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Petroleum & Petrochemical Engineering Journal
ISSN: 2578-4846

Origin, Depositional Environment and Thermal Maturity of some Source Rocks from Niger Delta Basin, Nigeria

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Research Article
Volume 6 Issue 4
Received Date: November 17, 2022
Published Date: December 27, 2022
DOI: 10.23880/ppej-16000318

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Abstract

Eleven (11) core samples from Agbada and Akata formations in the Niger Delta, Nigeria, were analyzed using gas chromatography-mass spectrometry to evaluate their paleodepositional conditions and source input as well as to determine their thermal maturity. The distribution of n-alkanes, isoprenoids, and biomarkers indicate a mixture (marine/terrigenous) organic matter source input for Agbada and Akata formation sediments deposited in marine environment. Low values of Phytane/$n\mathrm{C}_{18}$ (0.45 to 1.32) and Pristane/$n\mathrm{C}_{17}$ (0.37 to 1.8) indicates Marine organic matter contribution and anoxic-suboxic (Type II/III kerogens) depositional conditions of extract for Agbada and Akata Formations. The Carbon Preference Index (CPI) values for all analysed samples are slightly greater than 1.0 indicate a mixed input of marine and terrigenous organic matter deposited under relatively reducing (dysoxic) conditions. The high concentration of Oleanane in studied samples reveals that source rocks are tertiary age and belong to marine deltaic depositional environment. Moderate to higher Gammacerane index values ranging from 0.06 to 0.11, suggests water-column stratification, potentially due to hypersalinity for Isan oilfield well samples from Agbada formation. Biomarker maturity parameters suggest that the sediments have reached the early stages of hydrocarbon generation.

Keywords: Biomarker; Depositional environment; Niger Delta; Source rock; Thermal maturity

Introduction

Petroleum geochemistry is used as the basic science to understand the properties of source rocks, productive and non-productive areas, oil migrations, oil field development and sustainable production [1]. To evaluate source rock, various laboratory advanced geochemical analyses methods, rapid and inexpensive, are used [2]. Among these techniques, we can cite Rock-Eval pyrolysis, organic petrography (kerogen type analysis, maceral analysis, vitrinite reflectance), scanning fluorescence, gas chromatography, and stable isotope analyses. Gas chromatography-mass spectrometry provides valuable data on the chemical composition of solvent-soluble organic matter in samples that can help identify sources of contamination as well as support and enhance interpretations based on organic petrology and pyrolysis techniques.

Biomarker parameters have been widely used effectively in the characterization of the environmental conditions during the deposition of organic matter, the source input and the assessment of maturation level of potential source rocks [2,3].

Preliminary organic geochemical studies of samples from the Niger Delta conducted with gas chromatography-mass spectrometry (GC-MS) by Ekweozor CM, et al. [4] using αβ-hopanes and oleananes for fingerprinting crude oil with respect to their source, demonstrated the same result concerning the two main source rocks which were the Agbada and Akata formations as obtained by Evamy BD, et al. [5]. Bustin RM [6] found that composition of the organic matter and the relatively high pristane/phytane ratio indicate a predominantly detrital terrestrial source. However, the decrease in the pristane/phytane ratio in the younger strata is difficult to explain, but may reflect a decrease in oxidation associated with faster burial.

According to Haack RC, et al. [7], the principal sources for oil and gas in the Niger Delta are Type II, Type II/III and Type III kerogens and assumed that oil and gas in the Niger Delta originated mainly from terrigenous and nearshore marine source rock. The occurrence of oleanane in Nigerian oils points to Late Cretaceous or younger source rocks [8]. In the Niger Delta province, Tuttle, et al. [9] have highlighted one petroleum system: the tertiary petroleum system of the Niger Delta (Akata-Agbada). They claimed that the main source rock is the Upper Akata Formation, the delta marine shale facies, possibly with the contribution of interbedded marine shales of the Lower Agbada Formation. This result is not adequacy with the work of Akinlua A, et al. [10] based on geochemical analysis of rock samples from three offshore fields and oil samples from offshore and onshore fields in the western Niger Delta revealed complex mixtures of organic matter and showing early mature to mature source rocks deposited in alternating oxic and anoxic environments; the results of this study highlighted that the Niger Delta has two petroleum systems, though the terrigenous system is more predominant.

The studies of Onojake, et al. [11], Ekpo BO, et al. [12], conducted on oil samples from Niger Delta revealed mixed sources (marine and terrestrial kerogen), thermally mature and deposited under oxidizing condition. And the recent study of Faboya OL, et al. [13] concluded that the distribution of molecular biomarkers and isotopic composition in the oils indicated that they were formed from thermally mature source rocks of a mixed source but with greater input from marine organic matter deposited under suboxic conditions.

Aware of the diverse and contradictory results on Niger Delta source rocks characterization, this present study aims to improve our knowledge and provide relevant information needed to answer exploration questions related to type of source input, conditions of depositional environment and thermal maturity of some source rocks of the basin.

Geological Setting of Niger Delta Basin

The Niger Delta is one of the most prolific petroleum provinces in the world, it is located in the Southern Nigeria margin of the Gulf of Guinea., with latitude 4°49’ N and longitude 6°0’ E [14]. The Niger Delta sedimentary basin covers an area of about 256,000 km^2 [15]. It is bounded to the south by the Gulf of Guinea and the north by older tectonic elements (Cretaceous) including the Anambra Basin, the Abakaliki uprising and the Afikpo syncline, and to the east and west by the Cameroon volcanic line and the Dahomey basin respectively (Figure 1b). The Niger Delta basin began to form in the Cretaceous when the African plate separated from the South American plate; the basin is delimited by rift faults on its northwest and northeast edges [16].

After the rifting, gravity tectonics became the main deformation process [9]. Pre- and syn-sedimentary tectonics described by Evamy BD, et al. [5] and Knox GJ, et al. [17] characterized the evolution of the Niger Delta basin. The regressive clastic sequence in the Niger Delta began to form in the Paleocene and has since formed sediments which now reaches a thickness of 12,000 m [5]. The Niger Delta Basin consists of three main lithostratigraphic units of Cretaceous to Holocene origin (Figure 1a). These units represent the prograding depositional environments which are distinguished mainly based on shale-sand ratios and are continental, transitional, and marine environment [18]. This Tertiary sequence in the Niger Delta consists of the three formations that are locally designated in ascending order (from the bottom) the Akata Formation, Agbada Formation, and Benin Formation [9,19].

At the base of the system is the Akata Formation, a sequence of planktonic foraminifera-rich non-compacted transgressive Paleocene-to-Holocene marine shale, clays, and silt. This interstratified unit of sandstone and shale is called the Agbada Formation (Recent Eocene). The Agbada Formation represents the delta system (delta front, fluvio-deltaic facies) of the sedimentary sequence [9]. The Agbada Formation is overlain by the third formation, the Benin Formation, a last continental deposit from the Eocene to Recent alluvial and upper coastal plains [20].

