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Organic Geochemistry and Rock-Eval Pyrolysis of Eocene fine Sediments, East Ketungau Basin, West Kalimantan

Geokimia Organik dan Pirolisis Rock-Eval Batuan Sedimen halus berumur Eosen, Cekungan Ketungau Timur, Kalimantan Barat

M.H. Hermiyanto Zajuli and Suyono

Geological Survey Institute, Geological Agency, Jln. Diponegoro 57 Bandung - 40122

Abstract

Indonesia contains many Paleogene and Neogene basins which some of them have been proven to be a very prolific producer of oil and gas. A study on the result of Rock-Eval pyrolysis and biomarker undertaken on the Eocene Mandai Group was able to assess hydrocarbon potential of the Paleogene fine sediments in the frontier basin, especially West Kalimantan area. East Ketungau Basin is located in the western Kalimantan, bounded with Melawi Basin by the Semitau High in the south and West Ketungau Basin in the west. The Mandai Group was deposited in the East Ketungau Basin during Eocene, consisting of sandstone and mudstone facies. Mudstone facies comprises shale, claystone, and coal. Seven samples of Eocene fine sediments collected from East Ketungau Basin were analyzed by Rock-Eval pyrolisis and three samples for biomarker to evaluate their hydrocarbon potential. The Rock-Eval pyrolisis result of Mandai Group shows that TOC value of this facies ranges from 0.34 % to 5.16 %, Potential Yield (PY) between 0.06 and 4.78 mg HC/g rock, and Hydrogen Index (HI) from 12 to 89. Based on that result, the fine sediments of Mandai Group are included into a gas prone source rock potential with poor to fair categories. Moreover T_{max} values vary from 426^o C to 451^o C. The Eocene fine sediments of Mandai Group fall under kerogen type III. Based on T_{max} and biomarker analyses, the maturity of the sediments is situated within immature to mature level. The fine sediments of Mandai Group were deposited in a terrestrial to marine environment under anoxic to sub-oxic condition.

Keywords: East Ketungau Basin, Eocene, Rock-Eval pyrolysis, biomarker

Sari

Indonesia ditempati oleh sejumlah Cekungan Paleogen dan Neogen yang beberapa di antaranya terbukti dapat menghasilkan minyak dan gas. Studi tentang pirolisis Rock-Eval dan biomarker batuan sedimen halus berumur Eosen akan memberikan gambaran potensi hidrokarbon Paleogen pada cekungan-cekungan frontier, khususnya di daerah Kalimantan Barat. Cekungan Ketungau Timur yang terletak di Kalimantan Barat dibatasi oleh Tinggian Semitau dengan Cekungan Melawi di bagian selatan dan Cekungan Ketungau Barat di bagian barat. Kelompok Mandai yang terendapkan di Cekungan Ketungau Timur pada Eosen, terdiri atas fasies batupasir dan batulumpur. Fasies batulumpur berupa serpih, batulempung, dan batubara. Tujuh percontoh batuan sedimen halus berumur Eosen dari Cekungan Ketungau Timur dianalisis dengan pirolisis Rock-Eval dan tiga percontoh dengan biomarker untuk mengevaluasi potensi hidrokarbonnya. Hasil pirolisis Rock-Eval pada batuan sedimen halus Kelompok Mandai menunjukkan bahwa TOC berkisar dari 0,34% sampai 5,16%, Potential Yield (PY) 0,06 - 4,78 mg HC/g rock, dan Indeks Hidrogen (HI) dari 12 sampai 89. Berdasarkan hasil analisis tersebut, batuan sedimen halus Kelompok Mandai termasuk ke dalam batuan induk yang menghasilkan gas dengan kategori jelek sampai sedang. T_{maks} batuan sedimen halus berkisar dari 426^o C sampai 451^o C. Bahan organik batuan sedimen halus Kelompok Mandai berumur Eosen ini tergolong ke dalam kerogen tipe III. Berdasarkan analisis T_{maks} dan biomarker, kematangan batuan sedimen tersebut berada pada tingkat belum matang sampai matang. Batuan sedimen halus Grup Mandai diendapkan di lingkungan darat (terrestrial) sampai laut dengan kondisi anoksik sampai sub-oksik.

Kata kunci: *Cekungan Ketungau Timur, Eosen, pirolisis Rock-Eval, biomarker*

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Introduction

Indonesia is occupied by many Paleogene and Neogene basins. Some Neogene basins were proven to be prolific producers of oil and gas. The East Ketungau Basin is one of the Paleogene frontier basins in the western Kalimantan, and it accommodates the junction of three of Kalimantan's four provinces, those are West, East, and Central Kalimantan. The basin is situated 60 km south of Putussibau, Kapuas Hulu Regency, bordered by the equator and latitude 1^o N, and longitudes 112^o 30' E and 114^oE (Figure 1).

