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# API GRAVITIES AND GEOCHEMICAL EVALUATION OF CRUDE OILS FROM SAPELE, NIGER – DELTA, NIGERIA

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# ABSTRACT

The investigation is to provide information on source organic matter input, depositional conditions and the correlation between crude oils recovered from Sapele oilfield in the Niger Delta. A suite of twenty-five crude oils from the Agbada reservoirs (synsedimentary) of the Tertiary Niger Delta (Southern Nigeria) were analysed based on API gravities and geochemically compared with extracts from source rock of the Akata and Agbada Formations. The Sapele shallow reservoirs occur between the depths of 4000ft and 6000ft, containing heavy crudes with API gravities 20 – 22 degrees. The deep reservoirs lie within 7000ft and 12000ft accumulating the light crudes with API gravities of 24.70-35.60 degrees, and viscocity of 1.64cP. The investigated biomarkers indicated that the Sapele oils were derived from mixed marine and terrigenous organic matter and deposited under suboxic conditions. This has been achieved from normal alkane and acyclic isoprenoids distributions, terpane and sterane biomarkers. These oils were also generated from source rock with a wide range of thermal maturity and ranging from early-mature to peak oil window. Based on molecular indicators of organic source input and depositional environment diagnostic biomarkers, one petroleum system operates in the Niger Delta Region; as observed on the source rocks from the Agbada organic – rich shale sediments. Therefore, the hydrocarbon exploration processes should be concentrating on the Akata and Agbada area of the Tertiary strata for determining the source kitchen.

**KEYWORDS:** API Gravity, isopreniods, terpanes, steranes, Depositional environment, Sapele.

# INTRODUCTION

The Sapele oil field is located in the northwestern part of the main hydrocarbon producing area of the Niger Delta, a few kilometers west of Sapele town within latitude 5°38' to 5°59'N and longitude 5°30' to 6°00'E (Fig. 1). Over 32 wells have been sunk in the development of the field. The hydrocarbon bearing structure is a NW-SE trending roll-over anticlinal structure that is situated on the downthrown side of the structure forming boundarv faults. The hydrocarbons are trapped in low relief, flat crested dip-closures at shallow depths gradually changing with depth to steeper, elongated fault bounded closures (Lambert-Aikhionbare and Shaw, 1981).

Sapele is one of the oil-rich and biggest oil producing area in the Niger Delta Basin found within the mid-Western Nigeria (Fig. 1). The dataset used in this study was taken from the most productive Bakana and Ogberikoko wells in the Sapele oilfields Niger Delta Region, located offshore and occupy the northwestern part of the Sapele Region (Fig. 1). Sapele is situated within the Tertiary Niger-Delta rift basin and contains several producing oilfields of various sizes, the largest of which are the Sapele and Oben oilfields (Fig. 1). The hydrocarbon bearing structures consist of simple

The hydrocarbon bearing structures consist of simple roll-over anticlines bounded to the north by a major east-west trending synsedimentary growth fault and dip-closed to the South, East, and West. Such

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growth faults are believed to be triggered by the presence of under-compacted clays that underlie the fluvio-marine deposits in which hydrocarbons are trapped (Hospers, 1971). Thicker deposits are found on the downthrown side of the synsedimentary or "growth" faults where the Sapele Field occurs. At depths, in the "H" sands, the main fault branches and delineates a smaller fault block to the northwest and the crest of the roll-over anticline is cut by two antithetic faults (Ajekaiye and Bally, 2002). The depositional sequence in the Sapele Field shows that the reservoir section consists of overall blocky to coarsening upwards sequences cut at the top by unconformity surfaces (Nwajide, 2006).

The geochemistry and heavy crudes of the Sapele oilfields have previously been studied by a number of

researchers (e.g., Mills, 1992; Idowu et al., 1993; King et al., 2003; Adekeye, 2004; Adekeye et al., 2006; Adekeye and Akande, 2010; Hakimi et al., 2011a,b; Al Areeg et al., 2011). The current paper deals with the geochemical evaluation of crude oils and source rock recovered from the Adbada Formation, Sapele oilfields. To determined biomarker distributions and use the resultant data to characterize the oil types and to assess the respective depositional environment, age and thermal maturity of their source rocks. Subsequently, using molecular composition data from both oil and source rock samples to determine oil to source rock correlation.



Fig. 1: Map of Sapele showing the location sampling sites (after Arise et al., 2015)

# **GEOLOGICAL SETTING**

Short and Stauble (1967), outlined the regional geology of the Niger Delta. The origin of the Niger Delta was attempted and they established that the Tertiary deltaic fill is represented by a strong diachronous sequence (Eocene- recent), which divided into three lithofacies units namely; the Akata, Agbada and Benin Formations (Fig. 2). Bustin (1988) established that the Niger Delta basin is divided into continental, marginal marine and marine facies. Haack *et al.* (2000) discussed the tertiary petroleum systems of the Niger Delta.

These three formations according to Short and Stable (1967), are locally designated from the bottom as Akata, Agbada and Benin formation respectively. Of all these three formations, the Agbada formation constitutes the main reservoir of hydrocarbon in the Niger Delta province.

(i) *Benin Formation:* The Benin formation consists predominantly of massive, highly porous, fresh – water sandstones with shale/ clay interbeds. These

sediments represent upper Delta – Plain deposits, so that the gravels and sandstones represent braided streams, point – bar channel fills, while shales and clays may represent back swamp – deposits (Weber, 1971). The thickness is variable but generally exceeds 2,000 meters in thickness (Weber and Daukoru, 1973) while Merki in his own, attributed that, the formation records 4,000 ft in thickness (Merki, 1970).

(ii) Agbada Formation: Weber and Daukoru (1973); explained the Agbada formation to the consisted of inter – bedded sand shales with a thickness of about 300 - 4,500 meters (Oghonyon *et al.*, 2015)); Merki, (1976), suggests that the interbedded sand and shales have a thickness of about 10,000 ft (in the center of the Delta). The sandy parts constituted the main hydrocarbon reservoirs, and the shales, the cap rock, Weber, (1971).

(iii) *Akata Formation:* The Akata Formation is mainly composed of marine shales with locally sandy and silty beds thought to have been laid down as

turbidites and continental slope channel fills. The formation is said to be the main source rock for the Niger Delta complex. Its thickness depends on shale diaprism and flowage which the formation has been subjected.

Stonily (1966) and Burke (1970 and 1972) analyzed and discussed the mega tectonics of the Niger Delta. The sedimentary tectonics of the tertiary delta was extensively described by Merki (1972) and Evamy et al. (1978). According to Burke (1972), the modern Niger Delta has three well developed submarine channels and numerous smaller gullies which extended from the mouth of the delta to the abyssal plain. Several other paleochannels have been recognized by Murat (1972); Omatsola and Cordey (1976) and Peters (1984). Clay deposits have been identified in several of the paleochannels as important regional seal within the Niger Delta complex. These clay deposits have been identified as regional seismic marker horizons in the shallow offshore and could be used to correlate stratigraphic events (Beka and Oti, 1995).

