Biomarker characteristics of Montney source rock, British Columbia, Canada

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HIGHLIGHTS

- Geochemical analyses of biomarker traces, elemental analysis, and pyrolysis provide a continuous profile of source rock.
- The OM source input, preservation conditions, and thermal maturation level were provided based on biomarker analysis.
- The results of the elemental analysis show that the Montney formation source rock was deposited in a marine environment.
- Biomarkers are considered an effective method for detailed and insightful information that helps evaluate any source rock.

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ABSTRACT

Montney Formation (MF) source rock located in northeastern British Columbia (BC), Canada, was analyzed to determine its depositional conditions and organic matter source input other than to determine their level of thermal maturity. The high total sulfur (TS) (2.23–20.86 wt.%) and good to very good total organic carbon (TOC) content (0.3–5.87 wt.%) in the analyzed samples give good evidence that the deposition of MF source rock was in a marine environment under reducing conditions. A mixed marine-terrestrial derived organic matter (OM) for the Montney source rock that was deposited in a marine dysoxic environment is deduced from the composition and distribution of different biomarker traces. Thus, the previous result is supported by the high short-chain n-alkanes ratio, accompanied by carbon preference index (CPI) around unity, high concentration of tricyclic terpanes, high C24 tricyclic/C24 tetracyclic, hopane/sterane ratios ranging from low to moderate, as well as the relationship between regular sterane compositions. During deposition of the MF source rock, it can be noticed that more land organic materials this was deduced according to the high waxiness index. From maturity ratios of Ts/(Ts + Tm), C32 22S/(22S + 22R) homohopane, moretane/hopane and 20S/(20S + 20R) and ββ/(ββ + αα)C29 it can give a conclusion that the source rock is mature to postmature of hydrocarbon generation.

1. Introduction

The Lower Triassic Montney Formation (MF) of the Western Canada Sedimentary Basin (WCSB) (Figure 1) is a world-class unconventional resource with 450 Tcf gas reserves, 14 520 million barrels of marketable natural gas liquids reserves, and 1125 million barrels of commercial oil reserves [1]. Although commonly described as shale, the MF is siltstone in most of its subcrop. MF is a multilayered accumulation of fine-grained sediments (shale, siltstone, sandstone) deposited in the offshore to shoreface environment [2].

Unconventional reservoirs have been studied intensively in the last two decades because they form cap rocks and are an essential and direct source of hydrocarbons, especially after the production of conventional storage tanks began to decline and the inability to cover the growing market needs. But these reservoirs need recent and in-depth studies using different techniques to create models as a reference for proper understanding and determining reservoir parameters.

Classification of source rocks and labeling the families of the crude oils became possible and easy to achieve by using petroleum geochemistry [3, 4, 5, 6, 7, 8, 9, 10]. Organic matter (OM) extract analysis is one of the most basic tests for determining paleo-preservation conditions, OM maturity, and the type of hydrocarbons generated [11, 12]. These parameters will help in locating hydrocarbons in the basin’s explored areas and various stratigraphic units [13]. This kind of analysis is also beneficial in developing tools describing, understanding, and predicting the formation of sweet spots of oil and gas, migration, basins thermal maturity history, and fluids that have passed through them all over exploration and production. The OM extract analyses include

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biomarkers, stable isotope ratios, hydrocarbon contents [8]. The biomarkers analysis using gas chromatography-mass spectrometry (GC-MS) is the key to this information. As a result, petroleum geochemistry has become a widely used tool in the oil and gas industry [14].

Source rock potential and OM maturity of the MF were the focus of most of the studies; very few organic geochemical investigations on the origin of OM and the preservation conditions during deposition have been made. Biomarkers were not heavily used in assessing the MF source rock because most previous interpretations relied heavily on pyrolysis methods, which indicated the largely gas-prone nature of the probable source rock in the MF without thoroughly investigating the source input and preservation conditions of the OM. Riediger [15] first made correlations for the oil-source rock of the Triassic source rocks in BC, which were established, based on biomarker traces; the results of the study revealed that the over mature stage of MF nearly in most of the studied area, which makes it difficult to assess its (original) source potential. The current study aims to provide a detailed overview of the OM source input, preservation conditions, and thermal maturation level of the MF source rock depending on a detailed biomarkers analysis.

2. Geological setting

The lower Triassic Montney sediments deposited in a basin presently known as the WCSB on the Pangean supercontinent west margin. The Peace River’s central basin is considered one of the essential sub-basins inside the WCSB [16, 17, 18, 19, 20]. The MF reaches up to 300 m of deltaic marine and submarine turbidites deposited in the peace river arc area of NE BC. The lower Triassic MF was assigned to the Griesbachian to Spathian in age [19] (Figure 2). In nearly most places, the Triassic sequence overlies unconformably overlies the Carboniferous to Permian (Belloy Formation) strata [15, 21, 22, 23]. The Triassic sequence’s cumulative thickness is approximately 1200 m in the westernmost outcrop in the Rocky Mountain bottoms [21]. The main sediment types include deeper water, interlaminated shale with siltstone, and fine-grained sandstone, which reveal a turbidity condition [21, 24, 25] (Figure 2). The stratigraphy and the paleogeography of the MF were established based on the Induan and Lower Olenekian aged deposits that contain the shallow marines and turbiditic facies [24, 26, 27]. The various sedimentary environments are presented, including Tidal and wave-dominated foreshore, shoreface, and offshore settings, forming the typical facies association and log pattern [27] (Figure 2).

The early Triassic was a time of biologic recovery as it immediately follows the End-Permian extinction, the most severe biologic perturbation in history [2, 29, 30]. Regionally extensive shallow water anoxia/dysoxia in conjunction with increased oceanic acidity is thought to have played a significant role in the extinction [31, 32, 33]. These conditions are assumed to have continued into the Early MF [32, 33]. On the basis of lithology, mineralogy, and well log character, the MF is formally divided into eight regionally extensive members. The major three are the Lower Montney Member, the Middle Montney Member, and the Upper Montney Member, which correspond to the informal units used by
industry geoscientists. The boundaries of these units correspond to those of main boundaries (Dienerian-Smithian and Smithian-Spathian) [24, 34, 35, 36].

