Compositional Heterogeneity of Hopanoid in Crude Oil: A case study of selected wells from Eric Field, Niger Delta Nigeria

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ABSTRACT- **This research aims at evaluating compositional heterogeneity of biomarkers in crude oils from Eric Field by means of biomarker parameters and ratios. Four oil samples were obtained from Eric Field Off-shore Niger Delta Nigeria. The oils were studied by means of gas chromatography mass spectrometry (GC-MS) to obtain information on origin, occurrence, environment of deposition and thermal maturity. The thermal maturity parameter calculated from GC/GC-MS analysis ranges from Ts/Ts+Tm (0.42-0.17), $C_{31}22S/C_{31}22S+22R$ (0.51-0.53), $C_{31}/C_{32}-C_{34}$ and $C_{30}Ol/C_{30}Ol+C_{30}H$ (0.16-0.590). Biomarker parameters and ratios calculated shows that the studied oil is from clay-rich organic matter input, deposited under suboxic-oxic condition with high marine organic material and mixed organic material (both marine and terrestrial) input. The lateral thermal maturity gradient indicates that the source rock is uniformly matured from North to South, these suggests high prospectivity from North to South of the Field. The Field section within the study area indicates variation in oil water contact due to faulting and tectonic activities. Assessment of compositional variation in these oil samples using biomarker ratios and parameters revealed compositional heterogeneity. This suggests that the reservoir is compartmentalized, and the fluids are not communicating.**

Keywords- **Homohopane; Hopanoid; Oleanane; Crude oil; Heterogeneity**

I. INTRODUCTION

Crude oil is a heterogeneous mixture of large number of organic compounds, commonly dominated by hydrocarbons. Compositional heterogeneity of crude oil has led to the development of different geochemistry technique, from its inception to recent, followed by the development of analytical techniques for the analysis of crude oils. The Biological markers or biomarkers are complex molecules derived from formerly living organisms, which are used to provide wide-ranging information on source rock composition heterogeneity in hydrocarbon from different reservoir within a field and have also played a vital role during exploration, development and production phase of hydrocarbon. Biomarkers are compounds such as Oleananes, hopanes,

Homohopanes, sesquiterpene etc. These compounds are measured in both oil and source rocks, and they can be used to establish a correlation between an oil samples, oil compositional heterogeneity and the original petroleum source rock. This study is majorly concerned with application of biomarker distribution in oil from difference oil fields to delineate oil correlation, compositional variation, reservoir compartmentalization and structural trends (faulting) history.
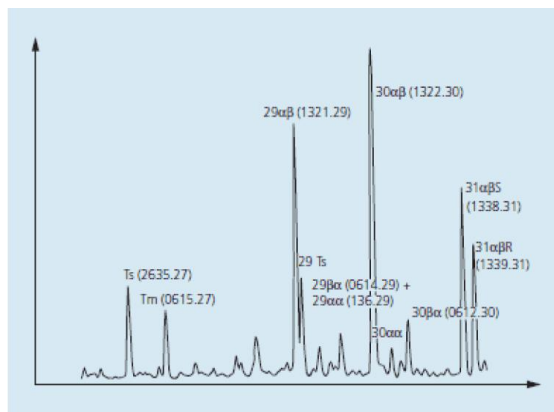

Fig.1: GC MS (m/z 191) hopane profile [1]

Ts-Trinorhopane, Tm-Trinorneohopane, $C_{29}\alpha\beta(H)$ - Norhopane, $C_{29}Ts(H)$-hopane, $29\alpha\beta(H)$-Norhopane, $29\alpha\alpha(H)$- Norhopane(fluka), $C_{30}\alpha\beta(H)$ Hopane, $C_{31}22S(H)$-Homohopane, $C_{31}22R(H)$- Homohopane

Hopanoids are lipids that are resistant to saponification and are abundant in animals and plants tissues; there belong to the triterpenoid family. Hopanoids are formed by the cyclization of squalane to a pentacyclic triterpanoid with a hopane skeleton which has four cyclohexane rings and one cyclopentane ring. Naturally occurring hopanoids have been identified in soils, sediments and other organic matter basically within marine environment. Hopanoids in sediments ranges from C_{27}- C_{35} usually the C_{30} isomers are the predominant form of hopanoids. Hopanoid are used for coal

exploration, petroleum exploration, development, production and spill remediation. Hopanoids are evidence of bacteria, primarily, high concentration of 17α(H), 21β(H)-Hopane are usually from non-marine source rocks. Hopanoids are also used to indicate the source of oil seeps on the water surface as indicator of active petroleum system beneath. Hopanes are important internal markers in environmental and petroleum remediation studies, due to their persistency and stability. By comparing Hopane fingerprint profiles, the source of the oil spill can be identified.

