COMPOSITIONAL VARIABILITY, MIGRATION AND MIXING OF CRUDE OILS IN THE COOPER AND EROMANGA BASINS

XINKE YU

B.Sc. (Chemistry)
M.Sc. (Organic Geochemistry)

Thesis submitted for the degree of
DOCTOR OF PHILOSOPHY
in
The Department of Geology and Geophysics

SEPTEMBER 2000

THE UNIVERSITY OF ADELAIDE

TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: PETROLEUM GEOLOGY OF THE COOPER AND EROMANGA BASINS

CHAPTER THREE: MATERIALS, METHODS AND EXPERIMENTS

CHAPTER FOUR: HYDROCARBON MAPPING BASED ON GC-FID ANALYSIS

CHAPTER FIVE: MIXED SOURCING MODEL BASED ON WHOLE-OIL GC-MS MEASUREMENTS

CHAPTER SIX: SECONDARY PETROLEUM MIGRATION

CHAPTER SEVEN: CONCLUSIONS

ABSTRACT

The Cooper/Eromanga Basin is one of the most important onshore petroleum provinces in Australia. It is located in the northeastern corner of South Australia and extends into the southwestern part of Queensland. The area of the Eromanga Basin is 1,000,000 km^2, and that of the underlying Cooper Basin is 13,000 km^2. Sediments of the Cooper Basin were deposited in glacial, fluvial and lacustrine environments, throughout the Permian and much of the Triassic. Deposition of fluvial, lacustrine and marine sediments in the Eromanga Basin commenced in the Early Jurassic and extended into the Cretaceous. Hydrocarbons have been recovered on test over a wide stratigraphic interval from the Early Permian Tirrawarra Sandstone to the Early Cretaceous Coorikiana Sandstone. More than six major potential hydrocarbon source rocks have been identified. These include the Patchawarra, Epsilon and Toolachee Formations of the Cooper Basin and the Poolowanna, Birkhead, and Murta Formations of the Eromanga Basin.

Considerable effort has been made over the last fifteen years to establish robust correlations between liquid hydrocarbons and potential source rocks, and thus to delineate petroleum migration pathways, within the Cooper/Eromanga petroleum province. However, due to the gross chemical similarity (including biomarker distributions) of the source rock extracts and reservoired oils, these problems have yet to be satisfactorily resolved. In order to better understand the processes of petroleum generation, migration and accumulation in the Cooper and Eromanga Basins, a multi-faceted study has been carried out in the following stages:

1. High resolution cryogenic GC-FID of whole oils and condensates (n = 123) to establish the limits of hydrocarbon compositional variation in the Cooper/Eromanga Basin.

2. Statistical analysis of GC-FID data (e. g. correlation, covariance, cluster analysis) to evaluate the relative importance of source and maturity, and also fractionation effects during secondary migration, in controlling the composition of these oils and condensates.

3. Measurement and comparison of the thermal maturities of the C_5–C_{15} and C_{15+} fractions of selected oils and condensates (n = 72) to ascertain whether or not they are the result of in-reservoir mixing of multiple hydrocarbon charges from kitchens of different thermal maturities.

4. Quantification (modelling) of the in-reservoir mixing of multiple hydrocarbon charges from different petroleum kitchens with the help of statistical analysis and computer digital imitation.

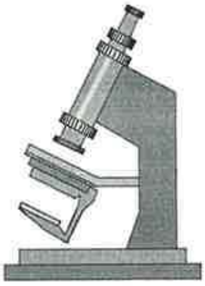
5. Reconstruction of long-distance secondary migration pathways and reservoir-filling histories on the southern flank of the Nappamerri Trough based on core-plug analysis using a novel device recently developed at the University of Cologne, the solvent flow-through solvent extraction (SFTE) cell. Following examination of isopach and structure maps and well completion reports, the Thurakinna, Garanjanie, Dirkala and Wancoocha Fields were selected for this part of the study. These fields comprise oil and gas accumulations in stacked Permian, Jurassic and Cretaceous reservoirs that lie along a fill-and-spill pathway previously thought to have been charged by updip migration from a Permian hydrocarbon kitchen. Residual oils recovered by SFTE (n = 20) and conventional bulk extraction of sandstones from the Permian Patchwarra Formation and Murteree Shale, the Jurassic Hutton Sandstone and Birkhead Formation, and the Cretaceous Murta Formation were compared with crude oils obtained by drill stem testing of the same units. These oils were analysed using MPLC, GC and GC-MS.

Cluster analysis of the whole-oil GC-FID data enabled the Cooper/Eromanga petroleums to be classified into three groups – Cooper-sourced oils and condensates; Eromanga-sourced oils; and mixed crudes derived from both Cooper and Eromanga source rocks (work of stages 1 and 2).

A mathematical model based on a comprehensive mass balance of light and heavy hydrocarbon components has been devised in order to better quantify the mixing ratios of discrete oils in a given reservoir. Computer digital imitation of this model closely matches the actual data distribution on cross-plots of light- *versus* heavy-end

maturities and the results of principal components analysis of the measured data. The relevance of this model to the Cooper and Eromanga Basins is demonstrated by way of three examples (work of stages 3 and 4).

The first application of SFTE technology to a major Australian petroleum province (work of stage 5) has confirmed significant lateral and vertical secondary migration of Permian oil in the southwestern Cooper and Eromanga Basins; and revealed a complex charge history for its Jurassic and Cretaceous reservoirs. Residual and DST oils recovered from sands in the Permian Patchawarra Formation and Murteree Shale are all of intra-Permian origin. Oil in the Jurassic reservoirs (Hutton, Birkhead) at Dirkala and Wancoocha displays a gross stratigraphic segregation according to maturity. The least mature oil (Rc = 0.7%) is located at the top of the oil column. These early oils, and the more mature residual oils lower in each structure (Rc = 0.7–0.8%), are all of Jurassic origin. Anomalously mature residual oils (Rc = 1.0–1.1%) at the base of the oil column in these two fields are of mixed Permian-Jurassic source affinity. They imply leakage of Permian hydrocarbons past the zero edge of the Nappamerri seal; and compartmentalisation of the Jurassic reservoirs. DST oils from Cretaceous reservoirs (Cadna-owie, Murta) in the study area have uniformly low maturities (Rc = 0.63–0.69%). Those at Wancoocha and Dirkala are of Jurassic (Birkhead) origin. However, the biomarker signature of Murta oil in the more basinward Garanjanie field indicates an additional contribution from a low-maturity Permian source.



STATEMENT OF ORIGINALITY

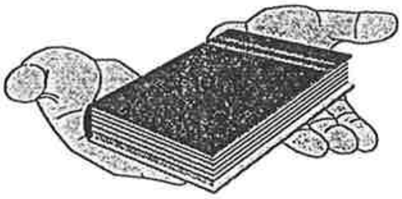
To the best of my knowledge and belief, and except where reference is made herein, this thesis contains no material published or written by another person, nor any material that has been accepted for the award of any other degree or diploma in any university. I give consent to my thesis, when deposited in the University Library, being available for photocopying and loan.

Xinke Yu

September 2000

DEDICATION

To my parents and my beloved daughter Guo



ACKNOWLEDGEMENTS

This research project was carried out with the assistance of an Overseas Postgraduate Research Scholarship, complemented by a University of Adelaide Scholarship. This financial support enabled me to undertake my doctoral studies in Australia and is highly appreciated.

The Department of Primary Industries and Resources, South Australia (PIRSA) funded the solvent flow-through extraction (SFTE) experiments conducted at the Geological Institute, University of Cologne and the related GC-MS analyses undertaken in the Organic Geochemistry Laboratory of the Department of Geology and Geophysics, University of Adelaide. My 3-month stay in Cologne was made possible by a European Association of Organic Geochemists (EAOG) Travel Grant. Santos Limited contributed oil samples to the study.

I am extremely grateful to my mentor, Associate Professor David M. McKirdy, for his keen supervision, guidance and constant support (both academic and personal) throughout my research. His critical reading and correction of the thesis left his clothes fitting somewhat looser!

Likewise, I am indebted to my friend and colleague Dr Khaled Arouri (Department of Geology and Geophysics) for his fruitful discussions and careful review of my thesis. His hospitality, encouragement and support will be treasured forever. Professor Detlev Leythaeuser, Dr Lorenz Schwark and their colleagues at the University of Cologne are sincerely thanked for their guidance and hospitality while I was working in their laboratories.

I would like to extent my deep appreciation and gratitude to Dr Qianyu Li (Department of Geology and Geophysics) for his academic support and personal encouragement. He kindly provided cluster and principal components analysis software. He also persuaded me to complete my degree when I was in psychological trouble.

I gratefully appreciate the help provided by the staff of the Department of Geology and Geophysics and the National Centre for Petroleum Geology and Geophysics. Some of them deserve special mention. Dr Nick Lemon donated oil/condensate samples. Professor Cedric Griffths (my former second supervisor) and Dr Peter Brooker provided much constructive discussion on the statistical aspects of my project. Mr John Stanley did the X-ray diffraction analyses of my salt extracts from the sandstone plugs. Further, I would like to express my thanks to Dr Keith Turnbull for his help around the laboratory; Mrs Sherry Proferes and Mr Ian Florance for their help with computer drafting and computing; and Mr Gerald Buttfield, Ms Kim Crawford, Mrs Yvonne Philp, Ms Sondra Gould, Mrs Sophia Craddock and Ms Sharon Gold for their friendly secretarial assistance.

Tony Hill, Elinor Alexander and the late Dr David Gravestock are warmly thanked for their constructive discussion and hospitality in providing convenient access to information from the PIRSA database.

I extend my sincere thanks to Mrs Lisa Brown, Mrs Cathy Li, Dr Baohong Hou, Mrs Esther Frakes and Mrs Alison McKirdy who gave me so much mental support and encouragement throughout the four years of my stay in Australia.

Finally, I would like to express my sincere appreciation to my friends: Dr Lin Huang, Dr Wei Zhang, Mr Li Sun, Mr Fuguei Cai, Mr Jian Li, Dr Guangguo Ying, Ms Xiaoming Chi, Ms Qingwei Zhang and Ms Yanqing Ding for their support and kind wishes. My thanks are also due to my beloved daughter, Guo, for tolerating the absence of her dad. Her high achievements in school are the greatest support and encouragement she could have given me, for which I shall be forever grateful!

CHAPTER ONE
INTRODUCTION

1.1 RATIONALE, AIMS AND SCOPE OF THE STUDY

The Cooper/Eromanga Basin is one of the most important onshore petroleum provinces in Australia (Figure 1.1). Since the first discovery of natural gas at Gidgealpa in 1963 and oil at Tirrawarra in 1970, 229 × 10^9 m^3 of recoverable raw gas and 17.5 × 10^6 kL of recoverable oil have been found in South Australia, and a total of 129 × 10^9 m^3 of gas and 4.6 × 10^6 kL of oil have been produced (as at 1 January 1998: Gravestock et al., 1998a). It supplies crude petroleum or its products to Adelaide and Sydney, as well as several regional centres (Figure 1.1)

Sediments of the Cooper Basin were deposited in glacial, fluvial and lacustrine environments during the late Carboniferous, the Permian and much of the Triassic. Deposition of fluvial, lacustrine and marine sediments in the Eromanga Basin commenced in the Early Jurassic and extended into the Cretaceous. Hydrocarbons have been recovered on test over a wide stratigraphic interval from the Lower Permian Tirrawarra Sandstone to the Lower Cretaceous Coorikiana Sandstone (Moussavi-Harami, 1996a,b). At least six major potential source rocks for the hydrocarbons have been identified. These include the Patchawarra, Epsilon and Toolachee Formations of the Cooper Basin and the Poolowanna, Birkhead and Murta Formations of the Eromanga Basin (Jenkins, 1989; Tupper and Burckhardt, 1990).

Considerable effort has been made over the last fifteen years or so to establish robust correlations between liquid hydrocarbons and potential source rocks, and thus to delineate petroleum migration pathways within the Cooper/Eromanga petroleum province (McKirdy, 1982; Kantsler et al., 1983; Vincent et al., 1985; Alexander et al., 1988, 1996; Heath et al., 1989; Jenkins, 1989; Michaelsen and McKirdy, 1989, 1996; Powell et al., 1989, 1991; Tupper and Burckhardt, 1990; McKirdy and Chivas, 1992; Alexander, 1996a; Boult et al., 1997, 1998). However, due to the gross chemical similarity (including biomarker distributions) of the source rock extracts and reservoired oils, these problems have yet to be satisfactorily resolved.

By studying the vertical and horizontal distribution of the hydrocarbon reservoirs in the Cooper and Eromanga Basins, Heath et al. (1989) proposed that most of the Eromanga-reservoired hydrocarbons were derived from Cooper Basin source rocks, and migrated vertically into the Eromanga sequence, where their physical and chemical characteristics were significantly altered. The results of exploratory drilling in the Lake Hope Block during 1988 seem to support this model. Jenkins (1989), based on his studies of Eromanga-specific biomarkers, also suggested that a considerable proportion of the Eromanga-reservoired oil was derived from source rocks in the Cooper Basin.

This conventional wisdom is strongly challenged by the work of the others. Michaelsen and McKirdy (1989, 1996), for example, concluded that migration from Permian source rocks into Eromanga Basin reservoirs had not occurred to any great extent in the southern Cooper Basin region and that many of the oils reservoired in the Eromanga Basin were generated *in situ*. McKirdy and Willink (1988) even proposed long-distance lateral migration of these oils towards the basin margin. Powell et al. (1989) also maintained that most of the oil reservoired in the Murta Formation of the Eromanga sequence is derived *in situ*. Based on their study of Araucariacean conifer biomarkers, Alexander et al. (1988) showed that large amounts of hydrocarbons in certain Eromanga reservoirs were of Jurassic origin.

Furthermore, Tuppper and Burckhardt (1990) concluded that mixing of Cooper and Eromanga Basin oils has occurred in some Murta Formation reservoirs. A recent geochemical study of oils and potential source rocks by Boreham and Summons (1999) led them to suggest that Eromanga Basin oil accumulations have received less than 25% of their charge from local Eromanga source rocks.

Clearly, the hydrocarbon charge histories of oil fields in the Cooper and Eromanga Basins are still poorly understood. A more comprehensive secondary migration scenario is required for the whole province, as well as more precise estimates of mixing ratios for individual reservoirs that have received multiple hydrocarbon

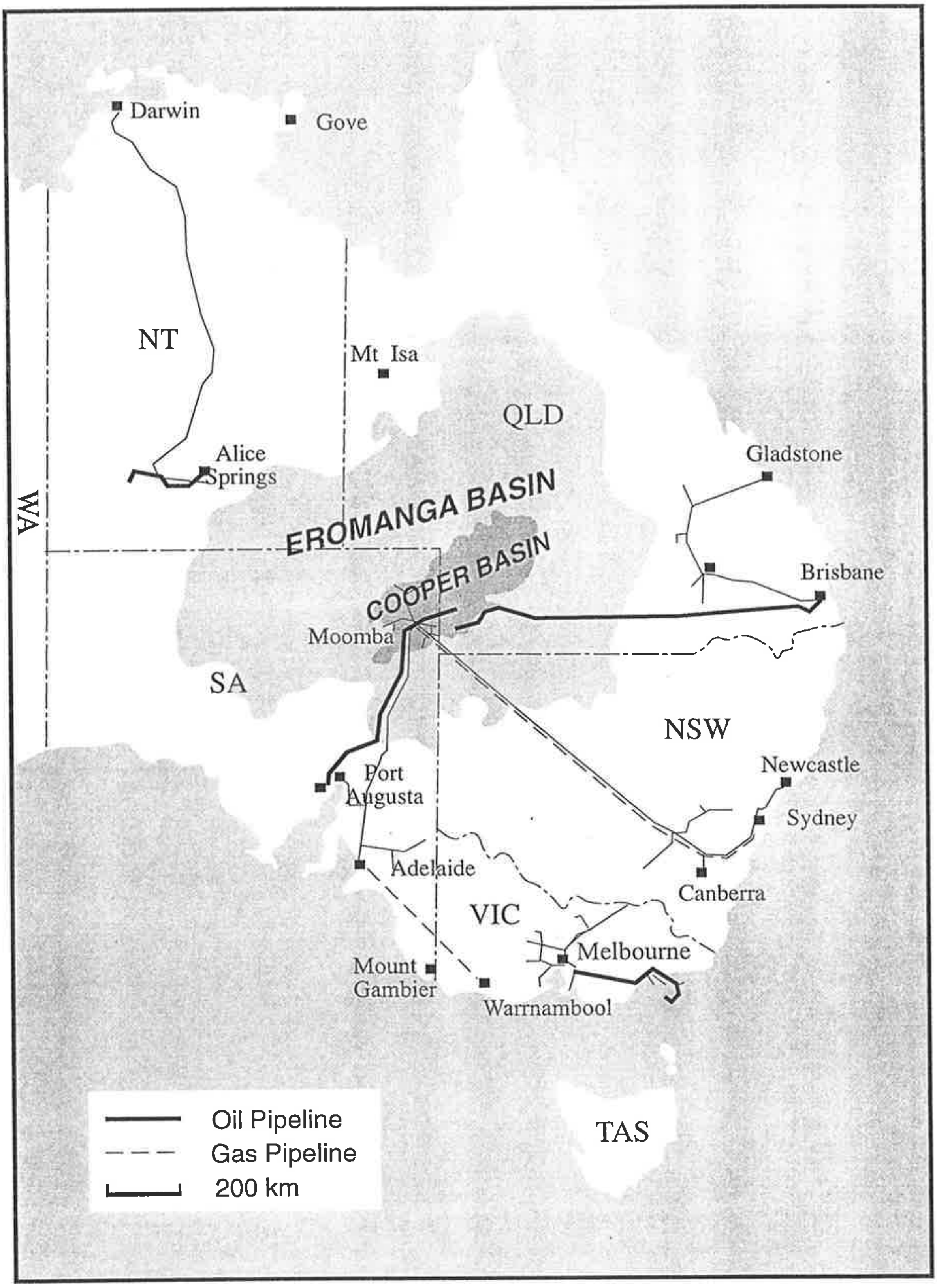


Figure 1.1 Location of Cooper and Eromanga Basins (adapted from Alexander and Hibburt, 1996).

charges from kitchens of different thermal maturity and/or different source rocks. These considerations provided the impetus for the present study which is a three-pronged investigation based on 1) establishment of the basin-wide variability in crude oil/condensate composition; 2) digital imitation and its application to the mixing of multiple hydrocarbon charges; and 3) characterisation of residual hydrocarbons in carrier beds along secondary migration pathways and in discrete reservoirs. This project has been carried out in the following stages:

1. Analysis by high-resolution cryogenic gas chromatography (with flame ionisation detection: GC-FID) of a large collection of whole oils and condensates (n = 123) in order to establish the limits of compositional variation for liquid petroleum in the Cooper/Eromanga Basin.

2. Statistical analysis of the resulting gasoline and kerosine-range hydrocarbon data (e.g. correlation, covariance, cluster analysis and principal components analysis) to evaluate the relative importance of source and maturity, and also fractionation effects during secondary migration (Thompson, 1987, 1988) in controlling the front-end composition of these oils and condensates.

3. Measurement and comparison of the thermal maturities of the C_5–C_{15} and C_{15+} fractions of selected oils and condensates (n = 72) to ascertain whether or not they are the result of in-reservoir mixing of multiple hydrocarbon charges from kitchens of different thermal maturity.

4. Quantification of the in-reservoir mixing of multiple hydrocarbon charges from different petroleum kitchens with the help of statistical analysis and computer-aided digital imitation.

5. Reconstruction of long-distance secondary migration pathways and reservoir-filling histories on the southern flank of the Nappamerri Trough based on core-plug analysis using a novel device recently developed at the University of Cologne, the solvent flow-through extraction (SFTE) cell (Schwark et al., 1997). Following examination of isopach and structure maps and well completion reports, the Thurakinna, Garanjanie, Dirkala and Wancoocha

Fields were selected for this part of the study. These fields comprise oil and gas accumulations in stacked Permian, Jurassic and Cretaceous reservoirs that lie along a fill-and-spill pathway previously thought by Heath et al. (1989) to have been charged by updip migration from a Permian hydrocarbon kitchen. Residual oils recovered by SFTE (n = 20) and conventional bulk extraction of sandstones from the Permian Patchwarra Formation and Murteree Shale, the Jurassic Hutton Sandstone and Birkhead Formation, and the Cretaceous Murta Formation were compared with crude oils obtained by drill stem testing of the same units. These oils were analysed using medium-pressure liquid chromatography (MPLC), gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

Stages 1 and 2 were aimed at surveying as many as possible whole oils and condensates from all over the Cooper/Eromanga Basin in order to determine whether they could be assigned to compositionally distinct groups. Cluster analysis of the whole-oil GC-FID data enabled these petroleums to be classified into three groups – Cooper-sourced oils and condensates; Eromanga-sourced oils; and mixed crudes derived from both Cooper and Eromanga source rocks. The main factors controlling the grouping were found to be source, migration, in-reservoir mixing and water-washing.

Stages 3 and 4 combined the compositional information acquired during Stages 1 and 2 with that obtained from high-resolution cryogenic GC-MS analysis of 72 representative samples from the original suite of oils and condensates. The resulting source and maturity data were processed statistically in a similar way to that used in the previous stages of the study. In order to explain the observed variations in the maturities of light-end and heavy-end hydrocarbons, as measured by isomeric ratios of various C_3-alkylbenezenes (Alexander et al., 1996) and the methylphenanthrene index (MPI-1: Radke and Welte, 1983), a mathematical model of in-reservoir mixing of hydrocarbon charges from different petroleum kitchens has been proposed. The model was verified by computer digital imitation and shown to quantify the mixing ratios of discrete oils in a given reservoir better than has previously been possible.

The first application of SFTE technology to a major Australian petroleum province (the work of stage 5) has confirmed significant lateral and vertical secondary migration of Permian oil in the southwestern Cooper and Eromanga Basins; and revealed a complex charge history for its Jurassic and Cretaceous reservoirs.

1.2 ORGANISATION OF THE THESIS

This thesis is organised into seven chapters. Chapter 1 outlines the rationale, aims and scope of the study. Chapter 2 is a review of the literature on the petroleum geology of the Cooper and Eromanga Basins. It provides the necessary geological background of the work undertaken, as well as the basics of the petroleum geochemistry of the region, including the relevant parameters of oil-to-source correlation. Chapter 3 details the materials and analytical methods employed. Cryogenic GC-FID data on the untopped oils and condensates are presented and discussed in Chapter 4. The recognition and quantification of in-reservoir mixing of hydrocarbon charges from different petroleum kitchens based on cryogenic GC-MS analysis of selected oils and condensates is dealt with in Chapter 5. The reconstruction of secondary migration pathways and reservoir filling histories for the Thurakinna, Garanjanie, Dirkala and Wancoocha Fields, based on the analysis of residual oils recovered by SFTE, is described in Chapter 6. The major findings and conclusions of the thesis are summarised in Chapter 7.

CHAPTER TWO

PETROLEUM GEOLOGY OF THE COOPER AND EROMANGA BASINS

2.1 GENERAL INFORMATION

The Cooper and Eromanga Basins together comprise one of the most significant onshore oil and gas provinces in Australia. This province is located in central-eastern Australia (Figure 1.1). The younger Eromanga Basin (or Great Artesian Basin, an important water resource in Australia) covers an area of 1,000,000 km^2, 360,000 km^2 of which lie in South Australia (Alexander and Hibburt, 1996). Deposition of fluvial, lacustrine and marine sediments in the Eromanga Basin commenced in the Early Jurassic and extended into the Cretaceous (Figure 2.1). The underlying Cooper Basin covers an area of 13,000 km^2, one third of which lies in south Australia. The unconformity at its upper surface varies in depth from 970 to 2800 m while the base of its deepest trough reaches about 4400 m below sea level (Gravestock et al., 1998a). Its non-marine sediments were deposited in glacial, fluvial and lacustrine environments and accumulated throughout the Permian and much of the Triassic (Figure 2.1). The Cooper Basin succession unconformably overlies Cambrian sedimentary and volcanic rocks of the Warburton Basin. The maximum total thickness of Permian to Recent sediment so far penetrated by drilling is 3850 m in the Nappamerri Trough (Alexander and Jensen-Schmidt, 1996).

2.2 TECTONIC HISTORY

Just like intracratonic basins elsewhere, the Cooper and Eromanga Basins have undergone slow episodic subsidence and low rates of deposition relative to rift basins (Alexander and Jensen-Schmidt, 1996). Their structural framework is a product of tectonic movements at least as old as the Late Devonian (Gravestock and Flint, 1995).

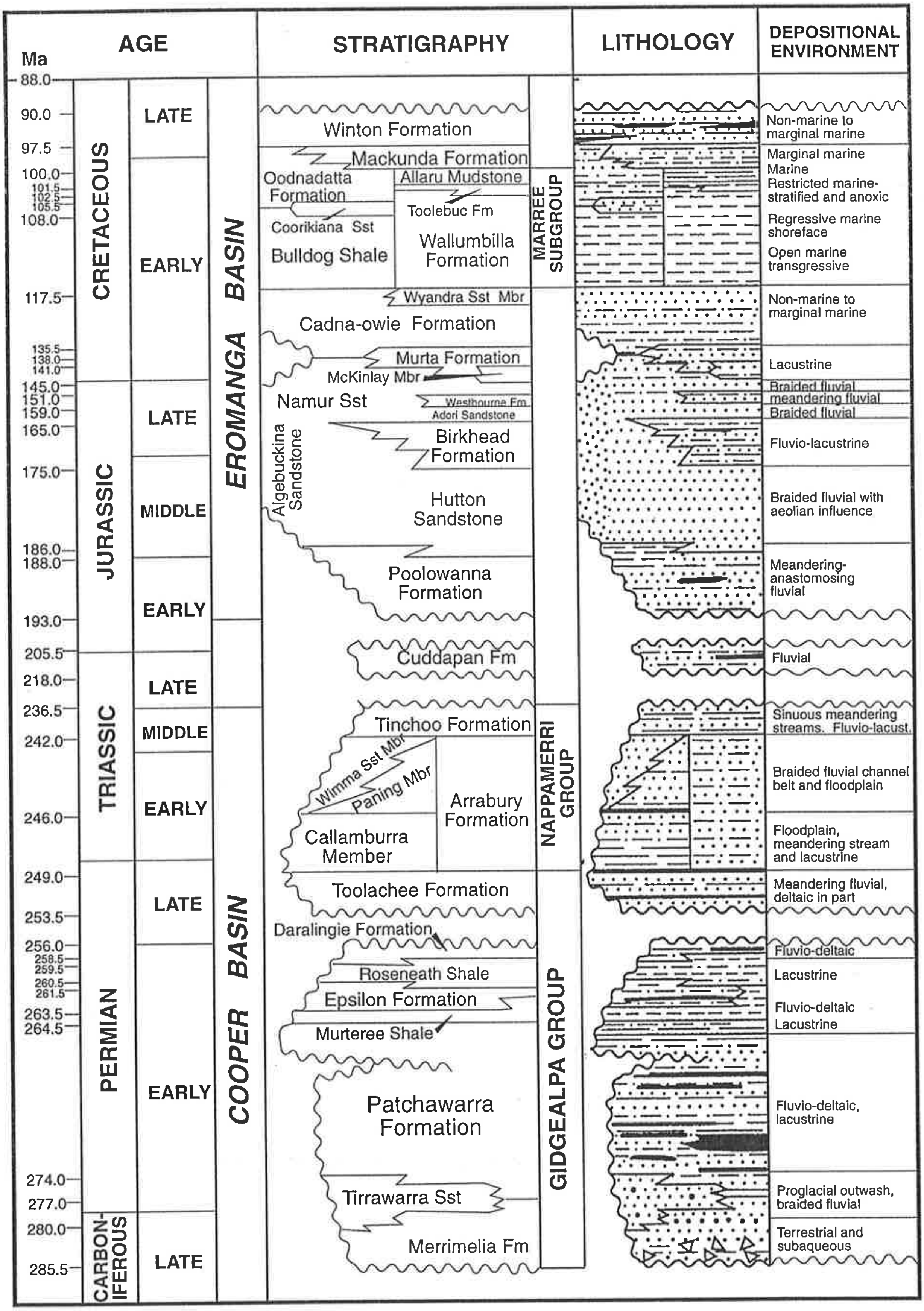


Figure 2.1 Generalised stratigraphic column and sequences of the Cooper and Eromanga Basins in South Australia (adapted from Moussavi-Harami, 1996).

Orogeny and epeirogeny cause deformation, uplift (or depression) and erosion of continental landmasses. Episodic subsidence is accompanied by deposition of sediment. The Cooper and Eromanga Basins display evidence of many significant tectonic movements and depositional episodes. In order of decreasing age, these are the Alice Springs Orogeny; Carboniferous–Triassic subsidence and deposition; Triassic uplift and erosion; Jurassic–Cretaceous subsidence and deposition; and Cainozoic tectonic movements (Alexander, 1996a; Alexander and Jensen-Schmidt, 1996; Hoffmann, 1989; Moussavi-Harami, 1996a,b). These events are considered in more detail below.

2.2.1 ALICE SPRINGS OROGENY

Devonian to Carboniferous (360-330 Ma) northwest-southeast orientated compression and uplift had a profound influence on shaping the original structure of the Cooper and Eromanga region. The compression and the resultant uplift probably were caused by the Alice Springs Orogeny (Gravestock and Flint, 1995). However, other workers variously attribute it to the Late Ordovician–Silurian Benambran Orogeny (Gatehouse, 1986), the mid-Carboniferous Kanimblan Orogeny (Apak et al., 1993, 1995), or a final phase of the Delamerian Orogeny (Roberts et al., 1990). The latter authors, using evidence from seismic sections and drillholes, identified overthrusts in Cambrian rocks beneath the Cooper Basin. These thrusts formed some of the most important structural features in the Cooper region: the arcuate domal Gidgealpa-Merrimelia-Innamincka Ridge and the Murteree-Nappacoongee Ridge (Figure 2.1), as well as the Birdsville Track Ridge which separates the Cooper and Simpson Basins (Figure 2.3).

2.2.2 CARBONIFEROUS–TRIASSIC DEPOSITION

From the Late Carboniferous to the Late Triassic, the Cooper and Eromanga Basins were regions of relative tectonic quiescence (Alexander and Jensen-Schmidt, 1996), and the prevailing subsidence and deposition were only interrupted by a brief interval of compression and uplift (Moussavi-Harami, 1996a,b). Up to 2,500 m of conglomerate, sandstone, siltstone, silty shale and coal were deposited in a variety of glacio-fluvial, fluvial, deltaic and lacustrine environments, within the Patchawarra and Nappamerri Troughs. The stacked non-marine depositional sequences are assigned to the Late

Carboniferous–Late Permian Gidgealpa Group and the Early–Middle Triassic Nappamerri Group (Alexander and Sansome, 1996: Figures 2.1 and 2.3). The Patchawarra, Epsilon and Toolachee Formations are important source rocks within the Gidgealpa Group.

This period of subsidence was followed by a brief (ca 2.5 Ma) interval of compression and uplift (starting at about 256 Ma: Figure 2.1) during which the southern Cooper Basin became a site of active erosion during the early Late Permian (Moussavi-Harami, 1996b). The resultant Daralingie Unconformity represents an erosional loss of 75–350 m of section, depending on location. According to Apak et al. (1993), this uplift was perhaps related to basement activity along older Palaeozoic or even Proterozoic northwest, meridional and northeast trends.

2.2.3 TRIASSIC EROSION

Sedimentation resumed with deposition of the Toolachee Formation and Nappamerri Group before prolonged uplift and erosion from Late Triassic to Early Jurassic (ca 236.5 to 193 Ma: Figure 2.1). This uplift was due to compressional deformation and regional tilting of the Cooper Basin toward the northwest. It resulted in removal by erosion of between 47 m and 285 m of Permian sediment in the southern Cooper Basin (Moussavi-Harami, 1996b). Erosion was particularly severe across the Dalhousie-McDills Ridge (Figure 2.3).

2.2.4 JURASSIC–CRETACEOUS SUBSIDENCE AND DEPOSITION

Down-warping within the Australian landmass created the Eromanga Basin and the sedimentation resuming during the Early Jurassic to Late Cretaceous without any major break (Moussavi-Harami, 1996b). Sedimentation in the Eromanga Basin was controlled by the topography of the unconformity surface at the top of the underlying Cooper Basin (Moussavi-Harami, 1996a,b). A ca 2.8 km-thick succession of lower non-marine, marine and upper non-marine sediments accumulated (Figures 2.1 and 2.3). The lower non-marine sequence (Poolowanna to Murta Formations) consists of sandstone, siltstone and shale with minor coal that were deposited in fluvial and lacustrine environments (Alexander and Samsome, 1996). The Poolowanna, Birkhead and Murta Formations are potential source rocks within this sequence, whereas the Hutton Sandstone is a good reservoir rock.

Subsidence ceased with the onset of regional east-west compression of basement rocks during the Late Cretaceous to Late Palaeocene (ca 90–60 Ma). This deformation caused considerable uplift and erosion (Moussavi-Harami, 1996b).

2.2.5 CAINOZOIC TECTONIC ACTIVITY

At least two phases of tectonic movement that are significant for the petroleum geology of the Cooper and Eromanga Basins have happened since Late Cretaceous. By this time, most of the Permian source rocks in the Patchawarra and Nappamerri Troughs and part of those in the overlying Eromanga sequence (here and in the Poolowanna Trough: Figure 2.3) had become mature enough to start generating hydrocarbons (Moussavi-Harami, 1996a,b; Tupper and Burckhardt, 1990). Reactivation of old faults by Cainozoic tectonic movements, and the formation of new ones, are likely to have had a major influence on hydrocarbon generation, expulsion, migration and accumulation. Fault activity provides heat for local petroleum generation and pathways for bulk migration, as well as destroying former traps and perhaps creating new ones.

Since the Late Jurassic Australia has drifted in a north-easterly direction from Antarctica towards collision with the South-East Asian and Pacific Plates. During this time the orientation of its continental compressive stress field has progressively changed from east-west to north-south (Alexander and Jensen-Schmidt, 1996). Thus, events on the margins of the Australian Plate may have strongly influenced Cainozoic deposition and structuring in the interior Cooper and Eromanga Basins.

From detailed seismic interpretation, Hoffmann (1989) recognised three episodes of tectonic extension and/or compression. The first of these occurred during the Late Cretaceous–Early Tertiary. It involved widespread extensional movement, which caused reactivation of pre-existing features in response to the rifting of the Tasman Sea. Two phases of compression followed, the first associated with the Middle Oligocene–

Miocene collision of the Australian and Pacific Plates. The second was an east-west compression, the cause and timing of which are not clear.

The significance of Cainozoic structuring in the Eromanga Basin has been recognised by many other researchers, including Sprigg (1986). During the Early Oligocene, major surface anticlines such as the Innamincka Dome and Birdsville Track Ridge formed (Moore and Pitt, 1984). Uplifts of the order of 350–500 m occurred around the margin of the basin (Alexander and Jensen-Schmidt, 1996). Evidence of Oligocene re-activation and uplift of these structures was also described by Wopfner (1985).

2.3 STRUCTURE

As shown in Figures 2.2 and 2.3, the South Australian part of the Eromanga Basin is separated by the Birdsville Track Ridge.into two depocentres, the Poolowanna Trough and the Cooper Basin region. The major troughs in the Cooper Basin (Patchawarra, Nappamerri and Tenappera) are separated by two main sets of structural highs, the Gidgealpa-Merrimelia-Innamincka (GMI) Trend and the Murteree-Nappacoongee (MN) Trend. This structural configuration is largely a product of the Alice Springs Orogeny and/or the Delamerian Orogeny, and is dominated by southwest-northeast oriented compressional features (see Section 2.2.1). Draped over the underlying structural grain and influenced by it, Permo-Triassic deposition in the Cooper Basin oscillated between the Nappamerri Trough and the Patchawarra Trough (Alexander and Jensen-Schmidt, 1996). The major sedimentary depocentre of the Eromanga Basin then shifted from the Cooper Basin region westward to the Poolowanna Trough in the Jurassic-Cretaceous, a time of tectonic quiescence with subsidence being the major mechanism creating space for deposition. Eromanga Basin deposition extended far beyond the limits of the Cooper Basin. All structuring within the Eromanga Basin is controlled by deposition over, and re-activation of, older tectonic trends.

The following discussion provides further details about three major structural highs: the GMI Trend, the MN Trend and the Birdsville Track Ridge.

2.3.1 GMI TREND

The GMI Trend, the most prominent structural high in the Cooper Basin, is an arcuate series of northeast-southwest oriented asymmetric, mildly compressional anticlinal features (Alexander and Jensen-Schmidt, 1996; Apak et al., 1993). It separates the Patchawarra Trough to the north and Nappamerri Trough to the south (Figures 2.2. and 2.3). Its northwest flank is controlled by high-angle thrust faults which were reactivated repeatedly throughout geological time, while the southern margin with the Nappamerri Trough exhibits a more complex array of gentle folds and smaller faults (Apak et al., 1993). The GMI Trend was formed prior to the deposition of the Cooper sequence during the Alice Springs Orogeny (Alexander and Jensen-Schmidt, 1996). Evidence from crustal unconformities led Apak et al. (1993) to suggest that the GMI Trend was uplifted in at least four distinct structural episodes, and that these phases of uplift caused the rejuvenation of pre-Permian faults. Seismic and other geological evidence suggests that, at the onset of deposition in the Eromanga Basin, the GMI Trend formed basement highs with a thin cover of Permo-Triassic sediments. Subsequent Mesozoic structuring over these ridges is due more to compaction of thick sediment in the adjacent Patchawarra and Nappamerri Troughs, than to loading and subsidence (Alexander, 1996a; Alexander and Jensen-Schmidt, 1996; Moussavi-Harami, 1996b).

2.3.2 MN TREND

Similar to the GMI Trend, the northeast-southwest oriented MN Trend is a complex structural high approximately 150 km long and 10–15 km wide consisting of many individual anticlines and faults (Apak et al., 1995). It separates the Nappamerri Trough to the northwest from the Tenappera Trough to the southeast and was in place during deposition of the Carboniferous to Triassic sediments of the Cooper Basin. The MN Trend resulted from the re-activation of basement folds and faults during compressional phases of uplift (Apak et al., 1995) and/or differential compaction (Alexander and Jensen-Schmidt, 1996; Moussavi-Harami, 1996b). It also formed a basement high when deposition of Eromanga Basin sediments commenced (Alexander and Jensen-Schmidt, 1996).

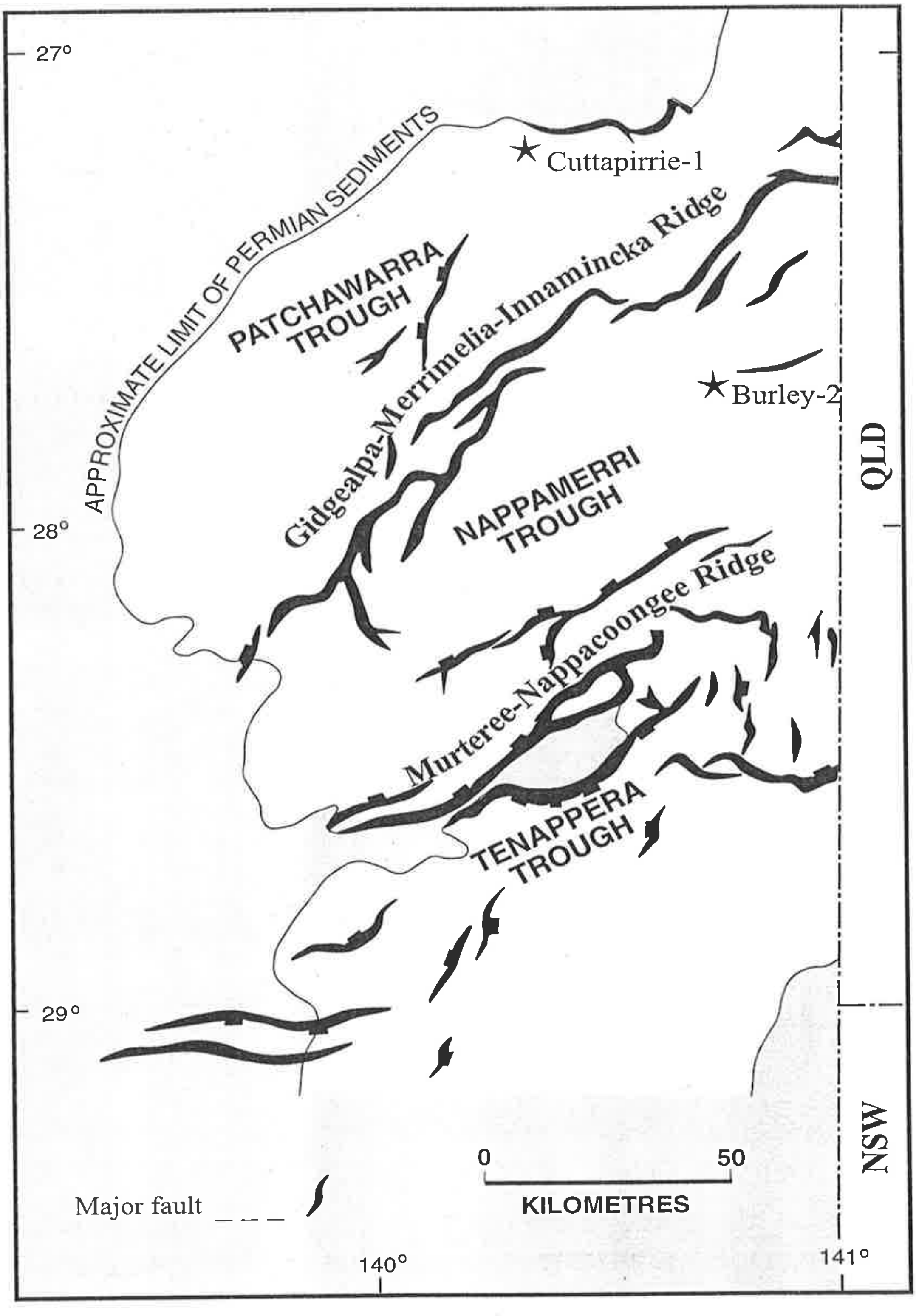


Figure 2.2 Main structures in South Australian section of the Cooper and Eromanga Basins, showing the approximate locations of the two wells from which formation depth data were used to describe the burial and maturity history (adapted from Alexander and Hibburt, 1996).

2.3.3 BIRDSVILLE TRACK RIDGE

The Birdsville Track Ridge (Figure 2.3), defined by surface exposures of the Late Cretaceous Winton Formation (Figure 2.1) and older units, is a northeast-southwest trending complex of domes and ridges that includes the Gason and Cordillo Domes (Alexander and Jensen-Schmidt, 1996, Fig. 4.4). These structural highs influenced deposition in the Cooper, Pedirka and Simpson Basins since Triassic sediments on-lap their margins. However, it appears that the structures had little relief during Eromanga Basin deposition.

2.4 DEPOSITIONAL SETTINGS AND STRATIGRAPHY

The stratigraphy and depositional environments of the Eromanga Basin have been under investigation for more than 40 years. For economic reasons, such studies became more refined and comprehensive in the Cooper region following the discovery of the first hydrocarbon-bearing reservoir in the underlying Permian sequence in 1963 (Alexander and Frears, 1995). Among the pioneering researchers were Kapel (1966), Martin (1967), and Gatehouse (1972). Hill and Gravestock (1995) and Krieg et al. (1995) provided comprehensive summaries of the sedimentology, stratigraphy and economic geology of the Cooper Basin and the Eromanga Basin, respectively. The most recent lithostratigraphic description of the Eromanga sequence is that by Alexander and Sansome (1996), and of the Cooper succession by Alexander et al. (1998). The following is a brief summary of these accounts, focussing on source and reservoir rocks.

2.4.1 DEPOSITIONAL ENVIRONMENTS AND PALAEOCLIMATES

During the late Palaeozoic, changing ocean circulation and orogenesis caused by the joining of Gondwana and Laurasia led to widespread glaciation. Highlands, such as the Birdsville Track Ridge and the platform on the southwest margin of the Cooper Basin, were glaciated during the Carboniferous and remained as topographical features during Early Permian deposition in the Cooper Basin.

Decay of the ice-sheet during the Early Permian as the climate ameliorated released enormous volumes of sediment which were deposited in various fluvio-glacial settings, including flood-basin lakes. These sediments formed the major part of the Gidgealpa Group comprising conglomerate, sandstone, siltstone, silty shale and coal (Figure 2.1).

Basin uplift during the Late Permian Daralingie Movement resulted in considerable erosion of the Early Permian section. Subsidence and deposition resumed in the Cooper Basin under meandering fluvial, deltaic, lacustrine and floodplain conditions, resulting in the Late Permian sandstones and coal measures of the Toolachee Formation and the interbedded sandstone, mudstone and minor coal of the Early–Middle Triassic Nappamerri Group. Orogenic movement and global climatic warming during the late Early Triassic to Middle Triassic caused widespread subaerial weathering and pedogenesis.

The cool, arid climate of the Early Jurassic gave way to moist cool conditions in the Late Jurassic. Following cold conditions with periods of ice formation in the Early Cretaceous (Frakes and Francis, 1988; De Lurio and Frakes, 1999) the climate then warmed during the Late Cretaceous as Australia drifted northwards. Early Jurassic–Late Cretaceous (193–90 Ma) deposition within the Eromanga Basin was relatively continuous and widespread. Terrestrial freshwater conditions prevailed, except for an Early Cretaceous marine transgressive phase that deposited thick shales (e.g. Bulldog Shale: Figure 2.1). During the time interval Early Jurassic to earliest Cretaceous, extensive sand-dominated braided fluvial systems drained into lakes and swamps through a landscape vegetated by conifers, cycads and ferns, whereas the Late Cretaceous upper non-marine sequence (Winton Formation) is the product of a meandering fluvial regime.

2.4.2 STRATIGRAPHY

A schematic ESE-WNW cross section (Figure 2.3) shows how the major stratigraphic units vary in thickness across the southwestern Cooper and Eromanga Basins. A generalised lithostratigraphic column is depicted in Figure 2.1. The following is a brief synopsis of the regional lithostratigraphy.

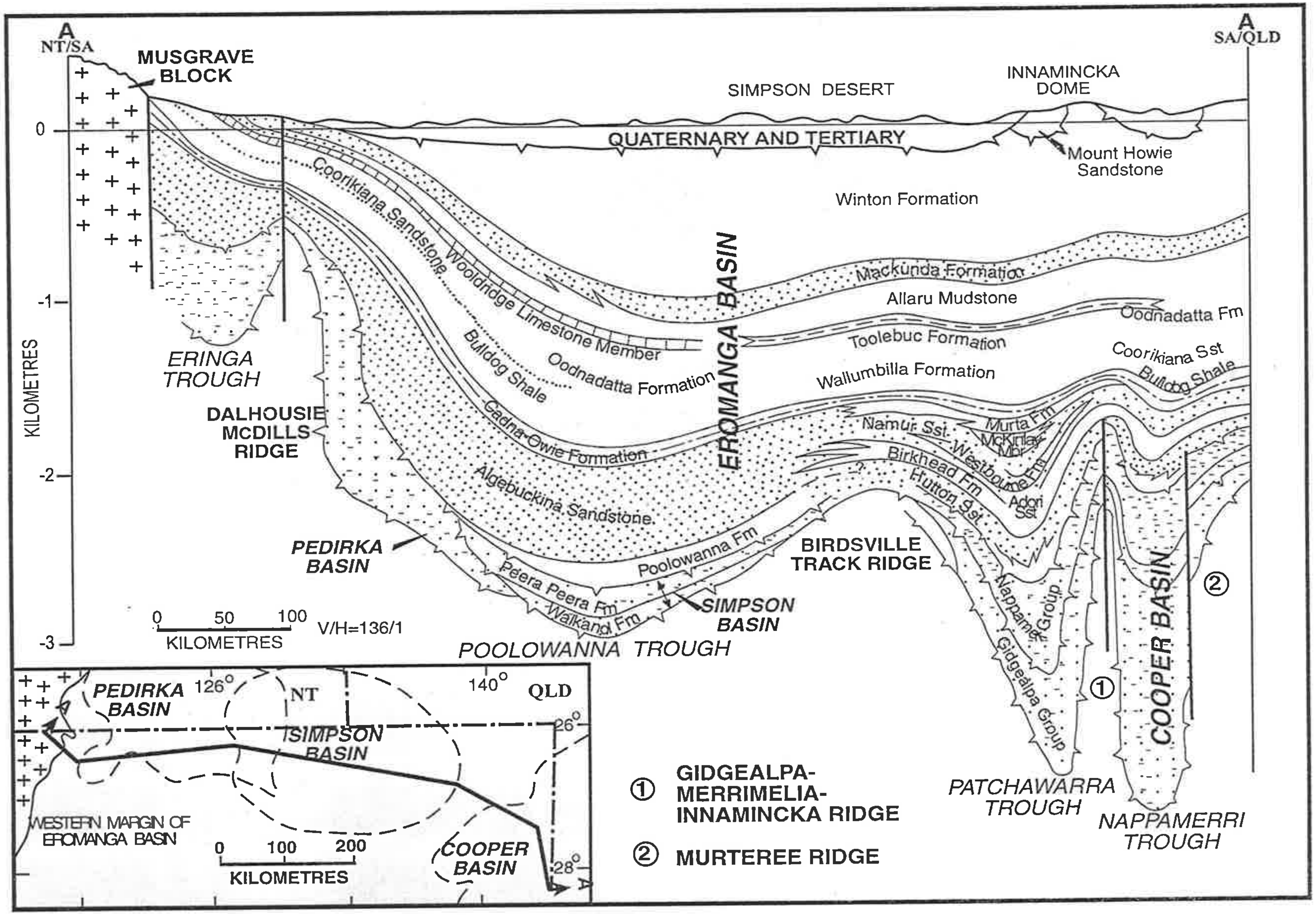


Figure 2.3 Schematic cross section of the Cooper and Eromanga Basins (from Alexander and Hibburt, 1996).

The Gidgealpa Group was deposited on glaciated Warburton Basin sediments or granitic basement. It comprises, in ascending order, the glacio-fluvial Merrimelia Formation and the braided fluvial, proglacial outwash Tirrawarra Sandstone, overlain by peat swamp and floodplain facies of the Patchawarra Formation. Two lacustrine units, the Murteree and Roseneath Shales, with intervening fluviodeltaic sediments of the Epsilon and Daralingie Formations, were deposited during a phase of continued subsidence. The Late Permian fluvial sandstones, lacustrine shales, and thin coals of the Toolachee Formation unconformably overlie the Early Permian section, and are in turn overlain by the Nappamerri Group.

The Gidgealpa Group is thickest in the Nappamerri Trough, whereas the thickest Nappamerri Group (>500 m) exists in the Nappamerri and Patchawarra Troughs (Figure 2.3). The Nappamerri Group consists of the Late Permian to Middle Triassic Arrabury Formation, comprising the lacustrine, floodplain and braided fluvial Callamburra, Paning and Wimma Sandstone Member, and the Middle Triassic fluvial lacustrine Tinchoo Formation. In the northern Patchawarra Trough, the group is locally overlain by sandstones, minor siltstone and coal beds of the Late Triassic Cuddapan Formation (Powis, 1989).

Bounded at the bottom and top by unconformities, the sedimentary record of the Eromanga Basin extends without major break from Early Jurassic to mid-Cretaceous and consists of a cyclic succession of sandstone and mudstone units (Figure 2.1). The sedimentary succession is composed of lower and upper terrestrial sequences and an intervening marine interval. Much of the lower sequence is medium- to moderately high-energy, cross-bedded fluvial sandstone. In ascending order, it comprises the Poolowanna Formation (sandstone, siltstone, shale and coal deposited in meandering fluvial to flood-plain settings); Algebuckina Sandstone (fluvio-lacustrine facies); Hutton Sandstone (braided fluvial facies); Birkhead Formation (siltstone, mudstone and coal deposited in lacustrine, peat-swamp and meandering fluvial environments); Adori Sandstone (braided fluvial facies); Westbourne Formation (lacustrine shale and siltstone); Namur Sandstone (braided fluvial facies); and Murta Formation (lacustrine-deltaic siltstone, shale and sandstone).

The upper non-marine sequence (Winton Formation), however, is mainly of lower energy, finer grained, flood-plain and lacustrine sandstone, siltstone and coal-swamp deposit. The intervening marine succession is a grey, fossiliferous mudstone-siltstone sequence with regressive marine sandstone intervals and a basal, non-marine to marginal marine sandstone–siltstone unit (Cadna-owie Formation).

2.5 SOURCE ROCKS

A comprehensive understanding of the source rocks in a petroleum-bearing basin — their occurrence, petrology and organic geochemistry, and their correlation with petroleum — is fundamental to the development of a regional exploration philosophy. This is particularly relevant in frontier areas but also has application in more mature provinces like the Cooper and Eromanga Basins. Research on source rocks of these two basins has been in progress for many years (Smyth, 1983; Smyth et al., 1984; Vincent et al., 1985; Alexander et al., 1988; Jenkins, 1989; Michaelsen and McKirdy, 1989; Powell et al., 1989; Armanios et al., 1995; Michaelsen and McKirdy, 1996; Boreham and Hill, 1998). A synopsis of the main source rocks in the study area is presented below. These are the Patchawarra and Toolachee Formations in the Cooper sequence and the Poolowanna, Birkhead and Murta Formations in the Eromanga sequence. Each will be discussed in terms of their depositional environment, total organic carbon (TOC) content, kerogen type (as determined by Rock-Eval pyrolysis) and thermal maturity.

2.5.1 PATCHAWARRA FORMATION

Deposited under an environment dominated by high-sinuosity fluvial systems flowing northward over a floodplain with peat swamps, lakes and gentle uplands, the Early Permian Patchawarra Formation is the thickest formation of the Gidgealpa Group (up to 680 m thick in the Nappamerri Trough: Alexander et al., 1998). Its coal and carbonaceous shale are the principal source rocks of the Cooper Basin, both in source richness and quality. The total thickness of the Patchawarra coals exceeds 60 m in the Weena Trough (in the southwestern corner of the basin; not shown in Figure 2.1) and ranges up to 40 m in the Patchawarra Trough, but rarely exceeds 10 m in Nappamerri Trough (Boreham and Hill, 1998).

The TOC content of shale in the Patchawarra Formation is up to 10%, whereas that of the carbonaceous shale and coaly shale facies is in the range 10–30%. The coal, by definition, has TOC values >30%. The hydrogen index (HI = 3– 346, mean = 132) and genetic potential, ($S_1 + S_2 = 0.04–37$, mean = 7.7 kg hydrocarbons per tonne) of the shales indicate potential to generate both gas and oil. Carbonaceous shale, coaly shale and coal exhibit a somewhat greater capacity for hydrocarbon generation ($S_1 + S_2 = 2–182$, mean = 54 kg hc/t) and a similar spread of kerogen quality (HI = 12–347, mean = 177). Oil-prone Patchawarra kerogen (HI > 200) ranges in composition from Type II to Type II/III (Boreham and Hill, 1998, Fig. 8.4).

The western Patchawarra Trough (Figure 2.2) represents the most important petroleum kitchen where thick shale and coal were deposited (Moussavi-Harami, 1996b) and now lie within the present-day oil generation window (vitrinite reflectance, R_o >0.65%: Boreham and Hill, 1998).

2.5.2 TOOLACHEE FORMATION

According to Hill and Gravestock (1995), the Late Permian Toolachee Formation comprises sandstone deposited in mixed-load fluvial channels of moderate to high sinuosity, overbank and floodplain lacustrine mudstone, and peat-swamp coal. It is ubiquitous across the Cooper Basin, except on parts of the GMI Ridge and southern Muteree Ridge. It reaches its maximum thickness of 160 m in the central Nappamerri Trough.

The coal and carbonaceous shale of the Toolachee Formation make it the second most important petroleum source rock unit in the Cooper Basin. The total coal thickness is greater than 35 m in the northern Patchawarra Trough (Boreham and Hill, 1998). TOC in the Toolachee shale facies ranges from 0.3 to 9.3% (mean = 3.8%), while the corresponding $S_1 + S_2$ values are from 0.1 to 19.5 (mean = 6.9) kg hc/t. Hydrogen indices (HI = 8–215, mean = 128) suggest minimal oil source potential. The far greater genetic potential of the coals (range = 21–187, mean = 61.5 kg hc/t) is paralleled by their improved kerogen quality (HI = 141–330, mean = 214). This kerogen is mainly of Type II/III composition.

Regional isopach and vitrinite reflectance maps of the Toolachee Formation source rocks (shale and coal) show that they are thickest and also mature for oil generation in the northern Patchawarra Trough (Figure 2.2: Boreham and Hill, 1998; Gravestock and Jensen-Schmidt, 1998).

2.5.3 POOLOWANNA FORMATION

The Early to Middle Jurassic Poolowanna Formation was deposited in an environment of high sinuosity fluvial channels meandering across a floodplain on which minor peat swamps developed (Alexander and Samsome, 1996). It consists of sandstone, interbedded with siltstone and shale, and thin, discontinuous coal seams and intraclast breccias (Krieg et al., 1995). Its maximum penetrated thickness is 205 m in Poolowanna-1 in the Poolowanna Trough (Figure 2.3: Alexander and Samsome, 1996). The interbedded coals and carbonaceous shales and siltstones are believed to be potential source rocks (Kagya, 1997).

TOC ranges from 5.1 to 42.1%, and the potential hydrocabon yield (S_1+ S_2) ranges from 11 to 160 kg hc/t in the Poolowanna Trough where the formation shows good to excellent source richness (Michaelsen and McKirdy, 1996). Hydrogen index values greater than 250 are exhibited by source rocks in both the Poolowanna Trough (HI up to 390) and in the Cooper region (HI up to 480), where the source potential for oil ranges from good (Type II/III kerogen) to very good (Type II kerogen: Michaelsen and McKirdy, 1996).

The maturity of the Poolowanna Formation source rocks reaches 0.9% R_o in the Poolowanna Trough (Michaelsen and McKirdy, 1996). They are only margiunally mature (0.5–0.6% R_o) in the Sturt-Tantanna area of the Patchawarra Trough (Kagya, 1997). Further east in the Cooper region, maturities up to 1.09% R_o have been recorded (Jenkins, 1989).

2.5.4 BIRKHEAD FORMATION

The Middle to Late Jurassic Birkhead Formation comprises interbedded siltstone, mudstone and sandstone with thin (<0.3 m), lenticular coal seams (Alexander and Sansome, 1996; Krieg et al., 1995). As the most important source rock unit in the Eromanga Basin, its organic-rich silts, muds and coals were deposited in lacustrine and peat swamp environments, cut by meandering fluvial channels. The thickness of the Birkhead Formation is greater than 150 m in both the Patchawarra and Nappamerri Troughs (Alexander and Sansome, 1996).

Source richness across the Birdsville Track Ridge (Figure 2.3) at Pandieburra-1, Poonarunna-1 and Putamurdie-1 is generally high but ranges from fair to excellent (TOC = 0.84–19.7%, $S_1 + S_2 = 1–98$ kg hydrocarbons per tonne rock) (Michaelsen and McKirdy, 1996). Source quality for oil is excellent here (resinite-rich Type II kerogen). Elsewhere Type II/III kerogen is the prevailing organic facies in the Birkhead Formation.

The Birkhead Formation source rocks are generally marginally mature to mature (R_o = 0.5–0.7%) around the margins of the underlying Cooper Basin, but the maturity of this unit increases to 1.3% at Burley-1 in the central Nappamerri Trough (Jenkins, 1989; Boult et al., 1997).

2.5.5 MURTA FORMATION

The Early Cretaceous lacustrine Murta Formation consists of finely interbedded siltstone, shale and sandstone (Alexander and Sansome, 1996; Krieg et al., 1995). It is widespread in the Eromanga Basin and reaches its maximum thickness (in excess of 90 m) in the Nappamerri Trough.

The Murta Formation is regarded as the shallowest unit of importance for hydrocarbon generation (Michaelsen and McKirdy, 1996). Its source richness and potential for hydrocarbon generation were studied in detail by Michaelsen and his co-workers (Michaelsen and McKirdy, 1989, 1996; Powell et al., 1989). Its TOC values (0.8–2.6%) and potential hydrocarbon yield ($S_1 + S_2 = 3$ to 12 kg hc/t), indicate fair to good source richness. HI values in the range 175–542 are characteristic of Type II and Type II/III kerogen with a significant oil and gas-generating potential.

Maturity of the Murta Formation is typically in the range 0.40–0.60% R_o (marginal for oil generation) in the Patchawarra and Tennapera Troughs, increasing to ca 1.0% at Burley-2 in the centre of the Nappamerri Trough (Figure 2.2; Tupper and Burckhardt, 1990).

2.6 RESERVOIRS

Petroleum reservoirs occur in nearly all the units of the Cooper and Eromanga Basins because sandstones are common throughout (Figure 2.1: Alexander, 1996b; Gravestock et al., 1998b). In the Cooper sequence, economic oil and/or gas occur within glacio-fluvial sandstones in the Merrimelia Formation (Williams and Wild, 1984; Chaney et al., 1997); glacial and fluvial sandstones in the Tirrawarra Sandstone (Seggie et al., 1994; Rezaee and Lemon, 1996; Seggie, 1997); fluvial channel, point bar and crevasse splay sandstones in the Patchawarra Formation (Gravestock et al., 1998b); fluvio-deltaic and shoreline sandstones in the Epsilon Formation (Fairburn, 1992; Alexander et al., 1998); fluvial channel and lacustrine delta sandstones in the Daralingie Formation (Kelemen, 1986; Gravestock et al., 1998b); fluvial channel, point bar and crevasse splay sandstone in the Toolachee Formation (Fairburn, 1989; Mackie et al., 1995); sands of the Callamurra, Paning and Wimma Members in the Arrabury Formation; and sandstone deposited in high-sinuosity fluvial channels of the Tinchoo Formation (Gravestock et al., 1998b).

In the Eromanga sequence, commercial oil/condensate flows have been obtained from fluvio-lacustrine sandstones in the Poolowanna Formation, Hutton Sandstone, Birkhead Formation, Namur Sandstone, Murta Formation and Cadna-owie Formation (Gravestock and Alexander, 1986, 1989; Heath et al., 1989; Alexander, 1996b; Boult et al., 1997, 1998).

The two most significant and representative hydrocarbon reservoir formations are discussed in more detail below – the gas and condensate-bearing Patchawarra Formation of the Cooper Basin, and the oil/condensate-bearing Hutton Sandstone of the Eromanga Basin.

2.6.1 PATCHAWARRA FORMATION

The Patchawarra Formation contains the most significant reservoirs of gas and/or condensate. Typical drillstem test (DST) flow rates are 2, 440, 268 m^3 of gas and 14 kL of condensate per day in Garanjanie-1; 174, 679 m^3 of gas and 2.9 kL of condensate per day in Gahnia-1; 146, 505 m^3 of gas and 0.3 kL of oil per day in Cooper Creek-2; and 42, 261 m^3 of gas per day in Beanbush-1 (Gravestock et al., 1998b). The total amount of gas produced from the Patchawarra Formation was 45.1 x 10^9 m^3 by the end of 1998 (Gravestock et al., 1998b).

The Patchawarra Formation is the thickest and most widespread Permian unit in the South Australian sector of the Cooper Basin (Alexander et al., 1998). It varies greatly in depth of burial, from 1,800 to 3,500 metre below sea level, with the deepest reservoirs occuring in the Nappamerri Trough (Hill and Gravestock, 1995). Its reservoirs were deposited as fluvial channel, point bar and crevasse splay sands. Their porosity ranges from 5 to 25%, with the modal frequency occurring at 15%. The permeability varies between 0.01 and 1,000 millidarcies (mD), but is mostly in the range 1–10 mD.

2.6.2 HUTTON SANDSTONE

The Hutton Sandstone is the most productive unit within the Eromanga Basin. Nearly half of the total crude oil produced from the Eromanga sequences in South Australia comes from reservoirs in the Hutton Sandstone that are sealed by the Birkhead Formation (Alexander, 1996b).

Underlying the Poolowanna Formation and overlain by the Birkhead Formation, the Hutton Sandstone reaches its greatest thickness in the Patchawarra Trough (Moussavi-Harami, 1996a,b). Toward the south, east and west, it becomes thin and is replaced by, or intertongues with, the Middle–Late Jurassic Algebuckina Sandstone (Figure 2.1). The reservoir facies of the Hutton Sandstone consists of mineralogically mature, fine to coarse-grained quartz sandstone (with minor amounts of feldspar) deposited as fluvial channel sands, gravel bars and crevasse splay sands (Alexander, 1996b; Alexander and Sansome, 1996).

The reservoir properties of the Hutton Sandstone are excellent (Alexander, 1996b). Its porosity varies widely from 8 to 28%, but is mostly in the range 20–24%. The permeability is even more variable, from 0.1 to 10,000 mD, although usually >1000 mD.

2.7 SEALS

The seals (cap rocks) of hydrocarbon accumulations in the Cooper and Eromanga Basin have not been rigorously studied, even though they are a vital component of risk analysis in petroleum exploration. Gravestock et al. (1998) summarised the Cooper Basin regional and intraformational seals, and Alexander (1996) reviewed those of the Eromanga Basin. Heath et al. (1989) noted a strong geographic relationship between hydrocarbon discoveries in the Eromanga sequence and the combined thickness of the Permo-Triassic seals in the underlying Cooper Basin. The Birkhead/Hutton seal/reservoir combination has been extensively studied by Boult and his co-workers (Boult et al., 1997, 1998).

2.8 BURIAL HISTORY AND SOURCE ROCK MATURATION

Thermal evolution of a source rock is controlled by the maximum temperature to which it is exposed and the duration of the heating (Tissot and Welte, 1984). As the source rock subsides, both the pressure and temperature build up, and the thermal maturity of its organic matter progressively increases. Burial depth determines the pressure, whereas the temperature is dependent on the heat flow and geothermal gradient. The burial and thermal history of the Cooper and Eromanga Basins has been studied most recently by Moussavi-Harami (1996a,b) and Deighton and Hill (1998), with the help of basin modelling computer software. Previous studies of the geothermal history and timing of maturation in these basins include those by Kantsler et al. (1983, 1986), Pitt (1986), Zhou (1989), Tupper and Burckhardt (1990) and Toupin et al. (1997).

A brief summary of the history of hydrocarbon generation in the Cooper and Eromanga Basins is presented here based on the modelling undertaken by Deighton and Hill (1998). Two representative areas are selected for discussion. These are the central Nappamerri Trough (represented by Burley-2) and the northwestern margin of the Patchawarra Trough (exemplified by Cuttapirrie-1: Figure 2.2).

2.8.1 PATCHAWARRA TROUGH

The burial and maturity history plot of Cuttapirrie-1 (Deighton and Hill, 1998, fig. 9.17) shows that the Patchawarra, Toolachee, Poolowanna and Birkhead source rocks all entered the oil window (>0.65% R_o) at ca 95 Ma. The Permian units reached the onset of wet gas generation (1.0% R_o) at ca 87 Ma and have remained in the wet gas window since then. Modelling of hydrocarbon generation indicates expulsion of some oil and minor gas from coals in the Patchawarra and Toolachee Formations, but little or no oil from the Jurassic units.

2.8.2 NAPPAMERRI TROUGH

The equivalent geohistory plot for Burley-2 (Deighton and Hill, 1998, fig. 9.13) indicates that the Permian source rock units entered the oil and gas windows very early because of high heat flow from basement granites during their deposition. The estimated geothermal gradient at this time was 80–110°C/km (compared with the present-day gradient of 61°C/km). Oil was expelled from the Patchawarra coals in the Late Permian and from the Toolachee coals in the mid-Cretaceous, when most of their gas was also generated. It was during the Cretaceous that the main Eromanga source rocks entered the oil generation window. They are now within the wet gas (Murta) and dry gas (Poolowanna, Birkhead) maturity zones.

2.9 OILS

Different varieties of crude oil and condensate occur in the Cooper and Eromanga Basins. Although most of them are obviously derived from terrestrial source rocks (Vincent et al., 1985; Heath et al., 1989; Hunt et al., 1989; Jenkins, 1989; Michaelsen and McKirdy, 1989; Powell et al., 1989; Tupper and Burckhardt, 1990; Boreham and Hill, 1998; Boreham and Summons, 1999), crudes that bear fingerprints of a marine carbonate origin do exist in basement rocks of the underlying Warburton Basin (Kagya, 1997; Yu and McKirdy, 1998; X. Sun, private communication, 1998). In general, oils and condensates reservoired in the Cooper Basin are typically medium to light crudes with paraffinic to paraffinic-naphthenic bulk compositions, and low to high wax contents (Hunt et al., 1989; Boreham and Hill, 1998). Most Permian oils contain significant dissolved gas and none show any evidence of water washing on the basis of their aromatic hydrocarbon distributions (Hunt et al., 1989; Yu and McKirdy, 1998). Oils in the Cretaceous reservoirs are normally light, non-waxy, low sulphur, paraffinic crudes (Vincent et al., 1985), although some waxy oils do occur in the Murta Formation along the MN Ridge (Figure 2.2: Michaelsen and McKirdy, 1989; Powell et al., 1989). Most of the Eromanga crudes, particularly those from Jurassic reservoirs, are non-waxy but show obvious signs of water-washing.

Boreham and Hill (1998) reported six geochemical parameters of oils from 161 selected wells covering both the South Australian and Queensland portions of the Cooper and Eromanga Basins. Table 2.1 is a statistical summary of the reported data. The following is a brief discussion of the physical and chemical properties of these oils and the geological factors that influence their variation.

2.9.1 GAS-TO-OIL RATIO

The gas-to-oil ratio (GOR) of a crude oil accumulation reflects the amount of natural gas associated with the oil. Crudes from the Cooper and Eromanga Basins have a large range of GOR values (Heath et al., 1989; Hunt et al., 1989). Oils from the Eromanga Basin typically contain about 9 m^3/kL natural gas, but those in Permian reservoirs range as high as 2950 m^3/kL.

2.9.2 POUR POINT

The pour point of a crude oil is another parameter reflecting its content of light hydrocarbons relative to heavy ends. Technically, it is a measure of the temperature at

Table 2.1 Descriptive statistics for geochemical parameters of oils from selected Cooper and Eromanga wells, South Australia and Queensland (based on the data of Boreham and Hill, 1998)

Description	$<C_{15}$	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}	OEP	API°
Cooper and Eromanga Crudes						
Mean	17.9	4.6	0.4	0.1	1.1	45.5
Standard Error	1.6	0.1	0.0	0.0	0.0	0.5
Median	16.3	4.4	0.4	0.1	1.1	45.7
Mode	0.8	3.3	0.3	0.1	1.1	47.5
Standard Deviation	15.5	1.3	0.3	0.0	0.0	4.7
Sample Variance	239.4	1.7	0.1	0.0	0.0	22.5
Kurtosis	0.4	0.7	25.4	8.3	12.0	-0.7
Skewness	0.9	0.8	4.1	2.4	-2.0	-0.3
Range	66.9	7.7	2.3	0.2	0.3	20.7
Minimum	0.0	1.7	0.1	0.0	0.8	34.2
Maximum	66.9	9.5	2.5	0.3	1.2	54.9
Sum	1767.8	733.7	67.5	14.1	172.1	4236.1
Count	99.0	161.0	161.0	161.0	161.0	93.0
Cooper Crudes						
Mean	19.0	4.8	0.4	0.1	1.0	44.6
Standard Error	3.6	0.2	0.0	0.0	0.0	1.1
Median	8.0	4.7	0.4	0.1	1.1	44.0
Mode	1.0	4.2	0.4	0.1	1.1	53.2
Standard Deviation	20.9	1.4	0.2	0.0	0.0	5.9
Sample Variance	437.9	1.9	0.0	0.0	0.0	35.4
Kurtosis	-0.6	-0.7	0.3	0.7	14.0	-1.3
Skewness	0.8	0.2	1.0	1.1	-2.5	-0.1
Range	66.9	6.0	0.9	0.1	0.3	19.0
Minimum	0.0	2.0	0.1	0.1	0.8	34.2
Maximum	66.9	7.9	1.0	0.2	1.2	53.2
Sum	645.5	194.8	18.3	3.9	43.0	1337.3
Count	34.0	41.0	41.0	41.0	41.0	30.0
Eromanga Crudes						
Mean	17.3	4.5	0.4	0.1	1.1	46.0
Standard Error	1.5	0.1	0.0	0.0	0.0	0.5
Median	17.1	4.3	0.3	0.1	1.1	45.9
Mode	29.1	3.3	0.3	0.1	1.1	50.9
Standard Deviation	11.8	1.3	0.3	0.0	0.0	4.0
Sample Variance	139.8	1.7	0.1	0.0	0.0	16.1
Kurtosis	-0.1	1.6	28.2	12.1	5.9	-0.6
Skewness	0.5	1.1	4.6	3.0	-1.1	-0.1
Range	52.5	7.7	2.3	0.2	0.2	18.2
Minimum	0.6	1.7	0.2	0.0	0.9	36.7
Maximum	53.1	9.5	2.5	0.3	1.2	54.9
Sum	1122.3	538.9	49.2	10.2	129.1	2898.8
Count	65.0	120.0	120.0	120.0	120.0	63.0

1. $<C_{15}$ = % weight loss of the whole oil by evaporation of volatile components over 24 hrs at room temperature
2. OEP = Odd over even predominance at n-C_{23} in normal alkane distribution $= (C_{21} + 6C_{23} + C_{25})/(4C_{22} + 4C_{24})$
3. Pr = Pristane,
4. Ph = Phytane

which the oil solidifies and is controlled by the wax content (essentially C_{23+} *n*-alkanes). The lower the pour point, the smaller the proportion of waxy, long-chain *n*-alkanes. The pour point of petroleum reservoired in the Cooper Basin ranges from –25 to 35°C (Hunt et al., 1989), whereas crudes from the Eromanga Basin have pour points that are marginally higher (–10 to 40°C: Heath et al., 1989).

2.9.3 API GRAVITY

Because of their high contents of gasoline and kerosine-range (C_5–C_{12}) hydrocarbons, the Cooper and Eromanga petroleums are typically medium to light (30–60° API: Heath et al., 1989; Hunt et al., 1989; Powell et al., 1989). Boreham and Hill (1998) reported an API range of 34–55° for 93 selected oils from South Australia and Queensland (see Table 2.1). Surprisingly, there is no significant difference between the Eromanga (range = 36.7–54.9°, mean = 46.0°, n = 63) and the Cooper (range = 34.2–53.2°, mean = 44.6°, n = 30) crudes. Powell and co-workers reported that the API gravities of oils from the Murta Formation, the shallowest of the main reservoirs, were at the top of the range (48–52°), although some heavier examples are cited by Boreham and Hill (as low as 41.2°).

2.9.4 LIGHT HYDROCARBON CONTENT

Light oils contain proportionally more volatile ($<C_{15}$) components than do heavy oils. The percentage of such components in the Cooper and Eromanga crudes varies from 0 to 66.9%, with a mean of 17.8% (Table 2.1). Based on the statistical means, Cooper crude (19%) is only slightly richer in volatile hydrocarbons than the average Eromanga crude (17.3%).

It must be kept in mind that the chemical composition of a crude oil changes very much during its passage from the sub-surface reservoir to the surface (England et al., 1987). Under the higher temperature and pressure conditions in the reservoir the oil contains far more methane and other gaseous components (hydrocarbons and non-hydrocarbons) than under the surface conditions. Methane and other volatile hydrocarbons are lost due to evaporation. This is a very significant factor that influences the measuring of properties such as API gravity and gasoline content. Handling procedures, including storage time and conditions, must be taken into account whenever these data are used to compare oils.

2.9.5 PRISTANE/PHYTANE

The pristand/phytane ratio (Pr/Ph) has long been regarded as a parameter indicating the redox potential of the source rock depositional environment and hence it is used in oil-to-oil and oil-to-source correlations (Powell and McKirdy, 1973; Didyk et al., 1978). However, Alexander et al. (1981) found that it could also be influenced by thermal maturation. The Pr/Ph ratio in Cooper and Eromanga Basin crudes varies from 1.7 to 9.5, with a statistical mean of 4.6 (Table 2.1). Values for the Cooper oils (range = 2.0–7.9, mean = 4.8) are similar to those of the Eromanga crudes (range = 1.7–9.5, mean = 4.5).

2.9.6 PRISTANE/N-HEPTADECANE AND PHYTANE/N-OCTADECANE

These isoprenoid/*n*-alkane ratios are both source and maturity dependent (Tissot and Welte, 1984). Among the 161 oils from the Cooper and Eromanga Basins analysed by Boreham and Hill (1998), the Pr/nC$_{17}$ ratio varies from 0.1 to 2.5, and the statistical mean is 0.4 (Table 2.1). The 41 Cooper oils (range = 0.1–1.0, mean = 0.4) differ little from the 120 Eromanga oils (range = 0.2–2.5, mean = 0.4). Similarly, the Ph/nC$_{18}$ ratio provides no discrimination between oils from the two basins (Table 2.1).

2.9.7 ODD-EVEN PREDOMINANCE IN N-ALKANES

The relative abundance of odd versus even carbon-numbered *n*-alkanes (OEP) may be used to obtain a rough estimate of the thermal maturity of non-marine petroleum source rocks and crude oils (Scalan and Smith, 1970). OEP values decrease with increasing source rock maturity, and are close to 1 in most crude oils (Tissot and Welte, 1984). However, although the Eromanga oils are less mature than those from the deeper Cooper reservoirs, their OEP values are essentially the same (Table 2.1). The 41 Cooper oils have OEP values in the range 0.8 to 1.2 (mean = 1.0), compared with 0.9 to 1.2 (mean = 1.1) for the 120 Eromanga oils.

2.10 OIL-SOURCE CORRELATION

Given the inability of the previously discussed geochemical parameters to distinguish different genetic families of oil in the Cooper and Eromanga petroleum province, other methods are needed for this purpose.

2.10.1 GASOLINE-RANGE HYDROCARBONS

Variations in the distribution of gasoline-range hydrocarbons (C_5–C_{10}) have been used to identify oils of different source and maturity (e.g. Thompson, 1987; Mango, 1990). The first geochemical studies of light hydrocarbons in oils from the Cooper and Eromanga Basins were by McKirdy (1985), Vincent et al. (1985) and Michaelsen and McKirdy (1989). However, one problem with this approach is that the gasoline fraction is very sensitive to alteration. For example, the concentrations of some light aromatic hydrocarbons, such as benzene, toluene and xylene, in crude oils are strongly influenced by fractionation during secondary migration and by other secondary alteration processes (Carpentier et al., 1996; Thompson, 1987, 1988).

Heath et al. (1989), Boreham and Hill (1998) and Boreham and Summons (1999) reported higher toluene/*n*-heptane ratios in the Cooper Basin oils compared to those in the Eromanga Basin. This was ascribed to the effects of fractionation on the Cooper-sourced petroleums during their long-distance migration and to water-washing of oils (of both Permian and Jurassic or Cretaceous origin) within the Eromanga reservoirs. This is consistent with the fact that the Eromanga Basin is actually part of the Great Artesian Basin, and that the Hutton Sandstone is one of the most significant aquifers in the region (Habermehl, 1986; Alexander, 1996a). This could be the only parameter that can effectively distinguish the Eromanga-reservoired oils from the Cooper-reservoired petroleums. The indigenous Cooper oils and condensates normally contain high concentrations of light aromatic hydrocarbons, whereas the Eromanga oils show very low concentrations regardless of their source. This problem will be reviewed and discussed extensively in Chapter 4.

2.10.2 BIOMARKERS

The distributions of conventional biomarkers (*n*-alkanes, acyclic isoprenoids, steranes and triterpanes) in oils from the Cooper and Eromanga Basins are extremely similar (Vincent et al., 1985; Jenkins, 1989). This is not surprising, as they have been generated from source rocks deposited under similar (fluvio-lacustrine) environments (Michaelsen and McKirdy, 1996; Boreham and Hill, 1998). However, some special biomarkers do occur in certain Eromanga oils. Alexander et al. (1988) identified age- and source-specific biomarkers derived from the resins produced by fossil Araucariacean conifers in source rocks of the Early Jurassic to Early Cretaceous sequence of the Eromanga Basin. In addition, Jenkins (1989) proposed that 25,28,30-trisnorhopane, 25,28,30-trisnormoretane (demethylated triterpanes of bacterial origin) and 19-norisopimarane (a diterpane of conifer resin origin) were Eromanga-specific biomarkers. He used the contents of these triterpanes to assess the hydrocarbon contribution of Eromanga petroleum kitchens to individual oil accumulations (maximum 40%, average <20% by volume). This will be discussed further in Chapter 5.

2.10.3 CARBON ISOTOPIC COMPOSITION OF N-ALKANES

The carbon isotopic composition of the various fractions of source rock bitumens and crude oils (saturated hydrocarbons, aromatic hydrocarbons, NSO compounds and asphaltenes) has long been used to identify different oil families, and in oil-source correlations (e.g. Sofer, 1984.; Al Arouri et al., 1998). The use of a Sofer-type $\delta^{13}C$ saturates *versus* $\delta^{13}C$ aromatics crossplot to distinguish oil families in the Cooper and Eromanga Basins was only partly successful (McKirdy, 1985; Vincent et al., 1985; Michaelsen and McKirdy, 1989).

GC-ir-MS (gas chromatography combined with isotope ratio-mass spectrometry) is a newly-developed technique which enables direct stable carbon isotope analysis of the effluent from a capillary gas chromatography column (Hayes et al., 1987; Freeman et al., 1990; Bjorøy et al., 1991). Carbon isotope compositions of individual *n*-alkanes in selected Cooper and Eromanga crude oils have recently been measured (Boreham and Hill, 1998; Boreham and Summons, 1999). The majority of these oils are characterised by *n*-alkane isotope profiles that become progressively lighter with increasing carbon number (i. e. they have negative *n*-alkane isotope gradients). The application of this technique to the recognition of oils with mixed sources will be discussed in more detail in Chapter 5.

2.10.4 MATURITY

Most of the sterane- and terpane-based maturity parameters (Peters and Moldowan, 1993) are not effective in distinguishing Cooper and Eromanga-sourced oils, because of the high maturity of the former crudes and their low concentrations in many condensates. Neither are the aromatic sterane parameters effective, because they also are not abundant enough. Under these circumstances, the methylphenanthrene index (MPI: Radke and Welte, 1983) has become the most important maturity parameter in describing the Cooper and Eromanga petroleums. Tupper and Burckhardt (1990), for example, used it to characterise the expulsion histories of the Cooper and Eromanga oils. Michaelsen and McKirdy (1989) and Powell et al. (1989) successfully employed it to demonstrate the unusually low maturities of Murta-derived oils. Generally speaking, the Cooper-derived crudes are more mature than the Eromanga-sourced oils, but there are many exceptions. Rc (calculated vitrinite reflectance based on MPI) of the Cooper petroleums ranges from 0.7 to 0.9%, while the Eromanga oils have Rc values ranging from 0.5 to 0.6%. The Rc maturities of the oils and condensates analysed here will be discussed in detail in Chapters 5 and 6.

CHAPTER THREE

MATERIALS, METHODS AND EXPERIMENTS

3.1 INTRODUCTION

The overall purpose of the present study was to analyse a suite of oil and core samples in order to gain further insights into the factors that control the variability of oil composition in the Cooper and Eromanga Basins. These factors may include multiple sources, migration and mixing of petroleum. The first part of the project involved the screening of 123 oil/condensate samples from wells distributed throughout the Cooper Basin and the overlying Eromanga Basin in both South Australia and Queensland, using whole-oil GC and GC-MS. The latter part of the study focussed on secondary migration. It was based on 53 core samples of source rock (coal, shale, siltstone) and reservoir/carrier bed sandstone, plus selected oils, from 11 wells in the Thurakinna, Garanjanie, Dirkala and Wancoocha Fields in the southwestern corner of the Cooper Basin (Figures 3.1 & 3.2).

The aforementioned samples were prepared and analysed using the joint facilities of two laboratories in Australia and Germany (viz. that of the Organic Geochemistry in Basin Analysis Group, Department of Geology and Geophysics, University of Adelaide; and the Laboratory for Organic and Environmental Geochemistry, Institute of Geology, University of Cologne). The techniques employed include gas chromatography (GC), gas chromatography combined with mass spectrometry (GC-MS), medium pressure liquid chromatography (MPLC), accelerated solvent extraction (ASE), Soxhlet extraction, ultrasonic extraction, solvent flow-through extraction (SFTE), thin-layer chromatography combined with flame ionisation detection (TLC-FID or IatroScan) and X-ray diffraction. Figure 3.3 summarises all these techniques in a flow chart.

All the whole oils/condensates were analysed directly by cryogenic GC-FID and GC-MS. Selected oils/condensates were evaporated under ambient conditions, and the residues were fractionated using MPLC. The saturate and aromatic fractions were analysed by GC-FID and GC-MS in Adelaide.

Cylindrical plugs (2 or 4 cm in diameter), oriented perpendicular to bedding, were cut from conventional cores of oil-bearing sandstones. The sequential extraction of residual "free" and "adsorbed" oils from these core plugs was carried out in Cologne using the solvent flow-through extraction (SFTE) device as described by Schwark et al. (1997). Employing this method, six fractions of extractable organic matter (EOM), inorganic salt and the residual sandstone plugs were obtained. The SFTE fractions were analysed on IatroScan-FID to determine their bulk chemical composition (i. e. contents of saturate hydrocarbons, aromatic hydrocarbons, NSO-compounds and asphaltene) and then fractionated by MPLC, yielding saturate, aromatic and resin fractions. The saturate and aromatic fractions were measured on GC-FID and GC-MS in the Adelaide laboratory. The inorganic salts were $AgNO_3$-tested and then analysed by X-ray diffraction. Selected residual (i.e. SFTE-extracted) sandstone plugs were ground and then extracted on ASE to test the efficiency of the SFTE. The EOM from ASE was weighed and analysed on IatroScan-FID.

Bulk samples of both source rock and reservoir/carrier bed sandstone lithofacies, taken from the same conventional cores from nine wells in the Thurakinna, Dirkala, Garanjanie and Wancoocha areas, were crushed and then Soxhlet- or ultrasonic-extracted. The EOM was deasphaltened (when necessary) and then fractionated by MPLC. The saturate and aromatic hydrocarbon fractions were analysed on GC-FID and GC-MS in the Adelaide laboratory.

In all cases (oils/condensates, residual oils and source rock extracts), the resin and asphaltene fractions were retained in Cologne for future analysis of nitrogen compounds (e.g. methylcarbazoles).

3.2 MATERIALS

3.2.1 OILS AND CONDENSATES

The oils and condensates assembled for this project are listed in Table 3.1, along with their basic geological information. Most of them are DST samples, the remainder being from production tests. The approximate locations of all the oil and gas fields in the South Australian sector of the study area are shown in Figure 3.1. Of the 123 oil/condensate samples, 11 (nos. 1–11) were provided by Santos specifically for the current PhD project; 43 (nos. 12–53, 91 and 92) were from the in-house collection of Associate Professor D.M. McKirdy and his Organic Geochemistry in Basin Analysis (OGBA) Group, Department of Geology and Geophysics, University of Adelaide; 27 (nos. 54–90) were from the personal collection of Dr N.M. Lemon, National Centre for Petroleum Geology and Geophysics (NCPGG); and 27 (nos. 93–119) had been previously donated by Santos for a recently completed PhD project (Kagya, 1997). The other four oils (nos. 120–123) were provided by the Department of Primary Industries and Resources, South Australia (PIRSA) for a pilot study of secondary migration of hydrocarbons in the Wancoocha area of the Cooper and Eromanga Basins.

GC-FID analysis of the whole oils and condensates, and comparison of the resulting chromatograms with those obtained from the artificial evaporation experiment (Section 3.3.6), allowed ready evaluation of sample quality (see last column and evaporation scale in footnote of Table 3.1). Two waxy oils (solid at room temperature) could not be analysed and one ‘condensate’ proved to be just water.

3.2.2 SANDSTONE CORE PLUGS

The Wancoocha, Dirkala, Garanjanie, and Thurakinna Fields (Figure 3.1) were selected as suitable for this study because of the availability of drill cores that intersected oil-impregnated sandstone and adjacent source rock lithologies. The presence of oil was indicated by fluorescence under UV light. A total of 48 pieces of core were obtained from the PIRSA Core Library.

A subset of 33 core samples were selected for plug drilling at the ACS Laboratory (Brisbane). The basic geological information on the plugs is given in Table 3.2. Figure 3.2 is a cross-section through the Wancoocha, Dirkala, Garanjanie, and Thurakinna Fields showing the approximate sampling depths of the core plugs.

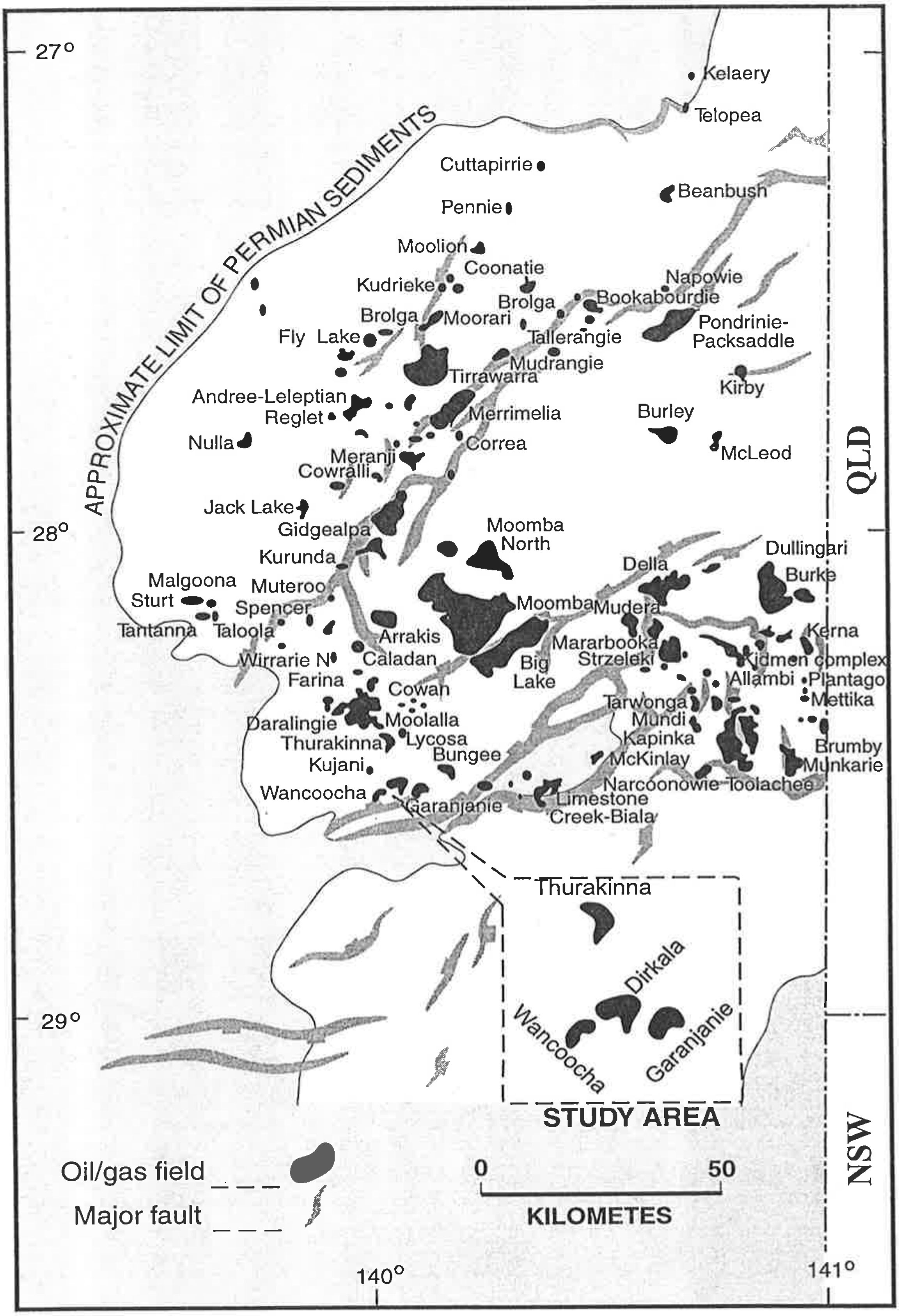


Figure 3.1 Locations of selected oil/gas fields in the Cooper and Eromanga Basins, South Australia. Insert shows the area of the secondary migration study.

Table 3.1 Oil and condensate samples: well, test, formation and quality

No*	GC run	WELL	DST #	TYPE	FORMATION	Quality**
1s	xyoil001	Tirrawarra-13	DST 4	Oil	Tirrawarra	4
2s	xyoil002	Tirrawarra-14	DST 3	Oil	Tirrawarra/Merrimelia	1, W
3s	xyoil003	Tirrawarra-64	DST 1	Oil	Tirrawarra	4
4s	xyoil004	Tirrawarra-70	DST 1	Oil	Tirrawarra	5
5s	xyoil005	Tirrawarra-70	DST 2	Cond	Patchawarra	4
6s	xyoil006	Taloola-1	DST 2	Oil	Namur	2
7s	xyoil007	Taloola-3	DST 2	Oil	Namur	2
8s	xyoil008	Taloola-2	DST 3	Oil	Namur	2
9s	xyoil009	Tantanna-2	DST 2	Oil	Namur	2
10s	xyoil010	Tantanna-1	DST 3	Oil	Birkhead/Namur	2,
11s	xyoil011	Tantanna-9	DST 3	Oil	McKinlay	2
12	xyoil012	Biala-1	DST 2	Oil	Namur	4
13	xyoil013	Mooliampah-1	DST 7	Oil	Adori	5
14	xyoil014	Munkah-2	DST 1	Cond	Patchawarra	2
15	xyoil015	Yanda-2	DST 2	Cond	Patchawarra	1
16	xyoil016	Kercummurra-1	DST 1	Oil	Cadna-Owie	5
17	xyoil017	Minkie-1	DST 4	Oil	Nappamerri	Waxy
18	xyoil018	Wilson-6	DST 2	Oil	Namur	5
19	xyoil019	Big Lake-37	DST 1	Oil	Birkhead	5
20	xyoil020	Mooliampah-1	DST 3	Oil	Namur	5
21	xyoil021	Epsilon-3	DST 5	Cond	Toolachee	4
22	xyoil022	Lepena-1	DST 3	Cond	Patchawarra	1
23	xyoil023	Epsilon-3	DST 3	Cond	Nappamerri	5
24	xyoil024	Spencer-4	DST 2	Oil	Birkhead	4
25	xyoil025	Wilson-6	DST 1	Oil	Hutton	4
26	xyoil026	Moolion-1	DST 1	Oil	Hutton	3
27	xyoil027	Tickalara-2	DST 5	Oil	Namur	4
28	xyoil028	Wancoocha-3	DST 3	Oil	Hutton	3
29	xyoil029	Jackson-28	DST 2	Oil	Westbourne	4
30	xyoil030	Tickalara-2	DST 1	Oil	Namur	5
31	xyoil031	Ulandi-1	DST 2	Oil	Namur	4
32	xyoil032	Wilson-2	DST 1	Oil	Murta	5
33	xyoil033	Kihee-2	DST 1	Oil	Murta	4
34	xyoil034	Thungo-2		Oil	Murta	5
35	xyoil035	Dilkera-2	DST 2	Oil	Murta	4
36	xyoil036	Maxwell-1		Oil	Murta	4
37	xyoil037	Maxwell-2	DST 1	Oil	Murta	5
38	xyoil038	Thungo-3		Oil	Murta	5
39	xyoil039	Thungo-1	DST 1	Oil	Murta	5
40	xyoil040	Maxwell South-1	DST 2	Oil	Murta	5
41	xyoil041	Thungo-1	DST 4	Oil	Westbourne	5
42	xyoil042	Thungo-4		Oil	Murta	5
43	xyoil043	Thungo-1		Oil	Murta	5

No*	GC run	WELL	DST #	TYPE	FORMATION	Quality**
44	xyoil044	Winna-1		Oil	Murta	3
45	xyoil045	Dilkera-2	DST 2	Oil	Murta	5
46	xyoil046	Nockatunga-4		Oil	Murta	5
47	xyoil047	Dilkera-1	DST 7	Oil	Murta	5
48	xyoil048	Koora-2	DST 4	Oil	Murta	3
49	xyoil049	Winna-2	DST 1	Oil	Murta	4
50	xyoil050	Winna-3	DST 1	Oil	Murta	3
51	xyoil051	Nockatunga-1		Oil	Murta	4
52	xyoil052	Maxwell-2		Oil	Murta	4
53	xyoil053	Nockatunga-3		Oil	Murta	4
54nl	xyoil054	Mooliampah-1	DST 2	Oil	Namur	4
55nl	xyoil055	Strzelecki		OIl	Namur	4
56nl	xyoil056	Meranji-1	DST 2	Oil	Namur	5
57nl	xyoil057	Tirrawarra-58	DST 3	Oil	Tirrawarra	4
58nl	xyoil058	Tirrawarra-57	DST 2	Oil	Tirrawarra	4
59nl	xyoil059	Gooranie-1	DST 2	Cond	Patchawarra	5
60nl	xyoil060	Merrimelia		Oil	Namur	5
61nl	xyoil061	Merrimelia-17	DST 4	Cond	Nappamerri	4
62nl	xyoil062	Wancoocha-2	DST 5	Oil	Hutton	3
63nl	xyoil063	Cook-1	DST 3	Oil	Hutton	4
64nl	xyoil064	Merrimelia		Oil	Nappamerri	5
65nl	xyoil065	Della-2		Cond	Toolachee	3
66nl	xyoil066	Woolkina		Oil	Tirrawarra	5
67nl	xyoil067	Moorari-3		Oil	Tirrawarra	4
68nl	xyoil068	Wancoocha-6		Oil	Murta	3
69nl	xyoil069	Wippo-1	DST 1	Cond	Patchawarra	4
70nl	xyoil070	Jackson South-4	DST 2	Oil	Birkhead	4
71nl	xyoil071	Moorari-3		Oil	Tirrawarra	1
72nl	xyoil072	Meranji-1	DST 5	Cond	Patchawarra	4
73nl	xyoil073	Jackson-2		Oil	Hutton	Waxy
74nl	xyoil074	Wilson South-1	DST 3	Oil	Hutton	3
75nl	xyoil075	Leleptian-1	DST 3	Cond	Patchawarra	1
76nl	xyoil076	Fly Lake-2		Oil	Tirrawarra	1
77nl	xyoil077	Merrimelia		Oil	Hutton	5
78nl	xyoil078	Daralingie		Cond	Permian	4
79nl	xyoil079	Alwyn-1	DST 1	Oil	Murta	5
80nl	xyoil080	Dullingari		Oil	Namur	5
81nl	xyoil081	Aroona-1	DST 3	Cond	Toolachee	3
82nl	xyoil082	Tirrawarra		Oil	Tirrawarra	5
83nl	xyoil083	Bagundi-1	DST 4	OIl	Patchawarra	1
84nl	xyoil084	Mooliampah-1	DST 1	Oil	Murta	5
85nl	xyoil085	Bookabourdie-4		Cond	Tirrawarra	4
86nl	xyoil086	Jackson-3		Oil	Westbourne	4
87nl	xyoil087	Nungeroo-1	DST 2	Oil	Namur	5
88nl	xyoil088	Nulla-1	DST 3	Cond	Patchawarra	3

No*	GC run	WELL	DST #	TYPE	FORMATION	Quality**
89nl	xyoil089	Daralingie-1		Cond	Patchawarra	4
90nl	xyoil090	Wancoocha-2	DST 4	Oil	Birkhead	2
91	xyoil091	Inland-1	DST 1	Oil	Hutton	4
92	xyoil092	Inland-1	DST 2	Oil	Namur	4
93m	xyoil093	Taloola-2	DST 1	Oil	Poolowanna	2
94m	xyoil094	Taloola-2	DST 2	Oil	Hutton	1
95m	xyoil095	Taloola-2	DST 3	Oil	Namur	1
96m	xyoil096	Tantana-1	DST 1	Oil	Poolowanna	3
97m	xyoil097	Tantana-1	DST 2	Oil	Hutton	1
98m	xyoil098	Tantana-1	DST 3	Oil	Namur	1
99m	xyoil099	Tantana-2	DST 1	Oil	Poolowanna	2
100m	xyoil100	Tantana-2	DST 2	Oil	Namur	1
101m	xyoil101	Tantana-9	DST 3	Oil	McKinlay	1
102m	xyoil102	Tantana-9	DST 4	Oil	Hutton	3
103m	xyoil103	Sturt-2	DST 1	Oil	Poolowanna	3 or 4
104m	xyoil104	Sturt-2	DST 2	Oil	Birkhead	1
105m	xyoil105	Sturt-3	DST 1A	Oil	Poolowanna	4
106m	xyoil106	Sturt-3	DST 1B	Oil	Birkhead	3 or 2
107m	xyoil107	Sturt-4	DST 1	Oil	Poolowanna	5
108m	xyoil108	Sturt-4	DST 2	Oil	Patchawarra	5
109m	xyoil109	Sturt-5	DST 1	Oil	Patchawarra	5
110m	xyoil110	Sturt-6	DST 1	Oil	Birkhead	1
111m	xyoil111	Sturt-6	DST 3	Oil	Patchawarra	4
112m	xyoil112	Sturt-6	DST 5	Oil	Patchawarra	3
113m	xyoil113	Sturt-7	DST 2	Oil	Mooracoochie	4
114m	xyoil114	Sturt-7	DST 3	Oil	Patchawarra	3
115m	xyoil115	Sturt-7	DST 5	Oil	Patchawarra	2
116m	xyoil116	Sturt-7	DST 4	Oil	Patchawarra	3
117m	xyoil117	Sturt-8	DST 1	Oil	Patchawarra	2
118m	xyoil118	Sturt East-2	DST 1	Oil	Patchawarra	2
119m	xyoil119	Poolowanna	DST 2	Oil	Poolowanna	Waxy
120p	xyoil120	Wancoocha-2	DST 3	Oil	Patchawarra	4
121p	xyoil121	Garanjanie-1	DST 1	Oil	Murta	4
122p	xyoil122	Dirkala-1	DST 1	Cond	Birkhead	3
123p	xyoil123	Dirkala-1	DST 6	Oil	Namur	4

*s Samples from Santos Limited
*m Samples from PhD study of Kagya (1997)
*p Samples provided by PIRSA
*nl Samples from N. M. Lemon (NCPGG)
All the remaining samples were from D. M. McKirdy's in-house collection
**1-5 Sample evaporation scale:
1 = very severe;
2 = severe;
3 = moderate;
4 = slight;
5 = very slight
**W Water

All the core plugs were extracted using SFTE, but only twenty contained enough EOM to satisfy the requirements for further analysis. The discussion in Chapter 6 is based mainly on the source and maturity data obtained from the residual oils in these twenty core plugs. Their lithological descriptions are included in Table 3.4.

3.2.3 CONVENTIONAL CORES

In addition to the aforementioned sandstone core plugs, another twenty conventional bulk core samples of both sandstones and putative source rocks were taken for comparative study. Their basic geological information is listed in Tables 3.3 & 3.4. The conventional core samples cover a wide spectrum of lithology (viz. sandstone, siltstone, shale and coal) and stratigraphy (viz. Murta Formation; Birkhead Formation; Epsilon Formation; and Patchawarra Formation: Figurre 3.2).

3.2.4 ORGANIC SOLVENTS

All AR grade organic solvents were distilled before use. In this project, the following solvents were used: *n*-hexane (for MPLC), methanol (for Soxhlet extraction, ultrasonic extraction, SFTE and MPLC), dichloromethane (for Soxhlet extraction, ultrasonic extraction, SFTE, ASE and IatroScan), petroleum ether (for deasphaltening), trichloromethane (for SFTE), benzene (for IatroScan), and toluene (for IatroScan). Occasionally, high purity commercial *n*-hexane and dichloromethane were used, directly, in diluting of samples for GC and GC-MS analysis.

3.2.5 SILICA GEL AND OTHER CHEMICAL REAGENTS

Silica gel was used in MPLC fractionation. For the pre-column, Silica Gel 100 (0.2-0.5 mm) and Silica Gel 100 (0.063-0.2 mm) were packed. The coarser silica gel was activated by heating for two hours at 600°C, and the finer one was activated by heating for one hour at 200°C. Silica Gel 60Å, activated by heating at 120°C, was packed in the main column.

Deionised water and AR grade silver nitrate were employed in processing the methanol-soluble inorganic salt(s) obtained from the SFTE of some core plugs.