3. Samples and methods

Thirty-four core samples were collected from four wells in the BC area (Figure 1). These wells were chosen to cross distinct lithofacies in a northeast-southwest direction. Before the geochemical studies, the collected samples were thoroughly cleaned. Geochemical analyses of the obtained samples were carried out at the Universiti Teknologi PETRONAS (UTP) and STRATOCHEM Laboratories, respectively. The samples were crushed to powder and separated into three parts; a small amount (1.5–2 mg) of the dry sample was used for elemental analysis using a PerkinElmer 2400 Elemental Analyzer (CHNO/S), which can provide measurements of the sulfur contents (TS) for preservation conditions. The second section was utilized for pyrolysis analysis and total organic carbon (TOC) measurement, with the SRA (source rock analyzer) employed to determine source rock potentiality and maturity. Pyrolysis analysis entails heating to 650 °C in an inert environment and measuring parameters such as S1, S2, and Tmax (Table 1). Following that, the hydrogen index (HI), production index (PI), and potential petroleum yield (PY) were computed (Table 1). Because of the possibility of interference between some classes of aromatic and saturate biomarkers, it is customary to separate saturates and aromatics components by liquid chromatography (MLPC, for example) before the examination so that each fraction may be studied separately. Both saturate and aromatic fractions were examined using an HP 6890 gas chromatograph outfitted with an HP 7683 auto-sampler, on-column injector, and the HP5973 mass selective detector (MSD); the sample preparation and investigation followed the procedure suggested by [37, 38, 39], and the results were used to determine the source of the organic material, maturity, and preservation conditions.

Figure 2. Ideal stratigraphic sequence of the MF [28].

4. Results and discussion

4.1. Organic-carbon and sulfur contents

Table 1 shows that the MF source rock samples have relatively good to very good TOC as 80% of the results fall in the range of 1–4%. The good enrichment of OM in terms of TOC results indicates that the OM preservation conditions were low to moderate when the source rock's sediments were being deposited or could be due to exhausting OM [40, 41, 42]. The TS wt.% of studied source rock samples from MF was high and ranged between 2.23 and 21.97 wt.% (Table 1). There is no apparent correlation between TOC and TS, as shown in (Figure 3); this indicates no relation between TS and OM sedimentation in the tested source rock samples. The origin and condition of preservation of OM in the marine environment were determined by the cross plot between TOC and TS contents as shown in (Figure 3) [43, 44], elucidated that the use of TS as an indicator of marine effect is stronger than the organic or pyritic sulfur in the sediments. The highly reducing hypersaline marine conditions were marked by TS > 2 wt.% [45], whereas the non-marine (freshwater) sediments have concentrations of TS < 0.5 wt.% [43, 46]. Thus, regarding the MF source rock understudy samples, which contain high TS > 2 wt.%, the interpreted depositional environment is marine under highly hypersaline-reducing conditions (Figure 3).

4.2. Type and characteristics of organic matter

The pyrolysis results of the analyzed samples (Table 1) were the reference for evaluating OM richness, type of kerogen, and maturity. The pyrolysis S1 and S2 results were 0.52–8.44 mg HC/g rock and 0.42–2.89 mg HC/g rock, respectively (Table 1), showing high S1 values regarding the S2 be explained by the high contamination or recent migration of hydrocarbons [47]. However, S2 values indicated that the generative potential of the MF source rock samples had fair to good (Figure 4), with comparatively low values of less than 2.89 mg HC/g rock (Table 1). The calculated HI and the low pyrolysis S1 and S2 yields were used to characterize the kerogen type. The low HI values, in the range of 33.02–209.45 mg HC/g TOC (Table 1) for the studied samples, places them in the kerogen type IV. A relationship was established using a pseudo van Krevelen graph of HI versus Tmax to infer the kerogen type [48].

4.3. Biomarkers

Biomarkers, considered geochemical fossils, are defined as complex organic compounds composed of carbon found in crude oils, bitumen, and petroleum source rocks because they can be used as indicators of depositional environments in the same way we use the physical remains of organisms [50, 51]. Also, they can be related to the original biochemical precursor even after undergoing accumulation, diagenesis, and catagenesis [50].

Total ion current (TIC) and single ion monitoring (SIM) modes were used to record the normal alkanes, isoprenoids, terpenes, and steranes distributions. The TIC and SIM mode mass chromatograms (m/z 85, m/z 191, and m/z 217) were used as a reference for the detailed biomarker characteristics investigated in this study. And their identification was based on retention time and previous work [9, 10, 52]. The concentration ratios of the biomarkers were used as indicators of source input of the OM and the paleoenvironmental conditions during deposition of the MF source rock [3, 4].

Gas chromatograms of saturate fractions from four representative samples are shown in (Figure 6). The distribution of n-alkanes was used to indicate the source input of the parent organic organisms [53]. For example, the short-chain n-alkanes < C20 means algal-sourced OM, while
the long-chain n-alkanes > C_{27} with odd over-even carbon numbers predominance indicates a land plant-derived OM [54, 55]. The chromatograms suggest that the analyzed extracts contain a diverse array of alkane compounds ranging from C_{6} to C_{36} n-alkanes (Figure 6). The unimodal distribution and widespread dominance of short-chain/low to medium molecular weight (n-C_{13} – n-C_{20}) and (n-C_{21} – n-C_{27}) n-alkanes contrasted significantly with the long-chain n-alkanes (n-C_{27} – n-C_{36}) in the majority of the analyzed samples. The well extracts (A01-17-080-18W6) demonstrate a predominance of short-chain n-alkanes with a low molecular weight n-C_{20} (Figure 6). The most index acyclic isoprenoid hydrocarbons through concentration are Pristane (Pr) and phytane (Ph) in which they used to reflect the depositional conditions of source rocks [56]. All the studied samples show a significant amount of acyclic isoprenoids (Table 2), as demonstrated by Pr/n-C_{17} versus Ph/n-C_{18} ratios, where it is generally <1 except for a few samples from well (11-25-77-20W6) >1. The ratio of Pr/Ph has been used as an indicator of the redox conditions during deposition and diagenesis [57, 58]. The formation of Ph (C_{20}) happens when the phytol of the chlorophyll loses a hydroxyl group, which was interpreted as a reducing type environment indicator, and when the phytol loses one carbon atom, it yields Pr (C_{19}), which was interpreted to be in oxidizing environments [3, 56, 59, 60]. Within the oil window, the Pr/Ph ratios of crude oils and source rocks have a weak correlation with the depositional redox conditions [56, 58, 61].

An OM derived mainly from land plants preserved under oxidizing conditions will give high Pr/Ph >3 ratios, while an OM of marine origin preserved under reducing conditions will provide ratios of Pr/Ph <1, and values between 1 and 3 suggest suboxic conditions [4].