II. MATERIALS AND METHODS

A. Samples and sampling

Crude oils were collected from wellhead during well testing from Eric Field located in the Offshore Niger Delta (See Fig. 3). Four samples were collected in a glass sample vials with depth ranging from 106442 - 14917ft and preserved in refrigerator before analysis.

B. Pre sample analysis

The samples used for the analysis were separated into aliphatic and aromatic fractions [3]. The samples were prepared by dissolving 60mg into 2mg of Alumina and five drops of Dichloromethane were added to the blend to achieve uniform concentration before injecting into GC-MS (Gas chromatography-mass spectrometry), the method adopted for this analysis is whole oil analysis full scan.

C. GC-MS analysis

All the crude oils samples from Eric Field were subjected to GC-MS analysis using HP5890 II GC with a syringe injector linked to HP 5972 MSD (Mass spectrometry detector), these was done to separate the samples. The internal temperature of GC was programmed at 4℃ per minute for 40℃-300℃ and was maintained with final internal temperature for 20 minutes. The carrier gas was Helium with flow rate of 1ml/min, pressure of 50KPa, and slit at 30ml/min. The identification and ionization were done in the HP 5972 MSD, with electron voltage of 70 eV, interface temperature of 300℃, filament current of 220μA, a multiplier voltage of 1600V and source temperature of 160℃. The process was monitored by HP Vectra 48 PC Chemstation computer in both full scan mode [3]. Hopanoid were detected and identified by extracting m/z=191 chromatograms. Peak integration was done using the RTE integrator [2], data was collected from the percentage report from the enhanced MSD Chemstation 2011 software by Agilent Technologies

D Peak identification and quantification

Hopanes were identified using m/z 191 chromatogram and pentacyclic. The peak area used for this study was extracted from the percent result of GC-MS analysis which comprises of retention time, peak height and corrected area (See Fig. 3, Table 1 and 2). The appropriate retention time for each peak were integrated in the chromatogram. The

corresponding corrected areas were recorded and retention time for each peak was checked up in the GC-MS analysis report (See Table 2). Peaks and compounds identified using m/z 191 chromatogram shows dominant Homohopane across the four wells (See Fig. 1).
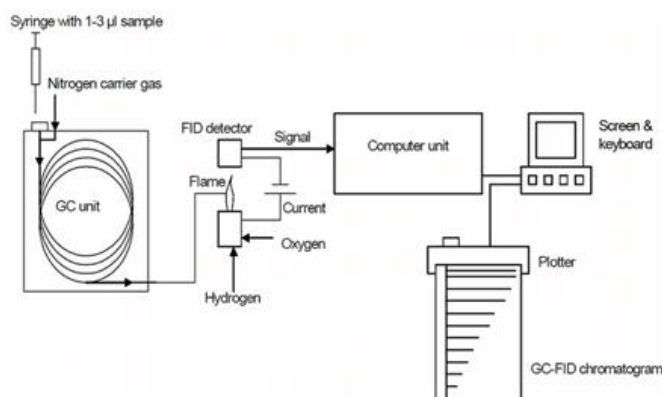

Fig. 2: Schematic diagram of GC-FID instrument by [1]

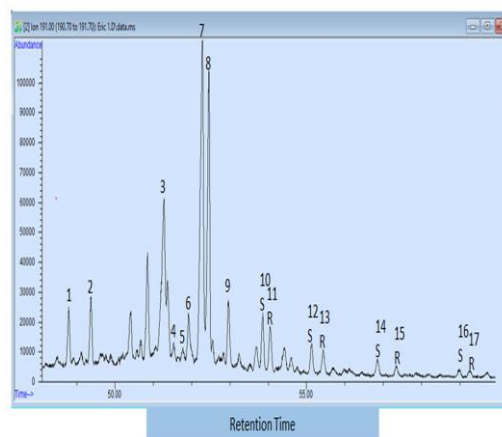Fig. 3: Map of southern Nigeria showing Eric Field [4]

