ORIGIN AND MIGRATION OF PETROLEUM IN THE GIDGEALPA RIDGE AREA, COOPER/EROMANGA BASINS, SOUTH AUSTRALIA

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Christian O.E. Hallmann

Nothing in nature is random…
A thing appears random only through
the incompleteness of our knowledge

Spinoza, *Ethics I*

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Declaration

Herewith I declare that to the best of my knowledge and belief, this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution, nor does it contain any material previously published or written by another person, except where due reference has been made in the text.

Christian Hallmann
December 23rd, 2004

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Abstract

The oil play of the Permo-Carboniferous Cooper and Jurassic-Cretaceous Eromanga Basins in South Australia is complicated to unravel due to the presence of multiple source rocks that bear similar geochemical characteristics and has consequently been subject to intense debate. The underlying Warburton Basin, although initially regarded an exploration target, subsequently has never been seriously considered to having participated in the oil play. The Cooper/Eromanga couplet is Australia's largest onshore petroleum province and still bears potential for undiscovered commodities, making a profound understanding of origin and migration of petroleum a prerequisite for efficient future exploration.

Being a typical example of structurally trapped oils in stacked fluvial sandstone reservoirs, the Gidgealpa Ridge was chosen as subject for this study. A suite of 13 sandstone cores, 11 source rocks and 24 drill stem test (DST) oils were processed at the University of Cologne by extraction, sequential extraction of sandstone cores to yield residual oils, preparative liquid chromatography and solid phase extraction to yield fractions of saturated hydrocarbons, aromatic hydrocarbons, maltene resins and a carbazole enriched fractions. While biomarker analyses on saturates and aromatics were performed by Dr. Khaled Arouri at the University of Adelaide, molecular characterisation of carbazoles and bulk geochemical characterisation was also done at the University of Cologne.

Sequentially extracted residual oils are particularly useful because they allow a temporal resolution of petroleum reservoir filling histories. While hydrocarbon compositions are quickly equilibrated over a few tens of metres in oil columns, there is substantial evidence that the same is not true for polar species such as e.g. carbazoles and for lateral variations in hydrocarbon composition. Carbazoles were initially regarded as molecular markers indicating relative migration distances. However, counterevidence soon appeared, showing the dependency of carbazole distributions on other factors.

The results of this study show that, while the distribution of benzocarbazoles seems to depend only on fractionation processes during primary and secondary migration, alkylated carbazole distribution patterns are governed by source rock facies. This new finding allowed the recognition of a Warburton Basin contribution in certain residual oil fractions, yielding the first conclusive evidence that Warburton Basin rocks bear a source potential and have actively participated in the oil play of the Cooper and Eromanga Basins.

The application of carbazole facies parameters, benzocarbazole migration parameters and aromatic maturity data on oils and residual oils from the Gidgealpa Field has allowed the reconstruction of its charging history. Generally, Cooper Basin oils exhibit large maturity variations but a uniformly short migration distance, indicating their origin from a nearby deep trough (eastern source kitchen). Eromanga Basin oils are characterized by similarly low maturity values but highly varying migration distances, suggesting that they were sourced by an extensive and shallow source kitchen. More precise consideration of the carbazole distribution in Eromanga Basin oils shows that the Gidgealpa Field has received two discrete Birkhead charges: a Late Cretaceous pulse from an eastern source kitchen, which migrated a short distance, and became locally displaced by a Tertiary charge from a western source kitchen, which had to migrate further before reaching the Gidgealpa Field.

Residual oil fractions from the sandy intervals of the Toolachee and Patchawarra Formations indicate that while the former is a source for Cooper Basin Family 2 oils, the latter can unambiguously be tied to the production of Cooper Basin Family 1 oils. After petroleum generation in the Patchawarra Formation, this petroleum was probably retained by the coaly Patchawarra source rock, and underwent further maturation before it was expelled as condensate-like light oil in gaseous solution.

The analysis of sequentially extracted residual oils promises to become a powerful tool in reservoir geochemical studies by adding a temporal resolution to otherwise time-integrated samples, thereby allowing a relatively precise reconstruction of an oil field’s charging history. The finding of facies dependent markers in the polar fraction of oils is a constructive motivation for further research into the facies and maturity dependency of NSO compounds. As many residual oils are characterized by minimum extracts yields and a high percentage of NSO compounds, conventional biomarker analyses are complicated and polar markers are necessary for a more precise evaluation.

Zusammenfassung

Die Rekonstruktion des *oil play* im Permo-Karbonischen Cooper und Jurassisch-Kretazischen Eromanga Becken in Süd Australien wird kompliziert durch die Anwesenheit mehrerer Erdölmuttergesteine, welche durch sehr ähnliche geochemische Charakteristika gekennzeichnet sind, und hat daher zu intensiven Debatten geführt. Während das unterlagernde Warburton Becken anfänglich ein Explorationsziel darstellte, wurde nachfolgend niemals ernsthaft an seine Teilnahme im *oil play* geglaubt. Das Cooper/Eromanga Becken ist Australiens größte Inlands-Erdölprovinz und enthält immer noch potentiell unentdeckte Erdölreserven, wodurch ein tiefgehendes Verständnis über den Ursprung und die Migration von Ölen eine Notwendigkeit für effektive zukünftige Explorationsaktivitäten darstellt.

Als ein typisches Beispiel von Ölen, welche in fluviatilen Sandstein Reservoiren struktureller Fallen gespeichert sind, wurde der Gidgealpa Rücken als Thema dieser Arbeit gewählt. Eine Serie von 13 Sandstein-Kernen, 11 Muttergesteinsproben und 24 drill stem test (DST) Ölen wurde mittels Extraktion, sequentieller Extraktion von Sandstein-Kernen, präparativer Flüssigchromatographie und Festphasenextraktion aufgearbeitet, um Fraktionen von gesättigten Kohlenwasserstoffen, aromatischen Kohlewasserstoffen, NSO Komponenten der Malten-Fraktion, und eine an Carbazolen angereicherte Fraktion zu erzeugen. Während Biomarker Analysen an aliphatischen und aromatischen Kohlenwasserstoffen von Dr. Khaled Arouri an der Universität zu Adelaide durchgeführt wurden, fand die molekulare Charakterisierung von Carbazolen sowie die Feststellung der relativen Anteile der ebengenannten Stoffklassen an der Universität zu Köln statt.

Sequentiell extrahierte Residualöle sind besonders nützlich weil sie eine zeitliche Auflösung der Füllungsgeschichte von Erdölreservoiren zulassen. Während sich Variationen in der Kohlenwasserstoffzusammensetzung einer Ölsäule rapide über einige zehn Meter an einander angleichen, gibt es zuverlässige Hinweise, dass dieses nicht für polare Stoffklassen, wie zum Beispiel Carbazole, und für laterale Kohlenwasserstoffvariationen gilt. Carbazole wurden anfänglich als molekulare Marker für relative Migrationsdistanzen betrachtet. Bald darauf erschienen jedoch Gegenbeweise, welche die Abhängigkeit der Carbazolverteilung von anderen Parametern zeigten.

Die Ergebnisse dieser Studie zeigen, dass, während die Verteilung von Benzocarbazolen nur von Fraktionierungsprozessen während primärer und sekundärer Ölmigration abhängt, das Verteilungsmuster von alkylierten Carbazolen von der Muttergesteinsfazies gesteuert wird. Diese neue Erkenntnis führte zu der Entdeckung eines Ölbeitrags des Warburton Beckens zu bestimmten Residualölfraktionen, und liefert den ersten eindeutigen Beweis für das Erdölpotential des Warburton Beckens und seiner Teilnahme an dem *oil play* der Cooper/Eromanga Becken.

Die Anwendung von Carbazol-Faziesparametern, Benzocarbazol-Migrationsparametern Reifedaten an Ölen und Residualölen aus dem Gidgealpa Ölfeld erlaubte die Rekonstruktion seiner Füllungsgeschichte. Cooper Becken Öle weisen in der Regel hohe Reifeunterschiede aber eine einheitlich kurze Migrationsdistanz auf. Dies deutet auf ihren Ursprung aus einem nahen, tiefen Trog (östliche Muttergesteinsregion). Öle des Eromanga Becken charakterisieren sich durch ähnlich niedrige Reifewerte aber stark variierende Migrationsdistanzen, welches auf ihren Ursprung aus einer breiten und flachen Muttergesteinsregion hinweist. Eine genauere Auswertung der Carbazol-Verteilungsmuster zeigt, dass das Gidgealpa Ölfeld zwei separate Ölpulse aus der Birkhead Formation empfangen hat: einen spätkretazischen Puls, welcher eine kurze Distanz wanderte, und durch einen zweiten, tertiären Puls aus der westlichen Muttergesteinsküche verdrängt wurde.

Residualöl-Fraktionen aus sandigen Intervallen der Toolachee und Patchawarra Formation zeigen, dass während die Toolachee Formation eine Quelle für Cooper Becken *'Family 2'*-Ölen darstellt, *‚Family 1'*-Öle definitiv mit der Patchawarra Formation in Verbindung gebracht werden können. Nachdem die Patchawarra Formation Öle generiert hatte, wurden diese von dem kohlehaltigen Patchawarra Muttergestein zurückgehalten, und erfuhren weitere Reifung bevor sie als Kondensate ausgetrieben wurden.

Die Analyse von sequentiell extrahierten Residualölen ist eine erfolgversprechende Technik in reservoir-geochemischen Studien weil sie eine zeitliche Auflösung von ansonsten kumulativen Proben erlaubt. Auf diese Weise ist es möglich, die Füllungsgeschichte eines Ölfeldes relativ präzise zu rekonstruieren. Die Entdeckung von faziesabhängigen Markern in der polaren Fraktion von Ölen stellt eine konstruktive Motivation dar für weitere Untersuchungen zu der Fazies- und Reifeabhängigkeit von NSO-Komponenten. Da viele Residualöle durch minimale Extraktausbeuten und einem hohen Gehalt an NSO-Komponenten gekennzeichnet sind, ist die Analyse von konventionellen Biomarkern kompliziert und „polare Marker" sind notwendig für genauere Aussagen.

CHAPTER ONE

Introduction

The oil play of the Permo-Carboniferous Cooper and Jurassic-Cretaceous Eromanga Basins (Fig. 1) in Australia is complicated to unravel due to the fact that most oil pools were sourced by a multitude of source rocks that bear similar geochemical characteristics. Source rocks vary in age but are similar in organic facies, making it difficult to distinguish between them. Furthermore, they are only accessible in elevated ridges and consequently little is known about their characteristics in the deep troughs that form the source kitchens.

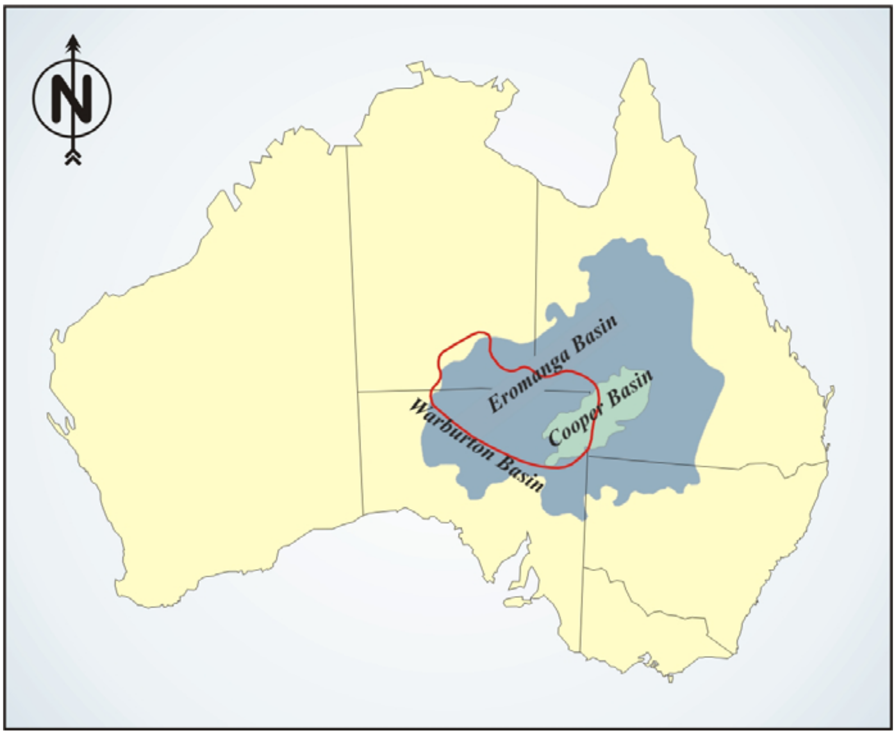

Figure 1 *The Jurassic-Cretaceous Eromanga Basin is underlain by the Permo-Triassic Cooper Basin. This couplet forms the largest onshore petroleum province in Australia. The partially marine Warburton Basin, which is of Palaeozoic age, underlies the Cooper/Eromanga Basins. Its source potential is currently subject to intense speculation but has been conclusively proven in this study.*

The Cooper/Eromanga Basins are underlain by the partially marine sequence of the Palaeozoic Warburton Basin, whose source potential is subject to controversy (Harvey and Hibburt, 1999; Boucher, *oral communication*) but has been proven in this study.

To increase the comprehension of origin, migration and mixing processes of oils in the Cooper and Eromanga Basins, an investigation named “Conditions and effects of hydrocarbon fluid flow in the subsurface of the Cooper-/Eromanga Basins” was initiated by the University of Adelaide, PIRSA and Santos Ltd., in which the University of Cologne participates as a research partner.

The petroleum-hosting stacked reservoirs of the Gidgealpa Ridge are a typical example of Cooper/Eromanga Basin petroleum accumulations. For this reason, the Gidgealpa Ridge area was chosen as a subject of this study. The obtained results may be transferable to other fields in the Cooper/Eromanga Basins that are characterised by a similar structural setting.

1.1 Scope of this thesis

Aim of this study is to reconstruct the origin and migration history of oils in the Gidgealpa Field by evaluation of the distribution of polar organic nitrogen compounds in source rock samples, DST oils and residual oils.

Aliphatic and aromatic biomarker data that has been made available by Dr. Khaled Arouri from the University of Adelaide was interpreted to determine the depositional environment of source rocks and explain the distribution of DST oils. Upon this backbone, the evaluation of carbazole geomarker distributions was based. Carbazoles were found in the polar fraction of drill stem test (DST) oils, source rock extracts and residual oils. In exception of aliphatic and aromatic biomarker analysis, all analyses were performed during the course of this study at the University of Cologne. These included gross composition analysis by thin layer chromatography – flame ionization detector (TLC-FID), solid phase extraction (SPE) of the maltene resins to obtain a purified carbazole fraction, and gas chromatography-mass spectrometry (GC-MS) of the latter.

It is anticipated that the results of this thesis will enhance our understanding of the oil play in the Cooper and Eromanga Basins and possibly reduce future exploration risk, as well as to improve understanding of the nature of carbazoles and their behaviour in the geosphere. As carbazoles still form a very speculative chapter of molecular organic geochemistry, the results of this thesis will be another piece, contributing to the big puzzle.

1.2 Study area

The Gidgealpa Field is located towards the southern end of the Gidgealpa-Merrimelia-Innamincka (GMI) Ridge (Fig. 2) and can be treated as a typical example of oilfields in stacked reservoirs of the Cooper/Eromanga basins.

Being one of the oldest hydrocarbon discoveries, a wide range of data is available on this area (e.g. Boreham and Summons, 1999; Boult *et al.*, 1997). The Gidgealpa Ridge consists of a metamorphic basement ridge that is onlapped by sedimentary sequences from the Permo-Carboniferous Cooper and the Jurassic-Cretaceous Eromanga Basins. High thicknesses of these sediments accumulated in three adjacent troughs, where they are underlain by the partially marine sequence of the Warburton Basin.

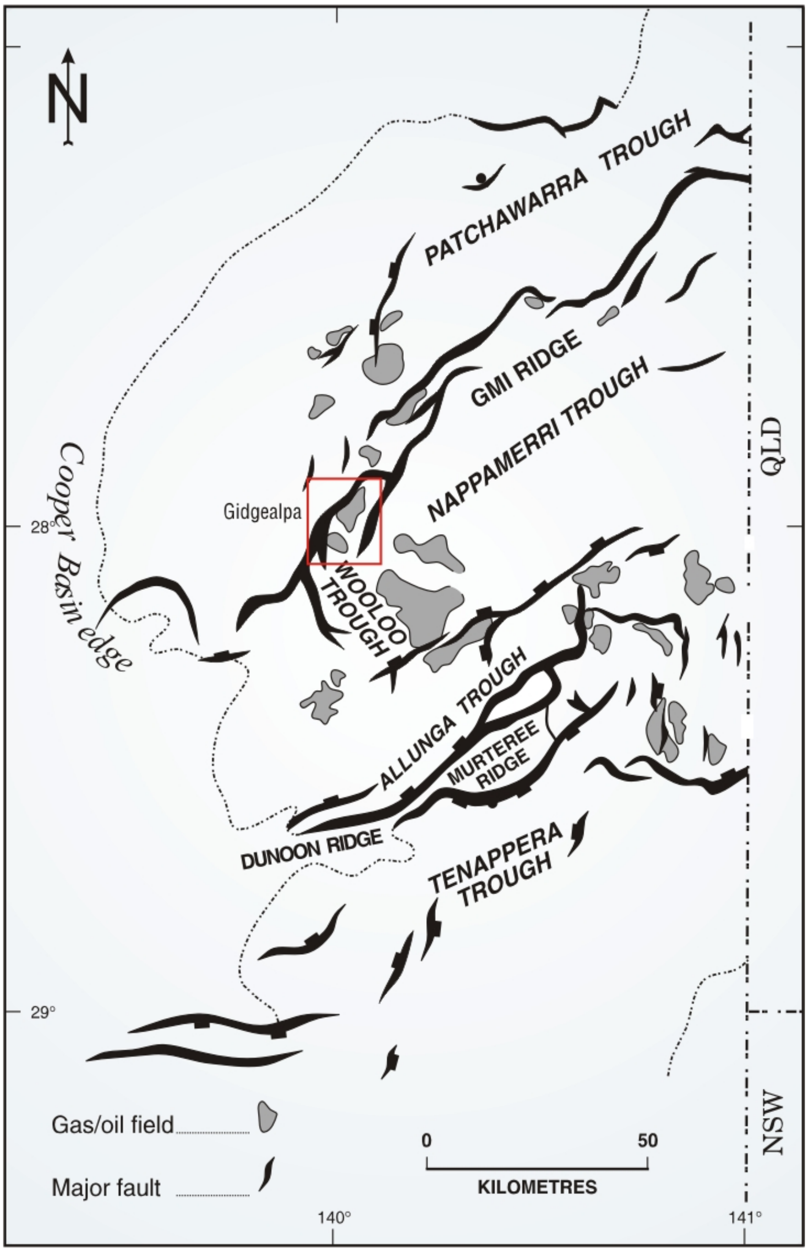

Figure 2 *The study area is situated towards the south-western end of the GMI Ridge and highlighted by the red frame. The two hydrocarbon accumulations that are depicted by the grey colour correspond to those of the southern and the northern Gidgealpa domes (modified after Alexander and Sansome, 1996).*

The Gidgealpa Field is a northeast to southwest trending asymmetric anticline on top of the Hutton Sandstone. It comprises a northern and a southern dome that are separated by a shallow saddle structure. While the northern dome mainly hosts gases and condensates that are reservoired within Permian fluvio-glacigenic sandstones, the southern dome contains oils in stacked fluviatile sandstone reservoirs of Jurassic-Cretaceous age.

1.3 History of petroleum exploration

The Cooper/Eromanga hydrocarbon province is Australia's largest onshore petroleum production and exploration region, currently producing approximately 3 x 10^9 m^3 of gas, 0.4 x 10^6 m^3 of condensate and 0.6 x 10^6 m^3 of oil per annum (based on values from 1997; Harvey and Hibburt, 1997). Exploration has been mainly undertaken by the Delhi-Santos Ltd (South Australia and Northern Territories Oil Search) consortium since the 1950s. The discovery of the first commercial gas reserve in the Toolachee Formation at the Gidgealpa-2 well (title page) in 1963 (Michaelsen, 2002) was followed by the first oil discovery in the Tirrawarra Formation of the Tirrawarra Field seven years later. The Gidgealpa gas field was first brought on line in 1969 (McIntyre *et al.*, 1997) and new near-field exploration and appraisal wells are still being drilled, e.g. Gidgealpa 58, which was completed in March 2004.

Although the production of mentioned commodities is declining since 1990, remaining proven reserves in the Cooper and Eromanga Basins are estimated on 5.5 x 10^6 m^3 oil and 100 x 10^9 m^3 gases. Furthermore, the Cooper and Eromanga Basins bear a potential for undiscovered reserves, which are estimated (50% probability) by PIRSA at 5.4 x 10^6 m^3 of recoverable oil and 56 x 10^9 m^3 of sales gas (Michaelsen, 2002).

Following these introducing words, chapter two and three elucidate the structural setting of the Cooper/Eromanga Basins and the Gidgealpa area, their sedimentary record and position in a petroleum geological context. An overview of the methods that were used to obtain results during this study is given in chapter four.

Results are discussed in chapter five, six and seven. Chapter five gives insight to the sources of oils and the facies of source rocks by evaluation of aliphatic biomarker data and the distribution of *n*-alkanes. Chapter six discusses the distribution of carbazoles in oils and source rock bitumens from the study area. In chapter seven, the results from carbazole analyses are combined with aromatic biomarker data to reconstruct the charging history of oil pools in the Gidgealpa Ridge by using a reservoir geochemical approach.

A summary of conclusions that were drawn from the obtained results is presented in chapter eight.

CHAPTER TWO

Regional Geology

2.1 Geological evolution of Australia

Australia’s Archaic cratons mainly comprise metamorphic series of felsic and mafic rocks. A large amount of sediments and basic volcanics were deposited during the Proterozoic. These sediments of the Nullagineum, Carpentarium and Adelaidean mainly occur in the larger basins and have been little influenced by metamorphosis.

After the Late Proterozoic break-up of Rodinia, Gondwana grew continuously during the Proterozoic and Palaeozoic due to accretional processes on its pacific side, which held on until the Triassic. In the active fault zone and on stable shelves, sediments that belong to the *Pre-Hercynian Megasequence* started accumulating in basins, one of which was the Warburton Basin. A peri-equatorial position of the Australian continent allowed the deposition of limestones under shallow-marine conditions. Sedimentation continued until the Early Carboniferous when the super-continent Pangaea started to form and the Hercynian Tectogenesis, locally termed the *Alice Springs Orogeny*, caused the deformation of accumulated deposits (Wopfner, 1997).
While Pangaea drifted southward, the southern parts of former Gondwana straddled the South Pole and became covered by ice sheets as the Permo-Carboniferous glaciation, which is thought to having been tectonically induced, heralded the start of the second stratigraphic megasequence, the *Pangaea Megasequence*. Due to the stabilisation of the Tasman Geosyncline in the East and the development of a taphrogenic system in the West, a number of intracratonic basins evolved that bear document of the glaciation by tillite deposits and glacial marks on the bedrock. On the eastern Australian margin, a compressive molasse basin, the Sydney Basin, evolved. In the West, a group of extensional basins that can be related to extensional dynamics in the newly established Tethys realm developed. Translational

movements in central Australia gave rise to a number of epicratonic basins that lack of any marine influence and include the Cooper Basin (Wopfner, 1997). A Sakhmarian transgression, caused by a postglacial eustatic sea level rise, allowed vast fluviodeltaic swamps to emerge, which are responsible for the large worldwide coal deposits of the Carboniferous and Permian. This peat-producing phase was set to an end during the Middle Triassic by *Cimmerian* tectonic activity, which caused the opening of a rift system that would later separate Australia from the rest of Gondwana.

The *Post-Cimmerian megasequence* runs from Late Triassic to Late Cretaceous. During the Jurassic, the North-South-trending rift, offshore what is currently Australia's South coast, proceeded further South (corresponding to a present-day eastward movement along the Australian South coast), opening up the Otway Basin. Further inland, the Eromanga and Murray Basins started to subside (Wopfner, 1997). Fluvial sedimentation dominated the Jurassic and allowed the deposition of extensive sandstone accumulations that bear good reservoir qualities for both, hydrocarbons and water. Therefore the Eromanga Basin is also named the Great Artesian Basin. A newly established subduction zone along the eastern Australian margin led to active volcanism and consequently to a varying input of volcanic arc derived (VAD) sediments into the central basins (Fig. 3; Boult *et al.*, 1998).

During the Neocomian, almost the complete continent became flooded by a marine ingression that was caused by the Cretaceous global sea level highstand, and led to the deposition of siliciclastics sediments and marine shales (Alexander and Sansome, 1996). While the basins in the south-eastern part of Australia were not affected, and lacustrine conditions were preserved until Middle Cretaceous, the Eromanga Basin saw a change to marine sedimentation. Meanwhile, the rift between Australia and Antarctica had reached the ocean-spreading phase. The uplift of the rift shoulders caused a tilt of the Australian continent and marine waters in the Eromanga Basin consequently regressed northward.

After the detachment from Antarctica from Australia, only few pericratonic basins (e.g. Gipsland Basin) remained and started or continued to subside during the Tertiary. Their sediments belong to the *Post-Laramic Megasequence* that started during the Palaeogene.

2.2 Tectonic setting

Wopfner (1997) subdivided the Australian continent in four geotectonic units, based on the pattern of gravitational anomalies. These are: the *Southwestern Craton*, the *North Australian Shield*, the *Tasman Geosyncline* and the *Transaustralian Faultzone*; the latter is also known as the Submobile Basinzone. The Warburton, Cooper and Eromanga Basins are located in the Transaustralian Faultzone, which came into existence during the Middle Proterozoic.

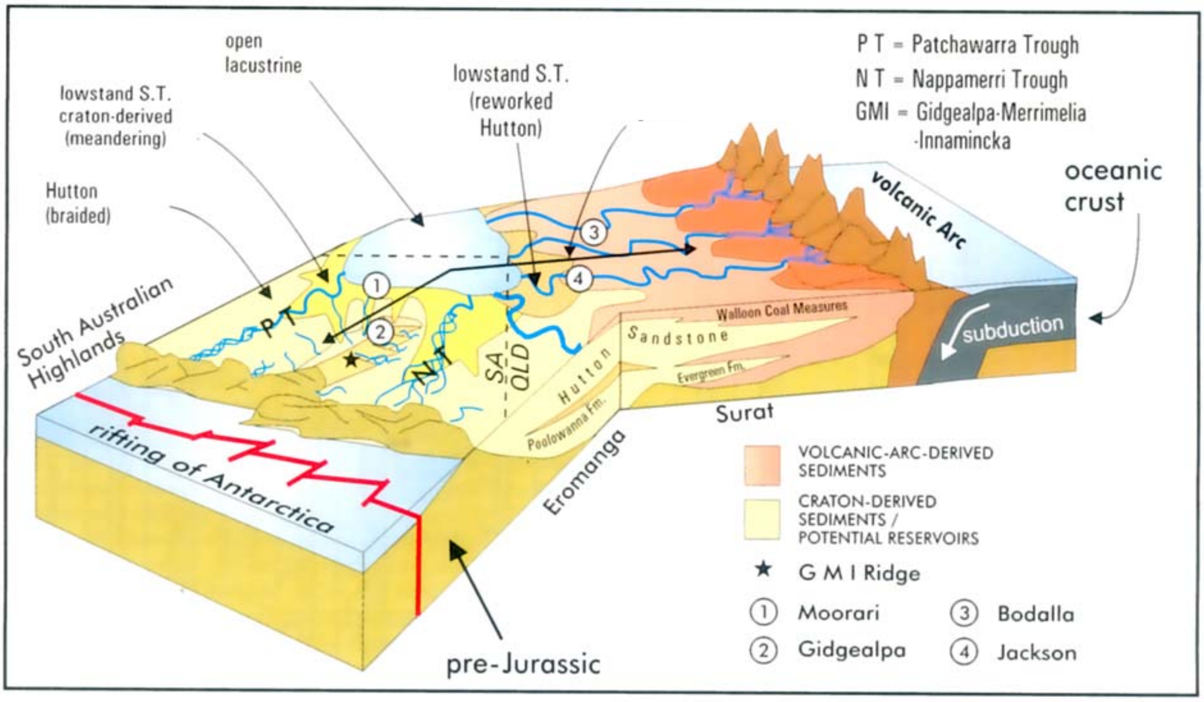

Figure 3 *Palaeogeographic setting of the Eromanga Basin during the upper Middle Jurassic, showing the sedimentary change of provenance from craton-derived sandstones to volcanic arc derived (VAD) sediments (From Boult et al., 1998).*

2.2.1 Warburton Basin

Wopfner (1972, *cf. Wopfner, 1997*) assigned Early Palaeozoic series that underlie the Permian deposits of the Cooper and Pedirka Basins to the Warburton Basin (Fig. 1 and 4). Warburton Basin sediments include thick Cambrian carbonate sequences, late-Adelaidean to early Cambrian Rhyolites and Ignimbrites, Ordovician Shales and Devonian Redbeds. The bedrock consists of Proterozoic phyllite, mica-slate and gneiss. During the Kanimbla orogeny, the Warburton Basin was intruded by tonalites (Gatehouse, 1986, *cf. Michaelsen, 2002*). In a sequence stratigraphic context, the Warburton Basin deposits can be assigned to the pre-Hercynian megacycle, which was dominated by marine sedimentation in the Transaustralian Fault Zone and on stable shelf regions north and south of it. The Warburton Basin has a complex tectonic history that is largely speculative due to a lack of reliable data and detailed study.

While the Warburton Basin sedimentary sequence was only mildly influenced by the Late Cambrian Delamerian orogen, early work on the Gidgealpa area suggests thrust-fault repeated sections, indicating a convergent tectonic regime (Sun, 1999 *and ref. therein*) that was triggered by the Carboniferous Alice Springs orogeny.

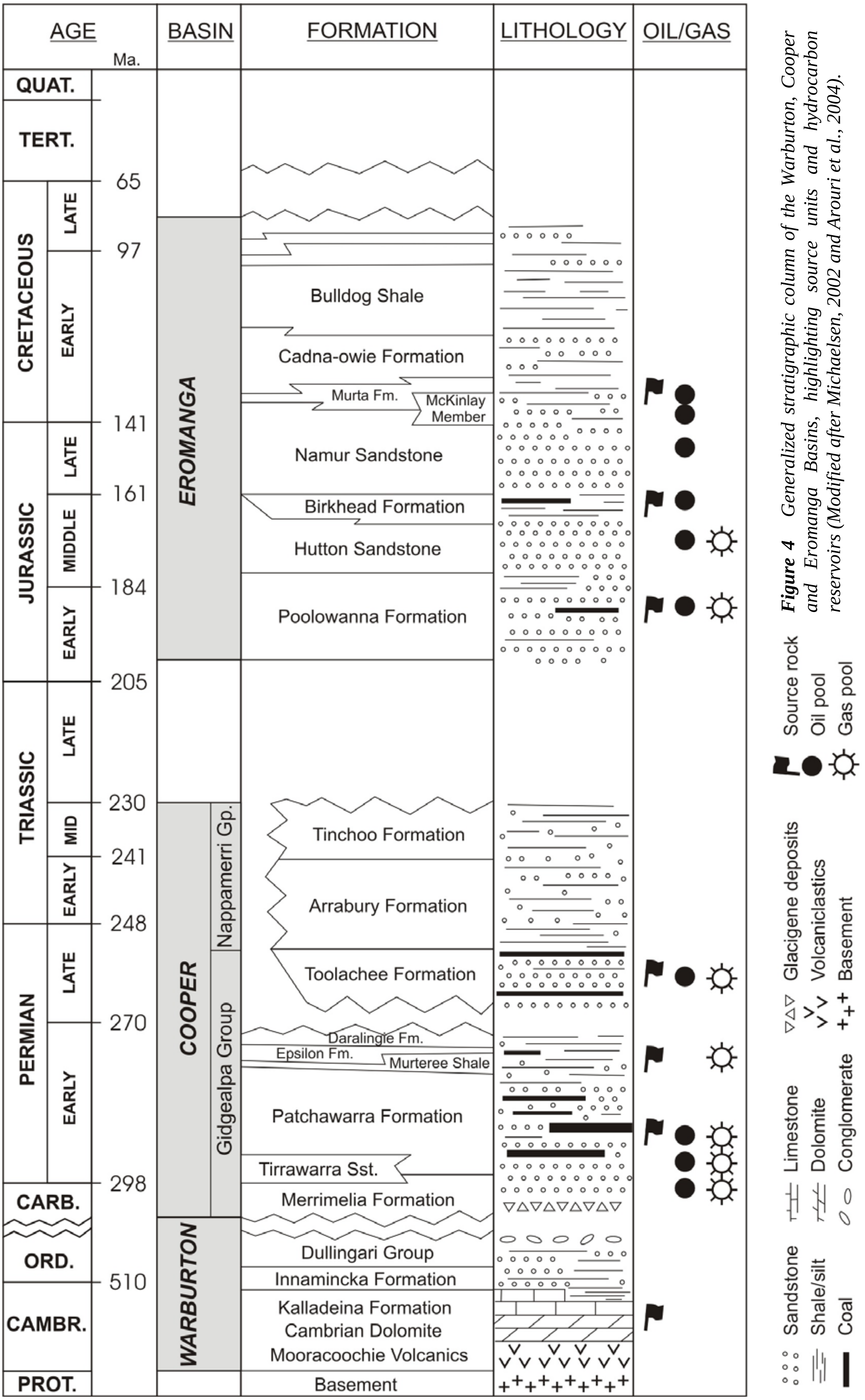

Figure 4 *Generalized stratigraphic column of the Warburton, Cooper and Eromanga Basins, highlighting source units and hydrocarbon reservoirs (Modified after Michaelsen, 2002 and Arouri et al., 2004).*

2.2.2 Cooper Basin

The Carboniferous to Triassic Cooper Basin is one of a number of remnant Late Carboniferous-Early Permian depocentres in the interior of Gondwana (Gravestock and Jensen-Schmidt, 1998). In contrast to other Mesozoic basins, the Cooper Basin developed as an intra-cratonic depocentre and lacks of any marine influence. Accumulation of sediments commenced after the Devonian-Mid Carboniferous Alice Springs orogeny, which is counted to the Hercynian tectogenetic cycle, and ceased at the end of the Middle Triassic (Fig. 4) as a consequence of basin-wide compression (Michaelsen, 2002). This tectonic compression event resulted in folding and uplift, and led to a ridge and trough morphology. Three major depressions developed, the Patchawarra, Nappamerri and Tenappera Troughs, which are separated by structural ridges, the Gidgealpa-Merrimelia-Innamincka (GMI) Ridge, the Murteree Ridge and the Nappacoongee Ridge (Fig. 2). The linear ridge trends are followed by fault zones that extend from the Cooper into the overlying Eromanga Basin. Late Triassic uplift resulted in erosion of Permian and Triassic strata from ridge crests. Sprigg (1961, *cf. Alexander and Jensen-Schmidt, 1996*) postulated that rejuvenation of existing pre-Permian faults and differential tectonics have controlled sedimentation on ridges by causing onlap onto the horst blocks. Michaelsen (2002) and sources therein however state that there is little if any argument for the reactivation of faults at intervals throughout the depositional history of the Cooper and Eromanga Basins.

2.2.3 Eromanga Basin

The Jurassic-Cretaceous Eromanga Basin is an epicratonic sag basin that formed as a consequence of crustal subsidence in the Early Jurassic (Alexander and Jensen-Schmidt, 1996). It entirely covers the Cooper Basin and most of the Warburton Basin. The main depocentres, in which high thicknesses of sediments accumulated during a period of tectonic quiescence, shifted westward from the Nappamerri and Patchawarra Troughs (Cooper area) to the Poolowanna Trough during its depositional history. These two depocentres are separated by the Birdsville Track Ridge, a major Northeast-Southwest trending structural feature. While the lower Eromanga Basin deposits are fluvial-terrestrial, younger strata have been influenced by a marine transgression (Fig. 4). Most regional and local faults of the Cooper Basin extend into the Eromanga sequence (Krieg, 1995, *cf. Michaelsen, 2003*).

2.2.4 Study area

The Gidgealpa field, a single four-way dip closed, draped anticline, is comprised of two culminations (North and South) that are separated by a relatively shallow saddle (Chen and Lonergan, 1991). It is located on the crest of the Gidgealpa-Merrimelia-Innamincka ridge (Fig. 2), an arcuate series of northeast-southwest trending en-echelon structures that form one of the three major Cooper Basin structural trends and separate the Nappamerri Trough to the East from the Patchawarra Trough to the west (Alexander and Sansome, 1996). Basement and near-basement faulting defines a number of fault blocks, which are interpreted to have moved relative to each other during the Early Permian and, in doing so, had a marked effect on deposition (McIntyre *et al.*, 1989).

Figure 5 shows the evolution of the Gidgealpa Ridge and adjacent troughs in a schematic ESE-WNW trending seismic section. The first frame (Fig. 5a) is levelled on the V-horizon, which is the top of the Patchawarra Formation seismic horizon, and shows the asymmetric geometry of the uplifted basement that caused onlap of the V-Z package of sediments, in which the Z-horizon represents the base of the Cooper Basin. The asymmetry was caused by an overthrusting of the basement to the Northwest. The seismic P-horizon corresponds to the top of Permian coal. The second frame (Fig. 5b) shows faults (F) that originate from the beginning subsidence of the Wooloo and Nappamerri Troughs, which caused the tilting of fault blocks. The C-horizon levelled frame (Fig. 5c), in which the C-horizon corresponds to the top Cadna-owie Formation, shows the difference between the flat floored Patchawarra Trough and the subsiding Wooloo Trough. Layer bound faults in marine Cretaceous sediments are related to compaction and expulsion of pore fluids. The present day low-amplitude fold pattern (Fig. 5d) was caused by Tertiary East-West directed compression.

2.3 Sedimentary record

2.3.1 Warburton Basin units

-Mooracoochie Volcanics

The Mooracoochie Formation comprises acid to intermediate volcanics, tuff and agglomerates of ignimbrite (Taloola Ignimbrite Member). The massive volcanics are porphyritic trachytes, shattered and penetrated by dacitic lava.

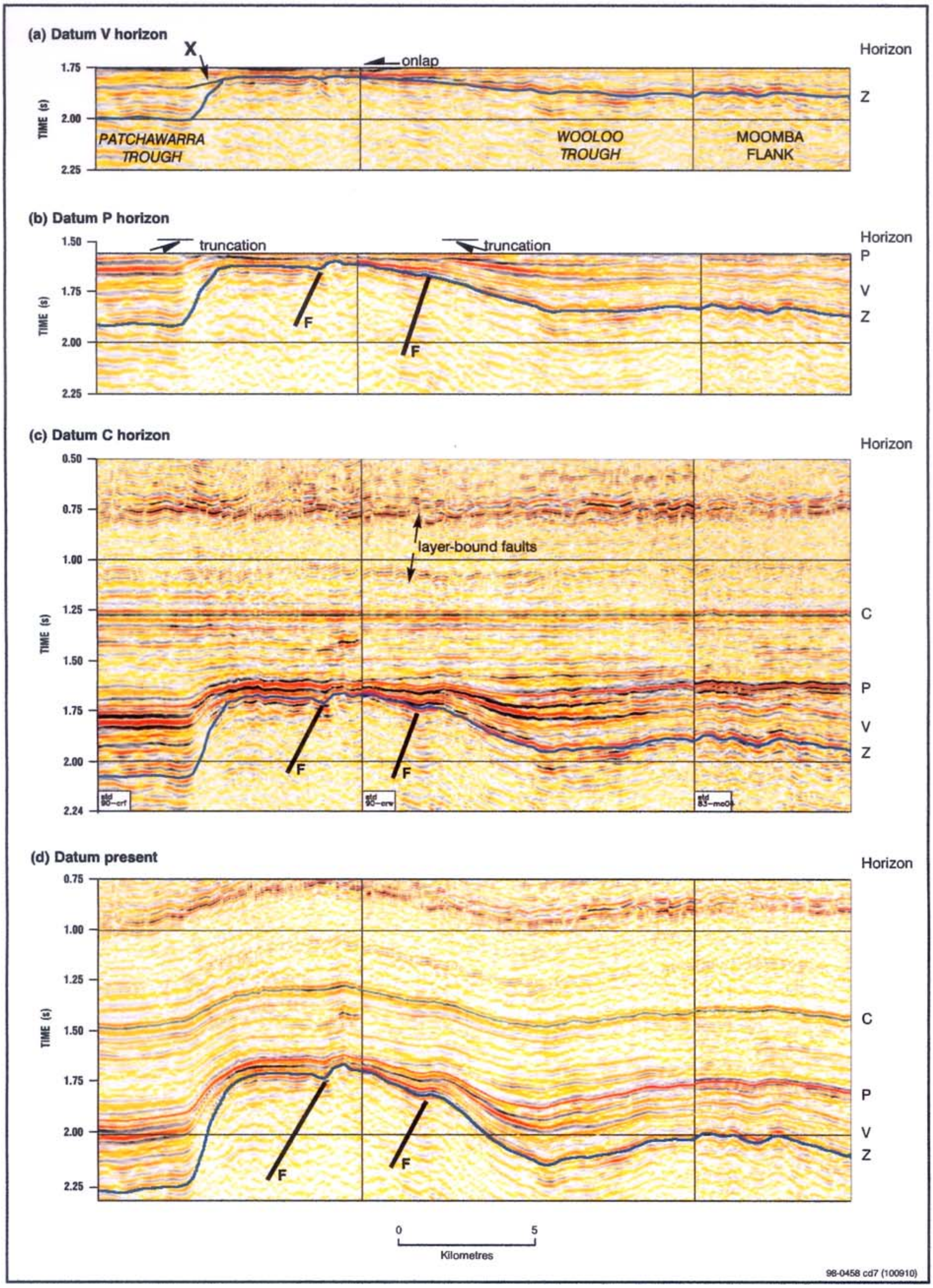

Figure 5 *A cross section through the Gidgealpa Ridge, levelled on the V, P and C horizons and the present datum surface, shows the evolution of the ridge and trough morphology and areas of sedimentation (from Gravestock and Jensen-Schmidt, 1998).*

-Diamond Bog Dolomite

The early Middle Cambrian dolomitic limestones are characterised by a vuggy and moldic porosity that indicates a marine highstand deposit, altered by sub-aerial exposure.

-Kalladeina Formation

The Kalladeina Formation comprises clastic and carbonate shelf lithologies that were deposited in a shallow marine environment. The carbonates consist of an ooid grainstone that is partially dolomitised. The upper Kalladeina Formation represents a highstand system tract that can be subdivided into three parasequences: early highstand aggradation, middle highstand progradation and late highstand regression. The lower Kalladeina Formation is seismically characterized by several cycles of catch-up and keep-up carbonate systems.
The Dullingarie Group is the basinal equivalent to the shelfal Kalladeina Formation. It locally contains black graptolitic shales.

-Innamincka Formation

The Innamincka Formation is characterised by stacked shoaling-upward parasequences of deltaic siltstones and rippled glauconitic sandstone, which may indicate a shallow stable shelf under the influence of frequent sea-level fluctuations. The increase of siliciclastic components at the expense of carbonate suggests an approaching shoreline. The *Pando Formation* sandstones and *Pondrinie Formation* extrusive basalts are locally restricted members within the Innamincka Formation.

2.3.2 Cooper Basin units

Gidgealpa Group

The lower series of non-marine Cooper Basin deposits are characterised by termino-glacial clastics, overlain by detritic sediments that are characterized by low-sulphur coal measures and mainly occur within the Patchawarra, Epsilon and Toolachee Formations (Gravestock *et al.*, 1998). The lateral extent, high thickness and low ash content of coals allow their comparison with high latitude blank mires. Diessel (1992, *cf. Alexander, 1996*) interpreted leaf cuticles within the coals as autumn leaf falls from Glossopterid fauna.

-Merrimelia Formation

Sediments of the Merrimelia Formation comprise a vast range of lithotypes that were created by rapid facies transitions in a glacial dominated environment. The formation covers a period from the Stephanian to the Asselian, during which its sediments have been deposited in troughs, onlapping topographic rises to the mid-flank regions of ridges throughout the Cooper Basin (Alexander, 1998).

Both, the Merrimelia Formation and the Tirrawarra Sandstone, form an integrated suite of sediments, deposited in terminoglacial and proglacial scenarios. During the maximum approach of the continental Merrimelia ice sheet, which started its growth during the Stephanian, the sediments of the Merrimelia Formation *sensu strictu* were deposited. As soon as a fluctuation of glacial influence occurred, triggered by the relative movement of the Australian subcontinent away from the Antarctic region, an interfingering sequence of Merrimelia type and Tirrawarra type sediments was deposited.

