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Biomarker characterisation and thermal maturity evaluation of Ganduman Formation, Sahabat area, Dent Peninsula, Sabah, Malaysia

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Abstract: Pliocene sediments of the Ganduman Formation is characterized by thick sand bodies in the lower Maruap Member while the upper Ganduman Formation is dominated by shale and carbonaceous material. In this study, an assessment is made on the biomarker distributions of these sediments and of their thermal maturity. Based on this study, the sediments are interpreted to be deposited under oxic to anoxic conditions in a probable lacustrine to fluvial deltaic setting with considerable marine influence. The extracted shale and coal samples suggest that these sediments are still immature for hydrocarbon generation. However, it is interesting to note that the extract of one immature sandstone sample is thermally mature which suggests the presence of non-indigenous, migrated hydrocarbons.

Abstrak: Sedimen Pliosen Formasi Ganduman dicirikan oleh badan-badan batu pasir tebal dari bahagian bawah Ahli Meruap sedangkan bahagian atas Formasi Ganduman didominasikan oleh syal dan bahan-bahan berkarbon. Di dalam kajian ini, suatu penilaian dilakukan ke atas taburan biomarker dari sedimen-sedimen tersebut dan ke atas kematangan termanya. Berdasarkan kajian ini, sedimen-sedimen ini ditafsirkan sebagai dienapkan dalam keadaan oksik ke anoksik berkemungkinan dalam persekitaran lakustrin ke delta berfluvius dengan mengalami pengaruh marin yang agak tinggi. Bahan ekstrak dari sampel-sampel syal dan arang batu mencadangkan yang sedimen-sedimen ini masih tidak matang bagi penjanaan hidrokarbon. Walaubagaimanapun suatu yang menarik adalah terdapat satu sampel batu pasir yang tidak matang tetapi ekstraknya adalah matang secara terma, dengan ini mencadangkan kehadiran hidrokarbon yang bukan berasal dari batu pasir tersebut tetapi yang telah berhijrah ke dalam batu pasir tersebut.

INTRODUCTION

Geological background

The Ganduman Formation on the Dent Peninsula, Sahabat area (Fig. 1) is Pliocene in age as suggested by fossil assemblages of Globigerinoids (Haile and Wong, 1965). The Ganduman Formation lies conformably on the Sebahat Formation (Ismail Che Mat Zin, 1994). The Ganduman, Sebahat and Togopi Formations together make-up the Dent group (Upper Miocene-Pleistocene) of the onshore and offshore NE Sabah basin. The Ganduman Formation mainly consists of grey limonitic quartzose sandstone containing undulating clay laminae, plant remains and lignite (Lower Ganduman, Maruap Member) and grey shale and sandstone with abundant carbonaceous materials, Upper Ganduman (Haile and Wong, 1965).

Onshore studies carried out by Ismail Che Mat Zin, (1994) concluded that the Ganduman Formation can be characterized by a very sandy nature and interpreted it to be deposited in a fluvial deltaic system. Channel features and very well preserved trough cross bedding are common. Moving eastward, the sediments become more sandy, and get into more marine environments. These sand bodies are interpreted as sand bars deposited in shallow marine environment. The depositional environment is increasingly marine eastward where the sandy facies changes to a shaly facies which demarcates the contemporaneous shelf edge limit during the deposition of the Ganduman Formation.

The Ganduman Formation of Dent Peninsula contains only poor to fair organic carbon with values ranging from 0.1 to 1.3 wt%. Dominant Kerogen is vitrinite and inertinite with minor oil-prone liptinite (Azlina Anuar and Abdul Jalil Muhamad, 1995).

Sample locations

The samples were collected from several locations in the Sahabat area during fieldwork carried out in March 2002. The samples locations are shown in Figure 1.

METHODOLOGY

Geochemistry

About 15 g of powdered samples were Soxhlet extracted for 72 hours using an azeotropic mixture of chloroform and methanol. The extracted materials were fractionated by column chromatography into three fractions: aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds. These fractions were further analyzed by Gas

Chromatography-Mass spectrometry (GC-MS).