Geologically, it is bounded by the Semitau High with Melawi Basin in the south, Lubuk Antu Mélange in the north, and Ketungau Basin in the west. The Mandai Group deposited in the East Ketungau Basin during Eocene, consists of sandstone and mudstone facies.

The first geological mapping in Putussibau and some of its tributaries was carried out by Molengraaff in 1894. Moreover, a joint co-operation between the Indonesian Geological Research and Development Center (GRDC) and Bureau of Mineral Resources of Australia-BMR (now Australian Geological Survey Organization, AGSO) from 1983 to 1989 had performed a geological mapping in this area.

More recent studies have performed a specific organic geochemical analysis to get new data and

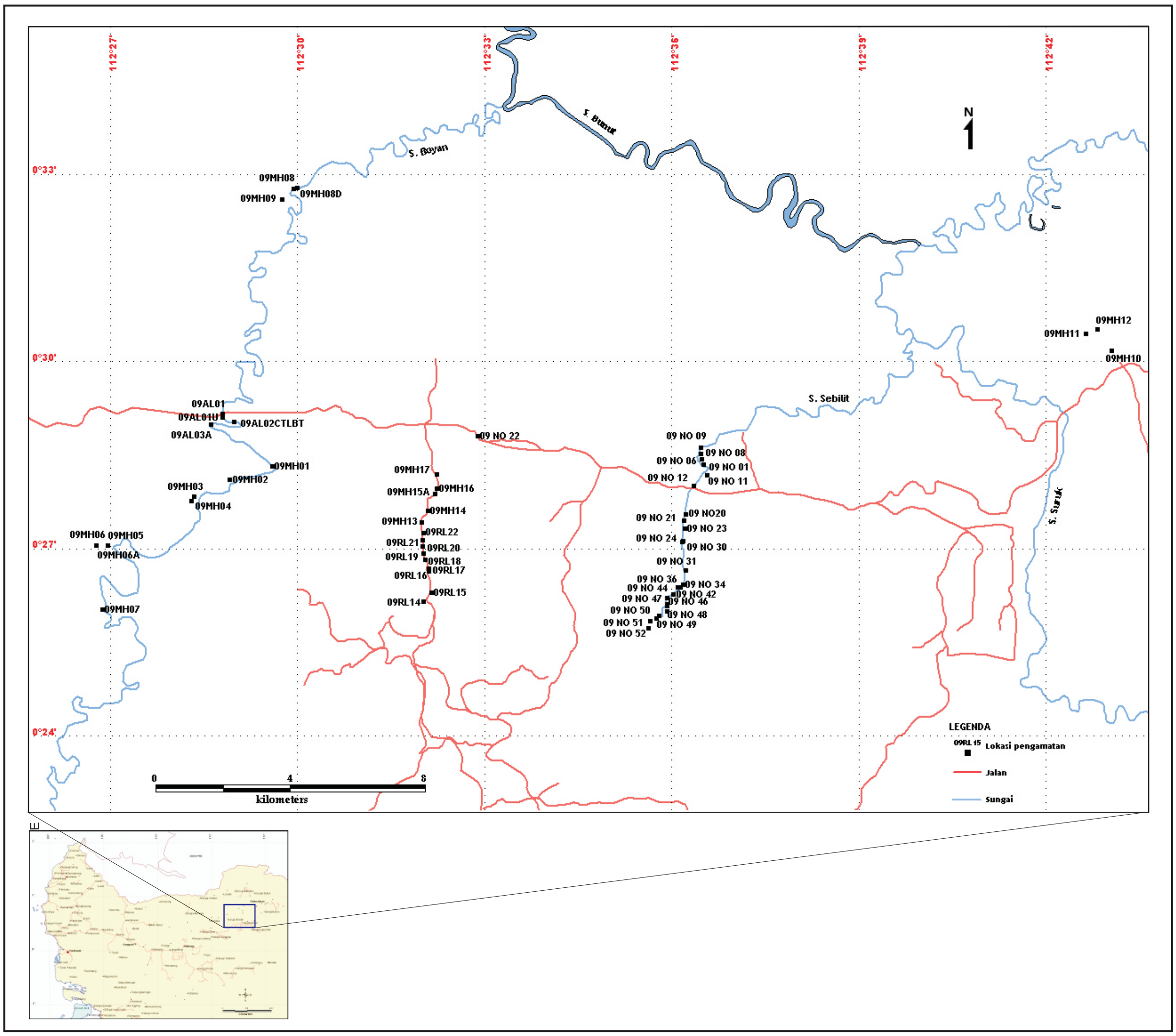

Figure 1. Location map of the study areas (blue square), 60 km south of Putussibau, Kapuas Hulu Regency.

to assess the probability of gas or oil potential in the area. Seven Eocene fine-grained surface samples from the East Ketungau Basin were analyzed by Rock Eval-pyrolisis and three samples by Chromatography Gas-Mass Spectrometry (GC-MS) methods to evaluate fine-grained rock quality and potential.

