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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°38ʹ to 5°59ʹN and longitude 5°30ʹ to 6°00ʹE (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 boundary 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

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 Areeq *et al*., 2011). The current paper deals with the geochemical evaluation of crude oils and source rock recovered from the Agbada 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.

Extent of erosional truncation

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/cm³, oil density ranging from 0.9 g/cm 3 to 0.97 $q/cm³$ 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).

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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 nparaffin/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 (n– paraffin/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°.

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 $(^{\circ}API)$	0.726	No Flow/kicked, LS/ SS SSITHP- $600\psi(LS)$, 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		
HC- of No. 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-C₁₇, Ph/ n-C₁₈ 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_{32} 22S/ (22S+22R), C_{29} / C_{30} , MC₃₀/ HC₃₀, HI, C₂₉ 20S/ (20S+20R), C₂₉ββ/ ($\beta\beta/\alpha\alpha$), 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_{17} , phytane/n- C_{18} , waxiness index, homohopane index, C_{27}/C_{29} regular sterane, C_{27} , C_{28} , C_{29} 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 $Σ(n-C_{21}$ n-C₃₁)/ Σ(n-C₁₅ - n-C₂₀) (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_{17} and Ph/ n-C₁₈ 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-C₁₇ and Ph/ n-C₁₈ 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_{10} - C_{36} 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 ($n-C_{10}$ $n-C_{20}$) with the presence of significant waxy alkanes $(+n-C_{25})$, 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_{17} and phytane/n- C_{18} 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.

Pr: pristane.

Ph: phytane.

CPI: carbon preference index (2[C₂₃ + C₂₅ + C₂₇ + C₂₉]/[C₂₂ + 2{C₂₄ + C₂₆ + C₂₈}+C₃₀]).

Waxiness degree: S (n-C₂₁-n-C₃₁)/S (n-C₁₅-n-C₂₀)

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

Ts: $(C_{27} 18\alpha(H)-22,29,30$ -trisnorneohopane).

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

 C_{29}/C_{30} : C_{29} norhopane/ C_{30} hopane.

 MC_{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/ $n-C_{17}$ and Ph/ $n-C_{18}$ 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_{32} 22S/ (22S+22R), C_{29} / C_{30} , MC₃₀/ HC₃₀, HI, C₂₉ 20S/ (20S+20R), C₂₉ββ/ ($\beta\beta/\alpha\alpha$), 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 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_{29} norhopane is generally half or less than that of C_{30} hopane in most of the studied oil samples (Fig. 4), with C_{29}/C_{30} 17 α (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 α (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_{31} homohopane and generally decreasing towards the C_{35} homohopane (Fig. 4). The distribution of the extended hopanes or homohopanes $(C_{31}-C_{35})$ 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. 4). 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_{28} and C_{29} regular steranes are calculated and the results are given in Table 3. The distributions of C_{27} / 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 $\beta\beta$ /($\beta\beta$ + αα) (Table 3). The relative distribution of $C_{27}-C_{29}$ 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 $C_{27}-C_{29}$ steranes which is an indicator of the mixed marine/ terrigenous organic matter (Fig. 6) as indicated by $Pr/n-C_{17}$ and Ph/ n-C₁₈ ratios (Fig. 5). This is also suggested by values of C_{27}/C_{29} 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.

