Department of Chemistry

Evaluating the source, age, thermal history and palaeoenvironments of deposition of Australian and Western Canadian petroleum systems: Compound specific stable isotopes coupled with inorganic trace elements

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Dedicated to Doruk&Chris

Declaration

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

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

Ercin MASLEN

Perth, May 21th 2010

Abstract

Petroleum geochemistry is an important scientific discipline used in the exploration and production of hydrocarbons. Petroleum geochemistry involves the applications of organic geochemistry to the study of origin, formation, migration, accumulation and alteration of hydrocarbons.

Key concepts and applications of petroleum geochemistry include understanding the petroleum systems, biomarkers and stable isotopes for oil-oil and oil-source rock correlations and controls on secondary processes (e.g. biodegradation, water-washing and migration-contamination) altering the composition and usually the quality of petroleum.

In this research, important concepts and novel techniques of petroleum geochemistry have been utilized for characterizing the source rocks, evaluating the thermal history of the source rocks, understanding the age (where possible), establishing the depositional environment and lithology of the source. More specifically, various innovative organic (biomarker and stable isotopes) and inorganic (trace elements) geochemical approaches were undertaken to establish source, age, thermal history and sedimentary depositional environments of petroleum systems in Western Australia and Western Canada petroleum basins.

The aim of the study presented in Chapter 2 was to understand the enigmatic occurrence of crocetane (an irregular C_{20} isoprenoid), that is usually found in sediments associated with gas hydrate settings and used as a molecular indicator for the anaerobic oxidation of methane (AOM), in Devonian sediments and crude oils containing molecular indicators of photic zone euxinia (PZE). This study comprised a detailed molecular and isotopic study of crocetane and Green Sulfur Bacteria (GSB)-derived carotenoids in Devonian sediments of the Western Canada Sedimentary Basin (WCSB) covering a range of thermal maturities. In addition, a series of oils generated from Devonian source rocks of the basin were analysed for crocetane. Crocetane was found in ten sediments from the WCSB and in seven Devonian WCSB crude oils. Its abundance was found to increase with thermal maturity, whereas the components generated from C_{40} derived

carotenoids of GSB decreased steadily. The preferred proposed natural product precursor for crocetane is thus GSB-derived carotenoids. This was corroborated by their similar structural features and the $\delta^{13}C$ value of combined crocetane and phytane in these samples. Based on the work presented in Chapter 2, it was concluded that crocetane can provide evidence for PZE conditions in highly mature sediments and crude oils of Devonian age.

Application of δD values of individual hydrocarbons (isoprenoids and *n*-alkanes) has a great potential to estimate the thermal maturity of sedimentary organic matter. In Chapter 3, to elucidate the effect of thermal history on the δD values of petroleum hydrocarbons, (i) a comprehensive literature review, focussing on variations in δD values of sediment extracts, crude oils (including bulk organic matter and hydrocarbon fractions as well as individual *n*-alkanes and isoprenoids) and kerogen was carried out and (ii) the application of δD values of hydrocarbons as a maturity parameter with new data from Devonian source-rocks in the WCSB was tested.

Previous work has been used to demonstrate systematic variation in D/H of individual compounds in sediments as a function of thermal maturity and our research in Chapter 3 extended the application of D/H of biomarkers to Devonian samples from the Duvernay Formation of the Western Canada Sedimentary Basin (WCSB) which is much older deposits (i.e. Devonian) than previously studied.

Based on the work presented in Chapter 3, the *n*-alkanes, pristane and phytane from relatively immature sediments have δD values that retain the isotopic signature of their natural product precursors, i.e. biosynthesised lipid components made up of acetyl and isoprene sub-units, respectively. With increasing maturity, pristane and phytane become more enriched in deuterium (D), while the *n*-alkanes generally remain at a constant isotopic composition until an overmature level is reached, at which point there occurs a significant enrichment of D in *n*-alkanes. The enrichment of D in pristane and phytane with increasing maturity correlated strongly with changes in traditional maturity parameters including vitrinite reflectance, T_{max}, and molecular parameters, providing evidence that D-enrichment is associated with thermal maturation.

The maturity indicator based on compound-specific δD values has proved useful in cases where traditional biomarker maturity parameters are ineffective, for example at high maturity levels (i.e. % R_o >1.0) or where their associated reactants and products either equilibrate, or are thermally degraded. In addition, such a maturity measurement is applicable to Devonian sediments, where vitrinite reflectance measurements cannot be made because the higher-plant precursors of vitrinite have not yet evolved.

In Chapter 4, an integrated study including organic (stable carbon isotopes of individual hydrocarbons) and inorganic (trace elements) geochemical data, along with statistical analysis (linear discriminant analysis) was carried out for the first time to assess the source and age characteristics of crude oils from Western Australian and Western Canada petroleum basins.

A novel rapid, reliable and accurate method of determination of major and trace element contents of crude oils was developed based on Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). This method has been applied for the first time to a series of petroleum samples for analysis of Fe, Mg, Al, Zn, Cu, Cr, Ni, Co, V, Tm, Mn, Ge, Dy, Si, Pb, B, Sn, Ti, Hg, As, Mo and Se at trace levels, with little or no sample pre-treatment. $\delta^{13}C$ values of individual hydrocarbons were carried out in a systematic manner to compliment the trace element data.

The scatter plot of two discriminant functions from the analysis of trace elements (V, Pb, B, Mg, Sn, Ti, Mo and Hg) in crude oils samples confirms the capability for separating samples into their petroleum basins. 91.3% correct classification of the samples analysed was achieved. Analysis using two discriminant functions of combined trace elements (Al, Cr, Ti, Fe, Cu, Si, Tm, Mn, Ge, and Dy) and $\delta^{13}C$ of Naphthalene (N), Biphenyl (Bp) resulted in 100% of samples being correctly classified according to their source rock age.

In summary, based on the work presented in Chapter 4, the application of linear discriminant analysis and the stable carbon isotope values and trace element concentrations has allowed the classification of crude oils to their geographical (or basinal) sources and age. The use of complimentary inorganic trace element and organic stable isotope techniques for crude oil samples has been demonstrated as a new highly discriminant tool for petroleum exploration.

The research presented in Chapter 5 is aimed at establishing the factors controlling the stable carbon isotopic compositions of individual aromatic hydrocarbons analysed by compound specific isotope analysis (CSIA) in crude oils from Western Australian petroleum basins of varying age and facies type but of similar thermal maturity. An evaluation of the data on $\delta^{13}C$ of individual aromatic hydrocarbons, like alkylbenzenes, alkylnaphthalenes, alkylphenanthrenes and methylated biphenyls has been carried out to confirm the source and age of these oils and to understand why the Sofer plot is ineffective in establishing source of Western Australian petroleum systems. Previous isotopic work on the oils was mainly based on their bulk $\delta^{13}C$ values of saturate and aromatic hydrocarbons. Western Australian oils seemed to follow an erroneous trend regarding their depositional environments (marine vs terrigenous) when they were assessed using only bulk isotopic values.

The interpretation of the data presented in Chapter 5 showed that the oils where the $\delta^{13}C$ of 1,6-DMN (dimethylnaphthalene) and 1,2,5-TMN (trimethylnaphthalene) isomers is most negative are probably derived from a marine source, whereas oils containing 1,6-DMN and 1,2,5-TMN with a less negative value are representative of a terrigenous source. The $\delta^{13}C$ values falling in between probably have mixed source(s). Less negative $\delta^{13}C$ values of 1-MP and 1,9-DMP isomers probably reflects the varying inputs of terrigenous organic matter to the source-rocks of the oils. In addition, plots of P (phenanthrene) /DBT (dibenzothiophene) and Pr (pristane)/Ph (phytane) versus $\delta^{13}C$ of DMP (dimethylphenanthrene), 1,6-DMN, 1,2,5-TMN, 1-MP (methylphenanthrene) and 1,9-MP are constructed to establish the end-members of terrigenous and marine sourced oils. The ratio of P/DBT and/or the ratio of Pr/Ph and $\delta^{13}C$ of aromatic isomers (such as 1,6DMN, 1,2,5-TMN, 1-MP and 1,9-MP) when coupled together, provide a novel and convenient way of establishing crude oil source rock origin and sometimes even lithologies.

In summary, oils from terrigenous depositional environments based on their bulk $\delta^{13}C$ values were classified as marine based on their $\delta^{13}C$ values of individual aromatic compounds. The compound specific isotope data of the aromatic hydrocarbons obtained for the oils may provide opposite conclusions regarding the source of the oils compared to bulk data using the Sofer plot. Thus,

great care must be taken when interpreting isotope values of hydrocarbons, particularly those that are only based on bulk parameters.

Ultimately, this project has demonstrated that analyses of molecular fossils (biomarkers) and their stable isotopic compositions ($\delta^{13}C$ and δD) complemented with trace element data provides an excellent novel tool for better understanding the basic concepts in petroleum basins and for solving a wide range of problems during petroleum exploration.

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Primary Publications

This thesis is assembled by publications, either published, in press or in review, which form the individual chapters and these are listed below.

CHAPTER 2

Maslen, E., Grice, K., Gale, J. D., Hallmann, C., Horsfield, B. Crocetane: A potential marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age, *Organic Geochemistry, 40, 1-11* (2009). Excellence Research Australia (ERA) A rated publication.

CHAPTER 3

Maslen, E., Grice, K., Dawson, D., Wang, S., Horsfield, B. Stable hydrogen isotopes of isoprenoids and *n*-alkanes as a proxy for estimating the thermal history of sediments through geological time, *Society for Sedimentary Geology Special Publication*, in press (2009). Excellence Research Australia (ERA) A* rated publication.

CHAPTER 4

Maslen, E., Grice, K., Pilgrim, T., Watling, J., Edwards, D. An integrated inorganic and organic isotopic geochemical study to evaluate the origin/age of Western Australian (WA) crude oils, *Science*, in preparation (2011). Excellence Research Australia (ERA) A* rated publication.

CHAPTER 5

Maslen, E., Grice, K., Le Métayer, P., Dawson D., Edwards, D. Stable carbon isotopic compositions of individual aromatic hydrocarbons as source and age indicators in oils from Western Australian basins, *Organic Geochemistry*, in press (2011). Excellence Research Australia (ERA) A rated publication.

Contribution of Others

The work presented in this thesis was primarily designed, experimentally executed, interpreted, and written by the first author of the individual manuscripts. Contributions by co-authors are described below.

CHAPTER 2

Ercin Maslen and Kliti Grice designed the organic geochemical experiments. Ercin Maslen performed experiments, interpreted results, and wrote the majority of the paper. All co-authors contributed to the writing of the paper. Julian Gale carried out computational chemistry after discussions with Ercin. Christian Hallmann assisted in identification of alkylated benzenes. Brian Horsfield provided samples.

CHAPTER 3

Ercin Maslen and Kliti Grice designed the organic geochemical experiments. Ercin Maslen performed experiments, interpreted results and wrote the paper. All co-authors contributed to the writing of the paper. Kliti Grice and Daniel Dawson provided intellectual input through discussions on the interpretation of the results. Brian Horsfield provided samples.

CHAPTER 4

Ercin Maslen, Kliti Grice, Tamara Pilgrim and John Watling designed organic and inorganic geochemical experiments. Ercin Maslen performed experiments, interpreted results and wrote the paper. All co-authors contributed to the writing of the paper. Tamara Pilgrim helped with inorganic geochemical experiments. Kliti Grice, Tamara Pilgrim, John Watling and Dianne Edwards provided intellectual input through discussions on the interpretation of the results. Dianne Edwards provided samples. Inorganic geochemical analyses were carried out at the University of Western Australia.

CHAPTER 5

Ercin Maslen and Kliti Grice designed the organic geochemical experiments. Ercin Maslen performed experiments, interpreted results and wrote the paper. All co-authors contributed to the writing of the paper. Kliti Grice, Pierre Le Metayer, Daniel Dawson and Dianne Edwards provided intellectual input through discussions on the interpretation of the results. Dianne Edwards provided samples.

Secondary Publications

Manuscripts and abstracts based on research that was conducted during the preparation of this thesis.

Peer-reviewed journal articles not part of thesis research

K. Grice, B. Nabbefeld, **E. Maslen** (2007): Source and significance of selected polycyclic aromatic hydrocarbons in sediments (Hovea#3, Perth Basin, Western Australia) spanning the Permian-Triassic boundary: *Organic Geochemistry* 38, 1795-1803. ERA A rated publication.

K. Grice, H. Lu, P. Atahan, M. Asif, C. Hallmann, P. Greenwood, **E. Maslen**, S. Tulipani, K. Williford, and J. Dodson (2009): New insights into the origin of perylene in geological samples, *Geochimica et Cosmochimica Acta* 73, 6531-6543. ERA A* rated publication.

P. Le Metayer, **E. Maslen**, K. Grice, D. Dawson, L. Fusetti, and B. van Aarssen (2010): Determining the origin and formation of low molecular weight aromatic hydrocarbons in petroleum using their stable carbon isotopic composition, *Geochimica et Cosmochimica Acta,* submitted. ERA A* rated publication.

Abstracts

***** Directly related to PhD.

***Maslen, E.**, Grice, K., Pilgrim, T., Watling, J., and Edwards, D. An integrated inorganic and organic geochemical study to evaluate the origin/age of crude oils in Australian petroleum systems. Poster Presentation, 10th Australasian Environmental Isotope and 3rd Australasian Hydrogeology Research Conference, December 2009, Perth, Australia. Best Student Poster Award.

*Maslen, E., Grice, K., Pilgrim, T., Watling, J., and Edwards, D. An integrated inorganic and organic geochemical study to evaluate the origin/age of crude oils in Australian petroleum systems using a novel LA-ICP-MS method and compound specific isotopic approach. Poster Presentation, 24rd International Meeting on Organic Geochemistry, September 2009, Bremen, Germany.

*Maslen, E., Grice, K., Pilgrim, T., Watling, J., and Edwards, D. An integrated inorganic and organic isotopic geochemical study to evaluate the origin/age of WA crude oils. Invited Oral Presentation, 18th Goldschmidt Conference, June 2009, Davos, Switzerland.

*Maslen, E., Grice, K., and Horsfield, B. Significance of Crocetane in Devonian source-rocks and crude oils from the Duvernay Formation and Bakken Shale. Poster Presentation, AOG Conference, September 2008, Adelaide, Australia.

*Maslen, E., Grice, K., Gale, J. D., Horsfield, B. The significance and origin of the biomarker crocetane in Devonian source rocks and crude oils (Western Canada Sedimentary Basin and Canning Basin, WA). Oral Presentation, AESC Conference, July 2008, Perth, Australia.

*Maslen, E., Grice, K., Gale, J, and Horsfield, B. Crocetane: A marker for photic-zone euxinia in Devonian source rocks (Duvernay formation, Western Canada Sedimentary Basin) and crude oils. Oral Presentation, EGU Conference, April 2008, Vienna, Austria.

*Maslen, E., Grice, K., Dawson, D., Horsfield, B. The Origin and Significance of Crocetane in Devonian Source Rocks and Crude Oils from the Western Canada Sedimentary Basin. Poster Presentation, 23rd International Meeting on Organic Geochemistry, September 2007, Torquay, England.

Le Métayer, P., **Maslen, E.**, Grice, K., Dawson, D., Fusetti, L., and van Aarssen, B. Stable carbon and hydrogen isotopic relationships of individual saturated and aromatic hydrocarbons in source rocks and petroleum, Poster

Presentation, 24rd International Meeting on Organic Geochemistry, 2009, Bremen, Germany.

Tulipani, S., Grice, K., Greenwood, P., Asif, M., Williford, K., **Maslen, E.**, Busetti, F. The significance of perylenequinones and their diagenetic alteration products in Devonian reefs (Canning Basin, WA), Poster Presentation, 24rd International Meeting on Organic Geochemistry, 2009, Bremen, Germany.

Kashiyama, Y., Chikaraishi, Y., Nomoto, S., Ogawa, N., Grosjean, E., Summons, R., **Maslen, E.**, Grice K., Godfrey, L., Falkowski, P., Kitazato H., Ohkouchi, N., Nitrogen isotopic analysis of maleimides obtained by chromic acid oxidation of kerogens. Poster Presentation, 24rd International Meeting on Organic Geochemistry, 2009, Bremen, Germany.

Horsfield, B., Muscio, G.P., Grice, K., di Primio, R., Kuhn, P. and **Maslen, E.** Gas Generation and Retention in the Bakken Shale, Williston Basin, Oral Presentation, AAPG Annual Convention, 2008, San Antonio, TX, USA.

Dawson, D., **Maslen, E.**, Grice, K., Alexander, R., Edwards, D. Oil-Source Correlation in the Vulcan Sub-basin (Timor Sea, Northern Australia): A Combined Molecular, δ13C and δD Approach. Poster Presentation, 23rd International Meeting on Organic Geochemistry, 2007, Torquay, England.

Grice, K., Nabbefeld, B., **Maslen, E.**, Summons, R. E., Hays, L., Twitchett, R. J., Turgeon, S., Algeo, T., Boetccher, M. E. Significance of Biomarkers for P/T and F/F Mass Extinctions. Oral Presentation-keynote, 17th Goldschmidt Conference, 2007, Cologne, Germany.

Grice, K., Hallmann, C., Atahan, P., **Maslen, E.**, Fenton, S., Nabbefeld, B., Summons, R., Hays, L., Twitchett, R., Lu, H., James, E., Greenwood, P., Dodson, J. and Böttcher, M.. Distributions of biomarkers and their stable carbon and hydrogen isotopes associated with mass extinction events and the evolution of vascular plants. The Royal Australian Chemical Institute INC Newsletter, 2007.

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Chapter 1

Introduction

Petroleum Geochemistry

Petroleum geochemistry has played an important role in the exploration and production of hydrocarbons. It is a discipline that includes the applications of organic geochemistry to the study of origin, formation, migration, accumulation and alteration of hydrocarbons. The processes leading to the deposition of sedimentary organic matter (OM) that can eventually yield hydrocarbons of commercial importance are one of the main areas of interest (Tissot and Welte, 1978; Hunt, 1996). Several geologic elements are necessary for hydrocarbons to accumulate in sufficient quantities to create a pool large enough to be worth producing. These elements include an organic-rich source rock to generate the hydrocarbons, a porous reservoir rock to store petroleum, and an impermeable trap to prevent the hydrocarbons from escaping (Figure 1.1) (Magoon and Dow, 1994).

More specifically, petroleum geochemistry is a tool that can improve exploration efficiency by identifying the processes that lead to the availability of petroleum in reservoirs. It is concerned with the processes involving OM leading to the formation and accumulation of petroleum. These processes include the

input, accumulation and preservation of OM in depositional environments, its burial history in the sediment, and eventually its alteration under thermal stress (maturation) in the subsurface which can lead to the formation of hydrocarbons.

Key concepts and applications of petroleum geochemistry include (1) petroleum systems (2) biomarkers and stable isotopes for oil-oil and oil-source rock correlations (3) three-dimensional basin modeling and (4) controls of secondary processes (e.g. biodegradation, water-washing and migration-contamination) that alter the composition and usually the quality of petroleum (Peters and Fowler, 2002).

The following sections describe the basic concepts of petroleum geochemistry.

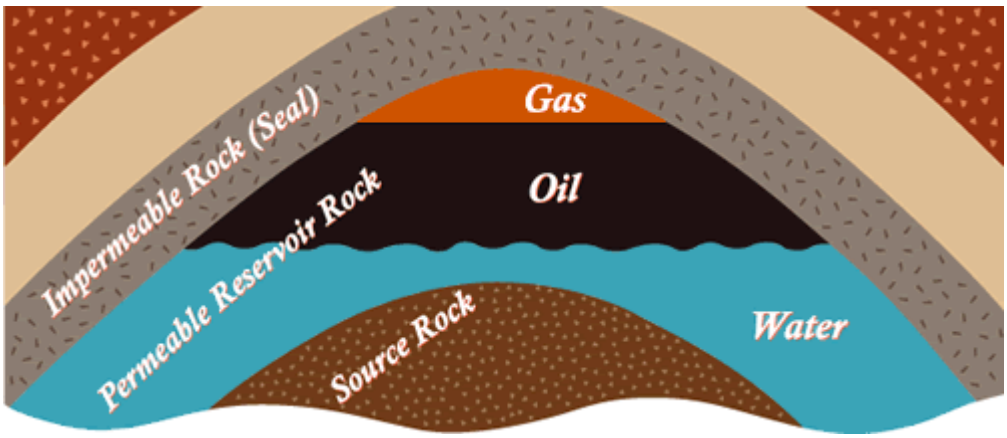

Figure 1.1 Essential elements for hydrocarbon accumulation (modified after source PhysicalGeography.net).

The carbon cycle

Carbon is the chemical basis for the evolution of life on Earth and one of the most abundant elements that exists. It is the major chemical constituent of OM ranging from simple hydrocarbons to highly complex molecules (such as DNA and RNA). The carbon cycle is the biogeochemical cycle by which carbon exchanges between the biosphere, geosphere, hydrosphere and atmosphere.

Figure 1.2 depicts a simplified version of the global carbon cycle and summarises the major reservoirs and sinks of the cycle (Killops and Killops, 2005; Retallack et al., 2007).

Carbon accumulates in the following major reservoirs (i) Biochemicals of living and dead organisms in the biosphere (ii) Carbon dioxide (CO_2) in the atmosphere (iii) OM in soils and water (iv) OM in the subsurface including debris, sediments, petroleum (oil and gas), humic substances in soils and sedimentary inorganic rock deposits and (v) Dissolved atmospheric CO_2 in oceans and lakes (vi) Calcified deposits made by certain marine organisms (Tissot and Welte, 1984).

Ecosystems gain most of their CO_2 from the atmosphere. Many organisms are photosynthetic and use CO_2 as their primary carbon source. With the addition of water and light energy, these organisms carry out photosynthesis to chemically convert the CO_2 to basic biochemical units. These units can then be chemically modified through the metabolic addition of other elements to produce more complex compounds like proteins, cellulose and amino acids (Durand, 1980; Grard et al., 2005). Some of the OM produced by photosynthetic organisms is passed down to other organisms *via* the food web. CO_2 enters the oceans by simple diffusion. Once dissolved in seawater, the CO_2 can also be precipitated into carbonate and/or bicarbonate. Some marine organisms biologically fix bicarbonate to produce calcium carbonate as shells and other body parts of corals, clams, oysters, some protozoa, and certain algae. When these organisms die, their shells and body parts sink to the ocean floor where they accumulate as carbonate-rich deposits. After long periods of time, these deposits are physically and chemically altered forming sedimentary rocks. Oceans are by far the biggest sink of carbon on Earth. Carbon is released from ecosystems as CO_2 by respiration in both plants and animals (Durand, 1980).

The mass of carbon accumulated in sediments is consequently very substantial and estimated at about 10^{16} tons compared to the estimated 10^{12} tons of carbon that exists in living biomass at the surface of the Earth (Durand, 1980; Waples, 1981).

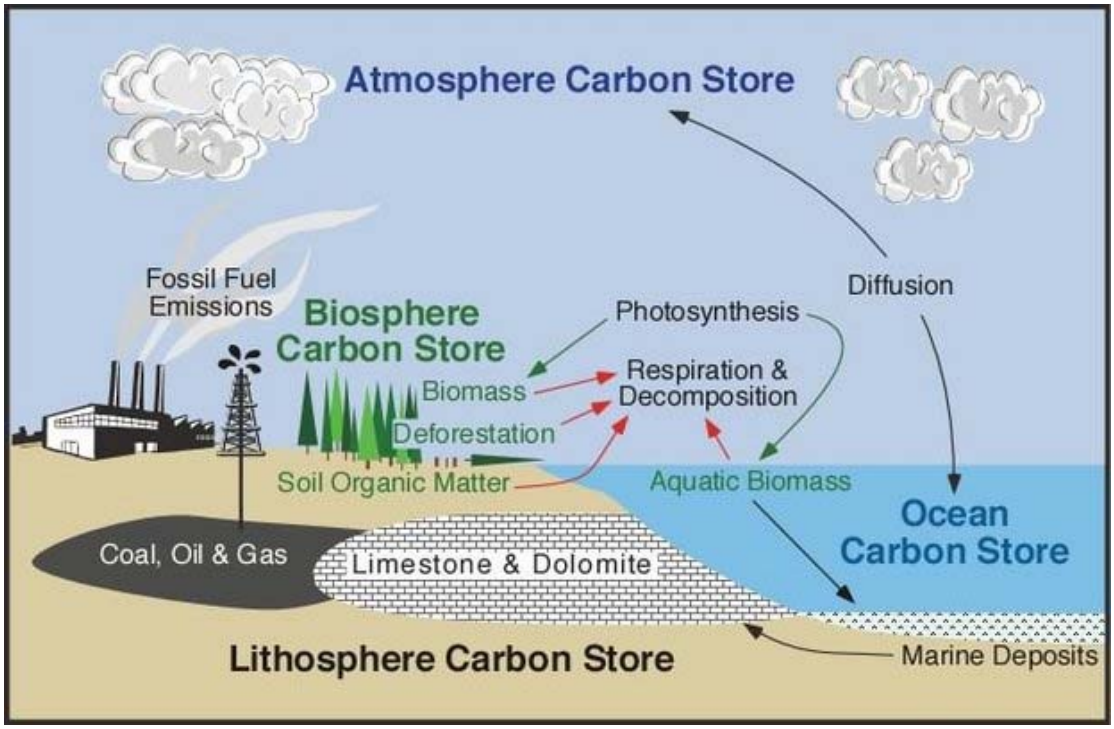

Figure 1.2 Global carbon cycle (modified after PhysicalGeography.net).

Sediments and sedimentary OM

Sediments are defined as unconsolidated grains of minerals, OM or pre-existing rocks that can be transported by water (fluviatile), wind (aeolian) or glaciers. Sediments can be deposited in various environments (e.g. Figure 1.3). Sedimentary rocks result from the deposition (sedimentation) and consolidation (lithification) in the subsurface (Press and Siever, 2001). The mineral composition of sediments is mainly determined by the parent rock lithology, whereas, the sedimentary OM in sediments derives from the remains of the organisms that once lived (i.e. Prokaryotes, Eukaryotes and Archeae).

Fine-grained sedimentary rocks (sediments) containing ≥1% OM and ≥0.5 wt.% total organic carbon (TOC) are potentially good petroleum source-rocks. If buried and heated (thermally matured) sufficiently, source-rocks have the potential to generate petroleum.

The burial and lithification process of sediments is called subsidence. The

accumulation of sediments can lead to the formation of sedimentary basins. During burial, pressure and temperature increase with time. Pressure is controlled by the weight of accumulated sediments which provokes a compaction and reduction of porosity. Temperature is controlled by a temperature gradient within the sediment column, the average of which is 30°C/km and the range is between 10°C/km to 50°C/km depending on the basin and its history (Salle and Debyser, 1976).

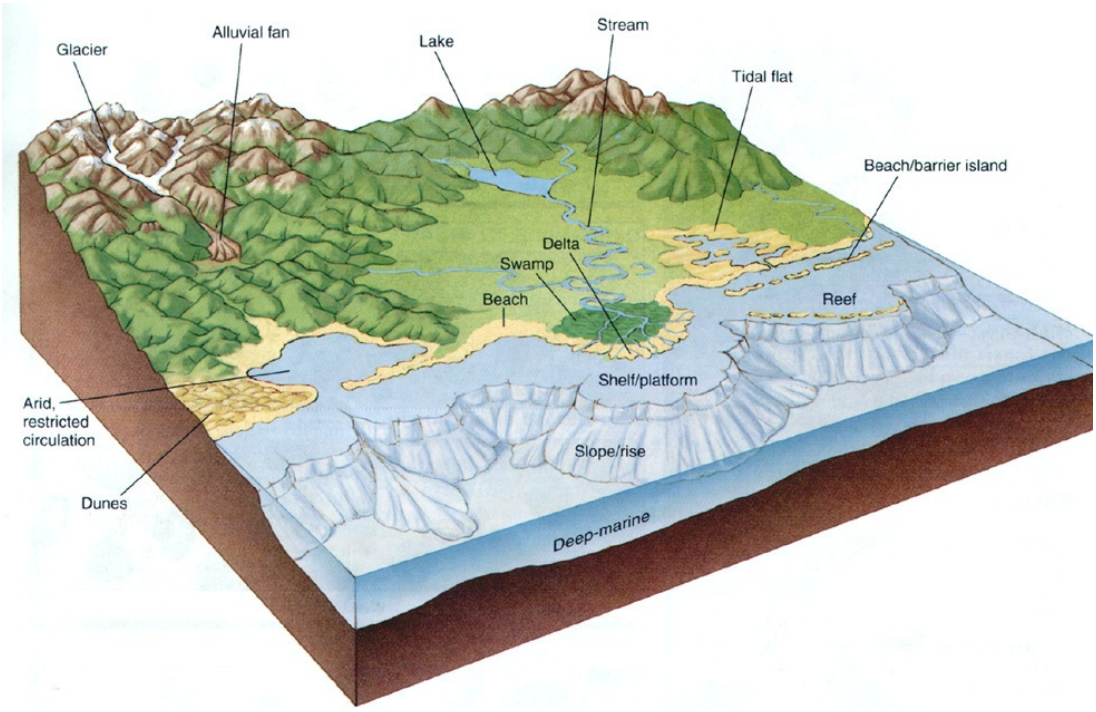

Figure 1.3 Typical sedimentary depositional environments (modified after Laboratory Manual for Physical Geology, Jones, 2001).

Within the surface waters of the marine environment, the main part of the detrital OM (95%) gets recycled by pelagic organisms (Killops and Killops, 2005). Benthic organisms then recycle small amounts of OM that reach the sediment surface. During sedimentation and early burial, several processes result in almost complete destruction of OM. Less than 0.1% of carbon produced as biomass by organisms may be preserved in sediments and thus can become

available for petroleum-related processes (Figure 1.4) (Schwartzkopf, 1990). To obtain OM-rich deposits, the remaining detritic OM needs to be incorporated into the sediments and conserved under specific conditions. OM is thus best preserved under low oxygen conditions (i.e. reducing conditions) (Demaison et al., 1984). In general, only < 0.1% of OM is preserved under oxygenated conditions and > 10% of OM is preserved under reducing conditions (e.g. Durand, 1980; Holser et al., 1988). However, the resident time of carbon present in sediments beneath the subsurface is much longer (several millions to several hundreds of millions of years) than that of carbon that exists in the ocean and atmosphere.

Significant amounts of OM are preserved in stagnant lakes and/or marine basins with restricted circulation (i.e. less oxygen is replenished within the water column). Anoxic basins (less than 0.1 mL/L of dissolved oxygen, Demaison and Moore, 1980) are generally found in enclosed areas with restricted water exchange (Figure 1.3). Anoxic bottom waters exist in enclosed seas, lagoons, and lakes where the access of oxygen to the sedimentation environment is restricted, and coastal zones with upwelling bringing the nutrients to the surface (Waples, 1981). River deltas located in areas of abundant vegetation are also favourable environments for the preservation of OM (Figure 1.3). A physical barrier as well as pronounced density stratification can prevent oxygen from reaching the deeper parts of the ocean (Demaison and Moore, 1980). These stagnant waters can either be thermally or salinity stratified. Thermal stratification occurs due to a temperature difference. Warmer (less dense) surface waters overlay colder (higher density) waters. Salinity stratification occurs due to salinity-dependent density differences, where less saline water (freshwater) overlays more saline water (hypersaline). In addition to the depositional conditions, other conditions are critical such as high primary productivity (algal), controlled by elevated nutrient inputs (i.e. phosphate, nitrate) and oxygen-availability during photosynthesis, allowing for primary producers to bloom (Suess, 1980; Betzer et al., 1984).

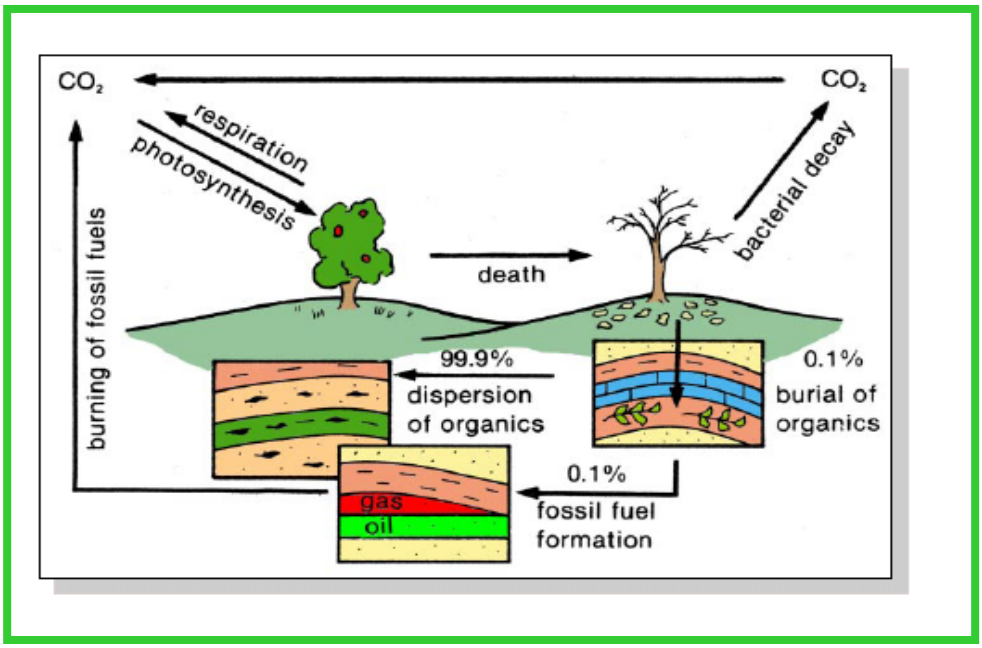

Figure 1.4 Preservation of organic matter in sediments (modified from Tissot and Welte, 1984).

The first stage that describes the alteration of deposited OM is referred to as diagenesis (Tissot and Welte, 1984). During this stage functional groups are generally removed from the natural product precursors (Huc, 1980). It differs from the succeeding stages in that it occurs at a restricted depth (usually less than a kilometre below the water-sediment interface) and at low temperatures (below 60°C). The transformations of the sedimentary OM during diagenesis are related to physico-chemical and biochemical processes rather than thermal processes. Diagenesis occurs up to an equivalent vitrinite reflectance (R_o) of 0.6% (Peters and Moldowan, 1993).

At the end of the diagenesis, all the processes lead to the transformation of sedimentary OM into two general fractions (i) bitumen, a low-molecular weight component which can be extracted from a potential source-rock using common organic solvents (e.g. dichloromethane and methanol, typically as 9:1 ratio) (ii) kerogen, a high-molecular-weight component which is insoluble in these solvents. The degradation and alteration (biological, physical and chemical) of the OM during transport, burial and early maturation can lead to stable, complex

macromolecules (i.e. kerogen, see below for more details) which can be dispersed and preserved in sedimentary horizons. Figure 1.5 is a schematic diagram showing the approximate percentage of the various molecular-weight fractions present in sedimentary OM.

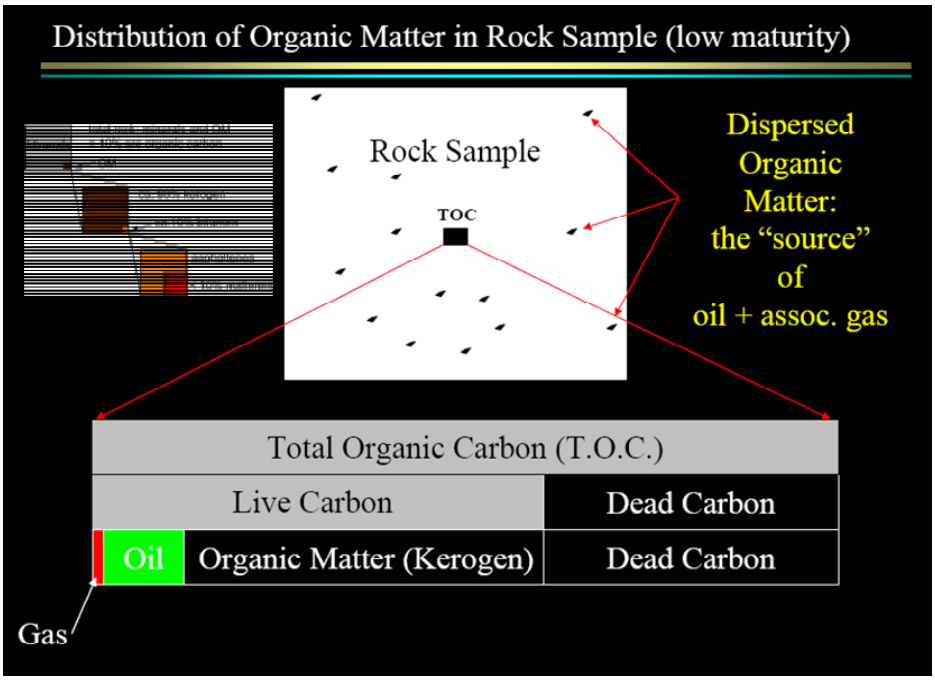

Figure 1.5 Approximate percentages for the composition of OM (modified after Humble Geochemical Services presentation).

Kerogen

Kerogen is the most abundant form of OM on Earth. Kerogen develops within early diagenesis, *via* polycondensation and defunctionalisation processes (Tissot and Welte, 1978) or *via* the selective preservation pathway (see below) (e.g. Tegelaar et al., 1989; Gelin et al., 1996; Zonneveld et al., 2009). The traditional pathway for the formation of kerogen involves biopolymers undergoing biochemical degradation, polymerization and recondensation, resulting in an insoluble product (Tissot and Welte, 1978). During the last few decades, an alternative method of kerogen formation has been postulated, based on observations that certain biopolymers (e.g. algaenans, bacterans) may be highly resistant to microbial degradation, indicating that these components can

be selectively preserved (Tegelaar et al., 1989; Zonneveld et al., 2009) .

Kerogens can be classified into four main types according to the nature of the OM that they contain and the depositional environments of the sediments which led to their formation: I, II (II-S) and III (Durand and Espitalie, 1973; Tissot and Welte, 1984; Killops and Killops, 2005). These kerogen types have different atomic ratios O/C and H/C whose evolution is represented in the van Krevelen (1961) diagram (Figure 1.6).

Type I kerogen is relatively rare and typically formed from algae (e.g. *Botryococcus braunii*) OM deposited in a lake (lacustrine environment) and has the potential to generate high quality oil (Figure 1.6). It contains a significant input from lipids, especially long-chain *n*-alkanes, mainly from bacterially decayed algal material or bacterial remains, forming algal macerals or amorphous structures, respectively. Compared to other kerogen types, Type I contains less aromatic and NSO components. The H/C can be as high as 1.9. It usually forms in fine-grained, organic-rich silts that are deposited under reducing conditions in oxygen restricted and shallow water columns (Tissot and Welte, 1984; Killops and Killops, 2005).

Type II kerogen is usually derived from a mixture of terrigenous and marine OM deposited in a marine environment and normally has the potential to give rise to oil and gas (Figure 1.6). It contains more aromatic and ketone structures than Type I, but also contains aliphatic components and organo sulfur containing compounds (Killops and Killops, 2005). Type II kerogens, containing a high percentage of organo sulfur (8-14%) are classified as Type II-S kerogens. They contain remains from mixed allochthonous phytoplankton, zooplankton, and microbial (bacterial) OM, but also allochthonous OM, from lipid-rich remains of higher plants (spores, pollen, cuticles, resins and waxes) (Killops and Killops, 2005). The H/C ratio reaches up to 1.4.

Type III kerogen is gas-prone and is formed mainly from terrigenous/woody matter typically deposited in a deltaic/paralic marine setting (Figure 1.6). It consists mainly of polyaromatic and ketone compounds and less aliphatic material (Tissot and Welte, 1984; Killops and Killops, 2005). The H/C ratio is 1 or less.

Type IV kerogen consists primarily of black opaque non-specific organic particles, probably derived from higher plant material, that was highly oxidised under terrigenous conditions and was transported prior to deposition. Type IV kerogens do not have any oil generative potential and little potential to generate gas (Durand and Espitalie, 1973; Tissot and Welte, 1984; Killops and Killops, 2005).

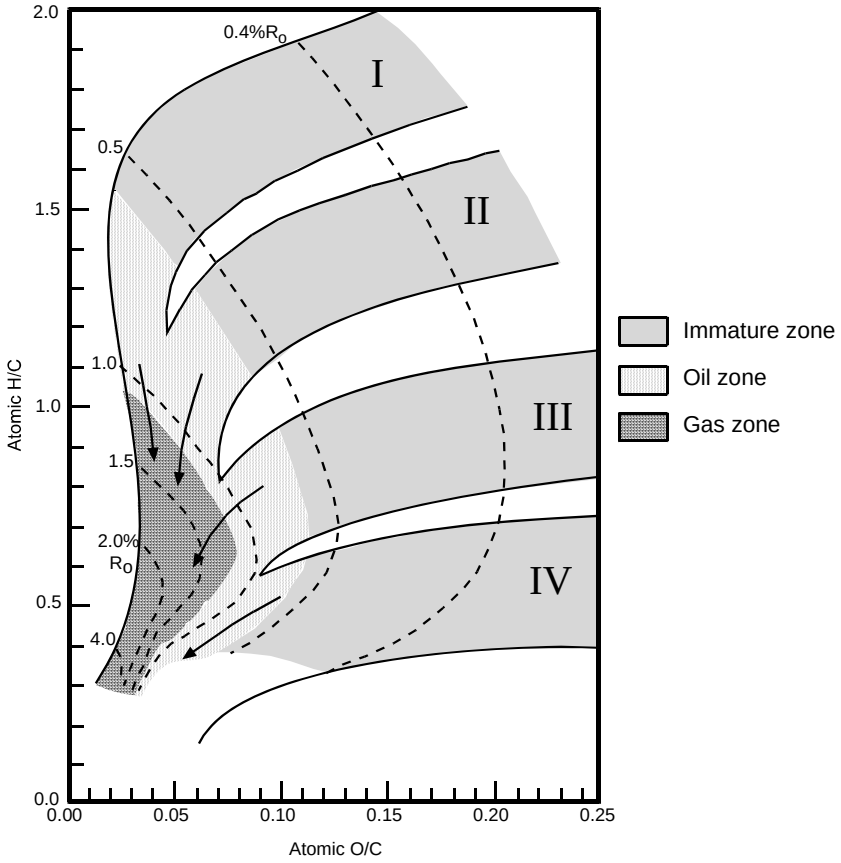

Figure 1.6 Types and chemical evolution of kerogen in response to increased levels of burial and thermal maturity presented on a van Krevelen diagram (arrows indicate increasing maturity) (after Tissot and Welte, 1978).

Bitumen

Bitumen is free OM present within a source-rock which can be similar in composition to crude oil. The term bitumen describes the liquid part of the petroleum and is defined as *in situ* hydrocarbons dispersed within fine-grained sedimentary rocks that can be extracted using organic solvents (Peters et al.,

2005). Bitumen is indigenous to the rock in which it is found unlike crude oil which has migrated away from the source-rock. Bitumen usually consists of three different groups of components, based on their relative polarity: aliphatic, aromatic, and NSO compounds (Tissot and Welte, 1978; Hunt, 1996).

Thermal maturity and generation of petroleum

Maturation is the chemical change in sedimentary OM, induced by burial and the action of temperature and pressure. Thermally driven chemical processes may convert the OM into petroleum. This continuum of processes is termed thermal maturation and is divided into three consecutive stages: diagenesis ($R_o < 0.5\%$), catagenesis ($0.5\% < R_o < 2.0\%$), and metagenesis ($2.0\% < R_o < 4.0\%$) (Figure 1.7) (Peters and Moldowan, 1993).

Kerogen formation is complete by the end of diagenesis. The mode of kerogen formation provides a strong influence on its structure and bulk composition, and thus on its oil- and gas-generating potential, during catagenesis. Catagenesis takes place over a depth range that can reach nearly 4 km below the water-sediment contact (temperatures range between 60°C and 150°C) (Figure 1.7) (Hunt, 1996). Sulfur-rich Type-II kerogen can generate oil at low levels of thermal stress. Low sulfur Type-II kerogen require more thermal energy to generate oil, and Type I and Type III kerogens require even more energy. Highly waxy oils appear to be generated from both wax ester and biopolymeric precursors, the first of which generates at an early stage of catagenesis and the other throughout catagenesis. The base of the oil window (occurring at $R_0 < 1.3\%$) appears to be controlled by the depletion of long chain components in the case of some terrigenous kerogens and by oil stability in the case of marine kerogens (Hunt, 1996). In the latter part of catagenesis, all potential source-rocks contain strongly enhanced proportions of hydrocarbon gases (wet gas) (Figure 1.7). Metagenesis is the second stage of thermal maturation and takes place at temperatures higher than 150°C. Throughout metagenesis, potential source-rock kerogens are strongly depleted in hydrogen and generated gas consists of methane (dry gas) and sometimes hydrogen

sulfide or nitrogen (Figure 1.7) (Hunt, 1996). At the end of metagenesis, solid residues tend to have a structure resembling graphite.