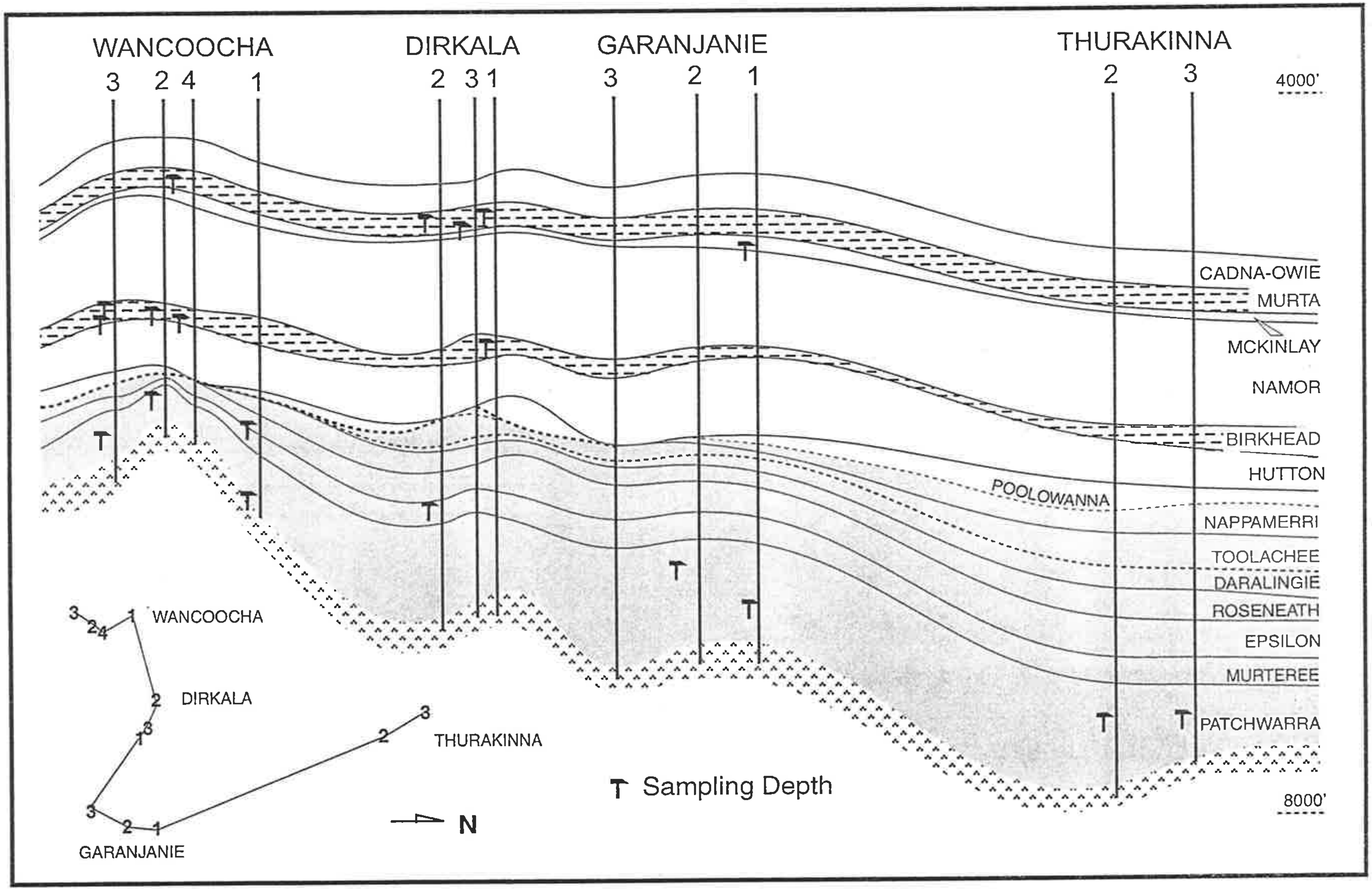


Figure 3.2 Sampling depths of the cores and oils for secondary migration study

Table 3.2 Sandstone core plug samples: well, depth, formation and lithology

Cologne No	UAUK No	Sample Type	Well	Depth (m) Middle	Depth (m) Top	Depth(m) Base	Top Depth (ft)	Top Depth (inch)	Base Depth (ft)	Base Depth (inch)	Formation Top	Formation Base	Lithology
980511	1	Core plug 1	Dirkala-1	1624.73	1624.71	1624.76	5330	5	5330	7	Birkhead	Birkhead	Sandstone
980512	3	Core plug 2	Dirkala-1	1626.81	1626.79	1626.84	5337	3	5337	5	Birkhead	Birkhead	Sandstone
980513	4	Core plug 3	Dirkala-1	1628.85	1628.80	1628.90	5343	10	5344	2	Birkhead	Birkhead	Sandstone
980514	5	Core plug 4	Dirkala-1	1631.88	1631.82	1631.95	5353	9	5354	2	Birkhead	Birkhead	Sandstone
980515	6	Core plug 5	Dirkala-1	1633.51	1633.44	1633.57	5359	1	5359	6	Birkhead	Birkhead	Sandstone
980516	7	Core plug 6	Dirkala-1	1637.84	1637.79	1637.89	5373	4	5373	8	Birkhead	Birkhead	Sandstone
980517	9	Core plug 7	Dirkala-2	1890.30	1890.24	1890.37	6201	7	6202	0	Murteree	Murteree	Sandstone
980518	11	Core plug 8	Dirkala-2	1894.96	1894.91	1895.01	6216	11	6217	3	Murteree	Murteree	Sandstone
980519	12	Core plug 9	Dirkala-3	1398.34	1398.32	1398.37	4587	8	4587	10	Murta	Murta	Sandstone
980520	13	Core plug 10	Dirkala-3	1407.66	1407.63	1407.69	4618	2.5	4618	5	Murta	Murta	Sandstone
980521	14	Core plug 11	Dirkala-3	1411.28	1411.22	1411.35	4630	0	4630	5	Murta	Murta	Sandstone
980522	15	Core plug 12	Garanjanie-2	2012.03	2011.98	2012.08	6601	0	6601	4	Patchwarra	Patchwarra	Sandstone
980523	17	Core plug 13	Garanjanie-2	2016.50	2016.48	2016.53	6615	9	6615	11	Patchwarra	Patchwarra	Sandstone
980524	19	Core plug 14	Garanjanie-2	2022.39	2022.34	2022.45	6635	0	6635	4	Patchwarra	Patchwarra	Sandstone
980525	21	Core plug 15	Thurakinna-2	2282.99	2282.95	2283.02	7490	0	7490	3	Patchwarra	Patchwarra	Sandstone
980526	22	Core plug 16	Thurakinna-2	2289.63	2289.60	2289.65	7511	10	7512	0	Patchwarra	Patchwarra	Sandstone
980527	24	Core plug 17	Thurakinna-2	2295.36	2295.32	2295.39	7530	7	7530	10	Patchwarra	Patchwarra	Sandstone
980528	25	Core plug 18	Thurakinna-3	2275.91	2275.89	2275.94	7466	10	7467	0	Patchwarra	Patchwarra	Sandstone
980529	26	Core plug 19	Thurakinna-3	2277.73	2277.69	2277.77	7472	9	7473	0	Patchwarra	Patchwarra	Sandstone
980530	29	Core plug 20	Thurakinna-3	2285.89	2285.87	2285.92	7499	7	7499	9	Patchwarra	Patchwarra	Sandstone
980531	30	Core plug 21	Thurakinna-3	2287.25	2287.21	2287.28	7504	0	7504	2.5	Patchwarra	Patchwarra	Sandstone
980532	32	Core plug 22	Wancoocha-1	1773.04	1773.02	1773.06	5817	0	5817	1.5	Epsilon	Epsilon	Sandstone
980533	33	Core plug 23	Wancoocha-1	1773.75	1773.68	1773.83	5819	2	5819	8	Epsilon	Epsilon	Sandstone
980534	35	Core plug 24	Wancoocha-1	1889.70	1889.63	1889.78	6199	7	6200	1	Patchwarra	Patchwarra	Sandstone
980535	36	Core plug 25	Wancoocha-1	1890.48	1890.44	1890.52	6202	3	6202	6	Patchwarra	Patchwarra	Sandstone
980536	37	Core plug 26	Wancoocha-3	1564.10	1564.08	1564.13	5131	6	5131	8	Birkhead	Birkhead	Sandstone
980537	39	Core plug 27	Wancoocha-3	1565.38	1565.31	1565.46	5135	6.5	5136	0.5	Birkhead	Birkhead	Sandstone
980538	40	Core plug 28	Wancoocha-3	1573.11	1571.39	1574.82	5155	6	5166	9	Birkhead	Birkhead	Sandstone
980539	42	Core plug 29	Wancoocha-3	1770.34	1770.25	1770.44	5807	11	5808	6.5	Patchwarra	Patchwarra	Sandstone
980540	44	Core plug 30	Wancoocha-3	1779.14	1779.11	1779.18	5837	0	5837	2.5	Patchwarra	Patchwarra	Sandstone
980541	46	Core plug 31	Wancoocha-4	1561.19	1561.13	1561.26	5121	10	5122	3	Birkhead	Birkhead	Sandstone
980542	47	Core plug 32	Wancoocha-4	1563.43	1563.37	1563.49	5129	2	5129	7	Birkhead	Birkhead	Sandstone
980543	48	Core plug 33	Wancoocha-4	1566.25	1566.21	1566.29	5138	6	5138	9	Birkhead	Birkhead	Sandstone

Table 3.3 Conventional core samples: well, depth, formation and lithology

Cologne No	UANK No	Sample Type	Well	Depth(m) Middle	Depth (m) Top	Depth (m) Base	Formation Top	Formation Base	Lithology
980544	49	Core 1	Dirkala-1	1634.78	1634.71	1634.84	Birkhead	Birkhead	Sandstone
980545	50	Core 2	Dirkala-1	1638.12	1638.09	1638.14	Birkhead	Birkhead	Sandstone
980546	51	Core 3	Dirkala-2	1888.99	1888.98	1889.01	Epsilon	Epsilon	Coal
980547	52	Core 4	Dirkala-3	1399.40	1399.36	1399.43	Murta	Murta	Heterolithic
980548	53	Core 5	Dirkala-3	1407.59	1407.57	1407.60	Murta	Murta	Silty shale
980549	54	Core 6	Garanjanie-1	2018.89	2018.88	2018.90	Patchawarra	Patchawarra	Coal
980550	55	Core 7	Garanjanie-1	2023.87	2023.87	2023.87	Patchawarra	Patchawarra	Sandstone
980551	56	Core 8	Garanjanie-1	2028.50	2028.50	2028.50	Patchawarra	Patchawarra	Sandstone
980552	57	Core 9	Thurakinna-2	2286.96	2286.96	2286.96	Patchawarra	Patchawarra	Siltstone
980553	58	Core 10	Thurakinna-2	2296.71	2296.71	2296.71	Patchawarra	Patchawarra	Shale, Coal
980554	59	Core 11	Thurakinna-3	2279.53	2279.52	2279.52	Patchawarra	Patchawarra	Sandstone
980555	60	Core 12	Wancoocha-1	1881.98	1881.98	1881.98	Patchawarra	Patchawarra	Coal
980556	61	Core 13	Wancoocha-1	1890.64	1890.64	1890.64	Patchawarra	Patchawarra	Coal
980557	62	Core 14	Wancoocha-3	1568.24	1568.24	1568.24	Birkhead	Birkhead	Sandstone
980558	63	Core 15	Wancoocha-3	1768.60	1768.60	1768.60	Patchawarra	Patchawarra	Sandstone
980559	64	Core 16	Wancoocha-3	1772.00	1772.00	1772.00	Patchawarra	Patchawarra	Sandstone
980560	65	Core 17	Wancoocha-3	1777.13	1777.13	1777.13	Patchawarra	Patchawarra	Coal
980561	66	Core 18	Wancoocha-4	1560.57	1560.57	1560.57	Birkhead	Birkhead	Sandstone
980562	67	Core 19	Wancoocha-4	1563.94	1563.90	1563.98	Birkhead	Birkhead	Siltstone
980563	68	Core 20	Wancoocha-4	1564.79	1564.79	1564.79	Birkhead	Birkhead	Coal

Table 3.4 Lithological descriptions of the analysed sandstone core plugs and conventional core samples (taken from well completion reports)

Sample	Well	Depth (m)	Formation	Lithology Description and Comments
980511	Dirkala-1	1624.7	Birkhead	Massive sandstone: clear to translucent, fine, minor and coarse, moderately well sorted, subangular to commonly subrounded, weak to moderate siliceous cement, minor to moderate white argillaceous matrix, trace lithics, common quartz overgrowths, fair to good visual porosity, strong fluorescence
980512	Dirkala-1	1626.8	Birkhead	Same as above, but thick siltstone underlying the sampling interval within 30 cm.
980513	Dirkala-1	1628.9	Birkhead	Massive sandstone: translucent to off white, occasionally fine, trace very fine, moderately well sorted, subangular to subrounded, moderate siliceous cement, moderate white argillaceous matrix, minor brown silty matrix, trace micromicaceous and carbonaceous specks, poor visual porosity, strong fluorescence. Close contact with siltstone on both the top within 10 cm and the bottom within 30 cm.
980514	Dirkala-1	1631.9	Birkhead	Sandstone: translucent, light grey, occasionally clear, fine to occasionally medium, moderately well sorted, subangular to commonly subrounded, week siliceous cement, common quartz overgrowths, minor to occasionally moderate white argillaceous matrix, trace lithics, firm to friable, fair visual porosity, strong fluorescence. Siltstone occurs around the sampling interval, within 10 cm at the bottom and 30 cm on the top.
980515	Dirkala-1	1633.5	Birkhead	Same as above, with trace siltstone around
980516	Dirkala-1	1637.8	Birkhead	Massive sandstone: clear to translucent, medium, minor and coarse, moderately well sorted, subangular to commonly subrounded, occasionally rounded, weak siliceous cement, common quartz overgrowths, trace to minor white argillaceous matrix, commonly clean, predominantly friable, occasionally firm, fair to good visual porosity, no fluorescence.

980517	Dirkala-2	1890.3	Murteree	Sandstone: light grey, very fine to medium, well sorted, subrounded, weak siliceous cement, white silty matrix, microcarbonaceous, plant root horizons, carbonaceous laminae with abundant muscovite, becoming thicker and more common with depth, very poor to fair visual porosity, rare vertical fractures. Fluorescence: trace, dull pale green/yellow with weak pale green yellow crush, thin ring to trace residue. Siltstone occurs around the sampling interval, one metre above is 60 cm-thick siltstone, a metre below very thick siltstone (several metres).
980518	Dirkala-2	1895.0	Murteree	No clear record, surrounded by siltstone, organic matter is probably in situ.
980519	Dirkala-3	1398.3	Murta	Sandstone: off white to colourless, very fine to fine, moderately to moderately well sorted, subrounded, siliceous cement, trace argillaceous matrix, rare lithic fragment, friable, poor porosity, no fluorescence.
980522	Garanjanie-2	2012.0	Patchawarra	Sandstone: light grey–brown, generally medium, occasionally very fine to fine, occasional bands pebbles, well to very poorly sorted, subangular to subrounded, common quartz overgrowths, siliceous cement, argillaceous matrix, friable to moderately hard, common carbonaceous grains, flecks and laminations in part, poor to fair visual porosity. Trace siltstone occurs below the sampling interval (10 cm).
980523	Garanjanie-2	2016.5	Patchawarra	Similar sandstone as above but surrounded by coal laminae in the top and bottom, which may influence the hydrocarbon composition of the organic matter in the sandstone. Siltstone occurs around the sampling interval (3 cm below and 2 cm above).
980528	Thurakinna-3	2275.9	Patchawarra	Sandstone with finely laminated carbonaceous siltstone, minor coaly laminae. Sandstone: clear to buff, fine to medium, silty, subangular, moderate sorting. Argillaceous siltstone: black to dark grey, argillaceous, highly carbonaceous. Abundant siltstone occurs in the sampling interval.
980529	Thurakinna-3	2277.7	Patchawarra	Same as above, but near siltstone on the top.

980531	Thurakinna-3	2287.0	Patchawarra	Interlaminated sandstone and siltstone. Sandstone: light grey brown, medium to coarse, clean to slightly argillaceous, well sorted, subangualr to subrounded, minor carbonaceous fragments and lithics. Siltstone: dark grey, argillaceous. Trace dull orange fluorescence, slow diffuse cut. Siltstone occurs around the sampling interval.
980536	Wancoocha-3	1564.1	Hutton	Sandstone with very minor interbeded siltstone. Sandstone: clear, rarely off white, medium grained, occasionally coarse grained, well sorted, angular to subrounded, week recrystallised siliceous cement, carbonaceous material and lithics, very friable, good visual porosity. Siltstone: brown, arenaceous, micromicaceous, carbonaceous, blocky, firm. Fluorescence: 100% bright yellow white patchy to solid fluorescence. Moderate to strong streaming moderately thick to thick ring residue.
980537	Wancoocha-3	1565.4	Hutton	Lithology same as above but less fluorescence: 30% dull yellow patchy, weak crush cut, very thin ring residue decreasing with depth.
980539	Wancoocha-3	1770.3	Patchawarra	Sandstone with rare interbedded siltstone. Sandstone: clear to light brown, medium to coarse grained, conglomeratic within the sampling interval, good visual porosity. Siltstone: dark grey to black, very carbonaceous, locally arenaceous, minor micaceous material, firm to moderately hard. Fluorescence: 100% moderately bright to bright yellow white patchy to solid, fast to very fast streaming cut, thick ring residue. It is conglomeratic in the sampling interval.
980540	Wancoocha-3	1779.1	Patchawarra	Same as above, but the sandstone within the sampling interval is very thin and sounded by siltstone. Its organic content is most likely be in situ or strongly influenced by the bitumen in the siltstone.
980541	Wancoocha-4	1561.2	Birkhead	Massive sandstone with minor siltstone clasts and coal spar. Sandstone: off white, fine to medium grained, subangular, moderately well sorted, occasional siliceous cement, trace carbonaceous flecks, friable to firm, fair to good visual porosity. Siltstone: dark grey, argillaceous in parts, carbonaceous in parts, firm to moderately hard. Coal: Black, earthy to vitreous brittle. Fluorescence: 100% moderately

				bright, solid, occasionally patchy, white fluorescence, slow streaming cut, thick ring to thin residue. Abundant siltstone in the sampling interval.
980542	Wancoocha-4	1563.4	Birkhead	Same as above. Thick siltstone 15 cm below.
980544	Dirkala-1	1634.8	Birkhead	Similar to 980515
980545	Dirkala-1	1638.1	Birkhead	Sandstone similar to that in 980515. The deepest sandstone sample within the Birkhead Formation, the furthest one away from the siltstone. Its petroleum should bear more deeper-sourced hydrocarbon fingerprint.
980554	Thurakinna-3	2279.5	Patchawarra	Sandstone: similar to 980528 and 980531, but relatively far away from siltstone.
980557	Wancoocha-3	1568.2	Birkhead	Sandstone: Same as in 980536, but 4 metres deeper. There exist 4 layers of blocky, firm carbonaceous siltstone between them. It could be more appropriate to treat 980557 as pure Hutton Sandstone, because there is nearly no siltstone below this interval. Hydrocarbons in Plug 980536 are probably more in situ than those in Core 980557.
980558	Wancoocha-3	1768.6	Patchawarra	Sandsotne: same as in Plug 980539, but not conglomeratic at all.
980559	Wancoocha-3	1772.0	Patchawarra	Sandstone: predominantly light brown to clear, coarse to very conglomeratic, moderate to well sorted, subangular to subrounded, week siliceous cement, very carbonaceous, plant fragments, very friable, excellent vugular porosity. Fluorescence: 100% bright white, solid fluorescence. Instant streaming cut, thin ring residue.
980561	Wancoocha-4	1560.6	Birkhead	Massive sandstone with siltstone clasts. Sandstone: off white, light grey, very fine to fine grained, occasionally medium, subangular to subrounded, moderately well sorted, siliceous cement, white argillaceous matrix, trace carbonaceous flecks, friable to moderately firm, poor to fair visual porosity. Fluorescence: 100% moderately bright to rarely bright, occasionally patchy, white fluorescence, moderately fast to fast streaming cut, thin ring to thin film residue. Siltstone: dark grey, occasionally black, argillaceous, hard.

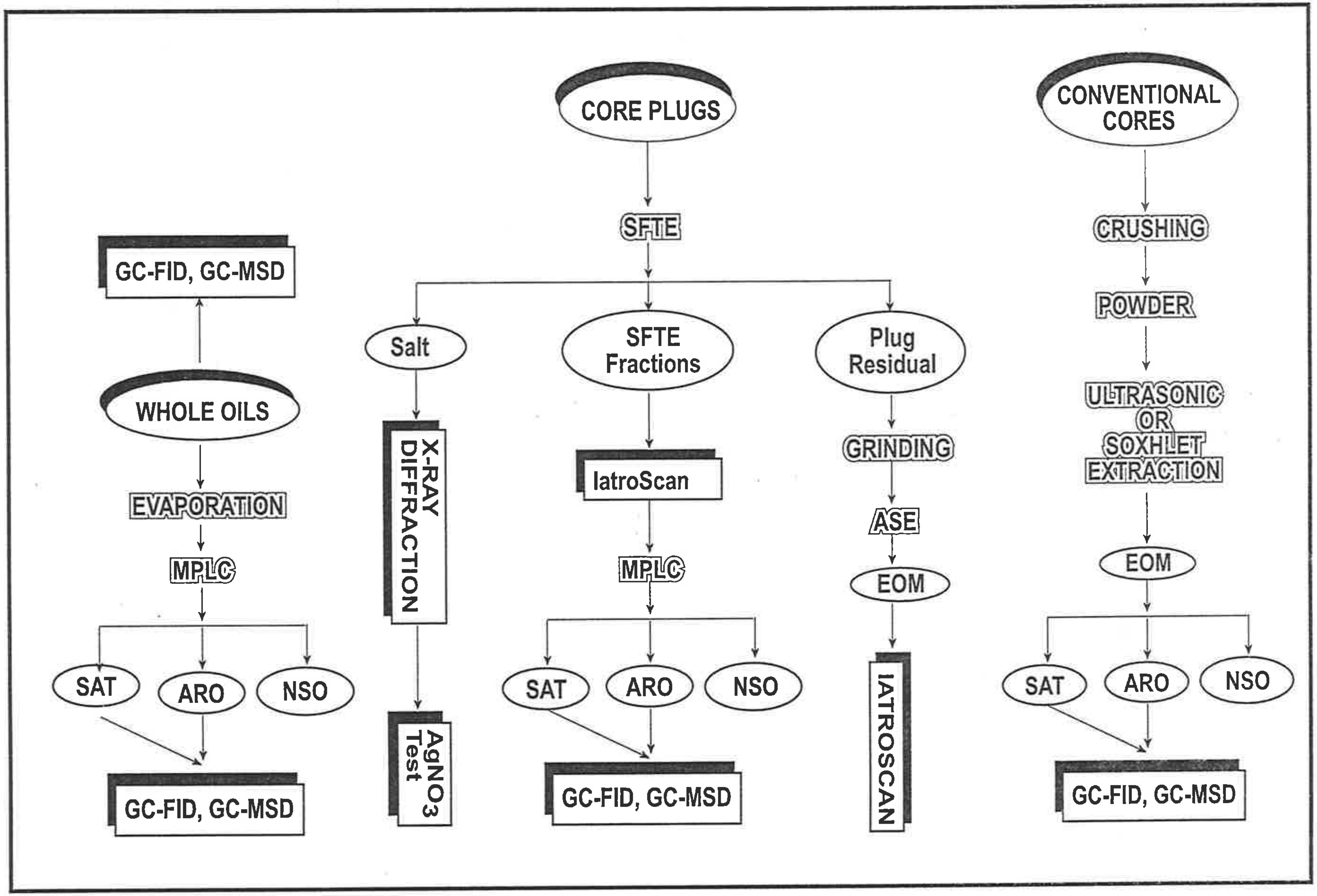


Figure 3.3 Flow chart of sample preparation and analysis

3.3. METHODS AND EXPERIMENTS

3.3.1 CRYOGENIC GC-FID INSTRUMENT

The whole research project was made possible by the recent purchase of a new Hewlett-Packard (HP) 6890 gas chromatograph (GC) coupled to a flame ionisation detector (FID) and a HP5973 mass selective detector (MSD). In addition to all the advanced features of the modern GC-FID and GC-MSD, it is also equipped with an electronic pneumatics control (EPC) and liquid nitrogen cryogenic system (NCS). Flow rate and/or pressure of the carrier gas and the gas supply to the FID and MSD are controlled precisely by the EPC. The oven temperature can be set much lower (–80°C) than the ambient temperature by using the liquid nitrogen cryogenic facility. By appropriately adjusting the EPC and NCS, it is not difficult to obtain high resolution for a whole-oil sample, across the entire range of C_3 to C_{45} hydrocarbons, with just one conventional 30-metre fused silica capillary column. The GC conditions developed in our laboratory can even quantitatively resolve methane and ethane.

3.3.2 GC-FID OF WHOLE OILS AND CONDENSATES

Cryogenic GC-FID analysis of the untopped oils and condensates was carried out on the aforementioned HP 6890 GC system. Depending on the gasoline content of the sample, 0.5 μl to 1.0 μL of crude oil/condensate was injected with a split ratio of 200:1 under an inlet temperature of 280 °C. Two minutes after the injection, the split flow was automatically reduced from 198.8 ml/min to 20 mL/min by the gas saver. The GC was fitted with a 30 m x 0.25 mm (i. d.) HP-5 fused silica capillary column coated with cross-linked 5% phenylmethylsiloxane (0.25 μm film thickness). Helium was used as carrier gas at a 6.8 psi head pressure to obtain a constant flow rate of 1.0 mL/min, or a linear velocity of 19 cm/sec. The oven temperature program was as follows: –60°C for 2 min; 20°C/min to 10°C and held for 1 min; 10°C/min to 20°C; 20°C/min to 40°C; 5.5°C/min to 240°C; 6°C/min to 310°C and held for 20 to 40 minutes. The FID temperature was 320°C. The flow rates to the detector were: hydrogen 30 mL/min and air 400 mL/min. A makeup gas flow of 29 mL/min (N_2)

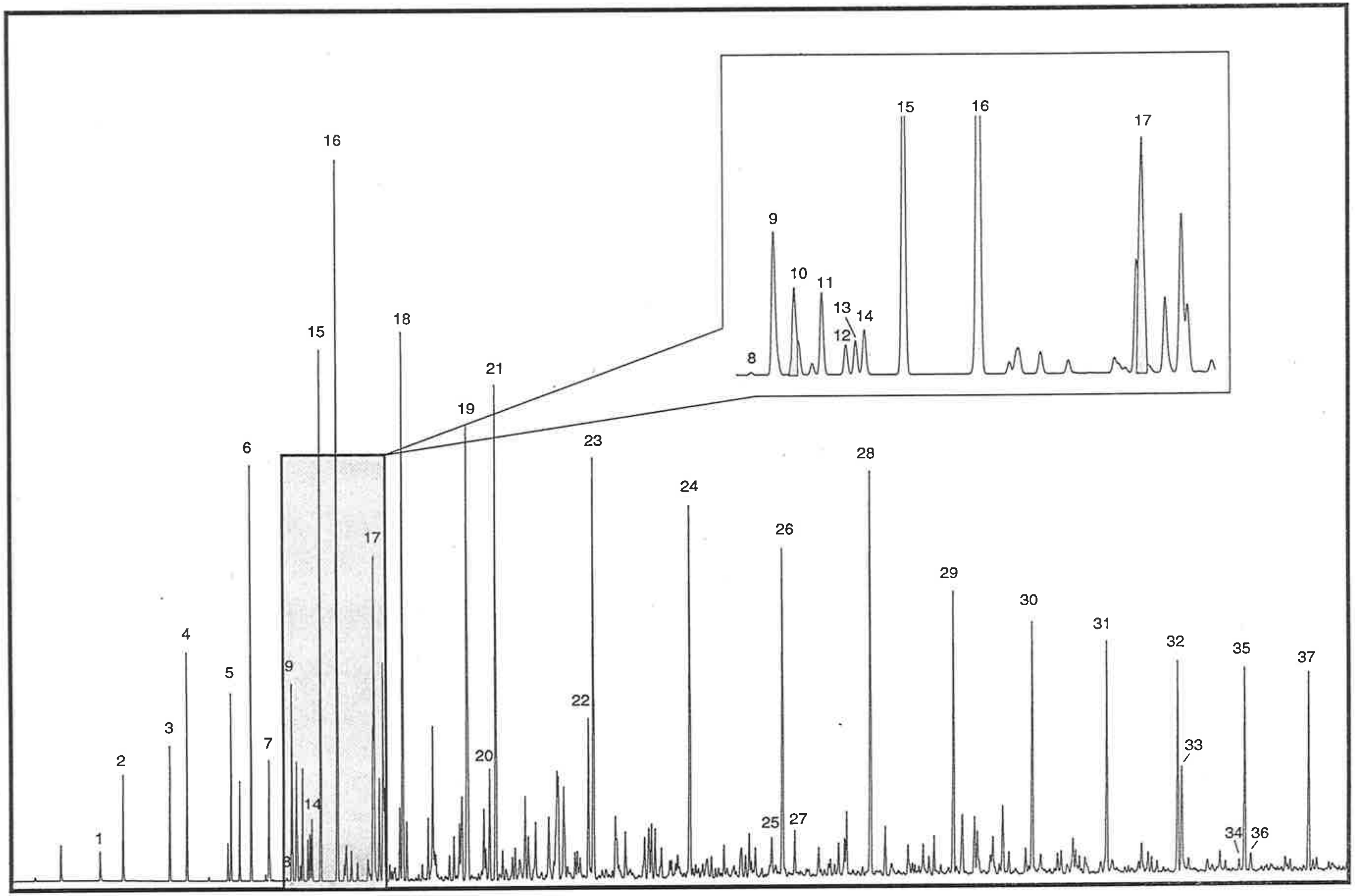


Figure 3.4 Typical GC-FID chromatogram of a whole oil with peak identification (see Table 3.5 for key)

Table 3.5 Peak identification in GC-FID analysis of whole oil

Peak No.	**Compound**	**Retention Time (min)**	**Standard RT (min)**
1	*iso*-butane	4.67	
2	*n*-butane	5.32	
3	*iso*-pentane	6.64	
4	*n*-pentane	7.13	
5	*iso*-hexane	8.37	
6	*n*-hexane	8.94	
7	methylcyclopentane	9.44	
8	benzene	9.94	9.94
9	cyclohexane	10.01	
10	2-methylhexane	10.21	
11	3-methylhexane	10.39	
12	*cis*-1,3-dimethylcyclopentane	10.54	
13	*trans*-1,3-dimethylcyclopentane	10.60	
14	*trans*-1,2-dimethylcyclopentane	10.66	
15	*n*-heptane	10.90	
16	methylcyclohexane	11.37	
17	toluene	12.41	12.41
18	*n*-octane	13.21	
19	xylene (p + m-)	15.03	15.07
20	unknown compound (o-xylene?)	15.67	15.68
21	*n*-nonane	15.84	
22	1,2,4-trimethylbenzene	18.46	
23	*n*-decane	18.60	
24	*n*-undecane	21.33	
25	naphthalene	23.65	
26	*n*-dodecane	23.95	
27	unknown compond	24.29	
28	*n*-tridecane	26.44	
29	*n*-tetradecane	28.79	
30	*n*-pentadecane	31.02	
31	*n*-hexadecane	33.13	
32	*n*-heptadecane	35.13	
33	pristane	35.25	
34	phenanthrene	36.89	
35	*n*-octadecane	37.04	
36	phytane	37.21	
37	*n*-nonadecane	38.89	
38	*n*-eicosane		

gave a combined flow rate from the column of 30 mL/min. Data were acquired and processed using a HP Vectra XA5 computer (with Pentium 166 MHz CPU) and ChemStation software.

An example of a whole-oil chromatogram is shown in Figure 3.4. The numbered peaks are identified as in Table 3.5. Compound identification was based on published retention times and the retention times of standards measured on our GC under the same conditions. The standards used in this project were benzene, toluene, ethylbenzene, *m*-, *p*- and *o*-xylene. Their retention times are also shown in Table 3.5.

3.3.3 GC-FID OF SATURATED HYDROCARBONS

GC-FID analysis of the saturate fractions prepared by MPLC was carried out on the aforementioned HP 6890 GC system. An HP 7373 liquid automatic sampler was used for the injection. The injection amount was 2 ml solution (10 mg/mL in DCM), with a split ratio of 40:1 under an inlet temperature of 280°C. Two minutes after the injection, the split flow was automatically reduced from ~40 mL/min to 20 mL/min by the gas saver. The GC was fitted with a 30 m x 0.25 mm i.d. HP-5 fused silica capillary column coated with cross-linked 5% phenylmethylsiloxane (0.25 μm film thickness). Helium was used as the carrier gas at a 6.8 psi head pressure to obtain a constant flow rate of 1.0 mL/min, or a linear velocity of 19 cm/sec. The oven temperature program was as follows: 70°C for 3 min; 6°C/min to 100°C and held for 1 min; 4°C/min to 200°C; 6°C/min to 310°C and held for 20 minutes. The FID temperature was 320°C. Flow rates to the detector were: hydrogen 30 mL/min and air 400 mL/min. A makeup gas flow of 29 mL/min (N_2) gave a combined flow rate from the column of 30 mL/min. Data were acquired and processed using a HP Vectra XA5 computer (with Pentium 166 MHz CPU) and ChemStation software. Peak identification was based on published retention times.

3.3.4 INJECTION TECHNIQUE FOR WHOLE-OIL GC ANALYSES

A consistent and appropriate injection method is crucial for reproducible whole-oil

GC analyses. Before any injection, the 5-microlitre (µL) syringe was thoroughly washed using petroleum spirit and then dichloromethane (DCM). This involved repeated flushing of the whole syringe, rinsing the plunger individually, and blow-drying the syringe in a stream of ultra-high purity nitrogen for at least one hour.

The detailed manual injection sequence is described below:

1. Draw air slowly into the syringe so that the tip of the plunger is at the 1.0 µL mark.

2. Insert the needle into the untopped oil, draw up the desired volume (0.4-0.8 µL), and then remove the syringe.

3. Draw a further 2 µL of air into the syringe. The oil sample is now isolated between two air gaps.

4. Remove any excess sample from the syringe by wiping the outside of the needle with a clean, lint-free tissue.

5. Hold the plunger in place while aligning the syringe over the injection port. Inject the sample by inserting the syringe needle into the injector until the barrel of the syringe rests on the injector. Press the plunger all the way into the syringe.

6. Press 'Start' on the GC keypad.

7. Wait several seconds to allow all traces of sample to enter the system, then remove the syringe from the injection port.

3.3.5 REPRODUCIBILITY TEST

The detection of subtle trends in oil compositional data places great demands on analytical reproducibility. To test the repeatibility of our new analytical method, six runs of one oil (Sturt-6) using the same GC conditions but different injection sizes were completed before the routine GC analysis of all 120 oils and condensates was undertaken. The amount injected ranged from 0.5 to 0.8 µL, which is within the range for obtaining adequate resolution and signal size. The reproducibility of representative ratios used in this project is summarised in Figure 4.5 and will be discussed in Chapter 4.

3.3.6 ARTIFICIAL EVAPORATION OF MURTA OIL

Loss of light ends from oil/condensate during sampling and storage is a serious problem for geochemists because it affects the accuracy of oil-oil correlations based on the ratios of crude oil components, particularly those in the C_5-C_{12} range. In order to evaluate the influence of evaporation, a laboratory imitation was designed using forced evaporation under capillary flow of nitrogen. Briefly, a sample of Murta oil from Nockatunga-3 (judged to be unaltered according to the published criteria of Holba et al., 1996) was artificially evaporated at ambient temperature (ca 20°C) under a capillary stream of ultra-high purity nitrogen. GC-FID analyses of the residual oil were undertaken at eleven stages during the course of the evaporation experiment, which lasted 48 hours. The times at which aliquots of oil were removed for GC analysis are listed in Table 3.6. The resulting whole-oil GC traces are shown in Figure 4.3.

Table 3.6 Experimental evaporation of an unaltered Murta oil (at 20°C under stream of N_2)

Test	1	2	3	4	5	6	7	8	9	10	11
Evaporation time in hours	0.0	1.5	3.0	4.5	6.5	8.5	10.5	12.5	18.0	31.0	48.0

All of the eleven GC traces were integrated. Values of selected compound ratios were calculated and plotted against the evaporation time (Figures 4.4a-d). These crossplots reveal that evaporation can severely limit the usage of some of the gasoline-range parameters which have previously been used for the purposes of oil characterisation and oil-oil correlation.

3.3.7 GC-MS OF WHOLE OILS AND CONDENSATES

Gas chromatography-mass spectrometry (GC-MS) of whole oils/condensates was performed on a HP 6890 GC coupled with a HP 5973 MSD in selected ion monitoring (SIM) mode. The capillary column specifications were: HP-5MS, 5% phenyl methyl siloxane, 30 meters long, 250 μm i.d. and 0.25 μm film thickness. The oven temperature was controlled by the same program as in the whole-oil GC-FID analysis (see Section 3.3.2). The injection was accomplished by the HP 7673 liquid automatic sampler (LAS), under the following control settings: sample pumps, 6; injection volume, 1.0 μL; syringe size, 10.0 μL; post-injection solvent A (DCM) washes, 8; viscosity delay, 0 second; plunger speed, fast. Helium was used as the carrier gas. The head pressure for the carrier gas was 2.1 psi. Typical MS conditions were: ionisation mode, electron impact (EI); electron energy, 70eV; source temperature, 230°C; and quad temperature, 150°C.

3.3.8 GC-MS OF SATURATED AND AROMATIC HYDROCARBONS

GC-MS analyses of the saturate and aromatic HPLC fractions were carried out on the same instrument using the same MS detection mode. The LAS controlling parameters were: sample pumps, 6; injection volume, 3.0 μL; syringe size, 10.0 μL; pre-injection solvent A washes (DCM), 3; pre-injection solvent B washes (*n*-hexane), 3; post-injection solvent A washes, 3; post-injection solvent B washes, 3; viscosity delay, 0 second; plunger speed, fast. Sample concentration was about 10 mg/mL in DCM. The GC conditions were the same as in the aforementioned GC-FID analysis of saturate and aromatic fractions (see Section 3.3.3). The capillary column and MS conditions were the same as for whole-oil GC-MS (see Section 3.3.7).

To make the GC-MS peak retention times match those in the GC-FID traces, a series of carrier gas head pressures were tested (6.8, 6.7,5.6, 4.3, 3.3, 2.1, and 1.7 psi), and 2.1 psi was finally chosen as the head pressure for the GC-MS analysis. By studying the retention time changes with the head pressure, an explanation of the "tridecane preference index" (TPI) was provided (see Chapter 4).

GC-MS peak identification was based on retention time, mass spectra and standard injections where possible. Pure standards (viz. 1,3,5-trimethylbenzene, propylbenzene and isopropylbenzene) and two whole-oil samples (viz. Oil 004 of the

Cooper Basin and Oil 013 of the Eromanga Basin: Table 3.1) were measured by full-scan GC-MS, under the same GC conditions as used for whole- oil analysis in SIM mode.

3.3.9 SOLVENT FLOW-THROUGH EXTRACTION OF CORE PLUGS

Solvent flow-through extraction (SFTE) is a novel extraction system for whole sandstone core plugs (Figure 3.5). It was recently developed in the Institute of Geology, University of Cologne, Germany. The solvent-extractable organic matter is sequentially extracted from the core plugs while preserving the original rock characteristics. The system and its operation have been detailed by Schwark et al. (1997). The following is a brief introduction to the technique.

Figure 3.5 is schematic diagram of the whole SFTE system and the details of the extraction cell. The personal computer controls the pneumatic switching valves, solvent flow rates, extraction time (adjusted according to the size of the core plug), fraction collector position, and the collection of the pressure data (for assessing the liquid permeability). The Hewlett-Packard HPLC (high-pressure liquid chromatograph) pump with a preparative head (0.5~30 mL/min) provides a maximum pressure of 450 bar. Two kinds of eluting solvents, DCM and a mixture of DCM and methanol (50:50 v/v), were used. The confining and back-pressure overflow valves together with the head and back-pressure gauges control the pressure. Two different extraction cells have been used to allow for two different sizes of core plugs (2 cm and 4 cm in diameter). The filter and the 16-port selection valve, in combination with a 16-place fraction collector, help the collection of the eluates from the core plugs.

The special design of the extraction cell and the solvent flow-path ensure that the solvent flows through the core plug, but not preferentially via the outer surface between the plug and the liner. Two metal frits and the end pieces are positioned at both ends of the plug. They are then placed in the liner of heat-shrinkable fluoro-ether polymer (FEP). The FEP-liner is heated gently with a blow-drier, with the result that the core plug and the end pieces are held tight and sealed by the shrinking

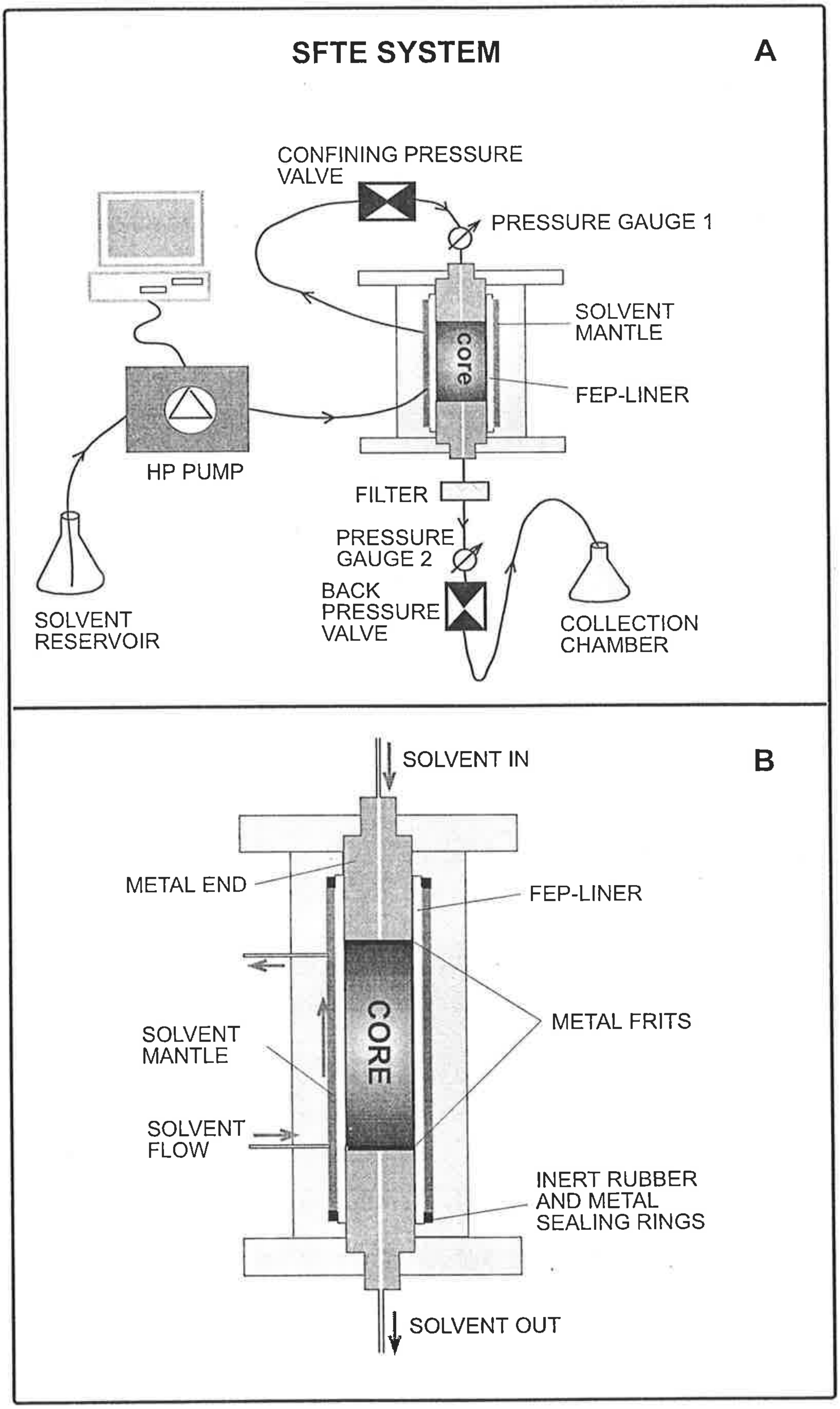


Figure 3.5 Solvent flow-through extraction (SFTE) system
a) the system b) the extraction cell

where it is sealed by a combination of metal, inert rubber O-rings, and two caps on each ends of the cell body. Solvent is pumped to fill the space between the outside of the FEP-lined plug and the inner wall of the extraction cell. When the head pressure exceeds the preset confining pressure (ca. 190 bar), the solvent is allowed to pass the confining pressure valve and flow through the capillary tube connecting to the cell inlet. It is vital in this design that the solvent flow path ensures a higher confining pressure. This is important in preventing the solvent from flowing, preferentially, via the outer surface of the core. Furthermore, by applying a back-pressure (ca. 50 bar lower than that of the confining pressure) at the outlet of the extraction cell, solvent is forced to flow through the entire pore system.

From each plug, six fractions of eluate were collected. The first three fractions were eluted by dichloromethane, and the other three with a mixture of DCM and methanol (50:50 v/v). The elution time was determined according to the size or mass of the core plug. For a plug of 80 g, the first 3 fractions were each about 40 mL, the fourth was about 20 mL, and the last two each about 60 mL.

Solvents in the collected fractions were removed on a rotary evaporator, at temperatures lower than 45°C and under negative pressure (DCM solution 600 mm Hg, solvent-mixture solution, 350~600 mm Hg). All the fractions were analysed by TLC-FID (IatroScan: see Section 3.3.11) to determine their bulk chemical compositions, quantifying the aliphatic hydrocarbons, aromatic hydrocarbons, NSO-compounds (resins) and asphaltenes. Selected SFTE fractions were further fractionated by MPLC (see Section 3.3.10). The MPLC saturates and aromatics were then analysed using GC and GC-MS.

To assess the efficiency of the SFTE, selected SFTE-extracted sandstone plugs were ground and extracted further by ASE (see Section 3.3.14).

3.3.10 MEDIUM-PRESSURE LIQUID CHROMATOGRAPHY

Instead of open-column liquid chromatography, a faster and more convenient MPLC technique was employed in fractionation of EOM from conventional cores, SFTE fractions, and topped crude oils and condensates. The non-commercial MPLC device was designed and assembled by H. Willsch (see Radke et al., 1980). Its schematic representation is shown in Figure 3.6.

An Hewlett-Packard preparative pump provided the elution solvent from the *n*-hexane reservoir. The pre-columns (10 cm long and 1 cm in diameter) were packed with 8–9 cm of silica gel 100 (0.063–0.2 mm) and 1 cm of silica gel 100 (0.2–0.5 mm). The main column (25 cm long and 1 cm in diameter) was packed with silica gel 60 Å (0.045–0.063 mm). The combination of a UV-photometer and a differential refractometer was used to monitor the separation between the saturate and aromatic hydrocarbon fractions.

About 500 μL of *n*-hexane was added to 10–50 mg of maltenes (asphaltene-free extractable organic matter). The whole solution was then transferred into the sample loop with a micro-syringe. The sample vial was rinsed at least twice with *n*-hexane (500 μl) to ensure that all the maltenes had been removed.

Once the sample is loaded on to the sample loop, all the ensuing procedures for a whole batch of samples are fully automatic. During the initial period, the first sample is carried by normal flow of *n*-hexane into the first pre-column where saturates are separated from the sample and collected. After the total aromatics have entered the main chromatographic column, and before the mono-aromatics have been eluted, flow through the chromatographic column is reversed by action of a back-flush valve and the flow rate increased from 8 mL/min to 12 mL/min. Pre-column valve indexing is performed at the same time, allowing solvent to pass through the second pre-column. Polar N, S and O-bearing compounds from the first sample will remain on the first pre-column which is detached from the solvent line. Thus, pure aromatics will be collected during the back-flushing procedure. The elution time for the saturates fraction was 4 min, and that for the aromatics was 6 min. The initial conditions are restored after this period (i.e. the back-flush valve is switched back and the flow rate is reduced to the initial setting. Sample loop valve indexing is then performed to introduce the second sample. Since the rotor motion is rather slow, dual 20-way valves have to be bypassed during indexing to prevent buildup of excessive pressure.

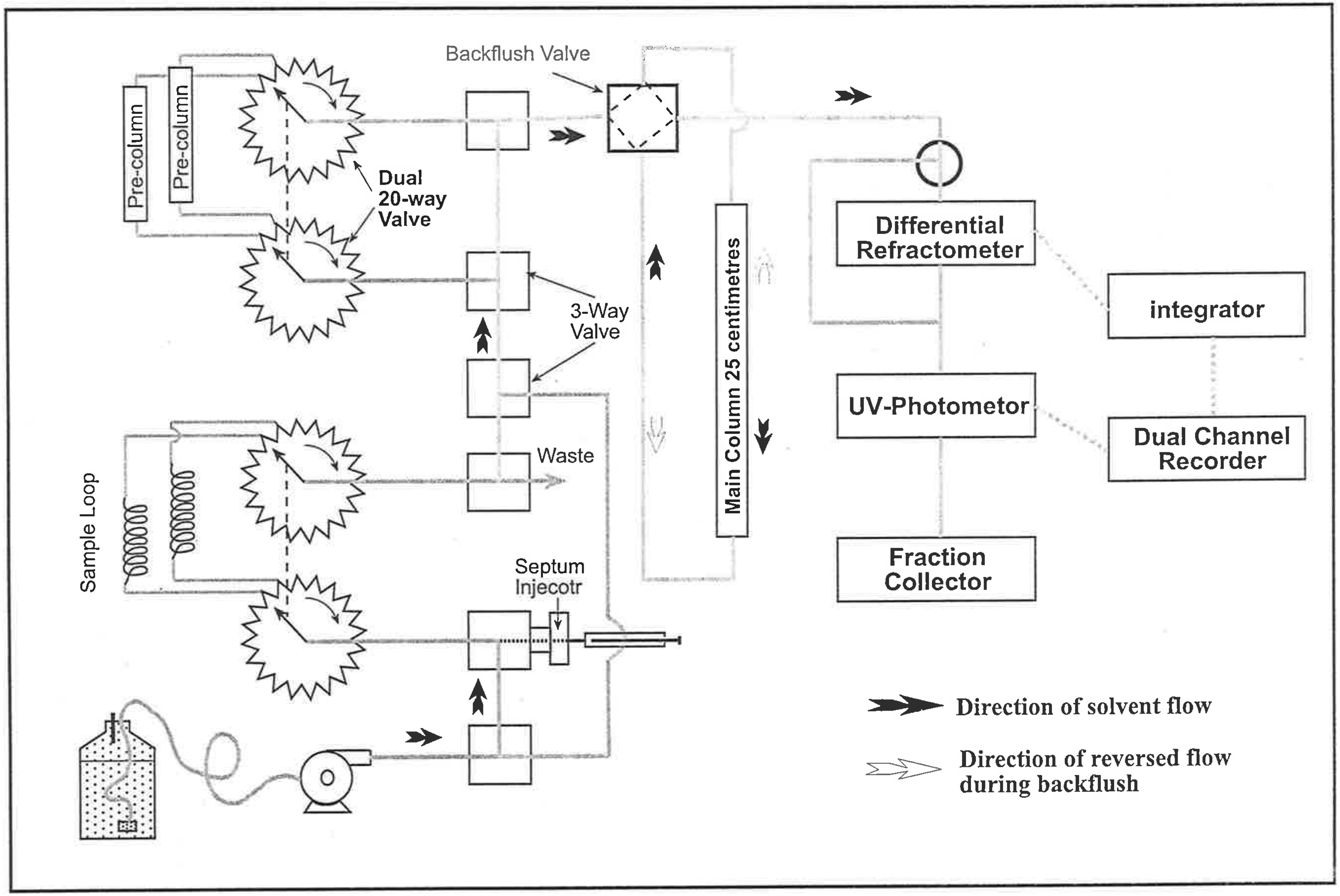


Figure 3.6 Schematic diagram of MPLC (medium pressure liquid chromatograph)

After separation of hydrocarbons had been completed for a given sample batch, the pre-columns were dismounted sequentially, and the polar NSO-compounds were recovered, by eluting with DCM/methanol (93:7 v/v) provided by another device (viz. a solvent reservoir connected to nitrogen cylinder to provide a pressure of approximately 2–6 bars).

Rotary evaporation was used for removal of solvent from the NSO-fraction, and a turbo evaporator for the saturated and aromatic hydrocarbon fractions. Selected saturate and aromatic hydrocarbon fractions (according to the amount obtained) were analysed by GC-FID and GC-MSD.

3.3.11 IATROSCAN

A Th-10 IatroScan equipped with an FID and interfaced to a Hewlett Packard integrator was used for quantification of the saturates, aromatics, resins and asphaltenes in the SFTE and ASE extracts. The IatroScan experiments were carried out according to the published procedure (Karlsen and Larter, 1989, 1991). Briefly, ~2μL aliquots of SFTE fractions dissolved in DCM (20 g/L concentration) were applied, dropwise, from a 5μl syringe, on to the rods (Chromarod Type A, alumina, pore diameter 150 Å). The rods were kept at ambient room conditions for about 3 min to dry. They were then developed in tanks of different mobile phases as follows: 30 min in *n*-hexane for saturates (to 100% of rod length), 12.5 min in toluene for aromatics (50%), and 3 min in DCM/MeOH (93:7 v/v) for the resins (25%). Between each stage of development, the rods were dried at room temperature for about 3 min. Peak identification and quantification were achieved by comparison with a standard. The standard was a DCM solution, containing 10.72 g/L of saturates, 6.92 g/L of aromatics, 2.57 g/L of resins, and 0.58 g/L of asphaltenes.

3.3.12 INORGANIC SALT TEST

To determine the type of salt recovered in some SFTE fractions, a 5% solution of $AgNO_3$ was added dropwise to an aqueous solution of the inorganic extract. A white precipitate indicated that the inorganic extract included halite (NaCl), according to the reaction:

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow \text{ (white)}$$

3.3.13 X-RAY DIFFRACTION

To confirm the above mineral identification X-ray diffraction analysis was also employed. The samples were prepared as smears by grinding in water with an agate mortar and pestle to form a thin slurry that was then spread on to a glass slide and allowed to dry.

The samples were scanned in a semi-automated Philips PW1050 diffractometer, incorporating a graphite monochromator and using a Co tube operating at 50 kV and 30 mA. The scans were logged as computer disc files, and displayed and processed using the CSIRO XPLOT computer program.

3.3.14 ACCELERATED SOLVENT EXTRACTION

Accelerated solvent extraction (ASE) is another new extraction technique (Richter et al., 1996) in which solid or semi-solid samples are enclosed in sample cartridges that are filled with extraction fluid. The samples are statically extracted under elevated temperature (50–200°C) and pressure (500–3000 psi) for a short period of time (5–10 minutes). Compressed gas is used to purge the sample extract from the cell into a collection vessel. A schematic diagram of the ASE system is shown is Figure 3.7.

The ASE experiments for this project were carried out on a Dionex ASE 200 instrument. Twenty SFTE-extracted sandstone plugs were selected (see Table 6.2) and ground in a mortar and pestle. About 10 g of rock powder was loaded into each extraction cell. The samples were then extracted in DCM for 20 min at 75°C and 50 bar. Nitrogen was used to purge the sample extracts. DCM was removed from the extract solution using rotary evaporation. The ASE extracts were then weighed and fractionated by IatroScan to assess the efficiency of the SFTE.

3.3.15 SOXHLET EXTRACTION

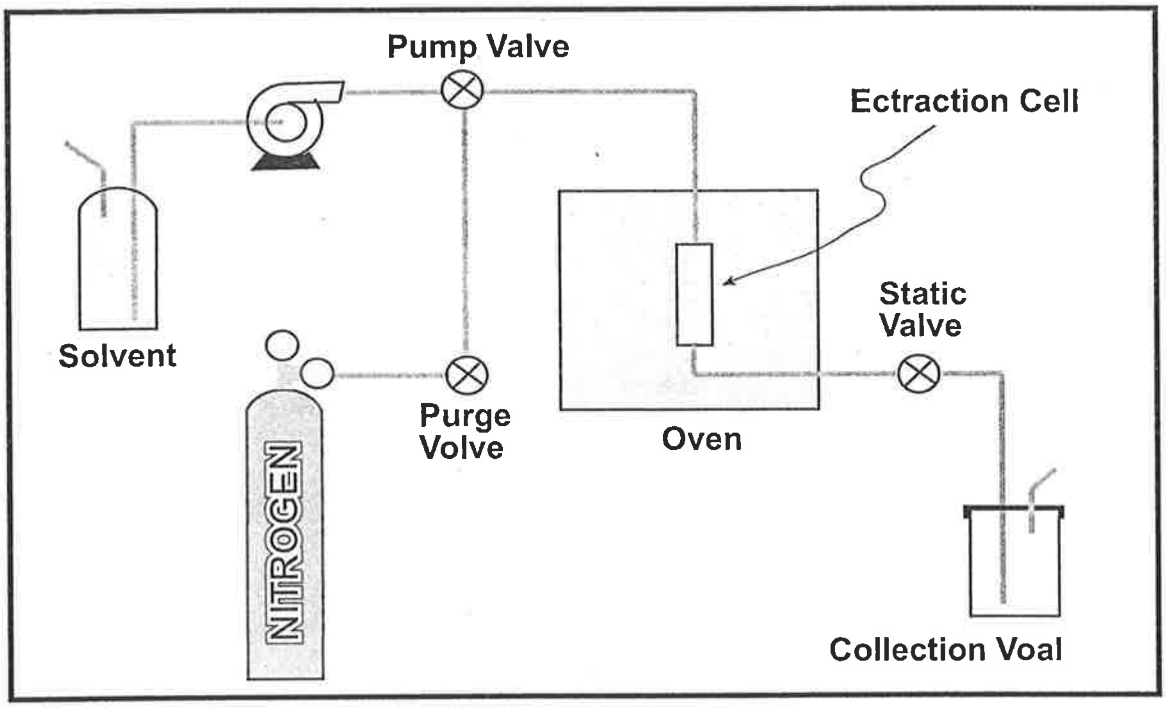


Figure 3.7 Schematic diagram of accelerated solvent extraction (ASE) system.

Core samples were crushed (80–200 mesh) and then Soxhlet extracted with an azeotropic mixture of DCM and methanol (97:3 v/v) for 72 hr (coal, shale and siltstone) or 60 hr (sandstone).

3.3.16 Ultrasonic Extraction

Ultrasonic extraction was employed in a preliminary survey of all the bulk core and core plug samples. Crushed core sections (ca. 1– 50 g, depending on the visual TOC) were extracted twice with DCM/methanol (95:5 v/v) in an ultrasonic bath for 1–2 hr, and then centrifuged. The supernatant was decanted and collected in a round-bottom flask. The residue was washed with additional solvent mixture, and centrifuged twice. The combined supernatants were concentrated by rotary evaporation and the residues were weighed. This weight gives a measure of the EOM content and hence a guide to the size of the plug needed for SFTE to yield adequate residual oil for further analysis.

CHAPTER FOUR

HYDROCARBON MAPPING BASED ON GC-FID ANALYSIS

4.1 INTRODUCTION

The origin of the Eromanga-reservoired oils has provided lively debate since the first discovery of oil in the sandstone of the Early to Middle Jurassic Poolowanna Formation at Poolowanna-1 in 1977 (O'Neil, 1996, 1998). Initially, Armstrong and Barr (1986) thought these Jurassic accumulations were derived from the organic-rich mudstone units of the Eromanga Basin. Michaelsen and McKirdy (1989) and Powell et al. (1989) maintained that most of the oil reservoired in the Murta Formation of the Eromanga sequence was derived *in situ*. Furthermore, using age- and source-specific biomarkers, Alexander et al. (1988) and Jenkins (1989) recognised Eromanga-sourced inputs to certain Jurassic and Cretaceous reservoirs. However, Heath et al. (1989) strongly believed that Permian shales and coals in the Cooper Basin sequence were the sources of the Eromanga-reservoired oils.

Recently, more and more researchers have proposed that many Eromanga-reservoired oils are the result of mixed sourcing (Alexander et al., 1996a; Boreham and Hill, 1998; Boreham and Summons, 1999; Michaelsen and McKirdy, 1999, 2000). Petroleum reservoired in an Eromanga reservoir could be a mixture of hydrocarbons derived from both the Cooper and Eromanga sources, and even from the Cambrian carbonates of the underlying Warburton Basin. But the mixing scenario is poorly understood, both qualitatively and quantitatively.

As mentioned in Chapter 1, one of the main aims of this project was to shed some new light on this question. This chapter presents the results from the first two steps of the project. One hundred and twenty-three oil/condensate samples were collected from more than 50 petroleum-producing fields and all but three were analysed by cryogenic GC-FID. These samples cover most of the reservoir formations in the Cooper and Eromanga Basins. All their GC traces were examined for peak identification and integration, and the oils/condensates grouped (classified) using hierarchical cluster analysis based on a set of twenty parameters (Table 4.1). Some of these parameters were adopted from the literature whereas others were newly created in an attempt to rigorously distinguish the Cooper-hosted oils from those in Eromanga reservoirs.

Based on this initial screening, a subset of 72 oils/condensates was selected for further GC-MS (SIM mode) analysis. The purpose of the GC-MS analysis was to obtain additional source-specific information that would allow the recognition and quantitative description of mixed charging of hydrocarbon reservoirs (see Chapter 5). One target area was chosen (Figures 3.1 & 3.2) to depict how Permian-derived hydrocarbons migrated from the Cooper to the Eromanga Basin, and then mixed with Eromanga-derived petroleum and pooled there (see Chapter 6).

This chapter, therefore, discusses the results of the GC-FID measurement and peak identification, sample quality control, data quality control, parameter selection and creation, variation of the parameters with reservoir formation, and hydrocarbon mapping based on the cluster analysis.

4.2 RESULTS AND DISCUSSION

4.2.1 GC-FID ANALYSIS OF WHOLE OILS

Biomarkers have been used in oil-to-source and oil-to-oil correlations for decades. However, recent studies show that the conventional approach of using several biomarker distributions (e.g. steranes and terpanes) in these correlations is not always successful. High-molecular-weight biomarkers are helpful but not always sufficient for correlation, especially when mixed sourcing occurs. To solve this problem, whole oils/condensates were injected directly into the GC-FID and GC-MS. This not only prevents the loss of information carried by the light-end components, but (in the

Table 4.1 Parameters for oil/condensate mapping and their specificity

1. Pr/Ph = pristane/phytane (source, maturity)
2. Pr/*n*-C_{17} = pristane/*n*-C_{17} (source, maturity, biodegradation)
3. Ph/*n*-C_{18} = phytane/*n*-C_{18} (source, maturity, biodegradation)
4. A = benzene/*n*-hexane (aromaticity: evaporative fractionation, water-washing)
5. A' = benzene/1c3-dimethylcyclopentane (aromaticity: evaporative fractionation, water-washing)
6. B = toluene/*n*-heptane (aromaticity: evaporative fractionation, water-washing)
7. B' = toluene/*n*-octane (aromaticity: evaporative fractionation, water-washing)
8. X = *m* + *p*-xylene /*n*-octane (aromaticity: evaporative fractionation, water-washing)
9. X' = *m* + *p*-xylene /*n*-nonane (aromaticity: evaporative fractionation, water-washing)
10. C = (*n*-hexane + *n*-heptane)/(cyclohexane + methylcyclohexane (paraffinicity: maturity)
11. I (isoheptane value) = [methyhexanes (2- + 3-)]/[dimethylcyclopentanes (1c3- + 1t3- + 1t2-)] (paraffinicity: maturity)
12. F = *n*-heptane/methylcyclohexane (paraffinicity: maturity)
13. H (heptane value) = 10 x *n*-heptane/(Σcyclohexane through methylcyclohexane excluding 1c2-dimethylcyclopentane) (paraffinicity: maturity)
14. R = *n*-heptane/2-methylhexane (paraffin, branching)
15. U = cyclohexane/methylcyclopentane (naphthene, branching)
16. New 1 = *o*-xylene/*n*-nonane (aromaticity: water-washing)
17. New 2 = 1,2,4-trimethylbenzene/*n*-decane (aromaticity: water-washing)
18. New 3 = naphthalene/unknown compound* (aromaticity: water-washing)
19. New 4 = TPI (tridecane preference index) = 3 x *n*-C_{13}/(*n*-C_{12} + *n*-C_{13} + *n*-C_{14}) (aromaticity: source? water-washing: see Section 3.2.1)
20. New 5 = phenanthrene/phytane (aromaticity: water-washing)

* = peak no.27 (Figure 3.4, Table 3.5).

case of mixed sourcing or multiple charging) also suppresses the overestimation of the contribution from the sources that contain relatively more heavy-end biomarkers.

Whole oil GC-FID has been used in studies of petroleum reservoir continuity and production management (Hwang et al., 1994; and references therein). With the development of GC techniques, peak resolution has improved, especially in the gasoline range. This allowed Dzou and Hughes (1993), Thompson (1987) and Curiale and Bromley (1996) to employ whole-oil GC in "migration fractionation" or "evaporative fractionation" studies. Holba et al. (1996) used it to investigate the history of reservoir filling and biodegradation in a field in the Gulf of Mexico. Recently, Boreham and Hill (1998) and Boreham and Summons (1999) identified five source-reservoir couplets in Cooper and Eromanga Basins by using whole-oil GC and other geochemical data.

In the present study excellent resolution was routinely achieved across the entire range of C_1 to C_{45} hydrocarbons with a 30-metre fused silica capillary column. As shown by the chromatograms in Figures 4.1a–c, for example, the resolution of peaks in C_{15+} range is no worse than that obtained by conventional GC using a 50-metre column. Baseline resolution is achieved between pristane and *n*-heptadecane (n-C_{17}) and between phytane and *n*-octadecane (n-C_{18}). Unlike conventional whole-oil chromatograms, in which the light-end components are commonly congested and poorly resolved (Hwang et al., 1994), the present chromatograms also display baseline resolution for most of the low-molecular-weight hydrocarbons (C_1-C_{10}). In particular, the C_1–C_5 alkanes are far more cleanly separated. Also, it is noteworthy that methane and ethane are still present in some of the Murta oils!

Figure 4.1a shows the GC-FID profile of an Eromanga oil (XYOIL53, Nockatunga-1, Murta Formation). Methylcyclohexane is the most abundant component, and *n*-heptane is the major peak in the *n*-alkane distribution that ranges from C_3 to C_{31} and displays no obvious odd or even carbon number predominance. By comparison, the gas chromatogram of a typical Cooper oil (XYOIL57, Tirrawarra-58, Tirrawarra Formation: Figure 4.2b) is very similar, except that it contains more aromatic hydrocarbons, such as toluene, xylene and naphthalene. Another obvious feature is the apparent predominance of tridecane (n-C_{13}) observed in all the Cooper oils/condensates. This is caused by the co-elution of n-C_{13} and 2-methylnaphthalene (Figure 4.2) and is discussed in the next section.

Not all the Cooper- and Eromanga-reservoired crude oils have unimodal GC-FID profiles, as shown in Figures 4.1a & b. Bimodal n-alkane distribution patterns are also common, skewed toward either the heavy end (n-C_{23}) or the light end (n-C_7). Some typical bimodal GC-FID traces can be seen in Chapter 5. Figure 4.1c is an example of a slightly bimodal n-alkane distribution that is strongly skewed toward the heavy end (maximum at n-C_{19}). Oils/condensates showing bimodal gas chromatograms were interpreted to be the results of mixed sourcing or multiple charging (further discussed in Chapter 5).

4.2.2 PEAK IDENTIFICATION

Identification of peaks in the gas chromatograms was accomplished based on retention time, external standards, and GC-MS analysis in full scan mode that permits mass spectral characterisation. The identified compounds were numbered as shown in Figure 3.4 and listed in Table 3.5. In fact, the retention times differed slightly between runs, and the retention times listed in Table 2.5 are those within one typical run.

A full-scan GC-MS was carried out to determine the structures of some of the aromatic compounds incorporated in the new parameters created in this study. Identifications of *o*-xylene (No. 20), 1,2,4-trimethylbenzene (No. 22), naphthalene (No. 25), and phenanthrene (No. 34) were confirmed by their mass spectra. The key ions in their mass spectra and retention times of these molecules are summarised in Table 4.2. Some other relevant compounds, used in the newly devised parameters that will be discussed in the next chapter, are also listed here.

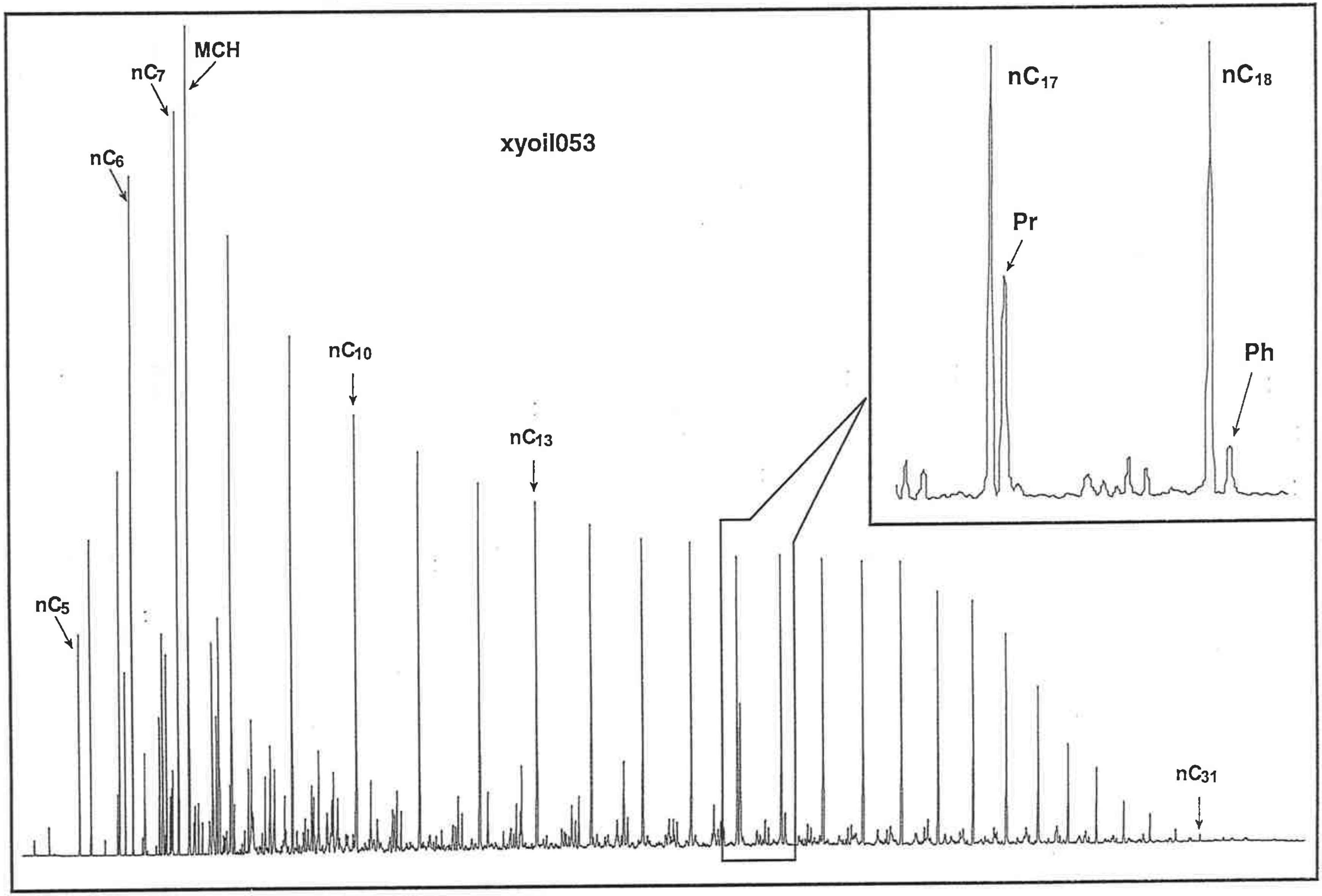


Figure 4.1a Typical GC-FID chromatogram of an Eromanga oil (xyoil053)

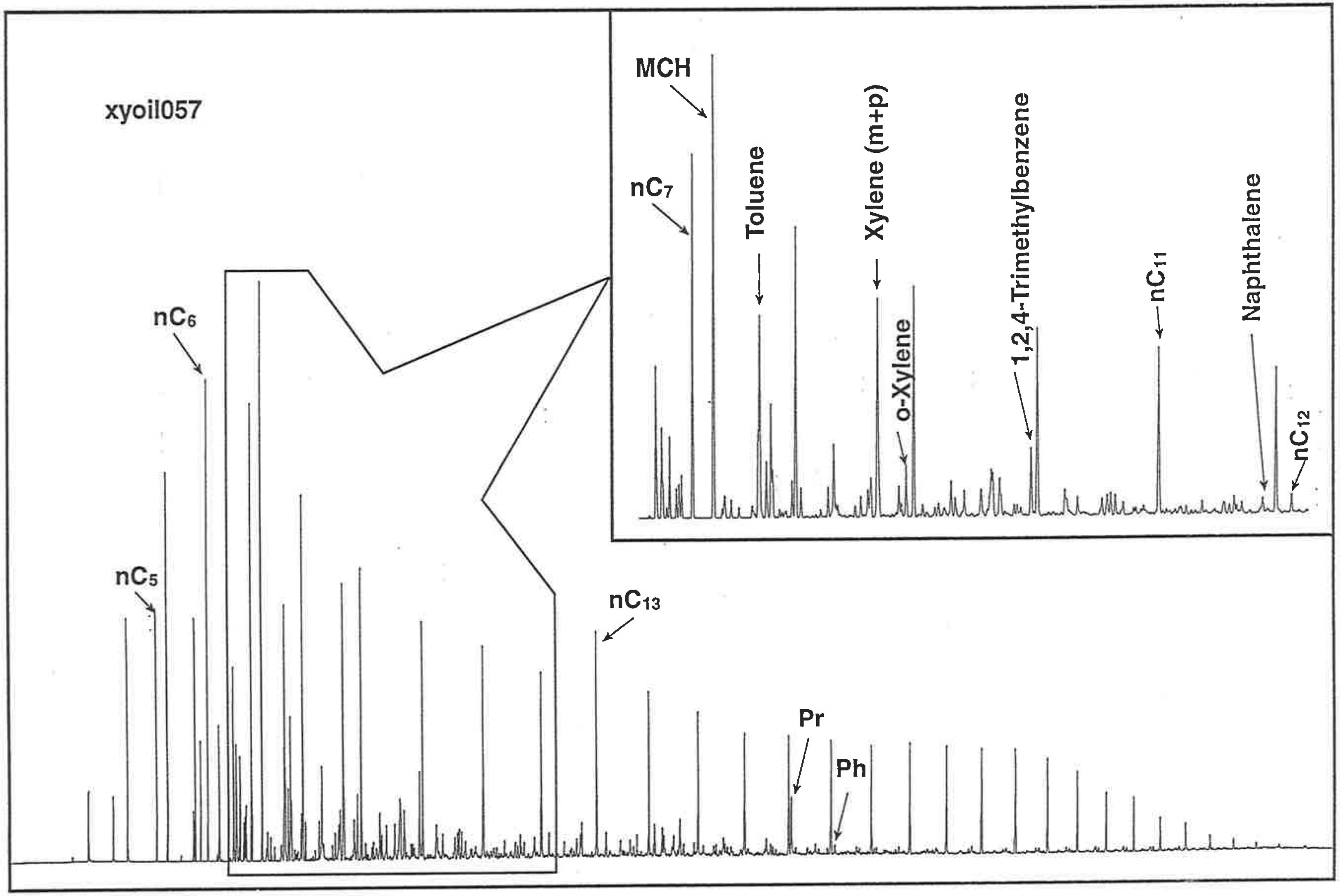


Figure 4.1b Typical GC-FID chromatogram of a Cooper oil (xyoil057)

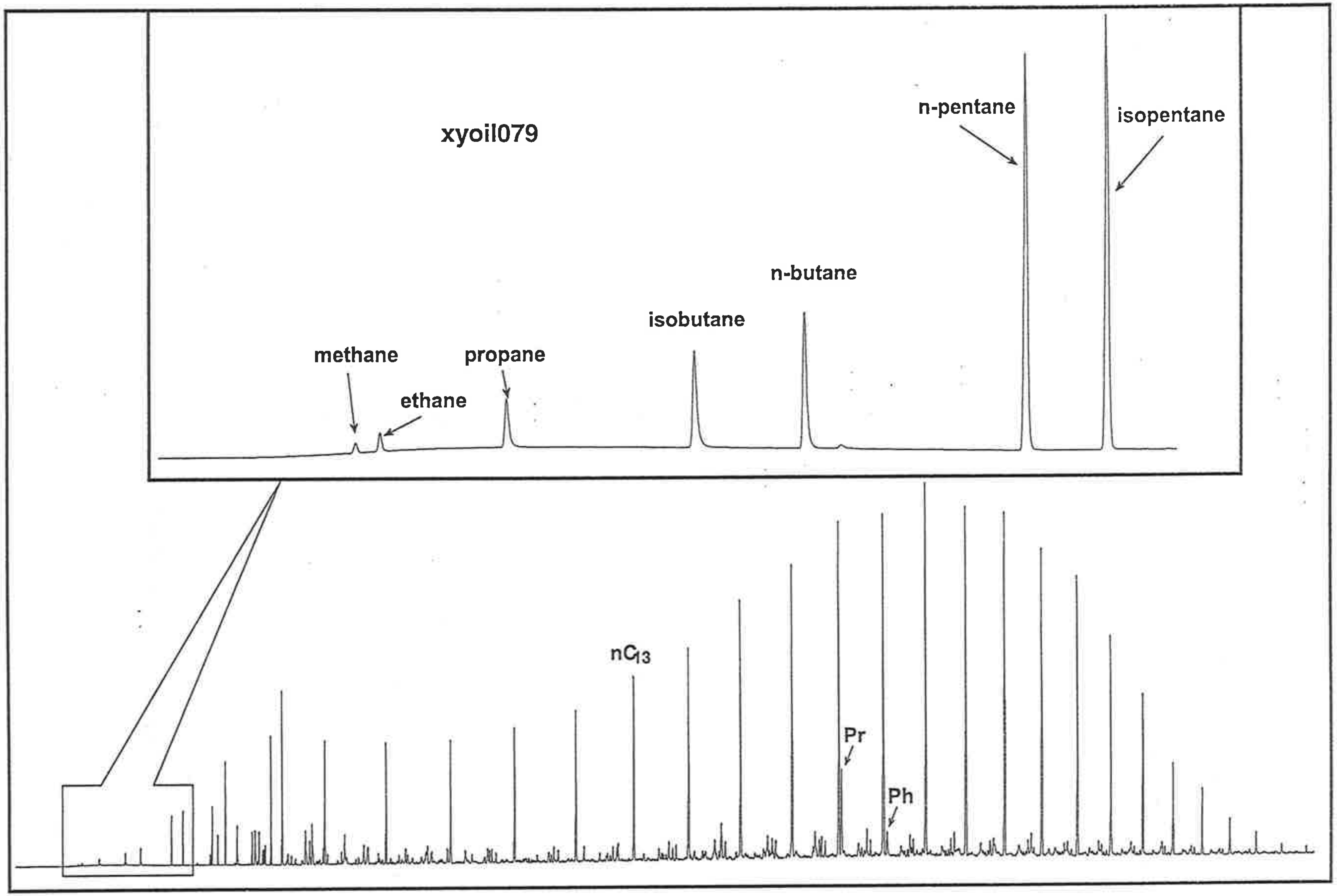


Figure 4.1c GC-FID chromatogram of a mixed-source oil reservoired in the Eromanga Basin (xyoil079)

Table 4.2 Retention times and key ions in mass spectra of some compounds involved in the whole-oil characterisation parameters

No	Molecular Weight	Name	Key Ions (m/z)	Retention Time (min.)
20	106	o-xylene	91, 106	14.77
21	128	*n*-nonane	57, 128	15.00
22	120	1,2,4-TMB	105, 120	17.72
23	142	*n*-octane	57, 142	17.90
25	128	naphthalene	128	23.16
26	168	*n*-dodecane	57, 168	23.58
34	178	phenanthrene	178	37.25
35	254	*n*-octadecane	57, 254	37.40
36	282	phytane	183, 282	37.60

One compound (No. 27 in Table 3.5) used in one of the new parameters (No. 19 in Table 4.1) remained unidentified. It elutes after n-C_{12} in whole-oil GC-FID traces. Its mass spectrum shows that the most abundant peaks are m/z 57, 71, 85, 113, 99, 127, 141 and 155, among which m/z 57 is the major ion and m/z 184 is the molecular ion. However, the identity of this compound will not be discussed further here since it does not influence the usefulness of the parameter in distinguishing the oils/condensates from the Cooper and Eromanga Basins.

What is worthy of mention is the co-elution of tridecane and an isomer of methylnaphthalene in the whole-oil GC-FID analysis (Figure 4.2). During the initial GC-FID survey (Yu and McKirdy, 1998), the apparent predominance of *n*-tridecane in the Cooper-reservoired crudes was noticed. Accordingly, a new parameter (New 4, the tridecane preference index, TPI: Table 4.1) was devised to exploit this phenomenon for the purpose of distinguishing those oils and condensates derived from the Cooper Basin. The tentative explanation for TPI values >1 was either that anomalously high *n*-tridecane levels do occur in Permian source rocks, or (more likely) that their organic matter contained a specific biomarker that co-elutes with *n*-tridecane.

Subsequently, the elevated TPI values were unveiled as an analytical artefact by full-scan-mode GC-MS analysis of Tirrawarra-reservoired oil, XYOIL004 (Tirrawarra-70, DST 1: Table 3.1). Six GC-MS runs, each under a different carrier-gas head-pressure, were carried out. The results are summarised in Figure 4.2 and the retention time changes with the head pressure are listed in Table 4.3.

Table 4.3 Retention time changes of 2- and 1-methylnaphthalene and *n*-tridecane with GC head pressure

GC-MS Run	Column Head Pressure (psi)	Retention time (min)		
		2-MN	*n*-Tridecane	1-MN
XYLAST-2	6.7	23.90	24.12	24.30
XYLAST-3	5.6	24.13	24.33	24.54
XYLAST-4	4.3	24.67	24.84	25.08
XYLAST-5	3.3	25.15	25.29	25.57
XYLAST-6	2.1	25.93	26.03	26.35
XYLAST-7	1.7	26.18	26.26	26.60

The retention times of the methylnaphthalenes are more sensitive to column head pressure than that of *n*-tridecane. As shown in Table 4.3, with head pressure increasing from 1.7 to 6.7 psi, the decrease in retention time for 2- and 1-methylnaphthalene was 2.28 and 2.30 min, respectively, whereas that for tridecane was only 2.14 min.

All the total ion current (TIC) mass chromatograms of the GC-MS scans and the GC-FID trace of XYOIL004 are compiled in Figure 4.2. The left column of the figure shows the complete chromatograms and the right column exhibits the expanded section around *n*-tridecane. On the top is the original GC-FID trace of XYOIL004, which shows an apparent "tridecane preference". With the decrease in GC head pressure from 6.7 to 1.7 psi, the resolution of 2-methylnaphthalene and *n*-tridecane deteriorates to the point where they nearly coelute. If the head pressure were to drop slightly below 1.7 psi, these molecules would co-elute completely, causing an apparent "tridecane predominance" in the TIC mass chromatograms.

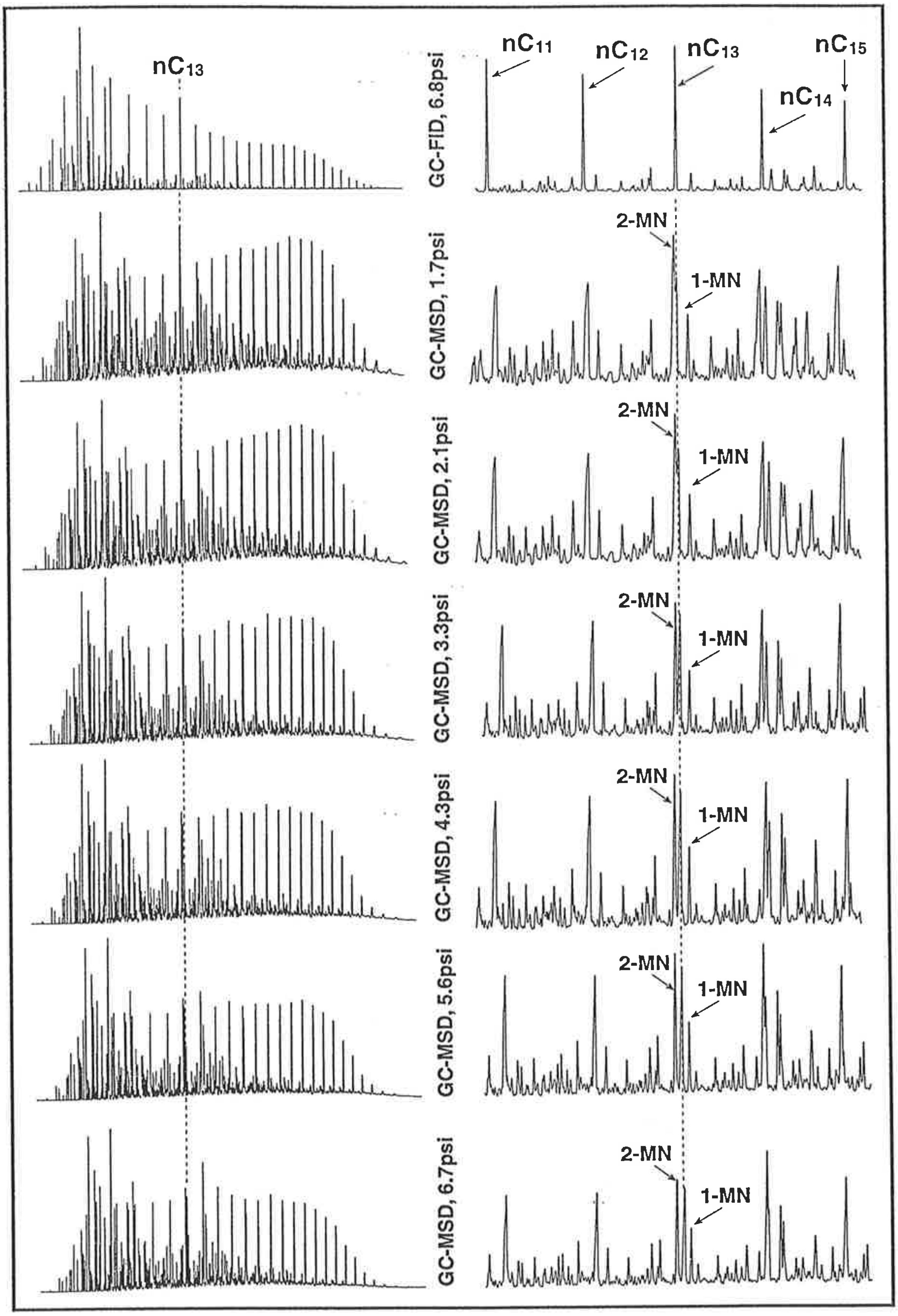


Figure 4.2 Chromatograms showing change of retention time of tridecane relative to the two methylnaphthalene isomers with increasing GC head pressure.

Though the "tridecane preference" in untopped Cooper-reservoired oils/condensates is in fact an analytical artefact, it is still useful for distinguishing Cooper and Eromanga oils/condensates. But it must be kept in mind that the phenomenon is caused by co-elution of a more water-soluble aromatic compound with a less water-soluble saturated hydrocarbon. Such co-elution is commonly an unavoidable problem in whole-oil GC-FID and GC-MS analyses.

Like other parameters based on aromatic and saturated hydrocarbons (Table 4.1), the so-called TPI is sensitive to water-washing. Thus, the "tridecane preference" in Cooper-reservoired petroleums is likely to disappear once they migrate, laterally and/or vertically, into stratigraphically younger traps within the Eromanga sequence.

4.2.3 DATABASE AND PARAMETERS

One hundred and eighteen whole-oil GC-FID traces were surveyed and integrated. The areas under the peaks of interest were recorded and compiled in a database. Twenty peak ratios (compositional parameters) were calculated and the results were summarised in Table 4.4. The parameters and their specificity are defined in Table 3.4. Fifteen of these parameters were selected and/or modified from the literature (Powell and Snowdon, 1979; Snowdon and Powell, 1979; Thompson, 1983, 1987, 1988; Schaefer and Littke, 1988; Dzou and Hughes, 1993; Hwang et al., 1994; Curiale and Bromley, 1996; Holba et al., 1996; Boreham and Hill, 1998; Boreham and Summons, 1999). The other five are newly-created parameters, based on careful inspection of the GC-FID traces.

4.2.4 ARTIFICIAL EVAPORATION AND PARAMETER EVALUATION

As explained in Section 3.3.6, an otherwise unaltered oil from the Murta reservoir at Nockatunga-3 was artificially evaporated for 48 hr. and its composition monitored at eleven stages during the experiment (see Table 3.6). The results are presented in Table 4.5 and Figures 4.3 & 4.4.

The GC profile of the unaltered oil (Figure 4.3a) is dominated by the C_5-C_{12} hydrocarbons. The C_5 alkanes, *n*-pentane and isopentane, have similar

Table 4.4 Values of ratios (parameters) for oil/condensate mapping (based on whole oil GC-FID measurements) (page 1/8)

Data File	GC method	Records in the GC Database	Formation	1	2	3	4	5	6
				Pr/Ph	Pr/nC17	Ph/nC18	A	A'	B
XYOIL001.D	XYOILT.M	Tirrawarra-13, DST 4	Tirrawarra	5.74	0.63	0.12	0.01	0.09	0.67
XYOIL003.D	XYOILT.M	Tirrawarra-64, DST 1, Tirrawarra	Tirrawatta	5.66	0.59	0.11	0.03	0.18	0.47
XYOIL004.D	XYOILT.M	Tirrawarra-70, DST 1, Tirrawarra Fr	Tirrawatta	5.63	0.62	0.12	0.01	0.08	0.77
XYOIL005.D	XYOILT.M	Tirrawarra-70, DST 2, Patchawarra Fr	Patchawarra	0.44	0.36	1.00	0.02	0.11	1.35
XYOIL006.D	XYOILT.M	Taloola-1, DST 2, Namur	Namur	6.69	0.86	0.13	0.02	0.06	0.27
XYOIL007.D	XYOILT.M	Taloola-3, DST 2, Namur	Namur	6.62	0.87	0.13	0.03	0.05	0.30
XYOIL008.D	XYOILT.M	Taloola-2, DST 3, Namur	Namur	6.30	0.86	0.14	0.02	0.06	0.29
XYOIL009.D	XYOILT.M	Tantanna 2, DST 2, Namur	Namur	6.42	0.78	0.13	0.02	0.05	0.33
XYOIL010.D	XYOILT.M	Tantanna 1, DST 3, Birkhead/Namur	Birk/Namur	7.95	1.20	0.17	0.02	0.04	0.37
XYOIL011.D	XYOILT.M	Tantanna 9, DST 3, McKinlay	Mckinley	7.55	1.20	0.17	0.02	0.04	0.50
XYOIL012.D	XYOILT.M	Biala-1, DST 2, Namur	Namur	2.90	0.27	0.08	0.02	0.07	0.16
XYOIL013.D	XYOILT.M	Mooliampah-1, DST 7, Adori	Adori	0.26	0.27	1.00	0.03	0.12	0.16
XYOIL014.D	XYOILT.M	Munkah-2, DST 1, Patchawarra	Patchawarra	0.22	0.19	1.00	0.05	0.13	2.27
XYOIL015.D	XYOILT.M	Yanda-2, DST 2, Patchawarra	Patchawarra	2.84	0.22	0.08	0.06	0.12	5.76
XYOIL016.D	XYOILT.M	Kercummurra-1, DST 1, Cadna-Owie	Cadna-Owie	4.50	0.46	0.11	0.01	0.14	0.07
XYOIL018.D	XYOILT.M	Wilson-6, DST 2, Namur	Namur	3.55	0.37	0.10	0.03	0.17	0.19
XYOIL019.D	XYOILT.M	Big Lake-37, DST 1, Birkhead	Birkhead	5.12	0.52	0.11	0.02	0.19	0.11
XYOIL020.D	XYOILT.M	Mooliampah-1, DST 3, Namur	Namur	2.91	0.26	0.09	0.03	0.12	0.12
XYOIL021.D	XYOILT.M	Epsilon-3, DST 5, Toolachee	Toolachee	2.93	0.22	0.09	0.02	0.17	1.64
XYOIL022.D	XYOILT.M	Lepena-1, DST 3, Patchawarra	Patchawarra	3.41	0.21	0.07	0.03	0.15	2.42
XYOIL023.D	XYOILT.M	Epsilos-3, DST 3, Nappamerri	Nappamerri	2.98	0.21	0.09	0.03	0.20	0.46
XYOIL024.D	XYOILT.M	Spencer-4, DST 2, Birkhend	Birkhead	4.14	0.38	0.09	0.02	0.13	0.08
XYOIL025.D	XYOILT.M	Wilson-6, DST 1, Hutton	Hutton	3.01	0.25	0.07	0.02	0.11	0.08
XYOIL026.D	XYOILT.M	Moolion-1, DST 1, Hutton	Hutton	7.78	1.65	0.21	0.08	0.11	0.35
XYOIL027.D	XYOILT.M	Tickalara-2, DST 5, Namur	Namur	2.92	0.24	0.07	0.02	0.13	0.11
XYOIL028.D	XYOILT.M	Wancoocha-3, DST 3, Hutton	Hutton	0.62	0.54	1.00	0.02	0.20	0.09
XYOIL029.D	XYOILT.M	Jackson-28, DST 2, Westbourne	Westboutne	2.87	0.25	0.08	0.01	0.10	0.10
XYOIL030.D	XYOILT.M	Tickalara-2, DST 1, Namur	Namur	3.45	0.30	0.08	0.01	0.14	0.09
XYOIL031.D	XYOILT.M	Ulandi-1, DST 2, Namur	Namur	3.33	0.33	0.09	0.02	0.06	0.18

Table 4.4 Values of ratios (parameters) for oil/condensate mapping (based on whoil GC-FID measurements) (page 2/8)

Data File	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	B'	X	X'	C	I	F	H	R	U	New 1	New 2	New 3	New 4	New 5
XYOIL001.D	0.63	1.05	1.15	0.83	1.62	0.69	2.82	4.07	1.91	0.23	0.37	0.95	1.22	n. d.
XYOIL003.D	0.47	0.92	0.98	0.76	1.86	0.52	2.18	2.30	1.39	0.17	0.37	0.68	1.19	n. d.
XYOIL004.D	0.63	1.17	1.15	0.85	1.54	0.65	2.73	4.34	1.85	0.23	0.38	0.99	1.23	n. d.
XYOIL005.D	0.91	1.47	1.31	0.54	1.67	0.45	2.22	3.93	3.24	0.25	0.35	1.22	1.19	n. d.
XYOIL006.D	0.04	0.28	0.11	1.36	1.52	1.21	3.74	4.09	0.41	0.00	0.00	0.16	1.02	n. d.
XYOIL007.D	0.04	0.28	0.11	1.38	1.45	1.24	3.72	3.93	0.44	0.00	0.00	0.16	1.02	n. d.
XYOIL008.D	0.04	0.28	0.11	1.42	1.53	1.24	3.73	3.88	0.48	0.00	0.00	0.16	1.00	n. d.
XYOIL009.D	0.04	0.27	0.11	0.96	1.25	0.85	3.16	3.89	0.57	0.00	0.00	0.20	0.99	n. d.
XYOIL010.D	0.03	0.26	0.11	1.40	1.41	1.30	3.92	4.63	0.48	0.00	0.00	0.13	1.02	n. d.
XYOIL011.D	0.04	0.27	0.10	1.30	1.33	1.18	3.70	4.18	0.43	0.00	0.00	0.13	0.99	n. d.
XYOIL012.D	0.09	0.24	0.20	0.78	1.19	0.61	2.51	3.35	0.70	0.03	0.05	0.25	1.01	n. d.
XYOIL013.D	0.09	0.18	0.16	1.02	1.86	0.87	3.05	3.11	0.93	0.02	0.04	0.28	1.03	n. d.
XYOIL014.D	0.95	2.29	0.96	0.36	1.44	0.35	1.91	4.27	4.17	0.18	0.22	0.93	1.12	n. d.
XYOIL015.D	2.45	4.39	2.50	0.24	0.99	0.25	1.46	5.14	6.90	0.46	0.41	2.20	1.29	n. d.
XYOIL016.D	0.06	0.16	0.17	2.25	2.61	1.60	4.23	3.83	0.87	0.02	0.02	0.23	1.02	n. d.
XYOIL018.D	0.16	0.46	0.23	0.72	1.68	0.48	2.07	2.48	1.11	0.04	0.03	0.14	1.02	n. d.
XYOIL019.D	0.09	0.25	0.23	1.50	2.67	1.10	3.53	3.36	1.13	0.03	0.06	0.19	1.05	n. d.
XYOIL020.D	0.07	0.21	0.20	1.05	1.81	0.92	3.13	3.22	0.77	0.02	0.04	0.28	1.04	n. d.
XYOIL021.D	1.39	1.36	1.46	0.50	1.77	0.42	1.97	3.38	4.20	0.27	0.27	1.20	1.10	n. d.
XYOIL022.D	1.18	9.86	0.78	0.38	1.35	0.32	1.64	3.43	3.29	0.20	0.42	1.47	1.16	n. d.
XYOIL023.D	0.48	0.68	0.80	0.65	1.84	0.45	2.07	2.92	1.98	0.13	0.22	0.31	1.03	n. d.
XYOIL024.D	0.06	0.19	0.16	1.68	2.27	1.23	3.83	3.55	0.74	0.01	0.02	0.22	1.02	n. d.
XYOIL025.D	0.06	0.17	0.17	1.72	2.25	1.44	4.10	4.25	0.85	0.02	0.03	0.27	1.01	n. d.
XYOIL026.D	0.22	1.08	0.21	0.22	0.83	0.18	1.07	2.57	1.51	0.04	0.03	0.09	1.06	n. d.
XYOIL027.D	0.09	0.26	0.27	0.94	1.61	0.69	2.67	3.12	0.96	0.03	0.08	0.32	1.06	n. d.
XYOIL028.D	0.06	0.17	0.16	3.54	4.59	2.96	5.13	3.60	0.68	0.00	0.00	0.15	1.00	n. d.
XYOIL029.D	0.11	0.57	0.58	0.99	1.52	0.68	2.76	4.19	1.53	0.08	0.20	0.30	1.06	n. d.
XYOIL030.D	0.11	0.30	0.36	1.16	1.76	0.74	2.80	3.19	1.07	0.06	0.13	0.27	1.04	n. d.
XYOIL031.D	0.09	0.26	0.19	0.76	1.14	0.60	2.48	3.47	0.69	0.01	0.03	0.25	0.98	n. d.

Table 4.4 Values of ratios (parameters) for oil/condensate mapping (based on whole oil GC-FID measurements) (page 3/8)

Data File	GC method	Records in the GC Database	Formation	1	2	3	4	5	6
				Pr/Ph	Pr/nC17	Ph/nC18	A	A'	B
XYOIL032.D	XYOILT.M	Wilson-2, DST 1, Murta	Murta	5.81	0.42	0.09	0.01	0.11	0.13
XYOIL033.D	XYOILT.M	Kihee-2, DST 1, Murta	Murta	5.01	0.42	0.09	0.01	0.11	0.07
XYOIL034.D	XYOILT.M	Thungo-2, Murta	Murta	4.41	0.42	0.10	0.01	0.11	0.10
XYOIL035.D	XYOILT.M	Dilkera-2 DST 2, Murta	Murta	5.32	0.42	0.09	0.01	0.11	0.08
XYOIL036.D	XYOILT.M	Maxwell-1, Murta	Murta	5.29	0.41	0.09	0.01	0.11	0.07
XYOIL037.D	XYOILT.M	Maxwell-2, DST 1, Murta	Murta	5.36	0.40	0.09	0.01	0.11	0.08
XYOIL038.D	XYOILT.M	Thungo-3, Murta	Murta	4.49	0.44	0.10	0.01	0.11	0.10
XYOIL039.D	XYOILT.M	Thungo-1, DST 1, Murta	Murta	4.53	0.42	0.10	0.01	0.11	0.11
XYOIL040.D	XYOILT.M	Maxwell South-1, DST 2, Murta	Murta	5.17	0.39	0.09	0.01	0.10	0.08
XYOIL041.D	XYOILT.M	Thungo-1, DST 4, Westbourne	Westboutne	3.53	0.39	0.10	0.01	0.09	0.05
XYOIL042.D	XYOILT.M	Thungo-4, Murta	Murta	4.43	0.42	0.10	0.01	0.11	0.11
XYOIL043.D	XYOILT.M	Thungo-1, Murta	Murta	4.44	0.43	0.10	0.01	0.11	0.11
XYOIL044.D	XYOILT.M	Winna-1, Murta	Murta	4.21	0.45	0.11	0.02	0.10	0.11
XYOIL045.D	XYOILT.M	Dilkera-2, DST 2, Murta	Murta	5.15	0.42	0.09	0.01	0.11	0.08
XYOIL046.D	XYOILT.M	Nockatunga-4, Murta	Murta	5.79	0.43	0.09	0.01	0.11	0.11
XYOIL047.D	XYOILT.M	Dilkera-1, DST 7, Murta	Murta	5.29	0.42	0.09	0.01	0.11	0.08
XYOIL048.D	XYOILT.M	Koora-2, DST 4, Murta	Murta	3.59	0.38	0.10	0.02	0.07	0.19
XYOIL049.D	XYOILT.M	Winna-2, DST 1, Murta	Murta	4.16	0.50	0.13	0.01	0.11	0.11
XYOIL050.D	XYOILT.M	Winna-3, DST 1, Murta	Murta	4.50	0.42	0.10	0.01	0.11	0.11
XYOIL051.D	XYOILT.M	Nockatunga-1, Murta	Murta	5.91	0.43	0.09	0.01	0.11	0.10
XYOIL052.D	XYOILT.M	Maxwell-2, Murta	Murta	5.29	0.40	0.09	0.01	0.11	0.07
XYOIL053.D	XYOILT.M	Nockatunga-3, Murta	Murta	3.70	0.58	0.15	0.02	0.15	0.07
XYOIL054.D	XYOILT.M	Mooliampah-1, DST 2, Namur	Namur	3.22	0.28	0.08	0.02	0.13	0.10
XYOIL055.D	XYOILT.M	Strzekecki, Namur	Namur	3.16	0.30	0.08	0.03	0.12	0.19
XYOIL056.D	XYOILT.M	Meranji-1, DST 2, Namur	Namur	4.18	0.41	0.09	0.02	0.12	0.12
XYOIL057.D	XYOILT.M	Tirrawarra-58, DST 3, Tirrawarra	Tirrawarra	5.40	0.61	0.12	0.01	0.09	0.66
XYOIL058.D	XYOILT.M	Tirrawarra-57, DST 2, Tirrawarra	Tirrawarra	5.54	0.63	0.12	0.01	0.09	0.61
XYOIL059.D	XYOILT.M	Gooranie-1, DST 2, Patchawarra	Patchawarra	4.60	0.52	0.12	0.01	0.12	1.03
XYOIL060.D	XYOILT.M	Merrimelia, Namur	Namur	3.79	0.34	0.10	0.02	0.18	0.11

Table 4.4 Values of ratios (parameters) for oil/condensate mapping (based on whole oil GC-FID measurements) (page 4/8)

Data File	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	B'	X	X'	C	I	F	H	R	U	New 1	New 2	New 3	New 4	New 5
XYOIL032.D	0.12	0.53	0.49	0.91	1.63	0.64	2.67	3.99	0.17	0.07	0.17	0.20	1.03	n. d.
XYOIL033.D	0.07	0.25	0.25	1.36	2.03	0.98	3.42	3.98	1.47	0.03	0.08	0.18	1.02	n. d.
XYOIL034.D	0.09	0.39	0.35	0.98	1.65	0.68	2.81	4.06	1.59	0.05	0.12	0.18	1.03	n. d.
XYOIL035.D	0.07	0.31	0.29	1.03	1.62	0.71	2.90	4.28	1.52	0.04	0.10	0.19	1.02	n. d.
XYOIL036.D	0.07	0.23	0.22	1.16	1.76	0.76	3.06	4.05	1.44	0.02	0.09	0.17	1.03	n. d.
XYOIL037.D	0.07	0.26	0.25	1.09	1.72	0.73	2.97	4.02	1.46	0.03	0.10	0.18	1.03	n. d.
XYOIL038.D	0.09	0.38	0.34	0.98	1.67	0.70	2.84	4.02	1.66	0.05	0.12	0.18	1.03	n. d.
XYOIL039.D	0.09	0.41	0.36	0.92	1.65	0.67	2.82	4.16	1.70	0.05	0.12	0.19	1.03	n. d.
XYOIL040.D	0.07	0.23	0.20	1.34	1.83	0.90	3.37	4.20	1.27	0.03	0.06	0.16	1.02	n. d.
XYOIL041.D	0.06	0.18	0.18	1.18	1.38	0.65	2.77	4.33	1.21	0.03	0.11	0.13	1.03	n. d.
XYOIL042.D	0.10	0.40	0.37	0.98	1.65	0.68	2.81	4.10	1.64	0.05	0.13	0.19	1.03	n. d.
XYOIL043.D	0.10	0.42	0.38	0.98	1.61	0.69	2.82	4.28	1.67	0.05	0.13	0.20	1.03	n. d.
XYOIL044.D	0.08	0.34	0.29	0.88	1.71	0.73	3.04	4.49	1.86	0.04	0.10	0.17	1.02	n. d.
XYOIL045.D	0.07	0.31	0.29	1.05	1.64	0.71	2.88	4.15	1.50	0.04	0.10	0.19	1.03	n. d.
XYOIL046.D	0.10	0.46	0.41	0.90	1.59	0.62	2.64	3.93	1.67	0.06	0.14	0.19	1.02	n. d.
XYOIL047.D	0.07	0.31	0.28	1.04	1.70	0.71	2.88	3.91	1.55	0.07	0.10	0.18	1.02	n. d.
XYOIL048.D	0.06	0.22	0.14	1.25	1.36	1.07	3.57	4.30	0.67	0.01	0.01	0.13	1.01	n. d.
XYOIL049.D	0.09	0.40	0.34	0.96	1.70	0.71	2.89	4.13	1.62	0.04	0.11	0.14	1.03	n. d.
XYOIL050.D	0.09	0.36	0.32	0.98	1.64	0.70	2.88	4.30	1.58	0.04	0.11	0.17	1.03	n. d.
XYOIL051.D	0.10	0.45	0.40	0.91	1.58	0.62	2.62	3.93	1.66	0.06	0.14	0.19	1.03	n. d.
XYOIL052.D	0.07	0.26	0.25	1.12	1.69	0.74	2.98	4.18	1.46	0.03	0.10	0.18	1.03	n. d.
XYOIL053.D	0.07	0.19	0.21	1.24	2.01	0.80	3.07	3.27	1.45	0.02	1.00	0.09	1.00	n. d.
XYOIL054.D	0.09	0.22	0.22	1.38	1.98	1.04	3.33	3.26	0.84	0.03	0.05	0.24	1.03	n. d.
XYOIL055.D	0.11	0.38	0.19	0.61	1.21	0.41	1.88	2.57	0.62	0.02	0.03	0.30	1.02	n. d.
XYOIL056.D	0.08	0.19	0.23	0.94	1.54	0.57	2.40	2.68	0.95	0.04	0.05	0.22	1.03	n. d.
XYOIL057.D	0.71	1.07	1.21	1.02	1.56	0.72	2.76	4.11	1.68	0.24	0.37	0.94	1.22	n. d.
XYOIL058.D	0.75	0.96	1.23	0.94	1.66	0.76	2.86	3.93	1.82	0.24	0.38	0.97	1.22	n. d.
XYOIL059.D	1.24	1.29	1.63	0.76	1.80	0.54	2.27	3.32	2.74	0.29	0.38	1.24	1.17	n. d.
XYOIL060.D	0.08	0.19	0.18	1.96	3.02	1.54	4.11	3.40	0.99	0.01	0.02	0.27	1.01	n. d.

