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BIOMARKER DISTRIBUTIONS OF THE CAMPANO-MAASTRICHTIAN NKPORO GROUP OF ANAMBRA BASIN, SOUTHEASTERN NIGERIA

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Abstract

Biomarkers are a group of compounds, primarily hydrocarbons, found in oils, rock extracts, recent sediment extracts, and soil extracts. The type/origin of the source rock, depositional environment/age and thermal maturity status of the organic matter contained in the samples were determined based on the distributions and abundance of aliphatic biomarkers in the shale extracts. From the biomarker analysis results, the n-Alkane in Nkporo and Enugu Formations ranges from C_{14}- C_{35} maximizing at C_{14} and C_{20}. This pattern of distribution indicates organic matter derived from marine organic sources. The pristane/phytane ratios of the Nkporo Formation samples range from 0.33-0.78 while that of Enugu Shale samples range from 0.65-0.75. These ratios indicate an anoxic depositional environment rich in marine organic matter. The resultant ratios of isoprenoids/n-alkanes (pristane/n-C_{17} and phytane/n-C_{18}) of Nkporo source rocks range from 0.19 to 2.47 and 0.08 to 1.25. While that of Enugu source rocks range from 0.24 to 0.43 and 0.07 to 0.14. These ratios reflect that most of the Cretaceous source rocks were derived from mixed organic sources, deposited under transitional environment and show a degree of maturation and no biodegradation. Also the nature of kerogen shows that the Nkporo and Enugu source rocks are of Type II/III. The CPI values of the Nkporo Formation range from 0.73 to 1.06 while that of the Enugu Shale range from 0.97 to 1.09 (Table 4.10) indicating that, these source rocks are mainly mature and most probably generated from marine organic sources (Bray and Evans, 1961). Also the plot of CPI against OEP and Pr/Ph against CPI shows that the Nkporo and Enugu source rocks are mature and deposited in a reducing environment respectively. The polycyclic hydrocarbon (triterpanes) distribution showed that the source rock is of marine organic source. The occurrence of oleanene isomers in Nkporo and Enugu samples indicates that it is of the Cretaceous or younger age. The presence of hopane, homohopane (C_{31}-C_{35}) and steranes in the samples showed that the Nkporo and Enugu samples are derived from marine organic sources and are of the early mature stage to generate hydrocarbon.

***Keywords**: GC-MS, Biomarkers; n-Alkanes; Isoprenoids; Triterpanes; Steranes.*

1. Introduction

Several authors have demonstrated the usefulness and organic petrologic methods of accessing the generative potential and characteristics of source rocks in the Anambra Basin [1-4]. The deposition of organic sediments in the Benue Trough was first reported by Murat [5] and examined in greater details by various workers [6-9]. The use of biomarkers as indicators of biogenic, paleoenvironmental, and geochemical processes on earth has been widely accepted [10-16]. Biomarkers are widely used in petroleum geochemical studies for source rock evaluation, oil-oil or oil-source rock correlations, basin evaluation and reservoir management [17]. The objective of this work is to determine the type/origin of the source rock, depositional environment/age and thermal maturity status of the organic matter contained in the samples of the Nkporo Group.

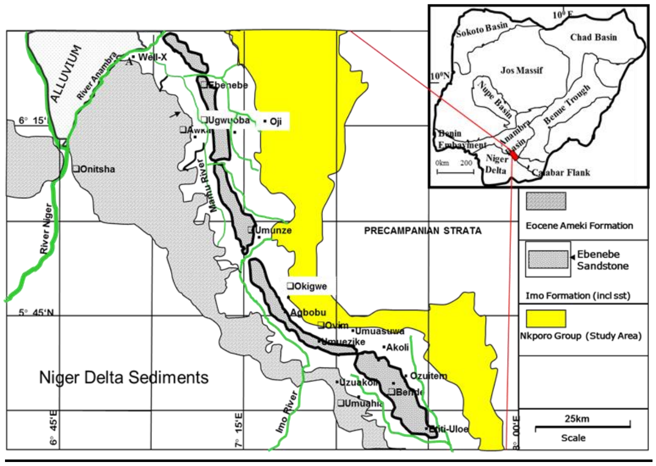

Fig. 1. Geologic map showing the study area

2. Methodology

The saturated hydrocarbon fractions were analyzed for biomarker using a gas chromatographic system coupled with a mass spectrometer (GC-MS). Compound separation was performed on an Agilent 6890 Series GC-instrument equipped with an injection system and a fused silica capillary column (SGE BPX5; 50m length, inner diameter = 0.22 mm, film thickness = 0.25 µm). Helium was used as carrier gas, and the temperature of the GC oven was programmed from 50°C (1 min) to 310°C at a rate of 3°C/min, followed by an isothermal phase of 10 min. The injector temperature was programmed from 52°C to 300°C at a rate of 12°C/sec. For compound identification, the gas chromatographic system was linked to a Finnigan MAT 95 XL mass spectrometer operating in the electron impact mode (70 eV). Full scan mass spectra were recorded from m/z 50 to 650 at a scan rate of 1 s per decade and an interscan delay of 0.2 s, resulting in a scan cycle time of 1.3 s. The GC-MS analysis was performed at the University of Ibadan, Oyo State, Nigeria.

3. Results and discussion

The type/origin of the source rock, depositional environment/age and thermal maturity status of the organic matter contained in the samples were determined based on the distributions and abundance of aliphatic biomarkers in the shale extracts. This was achieved by using the Gas Chromatography- Mass Spectrometry (GC-MS). Ten (10) samples of the Campano-Maastrichtian Nkporo Group (Six samples from Nkporo Formation and four samples from Enugu Shale) were analyzed. These samples have high TOC, Tmax and Vitrinite Reflectance values based on the results gotten from the source rock data. The Gas Chromatography- Mass Spectrometry (GC-MS) are calibrated into three major distributions; n-alkanes and Isoprenoid, Polycyclic Hydrocarbon (Triterpanes) and Steranes.

3.1. n-alkanes and isoprenoid distribution

The specific geochemical parameters, which have been assessed by the aid of C_{15} analysis, are: Normal alkanes, Isoprenoid (pristane/phytane ratio), isoprenoids/n-alkanes ratio and carbon preference index. These parameters can be used for interpreting some geochemical aspects of the studied source rocks such as origin, depositional environments, and biodegradation [18].

3.1.1. Normal alkanes (n-Alkanes)

The distribution of normal alkanes in the saturated hydrocarbons sheds light on the genetic origin of source rock. [19]. It is known that the amorphous sapropelic organic matter is characterized by a maximum peak concentration of C_{14}–C_{25}, reflecting marine organic sources [18].