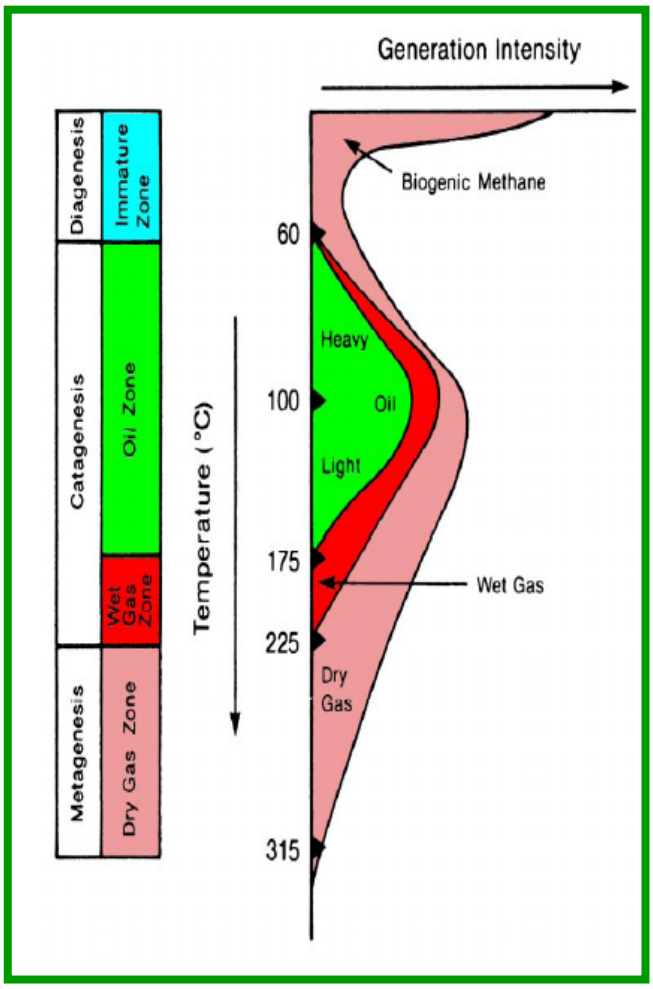

Figure 1.7 Simplified evolution of OM during and after sedimentation (modified after Peters et al. 2005).

Vitrinite reflectance is the most commonly measured thermal maturity parameter. With increasing maturity, coal rank and with changing chemical composition, the vitrinite macerals become increasingly reflective (Killops and Killops, 2005). Consequently, the reflection of a beam of normal incident white light from the surface of polished vitrinite is a function of maturity. This reflectivity is recorded in R_o (%).

Thermal maturity can also be assigned from biomarker distributions relying on the transformation of one precursor compound to a more stable product, depending on thermal conditions. The most commonly applied thermal maturity parameters are based on certain saturated and aromatic biomarkers resulting from either cracking or isomerisation reactions (e.g. Brocks and Summons, 2003 and references therein). Maturity parameters based on biomarkers and other compounds are used in the petroleum industry to estimate the oil and gas-generation potential of sedimentary basins. For example, the ratio of 22*S* / (22*S* + 22*R*) isomers of 17α(H)-homohopanes measures the gradual transformation of the biological 22R configuration to the more stable 22*S* epimer. The 22*S* / (22*S* + 22*R*) ratio reaches a thermodynamic equilibrium at a value of ~0.6, indicating a thermal maturity roughly corresponding to the early phase of oil generation (e.g. Zumberge, 1987).

Petroleum

Petroleum is a complex mixture of hydrocarbons. It includes hydrocarbons (sometimes biomarkers), gases, bitumen, migrated crude oil and pyrobitumen, but not kerogen (Figure 1.8). Crude oil can consist of saturated hydrocarbons, aromatic hydrocarbons, NSO compounds and metal porphyrin complexes containing vanadium, nickel and occasionally iron (Hunt, 1996).

Saturated hydrocarbons can be further divided into aliphatic and cycloaliphatic hydrocarbons. Aliphatic hydrocarbons comprise normal and branched alkanes. Cycloaliphatic hydrocarbons comprise monocyclic (e.g. alkylcyclohexanes) and polycyclic compounds (e.g. hopanes). Molecules classified as aromatic hydrocarbons include strictly aromatic compounds (ranging from benzene to polycyclic aromatic hydrocarbons-PAHs), their methylated and alkylated counterparts, hydroaromatic hydrocarbons, and aromatics containing heteroelements. NSO compounds are polar compounds containing heteroatomic elements (mainly N, S and O) in addition to C and H. They contain molecules such as alcohols, phenols, fatty acids, resins and asphaltenes.

Figure 1.8 Various petroleum samples from different producing petroleum basins (after geology.about.com).

Some petroleum hydrocarbons formed by degradation of the macromolecular structure of kerogen, with minimal alteration of their carbon skeletons, and can be directly related to their biological precursors. These compounds are commonly called "biomarkers". Molecular fossils or biomarkers that record evidence of past life (Eglinton et al., 1964) occur not only in kerogen but also in bitumen. Biomarkers can provide information about ecology and diversity of ancient communities. Many biomarkers analysed in sediments and oils have also been found in present day organisms (Eukaryotes, Prokaryotes and Archeae). Some other petroleum hydrocarbons are formed geosynthetically in the subsurface. Thus they are referred to as geosynthetic products. They comprise many aromatic hydrocarbons, several saturated hydrocarbons and NSO compounds (e.g. carbazoles). They cannot be directly related to natural product precursors of present day organisms. Geosynthetic compounds generally have no structural similarity to any biological precursors. However their distributions can give insights into the types of chemical processes that

occur in the subsurface during petroleum generation (Radke et al., 1982a; Bastow et al., 2000). Biomarkers and aromatic compounds are discussed in more detail in the following sections.

Biomarkers

Biomarkers can be source specific or non-specific. For example, isorenieratane (**I**) and some related compounds are derived from isorenieratene (**II**) that originated from the photosynthetic secondary carotenoid pigments of green/brown photosynthetic sulfur bacteria (e.g. *Chlorobiaceae*) (Summons and Powell, 1986; Summons and Powell, 1987; Kohnen et al., 1992; Grice et al., 1996). Thus isorenieratane (**I**) is a specific biomarker for green sulfur bacteria (GSB), and therefore photic zone euxinia (presence of hydrogen sulphide (H_2S), anoxic, see details below) depositional conditions for sediments (e.g. Grice et al., 2005).

Some other biomarkers can have more than one origin in which case they are of limited diagnostic value. For example, C_{20} regular isoprenoid phytane (**III**), which can derive from a variety of lipids in archaea, bacteria and chlorophyll *a* (**IV**) in algae and/or higher plants, and from bacteriochlorophylls (**V**) *a* and *b* of purple sulphur bacteria (e.g. Peters et al., 2005).

Biomarkers and their stable isotopic compositions have useful applications in petroleum geochemistry. Petroleum geochemists have employed biomarkers to understand the transformation of OM into petroleum, estimate the thermal maturity and geological age of reservoir oil, and correlate crude oil with potential source rocks (e.g. Philippi, 1965; Albrecht and Ourisson, 1969; Tissot and Welte, 1984; Peters and Moldowan, 1993). They have been used to evaluate the source of OM that provides information about palaeoenvironmental proxies (Grice et al., 1998; Grice et al., 2007). Biomarkers also became of increasing interest in our understanding of the remineralisation and burial of OM, crucial aspects of the global carbon cycle (e.g. Hedges et al., 1997; Eglinton and Repeta, 2004), the study of organisms and metabolisms that otherwise rarely leave a macro-fossil record (e.g. Moldowan and Talyzina, 1998; Hinrichs et al., 1999; Summons et al., 1999; Kuypers et al., 2001).

Aromatics in sediments and petroleum

Alkylated aromatic hydrocarbons which do not have a carbon skeleton resembling a natural product precursor, are thought to be formed through two major pathways resulting in a host of alkylated, dealkylated and isomerised components (Radke et al., 1982b; Ioppolo-Armanios et al., 1995; van Aarssen et al., 1999; Bastow et al., 2000) The main diagenetic processes are isomerisation (*via* methyl shift) and trans-alkylation (*via* methyl transfer) reactions (Radke et al., 1982a; Alexander et al., 1985; Strachan et al., 1988; van Aarssen et al., 1999; Bastow et al., 2000).

The abundance of aromatic hydrocarbons in Recent sediments is low. Furthermore, Erdman (1961) has shown the absence of low-molecular-weight (LMW) aromatic hydrocarbons in Recent sediments from various origins. This is in contrast to their importance in ancient sediments and crude oils. Alkylated aromatic hydrocarbons are common constituents of ancient sediments and petroleum. LMW alkylbenzenes are generally the most abundant aromatic hydrocarbons and, alkyl chains often have similar carbon number ranges as *n*-alkanes (Hunt, 1996). Alkylnaphthalenes and alkylphenanthrenes are also usually present but larger PAHs (described in detail below), such as chrysene (**VI**) are less abundant. Alkyl substituents on these PAHs take the form of methyl and ethyl groups, in contrast to the long alkyl chains present in alkylbenzenes. The short-chain alkylbenzenes are liquids, but the longer-chain members and also PAHs are generally solids under normal surface conditions (Hunt, 1996).

Alkylated aromatic compounds have received considerable attention as indicators of thermal maturity. It is now accepted that the thermal maturity level of source rocks and crude oils can often be assessed from the isomer distribution of aromatic compounds (e.g. Radke et al. 1982a; Alexander et al., 1985; Garrigues et al., 1986; van Aarssen et al., 1999). With increasing maturity these reactions lead to enrichment of the thermodynamically more stable isomers. In general, the compounds substituted at the α positions are less stable than isomers substituted at the β-substitution positions. Therefore, the β/α ratios for several groups of LMW aromatic compounds have been used to assess the thermal maturity of petroleum and source rocks (Radke et al., 1982a; Radke et al., 1990:

Radke et al., 1994; Alexander et al., 1995; Budzinski et al., 1995; van Aarssen et al., 1999; Nabbefeld et al., 2010). The methylphenanthrene index for example, is a commonly used parameter for assessing thermal maturity (Radke et al., 1982a).

Aromatic hydrocarbons with ≥ 2 rings are termed PAHs. The origin of PAHs in the (bio)geosphere may be attributed to two different sources in the absence of pollution by fossil fuels: (1) those produced from the (incomplete) combustion of fossil fuels and plant materials (generally dominated by unsubstituted PAHs) and/or (2) those that can be derived from natural biological precursors (transformed during sedimentary diagenesis and catagenesis).

Research over the last three decades has led to improved understanding of the sources of PAHs in environments. PAH distributions have been studied widely in soils (Blumer and Youngblood, 1975; Lichtfouse et al., 1997), in lake deposits (Laflamme and Hites, 1978; Giger and Schaffner, 1978; Gschwend and Hites, 1981; Fernández et al., 1996), in marine sediments (Youngblood and Blumer, 1975; Gschwend and Hites, 1981; Wilcock and Northcott, 1995) and in river estuarine sediments (Giger and Schaffner, 1978; Hites et al., 1980; Brown and Maher, 1992) as well as river particulates (Giger and Schaffner, 1978). In Recent sediments, incomplete combustion of organic materials (i.e. during wild fires) and residential and industrial heating activities are proposed as a major source for PAHs. PAHs found in recent sediments are mainly absorbed onto air transported particulate matter and can then be deposited within minerals (Blumer, 1976; Laflamme and Hites, 1978).

In contrast, less is known about the source and fate of PAHs in ancient samples, except specific higher-plant biomarkers, such as cadalene (**VII**), retene (**VIII**), and simonellite (**IX**) (Wakeham et al., 1980; Alexander et al., 1992; Ellis et al., 1996; Grice et al., 2005). Examples of PAHs from natural precursors are the gymnosperm plant-derived ones. These include cadalene, retene and simonellite (Simoneit et al., 1986; Laflamme and Hites, 1978; Wakeham et al., 1980), and the angiosperm higher-plant-derived aromatised tetracyclic and pentacyclic triterpenoids (Murray et al., 1997). Bicyclic and tricyclic diterpenoid compounds

are the major components of conifer resins, and are the proposed biological precursors of sedimentary biomarkers, retene and simonellite (e.g. Simoneit et al., 1986; Wakeham et al., 1980; Alexander et al., 1988, 1992; Ellis et al., 1996). The biomarker cadalene occurs widely in many different deposits (e.g. Alexander et al., 1994; van Aarssen et al., 1996). Cadinenes in plants, fungi, plant resins, fossil resins and in oils are the proposed precursors for cadalene (Simoneit et al., 1986). Perylene (**X**) has been found in marine sediments, lake and river sediments, oil shales, coals and crude oils. Perylene is believed to be biogenic product derived from its natural precursors via post-depositional transformation during early diagenesis. It has been hypothesised that there is a relationship of perylene to perylene quinone pigments abundant in wood-degrading fungi (Grice and Brocks, 2009 and references therein).

Photic zone euxinia (PZE)

Geological and paleontological evidence support the presence of ocean anoxia in shelf and abyssal environments (deep marine) in Earth's geologic past (e.g. Holland, 1984; Grotzinger and Knoll, 1995). In modern-day environments with stratified water columns, such as the Black Sea, sulfate reducing bacteria use sulfate, if available, as an electron acceptor in their metabolism, producing H_2S. Thus, high sulfide concentrations are produced by bacterially-mediated reduction of sulfate (Trull et al., 2001). As a result, the Black Sea has become sulfide rich (e.g., Arthur and Sageman, 2005). Similar conditions have occurred throughout the geological record. Such conditions are ideal conditions to preserve OM and have given rise to some of the best quality source-rocks. High concentrations of H_2S in the ocean are described as euxinic conditions (Hunt, 1996). In the very rare case, when the H_2S reaches the zone of light penetration (i.e. photic zone) conditions of photic zone euxinia (PZE) develop (Figure 1.9) (Grice et al., 2005).

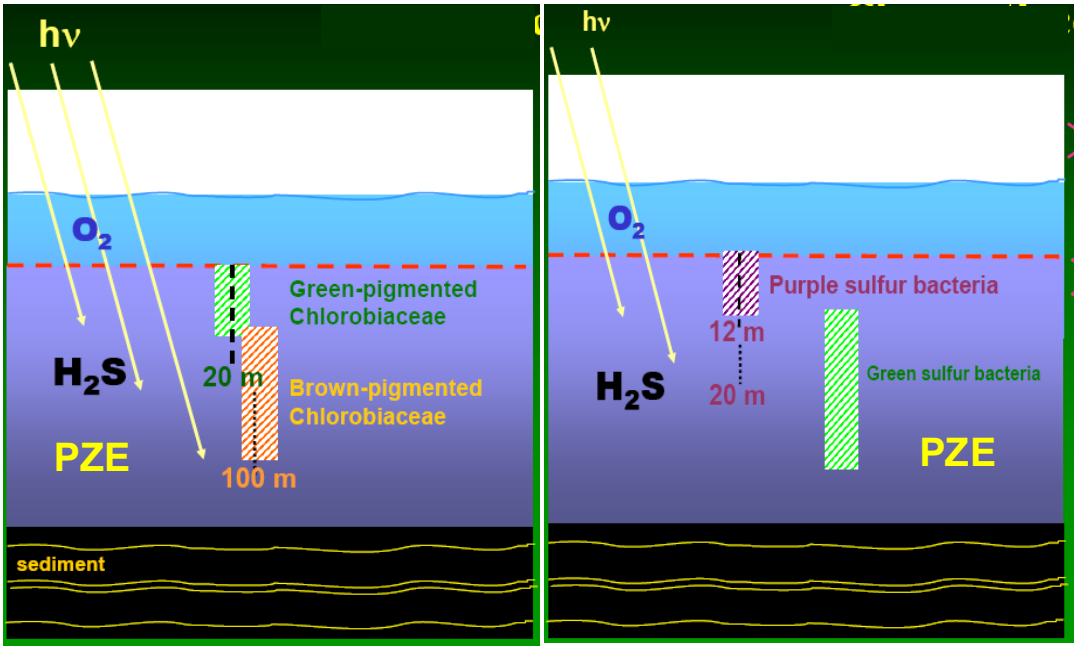

Figure 1.9 Photic zone euxinic (PZE) conditions and pigments associated with organisms that live under these conditions (modified after, Brocks and Pearson, 2005)

Only specialised organisms can survive under these conditions. Important organisms are the purple sulfur bacteria (PSB, these can also tolerate O_2 being obligate anaerobes), the brown sulfur bacteria (BSB) and the green sulfur bacteria (GSB) that live under PZE conditions (Pfennig, 1978). For example, GSB (Chlorobiaceae) are strictly anaerobic autotrophs that primarily use H_2S as an electron donor for photosynthesis (Pfennig, 1978). They can occur where euxinic conditions extend into the photic zone (Figure 1.9). Biomarkers derived from GSB are thus molecular indicators of PZE in depositional environments. Because carbon assimilation in GSB occurs *via* the reversed tricarboxylic acid cycle (TCA), their biomass and lipids are distinguished by ^{13}C enriched values relative to organisms that use the C3 pathway for CO_2 fixation (Quandt et al., 1977; Sirevag et al., 1977).

Biomarkers derived from GSB, include isorenieratane and aryl isoprenoids (**XI**). They have been reported in a petroleum drill core from Western Australia and in the global stratotype section in Meishan, South China spanning the P/Tr event (Grice et al., 2005; Cao et al., 2009). Along with sulfur

isotopes of sedimentary pyrite and high abundances of vanadyl porphyrins (**XII**), these biomarkers indicate the presence of PZE conditions during the largest mass extinction event of the Phanerozoic. It has been proposed that the release of toxic H_2S to the ocean surface and atmosphere played a critical role in the extinction (Kump et al., 2005).

Anaerobic oxidation of methane (AOM)

AOM is a microbial process occurring mainly in anoxic marine sediments. During AOM, methane is oxidized with sulfate as the terminal electron acceptor. According to current knowledge, AOM is mediated by a syntrophic consortium of methanotrophic archaea and sulfate-reducing bacteria (Raghoebarsing et al., 2006). They often form small aggregates or sometimes voluminous mats. In benthic marine areas with strong methane releases from fossil reservoirs (e.g. at cold seeps, mud volcanoes or gas hydrate deposits), AOM can be so high that chemosynthetic organisms like sulfur bacteria (e.g. Beggiatoa) or animals (clams, tube worms) with symbiont sulfide-oxidizing bacteria can thrive on the large amounts of H_2S that are produced during AOM. The production of bicarbonate from AOM can result in the precipitation of calcium carbonate or so-called authigenic carbonates. AOM is considered to be a very important process reducing the emission of the greenhouse gas methane from the ocean into the atmosphere. It is estimated that almost 90% of all the methane that arises from marine sediments is oxidized anaerobically by this process (Clayton, 1991).

Stable Isotopes in Petroleum Geochemistry

Stable isotopes

Stable isotope geochemistry is based on the relative and absolute concentrations of the elements and their stable isotopes on Earth. The stable isotopes of carbon (C) and hydrogen (H) are useful to discover the processes in sedimentary OM since they are usually the most abundant elements. For

example, carbon and hydrogen each have two stable isotopes, ^{12}C and ^{13}C and ^{1}H and ^{2}D, respectively. ^{12}C accounts for 98.899 weight %, whereas ^{13}C only accounts for 1.111 weight % of the total carbon pool (Tissot and Welte, 1978). ^{1}H accounts for 99.985 weight % and ^{2}D accounts for 0.0105 weight % of the total hydrogen pool.

Isotope fractionation is the physical phenomenon which causes changes in the relative abundance of isotopes due to their differences in mass (Urey, 1947). Isotopic fractionation occurs in nature during chemical, biochemical and physical processes depending on the strength of bonds (Hoefs, 1987). "Heavy" isotopes generally form stronger bonds than "light" isotopes. There are two categories of isotope effects: equilibrium and kinetic.

Equilibrium and kinetic isotope effects

An equilibrium isotope effect will cause one isotope to concentrate in one component of a reversible system that is in equilibrium (Hoefs, 1987). If it is the heavier isotope that concentrates in the component of interest, then that component is commonly referred to as enriched or heavy. If it is the light isotope that concentrates then the component is referred to as depleted or light. In most circumstances the heavy isotope concentrates in the component in which the element is bound more strongly and thus equilibrium isotope effects usually reflect relative differences in the bond strengths of the isotopes in the various components of the system.

A kinetic isotope effect occurs when one isotope reacts more rapidly than the other in an irreversible system or a system in which the products are swept away from the reactants before they have an opportunity to come to equilibrium (Hoefs, 1987). Normally, the lighter isotope will react more rapidly than the heavy isotope and thus the product will be lighter than the reactant.

Standards and notation

Stable isotope composition is expressed as a ratio calculated by the δ (delta) notation and is expressed in per mil (‰):

$$\delta_{sample} = [(R_{sample} - R_{standard})/R_{standard}] \times 1000 \text{ ‰} \qquad (\mathbf{1.1})$$

For carbon, R is the measured ratio of ^{13}C to ^{12}C for the sample and standard, respectively, relative to an international marine carbonate standard (i.e. Vienna Pee Dee Belemnite, VPDB)(Hoefs, 1987). For hydrogen, R is the measured ratio of D to H in a sample and standard, respectively, relative to the international Vienna Mean Ocean Water (SMOV) standard (Werner and Brand, 2001).

Stable isotope analysis

Stable isotopic compositions are most effectively determined using mass spectrometric methods (Hoefs, 1987). Two methods of determining stable isotope composition of a sample are commonly used; bulk stable isotope analysis and compound specific isotope analysis (CSIA).

Bulk stable isotope analysis

Bulk stable isotope analysis involves measurement of the stable isotopic composition of the total carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S) in a sample. Thus it is used to determine the isotopic composition of all compounds in the whole mixture and consequently only gives an average value for the entire complex mixture.

Compound specific isotope analysis (CSIA)

In contrast to bulk stable isotope analysis, CSIA involves the measurement of single compounds in a complex mixture (e.g. petroleum, natural gases, sediments, soils, groundwater, potable waters and extracts from plants) leading to more specific results and is conducted using a gas chromatograph - isotope ratio monitoring - mass spectrometer (GC-ir-MS). CSIA developments have included instruments capable of measuring $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$ and D/H (Hayes, 1993; Brand et al., 1994; Prosser and Scrimgeour, 1995).

The GC-ir-MS, whereby the gas chromatograph (GC) is linked to an isotope ratio mass spectrometer via a combustion interface is used for determining $^{13}C/^{12}C$ of individual organic components in complex mixtures of petroleum and

organic extracts from sedimentary material (Matthews and Hayes, 1978). The combustion interface either consists of a quartz tube containing CuO pellets (850°C) or a ceramic tube containing twisted CuO/Pt wires (850°C) (Matthews and Hayes, 1978; Hayes, 1993) yielding a gas analyte of CO_2 and by-product H_2O for each GC-separated component. H_2O is removed either with a Nafion trap or a liquid N_2 trap (-100°C). The isotope ratio mass spectrometer measures the abundances of the ions *m/z* 44 ($^{12}CO_2$), 45 ($^{13}CO_2$) and 46 ($^{12}C^{18}O^{16}O_2$). D/H CSIA requires that a GC is linked to an isotope ratio mass spectrometer via a pyrolysis furnace (e.g. Prosser and Scrimgeour, 1995; Burgøyne and Hayes, 1998). For this application the mass spectrometer measures the abundances of the ions *m/z* 3 (^{2}DH) and 2 ($^{1}H_2$). Contributions from H^{3+} produced in the ion source are corrected following *m/z* 3 analyses at two different pressures of the H_2 reference gas to determine the H^{3+} correction factor (Sessions et al., 1999; Dawson et al., 2004; Grice et al., 2007).

In order to identify the carbon skeletons of biomarkers in natural organic extracts of sediments and petroleum, GC-MS fingerprinting techniques have been used (Peters et al., 2005). It should be noted that GC-MS techniques are not always useful in establishing source. Stable C and H isotope measurements reveal more detailed information about the biosynthesis and sources of individual molecules (e.g. Brocks and Summons, 2003 and references therein). Thus, CSIA methods allow wide applications (e.g. palaeoenvironmental reconstruction) in biogeochemistry and have clearly revolutionised biomarker research (Freeman et al., 1990; Hayes, 1993; Grice et al., 1998; Grice et al., 2001; Brocks and Summons, 2003; Grice and Brocks, 2009). In the following sections, more detailed information will be provided about the applications of stable C and H isotopes in OM and petroleum.

$\delta^{13}C$ in OM and petroleum

The stable isotopic composition of OM is determined by its origin. The elements C and H are the main constituents of OM and play key roles in many biochemical, ecological, environmental, hydrologic and atmospheric processes.

Therefore stable isotopic compositions preserved in OM can provide powerful insights into these mechanisms.

The $\delta^{13}C$ values of petroleum including whole crude oils or bitumens, their fractions, and individual compounds, have been used to determine origin, age and the nature of depositional environment of the source (e.g. Sofer, 1984; Bjoroy et al., 1991; Chung et al., 1992; Andrusevich et al., 1998). In the subsurface, maturation has been reported to affect the stable isotopic composition of petroleum (Clayton, 1991). $\delta^{13}C$ values of kerogen, source-rock extracts and crude oils, and their associated fractions, and individual compounds (e.g. *n*-alkanes) have been found to increase with thermal maturity. The enrichment of ^{13}C in kerogen is thought to be a result of the thermal release of isotopically lighter products (Clayton, 1991). Secondary processes such as biodegradation have been reported to alter $\delta^{13}C$ values. Biodegradation can lead to an enrichment of ^{13}C in residual compounds, with the level of enrichment gradually decreasing with increasing molecular weight (e.g. George et al., 2002; Sun et al., 2005).

Sofer (1984) used the bulk carbon isotope ratios of aromatics against saturate fractions to separate oil families into waxy (terrigenous) and non-waxy (marine) oil types. This technique is still useful for correlation studies, but the source typing is less accurate. Chung et al. (1992) classified 621 post-Ordovician marine oils into four groups in terms of their depositional environment and the age of their source rocks, on the basis of $\delta^{13}C$ distribution, in conjunction with pristane/phytane ratios and sulfur contents. Andrusevich et al. (1998) reported bulk $\delta^{13}C$ values of the saturate and aromatic fractions of 514 oils. They found that both fractions become enriched in ^{13}C values with towards recent timescales.

δD in OM and petroleum

Hydrogen CSIA has shown great potential in petroleum geochemistry because hydrogen of all the elements has the largest mass difference between its two stable isotopes (H and D) and hence the largest natural variations in stable isotope ratios. The capability of measuring the δD values of individual

compounds in complex mixtures (e.g. petroleum) was developed over 10 years ago (e.g. Burgøyne and Hayes, 1998; Hilkert et al., 1999; Dawson et al., 2004; Schimmelmann et al., 2004; Pedentchouk et al., 2006). Therefore the accurate measurement of δD values of hydrocarbons in geological samples, considering the very low abundance of D in nature, is an analytical challenge.

The water in the world's oceans comprises the largest natural reservoir of hydrogen, and is essential in the global hydrological cycle. In marine and terrigenous environments, ocean water, and/or meteoric water produced by operation of the hydrological cycle, is used by inhabiting organisms. Therefore, the distribution of stable hydrogen isotopes in present day environments is mainly controlled by the natural processes in the global hydrological cycle.

To date there has been relatively limited research into the D/H composition of petroleum, particularly using a compound-specific approach. The reports that exist have investigated the relationship between δD values of whole crude oils and bitumens and their source (including organic matter type and depositional conditions), thermal maturity, as well as the effects of secondary processes such as biodegradation, mixing and migration (e.g. Hoering, 1977; Rigby et al., 1981; Li et al., 2001; Dawson et al., 2006; Pedentchouk et al., 2006). Sessions et al. (1999) studied the fractionation of hydrogen isotopes in lipid biosynthesis by different organisms. Anderson et al. (2000) reported δD values of individual *n*-alkanes and isoprenoids as evidence of large and rapid climate variability. Li et al. (2001) assessed the usefulness of hydrogen CSIA in petroleum correlation studies using a number of crude oil samples from the Western Canada Sedimentary Basin. Dawson et al. (2005 and 2006) have demonstrated the usefulness of δD of sedimentary aliphatic hydrocarbons to evaluate the maturity of source rocks and crude oils from the Perth Basin (WA) and Vulcan-sub Basin (Timor Sea). Pristane (Pr) and phytane (Ph) are significantly depleted in D compared to *n*-alkanes, although this difference decreases with increasing maturity due to thermal hydrogen isotopic exchange. The work by Dawson et al. (2005 and 2006) suggests that the δD measurement of sedimentary hydrocarbons represents a useful maturity parameter which also accounts for source-effects. Maslen et al. (2010) showed the application of the

D/H of biomarkers as a maturity proxy for Devonian source-rocks from the Western Canada Sedimentary Basin (WCSB) extending this application to much older sediments than previously studied.

Trace Elements in Petroleum and Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP MS)

The presence of trace elements in crude oils has been recognised for several decades. Trace element concentrations in petroleum samples have been undertaken in many studies (e.g. Lewan and Maynard, 1982; Odermatt and Curiale, 1991; Filby, 1994) and have been used for oil classification (Barwise, 1990; Frankenberger et al., 1994; Akinlua et al., 2008) and oil-oil/oil-source rock correlations (Barwise, 1990; Filby, 1994; Alberdi-Genolet and Tocco, 1999; Akinlua et al., 2007). Trace element abundances have also been used to resolve issues associated with petroleum refining, catalytic poisoning, corrosion and environmental matters (Oluwole et al., 1993; Olajire and Oderinde, 1993).

Trace element contents may predict crude oil origin, maturity, migration pathways and aid to establish source(s) of heavily biodegraded petroleum. Different analytical techniques have been used to determine trace element concentrations of crude oils. For example, Lang et al. (1990) and Hardway et al. (2004) used atomic absorption spectrometry (AAS) and others (Algadi and Al Swaidan, 1990) determined vanadium contents in crude oil by inductively coupled plasma mass spectrometry (ICP-MS). Sequential injection analysis followed by-ICP-MS has also been used to measure lead, nickel, and vanadium contents in crude oil (Al Swaidan, 1996). Vanadium, nickel, lead and mercury contents have also been measured in condensates by ICP-MS (Olsen et al., 1997). A novel rapid, reliable and accurate method of determination of major and trace element contents of olive oil has been developed based on Laser Ablation-ICP-MS (LA-ICP-MS) (Pilgrim et al., 2008).

Scopes of This Thesis

The overall aim of this PhD thesis is to evaluate the source, age, thermal history and palaeoenvironments of deposition of Australian and Western Canadian petroleum systems by using compound specific stable isotopes coupled with inorganic trace elements. Several different sediment and oil samples have been analysed in this study to establish a better understanding of the petroleum systems.

In Chapter 2, the main purpose is to understand the natural product precursor for the biomarker crocetane which has been previously used as a molecular indicator for AOM. Improved understanding of the source of crocetane in Devonian crude oils will help to comprehend the results with respect to significance of the paleoenvironment of the OM deposited and age of the oils. This chapter comprises a detailed molecular and isotopic study of crocetane and GSB-derived carotenoids in Devonian sediments of the Western Canada Sedimentary Basin (WCSB) covering a range of thermal maturities. A series of oils generated from Devonian source rocks of the basin have been analysed for crocetane to establish its general occurrence in Devonian samples. Understanding the source of crocetane will certainly aid oil–source correlation studies of petroleum systems (especially of Devonian age).

Implicit in the interpretation of δD values of OM is an understanding of the effect of sedimentary processes such as thermal maturation on the δD values of individual petroleum hydrocarbons (isoprenoids and *n*-alkanes). The intention of Chapter 3 is to provide an overview on previous work that demonstrates systematic variation in D/H of individual compounds in sediments as a function of thermal maturity and also to extend the application of D/H of biomarkers to Devonian samples from the Duvernay Formation of the WCSB. The purpose is to understand if a maturity indicator based on compound-specific δD values may prove useful in cases where traditional biomarker maturity parameters are ineffective. Another aim is to understand how this maturity measurement could be applicable to pre-Devonian sediments, where vitrinite

reflectance measurements cannot be made because the higher-plant precursors of vitrinite had not yet evolved.

Understanding of a petroleum system may not be achieved even by applying the traditional organic geochemical tools such as molecular and stable isotopic techniques of individual hydrocarbons and whole oil. Trace element contents may predict crude oil origin, maturity, migration pathways and establish sources of heavily biodegraded petroleum samples. The main aim in Chapter 4 is to apply a novel rapid, reliable and accurate method of determination of trace element contents of crude oils which has been developed based on Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). For the first time this method has been applied to a series of petroleum samples allowing analysis of a range of trace elements, with little or no sample pre-treatment. Once the method is developed, the second aim is to investigate the potential of using a combination of CSIA (carbon) approach and trace element data for crude oil samples from Western Australian (WA) and WCSB to establish their origin and age using Linear Discriminant Analysis (LDA).

In Chapter 5, the main aim is to establish the factors controlling the stable carbon isotopic compositions of individual aromatic hydrocarbons analysed by CSIA in crude oils from Western Australian petroleum basins of varying age, facies type but of similar thermal maturity. In order to understand the prevailing palaeoenvironmental conditions in Western Australian petroleum systems, it is intended to use the data on $\delta^{13}C$ of individual aromatic hydrocarbons, like alkylbenzenes, alkylnaphthalenes, alkylphenanthrenes and methylated biphenyls. Because the bulk $\delta^{13}C$ of saturate and aromatic fractions of crude oils have been previously used to differentiate sources (marine vs terrigenous) and since many Australian crude oils do not appear to follow this source separation trend, another purpose of Chapter 5 is to understand why the Sofer plot is ineffective in establishing source of these oils.

The ability to understand and track the source, age, thermal history and palaeoenvironments of deposition of petroleum is critical to the exploration and production of oil and gas reserves. The capability of using a variety of organic and inorganic geochemical methods on sediments and petroleum provides a new

outlook for monitoring sedimentary processes in the subsurface. Thus this allows insights into better understanding of the petroleum systems.

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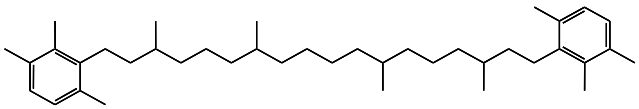
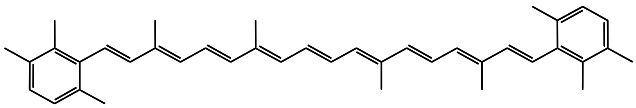
Appendix

Structures referred to in text

I Isorenieratane



II Isorenieratene



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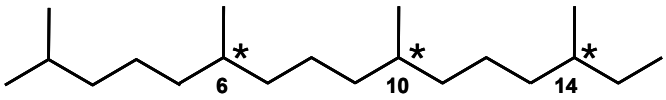
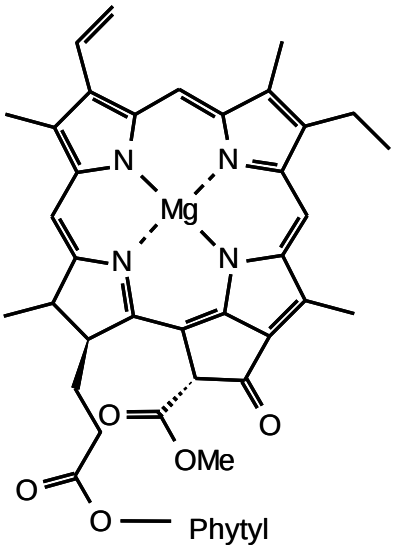
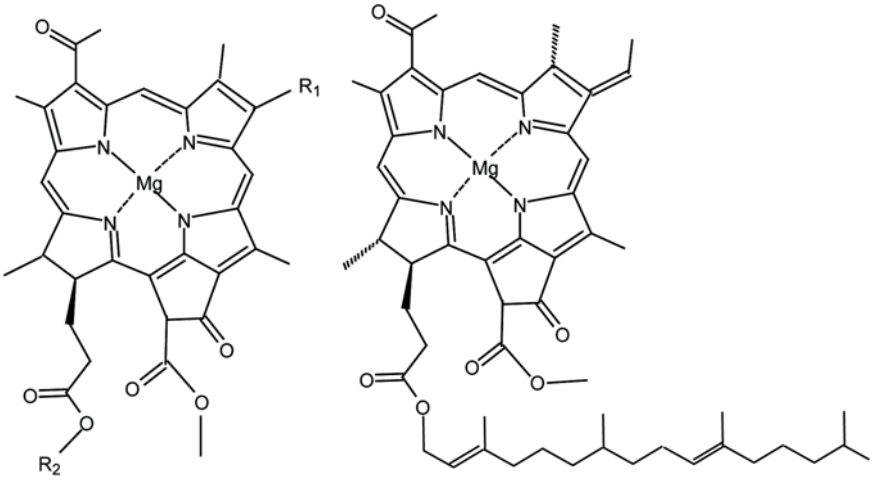


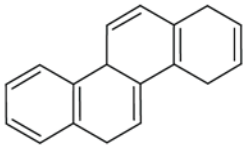
IV Chlorophyll *a*



V Bacteriochlorophyll *a & b*



VI Chrysene



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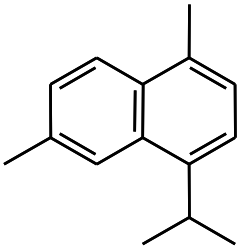
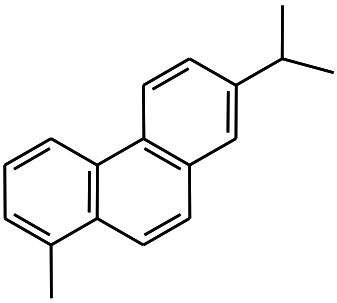
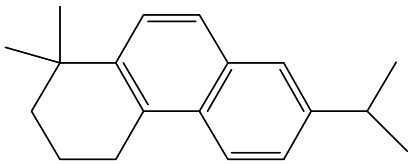


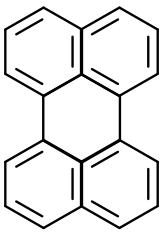
VIII Retene



IX Simonellite



X Perylene



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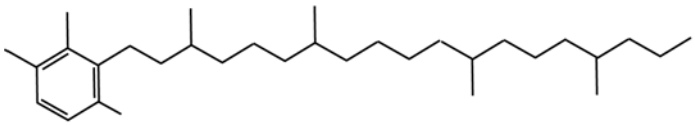

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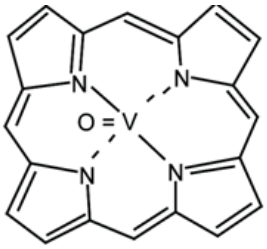

Chapter 2

Crocetane: A potential marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age

Ercin Maslen, Kliti Grice, Julian D. Gale, Christian Hallmann and Brian Horsfield

Organic Geochemistry, 40, 1-11 (2009).

Abstract

Crocetane, an irregular C_{20} isoprenoid, in sediments generally associated with gas hydrate settings, is a molecular indicator for the anaerobic oxidation of methane. Green sulfur bacteria (GSB) are the main source for specific aromatic carotenoids (e.g. isorenieratane) in sedimentary environments and are molecular indicators of photic zone euxinia (PZE). The present study comprises a detailed molecular and isotopic study of crocetane and GSB-derived carotenoids in Devonian sediments of the Western Canada Sedimentary Basin (WCSB) covering a range of thermal maturities. In addition, a series of oils generated from Devonian source rocks of the basin have been analysed for crocetane. Crocetane was found in ten sediments from the WCSB and in seven Devonian WCSB crude oils. Its abundance was found to increase with thermal maturity, whereas the components derived from C_{40} derived carotenoids decrease steadily. We were not able to identify 2, 6, 10, 15, 19-pentamethylicosane (PMI) neither in the Duvernay Formation sediments nor in the WCSB crude oils, consistent with previous findings. The preferred proposed natural product precursor for crocetane is thus GSB-derived carotenoids. This is corroborated by their similar structural features and the $\delta^{13}C$ value of combined crocetane and phytane in these samples. However, contributions from other carotenoids cannot be fully excluded. Crocetane can provide evidence for PZE conditions in highly mature samples and crude oils of Devonian age.

Keywords-

Crocetane, green sulfur bacteria, carotenoids, Devonian, Western Canada Sedimentary Basin, crude oils

Introduction

Crocetane (**I**), an irregular tail-to-tail C_{20} isoprenoid (2,6,11,15-tetramethylhexadecane) has been used as a molecular indicator for the anaerobic oxidation of methane in sediments derived from gas hydrate settings and methane-rich mud volcanoes (e.g. Elvert et al., 1999, 2000; Thiel et al., 1999; Pancost et al., 2000). This compound has been detected in sediments comprising archaea mediating oxidation by reverse methanogenesis in co-operation with sulfate reducing bacteria (Hoehler et al., 1994; Elvert et al., 1999; Thiel et al., 1999; Hinrichs et al., 2000; Pancost et al., 2000). In anoxic environments such as these, crocetane was found to be depleted in ^{13}C (e.g. -120 ‰) suggesting that it derives from organisms mediating the anaerobic oxidation of ^{13}C-depleted methane (e.g. Thiel et al., 1999; Pancost et al., 2000). Moreover, crocetane has been reported in Western Australian crude oils from the Canning Basin of Devonian age (Barber et al., 2001; Greenwood and Summons, 2003). However, the discrete source of crocetane in the Devonian and especially in crude oils still remains ambiguous.

The biomarker isorenieratane (**II**) is generally derived from the carotenoid isorenieratene (**III**), which is synthesised by photosynthetic green sulfur bacteria (*Chlorobiaceae*) (e.g. Summons and Powell, 1986; Requejo et al., 1992; Grice et al., 1996; Koopmans et al., 1996). Another C_{40} carotenoid, paleorenieratane (**IV**), also thought to be derived from GSB has been identified in Devonian-aged sediments and crude oils (Hartgers et al., 1994; Requejo et al., 1992). GSB are strict anaerobes that require light and hydrogen sulfide in stratified water columns to carry out photosynthesis and are thus markers for photic zone euxinia (PZE) in depositional environments. Because carbon assimilation in GSB occurs *via* the reversed tricarboxylic acid cycle (TCA), their biomass and lipids are distinguished by ^{13}C enriched values relative to organisms that use the C3 pathway for CO_2 fixation (Quandt et al., 1977; Sirevag et al., 1977). Sediments that contain crocetane and diaromatic carotenoids (**II** and **IV**), both representing euxinic conditions, are intriguing. One notable coincidence is

the occurrence of crocetane in Devonian crude oils that have been sourced from a type-II organic matter rich calcareous source rocks deposited under PZE conditions.

This paper comprises a detailed molecular and isotopic study of crocetane and GSB derived carotenoids (e.g. isorenieratane- **II** and paleorenieratane- **IV**) in calcareous sediments of the Western Canada Sedimentary Basin (WCSB, Upper Devonian Duvernay Formation) that cover a range of thermal maturities. In addition, a series of oils generated from Devonian source rocks of the basin have been analysed for crocetane to establish its general occurrence in Devonian samples. Understanding the source of crocetane will certainly aid oil–source correlation studies of petroleum systems (especially of Devonian age).

Materials and methods

Western Canada Sedimentary Basin: Devonian source rock and crude oil samples

The Upper Devonian Duvernay Formation, part of the Late Devonian Woodbend Group in the central Alberta region of the WCSB, has excellent hydrocarbon source potential (Stoakes and Creaney, 1984; 1985; Creaney and Allan, 1990; Chow et al., 1995) (Figure 2.1). It is an organic matter rich basinal carbonate succession that was deposited in palaeowater depths mostly greater than 100 m (Creaney and Allan, 1990). Total organic carbon (TOC) contents vary from 0.5% to 10.8% throughout the basin (Fowler et al., 2001). Hydrogen indices (HI) are reported to be between 500 and 600 mg HC/g TOC, indicative of a type II kerogen. The Duvernay Formation exhibits a range of maturity levels from immature to over mature. Oils generated from the Duvernay Formation are mostly paraffinic-aromatic oils with low sulfur contents (less than 0.5%) (Grantham and Wakefield, 1988; Requejo et al., 1991).

Detailed geological descriptions and reports of geochemical characteristics of bitumens and kerogens from the Duvernay Formation have

been provided by Creaney and Allan (1992) and Requejo et al. (1992). The stratigraphic succession of the Devonian in the WCSB is summarised in Figure 2.2.