The studied extracts show high relative concentrations of pristane mostly, with ratios of Pr/Ph lies mostly between 1 and 3, suggesting a mixed marine-terrestrial input OM that was preserved under anoxic to suboxic conditions. Except for the samples from well (15-34-080-18W6) that show Pr/Ph ratio less than 1 (Table 2). However, other source

| Well ID          | Max. depth (m) | Depth (m) | TS (wt.%) | TOC (wt.%) | S1 (mg/g) | S2 (mg/g) | Tmax (°C) | HI (mg/g) | Oil (mg/g) | PI (mg/g) | PY (mg/g) |
|------------------|----------------|-----------|-----------|------------|-----------|-----------|-----------|-----------|------------|-----------|-----------|
| 15-34-080-18W6   | 2062           | 2048.65   | 11.80     | 1.07       | 2.25      | 0.63      | 461       | 58.88     | 2.80       | 0.78      | 2.88      |
|                  |                | 2054.93   | 11.50     | 1.20       | 1.85      | 0.82      | 466       | 68.33     | 3.33       | 0.69      | 2.67      |
|                  |                | 2060.02   | 9.40      | 1.12       | 1.61      | 0.84      | 455       | 75.00     | 0.00       | 0.66      | 2.45      |
|                  |                | 1852.80   | 16.98     | 2.30       | 2.68      | 1.03      | 475       | 44.80     | 19.57      | 0.72      | 3.71      |
|                  |                | 1859.14   | 18.11     | 0.60       | 1.16      | 0.43      | 451       | 76.51     | 80.07      | 0.73      | 1.59      |
|                  |                | 1866.76   | 15.96     | 3.11       | 4.49      | 1.84      | 489       | 59.18     | 16.73      | 0.71      | 6.33      |
|                  |                | 1867.13   | 20.86     | 3.01       | 6.39      | 1.82      | 480       | 60.53     | 14.63      | 0.78      | 8.21      |
|                  |                | 1871.10   | 20.20     | 3.12       | 6.24      | 1.89      | 478       | 60.64     | 14.12      | 0.77      | 8.13      |
| 11-25-77-20W6    | 2834.5         | 2161.80   | 20.48     | 5.87       | 1.59      | 2.33      | 496       | 39.69     | 10.39      | 0.41      | 3.92      |
|                  |                | 2163.80   | 20.31     | 0.90       | 8.44      | 1.95      | 324       | 209.45    | 46.19      | 0.81      | 10.39     |
|                  |                | 2166.60   | 14.62     | 5.10       | 1.76      | 2.00      | 502       | 39.43     | 7.29       | 0.47      | 3.76      |
|                  |                | 2168.80   | 15.46     | 0.67       | 2.94      | 0.56      | 370       | 84.21     | 64.66      | 0.84      | 3.50      |
|                  |                | 2186.60   | 17.23     | 1.55       | 5.91      | 0.70      | 311       | 45.22     | 31.65      | 0.89      | 6.61      |
|                  |                | 2385.04   | 5.53      | 0.92       | 0.52      | 0.50      | 459       | 54.53     | 34.90      | 0.51      | 1.02      |
|                  |                | 2392.87   | 7.81      | 1.27       | 0.55      | 0.42      | 458       | 33.02     | 29.87      | 0.57      | 0.97      |
|                  |                | 2402.17   | 2.23      | 0.30       | 0.57      | 0.43      | 457       | 133.54    | 114.91     | 0.57      | 1.00      |
|                  |                | 2411.48   | 5.04      | 1.37       | 0.58      | 0.64      | 459       | 46.78     | 24.85      | 0.48      | 1.22      |
| 2017-080-18W6    | 2592.35        | 2420.67   | 4.47      | 2.36       | 0.88      | 1.07      | 474       | 45.30     | 17.36      | 0.45      | 1.95      |
|                  |                | 2429.81   | 5.77      | 2.10       | 0.94      | 1.26      | 486       | 60.75     | 16.39      | 0.43      | 2.20      |
|                  |                | 2438.76   | 5.41      | 1.90       | 0.98      | 1.02      | 477       | 52.50     | 17.50      | 0.49      | 2.00      |
|                  |                | 2447.88   | 4.82      | 1.93       | 1.04      | 1.11      | 477       | 57.51     | 17.10      | 0.48      | 2.15      |
|                  |                | 2457.33   | 4.75      | 3.00       | 1.65      | 1.56      | 486       | 51.97     | 11.33      | 0.51      | 3.21      |
|                  |                | 2465.14   | 3.31      | 1.42       | 0.96      | 0.51      | 471       | 35.97     | 21.16      | 0.65      | 1.47      |

TOC: Total organic carbon, wt.%,
S1: Volatile hydrocarbon (HC) content, mg HC/g rock.
S2: Remaining HC generative potential, mg HC/g rock.
HI: Hydrogen Index = S2 *100/TOC, mg HC/g TOC.
PY: Potential yield = S1 + S2 mg HC/g rock.
PI: Production Index = S1/(S1 + S2).TS: Sulfur content (wt.%).
materials than phytol from chlorophylls [62] and thermal maturity [63] may influence the Pr/Ph ratio.

The cross-plot of Pr/n-C17 versus Ph/n-C18 (Figure 7) is commonly used to interpret source rock depositional environment conditions and OM type [4, 64]. Accordingly, the mixed marine and terrestrial sources of OM that was the dominant source that was deposited under anoxic to suboxic conditions, except for the samples from well (15-34-080-18W6) which is derived from marine source, deposited in an anoxic environment, and that all the samples were in the mature stage. which is also consistent with the results obtained from the cross plot of TS and TOC illustrated in (Figure 3).

The carbon preference index (CPI) of n-alkanes was calculated according to the formula proposed by [3], which is \(2(C_{23} + C_{25} + C_{27} + C_{29})/[C_{22} + 2(C_{24} + C_{26} + C_{28} + C_{30})]\) to provide some deep understanding of the OM source and conditions during deposition. CPI value is greatly influenced by OM input. CPI <1.0 indicate reducing depositional conditions [65]. The CPI values for all the analyzed samples were around the unity (Table 2) and were plotted against the Pr/Ph ratios (Figure 8), which indicates that the OM deposited under relatively reducing (dysoxic) conditions and is in the matured and beyond level [65].

