Department of Chemistry

Organic geochemistry and novel isotopic approaches of fluvial-deltaic petroleum systems

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This thesis is presented for the Degree of
Doctor of Philosophy
of
Curtin University

July 2017

DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Jaime Cesar
Perth, July 23rd, 2017

ABSTRACT

The North West Shelf of Australia (NWS) is a world class province for gas generation. Potential source rocks of Triassic and Jurassic age in the NWS formed under fluvial-deltaic depositional settings, and contain significant gas/condensate accumulations. However, petroleum system formed under fluvial-deltaic depositional settings, and multiple uncertainties remain about the origin of the fluids, which has been assigned on limited fluid-source correlation data. The fluids in the basins are very light and arise from mixed terrigenous/marine organic-matter sources. The very low concentration of key organic compounds create challenges for fluid-source correlation and limit the differentiation available using traditional biomarker and isotope methods. An example is the Dampier sub-Basin, which has shown hydrocarbon potential in the Late Triassic, Middle and Late Jurassic stratigraphic intervals. However, the source rock for some of the fluids in the Rankin Platform remains uncertain. Therefore, a fundamental discrimination is required to improve our understanding of fluid families and properties, both within the known reservoirs and those yet to be identified, enabling explorationists to evaluate new plays in the NWS region. To generate new insights in this respect, this research aims to provide new molecular and isotopic tools using geosynthetic compounds and certain aromatic compounds that are detectable not only in source rock extracts but also in condensates. It is important to note that the thesis focuses on the description of the parameters and explains how these can be applied. In contrast, the fluid-source correlation studies represent confidential information that, only under approval of joint venture partners, will be released in upcoming publications.

In the Dampier sub-Basin, as well as in many other basins of the NWS, hydrocarbons have originated from land plant dominated organic facies. **Chapter 2** describes a palaeovegetation reconstruction for Dampier, over the the Late Triassic to Late Jurassic time interval. The predominance of retene (conifer marker) over other plant markers such as cadalene (derived from vascular plants in general) and 6-*iso*propyl-1-*iso*hexyl-2-methylnaphthalene (*ip*-iHMN, from bryophytes) indicate that conifer families probably dominated the vegetation. Conifer forests settled during the Late Triassic but did not grow during Early Jurassic times due to very arid conditions following a mass extinction event. Conifer plants began to thrive again in the Middle

to Late Jurassic after a more humid climate was established. Additionally, local changes in the deposition of plant debris were described by the ratio of retene to 1,3,6,7-tetramethylnaphthalene (retene/1,3,6,7-TeMN) in response to shoreline migrations (which, e.g., leads to changes in salinity and drainage patterns). High retene/1,3,6,7-TeMN ratios were recorded for the Middle Jurassic (up to 16 versus 0.6 in the Late Triassic) after abrupt increase of seal level, which suggests a major proximity to the source (conifer forests). The chapter is also the first palaeovegetation reconstruction, covering more than 50 Myr (million years) reported for the Northern Carnarvon Basin; and even though this can only be attributed to regional conditions, the approach might be a reference for other localities at different latitudes.

Another aspect of interest was the identification of the marine versus terrigenous characteristics of the organic matter, as traditional parameters (e.g. pristane: Pr/ phytane: Ph, sterane and hopane distributions) show similar values for the Triassic-Jurassic source rock intervals. **Chapter 3** describes a molecular and isotopic approach to discriminate organic facies using the molecular distribution of combustion-derived polycyclic aromatic hydrocarbons (PAHs) and their stable carbon isotopic composition. The approach also includes other aromatic compounds such as 1,3,6,7-Tetramethylnaphthalene (1,3,6,7-TeMN) and phenenthrene. The relative abundance of the PAHs was plotted against the difference between δ^{13}C values of 1,3,6,7-TeMN and each PAH. Samples that plotted below 0 for $\Delta^{13}C_{\text{(Combustion Marker-1,3,6,7 TeMN)}}$ are related to delta-plain/front-deltaic facies or coaly fluvial deltaic facies (*e.g.* samples from the Mungaroo Formation) whereas the positive region for $\Delta^{13}C_{\text{(Combustion Marker-1,3,6,7 TeMN)}}$ is assigned to transitional facies deposited under an estuarine/lagoonal environment (Brigadier Formation) and marginal marine environment (Legendre Formation). A similar separation for the samples was obtained using phenanthrene and other PAHs [i.e. $\Delta^{13}C_{\text{(Combustion Marker-Phe)}}$]. These new tools represent a non-biomarker approach to take into account for similar fluvial-deltaic systems as well as other cases where biomarker ratios are not discriminant.

Chapters 4 and **5** explore the potential of the molecular distribution of certain compound classes to indicate source rock lithofacies. **Chapter 4** describes how the distributions of benzo[*b*]naphtho[*d*]furans (BNFs: benzo[*b*]naphtho[2,1-*d*]furan, benzo[*b*]naphtho[1,2-*d*]furan, and benzo[*b*]naphtho[2,3-*d*]furan) in source rocks and fluids (crude oil and condensate) may represent a suitable parameter for source rock characterisation and fluid–source rock correlations. The formation of [1,2]BNF seems to be enhanced by clay catalysis. Lower [2,1]/[1,2]BNF ratios (or BNFr) were found in fluvial-deltaic source rocks (~1.2) compared to clay-depleted source rocks from marine environments (e.g. carbonate sequences, ~4.5). Triassic source rocks from the Dampier sub-Basin contain 25% w/w of clay and their BNFr ranges between 0.9 and 1.5. The BNFr increases up to 1.6-2.1 in the Middle-Jurassic source rocks with 14% w/w of clay content, and is the lowest for the Upper Jurassic Dingo Claystone (~0.8) with 29% w/w of clay minerals. The ternary plot of [2,1]-[1,2]-[2,3] BNFs could be applied for fluid-fluid and fluid-source rock correlations although the isomer [2,3]BNF is sometimes absent in the fluids (probably due to a maturity effect yet to investigate).

In **Chapter 5**, drimane-skeleton molecules (C_{15}-decalins), specifically the compounds 1,2,2,5,5-pentamethyl-*trans*-decalin and 1,1,2,5,5-pentamethyl-*trans*-decalin (or rearranged drimanes RD1 and RD2) and 18β(H)-drimane (D), in source rock extracts and petroleum fluids are described in detail. The ratio (RD1+RD2)/D was calculated for samples from the Dampier sub-Basin and compared to other localities reported in the literature. Samples with a higher clay content, e.g. claystones from the Brigadier Formation, exhibited higher rearranged drimane ratio (~6), compared to silty claystone from the Legendre Formation (~2) and silty mudstone from the Yanchang Formation (~2). The effects exerted by thermal maturity of the source rock and redox conditions of the depositional environment for this set of samples were shown to be minimal.

In **Chapter 6**, the research expands its scope to analytical advances for fluid screening, in a combined molecular, compound specific and site specific isotope approach using mononuclear aromatic compounds. Low-molecular-weight (LMW) aromatic hydrocarbons from petroleum have scarcely been studied because of their volatility and their relatively low abundances in source rocks for fluid-source correlations. However, they are important components in condensates which lack biomarkers (e.g. hopanes), and are also slightly more resistant to biodegradation compared to light aliphatics (more widely used for fluid screening of condensates). In this chapter the distribution of ethyltoluenes in fluvial-deltaic condensates is investigated. It showed an enhanced *meta*-selectivity of the *ortho*-*para*-*meta* isomerisation, suggesting a mineral catalytic effect, as it occurs during clay-catalysed synthesis of ethyltoluenes.

Isomers differ up to 6‰ in $\delta^{13}C$ values, however, this difference is not observed in fluids derived from carbonate source rocks. The site-specific isotope analysis of condensates was conducted using a Q-Exactive-GC Orbitrap-based-mass spectrometer. The difference between the isotope ratios of *meta*- and *para*-ethyltoluene, for the molecular ion (*m/z* 120) and the dimethylated fragment (*m/z* 105), indicated that a major isotope substitution occurs at the methyl end of the ethyl substituent in *meta*-ethyltoluene. The structural rearrangement under clay acid catalysis, and carbon-carbon cleavage during thermal evolution explain the isotopic differences detected between isomers. This study provides a new direction in isotope geochemistry of organic molecules (bigger than propane) and is also applicable to other research areas (e.g. environmental forensic and synthesis chemistry).

These findings will significantly contribute to overcome the challenges in defining petroleum systems from fluvial-deltaic depositional settings, and might drive petroleum geochemistry towards alternative parameters that can help address several geochemical interrogations even in marine-dominated facies with terrigenous input.

ACKNOWLEDGEMENTS

I could probably spend an entire chapter to acknowledge everybody who helped me in completing this very important stage of my life. Thank you all for making this journey an unforgettable experience.

Firstly, I would like to thank my supervisor, Prof. Kliti Grice for granting me the opportunity to work with her and the excellent Western-Australia Organic and Isotope Geochemistry Centre, her brilliant guidance and academic support, her generosity in motivating her students and especially offering them with opportunities to conduct high-quality research (*e.g.* participation in conferences and international collaborations with world-recognised laboratories). Kliti definitely is a huge influence in changing her students' lives for the better.

I gratefully acknowledge the Australian Research Council and Woodside Petroleum Ltd. for supporting this research, especially Dr. Daniel Dawson, Dr. Ines Melendez and Dr. Andrew Murray for their direction on studying petroleum systems from the North West Shelf. I also acknowledge the Institute of Geoscience Research for the top-up scholarship.

Special thanks to Geoff Chidlow, Dr. Alex Holman, Dr. Alan Scarlett and Peter Hopper for their technical support during the experimental work. I thank my colleagues, PhD students and post-docs, who created a lovely work environment and always contributed to my research with great discussions. Hendrik, Aileen, Svenja and Chloe were always very encouraging and my PhD life would have not been blissful without Sebastian Naeher and his friendship. Thanks to Matt, Calum, Su, Kuldeep, Gemma, Nannan, Danlei, Yali, Bettina, Prof. Marco and Cornelia for making this journey very enjoyable. Thanks also to my colleagues at the California Institute of Technology for bringing up some joyful working hours. Prof. John Eiler, Max, Laura, Brooke and Camilo made it a time not to forget.

I would also like to thank all the students and staff at Curtin University who helped and made me laugh along this journey. Special thanks to Buddhika and Holly, lovely forensic students that shared their PhD journeys with me. I love you ladies. Thanks

also to Harriet, Ina and Rhys for their support and getting my mind away from research from time to time.

Very special thanks to Ines for helping me to come to Australia, and for being a miracle. Ines and Andres are family to me, the little Venezuela. My housemates have also been my family, making me feel home and helping with organising the best birthday parties. Dayi, Lina, Samantha, Valentin, Aram, Diana and Juan occupy a very special place in my heart.

This thesis would not be possible without the support from Bianca, Tina, Flora, Mariela, and Charity as well. A lifetime is not enough to thank you for your companionship, helping me grow, loving me, and keeping me sane. Fay, Josh, and Russell, thank you for being there for me.

I foremost dedicate this thesis to my family: my mother Carmen for letting me fly, my siblings Jairo, Esther, Elena, and Raquel, and my father Jose for loving me. Finally, I dedicate this work to my country, Venezuela, and to those who sacrificed their lives defending our democracy.

PRIMARY PUBLICATIONS

The chapters integrating this thesis correspond to papers published or accepted with minor changes, submitted or in preparation, and are listed below.

Chapter 2

Cesar, J., Grice, K. (2017). New insights from plant biomarkers for Triassic-Jurassic palaeovegetation reconstructions in the Northwest Shelf of Australia. *Palaeogeography, Palaeoclimatology, Palaeoecology*, submitted (2017).

Chapter 3

Cesar, J., Grice, K. (2017). $\delta^{13}C$ of polycyclic aromatic hydrocarbons to establish the facies variations in a fluvial deltaic Triassic record (Dampier sub-Basin, Western Australia). *Organic Geochemistry, 107*, 59-68.

Chapter 4

Cesar, J., Grice, K. (2017). The significance of benzo[*b*]naphtho[*d*]furans in fluids and source rocks: New indicators of facies type in fluvial-deltaic systems. *Organic Geochemistry*, in press (2017).

Chapter 5

Cesar, J., Grice, K. (2017). Drimane-type compounds in source rocks and fluids from fluvial-deltaic depositional settings in the North-West Shelf of Australia. *Organic Geochemistry*, submitted (2017).

Chapter 6

Cesar, J., Eiler, J., Dallas, B., Chimiak, L., Raiteri, P., Grice, K. (2017). Molecular distribution and site-specific isotopes of ethyltoluenes in fluids as a diagnostic tool for lithofacies of source-rocks. In preparation for submission to *Nature Scientific Reports*.

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STATEMENT OF CONTRIBUTION OF OTHERS

The work presented in this thesis was primarily designed, experimentally executed, interpreted, and individual manuscripts were prepared by the firs author (Jaime Cesar). Contributions by colleagues are described below.

Chapters 2 and 3

Jaime Cesar and Kliti Grice designed the experiments. Jaime Cesar conducted all the experiments (sample preparation and analysis). The source rocks correspond to open-source cores from the Perth Core Library, and were sampled by Jaime Cesar with guidance from Kliti Grice. The writing of the manuscripts representing chapters 2 and 3 was conducted by Jaime Cesar and reviewed by Kliti Grice who also participated in the discussion and interpretation of the results. Kliti Grice provided analytical facilities. Financial support was provided by the Institute of Geoscience Research (TIGeR) and Woodside Energy Ltd.

Chapters 4 and 5

Jaime Cesar and Kliti Grice designed the experiments. Jaime Cesar conducted all the experiments (sample preparation and analysis). The source rocks correspond to open-source cores from the Perth Core Library, and were sampled by Jaime Cesar, with guidance from Kliti Grice. Woodside Energy Ltd. provided the fluid samples. The writing of the manuscripts representing Chapters 4 and 5 was conducted by Jaime Cesar and reviewed by Kliti Grice who also participated in the discussion and interpretation of the results. Kliti Grice provided analytical facilities. Infrastructural support was also provided by John de Leater Centre (Curtin University’s Microscopy & Microanalysis Facility), and financial support was provided by the Institute of Geoscience Research (TIGeR) and Woodside Energy Ltd.

Chapter 6

Kliti Grice and Jaime Cesar conceived the research and chose relevant samples. Jaime Cesar performed all the experiments at Curtin University and the California Institute of Technology. Woodside Energy Ltd. provided the fluid samples. John Eiler and Jaime Cesar designed the site-specific isotope analysis with academic and technical support from Brooke Dallas and Laura Chimiak at Caltech. Computational simulations were developed by Paolo Raiteri at Curtin University. All authors analysed the results and reviewed the manuscript. Kliti Grice and John Eiler provided analytical facilities at Curtin University and Caltech respectively. Financial support was provided by the Institute of Geoscience Research (TIGeR) and Woodside Energy Ltd.

SECONDARY PUBLICATIONS

The following correspond to manuscripts based on research conducted during the preparation of this thesis, and abstracts for conference presentations.

Peer reviewed journal article not part of this thesis:

Eiler, J., Cesar, J., Chimiak, L., Dallas, B., Grice, K., Griep-Raming, J., Juchela, D., Kitchen, N., Lloyd, M., Makarov, A., Robins, R., & Schwieters, J, (2017). Analysis of molecular isotopic structures at high precision and accuracy by orbitrap mass spectrometry. *The International Journal of Mass Spectrometry*, in press (2017).

Conference abstracts

Cesar, J., Eiler, J., Dallas, B., Chimiak, L., Raiteri, P., Grice, K. Isotope Effects in Low-Molecular-Weight Aromatic Compounds from Petroleum Hydrocarbons Originating from Fluvial-Deltaic Source Rocks. Goldschmidt International Conference, Paris, accepted in May 2017, oral presentation.

Cesar, J., Grice, K. The North West Shelf of Australia: Molecular and isotopic approach to discriminate organic facies in source rocks of Triassic vs Jurassic age. Australian Organic Geochemistry Conference (AOGC), Perth, November 2016, oral presentation.

Cesar, J., Grice, K. The North West Shelf of Australia: Origin of light hydrocarbons from the Dampier sub-Basin. Gordon Research Seminar & Conference in Organic Geochemistry, New Hampshire, July 2016, oral and poster presentations.

Cesar, J., Grice, K. Fundamental discrimination of fluids originating in source rocks of Triassic age vs Jurassic age in the Dampier sub-Basin. Australia. American Association of Petroleum Geologists - International Conference and Exhibition, Melbourne, August 2015, poster presentation.

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CHAPTER 1

INTRODUCTION AND OVERVIEW

ORGANIC GEOCHEMISTRY AND PETROLEUM GEOCHEMISTRY

Organic geochemistry studies the distribution, abundance and composition of the organic matter in the geosphere, at bulk and molecular levels (Kvenvolden, 2006; Rullkötter, 2001). After organisms decay, their biomass is incorporated into sediments in aquatic or terrestrial environments and is eventually buried to a greater depth. Under the influence of microbial activity, temperature, pressure and mineral catalysis, the organic matter undergoes a variety of complex chemical reactions which may lead to the formation of coal, oil and gas (petroleum) as the ultimate products (Tissot & Welte, 1984; Rullkötter 2001).

Organic geochemistry is closely associated with petroleum geochemistry (Kvenvolden, 2006) which concerns the variables that control the volume of oil and gas available, the distribution, richness and quality of source rocks, thermal maturity, and the timing of generation-migration-accumulation of the fluids and the formation of the trap (Nagy & Colombo, 1967; Peters & Fowler 2002). Currently, petroleum geochemistry plays an important role in finding resources that are difficult to locate, extract and produce. Numerous production complications can be solved by applying rapid and relatively inexpensive petroleum geochemical methods. For example, the analysis of reservoir fluids helps with the identification of reservoir continuity and compartments, as well as non-productive zones and commingled production (Kaufman, Ahmed, & Elsinger, 1990).

Bioproductivity and the carbon cycle

The first favourable condition for the accumulation and preservation of organic matter includes a significant input of organic moieties mainly derived (directly or indirectly) from primary producers such as higher plants in terrestrial environments, and phytoplankton and zooplankton in aquatic environments. A high amount of primary productivity leads to a greater amount of organic matter being deposited within sediments instead of being recycled in the water column. The second condition is a low energy deposition of low density particles together with an amount of inorganic sediments that does not dilute the organic matter significantly. The organic matter is then preserved and this is optimum in anoxic (and especially euxinic) conditions with high accumulation rates (Grice, Cao, *et al.*, 2005; Killops & Killops, 2005).

The accumulation of organic matter is tied to the production and decay of biomass. Most of the organic carbon is recycled in a cyclic process of a complex food chain related with the carbon dioxide (CO_2) in the atmosphere and oceans. Annually, more than 10% of the total atmospheric carbon dioxide is reduced by photosynthetic organism; and the vast majority of this is returned to the atmosphere as carbon dioxide by animal, microbial and plant metabolism, and by combustion (natural or anthropological) of the biomass (Burgess & Pletschke, 2010). As carbon dioxide is soluble in water, precipitation enables the drawdown of carbon dioxide from the atmosphere into the sediments through weathering of silicate rocks (Williams & Follows, 2011). Aditionally, CO_2 from the atmosphere dissolves in sea water to form carbonate and bicarbonate ions which are collectively referred as disoolved inorganic carbon and can eventually be incorporated in carbonate minerals (Williams & Follows, 2011). This part of the global carbon cycle is connected *via* a small outflow to the massive carbon reservoir of the lithosphere (**Figure 1.1**).

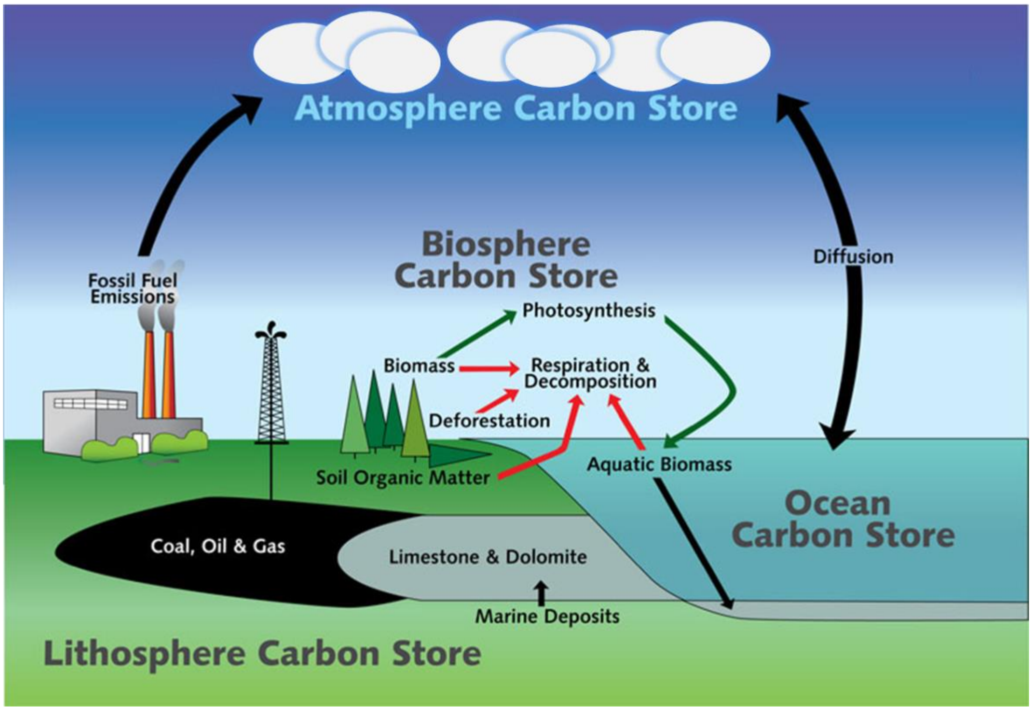

Figure 1.1: The Carbon cycle. Major sinks and sources of carbon and the main exchange processes between the geospheres (modified from New York State Department of Environmental preservation, 2017)

As described by Rullkötter (2001), the oceans contain the bulk of the carbon in the productivity cycle but only 2.5% of these 40 trillion metric tons of carbon are organic. Carbon in the atmosphere is of the same order of magnitude as the biomass in the continents. The exchange rate between the atmosphere and the oceans is of the order of 80 billion metric tons/year, whereas the annual production of biomass only exceeds 100 billion metric tons. Most of the organic carbon in the lithosphere is finely disseminated within sediments, and only one-thousandth of carbon occurs as fossil fuels. Less than 250 million metric tons/year of carbon reach the marine sediments; and the anthropogenic influence exerted by fossil fuel consumption and cement production sums 5 billion metric tons/year.

Transformation of the organic matter: diagenesis, catagenesis and metagenesis

The set of decomposition and metabolic processes that sedimentary organic matter undergoes is known a diagenesis. In organic geochemistry, diagenesis represents the alteration process of the products of primary and secondary productivity, which takes place before deposition and until the first stages of burial, under conditions of relatively low temperature and pressure (<50 °C and <300 bars respectively; Tissot &

Welte, 1984). Biological agents are the main actors during diagenetic transformations although some chemical reactions are promoted by catalysis over mineral surfaces (Tissot & Welte, 1984; Killops & Killops, 2005; Melendez, Grice, & Schwark, 2013). In general terms, these processes can be classified as microbial degradation, formation of geopolymers, and insolubilisation, which altogether lead to the formation of kerogen or final product of diagenesis (**Figure 1.2**). This complex organic geo-macromolecule is insoluble in organic solvents, as in acids or bases. Its chemical composition is strongly heterogeneous and varies greatly depending on the organic facies type (Durand & Espitalié, 1973; Vandenbroucke & Largeau, 2007; Rullkötter 2001).

The first scheme (**Figure 1.2a**) represents a series of random polymerisation and polycondensation of degraded biopolymers (Tissot & Welte, 1984). However, it has been demonstrated that kerogen can form due to a selective preservation pathway (**Figure 1.2b**) of highly resistant biopolymers (*e.g.* often highly aliphatic in structure) that survive decay compared to other biomolecules (Gelin *et al.*, 1999; Riboulleau, Derenne, Largeau, & Baudin, 2001)

When the sediments become buried more deeply due to continuing sedimentation and basin subsidence, they may enter the catagenesis stage which is the principal zone of hydrocarbon formation. Under the influence of increasing temperature (>50 C), pressure and geological time, hydrocarbons and other compounds are released from the kerogen network and incorporated into the bitumen phase which is the fraction of fossil organic matter soluble in organic solvents. Released fluids possess a range of low to high-molecular-weight hydrocarbons, plus, compounds containing heteroatoms (mainly nitrogen, sulfur and oxygen; commonly referred to as NSO compounds) which can account for a significant proportion of the total bitumen.

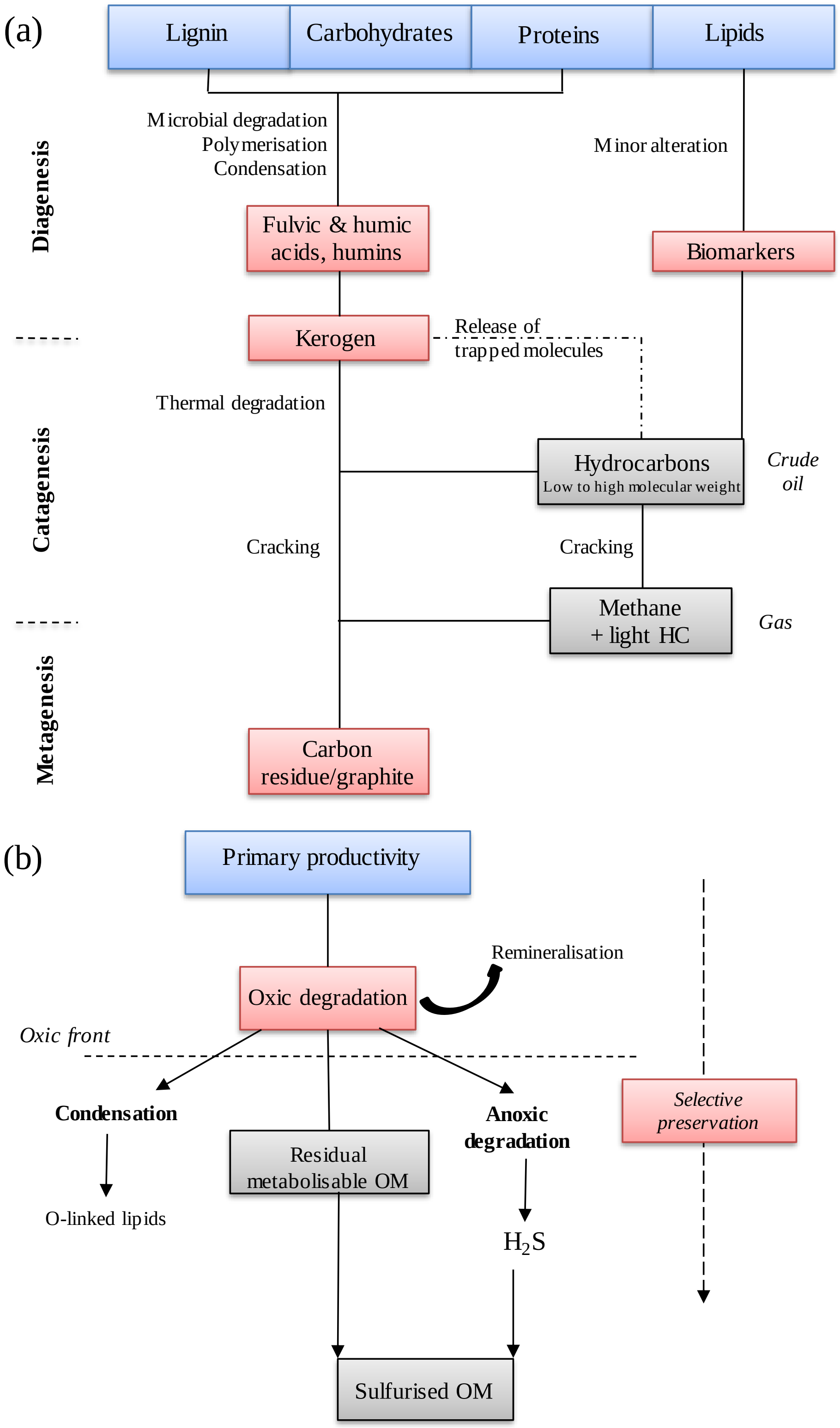

Figure 1.2: The formation of kerogen by (a) random polymerisation of labile molecules (modified from Tissot & Welte, 1984), and (b) Selective preservation (modified from Riboulleau *et al.*, 2001).

In later catagenesis, further thermal hydrocarbon generation from the kerogen as well as thermal cracking of the bitumen yield mainly gaseous hydrocarbons, predominantly methane. These reactions generally occur between 60 and 200 °C (Libes, 2009).

Specifically, Quigley and Mackenzie (1988) suggested that the formation of oil (and gas) from labile kerogen breakdown occurs between 100 and 150 °C, followed by gas formation from refractory kerogen breakdown at 150-220 °C, whereas oil to gas cracking takes place between 150 and 190 °C. The oil to gas generation also depends on the composition of the oil. Hig wax oils start generating gas at 180 °C with a peak at 225 °C, whereas marine oils are less stable and start generating gas at 170 °C with peak generation at 215 °C (Schenk, Di Primio & Horsfield, 1997). At higher temperatures (>200 °C) and great depth, the organic matter reaches metagenesis, during which only methane is stable, and the kerogen is converted to a carbon residue which may ultimately form graphite (Tissot & Welte, 1984, Rullkötter, 2001, Vandenbroucke & Largeau, 2007; Libes, 2009).

Kerogen types

Kerogen is widely classified as lacustrine algal (type I), marine or planktonic (type II), and terrestrial or humic (type III) according to the source organisms and the depositional environment. This classification ranges in the order of decreasing petroleum potential and therefore the H/C ratio (Durand & Espitalié, 1973).

Type I kerogen is highly aliphatic with an H/C atomic ratio often above 1.5 and O/C atomic ratio from 0.03 to 0.1 (Vandenbroucke & Largeau, 2007) and is usually associated with lacustrine environments (often associated with green algae Botryococcus). Type II kerogen contains a large amount of aromatics and many more alicyclic moieties than type I, with atomic ratios around 1.3 for H/C and 0.15 for O/C, and is commonly associated to moderately deep marine environments with planktonic input as the primary source with a minor contribution from land plant material. In contrast, the organic matter deposited in deltaic settings corresponds to kerogen type III; this originates from higher plants (frequently reworked) and exhibits H/C ratios lower than 0.8 and O/C ratios up to 0.3. The organic matter from coal depositional settings is also classified as type III kerogen and has variable sedimentary characteristics (Vandenbroucke & Largeau, 2007). Other kerogen types include kerogen II-S when the sulfur content reaches 8 wt% and the S/C ratio is above 0.04 (sulfur influences the kinetics of thermal decomposition of kerogen due to the weakness of S-C bonds, Orr, 1986), and kerogen type IV usually characterises humic coal or strongly altered (reworked) organic matter (Hardwood, 1977; Tissot, 1984).

The type of organic matter largely influences the chemical composition of the corresponding petroleum fluids and their mobility. Type II kerogen sourced petroleum fluids are very rich in aromatic and NSO compounds which facilitate the solubilisation of naphthenoaromatic molecules and therefore a pore filling by a fluid rich in heavy compounds. Instead, type I and III kerogens generally produce a paraffinic mobile fluid which will have a higher mobility than type II oils. This liquid phase can also carry in solution light aromatic compounds from kerogen type III (Penteado & Behar, 2000).

Petroleum exploration studies of deltaic settings have demonstrated that the oil versus gas potential of kerogen type III cannot be estimated simply from the H/C ratios or Rock-eval hydrogen index (Isaksen, Curry, Yeakel, & Jenssen,, 1998; Vandenbroucke & Largeau, 2007). Source rocks containing type III kerogen can be either oil-prone or gas-prone depending on the main components of the kerogen (Killops *et al.*, 1998) which are aromatic ligneous debris (gas potential) and aliphatic protective coatings (oil potential).

Biomarkers

The geochemical signature of petroleum fluids is usually the most accurate indication of the parent source rock and the processes that may have altered the fluids during or after emplacement into a reservoir. This signature is mainly obtained from the analysis of molecular fossils, generally termed biomarkers, which carry information concerning the composition, ecology and diversity of ancient environments. Specifically, biomarkers are compounds whose molecular skeleton can be related to its biological precursor lipid (usually sterols, hopanols, alcohols, phospho- and ether-lipids); they have been successfully applied to fluid-fluid and fluid-source correlation studies (Peters, Clifford, Walters, & Molodowan, 2005a; Grice & Brocks 2011; Grice & Eiserbeck, 2013). Biomarkers are commonly divided into the following groups: alkanes and acyclic isoprenoids, steranes and diasteranes, terpanes, aromatic steroids, hopanes, carotenoids derivatives, porphyrins and maleimides (Grice *et al.*, 1996; Grice, Schaeffer, Schwark, & Maxwell, 1997; Peters, Clifford, Walters, & Molodowan, 2005b; Grice & Eiserbeck, 2013). The studies of molecular structures, including biomarkers, combined with stable isotope measurements, are a usual and efficient practice in modern organic geochemistry (Galimov, 2006).

Under certain conditions, large populations of a specific organism can generate one or a few precursors which will turn into biomarkers. The presence of an unusual high concentration of these biomarkers will indicate a source input dominated by those precursor organisms. Biomarkers in petroleum fluids can be used to infer the depositional environment, type of organic matter, thermal maturity and age of the source rock. Additionally, the distribution of biomarkers in source rocks and fluids can show systematic variations related to stratigraphy (Peters *et al.*, 2005b). However, many of the fluids may not always contain specific biomarkers, thus the distribution and abundance of other compounds, *e.g.* aromatics, gasoline range compounds and diamondoids, provide additional geochemical information.

In a fluvial-deltaic sedimentary record, there is a variety of molecular fossils derived from land plants. Some of these molecules (see structures in **Appendix 1**), or higher plant biomarkers, include retene (I), cadalene (III) and 6-*iso*propyl-1-*iso*hexyl-2-methylnaphthalene (III) (Simoneit, 1985; van Aarssen, Alexander, & Kagi, 2000; Hautevelle, Michels, Malartre, & Trouiller, 2006; Otto & Wilde, 2001; Nguyen, Derenne, Largeau, Mariotti, & Bocherens, 2003; Asakawa, 2004). Efficient palaeoenvironmental reconstructions and petroleum exploration very often build on the understanding of the distribution of terrestrial organic matter and the processes controlling such distribution (Hedges, Keil, & Benner, 1997).

STABLE ISOTOPES GEOCHEMISTRY

Isotope geochemistry is the study of the relative and absolute concentrations of the elements and their isotopes in samples from the Earth and solar system (Hoefs, 2015). The measurements offer a powerful tool to investigate a range of scientific problems from the origins of the terrestrial planets, to past climate change, igneous processes and the source of elements in a variety of geological reservoirs (Hoefs, 2015).

Stable Isotopes

Stable isotopes are not radioactive but are energetically stable. Isotopes in the biosphere are dominated by lighter elements because the increase in mass caused by the addition of a single neutron is greatest for these elements (Sulzman, 2007). Isotope analyses in organic geochemistry are commonly performed on carbon, hydrogen, oxygen, nitrogen and sulfur (Sulzman, 2007). **Table 1.1** shows details of the stable isotopes of these elements.

Table 1.1: Stable isotopes commonly studied in organic geochemistry (Killops & Killops, 2005).

Element	Stable Isotope (% relative abundance)
Hydrogen	^{1}H (99.9844) ^{2}H or D (0.0156)
Carbon	^{12}C(98.89) ^{13}C (1.11)
Nitrogen	^{14}N (99.64) ^{15}N (0.36)
Oxygen	^{16}O (99.763) ^{18}O (0.1995)
Sulfur	^{32}S (95.02) ^{34}S (4.21)

Notation and standards

The isotopic difference between various materials is exceedingly small and the isotopic composition is expressed in parts per thousand deviations relative to an internationally accepted standard. **Table 1.2** shows the international standards of the main constituents of the organic matter. As described by Peters *et al.* (2005a), a negative value implies that the sample is depleted in the heavy isotope whereas a positive value means that the sample is isotopically enriched in the heavy isotope (see Eq. 1).

$$\delta\ (‰) = \left(\frac{R_{sample}}{R_{standard}} - 1\right) x\ 1000 \qquad \text{(Eq. 1)}$$

$$\text{Where, } R = \frac{Heavy\ isotope\ content}{Light\ isotope\ content} \qquad \text{(Eq. 2)}$$

Table 1.2: International standards for stable isotope analysis in organic geochemistry (Sulzman, 2007).

Element	International standard	$R_{standard}$
Hydrogen	Vienna Standard Mean Ocean Water (VSMOW)	0.00015576
Carbon	Vienna Pee Dee Belemnite (VPDB)	0.0112372
Nitrogen	Atmospheric nitrogen (air)	0.0036765
Oxygen	VSMOW in water. Generally VPDB in CO_2 and carbonates	VSMOW: 0.0020052 VPDB: 0.0020672
Sulfur	Vienna Canon Diablo meteorite troilite (VCDT)	0.0450045

Compound Specific Isotope Analysis (CSIA)

The combination of isotope and biomarker geochemistry has many advantages in the description of palaeoenvironments and petroleum systems. Compounds with a common biological origin show a similar isotopic composition and compound specific isotope analysis (CSIA) has become a powerful tool for reconstructing biogeochemical pathways of organic carbon (Peters *et al.*, 2005b). Stable carbon and hydrogen isotopes are efficient indicators of origin of the organic matter (source) (*e.g.* Freeman, Boreham, Summons, & Hayes, 1994; Grice, Audino, Boreham, Alexander, & Kagi, 2001; Gaines, Eglinton, & Rullkötter, 2009; Sessions, 2016).

The interpretation of CSIA is usually very challenging due to the complexity of the processes involved (isotopic exchange, biosynthesis, photosynthesis, isotopic composition of the source, alteration processes, etc.). However, CSIA has become a fundamental tool in accurately detecting fluid families with a common origin, and generating information consistent with other geochemical indicators. The technique is especially suitable for condensates although its use has not been widely reported. The very precise measurements allowed by baseline chromatographic separation is an advantage of CSIA of condensates. Individual light alkanes (*e.g.* alicyclic alkanes and *iso*alkanes) show wider variations in the isotopic composition compared to other *n*–alkanes which show minor or systematic changes in a particular sample (George, Borehamb, Minifiec, & Teermand, 2002; Peters *et al.*, 2005b).

Isotopic patterns of hydrocarbons represent a very useful tool for fluid-source correlations; H- and C-isotopic data combined can provide significantly enhanced resolution in complex systems where a single isotopic system may be insufficient (Schimmelmann *et al.*, 2004; Sessions, 2016).

Significance of $\delta^{13}C$

The stable carbon isotopic composition of individual biomarkers is preserved during diagenesis. The isotope content is biologically controlled and can be used to identify the source of some compounds and make estimations about the carbon cycling within a particular environment (Hayes, Takigiku, Ocampo, Callot, & Albrecht, 1987; Grice & Brocks, 2011). The isotopic values respond to a series of primary pathways which refer to all the products of photosynthesis, and secondary pathways which correspond to the subsequent biological and thermal transformations of these (Freeman, Hayes, Trendel, & Albrecht, 1990). The $\delta^{13}C$ value of a particular organism depends on its carbon fixation pathway and the abundance of its carbon source; whereas the $\delta^{13}C$ value of a particular compound relies on its biosynthetic pathway (Gaines *et al.*, 2009). **Figure 1.3** shows the typical values for different organisms, environments and geological deposits.

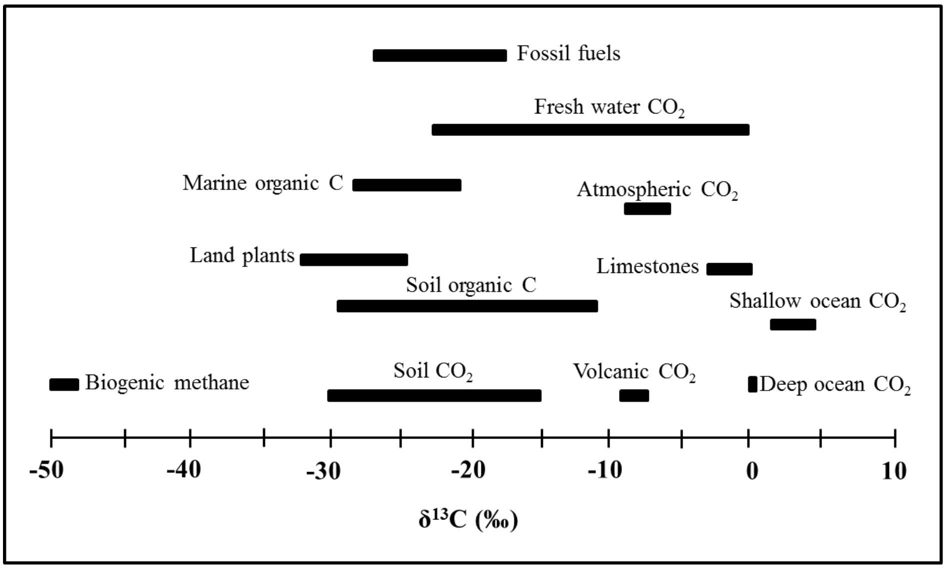

Figure 1.3: Typical $\delta^{13}C$ values in organisms, the environment, and geological deposits (Gaines *et al.*, 2009).

The $\delta^{13}C$ values have significant applications for fluid-fluid and fluid-source rock correlations, and can be correlated with other parameters such as biomarker distributions and palynology, as described in previous studies (*e.g.* Grice, Backhouse, Marshall, Alexander, & Logan, 2005). The stable carbon isotopic composition of compounds such as *n*-alkanes, pristane, phytane and hopanes can be used to distinguish the rock samples and the fluids originated from them (*e.g.* Guthrie *et al.*, 1996). For example, organic compounds from lacustrine environments are usually more depleted in ^{13}C than those accumulated in marine depositional settings (Gaines *et al.*, 2009).

More recently, CSIA of carbon has also been extended to individual aromatic hydrocarbons and has successfully distinguished source of hydrocarbons in Western Australia (Grice *et al.*, 2001; Grice, Nabbefeld, & Maslen, 2007; Nabbefeld, Grice, Summons, Hays, & Cao,, 2010; Maslen, Grice, Dawson, Le Métayer, & Edwards, 2011; Williford, Grice, Logan, Chen, & Huston, 2011; Williford, Grice, Holman, &

McElwain, 2014; Le Métayer *et al.*, 2014; Tulipani *et al.*, 2015, Cesar & Grice, 2017). For example, Maslen *et al.* (2011) demonstrated that CSIA enables the determination of marine or terrigenous end-members which cannot be distinguished by bulk isotopic composition of saturated and aromatic fractions. Fluids with more negative $\delta^{13}C$ values of 1,6-dimethylnaphthalene (1,6-DMN) and 1,2,5-trimethylnaphthalene (1,2,5-TMN) were associated with a marine source for organic matter, whereas those with more positive $\delta^{13}C$ corresponded to a mixed marine/terrigenous source. A similar source effect was suggested by Le Métayer *et al.* (2014) who also proposed that methyl transfer reactions might induce an isotopic fractionation that results in ^{13}C depletion with increasing degree of methylation of light aromatic hydrocarbons.