The lithology is solely controlled by the aquatic energy, which in turn depends on the distance from the glacial ice sheet. It ranges from poorly sorted, clast supported conglomerates, sandstones, and siltstones, which were deposited under high energetic conditions, to kettle hole deposits that exhibit rainout diamictites and dropstones.

The Merrimelia sandstones host a few minor hydrocarbon accumulations, which have been sourced down-dip from Cooper Basin source rocks (Michaelsen, 2002).

-Tirrawarra Sandstone

A local unconformity subdivides the Stephanian to Asselian Tirrawarra Sandstone into a lower part, belonging to the Merrimelia type facies, and an upper part, which is locally diachronous and intertongues with the Patchawarra Formation (Seggie, 1997, *cf. Alexander, 1998*). The upper section must although be distinguished from the ’Tirrawarra Sandstone-like’ facies of the Patchawarra Formation (Alexander *et al.*, 1998).

During further retreat of the glaciers in southerly direction, meltwater streams that flew to the North carried glacigenic material and reworked unconsolidated Merrimelia sediments. The first two of four sedimentological associations (Williams *et al.*, 1984), consist of longitudinal gravel bars with reworked Merrimelia and Warburton Basin material (1) and medium to coarse grained lithic sandstone with rare conglomerate, mudrock and coal bed (2) (Alexander, 1998). Low angle and planar cross bedded units are stacked, including coarsening up and fining up sequences. These two associations, of which the latter exhibits the better hydrocarbon-reservoir potential, belong to the Tirrawarra/Merrimelia facies. Associations three and four represent an evolution into a mixed load meandering fluvial system, consisting of stacked sandstone fining up sequences (3) and thick conglomerates with reworked Merrimelia clasts (4) that may have been sourced from adjacent palaeohighs (Alexander *et al.*, 1998). The Gidgealpa South field contains association 4 conglomerates, derived from the North Gidgealpa Palaeohigh (see also section on Patchawarra Formation).

Being the main oil reservoir in the Cooper Basin, the Tirrawarra Sandstone hosts approximately 80 % of all Cooper oils, which are located in the Tirrawarra Field (Michaelsen, 2002).

-Patchawarra Formation

Asselian to Artinskian Patchawarra deposits consist of fluvial, fine to medium grained sandstones, lacustrine siltstones and shales. In the Gidgealpa Field the basal Patchawarra layer is formed by a conglomerate of reworked Mooracoochie volcanics that have been eroded from the crest of the Gidgealpa Ridge. Coals, containing Type II to Type III kerogen, are widespread within these strata in the Patchawarra Trough, making it the main source kitchen for hydrocarbons in the Cooper Basin. Furthermore, the Patchawarra Formation serves as the most important gas-condensate reservoir in the Cooper Basin. Even though it is the thickest Permian unit, it has been eroded off heights such as e.g. the GMI-ridge.

The sedimentary environment has been interpreted as a highly sinuidal fluvial system, flowing northward (Stanmore and Johnstone, 1988) over a floodplain with peat swamps, lakes and gentle uplands (Stuart, 1976, *cf. Alexander et al., 1998*; Stanmore and Johnston, 1988) that feature point bars and crevasse splay deposits (Williams, 1995*, cf. Alexander, 1998*).

-Murteree Shale

During the Artinskian, a deep lake environment developed. This is documented by argillaceous, laminated shales that largely lack wave ripples and any evidence of turbiditic reworking. The fine-grained pyrite and muscovite containing Murteree Shale has been eroded of crestal areas.

The hydrocarbon potential is zero or very minor, at the most capable of producing negligible amounts of gas. It could, however, act as a seal in favourable conditions (Michaelsen, 2002).

-Epsilon Formation

Quartzose sandstones that were deposited in a fluviodeltaic and lacustrine shoreface setting toddled in dependency of regional trans- and regressions during the Artinskian to early Kungurian. Dispersed Type II kerogen coal seams do not contain enough organic material for the production of relevant amounts of hydrocarbons (Alexander, 1998; Michaelsen, 2002), but can contaminate passing hydrocarbon charges.

-Roseneath Shale

Conformably overlying the Epsilon Formation, the Roseneath Shale documents a return to lacustrine conditions. The depositional environment was similar to that of the Murteree Shale. Silt- and mudstones with interbedded fine-grained sandstones contain load marks and slump folds, indicating mass flows and slope instability during its deposition in Kungurian times (Stuart, 1976, *cf. Alexander et al., 1998*).

-Daralingie Formation

Sedimentation of Kungurian to Ufimian Daralingie beds was restricted to the Cooper Basin area south of the GMI Ridge. During the regression of the ’Roseneath Lake’, deltaic systems developed, which allowed the deposited of sandstones, shales and minor amounts of coal during their progradation to the northeast. Williams (1995, *cf. Alexander, 1998*) interpreted the sediments as delta front bars, lake-margin beach and lake-margin shoreface deposits that pass on to a fluvial channel, backswamp and marsh environment.

-Toolachee Formation

The uppermost unit of the Gidgealpa Group is represented by fine to coarse grained, buff to white sandstones, dark siltstones and carbonaceous shales. Thin (<3m), laterally continuous coal seams occur and, adjacent to structural heights, a basal conglomerate layer that contains clasts of reworked Warburton Basin material was deposited. Glossopteris leaves that are preserved on bedding planes in laminated siltstones give insight to the prevailing flora. Mackie *et al.* (1995, *cf. Alexander, 1998*) and Alexander (1998) interpreted the sedimentary structures to originate from ephemeral lakes and backswamps in the flood-basin. Sandstone packages document channels that were abandoned by chute and neck-cut-off and crevasse splays. The Toolachee Formation was divided into three sedimentary association by Mackie *et al.* (1995, *cf. Alexander, 1998*) and Williams (1995, *cf. Alexander, 1998*). The first association represents a fluvial system flowing to the North-East. Association two, being dominated by mudstones and coal seams, documents overbank flooding and flood-basin lakes. It is overlain by crevasse splay sandstones. In the Gidgealpa Field a third association exists, containing coarse-grained fining-upward packages, which Alexander *et al.* (1998) interpreted as high-sinuosity alluvial channels.

Nappamerri Group

Triassic sediments are developed in a redbed facies and reach maximum thicknesses in the Nappamerri and Patchawarra Troughs, where they onlap structural ridges. Of many stratigraphic arrangements, the Channon and Wood (1998) framework is adopted in this study. The Triassic coal gap makes these strata useless as source rocks but their high lateral extent turns them into useful regional seals.

-Arrabury Formation

Mudstones, siltstones and sandstones of the Tatarian to Anisian Arrabury Formation cover almost all of the Cooper Basin, including structural heights. It has although been eroded from the crest of the Murteree Ridge.

In contrast to the dark grey, organic rich siltstones and coals of the Toolachee Formation, the Arrabury Formation strata exhibit a drop in organic carbon content, a change in magnetic polarity and a major $\delta^{13}C_{org}$-excursion. Although they generally appear as redbed sediments, the deposition controversially took place during a rather humid palaeoclimate in a vegetated floodplain with ephemeral lakes. Symptoms of pedogenesis are present on exposed areas. Northeast-Southwest trending channel belts in the Patchawarra and Nappamerri Troughs indicate the presence of low-sinuosity rivers that cut the floodplain. The Arrabury Formation bears witness of the beginning Triassic coal gap.

-Tinchoo Formation

In contrast to the Queensland-sector of the Cooper Basin, much of the Tinchoo Formation has been eroded in South Australia. These Anisian to Ladinian strata are restricted to the northeastern Patchawarra Trough and the northern area of the Cooper Basin (Channon and Wood, 1989). Sedimentary structures suggest a deposition in fluvial channels that differed across the flood basin between high and low-sinuosity fluvial facies.

-Cuddapan Formation

Remnants of the eroded Cuddapan Formation are restricted to the Patchawarra Trough in South Australia. These deposits strongly resemble the overlying Poolowanna Formation. Sandstones, siltstones and coal interbeds were deposited during the Carnian and Norian in a high-sinuosity fluvial system with flood basin coal swamp development. The recovery of peat swamps, which reach high thicknesses in the time-equivalent Peera Peera Formation, (Simpson Basin) indicates the end of the Triassic coal gap.

2.3.3 Eromanga Basin units

-Poolowanna Formation

The Poolowanna Formation should be regarded as a silty and coaly facies of the Hutton Sandstone in the Cooper region of the Eromanga Basin (Fig. 1). In this same region, the facies of the Poolowanna Formation was strongly controlled by the palaeotopography of the Late Triassic unconformity surface. Carbonaceous siltstones and pale sandstones that contain rare coal seams were deposited during the Early to Middle Jurassic (Alexander and Sansome, 1996) and contain sedimentary structures which indicate a meandering to anastomosing fluvial palaeoenvironment with subordinate peat swamp development (Michaelsen, 2002).

-Hutton Sandstone

During the Middle Jurassic, braided streams transported sand into the Eromanga Basin. Upon arrival, these were further distributed across the basin by aeolian and lacustrine processes (Wiltshire, 1989, *cf. Alexander and Sansome, 1996*). A low sinuosity fluvial system with variable discharge was proposed for the Gidgealpa area (Williams, 1995, *cf. Alexander and Sansome, 1996*). The Quartz-arenite in the upper Hutton Sandstone and lower Birkhead Formation was dated on 1400 – 1900 Ma. in the Gidgealpa Field, and indicates a second or third sedimentary cycle after having been sourced from a cratonic provenance. The Hutton Sandstone is the most important Eromanga Basin hydrocarbon reservoir within the Cooper area of the Eromanga Basin.

-Birkhead Formation

The basal Birkhead Formation consists of sandstones that were derived from the same region as the upper Hutton Sandstones. During the Middle and Late Jurassic, however, a provenance change was noticed in the Gidgealpa Field (Fig. 3), from deposits of younger material (950 Ma). The lithology changes from a sandy facies to dark siltstones, mudstones and fine to medium grained sandstones with thin, lenticular coal seams (Alexander and Sansome, 1996). Coals reach maximum thicknesses in the Patchawarra and Nappamerri Troughs.

The change in depositional environment from a fluvial system to a lacustrine coal swamp environment, cut by meandering channels, is discussed to be either caused by a blockage or restriction of the Hutton fluvial system, or to result from climatic changes. Suddenly occurring volcaniclastic sandstones indicate the development of an active volcanic arc on the eastern coast of the Australian continent. Shallow lakes that covered the Pando and Wooloo Troughs inundated the floodplain and sealed the Birkhead Formation with a thick siltstone-shale unit.

-Namur Sandstone

The Late Jurassic to Early Cretaceous (Neocomian) Namur Sandstone represents the second most important petroleum reservoir in the Eromanga Basin. The Namur Sandstone consists of fine to coarse-grained sandstones with minor interbedded siltstone and mudstone. Conglomeratic interbeds of lithic and quartzose pebbles, mudstone intraclasts and carbonised plant fragments occasionally occur. Deposition took place under a low-sinuosity fluvial regime. A northern-directed palaeo-current was reconstructed (Alexander and Sansome, 1996) for the depositional environment that strongly resembled the environment during the deposition of Hutton sandstones.

-Murta Formation

A Late Neocomian marine transgression led to a change in depositional environment from a fluvial dominated plain to a lacustrine and paralic environment. This is attested by the presence of the planktonic green algae *Bottryococcus* and by palynological analyses (Michaelsen and McKirdy, 1989). The upper Murta Formation saw a change to a brackish marine environment that experienced slope-instability density currents, as indicated by Bouma sequences. The upper Murta Formation consists of dark grey siltstones, very fine-grained sandstones and shales.

Higher Eromanga Basin strata include the Cadna-owie Formation, Bulldog Shale, Coorikiana Sandstone, Oodnatta Formation, Mackunda Formation, Winton Formation and Mount Howie Sandstone. These will not be further discussed because they are not relevant to this study. While these higher Eromanga Basin deposits consist of clastic marine sediments, the deposits of the overlying Tertiary Lake Eyre Basin are generally fluvial and lacustrine.

CHAPTER THREE

Petroleum Geology

3.1 Introduction to the Cooper/Eromanga Basin petroleum province

The main difficulty with the Cooper and Eromanga Basin oil play concerns the sources of petroleum, which are hard to decipher due to highly similar characteristics of Cooper and Eromanga Basin source rocks. Furthermore, severe post-generative overprinting of primary geochemical signatures can trouble oil-source rock correlations. While during the first generation of petroleum exploration in the Cooper/Eromanga Basins, oil accumulations were believed to be exclusively sourced by Cooper Basin source rocks, more recently, the Jurassic Birkhead and the Cretaceous Murta Formations were found to have participated in the play. Currently, Cooper Basin reservoired oils are believed to be Cooper Basin sourced, while Eromanga Basin oil pools are thought to contain mixtures of Eromanga Basin sourced oils, and Cooper Basin sourced oils.

The results of this study herald the next step by providing conclusive evidence for the participation of pre-Permian Warburton Basin sourced oils in the oil play of the Cooper and Eromanga Basins.

3.2 Source Rocks

The Toolachee and the Patchawarra Formation are regarded as the richest source units in the Cooper Basin sedimentary sequence. Sources of hydrocarbons are coals and kerogenous shales. It seems contradictive that coals represent an oil-prone source facies while lacking a high amount of liptinite. Taylor *et al.* (1998) suggest that sub-microscopic alginate, which is dispersed in the inertinite matrix of coals, is the source of ’coaly’ oils. The lacustrine Murteree and Roseneath Shales appear to have little source potential (Hunt *et al.*, 1989, *cf.*

Boreham and Hill, 1996). Epsilon Formation shales exhibit a fair source potential and although thin, they can form local sources for hydrocarbons.
A factor that troubles oil-source rock correlations within the Cooper Basin is the presence of dispersed organic matter (DOM) within most non-marine, clastic units. Although this organic matter is inertinite-dominated, the small amounts of liptinite (vitrinite and liptinite <25%) are capable of contaminating oils with their organic geochemical signature.

The Eromanga Basin sedimentary sequence hosts two important Type II to Type III organic matter source rocks: the coaly/lacustrine Birkhead and the lacustrine/marine Murta Formation (Fig. 4). The Poolowanna Formation comprises organic rich, Type II to type III coals and carbonaceous shales in which *Bottryococcus*-type telalginite is relatively abundant (Kagya and McKirdy, 1996). It is capable of generating hydrocarbons and contaminating Permian oils, reservoired in the Poolowanna Formation, by adding a typical Poolowanna geochemical signature (see also chapter five and seven). The hydrocarbon generation potential of the Birkhead Formation is fair in the study area, but less than in the Western sector of the Eromanga Basin. The lacustrine/marine Murta Formation bears oil prone Type II organic matter and a high source potential in the Murteree Ridge Area (Fig.2). A second cluster of generative Murta source rocks is located in the Nappamerri Trough, where, however, the source potential is diminished.

The source potential of the pre-Permian Kalladeina Formation has been discussed after the discovery of an oil accumulation in the Mooracoochie Formation of the Warburton Basin. Harvey and Hibburt (1999), however, estimate the source potential to be modest, based on a total organic carbon (TOC) value of <0.85% and postulate these oils to having been sourced down-dip from Cooper Basin sources. As most wells that penetrated the Warburton Basin sedimentary sequence only reached the upper ’altered zone’, which has been severely oxidised, no conclusive statements can be made concerning its true hydrocarbon generation potential.

3.3 Reservoirs

Multi-zone high-sinuosity fluvial sandstones from the Patchawarra and Toolachee Formations form reservoirs of varying quality, from which gas is produced. Oil is produced principally from low-sinuosity fluvial sands within the Tirrawarra Sandstone and, towards the margin of the Cooper Basin, also from the Patchawarra Formation and from fluvial channel sands of the Merrimelia Formation. Shoreface and delta sands of the Epsilon and Daralingie Formation locally form smaller reservoirs

The principal Eromanga Basin sequence reservoirs in the Cooper region of the Eromanga Basin (Fig. 1) are the braided fluvial Hutton and Namur Sandstones, which are characterized by optimum porosities of up to 25 percent. Oil is also reservoired within the meandering fluvial Poolowanna and Birkhead Formations, the lacustrine shoreface McKinlay Member and lacustrine turbiditic sandstones from the Murta Formation.

The eastern Warburton Basin unconformably underlies the Cooper and Eromanga Basins in northern South Australia (Fig. 1). Although more than six-hundred wells have penetrated the Warburton Basin deposits, most of these are ’ratholes’ with less than forty metres penetration, making the Warburton Basin a high-risk exploration target. However, four wells have produced commercial volumes of oil from Warburton Basin reservoirs, which are thought to have migrated down-dip from Cooper Basin source rocks. Fracture analysis, carried out by Sun (1999), showed that most Warburton Basin rocks show fracture porosity, featuring high porosity but low permeability. Hence, the conclusion arises that Warburton Basin reservoirs are likely related to fractures or in fault contact to mature Permian source rocks.

3.4 Traps

While the Early Triassic Arrabury Formation is conventionally regarded as a regional seal for the Toolachee Formation, intra-formational shales and coals form local seals in most major reservoir units. Furthermore, the Murteree and Roseneath shales can be regarded as regional seals for Epsilon and Patchawarra Formation reservoirs.

Where the regional seal is thin or absent, multiple oil and gas pools are stacked in coaxial Permian-Mesozoic structures and may occur throughout the complete Cooper and Eromanga Basin sedimentary sequence (PIRSA website[1]). While anticlines have proven as reliable exploration targets, stratigraphic traps do occasionally occur, especially where Permian sediments are truncated by the overlying Eromanga Basin succession.

Eromanga Basin traps are dominantly anticlines with four-way dip closure or drapes over pre-existing highs. Seals consist of intra-formational siltstones and shales of the Poolowanna, Birkhead and Murta Formations.

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[1] http://www.pir.sa.gov.au/pages/petrol/prospectivity/prospectivity_cooper.htm

3.5 Oils

Oil and condensate are typically medium to light (30-60° API) and paraffinic with varying wax contents. Most Permian reservoired oils contain a significant amount of dissolved gas and do generally not show any evidence of water washing (Boreham and Hill, 1996). The main factor controlling intra oil-family heterogeneity is contamination during secondary migration through carrier rocks that contain disperse organic matter, insignificant for the production of hydrocarbons but extractable by hydrocarbons flowing along. Oils are not or only marginally affected by biological degradation, which can be attributed to ’reservoir sterilization’ during the Mid Cretaceous heatflow event (Wilhelms *et al.*, 2001).

Heath *et al.* (1989) noticed that stacked reservoirs in the Cooper and Eromanga Basins generally show a progression from low API gravity oils in the deeper reservoirs to the highest API gravity oil-condensates in the shallowest reservoir. Where API gravity data was present, this was also observed in the stacked reservoirs of the Gidgealpa Ridge. Three oil families, Cooper Basin Family 1 and 2, and Birkhead/Murta Formation oils can be distinguished. These will be covered in full detail in chapter five.

3.6 Thermal and subsidence history and expulsion events

The generalized subsidence curve of the Cooper and Eromanga Basins exhibits rapid burial during the Permian, a slowing down and even slight uplift during the course of the Triassic and Early Jurassic, and a renewed fast burial during the Cretaceous (Fig. 6). The Cooper Basin subsidence can be attributed to relaxing thermal anomalies that were induced by tectogenesis of granite during the Alice Springs orogeny. In contrast to the Cooper Basin subsidence that was paralleled by tectonic subsidence and constant sedimentary rates (generally less than 5m/My), the Eromanga Basin saw a drastic increase in sedimentation rate between 100 and 90 Ma (early Late Cretaceous) when burial increased to 60m/My along the Murteree Ridge and over 200m/My in the Patchawarra Trough.

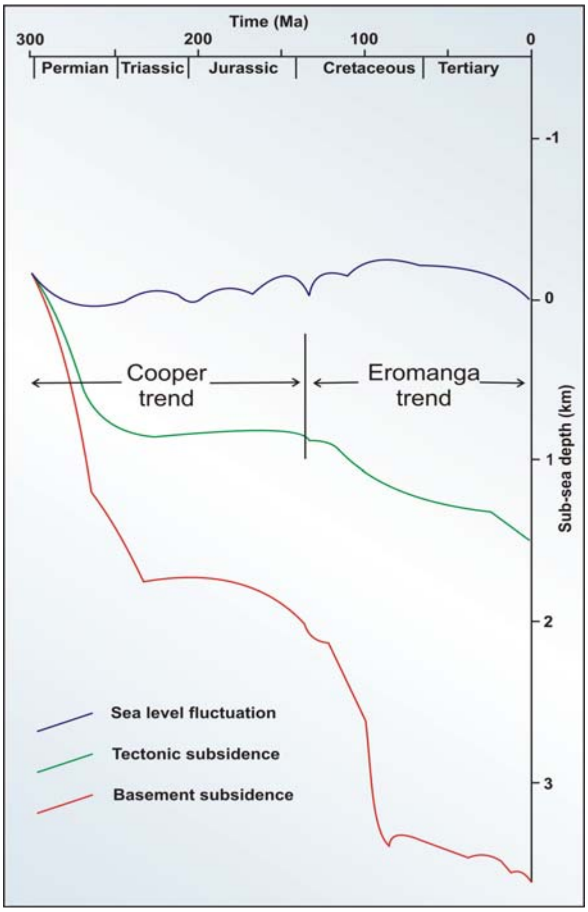


Figure 6 *The Cooper and Eromanga Basins have experienced different mechanisms of subsidence. The Early Jurassic saw a short-lived phase of erosion (Modified after Deighton and Hill, 1998).*

The palaeoheatflow model sees two distinct anomalies. A short-lived high heatflow event (Eromanga event; 120-130 mW/m²), whose origin is unknown, has been modelled from 90 to 85 Ma. A second thermal perturbation (Post-Eromanga event; 80-100 mW/m²) started at 5

Ma, after a 80 My low temperature phase (50-60 mW/m²), and is subject to active controversy. Other studies suggest the present-day heat flow to be normal, and the low temperature phase to have resulted from increased artesian flow in the past, laterally removing a high amount of heat.

Based on 1D basin modelling results, Michaelsen (2002) concludes that most localities in the Cooper region of the Eromanga Basin experienced four periods of oil expulsion.

- A Permo-Triassic (ca 250 Ma) expulsion event resulted from burial and maturation of the Patchawarra Formation in the Nappamerri Trough. Only minor amounts of oil and gas were expelled.
- During the late Early Cretaceous (ca 105 Ma) rapid burial of the entire Cooper and Eromanga Basin sequence allowed expulsion of hydrocarbons from the Patchawarra and Toolachee Formations. Expulsion from Jurassic source rocks locally commenced. Elevated heat flows in the Nappamerri Trough (granite emplacement) allowed the release of gas since the Middle Jurassic (ca 185 Ma).
- During the maximum burial in Late Cretaceous times (ca 90 Ma) Permian source rocks passed through the lower boundary of the oil generative window. Additionally, Eromanga Basin source rocks entered the peak phase of oil generation at around 100 Ma.
- Renewed burial during the Late Tertiary (20-5 Ma) allowed minor quantities of hydrocarbons to be expelled.

Moussavi-Harami (1996) postulates a present day active expulsion, which he bases on increased current heat flows.

3.7 Study area

The Gidgealpa Field comprises a northern and a southern dome that host structurally trapped hydrocarbon accumulations (Fig. 7). While the northern dome contains Toolachee and Patchawarra Formation gas pools and only a small Hutton Sandstone oil pool, the southern dome is dominated by liquid petroleum accumulations (Fig. 8). In addition to a number of Toolachee, Patchawarra and Tirrawarra Formation gas reservoirs, it contains five large oil pools, reservoired in the Poolowanna Formation, Hutton Sandstone, Birkhead Formation and Namur Sandstone.

Since source rocks are thin on the Gidgealpa Ridge or onlap against it, most oil and gas was expelled from adjacent troughs, where source rocks reach high thicknesses and maturity. Three potential kitchen areas can be distinguished: the Patchawarra Trough, the Nappamerri Trough and the rather shallow Wooloo Trough. The Patchawarra Formation reaches up to 40m total coal thickness in the Patchawarra Trough, but only rarely exceeds 10m in the

Nappamerri Trough. The same trend is observed for the Toolachee Formation that reaches thicknesses of over 35 m in the northern Patchawarra Trough. The Nappamerri Trough is rich in Nappamerri Group sediments that only contain discontinuous coal seams as potentially poor source rocks.

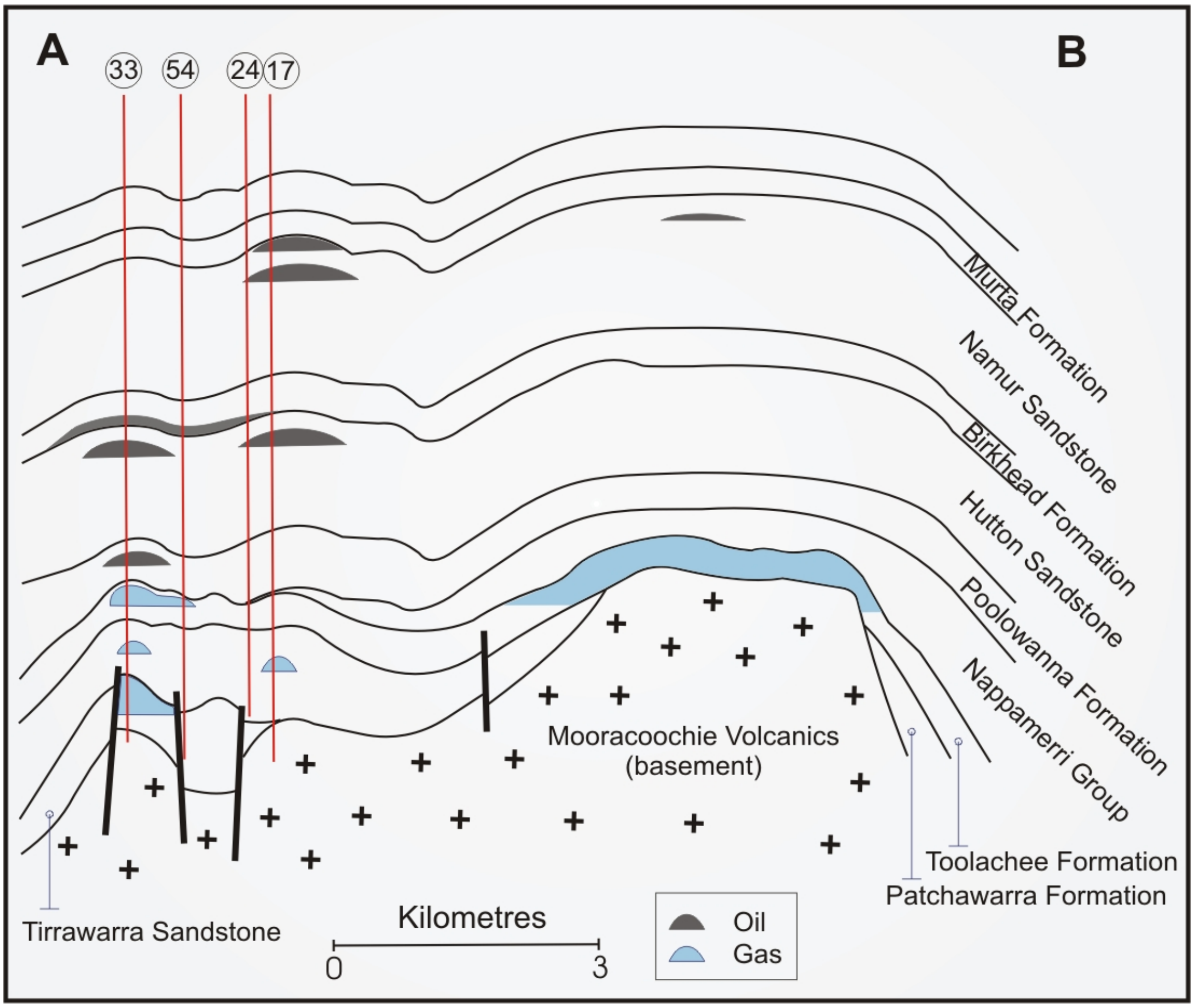


Figure 7 *A more or less North-South trending cross section through the Gidgealpa Domes (see figure 8 for section line) shows the location of hydrocarbon accumulations. These are mainly liquid in the Southern dome and gaseous in the Northern dome (modified after Boreham and Summons, 1999).*

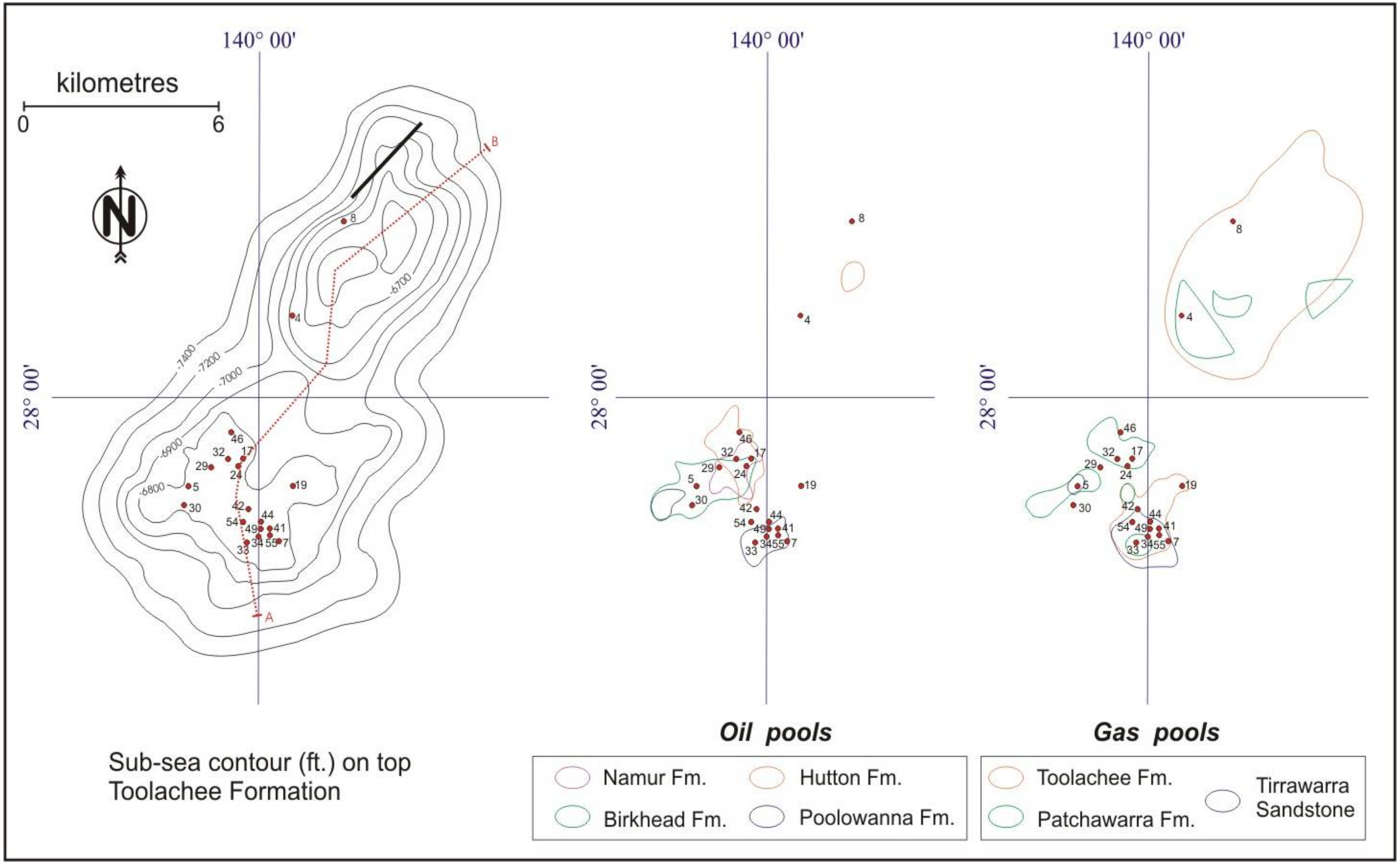


Figure 8 *The location of oil and gas accumulations in the Gidgealpa North and South domes. The cross section in Figure 7 is indicated by the dotted red line (modified after McIntyre et al., 1989).*

CHAPTER FOUR

Experimental

4.1 Sample selection and preparation

A suite of thirteen sandstone cores, eleven source rock extracts and twenty-four drill stem test (DST) oils were provided by the Department of Geology and Geophysics at the University of Adelaide, South Australia. Samples mainly cover oil pools in the southern Gidgealpa dome since the northern dome is dominated by gaseous petroleum accumulations.

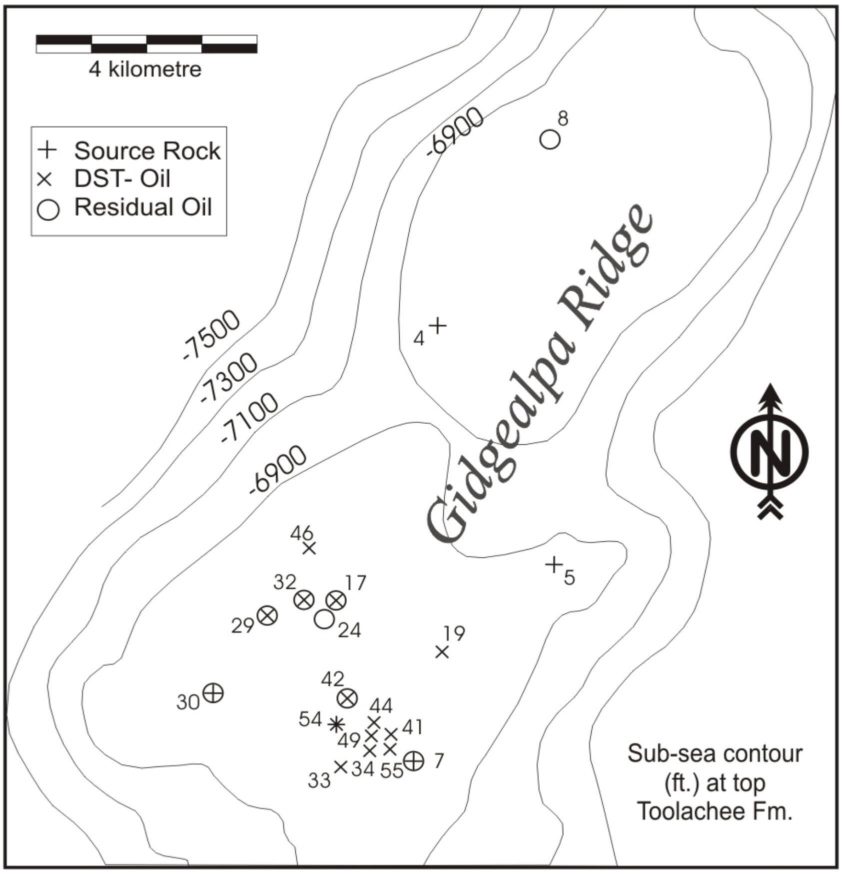


Figure 9 *Sub-sea contour map of the top Toolachee Formation, featuring sampled wells. Samples cover all oil pools in the southern Gidgealpa dome as well as carrier beds and potential source rocks.*

Source rock samples were brushed, rinsed under deionised water and dried at room temperature before extraction.

Sandstone core plugs, intended for sequential extraction, were cut from the sidewall of larger cores to adapt the size to the SFTE cells and to avoid contamination from drilling fluids that may have impregnated the core rim.

Source rock extracts

sample	formation	depth (ft.)
Well 4	Toolachee	6960'
Well 4	Patchawarra	7097'
Well 5	Toolachee	6888'
Well 5	Patchawarra	7134.5'
Well 5	Tirrawarra	7435.2'
Well 5	Cambr.Dol.	7951'
Well 7	Toolachee	6953.3'
Well 7	Kalladeina	7704'
Well 30	Birkhead	6029.2'
Well 30	Birkhead	6041.5'
Well 54	Patchawarra	7262.6'

Sandstone cores

sample	formation	depth (ft.)
Well 7 -45	Toolachee	6977'5"
Well 7 -47	Patchawarra	7125'
Well 7 -48	Tirrawarra	7288'1"
Well 8 -50	Toolachee	6932'10"
Well 17 -51	Hutton	6011'2"
Well 17 -52	Hutton	6086'5"
Well 24 -53	Namur	5189'
Well 29 -54	Birkhead	6042'2"
Well 29 -56	Hutton	6067'
Well 30 -57	Birkhead	6026'
Well 32 -58	Hutton	6012'
Well 32 -59	Hutton	6016'4"
Well 42 -61	Tirrawarra	7331'9"

DST oils

sample	formation	depth (ft.)
Well 17 DST1	Namur	5049'-5069'
Well 17 DST2a	Namur	5164'-5187'
Well 17 DST3	Birkhead	5916'-5950'
Well 17 DST4	Hutton	5981'-6000'
Well 17 DST6	Patchawarra	7100'-7428'
Well 19 DST1	Patchawarra	
Well 29 DST1	Birkhead	5968'-6014'
Well 32 DST2	Namur	5191'-5219'
Well 33 DST1	Hutton	
Well 33 DST4	Poolowanna	
Well 33 DST7	Patchawarra	
Well 34 DST2	Birkhead	6004'-6024'
Well 41 DST1	Tirrawarra	
Well 41 DST3	Toolachee	
Well 42 DST6	Hutton	6006'-6030'
Well 42 DST7	Namur	5204'-5217'
Well 44 DST2	Hutton	
Well 46 DST3	Poolowanna	
Well 46 DST6	Hutton	
Well 49 DST1	Poolowanna	6626'-6648'
Well 49 DST3	Epsilon	
Well 54 DST4	Namur	5188'-5212'
Well 54 DST6	Namur	5084'-5100'
Well 55 DST1	Poolowanna	

Table 1 *List of samples, i.e. source rock extracts, drill stem test oils and sandstone cores, of which the latter yielded between five and twenty residual oil fractions each, that were used in this study.*

4.2 Sequential flow through extraction

Sequential flow through extraction (SFTE) is a non-destructive extraction method, which allows recovery of discrete pore-filling oil pulses from an intact pore system, following the 'first in – last out'-principle (Schwark *et al.*, 1997).
Avoiding to grind samples prior to extraction prevents the generation of new mineral surfaces that can cause fractionation processes during extraction, and consequently falsify the study of migration fractionation processes. The main benefit of this method is, however, the potential to separately extract 'free oil' and discrete fractions of residual oils that are adsorbed as more or less discrete layers onto the mineral pore walls (Fig. 10 and 11).

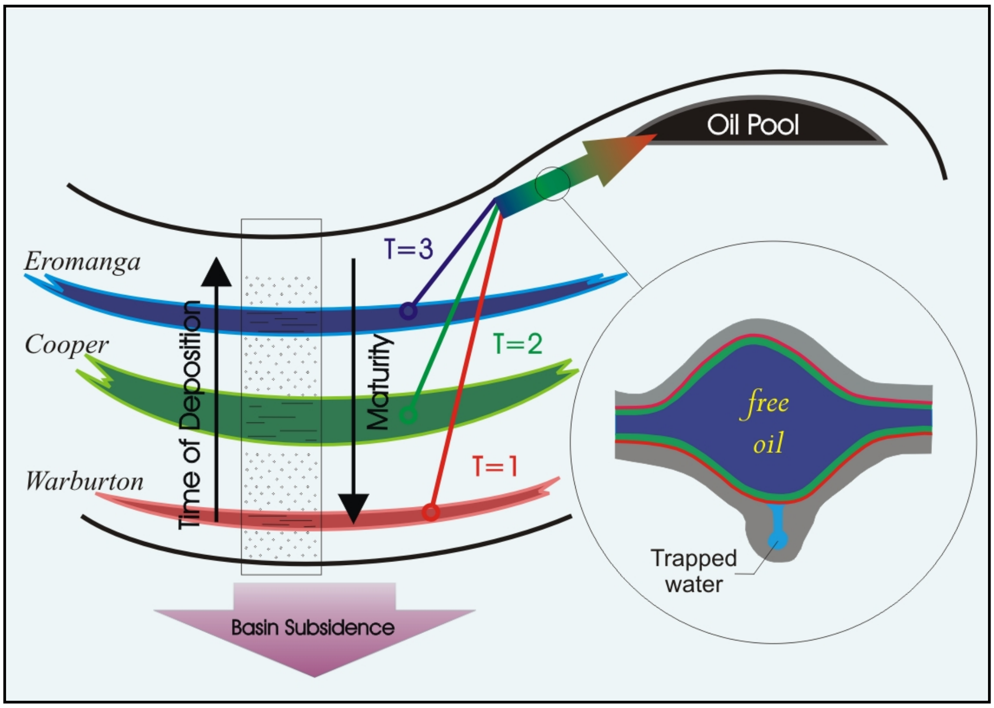


Figure 10 *During continuous basin subsidence, the three source rocks will successively enter the oil generative window (T1 – 3 = time steps). The generated petroleum migrates buoyantly until trapped to form an oil pool. Carrier and reservoir bed pore walls will thus successively be coated with layers of residual oils from the three source rocks.*

Larter and Aplin (1995), Stoddart *et al.* (1995) and Leythaeuser *et al.* (1988) noticed that core extracts contain a higher percentage in resins and asphaltenes than corresponding production oils from the same reservoir section. This is caused by selective adsorption of compounds onto mineral and/or organic phases during secondary migration, also termed geochromatography (Kroos *et al.*, 1991). After the passing of multiple petroleum pulses through a pore, a pseudo-layered system of adsorbed oils will develop, each layer representing an oil charge. During the first oil's dwell time in a pore space, polar compounds will experience interactions with the carrier rock mineral matrix and residual pore waters, resulting in a highly polar oil layer that is adsorbed onto the pore wall. When a second oil charge displaces the free oil phase of the first charge, it will encounter less active sites on the pore walls as these are already covered by a residual oil layer from the first charge. The first oil charge will be forced to enter smaller pores. Adsorbed oil layer number two will thus generally be less polar than number one since the ’polar docking stations’ have been preconditioned. The general state of the pore system gradually changes from ’water-wet’ to ’oil-wet’ and the polarity of subsequent residual oil layers decreases.

When a reservoir is sourced by only one source rock, this should be reflected by laboratory extract yields of a decreasing maturity, controlled by the continuous filling of the pore system with oils from a continuously maturing source kitchen. In case of in-reservoir-mixing of oils from different sources, the charging history can be reconstructed by observing changes in facies-dependent markers. The free oil, corresponding to the last charge and yielded by the first extraction step, should possess characteristics similar to DST or production oils.

The extraction was performed using dichloromethane (DCM) as the first solvent and a binary mixture of chloroform/methanol (1:1) as the second solvent (Fig. 11). Extraction with the second solvent started when colour was no longer observed in the DCM extracts. For a more detailed description the reader is referred to Schwark *et al.* (1997).

The SFTE extraction capacity was controlled in direct comparison to an automated solvent extraction method. Sixteen sandstone cores from the Strzelecki Field, QLD, were crushed after sequential flow through extraction and after crushing re-extracted by a *Dionex ASE 200* accelerated solvent extractor (ASE). The extract yields obtained by ASE, compared to the total extract yield, lie within the range of 0% to 5.3% (Table 2). Only two of sixteen samples showed a value higher than 1.5%, and the average value indicated that 98.6% of the total bitumens was extracted by SFTE.

