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Biomarker application in the recognition of the geochemical characteristics of crude oils from the five depobelts of the Niger Delta basin, Nigeria

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Abstract

Biomarker fingerprints of crude oils are useful indicators of origin of organic matter input in source rocks and depositional conditions which are useful indices for petroleum systems development within a hydrocarbon producing horizon. Twenty five (25) crude oil samples from the five depobelts of the Niger Delta basin, Nigeria were studied to describe their biomarker fingerprints, provide information on the origin of organic matter input in the source rock(s), determine depositional environmental conditions and thermal maturity of the crude oils. The study was based on biomarkers (steranes and hopanes), normal alkanes and acyclic isoprenoids (pristine and phytane) obtained from the gas chromatography–mass spectrometry (GC-MS) analyses performed on the saturated fractions of the crude oils. The results of pristine/phytane (Pr/Ph) ratios, Pr/n-C_{17} ratios, Ph/n-C_{18} ratios, C_{29}/C_{27} sterane ratios, sterane/hopane ratios, %C_{27}, %C_{28} and %C_{29} regular steranes, oleanane index, waxiness index, Ts/Tm ratios and Carbon Preference Index (CPI) values, indicated that the analyzed crude oils belong to the same family of oil and originated from terrigenous clastic source rock (s) containing land plant organic matter with minor marine organic matter input, deposited under oxic to sub-oxic paleoenvironmental conditions. The Pr/n-C_{17} versus Ph/n-C_{18} cross plot indicated marine algal type II and a mixed type II/III kerogen. The C32H:22S/(22S+22R) values together with Ts/(Ts + Tm), C29:20S/20S + 20R, oleanane index and CPI values indicated that most of the crude oils have reached thermal equilibrium with high thermal maturity levels.

Keywords: *Niger Delta, depobelts, source rocks, organic matter, Biomarker*

1. Introduction

The Niger Delta (Fig 1) is a hydrocarbon province with an estimated recovery of about 40 billion barrels of crude oil and over 40 trillion cubic feet of gas reserves (Adegoke et al. 2017). It is the major oil bearing province in Africa, making up about 70% of the total hydrocarbon reserves of the entire sub-Saharan Africa (Reijers 2011; Adegoke et al. 2017). The Niger Delta is the Cenozoic offlapping siliciclastic succession situated in the Gulf of Guinea, central part of West Africa (Fig 2). The delta developed on top of the Cretaceous marine strata of the Anambra Basin (Reijers et al. 1997 Corredor et al. 2005; Adegoke et al. 2017), as a major embankment that extended outwards in the process of subsidence and cooling of the oceanic crusts resulting from the separation of the African and the South American plates (Adegoke et al. 2017). The whole of the sedimentary wedge in the Niger Delta were laid in five discrete offlapping siliciclastic sedimentation cycles of fluviomarine systems known as depobelts. The mechanisms of sedimentation in these depobelts have been described using the escalator regression model (Knox and Omatsola 1989). These depobelts are self-contained entities with respect to hydrocarbon distribution, stratigraphy and structural framework (Adegoke et al. 2017).

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The stratigraphic successions in each of these depobelts begins with marine clays and ends with coarse grained sands both vertically and laterally basinward. The presence of major regional faults makes stratigraphic correlation within these depobelts difficult. Geochemical studies in the Niger Delta indicates that the hydrocarbons originated from land plants and other structureless organic matters of Type III Kerogen in Late Eocene to Pliocene aged rocks, deposited in the outer neritic to bathyal environments (Bustin 1988; Onyia et al. 2002). A recent study (Anyanwu et al. 2021) identified subtle geochemical differences among crude oils from the coastal and offshore Niger Delta, where the coastal crude oils appeared to be sourced from more of planktonic/bacterial organic materials, the offshore oils originated mainly from planktonic/land plants organic materials. Ekpo et al. (2018) using biomarkers from twenty-four crude oil samples from western offshore Niger Delta showed that the oils originated from same source rocks, deposited under an oxic paleoenvironmental condition with a mixture of marine and terrigenous organic inputs. Onojake et al. (2013) reported that crude oil samples from two fields in the Niger Delta originated from terrestrial organic sources and deposited in an oxygenated environment. Akinlua and Ajayi (2009) investigated the origin of crude oils from the central Niger Delta and indicated that the oils originated from organic matter of both terrestrial and marine sources deposited in an oxidized environment.

Similarly, Sonibare et al. (2008) analyzed ten crude oil samples from the onshore and offshore Niger delta and concluded that the oils originated from a mixed origin (marine and terrestrial kerogen). A detailed understanding of the petroleum systems within a hydrocarbon producing basin is an important aspect of petroleum exploration. Geochemical studies indicate that the Niger Delta petroleum belongs to one family (Bustin 1988; Onyia et al. 2002; GhasemShirazi et al. 2014; Sharifi Teshnizi et al. 2021), of a single petroleum system (Ekweozor et al. 1979). There is need to study the petroleum system in each of the five depobelts of the Niger Delta in order to ascertain if there are subtle geochemical differences and relationships. In this study, standard oil geochemical parameters were used to characterize crude oil samples from the five depobelts of the Niger Delta (Fig 2). The objective was to describe the biomarker fingerprints in the crude oils in order to provide information on the origin of organic matter input in the source rock(s), determine the depositional environmental conditions and thermal maturity of the crude oils.

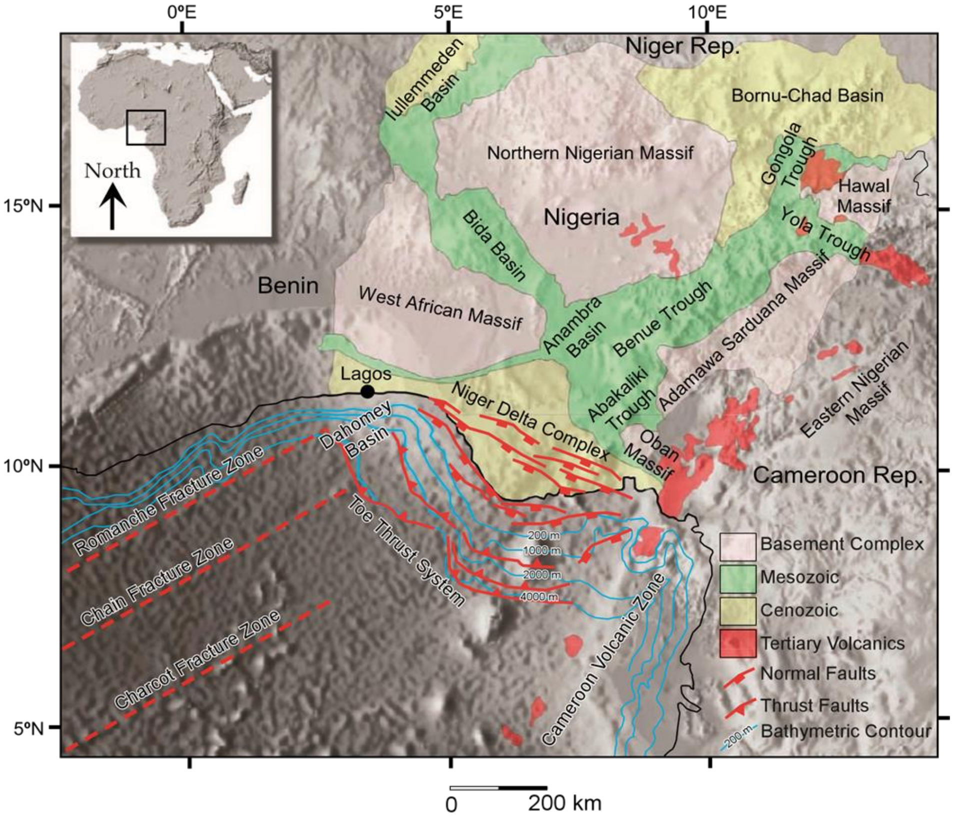

Fig 1. Regional location map of the Niger Delta showing the major sedimentary basins, tectonics and structural features: The topographic and bathymetric features are indicated as (shaded relief) gray-scale image (Corredor et al. 2005).

2. Geology of the Niger Delta basin

The break-up of Gondwana supercontinent is the fundamental events that lead to the evolution of the Niger Delta basin. The origin of this basin is linked to the same processes that formed the Benue Trough, which evolved from the failed arm of rift Triple Junction in the late Jurrassic when convention currents in the asthenosphere caused the break-up of the Gondwana Supercontinent (Burke 1972; Olade 1975). The Benue Trough is a conglomerate of series of pull-apart rifts, resulting from sinistral wrench faulting, structural readjustments (that occurred in the Santonian as a result of dissimilarities in the rate of Atlantic spreading in the Mesozoic) (Burke 1972; Genik 1993). This thermo-tectonic events lead to the folding, uplift and changes of depositional axis in the southern part of the Benue Trough. This resulted to subsidence in the west, south and southeast of the Abakaliki Anticlinorium and the prolongation of the Anambra Basin towards the Calabar area (Adegoke et al. 2017). At this time Anambra Basin was filled with Campanian to Early Paleocene sediments, as subsidence continued in the southern parts of the Benue Trough due to thermal contraction of the lithospheric plates (Turcotte 1977; Onuoha 1981), the Niger Delta Basin evolved (Adegoke et al. 2017; Jehangir Khan et al. 2021). The Benue Trough, the Anambra Basin, and the Niger Delta Basin are a conglomerate of basins stacked vertically in the southern part, and constrained lateral by the fracture zone positions (Fig 3; Fig 4; Fig 5).