Geological Setting

Subduction along the Sundaland margin can be traced back into Pre-Tertiary time, as evidenced by metamorphic rocks exposed in the Meratus Mountains (southeast Kalimantan) – and their associated accretionary complex. In addition, Cretaceous shelf sandstone and limestone, Triassic granite, and older metamorphic rocks are exposed in the central Borneo Range (Pieters *et al.,* 1987) that may represent back arc oceanic material, as well as associated accreted sedimentary and volcanic rocks that may have been thrusted onto the eastern margin of Sundaland in the Early Cretaceous (Sikumbang, 1990). The Cretaceous melange complex in central western Borneo Range namely Boyan Melange or the Melange zone includes the Semitau High.

The subsequent tectonic history of Mandai, Melawi, Ketungau, and West Kutei Basins during Late Cretaceous to Early Palaeogene is still a matter of debate – interpretations offered foreland basins or subduction related process. The East Ketungau Basin is defined as a foreland basin (Pieters *et al*. 1993) including the Melawi and west Kutei Basins occupied by widely distributed and remarkably synchronous basal Haloq Sandstone. On the other hand, William *et al*. (1986) argued that those three basins in western Kalimantan are present as intra mountain basins which expose Eocene Volcanics, i.e. Piyabung and Muller volcanics (subduction related) in this areas. Thus, the Boyan Melange represents an arc/high whilst the Schwaner Mountains in the south as a volcanic/magmatic arc.

The East Ketungau Basin is mainly made up of the Mandai Group existing as a flat lying to gentle dipping sandstone and mudstone facies during Late Eocene. Mudstone facies consists of shale, claystone, and coal, and it is well exposed in Sebilit, Boyan, and Semangut Rivers. Stratigraphically, these rock deposits are unconformable overlying the Selangkai Group and other basements in the Putussibau and Sintang Quadrangles.

Methods of Study

Achieving the aims of the study, specific geologic field investigations and laboratory techniques were carried out. Futhermore, the study was focused on the organic geochemical analysis. Eventually, fine sediments of the Mandai Group were selected from a representative section, which was followed by collecting rock samples for laboratory analysis purposes, such as Chromatography Gas-Mass Spectrometry (GC-MS) and Rock-Eval pyrolysis.

The Rock-Eval pyrolysis performed in the Lemigas Laboratory, was conducted on each sample of two replicates following standard procedures. Parameters determined include total organic carbon (TOC), T_{max}, and S_1, S_2, S_3 values. Furthermore GC-MS analysis was performed on three samples for n-alkane, sterane, and terpane. The analysis was also carried out in the Lemigas Laboratory.

Hydrocarbon Source Rock

Seven samples were collected from the East Ketungau areas for Rock-Eval pyrolysis (Table 1) and GC and GC-MS analyses (Table 2).

Organic Richness

The analysis shows that, total organic carbon (TOC) content of fine sediments of the Mandai Group varies from 0.34 % to 5.16 % with an average of 0.605%. The highest TOC content (5.16%) is contained within the shale (09 HH 10C), that crops out in the Boyan River area. Organic richness of the Mandai Group tends to be categorized as fair, while one sample (09 HH 10C) indicates a very good organic richness.

Table 1 presents that the Mandai shale has a potential yield from 0.06 to 4.78 mg HC/g rock; whilst the Mandai claystone is between 0.27 and 0.53 mg HC/g rock. Based on those potential yields, the Mandai shale is included into a fair category, whilst the Mandai claystone tends to indicate a poor category. Plotting on the TOC *versus* Potential Yield

Table 1. TOC and Rock-Eval Pyrolysis Data of fine Sediments from East Ketungau Basin