This study calculated the waxiness index using the \(\sum(n-C_{21}-n-C_{31})/\sum(n-C_{15}-n-C_{30})\) ratio. This index is an indicator used to determine the terrigenous sources input in the sediments relying on the presumption that terrigenous sources contribute with high molecular weight n-alkane components [4]. Samples from MF source rock generally show medium to high waxiness index (Table 2), indicating relatively a mixed source of OM of land plant biomarkers, mainly except for the samples from well (15-34-080-18W6), which shows relatively low waxiness index suggesting a marine source. This interpretation was corroborated by the cross-plot of waxiness and Pr/Ph ratio (Figure 9).

Hopane distributions of the analyzed samples were determined based on the SIM mode m/z 191 traces (Figure 10). Peak identifications of the m/z 191 chromatograms were made based on retention times and published literature [10, 52, 60, 67, 68]. The Peak assignments are shown in Appendix A, and the calculated ratios are listed in (Table 3). For all analyzed samples, the saturated hydrocarbon m/z 191 mass chromatograms reveal that pentacyclic and tricyclic terpanes are more abundant, while tetracycle terpanes are less abundant.

Hopanoids are important biomarkers indicators for bacterial-derived OM [69]. Their composition and distribution mainly consist of \((H)\)-norhopane C29 to C35 17\(\alpha\) (H) 21\(\beta\) with hopanes C29\(\alpha\) and C30\(\alpha\) as major compounds and are similar in most of the samples (Figure 9). However, the C29 hopane relative abundance is generally less than that of C30 hopane in most of the analyzed samples, with C29/C3017\(\alpha\) (H)-hopane ratios average of 0.65 (Table 3). The dominance of C30 hopane is an indicator of clay-rich source rocks [70]. The (H)-moretane 17\(\beta\)21\(\alpha\) was also detected in low concentrations in many analyzed samples.

Gammacerane is frequently used to determine the salinity-stratified water column and may indicate photic zone anoxia. It is believed to have evolved from tetrathymanol in bacterivorous ciliates that live at the interface between a high-salinity water layer and a lower-salinity upper layer [52, 71]. Gammacerane is present in low concentrations in all the
Figure 5. HI vs Tmax on a pseudo van Krevelen graph, showing quality and maturity of the kerogen in the analyzed MF samples [49].

Figure 6. Mass fragmentograms of saturated hydrocarbon fractions of four representatives MF shale samples.
rock samples may be a clue of high bacterial activities and an environmental condition that is marine (dysoxic), and also supports the assumption that the OM has been originated from algal origin under diageneric factors [9]. The C24/C23 tricyclic terpane ratio show low to medium values (Table 3) in the analyzed MF source rock samples; this is interpreted to mean that the OM is a mix of marine and terrestrial. The tricyclic terpane ratio of C26/C25 can be used to differentiate marine from lacustrine source rocks [9, 76]. The OM in the source rock of the MF was interpreted as mixed marine and terrigenous organic materials because of the low abundance of the C25 tricyclic terpane in comparison with the C26 tricyclic terpane in most of the analyzed samples (Table 9) [9, 77].

Another important biomarker group is the steranes (Table 4), which were determined based on m/z 217 traces. Appendix A contains a list of the Peak assignments. Fragmentograms for peak identification were generated using retention times and previously published literature (Figure 11) [10, 52, 60, 67, 68].

Higher plants and algae are the source of sterols which are believed to be the origin of steranes [78]. The regular steranes (C27, C28, and C29) relative proportions can vary very much from sample to sample and are influenced by the type of OM source [78], although it can be used as a paleoenvironmental condition indicator [79]. Where they suggested that the presence of C27 steranes in predominant quantities indicates a marine phytoplankton environment mostly, while the preponderance of the amount of C29 steranes may indicate a terrestrial environment mostly, and C28 abundancy might indicate an intense contribution by lacustrine algae. However, Volkman, et al. [74] later noted that some marine organisms participate in C29 steranes. Nichols, et al. [80] also noticed that marine diatoms contribute to significant amounts of C29 sterols during the spring bloom in freezing Antarctic waters.

The analyzed samples, however, show a higher proportion of C27 (30.3–55.9 %) and C29 (27.7–51.1 %) steranes compared to C28 (13.5–25 %) (Table 4), reflecting mixed aquatic and terrestrial OM [3] as illustrated by the ternary diagram of the regular sterane ratio (Figure 12A) and the cross plot of C27/C29 versus Pr/Ph ratio versus the Pr/Ph ratio (Figure 12B).

These results were consistent with the medium hopane/stearane ratios and the low to medium C28/C27 sterane ratios (Table 4). The Pr/Ph ratio cross-plots with both hopane/stearane and sterane C27/(C27 + C29) ratios (Figure 13A, B) further support this interpretation.

The interpreted marine depositional environment and dysoxic conditions were also supported by the hopane/stearane ratios, which range from 0.52 to 1.79, and moderate diasterane/stearane ratio 1.42–3.4 in the analyzed samples. The parameters of n-alkane and biomarker maturity

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**Table 2. Biomarker parameters of the selected MF source rock samples.**