The two molecular indicators, the ratio of dibenzothiophene/phenanthrene and the ratio of pristane/phytane, can be also used to infer crude oil source rock depositional environments and lithologies (Hughes *et al*., 1995). The 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 of dibenzothiophene/phenanthrene 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 C₃₂22S/ (22S+22R), C₂₉/ C₃₀, MC₃₀/ HC₃₀, HI, C₂₉ 20S/ (20S+20R), C₂₉ββ/ (ββ/αα), C₂₇/C₂₉, C₂₇, 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/ $n-C_{17}$, Ph/ $n-C_{18}$ 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_{32} 22S/(22S + 22R) homohopane, moretane/hopane and 20S/ (20S + 20R) and $ββ/ (ββ + αα) C₂₉$ 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_{32} 17α (H), 21β (H)-hopanes and 20S/ (20S + 20R) and $ββ/ (ββ + αα) C₂₉$ 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 ββ/(ββ + αα) and $20S/(20S + 20R)$ for C₂₉ sterane are plotted against ratio. This correlation reflects that the oils are early mature to peak oil window (Fig. 10). The relationship between isoprenoids $Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios (Fig. 6) reflects the same interpretation as do the moretane/hopane ratios consistent with low relative abundance of C_{30} 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 $+C_{25}$ 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.

Pr: pristane.

Ph: phytane.

CPI: carbon preference index (2[C₂₃ + C₂₅ + C₂₇ + C₂₉]/[C₂₂ + 2{C₂₄ + C₂₆ + C₂₈}+C₃₀]).

Waxiness degree: S (n-C $_{21}$ - n-C $_{31}$)/S (n-C $_{15}$ - n-C $_{20}$).

 $\rm C_{29}/C_{30}$: $\rm C_{29}$ norhopane/ $\rm C_{30}$ hopane.

 MC_{30}/HC_{30} : C_{30} moretane/ C_{30} hopane.

H Index: $(C_{35}/(C_{31} - C_{35})$ homohopane

Fig. 5: Phytane to n-C₁₈ alkane (Ph/n-C₁₈) versus pristane to n-C₁₇ alkane (Pr/n-C₁₇) ratios for Sapele crude oils and source rock extracts.

Fig. 6: Relationship between isoprenoid ratios and degree of waxiness S (n-C₂₁- n-C₃₁)/S (n-C₁₅ - n-C₂₀) for investigated crude oils from Sapele oilfield and source rock extracts in the Niger Delta Region.

Fig. 7: Ternary diagram of regular steranes (C_{27} - C_{29}) 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 $[C_{29}$ 22S/(22S + 22R) and C_{29} $\beta\beta/(\beta\beta + \alpha\alpha)$] 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 $ββ/(ββ + αα)$ for C_{29} 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_{30} moretane/ C_{30} 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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REFERENCES