Clumped-isotopes geochemistry

Clumped isotopes geochemistry studies the distribution and abundance of rare isotopes (*e.g.* ^{2}H, ^{13}C, ^{15}N, ^{18}O) in terms of their ordering in natural materials. It focusses on how they bond to each other instead of to light isotopes (which are often majority) within the same molecule/crystal (Eiler, 2007). The abundance of this preferential grouping of rare isotope "clumps" is controlled by factors such as: thermodynamic stability of heavy isotope clumps, thermo-gravitational fractionations, and growth temperature of minerals (Eiler, 2007). For example, the abundances of doubly substituted isotopologues of carbonate ions containing a ^{13}C and an ^{18}O $[(^{13}C^{18}O^{16}O_2)]^{-2}$ are controlled by a homogeneous equilibrium, and represent a peleothermometer tool because its equilibrium constant is a function of temperature (Schauable, Ghosh, & Eiler, 2006; Eiler, 2011). More importantly, this tool can be used without knowing the ^{18}O content of the waters from which the carbonate minerals grew.

Measuring clumped isotopes requires instrumentation with high sensitivity, high precision (usually 10^{-5}), and excellent mass resolving power or highly pure samples. Gas source isotope ratio mass spectrometry represents the technique that best meets these criteria and has been widely applied for clumped isotope studies (*e.g.* Schauble, Eiler, & Kitchen, 2003; Eiler & Schauble, 2004; Guo & Eiler, 2005).

Site-specific isotope analysis - SSIA

Site-specific isotope analysis evaluates the distribution of rare isotopes according to a particular position within a molecule/crystal (*e.g.* Brenninkmeijer & Rockmann, 1999). The target compounds are usually singly-substituted isotope species though the analysis applies the same principle of non-random distribution of rare isotopes within molecules and mineral structures (Eiler, 2007). For example, it has been demonstrated that carbon atoms integrating different functional groups within the same molecule or, carbon atoms more or less shielded, respond differently to isotopic fractionation effects (*e.g.* Blair *et al.*, 1985; Julien *et al.*, 2015). Recent developments have been reported for site-specific isotope analysis of hydrogen and carbon in organic molecules such as propane using high resolution isotope-ratio mass spectrometry (Piasecki *et al.*, 2016). This technique requires considerably less sample material compared to other techniques (50 µmol vs 10 mmol) frequently used for site-specific analysis (*e.g.* NMR and IR absorption spectroscopy).

PETROLEUM SYSTEMS

A petroleum system consists of an active or once-active source rock, the associated fluids and the geological components and processes responsible for the accumulation of these fluids (petroleum) to form (Perrodon, 1992). Characterising a petroleum system has the purpose of defining the geographic boundaries of oil and gas occurrence. Constant development in the study areas of generation, migration and accumulation of petroleum hydrocarbons helps identify new plays and improves the capability of geoscientists to allocate resources (Peters & Fowler, 2002). Each source rock develops its own petroleum system if all the elements are present (**Figure 1.4**). These elements correspond to facies that contained, transported and sealed in the fluids generated in the source rock. The fluids are connected with migration stringers and accumulation bodies; they can also mix with fluids from other petroleum systems in the same basin (Hantschel & Kauerauf, 2009).

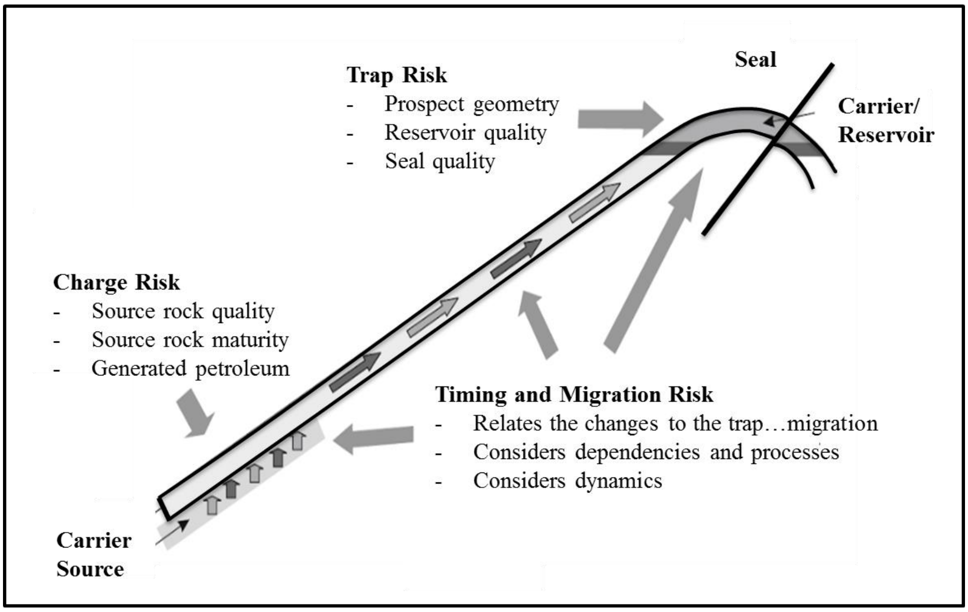

Figure 1.4: A petroleum system and its risk factors (modified from Hantschel & Kauerauf, 2009)

The definition of a petroleum system is also based on fluid-fluid and fluid-source rock correlations (Peters *et al.*, 2005b). A fluid–source rock correlation is a causal relationship, established between a crude oil and an oil-prone petroleum source rock, which is consistent with all known chemical, geochemical and geological information (Curiale, 2008). The correlations are based on the concept that some characteristics (parameters) of the migrated fluid are not significantly different from those of the remaining bitumen in the source rock. These similarities can be demonstrated in isotopic composition and molecular ratios. Fluid-source correlations are very important in understanding the origin and migration pathways of the fluids and defining new exploration plays. Geochemical correlations often rely on the analysis of biomarkers and compound specific isotope analysis (Peters *et al.*, 2005b).

Petroleum systems from deltaic settings

Typical organic matter in deltaic settings consists of kerogen type III (Vandenbroucke and Largeau, 2007). Terrestrial organic matter includes land plant-derived waxes, pollen and spores of higher plants. This represents the main component in coal-forming swamps and is highest in deltas, lower in lacustrine environments and lowest in open marine basins. The organic material can largely consist of ligneous debris which is predominantly aromatic, but there could also be a significant contribution of long-chain aliphatic compounds from the protective constituents of higher plants. For this reason the petroleum–generating capability of kerogen type III varies considerably (Hunt, 1996; Vandenbroucke & Largeau, 2007).

Gas-prone deltaic and coaly rocks generate fluids (gas and associated condensate) that are very poor in biomarkers (Peters *et al.*, 2005b). Additionally, routine analysis methods still do not meet the analytical requirement because of strong volatility of condensate oil (Wang *et al.*, 2012). Condensates are liquid hydrocarbons dissolved in compressed gas, both coexisting in a single-phase state and that obeys the law of retrograde condensation. A condensate has an average boiling point temperature below 200 °C and is composed of a mixture of gasoline and heavier oil fractions. The gasoline fraction (separated from the associated gases) has a boiling point of 130–160 °C (Chilingar, Buryakovsky, Eremenko, & Gorfunkel, 2005).

Many examples of deltaic petroleum systems occur in Southeast Asia and Australia. In this region, fluvial-deltaic sourced systems account for around 120 billion BOE [BOE: barrel of oil equivalent; 1 BOE = I bbl oil, 1 bbl condensate, or 6 million cubic feet (Mcf) gas at standard conditions; bbl: barrel] in-place and 50 billion BOE recoverable oil and gas whereas coals are responsible for sourcing 40 billion BOE of in-place oil and condensate, as well as 30 trillion cubic feet (Tcf) of gas (Howes, 1997). Around half of the larger petroleum systems in this regions (Central Sumatra, Baram, Malay, Gippsland, South Sumatra, Burma, Ardjuna, Carnarvon) are slightly to strongly oil-prone whereas the other half (Rankin, East Natuna, Central Luconia, North Sumatra, Browse, and Pattani) are strongly gas-prone (Howes, 1997).

Alteration processes in the reservoir

Reservoir conditions are not constant from the time they were filled with petroleum fluids. Several processes might be activated and can modify the chemical and physical properties of the fluids (Dembicki, 2017). Some of these processes include thermal alteration, thermochemical sulfate reduction (TSR), deasphalting, gas washing, water washing, biodegradation and evaporative fractionation.

When oil and gas coexist in the same reservoir, the compounds tend to distribute between the liquid and the gas phases according to a vapour-liquid equilibrium. Once some reservoir conditions change (*e.g.* due to lifting, fracturing), any leakage of gas or spillage of oil will cause a new partitioning equilibrium between the two phases resulting in evaporative fractionation. This process usually leads to a residual oil enriched in aromatic compounds and a gas phase that can migrate to shallower reservoirs (Thompson, 1987; Killops & Killops, 2005).

At certain times, the reservoir conditions are favourable for microbe communities to grow and degrade the fluids. This process is known as biodegradation and occurs at relatively low temperatures (35-80 ºC) and when enough water-soluble nutrients are supplied in formation water legs (Head, Jones, & Larter, 2003). The microbes will attack the fluid components according to their degradation simplicity; small hydrocarbons are consumed preferentially (at faster speed), followed by linear compounds which are consumed before their equivalent branched molecules, and branched structures are more easily degraded compared to their equivalent cyclic compounds (Peters & Moldowan., 1993). Biodegradation is also currently regarded as an anaerobic process (*e.g. via* methanogenesis, Jones *et al.*, 2008).

Formation waters can be an agent for further alteration due to the solubility of certain light hydrocarbons which can be removed in solution (Bailey, Krouse, Evans, & Rogers, 1973). Usually low-molecular-weight aromatics are more soluble than the equivalent saturates, and amongst saturates, cyclic structures are more soluble than their branched and linear isomers (Lafargue & Barker, 1988).

GEOLOGICAL SETTINGS

The North West Shelf of Australia

Samples for the current study were obtained from the Dampier sub-Basin, Northern Carnarvon Basin, in the North West Shelf of Australia (NWS). The North West Shelf is a world-class gas province composed of intra-cratonic sediments deposited during a Permo-Triassic pre-rift and subsequently overlayed by Jurassic to Cainozoic syn- and post-rift successions. These rift and post-rift deposits show a complex spatial and temporal distribution. The rifting initiated in the Oxfordian over the central Argo area. The rifting moved to the north of Timor during the Tithonian and then to the Cuvier area in the Valanginian. The final disposition of the deposits has controlled the hydrocarbon potential and efficiency of the petroleum systems of the margin (Longley *et al.*, 2002). Geographically, the NWS is known as the offshore and marginal basins areas flanking the northwest coast of Australia (**Figure 1.5).** Several samples from the

Maracaibo Basin [marine crude oils derived from the Upper Cretaceous La Luna Formation, a limestone source rock, (*e.g.* James, 2000)], in Venezuela, were also included for comparison of certain parameters.

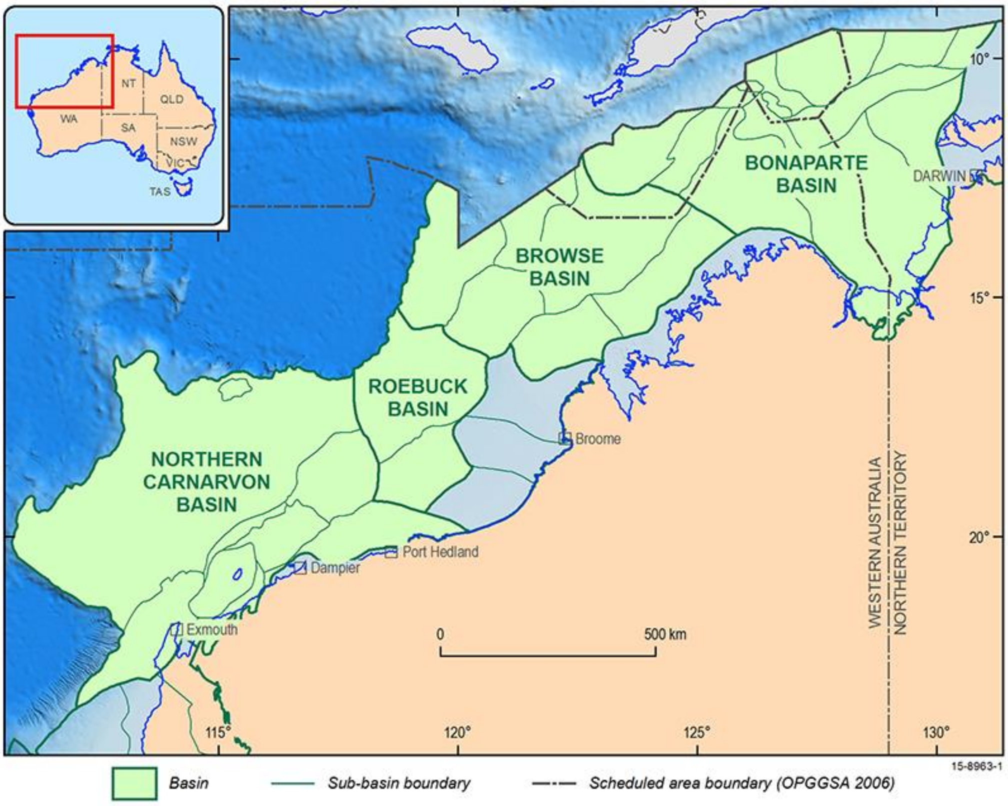

Figure 1.5: Petroleum basins of the North West Shelf of Australia (Geoscience Australia, 2015)

This region consists of the following basins: Northern Carnarvon, Roebuck, Browse and Bonaparte basins; and one orogenic belt also known as the Timor-Banda Orogen. The basins are commonly identified as part of the "Westralian Super-basin" or WASB (Yeates et. al., 1987) and are defined by a thick Late-Palaeozoic, Mesozoic, and Cainozoic sedimentary succession relating principally to the fragmentation of Gondwana (Metcalfe, 1999; Keep et. al., 2002).

The exploration in the NWS commenced in 1953 and more than 700 exploration wells had been drilled by 2001, with an estimation of 2.6 billion bbl of oil, 2.6 billion bbl of condensate and 152 Tcf of gas as reserves. The traps are mostly sandstones within rift-related horsts and tilt blocks, or sandstones within overlying drape folding, which accumulate the resources under Cretaceous seals. The province continues under exploration due to the reserves still undeveloped [119 Tcf of gas, and estimated 1400 MMbbls (Million barrels) of potential condensate] as well as the large potential volumes of hydrocarbons in untested deep-water basins of Mesozoic and Palaeozoic age. The future essentially depends on developing these resources and exploring for new traps.

The Carnarvon Basin

The Carnarvon Basin covers 535,000 km^2 offshore and 115,000 km^2 onshore in the North West Shelf and comprises stacked basins of early to middle Palaeozoic age overlain by Late Palaeozoic to Cainozoic elements of the Westralian Super-basin (Yeates *et al.*, 1987). The basin consists of two different areas: the Southern Carnarvon Basin is an onshore group of sub-basins with up to 7 km of Palaeozoic sediments, and its northern edge is truncated by the northeast-trending Northern Carnarvon Basin.

The Northern Carnarvon Basin encloses up to 15 km of Phanerozoic (mostly Mesozoic) sediments distributed among an inner complex of mainly Jurassic-Cretaceous depo-centres (Exmouth, Barrow, Dampier and Beagle sub-basins), an inner shelf area (Peedamullah and Lambert shelves) flanked by a north-westwards-deepening terrace, and a major platform of thick, flat-lying sediments (Exmouth Plateau), the inner flank of which is relatively elevated to form the Rankin Platform and Alpha Arch (Boreham, Hartung-Kagi, Hope, Offer, & Traynor,, 2000).

Enormous gas and gas/condensate fields are contained in the Carnarvon Basin, with medium to small oil fields, representing volumes of 1564 MMbls, 1076 MMbls, 829 MMbls and 70.9 Tcf of oil, condensate, liquefied petroleum gas (LPG) and gas discovered respectively. The Goodwyn field is the most important source of production in this region, with around 25% of the condensate and LPG reserves. Other relevant areas are the Barrow Island as the main source of oil reserves (35%), Wanaea field (15% of oil reserves) and the North Rankin field with 40 to 50% of the condensate. The fluid fields can be divided into two principal groups: those in the Triassic Mungaroo Formation reservoirs and those in the Early Cretaceous sandstones.

The Dampier sub–Basin

The Dampier sub-Basin represents an elongate northeast–southwest-trending depositional complex, in the Northern Carnarvon Basin (Edwards & Zumberge, 2005). In 2001, the Dampier sub-Basin contained 55 field discoveries and more than 120 exploration wells with a technical success rate of 41% and 22% for fields greater than

20 MMBOE (million barrels of oil equivalent) (Bradshaw *et al.*, 1994). The sub-basin is estimated to contain reserves of 34 Tcf of gas, 1037 MMbbls of condensate and 633 MMbbls of oil. Of these discovered estimated reserves, an estimated 15 Tcf of gas, 418 MMbbls of condensate and 440 MMbbls of oil remain to be developed (Edwards & Zumberge, 2005).

The formation and structural development of the Dampier sub-Basin was largely controlled by the break-up of eastern Gondwana and the separation of Greater India from Australia (Veevers *et al.* 1988), starting as a pull-apart basin and evolving into a marginal basin with carbonate sedimentation (Felton *et al.* 1993). The current stratigraphy records a 10 km section of syn-rift and post-rift sediments, from Permo-Triassic to recent age (Boote & Kirk, 1989), lying between the Rankin Trend and the Enderby Trend (Newman, 1994).

Structurally, the sub-Basin has the following configuration (see also **Figure 1.6):**

- Two linear synclinal depressions: the Lewis Trough and the Kendrew Terrace.
- An intra-basinal anticlinal trend: the Madeleine trend, separating the Lewis and Kendrew depressions.
- Another anticlinal trend: the Legendre trend, along the south-eastern flank of the Lewis Trough, parallel to the Rosemary fault system.

The major subsidence to form the Dampier sub-Basin occurred in the Oxfordian. Subsequently, the basin was infilled by Late Jurassic and Early Cretaceous sediments (relatively thick sequence), and stopped growing in the Albian (Newman, 1994).

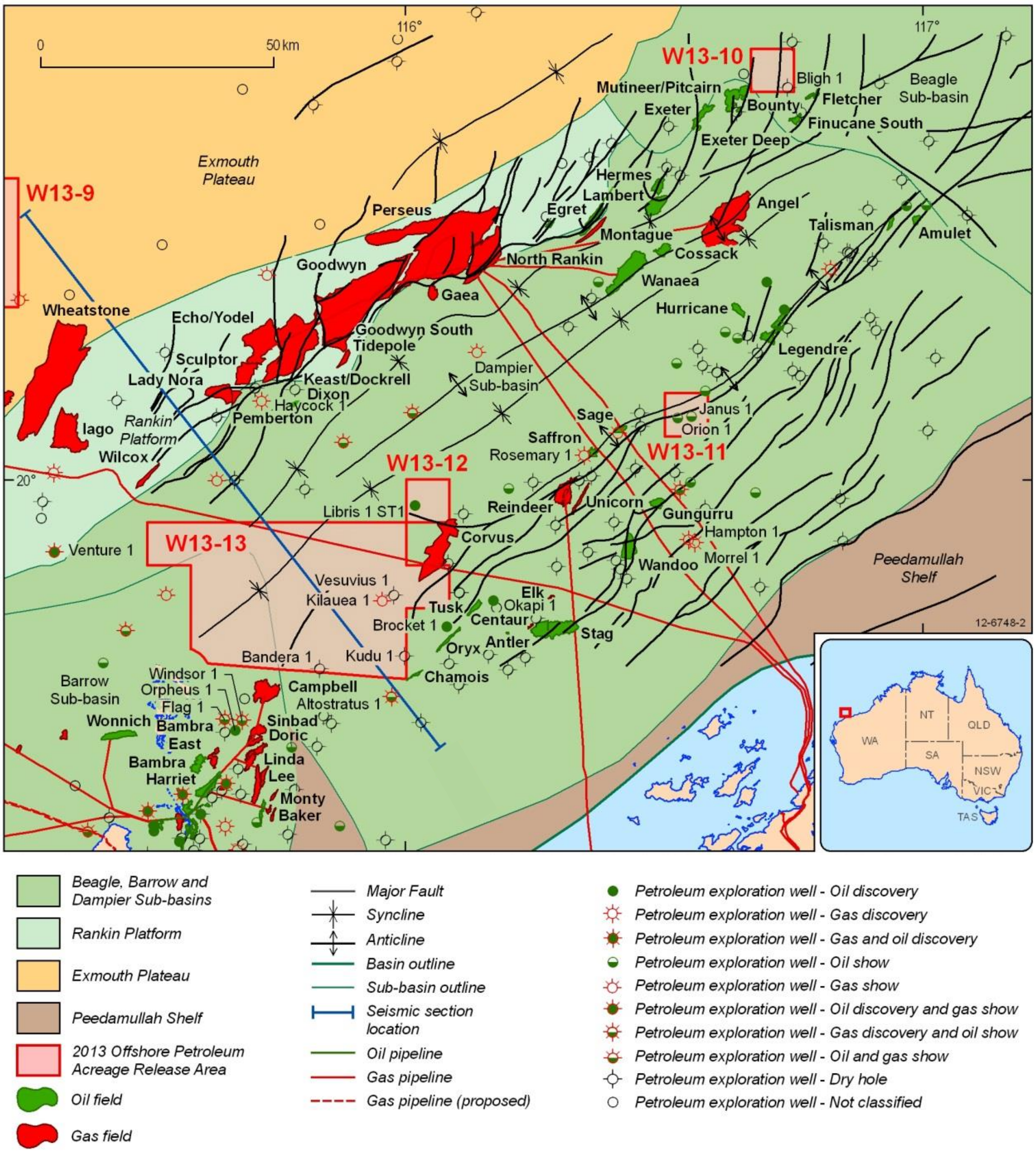

Figure 1.6: Structural setting of the Dampier, Beagle and Barrow sub-Basin, including the Release Areas (2013) and the petroleum fields and discoveries (modified from Geoscience Australia, 2013).

This basin is considered to be predominantly part of the Westralian 2 petroleum system according to the Bradshaw petroleum super-systems description (Bradshaw *et al.*, 1994). However, the concept of a petroleum system is not completely applicable to the offshore basins of Western Australia because the source rocks, in a regional context, are typically of poor quality and commonly occur at multiple stratigraphic levels (Longley *et al.*, 2002). The hydrocarbon potential of many source rocks cannot be ascertained because these rocks are either undrilled or penetrated solely on structural highs and basin margins. Therefore, fluid-source correlations can be only inferred.

Another complication is that in many cases the hydrocarbons generated from multiple source rocks have mixed in a single reservoir (Edwards & Zumberge, 2005).

Geoscience Australia (2013) described the source rocks in this sub-basin are the following:

- Late Jurassic marine Dingo Claystone (oil-prone).
- Early–Middle Jurassic fluvial-deltaic to marginal marine Legendre Formation (gas- and oil-prone).
- Early–Middle Jurassic marine to marginal marine Athol Formation (gas- and oil-prone).
- Early Jurassic marine Murat Siltstone (gas- and oil-prone).
- Late Triassic fluvial-deltaic to marine Brigadier Formation (gas-prone).
- Middle–Late Triassic fluvial to marginal marine Mungaroo Formation (gas-prone).

Several analyses have led to the identification of some clear families for the Dampier sub-Basin and hence have allowed inferences about the likely source rocks and kitchens (Woodside Offshore Petroleum, 1988a: Bastow, van Aarssen, Alexander, Kagi, & Liu, 2002; Edwards & Zumberge, 2005). However, many uncertainties still remain as all the relevant source rocks have some component of terrestrial organic matter and all are of Mesozoic age and therefore fundamental discrimination is limited. Furthermore, mixing of fluids creates difficulty in assigning the most important source because some components used for fluid-source correlation (*e.g.* biomarkers) are present in highly variable quantities.

The Rankin Platform

The Rankin Platform, also known as the Rankin Trend, is a structurally high area which delimitates the northwest boundary of the Dampier sub-Basin (Newman, 1994), and represents the north-western stable margin to the Barrow-Dampier rift, offshore Northern Carnarvon Basin (Stein, 1994). Its main structural fabric originated from a major east-west extension in the Early to Middle Jurassic. Later, the doming was caused by a major uplift during the Early or Middle Jurassic and erosion occurred removing over a kilometre of sediments from the crest. Post-Albanian restructuring in the Dampier sub-Basin also highlighted the structural form of the Rankin Platform (Newman, 1994). The sandstones of the Mungaroo Formation constitute the major reservoirs in the Rankin Platform, having the Muderong Shale as the seal. The early syn-rift Athol Formation seal is not seen in Mungaroo since it has been eroded. As a result any possible oil charge from the Mungaroo Formation source rocks is expected to have been lost before the deposition of the Muderong Shale (Stein, 1994).

AIMS OF THIS THESIS

The main purpose of this thesis is to contribute to the understanding of fluvial-deltaic petroleum systems in Western Australia by developing novel molecular and isotopic approaches for source rock and fluid screening. Fluvial-deltaic petroleum systems are very difficult to characterise because the organic matter is usually mixed (although predominantly kerogen type III) which can develop to oil- or gas-prone source rocks. Fluvial-deltaic geological records are widely distributed in Australia and sourced the main oil and gas/condensate accumulations in the North-West Shelf. However, many uncertainties still persist about fluid provenance because the potential source rocks have very similar organic facies. This thesis re-evaluates the history of fossil fuels in the Dampier sub-Basin from the stage of deposition of land plant debris. It subsequently identifies potential source rock signatures caused by organic-inorganic interactions during diagenesis, and explores future perspectives in fluid screening using novel light hydrocarbons parameters. The approaches described herein can also be applied to similar petroleum systems worldwide.

In **Chapter 2**, this research looks at the distribution of plant biomarkers in source rocks from Late-Triassic to Late-Jurassic age, with the purpose of identifying palaeovegetation changes potentially associated to climate and variations in the depositional settings (*e.g.* shoreline migrations). This section provides an overview on land plants input in the sedimentary basin over alternating fluvial-deltaic to marginal marine depositional environment.

Chapter 3 explores a non-biomarker compound class, the combustion-derived polycyclic aromatic hydrocarbons (PAHs) with the objective of distinguishing the marine versus terrigenous character of the organic matter. These properties were tested in source rock of Triassic age (the Mungaroo and Brigadier Formations) and Jurassic age (the Legendre Formation). The comparison of the molecular distribution and stable carbon isotopic composition of combustion products as well as key aromatic markers such as 1,3,6,7-tetramethylnaphthalene (microbe-derived) and phenanthrene (microbe-derived and combustion-derived) represents a new tool for organic facies discrimination.

The capability of certain parameters to preserve source rock signatures caused by organic-inorganic interactions (*i.e.* organic moieties/geopolymers-minerals) has not been widely explored. **Chapters 4** and **5** focus on non-biomarker compounds that potentially experience structural rearrangements over mineral catalysis. These are the drimane-type sesquiterpanes within the saturate fraction and the benzo[*b*]naphtho[*d*]furans (BNF) in the aromatic fraction respectively. In this way, isomerisation ratios of rearranged drimanes to drimane and benzo[*b*]naphtho[2,1-*d*]furan to benzo[*b*]naphtho[1,2-*d*]furan can be used to distinguish source rock lithofacies. These signatures are potentially preserved in the equivalent fluids.

Finally, **Chapter 6** suggests a new research area in isotope geochemistry for petroleum system studies. Stable carbon compound specific isotope analysis (CSIA) and site-specific isotope analysis (SSIA) have been combined to design a novel approach in petroleum geochemistry. This is based in low molecular weight (LMW) aromatic hydrocarbons which show extraordinary isotopic variations between structural isomers. This approach is significantly relevant to fluvial-deltaic petroleum systems because the generated fluids lack biomarkers and typical correlation tools cannot be applied.

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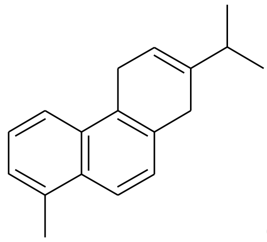
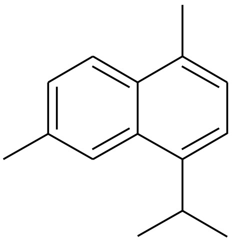
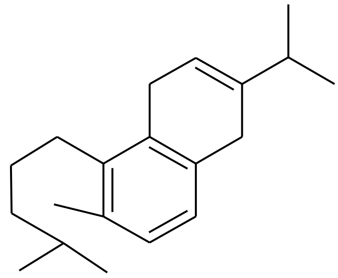
Appendix 1. Molecular structures of plant makers mentioned in the text



(I) Retene



(II) Cadalene



(III) 6-*iso*propyl-1-*iso*hexyl-2-methylnaphthalene (*ip*-*i*HMN)

CHAPTER 2

New insights from plant biomarkers for Triassic-Jurassic palaeovegetation reconstructions in the Northwest Shelf of Australia

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Palaeogeography, Palaeoclimatology, Palaeoecology, submitted (2017).

ABSTRACT

A palaeovegetation reconstruction for the Dampier sub-Basin, Northwest Shelf of Australia, has been described in this study, which covers the Late Triassic to Late Jurassic time interval. We propose the ratio of retene to 1,3,6,7-tetramethylnaphthalene (retene/1,3,6,7-TeMN) to trace changes in palaeoflora in response to shoreline migrations (which, *e.g.*, leads to changes in salinity). High retene/1,3,6,7-TeMN ratios were recorded for the Middle Jurassic after abrupt increase of seal level, which translates into proximity to the source (conifer forests) and redistribution of lowland vegetation communities. The higher plant fingerprint or HPF, instead, enabled the identification of plant distributions in response to climate, which indicated that conifers dominated the vegetation excepting during the Early Jurassic when other vascular plants were predominant (species that potentially synthesised cadalene over retene) due to very arid conditions. We also emphasise that the present approach has only local implications and the parameters used herein (including the higher plant parameter or HPP) might not applicable for global palaeoclimate studies.

Keywords: higher-plant, conifer, palaeoclimate, cadalene, retene, bryophyte

Introduction

The study of the evolution of land plants over geological time has been a key component to describe paleoclimates (Pancost % Boot, 2004). It is known that changes in temperature, humidity, sea level and proximity to the coast influence the type of plants that flourish in land (*e.g.* Hautevelle, Michels, Malartre, & Trouiller 2006). Typical tools for palaeoflora studies involve the identification and quantification of microfossils, *e.g.* pollen and spores, which can be attributed to specific plant taxa, but their preservation in marine environments is often limited (Traverse, 1989; Lindstrom, Erlstrom, Piasecki, Nielsen, & Mathiesen, 2017). Besides pollen and spores, higher plant biomarkers have also been measured to help construct palaeovegetation profiles. However, the reported molecular proxies are not widely applicable in time (intervals of a few tenths of million years) and the results of such studies are often fragmentary (Bird, 1995).

The analysis of higher plant biomarkers is particularly relevant in areas where the flux of terrestrial organic carbon into the marine environment is high (*e.g.*, Amazon fan; Hinrichs & Rullkötter, 1997), such as the Triassic-Jurassic deltas of the Northwest Shelf of Australia (Edwards & Zumberge, 2005; Jablonski, Preston, Westlake, & Gumley, 2013; Cesar & Grice, 2017). Exploring higher plant biomarker distributions in this region may be useful to detect climatic effects in palaeoflora distributions, as well as to understand the origin of the main hydrocarbon accumulations in Western Australia.

Earlier, Jiang, Alexander, Kagi, and Murray (1998) investigated palaeoflora distribution in response to climate as shown by the relative abundance of combustion derived polycyclic aromatic hydrocarbons (PAHs) and aromatic plant markers in the Northern Carnarvon Basin. van Aarssen, Alexander, and Kagi (2000) first reported palaevegetation changes in the Northwest Shelf (Northern Carnarvon Basin) using higher plant biomarkers, covering the Jurassic period over combined stratigraphy from different wells. They used the relative distribution of retene, cadalene and 6-*iso*propyl-1-*iso*hexyl-2-methylnaphthalene (*ip*-*i*HMN) as a fingerprint of the terrigenous organic matter input (or higher plant fingerprint, HPF). This indicator showed a positive correlation between wells located up to 1500 km apart. Retene is widely considered to derive from biditerpenoids synthesised by conifers (*e.g.* Simoneit, 1985; Hautevelle, 2006), although certain Upper Silurian – Lower Devonian rocks (pre-gymnosperm records) contain retene which probably derived from Early Palaeozoic bryophytes (Romero-Sarmiento, Riboulleau, Vecoli, & Versteegh, 2010). Retene has also been detected as a minoritary product derived from combustion of conifers (Simoneit, 2002). In contrast, cadalene derives from generic biosesquiterpenoids and thus can be produced from plant resins, cadinenes, cadinoles, fungi and even essential oils (Otto & Wilde, 2001; Nguyen, Derenne, Largeau, Mariotti, & Bocherens 2003; Asakawa, 2004; Lu, 2013). The source of *ip*-*i*HMN remains unknown although aromatisation-rearrangement reactions of certain land plant derived terpenoids have been suggested as a potential formation mechanism for this and similar compounds (Ellis, Singh, Alexander, & Kagi, 1996). Bryophytes were also suggested as a potential source for *iso*hexyl-alkyl-naphthalenes (Romero-Sarmiento, 2010).

van Aarssen *et al.* (2000) likewise applied the ratio of retene to the sum of retene and cadalene (higher plant parameter or HPP) which exhibited an apparent relationship with climate periods and correlated with global sea-level variations. However, the factors controlling the association between local climate, global sea level and land plant input were not specified. Also in the Northern Carnarvon Basin, Jiang, Alexander, Kagi, & Murray (2000) showed that cadalene and perylene were more abundant in facies described as shallow marine compared to fluvial-deltaic facies; and a regular depletion with increasing distance from the shoreline was identified. Further evidence of an association with depositional settings was shown by Grice, Backhouse, Marshall, Alexander, & Logan, (2005) who identified an increase in the relative abundance of retene in pro-distal deltaic facies. A palaeoclimatic global change was again suggested by Hautevelle *et al.* (2006) based on HPP profiles in the Jurassic section of the Paris Basin that were very similar to the profiles reported by van Aarssen *et al.* (2000). Nevertheless, also in the northern hemisphere, Grice, Riding, Foster, Naeher, and Greenwood (2015) reported different HPP profiles for a sequence of the same age in the Staffin Bay, northwest Scotland; and suggested that local controls (*e.g.* eustatic changes in the relief) potentially had a greater influence on the vegetation than climate.

These studies confirm the contribution of biomarkers to palaeovegetation reconstructions is valuable yet fragmentary. Nonetheless, and for first time, we present in this paper a more comprehensive study of plant biomarkers in the Northwest Shelf of Australia (over ~70 Myr). For this approach, we have incorporated the findings from the aforementioned studies and included a Late Triassic sequence (the Norian-Rhaetian Mungaroo and Brigadier Formations) as well as several Middle Jurassic (the Bathonian Legendre Formation) and Late Jurassic (the Tithonian Dingo Claystone Formation) samples from the Dampier sub-Basin in the Northern Carnarvon Basin.

Materials and methods

Geological settings

The Triassic sequence consists of the Mungaroo and Brigadier Formations (Late Norian – Rhaetian; North Rankin 5 well). The first represents a siliciclastic stratigraphy which main facies have been attributed to fluvial deltaic environments with local reducing conditions. The deposition occurred in a clastic depositional cycle with progradation into a marine environment followed by transgression. Thin coal layers are also present and have local importance (Longley *et al.*, 2002). The Brigadier Formation overlies the Mungaroo Formation and represents a very thinly interbedded claystone and sandstone with several intervals of fine to medium grained sandstone, and the depositional environment was paralic to shallow-marine (Hocking, Moors, & Van de Graaff, 1987). It records an increase in marine character compared to Mungaroo since the sediments accumulated under fluvial and transgressive processes in an estuarine setting (Woodside Energy Ltd., 1977).

The Middle Jurassic Legendre Formation (Perseus South 1 well) is a marginal marine sequence (Hocking, 1992), and was deposited in an estuarine system largely tidally influenced, with marine incursions (Woodside Energy Ltd., 1997). The lithology of this formation consists of silty claystone and laminated claystone (Woodside Energy Ltd., 1997). Lastly the Late Jurassic sediments were deposited in a restricted deep marine environment and formed the Dingo claystone (Wanaea 1 well) which is widely recognised as the source of liquid hydrocarbons in the Rankin Platform accumulations (Boreham, Hartung-Kagi, Hope, Offer, & Traynor, 2000; Edwards & Zumberge, 2005). **Figure 2.1** shows the well locations from which these sequences were sampled.

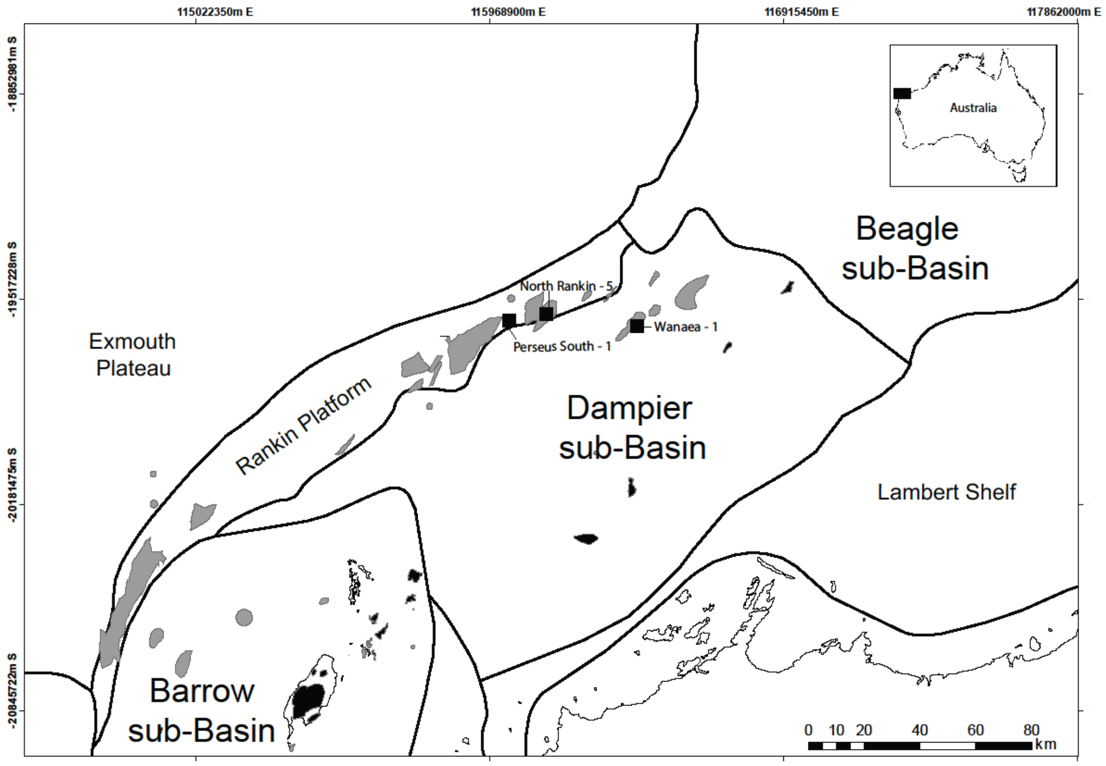

Figure 2.1. Well locations in the Dampier sub-Basin.

Samples and sample preparation

A set of 28 source rock samples was analysed for this study. A Milestone START-E microwave system was used to extract the bitumen, with a 9:1 mixture of dichloromethane (DCM) and methanol (MeOH). The temperature was ramped from room temperature (~25ºC) to 80ºC at 8 ºC/min and then held for 15 min. Approximately 5-10 mg of the extracted bitumen was separated into aliphatic, aromatic and polar fractions by small scale silica gel liquid chromatography as described elsewhere (Maslen, Grice, Le Métayer, Dawson, & Edwards, 2011). Aromatic hydrocarbons, including higher plant biomarkers, were analysed using gas chromatography - mass spectrometry (GC-MS).

GC-MS

The aromatic fractions were dissolved in *n*-hexane and analysed by GC-MS on a HP 6890 GC coupled to a HP 5973 mass selective detector (MSD) operating in electron ionisation mode (70 eV). 1 µL of each solution was injected using an HP 6890 auto-sampler. Chromatographic separation of compounds occurred on a WCOT fused silica capillary column (60 m X 0.25 mm i.d.) with a 0.25 µm 5% phenyl–methyl–silicon stationary phase (DB-5). The carrier gas was helium at a linear velocity of 1 mL/min. The temperature of the GC oven was programmed from 40ºC –325 ºC (at 3 ºC/min) and was held isothermally for 45 minutes at 325 ºC. Compound identification was achieved by comparing mass spectra and relative retention times with those previously reported in the literature (Jiang *et al.*, 1998, 2000; van Aarssen, Bastow, Alexander, & Kagi, 1999; 2000; Maslen *et al.*, 2011).

Results and discussion

Higher Plant Parameter (HPP) in the Late Triassic

The Higher Plant Parameter HPP [retene / (retene and cadalene)] was calculated for a Late Triassic sequence from the Dampier sub-Basin and varies between 0.5 and 0.9. The HPP profile showed a positive correlation with the global sea level curve from Haq and Alqahtani (2005) (**Figure 2.2**). However, similar values (0.2-0.9) were found in Jurassic records from the same basin (van Aarssen *et al.*, 2000), which implies the apparent correlation with global sea level is not linear during the Triassic and Jurassic periods. The variation range of HPP is very narrow compared to the more than 100 m fluctuation below and above the present sea level registered during the Triassic and the Jurassic, respectively. The HPP was defined by van Aarssen *et al.* (2000) based on the fact that retene and cadalene were the plant biomarkers with greatest variation in the sedimentary record but the authors advised that further investigation was needed to identify other factors controlling the HPP profiles.

We consider the HPP cannot be applied to identify global climatic effects because it only indicates how the population of conifers (adopting retene as a conifers marker) vary with respect to vascular plants in general (cadalene is not specific to a particular vascular plant type). This relationship not only depends on climate but also on the evolution of the depositional settings (*e.g.* due to shoreline position; Jiang *et al.*, 1998; Abbink, Van Konijnenburg-Van Cittert, & Visscher, 2004; Grice *et al.*, 2005).