Fig. 4: showing m/z 191 GC-MS for the oil samples

Table 1: peak identification

PEAK	COMPOUNDS	
1	C_{27}-17α(H)-22,29,30-Trinorhopane (c27mTs)	
2	C_{27}-18α(H)-22,29,30-Trinorneohopane (c27mTm)	
3	C_{29} -17α(H)Norhopane	
4	C_{29}- Tshopane	
5	C_{30} 17α(H)Diahopane	
6	C_{29}-Normoretane	
7	C_{30}-αβ(H)Oleanane	
8	C_{30}-17α(H), 21β(H)Hopane	
9	C_{30}-17β(H),21α(H)Moretane	
10 S	C_{31} 22S 17α (H)Homohopane	Homohopane
11R	C_{31} 22R 17α (H)Homohopane	
12 S	C_{32}22S 17α (H)Homohopane	
13R	C_{32}22R 17α (H)-Homohopane	
14 S	C_{33}22S 17α (H)Homohopane	
15 R	C_{33}22R 17α (H)Homohopane	
16 S	C_{34} 22S 17α (H)Homohopane	
17 R	C_{34} 22R 17α (H)Homohopane	

III.   RESULT AND DISCUSSION

A.   Result analysis

The diagnostic ratios were calculated from compound concentration i.e. concentration of the compound or peak area of the biomarkers fingerprint [5]. Biomarker parameters and ratios used for this study were obtained from the assessment of the oil, biomarker ratio and parameter calculation where based on [6], [7] guidelines.

Table: 2 Corrected extracted data from m/z chromatogram

Wells	Eric 1	Eric 2	Eric 3	Eric 4
C_{27}Ts	66972	66972	11561	11857
C_{27}Tm	89852	89852	56427	56427
C_{29}	290122	290122	201793	150029
C_{29}Ts	75510	75510	37057	37057
C_{30}Dh	20872	20872	96463	96463
C_{29}Nm	70968	70968	00000	00000
C_{30}Ol	622794	622794	459259	459259
C_{30}H	397620	397620	318116	318116
C_{30}M	96363	96363	63382	63382
C_{31}S	77851	77851	81323	81323
C_{31}R	72469	72469	71274	71274
C_{32}S	47063	47063	63377	63377
C_{32}R	36973	36973	44297	44297
C_{33}S	29250	29250	37095	37095
C_{33}R	12051	12051	25725	25725
C_{34}S	12270	12270	41802	41802
C_{34}R	12622	12622	20001	20001

The biochemical and biological compounds present or absent are used to identify the major source(s) of organic matter and predict possible depositional environment. The percentage concentration of organic matter in oils from GC and GC-MS analysis presents contribution input from different depositional environment, whereas the depositional environment of the samples studied was extrapolated from hopane, gammaccerane and Oleanane biomarker index. The existence of Oleanane in the oil samples is an indicative of higher terrigenous plants, and angiosperms (flowering plants). The ratios of Oleanane to Hopane provide vital information on environment of deposition and source rocks age. Oleanane index value greater than 0.2 indicates those samples were deposited during the Tertiary and in a marine deltaic environment. Whereas Oleanane index values less than 0.2 are characteristics of Cretaceous source rocks deposit in marine deltaic/shelf environments. (see Table 3).

The calculated geochemical parametric ratios derived from the hopanoids distribution using the m/z 191 chromatogram is presented in table 3 and are being used in characterizing the oils with respect to the environment of deposition, organic matter input and reservoir compartmentalization.

