RESEARCH ARTICLE OPEN ACCESS

C_{30} 4,23,24-Trimethylsteranes in Niger Delta Oils: Discriminates Depobelts and Suggests Possible Sub-Petroleum Systems.

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***Abstract*:**

Some oils from different depobelts in the Niger Delta Basin were geochemically examine for the presence of C_{30} methylsteranes which were to serve the purpose of discriminating the depobelts upon the hypothesis that they were deposited at different geological times and different paleoenvironment with different degrees of marine organic matter contribution. The oils were fractionated and the aliphatic fraction was subjected to GC-MS analysis. C_{30} 4-methysteranes and C_{30} 4,23,24-trimethysterane were identified in the oils from the EIC (extracted ion chromatogram) on m/z 231 from the TIC (total ion chromatogram). A bivariant plot of B against Pr/Ph, [B= 4,23,24-trimethylsteranes/(4,23,24-trimethylsterane+4-methylsterane)] showed a gradual gradient-wise increase from the Greater Ughelli oils to the Offshore oils. This compositional variations could be due to the fact that depobelts are geologically independent indvidual megasequences impling the potential existence of sub-petroleum systems.

Keywords **— Biomarkers, geochemistry, methylsteranes, Niger Delta.**

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I. INTRODUCTION

A. *Biological Markers*

Biological markers popularly abbreviated as biomarkers are within the circles of petroleum geochemistry known as chemical fossils, they are organic compounds in geological polymer (kerogen) which are generated alongside, petroleum, that bears an unambiguous structural formula that relates to the biological polymer. They are mostly derived from lipids in organisms. Their functional groups tend to be lost or modified, in some cases their functional group are modified beyond recognition [18]. Among other biomarkers such as oleanane, methylhopanes, steranes and hopanes are the methyl steranes.

Methylsteranes are a class of biomarker that has a methyl group attached to the regular steranes and entails C_{27}, C_{28}, C_{29} and C_{30} methylsteranes. The C_{30} methyl steranes has been used as diagnostic marker for marine environment. However, more specifically, the most significant of the C_{30} steranes are the 4-methylsteranes [18]. The C_{30} 4-methylsterane also have an analogue which is C_{30} 4,23,24 trimethylsterane, also known as dinosterane. The dinosteranes are uniquely derived from dinosterol (4α, 23, 24R-trimethyl-5α-cholest-22E-en-3β-ol) their precursor has been reported to be sourced from dinoflagellates. Dinoflagellates are eukaryotic organisms which are mostly marine plankton found mostly in marine environments.[1], but are also common in freshwater environments. The dinoflagellates are distributed based sea surface temperature, salinity and depth. Dinoflagellates

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exist as photosynthetic species and mixotrophic species, combining photosynthesis and ingestion of preys (phanotrophy) [14]. [16] states the existance of about 2000 species of which 1,700 species are of marine and benthic habitat, while 220 species are of freshwater habitat. The freshwater dinoflagellates are rarer relative to the marine denoflagellates, this observation has been attributed to parculiarity of their habitat[21].

The predominanat occurance of the C_{30} 4,23,24 trimethylsterane in preference to the C_{30} 4-methyl sterane is suggested to be possibly due to protection of the unsaturated dinosterol side-chain from oxidation due to anoxic conditions. Such a mechanism has been proposed to explain the relative abundance of C_{35} homohopanes in marine sediments through preferential preservation of hydroxyl groups (tetrahol) precursors [5], [10]

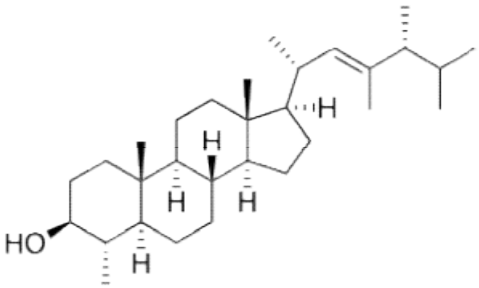

Figure 1a Dinosterol (Biological)

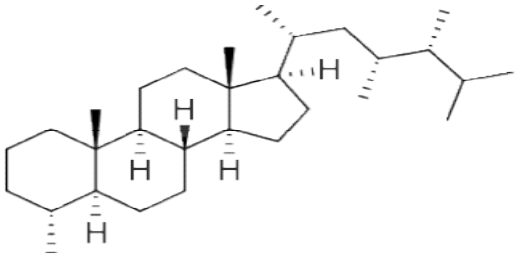

Figure 1b Dinosterane (Geological)

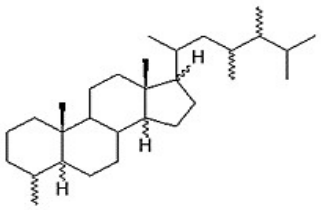

Figure 1c. C_{30} 4,23,24-trimethyl sterane

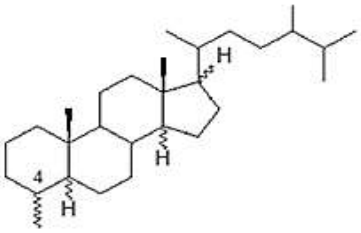

Figure 1d. C_{30} 4-methylsterane

Figure 1. Showing Dinosterol the biological form (precursor) (a) and the Dinosterane the geological form (product) (b) and the two major C_{30} Methylsteranes which are (c) C_{30} 4,23,24-trimethyl sterane and (d) C_{30} 4-Methylsterane.

