

Paleoenvironmental Implications from Biomarker Investigations on the Pliocene Lower Sajau Lignite Seam in Kasai Area, Berau Basin, Northeast Kalimantan, Indonesia

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Abstract

Pliocene age lignites from Lower Sajau seam, from borehole in Berau Basin, Northeast Kalimantan, Indonesia were investigated with respect to organic geochemistry by HPLC, GC and GC/MS. The analysis was conducted to drilling sequence of Kasai Coal Field, Berau Basin which has been applied to identify organic sources and maturity of organic matter. The result of normalized yields of the soluble organic matter (SOM) data indicates saturated and aromatic proportion of hydrocarbon are very low (under 10%), this was reflecting that lignite coal is still in immature stage. Moreover, biomarker hydrocarbon such as diterpenoids was not found from the sample that indicates absence of gymnosperm precursor in the paleo-peat. In contrast, there was great abundance of terpenoid biomarkers including lupane and oleanane showing domination of angiosperms indicate that angiosperm was dominated vegetation source. There also hopanoid biomarkers explaining acidic depositional environment in coal formation and microbes-affected conditions in peat formation process. Ratio of Tm/Ts shows paleomire where ratios value of Tm/Ts is in range of oxide condition.

Keywords

Paleoenvironment, Lignite, Sajau, Berau Basin, Biomarker

1. Introduction

In this paper, a geochemical research was conducted to a number of coal lignite samples from lower Sajau Formation in Berau Basin, northeastern Kalimantan in order to identify the biomarker presents as the indicator for paleoenvironmental assessment. Furthermore, several specific identified biomarkers have been used in maturity

determination. These two parameters are important in coal quality evaluation, also from these data, a coal depositional environment is established including the conditions and vegetations involved during depositional process which will be useful for future investigations into the evolutions of depositional environment from this interval.

2. Regional Geology

2.1. Regional Tectonics

Berau Basin is located as a part of Great Tarakan Basin (**Figure 1**) within Berau Regency Northeast Kalimantan. It has latitude of $1^{\circ}12'00''\text{S}$ - $2^{\circ}36'00''\text{S}$ and longitude of $116^{\circ}00'00''\text{E}$ - $118^{\circ}57'00''\text{E}$ with the total area of this basin approximately 150 km^2 West-East. In northern part, it has bounded by Mesozoic and older rocks of the Sampurna High, to the western part by the strongly folded Mesozoic to Eocene mélangé of the Kucing High, and to the southern part by Mangkalihah High separating the Berau Basin and Kutai Basin in the south. This high was associated with the Fault Zone along the north shore of the Mangkalihah Peninsula, and the basin extends toward the Makassar Trough of the Celebes Sea in eastern part.

The Kalimantan island was a relatively stable Sundaland in the Upper Mesozoic times. The tectonics in the northeast Kalimantan area was the result of collision between Indian and Eurasian Plates at 50 Ma [1]. This collision caused the back arc extension connected to subduction rollback in the west Pacific, and the opening of the Berau Basin by Rifting in the Eocene [2], however, thought that collision was less significant.

2.2. Regional Stratigraphy

Regional stratigraphy of Berau Basin was classified into pra-Tertiary, Tertiary, and Quaternary deposits (**Figure 2**). The oldest age rocks of Tertiary period is Danau Formation, consist of strong tectonics rocks and metamorf with highly significance thickness in the age of Permian-Carbon or Jurassic Cretaceous.

The basin-fill succession of the Berau Basin can be simply divided into 5 major cycles of sedimentation [3], there are cycle 1 (Late Eocene-Oligocene), cycle 2 (Early Miocene-Middle Miocene), cycle 3 (Middle Miocene-Late Miocene), cycle 4 (Pliocene) and cycle 5 (Quaternary). Every cycle reflects different lithological characteristics, which may have been associated to tectonism and relative sea-level changes leading to transgressive and regressive events.



Figure 1. Physiography map of berau basin in northeast Kalimantan.

