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Geochemical Characterizations of Crude Oils in Pendopo High and Limau Graben, South Sumatra Basin

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Abstract **–** There are several oil fields in Pendopo High and Limau Graben, South Palembang Subbasin, South Sumatra Basin. Crude oils from the Pendopo High and Limau Graben have been analyzed using geochemical methods. Some or all of the following analyses were completed on twenty-four oils. Two analysis methods, namely the $\delta^{13}C$ isotopic and biomarker compositions have been used to classify the oil types. Most of the oils are isotopically more depleted in $\delta^{13}C_{sat}$ (> -28‰) relative to the other four oil sample counterpart of the Pendopo High. All oil samples from The Pendopo High have Pr/Ph values < 4 and those from the Limau Graben > 4. In addition, biomarker ratio for hopanes/steranes from the Limau Graben shows small values compared with the Pendopo High. Geochemical cross plots of probabilities can also be used to distinguish oils derived from different source inputs. In the Limau Graben, tricyclic terpane data shows terrestrial patterns, while the Pendopo High shows deltaic patterns. The Limau Graben is derived from humic kerogen, while the Pendopo High is more towards mixed kerogen (humic and sapropelic kerogen). The depositional condition in the Limau Graben is anoxic to suboxic to oxic and mostly oxic condition, predominated by higher plants. While Pendopo High condition is anoxic to suboxic, predominated by algae. Oil in the Pendopo High is interpreted to be deltaic oil, whereas oil in the Limau Graben is a typical fluvial.

Keywords: biomarker, deltaic oil, fluvial, South Sumatra Basin

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Introduction

Various geochemical methods have been applied to oil samples in attempts to provide information on the sources and geological conditions, including stable isotopes, gas chromatography, and gas chromatography-mass spectrometry (Robinson, 1987; Suseno *et al.,* 1992; ten Haven and Schiefelbein, 1995; Rashid *et al.,*1998; Bishop, 2001; Peters *et al.,* 2005; Syaifudin *et al.,* 2015; and Syaifudin, 2016). In addition, the literature contains various interpretations as to how isotopic compositions of oils can be related to the organic matter and depositional environments of their source rocks. For example, stable isotope compositions of crude oils and their saturate and aromatic hydrocarbon fractions have been used by petroleum geochemists to provide information on the depositional environment of the source rocks generating the oils, and the relationships among oils (Peters *et al.,* 2005 and references therein). Biomarker composition can occur in different carbon ranges of crude oils (Peters *et al.,* 2005). In general, conventional biomarker compositions are characterized by sterane and triterpane families. Crude oil study, which utilizes the detailed geochemical analysis of a representative suite of samples, is an excellent way of identifying and comparing the samples that are sourced from the rock to a location of a relatively close area (Doust and Noble, 2008). Hence, their signatures are an invaluable tool for exploration because of their predictive capabilities.

Nederlandsche Koloniale Petroleum Maatschappij discovered Talang Akar field located in Pendopo High, South Sumatra Basin, Indonesia, in 1921 for producing the first oil from this area. The field was the biggest find in the country before World War-II. There are several oil fields have been discovered and most of them remain produce some oil to date. Geochemical study on oils from the Limau Graben and Pendopo High has been done by Suseno *et al.,* 1992. They found that the oils are characterized as fluvio-deltaic oil family, and were generated under some similarities in terms of geological phenomena (Bishop, 2001). This study was done to confirm that there are differences between crude oil samples in the Limau Graben and Pendopo High. The crude oil samples contained in the Limau Graben seem to have been deposited relatively more towards an oxidation condition (Pr/Ph > 4) as well as have higher marker than those in the Pendopo High (Tables 1 and 2). In the Limau Graben, tricyclic terpane data shows terrestrial patterns (C_{19} and C_{20} tricyclic terpanes are relatively abundant), while those in the Pendopo High indicate delta patterns (C_{19}, C_{20}, and C_{23} tricyclic terpanes are abundant) (Tables 3 and 4).

This paper focuses to discuss the successfully combined use of isotopic and biomarker indicators to distinguish and to separate the Pendopo High and Limau Graben crude oils based on their closed geographic locations. Although this preliminary work is based on a limited sample suite, the useful results justify an expanded study using more oils and analytical parameters.

The studied area is located in the Pendopo High area and Limau Graben, South Palembang Subbasin, South Sumatra Basin (Figure 1).

Methods and Materials

The analytical methods used in this study were capillary gas chromatography (GC); a standard gravitational column chromatography for hydrocarbon fractionation and saturate GC-MS for biomarker determination.

The whole oil sample was previously analyzed using a fast GC to find alkanes distribution. Fingerprinting analysis of the whole oil was carried out by using an Agilent 6890 N GC instrument coupled to a flame ionization detector (FID). The GC was fitted with a 10 m x 0.21mm i.d. DB-1 (J and W) fused-silica capillary column. Samples were injected using an Agilent 7673 auto sampler, with split/splitless mode injector.

For GC-MS analysis, the oil samples were separated into saturated hydrocarbon, aromatic hydrocarbon, and nonhydrocarbon fraction (polar compounds) by a preparative column chromatography. Isolation of branched and cyclic fraction from saturated hydrocarbons was carried out using a packed activated silicalite chromatographic column. Then the branched and cyclic fractions were introduced to a GC-MS instrument.