No.	Formation	Sample No. (09)	Sample Type	Analyzed Lithology	TOC (%)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	PY (mg/g)	S2/ S3	PI	PC	T_{max} (^{0}C)	HI	OI
1	Mandai Group	HH/10 C	OC	Shale, dkgy	5.16	0.17	4.61	1.66	4.78	2.78	0.04	0.40	426	89	32
2		HH/02 B	OC	Shale, brngy, lam w/ Sltst/ VFSst, oxidized	0.34	0.02	0.04	0.49	0.06	0.08	0.33	0.00	445**	12	145
3		HH/05 B	OC	Shale, gy	0.58	0.07	0.16	0.11	0.23	1.45	0.30	0.02	463**	27	19
4		NO/17 A	OC	Shale, gy	0.60	0.06	0.20	0.15	0.26	1.33	0.23	0.02	442	33	25
5		AL/01 M	OC	Claystone, yell-lt.brngy, weathered	0.46	0.06	0.21	0.40	0.27	0.53	0.22	0.02	430	45	86
6		AL/10	OC	Claystone, yell-lt.gy, weathered	0.46	0.27	0.26	0.83	0.53	0.31	0.51	0.04	451	57	181
7		AL/01 H	OC	Shale, gy	0.59	0.13	0.36	0.34	0.49	1.06	0.27	0.04	429	61	58

Remarks:

TOC : Total Organic Carbon

S1 : Amount of Free Hydrocarbon

S2 : Amount of Hydrocarbon released from kerogen

S3 : Organic Carbon Dioxide

PY : Amount of Total Hydrocarbon = ($S_1 + S_2$)

PI : Production Index = (S_1/ $S_1 + S_2$)

PC : Pyrolysable Carbon

T_{max} : Maximum Temperature (^{0}C) at the top of S_2 peak

HI : Hydrogen Index = (S_2/TOC) x 100

OI : Oxygen Index = (S_3/TOC) x 100

NDP : No Determination Possible

** : Unreliable T_{max} due to poor S_2

OC : Outcrop

Table 2. Result of Gas Chromatography (GC) and Gas Chromatography - Mass Spectrometry (GC-MS) Analyses

Gas Chromatography - Mass Spectrometry		Sample Code		
		NO 30	HH 08A	HH 11C
n-alkane ratio	pristane/phytane	2.21	4.47	2.65
	pristane/nC_{17}	1.13	1.3	5.01
	Phytane/nC_{18}	0.13	0.33	2.46
	Carbon Preference Index (CPI) 1	1.17	2.29	3.22
	Carbon Preference Index (CPI) 2	0.98	1.52	3.79
Triterpane ratio	C_{30} Moretane/C_{30} Hopane	0.39	0.78	0.75
	22S/(22S+22R)C_{31}	0.33	0.2	0.28
	Tm/Ts	1.97	47.20	8.51
	Ts/(Ts + Tm)	0.337	0.021	0.105
	C_{29}/C_{30} Hopane	0.83	0.76	0.52
Sterane ratio	C_{27}	44	33	43
	C_{28}	22	61	52
	C_{29}	34	0.04	0.06
	Hopane/sterane	4.87	11.19	9.35

(PY) diagram, the fine sediments of Mandai Group tend to indicate to be potential as a gas prone source rock (Figure 2).

Maturity and Kerogen Type Indicators

The maximum temperature (T_{max}) data indicate that the Mandai shale is characterized by the T_{max} value varying from 426 - 442°C, whilst the T_{max} value of Mandai claystone varies between 430°C and 451°C. Moreover, based on Hydrogen Index (HI) values, organic matter from the Mandai shale having HI from 12 – 89 and also the Mandai claystone that has HI between 45 and 57, both indicate type III kerogen. According to Waples (1985), type III kerogen is composed of terrestrial organic materials that lack of fatty or waxy components, with cellulose and lignin as the major contributors. This kerogen type is normally considered to generate mainly gas.

The maximum temperature (T_{max}) *versus* Hydrogen Index (HI) diagram (Figure 3) shows that thermal maturity of the organic matter of the Mandai Group fine sediments tends to be situated between an immature to mature level.

Determination of the Mandai Group maturity at the researched area (HH 08A, HH 11C, and NO 30) is also relied on a biomarker analysis. The samples of HH 08A, HH 11C, and NO 30 having moretane/hopane ratio of 0.79, 0.75, and 0.39 respectively indicate an immature level (Ro<0.6%). Plotting samples of HH 08A, HH 11C, and NO 30 on the diagram of Tm/Ts ratio *versus* C_{30} moretane/hopane, their thermal maturities tend to fall under an immature to early mature level (Figure 4).

Organic Matter Origin

Organic matter origin can be determined from normal alkane isoprenoid, sterane, and triterpane ratio. The isoprenoid ratio is pristane/phytane (Pr/Ph). Sterane was used as a photosynthetic biota indicator from terrestrial environment, whilst triterpane (from bacterial) often used as a depositional environment indicator.