Table: 3 Diagnostic ratios calculated from m/z 191 chromatogram

Wells	Eric 1	Eric 2	Eric 3	Eric 4
Ts/Ts+ Tm	0.42	0.42	0.17	0.17
C_{31}S/S+R	0.51	0.51	0.53	0.53
C_{29}/C_{29} Ts	3.84	3.84	8.92	8.92
C_{30}Ol/C_{30}Ol+C_{30}H	0.16	0.16	0.59	0.59
C_{30}M/C_{30}H	0.24	0.24	0.20	0.20
C_{30}D/C_{30}N	0.29	0.29	0	0
C_{34}/C_{31}-C_{34}	0.04	0.04	0.05	0.05
C_{31}R/C_{31}S+R	0.05	0.05	0.47	0.47
C_{29}Ts/C_{29}	0.26	0.26	0.11	0.18
C_{30}H/ C_{31}-C_{34}	1.32	1.32	0.83	0.83
C_{31}R/C_{31}H	0.18	0.18	0.22	0.22
C_{32}-C_{34}/C_{31}-C_{34}	0.18	0.18	0.60	0.52
C_{29}/C_{30}H	0.73	0.73	0.47	0.63
C_{33}-C_{34}/C_{31}-C_{34}	0.22	0.22	0.35	0.35

Wells highlighted in red is suggestive of Cretaceous source rocks deposited in marine deltaic/shelf environments while those in green is suggestive of Tertiary and marine deltaic deposits.
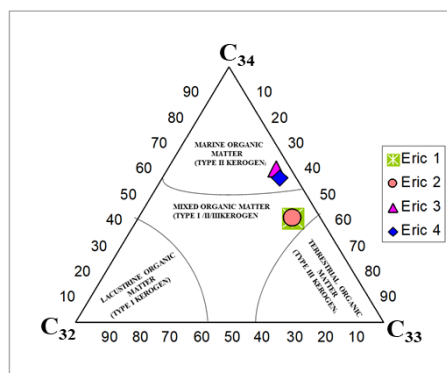
Fig. 5: Ternary plot of C_{32}, C_{33} and C_{34} Homohopane distribution in oil samples

B   Discussion

The discussion focuses on the environment of deposition, organic matter input, and reservoir compartmentalization inferred from the encountered oils in Eric Field.

1.   Depositional environment

The GC fingerprints of the oils from the Eric field show predominance of hopanoids between C_{31}- C_{34} in the oils which is typical of marine organic matter from algae and bacteria. The appropriate standard method of categorizing the amount of land derive organic matter in oil is to determine its degree of waxiness. The ternary plot indicates that the organic matter was deposited under suboxic/oxic condition, Eric 1 and Eric 2 shows high concentration of mixed organic input (type I, II and III kerogen) (See Fig. 5). The plot of C_{33}- C_{34} shows dominance of marine organic matter over terrestrial organic matter input into the source rock. This suggests that the organic matter input falls within the C_{33} and C_{34} (See Fig. 5).
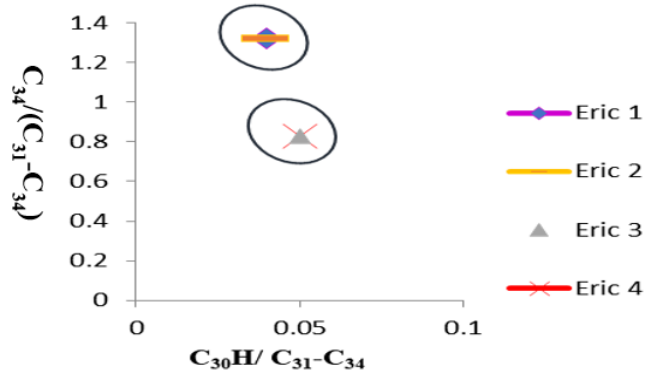

Fig. 6: Cross plot of $C_{34}/(C_{31}-C_{34})$ Vs $C_{30}H/C_{31}-C_{34}$ distribution

The distribution of $17\alpha,21\beta(H)$-31-homohopanes 22R+22S $C_{34}/(C_{31}-C_{34})$ in crude oils can be used as an indicator of oxic or anoxic conditions of environment during and immediately after deposition of the source sediments [4].