- Aboglila, S., Grice, K., Trinajstic, K., Dawson, D. and Williford, K.H., 2010. Use of biomarker distributions and compound. isotopes of carbon and hydrogen to delineate hydrocarbon characteristics in the East Sirte Basin (Libya). Org. Geochem., 41, 1249- 1258.
- Adekeye, O.A., 2004. Aspects of sedimentology, geochemistry and hydrocarbon potentials of Cretaceous-Tertiary sediments in the Dahomey Basin, south-western Nigeria. Unpublished Ph.D thesis, University of Ilorin, 202.
- Adekeye, O.A. and Akande, S.O., 2010. The Principal Source Rocks for Petroleum Generation in the Dahomey Basin, Southwestern Nigeria. Cont'al J. Earth Sci., $5(1)$: 42 – 55.
- Adekeye, O.A., Akande, S.O., Erdtman, B.D., Samuel, O.J. and Hetenyi, M. 2006. Hydrocarbon Potential Assessment of the Upper Cretaceous-Lower Tertiary Sequence in the Dahomey Basin Southwestern Nigeria. Nig. Assoc. Petrol. Expl. Bull., 19(1), 50-60.
- Ajekaiye, D.E. and Bally, A.W., 2002. Course Manual and Atlas of structural styles on reflection profiles from the Niger Delta. Ame. Assoc. Petrol. Geol. continuing Education Course Note Series No. 41, 107.
- Akaegbobi, I.M. and Schmitt, M., 1998. Organic facies, hydrocarbon source potential and the reconstruction of depositional paleoenvironment of Campano-Maastrichtian Nkporo shale in the Cretaceous Anambra Basin, Nigeria. Nig. Assoc. Petrol. Expl. Bull., 13(1), 1-19.
- Al-Areeq, N.M., Abu El Ata, A.S., Maky, A.F. and
Omran, A.A., 2011. Hydrocarbon Omran, A.A., 2011. Hydrocarbon Potentialities of some upper Jurassic Rock units in Masila block, Sayun-Masila Basin, Yemen. National research Center, Cairo. J. Appl. Geophys. 10(2), 147-168.
- Allen J.R.L., 1964. The Nigeria continental margin bottom sediments submarine morphology, and geological evolution. Mari. Geol., 1, 289 – 332.
- Amane, W. and Hideki, N., 1997. Geochemical characteristics of terrigenous and marine sourced oils in Hokkaido, Japan. Org. Geochem. 28, 27-41.
- Aquino Neto, F.R., Trendel, J.M., Restle, A., Connan, J. and Albrecht, P.A., 1983. Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleums. In: Bjorøy, M., et al. (Eds.), Advances in Organic Geochemistry, 1981. John Wiley and Sons, 659-667.
- Arise, R.O., Aboyewa, J.A. and Osioma, E., 2015. Biochemical Changes in Lumbricus terrestris and Phytoaccumulation of Heavy Metals from Ugberikoko Petroleum Flow Station Swamps, Delta State, Nigeria. Nig. J. Bas. Appl. Sci., 23(2), 141-155.
- Avbovbo, A.A., 1978. Tertiary lithostratigraphy of Niger Delta. Ame. Assoc. Petrol. Geol. Bull., 62, 295-300.
- Avbobbo, A.A and Ogbe, F.G., 1978. Tertiary lithostratigraphy of Niger Delta. Ame. Assoc. Petrol. Geol. Bull., 62, 295- 306.
- Bahram, A., Hossein, S., Mehrab, R. and Mehdi, K., 2016. Geochemical investigation of oils from Cretaceous to Eocene sedimentary sequences of the Abadan Plain, Southwest Iran. Mar. Petrol. Geol., 73, 609-619.
- Beka, F.T. and Oti, M.N., 1995. The distal offshore Niger Delta: frontier prospects of a mature petroleum province, in, Oti, M.N. and Postma, G., eds., Geology of Deltas: Rotterdam, A.A. Balkema, 237-241.
- Bray, E.E. and Evans, E.D., 1961. Distribution of nparaffins as a clue to recognition of source beds. Geochim. Cosmochim. Acta 22, 2-15.
- Brooks, J.D., Gould, K. and Smith, J.W., 1969. Isoprenoid hydrocarbons in coal and petroleum. Nat., 222, 257-259.
- Burke, K., 1972. Long shore drift, submarine canyons, and submarine fans in development of Niger Delta. Ame. Assoc. Petrol. Geol., 56, 1975-1983.
- Burke, K.C., Dessauvagie, T. F.J. and Whiteman, A.J., 1970. Geological history of the Benue Valley and adjacent areas. In. African Geology, eds. Dessauvagie, T.F.J. and Whiteman, A.J., Ibadan University Press, Ibadan. 187-205.
- Bustin, R.M., 1988. Sedimentology and characteristics of dispersed organic matter in Tertiary Niger Delta: origin of source rocks in a deltaic environment. Ame. Assoc. Petrol. Geol. Bull., 72, 277-298.
- Carim A.A. and HorsfalL, D.E., 1999. Hydrocarbon distribution and accumulations in the coastal swamp depobelt (a case study of the middle Miocene, NAOC experience). Nig. Assoc. Petrol. Expl. Bull., 14, 86 – 91.
- Chandra, K., Mishra, C.S., Samanta, U., Gupta, A. and Mehrotra, K.L., 1994. Correlation of different maturity parameters in the AhmedabadeMehsana block of the Cambay basin. Org. Geochem. 21, 313-321.
- Connan, J. and Cassou, A.M., 1980. Properties of gases and petroleum liquids derived from terrestrial kerogen at various maturation levels. Geochim. Cosmochim. Acta 44, 1-23.
- Demaison, G. and Huizinga, B.J., 1994. Genetic classification of petroleum systems using three factors: charge, migration, and entrapment, in, Magoon, L.B., and Dow, W.G., eds., The Petroleum System--From Source to Trap, AAPG Memoir 60: Tulsa. Ame. Assoc. Petrol. Geol. Bull., 73-89.
- Didyk, B.M., Simoneit, B.R.T., Brassell, S.C. and Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. Nat. 272, 216-222.
- Doust, H., and Omatsola, E., 1990. Niger Delta, in, Edwards, J. D., and Santogrossi, P.A., eds., Divergent/passive Margin Basins, AAPG Memoir 48: Tulsa, Ame. Assoc. Petrol. Geol. Bull., 239-248.
- Ebukanson, E.J. and Kinghorn, R.R.F., 1986. Maturity of organic matter in the Jurassic of southern England and its relation to the burial history of the sediments. J. Pet. Geol. 93, 259-280.