Table 4.4 Values of ratios (parameters) for oil/condensate mapping (based on whole oil GC-FID measurements) (page 5/8)

Data File	GC method	Records in the GC Database	Formation	1	2	3	4	5	6
				Pr/Ph	Pr/nC17	Ph/nC18	A	A'	B
XYOIL061.D	XYOILT.M	Merrimelia-17, DST 4, Nappamerri	Nappamerri	4.21	0.37	0.11	0.01	0.12	1.09
XYOIL062.D	XYOILT.M	Wancoocha-2, DST 5, Hutton	Hutton	4.87	0.54	0.13	0.02	0.19	0.09
XYOIL063.D	XYOILT.M	Cook-1, DST 3, Hutton	Hutton	4.28	0.41	0.11	0.01	0.11	0.06
XYOIL064.D	XYOILT.M	Merrimella, Nappamerri	Nappamerri	2.99	0.33	0.10	0.01	0.07	0.91
XYOIL065.D	XYOILT.M	Della-2, Toolachee	Toolachee	2.04	0.17	0.13	0.03	0.16	3.64
XYOIL066.D	XYOILT.M	Woolkina, Tirrawarra	Tirrawarra	5.16	0.59	0.13	0.01	0.09	0.65
XYOIL067.D	XYOILT.M	Moorari-3, Tirrawarra	Tirrawarra	5.42	0.68	0.13	0.01	0.08	0.68
XYOIL068.D	XYOILT.M	Wancoocha-6, Murta	Murta	3.52	0.33	0.10	0.01	0.12	0.08
XYOIL069.D	XYOILT.M	Wippo-1, DST 1, Patchawarra	Patchawarra	0.30	0.22	1.00	0.01	0.15	0.71
XYOIL070.D	XYOILT.M	Jackson South-4, DST 2, Birkhead	Birkhead	3.69	0.33	0.08	0.01	0.08	0.07
XYOIL071.D	XYOILT.M	Moorari-3, Tirrawarra	Tirrawarra	5.89	0.71	0.13	0.11	0.15	0.92
XYOIL072.D	XYOILT.M	Meranji-1, DST 5, Patchawarra	Patchawarra	4.31	0.38	0.09	0.01	0.10	0.90
XYOIL074.D	XYOILT.M	Wilson South-1, DST 3, Hutton	Hutton	6.09	0.91	0.16	0.02	0.12	0.13
XYOIL075.D	XYOILT.M	Leleptian-1, DST 3, Patchawarra	Patchawarra	2.86	0.65	0.27	0.07	0.12	7.01
XYOIL076.D	XYOILT.M	Fly Lake-2, Tirrawarra	Tirrawarra	6.35	0.77	0.13	0.12	0.18	0.78
XYOIL077.D	XYOILT.M	Merrimelia, Hutton	Hutton	3.88	0.34	0.10	0.02	0.17	0.11
XYOIL078.D	XYOILT.M	Daralingie	Permian	3.90	0.30	0.09	0.02	0.17	1.10
XYOIL079.D	XYOILT.M	Alwyn-1, DST 1, Murta	Murta	3.29	0.31	0.08	0.01	0.09	0.12
XYOIL080.D	XYOILT.M	Dullingari, Namur	Namur	4.18	0.36	0.10	0.01	0.15	0.09
XYOIL081.D	XYOILT.M	Aroona-1, DST 3, Toolachee	Toolachee	3.69	0.21	0.07	0.04	0.16	1.53
XYOIL082.D	XYOILT.M	Tirrawarra, Tirrawarra	Tirrawarra	5.21	0.60	0.12	0.01	0.09	0.64
XYOIL083.D	XYOILT.M	Bagundi-1, DST 4, Patchawarra	Patchawarra	3.08	0.21	0.07	0.08	0.12	3.55
XYOIL084.D	XYOILT.M	Mooliampah-1, DST 1, Murta	Murta	3.64	0.31	0.08	0.02	0.17	0.09
XYOIL085.D	XYOILT.M	Bookabourdie-4, Tirrawarra	Tirrawarra	2.52	0.20	0.09	0.05	0.24	2.94
XYOIL086.D	XYOILT.M	Jackson-3, Westbourne	Westboutne	2.90	0.25	0.07	0.01	0.10	0.10
XYOIL087.D	XYOILT.M	Nungeroo-1, DST 2, Namur	Namur	3.38	0.34	0.09	0.02	0.07	0.13
XYOIL088.D	XYOILT.M	Nulla-1, DST 3, Patchawarra	Patchawarra	2.52	0.24	0.12	0.02	0.10	2.32
XYOIL089.D	XYOILT.M	Daralingie-1, Patchawarra	Patchawarra	4.00	0.35	0.11	0.03	0.21	0.97
XYOIL090.D	XYOILT.M	Wancoocha-2, DST 4, Birkhead	Birkhead	4.81	0.47	0.11	0.03	0.20	0.12

Table 4.4 Values of ratios (parameters) for oil/condensate mapping (based on whole oil GC-FID measurements) (page 6/8)

Data File	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	B'	X	X'	C	I	F	H	R	U	New 1	New 2	New 3	New 4	New 5
XYOIL061.D	1.28	1.37	1.75	0.71	1.65	0.52	2.22	3.42	2.43	0.30	0.42	0.74	1.10	n. d.
XYOIL062.D	0.07	0.15	0.15	3.16	3.98	2.44	4.87	3.56	0.95	0.00	0.00	0.17	1.00	n. d.
XYOIL063.D	0.06	0.13	0.15	1.82	2.06	1.34	4.10	4.46	0.90	0.03	0.04	0.34	1.07	n. d.
XYOIL064.D	0.92	1.13	1.16	0.66	1.13	0.46	2.03	3.65	1.77	0.22	0.36	0.76	1.13	n. d.
XYOIL065.D	2.01	3.46	2.06	0.32	1.35	0.30	1.55	3.99	5.12	0.34	0.38	2.01	1.30	n. d.
XYOIL066.D	0.79	1.07	1.32	1.09	1.66	0.72	2.69	3.75	1.59	0.25	0.39	1.11	1.25	n. d.
XYOIL067.D	0.81	1.04	1.25	1.10	1.66	0.76	2.78	3.72	1.60	0.26	0.40	1.05	1.20	n. d.
XYOIL068.D	0.06	0.19	0.18	2.13	2.29	1.50	4.12	3.78	0.87	0.02	0.03	0.12	1.01	n. d.
XYOIL069.D	0.35	0.70	0.71	0.94	2.11	0.81	3.30	6.00	3.69	0.12	0.15	0.70	1.04	n. d.
XYOIL070.D	0.06	0.19	0.18	1.14	1.29	0.77	3.04	4.23	0.89	0.03	0.08	0.23	1.04	n. d.
XYOIL071.D	0.19	1.51	0.66	0.39	1.44	0.39	2.09	3.86	2.90	0.16	0.33	0.88	1.22	n. d.
XYOIL072.D	0.98	0.89	1.50	0.80	1.68	0.62	2.54	3.55	1.41	0.29	0.41	1.15	1.04	n. d.
XYOIL074.D	1.25	0.16	0.24	1.54	2.07	1.24	3.87	4.24	0.90	0.00	0.00	0.06	1.00	n. d.
XYOIL075.D	0.61	2.23	2.00	0.19	1.20	0.18	1.38	9.99	5.73	0.40	0.40	0.96	1.18	n. d.
XYOIL076.D	0.16	1.26	0.62	0.43	2.13	0.44	2.42	5.17	3.76	0.15	0.30	0.69	1.20	n. d.
XYOIL077.D	0.11	0.22	0.26	1.24	2.21	0.83	3.02	2.86	1.13	0.03	0.07	0.22	1.08	n. d.
XYOIL078.D	1.31	1.40	1.74	0.75	1.81	0.54	2.22	3.20	2.64	0.28	0.36	1.07	1.12	n. d.
XYOIL079.D	0.11	0.31	0.29	0.94	1.33	0.65	2.69	3.79	0.88	0.05	0.13	0.23	1.02	n. d.
XYOIL080.D	0.08	0.19	0.19	1.88	2.35	1.36	3.88	3.68	0.96	0.02	0.04	0.22	1.02	n. d.
XYOIL081.D	0.31	1.14	0.80	0.45	1.79	0.39	2.17	4.34	3.47	0.14	0.19	0.94	1.06	n. d.
XYOIL082.D	0.76	1.03	1.22	1.12	1.63	0.75	2.77	3.79	1.59	0.24	0.37	0.91	1.21	n. d.
XYOIL083.D	1.25	4.02	1.35	0.29	1.24	0.30	1.74	4.65	5.62	0.24	0.32	2.12	1.12	n. d.
XYOIL084.D	0.08	0.23	0.24	1.67	2.37	1.12	3.44	3.05	0.93	0.03	0.05	0.18	1.02	n. d.
XYOIL085.D	2.52	3.26	3.20	0.46	1.97	0.38	1.63	1.88	2.58	0.44	0.66	1.87	1.28	n. d.
XYOIL086.D	0.10	0.40	0.39	1.10	1.55	0.77	2.98	4.07	1.27	0.06	0.12	0.30	1.04	n. d.
XYOIL087.D	0.10	0.20	0.19	0.96	1.01	0.79	3.10	7.25	0.66	0.03	0.03	0.19	1.01	n. d.
XYOIL088.D	0.14	0.90	1.87	0.37	1.17	0.30	1.82	6.37	4.05	0.36	0.43	1.37	1.18	n. d.
XYOIL089.D	0.83	1.25	1.18	0.67	1.79	0.52	2.29	3.43	2.54	0.22	0.29	0.80	1.12	n. d.
XYOIL090.D	0.06	0.18	0.16	4.15	5.84	3.87	5.61	4.12	0.70	0.00	0.00	0.17	0.98	n. d.

Table 4.4 Values of ratios (parameters) for oil/condensate mapping (based on whole oil GC-FID measurements) (page 7/8)

Data File	GC method	Records in the GC Database	Formation	1	2	3	4	5	6
				Pr/Ph	Pr/nC17	Ph/nC18	A	A'	B
XYOIL091.D	XYOILT.M	Inland-1, DST 2, Namur	Namur	3.86	0.37	0.11	0.01	0.07	0.07
XYOIL092.D	XYOILT.M	Inland-1, DST 1, Hutton	Hutton	3.86	0.37	0.11	0.01	0.07	0.08
XYOIL093.D	XYOILT.M	Taloola-2, DST 1, Poolowanna	Poolowanna	4.65	0.42	0.10	0.04	0.16	0.15
XYOIL094.D	XYOILT.M	Taloola-2, DST 2, Hutton	Hutton	4.78	0.42	0.09	0.07	0.17	0.18
XYOIL095.D	XYOILT.M	Taloola-2, DST 3, Namur	Namur	6.34	0.86	0.14	0.04	0.06	0.44
XYOIL096.D	XYOILT.M	Tantana-1, DST 1, Poolowanna	Poolowanna	5.10	0.47	0.10	0.02	0.14	0.10
XYOIL097.D	XYOILT.M	Tantana-1, DST 2, Hutton	Hutton	6.47	0.77	0.13	0.04	0.06	0.48
XYOIL098.D	XYOILT.M	Tantana-1, DST 3, Birkhead/Hutton	Birk/Hutton	7.65	1.18	0.17	0.04	0.05	0.77
XYOIL099.D	XYOILT.M	Tantana-2, DST 1, Poolowanna	Poolowanna	5.04	0.46	0.10	0.08	0.17	0.18
XYOIL100.D	XYOILT.M	Tantana-2, DST 2, Namur	Namur	6.42	0.77	0.13	0.03	0.05	0.43
XYOIL101.D	XYOILT.M	Tantana-9, DST 3, McKinlay	Mckinley	7.59	1.20	0.17	0.04	0.05	0.69
XYOIL102.D	XYOILT.M	Tantana-9, DST 4, Hutton	Hutton	7.84	1.03	0.15	0.02	0.08	0.18
XYOIL103.D	XYOILT.M	Sturt-2, DST 1, Poolowanna	Poolowanna	6.17	0.99	0.16	0.02	0.17	0.12
XYOIL104.D	XYOILT.M	Sturt-2, DST 2, Birkhead	Birkhead	6.83	1.25	0.20			4.83
XYOIL105.D	XYOILT.M	Sturt-3, DST 1A, Poolowanna	Poolowanna	6.24	1.11	0.18	0.02	0.16	0.10
XYOIL106.D	XYOILT.M	Sturt-3, DST 1B, Birkhead	Birkhead	6.48	1.19	0.19	0.03	0.09	0.10
XYOIL107.D	XYOILT.M	Sturt-4, DST 1, Poolowanna	Poolowanna	6.30	1.11	0.18	0.02	0.16	0.11
XYOIL108.D	XYOILT.M	Sturt-4, DST 2, Patchawarra	Patchawarra	6.31	1.12	0.18	0.02	0.16	0.12
XYOIL109.D	XYOILT.M	Sturt-5, DST 1, Patchawarra	Patchawarra	6.18	1.04	0.17	0.02	0.17	0.11
XYOIL110.D	XYOILT.M	Sturt-6, DST 1, Birkhead	Birkhead	7.27	1.41	0.21	0.05	0.11	0.21
XYOIL111.D	XYOILT.M	Sturt-6, DST 3, Patchawarra	Patchawarra	5.71	0.85	0.16	0.03	0.18	0.11
XYOIL112.D	XYOILT.M	Sturt-6, DST 6, Patchawarra	Patchawarra	6.18	0.87	0.15	0.04	0.20	0.14
XYOIL113.D	XYOILT.M	Sturt-7, DST 2, Mooracoochie	Mooracoochie	6.11	0.86	0.15	0.12	0.45	0.50
XYOIL114.D	XYOILT.M	Sturt-7, DST 3, Patchawarra	Patchawarra	6.26	1.07	0.17	0.02	0.17	0.12
XYOIL115.D	XYOILT.M	Sturt-7, DST 5, Patchawarra	Patchawarra	6.23	1.06	0.17	0.03	0.17	0.13
XYOIL116.D	XYOILT.M	Sturt-7, DST 4, Patchawarra	Patchawarra	6.20	0.87	0.15	0.03	0.19	0.13
XYOIL117.D	XYOILT.M	Sturt-8, DST 1, Patchawarra	Patchawarra	6.24	1.11	0.18	0.02	0.14	0.12
XYOIL118.D	XYOILT.M	Sturt East-2, DST 1, Patchawarra	Patchawarra	6.25	1.06	0.18	0.02	0.16	0.13

Table 4.4 Values of ratios (parameters) for oil/condensate mapping (based on whle oil GC-FID measurements) (page 8/8)

Data File	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	B'	X	X'	C	I	F	H	R	U	New 1	New 2	New 3	New 4	New 5
XYOIL091.D	0.06	0.17	0.18	1.57	1.67	1.32	3.95	5.27	0.95	0.03	0.05	0.43	1.07	n. d.
XYOIL092.D	0.07	0.19	0.20	1.46	1.62	1.28	3.89	5.31	1.02	0.04	0.05	0.52	1.08	n. d.
XYOIL093.D	0.07	0.29	0.21	0.79	2.07	0.63	2.78	3.07	1.05	0.03	0.06	0.39	1.06	n. d.
XYOIL094.D	0.06	0.22	0.16	2.10	4.11	2.03	5.00	4.88	1.59	0.00	0.00	0.32	1.01	n. d.
XYOIL095.D	0.05	0.34	0.12	1.06	1.45	0.98	3.41	4.11	0.59	0.00	0.00	0.16	1.02	n. d.
XYOIL096.D	0.08	0.24	0.22	0.86	1.82	0.63	2.66	3.19	1.82	0.03	0.08	0.33	1.06	n. d.
XYOIL097.D	0.05	0.32	0.11	0.74	1.16	0.67	2.79	3.89	0.66	0.00	0.00	0.20	1.00	n. d.
XYOIL098.D	0.05	0.32	0.11	1.08	1.36	1.03	3.60	4.66	0.64	0.00	0.00	0.13	1.03	n. d.
XYOIL099.D	0.08	0.27	0.21	0.55	1.64	0.52	2.53	3.84	2.68	0.06	0.08	0.35	1.06	n. d.
XYOIL100.D	0.05	0.31	0.11	0.79	1.15	0.71	2.89	4.00	0.68	0.00	0.00	0.20	1.00	n. d.
XYOIL101.D	0.05	0.33	0.11	1.00	1.30	0.92	3.26	3.80	0.49	0.00	0.00	0.12	1.02	n. d.
XYOIL102.D	0.06	0.49	0.10	0.83	1.31	0.63	2.65	3.50	0.92	0.00	0.00	0.15	1.01	n. d.
XYOIL103.D	0.11	0.22	0.21	1.10	2.07	0.80	3.02	3.52	1.92	0.03	0.04	0.21	1.04	n. d.
XYOIL104.D	0.08	1.46	0.18	0.28		0.28	2.20			0.00	0.00	0.02		n. d.
XYOIL105.D	0.08	0.20	0.18	1.16	2.09	0.88	3.24	3.70	1.95	0.03	0.03	0.18	1.03	n. d.
XYOIL106.D	0.07	0.14	0.16	1.66	2.17	1.44	4.08	3.71	0.58	0.00	0.00	0.08	1.05	n. d.
XYOIL107.D	0.09	0.19	0.19	1.28	2.21	0.94	3.33	3.60	1.88	0.00	0.00	0.16	1.03	n. d.
XYOIL108.D	0.09	0.20	0.18	1.23	2.25	0.91	3.23	3.29	2.01	0.00	0.00	0.16	1.03	n. d.
XYOIL109.D	0.09	0.18	0.17	1.15	2.11	0.85	3.17	3.69	2.10	0.03	0.03	0.18	1.04	n. d.
XYOIL110.D	0.06	0.23	0.13	2.27	2.97	2.15	4.97	4.61	0.67	0.00	0.00	0.09	1.03	n. d.
XYOIL111.D	0.10	1.32	1.37	0.85	2.04	0.64	2.60	2.86	1.78	0.04	0.08	0.28	1.08	n. d.
XYOIL112.D	0.10	0.27	0.25	0.71	1.87	0.57	2.48	3.14	2.23	0.04	0.08	0.26	1.08	n. d.
XYOIL113.D	0.33	0.55	0.40	0.73	2.73	0.49	1.61	0.89	0.93	0.14	0.14	0.20	1.08	n. d.
XYOIL114.D	0.10	0.21	0.19	1.08	2.12	0.78	2.98	3.19	2.00	0.03	0.03	0.17	1.04	n. d.
XYOIL115.D	0.10	0.22	0.20	0.91	2.06	0.72	2.90	3.24	2.28	0.03	0.04	0.19	1.04	n. d.
XYOIL116.D	0.11	0.26	0.26	0.83	1.89	0.62	2.57	3.16	1.82	0.05	0.08	0.29	1.08	n. d.
XYOIL117.D	0.08	0.19	0.17	1.09	2.20	0.92	3.43	3.94	2.41	0.02	0.02	0.17	1.03	n. d.
XYOIL118.D	0.10	0.22	0.20	0.93	2.01	0.74	2.96	3.54	2.15	0.03	0.04	0.19	1.04	n. d.

concentrations to those of *n*-heptadecane; and are roughly half as abundant as the main peaks, *n*-heptane and methycyclohexane. Although not evident in the figure, this oil even contains propane and ethane.

As expected, the concentrations of the light hydrocarbons decrease significantly with prolonged evaporation. Within just 1.5 hr, the C_4 and lighter hydrocarbons had disappeared (see Figure 4.3b); and the content of C_5 and C_6 alkanes dropped to about half of their original levels. These changes imply that even short-term (e.g. overnight) storage of similar crude oils in the open air, or in containers with a large head-space, may significantly deplete the front-end components. Thus compositional parameters based on C_5 and C_6 hydrocarbon isomers are not very reliable for geochemical interpretation, particularly when the sample quality or handling history is not clear.

With increasing evaporation time, the contents of all the hydrocarbons lighter than *n*-C_8 decreased markedly. After 3 hr of evaporation, the butanes had disappeared from the GC trace (see Figure 4.3c); and the concentration of *n*-pentane became less than one-tenth of its original level. By 6.5 hr the C_5 components had evaporated (see Figure 4.3d), and *n*-hexane content had dropped to one-fifth of the original level. The main peak in the GC profile became *n*-octane. After 18 hr of evaporation the concentration of *n*-heptane became half that of *n*-octane; after 31 hr, one tenth; and after 48 hr, most of the components lighter than *n*-decane had disappeared. Thus, caution should be exercised when using any parameters that involve hydrocarbon isomers lighter than *n*-C_{10}.

The relative effect of evaporation on compound ratios used in the following discussion is shown in Figure 4.4 and Table 4.5. The more volatile the hydrocarbons incorporated in a parameter, the greater the impact of evaporation on its value. It is obvious that parameters R, U, C, F, A, A', B, and B' (see Table 4.1 for their definitions) are seriously modified by evaporation; all involve C_6 and C_7 hydrocarbons. On the contrary, parameters based on components in the C_{10+} range (viz. Pr/Ph, TPI, Pr/nC_{17}, Ph/nC_{18}, New 1, New 2, New 3 and, to a lesser degree, New 5: Table 4.1) are nearly constant with the evaporation. The only light

Table 4.5 Variation of selected parameters with artificial evaporation time

Evap Time (hr)	1	2	3	4	5	6	7	8	9	10
	Pr/Ph	Pr/nC17	Ph/nC18	A	A'	B	B'	X	X'	C
0.0	3.70	0.58	0.15	0.01	0.15	0.07	0.08	0.19	0.20	1.24
1.5	3.91	0.57	0.15	0.02	0.15	0.08	0.08	0.19	0.21	1.13
3.0	3.73	0.57	0.15	0.02	0.14	0.08	0.07	0.20	0.21	1.02
4.5	3.73	0.57	0.15	0.03	0.14	0.09	0.07	0.20	0.20	0.94
6.5	3.74	0.57	0.15	0.04	0.12	0.11	0.07	0.21	0.20	0.84
8.5	3.80	0.57	0.15	0.05	0.12	0.11	0.07	0.23	0.22	0.81
10.5	3.73	0.57	0.15	0.09	0.10	0.15	0.07	0.22	0.19	0.74
12.5	3.74	0.57	0.15	0.13	0.10	0.16	0.07	0.23	0.19	0.71
18.0	3.75	0.57	0.15		0.08	0.22	0.05	0.26	0.19	0.65
31.0	3.79	0.57	0.15		0.00	0.62	0.04	0.34	0.16	0.55
48.0	3.74	0.57	0.15							

Evap Time (hr)	11	12	13	14	15	16	17	18	19	20
	I	F	H	R	U	New 1	New 2	New 3	New 4	New 5
0.0	1.20	0.80	3.10	3.63	1.44	0.02	0.04	0.09	1.00	0.03
1.5	1.24	0.79	3.11	4.62	1.56	0.02	0.04	0.10	1.02	0.06
3.0	1.17	0.79	3.18	4.13	1.84	0.02	0.04	0.09	1.00	0.09
4.5	1.16	0.78	3.22	4.40	1.83	0.03	0.04	0.09	1.01	0.04
6.5	1.18	0.76	3.43	4.62	2.47	0.02	0.04	0.10	1.01	0.06
8.5	1.20	0.75	3.28	4.66	2.75	0.02	0.04	0.09	1.01	0.04
10.5	1.12	0.73	3.39	6.08	3.57	0.02	0.04	0.10	1.00	0.05
12.5	1.11	0.71	3.42	7.02	4.48	0.02	0.04	0.10	1.01	0.05
18.0	1.04	0.66	3.45	10.04	8.38	0.02	0.04	0.10	1.01	0.05
31.0	0.96	0.55	3.33	23.00		0.02	0.04	0.09	1.01	0.06
48.0						0.00	0.00	0.09	1.03	

hydrocarbon ratios that are not seriously compromised by evaporation are H (heptane value), I (isoheptane value), X (*m* + *p*-xylene/*n*-octane) and X' (*m* + *p*-xylene/*n*-C_9). The main reason for this stability during evaporation may be that the hydrocarbons involved in any one of these parameters have similar vapour pressures and so they are affected similarly by evaporation.

The five new parameters were developed based on the artificial evaporation experiment and careful inspection of all the whole-oil gas chromatograms. Their geochemical significance will be discussed later in this chapter. Cross-plots of these ratios against artificial evaporation time for the Nockatunga-3 (Murta) oil (Figure 4.4b & c) demonstrate that most of them display negligible variation under the conditions of the artificial evaporation experiment. They should be effective parameters, even in the case of poor quality of oil samples. Apparent random changes in the evaporation profiles of New 2, New 3 and New 5 (Figure 4.4c) are caused by the unusually low concentrations of the aromatic hydrocarbons (viz. naphthalene, 1,2,4-trimethylbenzene and phenanthrene) in this and other Eromanga oils. Their contents are too low to permit consistent integration of their peak area. This does not affect their validity in distinguishing between Cooper and Eromanga petroleums, because the aromatic compounds in question have concentrations ten times higher in the former crudes.

4.2.5 REPRODUCIBILITY OF THE GC-FID MEASUREMENTS

As described in Section 3.3.5, multiple injections of the same oil (Sturt-6, DST 1, Patchawarra?) were made to assess the analytical reproducibility of the GC-FID technique. The results are summarised in Table 4.6 and Figure 4.5.

The experimental results showed adequate reproducibility in the whole-oil GC-FID analysis for the purpose of this project. Deviations of the six runs are negligible relative to the difference between different samples (and especially between the Cooper and Eromanga crudes). As shown in Figure 4.5 and Table 4.6, the standard error for all the parameters among the six runs ranges from 0.1% to 5.9% with Pr/Ph showing the greatest error. The other largeset errors are 3.6%, 2.6% and 2.2% for

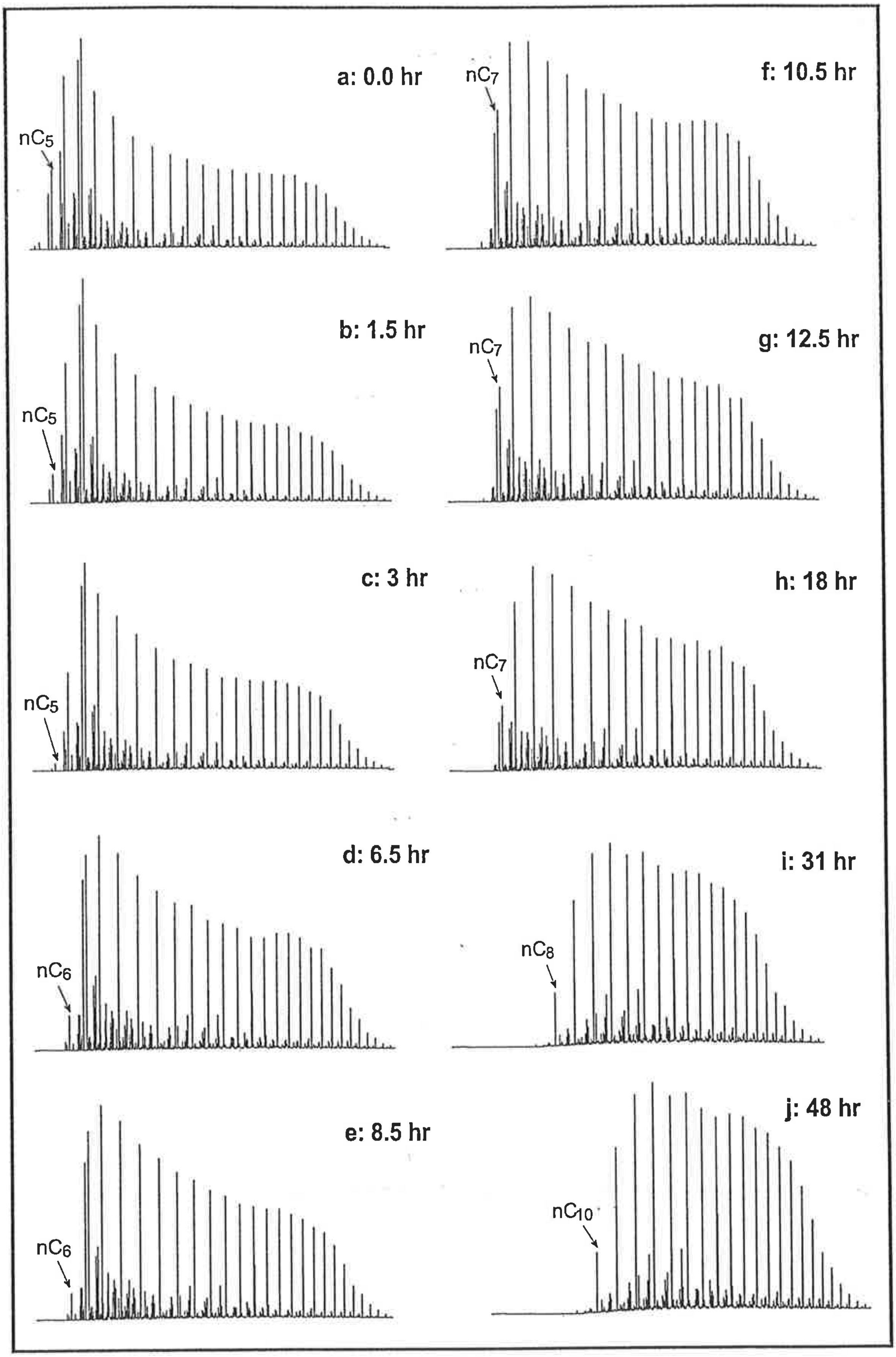


Figure 4.3 GC-FID chromatograms of a "whole oil" after artifical evaporation

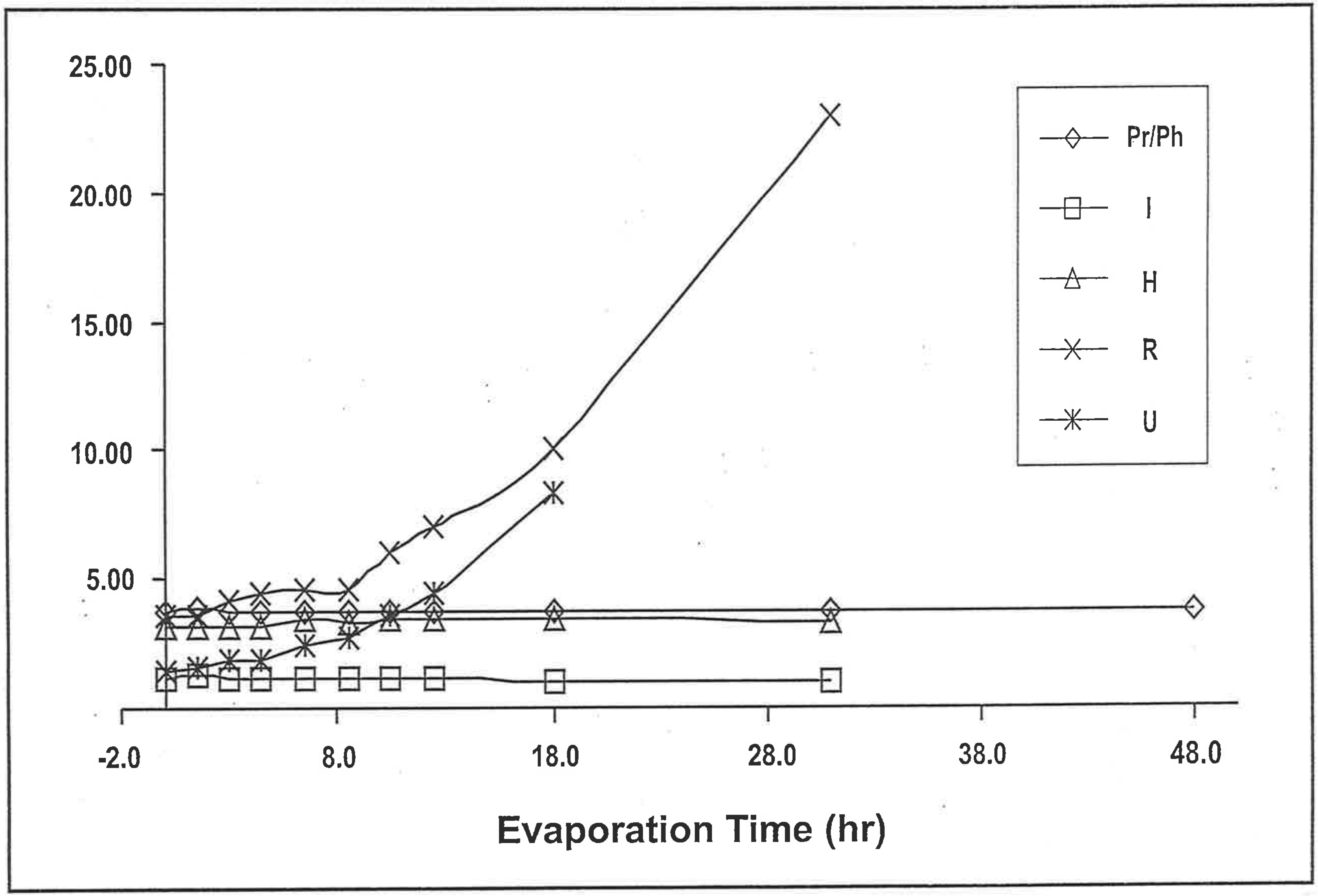


Figure 4.4a Variation of selected parameters with artifical evaporation time

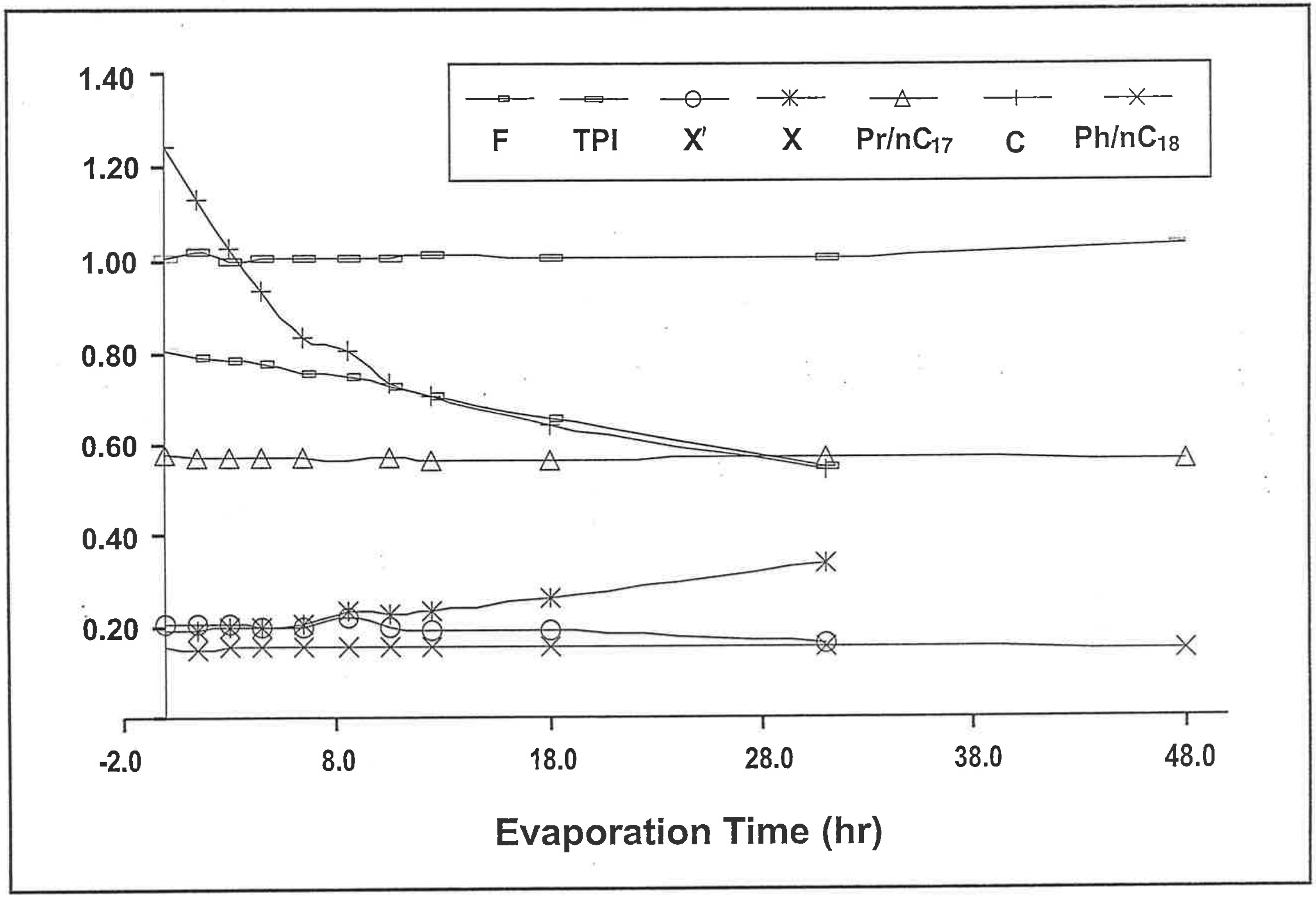


Figure 4.4b Variation of selected parameters with artifical evaporation time

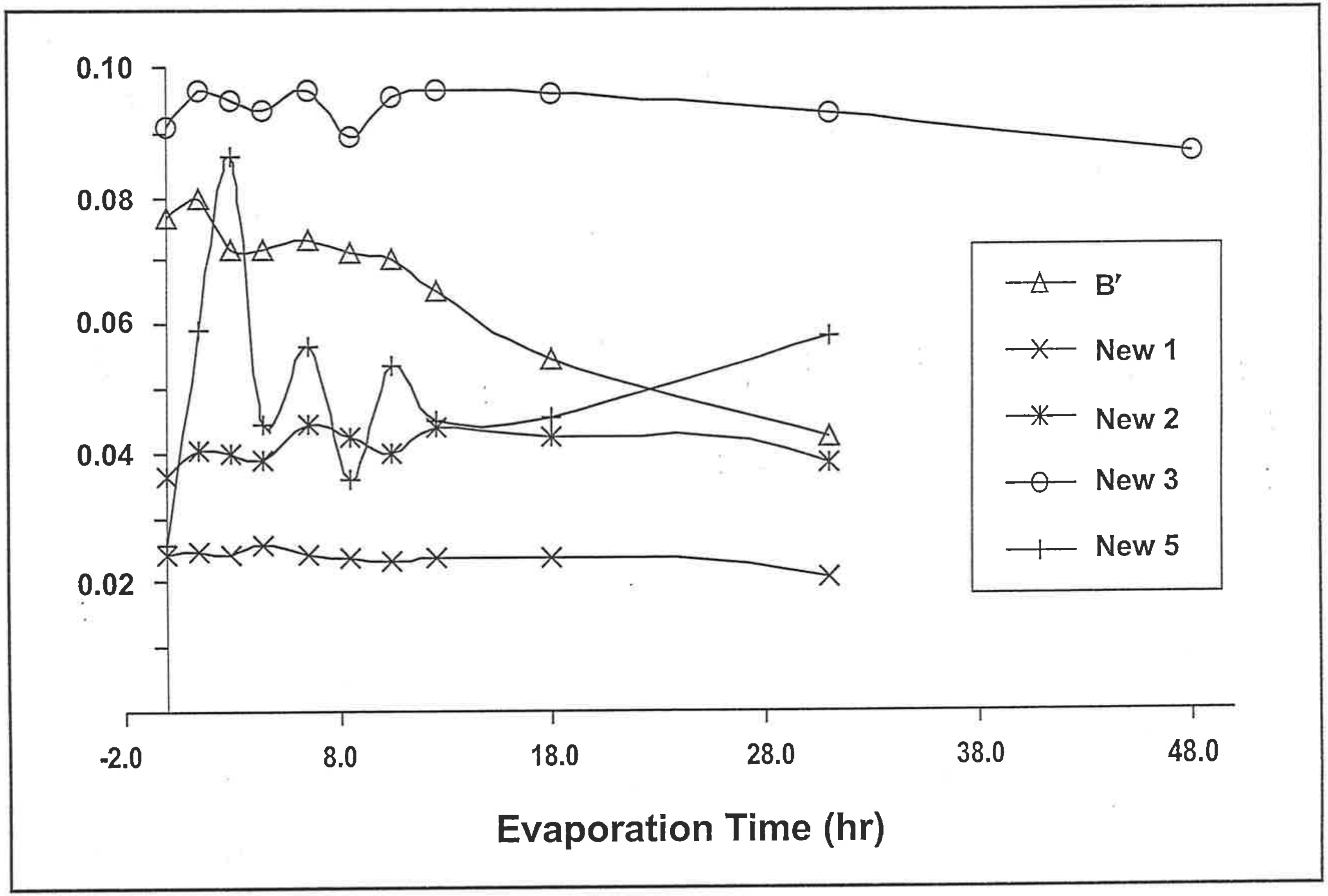


Figure 4.4c Variation of selected parameters with artifical evaporation time

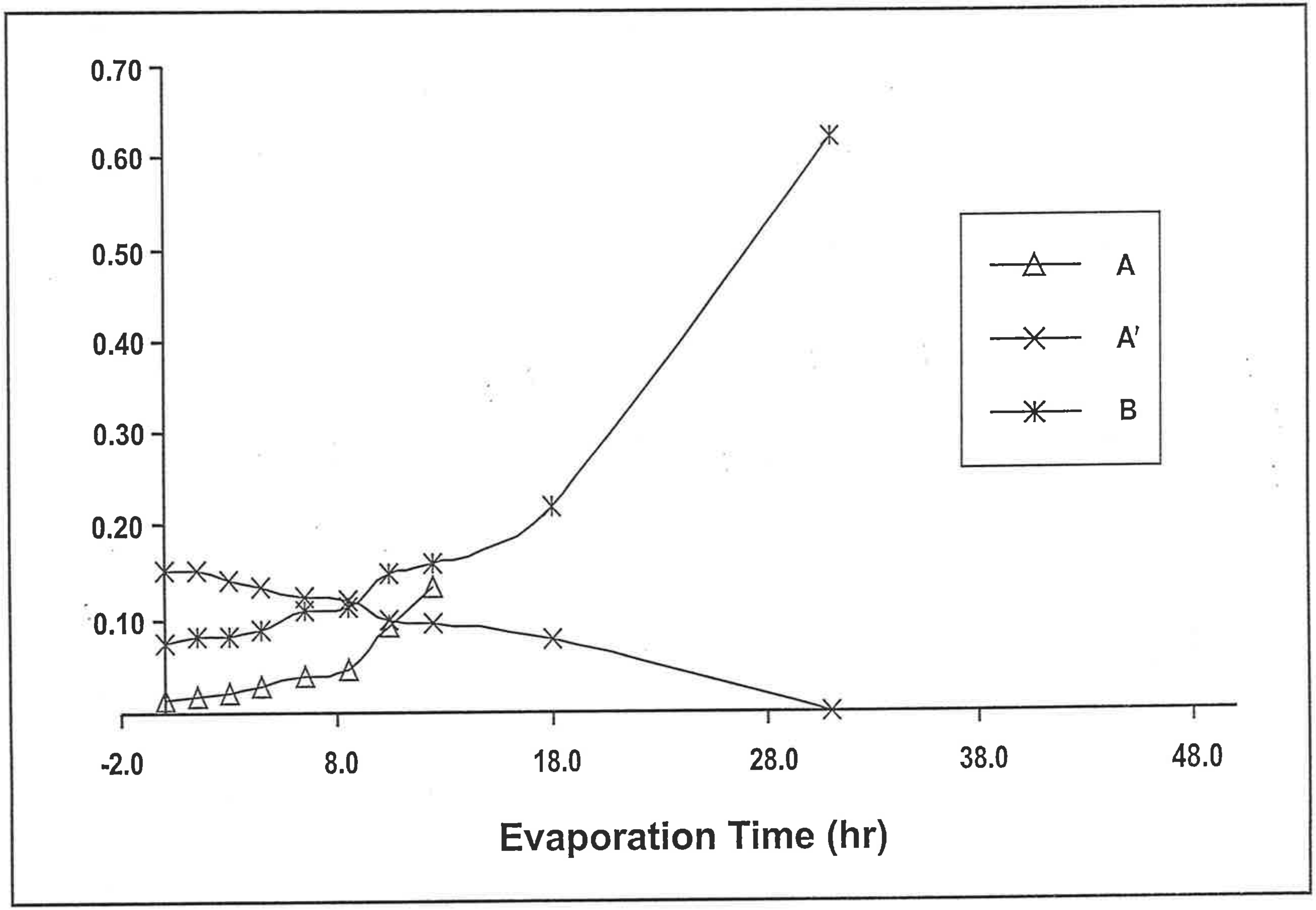


Figure 4.4d Variation of selected parameters with artifical evaporation time

parameters U, F and C, respectively. Errors for the remaining parameters are less than 1.3%.

4.2.6 DISTINGUISHING COOPER AND EROMANGA CRUDES

Gas chromatographic traces of typical Eromanga and Cooper crude oils are shown in Figure 4.1a & b. The Eromanga oil is from the Murta Formation in Nockatunga-3, and the Cooper crude is from the Tirrawarra Formation in Tirrawarra-58. By contrast with the Eromanga oil, it can be seen that the Cooper oil contains higher concentrations of aromatic hydrocarbons (viz. toluene, xylene, naphthalene, 1,2,4-trimethylbenzene and phenanthrene). Surprisingly, unlike the other low-molecular-weight aromatic compounds, benzene does not show any obvious concentration difference between the Cooper and Eromanga crudes. The most unusual characteristic of the Permian oils is their marked apparent tridecane preference in the *n*-alkane profile (see Figure 4.1b). As discussed in Section 4.2.2, this feature (caused by the coelution of *n*-tridecane with 2-methylnaphthalene: Figure 4.2) is absent in the Murta and other Eromanga-reservoired oils.

The aforementioned diagnostic features for distinguishing Cooper and Eromanga hydrocarbons are reflected in a variety of the parameters listed in Table 4.1. Parameters A, B, X, C, I, F, H, R and U (and their assigned significance) are compositional ratios employed by Thompson (1983, 1987, 1988) to classify petroleums in terms of their source, thermal maturity and degree of evaporative fractionation. Parameters A', B' and X' are variations of the original equivalent Thompson ratios. Compositional differences between the Cooper- and Eromanga-reservoired crude oils can be displayed using crossplots of these parameters versus reservoir formation (grouped in order of increasing stratigraphic age from left to right on the abscissa axis: see Figures 4.6 & 4.7). A complete set of these crossplots may be found in Appendix 1 (Figures A.1a–s). The newly developed parameters (e.g. New 1: Figure 4.6) are more effective than many of the conventional ones (e.g. H, Heptane Value: Figure 4.7) in distinguishing Cooper and Eromanga crude oils.

It will be shown below that, among all the parameters listed in Table 4.1, New 1–4 are the most effective in differentiating the Permo-Triassic oils from those in

Table 4.6 Reproducibility of selected parameters from six injections of the same whole-oil sample on GC-FID

Test	Pr/Ph	Pr/nC17	Ph/nC18	A	B	X	C	I	F	U	New 1	New 2	New 3	New 5
Run 1 (0.8 µl)	5.859	0.889	0.158	0.037	0.104	0.162	0.780	2.364	0.615	2.043	0.047	0.081	0.291	0.044
Run 2 (0.5 µl)	6.216	0.877	0.151	0.031	0.105	0.167	0.774	2.372	0.611	1.928	0.048	0.082	0.282	0.040
Run 3 (0.7 µl)	5.905	0.877	0.157	0.033	0.141	0.164	0.640	2.353	0.455	2.031	0.045	0.083	0.239	0.036
Run 4 (0.8 µl)	5.922	0.874	0.157	0.033	0.103	0.165	0.770	2.357	0.609	2.041	0.049	0.083	0.284	0.053
Run 5 (0.7 µl)	5.895	0.878	0.157	0.038	0.105	0.165	0.767	2.355	0.610	2.056	0.047	0.081	0.257	0.061
Run 6 (0.5 µl)	5.810	0.890	0.163	0.040	0.154	0.168	0.777	2.438	0.614	1.833	0.049	0.079	0.265	0.027
Result of data analysis														
Mean	5.935	0.881	0.157	0.035	0.119	0.165	0.751	2.373	0.586	1.989	0.047	0.081	0.270	0.044
S. E.*	0.059	0.003	0.002	0.001	0.009	0.001	0.022	0.013	0.026	0.036	0.001	0.001	0.008	0.005
Median	5.900	0.878	0.157	0.035	0.105	0.165	0.772	2.361	0.611	2.036	0.048	0.082	0.274	0.042
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
S. D.*	0.144	0.007	0.004	0.003	0.023	0.002	0.055	0.033	0.064	0.089	0.001	0.001	0.020	0.012
S. V.*	0.021	0.000	0.000	0.000	0.001	0.000	0.003	0.001	0.004	0.008	0.000	0.000	0.000	0.000
Kurtosis	4.544	-1.746	2.342	-0.903	-1.017	-0.992	5.857	5.046	5.973	0.783	0.698	0.400	-0.701	-0.515
Skewness	2.009	0.734	0.076	0.085	1.107	0.297	-2.412	2.213	-2.442	-1.392	-1.183	-0.896	-0.667	0.213
Range	0.406	0.016	0.012	0.010	0.051	0.006	0.139	0.085	0.160	0.223	0.004	0.004	0.052	0.034
Minimum	5.810	0.874	0.151	0.031	0.103	0.162	0.640	2.353	0.455	1.833	0.045	0.079	0.239	0.027
Maximum	6.216	0.890	0.163	0.040	0.154	0.168	0.780	2.438	0.615	2.056	0.049	0.083	0.291	0.061
Sum	35.608	5.285	0.943	0.211	0.712	0.991	4.508	14.239	3.514	11.933	0.284	0.489	1.618	0.261
Count	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
C. L. *	0.151	0.007	0.004	0.004	0.024	0.002	0.057	0.034	0.067	0.094	0.002	0.001	0.021	0.013

* S. E. Standard Error
S. D. Standard deviation
S. V. Sample Variances
C. L. Confidence Level (95%)

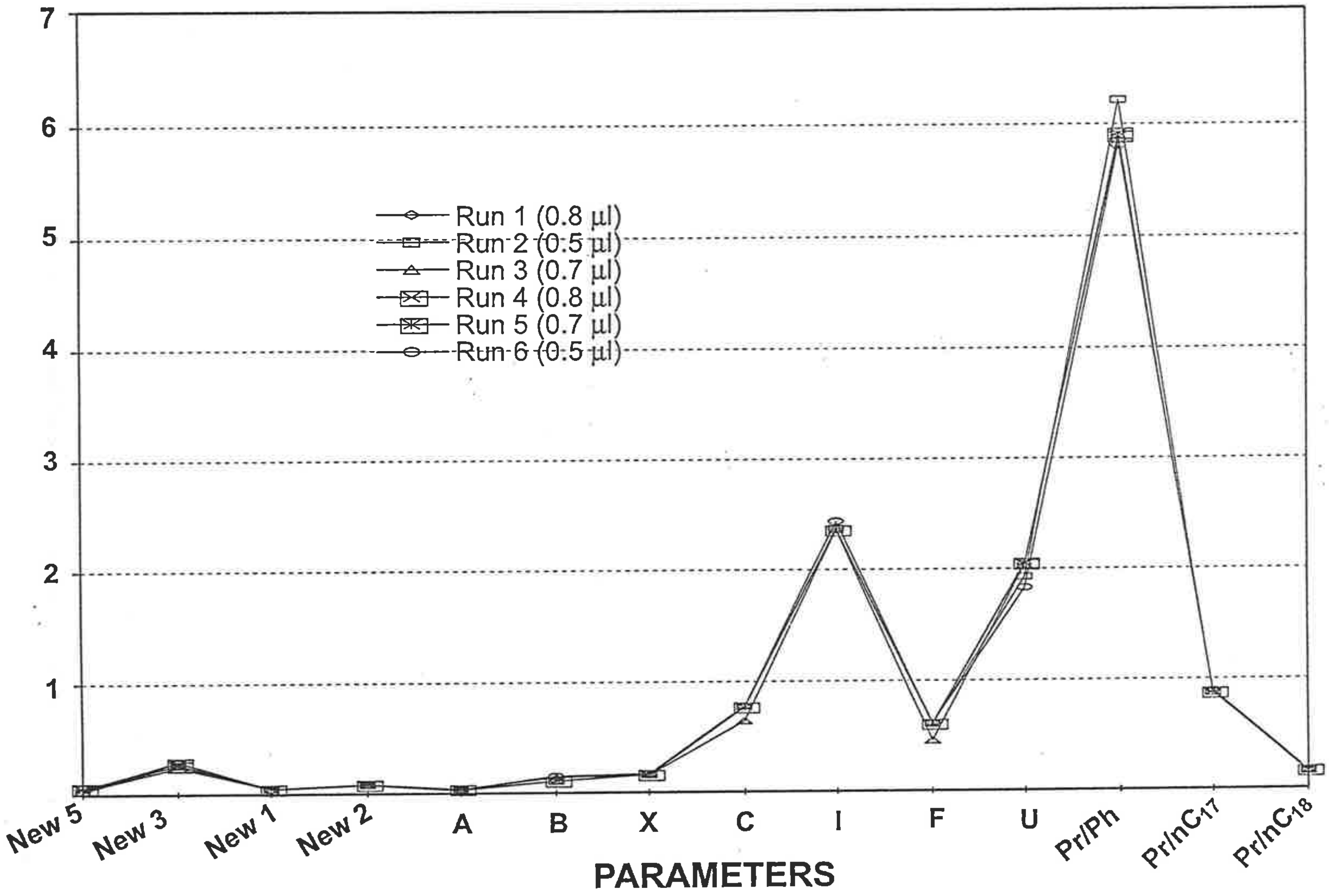


Figure 4.5 Reproducibilities of selected parameters from six injections (each of different size) of the same oil sample.

Eromanga reservoirs (see Figures 4.6 and A.1 m–p). Only three of Thompson's (1983, 1987, 1988) ratios, B, X and U, can match the effectiveness of the new ones (see Figures A.1e, f & l). Crossplots of the remaining parameters (A, F, C, I, H, R, Pr/nC$_{18}$, Ph/nC$_{18}$, and Pr/Ph) reveal no evident systematic differences between the Cooper and Eromanga crudes (see Figures 4.7 and A.1a–d, g–k).

The following sections discuss in detail how each of the parameters may be used in distinguishing Cooper and Eromanga crude oils, with a view to understanding the petroleum mapping based on cluster analysis. The results of statistical analysis for all the parameters are listed in Tables 4.7–4.9.

4.2.6.1 Pr/Ph

Being easily measured using simple gas chromatography, the relative abundance of pristane and phytane (Pr/Ph) is commonly applied in various aspects of organic geochemistry. Powell and McKirdy (1973) found that Pr/Ph ratio ranges from 5 to 11 among high-wax Australian oils/condensates sourced from non-marine source rocks, whereas in crude oils derived from marine organic matter the ratio ranges from 1 to 3. Clayton et al. (1987) distinguished 3 types of Paleozoic oil in the Northern Denver Basin based mainly on their Pr/Ph ratio and stable carbon isotope composition. Pr/Ph was initially proposed to indicate the redox potential of organic-rich sediments (Didyk et al., 1978). Schwark and Puttman (1990) reported that the Pr/Ph ratio also showed some relationship with palaeosalinity.

However, there are factors other than depositional environment that affect the Pr/Ph ratio. Firstly, the phytyl side chain of chlorophyll in phototrophic organisms is not the only precursor of pristane and phytane (Chappe et al., 1982; Illich, 1983; Goosens et al., 1984; ten Haven et al., 1987; Rowland, 1990). Secondly, the Pr/Ph value depends on the thermal maturation level of the host sediment or source rock from which the oil was derived (Brooks et al., 1969; Albrecht et al., 1976; Radke et al., 1980a; Alexander et al., 1981; Burnham et al., 1982; Connan, 1984; ten Haven et al., 1987)

Previous studies of the petroleum geochemistry of the Cooper and Eromanga Basins have used the pristane/phytane ratio to characterise the depositional environments of its source rocks and the source affinity of its oils (McKirdy, 1982, 1985; Vincent et al., 1985; Jenkins, 1989; Michaelsen and McKirdy, 1989; Powell et al., 1989; Michaelsen and McKirdy, 1996; Boreham and Hill, 1998; Boreham and Summons, 1999).

From the data of this project, it is evident that the Pr/Ph ratio provides little help in distinguishing Cooper and Eromanga petroleums (Tables 4.7–4.9; Figure A.1a). This may be a reflection of the similarity of the organic facies in the Cooper and Eromanga Basins. As displayed in Figure A.1a, the Pr/Ph values distribute erratically between and within the reservoir formations. Six Namur and thirteen other Eromanga-reservoired oils/condensates show very high values (Pr/Ph > 6), whereas crude oils reservoired in the Toolachee Formation and some (but not all) of those in the Patchawarra Formation tend to have somewhat lower values (Pr/Ph < 5).

The Pr/Ph ratios of the Eromanga-reservoired oils (range = 0.26–7.95, mean = 4.91) are only slightly greater than those for the Cooper oils and condensates (range = 0.22–6.35, mean = 4.13). Values for the whole sample set range from 0.22 (XYOIL014, Munkah-2, Patchawarra) to 7.95 (XYOIL010, Tantanna-1, Birkhead/Namur), with a mean of 4.67.

4.2.6.2 Pr/n-C_{17} and Ph/n-C_{18}

Being as easy as Pr/Ph to obtain by gas chromatography, the two isoprenoid/n-alkane ratios Pr/n-C_{17} and Ph/n-C_{18} are also commonly used in oil-to-oil correlation. However, they are readily affected by several geochemical processes. Both of them decrease with increasing thermal maturity, and this made Alexander et al. (1981) propose the using of the ratio (Pr+n-C_{17})/(Ph+n-C_{18}) because it is less affected by variations in thermal maturity. Biodegradation by aerobic bacteria is a secondary alteration process that also influences the two ratios, because the n-alkanes are generally attacked prior to the isoprenoids (Connan, 1984; Seifert and Moldowan, 1979; Zhang et al., 1988).

Like Pr/Ph, the Pr/n-C_{17} and Ph/n-C_{18} ratios are not very helpful in distinguishing the

Cooper and Eromanga crude oils. As shown in Figures A.1b & c, there are no regular patterns for the distributions of Pr/n-C_{17} and Ph/n-C_{18} according to reservoir unit. The values of Pr/n-C_{17} and Ph/n-C_{18} are highest in six Namur, several Birkhead/Hutton, eight Poolowanna and ten Patchawarra crudes. The majority of the Pr/n-C_{17} values distribute around 0.4, and the median of the Ph/n-C_{18} is 0.1 (see Table 4.7).

Again, statistical analysis shows that there is no clear contrast between the Cooper and Eromanga crude oils in terms of their Pr/n-C_{17} and Ph/n-C_{18} distribution patterns. In the Cooper crudes Pr/n-C_{17} ranges from 0.17 to 1.06 (mean = 0.49) (Table 4.9) whereas in the Eromanga petroleums it ranges from 0.24 to 1.65 (mean = 0.60) (Table 4.8). Though the difference between the two means is larger than 10% of their average value, it is still very difficult to use the Pr/n-C_{17} ratio to distinguish the crude oils reservoired in the Cooper and Eromanga Basins, because of the overlap in the two data ranges.

Similarly, the Ph/n-C_{18} ratios range from 0.07 to 0.27 (mean = 0.12) for the analysed Cooper oils/condensates (Table 4.9), and from 0.07 to 0.21 (mean = 0.12) for the analysed Eromanga crude oils (Table 4.8). It is even more difficult to use this ratio to distinguish the Cooper and Eromanga oils/condensates, because the data distribute in nearly the same pattern about the same mean for the two groups of crude oils.

4.2.6.3 Parameter C

Parameter C, which is the ratio of (n-hexane + n-heptane)/(cyclohexane + methylcyclohexane), was first proposed by Thompson (1983) as an indicator of paraffinicity and maturity. Later Thompson (1987, 1988) concluded that this ratio also decreased in a crude oil with loss of its light ends in the subsurface by the process of “evaporative fractionation” or “migration fractionation”.

From the trend illustrated in Figure A.1d it is evident that the Eromanga-reservoired oils generally have larger C values than the oils/condensates from Cooper reservoirs.

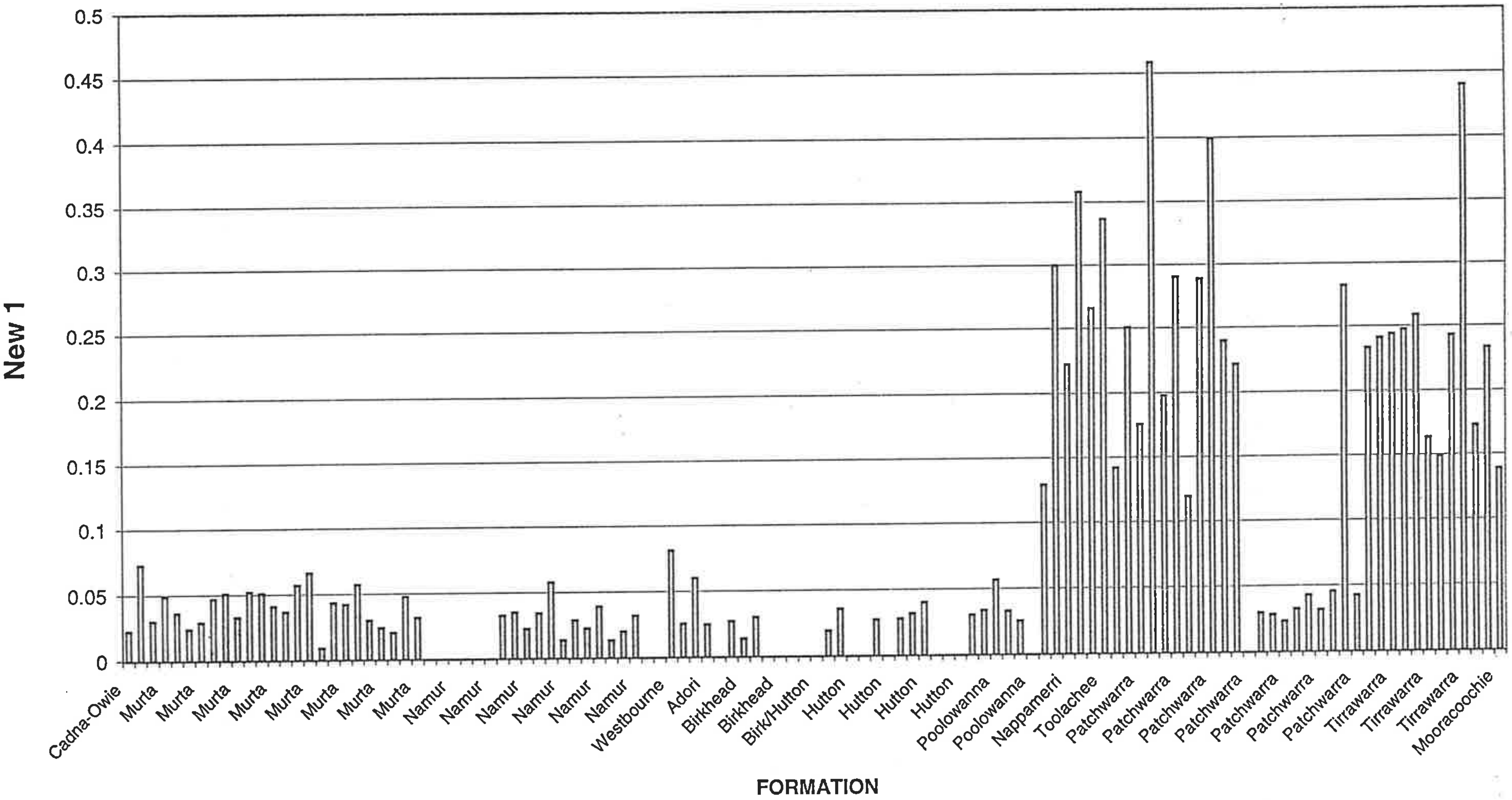


Figure 4.6 Variation of New 1 with reservoir strata, showing obvious difference between Cooper and Eromanga crudes

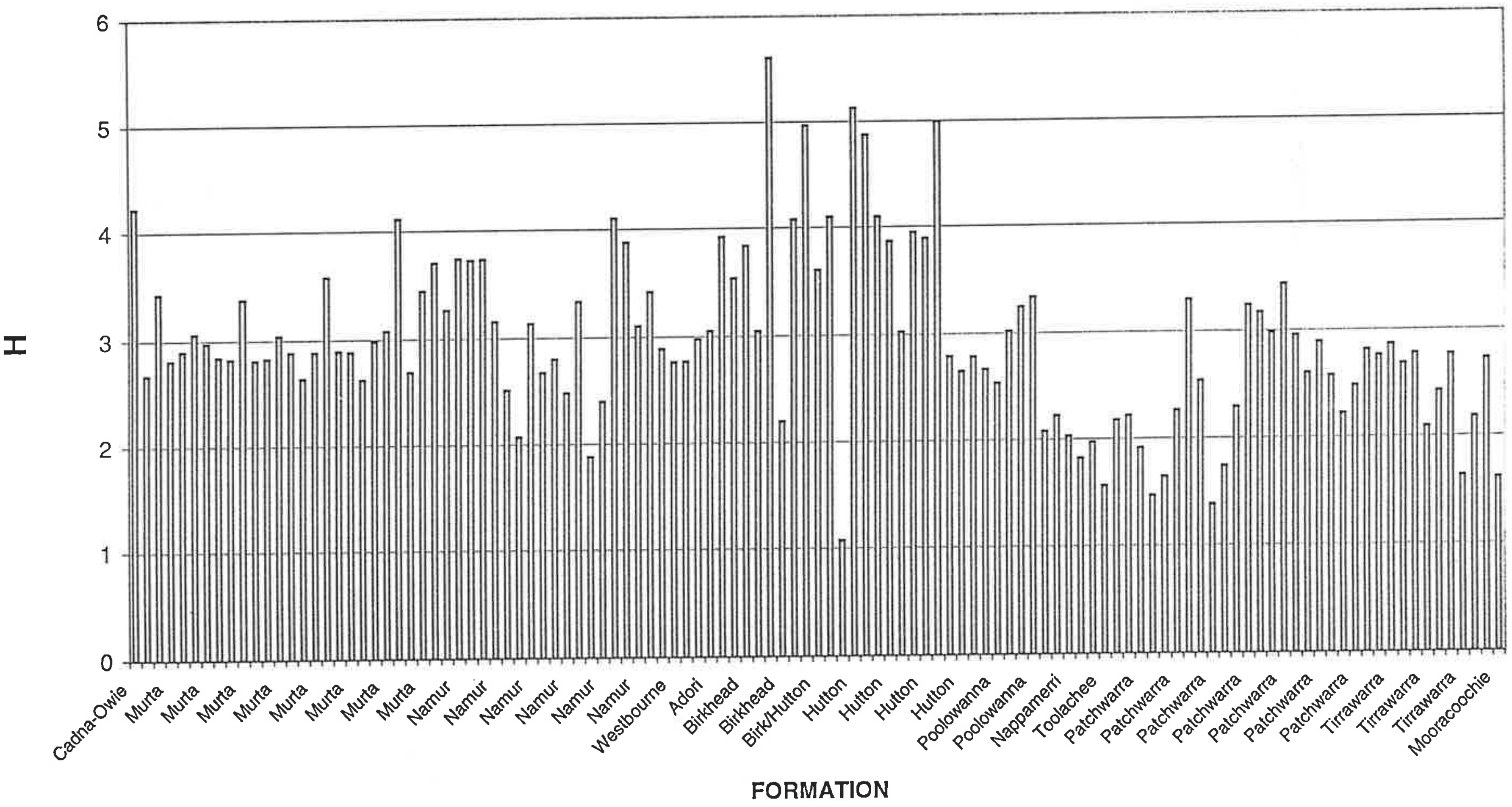


Figure 4.7 Variation of H with reservoir strata, showing a less obvious distinction between Cooper and Eromanga crudes

Although the majority of the C values in the Cooper population are =1.0, values larger than 1.2 occur in many of the Eromanga samples.

Statistical analysis of the data for parameter C shows the same trend. The C values of the whole set of 115 counted oils/condensates range from 0.19 to 4.15 (mean = 1.08: Table 4.7). Comparison of the 81 Eromanga-reservoired crude oils (range = 0.22–4.15, mean = 1.26: Table 4.8) with the 34 Cooper-reservoired petroleum (range = 0.19 to 0.12, mean = 0.66: Table 3.9) reveals that the mean of parameter C for the Eromanga-reservoired oils is about twice that for the Cooper-reservoired crudes.

Both migration and maturation could have influenced the distribution of C values in the Cooper and Eromanga crudes (Figure A.1d). Previous studies (e.g. Tupper and Burckhardt, 1990, using MPI) have shown that the latter oils are, on average, less mature than the former. Yet, according to the principles outlined by Thompson (1987,1988), any migration of petroleum light-ends from the Cooper to the Eromanga Basin (as proven to be the case in Chapters 5 and 6) should mean that the "paraffinicity" (and apparent maturity) of those petroleums pooled in the Eromanga strata are greater than that of the oils remaining in the Cooper Basin. Both processes would tend to enhance the C value of petroleum derived from the Cooper Basin and reservoired in the overlying sequences.

Whereas either "migration fractionation" or thermal evolution (or both of them together) could explain the distribution pattern of C values in Figure A.1d, the former is believed to be more important in the Cooper/Eromanga province. It is significant that the largest values of parameter C are displayed by Eromanga-hosted crudes from the Wancoocha Field (viz. 3.16 and 3.54 in the Hutton oils at Wancoocha-2 & 3; 4.15 in the Birkhead oil at Wancoocha-2; and 2.13 in the Murta oil at Wancoocha-6). This field is located on the southwestern margin of the Nappamerri Trough (Figure 3.1). Similarly, two fields on the southwestern flank of the Patchawarra Trough, Taloola and Sturt, (Figure 3.1), also contain oils with high values of parameter C (viz. 2.10 in Taloola-2, Hutton oil; and 2.27 in Sturt-6, Birkhead oil). In all these instances, the Eromanga oil pools are positioned near or beyond the zero edge of the Cooper Basin, allowing vertical migration of hydrocarbons past the regional

Nappamerri seal (Heath et al., 1989; Kagya, 1997). A similar migration scenario is likely at Cook-1 (Hutton: C = 1.82) and Kercummurra-1 (Cadn-Owie: C = 2.25), located just beyond the northern and southern edges, respectively of the Cooper Basin in Queensland. Other oils with high C values include those from the Merrimelia Field (Namur: C = 1.96) on the GMI Ridge (Figure 3.1) and the Wilson Field (Hutton: C = 1.68) on the Jackson-Naccowlah Trend, an extension of the GMI Ridge in Queensland (Vincent et al., 1985). Here major faults or erosional unconformities provide pathways for migration of Permian hydrocarbons into Eromanga reservoirs. It is not clear, however, why oil in the Namur Sandstone of the Dullingari Field has a high C value of 1.88.

Scenarios of long-distance migration from Cooper Basin source rocks into Eromanga reservoirs along faults or past the zero edge of the Cooper Basin (cf. Heath et al., 1989) are further elaborated in the following chapters.

4.2.6.4 Parameter H (Heptane Value)

The Heptane Value (H = 10 x n-heptane/(Σ all compounds eluting between cyclohexane and methylcyclohexane, excluding *cis*-1,2-dimethylcyclopentane) is another conventional light-hydrocarbon indicator of maturity in petroleum. It was one of two parameters first measured by Thompson (1979) in the C_2–C_7 hydrocarbons recovered from mudstones and shales, and chosen to evaluate "paraffinicity" (i.e. ratios of normal paraffins to naphthenes or, in the case of the second parameter, branched paraffins to naphthenes) in terms of stratal temperature. He later found that the Heptane Value is closely related to vitrinite reflectance, the most robust maturity indicator (Thompson, 1983). Schaefer (1992) and Schaefer and Littke (1988) reported similar relationships in Toarcian Shales. They proposed two equations relating vitrinite reflectance (Rm) to heptane and isoheptane values similar to those of Thompson: $Rm = 1.0 + 1.8 \log V$ and $Rm = 0.84 + 1.1 \log J$, where V = C_7 paraffin/C_7 naphthenes and J = (2-methylhexane + 3-methylhexane)/(*cis*-1,3- + *trans*-1,3- + *trans*-1,2- + *cis*-1,2-dimethylcyclopentane).

Figure 4.7 shows the distribution of Heptane Value (H) across the reservoir formations. The pattern is somewhat similar to that of parameter C discussed above in that the values are larger in the Eromanga-reservoired crude oils (range = 1.07–5.61; mean = 3.24) than in the Cooper-reservoired petroleums (range = 1.38–3.3; mean = 2.28). All the 11 oils with H values >4.0 are reservoired in the Eromanga sequence. These include oils from the same fields with high C values, viz. Wancoocha, Taloola, Sturt, Merrimelia, Wilson, Cook and Kercummurra which are adjacent to the pinchout of the Permo-Triasssic infra-basin, or at Merrimelia where the Eromanga reservoirs are unconformably underlain by the Permian section. Thus, parameters C and H have very similar geochemical significance.

Though petroleum paraffinicity is affected by various factors (such as kerogen type, maturity, migration and biodegradation) fractionation during the migration of Cooper-sourced hydrocarbons into the Eromanga reservoirs appears to be the main reason for the higher paraffinicity seen in certain Eromanga oils. Organic facies are very similar throughout the non-marine sequences of the Cooper and Eromanga Basins, and hence the hydrocarbons derived from them should have similar paraffinicity at the same maturity level. Although mixed charging of some Eromanga reservoirs has occurred (see Chapters 5 & 6), the average maturity of Cooper-reservoired crudes is greater than that of the Eromanga-reservoired oils (Boreham and Hill, 1998; Boreham and Summons, 1999). There is little or no evidence of biodegradation in either the Cooper or Eromanga Basin, probably because reservoir temperatures are too high (D.M. McKirdy, pers. comm., 2000).

Basin margin pinchout of regional seals and faults along anticlinal trends can provide the migration paths for Cooper-derived petroleums into younger horizons (Heath et al., 1989; Passmore, 1989). However, not all the Eromanga-reservoired oils are sourced entirely from the Cooper Basin. Hydrocarbons derived from Cooper sources can also mix in the Eromanga reservoirs with the local Eromanga-derived petroleum (Jenkins, 1989; Boreham and Hill, 1998; Boreham and Summons, 1999; Michaelsen and McKirdy, 1999, 2000). The distribution patterns of parameters H and C in the Cooper and Eromanga oils do not conflict with the above scenario.

4.2.6.5 Parameter I (Isoheptane Value)

Isoheptane Value (parameter I in Table 4.1) was first used as an indicator of petroleum paraffinicity and maturity by Thompson (1983, 1987). It is very similar to the parameter J of Schaefer and Littke (1988) and Schaefer (1992). In fact, the difference between the I and J values of common crude oils is negligible, because the concentration of *cis*-1,2-dimethylcyclopentane is very low in comparison with all the other 5 components incorporated in the parameters. Mango (1987, 1990a,b, 1997) reported an invariance of some ratios involving isoheptanes, but ten Haven (1996) proposed that caution should be exercised when applying Mango's ratios.

The distribution of I values among the reservoir strata in the Cooper and Eromanga Basins is depicted in Figure A.1f. The figure shows that the average Isoheptane Values are very similar for the crude oils from both basins and no discrimination is possible. The majority of the values fall in the range 1–2, but larger values (up to 5.84) do occur, most notably in Jurassic reservoirs in the Wancoocha and Taloola Fields. These fields are close to the margin of the Cooper Basin where high paraffinicity petroleums have already been noted. I values for the Eromanga-reservoired oils vary between 0.83 and 5.84 (mean = 1.90: Table 4.8), whereas for the Cooper-reservoired petroleum a narrower range is evident (I = 0.99–2.43), with a mean of 1.68 (Table 4.9).

4.2.6.6 Parameter F

Parameter F (= *n*-heptane/methylcyclohexane: Table 4.1) is another paraffinicity and maturity indicator proposed by Thompson (1987). Relative to the other parameters, it is easier to measure because both *n*-heptane and methylcyclohexane are very abundant and well resolved in whole-oil GC traces (see Figures 3.4 and 4.1). This parameter behaves in a similar manner to those of parameters C, H and I with respect to reservoir distribution (Figure A.1g). It is obvious that all values of F >1 occur in Eromanga-reservoired oils, whereas petroleum in the Cooper reservoirs has uniformly low F values (<1). The Eromanga oil samples with the highest F values are encountered in the fields that are most likely to have received Cooper-derived hydrocarbons. These include Wancoocha, Taloola and Sturt (Table 4.4) where the oil charging Jurassic reservoirs appears to have undergone compositional fractionation during migration.

4.2.6.7 Parameter U

Parameter U (cyclohexane/methylcyclopentane: Table 4.1) is one of several ratios suggested by Thompson (1987) to indicate the normality or branching of alkanes in a crude oil. In this case it measures the content of an unbranched (unsubstituted) naphthene relative to that of the corresponding branched (substituted) isomer. Its value increases in the residual light hydrocarbons left behind in a reservoir after evaporative fractionation has occurred (Thompson, 1987). In other words, migrated hydrocarbons have smaller U values than those remaining in the original accumulation; whereas unfractionated petroleum (reservoired *in situ*) has a U value intermediate between the migrated and residual crudes. Thus, if evaporative fractionation happens with the leakage of hydrocarbons from the Cooper Basin sequence into shallower Eromanga reservoirs, the U values of the migrated petroleum should be smaller than those of the residual Cooper-reservoired crude oils. This is proven to be the case by the U value distribution illustrated in Figure A.1h.

It is quite evident that U values of the Cooper-reservoired hydrocarbons (U = 0.93–6.90; mean = 2.84: Table 4.9) are larger than those of the Eromanga oils (U = 0.17–2.68; mean = 1.17: Table 4.8). A closer inspection reveals other more subtle differences among crude oils from different formations. Within the Cooper Basin, the U values of the Toolachee and Patchawarra-hosted hydrocarbons (>3) are larger than those in other reservoirs. Only a few Tirrawarra crude oils have U values larger than 2; and all but one of the Nappamerri oils share similar U values with the Poolowanna oils. Within the Eromanga Basin, the U values of oils reservoired in the Murta and Poolowanna Formations ($U \approx 2$) are larger than those encountered in the other Eromanga strata ($U < 1$).

The above U value distribution can be explained by the following scenario of petroleum generation and migration within Cooper and Eromanga Basins:

1. The majority of the hydrocarbons reservoired in the Tirrawarra Formation seem to have been generated from the deepest, most mature part of the Cooper sequence and remain *in situ*.

2. Hydrocarbons reservoired in the Toolachee and Patchawarra Formations seem to represent residual petroleum accumulations left behind after considerable partial migration of their light ends. This reflects the imperfect seals immediately overlying these two formations. Some of the Nappamerri-reservoired hydrocarbons may have migrated from these underlying reservoirs. This would explain why the Nappamerri petroleums have the lowest U values among the Cooper Basin crude oils.

3. Where the seals within and above the Nappamerri Group are not effective enough, the Toolachee- and Patchawarra-derived hydrocarbons seem to have migrated through the Triassic sequence into the Eromanga Basin, resulting in even smaller U values in the Hutton, Birkhead and Namur oils.

4. The somewhat higher U values of the Poolowanna and Murta oils (compared to other Eromanga accumulations) might be attributed to local hydrocarbon generation.

4.2.6.8 Parameter R

Compositional ratio R (*n*-heptane/2-methylhexane: Table 4.1) is a paraffin branching parameter proposed by Thompson (1987). However, it is not as effective as parameter U in distinguishing the Cooper and Eromanga hydrocarbons as can be clearly seen from Figure A.1i.

Though the largest value (9.99) belongs to a Cooper-reservoired petroleum (Leleptian-1, Patchawarra), the second largest (7.25) occurs in an Eromanga oil (Nungeroo-1, Namur) (Table 4.4). Statistical analysis shows the Cooper and Eromanga data sets to overlap and share a similar mean (3.9: Tables 4.8 and 4.9).

Table 4.7 Data analysis for parameters used in oil mapping

Result	Pr/Ph	Pr/nC17	Ph/nC18	A	B	X	C	I	F	H
Mean	4.67	0.56	0.12	0.02	0.55	0.71	1.08	1.84	0.84	2.95
Standard Error	0.16	0.03	0.00	0.00	0.10	0.11	0.06	0.06	0.05	0.08
Median	4.65	0.42	0.11	0.02	0.13	0.31	0.98	1.68	0.72	2.88
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	1.66	0.32	0.04	0.02	1.03	1.14	0.60	0.68	0.52	0.81
Sample Variance	2.77	0.10	0.00	0.00	1.06	1.31	0.36	0.46	0.27	0.65
Kurtosis	0.24	0.40	1.33	7.60	19.18	37.00	8.20	13.08	12.10	0.98
Skewness	-0.43	1.09	1.16	2.64	4.04	5.32	2.25	3.01	2.86	0.58
Range	7.73	1.47	0.20	0.11	6.96	9.73	3.97	5.00	3.69	4.54
Minimum	0.22	0.17	0.07	0.01	0.05	0.13	0.19	0.83	0.18	1.07
Maximum	7.95	1.65	0.27	0.12	7.01	9.86	4.15	5.84	3.87	5.61
Sum	537.60	64.81	13.02	2.83	62.70	81.20	124.65	209.20	97.16	339.24
Count	115.00	115.00	110.00	114.00	115.00	115.00	115.00	114.00	115.00	115.00
Confidence Level(95.0%)	0.31	0.06	0.01	0.00	0.19	0.21	0.11	0.13	0.10	0.15

Result	R	U	A'	B'	X'	New 1	New 2	New3	New 4
Mean	3.88	1.67	0.12	0.30	0.52	0.08	0.13	0.43	1.07
Standard Error	0.09	0.11	0.00	0.04	0.05	0.01	0.01	0.04	0.01
Median	3.88	1.49	0.11	0.09	0.24	0.03	0.08	0.22	1.03
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	0.00	0.00	#N/A	#N/A
Standard Deviation	0.98	1.18	0.05	0.48	0.58	0.11	0.15	0.46	0.07
Sample Variance	0.97	1.38	0.00	0.23	0.34	0.01	0.02	0.21	0.01
Kurtosis	13.97	4.86	11.59	7.97	4.33	1.73	0.62	3.83	1.46
Skewness	2.34	1.98	2.14	2.70	2.03	1.61	1.23	2.01	1.54
Range	9.10	6.73	0.41	2.49	3.10	0.46	0.66	2.18	0.32
Minimum	0.89	0.17	0.04	0.03	0.10	0.00	0.00	0.02	0.98
Maximum	9.99	6.90	0.45	2.52	3.20	0.46	0.66	2.20	1.30
Sum	442.46	190.08	14.20	34.13	59.84	9.71	14.96	49.81	122.53
Count	114.00	114.00	114.00	115.00	115.00	115.00	114.00	115.00	115.00
Confidence Level(95.0%)	0.18	0.22	0.01	0.09	0.11	0.02	0.03	0.08	0.01

Table 4.8 Data analysis for parameters of oils/condensates from the Eromanga Basin

Result	Pr/Ph	Pr/nC17	Ph/nC18	A	B	X	C	I	F	H
Mean	4.91	0.60	0.12	0.02	0.16	0.30	1.26	1.90	0.98	3.24
Standard Error	0.17	0.04	0.00	0.00	0.02	0.02	0.07	0.09	0.06	0.08
Median	4.81	0.42	0.10	0.02	0.11	0.26	1.09	1.69	0.80	3.05
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	1.57	0.34	0.04	0.01	0.14	0.19	0.61	0.77	0.55	0.74
Sample Variance	2.45	0.12	0.00	0.00	0.02	0.04	0.38	0.60	0.31	0.55
Kurtosis	0.19	0.09	-0.40	8.44	6.47	19.70	8.03	9.93	10.52	1.69
Skewness	-0.21	1.12	0.93	2.65	2.49	3.90	2.39	2.73	2.77	0.68
Range	7.70	1.41	0.14	0.07	0.72	1.33	3.93	5.00	3.69	4.54
Minimum	0.26	0.24	0.07	0.01	0.05	0.13	0.22	0.83	0.18	1.07
Maximum	7.95	1.65	0.21	0.08	0.77	1.46	4.15	5.84	3.87	5.61
Sum	397.31	48.30	9.29	1.68	13.27	24.40	102.06	152.10	79.64	262.54
Count	81.00	81.00	79.00	80.00	81.00	81.00	81.00	80.00	81.00	81.00
Confidence Level(95.0%)	0.35	0.08	0.01	0.00	0.03	0.04	0.14	0.17	0.12	0.16

Result	R	U	A'	B'	X'	New 1	New 2	New 3	New 4
Mean	3.87	1.17	0.12	0.08	0.22	0.03	0.05	0.20	1.03
Standard Error	0.08	0.06	0.00	0.00	0.01	0.00	0.01	0.01	0.00
Median	3.92	1.00	0.11	0.08	0.20	0.03	0.04	0.19	1.03
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	0.00	0.00	#N/A	#N/A
Standard Deviation	0.68	0.53	0.04	0.03	0.09	0.02	0.05	0.08	0.02
Sample Variance	0.46	0.28	0.00	0.00	0.01	0.00	0.00	0.01	0.00
Kurtosis	7.13	-0.37	-0.75	8.06	2.18	-0.42	-0.40	2.91	5.03
Skewness	1.43	0.52	0.10	1.84	1.33	0.33	0.70	1.17	1.38
Range	4.77	2.51	0.16	0.19	0.48	0.08	0.20	0.50	0.16
Minimum	2.48	0.17	0.04	0.03	0.10	0.00	0.00	0.02	0.98
Maximum	7.25	2.68	0.20	0.22	0.58	0.08	0.20	0.52	1.08
Sum	309.28	93.38	9.21	6.35	17.79	2.10	4.24	16.36	83.27
Count	80.00	80.00	80.00	81.00	81.00	81.00	80.00	81.00	81.00
Confidence Level(95.0%)	0.15	0.12	0.01	0.01	0.02	0.00	0.01	0.02	0.01

Table 4.9 Data analysis for parameters of oils/condensates from the Cooper Basin

Result	Pr/Ph	Pr/nC17	Ph/nC18	A	B	X	C	I	F	H
Mean	4.13	0.49	0.12	0.03	1.45	1.67	0.66	1.68	0.52	2.28
Standard Error	0.31	0.04	0.01	0.01	0.27	0.30	0.05	0.06	0.03	0.08
Median	4.26	0.45	0.12	0.03	0.90	1.16	0.71	1.66	0.52	2.22
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	1.78	0.26	0.04	0.03	1.56	1.75	0.26	0.34	0.17	0.49
Sample Variance	3.17	0.07	0.00	0.00	2.42	3.08	0.07	0.12	0.03	0.24
Kurtosis	-0.33	-1.02	6.28	2.01	5.15	14.41	-1.01	1.56	-0.97	-0.83
Skewness	-0.67	0.40	1.83	1.66	2.21	3.44	-0.06	0.45	-0.03	-0.06
Range	6.13	0.88	0.20	0.11	6.90	9.64	0.93	1.74	0.63	1.91
Minimum	0.22	0.17	0.07	0.01	0.11	0.22	0.19	0.99	0.18	1.38
Maximum	6.35	1.06	0.27	0.12	7.01	9.86	1.12	2.73	0.81	3.30
Sum	140.29	16.51	3.73	1.15	49.43	56.80	22.58	57.11	17.52	79.66
Count	34.00	34.00	31.00	34.00	34.00	34.00	34.00	34.00	34.00	35.00
Confidence Level(95.0%)	0.62	0.09	0.01	0.01	0.54	0.61	0.09	0.12	0.06	0.17

Result	R	U	A'	B'	X'	New 1	New 2	New 3	New 4
Mean	3.92	2.84	0.15	0.82	1.24	0.22	0.32	0.98	1.15
Standard Error	0.26	0.24	0.01	0.11	0.11	0.02	0.02	0.09	0.01
Median	3.73	2.49	0.14	0.75	1.22	0.24	0.36	0.95	1.16
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	1.49	1.42	0.07	0.62	0.64	0.11	0.13	0.52	0.08
Sample Variance	2.22	2.03	0.00	0.39	0.41	0.01	0.02	0.27	0.01
Kurtosis	8.00	0.90	10.41	1.49	1.69	0.07	0.77	0.46	-0.94
Skewness	2.01	1.16	2.61	1.19	0.84	0.14	-0.32	0.65	0.09
Range	9.10	5.97	0.38	2.42	3.00	0.43	0.63	2.00	0.27
Minimum	0.89	0.93	0.07	0.10	0.20	0.03	0.04	0.19	1.03
Maximum	9.99	6.90	0.45	2.52	3.20	0.46	0.66	2.20	1.30
Sum	133.18	96.70	5.00	27.78	42.06	7.61	10.72	33.45	39.26
Count	34.00	34.00	34.00	34.00	34.00	34.00	34.00	34.00	34.00
Confidence Level(95.0%)	0.52	0.50	0.02	0.22	0.22	0.04	0.05	0.18	0.03

4.2.6.9 Parameters A and A'

Parameter A (benzene/*n*-hexane: Table 4.1) was designed to indicate petroleum aromaticity, in the form of the relative abundance of aromatic compounds to normal alkanes of similar molecular weight (Thompson, 1983). Aromaticity increases in the remaining petroleum when evaporative fractionation takes place (Thompson, 1987), and decreases proportionately in the migrated hydrocarbons. This and similar compositional ratios also decrease with water washing (LaFargue and Barker, 1988; Heath et al., 1989; LaFargue and Le Thiez, 1996; Boreham and Hill, 1998; Boreham and Summons, 1999). According to LaFargue and his coworkers, light aromatic molecules, such as benzene and toluene, are removed first by water washing, followed by normal alkanes and then naphthenes. The ratio A' (benzene/*cis*-1,3-dimethylcyclopentane; Table 4.1) is a newly created parameter that is more sensitive to water washing, because naphthenes are less soluble than normal alkanes in the gasoline range.

Hydrogeologically, the carrier beds in the Cooper Basin are very different from the Eromanga sandstones, where the latter represent important aquifers of the Great Artesian Basin (Habermehl, 1986). Where anticlinal traps in the Eromanga Basin are not occupied by hydrocarbons, they are commonly water-saturated (Heath et al., 1989). In contrast, water supply to the Cooper Basin carrier beds is negligible. Hydrocarbons migrated from the Cooper Basin into the Eromanga strata experienced significant water washing on their journey through the water-saturated sequences of the Eromanga Basin. Chemical compositions of hydrocarbons that are locally derived and accumulated in Eromanga reservoirs should also be seriously affected by water washing.

Taking into account the hydrogeological setting of the Cooper and Eromanga Basins, there should be significant differences in aromaticity between the Cooper- and Eromanga-reservoired petroleums. Ratios A and A' of the Eromanga-reservoired hydrocarbons should be lower than that of the crude oils trapped in the Cooper Basin reservoirs. However, this is not the case. Distributions of A and A' values across the reservoir strata are surprisingly different from what was expected. There is no consistent enhancement of A and A' values in the Cooper-reservoired oils/condensates (Figures A.1j & k).

The values of parameter A in oils and condensates from the Cooper and Eromanga Basins are mostly <0.02; larger values were irregularly encountered in both basins (Table 4.7–4.9; Figure A.1j). Values in the Eromanga-reservoired oils (range = 0.01–0.08, mean = 0.02) differ little from those in the Cooper-reservoired hydrocarbons (range = 0.01–0.12, mean = 0.03).

The A' values are an order of magnitude higher (mostly <0.2) but show a similar distribution pattern to parameter A (Figure A.1k). Statistical data analysis indicates that there is no clear difference between Cooper- and Eromanga-reservoired petroleums (Tables 4.7–4.9).

The observed inconsistency in the distributions of A and A' can not be explained by water washing or evaporative fractionation, as these two processes would both cause systematic enhancement of the relative abundances of benzene in the Cooper oils and condensates. Instead, source difference could be an alternative interpretation, but this requires further study. Of particularly interest is the fact that petroleum from the Mooracoochie Volcanics shows the largest A and A' values (Figures A.1j & k).

4.2.6.10 Parameters B and B'

Unlike parameters A and A', ratios B and B' (which represent the relative abundance of toluene to its adjacent normal alkanes in the whole-oil GC trace) show positive relationships with water washing and/or evaporative fractionation (Table 4.1). These parameters, together with other aromatic ratios discussed in this chapter, are very effective in distinguishing the Cooper oils and condensates from the Eromanga-reservoired crudes.

The ratio B (toluene/*n*-heptane) is a parameter previously used to recognise evaporative fractionation (Thompson, 1987, 1988; Carpentier et al., 1996). Compared to the parent oil, the value of B increases in the residual heavy oil and decreases in the migrated "light" oil, when evaporative fractionation (Thompson,

1987) or migration fractionation (Curiale and Bromley, 1996) occurs. Eromanga-reservoired oils have smaller B values (range = 0.05–0.77; mean = 0.16) than the Cooper crudes (range = 0.11–7.01; mean = 1.14) (Tables 4.7–4.9; Figure A.1l). This could be attributed to migration fractionation. However, Heath et al. (1989), Boreham and Hill (1998), and Boreham and Summons (1999) interpreted the higher B values in the Cooper Basin oils, compared to those in the Eromanga oils, as indicative of greater water washing of the latter. It is difficult to demonstrate which process (evaporative fractionation or water washing) is more important in influencing the B value distribution for the oils/condensates of the Cooper and Eromanga Basins. This is because they would be expected to change the B value in the same direction upon migration of the Cooper-sourced petroleum into the overlying Eromanga sequence. Fortunately, both evaporative fractionation and water washing are related to a single petroleum geologically significant process – secondary migration. Migration of the Cooper Basin-derived petroleum via the Eromanga aquifers causes not only evaporative fractionation, but also water washing. Eromanga Basin oils have smaller B values, because they have migrated further, and hence have undergone greater migration fractionation and water washing. Cooper Basin oils are the least affected by water washing (Heath et al., 1989; Hunt et al., 1989), or migration fractionation, because of shorter migration distances from their Permian source rocks.

As shown in Figure A.1l, parameter B is clearly effective in distinguishing petroleums from the Cooper and Eromanga Basins, with the latter crudes having very small B values (mostly < 0.2). In contrast, while nine Patchawarra-reservoired samples from the Sturt area (XYOIL108, 109, 111, 112, 114–118) have B values <0.5, half of the Cooper-reservoired crudes have B values >1.0. The largest two values of 7.01 and 5.76 were recorded for the Patchawarra condensates from Leleptian-1 and Yanda-2, respectively. A similar picture is evident in the stratigraphic distribution of B' values (Figure A.1m).

The unexpectedly small B and B' values for the nine Patchawarra condensates could be interpreted as a function of water washing, as they all come from basin-margin traps that could be affected by the Eromanga aquifers (notably the Hutton

Sandstone). Sturt is one of the typical areas in which Cooper-derived petroleum has been discovered in the Eromanga reservoirs (Heath et al., 1989; Kagya, 1997; Michaelsen and McKirdy, 2000). As shown in the seismic section of the Nealyon-Taloola Nose (see figure 15 in Heath et al., 1989), the Hutton Sandstone of the Eromanga Basin directly overlies truncated Permian section, cut by faults close to the Cooper Basin margin. This makes it possible for the underground water in the Great Artesian Basin aquifers to access the Permian traps, leaching the petroleums reservoired there. The observed distributions of ratios B', X, X' and the other new aromatic parameters (New 1–5: Table 4.1) discussed below support this interpretation.

As demonstrated in the next chapter (Sections 5.2.2.1–5.2.2.5), the remarkably low B and B' values of the Patchawarra oils in the Sturt area can also be explained by a novel secondary migration scenario, viz. the migration of Eromanga-derived hydrocarbons into Cooper reservoirs. This interpretation is more feasible because it not only satisfies the water washing indicators (low B and B' values), but also explains the high values of retene/phenanthrene and other Eromanga-specific source parameters in these Permian-reservoired oils.

4.2.6.11 Parameters X and X'

Parameter X, defined as *m* + *p*-xylene/*n*-octane (Table 4.1), is another measure of petroleum aromaticity (Thompson, 1987). It increases in the remaining heavy oil, and decreases in the migrated "light" hydrocarbons, as a result of evaporative fractionation. It also decreasess in water- washed oils. The values of parameter X have a distribution pattern similar to that of ratio B (Figure A.1n) and display a clear contrast between the Eromanga- and Cooper-reservoired petroleums.

The average X value of the Cooper-reservoired oils and condensates (mean = 1.67; range = 0.22–9.86: Table 4.9) is greater than the largest value measured in the Eromanga oils (mean = 0.30; range 0.13–1.46: Table 4.8), clearly demonstrating the effectiveness of the X ratio in distinguishing Cooper and Eromanga crudes. The X values of all but three of the analysed Eromanga samples are <0.5. The values of all but eight of the oil/condensate samples from the Cooper Basin are >0.8, with the largest (X = 2.23–9.86) reported from Patchawarra, Toolachee and Tirrawarra samples. This lends further support to the suggestion that the Eromanga-reservoired petroleums have been severely water-washed and/or evaporation-fractionated due to migration processes, whereas crude oils preserved in the Cooper strata are the least affected by water washing and evaporative fractionation.

As shown in Figure A.1o, the values of parameter X' (*m* + *p*-xylene/*n*-nonane: Table 4.1) have a distribution pattern similar to those of parameter X. The Patchawarra oils in the Sturt area with very low X values also have extraordinarily small X' values, supporting the above interpretation. However, it must be pointed out that the contrast between the Cooper and Eromanga-reservoired hydrocarbons is more obvious when using the X' values.

4.2.6.12 Comparison of Effectiveness of A, B, X and A', B', X'

Parameters A', B' and X' are modified versions of the three aromaticity functions A, B and X originally defined by Thompson (1983, 1987). They were designed to reduce the influence of evaporation during sample storage and handling, and hence increase their effectiveness as useful tools in petroleum exploration. Taking into account that some light hydrocarbon loss is inevitable during storage and handling, an ideal parameter should include components that have the same partition ratio between their gaseous and liquid phases. The ratios A', B' and X' are less affected by evaporation than A, B and X because *cis*-1,3-dimethylcyclopentane, *n*-octane and *n*-nonane are less volatile than their counterparts, *n*-hexane, *n*-heptane and *n*-octane, respectively. Hence, A', B' and X' should, theoretically, be more effective in distinguishing Cooper and Eromanga hydrocarbons.

Inspection of their respective histogram plots (Figures A.1j–o, Appendix 1) reveals that the relative improvement in effectiveness of distinguishing Cooper and Eromanga-reservoired petroleum is as follows: X' > B' >> A'. In fact, for A' the improvement is not very evident at all.

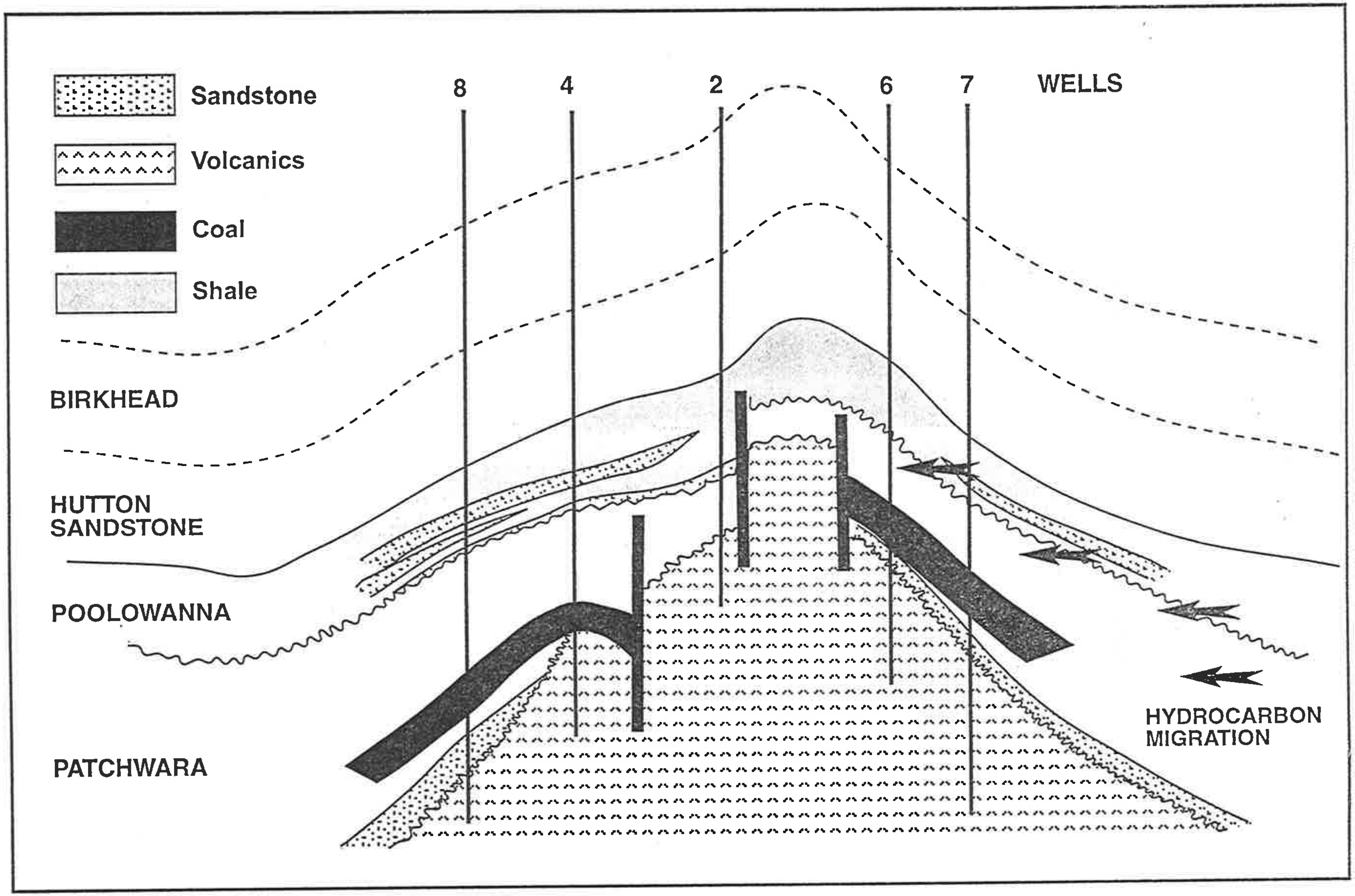


Figure 4.8 Schematic cross-section of Sturt Field showing hydrocarbon migration from Poolowanna Formation to Patchwarra Formation (after Kagya, 1997)

4.2.6.13 Interpretation of anomalous Behaviour of A and A'

Taking into account the hydrogeology of the Cooper and Eromanga Basins and the fact that benzene is the most water-soluble aromatic compound in petroleum, parameters A and A' should be the most effective, among the aromaticity parameters, in distinguishing their oils and condensates. Nevertheless, neither water washing nor migration fractionation can satisfactorily explain the irregular distributions of A and A' values among the reservoir strata, despite these two processes being expected to play a major role in affecting the concentrations of aromatic compounds in the oils and condensates of the Cooper/Eromanga province.