Basically, an invasion of the land due to sea-level increase translates into a reduction of the area inhabited by lowland vegetation which is not resistant to salt influence (Abbink *et al.*, 2004), and this increases the abundance of upland vegetation (*e.g.* conifer conifer consequently results in higher HPP values. Furthermore, the position of the shoreline is not only influenced by global sea level but also by several local factors such as tectonic events (uplifting/subsidence), erosion rates and inherited morphology, amongst others (Stive *et al.*, 2002).

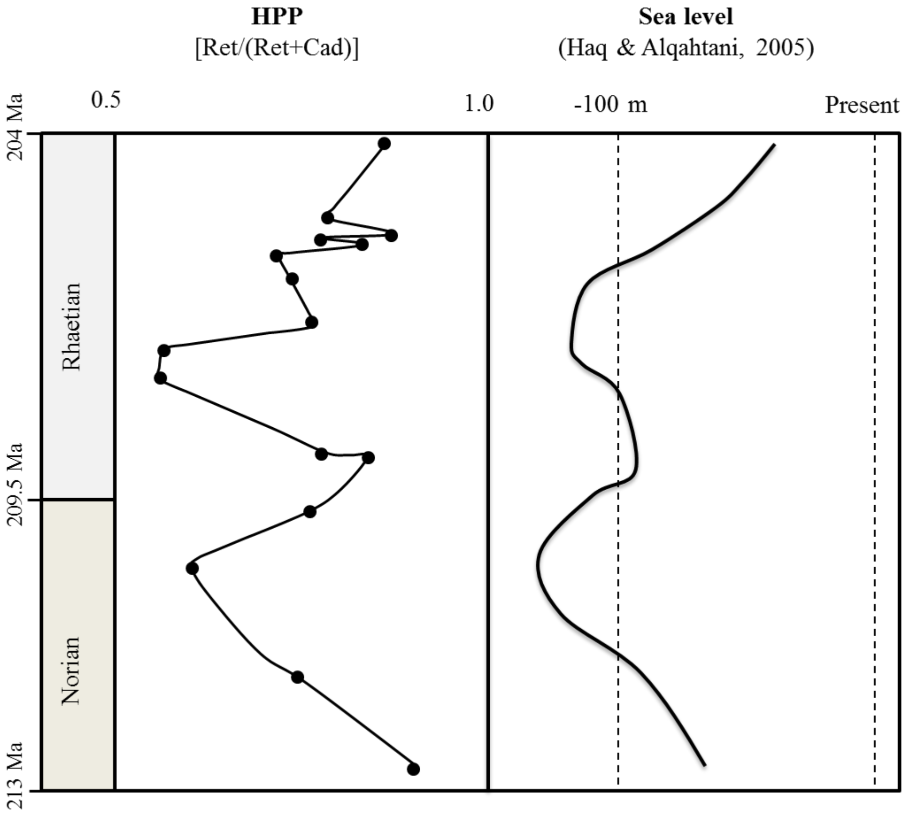

Figure 2.2. Higher Plant Parameter or HPP [retene / (retene and cadalene)] versus global sea level during the Late-Triassic (Haq & Al-Qahtani, 2005) in a sequence from North Rankin 5 well.

Palaeovegetation adaptations induced by changes in the depositional settings (shore-line position)

To overcome the limitations of HPP due to the non-specificity of cadalene, we propose the retene/1,3,6,7-TeMN ratio to trace variations in the depositional settings of the basin. Retene is more specific to conifer plants and is the most abundant plant marker in this particular sedimentary record (as shown by retene ≥50% relative to the other plant markers cadalene and *ip*-*i*HMN; **Table 2.1**). We measured the abundance of retene relative to 1,3,6,7-TeMN because this alkyl-naphthalene is microbe-derived and poorly correlated to land plan input (*e.g.* Jiang *et al.*, 1998). The 1,3,6,7-TeMN

Table 2.1. Plant biomarker parameters of the samples analysed in this study

Age[a]	***Formation***[a]	***Sample***[c]	***HPP***[d]	***Retene***[e]	***Cadalene***[e]	***%Retene***[f]	***%Cadalene***[f]	***%ip-iHMN***[f]	***%TOC***[b]	***%Ro***[b]
Tithonian	Dingo Claystone	W1(4)	0.7	1.6	0.6	67	24	8	<1	0.57-0.58
		W1(7)	0.9	3.4	0.4	84	11	5		
		W1(8)	0.8	1.2	0.3	63	15	21		
		W1(10)	0.8	0.9	0.2	70	17	13		
Bathonian	Legendre	PS1(24)	0.9	3.4	0.5	70	11	20	~2	0.54-0.56
		PS1(28)	0.9	15.7	2.2	67	9	23		
		PS1(27)	0.9	11.1	1.9	65	11	23		
		PS1(26)	0.9	5.3	0.6	75	8	17		
		PS1(25)	0.8	9.7	2.1	65	14	21		
		PS1(22)	0.9	9.9	1.4	68	10	22		
		PS1(21)	0.8	10.0	2.4	63	15	22		
		PS1(20)	0.8	11.2	2.3	67	14	19		
Rhaetian	Brigadier	NR5(89)	0.8	0.8	0.2	81	15	4	4.2	0.52-0.54
		NR5(93)	0.8	0.7	0.2	74	22	3	3.2	
		NR5(69)	0.9	1.4	0.2	81	14	5	3.9	
		NR5(70)	0.8	0.5	0.1	72	14	5	-	
		NR5(71)	0.8	0.6	0.1	79	18	3	-	
		NR5(74)	0.7	0.3	0.1	67	28	4	-	
		NR5(79)	0.7	0.5	0.2	71	27	2	-	
		NR5(80)	0.7	0.5	0.2	73	24	3	3.4	
		NR5(82)	0.6	0.3	0.2	53	42	5	1.3	
		NR5(85)	0.6	0.2	0.2	53	43	4	-	
		NR5(55)	0.8	1.6	0.5	73	23	4	-	
Norian	Mungaroo	NR5(57)	0.8	0.6	0.1	80	17	3	-	0.56-0.59
		NR5(62)	0.7	0.6	0.2	71	24	5	10.9	
		NR5(64)	0.6	0.8	0.6	55	38	7	-	
		NR5(31)	0.7	0.4	0.2	59	22	19	-	
		NR5(47)	0.9	1.5	0.2	83	11	6	3.0	

[a] Woodside Energy Ltd. (1977; 1988; 1997); Marshall and Lang (2013). [b] Woodside Energy Ltd. (1977; 1988; 1997); Phillips Australian Oil Company (1993); Marshall and Lang (2013). [c] Core samples from the wells Wanaea-1 (W-1), Perseus South 1 (PS1) and North Rankin 5 (NR5). [d] Calculated using peak areas for retene (*m/z* 219) and cadalene (*m/z* 183). [e] Retene and cadalene ratios relative to 1,3,6,7-TeMN (*m/z* 219, 183 and 184). [f] HPF (percentage of retene, cadalene and *ip*-*i*HMN) calculated using peak areas (*m/z* 219, 183 and 197).

is also present in sediments and crude oils of all ages and its application as a reference point to evaluate land plant input into marine settings is becoming a common practice in organic geochemistry (*e.g.* Van Aarssen *et al.*, 2000; Grice *et al.*, 2005; Romero *et al.*, 2011; Cesar & Grice, 2017). Using retene also has the advantage of the geographical distribution of conifer forests which predominantly grow on higher terrain (Abbink, 1998) and are part of the upland communities (Abbink *et al.*, 2004), whereas cadalene originates from vascular plants in general, many of which broadly distribute at variable distances from the seashore (*e.g.* upland, lowland and coastal communities; Abbink *et al.*, 2004). This may explain a lower variation in cadalene ratios (0.1-2) compared to retene ratios (0.2-16) as listed in Table 1. Abbink *et al.* (2004) also explained that upland communities, *e.g.* conifer forests, are less affected by sea-level variations which confirms that retene, as a conifer marker, might be a suitable tracer for shoreline migrations. In the following sub-sections we describe the overall palaeovegetation adaptation induced by depositional settings, as shown by retene/1,3,6,7-TeMN over geological time in the Dampier sub-Basin (**Figure 2.3**).

Late Triassic

During this time the global sea level was approximately 100 m below the present reference (Haq & Alqahtani, 2005). The retene/1,3,6,7-TeMN ratios are very low (≤1) which suggests the shoreline was far from the source (conifer forests) and the plant debris travelled long distances before deposition, which at the same time reduces the preservation of terrigenous markers (Hedges *et al.*, 1999). Moreover, *Pinaceae* probably was the dominant conifer family because neither tricyclic nor tetracyclic diterpanes (*e.g.* kaurane, phyllocladene, beyerane) were detected in the source rock extracts. These compounds derive from all conifer families (*e.g. Podocarpaceae, Araucariaceae*) except *Pinaceae* (Otto & Wilde, 2001; Hautevelle *et al.*, 2006). Similarly, there is no signal of phenolic abietanes which are typical in

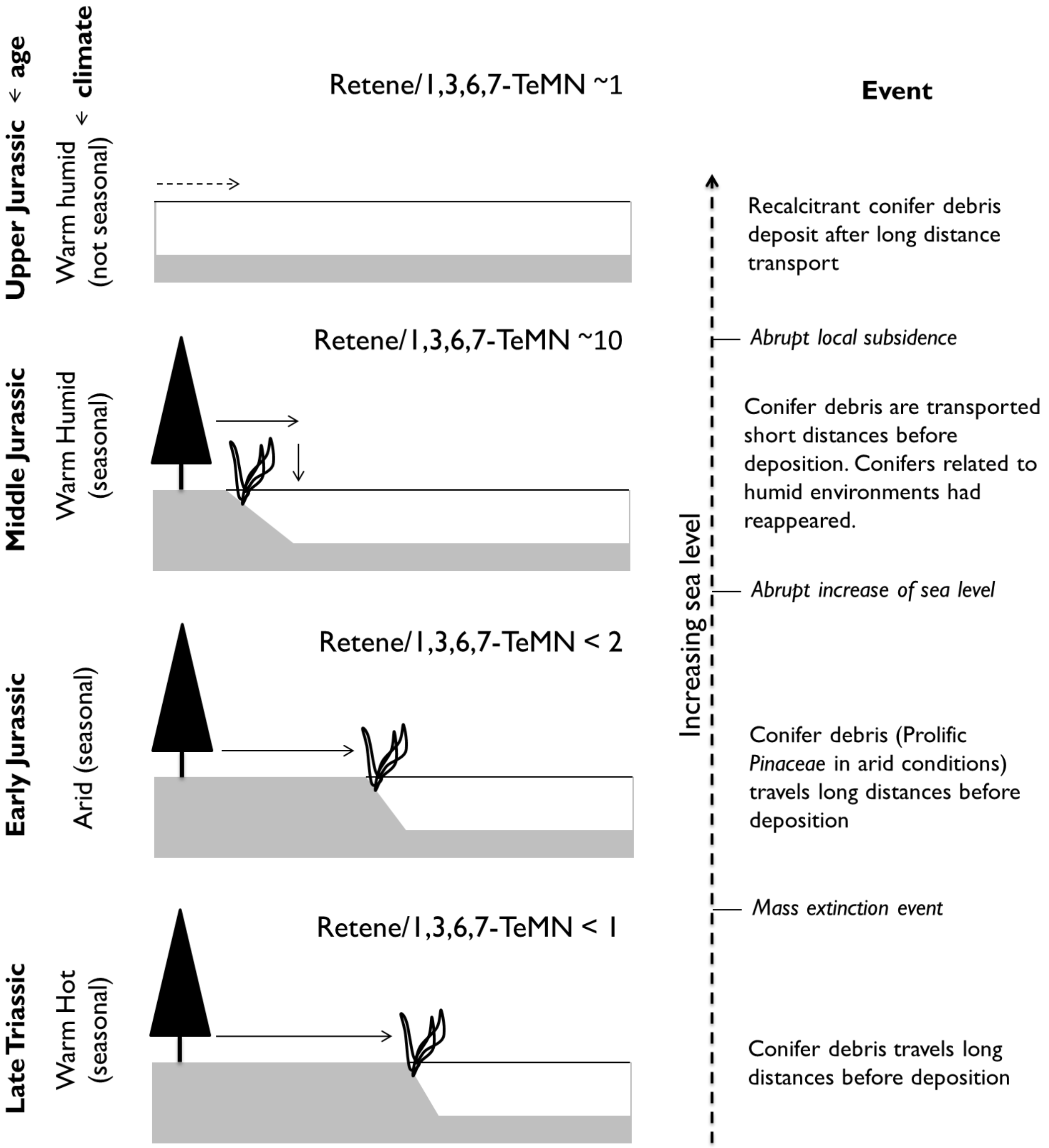

Figure 2.3. Palaeovegetation adaptations induced by changes in the depositional settings of the Dampier sub-Basin during Triassic-Jurassic times. Climate information from Parrish *et al.* (1996) and Scotese (2000).

Taxodiaceae and *Cupressaceae* families (Otto & Wilde, 2001; Hautevelle *et al.*, 2006). The presence of bicyclic (drimane-type) sesquiterpanes and the absence of tri- and tetracyclic diterpanes (**Figure 2.4a**) are also consistent with a *Pinaceae* origin for retene (Hautevelle *et al.*, 2006). The dry warm-hot Triassic climate (Preto, Kustatscher, & Wignall, 2010) might have restricted the conifer vegetation to *Pianaeae* since this is the conifer family that best adjusts to dry environments (Hautevelle *et al.*, 2006).

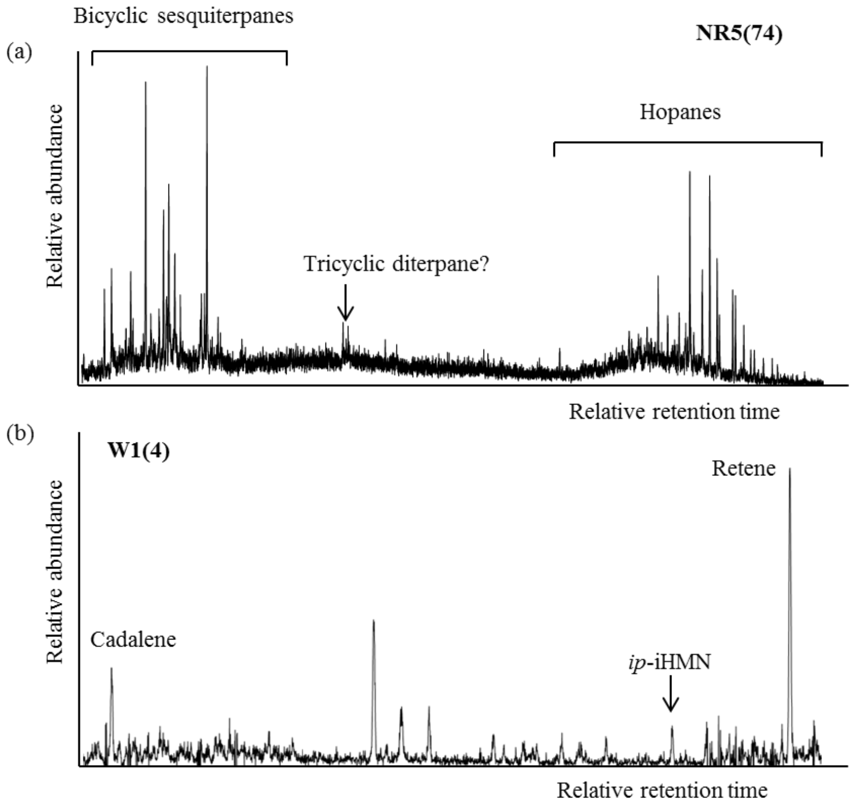

Figure 2.4. Partial chromatogram for compound identification. a) *m/z* 123 diterpanes from the sample NR5(74). b) *m/z* 183+197+219 retene, cadalene and 6-*iso*propyl-1-*iso*hexyl-2-methylnaphthalene (*ip-i*HMN) from the sample W1(4) (this sample has a relative distribution pattern more suitable compound identification).

Early Jurassic

The Early Jurassic registered a subtle increase in sea level that reached and settled around present sea level conditions (Haq & Alqahtani, 2005). The retene/1,3,6,7-TeMN ratios are slightly higher since the shoreline is now closer to the source (coniferous vegetation) and shorter transportation distance might have favoured the preservation of plant debris compared to Triassic times. The climate evolution towards arid conditions (Parrish *et al.*, 1996) probably enhanced the proliferation of *Pianaceae* over other conifer families, which was also the case during the same time interval in the Paris Basin (Hautevelle *et al.*, 2006). Samples from the Early Jurassic were not analysed in this study, thus we have based the interpretation on the results from Jiang *et al.* (1998), van Aarssen *et al.* (2000) and Grice *et al.* (2005). Also, this study does not attempt to address the Triassic-Jurassic mass extinction event.

Middle Jurassic

The Middle Jurassic started with an abrupt increase in global sea level (Haq & Alqahtani, 2005). This likely resulted in a rapid migration of the shoreline towards the continent and as a consequence promoted a localised change in vegetation. Probably, a significant portion of coastal and lowland vegetation declined due to variations in the depositional environment (*e.g.* increase in salinity due to proximity to the sea). The shoreline is closer to the upland sources, *e.g.* conifers, which might have also been affected by changes in the drainage patterns of the rivers. These new settings areexpressed in retene/1,3,6,7-TeMN ratios significantly higher (~10) than the reported values for older records. The conifers population was probably dominated by *Pinaceae* that proliferated in the Early Jurassic. However, there are some records of *Araucariaceae* in Late Toarcian – Early Alenian sediments (Grice *et al.*, 2005). During this time the climate evolved towards more humid conditions which may be the reason for the reappearance of other conifer families in certain locations.

Late Jurassic

The climate seasonality and sea level fluctuation pattern registered in the Middle Jurassic seem to have propagated until the Oxfordian, but during the Kimmeridgian-Tithonian these conditions were more stable and the sea level set at ~100 m above the present sea level (Ruban, 2015). Deltaic to shallow marine deposition was also terminated by abrupt subsidence at the start of the Callovian–Oxfordian rifting episode, and a restricted deep-marine environment became established throughout the inner Northern Carnarvon Basin (Felton *et al.*, 1993; Grice *et al.*, 2005). The land plants debris had to undergo prolonged transportation to reach the deep marine environment, which reduces the preservation of plant markers. This scenario translates into low retene/1,3,6,7-TeMN ratios (~2). The remaining question for this time interval is the absence of biomarkers indicative of conifer families other than *Pinaceae* despite the climate evolving to more humid conditions. We suggest the climatic seasonality during the Middle and Late Jurassic might have caused an uneven geographical distribution of conifer families that settle in humid environments.

Comparison with other localities

Hautevelle *et al.* (2006) found a HPP trend in the Paris Basin similar to that one described by van Aarssen *et al.* (2000) in Western Australia for the same age. The HPP values were, however, considerably lower (*e.g.* ≤0.6 in Paris compared to ~0.9 in Carnarvon during the Oxfordian), which is probably due to the limitations of using HPP with cadalene being ubiquitous to all land plants. From this study it is important to note the increase in the relative abundance of retene followed a change in the depositional settings. The highest abundances of retene are registered in the transition from siliciclastic sedimentation to the formation of carbonate platforms. During the Callovian and Oxfordian the Paris Basin was covered by a shallow sea which likely forced a vegetation adaptation and a reduction in lowland and coastal vegetation, as occurred during the Middle Jurassic in the Dampier sub-Basin. In another study, low HPP values (<0.4) were found in the Staffin Bay, Scotland (Grice *et al.*, 2015). The deposition occurred in open marine settings and the sequence consists predominantly of mudstones (Hudson & Trewin, 2002). Notably, the highest abundance of retene was registered after the drowning of the Belemnite Sands Member at the end of the Oxfordian. This member represents a sand bar in which higher plants could have grown and subsequently decayed during drowning of the bar. This is not the only report of the dependence of a particular plant marker on local depositional environment (Lindstrom *et al.*, 2017). For example, *cheirolepid* pollen is usually more abundant in marine secessions because *Cheirolepidiaceae* preferentially grows in coastal environments (Abbink, 1998).

The retene/1,3,6,7-TeMN ratio seems to be a suitable tracer of palaeovegetation adaptations due to changes in depositional settings, whereas other molecular parameters and palynology should be taken into account to determine climatic effects (*e.g.* certain biomarkers and/or pollen indicators of plant families that settle under specific climate). For example, also in the Carnarvon Basin, Dixon (2013) carried out a palynological analysis of a 40 m section of the Norian-age Mungaroo Formation from the well Knock-1 (more than 300 km east from North Rankin 5). Dixon identified local/temporary transitions in the delta-plain towards marginal marine facies as revealed by palynofacies assemblages, following the approach of sporomorphs ecogroups (SEGs) from Abbink *et al.* (2004), and found the lowland and tidally-influenced vegetation were the most affected during those depositional environment transitions. Moreover, retene/1,3,6,7-TeMN seems not to be biased by the organic matter content, and maturity affects can be ruled out for these immature sediments (see the corresponding %TOC and %Ro values in **Tables 2.1** and **2.2**).

Distribution of retene, cadalene and ip-iHMN in response to climate

As discussed in the HPP results section, besides climate there are many factors affecting the abundance of plant derived markers. These include local depositional settings (*e.g.* shoreline position), the geographical distribution of particular taxa, local tectonic events and the composition of the substrate (soil/rock), amongst others. However, if the purpose is to detect trends that follow palaeoclimate, the higher plant fingerprint from van Aarseen *et al.* (relative distribution of retene, cadalane and *ip-i*HMN; compounds identified in **Figure 2.4b**), observed over a wide geological time interval, might provide a better estimation (**Figure 2.5**), as Abbink *et al.* (2004) also advised that palaeovegetation changes in response to climate are more detectable as internal shifts within each SEG (especially in upland and coastal communities). We anticipate however that different distribution patterns might be obtained for sedimentary records outside the Dampier sub-Basin.

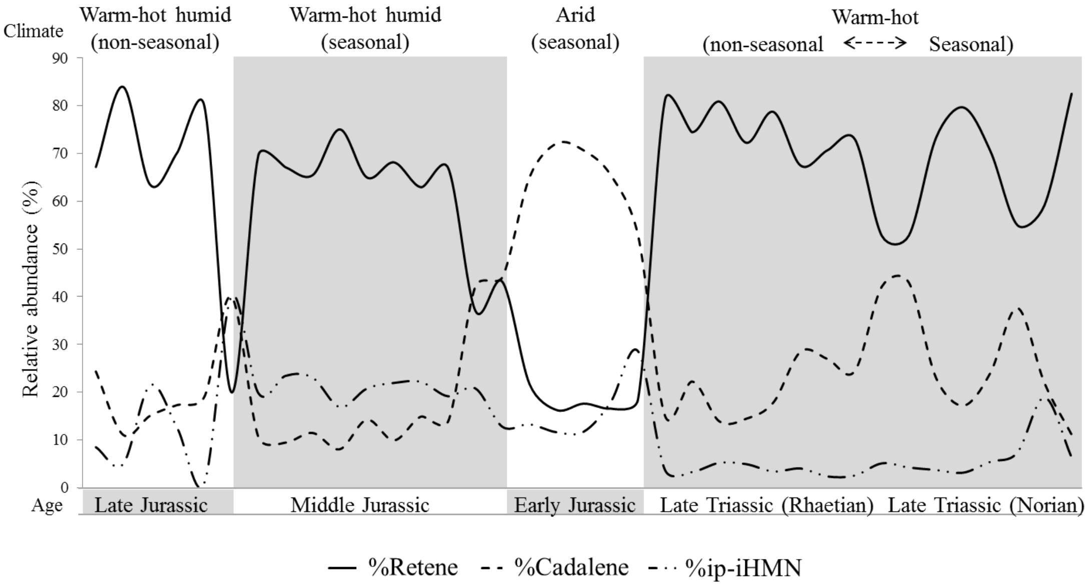

Figure 2.5. Distribution of retene, cadalene and *ip-i*HMN in response to climate, in the Dampier sub-Basin during the Triassic (this study) and Jurassic (Jiang *et al.*, 1998; van Aarssen *et al.*, 2000).

Table 2.2. Plant biomarkers parameters for the samples from other localities

Age	***Location***	***HPP***[e]	***Retene***[f]	***Cadalene***[f]	***%Retene***[g]	***%Cadalene***[g]	***%ip-iHMN***[g]	***%TOC***[h]
Oxfordian-Kimmeridgian	Carnarvon[a]	~0.9	-	-	~80	~20	<1	-
Middle Oxfordian	Paris[b]	~0.6	-	-	-	-	-	-
Middle Oxfordian	Staffin[c]	~0.1	-	-	~10	~90	<1	~3
Middle Callovian	Paris[b]	~0.1	-	-	-	-	-	-
Middle Callovian	Staffin[c]	~0.9	-	-	~95	<1	~5	~3
Callovian	Carnarvon[a]	~0.2	-	-	~20	~40	~40	-
Bathonian-Bajocian	Carnarvon[d]	0.5	2.1	2.4	-	-	-	1.3
Bathonian-Bajocian	Carnarvon[d]	0.5	1.7	1.7	-	-	-	1.3
Aalenian-Toarcian	Carnarvon[d]	0.3	2.3	6.9	-	-	-	1.9
Aalenian-Toarcian	Carnarvon[d]	0.2	1.3	5.6	-	-	-	1.8
Pliensbach-Hettangian	Carnarvon[d]	0.2	0.8	3.0	18	71	12	2.0
Pliensbach-Hettangian	Carnarvon[d]	0.2	0.7	2.7	-	-	-	1.7
Pliensbach-Hettangian	Carnarvon[d]	0.3	1.0	2.9	-	-	-	0.9

[a] Carnarvon (Delambre) (van Aarssen *et al.*, 2000). [b] Paris Basin (Hautevelle *et al.*, 2006). [c] Staffin Bay (Grice *et al.*, 2015). [d] Carnarvon (Delambre) (Jiang, 1998; Jiang *et al.*, 1998). [e] Calculated using peak areas for retene (*m/z* 219) and cadalene (*m/z* 183). [f] Retene and cadalene ratios relative to 1,3,6,7-TeMN (*m/z* 219, 183 and 184). [g] HPF (percentage of retene, cadalene and *ip-i*HMN) calculated using peak areas (*m/z* 219, 183 and 197). [H] Values from the corresponding studies

The distribution pattern of retene suggests that conifers were predominant among the vascular plants during the Late Triassic (53-80% of retene). A critical climatic variation towards arid conditions in the Early Jurassic reduced the population of conifers (16-22% of retene) and probably restricted it to the *Pinaceae* family. Conifer forests developed again after more humid conditions were established in the Middle and Late Jurassic (63-84% of retene). As discussed above (Section 3.1), cadalene is not a diagnostic marker because it can originate from many types of plant. However, it is important to note that cadalene is particularly abundant during the Early Jurassic (53-72%) which suggests this compound was probably associated with land plants that could grow under arid conditions. In fact, Grice *et al.* (2005) found higher concentrations of cadalene in sediments that contain abundant *Corollina spp.*, which has been related to a dry climatic episode in the Hettangian–Pliensbachian. Additionally, according to Abbink *et al.* (2004), *Corollina spp.* corresponds to the coastal SEG which together with the upland SEG represent the communities more sensitive to climate change.

With respect to *ip*-*i*HMN, it has been proposed this compound originates from aromatisation-rearrangement of phyllocladene- and pimarane- skeleton diterpenoids (Ellis *et al.*, 1996). However, these compounds were not detected in the samples thus an origin from plant resins for *ip*-*i*HMN can be ruled out. We consider here that bryophytes are a potential source (Romero *et al.*, 2010) since these plants also contain diterpenoids from the phyllocladene and pimarane class (Xie and Lou, 2009; Liu, Wang, & Loun, 2012). According to Abbink *et al.* (2004), the bryophytes integrate the river SEG which showed to be the least affected by climate. This might explain why the *ip*-*i*HMN curve does not drastically vary over geological time although different levels correspond to different time intervals (4%, 12%, 20%, and 10%, for the Late Triassic, Early Jurassic, Middle Jurassic and Late Jurassic respectively). It can also be observed that the population of bryophytes increased with more humid conditions in the Middle Jurassic (~22% of *ip*-*i*HMN) because these plants are more adapted to humid environments (*e.g.* He, X., He, K., & Hyvonen, 2016).

The redistribution of plants in the transition Middle to Late Jurassic might have been influenced by climate variations towards a non-seasonal regime and the local Callovian–Oxfordian rifting episode. Additionally, within the Triassic, two patterns could be further distinguished because the variation frequency is slightly different between the Norian and the Rhaetian. This is probably due to climate transition from more monsoon-seasonal in the Norian (coal layers as those found in the Mungaroo Formation are typical of monsoon climates; Sellwood & Valdes, 2006) towards predominantly arid climate with a short wet season in the Rhaetian (Scotese, 2000).

Finally, the approach presented here in can be applied to other sedimentary records worldwide but local factors need to be taken into account (*e.g.* depositional environment, tectonic events, and geology/geomorphology). But the same would not be applicable for records of Cretaceous age or younger because the appearance of angiosperms implies a complete redistribution of land plants and the new scenarios are more complex to address.

Conclusions

This study represents the most comprehensive palaeovegetation reconstruction (over 70 million years) reported so far for the Northwest Shelf using molecular proxies (plant biomarkers); and demonstrates that changes in the distribution of palaeoflora not only depended on climate but also on the depositional environment (shoreline position) and probably local tectonic events.

Retene seems to be a suitable tracer of changes in depositional settings due to shoreline migrations. This compound was found to be more abundant in shallow marine environments (transitional/pro-deltaic facies) due to proximity to the source after transgression. Cadalene instead is less diagnostic because it originates from vascular plants in general, which are widely distributed in different depositional environments.

The higher plant fingerprint evaluated over an extended time interval (at least ~50 Myr) can provide a better approximation of palaeoclimate. The population of conifer plants decreased with increasing arid climatic conditions and were probably restricted to the *Pinaceae* family which can adapt to arid environments. Plants other than conifers dominated over the Early Jurassic. These plants (*e.g. Corollina Torosa*) probably synthesised cadalene over retene during a dry climatic episode in the Hettangian–Pliensbachian. Conifers dominated again in the Middle and Late Jurassic where more humid conditions were established. Bryophytes also increased in abundance during the more humid Middle and Late Jurassic periods although this group in general is not very sensitive to climate change.

Acknowledgments

Jaime Cesar acknowledges Curtin University for an International scholarship and The Institute for Geoscience Research for a scholarship. K.G and J.C acknowledge the ARC for Linkage funding [LP150100341] and Woodside Energy Ltd. for supporting this research. Geoff Chidlow, Peter Hopper and Alex Holman are acknowledged for technical support.

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CHAPTER 3

$\delta^{13}C$ of polycyclic aromatic hydrocarbons to establish the facies variations in a fluvial deltaic Triassic record (Dampier sub-Basin, Western Australia)

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Organic Geochemistry, *107*, 59-68 (2017).

ABSTRACT

The $\delta^{13}C$ of polycyclic aromatic hydrocarbons (PAHs) was measured in a series of Triassic and Jurassic source rocks from the Dampier sub-Basin, Carnarvon Basin, North West Shelf of Australia. These sequences correspond to fluvial deltaic systems which integrate the Mungaroo, Brigadier and Legendre Formations, and the organic matter has been assigned as mixed terrigenous/marine material. The relative abundance of the PAHs was plotted against the difference between $\delta^{13}C$ values of 1,3,6,7-tetramethylnaphthalene (TeMN) and each PAH. We demonstrated here that samples plotting below 0 for $\Delta^{13}C_{\text{(Combustion Marker-1,3,6,7 TeMN)}}$ are related to delta-plain/front--deltaic facies or coaly fluvial deltaic facies (samples from the Mungaroo Formation - North Rankin-5, Goodwyn-9 and Goodwyn-5 wells) whereas the positive region for $\Delta^{13}C_{\text{(Combustion Marker-1,3,6,7 TeMN)}}$ is assigned to transitional facies deposited under an estuarine/lagoonal environment with a high sapropelic contribution (Brigadier Formation) and marginal marine environment (Legendre Formation). A similar separation for the samples was obtained with phenanthrene and other PAHs. The $\delta^{13}C$ of PAHs in combination with their distributions can be used to establish the facies type, *i.e.*, delta-plain/front-deltaic from estuarine/lagoonal in a dominantly fluvial deltaic record. Our research provides new tools to take into account for further applications in fluid-source rock correlation studies which represent the main challenge in assessing petroleum systems in the sub-Basin.

Keywords: polycyclic aromatic hydrocarbons, alkylnaphthalene, stable carbon isotopes, organic facies, fluvial-deltaic.

Introduction

Vascular plants are the main sources of terrestrial-derived organic matter in sediments and can contain high concentrations of biomacromolecules such as lignin, tannin, suberin and cutin (de Leeuw & Largeau, 1993). Certain alkylated aromatic compounds (*e.g.* cadalene and retene) have a strong association with higher plant precursors. Retene has been considered to be mainly sourced from resins of conifers (Simoneit, 1985; Hautevelle, Michels, Malartre, & Trouiller, 2006), although this molecule has also been found in Upper Silurian – Lower Devonian sediments (gymnosperms only evolved during the Late Devonian) for which Early Palaeozoic bryophytes were suggested as potential source (Romero-Sarmiento, Riboulleau, Vecoli, & Versteegh, 2010). Cadalene instead is produced not only from plant resins but also from cadinenes, cadinoles, fungi and a range of essential oils, and even certain bryophytes (Otto and Wilde, 2001; Nguyen Tu, Derenne, Largeau, Mariotti, & Bocherens, 2003; Asakawa, 2004).

Other aromatics include non-alkylated polycyclic aromatic hydrocarbons (PAHs) attributed to incomplete combustion (Killops and Massoud, 1992; Jiang *et al.*, 1998; Grice, Nabbefeld, & Maslen, 2007). These compounds cannot be associated to any specific type of plant taxa, but testify that fire events or volcanism may have taken place prior to and/or during the deposition of organic matter (Oros, Abas, Omar, Rahman, & Simoneit,, 2006; Iinuma *et al.*, 2007). PAHs are normally sorbed onto combustion-generated airborne and riverine particulate material and deposited within sediments (Killops and Massoud, 1992; Jiang *et al.*, 1998). The presence of combustion-derived PAHs can be attributed to the fusinite group (pyrofusinite) in the organic matter which has been often reported in coals (Falcon-Lang, 2000; Romero-Sarmiento, Riboulleau, Vecoli, Laggoun-Défarge, & Versteegh, 2011). In a few cases PAH compounds like benzo(*e*)pyrene and perylene have been shown to derive from algal sources and fungal wood pigments, respectively (Grice *et al.*, 2007, 2009; Tulipani *et al.*, 2015).

Phenanthrene is another PAH that has been widely used to distinguish the type of organic matter and depositional environment based on distribution, abundance (Alexander, Bastow, Fisher, & Kagi,, 1995; Budzinski *et al.* 1995; Hughes, Holba, & Dzou, 1995) and its stable carbon isotopic composition (Radke, Willsch, Leythaeuser,

& Teichmüller, 1982; Maslen, Grice, Le Métayer, Dawson, & Edwards, 2011; Le Métayer *et al.*, 2014) in petroleum and sediments. This compound has been shown to originate from combustion processes (Laflamme and Hites, 1978) as well as being generated during diagenesis from certain natural product precursors (Tan, Kong, & Monetti, 1996).

Additionally, amongst the aromatic compounds occurring in sediments are alkylnaphthalenes [monomethyl (MN), dimethyl (DMN), trimethyl (TMN), tetramethyl (TeMN) and pentamethyl naphthalenes (PeMN)] which have been applied as thermal maturity parameters of oils (van Aarssen, Bastow, Alexander, & Kagi, 1999). However, these alkylnapthalene parameters have little use in source-rock studies as they are largely influenced by source (van Aarssen *et al.*, 1999; Romero-Sarmiento *et al.*, 2011). For example, the 1,2,5-TMN has been shown to be derived from a bacterial source through degradation of the D-ring of the monoaromatic 8,14-secohopanoids (Püttmann and Villar, 1987; Grice, Audino, Boreham, Alexander, & Kagi, 2001) but this could also form by degradation of triaromatic tetracyclic triterpenoids at higher stages of coalification (Püttmann and Villar, 1987). The 1,3,6,7-TeMN is another compound also derived from a microbial precursor (van Aarssen *et al.*, 1999; Asif, Fazeelat, & Grice,, 2011; Romero-Sarmiento *et al.*, 2011).

In terms of compound specific isotope analyses (CSIA) of aromatic hydrocarbons (such as alkylnaphthalenes and PAHs) in oils and sediments, very few studies have been carried out (Grice *et al.*, 2001, 2007; Nabbefeld, Grice, Summons, Hays, & Cao, 2010; Maslen *et al.*, 2011; Williford, Grice, Logan, Chen, & Huston, 2011; Williford, Grice, Holman, & McElwain, 2014; Le Métayer *et al.*, 2014; Tulipani *et al.*, 2015). The work of Maslen *et al.* (2011) showed that CSIA allows for marine or terrigenous end-members to be determined which cannot be established by bulk δ^{13}C values of saturated and aromatic fractions. Maslen *et al.* (2011) evaluated the stable carbon isotopic composition of 1,6-DMN and 1,2,5-TMN from a set of oils from Western Australia. The oils with more negative δ^{13}C values for these compounds were associated with a marine source for organic matter, whereas those with more positive δ^{13}C values were suggested to represent a mixed marine/terrigenous source. A similar source effect was also considered to explain a large variation in δ^{13}C values for 1,6-

DMN, 1,2,5-TMN, 1,2,5,6-TeMN and alkylphenanthrenes in crude oils from the Northern Carnarvon Basin, Western Australia, by Le Métayer *et al.* (2014).

Our study is also based on the Northern Carnarvon Basin, specifically the Dampier sub-Basin though from a source rock perspective, and include the Mungaroo, Brigadier and Legendre Formations which represent potential sources for some of the gas/condensate accumulations in the Rankin Platform. These sediments were deposited in fluvial deltaic systems and the organic matter is assigned as mixed terrigenous/marine material. In this sub-Basin, it is still very challenging to define the contribution of every potential source rock to the hydrocarbon accumulations (Triassic vs Jurassic sources) due to very similar organic facies, similar depositional environment and very low concentration of key organic compounds (*e.g.* hopanes and steranes) in the fluids (Longley *et al.*, 2002). Therefore, the development of new parameters that better describe the variability of the source may have a significant impact in de-convoluting petroleum systems in the Dampier sub-Basin.

To help address these gaps we have measured the stable carbon isotopic compositions of 1,2,5,-TMN and 1,3,6,7-TeMN and certain PAHs on a set of samples from the Dampier sub-Basin. These samples show variations in the sedimentary facies type ranging from delta-plain facies towards front-deltaic, and estuarine/lagoonal with high sapropel content (Woodside Energy Ltd, 1977). Our research focuses on North Rankin – 5 which integrates a continuous sequence of the Mungaroo and Brigadier Formations and the contribution from these source rocks to the reservoirs is less certain (Longley *et al.*, 2002; Edwards & Zumberge, 2005; Jablonski, Preston, Westlake, & Gumley, 2013) though sample availability from the different wells was also a factor to consider for our selection. The fact of the organic facies being very similar and the anticipated presence of the afore-discussed aromatic compounds in the fluids (condensate and crude oil) facilitate the applicability of these parameters at a basin scale.

Materials and methods

Geological Setting

The Mungaroo Formation is a sandy sequence which conformably overlies the Locker Shale, and represents a siliciclastic stratigraphy dominantly argillaceous with two main fine-grained facies (i) brown claystone and (ii) grey claystone which have been attributed to fluvial deltaic environments with local reducing conditions. The sediments were deposited in a clastic depositional cycle with progradation into a marine environment followed by transgression. Additionally, thin coal layers occur having local importance (Longley *et al.*, 2002). Conformably overlying the Mungaroo Formation is the Brigadier Formation which corresponds to a very thinly interbedded claystone and sandstone as well as several intervals of fine to medium grained sandstone; and the depositional environment was paralic to shallow-marine after the drowning of the Mungaroo Formation delta environment (Hocking, Moors, & Van de Graaff, 1987). The sediments in the Brigadier Formation are far from simple to interpret although an increase in the marine character is apparent; these sediments packages are thought to record the intimate interplay of fluvial and transgressive processes in an estuarine setting (Woodside Energy Ltd., 1977). **Figure 3.1** shows the Mungaroo Delta in a Late Triassic palaeogeographic map.

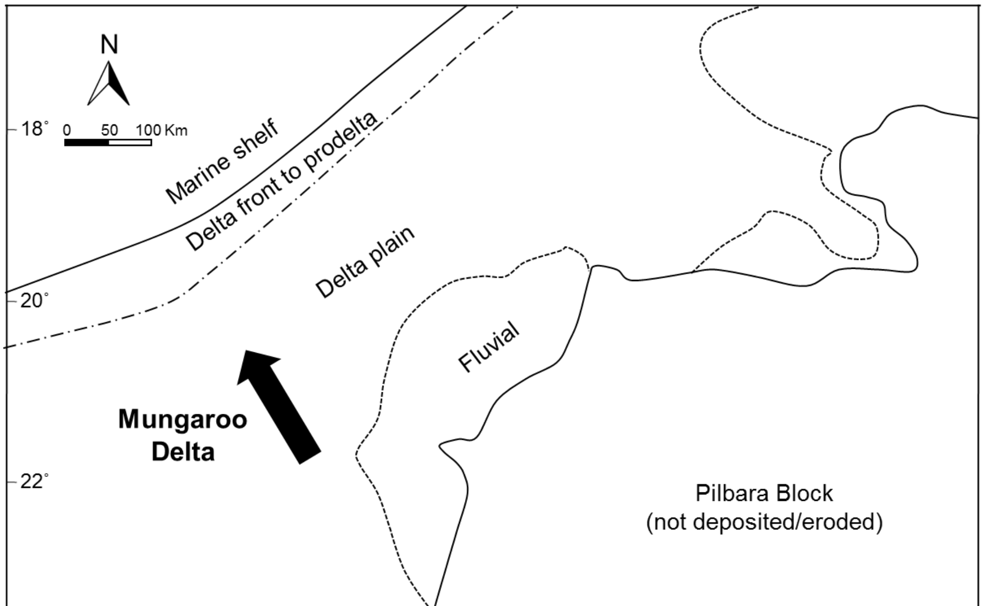


Figure 3.1. The Late Triassic palaeogeographic map of the Northern Carnarvon Basin (modified after Tao *et al.*, 2013).

The Legendre Formation represents a regressive deltaic to marginal marine sequence (Hocking, 1992) which potential source rock interval was deposited in an estuarine system largely tidally influenced, with marine incursions (Woodside Energy Ltd., 1997).

Samples and sample preparation

A set of 16 source rock samples was used for the study (Table 1). These come from the North Rankin-5 well in the Dampier sub-Basin (Figure 2). All the samples are of Triassic age and correspond to the Mungaroo and Brigadier Formations [%TOC up to 11 and 5 respectively and 430 ºC Tmax (Phillips Australian Oil Company, 1993)]. Additional samples of Triassic (Goodwyn-5, Goodwyn-9) and Jurassic age [Perseus South-1, up to 3 %TOC and 430 ºC Tmax (Woodside Energy Ltd., 1997)] were also included for comparison.