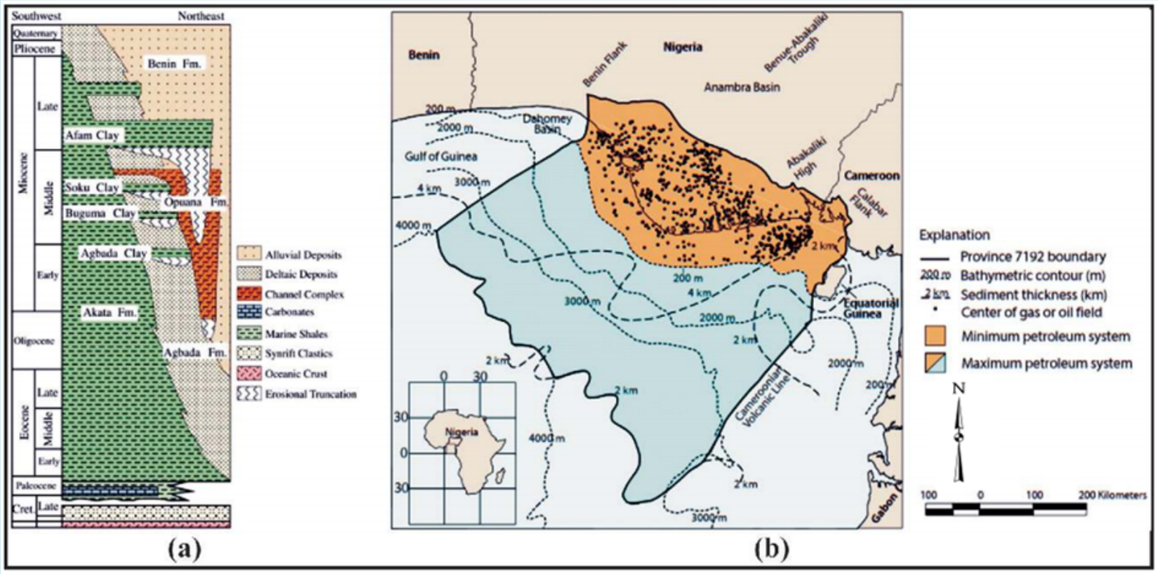

Figure 1: (a) Stratigraphic column showing the three formations of the Niger Delta [18]. (b) Niger Delta Map showing Province outline (petroleum system) and bounding structural features [9].

Materials and Methods

After Rock-Eval analysis, Biomarker analysis was performed on Eleven (11) core samples with good Total Organic Carbon (TOC more than 1 wt.%) and good petroleum potential using gas chromatography-mass spectrometry (GC-MS). Three (3) samples from Agbada formation wells and Eight (8) samples from Akata formation wells. The fractions of bitumen obtained after Soxhlet extraction were dissolved in *n*-hexane and analyzed using gas chromatography-mass spectrometry (GC-MS). The GC-MS analysis was performed using Perkin Elmer GC/MS Clarus 500. Chromatograms were acquired in scanning: 35–700 molecular weight and selected-ion-monitored (SIM) for compound identification and integration. The distribution of organic compounds in the bitumen extracts is monitored by fragmentograms of *n*-alkane (m/z 85), terpanes and hopanes (m/z 191) and steranes (m/z 217). The relative concentrations of particular compounds were calculated from peak areas.

Biomarkers were identified by comparison with previously published accounts [3,21,22]. These analyses were done in the laboratory of PETROCI (Société National d'Opération Pétrolière de la Cote d'Ivoire).

Result and Discussion

Biomarker distributions

Normal alkanes and isoprenoids distribution

The *n*-alkane hydrocarbons were distributed differently in samples obtained from different wells (m/z 85). The distributions were unimodal in these samples, and the dominant peaks of the samples from Agbada and Akata formations are distributed mainly between nC_{16} and nC_{23}, and the carbon number is distributed mostly between nC_{13} and nC_{37} (Figure 2). The *n*-alkane distribution in the Agbada and Akata core samples is dominated by short-chain n-alkanes suggesting sources of marine algae. Odd to Even predominance (OEP) has been observed in many recent sedimentary systems and is linked to contributions from algae, bacteria, fungi, and yeast [23]. The presence of terrestrial plant-derived organic matter is typically verified based on the presence of predominantly odd molecular weight *n*-alkanes, between C_{25} and C_{35}, which are linked with inputs of wax lipids derived from higher plants [23]. Isoprenoids (Pristane and Phytane) are present in significant amounts in the analyzed samples (Figure 2).

Triterpanes and Steranes Distribution

Triterpane and sterane distributions of the analyzed samples were determined based on m/z 191 (Figure 3) and m/z 217 (Figure 4) traces respectively. Peak identifications of the m/z 191 and m/z 217 fragmentograms were made on the basis of retention times and published literatures Peters KE, et al. [3], Hakimi MH, et al. [24], Weiss HM, et al. [25], Waples DW, et al. [26]. The identified peaks are listed in Table 1 and Table 2, and the calculated ratios are shown in Table 3 and Table 4. The m/z 191 mass chromatograms of the saturated hydrocarbon fractions of all the analyzed samples show moderate abundances of tricyclic terpanes with lower amounts of tetracyclic terpanes.

Tricyclic and tetracyclic terpanes are usually common in a marine environment and are believed to have their origin in algae, especially Tasmanites and bacteria [27-29]. Tricyclic terpanes (TT) C_{20}TT (t20) to C_{29}TT (t29) were identified in the shale samples of Agbada and Akata formations. The most prominent peak in the tricyclic terpanes series was that of C_{23}TT (t23), as shown in Figure 3, which is a clear indication of a marine input [29,30].

Hopanoids are important biomarkers for indicating organic matter that was derived from bacteria [31]. Their composition and distribution are similar in most of the samples and mainly consist of C_{28} to C_{35} 17α,21β(H)-hopanes with C_{29}αβ and C_{30}αβ hopanes as major compounds (Figure 3). The predominance of C_{30} hopane is often associated with clay-rich source rocks [23,32].

Moreover, pentacyclic terpanes from C_{27} to C_{35} were present. Of these, C_{30} (hopane) had the highest relative abundance samples of Agbada formation and moderate in Akata formations, whereas the abundance of C_{28} was unusually low. Trisnorhopane (C_{27}) and homohopanes (C_{31+}) appeared as doublets (18α(H)-trisnorneohopane (Ts) and 17α(H)-trisnorhopane (Tm) isomers); 22S and 22R epimers, respectively) in the Ion chromatograms for all of the studied shale samples (Figure 3).