Petrology

The studied samples were dried and brushed carefully to remove any superficial contaminations. They were then crushed to 2 mm size and mounted in a slow-setting resin. Subsequently the blocks were ground on a diamond lap until the surface became flat. Then they were polished on silicon carbide paper beginning with 300 grade followed by 800 and finally on 1,200 grade using isopropyl alcohol as a lubricant for shaly samples and water for coaly samples. Microscopical examination was performed using an oil immersion objective. Vitrinite reflectance was measured using plane-polarized, reflected "white light".

RESULTS

Carbon preference index

The carbon preference index (CPI) can be used to obtain a crude estimate of thermal maturity of petroleum. However, CPI values are also affected by the type of organic matter, not only by the maturity (Tissot and Welte, 1984).

The extracted samples collected from several locations within the Ganduman Formation, display different distributions of n-alkanes. For example Figures 2A and 2C which represent samples L1/S7 and L9/S5, show that they are dominated by medium molecular weight n-alkanes (C_{15}-C_{22}). The higher molecular-weight n-alkanes (C_{23}-C_{32}) have a slight odd-over-even number predominance. In contrast, Figure 2B which represents sample L2/S8 shows a bimodal distribution.

Table 1 illustrates the variety of CPI values for the whole extract samples used in this study. CPI values are in the range of 1.19 in sample L9/S5 to 3.52 in sample L6/S2.

Pristane/Phytane ratios

Powell and Mckirdy (1973) have used the Pr/Ph ratio in correlation studies. The Pr/Ph ratios of oils or bitumens have been used to indicate the redox potential of the source sediment (Didyk *et al.*, 1978). In the present study, the Pr/Ph ratios of the extracted sample display a slight variation in values among the samples analyzed. The Pr/Ph ratios are in the range of 1.22 to 1.64 except for a coal (L1/S7) and a shale (L6/S2) sample which possess Pr/Ph ratios of 0.92 and 0.87, respectively (Table 1).

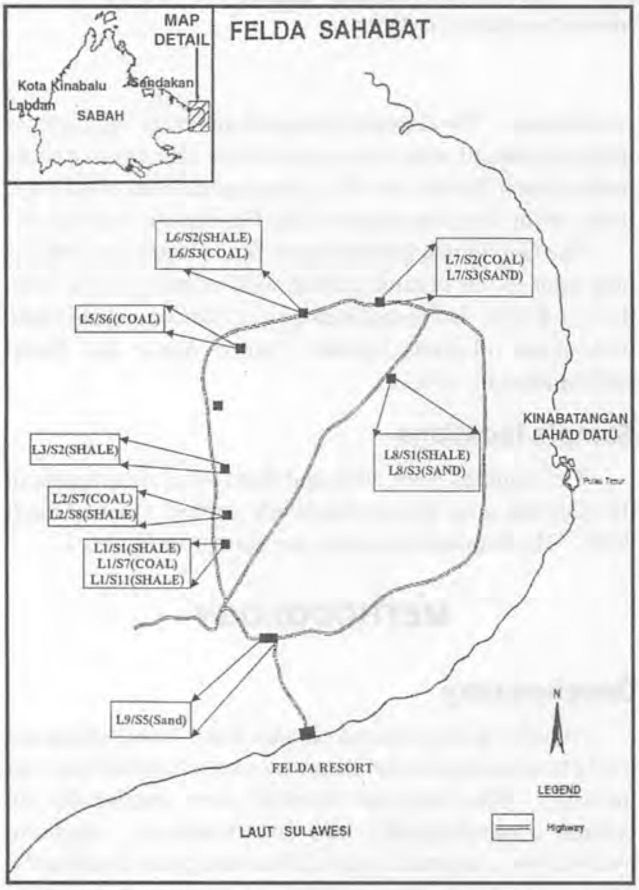

Figure 1. Map showing locations of samples in this study.