The irregular distribution of A and (to a lesser degree A') values amongst the reservoir strata necessitates the involvement of some random processes that may alter the benzene content of crude oils. The likelihood of a third hydrocarbon source (besides the Cooper and Eromanga kitchens) is remote, because any petroleum reservoired in the Eromanga Basin is likely to have been severely altered by water washing, particularly if long-distance secondary migration was involved. Evaporative loss of the light-ends during sampling, storage and handling could be a more plausible explanation. This is supported, at least to some extent, by the difference between the distributions of A and A' values along the reservoir strata (see Figures d and q in Appendix 1).

Considering molecular weights and chemical structures, the volatility of benzene is closer to that of 1,cis-3-dimethylcyclopentane than to that of *n*-hexane. In other words, the vapour-liquid equilibrium constant of benzene is closer to that of cis-1,3-dimethylcyclopentane than to that of *n*-hexane. Ratio A should, therefore, be more sensitive to evaporative loss of light hydrocarbons during storage and/or handling of crude oil samples, which is a random event. Hence, A values should primarily reflect the storage/handling history of the samples, and, to a lesser extent, their secondary migration. On the contrary, compositional ratio A' is less (relative to A, only) affected by random losses during sample handling, and so its distribution still shows (though not obviously) some relationship with migration fractionation in the subsurface. Further laboratory simulation experiments and field observations are necessary to prove this interpretation.

To test if the content of benzene is severely affected by random procedures, such as storage and handling of the petroleum samples prior to analysis, the relative concentrations of various other aromatic compounds were investigated using GC-MS measurements. The results are summarised in Appendix 2 (Table A.2, Figures A.2a–k).

Benzene is the smallest, and therefore the most volatile and water-soluble, of the aromatic hydrocarbons in petroleum. By comparison, toluene is less volatile and much less water soluble (LaFargue and Barker, 1988; LaFargue and Le Thiez, 1996). If the relative content of benzene is not affected by evaporative loss during sample handling, the ratio benzene/toluene in the Eromanga-reservoired oils should be smaller than that in the Cooper crudes. However, this is inconsistent with the observed distribution of this ratio among the reservoir strata (see Figure A.2a, Appendix 2). The relative content of benzene is not always larger in the Cooper-reservoired crude oils; very low benzene/toluene ratios also occur in some Cooper samples. This supports the above argument that the non-systematic distribution of benzene in the crude oils examined is most likely due to some artificial factor (e. g. storage and handling), hence preventing the proper application the Thompson's parameter A to this suite of samples. The concentration of benzene relative to other larger aromatic compounds, such as naphthalene and phenanthrene (see Figures A.2d & e in Appendix 2), displays a more distinct pattern: values are consistently low in Eromanga-reservoired oils, mainly due to water washing. However, some very low values are encountered in the Cooper oils, indicating their random loss of light aromatic hydrocarbons due to severe evaporation during storage and/or handling of the samples. The use of components insensitive to random evaporative loss is therefore warranted to obtain a clearer picture on the severity of water washing, as shown by the ratio naphthalene/phenanthrene (Figure A.2 f). Other aromatic ratios compiled in Appendix 2 are indicators of source input and will be discussed in Chapter 5.

In the following sections, the effectiveness of four newly created parameters will be discussed. It will be demonstrated that they are closely correlated, and are very effective in distinguishing Cooper-sourced and reservoired petroleums from those now found within the Eromanga Basin.

4.2.6.14 New parameter 1

New parameter 1 is the ratio of *o*-xylene to *n*-nonane (Table 4.1). It decreases with water washing of the crude oil. Its variation across the reservoir units of the sampled oils/condensates is shown as in Figure 4.6, which is representative of all the other new parameters compiled in Figures A.1p–s (Appendix 1). It is clearly evident that the Eromanga-reservoired oils have smaller values of New 1 (0.00–0.08; mean = 0.03) than do the Cooper crudes (0.03-0.46; mean = 0.22). Again, the smallest Cooper values were encountered in the Patchawarra reservoir of the Sturt Field (see Sections 4.2.6.10–11), where faults and truncations of the Permian units facilitate water washing, or alternatively where the geological structures allow Jurassic (Poolowanna-derived) hydrocarbons to migrate into the Patchawarra reservoirs. Further discussion of this scenario may be found in Chapter 5 (Sections 5.2.2.1–5).

4.2.6.15 New parameter 2

New parameter 2, the concentration of 1,2,4-trimethylbenzene relative to *n*-decane, is another potential parameter for water washing (Table 4.1). Its variation according to reservoir formation (Figure A.1q) is almost identical to that of ratio New 1. The Cooper-reservoired hydrocarbons exhibit significantly larger New 2 values (0.04–0.66; mean = 0.32) than do the Eromanga oils (0.00–0.20; mean = 0.05) (see also Tables 4.8 & 4.9). Again, samples from the Patchawarra reservoirs in the Sturt area have exceptionally low New 2 ratios.

4.2.6.16 New parameter 3

New parameter 3 (Table 4.1) measures the relative concentration of naphthalene and an unknown naphthene (see Figure 3.4 and Table 3.5 for peak number and its retention time). The chemical structure of the unknown compound is not clear because the mass spectrum extracted from the scan-mode GC-MSD is not adequate for complete elucidation. However, this does not detract from the effective use of the ratio in distinguishing Cooper and Eromanga petroleums.

As shown in Figure A.1r and Tables 4.8 & 4.9, the New 3 ratio varies with reservoir formation in a very similar manner to parameters New 1 and New 2. The average value for the Cooper-reservoired hydrocarbons is 0.98, which is four times larger than that of the Eromanga-hosted oils (0.20).

4.2.6.17 New parameter 4 (TPI)

From its definition in Table 4.1, TPI (tridecane preference index) should be a parameter reflecting the abundance of *n*-tridecane relative to the nearby normal alkanes. However, the apparent tridecane preference in the normal alkane profiles of the whole-oil gas chromatograms is caused by its coelution with 2-methylnaphthalene. This has been discussed in Section 4.2.2. To make it consistent with a former report (Yu and McKirdy, 1998), the term TPI will be used in the following discussion, though it is not literally correct.

It is evident from Figure A.1s (Appendix 1) that the Cooper-hosted oils and condensates have larger TPI values than the hydrocarbons preserved in the Eromanga reservoirs. The majority of the latter oils have TPI values <1.05, while most of the former crudes have much higher values, with the largest being from the Toolachee (1.30), Patchawarra (1.29), and Tirrawarra (1.28) reservoirs.

The difference between the Cooper and Eromanga hydrocarbons in terms of their TPI values is further demonstrated by statistical analysis (Tables 4.8 & 4.9). The range in TPI for the Eromanga oils is 0.98–1.08 (mean = 1.03), compared to 1.03–1.30 (mean = 1.15) for the Cooper samples. The mean Cooper TPI value is even greater than the largest TPI value measured in the Eromanga oils, implying lower 2-methylnaphthalene concentrations in the latter oils. This possibly reflects source differences (particularly in the indigenous Murta oils: Michaelsen and McKirdy, 1989; Powell et al., 1989), or water washing during the secondary migration of light oils from hydrocarbon kitchens in the Cooper Basin.

4.3 RELATIONSHIPS BETWEEN THE PARAMETERS

To clarify the geochemical significance of the aforementioned parameters, a statistical correlation study was carried out. This was helpful in selecting appropriate parameters for grouping (or mapping) the different types of oil and condensate found in the Cooper and Eromanga Basins. The resulting correlation coefficients (R^2) are listed in Table 4.10.

4.3.1 PARAMETERS A AND A'

As shown in Table 4.10, parameters A and A' (aromaticity: supposed indicators of evaporative fractionation and water washing) are not closely correlated to any of the other listed parameters, regardless of their geochemical significance, nor even to each other ($R^2 = 0.43$). The best correlation was between A' and I ($R^2 = 0.53$). This implies that neither A nor A' has recognisable geological significance. It seems that they cannot be used as indicators for evaporation/migration fractionation or water washing, presumably because they can be readily affected by random evaporative loss of benzene during storage and handling of crude oil samples, as discussed in Section 4.2.6.13. Parameters A and A', therefore, are not suitable for use in classifying the Cooper and Eromanga petroleums because they bear no obvious relationships with source, maturity or any secondary alteration processes.

4.3.2 PARAMETERS PR/PH, PR/N-C17 AND PH/N-C18

The three most conventional and easy-to-obtain parameters, Pr/Ph, Pr/n-C_{17} and Ph/n-C_{18}, are not suitable for grouping oils in the Cooper and Eromanga Basins either. Although they are closely correlated with each other, their correlation coefficients with respect to the other parameters are very low ($R^2 < 0.3$: Table 4.10).

The three parameters incorporating pristane and phytane have long been used as indicators of source, maturity and biodegradation in crude oils. Nevertheless, they are of little use in distinguishing Cooper from Eromanga hydrocarbons. Similarity of the depositional environments of source rocks in the Cooper and Eromanga sequences give rise to similar biomarker distributions (including Pr/Ph values) for their crude

Table 4.10 Correlation coefficients (R^2) of all the ratios used for oil mapping in the Cooper and Eromanga Basins

	Pr/Ph	Pr/C_{17}	Ph/C_{18}	A	B	X	A'	B'	X'	C	I	F	H	R	U	New 1	New 2	New 3	New 4
Pr/Ph	1.00																		
Pr/C_{17}	0.81	1.00																	
Ph/C_{18}	0.65	0.88	1.00																
A	0.11	0.21	0.25	1.00															
B	-0.31	-0.19	0.12	0.39	1.00														
X	-0.24	-0.21	-0.11	0.28	0.68	1.00													
A'	-0.13	-0.05	0.05	0.43	0.05	0.11	1.00												
B'	-0.34	-0.30	-0.14	0.17	0.72	0.69	0.15	1.00											
X'	-0.34	-0.31	-0.07	0.13	0.75	0.58	0.13	0.90	1.00										
C	0.23	0.29	0.18	0.11	-0.16	-0.10	-0.18	-0.24	-0.27	1.00									
I	-0.04	0.04	0.06	0.05	-0.25	-0.22	0.53	-0.18	-0.21	-0.03	1.00								
F	0.07	0.12	0.06	-0.14	-0.35	-0.35	0.04	-0.36	-0.41	0.13	0.82	1.00							
H	0.18	0.18	0.07	-0.28	-0.51	-0.50	-0.14	-0.53	-0.57	0.14	0.66	0.92	1.00						
R	-0.12	-0.07	0.17	0.01	0.43	0.06	-0.44	-0.04	0.12	-0.02	-0.15	0.04	0.11	1.00					
U	-0.34	-0.22	0.05	0.37	0.81	0.62	0.22	0.67	0.70	-0.24	-0.18	-0.47	-0.58	0.33	1.00				
New 1	-0.35	-0.32	-0.09	0.18	0.77	0.60	0.13	0.88	0.96	-0.30	-0.25	-0.45	-0.61	0.17	0.73	1.00			
New 2	-0.32	-0.37	-0.19	0.11	0.62	0.61	0.10	0.82	0.91	-0.30	-0.26	-0.48	-0.61	0.08	0.63	0.95	1.00		
New 3	-0.39	-0.37	-0.19	0.23	0.77	0.73	0.07	0.90	0.89	-0.25	-0.22	-0.38	-0.53	0.14	0.77	0.91	0.86	1.00	
New 4	-0.17	-0.13	0.04	0.24	0.62	0.58	0.11	0.76	0.82	-0.25	-0.23	-0.43	-0.54	0.08	0.64	0.86	0.86	0.83	1.00

oils and source rock bitumens. Mixed sourcing and negligible biodegradation could be other reasons that disqualify Pr/Ph, Pr/n-C_{17} and Ph/n-C_{18} from distinguishing the Cooper and Eromanga oils and condensates.

4.3.3 PARAMETER U AND RATIOS INCORPORATING OTHER AROMATIC COMPONENTS

The remaining 14 parameters listed in Table 4.1 are variably effective in distinguishing Cooper and Eromanga crude oils. Of these New 1, New 2, New 3, New 4 (TPI), B, B', X, X' and U are the most effective (see relevant figures in Appendix 1). With the exception of U, all these ratios involve aromatic components. They are all closely correlated to each other, with correlation coefficients varying between 0.86 and 0.96 (Table 4.10). Such high correlation coefficients indicate that these parameters are controlled by similar factors (secondary alteration). Water washing seems to be the most likely interpretation, as the aromatic compounds involved in these parameters are all susceptible to water washing.

Water washing has been widely interpreted as one of the most common secondary alteration process for hydrocarbons migrating within the Great Artesian Basin (Heath et al., 1989; Boreham and Hill, 1998; Boreham and Summons, 1999). That the values of the aromatic-based parameters are low in the Eromanga oils is consistent with the prevailing hydrological activity in the Eromanga carrier beds and reservoirs. The chemical composition of hydrocarbons generated from the Cooper source rocks would be seriously altered en route wherever they breach the Triassic regional seal and migrate into the Eromanga sequence. Hydrocarbons derived from local Eromanga petroleum kitchens would also be severely water washed, though to a lesser extent.

Evaporative fractionation could be another plausible cause for the selective loss of certain aromatic compounds, although probably less influential than water washing. Thompson (1987, 1988) used the ratios B and X as evaporative fractionation parameters. Heath et al. (1989) and Boreham and Summons (1999) ascribed the low concentrations of toluene and xylene in the Eromanga-reservoired petroleums to water washing within the Eromanga aquifers. Source differences are the least likely factor that could account for the observed variation in these compositional ratios, although Alexander et al. (1988) identified some Eromanga-specific aromatic biomarkers.

It must be pointed out that although parameter U has no aromatic component, it is discussed under this heading because its correlation coefficient shows a closer affinity to the aromatic water- washing parameters than to the evaporation/migration fractionation parameters.

4.3.4 PARAMETERS I, F AND H

Parameters I, F and H (all measures of paraffinicity: Table 4.1) are also closely related, though not as effective as the aromatic-based ratios in distinguishing Cooper and Eromanga oils/condensates (see Table 4.10 and relevant figures in Appendix 1). The correlation coefficients (R^2) are as follows: between F and H, 0.92; between I and F, 0.82; and between I and H, 0.66. As pointed out by Thompson (1987; 1988), these three parameters are controlled primarily by maturity but also reflect alteration of hydrocarbons caused by evaporative fractionation during secondary migration. Their values increase in the migrated light hydrocarbons and decrease in the residual heavy hydrocarbons. Distributions of I, F and H values with the reservoir strata (as discussed above) do indicate some secondary migration of the Cooper-derived hydrocarbons into the Eromanga reservoirs.

Furthermore, it must be emphasised that parameters H, I and F are far more susceptible to evaporation fractionation than to water washing. In contrast, the aromatic parameters are more readily influenced by water washing. In other words, parameters H, I and F should be mainly used as migration-related fractionation parameters, and the aromatic-related ratios as water washing indicators.

The remaining two parameters, C and R, are poorly correlated to each other and to all the other parameters discussed above. They are of little use in distinguishing Cooper and Eromanga hydrocarbons.

Based on the above discussion, an attempt was made at petroleum mapping (i. e. grouping) in the Cooper and Eromanga Basins using hierarchical cluster analysis and relying heavily on the three maturity and/or migration fractionation parameters (H, I and F) and nine water washing indicators.

4.4 CLUSTER ANALYSIS

Cluster analysis is a means of grouping samples on a hierarchical basis by matching mutually similar samples in pair-groups. The pairing is usually made on the basis of "minimum distance" or maximum similarity of two samples according to the parameters used to describe them. After the samples within the set become paired, the pairs are then treated as a single sample, with the parameters of the members arithmetically averaged to define the parameters of the pair-group. This averaging eventually results in distortion of the input data.

Cluster analysis has been used to group petroleum accumulations into families since the late 1970's. Powell and Snowdon (1979) grouped oils and condensates from the Scotian Basin, offshore Eastern Canada, into four categories using cluster and factor analyses. They used the same method when classifying the oils and condensates in the Beaufort-Mackenzie Basin (Snowdon and Powell, 1979). In order to identify the active petroleum systems in the Cooper and Eromanga Basins, Boreham and Hill (1998) and Boreham and Summons (1999) clustered the oils/condensates from these basins using various source parameters, enabling the characterisation of several source-reservoir couplets.

In the present study, more attention has been paid to the role of secondary migration in the Cooper and Eromanga Basins. Parameters were selected on the basis of their effectiveness in indicating secondary migration. Bearing in mind the hydrogeological contrast between the Cooper and Eromanga Basins, the aforementioned fourteen ratios that reflect water washing and/or maturity and migration fractionation were employed in cluster analysis of the oils and condensates from this large petroleum province. The results are presented in Table 4.11 and Figure 4.9.

4.5 MAPPING THE COOPER AND EROMANGA PETROLEUM FAMILIES

Grouping the oils and condensates into families and mapping them in a study area is a useful exercise from several aspects. It may enable one to determine how many sources have been effective in a basin, and may also help depict petroleum secondary migration scenarios. It may even provide some information about mixed sources and/or multiple charging of reservoirs. This type of information is helpful for both exploration and development.

4.5.1 DENDROGRAM AND HIERARCHICAL CLUSTERING DISTANCE

Figure 4.9 is the dendrogram from the hierarchical cluster analysis. For convenience, the distance (or similarity) between samples (or groups of samples) is shown in a numerical way (see Table 4.11). Small distance value means large similarity. That is to say, when two samples have a small clustering distance, they are closely correlated, i.e. derived from a similar source and/or having a similar thermal history. For example, the distance between two Murta oils, XYOIL034 (Thungo-3) and XYOIL042 (Thungo-4) is only 0.1. In contrast, the distance between a Cooper-reservoired oil (XYOIL001, Tirrawarra-13, Tirrawarra Formation) and an Eromanga oil (XYOIL006, Taloola-1, Namur Formation) is as large as 36 (see Table 4.11).

4.5.2 GROUPING OF THE OILS AND CONDENSATES

As shown in Figure 4.9, the whole set of 114 oil/condensate samples from all over the Cooper and Eromanga Basins can conceivably be classified into two families, Family I and Family II. Family II is further divided into two sub-families, namely Family IIA and IIB. The distance between Family I and II is 36.0, and between Family IIA and Family IIB is 16.7.0 (see Table 4.11). All the sub-families could be further sub-divided according to the degree of detail required, but this is not considered to be geochemically appropriate here.

The resolution (or separation) between two petroleum families is measured by the distance jump, that is the difference between the distances of two adjacent hierarchical levels. The larger the distance jump, the further the two petroleum families are from each other in composition, or the less similar the two petroleum families are. The distance between Families I and II is 36.0 with a distance jump within the two hierarchical levels of 15.4, which represents the largest distance jump in this cluster analysis. The distance between the two sub-families IIA and IIB is 17.6 with the distance jump being only 1.1.

From the distance jump, one can tell that there is large difference between the properties of hydrocarbons within Families I and II. The difference between the two sub-families (IIA and IIB) is relatively smaller. This is consistent with the geological frameworks of the hydrocarbon reservoirs in the Cooper and Eromanga Basins.

4.5.3 FAMILY I AND FAMILY II OILS

All the oils and condensates within Family I are from reservoirs in the Cooper Basin (refer to Figure 4.9 and Table 3.1). They are the least influenced by water washing and evaporation/migration fractionation, because they have experienced the shortest secondary migration distances (Heath et al., 1989; Boreham and Hill, 1998; Boreham and Summons, 1999). However, the 89 samples in Family II are from the Eromanga reservoirs, with the exception of nine crude oils that come from the Patchawarra Formation of the Cooper Basin (see below). Hydrocarbons reservoired in the Eromanga Basin have undergone severe secondary alteration, such as water washing and/or fractionation during their secondary migration. As the carrier beds through which they migrated are also aquifers of the Great Artesian Basin, the physical and chemical properties of these oils were significantly modified (Habermehl, 1986 and Heath et al., 1989).

The nine "exceptional" Cooper-reservoired oils/condensates of Family II are the same samples which have "exceptionally" low B, B', X, X', TPI, New 1, New 2 and New 3 values and high abundant Eromanga-specific biomarkers (refer to Section 5.2.2). Their special geochemical characteristics are attributed to the geological architecture of the Sturt area, where the Permian sequences are pinched out or truncated, and unconformably overlain by the Early Jurassic Poolowanna Formation. This "plumbing system" facilitated the west-southwest lateral migration of

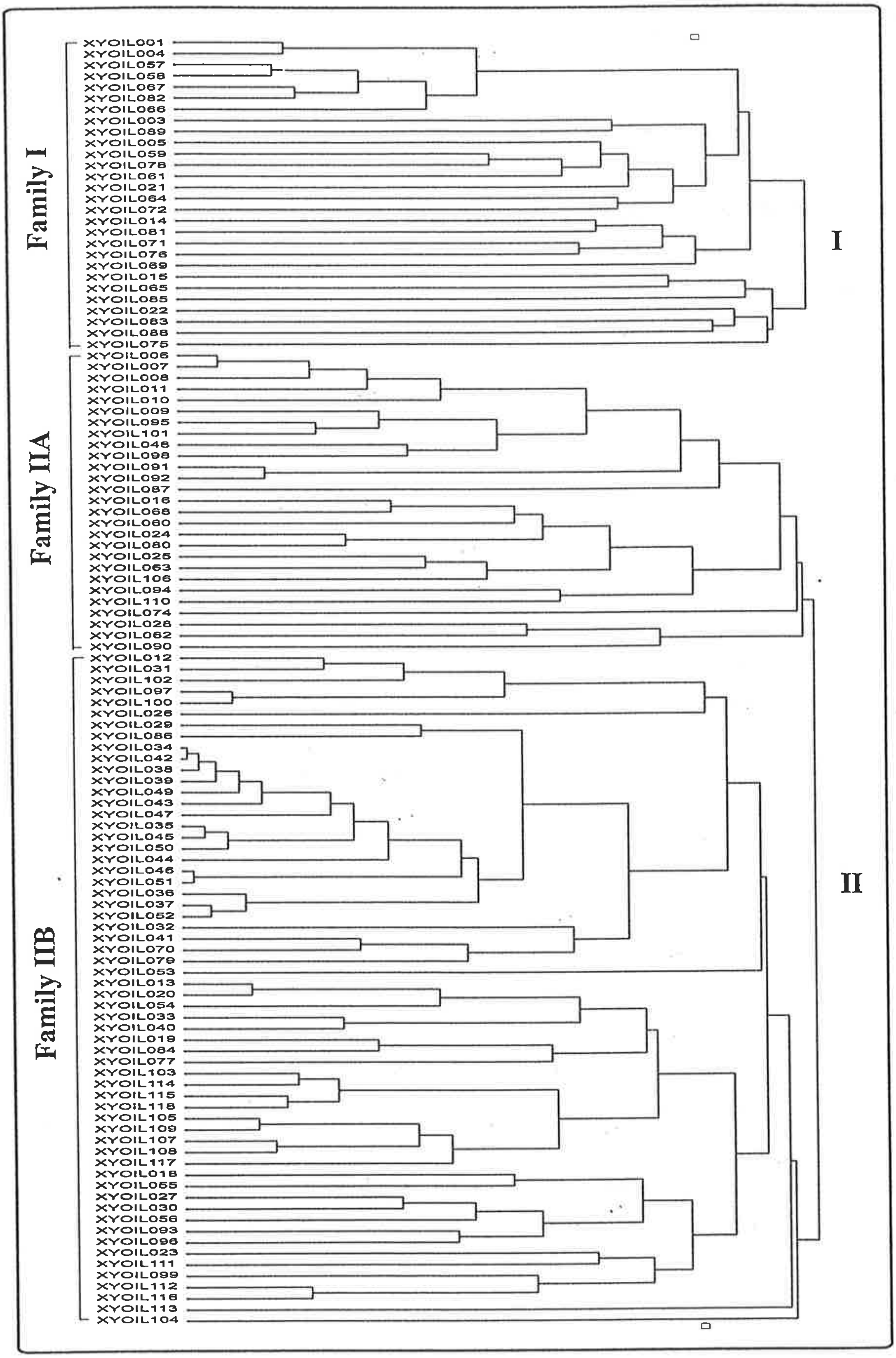


Figure 4.9 Dendrogram showing the major groupings of the Cooper and Eromanga oils and condensates.

Table 4.11 Hierarchical clustering history of the Cooper and Eromanga oils/condensates

Number of Cluster	Distance	Leader	Joiner	Number of Cluster	Distance	Leader	Joiner
114	0.104	XYOIL034	XYOIL042	57	1.300	XYOIL018	XYOIL055
113	0.111	XYOIL046	XYOIL051	56	1.340	XYOIL016	XYOIL060
112	0.132	XYOIL034	XYOIL038	55	1.348	XYOIL029	XYOIL034
111	0.151	XYOIL035	XYOIL045	54	1.353	XYOIL028	XYOIL062
110	0.203	XYOIL037	XYOIL052	53	1.368	XYOIL099	XYOIL112
109	0.203	XYOIL034	XYOIL039	52	1.371	XYOIL027	XYOIL093
108	0.205	XYOIL006	XYOIL007	51	1.146	XYOIL016	XYOIL024
107	0.208	XYOIL035	XYOIL050	50	1.483	XYOIL019	XYOIL077
106	0.241	XYOIL097	XYOIL100	49	1.505	XYOIL103	XYOIL105
105	0.249	XYOIL034	XYOIL049	48	1.512	XYOIL094	XYOIL110
104	0.257	XYOIL036	XYOIL037	47	1.517	XYOIL059	XYOIL061
103	0.266	XYOIL013	XYOIL020	46	1.651	XYOIL032	XYOIL041
102	0.269	XYOIL015	XYOIL019	45	1.814	XYOIL013	XYOIL033
101	0.335	XYOIL034	XYOIL043	44	2.047	XYOIL071	XYOIL076
100	0.342	XYOIL091	XYOIL092	43	2.056	XYOIL006	XYOIL009
99	0.393	XYOIL107	XYOIL108	42	2.096	XYOIL023	XYOIL111
98	0.398	XYOIL057	XYOIL058	41	2.134	XYOIL014	XYOIL081
97	0.405	XYOIL115	XYOIL118	40	2.151	XYOIL005	XYOIL059
96	0.413	XYOIL001	XYOIL004	39	2.196	XYOIL016	XYOIL025
95	0.441	XYOIL103	XYOIL114	38	2.209	XYOIL003	XYOIL089
94	0.449	XYOIL067	XYOIL082	37	2.265	XYOIL064	XYOIL072
93	0.645	XYOIL112	XYOIL116	36	2.277	XYOIL029	XYOIL032
92	0.468	XTOIL006	XYOIL008	35	2.431	XYOIL005	XYOIL021
91	0.509	XYOIL095	XYOIL101	34	2.481	XYOIL018	XYOIL027
90	0.511	XYOIL012	XYOIL031	33	2.739	XYOIL013	XYOIL019
89	0.515	XYOIL034	XYOIL047	32	2.821	XYOIL023	XYOIL099
88	0.569	XYOIL103	XYOIL115	31	3.237	XYOIL013	XYOIL103
87	0.572	XYOIL033	XYOIL040	30	3.293	XYOIL028	XYOIL090
86	0.576	XYOIL024	XYOIL080	29	3.304	XYOIL014	XYOIL071
85	0.592	XYOIL034	XYOIL035	28	3.429	XYOIL015	XYOIL065
84	0.606	XYOIL041	XYOIL070	27	3.470	XYOIL005	XYOIL064
83	0.629	XYOIL057	XYOIL067	26	3.536	XYOIL006	XYOIL091
82	0.666	XYOIL006	XYOIL011	25	3.655	XYOIL018	XYOIL023
81	0.724	XYOIL019	XYOIL084	24	3.892	XYOIL016	XYOIL094
80	0.725	XYOIL009	XYOIL095	23	3.920	XYOIL014	XYOIL069
79	0.731	XYOIL034	XYOIL044	22	4.056	XYOIL012	XYOIL028
78	0.753	XYOIL016	XYOIL068	21	4.122	XYOIL003	XYOIL005
77	0.762	XYOIL027	XYOIL030	20	4.454	XYOIL083	XYOIL088
76	0.768	XYOIL012	XYOIL102	19	4.582	XYOIL006	XYOIL087
75	0.771	XYOIL048	XYOIL098	18	5.791	XYOIL012	XYOIL029
74	0.781	XYOIL105	XYOIL107	17	6.073	XYOIL013	XYOIL018
73	0.784	XYOIL029	XYOIL086	16	6.098	XYOIL022	XYOIL083
72	0.813	XYOIL025	XYOIL063	15	6.163	XYOIL001	XYOIL003
71	0.846	XYOIL057	XYOIL066	14	6.296	XYOIL015	XYOIL085
70	0.884	XYOIL013	XYOIL054	13	7.571	XYOIL001	XYOIL014
69	0.887	XYOIL006	XYOIL010	12	7.954	XYOIL012	XYOIL053
68	0.909	XYOIL105	XYOIL117	11	8.319	XYOIL012	XYOIL013
67	0.917	XYOIL093	XYOIL096	10	8.557	XYOIL022	XYOIL075
66	0.928	XYOIL034	XYOIL046	9	9.471	XYOIL015	XYOIL022
65	0.986	XYOIL041	XYOIL079	8	9.517	XYOIL006	XYOIL016
64	1.063	XYOIL027	XYOIL056	7	10.006	XYOIL012	XYOIL113
63	1.114	XYOIL034	XYOIL036	6	12.011	XYOIL012	XYOIL104
62	1.119	XYOIL001	XYOIL057	5	12.368	XYOIL006	XYOIL074
61	1.154	XYOIL025	XYOIL106	4	14.312	XYOIL006	XYOIL028
60	1.188	XYOIL059	XYOIL078	3	16.485	XYOIL001	XYOIL015
59	1.193	XYOIL009	XYOIL048	2	17.581	XYOIL006	XYOIL012
58	1.212	XYOIL012	XYOIL097	1	36.025	XYOIL001	XYOIL006

Poolowanna-derived hydrocarbons into the underlying Patchawarra reservoirs (as previously discussed).

4.5.4 FAMILY IIA AND FAMILY IIB OILS

The two oil sub-families IIA and IIB are separated by little distance in their clustering history, indicating their overall similarity. The only observation worth making is that most of the mixed oils discussed in Chapter 5 fall into the second sub-family, implying that crude oils belonging to sub-family IIA bear most of the properties of typical Eromanga-derived hydrocarbons.

4.6 SUMMARY

A large suite of oils and condensates from all over the Cooper and Eromanga Basins (including both the South Australian and Queenslands sectors) were analysed using cryogenic gas chromatography. After careful inspection of the resulting GC-FID traces, 19 parameters were selected (seven of them newly created for this study) to characterise the Cooper and Eromanga hydrocarbons in terms of their source affinity, maturity and secondary alteration .

Fourteen of the chosen parameters, many involving aromatic hydrocarbons, proved to particularly helpful in distinguishing Cooper oils and condensates from those reservoired in the Eromanga Basin. The conventional ratios Pr/Ph, Pr/*n*-C_{17} and Ph/*n*-C_{18} were of little or no use.

To determine the relationship between the 19 parameters, statistical correlation of the measured data was employed. This showed that the aromatic-based parameters and one other (U = cyclohexane/methylcyclopentane) are closely correlated. They are the most effective parameters for characterising the Cooper and Eromanga petroleums. They indicate that water washing is the most prevalent type of secondary alteration undergone by the Eromanga-reservoired oils. The results also show that Thompson's three maturity/evaporative fractionation parameters (viz. H, I and F) are closely correlated. They are also effective, though to lesser degree, in distinguishing the Cooper and Eromanga crude oils, thereby indicating that another kind of secondary alteration – evaporative fractionation – has strongly influenced the chemical compositions of certain Eromanga-reservoired crude oils. Light hydrocarbon ratios involving benzene were found to be highly susceptible to random evaporative loss during the storage and handling prior to analysis.

Based on their effectiveness and correlatability, fourteen parameters were adopted in grouping the oils and condensates by means of hierarchical cluster analysis. The samples can be classified into two groups, Family I and II. Family II crude oils may be further divided into two sub-families, Family IIA and IIB. All the crude oils of Family I come from reservoirs within the Cooper sequence. They have undergone the least secondary migration and hence also the least water washing. However, they may be enriched in aromatic hydrocarbons as a result of evaporative loss of their light fractions. Most oils of Family II are from Eromanga reservoirs. Their chemical composition suggests that they have experienced severe water washing during secondary migration within the aquifers of the Great Artesian Basin and after accumulation in the Eromanga traps, regardless of their origin from Cooper or Eromanga kitchens. Although nine crude oils assigned to Family II are from Patchawarra reservoirs, the geological setting of the Sturt area makes possible both an intra-Poolowanna origin and/or their in situ water washing. Most the mixed crude oils identified in Chapter 5 fall into sub-family IIA.

CHAPTER FIVE

MIXED SOURCING MODEL BASED ON WHOLE-OIL GC-MS MEASUREMENTS

5.1 INTRODUCTION

Petroleum system logic is an important tool for exploration in frontier settings (Smith, 1994). The concept becomes complicated wherever more than one type of mature source rocks occurs. Which is the major source rock? What is the mixing ratio of hydrocarbons in a multiply charged reservoir? These are questions that must be answered before a comprehensive *petroleum system logic* can be achieved. Their answers, in turn, may strongly influence the strategy of future exploration and even production.

Quantitative assessment of the relative contributions of hydrocarbons by Permian and Mesozoic source rocks to reservoirs in the Eromanga Basin has been a problem since the first discovery of Jurassic oil at Poolowanna-1. Kantsler et al. (1983), Vincent et al. (1985), Powell et al. (1989), Michaelsen and McKirdy (1989) published geochemical data showing that Jurassic and Cretaceous sediments were the source of the Eromanga-reservoired petroleum. On the contrary, Heath et al. (1989) argued that most of the oils found in Eromanga reservoirs were derived from Permian source rocks, and migrated vertically into the Mesozoic sequence, where their physical and chemical characteristics were severely altered.

Jenkins (1989) was one of the pioneers in trying to estimate the contribution of intra-Eromanga sources to the petroleum reservoired there. He suggested that the occurrence of 25,28,30-trisnorhopane, 25,28,30-trisnormoretane and 19-norisopimarane in a crude oil signified an Eromanga source input. Using this criterion, the maximum Eromanga contribution to an individual oil accumulation was found to be 40%, though less than 20% was the volumetric average across the basin.

Even this volumetrically minor Eromanga contribution has been questioned (Tupper and Burckhardt, 1990) since 19-norisopimarane is not strictly confined to the Eromanga sequence but also occurs in Permian source rocks.

Using an alternative approach based on the carbon isotopic composition of individual *n*-alkanes, Boreham and Hill (1998) and Boreham and Summons (1999) estimated that the Eromanga input to mix-sourced oils reservoired in the Eromanga Basin was greater than 25%. A maximum contribution of 65% was assigned to Eromanga sources on the basis of isotopic mass balance. However, this estimation method is limited by the analytical uncertainty of 0.5‰ in the data obtained from the current commercial GC-ir-MS systems (Bjorøy and Hall, 1990; Bjorøy et al., 1991, 1994a,b; Boreham and Hill, 1998; Boreham and Summons, 1999). Hence, the isotope method for source contribution assessment is only useful when the contribution of the Eromanga source rocks is greater than 25%. Another recent innovation with the potential for quantitation was the use of mixing curves based on the aromatic source and maturity parameters, 1-methyl/9-methylphenanthrene and 2-methyl/1-methylphenanthrene (Michaelsen and McKirdy, 1999, 2000). However, all these methods are at best semi-quantitative, although the last one appears to have a resolution of ±10%.

Alexander et al. (1996) provided yet another approach to the recognition of mixed Cooper and Eromanga-derived oils in Eromanga reservoirs. They used two sets of aromatic maturity parameters, one based on gasoline-range components and the other on heavy-end aromatic hydrocarbons. By cross-plotting these parameters, they determined that the Sturt-7 (Poolowanna) oil appears to be a mixture of low-maturity heavier crude and high-maturity gasoline-range hydrocarbons. The Birkhead oil from Big Lake-37, however, contained lower-maturity gasoline-range hydrocarbons and heavier components of higher maturity.

Of the three aforementioned methods (viz. age-specific biomarkers, GC-ir-MS of individual *n*-alkanes, and maturity measurement of light *versus* heavy aromatic hydrocarbons) for the assessment of the mixing ratio of petroleum sourced from both the Cooper and Eromanga petroleum kitchens, the first is the least reliable. The

Eromanga contribution could readily be over-emphasised when a Cooper-derived condensate, which contains extremely low concentrations of high-molecular-weight biomarkers, is mixed with an Eromanga-sourced oil in which triterpenoid (Jenkins, 1989) and/or araucariacean (Alexander et al., 1988) biomarkers are abundant.

Carbon isotope compositions of individual *n*-alkanes in crude oils provide, no doubt, one of the most promising approaches to the problem of mixed charging of hydrocarbon reservoirs in the Eromanga Basin (Boreham and Summons, 1999). However, caution must be exercised when interpreting the isotope data, as it is easy to make a wrong estimate when only the average isotope composition of the *n*-alkanes is considered. Even the average slope of the *n*-alkane isotope profile – employed by Boreham and Hill (1998) and Boreham and Summons (1999) to assess the degree of mixing of Cooper and Eromanga-derived hydrocarbons – requires further refinement.

Several facts must be borne in mind when attempting to calculate the mixing ratio of Cooper and Eromanga-derived hydrocarbons in an individual oil accumulation:

- ☐ Organic matter from the Cooper and Eromanga Basins appears to be isotopically indistinguishable. The range in isotopic composition of organic matter (kerogen) 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) (Boreham and Hill, 1998). This is not surprising since the source rocks and oil accumulations in both basins have fairly similar gross chemical and biomarker compositions (see Section 1.1).

- ☐ The range of *n*-alkane carbon isotope values in different crude oils is similar to that within one sample (Boreham and Hill, 1998; Boreham and Summons, 1999). Among all the crudes analysed by Boreham and Summons (1999), the carbon isotopic composition of *n*-C_{10} ranges from –22.09‰ to –28.05‰; that of *n*-C_{20} from -21.86‰ to –27.59‰. By comparison, carbon isotope compositions of *n*-alkanes in an oil from the Birkhead Formation at Big Lake-38 range from –24.57‰ to –28.07‰; and in that from the Patchawarra Formation at Gidgealpa-17, –23.31‰ to –27.76‰.

- ☐ The oils and condensates from this province exhibit a large chemical variation. Whole-oil GC-FID measurements of 120 samples in the present study (see Chapter 4) indicates that it is quite common for a Cooper-derived condensate to comprise mostly gasoline- and kerosine-range hydrocarbons, whereas the Eromanga oils often contain mainly waxy hydrocarbons.

Taking into account the above observations, it is conceivable that any quantitative description which relies solely on the relative concentrations of conventional steranes and triterpanes (Vincent et al., 1985), or only on the araucariacean biomarker signature (Alexander et al., 1988) will be doubtful. Similarly, the validity of relying merely on the bulk carbon isotope composition, or on the average carbon isotopic composition of individual *n*-alkanes, or even on slopes of the *n*-alkane carbon isotope profiles, is debatable. For example, Alexander et al. (1996) recognised that some oils reservoired in the Eromanga Basin are composite accumulations produced by mixing of the light Permian condensates with local waxy Eromanga oils of different maturities. In this case, assessment based on biomarkers would not reflect the contribution of the Permian-sourced condensate, considering its much lower content of heavy-end hydrocarbons (and hence biomarkers). Interpretations biased towards the contribution of Eromanga-derived petroleum also arise when only the *n*-alkane isotopic gradient is considered (Boreham and Hill, 1998; Boreham and Summons, 1999). The following theoretical calculation will clarify these points.

For a hypothetical Eromanga-reservoired oil, which is a mixture of Permian condensate and Jurassic waxy oil, the following statements apply:

1. The Permian condensate, in which the *n*-alkane isotopic gradient is relatively steep (Boreham and Summons, 1999), contains abundant gasoline-range hydrocarbons and extremely low concentrations of biomarkers (e. g. steranes, triterpanes) and lacks araucariacean resin-derived aromatics. Here, the light-end hydrocarbons account for up to 99.99% of the total hydrocarbons with an average gasoline-range *n*-alkane isotopic composition of –27‰, compared to –23‰ for the minor heavy-end *n*-alkanes.

2. The Jurassic heavy oil, with a flat *n*-alkane isotopic profile, contains predominantly C_{20+} hydrocarbons (99.99%), whose *n*-alkane isotopic composition is –26‰ for both the light- and heavy-ends. Its retene/phenanthrene

ratio is 2, and the 25,28,30-trisnorhopane/C_{30}-hopane ratio is 5.

3. When the mixing ratio of the above two crudes is 50:50, the resulting oil contains 50% of the gasoline-range hydrocarbons (coming primarily from the Permian condensate) and 50% of the heavy-end components (primarily from the Jurassic waxy oil). Carbon isotope values for the light-ends are near –27‰, and for the heavy ends close to –26‰, resulting in a nearly flat *n*-alkane isotope profile (seemingly characteristic of a Jurassic oil). Note that the biomarker ratios in the mixed oil are identical to those in the Jurassic waxy oil. Thus, bias towards (and over-emphasis of) the Jurassic contribution always occurs when the interpretation of mixing ratios is based only on the biomarker data or *n*-alkane isotope gradient. In this case, the biomarker interpretation leads to the exaggerated assumption of a 100% contribution from the Jurassic oil, whereas the carbon isotopic slope calculation suggests a contribution of only 25% from the Permian condensate.

In an attempt to improve upon the previous efforts to quantify hydrocarbon mixing ratios and, hence, to determine more accurately the relative contributions of Cooper *versus* Eromanga sources to the known petroleum reserves in the region, a new method has been designed. This method is based on the concept of compositional mass balance and detailed consideration of the observed chemical and isotopic variations between and within individual samples. It is expressed here first in a generalised form. Then a simplified two-end-member expression is used to illustrate this approach and its application to the Cooper/Eromanga petroleum province.

In this chapter, compositional differences in the Cooper and Eromanga oils/condensates are displayed by using various molecular source and maturity parameters. Data processing tools, such as correlation, principal components analysis, factor analysis and computer digital imitation, are employed to link the geochemical data with the conceptional mathematical mixing model. Finally, the model was used to estimate the mixing ratios for several selected oil accumulations.

However, it must be pointed out that this model also has limitations. In its multiple-end-member form it is limited by difficulties of visualisation, the lack of sufficient pristine samples, and the costs of tedious computation and laboratory analysis.

The simplified two-end-member approach, on the other hand, is limited by the difficulty of finding the representative end-members, because source rocks expel hydrocarbons in not only one but many maturity stages, and source rock organic facies vary considerably. Finding the representative end-member also involves time-consuming computer system optimisation.

5.2 SAMPLES, PARAMETERS AND ANALYTICAL RESULTS

5.2.1 SAMPLES

From the total collection of 123 Cooper/Eromanga oils and condensates (Table 3.1), 72 samples were selected for this part of the study. All were considered to have sustained minimal evaporative loss of their light ends during storage. The samples, with their geological details, are listed in Table 5.1.

5.2.2 PARAMETERS

The whole oil/condensate samples were analysed by GC-MS in selected ion detection mode (as detailed in Chapter 3). Diagnostic ions for most of the conventional aromatic and saturated hydrocarbon biomarkers were monitored. Most of the saturate biomarkers are, unfortunately, not abundant enough to be satisfactorily detected, especially in the light oils and the condensates. In contrast, signals of the aromatic biomarkers in the mass chromatograms are easy to quantify, because they commonly have stable molecular ions from the ion source. Therefore, only the aromatic data were processed in this study. Representative mass chromatograms are shown in Figures 5.1–5.3. Peak identifications of all eight isomers of the C_3-substituted benzenes were made on the basis of their retention times and mass spectra. The mass spectra were obtained from the full scan GC-MS of a Permian oil (XYOIL001, Tirrawarra-13, DST 4, Tirrawarra Formation) and injections of pure standards (viz. 1,3,5-trimethylbenzene, *n*-propylbenzene and isopropylbenzene).

Table 5.1 Values of aromatic maturity and source parameters (see Table 5.2 for definition)

Samples	Well	DST		Formation	MPI	XYLI	ProB	MEBI
xyoil001	Tirrawarra-13	DST 4	Oil	Tirrawarra	1.354	0.760	0.325	0.829
xyoil004	Tirrawarra-70	DST 1	Oil	Tirrawarra	1.256	0.763	0.317	0.831
xyoil013	Mooliampah-1	DST 7	Oil	Adori	0.573	0.801	0.300	0.782
xyoil014	Munkah-2	DST 1	Cond	Patchawarra	1.075	0.826	0.274	0.814
xyoil015	Yanda-2	DST 2	Cond	Patchawarra	0.890	0.842	0.271	0.823
xyoil018	Wilson-6	DST 2	Oil	Namur	0.864	0.812	0.303	0.814
xyoil019	Big Lake-37	DST 1	Oil	Birkhead	0.967	0.818	0.300	0.838
xyoil020	Mooliampah-1	DST 3	Oil	Namur	0.603	0.792	0.291	0.784
xyoil021	Epsilon-3	DST 5	Cond	Toolachee	0.967	0.768	0.347	0.803
xyoil022	Lepena-1	DST 3	Cond	Patchawarra	0.865	0.761	0.242	0.810
xyoil023	Epsilon-3	DST 3	Cond	Nappamerri	0.982	0.801	0.290	0.837
xyoil024	Spencer-4	DST 2	Oil	Birkhead	0.572	0.802	0.260	0.806
xyoil025	Wilson-6	DST 1	Oil	Hutton	0.982	0.837	0.245	0.812
xyoil026	Moolion-1	DST 1	Oil	Hutton	0.512	0.758	0.339	0.762
xyoil027	Tickalara-2	DST 5	Oil	Namur	0.516	0.802	0.305	0.789
xyoil028	Wancoocha-3	DST 3	Oil	Hutton	0.542	0.778	0.258	0.777
xyoil029	Jackson-28	DST 2	Oil	Westbourne	0.921	0.859	0.278	0.837
xyoil030	Tickalara-2	DST 1	Oil	Namur	0.442	0.920	0.323	0.796
xyoil035	Dilkera-2	DST 2	Oil	Murta	0.562	0.862	0.278	0.836
xyoil037	Maxwell-2	DST 1	Oil	Murta	0.518	0.868	0.266	0.842
xyoil039	Thungo-1	DST 1	Oil	Murta	0.632	0.860	0.283	0.834
xyoil041	Thungo-1	DST 4	Oil	Westbourne	0.688	0.903	0.232	0.863
xyoil042	Thungo-4		Oil	Murta	0.608	0.861	0.282	0.835
xyoil047	Dilkera-1	DST 7	Oil	Murta	0.558	0.862	0.278	0.835
xyoil054	Mooliampah-1	DST 2	Oil	Namur	0.488	0.795	0.322	0.776
xyoil057	Tirrawarra-58	DST 3	Oil	Tirrawarra	1.601	0.777	0.319	0.839
xyoil058	Tirrawarra-57	DST 2	Oil	Tirrawarra	1.368	0.780	0.324	0.840
xyoil059	Gooranie-1	DST 2	Cond	Patchawarra	1.223	0.789	0.337	0.845
xyoil061	Merrimelia-17	DST 4	Cond	Nappamerri	1.080	0.784	0.309	0.838
xyoil062	Wancoocha-2	DST 5	Oil	Hutton	0.519	0.789	0.247	0.793
xyoil063	Cook-1	DST 3	Oil	Hutton	0.719	0.816	0.255	0.834
xyoil064	Merrimelia		Oil	Nappamerri	1.161	0.826	0.247	0.854
xyoil065	Della-2		Cond	Toolachee	1.143	0.798	0.317	0.838
xyoil066	Woolkina		Oil	Tirrawarra	1.216	0.789	0.320	0.847
xyoil067	Moorari-3		Oil	Tirrawarra	1.114	0.775	0.316	0.839
xyoil068	Wancoocha-6		Oil	Murta	0.432	0.830	0.328	0.821
xyoil069	Wippo-1	DST 1	Cond	Patchawarra	1.046	0.784	0.333	0.841
xyoil070	Jackson South-4	DST 2	Oil	Birkhead	0.770	0.844	0.248	0.776
xyoil071	Moorari-3		Oil	Tirrawarra	1.079	0.764	0.280	0.786
xyoil072	Meranji-1	DST 5	Cond	Patchawarra	0.945	0.762	0.384	0.839
xyoil073	Jackson-2		Oil	Hutton	1.055	0.769	0.235	0.791
xyoil074	Wilson South-1	DST 3	Oil	Hutton	0.906	0.810	0.249	0.801
xyoil075	Leleptian-1	DST 3	Cond	Patchawarra	1.040	0.762	0.343	0.795
xyoil076	Fly Lake-2		Oil	Tirrawarra	1.036	0.770	0.269	0.830
xyoil077	Merrimelia		Oil	Hutton	0.750	0.841	0.283	0.836
xyoil079	Alwyn-1	DST 1	Oil	Murta	0.467	0.815	0.291	0.808
xyoil081	Aroona-1	DST 3	Cond	Toolachee	0.930	0.784	0.332	0.819
xyoil082	Tirrawarra		Oil	Tirrawarra	1.378	0.786	0.321	0.842
xyoil083	Bagundi-1	DST 4	Oil	Patchawarra	0.904	0.842	0.225	0.811
xyoil084	Mooliampah-1	DST 1	Oil	Murta	0.544	0.791	0.359	0.765
xyoil085	Bookabourdie-4		Cond	Tirrawarra	1.560	0.811	0.354	0.849
xyoil086	Jackson-3		Oil	Westbourne	1.061	0.855	0.271	0.834
xyoil087	Nungeroo-1	DST 2	Oil	Namur	0.536	0.768	0.260	0.767
xyoil089	Daralingie-1		Cond	Patchawarra	0.935	0.786	0.338	0.827
xyoil090	Wancoocha-2	DST 4	Oil	Birkhead	0.517	0.791	0.268	0.773
xyoil093	Taloola-2	DST 1	Oil	Poolowanna	0.752	0.765	0.326	0.790
xyoil094	Taloola-2	DST 2	Oil	Hutton	0.616	0.736	0.262	0.758
xyoil095	Taloola-2	DST 3	Oil	Namur	0.399	0.733	0.261	0.734
xyoil107	Sturt-4	DST 1	Oil	Poolowanna	0.610	0.734	0.363	0.751
xyoil108	Sturt-4	DST 2	Oil	Patchawarra	0.591	0.731	0.360	0.751
xyoil109	Sturt-5	DST 1	Oil	Patchawarra	0.633	0.742	0.360	0.751
xyoil110	Sturt-6	DST 1	Oil	Birkhead	0.385	0.811	0.251	0.790
xyoil111	Sturt-6	DST 3	Oil	Patchawarra	1.008	0.745	0.346	0.776
xyoil113	Sturt-7	DST 2	Oil	Mooracoochie	0.877	0.730	0.332	0.771
xyoil114	Sturt-7	DST 3	Oil	Patchawarra	0.666	0.748	0.351	0.760
xyoil115	Sturt-7	DST 5	Oil	Patchawarra	0.666	0.738	0.350	0.760
xyoil116	Sturt-7	DST 4	Oil	Patchawarra	0.915	0.744	0.336	0.760
xyoil118	Sturt East-2	DST 1	Oil	Patchawarra	0.638	0.746	0.348	0.765
Xyoil120	Wancoocha-2	DST 3	Oil	Patchawarra	0.738	0.808	0.331	0.791
Xyoil121	Garanjanie-1	DST 1	Oil	Namur	0.481	0.754	0.316	0.732
Xyoil122	Dirkala-1	DST 1	Cond	Birkhead	0.551	0.799	0.295	0.826
Xyoil123	Dirkala-1	DST 6	Oil	Namur	0.521	0.743	0.273	0.748

Table 5.1 continued (2/4)

Samples	Well	DST		Formation	TMBI-1	TMBI-2	R/P
xyoil001	Tirrawarra-13	DST 4	Oil	Tirrawarra	0.705	0.787	0.016
xyoil004	Tirrawarra-70	DST 1	Oil	Tirrawarra	0.705	0.788	0.017
xyoil013	Mooliampah-1	DST 7	Oil	Adori	0.672	0.764	1.181
xyoil014	Munkah-2	DST 1	Cond	Patchawarra	0.720	0.783	0.004
xyoil015	Yanda-2	DST 2	Cond	Patchawarra	0.687	0.773	0.003
xyoil018	Wilson-6	DST 2	Oil	Namur	0.609	0.736	0.114
xyoil019	Big Lake-37	DST 1	Oil	Birkhead	0.635	0.760	0.081
xyoil020	Mooliampah-1	DST 3	Oil	Namur	0.616	0.723	1.484
xyoil021	Epsilon-3	DST 5	Cond	Toolachee	0.769	0.793	0.009
xyoil022	Lepena-1	DST 3	Cond	Patchawarra	0.751	0.788	0.002
xyoil023	Epsilon-3	DST 3	Cond	Nappamerri	0.784	0.788	0.058
xyoil024	Spencer-4	DST 2	Oil	Birkhead	0.660	0.742	0.763
xyoil025	Wilson-6	DST 1	Oil	Hutton	0.635	0.741	0.754
xyoil026	Moolion-1	DST 1	Oil	Hutton	0.515	0.686	0.395
xyoil027	Tickalara-2	DST 5	Oil	Namur	0.634	0.732	0.400
xyoil028	Wancoocha-3	DST 3	Oil	Hutton	0.560	0.698	2.576
xyoil029	Jackson-28	DST 2	Oil	Westbourne	0.754	0.798	0.796
xyoil030	Tickalara-2	DST 1	Oil	Namur	0.666	0.748	0.796
xyoil035	Dilkera-2	DST 2	Oil	Murta	0.768	0.802	2.196
xyoil037	Maxwell-2	DST 1	Oil	Murta	0.776	0.806	2.018
xyoil039	Thungo-1	DST 1	Oil	Murta	0.768	0.804	2.196
xyoil041	Thungo-1	DST 4	Oil	Westbourne	0.801	0.811	2.554
xyoil042	Thungo-4		Oil	Murta	0.768	0.805	2.151
xyoil047	Dilkera-1	DST 7	Oil	Murta	0.769	0.802	2.155
xyoil054	Mooliampah-1	DST 2	Oil	Namur	0.618	0.725	1.750
xyoil057	Tirrawarra-58	DST 3	Oil	Tirrawarra	0.708	0.798	0.031
xyoil058	Tirrawarra-57	DST 2	Oil	Tirrawarra	0.712	0.799	0.017
xyoil059	Gooranie-1	DST 2	Cond	Patchawarra	0.750	0.805	0.044
xyoil061	Merrimelia-17	DST 4	Cond	Nappamerri	0.758	0.800	0.025
xyoil062	Wancoocha-2	DST 5	Oil	Hutton	0.563	0.696	2.133
xyoil063	Cook-1	DST 3	Oil	Hutton	0.625	0.739	0.185
xyoil064	Merrimelia		Oil	Nappamerri	0.737	0.796	0.094
xyoil065	Della-2		Cond	Toolachee	0.787	0.795	0.001
xyoil066	Woolkina		Oil	Tirrawarra	0.725	0.807	0.019
xyoil067	Moorari-3		Oil	Tirrawarra	0.705	0.802	0.027
xyoil068	Wancoocha-6		Oil	Murta	0.682	0.763	1.329
xyoil069	Wippo-1	DST 1	Cond	Patchawarra	0.778	0.819	0.010
xyoil070	Jackson South-4	DST 2	Oil	Birkhead	0.701	0.757	1.816
xyoil071	Moorari-3		Oil	Tirrawarra	0.666	0.783	0.028
xyoil072	Meranji-1	DST 5	Cond	Patchawarra	0.787	0.828	0.309
xyoil073	Jackson-2		Oil	Hutton	0.569	0.752	1.580
xyoil074	Wilson South-1	DST 3	Oil	Hutton	0.573	0.700	0.924
xyoil075	Leleptian-1	DST 3	Cond	Patchawarra	0.718	0.779	0.004
xyoil076	Fly Lake-2		Oil	Tirrawarra	0.665	0.782	0.023
xyoil077	Merrimelia		Oil	Hutton	0.694	0.751	0.147
xyoil079	Alwyn-1	DST 1	Oil	Murta	0.686	0.767	1.689
xyoil081	Aroona-1	DST 3	Cond	Toolachee	0.771	0.800	0.007
xyoil082	Tirrawarra		Oil	Tirrawarra	0.708	0.800	0.020
xyoil083	Bagundi-1	DST 4	Oil	Patchawarra	0.678	0.767	0.005
xyoil084	Mooliampah-1	DST 1	Oil	Murta	0.634	0.727	1.953
xyoil085	Bookabourdie-4		Cond	Tirrawarra	0.833	0.845	0.002
xyoil086	Jackson-3		Oil	Westbourne	0.729	0.784	0.470
xyoil087	Nungeroo-1	DST 2	Oil	Namur	0.546	0.707	1.910
xyoil089	Daralingie-1		Cond	Patchawarra	0.747	0.794	0.006
xyoil090	Wancoocha-2	DST 4	Oil	Birkhead	0.581	0.707	0.901
xyoil093	Taloola-2	DST 1	Oil	Poolowanna	0.664	0.741	0.654
xyoil094	Taloola-2	DST 2	Oil	Hutton	0.469	0.645	1.182
xyoil095	Taloola-2	DST 3	Oil	Namur	0.484	0.674	2.530
xyoil107	Sturt-4	DST 1	Oil	Poolowanna	0.565	0.692	0.627
xyoil108	Sturt-4	DST 2	Oil	Patchawarra	0.564	0.691	0.632
xyoil109	Sturt-5	DST 1	Oil	Patchawarra	0.580	0.698	0.686
xyoil110	Sturt-6	DST 1	Oil	Birkhead	0.619	0.683	2.529
xyoil111	Sturt-6	DST 3	Oil	Patchawarra	0.639	0.721	0.242
xyoil113	Sturt-7	DST 2	Oil	Mooracoochie	0.559	0.675	0.588
xyoil114	Sturt-7	DST 3	Oil	Patchawarra	0.588	0.702	0.889
xyoil115	Sturt-7	DST 5	Oil	Patchawarra	0.594	0.703	0.821
xyoil116	Sturt-7	DST 4	Oil	Patchawarra	0.640	0.724	0.312
xyoil118	Sturt East-2	DST 1	Oil	Patchawarra	0.601	0.705	0.841
Xyoil120	Wancoocha-2	DST 3	Oil	Patchawarra	0.728	0.795	0.336
Xyoil121	Garanjanie-1	DST 1	Oil	Namur	0.551	0.704	1.832
Xyoil122	Dirkala-1	DST 1	Cond	Birkhead	0.703	0.706	0.572
Xyoil123	Dirkala-1	DST 6	Oil	Namur	0.463	0.671	1.362

Table 5.1 continued (3/4)

Samples	Well	DST		Formation	125/136-TMN	1,7/x-DMP	R/9-MP	1/9-MP
xyoil001	Tirrawarra-13	DST 4	Oil	Tirrawarra	0.428	0.326	0.032	0.747
xyoil004	Tirrawarra-70	DST 1	Oil	Tirrawarra	0.468	0.337	0.030	0.726
xyoil013	Mooliampah-1	DST 7	Oil	Adori	2.100	1.570	2.768	2.409
xyoil014	Munkah-2	DST 1	Cond	Patchawarra	0.750	0.210	0.009	0.650
xyoil015	Yanda-2	DST 2	Cond	Patchawarra	0.876	0.285	0.006	0.621
xyoil018	Wilson-6	DST 2	Oil	Namur	1.342	0.718	0.193	1.052
xyoil019	Big Lake-37	DST 1	Oil	Birkhead	0.882	0.972	0.102	1.204
xyoil020	Mooliampah-1	DST 3	Oil	Namur	1.858	1.784	3.174	2.668
xyoil021	Epsilon-3	DST 5	Cond	Toolachee	1.077	0.223	0.023	0.628
xyoil022	Lepena-1	DST 3	Cond	Patchawarra	0.775	0.299	0.005	0.618
xyoil023	Epsilon-3	DST 3	Cond	Nappamerri	1.354	0.284	0.095	0.663
xyoil024	Spencer-4	DST 2	Oil	Birkhead	1.558	1.672	1.487	1.838
xyoil025	Wilson-6	DST 1	Oil	Hutton	0.970	0.475	0.858	1.003
xyoil026	Moolion-1	DST 1	Oil	Hutton	2.276	0.771	0.764	0.806
xyoil027	Tickalara-2	DST 5	Oil	Namur	2.132	1.343	0.998	2.363
xyoil028	Wancoocha-3	DST 3	Oil	Hutton	2.189	1.853	4.959	1.867
xyoil029	Jackson-28	DST 2	Oil	Westbourne	0.900	0.560	1.144	1.363
xyoil030	Tickalara-2	DST 1	Oil	Namur	1.382	1.219	1.968	2.153
xyoil035	Dilkera-2	DST 2	Oil	Murta	1.130	1.281	3.903	1.430
xyoil037	Maxwell-2	DST 1	Oil	Murta	1.186	1.359	3.785	1.360
xyoil039	Thungo-1	DST 1	Oil	Murta	1.171	1.030	3.772	1.779
xyoil041	Thungo-1	DST 4	Oil	Westbourne	0.984	1.190	4.069	2.741
xyoil042	Thungo-4		Oil	Murta	1.039	1.049	3.995	1.891
xyoil047	Dilkera-1	DST 7	Oil	Murta	1.113	1.238	3.803	1.463
xyoil054	Mooliampah-1	DST 2	Oil	Namur	1.641	1.600	3.928	2.160
xyoil057	Tirrawarra-58	DST 3	Oil	Tirrawarra	0.526	0.383	0.034	0.747
xyoil058	Tirrawarra-57	DST 2	Oil	Tirrawarra	0.349	0.377	0.032	0.747
xyoil059	Gooranie-1	DST 2	Cond	Patchawarra	1.114	0.439	0.089	0.716
xyoil061	Merrimelia-17	DST 4	Cond	Nappamerri	1.029	0.274	0.044	0.616
xyoil062	Wancoocha-2	DST 5	Oil	Hutton	2.279	2.109	4.431	2.273
xyoil063	Cook-1	DST 3	Oil	Hutton	1.621	0.947	0.360	1.077
xyoil064	Merrimelia		Oil	Nappamerri	1.000	0.322	0.101	0.630
xyoil065	Della-2		Cond	Toolachee	0.643	0.208	0.004	0.649
xyoil066	Woolkina		Oil	Tirrawarra	0.405	0.365	0.034	0.721
xyoil067	Moorari-3		Oil	Tirrawarra	0.462	0.388	0.043	0.716
xyoil068	Wancoocha-6		Oil	Murta	3.002	0.885	2.734	1.185
xyoil069	Wippo-1	DST 1	Cond	Patchawarra	0.740	0.246	0.019	0.659
xyoil070	Jackson South-4	DST 2	Oil	Birkhead	1.119	1.219	3.976	2.514
xyoil071	Moorari-3		Oil	Tirrawarra	0.447	0.388	0.044	0.727
xyoil072	Meranji-1	DST 5	Cond	Patchawarra	0.931	0.403	0.600	0.911
xyoil073	Jackson-2		Oil	Hutton	1.002	0.510	1.626	1.108
xyoil074	Wilson South-1	DST 3	Oil	Hutton	1.695	0.960	1.397	1.350
xyoil075	Leleptian-1	DST 3	Cond	Patchawarra	1.183	0.240	0.010	0.596
xyoil076	Fly Lake-2		Oil	Tirrawarra	0.587	0.422	0.034	0.718
xyoil077	Merrimelia		Oil	Hutton	1.442	0.792	0.277	1.216
xyoil079	Alwyn-1	DST 1	Oil	Murta	1.167	0.791	3.190	1.027
xyoil081	Aroona-1	DST 3	Cond	Toolachee	0.979	0.247	0.015	0.638
xyoil082	Tirrawarra		Oil	Tirrawarra	0.361	0.383	0.037	0.742
xyoil083	Bagundi-1	DST 4	Oil	Patchawarra	0.688	0.305	0.010	0.631
xyoil084	Mooliampah-1	DST 1	Oil	Murta	1.704	1.380	3.637	1.316
xyoil085	Bookabourdie-4		Cond	Tirrawarra	0.519	0.217	0.006	0.671
xyoil086	Jackson-3		Oil	Westbourne	0.868	0.430	0.584	0.946
xyoil087	Nungeroo-1	DST 2	Oil	Namur	1.459	0.917	3.338	1.595
xyoil089	Daralingie-1		Cond	Patchawarra	1.023	0.285	0.013	0.673
xyoil090	Wancoocha-2	DST 4	Oil	Birkhead	1.667	1.174	1.796	1.459
xyoil093	Taloola-2	DST 1	Oil	Poolowanna	1.428	0.560	0.986	0.830
xyoil094	Taloola-2	DST 2	Oil	Hutton	1.463	0.515	1.821	0.901
xyoil095	Taloola-2	DST 3	Oil	Namur	2.895	1.049	5.785	1.483
xyoil107	Sturt-4	DST 1	Oil	Poolowanna	1.845	0.626	1.290	0.811
xyoil108	Sturt-4	DST 2	Oil	Patchawarra	1.830	0.613	1.273	0.774
xyoil109	Sturt-5	DST 1	Oil	Patchawarra	1.731	0.675	1.352	1.067
xyoil110	Sturt-6	DST 1	Oil	Birkhead	1.823	1.738	5.398	2.862
xyoil111	Sturt-6	DST 3	Oil	Patchawarra	1.286	0.460	0.344	0.689
xyoil113	Sturt-7	DST 2	Oil	Mooracoochie	2.105	0.260	0.737	0.635
xyoil114	Sturt-7	DST 3	Oil	Patchawarra	1.662	0.730	1.731	1.170
xyoil115	Sturt-7	DST 5	Oil	Patchawarra	1.611	0.727	1.577	1.261
xyoil116	Sturt-7	DST 4	Oil	Patchawarra	1.297	0.466	0.407	0.688
xyoil118	Sturt East-2	DST 1	Oil	Patchawarra	1.607	0.804	1.488	1.238
Xyoil120	Wancoocha-2	DST 3	Oil	Patchawarra	1.429	0.543	0.811	0.776
Xyoil121	Garanjanie-1	DST 1	Oil	Namur	2.933	0.755	3.309	0.752
Xyoil122	Dirkala-1	DST 1	Cond	Birkhead	1.975	1.319	1.235	1.553
Xyoil123	Dirkala-1	DST 6	Oil	Namur	2.360	0.746	2.974	1.469

Table 5.1 continued (4/4)

Samples	Well	DST		Formation	MA/MP	DNR-1	DNR-6	TNR-1
xyoil001	Tirrawarra-13	DST 4	Oil	Tirrawarra	0.031	17.021	5.189	1.940
xyoil004	Tirrawarra-70	DST 1	Oil	Tirrawarra	0.041	14.225	4.760	1.757
xyoil013	Mooliampah-1	DST 7	Oil	Adori	0.011	2.926	2.083	0.371
xyoil014	Munkah-2	DST 1	Cond	Patchawarra	0.061	9.230	3.426	0.886
xyoil015	Yanda-2	DST 2	Cond	Patchawarra	0.036	8.367	3.190	0.812
xyoil018	Wilson-6	DST 2	Oil	Namur	0.039	5.544	2.966	0.698
xyoil019	Big Lake-37	DST 1	Oil	Birkhead	0.012	6.142	3.657	0.903
xyoil020	Mooliampah-1	DST 3	Oil	Namur	0.006	2.601	2.019	0.410
xyoil021	Epsilon-3	DST 5	Cond	Toolachee	0.100	7.165	2.960	0.707
xyoil022	Lepena-1	DST 3	Cond	Patchawarra	0.035	8.814	3.649	0.810
xyoil023	Epsilon-3	DST 3	Cond	Nappamerri	0.035	6.383	3.107	0.576
xyoil024	Spencer-4	DST 2	Oil	Birkhead	0.016	3.826	2.450	0.494
xyoil025	Wilson-6	DST 1	Oil	Hutton	0.036	9.475	4.730	0.922
xyoil026	Moolion-1	DST 1	Oil	Hutton	0.259	2.406	1.691	0.397
xyoil027	Tickalara-2	DST 5	Oil	Namur	0.013	2.792	2.114	0.397
xyoil028	Wancoocha-3	DST 3	Oil	Hutton	0.036	2.530	1.518	0.348
xyoil029	Jackson-28	DST 2	Oil	Westbourne	0.000	6.521	3.129	0.860
xyoil030	Tickalara-2	DST 1	Oil	Namur	0.011	3.483	2.213	0.535
xyoil035	Dilkera-2	DST 2	Oil	Murta	0.024	5.810	2.719	0.591
xyoil037	Maxwell-2	DST 1	Oil	Murta	0.024	7.215	3.155	0.537
xyoil039	Thungo-1	DST 1	Oil	Murta	0.020	7.006	2.807	0.548
xyoil041	Thungo-1	DST 4	Oil	Westbourne	0.010	6.458	2.788	0.723
xyoil042	Thungo-4		Oil	Murta	0.036	6.433	2.824	0.665
xyoil047	Dilkera-1	DST 7	Oil	Murta	0.022	5.875	2.884	0.607
xyoil054	Mooliampah-1	DST 2	Oil	Namur	0.004	2.365	1.726	0.389
xyoil057	Tirrawarra-58	DST 3	Oil	Tirrawarra	0.046	17.240	5.341	1.996
xyoil058	Tirrawarra-57	DST 2	Oil	Tirrawarra	0.029	18.266	5.412	1.971
xyoil059	Gooranie-1	DST 2	Cond	Patchawarra	0.211	7.195	2.969	0.828
xyoil061	Merrimelia-17	DST 4	Cond	Nappamerri	0.035	7.748	3.424	0.800
xyoil062	Wancoocha-2	DST 5	Oil	Hutton	0.070	2.779	1.799	0.328
xyoil063	Cook-1	DST 3	Oil	Hutton	0.017	5.187	2.676	0.595
xyoil064	Merrimelia		Oil	Nappamerri	0.038	6.806	3.078	0.887
xyoil065	Della-2		Cond	Toolachee	0.120	10.504	3.930	0.930
xyoil066	Woolkina		Oil	Tirrawarra	0.029	13.973	4.876	1.685
xyoil067	Moorari-3		Oil	Tirrawarra	0.018	11.991	4.552	1.573
xyoil068	Wancoocha-6		Oil	Murta	0.061	2.340	1.449	0.270
xyoil069	Wippo-1	DST 1	Cond	Patchawarra	0.043	8.623	3.752	0.898
xyoil070	Jackson South-4	DST 2	Oil	Birkhead	0.026	5.750	3.420	0.699
xyoil071	Moorari-3		Oil	Tirrawarra	0.010	10.804	4.287	1.708
xyoil072	Meranji-1	DST 5	Cond	Patchawarra	0.068	8.021	3.446	0.809
xyoil073	Jackson-2		Oil	Hutton	0.036	4.972	3.236	0.842
xyoil074	Wilson South-1	DST 3	Oil	Hutton	0.083	3.816	2.598	0.502
xyoil075	Leleptian-1	DST 3	Cond	Patchawarra	0.114	6.688	2.579	0.732
xyoil076	Fly Lake-2		Oil	Tirrawarra	0.025	8.318	3.621	1.167
xyoil077	Merrimelia		Oil	Hutton	0.021	4.288	2.537	0.582
xyoil079	Alwyn-1	DST 1	Oil	Murta	0.072	5.945	3.158	0.611
xyoil081	Aroona-1	DST 3	Cond	Toolachee	0.088	7.346	3.188	0.758
xyoil082	Tirrawarra		Oil	Tirrawarra	0.028	17.361	5.388	1.894
xyoil083	Bagundi-1	DST 4	Oil	Patchawarra	0.047	9.640	3.960	1.031
xyoil084	Mooliampah-1	DST 1	Oil	Murta	0.028	2.349	1.651	0.394
xyoil085	Bookabourdie-4		Cond	Tirrawarra	0.022	16.466	5.384	1.497
xyoil086	Jackson-3		Oil	Westbourne	0.005	7.644	3.289	0.900
xyoil087	Nungeroo-1	DST 2	Oil	Namur	0.021	3.845	2.338	0.538
xyoil089	Daralingie-1		Cond	Patchawarra	0.079	7.286	3.234	0.786
xyoil090	Wancoocha-2	DST 4	Oil	Birkhead	0.083	3.172	1.970	0.362
xyoil093	Taloola-2	DST 1	Oil	Poolowanna	0.210	4.513	2.215	0.604
xyoil094	Taloola-2	DST 2	Oil	Hutton	0.291	3.159	1.908	0.517
xyoil095	Taloola-2	DST 3	Oil	Namur	0.081	3.148	1.849	0.219
xyoil107	Sturt-4	DST 1	Oil	Poolowanna	0.315	3.412	1.650	0.429
xyoil108	Sturt-4	DST 2	Oil	Patchawarra	0.476	3.380	1.645	0.422
xyoil109	Sturt-5	DST 1	Oil	Patchawarra	0.275	3.667	1.793	0.472
xyoil110	Sturt-6	DST 1	Oil	Birkhead	0.039	2.815	1.842	0.257
xyoil111	Sturt-6	DST 3	Oil	Patchawarra	0.089	5.655	2.604	0.730
xyoil113	Sturt-7	DST 2	Oil	Mooracoochie	0.133	3.912	2.105	0.448
xyoil114	Sturt-7	DST 3	Oil	Patchawarra	0.169	3.557	1.878	0.489
xyoil115	Sturt-7	DST 5	Oil	Patchawarra	0.016	3.833	1.954	0.513
xyoil116	Sturt-7	DST 4	Oil	Patchawarra	0.073	5.127	2.383	0.700
xyoil118	Sturt East-2	DST 1	Oil	Patchawarra	0.211	3.765	1.976	0.511
Xyoil120	Wancoocha-2	DST 3	Oil	Patchawarra	0.246	5.708	2.287	0.561
Xyoil121	Garanjanie-1	DST 1	Oil	Namur	0.224	2.656	1.677	0.246
Xyoil122	Dirkala-1	DST 1	Cond	Birkhead	0.060	3.183	1.934	0.391
Xyoil123	Dirkala-1	DST 6	Oil	Namur	0.029	3.121	1.893	0.338

Table 5.2 Definition and specificity of the aromatic parameters

No.	Parameter	S	Definition	m/z	Reference
1	XYLI	M	Σ(m+p)-xylenes/ Σ all xylene isomers	106	This study
2	ProB	M	propylbenzene/Σ (propylbenzene+isopropylbenzene)	120	This study
3	MEBI	M	Σ (1-methyl-3-ethyl-benzene+1-methyl-4-ethyl-benzene)/Σ all methyl-ethyl-benzenes	120	This study
4	TMBI-1	M	1,3,5-trimethylbenzene/Σ(1,3,5+1,2,3)-trimethylbenzenes	120	Alexander et al., 1996
5	TMBI-2	M	1,2,4-trimethylbezene/Σ(1,2,4+1,2,3)-trimethylbenzenes	120	Alexander et al., 1996
6	R/P	S	retene/phenanthrene	178, 219	This study
7	125/136-TMN	S	1,2,5-trimethylnaphthalene/1,3,6-trimethylnaphthalene	170	Alexander et al., 1988
8	1,7/x-DMP	S	1,7-dimethylphenanthrene/Σ (1,3+3,10+2,10+3,9+2,9)-dimethylphenanthrenes	206	Alexander et al., 1988
9	R/9-MP	S	retene/9-methylphenanthrene	192, 219	Alexander et al., 1988
10	1/9-MP	S	1-methylphenanthrene/9-methylphenanthrene	192	Alexander et al., 1988
11	MA/MP	S?	2-methylanthracene/9-methylphenanthrene	192	This study
12	DNR-1	M	Σ (2,7+2,6)-dimethylnaphthalene/1,5-dimethylnaphthalene	156	Radke et al., 1982
13	DNR-6	M	Σ (2,7+2,6)-dimethylnaphthalenes/Σ (1,4+2,3)-dimethylnaphthalenes	156	Alexander et al., 1985
14	TNR-1	M	2,3,6-trimethylnaphthalene/Σ (1,4,6+1,3,5)-trimethylnaphthalenes	170	Alexander et al., 1985
15	MPI	M	1.5 x Σ (2-MP + 3-MP)/Σ (0.69P+1-MP+9-MP)*	178, 192	Radke and Welte, 1983

- * When peal area of 1-MP is higher than that of 9-MP in Eromanga-sourced oils peak area of 1-MP is normalised to that of 9-MP.
- MP = methylphenanthrene, S = Specificity, M = Maturity, S = Source

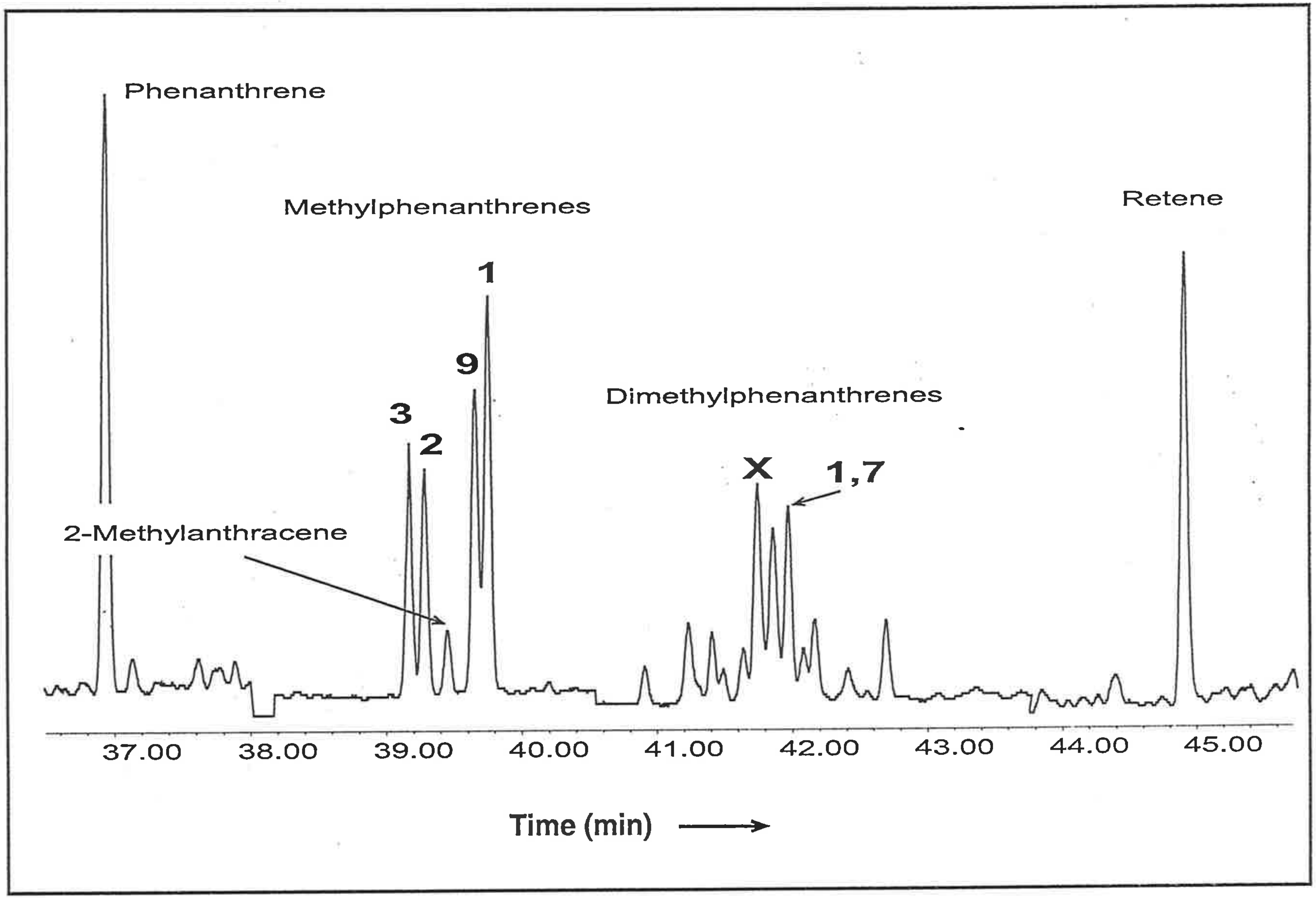


Figure 5.1 Partial *m/z* 178 + 192 + 206 + 219 mass chromatogram showing retention times of phenanthrene, methylphenanthrenes, dimethylphenanthrenes, 2-methylanthracene and retene (X = 1,3 + 3,1. + 2,10 + 3,9-dimethylphenanthrenes)

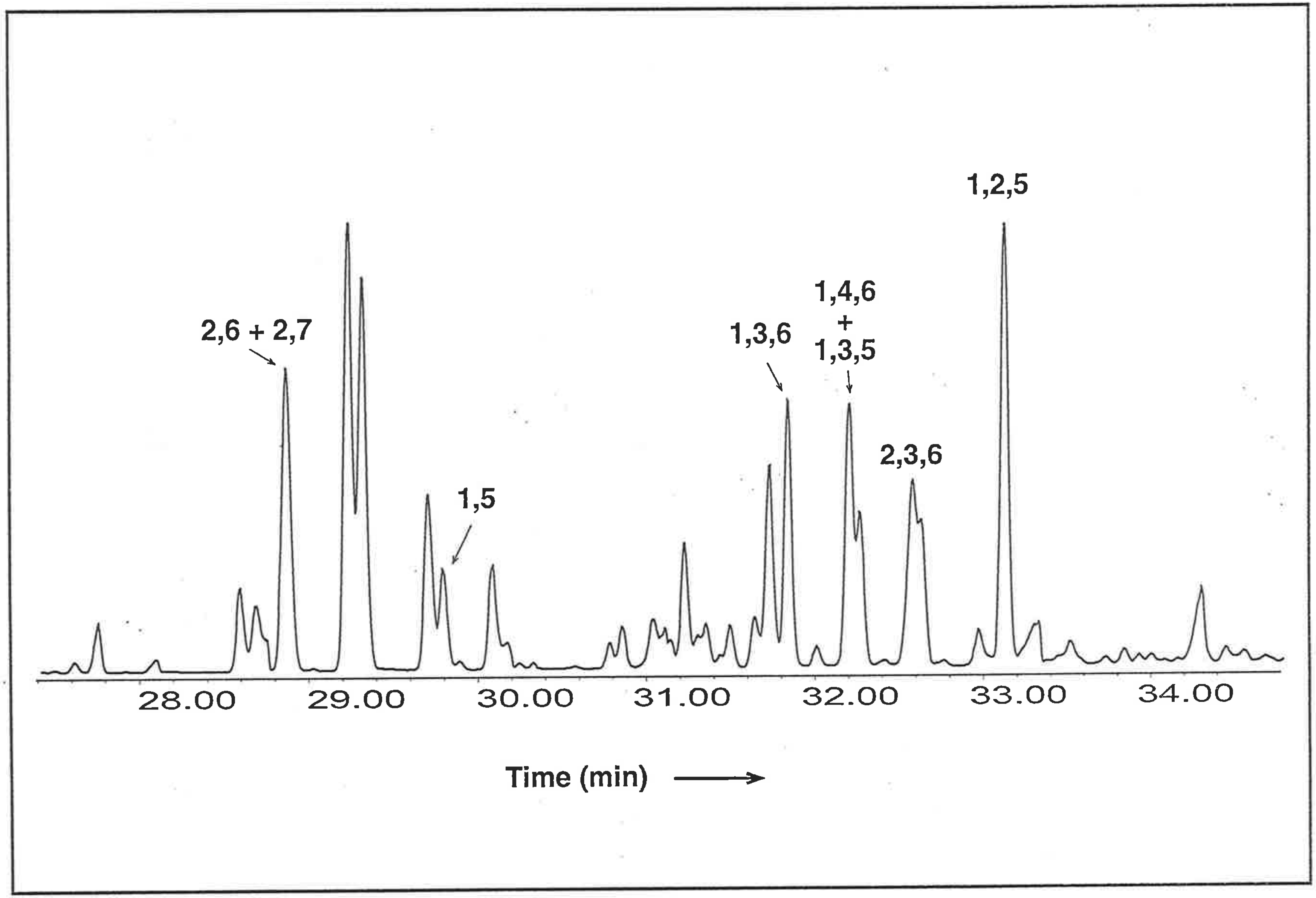


Figure 5.2 Partial *m/z* 156 + 170 mass chromatogram showing retention time of di- and tri-methylnaphthalenes

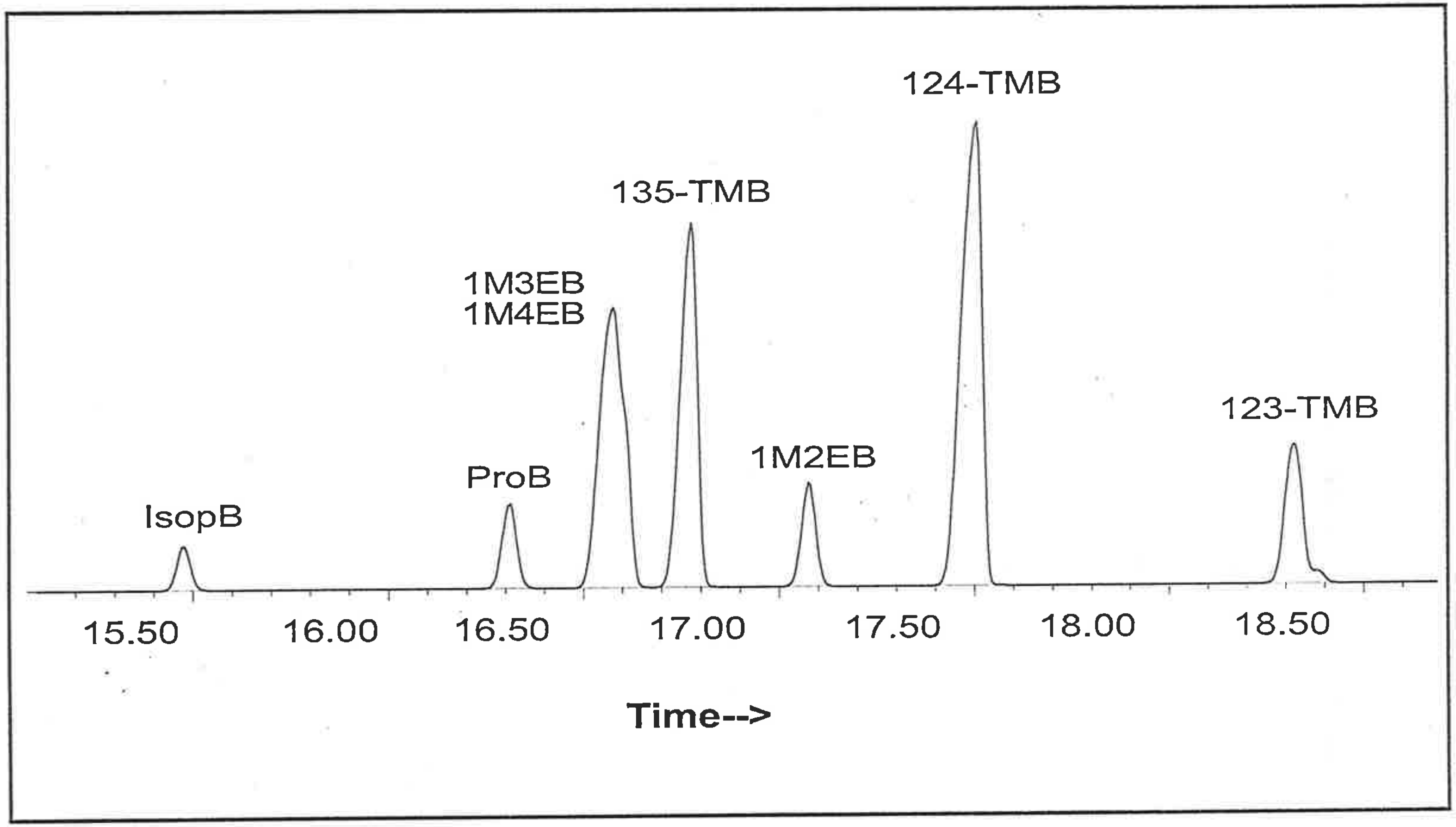


Figure 5.3 Partial m/z 120 mass chromatogram showing the retention times of C_3 substituted bezenes

Target peaks were integrated and various maturity and source parameters were calculated. The results are compiled in Table 5.1. Definitions of all the parameters discussed here are given in Table 5.2. Of the 15 aromatic parameters used, ten are from the literature (Radke et al., 1982; Radke and Welte, 1983; Alexander et al., 1985, 1988, 1996) and five are new. Among them, nine are maturity parameters (5 from the gasoline-range; 4 from the C_{12+} range) and six are source parameters (all from the C_{12+} range).

The following sections briefly introduce or review these parameters, and discuss their values in the Cooper/Eromanga oils and condensates.

5.2.2.1 Retene / Phenanthrene and Retene / 9-Methylphenanthrene

The ratio of retene to phenanthrene (R/P) is proposed here as a source parameter capable of distinguishing oils of Permian and Jurassic/Cretaceous origin in the Cooper and Eromanga Basins. Retene/9-methylphenanthrene (R/9-MP) is a similar parameter first employed by Alexander et al. (1988). Values of these two ratios are listed in Table 5.1, and their respective distributions between the reservoir horizons (with stratigraphic age increasing from left to right) are shown in Figures 5.4 & 5.5.

Retene (like 1-methylphenanthrene, 1,2,5-trimethylnaphthalene and 1,7-dimethylphenanthrene) is a well-known age-specific biomarker derived from natural products (resins) of the *Araucariaceae*, conifers of the Kauri pine group (native to the southern hemisphere, e. g. monkey-puzzle tree) that first appeared during the Early Jurassic (Alexander et al., 1988). High concentrations of these compounds (relative to those of other ubiquitous aromatic hydrocarbons of similar structure, such as phenanthrene) have been widely used to identify oils derived from Jurassic–Cretaceous source rocks in the Eromanga Basin (Alexander et al., 1988; Michaelsen and McKirdy, 1989, 1996; Boreham and Hill, 1998; Boreham and Summons, 1999). Several other ratios of this type (i.e. source-specific) are included in Table 5.2. However, considering the larger number of oils involved in this study, the conventional log-log plots designed by Alexander et al. (1988) have not been adopted. Instead the option of cross-plotting the various ratios against the reservoir strata was preferred (see Figures 5.4–5.7).

Except for five oils from the Sturt area (R/P = 0.6–0.9; R/9-MP = 0.7–1.7) and one from Wancoocha-2 (R/9-MP = 0.8), all of which are from the Patchawarra Formation, the other Cooper-reservoired crudes are characterised by very low values of these two ratios (= 0.1). The only oil from the Mooracoochie Volcanics (part of the Cambrian basement at Sturt-7) also displays an unexpectedly high retene level (R/P = 0.6; R/9-MP = 0.7). By way of contrast, the Eromanga-reservoired oils in general have high to very high relative concentrations of retene (R/P = 0.4–2.6; R/9-MP = 1.0–5.8). Notable exceptions are the oils in Middle–Late Jurassic reservoirs at Merrimelia (Hutton) and Big Lake (Birkhead) in South Australia and at Cook (Hutton), Jackson (Westbourne) and Wilson (Namur) in Queensland. These oils have retene concentrations intermediate between those of typical Cooper and Eromanga crudes. Interestingly though, these same reservoirs in other areas (Wancoocha-2 & 3, Thungo-1, Taloola-2 and Sturt-6) are the host for the oils with the highest R/P and R/9-MP ratios. On the other hand, the Murta oils display consistently high R/P and R/9-MP values.

The fact that some Eromanga-reservoired oils contain only very little retene suggests a Cooper source or mixed-sourcing (from both the Cooper and Eromanga Basins). The lower the R/P value is, the greater the contribution from the Cooper source rock(s). Where R/P values are >2.5, the Eromanga petroleum kitchens make the main, or probably exclusive, contributions to the local reservoirs; where the R/P values are <0.25, the predominant inputs to the Eromanga hydrocarbon accumulations come from the Cooper Basin. Quantitative interpretation of the mixed charge will be discussed later in this chapter, using a novel mixing model developed as part of this project (Yu et al., 2000a,b).

What is more interesting is the fact that some oils reservoired in the Patchawarra Formation (Cooper Basin) and Mooracoochie Volcanics (Warburton Basin) at the Sturt–Sturt East Fields have relatively large R/P and R/9-MP values. It is very likely that these hydrocarbons come from mature Eromanga source rocks (specifically the upper Poolowanna Formation: Kagya et al., 1996; Kagya, 1997) buried deeply in the

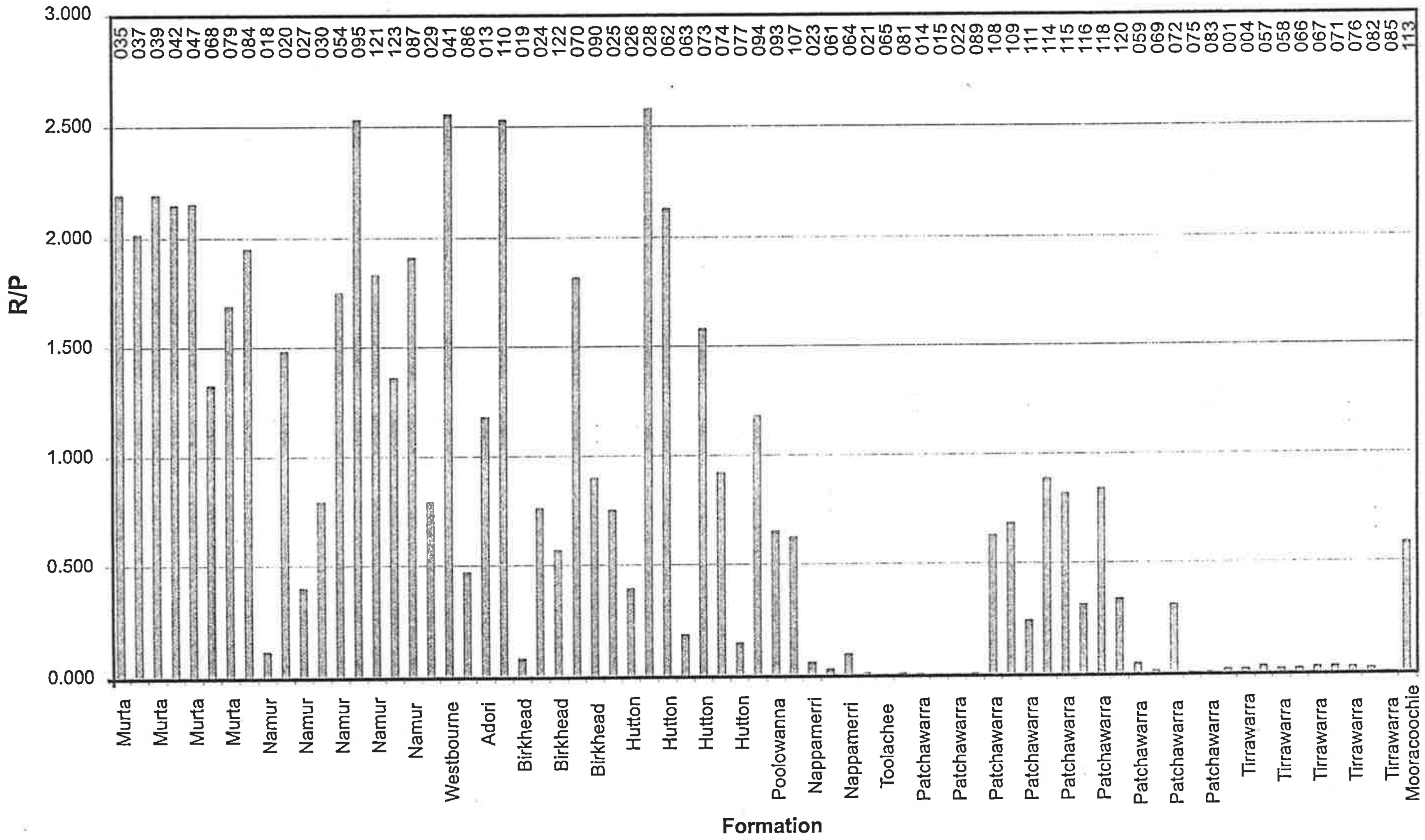


Figure 5.4 Variation of R/P with reservoir formation. Sample numbers (XYOILxxx) are shown along the top.

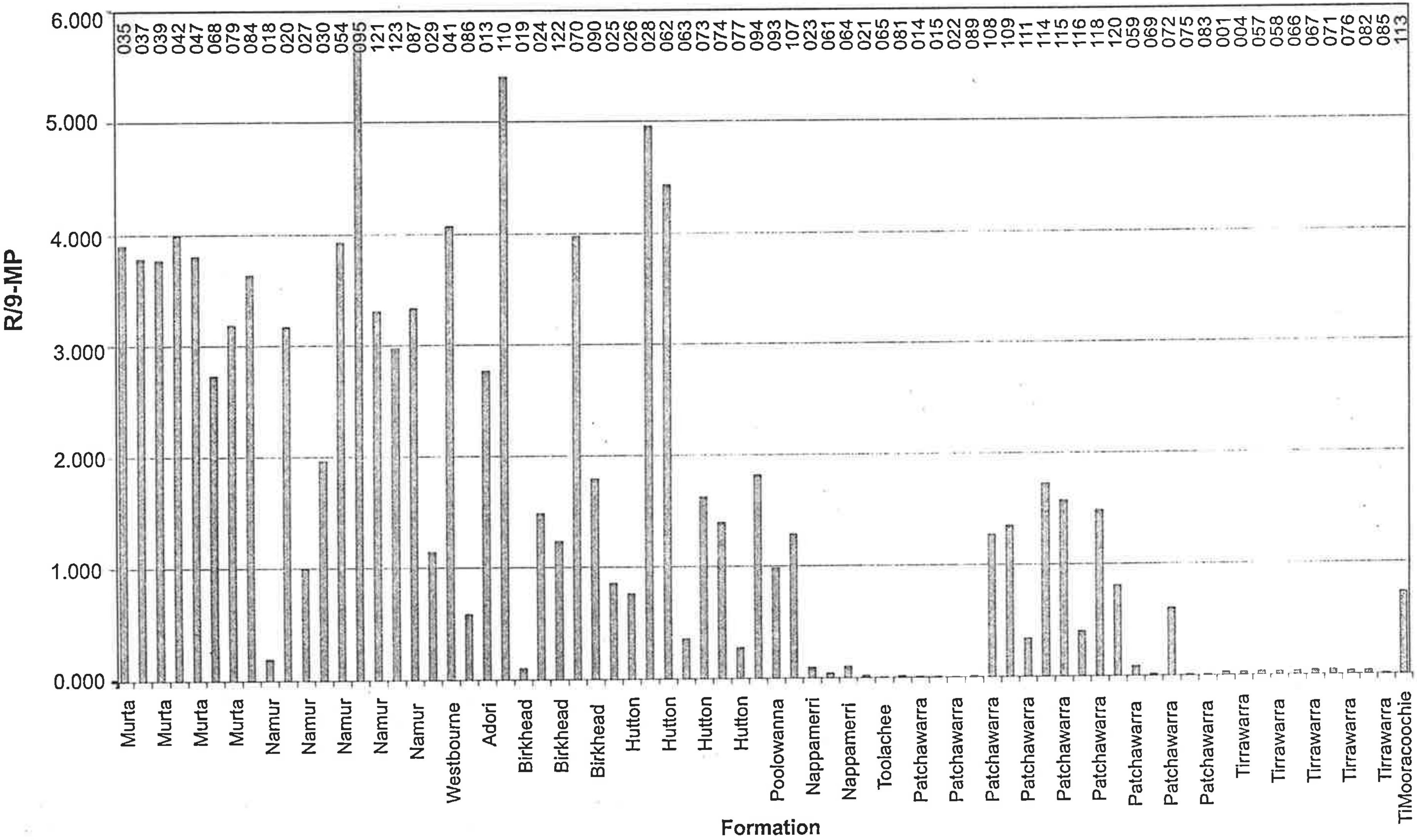


Figure 5.5 Variation of R/9-MP with reservoir formation. Sample numbers (XYOILxxx) are shown along the top.

Table 5.3 Descriptive statistics of the aromatic maturity and source parameters

	MPI	XYLI	ProB	MEBI	TMBI-1	TMBI-2	R/P	125/136-TMN	1,7/x-DMP	R/9-MP	1/9-MP	2-MA/9-MP	DNR-1	DNR-6	TNR-1
Mean	0.82	0.79	0.30	0.80	0.67	0.76	0.79	1.32	0.75	1.48	1.18	0.08	6.43	2.86	0.75
Std Error	0.03	0.00	0.00	0.00	0.01	0.01	0.10	0.07	0.06	0.19	0.07	0.01	0.48	0.13	0.05
Median	0.76	0.79	0.30	0.81	0.68	0.76	0.58	1.18	0.62	0.92	0.97	0.04	5.73	2.75	0.61
Mode	#N/A	#N/A	#N/A	0.76	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Std Deviation	0.29	0.04	0.04	0.03	0.09	0.05	0.83	0.62	0.48	1.63	0.61	0.09	4.05	1.09	0.44
Variance	0.09	0.00	0.00	0.00	0.01	0.00	0.70	0.39	0.23	2.65	0.37	0.01	16.42	1.18	0.20
Kurtosis	-0.33	0.16	-1.07	-1.06	-0.57	-1.01	-0.72	0.23	-0.05	-0.37	0.60	5.35	1.63	0.20	1.69
Skewness	0.60	0.66	-0.02	-0.36	-0.39	-0.34	0.80	0.65	0.90	0.92	1.22	2.21	1.42	0.73	1.53
Range	1.22	0.19	0.16	0.13	0.37	0.20	2.57	2.65	1.90	5.78	2.27	0.48	17.32	4.94	1.78
Minimum	0.39	0.73	0.23	0.73	0.46	0.64	0.00	0.35	0.21	0.00	0.60	0.00	0.95	0.47	0.22
Maximum	1.60	0.92	0.38	0.86	0.83	0.85	2.58	3.00	2.11	5.79	2.86	0.48	18.27	5.41	2.00
Sum	59.02	57.21	21.63	57.95	48.17	54.36	56.81	94.87	54.24	106.90	84.73	5.43	463.06	205.63	54.30
Count	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72

Patchawarra Trough further to the northeast. This is consistent with the geological structure of this area, where the Permian sequence is truncated and both it and the Cambrian sequence are unconformably overlain by the Poolowanna Formation, facilitating the west–southwest lateral migration of the Poolowanna-derived hydrocarbons into the underlying Patchawarra Formation and Mooracoochie Volcanics. This migration scenario is depicted in Figure 4.8.

