Biomarker signatures of Upper Cretaceous hydrocarbon source rocks from the Latrobe Group, Gippsland Basin

Lian Jiang*
Department of Earth and Planetary Sciences and Macquarie University Marine Research Centre
Macquarie University, Sydney, NSW, 2109, Australia
E-mail: lian.jiang@hdr.mq.edu.au

Simon C. George
Department of Earth and Planetary Sciences and Macquarie University Marine Research Centre
Macquarie University, Sydney, NSW, 2109, Australia
E-mail: simon.george@mq.edu.au

**presenting author asterisked*

SUMMARY

Gas chromatography-mass spectrometry analyses have been carried out to investigate the geochemical characteristics of the Latrobe Group shales and coaly shales from the Gippsland Basin, Australia. The depositional environment, source of organic matter and thermal maturity of hydrocarbon source rocks in the study area were evaluated using molecular biomarker analyses. The distribution of isoprenoid alkanes and pentacyclic triterpanes reveals an oxic environment with fresh water (pristane/phytane > 3.0, gammacerane index < 0.3). The carbon preference indices (CPI) and odd-to-even predominance ratios of the n-alkanes are higher than 1.0, suggesting terrigenous higher plant-derived organic matter in the sediments. The high predominance of C_{29} sterane over C_{27} sterane, as well as the occurrence of conifer and angiosperm biomarkers (e.g., labdane, isopimarane, phyllocladane, rimuane, oleanane, retene, anthracene, and cadalene), corroborates input from higher vascular land plants. Biomarker and aromatic thermal maturity indices, such as the methylphenanthrene index, the methylnaphthalene ratio, C_{31} 22S/(22S+22R) hopanes, C_{30} αβ/(αβ+βα) hopanes and C_{29} ααα 20S/(20S+20R) steranes, indicate rather thermally immature hydrocarbon source rocks, in agreement with the above CPI data. This maturity trend is also supported by the triaromatic sterane index [TA(I)/TA(I+II)], which is generally lower than 0.2.

Key words: Gippsland Basin, Latrobe Group, Hydrocarbon Source Rocks, Biomarker, Cretaceous

INTRODUCTION

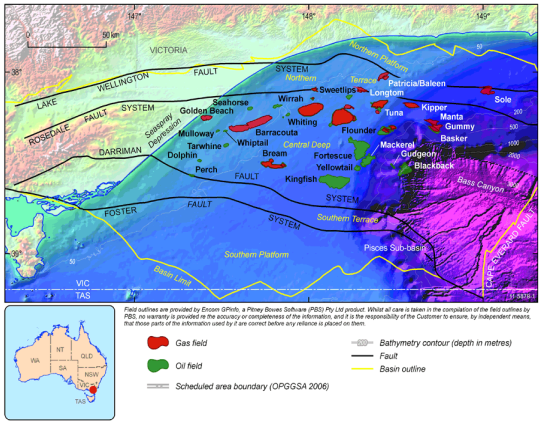

Figure 1: Digital terrain image of the Gippsland Basin showing the major tectonic elements (Geoscience Australia)

The Gippsland Basin is Australia's most prolific oil and gas province, with an area of approximately 46,000 square kilometres. The basin is one of the major post-Palaeozoic passive margin basins located along the southern continental shelf of Australia, and about three quarters of it lies under the waters of Bass Strait (Figure 1). Compared to many other prolific basins around the world, the Gippsland Basin is actually relatively under-explored. Due to a combination of its untapped potential and increasing demand for natural gas and oil, exploration within the Gippsland Basin is predicted to continue at the current robust levels. To date, most of the hydrocarbon accumulations in this basin are sourced from the Upper Cretaceous to Paleogene Latrobe Group, which is a sedimentary system dominated by marginal marine to lower coastal plain depositional environments (Edwards et al., 2015; Goldie Divko, 2015).