Furthermore, the organic matters which were derived from the remains of higher vascular plants (terrestrial) are characterized by a maximum concentration of n-paraffins at n-C_{25}–C_{29} [19]

The n-alkane in Nkporo and Enugu Formations ranges from C_{14}- C_{35} maximizing at C_{14} and C_{20}. The gas chromatograms of the n-Alkane in Nkporo and Enugu Formations ranges from C_{14}- C_{35} and are characterized by the predominance of the maximum peak of C_{14}. This pattern of distribution indicates organic matter derived from marine organic sources [17].

3.1.2. Isoprenoid

The most common isoprenoids which are used in this work have a pristane/phytane ratio. The pristane/phytane ratio has been used as an indicator of the depositional environment with a low specificity due to the interferences by thermal maturity and source inputs [17]. The pristane/phytane ratios of oil show some kind of correlation with the canonical variable (CV) values. They are found that the low pristane/phytane ratio (<1) and CV (<0.47) associates with carbonate oils, rich in marine organic matter and more than one of pristane/phytane ratio and CV (>0.47) indicates deltaic oils, derived from the contribution of terrestrial and detrital sediments.

The pristane/phytane ratios of the Nkporo Formation range from 0.33-0.78 while that of Enugu Shale ranges from 0.65-0.75 (Table 1). These ratios indicate an anoxic depositional environment rich in the marine organic matter [17].

Table 1. Source and depositional environment parameters computed from *n*-alkanes and isoprenoids distributions of Nkporo and Enugu Shale

Sample No.	C17	C18	Pr	Ph	Pr/Ph	Pr/nC17	Ph/nC18	CPI	CPI (1)	OEP	OEP (2)
NKP 03	26.857	30.605	27.06	30.605	0.77	0.19	0.08	1.06	0.98	0.48	0.94
NKP 07	26.842	30.304	27.046	30.574	0.55	0.22	0.09	0.84	0.63	0.43	0.73
NKP 08	26.839	30.295	27.035	30.565	0.57	0.34	0.12	1.06	0.87	0.50	0.91
NKP 12	26.835	30.300	27.025	30.596	0.33	2.47	1.25	0.87	0.81	0.87	0.81
NKP 16	26.836	30.296	27.027	30.575	0.78	0.22	0.06	0.85	0.39	0.27	0.60
NKP 17	26.840	30.301	27.032	30.571	0.72	0.25	0.07	0.73	0.58	0.36	0.72
ENU 20	26.832	30.300	27.031	30.572	0.75	0.24	0.07	0.97	0.75	0.44	0.85
ENU 21	26.842	30.299	27.023	30.560	0.65	0.30	0.08	0.98	0.48	0.27	0.72
ENU 24	26.845	30.305	27.113	30.571	0.76	0.43	0.14	1.09	0.91	0.55	0.96
ENU 25	26.846	30.309	27.040	30.584	0.68	0.27	0.11	0.99	0.85	0.50	0.87

Pr = Pristane Ph= Phytane CPI= Carbon Preference Index OEP= Odd-Even Preference
NKP- Nkporo Formation; ENU- Enugu Shale

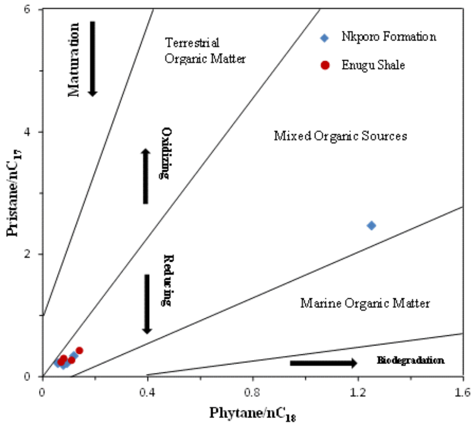

Fig. 2. Plots of Pr/nC17 against Ph/nC18 of showing the organic sources and maturation of Nkporo and Enugu Formation samples [20].

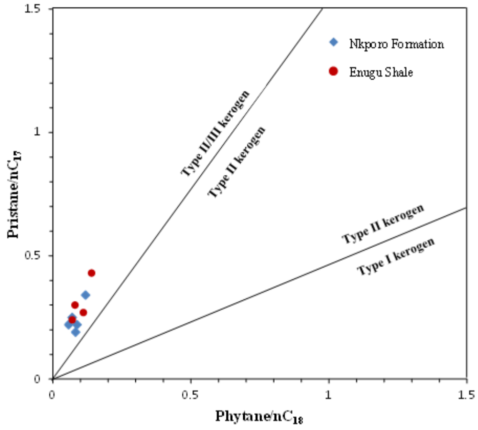

Fig. 3. Plots of Pr/nC17 against Ph/nC18 of showing the type of kerogen of Nkporo and Enugu samples [20]

3.1.3. Isoprenoids/n-Alkanes ratio

Pristane/n-C_{17} and phytane/n-C_{18} ratios have been used for oil–source rock correlation. These ratios are influenced by the nature of kerogen and extent of generation and maturation [17].

The resultant ratios of isoprenoids/n-alkanes (pristane/n-C_{17} and phytane/n-C_{18}) of Nkporo source rocks range from 0.19 to 2.47 and 0.08 to 1.25. While that of Enugu source rocks range from 0.24 to 0.43 and 0.07 to 0.14. (Table 1). These ratios reflect that most of the Cretaceous source rocks were derived from mixed organic sources, deposited under the transitional environment and show a degree of maturation and no biodegradation [20] (Fig. 2). Also, the nature of kerogen shows that the Nkporo and Enugu source rocks are of Type II/III kerogen (Fig. 3).

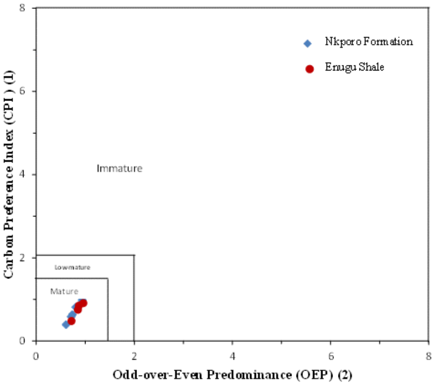

Fig. 4. Plots of CPI against OEP of Nkporo and Enugu samples [21]

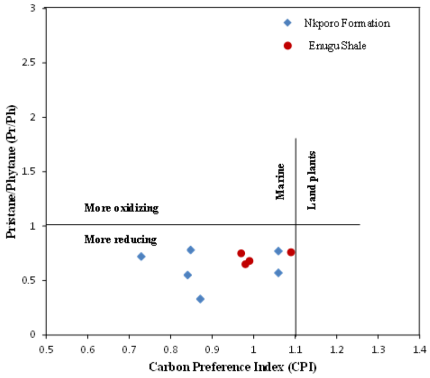

Fig. 5. Plots of Pr/Ph against CPI of Nkporo and Enugu Formation samples [21]