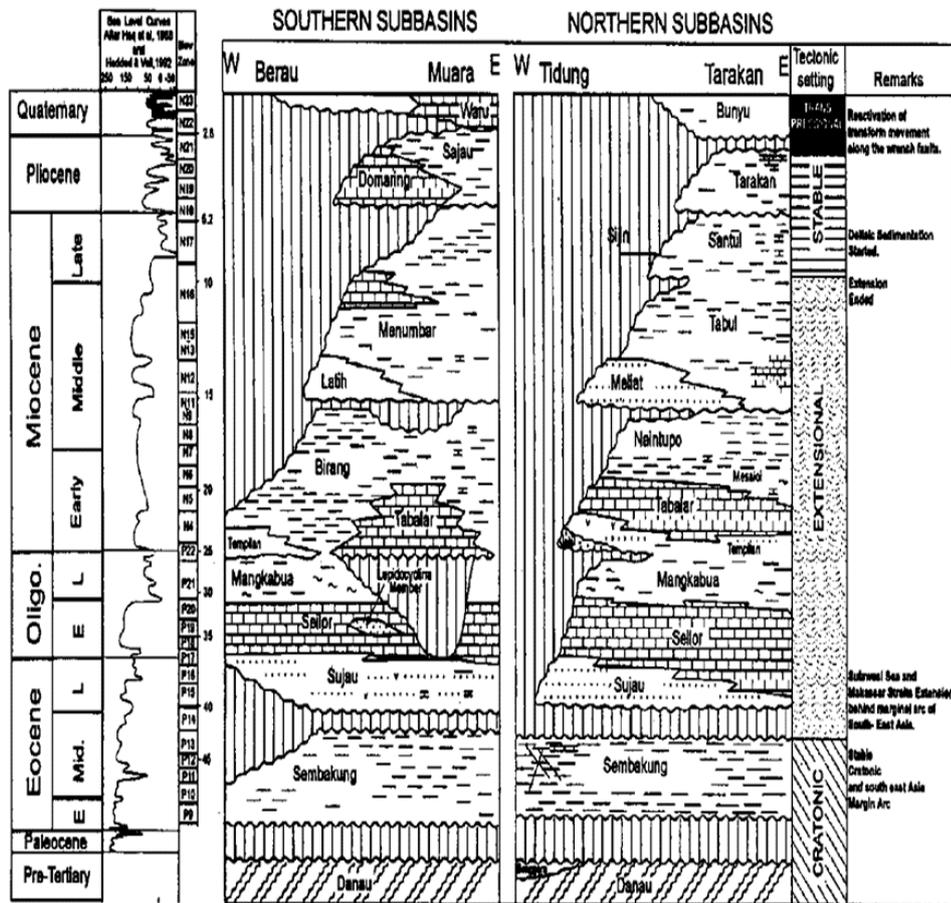


Figure 2. Stratigraphy of tarakan sub-basin (Achmad and Samuel, 1984).

The oldest sedimentary cycle is a syn-rift volcanic bearing siliciclastic-rich unit of the Middle to Upper Eocene which called Sekatak Group consisting of Sembakung Formation and the unconformably overlying Sujau and Malio Formations. This group were sedimented unconformably overlies pre-rift, Triassic to Cretaceous Sundaland basement rocks, also underlies the post-rift unconformity below the younger group sediments.

The youngest which called Simenggaris Group is divided into five lithostratigraphic units, Meliat/Latih (oldest), Tabul/Domaring, Tarakan/Sajau, and Bunyu (youngest) Formations.

The Sajau coal measures in Tanah Kuning, Mangkupadi in northern part and in the Kasai, Batu-Batu area southern part of the basin typically consist of siliciclastic rocks and coals. The Sajau formation is the one of two coal carrier formations in Berau Basin beside of Latih Formation. This formation consisting claystone, shales-tone, sandstone, conglomerates with interlaminated coal, also containing molluscs, quartzit, and mica. The lithological structure which can be found are cross and parallel lamination. The coal thickness in this formation is 0.2 - 1 m, black and brownish layer within 775 m of the total layers. The sedimentation process begin on the fluvial and deltaic system over Pliocene-Pleistocene period which conformably overlying Waru Formation.

3. Methods

Generally, there are three stages in this research, beginning with coal sampling from Sajau Formation in Kasai area, evaluating the geochemical characteristics through laboratory test using HPLC, GC, and GC/MS methods, and making interpretations from laboratory result to determine the conditions of depositional environment also the maturity assessment from all samples.

Two coal samples labeled S-003 and SG-19 has been examined in laboratory test. Firstly, solid coal samples were extracted during 24 hours until its change their phase into liquid. This concentrate liquids then filtered by

HPLC process to separate fractions including saturated, aromatic, NSO, and asphaltine. Furthermore, saturated and aromatics fractions were tested in GC instrument so that the chromatograph pattern could be identified. The GC instrument that used in this research is Varian Series 3400 Gas Chromatograph under standard conditions with $T_0 = 70^\circ\text{C}$, hold time I = 2 mins, Rate I = $8^\circ\text{C}/\text{min}$, T_f I = 280°C , hold time II = 45 mins, Rate II = $10^\circ\text{C}/\text{min}$, T_f II = 300°C , hold time III = 10 mins.

The remaining saturated and aromatics fractions were prepared in Mole Sieve Analysis for GCMS test on the next stage. The specific biomarkers were investigated from remaining saturated and aromatics fractions through GC/MS method. The GC/MS instruments used in this experiment is Shimadzu GCMS-QP2010 with Shimadzu GC-2010 in standard conditions with $T_0 = 120^\circ\text{C}$, hold time I = 2 mins, Rate I = $5^\circ\text{C}/\text{min}$, T_f I = 200°C , hold time II = 0.5 mins, Rate II = $5^\circ\text{C}/\text{min}$, T_f II = 300°C , hold time III = 30 mins. These GCMS standard conditions are slightly different with usual GCMS experiment, the base temperature is lower than usual to make it more effective for biomarker appearance.