This interpretation is also consistent with the discussion in Chapter 4 on the pronounced water-washing effects noted in the distributions of light aromatic hydrocarbons in the oils from the Patchawarra Formation and Mooracoochie Volcanics in the Sturt area. Water from the Great Artesian Basin aquifers carries the hydrocarbons generated from the Eromanga source rocks to the Patchawarra and Mooracoochie reservoirs, and leaches them, simultaneously, giving rise to petroleums deficient in light aromatic hydrocarbons and rich in araucariacean biomarkers.

5.2.2.2 Other Araucariacean Resin Signatures

The other parameters involving araucariaceaen aromatic biomarkers (viz. 1/9-MP, 1,7/x-DMP, and 125/136-TMN) show similar distribution patterns in which there is a less obvious contrast between Permian/Triassic and Jurassic/Cretaceous reservoir strata (Table 5.1 and Figure 5.6). The average values for the Eromanga oils are at least twice that of the Cooper accumulations. However, there are large variations (up to a factor of three) among the Eromanga petroleums, and high values are again observed in the Patchawarra/Mooracoochie crudes of the Sturt area. The same geological interpretation mentioned above (Section 5.2.2.1) applies here. Definitions of these parameters and a brief summary of their data distribution are presented below.

1,7/x-DMP

The ratio 1,7/x-DMP, represents the concentration of 1,7-dimethylphenanthrene relative to the sum of the chromatographically unresolvable 1,3 + 3,10 + 2,10 + 3,9-dimethylphenanthrenes. A value smaller than 0.8 was suggested to indicate a pre-

Jurassic source affinity (Alexander et al., 1988). Here, based on the data distribution and the aforementioned geological interpretation, the value of 0.5 is applied.

Descriptive statistics shows that the 1,7/x-MP in the analysed samples ranges from 0.21 to 2.11, with a mean of 0.75 and a median of 0.62. All but two Eromanga-reservoired oils and condensates have 1,7/x-DMP values >0.5, whereas all the Cooper crudes, excepting the six Patchawarra-reservoired accumulations mentioned earlier, have values <0.5 (Figure 5.3). The two exceptions of Eromanga-reservoired oils with evidently pronounced contributions from the Cooper Basin (1,7/x-DMP < 0.5) occur in the Hutton and Westbourne reservoirs at Wilson-6 and Jackson-3, respectively.

1/9-MP

The ratio of 1-methylphenanthrene to 9-methylphenanthrene (1/9-MP) also indicates the relative abundance of the araucariaceaen input (Alexander et al., 1988). For most of the Eromanga-reservoired oils, the 1/9-MP values are >1.0 (notice that this is also the value Alexander and co-workers suggested for distinguishing the Cooper and Eromanga hydrocarbons), implying predominant contributions from the Eromanga Basin source rocks. The three smallest values (<1.0) among the Eromanga crudes are 0.75 (Garanjanie-1, Namur), 0.81 (Moolion-1, Hutton) and 0.95 (Jackson-3, Westbourne) suggesting significant Permian charges to each of these reservoirs.

Among the Cooper-hosted hydrocarbons, all but four Patchawarra crude oils share 1/9-MP values below the 1.0 level. The 1/9-MP values of the exceptional Patchawarra crudes are even greater than that of the Poolowanna petroleum at Sturt-4, and nearly equivalent to those of the Hutton accumulations.

125/136-TMN

The last araucariaceae-specific source parameter introduced by Alexander et al. (1988) and used here is the ratio of 1,2,5-trimethylmaphthalene over 1,3,6-trimethylnaphthalene (125/136-TMN). In this data set the average 125/136-TMN ratio for the Eromanga oils is equivalent to the cut-off value (= 1.45) used by

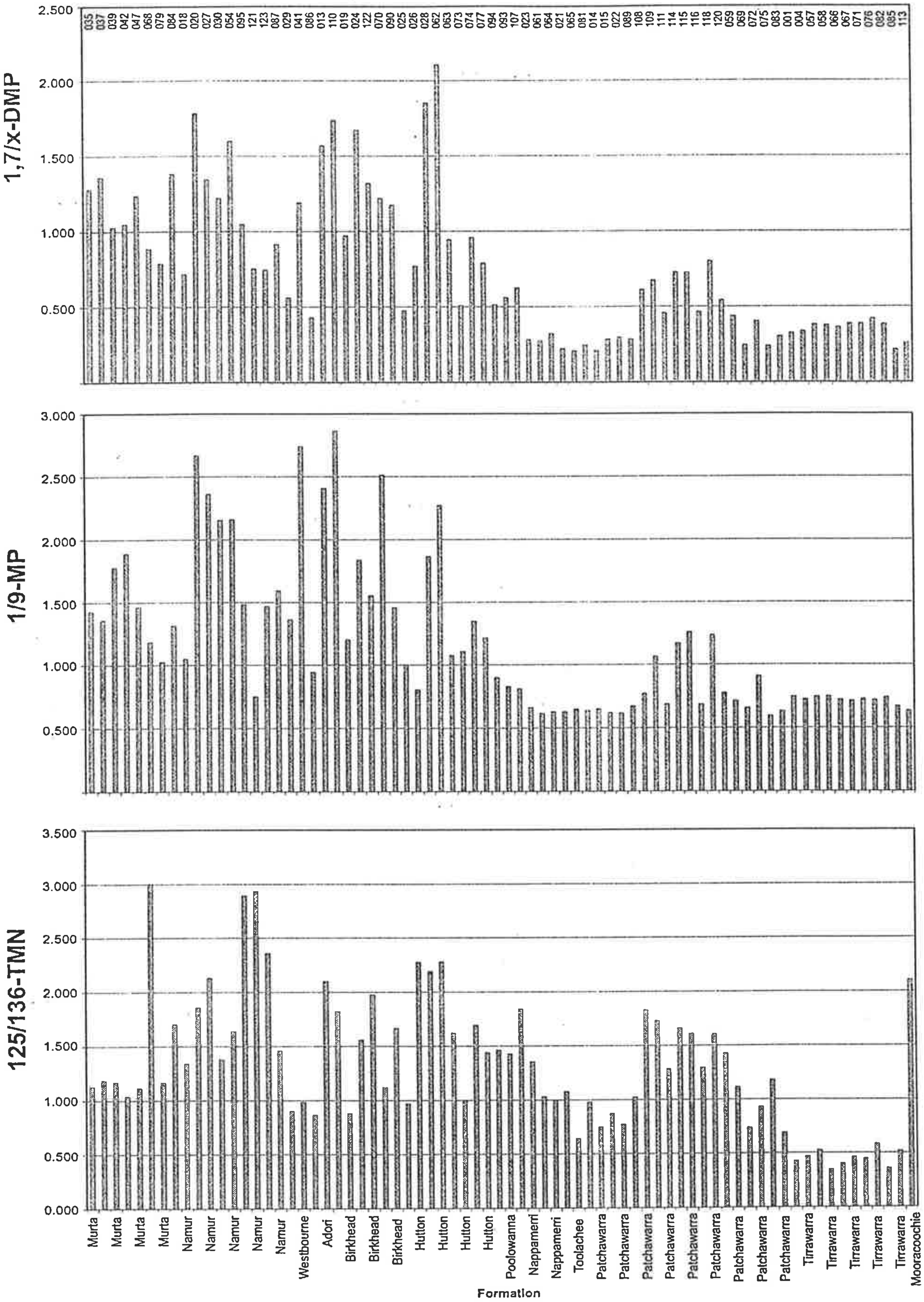


Figure 5.6 Variation of 1,7/x-DMP, 1/9-MP and 125/136-TMN with reservoir formation. Sample numbers (XYOILxxx) are shown along the top.

Alexander and his co-workers to separate their Cooper and Eromanga crudes. The average for the Cooper crudes is around 0.7. Among the highest 125/136-TMN values obtained from the Eromanga oils is that of the Namur crude at Garanjanie-1 (2.93). This conflicts with its low 1/9-MP value (see above). The smallest 125/136-TMN values are in the Birkhead oil from Big Lake-37 (0.88) and the two Westbourne oils from Jackson-3 & 28 (0.87 and 0.90) confirming their suspected Permian origin.

Among the Cooper-hosted oils and condensates, uniformly low 125/136-TMN values are encountered in the Tirrawarra Formation (0.35–0.47). Yet again, the hydrocarbons accumulated in the Patchawarra Formation and Mooracoochie Volcanics at Sturt and Sturt East have appreciably higher values (>1.45).

5.2.2.3 2-Methylanthracene / 9-Methylphenanthrene

The triaromatic hydrocarbon 2-methylanthracene is another compound that exhibits an unusual distribution within the Cooper/Eromanga oils and condensates. Its peak area in the m/z 178 + 192 + 206 + 234 chromatogram (Figure 5.1) of each oil and condensate was integrated, along with those of phenanthrene and the four isomeric methylphenanthrenes, and the ratio of 2-methylanthracene over 9-methylphenanthrene (MA/MP) was calculated. These MA/MP values are listed in Table 5.1 and their distribution with respect to reservoir strata is shown in Figure 5.7. Though its geochemical significance is not yet clear, this parameter does highlight the previously noted peculiarity of the hydrocarbons in the Patchawarra Formation and Mooracoochie Volcanics in the Sturt-Taloola area. This may indicate another, additional source input to the Cooper petroleum system in this particular area.

Descriptive statistics show that the MA/MP ratio ranges from zero to 0.48, about a mean of 0.08 (Table 5.3). As shown in Figure 5.7, some eleven oils and condensates possess extremely large (compared to the mean) MA/MP ratios. All but three of the ten largest MA/MP values were encountered in oils from the Poolowanna Formation, Patchawarra Formation and Mooracoochie Volcanics in fields located at or near the zero edge of the Cooper Basin, viz. Sturt, Sturt East and Taloola in the Patchawarra

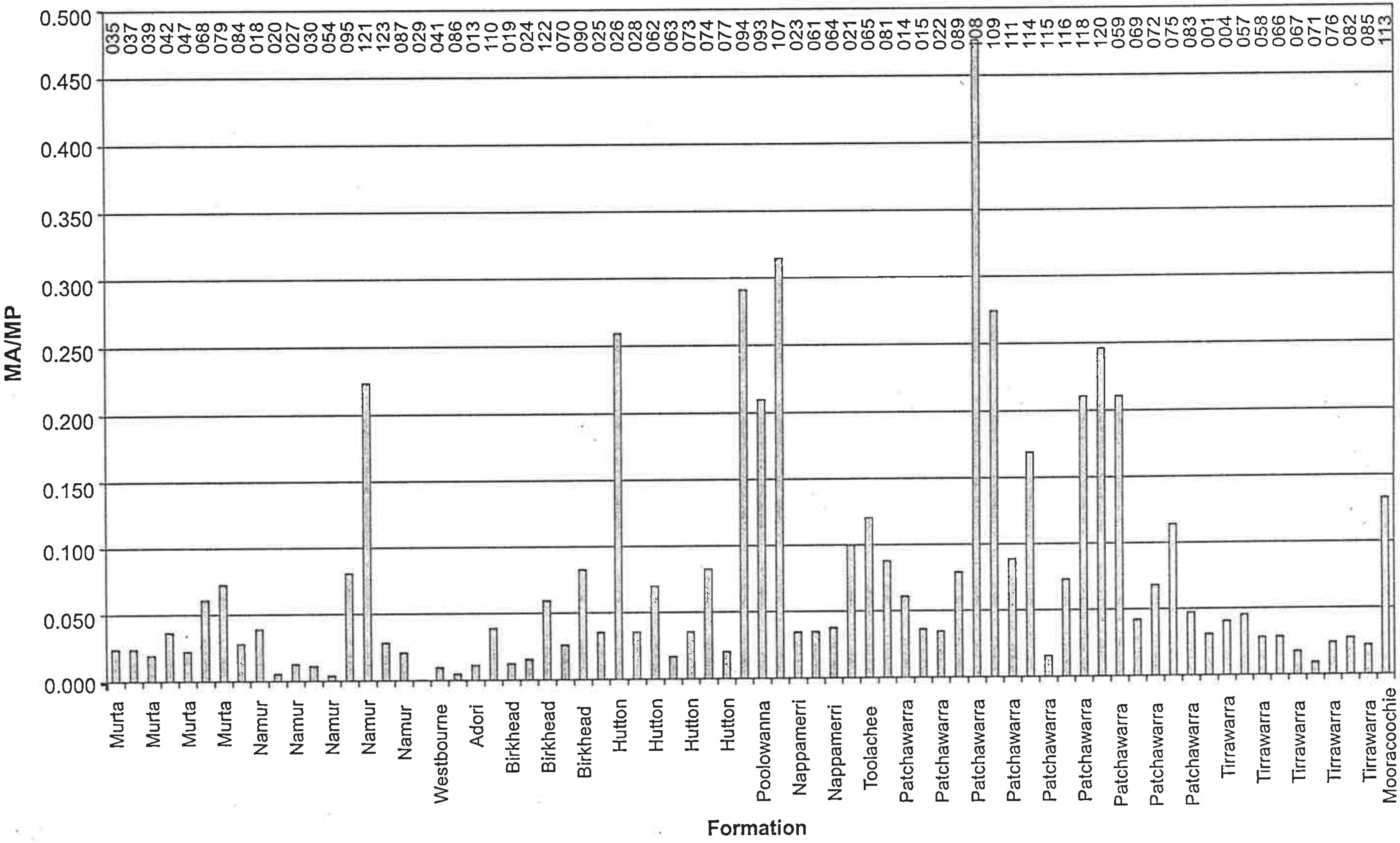


Figure 5.7 Variation of MA/MP with reservoir formation. Sample numbers (XYOILxxx) are shown along the top.

Trough, and Wancoocha in the Nappamerri Trough (Figure 3.1). Other crudes with high MA/MP values (>0.2) are those from Gooranie (Patchawarra) and Moolion (Hutton) in the central Patchawarra Trough, and Garanjanie (Namur) located ca 8 km east of Wancoocha in the Nappamerri Trough (see Chapter 6).

It seems that in addition to the typical Cooper source and the Eromanga source that contains araucariacean biomarkers, there exists a third source type in which the concentration of 2-methylanthracene is high. The latter could be a source rock facies within the lower Poolowanna Formation. Hydrocarbons produced from this hypothetical Poolowanna source could have been expelled into local intra-formational sandstones (e. g. XYOIL093, 094 & 107), or migrated laterally into the adjacent Patchawarra sandstone and Mooracoochie Vocanics (e. g. XYOIL059, 108, 109, 114, 118 & 120). In favourable geological settings (such as the presence of faults or thin seals) part of this hydrocarbon charge could have migrated upwards along the "highway" into the Eromanga Basin and accumulated there (XYOIL026 in Hutton Formation and XYOIL121 in Namur Sandstone).

Migration "highway" means a hydrocarbon migration pathway through which deeper-derived petroleum migrates vertically into younger strata and is reservoired there without encountering the locally generated hydrocarbons. This concept will be explained in more detail in Chapters 6 & 7. Oil/condensate samples XYOIL026 & 121 appear to belong to this category. Samples XYOIL018, 019, 063 & 077 may also be of this type. They accumulated in Eromanga traps, but contain low levels of araucariacean biomarkers and have low to high MPI maturity values.

However, it must be pointed out that this interpretation is somewhat speculative and needs further work to confirm it. Investigation of 2-methylanthracene abundance in the putative Poolowanna source rock could provide the most direct evidence.

5.2.2.4 Methylphenanthrene Index

Introduced by Radke and Welte (1983), the methylphenanthrene index (MPI) is one of the most widely used maturity parameters. It certainly has been an important part of many geochemical studies of the Cooper and Eromanga Basins (Alexander et al., 1988; Boreham et al., 1988; Jenkins, 1989; Michaelsen and McKirdy, 1989; Powell et al., 1989; Tupper and Burckhardt, 1990; Michaelsen and McKirdy, 1996). The original formula (1) is most suitable for data obtained from GC measurements on aromatic hydrocarbon fractions of EOM from Type III source rocks and their associated crude oils (Radke and Welte, 1983). Two modifications are necessary to make it suitable for GC-MS data on the Cooper and Eromanga oils and condensates. Firstly, the phenanthrene ion abundance was multiplied by a factor of 0.69 to adjust the MPI in formula 1 to an equivalent FID response (Formula 2). Secondly, the response of 1-MP was normalised to that of 9-MP when 1-MP is more abundant than 9-MP (as is very common in Eromanga samples).

$$MPI = \frac{1.5(2MP + 3MP)}{P + 1MP + 9MP} ------ (1)$$

$$MPI = \frac{1.5(2MP + 3MP)}{0.69P + 1MP + 9MP} --- (2)$$

When the maturity of Type III kerogen changes within the oil generation window (vitrinite reflectance, $R_o = 0.65–1.35\%$), there exists a linear relationship between R_o and MPI (i. e. $R_c = 0.6$ MPI + 0.4). Here R_o is the measured vitrinite reflectance and R_c refers to the calculated vitrinite reflectance based on the MPI. Using Australian coals and sediments of various types and ages Boreham et al. (1988) produced an alternative calibration (R_c = 0.7MPI + 0.22). However, Alexander et al. (1988) pointed out that the original Radke and Welte calibration is more suitable for the Cooper and Eromanga Basins. Although the term R_c is perhaps more familiar to petroleum geologists, the MPI data are used directly here to facilitate comparison of the maturities of gasoline-range and C_{12+} hydrocarbons. Both are expressed as ratios of aromatic compounds, viz. XYLI, ProB, MEBI, TMBI-1 and TMBI-2 for the light ends, and MPI, DNR-1, DNR-6 and TNR-1 for the heavy ends (see Table 5.2 for definitions).

The MPI data on the oils/condensates analysed in this study are listed in Table 5.1, and plotted against reservoir formation in Figure 5.8. Just as expected, the average MPI maturity of the crude oils reservoired in the Cooper Basin is higher than that of those from the Eromanga Basin. However, there are exceptions to this general rule in both the basins.

Descriptive statistics show that the mean MPI value of the 72 studied crude oils is 0.82. The minimum value is 0.39, which belongs to a Birkhead oil from Sturt-6 (XYOIL110). The most mature petroleum, with an MPI of 1.60, occurs in the Tirrawarra Formation at Tirrawarra-58 (XYOIL057). The average MPI maturity of the Cooper hydrocarbons (excepting the six Patchawarra oils from the Sturt area) is about 1.0, whereas the majority of the Eromanga crudes (excluding those interpreted as containing a large contribution from Permian source rocks) have an MPI of about 0.5. These MPI maturity data are generally consistent with previous reports (e. g. Tupper and Burckhardt, 1990).

Within the Cooper Basin, a quarter of the analysed crude oils have MPI values = 1.20, but the maturity of the exceptional Patchawarra hydrocarbons in the Sturt area (viz. XYOIL108, 109, 114, 115 & 118) are within the range for the Eromanga crudes, and are particularly similar to those of the Poolowanna oils. The “anomalously” low maturity of the Patchawarra petroleum in the Sturt area supports the aforementioned conclusion – deduced from its content of araucariacean biomarkers and 2-methylanthracene (see Sections 5.2.2.1–3) – that much of it is derived from the Poolowanna Formation.

The majority of the Eromanga-reservoired oils are of low maturity (MPI ~ 0.60), but a quarter of them have exceptionally high MPI values (0.86–1.06). These high-maturity Eromanga crude oils (viz. XYOIL018, 019, 025, 029, 073, 074 & 086) are even more mature than some pooled in the Nappamerri and Toolachee Formations of the Cooper Basin. They occur in the Wilson, Wilson South, Jackson and Big Lake Fields, all of which are located above or adjacent to major fault systems (Figure 2.2). Such faults facilitate the vertical migration of Cooper-derived hydrocarbons into Eromanga traps (Heath et al., 1989; Alexander et al., 1996; Boreham and Hill, 1998; Boreham and Summons, 1999).

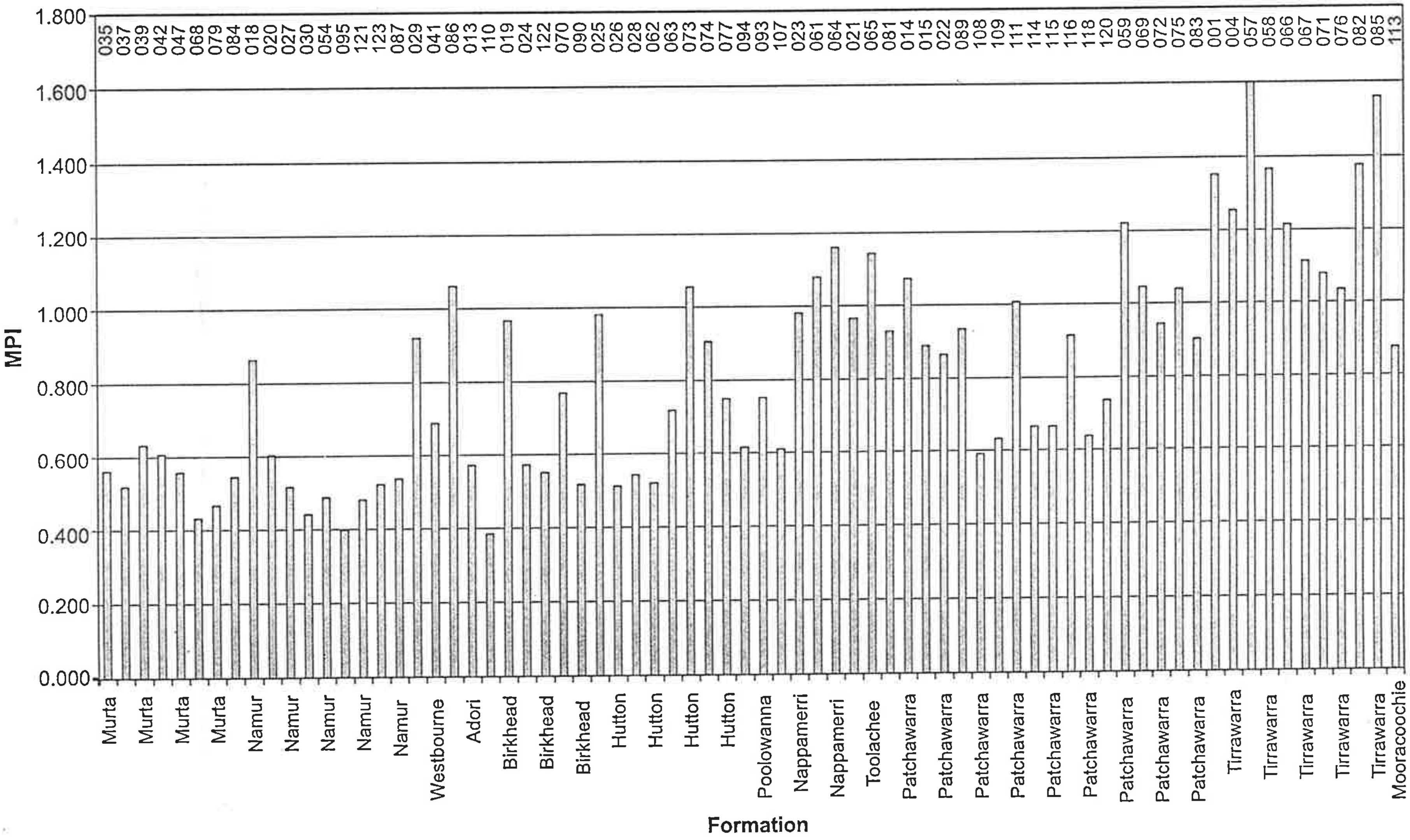


Figure 5.8 Variation of MPI with reservoir formation. Sample numbers (XYOILxxx) are shown along the top.

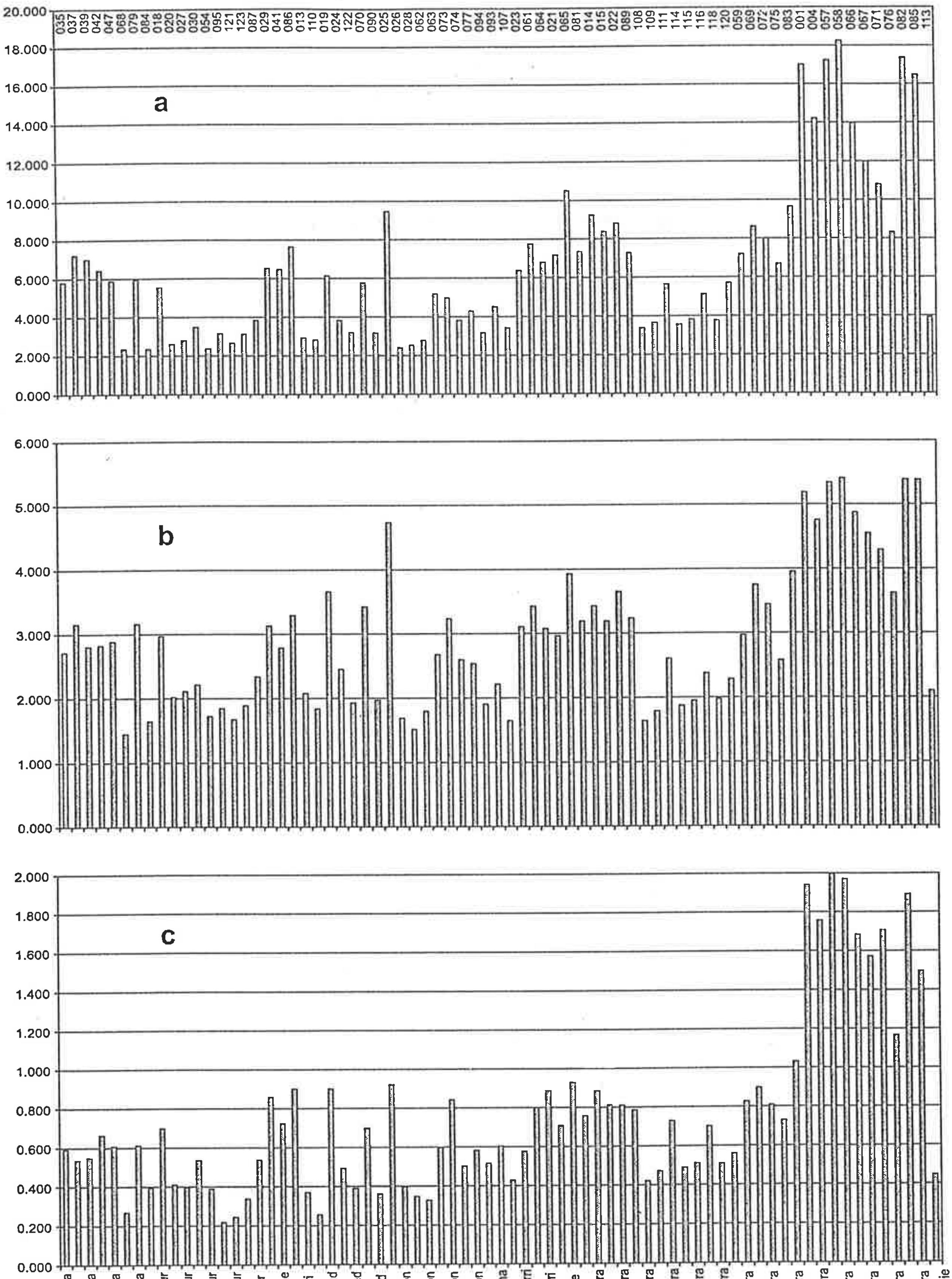


Figure 5.9 Variations of a) DNR-1, b) DNR-6 and c) TNR-1 with reservoir formation. Sample numbers (XYOILxxx) are shown along the top.

5.2.2.5 Other Heavy-end Aromatic Maturity Parameters

The ratios DNR-1 (Radke et al., 1982), DNR-6 (Alexander et al., 1985) and TNR-1 (Alexander et al., 1985) are commonly used aromatic maturity parameters based on the isomer distributions of dimethylnaphthalenes (DMNs) and trimethylnaphthalenes (TMNs: Figure 5.2). Their definitions are given in Table 5.2. The values of these ratios for the 72 oils and condensates are listed in Table 5.1 and plotted in Figure 5.9. Statistical summaries of the data are given in Table 5.3. Correlations between DNR-1, DNR-6, TNR-1 and MPI are displayed in Table 5.4.

Inspection of Figures 5.8 & 5.9 reveals a close similarity between the distribution patterns of the four aromatic maturity parameters (DNR-1, DNR-6, TNR-1 and MPI) with respect to reservoir formation. This is confirmed by their high correlation coefficients ($R^2 = 0.81–0.96$: Table 5.4). Each shows a higher average for the older Cooper crudes than for the younger Eromanga oils. The hydrocarbons accumulated in the Patchawarra Formation at Sturt and Sturt East again stand out as "anomalous" relative to the other Cooper Basin petroleums. Within the Eromanga Basin, all the crudes with greater MPI values (except XYOIL074) have similarly enhanced DNR-1, DNR-6 and/or TNR-1 values. In addition, there are four other Eromanga crudes with elevated maturities based on either DNR-1 (XYOIL039 & 042, both Murta oils from Thungo-1 & 4) or DNR-6 (XYOIL070 & 079, Birkhead and Murta oils from Jackson South-4 and Alwyn-1, respectively).

5.2.2.6 Light-end Aromatic Maturity Parameters

Inspired by the light- *versus* heavy-end maturity approach of Alexander et al. (1996), an attempt was made here to find some new maturity parameters based on aromatic hydrocarbons within the gasoline range. The aim of this part of the research was to better document the maturity of the C_5–C_{10} components in a crude oil, in the hope of recognising any maturity contrast between its light- and heavy-end hydrocarbons. Where such a contrast exists, there is the potential to exploit it as a quantitative measure of the proportions in which the multiple oil charges mixed in the reservoirs.

In addition to the two trimethylbenzene parameters proposed by Alexander et al.

(1996), three other ratios incorporating isomeric alkylbenzenes have been evaluated (Tables 5.1 & 5.2). The variation of all five ratios with reservoir formation in the 72 oils and condensates was inspected. However, as discussed later, only three of them (MEBI, TMBI-1 & TMBI-2) proved to be effective as maturity parameters. Cross-plotting the light-end maturities against those of the heavy-end components revealed some information about the mixing of Cooper and Eromanga petroleums. A generalised model was deduced from statistical analysis of the data set and a simplified two-end-member transformation is applied here to assess the mixing ratios. The five light-end aromatic maturity parameters and their variation with reservoir strata are introduced below, followed by a detailed explanation of the "mixing model" and its application.

MEBI

The methylethylbenzene index (MEBI = Σ(1-methyl-3-ethylbenzene + 1-methyl-4-ethylbenzene) / Σ(1-methyl-3-ethylbenzene + 1-methyl-4-ethylbenzene + 1-methyl-2-ethylbenzene) is a new maturity parameter. It is based on the fact that 1-methyl-3-ethylbenzene and 1-methyl-4-ethylbenzene are thermodynamically more stable than 1-methyl-2-ethylbenzene, and the reality of the co-elution of 1-methyl-3-ethylbenzene and 1-methyl-4-ethylbenzene in GC-MS analysis (Figure 5.3). As such, the MEBI value should increase with increasing thermal maturity of petroleum. The variation of MEBI with reservoir formation is displayed in Figure 5.10, from which the following observations can be deduced:

1. The MEBI values of the 72 analysed oils and condensates range from 0.73 to 0.86 (mean = 0.8). On average, the Cooper-reservoired hydrocarbons have larger MEBI values than that from the Eromanga Basin, consistent with the fact that the Cooper hydrocarbon kitchens are deeper and hence more mature. It should be noted, however, that the "exceptional" Patchawarra and Mooracoochie oils (XYOIL108, 109, 113, 114, 115, 116 & 118) in the Sturt area, which have larger R/P, R/9-MP and MA/MP ratios (see Sections 4.2.2.1, 2.2 and 2.5) and smaller MPI values (see Section 4.2.2.6), also retain low MEBI values (<0.76); consistent with a less mature Poolowanna source.

2. Extremely low MEBI values (< 0.74) of some Eromanga crudes (e.g. XYOIL095 and 121) are consistent with their extremely high R/P ratios, implying predominant or "pure" Eromanga sourcing. The majority of the Eromanga petroleums, with MEBI values larger than 0.74 are interpreted to be either of mixed source (from both the Cooper and Eromanga Basins), or mainly of Cooper origin(s). The larger the MEBI value, the greater the Permian source input.

3. Some Eromanga-reservoired hydrocarbons (XYOIL018, 019, 025, 029, 041, 063, 077 & 086) have MEBI values (0.81–0.86) similar to those of the Permian ones, indicating that their dominant light-end hydrocarbons come mainly from the Cooper sources. This is also consistent with their lower R/P and higher MPI values, as explained above.

TMBI-1 and TMBI-2

The trimethylbenzene index (TMBI-1 = 1,3,5-trimethylbenzene / Σ(1,3,5-trimethylbenzene + 1,2,3-trimethylbenzene) is one of several gasoline-range maturity parameters created by Alexander et al. (1996) but, in this instance, labelled by them TB-2. Its variation with reservoir strata is displayed in Figure 5.11a. It is evident that this stratigraphic distribution pattern is very similar to that of MEBI for both Cooper and Eromanga reservoirs. On average, hydrocarbons from the Cooper Basin have larger TMBI-1 values than do those from the Eromanga Basin. Exceptions, again, occur where the lowest values among the crude oils in pre-Jurassic-reservoirs occur in the Patchawarra Formation and Mooracoochie Volcanics of the Sturt area, supporting a non-Cooper source for both their light- and heavy-end hydrocarbons.

Another trimethylbenzene index (TMBI-2 = 1,2,4-trimethylbenzene / Σ(1,2,4-trimethylbenzene + 1,2,3-trimethylbemzene; equivalent to parameter TB-1 of Alexander et al., 1996) was measured in the same suite of oils. Its stratigraphic variation (Figure 5.11b) is nearly identical to those of MEBI and TMBI-1.

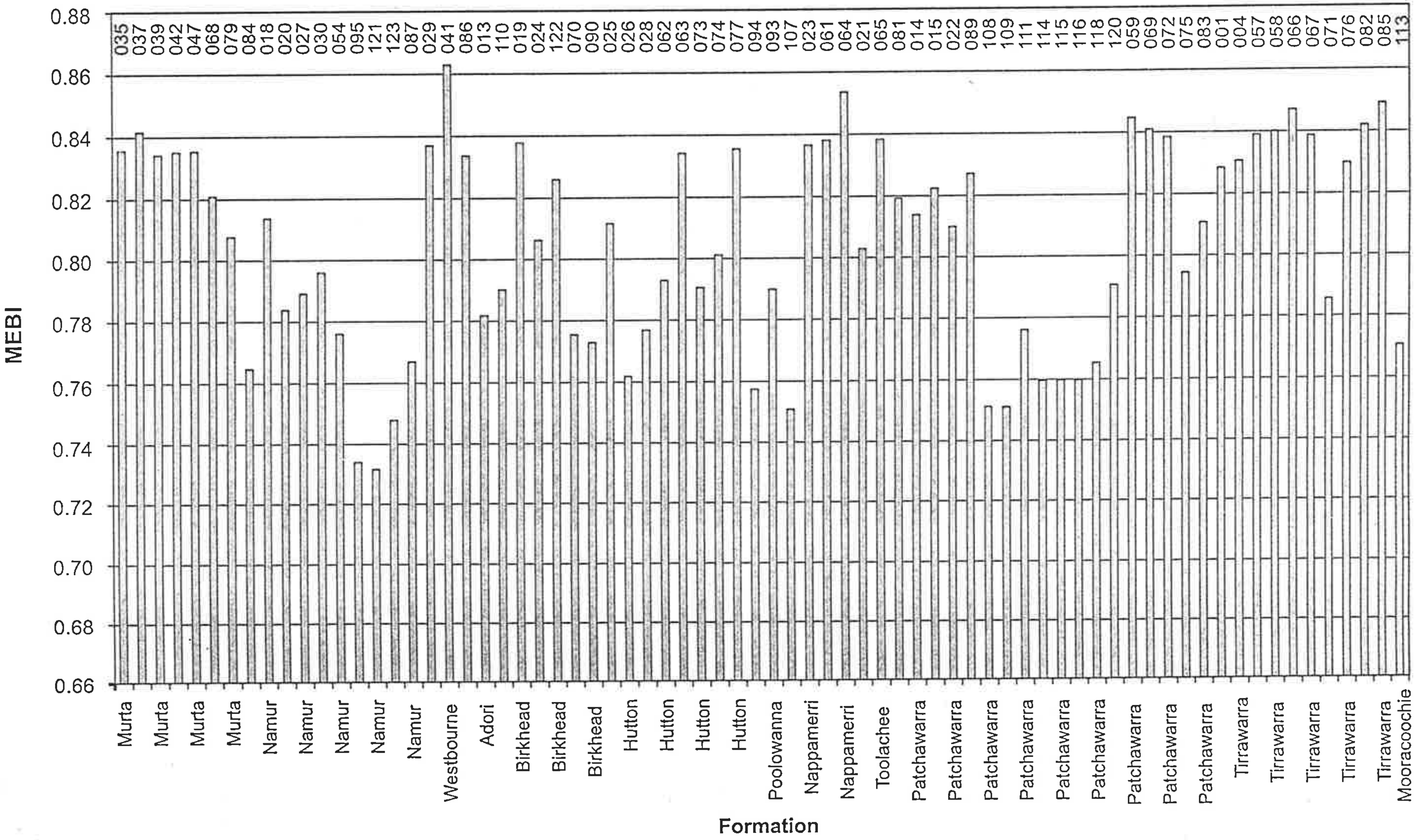


Figure 5.10 Variation of MEBI with reservoir formation. Sample numbers (XYOILxxx) are shown along the top.

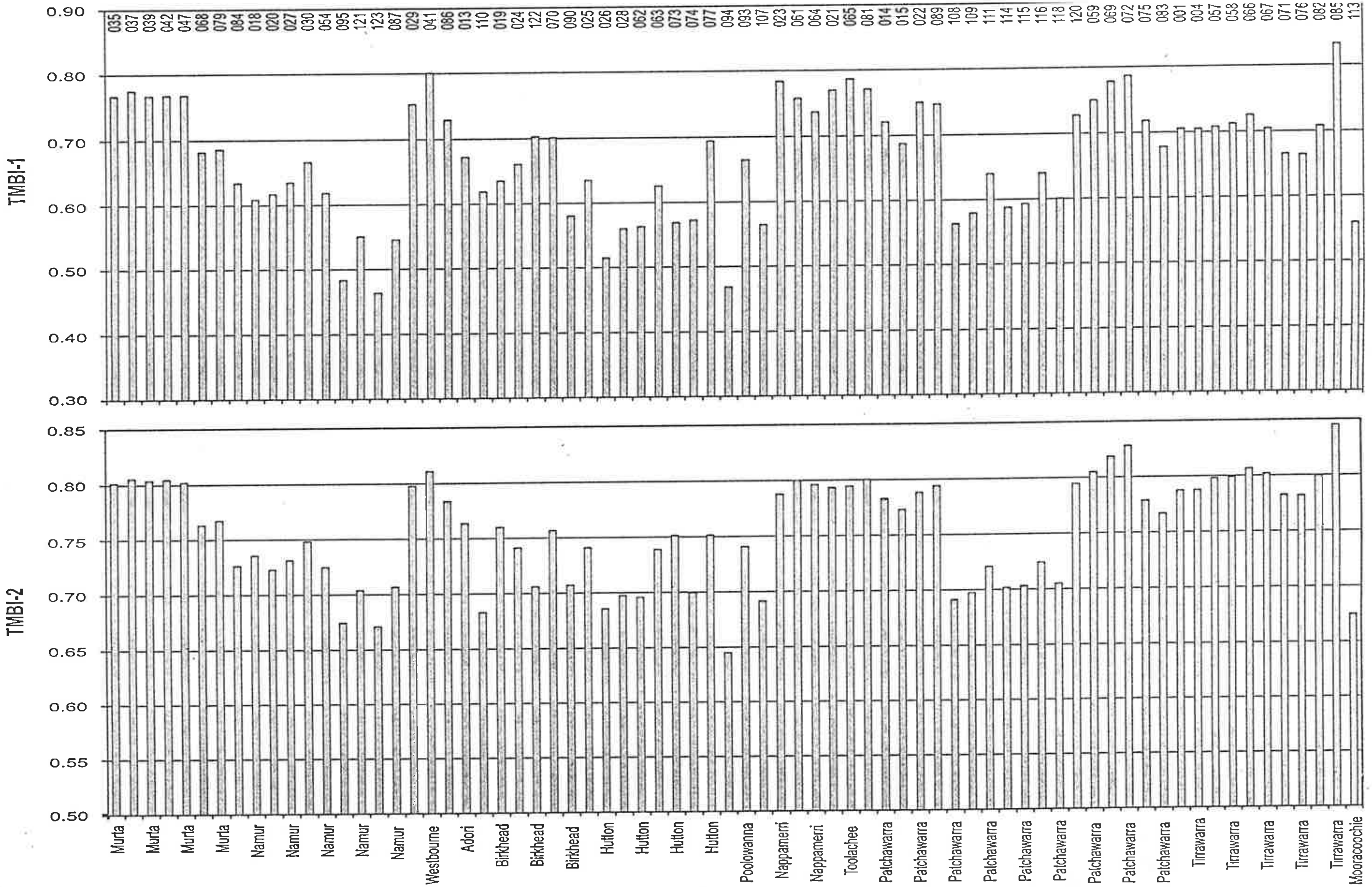


Figure 5.11 Variation of TMBI with reservoir formation. Sample numbers (XYOILxxx) are shown along the top.

XYLI and ProB

Two other ratios considered likely to respond to differences in the maturity of the light-end hydrocarbons are the xylene index (XYLI = $\Sigma(m + p)$-xylenes / Σ all xylene isomers) and the propylbenzene index (ProB = *n*-propylbenzene / Σ(*n*-propylbenzene + isopropylbenzene). Unfortunately, their respective variation patterns in the oils and condensates analysed for this study (Figures A.2h & c) do not mirror those evidenced by the aforementioned three parameters. This lack of correlation (see also Table 5.4) is probably due to the greater sensitivity of XYLI and ProB to secondary alteration processes like evaporation and water washing. The variation of these two parameters with reservoir formation will not be discussed further here.

5.2.3 CORRELATIONS BETWEEN PARAMETERS

To highlight the relationships between the 16 aromatic parameters employed herein, a correlation study has been carried out using the data compiled in Table 5.1. The results of the correlation analysis are compiled in Table 5.4, from which it can be seen that these parameters may be classified into three groups.

The first group is composed of the three light aromatic maturity parameters (MEBI, TMBI-1 and TMBI-2). Correlation coefficients (R^2) for MEBI and both TMBI-1 and TMBI-2 are 0.82 and 0.84, respectively, whereas that for TMBI-1 and TMBI-2 is 0.93. The correlation between these light-end maturity parameters and those based on the medium/heavy aromatics (DNR-1, DNR-6, TNR-1 and MPI) is less strong (R^2 = 0.42–0.71), indicating perhaps a significant number of mixed-source oils in the sample set. Considering its high correlation coefficients, TMBI-1 will be treated, in the following discussion, as representative of the three maturity parameters for the light-end hydrocarbons.

The second group includes those maturity parameters based on larger aromatic molecules (MPI, DNR-1, DNR-6 and TNR-1). All have high correlation coefficients (0.81–0.96). The strongest correlation is between DNR-1 and DNR-6, and the weakest between MPI and DNR-6. MPI will be used here to represent the maturity

Table 5.4 Correlation coefficients (R^2) of the aromatic maturity and source parameters (see Table 5.2) for definition)

	MPI	XYLI	ProB	MEBI	TMBI-1	TMBI-2	R/P	125/136 -TMN	1,7/x	R/9-MP	1/9-MP	DNR-1	DNR-6	TNR-1
MPI	1.00													
XYLI	-0.10	1.00												
ProB	0.17	-0.45	1.00											
MEBI	**0.56**	0.58	-0.16	1.00										
TMBI-1	**0.48**	0.52	0.09	**0.82**	1.00									
TMBI-2	**0.60**	0.47	0.05	**0.84**	**0.93**	1.00								
R/P	-0.70	0.24	-0.38	-0.32	-0.29	-0.34	1.00							
125/136-TMN	-0.78	-0.22	0.02	-0.67	-0.65	-0.74	**0.51**	1.00						
1,7/x-DMP	-0.72	0.28	-0.32	-0.25	-0.31	-0.40	**0.75**	**0.55**	1.00					
R/9-MP	-0.74	0.21	-0.33	-0.36	-0.31	-0.37	**0.98**	**0.56**	**0.79**	1.00				
1/9-MP	-0.61	0.39	-0.38	-0.17	-0.18	-0.28	**0.72**	**0.40**	**0.84**	**0.76**	1.00			
DNR-1	0.84	0.02	0.14	0.60	0.55	0.68	-0.51	-0.79	-0.55	-0.52	-0.46	1.00		
DNR-6	0.81	0.09	0.04	0.64	0.57	0.71	-0.50	-0.82	-0.51	-0.51	-0.41	**0.96**	1.00	
TNR-1	0.87	-0.02	0.10	0.54	0.42	0.60	-0.55	-0.82	-0.55	-0.57	-0.46	**0.94**	**0.90**	1

of the heavy-end hydrocarbons.

The third group includes all the source-related parameters. The largest correlation coefficients are between parameters R/P and R/9-MP (0.89), and between 1/9-MP and 1,7/x-DMP (0.88). To simplify the following discussion, the Araucariaceaen signature R/P will be used as the representative source parameter.

5.2.4 COMPARISON OF MATURITIES OF LIGHT AND HEAVY ENDS

To depict the relationship between the maturity of the heavy-end hydrocarbons in these oils and condensates and that of their gasoline-range hydrocarbons, MPI was plotted against MEBI, TMBI-1 and TMBI-2 using the data listed in Table 5.1.

The data distribution patterns are very similar in the resulting cross-plots (Figure 5.12–5.14), because the three light-end maturity parameters are very highly correlated (see Section 5.2.3). However, none of the cross-plots shows a well-defined relationship between light-end and heavy-end maturity. This is potentially of great significance in evaluating the mixing of hydrocarbons in both the Cooper and Eromanga Basins, as illustrated below.

Taking Figure 5.12 as an example, the data points do not fall on a straight line. In other words, for most samples MEBI and MPI do not have good linear relationship. Nevertheless, the majority of the oils and condensates do fall within a broad band (highlighted by shading in the figure). Where this occurs, mixing of oils with different maturities and different chemical compositions (i. e. different relative proportions of light-end and heavy-end components) may be inferred. The MEBI represents the "apparent maturity" of the light-ends of the mixed petroleum, whereas the MPI represents the "apparent maturity" of its heavy-end components. As explained in detail in Section 5.4, the values of both parameters are the *weighted* averages of the all the contributing petroleums, which need to be identified and assessed *separately*.

Only a few oils plot outside the shaded band (notably XYOIL035, 037, 039, 041, 042, 047, 068, 079 & 122 035, 042, 039, 122, and 079: Figure 5.12), most of which

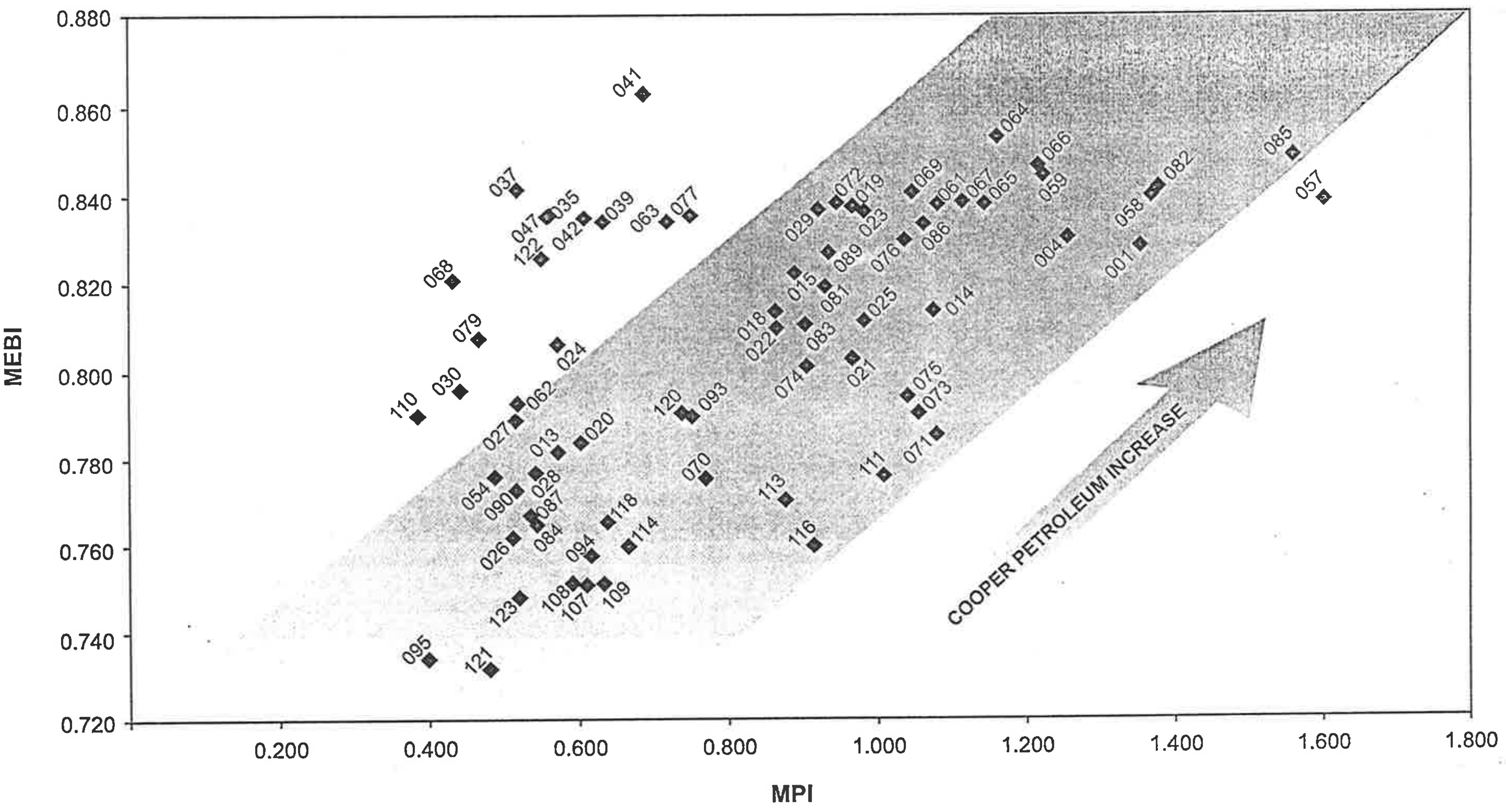


Figure 5.12 Cross-plot of MEBI versus MPI with sample numbers shows in three digits.

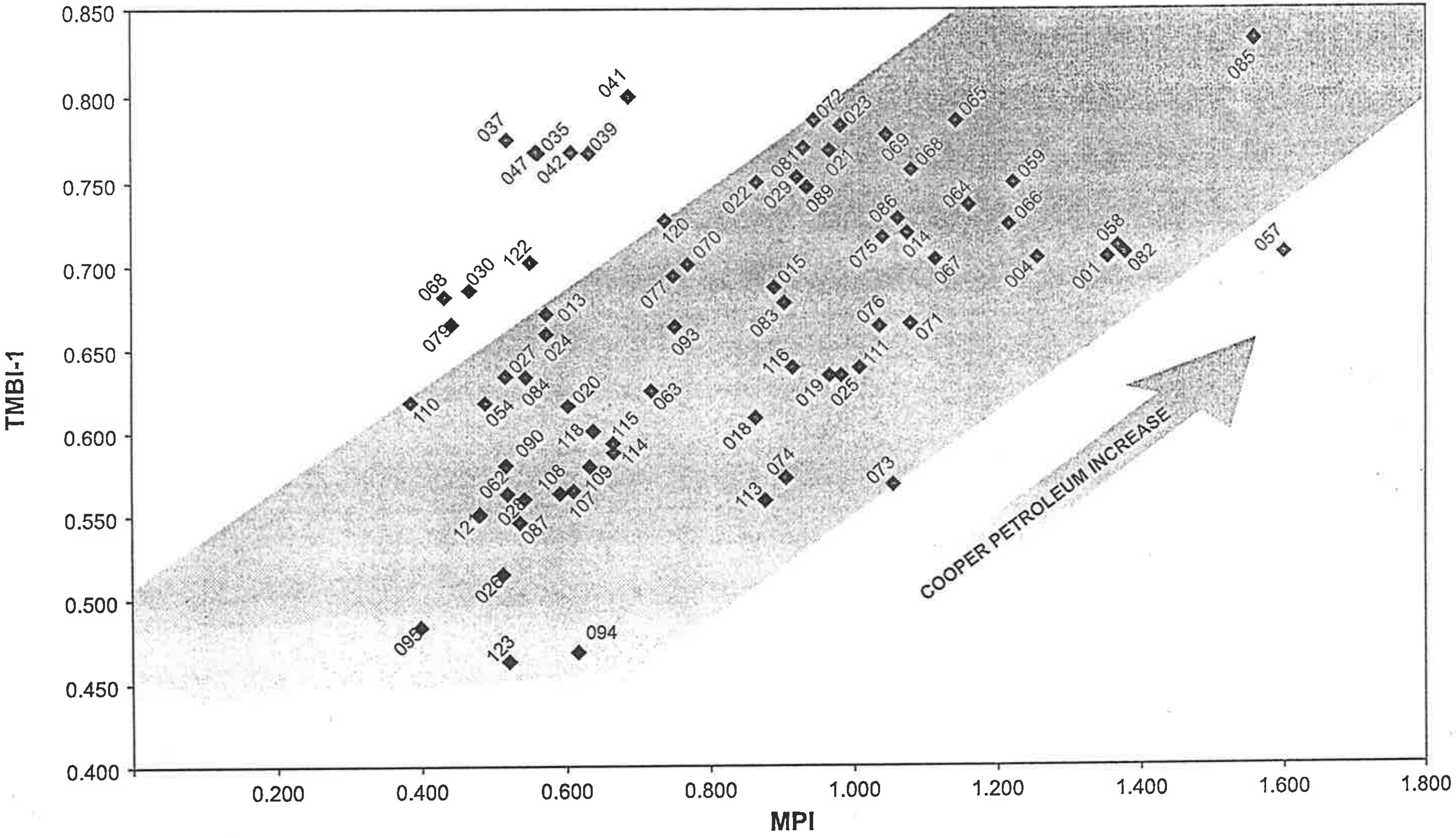


Figure 5.13 Cross-plot of TMBI-1 versus MPI with sample numbers shows in three digits.

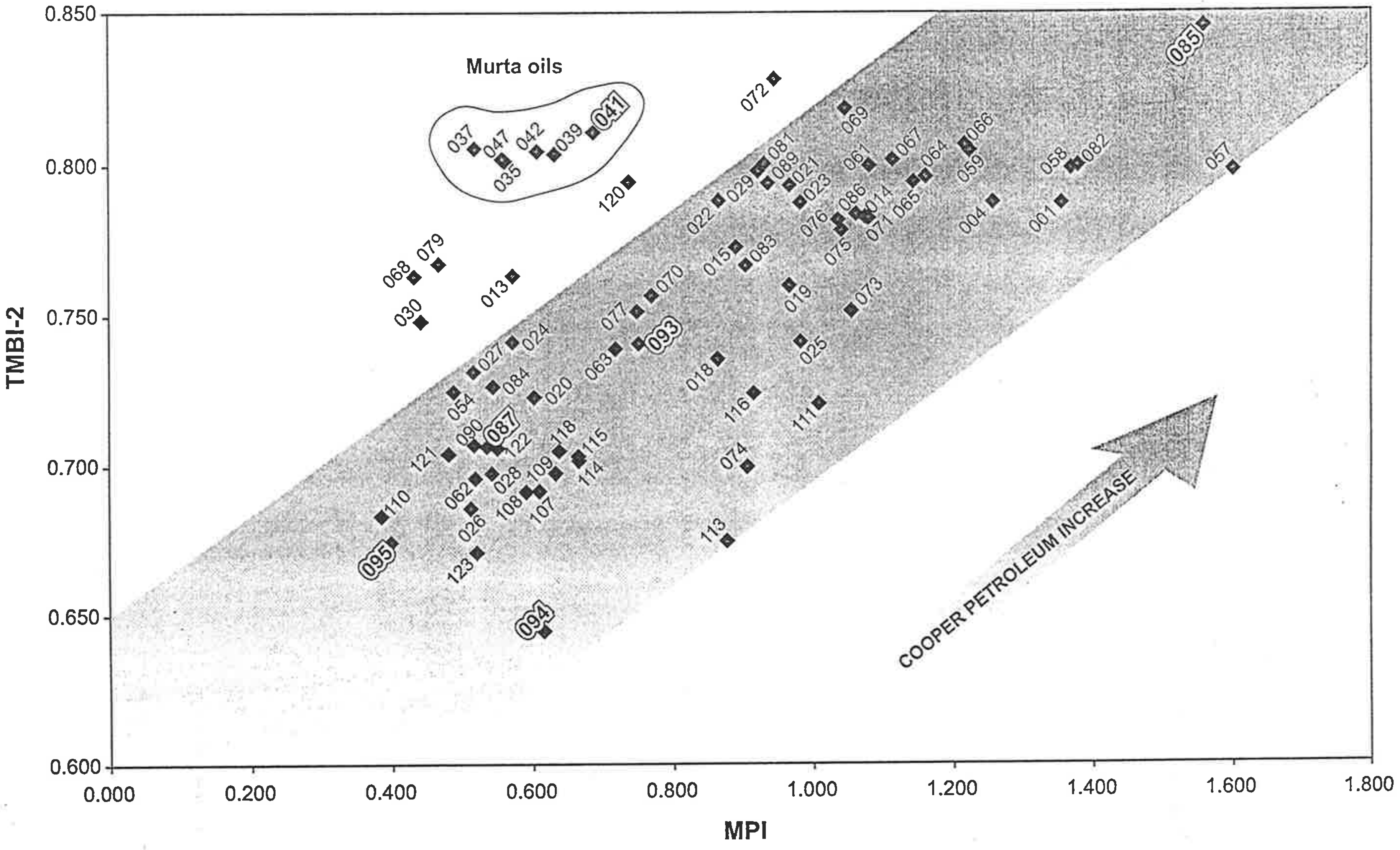


Figure 5.14 Cross-plot of TMBI-2 versus MPI with sample numbers shows in three digits

are from reservoirs in the Murta Formation (Table 5.1). Samples plotting in the lower-left end of the shaded band (e. g. XYOIL095, Taloola-2, Namur) represent "typical" Eromanga-derived oils, whereas those at the upper-right end (e. g. XYOIL085, Bookabourdie-4, Tirrawarra) represent typical Cooper and/or Warburton-derived petroleums. Higher maturities for both their light- and heavy-end components distinguish these condensates from the Eromanga-derived oils. In the middle of the band are the crudes of mixed origins. Finally, samples plotting outside the band can be interpreted as mixtures of Cooper and Eromanga-derived crudes, within each of which the contrast between the abundance of light-end and heavy-end hydrocarbons is large. In the aforementioned Murta oils, the locally derived input is dominated by less mature heavy-end hydrocarbons, whereas the Cooper contribution comprises mainly more mature, "extremely" water-washed and evaporation/migration-fractionationed, light-end hydrocarbons.

Similar data distribution patterns are observed on the TMBI-1 *versus* MPI (Figure 5.13) and TMBI-2 *versus* MPI (Figure 5.14) plots. The former will be employed as the representative plot in the following discussion of the oil mixing model.

5.3 PRINCIPAL COMPONENTS ANALYSIS

Principal components analysis is widely used in the statistical evaluation of geological data. The principal components are the eigenvectors of a variance-covariance (or correlation) matrix erected from a multi-variable database. The eigenvalues measure just how "principal" the components are. Such an analysis provides some insight into the database by helping to find the most significant factor(s) that control the distribution of the data. Unfortunately, it is often very difficult to give the "principal components" their definitive geological meaning. In this study, geochemical interpretations of the first two principal components have been made with the help of digital imitation of a two-end-member mixing model.

Principal components analysis of all the aromatic hydrocarbon data listed in Table 5.1 shows that the first eigenvector typically assumes a 75% loading, and the second eigenvector a 19% loading. In other words, the first and second principal

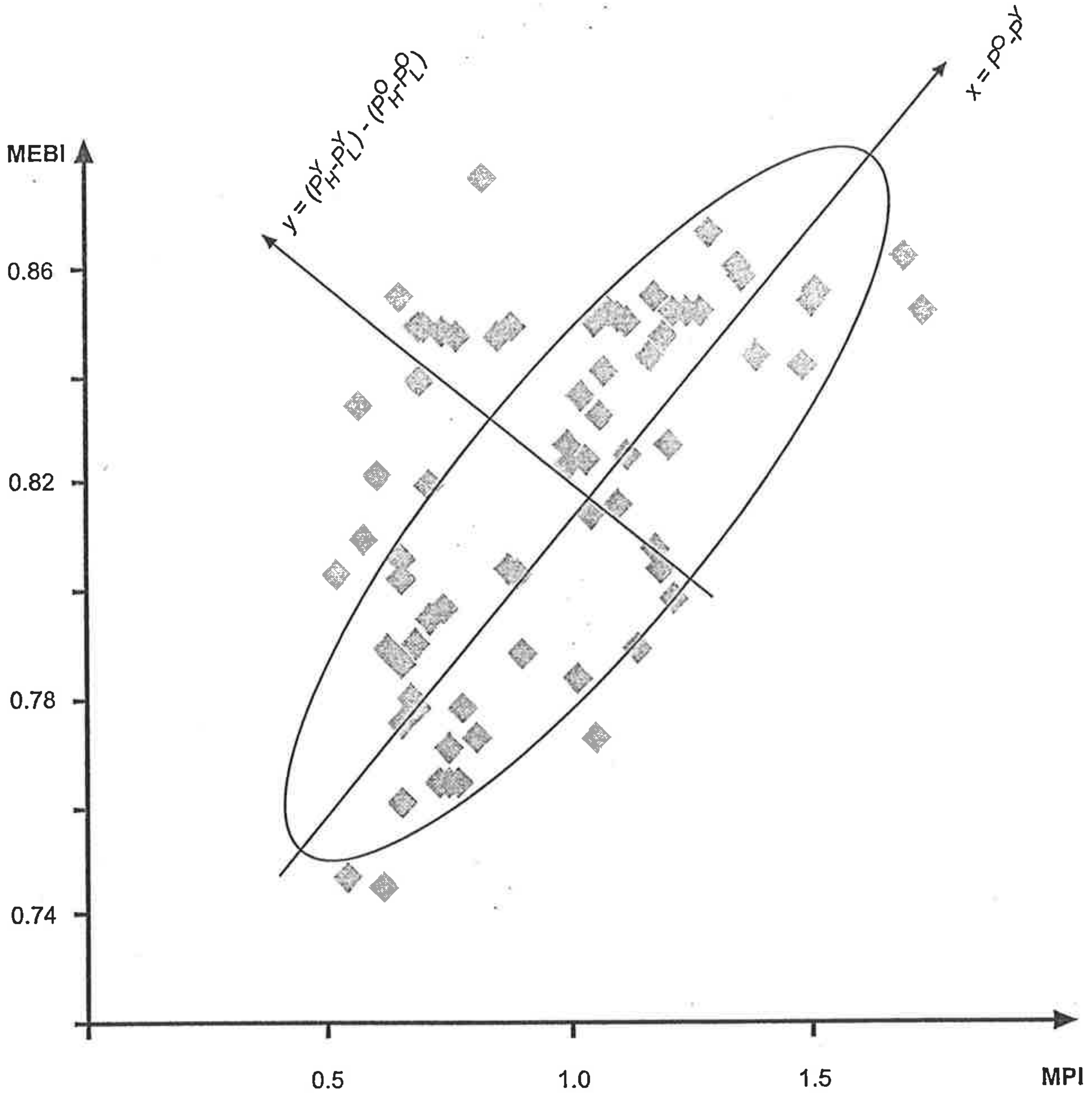


Figure 5.15 Projection of the two major principal components on the cross-plot of MEBI versus MPI

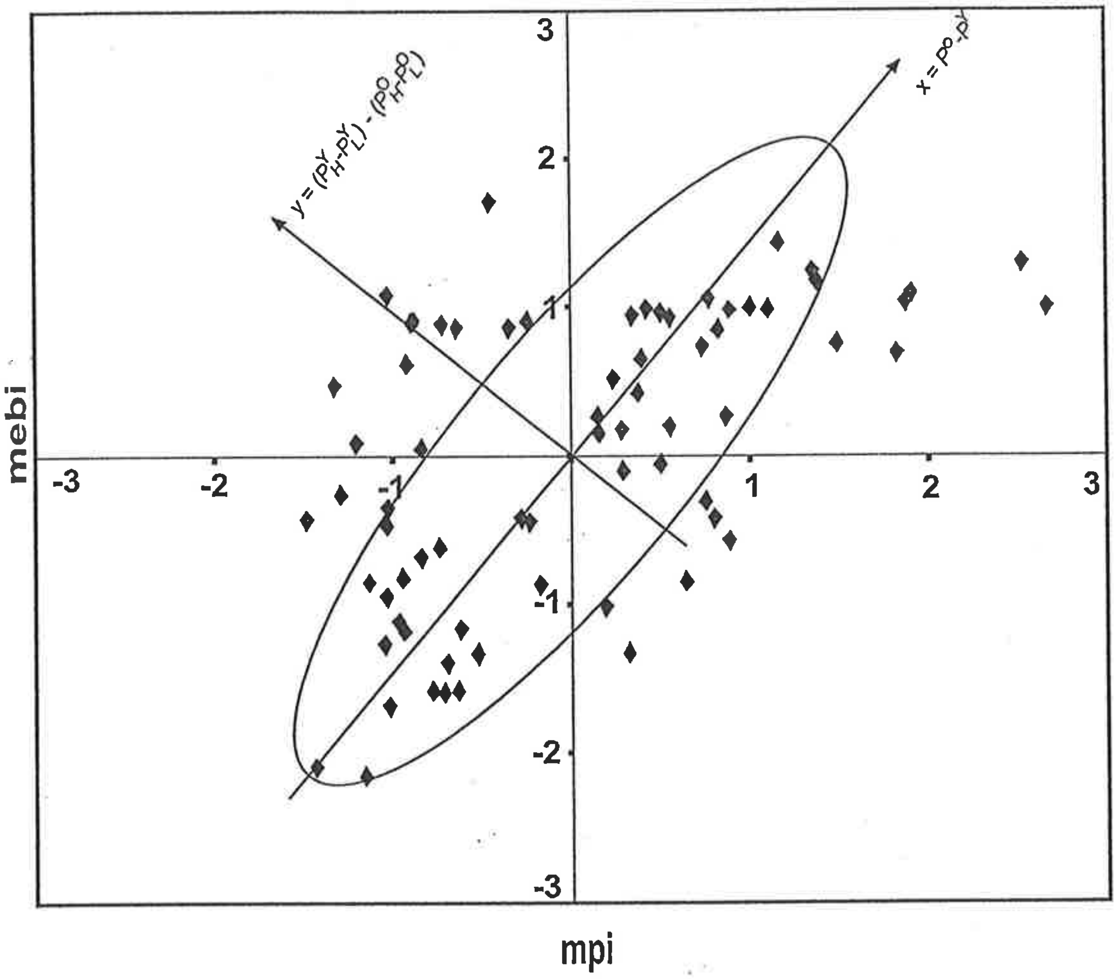


Figure 5.16 Standard normal form of MEBI *versus* MPI.

components are responsible for 75% and 19%, respectively, of the data variance. By neglecting all the other components (which together account for only 6% of the total variance), the first principal component may be assigned 80% responsibility for controlling the distribution of the data, leaving 20% of that control to the second principal component.

However, feeding a computer with a data matrix and making it work out the principal components is nothing more than playing a computer game. Only when the result can be interpreted does this exercise have any use or significance. What is the most powerful factor that controls the distribution of the oil compositional data listed in Table 5.1? What is the second?

To identify the most important geological or geochemical factors that influence the chemical composition of the oils interpreted to be mixed crudes from multiple sources, principal components analysis was run on simple data systems, such as those in Figures 5.12–5.14. Analysis of the MEBI *versus* MPI data set shows that the eigenvalue of the larger eigenvector is 1.56, and that of the other is 0.44. That is to say, the two principal components control 78% and 22%, respectively, of the data distribution on the MEBI *versus* MPI crossplot. For TMBI-1 *versus* MPI the equivalent values are 74% and 26%; and for TMBI-2 *versus* MPI they are 80% and 20%.

Adopting the eigenvalues of 80% and 20%, the relationship between the two eigenvectors can be expressed diagrammatically as shown in Figure 5.15. Here new Cartesian coordinates (composed of the first two eigenvectors) are projected on to the cross-plot of MEBI *versus* MPI. The elongated ellipse is defined by the first two eigenvectors of the variance-covariance matrix. The major axis of the ellipse represents the importance (80%) and direction of the first principal component; and the minor axis (perpendicular to the major axis and a quarter of its length) represents the second most important principal component (exerting 20% of the control on the data distribution).

A simplified two-oil mixing model and its digital imitation (see Section 5.4) show that the major axis represents the influence of the *mixing ratio of the two oils* ($x = P^O - P^Y$, where P^O = the portion of older, more mature oil, and P^Y = the portion of younger, less mature oil). The minor axis is determined by the *concentration difference between the light-end and heavy-end hydrocarbons in each of the two oils* ($y = (P^Y_H - P^Y_L) - (P^O_H - P^O_L)$: discussed in detail in the next section).

Figure 5.16 displays the direct result of principal components analysis on a standard normal form of the MEBI *versus* MPI plot, and illustrates why the Cartesian coordinates are projected in the manner shown in Figure 5.15. Further details can be found in Davis (1986).

5.4 MATHEMATICAL MODEL OF OIL MIXING

As indicated at the beginning of this chapter, a bias towards the heavy-end-dominant Jurassic or Cretaceous input will always occur when the interpretation of mixing of Cooper- and Eromanga-derived hydrocarbons is based only on biomarker ratios or the isotope gradient of individual *n*-alkanes. A new model for assessing the contribution of a single hydrocarbon source to the mixed petroleum has been designed based on mass balance considerations which take into account chemical and isotopic compositional variations *within* the individual oils that have mixed (intra-charge difference) as well as *between* them (inter-charge difference). The generalised form of this model can be applied to most of the conventional organic geochemical parameters (source, maturity, and isotopic composition) only if the components involved in the parameters have variable concentrations. A simplified two-oil form of the mixing model will be introduced to illustrate its application in the Cooper/Eromanga petroleum province.

5.4.1 THE GENERALISED FORM

According to mass balance, for an oil of multiple origins (*n* sources, each composed of *m* components, the "apparent" value of a certain property obeys the following formula (Figure 5.17):

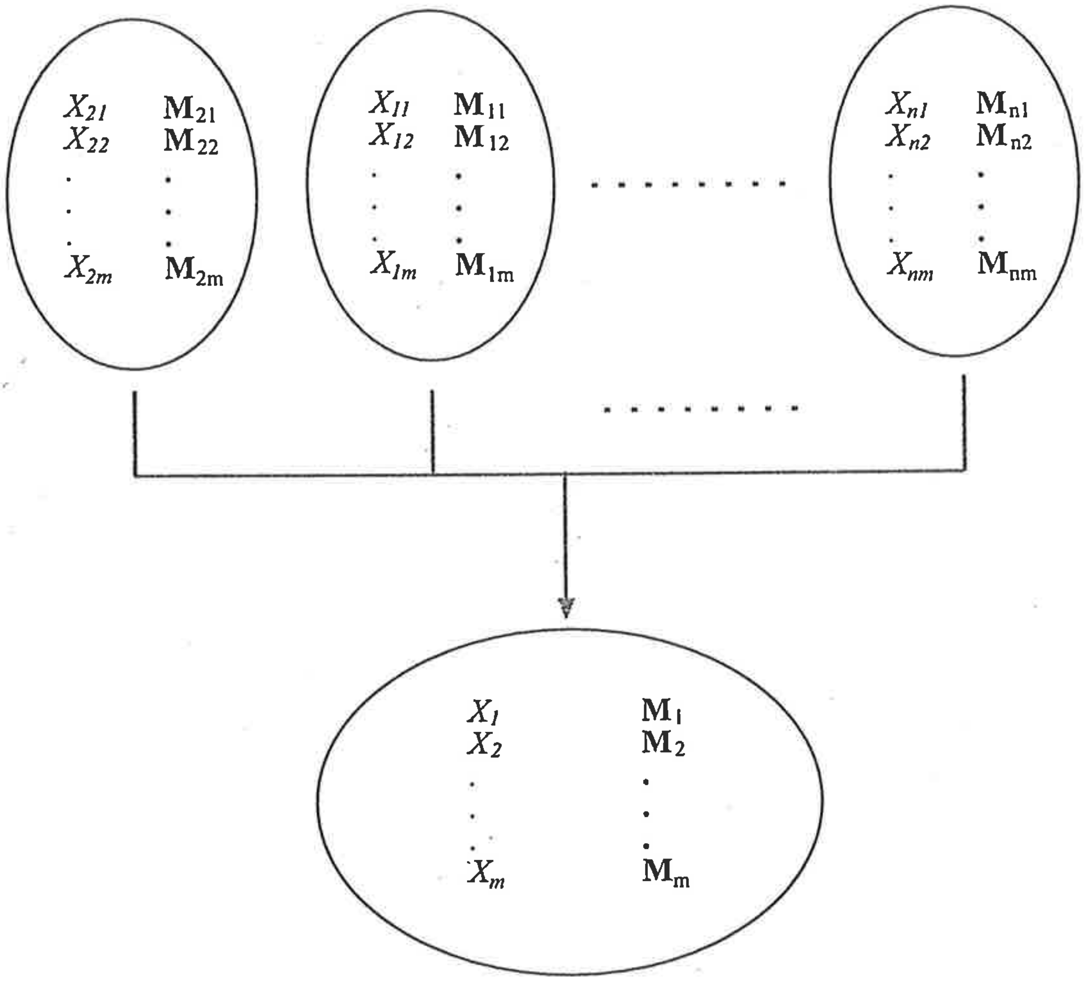


Figure 5.17 Schematic diagram showing a mixed oil composed of hydrocarbons from *n* sources, each of which contains *m* different components.

$$M_j = \sum_{i=1}^{n} M_{ij} \frac{x_{ij} y_i}{x_j}$$

$$x_j = \sum_{i=1}^{n} x_{ij} y_i$$

$$i = 1,2,3,\ldots n;$$

$$j = 1,2,3,\ldots m$$

$$m \geq n$$

where x_{ij} is the partial mole number of the *j*th component (and/or group of components) in the *i*th oil source; x_j is the partial mole number of the *j*th component (and/or group of components) in the mixed oil reservoir; y_i is the partial mole number of oil from the *i*th source in the mixed oil reservoir; M_{ij} is the value of a certain property (viz. isotope composition, MPI, Pr/Ph, or any other maturity/source ratio) of the *j*th component (and/or group of components) in the *i*th oil source; and M_j is the weighted average value of the property of the *j*th component (and/or group of components) in the mixed oil reservoir.

5.4.2 SIMPLIFIED TWO-OIL MIXING MODEL

With the help of computers, the calculations involved in solving the above equation are not a problem. However, once the potential sources (or mixing oils) number more than three, the visualisation and geological interpretation of the results from these calculations may become very complicated. Therefore a simplified two-end-member transformation is adopted here, imitated on the computer, and then applied to several case studies of the Cooper/Eromanga petroleum province. The reason for doing this is not just because of the above difficulty. In fact, this approach is also very practical, since all possible multi-charging problems can be solved, step by step, using the two-oil mixing model.

Suppose that the hydrocarbons in an oil reservoir come from two different sources of contrasting maturity. The high-maturity (older) source rock contributes P^O part of the hydrocarbons to the oil reservoir, and the low-maturity (younger) one contributes P^Y part (where $P^O + P^Y = 1$). Hydrocarbons expelled from each source rock contain both light and heavy ends of variable concentrations. The hydrocarbons contributed by the high-maturity source contain $P^O{}_L$ part of light ends and $P^O{}_H$ part of heavy ends, whereas the low-maturity source contributes $P^Y{}_L$ part of light hydrocarbons and $P^Y{}_H$ part of heavy hydrocarbons. $M^O{}_L$ and $M^O{}_H$ represent the maturities of the light and heavy ends, respectively, in the high-maturity oil; and $M^Y{}_L$ and $M^Y{}_H$ their maturities in the low-maturity oil. If M_L and M_H are the measured maturities of the light and the heavy ends of the mixture, respectively, the above multiple-member equation becomes:

$$M_H = M^O_H \times \frac{\dfrac{P^O_H P^O}{(P^O+P^Y)}}{\dfrac{P^O_H P^O}{(P^O+P^Y)}+\dfrac{P^Y_H P^Y}{(P^O+P^Y)}} + M^Y_H \times \frac{\dfrac{P^Y_H P^Y}{(P^O+P^Y)}}{\dfrac{P^O_H P^O}{(P^O+P^Y)}+\dfrac{P^Y_H P^Y}{(P^O+P^Y)}}$$

$$M_L = M^O_L \times \frac{\dfrac{P^O_L P^O}{(P^O+P^Y)}}{\dfrac{P^O_L P^O}{(P^O+P^Y)}+\dfrac{P^Y_L P^Y}{(P^O+P^Y)}} + M^Y_L \times \frac{\dfrac{P^Y_L P^Y}{(P^O+P^Y)}}{\dfrac{P^O_L P^O}{(P^O+P^Y)}+\dfrac{P^Y_L P^Y}{(P^O+P^Y)}}$$

i.e.

$$M_H = M^O_H \times \frac{P^O_H P^O}{P^O_H P^O + P^Y_H P^Y} + M^Y_H \times \frac{P^Y_H P^Y}{P^O_H P^O + P^Y_H P^Y}$$

$$M_L = M^O_L \times \frac{P^O_L P^O}{P^O_L P^O + P^Y_L P^Y} + M^Y_L \times \frac{P^Y_L P^Y}{P^O_L P^O + P^Y_L P^Y}$$

5.4.3 DIGITAL IMITATION

To illustrate the geochemical significance of the mixing model, digital imitation was accomplished on a personal computer, using the following assumptions:

- Maturities of both the light-end and the heavy-end fractions of the young oil are 1 (i.e. $M^Y{}_L = 1$; $M^Y{}_H = 1$).
- Maturities of both the light-end and the heavy-end fractions of the old oil are 100 (i.e. $M^O{}_L = 100$; $M^O{}_H = 100$).

The results of the digital imitation are depicted in Figure 5.18, a Cartesian cross-plot of M_L and M_H.

The following hypothetical reservoir charge scenarios demonstrate the dual influence of 1) the mixing ratio of the young and old oils; and 2) the relative abundance of light and heavy hydrocarbons within the individual young and old oils, on the position of the resulting mixed oil in Figure 5.18.

1. When both the young and old oils contain equal amounts of light and heavy hydrocarbons (i.e. $P^Y{}_L : P^Y{}_H = 1:1$ and $P^O{}_L : P^O{}_H = 1:1$), the maturity data of the mixed oil distribute along the straight line A. At point E, where the maturities of both the light and the heavy ends are 1, the mixing ratio between the young and old oils is 100:0. At point C, where the maturities of the light and heavy hydrocarbons are 100, the mixing ratio between the young and old oils is 0:100. At the mid-point of the straight line, where the maturities of the light and the heavy hydrocarbons are both 50, the young and old oils make the same contribution to the mixture (mixing ratio = 50:50).

2. Where the young oil comprises 1 part light-end hydrocarbons and 2 parts heavy-end hydrocarbons, and the old oil is made up of 2 parts light components and 1 part heavy components, M_L and M_H in the mixed oil increase along the curve EBC (1221) as the proportion of old oil rises. At the apex of the arc EBC, the mixing ratio is 50:50.

3. When the young oil contains 1 part light-end hydrocarbons and 5 parts heavy-end hydrocarbons, and the old oil consists of 5 parts light components and 1 part heavy components, the light and heavy-end maturities of the mixed oil increase along the curve EDC (1551). Again, at the top of the arc EDC, the mixing ratio is 50:50.

4. Where the young oil contains 5 parts light-end hydrocarbons and 3 parts heavy-end hydrocarbons, and the old oil comprises 3 parts light components and 5 parts heavy components, M_L and M_H in the mixed oil will plot along the curve EFC (5335) according to the relative contributions of old and young oil.

In a summary, the computer modelling indicates that the distribution pattern of the maturity data (MEBI *versus* MPI) in mixed oils is *not only influenced by the mixing ratio, but also by the chemical compositions of the individual contributing oils.* When the young oil contains more heavy components and the old contains more light components, the maturities of both the light and heavy ends in the mixture increase with the increasing contribution of the old oil, along a *curved* line. *The greater the curvature of the line, the bigger the compositional difference between the young and* *old oils.* In situations where the young oil contains more light than heavy components, and in the old oil the reverse is true, the maturity line curves down (see, for example, line EFC in Figure 5.18). Notice that the latter scenario is geologically unlikely in the Cooper/Eromanga petroleum province. This is shown by the fact that (with perhaps one exception, XYOIL057), no oils plot below the shaded band in Figures 5.12–5.14.

5.5 APPLICATIONS

The following are some applications of the mixing model to the task of interpreting the aromatic source and maturity data obtained on 72 oils and condensates from the Cooper and Eromanga Basins (Table 5.1). It seems that the model does provide a practical solution to the problem of recognising and quantifying multiple-sourced crude oils.

5.5.1. INTERPRETATION OF TMBI-1 VERSUS MPI AND SIMILAR CROSS-PLOTS

By comparing the data distribution patterns in the cross-plots of light- *versus* heavy-end maturity (Figures 5.12–5.14) with the results of principal components analysis (Figure 5.15) and the model maturity curves (Figure 5.18), it is evident that the actual data can be matched to that generated by digital imitation. Therefore, the imitation results can be used in the interpretation of the measured maturity data. In the following discussion, the cross-plot of TMBI-1 *versus* MPI (Figure 5.13) will be taken as an example to illustrate the application of the mixing model.

As discussed earlier, crude oil samples plotting in the grey band of Figure 5.13 contain similar proportions of light-end hydrocarbons and heavy-end components (and are equivalent to model oils falling on the straight line EAC in Figure 5.18). The contribution of Cooper-derived petroleum increases from left to right along the band. Condensate XYOIL085 (Bookabourdie-4, Tirrawarra: highlighted in Figure 5.14) contains the largest contribution from the high-maturity Permian source(s), and

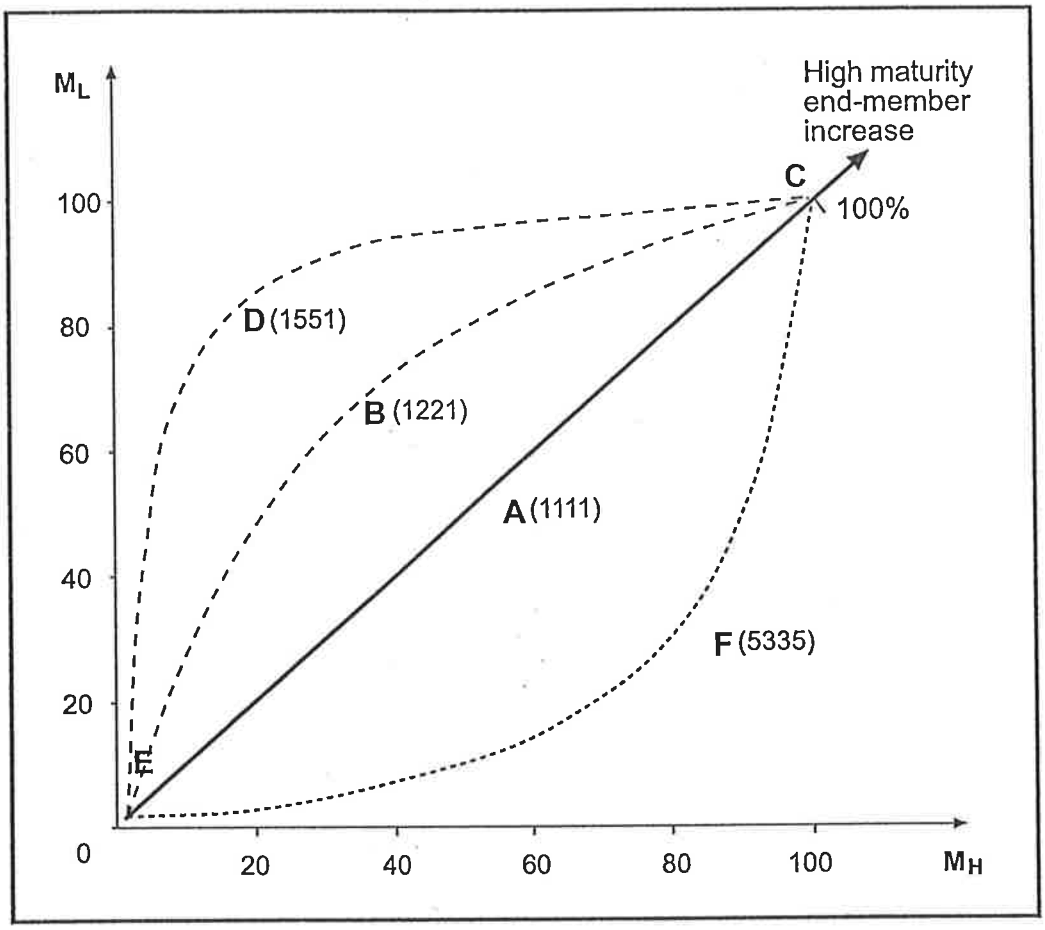


Figure 5.18 A representation of the digital imitation of the two-end-member mixing model.
E = low maturity end-member,
C= high maturity end member.
Numbers in brackets represent partial mole number of light components in immature oil, heavy components in immature oil, light components in mature oil, and heavy components in mature oil, repectively.

therefore may be treated as a "pure" Cooper-derived crude. In contrast, the contribution of Eromanga-derived petroleum increases towards the intercept. Oil XYOIL095 (Taloola-2, Namur: also highlighted in Figure 5.14) contains the smallest contribution from the low-maturity Jurassic or Cretaceous hydrocarbon kitchens, and hence may be regarded as a "pure" Eromanga-derived oil. However, use of the term "pure" here is not entirely appropriate. It would be more proper to treat these two end-members as the "least mixed" crudes.

All the other petroleums falling between them within the shaded band (Figures 5.12–5.14) can be treated mathematically as mixtures of the two end-member crudes. Realistically, all (or at least most) of the Cooper-reservoired petroleums contain no contribution from the Eromanga hydrocarbon kitchens (the Patchawarra and Mooracoochie oils in the Sturt area are exceptions caused by a special structural juxtaposition of source and trap). Nevertheless, it is still possible that some of the Cooper-hosted accumulations could be the result of multiple charges, or the mixing of contributions from Permian and Cambrian source rocks in the Cooper and Warburton Basins, respectively. Source-specific biomarkers (e. g. steranes and triterpanes) would provide some help in identifying the mixing of marine Warburton and non-marine Cooper petroleums.

Eromanga oils which fall into the lower left part of the shaded band in Figure 5.13 can be treated as mixtures of hydrocarbon inputs from both the Cooper and Eromanga source rocks. Such oils typically display a high maturity in their light-end hydrocarbons and bear Eromanga-specific biomarkers.

The Eromanga oils that fall outside of the grey band and in the upper-left area of Figure 5.13 are mixtures of high-maturity Cooper-derived hydrocarbons containing far more light-end components than heavy ends and low-maturity, heavy-end dominant Eromanga-derived hydrocarbons. They plot along mixing curve EDC (1551) in Figure 5.18. This interpretation is supported by the presence of araucariacean signatures in their di- and tri-aromatic hydrocarbons (Figures 5.1 & 5.2). Many of these oils are reservoired in the Murta Formation (see Section 5.5.3).

It is much less likely that an immature oil will contain relatively more light-end hydrocarbons than a mature oil. This is consistent with fact that there are no samples which fall into the area below the grey band in Figures 5.12–5.14, or along curve EFC (5335) in Figure 5.18, giving further credence to the mixing model presented here.

In summary, it can be said that samples plotting closer to the upper-right corner in Figures 5.12–5.14 contain more Cooper (and/or Warburton)-derived hydrocarbons, whereas samples plotting closer to the lower-left corner contain more Eromanga-derived contributions. The greater the contrast between the contents of light- and heavy-end hydrocarbons within the individual oil samples contributing to the mixture, the larger deviation from the central line (Figure 5.18).

5.5.2 XYOIL 85 (40%) + XYOIL 87 (60%) = XYOIL 41

Here, three samples (viz. XYOIL085, 087 & 041) were selected from among the Cooper/Eromanga oils and condensates analysed in this study. Along with their whole-oil GC traces (shown in Figure 5.19) their TMBI-1 and MPI maturities (Figure 5.13) and araucariaceae signatures (Table 5.1) will be compared. The consistency of the measured values in XYOIL041 with the calculated results for the postulated mixture of XYOIL085 & 087 proves that the proposed mixing model is useful in assessing the contributions of Cooper- and Eromanga-sourced hydrocarbons to Jurassic and Cretaceous reservoirs.

Considering all the available geochemical criteria, XYOIL085, a condensate from the Tirrawarra Formation at Bookabourdie-4, may be regarded as a typical Cooper-reservoired crude in that it is mainly (or entirely) sourced from the Cooper Basin. On the cross-plot of TMBI-1 *versus* MPI (Figure 5.13), this sample occupies the upper-right corner of the grey band (see also Figures 5.12 & 5.14). Its chemical composition is dominated by gasoline-range hydrocarbons. Based on its GC-FID profile (Figure 5.19a), its abundance of gasoline-range *n*-alkanes is about four times that of the C_{15+} components (4:1). Its TMBI-1 and MPI values are 0.83 and 1.56, respectively (see Table 5.1). The TMBI-1 value is about 30% larger than the average value of the Eromanga-reservoired hydrocarbons (Figure 5.11) whereas the MPI value is the second largest of all the studied samples (and twice the average value of the Eromanga-reservoired oils: Figure 5.8). This condensate bears no detectable araucariacean biomarker signature (Table 5.1).

In contrast, sample XYOIL087 is a crude oil from the Namur Sandstone at Nungeroo-1. Although located in an Eromanga reservoir, according to its position in Figure 5.13 it contains 30% Cooper-derived hydrocarbons. Its alkane distribution is dominated by C_{15+} hydrocarbons. The *n*-alkanes of this range are about four times as abundant as those in the gasoline-range (Figure 5.19b). It plots closer to the intercept in the TMBI-1 *versus* MBI cross-plot, and its TMBI-1 (0.56) and MPI (0.53) values are amongst the smallest of the sample set (Table 5.1; Figures 5.8 & 5.11). The di- and tri-aromatic hydrocarbons of this oil exhibit strong araucariacean signatures (e. g. R/P = 1.91; 125/136- TMN = 1.46; R/9-MP = 3.34; 1/9-MP = 1.60: Table 5.1).

$$M_H = M_H^O \times \frac{P_H^O P^O}{P_H^O P^O + P_H^Y P^Y} + M_H^Y \times \frac{P_H^Y P^Y}{P_H^O P^O + P_H^Y P^Y}$$

$$= 1.56 \times \frac{0.2 \times 0.4}{0.2 \times 0.4 + 0.8 \times 0.6} + 0.53 \times \frac{0.8 \times 0.6}{0.8 \times 0.6 + 0.2 \times 0.4} = 0.68$$

$$M_L = M_L^O \times \frac{P_L^O P^O}{P_L^O P^O + P_L^Y P^Y} + M_L^Y \times \frac{P_L^Y P^Y}{P_L^O P^O + P_L^Y P^Y}$$

$$= 0.83 \times \frac{0.8 \times 0.4}{0.8 \times 0.4 + 0.2 \times 0.6} + 0.56 \times \frac{0.2 \times 0.6}{0.2 \times 0.6 + 0.8 \times 0.4} = 0.76$$

i.e.

$$MPI = M_H = 0.68,$$

$$TMBI - 1 = M_L = 0.76$$

The gasoline-range *n*-alkane content of a theoretical mixture composed of 40% XYOIL085 and 60% XYOIL087 should be around two-thirds that of the heavy-ends. Accordingly, its position on the TMBI-1 *versus* MPI crossplot (Figure 5.13) would fall into the area above the grey band. Its calculated TMBI-1 and MPI values are 0.76 and 0.68, respectively (notice that in the calculation below, the relative proportions of light and heavy ends within the individual crude oils must be expressed in the form of partial mole numbers or percentages in the calculation).

The calculated results match fairly well the measured maturity and compositional data of sample XYOIL041, a crude oil from the Westbourne Formation at Thungo-1. Based on GC-FID measurement of peak areas (Figure 5.19c), its ratio of gasoline-range to C_{15+} *n*-alkanes is about 2 to 3. Its araucariacean signatures are strong and it has TMBI-1 and MPI maturities of 0.80 and 0.69, respectively (Table 5.1). This oil samples falls outside of the grey band in the TMBI-1 *versus* MPI cross-plot (Figure 5.13), in a position that is equivalent to a 60% Cooper contribution, which is nearly the same as what can be predicted (40% pure Cooper + 60% Eromanga with a 30% Cooper input). The excellent match between the calculated results and the experimental data lends support to the viability of the mixing model.

5.5.3 MURTA MIXED OILS

Considering its effectiveness as a regional seal, the Murta Formation in the Eromanga Basin is likely to be one of the youngest units that Cooper-derived hydrocarbons can access by secondary migration. It is also arguably the best location for petroleum geochemists to identify oil pools comprising hydrocarbons of mixed source, because once the mixing occurs, it will be quite obvious. Compared with the other oils accumulated in Eromanga reservoirs, hydrocarbons derived from intra-Murta source rocks are the least mature, containing predominantly C_{15+} components and Eromanga-specific biomarkers (Alexander et al., 1988; Michaelsen and McKirdy, 1989, 1996; Powell et al., 1989). They would be expected to fall in the lower-left corner on the TMBI-1 *versus* MPI cross-plot (Figure 5.13). In contrast, any Cooper-derived hydrocarbons that accumulated in Murta reservoir beds must bear the characteristics of long-distance-migrated, severely fractionated condensates (viz. high TMBI-1 and MPI maturities, and high contents of gasoline-range components). Accordingly, they should plot in the upper-right corner of the TMBI-1 *versus* MPI diagram.

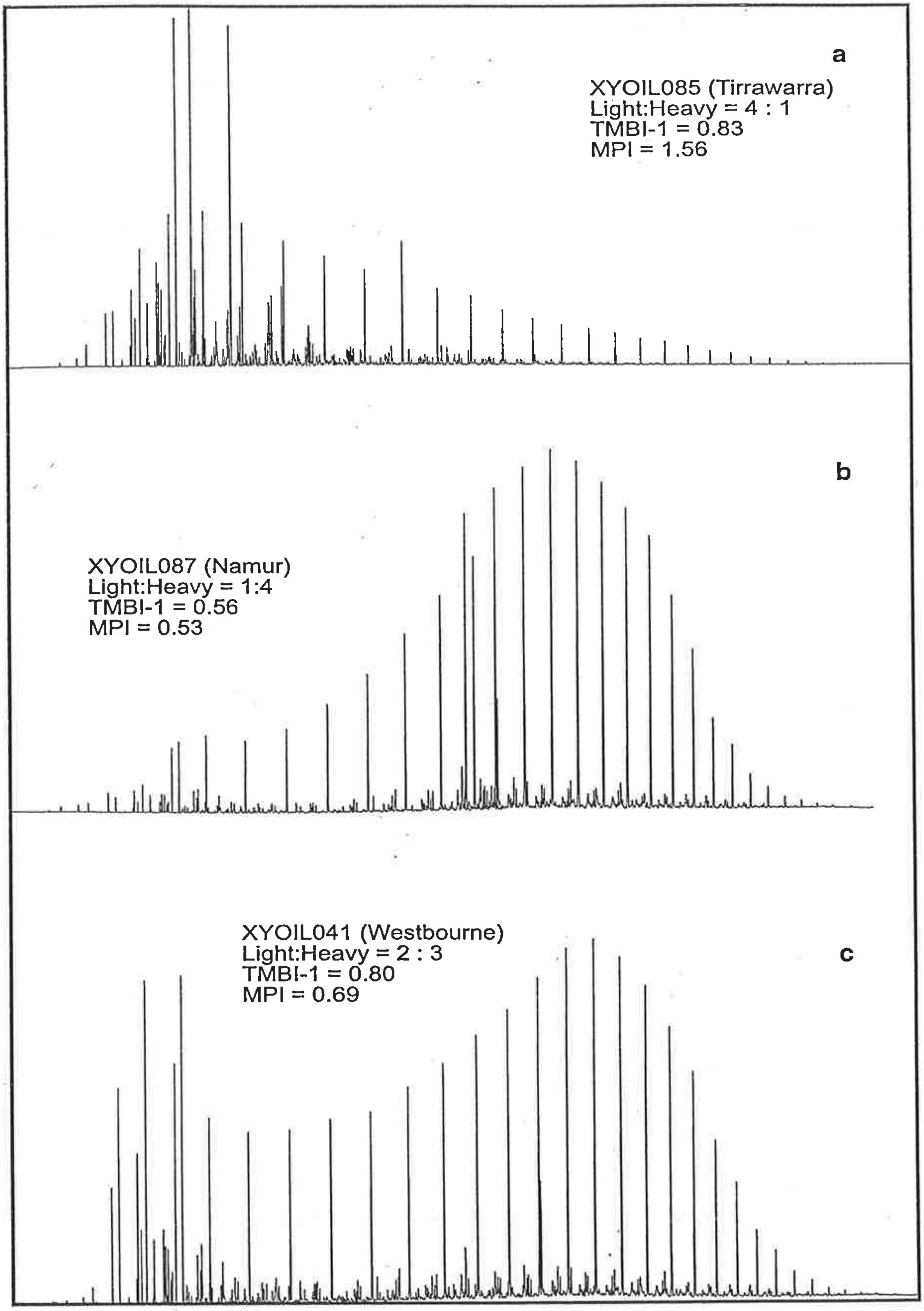


Figure 5.19 GC-FID chromatograms for whole-oils xyoil085, 087 and 041 with the relative abundance and measured maturity of their light (TMBI-1) and heavy (MPI) components

When these two types of petroleum are mingled together, the properties of both the crudes will be inherited, most evidently the dramatic maturity contrast (mature light-ends and immature heavy-ends), and detectable araucariacean signatures. Its MPI maturity will be similar to that of the Eromanga-derived hydrocarbons, because the Murta source rock makes the main contribution to its C_{15+} components. Its TMBI-1 value will be that of the Cooper petroleum, because Cooper-derived hydrocarbons dominate the light-end components. Taking into account the large maturity and compositional contrasts between the two mingling oils, the composite petroleum would be expected to fall well above the shaded band in the TMBI-1 *versus* MPI and similar cross-plots (Figures 5.12–5.14). This inference is supported by the actual geochemical data on oil samples XYOIL035, 037, 039, 042 and 047 (Table 5.1):

1. They are all from reservoirs within the Murta Formation.

2. They contain consistently high amounts of araucariacean biomarkers (e. g. retene: see the first five samples in Figure 5.4). The maximum R/P values in the 72 oils and condensates analysed exceed 2.5, whereas the average is below 1.0. In these five samples the R/P ratios are in the range 2.0–2.6. R/P values for the Cooper-reservoired condensates are near zero.

3. Their MPI values (0.56–0.69: Figure 5.8) are near the average for the Eromanga-reservoired oils. The average MPI value for the Cooper-hosted condensates is about 1.0.

4. Their TMBI-1 values (0.77–0.78) are almost identical and near the top of the range for the Eromanga crude oils (Figure 5.11). Their light-end maturity is even greater than that of the average Cooper-reservoired condensate (TMBI-1 = 0.7). This may be ascribed to evaporative and other fractionation during long-distance secondary migration from the Cooper kitchens to the Murta reservoirs.

5. They all fall above the shaded band in the TMBI-1 *versus* MPI and similar cross-plots (Figures 5.12– 5.14), implying that they are mixtures of typical Eromanga- and Cooper-derived hydrocarbons. The former are immature and contain predominantly C_{15+} components, whereas the latter are long-distance-migrated (and hence highly evaporation/migration fractionated) Permian condensates which have high light- and heavy-end maturities and comprise mostly gasoline-range hydrocarbons.

5.5.4 "PURE" COOPER-DERIVED PETROLEUM ACCUMULATIONS IN EROMANGA RESERVOIRS

Several crude oils in Eromanga reservoirs bear features characteristic of Cooper-derived hydrocarbons. In these oils, the light- and heavy-ends both have high maturities (relative to the other Eromanga crudes: Figures 5.8 and 5.11). They fall into the same area of the TMBI-1 *versus* MPI cross-plot occupied by the Cooper-reservoired petroleums (Figure 5.13). They contain very low concentrations of araucariacean biomarkers (Table 5.1). They could be "pure" Cooper-derived hydrocarbons that have migrated along a "highway" into the Eromanga Basin and become trapped there (see Section 6.3.6 for a detailed explanation of the "migration highway" concept).

XYOIL018 is one of the most typical Cooper-sourced, Eromanga-reservoired crude oils. It comes from the Namur Sandstone at Wilson-6. It contains extremely low levels of araucariacean biomarkers, having a very low R/P value of ~0.1 compared to the average value of ~1.0 for Eromanga petroleums (Figure 5.4). The MPI of this oil (0.83) is about twice the average value for all the Eromanga oils, and only slightly smaller than the average value for the Cooper samples. The TMBI-1 value (0.63) of this oil is also larger than the average of the Eromanga-reservoired oils and only slightly smaller than that of the Cooper condensates. On the cross-plot of TMBI-1 *versus* MPI, the Wilson-6 (Namur) oil plots in the same region as the Cooper-reservoired petroleums (Figure 5.13).

Another typical Cooper-derived Eromanga oil is XYOIL019 from the Birkhead Formation at Big Lake-37. It is very similar to XYOIL018, displaying a high maturity in both the light and heavy ends, and a low concentration of araucariacean resin biomarkers. Accordingly, it falls close to XYOIL018 in Figures 5.13 & 5.14. The other Eromanga-reservoired crude oils possibly derived from Permian source rocks are XYOIL086 (Jackson-3, Westbourne) and XYOIL077 (Merrimelia, Hutton).

The geological setting of these Eromanga traps containing Cooper-sourced crude oils helps explain their occurrence. The Wilson and Jackson Fields occur near the

Permian zero edge in the Queensland section of the Cooper Basin, whereas the Big Lake and Merrimelia oil pools, respectively, lie just above the erosional truncation of Permian carrier beds around prominent anticlinal trends. Faults are common in all the above areas. Such faulting along anticlinal trends, or Cooper Basin margin pinchouts, provide pathways along which Cooper-derived hydrocarbons can migrate into the younger horizons of the Eromanga Basin (Heath et al., 1989; Passmore, 1989).

5.5.5 VERTICALLY-STACKED RESERVOIRS

Crude oils XYOIL093, 094 & 095 are from the same well, Taloola-2, but different reservoir horizons (viz. the Poolowanna Formation, Hutton Formation and Namur Sandstone) on the southwestern margin of the Patchawarra Trough (Figure 3.1). Aromatic source and maturity data (Table 5.1; Figures 5.12–5.14) and the mixing model (Figures 5.17 & 5.18) indicate that the deeper the reservoir, the greater the hydrocarbon charge it has received from Cooper source rocks.

As may be inferred from Figures 5.13 & 5.14, the Poolowanna oil (XYOIL093) comprises about 55% Cooper-derived hydrocarbons, whereas in the Hutton oil (XYOIL094) the Cooper contribution is ~30%, and in the Namur crude (XYOIL095) it is even less (~20). This is consistent with the upward decrease in the strength of their respective araucariacean biomarker ratios (e. g. R/P = 2.5, 1.2 and 0.6: Table 5.1). The stratigraphic trend is clear: the shallower the reservoir, the greater its Eromanga hydrocarbon charge.

Maturity data are consistent with the araucariacean signatures (Table 5.1). The MPI and TMBI-1 values of the Poolowanna oil (0.75 and 0.66, respectively) are larger than those of the Hutton crude (0.62 and 0.47), whereas the Namur oil has the lowest maturity (0.48 and 0.40).

As mentioned previously, the Sturt-Taloola-Tantanna area provides a favourable environment for Permian hydrocarbons to migrate into the overlying Eromanga sequence (Heath et al., 1989; Passmore, 1989). Multiple vertically-stacked reservoirs are ideal for studying the mixing of hydrocarbons from the Cooper kitchen with local

Eromanga-sourced petroleum. If upward migration of Permian hydrocarbons into the Eromanga Basin occurs, oil pools in the Poolowanna Formation will hold more Cooper-sourced petroleum than will those in the Hutton Formation. This may be attributed to the sealing effect of intra-Poolowanna shales and coals. Considering the combined sealing effects of similar impermeable lithofacies within the intervening Birkhead and Westbourne Formations, it is only reasonable to expect that the Namur Sandstone will contain the least Permian input of all the three Jurassic reservoirs.

