



The Liburdinding Miocene Pamaluan Coal Mine, Pasir-Sub Basin, East Kalimantan:

Origin and palaeoenvironmental implications from biomarker studies

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Abstract

The coals from the Liburdinding coal mine in Paser regency, Pasir Sub-Basin, East Kalimantan, Indonesia were investigated with respect to organic geochemistry to determine their origin and to reconstruction the depositional environment. For this purpose, biomarker analyses have been done. The distribution of saturated and aromatic hydrocarbons of organic matter in a series of Miocene Pamaluan coal formation were identified. The rank of the Pamaluan coals ranged from sub-bituminous to bituminous coals (0.46–0.55% Ro), based on measurements of huminite/vitrinite reflectance. The predominance of diterpenoids in both the saturated and aromatic fractions indicated that the main sources of organic matter were gymnosperms (conifers). The presence of hopanoid biomarkers indicates the contribution of prokaryotic organisms, such as bacteria and fungi, whereas the identification of non-hopanoid triterpenoids implies a contribution of angiosperms to the coal organic matter. The variations in compositions of biomarkers indicate changes in the water level, due to seasonal drying of the mire, which caused vegetation differences in the palaeoplant communities and changes in the dysaerobic conditions during peatification.

Key word: Miocene, Pamaluan, coal, Sub-Pasir basin, biomarker.

Introduction

In the past few decades, molecular organic geochemistry has played an important role in the exploration of coals and fossil fuels generally. It involves the analysis of the soluble organic matter and identification of organic compounds with hydrocarbon skeletons related to biological molecules present in the tissues of living organisms (K. E. Peters, C.C. Walters, J. M. Moldowan, 2005; MacKenzie, A.S., Patience, R.L., Maxwell, J.R., 1981). These biomarkers allow for the recognition of the main input of organic matter (OM), identification of coal maturity, an indicator of the palaeoenvironment in which they were deposited.

Although the coal deposits are widespread in Pasir Regency, organic geochemical data are limited. The determine of origin and paleoenvironmental of

coal in Liburdinding Coal Mine are the objective of this study.

Geological Setting

The Liburdinding coal mine is located in the vicinity of the Paser Regency, East Kalimantan Province (Fig. 1) and is situated S. 00° 33' 34.9"/E. 117° 12' 15.5". There are seven (7) coal seams in the Liburdinding coal mine are present within Pemaluan Formation of Lower to Middle Miocene age. Geologically, the Liburdinding coal mine was situated in Pasir Basin. This basin is one of the Tertiary basin and well known as an area of major resources of oil, gas and coal in western Indonesia. The Pasir Basin is situated along the northwestern margin of the Paternoster Platform Shield in South Kalimantan.

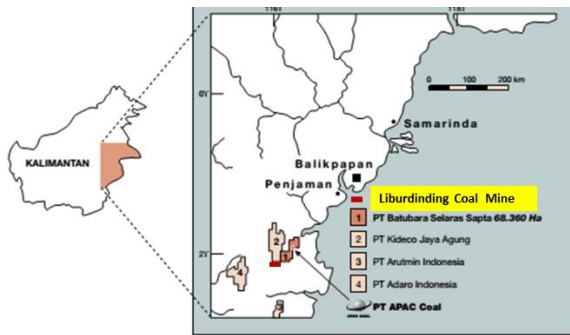


Figure 1. Liburdinding coal mine location, Paser Regency, East Kalimantan.

The basin is defined by the Meratus Ophiolitic Complex to the west and separated from the Kutei Basin to the north by a flexure related to the Adang Fault. The basin has a narrow opening to the south towards the Asem-Asem basin. The Barito Basin is an asymmetric basin, forming a foredeep in the eastern part and a platform approaching the Meratus Mountains towards the west (Fig. 2).

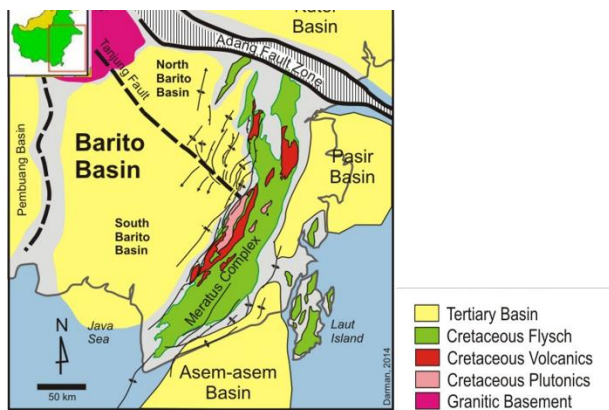


Figure 2. A geological summary map of Pasir Basin (Darman H., 2014)