The 17β,21α(H)-moretane was also detected in almost all the samples (Figure 3), though in moderate concentrations in the Akata samples. Moretanes are more abundant in organic material of terrestrial origin, but it is not known if they come from terrestrial plants or from microorganisms associated with those particular depositional environments [26].

The 18α(H)-oleanane, which is an important land plant-derived biomarker, was identified in high proportion in all the analyzed samples particularly in high concentrations in the rock extracts from Akata formation (Figure 3), supporting the presence of terrigenous organic matter input in the sediments [3,23]. Gammacerane is present in the sample from oilfield Isan (Figure 3), indicating a stratified water column in lacustrine depositional environments of source rock which resulted from hypersalinity [33]. The investigated rock extracts for Agbada formation wells are characterized by relatively moderate concentrations of 5α(H),14β(H),17β(H)-Cholestane or C_{27}-cholestane (30%) and low to slightly moderate abundance of 24-methyl-5α(H),14α(H),17α(H)-cholestane or C_{28}-ergostane (12–18%) and 24-ethyl-5α(H),14β(H),17β(H)-cholestane or C_{29}-stigmastane (50–58%) respectively (Figure 4 and Table 2), that indicate a marine and mixed marine/terrigenous origin [3]. Diasteranes is referred to as rearranged steranes and are present in significant amounts in all samples analyzed (Figure 4 and Table 2).

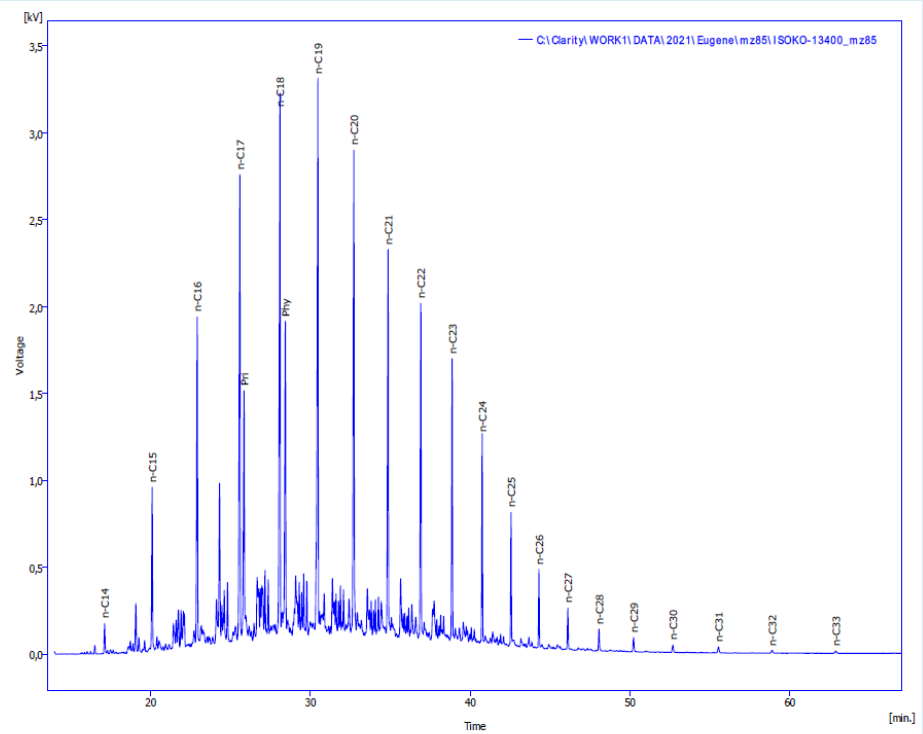

Figure 2: Gas chromatogram of a saturated hydrocarbon fraction (m/z 85) of rock extracts from Akata formation samples.

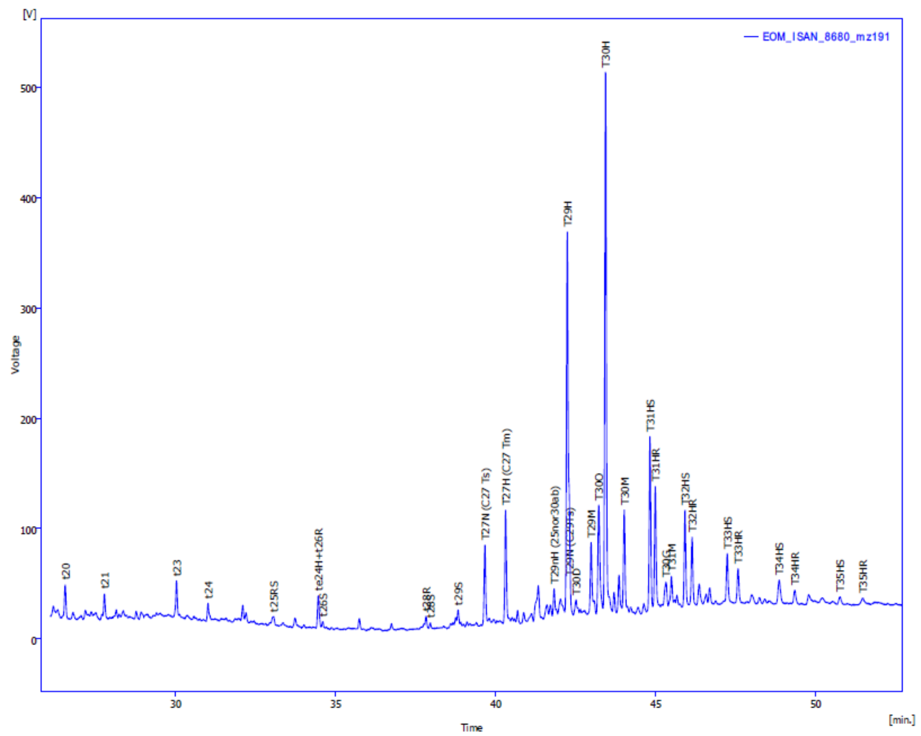

Figure 3: The m/z 191 mass fragmentogram of a saturated hydrocarbon fraction of rock extracts from Agbada formation samples.