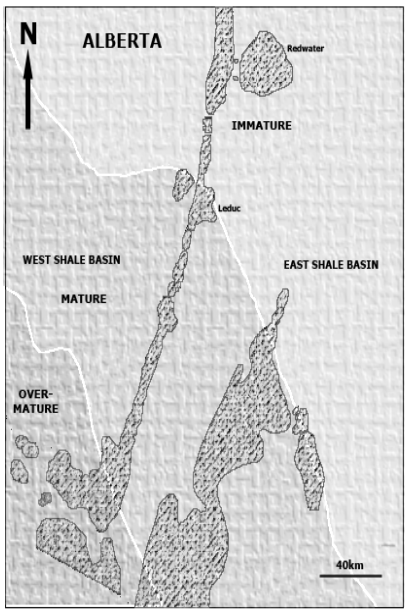

Figure 2.1 A map of east central Alberta Basin, showing the location of the wells from which the sediment samples penetrating the Devonian Duvernay Formation were prepared for use in this study (modified after Stoakes and Creaney, 1985).

The sediments used in this study consist of 10 samples from the Duvernay Formation which are characterised by TOC values ranging from 1.5% to 5.4% and HI values ranging from 55 to 591 mg HC/g TOC (Table 2.1). The thermal maturity of the source rock samples increases with depth as shown by T_{max} values varying between 414 and 441°C (Figure 2.3). Seven crude oils reservoired in various geological units in the WCSB, all Devonian in age, were also used in this study (Table 2.2).

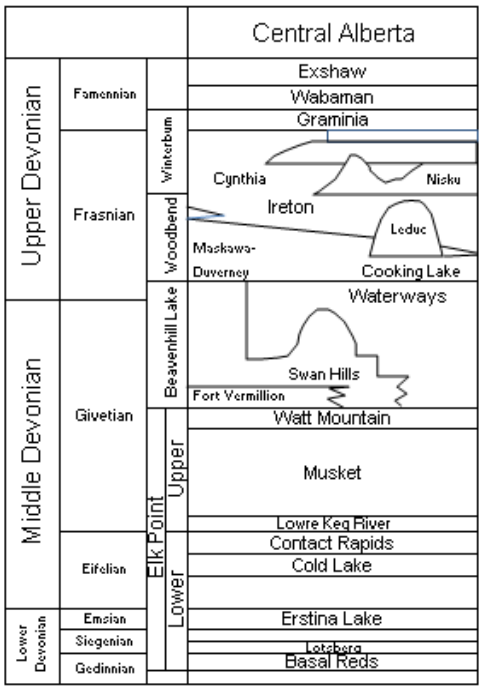

Figure 2.2 Generalized stratigraphic column of the Alberta Basin in the Western Canada Sedimentary Basin, showing the Devonian subsurface (modified after Wendte, 1992).

Locality	Depth (m)	TOC (wt.%)[a]	T_{max} (°C)[a]	HI (mg HC/g TOC)[a]
Redwater	1147.3	5.36	419	591
Redwater	1157.2	4.69	414	494
Imperial Kingman	1402.7	2.7	426	410
Imperial Kingman	1404.5	3.21	426	432
Leduc	1766.9	3.55	434	465
Leduc	1773	4.47	436	576
Ferrybank	2239.5	4.02	437	273
Ferrybank	2248.7	3.3	437	247
Imperial Cynthia	2971.5	1.48	440	55
Imperial Cynthia	2973.7	4.19	441	303

[a]TOC, total organic carbon; HI, hydrogen index

Table 2.1 Sample description, organic carbon (TOC %) and Rock-Eval pyrolysis parameters of source rocks studied from the Duvernay Formation, WCSB. Samples are listed in order of increasing maturity.

Sample	Depth (m)	Age-Source	Cr/Ph SIM *m/z* 169*
2204 Woodriver	1856	Nisku Fm	0.07
2221 Big Valley	1569.7	Duvernay Fm	0.04
2158 Clive	1868	Duvernay Fm	0.45
2177 Lone Pine	2362.8	Duvernay Fm	0.36
1634 Rich	2231	Winnipegosis Fm	0.08
207 Aquitane	1805.6	Keg River Fm	0.16
807 Zama	1516.5	Keg River Fm	0.31
Blina-1	-	Late Devonian	0.63**
Janpam North-1	-	Late Devonian	0.40***

*Ratios of crocetane to phytane (Cr/Ph) refer to measurements of the peak heights in *m/z* 169 ion chromatogram.
**The Cr/Ph ratio is from Barber et al. (2001).
***The Cr/Ph ratio is from Greenwood and Summons (2003).

Table 2.2 Devonian crude oil samples containing crocetane (WCSB and Canning Basin).

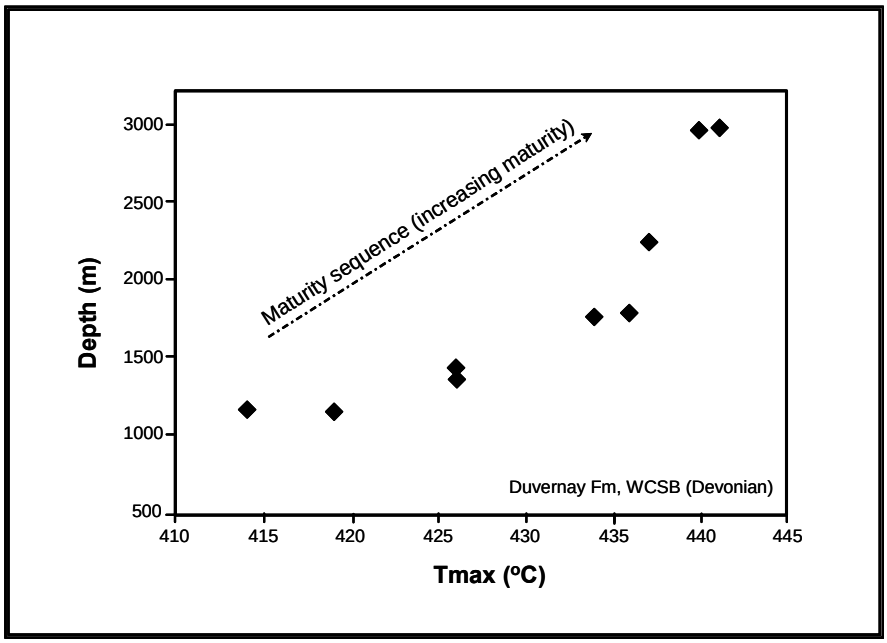

Figure 2.3 Depth profile showing maturities (T_{max} in °C) of studied sediment samples from the Duvernay Formation.

Sample preparation

The sediment samples were surface extracted using a solution of dichloromethane and methanol (9:1), and dried before grinding. The samples were then ground to a particle size of approximately 150 µm using a ring mill.

Solvent extractions

The Duvernay Formation samples were extracted using an automated accelerated solvent extractor (ASE 200 Dionex, Sunnyvale, CA, USA). The ground sediments were weighed into pre-extracted stainless steel extraction cells containing pre-rinsed glass fibre filters. The cells were loaded into the turret of the ASE. The cells were preheated at 100°C (2 min). A 9:1 mixture of dichloromethane and methanol was pumped into the cells using a pressure of 1000 psi for 5 min. The entire procedure was repeated until the solvent in the collection vial became colourless. Finally, the extracts were combined and the solvent was removed under a nitrogen purge.

Fractionation of crude oils and sediment extracts using column chromatography

The Duvernay Formation sediment extracts were fractionated using a large scale liquid chromatography method. The sediment extract was applied to the top of a large column (20 cm x 0.9 cm i.d.) containing activated silica gel (120°C, 8 h), which was prewashed with *n*-hexane. The saturated fraction was eluted with *n*-hexane (35 ml), the aromatic hydrocarbon fraction with a solution of dichloromethane in *n*-hexane (40 ml, 30%), and the polar fraction with dichloromethane and methanol (40 ml, 50%).

Devonian sourced crude oils were fractionated using a small scale column liquid chromatography method (Bastow et al., 2007). The sample was applied to the top of a small column (5.5 cm x 0.5 cm i.d.) containing activated silica gel (120°C, 8 h). The saturated fraction was eluted with *n*-hexane (2 mL), the

aromatic hydrocarbon fraction with a solution of dichloromethane in *n*-hexane (2 mL, 30%), and the polar fraction with dichloromethane and methanol (2 mL, 50%).

5A molecular sieving

Straight chain hydrocarbons were separated from branched and cyclic hydrocarbons by treating the saturated fractions with activated (250°C, 8 h) 5A molecular sieves (Murphy, 1969; Dawson et al., 2005; Grice et al., 2008) in cyclohexane. In a typical 5A molecular sieving separation, a portion of the saturate fraction in cyclohexane was added to a 2 mL vial, 3/4 of it filled with activated 5A molecular sieves. The vial was capped and placed into a preheated aluminium block (85°C, overnight). The resulting solution was then cooled and filtered through a small column of silica plugged with cotton wool (pre-rinsed with cyclohexane) and the sieves were rinsed thoroughly with cyclohexane yielding the branched/cyclic fraction (5A excluded).

Gas chromatography - mass spectrometry (GC-MS)

GC–MS analyses were performed on a Hewlett Packard (HP) 5973 mass spectrometer interfaced to a HP 6890 gas chromatograph fitted with a 60 m x 0.25 mm i.d. WCOT fused silica capillary column coated with 0.25 μm thick film (DB-5, J&W Scientific). In a typical analysis, the GC oven was programmed from 40°C to 310°C at 3°C/min with initial and final hold times of 1 and 30 min, respectively. Samples (in *n*-hexane) were injected in splitless mode using a HP 6890 series autosampler. The carrier gas used was ultra high purity helium with a constant flow rate of 1 mL/min.

For crocetane identification, the analyses were performed on the same instrument but fitted with a 60 m x 0.25 mm i.d. DB-1701 column coated with a 0.25 μm thick film (J&W Scientific). The mass spectrometer was operated in selected ion monitoring (SIM) mode to monitor *m/z* 113, 169, 183, 197 and 282.

An internal perdeuterated aromatic standard was added to the aromatic fraction for quantification purposes (see below also).

For alkylbenzene and alkylnaphthalene quantifications, weighed aliquots of crude oils were spiked with internal standards before the small scale silica column fractionation was performed. Aromatic fractions were purified as described by Bastow et al. (2007). Tri- and tetramethylbenzenes and tetramethlynaphthalenes were analysed in selected ion monitoring mode (SIM) scanning for the following ions: *m/z* 119 (trimethylbenzenes), *m/z* 133 (tetramethylbenzenes) and *m/z* 184 (tetramethylnaphthalenes). Compounds were quantified relative to d_8-naphthalene. No corrections for individual response factors were made.

Compound specific isotopic analyses (CSIA)

CSIA were performed on a Micromass IsoPrime instrument. Methods are described in Grice et al. (2008). The average values of three runs for each compound is reported and only results with a standard deviation of less than 0.4‰ were used. $\delta^{13}C$ values are reported in the δ-notation relative to the international Vienna Peedee belemnite (VPDB) standard.

Quantum mechanical calculations

Ab initio quantum mechanical calculations have been performed for selected cases in order to examine the relative energy of the systems. Given the size of the molecules to be studied, the hybrid functional B3LYP (Becke, 1993; Stephens et al., 1994) was selected as an appropriate Hamiltonian and calculations have been performed with both the 3-21G** and 6-31G** basis sets in order to evaluate the influence of this numerical factor on the results. B3LYP represents a hybrid density functional, based on the adiabatic connection method of Becke (1993), where the Becke gradient corrected exchange functional is mixed with the Hartree–Fock exchange and the Lee–Yang–Parr gradient-corrected correlation functional in a parameterized expression. 6-31G**

represents a basis set where core orbitals are presented by a linear contraction of 6 Gaussians and the valence orbitals are represented by a double-zeta combination of a 3 Gaussian contraction and a single further Gaussian. In addition, polarization functions are added for all atoms including hydrogen (Hehre et al., 1972).

All calculations have been performed using NWChem version 4.7 (Apra et al., 2005), with a fine grid for integration of the exchange correlation potential, implying a target accuracy for the total energy of 10^{-7} with respect to the quadrature. Full geometry optimisation was applied to all configurations to obtain the local minimum with an energy converged to better than 0.01 kJ/mol with respect to structural parameters. No correction has been made for zero point energy or finite temperature effects.

Results and discussion

Crocetane (I) in sediments and crude oils of WCSB

The branched/cyclic hydrocarbon fractions of a suite of Devonian aged sediments and crude oils from WCSB were analysed by GC–MS. Since both the suite of Duvernay oils and sediment samples examined represent a range of maturity levels, they present an opportunity to examine the formation of crocetane, through maturity from individual aromatic biomarker compounds isorenieratane (**II**) and paleorenieratane (**IV**) of GSB.

Studies concerning the GC elution behaviour of phytane (**V**) and crocetane (**I**) have been reported previously (e.g. Robson and Rowland, 1993; Thiel et al., 1999; Barber et al., 2001). Robson and Rowland (1993) achieved partial GC separation of these two compounds using an OV-1 stationary phase. Thiel et al. (1999) also achieved partial resolution of phytane (**V**) and crocetane (**I**) on a squalane column using hydrogen as a carrier gas. Barber et al. (2001) developed a method for analyses of these diastereomeric isoprenoids in sediments and crude oils using a β-cyclodextrin column using helium as a carrier gas. In this

study, we utilised a DB-1701 column (60 m, 0.25 mm i.d., J&W Scientific) of relatively greater polarity, which is more readily available commercially and can be routinely used in organic geochemical studies to achieve a similar separation of phytane (**V**) and crocetane (**I**). Single ion monitoring of *m/z* 169 and *m/z* 183 were used to determine the peak areas and thus the ratio of crocetane (**I**) relative to phytane (**V**) in sediments and crude oils (Table 2.2 and Figure 2.4). A calibration with artificial standards of crocetane (**I**) and phytane (**V**) was used in the analyses as described by Barber et al. (2001) and Greenwood and Summons (2003).

Crocetane was found to be present throughout the Duvernay Formation sequence and in all the Devonian crude oils (Table 2.2 and Figure 2.4). The relative abundance of crocetane (**I**) to phytane (**V**) i.e. Cr/Ph in the Duvernay Formation sediment samples gradually increases with thermal maturity represented by T_{max} values ranging between 414°C and 441°C (Figure 2.4). However, the Cr/Ph in the crude oils varies between samples (Table 2.2). Clive, Lone Pine and Zama crude oils show the highest relative abundances of crocetane having Cr/Ph of 0.45, 0.36, and 0.31, respectively. The remaining samples show much lower relative abundances of crocetane having Cr/Ph ranging between 0.16 and 0.04. The occurrence of crocetane (**I**) in various crude oil samples has been shown previously by Barber et al. (2001) and Greenwood and Summons (2003). It is apparent that crocetane (**I**) appears to be generally higher in Devonian aged oils (e.g. the Canning Basin, Western Australia) and Devonian oils from WCSB (this study).

Diaromatic carotenoids in sediments of WCSB

Aromatic carotenoids (such as isorenieratane- **II** and paleorenieratane- **IV**) contain one or more trimethyl substituted aromatic rings connected by an isoprenoid chain. The structural similarity of crocetane (**I**), the irregular tail-to-tail linked C_{20} isoprenoid 2,6,11,15-tetramethlyhexadecane, with these carotenoids and their co-occurrence in Devonian source rocks and crude oils in WCSB is interesting since it could imply a common origin. The diaromatic

carotenoids (**II** and **IV**) as well as aryl isoprenoids are important constituents of the aromatic hydrocarbon fractions of the Devonian Duvernay Formation (WCSB) and related oils (Summons and Powell, 1986; Requejo et al., 1991; Hartgers et al., 1994). Molecular and isotopic studies of these particular compounds show that two C_{40} diaromatic carotenoids (**II** and **IV**) have a significant contribution from carotenoids of photosynthetic GSB. Abundances (µg/g TOC) of the extractable aromatic hydrocarbons were determined for the Devonian Duvernay Formation source rock samples.

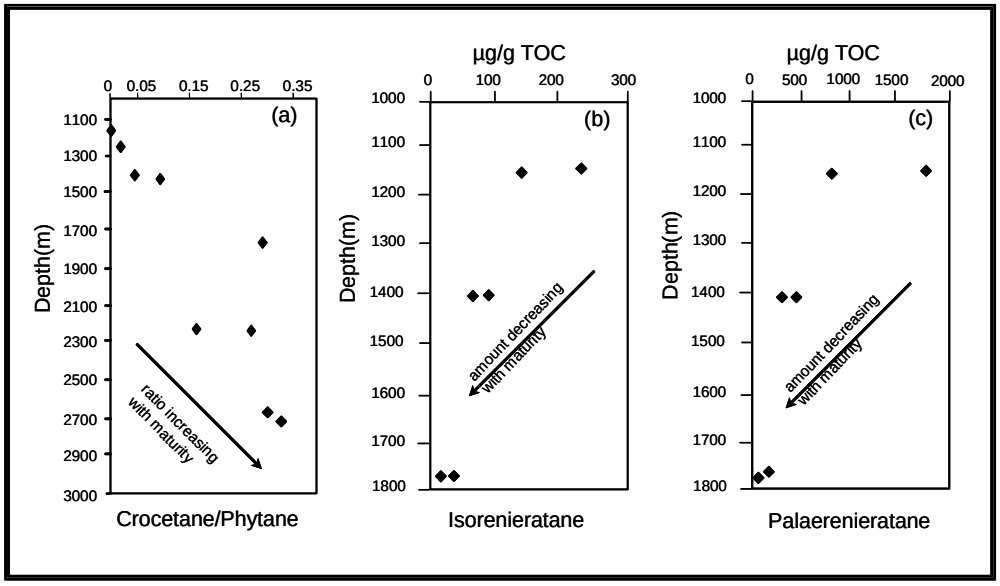

Figure 2.4 Plots of (a) Cr/Ph ratio versus depth (b) abundance of (**II**) versus depth and (c) abundance of (**IV**) versus depth from Duvernay Formation sediment extracts. The direction of the arrows indicates increasing and decreasing maturity.

The depth abundance profiles for isorenieratane (**II**) and paleorenieratane (**IV**) show a decrease in concentration from 236 to 8 µg/g TOC and from 1874 to 22 µg/g TOC, respectively, with depth (Figure 2.4). Both reach a minimum concentration at 1773 m, corresponding to a maturity of 436°C T_{max}. At a T_{max} of 437–441°C, concentrations of both compounds are below detection limit (Figure

2.4). These data show that the change in concentration of diaromatic carotenoids is proportional to thermal maturation of the organic matter present in the sediments. Another comparison of change in concentration of diaromatic carotenoids with a traditional maturity parameter, (C_{32}) homohopane 22S/22(S+R), was made to further assess whether the change in abundance of diaromatic carotenoid composition is directly related to maturity. The quantitative abundance of isorenieratane (**II**) shows that there is a similar decrease in concentration of isorenieratane (**II**) with an increase in C_{32} 22S/22(S+R) and thus rising thermal maturity (Figure 2.5). The concentration of isorenieratane (**II**) decreases from 236 to 0 µg/g TOC parallel to an increase in the ratio of C_{32} 22S/22(S+R) from 0.26 to 0.68. This data also supports that the variation in abundance of isorenieratane (**II**) is proportional to maturation.

With increasing maturation, the abundance of Cr/Ph in Duvernay source rock bitumens increases to a point, whereas diaromatic carotenoids decrease steadily. The Cr/Ph appear to correlate strongly with maturity, as shown by its correlation with T_{max} values (R^2 = 0.84). Similarly, the diaromatic carotenoid isorenieratane shows a strong correlation with depth (R^2 = 0.79).

Potential sources for crocetane (I) based on structure

Several potential sources for crocetane have been proposed previously and these include: (i) a diagenetic product of the C_{25} irregular isoprenoid, 2,6,10,15,19-pentamethylicosane (PMI, **VI** see Barber et al., 2001) reported in cultured organisms, microbial communities and sediments consisting of methanogenic (e.g. Koga et al., 1993; Schouten et al., 1997, 2001a,b) and methanotrophic archaea (Elvert et al., 1999; Thiel et al., 1999; Hinrichs et al., 2000; Pancost et al., 2000) and (ii) a direct biological precursor from microbial consortia consisting of methanotrophic archaea and sulfate reducing bacteria that are typically depleted in ^{13}C (e.g. Elvert et al., 1999; Thiel et al., 1999; Hinrichs et al., 2000; Pancost et al., 2000; Orphan et al., 2001), due to carbon assimilation from an isotopically depleted carbon source (i.e. biogenic methane).

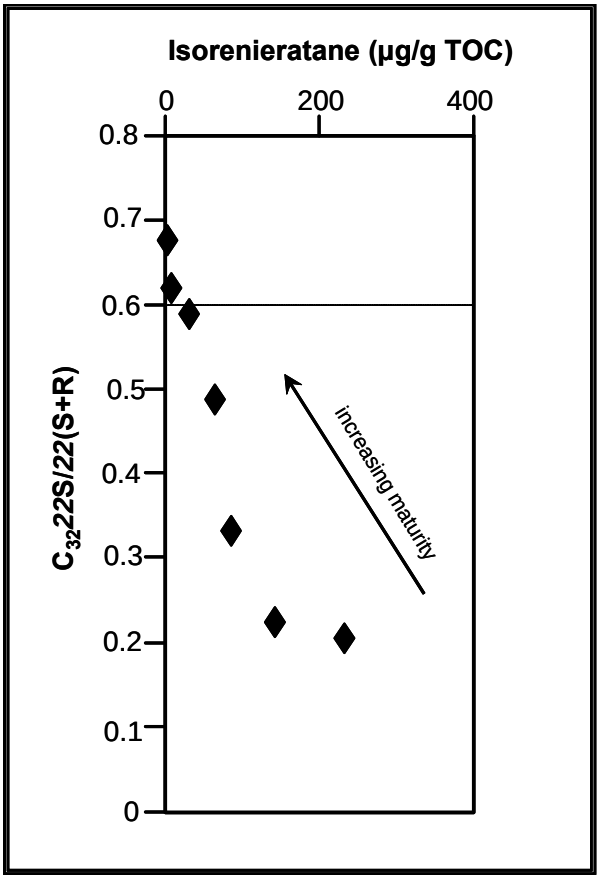

Figure 2.5 Plot of abundance of (**II**) versus the variation of a hopane maturity parameter (C_{32} homohopane 22S/22(S+R)) in Duvernay Formation sediment extracts. The direction of the arrow indicates increasing maturity.

However, in the Duvernay Formation sediments and the WCSB crude oils, we were not able to identify any PMI (**VI**). Only small amounts of a C_{25} regular isoprenoid were observed, consistent with the findings of Greenwood and Summons (2003). This data is also consistent with the notion that PMI (**VI**) has not yet been reported in samples predating the Cretaceous.

Based on structural grounds and the findings above, other potential sources for crocetane (**I**) include a variety of carotenoid derived biomarkers (e.g. lycopene (**VII**), β-carotene (**VIII**), β-isorenieratene (**IX**), isorenieratene (**III**),

renieratene (**X**) and paleorenieratene (**XI**), okenone (**XII**) *via* β-cleavage. Interestingly, sedimentary bitumens and oils of Palaeozoic age have been reported to contain high concentrations of carotenoid derivatives including a large array of carotenoid cyclisation and degradation products (Grice et al., 1996, 2005; Koopmans et al., 1996, 1997; Clifford et al., 1998; Sinninghe Damsté et al., 2001). These products also include aryl isoprenoids (e.g. Pedentchouk et al., 2004). In certain instances, β-carotene (**VIII**) can yield β-isorenieratane by aromatisation (Koopmans et al., 1998). Isorenieratane (**II**) can also be formed from β-carotene (**VIII**) by aromatisation of both cyclohexenyl moieties. The aryl isoprenoids, which can be formed by carbon-carbon bond cleavage of both isorenieratane (**II**) and β-isorenieratane, thus can have a mixed $\delta^{13}C$ signature (Grice et al., 1997; Koopmans et al., 1998; Pedentchouk et al., 2004). $\delta^{13}C$ analyses reported for isorenieratane (**II**) and paleorenieratane (**IV**) in the Duvernay Formation sediments (e.g. Hartgers et al., 1994) are consistent with a GSB source being significantly enriched in ^{13}C relative to algal biomarkers, in keeping with the use of the reversed TCA cycle in Chlorobiaceae (Evans et al., 1966), which can lead to biomass enriched in ^{13}C (Quandt et al., 1977; Sirevag et al., 1977). Given that no β-carotane, okenane, or lycopane components are evident in the Duvernay Formation sediments, it is likely that carotenoids such as isorenieratane (**II**), paleorenieratane (**IV**) and renieratane, derived from Chlorobiaceae, are the most likely sources for crocetane. However, contributions from other carotenoids cannot be fully excluded for reasons described above.

Potential sources of crocetane (I) based on $\delta^{13}C$

Crocetane (**I**) has been previously identified by its light isotopic signature confirming a source associated with anaerobic methane oxidation (Thiel et al., 1999; Peckmann et al., 2002; Birgel et al., 2006). The combined $\delta^{13}C$ data of Cr and Ph reported by Barber et al. (2001) does not show any evidence for a ^{13}C depleted source. However, a slight ^{13}C enrichment was observed (Barber et al., 2001). The $\delta^{13}C$ values of pristane and combined crocetane (**I**) with phytane (**V**) in samples from this study are shown in Table 2.3. Given that the preferred

precursor(s) for crocetane (**I**) are the carotenoids of GSB, phytane should be slightly less depleted in ^{13}C relative to pristane, assuming that pristane and phytane are predominantly sourced from the phytyl side chain of chlorophyll *a*. Contributions from halophilic archaea cannot be entirely excluded given that a C_{25} regular isoprenoid has been identified in these samples (Grice et al., 1998). Even so, $\delta^{13}C$ of the combined crocetane (**I**) and phytane (**V**) with increasing thermal maturity shows a greater $\Delta\delta$ difference to pristane, especially in the two deepest samples where the Cr/Ph is the highest. Taking into account the approximate percentage of crocetane (**I**) relative to phytane (**V**) in these samples, an estimated $\delta^{13}C$ value for crocetane (**I**) varies between -11 and -6‰, consistent with a GSB source.

In addition to the source effects mentioned above, the $\delta^{13}C$ data of pristane and phytane (**V**) show a maturity effect throughout the section. The $\Delta\delta$ difference of pristane from the least mature sample to most mature sample is 3.9‰, and for phytane (**V**) it is 5.4‰. The larger $\Delta\delta$ difference with regards to rising maturity for phytane (**V**) can be attributed to a greater contribution of ^{13}C enriched crocetane (**I**) from a GSB source.

Formation of crocetane (I) from Chlorobiaceae carotenoids

Crocetane (**I**) can arise from isorenieratene through β-cleavage. With increasing maturation, the ratio of Cr/Ph in Duvernay source rock bitumens increases, whereas the C_{40} derived carotenoid components decrease steadily. β-cleavage of long chain alkylthiophenes and alkylbenzenes has also been demonstrated by MSSV pyrolysis (at 300°C for 72 h) leading to generation of lower molecular weight alkylated thiophenes and benzenes (Sinninghe Damsté et al., 1998).

Additional diagenetic products of carotenoids include tetramethylbenzenes (TeMBs) (van Aarssen et al., 2007). An investigation on the relationship of 1,2,3,4-TeMB and 1,2,3,5-TeMB with Cr/Ph was carried out on the oils for this purpose. No TeMBs were present in the sediments, probably due to loss through evaporation. The occurrence of 1,2,3,4-TeMB and 1,2,3,5-TeMB both

in kerogen pyrolysates of Duvernay Formation sediment samples and in crude oils from the WCSB has previously been reported (Requejo et al., 1992; Hartgers et al., 1994). The abundance of crocetane (**I**) and the high concentration of 1,2,3,5-TeMB (µg/g oil) are evident in the Devonian oils studied herein (Figure 2.6). The strong relationship demonstrated for the concentration of 1,2,3,5-TeMB and Cr/Ph points to a common source i.e. Devonian aged GSB carotenoid (palaerenieratene, **XI**) for 1,2,3,5-TeMB and crocetane (**I**). On the other hand the 1,2,3,4-TeMB is low in concentration when crocetane (**I**) is relatively higher. The lack of a trend is probably related to multiple sources for the 1,2,3,4-TeMB (Pedentchouk et al., 2004) and a predominant GSB source for crocetane (**I**).

Sample, Depth (m)	***T_{max} (°C)***	**δ^{13}C Pr (‰)***	**δ^{13}C Ph (‰)***
G000542, 1147.3	419	-32.5 (0.39)^{3}	-31.6 (0.28)^{3}
G000584, 1402.7	426	-32.9 (0.18)^{3}	-32.4 (0.08)^{2}
G000553, 1766.9	434	-29.9 (0.09)^{3}	-29.6 (0.08)^{2}
G000557, 1773	436	-30.2 (0.07)^{3}	-29.4 (0.35)^{3}
G000595, 2239.5	437	-27.8 (0.38)^{3}	-28.3 (0.42)^{3}
G000601, 2971.5	440	-27.7 (0.12)^{3}	-26.1 (0.14)^{3}
G000603, 2973.7	441	-28.5 (0.14)^{2}	-26.22 (0.24)^{2}

* Numbers in parenthesis are standard deviations; superscript numbers are number of replicate analyses.

Table 2.3 δ^{13}C values of pristane (Pr) and phytane (Ph) for the WCSB sediment extracts from the Duvernay formation.

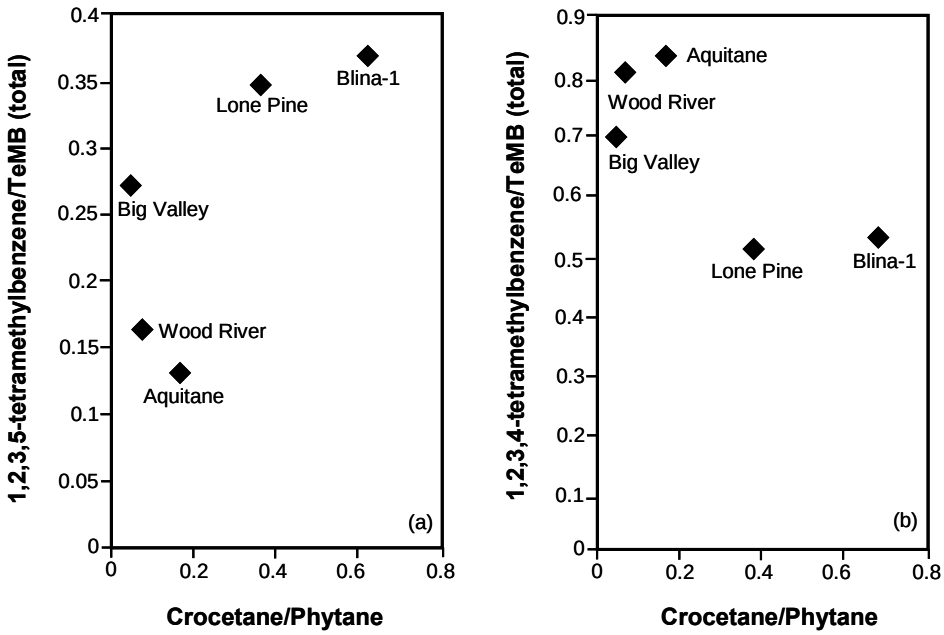

Figure 2.6 Plot of ratios of (a) 1,2,3,5-TeMB/TeMB (total) and (b) 1,2,3,4-TeMB/TeMB (total) versus Cr/Ph ratio in Devonian crude oils from WCSB and Canning Basin.

In order to demonstrate any difference in thermal stability of isorenieratane (**II**) and paleorenieratane (**IV**), or in their unsaturated forms of isorenieratene (**III**) and palaerenieratene (**XI**), respectively, ab initio quantum mechanical calculations were undertaken at the B3LYP/3-21** and B3LYP/6-31G** levels. For the unsaturated case, the conformation of the hydrocarbon backbone connecting the two benzene rings is unambiguous. However, for the saturated case there are four chiral centres and many possible local minima to be explored. In order to reduce the computational demands it has been assumed that the particular stereochemistry of the connecting hydrogen chain is unlikely to influence the preferential substitution pattern for benzene rings. Hence, in the present study the same conformation of the saturated hydrocarbon backbone is used for both isorenieratane (**II**) and paleorenieratane (**IV**) to ensure that any energy difference is solely related to the isomerism of the methyl substituents on the aromatic rings. Investigation of whether the methyl substitution pattern might induce a change of conformation is left for future work. Furthermore, it is

assumed the molecule adopts an extended conformation and that the influence of solvent is negligible. In aqueous environments the saturated species may undergo some degree of folding in order to lower the effective surface area. Again, this remains the subject of future research.

For the unsaturated species, the energy differences are 5.8 and 7.0 kJ/mol at the B3LYP/3-21G** and B3LYP/6-31G** levels, respectively, with palaerenieratene (**XI**) being the thermodynamically favoured molecule in both cases. The small change as a function of basis set suggests that the result is likely to be robust with respect to this factor. Furthermore, the preference for palaerenieratene (**XI**) can be understood in terms of competition between the desire to avoid steric hindrance between the hydrocarbon backbone and the methyl substituents of the terminal benzene rings and the preference to maintain conjugation; palaerenieratene (**XI**) has one less methyl group adjacent to the unsaturated backbone than isorenieratene (**III**).

Considering the case of isorenieratane (**II**) and paleorenieratane (**IV**), the energy difference is 0.4 kJ/mol in favour of isorenieratane (**II**) at the B3LYP/3-21G** level, which switches to a preference of 0.8 kJ/mol for paleorenieratane (**IV**), with the improvement in the basis set. Given the small energy difference and sensitivity to numerical parameters, the two molecules should be considered as indistinguishable in terms of energy within the limitations of the uncertainties of present day hybrid density functional theory. Again, this is consistent with physical intuition. Once the driver of trying to maintain conjugation between the benzene rings and the hydrocarbon backbone is removed, both molecules are equally able to adopt a conformation that minimises steric hindrance.

Geological significance of crocetane (I) in sediments and oils

The biomarker isorenieratane (**II**) and its diagenetic products are commonly reported in sediments and certain oils throughout the Phanerozoic and Paleozoic. Crocetane (**I**) which does not share an anaerobic methane oxidation source is only abundant in crude oils and sediments of Devonian age. There is one report of a low abundance of crocetane (**I**) in sediments of Triassic

age from the Kockatea shale (Greenwood and Summons, 2003). Grice et al. (2005) reported isorenieratane and aryl isoprenoids across the Permian/Triassic boundary in several sections, but no crocetane (**I**) was evident in these samples (Grice, unpublished). Interestingly, the chemical controls on the generation and destruction of diverse diagenetic products of carotenoids are as yet unsolved (see Sinninghe Damsté et al., 2001). As suggested by Brocks and Schaeffer (2008) the array of diagenetic products of carotenoids in Palaeoproterozoic sediments appear rather different to those reported in Phanerozoic sediments. Brocks and Schaeffer (2008) suggest that clues to this discrepancy may lie in the differences in water chemistry and ecology. Based on the abundance of crocetane in Devonian samples it is suggested that the array of diagenetic products of carotenoids in Paleozoic sediments are also rather different to those reported in post-Paleozoic sediments. Crocetane's occurrence in Palaeoproterozoic sediments has not yet been fully explored. Further work is necessary to understand the formation and controls on the diagenetic products of carotenoids in geological samples. In addition, pyrolysis experiments should be carried out in order to investigate the diagenetic source relationship between the diaromatic carotenoids and crocetane (**I**). Unfortunately there were not enough immature sedimentary samples available to carry out additional pyrolysis experiments in the present study.

Conclusions

A detailed molecular and isotopic study of crocetane (**I**) and GSB derived carotenoids in sediments of the WCSB (upper Devonian Duvernay Formation) covering a range of thermal maturities showed that the Cr/Ph steadily increases in the maturity sequence. The depth abundance profiles for GSB derived carotenoids show a decrease in concentration with depth and concomitant increase in the relative abundance of crocetane (**I**). Crocetane (**I**) was also found to be present in all seven WCSB crude oils analysed.

In the Duvernay Formation sediments and the WCSB crude oils, we were not able to identify PMI (**VI**), which is consistent with previous findings. Thus, the preferred proposed natural product precursor for crocetane (**I**) is GSB derived isorenieratene (**III**) and palaerenieratene (**XI**). This is based on their similar structural features and the $\delta^{13}C$ of combined crocetane (**I**) and phytane (**V**) in these samples. However, contributions from other carotenoids cannot be fully excluded. It is proposed that crocetane (**I**) arises from the β-cleavage of diaromatic carotenoid moieties of GSB that have been incorporated into the kerogen structure. Crocetane (**I**) can provide evidence for PZE conditions in highly matured samples and crude oils of Devonian age.

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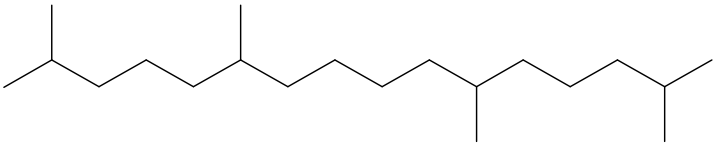
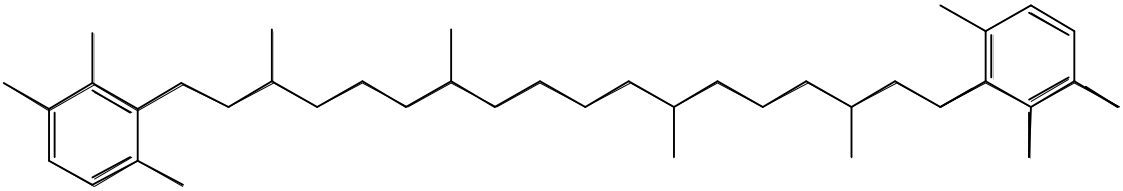
Appendix

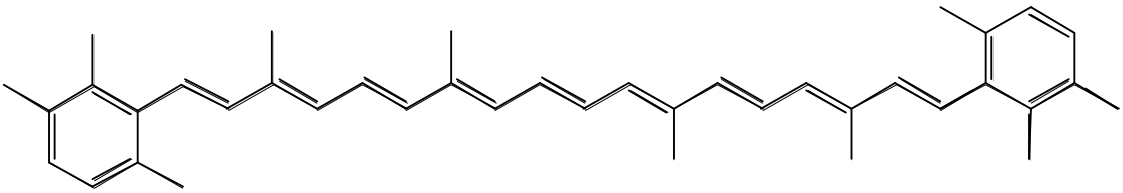
Crocetane (**I**)



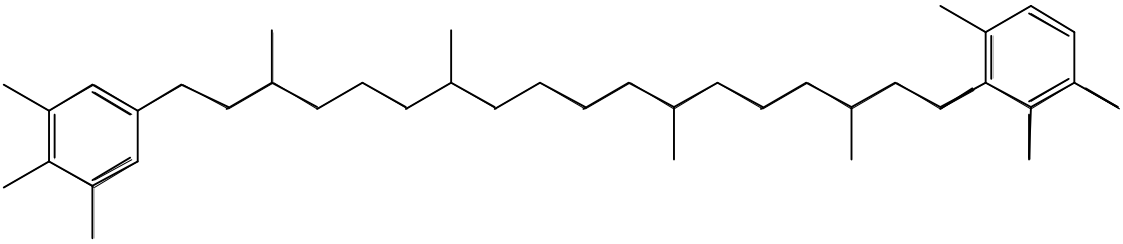
Isorenieratane (**II**)



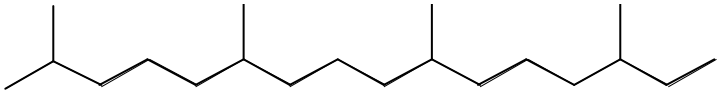
Isorenieratene (**III**)



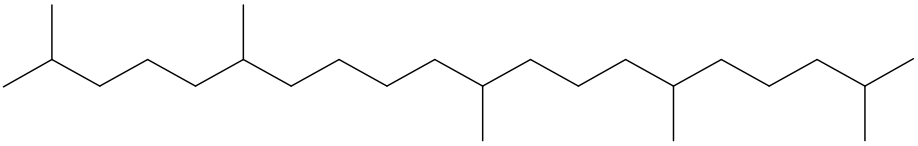
Palaerenieratane (**IV**)



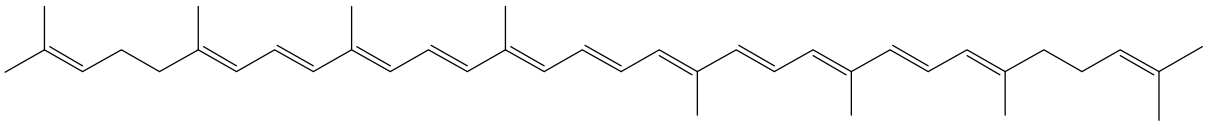
Phytane (**V**)



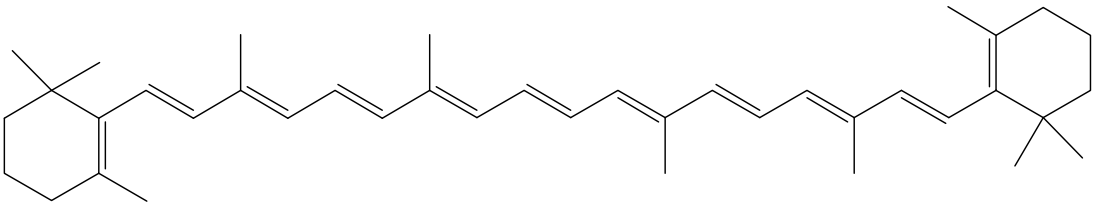
PMI (**VI**)



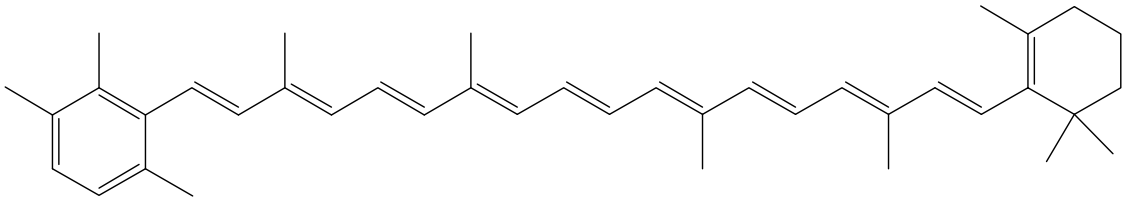
Lycopene (**VII**)



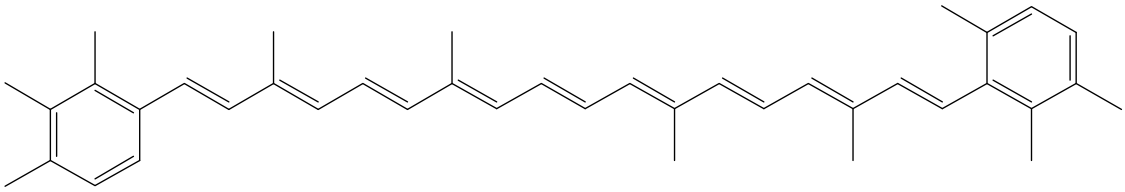
β-Carotene (**VIII**)



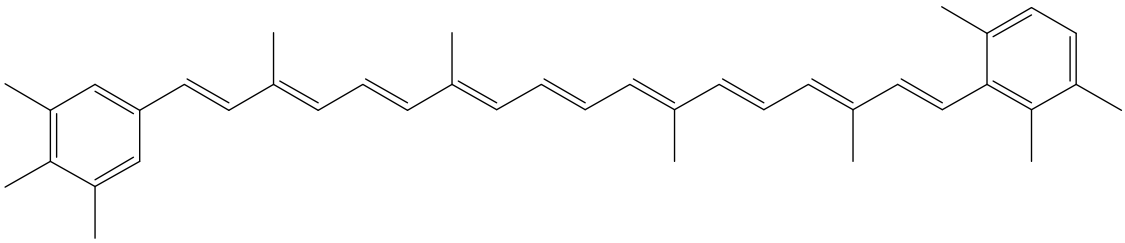
β-Isorenieratene (**IX**)



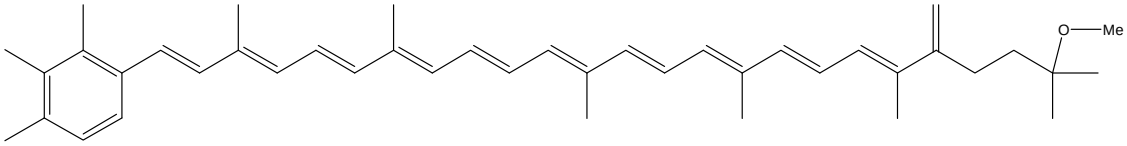
Renieratene (**X**)



Paleorenieretene (**XI**)



Okenone (**VIII**)



Chapter 3

Stable hydrogen isotopes of isoprenoids and *n*-alkanes as a proxy for estimating the thermal history of sediments through geologic time

Ercin Maslen, Kliti Grice, Daniel Dawson, Sue Wang and Brian Horsfield

Society for Sedimentary Geology (SEPM) Special Publication, in press.