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- Ejedawe, J.E., 1981. Patterns of incidence of oil reserves in Niger Delta Basin. Ame. Assoc. Petrol. Geol. Bull., 65, 1574-1585.
- Ejedawe, J.E., Coker, S.J.L., Lambert-Aikhionbare, D.O., Alofe, K.B. and Adoh, F.O., 1984. Evolution of oil-generative window and oil and gas occurrence in Tertiary Niger Delta Basin. Ame. Assoc. Petrol. Geol. Bull., 68, 1744-1751.
- Ekweozor, C. M., and Daukoru, E.M., 1984. Petroleum source bed evaluation of Tertiary Niger Delta—reply. Ame. Assoc. Petrol. Geol. Bull., 68, 390-394.
- Ekweozor, C. M., Okogun, J.I., Ekong, D.E.U. and Maxwell, J.R., 1979. Preliminary organic geochemical studies of samples from the Niger Delta, Nigeria: Part 1, analysis of crude oils for triterpanes. Chem. Geol., 27, 11-28.
- Ekweozor, C.M., and Okoye, N.V., 1980, Petroleum source-bed evaluation of Tertiary Niger Delta. Ame. Assoc. Petrol. Geol. Bull., 64, 1251-1259.
- ETU-FEOTOR, J.O. 1997. Fundamental of Petroleum Ecology, Paragraphics, Port Harcourt. **110-130**.
- Evamy, B.D., Haremboure, J., Kamerling, P., Knaap, W.A., Molloy, F.A., and Rowlands, P.H., 1978. Hydrocarbon habitat of Tertiary Niger Delta. Ame. Assoc. Petrol. Geol. Bull., 62, 277-298.
- Frankyl, F.J. and Cordry, E.A., 1967. The Niger Delta oil province recent development onshore and offshore: Maxico city, 7th would Petroleum congress proceedings, V. 1B 195-208.
- Frost, B.R., 1997. A Cretaceous Niger Delta Petroleum System, in, Extended Abstracts, AAPG/ABGP Hedberg Research Symposium, Petroleum Systems of the South Atlantic Margin, November 16-19, 1997, Rio de Janeiro, Brazil.
- Gürgey, K., 1999. Geochemical characteristics and thermal maturity of oils from the Thrace Basin (western Turkey) and western Turkmenistan. J. Pet. Geol., 22, 167-189.
- Haack, R.C., Sundararaman, P. and Dahl, J., 1997. Niger Delta petroleum System, in, Extended Abstracts, AAPG/ABGP Hedberg Research Symposium, Petroleum Systems of the South Atlantic Margin, November 16-19, 1997, Rio de Janeiro, Brazil.
- Haack, R.C., Sundaraman, P., Diedjomahor, J.O., Xiao, H., Gant, N.J., May, E.D. and Kelsch, K. 2000. The Niger Delta petroleum systems, Nigeria. In: Mello, M.R., Katz, B.J. (Eds.), Petroleum Systems of South Atlantic Margins. Am. Assoc. Petrol. Geo Mem., 73, 213–231.
- Hakimi, M.H., Abdullah, W.H. and Shalaby, M.R., 2012a. Geochemical and petrographic characterization of organic matter in the Upper Jurassic Madbi shale succession (Masila Basin, Yemen): origin, type and preservation. Org. Geochem. 49, 18-29.
- Hakimi, M.H., Abdullah, W.H. and Shalaby, M.R., 2012b. Molecular composition and organic petrographic characterization of Madbi source rocks from the Kharir oilfield of the Masila Basin (Yemen): palaeoenvironmental and maturity interpretation. Arab. J. Geosci., 5, 817-831.
- Hakimi, M.H., Abdullah, W.H. and Shalaby, M.R., 2011a. Organic geochemical characteristics and depositional environments of the Jurassic shales in the Masila Basin of Eastern Yemen. Geo Arabia, 16 (1), 47-64.