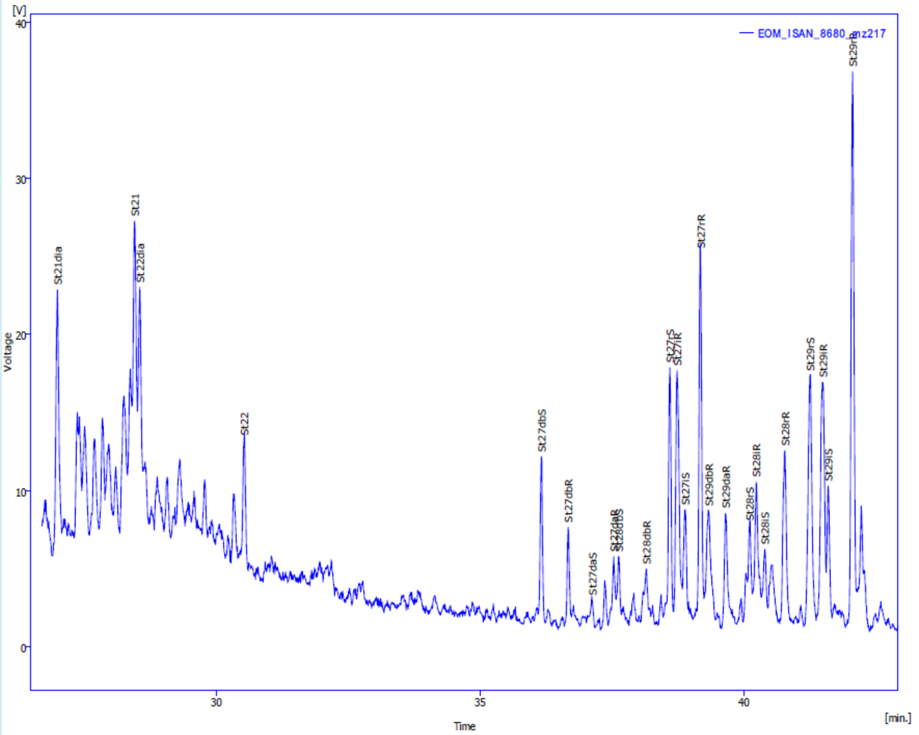

Figure 4: The m/z 217 mass fragmentogram of a saturated hydrocarbon fraction of rock extracts from Agbada formation samples.

Peak	Compound
t20	C20 Tricyclic terpane (Cheilanthane)
t21	C21 Tricyclic terpane
t23	C23 Tricyclic terpane
t24	C24 Tricyclic terpane
T25RS	C25 Tricyclic terpane 22S + 22R
te24H	C24 Tetracyclic terpane
t26S	C26 Tricyclic terpane 22S
t26R	C26 Tricyclic terpane 22R
T26RS	C26 Tricyclic 22S + 22R
t28R	C28 Tricyclic terpane 22R
t28S	C28 Tricyclic terpane 22S
t29R	C29 Tricyclic terpane 22R
T29S	C29 Tricyclic terpane 22S
T27N (C27 Ts)	18α(H), 22,29,30-trisnorneohopane (Ts)
T27H (C27 Tm)	18α(H), 22,29,30-trisnorhopane (Tm)
T28nH (C28ab)	17α(H), 21β(H)-28,30-bisnorhopane
T29nH (25nor30ab)	17α(H), 21β(H)-25-norhopane
t30R	C30 Tricyclic terpane 22R
t30S	C30 Tricyclic terpane 22S
T29H	17α,21β(H)-30-norhopane
T29N (C29Ts)	18α(H)-30-norneohopane
T30D	17α(H)-diahopane
T29M	17β,21α(H)-moretane
T30O	17α(H)-oleanane
T30H	17α,21β(H)-Hopane
T30M	17β,21α(H)-moretane
T31HS	17α,21β(H)-homohopane 22S
T31HR	17α,21β(H)-homohopane 22R
T30G	Gammacerane
T31M	17β(H), 21α(H)-homohopane (moretane)
T32HS	17α,21β(H)-bishomohopane 22S
T32HR	17α,21β(H)-bishomohopane 22R
T33HS	17α,21β(H)-trishomohopane 22S
T33HR	17α,21β(H)-trishomohopane 22R
T34HS	17α,21β(H)-tetrakishomohopane 22S
T34HR	17α,21β(H)-tetrakishomohopane 22R
T35HS	17α,21β(H)-pentakishomohopane 22S
T35HR	17α,21β(H)-pentakishomohopane 22R

Table 1: Identification of peaks in triterpanes (m/z 191) mass spectrograms.

Peak	Compound
St21dia	C21 diasterane
St21	C21 sterane
St22dia	C22 diasterane
St22	C22 sterane
St27dbS	13β(H), 17α(H)-cholestane 20S (diasterane)
St27dbR	13β(H), 17α(H)-cholestane 20R (diasterane)
St27daS	13α(H), 17β(H)-cholestane 20S (diasterane)
St27daR	13α(H), 17β(H)-cholestane 20R (diasterane)
St28dbS	24-methyl-13β(H), 17α(H)-cholestane 20S (diasterane)
St28dbR	24-methyl-13β(H), 17α(H)-cholestane 20R (diasterane)
St27Rs	5α(H),14α(H),17α(H)-Cholestane 20S
St27iR	5α(H),14β(H),17β(H)-Cholestane 20R
St27iS	5α(H),14β(H),17β(H)-Cholestane 20S
St27rR	5α(H),14α(H),17α(H)-Cholestane 20R
St29dbR	24-ethyl-13β(H), 17α(H)-cholestane 20R (diasterane)
St29daR	24-ethyl-13α(H), 17β(H)-cholestane 20R (diasterane)
St28rS	24-methyl-5α(H), 14α(H), 17α(H)-cholestane 20S
St28iR	24-methyl-5α(H), 14β(H), 17β(H)-cholestane 20R
St28iS	24-methyl-5α(H), 14β(H), 17β(H)-cholestane 20S
St28rR	24-methyl-5α(H), 14α(H), 17α(H)-cholestane 20R
St29rS	24-ethyl-5α(H), 14α(H), 17α(H)-cholestane 20S
St29iR	24-ethyl-5α(H), 14β(H), 17β(H)-cholestane 20R
St29iS	24-ethyl-5α(H), 14β(H), 17β(H)-cholestane 20S
St29rR	24-ethyl-5α(H), 14α(H), 17α(H)-cholestane 20R

Table 2: Identification of peaks in steranes (m/z 217) mass spectrograms.

Source Input and Depositional Environment

The biomarker distributions measured from GC-MS are used to interpret the organic matter source and depositional environment in this study. The ions m/z 85, m/z 191 and m/z 217 mass chromatograms are monitored in order to determine the peak area of *n*-alkanes, terpanes and steranes, respectively, which can be calculated as parametric ratios, is shown in Table 3 and Table 4.

Pr/Ph values range from 0.9 to 1.02 for Agbada formation and 0.73 to 1.23 for Akata formation (Table 3). These Pr/Ph values suggest alternating anoxic and dysoxic conditions during deposition of the sediments in these formations. A cross-plot of Pr/nC_{17} and Ph/nC_{18} values (Figure 5) suggests predominant mixed organic facies with some samples having strong contributions of terrestrial marine organic matter. Marine organic matter contribution and anoxic-suboxic (Type II/III kerogen) depositional conditions of extract for Agbada and Akata Formations are indicated by low Phytane/nC_{18} (0.45 to 1.32) and Pristane/nC_{17} (0.37 to 1.8).