B. *Niger Delta.*

The Niger Delta Basin is located in the Gulf of Guinea, it has been the beehive of hydrocarbon exploration and production since 1957, when the first well was brought on stream by the then Shell-British Petroleum [17].

The Niger Delta Basin is 12,000m thick with successions of sediments that resulted in the deposition of the main formations that consist the Niger Delta Basin which are the Benin formation, the most shallow, and is underlaid by the Agbada Formation, and which in turn is underlaid by the Akata Formation. However, [6] stated that the deposition of the Niger Delta Basin was according to the model of the Gulf of Mexico, that the deltaic sedimentation is a function of rate of deposition.

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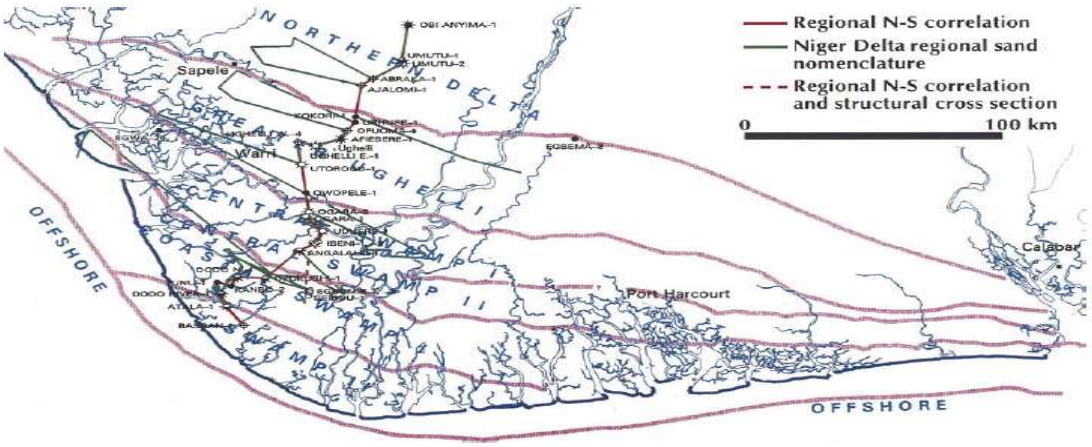

Figure 2. The Niger Delta Basin, showing the various depobelts that consists the basin [11]

and rate of subsidence, in building delta as that of the Niger delta, the regressive phases dominated where rate of deposition was greater than rate of subsidence resulting in ineffective dewatering thereby resulting in a high pressure basin [6].

The interplay of subsidence and rate of sediment deposition resulted in the deposition of discrete depobelts. [11] referring to the depobelts, unravelled that the Niger Delta was deposited inmegasequences with considerble internal lithological variation. [11] also stated that cycles of sea levels were out of phase with each other and with local subsidence and thus varible depositional processes and environments. Each megasequence was formed over a geological time interval of 5Ma and 30-60 km wide. Each of the depobelt consist of the three major formation that consist the Niger Delta, and corresponds to a break in regional dip being bounded seaward by growth fault and landward by counter regional fault/growth faults thus existing more as separate geological entities, having separate sedimentation (marker shales), deformation and petroleum history[17]. The existence of the three major formations in each of the depobelt with potentially separete stratigraphic petroleum elements and processes might infer separate sub-petroleum systems with subtle differencs.

[11] unravelled five (5) depobelts namely the Northern depobelt; the Greater Ughelli depobelt; Central swamp depobelt; Coastal swamp depobelt; and Offshore depobelt (figure1), while [6] recognized three (3) depobelts namely the Northern Delta province, the Central Delta province and the Distal Delta province [17].