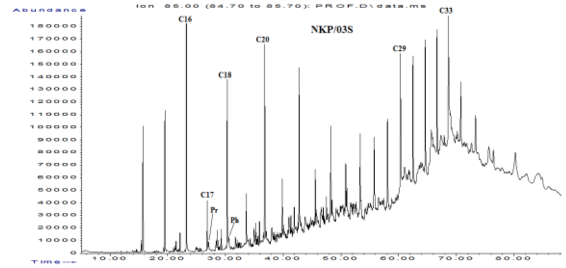

Fig. 6a. Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/03)

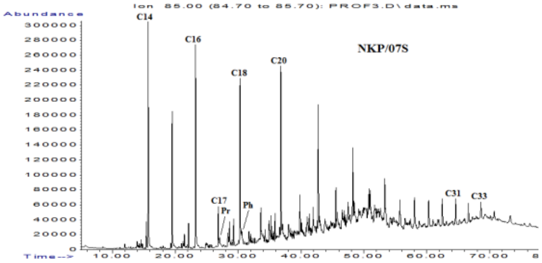

Fig. 6b. Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/07)

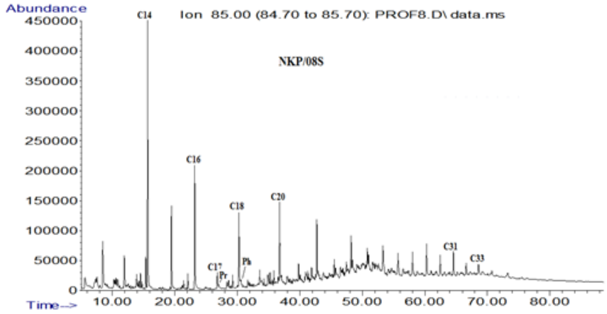

Fig. 6c. Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/08)

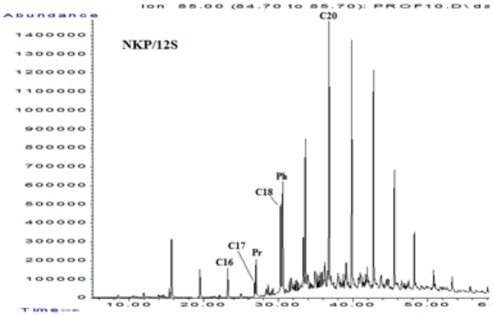

Fig. 6d. Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/12)

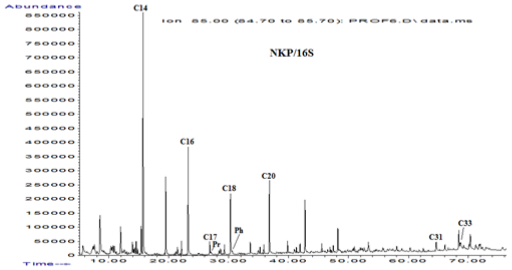

Fig. 6e. Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/16)

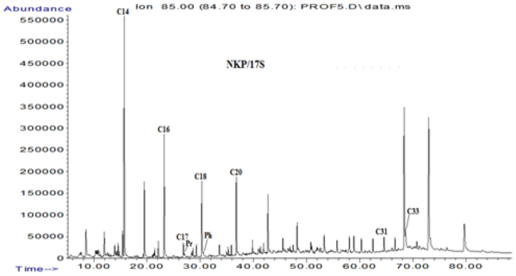

Fig. 6f. Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/17)

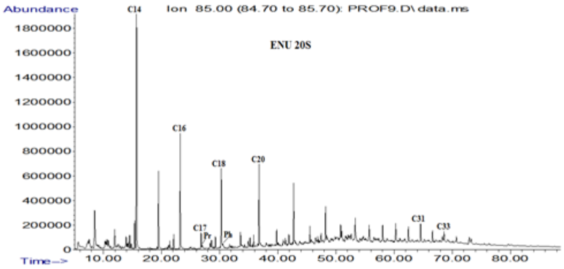

Fig. 6g. Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Enugu Shale (ENU/20)

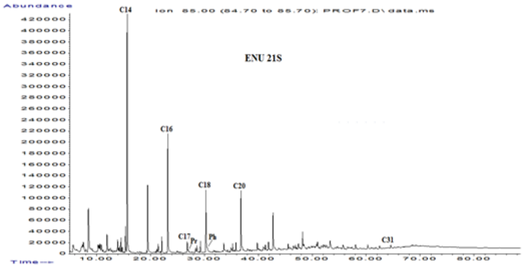

Fig. 6h. Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Enugu Shale (ENU/21)

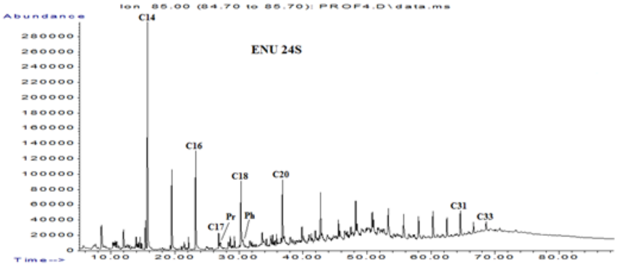

Fig. 6i. Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Enugu Shale (ENU/24)

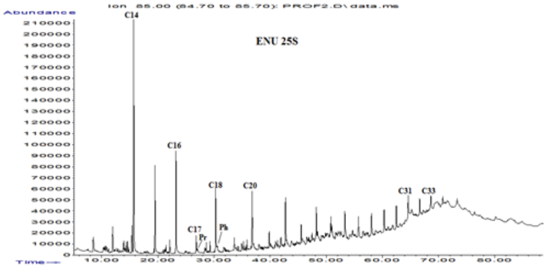

Fig. 6j. Gas chromatograms (mz 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Enugu Shale (ENU/25)

3.2. Polycyclic-hydrocarbons

Polycyclic-hydrocarbon biomarkers (triterpenes) are also considered to be the most powerful tool for oil–source rock correlation due to their resistance to biodegradation [22]. The most common polycyclic biomarker compounds used in this work are tricyclic and tetracyclic terpanes, moretanes, gammacerane, oleanane, and pentacyclic extended hopane. These compounds represent an unusual organic input to the sediment and are abundant in many crude oils generated from lacustrine source rocks, often associated with the hypersaline environment [23].

3.2.1. Tricyclic and tetracyclic terpanes

A series of tricyclic terpanes ranging from C19 to C29 are observed in Nkporo and Enugu Shale samples (Figs. 7 a,b,c,d,e,f,g,h,i and j). The source rocks have low percentages of C19-C26 tricyclic terpanes which indicate organic matter derived from marine origin [24]. The C24tetra/C26tri(R+S) ratios range between 0.63- 2.0 and 0.55-1.54 for the Nkporo Formation and Nkporo Shale respectively, probably both reflecting marine organic matter input [25] (Table 2).