Carbon preference index (CPI) of *n*-alkanes between nC_{22} and nC_{30} was also calculated to provide some insights into the source input and depositional conditions of the organic matter. CPI value that is less than 1.0 would indicate reducing depositional conditions [34]. The CPI values for all the analysed samples are slightly greater than 1.0 (Table 3). This indicates a mixed input of marine and terrigenous organic matter deposited under relatively reducing (dysoxic) conditions. The cross-plot of CPI against Pr/Ph (Figure 6) further supports this interpretation [34-36].

Waxiness index may be used to determine the amount of land-derived organic materials in the sediments [23]. The degree of Waxiness is expressed by the ΣC_{21}-C_{31}/ΣC_{15}-C_{20} ratios. Samples from Agbada and Akata formations generally contain low to moderate waxy ratios (0.13 - 1.07), reflecting mixed marine and land plant-derived biomarkers. The cross-plot of waxiness and Pr/Ph ratio further corroborates this interpretation (Figure 7).

The terrigenous/aquatic ratio (TAR) is also used as a valuable parameter of relative terrigenous versus aquatic organic matter input. TAR gives an additional way to assess the relative contributions of terrigenous (e.g., terrestrial plant) and aquatic (e.g., aquatic algae) organic matter, by comparing the abundances of short and long-chain *n*-alkanes. TAR values in Agbada and Akata core samples range between 0.02 to 0.48 (Table 3). These low values indicate a dominantly aquatic organic matter source (Figure 8), with more algal organic matter input as compared to vascular plants [37].

Marine and lacustrine crude oils are best discriminated using C_{31}R/C_{30} hopane in combination with C_{26}/C_{25} tricyclic terpanes parameters [23,38]. Akata formation samples display C_{26}/C_{25} tricyclic ratios around 1.0 and C_{31}R/C_{30} hopane ratios range between 0.23 to 0.35, indicating marine environment. However, Agbada formation studied samples show C_{26}/C_{25} tricyclic ratios that are greater than 1.0, with C_{31}R/C_{30} hopane ratios ranging from 0.23 to 0.59, indicating their mixed origin (Figure 9).

Formation	Wells	Depth (ft)	Pr/Ph	Pr/nC17	Ph/nC18	TAR	Waxiness	CPI
Agbada	Isan 9	6760	0,9	1,8	1,33	0,15	0,68	1,48
	Benin West	7840	1,03	0,61	0,68	0,06	0,30	1,04
	Isan 9	8680	0,94	0,62	0,68	0,48	1,07	1,23
Akata	Ubefan	9800	1	0,47	0,48	0,03	0,32	1,19
	Ughelli	11120	1,23	0,67	0,77	0,03	0,13	1,19
	Appara	11800	0,79	0,37	0,45	0,02	0,33	1,15
	Kokori	12140	0,82	0,56	0,6	0,05	0,54	1,16
	Eriemu	12200	0,78	0,57	0,62	0,04	0,43	1,11
	Warri River	12260	0,73	0,55	0,63	0,04	0,54	1,14
	Udeduma Cr.	12340	0,94	0,49	0,49	0,02	0,25	1,23
	Isoko	13400	0,82	0,56	0,6	0,05	0,54	1,16

Table 3: Normal Alkanes and isoprenoids ratios of the studied samples.

Pr : Pristane, Ph : Phytane, Pr/Ph : Pristane/Phytane, Pr/nC_{17} : Pristane/nC_{17}, Pr/nC_{18} : Pristane/nC_{18},

CPI : Carbon Preference Index=$[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33}) / (C_{24}+C_{26}+C_{28}+C_{30}+C_{32}) + (C_{25}+C_{27}+C_{29}+C_{31}+C_{33}) / (C_{26}+C_{28}+C_{30}+_{C32}+C_{34})] /2$,

TAR : Terrigenous/Aquatic Ratio = $(C_{27}+C_{29}+C_{31}) / (C_{15}+C_{17}+C_{19})$,

Waxiness : $\Sigma (nC_{21}-nC_{31}) / \Sigma (nC_{15}-nC_{20})$

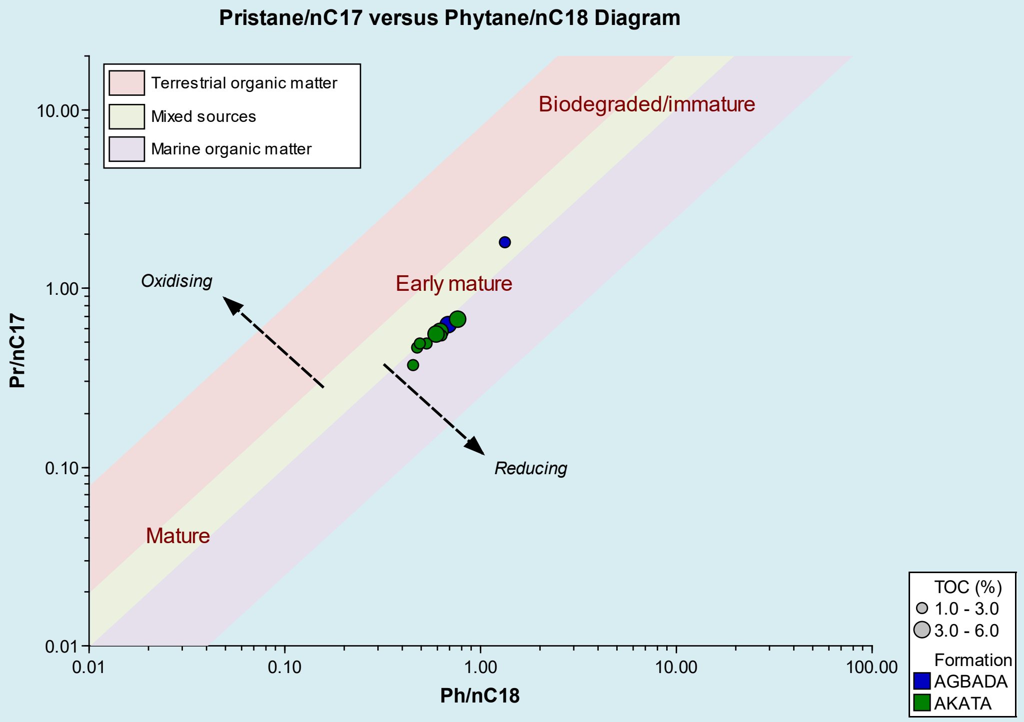

Figure 5: Plot of pristane/n-C17 versus phytane/n-C18 for the investigated samples (After [23]).