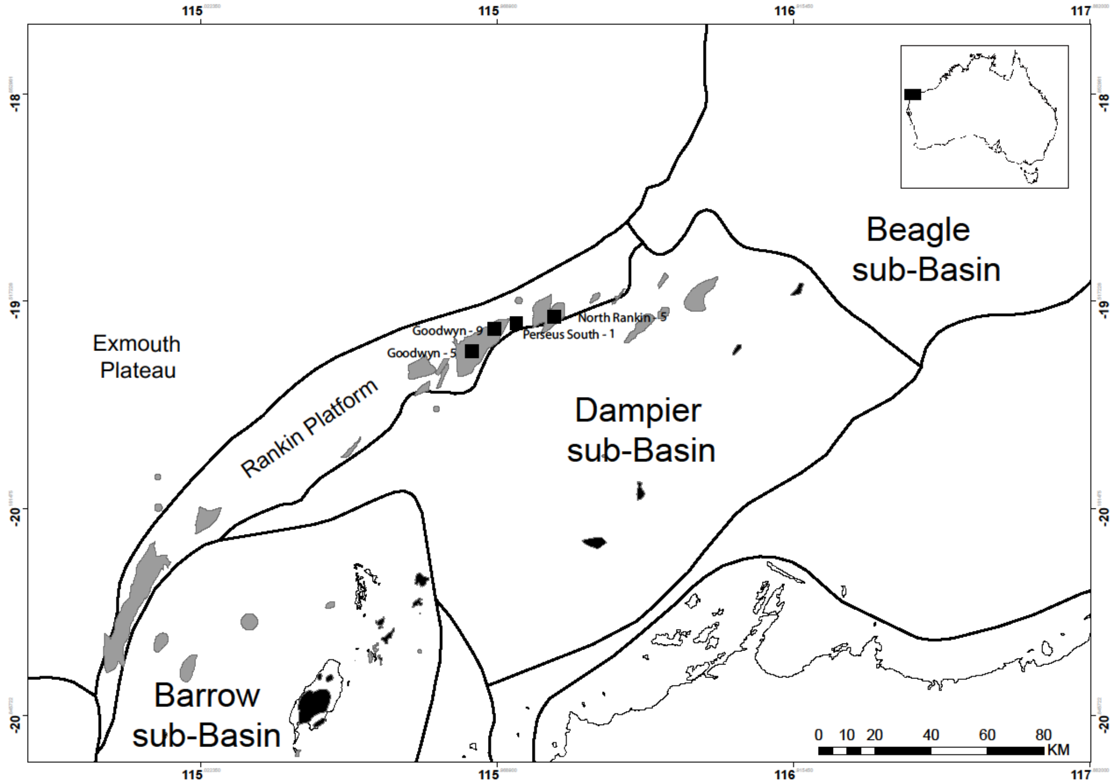


Figure 3.2. Well locations in the Dampier sub-Basin.

The bitumen was extracted (1 h) using a Milestone START-E microwave extraction system with a mixture 9:1 of dichloromethane (DCM) and methanol (MeOH) using a temperature program of 80 ºC for 15 min after a ramp of 8 ºC/min. Approximately 5-

10 mg of an aliquot of the bitumen was subsequently separated in aliphatic, aromatic and polar fractions by a small scale silica gel liquid chromatography as described elsewhere (Maslen *et al.*, 2011). Aromatic hydrocarbons including PAHs were analysed using gas chromatography - mass spectrometry (GC-MS) and gas chromatography – isotope-ratio mass spectrometry (GC-irMS).

Table 3.1 includes fundamental information about the samples. This is complemented with the **Figure 3.3** which summarises the stratigraphy in North Rankin – 5 and show, in general terms, how the facies are displayed; it also contains thermal maturity (expressed as Tmax from Rock-eval pyrolysis) and total organic carbon (%TOC) profiles Phillips Australian Oil Company, 1993; Woodside Energy Ltd., 1997).

GC-MS

The aromatic fractions were dissolved in *n*-hexane and analysed by GC-MS on a HP 6890 GC coupled to a HP 5973 mass selective detector (MSD) operating in electron ionisation mode (70 eV), and injections were of 1 µL of solution using an HP 6890 auto-sampler. The compounds were chromatographically separated on a WCOT fused silica capillary column (60 m X 0.25 mm i.d.) with a 0.25 µm 5% phenyl–methyl–silicon stationary phase (DB-5), and the carrier gas was helium at a linear velocity of 1 mL/min. The temperature program of the GC oven was programmed from 40 ºC – 325 ºC (at 3 ºC/min) and was held isothermally for 45 minutes at 325 ºC.

The identification of the compounds was achieved by comparing the mass spectra and the relative retention times with those previously reported in the literature (van Aarssen *et al.*, 1999; Grice *et al.*, 2001; Nabbefeld *et al.*, 2010; Maslen *et al.*, 2011).

GC-irMS

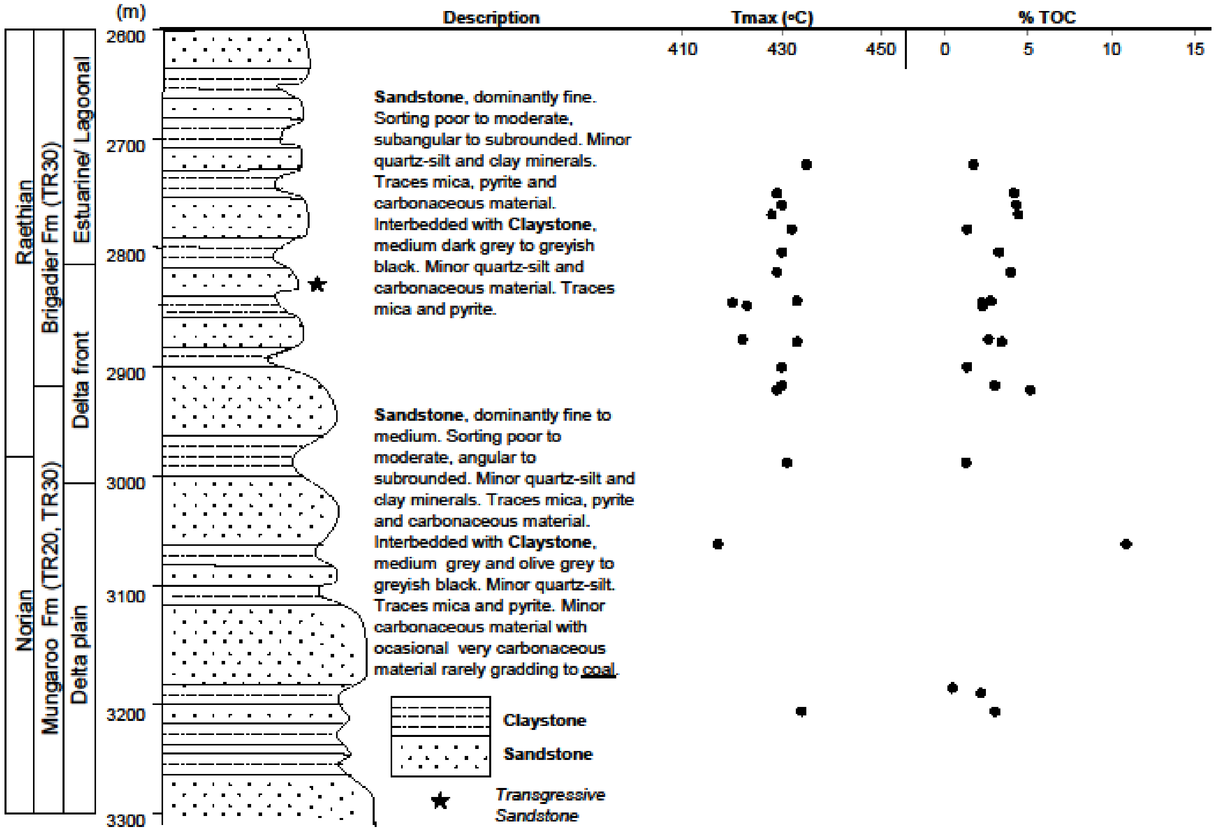
A Thermo Scientific Trace GC Ultra, connected to a Thermo Scientific Delta V Advantage irMS via a GC Isolink and Conflo IV was used for CSIA. 1 µL of each fraction was injected into a split-splitless injector operating in splitless mode, held at 280 °C. The same GC conditions as used above for GC-MS analyses were used for CSIA. Helium was used as carrier gas at a constant flow of 1.5 mL / min. GC column outflow passed through the GC Isolink combustion reactor (copper oxide and nickel

3.1. Fundamental data and selected molecular ratios (Fla, B*a*Py, B*e*Py and Cor relative to 1,3,6,7-TeMN) of the samples (Woodside Energy Ltd, 1977, 1979, 1987, 1997; Phillips Australian Oil Company, 1993; this study). Stratigraphic peaks from Marshall and Lang (2013). na.: non available.

Facies	*Sample ID*	*%TOC*	*Tmax (°C)*	*C_{29}sterane ββ/(αα+ββ)*	*Fla*	*BaPy*	*BePy*	*Cor*	*Cor/BaPy*	*BePy/Phe*
Estuarine (TR30)	NR-5(88)	1.71	435	0.35	1.18	0.79	0.95	0.07	0.09	0.06
	NR-5(89)	4.15	429	0.30	1.70	0.79	1.33	0.37	0.47	0.08
	NR-5(90)	4.3	430	0.33	2.65	1.44	1.79	0.34	0.24	0.08
	NR-5(91)	1.33	432	0.35	1.20	1.12	1.24	0.32	0.29	0.08
	NR-5(93)	3.24	430	0.33	1.85	1.39	1.58	0.48	0.35	0.07
	NR-5(69)	3.94	429	0.36	2.22	2.48	3.22	1.07	0.43	0.15
Delta front (TR20, TR30)	NR-5(77)	na	Na	0.31	1.88	1.86	1.75	0.42	0.22	0.08
	NR-5(78)	2.76	433	0.34	2.03	1.90	2.14	0.43	0.22	0.11
	NR-5(79)	na	Na	0.33	2.44	3.13	3.06	0.68	0.22	0.16
	NR-5(80)	3.41	433	0.35	2.44	2.78	2.62	0.73	0.26	0.15
	NR-5(82)	1.34	430	0.34	2.59	3.09	3.47	0.98	0.32	0.19
	NR-5(84)	2.99	430	0.32	3.09	5.40	5.06	1.24	0.23	0.21
	NR-5(85)	na	Na	0.30	2.39	3.15	2.92	0.60	0.19	0.17
	NR-5(55)	na	Na	0.34	9.61	7.57	6.69	2.81	0.37	0.15
	NR-5(64)	10.89	431	0.37	18.22	27.15	15.59	13.87	0.51	0.14
	NR-5(47)	3.01	434	0.40	21.74	17.93	26.79	6.27	0.35	1.23
	G-9(10)	2.40	432	0.34	13.26	13.64	17.33	4.22	0.31	0.26

Table 3.1 (Continued)

Facies	*Sample ID*	*%TOC*	*Tmax (°C)*	*C_{29}sterane ββ/(αα+ββ)*	*Fla*	*BaPy*	*BePy*	*Cor*	*Cor/BaPy*	*BePy/Phe*
Delta plain (TR20)	G-9(12)	na	Na	0.35	16.20	25.03	22.46	10.34	0.41	0.31
	G-9(15)	2.40	433	0.35	1.95	1.43	1.45	1.08	0.75	0.21
	G-9(16)	na	Na	0.37	23.13	14.32	15.39	12.31	0.86	0.15
	G-9(14)	3.00	435	0.36	26.71	47.76	41.06	16.26	0.34	0.13
	G-5(2)	na	Na	0.39	4.09	2.36	3.59	0.68	0.29	0.14
	G-5(3)	na	Na	0.38	7.69	3.20	4.31	0.85	0.26	0.09
Estuarine (J40.0_SB, J29.51_FS)	PS-1(22)	na	Na	0.32	6.71	4.40	9.00	3.21	0.73	0.29
	PS-1(24)	na	Na	0.31	3.42	3.19	6.64	3.22	1.01	0.20
	PS-1(27)	2.58	431	0.33	7.51	4.60	8.47	2.83	0.61	0.27
	PS-1(20)	na	Na	0.35	8.50	4.83	9.76	2.96	0.61	0.24
	PS-1(21)	na	Na	0.34	7.05	4.35	8.20	2.43	0.56	0.24
	PS-1(25)	na	Na	0.31	8.96	6.11	13.95	4.86	0.79	0.30
	PS-1(26)	na	Na	0.31	4.70	3.09	7.51	2.75	0.89	0.31
	PS-1(28)	na	Na	0.31	10.34	6.80	15.37	6.46	0.95	0.25



Sandstone, dominantly fine. Sorting poor to moderate, subangular to subrounded. Minor quartz-silt and clay minerals. Traces mica, pyrite and carbonaceous material. Interbedded with **Claystone**, medium dark grey to greyish black. Minor quartz-silt and carbonaceous material. Traces mica and pyrite.

Sandstone, dominantly fine to medium. Sorting poor to moderate, angular to subrounded. Minor quartz-silt and clay minerals. Traces mica, pyrite and carbonaceous material. Interbedded with **Claystone**, medium grey and olive grey to greyish black. Minor quartz-silt. Traces mica and pyrite. Minor carbonaceous material with ocasional very carbonaceous material rarely gradding to coal.

Figure 3.3. Stratigraphy of North Rankin – 5 well with thermal maturity (Tmax from Rock-eval pyrolysis) and total organic carbon (% TOC) profiles (Woodside Energy Ltd., 1977; Phillips Australian Oil Company, 1993; Marshall & Lang, 2013) .

oxide, held at 1000 °C) which combusted each peak to a separate peak of CO_2. The $\delta^{13}C$ values are expressed in parts per mil (‰) relative to the International Vienna Peedee Belemnite (VPDB) standard, and were calculated by Thermo Isodat software from the integration of the 44, 45 and 46 mass ions currents.

Every two sample measurements, a mixture of standards with known $\delta^{13}C$ values was analysed in order to insure instrument accuracy. Peaks co-eluting as well as those at very low concentrations were not considered for our interpretations. Only target compounds with standard deviation of less than 0.4‰ were taken into account.

Results and discussion

Distribution of combustion-derived PAHs

In general, the combustion-derived PAHs present in sediments are often not attributed to specific type of plants. Their occurrence instead can be related to charred or fusinised plant debris and often testify a fire event took place contemporarily with the deposition of organic matter (Falcon-Lang, 2000; Oros *et al.*, 2006; Iinuma *et al.*, 2007; Romero-Sarmiento *et al.*, 2011). However, the presence of these compounds is also indicative of terrestrial organic matter input. In this study, the relative abundance of selected PAHs has been compared to the relative abundance of 1,3,6,7-Tetramethylnaphthalene as implemented by Jiang *et al.* (1998). The origin of the 1,3,6,7-TeMN isomer has shown to be strongly associated with marine-derived organic matter (van Aarssen *et al.*, 1999; Asif *et al.*, 2011; Romero-Sarmiento *et al.*, 2011); therefore its relative abundance compared to the abundance of the PAHs can be used as an indicator of the type of organic matter accumulated.

The following combustion markers were identified in all the samples (see **Figure 3.4** for chromatographic distribution): pyrene (Pyr), benzo[*a*]pyrene (B*a*Py), benzo[*e*]pyrene (B*e*Py), coronene (Cor), fluoranthene (Fla), benzofluaranthenes (BFla), benzo[*g,h,i*]perylene (Bpery), chrysene (Chry), triphenylene (Tpn) and benzo[*a*]anthracene (B*a*An). Chrysene and triphenylene show a similar distribution to all other PAHs in these samples supporting a source predominantly from combustion rather than other sources (Killops and Massoud, 1992; Jiang *et al.*, 1998; Grice *et al.*, 2007; Nabbefeld *et al.*, 2010). Additionally, perylene and simonellite were found but these are assigned to other sources (Jiang *et al.*, 2000; Grice *et al.*, 2009); and thus have not been considered for our study.

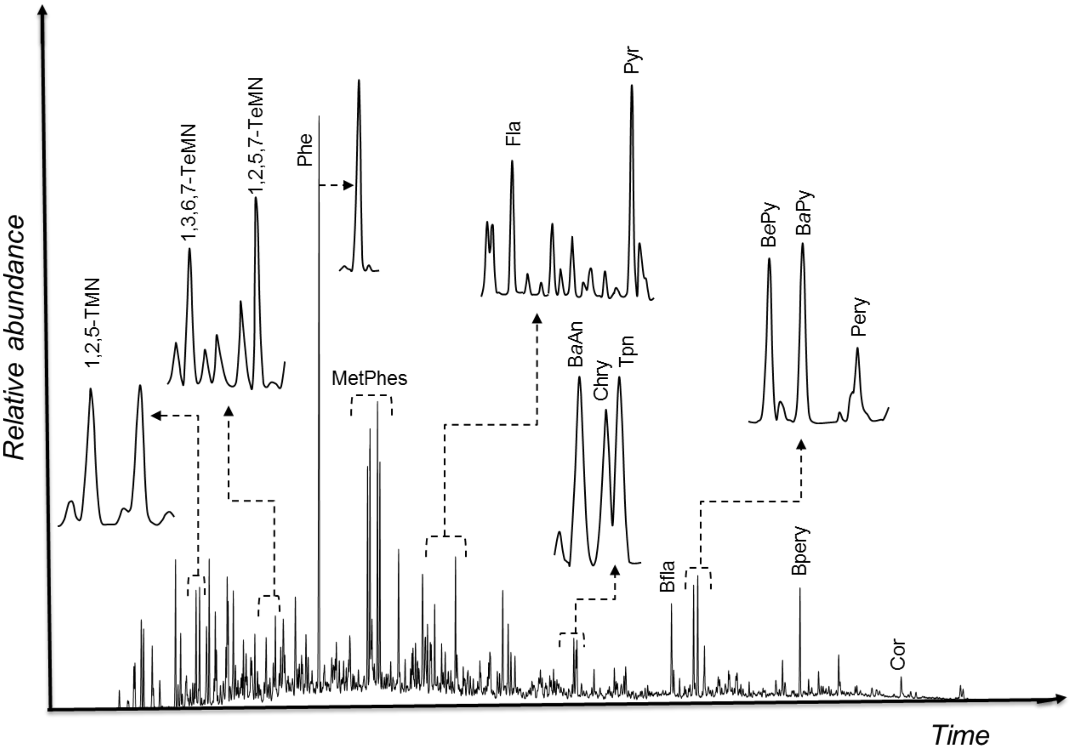


Figure 3.4. Total ion chromatogram of the aromatic fraction [sample NR-5(47)] with the identified compounds. 1,2,5-trimethylnaphthalene (1,2,5-TMN), 1,3,6,7-tetramethylnaphthalene (1,3,6,7-TeMN), 1,2,5,7-tetramethylnaphthalene (1,2,5,7-TeMN), phenanthrene (Phe), methylphenanthrenes (MetPhes), pyrene (Pyr), benzo[*a*]anthracene (B*a*An), triphenylene (Tpn), chrysene (Chry), coronene (Cor), benzo[*g*,*h*,*i*]perylene (Bpery), benzofluoranthenes (Bfla), benzo[*e*]pyrene (B*e*Py), benzo[*a*]pyrene (B*a*Py) and fluoranthene (Fla).

Figure 3.5 shows the relative abundance of the PAHs from combustion sources relative to the 1,3,6,7-TeMN isomer through a Triassic sequence (North Rankin - 5 well, Dampier sub-Basin). In general the PAH/1,3,6,7-TeMN ratios show a similar trend throughout the profile and thus point towards a common origin (see also Table 1 for selected molecular ratios as example). At the top of the sequence the PAH ratios are low and support a stronger marine influence. Towards the sediments that are described as front-deltaic to delta-plain the PAH ratios increase substantially. The preservation of these organic molecules in oxic settings also suggests a higher sedimentation rate and rapid burial which reduce the residence time of the organic matter in the zones of degradation (Peters, Clifford, Walters, & Molodowan, 2005a).

Higher %TOC values registered in the Mungaroo Formation might also be a consequence of a higher sedimentation rate since increasing %TOC has already been reported with increasing sedimentation rate in oxic settings (Stein, 1986). Jiang *et al.* (1998) also found that higher PAH/1,3,6,7-TeMN ratios correspond to high sedimentation rates.

In terms of the process originating the PAHs, low Cor/B*a*Py values (<1, see Table 1) can be assigned to combustion rather than volcanic activity as described by Williford *et al.* (2014). Frequent combustion is anticipated at this latitude due to very warm temperatures during the Triassic period (Preto, Kustatscher, & Wignall, 2010). The above PAHs are usually absorbed and stabilised in the particulates released from combustion (soot) and can be protected of a variety of environmental agents during fluvial or aeolian transportation (Killops and Massoud, 1992; Jiang *et al.*, 1998; Grice *et al.*, 2007).

On a more regional scale, Jiang *et al.* (2000) found a high abundance of combustion-derived compounds in the Northern Carnarvon Basin, specifically in the Delambre-1 well. They suggested the occurrence of forest fires as their main source which was also supported by palynological data. A contribution of combustion from fires associated with swamps and peat bogs was also considered. According to the above study, abundant vegetation and a humid and seasonal climate was favourable for frequent fires events. The findings in North Rankin – 5 described herein might represent a small-scale fire regime similar to that described in the Delambre-1 well. Furthermore, the wood soot accumulated within the sediments provides a solid matrix that stabilises PAHs (Rogge, Hildemann, Mazurek, Cass, & Simoneit,1998) as well as interactions between PAHs and clay minerals have been suggested to help stabilising these molecules (Jia, Zhao, Li, L., Li, X., & Wang, 2014).

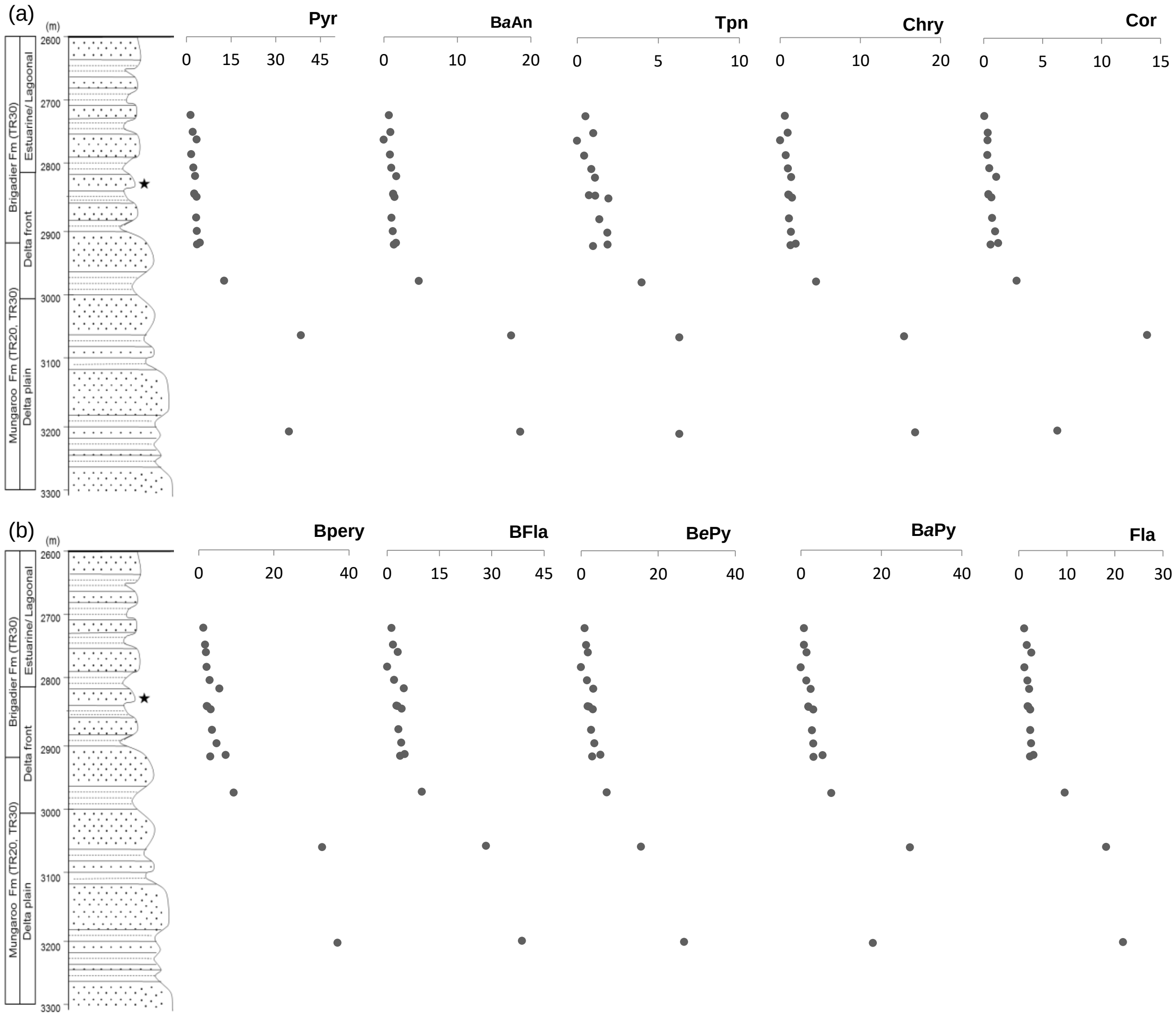


Figure 3.5. Distribution of combustion-derived PAHs through a Triassic sequence in North Rankin – 5. The ratio between each PAH and 1,3,6,7-TeMN has been plotted for:

(a): pyrene (Pyr), benzo[*a*]anthracene (B*a*An), triphenylene (Tpn), chrysene (Chry) and coronene (Cor).

(b): benzo[*g*,*h*,*i*]perylene (Bpery), benzofluoranthenes (Bfla), benzo[*e*]pyrene (B*e*Py), benzo[*a*]pyrene (B*a*Py) and fluoranthene (Fla).

δ^{13}C of PAHs and alkylnaphthalenes

CSIA was carried out on the samples to evaluate any possible source differentiation (see **Table 3.2** for isotopic values). In general terms, as can be observed in **Figure 3.6a** (fluoranthene as an example), the δ^{13}C of the PAHs does not display significant changes with depth except for the sample NR-5(93) in the Brigadier Formation where marine contribution increases. So δ^{13}C of 1,2,5 TMN, which has been shown before to be a useful measurement for establishing marine/terrigenous influences, was measured (Alexander, Bastow, Kagi, & Singh, 1992; Grice *et al.*, 2001; Sivan, Datta, & Singh, 2008; Asif *et al.*, 2011; Maslen *et al.*, 2011; Romero-Sarmiento *et al.*, 2011). In fact, when the depth profile of δ^{13}C of 1,2,5-TMN is plotted (**Figure 3.6b**, error bars non-visible at this scale), a major variability can be observed. The δ^{13}C values of 1,2,5-TMN are more negative where the marine influences increases towards the Brigadier Formation; the organic matter of marine origin is known to have lower δ^{13}C values (Gaines, Eglinton, & Rullkötter, 2009). Other samples from the Mungaroo Formation (*e.g.* from Goodwyn-9 and Goodwyn-5 wells, **Table 3.2**) also show more positive values than samples from Brigadier. As a result, compared The δ^{13}C of 1,3,6,7-TeMN and 1,2,5,7 TeMN were also measured; these and δ^{13}C of 1,2,5-TMN were plotted against the relative abundance of all PAHs. All PAHs show a similar trend with δ^{13}C of all these alkylnaphthalenes. For simplicity we have chosen 2 representative PAHs (B*e*Py and Cor) plotted against δ^{13}C of 1,2,5,7 TeMN and 1,3,6,7-TeMN (**Figure 3.7**).

In the interval of North Rankin-5 where the input of marine organic matter increases, the δ^{13}C values of 1,3,6,7-TeMN are lower, and the PAHs (terrigenous organic matter indicators) are relatively less abundant compared to delta-plain facies. Additional samples from other wells, (Goodwyn-5, Goodwyn-9 and Perseus South-1) have been included; and as anticipated, slightly higher δ^{13}C values of 1,3,6,7-TeMN occur where PAHs are relatively more abundant.

Table 3.2. δ^{13}C values with the corresponding standard deviation (σ). nd.: not-determined (due to very high error, very low abundance, or poor baseline separation).

Sample ID	*Fla*	*σ*	BePy	*σ*	BaPy	*σ*	*1,2,5-TMN*	*σ*	*1,3,6,7-TeMN*	*σ*	*1,2,5,7-TeMN*	*σ*	*Phe*	*σ*
NR-5(88)	-26.2	0.1	nd	nd	nd	nd	-26.7	0.0	-26.8	0.3	nd	nd	-24.5	0.2
NR-5(89)	-26.9	0.3	nd	nd	nd	nd	-28.2	0.1	-30.0	0.1	-24.8	0.3	-25.4	0.1
NR-5(90)	-26.7	0.1	-31.1	0.0	nd	nd	nd	nd	nd	nd	-25.0	0.3	-24.6	0.1
NR-5(91)	nd	nd	nd	nd	-25.9	0.4	-24.5	0.1	nd	nd	nd	nd	nd	nd
NR-5(93)	-31.8	0.2	nd	nd	nd	nd	-25.1	0.2	-26.4	0.1	-26.1	0.4	nd	nd
NR-5(69)	nd	nd	-25.8	0.3	nd	nd	-23.9	0.1	nd	nd	nd	nd	-23.4	0.3
NR-5(77)	nd	nd	nd	nd	-26.2	0.2	nd	nd	-31.2	0.2	nd	nd	nd	nd
NR-5(78)	-28.8	0.0	nd	nd	nd	nd	-27.3	0.1	-26.1	0.4	nd	nd	-26.0	0.4
NR-5(79)	-26.3	0.1	-26.6	0.1	-25.2	0.0	-29.5	0.4	nd	nd	-24.6	0.3	nd	nd
NR-5(80)	-26.2	0.0	-26.3	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
NR-5(82)	nd	nd	-26.2	0.2	-25.7	0.2	-23.9	0.0	nd	nd	nd	nd	-27.2	0.4
NR-5(84)	-28.2	0.4	-27.5	0.3	-26.4	0.0	-23.9	0.2	nd	nd	-25.2	0.3	nd	nd
NR-5(85)	-26.8	0.1	-26.9	0.3	-26.0	0.3	-27.2	0.2	-28.2	0.1	nd	nd	nd	nd
NR-5(55)	-26.5	0.2	-29.3	0.3	nd	nd	nd	nd	-24.0	0.4	nd	nd	-23.6	0.2
NR-5(64)	-26.5	0.1	-28.2	0.2	-28.6	0.2	nd	nd	nd	nd	nd	nd	-24.8	0.1
NR-5(47)	-25.9	0.4	-26.6	0.4	-26.8	0.3	-24.0	0.1	-25.7	0.0	nd	nd	nd	nd
G-9(10)	nd	nd	-26.5	0.1	-26.3	0.0	nd	nd	-26.6	nd	nd	nd	-24.6	0.1
G-9(12)	nd	nd	-25.8	0.0	-26.2	0.1	-24.3	0.4	-24.3	0.0	nd	nd	-25.1	0.2
G-9(15)	nd	nd	nd	nd	nd	nd	-24.3	0.0	nd	nd	-25.7	0.0	-25.9	0.3

Table 3.2. (Continued)

Sample ID	*Fla*	*σ*	*BePy*	*σ*	*BaPy*	*σ*	*1,2,5-TMN*	*σ*	*1,3,6,7-TeMN*	*σ*	*1,2,5,7-TeMN*	*σ*	*Phe*	*σ*
G-9(16)	nd	nd	-26.3	0.0	nd	nd	nd	nd	-24.7	0.2	-25.6	0.0	nd	nd
G-9(14)	nd	nd	nd	nd	-27.1	0.1	nd	nd	-24.0	0.1	nd	nd	nd	nd
G-5(2)	nd	nd	-27.6	0.1	-29.2	0.2	-26.3	0.4	nd	nd	nd	nd	nd	nd
G-5(3)	nd	nd	-29.3	0.1	-26.9	0.1	nd	nd	nd	nd	-25.5	0.2	-25.3	0.3
PS-1(22)	nd	nd	nd	nd	nd	nd	-25.8	0.3	nd	nd	-25.8	0.0	nd	nd
PS-1(24)	nd	nd	-24.6	0.3	nd	nd	-24.6	0.2	-26.8	0.4	-26.0	0.4	-24.6	0.2
PS-1(27)	nd	nd	-24.0	0.1	-24.1	0.4	-24.8	0.1	-27.6	0.2	-25.1	0.0	-26.8	0.1
PS-1(20)	nd	nd	-23.3	0.4	-24.2	0.0	-25.3	0.1	-26.0	0.1	nd	nd	-25.1	0.0
PS-1(21)	nd	nd	-23.6	0.4	-27.1	0.2	-24.3	0.1	nd	nd	nd	nd	-24.4	0.1
PS-1(25)	nd	nd	-22.9	0.2	-23.5	nd	nd	nd	-25.3	0.0	nd	nd	-24.6	0.0
PS-1(26)	nd	nd	-24.5	0.1	nd	nd	nd	nd			nd	nd	-27.9	0.2
PS-1(28)	nd	nd	-23.5	0.4	-23.1	0.2	nd	nd	-25.8	0.1	nd	nd	-25.3	0.1

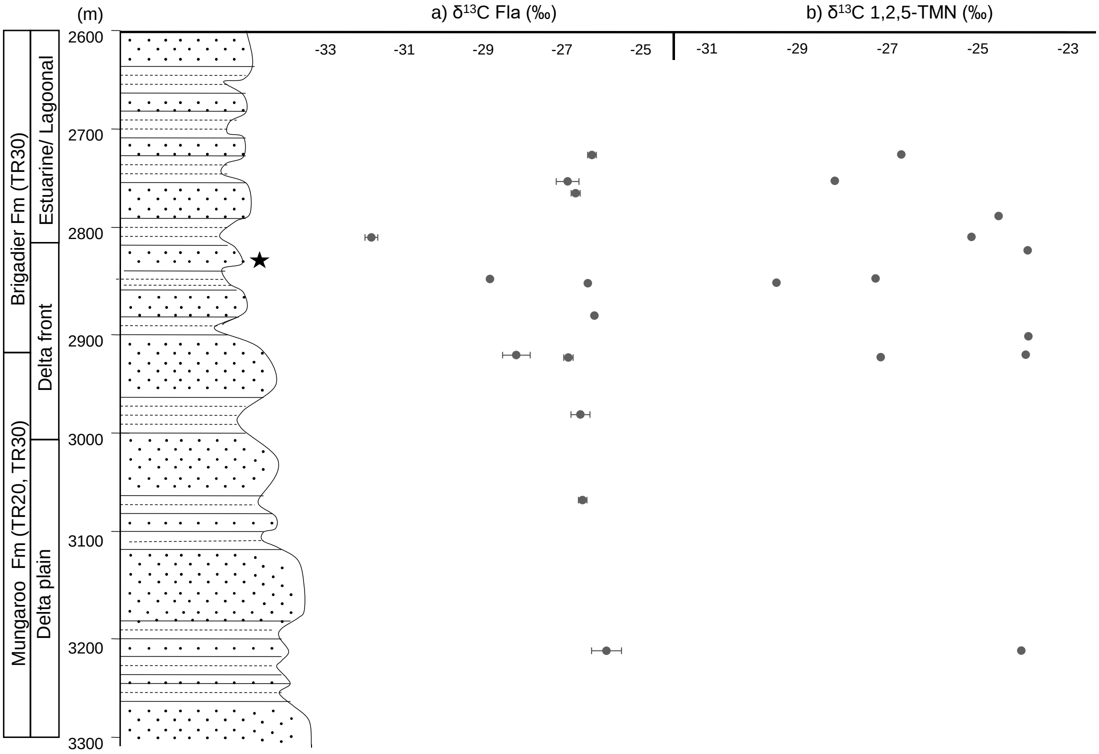


Figure 3.6. Depth profile of δ^{13}C values for (a): fluoranthene (Fla), and (b): 1,2,5-trimethylnaphthalene (1,2,5-TMN); in North Rankin – 5 well.

1,2,5,7-TeMN has been previously associated with a microbial origin (Alexander *et al.*, 1992). However, this compound could also be generated by alkylation of 1,2,5-TMN and therefore cannot be linked to a specific source (Bastow *et al.*, 2000). Bastow *et al.* (2000) found the abundance of certain alkylnaphthalanes is proportional to the abundance of their equivalent methylated compounds in the following order: 1,6-DMN to 1,4,6-TMN, 1,2,5-TMN to 1,2,5,7-TeMN, 1,2,3,5-TeMN to 1,2,3,5,7-PMN, and 1,2,3,5,6-PMN to 1,2,3,5,6,7-HMN. For our investigation, the δ^{13}C of 1,2,5,7-TeMN does not seem to be a suitable discriminating factor since no differentiation amongst the samples is obtained based on their δ^{13}C values (**Figure 3.7**). Therefore, here, we can consider the sedimentary alkylation reaction (from 1,2,5-TMN to 1,2,5,7-TeMN) as being responsible for the alteration (homogenisation) of the isotopic composition of 1,2,5,7-TeMN and the dissipation of any source signature on the isotopic composition of this molecule.

These results show that 1,2,5-TMN and 1,3,6,7-TeMN represent reliable indicators of marine organic matter input, and their δ^{13}C values allows discrimination of intervals with different marine influence on the depositional environment.

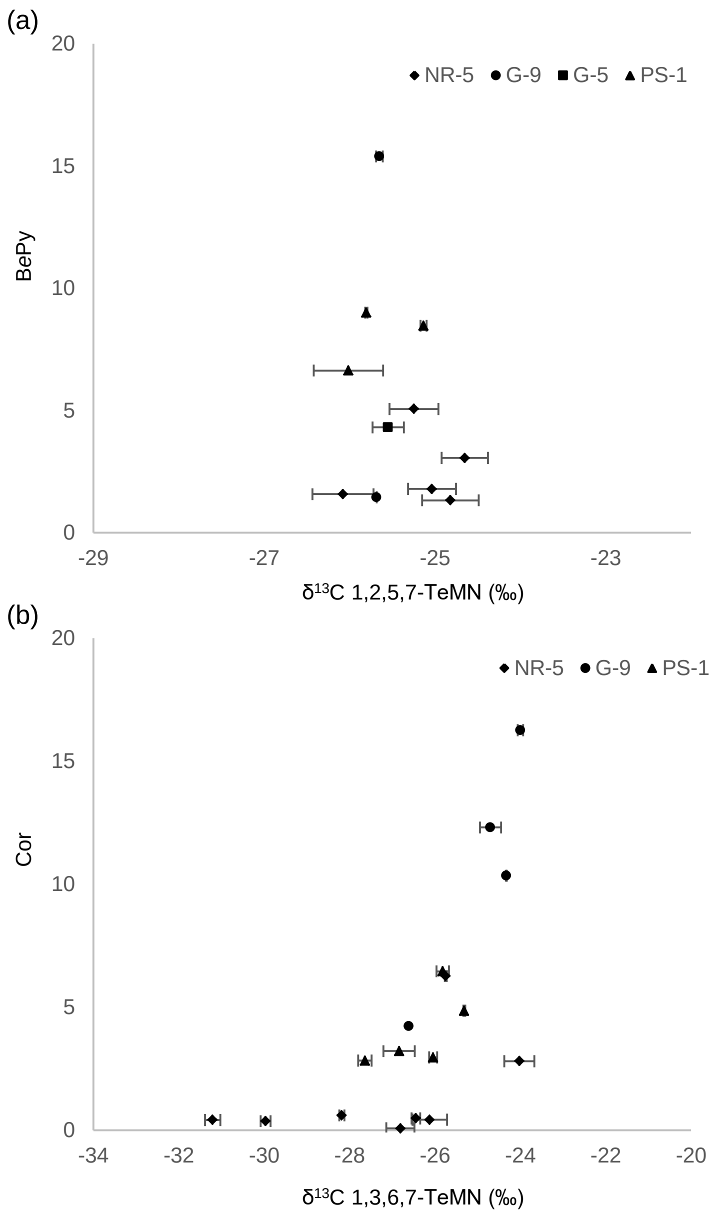


Figure 3.7 Sample discrimination obtained by correlating the δ^{13}C of the alkylnaphthalenes with the abundance of the combustion-derived PAHs (relative to 1,3,6,7-TeMN). (a): benzo[*e*]pyrene (B*e*Py) vs 1,2,5,7-tetramethylnaphthalene (1,2,5,7-TeMN); (b): corenane (Cor) vs 1,3,6,7-tetramethylnaphthalene (1,3,6,7-TeMN). Wells: North Rankin- 5 (NR-5), Goodwyn-5 (G-5), Goodwyn-9 (G-9) and Perseus South – 1 (PS-1).

$\Delta^{13}C_{(Combustion\ Marker\text{-}1367TeMN)}$

For further separation of the isotopic data, the relative abundance of the PAHs was plotted against the difference between δ^{13}C values of 1,3,6,7-TeMN and each PAH (**Figure 3.8a** as an example). As a result, a much better separation was obtained. The samples plotting below 0 for $\Delta^{13}C_{(Combustion\ Marker\text{-}1367TeMN)}$ relate to delta-plain/front-deltaic facies or coaly fluvial deltaic facies (samples from Mungaroo Fm. in Goodwyn-9, Goodwyn-5 and North Rankin – 5 wells) whereas the positive region for $\Delta^{13}C_{(Combustion\ Marker\text{-}1367TeMN)}$ relates to the samples corresponding to front-deltaic facies in transition towards an estuarine/lagoonal environment with a high sapropelic contribution (Brigadier Fm. in North Rankin – 5) and marginal marine environment (Legendre Fm. in Perseus South – 1). Our approach enables an improved assignment of the organo-facies type.

It is worth noting that thermal maturation can lead to the formation of other isomers and thus underestimates the signal of the source input, assigning the isomerisation to thermodynamic control in oils (van Aarssen *et al.*, 1999). However, for source rock extracts, the processes affecting the isomerisation have not been completely understood yet, and the alkylnaphthalene ratios (TMNr, TeMNr and PMNr) have not shown consistent trends (Bastow, Alexander, Sosrowidjojo, & Kagi, 1998). Thus source has been suggested to account for the unusual distributions of methylated naphthalenes with maturity (van Aarssen *et al.*, 1999, Romero-Sarmiento *et al.*, 2011).

$\Delta^{13}C_{(Combustion\ Marker\text{-}Phe)}$

As with 1,3,6,7-TeMN, the same approach was applied using the $\delta^{13}C$ of phenanthrene of samples from North Rankin - 5 and Perseus South -1 (**Figure 3.8b**). A similar separation for the samples was obtained as with other PAHs (see above). The positive region assigns the samples corresponding to estuarine/lagoonal facies or marginal marine environment whereas the samples from the front delta and delta plain intervals show negative values. The abundance of phenanthrene in the delta plain/front-deltaic facies might be largely dominated by combustion-derived phenanthrene and therefore its $\delta^{13}C$ are more positive, whereas in the facies with stronger marine character the $\delta^{13}C$ values (more negative) of this compound might also include the contribution of phenanthrene as a diagenetic product of a natural precursor more typical of marine environments.