GC-MS analyses of saturate fraction were performed using an Agilent 6890 Gas Chromatograph (GC) coupled to an Agilent 5973 series Mass Selective Detector (MSD) - computer data system (Chemstation). The GC was fitted with a 60 m x 0.25 mm i.d. DB- 5MS (J and W) fused-silica capillary column. Samples were injected using an Agilent 7673 auto sampler, with split/splitless mode injector. The MS condition was ionization mode: electron impact (EI), EM voltage was 1980 Volt; electron energy was 70 eV and source temperature 250°C.

Examination of fingerprint signatures for all samples were based on pristane, phytane of the whole oil chromatograms and triterpanes (m/z 191), and steranes (m/z 217) of saturated fractions.

Table 1. Biomarker Data of Oils in the Pendopo High

Wells in Pendopo High	$\delta^{13}C$ sats	$\delta^{13}C$ aroms	Ph/nC_{18}	Pr/nC_{17}	Pr/Ph	Tot Hop/Tot Ster
Pandawa-1	-27,36	-26,63	0,23	0,68	3,10	92,90
Pandawa-1	-29,50	-27,33	0,19	0,57	3,26	0
Pandawa-1	-29,11	-27,12	0,20	0,56	3,06	19,36
Pandawa-2	-26,40	-26,20	0,21	0,72	3,28	12,75
Pandawa-3	-28,70	-27,70	0,32	0,89	2,84	9,82
Pandawa-4	-27,10	-27,20	0,31	1,08	3,74	7,29
Pandawa-5	0	0	0,34	1,09	3,38	7,56
Pandawa-6	-27,90	-27,60	0,26	1,32	3,95	9,46

Table 2. Biomarker Data of Oils in the Limau Graben

No	Well in Limau Graben	$\delta^{13}C$ sats	$\delta^{13}C$ aroms	Ph/nC_{18}	Pr/nC_{17}	Pr/Ph	Tot Hop/Tot Ster
9	Orange-1	-28,7	-27,20	0,65	2,89	4,02	3,88
10	Orange-2	-29,50	-27,20	0,75	7,31	10,56	3,94
11	Orange-3	0	0	0,41	1,81	5,22	4,31
12	Orange-4	-29,80	-27,80	0,15	1,04	7,75	2,84
13	Orange-4	-29,30	-28,10	0,13	1,12	9,33	3,30
14	Orange-4	-29,70	-28,00	0,14	1,17	7,58	3,03
15	Orange-5	-28,30	-27,00	0,60	4,94	14,76	33,3
16	Orange-5	-29,10	-27,70	0,23	2,07	11,44	9,10
17	Orange-6	-29,00	-27,30	0,48	6,73	4,21	3,78
18	Orange-6	-29,90	-28,30	0,21	2,30	4,05	4,29
19	Orange-7	-29,40	-29,90	0,34	1,76	4,96	2,84
20	Orange-8	-29,10	-27,40	0,48	1,55	4,01	3,58
21	Orange-9	-28,90	-27,10	0,31	1,87	6,50	2,33
22	Orange-10	-29,30	-27,30	0,38	1,33	7,90	5,90
23	Orange-11	0	0	0,62	4,83	6,50	2,33
24	Orange-12	0	0	0,31	2,24	7,90	5,90

Table 3. Tricyclic Terpane Data of Oils in the Pendopo High

Wells	Norm% Tricyclics Terpane						
	B	C	D	E	F	G	H
	C19	C20	C21	C22	C23	C24	C25
Pandawa-2	18	16	21	0	22	16	7
Pandawa-3	20	161	17	0	20	18	10
Pandawa-4	18	15	17	3	18	18	12
Pandawa-5	18	15	16	0	19	19	12
Pandawa-6	19	15	14	5	17	17	14

Table 4. Tricyclic Terpane Data of Oils in the Limau Graben

Wells	Norm% Tricyclics Terpane						
	B	C	D	E	F	G	H
	C19	C20	C21	C22	C23	C24	C25
Pandawa-2	18	16	21	0	22	16	7
Pandawa-3	20	161	17	0	20	18	10
Pandawa-4	18	15	17	3	18	18	12
Pandawa-5	18	15	16	0	19	19	12
Pandawa-6	19	15	14	5	17	17	14