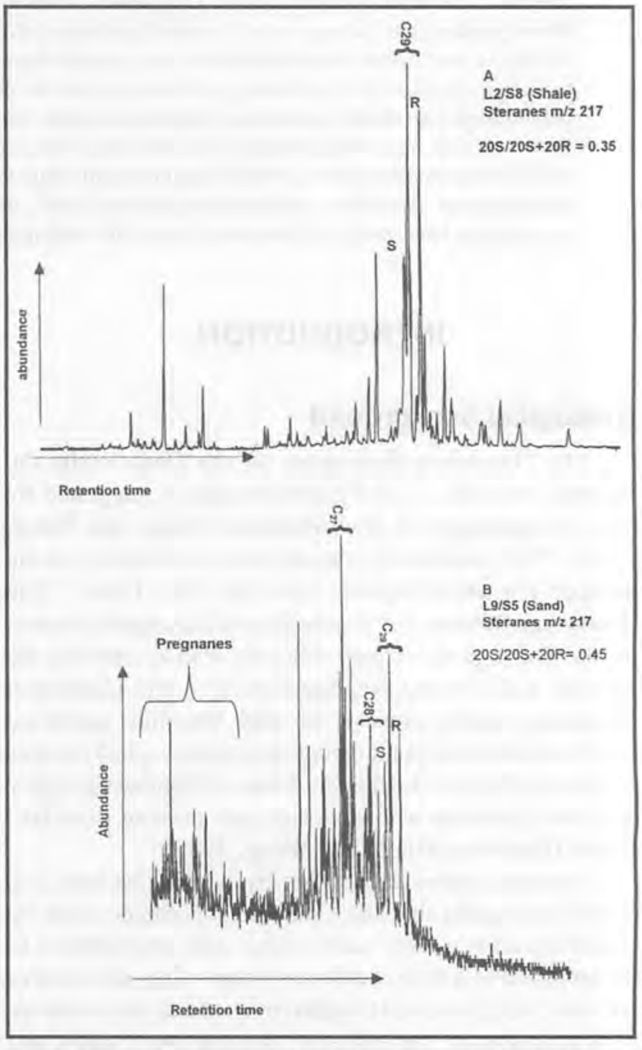

Figure 2. Total ion current (TIC) chromatogram of the aliphatic fraction: (A) Sample L1/S7, Coal; (B) Sample L2/S8 Shale; (C) Sample L9/S5, Sand.

Table 1. Biomarker parameters and vitrinite reflectance data (%Ro) (CPI after Bray & Evans, 1961; peaks abbreviation as discussed in text).

Sample No	Litho-logy	n-alkane Max	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	nC_{30}/nC_{17}	CPI $nC_{25}nC_{31}$	Ts/Tm	Ol/C_{30} hop	$C_{31}22S/22S+22R$ homohop	$C_{29}hop/C_{30}hop$	$C_{24}Tri/C_{29}hop$	$\%R_0$
L1/S7	Coal	nC_{14}	0.92	0.302	0.325	0.10	3.060	0.6	0.08	---	3.3.	0.33	0.38
L2/S7	Coal	nC_{15}	1.25	0.357	0.256	0.30	1.880	0.4	1.16	---	3.7	0.81	0.34
L2/S8	Shale	nC_{16}	1.45	0.477	0.323	0.70	2.032	0.6	0.5	---	13.7	0.51	---
L5/S6	Coal	nC_{15}	1.40	0.310	0.220	0.77	2.100	0.3	0.33	0.18	15.7	0.04	0.33
L6/S2	Shale	nC_{31}	0.87	0.700	0.285	2.40	3.521	0.7	0.16	0.16	2.8	0.42	0.25
L6/S3	Coal	nC_{31}	1.33	0.307	0.250	1.10	6.177	1.0	0.37	0.17	11.9	0.82	0.44
L7/S3	Sand	nC_{15}	1.22	0.379	0.281	0.20	3.375	0.8	0.08	0.48	1.8	1.23	0.23
L8/S1	Shale	nC_{14}	1.64	0.417	0.220	0.10	1.362	0.3	0.37	0.43	5.3	0.11	---
L8/S3	Shale	nC_{14}	1.38	0.375	0.254	0.04	1.507	0.5	0.63	---	4.6	0.20	---
L9/S5	Sand	nC_{18}	1.46	0.372	0.241	0.10	1.197	1.2	0.07	0.61	1.0	0.24	---