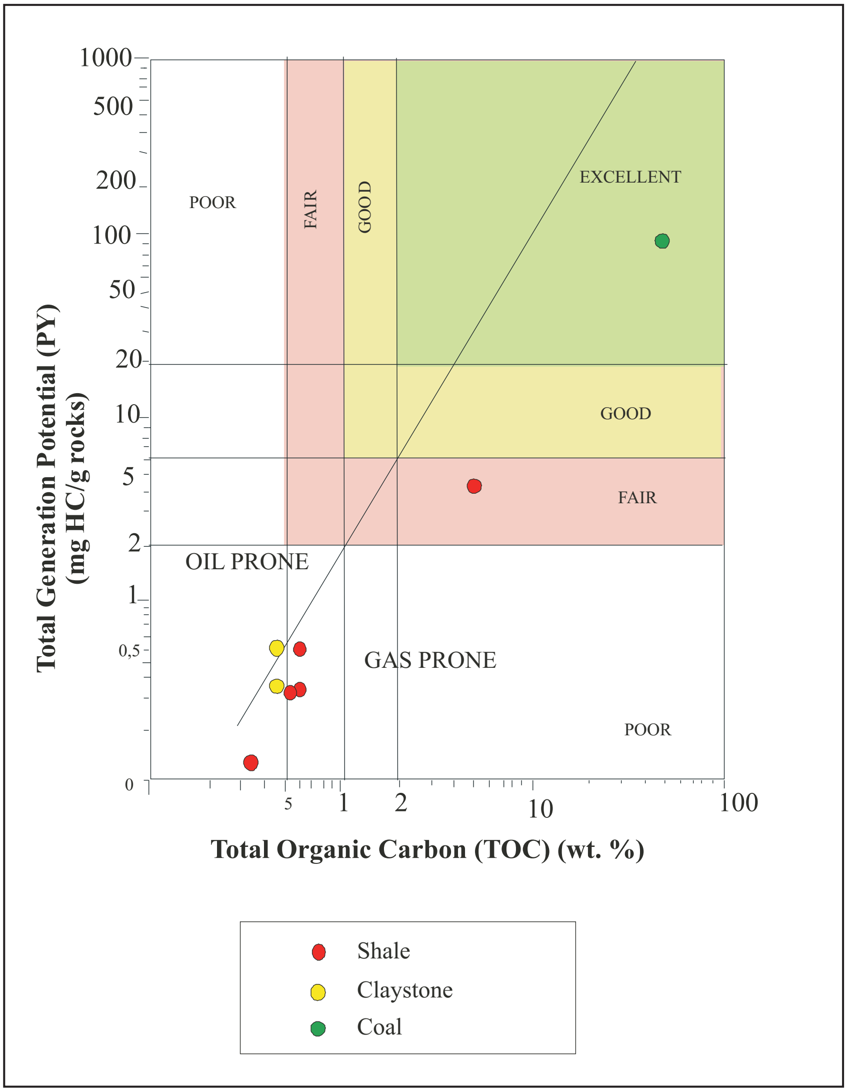

Figure 2. The diagram of some potential source rock of Mandai Group in East Ketungau Basin.

Peters and Moldowan (1993) suggested that for Pr/Ph ratio > 3, organic matter was originated from terrestrial plant (high plant), while Pr/nC17 > 0.6 was also from terrestrial plant (high plant). Crossplot hopane/sterane *versus* Pr/Ph (Figure 5) shows that samples of HH 08A, HH 11C, and NO 30, contain organic matter originated from algae with anoxic to sub-oxic condition.

Depositional Environment

Depositional environment was interpreted based on isoprenoid ratio Pr/Ph, Pr/nC17, Ph/nC18, and sterane (C27, C28, and C29). Powell and Mc Kirdy (1973; in Peters *et al*., 2005) suggested Pr/Ph ratio 5 - 11 show a depositional environment of non-marine under high waxy component, whilst ratio of 1 - 3 tends to indicate a marine environment with low waxy condition.