The stratigraphy of the Niger Delta basin is made up of the Cretaceous to Holocene clastic sediments which overlie oceanic crust and some remnants of the continental plate (Fig 6). Although the Cretaceous strata can only be inferred from the exposed lithological units of the closest basin, which is the Anambra Basin, because these strata have not been penetrated beneath the Niger Delta (Reijers et al. 1997; Corredor et al. 2005). Stratigraphy of the Tertiary Niger Delta is subdivided into three main Formations, these Formations represents depositional environments that are prograding (Short and Stauble 1965; Doust and Omatsola 1990; Kulke 1995). The Akata Formation occupies the basal part of the Tertiary Niger Delta. This Formation is marine in origin, with a thickness that ranges from 2000m at the distal end of the delta to about 7000m underneath the continental shelf (Doust and Omatsola 1990; Corredor et al. 2005).

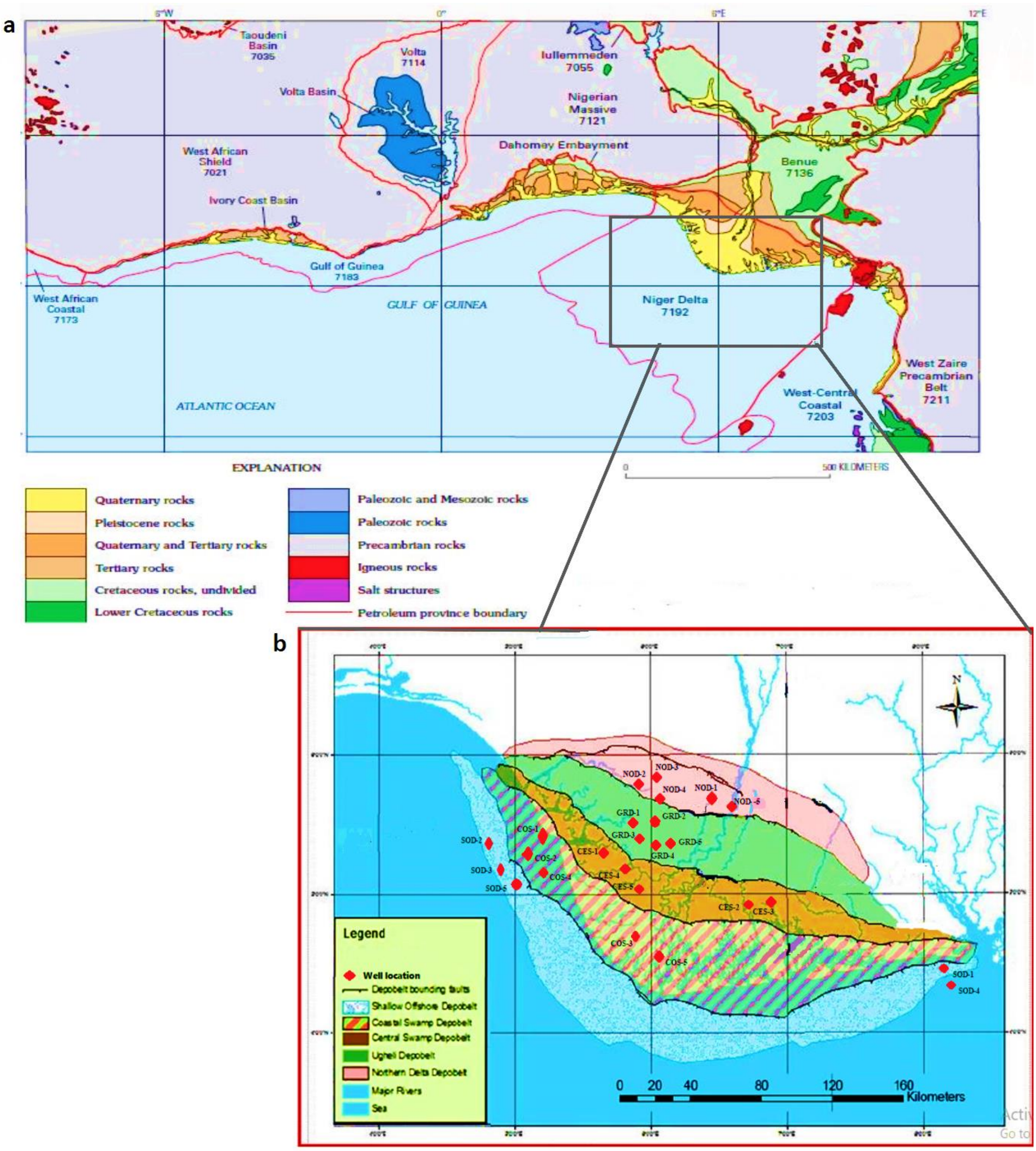

Fig 2. Location of the study area: A. Generalized geologic map of the Gulf of Guinea and surrounding areas (Brownfield and Charpentier 2006); B. Outline map of the Niger Delta. Red Stars show the locations of the twenty five wells in the five depobelts from which crude oil samples were collected for this study (modified from Okosun and Osterloff 2013).

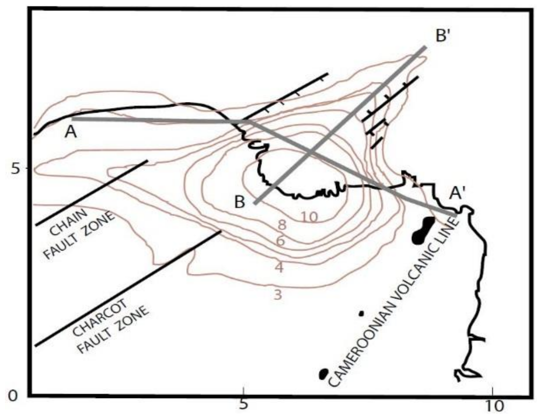

Fig 3. An extension of the Fracture Zones (Chain and Charcot Fracture Zones) into African Plate (Adegoke et al. 2017).

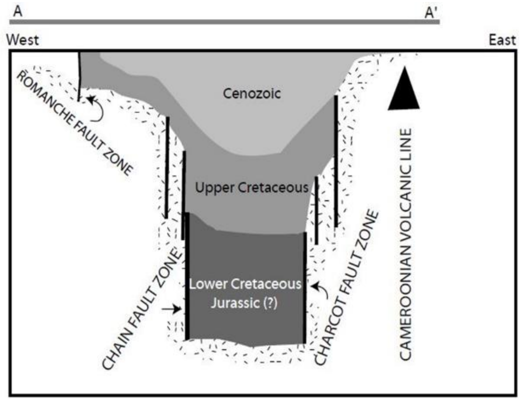

Fig 4. Cross section AA′ in Fig 3 showing the stacking pattern of basins in southern Nigeria (the southern Benue Trough, Anambra Basin, and the Niger Delta Basin) (Adegoke et al. 2017).

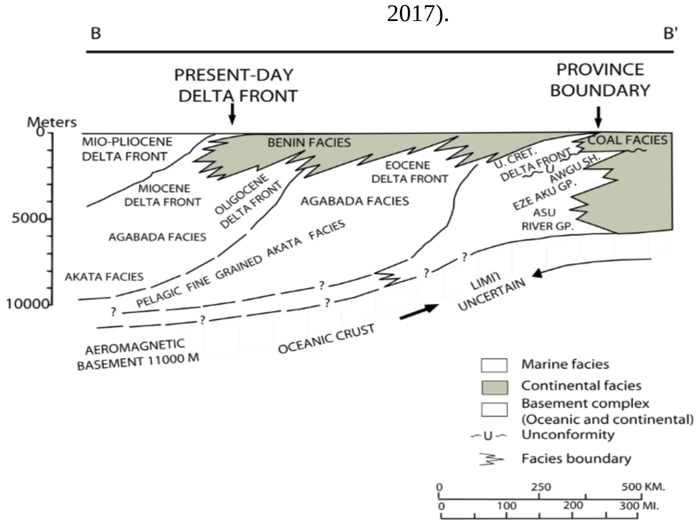

Fig 5. Northeast to Southwest cross section (BB′ section in Fig 3) showing the vertical and lateral lithofacie successions starting from the southern Benue Trough, through the Anambra Basin to the Niger Delta (Adegoke et al. 2017).

The Akata Formation has a thickness of about 5000m in the deep-water fold and thrust belts, due to repetitions of structures in this zone (Bilotti et al. 2005; Corredor et al. 2005). This Formation is made up of thick sequences of shales believed to be the major source rocks with minor amounts of turbidite sands representing possible reservoirs in deeper water regions. The Akata Formation generally lacks internal reflections on seismic sections (Fig 6). Overlying the Akata Formation, is the Agbada Formation which represents the major petroleum-bearing portion in the Niger Delta. This Formation ranged from Eocene to recent, and is made up of paralic clastic strata of more than 3500m thick, representing the true deltaic unit of the sequence (Corredor et al. 2005). The Benin Formation overlies the Agbada Formation, and it is made up of late Eocene to recent (Holocene) deposits of continental origin. This includes the alluvial and coastal-plain sediments of up to 2000m in thickness (Avbovbo 1978; Corredor et al. 2005).