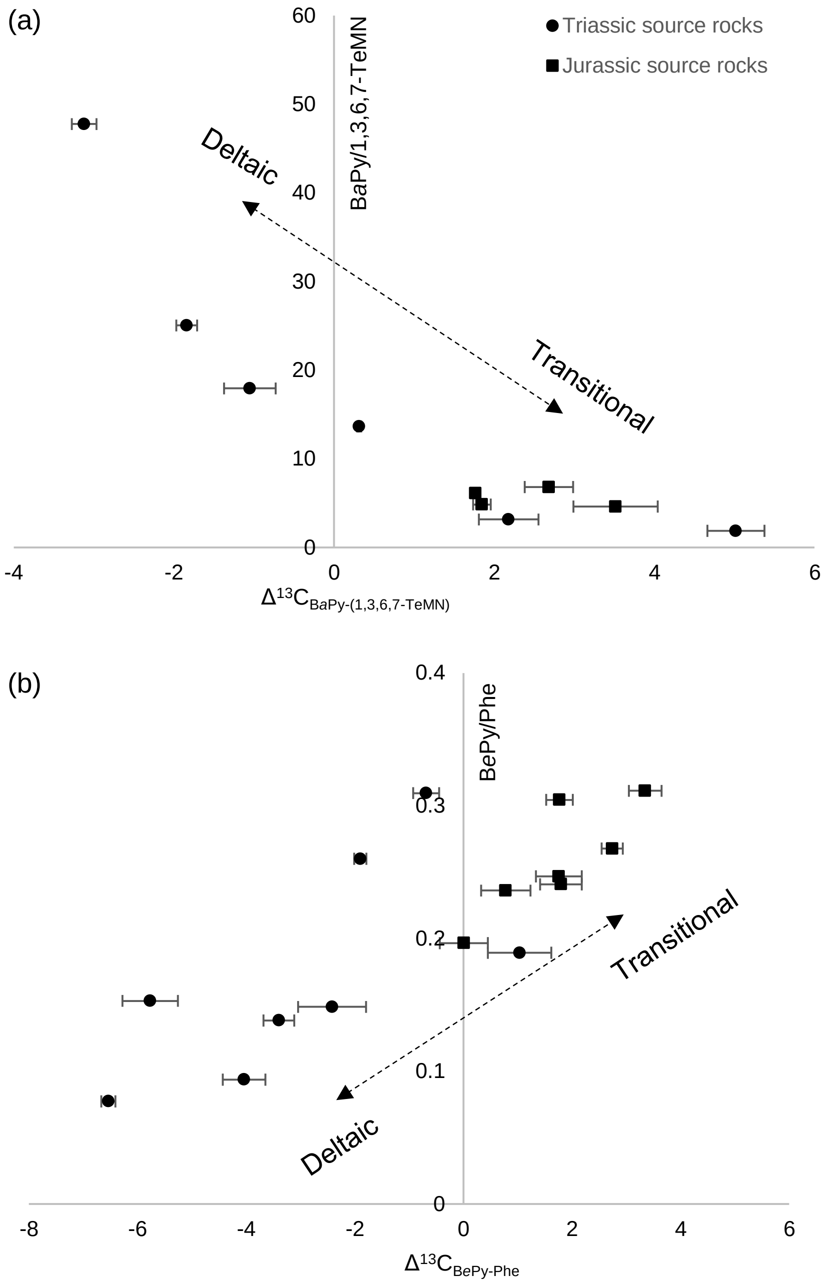


Figure 3.8. Facies discrimination using Δ^{13}C. (a): $\delta^{13}C_{B\mathit{a}Py}$-$\delta^{13}C_{1,3,6,7\text{-}TeMN.}$ (b): $\delta^{13}C_{B\mathit{e}Py}$-$\delta^{13}C_{Phe}$

Conclusions

Combustion-derived PAHs are suitable indicators of terrigenous organic matter and their relative abundance (measured against 1,3,6,7-TeMN) can be used to describe the original input of marine against terrigenous organic matter during deposition. Other compounds such as 1,2,5-TMN, 1,3,6,7-TeMN and phenanthrene are instead more sensitive to marine conditions in the depositional environment, as they exhibit lighter

$\delta^{13}C$ values where the input of marine organic matter increases. $\delta^{13}C$ of PAHs in combination with their distributions can be used to establish the facies type, *i.e.*, delta plain/front-deltaic from estuarine/lagoonal in a fluvial deltaic Triassic record (Dampier sub-Basin, Western Australia). Fluvial deltaic systems in Western Australia evolved in climatic conditions that differ from other periods of fluvial deltaic deposition around the globe. However, this study provides new parameters to research the heterogeneity and origin of organic source in other fluvial deltaic sequences.

Acknowledgments

Jaime Cesar acknowledges Curtin University for an International training scholarship and The Institute for Geoscience Research for a scholarship. K.G and J.C acknowledge the ARC for Linkage funding (LP150100341). Geoff Chidlow, Peter Hopper, Alex Holman are acknowledged for technical support.

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CHAPTER 4

The significance of benzo[b]naphtho[d]furans in fluids and source rocks: New indicators of facies type in fluvial-deltaic systems

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Organic Geochemistry, in press (2017).

ABSTRACT

The distributions of benzo[*b*]naphtho[*d*]furans (BNFs) in source rocks and fluids (crude oil and condensate) are shown to be useful indicators of facies type in fluvial-deltaic systems from the Dampier sub-Basin, North West Shelf, Australia. The stratigraphy in the Dampier sub-Basin represents a challenging petroleum system where the organic matter is very similar in most of the Triassic-Jurassic sequences. These sections consist of a fluvial-deltaic system with a low-rate increase of the marine influence towards the end of the Jurassic period. Potential applications of BNFs for source rock characterisation as well as fluid – source rock correlations have been reported for the first time. The formation of [1,2]BNF seems to be influenced by clay catalysis and the ratio [2,1]/[1,2]BNF can be used to describe lithofacies. This ratio is much lower in sediments from fluvial-deltaic systems compared to clay-depleted sediments from marine environments (*e.g.* carbonate sequences). For this study, the Triassic source rocks show ratios of 0.9-1.5 with 25% w/w of clay content in the rock whereas the ratios for the Middle Jurassic source rocks are around 1.6-2.1 with 14% w/w of clay content. The BNF ratio is lowest in the Late Jurassic samples (0.8) with 28 % w/w of clay minerals. Further work needs to be done on the factors controlling the abundance of the [2,3]BNF which is more abundant in source rocks compared to their equivalent fluids. The ternary plot of [2,1]-[1,2]-[2,3] BNFs could be applied to fluid-fluid and fluid-source rock correlations.

Keywords: benzo[*b*]naphto[*d*]furan, coal, fluid, clay catalysis, source rock, fluvial deltaic.

Introduction

Traditional biomarker parameters in petroleum geochemistry have a very wide range of applications although some limitations persist, especially in highly complex petroleum systems where mixed fluids from different charges are in the reservoir and several alteration processes have affected the accumulation (Volkman, Alexander, Kagi, Rowland, & Sheppard, 1984; Grice, Alexander, & Kagi, 2000; Le Métayer *et al.*, 2014). Occasionally, different source rocks can have very similar characteristics in terms of the organic facies type and it is therefore more challenging to establish fluid-source correlations. Thus more molecular indicators that are sensitive to variation in the facies type are needed to determine the source rock; particularly those parameters which are not affected by thermal maturity and fluids that are not altered by secondary processes such as biodegradation, evaporative fractionation and water washing.

Another challenge is the very low concentration of biomarkers in mature fluids, compared to the abundance of those compounds in source rocks (Peters & Moldowan, 1993). This is commonly the case with coal and other source rocks with type III kerogen which are gas and condensate prone (Bechtel, Karayigit, Bulut, Mastalerz, & Sachsenhofer, 2016). In such cases, the *n*-alkanes represent the main compound class available unless secondary alteration processes have also altered their distribution. In our study we investigated the importance of oxygenated polycyclic aromatic hydrocarbons (PAHs), such as benzo[*b*]naphtho[*d*]furans as proxies for facies type especially in fluids containing very low concentrations of biomarkers.

Benzo[*b*]naphtho[*d*]furans have been identified by authentic standards in fluids and source-rocks and were most abundant in coal and coaly shales (Li & Ellis, 2015). These compounds have also been detected in bitumen from fluvial-deltaic siltstone and charcoal from Jurassic records of wildfires in the Northern (Poland) and Southern (Argentina) hemispheres (Marynowski & Simoneit, 2009; Marynowski Scott, Zaton, Parent, & Garrido, 2011). There is currently no clear understanding about the factors controlling the isomerisation of benzo[*b*]naphtho[*d*]furans, and the source for these compounds is unknown. However, such oxygenated compounds are anticipated to derive from terrigenous organic matter, which would explain their particularly high abundance in coal and coaly shales (Li & Ellis, 2015).

A large number of studies have been conducted on other compounds bearing a similar structure. These include dibenzofurans (DBF), benzocarbazoles (BC) and benzonaphthothiophenes (BNThioPs). DBF is regarded as an indicator of terrigenous organic matter, particularly originating from woody plants (Mizukami, Kaiho, & Oba, 2014) by dehydration of polysaccharides (Pastorova, Botto, Arisz, & Boon, 1994) or oxidative coupling of phenols (Born, Louw, & Mulder, 1989); lichens have also been suggested as a potential source for this molecule (Radke, Vriend, & Ramanampisoa, 2000). High abundance of DBF has been found during the Late Permian previous to the P/Tr collapse; the abundance of this compound decreases significantly towards the Triassic, representing the disappearance of a low diversity arborescent cordaite-conifer-pteridosperm vegetation (Fenton *et al.*, 2007; Nabbefeld, Grice, Summons, Hays, & Cao, 2010).High DBF concentrations during the end-Permian were also attributed to a large supply of soil to ocean after an ecosystem collapse (Sephton *et al.*, 2005).

BC distributions have been used as migration parameters by applying the ratio of benzo[*a*]carbazole and benzo[*c*]carbazole; fluids that have migrated though clay-mineral/organic-matter-rich mudstones give a lower ratio of benzo[*a*]carbazole to benzo[*c*]carbazole compared to fluids that migrate through faults and other type of fractures (Larter *et al.*, 1996). Li *et al.* (2014) applied a similar ratio using the BNThioPs since their isomers [2,1] and [1,2] have similar structure to benzo [*a*] and [*c*] carbazoles, respectively.

A more comprehensive study on the BNFs carried out by Li *et al.* (2015) concluded that BNFs occur in fluids and source rocks from different depositional environments. Li *et al.* (2015) proposed that the [2,1] and [1,2] isomers could be important components for migration pathways like the BNThioPs. Vukovic *et al.* (2016) also reported a higher abundance of [2,1] and [1,2] BNFs compared to [2,3]BNF in pyrolysates from a sub-bituminous coal (having a vitrinite reflectance of 0.42%) and high volatile bituminous coal (having a vitrinite reflectance of 0.56%). They suggested that the water released from kerogen together with the clay minerals undergoes different reactions with the organic matter and that these might be the source of various oxygenated PAHs.

It is known that the abundance and type of clay minerals control the rearrangement of steranes to form diasteranes (Rubinstein, Sieskind, & Albrecht, 1975; Sieskind *et al.*, 1979) and high diasteranes/steranes ratios have been reported to indicate clay-rich sediments (Peters & Moldowan, 1993). More specifically, the clay/TOC (total organic carbon) ratio seems to also have an effect on the formation of diasteranes (van Kaam-Peters, Schouten, de Leeuw, & Sinninghe Damsté, 1997). However, only a few studies have been documented about the clay-mineral effect on the generation and transformation of PAHs. For example, Huang *et al.* (2016) reported no association of phenanthrene and alkylphenanthrenes with the lithology, but found the abundance of phenylphenanthrenes was associated with clay-rich lithology in sub-oxic environments.

Different intrinsic reactivities of various active sites of clay minerals have been reported in previous studies (Elsner, Schwarzenbach, & Haderlein, 2004; Gu *et al.*, 2011). Jia, Zhao, Li, L., Li, X., & Wang (2014) found that the effect of the clay minerals on the transformation of PAHs might include several stages of electron-exchange reactions leading to a decrease in the electron density of the PAHs and inducing the formation of organic cations. The metals contained in the clay would subsequently reduce and oxygenic species -such as water- would react with the carbo-cations to form oxygenated PAHs. The planar silicate surface provided by the clay minerals has also been shown to help stabilise the carbocation intermediates, since in a set of experiments with similar transition metal ions the radical organic cations did not form in aqueous solution and the electron transfer did not occur (Rupert, 1973; Polubesova, Eldad, & Chefetz, 2010).

Our study on the BNFs aims to establish their significance in petroleum systems from the Dampier sub-Basin, NW Shelf, Australia. The stratigraphy in the Dampier sub-Basin represents a challenging petroleum system where the organic matter is very similar in most of the Triassic-Jurassic sequences. These sections consist of a fluvial-deltaic system with a low-rate increase of the marine influence towards the end of the Jurassic. In this study, we suggest the BNFs might be potential indicators for source rock discrimination in a petroleum system like Dampier, and could be applicable to other petroleum systems derived from a similar depositional regime.

Geological Setting

The Triassic sections chosen for this study include the Mungaroo and Brigadier Formations. The Mungaroo Formation is a sandy section which conformably covers the Locker Shale, and comprises of a siliciclastic stratigraphy largely argillaceous with two main fine-grained facies (i) a brown claystone and (ii) a grey claystone which have been attributed to fluvial deltaic environments with regional reducing conditions. The sediments were deposited in a clastic depositional cycle with progradation into a marine environment followed by transgression (Longley *et al.*, 2002). The Brigadier Formation conformably covers the Mungaroo Formation and corresponds to a very thinly interbedded claystone and sandstones; the depositional environment was paralic to shallow-marine after the inundation of the Mungaroo Formation delta environment (Hocking, Moors, & Van de Graaff, 1987).

The Middle Jurassic samples belong to the Legendre Formation which denotes a regressive deltaic to marginal marine sequence that expanded to Dampier from the Beagle sub-Basin, and the sediments were supplied from fault blocks and platforms at the depocentre margins (Hocking, 1992). Later, in the Late Jurassic, sediments were deposited in a restricted deep marine environment and formed the Dingo claystone, a thick succession of claystone which is widely recognised as the source of liquid hydrocarbons to the Rankin Platform accumulations (Edwards, Hope, & Boreham, 2000; Edwards & Zumberge, 2005). **Figure 4.1** shows the well locations, and the Goodwyn field in the Dampier sub-Basin.

The fluids are from the Goodwyn field in the Rankin Platform reservoirs. The condensates from these gas/condensate accumulations are predominantly of terrigenous origin and the suggested sources include Middle to Late Jurassic and Late Triassic fluvial deltaic sequences (Edwards *et al.*, 2000; Edwards & Zumberge, 2005).

Published data from other samples have been included herein. These source rocks and their equivalent fluids are from typical marine carbonate, marine shale, lacustrine shale and fluvial-deltaic facies; see more details in Li and Ellis (2015). Lastly, several charcoal samples were included from the study of Marynowski and Simoneit (2009) who analysed charcoal fragments from Jurassic fluvial-deltaic records of wildfires in Northern Poland.

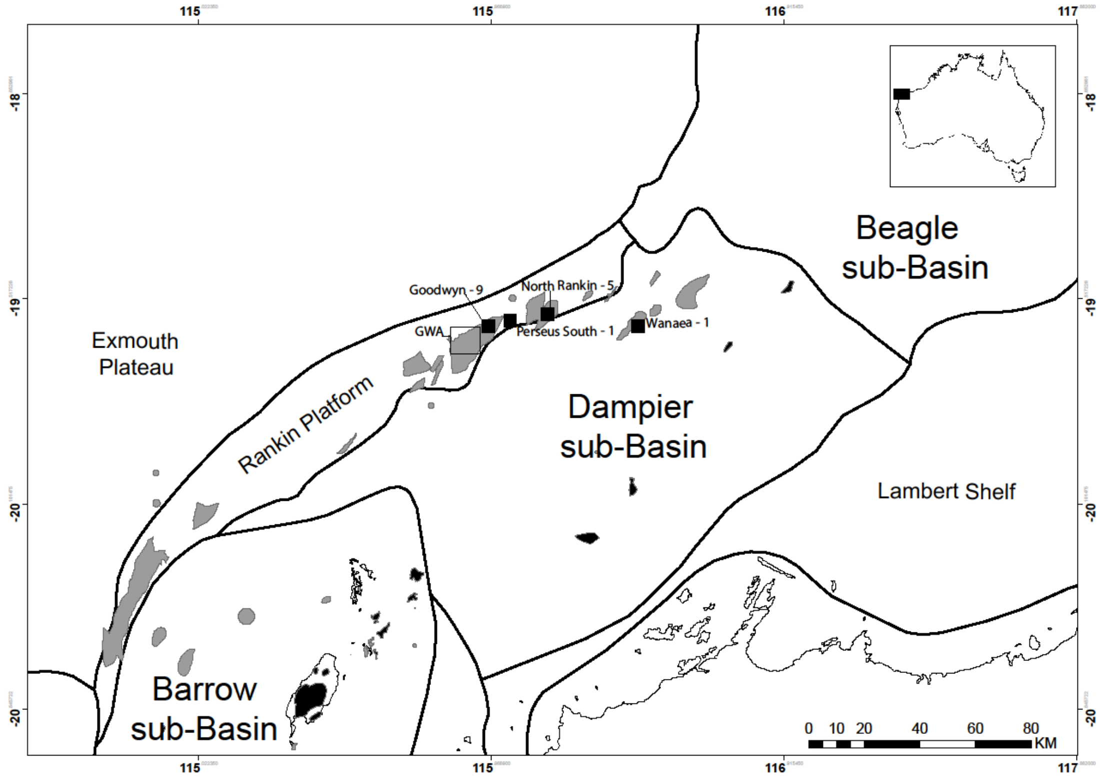

Figure 4.1. Location of the samples in the Dampier sub-Basin.

Materials and methods

Samples and sample preparation

A set of 29 source rock samples was used for the study. These were taken from the cores North Rankin-5 which covers the Mungaroo and Brigadier Formation (Triassic, 2-11% TOC and ~0.54% vitrinite reflectance), and Perseus South -1 which covers the Legendre Formation (Middle Jurassic, 2-5% TOC and ~0.54 % vitrinite reflectance) in the Dampier sub-Basin. Additional samples of Triassic (the Mungaroo Fm. in Goodwyn-9) and Late Jurassic age (the Dingo Claystone Fm. in Wanaea-1) were also included for comparison (**Table 4.1**). The fluids listed in **Table 4.2** correspond to 11 condensates from the Goodwyn field (**Figure 4.1**) and one sample from the Mondarra-1 well and one from the Gorgon-4 well have been included as a reference from the Perth Basin (marine shale facies) and Barrow sub-Basin (coal/carbonaceous shale facies) respectively (Edwards & Zumberge, 2005).

The bitumen was extracted (1 h) using a Milestone START-E microwave extraction system with a mixture of 9:1 dichloromethane (DCM) and methanol (MeOH) using a temperature program of 80 ºC for 15 min after a ramp of 8 ºC/min. An aliquot of approximately 5-10 mg of the bitumen was subsequently separated into saturated, aromatic and polar fractions by small scale silica gel liquid chromatography as described elsewhere (Maslen, Grice, Le Métayer, Dawson, & Edwards 2011); and this same chromatographic method was carried out on the condensates. Aliphatic and aromatic hydrocarbons (from bitumen and condensates) including BNFs were analysed using gas chromatography - mass spectrometry (GC-MS).

GC-MS

The samples were dissolved in *n*-hexane and analysed by GC-MS on a HP 6890 GC coupled to a HP 5973 mass selective detector (MSD) operating in electron ionisation mode (70 eV), and injection were of 1 µL of solution using an HP 6890 auto-sampler. The compounds in the aromatic fractions were chromatographically separated on a WCOT fused silica capillary column (60 m X 0.25 mm i.d.) with a 0.25 µm 5% phenyl–methyl–silicon stationary phase (DB-5), and the aliphatic fractions were analysed using an ultra-inert column (same dimensions as the DB5-5MS) with a 100% dimethylpolysiloxane DB-1MS phase. The carrier gas was helium at a linear velocity of 1 mL/min. The temperature program of the GC oven was programmed from 40 ºC –325 ºC (at 3 ºC/min) and was held isothermally for 45 minutes at 325 ºC.

The identification of the compounds was achieved by comparing the mass spectra and the relative retention times with those previously reported in the literature (Li *et al.*, 2014, Li & Ellis, 2014).

Table 4.1. Characteristics of the source rock samples (Woodside Energy Ltd., 1977; 1986; 1988; 1997; Li & Ellis, 2015, Marynowski & Simoneit, 2009; this study). The abundance is relative to the three BNF isomers. The clay content is measured as %w/w of kaolinite from X-ray diffraction analysis. C_{27} diasteranes/C_{27} steranes was measured in the *m/z* 217, and C_{31} diahopane/C_{31} hopane was measured in the *m/z* 191. M-B Fm.: transition between the Mungaroo Formation and the Brigadier Formation.

Sample/source	***Facies***	***%[2,1]BNF***	***%[1,2]BNF***	***%[2,3]BNF***	***[2,1]/[1,2]BNF***	***Ro (%)***	***C_{27}dia/C_{27}reg***	***C_{31}dia/C_{31}reg***	***% Clay***
Li & Ellis (2015)	Fluvial-deltaic shale	26.4	64.7	9.0	0.4	0.63	-	-	-
		32.8	56.8	10.4	0.6	0.50	-	-	-
	Marine shale	38.2	50.9	10.9	0.8	0.30	-	-	-
		44.7	33.6	21.7	1.3	-	-	-	-
	Lacustrine shale	60.5	15.8	23.7	3.8	0.58	-	-	-
	Marine carbonate	69.2	15.4	15.4	4.5	-	-	-	-
NR5(85)	Fluvial-deltaic claystone (estuarine facies, Brigedier Fm.)	41.8	31.8	26.4	1.3	0.52 to 0.54	0.32	0.75	-
NR5(93)		43.9	31.9	24.3	1.4		0.34	1.11	-
NR5(74)		42.9	28.6	28.5	1.5		0.25	1.06	-
NR5(70)		43.8	28.3	27.9	1.6		0.25	0.88	-
NR5(92)		43.5	31.6	24.9	1.4		0.26	0.89	-
NR5(79)		41.3	34.0	24.7	1.2		0.37	0.73	-
NR5(91)		42.9	28.7	28.4	1.5		0.25	1.07	24.6
NR5(82)	Fluvial-deltaic claystone (prodelta, M-B Fm.)	41.8	34.8	23.5	1.2	0.54 to 0.56	0.28	0.56	-
NR5(90)		42.6	34.4	23.0	1.2		0.23	1.10	-
NR5(55)		42.6	33.7	23.7	1.3		0.22	0.42	-
NR5(57)		41.9	36.0	22.1	1.2		0.20	0.50	-
NR5(88)		43.0	34.7	22.2	1.2		0.17	0.93	-
NR5(80)		41.4	34.2	24.3	1.2		0.25	0.64	-
NR5(89)		43.2	33.7	23.0	1.3		0.19	1.19	21.9

Table 4.1 (Continued)

Sample/source	*Facies*	*%[2,1]BNF*	*%[1,2]BNF*	*%[2,3]BNF*	*[2,1]/[1,2]BNF*	*Ro (%)*	*C_{27}dia/C_{27}reg*	*C_{31}dia/C_{31}reg*	*% Clay*
NR5(69)	Fluvial-deltaic claystone delta plain, Mungaroo Fm.)	43.2	28.7	28.1	1.5	-	0.26	0.95	18.5
NR5(84)		42.1	32.0	26.0	1.3	0.54	0.39	0.73	-
NR5(47)		41.0	27.9	31.2	1.5	-	0.24	1.21	-
G9(15)		38.5	40.0	21.5	1.0	0.58	0.54	0.97	-
G9(16)		39.1	39.3	21.6	1.0	-	0.47	1.03	-
PS1(20)	Fluvial-deltaic to marginal marine silty claystone (Legendre Fm.)	46.2	25.5	28.3	1.8	0.56	0.19	0.61	-
PS1(21)		46.1	25.2	28.7	1.8		0.11	0.63	-
PS1(22)		45.2	24.5	30.3	1.8		0.11	0.64	-
PS1(24)		47.0	29.8	23.1	1.6		0.21	0.64	-
PS1(25)		46.7	23.3	30.0	2.0		0.17	0.61	-
PS1(27)		46.1	23.5	30.5	2.0		0.14	0.67	-
PS1(28)		47.6	24.5	27.9	1.9		0.12	0.71	14.0
W- 1(7)	Marine claystone (Dingo claystone Fm.)	48.8	38.1	13.1	0.8	0.57	0.48	0.83	-
W-1(8)		50.5	40.1	9.5	0.8		0.64	0.87	27.5
W-1(10)		49.4	39.0	11.6	0.8		0.56	0.77	-
Marynowski & Simoneit (2009)	Charcoal	29.5	25.0	45.5	0.8	-	-	-	-
		48.1	28.4	23.5	0.6	-	-	-	-
		41.3	33.9	24.8	0.8	-	-	-	-
		56.6	25.3	18.1	0.4	-	-	-	-

Results and discussion

*Distribution of the Benzo[*b*]naphtho[*d*]furans in source rocks and fluids*

The BNFs were identified using the fragment ion *m/z* 218 and their relative retention time (Li & Ellis, 2015) as shown in **Figure 4.2.** The [2,1] isomer is usually more abundant than the [2,3]BNF. [2,3]BNF is commonly found at a very low relative abundance especially in fluids from the NW Shelf, as also observed in fluids by Li and Ellis (2015). In contrast the [1,2] BNF isomer exhibits the largest variability in fluids and source-rocks ranging between 15% and 60% abundance relative to the three isomers. Also the [1,2]BNF is present at lower relative abundance (~20%) in Jurassic-aged source rocks compared to fluids and Triassic-aged source rocks (30%).

By comparing the relative abundance of BNFs in different sample types (fluid and source-rocks extracts) a genetic relationship can be established (**Table 4.1**). Since our study does not cover a wide range of source-rock units and fluids we have included also the data from Li and Ellis (2015). There is a trend in the variation of % [1,2]BNF according to the facies type of source rocks and fluids, and a shift of 10-15 % [2,3]BNF decrease for the fluids (**Table 4.2**).

Geochemical significance

To better describe the geochemical significance and applications of the BNFs, we have applied a ternary plot to show the relative distribution (%) of BNF isomers in fluids and source rock extracts (**Figure 4.3**). As anticipated, it is clear that the main variation is observed on the axis corresponding to the [1,2]BNF isomer. This compound is more abundant in samples belonging to a fluvial-deltaic depositional environment including samples from the Dampier sub-Basin (Figure **4.4**). In our study, the samples from the Middle Jurassic Legendre Formation show a lower relative abundance of [1,2]BNF (~10% less than the Triassic samples). This could be attributed to a higher marine influence in the depositional environment compared to the Triassic source rocks deposited in a fluvial-deltaic regime consisting of more siliciclastic and carbonaceous material.

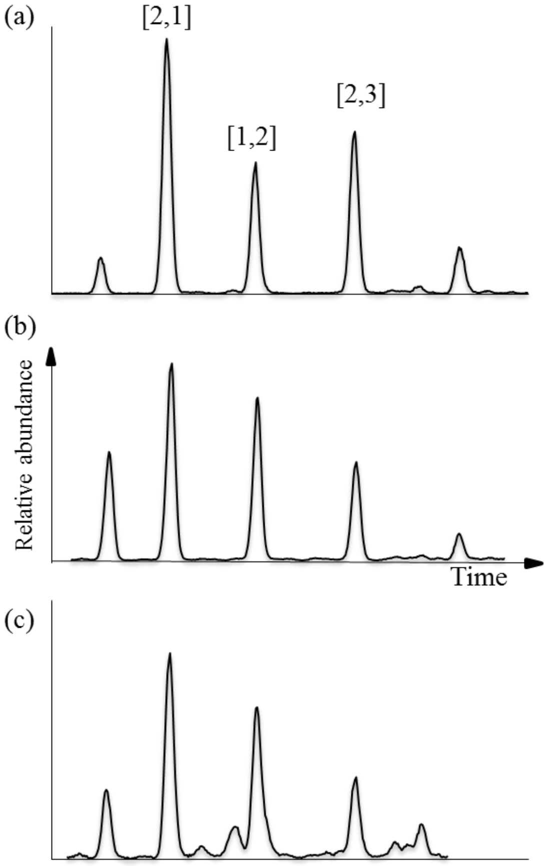

Figure 4.2. Mass fragmentogram *m/z* 218 showing the distribution of the benzo[*b*]naphtho[*d*]furans. [2,1]: benzo[*b*]naphtho[2,1-*d*]furan. [1,2]: benzo[*b*]naphtho[1,2-*d*]furan. [2,3]: benzo[*b*]naphtho[2,3-*d*]furan. In: a) Triassic source rock. b) Jurassic source rock. c) Condensate.

Table 4.2. Characteristics of the fluid samples (Li & Ellis, 2015; this study). Methylphenanthrene index MPI= (3+2)MP/[P+(1+9)MP].

Sample/source	***Facies***	***%[2,1]BNF***	***%[1,2]BNF***	***%[2,3]BNF***	***[2,1]/[1,2]BNF***	***MPI***
Li & Ellis (2015)	Fluvial/deltaic shale	30.6	57.4	12	0.5	-
		35.4	56.5	8.2	0.6	-
	Lacustrine shale	30.9	53	16.1	0.6	-
	Lacustrine shale	43.8	49.4	6.7	0.9	-
	Marine carbonate	42.3	35.2	22.5	1.2	-
	Marine shale	52.8	42.8	4.4	1.2	-
		57.8	35.6	6.7	1.6	-
		65.9	30.2	3.9	2.2	-
GWA-3	Fluvial/marine-deltaic shale	45.3	34.5	20.2	1.3	0.30
GWA-5		45.8	36.9	17.2	1.2	0.28
GWA-06		46.6	35.7	17.7	1.3	0.27
GWA-07		45.9	38.0	16.1	1.2	0.31
GWA-10		48.0	36.3	15.7	1.3	0.35
GWA-11		45.6	33.6	20.8	1.4	0.26
GWA-12		44.9	36.2	19.0	1.2	0.25
GWA-13		42.2	38.5	19.3	1.1	0.24
GWA-13B		46.4	39.1	14.5	1.2	0.24
GWA-14		43.3	39.1	17.6	1.1	0.30
GWA-16		44.2	38.4	17.4	1.2	0.35
Mondarra-1	Marine shale	42.4	45.8	11.8	0.9	0.63
Gorgon-4	Coal and carbonaceous claystone	45.2	44.4	10.4	1.0	0.61

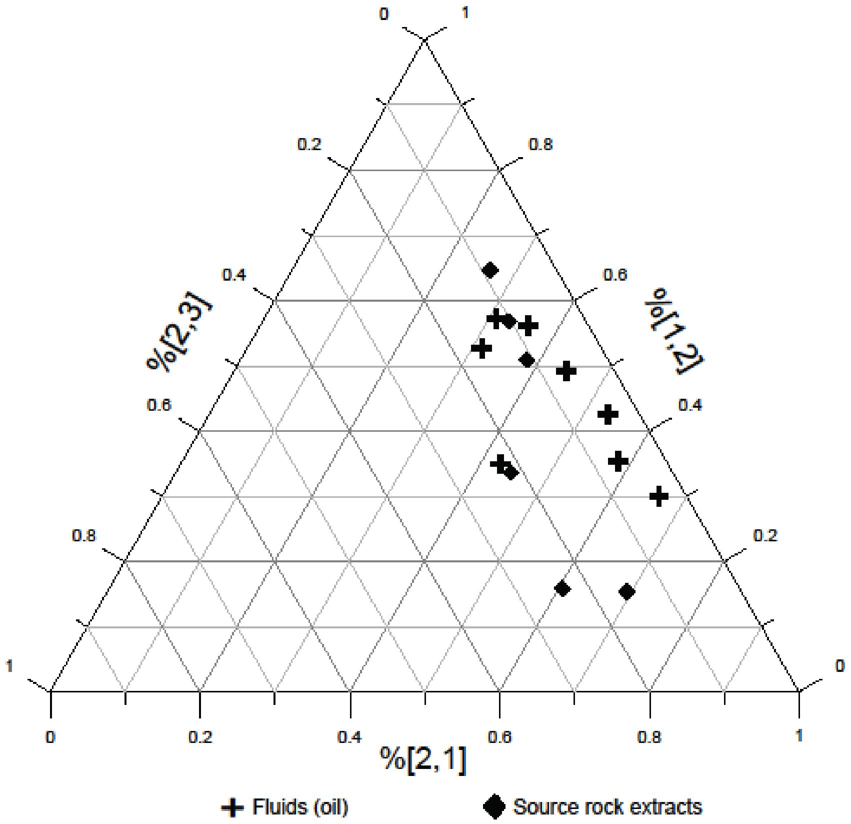

Figure 4.3. Ternary plot of [2,1], [1,2] and [2,3] BNFs for oils and source rocks from Li and Ellis (2015).

It is not yet clear which factors control the abundance of [2,3]BNF; however the % variability of [1,2]BNF can be ascribed to facies type. Thus the ratio [2,1]/[1,2]BNFs has been calculated to determine the relationship with the lithology. For example, based on the data from Li and Ellis (2015), fluvial-deltaic shales show lower [2,1]/[1,2]BNFs ratios (between 0.4-0.6) than marine shale and lacustrine shales (ratio between 1.3-3.8), respectively. The fluids coming from fluvial-deltaic shales also have much lower ratios (values between 0.5-0.6) compared to fluids from carbonate source rocks (ratios of around 1.2). However, the fluids from marine shales also exhibit low ratios (between 0.9-1.2). This could represent a stronger association to the clay content (*e.g.* proportion and type of minerals) rather than the depositional environment (fluvial-deltaic *vs* marine environment).

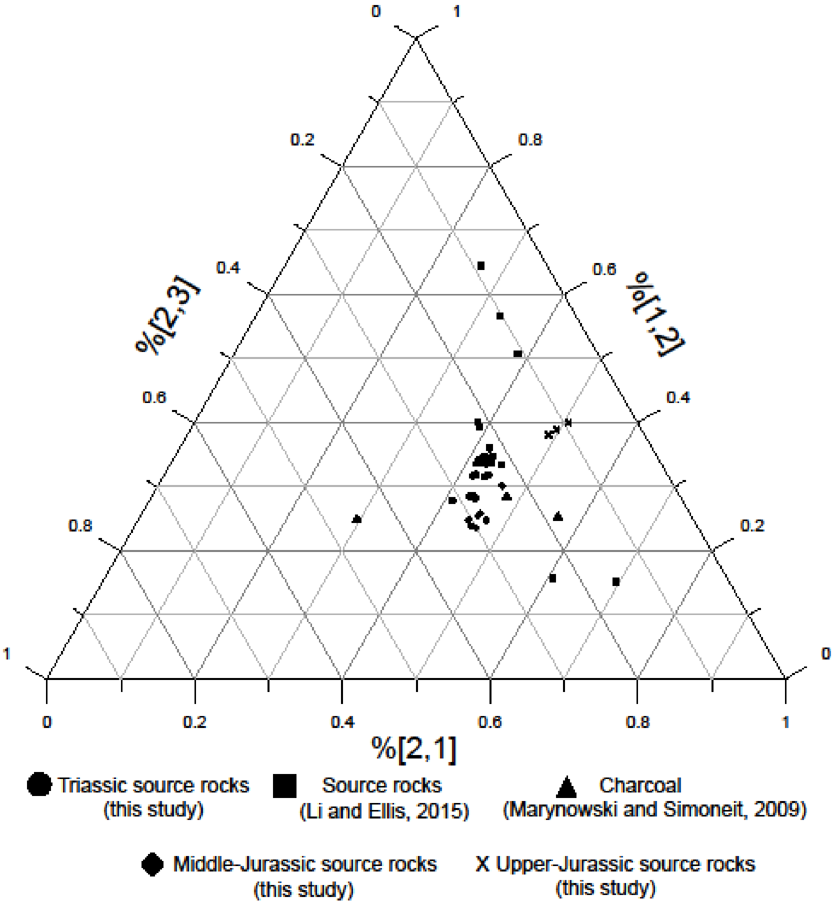

Figure 4.4. Ternary plot of [2,1], [1,2] and [2,3] BNFs for source rocks from Li and Ellis (2015) and source rocks from the Dampier sub-Basin for comparison.

Furthermore, we have compared the ratio [2,1]/[1,2]BNFs to the ratio of C_{27} diasteranes to C_{27} steranes (**Figure 4.5**) in the samples from this study. The formation of diasteranes has been shown to be influenced by mineral catalysis; higher clay content usually gives higher diasterane/sterane ratios (Rubinstein *et al.*, 1975; Sieskind *et al.*, 1979; van Kaam-Peters *et al.*, 1997). **Figure 4.5** shows that the predominance of the [1,2]BNF correlates with the ratio of C_{27} diasteranes/C_{27} steranes, suggesting clay catalysis as a possible mechanism for the formation of [1,2]BNF. Therefore, source rocks with higher clay content would be expected to have lower [2,1]/[1,2]BNFs ratio. For example, fluvial-deltaic Triassic calystones have a BNF ratio of ~1.3 and up to 25% w/w of clay, whereas the Middle Jurassic fluvial-deltaic to marginal-marine silty claystones have a ratio of ~1.8 and 14% w/w of clay minerals. Lastly, the Late Jurassic marine claystones have a BNF ratio of ~0.8 and the clay content reaches 28% w/w. The correlation between C_{27} diasteranes/C_{27} steranes and

BNF ratios also enabled the discrimination of more complex depositional settings such as the transition of the Mungaroo Formation to the Brigadier Formation (**Figure 4.5**).

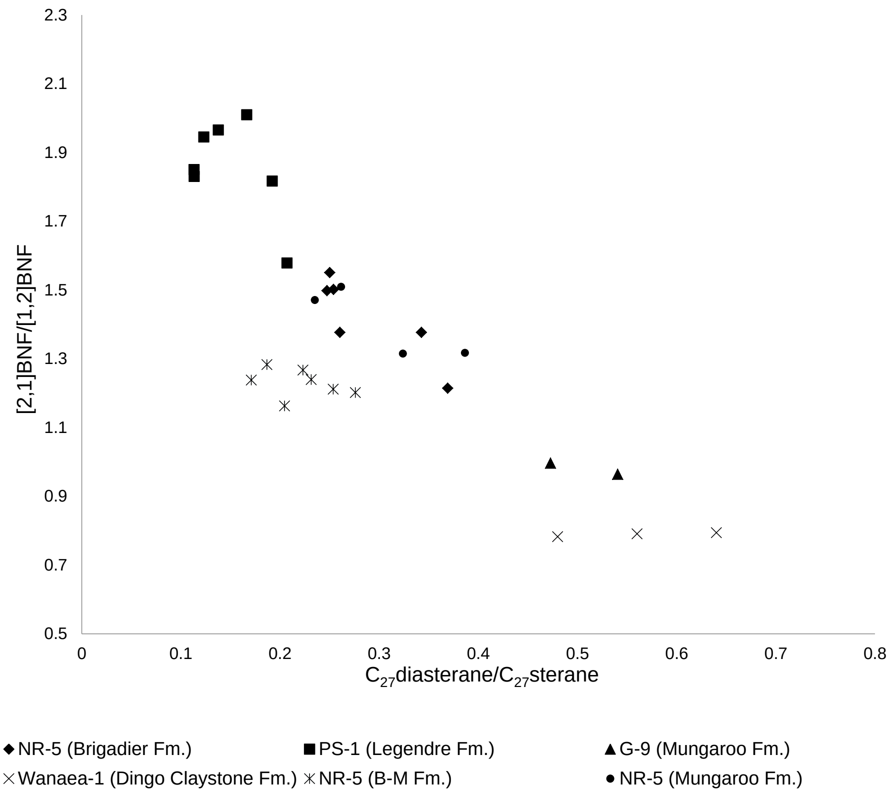

Figure 4.5. Correlation between [2,1]/[1,2]BNF ratio and rearranged steranes. B-M Fm.: transition between the Mungaroo and the Brigadier Formation).

The mineral catalysis operating in our system might be similar to that suggested by Jia *et al.* (2014) for the transformation of PAHs in the presence of clay minerals. We suggest the silicate surface in clays enhances the stability of the intermediate carbocation leading to the preferential formation of [1,2]BNF. This is consistent with a higher clay content and a lower [2,1]BNF to [1,2]BNF ratio. For the [2,3]BNF isomer no significant variations were observed except when comparing the source rocks to their associated fluids (**Figure 4.3**). It seems this isomer ([2,3]BNF) is usually more abundant in source rock compared to fluids. Therefore, rather than lithology, the process of thermal maturation may be controlling the formation of the [2,3]BNF isomer as it is also the case of [2,3]BNThioP in fluids (Li *et al.*, 2012; Li *et al.*, 2014)

The distribution of BNF compounds in charcoal (Marynowski & Simoneit, 2009) has also been included for comparison (**Figure 4.4**). A clay-catalysed rearrangement is discarded for these samples because BNFs and other compounds (*e.g.* polycyclic aromatic hydrocarbons) were well preserved in the charcoal fragments. This explains why the BNFs do not follow a particular distribution pattern; and the authors attributed the abundance of these compounds to combustion process as well as original unburned terrigenous organic matter. Other geochemical parameters have been reported in Table 1. A higher abundance of rearranged hopanes, measured as C_{31} diahopane/C_{31} hopane to indicate clay-catalysed rearrangement similar to diasterane/sterane ratios (Farrimond & Telnaes, 1996), are also consistent with lower BNF ratios (*e.g.* C_{31} diahopane/C_{31} hopane ratios of ~1 in the Mungaroo Fomation versus ~0.6 for the Legendre Formation). Additionally, there is no evidence of significant effects due to thermal maturity, as indicated by the vitrinite reflectance values (~0.55% in all the source rocks).

Potential applications for source rock – fluid and fluid – fluid correlations

Triassic-Jurassic sections of the NW Shelf are largely fluvial-deltaic systems. In this study, BNFs are useful indicators for source rock type. It is clear that the abundance of [1,2]BNF is mainly controlled by lithology therefore the ratio [2,1]/[1,2]BNF can be applied to differentiate facies type according to clay content. This would be a key parameter especially for samples where the [2,3] isomer is absent or at unmeasurable concentrations, and also where steranes and diasteranes are not present (highly mature oils and source rocks, *e.g.* Peters *et al.*, 2005b). Furthermore, the ternary plot can be applied to spatially correlate source rocks and fluids (**Figure 4.6**).