Various ratios of tricyclic terpanes have been used to distinguish marine carbonate, lacustrine, paralic, coal/resin and evaporitic source depositional environments [17,26-28]. The C_{22}/C_{21} tricyclic terpane ratio in the samples range from 0.25 to 1.47 for the Nkporo Formation and

0.57 to 1.07 for the Enugu Shale, suggesting organic matter were both deposited in fluvial/deltaic to the marine depositional environment [17] (Table 2). C_{24}tetra/C_{30}hopane ratio has also been used to assess depositional environment of source rock [17]. C_{24}tetra/C_{30}hopane ratios in the sample range between 0.09 and 0.14 for Nkporo Formation, while that of Enugu Shale is between 0.07 and 0.08. These values also indicate organic matter deposited in the fluvial/deltaic-marine depositional environment [17] (Table 2).

Table 2. Source and depositional environment parameters from tri- and tetracyclic terpanes of Nkporo and Enugu Shale

Sample No.	%C19-C21 triterpane	%C23 triterpane	C24tetra/C26(R+S) tri	C24tetra/ C30Hopane	C22/C21 triterpane
NKP/ 03	NIL	NIL	1.56	NIL	0.7
NKP/07	NIL	NIL	1.78	0.09	0.7
NKP/08	NIL	NIL	0.63	0.08	0.55
NKP/12	58.3	41.7	1.08	0.14	0.27
NKP/16	40.7	59.3	1.16	0.11	0.25
NKP/17	NIL	NIL	2	0.11	1.46
ENU/20	25.1	74.9	0.56	0.08	0.6
ENU/21	NIL	NIL	1.19	0.08	0.83
ENU/24	NIL	NIL	1.54	0.07	1.07
ENU/25	NIL	NIL	0.55	0.08	0.57

C24tetra/C30hopane = C24tetracyclic terpane/C30hopane;
C24tetra/C26(R+S)tri = C24tetracyclic terpane/C26(R+S)tricyclic terpane;
NKP- Nkporo Formation; ENU- Enugu Shale

3.2.2. Moretanes

High moretanes concerntration seemed to be abundant in organic materials of terrestrial origin [29]. Also very low moretanes concerntration seemed to be abundant in organic materials of marine origin (Figs. 7 a,b,c,d,e,f,g,h,i and j) shows that moretanes (peak MOR, see peak identification in Table 4) in the Nkporo and Enugu Shale extracts are has very low concentrations and slightly abundant, indicating contribution from marine sources [29]. Moretanes are less stable with an increase in maturity; this is because of their relatively low concentrations in oil samples [29] (Figs. 7 a,b,c,d,e,f,g,h,i and j).

3.2.3. Gammacerane

High gammacerane concentrations were originally considered to be markers for lacustrine facies. Gammacerane occurs in major or minor concentrations in many rocks that are definitely not of lacustrine origin as they are dominant in marine rocks [30]. The lacustrine environment had abundant gammacerane and considered also as a salinity marker [31]. Gammacerane (peak G, Figs. 7 a,b,c,d,e,f,g,h,i and j, see peak identification in Table 4) is only detected, in a relatively low amount, in the both Nkporo and Enugu source rock extract indicating input of marine organic matter in different saline environments.

3.2.4. Oleanane

Low or absent oleanane concentrations are originally considered to be markers for marine facies [32]. Also, high oleanane concentrations are originally considered to be markers for terrigenous facies [32]. Figs. 7 a,b,c,d,e,f,g,h,i and j shows that oleanane (peak OLE, see peak identification in Table 4) of the Nkporo and Enugu Shale extracts has very low concentrations, both indicating contribution from marine sources [29]. Oleananes are regarded as a reliable marker for angiosperm; being significant constituents of wood, roots, and bark in Cretaceous or younger effective source rocks in deltaic petroleum system [17,24,34-37]. There is the presence of oleananes in both Nkporo and Enugu Formations which is an indication of organic matter from higher land plants of Cretaceous or younger age.

3.2.5. Pentacyclic extended hopane

The unusually large amount of C_{35} extended hopane seems to be associated with marine carbonates or evaporites [38]. High C_{35}/C_{34} ratios in the marine environment with a low redox potential rather than with lithology as not all carbonate rocks have high C_{35} concentration [39]. The concentration of C_{35} extended hopane

(Figs. 7 a,b,c,d,e,f,g,h,i and j, see peak identification in Table 4) is more abundant in Nkporo and Enugu Shale. Such results indicate the marine input of the Nkporo and Enugu source rocks [38].

3.3. Hopanes and homohopanes

C_{29}/C_{30} hopanes ratios are generally high (>1) in oils generated from organic rich carbonates and evaporate [40]. The majority studied source rock samples, having lower concentrations of C_{29} than C_{30} hopane, with low C_{29}/C_{30} hopane ratios, range from 0.71 to 0.82 of the Nkporo source rocks and 0.59 to 0.79 of Enugu source rocks (Table 4), These data illustrate that the shale samples might be sourced from source rocks rich in carbonaceous organic matters.

C_{29} and C_{30}αβ-hopane occur in an appreciable amount in all the Nkporo and Enugu shale samples, indicating a significant contribution of prokaryotic organisms (i.e., bacteria, cyanobacteria, and blue algae) to the source organic matter.

The regular steranes/17α (H)-hopanes ratio reflects the input of eukaryotic (mainly algae and higher plants) versus prokaryotic (bacteria) organisms to the source rock [41]). The sterane/hopane ratio is relatively high in the marine organic matter, with values generally approaching unity or even higher. In contrast, low steranes and sterane/hopane ratios are more indicative of terrigenous and/or microbially reworked organic matter [41].

The sterane/hopane ratio values range from 0.07-0.27 for the Nkporo Formation and 0.05-0.32 for the Enugu Shale (Table 3). This indicates that the studied source rock can be considered generated from terrigenous organic matter source. The ratio values (<0.6) according to [32,42-43,] indicative of the incorporation of the high level of bacterial inputs commonly associated with terrigenous organic matter in shales (non-marine organic matter). The appreciable quantity of homohopanes (C31-C35) in all the samples suggest that bacteriohopanetetrol and other polyfunctional C35 hopanoids; bacteriohopanepolyols, aminopolyols, etc. [44], common in prokaryotic micro-organisms [45-46] were significant contributors to the biomass.