The regional geology and stratigraphic sequence of the Gippsland Basin are well documented in the literature (Brooks and Smith, 1969; George et al., 1998; Bernecker and Partridge, 2001; O'Brien et al., 2013, and references therein). Several studies related to the origin of organic matter, large-scale CO_2 storage possibilities, coal seam gas potential, and petroleum potential have also been reported. For example, Spyckerelle (1975) first reported the occurrence of several tetraaromatic and triaromatic hydrocarbons (e.g. 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene and 1,2,4,4a-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene) in the Yallourn lignite. A series of tricyclic diterpenoid hydrocarbons which might possibly be the precursors of bicyclic sesquiterpanes were found to be widely distributed in various crude oils thought to be of non-marine origin in the Gippsland Basin (Philp et al., 1981). These diterpanes were thought to be related to higher-plant input (Philp et al., 1981, 1983). Subsequently, Alexander et al. (1983) used synthetic standards to identify 4β-eudesmane and 8 β-drimane in oils from the Cormorant Field in the Gippsland Basin, and suggested that these biomarkers are probably derived from higher plant precursors and microbial sources, respectively. George et al. (1998) reported a fluid inclusion oil extract within the upper Latrobe Group reservoir at Blackback-2 which had a marine source influence. Other studies have considered the viability of the Gippsland Basin for large-scale Carbon Capture and Storage (CCS) in relation to containment and migration (O'Brien et al., 2008), and kinetic models for hydrocarbon generation from the Upper Cretaceous to Paleogene Latrobe Group coals and shales (Abbassi et al., 2016). Even though it is a mature basin for exploration, few biomarker analyses of hydrocarbon source rocks

in the Gippsland Basin have been published in the peer-reviewed literature (Chaffee et al., 1983a, 1983b, 1984, Volk et al., 2011, and reference therein).

This study aims to decipher biomarker distributions of Upper Cretaceous hydrocarbon source rocks from the Latrobe Group, Gippsland Basin based on gas chromatography-mass spectrometry (GC-MS) analyses, and evaluate their depositional environment, origins of organic matter and thermal maturity. The results not only improve our understanding of the geochemical characteristics of Upper Cretaceous hydrocarbons, but also provide insights into the remaining prospectivity and new exploration opportunities in less explored parts of the basin.

SAMPLES AND METHODS

Ten Upper Cretaceous samples, which were provided by Dr. Dianne Edwards for this study, were previously solvent extracted to provide kerogen fractions for a kinetics study (Abbassi et al., 2016). Six samples are from the Maastrichtian (2011032, 2011034, 20110130, 20110144, 20110149, and 20110252), and four samples are from the Campanian (20110035, 20110096, 20110097 and 20110128). For detailed information about depths, locations and Rock-Eval pyrolysis parameters of these samples, refer to Abbassi et al. (2016). The extractable organic matter (EOM) of each sample (approx. 10-20 mg), after sulphur elimination, was separated by column chromatography into aliphatic and aromatic hydrocarbon fractions using an activated silica gel column (45 mm). Total hydrocarbons (THC) were first eluted with a solution of n-hexane and dichloromethane (DCM) (4:1, v/v, 3 ml), and the polar fraction with a solution of methanol (MeOH) and DCM (1:1, v/v, 3 ml). Subsequently, the THC were separated into aliphatic and aromatic hydrocarbon fractions using n-hexane (2.6 ml) and n-hexane/DCM (4:1, v/v, 3.5 ml), respectively.

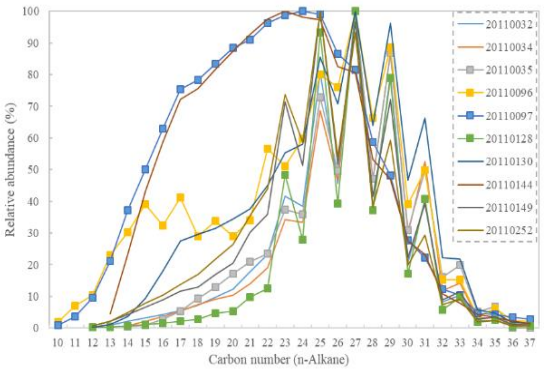

Figure 2: Normalised *n*-alkane profiles of aliphatic fractions of the Upper Cretaceous Latrobe Group hydrocarbon source rocks in the Gippsland Basin

GC-MS was carried out using an Agilent gas chromatograph (6890N) coupled to an Agilent mass selective detector (5975B) equipped with a DB-5MS fused silica capillary column (60 m × 0.25 mm i.d., film thicknesses 0.25 µm). The programmable temperature vaporisation (PTV) inlet was held at 40 °C for 3 min, and then was programmed to 310 °C (0.4 min. isothermal) at a rate of 700°C/min. Helium was used as the carrier gas with a rate of 1.5 ml/min (constant flow) and the EI source was operated at 70 eV. The GC oven was temperature programmed to start at 40 °C for 2 min, increase to 310 °C at a rate of 4 °C /min, and was then held at 310 °C for 40 min.

RESULTS AND DISCUSSION

Hydrocarbon source rocks from the Upper Cretaceous Latrobe Group, Gippsland Basin contain predominately C_{12} to C_{36} *n*-alkanes in the aliphatic fractions, with a maximum at *n*-C_{25} or C_{27} (Figure 2). The *n*-alkane profiles show three patterns: (a) a unimodal distribution with slight odd-over-even predominance (represented by samples 20110097 and 20110144); (b) a bimodal distribution, only in sample 20110096); (c) a unimodal distribution with a maxima and significant odd-over-even predominance at high molecular weight. The wax index ((*n*-C_{21} + *n*-C_{22})/(*n*-C_{28} + *n*-C_{29}) alkanes), carbon preference index (CPI), and odd-to-even predominance (OEP) ratios of Upper Cretaceous hydrocarbon source rocks are 0.19-1.9, 1.09-2.8, and 1.09-2.3, respectively. These ratios show that the organic matter was mainly derived from terrigenous higher plants. Compared to other samples, samples 20110097 and 20110144 have a larger aquatic organic matter input, given their higher wax index ratios and *n*-alkane profiles. The Pr/Ph ratios of all samples range from 3.8 to 11.5, and the Pr/*n*-C_{17} and Ph/*n*-C_{18} ratios are 0.71-8.1 and 0.12-0.89, respectively, indicating an oxidising depositional environment with Type III organic matter input.

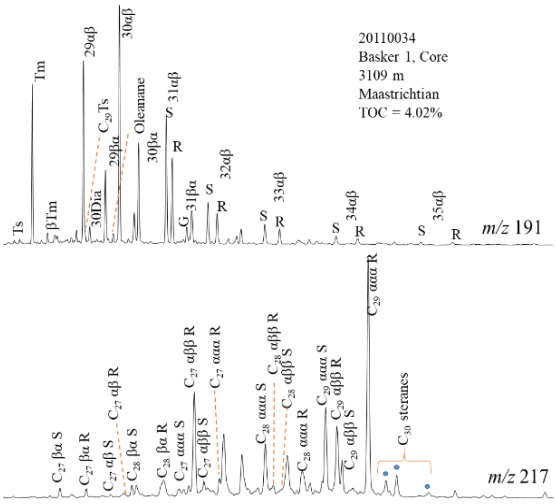

Figure 3: Partial *m/z* 191 and *m/z* 217 mass chromatograms of the aliphatic fraction of a typical Upper Cretaceous Latrobe Group hydrocarbon source rock in the Gippsland Basin. Notes: Dia = diahopane, G = gammacerane.

A series of sesquiterpanes, diterpanes and triterpanes are present in the samples. C_{14}-C_{16} bicyclic sesquiterpanes include drimane, homodrimane, and 4β(H)-eudesmane. Diterpanes are represented by 8β(H)-labdane, 4β(H)-19-norisopimarane, 18-norabietane, abietane, rimuane, C_{19}-17-nortetracyclane, *ent*-beyerane, isopimarane, 16α(H)-phyllocladane, 16β(H)-phyllocladane, and *ent*-16β(H)-kaurane. These compounds confirm a contribution of terrigenous higher plants to the organic matter. The distributions of pentacyclic triterpanes (hopanes) in the hydrocarbon source rocks are similar. Taking sample 20110034 as an example (Figure 3), hopanes are dominated by C_{30} αβ hopane with a range of C_{27}-C_{35} hopanes. C_{27} 17α(H)-22,29,30-trinorhopane (Tm) is significantly more abundant than C_{27} 18α(H)-22,29,30-trinorneohopane (Ts), and the C_{27} 17β(H)-22,29,30-trinorhopane (βTm) was also detected in all samples. Ts/(Ts+Tm) ratios are generally < 0.3, and C_{30} αβ/(αβ+βα) hopane values vary from 0.68-0.86. C_{31}-22S/(22S+22R) homohopane, which is a maturity indicator that equilibrates at 0.57-0.62 and shows high specificity for immature to early oil generation (Peters et al., 2005), has reached

equilibrium values. These hopane maturity parameters show that the samples have reached the early oil window, but not the peak oil generating threshold. The gammacerane index (G/C_{30} αβ hopane) is low and ranges from 0.04 to 0.23, indicating a fresh water environment. The oleanane index (oleanane/C_{30} αβ hopane) is 0.01-0.11 with a mean of 0.06, suggesting a relatively low input from angiosperms, which is consistent with the palynology data (Macphail, 2007).