Abstract

The effect of thermal maturation on the δD values of individual petroleum hydrocarbons (*n*-alkanes and regular isoprenoids) from sedimentary organic matter over geological timescales has been explored in six different sedimentary sequences covering a wide range of maturities, i.e. 0.53%–1.6% vitrinite reflectance (R_o or equivalent i.e. R_e, R_c). These include, new data and recently reported literature data on formations ranging in age from the Lower Cretaceous to the Permian. The application of the D/H of biomarkers as a maturity proxy for Devonian source-rocks from the Western Canada Sedimentary Basin (WCSB) is also presented here, extending this application to much older sediments than previously studied. In each case, pristane and phytane are predominantly derived from the lipid side chain of chlorophyll *a* present in most photosynthetic organisms, with an additional (but minor) contribution to pristane from tocopherol of land plants in selected cases. The *n*-alkanes represented contributions of algae, bacteria and in certain cases higher plants. In general, the *n*-alkanes, pristane and phytane from relatively immature sediments have δD values that retain the isotopic signature of their natural product precursors, i.e. biosynthesised lipid components made up of acetyl and isoprene sub-units, respectively. With increasing maturity, pristane and phytane become more enriched in deuterium (D), while the *n*-alkanes generally remain at a constant isotopic composition until an overmature level is reached, at which point there is a significant enrichment of D in *n*-alkanes. The enrichment of D in pristane and phytane with increasing maturity correlates strongly with changes in traditional maturity parameters including vitrinite reflectance, T_{max}, and molecular parameters, providing evidence that D-enrichment is associated with thermal maturation.

Introduction

Hydrogen is the lightest and most abundant chemical element in the universe and is present in water and all organic compounds. Hydrogen consists of two naturally-occurring stable isotopes, hydrogen (^{1}H) and deuterium (^{2}D). Hydrogen in hydrocarbons can be either bound to (i) primary, secondary or tertiary carbon atoms in alkyl moieties (Figure 3.1) (ii) carbon atoms in aromatics (aromatic C-bound hydrogen), or (iii) nitrogen, oxygen or sulfur atoms in polar compounds (N, O, S-bound hydrogen).

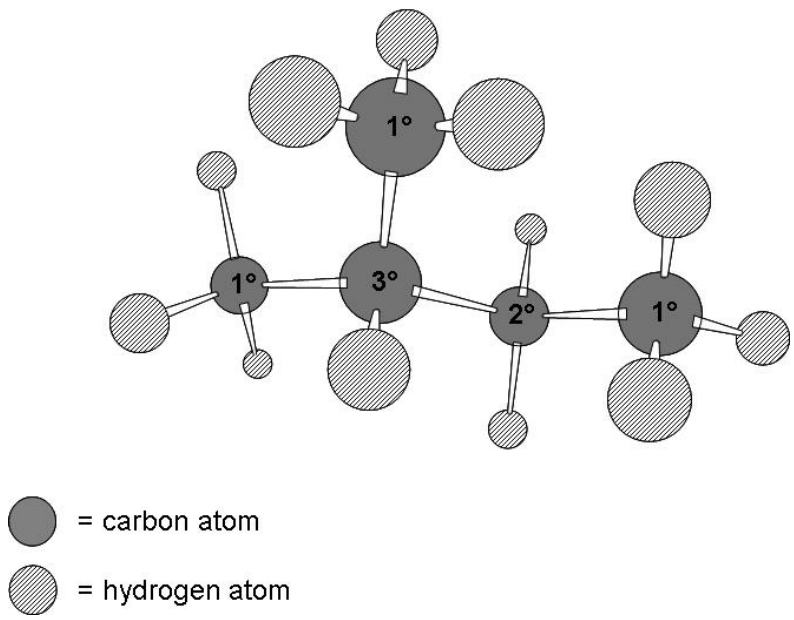


Figure 3.1 A structural diagram to illustrate the difference between primary, secondary and tertiary carbon positions.

The strength of the hydrogen bond differs considerably among different chemicals, which is a critical factor in assessing the exchangeability and therefore the rate of hydrogen exchange at different molecular positions in

organic components. For example, aliphatic C-bound hydrogen is linked via a strong covalent bond, and is often referred to as 'non-exchangeable hydrogen' (e.g. Epstein et al., 1976; Schimmelmann, 1991). In contrast, aromatic C-bound hydrogen is more susceptible to exchange due to the enhanced stability of aromatic systems and their ability to stabilize charged transition states. N, O, S-bound hydrogen is linked via weaker hydrogen bonds, making exchange very favourable.

The rate of exchange of hydrogen bound in alkyl moieties (i.e. part or portion of a molecule) depends on the extent of substitution of carbon atoms within the compound. For instance, compounds containing tertiary carbon atoms exchange their hydrogen atoms more easily and more rapidly than compounds containing secondary or primary carbon atoms (Figure 3.1). Although aliphatic C-bound hydrogen is often considered as 'non-exchangeable' hydrogen, a few reports describe aliphatic C-bound hydrogen exchange in model compounds under laboratory conditions. Alexander et al. (1984) heated meso-pristane with a deuterated clay (montmorillonite) catalyst at 160°C (670 h), and reported that approximately 60% of the total pristane (based on GC-MS analysis) was deuterated.

Based on ^{1}H NMR spectroscopic analysis, the same co-workers also reported that 40% of the methyl hydrogen, and 40% of methylene (secondary carbon) and methine (tertiary carbon) hydrogen were replaced by D. Estimated exchange half-lives were 2.1 and 1.5 years for primary and secondary hydrogen, respectively, which are much slower than those determined for naphthalene under comparable conditions (Alexander et al., 1982; Alexander et al., 1983; Sessions et al., 2004). Sessions et al. (2004) used compound-specific isotope-ratio mass spectrometry to examine *n*-icosane (n-C_{20}) incubated with heavy water (D_2O) on montmorillonite or silica under a range of temperatures. They reported exchange half-times ranging from ca. 10,000 years (at 60°C) to ca. 100,000 years (at 7°C), which are shorter than those reported for *n*-hexane (n-C_6) without a catalyst (Koepp, 1978). The faster exchange rate was attributed to the presence of a mineral catalyst. Larcher et al. (1986) studied alkyl hydrogen exchange in a series of acyclic isoprenoidal acids when heated at 160°C in the

presence of deuterated montmorillonite. GC-MS analysis of the methyl ester derivatives indicated that all of the isoprenoidal acids had undergone hydrogen exchange with water adsorbed on the clay surface, and exchange was most rapid at the carbon adjacent to the carboxyl group (Larcher et al., 1986).

The studies described above show that (i) aliphatic C-bound hydrogen can indeed undergo hydrogen exchange, although at significantly slower rates than aromatic C-bound and N,O,S-bound hydrogen; and (ii) the laboratory conditions under which alkyl hydrogen exchange has been observed in model compounds suggests that similar processes could occur in sedimentary organic matter during petroleum generation. The slower rate of exchange of C-bound hydrogen in aliphatic compounds is favourable to the measurement of δD values of hydrocarbons formed over geologic timescales, because the δD signature of their precursors are either preserved or only slightly altered, therefore allowing an assessment of the nature of their depositional environment.

A range of techniques have been used to artificially mature sedimentary organic matter. The techniques involve heating a sample in either an open or closed pyrolysis system. Artificial maturation experiments can also be performed under anhydrous or hydrous conditions. Hydrous experiments appear to more accurately reproduce the natural maturation process, and thus have been used more widely in D/H studies (Koepp, 1978; Hoering, 1984; Lewan, 1997; Schimmelmann et al., 1999; Leif and Simoneit, 2000; Sessions et al., 2004). It has been shown that water-derived hydrogen can exchange readily with aliphatic C-bound hydrogen during artificial maturation of sedimentary organic matter.

Published work on maturation in natural systems provides evidence of gradual D-enrichment of organic matter with increasing thermal maturity (Hoering, 1977; Rigby et al., 1981; Smith et al., 1982; Li et al., 2001). The effect of thermal maturation processes on the δD of individual hydrocarbons (regular isoprenoids and *n*-alkanes) have been recently studied (Dawson et al., 2005; Radke et al., 2005; Pedentchouk et al., 2006; Dawson et al., 2007). A large (ca. 115‰) biologically-derived offset between the δD values of *n*-alkanes and regular isoprenoids from immature sediments has been shown to gradually decrease with rising maturity, as the isoprenoids become enriched in D more

readily than the *n*-alkanes (Dawson et al., 2005). The D-enrichment in isoprenoids has been shown to correlate strongly with measured, calculated and equivalent (modelled) vitrinite reflectance (R_o, R_c, R_e, respectively), as well as other traditional molecular maturity parameters such as those based on biomarker ratios. This suggests that D/H exchange and the associated D-enrichment during maturation occurs, possibly via a mechanism involving carbocation-like intermediates (i.e. any cation containing an excess positive charge on one or more carbon atoms), which proceeds more rapidly with compounds containing tertiary carbon centres.

The potential of δD values of individual hydrocarbons (isoprenoids and *n*-alkanes) to estimate the thermal maturity of sedimentary organic matter warrants further investigation. A maturity indicator based on compound-specific δD values may prove useful in cases where traditional biomarker maturity parameters are ineffective, for example at high maturity levels (i.e. % R_o >1.0) or where their associated reactants and products either equilibrate, or are thermally degraded. In addition, such a maturity measurement could be applicable to pre-Devonian sediments, where vitrinite reflectance measurements cannot be made because the higher-plant precursors of vitrinite had not yet evolved. This paper reviews previous work that demonstrates systematic variation in D/H of individual compounds in sediments as a function of thermal maturity and extends the application of D/H of biomarkers to Devonian samples from the Duvernay Formation of the WCSB.

Materials and methods

Sample description and preparation

The Upper Devonian Duvernay Formation is an organic matter-rich basinal carbonate succession and one of the most prolific marine source rocks in the central Alberta region of the WCSB (Stoakes and Creaney, 1984; Creaney and Allan, 1990; Chow et al., 1995). The Duvernay Formation, in the central Alberta basin of the WCSB, exhibits a wide maturity range, from very immature in the

east to overmature in the west (Stoakes and Creaney, 1984). Samples in this study were taken from a number of different exploration wells covering a broad maturity range of the Duvernay Formation (Maslen et al., 2009). Table 3.1 shows the investigated source rock samples with their location, depth and Rock-Eval screening data. No vitrinite has been found in the studied sample set. The 8 Duvernay Formation sediment samples used in this study have TOC values ranging from 1.5 - 5.4% and HI values ranging from 55 - 591 mg HC/g TOC (Table 3.1). The thermal maturity of the source rock increases with depth with T_{max} values varying between 419° and 441°C. The sediment samples were surface-extracted using a solution of dichloromethane and methanol (9:1), and dried before grinding. The sediment samples were ground to a particle size of ≤150 µm using a ring-mill and were then extracted as described below.

Solvent extractions

The ground sediments were accurately weighed into pre-extracted stainless steel extraction automated accelerated solvent extractor (ASE) cells containing pre-rinsed glass-fibre filters. The samples were extracted using the ASE (ASE 200 Dionex, Sunnyvale, CA, USA) cells using the following method. The cells were preheated at 100°C (2 minutes). A mixture of dichloromethane and methanol (9:1) was pumped into the cells up to a pressure of 6895 kPa (1000 psi) for 5 minutes. The solvent residue was then purged with high-purity compressed nitrogen, flushing the solvent-extract from the cell into a collection vial. The entire procedure was repeated until the solvent in the collection vial became colourless. Finally, the solvent extracts were combined and the excess solvent was carefully removed under a nitrogen purge.

Locality	Depth (m)	TOC (wt.%)[a]	T_{max} (°C)[a]	HI (mg HC/g TOC)[a]	S_2 (mg/g)
Redwater	1147.3	5.4	419	591	31.7
Imperial Kingman	1402.7	2.7	426	410	11.06
Imperial Kingman	1404.5	3.2	426	432	13.88
Leduc	1766.9	3.6	434	465	16.5
Ferrybank	2239.5	4.0	437	273	0.99
Ferrybank	2248.7	3.3	437	247	8.17
Imperial Cynthia	2971.5	1.5	440	55	0.82
Imperial Cynthia	2973.7	4.2	441	303	12.7

[a]TOC, total organic carbon; HI, hydrogen index; T_{max}, determined temperature of maximum hydrocarbon generation during Rock-Eval pyrolysis

Table 3.1 Sample description, organic carbon (TOC %), Rock-Eval pyrolysis parameters of source rocks from the Duvernay Formation, WCSB. Samples are listed in order of increasing maturity (see Maslen et al. 2009 for further details).

Fractionation of sediment extracts using column chromatography

The extracts were fractionated using a large-scale liquid chromatographic method. The sediment extract was applied to the top of a large column (20 cm x 0.9 cm internal diameter) of activated silica gel (120°C, 8 hrs). The saturated fraction was eluted with *n*-hexane (35 mL), the aromatic hydrocarbon fraction with a solution of dichloromethane in *n*-hexane (40 mL, 30%), and the polar fraction with a solution of equal parts of dichloromethane and methanol (40 mL). Finally, the excess solvent was carefully removed under a nitrogen purge.

5A molecular sieving

Straight chain hydrocarbons were separated from branched and cyclic hydrocarbons by treating the saturated fractions with activated (250°C, 8 hrs) 5A molecular sieves (Murphy, 1969; Dawson et al., 2005; Grice et al., 2008) in cyclohexane. In a typical 5A molecular sieving separation, a portion of the saturate fraction in cyclohexane was added to a 2 mL vial ¾ full of activated 5A molecular sieves. The vial was capped and placed into a pre-heated aluminium block (85°C, overnight). The resulting solution was then cooled and filtered through a small column of silica (pre-rinsed with cyclohexane), and the sieves were rinsed thoroughly with cyclohexane yielding the branched/cyclic fraction (5A excluded). The *n*-alkanes were obtained by dissolving the sieve with HF acid as described by Grice et al. (2008).

Gas chromatography - mass spectrometry (GC-MS)

GC-MS analyses were performed on a Hewlett Packard (HP) 5973 interfaced to a HP 6890 gas chromatograph containing a 60m x 0.25mm internal diameter WCOT fused silica capillary column coated with a 0.25µm thick film (DB-5, J&W Scientific). The GC oven was programmed from 40°C to 310°C at 3°C/min with initial and final hold times of 1 and 30 minutes, respectively. Samples (in *n*-hexane) were injected (split/splitless, pulsed splitless mode) using a HP 6890 series autosampler. The carrier gas used was ultra high-purity helium at a constant flow of 1mL/min.

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

Compound specific isotope analyses (CSIA) of samples were carried out on a Micromass IsoPrime isotope ratio mass spectrometer coupled to a HP 6890 gas chromatograph (GC-ir-MS), utilizing a column identical to that used for GC-MS analysis (see above). For the external organic reference standards, the GC oven was programmed from 50°C to 310°C at 10°C/min with initial and final

hold times of 1 and 10 minutes, respectively. δD was calculated by integration of the *m/z* 2 and 3 ion currents of the hydrogen peaks produced by pyrolysis of the GC-separated compounds using chromium powder catalyst maintained at 1050°C. Contributions to *m/z* 3 from H_3^+ ions produced in the ion source were corrected (see Dawson, 2007 for details). δD values of individual compounds in the samples was calculated relative to that of reference gas pulses produced by allowing H_2 gas of a known D/H into the ir-MS. Reported values are the average and standard deviations of three to five analyses. δD are given in the delta notation in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW). Precision and accuracy of the instrument was determined daily via the analysis of a series of reference compounds.

Review of previous studies

It is generally accepted that maturation of organic matter during burial affects its stable carbon and hydrogen isotopic composition (e.g. Peters and Moldowan, 1993 and references therein). Other than source effects, temperature and time, in other words thermal maturity, are the primary factors driving these isotopic shifts (Seewald, 2001). D-enrichment with increasing thermal maturity is thought to be a result of hydrogen exchange with formation waters, which in most cases are significantly enriched in D relative to the organic hydrogen in sediments (Schoell, 1984).

Carbon isotope studies preceded hydrogen isotope studies for two pertinent reasons. First, analytical techniques in the past have experienced difficulties in measuring stable hydrogen isotopes. Second, conceptual difficulties exist in interpreting the δD results due to the fact that hydrogen in certain positions may undergo rapid exchange with a variety of hydrogen sources in the surrounding environment. However, recent developments of (1) a method for CSIA of hydrogen and (2) the laboratory standards for controlling the isotopic composition of easily exchangeable hydrogen in bulk organic samples have changed the situation, enabling geochemists to better understand hydrogen

isotopic changes accompanying the thermal maturation history of sediments through geological time.

In the present paper, we provide a comprehensive literature review, focussing on variations in δD values of sediment extracts, crude oils (including bulk organic matter and hydrocarbon fractions as well as individual *n*-alkanes and isoprenoids) and kerogen. Table 3.2 presents a summary of the sample details and their key parameters such as age, source, thermal maturity and corresponding range of δD values for each study. In a following section, we test the application of D/H of hydrocarbons as a maturity parameter with new data from Devonian source-rocks in the WCSB, extending the application of D/H measurements to much older sediments (i.e. Devonian) than previously studied.

Earlier Studies

Early studies on the distribution of D/H in coals and crude oils began with Schiegl and Vogel (1970), Redding (1978) and Schoell and Redding (1978). Schiegl and Vogel (1970) reported δD values from -140‰ to -127‰ for 19 samples of South African coals and from -112‰ to -92‰ for 6 German coals although no thermal maturity data were provided (Table 3.2). Redding (1978) recorded a wider range of δD values, from -154‰ to -65‰, for 24 coals of different origins and for a wide interval of thermal maturity, from 0.25% to 4.8% R_o. Schoell and Redding (1978) examined 26 crude oils of Ordovician to Late Tertiary age that yielded δD values from -160‰ to -90‰. They found enrichment in D with age in the bulk oils and within each series of saturated, aromatic and NSO hydrocarbon fractions. Hoering (1977) studied 11 whole oils and oil fractions with source rock ages from the Pliocene to the Precambrian and they found that organic matter in older samples had a tendency to be enriched in D.

Sample	Age	Thermal Maturity	Summary	Reference
South African coals	Permo- Carboniferous	not available	δD from -127‰ to -147‰ different climate conditions during deposition	Schiegl & Vogel ,1970
German & Netherland coals	Middle Carboniferous	not available	δD from -92‰ to -112‰ different climate conditions during deposition	Schiegl & Vogel, 1970
Coals from different origins & ranks	Unknown	Ro: 0.25%-4.8%	δD from -65.2‰ to -153.8‰	Redding, 1978
Crude oils	Ordovician- Late Tertiary	not available	δD from -90‰ to -160‰ increase in δD with age & increase through the series, saturate, aromatics & NSO compounds	Schoell & Redding, 1978
Crude oils and fractions	Precambrian-Pliocene	not available	older samples found to tend to be enriched in δD	Hoering, 1977
Kerogens from marine sediments	Unknown	Ro: 0.25%-2.5%	kerogen δD increases by 70-150 ‰ with maturity	Simoneit et al., 1978
Oils & alkane extracts, Australian coals	Cretaceous- Late Tertiary	not available	δD values increasing with depth	Rigby et al., 1981
Marine kerogens	Unknown	not available	kerogens near a dike intrusion are D-enriched	Simoneit & Mazurek, 1981
Australian coals, macrolithotypes	Permian-Miocene	Ro: 0.7%-1.04%	increase in δD values with increasing maturity	Smith et al., 1982
Coal lignite seam, Germany	Tertiary	Ro: 0.29%-2%	δD values of coals increases from -120‰ to -94 ‰ by contact metamorphism	Redding et al. 1980; Schoell 1984
Type-I, -II & -III kerogens	unknown	Ro: I 0.7-1.39%, II 2.1-2.5%, III 0.35-2.81%	all kerogen types show D enrichment with increasing maturity	Redding et al., 1980; Schoell, 1984
Coals occurring world-wide	unknown	not available	Gondwana coals with δD -135‰ to -170‰, American and European coals with δD -90‰ to -140 ‰, large hydrogen isotopic variations-primary, source controlled	Redding et al,. 1980

Sample	**Age**	**Thermal Maturity**	**Summary**	**Reference**
Crude oils and fractions from Viking Fm, WCSB	Cretaceous	not available	δD values increasing with depth for all fractions except NSO fractions	Schoell, 1984
Condensates	unknown	Ro: 0.5%-1.5%	δD values increasing with maturity	Schoell, 1984
Type-III kerogen, saturate, aromatic and NSO fractions, Mahakam Delta	Miocene	T_{max} 414-458°C	δD values increasing both in kerogen & in all the fractions with maturity	Schoell et al., 1983
Type-II and -III kerogen, saturate, aromatic, NSO fractions, North Sea	Jurassic	not available	δD values increasing in all the fractions with depth	Schou et al., 1985
Jurassic oils & saturate fractions	Jurassic	increasing maturity w/biomarker data	δD values vary around -78‰ ± 6‰ in oils and in sat fractions	Baker, 1987
Bitumen, Kupferschiefer Fm, Germany	Permian	not available	increase in δD values in bitumen near the intrusive body	Bechtel & Puttmann, 1992
Oils, condensates, saturate, aromatic fractions, NE Japan	unknown	oil window by biomarker data	δD values increasing with maturity except aromatic fractions	Waseda, 1993
Oils from lacustrine, marine-evaporitic & mixed source, Potiguar Basin, Brazil	Cretaceous	Oil window by biomarker data	At low levels of thermal maturity, 3 different paleoenvironments distinguished by their δD values (lacustrine -90‰, mixed -110‰, marine-evaporitic -120‰ to -135‰) with increasing thermal maturity, δD values converge around -110‰. Unique study showing decrease in δD values by increasing maturity	dos Santos Neto & Hayes, 1999

Sample	Age	Thermal Maturity	Summary	Reference
Oils, condensates, bitumens, asphaltenes, maltenes, Ukraine	unknown	Oil window	δD values increasing with maturity in older samples	Lukin, 1999
Type-I, -II, -II-S and -III kerogens (I-Green River Fm, Utah; II-New Albany Shale, Indiana IIS-Ghareb limestone, Jordan; III-Lignite in Wilcox Group, Texas)	(I- Eocene, II-Devonian-Mississipian IIS-Senonian, III-Paleocene)	Thermal maturation simulation	hydrogen in kerogen, bitumen, and expelled oil from most to least isotopically influenced by water-derived hydrogen in the order IIS>II≈III>I	Schimmelmann et al., 1999
n-alkanes & acyclic isoprenoids by CSIA in oils, WCSB	Ordovician-Cretaceous	Increasing maturity with biomarker data	δD values increasing for all *n*-alkanes with increasing maturity of the oils	Li et al., 2001
Type-II-S kerogens, Monterey Fm, Canada	Miocene	Ro: 0.23%-0.33% & 0.29%-0.42%	More mature kerogens are enriched in δD by ~40‰ relative to less mature kerogens	Schimmelmann et al., 2001
Oils, saturate, aromatic, nso fractions, *n*-alkanes (CSIA), kerogen, terrigenously sourced oils in Australia	Early Permian-Late Eocene	not available	Isotopic exchange in δD values is limited to the aromatic fractions not aliphatic fractions In oils derived from a single source, whole oil, fractions and *n*-alkanes have similar δD values δD increasing with carbon number in n-alkanes	Schimmelmann et al., 2004
n-alkanes and isoprenoids (CSIA) from bitumen and oils, Perth Basin, Australia	Early Triassic	Ro: 0.53-1.13% based on biomarkers	δD values of isoprenoids increase by ~150‰, n-alkanes by ~42‰ with increasing maturity	Dawson et al., 2005

Sample	Age	Thermal Maturity	Summary	Reference
n-alkane and isoprenoids (CSIA), Kupferschiefer and Posidonia Fm, Germany	Late Permian and Early Jurassic	Ro: 0.48-1.3% based on MPI	δD values increases with maturity, more for isoprenoids	Radke et al., 2005
n-alkanes (CSIA), terrigenous source rocks, China	Permian-Oligocene	not available	δD values from terrigenous source rocks vary between -140 to -250‰, and more negative than marine n-alkanes. Depletion in D values for n-alkanes in the order of saline lacustrine to freshwater lacustrine and to swamp	Xiong et al., 2005
Type-II and -III kerogens New Albany Shale & Exshaw Fm	Devonian-Mississippian	Ro: 0.3-3%	δD values increases with maturity up to Ro~1.8%	Lis et al, .2006
n-alkanes, isoprenoids, kerogen, Gabon basin, West Africa	Early Cretaceous	Ro: 0.55-0.7%	δD values of isoprenoids increase dramatically to similar values of n-alkanes at Ro 0.7% Kerogen and n-alkanes change slightly	Pedentchouk et al., 2006
n-alkanes and isoprenoids (CSIA) in bitumen and oils Vulcan Sub-basin, Northern Australia	Late Jurassic	Ro: 0.7-1.6%	δD values increases with maturity, both for n-alkanes and more for isoprenoids	Dawson et al., 2007

Table 3.2 A summary of δD measurements made on sediments and oils of varying maturity and age (Modified after Schimmelmann et al. (2006)

Simoneit et al. (1978) demonstrated the effect of maturation on the δD values of kerogens from marine sediments, presenting δD values of kerogens that increase from -150‰ to -70‰ with increasing maturity over a R_o range of 0.25% to 2.5%. Schoell et al. (1983) observed that type III kerogen, and associated saturated, aromatic and NSO fractions all trend towards more positive values in Miocene sediment samples from the Mahakam Delta (Indonesia) with increasing burial depth. δD values of kerogen and extractable fractions from the North Sea (Schou et al., 1985) and extracts from Australian coals (Rigby et al., 1981) show similar patterns.

These patterns are repeated in the δD values of specific organic compounds. Li et al. (2001) measured the δD values of individual *n*-alkanes and regular isoprenoids from a number of crude oils from the WCSB. The *n*-alkanes from a marginally mature crude oil displayed a range from -155‰ to -120‰ (averaging -134‰), while pristane and phytane gave δD values of -188‰ and -168‰, respectively (averaging -178‰). The *n*-alkanes, pristane and phytane were found to be more enriched in D in the more mature crude oil relative to respective δD values from the less mature crude oil. The *n*-alkane δD values range from -144‰ to -136‰, respectively (averaging -140‰) in the less mature crude oil and pristane and phytane δD values range from -131‰ to -97‰ (averaging -110‰) in the more mature crude oil. These data show trends consistent with the results obtained in this study and other reviewed literature.

Other studies, however, have documented a lack of isotopic trends in the organic matter with thermal maturity. For example, Baker (1987) investigated a suite of Jurassic oils and their saturate fractions, where δD values varied around -78‰ ± 6‰ regardless of maturity. Schimmelmann et al. (1999) later attributed these values to the organic matter being relatively enriched in D prior to maturation (δD values > -100‰).

Studies of δD in *n*-alkanes and isoprenoids – six studies

The effect of thermal maturation sedimentary processes on the δD values of individual petroleum hydrocarbons (*n*-alkanes and isoprenoids) over

geological timescales has only recently been explored. Studies of 6 different sedimentary sequences have been published to date: Perth Basin (marine, Western Australia, Dawson et al., 2005); Vulcan Sub-basin (two data sets, marine, northern Australia; Dawson et al., 2007); Kissenda Formation, (lacustrine, Gabon Basin; Pedentchouk et al., 2006); Poland (marine, Kupferschiefer; Radke et al., 2005); and Germany (marine, Posidonia Shale; Radke et al.; 2005). These 6 data sets cover a range of thermal maturities from 0.53%–1.6% R_o and ages from the Lower Cretaceous to the Permian.

Perth Basin, Australia

Comprehensive organic geochemical studies of sediments from the Lower Triassic marine Kockatea shale in the Perth Basin have been carried out by Thomas and Barber (2004) and Grice et al. (2005a; 2005b), including Rock-Eval pyrolysis, distributions of biomarkers and thermal maturity estimates. The Hovea member of the Kockatea shale is classified as a type II organic matter-rich source-rock (Thomas and Barber, 2004). Due to the problems associated with the direct measurement of vitrinite reflectance (% R_o) of sediments from the Kockatea Shale (Kantsler and Cook, 1979), Thomas and Barber (2004) calculated equivalent vitrinite reflectance values (% R_e) for the samples using basin-wide burial history modelling. The Perth Basin sediments span thermal maturities from immature to late mature (% R_e = 0.53 to 1.13) and have $Ts/(Ts+Tm)$ values (a maturity parameter based on the 18α(*H*)- and 17α(*H*)- trisnorhopanes; Seifert and Moldowan, 1981) ranging from 0.25 to 0.89 (Table 3.3).

The range of δD values of *n*-alkanes (from C_{12} to C_{32}), and the δD values of pristane and phytane from extracts of the Perth Basin sediments were reported by Dawson et al. (2005) and are summarized in Table 3.3. The ΔδD values were determined by subtracting the average δD value of the *n*-alkanes from the average δD value of pristane and phytane. Figure 3.2 shows average δD values of the *n*-alkanes, and the δD values of pristane and phytane versus depth in sediments obtained from the Perth Basin. Both *n*-alkanes and isoprenoids show clear trends of D-enrichment with depth, with the rate of enrichment more rapid in isoprenoids than in *n*-alkanes. δD values of *n*-alkanes from extant plants vary

from –187‰ to –152‰ representing the different photosynthetic assimilation processes (C3, C4 and CAM) and plant classes (e.g. Chikaraishi and Naraoka, 2001). δD values of phytol in aquatic plants and flagellates range from -278‰ to -357‰, respectively (Sessions et al., 1999).

Well, Depth m	R_e (%)	*Ts/(Ts+Tm)*	*n*-Alkanes δD Range (‰)*	δD Pr (‰)*	δD Ph (‰)*	ΔδD (‰)
BMR 10 973–976	0.53	0.30	-183 to -128 (13)[4]	-267 (7)[5]	-249 (4)[5]	-115
BMR 10 989–991	0.53	0.25	-188 to -130 (8)[5]	-278 (3)[3]	-266 (1)[3]	-116
Dongara 4 1674	0.60	0.32	-175 to -140 (8)[5]	-217 (3)[5]	-185 (0)[3]	-43
Dongara 4 1675	0.60	0.34	-157 to -112 (6)[5]	-208 (6)[5]	-166 (7)[5]	-55
Dongara 4 1678	0.60	0.38	-165 to -116 (5)[4]	-175 (6)[5]	-168 (2)[3]	-29
Yardarino 2 2289	0.78	0.76	-146 to -109 (8)[3]	-153 (3)[3]	-144 (1)[3]	-23
Yardarino 2 2290	0.78	0.79	-166 to -123 (7)[3]	-159 (7)[3]	-141 (3)[3]	-6
Arrowsmith 1 2494	1.13	0.89	-145 to -80 (4)[3]	-102 (16)[3]	-97 (16)[3]	3 (0)
Arrowsmith 2678	1.13	0.80	-123 to -73 (3)[3]	-121 (4)[3]	-108 (4)[3]	-19

ΔδD, difference between the average δD value of Pr and Ph and the average δD value of the *n*-alkanes (relative to VSMOW); * Numbers in parenthesis are standard deviations (average is shown for *n*-alkanes), superscript numbers are number of replicate analyses. R_e calculated vitrinite reflectance values (Thomas and Barber, 2004). *Ts*/(*Ts*+*Tm*), a maturity parameter based on the 18α(*H*)- and 17α(*H*)-trisnorhopanes.

Table 3.3 δD values of *n*-alkanes, pristane (Pr) and phytane (Ph), and corresponding ΔδD values (see below for definition) for the Perth Basin sediment extracts of the Kockatea shale (Dawson et al. 2005).

A large (ca. 115‰) biologically-derived offset between the δD values of *n*-alkanes from extant plants and δD values of phytol (i.e. lipid side chain of

chlorophyll *a* is a precursor of phytane) have been observed between the δD values of *n*-alkanes and pristane and phytane from immature sediments (Dawson et al., 2005; 2007). This large offset gradually decreases with increasing maturity, as the isoprenoids become enriched in D more rapidly than the *n*-alkanes.

The D-enrichment in isoprenoids correlates strongly with R_e and traditional molecular maturity parameters. Figure 3.2 also clearly shows that the change in δD values of pristane and phytane with depth, and their similar rates of D-enrichment suggest they probably exchange hydrogen at similar rates.

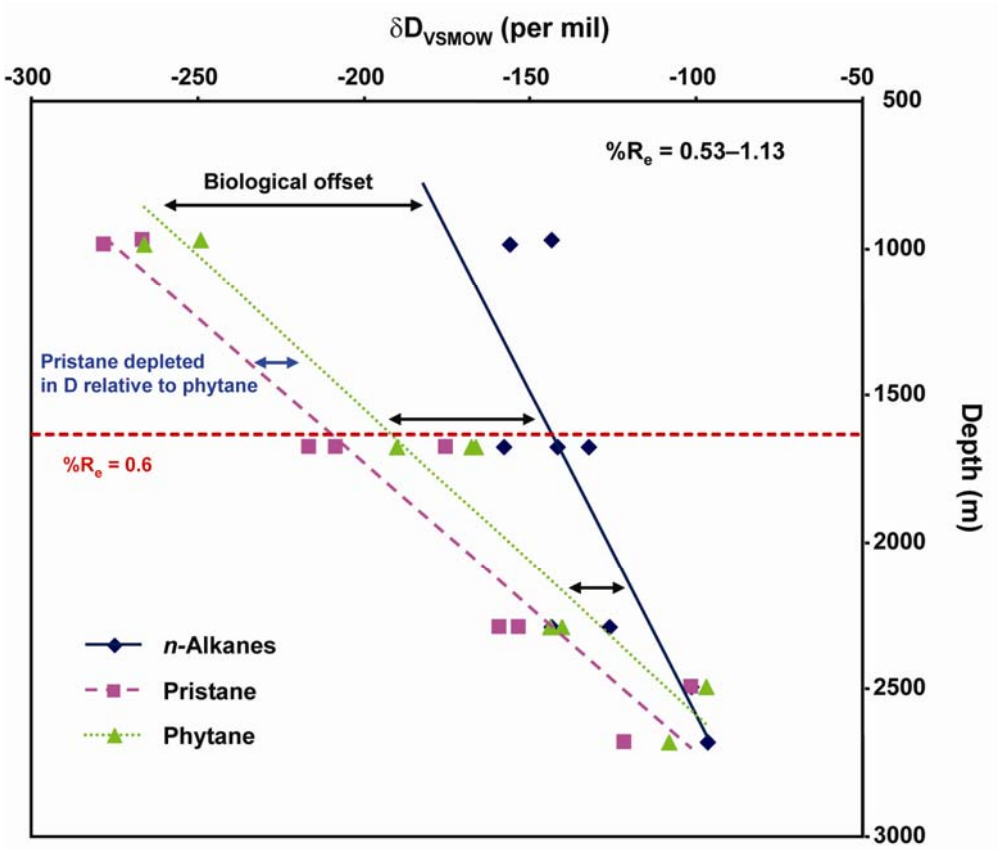


Figure 3.2 Average δD values of *n*-alkanes, and the δD values of pristane and phytane versus burial depth in extracts from Perth Basin sediments (Dawson et al., 2005).

It is possible (although unlikely) that the *n*-alkanes and isoprenoids exchange hydrogen at similar rates, and that the observed changes in their δD values with maturation is a result of the extent to which the compounds are out of isotopic equilibrium with formation water, which is typically enriched in D.

In relatively immature samples, pristane and phytane are on average much further away from the point of isotopic equilibrium than *n*-alkanes, because the isoprenoids' biological precursors are significantly more depleted in D compared to the precursors of the straight chain hydrocarbons. Therefore, for a given increment in hydrogen exchange, there would be a larger change in the δD value of the isoprenoids compared to that of the n-alkanes, even though the two compound classes are hypothetically exchanging hydrogen at the same rate (Dawson, 2007). This concept is illustrated in Figure 3.3.

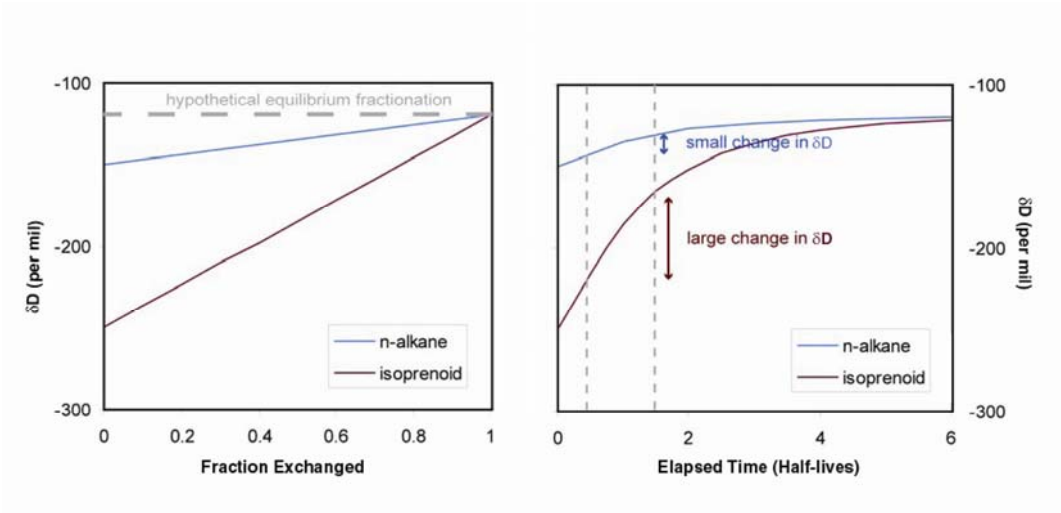


Figure 3.3 Modelled trends for (a) δD value versus fraction of total hydrogen exchanged, and (b) δD value versus elapsed time (half-lives) for an *n*-alkane and an isoprenoid (Dawson et al., 2007), A.L. Sessions, pers. comm.).

Vulcan Sub-basin, Australia

Comprehensive organic geochemical studies on sediment samples from the Paqualin-1 and Vulcan-1B wells (Upper Jurassic, Lower Vulcan Formation) in the Vulcan Sub-basin (Timor Sea, northern Australia) have been carried out by Smith and Sutherland (1991), van Aarssen et al. (1998a; 1998b) and Edwards et al. (2004). Smith and Sutherland (1991) and Edwards et al. (2004) reported Rock-Eval pyrolysis and R_o results. The Lower Vulcan Formation, intersected by the Paqualin-1 and Vulcan-1B wells, is classified as a type II/III source-rock. The Paqualin-1 sediments range in maturity from early mature to over-mature, with measured R_o from 0.62% to 1.6% and T_{max} values from 441°C to 455°C. The Vulcan-1B sediments cover a maturity range from early mature to post mature (% R_o = 0.69 to 1.3).

These sediments were analysed to study the effect of maturation on the δD values of individual hydrocarbons from sedimentary sequences, extending the original work of Dawson et al. (2005) on the Perth Basin to a higher level of maturity. The δD values of *n*-alkanes in extracts from the Paqualin-1 sediments average between -136‰ and -108‰, and the *n*-alkanes in extracts from the Vulcan-1B average between -146‰ and -110‰ (Figure 3.4a). The δD values of *n*-alkanes extracted from the sediments of lowest maturity are consistent with a source from the marine mudstones of the Lower Vulcan Formation, while the samples of higher maturity contain *n*-alkanes more enriched in D. The δD values of pristane and phytane in the Paqualin-1 samples average between -165‰ and -68‰, and in Vulcan-1B between -166‰ and -105‰ (Figure 3.4). It was reported that the Paqualin-1 sediments below ~3159 m seem to be relatively more mature than is reflected by their R_o values, based on a significant enrichment of D (ca. 21‰) in pristane and phytane relative to *n*-alkanes, signifying that the available R_o data do not accurately reflect maturity in this particular case (Dawson et al., 2007). Pristane and phytane are more rapidly enriched in D with ongoing maturation, similar to that observed in the Perth Basin sediments of Dawson et al. (2005). Pristane and phytane from post-mature Paqualin-1 sediments (% R_o = 1.6) are significantly enriched in D (ca. 40‰) relative to the *n*-alkanes.

This result indicates that D-enrichment continues at extremely high maturity, and continues to be more rapid for regular isoprenoids than *n*-alkanes. Published equilibrium fractionation factors between C-bound hydrogen and water for primary, secondary and tertiary C-H (Sessions et al., 2004 and references therein) do not allow for isoprenoids to be enriched in D relative to *n*-alkanes. However, the data presented by Dawson et al. (2007) indicate that the δD values of isoprenoids can, in fact, be more positive than *n*-alkanes.

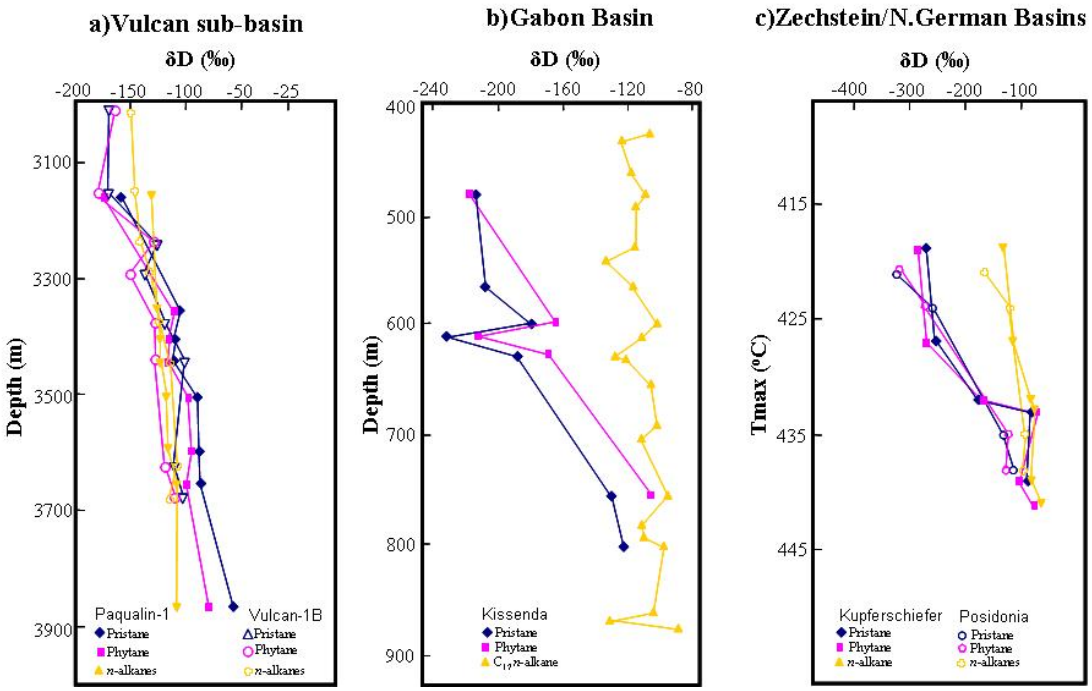


Figure 3.4 δD values of isoprenoids and *n*-alkanes with depth and T_{max} (°C). Data have been replotted from a) Dawson et al. (2007), where R_o varied from 0.62% to 1.6% and T_{max} from 441 to 455°C in the Paqualin-1 and R_o varied from 0.69% to 1.3% and T_{max} from 430 to 441°C in the Vulcan-1B well; b) Pedentchouk et al. (2006); c) Radke et al. (2005); no depth data were available from the Zechstein and North German Basins.

Gabon Basin, Africa

Samples from the well ONEZ-1, Lower Cretaceous, Gabon Basin represent a 450m thick section in the Kissenda Formation (Neocomian), covering about 7 million years of lacustrine deposition (Pedentchouk et al., 2006). The kerogen from most of the samples is classified as type I, based on Rock-Eval pyrolysis. Both bulk and biomarker indicators show an increase in organic matter thermal maturity (based upon $22S/(22S + 22R)C_{31}$ homohopanes (the value of 0.6 for this ratio is equivalent to R_o=0.6 (Peters and Moldowan, 1993)), $20S/(20S + 20R)$ C_{29} steranes (0.4, R_o = 0.6), and $Ts/(Ts + Tm)$ (0.5, R_o = 0.6) ratios, with depth from immature to early mature. The onset of oil generation was estimated to occur at a depth of 750m to 800m in this section (Pedentchouk et al., 2006).