Samples of HH 11C and NO 30 having Pr/Ph ratios of 2.65 and 2.21 respectively, tend to indicate a depositional environment of marine under low waxy component, while HH 08A having Pr/Ph ratio 4.47 is interpreted as a non-marine environment. Peters and Moldowan (1993) stated that a high ratio of Pr/Ph suggests a depositional environment from oxic condition under low salinity composition. Ternary

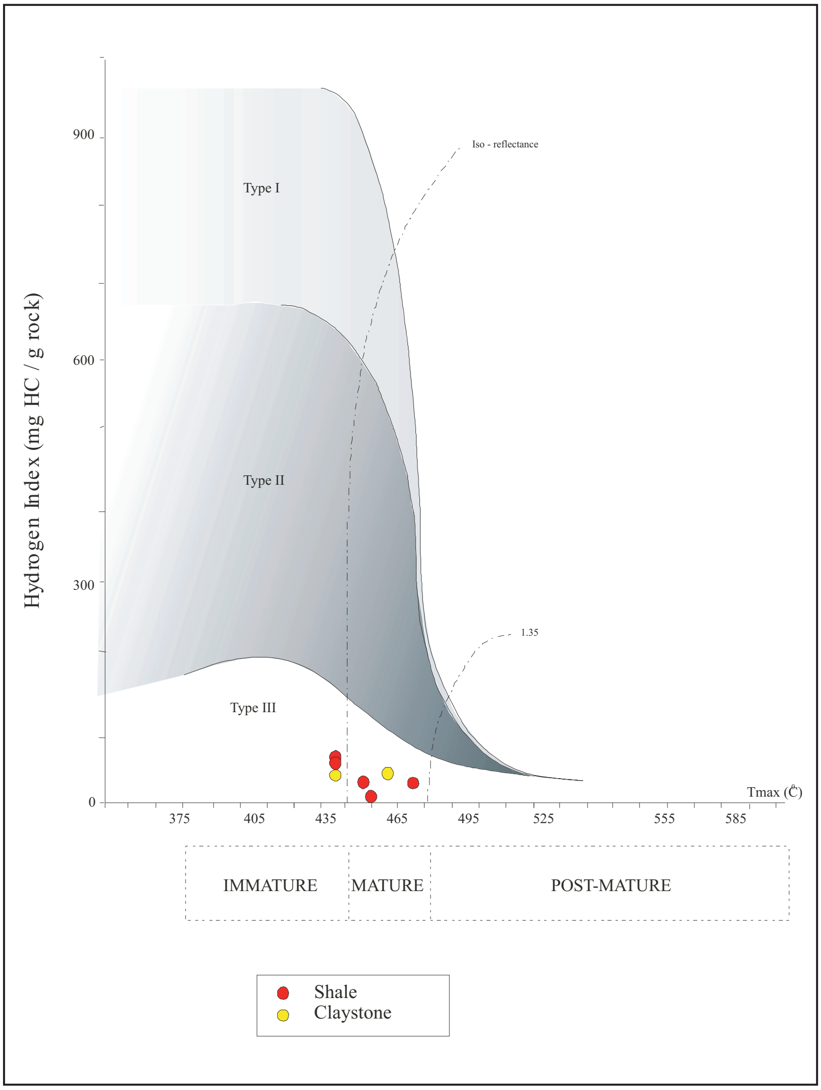

Figure 3. Diagram of *Hydrogen Index* (HI) versus T_{max}, show kerogen type of some potential source rock from Mandai Group in the studied area.

diagram crossplot of sterane (C27, C28, and C29) shows that samples HH 08A and HH 11C were derived from terrestrial environment, whilst NO 30 from an open marine environment (Figure 6).

Hydrocarbon Potential

On organic geochemistry and rock-eval pyrolysis analyses show Potential Yield (PY) of the Mandai shale is included into a fair category, whilst the Mandai claystone tends to indicate a poor category. The Mandai shale is more potential than the Mandai claystone; however both fine sediments clearly indicate a low potential category. Plotting on the TOC *versus* Potential Yield (PY) diagram, the fine sediments of Mandai Group tend to indicate to be potential as a gas prone source rock.

Discussions

The presence of highest TOC content (5.16%) in Boyan area is due to the association of shale with coal and shaly coal, that contains abundant organic matter. Figures 2 and 3 show plotting diagrams