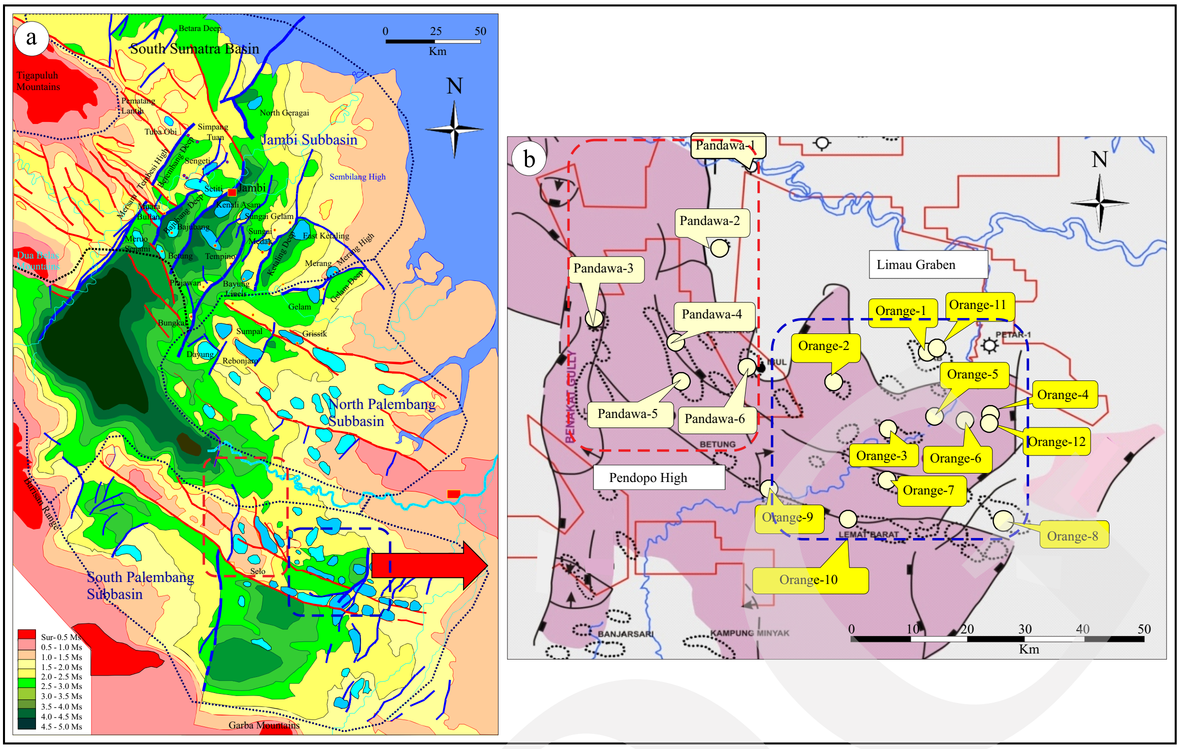

Figure 1. Location maps of (a) South Sumatra Basin and (b) studied area.

In this study, the oil analysed consist of twenty samples of carbon isotopes and twenty-four samples of biomarkers. Characterization has been based on qualitative and quantitative data. Qualitative data comprised evaluations which were based on chromatograms and mass-fragmentograms. Whereas the quantitative data consists of a series of cross plots, *eg*. Cross plot of carbon isotope $\delta^{13}C$ saturates-aromatics, distribution of C_{27}-C_{28}-C_{29} sterane, Pr/nC_{17}-Ph/nC_{18}, Pr/Ph-Pr/nC_{17}, carbon isotope $\delta^{13}C$ saturates-Pr/Ph, Pr/Ph-total hopane/total sterane, and ratio of C_{26}/C_{25} (tricyclic).

Regional Structural Geology

Geological structures that control the regional South Sumatra were influenced by three tectonic phases (Pulunggono *et al.*, 1992):

- Compression (Upper Jurassic - Lower Cretaceous)
- Tension (Upper Cretaceous - Lower Tertiary)
- Compression (Middle Miocene - Recent) .

The first phase: Started in Upper Jurassic - Lower Cretaceous, characterized by the subduction of India-Australia Plate as a movement mechanism to yield primary stress to the Sundaland trending N 30° W. This subduction resulted simple shear (N 300° E) as a strike-slip fault that was actively moved laterally. This was assumed as the cause of linearity trending N-S as an antithetic fault which was inactive.

The second phase: Commenced during Upper Cretaceous-Lower Tertiary, characterized by the change of subduction trend of the India-Australia Plate into N-S. This event resulted in the formation of some geological structures (fractures) caused by a tension force as a linearity with N-S direction. This phenomenon caused the formation of grabens and depressions, such as Benakat Gulley. Initiation of graben filling with Tertiary sediments was started.

The third phase: Commenced in the Middle Miocene-present, shown with, again, the change of the subduction direction into N 6° E, causing rejuvenation and inversion processes on the paleostructures by Plio-Pleistocene (N 330° E) and the uplifting of Barisan Montains and also the formation of some thrust faults with Lematang Fault pattern.

Regional Stratigraphy

Based on the tectonostratigraphy framework, Ryacudu (2008) divides Early Tertiary rock units in South Sumatra Basin as follows (Figure 2):

- Pre-rift sequences

This sequence consists of volcanic rocks of Kikim Formation and pre-Tertiary rocks. Kikim Formation are the oldest Tertiary rocks in South Sumatra Basin, consisting of volcanic rocks such as volcanic breccia, agglomerate, andesitic tuffs, and igneous rocks (as intrusions and lava flows). The age of Kikim Formation based on dating K-Ar is 54-30 Ma (Paleocene-Early Oligocene, Ryacudu, 2008).

- Syn-rift sequences

Syn-rift sequence consists of Lahat Group comprising Lemat and Benakat Formations with interfingering relationship (Ryacudu, 2008). The main constituent of Lemat Formation is coarse clastic rocks (sandstone) with Tuff and Conglomerate Members, while Benakat Formation is dominated by fine clastic rocks (shale). The Lemat Formation deposited in a fluvial environment. However, in the Pendopo High, Lemat Formation is likely to have a fluvio-deltaic environment. Shale of Benakat Formations interpreted as lake (lacustrine) sediments.