Table 3. Source, maturity and depositional environment parameters computed from the hopane and homohopane distributions of Nkporo and Enugu Formations

Sample No	Mortane/Hopane	Hop/Hop +Mortane	Ts/Ts+ Tm	Sterane/ Hopane	C_{35}/C_{30} Hopane	C_{29}/C_{30} Hopane	Ts/Tm	C_{35}/C_{34} αβS Hopane	Homohopane
NKP/07	0.30	0.77	0.66	0.09	0.21	0.80	1.95	0.42	0.05
NKP/08	0.17	0.85	0.57	0.27	0.07	0.71	1.34	0.5	0.04
NKP/12	0.2	0.83	0.51	0.25	0.1	0.80	1.04	0.79	0.07
NKP/16	0.29	0.78	0.46	0.07	NIL	0.82	0.86	NIL	NIL
NKP/17	0.32	0.76	0.54	nil	NIL	0.74	1.19	NIL	NIL
ENU/20	0.19	0.84	0.50	0.32	0.1	0.59	1.00	0.61	0.06
ENU/21	0.50	0.67	0.58	0.05	NIL	0.79	1.39	NIL	NIL
ENU/24	0.41	0.71	0.48	0.07	NIL	0.71	0.94	NIL	NIL
ENU/25	0.30	0.77	0.51	0.15	0.18	0.63	1.02	0.38	0.05

Mor/Hop = Moretane/Hopane (C30); Hop/Hop + Mor = Hopane/Hopane + Moretane (C30)
C32HH = C32homohopane;
Sterane/Hopane=C27+C28+C29steranes/[(C29+C30)αβhopane+(C31+C32+C33)αβ(R+S)homohopane]
C35/C30 = C35αβ(R+S) homohopane/ C30αβ hopane + C30βα moretane
Homohopane ratio ,C35/C34 αβS = C35αβS/C34αβS homohopane
Homohopane index = C35/ C31+C32+C33+C34+C35) αβ(R+S) homohopane

The C_{35}/C_{30} hopane ratio values range from 0.07 to 0.21 for the Nkporo Formation and 0.1 to 0.18 for Enugu Shale (Table 3), which reflects organic matter deposited in lacustrine environments [17]. The homohopane ratio (C35αβS/C34αβS) range from 0.42 to 0.79 for the

Nkporo Formation and 0.38 to 0.61 for the Enugu Shale. The homohopane index (C_{35}/C_{31} - C_{35}) range from 0.04 to 0.07 for the Nkporo Formation and 0.05 to 0.06 for Enugu Shale and 0.15 to 0.92 (Table 3). The low homohopane index of the samples indicates oxic condition during organic matter deposition [17,39,47-48]. Hopanes with αβ epimers are more prominent in all the samples while no ββ-epimer is detected. Homohopanes ranging from C31-C35 showed a notable predominance of the 22S over the 22R epimer. These observations reflect the high maturity status of the samples [17,49-50].

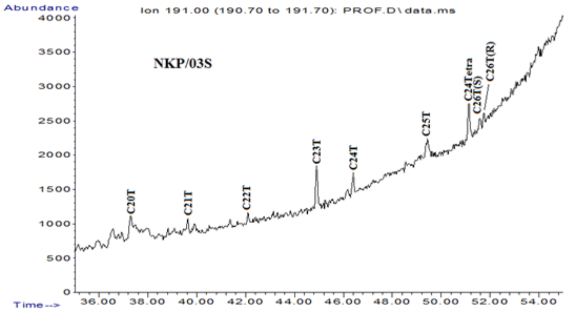

Figure 7a. Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/03)

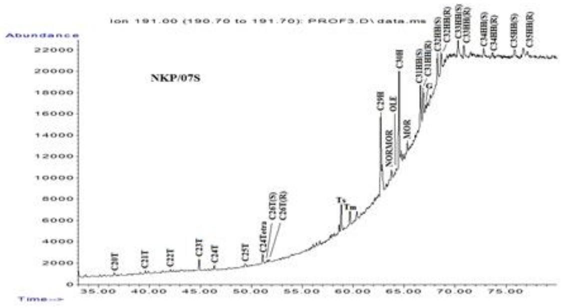

Figure 7b. Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/07)

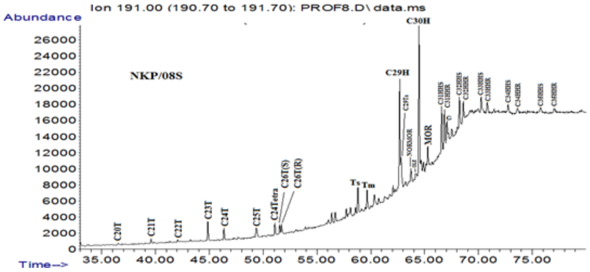

Figure 7c. Mass chromatograms (m/z 191) showing the distribution of polycyclic hydro-carbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/08)

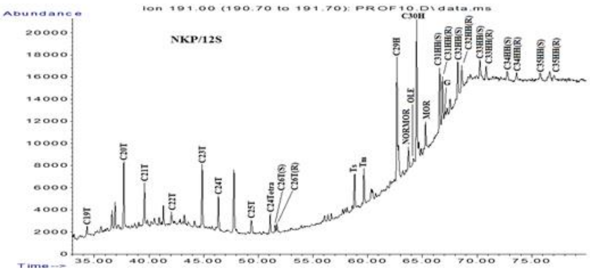

Figure 7d Mass chromatograms (m/z 191) showing the distribution of polycyclic hydro-carbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/12)

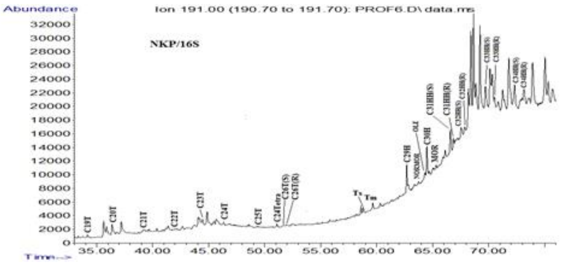

Figure 7e. Mass chromatograms (m/z 191) showing the distribution of polycyclic hydro-carbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/16)

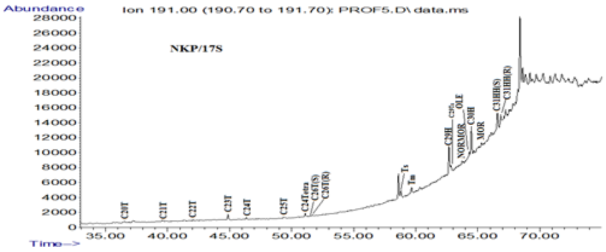

Figure 7f. Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/17)

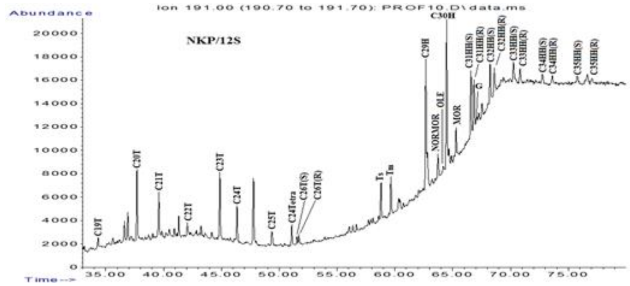

Figure 7g. Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Enugu Shale (ENU/20)