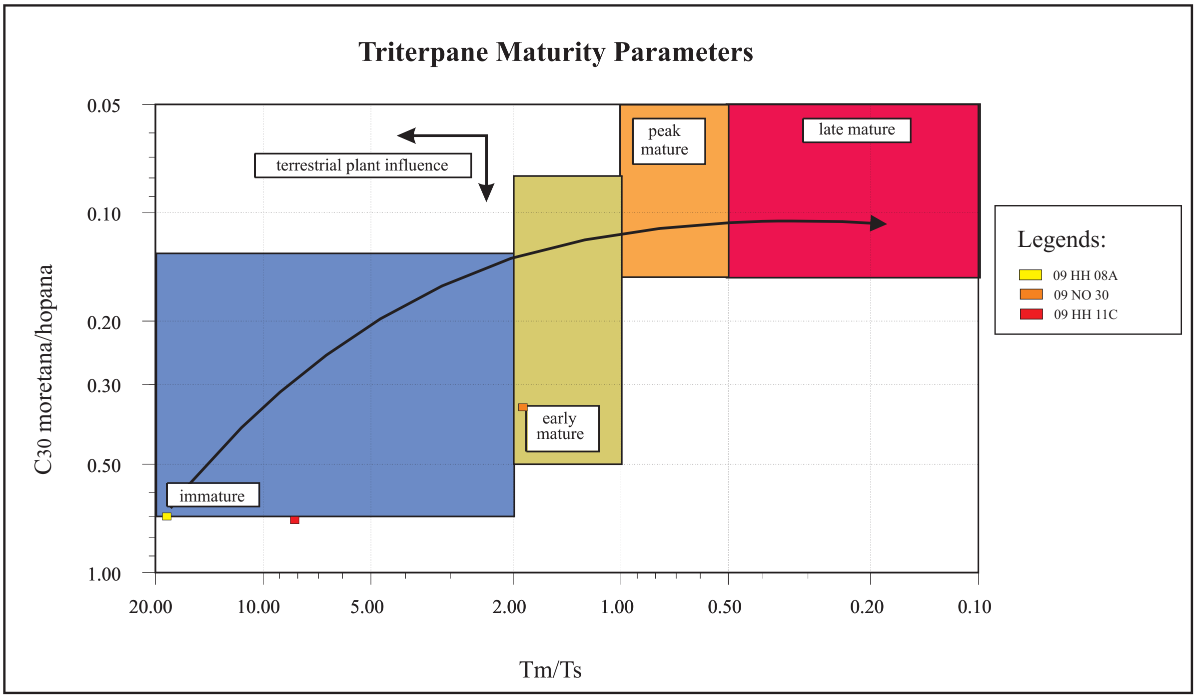

Figure 4. Diagram of maturity of some potential source rock from the Mandai Group in the studied area.

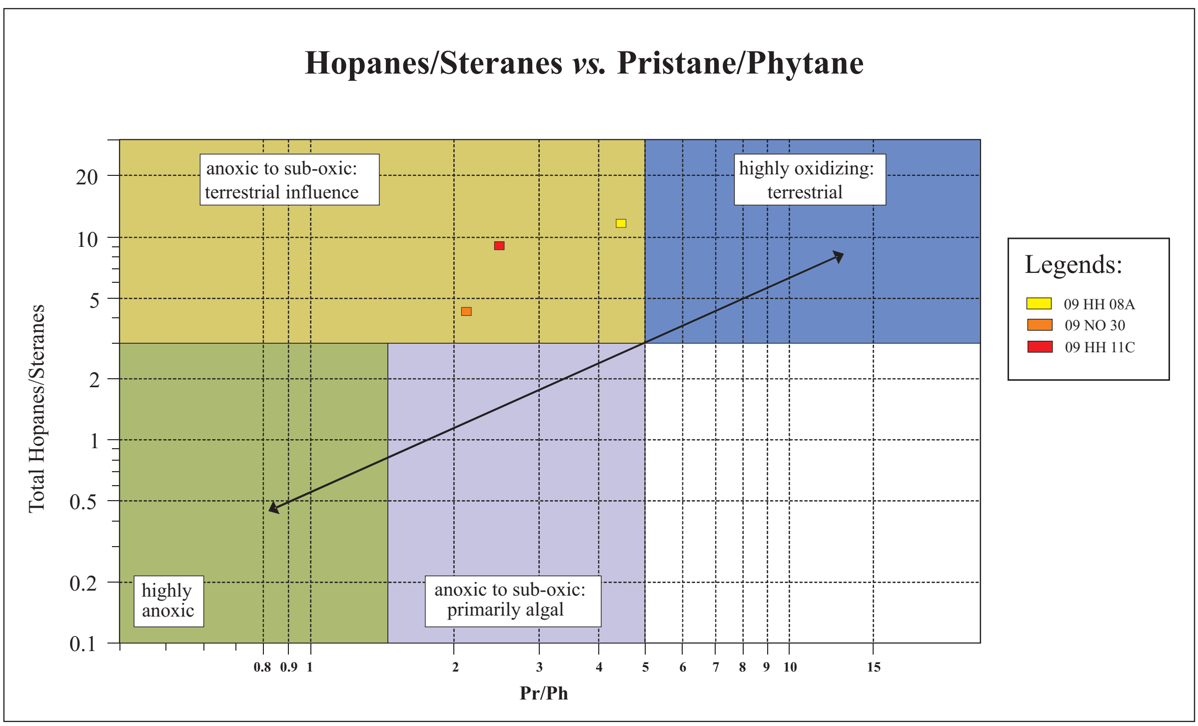

Figure 5. Ratio of hopane/sterane *versus* Pristane/Phytane, showing anoxic to sub-oxic condition of fine sediments of the Mandai Group.