- Post-rift sequences

Tanjungbaru Formation, originally considered as a GRM (Gritsand Member) formerly known as a member of Talangakar Formation. This unit is dominated by conglomeratic sandstone deposition system as the result of a braided river. Notwithstanding, in Pendopo High, Lower Talangakar Formation (GRM) is likely to have fluvio-deltaic environment. This member of Talangakar Formation commonly referred as a TRM (Transition Member) is proposed as Talangakar Formation. This formation consists of alternating sandstones and shales, with thin coal interbedded, deposited in a transition environment, *i.e.* a delta system to a shallow marine of Early Miocene. Baturaja Formation, Early Miocene (N5-N6) in age, composed of bioclastic limestone, calcarenite, bioclastic sandy limestones, and reefal bioherm with interbedded of calcareous shale, was deposited on the a carbonate platform. Upwards, Early Miocene to Middle Miocene Gumai Formation, is composed of calcareous mudstone containing fossil planktonic *Globigerina* and shales with

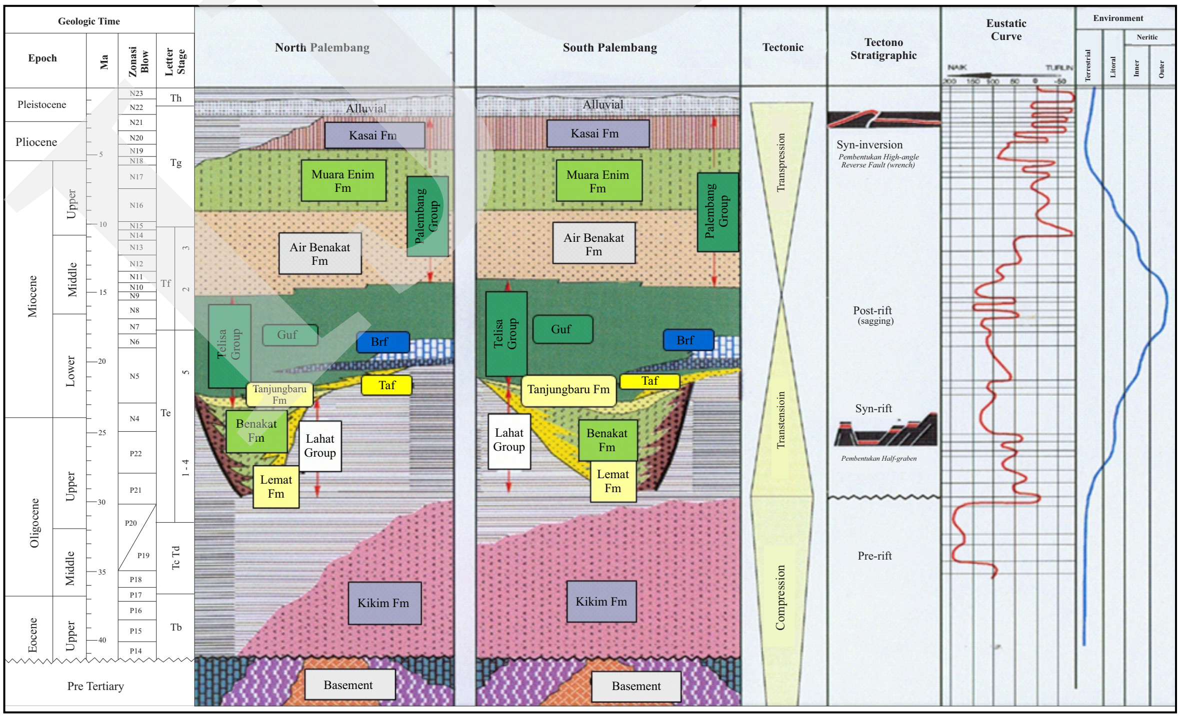

Figure 2. Regional stratigraphy of South Sumatra Basin (modified from Ryacudu, 2008).

glauconitic quartz sandstones. Deposited conformity on top of the Gumai Formation is Palembang Group, comprising of Air Benakat, Muara Enim, and Kasai Formations. Furthermore, the marine condition was getting shallow and then the overlying Kasai Formation was deposited in a terrestrial environment.

Results and Discussoin

Characterization of Oils in the Pendopo High and Limau Graben Areas

A qualitative comparison of biomarker characterizations between crude oil samples in the Pendopo High and Limau Graben is presented in Figure 3.

Based on data of H_{29} and H_{30} (hopane) distribution, the pattern of H_{29} <H_{30} indicates clastic sediments, while H_{29}>H_{30} is evaporates-carbonate sediment (Zumberge, 1984; Connan *et al.,* 1986; Price *et al.,* 1987; Waples and Machihara, 1991; Peters and Moldowan, 1993; Peters *et al.,* 2005; Hakimi *et al.,* 2011; Grosjean *et al.,* 2012; Xiangchun *et al.* 2013; ten Haven *et al.,* 1988 vide Rabbani *et al.,* 2014; Syaifudin *et al.,* 2015; Wang *et al.,* 2015; and Syaifudin, 2016). The crude oil samples from Pendopo High and Limau Graben are clastic sediments since it shows as pattern of 29_H<30_H.