[11] presented that the most earlier deposited depobelt which is the Northern depobelt was deposited during high sea level, through a falling sealevel to low sea level, which was during the Middle Eocene (54.6-38.0). It correspondingly resulted in the deposition of the Eponides-11 marker shale and eventually the Umutu Shale. During the Oligocene, the deposition of the dinocyst rich Orogho shale defined the base of the Greater Ughelli

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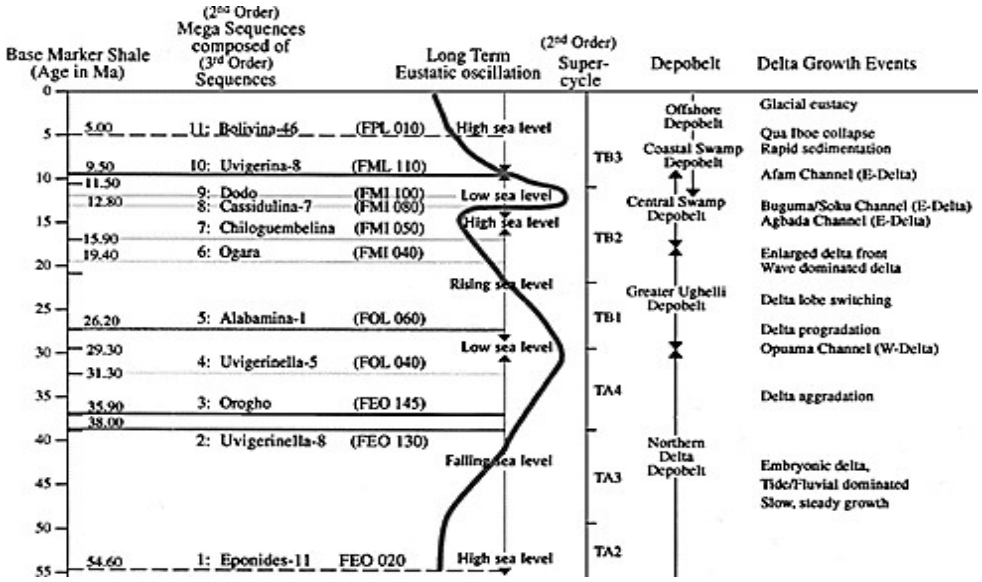

Figure 3. Evolutionary phases of the Niger Delta and their peculia characteristics. [11]

depobelt, it was deposited during rising sea level, which could had foster enhanced incursion of marine organisms which had been populated after the Jurrasic outburst of marine environments (Figure. 3). A channel formation (Opuma channel) was triggered by sea level fall and the corresponding sea level rise resulted in the slumping and gravity fill of the channel, later the deposition of the Uvigerinella-5 shale phased out the Greater Ughelli depobelt. In the Miocene, the deposition of the Ogara Shale triggered the deposition of Central Swamp depobelt and marked eustatic sea level rise. Subsidence rate increased from less than 700m/Ma to higher than 1000m/Ma, this triggered increased sedimentation.

The deposition of the Cassidulina-7 shale straddle the Greater Ugehlli bounderies with the Central Swamp and overlapping Coastal swamp depobelt. The Upper and Lower sequences are separated by significant sea level fall which resulted in the formation of Buguma Channel, Soku/Ekelewu Channels. The Late Miocene Uvigerina-8 shale is the bounderies between the Central Swamp and Coastal Swamp depobelt (figure. 3). The erossive events at 8.5Ma formed the Afam Channel which gradesbasinward into the a submarine canyon that incised sand that became part of a deep-water settings [11].

The hypothesis of this study rest on the fact that, the existence of separate depobelts with different depositional history, will infer different or slightly different source facies that consist the organic matter deposited in the matrix of the source rock. These organic matters have chemical fossils which are the custodian of inherent traits in the oils generated by the source rock, their paleoenvironment and facies constituents can be unravel by these chemical fossil records (biomarkers). These potential differences may infer potential sub-petroleum systems. The source rock, probably markers shales, could have been deposited in variable conditions which could be reflected on the compositional distribution of compounds in the oils. C_{30} 4,23,24-trimethylsterane (dinosterane) which is a marker for marine environment may discriminate the oils based on the subtle differential marine contributions to the organic matter. The major objective of this study includes developing

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and using a 4-methylsterane ratio to discriminate the Niger Delta oils in a lateral gradient that show subtle differences with respect to their depobelts, also use generic parametric ratios for discrimination of the oils. Dinoflagellates are the organism reported to biosynthesized 4-methyl sterols and invariably, Dinosteranes has been used as indicator for marine paleoenvironment of deposition [15].

II. Materials and Methods

A. Sampling

A suite of oil samples consisting about seventeen (17) samples was obtained from seventeen oil fields across the depobelts that consist the Niger Delta Basin. In accordance with confidentiality agreements the names of the fields are coded as used and inscribed in the samples and study location map (figure 3). All samples were duly obtained and supplied from the well head.
Samples were stored in sample glass vials with Teflon cover and stored in a refigerator untill samples were retrieved for analysis. Sample handling was consistent as required for a consistent chain of custody.