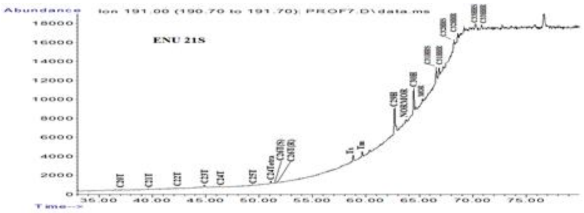

Figure 7h. Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Enugu Shale (ENU/21)

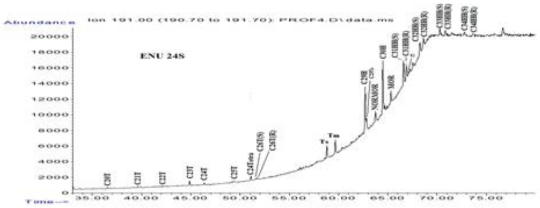

Figure 7i. Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Enugu Shale (ENU/24)

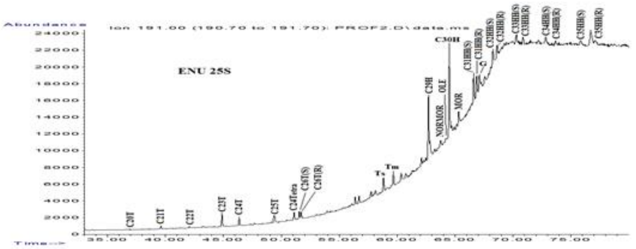

Figure 7j. Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Enugu Shale (ENU/25)

Table 4. Peak identification of triterpenes (m/z 191) fragmentograms

Peak	Compounds	Peak	Compounds
C19tri	C19 tricyclic terpanes	C30H	17α(H), 21β(H)-hopane C_{30}
C20tri	C20 tricyclic terpanes	MOR	Moretane
C21tri	C21 tricyclic terpanes	C31HHS	22S 17α (H), 21β(H)- 30-homohopane C_{31}
C22tri	C22 tricyclic terpanes	C31HHR	22R 17α (H) ,21β(H)-30-homohopane C_{31}
C23tri	C23 tricyclic terpanes	G	Gammacerane
C24tri	C24 tricyclic terpanes	C32HHS	22S 17α (H) ,21β (H)-30,31-bishomohopane C_{32}
C25tri	C25 tricyclic terpanes	C32HHR	22R 17α(H), 21β(H)-30,31-bishomohopane C_{32}
C24tetra	C24 tetracyclic terpanes	C33HHS	22S 17α(H) 21β(H)-30,31,32-trishomohopane C_{33}
C26tri	C26 tricyclic terpanes	C33HHR	22R 17α(H),21β(H)-30,31,32-trishomohopane C_{33}
Ts	18α(H)-22,29,30-trisnorneohopane Ts, C_{29}	C34HHS	22S 17α (H) ,21β (H)-30,31-bishomohopane C_{34}
Tm	17α(H)-22,29,30 Trisnorhopane Tm, C_{27}	C34HHR	22R 17α(H), 21β(H)-30,31-bishomohopane C_{34}
C29H	17α(H), 21β(H)-30- norhopane C_{29}	C35HHS	22S 17α(H) 21β(H)-30,31,32-trishomohopane C_{35}
NORMOR	Normoretane	C35HHR	22R 17α(H),21β(H)-30,31,32-trishomohopane C_{35}
OLE	Oleanane		

The ratio of Ts/Tm - Ts (trisnorneohopane) to Tm (trisnorhopane) more than (0.5) increases as the portion of shale in calcareous facies increases [22]. Also, this ratio was proved to be useful in paleofacies predictions, though not as decisive as mature parameters. Van Grass [56] stated that Ts/Tm ratios begin to decrease quite late during maturation, but Waples and Machihara [30] reported that Ts/Tm ratio does not appear to be appropriate for quantitative estimation of maturity. The Ts/Tm ratios range from 0.86 to 1.95 for the Nkporo source rock, while that of Enugu source rock range from 0.94 to 1.39 (Table 3). These relatively high ratios suggest that the studied source rocks were generated mainly from calcareous facies.

The Moretane/Hopane, Hopane/Hopane + Moretane and Ts/Ts + Tm, ratios for the Nkporo Formation range from 0.17 to 0.30; 0.77 to 0.85 and 0.51 to 0.66 respectively, while that of Enugu Shale ranges from 0.19 to 0.50, 0.67 to 0.84 and 0.48 to 0.58 respectively (Table 3). These values indicate samples that are within the early oil window [17,32,47]. The abundance of C_{35} pentacyclic extended hopane seems to be associated with marine carbonates or evaporites [38]. However, Peters and Moldowan [39] prefer to correlate high C_{35}/ C_{34} ratios in the marine environment with a low redox potential rather than with lithology as not all carbonate rocks have high C_{35} concentration. The concentration of C_{35} extended hopane (Fig. 4, see peak identification in Table 4) is more abundant in the Nkporo and Enugu Shale extracts. Such results indicate the marine input of the Nkporo and Enugu source rocks [38]. The C_{35}/C_{30} hopane ratio values range from 0.42 to 0.79 for the Nkporo source rock and 0.38 to 0.61 for Enugu source rock, which reflects organic matter deposited in marine environments [17] (Table 3).The *m/z* 191 showing the distributions of polycyclic hydrocarbons, hopanes and homohopanes in the samples are shown in Fig. 7 a,b,c,d,e,f,g,h,i and j of Nkporo and Enugu source rocks. Peak identities are listed in Table 4.

3.4. Steranes

The occurrence of C27 to C29 steranes was detected in Nkporo and Enugu Shale samples (Figs. 8 and 9). The sterane distributions for all the samples occur in the order of C29>C28>C27 (Table 5).

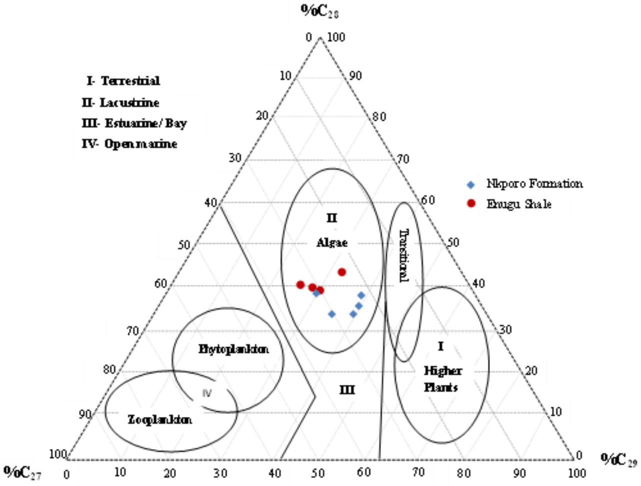

Fig. 8. Ternary plot of C_{27}, C_{28} and C_{29} Steranes distribution showing the environment of deposition of Nkporo and Enugu Shale samples [17]