Trisnorneohopane and trisnorhopane Ts/(Ts+Tm) ratios

The Ts/(Ts+Tm) ratio is known to be both maturity and source dependent (Peters and Molodwan, 1993). Molodwan *et al.* (1986) showed that this ratio can vary depending on organic facies. Examples of the extracted samples of the Ganduman Formation are shown in Figures 3A, 3B and 3C.

Most of the samples illustrate that Ts is less than Tm. Moreover, its concentration is very low in some samples resulting in very low Ts/(Ts+Tm) ratios except for the sand sample (L9/S5) which shows a relatively high abundance of Ts compared to Tm resulting in the highest Ts/(Ts+Tm) ratio among the studied samples.

Oleanane

18α(H) oleanane is believed to be derived from Cretaceous or younger higher plant material. It has been suggested that oleananes are derived from betulins and other pentacyclic triterpenes in angiosperms. The oleanane index is used in correlation and thermal maturity studies (Peters and Molodwan, 1993). In this study, the extracted samples show oleanane/C_{30} hopane ranging from low to relative high values. However, most samples have values <1 except for sample L2/S7 which has a value of 1.16. Table 1 shows that the samples L1/S7, L7/S3 and L9/S5 have values equivalent to 0.08, 0.08 and 0.07 respectively. While, remaining samples are in the range of 0.16 in sample L6/S2 to 0.63 in sample L8/S3.

Homohopane index 22S/(22S+22R)

The homohopanes (C_{31}-C_{35}) are believed to be derived from bacteriohopanetetrol and other polyfunctional C_{35} hopanes common in prokaryotic micro organisms (Ourisson *et al.*, 1978). The homohopane index has been used as an indicator of the redox potential (Eh) during and after deposition of the source rocks (Peters & Molodwan, 1993). This ratio is also used as maturity parameter (Ensminger, 1977).

The extracted samples from Ganduman Formation display values of 22S/(22S+22R) in the range of 0.16 to 0.61. However, some samples do not display a clear distribution of C_{31}-C_{35} peaks thus this ratio could not be determined.

