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

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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 anoxic environments 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 C29 sterane over C27 sterane, as well as the occurrence of conifer and angiosperm biomarkers (e.g., labdane, isopimarane, phyllocladane, rimuane, oleane, 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, C20/S/(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

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 CO2 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. 3,7-trimethyl-1,2,3,4-tetrahydrochrysene and 1,2,4,4a-tetramethyl-1,2,3,4,4a,5,6,14b-octahydrotocipene) 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 8β-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.

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 thickness 0.25 μm). The programmable temperature vapourisation (PTV) inlet was held at 40 °C for 3 min, and then was programmed to 310 °C (0.4 min. isotothermal) 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 Latrobe Group, Gippsland Basin contain predominately C12 to C30 n-alkanes in the aliphatic fractions, with a maximum at n-C25 or C27 (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-C21 + n-C23)/(n-C24 + n-C25) 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-C17 and Ph/n-C18 ratios are 0.71-8.1 and 0.12-0.89, respectively, indicating an oxidising depositional environment with Type III organic matter input.

A series of sesquiterpanes, diterpanes and triterpanes are present in the samples. C15-C18 bicyclic sesquiterpanes include dimane, homodimane, and 4β(H)-endosperane. Diterpanes are represented by 8β(H)-labdanane, 4β(H)-19-norisopimarane, 18-norabietane, abietane, rimuane, C15-17-nortetracyclic, ent-beyerane, isopimarane, 16α(H)-phyllocladane, 16β(H)-phyllocladane, and ent-16β(H)-kaurene. 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 C29 0βH hopane with a range of C27-C30 hopanes. C27 17α(H)-22,29,30-trinorhopane (Tm) is significantly more abundant than C27 18α(H)-22,29,30-trinorhopane (Ts), and the C27 17β(H)-22,29,30-trinorhopane (βTm) was also detected in all samples. Ts/(Ts+Tm) ratios are generally < 0.3, and C29 0βH/(0βH+1βH) hopane values vary from 0.68-0.86. C27-22S/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 (GC/C0 θβ hopane) is low and ranges from 0.04 to 0.23, indicating a fresh water environment. The oleanane index (oleanane/C0 θβ 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).

Rearranged steranes (C27-C29) are in low abundance compared to regular steranes (Figure 3). C27 and C29 diasterane/regular sterane ratios are low, with ranges of 0.08-0.37 and 0.15-0.51, respectively. C27-C29 regular steranes are dominated by C29 regular steranes, with C29/C27 mean 20R sterane ratios varying from 1.5-16, suggesting major to dominant input from higher land plants. C29 θβ(θβθ+ααα)/(22S+22R) sterane and C29 θβθθ/(θβθθ+θβαβ) 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, C0 θβθθ/(θβθθ+θβαβ) hopane and C31-22S/(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 methylnaphthalene 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 C21-C29 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