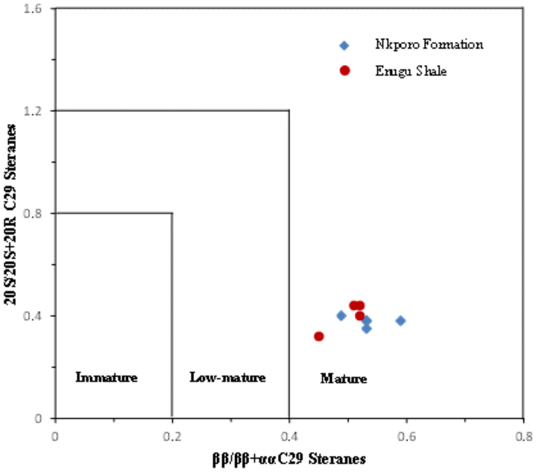

Fig. 9. Plot of 20S/20S+20R versus ββ/αββ+ααα of the Nkporo and Enugu source rock samples

Table 5. Source, maturity and depositional environment parameters computed from the sterane distributions of Nkporo and Enugu Formations

Sample No	%C27	%C28	%C29	%Diasterane/ Sterane	20S/20S+20R C29 Steranes	Bβ/ββ+ααC29 Sterane
NKP/ 03	-	-	-	-	NIL	NIL
NKP/07	39.1	22.4	38.5	1.19	0.38	0.53
NKP/08	29.8	31.3	38.9	0.32	0.4	0.49
NKP/12	39	27.1	33.9	0.82	0.38	0.53
NKP/16	35.9	30.9	33.2	2.55	0.38	0.59
NKP/17	39.8	24.9	35.3	1.47	0.35	0.53
ENU/20	30.2	32.1	37.7	0.41	0.44	0.52
ENU/21	30	30.3	39.7	1.47	0.32	0.45
ENU/24	32.9	24.6	42.5	1.05	0.4	0.52
ENU/25	27.5	32.2	40.3	0.35	0.44	0.51

The predominance of C27 sterane over C29 sterane reflects a greater input of marine relative to terrestrial organic matter [17,47,51-53]. The ternary plots of sterane distribution in (Fig. 8) indicate organic matter derived from marine materials deposited in lacustrine settings [17,47,51,54]. This observation is supported by C27/C29 ratios (Table 4.7), which range from 0.77 to 1.13 for the Nkporo samples and 0.68 to 0.80 for the Enugu samples [17]. The dominance of C30 steranes over dinosterol in these samples reflects typical marine source rocks [17].

The 20S/20S+20R and αββ/αββ+ααα C_{29} ratios range from 0.35 to 0.38 and 0.49 to 0.59 for the Nkporo Formation, while that of Enugu Shale range from 0.32 to 0.44 and 0.45 to 0.52 respectively (Table 5). These values show that the samples are mature and are within the early oil generative window [17,47] (Fig. 9).

3.4.1 Ratio of sterane to Pr/Ph

Conditions of the paleodepositional environment of the source rock were evaluated using a graph of C_{27}/ (C_{27}+C_{29}) sterane versus Pr/Ph (Fig. 10a and b).

The C_{27}/ (C_{27}+C_{29}) sterane versus Pr/Ph ratios ranges from 0.43 to 0.53 and 0.33 to 0.78 for the Nkporo Formation which indicate that the organic matter was deposited in a pelagic and anoxic environment, while that of Enugu Shale ranges from 0.41 to 0.44 and 0.65 to 0.76 which indicate that the organic matter was deposited in a coastal and anoxic environment [55] (Fig. 4.57a and b).

The *m/z* 217 mass chromatograms showing the distribution of steranes and diasteranes in all the samples are shown in Figs. 11 a,b,c,d,e,f,g,h and i. Peak identities are listed in Table 6.

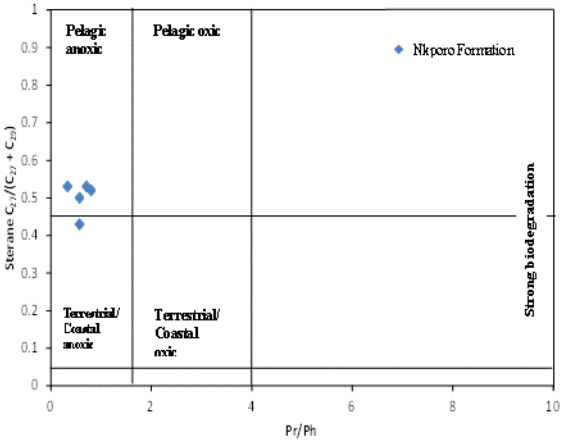

Fig. 10a. Plots of C_{27}/ (C_{27}+C_{29}) versus pristane/ phytane ratio of the Nkporo Formation samples [55]

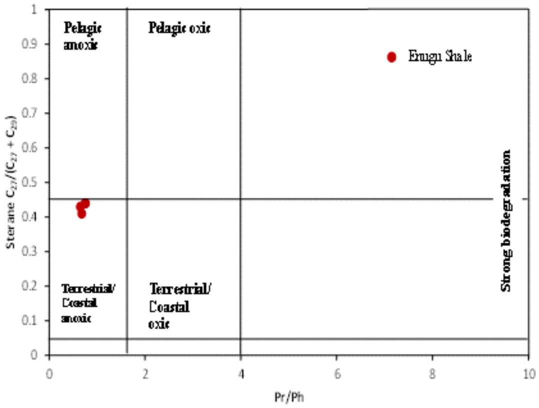

Fig. 10b. Plots of C_{27}/ (C_{27}+C_{29}) versus pristane/ phytane ratio of the Enugu Shale samples [55]

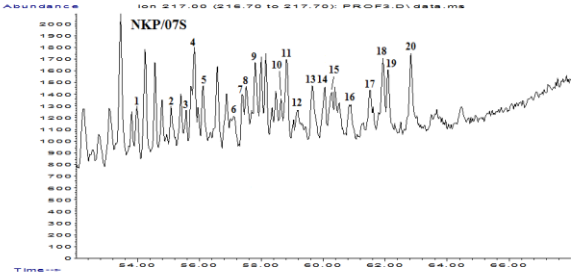

Figure 11a Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/07)

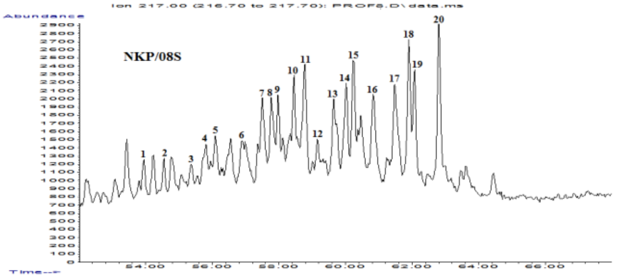

Figure 11b. Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/08)