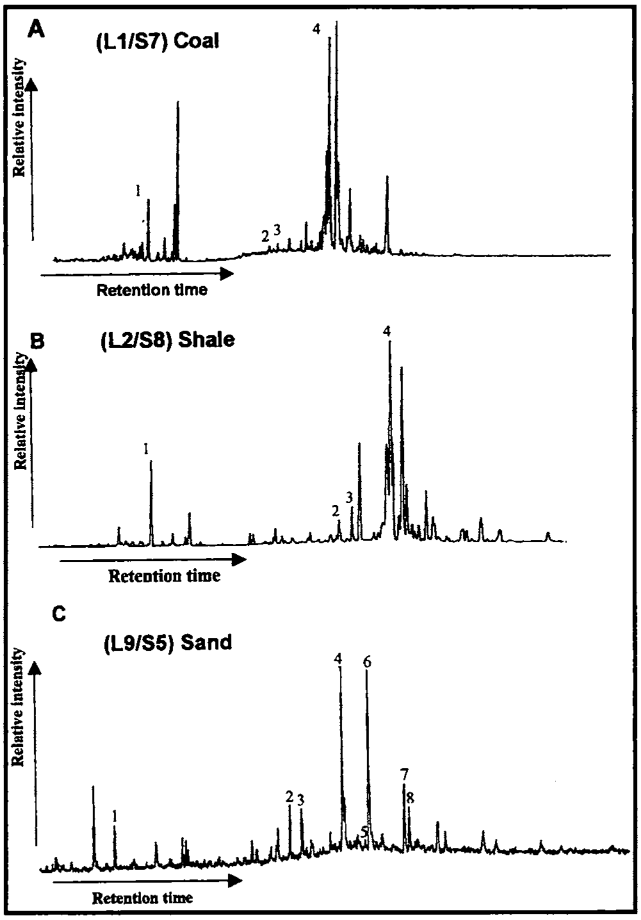

Figure 3. Triterpane m/z 191 mass fragmentograms. 1: C_{24} tricyclic terpanes; 2: Ts C_{27} 18α(H)-22,29,30 trisnorneohopane; 3: Tm C_{27} 17α(H)-trisnorhopane; 4: C_{29} 17α(H) norhopane; 5: C_{30} 18α(H) oleanane; 6: C_{30} 17α(H) hopane; 7: 22S homohopane; 8: 22R homohopane.

Tricyclic/C_{29} hopane

The tricyclic terpanes can be used as a source parameter when they are compared to a group of bacterial or algal lipids with markers that originate from different prokaryotic species (Hopane). And they are also useful in differentiating maturity and depositional environment.

C_{24} tricyclic/C_{29} ratios of the analysed extracts are shown in Table 1. Most of the ratios display low values less than 1 except for sample L7/S3 which has the highest value 1.23. However, the other values are in the range of 0.11 in sample L8/S1 to 0.82 represented by sample L6/S3.

DISCUSSION

Thermal Maturity

Thermal maturity describes the impact of heat during burial of sediments. This thermal exposure converts sedimentary organic matter into petroleum. Several parameters have been used as indicators of organic maturity such as mean vitrinite reflectance (%R_o), amount of extractable soluble organic matters, Carbon Preference Index (CPI) and, pentacyclic triterpane and regular sterane isomerisation ratios (Peters and Molodwan, 1993).

Vitrinite reflectance

Vitrinite reflectance (%R_o) is widely accepted by exploration geologists for measuring the thermal maturity of organic matter in sedimentary rocks (Bostick, 1979; Murchison, 1987; Hunt 1996). Vitrinite reflectance values increase with increasing rank. Vitrinite reflectance values of between 0.50% and 1.30% suggest the oil generation window while values less than 0.50% considered thermally immature. However, vitrinite reflectance values greater than 1.30% indicate gas window maturity (Tissot and Welte, 1984). Mean vitrinite reflectance values of the investigated samples are illustrated in Table 1. The analysed samples show low values in the range of 0.23 to 0.44%.

Regular steranes

One of the most important measures of maturity using biomarkers is the proportion of the two epimeric forms of 20R and 20S of the ααα steranes. This is commonly expressed as 20S/(20S+20R). The biologically produced form is exclusively the ααα form in the 20R configuration, but with increasing maturity the proportion of 20S increases as some of the 20R molecules change configuration (Waples and Machihara, 1991). Eventually an equilibrium between the two forms is reached, comprising approximately 55% 20S and 45% 20R. In this study, the isomerisation ratio is measured for C_{29} sterane and is shown in Figure 4. The 20S/(20S+20R) for the sand (L9/S5) sample is 0.45 whilst for the shale (L2/S8) is 0.35, and supports the relatively more mature nature of the hydrocarbon fraction within the sand and the immature nature of the hydrocarbon within the shale sample.

The mature hydrocarbon trace of the sandstone sample is compared to that of an offshore oil trace reported from NE Sabah Basin offshore Sabah (Leong and Azlina Anuar, 1999). This hydrocarbon trace bares a number of similarities to the Mutiara Hitam-1 RFT 2,089 m oil sample. It shows a smooth unimodal n-alkane envelopes between nC_{19} to nC_{31}, relatively high Pr/Ph ratio, Ts>Tm, low concentration of oleanane, and an almost equal concentration of C_{27} and C_{29} regular steranes. Early to mid mature oil window thermal maturity level is suggested from both the isomerisation ratio of C_{31} hopane and the C_{29} regular sterane. Such high maturity level for the extract of an immature rock suggests the presence of staining by migrated hydrocarbons. Based on biomarker distributions, a fluvial-deltaic source that has received significant marine influence is regarded as a probable source facies for the stain. A marginal fluvial marine source rock was also suggested for Mutiara Hitam-1 RFT 2089m sample (Leong and Azlina Anuar, 1999).