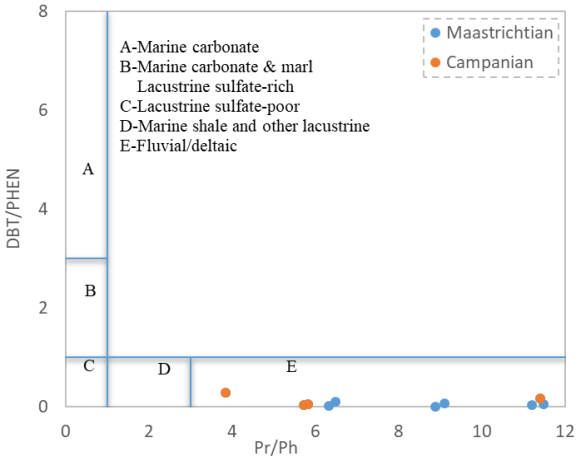

Figure 4: Cross-plot of dibenzothiophene/phenanthrene (DBT/PHEN) versus Pr/Ph for Upper Cretaceous Latrobe Group hydrocarbon source rocks in the Gippsland Basin (fields after Hughes et al., 1995).

Rearranged steranes (C_{27}-C_{29}) are in low abundance compared to regular steranes (Figure 3). C_{27} and C_{29} diasterane/regular sterane ratios are low, with ranges of 0.08-0.37 and 0.15-0.51, respectively. C_{27}-C_{29} regular steranes are dominated by C_{29} regular steranes, with C_{29}/C_{27} ααα 20R sterane ratios varying from 1.5-16, suggesting major to dominant input from higher land plants. C_{29} ααα 20S/(20S+20R) sterane and C_{29} αββ/(αββ+ααα) sterane ratios range from 0.22-0.45 and 0.22-0.59, respectively, also show an early oil window thermal maturity, as also suggested by CPI, OEP, C_{30} αβ/(αβ+βα) hopane and C_{31}-22S/(22S+22R) homohopane ratios.

Aromatic fractions of the rock extracts contain abundant naphthalene, phenanthrene, anthracene, cadalene, retene, fluorene, dibenzothiophene, dibenzofuran, biphenyl, and their alkyl derivatives, as well as pyrene, perylene, picene and chrysene. These distributions are consistent with the results from the aliphatic fractions that suggest a major contribution of organic matter from terrigenous plants. The methylnaphthalene ratio (MNR; 2-MN/1-MN) and the methylphenanthrene index (MPI-1; 1.5 × (3-MP + 2-MP)/(P + 9-MP + 1-MP)) are 1.15-1.6 and 0.24-0.96, respectively, consistent with thermal maturities in the early to mid-oil window. In addition, a series of C_{21}-C_{29} triaromatic steranes was detected in the samples. The triaromatic sterane index (TA(I)/TA(I+II)), which is a maturity parameter, is generally lower than 0.2, also indicating a relatively low maturity. The cross-plot of dibenzothiophene/phenanthrene (DBT/PHEN) versus Pr/Ph shows that the Upper Cretaceous source rocks were deposited in fluvial/deltaic environment.

CONCLUSIONS

Based on aliphatic and aromatic hydrocarbon and biomarker analyses of Upper Cretaceous hydrocarbon source rocks from the Latrobe Group, Gippsland Basin, the following conclusions can be drawn: (1) The depositional environment during the Upper Cretaceous was mostly an oxidising fluvial/deltaic environment, with fresh water. (2) The thermal maturity is relatively low and is in the early-middle oil generation window. (3) The organic matter was mainly derived from higher land plants (both gymnosperms and angiosperms).

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REFERENCES

Abbassi, S., Edwards, D.S., George, S.C., Volk, H., Mahlstedt, N., di Primio, R., Horsfield, B., 2016. Petroleum potential and kinetic models for hydrocarbon generation from the Upper Cretaceous to Paleogene Latrobe Group coals and shales in the Gippsland Basin, Australia. Organic Geochemistry, 91, 54-67.