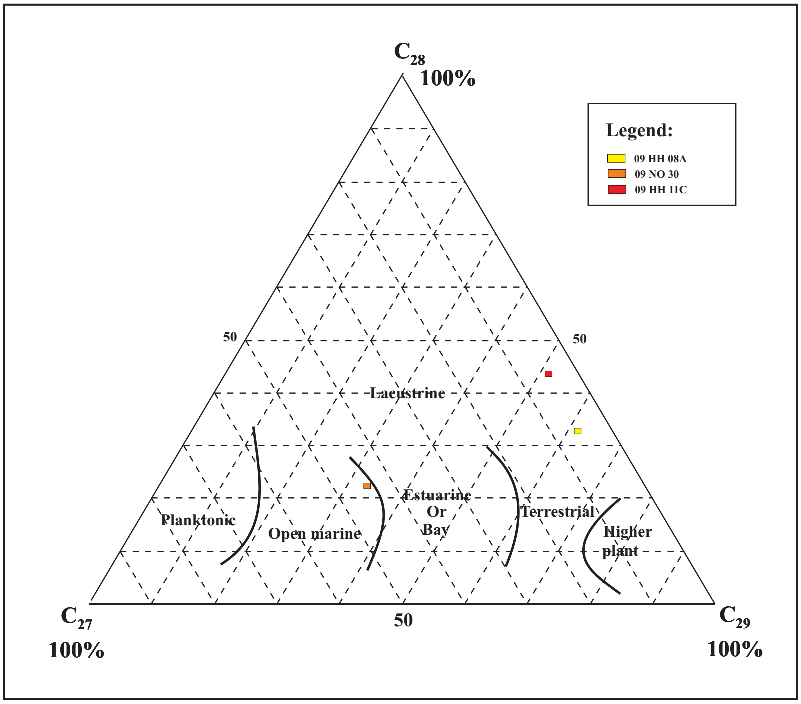

Figure 6. Ternary diagram of sterane that shows depositional environment of fine sediments Mandai Group (Huang dan Meinschein, 1979, *in* Waples and Machihara, 1991).

between TOC *versus* PY, and T_{max} *versus* HI, respectively. Both figures clearly indicate that the kerogen type and hydrocarbon potential are in a positive correlation. The Mandai Group fine sediments tend to contain type III of kerogen that is considered to generate mainly gas.

T_{max} value of the Mandai shale ranging from 426 - 442°C, and Mandai claystone from 430°C to 451C show that the maturity level of fine sediments is situated between an immature to mature stage. This condition is supported by biomarker analyses, which indicate an immature to early mature level as shown by Tm/Ts ratio (Figure 4). Tm/Ts ratio is not accurate, because it is possible to be influenced by organic material type (Waples and Machihara 1991). Tm/Ts ratio will decrease by the end of maturity (Waples and Machihara, 1991) at a variated of moretane/hopane ratio and 22S/(22R+22R) ratio. Increasing on the maturity degree influenced by Tm will progressively disappear, while Ts concentration relatively rises. Therefore, Tm/Ts ratio was used as a non-qualitative indicator for the relative maturity of fine sediments and oil, because both materials contain organic matter input from the same facies.

C_{30} moretane/hopane ratio has more unstable condition than 17 á (H)-hopane, therefore its concentration will decrease at the high maturity level. Most of moretane disappear at the early mature stage (Ro<0.6%), thereby the usage of the ratio is very limited. Waples and Machihara (1991) expressed that moretane/hopane ratio indicate a mature level if less than 0.15, while it is immature if the ratio is more than 0.15. Those ratio values can only be used as a qualitative immature indicator. Moretane/hopane ratio above 0.15 indicates that Ro value is less than 0.6%.

Conclusions

- Organic richness of fine sediments from the Mandai Group tends to be categorized as fair, while one sample (09 HH 10C) indicates a very good organic richness.
- Type III of kerogen considered to generate mainly gas is found in the fine sediments of the Mandai Group which appears to be a gas prone potential with poor to fair category.

- In accordance with Rock-Eval pyrolysis and GC-GCMS data, the maturation level of most of samples analyzed is immature to mature.
- Based on organic geochemistry and Rock-Eval pyrolisis, the Mandai shale has hydrocarbon potential more than claystone.
- Fine sediments of Mandai Group was deposited within a terrestrial to marine environment under anoxic to sub-oxic condition.

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