Sample	**Depth** [m]	**Formation**	**Porosity** [Φ]	**Perm.** [Ka]	**Extr.yield [mg/g]**		**Extract yield [%]**	
					SFTE	ASE	SFTE	ASE
Strzelecki-4	1430.42	Namur Sst	18.1	198	2.168	0.102	95.5	4.5
	1686.38	Hutton Sst	20.0	1159	7.657	0.043	99.4	0.6
	1694.51	Hutton Sst	20.0	303	8.472	0.042	99.5	0.5
	1697.65	Hutton Sst	14.5	466	3.496	0.052	98.5	1.5
	1699.56	Hutton Sst	17.8	901	3.878	0.024	99.4	0.6
	1702.07	Hutton Sst	15.7	784	1.692	0.000	100.0	0.0
Strzelecki-5	1421.89	Namur Sst	20.2	356	1.549	0.019	98.8	1.2
	1685.23	Hutton Sst	20.5	553	7.079	0.105	98.5	1.5
	1690.32	Hutton Sst	19.3	1080	8.112	0.043	99.5	0.5
Strzelecki-6	1413.96	Namur Sst	19.2	186	4.649	0.058	98.8	1.2
	1416.10	Namur Sst	20.1	295	4.353	0.026	99.4	0.6
	1420.26	Namur Sst	18.3	154	3.768	0.031	99.2	0.8
	1421.08	Namur Sst	19.5	165	3.291	0.038	98.9	1.1
Redman-1	2842.25	Pretty Hill Fm	17.7	33,9	1.032	0.058	94.7	5.3
						Average:	***98.6***	***1.4***

Table 2 *Comparison of the extraction efficiency of the SFTE apparatus versus ASE, a commonly used destructive extraction method, shows that SFTE extracts between 95% and 100% of the extractable organic matter (EOM) that is present in a pore system. The non SFTE-extractable organic matter is trapped by mineral precipitation in fluid inclusions and can only be recovered by destruction of the pore system.*

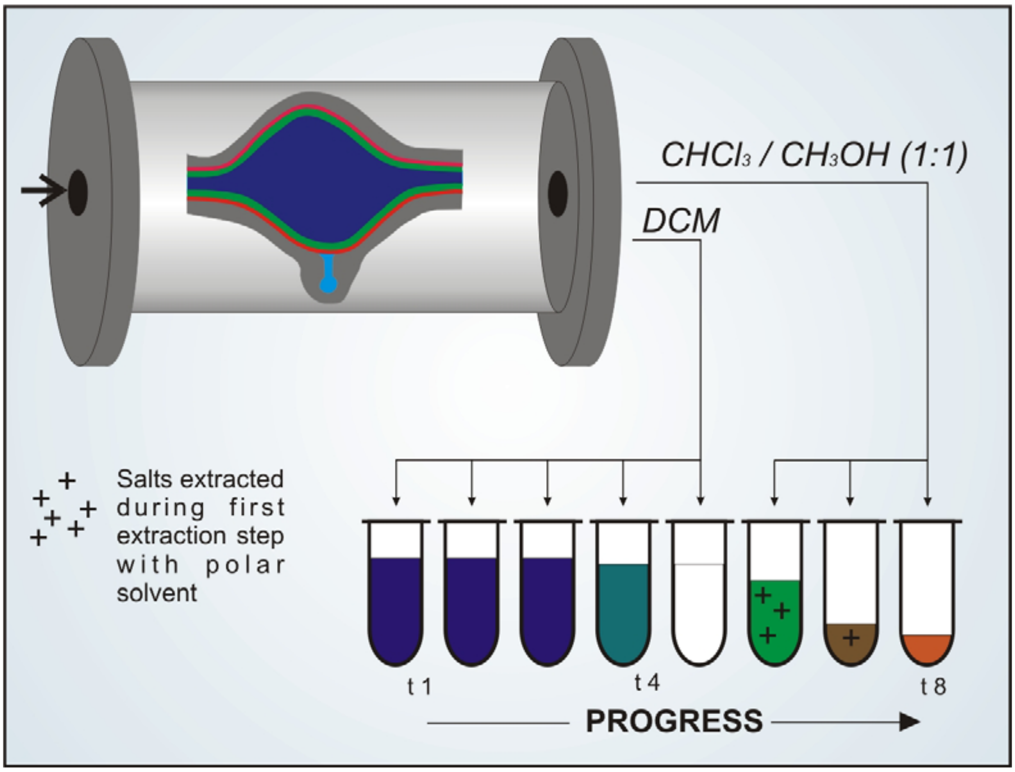


Figure 11 *The sequential flow through extraction mechanism uses a core plug that is fitted with a Teflon liner and flown through by solvents under high hydrostatic pressure in a closed cell. Solvent fractions are collected for a predetermined period each. As soon as a fraction appears colourless, a switch to a more polar solvent can be undertaken to extract the adsorbed residual oil layers that contain a higher amount of NSO compounds relative to hydrocarbons. The first fraction that is eluted with the more polar solvent frequently contains dissolved salts that have to be removed before further processing of the samples.*

4.3 Medium pressure liquid chromatography

Medium pressure liquid chromatography (MPLC) is a system for the semipreparative, semiautomatic separation of petroleum and organic rock extracts into discrete hydrocarbon compound classes.

Within the apparatus, resins are retained on pre-columns that are filled with silica (100Å, 0.063-0.2 mm) and topped by approximately 1 cm of coarser silica (100 Å, 0.2-0.5mm). While aromatic compounds are retained on a main column (60Å silica, 0.045-0.063mm) and later eluted by a backward solvent flow, aliphatic hydrocarbons can pass through the stationary phases freely. For a detailed description of this method the reader is referred to Radke *et al.* (1980).

All samples, i.e. source rock extracts, DST oils and residual oils, were separated into saturated hydrocarbons, aromatic hydrocarbons and resins, accepting the loss of asphaltenes in the *n*-hexane based system. Asphaltene incompatibility, caused by the insolubility of these large macromolecules in lower molecular weight hydrocarbons, raised the fear of a carbazole fractionation by co-precipitation with asphaltenes, as the solubility of *n*-carbazole in *n*-hexane is distinctively lower than that of other carbazole species (Fig. 12). Test mixtures of *n*-carbazole, 9-methylcarbazole, 9-phenylcarbazole and fluoren-9-one were analysed in four different concentrations per solvent by gas chromatography. The resulting diagrams (Fig. 12) represent the relative solubility of each compound in the used solvents. Co-solvents in real extracts facilitate full solubility in hexane.

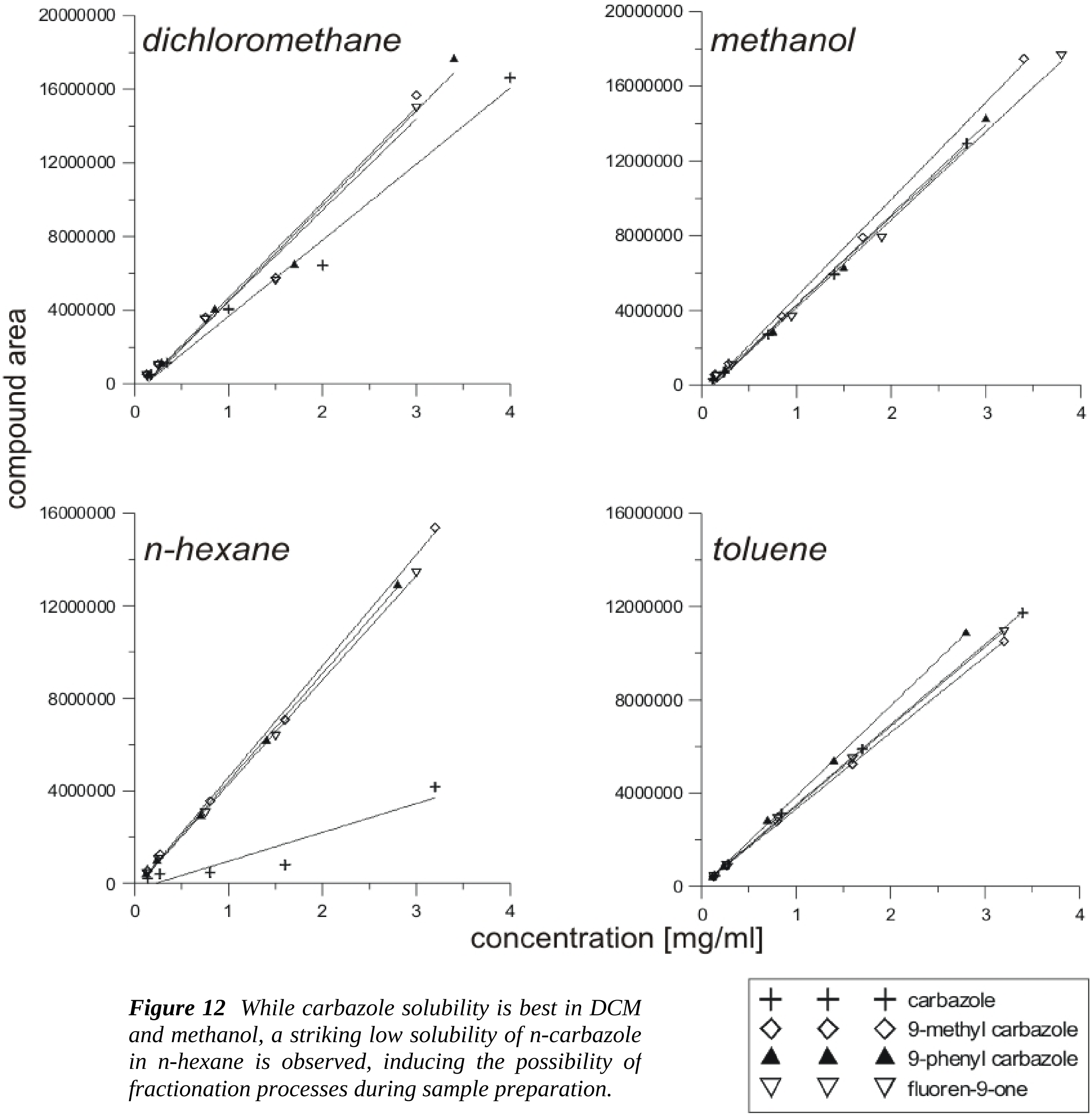


Figure 12 *While carbazole solubility is best in DCM and methanol, a striking low solubility of n-carbazole in n-hexane is observed, inducing the possibility of fractionation processes during sample preparation.*

4.4 Iatroscan TLC-FID

All residual oil fractions that were obtained by sequential flow through extraction of sandstone cores were screened for their bulk composition in terms of saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes (SARA). For a detailed description of this method the reader is referred to Karlsen and Larter (1991) and Bharati *et al*. (1993).

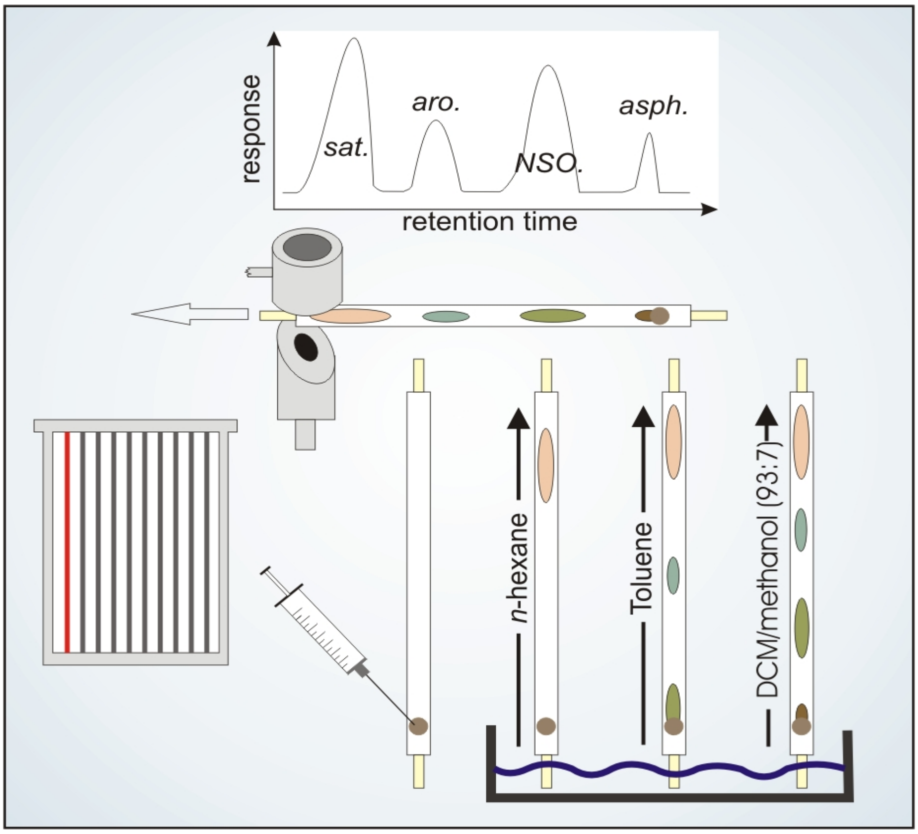


Figure 13 *The principle of thin layer chromatography implies the separation of a mixture into compound classes by a mobile (liquid) phase that moves relatively to a stationary (solid) phase. By using solvents of increasing polarity during successive steps, a separation into saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes can be achieved. In the figure, a cartoon is presented for the red rod, which is held together with nine of his peers in a metal rack. One whole rack can be analysed during one analytical run. After separation into compound classes, which occurs in solvent filled chambers, the solvent is evaporated from the rods; they are subsequently placed in an oven to evaporate lower molecular weight hydrocarbons for reasons of comparison. Analysis takes place in the Iatroscan apparatus, in which the rack that holds the rods is moved relative to a flame ionizing detector.*

Bitumens were dissolved in dichloromethane at a concentration of 10 µg/ml before 1 µl of the solution was applied onto a silica coated rod by using an automatically-driven syringe. Ten rods, held together in a rack, are successively placed in a number of solvent chambers where the capillary rise of the solvent in the stationary phase that covers the rods causes the separation of samples into discrete compound classes. After a 35 minute development in *n*-

hexane that allows the saturated hydrocarbons to rise with the solvent, the rods are placed for 15 minutes in toluene which separates the aromatic hydrocarbons from the NSO residue.

A final 5 minute-step in a dichloromethane/methanol [93:7] solvent mixture separates resins and asphaltenes. In between solvent chamber development steps, the rods are left to dry and, after the last step, the residual solvent and lower molecular weight hydrocarbons are evaporated in an oven at 60°C for 1 minute. This improves the comparability of results as different oils and bitumina have a varying content of gasoline-range hydrocarbons.

A Iatroscan TH-10 Mk IV (Iatron Laboratories, Japan), equipped with a flame ionizing detector (FID) was used for rod scanning. Quantification of compound classes was performed by a Hewlett Packard 3396 Series II integrator. The silica rods of the type Chromarod-S III have a pore diameter of 60Å and a particle size of 5µm. The FID was operated with pure grade hydrogen (190 ml/min) and air (2.1 l/min).

4.5 Solid phase extraction

Solid Phase Extraction (SPE) is a method to clean up and concentrate samples prior to molecular analysis, in view of improving detection limits (Fig. 14). The advantages over common liquid chromatography are the use of small amounts of solvent, a rapid sample throughput and the fact that no special equipment is needed. Typically, a stationary phase is chosen that has the potential to retain the analytes in dependency of the eluting solvent. After elution of interfering compounds, the solvent is switched to elute a fraction enriched in analytes.

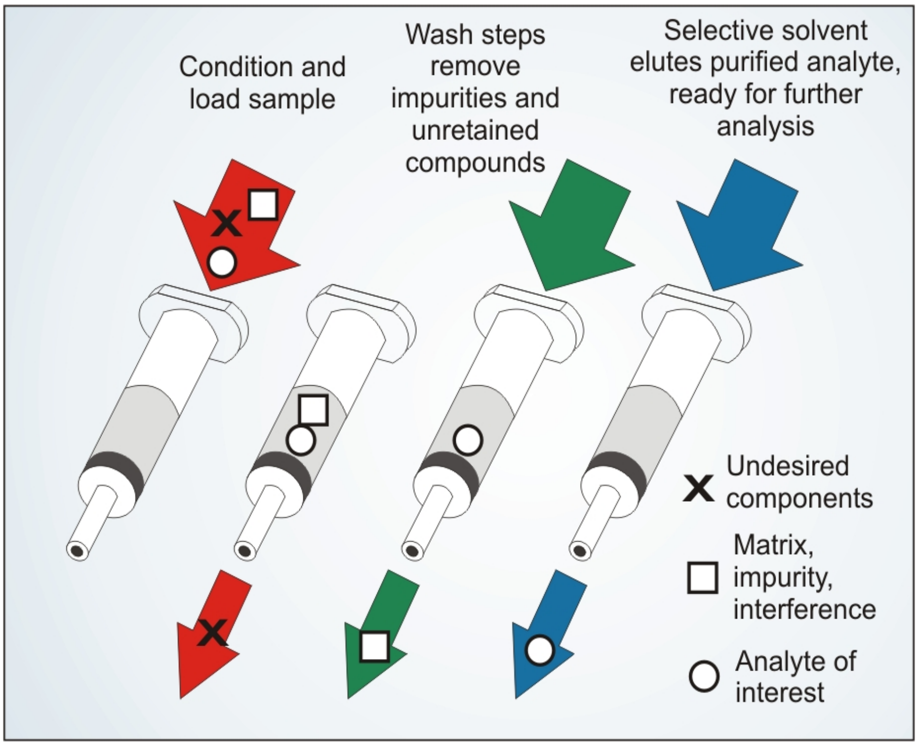


Figure 14 *SPE reduces interfering compounds and impurities by taking advantage of slight differences in polarity or ionic charge between the undesired components and the analytes (modified after several unknown sources).*

In this study, an existing two-step in-house SPE method was used to concentrate carbazole compounds and reduce fluorenone interferences.

The polar fraction, obtained by MPLC, was dissolved in 100 µl DCM and loaded on top of a 3 ml glass column that was filled with 500mg silica, which was activated at 110°C for one hour. Residual hydrocarbons were eluted with 1.5 ml *n*-hexane. The neutral nitrogen fraction, which contains the carbazoles, was subsequently eluted with 5 ml toluene/*n*-hexane (1:1) and allowed to dry. Further elution steps can be undertaken to recover amines (acidic nitrogen compounds) with toluene and basic nitrogen compounds with toluene/diethylether (1:1). If any asphaltenes are present, they can be recovered with tetrahydrofurane (THF).

The neutral nitrogen fraction was dissolved in 100 µl DCM and loaded on top of a 3 ml glass column, filled with -NH_2 substituted silica (aminopropyl phase). Anthraquinones were eluted with 6 ml *n*-hexane/DCM (95:5) and the carbazole containing fraction was eluted with 4 ml DCM. Glass columns were used to minimize contamination by phthalates that are contained in plastic columns, where they function as plasticizers. Phthalates can be leached by organic solvents and coelute with carbazoles on most GC columns.

During the course of this study, an improved separation scheme for carbazoles was elaborated. This involves an intermediate step, in which interfering compounds are reduced by borohydride (BH_4). Preliminary results indicate that fluorenones are indeed reduced to fluorenols, which have a different polarity, and can be eliminated during the second SPE step. Furthermore, a reduced interference by phthalates was observed. The extensive evaluation that is required for the interpretation of the results that were obtained from these tests will however adjourn this interpretation to a future time.

4.6 Gas chromatography and mass spectrometry

For analysis of carbazoles, a Hewlett Packard 6890 gas chromatograph was used, interfaced to a Chromtech Kodiak 1200 triple sector quadrupole mass spectrometer. The GC was equipped with a PVT injection system, operated in splitless mode, and a HP 5 fused silica capillary column (5% phenyl, 95% methylsilicone) of 30 m length, 0.25 mm inner diameter and 0.25 µm film thickness. Helium was used as the carrier gas with a flow of 0.7 ml/minute. The oven temperature was programmed as followed: 60°C held for two minutes, then programmed at 20°C/minute to 180°C, kept isotherm for 1 minute and programmed at 4°C/minute to 310°C and held at final temperature for 10 minutes.

In electron impact (EI) mode, the MS was operated at an electron energy of 70 eV and a source temperature of 200°C. Carbazoles were detected in selective ion monitoring (SIM) mode, scanning for following ions (mass to charge ratio): 149 (phthalates), 167 (*n*-carbazole), 181 (methylcarbazoles), 195 (dimethylcarbazoles), 209 (trimethylcarbazoles), 217 (benzocarbazoles), 231 (methylbenzocarbazoles), 243 (phenylcarbazole) and 245 (dimethylbenzocarbazoles). Mass spectra were recorded at a scan rate of 0.7 s/decade.

The quantitative amounts were determined relative to 9-phenylcarbazole as an internal standard. No corrections were made for specific response factors of individual compound.

CHAPTER FIVE

Source facies

The saturated and aromatic hydrocarbon fractions were extracted and separated at the Organic Geochemistry Department of the University of Cologne and analysed via GC/MS by Dr. Khaled Arouri at the University of Adelaide. Results of aliphatic biomarker analyses are presented briefly in this chapter to construct a backbone, on which the evaluation of carbazole distributions can be based. In particular, elucidation of the depositional environment of source rocks and the distribution and association of oils is presented.

5.1 *n*-Alkane distribution

Typically, the oil play of the Cooper and Eromanga Basins hosts three to four oil families that can in some cases be readily distinguished by the *n*-alkane profile of whole oil gas chromatograms (Figure 15). Extensive mixing however creates the necessity to use molecular markers to distinguish and quantify participating oils. Cooper Basin oils are subdivided in Family 1 and 2 oils. Family 1 oils have a *n*-alkane distribution with a maximum around nC_7, whereas the *n*-alkane distribution of Family 2 oils is skewed towards carbon numbers in the nC_{13} to nC_{23} range (Michaelsen, 2002). Waxy oils can be produced from source rocks that received a high input of vascular plants, which has been the case throughout the Cooper Basin sedimentary sequence. High amounts of rearranged hopanes (17α-diahopanes and 18α-neohopanes) over normal hopanes in Family 2 oils point to catalytic processes on clay minerals, making shaly sections of the Toolachee Formation a favourable source. Family 1 oils bear a normal hopanoid signature and were generally produced at higher maturities (1.0 - 1.1% Ro) than Family 2 oils (0.9 – 1.0% Ro). They were probably generated from coaly Patchawarra Formation source rocks during the peak phase of oil generation, but were retained by the coaly nature of the source rock. Only at a later time, when more petroleum of a, by now, higher maturity was produced did efficient expulsion start. Bimodal *n*-alkane distributions as shown in figure 15 may either point to mixing between Family 1 and 2 oils, or to a more efficient expulsion from Family 1 source rocks. This can be distinguished by the hopanoid signature.

Eromanga Basin oils were generated at surprisingly low maturities from the lacustrine Birkhead and Murta Formations. They have highly variable proportions of waxy *n*-alkanes and are consequently variably similar to Cooper Basin Family 1 and 2 oils. As the Birkhead Formation is also coal bearing, the source rock lithology may possibly exert a control on the *n*-alkane profile, oils being more condensate-like and less waxy, the more organic matter the source rock contains (by retention of higher molecular weight hydrocarbons). Water washing is a widespread phenomenon in the Eromanga Basin, resulting in oils that were stripped off their gasoline range hydrocarbons, making them appear like high-wax oils. The study area mainly hosts light Jurassic oils as shown in figure 15, suggesting Birkhead Formation coals as a source.

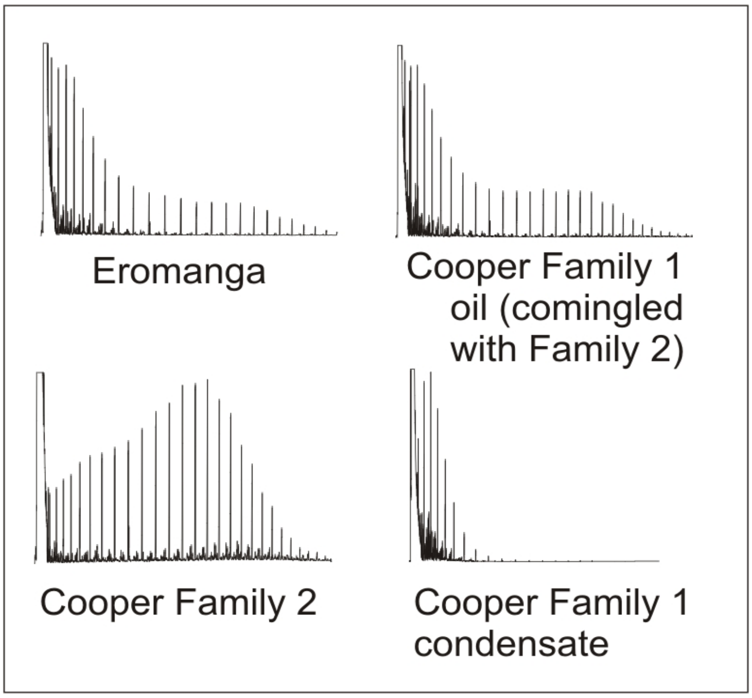


Figure 15 *Typical GC traces of Cooper and Eromanga Basin oil types. The (commingled) Cooper Basin Family 1 oil and the Eromanga Basin Birkhead Fm sourced oil resemble each other but can be distinguished by the lower maturity of Jurassic oils.*

5.2 Isoprenoid Biomarkers

5.2.1 Pristane and Phytane

The acyclic isoprenoids pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$) derive primarily from the phytyl side chain, which is cleaved from chlorophyll during diagenesis to form the unsaturated *n*-alcohol phytol (Killops and Killops, 1993). While oxic to suboxic conditions during deposition allow phytol oxidation to phytenic acid, decarboxylation to pristene and reduction to pristane, an anoxic depositional environment forces phytol reduction to form dihydrophytol and subsequently phytane. Apart from uncertainties that can be evoked by an archaebacterial input, depositional salinity variations and gas chromatographic coelution, the pristane/phytane ratio is considered as a useful indicator of the palaeoenvironmental redox state (Peters and Moldowan, 1993). The isoprenoid/*n*-paraffin ratio decreases during maturation as a result of continuous *n*-paraffin generation from the source rock kerogen, and increases by the action of petroleum degrading micro-organisms that tend to attack paraffins prior to isoprenoids.

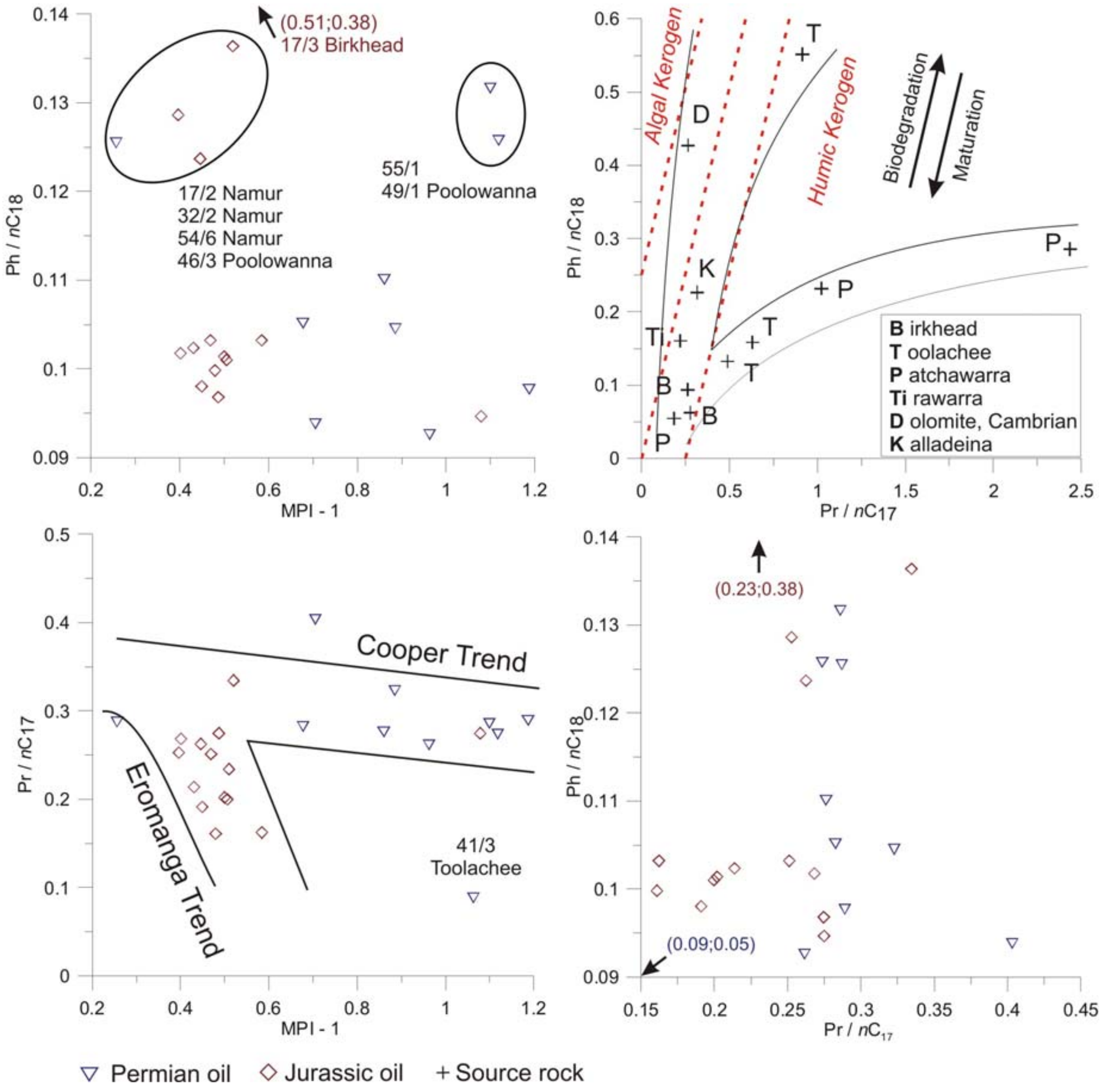


Figure 16 *The distribution of acyclic isoprenoids and paraffins in source rock extracts (+) is an indicator of source rock kerogen type. While the Pr/nC$_{17}$ and Ph/nC$_{18}$ ratios generally reflect maturation or biological degradation in oils, their distribution in the oils that were studied (▽, ◇) seems to be governed by the source rock type and possibly lithology.*

5.2.2 Results and discussion

The pristane/heptadecane versus MPI – 1 plot has a bifurcate trend: with increasing maturity Pr/*n*C_{17} of Permian oils decreases slower than that of Jurassic oils (Fig. 16). The Birkhead Formation, being the main Eromanga Basin source rock, during maturation produces more *n*-alkanes in the C_{17} range than the Cooper Basin source rocks, the Patchawarra and Toolachee Formations respectively. Elevated phytane/octadecane values may be attributed to varying Eh conditions in the source rocks.

All source rocks except the Cambrian Dolomite have sourced their oils from humic Type III kerogen (Fig. 16), which is a common feature of terrestrially dominated sedimentary sequences like that of the Cooper Basin. Those humic source rocks that seem to have received a little algal input may be the remainders of peat swamps that became flooded and colonised by lacustrine algae. This should then be reflected by their hopanoid and steroid distribution.

5.2.3 Hopanoids

Hopanoids are pentacyclic triterpenoids, which originate from amphiphilic prokaryotic membrane lipids that form a bilayer to protect the bacterial cytoplasm. Reduction of biological precursor hopanepolyols and hopanoic acids yields hopanes with a 17β(H), 21β(H) configuration. In C_{31}-C_{35} homohopanes (Fig. 17) an additional chiral centre is present at C-22, and biosynthesized in the 22R configuration. This is converted to an equilibrium mixture of 22R and 22S during thermal maturation.

During diagenesis, the biosynthesised 17β(H), 21β(H) hopanes (ββ) become unstable and are converted to βα-hopanes (moretanes) and αβ-hopanes. Due to differentially high energy barriers, the reverse reaction does not occur, and the formation of αβ-hopanes is favoured. At higher temperature levels, the conversion of βα-hopanes to αβ-hopanes becomes possible through a ββ-hopane intermediate. The βα / αβ -hopane ratio thus decreases during thermal maturation from approximately 0.8 to values of 0.05 in mature source rocks (Peters and Moldowan, 1993).

The ratio of the more stable C_{27} 18α(H)-22,29,30-trisnorneohopane (Ts) versus the less stable C_{27} 17α(H)-22,29,30-trisnorhopane (Tm) is a maturity indicator that covers higher maturity ranges. Conversion of C_{27} 17β(H) to 17α(H) (Tm) reaches completion at a maturity level after the disappearance of 17β(H), 21β(H) hopanes, prior to the onset of intense hydrocarbon generation. However, the Ts/(Ts+Tm) ratio is only reliable as a maturity indicator when oils and bitumina from a common source of consistent organic facies are evaluated (Peters and Moldowan, 1993) as the ratio is very source-sensitive (McKirdy *et al.,* 1983; Rullkötter *et al.*, 1985; Moldowan *et al.*, 1986, all cited from Peters and Moldowan, 1993; Rullkötter and Marzi, 1988).

Rearranged hopanes, i.e. C_{29} and C_{30} 17α(H)-diahopanes (C_{29}* and C_{30}*) are thought to be formed by rearrangement of a hopanoid that carries a functional group in the D-ring. Peters and Moldowan (1993) assume that C_{30}* is derived from bacterial input into a sediment containing clays, and that deposition under oxic or suboxic conditions favours its formation. This is consistent with the common appearance of terrestrial oils with high amounts of rearranged hopanes.

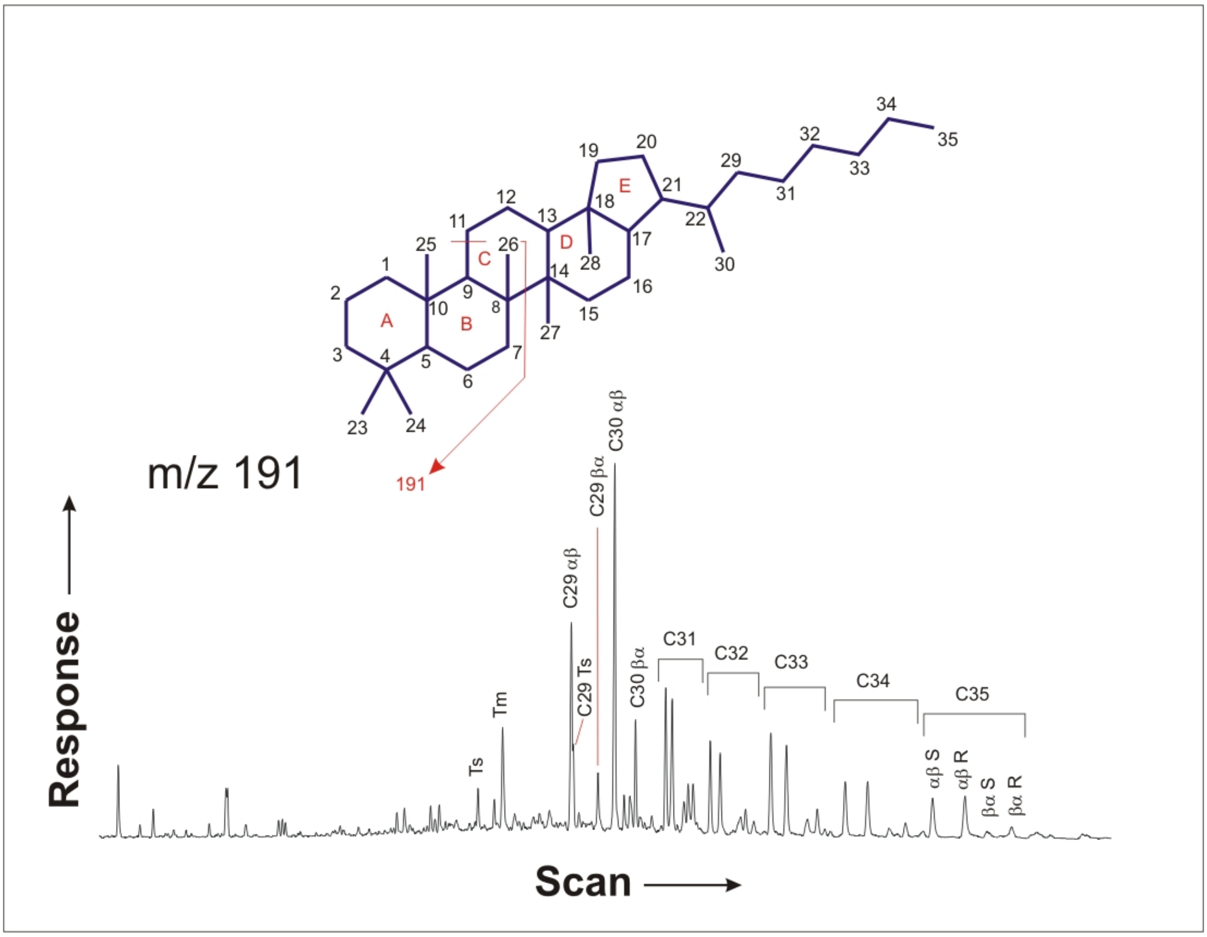


Figure 17 *The hopanoid carbon skeleton, which is depicted above, disintegrates characteristically and thereby produces an m/z 191 fragment. The mass fragmentogram below shows the elution order of various hopanoid molecules in a sample from the Permian Kupferschiefer. The dominating C_{30} αβ peak is misleading: C_{30} αβ hopane produces two 191 fragments, therefore almost doubling the peak area.*

5.2.4 Steroids

Steroids are the phytogenetic counterparts to hopanes and derive from eukaryotic cell membrane sterols. Similarly to hopanes, they are thought to increase the rigidity and strength of the membrane. As the configuration at most of the chiral carbons (Fig. 18) in the newly formed steranes is unaffected by diagenetic reactions, that of the original biogenic steroid is inherited (Killops and Killops, 1993), predominantly being the 5α(H), 8β(H), 9α(H), 10β(CH_3), 13β(CH_3), 14α(H), 17α(H), 20R configuration.

Ternary sterane plots of C_{27}, C_{28} and C_{29} steranes are a popular way to distinguish oil populations that belong to different source rocks or organic facies. Generally, a predominant C_{29} sterane signal indicates a vascular plant input, especially when accompanied by high Pr/Ph values. High C_{27} or C_{28} values, on the other hand, suggest an origin from aquatic organisms. However, C_{29} steranes are also found in pre-Mesozoic oils, which were sourced from rocks that were deposited before higher plants evolved.

Isomerisation at C-20 in C_{29} 5α(H), 14α(H), 17α(H) steranes converts the biogenically inherited 20R configuration to a mixture of 20R and 20S. Isomerisation at C-14 and C-17 in both, the 20S and 20R C_{29} regular steranes causes an increase in the ratio ββ / (ββ + αα) from nonzero values to approximately 0.7, which corresponds to a vitrinite reflectance equivalent of 0.9% Ro. While, again, hypersaline source rocks may favour the production of ββ steranes by reactions with sulphur, laboratory heating experiments suggest that the ratio is affected by different source rock types (Peters and Moldowan, 1993).

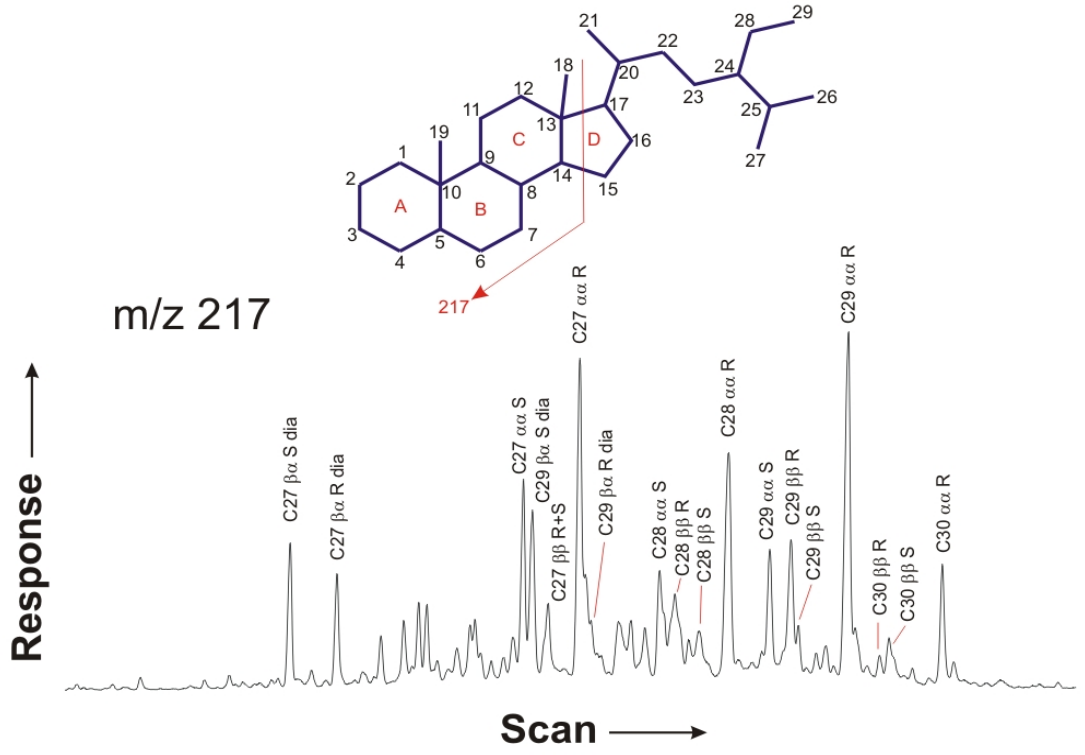


Figure 18 *In contrast to the five-ringed hopanoids, the steroid backbone consists of only four rings. The typical mass fragment, on which steranes are measured during GC-MS analyses, is m/z 217. Although more steroids exist, the most important* C_{27}*,* C_{28} *and* C_{29} *variations are shown in the mass fragmentogram of a Kupferschiefer sample.*

5.2.5 Results and discussion

Among the source rock samples, only the Cambrian dolomite has elevated C_{35}/C_{31} hopane values, which is indicative for its deposition under truly anoxic, and possibly hypersaline conditions. This finding supports the high amount of algal kerogen that is present within this sample (Fig. 16) and is further strengthened by having the lowest Pr/Ph value of all source rocks.

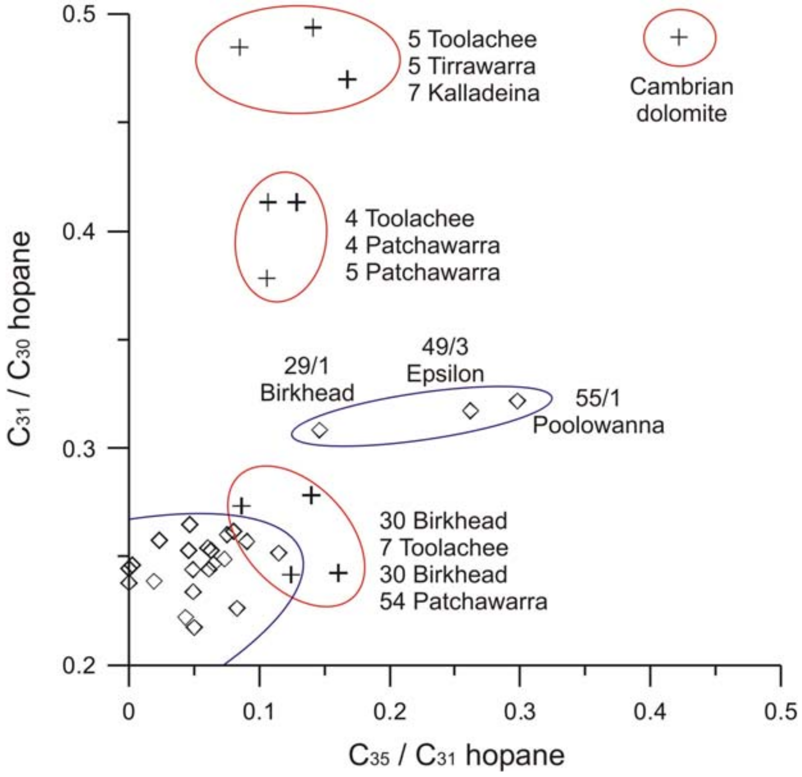
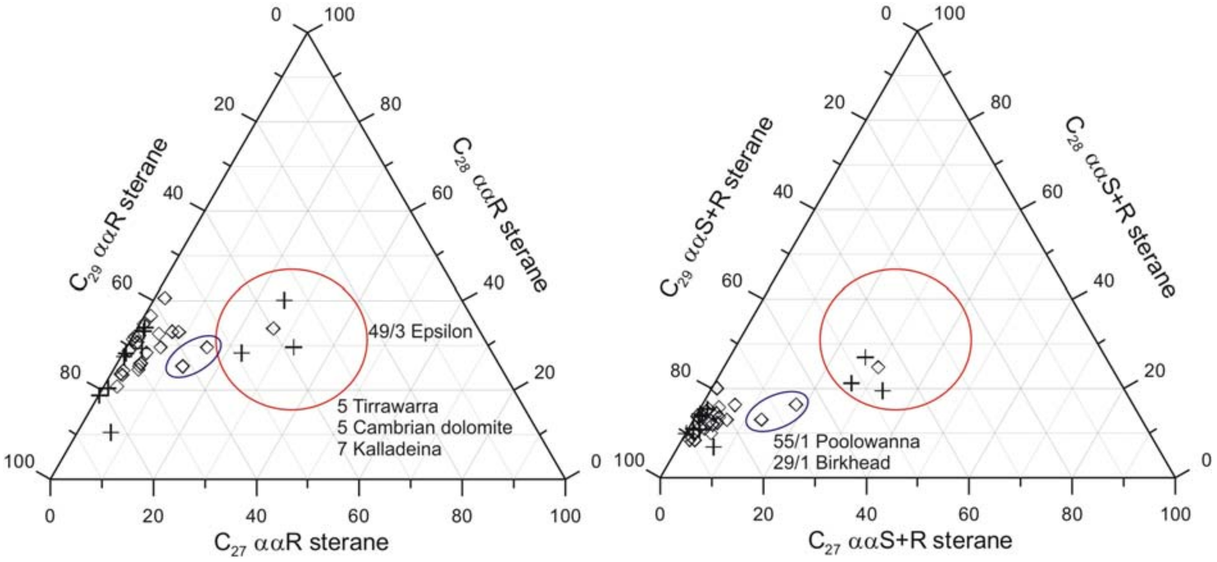


Figure 19 *This figure utilizes the distribution of homohopanes in oils (◇) and source rock extracts (+) to reveal the redox conditions during source rock deposition and the amount of bacterial contribution to the source rock.*

Concerning the C_{31}/C_{30} hopane ratio, which should reflect bacterial activity in the depositional environment, a large scatter exists among the remainder source rock samples. Nevertheless, three distinct clusters can be distinguished (Fig. 19). The highest amount of bacterial material, as expected, seems to be present within the two other pre-Permian to Early Permian Warburton Basin samples. The Toolachee sample from well No.5 stood out before with elevated phytane/octadecane values and has probably received a different input in organic matter than other Toolachee samples. While Jurassic Birkhead Formation source rocks were least reworked by bacterial communities, the remainder Toolachee and Patchawarra samples take an intermediate position.