High C_{34} homohopanes is an indicator of reducing marine conditions during deposition, whereas low C_{34} homohopane concentrations are generally observed in oxidizing water conditions during deposition [8]. The data given in Table 4 and displayed in Fig. 5 show variations in $C_{34}/(C_{31}-C_{34})$ ratios among the Eric 1, Eric 2 and Eric 3, Eric 4 oil samples, and are most likely caused by subtle source input changes in each reservoir. The Eric 3 and Eric 4 oil samples are characterized by high $C_{34}/(C_{31}-C_{34})$ ratio (see Table 3 and Fig. 6), suggesting that these oils were generated from marine sources influenced by suboxic conditions of the depositional environment. Furthermore, the resulting low $(C_{34}/C_{31}-C_{34})$ in oils (see Table 3), suggest that anoxic conditions did not occur during the time of deposition of their relevant source rocks

2.   Hopane Maturity Parameters Ts/Ts + Tm

All the crude oil from Eric Field have a predominance of 17α (H)22, 29, 30- trisnorhopane (Tm) over $18\alpha(H)22,29,30$-trisnorhopane (Ts). This feature is displayed by the m/z 191 chromatogram (See Fig. 4). Ts/Ts+Tm ratios display maturity trends comparable to the maturity indicators, C_{31} S/ (S + R). Fig. 7, illustrates the relationship between two maturity parameters, the C_{31} 22S/(22S+22R) ratio and the Ts/Ts+Tm hopane ratios of the studied crude oil. Eric 1 and 2 oils have higher Ts/Ts+Tm ratios of 0.42, whereas Eric 3 and 4 oils exhibit lower values of 0.17. Eric 3 and 4 oils exhibits low thermal history as compared to Eric 1 and 2 oils (see Table 3). Ts/Ts+Tm maturity is based on the conversion of C_{29} to C_{29}Ts during catagenesis stage and is also sensitive to source deposition characteristics [9].
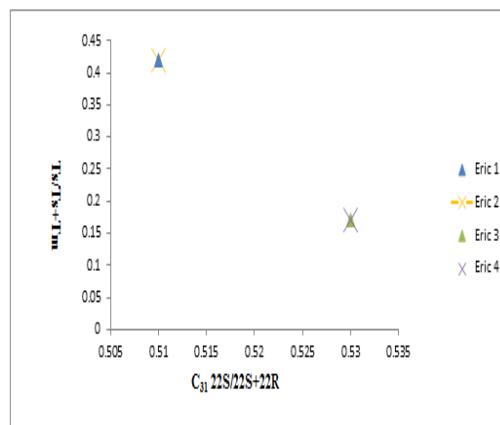

Fig. 7: plot of $C_{31}S/C_{31}S+R$ VS Ts/Ts+Tm distribution

The plot of Ts/Ts+Tm against $C_{31}22S/22S+22R$ shows that the oils from different wells has similar maturity and a linear relationship of both parameters exists. The value of C_{31} 22S/ 22S+22R ranges from 0.51-0.53 (See Table 3) which is close to the equilibrium value of 0.6 and indicates that the oils are most likely to be generated at the early oil window.

3. Reservoir compartmentalization

Reservoir compartmentalization is one of the key objectives in reservoirs reviews and characterization, especially during appraisal, development and production phase. A reservoir is compartmentalized if the reservoir fluids cannot flow freely from one end of the reservoir to another over production time scale. The most common driving mechanisms for reservoir compartmentalization within Southeastern offshore Niger delta is faulting and depositional heterogeneity, the fault may be a sealing or non-sealing fault. Sealing fault or static seals are completely sealed and capable of withholding reservoir fluid over geological time, while non-sealing faults or dynamic seals are low to very low permeability flow baffles that reduce petroleum cross-flow to infinitesimally slow rates. The non-sealing faults allow fluids and pressure to equilibrate across a boundary over geological time scales.