During the Paleocene to Earliest Eocene, marine shales accumulated over much of the Niger Delta resulting to the deposition of the Early – Middle Eocene coarse grained materials of the Agbada Formation in the Northern depobelt while the marine Akata Formation shales were deposited further offshore (Reijers et al. 1997). Paleontological studies of well samples from the Northern depobelt indicated normal marine saline waters, oxygenated conditions and normal temperature conditions of sediment deposition (Ukpong and Anyanwu 2018a; Ukpong and Anyanwu 2018b; Salari and Yazdi 2017). The development of syn-sedimentary growth faults close to the coastlines enabled sands and fines to be trapped along the coast resulting in the progradation of the delta during the Oligocene and Earliest Miocene. The deposition of sediments was very much affected by the long shore currents which helped in the distribution of the sediments and the formation of a thick clastic sequence referred to as the Greater Ughelli depobelt (Reijers et al. 1997), having an abundance composition of the siliciclastic sediments of the Agbada Formation deposits (Ukpong et al. 2017).

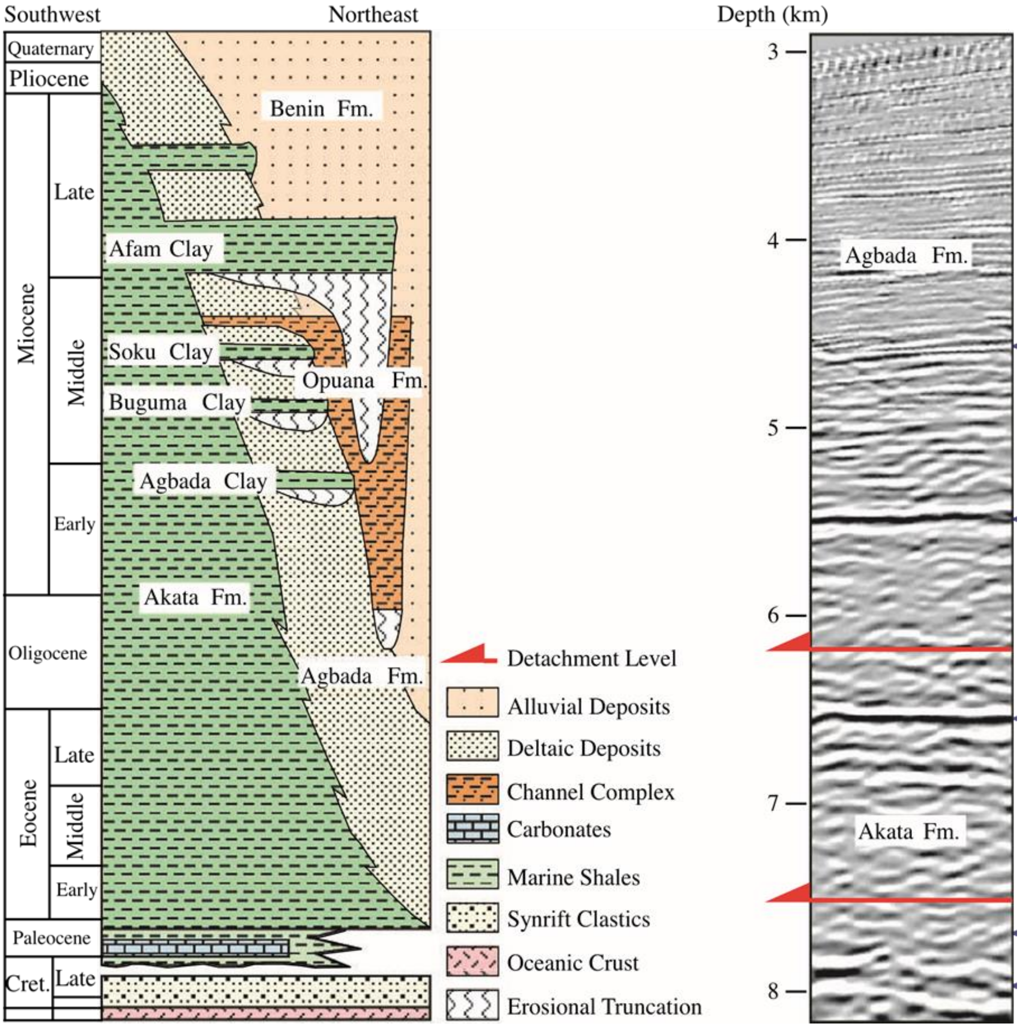

Fig 6. Diagrammatic description of the regional stratigraphy of the Niger Delta basin and the variable density-seismic display of the major stratigraphic sections (Corredor et al. 2005).

The paleohigh of the Abakaliki uplift which was active during this time separated the developing Niger Delta into different units each with its own characteristic paleodrainage pattern resulting to sediments deposition in the Central Swamp and the northern part of the present-day Coastal Swamp depobelts (Reijers et al. 1997). The Coastal Swamp and Shallow Offshore depobelts were formed during periods of steady delta progradation in the Late Miocene to Pliocene ages (Reijers et al. 1997).

3. Materials and methods

A suit of twenty five (25) crude oil samples from twenty five (25) oil producing wells were randomly collected from the five depobelts of Niger Delta basin (Fig 2), for this study. The crude oils were sampled from the wellheads under atmospheric conditions. Fractionation of the crude oil samples into saturates, aromatics and NSOs was carried out following standard procedures involving column chromatography with hexane, toluene and methanol respectively (Eneogwe et al. 2002). Evaporation of solvents were done in a stream of nitrogen. Gas chromatography-mass spectrometry (GC-MS) analyses were carried out on the saturated hydrocarbon fractions by using an Agilent HP5 ms column. The oven operating temperature condition for the GC MS was held at 55 °C for 1 min, 25°C/min. to 320°C held for 35 min. Sample injection was by splitless mode at an injector temperature of 290 °C, the electron ionization mode was 70 eV. The carrier gas was helium (He) at constant flow condition. The EI Scan mode was used to analyse the samples with source and quadrupole temperatures of 350°C and 150°C respectively. The data was processed using Chem Station G1701BA software, peak integration was done using the RTE integrator. Peak identification was based on retention times and comparison with set standards, literatures and elution order of compounds (Peters et al. 2005; Wang et al. 2006). The peak area of individual compounds was transferred to an Excel spreadsheet for calculation of ratios, preparation of tables and plotting.

4. Results and Discussion

4.1. n-Alkanes and acyclic isoprenoids

The n-alkanes distribution is very useful in determining source input of organic matter (Duan and Ma 2001). The representative chromatograms ion (m/z 71) of the saturated fractions showing n-alkanes and acyclic isoprenoids distribution are shown on Fig 7. The acyclic isoprenoids in the form of pristane and phytane occur in appreciable amounts in the crude oil samples. The major source of pristine and phytane is the phytyl side chain of chlorophyll (a) in phototrophic organisms and bacteriochlorophyll (a) and (b) in purple sulfur bacteria (Powell and McKirdy 1973). Pristane (Pr) and phytane (Ph) ratios less than one (Pr/Ph <1) in crude oil show anoxic source-rock deposition environment, while Pr/Ph >1 show oxic conditions of deposition (Didyk et al. 1978). Very high values of greater than or equal to three (≥ 3) indicate high oxidizing conditions associated with sources from terrestrial organic matter input (ten Haven et al. 1987; Peters et al. 2005). The Pr/Ph ratio for the crude oils from the Northern depobelt ranged from 0.75 to 3.87, 0.99 to 1.79 for Greater Ughelli oils, 0.63 to 2.08 for Central swamp oils, 1.01 to 1.57 for Coastal swamp oils and 0.62 to 4.61 for Shallow offshore oils (Table 1). The distribution of the isoprenoid ratios suggests an oxic to suboxic depositional conditions in all the depobelts. The cross plot of the Pr/n-C_{17} versus Ph/n-C_{18} was used to identify the organic matter contributions and depositional environments of the crude oils (Fig 8). The Pr/ n-C_{17} ratio ranged from 0.12- 12.53 while the Ph/n-C_{18} values ranged from 0.17-8.10 in all the depobelts. The values observed for the Pr/Ph ratios as well as the relationship between Pr/n-C_{17} versus Ph/n-C_{18} observed in almost all the oils from the five depobelts suggest major source input from mixed marine- terrestrial organic matter of Type II/III kerogen and marine algal organic matter of Type II Kerogen deposited under oxic-suboxic paleoenvironmental conditions (Fig 8; Peters et al. 1999). The distribution patterns of the n-alkanes and isoprenoids on the mz 71 chromatograms (Fig 7) shows biodegradation effect on the crude oils. The conspicuous chromatographic baseline hump represents the unresolved complex mixture (Peters et al. 2005). The sampled crude oils showed varying degrees of biodegradation (Fig 7). Biodegradation of crude oils is a function of bacterial alteration of the crude oil compositions (Peters et al. 2005; El-Sheshtawy et al. 2020). El-Sheshtawy et al (2020) demonstrated the effect of bacterial alteration on two shale samples from the Campanian Oil Shale of Egypt. Intense bacterial alteration of organic materials under sulfidic/anoxic conditions encourages the enrichment of metals such as Molybdenum (Mo), Nickel (Ni), and Vanadium (V) (Farouk et al. 2020), heteroatomic compounds (NSO's) with a corresponding removal of n-alkanes and saturated hydrocarbons (Peters et al. 2005).