- Hakimi, M.H., Abdullah, W.H. and Shalaby, M.R., 2011b. Organic geochemical characteristics of crude oils from the Masila Basin, eastern Yemen. Org. Geochem., 42, 465-476.
- Hakimi, M.H., Abdullah, W.H. and Shalaby, M.R., 2010. Source rock characterization and oil generating potential of the Jurassic Madbi Formation, onshore East Shabowah oilfields, Republic of Yemen. Org. Geochem., 41, 513-521.
- Hedberg, H.D., 1968. Significance of high-wax oil with respect to genesis of petroleum. Ame. Assoc. Pet. Geol. Bull., 52, 736-750.
- Hospers, J., 1965. Gravity field and structure of the Niger Delta, Nigeria, West Africa. Geol. Soc. Ame. Bull., 76, 407-422.
- Huang, W.Y. and Meinschein, W.G., 1979. Sterols as ecological indicators. Geochim. Cosmochim. Acta 43, 739-745.
- Hughes, W.B., Holba, A.G. and Dzou, L.I.P., 1995. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. Geochim. Cosmochim. Acta 59, 3581-3598.
- Idowu, J.O., Ajiboye, S.A., Ilesanmi, M.A. and Tanimola, A., 1993. Origin and significance of organic matter of Oshosun Formation south-western Dahomey Basin Nigeria. J. Min. Geol., 29, 9-17.
- Johns, R.B., 1986. Biological Markers in the Sedimentary Record. Elsevier, Amsterdam.
- King, W.A., Mills, B.R., Gardiner, S. and Abdillah, A.A., 2003. The Masila fields, Republic of Yemen. In: Halbouty, M.T. (Ed.), Giant Oil and Gas Fields of the Decade 1990-1999. Ame. Assoc. Petrol. Geol., Mem., 78, 275- 295.
- Kulke, H., 1995. Nigeria, in, Kulke, H., ed., Regional Petroleum Geology of the World. Part II: Africa, America, Australia and Antarctica: Berlin. Gebrüder Borntraeger, 143-172.
- Lambert-Aikhionbare, D.O., and Ibe, A.C., 1984. Petroleum source-bed evaluation of the Tertiary Niger Delta: discussion. Ame. Assoc. Petrol. Geol. Bull., 68, 387-394.
- Lambert-Aikhionbare, D.O. and Shaw, H.F., 1981. Petroleum source-bed evaluation of Tertiary Niger Delta discussion. Ame. Assoc. Petrol. Geol. Bull., 68, 387 – 390.
- Large, D.J. and Gize, A.P., 1996. Pristane/phytane ratios in the mineralized Kupferschiefer of the Fore-Sudetic Monocline, southwest Poland. Ore Geol. Rev. 11, 89-103.
- Larter, S.R., Head, I.M., Huang, H., Bennett, B., Jones, M., Aplin, A.C., Murray, A., Erdmann, M., Wilhelms, A. and Di Primio, R., 2005. Biodegradation, Gas destruction and methane generation in deep subsurface petroleum reservoirs: an overview. In: Dore, A.G., Vining, B. (Eds.), Petroleum Geology: Northwest Europe and Global Perspectives: Proceedings of the 6th Petroleum Geology Conference. Geol. Soc., London, 633-640.
- Lewan, M.D., 1984. Factors controlling the proportionality of vanadium to nickel in the bitumen of organic sedimentary rocks. Geochimica et Cosmochimica Acta, 48, 2231-2238**.**
- Lewan, M.D., and Maynard, J.B., 1982, Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. Geochimica et Cosmochimica Acta, 46, 2547-2560.