On the other hand, Bouvier *et al.* (1989), report on the three dimensional seismic interpretation by employing fault sealing method in the Nun river field of the Niger Delta. He suggested that the complexities of the subsequent sealing of fault structures were clearly observed and are made plain by day. Furthermore, various theories and discussions have been put forward for the Niger Delta. Another for instance, Frank and Cordey (1967); Weber and Daukoru (1975); they all concluded that the major factors that control hydrocarbon distribution within the field were literal spill-point at the termination of discontinuous faults and seals or lack of seal along fault planes.

Petroleum occurs throughout the Agbada Formation of the Niger Delta; however, several directional trends form an "oil-rich belt" having the largest field and lowest gas/oil ratio (Ejedawe, 1981; Evamy *et al.*, 1978; Doust and Omatsola, 1990).

Stacher (1995), using sequence stratigraphy, developed a hydrocarbon habitat model for the Niger Delta. The model was constructed for the central portion of the delta, including some of the oil-rich belt, and relates deposition of the Akata Formation (the assumed source rock) and the sand/shale units in the Agbada Formation (the reservoirs and seals) to sea level.



Fig. 2: Stratigraphic column showing the three formations of the Niger Delta. Modified from Shannon and Naylor (1989) and Doust and Omatsola (1990).

### METHODOLOGY

The well correlation was done using the full suites of logs and all the available data from existing wells. Well developed within the shales stratigraphic sequence was used as reference datum for the correlation. The shales exhibit relatively uniform thickness across the field and are served as useful markers. These markers were picked based on the Gamma ray log and Resistivity log signature correlation from the neighbouring wells (Fig. 3). The correlations for deep and shallow reservoirs are distinguished based on their API gravities and nparaffin/naphthene for the selected Sapele wells.

Shale volume is evaluated using the methods of Gamma Ray (GR) and Density or Density-Neutron separation as shale indicators. Detailed analyses of the methods showed that GR was more representative in evaluation of volume of shale across the Sapele shallow reservoirs. The Density and Neutron are affected by borehole washout encountered as a result of the unconsolidated nature of the Sapele shallow reservoirs. Porosity was estimated for the reservoirs from density- Neutron log which is available in all the wells used in this study. A matrix/grain density of 2.65 g/cm<sup>3</sup>, oil density ranging from 0.9 g/cm<sup>3</sup> to 0.97 g/cm<sup>3</sup> which is consistent with values obtained from the MDT result. The Simandoux Model has been chosen for the evaluation of water saturation. This model was developed for the interpretation of the resistivity in shaly sands, and is particularly adapted to the shaly sand reservoirs. The underlying Physics of the Simandoux water saturation model is that the total conductivity of the formation depends on the conductivities of water and shale.

Detailed geochemical investigations of twenty-five crude oils representing different petroleum reservoirs and four selected samples from source rock of Agbada Formation were analysed. The geochemical data on the crude oils and the source rock will be used in order to classify the oils genetic families and oil-source rock correlation.



Fig. 3: Correlation panel of deep and shallow Reservoirs of selected Sapele wells.

The oil-source rock correlation is essential to define the petroleum system present in the Sapele Region. Sample preparation and analyses were performed at Trican Geological Solutions, Alberta, Canada. Details on analytical methods and compound identifications are described in Peters and Moldowan (1993).

Asphaltenes were precipitated from the crude oils by adding a 40mil excess of n-hexane. The precipitated asphaltenes were filtered. The hexane soluble material was separated by liquid chromatography into saturated hydrocarbons. For aromatic hydrocarbons, sand resins on alumina and silica were used for 2 h at 200 °C to activate the aromatization. The saturate and aromatic fractions were subjected to GCFID and GC-MS analyses for biomarkers. A standard oil sample 10mil weighed on chemical balance was used analysis to ensure quality control and as a reference index for compound identification and for absolute quantification of steranes (Seifert and Moldowan, 1979).

After initial screening by Rock-Eval Pyrolysis and total organic carbon determination, four organic-rich samples were selected for further detailed studies. The rock samples were selected from organic-rich shale intervals within the Agbada Formation (Fig. 2).

Rock samples were crushed to a fine powder and then extracted with an azeotropic mixture of dichloromethane and methanol (93:7 v/v). The total organic extracts were fractionated using open column liquid chromatography to separate saturates, aromatics and polar compounds. Further GC-FID, GC-MS analyses were used as for the oil samples. For the analysis of biomarkers, the fragmentograms for steranes (m/z 217) and triterpanes (m/z 191) were recorded. Individual components were identified by comparison of their retention times and mass spectra with published data (Philpi, 1985; Peters and Moldowan, 1993; Hakimi et al., 2011b; Hakimi et al., 2012b). Relative abundances of triterpanes and steranes were calculated by measuring peak heights in the m/z 191 and m/z 217 fragmentograms, respectively.

#### **RESULTS AND DISCUSSION**

#### **API Gravity Characterization**

The API gravity of the oils ranges between 24.70 and 35.60° with a mean value of 29.56° (heavy to light oils). The API gravity and depth can well be correlated (Table 2). The oil within the delta has a gravity range of 16-50° API, with the lighter oils having a greenish-brown color (Whiteman 1982). Fifty-six percent of Niger Delta oils have API gravity between 30° and 40° (Thomas, 1995). Most oils fall within one of two groups. The first group are light paraffin based, waxy oils from deeper reservoirs (wax content up to 20%, but commonly around 5%; Kulke, 1995; Doust and Omatsola, 1990; high n-paraffin/naphthene of 0.86). The second group of oils

are biodegraded and from shallow reservoirs. They have lower API gravity (average API of 26°; Kulke, 1995) and are naphthenic non-waxy oils (nparaffin/naphthene = 0.37). Biodegradation and washing is extreme in some Pleistocene sands of the Agbada Formation, forming extra heavy oils (API 8-20°). Oils with less than 25° API account for only 15% of the Niger Delta reserves (Thomas, 1995). The concentration of sulfur in most oils is low, between 0.1 % and 0.3 % (Mbendi, 1996), with a few samples having concentrations as high as 0.6 % (Nwachukwu et al., 1995). A limited data set (Mbendi, 1996; Nwachukwu et al., 1995) shows a negative correlation between API gravity and sulfur content, suggesting that sulfur content is likely related to oil degradation.

The field has been divided into Sapele shallow and deep. The shallow reservoirs between the depths of 4000 and 6000ft contain heavy hydrocarbons with API gravities 20-22°. The deep reservoirs lie within 7000 and 12000ft accumulating the light crudes with API gravities of magnitude 38-45 degrees, and viscosity about 1.64 cP.

Kulke (1995) and Doust and Omatsola (1990) revealed from accumulated data that the low API gravity crudes occur within the shallow depths at the range of 4308 - 5803ft. The API gravity within the depth range was 20 - 21° (15 wells), with an off-mark case of API gravity 13° (very heavy crude type). The saturation pressure prevalent in this zone of reservoirs range from 90 to 176 psia (Pounds per square inch absolute), while average number fell in the range of 285-375psia and the off-mark case of 67 psia that bears the lowest API gravity of 13°. The depth range of higher values of API gravities corresponding to light crudes goes from 10,005-10,445ft, API gravities ranging from 37-45°. Remarkably the viscosity of the heavy crudes of low API gravities ranged from 14.4 - 35.5° with an exceptional off-mark viscosity of 82.7cP. The crude oils from Sapele oilfield have API gravity values in the range of 20.4-35.6°.

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Sapele Wells	20	27	28	29	31	32
Av Phi	0.2			0.23-0.291		0.28
N/G				0.76		0.62
Av Sw				0.29		0.60
Av Perm (mD)	280			3250		3418
Oil Gravity (° <b>API)</b>	0.726	No Flow/kicked,LS/ SS SSITHP- 600psi(LS), 300psi(SS)	21?/No flow	22	21	21
Oil rate (bopd)				750		1612
GOR (scf/stb)	0.04			31		615
BSW (%)	50			75		15
Bean						45
size/choke						
(Hz)						
Driller		Lonestar				
Well Type		Development	Development			
Target Reservoir/Gro ss thickness	H1000 H2000	G9000, G9100	G5600/88ft, G6100/, G7000/	A2000- C3000		
Total Depth (TD)	11543	11,502 ft	11,120ftah	8252ftah		
No. of HC- bearing Sands	2	16	16	12	15	
Expected Lifecycle (MMstb)		1.06 0.98	2.60 2.77	1.06MMstb		

Table 1: Reservoir Petrophysical Properties: API Gravities, Density, Porosity, Permeability, etc.

# **Geochemical Evaluation**

The saturated hydrocarbon content of the crude oils ranges between 40.00 and 65.90 with an average of 49.70, aromatics from 28.00 to 46.50 with an average of 38.03, asphaltenes from 3.40 and 15.30 with an average of 8.01, resins from 1.30 and 8.40 with an average of 4.27 while saturated/aromatic hydrocarbon ratio have an average of 1.35 (Table 2). These are corroborated by the average waxiness, Pristane/Phytane (Pr/Ph), Pr/ n-C<sub>17</sub>, Ph/ n-C<sub>18</sub> and carbon preference index (CPI) values for the crude oils and shales which are 0.92 and 1.03°, 1.77 and 1.96, 0.58 and 0.96, 0.38 and 0.64, and 0.98 and 1.01(Tables 2 and 4), respectively. In agreement with the obtained results are average C<sub>32</sub>22S/ (22S+22R),  $C_{29}/C_{30}$ ,  $MC_{30}/HC_{30}$ , HI,  $C_{29}$  20S/ (20S+20R),  $C_{29}\beta\beta/$ ( $\beta\beta/\alpha\alpha$ ),  $C_{27}/C_{29}$ ,  $C_{27}$ ,  $C_{28}$  and  $C_{29}$  values for the crude oils and shales which are 0.57 and 0.59, 0.43 and 0.40, 0.11 and 0.14, 0.09 and 0.09, 0.53 and 0.53, 0.54 and 0.51, 0.85 and 1.01, 35.03 and 40.33, 21.81 and 19.43, and 42.19 and 40.23 (Tables 3 and 4), respectively. The Ts/Tm and  $C_{29}$  TS/ $C_{29}$  for the crude oils ranges from 1.09 to 1.92 and 0.40 to 0.80 with an average of 1.34 and 0.59 (Table 3), respectively.

The dibenzothiophene/phenanthrene (DBT/Phen) value for crude oils ranges from 0.22 to 1.04 with an average of 0.40 (Table 3). The methyl dibenzothiophene ratio (MDR) yield ranges from 1.41 to 2.25 (Table 3). The average value of the MDR is (1.64). The methyl phenanthrene index (MPI) for the crude oils ranges from 0.50 to 0.62 (average 0.56)

Geochemical analyses of Niger Delta oils generally indicate land plant material and structurelss organic matter (SOM) as the major source of the hydrocarbons (Stacher, 1995). Source rock anaylses have shown that clays from (1) the lower coastal plain, (2) the marine-deltaic depositional areas (prodelta) and (3) the fully marine areas can be enriched in both land plant material and structureless organic matter. Lower coastal plain deposits (1), such as swamp clays and coals, are rarely preserved in-situ in large volumes in the Niger Delta. These sediments are usually reworked and re-deposited as marine-deltaic clays (2) and full marine clays (3).

Marine-deltaic clays form part of deeper, prospective Niger Delta well sections characterized by shales with sand interbeds. Source rock analyses show peaks of organic material with individual parasequences. However, significant source rock thicknesses are rarely encountered.

Marine clays (3), which are interpreted to be present in large volumes at greater depths, are referred to in the literature as Akata shale (Stacher, 1995). A number of authors have concluded that source rocks of economic significance are to be found in the Akata shales (Weber and Daukoru, 1975; Evamy *et al.*, 1978; Ekweozor and Daukoru, 1984; Weber, 1986). Because of the over-pressure encountered in deep exploration wells major sequences of Akata shales have rarely been penetrated.

Geochemical characteristics were used to identify groups of genetically related oils, to correlate oils with source rocks and to describe the probable source rock organic facies and depositional environment conditions. Based on these geochemical characteristics, the investigated oils were classified into one genetic oil family.

The source rock of this oil family contains a mixture of aquatic (algal and bacterial) and terrigenous organic matter that were deposited in a marine environment and were preserved under suboxic conditions. The depositional environment and organic facies were examined based on normal alkanes, isoprenoids, sterane, and triterpane distributions (Fig. 4). The geochemical parameters or ratios used are pristane/phytane, pristane/n-C<sub>17</sub>, phytane/n-C<sub>18</sub>, waxiness index, homohopane index, C27/C29 regular sterane, C27, C28, C29 regular steranes, dibenzothiophene/phenanthrene, presence or absence of tricyclic terpanes (Tables 2 and 4). A number of cross plots or triangular plots using these ratios have also been constructed (Figs. 4 - 9). A description of the geochemical characteristics of the oil family follows:

Oils derived from terrestrial organic matter such as those in the Niger Delta have high Pr/Ph ratios. If the oils are derived from terrestrial organic matter younger than mid-Cretaceous, then the oleanane: $C_{30}$ -hopane ratios are high as well (Ekweozor and Okoye, 1981).

### The properties of crude oils from Sapele oilfield

The crude oils have high saturated and aromatic fractions ranging from 40.0% to 65.9% and 28.0%-46.5%, respectively (Table 2). The high saturated and aromatic fractions with low amount of asphaltenes from 3.40 and 15.30 with an average of 8.01, resins from 1.30, 8.40 with an average of 4.27, saturated/aromatic hydrocarbon ratio have an average of 1.35 and average pristane/phytane (Pr/Ph) values for the crude oils and shales are 1.77 and 1.96 components (Table 2 and 4) indicate that these oils are naphthenic oils and no sign of biodegradation. The bulk property and composition of these analysed crude oils indicates that only one oil type is present.

Biodegradation process may occur in an oil reservoir, and the process dramatically affects the fluid properties of the hydrocarbons (e.g., Miiller *et al.*, 1987; Bahram *et al.*, 2016). The early stages of oil biodegradation are characterized by the loss of nalkanes or normal alkanes followed by loss of acyclic isoprenoids (e.g., pristane and phytane).

Compared with those compound groups, other compound classes (e.g., highly branched and cyclic saturated hydrocarbons as well as aromatic compounds) are more resistant to biodegradation (Larter *et al.*, 2005; Aboglila *et al.*, 2010). In this respect, there is no sign of biodegradation among the studied oil samples, where the analysed oils contain a complete suite of n-alkanes in the low-molecular weight region and acyclic isoprenoids (e.g., pristane and phytane; Fig. 4). This indicated that the analysed oil samples generally contain more saturated hydrocarbons than aromatic hydrocarbons with saturate/aromatic ratios >1 (Table 2).

The degree of waxiness is used to categorize the amount of land derived organic material in oil, assuming that terrigenous material contributes a high molecular weight normal paraffin component to the oil (Hedberg, 1968; Connan and Cassou, 1980; Johns, 1986).

Recent studies about oil classification by source input have relied heavily on waxiness as an environmental source input parameter (Connan and Cassou, 1980; Aboglila *et al.*, 2010). The degree of waxiness in this study is expressed by the  $\Sigma(n-C_{21} - n-C_{31})/\Sigma(n-C_{15} - n-C_{20})$  (Table 2). The calculated ratio of waxiness ranges from 0.53 to 1.27 (Table 2), suggesting that these oils have been derived from algal and/or bacterial and lower terrigenous organic matter contribution (Brooks *et al.*, 1969; Tissot and Welte, 1984; Bahram *et al.*, 2016).

Biomarker characteristics as indication for organic matter input and depositional conditions n-alkanes and isoprenoids

The geochemical results for crude oils and shales samples for pristane/phytane (Pr/Ph), Pr/ n-C<sub>17</sub> and Ph/ n-C<sub>18</sub> values range from 1.55-2.05 and 1.82-2.02, 0.41-0.77 and 0.90-1.05, and 0.27-0.52 and 0.57-0.75 (Tables 2 and 4), respectively. These parameters Pr/Ph, Pr/ n-C<sub>17</sub> and Ph/ n-C<sub>18</sub> contain average values for the crude oils and shales which are 1.77 and 1.96, 0.58 and 0.96, 0.38 and 0.64 (Tables 2 and 4), respectively.

There has been much discussion about the source rock for petroleum in the Niger Delta (e.g. Evamy et al., 1978; Ekweozor et al., 1979; Ekweozor and Okoye, 1980; Lambert-Aikhionbare and Ibe, 1984; Bustin. 1988: Doust and Omatsola. 1990). Possibilities include variable contributions from the marine interbedded shale in the Agbada Formation and the marine Akata shale, and Cretaceous shale (Weber and Daukoru, 1975; Evamy et al., 1978; Ejedawe et al., 1979; Ekweozor and Okoye, 1980; Ekweozor and Daukoru, 1984; Lambert-Aikhionbare and Ibe, 1984; Doust and Omatsola, 1990; Stacher, 1995; Frost, 1977; Haack et al., 1997).

The gas chromatograms of saturated hydrocarbon fractions from representative shale and oil samples from Sapele oil field are shown in Figure 4 and derived parameters are listed in Table 2.

The saturated gas chromatograms of the oil samples display a full suite of saturated hydrocarbons between C<sub>10</sub> - C<sub>36</sub> n-alkanes and isoprenoids pristane (Pr) and phytane (Ph) (Fig. 4). The similarity in the distribution patterns of nalkanes with most abundant constituents (extending to  $C_{35}$ ) suggests that the studied oils are derived from one source and that no biodegradation has occurred. The n-alkane distribution of the oils also show a predominance of low to medium molecular weight compounds (n-C<sub>10</sub> n-C<sub>20</sub>) with the presence of significant waxy alkanes (+n-C<sub>25</sub>), suggesting a significant high contribution of marine organic matter with minor terrigenous organic matter contribution (Brooks *et al.*, 1969; Powell and McKirdy, 1973; Tissot *et al.*, 1978; Ebukanson and Kinghorn, 1986; Murray and Boreham, 1992; Aboglila *et al.*, 2010).

Acyclic isoprenoids occur in a significant amount in all oil samples (Fig. 4) and diagnostic biomarker ratios are listed in Table 2. The pristane/phytane (Pr/Ph) ratio is one of the most commonly used geochemical parameters and has been widely invoked as an indicator of the redox conditions in the depositional environment and source of organic matter (Didyk *et al.*, 1978; Powell, 1988; Chandra *et al.*, 1994; Large and Gize, 1996; Bahram *et al.*, 2016).

High Pr/Ph (>3.0) indicates oxic conditions often associated with terrigenous organic matter input, while low values (<1.0) typify anoxic conditions, commonly hypersaline or carbonate environments (Peters *et al.*, 1995, 2005) and values between 1.0

and 3.0 suggest intermediate conditions (suboxic conditions) (Philp, 1985; Amane and Hideki, 1997; Aboglila et al., 2010). In the present study, pristine concentrations occurred relative high; possessing pristane/phytane (Pr/Ph) ratios in the range of 1.55 -2.05 which suggests that the studied oils considered being derived from source rock containing mixed organic facies and suboxic depositional conditions. Furthermore, lower amounts of acyclic isoprenoids to n-alkanes (Fig. 4), thus gives a distinctive low pristane/n-C<sub>17</sub> and phytane/n-C<sub>18</sub> ratios in the range of 0.41 - 0.77 and 0.27 - 0.52, respectively which also corresponding to mixed organic matter deposited under suboxic conditions (Fig. 5). This is supported by the plot of Pr/Ph vs. degree of waxiness which indicates only one oil type generated from mixed marine organic matter deposited in suboxic conditions (Fig. 6).



Fig. 4: Gas chromatography traces and m/z 191, m/z 217 mass fragmentograms for shale and oil from Sapele oil field.

### Table 2: Bulk organic geochemical data for crude oil samples from Sapele oilfield, Niger Delta Region.

Sample	Well	Sample	Depths	API	Hydrocarbons		Non-hydroca	arbons	Saturate/	Waxiness	N-Alkan	e and Isc	preniods	
N0.	N0.	Name	(m)	Gravity	Saturate	Aromatic	Asphaltenes	Resins	Aromatic	(°C)	Pr/Ph	Pr/	Ph/	CPI
				(°)								n-C <sub>17</sub>	n-C <sub>18</sub>	
SAP-1	20	Crude Oil	3518	27.90	47.40	39.60	8.20	4.80	1.20	0.82	1.81	0.62	0.40	0.99
SAP-2	"	n	3519	29.30	50.40	37.30	7.40	4.90	1.40	0.94	1.85	0.57	0.36	0.98
SAP-3	"	n	3521	24.70	43.20	43.90	7.90	5.00	1.00	0.53	1.77	0.76	0.48	0.97
SAP-4	"	n	3523	24.70	41.00	46.50	6.40	6.10	0.90	0.68	1.76	0.64	0.42	0.99
SAP-5	"	n	3525	24.60	42.70	44.50	7.30	5.50	1.00	0.63	1.80	0.67	0.43	0.96
SAP-6	27	n	3506	24.40	44.70	40.40	9.00	5.90	1.10	0.68	1.79	0.65	0.42	0.98
SAP-7	"	n	3509	25.80	44.70	40.40	9.00	5.90	1.10	0.64	1.71	0.77	0.52	0.97
SAP-8	"	n	3511	26.50	47.40	40.60	7.40	4.60	1.20	0.69	1.76	0.72	0.46	0.98
SAP-9	"	n	3512	29.90	49.70	36.60	10.30	3.40	1.40	1.03	1.78	0.56	0.37	0.99
SAP-10	28	n	3389	29.90	49.50	37.00	10.80	2.70	1.30	0.79	1.90	0.62	0.40	1.00
SAP-11	"	n	3391	31.80	53.20	37.00	6.70	3.10	1.40	1.01	1.85	0.57	0.37	0.98
SAP-12	"	n	3392	32.30	53.10	37.30	7.40	2.20	1.40	1.06	1.81	0.56	0.37	0.98
SAP-13	"	n	3395	31.90	57.70	34.70	5.30	2.30	1.70	1.05	1.77	0.55	0.37	0.98
SAP-14	29	"	2515	27.70	46.00	39.00	10.10	4.90	1.20	0.92	1.70	0.61	0.42	0.98
SAP-15	"	n	2517	30.10	52.40	37.10	7.10	3.40	1.40	0.99	1.82	0.57	0.37	0.99
SAP-16	"	"	2520	30.30	51.60	37.10	8.20	3.10	1.40	0.83	1.78	0.59	0.39	0.99
SAP-17	"	n	2523	31.40	51.70	38.30	6.30	3.70	1.30	0.99	1.76	0.57	0.39	0.98
SAP-18	31	n	2569	28.80	40.00	43.90	9.00	7.10	0.90	1.03	1.64	0.51	0.37	0.99
SAP-19	"	n	2571	28.40	46.00	38.80	10.10	5.10	1.20	1.04	1.61	0.51	0.38	1.00
SAP-20	"	n	2573	28.10	43.60	37.50	14.60	4.30	1.20	1.04	1.58	0.52	0.38	0.98
SAP-21	"	n	2574	33.70	56.30	37.80	4.60	1.30	1.50	1.27	1.67	0.42	0.30	0.99
SAP-22	32	n	2947	33.50	60.20	32.40	3.40	4.00	1.90	1.09	1.99	0.48	0.27	0.98
SAP-23	"	n	2949	33.80	65.90	28.00	3.60	2.50	2.40	1.12	2.05	0.48	0.27	0.96
SAP-24	"	n	2950	33.80	53.30	33.50	4.80	8.40	1.60	1.03	1.68	0.46	0.31	0.98
SAP-25	"	н	2952	35.60	50.70	31.50	15.30	2.50	1.60	1.21	1.55	0.41	0.31	0.97

 $\begin{array}{l} \mbox{Pr: pristane.} \\ \mbox{Ph: phytane.} \\ \mbox{CPI: carbon preference index } (2[C_{23} + C_{25} + C_{27} + C_{29}]/[C_{22} + 2\{C_{24} + C_{26} + C_{28}\} + C_{30}]). \\ \mbox{Waxiness degree: S } (n-C_{21} - n-C_{31})/S } (n-C_{15} - n-C_{20}) \end{array}$ 

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Sample	Well	Sample	Depths	3	Sa	turated bio	marker di	stribution	S						Α	romatic bior	narker dis	tributio	ns			
N0. N0. Name	Name	I0. Name	0. Name	Name	Name	(m)	Triterp	Triterpanes and terpanes (m/z191						Steran	es (m/z217)	)			Phen	Steroids	Phen	%Ro
				C <sub>32</sub> 22S/	C <sub>29</sub> /	Ts/Tm	MC30/	<b>C</b> <sub>29</sub>	н	C <sub>29</sub> 20S	/ C <sub>29</sub> ββ/	C <sub>27</sub> /C <sub>29</sub>			-	DBT Phen	MDR	MPI	•			
				(22S+22R)	<b>C</b> <sub>30</sub>		HC <sub>30</sub>	Ts/C <sub>29</sub>		(20S+20R)	(ββ/αα)	Regular	Reg	ular Stera	nes (%)							
												Steranes	<b>C</b> <sub>27</sub>	<b>C</b> <sub>28</sub>	<b>C</b> <sub>29</sub>							
SAP-1	20	Crude Oil	3518	0.57	0.41	1.17	0.12	0.53	0.10	0.54	0.54	0.88	36.90	21.40	41.70	0.24	1.68	0.51	0.71			
SAP-2	"	"	3519	0.58	0.40	1.25	0.15	0.62	0.10	0.55	0.54	0.87	35.90	22.80	41.30	0.23	1.61	0.59	0.75			
SAP-3	"	"	3521	0.57	0.42	1.33	0.13	0.57	0.10	0.55	0.53	0.84	35.50	22.00	42.50	0.28	1.61	0.62	0.77			
SAP-4	"	"	3523	0.58	0.42	1.09	0.13	0.54	0.10	0.52	0.53	0.85	36.20	21.40	42.40	0.28	1.81	0.62	0.77			
SAP-5	"	"	3525	0.58	0.42	1.18	0.12	0.56	0.10	0.51	0.54	0.87	36.20	22.10	41.60	0.29	1.60	0.62	0.77			
SAP-6	27	"	3506	0.57	0.41	1.14	0.11	0.61	0.10	0.52	0.54	0.82	35.10	22.10	42.80	0.27	1.53	0.62	0.77			
SAP-7	"	"	3509	0.57	0.42	1.26	0.13	0.56	0.10	0.51	0.55	0.88	36.30	22.60	41.10	0.26	1.51	0.60	0.76			
SAP-8	"	"	3511	0.57	0.41	1.12	0.13	0.60	0.10	0.55	0.55	0.85	36.10	21.60	42.30	0.25	1.61	0.61	0.77			
SAP-9	"	"	3512	0.57	0.40	1.31	0.09	0.61	0.09	0.54	0.56	0.83	35.60	21.60	42.70	0.22	1.58	0.56	0.74			
SAP-10	28	"	3389	0.56	0.41	1.39	0.10	0.60	0.09	0.58	0.56	0.83	35.50	21.70	42.80	0.23	1.59	0.56	0.74			
SAP-11	"	"	3391	0.57	0.39	1.41	0.10	0.63	0.09	0.53	0.56	0.86	36.00	22.00	42.00	0.22	1.56	0.54	0.72			
SAP-12	"	"	3392	0.57	0.41	1.37	0.10	0.59	0.08	0.54	0.56	0.81	35.60	20.40	44.00	0.22	1.52	0.55	0.73			
SAP-13	"	"	3395	0.57	0.40	1.25	0.10	0.62	0.08	0.55	0.57	0.84	35.90	21.60	42.50	0.40	1.52	0.54	0.72			
SAP-14	29	"	2515	0.57	0.45	1.24	0.09	0.52	0.09	0.54	0.51	0.85	35.70	22.40	41.90	0.46	1.42	0.57	0.74			
SAP-15	"	"	2517	0.57	0.42	1.57	0.10	0.60	0.09	0.55	0.53	0.84	35.20	22.80	41.90	0.40	1.51	0.56	0.74			
SAP-16	"	"	2520	0.58	0.42	1.34	0.09	0.58	0.08	0.53	0.53	0.93	36.40	24.60	39.00	0.45	1.43	0.55	0.73			
SAP-17	"	"	2523	0.57	0.41	1.68	0.10	0.61	0.09	0.52	0.51	0.84	35.40	22.30	42.30	0.44	1.48	0.54	0.72			
SAP-18	31	"	2569	0.57	0.46	1.31	0.07	0.52	0.09	0.51	0.52	0.80	34.20	22.90	42.90	0.69	1.41	0.50	0.70			
SAP-19	"	"	2571	0.57	0.47	1.23	0.06	0.53	0.09	0.51	0.51	0.82	35.40	21.20	43.40	0.74	1.47	0.51	0.71			
SAP-20	"	"	2573	0.57	0.46	1.34	0.06	0.51	0.09	0.51	0.52	0.86	36.10	21.70	42.20	0.76	1.46	0.50	0.70			
SAP-21	"	"	2574	0.56	0.46	1.56	0.11	0.64	0.09	0.53	0.56	0.90	36.80	23.30	40.80	1.04	1.96	0.52	0.71			
SAP-22	32	"	2947	0.57	0.36	1.92	0.22	0.79	0.10	0.56	0.55	0.92	36.70	23.30	40.00	0.26	2.06	0.58	0.75			
SAP-23	"	"	2949	0.57	0.37	1.65	0.23	0.80	0.10	0.51	0.54	0.93	41.60	13.90	44.60	0.25	2.25	0.57	0.74			
SAP-24	"	"	2950	0.58	0.63	1.12	0.08	0.40	0.13	0.50	0.54	0.81	34.60	22.60	42.90	0.57	1.61	0.57	0.74			
SAP-25	"	"	2952	0.58	0.46	1.17	0.09	0.58	0.10	0.52	0.57	0.83	35.80	21.00	43.20	0.67	2.11	0.52	0.71			

Table 3: A typical geochemical parameter distributions for crude oil samples from Sapele oilfield, Niger Delta Region.

Ts: (C<sub>27</sub> 18α(H)-22,29,30-trisnorneohopane).

Tm:  $(C_{27} 17\alpha(H)-22,29,30$ -trisnorhopane).

 $C_{29}/C_{30}$ :  $C_{29}$  norhopane/ $C_{30}$  hopane. M $C_{30}/HC_{30}$ :  $C_{30}$  moretane/ $C_{30}$  hopane H Index: ( $C_{35}/(C_{31} - C_{35})$  homohopane. DBT/Phen: dibenzothiophene/phenanthrene.

MDR: MDR, 4-MDBT/1-MDBT.

MPI: Methylphenanthrene Index. %Ro: 0.60 \* MPI + 0.40.

#### Triterpanes and steranes

The geochemical results are corroborated by the average pristane/phytane (Pr/Ph), Pr/ n-C<sub>17</sub> and Ph/ n-C<sub>18</sub> values for the crude oils and shales which are 1.77 and 1.96, 0.58 and 0.96, 0.38 and 0.64 (Tables 2 and 4), respectively. In agreement with the obtained results are average C<sub>32</sub>22S/ (22S+22R),  $C_{29}/C_{30}$ ,  $MC_{30}/HC_{30}$ , HI,  $C_{29}$  20S/ (20S+20R),  $C_{29}\beta\beta/$ ( $\beta\beta/\alpha\alpha$ ), C<sub>27</sub>/C<sub>29</sub>, C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub> values for the crude oils and shales which are 0.57 and 0.59, 0.43 and 0.40, 0.11 and 0.14, 0.09 and 0.09, 0.53 and 0.53, 0.54 and 0.51, 0.85 and 1.01, 35.03 and 40.33, 21.81 and 19.43, and 42.19 and 40.23 (Tables 3 and 4), respectively. The Ts/Tm and C<sub>29</sub> TS/C<sub>29</sub> for the crude oils ranges from 1.09 to 1.92 and 0.40 to 0.80 with an average of 1.34 and 0.59 (Table 3), respectively.

The distributions of steranes and triterpanes are commonly studied using GC-MS by monitoring the ions m/z 217 and m/z 191, respectively (Brooks et al., 1969; Peters et al., 2005; Aboglila *et al.*, 2010). The distributions of triterpanes and steroidal saturate biomarkers are very similar in the studied oils (Fig. 4). The fingerprint of peaks for steranes and triterpanes are shown in Figure 4. The similarity in the distribution patterns of m/z 191 and m/z 217 mass fragmentograms suggest that the studied oils are classified into one oil family (Fig. 4).

The m/z 191 mass fragmentograms of the saturated hydrocarbon fractions of all the oil samples analysed display high proportions of hopanes relative to tricyclic terpanes (Fig. 5). The relative abundance of C<sub>29</sub> norhopane is generally half or less than that of C<sub>30</sub> hopane in most of the studied oil samples (Fig. 4), with  $C_{29}/C_{30}$  17 $\alpha$  (H) hopane ratios in the range of 0.36-0.47 (Table 3), indicating that hydrocarbons generated from clay-rich source rock (Gürgey, 1999; Bahram et al., 2016). The oils possess Ts/Tm ratio in the range of 1.09-1.92 (Table 3). However, values of Tm ( $C_{27}$  17 $\alpha$ (H)-22,29,30- trisnorhopane) and Ts ( $C_{27}$ 18α(H)-22,29,30-trisnorneohopane) are well known to be influenced by maturation, type of organic matter, and lithology (Moldowan et. al., 1985). The studied oil samples contain a mixture of land and marine derived organic matter; thus, the variation of Ts/Tm ratios appear to be more strongly influenced by maturity instead of source input. Extended hopanes are dominated by the C<sub>31</sub> homohopane and generally decreasing towards the C<sub>35</sub> homohopane (Fig. 4). The distribution of the extended hopanes or homohopanes (C<sub>31</sub>-C<sub>35</sub>) has been used to evaluate redox conditions based on homohopanes index (Peters et al., 2005). This, in turn, suggests that the studied oils were derived from source rock deposited under suboxic conditions. In support, relatively lower homohopanes index were obtained for the studied oils in the range of 0.08-0.13 (Table 3). Typically, such a distribution of homohopanes also commonly represents clastic facies (Waples and Machihara, 1991) or a clay-rich character (Obermajer et al., 1999) as indicated by the predominance of  $C_{30}$ hopane in the m/z 191 mass fragmentograms (Fig. Tricyclic terpane concentrations are also present

in significant quantities (Fig. 4). The tricyclic terpane concentrations detected in the studied oils supports contribution from marine-derived organic matter to the source rocks (Aquino Neto et al., 1983; Philp, 1985; Waples and Machihara, 1991).

The distributions of diasterane and the sterane ( $C_{27}$ ,  $C_{28}$  and  $C_{29}$ ) are characterized by the m/z 217 ion chromatograms (Fig. 4). Relative abundances of  $C_{27}$ , C<sub>28</sub> and C<sub>29</sub> regular steranes are calculated and the results are given in Table 3. The distributions of C<sub>27</sub>/  $C_{28}/C_{29}$  regular steranes for all oil samples are very similar ( $C_{29} > C_{27} > C_{28}$ ) as are the ratios of  $C_{27}/C_{29}$ regular steranes and the thermal maturity indicators  $C_{29} 20S/(20S + 20R)$  and  $\beta\beta/(\beta\beta + \alpha\alpha)$  (Table 3). The relative distribution of C27-C29 regular steranes is used to indicate source of organic matter input (Huang and Meinschein, 1979; Waples and Machihara, 1991; Bahram et al., 2016). Based on this classification, the studied oil samples are derived from similar types of organic matter (Fig. 7). The oil samples composed of C27-C29 steranes which is an indicator of the mixed marine/ terrigenous organic matter (Fig. 6) as indicated by Pr/n-C<sub>17</sub> and Ph/ n-C<sub>18</sub> ratios (Fig. 5). This is also suggested by values of C27/C29 regular steranes ratio (Fig. 8) and the presence of tricyclic terpane in the m/z 191 mass fragmentograms (Fig. 4).

#### Dibenzothiophenes

The dibenzothiophene/phenanthrene (DBT/Phen) value for crude oils ranges from 0.22 to 1.04 with an average of 0.40 (Table 3). The average Pr/Ph ratio values for the crude oils and shales is 1.77 and 1.96 (Tables 2 and 4) respectively.

molecular indicators, The two the ratio of dibenzothiophene/phenanthrene and the ratio of pristane/phytane, can be also used to infer crude oil rock depositional environments source and (Hughes lithologies al., 1995). The et dibenzothiophene/phenanthrene ratio of Sapele oils ranges from 0.22 to 1.04 (Table 3). Such a range indicates that these oils have been derived from paralic/clastic source input (Sivan et al., 2008). Furthermore, the ratio of dibenzothiophene/ phenanthrene is plotted against pristane/phytane ratio, the values fall in a typical pattern indicating organic matter from the same source. The cross plot dibenzothiophene/phenanthrene of versus pristane/phytane indicates that Sapele oils are derived from marine shales (Fig. 9).

#### Thermal maturity of crude oils

The results of geochemical analysis comprise average  $C_{32}22S/(22S+22R)$ ,  $C_{29}/C_{30}$ ,  $MC_{30}/HC_{30}$ , HI,  $C_{29}20S/(20S+20R)$ ,  $C_{29}\beta\beta/(\beta\beta/\alpha\alpha)$ ,  $C_{27}/C_{29}$ ,  $C_{27}$ ,  $C_{28}$  and  $C_{29}$  values for the crude oils and shales which are 0.57 and 0.59, 0.43 and 0.40, 0.11 and 0.14, 0.09 and 0.09, 0.53 and 0.53, 0.54 and 0.51, 0.85 and 1.01, 35.03 and 40.33, 21.81 and 19.43, and 42.19 and 40.23 (Tables 3 and 4), respectively. The Ts/Tm and  $C_{29}$  TS/ $C_{29}$  for the crude oils ranges from 1.09 to 1.92 and 0.40 to 0.80 with an average of 1.34 and 0.59 (Table 3), respectively. In

corroboration with the average Pr/Ph, Pr/ n-C<sub>17</sub>, Ph/ n-C<sub>18</sub> and carbon preference index (CPI) values for the crude oils and shales which are 1.77 and 1.96, 0.58 and 0.96, 0.38 and 0.64 (Tables 2 and 4), respectively. The methyl dibenzothiophene ratio (MDR) yield ranges from 1.41 to 2.25 (Table 3). The average value of the MDR is (1.64). The methyl phenanthrene index (MPI) for the crude oils ranges from 0.50 to 0.62 (average 0.56), while the vitrinte reflectance (%Ro) range between 0.70 and 0.77 (average 0.74).

In this study, a variety of biomarker maturity indicators have been used to evaluate the level of thermal maturity of the Sapele oils; these include pentacyclic triterpanes and sterane isomer ratios, methyl phenanthrene index (MPI) and methyl dibenzothiophene ratio (MDR) (Table 3). In gas chromatography - mass spectrometry (GC-MS), biomarker maturation parameters such as C<sub>32</sub> 22S/(22S + 22R) homohopane, moretane/hopane and 20S/ (20S + 20R) and  $\beta\beta/(\beta\beta + \alpha\alpha)$  C<sub>29</sub> sterane ratios, were used as maturity indicators (Mackenzie et al., 1980; Waples and Machihara, 1991; Peters and Moldowan, 1993; Peters et al., 2005). The ratios of 22 S/(22R + 22 S) for C<sub>32</sub> 17α (H), 21β (H)-hopanes and 20S/ (20S + 20R) and  $\beta\beta/(\beta\beta + \alpha\alpha)$  C<sub>29</sub> sterane are ranging from 0.56 to 0.58, 0.50 to 0.56 and 0.51 to 0.57, respectively (Table 3) suggesting that they have reached equilibrium (Seifert and Moldowan, 1986) and that the oil window has been reached. Furthermore, the maturity ratios of  $\beta\beta/(\beta\beta + \alpha\alpha)$  and 20S/(20S + 20R) for C<sub>29</sub> sterane are plotted against ratio. This correlation reflects that the oils are early mature to peak oil window (Fig. 10). The relationship between isoprenoids Pr/n-C17 and Ph/n-C18 ratios (Fig. 6) reflects the same interpretation as do the moretane/hopane ratios consistent with low relative abundance of C<sub>30</sub> moretane (Waples and Machihara, 1991). Moretane converts to  $C_{30}$  hopane with increasing thermal maturity (Seifert and Moldowan, 1986), and thus, moretane decreases as thermal maturity increases. The ratio of moretane to their corresponding hopanes decreases with increasing thermal maturity, from about 0.8 in immature sediments to about 0.05-0.15 in mature source rocks and oils (Mackenzie et al., 1980; Seifert and Moldowan. 1986). The studied oils have moretane/hopane ratio in the range of 0.07-0.23, suggesting the oils samples were generated from early to peak mature source rock.

The methyl phenanthrene index (MPI) and methyl dibenzothiophene ratio (MDR) were also used as thermal maturity indicators. The methyl phenanthrene index (MPI) (Radke and Welte, 1983) yields calculated vitrinite reflectance (%Ro), whereas the maturity parameter equivalent to vitrinite reflectance (%Ro) calculated based on methyl

dibenzothiophene ratio (Table 3). The Sapele oils have vitrinite reflectance %Ro values in the range of 0.70-0.77 indicating that the oils are thermally mature.

Bustin (1988), in a detailed source-rock study on side-wall core and cuttings from the Agbada-Akata transition or uppermost Akata Formation, concluded that there are no rich source rocks in the delta. With respect to oil potential, Bustin (1988) claims that the poor source-rock quality has been more than compensated by their great volume, excellent migration pathways, and excellent drainage. The oil potential is further enhanced by permeable interbedded sandstone and rapid hydrocarbon generation resulting from high sedimentation rates. The total organic-carbon (TOC) content of sandstone, siltstone, and shale in his study varies (average of 1.4 to 1.6% TOC). The content, however, seems to vary with age of the strata-a trend of decreasing content with decreasing age (average of 2.2% in the late Eocene compared to 0.9% in Pliocene strata).

Bustin's Eocene TOC average compares well with the averages of 2.5% and 2.3% obtained for Agbada-Akata shales in two wells (Udo and Ekweozor, 1988). Ekeweozor and Okoye (1980) report TOC values from 0.4 to 14.4% in both onshore and offshore paralic sediments. Nwachukwu and Chukwura (1986) report values as high as 5.2% in paralic shales from the western part of the delta. The higher TOC contents are limited to thin beds and are only easily recognized in conventional cores (Doust and Omatsola, 1990).

# Inferred oil-source correlation

The methyl dibenzothiophene ratio (MDR) yield ranges from 1.41 to 2.25 (Table 3). The average value of the MDR is (1.64). The methyl phenanthrene index (MPI) for the crude oils ranges from 0.50 to 0.62 (average 0.56)

The Tertiary marine Akata Formation is a recognized source rock in the Niger-Delta Basin and has generated oil that has been found in Agbada reservoirs. The idea for this section is to investigate the genetic link between the oils recovered from Sapele oilfield in the Niger Delta Region of the Agbada Formation. In an attempt to develop an oilsource rock correlation the extracted soluble bitumen from four samples of the Agbada shale and analysed their biomarkers using GC and GC-MS analyses. Overall, the oil data closely match the Tertiary source rock data. Key factors include biomarker parameters (Table 3) and the similar positions on the cross-plots (Figs. 5-10). Extract from the Agbada shale has nearly equal quantity of +C<sub>25</sub> n-alkane waxy component to the oil samples (Table 4).

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Table 4: Biomarker parameters distributions for Sapele crude oils and shale source rock extracts for correlation.

Samples	Reservoir/	n-alkan	e and Isop	orenoids			Triterpanes a	and Terpar	nes (m/z 19	1	Steranes an					
	Source	Pr/Ph	Pr/C <sub>17</sub>	Ph/C <sub>18</sub>	CPI	Waxiness	C <sub>32</sub> 22S/	C <sub>29</sub> /C <sub>30</sub>	MC <sub>30</sub> /	н	C <sub>29</sub> 20S/	C <sub>29</sub> ββ/	C <sub>27</sub> /C <sub>29</sub>	Regular steranes (		s (%)
	Rock age					degree	(22S+22R)		HC <sub>30</sub>		(20S+20R)	(ββ+αα)	regular	<b>C</b> <sub>27</sub>	C <sub>28</sub>	C <sub>29</sub>
													steranes			
Sapele Oils	Tertiary	1.55- 2.05	0.41- 0.77	0.27- 0.52	0.96 - 1.00	0.53- 1.27	0.56- 0.58	0.36- 0.63	0.06- 0.23	0.08- 0.13	0.50- 0.58	0.51- 0.57	0.80- 0.93	34.2- 41.6	13.9- 24.6	39.0- 44.6
Sapele Shale	"	1.99	0.98	0.62	1.00	1.01	0.59	0.37	0.15	0.09	0.54	0.51	0.93	38.00	21.20	40.80
		2.02	0.92	0.57	0.99	1.03	0.58	0.40	0.13	0.09	0.52	0.52	1.02	40.00	20.60	39.30
		1.99	0.90	0.62	1.01	1.03	0.59	0.42	0.15	0.08	0.53	0.50	0.98	39.70	19.60	40.70
		1.82	1.05	0.75	1.04	1.06	0.58	0.39	0.14	0.08	0.51	0.50	1.09	43.60	16.30	40.10

Pr: pristane.

Pr: pristane. Ph: phytane. CPI: carbon preference index  $(2[C_{23} + C_{25} + C_{27} + C_{29}]/[C_{22} + 2\{C_{24} + C_{26} + C_{28}\}+C_{30}])$ . Waxiness degree: S  $(n-C_{21}-n-C_{31})/S$   $(n-C_{15}-n-C_{20})$ .  $C_{29}/C_{30}$ :  $C_{29}$  norhopane/ $C_{30}$  hopane. MC<sub>30</sub>/HC<sub>30</sub>:  $C_{30}$  moretane/ $C_{30}$  hopane. H Index:  $(C_{35}/(C_{31} - C_{35})$  homohopane



Fig. 5: Phytane to  $n-C_{18}$  alkane (Ph/n-C<sub>18</sub>) versus pristane to  $n-C_{17}$  alkane (Pr/n-C<sub>17</sub>) ratios for Sapele crude oils and source rock extracts.



Fig. 6: Relationship between isoprenoid ratios and degree of waxiness S (n-C<sub>21</sub>- n-C<sub>31</sub>)/S (n-C<sub>15</sub> - n-C<sub>20</sub>) for investigated crude oils from Sapele oilfield and source rock extracts in the Niger Delta Region.



Fig. 7: Ternary diagram of regular steranes (C<sub>27</sub>- C<sub>29</sub>) showing the relationship between sterane compositions, source organic matter input (modified after Huang and Meinschein, 1979).



Fig. 8: A plot of pristane/phytane versus  $C_{27}/C_{29}$  regular steranes, indicating organic matter input and depositional conditions.



Fig. 9: Cross plot of dibenzothiophene/phenanthrene (DBT/Phen) versus pristane/phytane (Pr/Ph) ratios provides a novel, convenient and powerful way to infer crude oil source rock depositional environments and lithologies (Hughes *et al.*, 1995).



Fig. 10: A range of thermal maturity based on two maturity related biomarker parameters [C<sub>29</sub> 22S/(22S + 22R) and C<sub>29</sub>  $\beta\beta/(\beta\beta + \alpha\alpha)$ ] for the studied oil samples and source rock extracts.

The steranes distribution shows composed of  $C_{27}$ - $C_{29}$  regular steranes and relatively low  $C_{27}/C_{29}$  regular steranes ratios (Figs. 7 and 8; Table 4), suggest a combination of marine and terrestrial organic matter input (Moldowan et al., 1985; Peters and Moldowan, 1993; Bahram et al., 2016),

On a plot of ratios 22S/(22S + 22R) and  $\beta\beta/(\beta\beta + \alpha\alpha)$  for C<sub>29</sub> steranes, the Agbada Formation is considered thermally immature to mature and the oil window has been reached (Fig. 10). Therefore the Agbada source for the crude oil can be suggested. The C<sub>30</sub> moretane/C<sub>30</sub> hopane ratios are also consistent with the level of thermal maturity (Table 4).

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### CONCLUSION

The Sapele Oil Field located few kilometers west of Sapele town west of the Niger delta has over 32 oil wells (pre-covid19), with the hydrocarbon bearing structure as NW-SE trending roll-over anticlinal deposit. The hydrocarbons are majorly trapped in relatively shallow depths of dip closures. The depositional sequence revealed blocky to coarsening upwards sequences cut at the top by unconformity surface. Associated deposits showed tidal and distributary channels and shallow sands of coastal deltaic sediments majorly of shoreface deposits and channel sands.

The heavy oils are found in shallow sands, while the light oils are found in deep sands. The field is divided into Sapele Shallow and deep. The Sapele shallow reserves occur between the depths of 4000ft and 6000ft, containing heavy hydrocarbons with API gravities 20 – 22 degrees. The deep reservoirs lie within 7000ft and 12000ft accumulating the light crudes with API gravities of 38-45 degrees, and viscocity of 1.64 cP.

Geochemical characterization based upon biomarker components coupled with the bulk geochemical parameters were used to arrive at a clear characterization and classification of the Sapele crude oils in the Niger Delta Region. The fingerprints have been achieved from the acyclic isoprenoids, triterpane and sterane biomarkers.

The investigated biomarkers of Sapele oils are characterized by a dominance of low to medium molecular weight n-alkane compounds with the presence of waxy alkanes (+n- $C_{25}$ ), moderately high Pr/Ph ratio (1.55-2.05), relatively low  $C_{35}$  homohopane index, composed of  $C_{27}$ - $C_{29}$  regular steranes, relatively low  $C_{27}/C_{29}$  regular steranes, and

the presence of tricyclic terpanes as well as relatively low dibenzothiophene/ phenanthrene ratios. These data indicate that the oils were generated from source rock containing a mixture of aquatic (algal and bacterial) and terrigenous organic matter that were deposited in suboxic marine conditions. Maturity estimates based on biomarker maturity parameters indicate that all oils had reached and/or surpassed the peak of the oil window.

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