APPLICATION OF OLEANANE AND STERANE INDEX FOR BIOSTRATIGRAPHIC AGE DETERMINATION: EXAMPLES FROM KANGEAN OILS, NORTHEAST JAVA BASIN

APLIKASI INDEKS OLEANANE DAN STERANE SEBAGAI PENENTU UMUR BIOSTRATIGRAFI: BERDASARKAN SAMPLE MINYAK KANGEAN, CEKUNGAN JAWA TIMUR UTARA

Himawan Sutanto[1] and **Junita Trivianty Musu**[1]
"LEMIGAS" R&D Centre for Oil and Gas Technology
Jl. Ciledug Raya, Kav. 109, Cipulir, Kebayoran Lama, P.O. Box 1089/JKT, Jakarta Selatan 12230 INDONESIA
Tromol Pos: 6022/KBYB-Jakarta 12120, Telephone: 62-21-7394422, Facsimile: 62-21-7246150
Email: himawan@lemigas.esdm.go.id; junita@lemigas.esdm.go.id

First Registered on April 8th 2014; Received after Corection on April 25th 2014
Publication Approval on: April 30th 2014

ABSTRAK

Cekungan Jawa Timur Utara diketahui sebagai cekungan mature berumur Kenozoikum. Pengertian ini mengesampingkan kemungkinan cekungan ini berumur lebih tua dari Kenozoikum yang menyebabkan strategi eksplorasi saat ini hanya tertuju kepada sedimen berumur Kenozoikum. Batuan sumber pada cekungan ini juga dipercaya berasal dari sedimen berumur Kenozoikum, terutama Formasi Ngimbang, yang terbentuk antara Eosen Akhir hingga Oligosen Awal pada awal terbentuknya syn-rift. Di sisi lain, kemunculan Alisporites sp di daerah ini menunjukkan batuan sumber potensial berasal dari sedimen berumur Kapur. Namun, hal ini masih menjadi perdebatan dengan kehadiran Alisporites similis di Cekungan Serawak, Malaysia yang kemunculannya hingga Paleosen. Tiga sampel minyak mentah yang berasal dari Lapangan Kangean, Cekungan Jawa Timur Utara yaitu NEJB-748, NEJB-749 dan NEJB-750 diteliti dengan menggunakan kromatografi gas (GC) dan kromatografi gas/spektrometer masa (GC/MS). Sampel minyak mentah yang berasal dari Lapangan Kangean ini diklasifikasikan sebagai campuran minyak dengan material organik yang berasal dari laut dan darat yang diendapkan pada kondisi oksidasi dan reduksi. Minyak ini mempunyai indeks Oleanane dan Sterane rendah yang mengarah kepada kesimpulan bahwa minyak ini berasal dari batuan sumber berumur Kapur.

Kata kunci: Cekungan Jawa Timur Utara, Formasi Ngimbang, Kapur, batuan sumber, lingkungan pengendapan, indeks Oleanane dan Sterane, penentuan umur.

ABSTRACT

Northeast Java Basin is known as mature Cenozoic basin, yet this understanding override possibility of sediment older than Cenozoic. This thoughthas brought current exploration strategy of this basin concerning within only Cenozoic sediments. Therefore, it is believed that the source rock in this basin was also derived from Cenozoic sediments, especially the Ngimbang Formation, which was formed during Late Eocene to Early Oligocene in the stage of Early Synrift. On the other hand, the occurrence of Alisporites sp has pointed Cretaceous sediments is a potential source rock. However, it is still debatable due to the presence of Alisporites similis in Serawak Basin of Malaysia, which is present until Paleocene. Three crude oils from the Kangean oil fieldNortheast Java Basin, namely NEJB-748, NEJB-749 and NEJB-750have been investigated using gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS).Kangean oils are classified as mixed oil with organic matter originated from marine and terrestrial deposited under oxidizing and reducing conditions. Moreover, Kangean oils show very low oleanane and steraneindexthat may lead us to the conclusion that the oils were originated from Cretaceous source rock.

Keywords: *Northeast Java Basin, Cretaceous, Ngimbang Formation, source rocks, depositional environment, Oleanane and Sterane Index, age determination*

I. INTRODUCTION

Northeast Java Basin, where Kangean as the study area is a part of it, is a mature Tertiary Basin for most of researchers, and it is classified as a mature Cenozoic Basin (Figure 1). These thoughts have over ridden possibility of the presence of sediments older than Paleogene, which lead to the current exploration strategy of the basin which concern Cenozoic sediments only. Therefore, the source rocks of the basin was also believed derived from Paleogene sediment, especially the Ngimbang Formation which was formed during Late Eocene to Early Oligocene in stage of Early Synrift (Doust & Noble 2008; Satyana & Purwaningsih 2003).

For those who believed in no Pre-Paleogene sediments, had classified this section into Pre-Ngimbang Formation without a definite age determination (Satyana & Purwaningsih 2003). However, few researchers who believed in the presence of older than Cenozoic sediment, classified this section into Mesozoic with Cretaceous age determination based on the presence of *AlisporitesSp* and seismic stratigraphic interpretation (Dinkelman et al. 2008; Ichimaru et al. 2009; Figure 2). The idea about Mesozoic sediments in Northeast Java Basin is also supported bythe tectonic evolution in this region done by Sribudiyani et al. 2003 (Figure3).

The aim of this study is to determine the evidence of the presence of Cretaceous or older source rock at Northeast Java Basin from hydrocarbon. The result of the study is important in order to have better understanding for exploration strategy in the near future.The study applies petroleum geochemistry with GC and GC/MS using biomarkers data to evaluate the possibility of Cretaceous source rock within the basin.