Table 1. n-Alkanes and acyclic isoprenoids ratios of the crude oils from the five depobelts of the Niger Delta

SAMPLES	Pr/Ph	Pr/(Pr + Ph)	Pr/n-C17	Ph/n-C18	CPI	Waxi. Index
Northern Depobelt						
NOD-1	3.87	0.79	2.95	0.43	1.17	1.51
NOD-2	0.75	0.43	0.19	1.08	1.14	0.76
NOD-3	1.76	0.64	1.12	0.71	1.05	3.23
NOD-4	1.9	0.65	0.74	0.46	1.03	1.67
NOD-5	-	-	-	-	-	-
Greater Ughelli						
GRD-1	0.99	0.5	0.32	0.46	1.1	1.08
GRD-2	1.71	0.63	0.25	0.31	1.1	1.24
GRD-3	1.04	0.51	0.26	0.53	0.99	0.69
GRD-4	1.69	0.59	0.23	0.33	1.11	1.22
GRD-5	1.01	0.53	0.33	0.5	1.13	1.1
Central Swamp						
CES-1	2.08	0.68	0.9	1.2	0.92	0.05
CES-2	0.65	0.4	0.51	2.6	1.02	1.4
CES-3	0.63	0.39	0.5	2.59	1.01	1.41
CES-4	0.98	0.5	1.08	0.41	1.06	0.37
CES-5	2.01	0.66	0.89	1.22	1.03	0.09
Coastal Swamp						
COS-1	1.21	0.55	0.83	1.32	0.99	3.09
COS-2	1.01	0.5	0.54	0.6	0.68	1.31
COS-3	1.23	0.54	0.8	1.29	1.01	2.9
COS-4	1.57	0.61	0.66	0.73	0.93	1.42
COS-5	1.35	0.56	0.82	1.33	0.98	3.1
Shallow Offshore						
SOD-1	0.62	0.38	0.25	9.23	1.21	1.79
SOD-2	2.85	0.74	0.63	0.25	1.24	1.78
SOD-3	1.63	0.62	3.51	1.85	0.87	5.43
SOD-4	4.61	0.82	12.53	0.17	0.87	0.09
SOD-5	0.63	0.41	0.28	8.1	1.22	1.8

*Pr- Pristane, Ph- Phytane

* Pr/(Pr + Ph) - Pristine/ (Pristine + Phytane)

*CPI- Carbon Preference Index = Odd number n-alkanes/even numbered n-alkanes (Bray and Evans, 1961).

*Waxiness Index (Wax. Index)– Σ (n-C21- n-C31)/Σ (n-C15 - n-C20)

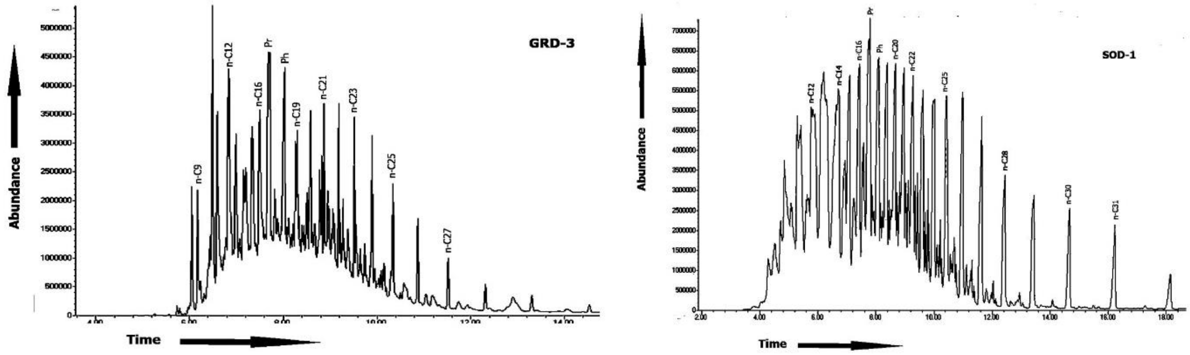

Fig 7. Representative mass chromatograms (71 m/z ion) for the crude oil samples from the five depobelts of the Niger Delta. Pr = pristine and Ph = phytane.

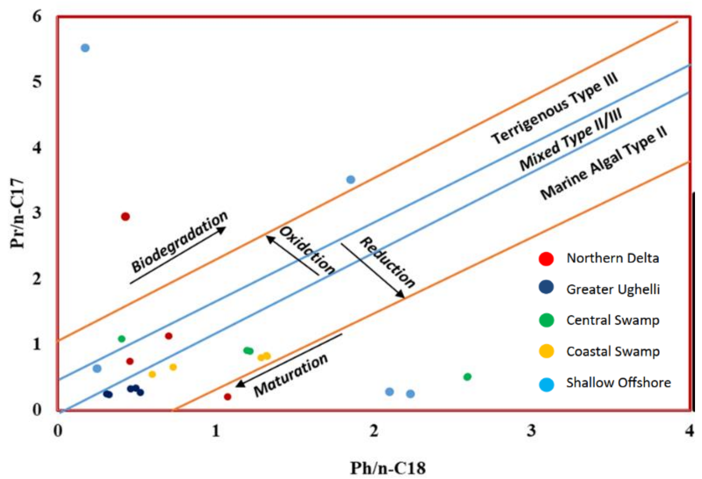

Fig 8. Plot of pristane/n-C17 versus phytane/n-C18 used to infer paleoenvironment and the precursor organic matter in the source rock (Peters et al. 1999). The increase in thermal maturity is shown using the arrow pointing towards the lower left while increasing biodegradation is demonstrated using the arrow pointing to the upper right.

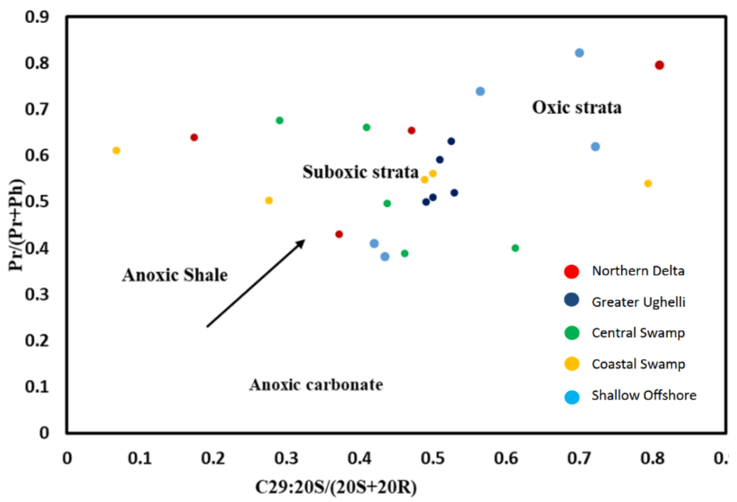

Fig 9. Cross plot of C_{29}: 20S/(20s+20R) versus Pr/(Pr + Ph) ratios for the crude oil samples from the five depobelts of the Niger Delta. The arrow show direction of thermal maturation

The Pr/n-C_{17} versus Ph/n-C_{18} relationships in the crude oils suggests major terrestrial input. The calculated Pr/(Pr + Ph) values correlated well with the C_{29}: 20S/(20S+20R) values for the Niger Delta oils (Fig 9). The ratio of Pr/(Pr + Ph) will increase with an increase in the clay content (acidity), and is related to the redox potentials of the environment during sediment deposition (Moldowan et al. 1986; Ten Haven et al. 1987; Moldowan et al. 1994).

The calculated Carbon preference index (CPI) values were also used to interpret the depositional environmental conditions (Peters et al. 2005). The Niger Delta oils contain relatively low to moderate ranges of Carbon preference index values. CPI values ranged from 1.03 to 1.17 for the Northern depobelt oils, 0.99 to 1.13 for the Greater Ughelli oils, 0.92 to 1.06 for the Central Swamp oils, 0.68 to 1.01 for the Coastal Swamp oils and 0.87 to 1.24 for the Shallow Offshore oils (Table 1). Cross plot of CPI versus Pr/Ph ratios of the analyzed crude oil samples from the Niger Delta (Fig 10), indicates more oxidizing environmental condition than a reducing condition of deposition (Waples 1983). This agreed with the correlation between pristane/(pristane + phytane) and C_{29}: 20S/(20S+20R) (Fig 9), which indicated an oxic to suboxic paleoenvironmental conditions of deposition (Moldowan et al. 1994). The degree of waxiness which is usually expresses as Σ (n-C_{21}- n-C_{31})/Σ (n-C_{15} - n-C_{20}) was applied to determine the amount of terrestrial organic matter input in the crude oils source rocks. This technique is based on the idea that land derived organic materials is a major contributor to higher molecular weight n-paraffin in crude oil and therefore can be useful as a source parameter (Hedberg 1968; El Diasty and Moldowan 2012). The Niger Delta oils contains waxy oils in abundance (waxiness >1) (Table 1). The waxiness index ranged from 0.76 to 3.23 for crude oils from the Northern depobelt, 0.69 to 1.24 for Greater Ughelli oils, 0.05 to 1.491 for Central Swamp oils, 1.31 to 3.10 for Coastal Swamp oils and 0.09 to 5.43 for the Shallow Offshore oils. The cross plot of Pr/Ph ratio versus waxiness index indicates an increasing composition of terrestrial plant organic materials and oxygen rich conditions of deposition for the analyzed crude oil samples (Fig 11).