The distribution of δD values of *n*-C_{17}, pristane and phytane from the Kissenda Formation, from a depth interval covering a thermal maturity range from immature to early mature, is shown in Figure 3.4b. This study reported changes in δD values of *n*-alkanes and isoprenoids against δD of kerogen through the transition from thermally immature to early mature organic matter. Substantial differences in δD values (up to 40‰ for *n*-C_{17}, up to 30‰ for *n*-C_{29} and up to 10‰ for bulk kerogen) were evident from one sample to the next throughout the ONEZ-1 well. However from the top of the well to the bottom, in general, δD values of individual *n*-alkanes showed a slight D-enrichment with depth and/or maturity. A general trend of increasing δD values with increasing *n*-alkane chain length was an interesting feature observed for all the samples. The δD values of kerogen samples were found to overlap with the δD values of *n*-alkanes; this was attributed to the kerogen being preferentially enriched in D due to its overall higher susceptibility to H-transfer in comparison with saturated hydrocarbons (Schimmelmann et al., 1999). The largest δD offset (100 ‰) between the *n*-alkanes and isoprenoids is observed in the upper section of the core, due to the δD values of the isoprenoids being more greatly affected by hydrogen exchange than the *n*-alkanes due to the greater extent of preservation of δD values at the shallower burial depth resulting from a lower thermal maturity.

Zechstein and Northern German Basins, Europe

Two stratigraphic sections from northern Europe with different thermal histories were investigated by Radke et al. (2005): the Permian Kupferschiefer from the Zechstein Basin; and the Lower Jurassic Posidonia Shale, from the Vlotho Massif, Northern German Basins. Kupferschiefer samples come from the Lower Permian Basal Zechstein "Kupferschiefer" horizon of the barren-zone, NE Poland Zechstein Basin (Bechtel et al., 2000). Both sedimentary sequences contain type II algal kerogen. Samples from the two sequences represent a range of thermal maturity from 0.48 to 1.3% R_o, determined by vitrinite reflectance measurements and equivalent reflectance values calculated from the methylphenanthrene index. Thermal maturation of the Kupferschiefer horizon from the Early Zechstein Basin of Poland was associated with burial, while the Posidonia Shale experienced contact metamorphic thermal maturation related to a magmatic intrusion during the Lower Cretaceous.

The δD values of individual alkanes and isoprenoids in the Kupferschiefer samples range from -198‰ to -53‰ and -281‰ to -84‰, respectively. The δD values of the *n*-alkanes and isoprenoids show a positive correlation with thermal maturity (Figure 3.4c). D-enrichment in isoprenoids, in particular, correlates strongly with traditional molecular maturity parameters, for example the methylphenanthrene index (0.4 to 1.5 MPI-1). The mean δD values of phytane and pristane range between -275‰ in the immature and to -147‰ in the mature Kuperschiefer samples (Figure 3.4). The D enrichment in the alkanes is +45‰ from the immature to the mature sample. Consistent with the earlier work of Dawson et al. (2005), again the rate of enrichment of δD with increasing maturity is more rapid for the isoprenoids than for the *n*-alkanes.

The δD values of alkanes from Posidonia sediments vary between -204‰ and -76‰. The D enrichment in the alkanes is +67‰ from the immature to the mature sample (Figure 3.4). In the Posidonia shales, the δD values of isoprenoids are between -317‰ and -123‰ in immature and mature samples, respectively. Different timescales and temperature regimes during burial of sediments in the Kupferschiefer and Posidonia Shale probably led to different hydrogen isotope fractionations within the same compound class.

Results from the Duvernay Formation, Western Canada Sedimentary Basin

Devonian strata include extremely important sources of hydrocarbons in the WCSB, accounting for 55% of oil reserves and 27% of gas reserves in that basin (Fowler et al., 2001). The Upper Devonian Duvernay Formation, part of the Late Devonian Woodbend Group in central Alberta of the WCSB, has excellent hydrocarbon source potential and is a major source for oil and gas in the basin (Stoakes and Creaney, 1984, 1985; Creaney and Allan, 1990; Chow et al., 1995). Comprehensive organic geochemical characteristics of sediments from the Duvernay Formation are reported by Creaney and Allan (1992) and Requejo et al. (1992). The Duvernay Formation maturity increases from very immature in the east to overmature in the west in central Alberta of the WCSB (Stoakes and Creaney, 1985).

The range of δD values of *n*-alkanes and the δD values of pristane and phytane from extracts of the Duvernay Formation sediments are shown in Figure 3.5 and summarized in Table 3.4 (including the number of individual analyses, range and standard deviation for each sample). The δD values of *n*-alkanes (n-C_{10} to n-C_{32}) in extracts from the Duvernay Formation sediments average between -163‰ and -92‰. The δD values of pristane and phytane in the Duvernay Formation samples range between -260‰ and -116‰ and between -282‰ and -103‰, respectively. Figure 3.5 shows a clear linear relationship of D-enrichment in isoprenoids and *n*-alkanes with increasing thermal maturity, represented by the T_{max} parameter. The δD values of pristane and phytane change at similar rates with increasing maturation, suggesting they exchange hydrogen at similar rates. The difference between the δD values of *n*-alkanes and isoprenoids gradually decreases with thermal maturity (Table 3.4). While pristane and phytane become more rapidly enriched in D with increasing maturity, *n*-alkanes are less rapidly enriched in D (if at all) until a relatively more mature stage is reached. The outcomes of demonstrating a correlation between D/H of biomarkers and maturity parameters for Devonian source-rocks from WCSB shows a strong link to the previous work.

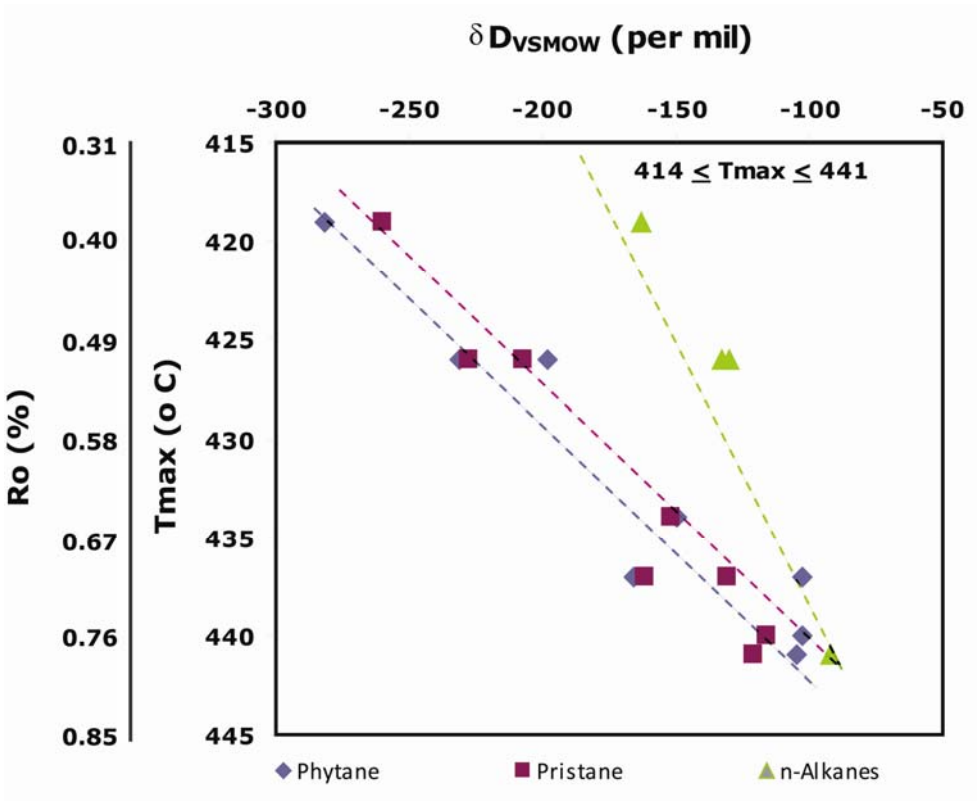


Figure 3.5 Average δD values of pristane, phytane and *n*-alkanes versus thermal maturity (T_{max}°C) in samples from the Duvernay Formation, WCSB. (The formula for deriving R_o, vitrinite reflectance from T_{max} is $R_o(\%)=(0.0180*T_{max})-7.16$ and is taken from Jarvie et al., 2001).

Sample, Depth m	T_{max} (°C)	δD Pr (‰)	δD Ph (‰)	average δD *n*-alkanes (‰)	ΔδD (‰)
G000542, 1147.3	419	-260 (7)[3]	-282 (5)[3]	-163	-108
G000584, 1402.7	426	-228 (13)[3]	-231(29)[3]	-130	-100
G000587, 1404.5	426	-207 (5)[2]	-198 (0)[2]	-133	-75
G000553, 1766.9	434	-152 (1)[3]	-150 (0)[3]	n.d.	n.d.
G000595, 2239.5	437	-162 (7)[3]	-166 (11)[3]	n.d.	n.d.
G000599, 2248.7	437	-131 (7)[3]	-103 (4)[3]	n.d.	n.d.
G000601, 2971.5	440	-116 (1)[2]	-103 (2)[2]	n.d.	n.d.
G000603, 2973.7	441	-121 (6)[3]	-105 (8)[3]	-92	-21

Superscript numbers are number of replicate analyses; numbers in brackets are standard deviations; ΔδD, difference between the average δD value of Pr and Ph and the average δD value of the *n*-alkanes (relative to VSMOW), n.d. not determined

Table 3.4 δD values of pristane (Pr), phytane (Ph) and *n*-alkanes for the WCSB (Duvernay Formation) sediment extracts.

Discussion

The δD values of individual hydrocarbons (*n*-alkanes and isoprenoids) can be used to estimate the thermal maturity of sedimentary organic matter from source-rocks. The application of D/H of individual hydrocarbons as a maturity parameter for Devonian source-rocks from WCSB has been presented here, extending the application of D/H measurements to much older sediments than previously studied. Figure 3.6 shows a plot of T_{max} against the ΔδD values (determined by subtracting the average δD value of the *n*-alkanes from the average δD value of pristane and phytane) for the several sedimentary sequences discussed in this review (Vulcan Sub-basin, Zechstein Basin, Northern German Basin and WCSB). A good correlation is evident (R^2=0.74), even though this data set includes sediments of different age, facies and source-rock/kerogen type. It is clear that ΔδD values provide a good approximation of thermal maturity of sediments. These systematic hydrogen isotopic trends with thermal maturity can provide an estimate of thermal maturity in cases where none of the traditional parameters can be used.

Investigating mechanism(s) of hydrogen exchange

Fundamental chemical principles, together with observations of stereochemical changes occurring during thermal maturation, provide insight into possible thermally-induced mechanisms by which organic matter in the sedimentary environment might exchange hydrogen with its surrounding water, resulting in D-enrichment. *n*-alkanes and the isoprenoids pristane and phytane are quantitatively the most significant hydrocarbon components of crude oils. While they belong to a similar compound class (alkanes), *n*-alkanes and regular isoprenoids exhibit some fundamental chemical differences that result in significantly different behaviours during various types of chemical reactions. The *n*-alkanes are straight-chain hydrocarbons containing only primary (methyl) and secondary (methylene) carbon atoms (Figure 3.1). Regular isoprenoids, however, also contain tertiary (methine) carbon atoms. Some chemical

processes, for example carbon-carbon bond cleavage, occur more readily at tertiary carbon atoms due to the ability of additional alkyl substituents to stabilize charged transition states (e.g. carbocations or radicals) through inductive and resonance effects. For this reason, hydrogen exchange readily occurs at tertiary carbons, and even more readily at carbon atoms adjacent to the tertiary centres (e.g. Alexander et al., 1984).

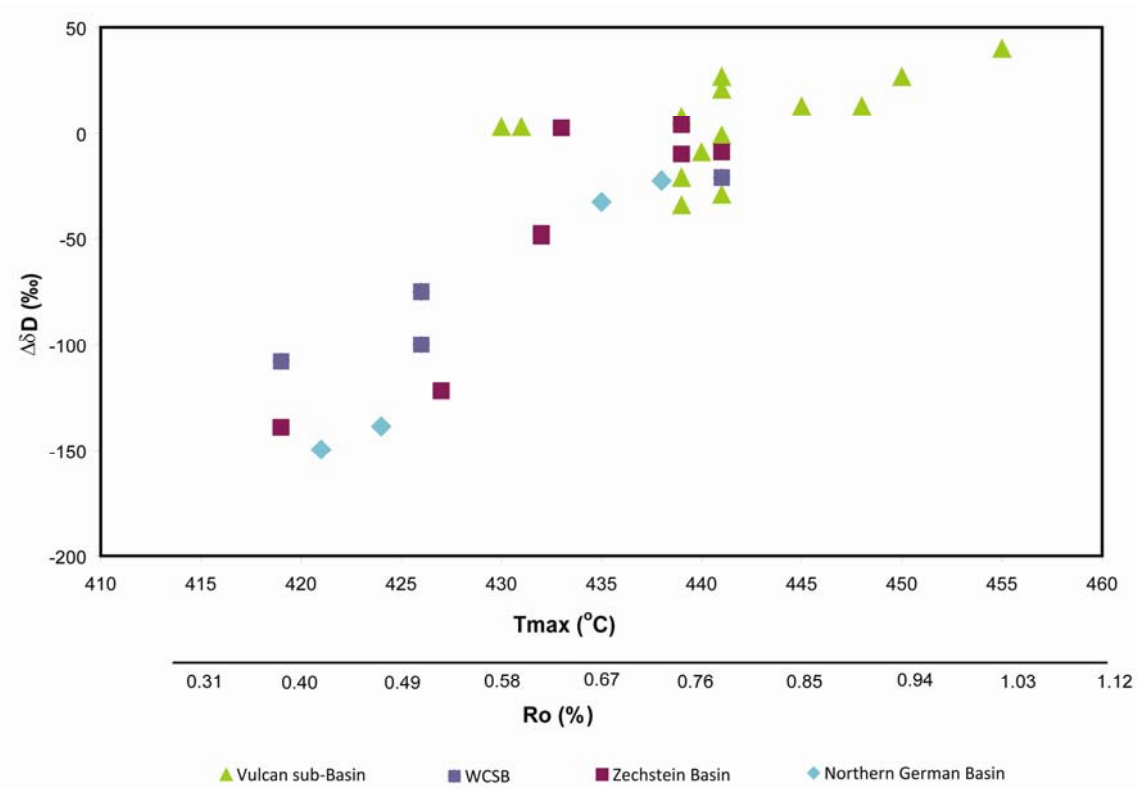


Figure 3.6 Combined results ΔδD vs T_{max} (°C) for several sedimentary basins. (ΔδD is the difference between the average δD value of pristane and phytane and the average δD value of *n*-alkanes), (The formula for deriving R_o, vitrinite reflectance from T_{max} is R_o (%)=(0.0180*T_{max})-7.16 and is taken from Jarvie et al., 2001).

Structural changes of molecules, such as stereochemical inversion or rearrangement of chiral centres, provide insight into the mechanism of hydrogen

exchange. Pristane and phytane both contain chiral carbons, and thus are ideal candidates for stereochemical studies. The pristane molecule is symmetrical, with two chiral centres at C-6 and C-10 resulting in three diastereomers, 6(*R*),10(*R*)-pristane (*RR*); 6(*S*),10(*S*)-pristane (*SS*) and 6(*R*),10(*S*)-pristane (*RS*, *meso*). All 3 have been discovered in sedimentary organic matter, but only meso-pristane retains the configuration of the precursor, while the *RR* and *SS* enantiomers form from the isomerisation of the meso compound during maturation (Patience et al., 1978). For example, the immature Messel Shale (Eocene, Germany) contains only *meso*-pristane, while the thermally mature Irati shale (Permian, Brazil) contains a 1:1 mixture of the *meso* and *RR*/*SS* isomers, respectively (Patience et al., 1978). Phytane has three chiral centres at C-6, C-10 and C-14, resulting in 8 diastereomers, with the 8 possible configurations at the chiral centres being *RRR*, *SSS*, *RRS*, *SSR*, *RSR*, *SRS*, *SRR* and *RSS*, respectively. All 8 occur in sedimentary organic matter (Patience et al., 1980).

Dawson et al. (2005, 2007) used pristane and phytane diastereomer ratios (PrDR' and PhDR, respectively; see also Hansen et al., 2003) to monitor the extent of hydrogen exchange of pristane and phytane in Perth Basin and Vulcan Sub-basin sediments. The plots in Figure 3.7 show (a) PrDR' versus the δD value of pristane, and (b) PhDR versus the δD value of phytane, for the Perth Basin and Vulcan Sub-basin sediments (Dawson et al., 2007). Dawson et al. (2005) showed that PrDR' and PhDR derived from the Perth Basin sediments increase and approach a value of 1 from initial values of 0.71 and 0.77, respectively, with the increase concurring with enrichment in D. The values increased linearly with a moderate-strong relationship up to PrDR' and PhDR values of 0.93 and 0.95, respectively for two late-mature samples. On the other hand, the Vulcan Sub-basin sediments start at PrDR' and PhDR values of approximately 0.85 (corresponding to 85% epimerisation) at their lowest maturity level (early mature, R_o = 0.62%). Significant epimerisation (~ 85 – 90%) of Pr and Ph has occurred in all the Vulcan Sub-basin sediments analysed by Dawson et al. (2007). This is consistent with results obtained from the Perth Basin sediments, where 85-90% epimerisation had also occurred at an equivalent level of thermal maturity (Dawson et al., 2007).

Patience et al. (1978) suggested an equilibrium mixture of approximately 1:1 of the *RS* and *RR*/*SS* diastereomers of pristane would be reached as a result of epimerisation during maturation. Patience et al. (1980) separated the diastereomers of phytane in a crude oil into two partially resolved peaks with a 1:1 ratio, and Mackenzie et al. (1980) found that the extent of isomerisation of phytane with maturation appeared to be virtually identical to that of pristane. The values of PrDR' and PhDR obtained from the immature Perth Basin sediments (0.71 and 0.77, respectively) suggested that significant epimerisation had already occurred at a relatively low maturity level (R_e = 0.53%; Dawson et al., 2007). For example, a PrDR' of 0.71 indicates there has been approximately 70% conversion of meso-pristane to RR- and SS-pristane in these immature samples, even though pristane appears to have essentially retained its precursor's isotopic composition (δD = -278 ‰, Dawson et al., 2007) The conversion approaches 85–90% at an early mature level, equivalent to an R_e value of 0.78 %.

The extent of epimerisation in the immature and early mature Perth Basin samples would suggest significant hydrogen exchange and thus significant modification of indigenous δD signatures; however this was clearly not the case (Dawson et al., 2007). Indeed, pristane and phytane have largely retained the isotopic composition of their precursors (see above).

A mechanism has been proposed which can account for both D/H exchange, and epimerisation of pristane and phytane in the sedimentary environment (Figure 3.8; Dawson et al., 2007). Upon interaction with a catalytic surface, a compound containing tertiary carbon centres may form an intermittent alkene structure via a tertiary carbocation-like species. The hydrogen attached to the carbon adjacent to the tertiary carbon may then separate, and exchange with other 1H or D atoms in the vicinity. Then the resulting sp2 hybridised tertiary carbocation undergoes 1H (or D) reattachment resulting in additional hydrogen exchange along with epimerisation of the chiral centre.

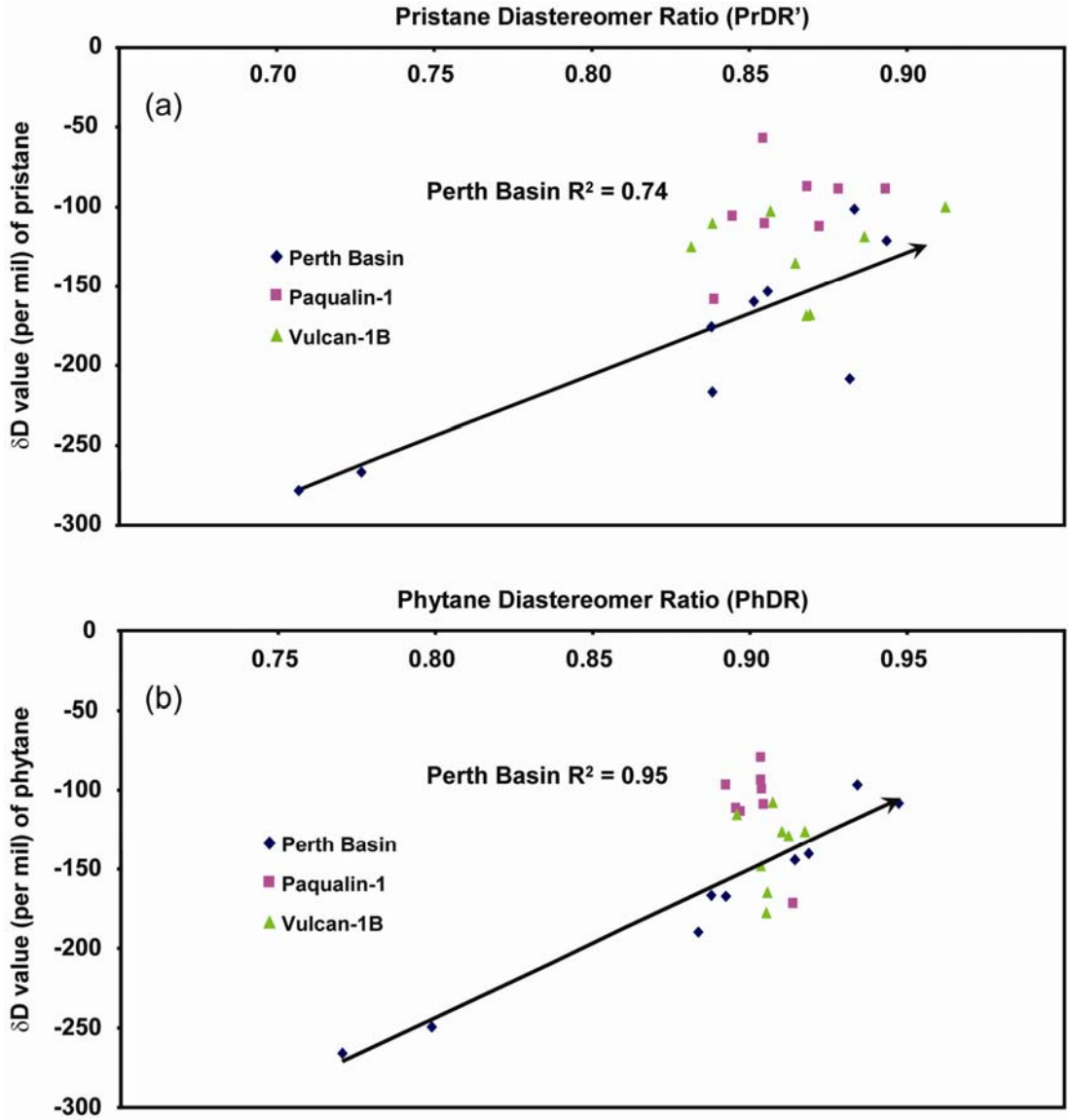


Figure 3.7 Plot of (a) the δD value of pristane versus the pristane diastereomer ratio (PrDR') and (b) the δD value of phytane versus the phytane diastereomer ratio (PhDR) for the Vulcan Sub-Basin sediment extracts, superimposed on the data obtained from the Perth Basin sediment extracts (Dawson et al., 2005; Dawson et al., 2007). The direction of the arrow indicates increasing maturity. Both PrDr' and PhDR increase as a function of thermal maturity.

Conclusions

The earlier studies described here and the new study of the Duvernay Formation demonstrates that the δD values of the *n*-alkanes, pristane and phytane are affected by thermal maturation. In general, the *n*-alkanes, pristane and phytane of immature sediments have initial δD values that represent the accepted isotopic composition of their natural product precursors. With increasing maturity, pristane and phytane become more enriched in D while the *n*-alkanes generally remain at a constant isotopic composition, until a mature-late mature-overmature level is reached where there is a significant enrichment of D in *n*-alkanes. With increasing maturity, the hydrocarbon compounds become enriched in D through hydrogen exchange, with the isoprenoids becoming enriched more quickly than the *n*-alkanes. Significant epimerisation of pristane and phytane during early maturation suggests that hydrogen exchange occurs at the tertiary carbons of these hydrocarbons, however it does not result in a significant alteration of precursor-derived δD values. Dawson et al. (2007) suggested that, perhaps hydrogen exchange and epimerisation proceed via different mechanisms during the early stages of maturation. These results provide an important insight into chemical processes that may occur in the subsurface during petroleum formation and generation.

It still remains uncertain whether the application of D/H of individual hydrocarbons as a precise maturity tool for pre-Devonian sedimentary rocks (i.e. predating the evolution of higher plants and those containing no vitrinite) is applicable. The results also emphasise the care needed when interpreting δD values in the context of the source(s) of hydrocarbons in sediments of high thermal maturity, particularly those hydrocarbons with a high reactivity towards hydrogen exchange. The effect of maturation on indigenous δD values may result in an erroneous interpretation.

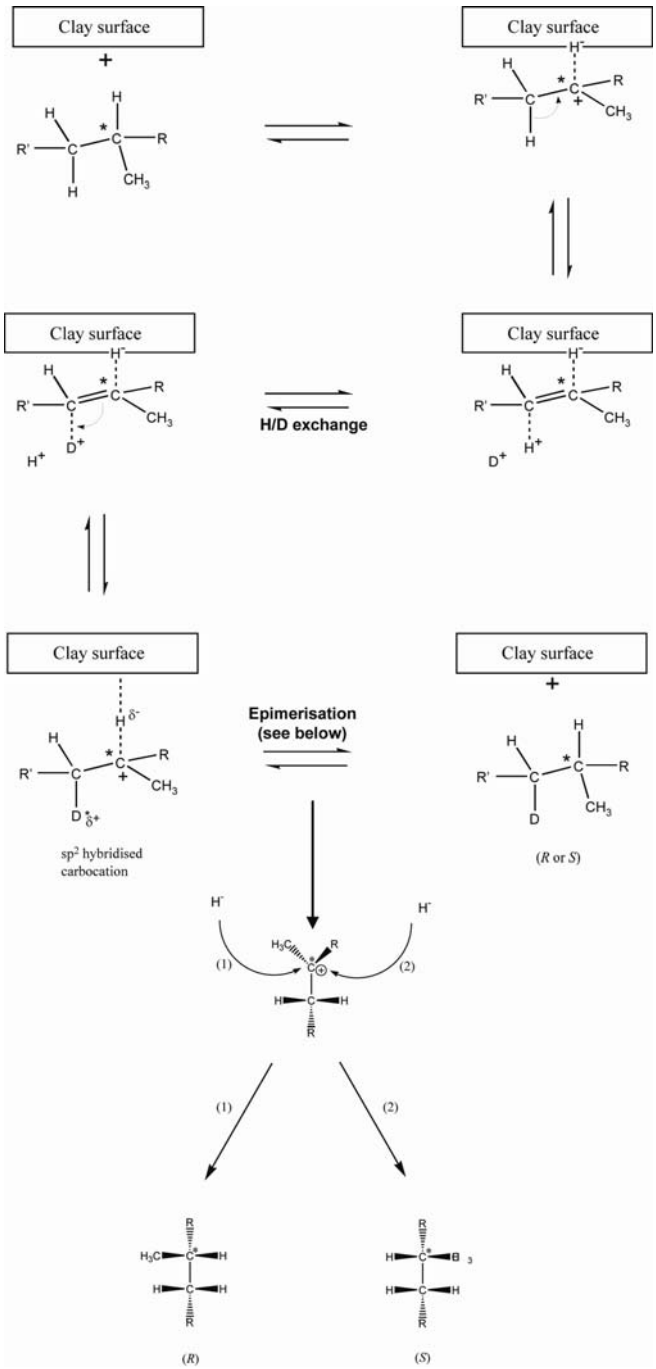


Figure 3.8 Mechanism of hydrogen exchange (after Alexander et al., 1984), and epimerisation of a chiral centre, where R' ≥ R in terms of substituent priority, and R ≠ CH_3. * denotes a chiral centre (Dawson et al., 2007).

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Chapter 4

An integrated inorganic and organic isotopic geochemical study to evaluate the origin/age of Western Australian (WA) crude oils

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Science, in preparation.

Abstract

Selected trace elements in oils have been previously used for oil-oil and oil-source rock correlations. Trace element contents may predict crude oil origin, maturity, migration pathways and establish sources of heavily biodegraded petroleum samples. A novel rapid, reliable and accurate method of determination of major and trace element contents of crude oils has been developed based on Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). For the first time this method has been applied to a series of petroleum samples for analysis of Fe, Mg, Zn, Cu, Cr, Ni, Co, V, As, Mo and Se at trace levels, with little or no sample pre-treatment. Carrying out $\delta^{13}C$ of individual hydrocarbons in a systematic manner may provide a better understanding on the origins of crude oils in Australian petroleum systems. Oils analysed include a series from Australian and Western Canadian basins of different geological age. The application of linear discriminant analysis of the stable carbon and hydrogen isotope ratios and trace element concentrations has allowed the classification of crude oils to their geographical (or basinal) sources and age. The use of complementary inorganic and organic isotope techniques for the petroleum samples may provide a new highly discriminant tool for petroleum exploration.

Keywords-

Trace elements, stable isotopes, crude oil, laser ablation-inductively coupled plasma-mass spectrometry, isotope ratio mass spectrometry, discriminant analysis

Introduction

Organic geochemistry can be utilized to enhance the effectiveness of the exploration of sedimentary basins for petroleum (oil and natural gas). During the initial stages of exploration, when there are only a few wells drilled and no accumulations are discovered, modern geochemical techniques can be useful for selecting major source rock groups. Once petroleum is discovered it is important to classify hydrocarbons into their families and correlate them to their major source rock(s). The classification of hydrocarbons into their oil families has often proven difficult. Crude oils consist of a mixture of hydrocarbons, including saturated, aromatic and NSO components (Hunt, 1996). Commonly used organic geochemical tools to classify crude oils include molecular and stable isotopic techniques (mainly $^{13}C/^{12}C$) of individual hydrocarbons and whole oil (Hunt, 1996). Classification of some sedimentary basins may not be achieved by applying these traditional organic geochemical tools (Hunt, 1996).

The presence of trace elements in crude oils has been recognised for several decades. Trace element concentrations in petroleum samples have been undertaken in several studies (e.g. Lewan and Maynard, 1982; Odermatt and Curiale, 1991; Filby, 1994) and have been used for oil classification (Barwise, 1990; Frankenberger et al., 1994; Akinlua et al., 2008) and oil-oil/ oil-source rock correlations (Barwise, 1990; Filby, 1994; Alberdi-Genolet and Tocco, 1999; Akinlua et al., 2007). Trace element abundances have also been used to resolve issues associated with petroleum refining, catalytic poisoning, corrosion and environmental matters (Oluwole et al., 1993; Olajire and Oderinde, 1993). Although several earlier trace element studies have been conducted on crude oils, these have been generally limited to smaller sample sets and a restricted number of trace elements.

Trace element contents may predict crude oil origin, maturity, migration pathways and aid in establishing source(s) of heavily biodegraded petroleum. Different analytical techniques have been used to determine trace element concentrations of crude oils. For example, Lang et al. (1990) and Hardway et al.

(2004) used atomic absorption spectrometry (AAS) and others (Algadi and Al Swaidan, 1990) determined vanadium contents in crude oil by inductively coupled plasma mass spectrometry (ICP-MS). Sequential injection analysis followed by ICP-MS has also been used to measure lead, nickel, and vanadium contents in crude oil (Al Swaidan, 1996). Vanadium, nickel, lead and mercury contents have also been measured in condensates by ICP-MS (Olsen et al., 1997).

A novel rapid, reliable and accurate method of determining major and trace element contents of olive oil has been developed based on Laser Ablation-ICP-MS (LA-ICP-MS) (Pilgrim et al., 2008). For the first time this method has been applied to a series of petroleum samples allowing analysis of 66 trace elements including Fe, Mg, Zn, Cu, Cr, Ni, Co, V, As, Mo and Se at trace levels, with little or no sample pre-treatment.

Bulk stable carbon isotopic analyses of saturate and aromatic fractions of crude oil have been previously used to differentiate marine from non-marine sources (Sofer, 1984), however, Australian crude oils do not appear to follow this trend (Edwards et al., 2005) (Figure 4.1). Carrying out $\delta^{13}C/\delta D$ of individual hydrocarbons (of known origin and both non-marine and marine) in a systematic manner may provide a better understanding of the origin of crude oils in Australian petroleum systems.

Studies to date have typically relied on classification and discrimination of crude oil samples either based on molecular and isotope geochemistry or trace element data rather than investigating the potential of amalgamating both techniques to provide a rigorous assessment. The use of complementary inorganic trace element and organic stable isotope techniques for crude oil samples may provide a new highly discriminant tool for petroleum exploration. The current study investigates the potential of using a combination of compound specific isotope (CSIA) (carbon) approach and trace element data for 27 crude oil samples from Western Australian (WA) and Western Canada Sedimentary basins (WCSB) to establish their origin and age. Linear Discriminant Analysis (LDA) has been applied to obtain separation of individual petroleum basins and to identify origin and age of the oils.

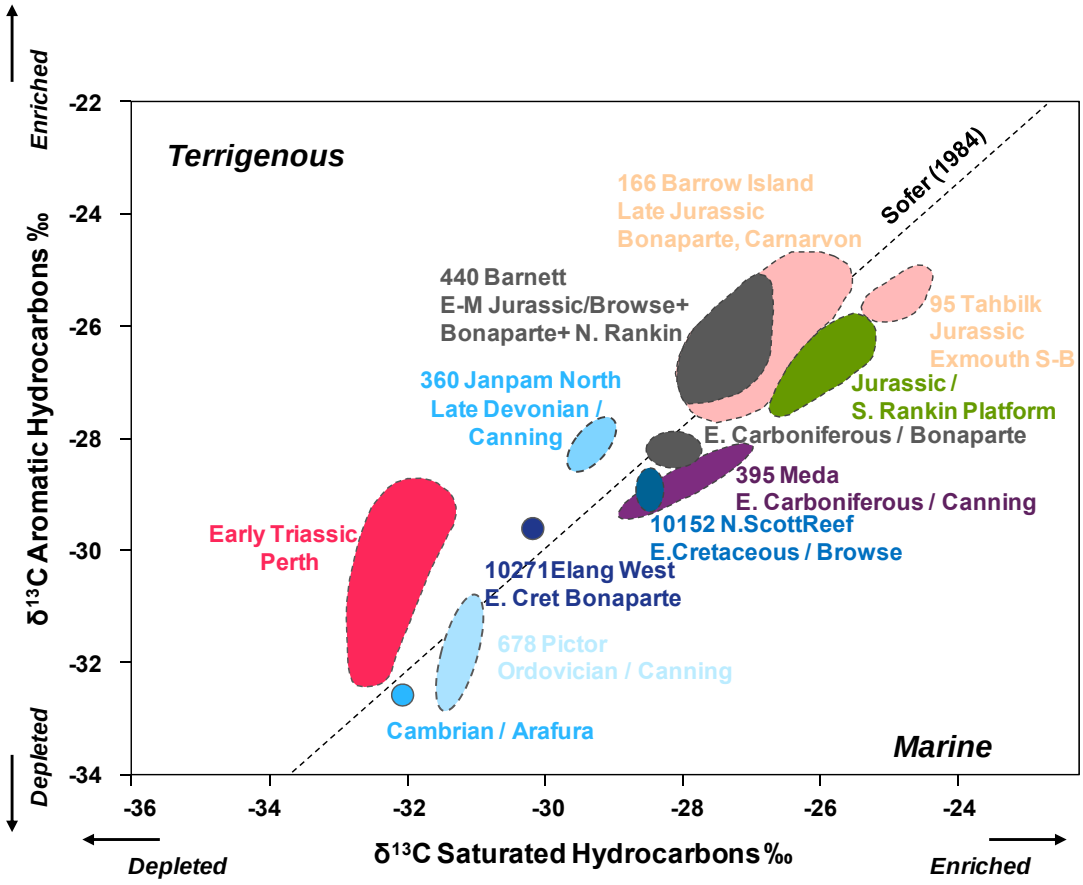


Figure 4.1 $\delta^{13}C$ of the saturated versus aromatic hydrocarbon fractions for Western Australian oils (Sofer Plot) (Edwards et al., 2005).

This study describes the deviations in trace element abundances of crude oils from different geological ages and from a variety of petroleum basins. It is anticipated that the trace element content data may provide information about an oil's source, and thus can be used for classification purposes. This data combined with the CSIA of selected aromatics has been subjected to LDA to achieve an advanced classification tool.

Studied samples

CSIA (carbon) and trace element analyses were carried out on 27 Mesozoic and Palaeozoic oils from WA and WCSB basins (Figure 4.2 and Table 4.1).

In order to understand the relationship between the crude oils within and between basins a comprehensive geochemical study has characterised the crude oil accumulations of Western Australian basins into genetically related families (Edwards et al., 2005). From a total of 316 samples, 33 oil/condensate families were identified in the Western Australian basins—Bonaparte (ten), Browse (two), Canning (four), Carnarvon (eleven) and Perth (six) (Figure 4.1). Using the organic geochemical characteristics of each family, the nature of their source facies, thermal maturity level and degree of preservation has been determined (Edwards et al., 2005).

A set of standardised geochemical protocols including bulk geochemical, molecular and bulk stable carbon isotopic analyses have been used. However, CSIA of individual aromatic hydrocarbons in crude oils have not been previously carried out and have therefore been measured in this study. Twenty seven oil samples representing a variety of ages and origins have been chosen to test the potential of using a combination of trace element data and CSIA in order to establish an origin and age correlation tool. The previous work on the oils used in this study is summarised below according to the basins in which they were produced.

Crude oils of Western Australian (WA) basins

Bonaparte Basin

Oil–oil correlations using biomarkers and stable carbon isotopes have defined two Paleozoic and eight Mesozoic oil families within the Bonaparte Basin (Edwards et al., 2005). All of the oils and condensates (Tahbilk, Corallina, Sunset West, Table 4.1) recovered from the Vulcan Sub-basin and northern Bonaparte Basin are of Mesozoic age. With the exception of a marine oil at Elang West, most

of the hydrocarbon accumulations discovered in these two regions were sourced by Jurassic marine mudstones containing variable amounts of terrigenous organic matter (OM) (see also Dawson et al., 2007). The Elang West oil is believed to be sourced from a marine shale within the Early Cretaceous Echuca Shoals Formation (Preston and Edwards, 2000).

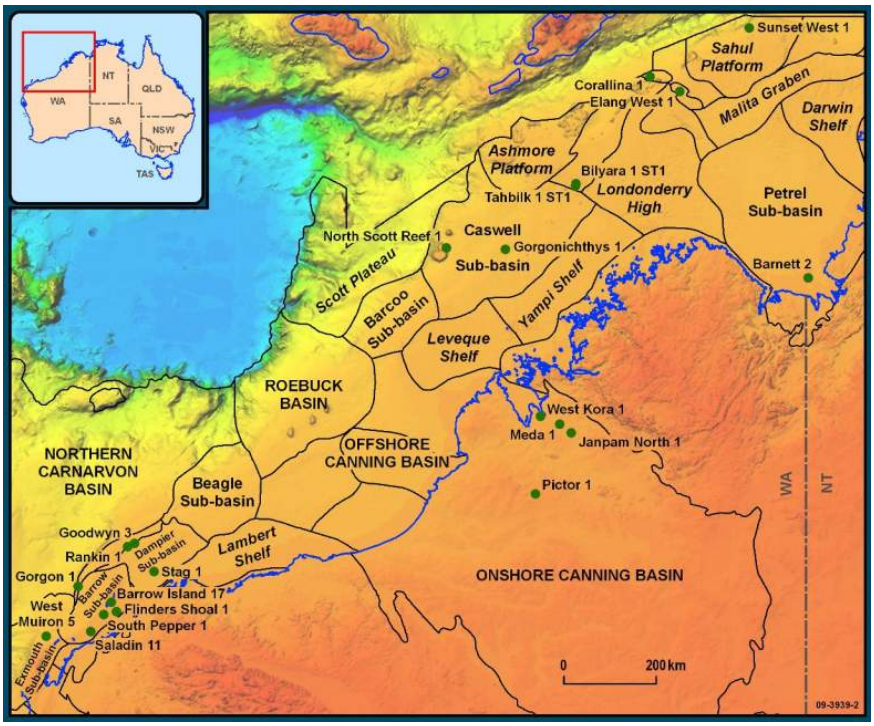


Figure 4.2 A map of the Carnarvon, Canning, Browse and Bonaparte Basins in Western Australia showing the location of petroleum exploration wells. The wells shown in green dots are the samples used in this study.

Browse Basin

The Scott Reef and North Scott Reef oils (North Scott Reef and Gorgon-Ichthys, Table 4.1) of the Browse Basin are non-biodegraded hydrocarbon accumulations that were derived from marine source rocks that contain abundant terrigenous OM (Edwards et al., 2005). These oils have not been correlated to a given source rock in the Browse Basin (Boreham et al., 1997).

Hence, by a process of elimination, Triassic and Early to Middle Jurassic OM-rich units could be the source of these oils (Edwards et al., 2005).

Canning Basin

The Dodonea oil (Table 4.1) in the Canning basin shows molecular features that are diagnostic of an extinct organism Gloeocapsomorpha prisca– resulting in a source input with a high odd-over-even predominance in the C_{13}–C_{19} *n*-alkane range. The Dodonea oil has been correlated to source rocks in the Ordovician Upper Goldwyer Formation that were deposited in a tropical epicontinental sea (Foster et al., 1986; Hoffman et al., 1987). The Pictor oil (Table 4.1) is also assigned to the same age and origin. The distinguishing features of the Ordovician-sourced oils are their significant depletion in ^{13}C (average $\delta^{13}C$ = -31.3 ‰), low sterane to hopane ratios and a slightly higher abundance of the C_{29} steranes relative to the C_{27} and C_{28} steranes (Edwards et al., 2005).

The oils from Blina and Janpam North (Table 4.1) are derived from Late Devonian marine marls and have a diagnostic biomarker signature that includes low pristane /phytane (Pr/Ph) ratios, high sterane/hopane ratios, a predominance of steranes relative to diasteranes, and abundant gammacerane and 30-norhopanes (Edwards et al., 2005). Similar biomarker distributions are observed in source rock extracts of the Late Devonian Gogo and Pillara Formations (Edwards et al., 1997). These oils also contain the biomarker crocetane (Barber et al., 2001; Greenwood and Summons, 2003) which is thought to be derived from the carotenoids of green sulfur bacteria (Maslen et al., 2008) indicative of photic zone euxinic conditions during deposition of the source-rock.

Meda, Sundown and West Kora oils (Table 4.1) are derived from Early Carboniferous marine, clay-rich mudstones, consistent with high diasteranes/sterane ratios. These oils are depleted in ^{13}C (mean average $\delta^{13}C$ = -28.0 ‰). They have an unusual terpane signature that has also been identified in source rock extracts of the Early Carboniferous Laurel Formation in the Fairfield Group. This formation has been proposed as the source of these Canning Basin oils by Brown et al. (1984), Goldstein (1989) and Kennard et al. (1994).

Sample ID	Basin	Field	Well	Depth (m)	Reservoir Formation	Reservoir Age	Source Age
Western Australian							
82	Carnarvon/Barrow	Flinders Shoal	1; DST 1A	786.1-799.2	Birdrong	Early Cretaceous	Jurassic
357	Carnarvon/Exmouth	West Murion	5; DST 1	1045-1063	Barrow Gp	Early Cretaceous	Jurassic
233	Carnarvon/N. Rankin	Rankin	1; FIT 8	2954	Mungaroo	Late Triassic	Triassic-Jurassic
10263	Carnarvon/Dampier	Stag	1; RFT 2	718.7	Muderong	Early Cretaceous	Jurassic
10057	Carnarvon/Barrow	Saladin	11	1647-2436	Mardie	Early Cretaceous	Jurassic
10271	Bonaparte/Flamingo High	Elang West	1; DST 1	3007-3016	Jamieson - Flamingo	Early-Late Cretaceous	E.Cretaceous
199995	Bonaparte/Vulcan	Tahbilk	1; RFT 1	2690.2	Montara	Late Jurassic	Jurassic
10300	Bonaparte/Laminaria High	Corallina	1; DST 1	3186-3196	Laminaria	Middle-Late Jurassic	Jurassic
1999354	Bonaparte/Sahul Platform	Sunset West	1; DST 1A	2189-2207	Laminaria-Plover	Middle Jurassic	E.-M. Jurassic
10152	Browse/Scott Reef	N. Scott Reef	1; RFT 1	4223-4283	unnamed	Early Jurassic	E.-M. Jurassic
98	Browse/Yampi Shelf	Gorgonichthys	1		Plover	Middle Jurassic	E.-M. Jurassic
678	Canning	Pictor	2; PT 2	929-956	Nita	Ordovician	Ordovician
299	Canning	Dodonea	1; DST 1	1519-1553	Goldwyer	Ordovician	Ordovician
10008	Canning	Blina	2; DST 5	1470-1489	Nullara	Late Devonian	Devonian
360	Canning	Janpam North	1; DST 1	1644-1661	Nullara	Late Devonian	Devonian
10136	Canning	West Kora	1; PT 1	1735-1751	Anderson	Early Carboniferous	E. Carboniferous
395	Canning	Meda	1; DST 9A	1557-1564	Laurel	Late Carboniferous	E. Carboniferous
363	Canning	Sundown	4; DST 1	1169-1480	Grant or Anderson	Carboniferous	E. Carboniferous
Western Canada							
2204	Alberta	Woodriver		1856	Nisku	Late Devonian	Devonian
2177	Alberta	Lone Pine		2362.8	Leduc/Nisku	Late Devonian	Devonian
2221	Alberta	Big Valley		1569.7	Leduc/Nisku	Late Devonian	Devonian
2158	Alberta	Clive		1868	Leduc/Nisku	Late Devonian	Devonian
207	Alberta	Aquitane		1805.6	Keg River	Middle Devonian	Devonian
807	Alberta	Zama		1516.5	Muskeg	Middle Devonian	Devonian

Table 4.1 Location, reservoir and age data of crude oils from Western Australia and WCS Basins.