Several terminology used in this study are explained to ease the readers in understanding the paper. They include biomarkers, gas chromatography (GC) finger print, *triterpanes* and *steranes*. Biological markers or biomarkers are molecular fossils originated from living organisms, and these complex compounds are composed of carbon, hydrogen and other elements. Biomarkers occur in sediments, rocks and crude oils and show little or no change in structure from their parent organic molecules in

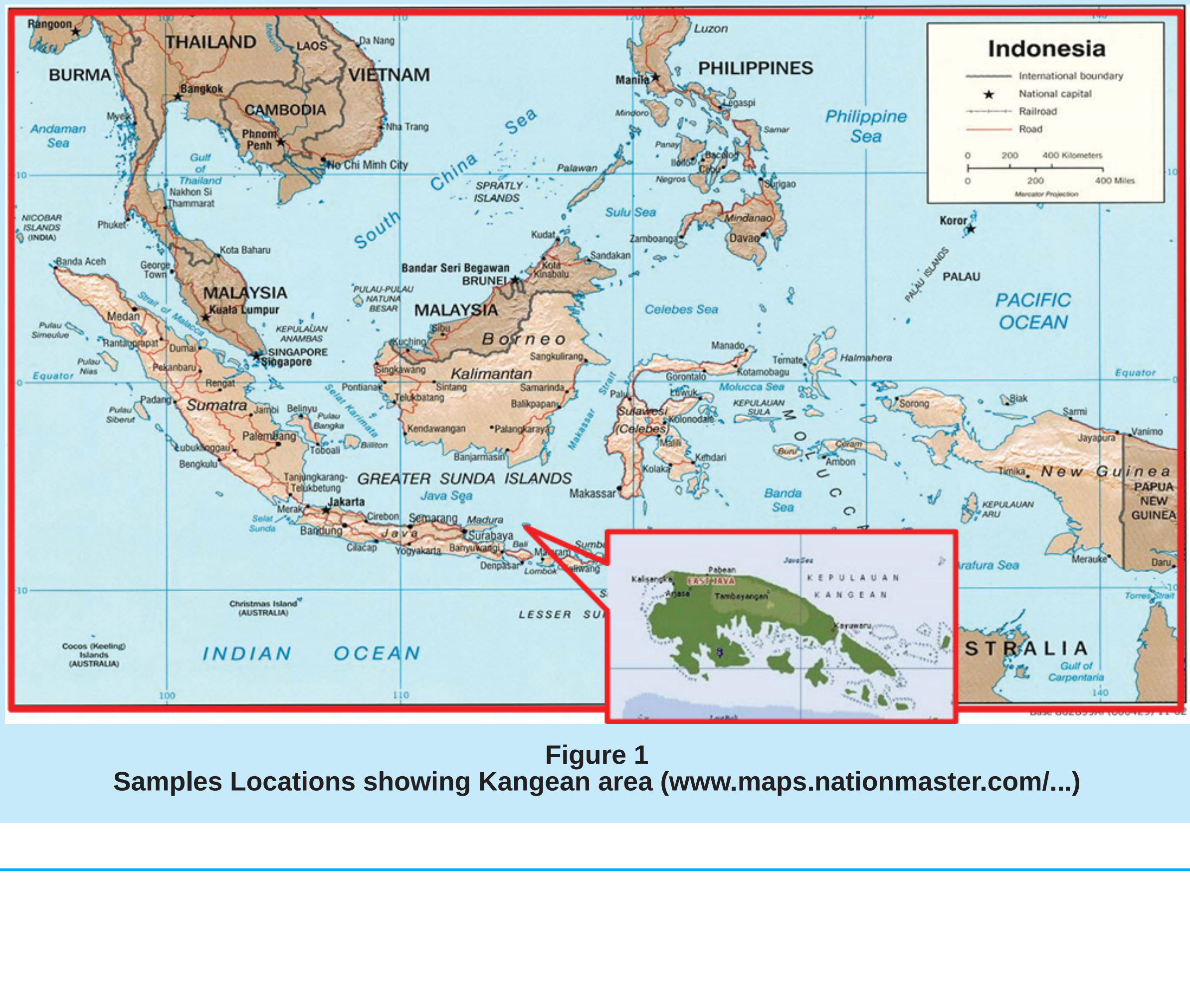


Figure 1
Samples Locations showing Kangean area (www.maps.nationmaster.com/...)

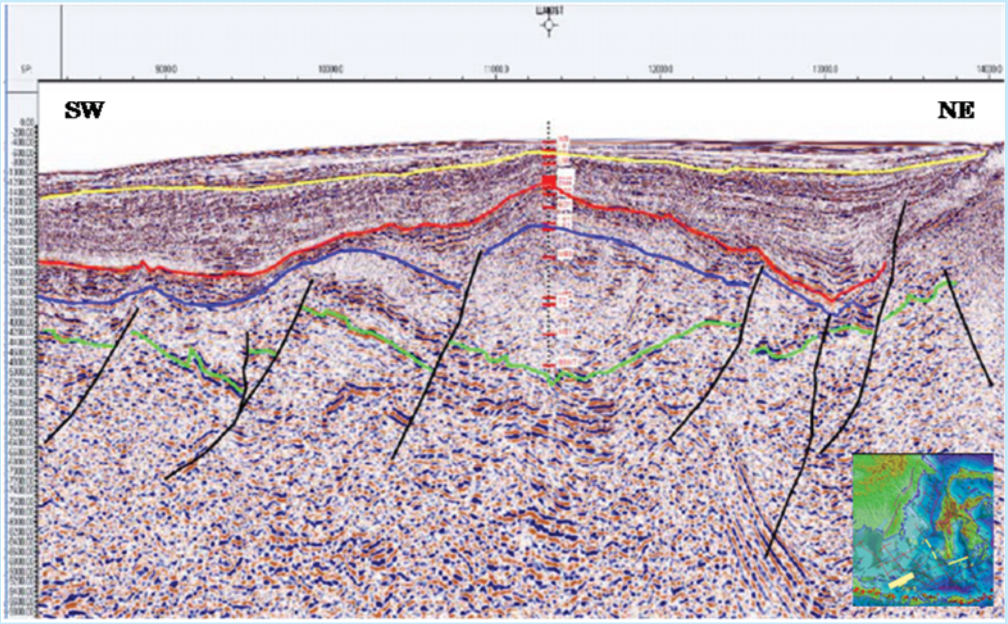


Figure 2
Image of seismic cross section from L-40-1 with total vertic section is 9800 m. Yellow colored reflector is a Lower Pliocene surface, and the green is top cretaceous (Dinkleman et al. 2008)

living organisms. Biomarkers are useful due to their complex structures that reveal more information about their origins than other compounds. Biomarkers used in this study include *triterpanes* and *steranes*. Many *terpanes* in petroleum originated from bacteria (*prokaryotic*) membrane lipids. These bacterial *terpanes* include several homologous series, including *aciclyc*, *bicyclic, tetracyclic*, and *pentacyclic* compounds. *Pentacyclictriterpenoids*, including precursor of *hopane*, occur in *prokaryotes* and higher plants but appear to absent in *eukaryotic* algae (Peters et al. 2005). *Streanes* are a class of 4-cyclic compounds derived from steroids or sterols via diagenetic and catagenetic degradation and saturation. The *sterane* structure constitutes the core of all *sterols*. *Steranes* are sometimes used as biomarkers for the presence of *eukaryotic* cells. *Steranes* may be rearranged to *diasteranes* during diagenesis (C-27 to C-30, rearrangement at C-18 and C-19, no R at C-24). Oils from clastic source rocks tend to be rich in *diasteranes*.

Gas chromatography fingerprint can indicate certain types of source organic matter input. Bimodal *n*-alkane distributions, and those skewed toward the range nC_{23}-nC_{31}, are usually associated with terrigenous higher-plant waxes. The C_{27}, C_{29}, and C_{31} *n*-alkanes in crude oils and source-rock extract mainly from higher-plant epicuticular waxes. Alga contributions to source rocks and oils are commonly indicated by abundant shorter-chain n-alkanes, particularly nC_{17}. Bitumens and oil related to carbonate source rocks commonly show even carbon-number *n*-alkane predominance, an odd predominance in n-alkanes common in many lacustrine and marine oils derived from shale source rocks (Peters et al. 2005). Moreover, hydrocarbon derived from a deltaic source rock typically has predominance of medium weight n-alkanes (Napitupulu et al. 1997).

II. METHODOLOGY

The study uses three (3) crude oils from Kangean oil, Northeast Java Basin, taken from Eocene Ngimbang Carbonate Formation with top reservoir at of approximately 4200 feet depth. The samples are NEJB-748, NEJB-749 and NEJB-750. All samples were determined using GC and GC/ MS and sent to laboratory for preparation and analysis. GC analyses of diluted hydrocarbons(50 mg of samples were diluted with hexane) were performed on GC series with DB-1 (J&W) fused-silica capillary column (10 m x 0.21 mm i.d) using split less injection. Each sample was injected using an auto sampler. 150 mg of

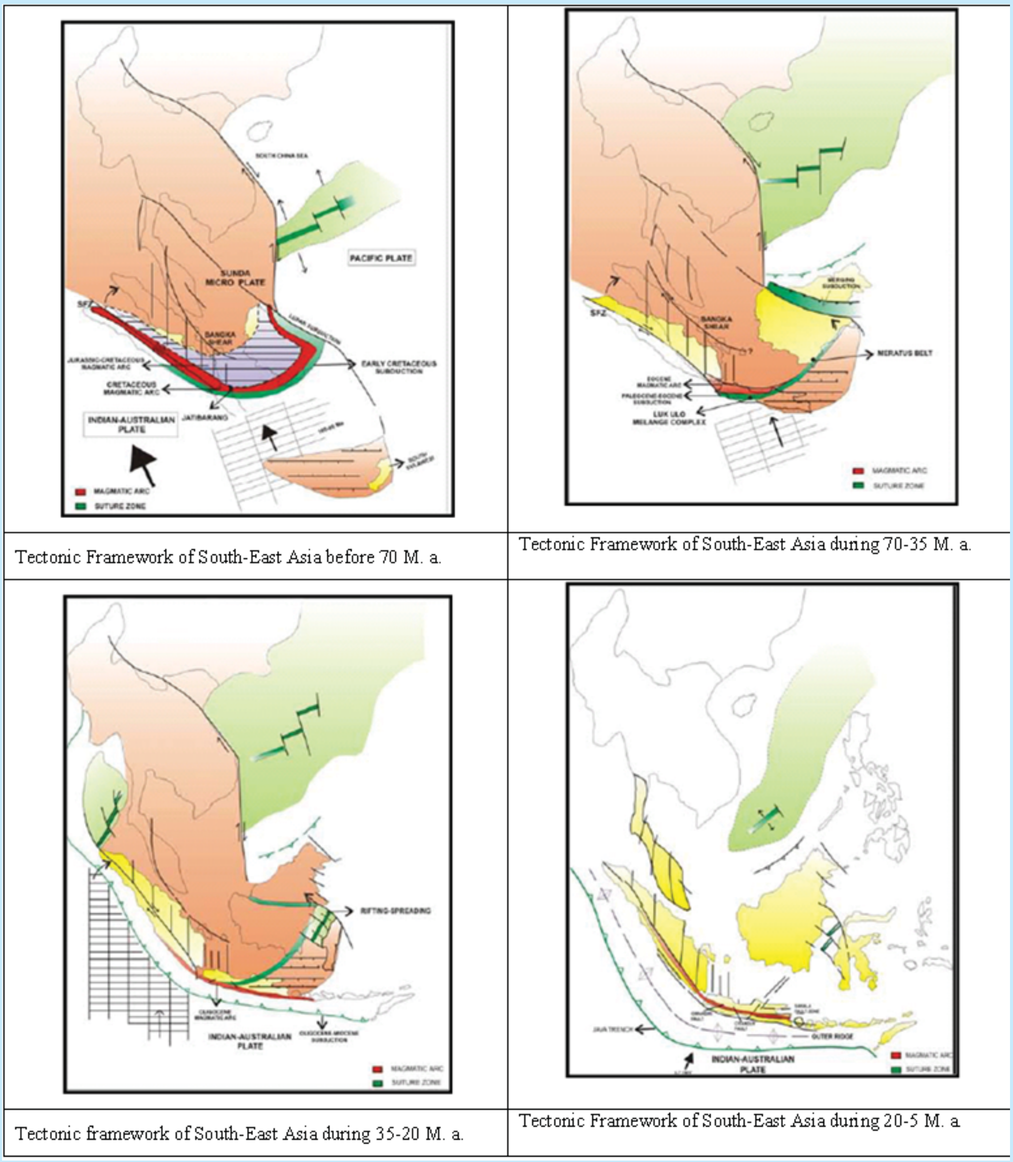


Figure 3
Tectonic evolution of western Indonesia (Sribudiyani et al. 2003)

each sample was diluted to be extracted using column chromatograph with diameter of column (Ø) is 1 cm. 3 cm of alumina and 7 cm of silica gel were added inside the column to separate saturate and aromatic fractions, extraction of saturate fraction using 16 ml of hexane, while aromatic using 16 ml of hexane and dichloromethane (DCM) with ratio 3:1. 1 μl of each saturate and aromatic fractions analyzed to GC/MS mass selective detector (MSD) – computer data system. The GC was fitted with a 60m x 0.25mm inner diameter (i.d) DB-5MS (J&W) fused-silica capillary column. Samples were injected using an auto sampler, with split/splitless mode injector. The MS condition is ionized mode (electron impact - EI, EM voltage was 1980 Volt; electron energy was 70 eV and source temperature 250°C).

III. RESULTS AND DISCUSSION

A. n-Alkanedistribution determination

As suggested by Peters et al. (2005) oils with odd-numbered n-alkane predominance in the gas chromatogram (Figure 4) are common in many lacustrine and marine oils derived from shaly source rock. Moreover, oil with bimodal distribution of n-alkane indicated terrestrial organic matter origin influenced. As seen in Figure 4, Kangean oils show bimodal distribution, which are then interpreted to be terrestrial oil. However, from their Pristane and Phytane ratio (Pr/Ph), ranging from 1.5 to 2.5 andPr/ *n*-C_{17}, ranging from 0.1 to 0.3, and also supported by cross plot of Pr/*n*-C_{17} versus Pr/*n*-C_{18}, as in Figure 5, Kangean oils are believed originated as mixed oil.

B. Triterpane determination

Many *terpanes* in petroleum including *triterpanes*, *oleananes* and *hopanes* originated from bacteria (*prokaryotic*) membrane lipids. *Triterpanes* used

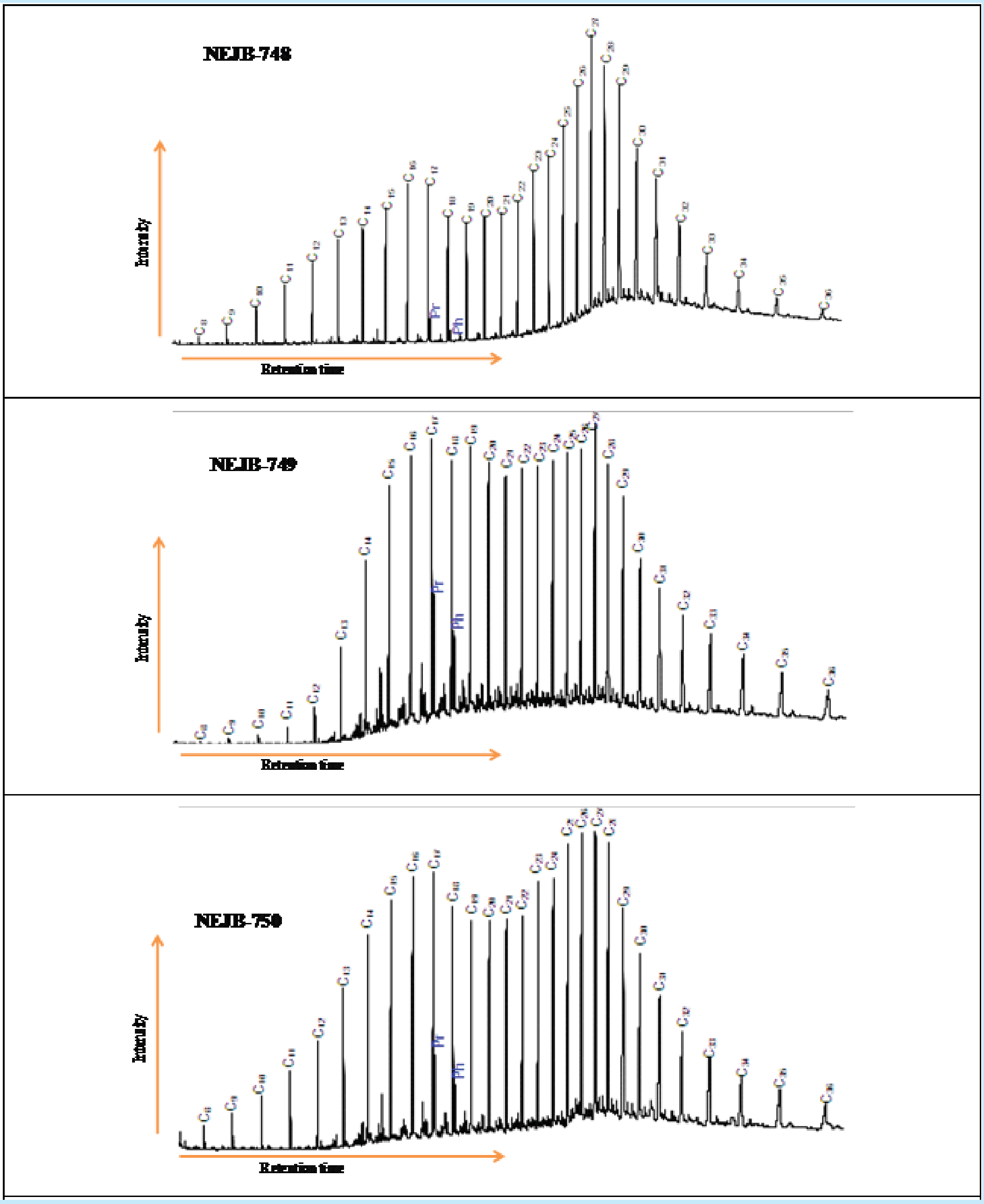


Figure 4
C_{7+} Whole oil chromatogram of Kangean oils

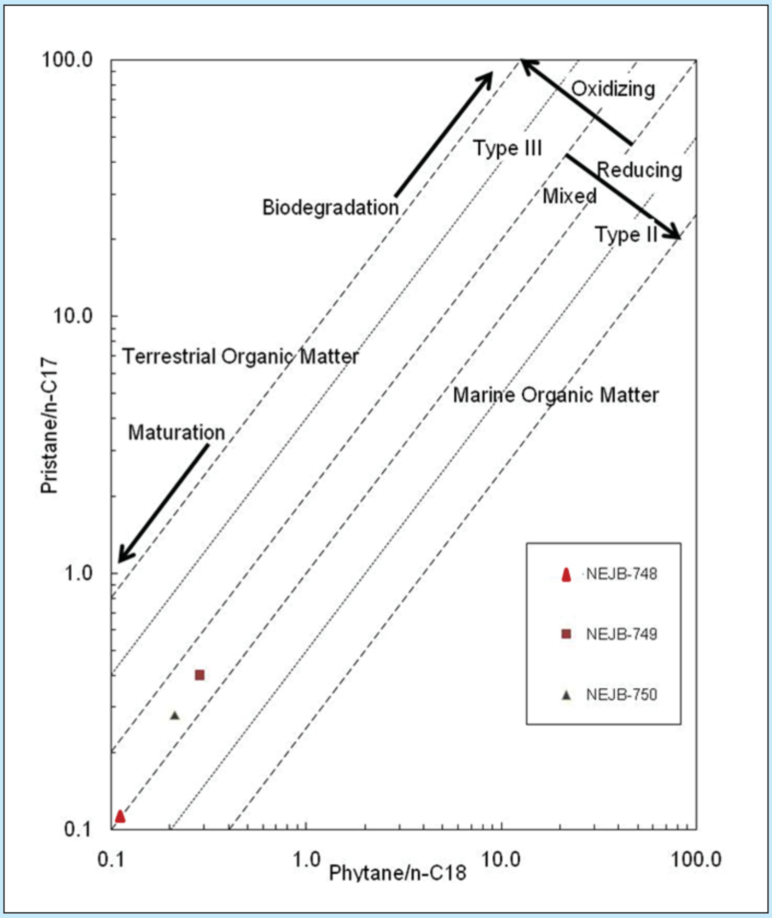


Figure 5
Cross Plot Pr/n-C_{17} versus Ph/$n$$C_{18}$ of Kangean oils

in this study are biomarkers with fragment ion *m/z* 191. Most crude oils show C_{29}/C_{30} *hopane m/z* 191 peak ratios less than 1 for hydrocarbon originated from shales (deltaic or terrestrial depositional environments) especially with high terrestrial organic matter input, howevehe ratio will be higher than 1, if the crude oils were originated from carbonates. Most researchers used *triterpanes* as a biomarker to determine source of organic matter and depositional environment (Peters et al. 2005). Other *terpanes* such as *oleanane* and *hopane* are also used in the study. *Oleanane* index (*Oleanane/*C_{30}*hopane*) is used to determine biostratigraphic age of hydrocarbon or sediments. *Oleanane* index more than 20% are diagnostic of Tertiary or younger source rock and related oils (Moldowan et al. 1994). Kangean oils show very low abundance of *oleanane* (Figure 6) with *oleanane* index less than 20% (Tabel 1).

Table 1
Oleanane index of angean oils

Samples		%ol(ol+hopane)
NEJB-748	Kangean oils	9.5
NEJB-749		12
NEJB-750		9.2

Table 2
Sterane index of angean oils

Samples		Sterane index (C28/C29 sterane)
NEJB748	Kangean oils	0.5
NEJB749		0.7
NEJB750		0.6

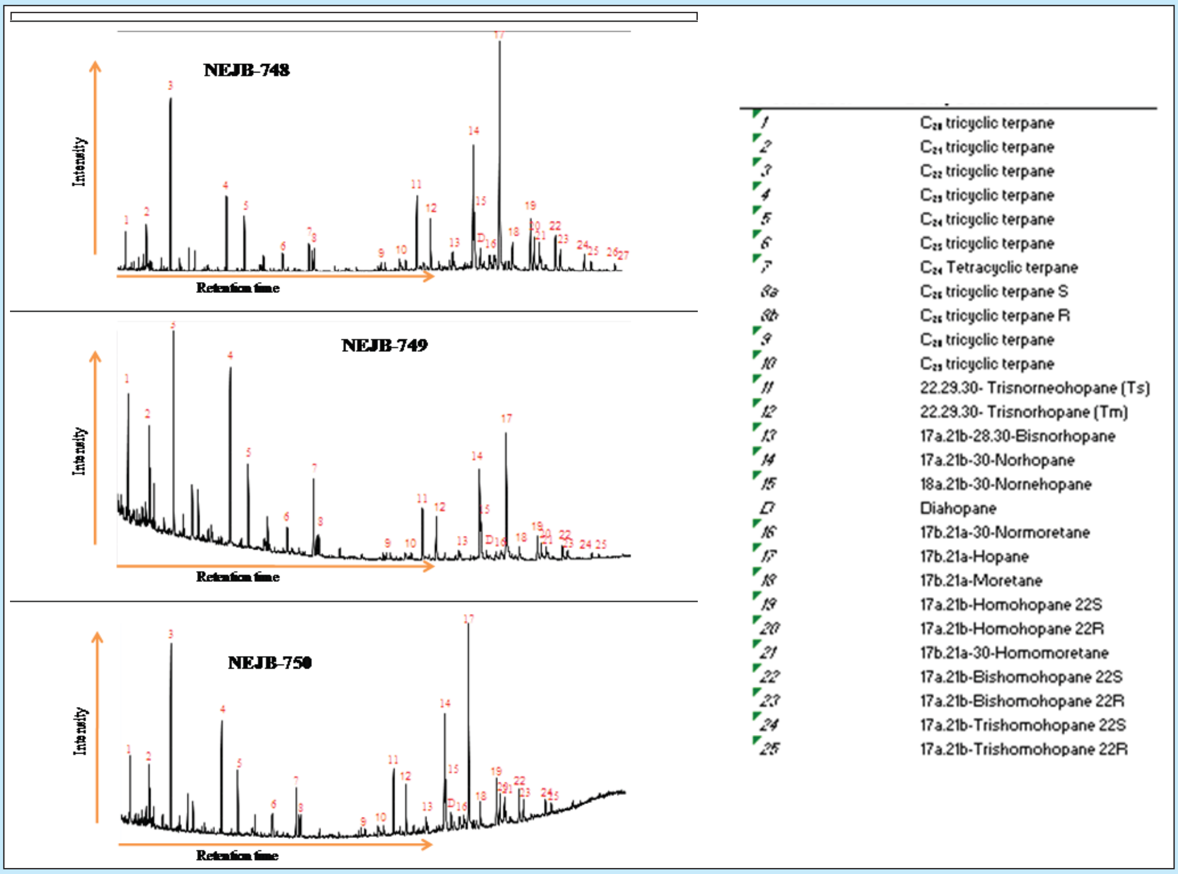


Figure 6
m/z 191 fragmentograms of Kangean oils showing fery low abundance of oleanane

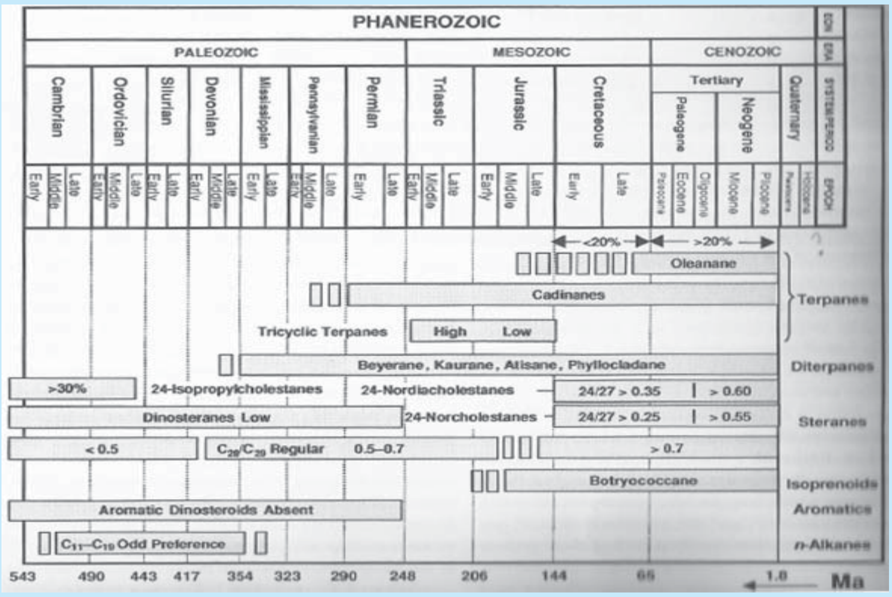
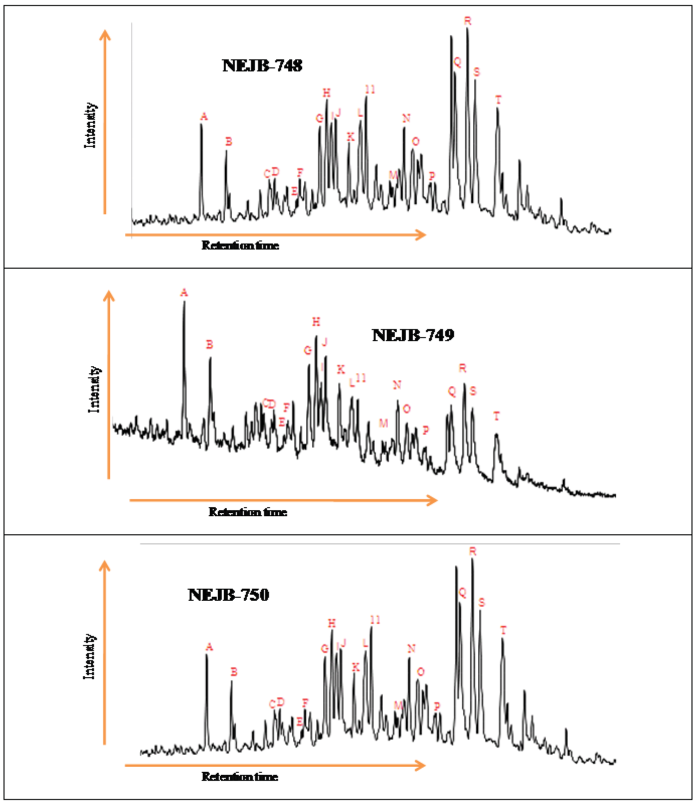


Figure 7
Age-related biomarkers help to infer the source rocks for crude oils (Peters and Moldowan, 2005)



Peak Label	Compound Name
A	13β,17α-Diacholestane 20S
B	13β,17α-Diacholestane 20R
C	24-Methyl-13β,17α-Diacholestane 20S
D	24-Methyl-13β,17α-Diacholestane 20R
E	24-Methyl-13α,17β-Diacholestane 20S
F	24-Methyl-13α,17β-Diacholestane 20R
G	5α,14α,17α-Cholestane 20S
H	5α,14β,17β-Cholestane 20R
I	24-Ethyl-13α,17β-Diacholestane 20S
J	5α,14β,17β-Cholestane 20S
K	5α,14α,17α-Cholestane 20R
L	24-Ethyl-13α,17β-Diacholestane 20R
11	22,29,30- Trisnorneohopane (Ts)
M	24-Methyl-5α,14α,17α-Cholestane 20S
N	24-Methyl-5α,14β,17β-Cholestane 20R
O	24-Methyl-5α,14β,17β-Cholestane 20S
P	24-Methyl-5α,14α,17α-Cholestane 20R
Q	24-Ethyl-5α,14α,17α-Cholestane 20S
R	24-Ethyl-5α,14β,17β-Cholestane 20R
S	24-Ethyl-5α,14β,17β-Cholestane 20S
T	24-Ethyl-5α,14α,17α-Cholestane 20R

Figure 8
m/z 217 fragmentograms of Kangean oils

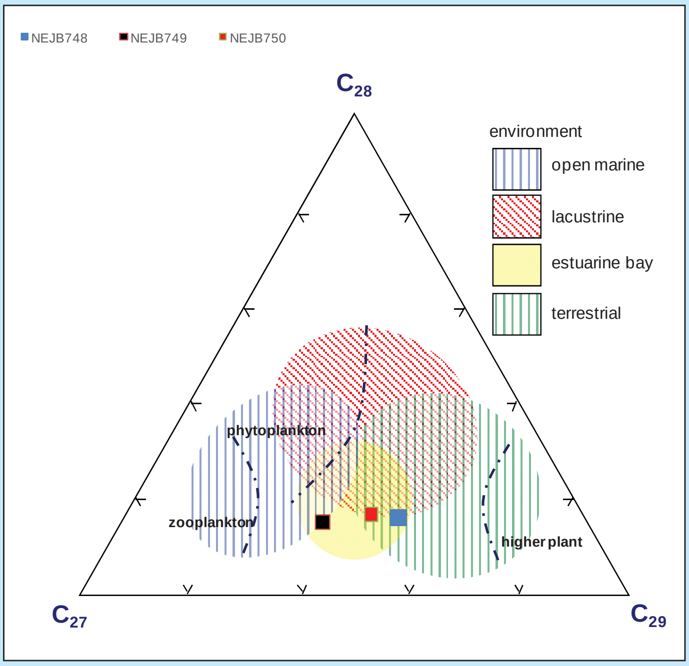


Figure 9
Sterane composition (Moldowan et al. 1985)

C. Sterane

Like *triterpanes*, most researchers use *steranes* with fragment ion *m/z* 217 for determining source of organic matter and depositional environment for hydrocarbon and sediments especially related to marine condition. Furthermore C_{28}/C_{29}*sterane* can also be used for biostratigraphic age determination for crude oils from marine source rock with little or no terrigenous organic matter input. The ratio of *sterane* index (Figure 7) less than 0.5 shows of lower Paleozoic and older oils, 0.47 – 0.7 for Upper Paleozoic to Lower Jurrasic oil, and greater than 0.7 for Upper Jurrasic to Miocene oil (Grantham & Wakefield, 1988). GCMS reveals that Kangean oils are originated from marine to terrestrial environment (Figure 8), as a result of their *sterane* composition (Figure 9) with *sterane* index ranging from 0.5 to 0.7 (Tabel 2).

Kangean oils show n-alkane bimodal distribution which is inconsistence with the ratios of Pr/Ph,Pr/*n*-C_{17},and the cross plot of Pr/*n*-C_{17} versus Pr/*n*-C_{18} results. The bimodal distribution of n-alkane shows that the Kangean oil is terrestrial originated,whereas the ratio of Pr/Ph,Pr/*n*-C_{17},and cross plot of Pr/*n*-C_{17} versus Pr/*n*-C_{18}revealed that the origin of Kangean oils are believed to have originated from marine and terrestrial organic matter. Due to this inconsistency results in determining depositional environment with these methods, therefore to have accuracy in age determination this study uses both oleanane and sterane index. This thought is in accordance with Moldowan et al. (1994), they provided that oleanane is a marker for flowering plant, which is only suite for terrestrial origin, whereas sterane is relatedto marine origin.

IV. CONCLUSIONS

Based on the above analyses, Kangean oils are then classified as mixed oil with organic matter originated from marine and terrestrial deposited under oxidizing and reducing conditions in shale source rock as a result of several point in *n*-alkane distributions. Application of oleanane and sterane index lead to oils originated from Cretaceous source rock. However, profound research about age determination biomarker should be carried out to give better result and understanding of basin and tectonic evolution in Northeast Java Basin as a breakthrough for the exploration concept. More additional samples are required to analyses for better understanding and undisputed conclusion.

This study is limited by the used of *triterpanes* and *steranes* only, which cannot give accurate depositional environment determination. The cross plot shows all samples lie on the mixture areas between marine and terrestrial environment. Deterium isotopes is recommended to be applied in the future study to assure the exact depositional environment.

ACKNOWLEDGMENT

We would like to express our sincere gratitude to: Ministry of Energy and Mineral Resources, Directorate General of Oil and Gas, PPPTMGB"LEMIGAS", Republic of Indonesia and Kangean Energy Indonesia Ltd. with their samples and regulation support to our research.

REFERENCES

Dinkelman, M. G., Granath, J. W., Emmet, P. A., & **Bird, D. E.,** 2008, Deep Crustal Structure of East Java Sea Back – Arc Region from Long – Cable 2D Seismic Reflection Data Integrated with Potential Field Data, *Proceed. Indonesian Petroleum Assoc., 32nd Ann. Conv.*

Doust, H. & **Noble, A. R.**, 2008, Petroleum System of Indonesia, *Marine and Petroleum Geology* 25, 103 – 129.

Grantham, P. J. & **Wakefield, L. L.,** 1988, Variations in the sterane carbon number distributions of marine source rock derived crude oils trough geological time, *Organic Geochemistry*, 12, 61 -73.

Hall, R., Late Jurrassic-Cenozoic reconstructions of Indonesian region and the Indian Ocean , *Tectonophysics* 570-571, 1-41.

Ichimaru, Y., Nishita, H., Honda, T., & **Sutanto, H.,** 2010, The Dynamic of Hydrocarbon Migration and Accumulation around Kangean Island, East Java, Indonesia, *The Annual Meeting of Japanese Assoc. for Petroleum Technology, 2010 (in Japanese).*

Moldowan, J. M., Dahl, J., & **Huizinga, B. J., et al.** 1994, The molecular fossil record of oleanane and its relation to angiosperms, Science, 265, 768 – 71.

Moldowan, J. M., Seifert, W. K., & **Gallegos, E. J.,** 1985, Relationship between petroleum composition and depositional environment of petroleum source rocks, *American Association of Petroleum Geologist Bulletin*, 69, 1255 – 68.

Napitupulu, H., Mitterer, M. R., & **Morelos-Garcia, A., J.,** 1997, Differentiation of Oils from the NW

Java Basin into Three Oil Type Based on Biomarker Composition, *Proceedings of an International Conference on Petroleum System of SE Asia and Australia*, 667-679.

Peters, E. K., Walters, C. C., Moldowan, M. J., 2005, The Biomarker Guide, Volume 2, 499- 617.

Satyana, A. H. & **Purwaningsih, M. E. M.**, 2003, Geochemistry of the East Java Basin: New Observations on Oil Grouping, Genetic Gas Type and Trends of Hydrocarbon Habitats, *Proceed. Indonesian Petroleum Assoc., 29th Ann. Conv.*

Sribudiyani, Muchsin, N., Ryacudu, R., Kunto, T., Astono, P., Prasetya, I., Sapiie, B., Harsolumakso, H. A., & **Yulianto, I.,** 2003, The Collision of The East Java Microplate and its Implication for Hydrocarbon Occurrences in The East Java Basin, *Proceed. Indonesian Petroleum Assoc.29th Ann. Conv*.

Susanto H., 2012, Cretaceous Source Rocks in Kangean Oil Fields, Indonesia, as Suggested by Biomarkers in Oils, unpublished thesis Hokkaido University, 1-40.

Map of Indonesia, 2012, www.maps.nationmaster,com/...,