4.2 Sterane biomarker fingerprints

Steranes measured using GC-MS and monitored with ion (m/z 217+218) are important biomarker groups that are capable of retaining the characteristic structure of precursor organic compounds in petroleum hydrocarbons. Thus, they can yield very important information useful to interpret genetic relationships and depositional conditions of the organic matters in crude oil. The representative GC-MS chromatograms of steranes distribution are shown in Fig 12a to Fig 12c. Table 2 shows the diagnostic biomarker (steranes and hopanes) ratios of the crude oils from the five depobelts of the Niger Delta basin. The peaks identification is shown on Table 3. The steranes are known to be associated with the sterols found in eukaryotic organisms such as algae and higher plants but are absent in the prokaryotes. A study of recent marine and continental sediments showed that the distribution of C_{27}, C_{28}, and C_{29}-sterol homologs on a ternary plots could be used to indicate ecosystems and source input of organic matter in crude oil and source rocks (Huang and Meinschein 1979). The dominance of C_{27} steranes were used to indicate source input from marine algae while predominance of C_{29} sterols were used to indicate source inputs from land plant and from cyanobacteria (Huang and Meinschein 1979). As shown in the chromatograms (Fig 12a to Fig 12c), the C_{27}, C_{28}, and C_{29}-sterol homologs are almost of equal proportion in all the analyzed oil samples.

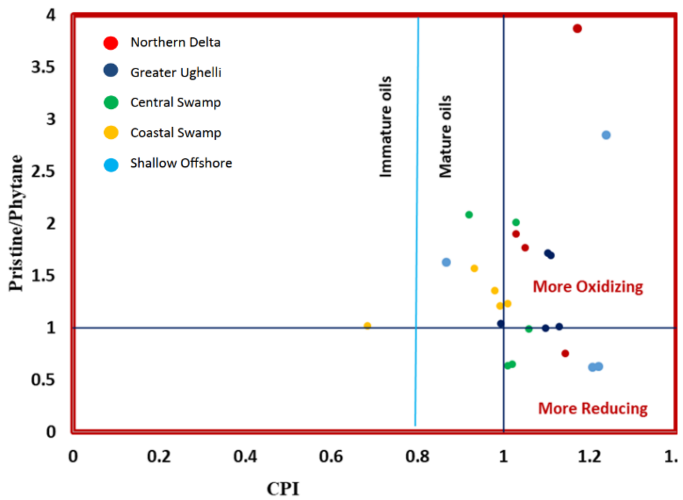

Fig 10. Cross plot of CPI versus Pristine/Phytane ratios for the crude oil samples from the five depobelts of the Niger Delta.

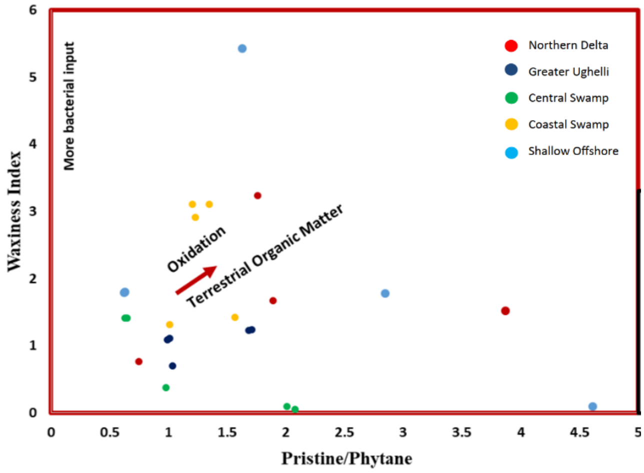

Fig 11. Cross plot of pristine/phytane ratio versus waxiness index (El Diasty and Moldowan 2012).

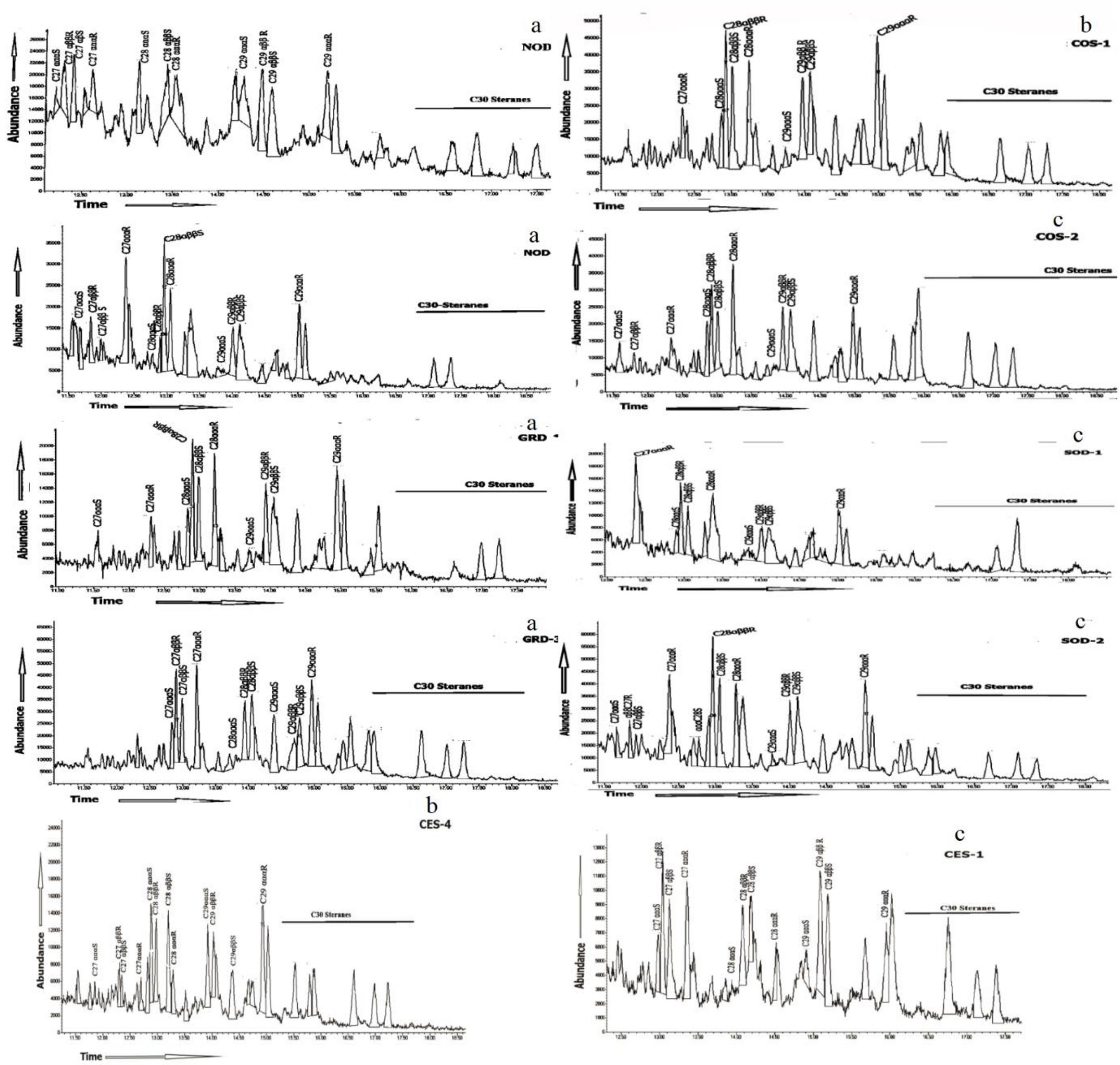

Fig. 12 Representative mass chromatograms 217+218 m/z ion for crude oil samples a)from the Northern (NOD) and Greater Ughelli (GRD) depobelts of the Niger Delta b) from the Central Swamp depobelt (CES) of the Niger Delta c) from the Coastal Swamp (COS) and Shallow Offshore (SOD) depobelts of the Niger Delta

The ternary plot (Fig 13), showed that this crude oils originated from a siliciclastic mixed marine and terrestrial sources, with major organic matter input from eukaryotic organisms (marine algae and land plants) and planktonic bacterial (Huang and Meinschein 1979; Peters et al. 2005). This observation agrees with Ekpo et al. (2018) that used biomarker ratios from twenty-four crude oil samples from western offshore Niger Delta to show that the oils originated from a mixture of marine and terrigenous organic matter input. The distribution of the percentage regular steranes (C_{27}, C_{28} and C_{29}) also show that the crude oils are genetically related, belonging to one source family (Fig 12a to Fig 12c; Table 2).