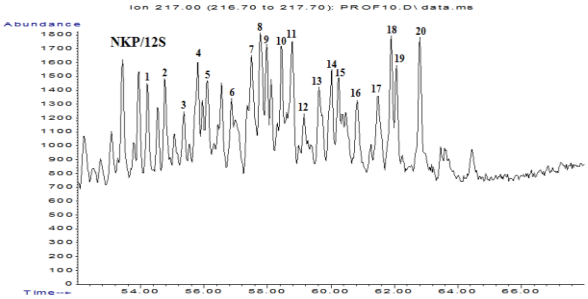

Figure 11c. Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/12)

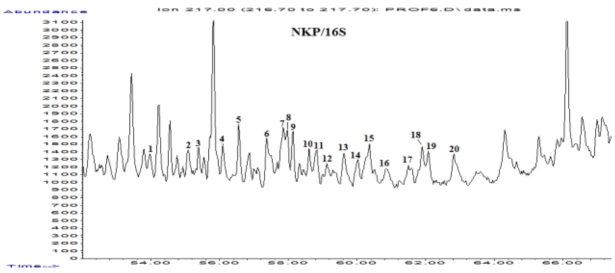

Figure 11d.Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/16)

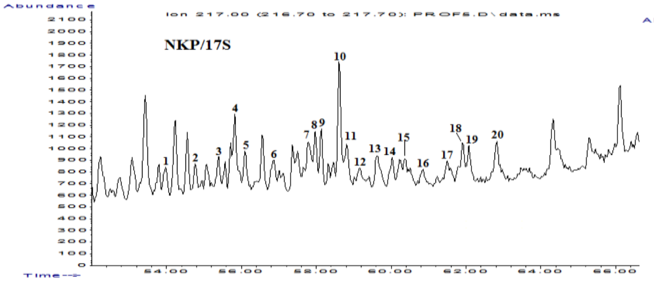

Figure 11e. Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/17)

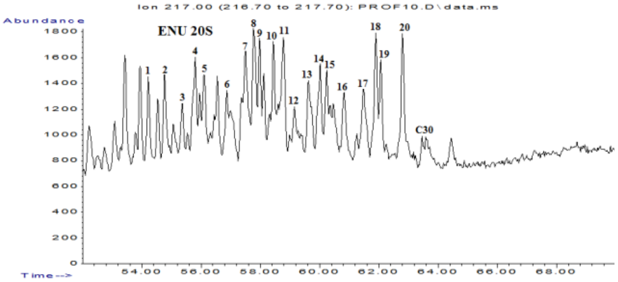

Figure 11f. Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Enugu Shale (ENU/20)

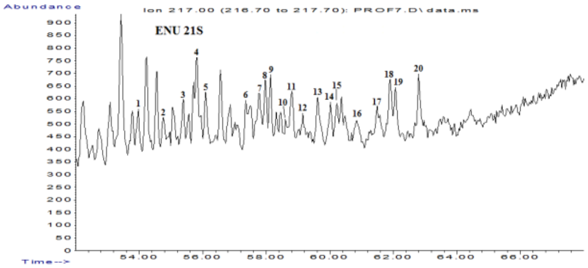

Figure 11g. Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Enugu Shale (ENU/21)

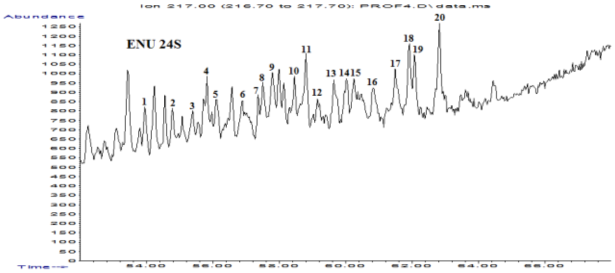

Figure 11h. Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Enugu Shale (ENU/24)

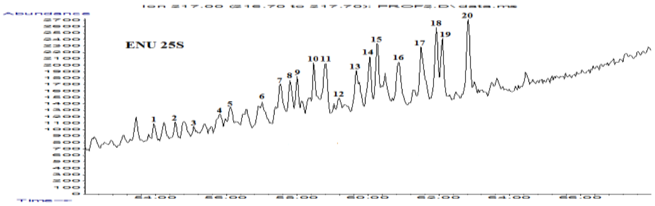

Figure 11i. Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Enugu Shale (ENU/25)

Table 6. Peak identification of Steranes and Diasteranes (m/z 217) fragmentograms

Peak	Compounds	Peak	Compounds
1	20S 13β, 17α-diacholestane C_{27}	12	20S 24-ethyl-13α,17β-diacholestane C_{29}
2	20R 13β, 17α-diacholestane C_{27}	13	20S 24-methyl-14α,17α-cholestane C_{28}
3	20S 13α,17β-diacholestane C_{27}	14	20R 24-methyl-14β,17β-cholestane C_{28}
4	20S 24-methyl-13β,17α-diacholestane C_{28}	15	24-methyl-14α,17α-cholestane C_{28}
5	20R 24-methyl-13β,17α-diacholestane C_{28}	16	20R 24-methyl-14α,17α-cholestane C_{28}
6	20R 24 methyl -13β,17α-diacholestane C_{28}	17	20S 24-ethyl-14α,17β-cholestane C_{29}
7	20R 24 methyl -13α,17β-diacholestane C_{28} + 20S 14α,17α cholestane C_{27}	18	20R 24-ethyl-14β,17α-cholestane C_{29}
8	20S 24 ethyl -13β,17α-diacholestane C_{29} + 20R 14β,17β cholestane C_{27}	19	20S 24-ethyl-14β,17β-cholestane C_{29}
9	20R 24 methyl -13α,17β-diacholestane C_{28} + 20S 14β,17β cholestane C_{27}	20	20R 24-ethyl-14α,17α-cholestane C29
10	20R 14α,17α-cholestane C_{27}	C_{30}	C_{30} sterane
11	20R 24-ethyl-13β,17α-diacholestane C_{29}		

5. Conclusion

The distributions of *n*-alkanes showed that Nkporo and Enugu samples were formed from organic matter derived from both mixed organic sources and deposited in transitional environments. The Pr/Ph ratios of samples from Nkporo and Enugu samples reflect organic matter deposition under anoxic conditions marine. The presence of hopane, homohopane (C_{31}-C_{35}) in all the samples showed that bacteriohopanetetrol and other polyfunctional C_{35} hopanoids common in prokaryotic microorganisms have significant contributions to the organic matter. The occurrence of oleanene isomers in Nkporo and Enugu samples favoured marine organic matter deposited in lacustrine environment. In addition, the detection of gammacerane in Nkporo and Enugu samples represents marine water stratification during organic matter source deposition. The abundance of C_{29} Steranes and diasteranes in the samples indicate marine input of the organic matter.

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