5.6 SUMMARY

1. The araucariacean resin biomarkers of Alexander et al. (1988), and the retene/phenanthrene ratio introduced in this study, afforded source signatures that are effective in distinguishing Eromanga (Jurassic and/or Cretaceous)-derived oils from those of Permian origin in the Cooper Basin.

2. All the Poolowanna-reservoired crude oils from the Sturt and Sturt East Fields contain 2-methylanthracene. This compound is also abundant in some oils recovered from the Patchawarra Formation and Mooracoochie Volcanics in this area. Its concentration is also very high in the Garanjanie-1 (Namur) and Moolion-1 (Hutton) oils. The presence of 2-methylanthracene may imply the existence of another source facies besides those already identified in the Cooper and Eromanga sequences. Further geological and geochemical studies are needed to evaluate this possibility.

3. In addition to TMBI-1 and TMBI-2 (after Alexander et al., 1996), MEBI is another effective parameter for monitoring the maturity of the gasoline-range hydrocarbons in crude oils from the Cooper and Eromanga Basins. Anomalously high values of TMBI-1, TMBI-2 and MEBI in certain Eromanga-reservoired oils indicate inputs from Permian (Cooper) source kitchens.

4. Principal components analysis of aromatic source and maturity data on 72 oils and condensates, subsequently confirmed by digital imitation, gave rise to a mathematical model for assessing the relative contributions of Cooper and Eromanga crudes to the mixed oils found in certain Eromanga reservoirs. This model has proved to be successful in identifying such oils, explaining their light- *versus* heavy-end composition, and interpreting their origin.

CHAPTER SIX

SECONDARY PETROLEUM MIGRATION

6.1 INTRODUCTION

Although several different approaches have been tried, understanding the processes of secondary hydrocarbon migration, one of the most important constraints on exploration concepts and production strategies, remains the least understood. England and his co-workers made a concerted effort to understand the scenarios of reservoir filling and in-reservoir mixing (England et al., 1987, 1990, 1995; England and Mackenzie, 1989; England, 1990). Larter and others have pioneered the use of molecular odometers in research on secondary migration of petroleum within carrier beds (Li et al., 1992; Yamamoto, 1992; Larter et al., 1996). The compositional heterogeneity of petroleum within an individual reservoir and between different reservoirs has been the subject of many recent studies (Karlsen and Larter, 1989, 1991; Leythaeuser and Rückheim, 1989; Horstad et al., 1990, 1995; Larter et al., 1990; Larter and Aplin, 1995; Mason et al., 1995; Smalley et al., 1995; Stoddart et al., 1995). Other techniques used to study secondary hydrocarbon migration and reservoir filling are fluid inclusions (Horsfield and McLimans, 1984; McLimans, 1987; Eadington et al., 1991; Karlsen et al., 1993), microscopic investigation (Rasmussen, 1997) and numerical simulations (Forbes et al., 1991).

Recently, a new methodological approach, solvent flow-through extraction (SFTE), has been pioneered at the University of Cologne (Schwark et al., 1997). Its technical details have been described in Chapter 3. Briefly, SFTE allows stepwise sequential extraction of residual petroleum fluids from sandstone core plugs, which in turn may be used to reconstruct the charge history of an oil-filled reservoir rock. That is to say those parts of a heterogeneous pore system which were filled by petroleum last in the subsurface can in this experimental procedure be emptied first. Thus, individual petroleum charges which may have filled a trap over an extended period of geologic time can be retrieved separately from oil-saturated reservoir rocks and/or carrier beds.

What are the origins of the crude oils in Cooper and Eromanga Basins? Are all of them sourced from the Permian sequences (as argued by Heath et al., 1989), or have pre-Permian, Jurassic and Cretaceous source rocks contributed, and if so, how much? These are questions that have puzzled Australian petroleum geologists and geochemists for many years.

Until now, the most promising ways to discriminate between Cooper and Eromanga-sourced oil have been their apparent maturity differential, relative abundances of various biomarkers, and carbon isotope compositions of individual *n*-alkanes (Section 2.10). Oil-source rock correlations should work well in a basin system with contrasting organic facies of varying thermal maturities, and where each oil accumulation was the product of a single charge. However, it is clear from the Cooper/Eromanga basin architecture, the overlapping chemistry of its hydrocarbons, and discussions in Chapter 4 and 5 of this thesis, that many of the Jurassic and Cretaceous reservoirs have a multiple-charge history.

Oil-bearing reservoirs do not acquire their hydrocarbons instantaneously. Some commercial oil pools have taken ~5 m.y. or more to accumulate (England et al., 1987; England and Mackenzie, 1989). In cases where the reservoir filled slowly, source-rock burial and maturation commonly continued in the drainage area supplying petroleum of progressively higher maturity to the carrier bed and ultimately to the trap (Brooks et al., 1987). Therefore, over the course of its filling history, the trap receives petroleum charges with different molecular compositions and thermal maturity signatures. The extent to which these petroleum fluids mix *in situ* after reaching the trap depends largely on the petrophysical heterogeneity of the reservoir (England et al., 1987). If the rate of mixing was low, geochemical analysis of oil-stained reservoir rocks (i.e. core plugs as opposed to oils/condensates recovered during drill stem and repeat formation tests) allows reconstruction of the accumulation history (Schwark et al., 1997). Both the timing and direction of charge can be assessed, as well as the sequence of filling of individual pay zones in fields with stacked reservoirs (e.g. Leythaeuser and Rückheim, 1989). An obvious application of such studies is the recognition and mapping of spatial heterogeneities of petroleum compositions within individual fields, which in turn may significantly affect their oil production behaviour (Leythaeuser et al., 1988). Even where the rate of in-reservoir mixing is high and the resulting hydrocarbon pool is chemically homogeneous, it is important to realise that the produced oil or condensate is the compositional average of the early and late charges which may have been compositionally quite distinct. Thus, at best, a DST oil sample represents the *integrated* charge of the tested zone of the reservoir. These considerations need to be borne in mind when attempting oil-source correlation in the Cooper and Eromanga Basins.

Based on the findings presented in Chapter 4 and 5, and the realisation that meaningful oil-to-oil and oil-to-source correlation are not possible without first taking into account the fractionation processes which may occur during migration of hydrocarbon fluids from the petroleum kitchens to the traps, the SFTE technique has been employed to better understand the conditions and effects of fluid flow on the scale of the pore network within the reservoir and/or carrier beds of the Thurakinna, Garanjanie, Dirkala and Wancoocha Fields.

Eighteen sandstone core plugs of reservoir and/or carrier beds have been SFTE-extracted (Table 6.1). The extraction yields are listed in Tables 6.2 and corrected for co-extracted salt in Table 6.4. The results of conventional core analysis (where available from well completion reports and the PEPS database) are summarised in Table 6.3. All the SFTE fractions (6 from each plug) were measured on Iatroscan to determine their bulk compositions (concentrations of the aliphatics, aromatics, resins and asphaltenes: Table 6.5). Selected SFTE-extracted core plugs were crushed and extracted on using accelerated solvent extraction (ASE) to test the efficiency of the SFTE (see Table 6.2 for the results).

Twenty conventional core samples of sandstone, siltstone and coal were extracted using standard Soxhlet extraction or ultrasonication (Table 6.1). Seven DST oils were evaporated under ambient conditions for two days to make the quantification match that of the extracts (Table 6.1).

Table 6.1 Source and maturity data on core plugs, cores and DST oils (1/3)

No.	Sample	Well	Sample Type	Lithology/DST	Formation
1	980511-1	Dirkala-1	Core Plug	Sandstone	Birkhead
2	980512-1	Dirkala-1	Core Plug	Sandstone	Birkhead
3	980513-1	Dirkala-1	Core Plug	Sandstone	Birkhead
4	980513Σ	Dirkala-1	Core Plug	Sandstone	Birkhead
5	980514-1	Dirkala-1	Core Plug	Sandstone	Birkhead
6	980515-1	Dirkala-1	Core Plug	Sandstone	Birkhead
7	980517-1	Dirkala-2	Core Plug	Sandstone	Murteree
8	980517Σ	Dirkala-2	Core Plug	Sandstone	Murteree
9	980522-1	Garanjanie-2	Core Plug	Sandstone	Patchawarra
10	980523-1	Garanjanie-2	Core Plug	Sandstone	Patchawarra
11	980528-1	Thurakinna-3	Core Plug	Sandstone	Patchawarra
12	980531-1	Thurakinna-3	Core Plug	Sandstone	Patchawarra
13	980531Σ	Thurakinna-3	Core Plug	Sandstone	Patchawarra
14	980536-1	Wancoocha-3	Core Plug	Sandstone	Hutton
15	980539-1	Wancoocha-3	Core Plug	Sandstone	Patchawarra
16	980540-1	Wancoocha-3	Core Plug	Sandstone	Patchawarra
17	980541-1	Wancoocha-4	Core Plug	Sandstone	Birkhead
18	980542-1	Wancoocha-4	Core Plug	Sandstone	Birkhead
19	980544	Dirkala-1	Core	Sandstone	Birkhead
20	980545	Dirkala-1	Core	Sandstone	Hutton
21	980546	Dirkala-2	Core	Coal	Epsilon
22	980547	Dirkala-3	Core	Heterolithic	Murta
23	980548	Dirkala-3	Core	Silty shale	Murta
24	980549	Garanjanie-1	Core	Coal	Patchawarra
25	980550	Garanjanie-1	Core	Sandstone	Patchawarra
26	980552	Thurakinna-2	Core	Siltstone	Patchawarra
27	980554	Thurakinna-3	Core	Sandstone	Patchawarra
28	980555	Wancoocha-1	Core	Coal	Patchawarra
29	980556	Wancoocha-1	Core	Coal	Patchawarra
30	980557	Wancoocha-3	Core	Sandstone	Hutton
31	980558	Wancoocha-3	Core	Sandstone	Patchawarra
32	980559	Wancoocha-3	Core	Sandstone	Patchawarra
33	980560	Wancoocha-3	Core	Coal	Patchawarra
34	980561	Wancoocha-4	Core	Sandstone	Birkhead
35	980562	Wancoocha-4	Core	Siltstone	Birkhead
36	980563	Wancoocha-4	Core	Coal	Birkhead
37	980564	Dirkala-1	DST Oil	DST 1	Birkhead
38	980565	Dirkala-1	DST Oil	DST 6	Murta
39	980568	Garanjanie-1	DST Oil	DST 1	Murta
40	980569	Wancoocha-2	DST Oil	DST 3	Patchawarra
41	980570	Wancoocha-2	DST Oil	DST 4	Birkhead
42	980571	Wancoocha-2	DST Oil	DST 5	Birkhead
43	980572	Wancoocha-6	DST Oil	DST 1	Murta

Table 6.1 continued (2/3)

No.	Depth (m)	1,7-DMP	R/9-MP	R/P	2-MA	1-MP	125-TMN
		X - DMP			9-MP	9-MP	136-TMN
1	1624.74	1.24	1.76	1.64	0.01	1.51	5.66
2	1626.82	1.41	1.26	0.97	0.00	1.57	4.79
3	1628.85	1.57	0.78	0.41	0.01	1.61	4.20
4	1628.85	1.58	0.78	0.40	0.02	1.63	5.05
5	1631.89	1.57	0.91	0.68	0.00	1.62	3.86
6	1633.51	1.33	0.85	0.34	0.02	1.59	2.94
7	1890.31	0.58	0.24	0.09	0.14	0.68	
8	1890.31	0.51	0.26	0.10	0.25	0.65	1.61
9	2012.04	0.53	0.17	0.09	0.05	0.81	1.32
10	2016.51	0.52	0.13	0.06	0.09	0.78	1.16
11	2275.92	0.40	0.06	0.05	0.02	0.76	0.94
12	2287.25	0.44	0.09	0.07	0.01	0.77	1.03
13	2287.25	0.43	0.07	0.06	0.02	0.78	1.57
14	1564.11	2.11	5.29	6.75	0.00	1.96	3.65
15	1770.35	0.56	0.34	0.21	0.00	0.70	2.02
16	1779.15	0.67	0.10	0.03	0.04	0.73	2.51
17	1561.20	2.32	5.89	6.75	0.00	2.25	7.31
18	1563.43	2.26	7.51	10.43	0.00	2.26	6.11
19	1634.78	1.39	1.64	0.81	0.03	1.55	4.34
20	1638.12	0.65	0.98	0.75	0.00	1.06	3.15
21	1889.00	0.46	0.25	0.12	0.31	0.58	1.59
22	1399.40	1.14	1.05	0.38	0.03	1.05	5.88
23	1407.59	1.10	1.20	0.53	0.03	1.39	5.16
24	2018.89	0.48	0.13	0.06	0.24	0.65	1.29
25	2023.87	0.63	0.10	0.04	0.06	0.78	1.76
26	2286.97	0.44	0.03	0.01	0.04	0.77	1.12
27	2279.52	0.49	0.19	0.14	0.03	0.81	0.94
28	1881.99	0.53	0.09	0.04	0.20	0.63	3.14
29	1890.65	0.48	0.12	0.05	0.21	0.62	2.63
30	1568.25	0.67	0.82	0.68	0.00	1.07	1.54
31	1768.60	0.59	0.25	0.15	0.00	0.69	1.64
32	1772.01	0.56	0.27	0.15	0.05	0.72	1.58
33	1777.14	0.62	0.08	0.03	0.16	0.64	3.00
34	1560.58	2.53	2.72	1.35	0.01	2.42	5.66
35	1563.94	2.53	2.08	1.00	0.02	2.34	6.18
36	1564.79	2.39	3.22	1.58	0.05	2.16	6.39
37	1620.01	1.39	1.34	0.68	0.07	1.55	4.08
38	1406.19	0.88	2.84	1.50	0.06	1.38	3.64
39	1415.80	0.77	3.07	2.13	0.10	0.71	5.97
40	1741.02	0.65	0.81	0.38	0.13	0.78	4.41
41	1554.33	2.12	4.50	2.60	0.10	2.15	2.88
42	1566.06	1.21	1.80	0.98	0.11	1.44	1.02
43	1310.03	1.17	2.47	1.48	0.06	1.04	0.82

Table 6.1 continued (3/3)

No.	25,28,30-TNH(M)/(Ts + Tm)	TNR-1	DNR-1	DNR-6	Ts/(Tm+Ts)	MPI-1	Rc(1)	Ro
1	0.15	0.66	2.42	1.38	0.20	0.69	0.81	
2	0.11	0.62	2.37	1.38	0.22	0.65	0.79	
3	0.13	0.60	2.50	1.45	0.19	0.56	0.74	
4	0.17	0.58	1.19	0.74	0.20	0.51	0.71	
5	0.20	0.77	3.27	1.74	0.18	0.64	0.78	
6	n.d.	0.77	2.63	1.47	n.d.	0.61	0.77	
7	0.00	0.91	4.81	1.70	0.17	0.69	0.81	
8	0.00	0.94	3.74	1.26	0.18	0.67	0.80	
9	0.00	0.99	3.99	1.49	0.33	0.95	0.97	
10	0.00	0.95	5.16	1.95	0.34	0.82	0.89	
11	0.00	1.00	4.85	2.13	0.68	0.97	0.98	
12	0.00	0.98	3.82	1.79	0.83	1.00	1.00	
13	0.00	1.01	1.51	0.69	0.73	1.07	1.04	
14	0.08	0.64	2.31	1.33	0.06	0.66	0.80	
15	0.00	0.75	4.92	1.85	0.37	0.88	0.93	
16	0.00	0.92	5.12	1.82	0.27	0.70	0.82	
17	0.03	0.58	2.95	1.60	0.07	0.58	0.75	
18	0.07	0.59	2.24	1.30	0.07	0.58	0.75	
19	1.61	0.66	2.04	1.17	0.23	0.55	0.73	
20	n.d.	0.89	1.63	0.84	n.d.	1.10	1.06	
21	0.00	0.75	3.55	1.29	0.03	0.65	0.79	0.69
22	n.d.	0.53	1.60	0.94	n.d.	0.31	0.59	
23	1.56	0.55	2.33	1.37	0.11	0.39	0.63	
24	0.00	0.82	4.36	1.69	0.14	0.72	0.83	0.73
25	0.00	0.96	3.23	1.27	0.26	0.81	0.89	
26	0.00	1.12	4.28	1.78	0.21	0.91	0.94	
27	0.00	1.10	4.46	1.87	0.36	1.19	1.11	
28	0.00	0.82	3.06	1.07	0.03	0.68	0.81	
29	n.d.	0.80	3.20	1.15	n.d.	0.68	0.81	0.71
30	0.08	1.04	2.45	1.14	0.32	1.23	1.14	
31	0.00	0.70	3.29	1.37	0.36	0.87	0.92	
32	0.00	0.89	5.56	2.03	0.35	0.92	0.95	
33	0.00	0.76	3.38	1.30	0.05	0.64	0.78	0.66
34	0.06	0.46	1.85	1.17	0.07	0.49	0.69	
35	0.00	0.52	1.81	1.17	0.14	0.47	0.68	
36	0.00	0.49	2.02	1.23	0.09	0.45	0.67	0.69
37	0.17	0.49	2.65	1.60	0.20	0.52	0.71	
38	0.50	0.48	3.47	3.82	0.29	0.48	0.69	
39	0.88	0.39	2.10	1.35	0.30	0.46	0.68	
40	0.00	0.66	4.91	2.00	0.35	0.70	0.82	
41	0.07	0.41	2.61	1.35	0.07	0.48	0.69	
42	0.00	0.43	2.53	1.54	0.10	0.49	0.69	
43	0.43	0.35	1.95	1.16	0.27	0.39	0.63	

Ro = measured vitrinite reflectance

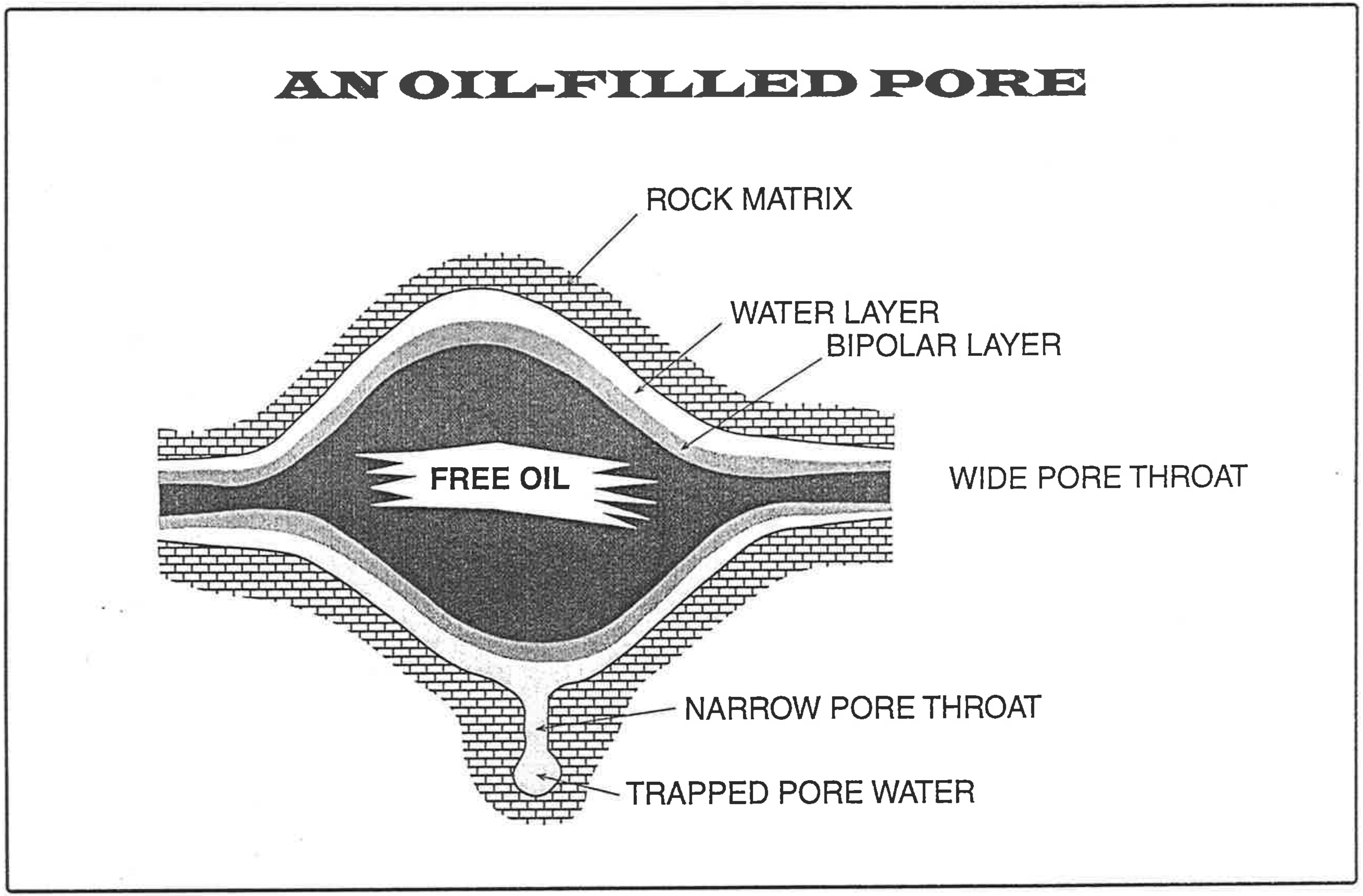


Figure 6.1 Schematic diagram showing the distribution of fluid in a pore of a sandstone reservoir

All the SFTE fraction 1 samples, several combined SFTE fraction 5 and 6 samples, the conventional extracts of sandstones and source rocks, and the topped oils were deasphaltened and fractionated by MPLC. The MPLC yields are compiled in Table 6.6. The aliphatic (saturated) and aromatic fractions from the MPLC were analysed by GC-FID and GC-MS. Values of various source and maturity parameters are compiled in Table 6.1.

Based on the data from these experiments, a secondary hydrocarbon migration scenario within the Warburton, Cooper and Eromanga Basins has been proposed.

6.2 DISTRIBUTIONS OF FLUIDS WITHIN THE PORE NETWORK

The SFTE technique is designed to reveal the distributions of fluids within the pore networks of reservoir and/or carrier beds (see Figure 6.1 for a conceptual model) and hence to reconstruct their petroleum charging history. What is the function of the migration "front", which normally comprises the less mature petroleum from the source rock? Is the formation water, which initially saturates the pore system, replaced by the petroleum front completely or only partly? If partly, what is the proportion? What is the distribution pattern of the fluids (petroleum and residual formation water) within the pores? How much petroleum does it take to wet the pores, and hence pave the way for later migration? SFTE yield data obtained in this study were used to compare the secondary petroleum migration process in the study area, both qualitatively and quantitatively, with that outlined in the following scenario (after Schwark et al., 1997):

- Residual formation water and petroleum are distributed in layers within the connected pores of the sandstone reservoir or carrier bed. From the mineral wall to the centre of the pore, the sequence is water, "adsorbed oil" and "free oil" (Figure 6.1).
- Migration fronts, which are composed of the early expulsion products of the source rocks (and hence are less mature and more polar), *partly* displace the formation water.

- ☐ Part of the formation water, in which inorganic salts are dissolved, is adsorbed on the mineral surfaces of the pore wall. Formation water in the smaller pores (Figure 6.1) can't be replaced by petroleum because of the larger capillary pressures that must be overcome when negotiating the narrow pore throats.
- ☐ Part of the petroleum migration front is adsorbed on the inner surface of the pores, next to the residual water layer, effectively becoming "adsorbed oil" that wets (or "paves") the migration path for the later arriving oil.
- ☐ The central parts of the large pores that are connected by wide pore throats become conduits for migrating oil.
- ☐ Some pore throats are just big enough to be penetrated by the migration front, but are not accessible by the later migrating petroleum. The petroleum within them actually becomes "adsorbed oil".
- ☐ Some large pores are connected to the main migration conduits by narrow pore throats. Crude oil trapped in them is another type of "adsorbed oil".
- ☐ The later arriving oil (normally more mature and less polar) occupies the middle spaces of the pores and corresponds to the "free oil". The "free oil" arrives in the pores last but is extracted first by the less polar solvents in SFTE technique.
- ☐ "Adsorbed oil" on the inner water-wet surfaces of carrier beds, and that occluded within the aforementioned two types of pores, together correspond to the migration loss.
- ☐ Not all the "adsorbed oil" is recoverable by SFTE extraction. Those parts of the "adsorbed oil" within the pores that are not well connected to the main petroleum migration conduits remain in the core plugs even after SFTE step 6. They are only recoverable by ASE extraction of the crushed SFTE-extracted plugs.

6.2.1 SFTE YIELDS

Taking into account the mass and oil saturation of the core plugs (Tables 6.2 & 6.3), and the requirements for adequate GC and GC-MS injection amounts, the SFTE device was programmed to recover most of the "free oil" in fractions 1–3 and the "adsorbed oil" in fractions 5 and 6. Fraction 4 was designed to be a transitional extraction. Taking a plug of 80 g as an example, the first three fractions each comprised 40 ml of extract solution, the forth fraction only 20 ml, and the last two 60 ml each. So, the combination of fractions 1 through 3 corresponds to the aforementioned "free oil" which occupies the central pore spaces (Figure 6.1) and may be compared with the corresponding DST and/or production oil. The combination of fractions 5 and 6 corresponds to the "adsorbed oil", which is adjacent to the water-wet pore wall and is more polar than the "free oil". After extraction, approximately 10 g was cut from the core plug and crushed for ASE to check the efficiency of the SFTE and estimate the petroleum loss during the secondary migration. In the case of a carrier bed, the combination of total ASE yield and SFTE fractions 5 and 6 corresponds to the loss of petroleum during secondary migration.

6.2.1.1 "Free oil"

As shown in Table 6.2 and depicted in Figure 6.2, the SFTE yields normally decrease through the first three fractions. In the case of core plug 980511 (Dirkala-1, Birkhead), the yield of fraction 1 is 1129.6 ppm; that of the fraction 2 is 45.2 ppm; and fraction 3, 14.7 ppm. All the other plugs, except 980518, 980519 and 980529, show similar but less pronounced trends. This is not surprising because the first three fractions are all eluted using the same solvent (dichloromethane) at the same flow rate.

How fast the yield decreases with the progress of the extraction is mainly controlled by the permeability of the core. The better the permeability, the faster the efficiency decreases, as shown by the comparison between the extract yield profiles (Figure 6.2) of plugs 980511 (280 mD) and 980512 (105 mD), both from the Birkhead Formation in Dirkala-1. A similar example supporting this interpretation is provided by plugs 980541 (1427 mD; fraction 1 = 633.4 ppm, fraction 2 = 3.8 ppm) and 980542 (839 mD; fraction 1 = 87.8 ppm, fraction 2 = 1.8 ppm) from the Birkhead Formation in Wancoocha-4.

The three exceptions (plugs 980518, Dirkala-2, Murteree; 980519, Dirkala-3, Murta;

and 980529, Thurakinna-3, Patchawarra) all have low contents of "free oil". For plug 980529, the measured yields of fractions 1 through 3 are zero. For plug 980519, the first three fractions have bulk chemical compositions (measured using IatroScan) that are similar to those of the last three fractions. All six fractions exhibit "adsorbed oil" properties, containing more asphaltenes and resins and less aliphatics (see discussion in Section 6.2.2).

6.2.1.2 "Adsorbed oil"

It is meaningless to compare the yield of fraction 4 with those of the other fractions, because the extraction time is shorter, and, more importantly, the polarity of the eluting solvent is transitional. After the completion of extraction step 3, a mixture of dichloromethane and methanol (50:50 v/v) is used for eluting the last of the residual oil. When the former solvent (DCM) is completely replaced by the latter mixture, the extraction behaviour once again is controlled by the porosity and permeability of the core. It is not predictable without detailed core analysis results. Neither is it worth monitoring, considering the costs and its significance. However, based on past experience, a 20 ml elution volume is enough to complete the solvent transition for most types of core plugs. Conceivably, the bulk chemical composition of the transitional fraction 4 should be between that of the fractions 1, 2 & 3 and fractions 5 & 6 (see discussion in Section 6.2.2).

Neglecting the transitional fraction 4, yields of "adsorbed oil" show a similar trend to those of the "free oil" fractions, decreasing with the extraction time (or eluting solvent volume). As shown in Table 6.2, from fraction 5 to 6, the yield drops from 111.9 to 19.9 ppm for plug 980511; from 138.9 to 6.9 ppm for plug 980513; and from 148.4 to 6.9 ppm for plug 980514. Plug 980518 is the only exception, in which the yield of fraction 6 (62.1 ppm) is larger than that of fraction 5 (14.1 ppm).

The explanation of the decreasing of yield is the same as that for the "free oils". However, there is no obvious explanation for what happened in the case of plug 980518. Temporary pump failure and/or blockage within the extraction cell are possible causes, since most of the extractions were carried out overnight without an operator in attendance.

Table 6.2 SFTE yields from core plugs

Well	Sample	Mass of the 6 SFTE Fractions (mg)								Plug mass (g)	Extract Concentration (ppm)						ASE sample (g)	ASE yield (mg)	ASE yield (ppm)
		1	2	3	4	5	Cal. 5	6	Cal. 6		1	2	3	4	5	6			
Dirkala-1	980511	92.4	3.7	1.2	1.4	57.4	9.2	30.6	1.6	81.8	1129.6	45.2	14.7	17.1	111.9	19.9	11.0	0.0	0.0
Dirkala-1	980512	49.2	6.5	1.5	1.8	31.3	4.3	12.5	0.9	83.1	592.1	78.2	18.1	21.7	52.0	10.7	10.0	0.0	0.0
Dirkala-1	980513	68.8	15.8	1.1	3.2	38.8	15.4	7.0	2.2	111.0	619.8	142.3	9.9	28.8	138.9	19.4	10.0	1.0	100.0
Dirkala-1	980514	40.1	3.1	0.3	1.9	67.2	15.7	11.3	0.7	105.6	379.7	29.4	2.8	18.0	148.4	6.9	10.5	0.0	0.0
Dirkala-1	980515	4.6	1.2	0.3	2.3	27.8	1.4	19.3	1.4	103.4	44.5	11.6	2.9	22.2	13.3	13.2	10.1	0.0	0.0
Dirkala-1	980516	1.2	0.2	0.5	1.4	49.9	2.0	29.6	0.7	97.6	12.3	2.0	5.1	14.3	20.2	6.8	9.8	0.0	0.0
Dirkala-2	980517	43.3	5.8	0.4	14.6	20.2	6.8	9.9	2.6	116.6	371.4	49.7	3.4	125.2	58.3	22.0	9.4	0.6	63.8
Dirkala-2	980518	0.7	0.8	0.0	2.0	32.6	1.8	59.2	8.0	129.4	5.4	6.2	0.0	15.5	14.1	62.1	11.1	0.0	0.0
Dirkala-3	980519	0.5	0.8	0.7	0.7	1.5	0.4	1.3	0.2	32.0	15.6	25.0	21.9	21.9	11.6	7.2	9.5	0.3	31.6
Dirkala-3	980520																		
Dirkala-3	980521																		
Garanjanie-2	980522	4.5	0.0	0.0	1.1	16.1	1.1	9.6	0.2	106.5	42.3	0.0	0.0	10.3	10.2	2.1	12.9	0.0	0.0
Garanjanie-2	980523	17.9	0.1	0.5	0.3	14.2	0.9	6.6	0.3	110.3	162.3	0.9	4.5	2.7	8.3	2.5	10.3	0.0	0.0
Garanjanie-2	980524																		
Thurakinna-2	980525																		
Thurakinna-2	980526																		
Thurakinna-2	980527																9.4	0.8	85.1
Thurakinna-3	980528	14.5	1.6	0.0	1.1	17.7	0.9	5.7	0.2	132.0	109.8	12.1	0.0	8.3	6.7	1.6	9.5	0.0	0.0
Thurakinna-3	980529	0.0	0.0	0.0	2.0	19.1	5.9	8.9	4.1	119.6	0.0	0.0	0.0	16.7	49.0	33.9	9.5	0.2	21.1
Thurakinna-3	980530																9.4	0.5	53.2
Thurakinna-3	980531	10.5	0.8	0.0	5.0	10.0	1.9	10.1	1.0	104.2	100.8	7.7	0.0	48.0	17.9	9.8	9.7	0.1	10.3
Wancoocha-1	980532																		
Wancoocha-1	980533																		
Wancoocha-1	980534																		
Wancoocha-1	980535																		
Wancoocha-3	980536	11.0	2.2	0.4	0.8	28.5	4.0	18.5	0.8	78.6	139.9	28.0	5.1	10.2	51.1	10.4	10.2	0.2	19.6
Wancoocha-3	980537	3.4	0.0	0.0	0.3	17.8	0.9	26.3	0.9	104.1	32.7	0.0	0.0	2.9	8.8	8.9	9.7	0.0	0.0
Wancoocha-3	980538																		
Wancoocha-3	980539	142.7	2.7	0.8	2.5	42.2	11.2	8.5	0.7	112.3	1270.7	24.0	7.1	22.3	99.4	6.6	9.4	0.0	0.0
Wancoocha-3	980540	49.2	4.7	1.8	16.7	18.3	5.2	2.4	1.1	119.0	413.4	39.5	15.1	140.3	43.9	9.2	9.7	0.0	0.0
Wancoocha-4	980541	66.7	0.4	0.1	1.2	15.2	2.8	2.8	0.7	105.3	633.4	3.8	0.9	11.4	26.3	7.0	9.5	0.0	0.0
Wancoocha-4	980542	9.9	0.2	0.2	1.9	13.2	4.0	8.8	0.6	112.7	87.8	1.8	1.8	16.9	35.4	5.6	9.6	0.0	0.0
Wancoocha-4	980543																		

Cal. = Calibrated mass from Iatroscan data

Table 6.3 Results of core analysis (extracted from well completion reports and/or PEPS database)* and ratios of "adsorbed oil" to "free oil"

Samples	Wells	Permeablilty (mD) K. A.	Porosity (%) He Injection	Residual Saturation (%) Oil	Residual Saturation (%) Water	Original Saturation (%) Oil	Original Saturation (%) Water	Residual oil / Original oil	"Adsorbed oil" / "Free oil"
980511	Dirkala-1	280.0	21.5	19.3	39.5	60.5	39.5	0.32	0.11
980512	Dirkala-2	105.0	19.4	9.4	43.4	56.6	43.4	0.17	0.11
980513	Dirkala-3	513.0	22.6	5.7	51.4	48.6	51.4	0.12	0.27
980514	Dirkala-4	392.0	25.2	5.2	60.8	39.2	60.8	0.13	0.29
980515	Dirkala-5	32.0	18.9	2.8	69.2	30.8	69.2	0.09	0.45
980516	Dirkala-6	873.0	24.9	0.0	83.8	16.2	83.8	0.00	0.68
980517	Dirkala-2	28.0	18.0	0.1	32.0	68.0	32.0	0.00	0.39
980519	Dirkala-3	0.0	7.1						0.54
980520	Dirkala-4	0.2	10.5						
980521	Dirkala-5	8.1	20.8						
980522	Garanjanie-2	233.0	17.4	0.1	32.4	67.6	32.4	0.00	0.35
980523	Garanjanie-2	1989.0	22.1	0.2	35.7	64.3	35.7	0.00	0.07
980524	Garanjanie-4	0.1	11.0	0.3	70.4	29.6	70.4	0.01	
980525	Thurakinna-2	0.8	11.2	0.6	32.8	67.2	32.8	0.01	
980526	Thurakinna-3	0.4	12.6	0.2	53.9	46.1	53.9	0.00	
980527	Thurakinna-4	0.6	11.9	0.2	48.2	51.8	48.2	0.00	
980528	Thurakinna-3	0.2	11.0	0.2	61.1	38.9	61.1	0.01	0.12
980529	Thurakinna-4	0.2	10.0	0.2	50.0	50.0	50.0	0.00	1.00
980530	Thurakinna-5	0.0	6.8	1.4	60.9	39.1	60.9	0.04	
980531	Thurakinna-6	0.0	9.4	0.3	60.0	40.0	60.0	0.01	0.44
980534	Wancoocha-1	15.0	16.1	1.2	58.4	41.6	58.4	0.03	
980535	Wancoocha-2	61.0	16.3	0.0	53.5	46.5	53.5	0.00	
980536	Wancoocha-3	122.0	19.9	10.5	60.2	39.8	60.2	0.26	0.34
980537	Wancoocha-4	307.0	22.4	0.1	71.9	28.1	71.9	0.00	0.39
980538	Wancoocha-5	1649.0	2.4	0.0	82.5	17.5	82.5	0.00	
980539	Wancoocha-6	70.0	16.4	4.0	50.0	50.0	50.0	0.08	0.09
980540	Wancoocha-7	1.3	18.1	5.2	52.2	47.8	52.2	0.11	0.29
980541	Wancoocha-4	1427.0	24.3	14.8	44.4	55.6	44.4	0.27	0.06
980542	Wancoocha-5	839.0	22.4	15.0	42.1	57.9	42.1	0.26	0.39

* Data interpolated and/or extrapolated where the sample depths are not those of the analysed cores

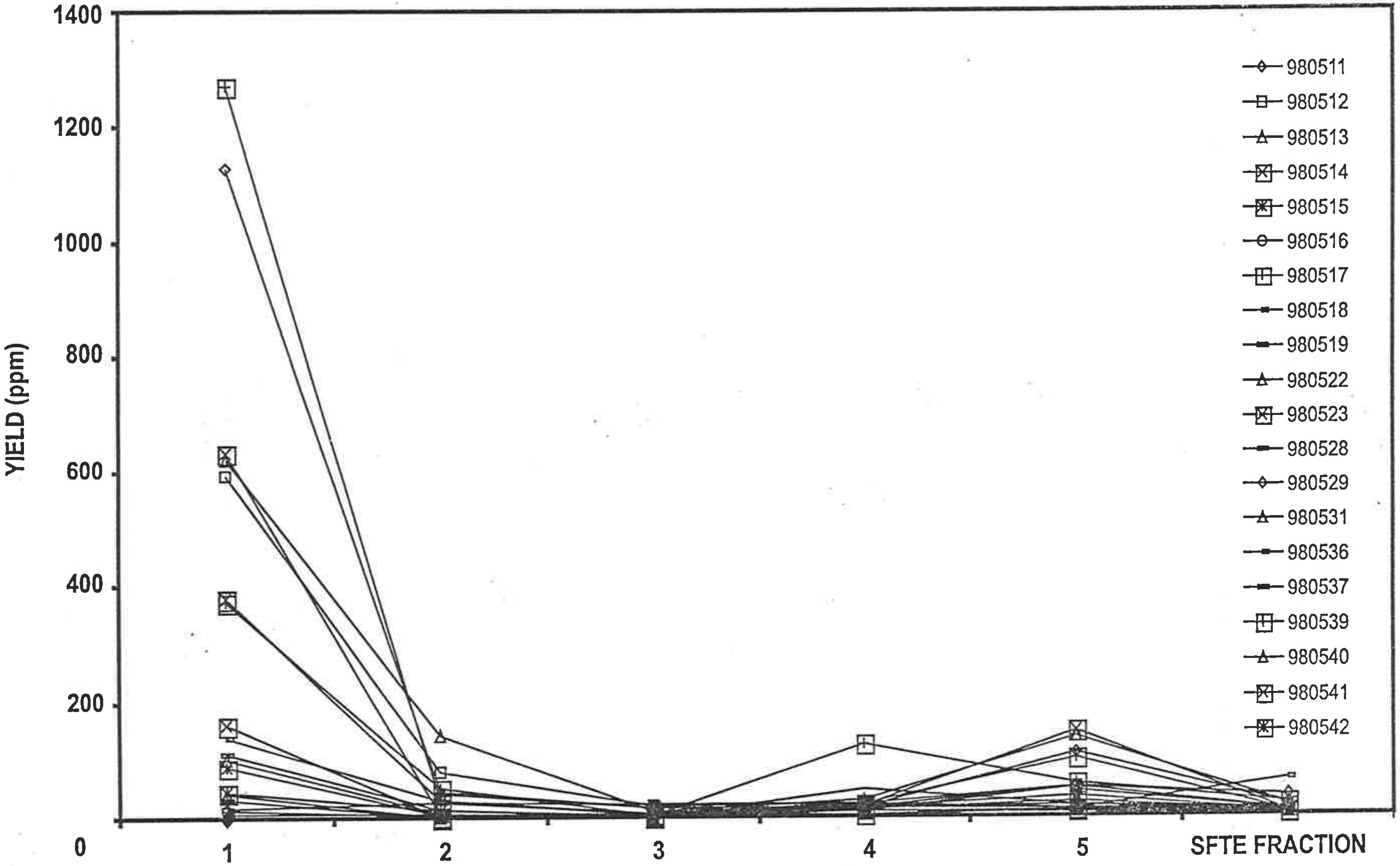


Figure 6.2 Change of SFTE yield with progress of extraction for 20 core plugs

6.2.1.3 ASE

The ASE yields obtained from the 18 SFTE-extracted plugs are listed in the last column of Table 6.2. For 70% of the plugs the yield was zero indicating that all their residual oil is located in accessible, connected pore space. For the remaining plugs, 10–100 ppm of their residual oil was recovered by ASE. The ASE yields represent those parts of the "adsorbed oils" that are preserved in the smaller pores or in large pores that are connected to the main migration conduits by narrow pore throats. For the reason of capillary pressure, the extraction solvent can't access them. Together with the SFTE fractions 5 and 6, they correspond to the petroleum lost during secondary migration within carrier beds.

6.2.1.4 Petroleum Loss *en route* during Secondary Migration

During secondary petroleum migration and reservoir filling, the migration fronts replace parts of the pre-existing formation water, wetting or "paving" the migration pathways for the later arriving hydrocarbons. In addition to some polar components (e.g. NSO-compounds) from the later arriving petroleum, parts of the crude oil front interact with the water layer to form the bipolar layer illustrated in Figure 6.1, thus becoming "adsorbed oil". Such "adsorbed oils" are immobile, and remain behind during the secondary migration process.

In order to establish some link between the petroleum migration loss and the SFTE data, several calculations were made. The results are compiled in Table 6.3 along with the available data on permeability, porosity, and residual oil/water saturation. Original oil saturation was calculated thus: original oil saturation = 100 – water saturation. The two ratios, residual oil saturation/original oil saturation and "adsorbed oil"/"free oil", provide a semi-quantitative estimate of the likely losses of petroleum *en route* during secondary migration where the sandstone is a carrier bed, or during production where the sandstone is a reservoir.

As shown in Table 6.3, ratio of "adsorbed oil" to "free oil" ranges from 6% in the Birkhead Formation at Wancoocha-4 to 100% in the Patchawarra Formation at Thurakinna-4, and the average is about 34%. If used to calculate petroleum losses during secondary migration in the study area, this average value is generally consistent with data from reservoir engineering studies (D. Leythauser, private communication, 1997). However, the average value of the ratio of "adsorbed oil" to "free oil" from SFTE measurements can at best only be a rough estimate of the hydrocarbon loss attributable to secondary migration. Its application to petroleum development and production needs further research. At the very least, there need to be some calibrations that take into account the evaporative loss of light hydrocarbons involved in the process of bringing the core from underground to the surface, and thereafter during storage. Thus, the actual migration losses (under subsurface conditions) must be less than indicated by this calculation.

Core analysis data from well completion reports were also employed, tentatively, to assess the migration loss in the study area. From Table 6.3, it is shown that about half of the pore volume is saturated by residual water in these cores under surface conditions. Formation water must occupy a similar amount of pore space in the subsurface, because water volume does not change much with changes of temperature and pressure. This value is also consistent with the conclusion of England et al. (1987) that the petroleum must fill ~50% of the available rock pore volume in order to create an interconnected pathway, allowing movement to occur. Residual oils (remaining in the cores under surface conditions) occupy no more than 19% of the pore space (Table 6.3).

What occupies the remaining ~30% of the pore space under subsurface conditions? Based on the findings of England et al. (1987), it is proposed here that this part of the pore space is occupied by light hydrocarbons. From the North Sea example documented in Table 1 of England et al. (1987), it can be seen that methane and other light hydrocarbons (smaller that C_6) are the predominant components of the subsurface petroleum liquid, accounting for more than 70 mol %. Because of their great volatility, the majority of these components disappear due to evaporation while the core is being brought from underground to the surface. Only the heavy parts of the petroleum remain in the pores. They comprise the residual oil and take up less than 20% of the total pore space.

Among the present suite of residual oils, an average of 34% is adsorbed "permanently" to the water-wet pore walls. So the calibrated calculation of petroleum loss *en route* during secondary migration should be larger than 14%. Therefore, the best estimate of migration loss in the study area falls in the range 14% ("adsorbed" portion of the residual oil) to 40% (all the residual oil).

6.2.1.5 Inorganic salt

During the SFTE extraction, inorganic salt (identified as halite, NaCl, by XRD) was recovered with fractions 5 and 6 of every core plug (Table 6.4). The salt appeared as white crystal on the inner wall of the flask during rotary evaporation. It was collected by first cautiously rinsing the EOM from the flask with DCM, and then dissolving the inorganic residue in deionised water. The salt was recovered by evaporation of the aqueous solution at 50 °C and weighed.

An alternative way of quantifying the salt content is by calculation based on the IatroScan measurements, according to the following formula (the calculation details are discussed in the next section):

Mass of salt (mg) = Combined mass of SFTE fractions 5 & 6 – [Volume of fractions 5 & 6 (ml) x Σ FID responses of fractions 5 & 6 x Σ Concentration of the standards (mg/ml) / Σ FID responses of the standards].

Table 6.4 lists the observed or calculated yields of the salt, and the actual and corrected masses of total EOM for comparison. The last six rows of data in this table show the results of an SFTE experiment in which a plug of Patchawarra sandstone from Garanjanie-4 (980524) was extracted only by DCM:MeOH (50:50 v/v). Salt yields decrease with extraction time (or volume), from 50.1 ppm in fraction 1 to 0.9 ppm in fraction 6. There is no need of any explanation, because methanol to salt is just like dichloromethane to EOM. Methanol dissolves the salt, and the yield decreases with the progress of the extraction as expected, because the content of saline pore water in the plug is limited.

As shown in Table 6.4, there is no evident relationship between salt content and reservoir formation. Neither does the salt content relate to the EOM content, permeability, porosity, residual water and oil saturation (Table 6.3). It is beyond the scope of this study to investigate the factors that control the salt content in

Table 6.4 Yields of salt and EOM from core plugs

Sample	Formation	Core plug (g)	Total extract (mg)	EOM calc.# (mg)	Salt (ppm)	Total salt (Fractions 5+6) (ppm)
980511-5*	Birkhead	81.8	57.4	9.2	590	944
980511-6*	Birkhead	81.8	30.6	1.6	354	
980512-5*	Birkhead	83.1	31.3	4.3	325	465
980512-6*	Birkhead	83.1	12.5	0.9	140	
980513-5*	Birkhead	111.0	38.8	15.4	211	254
980513-6*	Birkhead	111.0	7.0	2.2	44	
980514-5*	Birkhead	105.6	67.2	15.7	488	588
980514-6*	Birkhead	105.6	11.3	0.7	100	
980515-5*	Birkhead	103.4	27.8	1.4	256	435
980515-6*	Birkhead	103.4	19.3	0.7	180	
980516-5*	Birkhead	97.6	49.9	2.0	491	688
980516-6*	Birkhead	97.6	29.6	0.7	297	
980517-5	Murteree	116.6	20.2	6.8	435	657
980517-6	Murteree	116.6	9.9	2.6	222	
980518-5	Murteree	129.4	32.6	1.8	249	653
980518-6	Murteree	129.4	59.2	8.0	405	
980519-5*	Murta	32.0	1.5	0.4	35	69
980519-6*	Murta	32.0	1.3	0.2	34	
980522-5	Patchawarra	106.5	16.1	1.1	447	591
980522-6	Patchawarra	106.5	9.6	0.2	144	
980523-5	Patchawarra	110.3	14.2	0.9	228	298
980523-6	Patchawarra	110.3	6.6	0.3	70	
980528-5	Patchawarra	132.0	17.7	0.9	161	209
980528-6	Patchawarra	132.0	5.7	0.2	48	
980529-5*	Patchawarra	119.6	19.1	5.9	111	151
980529-6*	Patchawarra	119.6	8.9	4.1	41	
980531-5*	Patchawarra	104.2	10.0	1.9	78	176
980531-6	Patchawarra	104.2	10.1	1.0	98	
980536-5	Hutton	78.6	28.5	4.0	599	964
980536-6	Hutton	78.6	18.5	0.8	365	
980537-5	Hutton	104.1	17.8	0.9	601	1062
980537-6	Hutton	104.1	26.3	0.9	461	
980539-5	Patchawarra	112.3	42.2	11.2	300	374
980539-6	Patchawarra	112.3	8.5	0.7	74	
980540-5	Patchawarra	119.0	18.3	5.2	217	218
980540-6	Patchawarra	119.0	2.4	1.1	10	
980541-5	Birkhead	105.3	15.2	2.8	206	240
980541-6	Birkhead	105.3	2.8	0.7	34	
980542-5	Birkhead	112.7	13.2	4.0	195	286
980542-6	Birkhead	112.7	8.8	0.6	91	
980524-1	Patchawarra	113.7			50	
980524-2	Patchawarra	113.7			31	
980524-3	Patchawarra	113.7			7	
980524-4	Patchawarra	113.7			4	
980524-5	Patchawarra	113.7			1	
980524-6	Patchawarra	113.7			1	

* The yield of salt was calculated from Iatroscan data for these samples

\# EOM yield calculated from Iatroscan data these carrier bed and reservoir sandstones. Nevertheless, the salt obtained by SFTE does indicate that saline pore water co-exists with petroleum in all the sandstones sampled. Given their role as aquifers in the Eromanga Basin, it is perhaps not surprising that the highest salt contents (>900 ppm) were found in the Hutton and Birkhead formations. If the petroleum carries some soluble minerals from its source rocks, detailed analysis of the solutes might provide some help for oil-to-source correlation. Or if the petroleum leaves traces of source-related minerals along its migration route, this type of analysis could be a key to understanding the petroleum migration scenario.

6.2.1.6 Calibration Based on IatroScan Measurements

Identification of the inorganic salt halite in SFTE fractions 5 & 6 is a small but significant improvement for the SFTE technique. In previous studies at Cologne University, this material was treated as high molecular weight wax (D. Leythauser, personal communication, 1998). Such mis-identification would lead to over-estimation of the "adsorbed oil" and hence an incorrect understanding of the distribution of fluids in the pore network.

Calibration of SFTE fractions 5 & 6 using IatroScan data is another improvement to the conventional calculation procedure used in previous studies of this type. This calibration also allows quantification of the inorganic salt (Table 6.4). The calculation procedures used herein are expressed as in the following summary:

Total EOM (mg) = Aliphatics (mg) + Aromatics (mg) + Resins (mg) + Asphaltenes (mg)

Aliphatics (mg) = Solution volume (of any fraction) (ml) x Aliphatics concentration in the standard (mg/ml) x [FID response of sample/FID response of the standard]

Aromatics (mg) = Solution volume (of any fraction) (ml) x Aromatics concentration in the standard (mg/ml) x [FID response of sample/FID response of the standard]

Resins (mg) = Solution volume (of any fraction) (ml) x Resins concentration in the standard (mg/ml) x [FID response of sample/FID response of the standard]

Asphaltenes (mg) = Solution volume (of any fraction) (ml) x Asphaltenes concentration in the standard (mg/ml) x [FID response of sample/FID response of the standard]

Mass of salt (mg) = Weighed total EOM (mg) – Calibrated total EOM (mg)

As shown in Table 6.2, there are large differences between the masses of SFTE fractions 5 & 6 and the results after calibration by Iatroscan, especially when the EOM content of the plugs is low. For example, the weighed masses of fractions 5 & 6 in plug 980511 were 57.4 and 30.6 mg, respectively, but the actual masses are only 9.2 and 1.6 mg after the calibration (total EOM = 1339 ppm). The relative error is 70%. When the EOM content is low, this error is even larger. For plug 980518, weighed masses of fractions 5 & 6 were 32.6 and 59.2 mg, respectively, and the corrected masses are 1.8 and 8.0 mg (total EOM = 103 ppm). The relative error in this case is 196%. Unless corrected, this error seriously inflates the amount of "adsorbed oil", hence distorting our understanding of the distributions of fluid (including water and crude oil) and the estimation of petroleum loss *en route* during secondary migration. Caution should always be exercised whenever methanol and/or ethanol are used as extracting solvents.

6.2.2 BULK CHEMICAL COMPOSITION

Bulk chemical compositions (i.e. relative proportions of aliphatic hydrocarbons, aromatic hydrocarbons, resins and asphaltenes) of several types of EOM (viz. core plug SFTE fractions 1 through 6; and conventional bulk extracts of sandstone and source rock core samples) are compared with those of seven DST oils (Tables 6.5 & 6.6). It must be pointed out that the compositional data for these different types of extract are based on different measurements. Bulk compositions of the SFTE fractions were determined by IatroScan analysis. For the conventional cores of sandstone and source rock (samples 980544 to 980563) and the DST oils (samples 980564 to 980572), the compositions were determined by deaphaltening, MPLC fractionation of the maltenes and weighing of the four groups of components (saturated and aromatic hydrocarbons, resins and asphaltenes). Aliquots of DST oils were weighed and then evaporated under ambient laboratory conditions for 48 hr. The topped oils were MPLC fractionated without prior deasphaltening because of their very low asphaltene contents.

The bulk chemical compositions of all the core plug SFTE fractions are listed in Table 6.5 and those of the conventional core extracts and DST oils are compiled in Table 6.6. Notice that MPLC-derived compositions of 27 selected SFTE fractions are also listed in Table 6.6. It is evident that the MPLC and IatroScan measurements are broadly consistent. Bulk chemical compositions of representative examples of all three types of materials are depicted in Figure 6.3. To make it convenient for the following discussion, the term "polarity" will be used to describe the relative abundances of the four groups of components (viz. aliphatics, aromatics, resins and asphaltenes). The greater its content of saturated and aromatic hydrocarbons, the less polar is the EOM or oil.

6.2.2.1 DST Oils

Compared with conventional core extracts and the core plug SFTE fractions, DST oils have the lowest polarity (Tables 6.5 & 6.6; Figure 6.3). They contain no detectable asphaltenes, very little resins, but abundant aliphatic hydrocarbons. Aliphatic abundances in the oils range from 79.4% (980567) to 93.5% (980570), with an average of 87.1%. Few SFTE fraction-1s and sandstone bulk EOM samples reach this level. The average aromatic hydrocarbon and resin contents are 12.0% and 0.5%, respectively.

6.2.2.2 SFTE Fractions

Figure 6.3 depicts the systematic change in the bulk chemical composition of the SFTE fractions of Plug 980512. The aliphatic contents decrease from 86.2% in fraction 1, through 84.2, 77.8, 30.5 and 14.5%, to 12.2% in fraction 6, whereas the corresponding asphaltene contents increase in the order 2.9, 3.2, 4.3, 31.8, 60.0 and 67.8%. The average aliphatic content of the first three fractions is 82.7%, and that of the last two fractions is only 13.4% (notice that Fraction 4 is not counted because it is treated as a transitional extraction). In contrast, the average asphaltene content of the first three fractions is only 3.5%, and that of the last two is 63.9%.

Compared with the last two SFTE fractions and the EOM from the two source rock samples, the first three SFTE fractions have bulk chemical compositions that are the most similar to those of the DST oils (Figure 6.3; Tables 6.5 & 6.6). This explains why they are regarded as "free oil". They are less polar and less soluble in water than the other SFTE fractions. The "free oils" are what remains (under surface conditions)

Table 6.5 Bulk compositions of SFTE fractions based on Iatroscan measurements (1/3)

Fraction	Plug	EOM	Yield (% total EOM)		Relative concentration (% SFTE fraction)			
	[g]	[mg]	Relative	Cumulative	Aliph	Arom	Resin	Asph
980511-1	81.8	92.40	84.4	84.4	88.9	3.7	5.4	2.0
980511-2	81.8	3.70	3.4	87.8	85.0	3.3	8.8	3.0
980511-3	81.8	1.20	1.1	88.9	83.7	3.5	8.4	4.5
980511-4	81.8	1.40	1.3	90.2	29.6	1.8	45.8	22.8
980511-5	81.8	9.15	8.4	98.5	5.6	0.0	13.2	81.2
980511-6	81.8	1.63	1.5	100.0	0.0	0.0	13.3	86.7
980512-1	83.1	49.20	73.0	73.0	86.2	3.2	7.8	2.9
980512-2	83.1	6.50	9.6	82.6	84.2	2.7	9.9	3.2
980512-3	83.1	1.50	2.2	84.9	77.8	3.0	15.0	4.3
980512-4	83.1	1.80	2.7	87.5	30.5	0.8	36.9	31.8
980512-5	83.1	4.32	6.4	93.9	14.4	0.0	25.6	60.0
980512-6	83.1	0.89	1.3	95.3	12.2	0.0	20.0	67.8
980513-1	111.0	68.80	64.6	64.6	86.9	2.4	9.3	1.4
980513-2	111.0	15.80	14.8	79.5	80.9	3.5	13.5	2.1
980513-3	111.0	1.10	1.0	80.5	70.5	4.5	23.1	1.8
980513-4	111.0	3.20	3.0	83.5	33.6	1.7	42.5	22.1
980513-5	111.0	15.42	14.5	98.0	24.5	0.0	48.0	27.6
980513-6	111.0	2.15	2.0	100.0	14.0	0.0	62.1	23.9
980514-1	105.6	40.10	64.9	64.9	81.5	1.6	15.3	1.7
980514-2	105.6	3.10	5.0	69.9	61.2	2.1	34.1	2.6
980514-3	105.6	0.30	0.5	70.4	68.9	1.3	26.9	2.9
980514-4	105.6	1.90	3.1	73.5	16.8	0.2	49.0	34.0
980514-5	105.6	15.67	25.4	98.8	8.9	0.0	44.0	47.1
980514-6	105.6	0.73	1.2	100.0	17.3	0.0	24.1	58.6
980515-1	103.4	4.60	41.2	41.2	28.8	5.4	59.3	6.5
980515-2	103.4	1.20	10.8	52.0	9.3	3.6	75.2	11.9
980515-3	103.4	0.30	2.7	54.7	9.1	0.0	70.3	20.6
980515-4	103.4	2.30	20.6	75.3	0.0	0.0	32.1	67.9
980515-5	103.4	1.38	12.4	87.7	0.0	8.1	21.0	70.9
980515-6	103.4	1.37	12.3	100.0	0.0	0.0	10.7	89.3
980516-1	97.6	1.20	20.2	20.2	43.5	1.5	52.7	2.3
980516-2	97.6	0.20	3.4	23.6	29.7	0.0	63.8	6.6
980516-3	97.6	0.50	8.4	32.0	31.8	0.0	47.1	21.1
980516-4	97.6	1.40	23.6	55.6	5.8	0.0	45.8	48.4
980516-5	97.6	1.97	33.2	88.8	0.0	0.0	27.0	73.0
980516-6	97.6	0.66	11.2	100.0	7.1	6.1	11.9	75.0
980517-1	116.6	43.30	58.9	58.9	83.9	2.9	11.4	1.9
980517-2	116.6	5.80	7.9	66.8	83.5	6.0	9.1	1.4
980517-3	116.6	0.40	0.5	67.4	83.5	4.7	10.5	1.3
980517-4	116.6	14.60	19.9	87.2	61.6	3.7	23.7	11.1
980517-5	116.6	6.80	9.3	96.5	54.0	2.6	26.3	17.0
980517-6	116.6	2.57	3.5	100.0	57.6	2.2	27.3	12.9

Table 6.5 continued (2/3)

Fraction	Plug [g]	EOM [mg]	Yield (% total EOM) Relative	Cumulative	Relative concentration (% SFTE fraction) Aliph	Arom	Resin	Asph
980518-1	129.4	0.70	5.2	5.2	49.3	6.8	39.6	4.3
980518-2	129.4	0.80	6.0	11.2	58.6	6.8	30.8	3.9
980518-3	129.4	0.00	0.0	11.2	50.1	7.3	39.1	3.5
980518-4	129.4	2.00	15.0	26.2	17.0	0.9	61.8	20.2
980518-5	129.4	1.83	13.7	39.9	16.3	0.0	22.2	61.4
980518-6	129.4	8.04	60.1	100.0	11.1	0.0	41.0	47.9
980519-1	32.0	0.50	15.1	15.1	15.7	6.2	58.8	19.3
980519-2	32.0	0.80	24.2	39.3	28.8	6.2	52.7	12.2
980519-3	32.0	0.70	21.2	60.4	18.9	0.0	48.2	33.0
980519-4	32.0	0.70	21.2	81.6	14.4	0.8	49.6	35.2
980519-5	32.0	0.37	11.3	92.9	8.3	2.8	43.0	45.8
980519-6	32.0	0.23	7.1	100.0	20.4	6.1	55.2	18.3
980522-1	106.5	4.50	65.1	65.1	70.1	1.8	23.0	5.1
980522-2	106.5	0.00	0.0	65.1	67.6	0.0	16.2	16.2
980522-3	106.5	0.00	0.0	65.1	34.3	0.0	24.0	41.8
980522-4	106.5	1.10	15.9	81.0	11.6	2.0	21.0	65.4
980522-5	106.5	1.09	15.8	96.8	0.0	0.0	13.3	86.7
980522-6	106.5	0.22	3.2	100.0	0.0	0.0	34.3	65.7
980523-1	110.3	17.90	89.5	89.5	83.3	1.7	11.8	3.2
980523-2	110.3	0.10	0.5	90.0	76.6	3.5	14.7	5.1
980523-3	110.3	0.50	2.5	92.5	65.7	3.5	14.9	15.9
980523-4	110.3	0.30	1.5	94.0	6.9	0.4	44.3	48.4
980523-5	110.3	0.91	4.5	98.6	11.1	0.0	18.6	70.2
980523-6	110.3	0.28	1.4	100.0	17.7	0.0	22.3	60.1
980528-1	132.0	14.50	79.3	79.3	67.9	4.0	23.2	4.9
980528-2	132.0	1.60	8.7	88.0	57.9	5.2	32.0	4.9
980528-3	132.0	0.00	0.0	88.0	47.3	5.8	31.7	15.1
980528-4	132.0	1.10	6.0	94.0	10.3	0.2	26.8	62.7
980528-5	132.0	0.88	4.8	98.8	44.6	0.0	12.7	42.7
980528-6	132.0	0.21	1.2	100.0	21.9	0.0	19.1	59.0
980529-1	119.6	0.00	0.0	0.0	50.1	1.1	35.8	13.0
980529-2	119.6	0.00	0.0	0.0	66.6	5.9	25.8	1.8
980529-3	119.6	0.00	0.0	0.0	73.6	4.0	19.4	2.9
980529-4	119.6	2.00	16.2	16.2	49.1	0.8	27.8	22.3
980529-5	119.6	5.86	47.4	63.6	76.4	1.6	14.7	7.2
980529-6	119.6	4.50	36.4	100.0	69.6	1.7	20.9	7.8
980531-1	104.2	10.50	54.7	54.7	76.3	3.3	17.4	3.0
980531-2	104.2	0.80	4.2	58.9	47.0	4.7	43.5	4.7
980531-3	104.2	0.00	0.0	58.9	36.8	3.7	55.2	4.2
980531-4	104.2	5.00	26.1	85.0	24.1	2.5	32.4	41.0
980531-5	104.2	1.86	9.7	94.7	42.4	0.0	30.7	26.9
980531-6	104.2	1.02	5.3	100.0	48.5	1.7	15.9	33.9

Table 6.5 continued (3/3)

Fraction	Plug	EOM	Yield (% total EOM)		Relative concentration (% SFTE fraction)			
	[g]	[mg]	Relative	Cumulative	Aliph	Arom	Resin	Asph
980536-1	78.6	11.00	57.2	57.2	78.3	2.7	16.0	3.0
980536-2	78.6	2.20	11.4	68.6	86.2	2.2	9.5	2.1
980536-3	78.6	0.40	2.1	70.7	84.2	1.9	8.7	5.2
980536-4	78.6	0.80	4.2	74.8	40.7	1.7	46.5	11.1
980536-5	78.6	4.02	20.9	95.7	13.9	0.0	28.0	58.0
980536-6	78.6	0.82	4.3	100.0	23.7	0.0	25.0	51.3
980537-1	104.1	3.40	61.3	61.3	27.4	1.7	64.6	6.3
980537-2	104.1	0.00	0.0	61.3	27.9	1.9	48.9	21.2
980537-3	104.1	0.00	0.0	61.3	39.4	3.5	28.9	28.2
980537-4	104.1	0.30	1.6	66.7	2.8	0.0	56.2	41.1
980537-5	104.1	0.92	16.6	83.3	7.9	0.0	15.3	76.9
980537-6	104.1	0.93	4.8	100.0	0.0	0.0	9.6	90.4
980539-1	112.3	142.70	88.9	88.9	82.1	4.6	10.6	2.7
980539-2	112.3	2.70	1.7	90.5	79.9	4.7	12.7	2.8
980539-3	112.3	0.80	0.5	91.0	79.4	4.4	13.4	2.9
980539-4	112.3	2.50	1.6	92.6	6.6	0.0	54.8	38.6
980539-5	112.3	11.16	6.9	99.5	0.3	0.0	40.8	58.9
980539-6	112.3	0.74	0.5	100.0	17.1	5.2	14.5	63.3
980540-1	119.0	49.20	62.5	62.5	67.1	2.4	26.3	4.1
980540-2	119.0	4.70	6.0	68.5	82.8	2.7	11.9	2.7
980540-3	119.0	1.80	2.3	70.8	82.5	2.4	11.5	3.6
980540-4	119.0	16.70	21.2	92.0	13.9	0.0	57.6	28.5
980540-5	119.0	5.22	6.6	98.6	7.9	0.0	30.7	61.4
980540-6	119.0	1.09	1.4	100.0	7.1	0.0	48.3	44.6
980541-1	105.3	66.70	92.8	92.8	80.2	3.3	12.4	4.1
980541-2	105.3	0.40	0.6	93.3	81.7	2.0	14.1	2.3
980541-3	105.3	0.10	0.1	93.4	68.0	0.0	17.5	14.5
980541-4	105.3	1.20	1.7	95.1	1.4	0.0	50.6	48.0
980541-5	105.3	2.77	3.9	99.0	0.0	0.0	14.8	85.2
980541-6	105.3	0.74	1.0	100.0	9.2	0.2	33.8	56.7
980542-1	112.7	9.90	58.9	58.9	45.9	2.2	39.9	12.1
980542-2	112.7	0.20	1.2	60.1	42.1	2.0	44.5	11.4
980542-3	112.7	0.20	1.2	61.2	34.1	0.0	24.0	41.9
980542-4	112.7	1.90	11.3	72.5	0.9	0.0	43.7	55.4
980542-5	112.7	3.99	23.7	96.2	0.0	0.0	12.3	87.7
980542-6	112.7	0.63	3.8	100.0	0.0	0.0	11.8	88.2

1. Extract mass of Fraction 5 and 6 were calibrated based on IatroScan measurements.
2. Aliphatics, aromatics, resin and asphaltene were quantified based on a standard mixture containing:
   aliphatics = 10.72 mg/L
   aromatics =0.92 mg/mL
   resin = 2.57 mg/mL
   asphaltene = 0.58 mg/mL

Table 6.6 MPLC yields for core plugs, cores and DST oils

Sample	Sample type	EOM (mg)	Asphaltene mg	Asphaltene % EOM	Maltene mg	Maltene % EOM	Aliphatics mg	Aliphatics % EOM	Aromatics mg	Aromatics % EOM	Resins mg	Resins % EOM
980511-1	Plug	38.5	8.2	21.3	30.3	78.7	25.9	67.3	2.4	6.2	2.0	5.2
980511-5	Plug	9.2	8.8	95.6	0.4	4.4	0.1	1.1	0.0	0.0	0.3	3.3
980512-1	Plug	35.1	6.2	17.7	28.9	82.3	24.9	70.9	1.5	4.3	2.5	7.1
980512Σ	Plug	7.6	5.6	73.7	2.0	26.3	1.4	18.4	0.0	0.0	0.6	7.9
980513-1	Plug	38.2	5.7	14.9	32.5	85.1	26.9	70.4	1.8	4.7	3.8	9.9
980513-5	Plug	15.4	10.3	66.9	5.1	33.1	3.2	20.8	0.4	2.6	1.5	9.7
980514-1	Plug	33.4	3.0	9.0	30.4	91.0	24.7	74.0	0.9	2.7	4.8	14.4
980514-5	Plug	15.7	14.9	94.9	0.8	5.1	0.3	1.9	0.0	0.0	0.5	3.2
980515-1	Plug	4.6	2.0	43.5	2.6	56.5	1.1	23.9	0.1	2.2	1.4	30.4
980515Σ	Plug	4.0	4.0	100.0								
980517-1	Plug	36.1	10.4	28.8	25.7	71.2	20.8	57.6	1.5	4.2	3.4	9.4
980517Σ	Plug	14.0	3.5	25.0	10.5	75.0	7.6	54.3	0.8	5.7	2.1	15.0
980522-1	Plug	4.5	0.8	17.8	3.7	82.2	3.1	68.9	0.0	0.0	0.6	13.3
980523-1	Plug	17.9	1.6	8.9	16.3	91.1	13.6	76.0	0.7	3.9	2.0	11.2
980528-1	Plug	14.5	-0.8	-5.5	15.3	105.5	12.4	85.5	0.5	3.4	2.4	16.6
980531-1	Plug	10.5	0.2	1.9	10.3	98.1	7.9	75.2	0.7	6.7	1.7	16.2
980531Σ	Plug	6.1	4.1	67.2	2.0	32.8	1.2	19.7	0.1	1.6	0.7	11.5
980536-1	Plug	11.0	1.6	14.5	9.4	85.5	7.7	70.0	0.7	6.4	1.0	9.1
980536-5	Plug	4.0	3.4	85.0	0.6	15.0	0.3	7.5	0.1	2.5	0.2	5.0
980539-1	Plug	35.7	6.1	17.1	29.6	82.9	25.6	71.7	1.8	5.0	2.2	6.2
980539Σ	Plug	12.3	7.8	63.4	4.5	36.6	0.4	3.3	0.2	1.6	3.9	31.7
980540-1	Plug	35.1	5.9	16.8	29.2	83.2	21.5	61.3	1.3	3.7	6.4	18.2
980540Σ	Plug	17.7	11.6	65.5	6.1	34.5	1.8	10.2	0.1	0.6	4.2	23.7
980541-1	Plug	37.0	8.1	21.9	28.9	78.1	23.7	64.1	2.2	5.9	3.0	8.1
980541Σ	Plug	5.4	5.1	94.4	0.3	5.6	0.0	0.0	0.0	0.0	0.3	5.6
980542-1	Plug	9.9	2.9	29.3	7.0	70.7	4.2	42.4	0.4	4.0	2.4	24.2
980542Σ	Plug	6.0	6.0	100.0					0.0	0.0	0.1	1.7
980544	Core	34.3	24.3	70.8	10.0	29.2	2.6	7.6	1.8	5.2	5.6	16.3
980545	Core	7.6	4.5	59.2	3.1	40.8	0.5	6.6			2.6	34.2
980546	Core	50.3	35.3	70.2	15.0	29.8	3.7	7.4	4.7	9.3	6.6	13.1
980547	Core	15.8	12.8	81.0	3.0	19.0	0.4	2.5	0.6	3.8	2.0	12.7
980548	Core	48.8	34.4	70.5	14.4	29.5	2.1	4.3	3.1	6.4	9.2	18.9
980549	Core	49.7	35.7	71.8	14.0	28.2	3.4	6.8	4.5	9.1	6.1	12.3
980550	Core	9.8	4.2	42.9	5.6	57.1	3.6	36.7	0.2	2.0	1.8	18.4
980552	Core	42.6	33.3	78.2	9.3	21.8	1.6	3.8	3.6	8.5	4.1	9.6
980554	Core	14.1	5.7	40.4	8.4	59.6	5.1	36.2	0.8	5.7	2.5	17.7
980555	Core	40.4	31.5	78.0	8.9	22.0	1.7	4.2	2.9	7.2	4.3	10.6
980556	Core	33.7	25.8	76.6	7.9	23.4	0.9	2.7	2.0	5.9	5.0	14.8
980557	Core	7.8	4.8	61.5	3.0	38.5	1.2	15.4			1.8	23.1
980558	Core	35.5	1.5	4.2	34.0	95.8	28.3	79.7	2.4	6.8	3.3	9.3
980559	Core	60.6	3.8	6.3	56.8	93.7	47.5	78.4	3.4	5.6	5.9	9.7
980560	Core	44.5	31.0	69.7	13.5	30.3	4.6	10.3	2.6	5.8	6.3	14.2
980561	Core	57.3	14.6	25.5	42.7	74.5	33.5	58.5	2.2	3.8	7.0	12.2
980562	Core	43.1	26.2	60.8	16.9	39.2	8.2	19.0	1.3	3.0	7.4	17.2
980563	Core	48.6	31.0	63.8	17.6	36.2	3.1	6.4	3.8	7.8	10.7	22.0
980564	Oil	51.0			15.6		14.1	90.4	1.4	9.0	0.1	0.6
980565	Oil	51.8			27.0		23.1	85.6	3.5	13.0	0.4	1.5
980568	Oil	51.4	Total		27.6	Total	25.1	90.9	2.1	7.6	0.4	1.4
980569	Oil	52.8	Mass		33.6	Mass	28.6	85.1	4.2	12.5	0.8	2.4
980570	Oil	42.4			12.3		11.5	93.5	0.8	6.5	0.0	0.0
980571	Oil	46.9			16.3		15.2	93.3	1.1	6.7		
980572	Oil	48.9			23.8		20.4	85.7	2.8	11.8	0.6	2.5

Σ = Combination of fractions 5 and 6 from SFTE

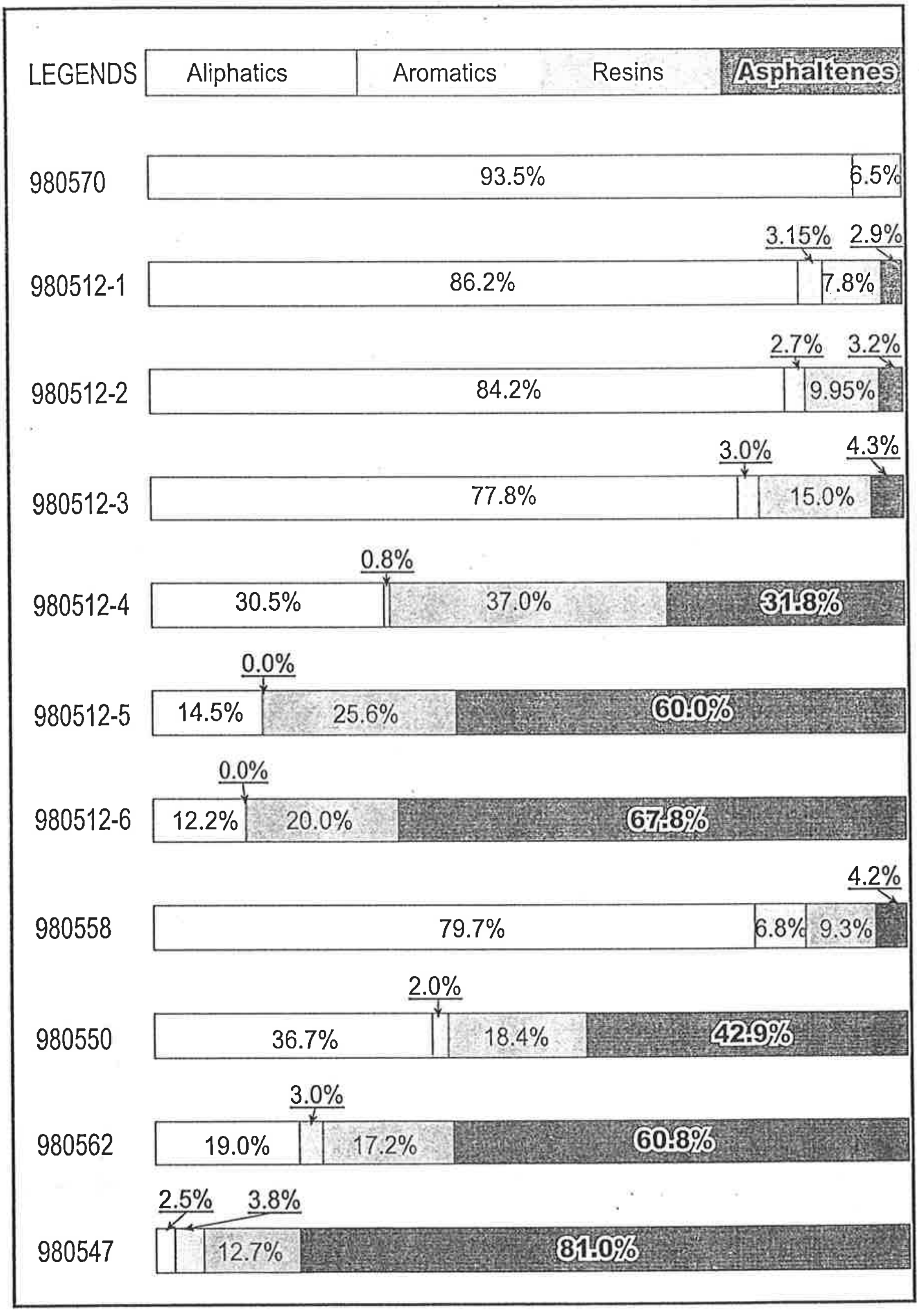


Figure 6.3 Bar diagram comparing the bulk compositions of a DST oil (980570), SFTE fractions of residual oil in a sandstone core (980512-1 to 6), bulk sandstone extracts (980558 & 980550) and EOM from source rocks (980562 & 980547).

of the mobile hydrocarbon phase within in a migrating "petroleum river" (under subsurface conditions). They occupy the central part of each individual pore within thc connected pore network of the carrier bed and/or reservoir sandstone.

The last two SFTE fractions comprise predominantly resins and asphaltenes (average = 86.7%). This is why they are regarded as "adsorbed oil". Since this oil is more polar and hence hydrophilic, it is adsorbed on the water mantling the pore wall where it forms a relatively static bipolar phase that "lubricates" petroleum migration.

Most of the other measured plugs show a similar pattern of bulk chemical composition across the six SFTE fractions. A representative exception, in which aliphatic hydrocarbons are not the dominant components in the first three SFTE fractions, is plug 980529. Here the average aliphatic content of the last two fractions (73.0%) is even larger than that of the first three (55.3%: Table 6.5). This is caused by errors in the IatroScan measurements that arise when there is not an adequate amount of EOM. To meet the required sensitivity for common plugs, the standard prepared for the IatroScan measurements of the SFTE fractions comprises mainly aliphatic hydrocarbons (72.3%; see footnote 2 of Table 6.5 for concentrations of the other components). Whenever the aliphatic content falls below the detection limit, a large error occurs because of "noise" peaks in the FID and/or the response of residuals from the last measurement. Note: the IatroScan rods are used repeatedly and cleaned two times by burning with hydrogen flame of the FID after each sample measurement. The weights of the first three SFTE fractions obtained from this plug are all zero (Table 6.2). The other exceptions are plugs 980515, 516, 518, 519, 531 & 537 (Tables 6.2 & 6.5). The yields of one or more of their SFTE fractions were too low for reliable IatroScan measurements.

6.2.2.3 Extracts from Conventional Sandstone Cores

The bulk chemical compositions of Soxhlet extracts of eight conventional sandstone cores are listed in Table 6.6 (samples 980544, 545, 550, 554, 557–559 & 561). Two of these extracts (550 and 558, from the Patchawarra Formation in Garanjanie-1 and Wancoocha-3, respectively) are selected to illustrate the pertinent features of their bulk compositions (Figure 6.3). As expected, their compositions fall between those of the "free oils" and "adsorbed oils". Of the two extracts, the second is far less polar (79.7% aliphatics, 6.8% aromatics, 9.3% resins and 4.2% asphaltenes) than the first (36.7% aliphatics, 2.0% aromatics, 18.4% resins and 42.9% asphaltenes), possibly reflecting differences in their respective pore size distributions.

It is reasonable for the chemical composition of the sandstone bulk extract to fall between those of the "free oil" and "adsorbed oil", because as the whole EOM it is the composite of all the SFTE fractions.

6.2.2.4 Extracts from Source Rocks

Considering the preferential expulsion of aliphatic hydrocarbons from non-marine source rocks during primary migration and the strong adsorption of polar compounds to the source rock matrix, it is likely that the EOMs of the shales, siltstones and coals (Table 6.1) will have the greatest polarities. In fact the experimental data show that their polarities are even greater than those of the "adsorbed oil" SFTE fractions. For example, siltstone extract 980547 (Dirkala-3, Murta, Rc = 0.59%) contains only 2.5% aliphatics and 3.8% aromatics, but its asphaltene content is 81.0% (Table 6.6; Figure 6.3). EOM from the somewhat more mature siltstone 980562 (Wancoocha-4, Birkhead, Rc = 0.68%) is composed of 19.0% aliphatics, 3.0% aromatics, 17.2% resins and 60.8% asphaltenes. Bulk chemical compositions of EOM from the other source rock samples (980546, 548, 549, 555, 556, 560, 562 & 563) are listed in Table 6.6.

6.2.3 MATURITY

Various molecular maturity parameters were measured in most of the SFTE fraction 1 samples, and in all the conventional core extracts (reservoir and source) and DST oils. These maturity data are compiled in Table 6.1 (page 3). Of the fifteen sandstone core plugs which yielded sufficient "free oil" (SFTE fraction 1) for GC-MS analysis, only three also had enough "adsorbed oil" (fractions 5 & 6, separately or combined) for the same analysis. These plugs, and the MPI-derived Rc values of their respective "free oil" and "adsorbed oil" fractions, are as follows:

Plug	*Well/Reservoirs*	*Free (fraction 1)*	*Adsorbed (fractions 5 & 6)*
980513	Dirkala-1 (Birkhead)	0.71%	0.74%
980517	Dirkala-2 (Murteree)	0.81%	0.80%
980531	Thurakinna-3 (Patchawarra)	1.00%	1.04%

Contrary to the findings of Schwark et al. (1997), the "free oils" in these reservoir sands are not consistently more mature than the "adsorbed oils". There is no obvious explanation for this, and the maturity data on the combined fractions 5 & 6 will not be used in the following discussion. The maturity of the "free oil" fractions is discussed further in Section 6.3.

6.2.4 REVISED PORE-SCALE MODEL OF FLUID DISTRIBUTION

Based on the bulk compositions of the "free oils" and "adsorbed oils" recovered sequentially by SFTE, and the NaCl contents of the pore waters removed in extraction steps 5 & 6, a conceptual distribution pattern may be deduced for the fluids present in the reservoir/carrier beds of the study area. This model of fluid distribution can be described, by reference to Figure 6.1, in the following manner:

- Within sandstone carrier beds and/or reservoir rocks, pore sizes and the throats connecting them are not uniform.
- Prior to the arrival of petroleum, the pores are occupied by water in which various kinds of inorganic salts are dissolved.
- About half of the previously existing water in the pore network is replaced by migrating petroleum only when the pores and the throats connecting them are large enough.
- The other half of the pore water is adsorbed on the pore walls where it exists as layer of immobile water.
- The polar parts of the petroleum migration front are adsorbed on the water mantling the mineral surfaces, forming a discrete layer of "adsorbed oil". The result is a layer similar to a bipolar cell membrane (Figure 6.1). Thus, the "adsorbed oil" wets the main secondary migration conduits for the subsequent oil

charge.

- The later arriving crude oil – the so-called “free oil” – occupies the central parts of the larger connected pores that form the migration pathway.
- The “adsorbed oils” are richer in polar compounds, whereas the “free oils” are richer in aliphatic and aromatic hydrocarbons.
- In these non-marine Permian and Jurassic reservoirs, the “free oils” and “adsorbed oils” do not differ significantly in their maturity.

6.3 SECONDARY PETROLEUM MIGRATION SCENARIO

6.3.1 INTRODUCTION

Oil generation, migration and preservation in the Cooper/Eromanga province have long been investigated in a way that treats the two basins as separate petroleum systems (Alexander et al., 1988; Heath et al., 1989; Jenkins, 1989; McKirdy, 1982; Michaelsen and McKirdy, 1989; Powell et al., 1989; Tupper and Burckhardt, 1990). After nearly 20 years of disputation over the source(s) of the oils in the two basins, the hydrocarbon generation-migration-accumulation scenario is still not clear.

Exploration activity has concentrated in the Eromanga Basin where it overlies the Cooper Basin, largely because the oil in Eromanga reservoirs is regarded by many as the result of vertical migration from Permian source rocks (Alexander, 1996a). After studying the vertical and horizontal distribution of hydrocarbon accumulations in the Cooper/Eromanga petroleum system, Heath et al. (1989) proposed that most of the Eromanga-reservoired hydrocarbons were derived from Cooper Basin source rocks, having migrated vertically into the Eromanga sequence, where their physical and chemical characteristics were significantly altered. Exploratory drilling in the Lake Hope Block during 1988 seems to support this model. Jenkins (1989), based on his studies of Eromanga-specific biomarkers, also suggested that a considerable proportion of the Eromanga-reservoired oil was derived from source rocks in the Cooper Basin.

The lateral and vertical distributions of Rc values for the DST oils/condensates, residual oils and source rock extracts in the present suite of samples from the Thurakinna-Garanjanie-Dirkala-Wancoocha area, suggest that petroleums reservoired in this part of the Nappamerri Trough are the result of multiple charging and in-reservoir mixing.

6.3.2 CALCULATED VITRINITE REFLECTANCE (RC)

There exist at least six proven source rock units in the Cooper/Eromanga petroleum province. These include the coals and shales of the Patchawarra and Toolachee Formations in the Cooper Basin; and the Poolawanna (shale, coal), Birkhead (shale, coal) and Murta (shale, siltstone) Formations in the Eromanga Basin. Cambrian carbonates in the underlying Warburton Basin could also be the source of hydrocarbons reservoired in the Mooracoochie Volcanics of the Sturt Field, and other especially mature petroleum accumulated elsewhere in the Cooper/Eromanga Basins. Molecular source and maturity parameters of the type listed in Table 6.1 are the tracers by which the history of hydrocarbon expulsion and migration can be reconstructed. When petroleum in a compartmentalised reservoir has a wide range of maturity values, it must be a mixture of hydrocarbons from more than one source (mixed sourcing), and/or more than one period of expulsion from the same source rock (multiple charging).

Although vitrinite reflectance (Ro, %) is the most credible maturity parameter, it has many limitations. Ro may be measured from coals and other carbonaceous sediments (shales, siltstones) which contain sufficient vitrinite phytoclasts for a statistically valid measurement. However, the content of vitrinite is often very low or even absent in other lithologies, such as carbonate and sandstone. The need for a complementary maturity parameter is most obvious in the case of crude oils. Rc, a calculated value of vitrinite reflectance based on the methylphenanthrene index (MPI: Table 5.2), is a maturity parameter that is equally applicable to reservoired oil, residual oil in sandstone and hydrocarbons in source rocks. Radke and Welte (1983) found that when the Ro of Type III kerogen changes within the hydrocarbon generation window (Ro = 0.65-1.35%), there exists a linear relationship between it and MPI (viz. $Rc = 0.6MPI + 0.4$). Ro is the *measured* vitrinite reflectance and Rc refers to *calculated* vitrinite reflectance based on the MPI. Boreham et al. (1988) proposed an alternative calibration based on Australian coals and carbonaceous shales. However, Alexander et al. (1988) used the original calibration of Radke and Welte in their study of oils and source rocks in the Eromanga and Cooper Basins (also see Section 6.3.3).

Oil maturity (Rc) may be compared with the reservoir and source maturity (Ro) to define expulsion maturity windows for oil expulsion from Cooper and Eromanga source rocks. Recent work by Hunt et al. (1989) on hydrocarbon distributions in the Cooper Basin proposed that its source rocks have expelled significant hydrocarbons only at maturity levels greater than 0.95% Ro. The results obtained in the present study for intra-Permian oils and residual oils (see section 6.3.7.3) suggest that a more likely maturity threshold is 0.8% Ro. When calculating MPI values in the present study, 1-MP was normalised to 9-MP in those samples for which 1-MP exceeds 9-MP, which is very common in Eromanga-derived hydrocarbons because of their araucariacean input. The resulting MPI and Rc data on the SFTE extracts (fraction 1), bulk sandstone and source rock extracts and DST oils (Table 6.1) were investigated to determine their implications (if any) for secondary migration of hydrocarbons in the study area.

As an internal check on data quality, vitrinite reflectance was measured in five coals (Table 6.1). The resulting Ro values are in good agreement with their corresponding Rc values, depending on which calibration is used, as shown below:

Sample	Well/Formation	Ro %	Rc % (1)	Rc % (2)
980546	Dirkala-2 (Epsilon)	0.69	0.79	0.68
980549	Garanjanie-1 (Patchawarra)	0.73	0.83	0.72
980556	Wancoocha-1 (Patchawarra)	0.71	0.81	0.70
980560	Wancoocha-3 (Patchawarra)	0.66	0.78	0.67
980563	Wancoocha-4 (Birkhead)	0.69	0.67	0.54

(1) Radke and Welte (1983) calibration (2) Boreham et al. (1988) calibration

Although based on a very small number of relatively immature coals, these data appear to suggest that calibration (1) is appropriate for Jurassic samples, whereas calibration (2) should be used for Permian samples. However, the Permian DST and residual oils are in fact more mature than the above coals, and fall in the range (>0.8% Rc) where calibration (1) is applicable.

6.3.3 PRESENTATION OF RC DATA

The Rc data in Table 6.1 are projected onto a cross section of the study area (Figure 6.4) to illustrate the stratigraphic variation of oil maturity and allow its comparison with reservoir maturity.

In general, the maturity of the DST oils increases with reservoir age. The Patchawarra oil at Wancoocha-2 is the most mature (Rc = 0.82%). The Birkhead oils at Dirkala-1 (Rc = 0.71%) and Wancoocha-2 (Rc = 0.69%) are somewhat less mature, whereas those in the Murta Formation at Wancoocha-6, Dirkala-1 and Garanjanie-1 display the lowest maturity (Rc = 0.63–0.69%).

Similarly among the residual oils, there exists a general trend of increasing Rc with sample depth in the three fields with stacked reservoirs (Figure 6.4). However, within individual reservoirs (e.g. the Hutton at Dirkala-1 and Wancoocha-3; and the Birkhead at Dirkala-1 and Wancoocha-4) there is considerable variation in oil maturity. This indicates that there is no unique source for all the reservoired oils in this part of the Cooper and Eromanga Basins.

6.3.4 A GENERALISED MODEL OF SECONDARY MIGRATION

In order to explain the distribution of Rc data in the geological setting shown in Figure 6.4, a new model of oil generation, migration and accumulation is proposed for the southwestern margin of the Cooper and Eromanga petroleum province (Figure 6.5). In summary, petroleum reservoired in the study area is the result of multiple sources and/or multiple charging. Petroleum in some units (notably the Hutton Sandstone) is heterogeneous in its heavy-end maturity (Rc), indicating that the reservoir is compartmentalised. Most Murta oils are mixtures of hydrocarbons formed both *in situ* and elsewhere (e.g. in the Birkhead, Poolowanna, Toolachee or Patchawarra

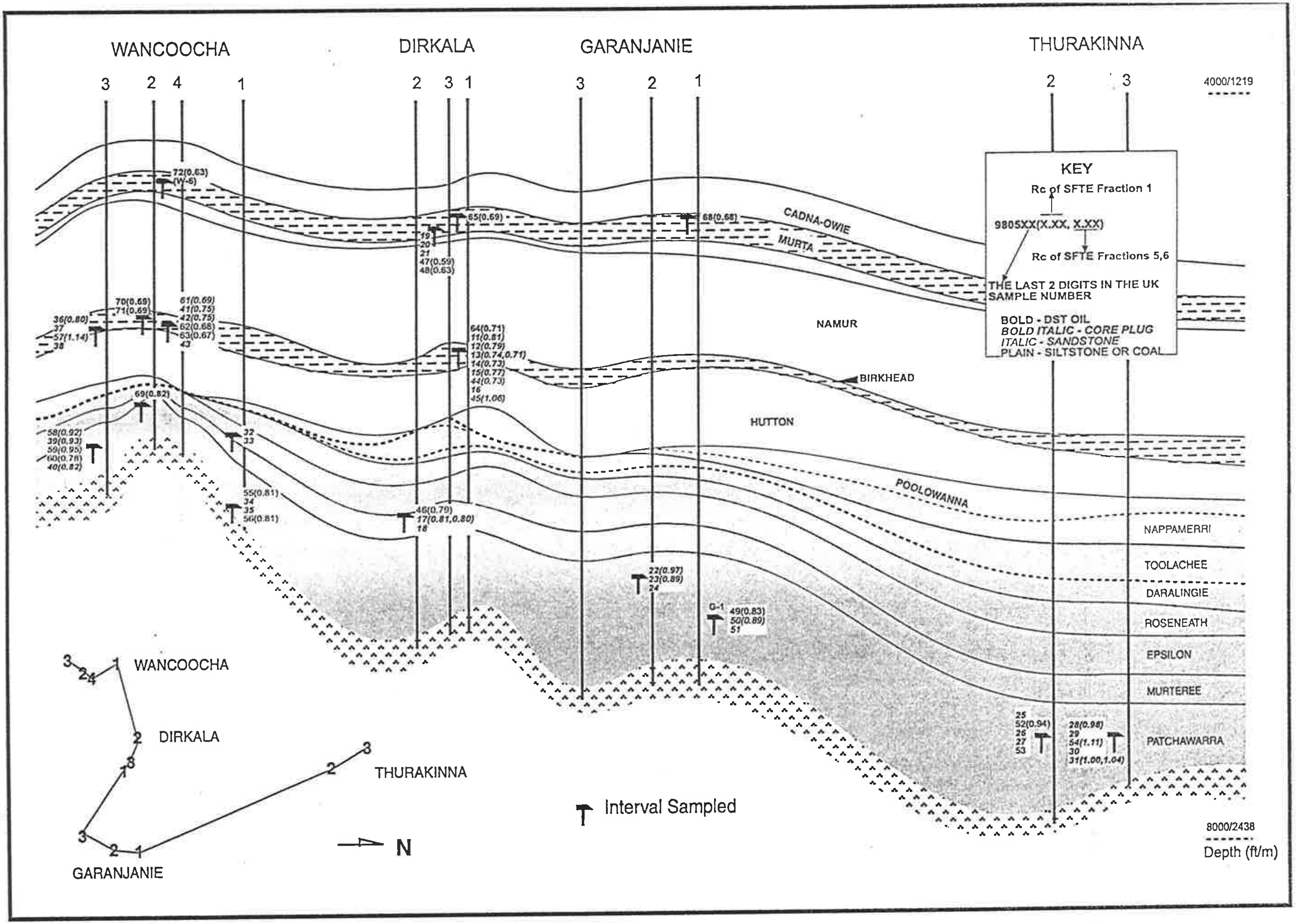


Figure 6.4 Cross section of the study area showing stratigraphic relationship of core plugs, conventional core samples and DST oils with their Rc data

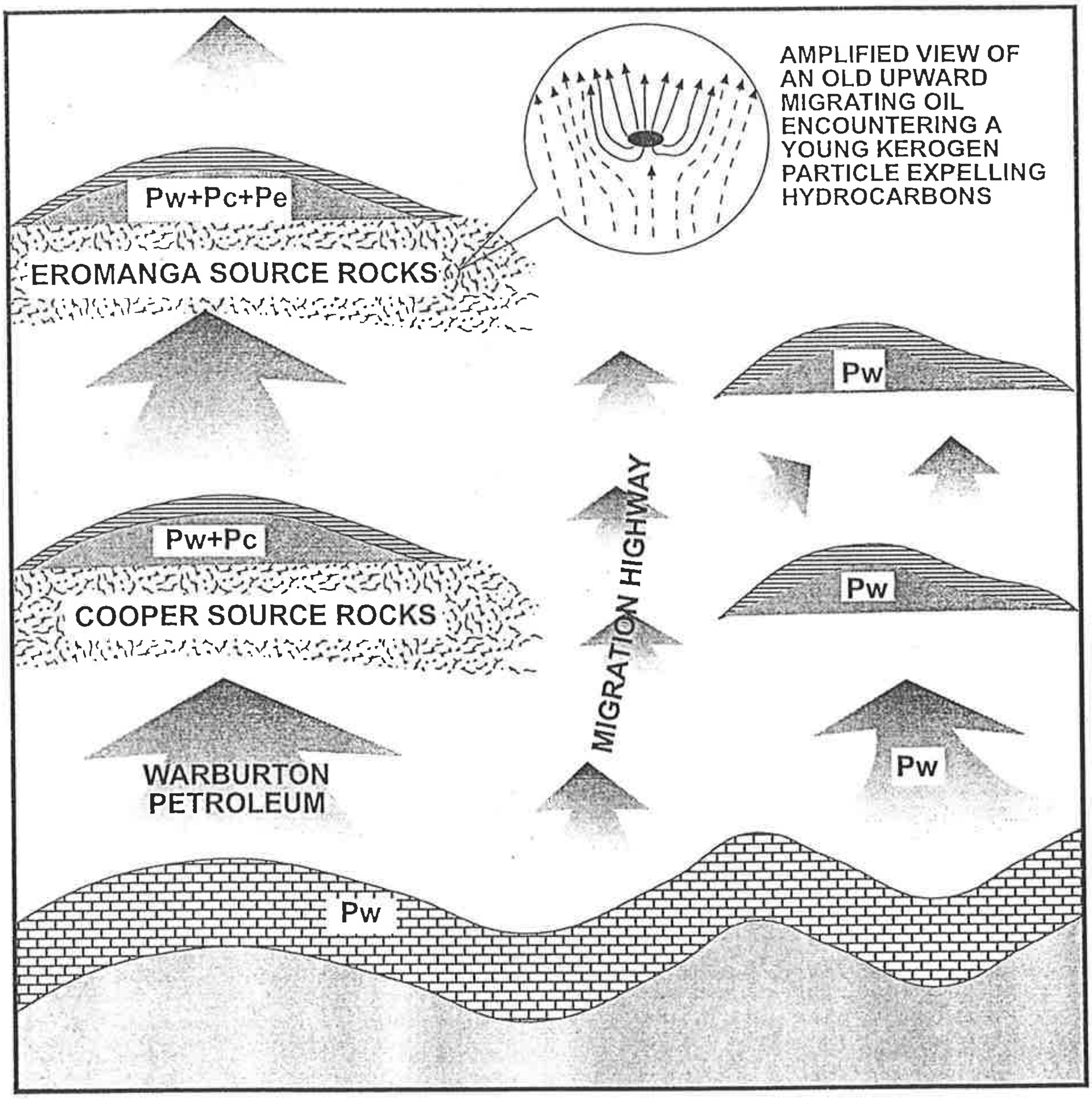


Figure 6.5 Cartoon illustrating the essential elements of the proposed petroleum generation-migration-accumulation scenario

Pw = Petroleum derived from Warburton Basin
Pc = Petroleum derived from Cooper Basin
Pe = Petroleum derived from Eromanga Basin
Migration Highway = migration pathway via sandstone carrier beds and/or active faults

Formations). Similar multi-sourcing situations are possible in Jurassic (Birkhead, Hutton) oil accumulations, and may even have happened in Permian reservoirs (Murteree, Patchawarra) if they received part of their hydrocarbon charge from the underlying Warburton Basin.

The following observations, based on the Rc data from the study area, support this model:

1. Oils accumulated in the Murta Formation are more mature than local putative source rocks. The average Rc value for intra-Murta source rocks at Dirkala is 0.62%, but that of the DST oil is 0.69%. This indicates that there has been an input of more mature hydrocarbons from a deeper source.

2. Source rocks in the Birkhead Formation at Wancoocha (Rc ~ 0.67%) are less mature than the DST oil (Rc = 0.69%) and residual oils in adjacent sandstone reservoir rocks or carrier beds (average Rc = 0.83%), implying mixing of Cooper (and maybe Warburton)-derived hydrocarbons in the Birkhead/Hutton reservoirs. Particularly noteworthy are the two extraordinarily mature residual oils from the base of the Birkhead/Hutton oil column at Dirkala (Rc = 1.06%) and Wancoocha (Rc = 1.14%). These contain biomarker evidence (discussed in Section 6.5) of having come (at least partly) from more mature source rocks in the underlying Cooper (or perhaps Warburton) Basin.

3. Residual oils in sandstones of the Patchawarra Formation are more mature than the local interbedded coals. This is strong evidence that there must exist a deeper petroleum kitchen, either in the underlying Warburton carbonate sequence or, more likely, further north where the Patchawarra Formation is buried more deeply (Figure 6.4). The latter scenario implies significant *lateral* secondary migration.

4. The deepest core plug from the Patchwarra Formation in Thurakinna-3 also contains residual oil with elevated maturities (Rc = 1.00–1.04%). These values are larger than that of the local coal in Thurakinna-2 (Rc = 0.94%). This residual oil could only come from a deeper source.

5. Whole-oil cryogenic GC-FID and GC-MS data (discussed in Chapters 4 and 5) also provide evidence that many Cooper/Eromanga petroleum accumulations are the result of mixed sourcing and multiple charging of the reservoir.

6.3.5 LATERAL VARIATION OF MATURITY

In order to prove that the distribution pattern of Rc values illustrated in Figure 6.4 supports the above scenario of hydrocarbon generation, migration and accumulation in the southwestern Cooper/Eromanga province, the oil and source rock maturities of each formation are discussed, individually.

6.3.5.1 Murta Formation

In the Murta Formation, Rc values of three DST oils range from 0.63% at Wancoocha-6 to 0.69% at Dirkala-1, with an average of 0.67%. This mean Rc value is 0.04–0.08% larger than those of the two samples of putative source rock in Dirkala-3 (980547, 1399.4 m, Rc = 0.59%; and 980548, Rc = 0.63%, 1407.6 m). Both source rock samples are silty shales.

It is reasonable that the deeper source rock is slightly more mature than the shallower one. However, the trend of maturity change with depth of the DST oils is not obvious. The maturities of these three oils are consistent with their derivation from intra-Murta source beds down dip from their respective well locations. For example, the Wancoocha-6 (Murta) oil may have originated from a Cretaceous hydrocarbon kitchen in the vicinity of the Dirkala field (Figure 6.4).

The fact that the DST oil is more mature than the local putative source rock at a similar depth could also be explained as the result of the mixing of more mature petroleum from a deeper source with less mature petroleum from a shallower source rock. The Garanjanie-3 (Murta) oil accumulation is one that seems to have received part of its charge from hydrocarbons produced in Cooper (or Warburton) source rocks. This would explain its anomalously low 1,7/x-DMP and 1/9-MP values (see sample 980568 in Figures 6.8b & c). These Permian (± Cambrian) hydrocarbons migrated upwards into the Eromanga succession, possibly leaching the Birkhead kerogen *en route*, and finally accumulated, together with petroleum expelled from the Birkhead and Murta source rocks, in the Murta reservoir.

Such upward migration of deeper-sourced hydrocarbons is evidenced by the discovery in some sandstone samples of residual oils that are much more mature than all the local organic materials (see the following discussion).

6.3.5.2 Birkhead and Hutton Formations

The distribution of Rc values in the Birkhead and Hutton Formations of the Dirkala and Wancoocha fields (Figure 6.4) provides further evidence for the above petroleum migration scenario summarised in Figure 6.5. Hydrocarbons from Cooper (±Warburton) sources migrated upwards and mixed with petroleum generated in the local Eromanga source rocks. The mixture accumulated in any Birkhead and/or Hutton traps it encountered along the secondary migration pathways.

Three Birkhead DST oil samples were analysed, two from Wancoocha-2 (980570 & 980571) and the other from Dirkala-1 (980564). The Rc values of the Wancoocha oils are 0.69%, and that of the deeper Dirkala crude is 0.71%.

The two putative source rock samples, 980562 (siltstone) and 980563 (coal), are both from the Birkhead Formation in Wancoocha-4. They have similar maturities (Rc = 0.68% and 0.67%, respectively).

Among the fourteen Birkhead/Hutton sandstone extracts, seven are from Dirkala-1, five are from Wancoocha-4, and two are from Wancoocha-3. Their Rc values fall mostly in the range 0.69–0.81%. Notable exceptions are the two Hutton extracts from the base of the residual oil columns in Dirkala-1 (980545, Rc = 1.06%) and Wancoocha-3 (980557, Rc = 1.14%). Otherwise, there is no systematic trend of changing maturity with depth.