High values (>1) of $\%C_{29}/\%C_{27}$ sterane ratios are used to indicate origin from land plants (terrigenous environment) while lower values (< 1) indicate origin from marine planktonic bacterial (Peters et al. 2005; Peters and Moldowan 1993). The $\%C_{29}/\%C_{27}$ regular sterane ratios ranged from 1.00 to 1.70 for the Northern depobelt oils, 1.12 to 1.53 for Greater Ughelli oils, 1.00 to 3.78 for Central Swamp oils, 0.46 to 1.69 for Coastal Swamp oils and 0.95 to 1.84 for the Shallow Offshore oils (Table 2). These values observed for the $\%C_{29}/\%C_{27}$ regular sterane ratios indicates source organic matter origin from land plants (terrigenous environment), except for some crude oil samples from the Coastal Swamp that showed lower values (>1) for $\%C_{29}/\%C_{27}$ sterane ratios (Table 2). High concentrations of steranes and higher steranes/hopanes ratio (≥1) are used to indicate input from marine organic matters of planktonic and benthonic algal origin (Peters et al. 2005). Similarly, low steranes and lower steranes/hopanes ratio (≤ 1) are used to indicate terrestrial input or microbially reworked organic matter (Tissot and Welte 1984; Peters et al. 2005). The ratio of regular steranes/17α-hopanes observed for the analyzed crude oil samples were very low (≤ 1) (Table 2). This indicates major source input from terrestrial materials or microbial reworked organic matter (Tissot and Welte 1984; Peters et al. 2005).

Table 2. Diagnostic biomarker (Steranes and Hopanes) ratios of crude oils from the five depobelts of the Niger Delta basin

SAMPLES	C28/C29 Steranes	C29/C28 Steranes	C29/C27 Steranes	% C29	%C28	%C27	C29: 20S/ (20S+20R)	Ster./Hop	Ts/ (Ts+Tm)	Ts/Tm	Olea. index	C31H/ C30H	Mor./ C30Hop	C32H: 22S/ (22S + 22R)
Northern Depobelt														
NOD-1	0.94	1.07	1.67	39.4	36.94	23.66	0.81	0.14	0.66	2.28	0.89	0.34	0.21	0.60
NOD-2	0.39	2.57	1.7	50.54	19.65	29.81	0.37	0.06	0.54	1.16	0.39	0.34	0.17	0.58
NOD-3	0.91	1.1	1.28	37.25	33.72	29.03	0.17	0.19	0.7	2.36	0.97	0.33	0.2	0.58
NOD-4	0.7	1.4	1.00	37.0	25.85	37.09	0.4	0.13	0.59	1.41	0.75	0.36	0.13	0.57
NOD-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Greater Ughelli														
GRD-1	0.93	1.08	1.51	38.6	35.87	25.53	0.49	0.19	0.54	1.17	0.75	0.36	0.16	0.54
GRD-2	0.79	1.27	1.12	37.34	29.41	33.25	0.53	0.14	0.48	0.91	0.84	0.34	0.16	0.56
GRD-3	0.92	1.06	1.52	40.6	33.87	25.53	0.5	0.18	0.44	0.78	0.71	0.32	0.16	0.59
GRD-4	0.81	1.25	1.19	39.32	27.41	33.27	0.51	0.15	0.49	0.89	0.83	0.34	0.15	0.56
GRD-5	0.9	1.04	1.53	40.5	32.97	26.53	0.52	0.18	0.53	0.16	0.76	0.35	0.16	0.52
Central Swamp														
CES-1	0.52	1.93	1.01	39.9	20.71	39.38	0.29	0.16	0.45	0.81	0.91	0.32	0.16	0.57
CES-2	0.62	1.61	1.00	38.16	23.73	38.11	0.61	0.2	0.83	4.78	0.95	0.34	0.19	0.57
CES-3	0.76	1.31	1.19	38.4	29.22	32.39	0.46	0.36	0.5	0.99	0.64	0.39	0.24	0.57
CES-4	0.56	1.79	3.78	54.81	30.68	14.51	0.44	0.15	0.47	0.88	0.89	0.33	0.17	0.64
CES-5	0.53	1.9	1.03	40.11	19.61	39.37	0.41	0.19	0.48	0.82	0.93	0.35	0.16	0.55
Coastal Swamp														
COS-1	0.58	1.73	0.99	38.64	22.38	38.97	0.49	0.21	0.52	1.08	0.9	0.35	0.19	0.55
COS-2	0.54	1.85	1.13	41.29	22.29	36.42	0.28	0.16	0.43	0.74	0.9	0.34	0.19	0.58
COS-3	1.14	0.88	0.46	23.29	26.58	50.13	0.79	0.51	0.61	1.54	0.7	0.23	0.12	0.61
COS-4	0.45	2.23	1.69	49.03	21.94	29.03	0.07	0.31	0.5	1	0.39	0.33	0.17	0.59
COS-5	0.56	1.69	1.02	40.74	20.38	38.87	0.5	0.22	0.51	1.06	1.01	0.33	0.18	0.56
Shallow Offshore														
SOD-1	1.07	0.93	1.06	33.2	35.57	31.23	0.43	0.09	0.6	1.47	0.43	0.29	0.23	0.60
SOD-2	1.53	0.66	0.95	27.98	42.69	29.33	0.56	0.28	0.52	1.09	0.99	0.29	0.26	0.59
SOD-3	0.53	1.89	1.84	48.23	25.49	26.27	0.72	0.07	0.51	1.06	4.67	0.27	0.17	0.58
SOD-4	0.55	1.91	1.6	50.24	22.48	27.27	0.7	0.09	0.53	1.08	4.76	0.3	0.18	0.56
SOD-5	1.06	0.86	1.08	40.1	28.67	31.33	0.42	0.1	0.55	1.5	0.42	0.3	0.22	0.6

*C_{29}: 20S/(20s+20R) - C_{29} αα 20S stigmastane/(C_{29} αα 20S stigmastane + C_{29} αα 20R stigmastane)
* Ster./Hop. - Regular Steranes /17α-hopanes
* Ster – Steranes, * Hop- Hopane , *$\%C_{27}$ Steranes, *$\%C_{28}$ Steranes, *$\%C_{29}$ Steranes, *Oleanane index (Olea. Index) - α-oleanane/ C_{30} 17α (H)-hopane
*Ts/(Ts+Tm):- 18α(H)-trisnorhopane /(18α(H)-trisnorhopane +17α(H)-trisnorhopane)
*Ts/Tm: 18α(H)-trisnorhopane/17α(H)-trisnorhopane
*$C_{31}H/C_{30}H$- C_{31}-17a(H), 21b(H)-30 homohopane (22S+22R)/2/ (C_{30} 17α (H)-hopane)
*Mor./C_{30}Hop- C_{30}-17b(H), 21a(H)-moretane/ C_{30} 17α (H)-hopane
*$C_{29}/C_{30}H$- C_{29} Tm 17a(H)21b(H)-norhopane/C_{30} 17α (H)-hopane
*$C_{32}H$: 22S/(22S + 22R) - C_{32}-17a(H), 21b(H)-30 bishomohopane (22S)/ (C_{32}-17a(H), 21b(H)-30 bishomohopane (22S)+ C_{32}-17a(H), 21b(H)-30 bishomohopane (22R)

4.3 Hopane (m/z 191) biomarker fingerprints

Just like the steranes, hopanes biomarkers are very important because they retain the characteristic skeletons of the original organic compounds in petroleum and source rocks. The hopanes are monitored on mass chromatogram ion (m/z=191), and are commonly used to determine genetic relationships between crude oils and their source rock depositional environment (Hunt 1996). The mass chromatograms showing the distribution of the hopanes are shown on Fig 14a to Fig 14e. The hopane biomarker ratios (Table 2) suggested source deposition in an oxic to sub-oxic environmental conditions. The hopanes originates from bacteriohopanetetrol and polyfunctional C_{35} hopanoids of prokaryotic microorganisms (Ourisson et al. 1984; Peters et al. 2005). The ratio of Ts (trisnorneohopane) to Tm (trisnorhopane) more than (0.5) has been found to increase as the shale ratio increases, also Ts/Tm ratios begins to decrease later in the course of thermal maturity (Hunt 1996; Van Grass 1990). The Ts/Tm ratios for the Northern depobelt oils ranged from 1.16 to 2.36, 0.16 to 1.17 for the Greater Ughelli oils, 0.81 to 4.78 for Central Swamp oils, 0.54 to 1.54 for the Coastal Swamp oils and 1.06 to 1.50 for the Shallow Offshore oils. The Ts/Tm ratios for the Niger Delta oils showed high values greater than 0.5 (Ts/Tm > 0.5) for all the crude oil samples, except two oil samples (GRD- 1 and GRD-5) in the Greater Ughelli depobelt. This values indicated thermally matured shale source rocks for the crude oils (Hunt 1996; Van Grass 1990). The oleanane index is expressed in this study as 18α (H)-oleanane /C_{30} 17α (H)-hopane. Moderate values for oleanane index was observed in the crude oils from the Northern depobelt (0.39-0.97), the oleanane index for the Greater Ughelli ranged from 0.71 to 0.84, 0.64 to 0.95 and 0.39 to 1.01 for the Central Swamp and Coastal Swamp respectively, and 0.42 to 4.76 for the Shallow offshore depobelt (Table 2). The abundance of oleanane as well as high oleanane index values have been reported in the Tertiary Niger Delta crude oils and source rock (Ekweozor et al. 1979; Udo and Ekweozor 1990; Onojake and Abrakasa 2021). This is an indication of an abundance of higher-plant macerals organic matter (Udo and Ekweozor 1990). A cross plot of oleanane index against the biostratigraphic ages of the depobelts showed gradual increase in the oleanane fingerprints from the older depobelts to the younger ones (Fig 15). Oleanane occurrences in crude oils have been widely used to indicate source inputs from higher-plants of Cretaceous and younger ages. This biological markers are derived from betulins and taraxerene (ten Haven and Rullkotter 1988; Grantham et al. 1983), including other pentacyclic triterpenoids (Whitehead 1974). The increasing oleanane fingerprints from the older depobelts to the younger ones appear to have resulted from increasing terrestrial organic matter input and/or thermal maturity of the source rocks (Moldowan et al. 1994). The Ts/(Tm+Ts) ratio is known to be controlled to some extent by the redox potential of the sediments during the time deposition, and it is also dependent on maturity. The Ts is relatively more stable than the Tm, and as such the Ts/(Ts+Tm) ratios increases with an increase in the thermal maturity as demonstrated using the relationship of Ts/(Ts + Tm) ratio and C29 20S/(20S + 20R) sterane ratio (Fig 16).