Three oils are notably distinctive. These are 29/1 from the Birkhead Fm., 55/1 from the Poolowanna Fm. and the Epsilon Formation oil 49/3. The Epsilon oil, featuring the strongest deviations, could represent a self-sourced system. This, however, is not the case for the other two oils. While the Poolowanna oil might be influenced by minor amounts of indigenously produced petroleum, no explanation was found for the Birkhead oil, which does not show any other anomalies that could distinguish it from the typical Namur-Birkhead-Hutton oil family.



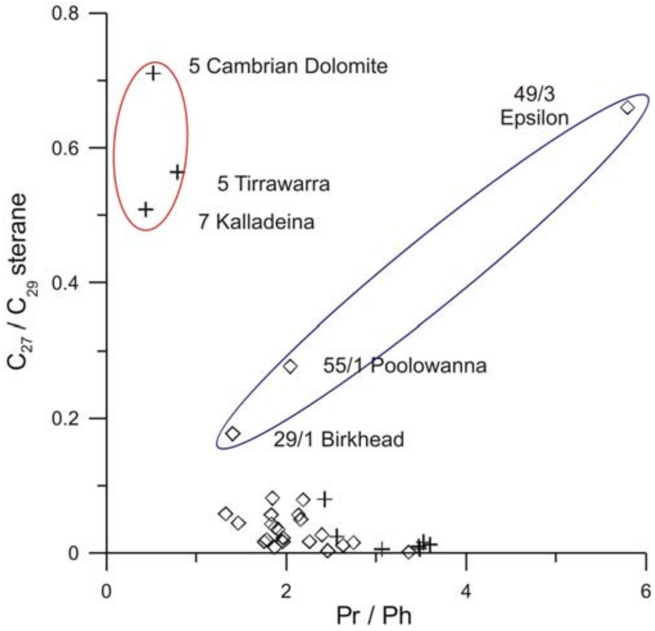


Figure 20 *The distribution of C_{27}, C_{28} and C_{29} steranes in source rock extracts (✚) and oils (◇) reveals that the three pre-Permian source rocks received a higher algal input. Three oil samples seem to originate from a different source than the remainder oil samples by exhibiting relatively elevated C_{27} sterane concentrations*

The relative distribution of C_{27}, C_{28} and C_{29} steranes supports previous findings. All three pre-Permian source rocks have received a higher input of algal material (Fig. 20), which is reflected in elevated relative C_{27} and C_{28} sterane concentrations. The three afore mentioned DST oils that feature elevated C_{31}/C_{30} hopane ratios are also characterised by elevated C_{27}/C_{29} sterane ratios.

CHAPTER SIX

Carbazoles

Nitrogen compounds in petroleum have been studied for many years (Snyder, 1965; Dorbon *et al.*, 1984), largely because of the roles of the compounds as health hazards, their involvement in catalyst poisoning, and their contribution to sludge formation in distillate products (Li *et al.*, 1994).

In 1986, Charlesworth noticed that organically bound nitrogen in a kerogen pyrolysates is adsorbed by clay minerals, the activity of minerals correlating with their ion exchange capacity and the polarizability of the exchangeable kation. Yamamoto (1991) compared alkylbenzoquinolines in crude oils and source rock extracts and attributed the variation in nitrogen-shielded isomers and nitrogen-exposed isomers to geochromatographic phenomena. During the 1990's this idea was picked up by the *NRG* research group at the University of Newcastle upon Tyne, which started intense research into the distribution of carbazoles (Fig. 1) in petroleum and source rock bitumina. After initial results, which suggested that the distribution of carbazoles was controlled by fractionation processes during secondary migration (Li *et al.*, 1994, 1995; Larter *et al.*, 1995, 1996; Schwark *et al.*, 1997), it soon became clear that other parameters such as maturity (Li *et al.*, 1997; Clegg *et al.*, 1998; Horsfield *et al.*, 1998), source facies (Clegg *et al.*, 1997; Bakr and Wilkes, 2002; Hallmann *et al.*, 2003, Hallmann *et al.*, 2004) and biodegradation (Chunmin *et al.*, 1999; Huang *et al.*, 2003) did exert a strong control in certain cases.

In this chapter the distribution of carbazole, methylcarbazoles, dimethylcarbazole and benzocarbazole in DST oils, source rock extracts and residual oils will be depicted and tentatively explained. C3 carbazoles will be covered briefly as their detailed molecular characterisation is not feasible due to the large number of isomers and the lack of reference standards.

6.1 Introduction

Most organic nitrogen compounds in crude oils are present as alkylated aromatic heterocycles with a predominance of neutral pyrrolic structures over basic pyridinic forms (Li *et al.*, 1994). Carbazoles, be they alkylated or arenic, all belong to the group of neutral polar compounds and contain *n*-carbazole, a diarenic pyrrole ring, as a basic skeleton (Fig. 1). A high polarity, caused by the nitrogen, makes these species sensitive to adsorptive interaction with clay mineral kations (Broholm *et al.*, 1994) or solid organic matter by hydrogen bonding. While oxygen containing compounds such as phenols, carboxylic acids and others are also prone to adsorb on polar surfaces (Larter *et al.*, 2000; Taylor *et al.*, 1997; Lucach *et al.*, 2002), they are highly sensitive to alteration by water washing processes, and consequently not suited to study fractionation processes during secondary petroleum migration.

Our knowledge of the origin of non-porphyrinic nitrogen compounds in the geosphere is limited (Li *et al.*, 1995). The possible biological origins of carbazoles remain unclear but can possibly be traced to alkaloids, proteins and pigments in terrestrial plants and algae (Snyder, 1965; Horsfield *et al.*, 1998).

Table 1 gives a summarized overview of the results that have to data been obtained during studies that aimed at the elucidation of carbazole distributions.

Alkylcarbazoles

Expulsion	* Liaho Basin shales have lower alkylcarbazole/(alkyl- + benzocarbazole), higher exposed isomers and lower C3/C2 ratios for alkylcarbazoles relative to corresponding oils[2].
Secondary Migration	* Reduced concentrations and elevated C2/(C0+C1+C2) ratio were observed in first eluting oils during a laboratory experiment. Normalization of both occurred after continuous oil flow, however without reaching the original values.[5]
Maturity	* All carbazole derivates reach their maximum yield in Posidonia Shale source rocks at 0.88%Ro (except *n*-carbazole at 0.53%). Systematic variations up to 0.88% suggest selective isomerization/destruction/generation of carbazole derivates[8]. * An overall decrease in carbazole concentration is observed up to 0.81%Ro in Sonda de Campeche carbonate source rocks, after which values steeply rise to a maximum at 1.09%Ro.[9] * 1-/4-MC, 1,8-/2,4- and 1,3-/2,4-DMC show an increase with maturity up to 0.74%Ro, followed by a decline with higher maturity in Duvernay Fm source extracts[10].
Facies	* Positive correlation of Pr/Ph vs. 1,8-DMC/(1,8-DMC+1-EC) and API gravity vs. 1-MC/(1-MC+1-EC) in oils from the Gulf of Suez[3] * Prevailing C4-C5 carbazoles in *LowerKR* (marine transgression, photic zone anoxia) versus prevailing carbazole and C1 carbazole in *UpperKR* (regressive, restricted, hypersaline) in bitumens from Keg River (KR) carbonate source rocks[8]
Biodegradation	* Concentrations increase slightly during early stages, but decreases dramatically after level 4*. Susceptibility is higher than for benzocarbazoles and decreases with increasing carbon number of alkyl substituent. Shielded isomers are preferentially degraded.[4]

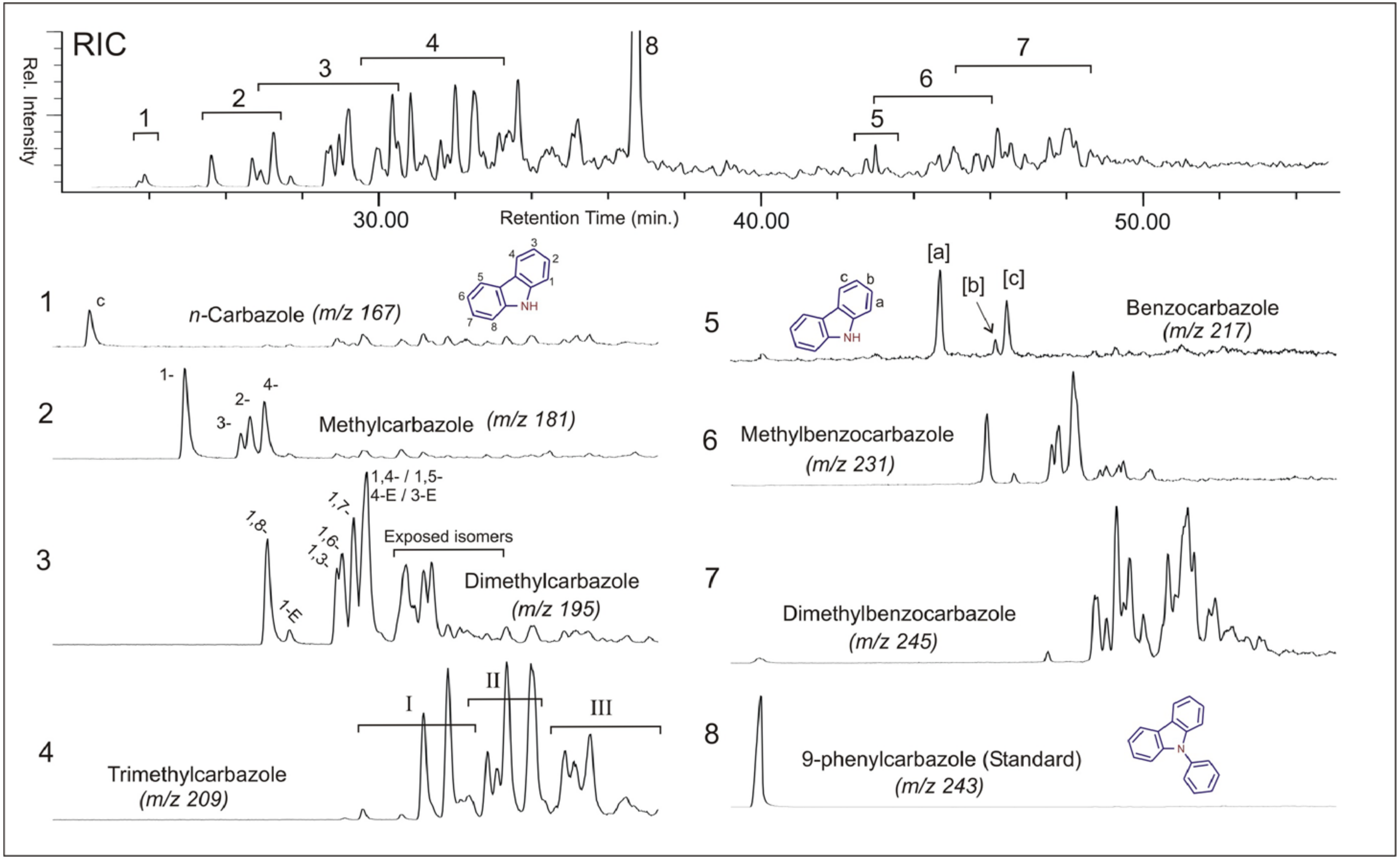


Figure 21 *A carbazole enriched fraction was won by a two-step solid phase extraction from maltene resins after MPLC separation of oils and source extracts. Molecular carbazole analysis was performed using gas chromatography-mass spectrometry in "selective ion monitoring" (SIM) mode. Due to a large amount of isomers and a lack of reference standards, C3 carbazoles were only characterized as shielded (I), partially shielded (II) and exposed (III), based on their theoretical order of elution.*

Benzocarbazoles

Expulsion	* Increase in concentration up to 0.85%Ro (generation) followed by decrease due to expulsion or dilution with newly generated hydrocarbons in N.Sea oils and source rocks[7]. * Positive correlation of BC [a]/[a]+[c] versus TOC in source rock extracts[7]. * Tenfold concentration in clastic source rock extracts relative to equivalent, nearby-reservoired petroleum in the North Sea.[7] * No expulsion fractionation in the carbonate Sonda de Campeche petroleum system[9].
Secondary Migration	* Decreasing BC ratio with increasing distance from a reference oil in oils from clastic source rocks in the Canadian Foreland Basin.[1] * Reduced [a]/[a]+[c] benzocarbazole ratio and benzocarbazole concentrations in first eluting oils during a laboratory core-flood experiment. Normalization occurred after continuous flow, however without reaching original values.[5] * Large reductions in the [a]/[a]+[c] benzocarbazole ratio were observed in an iso-mature oil suite from the Omani Dhahaban petroleum system with increasing distance from the inferred source kitchen.[6]
Maturity	* Increase in benzocarbazole concentration observed in clastic Posidonia Shale source rocks in the maturity range 0.36-1.29% Ro[8] * BC ratio increased from 0.4 to 0.6 between 0.48 and 0.88% Ro in Posidonia Shale source rocks, and from 0.4 to almost 0.7 between 0.35 and 1.1% in Tithonian carbonate source rocks and oils from the Sonda de Campeche. In the latter source rock samples a reversal occurred at 1.1%Ro[9]. * No correlation between BC ratio and maturity in N.Sea source rocks and oils[7].
Facies	* Increasing BC ratio and concentrations with rising API gravity, Pr/Ph and Ts/(Ts+Tm) in a maturity independent oil suite from the Gulf of Suez.[3]
Biodegradation	* Benzocarbazole concentrations and the Benzocarbazole Ratio decrease after level 4*[4].

[1]Larter *et al.*, 1996; [2]Li *et al.*, 1995; [3]Bakr and Wilkes, 2002; [4]Huang *et al.*, 2003; [5]Larter et al., 2000; [6]Terken and Frewin, 2000, 2001; [7]Bennet et al., 2002; [8]Clegg et al., 1997; [9]Horsfield et al., 1998; [10]Li et al., 1997; *Peters and Moldowan Biodegradation Scale (Peters and Moldowan, 1993)

Table 3 *A summarised overview of previous study results reflect that the distribution of carbazoles in oils and source rock extracts can be controlled by a variety of parameters.*

6.2 Maturity, expulsion and facies controls

Bennet et al. (2002) noticed an increase in benzocarbazole concentration in source rock extracts and oils (North Sea) up to 0.85%Ro (generation) followed by a decrease due to expulsion or dilution by newly generated hydrocarbons. Source rock extracts reached tenfold concentration of equivalent oils. This parabolic shape of carbazole concentration versus maturity, defined by generation and expulsion, was observed in most studies (Clegg *et al.*, 1998; Li *et al*, 1997).

In regard of alkylated aromatic maturity parameters such as the methylphenanthrene and methyldibenzothiophene indices, it is not far fetched to assume alkylated carbazoles, especially the C1 substituted isomers, to also undergo isomerization reactions during thermal maturation.

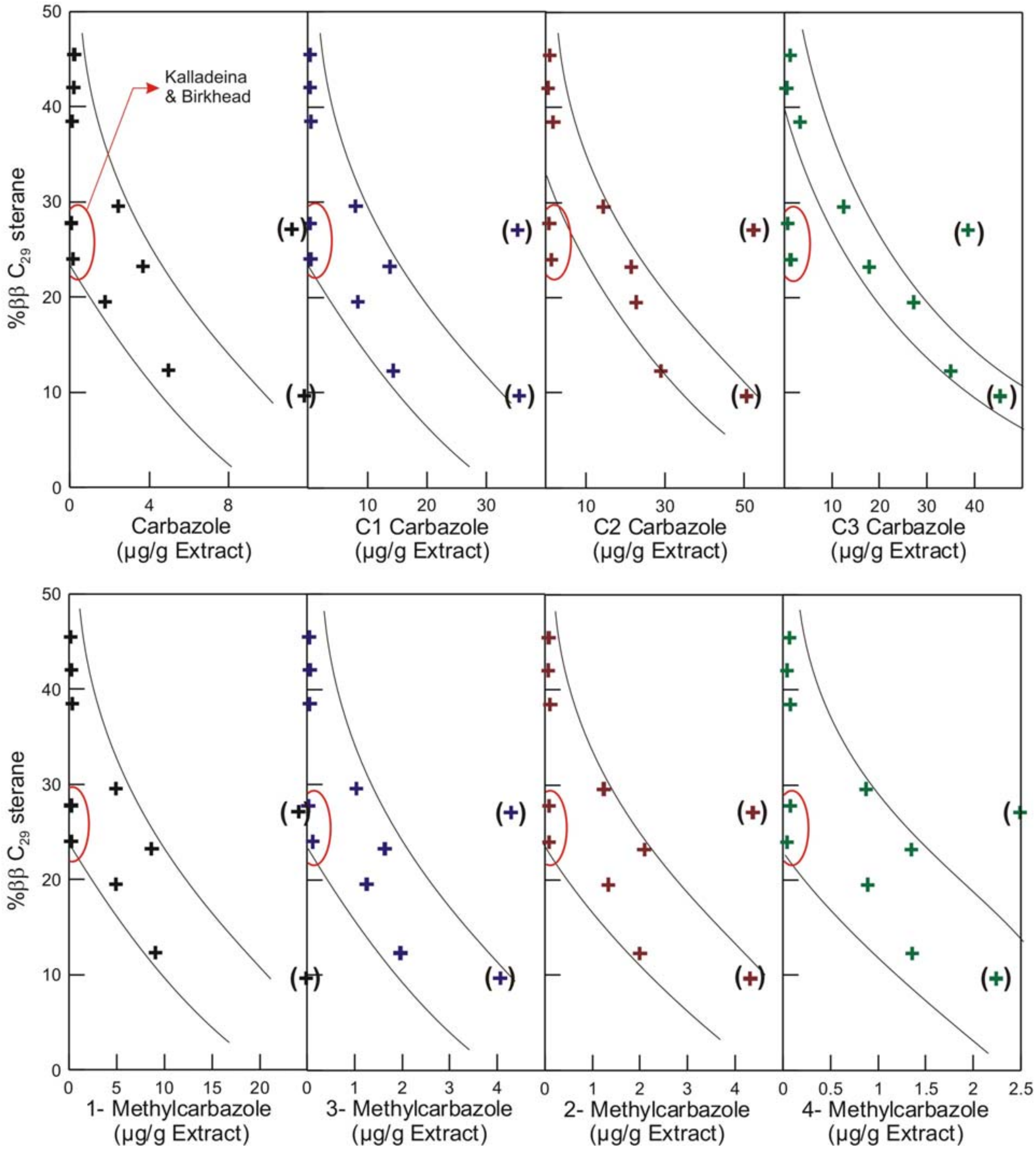


Figure 22 *In contrast to previous studies, source rock extracts from the Cooper/Eromanga Basin show decreasing carbazole concentrations with increasing maturity. As the decreasing trend is also observed in immature samples, this phenomenon cannot be a result of petroleum expulsion. Shaly samples from the Toolachee Fm. are shown in brackets.*

Source rocks from the Cooper/Eromanga Basins exhibit a general decrease in carbazole concentrations with increasing maturity. C3 and C2 carbazoles are the dominating species with concentrations of 30-50 (μg/g extract) in immature source rock samples, while C1 carbazoles are always lower than 10 (μg/g extract). Among the C1 isomers, 1-methylcarbazole is dominating and 4-methylcarbazole concentrations are lowest. Benzocarbazoles are strongly dominated by the benzo[a]carbazole and the benzo[c]carbazole isomer. Both are also present in low concentrations, ranging between 0.5 and 5 (µg/g extract), with one outlier that is characterized by a value of almost 10 (µg/g extract).

As the oils only cover a narrow maturity range, a correlation of carbazole concentrations with maturity could not be established, which however does not mean that it is not existent. Carbazole concentrations in oils are much lower than in source rock extracts. C2 and C3 carbazoles are dominant again with concentrations in the 0.5-0.8 (µg/g extract) range, while C1 carbazoles only reach 0.2-0.8 and *n*-carbazole is very low with values around 0.1 (µg/g extract). Benzocarbazole concentrations range between 0.02 and 0.2 (µg/g extract).

The trend of decreasing carbazole concentration in source rocks of increasing maturity is not likely to be a result of expulsion since 5 out of 11 source rocks have maturities lower than 25% ββ C_{29} sterane, which roughly corresponds to the onset of oil generation. A negative correlation of concentration and maturity is in contrast to all previously published results and, as this is the first study on carbazoles in oils that were sourced from humic coals, might be a feature that is exclusive to coals. The two source rock samples that constantly feature highest carbazole concentrations are shaly samples from the Toolachee Formation and may be considered separately from the remainder coaly samples. By doing so, the Toolachee system seems to show indeed a slight increase in C1, C2 carbazole, 2-, 3- and 4-methylcarbazole concentrations with increasing maturity. An observation that is made on two samples does however not provide firm evidence for a contrary trend of Cooper/Eromanga Basin shales and coals. The two constantly low samples in figure 22 (red circle) cannot be explained.

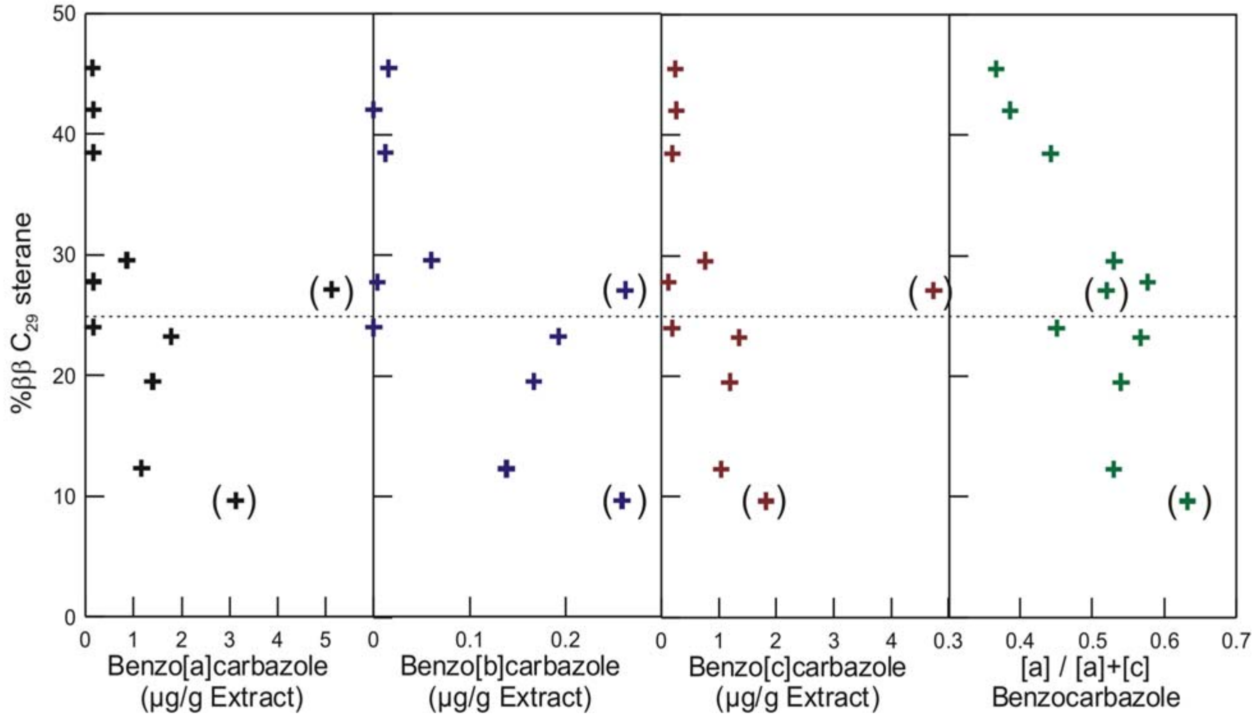


Figure 23 *Benzocarbazole concentrations increase in coaly (✚) and shaly ((✚)) source rocks up to a maturity of 25% ββ in* C_{29} *steranes, which corresponds to the onset of oil generation. The following decrease can be attributed to petroleum expulsion. The dotted line indicates the onset of oil generation.*

The concentration of all three benzocarbazole isomers increases up to the onset of oil generation (25% ββ C_{29} sterane) when considering the coaly source rocks and the two shaly Toolachee Formation source rock samples (in brackets) separately. This is a consequence of continuous benzocarbazole generation in the source rock, and is in agreement with previous studies. After the onset of oil generation, the concentration decreases rapidly and remains low. Both, benzocarbazole concentrations and their increase are higher in the shaly Toolachee Formation samples than in the coaly samples. The benzocarbazole [a]/([a]+[c]) ratio shows an increasing trend up to the onset of oil generation, and a reversal afterwards. While the rising ratio is a result of preferred benzo[a]carbazole generation over benzo[c]carbazole, the decrease during expulsion is contrasting with the typical benzocarbazole fractionation behaviour (Larter *et al.*, 1996, 2000).

The general idea of geochromatographic fractionation processes involves hydrogen bonding of the polar nitrogen group to clay mineral kations or active sites in solid organic matter. Benzocarbazoles have been shown to be depleted in benzo[a]carbazole over benzo[c]carbazole during migration. However, in terms of shieldedness of the nitrogen function, benzo[a]carbazole is the most shielded of all benzocarbazole isomers. Larter *et al.* (1996) mentioned the spatial molecular arrangement, benzo[a]carbazole being rather rod-shaped and benzo[c]carbazole featuring a sub-spherical shape. The idea of sorption onto clay minerals and solid organic matter was however not given up and supported by the effective dipolemoment. Benzo[a]carbazole has an effective dipolemoment of 1.41 debye units along the c-axis (length axis) of the molecule, whereas the sub-spherical benzo[c]carbazole has a dipolemoment of 1.75 debye units that is oriented closer to the major axis of the molecule. These differences suggest that solid-phase sorption characteristics and organic solvent solubilities would be quite distinct (Larter *et al.*, 1996). Schwark (*Habilitation thesis, 2000)* found a positive correlation between the benzocarbazole ratio and the 1- / 9-methylphenanthrene ratio in oils from the Brazilian Reconcavo Basin. Together with the benzocarbazole shape, this finding suggests the possibility of “molecular sieve-like” fractionation of compounds, thin and narrow shaped molecules being filtered out while bulky molecules become enriched in a migrating fluid.

The decrease of benzocarbazole ratio values with increasing expulsion from coaly Cooper/Eromanga Basin source rocks is the first evidence against the molecular sieve theory. I would therefore like to suggest that two fractionation mechanisms exist, competing with each other in dependence of the amount of organic matter and natural molecular sieves. In settings with little organic matter present (i.e. secondary migration or expulsion from a organic-lean clastic source rock), the molecular sieve fractionation mechanism will prevail, leading to a depletion in benzo[a]carbazole of the migrating charge and an enrichment in retaining phases. However, when much organic matter is present (e.g. coal source rocks) the molecular sieve fractionation will be outcompeted by normal adsorptive hydrogen bonding processes.

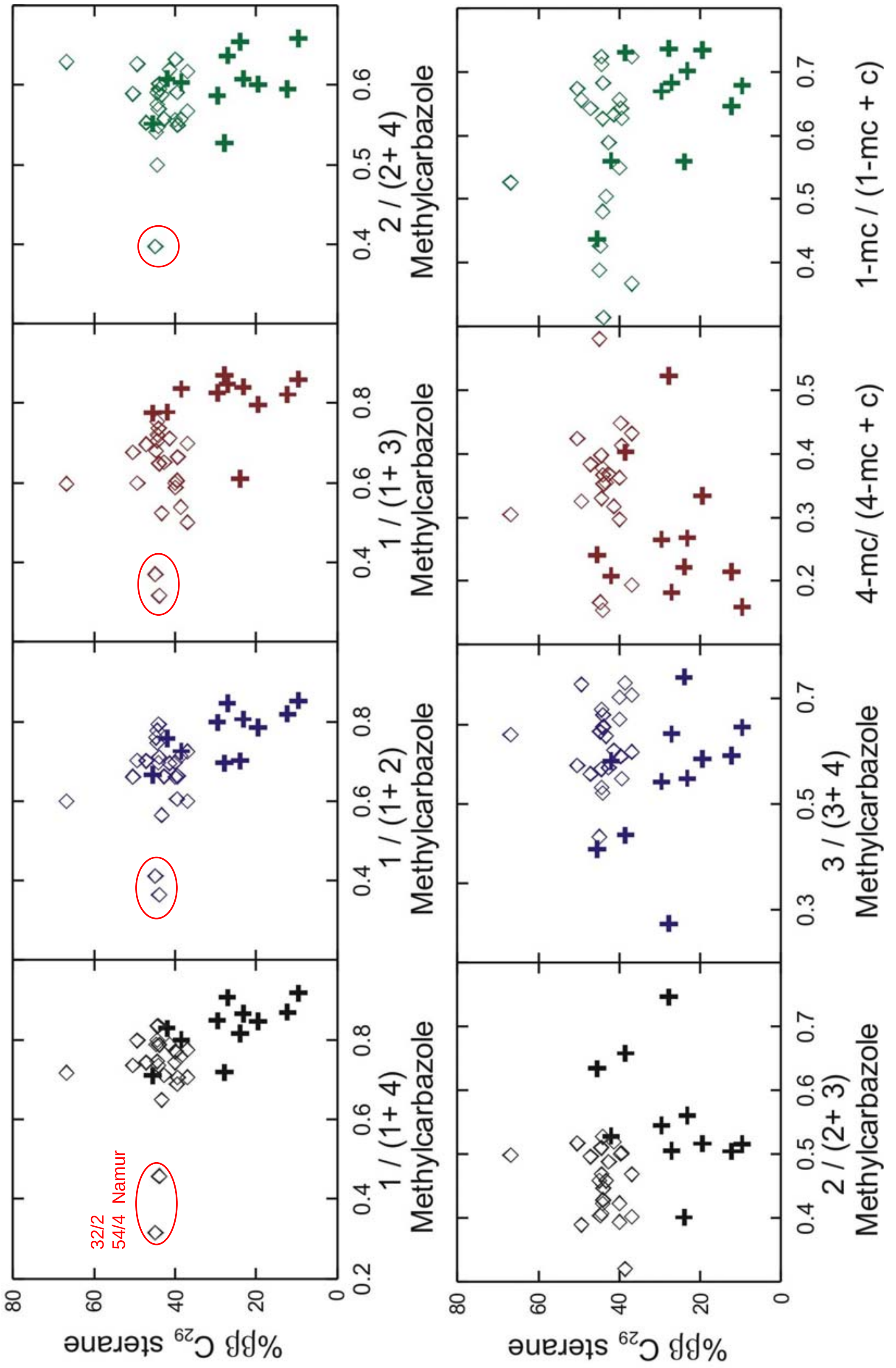


Figure 24 *Isomeric variations in C1 alkylated carbazoles can reflect expulsion, maturity-driven isomerization reactions, methylation/ demethylation or the selective release of different pyrrolic nitrogen components due to the decrease in the efficiency of bitumen trapping by the source rock (Li et al.,1997). Two Namur-reservoired DST oils are consistent outliers but cannot be explained.*

Isomeric variations with increasing maturity of mono-alkylated carbazoles are hard to decipher due to the presence of more than one source system. The clearest trend is observed in the 1/(1+4) and 1/(1+2) methylcarbazole ratios, and to a lesser degree in the 1/(1+3) and 2/(2+4) ratios. These trends follow the expected expulsion effects, in which the rather nitrogen-shielded 1-methylcarbazole is preferentially expelled and the exposed isomers experience stronger retention with increasing distance of the methyl group from the nitrogen, thus becoming enriched in the source rocks.

In the case of 1/(1+4), 1/(1+2) and 2/(2+4) methylcarbazole ratios, however, reservoired oils feature values that are similar to those of the most mature source rocks, which is contrasting the idea of fractionation during expulsion and would suggest that the aforementioned changes are not a consequence of primary migration, but an evidence that maturity exerts a strong control on the distribution of methylcarbazoles. While oils should become enriched in all parameters that are shown in Fig. 24 during migration, the only parameter that does is the 3/(3+4) methylcarbazole ratio. For other parameters oils have either similar values to source rocks or show even lower values, indicating a control by other factors.

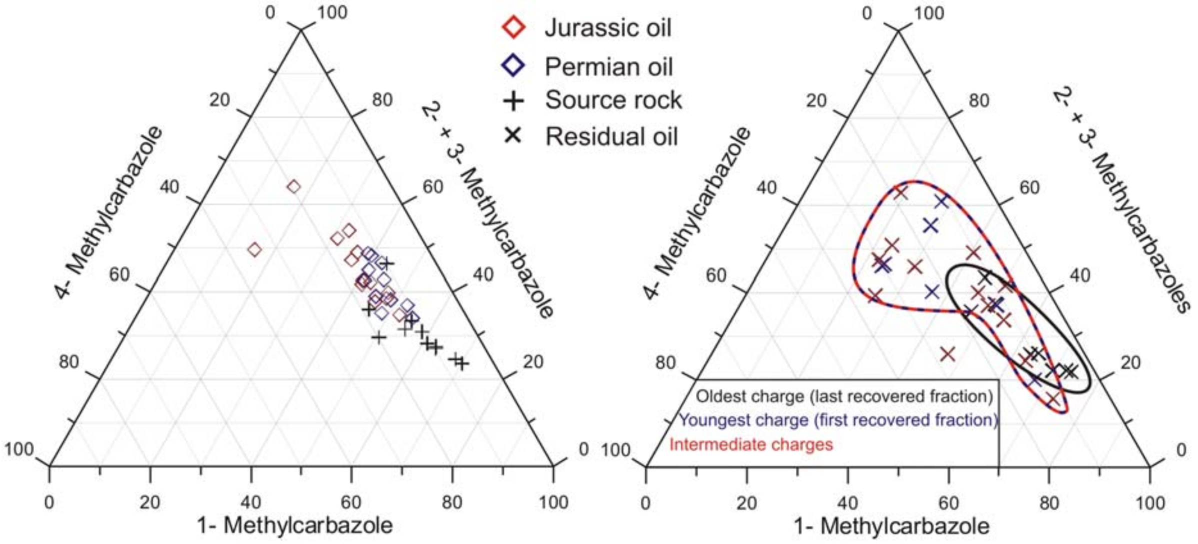
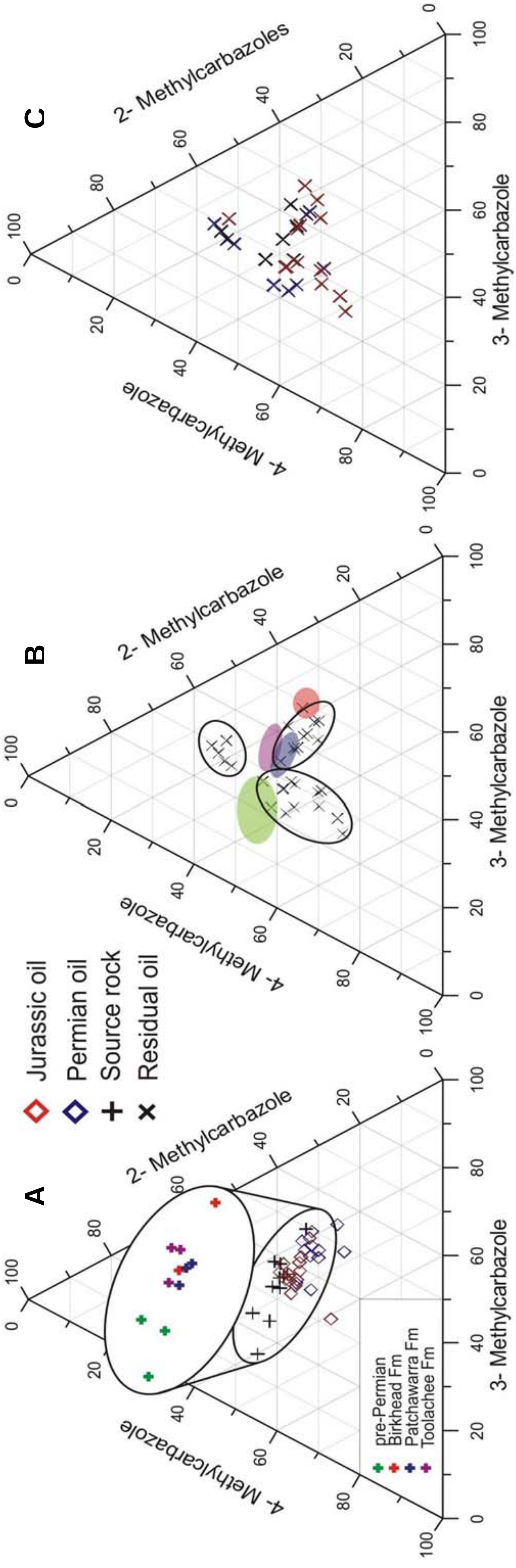


Figure 25 *Expulsion (left ternary diagram) and secondary migration (right ternary diagram) appear to exert only a restricted control on the distribution of C1 alkylated carbazoles.*

A triplot that exhibits the relative abundances of 1-methylcarbazole, 2- + 3-methylcarbazoles and 4-methylcarbazole shows that the main variation is found in the amount of 1-, 2- and 3-methylcarbazoles, oils being rather enriched in 2- and 3-methylcarbazole relative to source rocks (Fig. 25, left triplot). The distribution of residual oils (Fig. 25, right triplot) is similar to that of DST oils and source rocks. Comparison of residual oil fractions however can yield valuable information on fractionation processes that occur during secondary migration. The oldest charge that has entered a pore system will have encountered the most polar (water-wet) pore systems, while subsequent charges have met a decreasingly polar system due to residual oil adsorption of previous charges. The oldest charge appears to contain increased 1-methylcarbazole concentrations, while all subsequent charges cannot be kept apart, but feature increased 2- and 3-methylcarbazole concentration, which is again contrasting to the expected fractionation behaviour.



When excluding 1-methylcarbazole from the plot, a completely different story arises. The source rock samples plot together genetically (Fig. 26 A), suggesting that facies of the source rock is the main factor that controls the distribution of mono-alkylated carbazoles. The DST oils are all divided between Jurassic and Permian source rock samples, showing a rather low spread. Residual oils, however, plot together in three distinct clusters (Fig. 26 B). One of these seems to originate from mixing of Jurassic oils (red shaded area) and Permian oils (violet and blue shaded areas), similar to the DST oils. The two other clusters are more enigmatic. The highest 2-methylcarbazole concentrations are represented by residual oils that were recovered from the Namur Sandstone, possibly suggesting the participation of Cretaceous Murta Formation oils to the mixing of this cluster.

The lower cluster, which is characterized by high 4-methylcarbazole values, might be a mixing product of Cooper Basin and Warburton Basin sourced oils.

Figure 26
A *- Methylcarbazole distributions are controlled by source rock facies. DST oils are mixtures of Permian and Jurassic endmember oils.*
B *- Residual oils appear to have mixed in 3 clusters: Cooper-Eromanga, Cooper-Warburton and a mixture with contributions from a yet unknown source. Coloured fields indicate the location of source rocks (from A).*
C *– Methylcarbazole distributions are not steered by fractionation processes. For colour coding see Fig. 25 and 26 A.*

When the distribution of residual oil is considered in terms of oldest and youngest charge (Fig. 26 C), no trend is visible, suggesting that facies is indeed the controlling factor on the distribution of methylcarbazoles in oils, residual oils and source rock extracts.

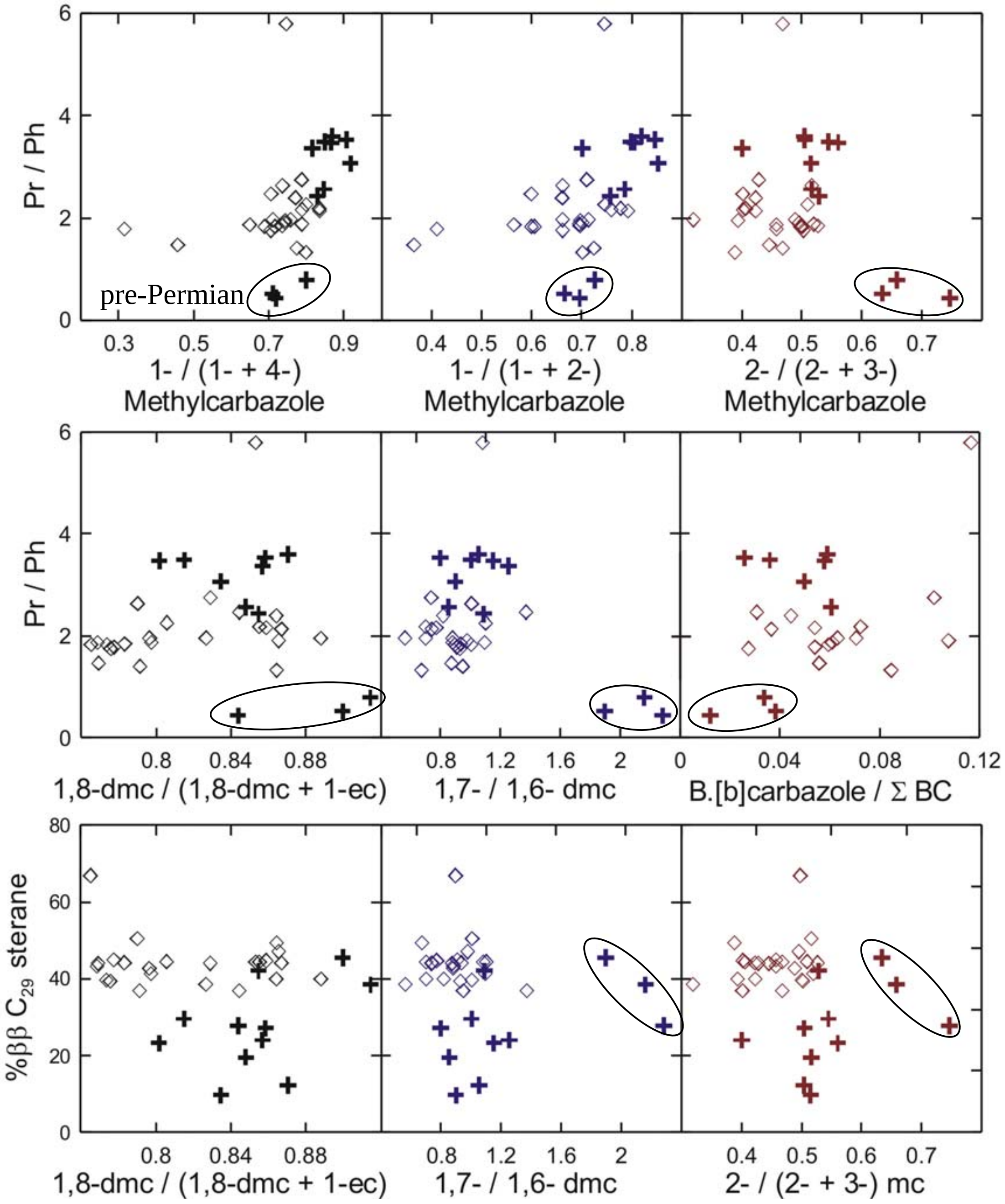


Figure 27 *The pristane/phytane ratio appears to correlate with alkylated carbazoles. This dependency might however only appear due to the position of the three pre-Permian source rock samples. The ratios of 1,8-dmc/(1,8-dmc+1-ec), 1,7-/1,6-dmc and 2-/(2-+3-)mc do not depend on maturity.*

The pristane/phytane ratio is primarily an indicator of redox conditions during sediment deposition. The three pre-Permian source rocks have values <1, indicating their deposition under reducing, anoxic conditions. The remainder source rocks that originate from the

Cooper and Eromanga Basin sedimentary sequences are characterised by values between 2 and 4, which is typical for terrestrial source rocks that were deposited under oxic conditions.