B. *Sample preparation.*

Samples were prepared for analysis by fractionation, which is a process of separating crude oils into its major constituents, which are aliphatics, aromatics and the polars. The polars are made up of asphaltenes and polar compounds which are the oxygen compounds e. g. phenols, carboxylic acids; nitrogen compounds e.g. carbazoles; and sulphur compound e.g. thiophenes. In this study the aliphatics were the fraction of interest. The method of [2] was adopted.
The oils were measured (60 mg) on to alumina (2 mg) (AnalaR grade supplied by BDH, England), on to that, 5 drops of dichloromethane (DCM) (AnalaR grade supplied by BDH, England) were added to blend the oil and thealumina for introduction of the samples into the column. The chromatographic column (50cm in length, and 0.5cm internal diameter, supplied by BDH, England) was packed with silica gel (SiO2) 60 size, 0.063–0.2mm (70–230) mesh (AnalaR grade supplied by BDH, England); the silica gel served as the stationary phase. The mobile phase was light petroleum ether (30°–40°) (AnalaR grade supplied by BDH England).

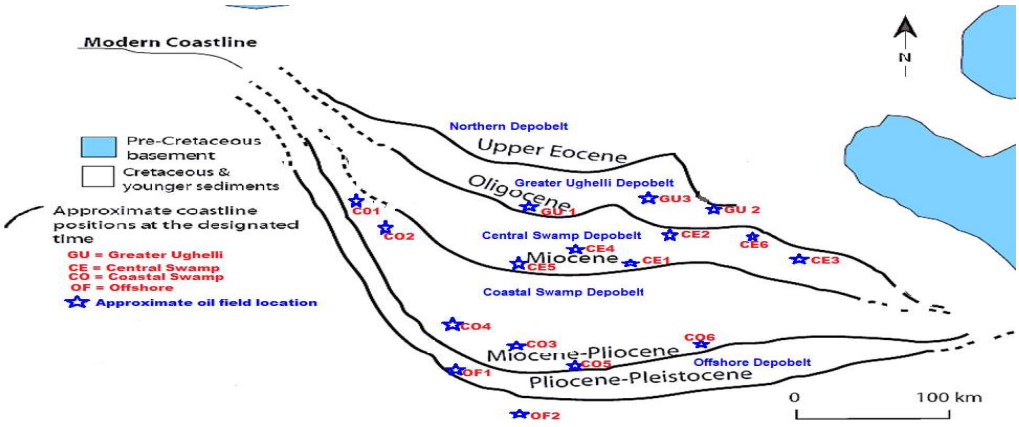

Figure 4. Map showing the Niger delta depobelts and sample sites (oil fields) (Tuttle, et al., 1999)

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The oils were mixed into a blend with activated alumina and introduced into the column; the aliphatics and the aromatics were eluted using 70 ml each of petroleum ether and dichloromethane (AnalaR grade supplied by BDH, England). The aliphatic fraction was evaporated with rotary evaporator and the fraction left was further reduced under nitrogen gas stream to a concentration of 1 mg of extract per 100µl of DCM as required for Gas Chromatography/Mass Spectrometry (GC–MS) analysis [2].

C. GC-MS Analysis.

Gas chromatography/mass spectrometry (GC–MS) is a hybrid technique of analysis; it couples separation capabilities of gas chromatograph (GC) and the detection competences of the mass spectrometry (MS) to evaluate biomarkers [9].
The laboratory procedure is as follows;
The saturated hydrocarbon fractions were subjected to gas chromatography/mass spectrometry (GC–MS) analysis using a HP5890 II GC with a split/splitless injector linked to a HP 5972 MSD.
The GC was temperature programmed for 40–300 °C at 4 °C per minute and held at final temperature for 20 min. The carrier gas was helium (flow rate 1 ml/min, pressure of 50 kPa, slit at 30 ml/min). The ionization and identification were carried out in the HP 5972 MSD which was equipped with electron voltage of 70 eV, filament current of 220 µA, source temperature of 160 °C, a multiplier voltage of 1600 V, and interface temperature of 300 °C.
The acquisition was monitored by a HP Vectra 48 PC. The acquisition was controlled by HP Vectra 48 PC chemstation computer in both full scan and selected ion mode (30 ions 0.7 cps 35 m dwell) for greater sensitivity. HP is currently known as Agilent, UK [2], [9].
The EIC (extracted ion chromatogram) for methylsteranes were obtainedusing m/z = 231from the TIC (total ion chromatograms), methylsteranes were identified by comparing mass chromatogram and mass spectra with those of standards in library and from literature. Peak integration was performed using the RTE integrator [10].

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III. Results and Discussion.

Table 1. 4-Methylsteranes and other generic data of some Niger Delta Oils.

B=(Y/Y+Z), A= (Z/Z+Y),
Y=total C_{30} 4,23,24-trimethylsterane, Z=total C_{30}4-methysterane,
Pr=Pristane, Ph=Phytane, Wax=waxiness (nC_{21} to nC_{31})/(nC_{15} to nC_{20}), TAR (nC_{17} to nC_{19})/(nC_{27} to C_{29})
GU=Greater Ughelli, CE=Central Swamp, CO=Coastal Swamp, OF= Offshore Depobelts.