The Ts (Ts+Tm) ratios and the C_{29}: 20S/(20S+20R) ratio are maturity indicators, C_{29}: 20S/(20S+20R) ratio increases from 0.0 to about 0.5 (0.52-0.55= attending equilibrium) with continues increase in maturity, this variation in ratio might be a function of isomerization and/or the greater stabilization of the 20S epimer when compared with the 20R epimer (Hunt 1996; Dahi et al. 1999). The C_{29}: 20S/(20S+20R) ratio approaches equilibrium value at/or before the peak of the oil generative window, this is quite distinct from the Ts / (Ts+Tm) ratio which approaches its endpoint around the end of the oil generative window (Peters and Moldowan 1993).

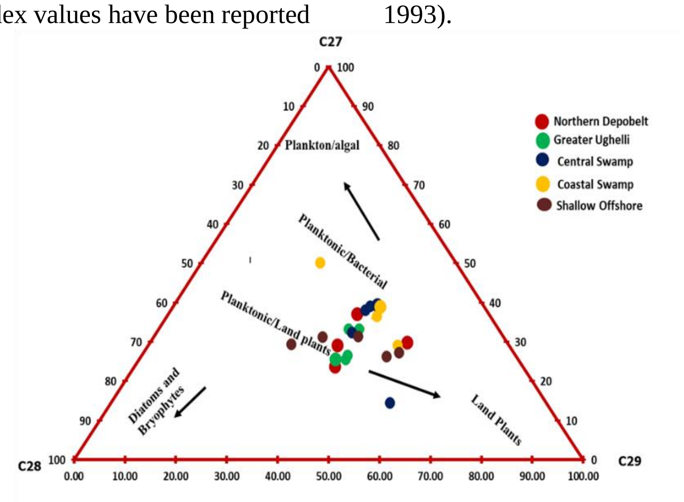

Fig 13. Ternary plot showing the distribution of steranes (C_{27}, C_{28} & C_{29}) for the analysed crude oils from the five depobelts of the Niger Delta (modified after Huang and Meinschein 1979).

Table 3. Identification of peaks on m/z 191 (hopanes) and m/z 217+218 (steranes) mass chromatograms

Peak	Compound name	Peak	Compound name
Ts	18α(H)- trisnorneohopane	C27αββR	C_{27} 13β(H) 17α(H) Diacholestane (20R)
		C27αββS	C_{27} 5α(H) 14β(H) 17β(H) cholestane (20S)
Tm	17α(H)-trisnorhopane	C27αααR	C_{27} 5α(H) 14α(H) 17α(H) cholestane (20R)
		C28αααS	C_{28} 5α(H) 14α(H) 17a(H) ergostane (20S)
αβC29Hop	C_{29} Tm 17a(H)21β(H)-norhopane	C28αββR	C_{28} 5α(H) 14β(H) 17β(H) cholestane (20R)
C29Ts	C_{29} 18α(H) norneohopane (29Ts)	C28αββS	C_{28} 5α(H) 14β(H) 17β(H) cholestane (20S)
βαC29Diahop	C_{29} 17α(H), 21β(H)-25-dinorhopane		
α -ole	18α (H) -oleanane		
αβC30Hop	C_{30} 17α (H)-hopane	C28αααR	C_{28} 5α(H) 14α(H) 17α(H) ergostane (20R)
βαC30Mor	C_{30} 17β(H), 21α(H)-moretane	C29αααS	C_{29} 5α(H) 14α(H) 17α(H) stigmastane (20S)
αβC31SHop	C_{31} 17α(H), 21β(H)-30 homohopane (22S)		
αβC31RHop	C_{31} 17α(H), 21β(H)-30 homohopane (22R)	C29αββR	C_{29} 5α(H) 14β(H) 17β(H) stigmastane (20R)
αβC32SHop	C_{32} 17α(H), 21β(H)-30 bishomohopane (22S)	C29αββS	C_{29} 5α(H) 14β(H) 17β(H) stigmastane (20S)
αβC32RHop	C_{32} 17α(H), 21β(H)-30 bishomohopane (22R)	C29αααR	C_{29} 5α(H) 14α(H) 17α(H) stigmastane (20R)
C27αααS	C_{27} 5α(H) 14α(H) 17a(H) cholestane (20S)		

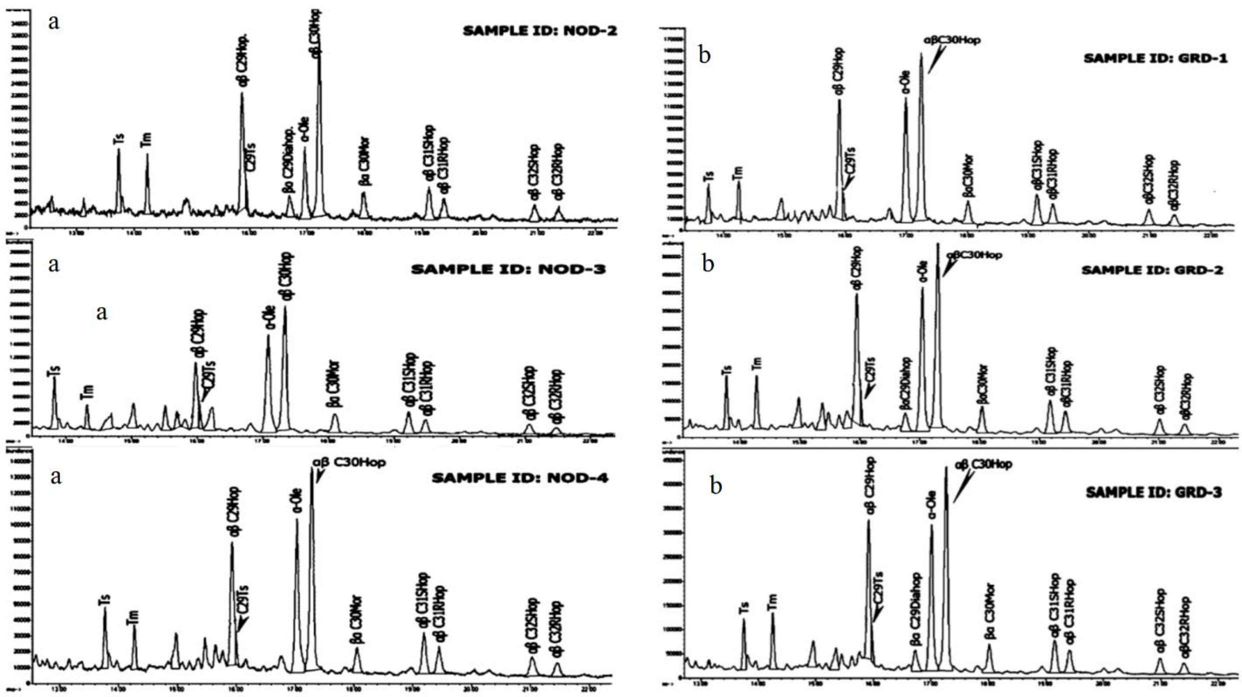

Fig 14. Representative mass chromatograms (m/z 191) showing the distribution of hopanes in the analyzed crude oils from the a) Northern Depobelt of the Niger Delta b) Greater Ughelli depobelt of the Niger Delta