While no correlation was observed between the Pr/Ph ratio and the distribution of alkylated carbazoles in oil (Fig. 27), source rock extracts exhibit a linear relationship between Pr/Ph and 1/(1+4) methylcarbazole, Pr/Ph and 1/(1+2) methylcarbazole and a negative linear relationship between 2/(2+3) methylcarbazole. However, these trends are defined to a high degree by the pre-Permian source rocks and it is doubtful whether the trends would be recognized in absence of the pre-Permian samples. No samples with Pr/Ph values between 1 and 2 were present. However, these could shed more light on the relation of Pr/Ph and alkylcarbazoles. Similar to the findings of Bakr and Wilkes (2002), a linear relationship exists between Pr/Ph and 1,8-dmc/(1,8-dmc + 1-ec), however with four outliers. One of these is the Cambrian Dolomite and it seems that this might be due to the carbonate lithology. The observed correlation of Pr/Ph with 1,8-dimethylcarbazole thus seems to be restricted to siliciclastic lithologies.

Oldenburg *et al.* (1999) suggested benzo[b]carbazole as an indicator for terrestrially dominated sedimentation in a deltaic setting offshore Norway. This idea is supported by the characteristics of the pre-Permian Cambrian Dolomite sample. This carbonate rock features the lowest Pr/Ph values, has definitely received no terrestrial input and is characterized by the lowest relative benzo[b]carbazole values (Fig. 6). The two other pre-Permian samples were also deposited under reducing conditions but are rather silty, indicating a higher lithological input from the mainland that may be responsible for their higher benzo[b]carbazole values. The coaly and shaly Cooper and Eromanga Basin source rocks feature elevated Pr/Ph and benzo[b]carbazole / Σ benzocarbazole ratios. However, the absolute benzo[b]carbazole concentrations are very low for dominantly terrestrial source rocks (Fig. 2) and lie in the 0-0.2 (µg/g extract) range for coals and 0.2-0.3 (µg/g extract) for the shaly Toolachee Formation samples. Li *et al.* (1997) reported values up to 3.4 (µg/g extract) for marine carbonate source rocks from Duvernay Formation. Furthermore it is surprising to find the highest absolute concentrations in the shaly Toolachee Fm. samples rather than in the coaly samples.

6.3 Warburton Basin input

Although initially an exploration target, the Cambrian sediments of the Warburton Basin subsequently were never seriously considered to have participated in the oil play, possibly due to a lack of subsurface information as a consequence of limited penetration by only a few widespread wells.

The discovery of oil in the pre-Cooper Mooracoochie Volcanics at Sturt-6 & 7 sparked renewed interesting the Warburton Basin. Based on his biomarker and isotopic studies, Kagya (1997) concluded that these oil accumulations were most likely sourced by Permian and Jurassic source rocks, respectively, and subsequently migrated down-dip into porous Warburton strata. Sun (1999) noticed high fracture porosity in the eastern part of the Warburton Basin, which could act as a conduit for migration. Previous dismissal of the Warburton sequence as a source of hydrocarbons was based on its low generative potential as measured by TOC and Rock-Eval analyses. As most of the core samples analysed come from the upper part of the basinal succession that has been subject to severe weathering and oxidation, these results might not reflect the true nature of the Warburton Basin’s source rocks (Hallmann *et al.*, 2004).

While a successful distinction between oils of a Jurassic (Birkhead) origin and those of a Permian (Patchawarra and Toolachee) origin can be made by combining maturity values with the amount of post-Triassic *Araucariacaean* markers (Alexander et al., 1988), this approach does not permit any further differentiation of pre-Jurassic oils. The ratio of 1- / 9-methylphenanthrene in sediment extracts rises dramatically after the Triassic/Jurassic boundary as a consequence of the extensive spread of the *Araucariacaea* conifer family throughout the Australian continent. These plants produced 1-methylphenanthrene, 1,7-dimethylphenanthrene, 1,2,5-trimethylnaphthalene and 1-methyl-7-isopropyl-phenanthrene (retene) as characteristic markers (see also chapter seven).

The combination of Araucariacaean biomarker ratios with certain alkylcarbazole ratios, which were found to be dependent on source facies, allows to a higher genetic resolution of oil samples. Figure 28 shows that while the 1- / 9-methylphenanthrene ratio is capable of distinguishing oils and source rocks of Jurassic/Cretaceous and pre-Jurassic age, the 3- / 2-methylcarbazole ratio can differentiate between Permian and pre-Permian source rocks and oils.

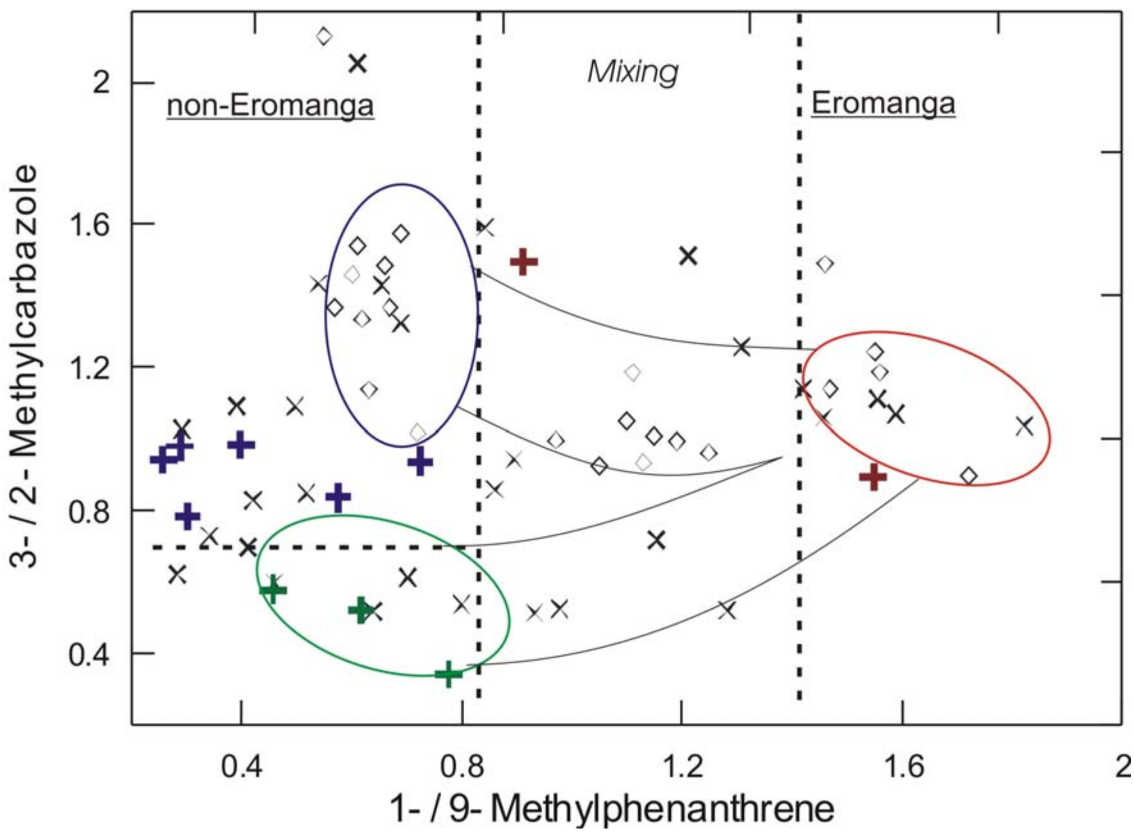


__Figure 28__ While the relative amount of the Araucariacaean marker 1-methylphenanthrene is capable of distinguishing between Eromanga Basin oils and pre- Eromanga Basin oils, the 3-/2-methylcarbazole ratio can add a higher resolution and discriminate between Permian and pre-Permian oils (for symbol legend see Figs. 25 and 26).

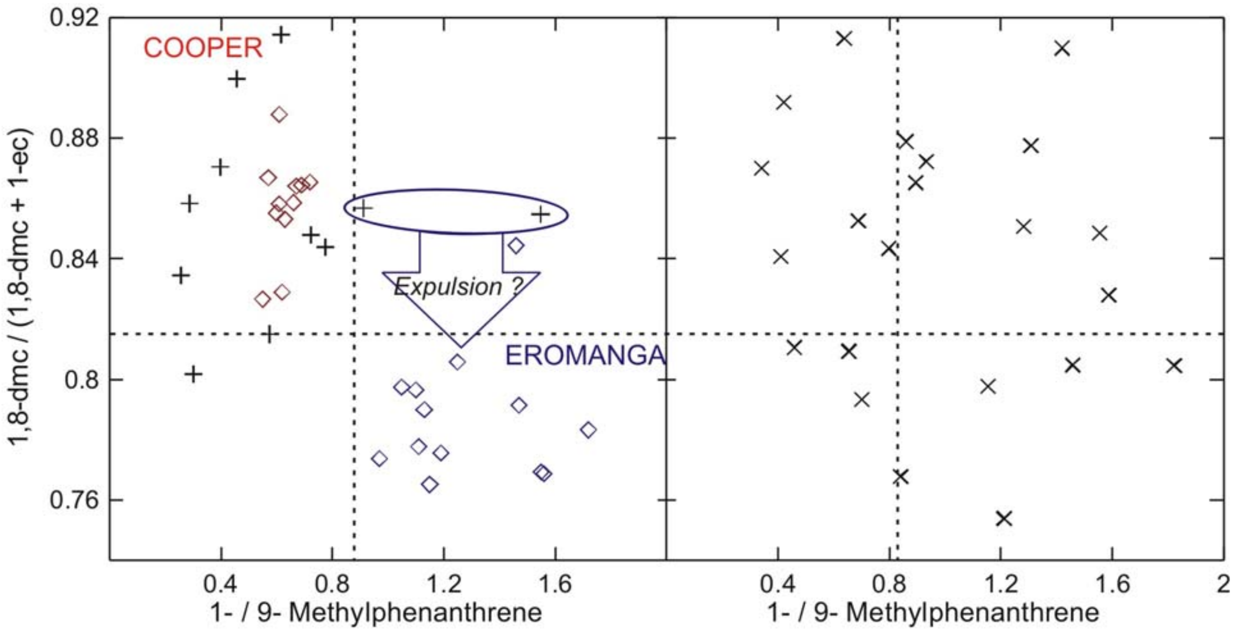


__Figure 29__ The 1,8-dimethylcarbazole/(1,8-dmc + 1-ethylcarbazole) ratio seems to be a similarly potent discriminant of Cooper and Eromanga Basin derived oils (◇) as the conventionally used 1-/9-methylphenanthrene ratio. The spread of residual oils (✕) and source rock extracts (✚) however suggest that other parameters also exert a control on this ratio. The large offset between Eromanga Basin source rocks and DST oils, which is not observed for Cooper Basin samples, might indicate fractionation processes during expulsion or oil staining of Eromanga source rocks with Cooper oils.

Also the 1,8-dimethylcarbazole / (1,8dmc + 1-ethylcarbazole) ratio appears to be a potential candidate for distinguishing petroleum systems in the Cooper and Eromanga Basins. Although pre-Permian source rocks and oils cannot be resolved from Permian samples, the 1,8-dmc/(1,8-dmc+1-ec) ratio and the 1-/9-methylphenanthrene parameter are similarly capable to distinguish between Cooper and Eromanga Basin oils. The distribution of residual oils is however disillusioning and indicates that other parameters must also exert a control on the 1,8-dmc/(1,8-dmc+1-ec) ratio.

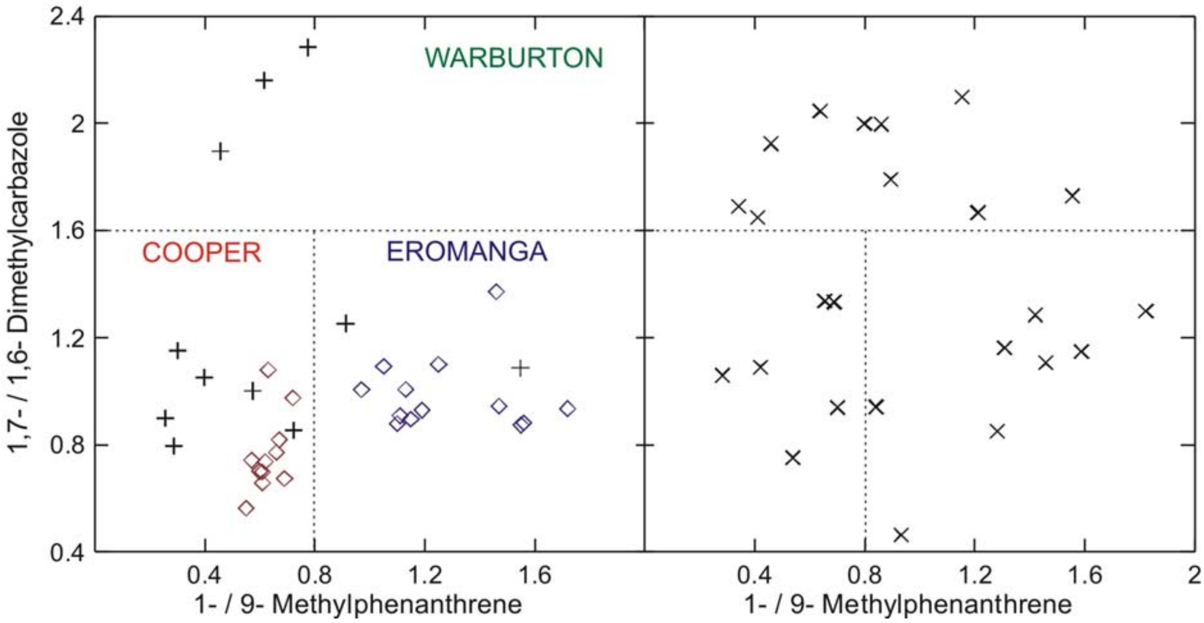


Figure 30 *The 1,7-/1,6- dimethylcarbazole ratio is found to be a very strong and useful parameter for the discrimination of Permian and pre-Permian oils (◇), source rocks (✚) and residual oils (✕).*

The strongest marker for discriminating a Warburton Basin source input was found in the 1,7-/1,6- dimethylcarbazole ratio, which is >1,8 in Warburton Basin source rocks and <1,3 in Cooper and Eromanga Basin source rocks. Combined with the 1-/9-methylphenanthrene ratio, this parameter has the potential to add a new resolution to oil samples from the Cooper/Eromanga/Warburton(!) Basin petroleum system.

While all DST oils featured 1,7-/1,6- dmc values lower than 1,5, indicating that these represent mixes that were exclusively sourced from Cooper and Eromanga Basin source rocks, 10 residual oils are characterised by values that are larger than 1.6, which indicates that these have received an input from the Warburton Basin. Unfortunately, the peaks after GC-MS analysis were too small for quantification in a number of samples.

Table 4 gives an overview of residual oil samples that are considered to having received a pre-Permian input as determined by three distinct carbazole parameters. While samples that only appear in one column must not necessarily have received a pre-Permian contribution, samples that do appear in more than one column can be considered to definitely contain a pre-Permian component.

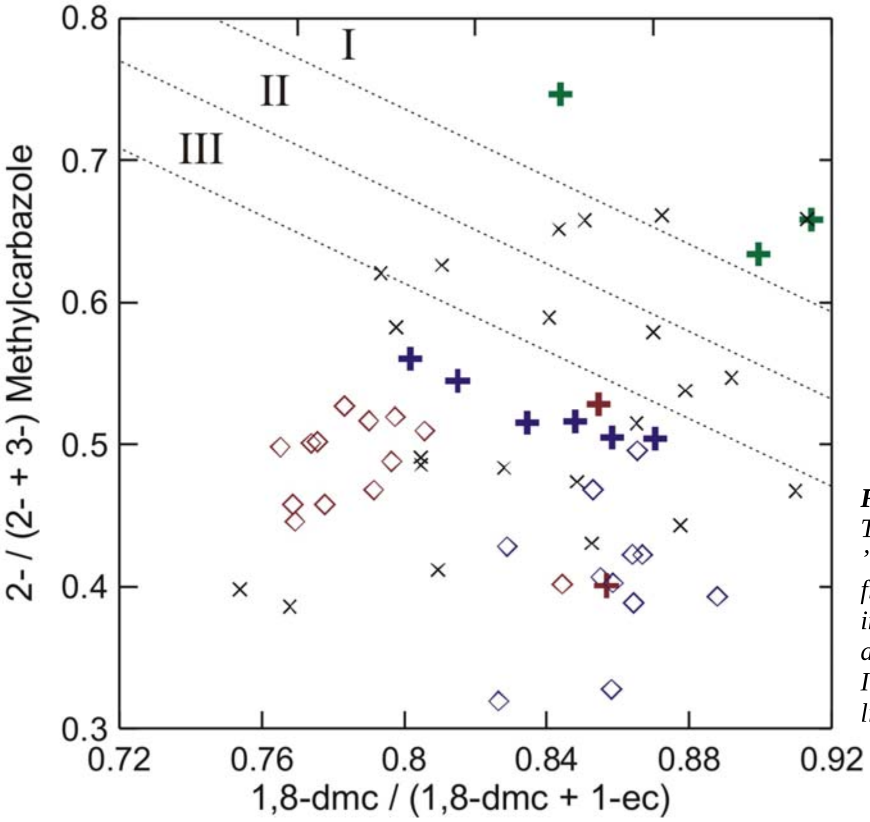


Figure 31
Three zones of 'Warburton Basin affinity' were established in a cross plot of alkylcarbazole ratios. Individual samples are listed in Table 4.

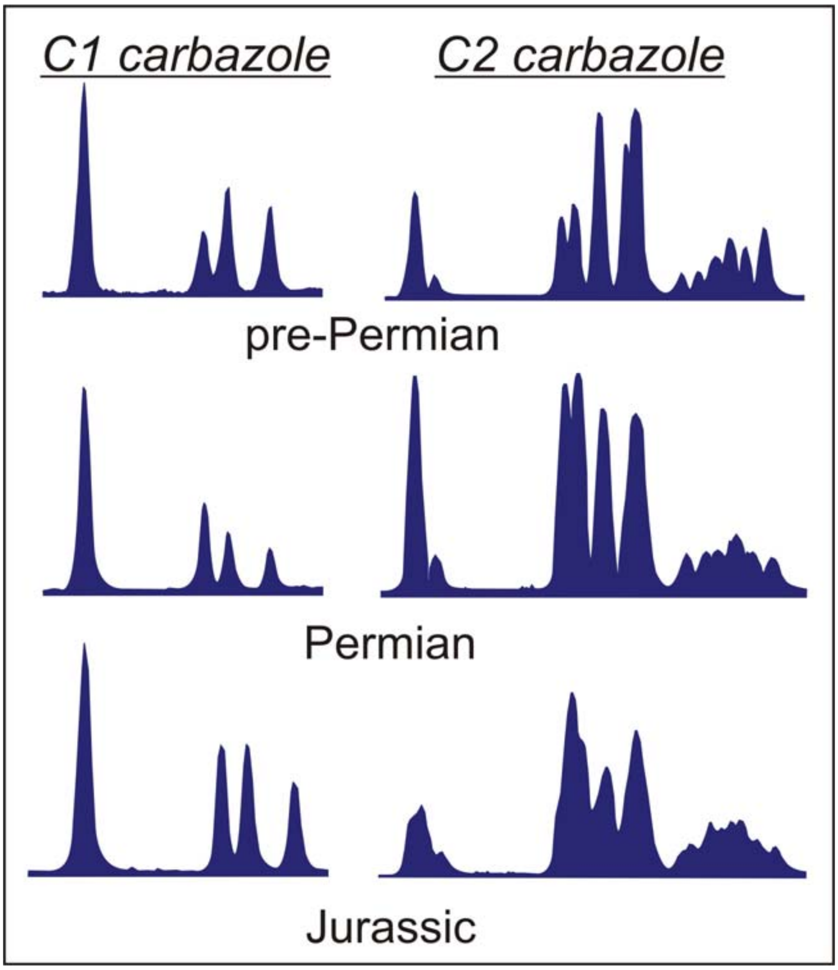


Figure 32 *Typical methyl- (m/z 181) and dimethylcarbazole (m/z 195) mass fragmentograms from Jurassic, Permian and pre-Permian oils. The distribution of alkylated carbazoles is mainly steered by the source facies in the Cooper/Eromanga Basins and typical carbazole traces can be easily recognised.*

3-/2-MC *vs.* 1-/9-MPI	1,7-/1,6-DMC *vs.* 1-/9-MPI	2-/(2-+3-)MC *vs.* 1,8- DMC/(1,8- + 1-EC)
Pre-Permian - 8/50 – 2 Toolachee - 8/50 – 3 Toolachee - 8/50 – 2a Toolachee - 7/45 – 2 Toolachee - 7/45 – 4 Toolachee - 17/52 – 1a+2a Hutton - 42-61 – 5a Tirrawarra Mixed with Jurassic - 32/59 – 2a Hutton - 30/57 – 3a Birkhead - 17/51 – 4a Hutton - 29/56 – 2 Hutton	Pre-Permian - 8/50 – 3 Toolachee - 8/50 – 2a Toolachee - 17/52 – 1a+2a Hutton - 42/61 – 5a Tirrawarra - 7/45 – 2 Toolachee Possibly mixed with Jurassic - 17/52 – 2 Hutton - 17/52 – 4 Hutton - 30/57 – 2a Birkhead - 32/58 – 2a Hutton - 32/59 – 2a Hutton	Class I - 7/45 – 2 Toolachee - 29/56 – 2 Hutton Class II - 30/57 – 3a Birkhead - 8/50 – 2a Toolachee Class III - 42/61 – 5 Tirrawarra - 7/45 – 4 Toolachee - 7/47 – 2 Patchawarra - 17/52 – 2 Hutton - 8/50 – 3 Toolachee - 17/52 – 4 Hutton

Table 4 *Residual oil samples that are thought to have received some input from the Warburton Basin by different carbazole parameters are compared*

Contribution of Warburton Basin sourced oils to the overlying Cooper and Eromanga Basin sedimentary sequences was only found in residual oils. These were recovered from intact sandstone cores by sequential extraction and would, due to their small amount, be diluted beyond detectability during conventional extraction procedures. Often belonging to older oil charges, these residual oils consist of a distinct higher amount of NSO compounds. Last recovered residual oils may contain up to 95% resins. Even if an input from the Warburton Basin could be determined using aliphatic or aromatic biomarkers, the small amount of residual oils and the extremely low hydrocarbon content would not permit a trustworthy identification. Therefore, it is of vital importance for application of sequentially extracted residual oils in reservoir geochemical studies, to find polar compounds whose distribution is steered by facies and maturity. After calibrating these for each petroleum system or geological setting against source rock extracts, residual oils become a powerful tool that adds a temporal resolution to a petroleum system, while conventional methods would only permit a cumulative signal.

In contrast to expectations, a pre-Permian input is not restricted to the last eluting residual oil fractions that correspond to the first pore-entering oil pulse. During deposition of the

Warburton Basin sedimentary sequence, which occurred on a stable shelf, the *’ridge and trough’* morphology that characterizes the Cooper and Eromanga Basins was not yet present as it is a consequence of the Carboniferous Alice Springs orogeny. Potential Warburton Basin source rocks should thus have similar lateral thicknesses. If any petroleum was expelled, the trough areas will have done so before the onset of petroleum generation in Cooper and Eromanga Basin source rocks. The ridge and flank areas, however, in which Warburton Basin strata should be present in similar thicknesses as in troughs, could have expelled petroleum at later times, conjoined with Cooper and Eromanga Basin source rocks.

6.4 Migration fractionation

Larter *et al.* (2000) proved that fractionation of carbazoles occurred in a laboratory experiment simulating geochromatography in secondary petroleum migration under subsurface conditions. In this experiment, a brine-saturated siltstone core (1000*5cm) was flown through by a predefined oil under 70°C and 48.3 MPa, with a pressure differential of 4.8 MPa. Oil flew for 89 days and occurred after 58 days. At this point, 121 ml oil had been injected into the core at a rate of 2.4ml/day. While no variation was encountered in widely used hydrocarbon biomarker ratios, nitrogen compounds (carbazole, methylcarbazole and benzocarbazole) were reduced in the first eluting oils and rose to values near 80% of the initial oil by the end of the experiment. Benzocarbazoles were completely absent in the first oil samples and the *a/(a+c)* ratio rose from around 0.6 in the first eluting oil that contained benzocarbazoles, to a value of 1.0 (normalized to the initial oil) that was reached after ca. 165 ml oil had been injected. The sum C2/ sum (C0-C2) decreased from ca. 0.87 in the first eluting oil to approx. 0.77 after 160ml had been injected and stayed constant, not reaching the 0,76 value of the original oil. Alkylphenols only reached around 20% of their initial concentration, indicating an even stronger adsorption.

The benzocarbazole *a/(a+c)* ratio of studied oils does not depend on maturity or facies (Fig. 33), and a fractionation during secondary migration is supported by the decrease in absolute benzocarbazole concentration with decreasing benzocarbazole *a/(a+c)* ratio (Fig. 34), which is thought to roughly reflect the distance that an oil has migrated. The samples in the red circle (Fig. 34) are reservoired in the Poolowanna and Epsilon Formation, respectively. These formations are known for their capacity of generating indigenous petroleum. Not having migrated, the *in situ* produced oil will raise the benzocarbazole *a/(a+c)* ratio of other oils that are reservoired within the Poolowanna and Epsilon Formation.

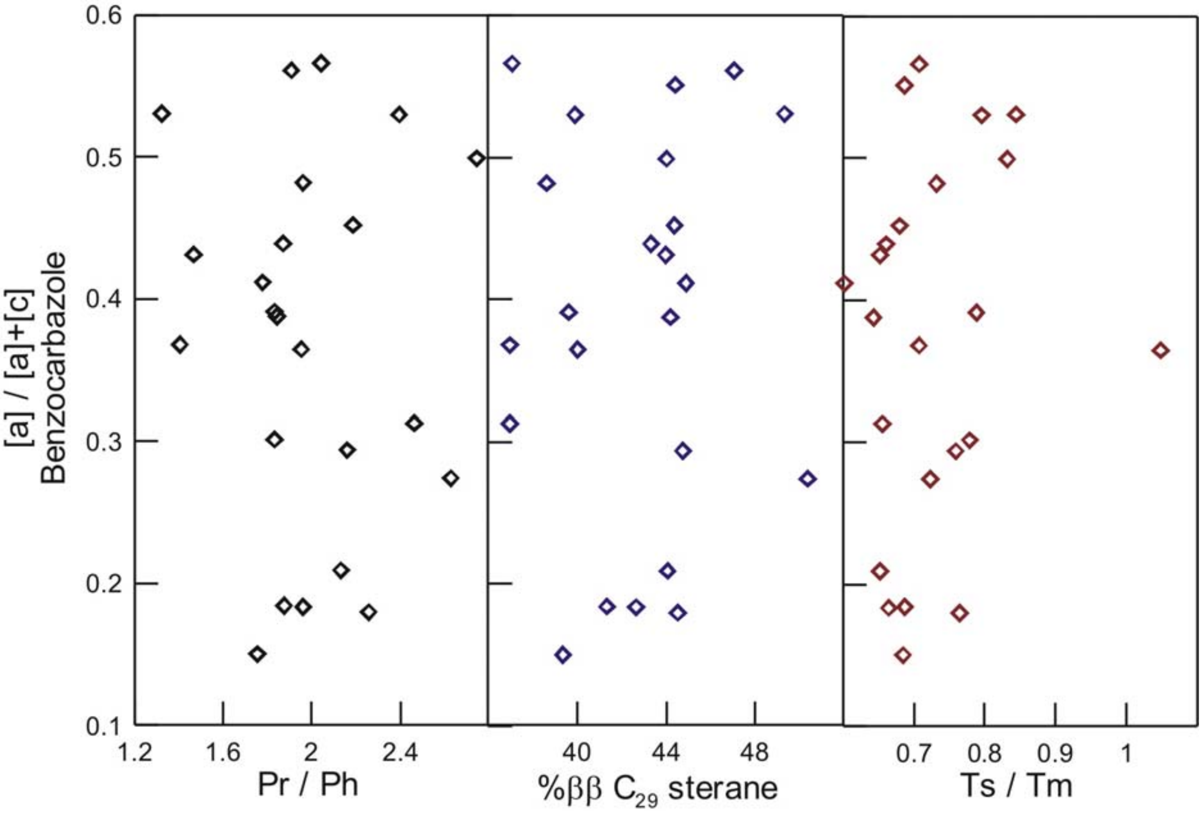


Figure 33 *The benzocarbazole a/(a+c) of oils (◇) does not depend on either maturity or source facies and is thought to reflect geochromatographic fractionation processes during secondary migration.*

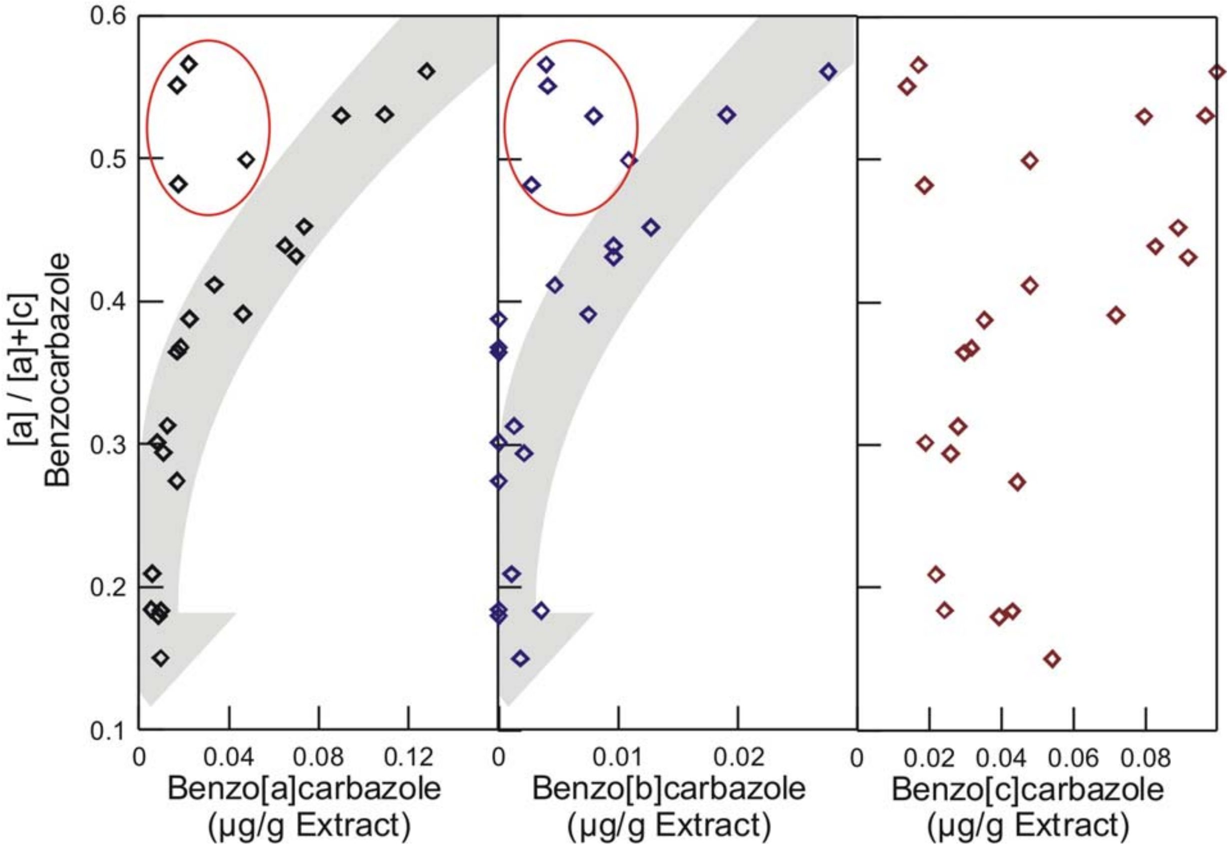


Figure 34 *The absolute decrease in benzocarbazole concentrations in oils (◇) with decreasing benzocarbazole a/(a+c) ratio supports the idea that this ratio is controlled by fractionation processes during secondary petroleum migration. Samples in the red circle were contaminated by indigenously produced petroleum in Poolowanna and Epsilon Formation reservoirs.*

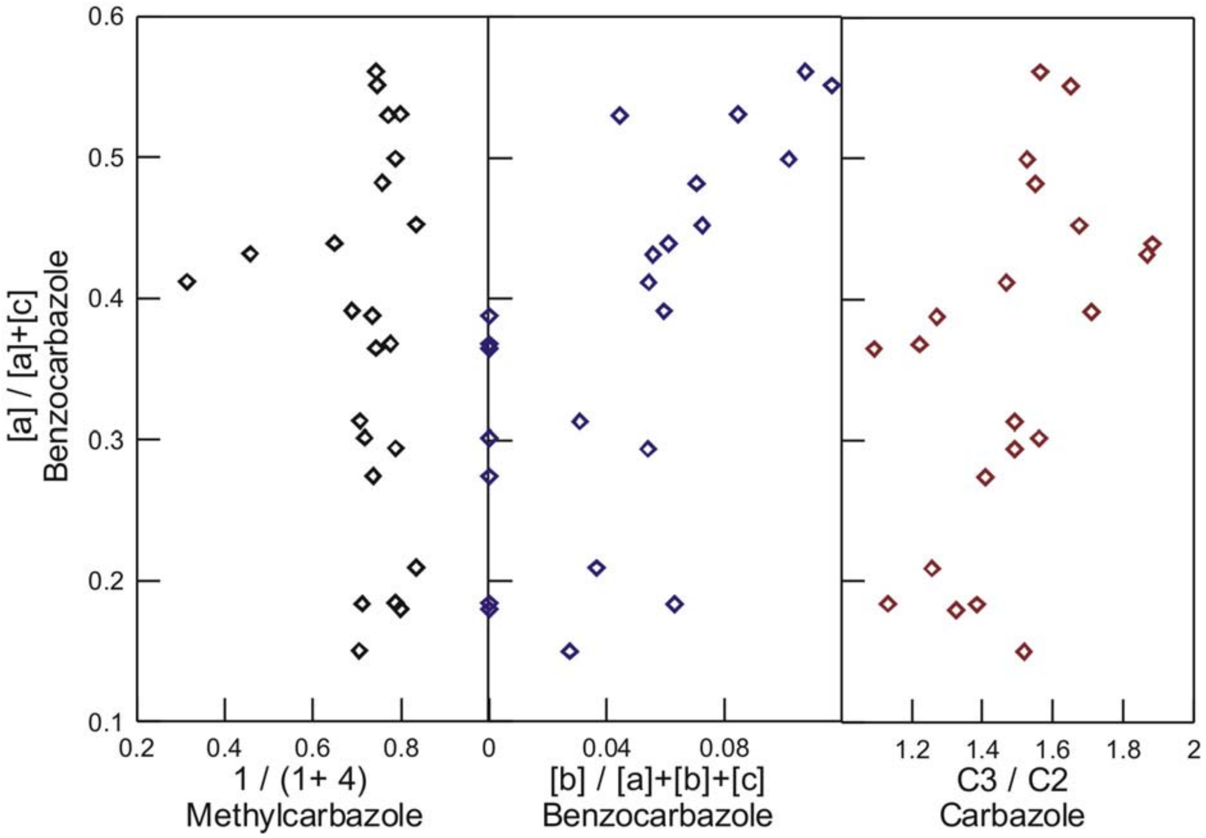


Figure 35 *Assuming the benzocarbazole a/(a+c) ratio to be a marker of relative migration distance, a fractionation of benzo[b]carbazole and a very slight, somewhat blurred, fractionation of the trimethylcarbazoles/dimethylcarbazole ratio does also occur. The 1/(1+4) carbazole ratio was suggested as a migration and maturity marker in previous studies but was shown here to depend rather on source facies.*

Along with the fractionation of benzocarbazoles during secondary migration, the ratio of C3 alkylated carbazoles/C2 alkylated carbazoles and that of benzo[b]carbazole/Σ benzocarbazole also decreases.

The retention of C3 carbazoles is paralleled by a reduction in exposed isomers in both, C3 and C2 carbazoles (Fig. 36). The retention of nitrogen exposed isomers on mineral and/or organic phases during migration is based on hydrogen bonding between the nitrogen and active kations in clay minerals or solid organic matter. The fractionation of C3/C2 carbazoles can neither be explained by a degree of shieldedness, nor by size-exclusion effects. A varying orientation of the effective dipolemoment might possibly be the reason for differential fractionation. The source rocks, which are expected to retain the nitrogen exposed species during petroleum expulsion, would be expected to be strongly enriched in exposed C2 and C3 carbazole isomers. They are, however, not, and seem to be characterized by similar values as the analyzed oils (Fig. 36), which may either point to a lack of fractionation during primary migration, indicating that the main fractionation occurs during secondary petroleum migration, or suggest that the source rock samples have not yet expelled any petroleum. The latter is rather improbable as half of the source rock samples have maturity values that correspond to the oil generative window.

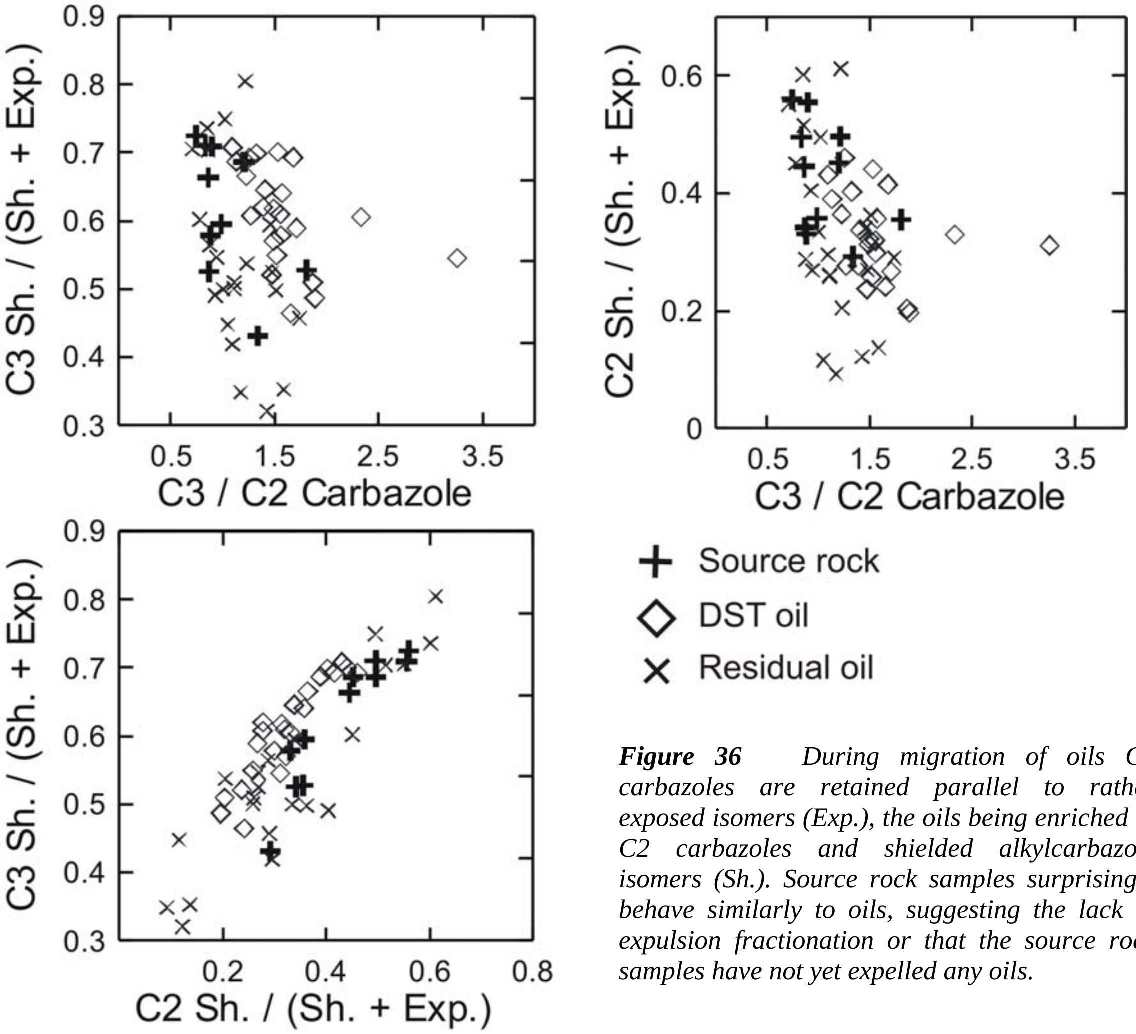


Figure 36 *During migration of oils C3 carbazoles are retained parallel to rather exposed isomers (Exp.), the oils being enriched in C2 carbazoles and shielded alkylcarbazole isomers (Sh.). Source rock samples surprisingly behave similarly to oils, suggesting the lack of expulsion fractionation or that the source rock samples have not yet expelled any oils.*

Figure 37 is the key to understanding the fractionation processes that occur during primary and secondary migration. In terms of C1, C2 and C3 carbazoles, source rocks are enriched in C1 carbazoles and depleted in C3 carbazoles relative to oils (Fig 37, *upper left*), suggesting a retention of C1 carbazoles by hydrogen bonding of the carbazole nitrogen, which is generally less shielded by a methyl group than by three methyl groups, or an ethyl and one methyl group. During secondary migration, the first charge (that probably met an empty, water-wet pore system) was preferentially depleted in C3 carbazoles, while in subsequent charges successively less C3 carbazoles and increasingly more C1 and C2 carbazoles were retained (Fig. 37, *upper right*).

The *shielded-partially shielded-exposed* diagram suggests that DST oils contain a larger proportion of exposed C2 carbazoles than source rocks (Fig. 37, *middle left*), which is highly surprising and can again only be explained by the fact that source rocks have not yet expelled oils, respectively have only expelled minor amounts (those with a higher amount of exposed isomers).

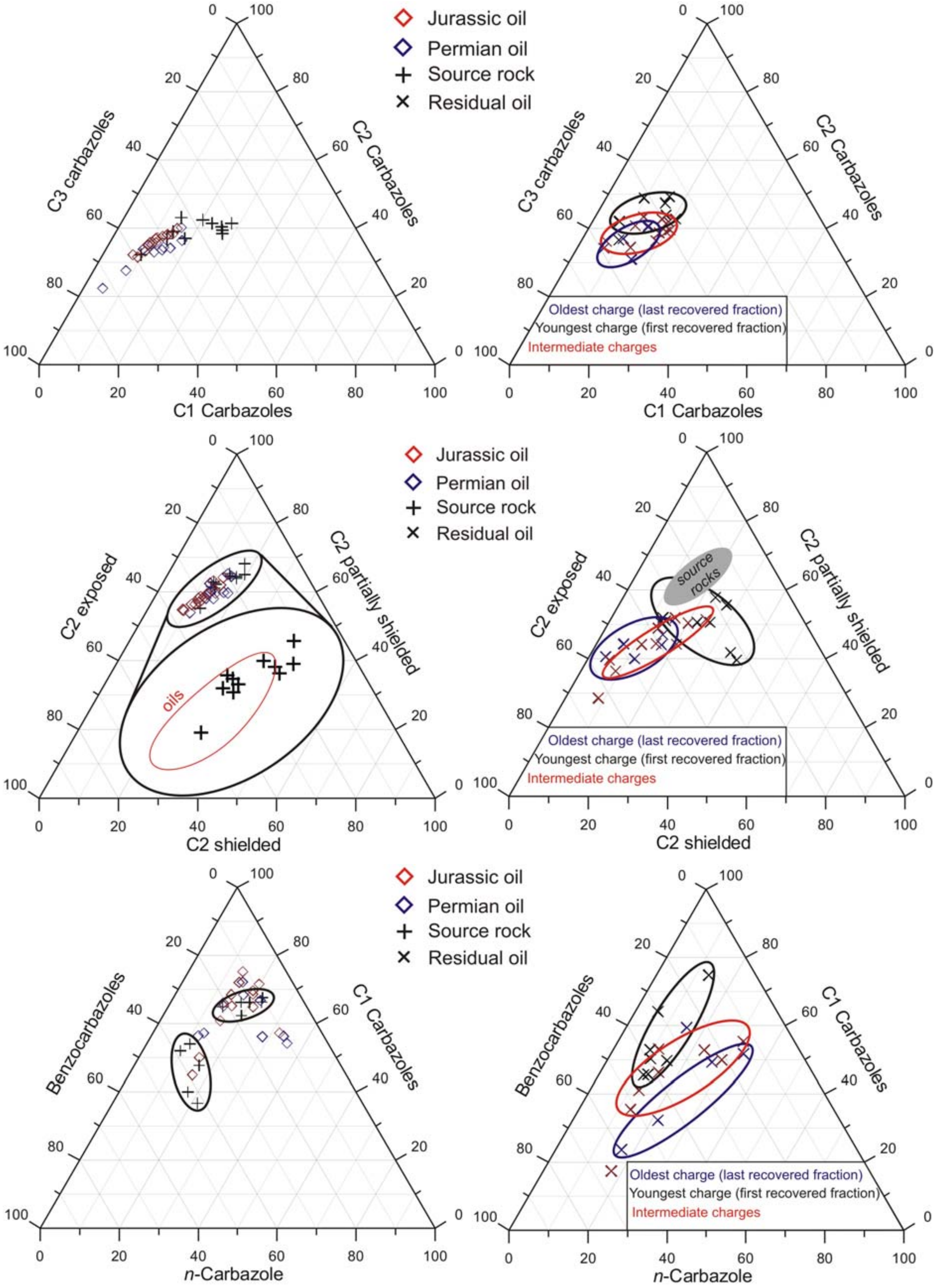


Figure 37 *Fractionation of carbazole compound classes and isomers during primary and secondary migration is depicted by showing compositional variability between oils and source rocks on one hand and residual oil fractions that correspond to first, middle or last fill on the other.*

When considering the fractionation during secondary migration in residual oils, the distribution of shielded and exposed isomers makes sense, the first oil charge being enriched in exposed C2 carbazoles while the latest charge is characterized by elevated relative amounts of shielded and partially shielded isomers (Fig. 37, *middle right*).