For example, in this study, the fluids evaluated exhibit a [2,1]/[1,2]BNF ratio of 1.2 +/-0.1 , and this suggests a common source or source rocks with very similar lithofacies. These samples are also ~10% depleted in [2,3]BNF compared to the Triassic source rock extracts as it was shown between source rocks and their equivalent fluids in the study of Li and Ellis (2015). However, based on the ternary plot (**Figure 4.6**), source discrimination for these condensates cannot be established between Late Jurassic and Late Triassic source rocks. Both intervals have been reported to source the Rankin Trend accumulations and have also been challenging to differentiate using routine geochemical parameters (Edwards & Zumberge, 2005; Jablonski, Preston, Westlake, & Gumley, 2013; Petroleum Division and Geological Survey of Western Australia, 2014). Further investigation is required for [2,3]BNF which may equilibrate at early stages during the thermal maturation process, and it is therefore not applicable for fluid-fluid or fluid-source rock correlations at advanced stage of maturity. Thermal maturity effects on the [2,1]/[1,2]BNF ratio, instead, could not be identified based on the methylphenanthrene index values (Table 2). Lastly, low BNF ratios in fluids from the Perth Basin and Browse sub-Basin (Table 2) are also consistent with the corresponding siliciclastic source rocks, marine shale and coal/carbonaceous claystone respectively.

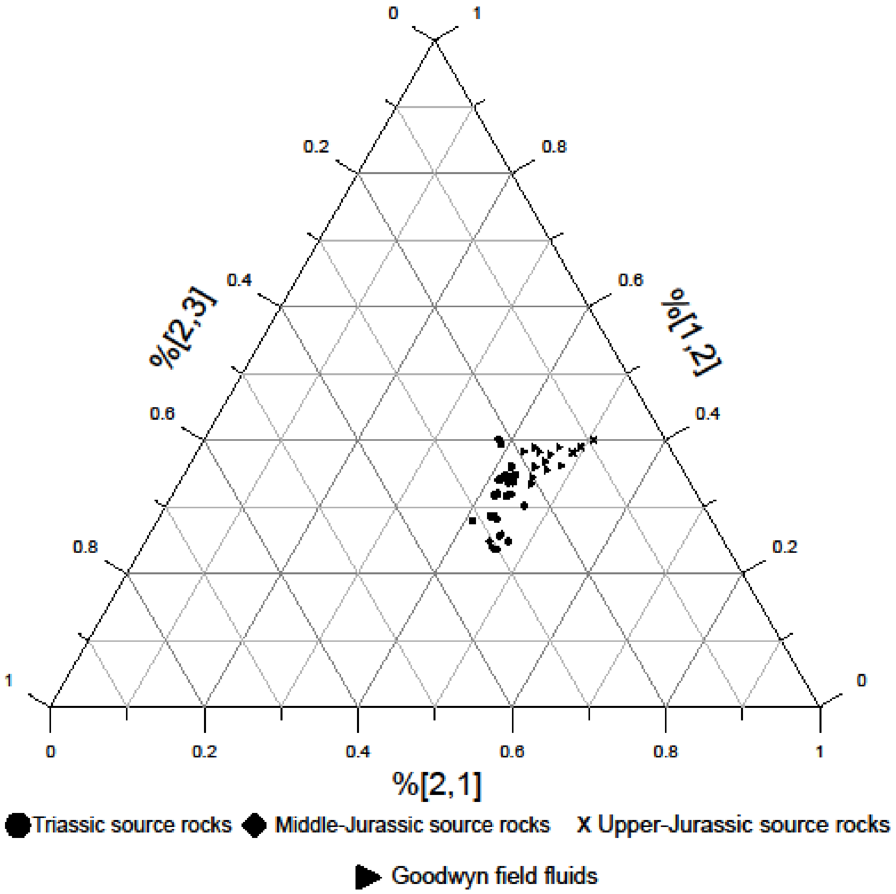

Figure 4.6. Ternary plot of [2,1], [1,2] and [2,3] BNFs for source rocks and condensates from this study.

Conclusions

Potential applications of the benzo[*b*]naphtho[*d*]furans for source rock characterisation as well as fluid – source rock correlations have been reported for the first time. The formation of [1,2]BNF seems to be influenced by clay catalysis and the ratio [2,1]/[1,2]BNF can be used to describe lithofacies. This ratio is much lower in sediments from fluvial-deltaic systems compared to sediments from marine environments. Further work needs to be done on the factors controlling the abundance of the [2,3]BNF which is only abundant in source rocks compared to their equivalent fluids. The ternary plot of [2,1]-[1,2]-[2,3] BNFs could be applied to fluid-fluid and fluid-source rock correlations.

Acknowledgments

Jaime Cesar acknowledges Curtin University for an International training scholarship and The Institute for Geoscience Research for a scholarship. K.G and J.C acknowledge the ARC for Linkage funding (LP150100341) and Woodside Petroleum Ltd. for supporting this research. Geoff Chidlow, Peter Hopper, Alex Holman are acknowledged for technical support.

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CHAPTER 5

Drimane-type compounds in source rocks and fluids from fluvial-deltaic depositional settings in the North-West Shelf of Australia

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Organic Geochemistry, submitted (2017).

ABSTRACT

Fluvial-deltaic petroleum systems with gas-prone source rocks are difficult to assess because the released fluids generally lack biomarkers and this limits the implementation of traditional organic geochemistry screening. However, there are a number of compound classes yet to be investigated in order to establish novel parameters for correlation studies in fluvial-deltaic geological settings. In this study we have focused on drimane-skeleton molecules (C_{15}-decalins), particularly the compounds 1,2,2,5,5-pentamethyl-*trans*-decalin and 1,1,2,5,5-pentamethyl-*trans*-decalin (termed herein as rearranged drimanes RD1 and RD2, respectively) and drimane (D), in source rock extracts and fluids from fluvial-deltaic petroleum systems in the Carnarvon Basin, North-West Shelf of Australia (NWS). We have calculated the ratio (RD1+RD2)/D as proposed by Ji *et al.* (2016) and compared their results with samples from the NWS. Our compilation of rearranged drimane ratios for a variety of lithologies suggests clay-catalysed rearrangement of C_{15}-decalins in siliciclastic source rocks from fluvial-deltaic depositional environments. Therefore, the mineral content seems to be a key factor controlling the isomerisation of decalins. Samples with higher clay content, such as claystone from the Brigadier Formation, have higher (RD1+RD2)/D ratios (~6) and higher C_{29} diasterane / C_{29} sterane (~1.1) compared to silty claystone from the Legendre Formation (~2 and ~0.8 respectively). The effects exerted by thermal maturity of the source rock and redox conditions of the depositional environment require further investigation, although samples from the Yanchang Fomation and La Luna Formation, where deposition occurred under more reducing conditions, exhibit lower rearranged drimane ratios (<2).

Keywords: drimane, rearranged-drimane, homodrimane, clay-catalysis, fluvial-deltaic.

Introduction

Source rocks containing Type III kerogen can be either oil-prone or gas-prone depending on the kerogen composition such as the proportions of aromatic lignin-derived compounds to aliphatic components (Killops *et al.*, 1998). In the case of gas-prone deltaic and coaly source rocks, the gas-associated fluids or "condensates" generated often lack biomarkers; therefore fluid-source correlations based on a biomarker approach are limited (Peters, Clifford, Walters, & Molodowan, 2005). With respect to compound specific isotope analysis (CSIA), the analysis of a condensate is possible if precise measurements are allowed by baseline chromatographic separation although CSIA of condensates is not a common practice (Peters *et al.*, 2005; Le Métayer *et al.*, 2014). Additionally, gasoline range hydrocarbons (C_5-C_{13}), major components of condensates, are sensitive to alteration processes in the reservoir compared to high-molecular-weight compounds (Thompson, 1983; 1987; Halpern, 1995; Peters *et al.*, 2005). The analysis of certain compound classes present in condensates, which are yet to be evaluated for applications in petroleum correlation studies, may help overcome these limitations. Here we have focused on specific bicyclic alkanes (decalins) or sesquiterpanes which are more resistant to alteration processes compared to other light hydrocarbons, and are widely distributed in source rocks and petroleum fluids (crude oils and condensates).

Amongst the sesquiterpanes, abundant compounds in fluids and bitumens often include drimane, homodrimane and other drimane-skeleton C_{15}-decalins (Nytoft, Samuel, Kildahl-Andersen, Johansen, & Jones, 2009, Chattopadhyay & Dutta, 2014, Ji, He, Zhang, Wu, & Li, 2016). Several sources have been suggested for these compounds which are ubiquitously distributed under different depositional environments (Luo *et al.*, 1991). Their sources include terpenoids and steroids from higher plants (Bendoraitis, 1974; Philp, Gilbert & Friedrich, 1981; Hautevelle, Michels, Malartre, & Trouiller, 2006), microbial degradation products from angiosperm markers such as oleanane (Nytoft *et al.*, 2009) and breakdown products of hopanoids (Alexander, Kagi, Noble, & Volkman, 1984). Amongst the drimane-type components only the 8β-(H) epimers of drimane and homodrimane have been identified in fluids and bitumens because their isomerisation with the 8α-(H) epimers reaches equilibrium at very early stages of thermal evolution (*i.e.* before the onset of hydrocarbon generation) and corresponds to 99% and 96% of the 8β-(H) epimers for drimane and homodrimane, respectively (Noble, Alexander, Kagi, & Knox, 1986).

The 2,2,4*a*,7,8-pentamethyl-*trans*-decalin and 2,2,4*a*,7,8-pentamethyl-*cis*-decalin were first identified by Nytoft *et al.* (2009). They proposed that these molecules are degradation products of oleanane since they are only reported in samples containing abundant angiosperm inputs. Their structure corresponds to rings "D" and "E" of oleanane although they may also form from oleanoids functionalised in ring B or C. The 1,2,2,5,5-pentamethyl-*trans*-decalin (RD1) and 1,1,2,5,5-pentamethyl-*trans*-decalin (RD2), in contrast, are more widely distributed in fluids and source rocks lacking angiosperm inputs. These two molecules are rearranged drimanes. A recent study by Ji *et al.* (2016) suggested that the abundance of rearranged drimanes decreased with increasing maturity with respect to drimane (D) as expressed by the ratio (RD1+RD2)/D. This parameter showed a positive correlation with the 17α-22,29,30-trisnorhopane (Tm)/ 18α-22,29,30-trisnorneohopane (Ts) ratio [adapted from the Ts/(Ts+Tm) maturity parameter, Seifert & Moldowan, 1978] in a mudstone/oil-shale sequence from the Yanchang Formation, China. It was suggested that reducing conditions might inhibit the rearrangement of drimane to rearranged drimanes, whereas other studies have proposed clay mineral catalysis to be the main factor controlling their isomerisation (Alexander *et al.*, 1984; Weston, Philp, Sheppard, & Woolhouse, 1989; Zhang, Li, Yang, Yang, & Wang, 2004).

In our study we have measured the (RD1+RD2)/D ratio for source rocks and fluids originating from fluvial-deltaic petroleum systems from the North-West Shelf of Australia, and we have compared our results with the data of Ji *et al.* (2016). We provide a new application of the (RD1+RD2)/D ratio from a range of different lithologies (oil shale, siltstone, fluvial-deltaic claystone, mudstone, silty mudstone, sandy mudstone and carbonaceous mudstone), and report an association between the facies type, specifically the clay-minerals content of the source rocks, and the rearrangement of drimane-skeleton compounds as shown by increasing (RD1+RD2)/D ratios with higher clay content.

Materials and methods

Geological Setting

The Brigadier Formation (Late Triassic) is composed of very thinly interbedded claystone and sandstone alternating with several intervals of fine to medium grained sandstones. This sequence conformably overlies the Mungaroo Formation; and the sediments were deposited under a paralic to shallow-marine environment after the drowning of the Mungaroo delta environment (Hocking, Moors, & Van de Graaff, 1987). The lithology is integrated by claystone with minor sandstone bands and siltstone (Woodside Energy Ltd., 1977). Later, in the Middle Jurassic, the sediments were deposited under a largely tidally-influenced estuarine environment and formed the Legendre Formation which represents a regressive deltaic to marginal marine sequence (Hocking, 1992); the lithology of this formation consists of silty claystone and laminated claystone (Woodside Energy Ltd., 1997). The Yanchang Formation (Middle to Upper-Triassic), in Northern China, represents the dominant source rocks in the Ordos Basin and consists of an organic-matter-rich mudstone sequence interbedded with shale, and sandstones of different thickness that form the reservoirs (Yu, Yang, & Du, 2010).

Samples and sample preparation

20 source rock samples and 15 different fluids were used for this study. The Triassic source rock samples come from the North Rankin 5 well whereas Jurassic source rocks are from the Perseus South 1 well, in the Dampier sub-Basin. The fluids come from some of the main gas/condensate accumulations in the Northern Carnarvon Basin, North-West Shelf of Australia, and from the Maracaibo sub-Basin, Venezuela.

The bitumen was extracted (1 h) using a Milestone START-E microwave extraction system with a mixture 9:1 of dichloromethane (DCM) and methanol (MeOH) using a temperature program of 80 ºC for 15 min after a ramp of 8 ºC/min. Approximately 5-10 mg of an aliquot of the bitumen was subsequently separated into aliphatic, aromatic and polar fractions by small scale silica gel liquid chromatography as described elsewhere (Maslen, Grice, Le Métayer, Dawson, & Edwards., 2011). Aliphatic and aromatic hydrocarbons were analysed using gas chromatography - mass spectrometry (GC-MS).

Tables 5.1 and **5.2** include fundamental information about the samples and basic ratios for source rock extracts and fluids calculated from the GC-MS analysis. Sample locations are shown in **Figure 5.1**.

GC-MS

The aliphatic and aromatic fractions from source rock extracts were dissolved in *n*-hexane whereas those from the fluids were dissolved in *n*-pentane, and subsequently analysed by GC-MS on an HP 6890 GC coupled to an HP 5973 mass selective detector (MSD) operating in electron ionisation mode (70 eV). Injections were of 1 µL of solution using an HP 6890 auto-sampler. The compounds were chromatographically separated on a DB-5MS Ultra inert column (60 m X 0.25 mm i.d.) with a 0.25 µm phenyl-arylene polymer for the aromatic fractions, and a DB-1MS ultra inert column (same dimensions as the DB5-5MS) with 100% dimethylpolysiloxane phase was used for the aliphatic fractions. The carrier gas was helium at a linear velocity of 1 mL/min. The temperature of the GC oven was programmed from 40 ºC –325 ºC (at 3 ºC/min) and was held isothermally for 45 minutes at 325 ºC.

Identification of the compounds was achieved by comparing the mass spectra and the relative retention times with those previously reported (Nytoft *et al.*, 2009; Chattopadhyay & Dutta, 2014; Ji *et al.*, 2016); and the (RD1+RD2)/D ratios were calculated using the peak areas of each compound as measured from the chromatograms *m/z* 193 for RD1 and RD2 and *m/z* 123 for drimane, as implemented by Ji *et al.*, (2016). Pr/Ph ratios for this study were calculated by using the peak areas of these isoprenoids from the total-ion-chromatogram (TIC). The C_{29} diasterane to C_{29} sterane ratio was calculated using the peak areas of C_{29} 13β,17α(H) 20*S*+20*R* diasteranes (with minimal interference of C_{27} 5α,14β,17β(H)20R sterane), C_{29} 5α,14β,17β(H) 20*S*+20*R* steranes and C_{29} 5α,14α,17α(H) 20S+20R steranes, from the fragmentgram of *m/z* 217. The C_{30} diahopane (C_{30}X) to C_{30} hopane ratio was calculated using the peak areas of C_{30} 17α diahopane and C_{30} 17α hopane from the *m/z* 191.

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Table 5.1. Fundamental data and selected molecular ratios of the source rock samples (Woodside Energy Ltd, 1977, 1997; this study). Brigadier Formation (B. Fm) and Legendre Formation (L. Fm). -: not determined.

Sample	*Lithofacies*	*Tmax (°C)*	*%TOC*	*S_2(mg/g)*	*Pr/Ph*	*Pr/nC_{17}*	*(RD1+RD2)/D*	*HD/D*	$C_{29\text{diasterane/sterane}}$	C_{30X}/C_{30H}
NR-5(1)	Fluvial-deltaic claystone (B. Fm)	432	1.71	2.4	1.9	0.5	5.2	1.9	1.08	0.15
NR-5(2)		431	-	2.1	2.4	1	4.8	3.5	0.95	0.13
NR-5(3)		430	3.24	2.2	0.8	0.3	5.5	2.4	1.14	0.16
NR-5(4)		430	2.76	1.9	2.4	0.5	6.7	2	1.12	0.14
NR-5(5)		430	-	1.8	1.7	0.5	6.5	2.3	1.26	0.15
NR-5(6)		431	-	2.3	2.0	0.6	5.6	1.6	0.91	0.13
NR-5(7)		430	2.25	1.3	2.2	0.3	6.4	1.4	1.20	0.15
NR-5(8)		-	-	-	2.2	0.7	4.3	1.6	1.00	0.13
NR-5(9)		nd	-	-	1.8	0.8	5.1	3.4	1.10	0.13
NR-5(10)		431	1.8	5.2	2.6	0.5	5.7	2.7	1.17	0.15
NR-5(11)		430	-	-	1.8	0.4	4.7	0.9	1.10	0.14
NR-5(12)		-	-	-	1.7	0.7	4.5	3.9	1.00	0.15
NR-5(13)		432	2.6	1.0	1.9	0.3	4.7	1.7	1.10	0.16
NR-5(14)		-	-	-	2.3	0.5	6.3	1.3	1.05	0.13
PS-1(1)	Fluvial-deltaic claystone (L. Fm)	432	2.0	1.6	2.6	0.3	1.3	2.3	0.80	0.07
PS-1(2)		431	-	1.6	1.8	0.1	1.7	1.5	0.83	0.09
PS-1(3)		431	3.6	1.9	4.1	0.3	2.0	1.2	0.90	0.08
PS-1(4)		431	-	2.0	1.81	0.1	2.4	1.6	0.86	0.10
PS-1(5)		431	2.1	1.6	2.66	0.2	1.9	2.2	0.72	0.08
PS1(6)		431	2.6	2.8	2.3	0.3	2.1	1.3	0.81	0.09
PS1(7)		431	2.1	1.3	2.1	0.2	2.1	1.5	0.84	0.07

Table 5.2. Fundamental data and selected molecular ratios of the fluids from this study. MPI= (3+2)MP/[P+(1+9)MP]. TeMNr= 1,3,6,7-TeMN/[(1,3,6,7+1,2,5,6+1,2,3,5)-TeMN].

Sample	*Source lithofacies*	*MPI*	*TeMNr*	*Pr/Ph*	*Pr/nC$_{17}$*	*(RD1+RD2)/D*	*HD/D*
Angel-1	Fluvial-deltaic shale	0.67	0.73	4.0	0.4	6.6	1.0
Barrow Is		0.46	0.74	2.9	0.3	8.9	1.0
Dockrell-1		0.45	0.73	3.6	0.4	8.1	1.1
Echo-1		0.28	0.52	3.3	0.6	7.3	0.7
Goodwyn-9		0.73	0.66	5.9	0.8	5.7	1.1
Gorgon-4		0.61	0.90	3.0	0.2	8.5	0.7
NR-1		0.78	0.58	3.4	0.5	10.0	0.8
NR-3		0.40	0.62	3.1	0.4	6.4	0.9
Tidepole-1		0.46	0.73	3.4	0.5	7.8	1.0
Barrow		0.51	0.67	3.0	1.4	8.1	0.9
La Luna 1	Limestone	0.50	0.26	0.5	0.4	1.5	0.67
La Luna 2		0.48	0.23	0.6	0.4	1.3	0.76
La Luna 3		0.50	0.19	0.6	0.4	1.8	0.56
La Luna 4		0.49	0.19	0.5	0.4	1.5	0.68
La Luna 5		0.50	0.25	0.6	0.4	0.8	1.18

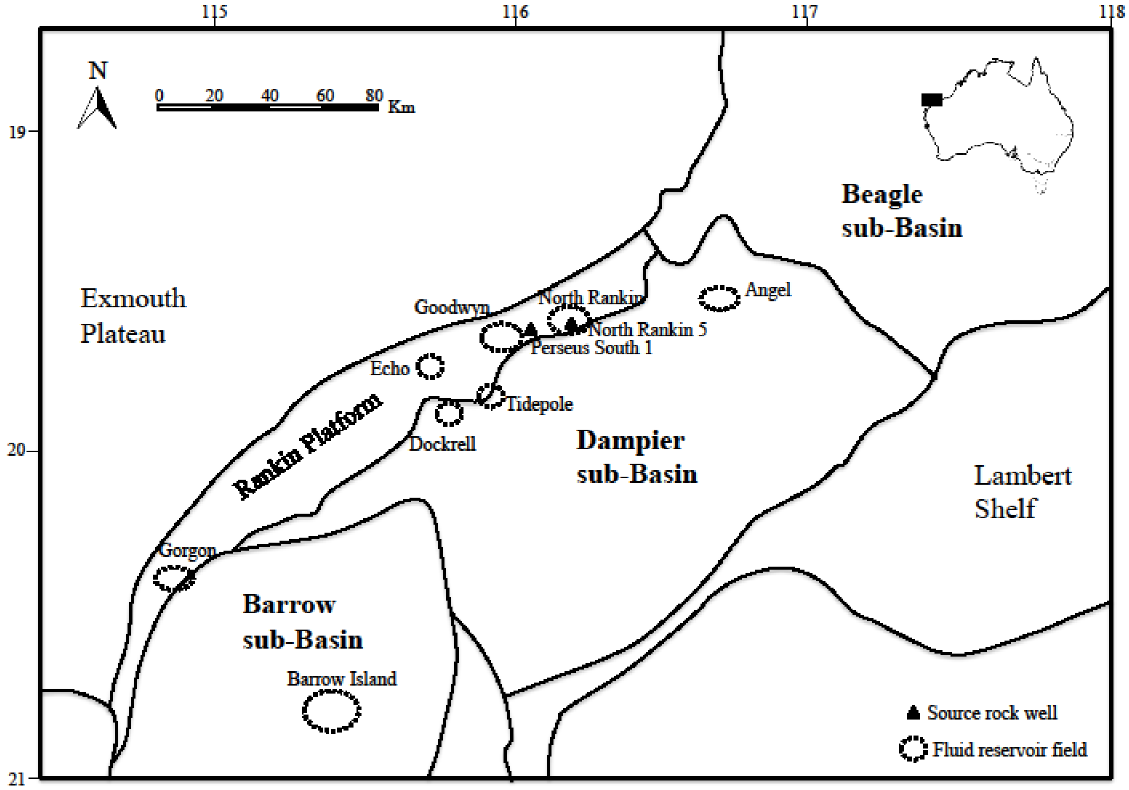

Figure 5.1. Location of the source rock cores and gas/condensate fields (Longley *et al.*, 2002; Edwards & Zumberge, 2005).

X-Ray Diffraction (XRD) analysis

X-ray diffraction analysis was conducted on four rock samples at the X-ray laboratory of the John de Laeter Centre, Curtin University, using a powder diffractometer D8 Advance (Bruker AXS, Germany), with a copper K alpha radiation source (@40kV & 40mA) and a LynxEye detector. A 2theta scan range of 7 – 120° with a step size of 0.015 were used for scanning; and the time/step ratio was 0.7s for a total scan time of approximately 90 min. Corundum was used as the internal standard for mineral quantification. DIFFRAC.EVA was used for mineral identification and DIFFRAC.SUITE TOPAS rietveld software was applied for phase quantification, using corundum as internal standard.

Results and discussion

Distribution of bicyclic alkanes in fluvial-deltaic source rock extracts and fluids

Figure 5.2 shows the main compounds identified for this study. These correspond to 8β-(H)-drimane (D) and 8β-(H)-homodrimane (HD) in the *m/z* 123 mass chromatogram, and 1,2,2,5,5-pentamethyl-*trans*-decalin (RD1) and 1,1,2,5,5-pentamethyl-*trans*-decalin (RD2) in the *m/z* 193 mass chromatogram. In these rocks, which all contain Type III kerogen, bicyclic alkanes may have predominantly originated from conifer resins since there was a significant input of terrigenous organic matter in the Carnarvon Basin (Longley *et al.*, 2002; Edwards & Zumberge, 2005; Cesar and Grice, 2017). It can also be inferred that plants from the *Pinaceae* family had the major contribution since tri- and tetracyclic diterpanes, which are indicative of other conifer families (Podocarpaceae, Araucariaceae and Taxodiaceae), were absent (Grice, Audino, Boreham, Alexander, & Kagi, 2000; Grice, Riding, Foster, Naeher, & Greenwood, 2015; Hautevelle *et al.*, 2006, Romero-Sarmiento, Riboulleau, Vecoli, Laggoun-Défarge, & Versteegh, 2011, Fabiańska & Kurkiewicz, 2013). Also, the absence of 2,2,4*a*,7,8-pentamethyl-*trans*-decalin and 2,2,4*a*,7,8-pentamethyl-*cis*-decalin is consistent with the findings of Nytoft *et al.* (2009) and supports the notion that these molecules are derived from oleanoids. Further their absence in source rocks that predate the evolution and proliferation of angiosperms (Jurassic or older) is anticipated.

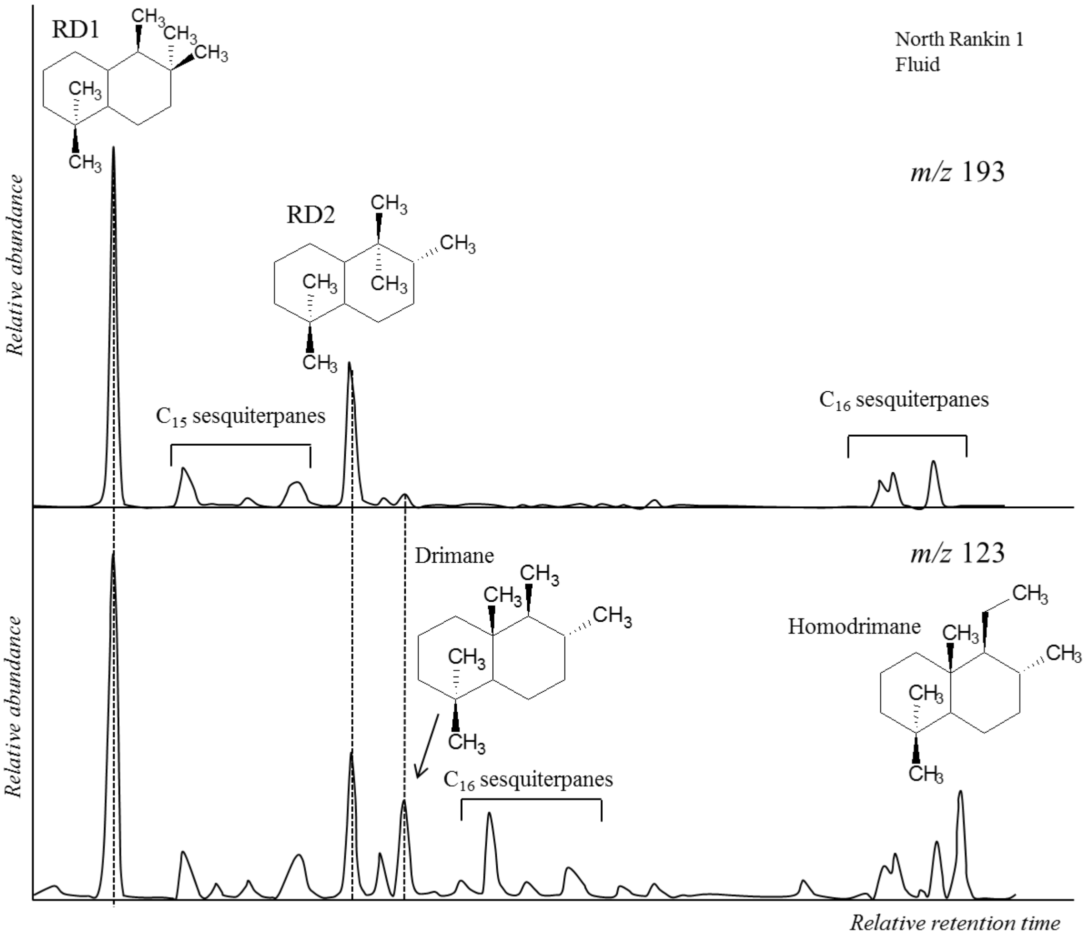

Figure 5.2. Fragmentograms *m/z* 123 and 193 showing the drimane-skeleton compounds identified in this study.

It is noteworthy that the distribution patterns are very similar in fluids and source rocks from equivalent lithofacies except for the homodrimane. This compound was found to be more abundant, relative to drimane, in the source rock extracts compared to the fluids (see **Tables 5.1**, **5.2 and 5.3**). Explaining this trend might not be a straightforward process since several factors should be considered. On one hand, Weston *et al.* (1989) suggested a source effect since drimane and homodrimane would arise from the cleavage of different bonds in ring "C" of the hopanoids; and the breaking-bond may be determined by the catalytic nature of the mineral matrix of the source rock. On the other hand, Luo *et al.* (1991) suggested a thermal maturity effect after finding an increase in the D/HD ratio until a vitrinite reflectance of 1.4% and a progressive decrease after that. We consider that H_2C-CH_3 cleavage at the ethyl group during the thermal evolution of the organic matter might explain higher D/HD ratios in fluids compared to source rock extracts; however, the relationship with other maturity parameters is not obvious (see **Tables 5.1, 5.2** and **5.3**). Migration and biodegradation effects have also been suggested to influence the distribution of homodrimane (Ji *et al.*, 2016) but our samples have not been subjected to any significant biodegradation.

Table 5.3. Fundamental data and selected molecular ratios of the source rock samples and fluids from Ji et al. (2016). -: not determined.

Sample	*Lithofacies*	*Tmax (°C)*	*Pr/Ph*	*Pr/nC₁₇*	*(RD1+RD2)/ D*	*HD/D*
3-X30	Oil shale (Y. Fm)	442	1.4	0.2	1.4	0.9
11-X30		448	1.9	0.3	2.1	0.9
12-X44		442	1.4	0.2	1.3	1.0
37-X44		449	1.8	0.2	1.5	1.6
40-3X44		449	1.6	0.3	1.3	2.4
86-X40		449	1.7	0.2	1.6	1.9
3-3X30	Silty mudstone (Y. Fm)	448	1.4	0.4	2.4	3.0
24-X30		448	3.9	1.6	2.8	3.0
8-X30		457	2.0	0.8	1.9	3.2
49-X30		454	1.0	0.6	1.7	3.4
51-X30		457	1.2	0.6	1.5	1.9
40-X44		438	1.1	0.5	3.0	1.6
8-X44		438	1.5	0.2	1.6	1.6
19-X44		443	1.3	0.4	2.1	1.5
45-X44		450	1.6	0.4	1.6	1.8
84-X40		446	1.5	0.3	2.4	1.6
23-X44	Carbonaceous mudstone (Y. Fm)	442	1.6	0.3	2.1	1.4
47-X30		447	4.0	1.0	1.5	1.3
46-X44		443	4.2	1.9	1.8	2.8
1-X44	Siltstone (Y. Fm)	441	1.4	0.5	1.5	1.5
7-X30	Sandy mudstone (Y. Fm)	451	1.6	0.5	2.1	3.9
13-X44	Argillaceous sandstone (Y. Fm)	440	1.4	0.3	1.9	1.1
28-X44	Mudstone (Y. Fm)	448	1.6	0.5	2.5	2.0

Table 5.3. (Continued)

Sample	*Lithofacies*	*Tmax (°C)*	*Pr/Ph*	*Pr/nC_{17}*	*(RD1+RD2)/ D*	*HD/D*
		Fluids				
36-N4	Oil shale (Y. Fm)	-	1.5	0.3	1.8	1.5
88-Zh42		-	1.8	0.3	1.8	2.5
94-M9		-	1.0	0.4	2.6	1.2
102-Zh5		-	1.0	0.2	0.9	1.2
Y-X29-23	Unknown interval (Y. Fm)	-	1.3	0.5	1.0	0.7
Y-X28-16		-	1.2	0.6	1.0	0.8
Y-X36-24		-	1.2	0.5	1.0	0.7
Y-X1-67		-	1.2	0.6	0.9	0.8
Y-X1-81		-	1.2	0.6	1.0	0.8
Y-X163		-	1.4	0.4	1.1	0.8
Y-D75-68		-	1.3	0.5	0.9	0.8
Y-X130		-	1.3	0.6	1.1	0.9

Rearranged drimane ratio in source rock extracts

Figure 5.3 shows (RD1+RD2)/D for the source extracts analysed by Ji *et al.* (2016) and the ones analysed in our study. The association with redox conditions of the depositional environments is not obvious since samples with similar (RD1+RD2)/D show differing Pr/Ph ratios (Figure **5.3a**). However, the overall distribution might suggest that lower rearranged drimane ratios are found in sediments deposited under more reducing conditions (e.g. the Yangchan Formation). Some clear exceptions to this rule are the carbonaceous mudstones from the Yangchan Formation. The mineralogical composition of the source rocks samples from Yangchan are not reported but we could infer the clay/TOC ratio might be playing a role in the low abundance of rearranged drimanes in these mudstones compared to the oil shales. Previously, van-Kaam Peters et al., (1998) found that low clay/TOC ratios are related to low diasterane/sterane ratios, indicating that the proportion of clay minerals to organic matter influences the rearrangement of sterenes to form diasterenes. It is challenging, however, to extrapolate such effect on the isomerisation of drimanes because Ji et al., (2016) did not report the clay content of the samples and the rearranged drimane ratio varied only between 1.0 and 3.0 for a wide range of organic matter content (TOC from 0.3 to 40%).

An association with thermal maturity is not clear since samples with different Pr/n-C_{17} values show similar rearranged drimane ratios (*e.g.* carbonaceous mudstone and siltstone, **Figure 5.3b**). Even if other maturity parameters such as Tmax (rock-eval pyrolysis, Table **5.1** and **5.3**) are considered, it can be observed that samples with very different maturity (Mudstone -Yanchang Fm and Silty claystone – Legendre Fm) exhibit similar rearranged drimane ratios. Therefore the (RD1+RD2)/D ratios for the different source rock types seems to be related to the lithology of the source rocks, and probably the redox conditions of the depositional environment. These interpretations are proposed keeping in mind that the abundance of the isoprenoids Pr and Ph is affected by the source organic matter and thermal maturity of the source rock (Peters, Fraser, Amris, Rustanto, & Hermanto, 1999). Alexander et al., (1984), nonetheless, had proposed that rearranged drimanes are diagenetic products rather than thermo-catalytic because they are commonly found in immature sediments.

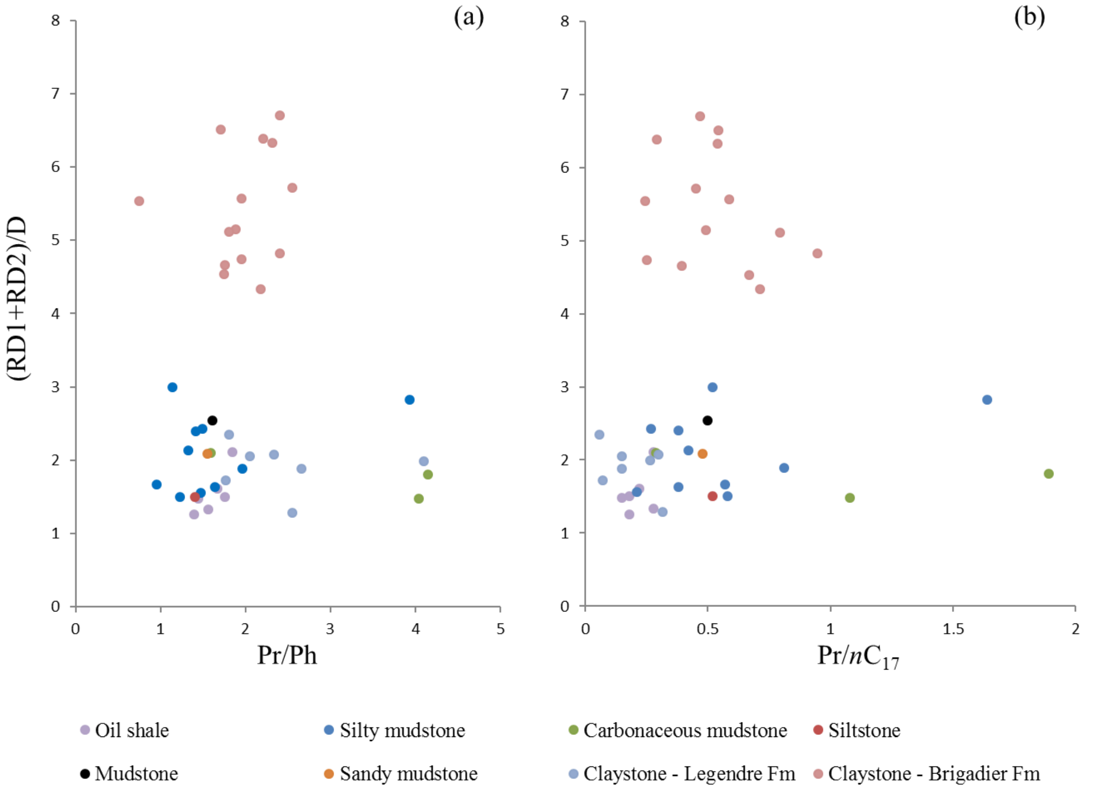

Figure 5.3. Rearranged drimane ratio (RD1+RD2)/D vs redox conditions and thermal maturity according to a) Pr/Ph and b) Pr/n-C_{17}, in source rock extracts.

The isomerisation of Ts and Tm has not been used for correlations with the rearranged drimane ratios of the set of samples from this study because this maturity parameter is also affected by lithology (Moldowan, Sundararaman, & Schoell, 1986). Therefore, Ts/Tm ratios of bitumen from a variety of lithologies cannot be used for comparative purposes.

Rearranged drimane ratio in fluids

Similarly to the source rocks, there is no clear correlation between the rearranged drimane ratio and thermal maturity expressed as Pr/n-C_{17} values in the fluids (**Figure 5.4a**). For example, fluids from the Dampier sub-Basin (siliciclastic source) have Pr/n-C_{17} ratios within the range of the fluids from the Yanchang Formation (mudstone and oil shale) and La Luna (limestone sourced) and their rearranged drimane ratios are different (~7.0 versus ~1.0, respectively). Additionally, although other maturity ratios could not be used to compare both sets of samples due to the absence of biomarkers in the fluvial-deltaic fluids, we have included the methylphenenthrene index (MPI) and tetramethylnaphthalene ratio (TMNr) of the condensates and crude oil from Maracaibo

(**Table 5.2**) and they do not show a clear influence on the (RD1+RD2)/D ratios. For instance, Angel-1 and North Rankin-3 condensates have very similar rearranged drimane ratios (~6.5) but different MPI values (0.67 and 0.40 respectively). This is considering that the organic matter types and lithologies in the Northern Carnarvon basin are similar (Cesar & Grice, 2017; Edwards & Zumberge, 2005) thus the effects of source and lithology on the MPI and TeMNr values are minimum.

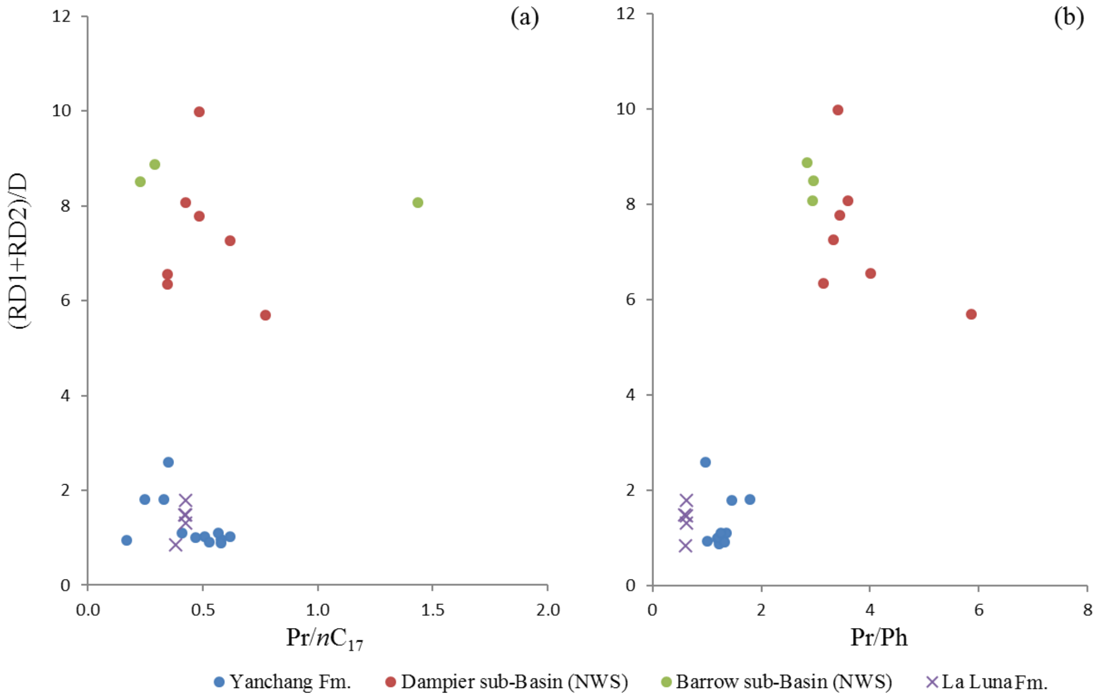

Figure 5.4. Rearranged drimane ratio (RD1+RD2)/D vs redox conditions and thermal maturity according to a) Pr/*n*-C_{17} and b) Pr/Ph, in fluids

With respect to redox conditions of the depositional environment, the data shows that lower Pr/Ph ratios are associated with lower rearranged drimane ratios (**Figure 5.4b**). Even though this is consistent with the suggestion of Ji *et al.* (2016) that reducing conditions inhibit the rearrangement, such effect is difficult to separate from the lithological effect because, for example, the formation of marine carbonates usually occurs in anoxic/euxinic conditions which result in low Pr/Ph ratios whereas higher ratios are recorded in fluvial deltaic basins where the deposition of sediments generally occurs under oxic conditions (Zumberge, 2000, personal communication in Peters *et al.*, 2005).