From data of homohopane distribution which decreased regularly from C_{31} to C_{35}, the crude oil samples from Pendopo High and Limau Graben are interpreted as depositional environment which associated with clastic sediments (Waples and Machihara, 1991) or more oxidizing conditions (Peters and Moldowan, 1993; Hakimi *et al.,* 2011).

A terrestrial environment is characterized by high C_{19} and C_{20} tricyclic terpane (Philp and Gilbert, 1986; Peters and Moldowan, 1993; Hanson *et al.,* 2000; Grice *et al.,* 2001; George *et al.,* 2004; Volk *et al.,* 2005; Zhang and Huang 2005; Peters *et al.,* 2005; George *et al.,* 2007; Hao *et al.,* 2011; Asif *et al.,* 2011; Adedosu *et al.,* 2012; Alberdi *et al.,* 2001 vide Rabbani *et al.,* 2014; Tao *et al.,* 2015; Wang *et al.,*, 2015). Crude oil samples from the Limau Graben show C_{19} and C_{20} tricyclic terpanes are more abundant (Figure

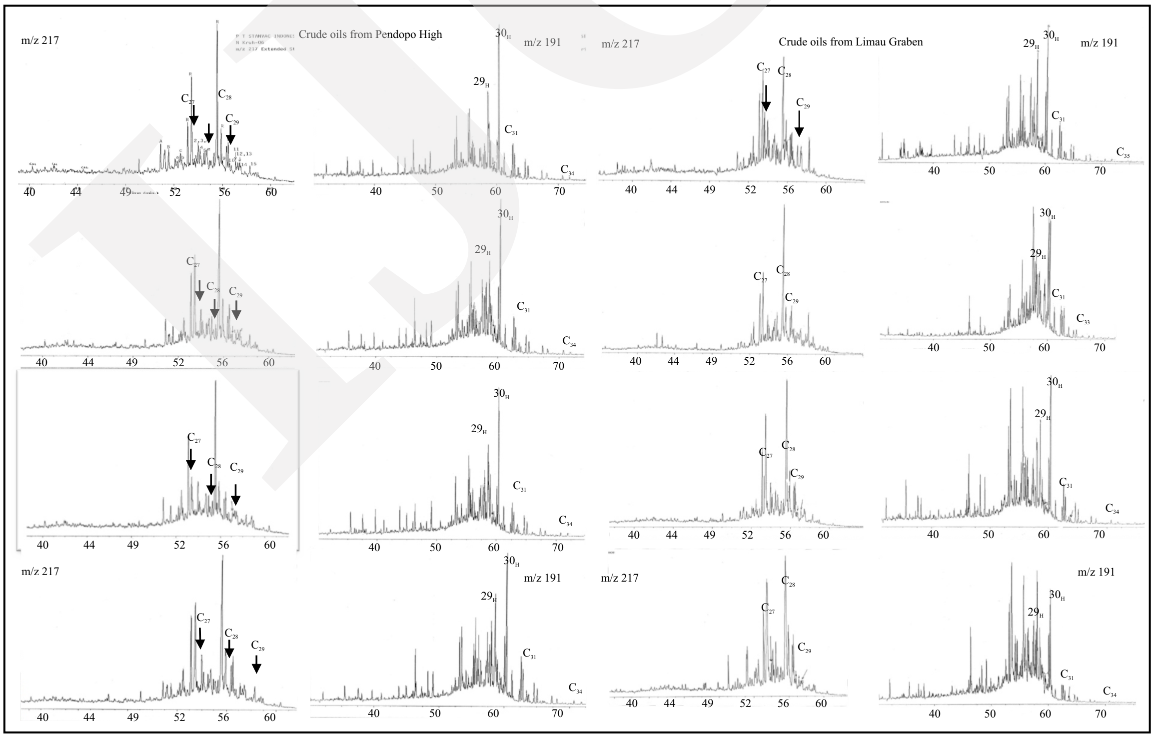

Figure 3. Comparison of biomarker characterization qualitatively between crude oils in the Pendopo High (left) and Limau Graben (right).

4). C_{23} tricyclic terpane is often predominant in crude oils of a marine source (Aquino Neto *et al.*, 1983; Zumberge, 1987; Burwood *et al.*, 1992; Peters and Moldowan, 1993; Hanson *et al.*, 2000; Zhang and Huang, 2005; Hakimi *et al.*, 2011; Tao *et al.*, 2015). Crude oil samples in the Pendopo High besides show predominant C_{19} and C_{20} tricyclic terpanes, they also contain relatively high concentration of C_{23} tricyclic terpane.

Based on these data, crude oil in the Limau Graben is interpreted to be originated from terrestrial source rocks, and the crude oil samples from the Pendopo High are interpreted to be derived from deltaic source rocks (Figure 4).

Quantitative Characterization

Pristane/phytane (Pr/Ph) ratios have been used to assess the redox potential of the depositional environment and the source of organic matter (Didyk *et al.*, 1978; Tissot and Welte, 1984; Zhang and Huang, 2005; Peters *et al.* 2005; Duan *et al.*, 2008; Hao *et al.*, 2011; Hakimi *et al.*, 2011; Adedosu *et al.* 2012; Cheng *et al.*, 2013; and Tao *et al.*, 2015) or reflect the relationship between contributing organisms and the chemistry of the environment (Mello and Maxwell, 1990).

The cross plot of Pr/Ph - Pr/nC_{17}, as proposed by Robinson (1991) (Figure 5a), shows that crude oil samples from Pendopo High fall into an anoxic

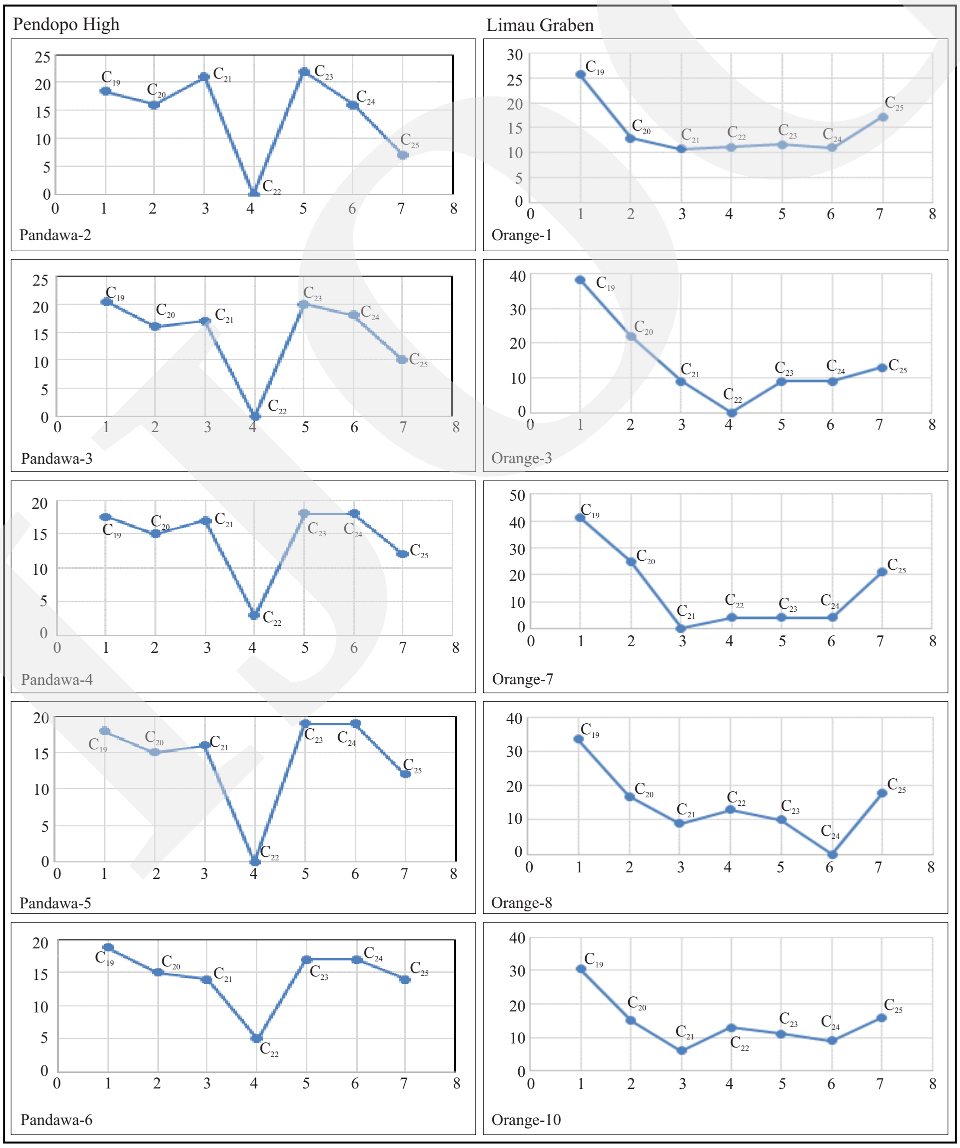

Figure 4. Comparison of tricyclic terpanes between crude oils in the Pendopo High (left) and the Limau Graben (right).

to suboxic category and was dominated by algae. While crude oil samples from Limau Graben fall into anoxic to oxic, mostly oxic, predominated by higher plants. The crude oil samples contained in the Limau Graben seem to have been deposited relatively more towards an oxidation condition (Pr/Ph > 4) as well as to have the higher marker than the crude oil samples in the Pendopo High.

The cross plot Pr/nC_{17} - Ph/nC_{18} (see Figure 5b) as proposed by Connan and Cassou (1980), shows that crude oil samples from Pendopo High and Limau Graben derived from humic kerogen, but in the Pendopo High they are more towards mixed kerogen (humic and sapropelic kerogen) (Sabra, 2021). The cross plot of carbon isotope $\delta^{13}C$ saturates - aromatics as proposed by Sofer (1984), shows that crude oil samples from Pendopo High (Figure 6a) are mostly derived from alga, and the saturate fraction are heavier than crude oil samples from Limau Graben.

The cross plot of carbon isotope $\delta^{13}C$ saturates - Pr/Ph, as proposed by Bishop (2001) (Figure 6b), shows that crude oil samples from Limau Graben are more oxic than crude oil samples from Pendopo High.