| Well name                  | Sample Depth (m) | Pr/n-C27 | Ph/n-C18 | Pr/Ph | CPI | Waxiness |
|----------------------------|------------------|----------|----------|-------|-----|----------|
| 15-34-080-18W6             | 2048.65          | 0.41     | 0.53     | 0.80  | 1.05| 0.36     |
|                            | 2054.93          | 0.44     | 0.54     | 0.81  | 1.04| 0.35     |
|                            | 2060.02          | 0.46     | 0.59     | 0.80  | 1.09| 0.33     |
| b-0931/094-B-09            | 1852.80          | 0.83     | 0.66     | 1.52  | 1.00| 0.37     |
|                            | 1859.14          | 0.83     | 0.68     | 1.49  | 1.01| 0.40     |
|                            | 1866.76          | 0.87     | 0.71     | 1.51  | 1.01| 0.39     |
|                            | 1867.13          | 0.92     | 0.74     | 1.43  | 1.05| 0.47     |
|                            | 1871.10          | 0.85     | 0.71     | 1.38  | 1.03| 0.45     |
|                            | 1883.01          | 0.91     | 0.74     | 1.33  | 1.01| 0.60     |
|                            | 1890.61          | 0.78     | 0.63     | 1.50  | 0.99| 0.42     |
|                            | 1933.04          | 0.70     | 0.52     | 1.63  | 0.94| 0.44     |
|                            | 1948.10          | 0.82     | 0.66     | 1.37  | 0.98| 0.52     |
|                            | 1973.10          | 0.83     | 0.66     | 1.38  | 0.93| 0.51     |
|                            | 1983.10          | 0.80     | 0.65     | 1.42  | 0.94| 0.60     |
|                            | 1999.50          | 0.72     | 0.56     | 1.51  | 0.96| 0.42     |
| 11-25-77-20W6              | 2142.10          | 1.11     | 0.83     | 1.16  | 1.05| 0.85     |
|                            | 2148.60          | 0.91     | 1.09     | 0.88  | 1.08| 0.90     |
|                            | 2152.00          | 0.57     | 0.55     | 1.76  | 1.02| 0.54     |
|                            | 2159.80          | 0.80     | 0.80     | 1.19  | 1.08| 1.42     |
|                            | 2161.80          | 0.42     | 0.29     | 2.25  | 1.09| 0.39     |
|                            | 2163.80          | 1.61     | 1.29     | 0.88  | 1.06| 1.63     |
|                            | 2166.60          | 0.56     | 0.47     | 1.89  | 1.06| 0.66     |
|                            | 2168.80          | 1.31     | 1.07     | 1.13  | 1.09| 0.98     |
|                            | 2186.60          | 1.13     | 0.98     | 1.21  | 1.00| 0.90     |
| A01-17-80-18W6             | 2385.04          | 0.48     | 0.41     | 1.36  | 0.99| 0.60     |
|                            | 2392.87          | 0.68     | 0.53     | 1.48  | 0.99| 0.56     |
|                            | 2402.17          | 0.66     | 0.52     | 1.49  | 0.95| 0.59     |
|                            | 2411.48          | 0.79     | 0.62     | 1.55  | 0.99| 0.48     |
|                            | 2420.67          | 0.73     | 0.57     | 1.54  | 1.01| 0.47     |
|                            | 2429.81          | 0.71     | 0.56     | 1.53  | 1.00| 0.46     |
|                            | 2438.76          | 0.69     | 0.53     | 1.60  | 1.00| 0.43     |
|                            | 2447.88          | 0.83     | 0.63     | 1.53  | 1.02| 0.51     |
|                            | 2457.33          | 0.53     | 0.40     | 1.60  | 1.00| 0.43     |
|                            | 2465.14          | 0.58     | 0.42     | 1.69  | 1.00| 0.37     |

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**Figure 7.** Plot of Pr/n-C17 vs Ph/n-C18 demonstrating the OM source, preservation conditions, and the maturity of the MF source rock [4, 64].
data were used in this study to assess the level of maturity of the MF source rock. The ratio of odd to even carbon numbered n-alkanes can be used to estimate the sediments' organic maturation level [3, 4, 82]. These measurements include the CPI; using the formula proposed by Peters and Moldowan [3], CPI values >1 or <1 indicate thermal immaturity, while the OM that is thermally matured has values of CPI = 1. As a result, the CPI for the analyzed samples was around unity (Table 1); this provides compelling evidence that the vast majority of the samples under investigation are thermally mature (Figure 7) [82]. All of the samples have reached a stage of maturity that is conducive to hydrocarbon production, as determined by the relationship between Pr/n-C 17 and Ph/n-C 18 (Figure 6).

The biomarker maturation parameters obtained from the m/z 191 and m/z 217 SIM mode, such as Ts/(Ts + Tm), C32 [22S/(22S + 22R)] homohopane, moretane/hopane and [20S/(20S + 20R)] and \([\beta\beta/(\beta\beta + \alpha\alpha)]\) C29 sterane ratios, were generally used as maturity markers [67, 83]. However, the source input and thermal maturation factors and other ratios may influence the Ts/(Ts + Tm) ratio [3]. Seifert and Moldowan [84] have related the increase in Ts to Tm ratio to the maturity increasing as the Tm is unstable compared to Ts during the catagenesis stage.

The Ts/(Ts + Tm) ratio for all the studied samples shows a range of 0.58–0.68 (Table 2); this signifies mature to postmature for all the analyzed samples. C31-hopane is the most common homohopanes in all the analyzed samples. In most of the samples, S-isomers predominate over R-isomers among the homohopanes (C31–C34), indicating that the sample has reached its mature state. Furthermore, Seifert and Moldowan [85] discovered that the [22S/(22S + 22R)] homohopane ratio increases from 0 to 0.6 during the process of thermal maturity. But during the postmature stages, the ratio ranges from 0.57 to 0.62; these findings support the notion that the samples have progressed beyond the mature stage and have reached the postmature stage.

The [22S/(22S + 22R)] isomerization values are calculated using the C31 or C32-homohopane results. The C32 [22S/(22S + 22R)] ratios for the analyzed samples range from 0.56 to 0.63, indicating thermally mature for hydrocarbon generation.

Figure 8. A cross plot of CPI versus Pr/Ph indicates the OM’s preservation conditions and maturity for the studied MF samples (modified after Meyers and Snowdon [65]).

Figure 9. Waxiness index vs Pr/Ph ratio cross-plot showing the source input of the OM and depositional conditions ([66]).
Thermal maturity reduces the concentrations of C29-hopanes and C30-moretanes in comparison to the corresponding hopanes [4] because of the lower thermal stability of the C30-(H) moretanes compared to the C29-(H) hopanes. With increasing OM maturity, the C30-M/C30-H ratio decreases from about 0.8 in immature bitumen to less than 0.15 in mature source rocks and 0.05 in oils [4, 83, 85].

![Figure 10. Mass fragmentograms measured in the SIM mode (m/z 191) of terpenoids for four samples representing the four wells from the study area.](image)

Table 3. Calculated parameters of hopanes biomarker from the SIM mode (m/z191) of the analyzed samples.