Further evidence of clay-catalysed rearrangement

A well know example of clay-catalysed rearrangement is the formation of diasteranes from steranes precursors. It has been reported the abundance and type of clay minerals control such rearrangement (Rubinstein, Sieskind, & Albrecht, 1975; Sieskind, Joly, & Albrecht, 1979) and high diasteranes/steranes ratios have been found to indicate clay-rich sediments (Peters & Moldowan, 1993; van Kaam-Peters, Schouten, de Leeuw, & Sinninghe Damsté, 1997; Nabbefeld *et al.*, 2010). Therefore we have calculated the C_{29} diasterane/C_{29} sterane ratio of the source rock extracts and used this as an indicator of clay mineral effects on alkyl rearrangement in polycyclic aliphatic hydrocarbons. **Figure 5.5** shows a positive correlation between rearranged drimane ratio and C_{29} diasterane/C_{29} sterane ratio of source rock samples from the Dampier sub-Basin. This suggests the formation of 1,2,2,5,5-pentamethyl-trans-decalin (RD1) and 1,1,2,5,5-pentamethyl-trans-decalin (RD2) from drimane precursors might occur as regular steranes precursors rearrange to form diasteranes in the presence of clay minerals, which involves backbone rearrangement and carbonium intermediates. A similar correlation was also found by Alexander et al., (1984) in crude oils from Australia (even in samples predating the evolution of higher plants) thus the rearranged drimane ratio could be explored as a correlation tool for a wide range of petroleum fluids in the region (and the corresponding oil-prone and gas-prone source rocks).

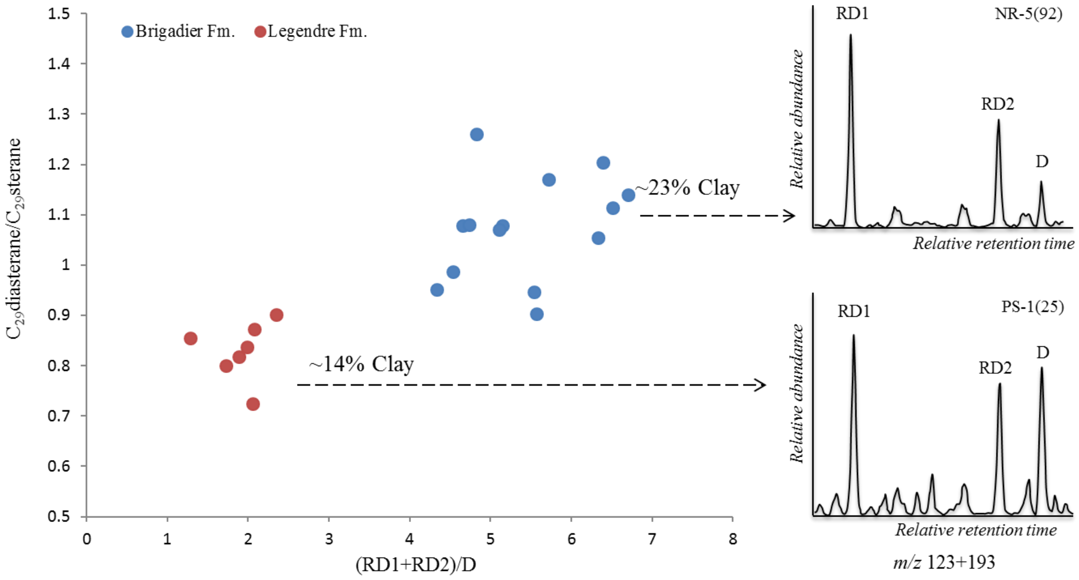

Figure 5.5. Correlation between the rearranged drimane ratio (RD1+RD2)/D and C_{29} diasterane/ C_{29} sterane ratio including the clay content of the source rocks.

For this set of sample, however, some chromatographic interference was found due to co-elution of C_{27} 5α,14β,17β(H)20R and C_{29} 13β,17α(H) 20S diasterane as shown on **Figures 5.6a** and **5.6b**. We consider herein that such interference is minimal as the organic facies of the two formations are very similar (Edwards and Zumberge, 2005; Cesar and Grice, 2017). Furthermore, the diahopane/hopane ratio has been included as this has also been used to indicate clay-catalysed rearrangement (e.g. Asif, Fazeelat & Grice, 2011; Yang, Liu & Feng, 2016) and the chromatography using the fragment of *m/z* 191 offers a better resolution (**Figure 5.6c**). The diahopane ratio ($C_{30}X/C_{30}H$) was consistent with diasterane ratios and samples from the Brigadier Formation exhibit higher $C_{30}X/C_{30}H$ values (~0.14) compared to the Legendre Formation (0.08).

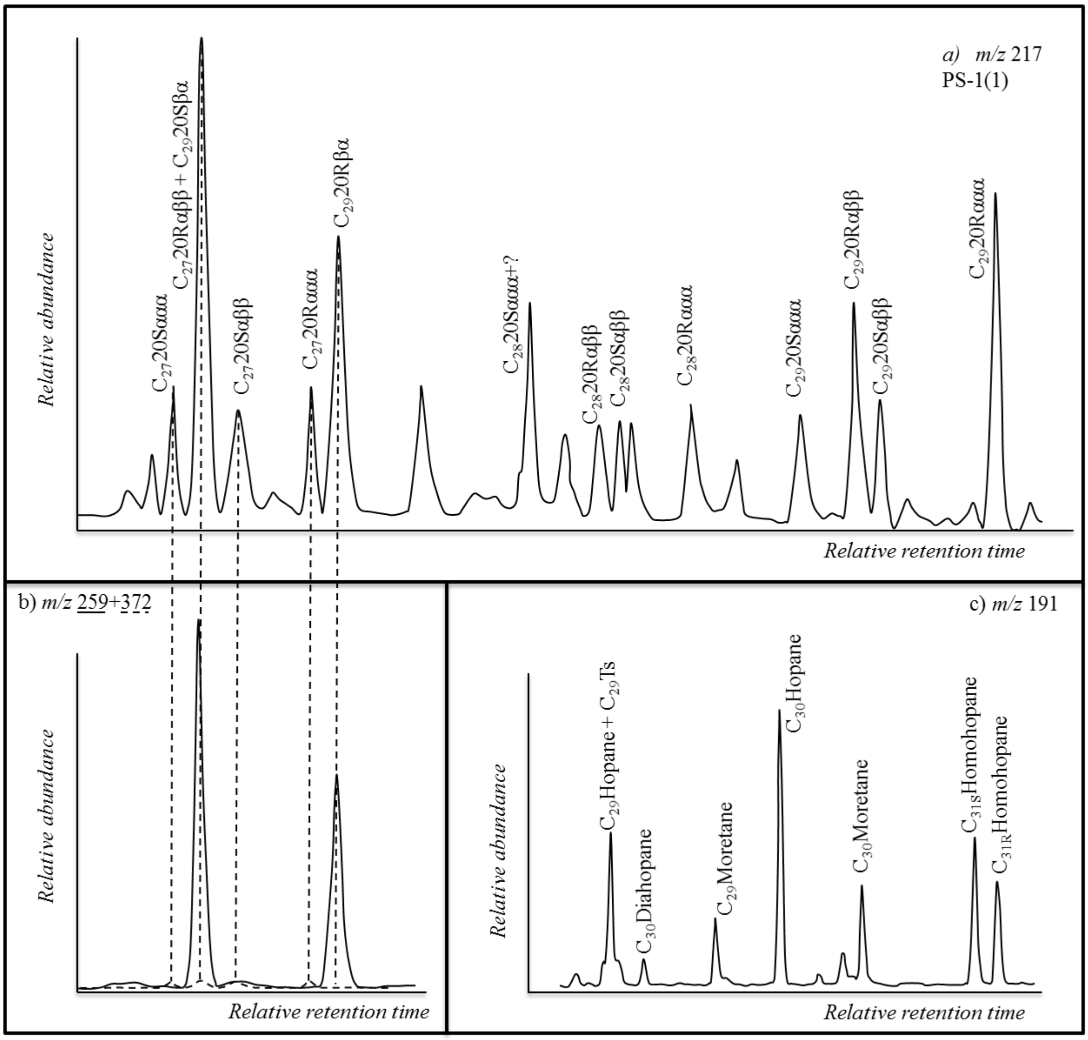

Figure 5.6. a) Peak areas used for the C_{29} diasterane/ C_{29} sterane ratio. b) *m/z* 259 (for C_{29} diasteranes) + 372 (for C_{27} steranes) partial fragmentogram showing the interference due to C_{27} 5α,14β,17β(H)20R

It is challenging to investigate the effect reported by van-Kaam Peters et al., (1998) in our set of samples because they have similar geochemical properties (the mentioned study evaluated samples with very contrasting characteristics, TOC from 1 to 53% and clay content from <1 to 70%). However, X-ray diffraction analysis was conducted on some source rock samples (**Table 5.4**) to investigate mineral effects. In the Brigadier Formation, the clay content of the rock reaches 23% w/w and the (RD1+RD2)/D values range between 5.2 to 6.7, whereas lower rearranged drimane ratios were found in the Legendre Formation (1.3-2.4) which has also a lower content of clay minerals (~14% w/w). Therefore, the rearrangement of the methyl groups in these bicyclic sesquiterpanes (RD1, RD2 and drimane) might be enhanced by clay-mineral catalysis as it is in the case in the transformation of sterenes to diasterenes. The overall trend shows that clay/TOC ratios are higher in the Brigadier Formation compared to the Legendre Formation (**Figure 5.7**), which is consistent with a similar effect found for diasteranes/steranes ratios by van-Kaam Peters et al. (1998).

Table 5.4.

Clay content of selected source rock samples. The clay content corresponds to % of kaolinite (other clay minerals, e.g. smectite, were present at ≤1%).

Sample	*% Clay*	*Clay/TOC*
PS-1(1)	13.9	7
PS-1(3)	14.3	4
PS-1(5)	14.0	7
NR-5(7)	21.9	10
NR-5(4)	24.6	11
NR-5(10)	22.5	13

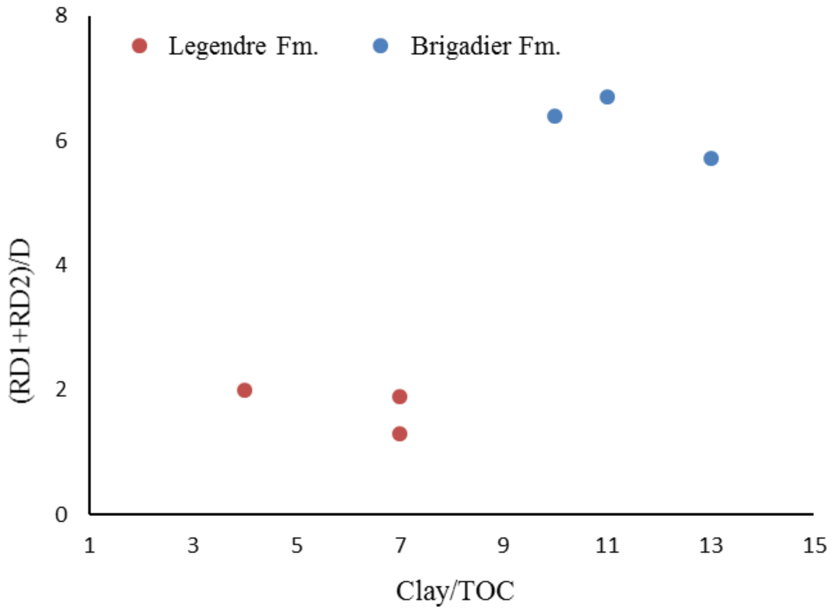

Figure 5.7. Rearranged drimane ration versus the clay/TOC of the Brigadier and Legendre Formation

The source rock samples used for this study are immature and of similar maturity which decreases maturity effects on the calculated ratios. Nevertheless, it is important to note the diasteranes/steranes ratio is also affected by thermal maturity since once they are formed, diasteranes are more stable than regular steranes. Thus, the use of the diasteranes/steranes ratio in fluid-source rock correlation studies requires caution (Rullkötter, Aizenshtat, & Spiro, 1984; Peters, Moldowan, & Sundararaman, 1990). A similar case might be present in the rearrangement of bicyclic alkanes since the isomers having an angular carbon atom in the molecule (*e.g.* drimane) are less stable at high temperatures (Gordadze, Okunova, Giruts, Erdnieva, & Koshelev, 2011). Therefore, a fluid-source rock correlation using the distribution of drimane-skeleton compounds might not be a straightforward process. This requires further investigation along with other factors that may affect the distribution of these compounds in petroleum fluids, such as migration pathways (Zhang *et al.*, 2004) and water washing (Kuo *et al.*, 1994). Biodegradation, however, seems to have a minimal effect on the distribution of C_{15}-decalins (Philp et al., 1981; Williams et al., 1986; Fazeelat et al., 2011; Cortes et al., 2013; Cortes, 2013; Fazeelat *et al.*, 2011; Williams, Bjorøy, Dolcater, & Winters, J 1986; Wang *et al.*, 2016).

Conclusions

A compilation of the rearranged drimane ratio from source rocks and fluids of different lithologies has been reported for the first time, including fluvial-deltaic gas-prone source rocks from Western Australia. This approach suggests the distribution of 1,2,2,5,5-pentamethyl-trans-decalin (RD1) and 1,1,2,5,5-pentamethyl-trans-decalin (RD2) are highly influenced by the lithofacies of the source rock as well as the redox conditions of the depositional environment. In siliciclastic source rocks from similar depositional settings, such as the Brigadier and Legendre Formations in the Dampier sub-Basin, high clay content might facilitate the formation of these compounds by acid-clay-catalysed rearrangement as previously observed for diasteranes. In general terms, claystones show higher rearranged drimanes ratios compared to other siliciclastic source rocks with lower clay content (siltstones) and carbonates; and the same trend seems to be largely preserved in the fluids (crude oils and condensates). This parameter can be explored in a variety of petroleum systems in Australia since its potential relationship with clay-catalysed rearrangement has also been found in Australian crude oils, thus rearranged drimanes can be evaluated for source screening independently of their biological precursors.

Acknowledgments

Jaime Cesar acknowledges Curtin University for an International training scholarship and The Institute for Geoscience Research for a scholarship. K.G and J.C acknowledge the ARC for Linkage funding [LP150100341]. Geoff Chidlow and Peter Hopper are acknowledged for technical support. The authors also acknowledge the use of Curtin University's Microscopy & Microanalysis Facility, whose instrumentation has been partially funded by the University, State and Commonwealth Governments. Jaime Cesar and Kliti Grice specially acknowledge the contribution from reviewers and the editor to improve this scientific contribution.

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CHAPTER 6

Molecular distribution and site-specific isotopes of ethyltoluenes in fluids as a diagnostic tool for lithofacies of source-rocks

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In preparation for submission to *Nature Scientific Reports*

ABSTRACT

Low-molecular-weight (LMW) aromatic compounds in hydrocarbon fluids have scarcely been studied due to their volatility and their relatively low abundances in source rocks for fluid-source correlations. However, LMW aromatics are important components in condensates which lack biomarkers (*e.g.* hopanes) for correlation studies. These compounds are also more resistant to biodegradation compared to light aliphatics which are more widely used for fluid screening. We have investigated the distribution of ethyltoluenes in fluvial-deltaic condensates which show an enhanced *meta*-selectivity of the *ortho-para-meta* isomerisation, suggesting a mineral catalytic effect, as it occurs during the clay-catalysed synthesis of ethyltoluenes. More interestingly, Isomers differ up to 6‰ in $\delta^{13}C$ values. Condensates from the Northern Carnarvon Basin, North West Shelf of Australia, have been analysed by gas chromatography (GC-MS) and compound specific isotope analysis (CSIA) of stable carbon. Interpretations are also supported by site-specific isotope analysis using a Q-Exactive-GC Orbitrap-based-mass spectrometer. We suggest carbon-carbon cleavage during thermal evolution and isomerisation rearrangement under clay acid catalysis explain the isotopic differences reported in isomers of ethyltoluene. This study opens a new window in site-specific isotope geochemistry of organic molecules and for further research on novel isotopic applications of light aromatics in petroleum geochemistry.

Introduction

Defining a petroleum system requires the correlation between a petroleum fluid (crude oil, gas and/or condensate) and a source rock. This is based on the conception that certain compositional parameters of the migrated fluid do not significantly differ from those in the source rock bitumen (Waples & Curiale, 1999). Over decades, this conception has subjected the estimations of hydrocarbons occurrence to the analysis of molecular fossils in order to trace the source of organic matter and establish thermal maturity levels of source rocks and fluids. However, these two variables are often difficult to discriminate because the transformations during the thermal evolution of the organic matter usually overprint the source indicators (*e.g.* isomerisation ratios and isotopic composition of certain compounds).

The very low abundance of biomarkers in condensates also becomes a significant restriction to trace the source(s) for gas/condensate accumulations. A step forward to address these gaps may rely on looking at compounds that preserve a source rock signature despite unknown biological precursors, and are present in crude oils and condensates. Our study demonstrates that low-molecular-weight (LMW) hydrocarbons such as di-alkylated benzenes meet these criteria and can be further explored.

Very few studies have been conducted on LMW aromatic compounds to describe organic facies (*e.g.* Maslen, Grice, Métayer, Dawson, & Edwards, 2011; Le Métayer *et al.*, 2014; Cesar & Grice, 2017) and design thermal maturity indicators (*e.g.* van Aarssen, Bastow, & Alexander, R., & Kagi, 1999; Cheng, Wanga, Huang, Wanga, & Simoneit, 2014; Zhang, Huang, Su, Liu, & Zhang, 2015). It is very challenging to assess the source of light hydrocarbons, particularly mono-nuclear aromatic compounds, because they represent break-down products from more complex structures and/or can ubiquitously form after cyclisation-aromatisation and subsequent isomerisation/methylation of a variety of compounds (*e.g.* Gallegos, 1981; Langworthy, Tornabene, & Holzer, 1982; Hartgers, Sinninghe, & De Leeuw, 1994; Ellis, Singh, Alexander, & Kagi,, 1995; Pedentchouk, Freeman, Harrisa, Clifford, & Grice, 2004). These compounds have also not been widely explored because it is difficult to detect them in source rocks due to their high volatility, and their low relative abundance in bitumen (Odden, Patience, & Van Graas, 1998; Odden, 1999).

There is a significant potential from current advances in analytical instrumentation to further investigate light aromatic hydrocarbons which might have been undervalued in the past due to analytical restrictions. So for this research, we have chosen a compound class scarcely evaluated in petroleum geochemistry and isotope geochemistry studies (Albaiges, Algabe, Clavell, & Grimalt, 1986; Cheng *et al.* 2014). These are the alkyltoluenes, specifically *ortho*- (1-ethyl-2-methylbenzene), *meta*- (1-ethyl-3-methylbenzene) and *para*- (1-ethyl-4-methylbenzene) ethyltoluene isomers, which are chromatographically well-resolved compared to xylenes (*meta*- and *para*- xylenes co-elute using conventional chromatographic settings) and are present in measurable concentrations in crude oils and condensates (Kissin, 1998).

Our research discusses the principles behind the molecular distribution of ethyltoluenes in fluvial-deltaic condensates and the factors controlling their individual stable carbon isotopic compositions from compound specific isotope analyses (CSIA). Their potential relationships with source rock lithofacies have been evaluated. However, improving the scope of the interpretations also requires analytical tools that can constrain more than molecule-averaged isotopic properties. Hence we have conducted the site-specific isotope analysis (SSIA) of stable carbon in ethyltoluenes from petroleum to investigate into isotopomers distribution. Isotopomers are two or more variants of a molecule that differ in the symmetrically non-equivalent location of an isotopic substitution (Eiler, 2007). In this way, we also explore an analytical field, for petroleum studies, that had been restricted to gasses (Gao *et al.*, 2016; Piassecki *et al.*, 2016).

The isotopic composition at different carbon positions within a single molecule has demonstrated to detect large isotope effects even for compounds where the bulk isotope effect is negligible (Remaud *et al.*, 2015) and provide valuable insights in the origin and formation mechanism of natural and synthetic products as well as for mechanistic studies of different chemical reactions (Gauchotte-Lindsay & Turnbull 2016 for a review). Recent SSIA of hydrogen and carbon in organic molecules such as propane have been conducted using high resolution isotope-ratio mass spectrometry (Piasecki *et al.*, 2016) which requires considerably less sample material (*e.g.* 50 µmols vs. 10 mmols) compared to other techniques frequently used for site-specific analysis (*e.g.* NMR and IR absorption spectroscopy). However, we pioneer herein the first application from SSIA of light aromatic hydrocarbons analysed by a Thermo Scientific Q-Exactive gas chromatographer coupled to an Orbitrap mass analyser, which provides an exceptional mass resolution and high sensitivity (Eiler *et al.*, 2017).

The first ever SSIA of gasoline range hydrocarbons from natural samples and the selective carbon isotopes distribution in alkyl-benzenes from petroleum fluids are breaking the barriers in the organic geochemistry of low-molecular-weight aromatic compounds for petroleum systems analysis. Recent advances in Orbitrap – isotope ratio mass spectrometry are exposing a new series of diagnostic tools to help address the biggest challenge in hydrocarbons exploration: identifying the source. This scientific approach also makes a fundamental contribution to organic chemistry (*e.g.* in deciphering reaction pathways) for implementations in other research areas such as environmental science, microbiology and synthetic chemistry.

Results

Meta-selectivity in ethyltoluenes from petroleum fluids

According to the calculations from Alberty (1985), the equilibrium concentrations of ethyltoluenes (at 227 ºC) are 50.2% *m*-ET, 36.0% *p*-ET and 13.8% *o*-ET. The relative abundance of ethyltoluenes in the petroleum samples analysed herein deviate from thermodynamic equilibrium (**Table S6.1**): the fluids derived from fluvial-deltaic source rocks contain up to 62% of *m*-ET whereas only 40% of *m*-ET was found in the fluids derived from carbonate source rocks. These distribution patterns are compared in **Figure 6.1** together with a reference value from clay-catalysis experiments for the synthesis of ethyltoluenes, and pyrolysis of oil shales. **Table S6.2** also provides an overview about the catalytic experiments which found an increase in the relative abundance of *m*-ET due to *para*-*meta* isomerisation (followed by *ortho*-*meta* isomerisation) with decreasing SiO_2/Al_2O_3 ratio of the catalyst. For example, Lee and Wang (1985) produced 50% of *m*-ET, 34% of *p*-ET and 16% of *o*-ET using a catalyst with a SiO_2/Al_2O_3 ratio of 90 whereas Ogunbadejo, Osman, Arudra, Aitani, & Al-Khattaf, (2015) decreased this ratio to 80 and obtained 61% of *m*-ET, 28% of *p*-ET and 11% of *o*-ET. This *meta*-selectivity is similar to the one detected in the fluvial-deltaic condensates. Ethyltoluenes were also detected after artificial maturation of oil shales. In those pyrolysis experiments Kissin (1998) determined 53% *meta*-selectivity, followed by 28% of *p*-ET and 19% of *o*-ET.

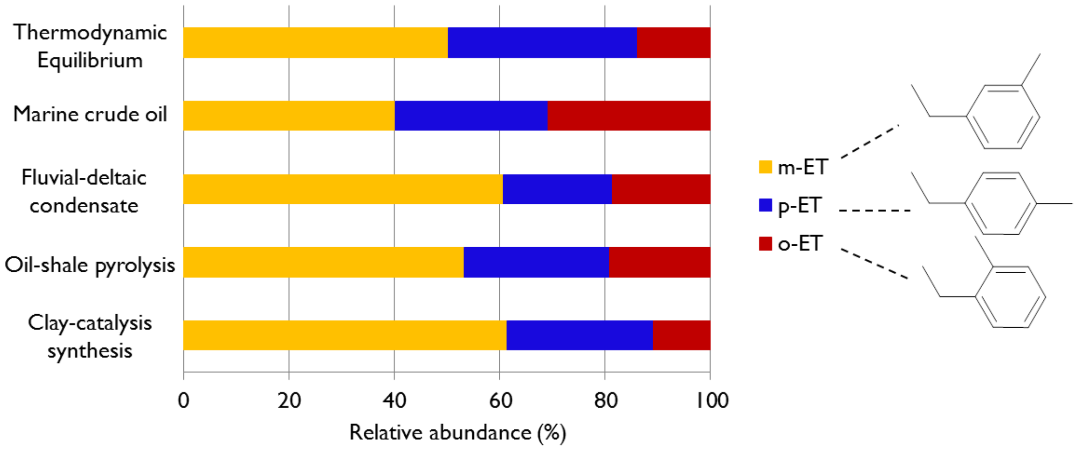

Figure 6.1. Distribution pattern of ethyltoluenes in a marine crude oil (Carbonate-180) and a fluvial-deltaic condensate (GWA-14) in comparison with the thermodynamic equilibrium concentrations at 227 °C (Alberty, 1985) and the distribution obtained from clay-catalysis experiments (MFI-80, Ogunbadejo *et al.*, 2015). MFI: Mordenite Framework Inverted zeolite.

Extraordinary variation in isotopic composition ($\delta^{13}C$) between structural isomers

Besides the particular distribution patterns identified for the relative abundance of ethyltoluenes, the isotopic composition of these compounds also showed distinctive ranges of variation (the $\delta^{13}C$ values are listed in **Table S6.3**). For example, in fluvial-deltaic condensates, the variation between two isomers ranges from less than 1‰ to 6‰, and as a general trend the difference is greater between *meta*- and *para*- isomers. The isotopic values of ethyltoluenes in marine crude oil, instead, did not show a particular trend and the $\delta^{13}C$ of *m*-ET and $\delta^{13}C$ of *p*-ET differ by less than 1‰.

Because the main difference between the geological settings for the formation of the fluids is the lithology of the source rocks, we have included a lithological indicator in order to further investigate potential mineral effects. It has been shown that rearranged drimane compounds are more abundant (compared to drimane) in fluids from fluvial-deltaic claystones than in fluids from carbonate source rocks probably due to clay-catalysed rearrangement (see **Chapter 5**). Hence we have included the rearranged drimane ratio (Ji, He, Zhang, Wu, & Li, 2016) for comparison (see RD/D values in **Table S6.1**). For this particular set of samples, those fluids with rearranged drimane ratios above 10.0 also show greater isotopic difference between δ^{13}C*m*-ET and δ^{13}C*p*-ET (~4‰). This difference is lower in fluids with lower rearranged drimane ratios (*e.g.* 1.4‰ in Angel-1 with a RD/D equals to 6.6) and lowest in the marine crude oils (also lowest RD/D, values <2). It is worth mentioning that other lithological indicators, *e.g.* diasteranes/steranes ratio (van Kaam-Peters, Schouten, de Leeuw, & Sinninghe Damsté, 1997; Nabbefeld *et al.*, 2010) were not applied since these compounds were not detected in the condensates.

Novel SSIA of hydrocarbons using Orbitrap‒isotope ratio-mass spectrometry

SSIA was implemented to investigate whether the large variations in δ^{13}C values (CSIA) were attributed to site-specific isotope distributions within the molecule. *Ortho*-, *para*- and *meta*-ethyltoluene, from a sample with a large isotopic difference amongst the isomers, were analysed by SSIA and the ^{13}C/^{12}C ratios were calculated for the molecular ion 120 Da and the fragment of 105 Da. The difference in ^{13}C/^{12}C was 2.6‰ between *m*-ET and *o*-ET and 4.1‰ between *m*-ET and *p*-ET for the molecular ion (**Table S6.4**). These results are consistent with the δ^{13}C values obtained using CSIA. For the fragment of 105 Da, variations in ^{13}C/^{12}C ratios were found to be reduced up to a difference of 0.5‰ between *m*-ET and *o*-ET and 1.8‰ between *m*-ET and *p*-ET. This fragment corresponds to the di-methylated benzene ring which is stabilised by hyper-conjugation. Fragmentation at the methyl group is not predictable because this process generates an aryl-cation that is very unstable compared to the di-methylated fragment (the fragmentation pattern was also tested using a labelled standard 3ethyl-d_5-toluene).

Discussion

A detailed analysis of isomerisation of ethyltoluenes has been reported in a substantial number of papers on the synthesis of these molecules due to their commercial usage in the petrochemical industry (US Patent No. 4,230,836; US Patent No. 4,490,570). The experiments have evaluated the role of clay catalysis in enhancing *para*-selectivity during the formation of ethyltoluenes and cymenes (*iso*propyltoluenes), which has significant economic repercussions (Lee & Wang, 1985; Paparatto, Moretti, Leofanti, & Gatti, 1987; Parikh, 2008; Odedario & Al-Khattaf, 2011; Atanda, Aitania, & Al-Khattaf, 2015, Ogunbadejo *et al.*, 2015; Ogunbadejo, Aitani, Cejka, Kubu, & Al-

Khattaf, 2016). Temperature was found to enhance *para*-selectivity whereas clay catalysis increases *meta*-selectivity, and the catalytic effect depends on the crystal size and the SiO_2/Al_2O_3 ratio of the catalyst (a measure of acid sites on the clay surface). If we extrapolate this approach to a geological context, clay minerals in siliciclastic source rocks might have a similar effect on the isomerisation of ethyltoluenes, and thus potential applications to trace the source rock can be investigated. Highly appropriate examples for such consideration are the gas-prone petroleum systems from the North-West Shelf of Australia, where the fluids originated from fluvial-deltaic claystones and/or clay-rich shales, and many uncertainties still persist about fluid provenance (Longley *et al.*, 2002, Edwards & Zumberge, 2005).

Figure 6.2 shows the suggested mechanism for the isomerisation of ethyltoluenes in a siliciclastic source rock. The same was adapted from Forni and Amarilli (1978) and further developed based on the findings from the clay-catalysed synthesis experiments (*e.g.* Atanda *et al.*, 2015, Ogunbadejo *et al.*, 2015). According to this mechanism, the rearrangement of alkyl groups is controlled by acid-catalysis on the mineral surface and also driven by the shape selectivity of the source rock and the stability of potential intermediates. Paparatto *et al.* (1987) explained the catalysis consists of two stages: the first reaction is shape-selective and drives the reaction towards the isomer with lowest steric hindrance and thermally more stable which is *para*-ethyltoluene, in the second reaction this compound diffuses through the pores and comes into contact with acid sites of the external mineral surface and isomerises towards *meta*-ethyltoluene over high contact times. In the case of petroleum fluids, geological time, thermal maturity, clay content, and source rock porosity suggest favourable conditions for this isomerisation to occur.

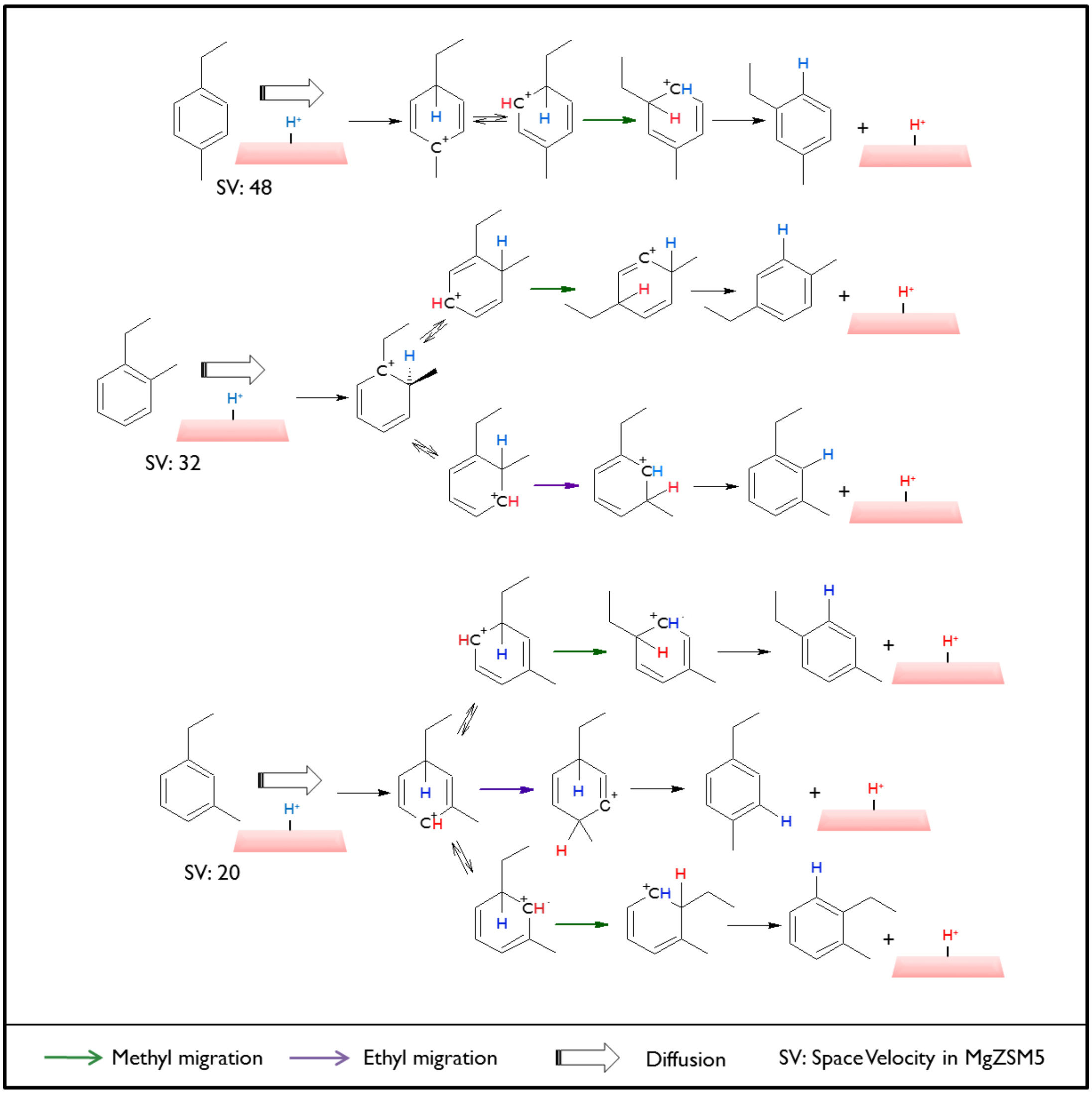

Figure 6.2. Proposed mechanism for the isomerisation of ethyltoluenes under clay mineral catalysis. A: clay-catalysis on *p*-ET involving protonation at the ethyl-bonded carbon and ethyl migration. B: clay-catalysis on *o*-ET involving protonation at the methyl-bonded carbon and ethyl/methyl migration. C: clay-catalysis on *m*-ET involving protonation at the ethyl-bonded carbon and ethyl migration. These pathways are suggested based on reported literature and fundamental principles of organic chemistry, however, several other rearrangements are also possible.

This mechanism we suggest considers the incorporation of a proton (H+ from the clay) at the carbon bonded to the ethyl group since the higher electronic density of this substituent increases the basic character of this carbon atom (Dewick, 2006). Subsequently, according to the migratory character of alkyl substituents, the ethyl group is more prone to migrate than the methyl group due to the capability of the first one to stabilise a positive charge more effectively (Witsuba & Ruchardt, 1981;

Cammell & Andersen, 2000). We consider, however, that the acid catalysis of *ortho*-ethyltoluene might operate through a slightly different pathway because steric hindrance potentially influences the rearrangement. Given that the alkyl groups are at the positions 1 and 2, the geometry of the structure protonated at the methyl side or carbon number 2 is to some extent more stable than the geometry obtained after protonation at the ethyl side or carbon number 1 (Table **S6.5** and **Figure S6.1** contain the zero point energy values of the optimised geometries of the protonated structures from computational simulations). Therefore, the isomerisation for *ortho*-ethyltoluene, as shown in **Figure 6.2B**, more likely starts by protonation at the methyl-substituted carbon followed by methyl and/or ethyl migration.

The reaction pathways proposed in **Figure 6.2** (A-C) can explain the accumulation of *meta*-ethyltoluene over geological time since the *para-meta* and *ortho-meta* transformations involve more stable intermediates (tertiary carbocations) and are therefore more prone to occur (Dewick, 2006). Additionally, *meta*-ethyltoluene has a lower diffusion rate through porous media such a source rock (see the corresponding space velocity values or SV in **Figure 6.2** for the molecular transport of ethyltoluenes in MgZSM5 calculated by Chen, Degnan, & Morris, 1994), which at the same time restricts its contact with the mineral surface. *Para*-ethyltoluene potentially represents the main source for *m*-ET because it has the highest diffusion rate which stimulates a more effective contact with acid sites of the mineral surface. The consumption of *p*-ET is also consistent with clay-catalysed rearrangements according to high relative abundance of rearranged drimanes (**Table S6.1**). *Ortho*-ethyltoluene, instead, has an intermediate diffusion rate, is the thermodynamically least stable (Alberty, 1985) and can isomerise towards *para*- and *meta*- compounds. Therefore assessing the rearrangement of *o*-ET is yet challenging. Nevertheless, we can infer the shape selective reaction or first stage according to Paparatto *et al.* (1987), mainly consists of *ortho-para* isomerisation which is also kinetically faster (Atanda *et al.*, 2015); an indication for this is the constant *ortho*/*para* ratio in the fluids despite the abundance of *m*-ET. Furthermore, the *ortho-para* isomerisation might be useful to indicate the architecture (*e.g.* porosity) of the source rock because the *o*-ET/*p*-ET ratio was found to be different only for distinctive source rock types (*e.g.* coaly facies from Gorgon-4, carbonate facies from La Luna, and marine shales in the Barrow Island). In general terms, as the ultimate product of the isomerisation, enhanced *meta*-selectivity in petroleum fluids might respond to mineral catalysis (thus to source rock lithofacies) as it responses to clay catalysis in the synthesis of ethyltoluenes.

In previous studies using petroleum samples, Ellis *et al.* (1995) concluded that, for mature crude oils, those from carbonate source rocks will exhibit higher proportions of *ortho* isomers whilst those derived from clay-rich source rocks will have higher abundance of *meta* isomers; this *meta*-selectivity was attributed to apparent clay-catalysed isomerisation reactions. Structural rearrangements were also suggested for the shale pyrolysis experiments of Kissin (1998). However, the *meta*/*para* ratio obtained after pyrolysis was lower than the ratios found for the fluids from this study. Those cracking experiments were conducted in enclosed system (sealed glass ampules) which restricts the diffusion of the compounds and stimulates the reverse isomerisation reactions. Kissin (1998) also proved the catalytic effect was mainly mineral dependent as adding organic-free shale rock to the oil shale accelerated the formation of light aromatic hydrocarbons during pyrolysis.

The isotopic composition associated to the molecular distribution of ethyltoluenes is more complex to address. In first place more negative δ^{13}C*p*-ET values are consistent with the shape-selective reaction aforementioned and *p*-ET becomes lighter than *o*-ET through a normal kinetic isotope effect through rearrangement. However, rearrangement reactions by themselves cannot explain the more positive δ^{13}C values of *m*-ET because as the ultimate product, a lighter isotopic composition would be expected. There must be another process responsible for the consumption of the *meta*-isomer that causes the ^{13}C enrichment of the remaining *m*-ET. We suggest herein that after the accumulation of *m*-ET due to *para*-*meta* and *ortho*-*meta* transformations, this isomer is consumed by thermal cleavage to form other compounds (*e.g.* dimethyl-benzenes) undergoing a large primary normal isotope effect (see simplified mechanism for thermal cleavage of *m*-ET in **Figure 6.3**).

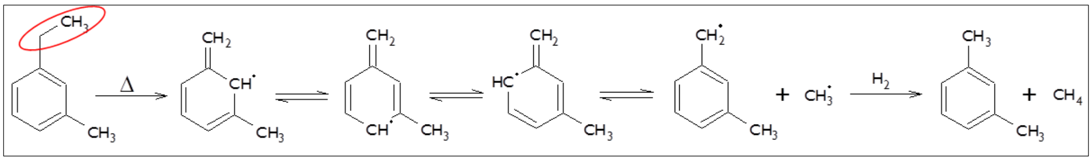

Figure 6.3. Simplified mechanism for the consumption of *m*-ET through ethyl cleavage.

The site specific isotope analysis suggests that the isotopomers of *m*-ET with ^{13}C-^{13}C and ^{12}C-^{13}C bonds integrating the ethyl substituent are the most abundant in the condensate. Even though these isotopomers concentrate after thermal cracking, their abundance is indirectly associated to the isomerisation rate towards *m*-ET due to clay-catalysed rearrangements, *i.e.* the more *m*-ET is formed the more has to be consumed by thermal cracking to drive the system towards equilibrium. It is worth mentioning that thermal maturation can also stimulate the reverse rearrangement of *m*-ET towards *ortho* and *para* isomers which requires further investigation.

There is a high potential in the molecular and isotopomeric distributions of ethyltoluenes to represent a well-preserved source rock signature after primary migration. Secondary migration presumes a lower temperature than source rock conditions thus further cracking is not expected (unless another process, *e.g.* a tectonic event, rises up the temperature). At the same time, secondary migration occurs though a rock with higher porous size and permeability (*e.g.* sandstone), therefore the effect of shape-selectivity and effective contact with mineral surface are significantly diminished (*e.g.* Schmidt & McDonald, 1979).

We have demonstrated that ethyltoluenes from complex mixtures, *e.g.* petroleum fluids, represent a compound class with large intramolecular isotope ratio heterogeneity. This sets the scene for a new direction in isotope geochemistry to outline the history of fossil fuels accumulations implementing for first time an intramolecular approach on liquid hydrocarbons. Further investigation in the isotopomers distribution of LMW aromatic hydrocarbons will significantly improve our understanding of petroleum systems in Western Australia as well as for similar petroleum basins worldwide. Some of these findings on similar compound classes will be reported in upcoming papers.

Methods

A set of twenty fluids was used for this study. Fifteen fluids are terrigenous condensates originating from siliciclastic source rocks from the North West Shelf of Australia (**Table S6.1**); and five crude oil samples from carbonate source rocks (La Luna Formation, Venezuela) were included for comparison. The aromatic fractions were isolated by small scale silica gel liquid chromatography and subsequently analysed by gas chromatography – mass spectrometry (GC-MS) and gas chromatography – isotope-ratio mass spectrometry (GC-irMS). Specific details on these methods can be found in the supplementary material (**Appendix 6**).

Site-specific Isotope Analysis (SSIA)

A sample with a large variation in the $\delta^{13}C$ isotopic values was selected for SSIA using a Thermo Scientific Q-Exactive GC containing an Orbitrap mass analyser. 5 µL of aromatic fraction were manually injected into the GC. The oven was programmed from 40 ºC to 70 ºC at 3 ºC/min and was held isothermally for 6 minutes; the temperature was subsequently ramped until 110 ºC at 3 ºC/min and held isothermally for 40 min. A peak broadener setting was used for the analysis of target compounds. Further details of this method will be available in the work of Eiler *et al.*, (2017) as well as the in **Appendix 6** (**Figure S6.2**) but briefly, this consists of the exclusive analysis of a target component during a wide time interval which results in a very broad chromatographic peak. This is achieved by manipulating a set of two valves which enables: (i) the trapping of a target compound in a vial that acts as a reservoir which accumulates the component of interest, and its subsequent analysis in the mass spectrometer over a period of approximately 60 min, (ii) the analysis of non-target compounds directly eluting from the GC column in order to monitor any possible chromatographic changes (*e.g.* variations in retention time), followed by (iii) the disposal of solvent and any undesirable compounds to waste. Mass spectrometer conditions were as follows: automatic gain control (AGC) target of $1x10^6$, injection time of 3,000 ms, and resolution of 180,000. The principles for signal processing of Orbitrap analysis were reported by Makarov, 2000. Briefly, $^{13}C/^{12}C$ ratios (number of ^{13}C-containing ions divided by the number of ^{12}C-containing ions) are calculated for every single scan during the time of analysis (~1000 scans per peak) and subsequently weighted to the absolute intensity at each data point. Each scan consists of the same amount of ions sent from the C-trap into the Orbitrap analyser.