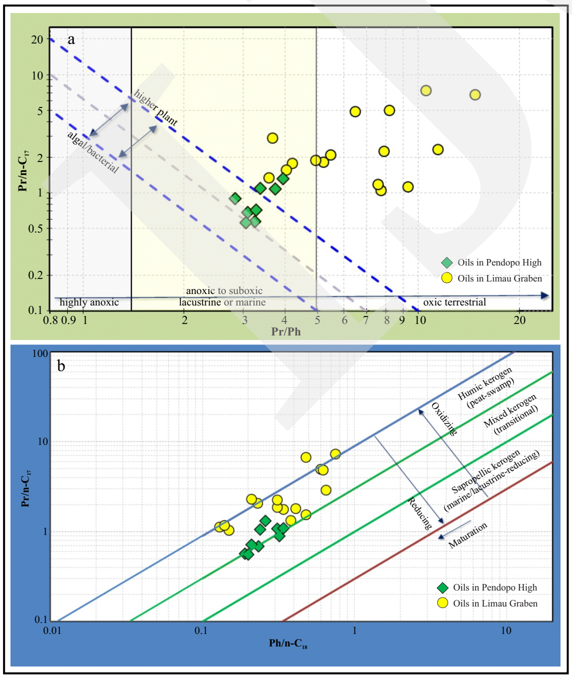

Figure 5. Cross plot of Pr/Ph - Pr/nC_{17} (a), Pr/nC_{17} - Ph/nC_{18} (b). Crude oils in the Pendopo High and Limau Graben.

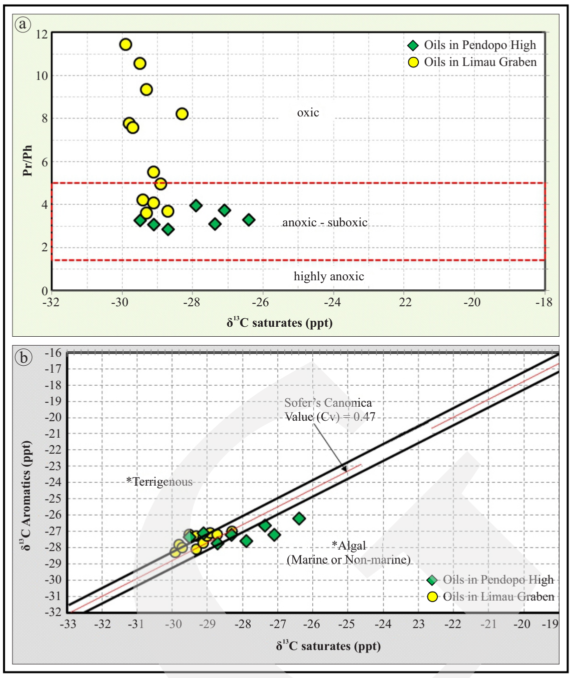

Figure 6. Cross plot of (a) carbon isotope $\delta^{13}C$ saturates - aromatics and (b) carbon isotope $\delta^{13}C$ saturates - Pr/Ph, crude oils in the Pendopo High and Limau Graben.

The cross plot of Pr/Ph - total hopane/sterane crude oils in the Pendopo High and Limau Graben as proposed by Robinson (1991) (Figure 7), shows that crude oil samples from Pendopo High fit to an anoxic to suboxic terrestrial influence, while crude oil samples from Limau Graben mostly fall into a highly oxidizing terrestrial.

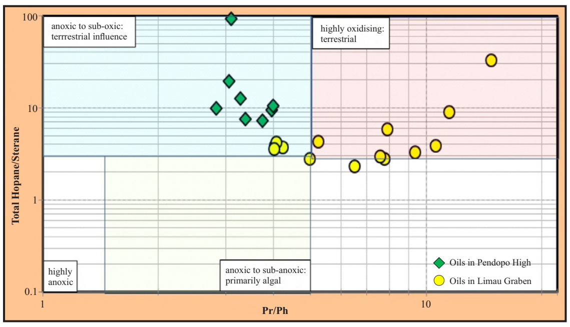

Figure 7. Cross plot of Pr/Ph - total hopane/sterane, crude oils in the Pendopo High, and Limau Graben.

The isopach map of Lemat and Lower Talangakar Formations (Figure 8) as source rocks, and the possibility of oil migration pathways prior Plio-Pleistocene, while the Top structure map of Talangakar Formation, and the possibility of oil