Fields	A	B	Pr/Ph	TAR	WAX	Pr/nC_{17}	Ph/nC_{18}
GU1	0.63	0.37	4.71	0.3	1.13	6.05	0.81
GU2	0.59	0.42	3.83	0.14	7.88	3.15	0.95
GU3	0.58	0.41	0.96	0.74	2.42	1	1
CE2	0.53	0.47	3.49	3.06	0.74	0.78	0.25
CE3	0.65	0.35	2.01	1.91	0.88	1.19	0.66
CO1	0.67	0.32	2.23	2.6	0.77	2.04	1.01
C03	0.42	0.58	2.9	2.7	0.78	2.07	1
CO8	0.64	0.36	2.5	1.97	1.39	1.6	1.62
OF1	0.66	0.72	1.94	2.36	0.81	2.15	1.41
OF2	0.68	0.68	2.32	2.97	0.4	0.63	0.34

A. C_{30} 4-Methylsteranes in Niger Delta Oils

C_{30} 4-methylsterane has been identified in oils from China, (particularly the South China Sea) Brazilian marginal oils, Libyian oils, and oils from Sumatran, Indonesia. C_{30} 4-methyl steranes has been identified in Nigerian Niger Delta oils in this study. C_{30} 4-methylsteranes were identified by extracting their mass chromatogram at 231 m/z from a full scan of the aliphatic fraction of the Niger Delta oils (though selected ion monitoring is more sensitive). The initial identification of the C_{30} 4-methlyseries was done by overlying the m/z 217 chromatogram to the m/z 231chromatogram as in figure 5 [8]. The typical distribution of C_{30} methylsteranes in a typical Nigerian oil is represented in figure 6.

B. Abundance of C_{30} 4-methylsteranes in Niger Delta Oils.

The result in table 1, which shows various parametric ratios calculated from m/z 231 indicates thattotal C_{30} 4,23,24-trimethylsteranes has higher values relative to the C_{30} 4-methylsteranes in a ratio of averagely 55%-67% relative 45%-33%. The data showed that there is a lateral variation of the ratio across the depobelts. This observation may be explained by the varible environment of deposition of the endmember marker shales for each of the depobelts. The C_{30} 4-methylsteranes are normaly abundant in lacustrine and lake type environments, while the trimethylsteranes are normally found in marine type/influenced environments [5],[1].

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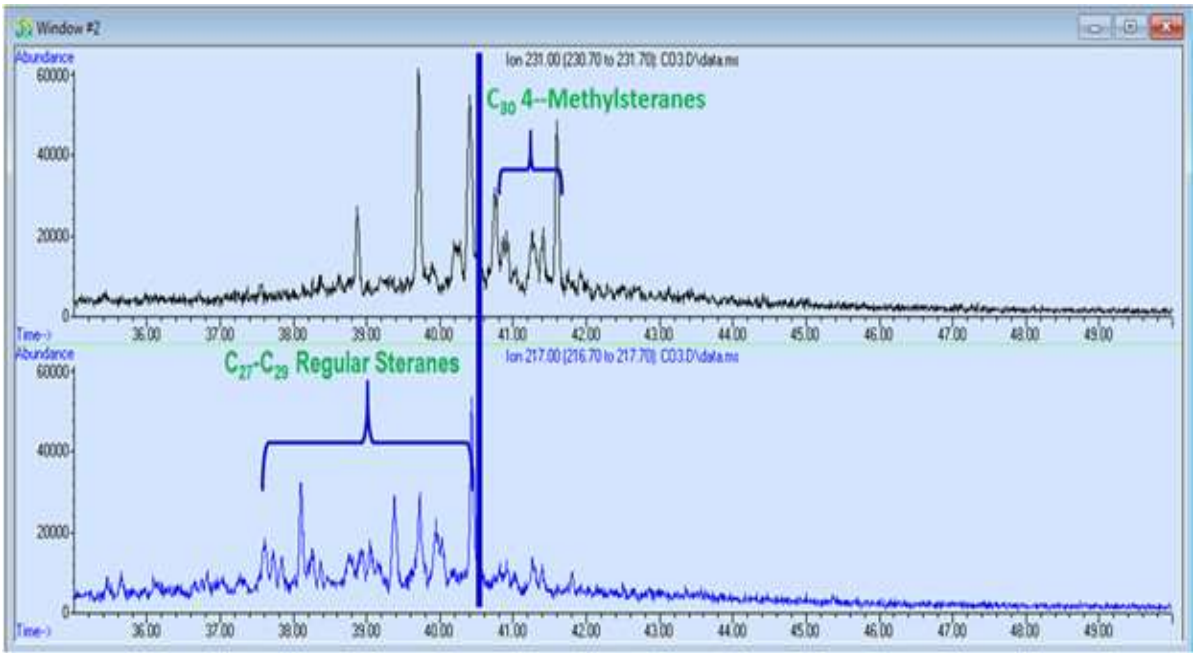

Figure 5. An overlay of m/z 217 (regular steranes) to m/z 231 (4-methylsteranes) showing the C_{30} 4-methylsteranes in the m/z 231 mass chromatograms.