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Appendix 6. Supplementary Online Material

Table S6.1. Total molecular data. Relative abundance of ethyltoluenes measured from the total ion chromatogram of the aromatic fraction. Rearranged drimane ratio RD/D: (RD1+RD2)/Drimane. *m*: *meta*, *p*: *para*, *o*: *ortho*.

Sample	**%*m*-ET**	**%*p*-ET**	**%*o*-ET**	**RD/D**
Echo-1	58.9	21.7	19.4	7.3
Gorgon-4	61.5	23.0	15.5	8.5
Dockrell-1	57.9	21.9	20.2	8.1
Tidepole-1	57.5	22.1	20.3	7.8
GWA-3	60.9	20.1	19.0	13.2
GWA-5	60.5	16.3	23.2	13.0
GWA-06	60.6	19.6	19.8	12.2
GWA-07	60.3	20.4	19.3	12.5
GWA-10	60.1	20.9	19.0	13.6
GWA-11	60.2	20.5	19.3	10.2
GWA-12	60.4	20.7	19.0	11.5
GWA-13	60.0	21.2	18.8	12.7
GWA-14	60.5	20.4	19.1	13.8
GWA-16	60.7	20.6	18.7	13.7
Angel 1	58.5	24.1	17.4	6.6
NR1	59.6	21.2	19.2	10.0
NR3	56.8	22.6	20.6	9.2
Barrow	53.5	24.3	22.1	8.1
Barrow Island	55.9	23.9	20.2	8.9
Goodwyn-9	61.0	20.6	18.3	7.6

Table S6.1 (Continued)

Sample	**%*m*-ET**	**%*p*-ET**	**%*o*-ET**	**RD/D**
Carbonate-180	39.1	28.7	32.2	1.5
Carbonate-74	40.2	28.9	30.8	1.3
Carbonate-176	39.7	27.8	32.4	1.8
Carbonate-186	40.3	27.3	32.4	1.5
Carbonate-187	41.6	28.3	30.1	0.8
Equilibrium (227 ºC)	50.2	36.0	13.8	-

Table S6.2. Examples of clay catalysis experiments for the synthesis of ethyltoluenes, and oil-shale pyrolysis.

Authors	**Experiment**	**SiO_2/Al_2O_3**	**% *m*-ET**	**% *p*-ET**	**% *o*-ET**
Lee & Wang (1985)	Alkylation of toluene with ethylene (HZSM-5 zeolite, 275ºC)	90	50	34	16
Ogunbadejo *et al*. (2015)	Alkylation of toluene with ethanol (MFI zeolites, 300ºC)	80	61	28	11
Ogunbadejo *et al*. (2015)	Alkylation of toluene with ethanol (MFI zeolites, 350ºC)	180	50	49	1
Atanda *et al*. (2015)	Alkylation of toluene with ethanol (ZSM-5 zeolite, 300ºC)	80	61	28	11
Kissin (1998)	Artificial oil shale maturation (350 ºC, 24h)	shale	53	28	19

Table S6.3. Total isotopic data. Standard deviation (σ) of δ^{13}C reported for duplicates. Δ: difference between two δ^{13}C values. *m*: *meta*, *p*: *para*, *o*: *ortho*.

Sample	**δ^{13}C*p*-ET**	**σ**	**δ^{13}C*o*-ET**	**σ**	**δ^{13}C*m*-ET**	**σ**	**Δ^{13}C*m*-*p***	**Δ^{13}C*m*-*o***
Echo-1	-25.9	0.38	-24.7	0.38	-25.1	0.44	0.8	-0.4
Gorgon-4	-26.1	0.35	-24.3	0.11	-26.1	0.41	0.1	-1.8
Dockrell-1	-24.3	0.27	-24.5	0.04	-24.1	0.04	0.3	0.4
Tidepole-1	-25.5	0.18	-23.8	0.04	-25.1	0.04	0.4	-1.3
GWA-3	-28.8	0.10	-28.4	0.04	-23.0	0.23	5.8	5.4
GWA-5	-28.1	0.14	-26.1	0.19	-22.8	0.16	5.2	3.2
GWA-06	-27.0	0.08	-25.9	0.24	-23.4	0.05	3.6	2.5
GWA-07	-27.1	0.16	-25.7	0.00	-23.4	0.26	3.6	2.2
GWA-10	-27.8	0.17	-26.2	0.13	-24.1	0.00	3.7	2.1
GWA-11	-26.9	0.08	-26.1	0.44	-23.6	0.06	3.3	2.5
GWA-12	-27.5	0.10	-26.8	0.04	-23.7	0.00	3.8	3.1
GWA-13	-27.8	0.04	-27.6	0.32	-23.7	0.15	4.1	3.9
GWA-14	-27.2	0.14	-26.0	0.30	-23.1	0.19	4.2	2.9
GWA-16	-28.2	0.30	-26.9	0.44	-24.3	0.18	3.9	2.6
Angel 1	-25.0	0.10	-25.7	0.07	-23.6	0.05	1.4	2.1

Table S6.3 (Continued)

Sample	δ^{13}C*p*-ET	σ	δ^{13}C*o*-ET	σ	δ^{13}C*m*-ET	σ	Δ^{13}C*m-p*	Δ^{13}C*m-o*
NR1	-24.4	0.00	-24.6	0.17	-23.0	0.10	1.4	1.6
NR3	-26.8	0.04	-24.9	0.04	-20.8	0.00	5.9	4.1
Barrow	-26.8	0.04	-26.9	0.26	-25.4	0.31	1.3	1.5
Barrow Is	-27.4	0.25	-24.9	0.27	-24.7	0.09	2.8	0.2
Goodwyn-9	-27.7	0.18	-25.0	0.09	-24.0	0.31	3.8	1.0
Carbonate 180	-28.8	0.31	-28.3	0.12	-28.2	0.21	0.6	0.1
Carbonate 74	-27.9	0.12	-28.5	0.12	-28.8	0.19	-0.9	-0.3
Carbonate 176	-29.0	0.20	-28.5	0.39	-28.5	0.15	0.6	0.0
Carbonate 186	-28.3	0.28	-27.3	0.05	-29.2	0.25	-0.9	-1.9
Carbonate 187	-28.2	0.11	-28.2	0.17	-27.9	0.28	0.3	0.3
Equilibrium (227 ºC)	-	-	-	-	-	-	-	-

Table S6.4. Stable carbon site-specific isotope analysis of ethyltoluenes. Sample GWA-5. Standard deviation (σ) of $^{13}C/^{12}C$ reported for duplicates. *m*: *meta, p*: *para, o*: *ortho*.

m/z	**120**	**105**
$^{13}C/^{12}C$*m*-ET	0.0937075	0.0884470
σ	0.0000718	0.0000314
$^{13}C/^{12}C$*o*-ET	0.0934494	0.0883985
σ	0.0000408	0.0000442
$^{13}C/^{12}C$*p*-ET	0.0932976	0.0882656
σ	0.0000817	0.0000610
$^{13}C/^{12}C$(*m-o*)	0.0002581	0.0000485
$^{13}C/^{12}C$(*m-p*)	0.0004099	0.0001813

Table S6.5. Difference in zero point energy between the intermediate protonated at the ethyl-bonded carbon ($^+$C2) and the intermediate protonated at the methyl-bonded carbon ($^+$C1) in kJ/mol for *ortho*, *meta* and *para* configurations.

	ΔZPE$_{(^+C2-^+C1)}$ (kJ/mol)
Ortho	2.05
Para	-5.14
Meta	-5.45

Supplementary Methods

Gas chromatography – mass spectrometry (GC-MS)

The aromatic fractions were isolated by small scale silica gel liquid chromatography as described elsewhere (Maslen et al., 2011), using *n*-pentane instead of *n*-hexane. Subsequently, the fractions were analysed by gas chromatography – mass spectrometry (GC-MS) on an HP 6890 GC coupled to an HP 5973 mass selective detector (MSD) operating in electron ionisation mode (70 eV), and injections were of

1 µL of solution using an HP 6890 auto-sampler. The compounds were chromatographically separated on a WCOT fused silica capillary column (60 m X 0.25 mm i.d.) with a 0.25 µm 5% phenyl–methyl–silicon stationary phase (DB-5), and the carrier gas was helium at a linear velocity of 1 mL/min. The temperature of the GC oven was programmed from 40 ºC –325 ºC (at 3 ºC/min) and was held isothermally for 45 minutes at 325 ºC. Compound identification was achieved by comparing the mass spectra and the relative retention times with those previously reported in the literature (Thompson, 1987; Hartgers, Sinninghe, & De Leeuw,.1994; Halpern, 1995).

Gas chromatography – isotope ratio-mass spectrometry (*GC-ir-MS)*

A Thermo Scientific Trace GC Ultra connected to a Thermo Scientific Delta V Advantage irMS via a GC Isolink and Conflo IV was used for compound specific isotope analysis (CSIA) of carbon by gas chromatography – isotope-ratio mass spectrometry (GC-irMS). 1 µL of each fraction was injected into a split-splitless injector operating in splitless mode, held at 280 °C. The same GC conditions as used above for GC-MS analyses were used for CSIA. Helium was used as carrier gas at a constant flow of 1.5 mL/min. GC column outflow passed through the GC Isolink combustion reactor (copper oxide and nickel oxide, held at 1000 °C) which combusted each peak to a separate peak of CO_2. The $\delta^{13}C$ values are expressed in parts per mil (‰) relative to the International Vienna Peedee Belemnite (VPDB) standard and were calculated by Thermo Isodat software from the integration of the 44, 45 and 46 mass ions currents. Every two sample measurements, a mixture of standards with known $\delta^{13}C$ values was analysed in order to insure instrument accuracy. Peaks co-eluting, as well as those at very low concentrations, were not considered for our interpretations. Only target compounds with a standard deviation of less than 0.4 ‰ were taken into account.

Computational simulations

The structures of the protonated isomers have been optimised in gas phase at the DFT (Density Functional Theory) level of theory with the NWChem code using the 6-311G* basis set and the B3LYP exchange and correlation functional. The vibrational frequencies have been calculated for all compounds to ensure that they were stable states and their free energies were computed by adding the zero point energy and the translational rotational and vibrational entropic contributions to the total DFT energy. The calculations show that all the proposed reaction pathways are thermodynamically accessible. An important aspect that has not been explored in these calculations is the activation energy required to form the intermediate species. These calculations are much more computationally demanding, particularly because the proton (H^+) comes from a clay mineral, which plays a key role in initiating these reactions and therefore should be explicitly included in the calculation.

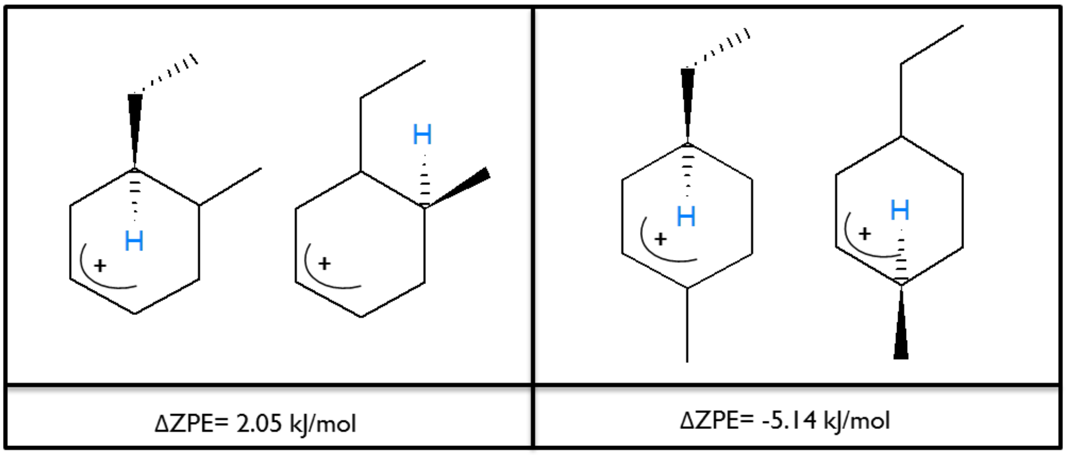

Figure S6.1. Stability of the molecular geometry of the protonated intermediates (ethyl-protonated–methyl-protonated) in A: *ortho-* configuration, and B: *para-* configuration.

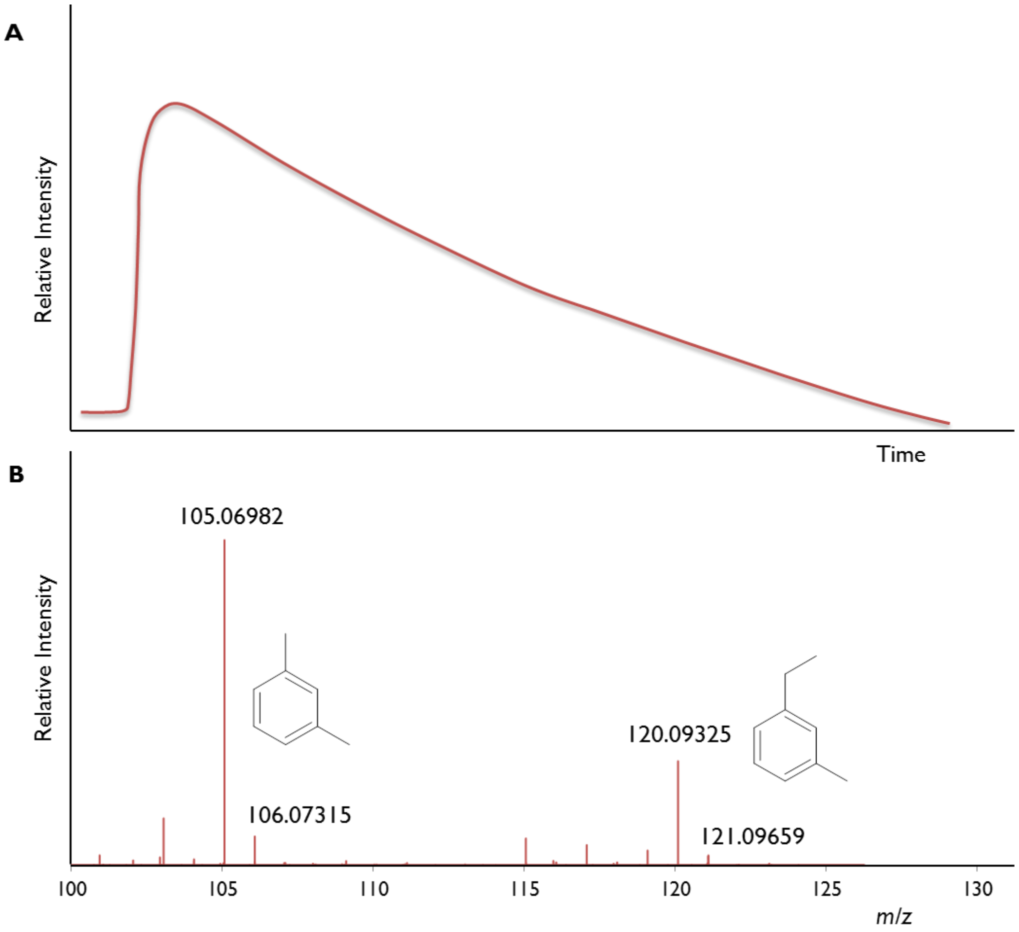

Figure S6.2. Instrumental signal from the GC – Q-Exactive – Orbitrap-irMS. A: Chromatogram of *meta*-ethyltoluene (sample GWA-05) using peak-broadener settings. B: corresponding mass spectrum in the window *m/z* 100-125 with the ^{12}C and ^{13}C peaks indicated.

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CHAPTER 7

Conclusions and Outlook

The thesis provides novel molecular and isotopic tools for geochemical screening of source rocks and fluids from fluvial-deltaic petroleum basins. This has potential applications to other petroleum basins around the world.

Several new parameters for distinguishing age and source-rock facies from complex depositional settings, such as deltas, have been identified providing new applications in the field petroleum geochemistry. These tools will play an important role in petroleum geochemistry when biomarker indicators are not available for correlation studies (*e.g.* between gas-prone source rocks and condensates). Further work will be undertaken by Eiler *et al.*, to finalise the last chapter.

Triassic-Jurassic land plants: the source of hydrocarbons in the Dampier sub-Basin

This research demonstrates that changes in the distribution of palaeoflora not only relied on climate but also on the depositional settings (shoreline position) of the Dampier sub-Basin. A major proximity to up-land vegetation, due to inland migration of the shoreline, resulted in high retene/1,3,6,7-TeMN ratios (retene being in this case attributed to a source from conifer resins). Retene was found to be more abundant in shallow marine environments (transitional/pro-deltaic facies) due to proximity to the source after transgression. Climatic effects, in contrast, were detected as internal shifts within up-land vegetation. For example, among the conifer families, the presence of only bicyclic sesquiterpanes indicated *Pinaceae* to be predominant under the warm-hot Triassic-Jurassic climate in Western Australia. Tricyclic and tetracyclic diterpanes that are synthesised by other conifer families were not detected, as these plants might have not prospered because they require more humid environments to settle.

The palaeovegetation reconstruction over the Late Triassic to Late Jurassic in the Dampier sub-Basin indicates conifer debris as the main land plant source to the basin. Conifer forests proliferated during the dry-seasonal Late Triassic and the humid Middle and Late Jurassic. Climatic conditions during the Early Jurassic were too dry for up-land vegetation to prosper, and the land plant population was probably restricted to low-land/coastal vegetation. This might also explain why the Early Jurassic claystones in the Dampier sub-Basin show only low to moderate source rock potential (*e.g.* the Athol Formation).

With respect to other plant markers, cadalene was not diagnostic in this study as it originates from a variety of vascular plants (not only conifers). However, this marker is most abundant in the Early Jurassic which suggests that low-land/coastal vegetation, which settled in arid conditions, synthesised natural product precursors that lead to the biomarker cadalene. Additionally, 6-*iso*propyl-1-*iso*hexyl-2-methylnaphthalene (*ip*-*i*HMN) probably originated from bryophytes. These plants are more adapted to humid environments, which might explain why *ip*-*i*HMN was found to be more abundant in the Middle Jurassic after a humid climate had been established.

Organic facies type and potential source rock signatures based on non-biomarker parameters

One of the main challenges in the Dampier sub-Basin is the similarity of organic facies of potential source rocks. Parameters such as pristane/phytane ratios or sterane distributions have shown similar values through the Triassic-Jurassic record. Therefore, it was of interest to evaluate the applicability of non-biomarker compound classes in the discrimination of the marine versus terrigenous character of the organic facies of potential source rocks. Combustion-derived PAHs [pyrene (Pyr), benzo[*a*]pyrene (B*a*Py), benzo[*e*]pyrene (B*e*Py), coronene (Cor), fluoranthene (Fla), benzofluaranthenes (BFla), benzo[*g*,*h*,*i*]perylene (Bpery), chrysene (Chry), triphenylene (Tpn) and benzo[*a*]anthracene (B*a*An)] were found to be suitable indicators of terrigenous organic matter as they form after combustion of land plants. The ratios of the combustion-derived PAHs to 1,3,6,7-TeMN were usually twenty times higher in delta plain facies compared to estuarine environments. The ratios of the combustion-derived PAHs to phenanthrene were, on the other hand, lower in the delta plain because the combustion process also generates phenanthrene. Furthermore, in comparison with the combustion-derived PAHs, phenanthrene and 1,3,6,7-TeMN showed greater variation of $\delta^{13}C$ values (up to up to and 4‰ and 7‰ respectively). This is because these two compounds can be affected by marine organic matter input (*e.g.* phenanthrene as a diagenetic product of steroids, and 1,3,6,7-TeMN derived from microbes). As a result, the parameters $\Delta^{13}C_{CombMarker-1,3,6,7\text{-}TeMN}$ and $\Delta^{13}C_{CombMarker-Phe}$ enable facies discrimination in transitional settings, for example, from more terrigenous in the Triassic towards slightly more marine in the Jurassic. The $\delta^{13}C$ of 1,2,5-TMN showed considerable variation (up to 6‰). This compound has the potential to be more indicative of local transitions in the depositional environment although its abundance in the extracted bitumen was not always suitable for isotopic measurements.

Another aspect explored in the research was the identification of source rock signatures due to molecular rearrangement of certain non-biomarker compound classes such as benzo[*b*]naphtho[*d*]furans (BNFs) and bicyclic sesquiterpanes. The formation of [1,2]BNF (benzo[*b*]naphtho[1,2-*d*]furan) seems to be enhanced by the presence of clay minerals in the source rock; and the ratio [2,1]/[1,2]BNF can be used to indicate lithofacies type. The BNF ratios were higher in the Mungaroo Formation compared to the Legendre Formation probably due to higher clay content (24% versus 14% w/w). This parameter seems to be consistent in the fluids, although further investigation is required on the relative distribution of the isomers (benzo[*b*]naphtho[2,1-*d*]furan benzo[*b*]naphtho[1,2-*d*]furan or [1,2]BNF, and benzo[*b*]naphtho[2,3-*d*]furan or [2,3]BNF) as the fluids were usually more depleted in [2,3]BNF compared to the source rock extracts.

In the same manner clay catalysis seems to facilitate the rearrangement of 8β-(H)-drimane (D) to form rearranged drimanes [1,2,2,5,5-pentamethyl-trans-decalin (RD1) and 1,1,2,5,5-pentamethyl-trans-decalin (RD2)] which results in higher rearranged drimane ratios [D/(RD1+RD2)]. Carbonate-dominated facies exhibited lower rearranged drimane ratios (~2) than fluvial-deltaic claystones (up to 7). In general terms, low BNF (0.7-1.3) ratios and high rearranged drimane ratios (6-10) are typical of source rocks and fluids from the Dampier sub-Basin. These parameters were also consistent with the diasteranes/steranes ratios measured in the source rock extracts.

New directions in molecular and isotope geochemistry of petroleum hydrocarbons

Low-molecular-weight (LMW) aromatic compounds are usually excluded in petroleum studies because they can have multiple sources and represent a very small part of the total composition of crude oils (up to 1%). However, light aromatics are important components in condensates, they are more resistant to biodegradation compared to their aliphatic counterparts, and some of the mononuclear aromatic compounds are chromatographically well resolved. In this particular case, the distribution of *ortho-, para-* and *meta-* ethyltoluene isomers was found to be distinctive for fluids derived from claystones compared to fluids derived from carbonate source rocks. The distinction is based on the enhanced *meta*-selectivity of the isomerisation due to clay-catalysed rearrangement. This was further supported by extensive research reported on clay-catalysed synthesis of ethyltoluenes, and by similar distributions found in alkyltoluene isomers from petroleum. This also demonstrated that, based on fluid screening, inferences about the characteristics of the source rock can be established despite such compounds being absent in source rock extracts. More interestingly, the isotopic signature of ethyltoluenes from fluvial-deltaic condensates was also different to the isotopic values found in marine crude oils. An extraordinary variation of up to 6‰ was found between the $\delta^{13}C$ of ethyltoluene isomers from the condensates whereas *ortho- para-* and *meta*-ethyltoluene from marine crude oils showed no variation in $\delta^{13}C$.

Research focused on light aromatics provided opportunities to overcome analytical boundaries to generate novel geochemical information. This project initiated the implementation of site-specific isotope analysis (SSIA) of hydrocarbons from complex mixtures (*e.g.* a petroleum condensate) which had not previously been attempted. The SSIA of low-molecular-weight aromatic compounds demonstrated that intramolecular isotope distributions in ethyltoluenes are not random. For example, isotopomers of *meta*-ethyltoluene with ^{13}C substitution at the ethyl branch are preferentially concentrated during thermal evolution of the organic matter. This process is intimately related to the enhanced *meta*-selectivity of the molecular distribution in fluids derived from fluvial-deltaic claystones, due to clay-catalysed rearrangement of *ortho* and *para* isomers. This new intramolecular approach provides a major level of detail for the analysis of petroleum fluids.

Recommendations for future work

New insights in fluid to source correlations in the Dampier sub-Basin are currently under evaluation by joint venture partners involved in hydrocarbon exploration of the Rankin trend. This information is not presented in this work as it directly affects the business and confidentiality policies of the companies involved. However, the application of the approaches presented in this research to other sub-Basins from the Northern Carnarvon Basin, particularly those with better defined petroleum systems, is recommended.

Further investigation in the isotopomers distribution of LMW aromatic hydrocarbons will significantly improve our understanding of petroleum systems in Western Australia and other petroleum basins worldwide. The new tool developed in collaboration with The California Institute of Technology will also have a significant impact in other research areas such as synthesis chemistry, forensic and environmental sciences. Determining the fragmentation pattern of several light aromatic compounds (*e.g.* trimethylbenzenes) using isotopic-labelled standards will help to facilitate new methods for SSIA of these compound clasess. Besides, carrying on experimental simulations of hydrocarbon to mineral interactions is also recommended to improve our understanding of the isotopic fractionation effects during thermal cracking and migration of the fluids.

Finally, the incorporation of the data into basin modelling will also improve our understanding of petroleum systems from the region. On this respect, collaboration with industry partners will play a key role in designing computational tools to incorporate these new geochemical data into the corresponding basin models. These novel geochemical sugnatures might reveal new insights in migration pathways and therefore current distribution of hydrocarbon resources within the basin, which have not been detected by traditional geological, geophysical and geochemical modelling approaches.

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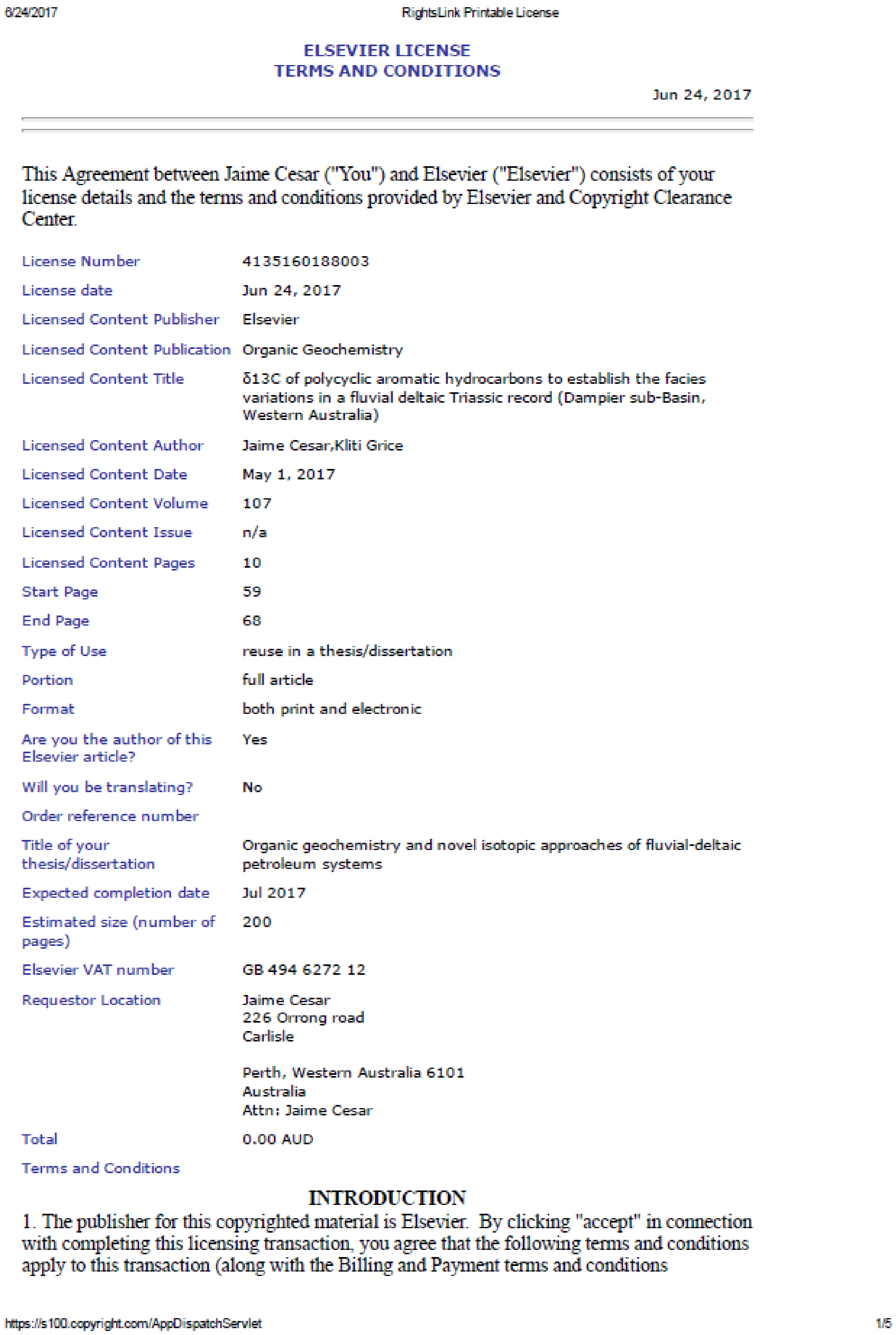

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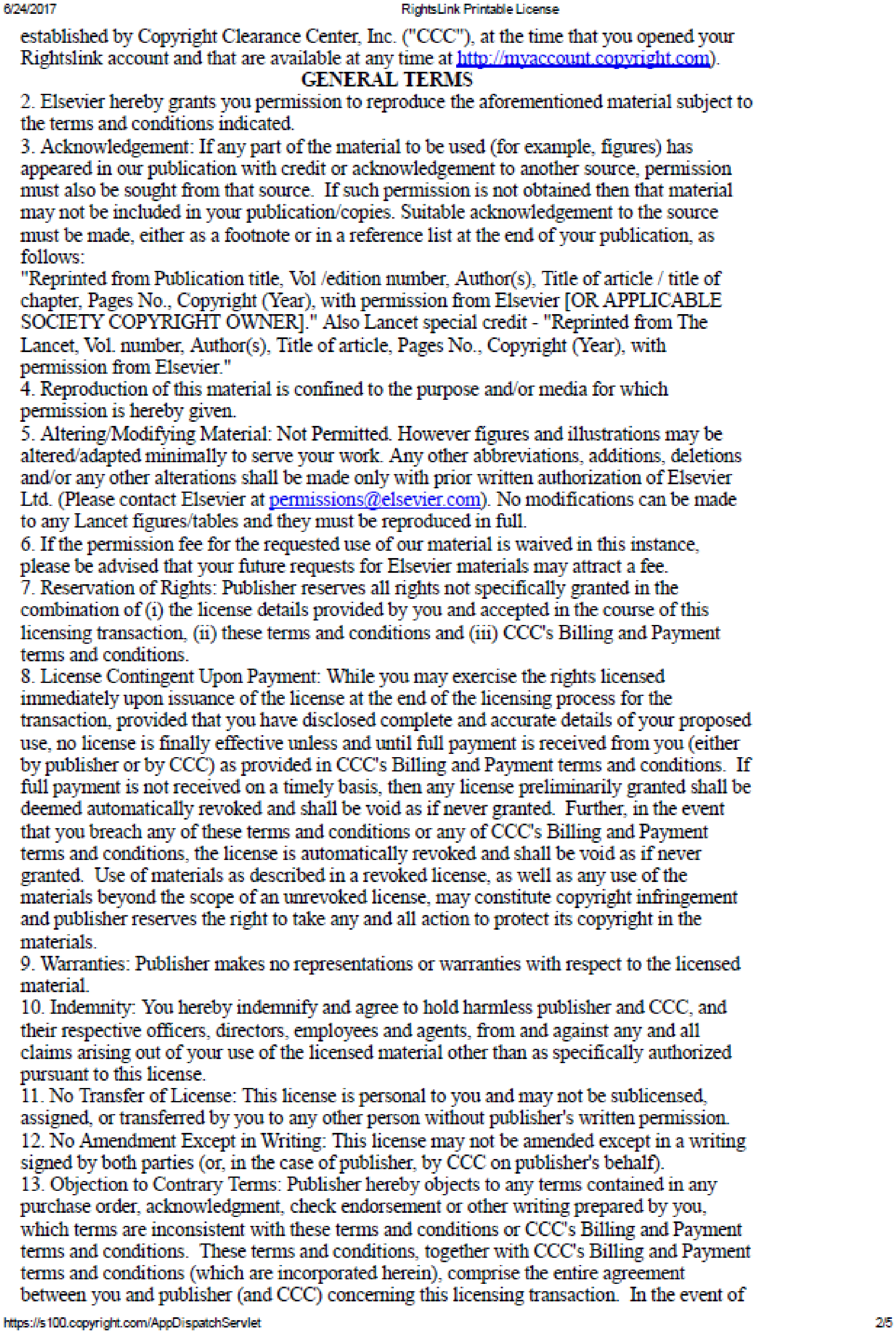

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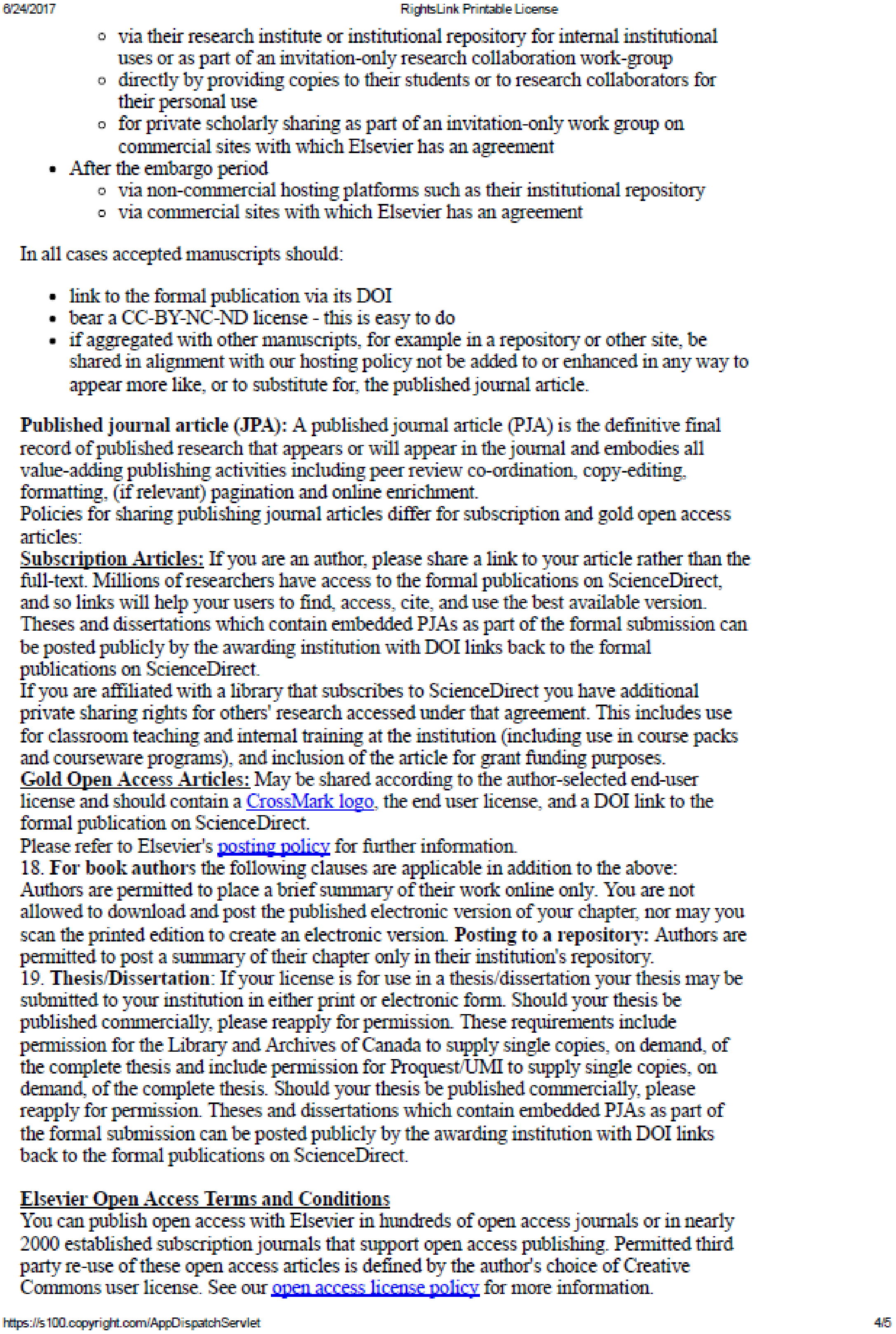

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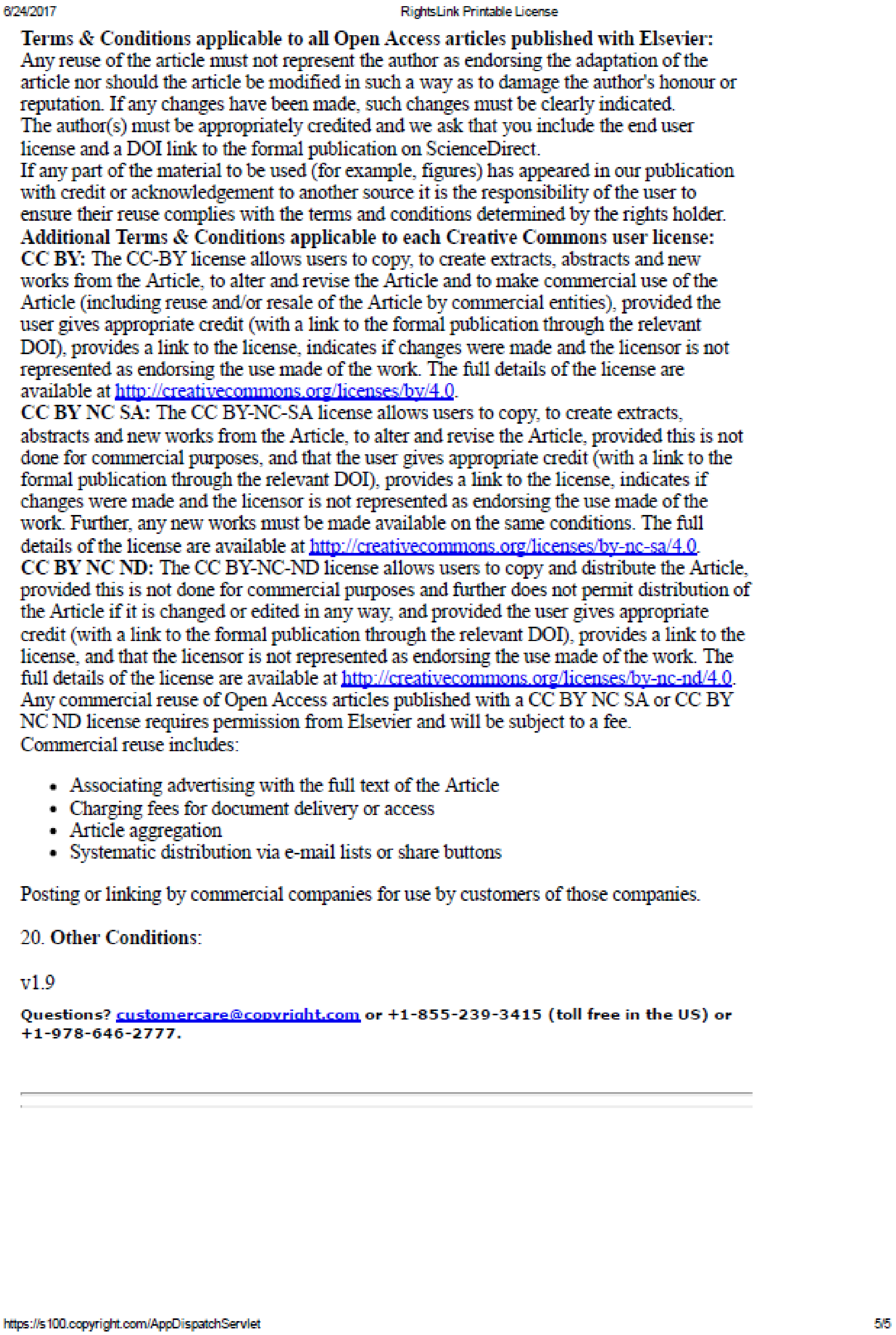

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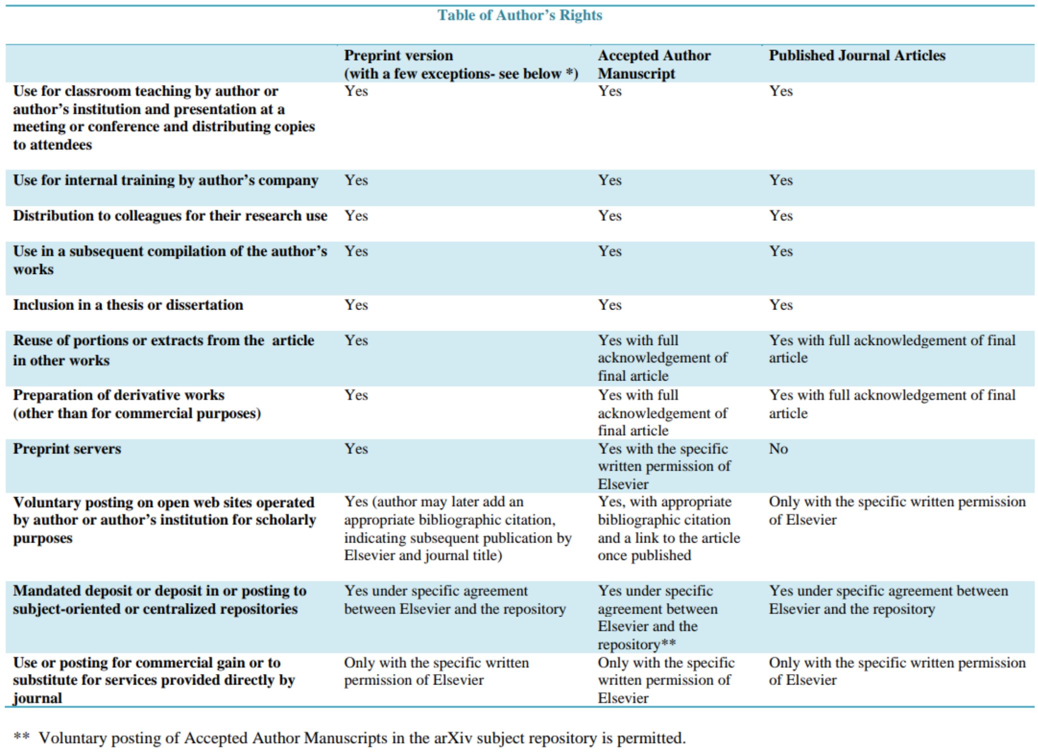

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