In terms of the relative amount of carbazole, C1 carbazole and benzocarbazole, the oldest charge has the highest carbazole and benzocarbazole content. The younger charge is enriched in C1 carbazoles (Fig. 37, *lower right*). The distribution of these in source rocks is steered by a mechanism that cannot be explained with the information available. Two clusters of source rocks exist. The Birkhead Formation source rocks and the three pre-Permian source rocks have similarly high amounts of benzocarbazole (around 40%) and low amounts of C1 carbazole (40-50%) while Permian Toolachee and Patchawarra Formation samples are similar in having low benzocarbazoles (10-20%) and high C1 carbazoles (60-70%). The distribution of Permian and Jurassic DST oils does not allow to draw any conclusion.

6.5 Synopsis

In contrast to literature reports of previous studies, the concentration of carbazoles in the Cooper/Eromanga Basins decreases with increasing maturity. C3 and C2 are the dominating species and carbazole concentrations are always higher in source rocks than in oils and residual oils. Oils do not exhibit a maturity dependency for the concentration of any compound or carbazole parameter.

When considering coaly samples and two shaly samples (Toolachee Fm.) separately, both the benzocarbazole *a/(a+c)* ratio and individual benzocarbazole isomer concentrations increases up to a maturity value of 25% ββ C_{29} sterane, which is equivalent to the onset of oil generation (0.6% Ro), after which a reversal takes place. This can be attributed to either the generation of new hydrocarbons or to expulsion effects.

The benzocarbazole *a/(a+c)* ratio in oils is not dependent on maturity or source facies and individual benzocarbazole concentrations decrease in parallel to a decreasing benzocarbazole ratio, which suggests fractionation processes during secondary petroleum migration to be the parameter that controls benzocarbazole distribution in oils.

The distribution of C1 and C2 alkylated carbazole species appears to be governed by the source facies and the ratio of 1,7-/1,6-dimethylcarbazole, 2-/(2-+3-) methylcarbazole and 1,8-dimethylcarbazole/(1,8-dmc+1-ethylcarbazole) can be used to discriminate oils that contain a Warburton Basin sourced component against the remainder Cooper and Eromanga Basin sourced oils. A minor maturity dependency is present for the relative amount of 1-methylcarbazole. Attribution of fractionation processes to primary migration is troublesome since it is not known whether the source rock samples have indeed expelled any petroleum.

However, the distribution of first- vs. last charge residual oils indicates that C3 carbazoles are preferentially retained over C2 and C1 carbazoles and exposed isomers over shielded and partially shielded isomers during secondary oil migration.

CHAPTER SEVEN

Filling and Mixing

This chapter aims at the evaluation of combined carbazole and aromatic hydrocarbon signatures in view of reconstructing the extent of oil mixing between oils that exhibit a Jurassic affinity and those that can be associated with Permian source rocks, and establishing the main direction of secondary migration by considering intra-reservoir maturity gradients and migration distance as suggested by the benzocarbazole *a/(a+c)* ratio. While hydrocarbon compositions are quickly equilibrated vertically over a few tens of metres in reservoired petroleum columns (England, 1990) there is substantial evidence that the same is not true for polar species such as resins and asphaltenes (Stoddart *et al.*, 1995), making residual oil carbazoles particularly useful for a temporal resolution of an oil charging history.

7.1 Aromatic hydrocarbon parameters

7.1.1 Methylphenanthrenes

Radke *et al.* (1983) developed a thermal maturity indicator based on methyl group isomerism in phenanthrene molecules (Fig. 38). The so called methylphenanthrene index (MPI) considers the relative abundance of phenanthrene and four of its methylated analogues (1-MP, 2-MP, 3-MP and 9-MP).

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

Steric hindrance between hydrogen atoms and the methyl group in 1-MP and 9-MP leads to a diminished thermodynamic stability of these two isomers. With increasing maturity they are converted into 2-MP and 3-MP by mobilization of the methyl groups. In addition, methylation

of phenanthrene does occur (Killops and Killops, 1993). An MPI range of 0.45–1.6 defines the zone of oil generation (~ 0.6–1.35%Ro); beyond this zone the MPI decreases again.
Variations in organic matter type and facies can influence the aromatic isomer patterns, especially the alkylphenanthrene distributions (Radtke, 1987). Also phase changes during secondary migration can have a remarkable effect on aromatic maturity parameters. The effect of phase changes, however, has a stronger impact on the distribution of alkylated naphthalenes (Larter *et al.*, 1991), which feature a lower molecular weight.

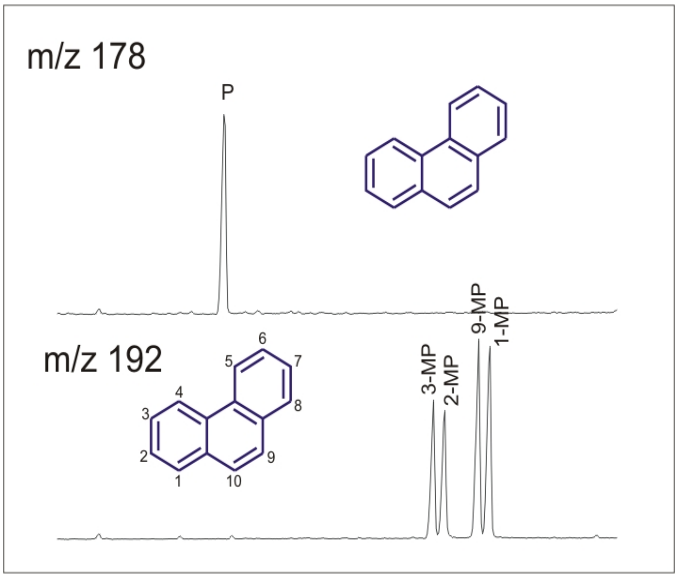


Figure 38 *Phenanthrene (P) and its four methylated isomers (MP), whose distributions are controlled by maturity, are measured by GC-MS on mass to charge ratios (m/z) 178 and 192.*

An apparent vitrinite reflectance value (R_C) can be calculated from the MPI-1 by using two formulas for samples of a lower, respectively higher maturity than 1.35% Ro, as the MPI – 1 increases throughout the oil generative window but reaches a maximum at approximately 1.35% Ro, after which it decreases again (Radtke and Welte, 1983).

$$\% \, Rc = 0.60 \, (MPI\text{-}1) + 0.40 \quad (\text{when } Ro<1.35\%)$$

$$\% \, Rc = -0.60 \, (MPI\text{-}1) + 2.30 \quad (\text{when } Ro>1.35\%)$$

7.1.2 Araucariacean markers

Alexander *et al.* (1988, 1992) used aromatic biomarkers of the post-Triassic conifer family *Araucariaceae* (Fig. 39) to distinguish between oils derived from the Permo-Triassic Cooper Basin and those derived from the overlying Jurassic-Cretaceous Eromanga Basin. While various *Araucariacean* aromatic biomarkers including 1,2,5-trimethylnaphthalene (Agathalene), 1,7-dimethylphenanthrene, 1-methylphenanthrene and retene (1-methyl-7-isopropyl-phenanthrene) are particularly abundant in Jurassic sediments and oils, they are virtually absent in pre-Jurassic strata. In *Araucariacean* conifers, the precursors of these molecules are found in leaves, where they function as resin constituents.

Mixing plots that compare 1-/9-methylphenanthrene and 2-/1-methylphenanthrene (Fig. 40) were utilized to determine the extent of mixing between Cooper Basin and Eromanga Basin oils. These plots were established by Michaelsen and McKirdy (1999) from the University of Adelaide, and more recently used by Arouri *et al.* (2004a and b) who experimented with artificial mixes of endmember oils to decipher endmember areas, mixing paths and the according mixing ratios (Fig. 40).

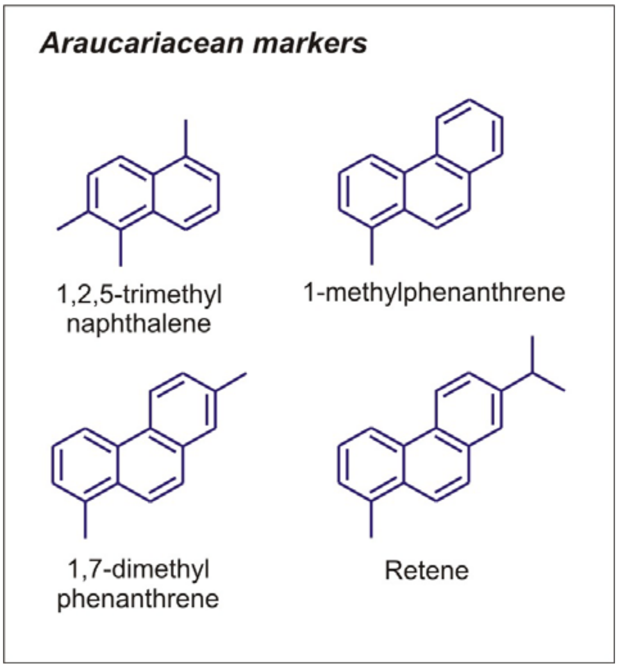


Figure 39 *These four aromatic biomarkers indicate a source specific input from the conifer family Araucariacea, when found in sediments or oils. In the plants they function as leaf resin constituents.*

7.1.3 Maturity discrepancies

An interesting feature upon comparison of DST oils and the first residual oil fractions from respectively adjacent core locations (Fig. 42), thus representing virtually one and the same oil, is the constantly elevated maturity of the residual oils. This was observed throughout all samples and thus cannot be attributed to random errors or different laboratory work-up procedures. The same phenomenon was noticed by Horstad *et al.* (1990), who found that aromatic hydrocarbon maturity parameter estimates from depth equivalent DST and core extract samples differed. His suggestion that these differences might result from fractionation effects during well testing still remains unproven (Larter *et al.*, 1991). The MPI-1 discrepancy in this study was seen to be steered by the distribution of phenanthrene, but due to its complexity will not be elaborated any further.

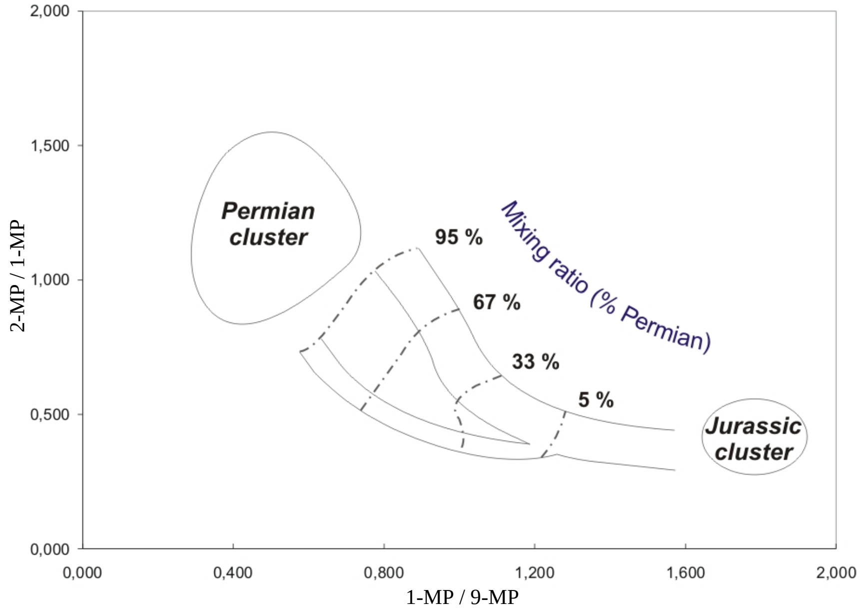


Figure 40 *Mixing plots of Araucariacean input versus maturity, show Jurassic samples to cluster in the lower right (high 1-MP), while Permian samples can be found in the left of the diagram. A distinction between Cooper Basin Family 1 and 2 oils is based on maturity values.*
The extent of oil mixing has been experimentally determined by mixing analyses of endmember oils (Arouri et al., 2004a).

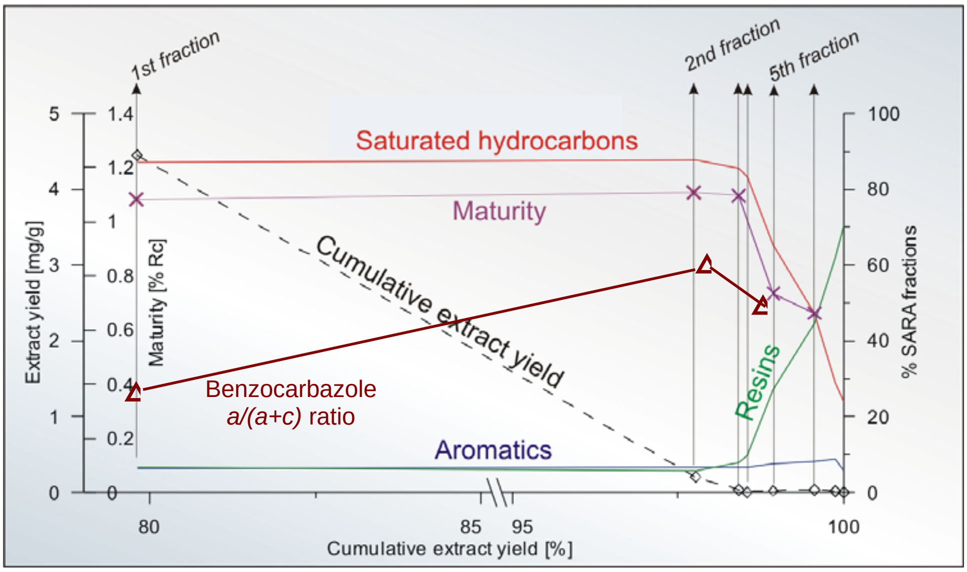


Figure 41 *Sandstone cores were sequentially extracted in an SFTE apparatus (Schwark et al., 1997). These plots yield information about the gross composition, maturity, extract yield and migration distance (benzocarbazole ratio) of subsequently extracted oil fractions. Fraction one was first recovered from the core, implying that it was the last oil charge to enter it. The last recovered fractions were the first to enter the pore system. The colour and symbol scheme is kept throughout this chapter.*

Residual oils that are obtained by sequential flow through extraction (SFTE) of sandstone cores exhibit a consistent compositional change in terms of the relative amount of saturates, aromatics, resins and asphaltenes (SARA) during the extraction process (Fig. 41). The first residual oil fractions, which are obtained by extraction with DCM, a solvent of medium polarity, resemble conventional DST or production oils. These first fractions are termed “free oil” and account for up to 98 percent of the total bitumen that is present within a pore system. The true residual oils, i.e. the bitumina that are adsorbed onto pore walls or trapped within smaller pores, can only be recovered by solvents of a higher polarity (e.g. a mixture of chloroform and methanol).

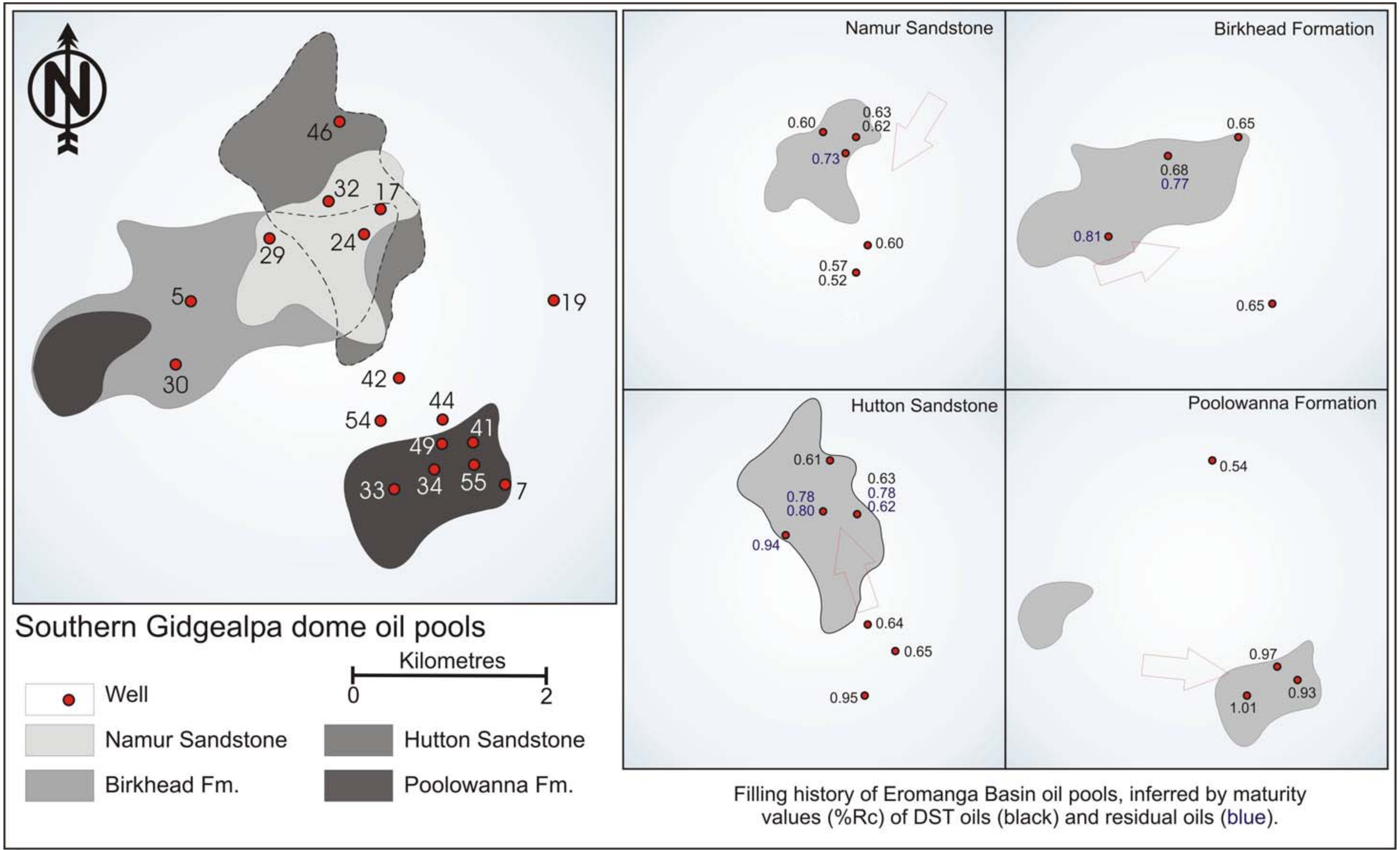


Figure 42 *The filling of discrete oil pools was tentatively reconstructed using the gradient of maturity that was present throughout the fields on a lateral scale. Strong mixing between mainly Permian and Jurassic oils, however, blurs the extracted information. Carbazole distributions prove to deal more successfully with this task. Two clusters of oil pools exist as seen in the left figure: a northern cluster of pools and a southern cluster of pools.*

The

se residual oils contain an increasing amount of polar NSO compounds, which correlates with their time of entering into the pore system. The first charge has experienced stronger adsorption of its polar compounds onto the water-wet pore system than subsequent charges, which entered an oil-wet pore system that was already preconditioned with a residual oil layer.

7.2 Eromanga Basin reservoirs

Oil that is reservoired within the Eromanga Basin reflects a complicated interplay between influence of Cooper, Eromanga and Warburton Basin source units. The main Eromanga Basin source rock is the Birkhead Formation that hosts shales and coals of Type II to Type III organic matter. The stratigraphically lowest Eromanga Basin reservoir, the Poolowanna Formation, has not received any input of Jurassic oils.

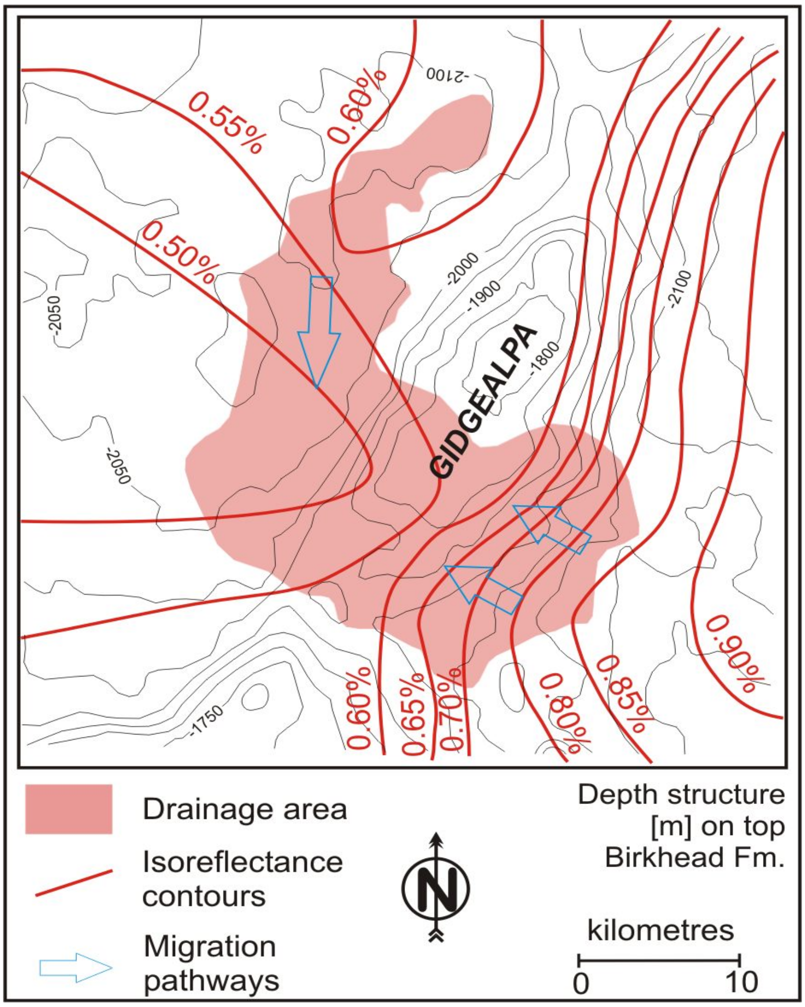


Figure 43 *This isoreflectance map of the Birkhead Formation in the vicinity of the Gidgealpa ridge suggests that two source kitchens have expelled petroleum. The eastern kitchen expelled its first charge during the Late Cretaceous, while the western kitchen started to expel petroleum during the Tertiary. The reservoired Birkhead oils have maturities in the 0.52-0.63% Ro range. The eastern kitchen, which should have entered the late peak phase of oil generation during the Tertiary, did either not expel a volumetrically significant second charge, or this charge did not migrate towards the Gidgealpa Ridge (modified after Boult et al., 1998).*

7.2.1 Filling of the Namur Sandstone

The Namur Sandstone has received a Permian input as can be seen in figure 44. However, as it is shielded from the underlying formations by the Birkhead Formation, the Namur Sandstone is thought to be rather a site of mixing between Birkhead Formation sourced oils and Murta Formation oils where the Murta Formation has a source potential and a sufficiently high maturity. No pre-Permian oil has entered the Namur Sandstone.

The distribution of values for the benzocarbazole ratio (BC) in Namur reservoired oils exhibits two maxima: around 0.15-0.18 and around 0.43 (see Appendix). This suggests that two discrete oil charges from the Birkhead Formation have entered the reservoir. While the lower values are restricted to the northern reservoir cluster (Fig. 42), the higher values occur at the southern cluster. Figure 43 shows that the Birkhead Formation has two source kitchens near the Gidgealpa dome. During the Late Cretaceous phase of maximum burial, oils were expelled from the eastern source kitchen and entered the Namur reservoir after having had migrated a short distance (higher BC values). Only 70 Ma later, during the Tertiary, the Birkhead Formation, west of the Gidgealpa Ridge, entered the oil generative window and expelled an oil charge that had to migrate further before reaching the Namur reservoir from the west. Upon arrival, it partially displaced the older Birkhead charge in the northern oil pool cluster but did not migrate to the southern cluster of reservoirs, due to the four way draped dome geometry of the Gidgealpa Ridge. This process is reflected by a sandstone core from well 24 (northern oil pool cluster), which first received a Permian Family 1 charge (Patchawarra source), followed by a Permian Family 2 charge (Toolachee source), a subsequent short distance migrated Birkhead charge and at last a long distance migrated Birkhead charge (Fig. 45).

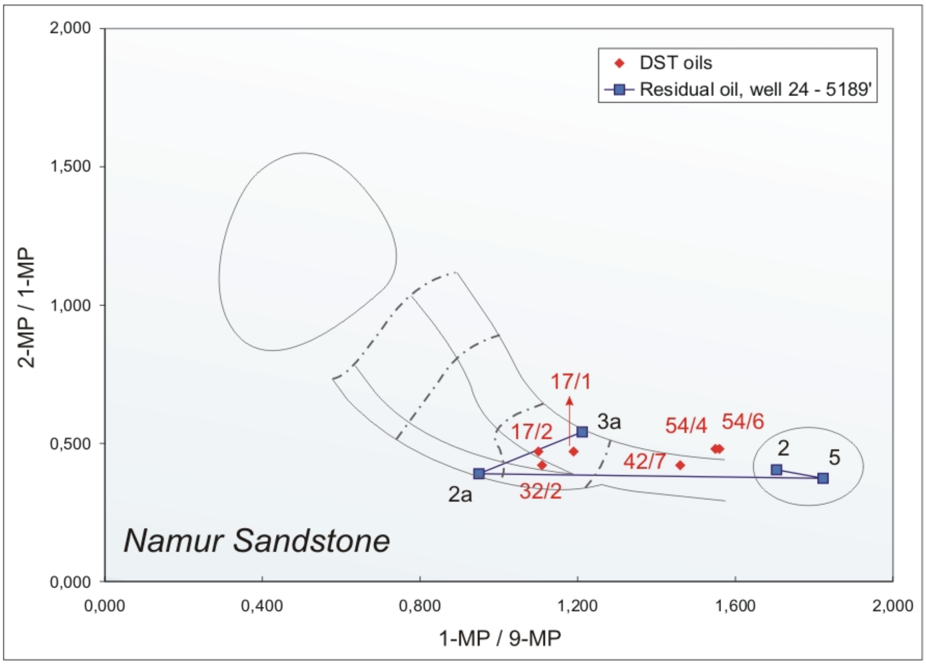


Figure 44 Although Namur Sandstone reservoired oils are mainly composed of pure Eromanga Basin oil, sourced by the Birkhead and/or Murta Formations, an influence of upward-leaked Cooper Basin derived oils is visible in the 1MP/9MP distribution.

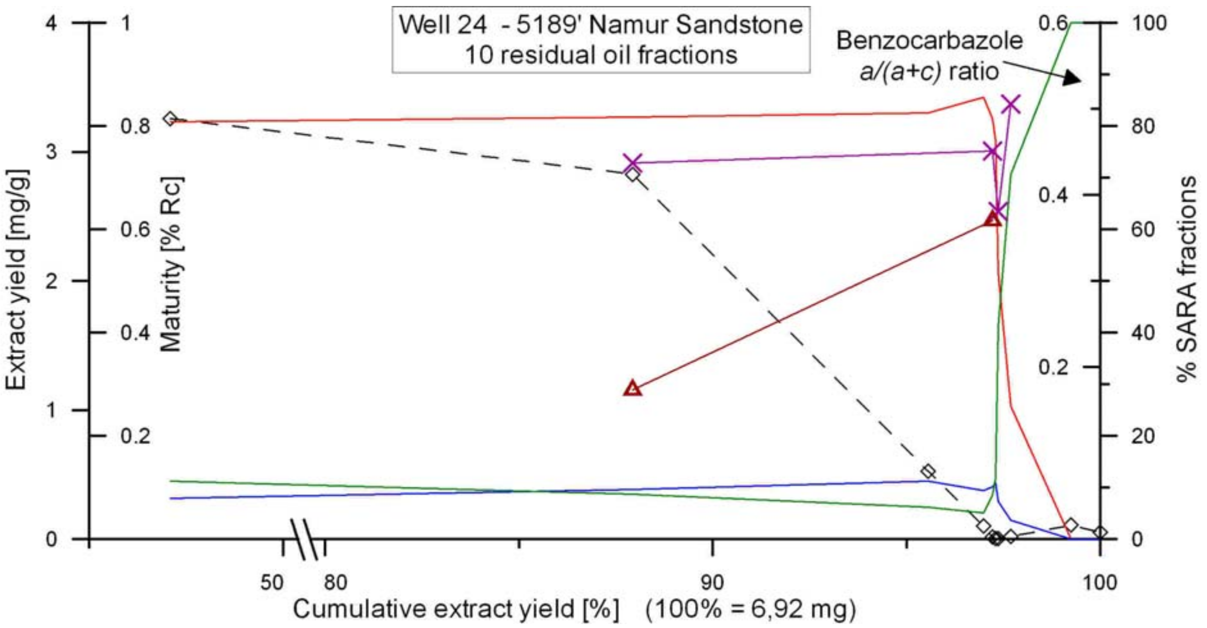


Figure 45 *This sequential extraction chart of a Namur Sandstone core plug shows that the first two fractions are somewhat equally mature and of mainly Jurassic origin. Varying migration distances, as suggested by the benzocarbazole a/(a+c) ratio however suggest their origin from two discrete source kitchens. The last two fractions bear a Permian signal (Figure 44); the maturity gradient (second charge more mature than first charge) suggests that the first charge was a Patchawarra (Family 1) oil while the second charge probably originated from the Toolachee Formation (Family 2).*

7.2.2 No second charge for Birkhead reservoirs

The benzocarbazole ratio for most Birkhead oils lies around values of 0.37-0.40, which are similar to those of the first oil charge that entered the Namur reservoir. This allows the conclusion that the Birkhead Formation sourced oils that are reservoired within sandier parts of the formation originate from the eastern source kitchen (Fig. 43). As not a single oil sample with a lower BC value was encountered, the Tertiary Birkhead Formation charge, which was sourced by the western kitchen area, is probably restricted in its migration to the Namur Sandstone.

The first pore filling oil pulse in well 30 was shown to be sourced by Warburton Basin source rocks (see chapter six). The fractions that represent this pulse (2a and 3a) are characterized by lower BC values of 0.19 and 0.20 respectively, which is in agreement with their origin from the deepest Warburton Basin strata. While these samples appear like normal Jurassic samples on the *Araucariacean* mixing plot after Michaelsen and McKirdy (1999), the ratio of 1,7-/1,6-dimethylcarbazole and 2-/3-methylcarbazole reveal their pre-Permian origin (Fig. 30, chapter six).

The mixing plot reveals that Birkhead oils generally appear to be less mixed with Permian oils. Well 34 bears a strong Permian signal (Fig. 46), which is not surprising as it is situated above a Poolowanna reservoir, filled exclusively with Permian oil (Fig. 42). Neighbouring well 33 contains purely Permian oil in the Hutton Sandstone, possibly spilled from the underlying Poolowanna Formation. The reason for this can be sought after in the low sealing capacity of intra-Poolowanna Formation shales.

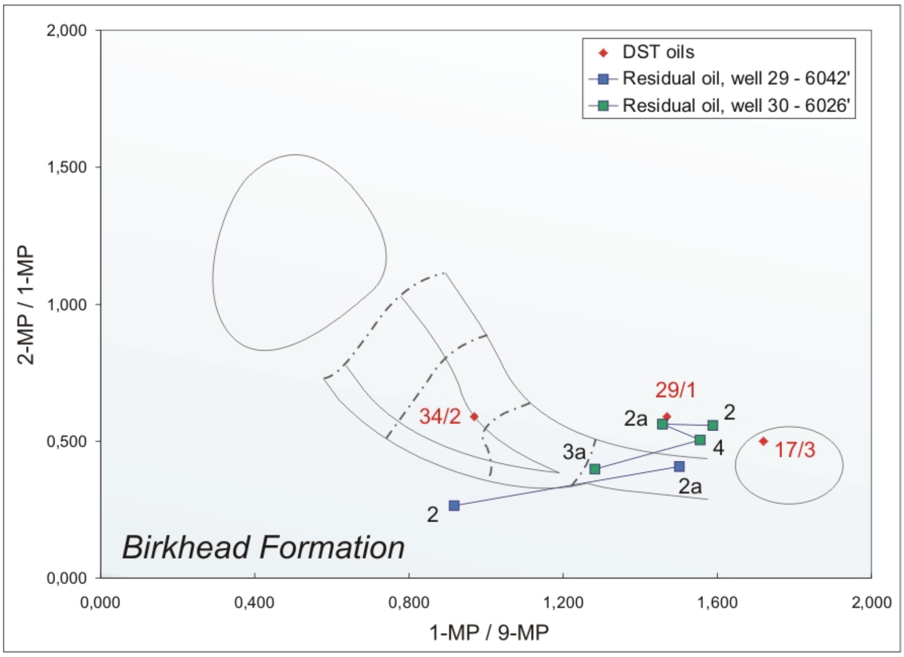


__Figure 46__ Most Birkhead Formation reservoired bitumens seem to be of a relatively pure Jurassic origin. It is highly surprising to find Permian influence in wells 34 and in the most recent (!) oil charge in the deeper sample from well 29. This (probably Family 2) charge has not yet reached the well 29 DST oil, which is situated only a few metres higher in the sedimentary column, suggesting a relatively recent leakage.

The second residual oil fraction from well 29, represents the ’free oil’ and should be comparable to the overlying well 29 DST oil, but it testifies to having received a relatively high Permian oil content (Fig. 46). The strong Jurassic signature of fraction 2a from the same sample suggests that this Permian oil has entered the Birkhead Formation in well 29 very recently, after the main Late Cretaceous Birkhead charge had accumulated (the Tertiary charge was restricted to the Namur Sandstone). As the DST oil in the hanging wall part of well 29, is mainly Jurassic, the Permian oil must have migrated up-dip from the underlying Hutton Sandstone and Poolowanna Formations, rather suggesting seal failure than a constantly low sealing capacity.

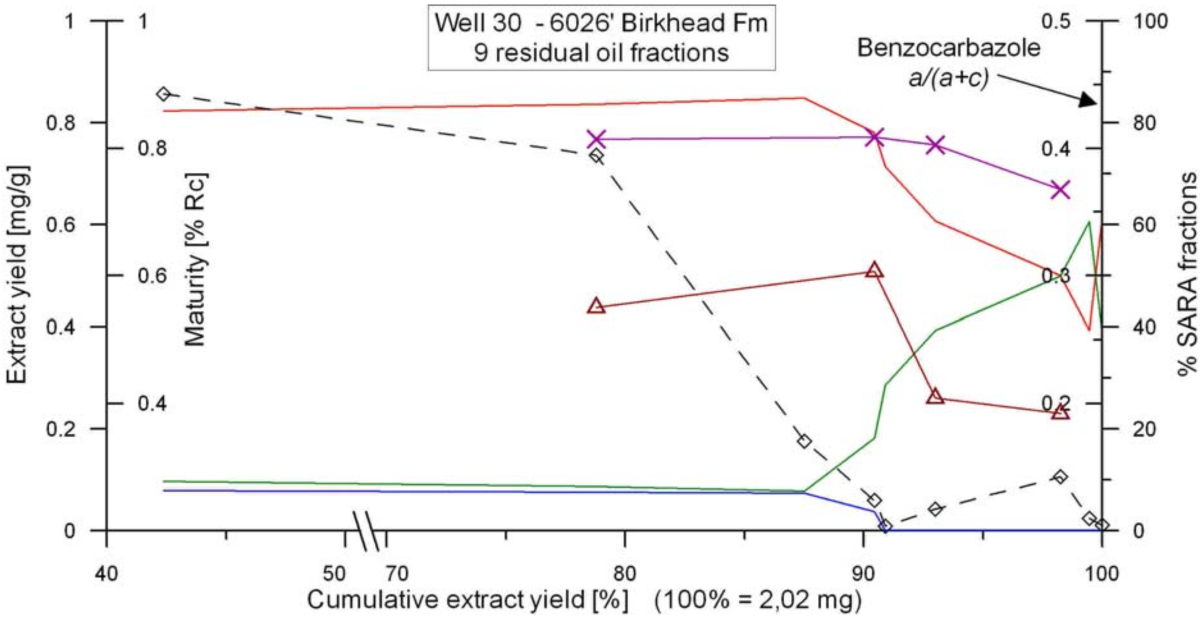


Figure 47 *The last residual oil fractions from this core carry a pre-Permian carbazole signature (chapter 6). Younger charges are characteristic Birkhead Formation oils that were sourced from the eastern kitchen area. The increase in extract yield and hydrocarbon content during the last stages of the extraction process suggest the release of trapped bitumen by pore fracturing.*

7.2.3 Hutton Sandstone – a site of active oil mixing

The Hutton Formation reservoired oils and residual oils probably represents the most complex mixes between two Birkhead Formation charges, a pre-Permian input and at least two Cooper Basin oil charges.

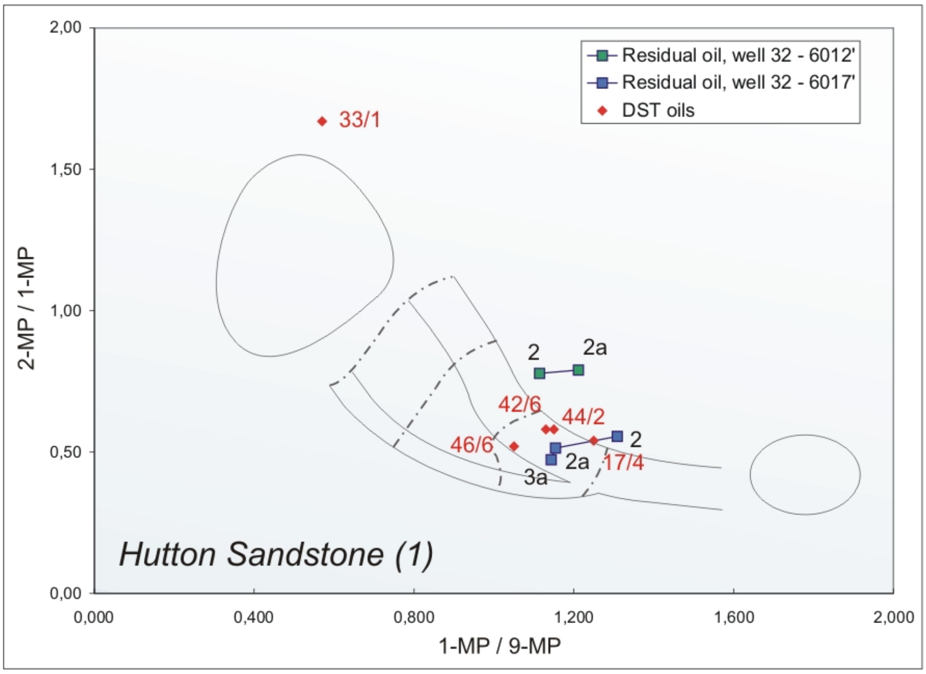


Figure 48 *In well 33, the Hutton Sandstone received a strong input of Permian oil, which probably migrated up-dip from underlying Poolowanna Formation reservoirs. The lack of gas accumulations in the Hutton Sandstone, however, excludes that this oil originates from underlying Cooper Basin oil pools, which are overlain by a gas leg.*

The occurrence of exclusively Permian-sourced oil in well 33 immediately jumps to the eye and suggests a leakage from the underlying Poolowanna-reservoired Permian oil pool. The neighbouring well 34 contains a Permian influence of estimated 35-40 % in a Birkhead-reservoired DST oil. Since no Namur-reservoired samples from this area are contaminated by Permian oil, the Birkhead Formation proves to be a tight seal. The aforementioned Birkhead sample is only characterized by a moderate Permian influence, and the Jurassic oil seems to be not fully displaced. One can thus argue in favour of either a very recent leaking event, or the leakage to having been minimal. Sample 33/1 is a relatively dense oil, which means that any Permian gas or gas-condensate must have been lost. Since, however, no gas accumulations are found within higher Eromanga strata in this small area, while they are present in lower Cooper Basin strata (i.e. Toolachee Fm., Patchawarra Fm., and Tirrawarra Sandstone), it must be concluded that the Poolowanna Formation oil pools in the southern oil pool cluster did not form by spilling of oil from underlying Permian hydrocarbon accumulations. The benzocarbazole ratio of these oils shed more light on this enigma: Permian Family 1 oils that are reservoired within the lower Toolachee Fm., Patchawarra Fm. and Tirrawarra Sandstone were locally generated and expelled from nearby situated Patchawarra Formation source rocks and bear relatively high BC-values of around 0.5. This argues for of a short migration distance. In contrast, the Permian Family 1 oils that are reservoired within the Poolowanna Formation and have leached into the Hutton Sandstone are characterized by far longer migration distances as indicated by their benzocarbazole ratio that lies between 0.21 and 0.25 (Fig. 60). Poolowanna-Hutton leakage can be explained by failure of the intra-Poolowanna shales’ sealing capacity. The Poolowanna-Hutton couplet is, on the other hand, separated from the underlying gas and oil pools by the tightly sealing Triassic Nappamerri Formation.

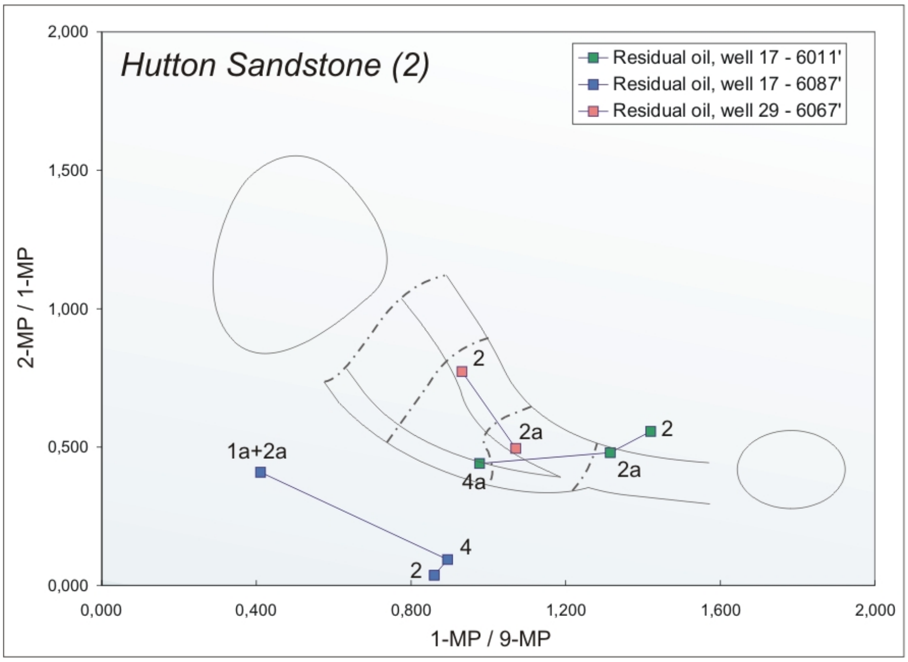


Figure 49 The deepest sample from well 17 reveals strong mixing with a Cooper Basin Family two oil.