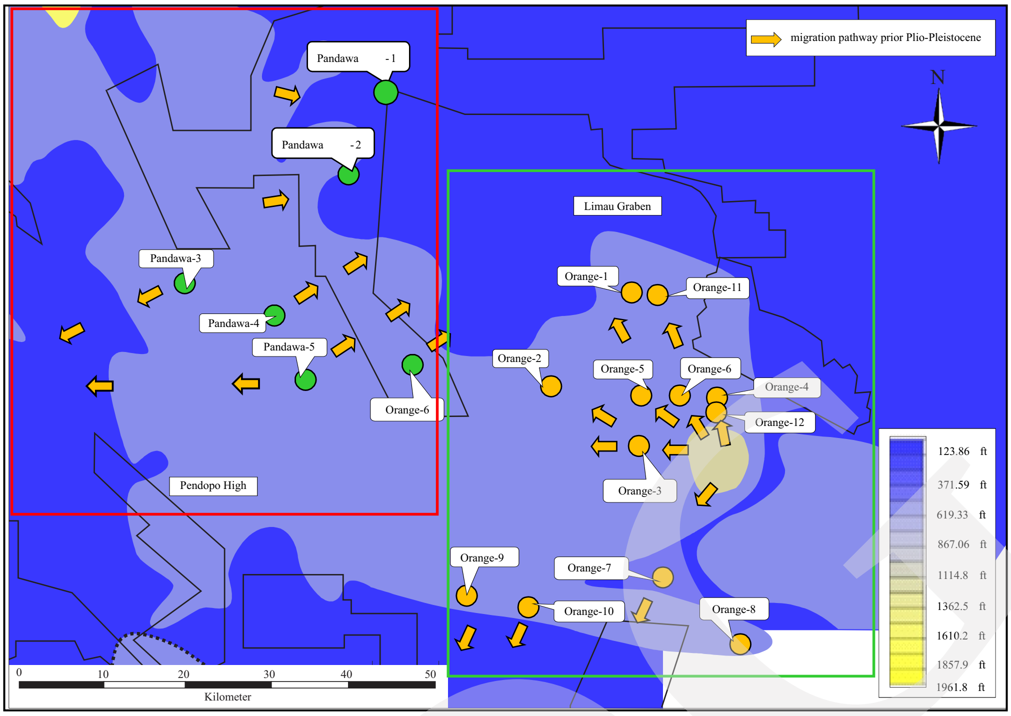

Figure 8. Isopach map of the Lemat and Lower TAF as source rocks,and the possibility of oil migration pathways prior Plio-Pleistocenee.

migration pathways after Plio-Pleistocene are exhibited in Figure 9.

Based on these data, crude oil samples from the Pendopo High are interpreted to be a deltaic oil

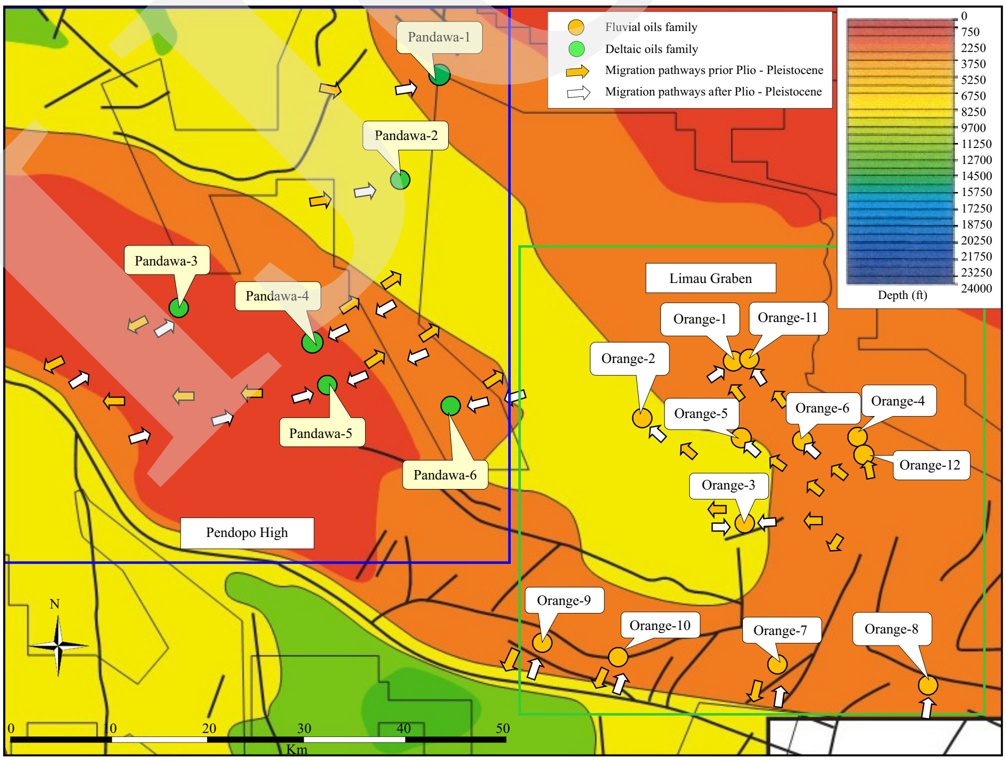

Figure 9. Top structure map of the Talangakar Formation, and the possibility of oil migration pathways after Plio-Pleistocenee.

family, whereas crude oil samples from the Limau Graben are categorized as the fluvial oil family.

Conclusions

Based on tricyclic terpane data, the crude oil samples from Pendopo High are interpreted to be derived from a deltaic environment, while those from Limau Graben are deciphered derived from a fluvial environment.

The crude oil samples from Limau Graben seem to have been deposited relatively more towards an oxidation condition (Pr/Ph > 4) as well as have higher plant marker than the crude oil samples from Pendopo High.

Crude oil samples from Limau Graben and Pendopo High have been derived from a humic kerogen, however those found in the Pendopo High indicate more towards mixed kerogen (humic and sapropelic kerogen).

The $\delta^{13}C$ saturate fraction from crude oil samples from Pendopo High is heavier than crude oil samples from Limau Graben ($\delta^{13}C$ saturate fraction Pendopo High -26.4 to -29.5, while in Limau Graben -28.3 to -29.8.

In general, crude oil samples from the Pendopo High are interpreted to be deltaic oil family, whereas crude oil samples from Limau Graben are typical a fluvial oil family.

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