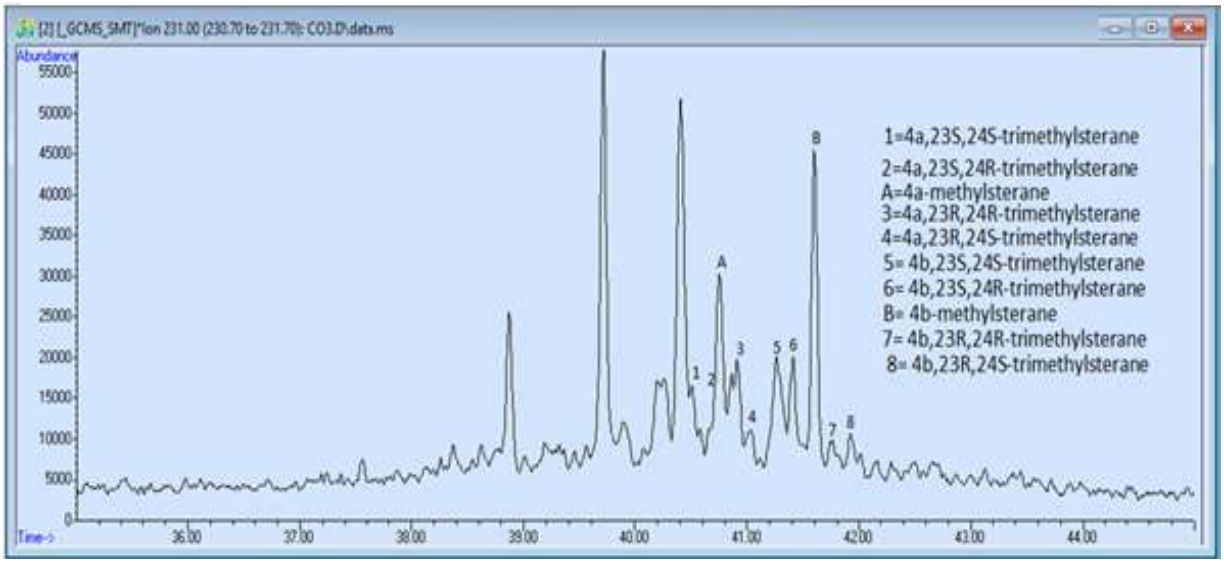

Figure 6. m/z 231 mass chromatogram of sample **CO3** showing the distribution of C_{30} 4-methlysterane and C_{30} 4, 23,24 trimethylsterane. The mass chromatograms showed that the C_{30} 4-methylsteranes are fewer but larger peaks compared to the C_{30} 4,23,24-trimethylsteranes.

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C. Implication for sub petroleum systems

The presence of C_{30} methylsteranes in an oil implies that the oil was generated by organic matter deposited in marine type environment. The depobelts exist as megasequences, these were deposited at seemingly regular intervals of 5Ma. The environment of deposition varied from rising sea level to falling sea level. The evolutionary trends as represented in Figure. 3, showed various degrees of marine incursion during the deposition of the depobelts, the Northern Delta was deposited during progression from a high sea level to a low sea level. The Greater Ughelli was deposited during rising sea level, while the Central Swamp was deposited during sessions of rising sea level, then the Coastal Swamp and the Offshore were deposited during rising sea level (Figure 3) [11]. This invariably implies that different degrees of marine incursion had occur at different phases of the deposition of the Niger Delta. Holistically, there would be variable marine organic matter contributions to different shales which could have been deposited at these phases.

The validation of the variableness and the fact that the megasequences are independently different depobelts implies that the petroleum geochemistry of the shales may indicate some significant or subtle variations which may infer differences in generated petroleum, and consequently different sub-petroleum systems.

In this study, C_{30} methylstreanes which consist, C_{30} 4-methylsteranes and C_{30} 4,23,24-trimethylsteranes had been used as marker for lacustrine and marine type environment respectively, however, the C_{30} 4-methylsterane is used as marker for lake/lacustrine environment, while the C_{30} 4,23,24-trimethylsterane had been used as marker for marine environment [20]. The use of both markers as parametric ratio for discriminant crossplot will serve as a varitable tool for highlighting the compositional variation of C_{30} 4-methylsteranes and C_{30} 4,23,24-trimethylsteranes across the depobelts of the Niger Delta Basin. The petroleum system concept has portrayed the Niger Delta Basin to consist a single homogenous endmember source rock [6], however the depobelts concept highlights the existence of independent megasequences with independent petroleum histories [17].