Carnarvon Basin

The crude oils (Flinders Shoal, West Murion, Rankin, Stag, Saladin, Table 4.1) from the Carnarvon Basin display a large range in organic geochemical properties. Some of the oils are formed from numerous source rock units. Others are formed from multiple phases of generation and expulsion of hydrocarbons trapped within any given structure. In addition, the geochemical source signature and degree of thermal maturity of the oils have been complicated by secondary alteration processes in the majority of these petroleum accumulations (Edwards et al., 2005). It is believed that the source units range in age from the Triassic to the Jurassic, with the majority of the oil accumulations being sourced from the Late Jurassic Dingo Claystone—a marine source rock that contains a significant amount of land-plant derived OM.

Crude oils of Western Canada Sedimentary Basin (WCSB)

A suite of 27 oils from predominantly the Nisku reservoirs of the Western Canada Sedimentary Basin (WCSB) including oils of Woodriver, Lone Pine and Big Valley (Table 4.1) in central and southern Alberta have been evaluated and can be classified into 6 groups or families based on stable carbon isotope ratios of individual gasoline range (C_5-C_{10}) compounds (Harris et al., 2003). The majority of oils used in this study show characteristics of generation from a common source rock, the Upper Devonian Duvernay Formation. Systematic isotope distributions in straight chain and branched alkanes can help to delineate a common source rock along with the influence of secondary alteration processes such as biodegradation, evaporation and thermochemical sulfate reduction. Like the Canning Basin oils of Devonian age (see above), these oils also contain crocetane derived from the carotenoids of green sulfur bacteria (Maslen et al., 2008) supporting photic zone euxinic conditions.

Analytical Methods

Analytical procedures are described below. Procedural blanks were carried out in parallel to account for any background contamination.

Inorganic geochemical analyses

LA-ICP-MS

A series of multi-element oil matrix standards (0, 0.1, 0.25, 0.5, 0.75, 1, 2 and 5ppm) was made using Conostan® organo-metallic standard (S21 + Co, In, K, Li, Sb & Sr 500ppm (wt)) and base oil (Conostan® 20 base oil) (Conostan Division, Conoco Specialty Products Inc., Oklahoma).

Where sample mass was allowed, samples were spiked to 1ppm La with lanthanum Conostan® organo-metallic standard (5000ppm) (Conostan Division, Conoco Specialty Products Inc., Oklahoma) to allow for data normalisation.

Samples and standards (40µL) were placed into the well of a custom designed Perspex disc (Figure 4.3) (Pilgrim et al., 2009) using a pipette prior to analysis.

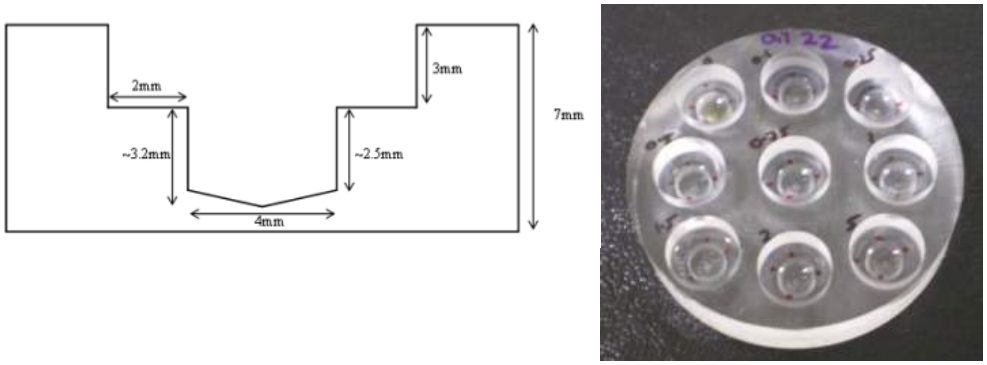


Figure 4.3 A schematic diagram and a photo showing dimensions of sample disk used during the study (Pilgrim et al., 2009).

LA-ICP-MS analysis was carried out using a New Wave UP213 LA system coupled to an Agilent 7500cs ICP-MS (Table 4.2). A manual tap system was incorporated into the system to control the flow of gas through the laser cell and to prevent contamination of the controlling solenoids by the oil. Argon was used as a carrier gas (1.2 $Lmin^{-1}$) with the addition of helium (45% v/v) to improve the sensitivity. NIST 610 glass standard was used to optimise the instrumental conditions, with a 2ppm Conostan® organo-metallic standard used to optimise the system parameters for the ablation of a non-solid matrix (Figure 4.4). Samples were ablated using optimised laser settings (65µm spot, 5Hz, 80% power, 7.53 J/cm^2).

Extract lens 1	-159 V	Cell Exit	-46 V
Extract lens 2	-15.5 V	Sample Depth	5.2 mm
Omega Bias-cs	-46 V	Torch - horizontal	-0.7 mm
Omega Lens-cs	8.8 V	- vertical	0.4 mm
Cell Entrance	-38 V		

Table 4.2 Example of typical daily tune parameters for ICP-MS

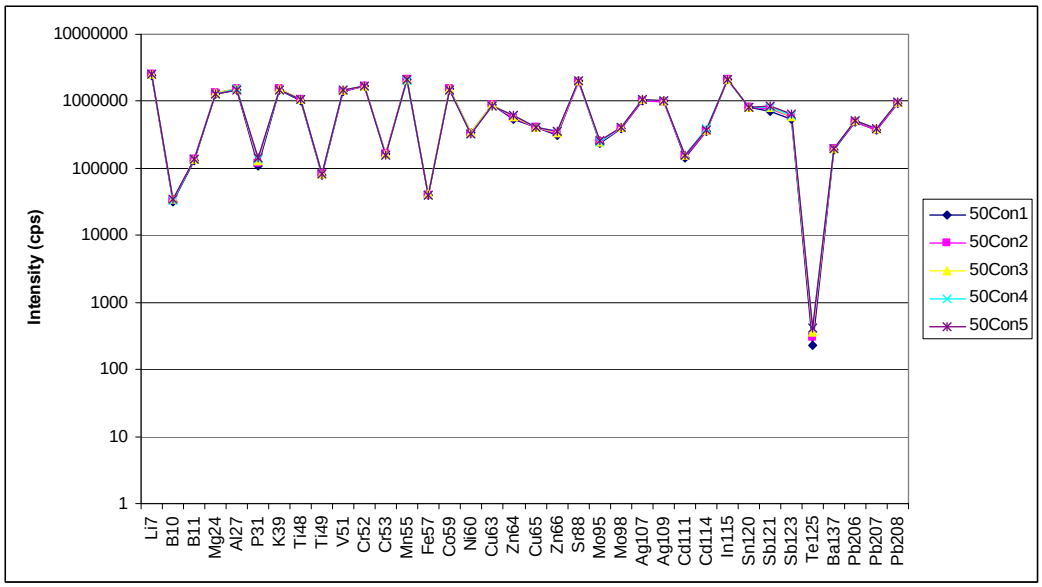
A 2ppm Conostan® standard was analysed every ten samples to monitor instrumental drift. Samples were pre-ablated (ten seconds) to allow a stable signal to be formed prior to full-quantitative data collection by the MS. Samples were analysed at least in duplicate.

Organic geochemical analyses

Separation of oils

The crude oils described above were fractionated using small-scale column liquid chromatography (Bastow et al. 2007). The sample (10 mg) was applied to the top of a small column (5 cm x 0.5 cm i.d.) of activated silica gel

(150°C, 8 hrs). The saturated hydrocarbon fraction was eluted with hexane (2 mL); the aromatic hydrocarbon fraction with dichloromethane in hexane (2 mL, 20%); and the polar fraction with a mixture of dichloromethane and methanol (2 mL). The saturated and aromatic hydrocarbon fractions were analysed by Gas-chromatography mass spectrometry (GC-MS).



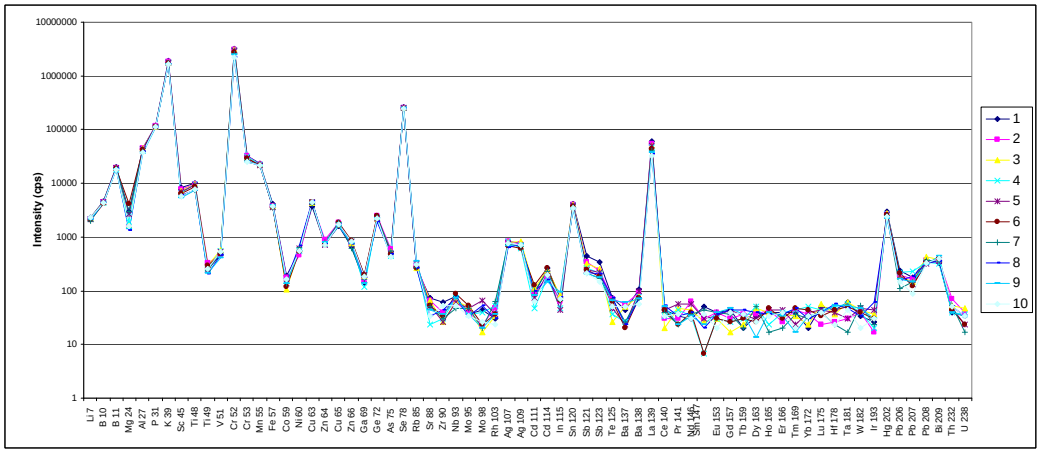


Figure 4.4 Graph showing the isotope distribution and reproducibility obtained for multiple analyses of Conostan multi element standard and of a single sample (Pilgrim et al., 2009).

GC-MS

GC-MS analysis was performed using a HP 5973 MSD interfaced to HP 6890 gas chromatograph, which was fitted with a DB-1 capillary column (J and W Scientific, 60 m, 0.25 mm inner diameter, 0.25µm phase thickness). The GC oven was ramped from 40°C to 300°C at a heating rate of 3°C /min with initial and final hold times of 1 and 30 minutes, respectively. Samples were dissolved in *n*-hexane and injected on-column using a HP 6890 auto-sampler. Helium was used as the carrier gas at a linear velocity of 28 cm/s with the injector operating at constant flow. The MS was operating with an ionisation energy of 70 eV, a source temperature of 180°C and an electron multiplier voltage of 1800V, scanning a mass range of 50 to 550 amu.

Aromatic hydrocarbon compounds were identified by comparison of mass spectra and by matching retention times with those of reference compounds reported previously (Grice et al., 2007). Between 2 and 10 ng/µL injected of each biomarker component was required for accurate GC-MS analyses. Results were integrated using the HP ChemStation Data Analysis program.

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

CSIA were carried out on a Micromass IsoPrime mass spectrometer connected to a HP 6890 gas chromatograph fitted with a similar column to that used for GC-MS analysis (above). The GC oven, injection conditions and carrier were the same as to those described for GC-MS analysis. For the external organic reference standards, the GC oven was programmed from 50 to 310°C at a rate of 10°C /min with initial and final hold times of 1 and 10 minutes, respectively. The aromatic fraction was injected using pulsed splitless mode (30 seconds hold time at 15 psi above the head pressure of the column and 35 seconds for purge). The flow rate used was 1 mL/min. The GC oven was programmed from an initial temperature of 40°C (1 min) over a temperature ramp of 3°C/min to 300°C and held for 30 min. The $\delta^{13}C$ compositions of the analysed compounds are reported

relative to reference gas pulses of CO_2 of known $\delta^{13}C$ composition (Coleman Instrument grade, BOC Gases Australia Ltd.).

Average values of at least two runs for each compound within each sample were determined and only results with a standard deviation of less than 0.4% used. $\delta^{13}C$ values are reported in the δ-notation relative to the international Vienna Peedee Belemnite (VPDB) standard.

Statistical analysis

Data were analysed using SPSS for Windows release 16.0. Stepwise discriminant analysis was carried out to establish the degree of grouping and separation of samples. The procedure generates a set of discriminant functions based on linear combinations of the predictor variables that provide the best discrimination between the groups. A database was generated which contained both trace element and CSIA data for each of the samples. Replicate analyses were included in the dataset. Cross-validation was carried out on the obtained classifications to give an indication of the degree of separation obtained.

Results and Discussion

A comprehensive organic geochemical study of oils from Western Australian basins has been carried out previously by Edwards et al. (2005). In the course of this study, each oil sample was assigned an oil family. The study also provided an age assessment for each oil and paleoenvironmental depositional conditions of their source rocks. This study led to the identification of at least 33 oil families, in Western Australian basins of Bonaparte, Browse, Canning, Carnarvon and Perth, with source ages varying from Ordovician to Triassic.

The current study samples comprise 20 crude oils from Western Australian (WA) petroleum basins (Carnarvon, Bonaparte, Browse, Canning) and seven oils from the WCSB, Alberta with source ages ranging from Ordovician to

Triassic (Figure 4.2 and Table 4.1). The 20 crude oil samples from Western Australian petroleum basins belong to six different oil families with source ages of Ordovician, Devonian, Early Carboniferous, Triassic, Jurassic and Early Cretaceous. Oils from WCSB are derived from Devonian-aged source rocks.

In the present work, 66 trace elements were determined in 12 oils and CSIA of individual aromatic hydrocarbons were performed on 27 oils (Table 4.3).

Sample ID	DMB	TeMB	N	MN	Bp	P
		$\delta^{13}C$(‰)				
Western Australian						
82	-25.0 (0.08)^2	-27.0 (0.07)^2	-27.3 (0.09)^2	-27.4 (0.08)^2	-28.7(0.12)^2	-27.2 (0.03)^2
233	-26.4 (0.06)^2	-26.6 (0.09)^2	-27.8 (0.03)^2	-27.7 (0.08)^2	-25.0 (0.04)^2	-27.0 (0.01)^2
10271	-23.6 (0.12)^2	-25.2 (0.18)^2	-24.3 (0.21)^2	-24.4 (0.25)^2	-23.6 (0.22)^2	-23.8 (0.20)^2
166	-25.6 (0.09)^2	-27.6 (0.03)^2	-26.1 (0.05)^2	-24.1 (0.01)^2		-26.3 (0.08)^2
10152	-24.7 (0.21)^2	-25.3 (0.23)^2	-26.3 (0.23)^2	-27.0 (0.21)^2	-23.8 (0.15)^2	-25.5 (0.12)^2
10057	-25.1 (0.13)^2	-27.0 (0.15)^2	-25.3 (0.12)^2	-27.4 (0.14)^2	-26.1 (0.15)^2	-28.2 (0.11)^2
678	-27.4 (0.01)^2	-28.7 (0.04)^2	-28.3 (0.07)^2	-30.0 (0.08)^2	-26.9 (0.03)^2	-28.1 (0.02)^2
360	-28.5 (0.45)^2	-31.3 (0.41)^2	-26.8 (0.35)^2	-26.6 (0.31)^2	-27.3 (0.33)^2	-29.5 (0.33)^2
10136	-27.5 (0.22)^2	-28.7 (0.27)^2	-28.2 (0.22)^2	-30.3 (0.18)^2	-28.8 (0.08)^2	-29.4 (0.10)^2
10300	-28.4 (0.18)^2	-28.1 (0.14)^2	-26.7 (0.15)^2	-27.3 (0.18)^2	-25.5 (0.20)^2	-26.6 (0.24)^2
98	-23.4 (0.07)^2	-28.8 (0.04)^2	-26.1 (0.02)^2	-27.8 (0.07)^2	-27.8 (0.08)^2	-28.0 (0.07)^2
95	-25.7 (0.45)^2	-27.3 (0.42)^2	-24.2 (0.40)^2	-22.2 (0.33)^2	-25.3 (0.31)^2	-24.1 (0.29)^2
354	-25.7 (0.11)^2	-27.7 (0.15)^2	-25.9 (0.12)^2	-23.7 (0.05)^2	-25.9 (0.01)^2	-27.2 (0.03)^2
881		-27.8 (0.07)^2				
166	-25.6 (0.51)^2	-27.6 (0.49)^2	-26.1 (0.23)^2	-24.1 (0.38)^2		-26.3 (0.44)^2
154	-25.3 (0.12)^2	-26.3 (0.14)^2	-23.4 (0.12)^2	-24.3 (0.11)^2	-25.2 (0.10)^2	-24.1 (0.12)^2
128	-25.3 (0.33)^2	-26.8 (0.29)^2	-23.6 (0.24)^2	-24.0 (0.25)^2	-25.2 (0.25)^2	-24.5 (0.21)^2
36	-25.7 (0.22)^2	-26.7 (0.19)^2	-23.1 (0.21)^2	-24.3 (0.21)^2	-25.2 (0.24)^2	-25.6 (0.18)^2
395	-28.1 (0.28)^2	-30.3 (0.22)^2	-27.7 (0.20)^2	-27.0 (0.24)^2	-27.7 (0.28)^2	-29.5 (0.21)^2
440	-25.9 (0.18)^2	-27.3 (0.14)^2	-24.0 (0.11)^2	-24.6 (0.17)^2	-25.8 (0.14)^2	-25.0 (0.14)^2
Western Canada						
2177	-27.8 (0.48)^2	-28.4 (0.41)^2	-27.0 (0.35)^2	-27.1 (0.35)^2	-27.1 (0.28)^2	-27.6 (0.28)^2
2204	-28.3 (0.08)^2	-29.8 (0.05)^2	-27.7 (0.08)^2	-27.9 (0.02)^2	-26.3 (0.08)^2	-27.3 (0.09)^2
207	-29.4 (0.05)^2	-29.7 (0.06)^2	-26.6 (0.08)^2	-27.3 (0.02)^2	-28.5 (0.05)^2	-27.2 (0.12)^2
2221	-29.2 (0.12)^2	-30.9 (0.18)^2	-28.4 (0.11)^2	-29.0 (0.14)^2	-30.2 (0.17)^2	-28.3 (0.18)^2
2158	-28.3 (0.05)^2	-29.1 (0.03)^2	-27.4 (0.07)^2	-27.9 (0.05)^2	-26.2 (0.02)^2	-27.7 (0.14)^2
807	-29.5 (0.04)^2	-31.3 (0.01)^2	-25.9 (0.01)^2	-28.8 (0.02)^2	-28.6 (0.07)^2	-29.3 (0.11)^2
1634	-29.2 (0.18)^2	-29.9 (0.12)^2	-27.7 (0.09)^2	-28.2 (0.08)^2	-28.4 (0.05)^2	-26.9 (0.09)^2

* Numbers in parenthesis are standard deviations; superscript numbers are number of replicate analyses.

Table 4.3 Results of $\delta^{13}C$ of individual aromatic hydrocarbons from crude oils analysed in this study (DMB, dimethylbenzene, TeMB, tetramethylbenzene, N, naphthalene, MN, methylnaphthalene, Bp, biphenyl, P, phenanthrene).

All of the analysed crude oil samples display significant amounts of low-molecular-weight aromatic hydrocarbons, including alkylbenzenes (B), alkylnaphthalenes (N), alkylphenanthrenes (P) and alkylbiphenyl (Bp). $\delta^{13}C$ measurements were obtained for most of these compounds. Each of the investigated series of compounds contains numerous isomers. In order to simplify the results, the $\delta^{13}C$ of each isomer series are condensed into an average range of $\delta^{13}C$ values. The $\delta^{13}C$ measurements of individual aromatic compounds obtained in this study are given in Table 4.3. The compounds used in the LDA in this study are dimethylbenzenes (DMB), tetramethylbenzenes (TMB), naphthalene (N), methylnaphthalenes (MN), biphenyl (Bp) and phenanthrene (P) (Table 4.3). $\delta^{13}C$ of individual low-molecular-weight aromatic compounds vary within their groups (e.g. N, -23.1‰ to -28.4‰) dramatically (Table 4.3). With increasing number of methyl groups on each aromatic moiety there is a systematic depletion in ^{13}C. This trend has been attributed to a ^{13}C-depleted methyl pool recently described by Le Metayer et al. (2010). With increasing age (i.e. source) of crude oils, there is a systematic shift in $\delta^{13}C$ values for B, N, Bp and P. Mesozoic-aged oils are typically enriched in ^{13}C relative to Palaeozoic sourced oils.

A number of studies have used trace element abundances to group crude oils into families (Barwise, 1990; Frankenberger et al., 1994; Akinlua et al., 2008). A small number of these studies have applied statistical methods to classify oils (Frankenberger et al., 1994; Hitchon and Filby, 1984). However, only a limited number of trace elements were used in the latter studies. With their limited data set, successful classification by these statistical means was relatively low. In this study, stepwise multiple discriminant function analysis was performed to classify crude oils on a basin-wide basis by using a combination of trace element and CSIA data from aromatic hydrocarbons.

Petroleum basin separation

Three separate analyses were performed in an attempt to achieve the best oil classification. Stepwise multiple discriminant analysis was used on 1)

combination of trace element and stable carbon isotope data (i.e. $\delta^{13}C$ of individual aromatic compounds); 2) stable carbon isotope data only; and 3) trace element data only.

Stepwise multiple discriminant analysis, using the combination of trace element and stable carbon isotope data in two discriminant functions, resulted in only 73% of the original group cases being correctly classified (Figure 4.5). The variables used to accomplish this classification were $\delta^{13}C$ of P, DMB, MN, N and Mo, Sc, Ti, B, Hf.

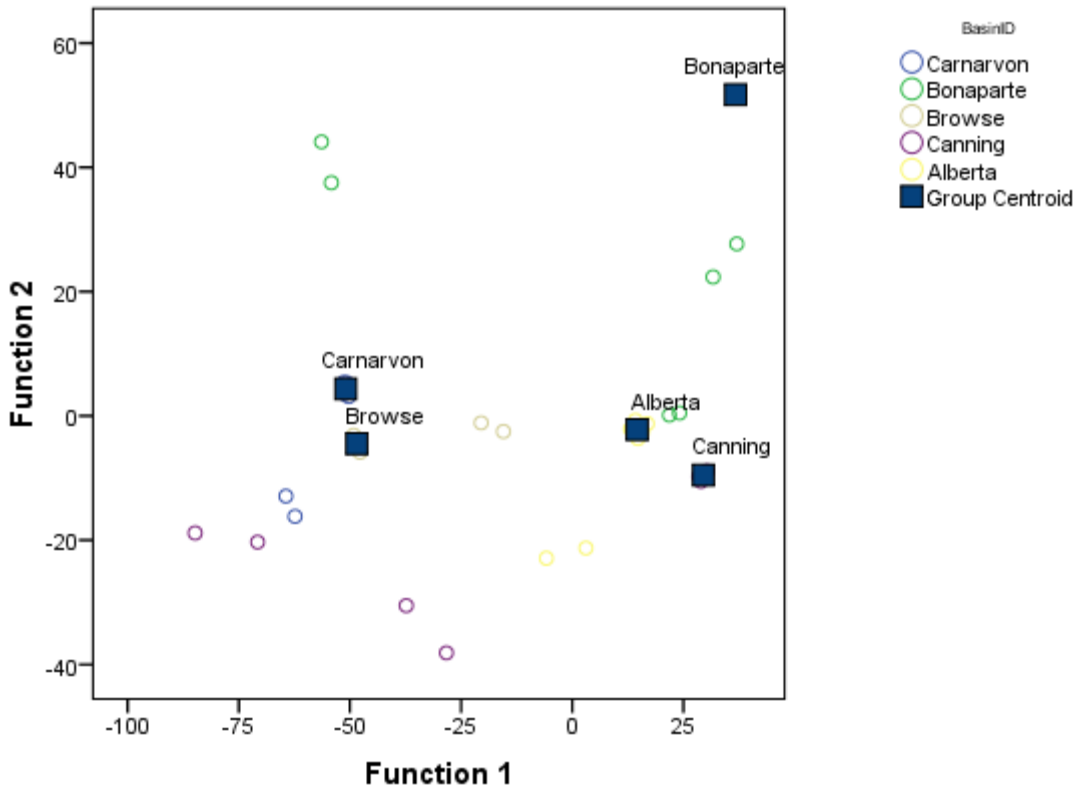


Figure 4.5 Scatter plot of two discriminant functions showing poor separation between basins of Western Australia (Carnarvon, Bonaparte, Browse, Canning) and WCSB (Alberta).

The second analysis, using stable carbon isotope data of individual aromatic compounds, using two discriminant functions, resulted in only 83% of

the samples being correctly classified (Figure 4.6). The variables used here for this classification were $\delta^{13}C$ of DMB and P.

The scatter plot of two discriminant functions from the analysis of trace elements in crude oils samples confirms the capability for separating samples into their petroleum basins - Carnarvon, Bonaparte, Browse, Canning, Alberta (Figure 4.7). Using two discriminant functions, 91.3% of the samples are correctly classified. The variables used to achieve this classification were V, Pb, B, Mg, Sn, Ti, Mo and Hg (given in order of their entry into the equations). The only outlier of the oil samples in Bonaparte Basin was Elang West oil sample, which groups closer to the Browse Basin. This can be explained by the fact that oils from Bonaparte Basin are mainly sourced from marine organic matter with varying amounts of terrigenous input (Edwards et al., 2005). Elang West is only sourced from marine-derived OM.

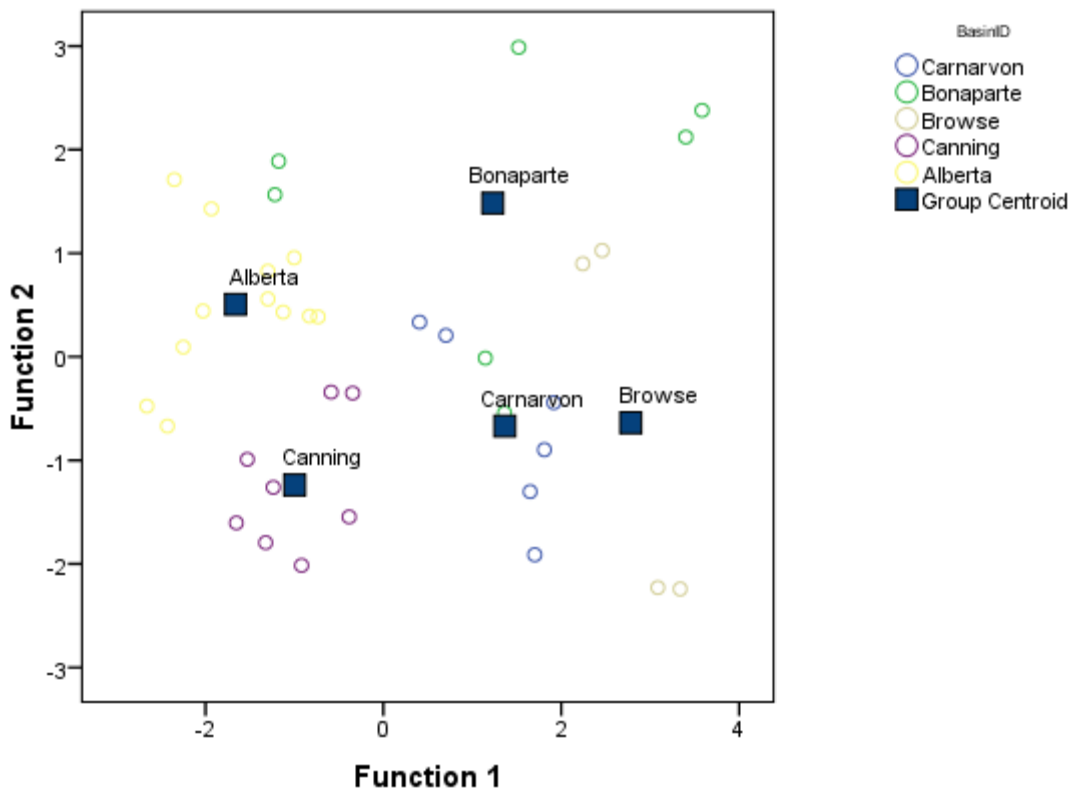


Figure 4.6 Scatter plot of two discriminant functions showing poor separation between basins of Western Australia (Carnarvon, Bonaparte, Browse, Canning) and WCSB (Alberta).

It is evident that stepwise multiple discriminant analysis using trace elements is an effective tool for classification of different petroleum systems (i.e. basin). Specifically, V, Pb, B, Mg, Sn, Ti, Mo and Hg were significant discriminators of the grouped data sets.

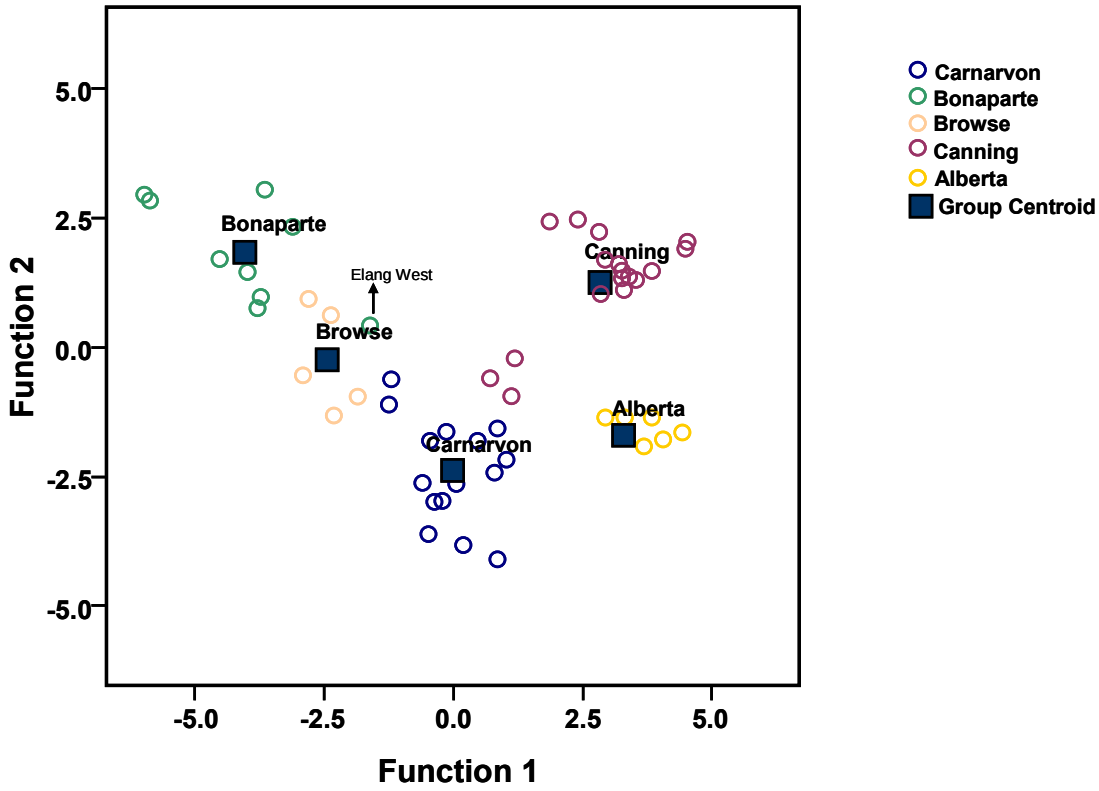


Figure 4.7 Scatter plot of two discriminant functions showing separation between basins of Western Australia (Carnarvon, Bonaparte, Browse, Canning) and WCSB (Alberta).

Source age separation

After separation of the oil samples into their petroleum basins, a further investigation was undertaken to explore the possibility of establishing whether the crude oils could be separated according to their source-rock age. The

discriminant analysis was repeated using a database with classification according to age, as previously defined (Edwards et al., 2005).

As with the basinal separation analysis, three separate stepwise multiple discriminant analyses were performed. Using stable carbon isotope data only in the discriminant analyses, it was not possible to separate the samples according to their source age. Using two discriminant functions, only 62.2% of the samples were correctly classified (Figure 4.8). The variables used in this classification were $\delta^{13}C$ of TeMB and N. Based on this data Triassic and Jurassic samples group together, whereas the Devonian samples are much more widespread.

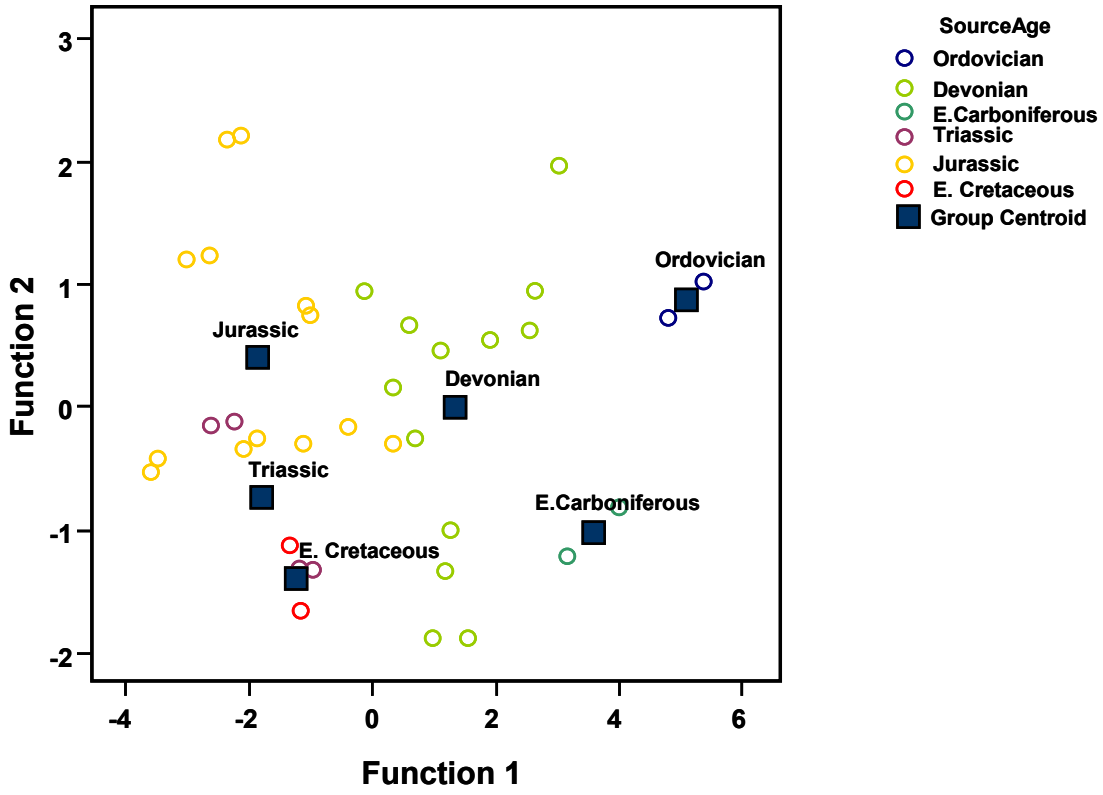


Figure 4.8 Scatter plot of two discriminant functions showing poor separation between source ages of Western Australia (Carnarvon, Bonaparte, Browse, Canning) and WCSB (Alberta).

The scatter plot of two discriminant functions from the analysis of trace elements only in crude oils samples resulted in a better classification than using stable isotope data only. Using two discriminant functions, 94.3% of the samples are correctly classified (Figure 4.9). The variables used to achieve this classification were Al, Tb, Tm, Hf, and Zn.

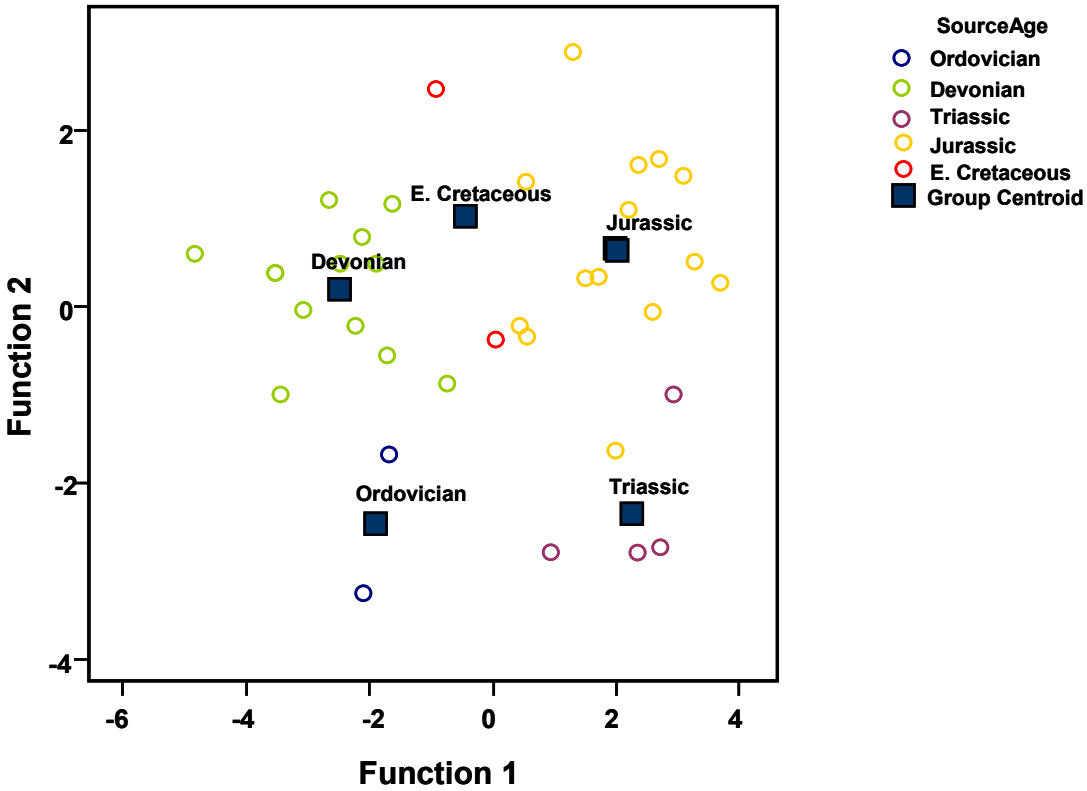


Figure 4.9 Discriminant plot showing separation between source ages of Western Australia (Carnarvon, Bonaparte, Browse, Canning) and WCSB (Alberta).

Analysis using two discriminant functions of combined trace elements and $\delta^{13}C$ of individual aromatics resulted in 100% of samples being correctly classified according to their source rock age (Figure 4.10). The variables used to achieve this classification were $\delta^{13}C$ of N, Bp and Al, Cr, Ti, Fe, Cu, Si, Tm, Mn, Ge, and Dy.

Source age separation is best achieved using both trace elements and $\delta^{13}C$ in stepwise multiple discriminant analysis. Significant discriminators of the grouped dataset were $\delta^{13}C$ of N, Bp and Al, Cr, Ti, Fe, Cu, Si, Tm, Mn, Ge, and Dy.

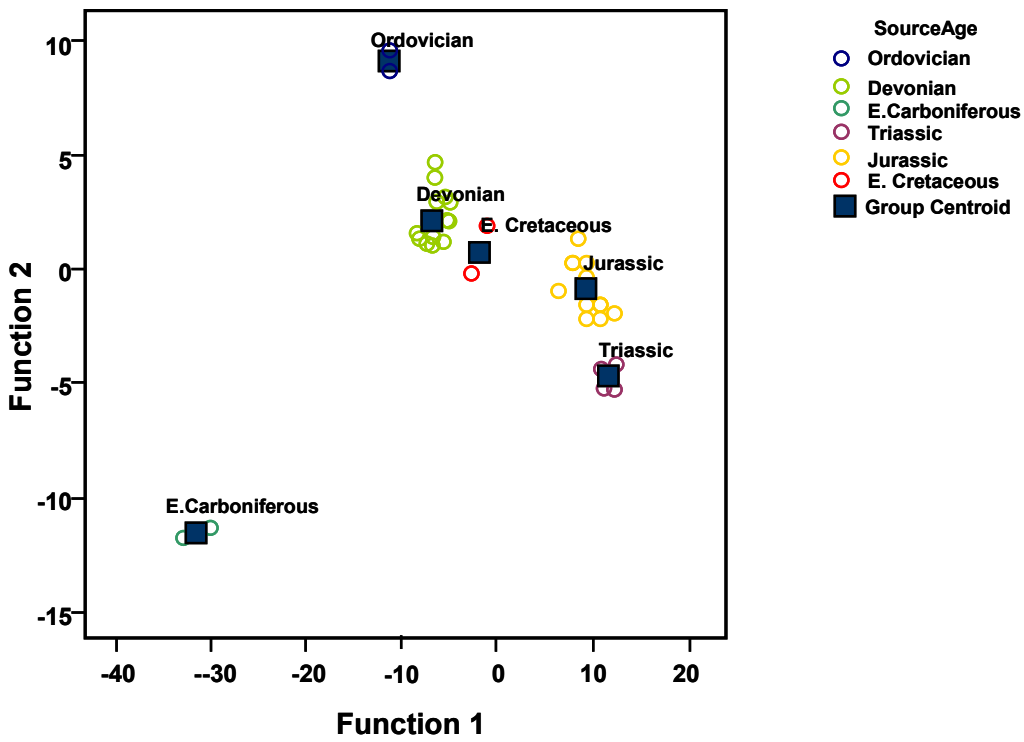


Figure 4.10 Discriminant plot showing effective separation between source ages of Western Australia (Carnarvon, Bonaparte, Browse, Canning) and WCSB (Alberta).

Trace elements

The analyses of trace elements in crude oils have been known for many decades (Lewan and Maynard, 1982; Ellrich et al., 1985; Barwise, 1990; Odermatt and Curiale, 1991). Although the amounts reported are generally low, it is evident that they play a significant role in deciphering the origin of crude

oils. The trace elements which are thought to be organically-bound to crude oils are V, Ni, Mo, Cr, Co, Fe, Cu, Zn and Mn (Filby, 1973; Odermatt and Curiale, 1991; Alberdi-Genolet and Tocco, 1999; Sajgo et al., 2009). These trace elements are bound through organometallic complexes (porphyrins) and/or partly as high-molecular-weight complexes associated with the asphaltene fraction of crude oils (Olsen et al., 1997; Lewan, 2009).

Nickel (Ni) and Vanadium (V)

High concentrations of V (up to 104 ppm) and Ni (up to 103 ppm) have been found in a variety of naturally occurring organic materials such as crude oils, asphalts and OM (Lewan and Maynard, 1982). There is no evidence on the timing of organo-metallic complex formation (involving V and Ni). However, low concentrations of V and Ni have been reported in surface sediments (Shiobara and Taguchi, 1975) and much higher concentrations are reported in buried (Louda and Baker, 1981) and thermally mature sediments (Shiobara and Taguchi, 1975) suggesting that chelating probably occurs in unconsolidated sediments prior to lithification.

Ni and V are the two most abundant metals in petroleum with Ni reaching concentrations up to 340 ppm and V up to 1580 ppm (Barwise, 1990). Most of the crude oils in WA and WCS basins have high V and Ni concentrations with V values reaching up to 137664 ppb and Ni reaching up to 401585 ppb (Table 4.4). Lewan and Maynard (1982) stated that the enrichment of V and Ni in sedimentary OM supports a source from phytoplankton and sub-mergent plants. Phytoplanktonic pigments (i.e. autochthonous derived chlorophylls) are the most likely source of tetrapyrroles because they are more easily preserved cf. tetrapyrroles derived from land plants (i.e. allochtonous). Organic matter in marine source rocks often contain abundant components (porphyrins) derived from chlorophylls and bacteriocholorophylls derived from phytoplankton and photosynthetic bacteria, respectively (Peters and Moldowan, 1993)

Redox potential (Eh), pH, and the concentration of sulfur/sulfide in the environment of deposition play a key role in chelating metals to OM (Odermatt and Curiale, 1991). Therefore, the proportion of trace metals in tetrapyrroles is

dependent on pH, Eh and activity of sulfur species of the sediment pore waters during deposition and during the early stages of diagenesis (Lewan and Maynard, 1982). This proportion is actually unaffected by the process of hydrocarbon formation and transferred to expelled oils (Lewan, 2009).