The Pasir Basin commenced its development in the Late Cretaceous, following a micro-continental collision between the Paternoster and SW Borneo microcontinents. Early Tertiary extensional deformation occurred as a tectonic consequence of that

oblique convergence. In Liburdinding Coal Mine, the Late Cretaceous uplifted caused displacement of Haruyan Formation which contains of ultrabasic rocks which were then intruded by granite, granodiorite and diorite; a NE-SW horst-graben structural was developed and became accommodation space for lacustrine sediment of the Tanjung and Pamaluan Formations. The Pasir Basin is underlain by Jurassic Cretaceous ultrabasic rocks and the Jurassic Pitap Formation. These are overlain by the Tanjung, Berai, Pamaluan, and covered by Quaternary alluvium. Research indicates that coal is formed mainly in the Tanjung, Pamaluan Formations within the basins. A generalised stratigraphic column is shown in Figure 3.

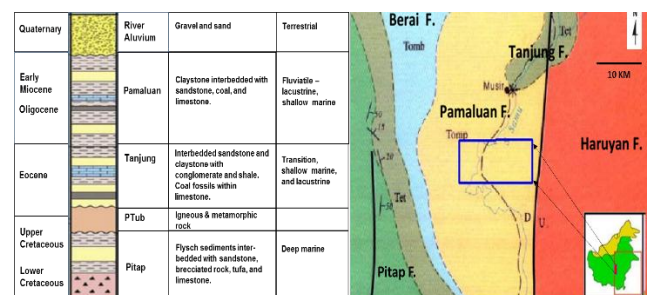


Figure 3. Geological Map and general stratigraphic column in Liburdinding and surrounding area.

The Pamaluan Formation consists of quartz sandstone intercalation with claystone, shale, limestone and siltstone, well bedded quartz Sandstone is the major constituent of rock, blackish grey to brownish, fine to medium grained, well sorted, sub-rounded to rounded, compact, carbonaceous or calcareous. Locally, contains cross bedded and parallel laminated. Thickness of layer between 1 -2 m. Claystone, thickness 45 cm in average. Shale, brownish grey to dark grey, compact, thickness of layers about 10 – 20 cm. Grey Limestone, massive, medium – coarse grained, locally bedded, contains of large foraminifera. Siltstone, blackish to dark grey is no blank line between sections and continue as shown.

Experimental

The coal samples has been examined in geochemistry 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 asphaltenes. 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 T₀ = 70°C, hold time I = 2 min, Rate I = 8°C/min, T_f I = 280°C, hold time II = 45 min, Rate II = 10°C/min, T_f II = 300°C, hold time III = 10 min.

The saturated and aromatics fractions were prepared in Mole Sieve Analysis for GCMS test on the next stage. The specific biomarkers were investigated from 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 T₀ = 120°C, hold time I = 2 min, Rate I = 5°C/min, T_f I = 200°C, hold time II = 0.5 min, Rate II = 5°C/min, T_f II = 300°C, hold time III = 30 min. 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.

Identification of individual compounds was accomplished based on retention time in the total ion current (TIC) chromatogram and comparison of the mass spectra with published data. All the biomarkers were identified from GC and GCMS instrument using GCMS Postrum Analysis with several libraries BENZODIAZEPINE, PESTEL_3, NIST 08, WILEY and R. P. Philp (1985). The peak areas from the gas chromatograms in relation to that of internal standards were used to calculate the relative percentages and absolute concentrations of different compound groups in the saturated and aromatic hydrocarbon fractions.

Results and discussion

Bulk Geochemistry Parameters

The normalized yields of the soluble organic matter (SOM) are listed in Table 1 together with the

relative proportions of saturated and aromatic hydrocarbons, NSO compounds and asphaltenes of the SOM.

Table 1. Bulk organic geochemical of EOM & n-alkane

No.	Sat.	Aro.	NSO	Asph.	CPI	Pr/Ph
PM-4	17	3	12	68	3.1	0.9
PM-8	12	7	14	76	3.6	1.2
PM-18	26	5	25	44	4.1	1.4
PM-21	15	9	20	56	5.9	1.7

From the Table 1; the EOM yield vary between 11.5 and 38.2 mg/g C_{org}. The average proportion of hydrocarbons (saturate and aromatic fractions) 23% (with min 19% and max 31%), it is supported that the coal were immature to early mature stage (0.46–0.55% Ro; with average Ro = 0.48%). The NSO and asphaltenes were dominated in the EOM (more than 50%).

n-Alkanes, isoprenoids

The n-alkane patterns are dominated by long-chain n-alkanes with a marked odd-over-even predominance and maximum intensities in the n-C₂₇ to n-C₃₁ range. The high values of the carbon preference index (CPI = 3.1 to 5.9, according to Bray and Evans, 19613) are consistent with the classification of the coals as subbituminous B (Tissot and Welte, 1984). The relative proportions of mid-chain (n-C_{21–25}) and long-chain (n-C_{27–31}) n-alkanes relative to the sum of n-alkanes show minor variations with depth and illustrate the predominance of n-alkanes of high molecular weight.

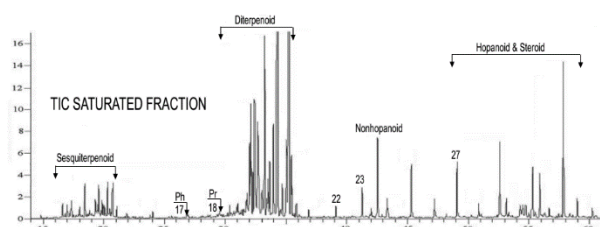


Figure 4. TIC chromatogram saturated fraction of Pamaluan coal sample

The dominance of long-chain lipids, indicated that the terrestrial plants were to be the main organic matter

source for coal (Eglinton and Hamilton, 1967). The n-alkanes of low molecular weight (<C₂₅) were small amount identified in coal samples (9% to 29% of the total n-alkane concentrations). This condition was explained that the algae and microorganism were predominantly as an OM source to coals (Cranwell, 1977). The mid-chain n-alkanes were dominantly in the lower seam comparing to the upper coal seam; indicated that the algae and microorganism were influence more bigger in the upper coal seams.

Mostly of the coals are pristane/phytane ratios (Pr/Ph) above 1.0 (Figure 4 which interpreted that coal was deposited under dysaerobic conditions.

Sesquiterpenoids, diterpenoids, nonhopanoid and triterpenoids

In the saturated fraction (Figure 4) of coal samples were identified the cadalane and drimane type in small amount. Also detected in the saturated hydrocarbons a pimarane, abietane, and C₁₉ to C₂₀ range phyllocladane-type diterpenoids. The tetra- and pentacyclic triterpenoids of the oleanane (olean-12-ene, olean-13(18)-ene), ursane (urs-12-ene) and lupine (des-A-lupane) type have been described.

The sesquiterpenoid type of cadalene (H) and retene was found significantly in aromatic fraction of coal samples (Figure 5). Abietene-type was also detected in this fraction. In addition, The monoaromatic pentacyclic triterpenoids identified as 24,25-dinoroleana-1,3,5(10),12-tetraene, 24,25-dinorursa-1,3,5(10),12-tetraene, and 24,25-dinorlupa-1,3,5(10)-triene have been identified.

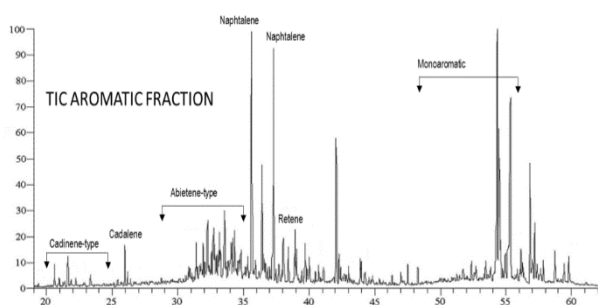


Figure 5. TIC chromatogram aromatic fraction of Pamaluan coal sample

Hopanoids

The hopanoids are abundant in the Pamaluan coals. The hopane composition in all samples which have identify on m/z 191 (Figure. 6) is characterized by the presence $\beta\beta$ - and $\alpha\beta$ -type hopanes from C₂₇ to C₃₁, with an exception of C₂₈ homologues. The C₃₀ 17(21)-hopane is the most abundant hopanoid in the saturated fraction of the coals samples. The abundance of hopanoids suggested that there were direct bacterial contribution of this compound (Ourisson, et al., 1979; Wakeham, 1990; Volkman, 1976).

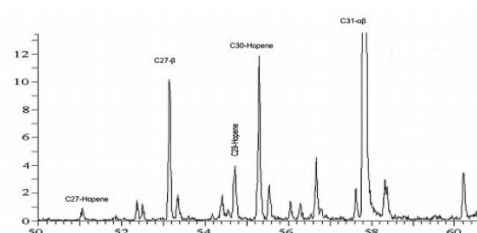


Figure 6. Mass fragmentogram of m/z 191 of coal sample from Pamaluan Formation

All samples contain unsaturated hop-17(21)-ene and hop-22(30)-ene. These compound were usually found in living organisms and has been found among diagenetic products in recent sediments. Under severe environmental condition, the hopanes diagenetic path evolution of hop-22(29)-ene (diploptene) can converted via hop-21(22)-ene and hop 17(21)-ene into neohop-13(18)-ene, and possibly into neohop-12(13)-ene. Therefore, presence of unsaturated hopenes with saturated hopanes in the coal, can be considered as precursors of saturated hopanes in coals, supported that microbial activity has been worked intensively in the lignite, an also confirming it's lower level of maturity or its less evolved diagenetic stage (Simoneit, 1986). Also, Brassell (1990) found that hop-22(29)-ene is a diagenetic product of from diplopterol. Diplopterol has been found in several eukaryotic phyta, such as ferns, mosses, lichens and fungi, but also in hopanoid producing bacteria. The C₃₁17 α (H) 21 β (H)-homohopane is moderately found in sample; it was suggested stronger reducing conditions and strong bacterial decomposition.



Conclusion

The depositional condition and origin of Pamaluan coal of Oligo – Miocene from the Pasir Basin, in Liburdinding Coal Mine site, have been evaluated using coal organic geochemistry.

The composition of the geochemical fossils were shown that the peat-forming vegetation dominated by gymnosperm plants, followed by prokaryotic organisms and angiosperms. The plant precursors of Pamaluan dominated from gymnosperm families *Podocarpaceae*, *Cupressaceae*, *Pinaceae* and *Taxodiaceae*

Based on higher pristane/phytane ratios of the Pamaluan coals, interpreted as indicating dysaerobic to aerobic conditions in this part of the mire.

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References

- Brassell, S.C., Comet, P.A., Eglinton, G., Isaacson, P.J., McEvoy, J., Maxwell, J.R., Thompson, I.D., Tibbetts, P.J.C., Volkman, J.K.. The origin and fate of lipids in the Japan Trench. In: Douglas, A.G., Maxwell, J.R. (Eds.), *Advances in Organic Geochemistry*. Pergamon Press, Oxford, 1989, pp. 375–392.
- Darman H., A geological summary map of Barito Basin and Meratus Complex, 2014
- de Leeuw J. W. and Baas M. (1986) Early-stage diagenesis of steroids. In *Biological Markers in the Sedimentary Record* (Edited by Johns R. B.), 1986, pp. 101-124. Elsevier, Amsterdam.
- Gagosian R. B., S. O., Smith and G. E., Nigrelli, Vertical transport of steroid alcohols and ketones measured in sediments trap experiments in the Equatorial Atlantic Ocean, *Geochim. Cosmochim. Acta*, 1982, 46, 1163-1172.
- K. E. Peters, C.C. Walters, J. M. Moldowan, *The Biomarker Guide, Vol. 2: Biomarkers and Isotopes in the Petroleum Exploration and Earth History*, Cambridge University Press, Cambridge, UK, 2005, p. 483–486, 499–500
- MacKenzie, A.S., Patience, R.L., Maxwell, J.R., Molecular changes and the maturation of sedimentary organic matter. In: Atkinson, G., Zuckermann, J.J. (Eds.), *Proc. 3rd Annu. Karcher Symp. Origin and Chemistry of Petroleum*. Pergamon, Oxford, 1981, pp. 1 – 31.
- Nishimura M., 5 β -isomers of stanols and stanones as potential markers of sedimentary organic quality and depositional paleoenvironments. *Geochim. Cosmochim. Acta* 1982, 46, 423-432.
- Ourisson, G., Albrecht, P., Rohmer, M., The hopanoids paleochemistry and paleobiochemistry of a group of natural products. *Pure Appl. Chem.* 1979, 51, 709–729
- R. P. Philp, *Fossil Fuel Biomarkers. Applications and Spectra*. Elsevier, Amsterdam, The Netherlands, 1985, pp. 12–33, 188, 259
- Simoneit, B.R.T., Grimalt, J.O., Wang, T.G., Cox, R.E., Hatcher, P.G., Nissenbaum, A., Cyclic terpenoids of contemporary resinous plant detritus and of fossil woods, amber and coal. *Org. Geochem.* 10, 1986, 877–889
- Tissot, B.T., Welte, D.H., *Petroleum Formation and Occurrences*, 2nd ed. Springer, Berlin. 1984, 699 pp.
- Volkman, J.K., Allen, D.I., Stevenson, P.L., Burton, H.R., 1986. Bacterial and algal hydrocarbons from a saline Antarctic lake. *Ace Lake. Org. Geochem.* 10,, 1986, 671–681.
- Wakeham, S.G., Algal and bacterial hydrocarbons in particulate material and interfacial sediment of the Cariaco-Trench. *Geochim. Cosmochim. Acta* 54, 1990, 1325–1336.