All the biomarkers were identified from GC and GCMS instrument using GCMSPostsum Analysis with several libraries BENZODIAZEPINE, PESTEL_3, NIST 08, WILEY and [4].

4. Results

4.1. HPLC Analysis

In this research, the first parameter were found from HPLC process of two samples (**Table 1**).

The tables above shows a very low percentage (<10%) of saturated and aromatics fractions which significantly different with NSO and asphaltine percentage that can be found of two samples. In this result, the main characteristics of coal has been proven according to a great abundance of asphaltine (>50%) also high amount of NSO with saturated and aromatics are under 10%.

4.2. GC Analysis

The two saturated samples has been injected to GC instruments in order to find the chromatograph of each sample. Those chromatograph will showing all the general biomarkers distribution and percentage of UCM (Unresolved Complex Mixture) area. Generally, both samples shows the domination of long chain carbons rather than short chain carbon with large area of UCM which defined as moderately degraded (**Figure 3**).

The distributions of n-alkana shows that long chain carbon domination begin with medium carbon in $n\text{C}_{22}$ then reach the highest abundance when $n\text{C}_{31}$ with percentage is more than 30% (**Table 2**).

Based on Moldowan *et al.*, 1992 [5], peak domination of long chain carbon which shows in a larger retention time proves that the maturity of coal samples is remain in immature stage.

Furthermore, the percentage of pristane and phytane is very low in all samples (**Figure 4**), so it needs larger magnification to identify both pristane and phytane to determine redox conditions during sedimentation.

All the identified pristane and phytane then will be calculate to find the ratio value (**Table 3**).

Table 1. Liquid chromatography results from two samples.

Sample	Empty Vial (gr)	Vial + Fraction (gr)	Wt of Fraction (mg)	Total (mg)	Normalized (%)	Total (%)
S-003	7.1192	7.1206	1.4	84.8	Sat	1.65
	7.1078	7.1099	2.1		ARO	2.48
	7.0812	7.1131	31.9		NSO	37.62
	7.2371	7.2865	49.4		Aspl	58.25
	7.1714	7.176	4.6		Sat	2.24
SG-19	7.1777	7.1835	5.8	205.2	ARO	2.83
	7.1801	7.2211	41		NSO	19.98
	7.1136	7.2674	153.8		Aspl	74.95

Table 2. Normalised percent of n-paraffins.

Component	S-003 Wt. %	SG-19 Wt. %	Type of Carbon Chain
N-Paraffins			
nC15	0.13	0.49	Short Chain Carbon
nC16	0.15	0.23	
nC17	0.22	0.96	
nC18	0.41	0.78	
nC19	0.21	0.50	
nC20	0.53	1.19	Medium Chain Carbon
nC21	0.50	1.34	
nC22	2.37	1.29	
nC23	1.15	1.56	
nC24	3.01	4.06	
nC25	3.66	5.52	Long Chain Carbon
nC26	1.80	3.26	
nC27	8.03	18.15	
nC28	2.70	2.72	
nC29	22.41	10.95	
nC30	5.37	3.50	
nC31	32.69	33.59	
nC32	4.36	2.92	
nC33	9.95	6.62	
nC34	0.34	0.37	
Total	100	100	

Table 3. Pristane/phytane ratio calculation.

Component	S-003	SG-19
Pris/Phy	1.49	1.38
Pris/nC17	0.48	0.41
Phy/nC19	0.18	0.37
nC31/nC19	157.86	67.10
CPI	4.86	5.20

4.3. GCMS Analysis

In GCMS analysis, saturated fractions have been used for biomarkers identification for depositional environment and maturity assessment of each samples. For saturated, several majors biomarkers have been discovered such as Terpanes from ion m/z 191, Steranes from ion m/z 217, and Bicyclic from ion m/z 123. Those biomarkers appears as peak of MIC (Mass Ionic Carbon) chromatograph which will be calculated in percentage as the paleoenvironmental implications. Beside that, TIC (Total Ionic Carbon) chromatograph could be used to determine the distribution of three majors biomarker above [6] (**Figure 5**).

4.4. Terpanes (m/z 191)

Both of samples shows tricyclic diterpane, Tm, Ts, hopanes, moretanenes and olenanes, and gammacerane that

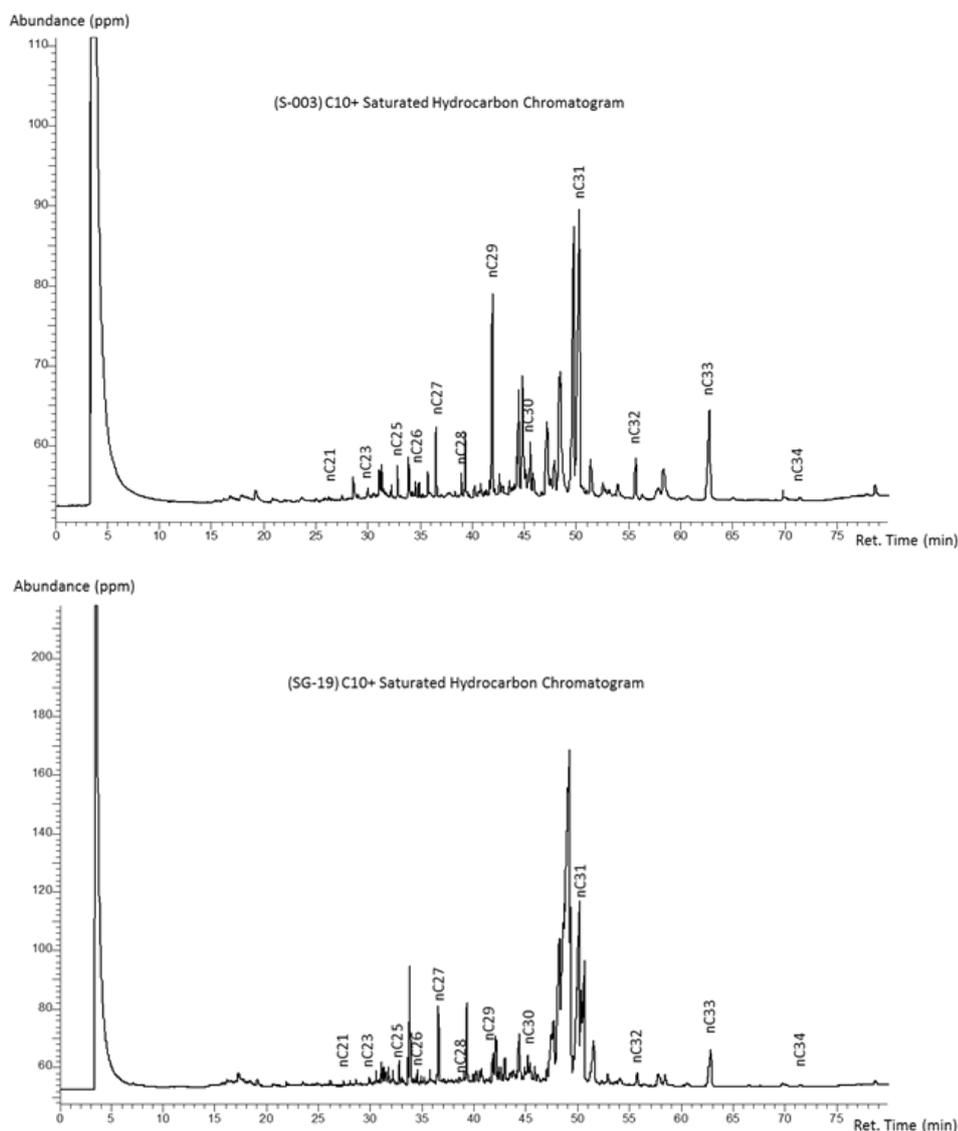


Figure 3. GC Chromatograph of saturated samples.

spreading along retention time 28 - 42.5 mins within temperature 242.5 - 300 C. But, unfortunately gammace-rane could not be identified in ion m/z 191, but it has be shown in chromatograph ion m/z 412. All the identified biomarkers have been calculated as shown below (Table 4).

4.5. Steranes (Ion m/z 217)

Several biomarkers from steranes has been discovered from chromatograph ion m/z 217 there are diacholestane, cholestane, cyclic alkane, and methylated sterane. Those biomarkers were dispersed in retention time 12 - 40 mins with temperature 170 - 300 C. But diacholestane and cholestane from all samples can only identified from ion m/z 205 (Table 5).

4.6. Bicyclane (Ion m/z 123)

A number of biomarkers have been found from chromatograph ion m/z 123 including bicyclic, pentamethyldecahydronaphtalene, drimane, and homodrimane. Those compounds were distributed thoughr retention time 9 - 43 mins within temperature 150 - 300 C. Those biomarkers also calculating in the table below (Table 6).

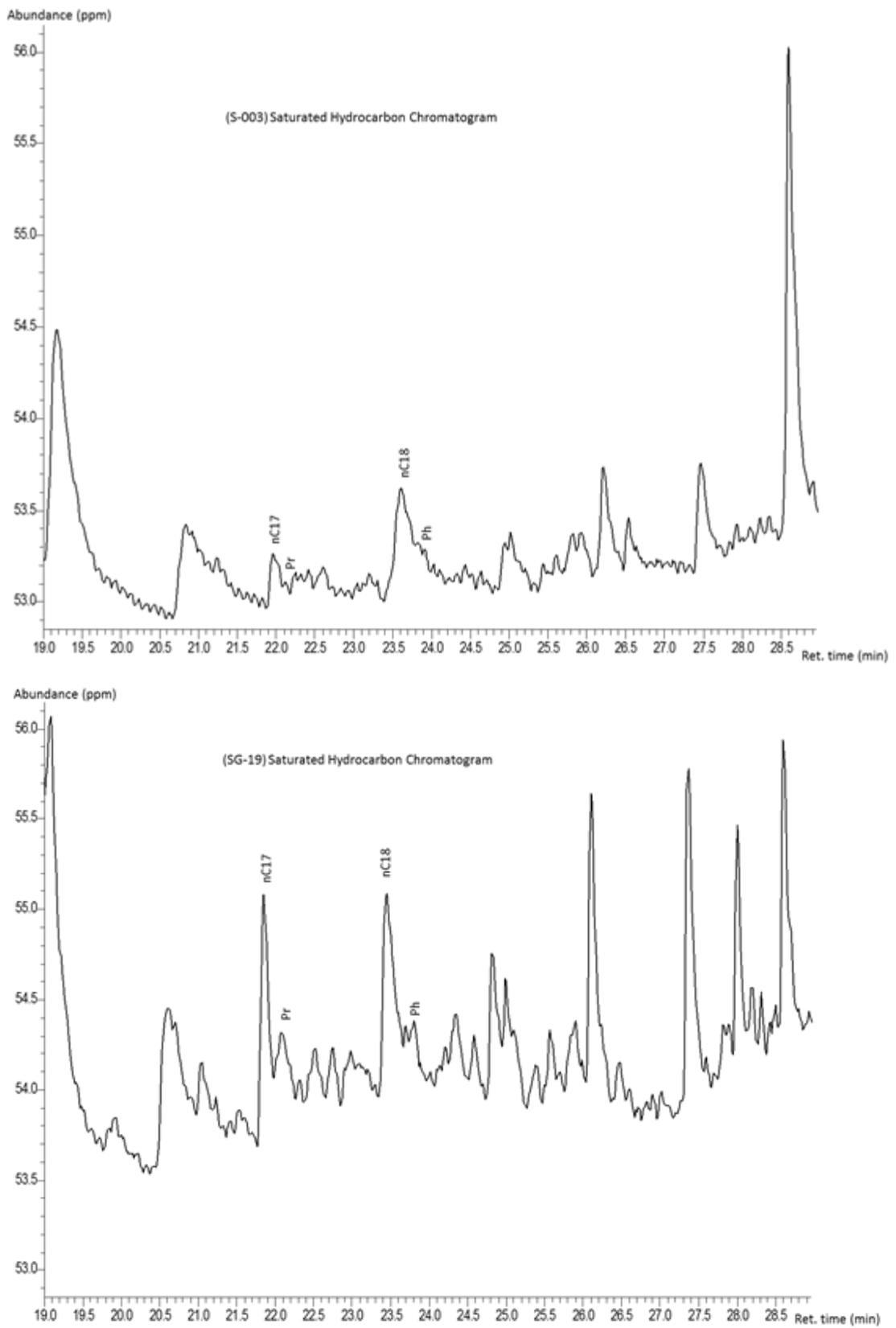


Figure 4. GC extension chromatogram from saturated samples.

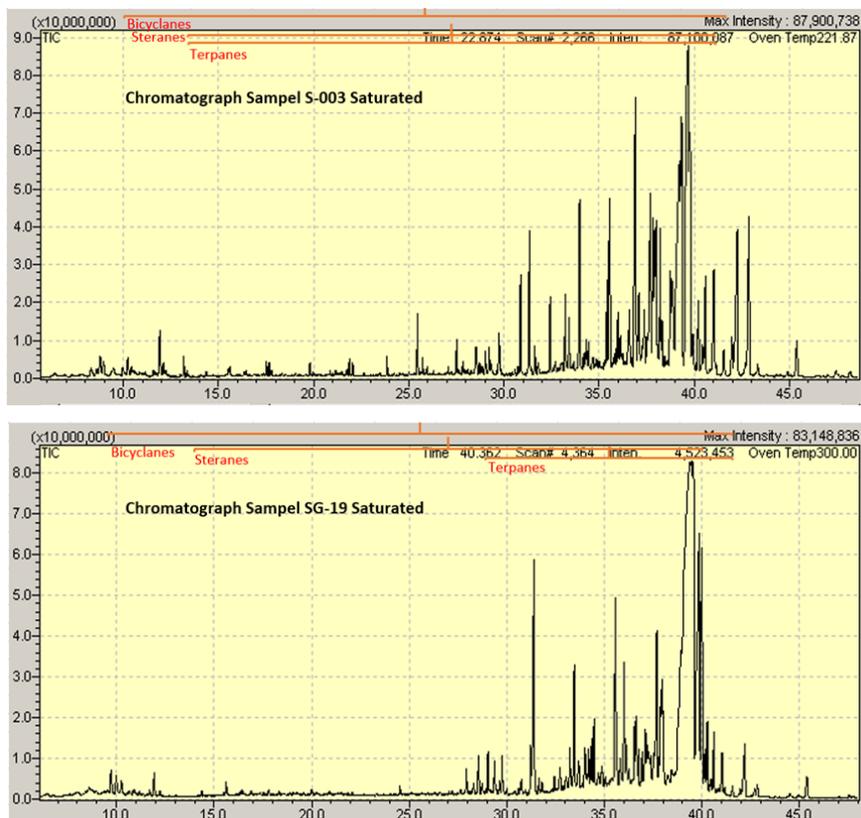


Figure 5. TIC chromatograph of saturated samples.

Table 4. Triterpane Data (ion m/z 191).

Sample Depth (metres/feet)	Tm Ts	Total % C19-C31 Tricy	Total % Hop	% C30 Resins + OL	C29 α , β Hopane		C29 Moretane	C30 Moretane	C30 Hopane		22S/22R		C30 α , β Hop OL	GMx100 C30 α , β Hop
					C30 α , β Hopane	C29 Hopane			C29-C30 Moretanes	C31	C32			
S-003	3.29	0.00	95.65	3.47	1.33	0.88	3.99	0.19	2.30	0.00	0.47	54.89		
SG-19	1.95	0.00	88.77	10.74	4.06	0.12	1.27	0.57	1.13	0.00	0.18	24.60		

Table 5. Sterane Data (ion m/z 217).

Sample Depth (metres/feet)	Total Hopane Total Sterane	C ₂₇ α , β Hop Total Dtx C ₂₇	% α 20R Steranes			C ₂₇ α , β 20R C ₂₈ α , β 20R	Total C ₂₇ -AM Total Dtx C ₂₇	Total C ₂₇ -AM, Dtx C ₂₇ Total Dtx C ₂₇	C ₂₇ α , β 20S C ₂₈ α , β 20R	C ₂₇ α , β 20R-20S C ₂₈ α , β 20R-20R	C ₂₇ α , β 20R C ₂₈ α , β 20R	C ₂₇ α , β 4M Ster C ₂₇ α , β Dtx	Total C ₂₇ - α , β Dtx Total C ₂₇ - α , β Dtx
			C ₂₇	C ₂₈	C ₂₉								
S-003	5.07	0.12	10.24	4.79	84.97	0.12	0.16	0.16	0.66	0.17	0.00	0.00	0.04
SG-19	10.56	0.39	16.51	28.91	54.58	0.30	0.26	0.26	0.50	0.82	0.00	0.00	0.00

Table 6. Bicyclane Data (ion m/z 123).

Sample Depth (metres/feet)	Drimane		C ₁₅ Rearranged Bicyclics	Drimane
	Homodrimane		C ₃₀ α , β Hopane	
S-003	0.3012		6.7661	3.1764
SG-19	0.1457		10.4374	1.1006

4.7. Gammacerane (Ion m/z 412)

In source rock sample, gammacerane usually appear on chromatograph m/z 191 and m/z 412, but in these samples, gammacerane can only find in m/z 412 which further identified as Gammacerane and Norgammacerane with calculation as the table below (Table 7).

4.8. Lupane (Ion m/z 177)

Lupane is a unique biomarker that indicates the domination of terrestrial source during sedimentation process and identically found in coal samples. Moreover, lupane is strongly associated with oleananes as an implications of sample which came from terrestrial with high effecting by vegetation sources. Lupane generally found in long chain carbon within retention time 35 - 45 mins in temperature around 290 - 300 C. There are two identified lupane in this ion m/z 177, such as lupane and lup-20(29)-en-3-ol.

In other MIC chromatograph, there also some association between gammacerane, oleananes, and lupanes which can be found in ion m/z 163, ion m/z 231, ion m/z 259, ion m/z 370, and ion m/z 398.

5. Discussion

5.1. Maturity Assessment

The coal maturity could be determine from several parameters which have been identified in this research. The first parameter was recognized from extraction data from two samples

Based on extract composition plot, we can examine that the maturity of both samples are still in immature coal stage according to very high abundance of NSO and asphaltine from these samples (Figure 6).

The other parameter that can be used for maturity determination is triterpane from MIC chromatograph ion m/z 191. The result of calculations are plotting in crossplot below (Figure 7).

Table 7. Gammacerane data (ion m/z 412).

Sampel	Retention Time	Abundance of Gammacerane	Total Triterpane	Grand Total Sterane	Total Drimane	% GM
S-003	39.761	54003	5970020	1261265	3464652	5.00
SG-19	39.845	59291	11160982	1123477	4855201	3.50

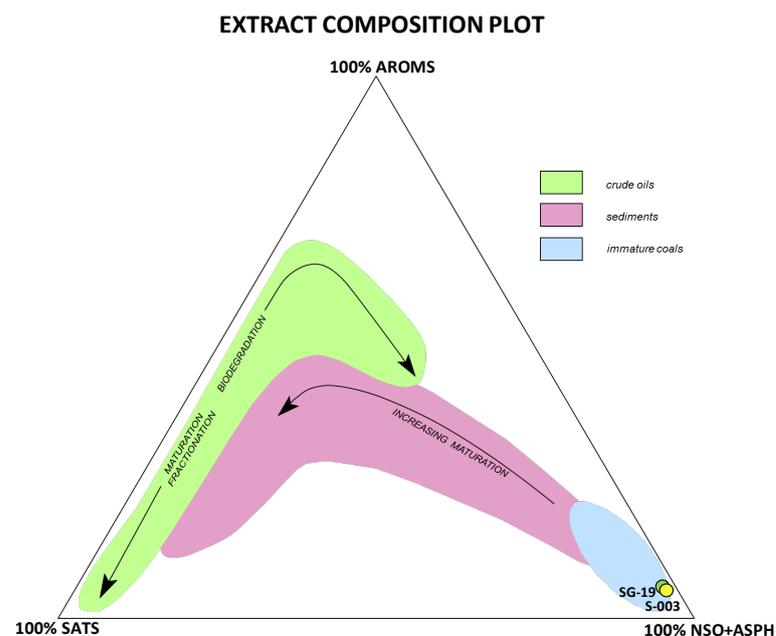


Figure 6. Extract composition plot.

Crossplot of Triterpane Maturity Parameters

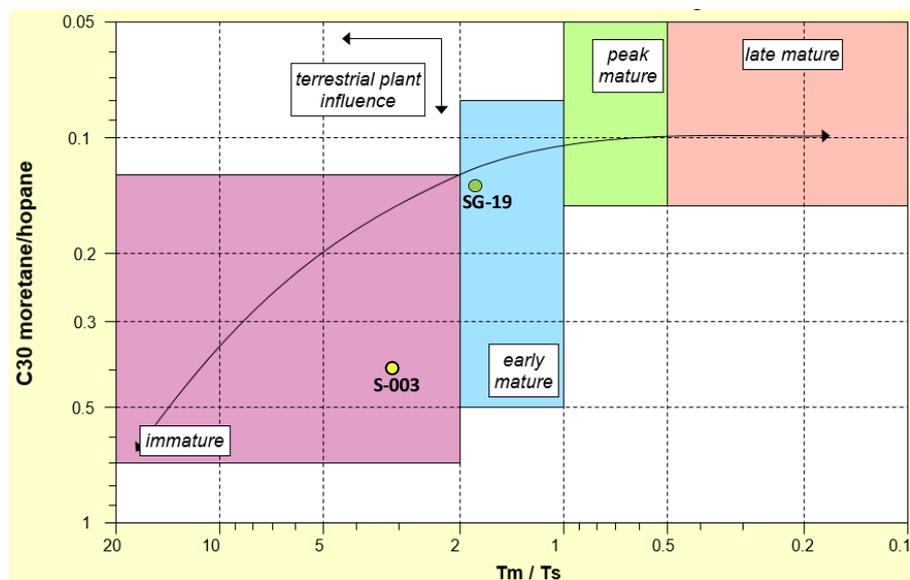


Figure 7. Crossplot of triterpane maturity parameters.

The diagram above describes the maturity of sample S-003 is slightly different with sample SG-19. Sample S-003 was plotted in immature area with higher terrestrial influence than SG-19, while sample SG-19 was plotted in the edge of early mature area. That diagram support the result of extraction composition plot.

5.2. Depositional Environment Assessment

Some parameters have been used to determine the conditions during sedimentation and conditions of depositional environment of each samples. All parameters in this research were interpreted in the form of crossplot diagram (**Figure 8**).

From the crossplot above, sample S-003 is in the edge of terrestrial source area while SG-19 is in mixed organic input. So, sample S-003 have been dominated by terrestrial source than SG-19 while sedimentation process.

The **Figure 9**, shows that all the samples are in highly anoxic condition with very low ratio value of Pr/Ph. It is related to the high salinity of environment while sedimentation that shows by highly abundance of gammacerane.

The other parameter which support terrestrial input domination is highly amount of oleananes which can be identified from several chromatograms proves that depositional environment was dominated by terrestrial input especially vegetation source. The other parameters are the great abundance of lupane and cholestane which indicates vegetation input in terrestrial settings. There also cadinanes, that found in MIC chromatograph ion m/z 156 that also implicates terrestrial input especially angiosperm domination rather than gymnosperm.

The absence of diterpenoids in all samples of ion m/z 191 can be an indicator of terrestrial input without or less in gymnosperms domination. The other parameters such as beta-Carotane and Carotenoids has been used to determine the lacustrine settings of deposition, but those parameters were cannot be found in both coal samples.

Based on that diagram (**Figure 10**), sample S-003 was identified in higher plant source domination while sample SG-19 is in terrestrial setting. So it has been proven that all samples were deposited in terrestrial sources domination.

Based on previous diagram, sample S-003 and SG-19 were plotted in area of highly terrestrial input due to great abundance of oleananes which can be found in most of MIC chromatograms (**Figure 11**).

6. Conclusion

Pliocene Sajau Formation is in immature-early mature stage. The depositional environment of this formation is

Pristane/nC₁₇ vs. Phytane/nC₁₈ Diagram

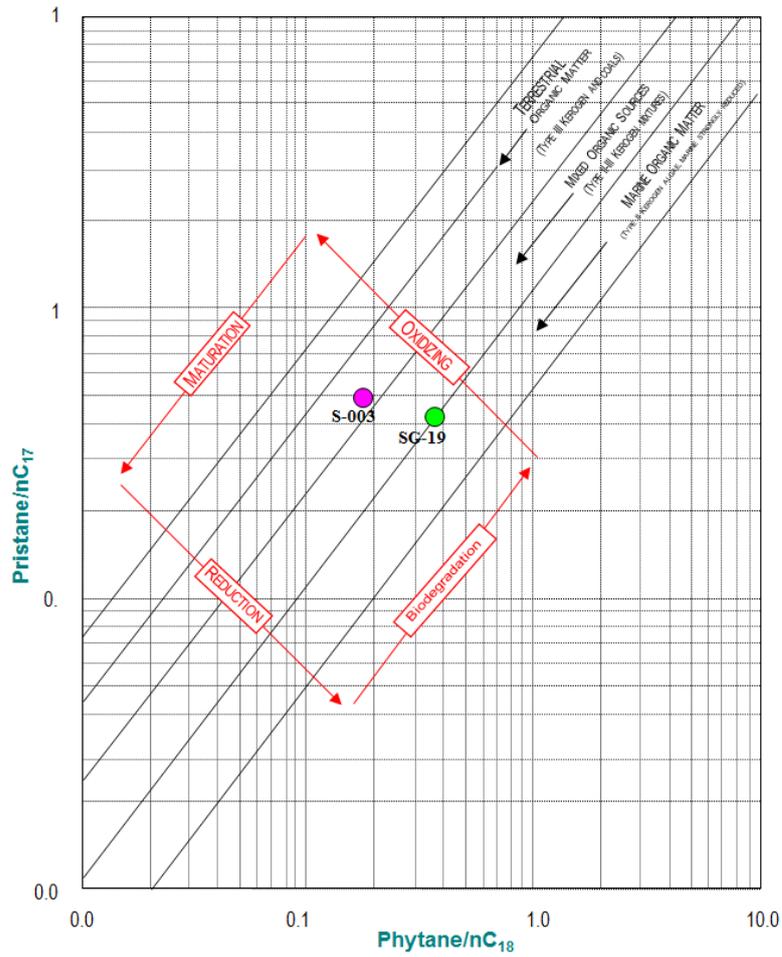


Figure 8. Pristane/phytane crossplot diagram [7].

Pristane/nC₁₇ vs Pristane/Phytane

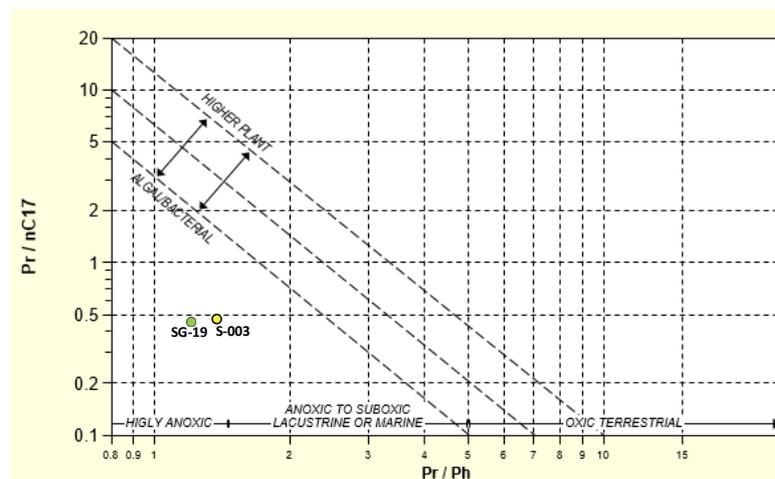


Figure 9. Crossplot between Pr/nC₁₇ and Pr/Ph.

terrestrial settings with the domination of terrestrial input such as vegetation sources especially angiosperms. The condition of depositional environment during sedimentation is hypersaline and anoxic to suboxic conditions.

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