However, not all Poolowanna DST oil samples from the southern oil pool cluster feature the aforementioned low benzocarbazole *a/(a+c)* values (BC). DST oils from well 49 and 55 have BC values of 0.48 and 0.57, which would again favours the idea of oil leakage from underlying Cooper Basin reservoirs. The absence of gaseous hydrocarbons from Poolowanna and Hutton reservoirs, however, definitely excludes this idea and the reason for the elevated BC values may be sought in local coal seams. In terms of the Ph/nC_{18} ratio, the Poolowanna Fm. DST oil from well 33 seems to be a normal Permian oil. The samples from wells 49 and 55, which feature the elevated benzocarbazole ratios in question, have an elevated Ph/nC_{18} ratio, which is thought to be a consequence of indigenously produced petroleum. Furthermore, the sample from well 55 has a higher relative abundance of C_{27} and C_{28} steranes. This locally produced oil would have migrated only minimal distances and, by mixing with a far migrated Permian charge, may have elevated the initially low BC values by contamination. The pristine migration signal is still found in well 33, where the Poolowanna Formation has produced no indigenous petroleum.

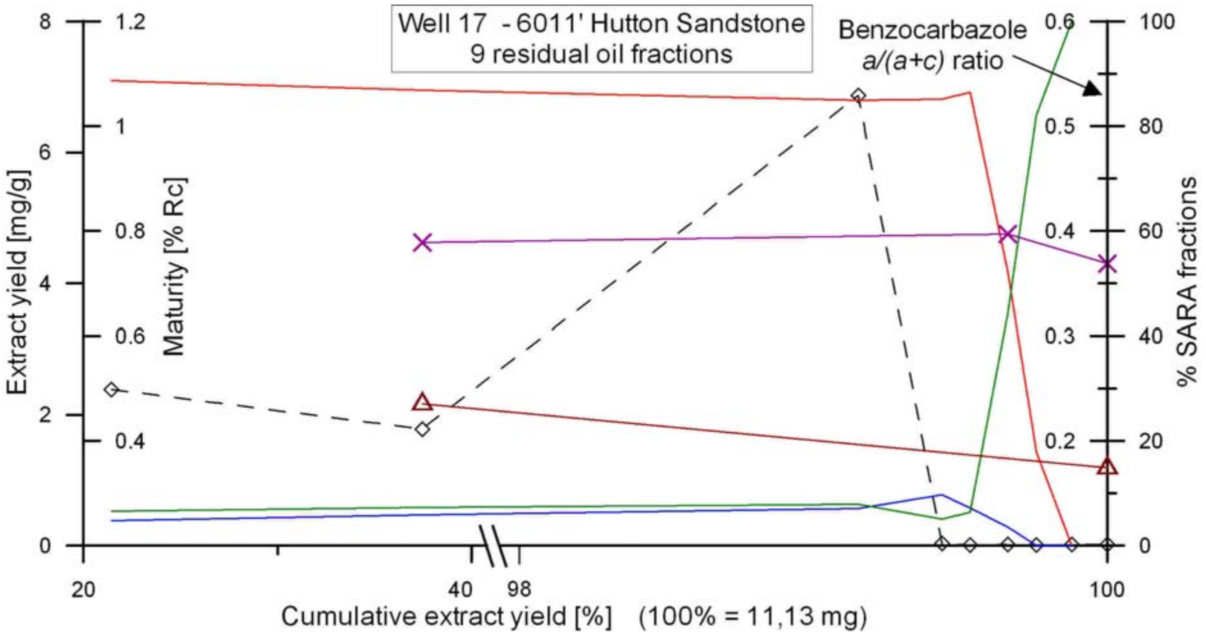


Figure 50 *The upper sandstone core from well 17 is situated within the Hutton oil leg, as can be seen by the high cumulative extract yield. Its last residual oil fraction was shown to bear a slight pre-Permian signal (see chapter 6).*

The Hutton Formation is represented by three samples from well 17. DST 4 was sampled from the oil leg of the Hutton Formation oil pool. The upper core (Fig. 50) yielded a cumulative extract of 11.13mg, which suggests that it is still situated in the oil leg. The lower core, however, only yielded a total of 1.35mg bitumen, suggesting that it was sampled from a palaeo-oil zone in the water-leg underneath the oil accumulation. It is therefore more than surprising to see that the residual oil fractions from this sample do not increase in polarity as the extraction process proceeded (Fig. 51).

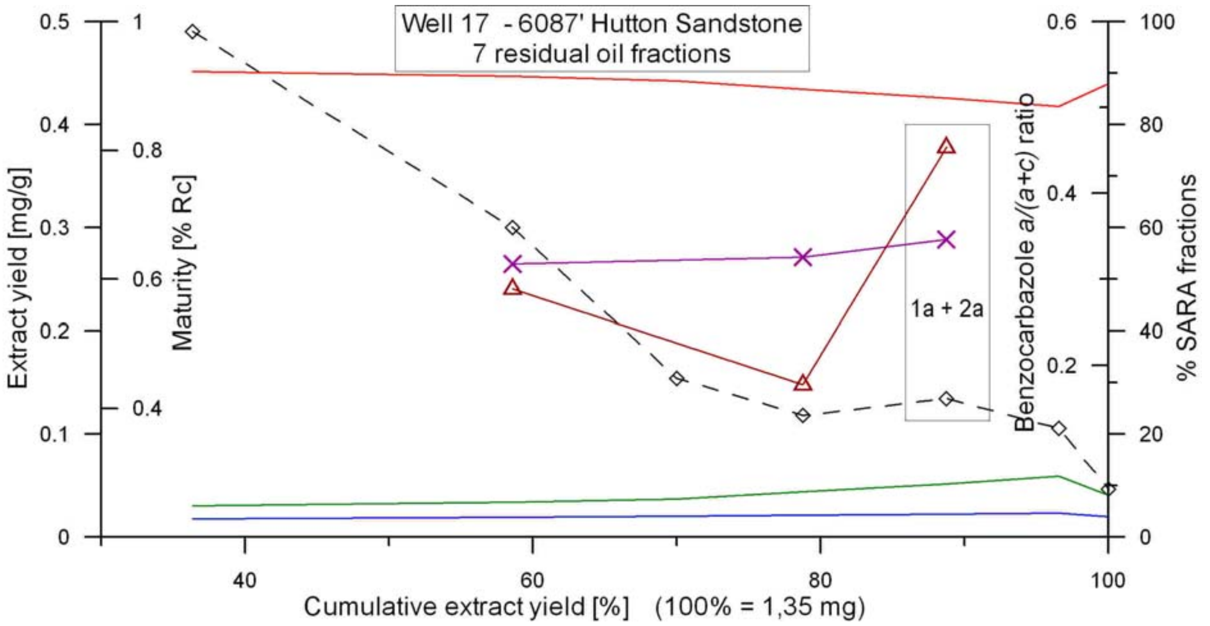


Figure 51 *The lower sandstone core only yields 1.35mg bitumen and is probably situated in the water leg beneath the Hutton oil pool, indicating a palaeo oil zone.*

Combined residual oil fractions 1a and 2a from the lower core in well 17 (Fig. 51) do appear to contain a Warburton Basin content (Fig. 28 and 30, chapter six). This is, however, unlikely to be responsible for the low total NSO-content of this sample, and a reasonable explanation was not found. The higher core from well 17 (Fig. 50) was also found to contain a slight pre-Permian component (Fig. 28, chapter six), which is also lower than in the deeper core. This co-occurrence of two samples that are characterized by a pre-Permian input and the upward diminishing pre-Permian signal may indicate a palaeo-migration conduit of pre-Permian oils. As the signal is not equally strong in both, relatively closely spaced samples one can argue in favour of only small amounts of pre-Permian petroleum. The Hutton reservoir was thus probably never completely filled with pre-Permian oil and subsequently displaced/spilled.

The palaeo-oil zone, which is represented by the lower sandstone core from well 17, indicates that this zone once was part of the oil leg. It is hard to reconstruct why the oil-water contact has moved, but East-West directed compressional tectonics during the Tertiary may have played a role. On the other hand, as some Permian oil has entered the Namur Sandstone, one could argue in favour of a leaking seal, which would have led to a decreasing oil leg and a palaeo-oil zone.

7.2.4 The Poolowanna Formation – no access for Jurassic oils

Although rather a transitional reservoir between the Permian and Jurassic sedimentary sequences, the Poolowanna Formation hosts oils that are of a predominantly Permian origin. Of two existing oil pools, only one was sampled. This hydrocarbon accumulation, which is situated in the southern cluster of oil pools, is represented by three DST oils that all three bear a distinct Permian Family 1 signature (Fig. 52). They can, however, not be unambiguously linked to a Patchawarra Formation source rock. Figure 57 shows that these oils have an *n*-alkane distribution that is skewed towards higher homologues. They thus appear rather to be over-mature Toolachee-sourced Cooper Basin Family 2 oils. A minor Family 1 content is suggested by the bimodality in the lower *n*-alkane range.

Well 46 is situated below the northern oil pool cluster, and the Poolowanna Formation does not host an oil pool here. Nevertheless, hydrocarbons are present and feature an immature Cooper Basin Family 2 signal. Evaluation of aliphatic hydrocarbons (chapter 5) has revealed that Poolowanna hosted oils are characterized by a deviating trend from other oils in a number of plots, which is attributed to the in-situ generation of minor amounts of oils from indigenous oil-prone coal seams. This was discussed before in the Hutton Sandstone-section.

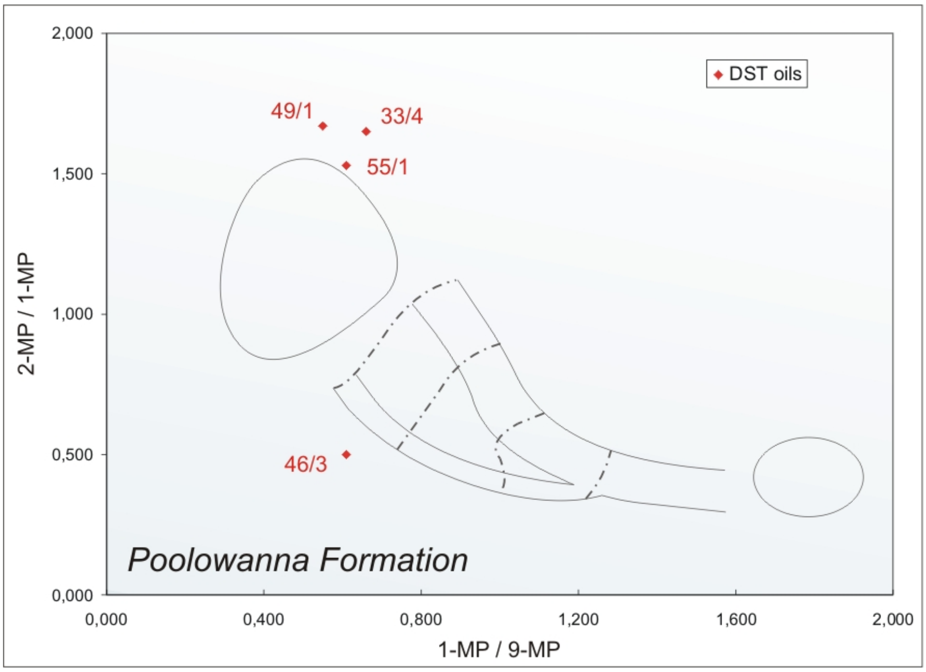


Figure 52 *Three DST oils from the Poolowanna Formation exhibit a strong Cooper Basin Family 1 affinity. All three were sampled at the southern oil pool cluster. Sample 46/3 represents a bitumen derived from the northern cluster and exhibits a Cooper Basin Family two affinity. Sample 33/4 is the only Poolowanna reservoired oil that has not been contaminated by indigenously produced petroleum (see chapter 5) and reflects the original characteristics of the Permian oil charge. It features low BC values (far distance migrated), while all other samples have elevated BC values, indicating a low migration distance or in-situ generation.*

7.3 Cooper Basin reservoirs

Generally the play of Cooper Basin reservoired oil is less complex that that of the Eromanga Basin as it contains one variable less, i.e. Jurassic oils. Downdip migration of Jurassic Birkhead Formation oils has not occurred; neither did any Jurassic oil enter due to juxtaposition in trough areas. The Toolachee and Patchawarra Formations are both source rock and reservoir, having produced Cooper Basin Family 1 oils and the slightly less mature Cooper Basin Family 2 oils.

7.3.1 Warburton Basin influx

Since the Toolachee Formation is also the source of low maturity Cooper Basin Family 2 oils, one could suspect to find residual traces of these liquids in Toolachee strata. The *Araucariacean* cross-plot (Fig. 53) does indeed seem to provide evidence for the Toolachee Formation as a source of the Family 2 oils. Both sequentially extracted cores appear to host pure Family 2 oils as the last residual oil fraction (2a and 3a), i.e. the oil that entered the pore space first. The alkylcarbazole signature (chapter six), however, suggests that these samples have received a strong pre-Permian input. While residual oils No. 3 and 2a from the well 8 Toolachee sample appear as pre-Permian influenced by the 1,7-/1,6- dimethylcarbazole and the 1,8-dimethylcarbazole/(1,8-dimethylcarbazole+1-ethylcarbazole) parameter but not by the 3-/2- methylcarbazole parameter, residual oil No.2, representing the most recent charging event, is characterized as strongly pre-Permian influenced by all three parameters! Also the Toolachee residual oil samples from well 7, which is situated in the southern Gidgealpa dome, appear to be partially Warburton Basin derived. Here, only residual oil No. 2 and 4, again representing the latest charge, bear the distinct carbazole signal. This is remarkable, as it is suggesting that an oil charge from the Warburton Basin has entered the Gidgealpa reservoirs very recently. As discussed in chapter six, the shelfal limestone source rocks from the Warburton Basin are not restricted to the troughs, which evolved at later stages. It can thus be assumed that a Warburton Basin source unit that is either situated beneath the GMI Ridge or on its flanks has recently entered the oil generative window and released a low maturity petroleum charge (Fig. 55). An interim accumulation of Warburton oil in a trap structure that recently failed and sent an oil charge up the migration path would be another explanation.

Residual oil fraction No. 2 from the Patchawarra Formation in well 7 bears a slight pre-Permian signal that is indicated by the 3-/2- methylcarbazole ratio only. We are again dealing with a last-fill fraction! As, however, the pre-Permian signal is only very weak in this footwall part of well 7, the oil charge can be concluded to not having migrated up-dip *in situ*, but rather having entered the Gidgealpa Field laterally, probably by migrating along the lower Triassic Nappamerri seal. In the case of the Patchawarra sample, a localized down-dip migration can potentially have occurred due to local porosity and permeability anomalies.

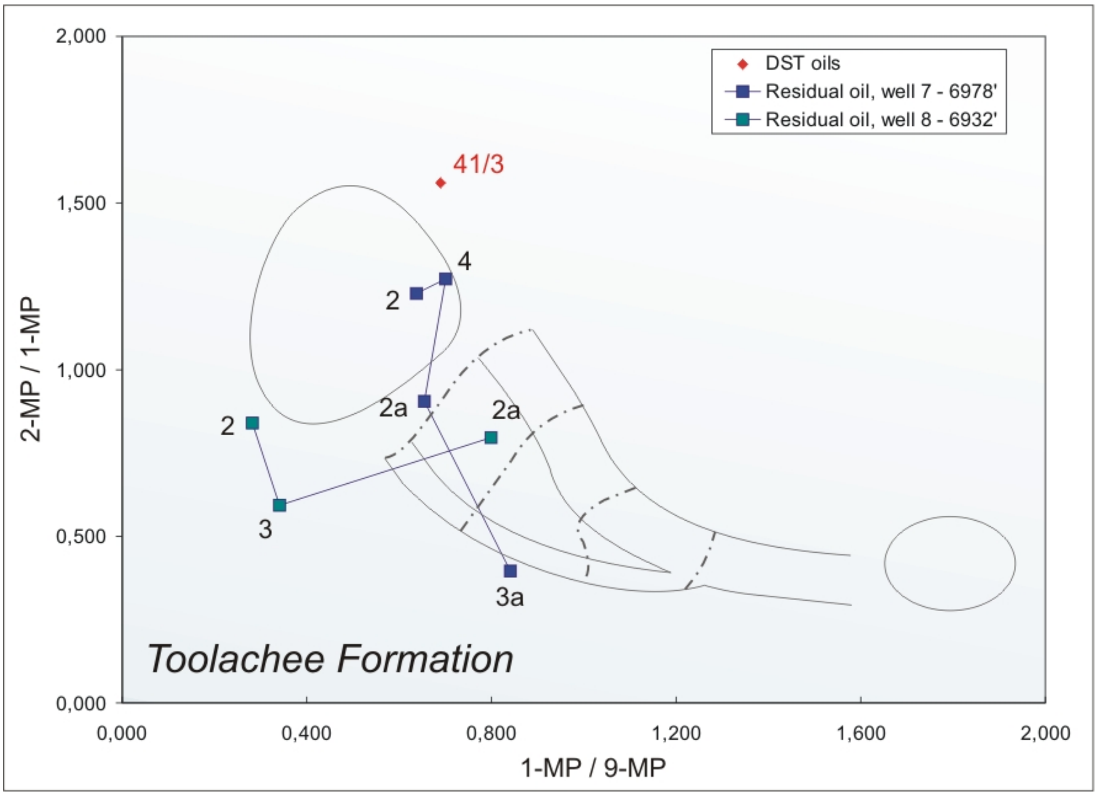


Figure 53 *While the low mature first charges in sandier intervals of the Toolachee Formation appear like low mature Cooper Basin Family 2 oils, they actually are strongly mixed with an oil charge from the Warburton Basin that must have entered the Gidgealpa Field relatively recently.*

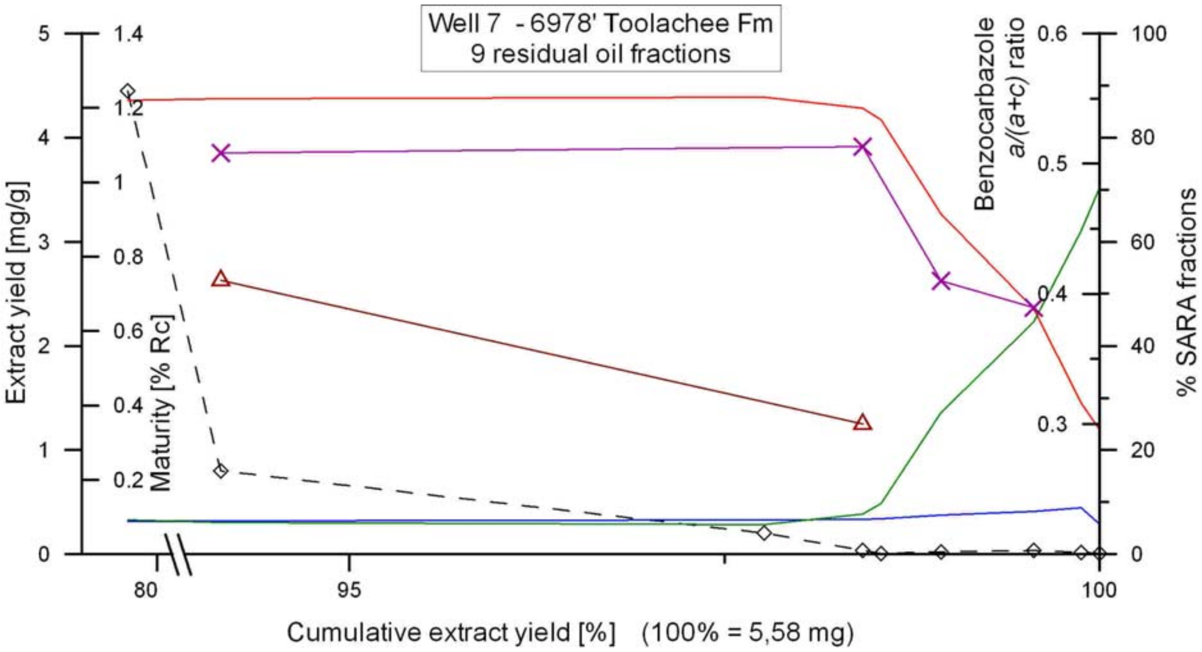


Figure 54 *The increasing maturity trend of the last two residual oils reflects the maturation of the Toolachee source kitchen. The first two residual oils, which reflect the most recent charge, are strongly mixed with petroleum that was sourced from Warburton Basin source rocks.*

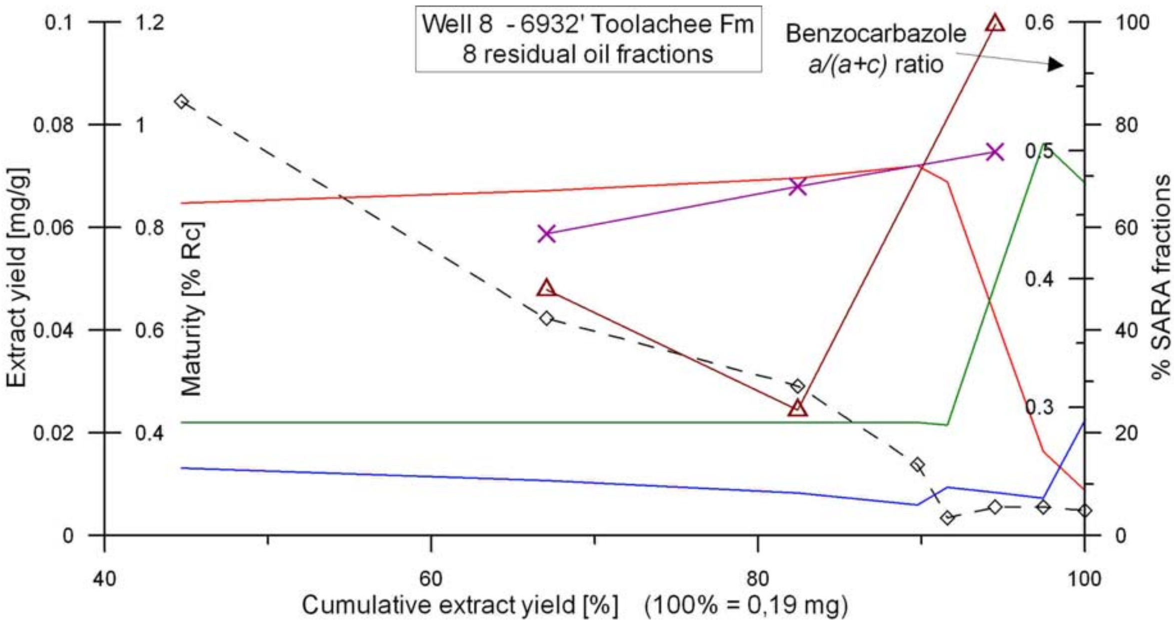


Figure 55 *Well 8, situated in the Northern Gidgealpa Dome, has experienced a strong influx of Warburton Basin oils. The low cumulative extract yield, however, rather suggests that this sample represents a palaeo-migration conduit that was flown through by a stringer of migrating oil.*

Toolachee and Patchawarra Fm	Hutton Sst.	Birkhead Fm
Well 8 (*To*) Fr. 2 - 0.39 ***A*** Fr. 3 - 0.30 ***B*** Fr. 2a - 0.60 ***C*** Well 7 (*To*) Fr. 2 - 0.41 ***A*** Fr. 4 - 0.30 ***B*** Fr. 2a - X Fr. 3a - X Well 7 (*Pa*) Fr. 2 - 0.42 ***A*** *Fr. 4 - not Warburton* *Fr. 2a - not Warburton*	Well 29 Fr.2 - 0.26 ***A'*** *Fr. 2a- not Warburton* Well 17 (*lower*) Fr. 2 - 0.29 ***A'*** Fr. 4 - 0.18 ***B'*** Fr. 1a+2a - 0.45 ***C'*** Well 17 (*higher*) *Fr. 2 - not Warburton* *Fr. 2a - not Warburton* Fr. 4a - 0.18 ***B'***	Well 30 *Fr. 2 - not Warburton* *Fr. 4 - not Warburton* Fr. 2a - 0.20 ***B'*** Fr. 3a - 0.19 ***B'***

Table 5 *Sandstone cores that have received an oil charge from the Warburton Basin show a similar pattern of benzocarbazole a/(a+c) ratios in comparable residual oil fractions. Hutton residual oils exhibit an A'B'C' trend that is similar to the ABC trend of Toolachee and Patchawarra Fm. residual oils, but seem to have migrated a longer distance.*

Table 5 compares the benzocarbazole *a/(a+c)* ratio of residual oils from throughout the Cooper and Eromanga Basins in the Gidgealpa area that contain a pre-Permian component. Interestingly, a very consistent trend is observed. All Cooper Basin sandstone cores (i.e. Patchawarra and Toolachee Fm.) received a medium far migrated (BC = 0.30) charge (***B***), followed by a less far migrated (BC = 0.39-0.42) charge (***A***). The Toolachee sample from well 8, being the only sample that contains detectable benzocarbazoles in its first pore-filling residual oils, has oldest residual oil fractions that are characterised by BC values of 0.60, indicating an extremely short migration distance, or a lowered benzocarbazole fractionation behaviour during secondary migration. This charge will henceforth be referred to as charge ***C***.

Those sandstone cores from the Hutton Sandstone that bear a pre-Permian signal exhibit exactly the same trend, but residual oils appear to have consistently migrated further, which is indicated by generally lower benzocarbazole *a/(a+c)* values. These further migrated charges will be referred to as charge ***A'***, ***B'*** and ***C'***.

Since very little is known about the true source potential of Warburton Basin source rocks and its spatial distribution, sensible reconstruction in terms of oil charges from the Warburton Basin are hard to establish. The first charge, *C* and *C'*, are represented by notably high BC values that would in fact suggest *in situ* generated bitumen. As the Toolachee formation source rock samples that was drilled in the study area are currently only marginally mature to early mature for oil generation, an *in situ* generation of charge *C* can be excluded. It is more likely that a deep Warburton source, located somewhere underneath the Gidgealpa Ridge entered the oil generative window while the Gidgealpa source rocks were still immature. The virtually absent fractionation suggests that non-sealing faults that extend from the Cooper into the Warburton sequence acted as migration conduits and allowed fast and efficient transport of the Warburton oil charge. Once arrived in the Cooper Basin sedimentary sequence, which is characterised by much dispersed organic matter, fractionation processes soon affected the migrating charge, leading to a lowered BC value by the time that the Warburton charge reached the Hutton Sandstone.

While the subsequently following Warburton charge B seems to have travelled a long distance (BC = 0.30 in charge B; 0.17-0.20 in charge B') the fractionation that is induced by Permian coal measures is observed again. This leads to the benzocarbazole *a/(a+c)* ratio variation between charge B in Permian sandstone pores, and charge B' in Hutton sandstone pores. The migration distance of charge A was, again, shorter. The discrepancy between Permian (A) and Jurassic samples (A') is still observed. More information on the origin and migration of Warburton Basin oils can not be extracted from the data currently available. The consistent trend that is observed throughout a range of samples however suggests that probably more than one kitchen area and consequently various mechanisms of expulsion and migration will have to be encountered.

7.3.2 Family one versus Family two oils

The residual oil samples No. 2a and 3a from well 7, which have not received any input from the Warburton Basin, confirm the Toolachee Formation as a source of Cooper Basin Family 2 oils. They indicate that the first generated oil that was expelled from source intervals in the Toolachee Formation has a low mature signal.

The Patchawarra Formation released Cooper Basin Family 1 oils at somewhat higher maturities than the Toolachee Formation, when the latter expelled its Family 2 oils. Could Cooper Basin Family 2 oils represent a low mature charge from the Patchawarra Formation? The analyzed core (Fig. 56) excludes this idea. The first pore-filling charge that passed through sandy intervals of the Patchawarra Formation source rocks was not a fluid in the maturity range of a Family 2 oil as in the case of the Toolachee sample (Fig. 53), but rather a fluid of higher maturity. The maturity gradient of the sequentially extracted bitumina (see 2-/1- methylphenanthrene in Fig. 56) reflects the maturation of the source rock.

The higher maturity of Family 1 oils can probably be attributed to the retention of oils in Patchawarra coals, where these could mature in-between generation and expulsion, which occurred in gaseous solution.

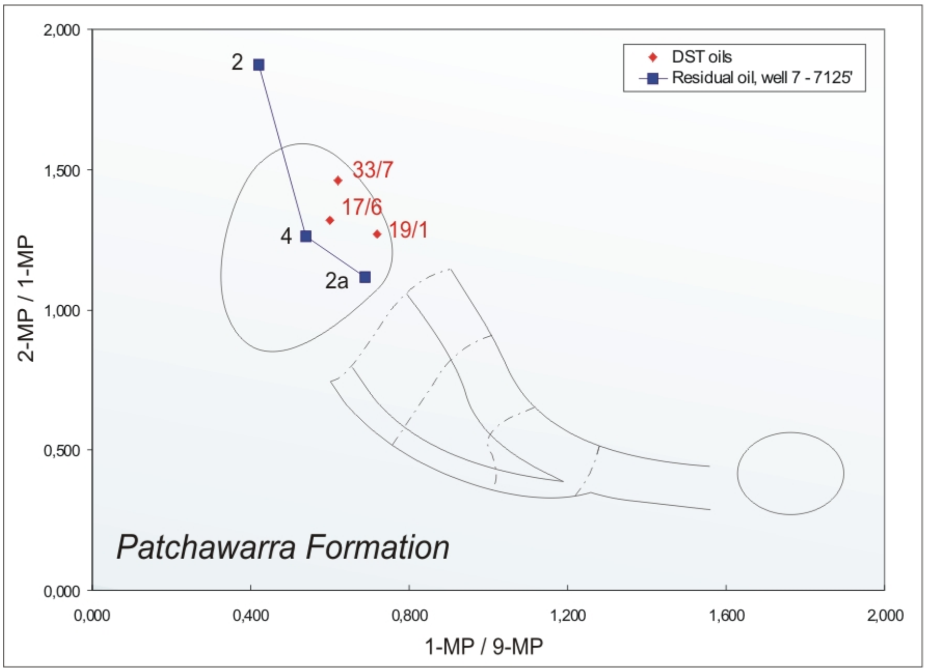


Figure 56 *The Patchawarra Formation has clearly not received any input from other source rocks. DST oils and residual oils plot closely together, while the sequentially extracted residual oils exhibit a trend of increasing maturity that is in agreement with continuous subsidence of the source kitchen.*

7.4 Synopsis

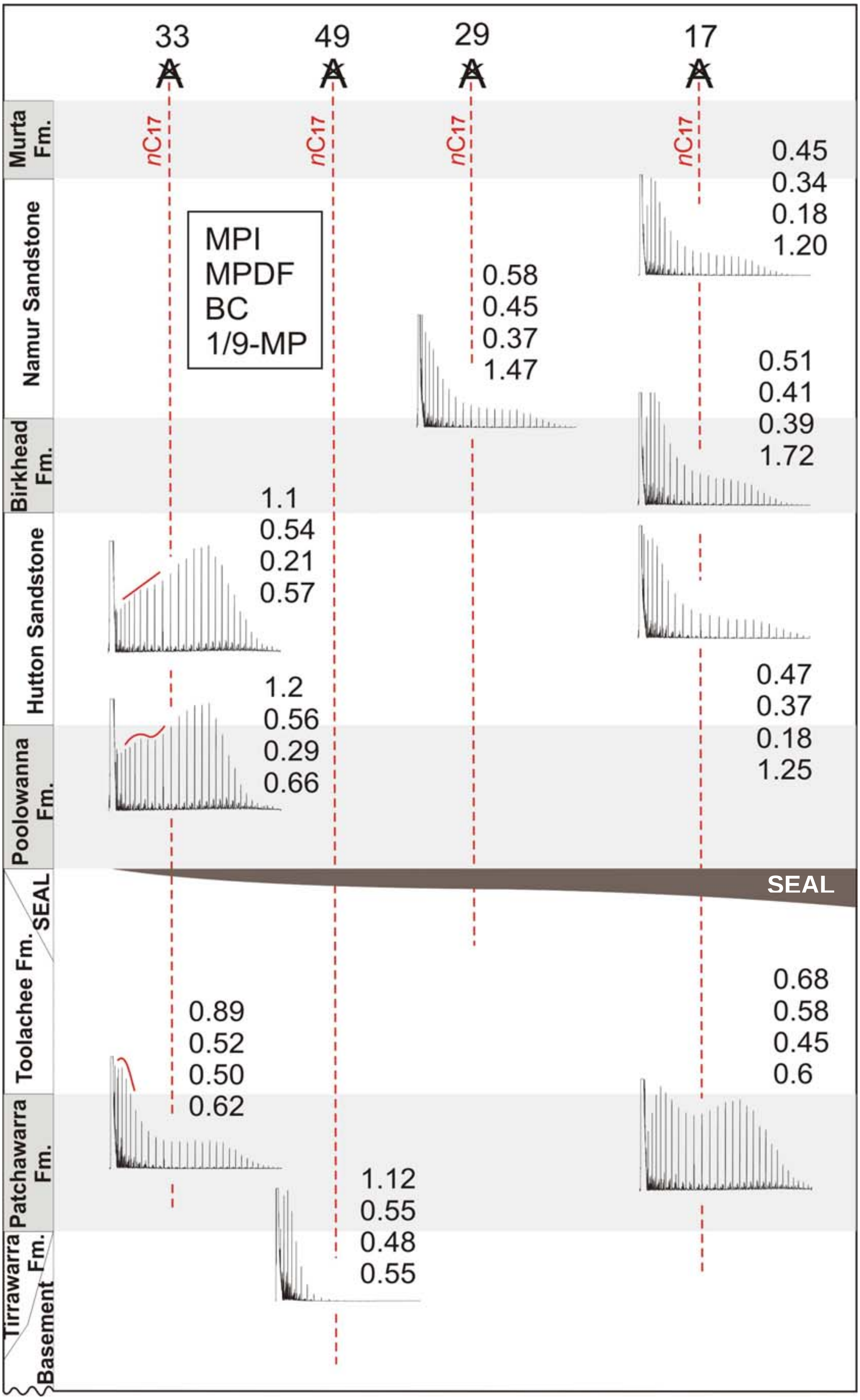


Figure 57 *Selected GC traces from the southern oil pool cluster (well 33 and 49) and the northern cluster (well 29 and 17). See figure 7 for the location of the wells.*

Figure 57 represents a schematic cross section through the southern Gidgealpa Dome. Wells 33 and 49 correspond to the southern cluster of oil pools and well 17 and 29 to the northern cluster of oil pools. These clusters formed due to two culminations in dome geometry and will henceforth be referred to as the northern and southern cluster respectively.

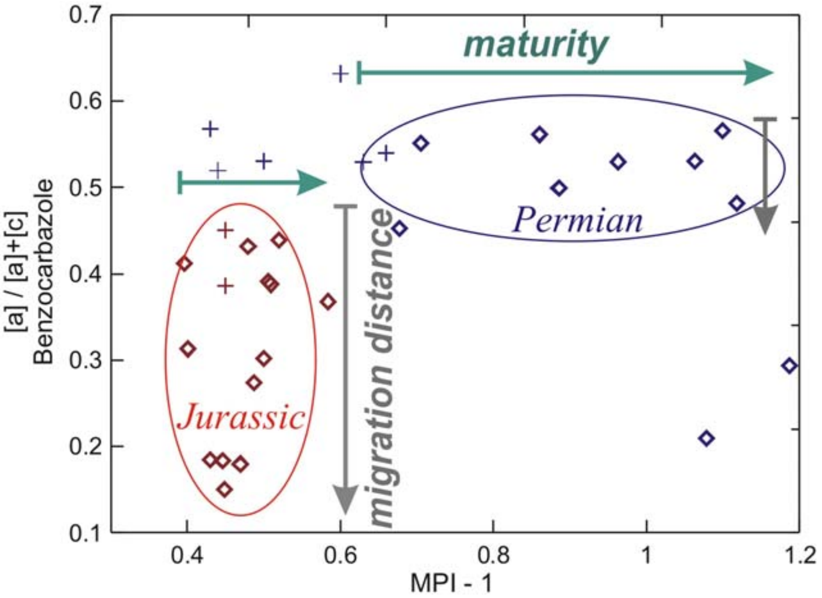


Figure 58 *Cooper Basin oils generally exhibit large maturity variations but a uniformly short migration distance, indicating their origin from a nearby deep trough (eastern source kitchen). Eromanga Basin oils are characterized by similarly low maturity values but highly varying migration distances, suggesting that they were sourced by an extensive and shallow source kitchen.*

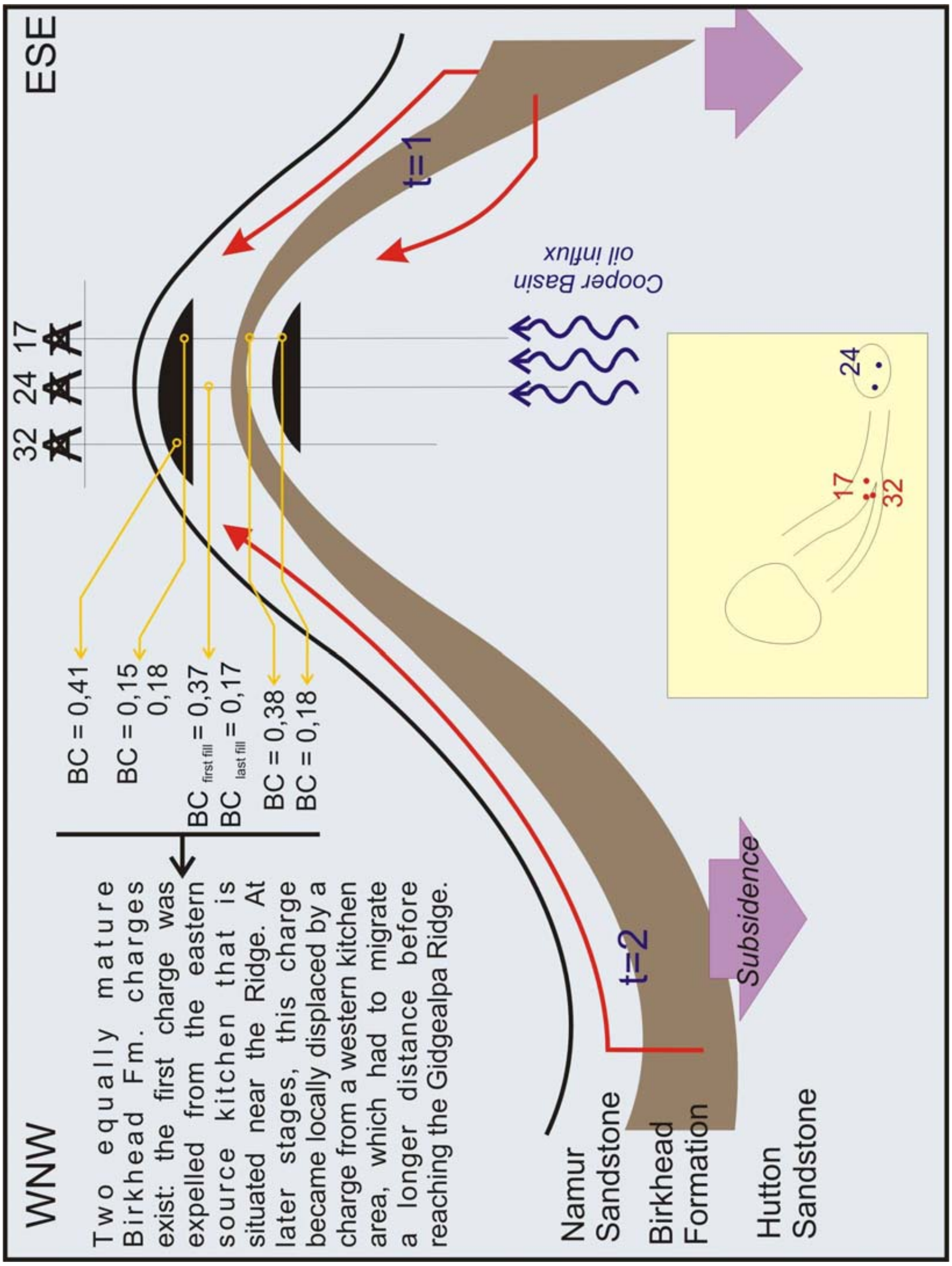
Birkhead charges

The Eromanga sequence only contains oil accumulations in the northern cluster, which was filled by two discrete Birkhead oil charges. The first Jurassic charge was release from the eastern source kitchen and migrated a short distance before arriving at the Gidgealpa Ridge. Here it passed the southern cluster, leaving some residual oil traces, to accumulate in the northern cluster. The second charge was released from a western source kitchen and directly filled the northern cluster, locally displacing the oil from the first charge, without ever having passed through the southern cluster. Hence two BC values (around 0.4 and around 0.17) occur in the northern cluster, while only values around 0.4 occur in the southern cluster. Migration of the second charge was restricted to the Namur Sandstone. In figure 57, the Birkhead oils can be recognised by their high 1-/9- methylphenanthrene ratio (>1). A schematic figure of the Jurassic charging history is given in figure 61.

Permian charges

Permian reservoirs in the southern cluster host gas and gas-condensate accumulations in the Toolachee, Patchawarra and Tirrawarra Formations. Relatively high benzocarbazole *a/(a+c)* ratios suggest that these were produced in the immediate vicinity of the Gidgealpa Ridge (Fig. 59). The overlying Poolowanna Formation also hosts Permian oils. These were however not produced by leakage from underlying accumulations as 1) no gas is present in the

Jurassic sedimentary sequence, 2) Poolowanna-reservoired Permian oils exhibit lower benzocarbazole *a/(a+c)* ratios, and 3) their GC fingerprints do not match (Fig. 57). These ’heavier’ Family 2 oils were generated at further distances from the Gidgealpa Ridge by a Toolachee Fm. source kitchen, and entered the Poolowanna Fm. laterally. The Permian-reservoired gas-condensates exhibit a typical Family 1 signature and were locally produced by the Patchawarra Fm.



Two equally mature Birkhead Fm. charges exist: the first charge was expelled from the eastern source kitchen that is situated near the Ridge. At later stages, this charge became locally displaced by a charge from a western kitchen area, which had to migrate a longer distance before reaching the Gidgealpa Ridge.

Figure 59 *The Birkhead Formation has expelled two oil charges from kitchen areas that are situated East, respectively West of the Gidgealpa Ridge. Their charges can be separated by the migration distance as inferred from the benzocarbazole a/(a+c) ratio.*

In contrast to the Nappamerri Formation, which is a tight seal that separates the Cooper from the Eromanga sedimentary sequences, intra-Poolowanna Formation shales do not have optimum sealing capacities and leaked recently, allowing Permian oil to escape into the overlying Hutton Sandstone (Fig. 57). The northern cluster of reservoirs was not affected since the Poolowanna Fm. here contains no oil accumulation.

The Permian oil that is reservoired in Permian strata beneath the northern cluster of oil pools interestingly appears to be a mixture of Permian Family 1 and 2 oils (Fig. 57) as indicated by its bimodal *n*-alkane distribution. The Family 2 in the Poolowanna Fm. probably entered from the East. This is supported by the fact that the Toolachee Formation is characterised by mainly shaly lithologies, which are thought to having produced the heavier Family 2 oil, in the Wooloo Trough area (East of the Gidgealpa Ridge) while it is characterised by mainly coaly lithologies in the Patchawarra Trough (West of the Gidgealpa Ridge).

Warburton Basin oil charges

A number of residual oils that were recovered from sandstone cores from the Permian Toolachee and Patchawarra Formation, and from the Jurassic Hutton and Birkhead Formations, were shown to contain a pre-Permian component that is thought to having been sourced by Warburton Basin source rocks. Very restricted knowledge of the source potential and distribution of source rocks in the Warburton Basin sequence make it hard to reconstruct the migration of these charges. However, a consistent trend was observed throughout all extracted cores, suggesting that the first charge was sourced in the immediate vicinity of the Gidgealpa Ridge and probably migrated along non-sealing faults where minimal fractionation processes occurred. This has happened before the Permian source rocks entered the oil generative window. Interestingly, also a very recent charging from the Warburton Basin can be detected. However, no sensible reconstruction of migration pathways was possible. Permian-reservoired pre-Permian-generated residual oils have consistently higher benzocarbazole $a/(a+c)$ ratios than Jurassic-reservoired pre-Permian residual oils. This indicates that strong molecular fractionation processes occur during petroleum migration through coaly sediments.