The maturities of SFTE fraction 1 and the combined fractions 5 and 6 were measured for plug 980513 (Dirkala-1, Birkhead). Rc value of the first fraction (0.74%) was slightly higher than that of fractions 5 and 6 (0.71%). This is consistent with earlier observations based on samples from the North Sea (Schwark et al., 1997).

In the absence of appropriate experimental data, any interpretation of this maturity difference must remain somewhat speculative. It could be ascribed to "differential adsorption" and/or multiple charging. The migrating petroleum "front" from any kitchen comprises earlier generated, and hence less mature, hydrocarbons. They enter the pore system of the carrier or reservoir bed where they wet the pore walls and "pave" the migration conduit, thus corresponding to the bipolar layer or "adsorbed oil" (= fractions 5 & 6) in Figure 6.3. Later oil, generated in the source rock at continuously increasing maturity levels, is of higher maturity when entering the carrier bed and corresponds to the "free oil" (= fractions 1 & 2). Any differential adsorption of the methylphenanthrene isomers would obviously affect the MPI and Rc of these SFTE fractions. This phenomenon needs further investigation.

The position of the oil-water contact (OWC) is known for one of the wells in this study (Dirkala-1) and may be relevant to the interpretation of its Rc data displayed in Figure 6.4. Core plugs 980511 and 980512 are from above the OWC and their residual oils have Rc values of 0.81 and 0.79%, respectively. Plugs 980513, 980514 and 980515 come from below the OWC and contain oils that are less mature (Rc = 0.74, 0.73 & 0.77%, respectively). This pattern of Rc values seems to be controlled by the buoyancy of oil relative to water. The later arrived (and hence maturer) petroleum corresponds to the "free oil", which migrates above the OWC. The pore system beneath the OWC contains more "adsorbed oil" which is composed mainly of the less mature initial petroleum charge.

As shown in Figure 6.2, two of the three Wancoocha-4 (Birkhead) sandstones (980541 and 980542) share the same Rc value for SFTE fraction 1 (0.75%) whereas the bulk extract of another (980561) has an Rc of only 0.69%. This is consistent with the above interpretation because the latter sample, which lies above the other two, is a mixture of "free oil" and less mature "adsorbed oil".

Two Wancoocha-2 (Birkhead) DST oils also share an Rc value of 0.69%. This value is similar to those of the two source rock cores (980562, 0.68%; and 980563, 0.67%) from the neighbouring well, Wancoocha-4, indicating that the oil is predominantly of local intra-Birkhead origin.

As already indicated in Section 6.3.4, the two exceptionally mature residual oils from the base of the oil-bearing zones of the Hutton Sandstone in Dirkala-1 (980545, Rc = 1.06%) and Wancoocha-3 (980557, Rc = 1.14%) are almost certainly mixtures of migrated Permian and local Jurassic oil.

6.3.5.3 Permian Formations

Just like those of the Murta, Birkhead and Hutton Formations, the Rc distribution pattern in the Permian succession (Figure 6.4) also supports the idea that its petroleum is out of place and has migrated from source rocks deeper in the Cooper Basin.

In the Patchawarra Formation at Thurakinna, only one source rock sample (980552, siltstone) was measured. Its maturity (Rc = 0.94%) is lower than that of all the residual oils (Rc = 0.98–1.11%). This can only be explained if the oil originated in a deeper petroleum kitchen, probably located to the north of the Thurakinna field, because sample 980552 is the deepest and most mature source rock in the study area (Table 6.1, Figure 6.4).

Permian units in the other three up-dip field locations show similar Rc discrepancies between oils and local source facies:

Field (Formation)	DST Oil	ResidualOil	Source
Garanjanie (Patchawarra)	0.89–0.97	0.83	
Dirkala (Epsilon/Murteree)	0.80–0.81	0.79	
Wancoocha (Patchawarra)	0.82	0.82–0.95	0.78–0.81

6.3.6 VERTICAL VARIATION IN MATURITY

In all the three main petroleum-bearing sequences (Cretaceous, Jurassic and Permian) within the study area, it is a common phenomenon that the residual oils are more mature than the local putative source rocks (as measured by Rc). This is evidence for the idea of deeper-sourced hydrocarbons migrating upward, leaving their traces in the carrier bed, and eventually mingling in the reservoir with locally generated petroleum to form accumulations of mixed crude oil.

The observed vertical variation of oil maturity in the three fields with more than one reservoir (Figure 6.4) similarly provides evidence for the above petroleum generation-migration-accumulation scenario. On the basin scale, Rc values of oils in the younger Eromanga Basin are typically smaller than those of oils from the older underlying Cooper Basin, indicating that the shallower basin did contribute hydrocarbons to the petroleum reservoired in it. On a smaller scale (within one reservoir-seal combination), larger Rc values (relative to that of the local DST oil) in the residual oils may indicate that they are traces of the upward migration of deeper-sourced hydrocarbons into shallower reservoirs.

Sometimes, an individual residual oil sample may have a similar Rc maturity to that of the local putative source rock. This always happens when the reservoir is a thin sandstone layer (or lens) within the source rock unit. Plug 980528 (Thurakinna-3, Patchawarra, Rc = 0.98%) is one such example (Table 3.3, Figure 6.4). The sandstone in this case is only 5 cm thick and it occurs within an interval of siltstone and coal, of which the Rc value is 0.94%.

6.3.6.1 Garanjanie Area

Within the Garanjanie area there are two oil-bearing reservoirs, one in the Patchawarra Formation and the other in the Murta Formation. The Murta DST oil at Garanjanie-1 is (Rc = 0.68%) is much less mature than the Patchawarra source rock (980549, coal: Rc = 0.83%) and residual oil 980550 (Rc = 0.89%) in the same well. It is also less mature than the Patchawarra residual oils from core plugs 980522 (Rc = 0.97%) and 980523 (Rc = 0.89%) at Garanjanie-2 (Figure 6.4). These Rc maturity data provide no hint of any contribution of Patchawarra-derived hydrocarbons to the Murta reservoir in this field (as mentioned in Section 6.3.5.1).

Particularly noteworthy are the comparative maturities of the Patchawarra coal at Garanjanie-1 (Rc = 0.83%), the underlying residual oil (Rc = 0.89%), and the two shallower residual oils at Garanjanie-2 (Rc = 0.97 and 0.89%). The latter two oils are only 4.5 m apart and yet have quite different maturities. The less mature one comes from a level of the reservoir that appears to have had less access (possibly because of adjacent thin coal laminae or other permeability barriers) to hydrocarbons migrating from deeper source facies, elsewhere in the Patchawarra Formation (and/or source rocks in the Warburton Basin).

6.3.6.2 Dirkala Area

Except for the residual oil from the base of the petroliferous interval in the Hutton Sandstone at Dirkala-1 (conventional core 980545: Rc = 1.06%), there are no oil samples that show abnormal maturities. The anomalously high maturity of this oil has been discussed in Sections 6.3.4 & 6.3.5.2. It indicates hydrocarbon migration from kitchens in the underlying Cooper and/or Warburton Basins. Such vertical migration into the overlying Eromanga Basin is possible here because the Dirkala field is located beyond the zero edge of the Nappamerri Group which elsewhere forms a regional seal (Figure 6.4).

Another phenomenon worthy of mention is that the Murta DST oil in the Dirkala field is maturer than the local source rocks (Table 6.1, Figure 6.4), indicating hydrocarbon contributions from deeper sources (Cooper Basin). This has been proved by whole-oil GC-MS, as discussed in Chapter 5. There, it has been pointed out that the inconsistency between the light-end and heavy-end components in many Murta oils – light ends are more mature than the heavy ends – is caused by the contributions of gasoline-rich Cooper-derived crude oil.

6.3.6.3 Wancoocha Area

Within the Wancoocha field, all varieties of samples (viz. DST oils, conventional cores of both sandstone and source rocks, and sandstone core plugs) were available for the Birkhead/Hutton and Patchawarra intervals, and most yielded maturity and source data.

Those from the Birkhead Formation are all from similar depth. They are ideal samples for observing the effects of contributions from deeper-derived petroleum on the distribution of maturity data. The maturity of the two Birkhead DST oils (Rc = 0.69%) is almost identical to that of the two source rocks (980562, Rc = 0.68%; 980563, Rc = 0.67%), indicating that they are of local origin. The residual oils in the core plugs are appreciably more mature (Rc = 0.75–0.80%) and appear to be derived from more mature Jurassic source rocks.

In marked contrast, the maturity of residual oil in the Hutton Sandstone core 980557 (Rc = 1.14%) is the highest of all the measured samples in this study. This oil is even maturer than the deepest Cooper Basin source rock within the study area. Petroleum with this maturity is evidently not from the local source rock of the Birkhead Formation. Neither could it possibly be derived from the Cooper sequence immediately below it. It can only come from petroleum kitchens in deeper parts of the Cooper (or Warburton) Basin. This is among the strongest evidence in support of the model of secondary hydrocarbon migration summarised in Figure 6.5.

6.3.7 OTHER MATURITY PARAMETERS

The above secondary petroleum migration scenario is deduced from the Rc maturity data. In order to see if other maturity parameters support this scenario, the dimethylnaphthalenes, trimethylnaphthalenes and triterpanes were quantified, and the values of selected maturity parameters were calculated. The resulting maturity data are compiled in Table 6.1.

Unfortunately, the abundances of mono- and tri-aromatic steroids in these oils are inadequate for maturity calculations. Maturity parameters based on the isomerisation of steranes and homohopanes were not considered because of their limitations at maturities greater than 0.8% Rc (Peters and Moldowan, 1993). Ts/(Ts+Tm) data are also unreliable because of the very low concentration of 22,29,30-trisnorneohopane (peak Ts is difficult to identify in some *m/z* 191 mass chromatograms). This explains why the most commonly applied maturity parameters in research on the petroleum geochemistry of the Cooper and Eromanga Basins are MPI (and the corresponding Rc), DNR and TNR (Alexander et al., 1986, 1996; Michaelsen and McKirdy, 1989, 1996).

According to data analysis, the correlation coefficients between Rc and DNR-1 & 6 are smaller than 0.3, whereas that between Rc and TNR-1 is 0.85. There is no proper explanation for the poor correlation between Rc and DNR. It may be caused by the relatively low molecular weight of the dimethylnaphthalenes, which means that they are more prone to selective removal by water washing, a common phenomenon in the Eromanga Basin.

Based on the results of data analysis, the distribution pattern of TNR-1 among the samples was selected for comparison with that of Rc. Figure 6.6 shows the distributions of Rc and TNR-1 across the strata sampled (with the stratigraphic age increasing from left to right). Obviously, the two distributions are similar. Patchawarra residual oil 980554, whose Rc value is 1.11%, has a TNR-1 value of 1.10, one of the largest measured. Likewise, the two Hutton residual oils (980545 and 980557) that are appreciably more mature than the other Jurassic oils also have abnormally large TNR-1 values (1.63 and 2.45, respectively: Table 6.1, Figure 6.6b).

6.4 SOURCE-SPECIFIC BIOMARKERS

In order to find more support for the secondary petroleum migration scenario introduced in Section 6.3, Eromanga-specific biomarkers, such as 25,28,30-trisnorhopane and 25,28,30-trisnormoretane (Jenkins, 1989), and the araucariacean resin markers (viz. 1,2,5-trimethylnaphthalene, 1-methylphenanthrene, 1,7-dimethylphenanthrene and retene: Alexander et al., 1988) were investigated. Peak areas of the target molecules in the relevant mass fragmentograms (*m/z* 170, 178, 191, 192, 206 & 219) were integrated and the ratios 1,7-DMP/x-DMP, R/9-MP, R/P, 1-MP/9-MP, 125-TMN/136-TMN and (25,28,30-TNH + 25,28,30-TNM)/(Tm + Ts) were calculated. Definitions of the first four ratios are given in Table 5.2, whereas the last ratio is a measure of the abundance of Jenkins' Eromanga-specific (but orphan) biomarkers relative to the combined concentrations of 22,29,30-trisnorneohopane (Ts) and 22,29,30-trisnorhopane (Tm). All the biomarker data are compiled in Table 6.1, and depicted in Figures 6.7 through 6.9. From the following discussion, it can be seen that the proposed migration scenario is consistent with the biomarker data.

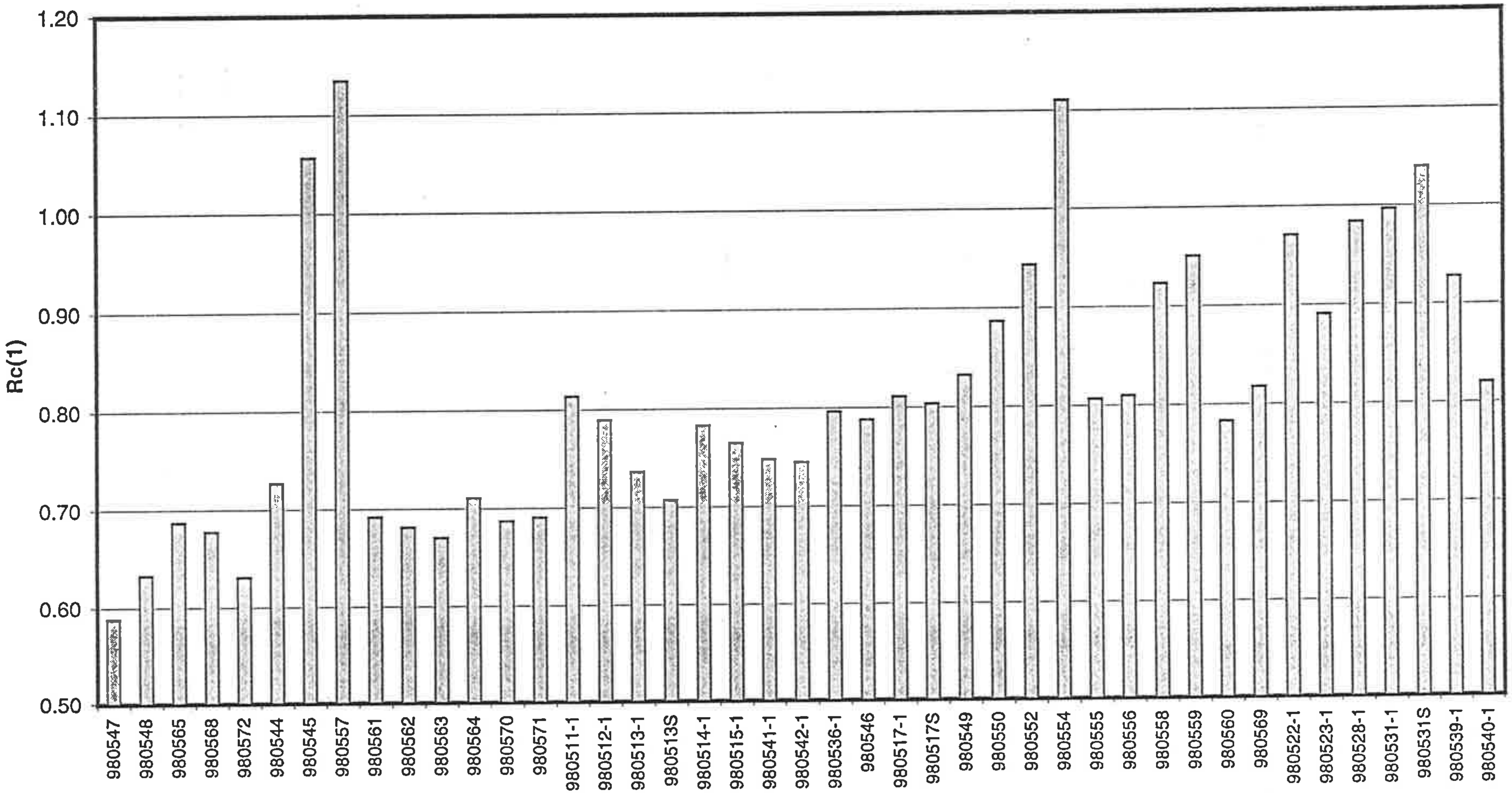


Figure 6.6a Variation of Rc in SFTE and associated samples (Table 6.1). Stratigraphic age increases from Cretaceous (left) to Permian (right).

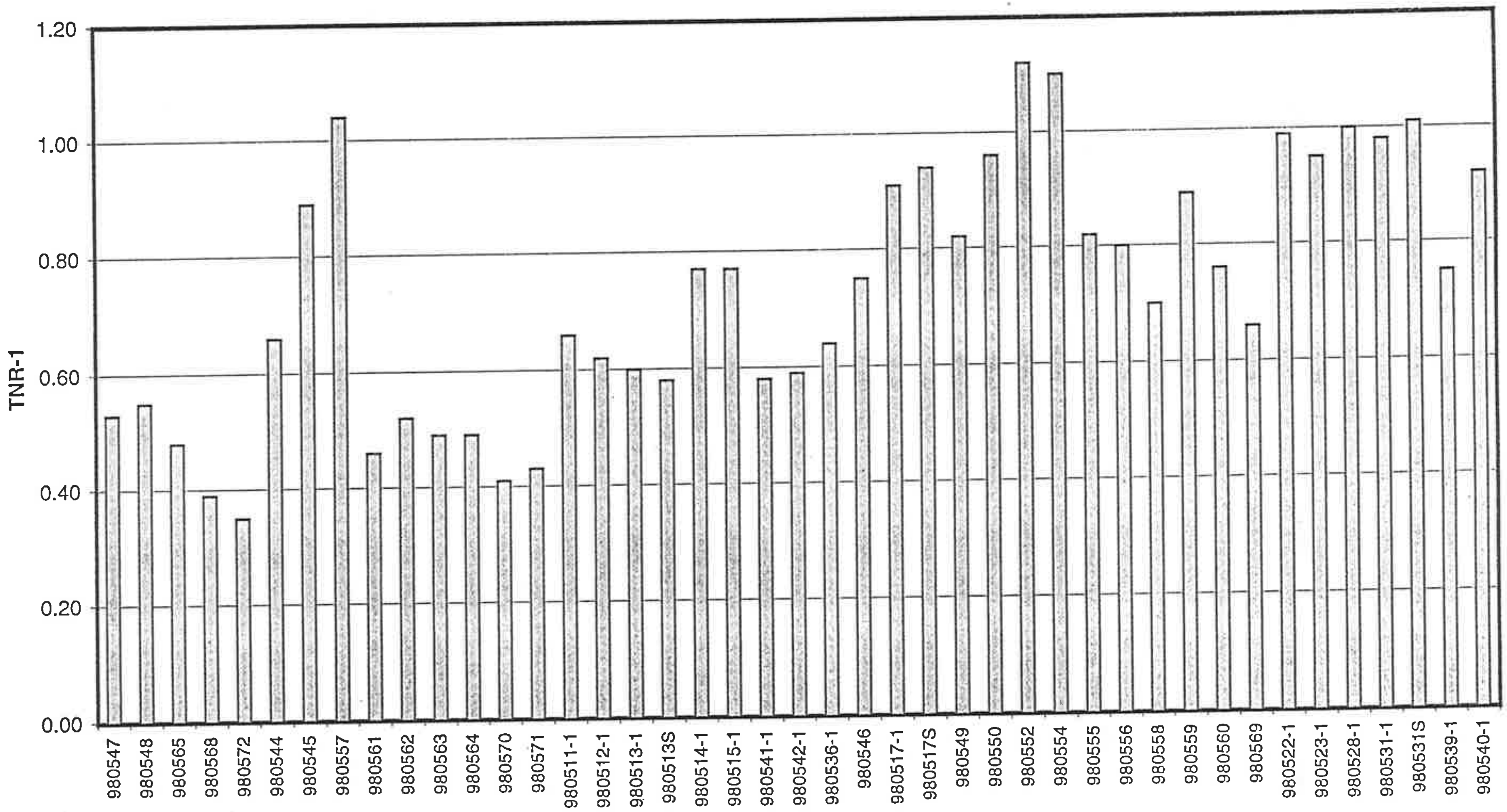


Figure 6.6b Variation of TNR-1 in SFTE and associated samples (Table 6.1). Stratigraphic age increases from Cretaceous (left) to Permian (right).

6.4.1 RETENE/9-METHYLPHENANTHRENE & RETENE/PHENANTHRENE

According to Alexander et al. (1988), retene is abundant in Eromanga-derived petroleum, its concentration relative to that of the commonly occurring 9-methylphenanthrene reflecting the contribution of hydrocarbons from Jurassic or Cretaceous source rocks. Figure 6.7a shows the variation of this ratio with the host formation (the stratigraphic age, as before, increasing from left to right). Figure 6.7b is the equivalent plot for the ratio of retene to phenanthrene.

All the samples from the Cooper sequence (including DST oils, residual oils and source rocks) have R/9-MP values <1.0, and R/P values <0.5. In contrast, the majority of the Eromanga samples have values above these levels. This is not surprising because retene is an araucariacean biomarker and therefore only occurs, abundantly, in Jurassic and Cretaceous source rocks. The biomarker distribution patterns illustrated in Figure 6.7 are consistent with the Cooper crude oils being products of Permian (± Cambrian) source rocks. On the other hand, the Eromanga petroleums are either entirely of Jurassic and/or Cretaceous origin, or mixtures of hydrocarbons from intra-Eromanga and Permian (± Cambrian) source beds.

The idea of a "migration highway" (Figure 6.5), via which hydrocarbons generated from intra-Cooper (and/or Warburton) source rocks migrate directly into Eromanga reservoirs, without meeting much local petroleum, finds some support in the low retene contents of the two anomalously mature Hutton residual oils, 980545 (Dirkala-1) and 980557 (Wancoocha-3). Figure 6.7 shows that the R/9-MP values of these two samples are also below 1.0, indicating that they are the purest Cooper (and/or Warburton) products encountered in the Eromanga Basin. In fact, these two residual oils are the most powerful evidence obtained in this study for petroleum migration from the Cooper and/or Warburton Basins into the Eromanga Basin.

Other samples Eromanga residual oils that have low retene contents are those from core plugs 980513, 980514 and 980515 (Dirkala-1, Birkhead). However, in this case, their maturities are similar to those of the local source rocks, suggesting an intra-Eromanga origin.

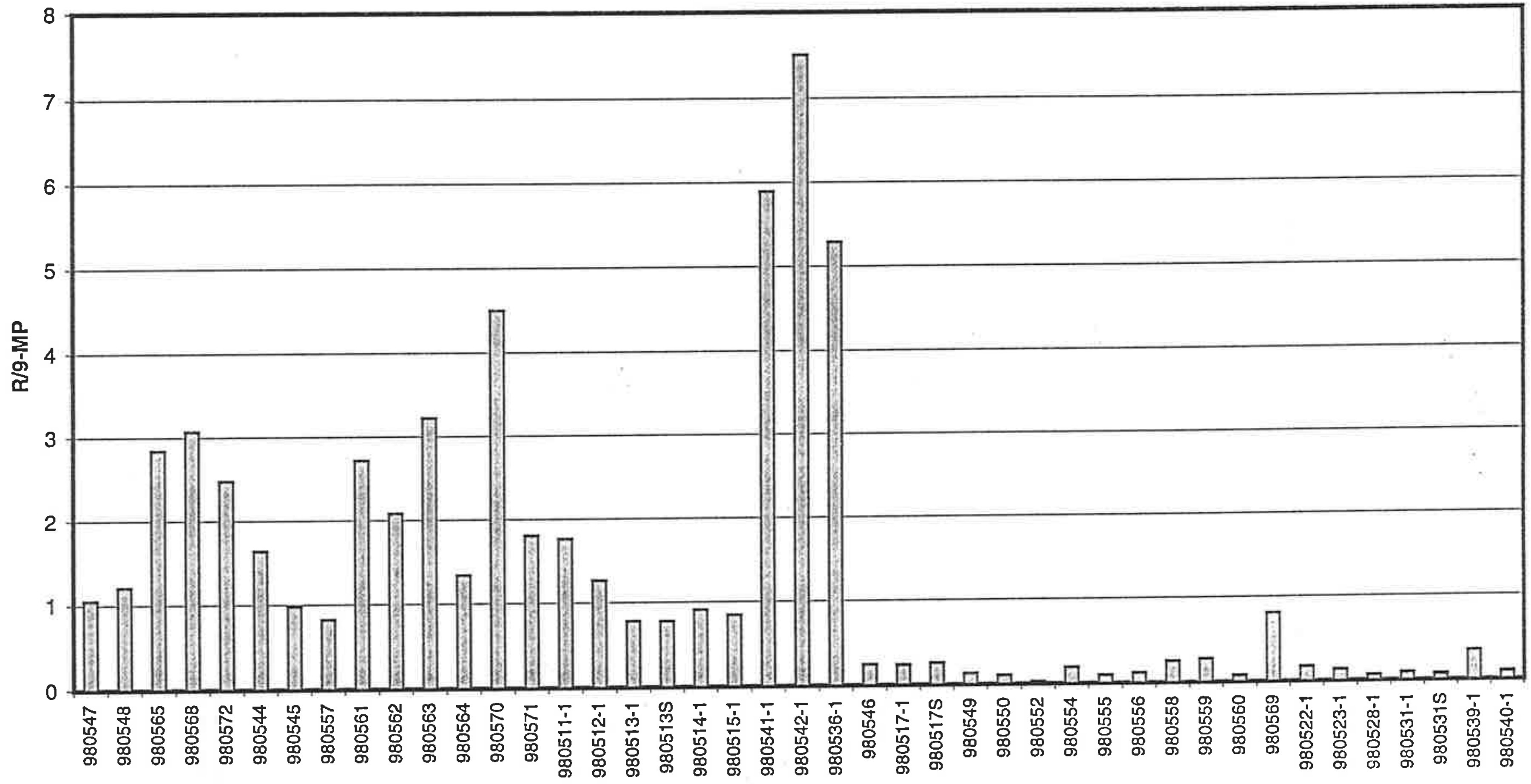


Figure 6.7a Variation of R/9-MP in SFTE and associated samples (Table 6.1). Stratigraphic age increases from Cretaceous (left) to Permian (right).

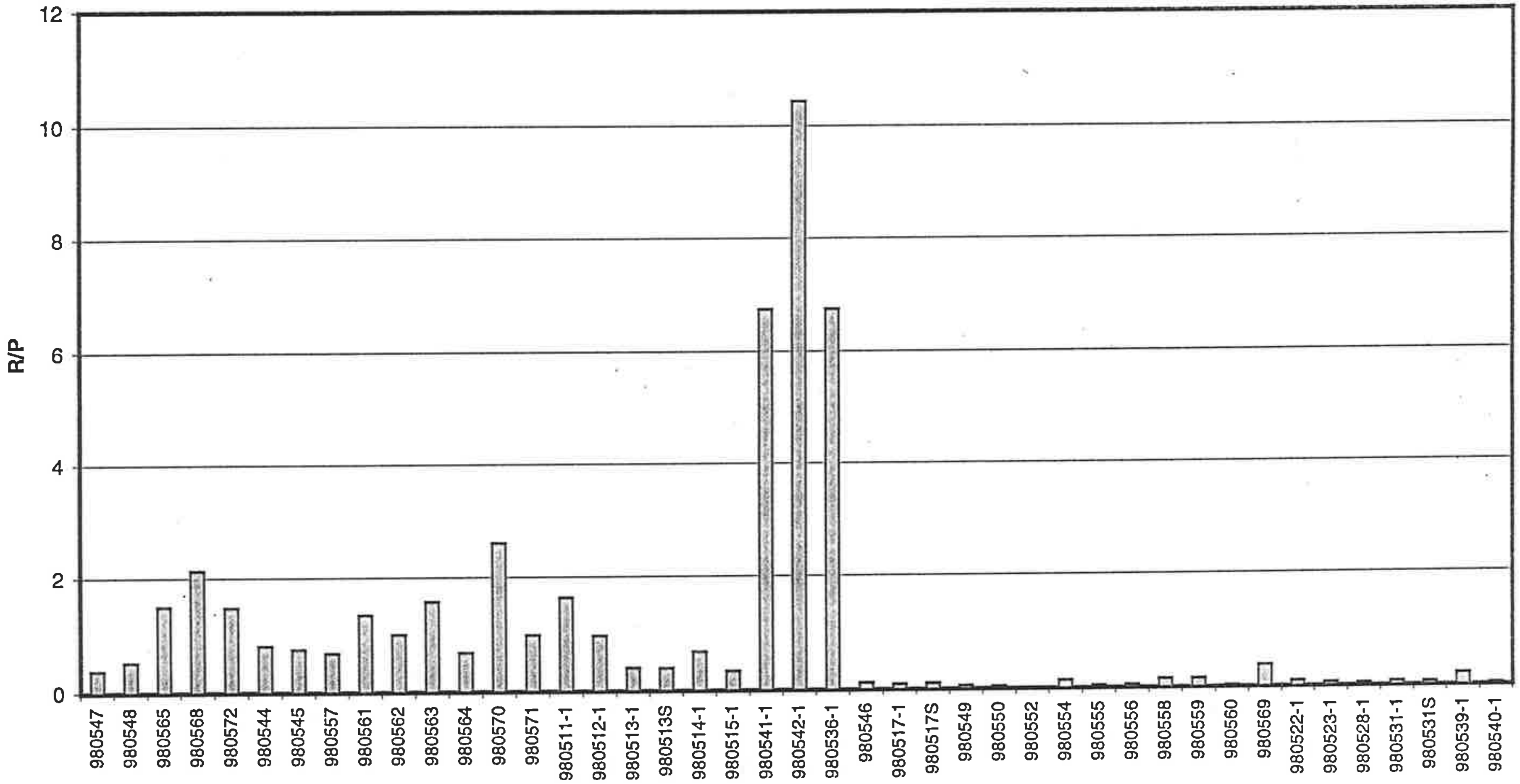


Figure 6.7b Variation of R/P in SFTE and associated samples (Table 6.1). Stratigraphic age increases from Cretaceous (left) to Permian (right).

6.4.2 OTHER ARAUCARIACEAN SIGNATURES

The variation of three other aromatic biomarker ratios that reflect the contribution of araucariacean resins to the source rock is illustrated in Figure 6.8. It is evident that all of them show a similar trend in which there is a fairly sharp distinction between Eromanga samples on the left (high values) and Cooper samples on the right (low values). However, it must be pointed out that some Eromanga samples may have relatively low values of one or two araucariacean signatures, but have higher values for the other signatures. For example, Murta source rocks 980547 and 980548 from Dirkala-3, and Birkhead residual oils 980513, 980514 and 980515 from Dirkala-1, have low values of R/9-MP and R/P, but higher (otherwise normal Eromanga) values of 1,7-DMP/x-DMP, 1-MP/9-MP and 1,2,5-TMN/1,3,6-TMN.

Residual oils in the Hutton sandstone cores 980545 and 980557 are the only two samples that are not only clearly more mature than indigenous Eromanga sedimentary organic matter, but also have consistently very low levels of araucariacean biomarkers. Thus, both their source and maturity characteristics support secondary petroleum migration from the Cooper into the Eromanga Basin.

6.4.3 25,28,30-TNH &TNM / (TS + TM)

Although of unknown origin, the two C_{27} triterpenoids 25,28,30-trisnorhopane and 25,28,30-trisnormoretane have been used as Eromanga-specific biomarkers (Jenkins, 1989). Their combined concentration relative to that of Ts and Tm was calculated from the *m/z* 191 mass chromatograms (in which they co-elute just after Ts) for all but four of the samples in Table 6.1. The variation of the ratio across the formations sampled is depicted in Figure 6.9.

It is very clear from Figure 6.9 that all the Cooper samples contain no detectable amounts of the above two biomarkers. On the other hand, their abundances in most of the Eromanga samples are relatively high. Particularly significant is their low concentration (or absence) in the two residual oils from the Hutton Sandstone (cores 980545 and 980557), whose maturities are extremely high relative to their Eromanga host sediments. Once again, the source and maturity signatures of these oils are

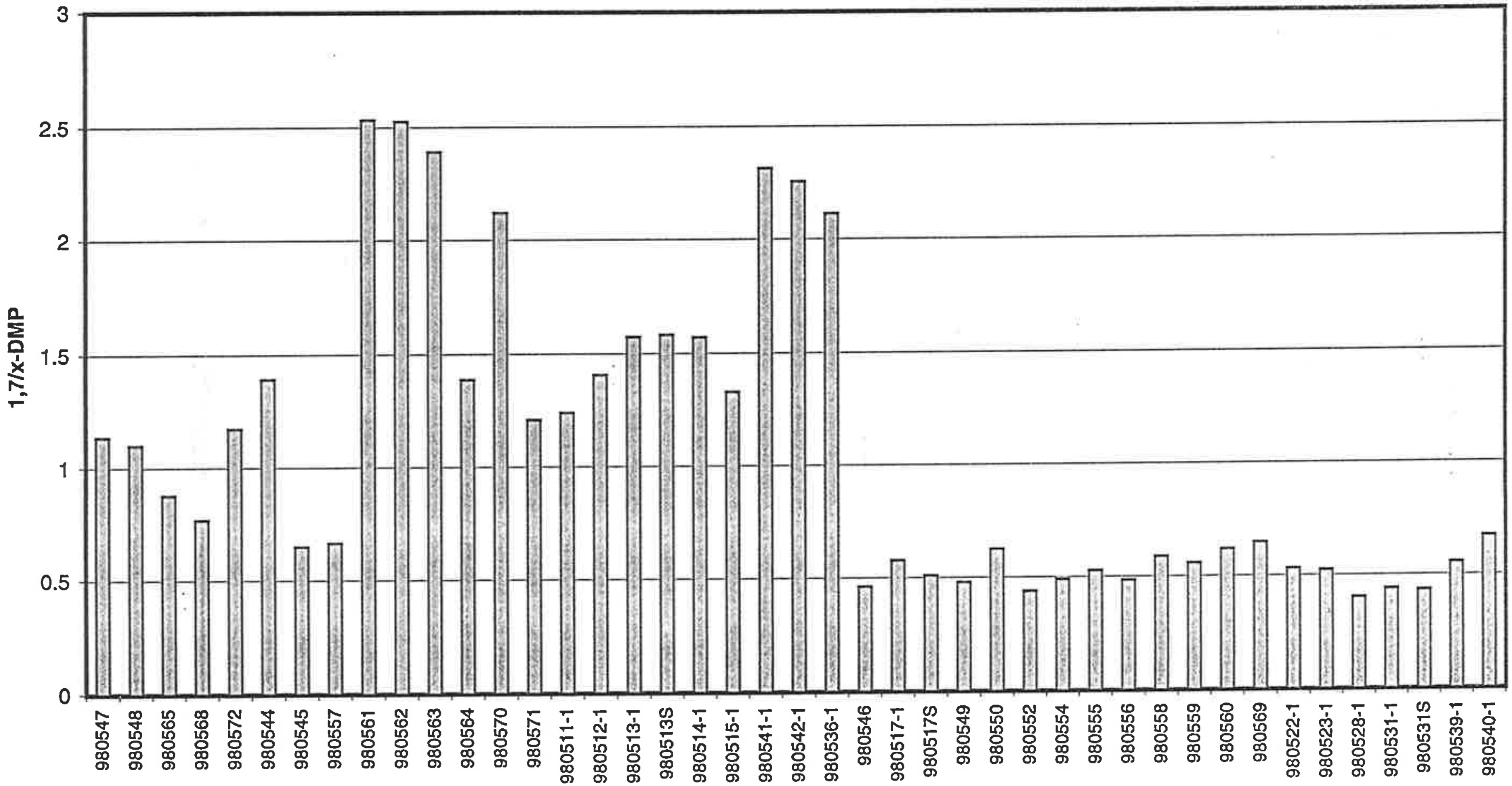


Figure 6.8a Variation of 1,7/x-DMP in SFTE and associated samples (Table 6.1). Stratigraphic age increases from Cretaceous (left) to Permian (right).

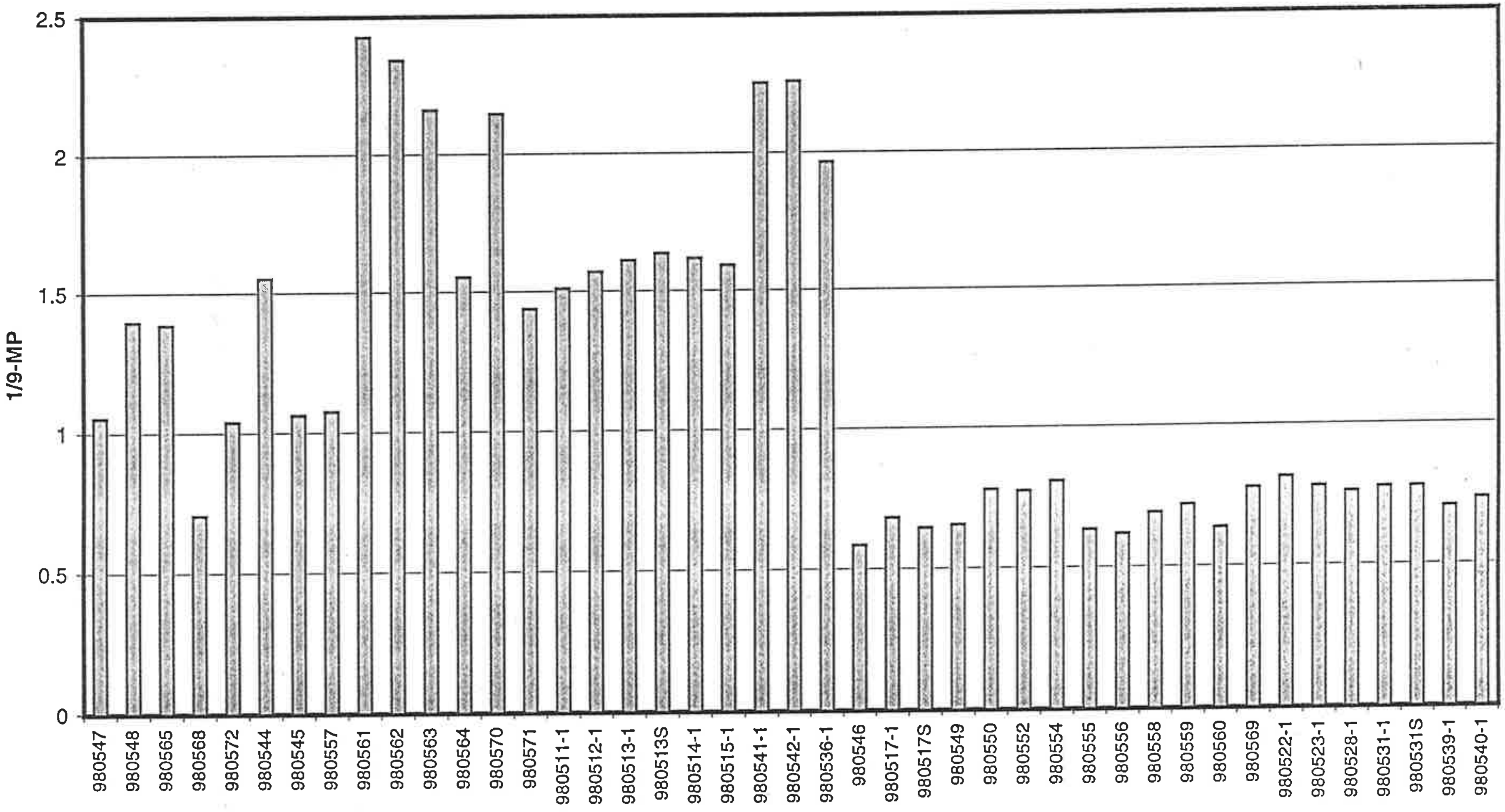


Figure 6.8b Variation of in 1/9-MP and associated samples (Table 6.1). Stratigraphic age increases from Cretaceous (left) to Permian (right).

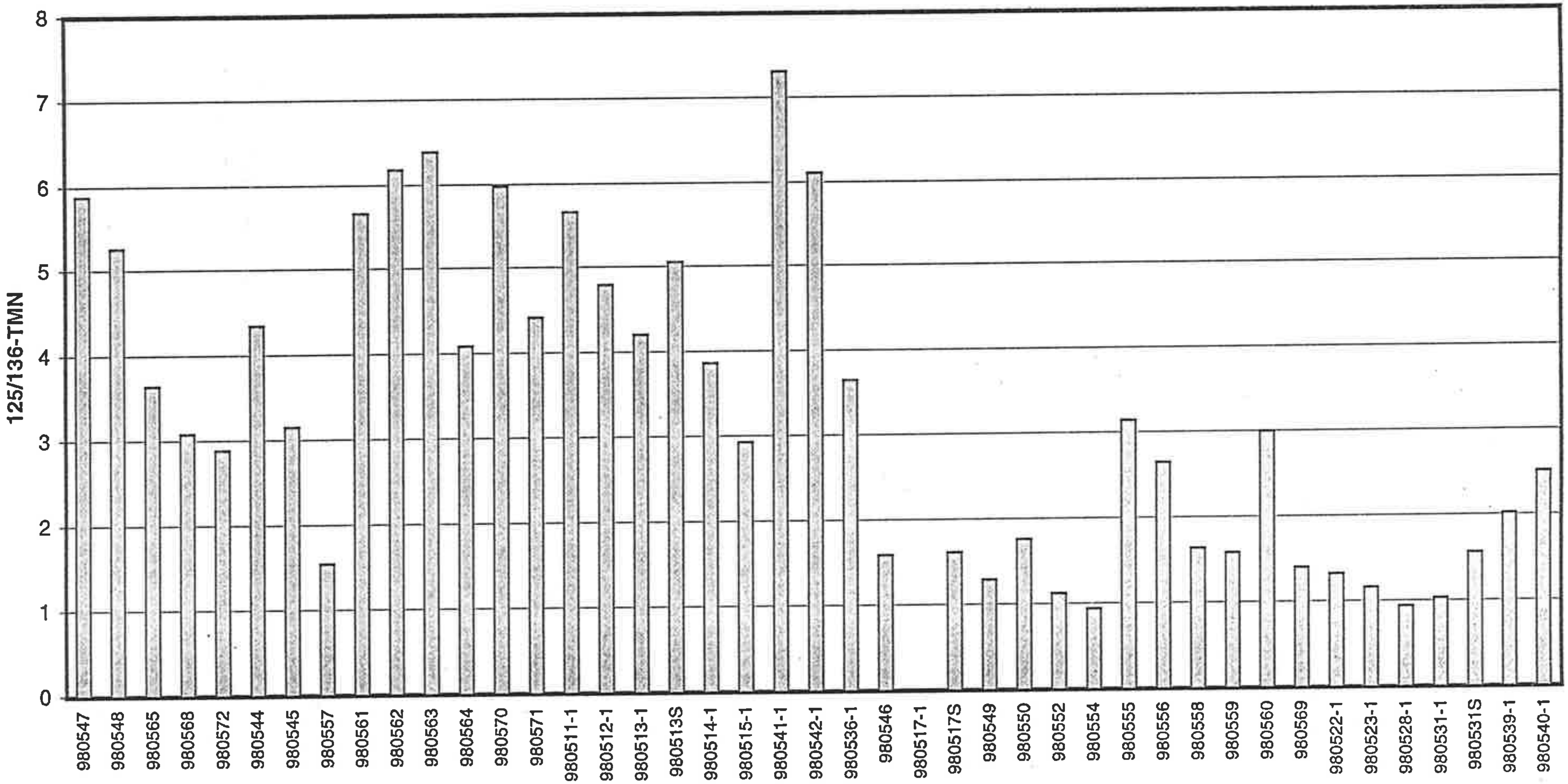


Figure 6.8c Variation of 125/136-TMN in SFTE and associated samples (Table 6.1). Stratigraphic age increases from Cretaceous (left) to Permian (right).

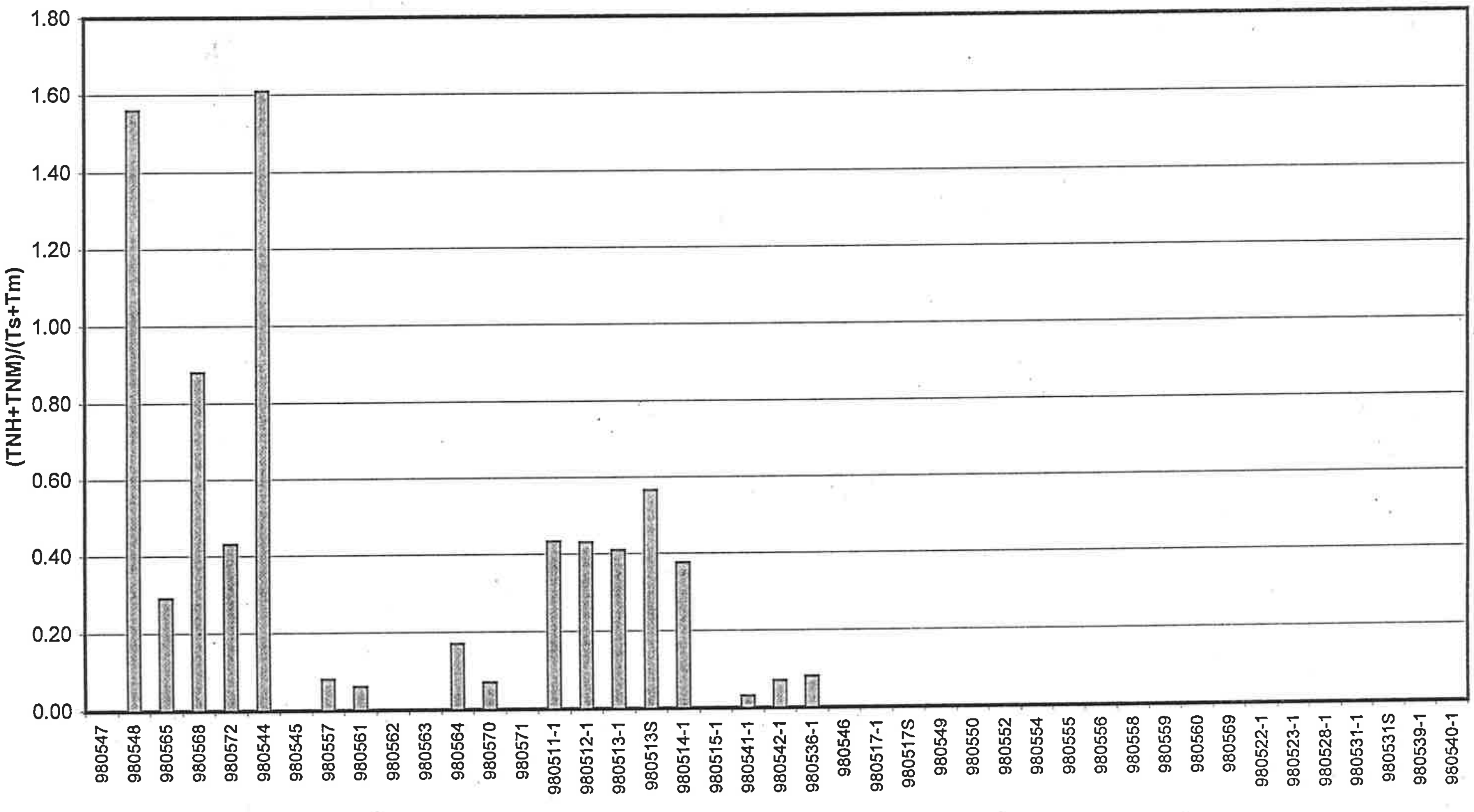


Figure 6.9 Variation of 25,28,30-TNH & TNM/(Ts+Tm) in SFTE and associated samples (Table 6.1). Stratigraphic age increases from Cretaceous (left) to Permian (right).

consistent in indicating a predominant contribution from the Cooper (and/or Warburton) Basin.

6.5 GENERATION-MIGRATION-ACCUMULATION MODEL

Figure 6.5 is a cartoon showing the essential elements of a generalised petroleum generation-migration-accumulation scenario that is consistent with the source and maturity data presented in this chapter. Carbonate in the Warburton Basin and coal, shale and siltstone in the Cooper and Eromanga Basins are all putative source rocks for the petroleum found in the study area. The presence of Cambrian carbonate source beds in the underlying Warburton Basin sequence is inferred from their intersection in other exploration wells (Gatehouse, 1986). These carbonates of the Kalladeina Formation contain 0.25–1.4% TOC and, in the Gidgealpa area (Figure 3.1), have attained maturities in the range Rc = 0.9–1.3% (Roberts et al., 1990). The local Cooper source rocks (coal and shale) are capable of producing petroleum with Rc values that range from 0.8 to 0.95%, whereas those in the Eromanga sequence (coal, shale and siltstone) have been expelling crude oils of somewhat lower maturity (Rc = 0.6-0.7%).

Hydrocarbons generated in the Warburton organic-rich carbonates migrated upwards into Cooper Basin and met the source rocks there, leaching them. Hydrocarbons from both the Warburton and Cooper Basins mixed, and accumulated in the Cooper reservoirs, forming petroleum with maturities intermediate between those of the Cooper source rocks and the Warburton-sourced hydrocarbons. Part of the mixed (Cambrian and Permian) petroleum migrated further upward and met the source rocks in Eromanga Basin, leaching out their liquid hydrocarbons and mingling with them. The final mixture (comprising Cambrian, Permian, Jurassic ± Cretaceous hydrocarbons) accumulated in traps within the Eromanga Basin, forming crude oil with Rc values larger than those of the Eromanga source rock(s) and smaller than those of the Cooper and Warburton source rocks. The insert in Figure 6.5 shows an enlarged view of the upward migrating older oil encountering a younger kerogen particle, leaching and mingling with its newly expelled hydrocarbons. In the centre of the diagram, a "migration highway" is shown to explain the occurrence of extraordinarily mature residual oils in Cooper or Eromanga reservoir sandstones.

This may happen when the upward migration pathway of the hydrocarbons bypasses active younger (or less mature) source beds and other oil accumulations, or coincides with faults. The two reservoirs on the right hand side of Figure 6.5 are the results of this kind of migration-accumulation scenario. Residual oil in the Patchawarra Formation at Thurakinna-2 (Cooper Basin) and residual oils 980545 and 980557 in the Hutton Sandstone at Dirkala-1 and Wancoocha-3 (Eromanga Basin) belong to this category.

6.6 SUMMARY

From the bulk and molecular compositions of a suite of DST oils, SFTE extracts of sandstone core plugs, and conventional Soxhlet and ultrasonic extracts of sandstones and source rocks, a secondary petroleum migration scenario has been deduced for the Thurakinna-Garanjanie-Dirkala-Wancoocha area of the Cooper/Eromanga petroleum province. This scenario is composed of the following aspects:

1. Crude oils occurring in the Cooper/Eromanga petroleum system are sourced from both the Cooper and Eromanga (and possibly also Warburton) Basins.
2. It is quite common for Eromanga-reservoired petroleum to be a mixed charge from Eromanga and Cooper (± Warburton) source rocks.
3. Some Cooper petroleum accumulations could be mixtures of hydrocarbons from both the Cooper and Warburton Basins, particularly if they contain compounds characteristic of carbonate source rocks (e.g. benzothiophenes).
4. Cooper-derived hydrocarbons migrate laterally within Permian carrier beds, remaining in Permian reservoirs only when proper structures are encountered.
5. Faults and/or basin-margin pinchouts provide migration paths along which Permian petroleum can escape into the overlying Eromanga sequence.
6. There the Cooper-derived hydrocarbons may accumulate by themselves or mingle with indigenous Eromanga petroleum. This is depicted in Figure 6.5 where the concepts of "migration highways" and leaching of younger source

rocks by more mature, upward migrating petroleum are emphasised.

7. Around the basin-margin pinchouts, Eromanga-derived hydrocarbons can migrate laterally, via the Late Triassic-Early Jurassic unconformity (Figure 2.1), into Cooper reservoirs.

This migration model is consistent with aromatic maturity data (MPI-derived Rc, TNR-1) and biomarker data (notably the araucariacean signatures based on 1,2,5-trimethylnaphthalene, 1-methylphenanthrene, 1,7-dimethylphenanthrene and retene; and the abundance of 25,28,30-trisnorhopane and 25,28,30-trisnormoretane). It is also supported by the discussion in Chapters 4 & 5.

Fluids (saline water and petroleum) are distributed in the pores of sandstone carrier beds and reservoirs layer by layer. From the pore wall to the centre of the pore space these are: water (containing dissolved inorganic salts), "adsorbed oil" and "free oil". Based on the analytical results of this study, the main type of inorganic salt is NaCl; "free oil" is similar to the DST oil recovered from the same reservoir; and "adsorbed oil" is enriched in polar components (i.e. resin and asphaltenes).

Petroleum must occupy more than half of the available pore volume to form an interconnected pathway for secondary migration. Petroleum losses *en route* during secondary migration are estimated to have been 14–40%. These estimates are consistent with the bulk chemical compositions of the residual oils in these sandstone cores; the difference between the chemical compositions of crude oil under subsurface and surface conditions, as reported in the literature; and the available core analysis data on residual water and oil saturation.

For the first time in SFTE experiments, inorganic salt was identified in the extracts of oil-bearing sandstone core plugs. Detailed analysis of the metal ions in the residual pore water could prove to be helpful in oil-to-source correlation and reconstructing secondary migration pathways.

Finally, IatroScan was shown to be an efficient tool for calibrating SFTE yields, especially when there are dissolved inorganic salts in the aqueous phase of the residual fluids.

CHAPTER SEVEN

CONCLUSIONS

The principal findings of this regional investigation of crude oil composition in the southwestern Cooper/Eromanga Basin are summarised below.

7.1 NEW COMPOSITIONAL PARAMETERS

Thirteen new petroleum geochemical parameters were created based on thermodynamic considerations and the existing literature. Most of them proved to be effective in describing and grouping Cooper/Eromanga oils and condensates according to their source affinity and maturity.

7.2 MIXING MODEL

The novel mixed sourcing model described in Chapter 5 is not only theoretically more comprehensive than existing approaches (i.e. those based on biomarkers and isotopes) but also consistent with the geology of the study area, as presently understood. Both the abundance and specified property (chemical and/or isotopic) of the light and heavy fractions are mathematically taken into account. Digital imitation of this model fits the actual geochemical data very well. The model therefore provides a logical and satisfactory explanation for much of the gross variability of crude oil composition observed throughout the southern Cooper and Eromanga Basins. Crude oils occurring in the Cooper/Eromanga petroleum system originated from source rocks in both the Cooper and Eromanga (and possibly also Warburton) Basins.

7.3 NEW INSIGHTS ON SECONDARY OIL MIGRATION

Comparison of the bulk and molecular compositions of DST oils, residual oils in sandstones and source rock bitumens from the Thurakinna, Garanjanie, Dirkala and Wancoocha fields (Chapter 6) threw new light on the process of secondary migration and reservoir filling in the Cooper/Eromanga petroleum province. Cooper-derived hydrocarbons migrate laterally within Permian carrier beds (over distances of up to 8 km: McKirdy et al., 2000), remaining in Permian reservoirs only when intact structures are encountered. Faults and/or the zero edge of the Nappamerri regional seal near the basin margin provide escape routes along which Permian petroleum can migrate into the overlying Eromanga sequence. This has occurred at Garanjanie, Dirkala and Wancoocha where examples of individual Eromanga reservoirs charged by both Permian and Jurassic hydrocarbons were documented. Moreover, the oil column in the Hutton and Birkhead reservoirs exhibits a gross stratigraphic segregation, with less mature oil of Jurassic origin at the top and more mature oil at the base. At Wancoocha and Dirkala, the latter oil is of mixed Permian-Jurassic origin.

For the first time in SFTE experiments, inorganic salt was identified in the extracts of oil-bearing sandstone core plugs. Such material was previously treated as high-molecular-weight wax. This finding is significant for understanding the petroleum/water fluid distribution in a sandstone pore and for calibration of the SFTE yields. Identification of the cations in the residual pore water is potentially useful in oil-to-source correlation and reconstructing secondary migration pathways.

The conceptual distribution of petroleum and aqueous fluids within a typical sandstone pore was revised. From the wall to the centre of the pore the sequence is thought to be: water (containing dissolved inorganic salts), "adsorbed oil" and "free oil". The "free oil" is similar to the DST oil recovered from the same reservoir whereas the "adsorbed oil" is enriched in polar resins and asphaltenes. In this part of the Cooper/Eromanga Basin, some 14–40% of the total oil expelled from the source kitchen(s) is estimated to have been lost as residual oil in the carrier beds *en route* to the trap.

Finally, a special petroleum generation-migration-accumulation play was identified in the Sturt-Taloola area on the southwestern flank of the Patchawarra Trough. Here hydrocarbons generated within the source facies of the Poolowanna Formation, the basal unit of the Eromanga Basin sequence, migrated downwards into the underlying older Cooper Basin where they accumulated in a basin margin pinch-out of the Patchawarra Formation.

REFERENCES

AL-AROURI K. R., MCKIRDY D. M. AND BOREHAM C. J. (1998) Oil-source correlations as a tool in identifying the petroleum systems of the southern Taroom Trough, Australia, *Organic Geochemistry* **29**, 713-734.

ALBRECHT P., VANDENBROUCKE M. AND MANDENGUE M. (1976) Geochemical studies on the organic matter from the Douala Basin (Cameroon). I. Evolution of the extractable organic matter and the formation of petroleum. *Geochimica et Cosmochimica Acta* **40**, 791-799.

ALEXANDER E. M. (1996a) Petroleum geology of the Eromanga Basin. *MESA J.* **2**, 28-34.

ALEXANDER E. M. (1996b) Reservoirs and seals. In *The Petroleum Geology of South Australia. Vol. 2: Eromanga Basin* (eds. E. M. Alexander and J. E. Hibburt). South Australian Department of Mines and Energy Report Book 96/20, pp. 141-147.

ALEXANDER E. M. AND FREARS B. (1995) *Petroleum Exploration and Development in South Australia.* South Australia. Department of Mines and Energy. Report Book 95/38, 77 p.

ALEXANDER E. M., GRAVESTOCK D. I., CUBITT C., AND CHANEY A. (1998) Lithostratigraphy and environments of deposition. In *The Petroleum Geology of South Australia. Vol. 4: Cooper Basin* (eds. D. I. Gravestock, J. E. Hibburt, and J. F. Drexel). South Australian Department of Primary Industries and Resources Report Book 98/9, pp. 69-115.

ALEXANDER E. M. AND HIBBURT J. E. (1996) *The Petroleum Geology of South Australia, Vol. 2: Eromanga Basin.* South Australian Department of Mines and Energy Report Book, 96/20.

ALEXANDER E. M. AND JENSEN-SCHMIDT B. (1996) Structural and tectonic history. In *The Petroleum Geology of South Australia. Vol. 2: Eromanga Basin* (eds. E. M. Alexander and J. E. Hibburt). South Australian Department of Mines and Energy Report Book 96/20, pp. 33-45.

ALEXANDER E. M. AND SANSOME A. (1996) Lithostratigraphy and environments of deposition. In *The Petroleum Geology of South Australia. Vol. 2: Eromanga Basin* (eds. E. M. Alexander and J. E. Hibburt). South Australian Department of Mines and Energy Report Book 96/20, pp. 49-86.

ALEXANDER R., BASTOW T. P. AND KAGI R. I. (1996) Novel approaches to the determination of the origins of petroleum hydrocarbons in the Cooper-Eromanga basin system. *Unpublished report to the Department of Mines and Energy of South Australia.*

ALEXANDER R., KAGI R. AND WOODHOUSE G. W. (1981) Geochemical correlation of Windalia oil and extracts of Winning Group (Cretaceous) potential source rocks, Barrow subbasin, Western Australia. *AAPG Bulletin* **65**, 235-250.

ALEXANDER R., KAGI R. I., ROWLAND S. J., SHEPPARD P. N. AND CHIRILA T. V. (1985) The effects of thermal maturity on distributions of dimethylnaphthalenes and trimethylnaphthalenes in some ancient sediments and petroleums. *Geochimica et Cosmochimica Acta* **49**, 385-395.

ALEXANDER R., LARCHER A. V., KAGI R. I. AND PRICE P. L. (1988) The use of plant-derived biomarkers for correlation of oils with source rocks in the Cooper/Eromanga Basin system, Australia. *The APEA Journal.* **28**(1), 310-324.

ALEXANDER R., STRACHAN M. G., KAGI R. I., AND VAN BRONSWIJK W. (1986) Heating rate effects on aromatic maturity indicators. *Organic Geochemistry* **10**, 997-1003.

APAK S. N., STUART W. J. AND LEMON N. M. (1993) Structural-stratigraphic development of the Gidgealpa-Merrimelia-Innamincka Trend with implications for petroleum trap styles, Cooper Basin, Australia. *The APEA Journal* **33**(1), 94-104.

APAK S. N., STUART W. J. AND LEMON N. M. (1995) Compressional control on sediment and facies distribution SW Nappamerri Syncline and adjacent Murteree High, Cooper Basin. *The APEA Journal* **35**(1), 190-202.

ARMANIOS C., ALEXANDER R., SOSROWIDJOJO I. B. AND KAGI R. I. (1995) Identification of bicadinanes in Jurassic organic matter from the Eromanga Basin, Australia. *Organic Geochemistry* **23**, 837-843.

ARMSTRONG J. D. AND BARR T. M. (1986) The Eromanga Basin, an overview of exploration and potential. In *Contributions to the Geology and Hydrocarbon Potential of the Eromanga Basin* (eds. D. I. Gravestock, P. S. Moore and G. M. Pitt). Geological Society of Australia Special Publication **12**, pp. 25-38.

BJORØY M. AND HALL K. (1990) Stable carbon isotope ratio analysis on single components in crude oils by direct gas chromatography-isotope analysis. *Trends Analytical Chemistry* **9**(10), 331-337.

BJORØY M., HALL K., GILLYON P. AND JUMEAU J. (1991) Carbon isotope variations in *n*-alkanes and isoprenoids of whole oils. *Chemical Geology* **93**, 13-20.

BJORØY M., HALL P. B. AND MOE R. P. (1994a) Stable carbon isotope variation of *n*-alkanes in Central Graben oils. *Organic Geochemistry* **22**, 355-381.

BJORØY M., HALL P. B. AND MOE R. P. (1994b) Variation in the isotopic composition of single compounds in the C_4-C_{20} fraction of oils and condensates. *Organic Geochemistry* **21**, 761-776.

BOREHAM C. J., CRICK I. H. AND POWELL T. G. (1988) Alternative calibration of the Methylphenanthrene Index against vitrinite reflectance: Application to maturity measurements on oils and sediments. *Organic Geochemistry* **12**, 289-294.

BOREHAM C. J. AND HILL A. J. (1998) Source rock distribution and hydrocarbon geochemistry. In *The Petroleum Geology of South Australia. Vol. 4: Cooper Basin* (eds. D. I. Gravestock, J. E. Hibburt, and J. F. Drexel). South Australian Department of Primary Industries and Resources Report Book 98/9, pp. 129-142.

BOREHAM C. J. AND SUMMONS R. E. (1999) New insights into the active petroleum systems in the Cooper and Eromanga Basins, Australia. *The APPEA Journal* **39**(1), 263-296.

BOULT P. J., LANZILLI E., MICHAELSEN B. H., MCKIRDY D. M. AND RYAN M. J. (1998) A new model for the Hutton/Birkhead reservoir/seal couplet and the associated Birkhead-Hutton (!) petroleum system. *The APPEA Journal* **38**(1), 724-744.

BOULT P. J., RYAN M., J., MICHAELSEN B. H., MCKIRDY D. M., TINGATE P. R., LANZILLI E. AND KAGYA M. L. N. (1997) The Birkhead-Hutton (!) petroleum system of the Gidgealpa area, Eromanga Basin, Australia. In *Petroleum Systems of SE Asia and Australia* (eds. J. V. C. Howes and R. A. Noble). Proceedings of IPA Conference, Jakarta, pp. 213-235.

BROOKS J., CORNFORD C. AND ARCHER R. (1987) The role of hydrocarbon source rocks in petroleum exploration. In *Marine Petroleum Source Rocks* (eds. J. Brooks and A. J. Fleet). Geological Society Special Publication **26**, pp. 17-46.

BROOKS J. D., GOULD K. AND SMITH J. W. (1969) Isoprenoid hydrocarbons in coal and petroleum. *Nature* **222**, 257-259.

BURNHAM A. K., CLARKSON J. E., SINGLETON M. F., WONG C. M. AND CRAWFORD R. W. (1982) Biological markers from Green River kerogen decomposition. *Geochimica et Cosmochimica Acta* **46**, 1243-1251.

CARPENTER B., UNGERER P., KOWALEWSKI I., MAGNIER C., COURCY J. P. AND HUC A. Y. (1996) Molecular and isotopic fractionation of light hydrocarbons between oil and gas phase. *Organic Geochemistry* **24**, 1115-1139.

CHANEY A. J., CUBITT C. J. AND WILLIAMS B. P. J. (1997) Reservoir potential of glacio-fluvial sandstones: Merrimelia Formation, Cooper Basin, South Australia. *The APPEA Journal* **37**(1), 154-176.

CHAPPE B., ALBERCHT P. AND MICHAELIS W. (1982) Polar lipids of archaebacteria in sediments and petroleum. *Science* **217**, 65-66.

CLAYTON J. L., KING J. D., THRELKELD C. N. AND VULETICH A. (1987) Geochemical correlation of Paleozoic oils, Northern Denver Basin – Implications for ecploration. *AAPG Bulletin* **71**, 103-109.

CONNAN J. (1984) Biodegradation of crude oils in reservoirs. In *Advances in Petroleum Geochemistry Vol. 1* (eds. J. Brooks and D. H. Welte), pp. 298-355. Academic Press, London.

CURIALE J. A. AND BROMLEY B. W. (1996) Migration induced compositional changes in oils and condensates of a single field. *Organic Geochemistry* **24**, 1097-1113.

DAVIS J. C. (1986) *Statistics and Data Analysis in Geology*. John Wiley and Sons.

DEIGHTON I. AND HILL A. J. (1998) Thermal and burial history. In *The Petroleum Geology of South Australia, Vol. 4: Cooper Basin* (eds. D. I. Gravestock, J. E.

Hibburt and J. F. Drexel). South Australian Department of Primary Industries and Resources Report Book 98/9, pp. 143-155.

DeLurio J. L. and Frakes L. A. (1999) Glendonites as a palaeoenvironmental tool: Implications for early Cretaceous high latitude climates in Australia. *Geochimica et Cosmochimica Acta* **63**, 1039-1048.

Didyk B. M., Simoneit B. R. T., Brassell S. C. and Eglinton G. (1978) Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature* **272**, 216-222.

Dzou L. I. P. and Hughes W. B. (1993) Geochemistry of oils and condensates, K Field, offshore Taiwan: a case study in migration fractionation. *Organic Geochemistry* **20**, 437-462.

Eadington P. J., Hamilton P. J. and Bai G. P. (1991) Fluid history analysis: a new concept for prospect evaluation. *The APEA Journal* **31**(1), 282-294.

England W. A. (1990) The organic geochemistry of petroleum reservoirs. *Organic Geochemistry* **16**, 415-425.

England W. A., Muggeridge A. H., Clifford R. J. and Tang Z. (1995) Modelling density-driven mixing rates in petroleum reservoirs on geological time-scale, with application to the detection of barriers in the Forties Field (UKCS). In *The Geochemistry of Reservoirs* (eds. J. M. Cubitt and W. A. England). Geological Society Special Publication **86**, 185-201.

England W. A. and Mackenzie A. S. (1989) Some aspects of the geochemistry of petroleum fluids. *Geologische Rundschau* **78**(1), 291-303.

England W. A., Mackenzie A. S., Mann D. M. and Quigley T. M. (1987) The movement and entrapment of petroleum fluids in the subsuface. *Journal of the Geological Society* **144**, 327-347.

ENGLAND W. A., MANN D. M. AND MANN A. L. (1990) "Migration from Source to Trap" and "Trap Filling and Mixing". *AAPG Handbook of Petroleum Geology.* Tulsa. Oklahoma.

FAIRBURN W. A. (1989) The geometry of Toolachee Unit 'C' fluvial sand trands, Moomba Field, Permian Cooper Basin, South Australia. In *The Cooper and Eromanga Basins, Australia* (ed. B. J. O'Neil), Proceedings of Petroleum Exploration Society of Australia, Society of Petroleum Engineers, Australian Society of Exploration Geophysicists (SA Branches), Adelaide, pp. 239-250.

FAIRBURN W. A. (1992) Geometry of reservoir trends in the Epsilon Formation sands, southern Cooper Basin, South Australia. *The APEA Journal* **32**(1), 339-358.

FORBES P. L., UNGERER P. M., KUHFUSS A. B., RIIS F. AND EGGEN S. (1991) Compositional modeling of petroleum generation and expulsion: trial application to a local mass balance in the Smorbukk Sor Field, Haltenbanken area, Norway. *AAPG Bulletin* **75**, 873-893.

FRAKES L. A. AND FRANCIS J. E. (1988) A guide to Phanerozoic cold polar climates, from high-latitude ice-rafting in the Cretaceous. *Nature* **333**, 547-549.

FREEMAN K. H., HAYES J. M., TRENDEL J. M. AND ALBRECHT P. (1990) Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons. *Nature* **343**, 254-266.

GATEHOUSE C. G. (1972) Formation of the Gidgealpa Group in the Cooper Basin. *Australasian Oil and Gas Review* **18**(12), 10-11.

GATEHOUSE C. G. (1986) The geology of the Warburton Basin in South Australia. *Australian Journal of Earth Sciences* **33**, 161-180.

GOOSSENS H., DE LEEUW J. W., SCHENCK P. A. AND BRASSELL S. C. (1984) Tocopherols as likely precursors of pristane in ancient sediments and crude oils. *Nature* **312**, 440-442.

GRAVESTOCK D. I. AND ALEXANDER E. M. (1986) Porosity and permeability of reservoirs and caprocks in the Eromanga Basin, South Australia. *The APEA Journal* **26**(1), 202-213.

GRAVESTOCK D. I. AND ALEXANDER E. M. (1989) Petrophysics of oil reservoirs in the Eromanga Basin, South Australia. In *The Cooper and Eromanga Basins, Australia* (ed. B. J. O'Neil), Proceedings of Petroleum Exploration Society of Australia, Society of Petroleum Engineers, Australian Society of Exploration Geophysicists (SA Branches), Adelaide, pp. 141-151.

GRAVESTOCK D. I. AND FLINT R. B. (1995) Post-Delamerian compressive deformation. In *The Geology of South Australia. Vol. 2, The Phanerozoic* (eds. J. F. Drexel and W. V. Preiss). South Australian Geological Survey Bulletin **54**, pp. 109-119.

GRAVESTOCK D. I. AND JENSEN-SCHMIDT. (1998) Structural setting. In *Petroleum Geology of South Australia, Volume 4: Cooper Basin* (eds. D. I. Gravestock, J. E. hibburt, and J. F. Drexel). South Australian Department of Primary Industries and Resources Report Book 98/9, pp. 49-69.

GRAVESTOCK D. I., HIBBURT J. E. AND DREXEL J. F. (1998a) *The Petroleum Geology of South Australia. Vol. 4: Cooper Basin.* South Australian Department of Primary Industries and Resources Report Book 98/9.

GRAVESTOCK D. I., ALEXANDER E. M., MORTON J. G. G. AND SUN X. (1998b) Reservoirs and Seals. In *The Petroleum Geology of South Australia. Vol. 4: Cooper Basin* (eds. D. I. Gravestock, J. E. Hibburt, and J. F. Drexel). South Australian Department of Primary Industries and Resources Report Book 98/9, pp. 157-180.

HABERMEHL M. A. (1986) Regional groundwater movement, hydrochemistry and hydrocarbon migration in the Eromanga Basin. In *Contributions to the Geology and Hydrocarbon Potential of the Eromanga Basin* (eds. D. I.

Gravestock, P. S. Moore, and G. M. Pitt). Geological Society of Australia. Special Publication **12**, pp. 353-376.

Hayes J. M., Takigiku R., Ocampo R., Callot H. J. and Albrecht P. (1987) Isotopic compositions and probable origins of organic molecules in the Eocene Messel Shale. *Nature* **329**, 48-51.

Heath R., McIntyre S. and Gibbins N. (1989) A Permian origin for Jurassic reservoired oil in the Eromanga Basin. In *The Cooper and Eromanga Basins, Australia* (ed. B. J. O'Neil), Proceedings of Petroleum Exploration Society of Australia, Society of Petroleum Engineers, Australian Society of Exploration Geophysicists (SA Branches), Adelaide, pp. 405-416.

Hill A. J. and Gravestock D. I. (1995) Cooper Basin. In *South Australia Geological Survey Bulletin*, Vol. 54 (eds. J. F. Drexel and W. V. Preiss). The Geology of South Australia. Vol.2, The Phanerozoic. pp. 78-87.

Hoffmann K. L. (1989) The influence of pre-Jurassic tectonic regimes on the structural development of the southern Eromanga Basin, Queensland. In *The Cooper and Eromanga Basins, Australia* (ed. B. J. O'Neil), Proceedings of Petroleum Exploration Society of Australia, Society of Petroleum Engineers, Australian Society of Exploration Geophysicists (SA Branches), Adelaide, pp. 351-328.

Holba A. G., Dzou L. I. P., Hickey J. J., Franks S. G., Moy S. J. and Lenney T. (1996) Reservoir geochemistry of South Pass 61 Field, Gulf of Mexico: compositional heterogeneities reflecting filling history and biodegradation. *Organic Geochemistry* **24**, 1179-1198.

Horsfield B. and McLimans R. K. (1984) Geothermometry and geochemistry of aqueous and oil-bearing fluid inclusions from Fateh Field, Dubai. *Organic Geochemistry* **6**, 733-740.

HORSTAD I., LARTER S. R., DYPVIK H., AGAARD P., BJØRNVIK A. M., JOHANSEN P. E. AND ERIKSEN S. (1990) Degradation and maturity controls on oil field petroleum column heterogeneity in the Gullfaks field, Norwegian North Sea. *Organic Geochemistry* **16**, 497-510.

HORSTAD I., LARTER S. R. AND MILLS N. (1995) Migration of hydrocarbons in the Tampen Spur area, Norwegian North Sea: a reservoir geochemical evaluation. In *The Geochemistry of Reservoirs* (eds. J. M. Cubitt and W. A. England). Geological Society Special Publication **86**, pp. 159-183.

HUNT J. W., HEATH R. S. AND MCKENZIE P. F. (1989) Thermal maturity and other geological controls on the distribution and composition of Cooper Basin hydrocarbons. In *The Cooper and Eromanga Basins, Australia* (ed. B. J. O'Neil), Proceedings of Petroleum Exploration Society of Australia, Society of Petroleum Engineers, Australian Society of Exploration Geophysicists (SA Branches), Adelaide, pp. 509-523.

HWANG R. J., AHMED A. S. AND MOLDOWAN J. M. (1994) Oil composition variation and reservoir continuity: Unity Field, Sudan. *Organic Geochemistry* **21**, 171-188.

ILLICH H. A. (1983) Pristane, phytane, and lower molecular weight isoprenoid distributions in oils. *AAPG Bulletin* **67**, 385-393.

JENKINS C. C. (1989) Geochemical correlation of source rocks and crude oils from the Cooper and Eromanga Basins. In *The Cooper and Eromanga Basins, Australia* (ed. B. J. O'Neil), Proceedings of Petroleum Exploration Society of Australia, Society of Petroleum Engineers, Australian Society of Exploration Geophysicists (SA Branches), Adelaide, pp. 524-540.

KAGYA M. L. N. (1997) *The source rock and petroleum geochemistry of the Early Jurassic Poolowanna Formation, Eromanga Basin.* Unpublished PhD Thesis, University of Adelaide.

KAGYA M. L. N., MCKIRDY, D. M. AND MICHAELSEN, B. H. (1997). Carbon isotope and biomarker signatures of oils and early Jurassic non-marine source rocks in the western Cooper/Eromanga Basin, South Australia. *4th Conference on Petroleum Geochemistry in the Afro-Asian Region, Arusha, Tanzania: Programme and Abstracts*, pp. 36-37.

KANTSLER A. J., COOK A. C. AND ZWIGULIS M. (1986) Organic maturation of the Eromanga Basin. In *Contributions to the Geology and Hydrocarbon Potential of the Eromanga Basin* (eds. D. I. Gravestock, P. S. Moore, and G. M. Pitt). Geological Society of Australia Special Publication **12**, pp. 305-322.

KANTSLER A. J., PRUDENCE T. J. C., COOK A. C. AND ZWIGULIS M. (1983) Hydrocarbon habitat of the Cooper/Eromanga Basin, Australia. *The APEA Journal.* **23**(1), 75-92.

KAPEL A. J. (1966) The Cooper's Creek Basin. *The APEA Journal.* **6**, 71-75.

KARLSEN D. A. AND LARTER S. R. (1989) A rapid correlation method for petroleum population mapping within individual petroleum reservoirs: applications to petroleum reservoir description. In *Correlation in Hydrocarbon Exploration NPF* (ed. J. D. Collinson), pp. 77-85. Graham & Trotman, London.

KARLSEN D. A. AND LARTER S. R. (1991) Analysis of petroleum fractions by TLC-FID: Applications to petroleum reservoir description. *Organic Geochemistry* **17**, 603-617.

KARLSEN D. A., NEDKVITNE T., LARTER S. R. AND BJØRLYKKE K. (1993) Hydrocarbon composition of authigenic inclusions: Application to elucidation of petroleum reservoir filling history. *Geochimica et Cosmochimica Acta* **57**, 3641-3659.

KELEMEN S. G. (1986) Sales gas and ethane storage projects – Moomba Field, lower Daralingie Beds. *The APEA Journal* **26**(1), 405-419.

KRIEG G. W., ALEXANDER E. M. AND ROGERS P. A. (1995) Eromanga Basin. In *The Geology of South Australia. Vol.2, The Phanerozoic* (eds. J. F. Drexel and W. V. Preiss). South Australian Geological Survey Bulletin **54**, pp. 101-127.

LAFARGUE E. AND BARKER C. (1988) Effect of water washing on crude oil composition. *AAPG Bulletin* **72**, 263-276.

LAFARGUE E. AND LE THIEZ P. (1996) Effect of water washing on light ends compositional heterogeneity. *Organic Geochemistry* **24**, 1141-1150.

LARTER S. R. AND APLIN A. C. (1995) Reservoir geochemistry: methods, applications and opportunities. In *The Geochemistry of Reservoir* (eds. J. M. Cubitt and W. A. England). Geological Society Special Publication **86**, pp. 5-32.

LARTER S. R., BJØRLYKKE K. O., KARLSEN D. A., NEDKVITNE T., EGLINTON T., JOHANSEN P. E., LEYTHAEUSER D., MASON P. C., MITCHELL A. W. AND NEWCOMBE G. A. (1990) Determination of petroleum accumulation histories: Examples from the Ula field, Dentral Graben, Norwegian North sea. In *North Sea Oil and Gas Reservoirs-II.* (eds. A. T. Buller, E. Berg, O. Hjelmeland, J. Kleppe, O. Torsaeter and J. O. Aasen). Proceedings of the North Sea Oil and Gas Reservoir Conference, pp. 319-330. Graham and Trotman, London.

LARTER S. R., BOWLER B. F. J., LI M., CHEN M., BRINCAT D., BENNETT B., NOKE K., DONOHOE P., SIMMONS D., KOHNEN M., ALLAN J., TELNAES N. AND HORSTAD I. (1996) Molecular indicators of secondary oil migration distances. *Nature* **383**, 593-597.

LEYTHAEUSER D., RADKE M. AND WILLSCH H. (1988) Geochemical effects of primary migration of petroleum in Kimmeridge source rocks from Brae field area, North Sea. II: Molecular composition of alkylated naphthalenes, phenathrenes, benzo- and dibenzothiophenes. *Geochimica et Cosmochimica Acta* **52**, 2879-2891.

LEYTHAEUSER D. AND RÜCKHEIM J. (1989) Heterogeneity of oil composition within a reservoir as a reflection of accumulation history. *Geochimica et Cosmochimica Acta* **53**, 2119-2123.

LI M., LARTER S. R. AND STODDART D. (1992) Liquid chromatographic separation schemes for pyrrole and pyridine nitrogen aromatic heterocycle fractions from crude oils suitable for rapid characterization of geochemical samples. *Analytical Chemistry* **64**, 1337-1344.

MACKIE S. J., GRASSO C. A. AND MCGUIRE S. R. (1995) Reservoir characterisation of the Toolachee Unit 'C' in the Moomba/Big Lake area: focussing on minimising risk. *The APEA Journal* **35**(1), 92-105.

MANGO F. D. (1987) An invariance in the isoheptanes of petroleum. *Science* **237**, 514-517.

MANGO F. D. (1990a) The origin of cycloalkanes in petroleum. *Geochimica et Cosmochimica Acta* **54**, 23-37.

MANGO F. D. (1990b) The origin of light hydrocarbon in petroleum: A kinetic test of the steady-state catalytic hypothesis. *Geochimica et Cosmochimica Acta* **54**, 1315-1323.

MANGO F. D. (1997) The light hydrocarbons in petroleum: a critical review. *Organic Geochemistry* **26**, 417-440.

MARTIN C. J. (1967) The Gidgealpa and Merrimelia Formation in the Coopers Creek Basin. *Australasian Oil and Gas Journal* **14**, 29-35.

MASON P. C., BURWOOD R. AND MYCKE B. (1995) The petroleum charging histories of Palaeogene-reservoired fields in the Outer Witch Ground Graben. In *The Geochemistry of Reservoirs* (eds. J. M. Cubitt and W. A. England). Geological Society Special Publication **86**, pp. 280-301.

McKirdy D. M. (1982) *Petroleum geochemistry and source-rock potential of the Cooper Basin and superjacent Eromanga Basin.* Unpublished report for Delhi Petroleum Pty. Ltd.

McKirdy D. M. (1985) Rapid evaluation of non-marine petroleum source rocks. *National Energy Research, Development and Demonstration Program, Project 261, End-of-Grant Technical Report.*

McKirdy D. M. and Chivas A. R. (1992) Nonbiodegraded aromatic condensate associated with supercritical carbon dioxide, Otway Basin: implications for primary migration from terrestrial organic matter. *Organic Geochemistry* **18**, 611-627.

McKirdy D. M. and Willink R. J. (1988) *Migration of hydrocarbons and groundwater towards PEL-31, southeastern Eromanga Basin, South Australia.* Unpublished report for Adelaide Petroleum NL.

McLimans R. K. (1987) The application of fluid inclusions to migration of oil and diagenesis in petroleum reservoirs. *Applied Geochemistry* **2**, 585-603.

Michaelsen B. H. and McKirdy D. M. (1989) Organic facies and petroleum geochemistry of the lacustrine Murta Member (Mooga Formation) in the Eromanga Basin, Australia. In *The Cooper and Eromanga Basins, Australia* (ed. B. J. O'Neil), Proceedings of Petroleum Exploration Society of Australia, Society of Petroleum Engineers, Australian Society of Exploration Geophysicists (SA Branches), Adelaide, pp. 541-558.

Michaelsen B. H. and McKirdy D. M. (1996) Source rock distribution and hydrocarbon geochemistry. In *The Petroleum Geology of South Australia. Vol. 2: Eromanga Basin* (eds. E. M. Alexander and J. E. Hibburt). South Australian Department of Mines and Energy Report Book 96/20, pp. 101-110.

MICHAELSEN B. H. AND MCKIRDY D. M. (1999) Aromatic hydrocarbon signatures of oils from the Cooper and Eromanga Basins, central Australia: Evidence of multiple sources and in-reservoir mixing. *19th International Meeting on Organic Geochemistry, Istanbul, Turkey, Abstracts*, pp. 645-646.

MICHAELSEN B. H. AND MCKIRDY D. M. (2000) Migration and mixing of oils in the Cooper/Eromanga Basin. *Australian Organic Geochemistry Conference 2000, Townsville, Abstracts* (2 p.)

MOORE P. S. AND PITT G. M. (1984) Cretaceous of the Eromanga Basin – implications for hydrocarbon exploration. *The APEA Journal* **24**(1), 269-286.

MCKIRDY D. M., YU. X., LEYTHAEUSER D., SCHWARK L. AND AROURI K. R. (2000) A pilot FTSE study of secondary migration and reservoir filling in the Cooper/Eromanga Basin, South Australia. *Australian Organic Geochemistry Conference 2000, Townsville, Abstracts* (2 p.)

MOUSSAVI-HARAMI R. (1996a) Burial history. In *The Petroleum Geology of South Australia. Vol. 2: Eromangà Basin* (eds. E. M. Alexander and J. E. Hibburt). South Australian Department of Mines and Energy Report Book 96/20, pp. 125-140.

MOUSSAVI-HARAMI R. (1996b) Burial history of the Cooper Basin region in South Australia. *PESA Journal* **24**, 57-76.

O'NEIL B. J. (1996) History of petroleum exploration and development. In *The Petroleum Geology of South Australia. Vol. 2: Eromanga Basin* (eds. E. M. Alexander and J. E. Hibburt). South Australian Department of Mines and Energy Report Book 96/20, pp. 11-32.

O'NEIL B. J. (1998) History of petroleum exploration and development. In *The Petroleum Geology of South Australia. Vol. 4: Cooper Basin* (eds. D. I.

Gravestock, J. E. Hibburt, and J. F. Drexel). South Australian Department of Primary Industries and Resources Report Book 98/9, pp. 7-36.

PASSMORE V. L. (1989) Petroleum accumulations of the Eromanga Basin: a comparison with other Australian Mesozioc accumulations. In *The Cooper and Eromanga Basins, Australia* (ed. B. J. O'Neil), Proceedings of Petroleum Exploration Society of Australia, Society of Petroleum Engineers, Australian Society of Exploration Geophysicists (SA Branches), Adelaide, pp. 371-389.

PETERS K. E. AND MOLDOWAN J. M. (1993) *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments.* Prentice Hall, Englewood Cliffs, New Jersey.

PITT G. M. (1986) Geothermal gradients, geothermal histories and the timing of thermal maturation in the Eromanga-Cooper Basins. In *Contributions to the Geology and Hydrocarbon Potential of the Eromanga Basin* (eds. D. I. Gravestock, P. S. Moore, and G. M. Pitt). Geological Society of Australia Special Publication **12**, pp. 323-351.

POWELL T. G., BOREHAM C. J., MCKIRDY D. M., MICHAELSEN B. H. AND SUMMONS R. E. (1989) Petroleum geochemistry of the Murta Member, Mooga Formation, and associated oils, Eromanga Basin. *The APEA Journal* **29**(1), 114-129.

POWELL T. G. AND MCKIRDY D. M. (1973) Relationship between ratio of pristane to phytane, crude oil composition and geological environment in Australia. *Nature* **243**, 37-39.

POWELL T. G. AND SNOWDON L. R. (1979) Geochemistry of crude oils and condensates from the Scotian Basin, offshore Eastern Canada. *Bulletin of Canadian Petroleum Geology* **27**, 453-466.

POWELL T. G., BOREHAM C. J., SMYTH M., RUSSELL N. AND COOK A. C. (1991) Petroleum source rock assessment in non-marine sequences: pyrolysis and petrographic analysis of Australian coals and carbonaceous shales. *Organic Geochemistry* **26**, 19-31.

RADKE M., SCHAFFER R. G., LEYTHAEUSER D. AND TEICHMULLER M. (1980a) Composition of soluble organic matter in coals: relation to rank and liptinite fluorescence. *Geochimica et Cosmochimica Acta* **44**, 1787-1800.

RADKE M., WILLSCH H. AND WELTE D., H. (1980b) Preparative hydrocarbon group type determination by automated medium pressure liquid chromatography. *Analytical Chemistry* **52**, 406-411.

RADKE M. AND WELTE D. H. (1983) The methylphenanthrene index (MPI): a maturity parameter based on aromatic hydrocarbons. In *Advances in Organic Geochemistry 1981* (eds. M. Bjoroy et. al.), pp. 504-512. Wiley, Chichester.

RASMUSSEN B. (1997) Fluorescent growth bands in irradiated-bitumen nodules: evidence of episodic hydrocarbon migration. *AAPG Bulletin* **81**, 17-25.

REZAEE M. AND LEMON N. M. (1996) Controls on pore geometry in the Tirrawarra Sandstone reservoir, Cooper Basin, Australia. *PESA Journal* **24**, 116-138.

RICHTER B. E., JONES B. A., EZZELL J. L. AND PORTER N. L. (1996) Accelerated solvent extration: A technique for sample preparation. *Analytical Chemistry* **68**, 1033-1039.

ROBERTS D. C., CARROLL P. G. AND SAYERS C. J. (1990) The Kalladeina Formation – a Warburton Basin Cambrian carbonate play. *The APEA Journal* **30**(1), 166-183.

ROWLAND S. J. (1990) Production of acyclic isoprenoid hydrocarbons by laboratory maturation of methanogenic bacteria. *Organic Geochemistry* **15**, 9-16.

SCALAN R. S. AND SMITH J. E. (1970) An improved measure of the odd-even predominance in the normal alkanes of sediment extracts and petroleum. *Geochimica et Cosmochimica Acta* **34**, 611-620.

SCHAEFER R. G. (1992) Zur geochemie nidrigmolekularer kohlenwasserstoffe im Posidonienschiefer der Hilsmulde. *Erdol and Kohle - Erdgas* **45**, 73-78.

SCHAEFER R. G. AND LITTKE R. (1988) Maturity-related compositional changes in the low-molecular-weight hydrocarbon fraction to Toarcian shales. *Organic Geochemistry* **13**, 887-892.

SCHWARK L. AND PUTTMANN W. (1990) Aromatic hydrocarbon composition of the Permian Kuperschiefer in the Lower Rhine Basin, NW Germany. *Organic Geochemistry* **16**, 749-761.

SCHWARK L., STODDART D., KEUSER C., SPITTHOFF B. AND LEYTHAEUSER D. (1997) A novel sequential extraction system for whole core plug extraction in a solvent flow-through cell – application to extraction of residual petroleum from an intact pore-system in secondary migration studies. *Organic Geochemistry* **26**, 19-31.

SEGGIE R. J. (1997) Reservoir characterisation of the Moorari/Woolkina field complex, Cooper Basin. *The APPEA Journal* **37**(1), 70-86.

SEGGIE R. J., LANSOM P. B., HAMLIN H. S. AND JOHNSON G. A. (1994) The Tirrawarra oil field: field revitalisation through reservoir description and characterisation. *The APEA Journal* **34**(1), 33-54.

SEIFERT W. K. AND MOLDOWAN J. M. (1979) The effect of biodegradation on steranes and terpanes in crude oils. *Geochimica et Cosmochimica Acta* **43**, 111-126.

SMALLEY P. C., DODD T. A., STOCKDEN I. L., RÅHEIM A. AND MEARNS E. W. (1995) Compositional heterogeneities in oil field formation waters: identify them, using them. In *The Geochemistry of Reservoirs* (eds. J. M. Cubitt. and W. A. England). Geological Society Special Publication **86**, pp. 59-69.

SMITH J. T. (1994) Petroleum system logic as an exploration tool in a frontier setting. In *The Petroleum System – from Source to Trap* (eds. L. B. Magoon and W. G. Dow). *AAPG Memoir* **60**, pp. 25-72.

SMYTH M. (1983) Nature of source material for hydrocarbons in Cooper Basin, Australia. *AAPG Bulletin* **67**, 1422-1428.

SMYTH M., COOK A. C. AND PHILIP R. P. (1984) Birkhead revisited: Petrological and geochemical studies of the Birkhead Formation, Eromanga Basin. *The APEA Journal* **24**(1), 230-242.

SNOWDON L. R. AND POWELL T. G. (1979) Families of crude oils and condensates in the Beaufort-Mackenzie Basin. *Bulletin of Canadian Petroleum Geology* **27**, 139-162.

SOFER Z. (1984) Stable carbon isotope composition of crude oils: application to source depositional environment and petroleum alteration. *AAPG Bulletin* **68**, 31-49.

SPRIGG R. C. (1986) The Eromanga Basin in the search for commercial hydrocarbons. In *Contributions to the Geology and hydrocarbon potential of the Eromanga Basin* (eds. D. I. Gravestock, P. S. Moore, and G. M. Pitt). Geological Society of Australia Special Publication **12**, pp. 9-12.

STODDART D. P., HALL P. B., LARTER S. R., BRASHER J., LI M. AND BJORØY M. (1995) Reservoir geochemistry of the Eldfisk Field, Norwegian North Sea. In *The Geochemistry of Reservoi*rs (eds. J. M. Cubitt and W. A. England). Geological Society Special Publication **86**, pp. 257-297.

TEN HAVEN H. L. (1996) Application and limitation of Mango's light hydrocarbon parameters in petroleum correlation studies. *Organic Geochemistry* **24**, 957-976.

ten Haven H. L., de Leeuw J. W., Rullkoetter J. and Sinninghe Damsté J. S. (1987) Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. *Nature* **330**, 641-643.

Thompson K. F. M. (1979) Light hydrocarbons in subsurface sediments. *Geochimica et Cosmochimica Acta* **43**(5), 657-672.

Thompson K. F. M. (1983) Classification and thermal history of petroleum base on light hydrocarbon. *Geochimica et Cosmochimica Acta* **47**, 303-316.

Thompson K. F. M. (1987) Fractionated aromatic petroleums and the generation of gas-condensates. *Organic Geochemistry* **11**, 573-590.

Thompson K. F. M. (1988) Gas-condensate migration and oil fractionation in deltaic systems. *Marine and Petroleum Geology.* **5**, 246-273.

Tingate P. R. and Luo P. (1992) Silica diagenesis and pore development in Permian sandstones, southern Cooper Basin. *The APEA Journal* **32**(1), 325-338.

Tissot B. P. and Welte D. H. (1984) *Petroleum Formation and Occurrence.* Springer-Verlag, Berlin.

Toupin D., Eadington P. J., Person M., Morin P., Wieck J. M. and Warner D. (1997) Petroleum hydrogeology of the Cooper and Eromanga Basins, Australia: Some insights from mathematical modelling and fluid inclusion data. *AAPG Bulletin* **81**, 557-603.

Tupper N. P. and Burckhardt D. M. (1990) Use of the methylphenanthrene index to characterise expulsion of Cooper and Eromanga Basin oils. *The APEA Journal* **30**(1), 375-385.

Vincent P. W., Mortimore I. R. and McKirdy D. M. (1985) Hydrocarbon generation, migration and entrapment in the Jackson-Naccowlah area, ATP 259P, Southwestern Queensland. *The APEA Journal* **25**(1), 62-84.

WILLIAMS B. P. J. AND WILD E. K. (1984) The Tirrawarra Sandstone and Merrimelia Formation of the southern Cooper Basin, South Australia – the sedimentation and evolution of a glaciofluvial system. *The APEA Journal* **24**(1), 377-392.

WOPFNER H. (1985) Some thoughts on the post-orogenic development of northeastern South Australia and adjoining regions. In *Stratigraphy, Palaeontology, Malacology. Papers in Honour of Dr Nell Ludbrook* (ed. J. M. Lindsay). South Australian Department of Mines and Energy Special Publication **5**, pp. 365-372.

YAMAMOTO M. (1992) Fraction of azaarenes during oil migration. *Organic Geochemistry* **19**, 389-402.

YU X. AND MCKIRDY D. M. (1998) *A preliminary survey of petroleum composition in the Cooper/Eromanga Basin using cryogenic GC-FID analysis of untopped oils and condensates*. Report for Santos Limited.

YU X., AROURI, K. R., MCKIRDY, D. M. AND HILL, A. J. (2000a) A new approach to the estimation of mixing ratios in reservoirs containing multiple oil charges. In *Second Sprigg Symposium: Frontier Basins, Frontier Ideas* (compiler G.R. Wood), Geological Society of Australia Abstracts **60**, 80-83.

YU X., AROURI, K. R., MCKIRDY, D. M. AND HILL, A. J. (2000b) A new approach to the estimation of mixing ratios in reservoirs containing multiple oil charges. *Australian Organic Geochemistry Conference 2000, Townsville, Abstracts* (2 p.)

ZHANG D., HUANG D. AND LI J. (1988) Biodegraded sequence of Karamay oils and semi-quantitative estimation of their biodegraded degrees in Junggar Basin, China. *Organic Geochemistry* **13**, 295-302.

ZHOU S. (1989) Subsidence history of the Eromanga Basin, South Australia. In *The Cooper and Eromanga Basins, Australia* (ed. B. J. O'Neil), Proceedings of

Petroleum Exploration Society of Australia, Society of Petroleum Engineers, Australian Society of Exploration Geophysicists (SA Branches), Adelaide, pp. 329-335.

APPENDIX ONE

Figures showing variation of compositional ratios with reservoir strata. Based on GC-FID measurements of 115 oils and condensates from the Cooper and Eromanga Basins.