In bid to observed the variation of marine contributions in oils obtained across the depobelts from the Northern Delta to the Offshore depobelts, the plot of C_{30} 4,23,24-trimethylsteranes against Pr/Ph was employed in Figure 7.

In an earlier study, [7] used C_{30} 4-methysterane to unravel oil families in the Weixinan Sub-basin in South China Sea. [8] in their study delinated the existence of different species of dinoflgellates across the Qaidam Basin, in North West China. This proved the contribution of dinoflagellates to the Palaeogene crude oil in the Qaidam Basin.

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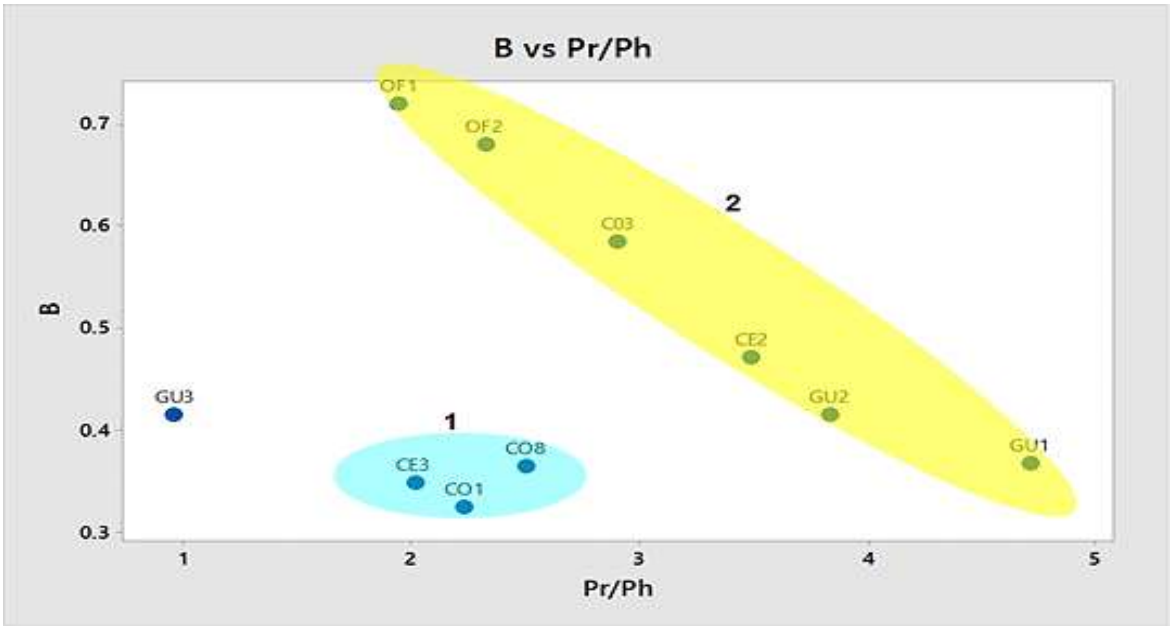

Fig.7. A bivariant plot of B against Pr/Ph, [B= trimethysteranes/(4-methylsterane+trimethylsteranes)] GU=Greater Ughelli, CE=Central Swamp, CO=Coastal Swamp, OF= Offshore Depobelts