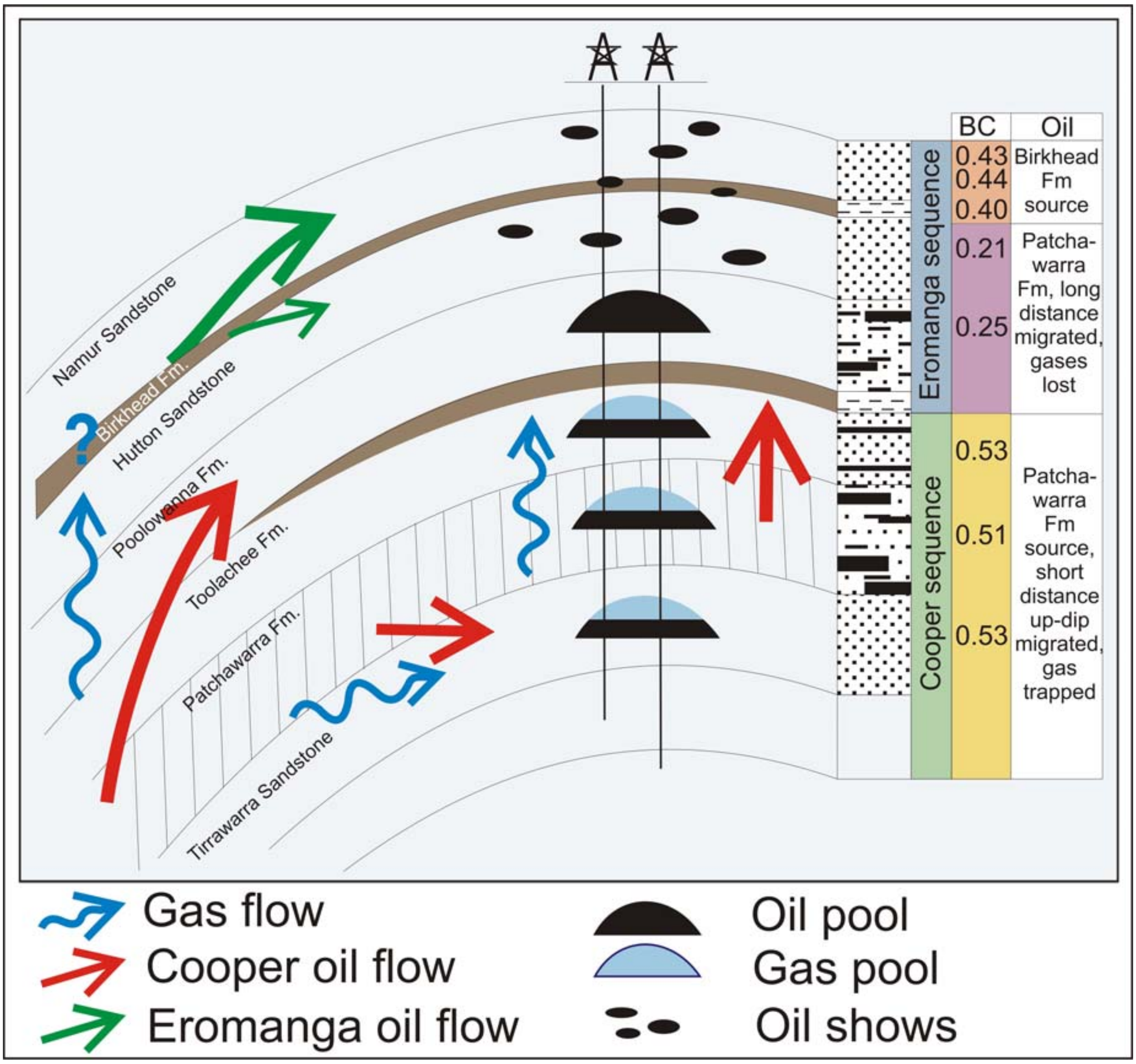


Figure 60 *A schematic cross section through the southern cluster of oil pools shows the secondary migration routes of Permian and Jurassic oils. Absence of gaseous hydrocarbons between the Nappamerri and Birkhead seals indicates a different source to underlying accumulations. This thesis is supported by the migration distance as inferred from the benzocarbazole ratio.*

CHAPTER EIGHT

Conclusions

Source rock characteristics

Source rock samples occur in the Eromanga, Cooper and Warburton Basin sedimentary sequence. All three pre-Permian Warburton Basin source rocks were deposited under reducing conditions; the Cambrian Dolomite under the strongest reducing conditions. In contrast to source rocks from the Cooper and Eromanga Basins, which are characterized by humic kerogen, the Warburton Basin source rocks received an algal input and the Cambrian Dolomite is characterized by mainly algal dominated kerogen.

DST oil characteristics

Evaluation of DST oils revealed the contamination of Permian oils that are reservoired in the Poolowanna and Epsilon Formations by indigenously generated petroleum. Both the Poolowanna and the Epsilon Formation are capable of producing small amounts of petroleum *in situ* and contaminate the Patchawarra- or Toolachee-sourced oils that are reservoired in these strata with a distinct geochemical signature.

Carbazole distribution

During maturation of source rocks, carbazole concentrations decrease consistently. This was not observed in any previous studies and is attributed here to dilution with newly-generated hydrocarbons before expulsion occurs.

The distribution of alkylated carbazoles was shown to depend mainly on source facies. Ratios of 1,7-/1,6- dimethylcarbazole, 3-/2- methylcarbazole and 1,8-dimethylcarbazole /(1,8-dmc+1-ethylcarbazole) are capable of discriminating between residual oils that contain a pre-Permian Warburton-sourced component and residual oils that do not.

The benzocarbazole *a/(a+c)* ratio of oils is not dependent on either facies or maturity. A parallel decrease in the ratio and in absolute benzocarbazole concentrations shows that the benzocarbazole *a/(a+c)* ratio is controlled by fractionation processes during secondary migration. Oils that were contaminated by petroleum that was produced *in situ* in the reservoir feature elevated benzocarbazole *a/(a+c)* ratios, indicative of a short migration distance.
While the distribution of nitrogen-shielded, -partially shielded and -exposed isomers in residual oils can be related to fractionation processes during secondary migration, the similarity of DST oils and source rock extract did not allow a conclusive statement.

Contribution of Warburton Basin source rocks

A number of residual oils feature carbazole signatures that suggest these oils to contain a pre-Permian component. This indicates that the Warburton Basin contains source rocks that are capable of generating petroleum, and that this petroleum has participated in the oil play of the Cooper/Eromanga Basins. Two charges are recognised, of which the last has entered the Gidgealpa Ridge very recently from nearby sources, as indicated by the high benzocarbazole *a/(a+c)* ratio. Restricted information about the Warburton Basin, however, precludes a sensible reconstruction of the charging history.

Oil charges from the Birkhead Formation

The Birkhead Formation has expelled two oil charges of a similarly low maturity. The first charge was released from a source kitchen to the east of the Gidgealpa Ridge and migrated a short distance through the southern cluster of reservoirs to reach the northern cluster. A second charge was released from a western source kitchen and had to migrate a longer distance before reaching the Gidgealpa Ridge. Upon arrival at the northern cluster of reservoirs it locally displaced the first charge. Due to the Gidgealpa dome geometry, the southern cluster of reservoirs has not witnessed the second charge.

Origin of Cooper Basin Family 1 and Family 2 oils

Sequential extraction of intra-source rock sandstone cores from the Toolachee and Patchawarra Formations, respectively, have shown that while the Toolachee Formation definitely is the source of Cooper Basin Family 2 oils, the Patchawarra Formation can be unambiguously tied to the production of Cooper Basin Family one oils. It can be excluded that Family two oils represent an immature charge from the Patchawarra Formation.

Seal failure in the Gidgealpa Field

Permian oil accumulations that are reservoired within the Poolowanna Formation are sealed exclusively by intra-Poolowanna Formation shales. Spilling of oil from the Poolowanna oil pools to the overlying Hutton Sandstone indicates failure of the Poolowanna seals, which must have occurred recently.

Oil-condensate charges from Cooper Basin source rocks

Oil that is reservoired within the Permian section of the Gidgealpa Ridge and sealed by the Triassic Nappamerri Formation appears to be exclusively Permian-sourced and has not received any input from Jurassic oils.

The overlying Poolowanna Formation also hosts Permian oils that were, however, not spilled from the underlying oil pools. The Permian oil accumulations are overlain by a gas leg, while no gas was encountered in the overlying Poolowanna and Hutton Formations. The benzocarbazole *a/(a+c)* ratio suggests that the Permian reservoired oils were sourced from nearby kitchens and did not migrate a far distance. The Poolowanna-reservoired Permian oil is characterised by higher migration distances, suggesting that it has entered the Gidgealpa Ridge laterally from regions where the Nappamerri seal is absent and gases were lost.

Future work

This study has provided the first conclusive evidence for the participation of the Warburton Basin in the oil play of the Cooper/Eromanga Basins. Although currently not an exploration target, further investigation of the Warburton Basin appears promising.

The use of sequentially extracted residual oils in reservoir geochemical studies is an extremely efficient way of reconstructing the charging history an oil field. As, however, most residual oils are characterised by minor extract yields and a high percentage of polar compounds, conventional biomarker analyses are troubled. The finding of facies-dependent markers in the NSO fraction of oils, as demonstrated in this study, is a constructive motivation for further research into the facies and maturity dependency of NSO compounds.

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APPENDIX I

Abbreviations and Units

Abbreviations

Ali.	Aliphatic (saturated) hydrocarbons
Aro.	Aromatic hydrocarbons
ASE	Accelerated Solvent Extraction
BC	Benzocarbazole a/(a+c) ratio
BIF	Banded Iron Formation
cf.	Cited from
DCM	Dichloromethane
DST	Drill Stem Test
Eh	Oxidising potential
FID	Flame Ionizing Detector
Fm	Formation
GC	Gas Chromatography
Gidg.	Gidgealpa
GMI	Gidgealpa- Merrimellia- Innamincka
HC	Hydrocarbons
HPLC	High Performance Liquid Chromatography
HP-5	Hewlett Packard -5 GC column
LC	Liquid Chromatography
m/z	Atomic mass-to-charge ratio
Ma	Million years before present
MP	Methylphenanthrene
MPDF	Methyl Phenanthrene Distribution Factor
MPLC	Medium Pressure Liquid Chromatography
MS	Mass Spectrometry
My	Million years, absolute
NSO	Nitrogen-Sulphur-Oxygen
OM	Organic Matter
P	Phenanthrene
Ph	Phytane
PIRSA	(department of) Primary Industries and Resources, South Australia
Pr	Pristane
Rc	Calculated vitrinite reflectance (from MPI-1)
Ro	Mean of maximum vitrinite reflectance
SA	South Australia
SFTE	Sequential Flow Through Extraction
SIM	Selective Ion Monitoring
SPE	Solid Phase Extraction
Sst.	Sandstone
TC	Total Carbon
TLC	Thin Layer Chromatography
TOC	Total Organic Carbon

Units

°API	Degree ’American Petroleum Industry’ (measurement of oil density)
°C	degree Celsius
eV	electron volt
µg	microgram
µl	microlitre
cm	centimetre
kg	kilogram
km	kilometre
m	metre
m^3	cubic metre
mg	milligram
min	minute
ml	millilitre
s	second

APPENDIX II

Data Tables

Biomarker Ratios

Well	Sample	Depth [ft.]	Formation				%ββ					C35 / C31	C31 / C30	% sterane (ααS + ααR)		
	No.			MPI - 1	1-mp/9-mp	2-mp/1-mp	C_{29} sterane	Ts / Tm	Pr / Ph	Pr / nC_{17}	Ph / nC_{18}	hopane	hopane	C27	C28	C29
Source rocks																
4		6960	Toolachee	0.44	0.29		27.10	0.05	3.53	0.63	0.16	0.11	0.41	1.32	15.51	83.18
4		7097	Patchawarra	0.5	0.58		29.56	0.07	3.48	1.02	0.23	0.13	0.41	0.51	14.34	85.16
5		6888	Toolachee	0.43	0.30		23.23	0.03	3.47	0.91	0.55	0.08	0.48	0.87	11.02	88.11
5		7134,5	Patchawarra	0.63	0.40		12.30	0.07	3.59	2.44	0.29	0.11	0.38	1.05	14.08	84.87
5		7435,2	Tirrawarra	0.63	0.62		38.47	0.64	0.79	0.22	0.16	0.17	0.47	26.33	27.01	46.67
5		7951	Cambr.Dol.	1.54	0.46		45.49	0.88	0.52	0.26	0.43	0.42	0.49	33.41	19.57	47.01
7		6953,3	Toolachee	0.6	0.26		9.65	0.09	3.06	0.49	0.13	0.09	0.27	0.50	13.73	85.77
7		7704	Kalladeina	0.75	0.78		27.77	0.44	0.44	0.32	0.23	0.14	0.49	26.56	21.24	52.20
54		7262,6	Patchawarra	0.66	0.72		19.51	0.50	2.56	0.19	0.05	0.12	0.24	2.12	10.88	87.01
30		6029,2	Birkhead	0.45	1.55		42.04	0.54	2.43	0.26	0.09	0.16	0.24	6.86	6.97	86.18
30		6041,5	Birkhead	0.45	0.91		24.00	0.21	3.36	0.28	0.06	0.14	0.28	0.09	9.94	89.97
DST oils																
17	DST 1	5049'-5069'	Namur	0.45	1.19	0.47	39.35	0.68	1.75	0.19	0.10	0.06	0.25	1.44	13.62	84.94
	DST 2a	5164'-5187'	Namur	0.45	1.1	0.47	42.63	0.67	1.96	0.26	0.12	0.05	0.26	1.47	10.20	88.34
	DST 3	5916'-5950'	Birkhead	0.51	1.72	0.5	44.19	0.64	1.84	0.23	0.38	0.08	0.26	6.28	16.35	77.37
	DST 4	5981'-6000'	Hutton	0.47	1.25	0.54	44.51	0.76	2.26	0.25	0.10	0.05	0.25	1.43	14.98	83.59
	DST 6	7100'-7428'	Patchawarra	0.68	0.60	1.32	44.37	0.68	2.19	0.28	0.11	0.08	0.26	6.34	13.07	80.59
19	DST 1		Patchawarra	0.86	0.72	1.27	47.06	2.16	1.91	0.28	0.11	0.02	0.26	3.02	11.07	85.91
29	DST 1	5968'-6014'	Birkhead	0.58	1.47	0.59	36.95	0.71	1.41	0.16	0.10	0.15	0.31	13.06	13.09	73.85
32	DST 2	5191'-5219'	Namur	0.40	1.11	0.42	44.88	0.60	1.78	0.25	0.13	0.07	0.25	1.64	15.49	82.88
33	DST 1		Hutton	1.08	0.57	1.67	44.05	0.65	2.13	0.27	0.09	0.05	0.23	4.83	10.03	85.14
	DST 4		Poolowanna	1.19	0.66	1.65	44.75	0.76	2.16	0.29	0.10	0.04	0.22	4.16	11.95	83.88
	DST 7		Patchawarra	0.89	0.62	1.46	44.01	0.83	2.74	0.32	0.10	0.08	0.23	1.36	8.55	90.09
34	DST 2	6004'-6024'	Birkhead	0.51	0.97	0.59	39.61	0.79	1.83	0.20	0.10	0.00	0.24	3.47	15.83	80.70
41	DST 1		Tirrawarra	0.96	0.67	1.24	39.89	0.80	2.39	0.26	0.09	0.05	0.22	2.40	8.51	89.10
	DST 3		Toolachee	1.06	0.69	1.56	49.34	0.84	1.32	0.09	0.05	0.11	0.25	4.79	12.37	82.84
42	DST 6	6006'-6030'	Hutton	0.49	1.13	0.58	50.39	0.72	2.63	0.27	0.10	0.00	0.24	0.91	20.11	78.98
	DST 7	5204'-5217'	Namur	0.40	1.46	0.42	36.94	0.66	2.46	0.27	0.10	0.07	0.25	0.29	13.91	85.80
44	DST 2		Hutton	0.50	1.15	0.58	66.90	0.78	1.83	0.20	0.10	0.05	0.24	4.62	13.60	81.78
46	DST 3		Poolowanna	0.26	0.61	0.50	40.00	1.05	1.95	0.29	0.13	0.02	0.24	1.58	9.94	88.49
	DST 6		Hutton	0.43	1.05	0.52	41.33	0.69	1.88	0.21	0.10	0.09	0.26	3.18	12.36	84.46
49	DST 1	6626'-6648'	Poolowanna	1.12	0.55	1.67	38.61	0.73	1.96	0.27	0.13	0.00	0.25	1.95	11.51	86.54
	DST 3		Epsilon	0.71	0.63	1.25	44.42	0.69	5.79	0.40	0.09	0.26	0.32	29.91	24.78	45.31
54	DST 4	5188'-5212'	Namur	0.48	1.55	0.48	43.98	0.65	1.47	0.16	0.10	0.06	0.24	3.65	14.50	81.85
	DST 6	5084'-5100'	Namur	0.52	1.56	0.48	43.32	0.66	1.87	0.33	0.14	0.06	0.25	0.70	13.39	85.91
55	DST 1		Poolowanna	1.10	0.61	1.53	37.04	0.71	2.04	0.29	0.13	0.30	0.32	18.11	16.45	65.44

Phenanthrene data

Well	Sample No.	fraction	Depth [ft.]	Formation	MPI - 1	1-mp/9-mp	2-mp/1-mp
Residual oils							
7	45	2	6977'5"	Toolachee	1.13	0.64	1.23
		4			1.16	0.70	1.27
		2a			0.56	0.65	0.90
		3a			0.44	0.84	0.40
7	47	2	7125'	Patchawarra	1.16	0.42	1.87
		4			0.91	0.54	1.26
		2a			1.05	0.69	1.12
7	48	2	7288'1"	Tirrawarra	1.11	0.76	1.11
		6			2.00	0.52	1.64
		10			1.60	0.50	1.54
		14			1.23	0.48	1.42
		2a			0.63	0.29	0.93
		4a			1.15	0.38	1.29
		6a			1.14	0.39	1.34
8	50	2	6932'10"	Toolachee	0.65	0.28	0.84
		3			0.80	0.34	0.59
		2a			0.91	0.80	0.80
17	51	2	6011'2"	Hutton	0.63	1.42	0.56
		2a			0.66	1.32	0.48
		4a			0.56	0.98	0.44
17	52	2	6086'5"	Hutton	0.37	0.86	0.04
		4			0.39	0.89	0.09
		1a+2a			0.44	0.41	0.41
24	53	2	5189'	Namur	0.55	1.70	0.40
		5			0.59	1.82	0.37
		2a			0.39	0.95	0.39
		3a			0.74	1.21	0.54
29	54	2	6042'2"	Birkhead	0.61	0.92	0.26
		2a			0.59	1.50	0.41
29	56	2	6067'	Hutton	0.90	0.93	0.77
		2a			0.68	1.07	0.50
30	57	2	6026'	Birkhead	0.69	1.59	0.56
		4			0.70	1.46	0.56
		2a			0.68	1.56	0.50
		3a			0.56	1.28	0.40
32	58	2	6012'	Hutton	0.63	1.11	0.50
		2a			0.65	1.21	0.46
32	59	2	6016'4"	Hutton	0.66	1.31	0.56
		2a			0.65	1.15	0.51
		3a			0.61	1.14	0.47
42	61	2	7331'9"	Tirrawarra	1.11	0.60	1.38
		4			0.16	0.36	0.84
		2a			1.18	0.73	1.21
		5a			1.14	0.46	1.26

Carbazoles (ng/g extract)

				carbazole	C1 carbazoles				C2 carbazoles						
									shielded	*partially shielded*					*exposed*
Well	Sample No.	Depth [ft.]	Formation		1-mc	3-mc	2-mc	4-mc	1,8-dmc	1-et	1,3-dmc	1,6-dmc	1,7-dmc	1,4- +1,5- dmc 4- + 3- ec	
Source Rocks															
4		6960	Toolachee	11.167	24.068	4.283	4.370	2.494	7.982	1.317	8.342	9.812	7.817	9.687	7.313
4		7097	Patchawarra	2.423	4.903	1.037	1.241	0.876	1.827	0.415	1.997	2.295	2.300	2.913	2.796
5		6888	Toolachee	3.687	8.665	1.637	2.089	1.348	3.038	0.751	3.278	2.880	3.320	4.382	3.859
5		7134,5	Patchawarra	4.969	9.061	1.964	1.998	1.360	4.512	0.671	4.216	4.131	4.347	5.828	5.257
5		7435,2	Tirrawarra	0.113	0.305	0.060	0.115	0.076	0.234	0.022	0.123	0.160	0.346	0.501	0.464
5		7951	Cambr.Dol.	0.210	0.163	0.047	0.082	0.067	0.113	0.013	0.080	0.079	0.150	0.225	0.306
7		6953,3	Toolachee	11.814	24.904	4.058	4.315	2.239	8.200	1.625	6.751	8.934	8.037	9.157	7.876
7		7704	Kalladeina	0.072	0.202	0.030	0.088	0.079	0.091	0.017	0.059	0.067	0.153	0.239	0.217
54		7262,6	Patchawarra	1.778	4.910	1.255	1.340	0.891	3.070	0.550	3.192	3.790	3.237	4.467	4.398
30		6029,2	Birkhead	0.177	0.225	0.064	0.072	0.046	0.066	0.011	0.085	0.081	0.088	0.126	0.148
30		6041,5	Birkhead	0.156	0.198	0.126	0.084	0.044	0.157	0.026	0.250	0.156	0.195	0.245	0.329
DST oils															
17	DST 1	5049'-5069'	Namur	0.055	0.093	0.047	0.047	0.039	0.070	0.020	0.106	0.106	0.099	0.139	0.258
	DST 2a	5164'-5187'	Namur	0.093	0.134	0.071	0.068	0.054	0.099	0.025	0.151	0.156	0.137	0.191	0.325
	DST 3	5916'-5950'	Birkhead	0.097	0.162	0.063	0.071	0.058	0.095	0.026	0.117	0.136	0.127	0.199	0.316
	DST 4	5981'-6000'	Hutton	0.051	0.133	0.044	0.045	0.033	0.090	0.022	0.112	0.106	0.117	0.165	0.166
	DST 6	7100'-7428'	Patchawarra	0.116	0.287	0.120	0.082	0.057	0.281	0.047	0.285	0.325	0.228	0.342	0.462
19	DST 1		Patchawarra	0.307	0.552	0.240	0.236	0.191	0.552	0.086	0.518	0.564	0.550	0.845	1.148
29	DST 1	5968'-6014'	Birkhead	0.062	0.163	0.070	0.062	0.047	0.104	0.027	0.102	0.132	0.125	0.173	0.229
32	DST 2	5191'-5219'	Namur	0.054	0.035	0.059	0.050	0.075	0.054	0.015	0.097	0.088	0.080	0.114	0.224
33	DST 1		Hutton	0.094	0.087	0.031	0.023	0.017	0.045	0.007	0.052	0.051	0.037	0.067	0.061
	DST 4		Poolowanna	0.132	0.098	0.046	0.031	0.026	0.055	0.009	0.076	0.069	0.054	0.094	0.135
	DST 7		Patchawarra	0.127	0.274	0.149	0.111	0.074	0.292	0.060	0.288	0.307	0.227	0.361	0.446
34	DST 2	6004'-6024'	Birkhead	0.081	0.146	0.095	0.095	0.066	0.114	0.033	0.174	0.169	0.170	0.251	0.405
41	DST 1		Tirrawarra	0.066	0.126	0.088	0.064	0.037	0.163	0.026	0.229	0.208	0.171	0.235	0.417
	DST 3		Toolachee	0.096	0.183	0.122	0.078	0.046	0.166	0.026	0.247	0.234	0.157	0.236	0.391
42	DST 6	6006'-6030'	Hutton	0.050	0.103	0.049	0.053	0.037	0.080	0.021	0.120	0.116	0.116	0.161	0.198
	DST 7	5204'-5217'	Namur	0.125	0.073	0.073	0.049	0.030	0.080	0.015	0.142	0.074	0.101	0.126	0.208
44	DST 2		Hutton	0.042	0.047	0.032	0.031	0.018	0.043	0.013	0.064	0.067	0.060	0.074	0.132
46	DST 3		Poolowanna	0.096	0.117	0.078	0.051	0.041	0.097	0.012	0.117	0.122	0.086	0.151	0.145
	DST 6		Hutton	0.067	0.115	0.047	0.050	0.031	0.077	0.020	0.102	0.084	0.092	0.126	0.151
49	DST 1	6626'-6648'	Poolowanna	x	0.052	0.045	0.021	0.017	0.032	0.007	0.052	0.056	0.032	0.059	0.082
	DST 3		Epsilon	x	0.052	0.020	0.018	0.018	0.027	0.005	0.031	0.031	0.034	0.055	0.098
54	DST 4	5188'-5212'	Namur	0.071	0.032	0.070	0.057	0.038	0.059	0.018	0.118	0.109	0.095	0.137	0.302
	DST 6	5084'-5100'	Namur	0.069	0.070	0.064	0.054	0.038	0.054	0.016	0.105	0.106	0.093	0.129	0.286
55	DST 1		Poolowanna	0.077	0.064	0.044	0.022	0.025	0.038	0.006	0.050	0.052	0.034	0.062	0.086

Carbazole (ng/g extract)

				Benzocarbazoles			C3 carbazoles			SUM		
Well	Sample No.	Depth [ft.]	Formation	B[a]C	B[b]C	B[c]C	*shielded*	*p. shielded*	*exposed*	C1	C2	C3
Source Rocks												
4		6960	Toolachee	5.118	0.262	4.732	15.951	16.614	6.060	35.215	52.270	38.624
4		7097	Patchawarra	0.857	0.060	0.759	4.372	5.929	2.218	8.055	14.544	12.520
5		6888	Toolachee	1.775	0.192	1.352	6.605	8.572	2.700	13.739	21.507	17.877
5		7134,5	Patchawarra	1.168	0.138	1.037	13.137	15.835	6.001	14.384	28.962	34.974
5		7435,2	Tirrawarra	0.154	0.012	0.195	0.938	1.564	0.841	0.556	1.851	3.343
5		7951	Cambr.Dol.	0.144	0.016	0.250	0.318	0.552	0.419	0.360	0.966	1.289
7		6953,3	Toolachee	3.121	0.259	1.818	17.483	20.652	7.173	35.516	50.580	45.308
7		7704	Kalladeina	0.168	0.004	0.124	0.228	0.349	0.166	0.400	0.844	0.743
54		7262,6	Patchawarra	1.397	0.167	1.190	9.988	12.625	4.559	8.397	22.704	27.171
30		6029,2	Birkhead	0.168	0.000	0.266	0.156	0.227	0.140	0.408	0.604	0.523
30		6041,5	Birkhead	0.153	0.000	0.187	0.418	0.638	0.284	0.453	1.359	1.340
DST oils												
17	DST 1	5049'-5069'	Namur	0.010	0.002	0.054	0.368	0.542	0.302	0.226	0.798	1.212
	DST 2a	5164'-5187'	Namur	0.010	0.004	0.043	0.503	0.688	0.308	0.327	1.084	1.500
	DST 3	5916'-5950'	Birkhead	0.022	0.000	0.035	0.423	0.597	0.273	0.354	1.017	1.293
	DST 4	5981'-6000'	Hutton	0.009	0.000	0.039	0.405	0.450	0.175	0.255	0.778	1.031
	DST 6	7100'-7428'	Patchawarra	0.074	0.013	0.089	1.307	1.415	0.578	0.546	1.970	3.300
19	DST 1		Patchawarra	0.128	0.027	0.100	2.371	2.968	1.332	1.219	4.262	6.671
29	DST 1	5968'-6014'	Birkhead	0.018	0.000	0.032	0.407	0.478	0.205	0.342	0.892	1.091
32	DST 2	5191'-5219'	Namur	0.034	0.005	0.048	0.273	0.462	0.251	0.218	0.671	0.986
33	DST 1		Hutton	0.006	0.001	0.022	0.169	0.160	0.075	0.158	0.321	0.404
	DST 4		Poolowanna	0.011	0.002	0.026	0.241	0.311	0.181	0.202	0.492	0.733
	DST 7		Patchawarra	0.048	0.011	0.048	1.249	1.242	0.535	0.608	1.980	3.025
34	DST 2	6004'-6024'	Birkhead	0.046	0.007	0.072	0.698	1.066	0.486	0.402	1.316	2.250
41	DST 1		Tirrawarra	0.090	0.008	0.080	1.440	2.076	1.199	0.316	1.448	4.715
	DST 3		Toolachee	0.109	0.019	0.097	1.164	1.476	0.758	0.430	1.458	3.397
42	DST 6	6006'-6030'	Hutton	0.017	0.000	0.044	0.425	0.487	0.233	0.241	0.812	1.144
	DST 7	5204'-5217'	Namur	0.013	0.001	0.028	0.363	0.524	0.225	0.224	0.746	1.113
44	DST 2		Hutton	0.008	0.000	0.019	0.212	0.342	0.154	0.128	0.453	0.708
46	DST 3		Poolowanna	0.017	0.000	0.030	0.300	0.375	0.124	0.287	0.731	0.799
	DST 6		Hutton	0.005	0.000	0.024	0.285	0.323	0.130	0.243	0.652	0.738
49	DST 1	6626'-6648'	Poolowanna	0.017	0.003	0.019	0.158	0.235	0.101	0.134	0.319	0.494
	DST 3		Epsilon	0.017	0.004	0.014	0.119	0.207	0.138	0.107	0.281	0.464
54	DST 4	5188'-5212'	Namur	0.070	0.010	0.092	0.418	0.743	0.403	0.198	0.838	1.565
	DST 6	5084'-5100'	Namur	0.065	0.010	0.083	0.379	0.706	0.400	0.227	0.789	1.485
55	DST 1		Poolowanna	0.022	0.004	0.017	0.150	0.226	0.103	0.154	0.329	0.479

Carbazoles (ng/g extract)

					carbazole	C1 carbazoles				C2 carbazoles						
										shielded	*partially shielded*					*exposed*
Well	Sample No.	fraction	Depth [ft.]	Formation		1-mc	3-mc	2-mc	4-mc	1,8-dmc	1-et	1,3-dmc	1,6-dmc	1,7-dmc	1,4- +1,5- dmc 4- + 3- ec	
Residual oils																
7	45	2	6977'5"	Toolachee	0.009	0.078	0.008	0.015	0.005	0.167	0.016	0.079	0.053	0.108	0.134	0.116
		4			0.016	0.014	0.004	0.007	0.002	0.019	0.005	0.011	0.012	0.011	0.016	0.024
		2a			0.122	0.100	0.044	0.031	0.028	0.061	0.014	0.034	0.049	0.066	0.075	0.205
		3a			0.069	0.069	0.040	0.025	0.019	0.031	0.009	0.021	0.033	0.031	0.052	0.165
7	47	2	7125'	Patchawarra	0.024	0.063	0.022	0.027	0.024	0.062	0.007	0.040	0.063	0.069	0.107	0.188
		4			0.017	0.015	0.011	0.008	0.004	0.005	0.003	0.007	0.008	0.006	0.011	0.033
		2a			0.043	0.040	0.017	0.013	0.009	0.021	0.004	0.016	0.014	0.018	0.027	0.060
7	48	2	7288'1"	Tirrawarra	x	x	x	x	x	x	x	x	x	x	x	x
		6			x	0.005	0.004	0.004	0.004	x	x	x	x	x	x	x
		10			0.034	0.009	0.007	0.006	0.012	x	x	x	x	x	x	x
		14			x	x	x	x	x	x	x	x	x	x	x	x
		2a			x	0.026	0.007	0.007	0.015	x	x	x	x	x	x	x
		4a			0.010	0.011	x	x	0.007	x	x	x	x	x	x	x
		6a			0.007	0.017	0.017	0.015	0.020	x	x	x	x	x	x	x
8	50	2	6932'10"	Toolachee	0.025	0.064	0.010	0.016	0.011	0.055	0.051	0.019	0.030	0.032	0.030	0.064
		3			0.052	0.103	0.017	0.023	0.020	0.074	0.011	0.027	0.033	0.056	0.070	0.150
		2a			0.306	0.173	0.066	0.124	0.109	0.098	0.018	0.115	0.112	0.223	0.311	0.840
17	51	2	6011'2"	Hutton	x	0.026	0.004	0.004	0.002	0.060	0.006	0.018	0.020	0.026	0.015	0.044
		2a			0.266	x	x	x	x	x	x	x	x	x	x	x
		4a			0.226	0.092	0.061	0.117	0.051	x	x	x	x	x	x	x
17	52	2	6086'5"	Hutton	0.014	0.046	0.007	0.008	0.006	0.043	0.006	0.024	0.019	0.038	0.040	0.039
		4			0.052	0.127	0.013	0.014	0.020	0.066	0.010	0.030	0.035	0.063	0.065	0.113
		1a+2a			0.040	0.103	0.013	0.018	0.020	0.060	0.011	0.030	0.035	0.058	0.065	0.169
24	53	2	5189'	Namur	x	x	x	x	x	x	x	x	x	x	x	x
		5			0.011	0.006	0.007	0.006	0.008	0.011	0.003	0.006	0.013	0.017	0.021	0.086
		2a			0.016	x	x	x	x	x	x	x	x	x	x	x
		3a			0.052	x	x	x	x	x	x	x	x	x	x	x
29	54	2	6042'2"	Birkhead	x	x	x	x	x	x	x	x	x	x	x	x
		2a			0.013	x	x	x	x	x	x	x	x	x	x	x

Carbazoles (ng/g extract)

					carbazole	C1 carbazoles				C2 carbazoles						
										shielded	*partially shielded*					*exposed*
Well	Sample No.	fraction	*Depth [ft.]*	Formation		1-mc	3-mc	2-mc	4-mc	1,8-dmc	1-et	1,3-dmc	1,6-dmc	1,7-dmc	1,4- +1,5- dmc 4- + 3- ec	
Residual oils																
29	56	2	6067'	Hutton	0.043	0.064	0.021	0.040	0.016	0.043	0.006	0.040	0.060	0.028	0.051	0.122
29		2a			0.027	x	x	x	x	x	x	x	x	x	x	x
30	57	2	6026'	Birkhead	0.022	0.053	0.011	0.010	0.007	0.046	0.010	0.032	0.031	0.036	0.028	0.068
30		4			0.160	0.236	0.076	0.072	0.053	0.108	0.026	0.073	0.111	0.123	0.125	0.267
30		2a			0.047	0.101	0.046	0.042	0.031	0.052	0.009	0.042	0.037	0.065	0.082	0.175
30		3a			0.065	0.028	0.021	0.039	0.011	0.029	0.005	0.031	0.032	0.027	0.047	0.098
32	58	2	6012'	Hutton	x	x	x	x	x	x	x	x	x	x	x	x
32		2a			0.073	0.024	0.048	0.032	0.023	0.015	0.005	0.010	0.013	0.022	0.026	0.156
32	59	2	6016'4"	Hutton	0.029	0.085	0.035	0.028	0.020	0.078	0.011	0.038	0.043	0.050	0.044	0.084
32		2a			0.351	0.208	0.189	0.263	0.230	0.142	0.036	0.137	0.197	0.414	0.524	1.762
					x	x	x	x	x	x	x	x	x	x	x	x
42	61	2	7331'9"	Tirrawarra	x	x	x	x	x	x	x	x	x	x	x	x
		4			x	x	x	x	x	x	x	x	x	x	x	x
		2a			x	x	x	x	x	x	x	x	x	x	x	x
		5a			0.099	0.036	0.026	0.044	0.046	0.026	0.006	0.036	0.050	0.096	0.137	0.434

Carbazole (ng/g extract)

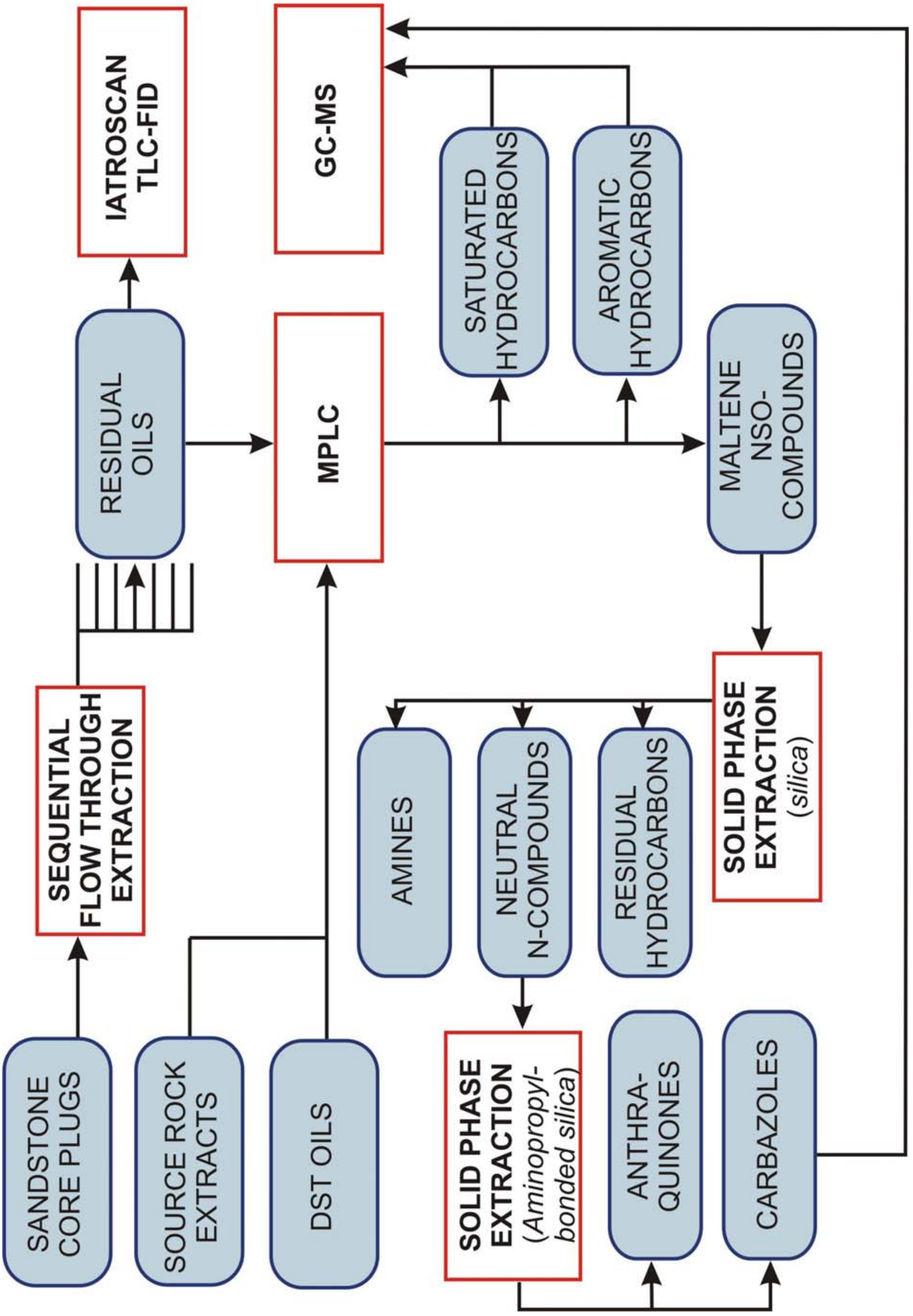
Well	Sample No.	fraction	Depth [ft.]	Formation	Benzocarbazoles			C3 carbazoles			SUM		
					B[a]C	B[b]C	B[c]C	*shielded*	*p. shielded*	*exposed*	C1	C2	C3
Residual oils													
7	45	2	6977'5"	Toolachee	0.019	0.003	0.028	0.430	0.282	0.104	0.106	0.672	0.817
		4			0.002	0.001	0.004	0.049	0.035	0.016	0.028	0.099	0.101
		2a			x	x	x	0.156	0.188	0.130	0.203	0.505	0.474
		3a			x	x	x	x	x	x	0.153	0.342	x
7	47	2	7125'	Patchawarra	0.009	0.001	0.012	0.244	0.325	0.221	0.136	0.535	0.789
		4			0.003	0.002	0.013	0.031	0.034	0.026	0.038	0.074	0.091
		2a			0.007	0.018	0.013	0.079	0.103	0.094	0.079	0.159	0.276
7	48	2	7288'1"	Tirrawarra	0.010	0.021	0.035	0.091	0.090	0.098	x	x	0.280
		6			0.032	0.014	0.050	x	x	x	0.017	x	x
		10			0.050	0.014	0.065	x	x	x	0.034	x	x
		14			0.005	0.001	0.006	x	x	x	x	x	x
		2a			0.078	0.035	0.127	x	x	x	0.055	x	x
		4a			0.078	0.038	0.015	x	x	x	x	x	x
		6a			0.047	x	0.013	x	x	x	0.069	x	x
8	50	2	6932'10"	Toolachee	0.036	0.005	0.055	x	x	x	0.102	0.282	x
		3			0.036	0.015	0.086	0.199	0.239	0.200	0.163	0.422	0.638
		2a			0.020	0.100	0.014	0.455	1.027	0.965	0.473	1.718	2.447
17	51	2	6011'2"	Hutton	0.008	0.002	0.027	0.084	0.046	0.030	0.037	0.189	0.161
		2a			x	x	x	#WERT!	#WERT!	#WERT!	x	x	x
		4a			0.141	0.000	0.668	#WERT!	#WERT!	#WERT!	0.321	x	x
17	52	2	6086'5"	Hutton	0.014	0.001	0.036	0.069	0.050	0.029	0.067	0.208	0.147
		4			0.033	0.010	0.154	0.125	0.098	0.130	0.174	0.381	0.353
		1a+2a			0.022	0.016	0.027	0.141	0.131	0.195	0.154	0.428	0.467
24	53	2	5189'	Namur	0.001	0.001	0.005	x x	x x	x	x	x	x
		5			0.003	x	0.005	0.058	0.085	0.106	0.028	0.157	0.248
		2a			x	x	x	x	x	x	x	x	x
		3a			x	x	x	x	x	x	x	x	x
29	54	2	6042'2"	Birkhead	x	x	x	x	x	x	x	x	x
		2a			0.006	0.001	0.004	x	x	x	x	x	x

Carbazole (ng/g extract)

					Benzocarbazoles			C3 carbazoles			SUM		
Well	Sample No.	fraction	Depth [ft.]	Formation	B[a]C	B[b]C	B[c]C	*shielded*	*p. shielded*	*exposed*	C1	C2	C3
Residual oils													
29	56	2	6067'	Hutton	0.025	0.002	0.071	0.105	0.121	0.081	0.140	0.351	0.307
		2a			x	x	x	x	x	x	x	x	x
30	57	2	6026'	Birkhead	0.020	0.003	0.053	0.080	0.062	0.053	0.082	0.251	0.195
		4			0.184	0.025	0.424	0.259	0.318	0.260	0.437	0.834	0.836
		2a			0.0281	0.009766	0.10933	0.161	0.190	0.161	0.220	0.462	0.511
		3a			0.026	0.005	0.110	0.090	0.122	0.087	0.098	0.270	0.299
32	58	2	6012'	Hutton	x	x	x	x	x	x	x	x	x
		2a			0.005	0.004	0.045	0.080	0.080	0.098	0.126	0.246	0.258
32	59	2	6016'4"	Hutton	0.0275	0.001991	0.09026	0.133	0.109	0.056	0.168	0.349	0.298
		2a			0.055	#WERT!	0.156	0.798	1.469	1.494	0.890	3.211	3.762
					x	x	x	x	x	x	x	x	x
42	61	2	7331'9"	Tirrawarra	0.002	0.010	0.006	0.022	0.027	0.027	x	x	0.076
		4			x	x	x	0.066	0.049	0.066	x	x	0.181
		2a			0.006	0.030	0.014	x	x	x	x	x	x
		5a			x	x	x	0.238	0.541	0.577	0.153	0.785	1.356

APPENDIX III

Flow Chart


SANDSTONE CORE PLUGS
SOURCE ROCK EXTRACTS
DST OILS
SEQUENTIAL FLOW THROUGH EXTRACTION
RESIDUAL OILS
IATROSCAN TLC-FID
MPLC
GC-MS
SATURATED HYDROCARBONS
AROMATIC HYDROCARBONS
MALTENE NSO-COMPOUNDS
SOLID PHASE EXTRACTION (silica)
AMINES
NEUTRAL N-COMPOUNDS
RESIDUAL HYDROCARBONS
SOLID PHASE EXTRACTION (Aminopropyl-bonded silica)
ANTHRA-QUINONES
CARBAZOLES