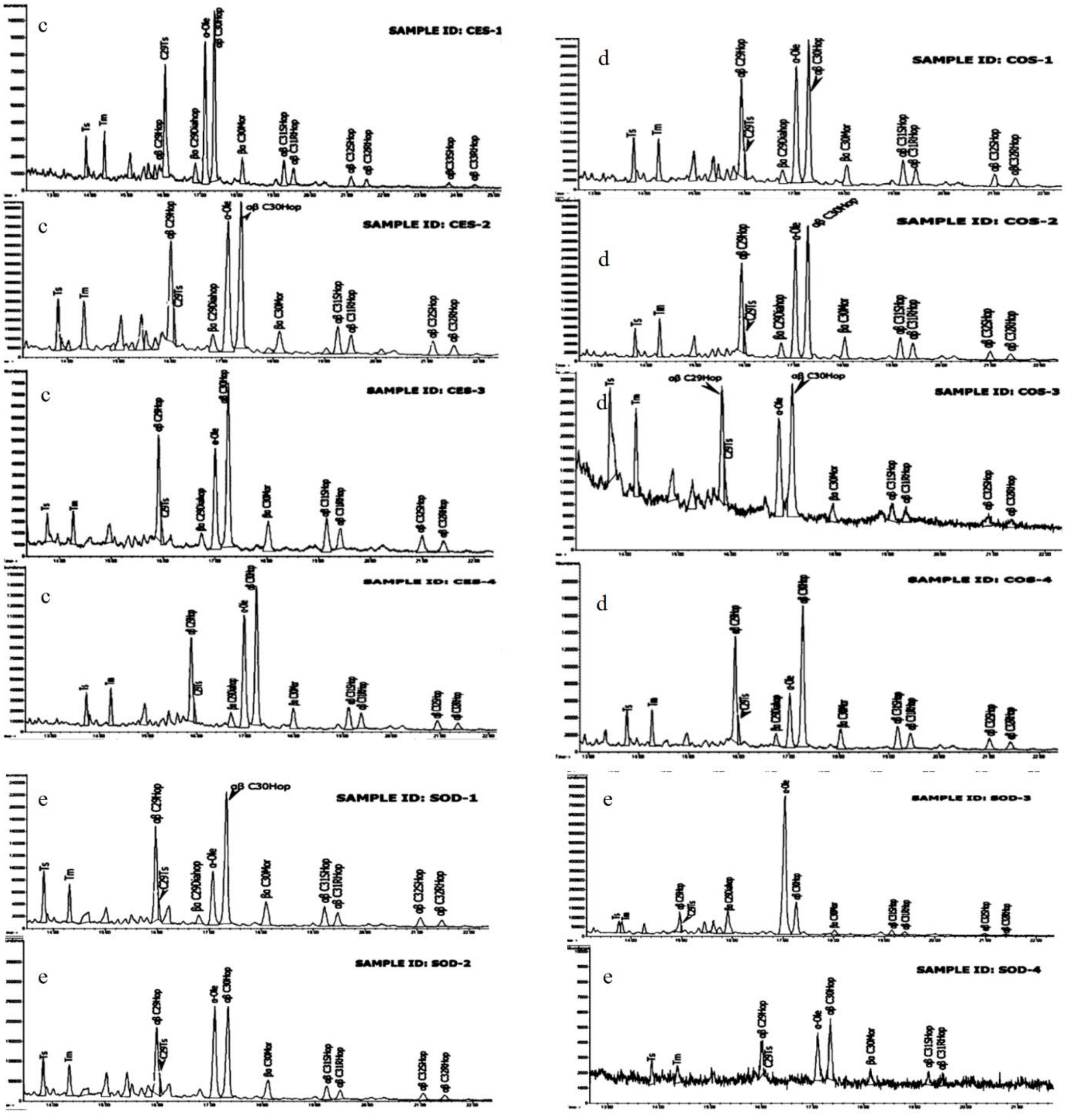

Fig 14. Continued. Representative mass chromatograms (m/z 191) showing the distribution of hopanes in the analyzed crude oils from the c) Central Swamp depobelt of the Niger Delta d) Costal swamp depobelt of the Niger Delta e) Shallow offshore depobelt of the Niger Delta

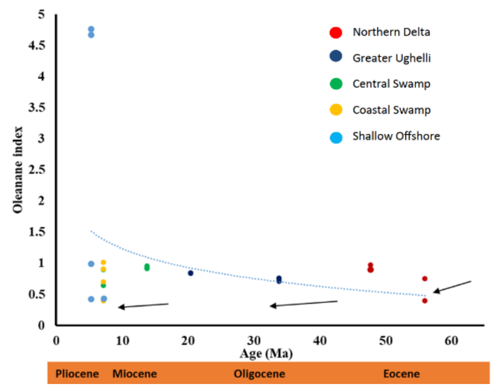

Fig 15. Oleanane index (vertical lines) from the twenty five analyzed representative crude oil samples from the five depobelts of the Niger Delta, horizontal axis indicate the geological/biostratigraphic ages of the depobelts (Reijers et al. 1997); the arrows show the direction of delta progradation and depobelts evolution.

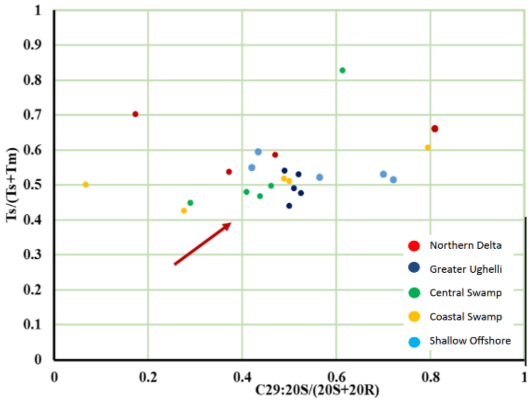

Fig 16. C29 20S/(20S + 20R) regular sterane ratio versus Ts/(Ts + Tm) ratio for the analyzed crude oil samples from the five depobelts of the Niger Delta: The direction of increasing thermal maturity is shown with the red arrow (Hunt 1996).

This means that after the peak point of the oil- generative window, the C_{29}: 20S/ (20S+20R) ratio will remain constant, maintaining the equilibrium value, only Ts/(Ts+Tm) ratio will be increasing with the increase in the thermal maturity. The Ts / (Ts+Tm) ranged from 0.54 to 0.70 for the Northern depobelt oils, 0.44 to 0.54 for greater Ughelli oils, 0.45 to 0.83 for Central Swamp oils, 0.43 to 0.61 for Coastal Swamp oils and 0.51 to 0.60 for Shallow Offshore oils (Table 2). The Ts/(Ts + Tm) ratios and C_{29}:20S/20S + 20R ratio values do not show much significant differences across the five depobelts. This might be related to similarities in source organic matters and/or conditions of deposition of these oils (Dahi et al. 1999). The C_{29} 20S/(20S + 20R) sterane ratio for the Northern depobelt oils ranged from 0.17 to 0.81, 0.49-0.53, for the Greater Ughelli oils, 0.29-0.61 for the Central Swamp oils, 0.07 to 0.79 for the Coastal Swamp oils and 0.42 to 0.72 for the Shallow offshore oils (Table 2). Fig 16 shows Ts/(Ts + Tm) ratio versus C_{29} 20S/(20S + 20R) regular sterane ratio of the crude oils. The Ts/(Ts + Tm) values show that some of the oils had already attained thermal equilibrium while some are just close to thermal equilibrium. The C_{32}H: 22S / (22S+22R) hopane ratio also indicated thermal maturity for the crude oils. C_{32}H: 22S / (22S+22R) ratio increases from 0 - 0.6 to reach equilibrium during thermal maturity, and values of 0.50 to 0.54 are indicative of oil generative window (El-Sabagh et al. 2017). Crude oil samples from the Northern depobelt have C_{32}H: 22S/(22S+22R) values that ranged from 0.57 to 0.60, 0.52 to 0.59 for the Greater Ughelli oils, 0.55 to 0.64 for Central Swamp oils, 0.55 to 0.61 for the Coastal Swamp oils and 0.56 to 0.60 for Shallow Offshore oils. These values suggested that most of these crude oils have reached thermal equilibrium with a high thermal maturity level (Fig 17; El-Sabagh et al. 2017).

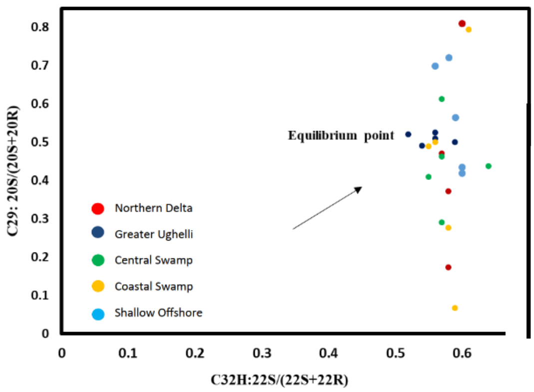

Fig 17. Cross plot of C_{32}H: 22S/ (22S+22R) versus C_{29}: 20S/ (20S+20R); the arrow show the direction of increasing thermal maturity (El-Sabagh et al. 2017).

5. Conclusions

The results of biomarker characterization by Gas chromatography–Mass spectrometry (GC-MS) indicated that the analyzed crude oils belong to the same family (a single petroleum system) with source organic matter originating from land plants (terrigenous environment) and minor organic matter input from planktonic diatoms/bacterial. Palaeoenvironmental analysis base on (Pr/Ph), Pr/n-C_{17}, Ph/n-C_{18} ratio, indicated sub-oxic to oxic paleoenvironmental conditions of deposition. The ratios of n-alkanes and the acyclic isoprenoids indicated mainly marine algal type II and a mixed type II/III kerogen for the studied crude oils. Most of the crude oil samples have C32H: 22S/(22S+22R) values that suggested they have reached thermal equilibrium with a high thermal maturity level. This is supported by the Ts/(Ts + Tm), C29:20S/20S + 20R, oleanane index and CPI values. The biomarker characteristics and distribution pattern in the various depobelts can be used as a fingerprints for crude oil and source rocks correlation across the Niger Delta.

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