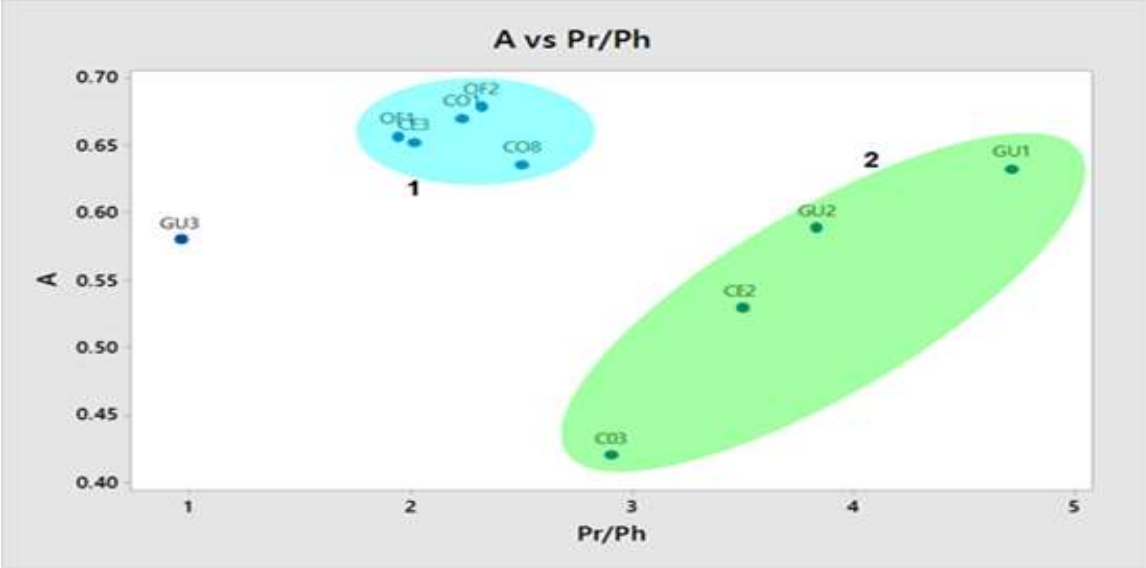

Fig. 8. A bivariant plot of A against Pr/Ph, [A= 4-methysteranes/(4-methylsterane+trimethylsteranes)] GU=Greater Ughelli, CE=Central Swamp, CO=Coastal Swamp, OF= Offshore Depobelts.

The contributions of C_{30} 4,23,24-trimethylsteranes in oils from different depobelts in the Niger Delta Basin showed a gradiential increase from the Northern Depobelt to the Offshore depobelt. This observation implies that there was an increasing marine paleoenvironment during the deposition of the megasequences that constitutes the depobelts. In an earlier study, [9] showed a gradual increase in the C_{33}-C_{35} homohopanes (hopanoids) in the Offshore oils relative to the Onshore oils, which was explained as due to increasing marine contributions from the Northern Delta (Umutu) through the swamps (Kolo Creek, Afam, Nembe Creek) to the Offshores (Enang, Abo) [9]. In another related study, [4] showed that a biodegradation parametric ratio indicate that the Offshore and Coastal Swamp oils were observed to be more degraded compared to the Onshore oils, implying that biodegradation increases from the Northern depobelt to the Offshore depobelt.

The bivarient plot in figure 7., show a discrimination of the oils into group 1 and 2. The group 2 oils showed a gradual gradient-wise increase in the contribution of C_{30} 4,23,24,-trimethylsteranes from the Greater Ugehlli oils to the Offshore oils. The variation in C_{30} 4,23,24,-trimethylsteranes contribution, with respect to the existing independent megasequences could imply the existence of sub-petroleum systems. The variability in the source rock could be attributed to the slightly different paleoenvironments under which the source rocks were deposited at various geological times. The group 1 oils could be suggested to be mixed oils having similar compositional distribution with similar paleo/redox environmental indicator. The filling of the incised channels during the Late Oligocene to Middle Miocene in the Central and Coastal Swamp depobelts and the overlapping commencement of the deposition of the Coastal depobelt before the conclusive deposition of the Central Swamp depobelt [11], may explain similarity of the clustered of oils in group1 in figure.7.

[12] in their study unravelled that most Nigeria oils used in the suite of oils for the study bear characteristics of oils generated from marine organic matter deposited in deltaic environment [12].discriminates the oils into groups 1 and 2. Group 2 show a gradual but gradient-wise increase in C_{30} 4-methylsterane contributions in the oils from the Coastal Swamp depobelt to a maximum in the Greater Ughelli oils. This implies a gradual increase in lake/lacustrine type paleoenvironment from the Coastal depobelt to the Greater Ughelli depobelt. This may also suggest different source rocks for the oils and invariably different sub-petroleum systems.

IV. CONCLUSION.

The depobelt concepts highlights the presence of independent megasequences which consist the Niger delta basin. C_{30} 4-methylsteranes and C_{30} 4,23,24-trimethylsteranes were identified in some Niger Delta Oils, which were obtained across the basin from the Greater Ughelli to the offshore depobelts. Parametric ratio for the C_{30} 4,23,24-trimethylsteranes showed gradual but gradient-wise variation in increasing order from the Northern depobelt to the offshore depobelt implying increasing marine paleoenvironment during the deposition of the depobelts. C_{30} 4-methylsterane show increasing order from the offshore depobelt to the Greater Ughelli depobelt, implying increasing lake/lacustrine type environment. These variations in corroboration with the megasequences (depobelts) implies existence of sub-petroleum systems in the Niger Delta basin.

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ACKNOWLEDGEMENT

The authors are grateful to World Bank for providing the research grant for this study via African Centre of Excellence for Oilfield Chemicals Research.

We also wish to acknowledge the supports of the Department of Petroleum Resources of the Ministry of Petroleum Resources, Nigeria, the Production Chemistry Department of Shell Petroleum Development Company as well as the University Liaison Office of Shell Petroleum Development Company, Port Harcourt Nigeria towards the success of this research work.

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