The observed geochemical heterogeneity (different fluid composition between the wells), indicates the presence of fluid flow barrier (reservoir compartmentalization due to faulting). The geochemical changes in composition of these oils might be due to depositional heterogeneity or petroleum filling history. Proper evaluation and identification of these compartments and their distribution within the field can help to guide the development of reservoirs, because it provides better strategies, excellent estimate of reserves and basis for quantification of future production problems. The field section in the study area shows prominent faults demarcating various wells with different biomarker parameters. The calculated biomarker parameter shows that Eric 1 and 2 wells are similar in composition, while Eric 3 and 4 wells have similar composition (see Table 3). A non-sealing minor fault can be observed between Eric 1 and 2. The faulting is believed to be associated with minor throw and the compositional homogeneity between oils from Eric 1 and 2 suggests that the fault is a non-sealing fault.
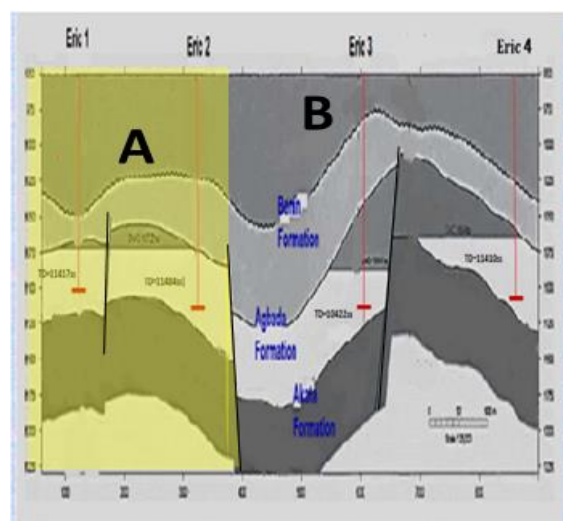

Fig. 8: Field section of Eric Field

As expected, compositional heterogeneity exist in oils from Eric 2 and 3. This is due to the high throw sealing fault situated between both wells (see Fig 8). The fault between Eric 3 and 4 appears to have a huge throw and one would expect oils from both wells to be compositionally dissimilar. However, the compositions of oils from both wells were similar indicating that they are either recharged from the same source kitchen or that the faulting occurred after the oil accumulation (post depositional faulting). In general, two compartments were established; compartment A (Eric 1 and 2) and compartment B (Eric 3 and 4).

IV. CONCLUSION

The analysis indicates that the source rock is made up of marine organic matter with minimal terrestrial organic matter input. Biomarker parameters and ratios show that the source rock was deposited under suboxic conditions probably within the marine deltaic environment where there is abundant supply of marine organic matter. This suggests that it is of type II kerogen. The existence of Oleanane in the oil samples is indicative of higher terrigenous plants, and angiosperms (flowering plants). The ratio of Oleanane to Hopane suggests that the source rock is of marine/deltaic environments and of Tertiary and Cretaceous age. Reservoir compartmentalization assessment based on the biomarker ratio indicates that the reservoir is compartmentalized due to the compositional variation of oils within the field. This study demonstrates that compositional variation of oils within a field is useful in reservoir compartmentalization investigation.

REFERENCES

[1] Pedersen, J. (2002). Typical oils, Unusual Condensates and Bitumens of the Norwegian Continental Shelf: an organic geochemical study, and. Scient. Thesis in Geology, Department of Geology, University of Oslo.

[2] Abrakasa, S. and Mohammad, A. B. (2011). Organic Geochemistry Assessment of the Source Depositional Environment and Migration Trend of oils in the Nembe Creek E 1.0 and Kolo Creek E 2.0 Reservoirs, Archives of Applied Sciences Research.

[3] Abrakasa, S. (2006). Newly identified Molecular Marker Compound in Some Nigerian oils. Nigeria Journal of Chemical Research.

[4] Peters, K.E., Walters, C. C. and J. M. Moldowan (2005). The biomarker guide: biomarkers and isotopes in the environment and human history (2nd edition). Cambridge, UK: Cambridge University Press.

[5] Yassar, M. M., Rania, E. M. (2012). Biomarkers, chromatography and its Applications, Dr. Sasikumar Dhanarasu.

[6] Peters, K. E., and Moldowan, J. W. (1993). The Biomarker Guide Interpreting Molecular Fossils in Petroleum and Ancient Sediments, Prentice Hall, New Jersey.

[7] Peters, K.E., Walters, C. C. and J. M. Moldowan (2005). The biomarker guide: biomarkers and isotopes in the environment and human history (2nd edition). Cambridge, UK: Cambridge University Press.

[8] Peters K. E, Moldowan JM (1991): Effects of source, thermal maturity, and biodegradation on the distribution and isomerization of homohopanes in petroleum. Org Geochem.

[9] Tuttle, M.L., Brownfeld, M.E., and Charpentier, R.R., (1999). Tertiary Niger Delta (Akata-Agbada) Petroleum System (701901), Niger Delta Province, Nigeria, Cameroon, and Equatorial Guinea: U.S. Geological Survey.

[10] Seifert, W. K. and Moldowan, J. M. (1978). Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils.