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The Occurrence and Distribution of Oleanane Biomarkers in Crude Oils as an Index

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Abstract

Oleanane biomarkers are age diagnostic indicators and source of organic matter input in fossil fuels which can unravels the stage of development of a petroleum system in the petroleum generating rock. Representative samples of crude oil obtained from two separate fields in the southern Nigeria province were evaluated geochemically using Gas Chromatography–Mass Spectrometry. The data obtained from the analysis of the crude oil samples revealed the presence of the 18α (H)-oleanane biomarker. The occurrence of 18α (H)-oleanane biomarker in the Niger Delta oils provides diagnostic evidence on age and organic matter source in all samples. The results of the Oleanane indices for all samples ranged from 0.32 to 1.03 (> 0.30), which suggests that the oils are from Tertiary age source rocks with resilient terrestrial organic matter input. Only crude oil sample KD03 had an Oleanane index of 0.03 (< 0.30), which shows crude oils derived from a late cretaceous or younger age with some marine input. The presence of 18α (H)-Oleanane in Niger Delta crude oils is a confirmation of an earlier postulation that most crude oils from the region had a greater terrestrial organic matter input.

Keywords: Oleananes, Biomarkers, Terrestrial, Angiosperms, Gas Chromatography– Mass Spectrometry.

Introduction

Biomarkers are compounds having carbon-based structures with their carbon skeletons traced to plants and animals. They are abundant in sediments, oil, and other rocks derived from hydrocarbons. Most biomarker structures are preserved with little change through the period of diagenesis and catagenesis. Their occurrence in fossil fuels and source rocks generally infers paleoenvironmental conditions, thermal maturity, organic matter source, genetic similarity genetically between various categories of oils and the generating source -rock from which the crude oils were formed. The Oleanane biomarker is a pentacyclic triterpene existing in two isomeric forms of 18α (H)-oleanane and 18β (H)-oleanane. Their source is the plants with the alpha (α) configuration having the utmost stability thermodynamically, confirming it as the most dominant structure in petroleum generating rocks and thermally matured crude oil [1]. Therefore, the 18α (H)-oleanane biomarker is one of the significant terrestrial plant diagnostic biomarkers of angiosperms (Figure 1).

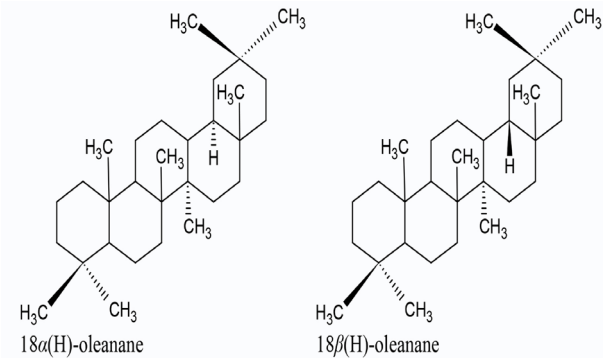

Fig. 1 Structure of oleanane Isomers

Therefore, the discovery of the 18α (H)-oleanane biomarker in fossil fuels and crude oils are used as an index for the age which unravels the stage of development of a petroleum system and the type of organic matter in the petroleum generating rock. Many researchers have applied the 18α (H)-oleanane index as an age indicator and source of organic matter [2, 3]. The existence of 18α (H)-oleanane in rocks generating petroleum/

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crude oils has also been used as an index of terrestrial organic input [4, 5]. The main reason is that the 18 (H)-oleanane biomarker is an angiosperm derivative of terrestrial plant origin. Many researchers, such as Rullkotter et al [6], revealed that the oleananes were produced by the process of diagenesis and catagenesis modification of several 3β-functionalized angiosperms. They are usually incorporated into petroleum during the generation process, and hence, they are employed in crude oil and source rock correlation studies. The source of flora which contains 18α (H)-oleanane precursors is fundamentally angiosperms recognized as the Late Cretaceous or younger [7].

A few exemptions from the research showed 18α (H)-oleanane was shown to be present in rocks older than the Late Cretaceous in moderate abundance in the Paja Formation of the Magdalena Basin, which was dated as of the Late Hauterivian-Barremian [8].

The biomarker 18α (H)-oleanane originates only in Tertiary and Cretaceous source rocks and oils that less than 130 million years old. The occurrence of 18α (H)-oleanane in benthic sediments was earlier used to establish a petrogenic source in Prince William Sound, collectively with its absence in Alaska North Slope crude oil and specifically in Exxon-Valdez oil and its residue [9, 10].

It has previously been discovered that the presence of 18 α(H)-oleanane establishes the age of the oil or source rock as of late cretaceous or Early Tertiary. There were several indications of 18 α(H)-oleanane in samples older than the late cretaceous, including Middle Jurassic marine siltstones from the Tyumen Formation in West Siberia, Russia; a Pennsylvanian coal ball from Illinois, USA; Middle Jurassic Brora coal in Scotland; Upper Permian rock extracts from Guizhou Province, China; and the Paja Formation, Upper Magdalena Basin, Colombia biostratigraph [11-13]. Explanations for these early occurrences of 18α (H)-oleanane were generally tentative, but possibilities were proposed by Moldowan et al [11] included a separate lineage leading to the angiosperms, such as stem-angiophytes that left their chemical signature long before plants with unmistakably angiospermous features were preserved, and related angiosperm sister groups that may have had the capability to produce the precursors to 18α (H)-oleanane [14,15]. 18α (H)-oleanane was applied in the characterization of crude oils from the Anaco area and Maturin subbasin in Venezuela were the studied places to indicate the organic matter source and age evaluation of the petroleum system [1]. The oleananes are usually formed by loss of the ring and aromatization reactions, and most of the reactions occur during the early stages of diagenesis. They are generally mediated by microbial and photochemical processes [16]. The products of the aromatization processes of plant triterpenoids can also serve as the source of specific biomarkers used to trace terrestrial organic matter input and transformations in vegetation and paleoenvironments [17]. On the other hand, their distributions could be used in recent and new sediments to redistribute specific plant inputs and deduce associated ecological and environmental alterations, including anthropogenic impacts [18].

Geological Setting of the Study Area

The study area where crude oil samples were collected was in the Niger Delta, Nigeria. It is located in the Gulf of Guinea with three geologic formations: Benin, Agbada and Akata Formations [19]. The study area (Niger Delta) is classified as one of the major hydrocarbon provinces that exist worldwide, producing about 34.5bbs of oil and 93.8 trillion cubic feet (ft^3) of gas. The depobelt of the area is the foremost regressive delta, having an expanse of 300,000 km^2, a sediment capacity of 500,000 km3 and a sediment depth of more than 10 km in the basin depocenter [20, 21]. The petroleum system of the study area (Niger Delta) was defined as the Tertiary or Akata –Agbada Petroleum System (Fig. 2a).

The boundary of the study area is identical to southern Nigeria geology and south-western Cameroon with a boundary at the north as that of the Benin border (Fig. 2a). Outliers of the Cretaceous delineate by outliers of the Cretaceous on the Abakaliki high and eastern part by the Calabar boundary, an axis line flanked by the Precambrian. The Cameroon volcanic contour delimits the shoreline boundaries of the region to the eastern border of the Dahomey basin to the west, and the 2 Km thick sediments contour or the four-thousand-meter bathymetric outline in zones having a sediment depth of more than 2 Km towards the south [22]. Fig. 2b is the map of the Niger Delta showing two producing fields where samples were collected.

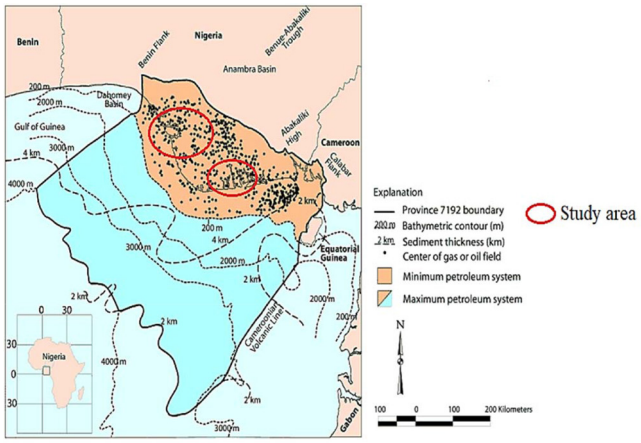

Fig. 2a Map of the Niger Delta showing Province outline. Source: U. S. Geological Survey Open File Report)

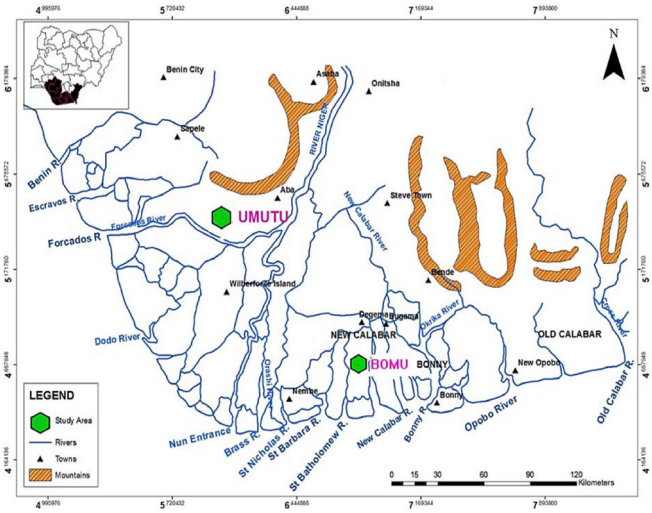

Fig. 2b Map of the Niger Delta showing two fields where samples were collected.

Stratigraphic Column of the Niger Delta

The Niger Delta consists of three broad formations: hydrocarbon habitats, the Akata, Agbada, and Benin formations. The Akata formation is situated at the base of the delta, and it is of marine origin. It exists from the Paleocene to the present day, has high pressure, and underpins the entire delta. It is comprised of thick shale arrangements, which are potential source rocks, turbidite sand, potential reservoirs in deep water, and small amounts of clay and silt (Fig. 2c).

The characteristics of the Akata formation formed in low stands at the time terrestrial organic matter and clays were transported to deep water areas are characterized by low energy conditions and oxygen deficiency [23]. According to Doust and Omotsola [24], the estimated thickness of the formation is about 7,000 meters thick. The second is the Agbada formation, which consists of sand and shale. It is the main petroleum-bearing unit that began in the Eocene, and it has continued to the present day.

The formation is made up of paralic siliciclastic that is more than 3700 meters thick and represents the sequence's actual deltaic area.The clastics accumulated in the delta-front, delta-topset, and fluvio-deltaic environments. In the lower Agbada Formation, shale and sandstone beds were deposited at equivalent magnitudes. Nevertheless, the upper portion is typically sand with minute shale interbeds. The Benin formation that follows the Agbada formation is a late Eocene to a recent continental deposit of sedimentary and upper coastal plain sands up to 2000 m thick [25]. The upper Benin formations consist of freshwater bearing, continental sand, and gravel stone. The formation is a late continental Eocene to a recent deposit of sedimentary and upper coastal plain sands with a thickness of up to 2000 m [25,26].

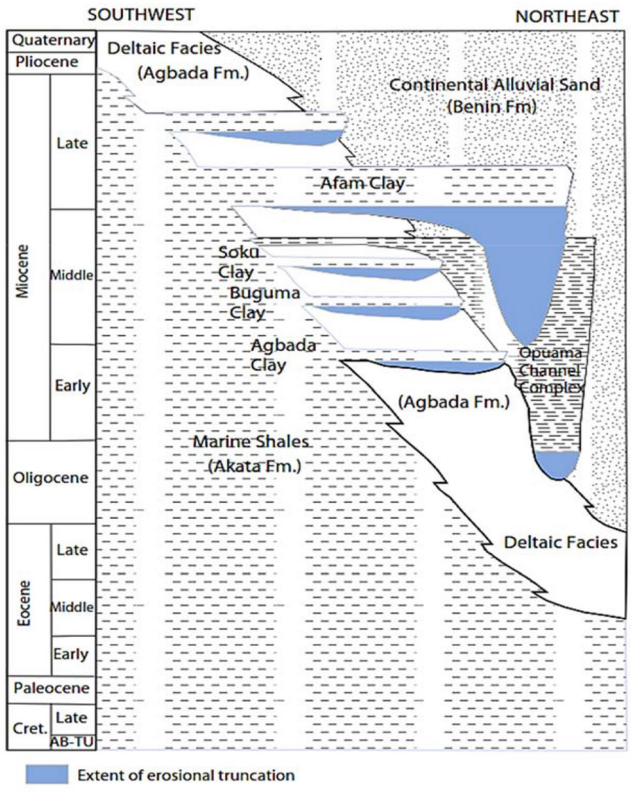

Fig. 2c Stratigraphic column showing the three formations of the Niger Delta. Modified from Doust and Omatsola (1990)

This research is aimed at using the oleanane biomarker as an age diagnostic index and source of organic matter in crude oils from two fields in the southern Niger Delta, Nigeria.

Materials and Method

Sample Collection

Seven (7) representative samples of crude oil were obtained at different depths, from 9800 ft to 10400 ft, from two (2) onshore producing fields in the southern Niger Delta. Deionized water and nitric acid (HNO_3) were used to rinse the glass vials and dried properly before sampling. The sampled crude oils were placed in a cooler that contained ice blocks and the temperature was maintained at about 4°C prior to the laboratory analysis.

Fractionation of Oil

The fractionation process comprises separating the crude oil samples into saturates, aromatics hydrocarbons and polar compounds by column chromatographic methods. Dichloromethane and petroleum ether were used to rinse the glass column at a length of 50 cm and an internal diameter of 0.5 cm. Cotton wool was then used to pad the column, which supports the silica gel (SiO) stationary phase. It was filled with petroleum ether, then silica gel was added. It was followed by the addition of two grams of alumina to stabilize the surface. The crude oil samples were carefully poured in, and then the emissions were released. The aliphatic fraction was eluted with 70 ml of petroleum ether, then 70 ml of dichloromethane (DCM) was added to elute the aromatic fractions. 70 ml of methanol was further added to elute the polar fractions (resins). A stream of N2 was used to reduce the aliphatic fractions' dryness and was diluted with dichloromethane before Gas Chromatography-Mass Spectroscopy (GCMS) analysis.

Gas Chromatography-Mass Spectroscopy (GC-MS) Analysis

The aliphatic hydrocarbon fraction of the fractionated crude oil samples were analyzed with GC-MS with a Hewlett-Packard 5890II and a split/splitless injector at 280 °C linked to a Hewlett-Packard 5972MSD. Seventy electron voltage (70eV) was used, and 220 microamperes the current of the filament with a source temperature of 160 °C, a multiplier voltage of 1600 volts and the temperature at the interface was 300 °C.

The acquisition was measured with an HP Vectra PC chemstation computer in full scan and selected ion mode. One microlitre of the sample was injected by an HP7673 auto-sampler, and it took approximately one minute for the split to open. This is followed by separation, which is done on a silica capillary column (30 m × 0.25 mm id.) coated with 0–25 µm, 5% phenylmethyl silicone (HP-5). The temperature of the gas chromatograph was set between 40 °C – 300 °C at 4 °C per minute and made to remain stable at an ultimate temperature of twenty minutes. Helium, which had a flow rate of 1 ml/min and a pressure of 50 kPa, slit at 30 ml/min, was the carrier gas. The data were obtained on DAT tape and processed later using Chemstation G1701BA (B.01.00 1989-1998) software. The RTE integrator was used for peak integration.

Results and Discussion

Oleananes are diagenetic products of various 3-functionalized angiosperm (flowering plants) triterpenoids [27]. The 18β (H)-oleanane is the naturally occurring isomer of the oleananes, but is thermally less stable and so undergoes isomerization gradually [28,29]. The ratio of 18α (H)-/18β (H)-Oleanane has been used by various researchers as a thermal maturity indicator. In his research, it was proposed by Armanios [30] that 18α (H)-Oleanane is the resultant product of the hydrogenation of 18α (H)-olean-12-ene in somewhat immature samples. The same researcher further established that Olean-18-ene is lost more than the frequency at which it is formed 18β(H)-oleanane, while 18α(H)-Olean-12-ene undergoes a very slow reaction to produce 18α(H)-Oleanane. As they become more mature, 18β (H)-oleanane might be preferentially destroyed or isomerize to 18α (H)-oleanane, which is more thermally stable. The pattern of diagenesis and early catagenesis of the oleanane biomarker is shown in Fig. 3.

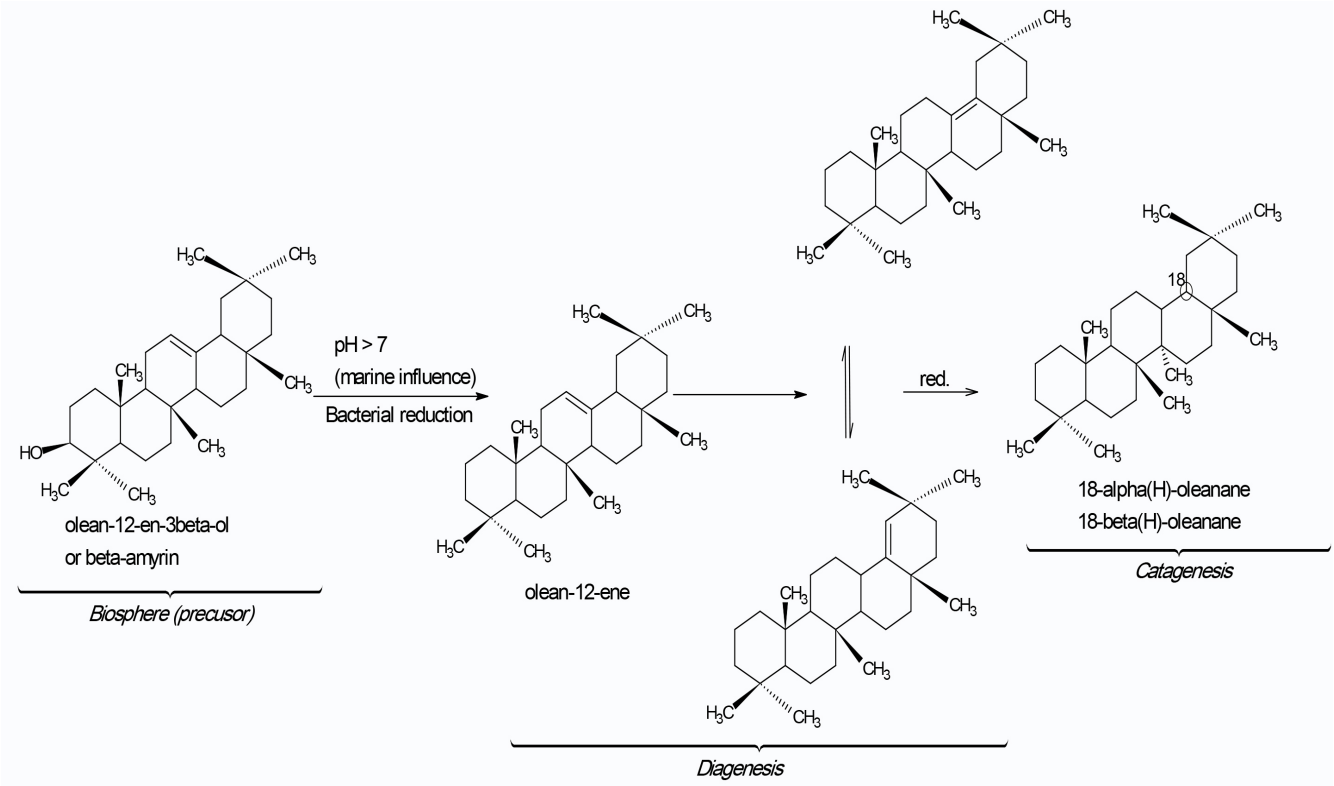

Fig. 3 Pattern of diagenesis and early catagenesis of oleanane biomarker (after ten Haven et al., 1988).

The oleanane index (Oleanane / (Oleanane+ C_{30}αβ-hopane) is a valuable parameter for source rock age determination was described by Moldowan et al. [8]. The early cretaceous or younger age show values of 0.03, while a higher oleanane index, greater than 0.3, is suggestive of oils which are derivatives of source rocks of the Tertiary age [31].

The presence of Oleanane was detected in all crude oil samples from this study, as indicated by a peak on the chromatograms representing 18α (H)-oleanane and 18β (H)-oleanane (Figures 4a, b, c, d).

Prominent authorities, like Ekweozor et al. [32], Philip and Gilbert [33], have suggested that the occurrence of oleananes in oil is a pointer to a terrestrial input into the oil-prone petroleum source rocks and shales deposited in a deltaic paleoenvironment.

A relatively low oleanane index in crude oil samples could be due to several factors, including the nature of the original depositional environment, crude oil maturity, or geological age. The ratio of the 18α (H)-oleanane/18β (H)-oleanane increases with maturity, possibly suggesting an isomerization of the beta (β) isomer to the alpha (α) isomer [34].

It was proposed by researchers such as Philp et al. [35] that as oil maturity increased, the ratio of 18α (H)oleanane/18β (H) oleanane did too. According to research, the 18α (H)-oleanane isomer is found in small quantities relative to its analog in more mature samples, but it becomes increasingly significant as depth increases. This may suggest that the 18β (H) oleanane is generated primarily by reducing an unsaturated molecule, which may isomerize into the alpha (α) isomer. Both 18α (H)-oleanane and isomers were discovered near the base of the late cretaceous in sediment and oil extracts. It suggests that the presence of oleananes is more related to a specific form of organic matter in angiosperms than to a certain age (tertiary), as reported earlier. Oleananes have been identified at the base of the late cretaceous; however, it expands the potential use of oleananes as genetic markers in sediments older than the tertiary [34, 35].

The results of the oleanane indices for all samples ranged from 0.32 to 1.03 (> 0.30) (Table 1), which is suggestive of crude oils originally from source rocks of Tertiary age with resilient terrestrial organic matter (a strong or higher plant) input.

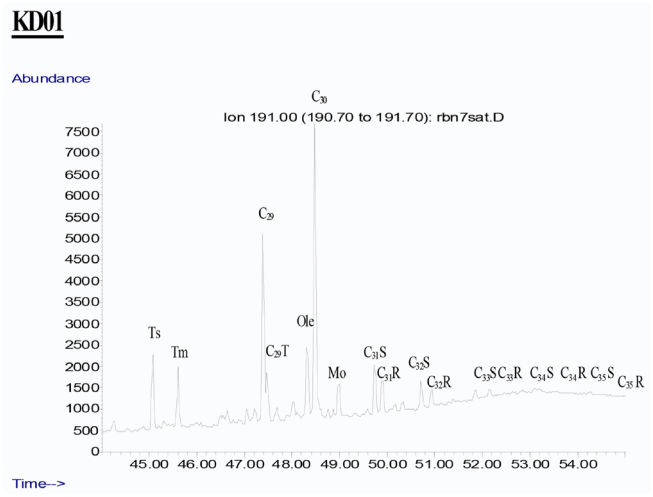

Fig. 4a Representative GC- MS Chromatograms of m/z 191 for crude oil samples.

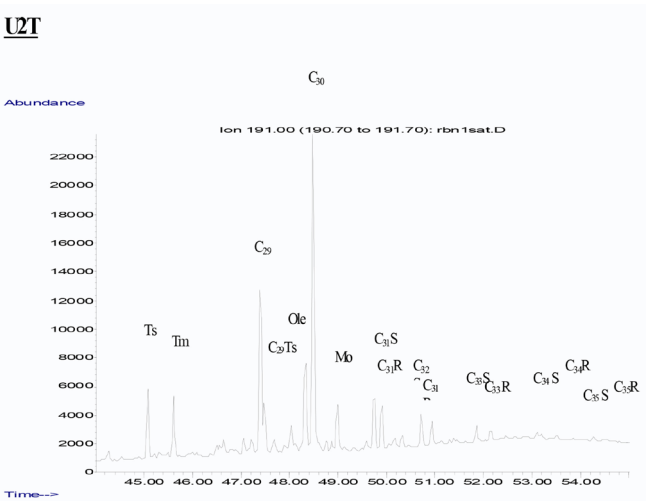

Fig. 4c Representative GC- MS Chromatograms of m/z 191 for crude oil samples.

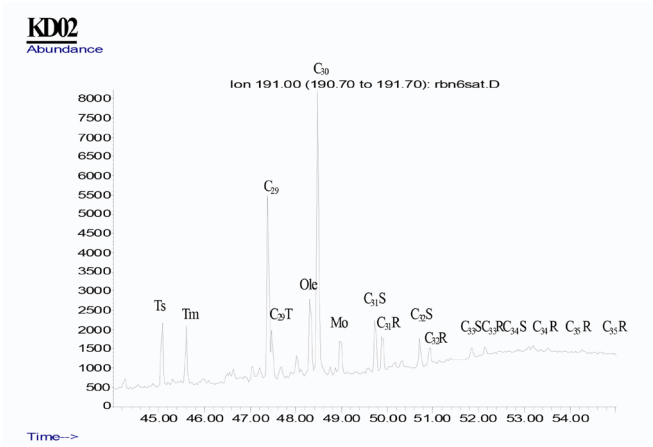

Fig. 4b Representative GC- MS Chromatograms of m/z 191 for crude oil samples.

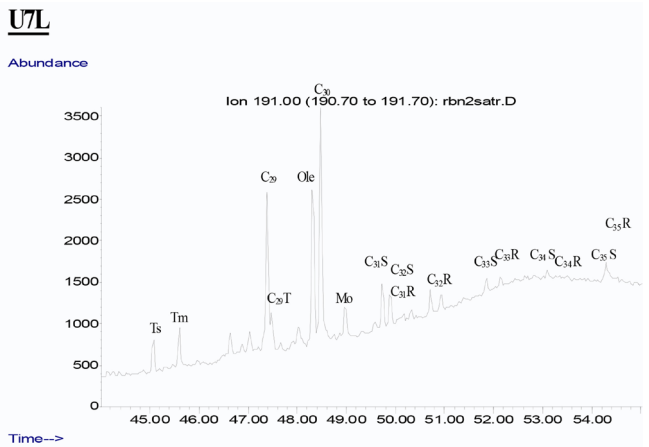

Fig. 4d Representative GC- MS Chromatograms of m/z 191 for crude oil samples.

Table 1 Calculated biomarker ratios in some Niger Delta crude oil samples.

		Sample					
Biomarker ratios	U2T	U7L	U4L	U45	KD01	KD02	KD03
Ts/Tm	1.19	0.82	0.79	0.86	1.25	1.15	1.47
Ts/(Ts + Tm)	0.54	0.45	0.44	0.46	0.56	0.53	0.59
C_{29}/C_{30}hop	0.62	0.65	0.69	0.67	0.64	0.65	0.60
Ole Index	0.37	0.72	0.72	1.03	0.32	0.31	0.03
Homo Index	0.03	0.04	0.01	0.01	0.04	0.04	0.05
C_{30M}/C_{30hop}	0.15	0.14	0.17	0.17	0.17	0.14	0.15
Sterane/hopane	0.08	0.14	0.13	0.20	0.09	0.06	0.02
22S/(22S+22R)	0.56	0.52	0.56	0.55	0.55	0.58	0.55
C_{30}*/C_{29}Ts	6.57	8.35	6.86	7.39	7.03	7.20	6.36
20S/(20S+20R)	0.60	0.50	0.51	0.50	0.63	0.55	0.46

Tm: 17α (H), 22, 29, 30-trisnorhopane; Ts:18α(H), 22, 29, 30-trisnorneohopane; Ole Index (Ol/C_{30}: Oleanane/C_{30} hopane); Homo Index: Homohopane Index (C_{35} homohopane S + R)/(C_{31} + C_{32} + C_{33} + C_{34} + C_{35} homohopanes S + R); $C_{30}M/C_{30}$hop: C_{30} mortane/C_{30} hopane; 22S/(22S+22R): 17α (H), 21β (H)-bishomohopane (22 S)/ [17α (H), 21β (H)-bishomohopane (22 S) + 17α (H), 21 β (H)-bishomohopane (22 R)] of $C_{31\text{-}32\text{-}33}$; C_{30}*/C29Ts: 17 α (H) hopane/18α (H)-

Crude oil sample KD03 showed an oleanane index of 0.03 (< 0.30), suggestive of an early cretaceous or younger age, which is an indication of a marine source with negligible terrestrial input [31,36]. During the early cretaceous phase, only the intermittent existence of angiosperm plants had been recorded, and by the commencement of the late cretaceous, they were usually the flora. The concentration of oleananes usually increases during the tertiary stages [8,37]. Ekweozor and Udo [38] have proposed an upsurge in the oleanane ratio from low values in immature source rocks to a maximum at the top of the oil-generating window. Moreover, at elevated maturity levels, the oleanane index tends to increase by the destruction of hopanes. Highly matured crude oils show a greater oleanane index than the source organic matter in the immature or low-maturity-level source rock. Riva et al. [34] stated that there are greater relationships between the ratio of Oleanane and its isomers and other indices used for maturity, such as the Ts/Tm.

The findings of this study agree with those of other researchers, such as Ekweozor et al. [32], who found out that crude oils from the Tertiary Niger Delta, which originated from marine shales of the Tertiary Akata formation with significant terrigenous higher plant input, had a high oleanane content. Peters et al. [12] stated that Oleanane and its interrelated triterpenoid skeletons occur geologically in materials limited to the cretaceous and after. The presence of oleananes has also been useful for age assessment of petroleum source rocks; the existence of oleananes practically without doubt specifies a Cretaceous or younger origin, and a higher oleanane to hopane ratio (oleanane index > 0.2) infers a Paleogene or younger origin [40].

Several researchers have used the Oleanane index as an age determining parameter in crude oil correlation studies, but caution should be exercised because, during the process of oil migration in reservoirs, crude oils in the reservoirs are likely to be contaminated with oleananes of the same nature [41,42]. Studies have also shown Oleananes to be a reliable indicator of a higher plant source material derived from higher plant triterpenoids rather than a bacterial origin.

Conclusions

Geochemical studies of crude oils from the Niger Delta have revealed high concentrations of oleananes in a variety of oils and shales from the Delta region. This research has shown that the existence of 18α (H)-oleanane in crude oil and petroleum source rocks is an indicator of the input of terrestrial organic matter. This is because 18α (H)-oleanane originates from a terrestrial diagnostic biomarker resulting from angiosperms previously verified in Cretaceous and younger sediments. It substantiates the presence of tertiary source rocks with terrestrial organic matter.

Oleananes, a biomarker, is a diagnostic index of source rock age and the land plant input of angiosperms, which provides valuable geochemical information on the organic matter source and the age of the oil. Although previous studies have concluded source and age information of crude oils using the oleanane index, it is important to substantiate and validate this because it may portend or be a pointer of the reservoir's age. 18α(H)-Oleanane has naturally been described to be a derivative of an angiosperm source. There were numerous propositions for these initial existences of 18α(H)-Oleanane, which it includes the proposition that angiosperms and associated kinds, fragmented off from the gymnosperms far-off than hitherto anticipated. Consequently, their occurrence in crude oil sets an age constraint for the petroleum system. The occurrence of 18α (H)-Oleanane in crude oils designates an age range for the hydrocarbons from cretaceous or younger and higher in tertiary sediments, which coincide with the evolution of angiosperms are indicative of both (1) source rock age and (2) terrestrial input, which both of them are beneficial biomarkers or molecular fossils in crude oil correlation studies and petroleum geochemistry generally.

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Nomenclatures

KD03: GC-MS: Gas Chromatography-Mass Spectroscopy RTE integrator

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