Other biomarker parameters

Carbon preference index (CPI) values of significantly above (odd preference) or below (even preference) 1.0

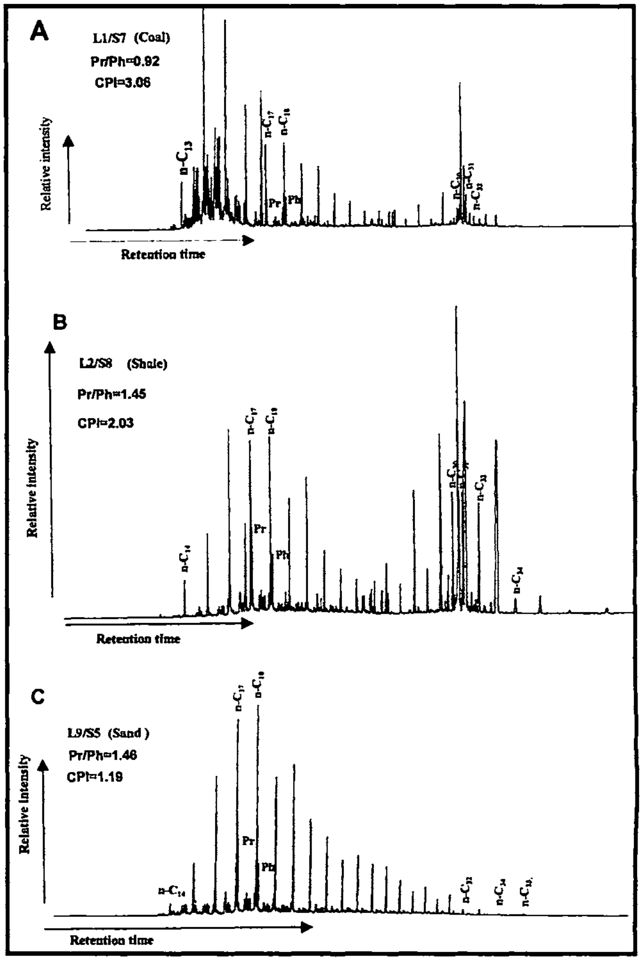

Figure 4. Steranes m/z 217 mass fragmentograms. (A) Sample L2/S8, shale and (B) Sample L9/S5, sand.

indicates a sample is thermally immature (Peters and Molodwan, 1993). The carbon preference index values, however, are affected by type of organic matter and the degree of maturity (Tissot and Welte, 1984). According to Bray and Evans (1961), high CPI value indicates immature sediments but near unity or just below is typical of mature crude oils.

By using the Bray and Evans Formula, values of CPI have been obtained (see Table 1). Most of the studied samples display high values of CPI indicating preference of odd over even n-alkanes. The high CPI values are a good indicator that these extracted samples are still thermally immature.

The Ts/(Ts+Tm) ratio sometimes reported as (Ts/Tm) is both maturity and source dependent. Moldowan *et al.* (1986) showed that the ratio can vary depending on organic facies. In Linyi Basin, China, a systematic increase in relative abundance of Ts and a decrease in trisnorhopane compared to Tm with depth was reported. In general, for the studied samples, values of Ts/Tm are less than 1. With acceptance that maturity is increasing with increasing Ts/Tm ratio and vice versa, the extracted samples appear to be still immature except for sample L9/S5 which displays a high ratio of 1.2. And hence, the Ts/Tm ratio indicates that this sample is mature. Correlation between vitrinite reflectance data and Ts/Tm for sample L9/L5 could not be done due to lack of vitrinite and coalified materials in the sand sample. The lack of organic matter itself is a testimony to the hydrocarbon not being indigenous of the sand.

C_{31} or C_{32} 22S/22S+22R hopane ratio rises from zero to about 0.6 at equilibrium (Seifert and Molodwan, 1986) during maturation. Values in the range 0.50 to 0.54 have barely entered oil generation, while ratios range from 0.57 up to 0.62 indicates that the oil window has been reached. Most of the extracted samples display very low values in the range from 0.16 to 0.48. A high value of 0.61 was recorded in sample L9/S5 which suggests that this hydrocarbon is migratory.

Type of organic matter and depositional environment

Conclusions on correlations, source, and depositional environment should always be based on through available geochemical information, including other biomarker, isotopic, and supporting data (Peters and Molodwan, 1993). Volkman and Maxwell (1986) summarised the use of biomarkers in petroleum for reconstructing source rock depositional environment and organic matter input.

The pristane/phytane ratio can be used as an indicator of redox conditions in ancient sediments (Didyk *et al.*, 1978). Values above 3.0 are considered to indicate dysoxic to oxic sediments, values below 1.0 indicate anoxic conditions, and values between 1.0 and 3.0 suggest intermediate conditions. However, Volkman and Maxwell (1986) do not recommend using Pr/Ph ratio in samples of low thermal maturity to describe paleoenvironment. In the samples studied here, as discussed in the thermal maturity ratios, most of the samples have not reached the oil generation window. And hence, other parameters such as Pr/nC_{17}, Ph/nC_{18} and Ts/Tm could be use to describe the paleoenvironment. High concentration of medium molecular weight normal alkanes (nC_{15}, nC_{17} and nC_{19}) indicate that the origin of organic matter is algal deposited under lacustrine and marine conditions, while high concentration of low molecular weight of nC_{27}, nC_{29} and nC_{31} represent higher plant origin and the sediments have been deposited under oxic condition (Gelpi *et al.*, 1970; Tissot and Welte, 1984).

Most of the extracted samples from Ganduman Formation display low values <1 of $nC_{30}/nC17$ ratio indicating primarily marine influence except for samples L6/S2 and L6/S3 which display values >1 indicating terrestrial influence or probably transition areas. Moreover, sample L2/S8 illustrated in Figure 2B show bimodal distribution dominated by low molecular weight (nC_{15}, nC_{17}, nC_{19}) and high molecular weight (nC_{27}, nC_{29}, nC_{31}) n-alkanes. Thus, maybe the shale was deposited under anoxic conditions but with considerable amounts of high plant originated from inland. However, the remaining samples show higher abundance of low molecular weight normal alkanes than abundance of high molecular weight normal alkanes. This could indicate that the shales and coals were influenced by brackish and/or marine conditions of deposition.

The ratio of C_{27} trisnorneohopane (Ts), relative to C_{27} trisnorhopane (Tm) can be use as a facies parameter for related oils Ts/Tm values below 1.0 imply lacustrine, saline, marine evaporite or marine carbonate depositional environment, while values above 1.0 indicate lacustrine fresh water or marine deltaic environment. According to the Ts/Tm data in Table 1 most of the samples have ratios less than 1 indicating lacustrine, saline or marine conditions except for sample L9/S5 which shows a value greater than 1 indicating lacustrine fresh water or marine deltaic environment.

Results represented by ratios Pr/nC_{17}, nC_{30}/nC_{17}, C_{24} tricyclic/C_{29} norhopane and Ts/Tm show variation in values. As discussed earlier, most of studied samples show that the organic matter originated from marine source rocks, while the others display mixed organic sources.

CONCLUSIONS

Based on biomarker ratios such as nC_{30}/nC_{17}, Ts/Tm and Pr/nC_{17} the sediments were considered to have been deposited under oxic to anoxic conditions of deposition, probably within lacustrine to fluvial deltaic setting with considerable marine influence. The vitrinite reflectance data obtained from examined polished surfaces of the studied samples showed that the sediments of the Ganduman Formation are thermally immature as suggested by biomarkers parameters such as CPI, Pr/Ph, Ts/Tm, oleanane/C_{30} hopane as well as the hopane and sterane isomerisation ratios. These results are supported by the vitrinite reflectance data. On the other hand, results which are obtained from sand sample L9/S5 show that the hydrocarbons are thermally mature. Thus, this mature hydrocarbon is considered to be migrated hydrocarbons from other mature source rocks.

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