Formations	Wells	Depth (ft)	Ts/ (Ts+Tm)	Ol/ C30H	C31 22S/22R+22S	Ga/ C30H	C31R/ C30H	C26/C25 Tricyclic	C29 20S/ (20S+20R)	C29 ββ/ (ββ+αα)
Agbada	Isan 9	6760	0,36	0,36	0,45	0,11	0,35	2,65	0,11	0,66
	Benin West	7840	0,74	0,32	0,54	0	0,33	2,6	nd	nd
	Isan 9	8680	0,42	0,27	0,57	0,07	0,23	1,53	0,3	0,62
Akata	Ubefan	9800	0,32	0,84	0,57	0	0,39	1,09	nd	nd
	Ughelli	11120	nd	nd	nd	Nd	nd	Nd	nd	nd
	Appara	11800	0,33	0,73	0,5	0	0,33	1,36	nd	nd
	Kokori	12140	0,46	1,03	0,51	0	0,28	1,29	nd	nd
	Eriemu	12200	0,24	0,71	0,55	0	0,3	0,9	nd	nd
	Warri River	12260	0,38	0,31	0,59	0	0,37	1	nd	nd
	Udeduma Cr.	12340	0	1,19	0,55	0	0,23	1,15	nd	nd
	Isoko	13400	0,47	0,32	0,43	0	0,56	0,8	nd	nd

Table 4: Triterpane (m/z 191) and Sterane (m/z 217) biomarker parameters calculated from mass chromatograms of the analyzed samples.

Ts/(Ts+Tm)=18α-22,29,30-trisnorneohopane/(18α-22,29,30-trisnorneohopane+17α-22,29,30-trisnorhopane); Ga/C_{30}H = gammacerane/ C_{30} 17α(H),21β(H)-hopane ; Ol/C_{30}H =18α(H)-oleanane/C_{30} 17α(H),21β(H)-hopane ; BNH/C_{30}H = 17α(H), 21β(H)-28,30-bisnorhopane/C_{30} 17α(H),21β(H)-hopane ; C_{31} 22S/(22S+22R) = C_{31}17α(H),21β(H) 22S/[C_{31}17α(H),21β(H) 22(R + S)] ; C_{29}H/C_{30}H = C_{29}17α(H),21β(H)-hopane/C_{30}17α(H),21β(H)-hopane ; C_{26}/C_{25} tricyclic= C_{26} tricyclic terpane/C_{25} tricyclic terpane; ββ/(ββ + αα) = [5α(H),14β(H),17β(H)(20R + 20S)C_{29}sterane]/[5α(H),14β(H),17β(H)(20R + 20S) + 5α(H),14α(H),17α(H)(20R + 20S)]C_{29} steranes ; 20S/(20S + 20R) : C_{29} 5α(H),14α(H),17α(H),20S/[C_{29} 5α(H),14α(H),17α(H),20(S + R)].

Oleanane is present in all the samples studied. It is believed to be derived from pentacyclic triterpenes in some angiosperms [39]. The results in Table 4 show that all studied samples display Oleanane Index ($Ol/C_{30}H$) values more than 0.2, which indicates that these samples were generated from the Tertiary source rocks, with the presence of terrigenous organic matter input in the sediments [3,23]. Figure 10 indicates that the studied source rocks belong to marine deltaic depositional environment for the Tertiary source rock [39]. Samples Isan 9 (6760 ft) and Isan 9 (8680 ft) have moderate to higher Gammacerane index ($Ga/C_{30}H$) values ranging from 0.06 to 0.11 (Table 4), that suggest water-column stratification, potentially due to hypersalinity [33].

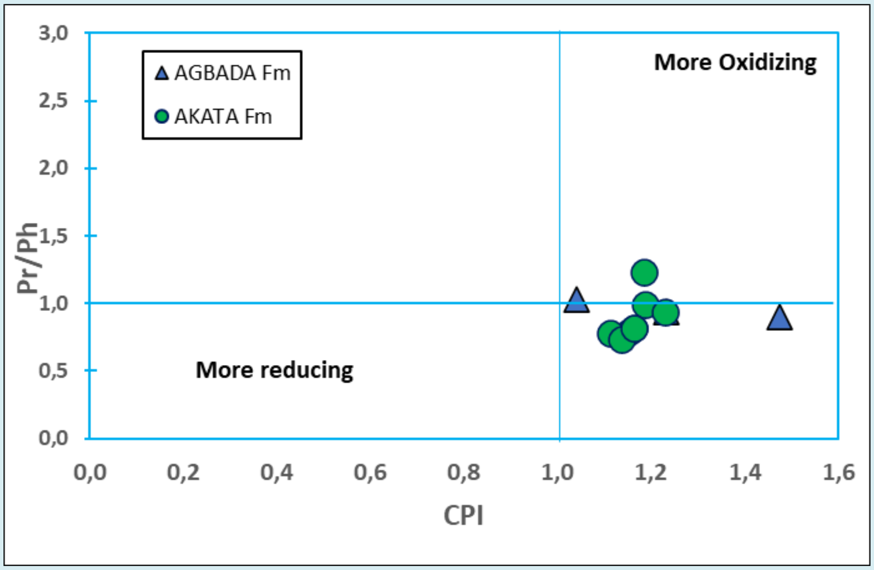

Figure 6: Plot of Pristane/phytane versus CPI, indicating the depositional environment conditions of the studied samples [35].

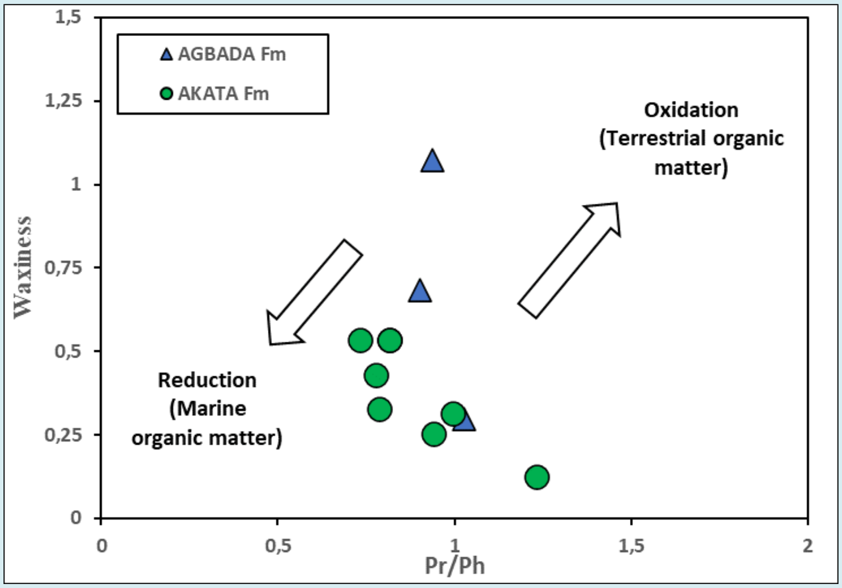

Figure 7: Cross-plot of waxiness index versus pristane/phytane ratios, indicating the depositional environment conditions of the studied samples (Modified after [40]).