| Well name | Sample depth | Tm/Ts | Ts/ (Ts + Tm) | C29H/C30H | C30M/C30H | C31 22S/ (22S + 22R) | C32 22S/ (22S + 22R) | C29N/C30H | C31R/C30H | G/C30H | C25TT/C26TT | C24TT/C24TET | C24TT/C23TT | C24TET/C30H |
|-----------|--------------|-------|---------------|-----------|-----------|----------------------|----------------------|-----------|-----------|--------|-------------|--------------|-------------|-------------|
| 15-34-080-18W6 | 2048.65 | 0.52 | 0.58 | 0.62 | 0.14 | 0.49 | 0.56 | 0.58 | 0.27 | 0.07 | 1.27 | 3.86 | 0.63 | 0.28 |
| 2054.93 | 0.51 | 0.59 | 0.62 | 0.12 | 0.52 | 0.57 | 0.55 | 0.25 | 0.05 | 1.23 | 1.74 | 0.45 | 0.24 |
| 2060.02 | 0.49 | 0.58 | 0.69 | 0.13 | 0.55 | 0.62 | 0.62 | 0.27 | 0.06 | 1.28 | 3.56 | 44.0 | 0.24 |
| B-93-1/94-B09 | 1852.80 | 0.52 | 0.58 | 0.62 | 0.14 | 0.49 | 0.56 | 0.62 | 0.25 | 0.07 | 1.49 | 3.21 | 0.55 | 0.22 |
| 1859.14 | 0.51 | 0.59 | 0.65 | 0.12 | 0.52 | 0.57 | 0.55 | 0.27 | 0.05 | 1.37 | 3.19 | 0.54 | 0.18 |
| 1866.76 | 0.49 | 0.58 | 0.69 | 0.13 | 0.55 | 0.62 | 0.52 | 0.26 | 0.07 | 2.86 | 4.72 | 0.61 | 0.26 |
| 1867.13 | 0.50 | 0.63 | 0.67 | 0.12 | 0.53 | 0.60 | 0.64 | 0.28 | 0.06 | 1.06 | 3.21 | 0.63 | 0.18 |
| 1871.10 | 0.51 | 0.62 | 0.64 | 0.11 | 0.55 | 0.63 | 0.68 | 0.27 | 0.04 | 1.18 | 3.51 | 0.58 | 0.18 |
| 1883.01 | 0.51 | 0.61 | 0.65 | 0.11 | 0.54 | 0.61 | 0.61 | 0.27 | 0.04 | 1.25 | 4.93 | 0.60 | 0.22 |
| 1898.61 | 0.50 | 0.64 | 0.60 | 0.12 | 0.54 | 0.61 | 0.57 | 0.26 | 0.04 | 1.56 | 2.06 | 0.38 | 0.21 |
| 1933.04 | 0.48 | 0.68 | 0.63 | 0.13 | 0.50 | 0.57 | 0.63 | 0.25 | 0.06 | 1.61 | 3.89 | 0.43 | 0.24 |
| 1948.10 | 0.50 | 0.67 | 0.64 | 0.14 | 0.51 | 0.58 | 0.60 | 0.26 | 0.07 | 1.67 | 3.38 | 0.49 | 0.24 |
| 1973.10 | 0.48 | 0.68 | 0.63 | 0.13 | 0.51 | 0.58 | 0.67 | 0.26 | 0.06 | 1.61 | 3.76 | 0.55 | 0.19 |
| 1983.10 | 0.50 | 0.66 | 0.64 | 0.13 | 0.50 | 0.56 | 0.62 | 0.25 | 0.06 | 1.68 | 2.49 | 0.62 | 0.18 |
| 1999.50 | 0.49 | 0.67 | 0.60 | 0.12 | 0.51 | 0.59 | 0.59 | 0.25 | 0.05 | 1.25 | 3.20 | 0.61 | 0.23 |
| B-93-1/94-B09 | 2142.10 | 0.51 | 0.66 | 0.66 | 0.11 | 0.53 | 0.60 | 0.66 | 0.29 | 0.04 | 1.12 | 3.80 | 0.62 | 0.24 |
| 2148.60 | 0.49 | 0.67 | 0.66 | 0.12 | 0.52 | 0.59 | 0.66 | 0.26 | 0.05 | 1.01 | 1.52 | 0.62 | 0.24 |
| 2152.00 | 0.53 | 0.65 | 0.67 | 0.13 | 0.52 | 0.61 | 0.67 | 0.28 | 0.05 | 0.85 | 3.13 | 0.72 | 0.19 |
| 2159.80 | 0.50 | 0.67 | 0.65 | 0.11 | 0.52 | 0.62 | 0.65 | 0.26 | 0.05 | 0.99 | 2.70 | 0.70 | 0.21 |
| 2161.80 | 0.52 | 0.66 | 0.67 | 0.12 | 0.54 | 0.58 | 0.67 | 0.26 | 0.05 | 0.98 | 2.79 | 0.67 | 0.19 |
| 2163.80 | 0.50 | 0.67 | 0.65 | 0.11 | 0.51 | 0.61 | 0.65 | 0.27 | 0.05 | 1.06 | 3.34 | 0.66 | 0.20 |
| 2166.60 | 0.51 | 0.66 | 0.65 | 0.11 | 0.53 | 0.61 | 0.65 | 0.25 | 0.04 | 0.95 | 3.10 | 0.75 | 0.18 |
| 2168.80 | 0.55 | 0.65 | 0.66 | 0.12 | 0.53 | 0.58 | 0.66 | 0.25 | 0.04 | 1.16 | 3.20 | 0.61 | 0.25 |
| 2186.60 | 0.49 | 0.67 | 0.67 | 0.11 | 0.52 | 0.59 | 0.67 | 0.25 | 0.04 | 1.07 | 3.40 | 0.63 | 0.27 |

(continued on next page)
values obtained for the analyzed MF source rock samples lie in the range of 0.11–0.14 and suggest that they are postmature between the oil to the dry gas windows; this corresponds to the previous maturity results above.

Diasteranes are present in considerable amounts in most of the analyzed samples (Figure 10). Diasteranes are believed to be more stable than steranes at high thermal maturity, and they are believed to be produced during diagenesis and early catagenesis by the transformation of sterols [3, 9]. These maturation interpretations were supported by the diasterane/regular sterane ratios calculated from the mass fragmentograms of the 217 ion m/z. The ratio of diasterane to sterane in the analyzed samples ranges from 1.42 to 3.4, indicating that the majority of the samples are mature in terms of hydrocarbon generation. The C29-5α, 14α,17α(H)-[20S/(20S + 20R)] and the ββ/(ββ + αα) for C29 steranes are other parameters calculated from the same ion mass fragmentograms for evaluating the maturity level these ratios are believed to increase with increasing thermal maturity [9]. Gallegos and Moldowan [86] proposed that the steranes C29 [20S/(20S + 20R)] ratio equilibrates at 0.52 to 0.55; these numbers, however, are likely exaggerated, with the actual value being closer to 0.5 in oils and source rocks. They reported that other C29 sterane isomers usually contaminate the peak corresponding to the C29 5α isomer. On the other hand, the lithofacies types may affect the ββ/(ββ + αα) [3, 87]. According to Korkmaz and Gülbay [88], some of the inconsistencies in the extent of sterane isomerization can be attributed to other factors such as organic facies, environment, and lithology, so the values may not be wholly equilibrated. The ranges of the 20S/(20S + 20R) and ββ/(ββ + αα) values for the MF source rock samples are 0.4–0.65 and 0.44 to 0.64, respectively; these values indicate that the analyzed samples are thermally mature enough to generate hydrocarbons (Table 4).