Alexander, R., Kagi, R., Noble, R., 1983. Identification of the bicyclic sesquiterpenes drimane and eudesmane in petroleum. Journal of the Chemical Society, Chemical Communications, 226-228.

Bernecker, T., Partridge, A.D., 2001. Emperor and Golden Beach subgroups: the onset of Late Cretaceous sedimentation in the Gippsland Basin, SE Australia, Eastern Australasian Basins Symposium. A Refocused Energy Perspective for the Future, Petroleum Exploration Society of Australia, Special Publication, 391-402.

Brooks, J.D., Smith, J.W., 1969. The diagenesis of plant lipids during the formation of coal, petroleum and natural gas—II. Coalification and the formation of oil and gas in the Gippsland Basin. Geochimica et Cosmochimica Acta, 33, 1183-1194.

Chaffee, A.L., Perry, G.J., Johns, R.B., 1983a. Pyrolysis—gas chromatography of Australian coals. 1. Victorian brown coal lithotypes. Fuel, 62, 303-310.

Chaffee, A.L., Perry, G.J., Johns, R.B., 1983b. Pyrolysis—gas chromatography of Australian coals. 2. Bituminous coals. Fuel, 62, 311-316.

Chaffee, A.L., Strachan, M.G., Johns, R.B., 1984. Polycyclic aromatic hydrocarbons in Australian coals II. Novel tetracyclic components from Victorian brown coal. Geochimica et Cosmochimica Acta, 48, 2037-2043.

Edwards, D.S., Ahmed, M., Bernecker, T., Boreham, C.J., Se, G., Goldie-Divko, L., Gorter, J., Hall, L., Langford, R.P., Mitchell, C., Volk, H., 2015. A Geochemical Overview of Gippsland Basin Hydrocarbon Accumulations, International Conference & Exhibition.

George, S.C., Eadington, P.J., Lisk, M., Quezada, R.A., 1998. Geochemical comparison of oil trapped in fluid inclusions and reservoired oil in Blackback oilfield, Gippsland Basin, Australia. Petroleum Exploration Society of Australia Journal, 26, 64-81.

Geoscience Australia, viewed 20 August 2017, <http://www.ga.gov.au/scientific-topics/energy/province-sedimentary-basin-geology/petroleum/offshore-southern-australia/gippsland>

Goldie Divko, L.M., 2015. A review of gas prospectivity: Gippsland region. Department of Economic Development, Jobs, Transport and Resources, Victorian State Government.

Hughes, W.B., Holba, A.G., Dzou, L.I.P., 1995. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. Geochimica et Cosmochimica Acta, 59, 3581-3598.

Macphail, M., 2007. Australian palaeoclimates: Cretaceous to Tertiary a review of palaeobotanical and related evidence to the year 2000, CRC LEME Special Volume Open File Report.

O'Brien, G.W., Tingate, P.R., Goldie Divko, L.M., Harrison, M.L., Boreham, C.J., Liu, K., Arian, N., Skladzien, P., 2008. First order sealing and hydrocarbon migration processes, Gippsland Basin, Australia: Implications for CO_2 geosequestration.

O'Brien, G.W., Tingate, P.R., Goldie Divko, L.M., Miranda, J.A., Campi, M.J., Liu, K., 2013. Basin-scale fluid flow in the Gippsland Basin: implications for geological carbon storage. Australian Journal of Earth Sciences, 60, 59-70.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide. Cambridge University Press.

Philp, R.P., Gilbert, T.D., Friedrich, J., 1981. Bicyclic sesquiterpenoids and diterpenoids in Australian crude oils. Geochimica et Cosmochimica Acta, 45, 1173-1180.

Philp, R.P., Simoneit, B.R.T., Gilbert, T.D., 1983. Diterpenoids in crude oils and coals of South Eastern Australia, Advances in Organic Geochemistry 1981. Wiley, Chichester, 698-704.

Spyckerelle, C., 1975. Constituents Aromatiques de sédiments. Ph.D. Thesis, University of Strasbourg, France.

Volk, H., Ahmed, M., Gong, S., Boreham, C., Tingate, P., Sherwood, N., Edwards, D., 2011. Distribution of land plant markers in oils from the Gippsland Basin. The Australian Petroleum Production and Exploration Association Journal, 51, 740-740.