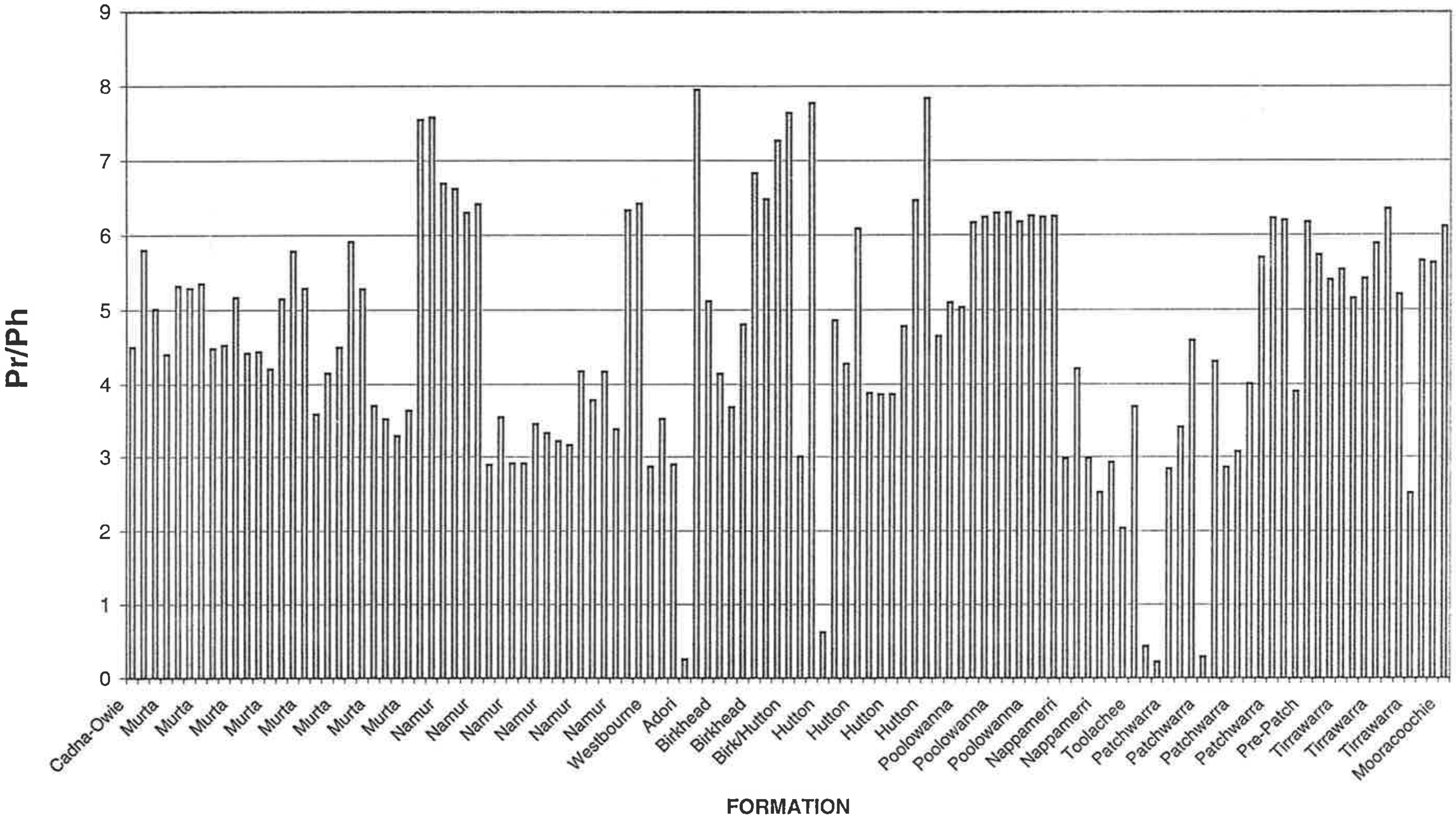


Figure A.1a Variation of Pr/Ph with reservoir formation

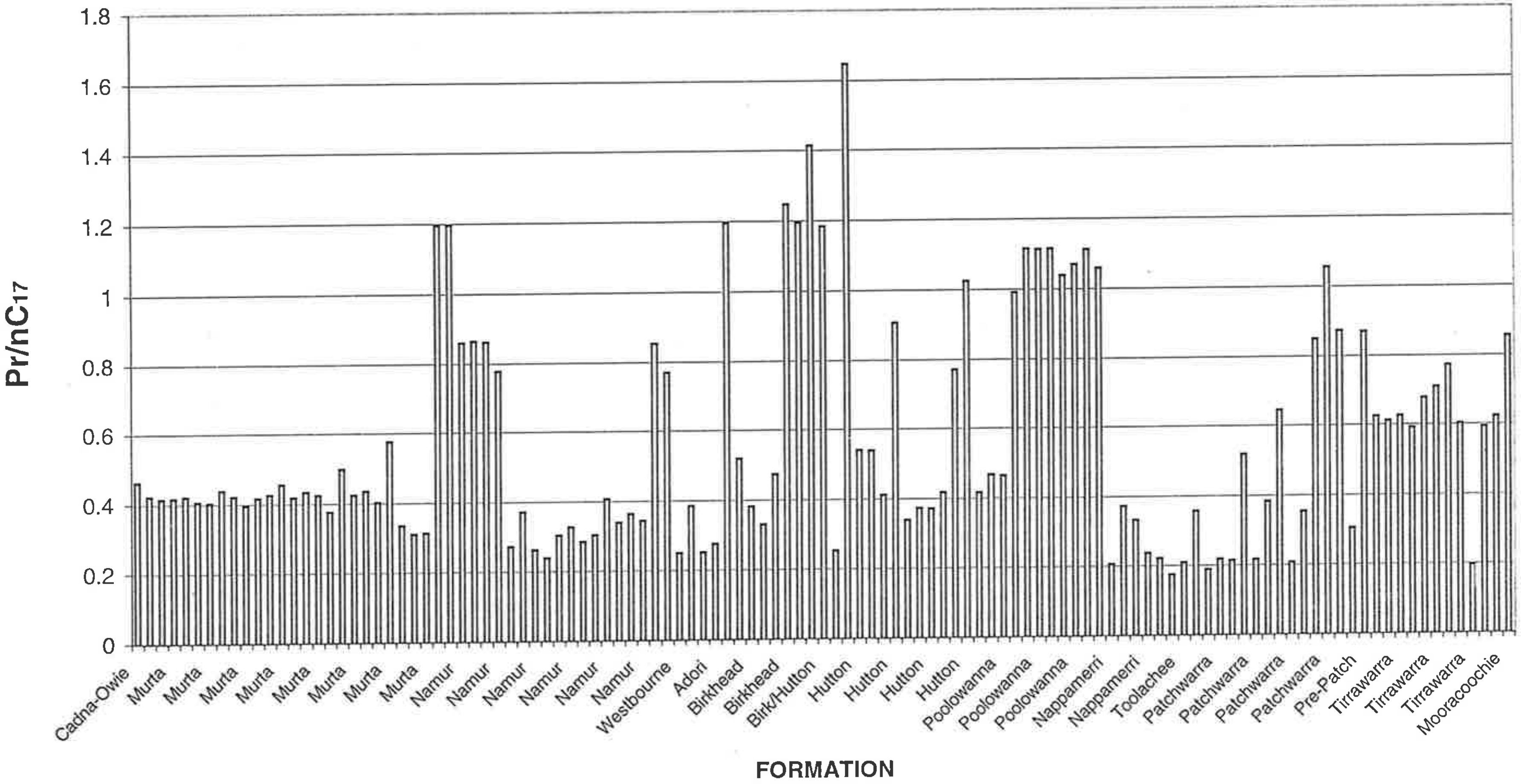


Figure A.1b Variation of Pr/nC_{17} with reservoir formation

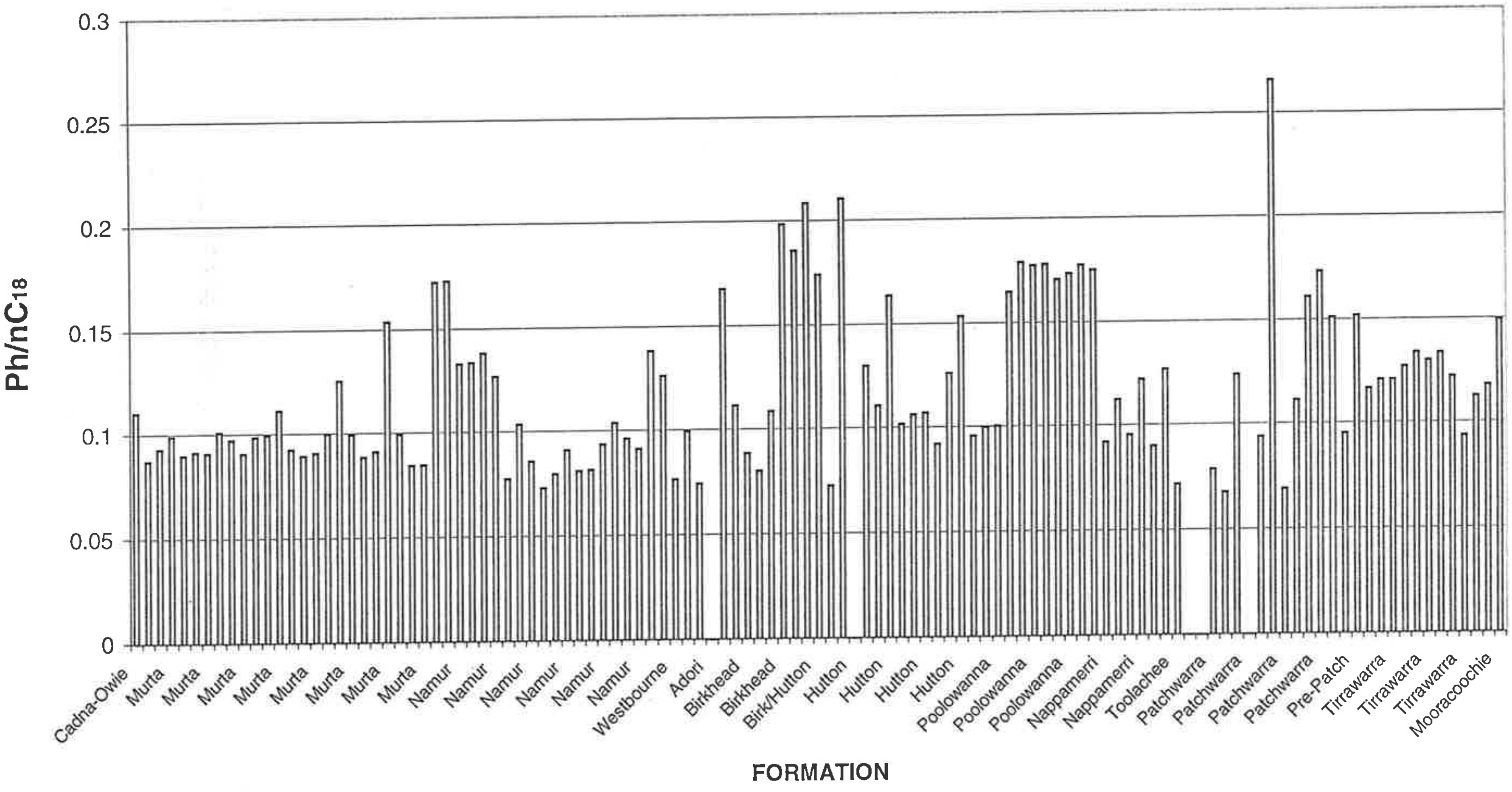


Figure A.1c Variation of Ph/nC_{18} with reservoir formation

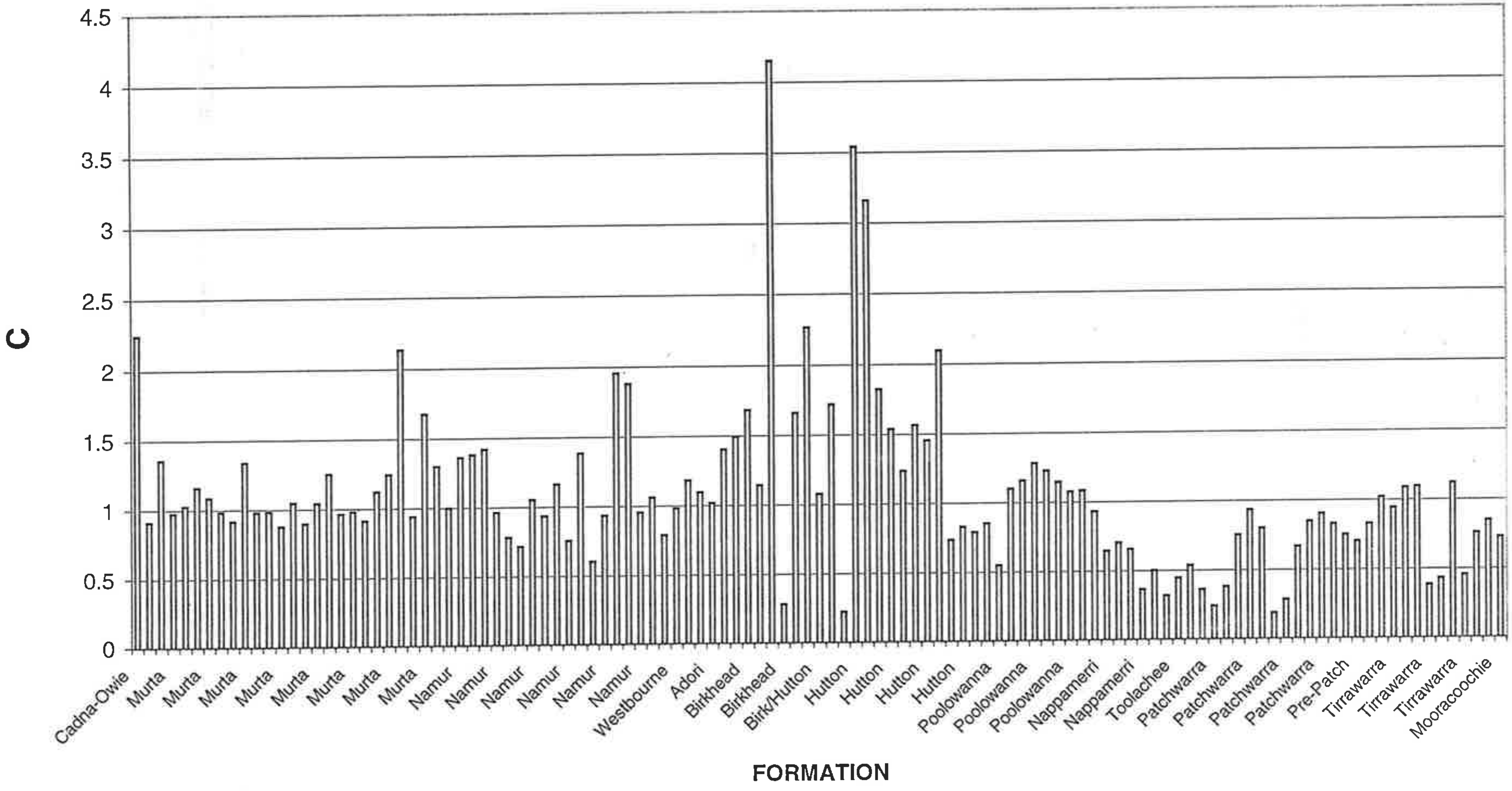


Figure A.1d Variation of C with reservoir formation

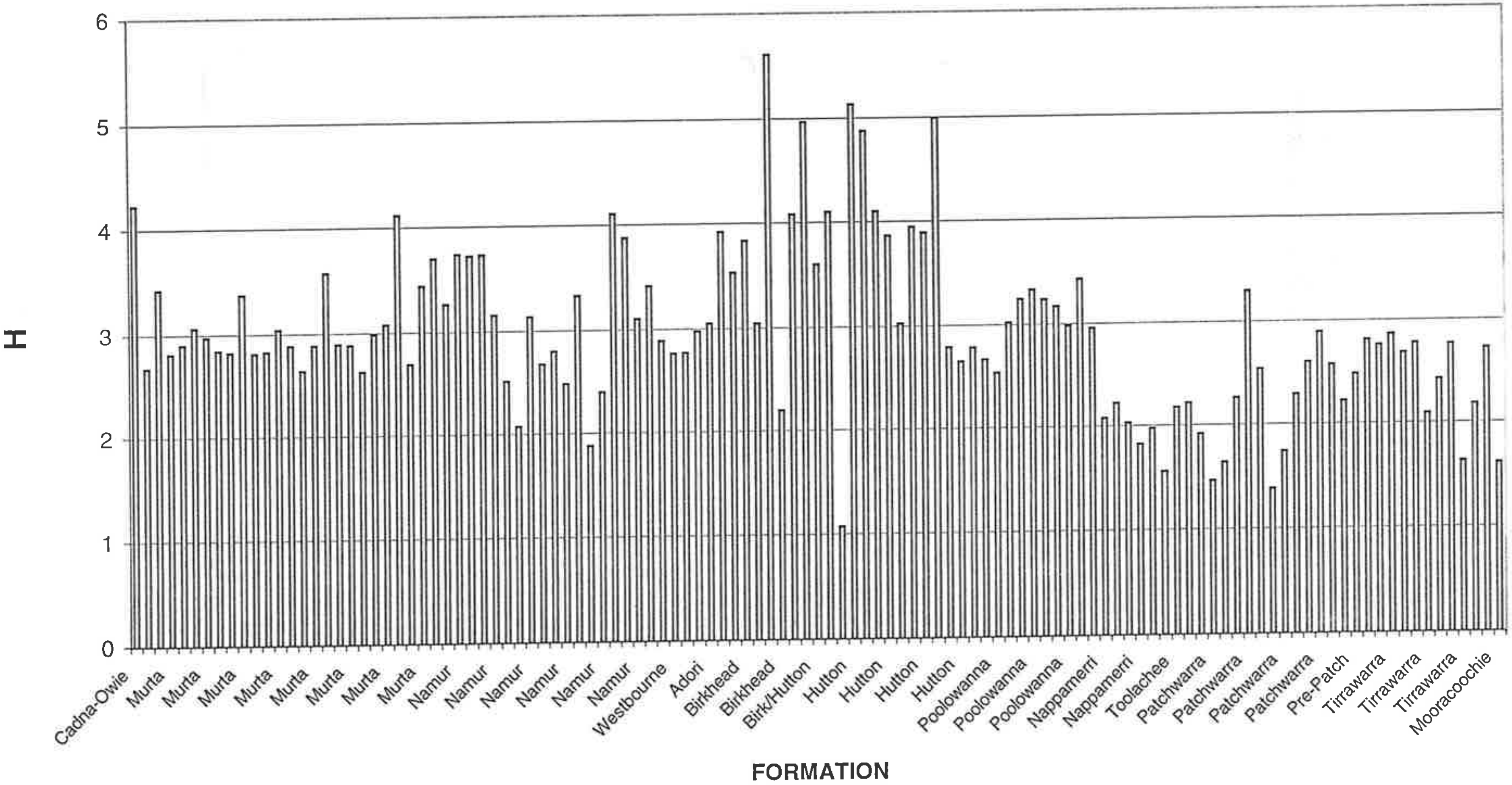


Figure A.1e Variation of H with reservoir formation

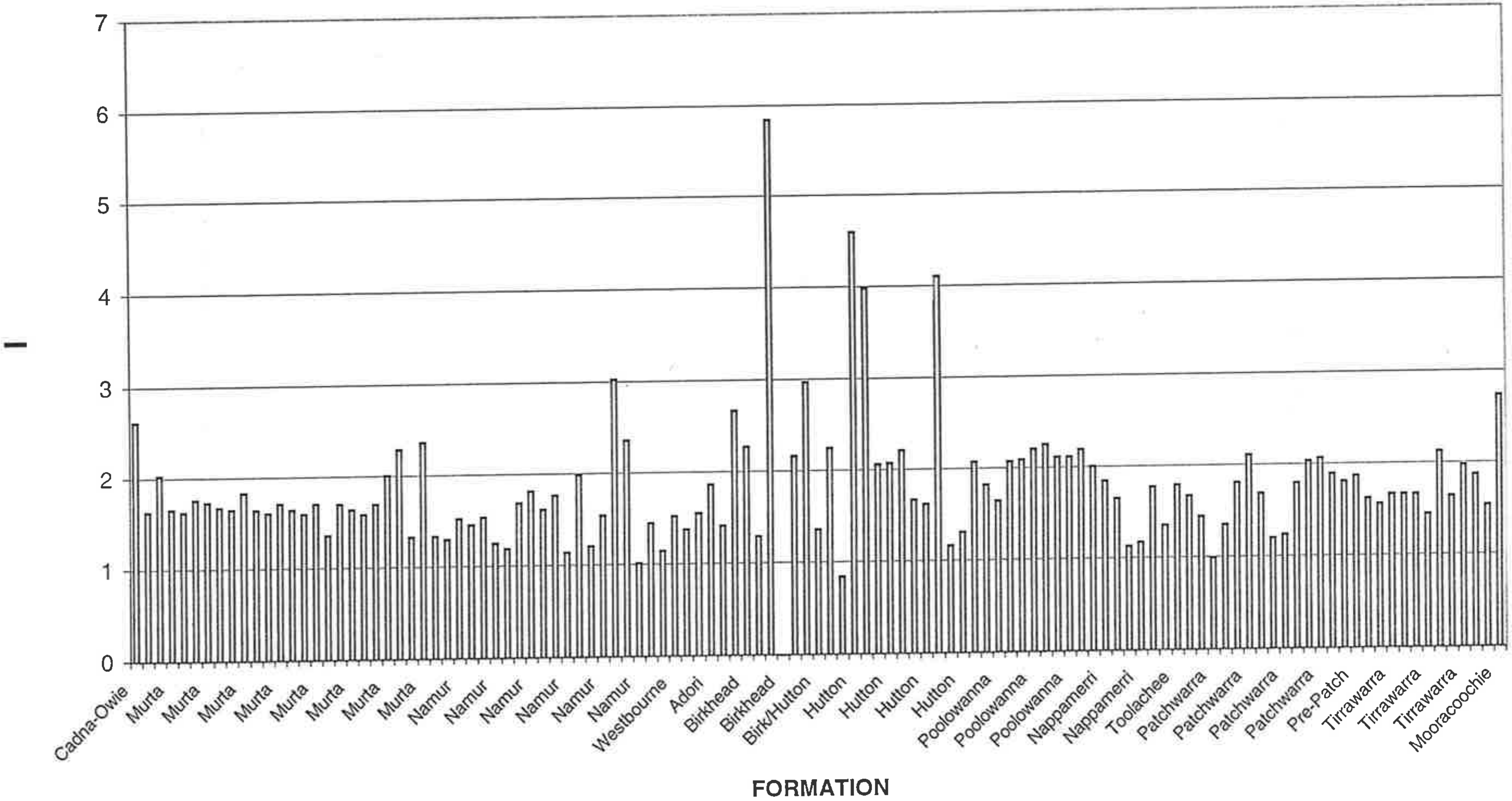


Figure A.1f Variation of I with reservoir formation

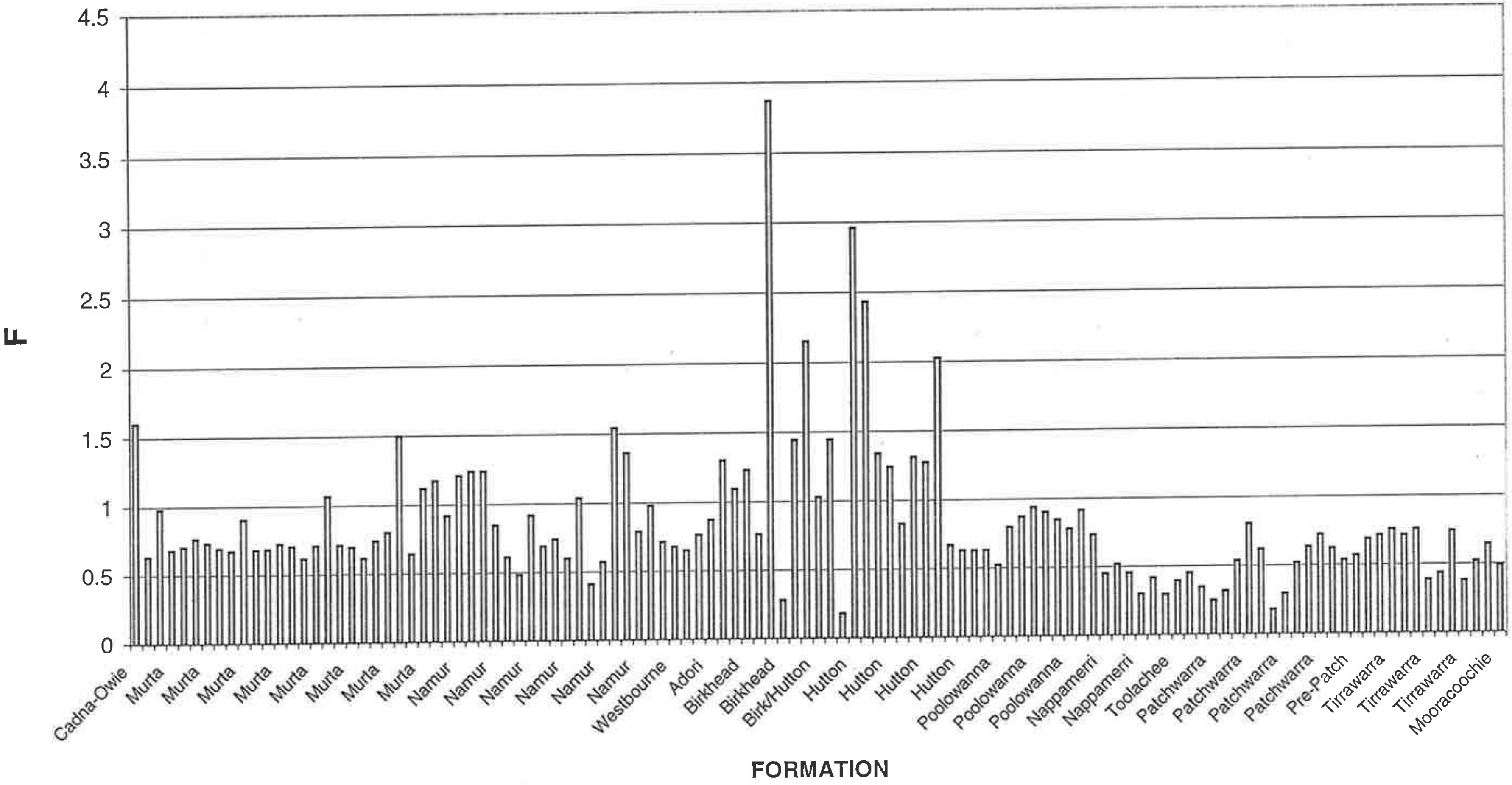


Figure A.1g Variation of F with reservoir formation

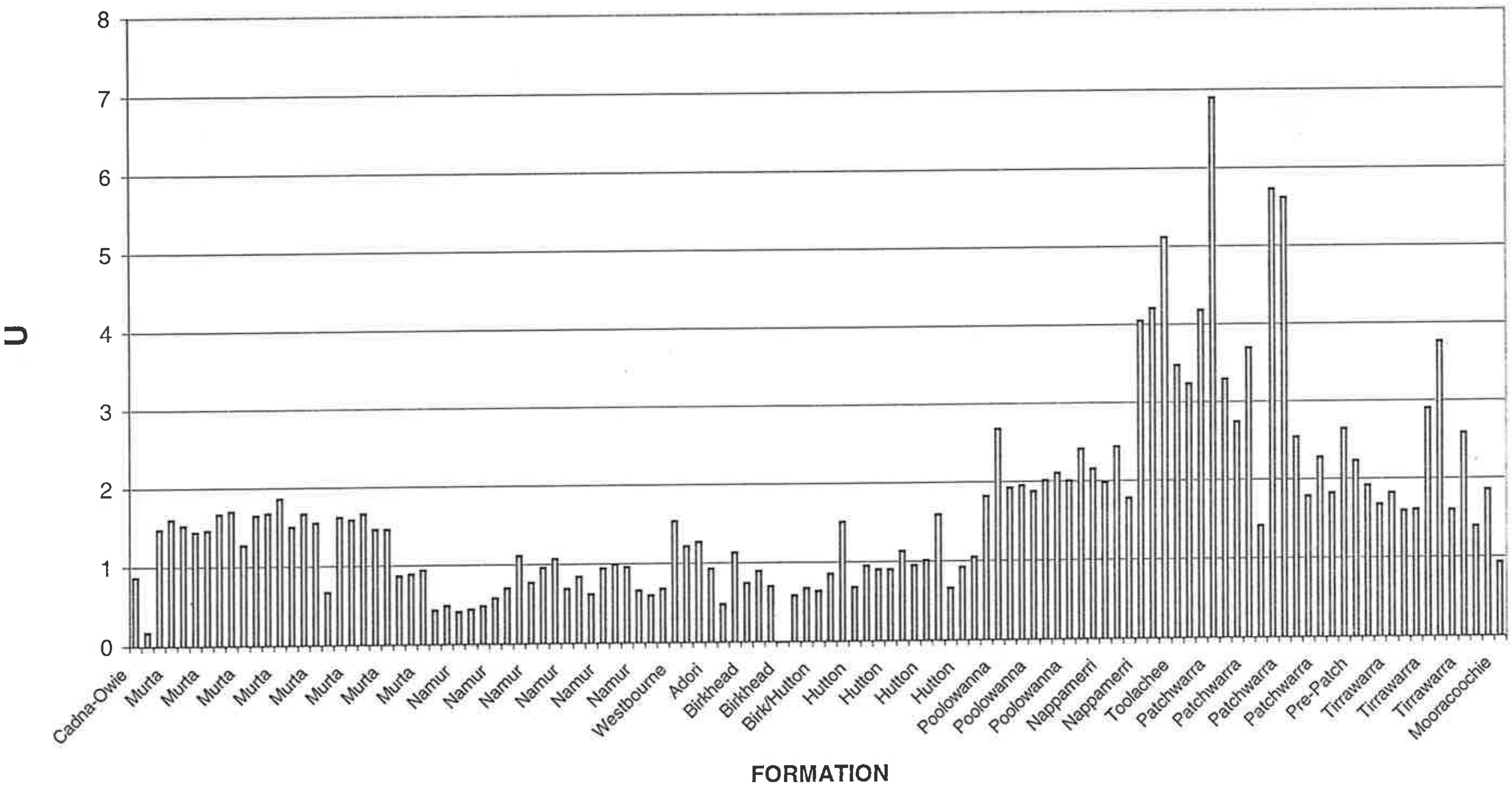


Figure A.1h Variation of U with reservoir formation

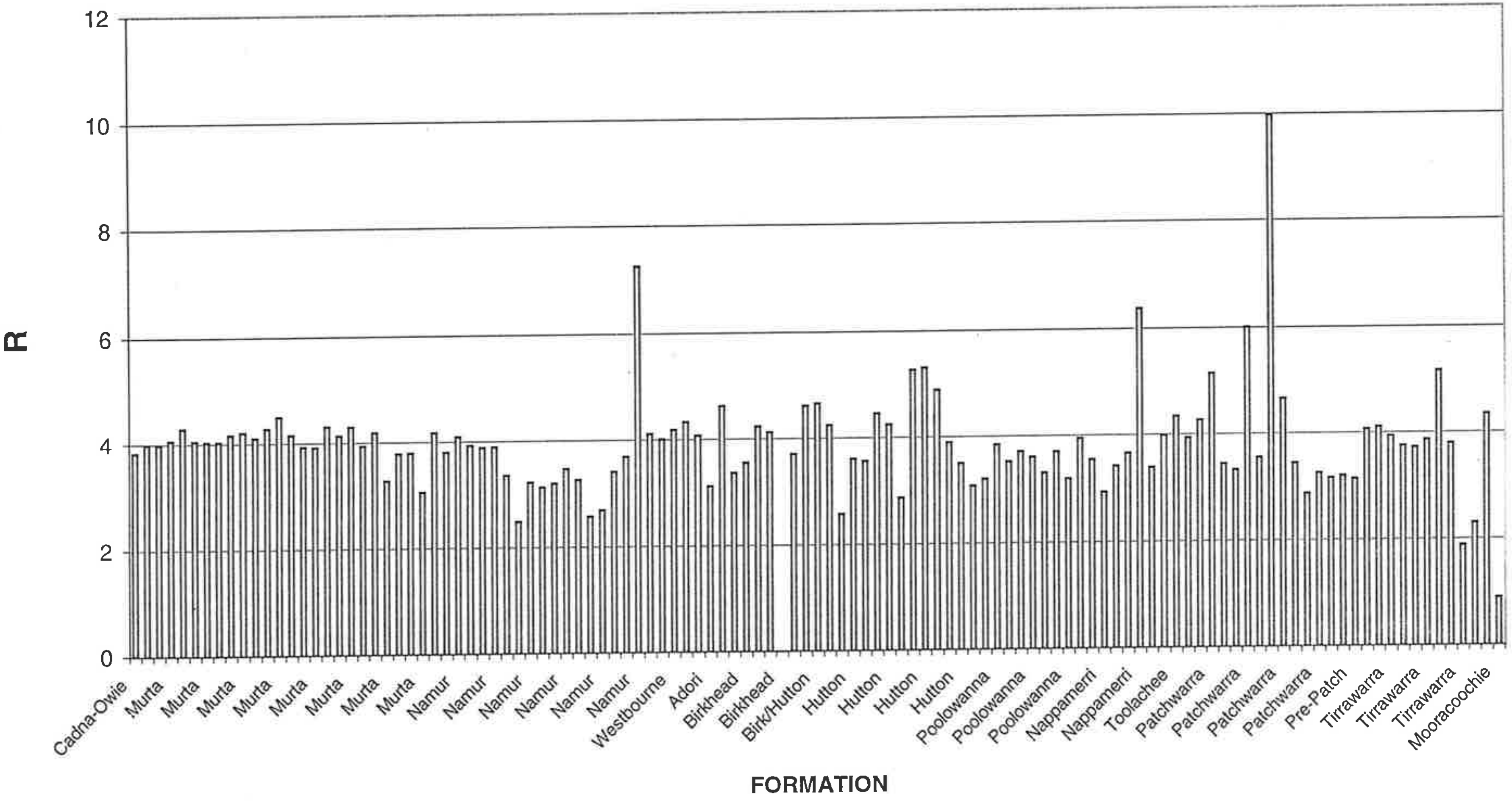


Figure A.1i Variation of R with reservoir formation

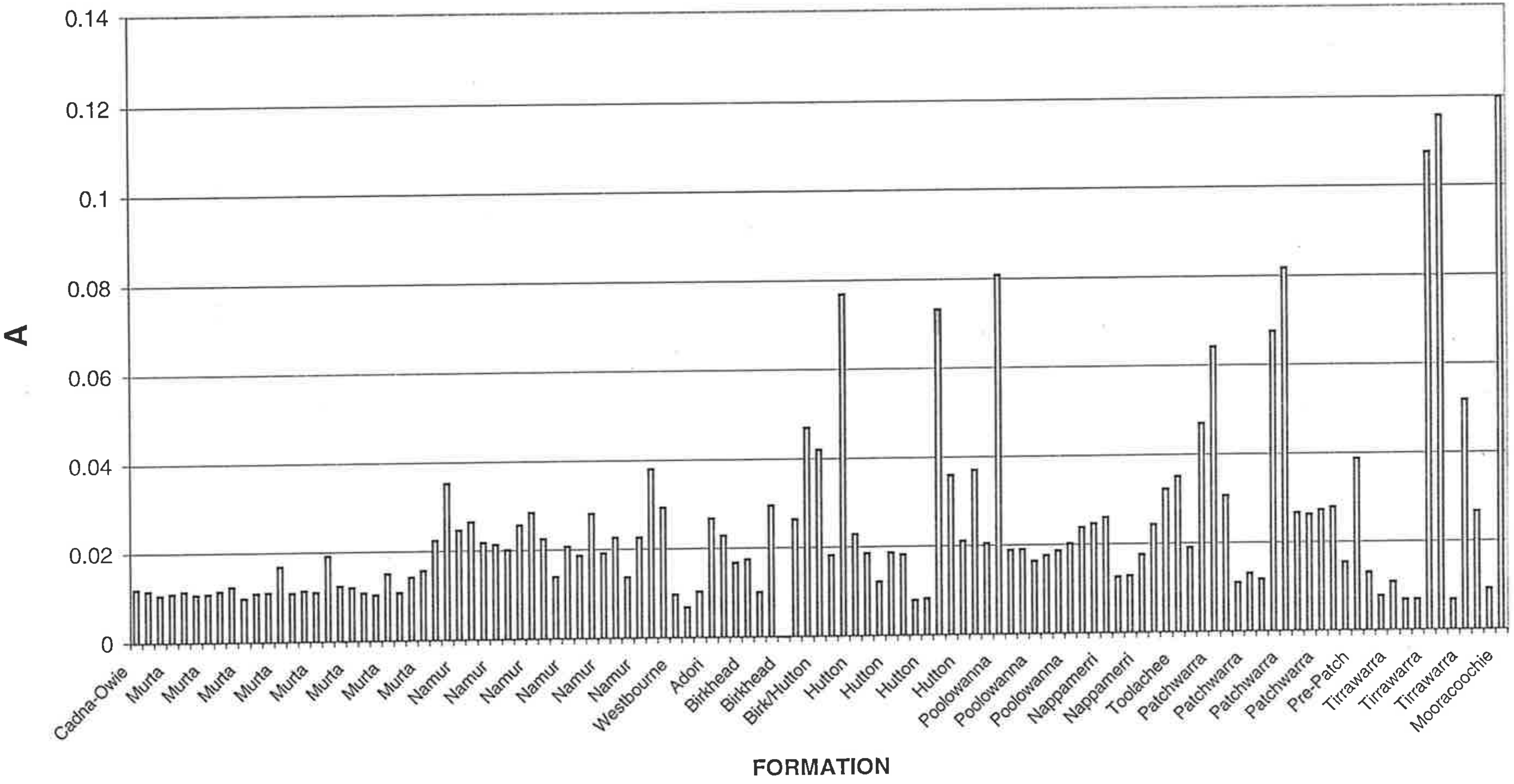


Figure A.1j Variation of A with reservoir formation

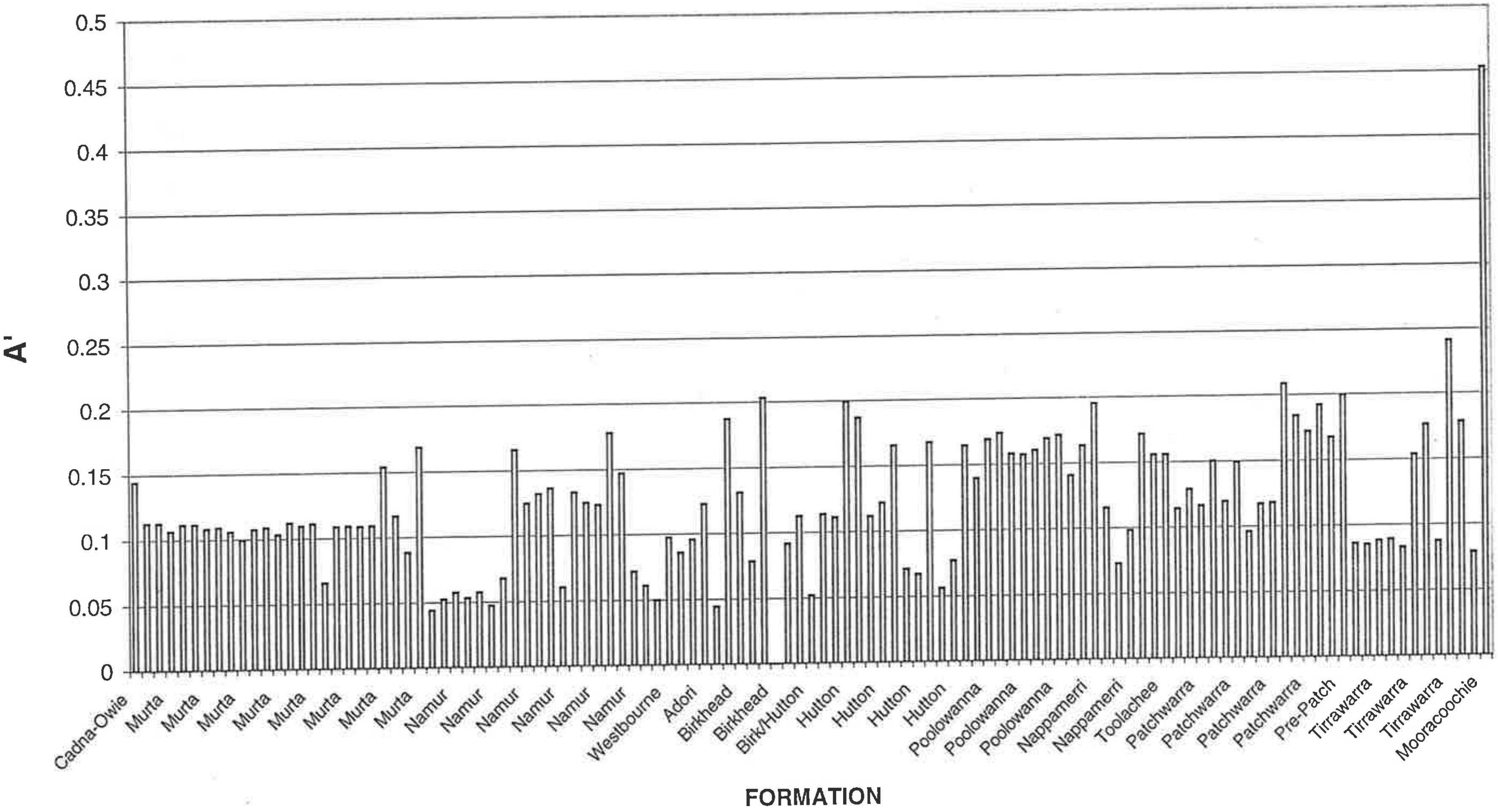


Figure A.1k Variation of A' with reservoir formation

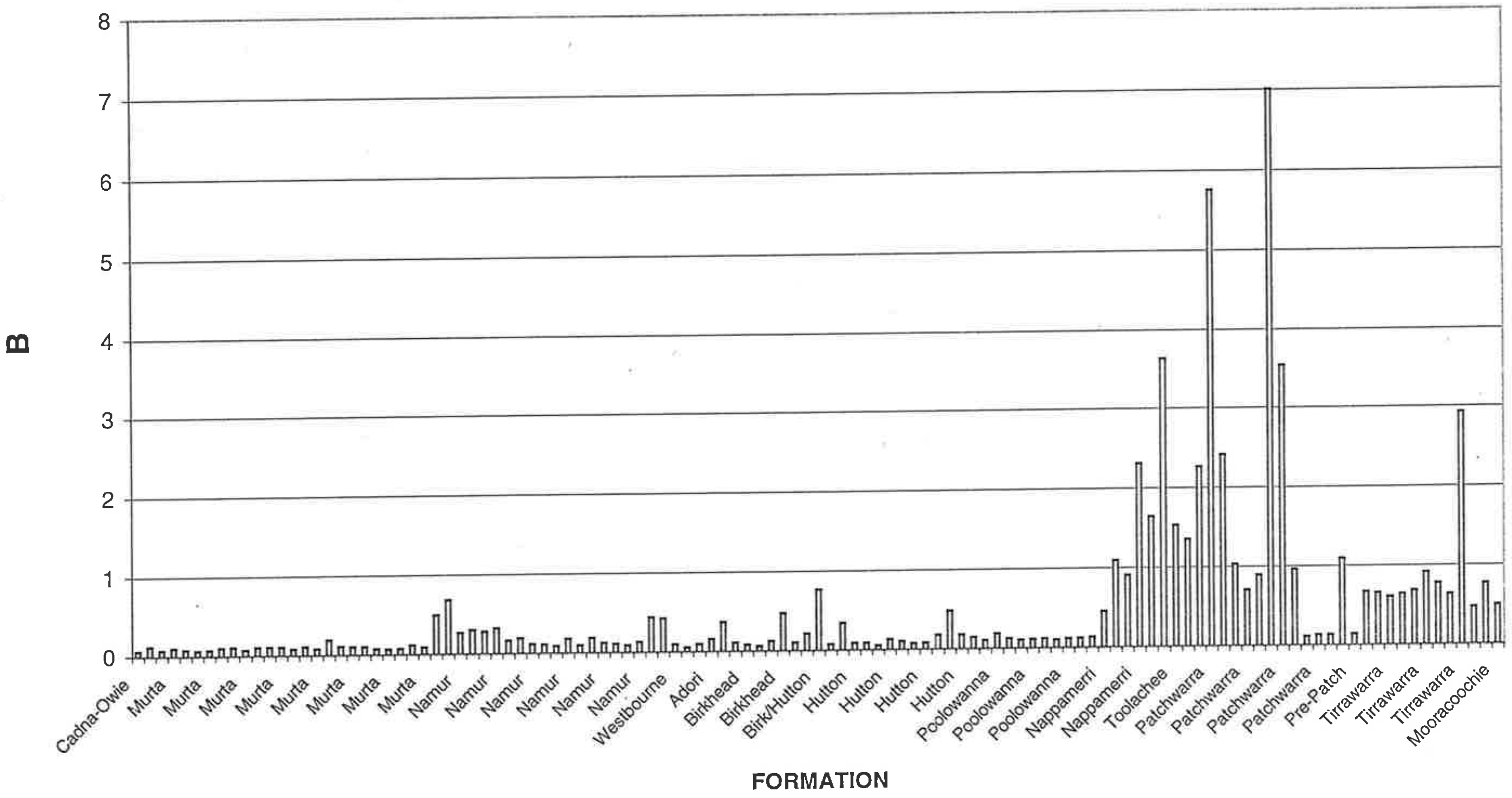


Figure A.11 Variation of B with reservoir formation

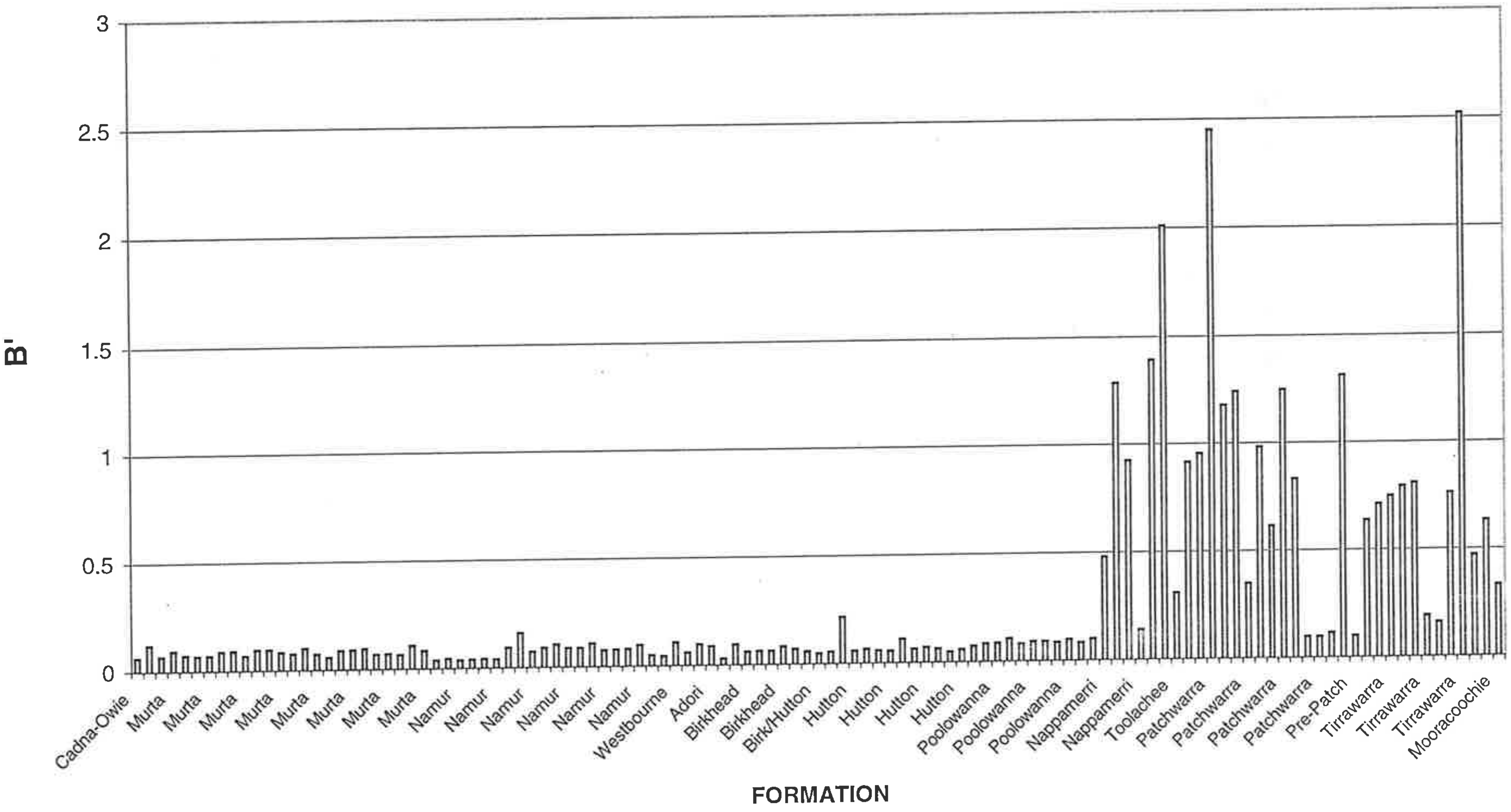


Figure A.1m Variation of B' with reservoir formation

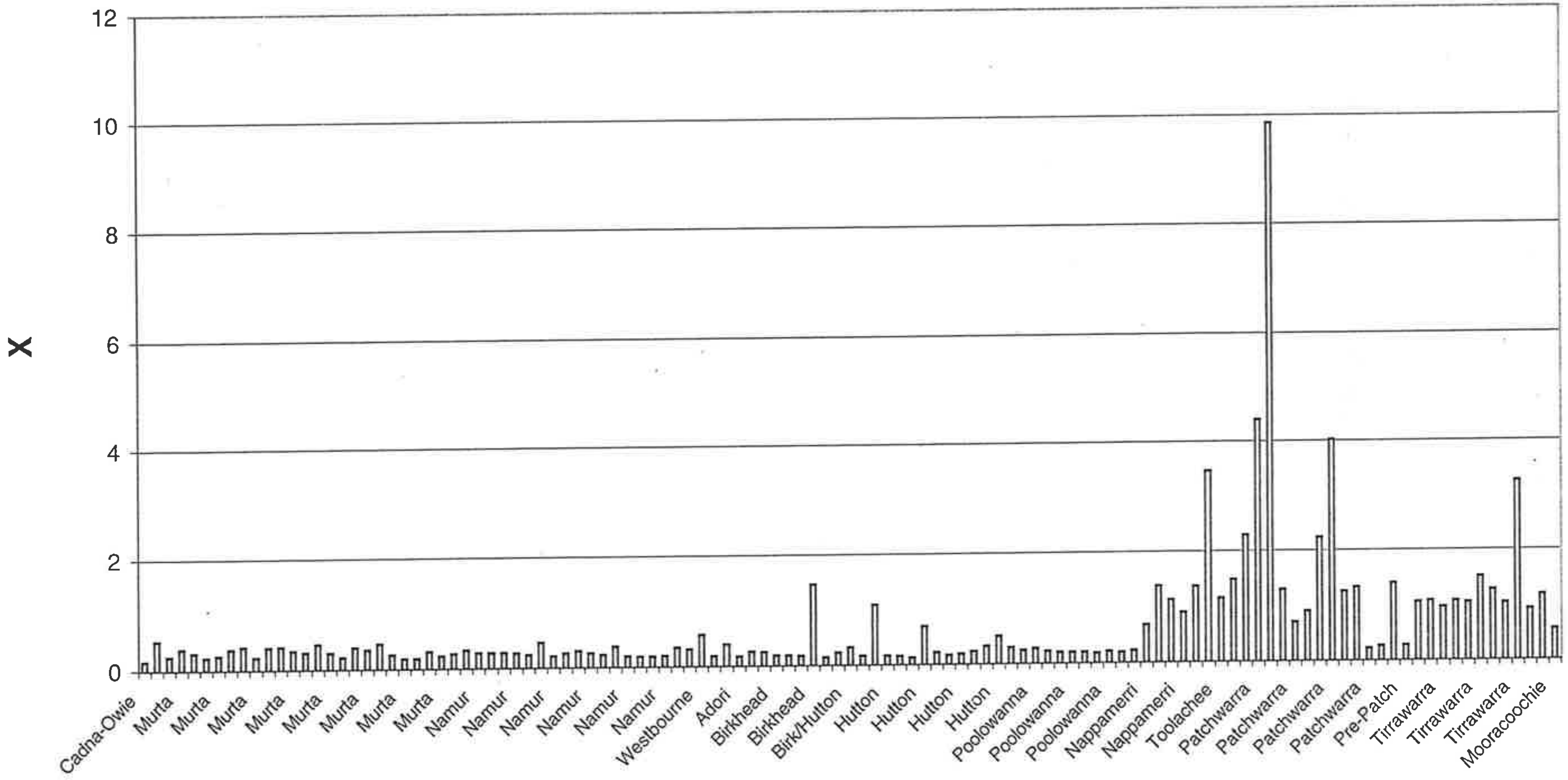


Figure A.1n Variation of X with reservoir formation

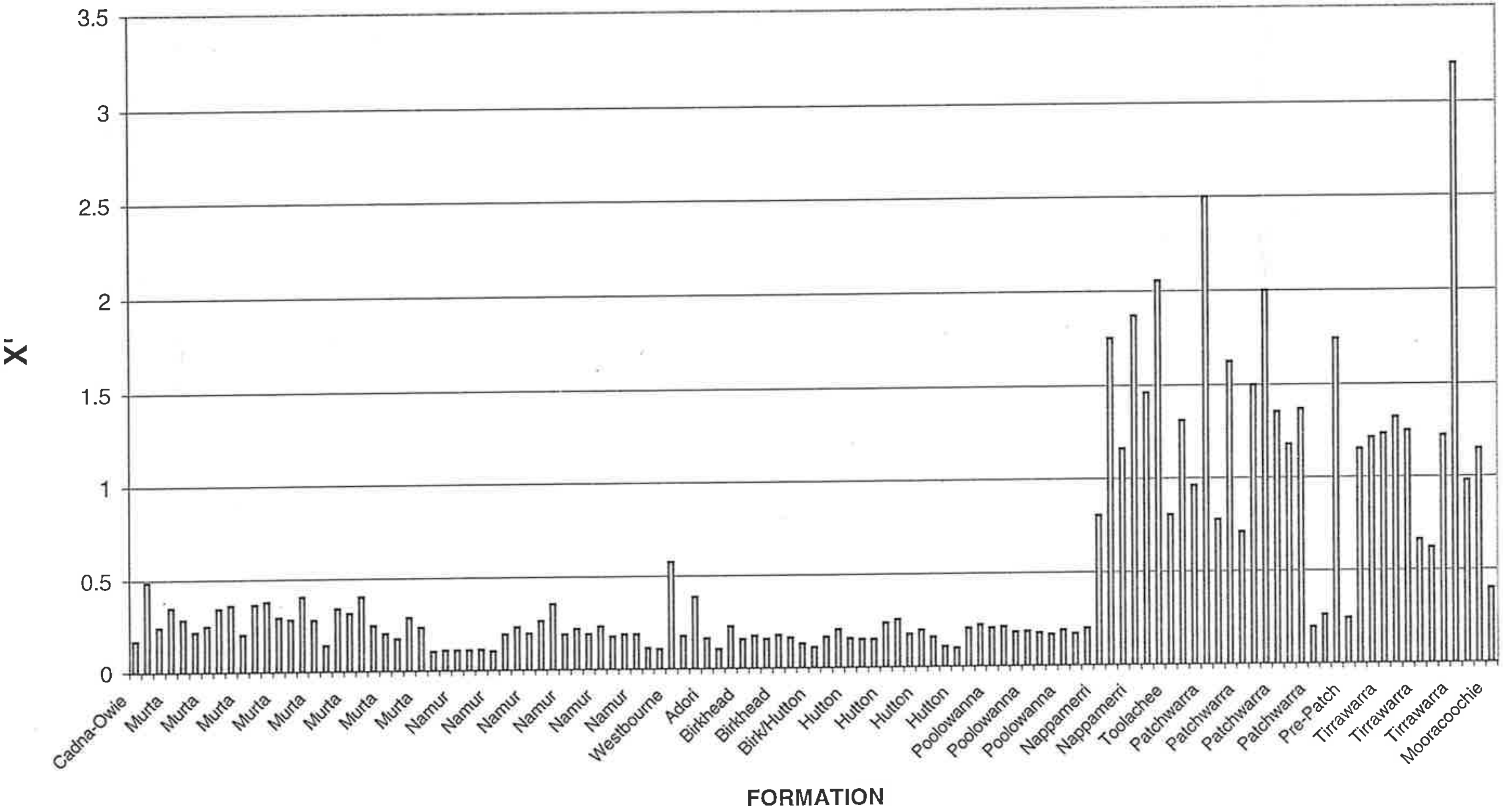


Figure A.1o Variation of X' with reservoir formation

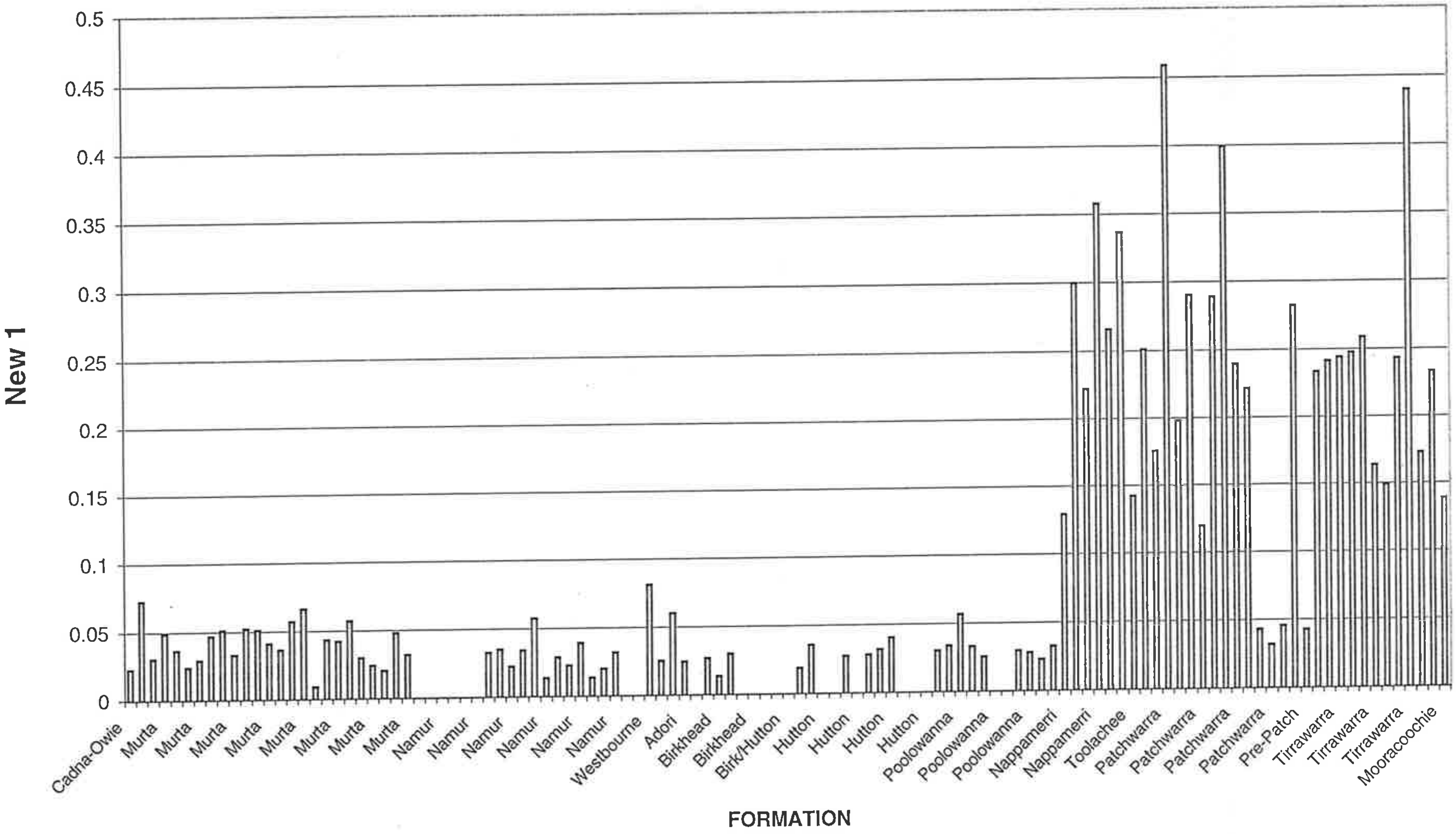


Figure A.1p Variation of New 1 with reservoir formation

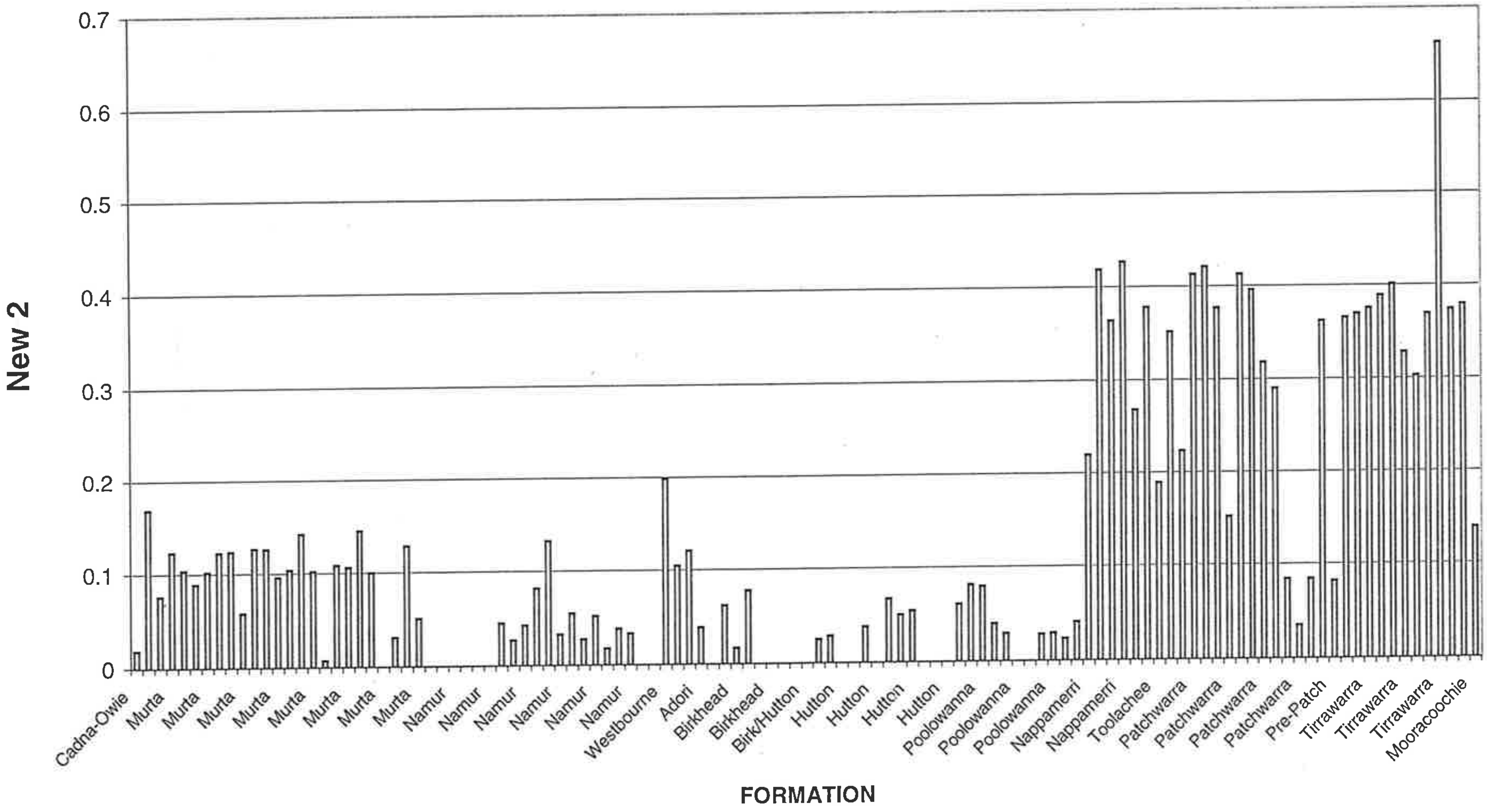


Figure A.1q Variation of New 2 with reservoir formation

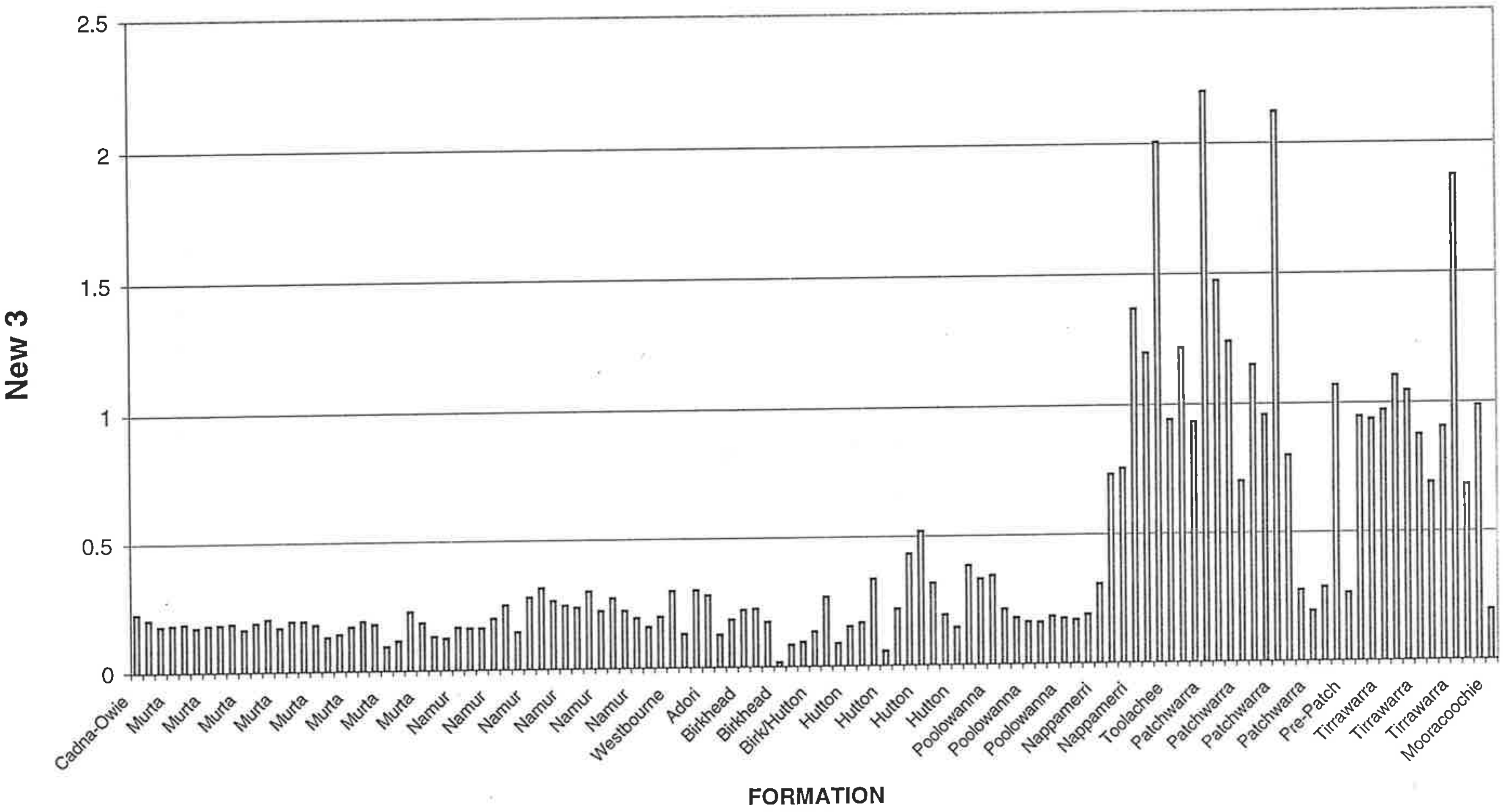


Figure A.1r Variation of New 3 with reservoir formation

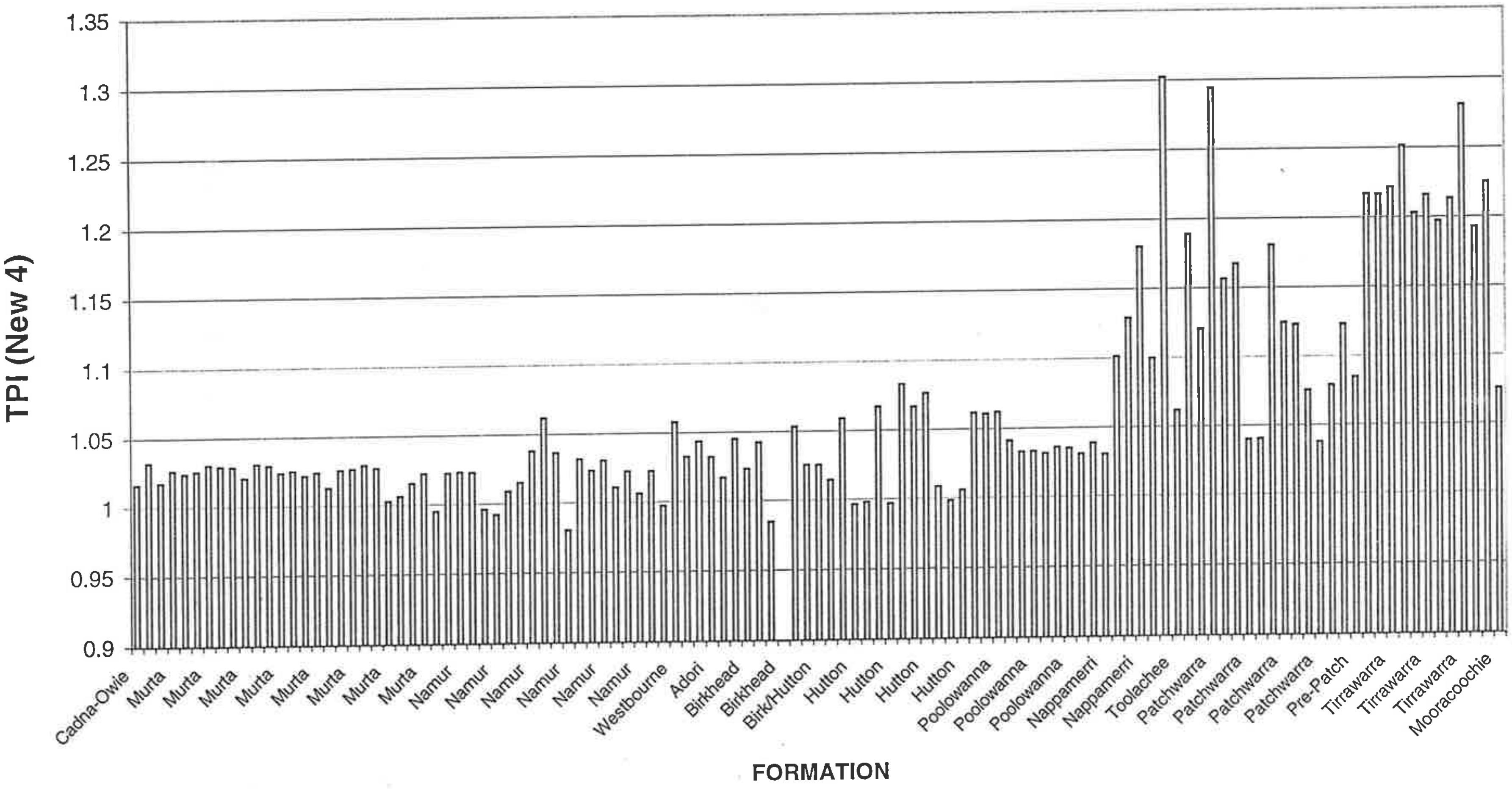


Figure A.1s Variation of TPI (New 4) with reservoir formation

APPENDIX TWO

Database and figures showing changes of aromatic compositional ratios with reservoir strata. Based on GC-MS analysis of 72 DST oils/condensates from the Cooper and Eromanga Basins.

Table A.2 Database of some aromatic hydrocarbon ratios in Cooper and Eromanga crude oils

Sample	Formation	Ben/Tol	Tol/proB	pro/ipro-B	Ben/Naph	Ben/Phe	Naph/Phe	Ret/Phe	Phe/Pr	Ret/Pr	o/mp-Xyl
XYOIL035	Murta	0.046	1.347	2.601	0.062	0.092	1.483	2.196	0.065	0.144	0.160
XYOIL037	Murta	0.046	0.811	2.755	0.041	0.072	1.769	2.018	0.057	0.115	0.152
XYOIL039	Murta	0.024	2.290	2.533	0.046	0.094	2.062	2.196	0.063	0.137	0.163
XYOIL042	Murta	0.033	2.361	2.549	0.065	0.126	1.945	2.151	0.064	0.137	0.162
XYOIL047	Murta	0.045	1.356	2.603	0.062	0.086	1.384	2.155	0.064	0.139	0.160
XYOIL068	Murta	0.111	1.814	2.051	0.058	0.087	1.506	1.329	0.127	0.169	0.205
XYOIL079	Murta	0.068	2.253	2.436	0.047	0.115	2.417	1.689	0.076	0.129	0.227
XYOIL084	Murta	0.100	3.288	1.784	0.113	0.285	2.528	1.953	0.102	0.199	0.264
XYOIL018	Namur	0.178	6.324	2.302	0.126	0.180	1.424	0.114	0.259	0.029	0.231
XYOIL020	Namur	0.182	2.173	2.438	0.070	0.115	1.649	1.484	0.435	0.645	0.263
XYOIL027	Namur	0.187	2.868	2.278	0.158	0.185	1.171	0.400	0.700	0.280	0.247
XYOIL030	Namur	0.133	3.049	2.093	0.154	0.240	1.560	0.796	0.199	0.158	0.087
XYOIL054	Namur	0.168	2.657	2.102	0.113	0.190	1.687	1.750	0.209	0.366	0.258
XYOIL087	Namur	0.156	3.588	2.842	0.058	0.068	1.158	1.910	0.093	0.178	0.302
XYOIL095	Namur	0.090	0.829	2.824	0.007	0.003	0.489	2.530	0.028	0.070	0.365
XYOIL121	Namur	0.139	2.807	2.163	0.054	0.145	2.693	1.832	0.031	0.056	0.327
XYOIL123	Namur	0.138	3.172	2.660	0.041	0.061	1.503	1.362	0.172	0.235	0.345
XYOIL029	Westbourne	0.009	2.262	2.603	0.009	0.006	0.704	0.796	0.530	0.422	0.164
XYOIL041	Westbourne	0.118	0.118	3.317	0.037	0.007	0.195	2.554	0.115	0.295	0.107
XYOIL086	Westbourne	0.028	2.668	2.693	0.020	0.013	0.621	0.470	0.544	0.256	0.169
XYOIL013	Adori	0.135	6.334	2.336	0.170	0.261	1.535	1.181	0.514	0.607	0.248
XYOIL019	Birkhead	0.167	5.161	2.331	0.110	0.116	1.060	0.081	0.576	0.047	0.223
XYOIL024	Birkhead	0.086	0.634	2.843	0.010	0.010	1.015	0.763	0.163	0.124	0.246
XYOIL070	Birkhead	0.105	1.280	3.033	0.040	0.022	0.540	1.816	0.192	0.350	0.185
XYOIL090	Birkhead	0.151	4.574	2.734	0.065	0.064	0.981	0.901	0.095	0.085	0.265
XYOIL110	Birkhead	0.029	1.587	2.980	0.006	0.003	0.512	2.529	0.026	0.066	0.233
XYOIL122	Birkhead	0.002	0.386	2.394	0.000	0.000	0.787	0.572	0.230	0.132	0.251
XYOIL025	Hutton	0.142	1.832	3.080	0.034	0.021	0.618	0.754	0.321	0.242	0.195
XYOIL026	Hutton	0.029	3.271	1.952	0.005	0.012	2.374	0.395	0.049	0.019	0.319
XYOIL028	Hutton	0.172	3.730	2.877	0.062	0.060	0.976	2.576	0.114	0.293	0.286
XYOIL062	Hutton	0.187	2.607	3.054	0.050	0.045	0.897	2.133	0.127	0.270	0.267
XYOIL063	Hutton	0.130	3.263	2.921	0.048	0.034	0.710	0.185	1.841	0.340	0.226
XYOIL073	Hutton	0.194	14.244	3.252	0.364	0.197	0.543	1.580	0.166	0.262	0.300
XYOIL074	Hutton	0.185	7.278	3.011	0.134	0.097	0.722	0.924	0.040	0.037	0.234
XYOIL077	Hutton	0.180	4.695	2.540	0.186	0.293	1.570	0.147	1.322	0.195	0.189

Table A.2 Database of some aromatic hydrocarbon ratios in Cooper and Eromanga crude oils (continued)

Sample	Formation	Ben/Tol	Tol/proB	pro/ipro-B	Ben/Naph	Ben/Phe	Naph/Phe	Ret/Phe	Phe/Pr	Ret/Pr	o/mp-Xyl
XYOIL094	Hutton	0.029	1.242	2.819	0.002	0.002	0.955	1.182	0.124	0.146	0.358
XYOIL093	Poolowanna	0.005	0.573	2.065	0.000	0.001	1.706	0.654	0.226	0.148	0.307
XYOIL107	Poolowanna	0.111	5.381	1.752	0.070	0.138	1.974	0.627	0.038	0.024	0.362
XYOIL108	Poolowanna	0.121	4.508	1.777	0.062	0.127	2.040	0.632	0.036	0.023	0.368
XYOIL109	Poolowanna	0.109	4.375	1.780	0.060	0.137	2.284	0.686	0.047	0.033	0.347
XYOIL113	Poolowanna	0.060	1.073	2.016	0.021	0.050	2.360	0.588	0.031	0.018	0.370
XYOIL023	Nappamerri	0.244	8.957	2.450	2.990	32.459	10.854	0.058	0.536	0.031	0.248
XYOIL061	Nappamerri	0.333	16.494	2.235	2.951	46.007	15.590	0.025	0.552	0.014	0.275
XYOIL064	Nappamerri	0.317	13.885	3.042	1.430	2.032	1.421	0.094	1.071	0.101	0.210
XYOIL021	Toolachee	0.302	20.377	1.882	1.300	24.396	18.761	0.009	1.037	0.009	0.302
XYOIL065	Toolachee	0.298	15.323	2.154	0.268	2.026	7.563	0.001	4.873	0.005	0.252
XYOIL081	Toolachee	0.084	7.610	2.013	0.144	1.591	11.045	0.007	0.784	0.005	0.275
XYOIL014	Patchwarra	0.077	9.682	2.656	0.020	0.125	6.122	0.004	1.710	0.007	0.210
XYOIL015	Patchwarra	0.100	20.474	2.695	0.011	0.032	2.769	0.003	2.904	0.008	0.187
XYOIL022	Patchwarra	0.141	1.351	3.128	0.020	0.135	6.706	0.002	1.157	0.003	0.315
XYOIL059	Patchwarra	0.313	25.851	1.971	1.254	4.436	3.538	0.044	0.877	0.039	0.267
XYOIL069	Patchwarra	0.168	17.342	2.005	0.983	10.550	10.730	0.010	0.756	0.007	0.275
XYOIL072	Patchwarra	0.362	35.785	1.607			15.464	0.309	0.428	0.132	0.313
XYOIL075	Patchwarra	0.014	8.979	1.914	0.022	0.139	6.365	0.004	0.910	0.004	0.312
XYOIL083	Patchwarra	0.079	6.098	3.441	0.011	0.078	6.795	0.005	1.471	0.008	0.188
XYOIL089	Patchwarra	0.229	14.563	1.955	0.722	9.310	12.898	0.006	0.467	0.003	0.272
XYOIL111	Patchwarra	0.049	1.764	1.892	0.015	0.023	1.593	0.242	0.207	0.050	0.343
XYOIL114	Patchwarra	0.075	2.533	1.846	0.023	0.057	2.494	0.889	0.051	0.045	0.337
XYOIL115	Patchwarra	0.050	2.686	1.853	0.017	0.040	2.282	0.821	0.057	0.047	0.355
XYOIL116	Patchwarra	0.044	1.527	1.979	0.011	0.022	2.027	0.312	0.170	0.053	0.343
XYOIL118	Patchwarra	0.046	2.893	1.878	0.018	0.039	2.159	0.841	0.057	0.048	0.340
XYOIL120	Patchwarra	0.114	20.755	2.025	0.416	2.366	5.689	0.336	0.123	0.041	0.238
XYOIL001	Tirrawarra	0.135	9.643	2.073	0.214	0.429	2.002	0.016	1.828	0.030	0.316
XYOIL004	Tirrawarra	0.156	8.635	2.156	0.226	0.490	2.170	0.017	1.858	0.031	0.311
XYOIL057	Tirrawarra	0.229	13.707	2.135	0.529	1.804	3.411	0.031	0.982	0.030	0.286
XYOIL058	Tirrawarra	0.212	15.374	2.082	0.581	1.207	2.078	0.017	1.721	0.029	0.282
XYOIL066	Tirrawarra	0.267	15.994	2.126	0.788	1.912	2.425	0.019	1.881	0.036	0.268
XYOIL067	Tirrawarra	0.275	13.945	2.163	0.775	1.772	2.288	0.027	1.508	0.041	0.291
XYOIL071	Tirrawarra	0.007	1.219	2.573	0.001	0.001	1.763	0.028	1.436	0.040	0.310
XYOIL076	Tirrawarra	0.005	1.071	2.712	0.000	0.001	1.767	0.023	1.102	0.026	0.299
XYOIL082	Tirrawarra	0.262	16.483	2.115	0.758	1.715	2.261	0.020	1.642	0.032	0.273
XYOIL085	Tirrawarra	0.305	16.253	1.825	1.038	3.443	3.316	0.002	5.304	0.013	0.233

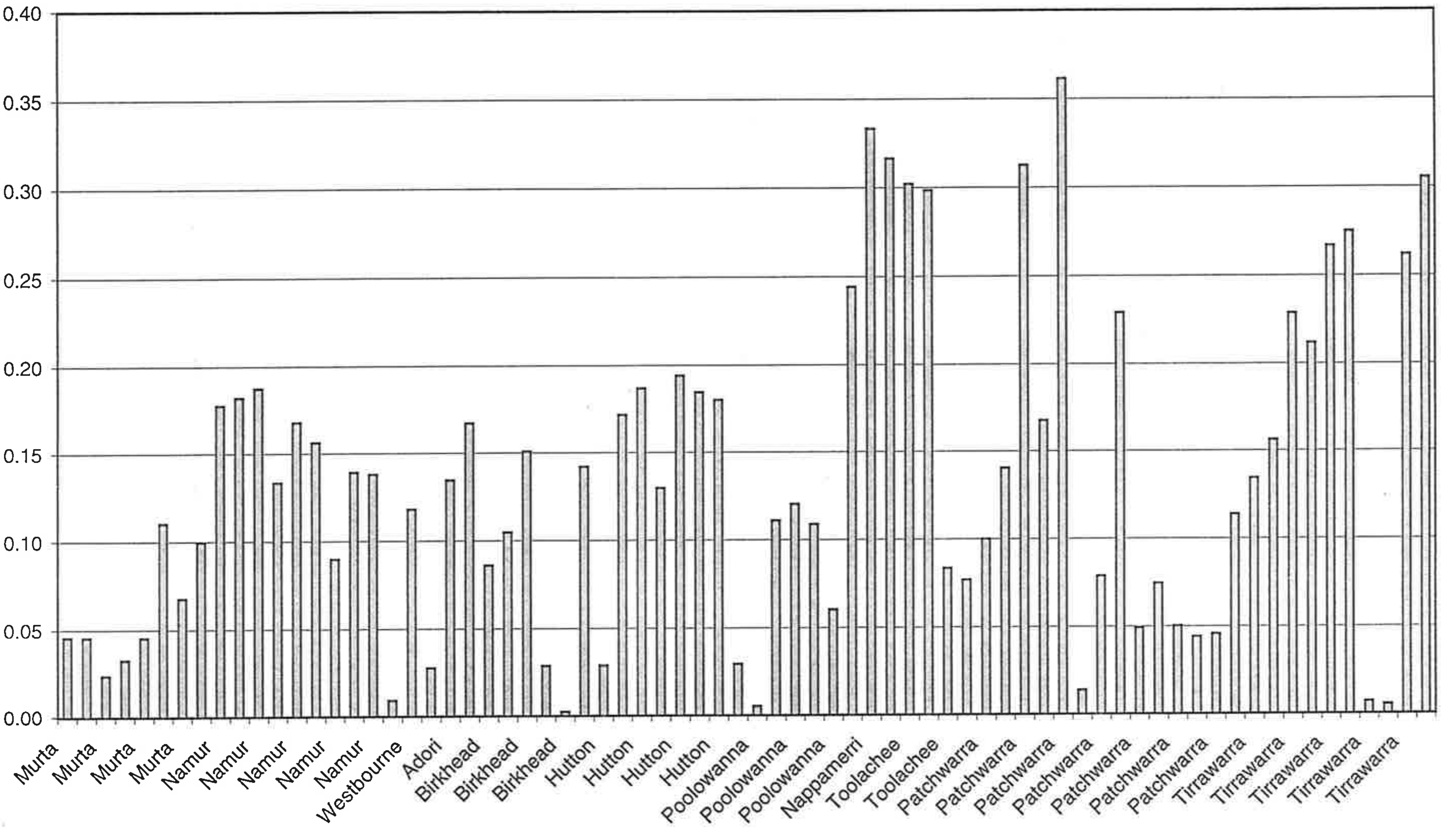


Figure A.2a: Benzene/Toluene

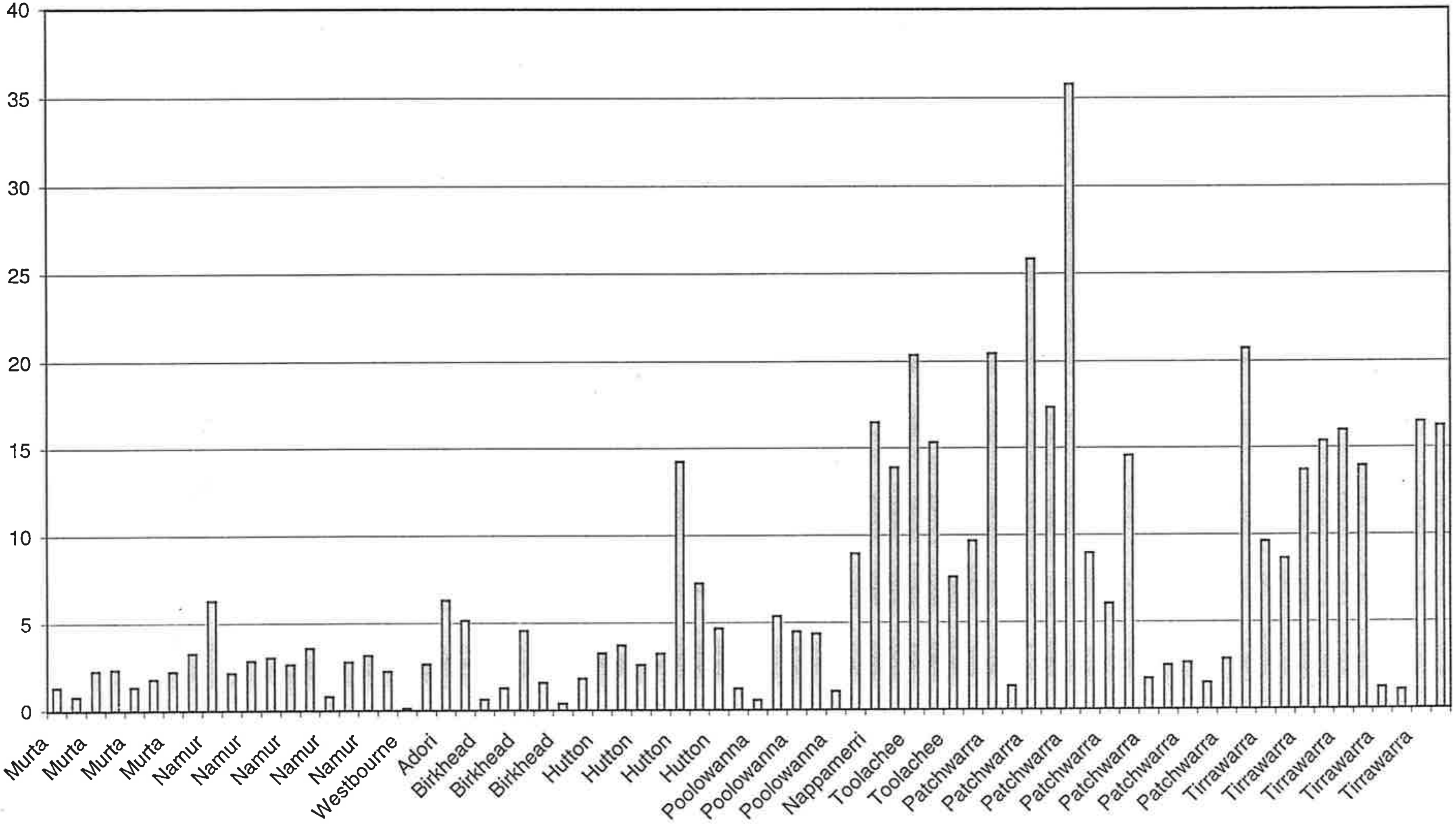


Figure A.2b: Toluene/Propylbenzene

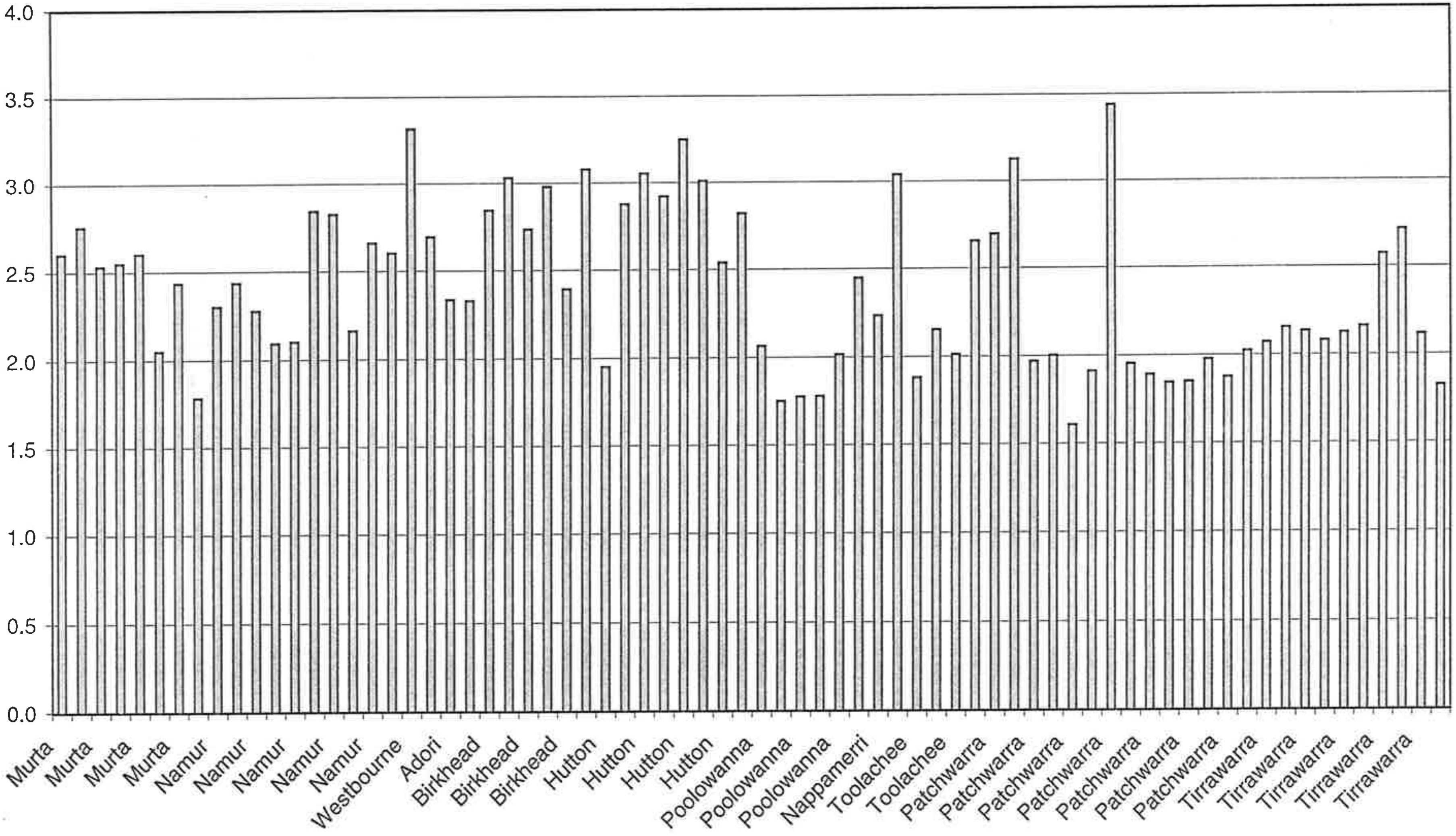


Figure A.2c: Propylbenzene/Isopropylbenzene

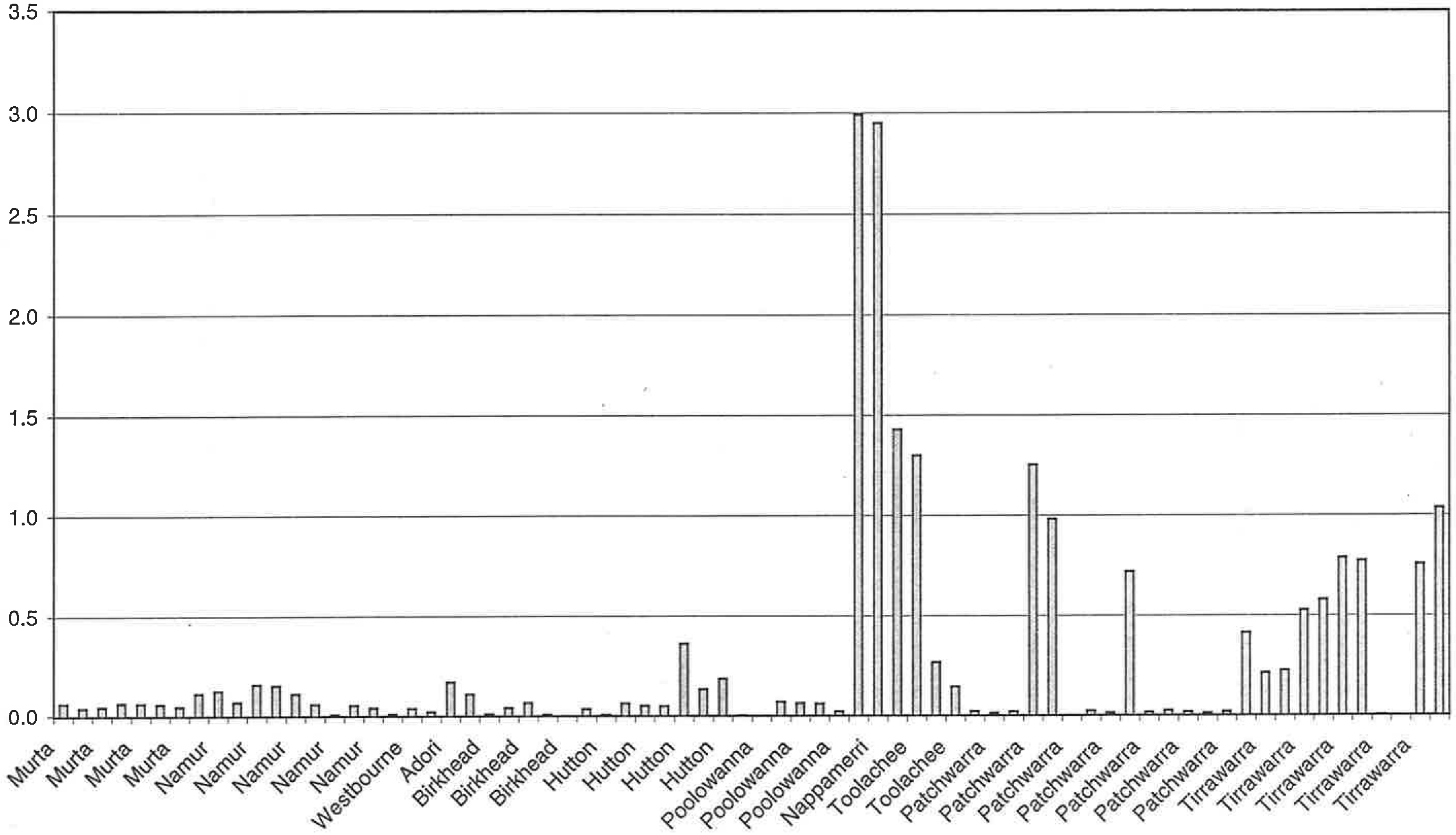


Figure A.2d: Benzene/Naphthalene

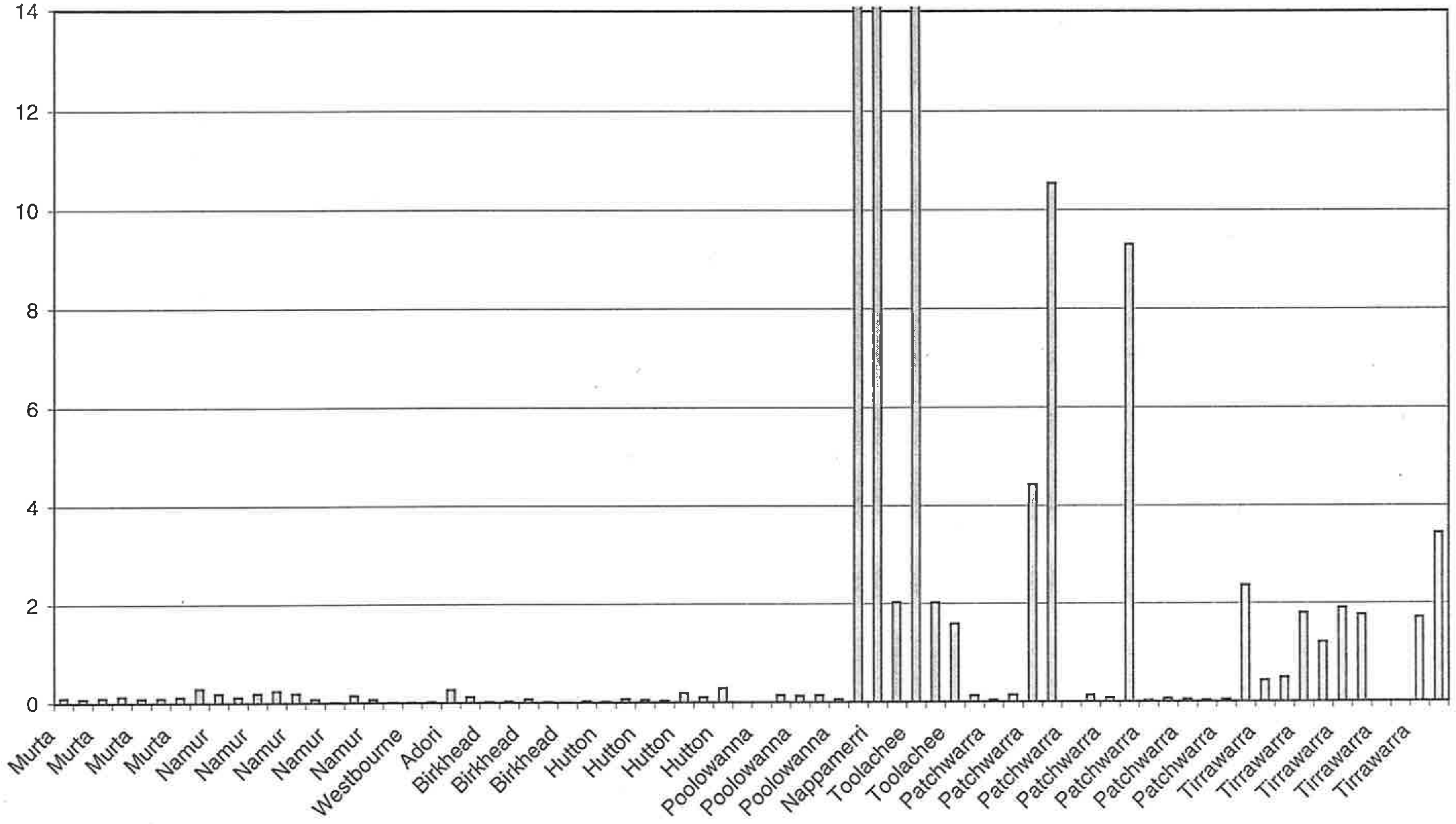


Figure A.2e: Benzene/Phenanthrene

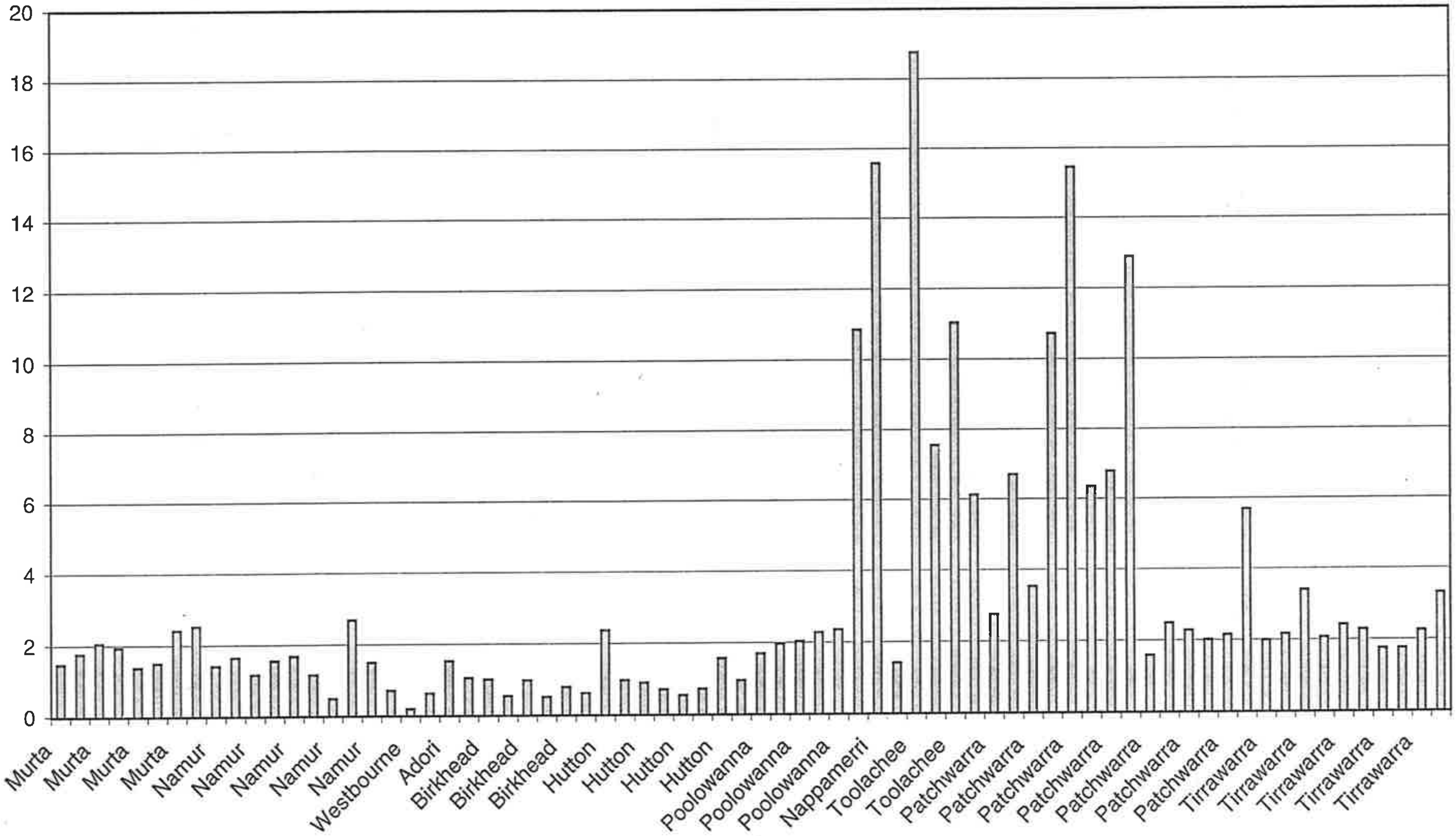


Figure A.2f: Naphthalene/Phenanthrene

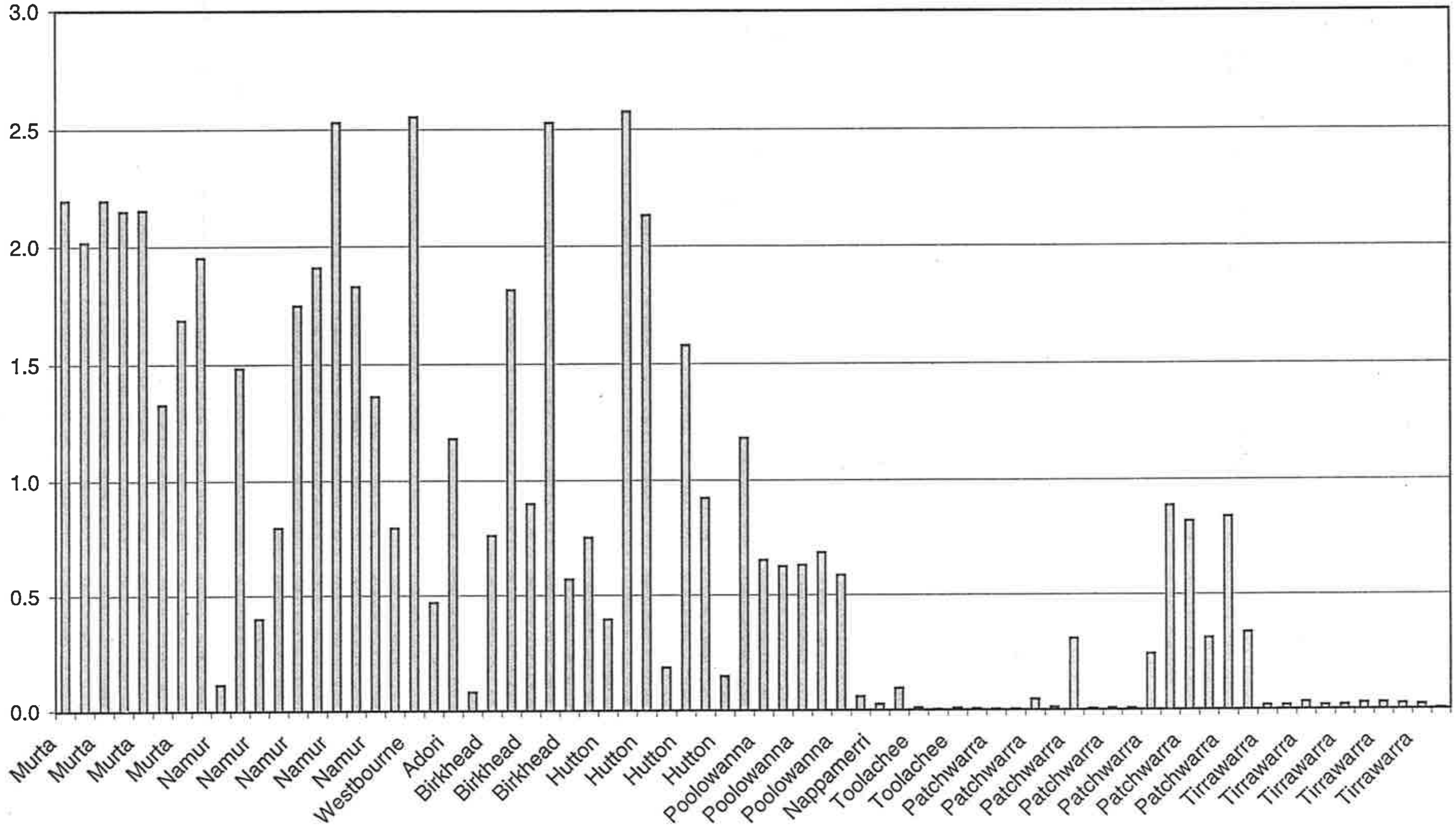


Figure A.2g: Retene/Phenanthrene

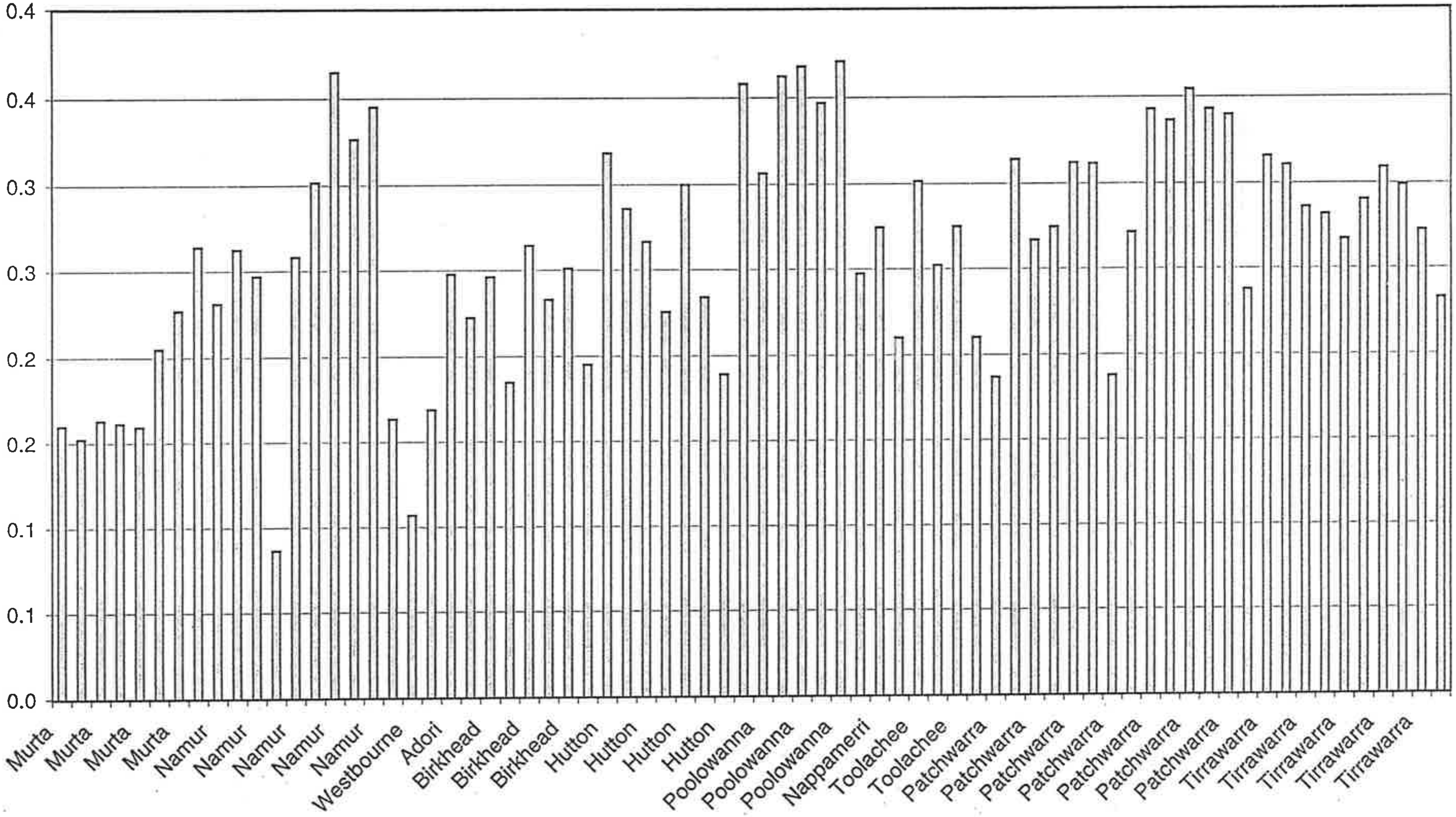


Figure A.2h: o-Xylene/(m+p)-Xylenes