Table 3 (continued)

| Well name | Sample depth | Hopanes (Thermal maturity) | Tricyclic (TT) and tetracyclic (TeT) terpanes (OM input & preservation conditions) |
|-----------|--------------|---------------------------|--------------------------------------------------------------------------------|
|           |              | Tm/Ts | Ts/ (Ts + Tm) | C29H/C30H | C30M/C30H | C31 22S/ (25 + 22R) | C32 22S/ (25 + 22R) | C29N/C30H | C31R/C30H | G/ C30H | C25TT/ C26TT | C24TT/ C24TET | C24TT/ C23TT | C24TET/ C30H |
| A01-17-080-18W6 | 2385.04 | 0.53 | 0.68 | 0.65 | 0.14 | 0.52 | 0.59 | 0.63 | 0.28 | 0.07 | 1.09 | 3.77 | 0.61 | 0.21 |
| A01-17-080-18W6 | 2392.87 | 0.54 | 0.67 | 0.65 | 0.14 | 0.53 | 0.60 | 0.65 | 0.29 | 0.07 | 1.12 | 1.63 | 0.60 | 0.19 |
| A01-17-080-18W6 | 2402.17 | 0.52 | 0.68 | 0.66 | 0.13 | 0.53 | 0.60 | 0.63 | 0.27 | 0.06 | 1.13 | 3.41 | 0.61 | 0.21 |
| A01-17-080-18W6 | 2411.48 | 0.53 | 0.66 | 0.67 | 0.13 | 0.54 | 0.62 | 0.67 | 0.27 | 0.06 | 1.23 | 3.04 | 0.61 | 0.23 |
| A01-17-080-18W6 | 2420.67 | 0.53 | 0.67 | 0.65 | 0.14 | 0.53 | 0.59 | 0.64 | 0.28 | 0.04 | 1.10 | 2.90 | 0.63 | 0.22 |
| A01-17-080-18W6 | 2429.81 | 0.51 | 0.66 | 0.67 | 0.12 | 0.52 | 0.60 | 0.65 | 0.29 | 0.05 | 1.09 | 2.90 | 0.63 | 0.22 |
| A01-17-080-18W6 | 2438.76 | 0.51 | 0.67 | 0.66 | 0.12 | 0.54 | 0.61 | 0.66 | 0.28 | 0.04 | 1.06 | 3.87 | 0.61 | 0.20 |
| A01-17-080-18W6 | 2447.88 | 0.52 | 0.65 | 0.67 | 0.11 | 0.55 | 0.62 | 0.63 | 0.28 | 0.05 | 1.05 | 2.85 | 0.59 | 0.20 |
| A01-17-080-18W6 | 2457.33 | 0.53 | 0.64 | 0.66 | 0.11 | 0.53 | 0.60 | 0.67 | 0.27 | 0.05 | 1.05 | 3.33 | 0.60 | 0.21 |
| A01-17-080-18W6 | 2465.14 | 0.52 | 0.63 | 0.65 | 0.12 | 0.53 | 0.60 | 0.64 | 0.26 | 0.07 | 1.07 | 3.56 | 0.62 | 0.19 |

C29/C30: C29 norhopane/C30hopane. C31R/C30 = C31 regular homohopane/C30 hopane. G/C30: Gammacerane/C30 hopane. C30M/C30H = C30 moretane/C30 hopane. Ts: (C27 18α(H)-22,29,30-trisnorhopane). Tm: (C27 17α(H)-22,29,30-trisnorhopane).

Figure 11. M/z 217 mass fragmentogram measured in SIM mode of sterane hydrocarbon fractions of the four MF source rock samples.
Table 4. Parameters for the sterane biomarker derived from the m/z 217 fragmentograms of the analyzed samples.

| Sample ID   | Depth (m) | Thermal maturity | Source input and depositional conditions | Regular steranes (%) | C27/(C27 + C30) | Ster-C27/Ster-C29 | Hop/Ster | Diaste/Ster |
|-------------|-----------|------------------|------------------------------------------|-----------------------|-----------------|-------------------|----------|-------------|
| Ster-C29 20S/(20S + 20R) Ster-C29 f/(f+ α) | %C27 | %C28 | %C29 |
| 15-34-080-18W6 | 2048.65 | 0.46 | 0.51 | 50.6 | 21.1 | 28.3 | 0.64 | 1.79 | 1.79 | 1.42 |
| | 2054.93 | 0.49 | 0.52 | 53.4 | 18.9 | 27.7 | 0.66 | 1.93 | 1.75 | 1.9 |
| | 2060.02 | 0.44 | 0.53 | 51.6 | 20.3 | 28.1 | 0.65 | 1.84 | 1.56 | 1.6 |
| B-93-L/94-B09 | 1852.8 | 0.48 | 0.56 | 31.0 | 19.0 | 50.0 | 0.38 | 0.62 | 0.67 | 2.34 |
| | 1859.14 | 0.45 | 0.53 | 40.8 | 18.2 | 41.0 | 0.5 | 1 | 0.65 | 3.01 |
| | 1866.76 | 0.40 | 0.44 | 30.3 | 20.7 | 49.0 | 0.38 | 0.62 | 0.63 | 2.21 |
| | 1867.13 | 0.45 | 0.51 | 30.7 | 24.0 | 45.3 | 0.4 | 0.68 | 0.66 | 2.36 |
| | 1871.1 | 0.43 | 0.48 | 31.4 | 25.0 | 43.6 | 0.42 | 0.72 | 0.66 | 2.46 |
| | 1883.01 | 0.51 | 0.57 | 30.9 | 22.9 | 46.2 | 0.4 | 0.67 | 0.68 | 3.11 |
| | 1898.61 | 0.46 | 0.54 | 31.4 | 18.5 | 50.1 | 0.39 | 0.63 | 0.65 | 2.29 |
| | 1933.04 | 0.45 | 0.52 | 34.4 | 17.3 | 48.3 | 0.42 | 0.71 | 0.65 | 3 |
| | 1948.1 | 0.48 | 0.57 | 34.6 | 17.8 | 47.6 | 0.42 | 0.73 | 0.65 | 2.89 |
| | 1971.3 | 0.45 | 0.51 | 32.0 | 16.9 | 51.1 | 0.39 | 0.63 | 0.69 | 2.46 |
| | 1983.1 | 0.43 | 0.48 | 34.4 | 16.4 | 49.2 | 0.41 | 0.7 | 0.69 | 2.56 |
| | 1999.5 | 0.51 | 0.57 | 38.0 | 15.1 | 46.9 | 0.45 | 0.81 | 0.67 | 3.4 |
| 11-25-077-20W6 | 2142.1 | 0.55 | 0.61 | 40.0 | 15.3 | 44.7 | 0.47 | 0.89 | 0.67 | 3.34 |
| | 2148.6 | 0.50 | 0.58 | 41.1 | 15.4 | 43.5 | 0.49 | 0.94 | 0.67 | 2.82 |
| | 2152 | 0.45 | 0.49 | 41.8 | 16.1 | 42.1 | 0.5 | 0.99 | 0.71 | 2.05 |
| | 2159.8 | 0.50 | 0.56 | 43.1 | 16.9 | 40.0 | 0.52 | 1.08 | 0.69 | 2.46 |
| | 2161.8 | 0.48 | 0.53 | 44.0 | 16.4 | 39.6 | 0.53 | 1.11 | 0.69 | 2.56 |
| | 2163.8 | 0.56 | 0.62 | 46.7 | 15.1 | 38.2 | 0.55 | 1.22 | 0.67 | 3.4 |
| | 2166.6 | 0.51 | 0.59 | 55.9 | 13.5 | 30.6 | 0.65 | 1.83 | 0.65 | 2.18 |
| | 2168.8 | 0.50 | 0.57 | 43.6 | 17.3 | 39.1 | 0.53 | 1.12 | 0.66 | 2.8 |
| | 2186.6 | 0.53 | 0.62 | 47.8 | 16.6 | 35.6 | 0.57 | 1.34 | 0.65 | 3.09 |
| A01-17-080-18W6 | 2385.04 | 0.63 | 0.62 | 33.8 | 17.9 | 48.3 | 0.41 | 0.7 | 0.66 | 2.25 |
| | 2392.87 | 0.65 | 0.64 | 33.8 | 17.0 | 49.2 | 0.41 | 0.69 | 0.67 | 3.18 |
| | 2402.17 | 0.62 | 0.61 | 31.6 | 21.1 | 47.3 | 0.4 | 0.67 | 0.66 | 2.05 |
| | 2411.48 | 0.60 | 0.59 | 37.9 | 19.6 | 42.5 | 0.47 | 0.89 | 0.68 | 2.31 |
| | 2420.67 | 0.59 | 0.58 | 31.1 | 19.8 | 49.1 | 0.39 | 0.63 | 0.66 | 2.38 |
| | 2429.81 | 0.60 | 0.59 | 32.9 | 20.0 | 47.1 | 0.41 | 0.7 | 0.68 | 2.15 |
| | 2438.76 | 0.65 | 0.64 | 33.7 | 21.3 | 45.0 | 0.43 | 0.75 | 0.69 | 3.05 |
| | 2447.88 | 0.62 | 0.61 | 35.2 | 22.2 | 42.6 | 0.45 | 0.83 | 0.52 | 2.86 |
| | 2457.33 | 0.62 | 0.61 | 39.8 | 20.3 | 39.9 | 0.5 | 1 | 0.53 | 2.65 |
| | 2465.14 | 0.63 | 0.62 | 39.6 | 19.4 | 41.0 | 0.49 | 0.97 | 0.56 | 2.48 |

Figure 12. A: a ternary diagram of C27, C28, and C29 ααα 20R steranes; B: Cross plot of C27/C29 ααα 20R sterane ratio versus Pr/Ph ratio, showing the depositional environment and OM type of MF source rock (modified after Huang and Meinschein [79]).
5. Conclusions

The source rock of the MF in the northeastern part of the BC area, Canada, was analyzed using bulk organic geochemical methods. The results achieved in this study give strong indications as follows:

1. The MF is organically good to very good source rock with an average TOC of 2.1 wt.%. Moreover, the high TS > 2 wt.% in the MF source rock indicates low oxygen deposition in a marine environment.

2. A mixed marine and terrestrial OM source input for MF source rock was deduced by the prevalence of the short-chain \( n \)-alkanes, CPI around unity, and high concentration of tricyclic terpanes and \( C_{24} \) tri/\( C_{24} \) tetra and low hopane/sterane ratios. In addition, the cross-plots of \( Pr/n-C_{17} \) versus \( Ph/n-C_{18} \), as well as the ternary diagram showing the relationship between regular sterane compositions, both found similar results, suggesting that the sediments studied had a mix of marine and terrigenous OM input.

3. The OM influx indicates that more marine input was toward the northeastern part, while mixed input was toward the southwestern region.

4. Dysoxic conditions were the dominant conditions during the OM deposition.

5. The waxiness index gives evidence of the terrigenous organic materials influx during the deposition of the MF source rock.

6. Different biomarker maturity data indicated that the source rock of the MF had reached the maturity stages of hydrocarbon generation.

Declarations

Author contribution statement

Azzam Barham: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Mohd Ismail: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.
Maman Hermana: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.
N.S. Zainal Abidi: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Appendix A. Peak designations for alkane hydrocarbons in saturated fraction gas chromatograms in the m/z 191 and 217 mass fragmentograms.

| m/z 191 | Compound | Peak no. |
|---------|----------|---------|
| TR C21  | C21 Tricyclic (Cheilanthane) | C21 |
| TR C22  | C22 Tricyclic (Cheilanthane) | C22 |
| TR C23  | C23 Tricyclic (Cheilanthane) | C23 |
| TR C24  | C24 Tricyclic (Cheilanthane) | C24 |
| Tetra C24 | C24 Tetracyclic | C24 |

| m/z 217 | Compound | Peak no. |
|---------|----------|---------|
| S21     | C21 sterane | C21 |
| S22     | C22 sterane | C22 |
| DIA27S | C27 σx 20S diasterane | C27 |
| DIA27R | C27 βα 20R diasterane | C27 |
| DIA28SA | C28 σx 20S diasterane (a) | C28 |

Figure 13. A: Cross-plot of Hopanes/Steranes vs Pr/Ph ratios; B: Cross-plot of \( C_{27}/(C_{27} + C_{29}) \) regular steranes vs Pr/Ph ratios showing depositional environment conditions and source input [81].

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