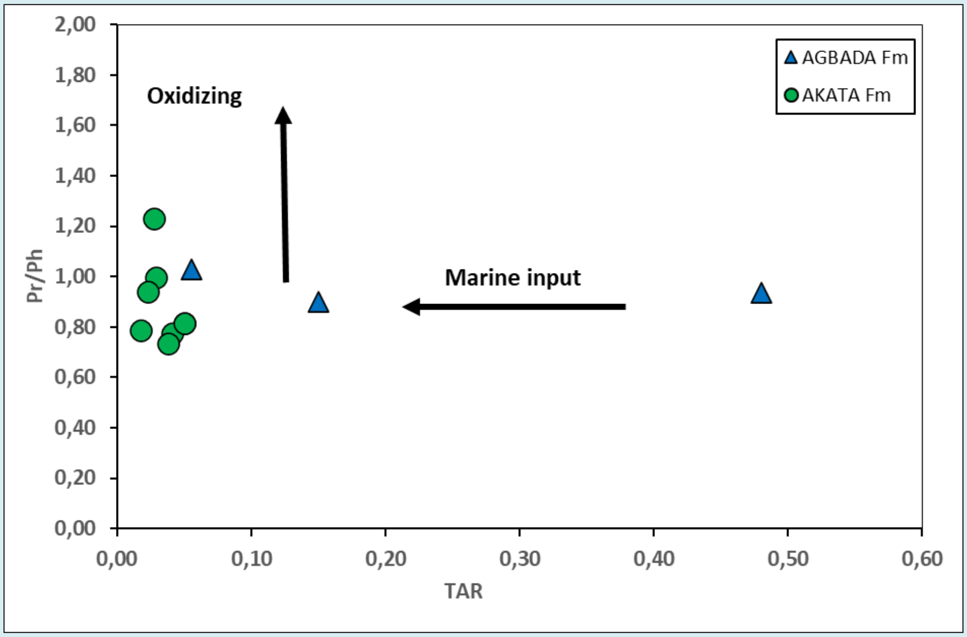

Figure 8: Cross-plot of Pristane/Phytane versus terrigenous/aquatic ratios, indicating the depositional environment conditions of the studied samples.

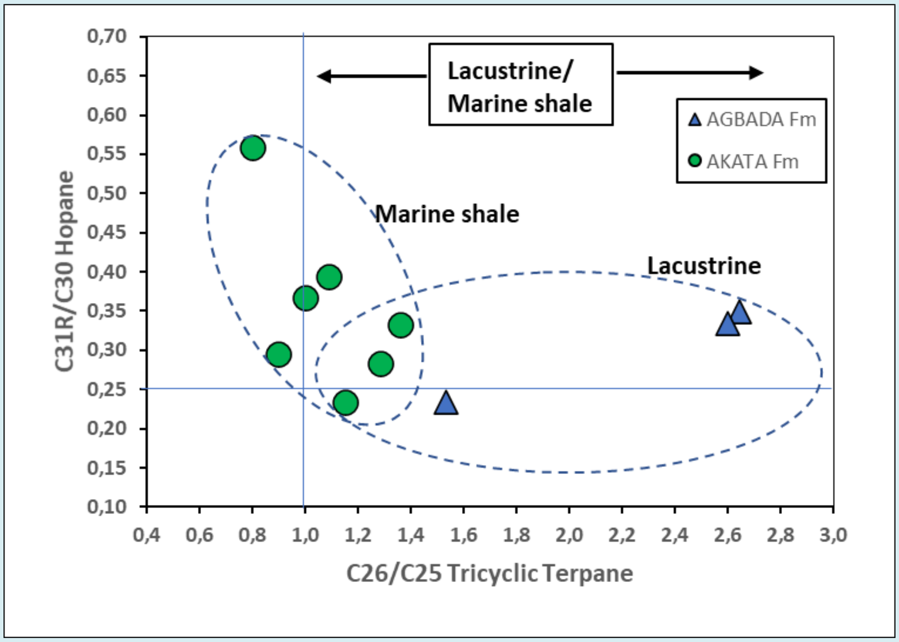

Figure 9: Plot of C_{26}/C_{25} tricyclic terpane versus C_{31} 22R/C30 hopane cross-plot for Agbada and Akata formation samples, showing depositional environments (modified after [23]).

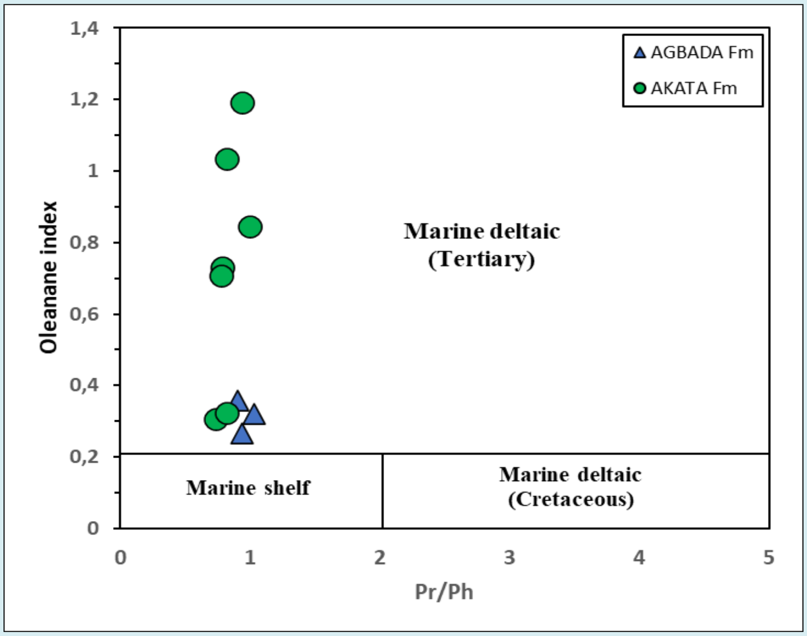

Figure 10: Plot of oleanane index values versus the pristane to phytane (Pr/Ph) ratio, indicating the depositional environment of the shale from Agbada and Akata formations.

Thermal Maturity Assessment

To understand the change of organic matters in rocks during diagenetic process the study of thermal maturity is used [41]. Biomarkers maturity parameters such as CPI, Ts/(Ts + Tm), C_{31} 22S/(22S + 22R) Hopane, 20S/(20S + 20R) and ββ/(ββ + αα) C_{29} sterane ratios were used as maturity indicators.

The Agbada formation samples have Carbon preference index (CPI) values that range from 1.04 to 1.48 (Table 3), which suggests moderate thermal maturity to immature source rocks. The extracts of Akata shale were all between 1.11 and 1.23 (Table 3), indicating immature to early mature source rocks. None of the samples were above 1.5.

C_{31} homohopane 22S/(22S+22R) isomerization ratio determines the configuration of homohopane molecules between biological form (22R) and geological form (22S). Ratio ranges from 0 to 0.6 indicating equilibrium during maturation. Early stage of oil generation values between 0.50 and 0.54. The Homohopane isomerization ratio can be calculated from any or all of C_{31}–C_{35} homohopanes. In this study, C_{31} homohopane is used as biomarker maturity indicator showing 22S/(22S+22R) ratio ranging from 0.45 to 0.57 for Agbada formation samples and ranging from 0.43 to 0.59 for Agbada formation samples (Table 4). The ratios suggest that organic matters have been reached at immature stage to early oil window (Figure 11).

The ratio of Ts (C_{27} 18α(H),22,29,30-trisnorneohopane) and Tm (C_{27} 17α(H),22,29,30-trisnorhopane), so called Ts/(Ts+Tm), is used to determine thermal maturity stage. Tm is less stable and converts to Ts during catagenesis. Therefore, the high value of this ratio represents low amounts of Tm with higher thermal maturity of organic matter [42]. The studied samples are mainly from siliciclastic rocks derived from terrestrial source. Thus, the variation of Ts/Tm ratios appears to be more strongly influenced by maturity instead of source inputs. Ts/(Ts+Tm) ratios from Agbada formation samples range from 0.36 to 0.74 suggesting early mature to late mature organic matter. Ts/(Ts+Tm) ratios from Akata formation samples range from 0 to 0.47 as presented in Table 4 indicating that the organic matter is in immature to early mature stage. The result of Ts/(Ts+Tm) ratios consistent with hopane isomerization ratio (Figure 11). The Plot of Pristane/nC_{17} versus Phytane/nC_{18} shows also immature to early mature organic matter for all investigated samples (Figure 5).

Other maturity parameters calculated from the m/z 217 ion mass fragmentograms are the C_{29}-5α,14α,17α(H)-20S/(20S + 20R) and the ββ/(ββ + αα) for C_{29} steranes. These ratios increase with increasing thermal maturity [23]. Although it has been stated that the 20S/ (20S + 20R) ratio equilibrates at 0.52 to 0.55 [43]. The values of 20S/(20S + 20R) and ββ/(ββ + αα) for the Agbada formation samples range from 0.11 to 0.3 and 0.62 to 0.66, respectively. These values suggest that the analyzed samples are early mature to thermally mature for hydrocarbon generation (Table 4).

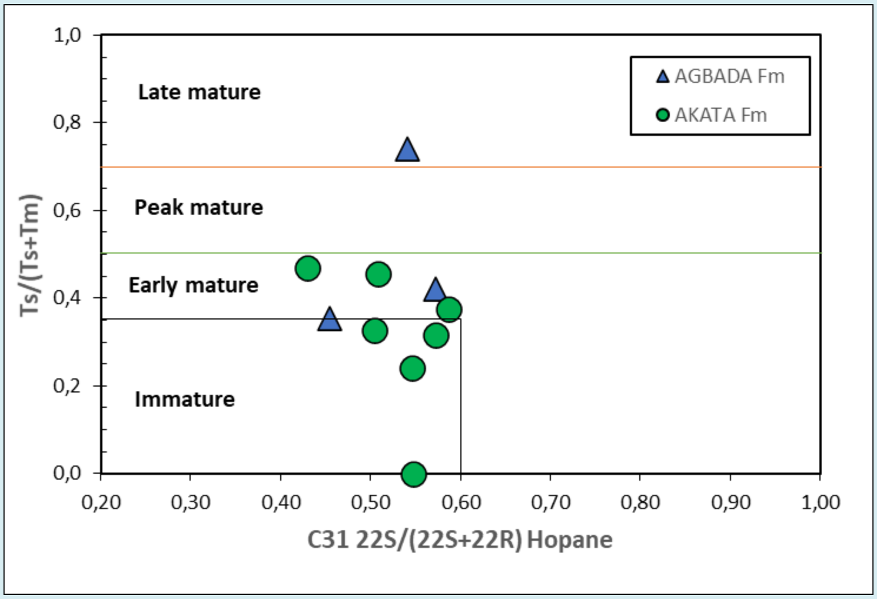

Figure 11: Cross-plot between the ratios of the Ts/(Ts+Tm) and C_{31} 22S/(22S+22R) homohopane.

Conclusion

The molecular geochemical analyses of selected samples from Agbada and Akata formations from Niger Delta (Nigeria) revealed that source rocks are type III (Terrestrial) and mixed origin (II/III - marine and terrigenous), deposited under anoxic to dysoxic conditions. The distribution of biomarkers and metrics such as Pr/Ph, CPI, Waxiness, and TAR suggests a mixed intake of marine and terrigenous organic matter deposited under reducing (dysoxic) conditions. Low Phytane/nC_{18} (0.45 to 1.32) and Pristane/nC_{17} (0.37 to 1.8) values in Agbada and Akata formation rock extracts suggest marine organic matter contribution and anoxic-suboxic (Type II/III kerogens) depositional settings. The Oleanane Index (Ol/C_{30}H) values in all of the samples studied are more than 0.2, suggesting that they were produced from Tertiary source rocks containing terrigenous organic matter in the sediments. In a marine deltaic depositional context, the Tertiary source rocks developed. The presence of Gammacerane in samples from the Isan oilfield's Agbada deposit indicated water-column stratification, perhaps owing to hypersalinity. The Agbada formations were the only formations that showed lacustrine characteristics. It could suggest a link with the Neocomian source rock of the Lower Cretaceous which is lacustrine and most of the tar sands of the western Niger Delta show lacustrine features. Biomarkers maturity metrics such as CPI, Ts/(Ts+Tm), 22S/(22S+22R) C_{31} Hopane, 20S/(20S+20R), and ββ/(ββ+αα) C_{29} sterane ratios were used as maturity indicators. These maturity indicators indicate that hydrocarbon production in the sediments is still in its early phases.

Nomenclatures/Abbreviations

C	Carbon
C_{29}	Total number of carbon present in a biomarker
CPI	Carbon Preference Index
DCAR	CENTRE OF ANALYSIS AND RESEARCH DIRECTION
Ga	Gammacerane
GC-MS	Gas chromatography-mass spectrometry
H	Hopane
m/z	Mass to charge ratio
OEP	Odd to Even Predominance
Ol	Oleanane
PETROCI	NATIONAL SOCIETY OF PETROLEUM OPERATIONS OF COTE D'IVOIRE
Ph	Phytane
Pr	Pristane
R	Asymmetric carbon in ring that obeys clockwise conventions
S	Asymmetric carbon in ring that obeys anticlockwise convention
SIM	Selected ion monitored
t	Terpane
TAR	Terrigenous to aquatic ratio

TT	Tricyclic terpanes
á	Asymmetric carbon in ring with functional group (usually H) down
â	Asymmetric carbon in ring with functional group (usually H) up

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