Sample ID	S (%)	V^{51}	Cr^{53}	Mn^{55}	Fe^{57}	Co^{59}	Ni^{60}	Se^{82}	Mo^{98}
Western Australian									
82	0.07	5752	223479	71106	254665	7231	7688	7194	3435
357	0.20	6506	211089	73505	355523	8379	8083	8328	4196
233	0.03	6800	186629	76806	444039	10002	7599	8804	4766
10263	0.10	8564	276769	80114	514889	13734	12757	10272	6527
10057	0.01	8688	240691	82936	549225	13970	20083	10577	6624
10271	0.09	11061	217980	87407	513650	12695	41965	9988	5934
95	na	33050	245654	64321	265776	6199	4869	8163	2712
10300	0.03	43799	188256	51004	365344	5870	5218	6405	2336
354	0.01	37068	255074	62856	292269	6258	4243	8142	2835
10152	0.02	8607	345266	76205	458407	12057	5446	9959	6175
98	na	29606	212257	61121	251847	6106	4777	7915	2428
678	0.03	8079	214610	91795	567574	14216	5719	10994	6685
299	0.16	42515	212775	80302	424677	8639	16290	8570	2492
10008	na	32541	211500	63638	228067	5160	9430	6775	1418
360	0.22	37212	222294	69027	259957	24945	70351	7039	2021
10136	0.03	66690	204646	66277	558308	7633	4461	8168	3263
395	0.05	39910	218001	70683	329576	6526	3891	7976	1870
363	0.11	42947	217767	88298	474902	9717	8642	9705	2968
Western Canada									
2204	na	104894	188530	59277	680957	8808	176231	7618	2757
2177	na	66213	192458	62474	532249	7225	16738	7881	2927
2221	na	137664	231837	70713	285626	7323	401585	7840	2074
2158	na	42805	216144	84361	473749	9604	8153	9692	2610
207	na	71978	218786	71512	580988	7864	42347	8924	3599
807	na	42962	222564	96091	503820	10766	11382	10594	3074

Table 4.4 Selected trace element concentrations (ppb) in crude oils of this study. Sulfur data is taken from Edwards et al. (2005). (na: not applicable).

Barwise (1990) stated that there is systematic variations in Ni and V contents of crude oils and this can be related to source rock and/or depositional environment. Moderate quantities of trace elements are found in oils derived from marine shales and lacustrine source rocks; however, only low concentrations of Ni and V are found in terrigenous-derived oils. Similarly, the oils in this study were assigned to a predominant marine source (e.g. Canning

Basin and WCSB oils) show high V and Ni concentrations (up to 137664 ppb and 401585 ppb, respectively) compared to those from a predominantly terrigenous source (e.g. Bonaparte Basin, up to 43799 ppb and 5218 ppb, respectively) (Table 4.4).

V and Ni concentrations have been shown to have a direct relationship with thermal maturity (Sajgo et al., 2009). The concentrations of V and Ni in some of the oils of the present study are also consistent with their thermal maturity (Figure 4.11). This can be observed from the data given in Table 4.5. Methylphenanthrene Index (MPI) and calculated vitrinite reflectance values (Vre) have been used to establish the thermal maturity of the crude oils analysed in this study (Edwards et al., 2005). As shown in Table 4.5, oils of low thermal maturity i.e. with low MPI and Vre values (0.10 and 0.46, respectively) show the highest V and Ni concentrations (137664 and 401585 ppb, respectively) relative to the oils of higher maturity with high MPI and Vre values (1.08 and 1.05, respectively) (V and Ni, 6800 ppb and 7599 ppb, respectively). These trace elements in Figure 4.11 demonstrate direct maturity dependence for the crude oils shown in the Table 4.5. The influence of thermal maturity on other trace elements (Co, Mo, Zn, Table 4.4) are more complicated, partly governed by source facies and migration effects (Sajgo et al., 2009).

Iron (Fe) and Manganese (Mn)

Fe was detected in high concentrations (values reaching up to 680957 ppb, Table 4.4) in all oil samples analysed. Fe may be present in oils as suspended inorganic compounds or attached as organometallic complexes (Franceskin et al., 1986). Fe also occurs as a pollutant introduced through corrosion and/or from drilling fluids during the extraction of oil (Valkovic, 1978). Fe is high in all oil samples analysed which suggests that it may have been introduced through corrosion and/or from drilling fluid (Valkovic, 1978).

Mn is present in all oils, although the concentrations are not as high as Fe (values reaching up to 96091 ppb, Table 4.4). The concentration of Mn in crude oil has often been reported to be low (<1000 ppb, Lopez and Lo Monaco, 2004; Franceskin et al., 1986). The origin of Mn in crude oils is unknown (Curiale,

1984). The reason for Mn existing in high concentrations in the oils studied here may be attributable either to oil migration and/or to its introduction during oil extraction (i.e. similar to Fe, see above).

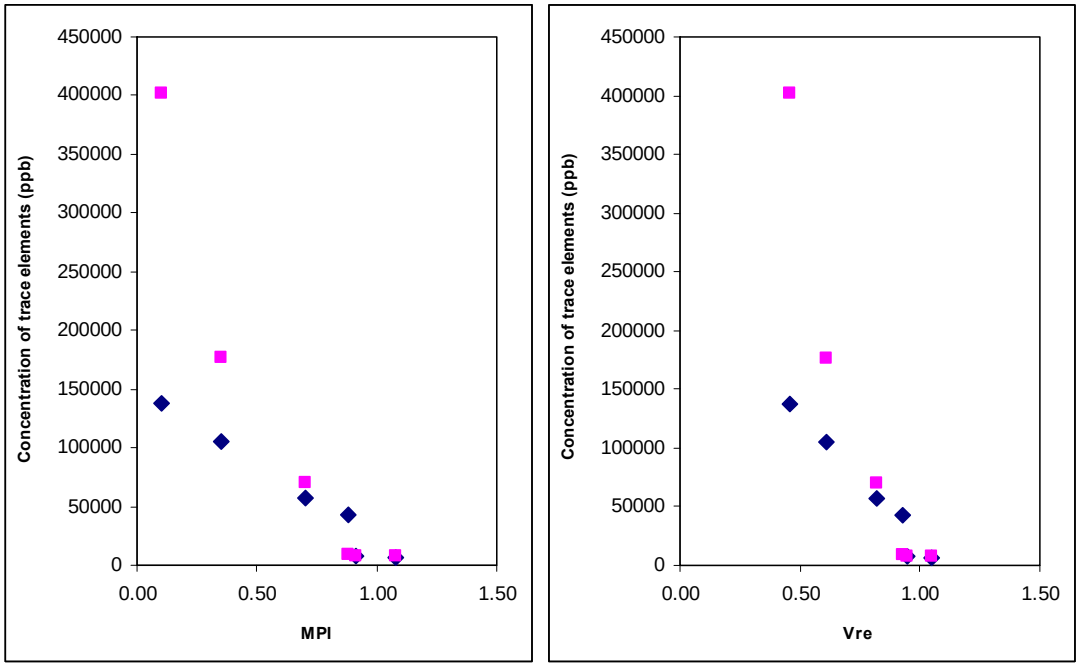


Figure 4.11 Diagram illustrating maturity dependence of V and Ni concentrations (ppb) in crude oils of this study, squares representing Ni and diamonds representing V (Methylphenanthrene Index: MPI, calculated vitrinite reflectance : Vre, maturity data taken from Edwards et al., 2005).

Sample ID	V^{51}	Ni^{60}	MPI	Vre
233	6800	7599	1.08	1.05
678	8079	7719	0.91	0.95
363	42947	8642	0.88	0.93
360	57212	70351	0.70	0.82
2204	104894	176231	0.35	0.61
2221	137664	401585	0.10	0.46

Table 4.5 Maturity sensitive V and Ni concentrations (ppb) in crude oils of this study (Methylphenanthrene Index: MPI, calculated vitrinite reflectance: Vre, maturity data taken from Edwards et al., 2005).

Chromium (Cr) and Cobalt (Co)

Cr in oils is thought to originate from biological tissues where it is an essential nutrient (Valkovic, 1978). The high concentration of Cr (values reaching up to 345266 ppb, Table 4.4) in the oils studied herein is probably representative of Cr content from the original OM.

Co is a trace element also from a biological source like Cr. It is an essential element in green and blue green algae, as well as certain fungi and bacteria (Valkovic, 1978). The consistent elemental concentration of Co in the studied oils indicates it as an organically bound trace element.

Molybdenum (Mo)

Mo in crude oils can be associated with enzymatic systems (nitrate reductase, nitrogenise) in nitrogen-reducing bacteria, which can be carried in the oil-bearing strata by surface water percolation (Gleim et al., 1975). The oceanic behaviour of Mo in sediments has a potential as a proxy indicator of physicochemical conditions (Emerson and Huested, 1991). Concentrations of Mo increase with increasing anoxic conditions at the water-bottom surface. Several researchers have associated Mo with humic acids in OM (Nissebaum and Swaine, 1976; Calvert and Price, 1983). Other researchers have reported Mo with sulfur (Glikson et al., 1985). It is thought that Mo can be selectively removed in solution as thyomolybdate during pyrite precipitation (Bertine, 1972). For all oils the Mo concentrations show a steady and consistent trend (Table 4.4).

Conclusions

This study investigated the potential of using a combination of CSIA and trace element data for 27 crude oil samples from Western Australian (WA) and Western Canada Sedimentary basins (WCSB) to establish their origin and age. Linear Discriminant Analysis (LDA) was applied to obtain separation of individual petroleum basins and to identify the origin and age of the oils.

The scatter plot of two discriminant functions from the analysis of trace elements (V, Pb, B, Mg, Sn, Ti, Mo and Hg) in crude oils samples confirms the capability for separating samples into their petroleum basins. 91.3% correct classification of the samples analysed was achieved.

Analysis using two discriminant functions of combined trace elements (Al, Cr, Ti, Fe, Cu, Si, Tm, Mn, Ge, and Dy) and $\delta^{13}C$ of N, Bp resulted in 100% of samples being correctly classified according to their source rock age.

The use of complementary inorganic trace element and organic stable isotope techniques for crude oil samples can be used as a new highly discriminant tool for petroleum exploration.

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Chapter 5

Stable carbon isotopic compositions of individual aromatic hydrocarbons as source and age indicators in oils from western Australian basins

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Abstract

The present study aims to establish the factors controlling the stable carbon isotopic compositions ($\delta^{13}C$) of individual aromatic hydrocarbons analysed by compound specific isotope analysis (CSIA) in crude oils from western Australian petroleum basins of varying ageand facies type.. This paper reports data on $\delta^{13}C$ of individual aromatic hydrocarbons, like alkylbenzenes, alkylnaphthalenes, alkylphenanthrenes and methylated biphenyls. The main aims are to confirm the origin (source) and age of these oils based on CSIA of selected aromatic compounds and to understand why the Sofer plot is ineffective in establishing source of western Australia petroleum systems. The bulk $\delta^{13}C$ of saturate and aromatic hydrocarbon fractions of crude oils have been previously used to differentiate sources, however, many Australian crude oils are not classified correctly using this method.The oils were classifed as marine by the $\delta^{13}C$ values of individual aromatic compounds and as terrigenous based on the bulk $\delta^{13}C$ data. The oils where $\delta^{13}C$ values of 1,6-DMN and 1,2,5-TMN isomers are most negative are indicative of a marine source, whereas oils containing with less negative values for the 1,6-DMN and 1,2,5-TMN arederived from marine source rocks that contain a significantterrigenous component. Similarly oils with theleast negative $\delta^{13}C$ values for the 1-MP and 1,9-DMP isomers reflects varying inputs of terrigenous organic matter to their marine source rocks . Plots of P/DBT and Pr/Ph concentration ratios versus $\delta^{13}C$ values of DMP, 1,6-DMN, 1,2,5-TMN, 1-MP and 1,9-MP are constructed to establish the relative amount of terrestrially-derived organic matter contributing to the source rock of a series of marine oils.The ratios of P/DBT and Pr/Ph plotted against the $\delta^{13}C$ values of the aromatic isomers (such as 1,6DMN, 1,2,5-TMN, 1-MP and 1,9-MP) provide a novel and convenient way to discriminate betweenoils derived from different source rocks that contain varying amounts of marine and terrigenous-derived organic matter.

Keywords-

Aromatic hydrocarbons, compound specific isotopic analyses (CSIA), age, source, petroleum, Western Australia.

Introduction

Alkylated aromatic hydrocarbons such as alkylbenzenes (ABs), alkylnaphthalenes (ANs), alkylphenanthrenes (APs) and biphenyls (BPs) are common constituents of petroleum and sedimentary organic matter (OM). Variations in the molecular distributions of aromatic hydrocarbons have received considerable attention in the field of organic geochemistry as indicators of source, thermal history, facies type and palaeoenvironments of source rocks offering petroleum potential (Radke et al., 1982a,b; Alexander et al., 1985; van Aarssen et al., 1999; Grice et al., 1998, 2001, Nabbefeld et al., 2010; Aboglila et al., 2010; Williford et al., 2011). The distributions of alkylated aromatic hydrocarbons are highly variable amongst oil samples since they are controlled by the effects of source, thermal maturity and secondary alteration processes such as biodegradation (Budzinski et al., 1995; Bastow et al., 1998; van Aarssen et al., 1992, 1999; Trolio et al., 1999).

Aromatic compounds are mainly formed by geosynthetic processes, resulting in a host of isomerised, alkylated and dealkylated components (Alexander et al., 1985; Ioppolo-Armanios et al., 1995). Previous work has primarily focused on molecular distributions of aromatic hydrocarbons, especially in relation to sedimentary methylation processes accounting for the occurrence of compounds not derived from natural product precursors. However, previous researchers have suggested that natural product precursors derived from microbes and land plants may be source(s) for some aromatic hydrocarbons reported in sediments and crude oils (Puttman and Villar, 1987; Forster et al., 1989; Grice et al., 2009).

Some aromatic compounds are thought to form in the subsurface *via* methyl shift and/or transalkylation reactions, and in a study of Australian brown

coals 1-2,methyl shift reactions also occur prior to or during aromatization (Radke et al., 1982; Strachan et al., 1988). Based on molecular parameters these reactions have been used to assess thermal history. In general, as thermal maturity increases the more stable geosynthetic isomers are formed. Thus the relative abundance of the isomers derived from natural product precursors decrease with rising thermal maturity (e.g. Radke et al., 1982; van Aarssen, et al., 1999). Aromatic compounds with alkyl groups in an α position are less stable than those with alkyl groups in a β position. Thus ratios of β-substituted and α-substituted aromatic hydrocarbons have been used to assess the degree of thermal alteration of OM in sediments and crude oils (Radke et al., 1986; Alexander et al., 1995; van Aarssen et al., 1999; Le Mateyer et al., 2010). Recently it has been demonstrated that the more stable β isomers of methylnaphthalene (MN) and methylphenanthrene (MP) are relatively more abundant in a bitumen associated with kerogen referred to as Bitumen II (Nabbefeld et al, 2010). The difference between the methylnaphthalene ratio (MNR) of freely extracted bitumen (i.e. Bitumen I) and Bitumen II, when plotted against the ratio of clay to total organic carbon (clay/TOC) show an excellent correlation. The highest clay/TOC ratio related to the largest difference in MNR for the respective bitumens, consistent with the more stable β isomers being preferentially retained within the clay/kerogen matrix.

The bulk stable carbon isotopic composition ($\delta^{13}C$) of OM has been used to study secular change in the global carbon cycle (e.g. Chung et al., 1992; Summons et al., 1995; Andrusevich et al., 1998), which in the geological record has resulted in changes in the $\delta^{13}C$ values of inorganic carbon sources (e.g. primary carbonates). Sedimentary OM $\delta^{13}C$ is driven by water column carbon cycling through organic matter pools, fractionation during photosythesis, and respiration products contributing to atmospherically derived dissolved organic carbon (e.g. Goericke et al., 1994; Hayes, 1993; Popp et al., 1998). Therefore, oil-source correlations based on $\delta^{13}C$ values of sedimentary OM are often applied to estimate the age (time of deposition) of a potential source rock (e.g. Chung et al., 1992; Summons et al., 1995; Andrusevich et al., 1998). Bulk isotopic analysis of

organic carbon has been used to classify marine and non-marine (terrigenous) crude oils by plotting the bulk $\delta^{13}C$ values of the saturated hydrocarbon fraction against bulk $\delta^{13}C$ values of aromatic hydrocarbon fraction to infer genetic relationships (Sofer, 1984). Chung et al. (1992) classified over 600 post-Ordovician marine crude oils into four groups, in terms of their depositional environment and age of their source, on the basis of $\delta^{13}C$ values combined with pristane/phytane (Pr/Ph) ratios and total organic sulphur content. Andrusevich et al. (1998) reported bulk $\delta^{13}C$ values of the saturated and aromatic hydrocarbon fractions of over 500 oils. They found that both fractions are enriched in ^{13}C with decreasing geological age including three major isotopic shifts at the Cambrian/ Ordovician, Triassic/ Jurassic and Paleogene/ Neogene boundaries.

In Australian petroleum systems, marine and non-marine crude oils do not appear to fit the Sofer plot (Edwards et al., 2005). For example, oils interpreted to have been generated from a marine source rock are classified as terrigenous sourced on the Sofer plot, while oils interpreted to be generated from a terrigenous source rock are classified as marine.

The present study aims to establish factors controlling the $\delta^{13}C$ of individual aromatic hydrocarbons (ABs, ANs, APs and BPs) in crude oils from western Australian petroleum basins of varying age, facies type and thermal maturities. The main aims are to confirm the source and age of these oils based on $\delta^{13}C$ of selected aromatic compounds and to understand why the Sofer plot is ineffective in establishing source of hydrocarbons in western Australian petroleum systems.

Sample material

A set of 19 Mesozoic and Palaeozoic oils from western Australian petroleum basins was used for the present study, representing fluids derived from a range of source rock types and ages. These oils were chosen according to the depositional setting, dominant lithology of their source rocks, API values of

the crude oils (showing a good correlation with biodegradation) and their thermal maturities (the database of Geoscience Australia is used; Edwards and Zumberge, 2005). The oils which were used to show the effects of source on the $\delta^{13}C$ of aromatic hydrocarbons (Barrow Island, Elang West, Tahbilk, Barnett, North Scott Reef, Pictor and Meda) have thermal maturities spanning the oil window based on calculated vitrinite reflectance (VRc ranging between 0.51 and 0.95, Edwards et al., 2005). The remainder of the oils (e.g. Flinders Shoal, Gorgon, West Kora) were included for their age. Mainly, oils with no degradation were selected. Only two oils namely West Kora and Flinders Shoal with API values of 23 and 25.3respectively, are characterised as being mildly and heavily biodegraded. (Edwards and Zumberge, 2005). The locations of the oil samples are shown in Figure 5.1. Table 5.1 lists the crude oils analysed in this study along with the geological age of their inferred source rock, source rock type, reservoir formation, and information relating to sample origin including depth, field and sedimentary basin (the database of Geoscience Australia is used; Edwards and Zumberge, 2005).

In order to understand the relationship of the crude oils within and between basins, the study by Edwards and Zumberge (2005) led to the characterisation of a representative set of crude oils into 33 genetically-related families. From a total of 316 samples, 33 oil/condensate families were identified in the western Australian Basins—Bonaparte (n=10), Browse (n=2), Canning (n=4), Carnarvon (n=11) and Perth (n=6) (Figure 5.1). These samples were characterized by bulk geochemical, molecular and bulk $\delta^{13}C$ analyses.Compound specific isotope analysis (CSIA) of individual aromatic hydrocarbons has been carried out in this study. To our knowledfe this is the first reported $\delta^{13}C$ data for aromatic hydrocarbons in these crude oils.

Analytical Methods

The analytical procedures used are described below. Procedural blanks were carried out in parallel to account for any background contamination.

Separation of oils

The crude oils (described above) were fractionated using a small-scale column liquid chromatography method (Bastow et al. 2007). The sample (10 mg) was applied to the top of a mini column (5 cm x 0.5 cm i.d.) of activated silica gel (150 °C, 8 h). The saturated hydrocarbon fraction was eluted with n-hexane (2 mL); the aromatic hydrocarbon fraction with dichloromethane in n-hexane (2 mL, 20%); and the polar fraction with a mixture of dichloromethane and methanol (2 mL, 50%). The saturated and aromatic hydrocarbon fractions were analysed without any solvent evaporation by gas-chromatography-mass spectrometry (GC-MS). Aromatic hydrocarbon fractions were analysed by gas chromatography-isotope ratio mass spectrometry (GC-irMS).

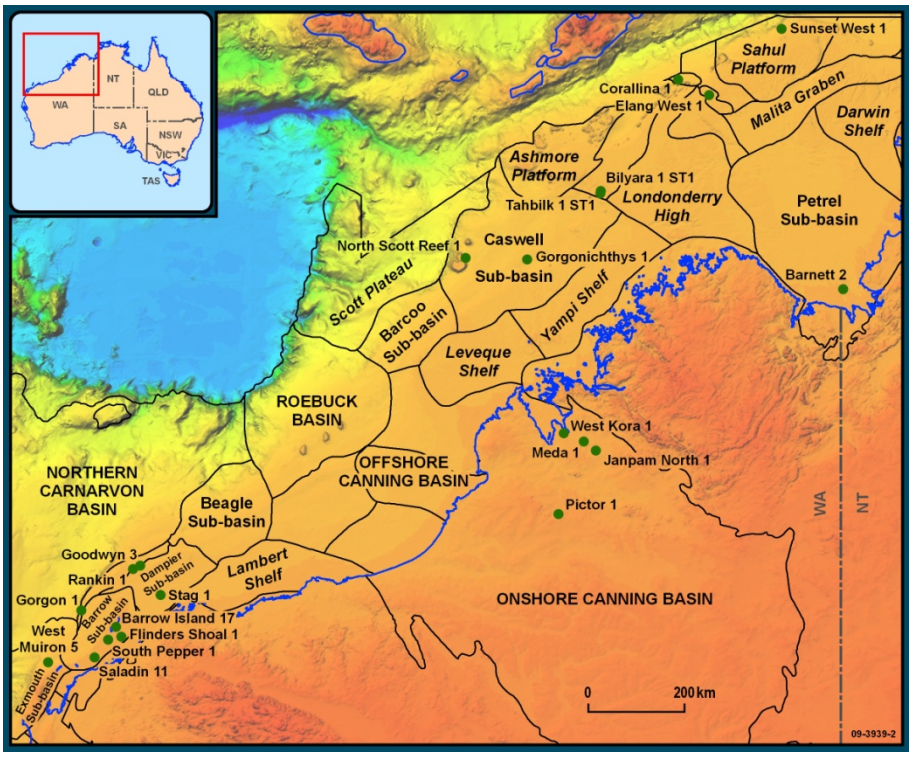

Figure 5.1 A map of the Carnarvon, Canning, Browse and Bonaparte Basins in western Australia showing the location of petroleum exploration wells. The wells shown in green dots are the samples used in this study

Sample ID	Basin	Field	Depth (m)	Reservoir Formation	Reservoir Age	Source Age	API	VRc	Biodegradation	Source Type
82	Carnarvon/Barrow	Flinders Shoal	786.1-799.2	Birdrong	E. Cretaceous	Jurassic	25.30	0.63	heavy	Distal Marine Shale/Paralic-Deltaic Marine Shale
881	Carnarvon/Barrow	South Pepper	2214-2217	Barrow Gp	E. Cretaceous	Jurassic	43.80	0.76	polyhistory	Paralic-Deltaic Marine Shale
166	Carnarvon/Barrow	Barrow Island	2282.9-2312.2	Muderong	E. Cretaceous	Jurassic	36.70	0.78	polyhistory	Paralic-Deltaic Marine Shale
233	Carnarvon/N. Rankin	Rankin	2954	Mungaroo	L. Triassic	Triassic-Jurassic	33.60	1.05	polyhistory	Distal Marine Shale/Paralic-Deltaic Marine Shale
128	Carnarvon/N.Rankin	Goodwyn	2879-2891	Mungaroo	L. Triassic	Triassic-Jurassic	52.50	0.80	polyhistory	Paralic-Deltaic Marine Shale
154	Carnarvon/S.Rankin	Gorgon	3973-4002	Mungaroo	L. Triassic	Triassic-Jurassic	45.10	0.79	non-degraded	Distal Marine Shale/Paralic-Deltaic Marine Shale
10057	Carnarvon/Barrow	Saladin	1647-2436	Mardie	E. Cretaceous	Jurassic	53.40	0.69	polyhistory	Distal Marine Shale/Paralic-Deltaic Marine Shale
10271	Bonaparte/Flamingo High	Elang West	3007-30016	Jamieson - Flamingo	E.-L. Cretaceous	E. Cretaceous	39.00	0.68	non-degraded	Distal Marine Shale
1999095	Bonaparte/Vulcan	Tahbilk	2690.2	Montara	L. Jurassic	Jurassic	34.70	0.51	non-degraded	Paralic-Deltaic Marine Shale
36	Bonaparte/Vulcan	Bilyara	2708	Montara	L. Jurassic	E.-M. Jurassic	33.90	0.73	non-degraded	Paralic-Deltaic Marine Shale
440	Bonaparte/Petrel	Barnett	1491-1497	U.Kuriyippi	L.Carboniferous-E.Permian	E. Carboniferous	36.90	0.86	polyhistory	Distal Marine Shale
10300	Bonaparte/Laminaria High	Corallina	3186-3196	Laminaria	M.-L. Jurassic	Jurassic	58.20	0.62	non-degraded	Paralic-Deltaic Marine Shale
1999354	Bonaparte/Sahul Platform	Sunset West	2189-2207	Laminaria-Plover	M. Jurassic	E.-M. Jurassic	61.80	0.53	non-degraded	Fluvio-deltaic
10152	Browse/Scott Reef	N.Scott Reef	4223-4283	unnamed	E. Jurassic	E.-M. Jurassic	47.90	0.89	non-degraded	Paralic-Deltaic Marine Shale
20019098	Browse/Yampi Shelf	Gorgonichthys	n/a	Plover	M.Jurassic	E.-M. Jurassic	n/a	n/a	n/a	Fluvio-deltaic
678	Canning	Pictor	929-956	Nita	Ordovician	Ordovician	43.80	0.95	non-degraded	Distal Marine Shale
360	Canning	Janpam North	1644-1661	Nullara	L. Devonian	Devonian	23.00	0.82	mild	Calcarerous Marine Shale
10136	Canning	West Kora	1735-1751	Anderson	E. Carboniferous	E. Carboniferous	46.90	0.67	polyhistory	Distal Marine Shale
395	Canning	Meda	1557-1564	Laurel	L. Carboniferous	E. Carboniferous	39.00	0.72	non-degraded	Distal Marine Shale

n/a; not available
E.; Early, L.; Late, M.; Middle, API; American Petroleum Institute gravity measurement

Table 5.1 Location, reservoir and age data of crude oils from western Australian basins. API, VRc (calculated vitrinite reflectance) data is taken from Edwards et al. (2005). Mild and heavy biodegradation approximately corresponds to the levels 2-4, 5-7, respectively (Volkman et al., 1984; Peters and Moldowan, 1993; Grice et al., 2000). The term polyhistory is used for reservoirs that have experienced several phases of recharge.

5A Molecular sieving

Straight chain hydrocarbons were separated from the branched and cyclic hydrocarbons by treating the saturated fractions with activated (250 ^{o}C, 8 h) 5A molecular sieves (Murphy, 1969; Dawson et al., 2005; Grice et al., 2008) in cyclohexane. In a typical 5A molecular sieving separation, a portion of the saturated fraction in cyclohexane was added to a 2 mL vial, half of it filled with activated 5A molecular sieves. The vial was capped and placed in a pre-heated aluminum block (85 ^{o}C, overnight). The resulting solution was then cooled and filtered through a small column of silica plugged with cotton wool (pre-rinsed with cyclohexane) and the sieves were rinsed thoroughly with cyclohexane yielding the branched/cyclic fraction (5A excluded). The branched/cyclic fractions were analysed by Gas-Chromatography Mass Spectrometry (GC-MS).

GC-MS

GC-MS analysis was performed using a HP5973 MSD interfaced to HP6890 GC, which was fitted with a DB-1 capillary column (J and W Scientific, 60 m, 0.25 mm internal diameter, 0.25μm phase thickness). The GC oven was programmed from 40°C to 300°C at a heating rate of 3°C/min with initial and final hold times of 1 and 30 minutes, respectively. Samples were dissolved in n-hexane and injected (split/splitless injector) by a HP6890 auto-sampler using pulsed-splitless mode. Helium was used as the carrier gas at a linear velocity of 28 cm/s with the injector operating at constant flow. The MS was operating with an ionisation energy of 70 eV, a source temperature of 180°C an electron multiplier voltage of 1800V, and a scanning a mass range of 50 to 550 amu.

Aromatic hydrocarbon compounds were identified by comparison of mass spectra and by retention times matching with those of reference compounds reported previously (Budzinski et al., 1992; Radke, 1987; Grice et al., 2007). Between 2 and 10 ng/μL injected of each biomarker component was

required for accurate GC-MS analyses. Peak areas of each compound were integrated using the HP ChemStation Data Analysis software.

GC-ir-MS

CSIA were carried out on a Micromass IsoPrime isotope ratio mass spectrometer connected to a HP 6890 GC fitted with the same column to that used for GC-MS analysis (above). The GC oven, injection conditions and carrier used were the same as those described for GC-MS analysis. For the external organic reference compounds, the GC oven was programmed from 50 to 310°C at 10°C/min with initial and final hold times of 1 and 10 minutes, respectively. The aromatic hydrocarbon fraction was injected using pulsed splitless mode (30 seconds hold time at 15 psi above the head pressure of the column and 35 seconds purge time). The flow rate used was 1 mL/min. The GC oven was programmed from an initial temperature of 40°C (1 min) over a temperature ramp of 3°C/min to 300°C and held for 30 min. A CO_2 reference gas standard (calibrated to Vienna Peedee Belemnite, VPDB) with a known $\delta^{13}C$ value was analysed in the irms and $\delta^{13}C$/ of each aromatic component are reported in the δ notation (in ‰) relative to the international standard (VPDB). Average values of at least two runs for each compound within each sample were determined and only $\delta^{13}C$ results with a standard deviation of less than 0.4% were used. A mixture of standard components with known $\delta^{13}C$ values was analysed daily in order to monitor the instrument's performance, precision and accuracy.

Results and Discussion

Experimental remarks

$\delta^{13}C$ values of selected aromatic hydrocarbons, API gravity, VRc, and ratios of Pr/Ph and P/DBT were determined for 19 western Australian oils and are shown in Tables 5.1 and 5.2.

Sample ID	DMB	TMB	TeMB	PMB	N	MN	DMN	1,6 DMN	TMN	1,2,5 TMN	BP	MBP	DMBP	P	MP	1MP	DMP	1,9 DMP	TMP	Pr/Ph	P/DBT
											$\delta^{13}C$(‰)										
Western Australian																					
82	-25.0	-26.0	-27.0	-27.3	-27.3	-27.4	-28.1		-27.0		-28.7	-26.1	-26.1	-27.2	-27.3		-28.4		-28.0		
881		-27.0	-27.8	-28.5																	
166	-25.6	-25.9	-27.6		-26.1	-24.1	-25.3	-24.1	-26.5	-25.4		-27.0	-26.0	-26.3	-25.7	-25.5	-25.5	-25.4	-28.8	2.68	13.18
233	-26.4	-26.3	-26.6	-25.5	-27.8	-27.7	-26.0		-27.8		-25.0	-24.7	-26.7	-27.0	-27.7		-28.2		-29.5		
128	-25.3	-26.2	-26.8	-27.0	-23.6	-24.0	-25.3		-27.9		-25.2	-25.1		-25.5	-24.7		-25.4		-27.6		
154	-25.3	-26.4	-26.3		-23.4	-24.3	-25.3		-28.8		-25.2	-24.9		-24.1	-24.3						
10057	-25.1	-26.1	-27.0	-27.2	-25.3	-27.4	-28.3		-28.1		-26.1	-26.8	-28.9	-28.2	-27.8		-28.3				
10271	-23.6	-24.3	-25.2		-24.3	-24.4	-25.3	-23.5	-25.4	-24.4	-23.6	-23.9	-24.4	-23.8	-24.3	-24.1	-28.0	-28.0	-28.3	2.84	11.38
95	-25.7	-26.3	-27.3	-26.7	-24.2	-22.2	-23.9	-25.4		-23.5	-25.3	-26.2	-26.4	-24.1	-24.8	-24.1	-26.7	-26.5	-27.0	2.47	7.30
36	-25.7	-27.1	-26.7		-23.1	-24.3	-24.8		-25.8		-25.2	-25.7	-26.0	-25.6	-27.3		-28.1		-29.9		
440	-25.9	-26.5	-27.3	-28.3	-24.0	-24.6	-25.2	-24.7	-26.6	-24.1	-25.8	-26.5	-26.5	-25.0	-24.8	-24.7	-25.1	-25.1	-27.0	1.19	5.74
10300	-28.4	-26.7	-28.1	-26.2	-26.7	-27.3	-25.6				-25.5	-26.5		-26.6	-26.7						
354	-25.7	-27.5	-27.7	-26.2	-25.9	-23.7	-26.5		-25.5		-26.0		-25.5	-27.2	-28.5						
10152	-24.7	-25.1	-25.3		-26.3	-27.0	-28.0	-25.5	-27.4	-26.3	-23.1	-23.6	-25.4	-25.5	-27.8	-27.5	-26.7	-26.7	-26.7	3.34	19.78
98	-23.4	-26.0	-28.8	-26.3	-26.1	-27.8	-27.1		-28.1		-27.8	-25.6	-27.0	-28.0	-27.8		-27.0		-27.5		
678	-27.4	-28.1	-28.7	-31.0	-28.3	-30.0	-30.2	-28.1	-30.2	-28.4	-26.9	-28.9		-28.1	-29.1	-29.1	-30.0	-30.0		1.97	5.84
360	-28.5	-29.7	-31.3	-30.8	-26.8	-26.6	-27.5	-27.1	-27.7	-27.0	-27.3	-27.4	-27.1	-29.5	-29.0	-28.5	-30.2	-30.1	-30.2	0.47	3.11
10136	-27.5	-28.1	-28.7	-27.8	-28.2	-30.3	-31.6		-32.0		-28.8	-29.3	-29.5	-29.4	-30.2						
395	-28.1	-29.3	-30.3	-31.8	-27.7	-27.0	-27.8	-27.5	-27.4	-27.1	-27.7	-27.9	-27.7	-29.5	-29.3	-29.3	-30.4	-30.3	-30.5	1.4	3.35

Table 5.2 Results of $\delta^{13}C$ of individual aromatic hydrocarbons from crude oils analysed in this study (DMB, dimethylbenzene; TMB, trimethylbenzene; TeMB, tetramethylbenzene; PMB, pentamethylbenzene; N, naphthalene; MN, methylnaphthalene; DMN, dimethylnaphthalene; TMN, trimethylnaphthalene; BP, biphenyl; MBP, methylbiphenyl; DMBP, dimethylbiphenyl; P, phenanthrene; MP, methylphenanthrene; DMP, dimethylphenanthrene; TMP, trimethylphenanthrene; Pr, Pristane; Ph, Phytane; DBT, dibenzothiophene).

Almost all samples studied contain high relative abundances of the aromatic compounds identified above. $\delta^{13}C$ values were obtained for various sub-classes of the aromatic hydrocarbon fractions such as DMB, TMB, TeMB, PMB, N, MN, DMN, TMN, BP, MBP, DMBP, P, MP, TMP, and for several isomers of the aromatic fraction such as 1,6- DMN, 1,2,5-TMN, 1-MP and 1,9-DMP (acronyms are defined in Table 5.2). In order to simplify the results, the $\delta^{13}C$ values of each isomer series were averaged since they were quite similar (within ≤ ± 0.4‰). However, some specific isomers particularly the ones thought to be mainly influenced by source and depositional environment (Budzinski et al., 1995; Radke et al., 1986) are reported separately. These include 1,2,5-TMN, 1,6-DMN and 1,9-DMP (Table 5.2).

$\delta^{13}C$ values of the individual aromatic compounds in the crude oils range from -22.2‰ to -32‰ (Table 5.2) and the bulk $\delta^{13}C$ of the aromatic hydrocabron fractions measured in a previous study for the same set of oils range between -25.4‰ to -29.9‰ (Figure 5.2, Edwards et al., 2005). The range of $\delta^{13}C$ values for the individual aromatic compounds in this study is much broader than the bulk $\delta^{13}C$ of the corresponding aromatic fractions. The bulk $\delta^{13}C$ of the saturated and aromatic hydrocarbon fractions of crude oils have been used to differentiate marine from non-marine sources (Sofer, 1984), however, many Australian crude oils are not differentiated during this method (Edwards and Zumberge, 2005) (Figure 5.2). For example, oils derived from marine source rocks are classified as terrigenous based on the Sofer plot. The Barnett and Janpam North oil has been correlated to a marine source by Edwards and Zumberge (2005). However, in the Sofer plot (Figure 5.2), this oil is classified as terrigenous based on the bulk $\delta^{13}C$ values of the saturated and aromatic hydrocarbon fractions. On the other hand, North Scott Reef condensate is classified as having a marine source on the Sofer plot even though it has previously been correlated to a mixed marine and terrigenous source using biomarker parameters (Figure 5.2). The $\delta^{13}C$ values of the aromatic hydrocarbons obtained for these oils may provide opposing conclusions regarding the source of the oils compared to Sofer plot ($\delta^{13}C$ saturated versus $\delta^{13}C$ aromatic hydrocarbons).

Both relative abundances and $\delta^{13}C$ values of individual aromatic compounds in crude oils are probably controlled by their source, relative thermal maturity and age of their source rock. In addition, it is known that secondary alterations such as biodegradation, in-reservoir mixing and water washing can alter the composition of aromatic hydrocarbons in crude oils (e.g. Volkman et al., 1984, Trolio et al., 1999). The following sub-sections describe these effects on $\delta^{13}C$ for the various aromatic compounds.

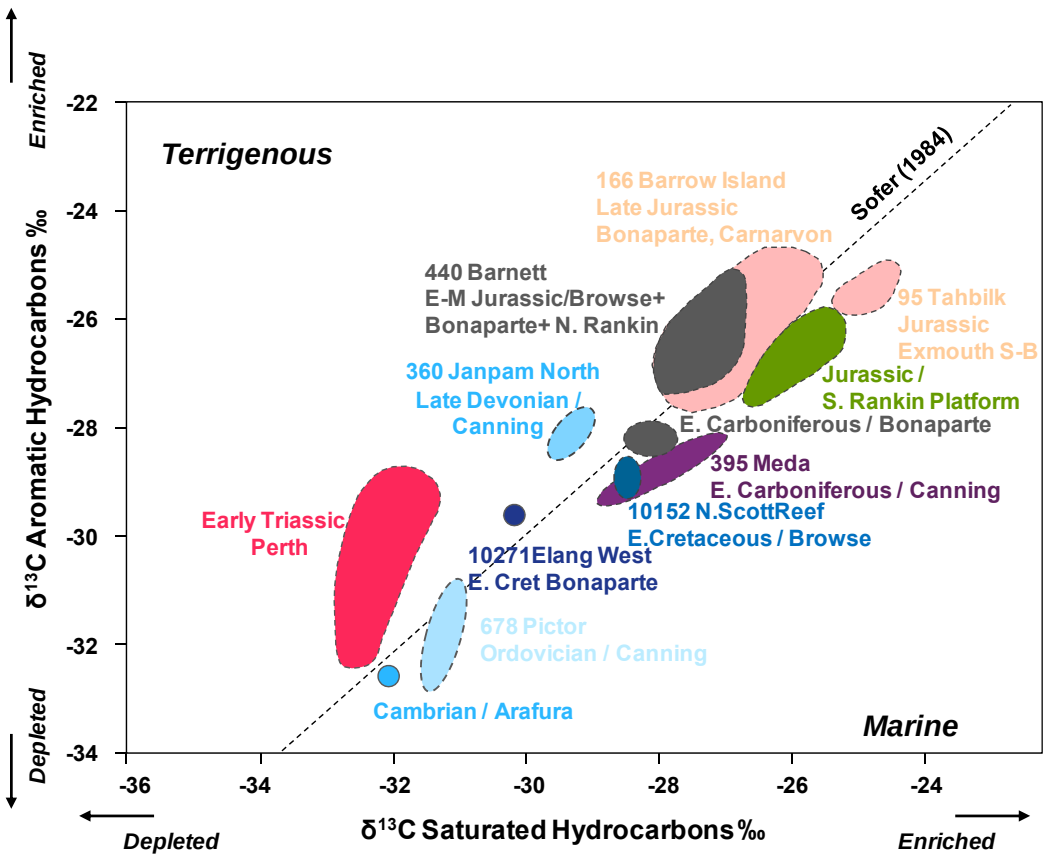

Figure 5.2 $\delta^{13}C$ of the saturated versus aromatic hydrocarbon fractions for Western Australian oils (Sofer Plot) (Edwards et al., 2005). Some oils with carbon isotope data of individual aromatic compounds analysed in this study are plotted on the diagram.

It is noted that there is generally a depletion in the $\delta^{13}C$ of individual aromatic compounds, both with increasing methylation and increasing number of aromatic rings (e.g. Figures 5.3 and 5.4). This trend is evident for all the oils analysed in this study (e.g. Figsures 5.3 and 5.4). With decreasing methylation, $\delta^{13}C$ of ABs and APs within their sub-groups show a more obvious depletion compared to ANs (e.g. Figures 5.3 and 5.4). In the study of Le Metayer et al. (2010), $\delta^{13}C$ values of ANs are shown to be strongly related to thermal maturity, contrary to the $\delta^{13}C$ of ABs and APs.

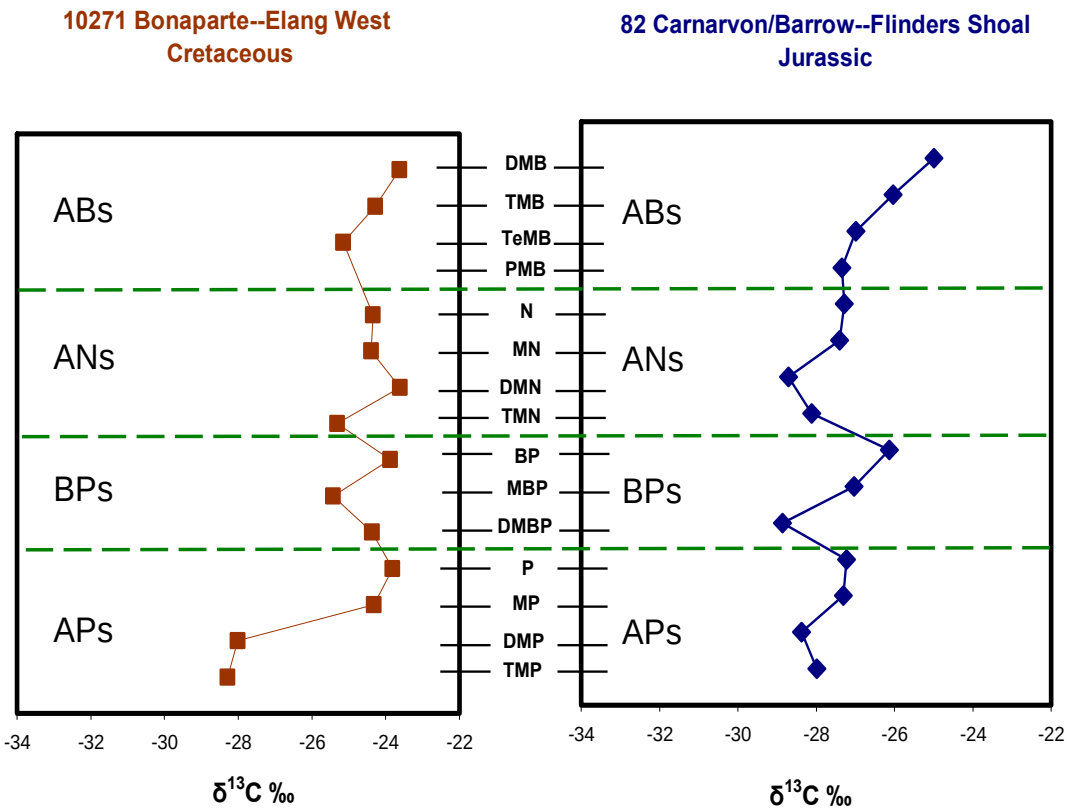

Figure 5.3 Trends of $\delta^{13}C$ of individual aromatic compounds in crude oils of Mesozoic age in selected WA basins (ABs: alkylbenzenes, ANs: alkylnaphthalenes, BPs: biphenyls, APs: alkylphenanthrenes, other abbreviations given in Table 5.2).