Mackenzie, A.S., Patience, R.L., Maxwell, J.R., Vandenbroucke, M. and Durand, B., 1980. Molecular parameters of maturation in the Toarcian shales, Paris Basin, France. Changes in the configuration of acyclic isoprenoids alkanes, steranes and triterpanes. Geochim. Cosmochim. Acta 44, 1709-1721.

Mbendi, 1996. <http://mbendi.co.za/cyngoi.html>

- Merki, P.J., 1972. Structural geology of the Cenozoic Niger Delta: 1st Conference on African Geology Proceedings, Ibadan University Press, 635-646.
- Tuttle, M.L.W., Charpentier, R.R. and Brownfield, M.E., 1999. The Niger Delta Petroleum System: Niger Delta Province, Nigeria, Cameroon, and Equatorial Guinea, Africa U.S. Geological Survey, Open file report 99- 50-H, 1-63.
- Miiller, D.E., Holba, A.G. and Huges, W.B., 1987. Effects of biodegradation on crude oils. In: Meyer, R.F. (Ed.), Exploration for Heavy Crude Oil and Natural Bitumen. Ame. Assoc. Petrol. Geol. Stud., 233-241.
- Mills, S.J., 1992. Oil discoveries in the Hadramaut: how Canadian oxy scored in Yemen. Oil Gas J., 49, 52.
- Moldowan, J.M., Seifert, W.K. and Gallegos, E.J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. Am. Assoc. Pet. Geol. Bull. 69, 1255-1268.
- Murat, R.C., 1972. Stratigraphy and paleogeography of the Cretaceous and lower Tertiary in southern Nigeria. In: African Geology (Ed. by DESSAUVAGIE, T.F.J. and WHITEMAN, A.J.), Ibadan University press, Ibadan, Nigeria, 251-266.
- Murray, A.P. and Boreham, C.J., 1992. Organic Geochemistry in Petroleum Exploration. Australian Geological Survey Organization, Canberra, 230.
- Nabil, M.A. and Abubakr, F.M. 2015. Organic geochemical characteristics of crude oils and oil-source rock correlation in the Sunah oilfield, Masila Region, Eastern Yemen. Mar. Petrol. Geol., 63(20), 17-27.
- Nwachukwu, J.I., and Chukwurah, P. I., 1986. Organic matter of Agbada Formation, Niger Delta, Nigeria. Ame. Assoc. Petrol. Geol. Bull, 70, 48-55.
- Nwachkwu, J.I., Oluwole, A.F., Asubiojo, O.I., Filby, R.H., Grimm, C.A., and Fitzgerald, S., 1995. A geochemical evaluation of Niger Delta crude oils, in, Oti, M.N., and Postma, G., eds., Geology of Deltas. Rotterdam, A.A. Balkema, 287-300.
- Nwajide, C.S., 2006. Outcrop analogues as a learning facility for subsurface practitioners: the value of geological field trips. Petrol. Tra. J., 3, 58 – 68.
- Obermajer, M., Fowler, M.G. and Snowdon, L.R., 1999. Depositional environment and oil generation in Ordovician source rocks from southwestern Ontario, Canada: organic geochemical and petrological approach. Am. Assoc. Pet. Geol. Bull., 83, 1426-1453.
- Oghonyon, R, Njoku, A.F. and Itiowe, K., 2015. Seismic and Petrophysical Characterization of Selected Wells, Niger Delta. Int. J. Sci. Inv. Today, 4(1), 054-067.
- Peters, K.E. and Moldowan, J.M., 1993. The Biomarker Guide: Interpreting Molecular Fossils, Petroleum and Ancient Sediments. Prentice Hall, New Jersey, 363.
- Peters, K.E., Walters, C.C. and Moldowan, J.M., 2005. The Biomarker Guide. Cambridge University Press, UK, 1155.
- Philp, R.P., 1985. Biological markers in fossil fuel production. Mass Spectrom. Rev. 4, 1-54. Powell, T.G., 1988. Pristane/phytane ratio as environmental indicator. Nat., 333, 604.
- Powell, T.G. and Mckirdy, D.M., 1973. Relationship between ratio of pristane to phytane, crude oil composition and geological environment in Australia. Nat. Phys. Sci., 243, 37-39.
- Seifert, W.K. and Moldowan, J.M., 1986. Use of biological markers in petroleum exploration. In: Johns, R.B. (Ed.), Methods in Geochemistry and Geophysics 24, 261-290.
- Seifert, W.K. and Moldowan, J.M., 1979. The effect of biodegradation on steranes and terpanes in crude oils. Geochim. Cosmochim. Acta 43, 111-126.
- Shannon, P. M., and Naylor, N., 1989. Petroleum Basin Studies: London, Graham and Trotman Limited, 153-169.
- Short, K.C. and Stäuble, A.J., 1967. Outline of geology of Niger Delta. Ame Assoc. Petrol. Geol. Bull., 51, 761-779.
- Sivan, P., Datta, G.C. and Singh, R.R., 2008. Aromatic biomarkers as indicators of source, depositional environment, maturity and secondary migration in the oils of Cambay Basin, India. Org. Geochem. 39, 1620-1630.
- Stacher, P., 1995. Present understanding of the Niger Delta hydrocarbon habitat, in, Oti, M.N., and Postma, G., eds., Geology of Deltas. Rotterdam, A.A. Balkema, 257-267.
- Thomas, 1995. Niger delta oil production, reserves, field sizes assessed. Oil Gas J., 13, 101-103.
- Tissot, B.P., and Welte, D.H., 1984. Petroleum Formation and Occurrence: Berlin, Springer-Verlag, 518.
- Tissot, B.P., Deroo, G. and Hood, A., 1978. Geochemical study of the Uinta Basin: formation of petroleum from Green river formation. Geochim. Cosmochim. Acta 42, 1469-1485.
- Udo, O.T., and Ekweozor, C.M., 1988, Comparative source rock evaluation of Opuama Channel Complex and adjacent producing areas of Niger delta. Nig. Assoc. Petrol. Expl. Bull., 3(2), 10-27.
- Waples, D.W. and Machihara, T., 1991. Biomarkers for Geologists e a Practical Guide to the Application of Steranes and Triterpanes in Petroleum Geology. Ame. Assoc. Petrol. Geol. Meth. Expl. Se., 9, 91.
- Weber, K.J. (1971): Sedimentological aspect of oil fielding the Niger Delta. Geol. Minjbouw, 50, 559-576.
- Weber, K.J., 1987. Hydrocarbon distribution patterns in Nigerian growth fault structures controlled by structural style and stratigraphy. J. Petrol. Sc. Eng., 1, 91-104.
- Weber, K.J., and Daukoru, E.M., 1975. Petroleum geology of the Niger Delta: Proceedings of the Ninth World Petroleum Congress, volume 2, Geology: London, Applied Science Publishers, Ltd., 210-221.
- Whiteman, A., 1982. Nigeria: Its Petroleum Geology, Resources and Potential: London, Graham and Trotman, 394.