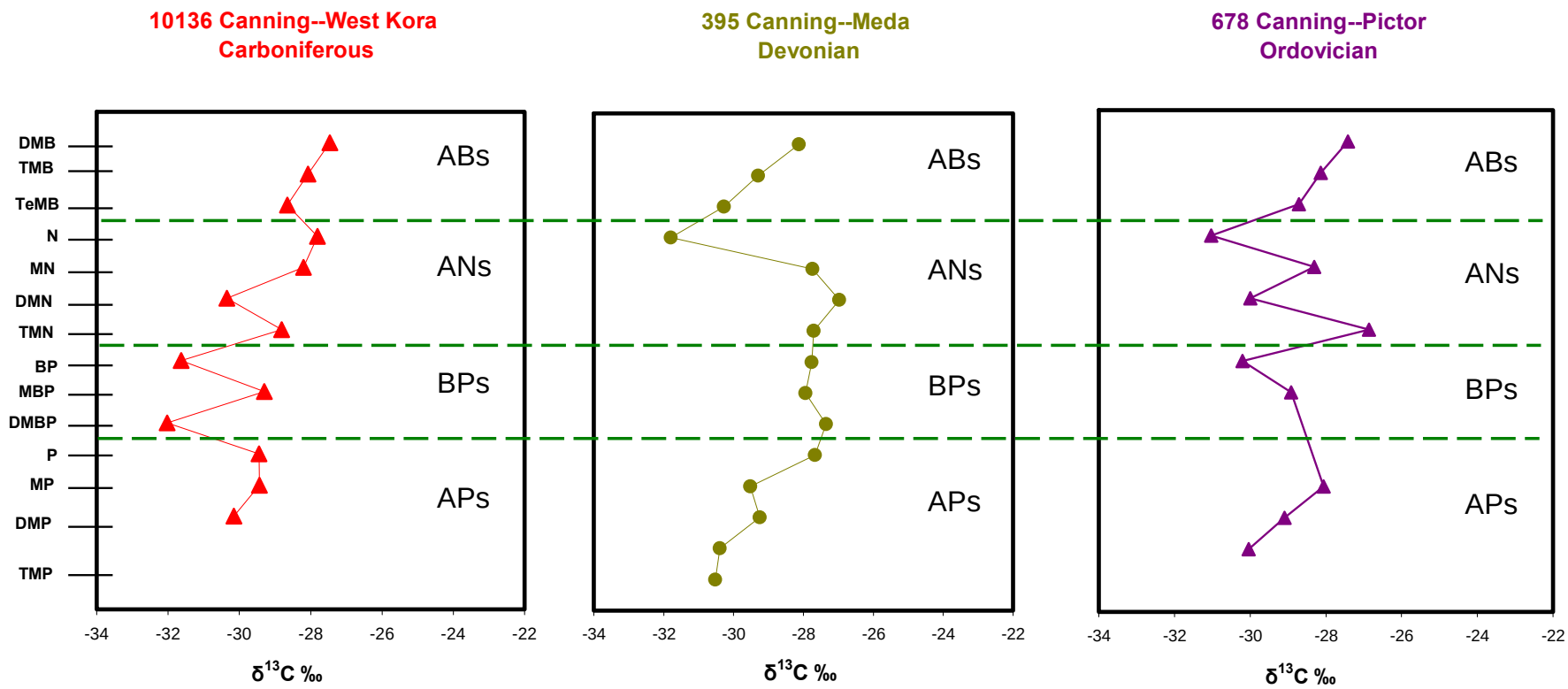

Figure 5.4 Trends of $\delta^{13}C$ of individual aromatic compounds in crude oils of Palaeozoic age in selected WA basins (ABs: alkylbenzenes, ANs: alkylnaphthalenes, BPs: biphenyls, APs: alkylphenanthrenes, other abbreviations given in Table 5.2).

$\delta^{13}C$ of aromatic isomers indicative of source

$\delta^{13}C$ measurements were carried on 1,6-DMN, 1,2,5-TMN, 1-MP, and 1,9-DMP for eightoils from different western Australian basins generated from source rock of various ages (Table 5.2, Figure 5.5). The source effects on $\delta^{13}C$ of the individual aromatic isomers are discussed in this section.

$\delta^{13}C$ values of 1,6-DMN from each oil are given in Table 5.2. The largest $\delta^{13}C$ difference for 1,6-DMN (4.6 ‰) is observed between the Pictor (Canning Basin) and Elang West (Bonaparte Basin) oils. The 1,6-DMN is an isomer which is thought to be derived largely from OM of higher plants (Alexander et al., 1992); an aromatization product of several natural product precursors (Puttmann and Villar, 1987; Alexander et al., 1992). It is assumed that the difference in $\delta^{13}C$ values of 1,6-DMN in the oils is indicative of the relative amounts of marine versus terrigenous derived organic matter within their source rocks(Figure 5.5). The oils where the $\delta^{13}C$ of 1,6-DMN isomer is most negative are probably derived from marine source rock, whereas oils containing 1,6-DMN with less negative $\delta^{13}C$ values are representative of an increasing contribution of terrigenous derived organic matter to their marine source rock.

Generally the higher $\delta^{13}C$ values of organic matter suggest a higher contribution of terrestrial plant material to the marine biomass, due to the pre-Miocene having ^{13}C enriched terrestrial organic matter relative to marine organic matter (e.g. Lewan, 1986; Popp et al., 1989). Based on the $\delta^{13}C$ data for the 1,6-DMN isomer, it appears to have a marine source but it is unclear what the natural precursor would be.

In Figure 5.5, the arrow represents an increase in terrigenous/deltaic facies source for the oils. When we compare these results with the Sofer plot (Figure 5.2), it is interesting to note that the oils classified as having terrigenous origin i.e. Janpam North (Canning Basin) are interpreted to have a marine source based on the $\delta^{13}C$ value of the 1,6-DMN isomer.

Conifer resins and their catagenetic products in oils and sediments are isotopically heavy compared with angiosperm resins and compounds derived there from (Murray et al., 1998). This distinction has existed since at least the

late Mesozoic and is probably a result of fundamental differences in the gas exchange behaviour of conifers and angiosperms and their relative efficiencies of carbon assimilation. Hence, the heavier $\delta^{13}C$ values are consistent with a mixed marine/terrigenous source for these oils. Modern plant resins are isotopically depleted compared to their fossil counterparts. The reasons for this are not yet clear but may include secular change in the isotopic composition and partial pressure of atmospheric CO_2. Resin-derived compounds in oils and sediments, especially those associated with conifers, are isotopically heavier than other hydrocarbons (Murray et al., 1998).

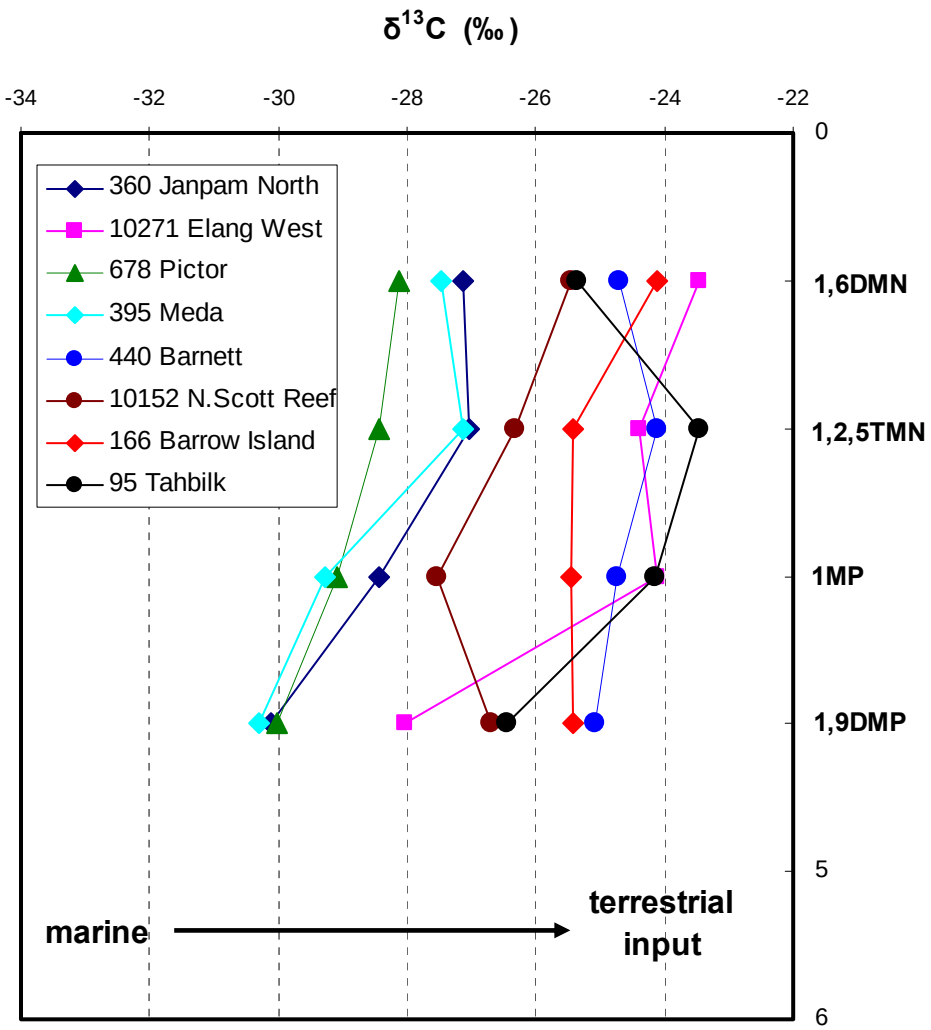

Figure 5.5 Graph showing the distribution of $\delta^{13}C$ of 1,6-DMN (dimethylnaphthalene), 1,2,5-TMN (trimethylnaphthalene), 1-MP (methylphenanthrene), 1,9-DMP (dimethylphenanthrene) in crude oils of WA Basins. Same legend is used in Figures 5.6, 5.7, 5.8 and 5.9.

$\delta^{13}C$ values of 1,2,5-TMN for each oil are given in Table 5.2. The largest difference for 1,2,5-TMN (4.9 ‰) is observed between the Tahbilk (Bonaparte Basin) and Pictor (Canning Basin) oils. The oils from the Canning Basin where 1,2,5-TMN is most negative are derived from marine sources, whereas oils containing 1,2,5-TMN with a more positive $\delta^{13}C$ value are derived from a mixed marine/terrigenous source. Similarly, Le Metayer et al. (2010) has suggested that of all the TMN isomers, 1,2,5-TMN isomer is most influenced by source. 1,2,5-TMN is suggested to be bacterial in origin, resulting from the degradation of D-ring monoaromatic 8,14-secohopanoids representing a dominant marine source (Puttmann and Villar, 1987). In Figure 5.5, based on $\delta^{13}C$ values of 1,2,5-TMN it can be interpreted that Pictor with the most depleted $\delta^{13}C$ value is a marine sourced oil whereas the Tahbilk oil with the most enriched $\delta^{13}C$ value is derived from a source rock that contains a mixture of marine and terrigenous derived organic matter. In addition to Pictor, Meda and Janpam North have depleted $\delta^{13}C$ values for 1,2,5-TMN representing a marine source for these Canning Basin oils. Barnett, Elang West, Barrow Island and North Scott Reef plot inbetween the Canning Basin oils and Tahbilk oil, probably due to varying terrigenous input to their source rock based on the $\delta^{13}C$ values of 1,2,5-TMN.

Budzinski et al. (1995) have investigated the source effect on the MP, DMP and TMP distributions for various crude oils and source rocks. From these studies, it has been established that the MPs are mostly influenced by source. 1-MP is generally dominant in terrigenously-sourced oils (Heppenheimer et al., 1992), while 9-MP is generally dominant in marine-sourced oils (Isaksen, 1991). The 2-MP and 3-MP isomers are usually dominant compounds in highly mature lacustrine and/or marine sourced oils (Radke et al., 1986).

The stable carbon isotopic compositions of Ps and MPs reported previously in coaly shales and coals at marginal to full thermal maturity are consistent with organic matter type rather than maturity (Radke et al., 1998). These authors reported that maturity differences in Lower Jurassic Posidonia shale samples had little effect on $\delta^{13}C$ of Ps and MPs. Similar results were also reported by Clayton and Bjorøy (1994) for a number of North Sea crude oils. Radke et al. (1998) reported that sediments containing marine derived organic

matter had Ps and MPs up to 7‰ more depleted in ^{13}C compared with those containing terrigenous derived organic matter.

In Figure 5.5, $\delta^{13}C$ values of 1-MP and 1,9-DMP in the Canning Basin oils range from -28.5‰ to -29.3‰ and -30.0‰ to -30.3‰, respectively. For oils from the other basins (Bonaparte, Carnarvon, Browse), the $\delta^{13}C$ values of 1-MP and 1,9-DMP ranges from -24.1‰ to -27.5‰ and -25.1‰ to -28.0‰, respectively. $\delta^{13}C$ values of 1-MP and 1,9-DMP are less negative probably reflecting the varying inputs of terrigenous organic matter to the source-rocks of these oils (North Scott Reef, Elang West, Tahbilk, Barnett, Barrow Island).

Relationship of aromatic ratios and $\delta^{13}C$ of aromatic isomers indicative of source

Hughes et al. (1995) have provided a novel way to identify the depositional environment of a source rock and associated lithologies using the ratio of DBT/P against the Pr/Ph. They measured these ratios for 75 crude oils from 41 known source rocks ranging in age from Ordovician to Neogene and classified them into the following groups; marine carbonate, lacustrine sulfate poor, marine / lacustrine shale / fluvial deltaic carbonaceous shale and coal. Similarly, Edwards and Zumberge. (2005) used Pr/Ph and P/DBT parameters to classify marine and terrigenous oils.

P/DBT, Pr/Ph ratios of the western Australian crude oils and $\delta^{13}C$ of source related aromatic isomers are given in Table 5.2. The relationship between $\delta^{13}C$ of 1,6-DMN and P/DBT, Pr/Ph of the oils are shown in Figure 5.6. The plot reveals that oils generated by source rocks of similar depositional environment and lithologies tend to group together. Thus, oils derived from marine anoxic carbonate rich source rocks have a low P/DBT and a low Pr/Ph and, $\delta^{13}C$ for 1,6-DMN is the most negative. In contrast, oils either from terrigenous silisiclastic or with a terrigenous source input have a high P/DBT and a high Pr/Ph together with enriched $\delta^{13}C$ values for 1,6-DMN (Figure 5.6).

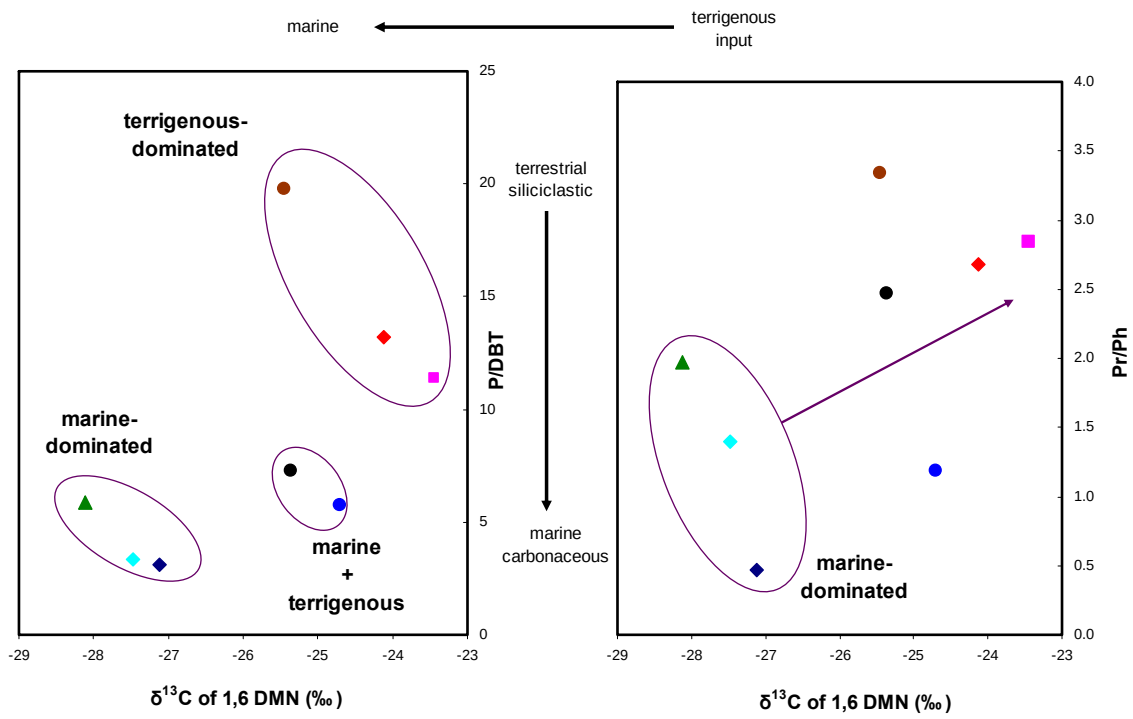

Figure 5.6 Plots of $\delta^{13}C$ of 1,6-DMN (DMN: dimethylnaphthalene) versus (a) P/DBT (P: phenanthrene, DBT: dibenzothiophene and (b) Pr/Ph (Pr: Pristane, Ph: Phytane) ratios in WA crude oils as an indication of source. (Arrow shows the increasing input of terrigenous source). The legend in Figures 5.5 is used.

The Janpam North, Pictor and Meda oils have a low P/DBT ratio and $\delta^{13}C$ of 1,6-DMN is most depleted. These oils are from a marine source (Figure 5.6a). Janpam North oil with a low Pr/Ph ratio relative to the other marine oils of the Canning Basin (Pictor and Meda) represents a more calcareous source rather than a shaley source rock (Figure 5.6b). Crocetane, an irregular tail-to-tail C20 isoprenoid, was found to be present in Canning Basin oils (Maslen et al., 2009). Crocetane coelutes with phytane. However the percentage of crocetane is low in abundance and therefore has a negligible influence on Pr/Ph ratio for the Canning basin oils.

The $\delta^{13}C$ values of aromatic isomers (1,6-DMN and 1,2,5-TMN) of the Barnett oil suggest a mixed source,, however when these data are plotted with the P/DBT and Pr/Ph ratios (Figures 5.6b, 5.7b and 5.8b) it points to a marine source similar to the Canning Basin oils. The Barnett oil shows a distinction from the other mixed source oils with its Pr/Ph ratio plotting inbetween the Canning

Basin oils and the other western Australian oils (Figures 5.6b, 5.7b and 5.8b). Elang West, North Scott Reef, Barrow Island and Tahbilk oils show highly variable P/DBT and Pr/Ph ratios reflecting varying degrees of terrigenous inputs to their marine source rocks. When $\delta^{13}C$ of 1,6-DMN (Figure 5.6b), 1,2,5-TMN (Figure 5.7b) and DMP (Figure 5.8b) are coupled with Pr/Ph ratios, these oils plot together with higher Pr/Ph ratios and less negative $\delta^{13}C$ of selected aromatic isomers(1,6-DMN, 1,2,5-TMN) relative to Canning Basin oils and to Barnett oil.

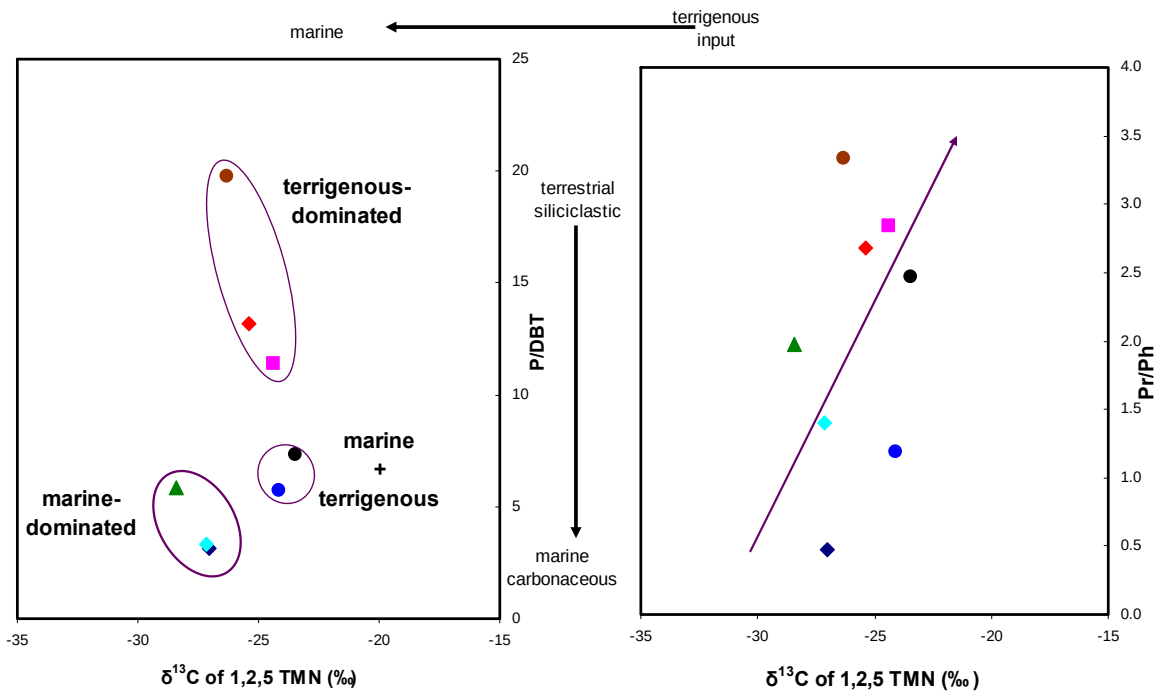

Figure 5.7 Plots of $\delta^{13}C$ of 1,2,5-TMN (TMN: trimethylnaphthalene) versus (a) P/DBT (P: phenanthrene, DBT: dibenzothiophene and (b) Pr/Ph (Pr: Pristane, Ph: Phytane) ratios in WA crude oils as an indication of source. (Arrow shows the increasing input of terrigenous source). The legend in Figures 5.5 is used.

$\delta^{13}C$ of 1,2,5-TMN (Figure 5.7a) and $\delta^{13}C$ of DMP (Figure 5.8a) are coupled with P/DBT ratios to discriminate any source effects in WA oils. As discussed above, the Canning Basin oils (Janpam North, Pictor and Meda) group together with their low P/DBT ratios and more negative $\delta^{13}C$ values reflecting a marine source. However, compared to other plots where it shows a greater marine contribution (Figures 5.6b, 5.7b and 5.8b), Barnett oil plots closer to the other western Australian oils from Bonaparte, Carnarvon and Browse Basins reflecting

a higher terrigenous input (Figures 5.6a, 5.7a and 5.8a). Elang West, North Scott Reef, Barrow Island and Tahbilk oils make a group with high P/DBT ratios and less negative $\delta^{13}C$ values representing varying contributions of terrigenous organic matter to their marine source.

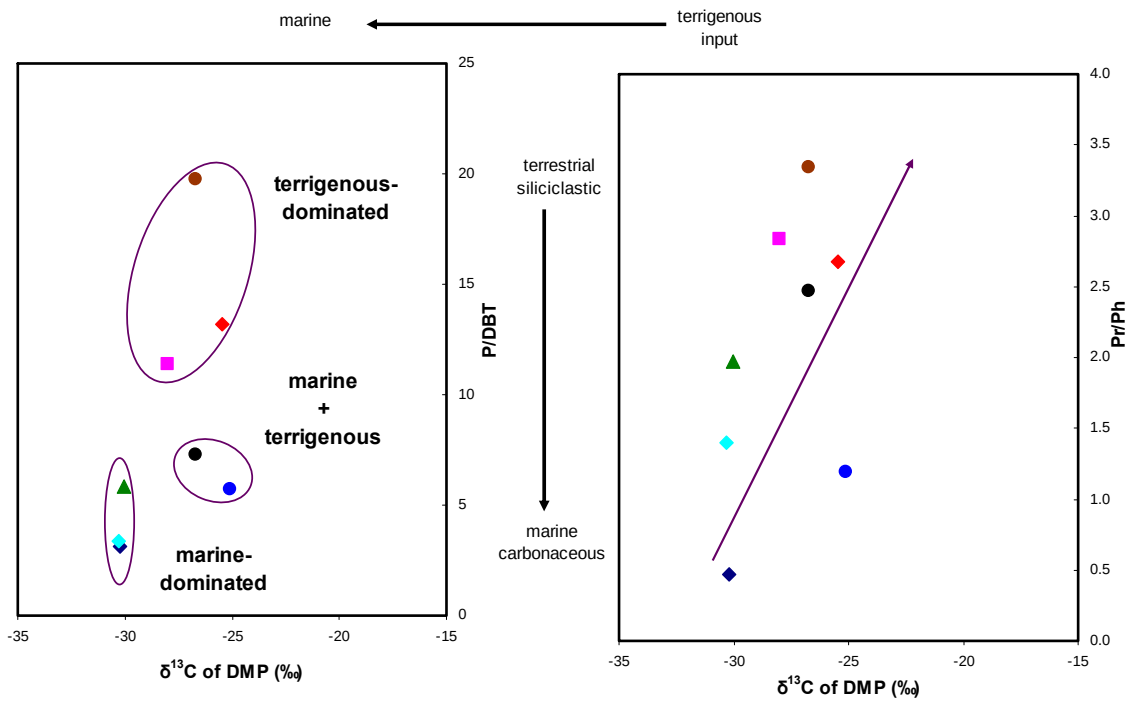

Figure 5.8 Plots of $\delta^{13}C$ of DMP (DMP: dimethylphenanthrene) versus (a) P/DBT (P: phenanthrene, DBT: dibenzothiophene and (b) Pr/Ph (Pr: Pristane, Ph: Phytane) ratios in WA crude oils as an indication of source. (Arrow shows the increasing input of terrigenous source). The legend in Figures 5.5 is used.

As discussed above (section 4.2), by studying the relative ratios of APs from oils of different sources, Budzinski et al. (1995) proposed that several specific MP, DMP and TMP isomers can be characteristic either of marine carbonate or terrigenous siliciclastic depositional environments. Using the isotopic approach, Radke et al. (1998) proposed that $\delta^{13}C$ of P and MPs reflect organic matter type rather than thermal maturity. Amongst all the alkylated Ps, the MPs have been shown to be the most indicative of source(s). Plots of P/DBT versus $\delta^{13}C$ of 1-MP and 1,9-MP (Figure 5.9a and b, respectively) are constructed to establish the end-members of terrigenous and marine sourced oils. Figures 5.9a and 5.9b classify the oils of the Canning Basin (Pictor, Meda and Janpam

North) as marine having low P/DBT ratios and the most negative $\delta^{13}C$ values for 1-MP and 1,9-MP isomers. In the other five oils an increasingterrigenous component to their marine sources is indicated by theirhigher P/DBT ratios and more positive $\delta^{13}C$ values for 1-MP and 1,9-MP in the order of Barnett, Tahbilk, Elang West, Barrow Island and North Scott Reef.. From most terrigenously sourced (all with less negative $\delta^{13}C$ values relative to Canning Basin oils) to least terrigenously sourced the oils can be put in an ordered as follows; N.Scott Reef, Barrow Island, Elang West, Tahbilk, Barnett oils (Figures 5.9a and 5.9b).

As a general conclusion, for the comparison of the oils that we have analysed with thoseidentified on the Sofer plot showed that Pictor and Meda (Canning Basin) oilsfollow the same trend based on $\delta^{13}C$ values of individual aromatics (marine-sourced). On the other hand, Canning Basin oil,Janpam North, gives a marine signature based on $\delta^{13}C$ of individual aromatic hydrocarbons in contrast to its terrigenous signature based on bulk $\delta^{13}C$ data from the Sofer plot. From the $\delta^{13}C$ data of the aromatic isomers (1,6-DMN, 1,2,5-TMN, 1MP and 1,9DMP) the Tahbilk oil provides a different conclusion to that drawn from the Sofer plot, showing a significant input of terrigenous organic matter to the parent marine source rock.

Therefore the $\delta^{13}C$ values of individual aromatic compounds provides an insight to classify western Australian oils based on their source signature.

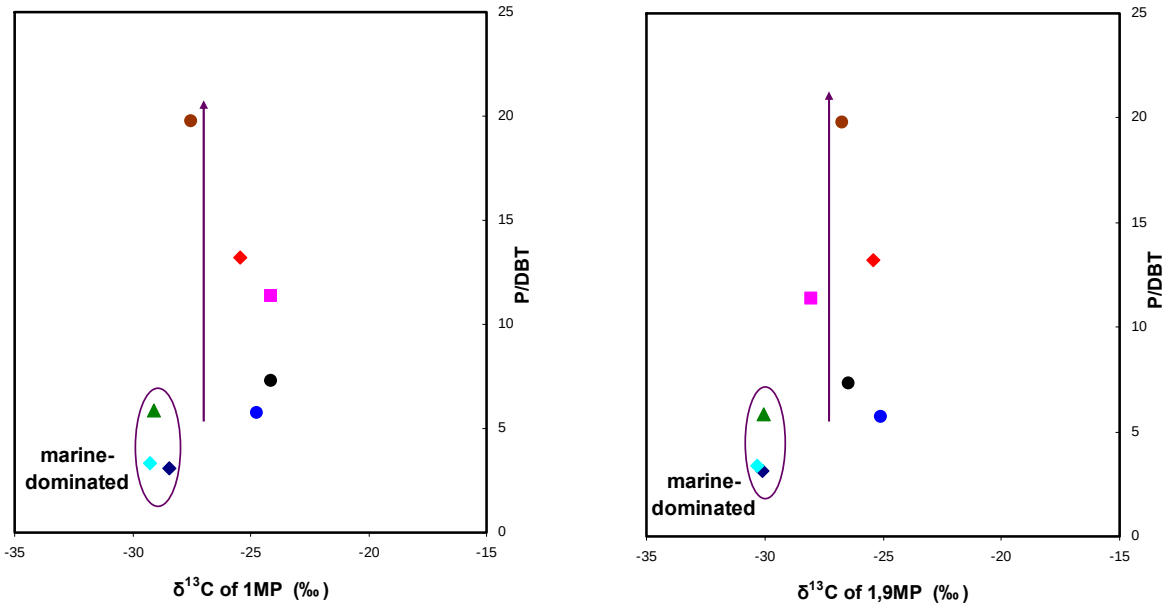

Figure 5.9 Plots of P/DBT verus (a) $\delta^{13}C$ of 1-MP (b) $\delta^{13}C$ of 1,9-MP in WA crude oils as an indication of source. (Arrow shows the increasing input of terrigenous source). The legend in Figures 5.5 is used.

$\delta^{13}C$ of aromatic sub-classes (age and basin)

Attempts have been previously made to correlate oils to their geological age and origin (e.g. Andrusevich et al., 1998; Sofer, 1984; Maslen et al., 2010). Most of the previous studies have used molecular characteristics and bulk $\delta^{13}C$ of saturated and aromatic hydrocarbons. Previous applications of bulk $\delta^{13}C$ for constraining the geologic ages of crude oils and their respective petroleum basins have only been met with limited success. This is a consequence of the large range of bulk $\delta^{13}C$ values for crude oils from any specific age. In general, oils tend to become enriched in ^{13}C with decreasing geological age (Andrusevich et al., 1998). Such changes are thought to be independent of the source rocks from which the oils are derived.

$\delta^{13}C$ distributions of individual aromatic sub-classes (ABs, ANs, BPs and APs) of two Mesozoic and three Palaeozoic oils from western Australian petroleum basins are illustrated in Figures 5.3 and 5.4. We have attempted to establish if there is any trend in $\delta^{13}C$ values of individual aromatic hydrocarbons with the age and basin of the oils. A Cretaceous oil, Elang West, from the

Bonaparte Basin (Figure 5.3a) ($\delta^{13}C$ of individual aromatics ranges between -23.6 ‰ to -28.3) has less negative ^{13}C values than Flinders Shoal a Jurassic aged oil from the Carnarvon (Figure 5.3b) ($\delta^{13}C$ ranges between -25.0 to -28.7 ‰). These data are consistent with the previous study of Andrusevich et al. (1998) showing that oils become enriched in ^{13}C in both saturated and aromatic hydrocarbons with decreasing age. The change in $\delta^{13}C$ of these two oils is believed to be directly age and source related since their thermal maturities are similar (Table 1, VRc = 0.63 and 0.68 for Elang West and Flinders Shoal, respectively). The Flinders Shoal is a mixture of heavily biodegraded and non-degraded oil (Grice et al, 2000). It is likely that the aromatic hydrocarbons in Flinders Shoal are mainly derived from the non-degraded oil however, biodegradation may still have had an effect on the $\delta^{13}C$ of individual aromatic hydrocarbons.

The Carboniferous aged West Kora oil from the Canning Basin (Figure 5.4a) has individual aromatic hydrocarbons with $\delta^{13}C$ values ranging between -27.5 ‰ and -32 ‰ (Table 5.2). The Devonian aged Meda oil from the Canning Basin has $\delta^{13}C$ values ranging from -27.0 ‰ to -31.8 ‰ (Figure 5.4b and Table 5.2). Ordovician Pictor oil from the Canning Basin has $\delta^{13}C$ values ranging from -26.9 ‰ to -31.0 ‰ (Table 5.2). Contrary to the Mesozoic oils shown in Figure 5.3, the Palaeozoic oils do not follow the trend of enrichment in ^{13}C with decreasing geologic age. The Ordovician oil Pictor has the most enriched $\delta^{13}C$ values of individual aromatic hydrocarbons on average relative to Carboniferous West Kora and Devonian Meda oils, even though it was the oldest oil analysed (Figure 5.4c). The change in ^{13}C values of the Ordovician oil might be more affected by thermal maturity rather than age since the Ordovician oil is the most mature oil of the Palaeozoic oils in the present study (VRc = 0.95, Table 5.1). However, in general Mesozoic oils in western Australian basins have more enriched $\delta^{13}C$ values of aromatic sub-classes relative to the older Palaeozoic oils.

Conclusions

Molecular approach have been complemented with compound specific isotope (CSIA) approach for individual aromatic compounds in western Australian crude oils to differentiate source and age.. $\delta^{13}C$ values were obtained for various sub-classes of the aromatic fractions such as DMB, TMB, TeMB, PMB, N, MN, DMN, TMN, BP, MBP, DMBP, P, MP, TMP, and for several isomers of the aromatic fraction such as 1,6- DMN, 1,2,5-TMN, 1-MP and 1,9-DMP.

The bulk $\delta^{13}C$ of saturates and aromatic hydrocarbon fractions of crude oils have been previously used to differentiate sources, however, many Australian crude oils are not classified correctly using this method. Oils with a marine source affinity interpreted from their $\delta^{13}C$ values of individual aromatic compounds are classified as terrigenous based on their bulk $\delta^{13}C$ values. The CSIA data of the aromatic hydrocarbons obtained for the oils provides opposite conclusions regarding the source of the oils compared to bulk data (Sofer plot).

The oils where the $\delta^{13}C$ value of the 1,6-DMN and 1,2,5-TMN isomers is most negative are probably derived from marine sources, whereas oils containing 1,6-DMN and 1,2,5-TMN with a less negative $\delta^{13}C$ values are representative of mixed marine and terrigenous sources. Less negative $\delta^{13}C$ values of 1-MP and 1,9-DMP isomers probably reflects the varying inputs of terrigenous organic matter to the marine source-rocks of the oils .

Plots of P/DBT and Pr/Ph concentrations versus $\delta^{13}C$ isotope ratios of DMP, 1,6-DMN, 1,2,5-TMN, 1-MP and 1,9-MP are constructed to establish the end-members in a series of oils who's marine source rocks contain increasing amounts of terrigenous organic matter..

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Chapter 6

Conclusions and Outlook

The results presented in this PhD thesis, significantly contribute to our scientific knowledge for evaluating the source, age, thermal history and palaeoenvironments of deposition of different petroleum systems. The chapters in this thesis describe various novel organic (biomarker and stable carbon and hydrogen isotopes) and inorganic (trace elements) geochemical approaches to establish answers for better understanding the Australian and Western Canadian petroleum systems.

In Chapter 2, a detailed molecular and isotopic study of crocetane and GSB-derived carotenoids in Devonian sediments of the Western Canada Sedimentary Basin (WCSB) covering a range of thermal maturities has been carried out. In addition, a series of oils generated from Devonian source rocks of the basin and a few oils from Australian Canning Basin have been analysed for crocetane. Crocetane was found in ten sediments from the WCSB and in seven Devonian WCSB crude oils. Crocetane, an irregular C_{20} isoprenoid, in sediments generally associated with gas hydrate settings, has been used as a molecular indicator for the AOM and related depositional environments. Green sulfur

bacteria (GSB) are the main source for specific aromatic carotenoids (e.g. isorenieratane) in sedimentary environments and serves as molecular indicators of photic zone euxinia (PZE). In Chapter 2, it is shown that crocetane abundance increases with thermal maturity, whereas the components derived from C_{40} derived carotenoids decrease steadily in the maturity sequence. The depth abundance profiles for GSB derived carotenoids show a decrease in concentration with depth and concomitant increase in the relative abundance of crocetane.

The main aim of the study was to understand the occurrence of crocetane in a different depositional environment and age than previously proposed. The findings of the Chapter 2 concluded that the preferred proposed natural product precursor for crocetane is GSB derived isorenieratene and palaerenieratene. This is based on their similar structural features and the $\delta^{13}C$ of combined crocetane and phytane in these samples. However, contributions from other carotenoids cannot be fully excluded. It is proposed that crocetane arises from the β-cleavage of diaromatic carotenoid moieties of GSB that have been incorporated into the kerogen structure. Thus, crocetane can provide evidence for PZE conditions in highly matured samples and crude oils of Devonian age.

Based on the work presented in Chapter 3, δD values of individual petroleum hydrocarbons (*n*-alkanes and regular isoprenoids) from sedimentary OM and in crude oils can provide information on thermal history of the petroleum basins. In Chapter 3, the effect of thermal maturation on the δD values of individual petroleum hydrocarbons (*n*-alkanes and regular isoprenoids) from sedimentary organic matter over geological timescales has been explored in six different sedimentary sequences covering a wide range of maturities, i.e. 0.53%–1.6% vitrinite reflectance (R_o or equivalent i.e. R_e, R_c). These include new data and recently reported literature data on formations ranging in age from the Lower Cretaceous to the Permian.

In general, the *n*-alkanes, pristane and phytane from relatively immature sediments have δD values that retain the isotopic signature of their natural product precursors, i.e. biosynthesised lipid components made up of acetyl and isoprene sub-units, respectively. With increasing maturity, pristane and phytane

become more enriched in deuterium (D), while the *n*-alkanes generally remain at a constant isotopic composition until an overmature level is reached, at which point there is a significant enrichment of D in *n*-alkanes. The enrichment of D in pristane and phytane with increasing maturity correlates strongly with changes in traditional maturity parameters including vitrinite reflectance, T_{max}, and molecular parameters, providing evidence that D-enrichment is associated with thermal maturation.

The research presented in Chapter 3 also showed that such a maturity measurement could be applicable to Devonian sediments, where vitrinite reflectance measurements cannot be made because the higher-plant precursors of vitrinite had not yet evolved. The study extended the application of D/H of biomarkers to Devonian samples from the Duvernay Formation of the Western Canada Sedimentary Basin (WCSB). Similar to previous work, with increasing thermal maturity, pristane and phytane are rapidly enriched in D, compared to slower D-enrichment of the *n*-alkanes in Duvernay Formation samples.

It still remains uncertain whether the application of D/H of individual hydrocarbons as a precise maturity tool for pre-Devonian sedimentary rocks is applicable. The results also emphasise the care needed when interpreting δD values in the context of the source(s) of hydrocarbons in sediments of high thermal maturity, particularly those hydrocarbons with a high reactivity towards hydrogen exchange. The effect of maturation on indigenous δD values may result in an erroneous interpretation.

In Chapter 4, the use of complementary inorganic and organic isotope techniques for the crude oils samples has been tested to understand if they provide a new highly discriminant tool for petroleum exploration (origin and age of the crude oils). Studies to date have typically relied on classification and discrimination of crude oil samples based either on molecular and isotope geochemistry or on trace element data rather than investigating the potential of amalgamating both techniques to provide a vigorous assessment.

Trace element contents may predict crude oil origin, maturity, migration pathways and establish sources of heavily biodegraded petroleum samples. A novel rapid, reliable and accurate method of determination of major and trace

element contents of crude oils has been developed based on Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). For the first time, this method has been applied to a series of petroleum samples for analysis of Fe, Mg, Zn, Cu, Cr, Ni, Co, V, As, Mo and Se at trace levels, with little or no sample pre-treatment. In addition, $\delta^{13}C$ of individual hydrocarbons in crude oils in a systematic manner has been carried out for a better understanding of the origins of crude oils in Australian petroleum systems. Oils analysed include a series from different Australian basins of different geological age.

Based on the work presented in Chapter 4, the scatter plot of two discriminant functions from the analysis of trace elements (V, Pb, B, Mg, Sn, Ti, Mo and Hg) in crude oils samples confirms the capability of separating samples into their petroleum basins. 91.3% correct classification of the samples analysed was achieved. Analysis using two discriminant functions of combined trace elements (Al, Cr, Ti, Fe, Cu, Si, Tm, Mn, Ge, and Dy) and $\delta^{13}C$ of N, Bp resulted in 100% of samples being correctly classified according to their source rock age.

The application of linear discriminant analysis of the stable carbon isotope ratios and trace element concentrations has allowed the classification of crude oils to their geographical (or basinal) sources and age (Chapter 4).

The study presented in Chapter 5 aimed to establish the factors controlling the stable carbon isotopic compositions of individual aromatic hydrocarbons analysed by CSIA in crude oils from Western Australian petroleum basins of varying age, facies type but of similar thermal maturity. A series of oils were analysed for $\delta^{13}C$ of individual aromatic hydrocarbons, like alkylbenzenes, alkylnaphthalenes, alkylphenanthrenes and methylated biphenyls. The study has been based on confirming the origin (source) and age of these oils based on CSIA of selected aromatic compounds and understanding why the Sofer plot is ineffective in establishing source of Western Australian petroleum systems. Because the bulk $\delta^{13}C$ of saturate and aromatic fractions of crude oils have been previously used to differentiate sources and because many Australian crude oils do not appear to follow this trend, oils from both marine and terrigenous basins have been studied to see if the CSIA data of the aromatic hydrocarbons obtained

for the oils provide different conclusions regarding the source of the oils compared to bulk data (Sofer plot).

In Chapter 5, it is shown that the oils where the $\delta^{13}C$ of 1,6-DMN and 1,2,5-TMN isomers is most negative are probably derived from marine sources, whereas oils containing 1,6-DMN and 1,2,5-TMN with a less negative value are representative of a terrigenous source. The $\delta^{13}C$ values falling in between probably have mixed source(s). Less negative $\delta^{13}C$ values of 1-MP and 1,9-DMP isomers probably reflect the varying inputs of terrigenous organic matter to the source-rocks of the oils . Plots of P/DBT and Pr/Ph versus $\delta^{13}C$ of DMP, 1,6-DMN, 1,2,5-TMN, 1-MP and 1,9-MP are constructed to establish the end-members of terrigenous and marine sourced oils. The ratio of P/DBT and/or the ratio of Pr/Ph and $\delta^{13}C$ of aromatic isomers (such as 1,6DMN, 1,2,5-TMN, 1-MP and 1,9-MP) when coupled together, provide a novel and convenient way of establishing crude oil source rock origin and sometimes even lithologies.

In summary, it is apparent that important source, age, thermal history and palaeoenvironmental information can be obtained from the molecular, carbon and hydrogen isotope values of individual hydrocarbons and from trace element data preserved in sedimentary organic matter and crude oils in different petroleum systems.

Future work

Novel findings are presented within this thesis. However, much additional work could be carried out. It is clear that thermal maturation alter the δD values of certain compounds types to a greater extent than others (Chapter 3), however the investigation of a wider range of compounds in different settings (i.e. hydrothermal fluids) is necessary to confirm these findings. In addition, although the potential of δD values of individual hydrocarbons to assess the thermal history has been demonstrated for Devonian samples, it would be desirable to show the application of maturity measurement to pre-Devonian sediments and oils. There has been little research into the effect that other alteration events such as biodegradation and water washing have on the δD values of individual

hydrocarbons. Further work in this area would allow more confident and comprehensive interpretation of stable isotope values of hydrocarbons present in the samples exposed to the secondary processes.

The trace elements in crude oils, the δD values and the $\delta^{13}C$ parameters of individual hydrocarbons in sedimentary organic matter and in oils, in combination with other molecular parameters and petroleum basin's geological history have useful applications in oil-source correlations, aging the oils and understanding the depositional environments of the petroleum systems (Chapter 4 and 5). Further work could focus on the analysis presented in Chapter 4 and 5 of a wider range of crude oils derived from source rocks deposited in various types of depositional environments and ages. An understanding of the effects of different depositional environments, ages and lithologies on the different organic and inorganic geochemical parameter could prove to be useful for better understanding of the petroleum systems.

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