Contents lists available at ScienceDirect

# Heliyon

journal homepage: www.heliyon.com

# The assessment of potential source rocks of Maastrichtian Araromi formation in Araromi and Gbekebo wells Dahomey Basin, southwestern Nigeria

Olabisi A. Adekeye<sup>a</sup>, Samuel O. Akande<sup>a</sup>, James A. Adeoye<sup>b,\*</sup>

<sup>a</sup> University of Ilorin, Ilorin, Nigeria

<sup>b</sup> Mountain Top University, Ibafo, Nigeria

#### ARTICLE INFO

*Keywords:* Geochemistry Geology

#### ABSTRACT

Drilled core samples of the Araromi Formation in the eastern Dahomey basin penetrated by Araromi and Gbekebo exploratory wells were investigated to establish the source rocks potentials in the onshore area of the basin. The sediments are of Maastrichtian age deposited in the shallow marine environment with varying thicknesses.

Rock-Eval data of forty seven (40) shales give Total Organic Carbon (TOC) range of 0.50–4.78 wt%, Hydrogen Index (HI) value range of 1 - 327mgHC/gTOC,  $T_{max}$  values from 398 °C–437 °C and Source Potential (SP) values range from 0.01 - 14.56kgHC/ton of rock. The maceral compositions of the shales are liptinite (av. 26.0%), abundance vitrinite (av. 38.1%) and inertinite (av. 35.9 %) with vitrinite reflectance (VR<sub>0</sub>) ranging from 0.51 - 0.68 %R<sub>o</sub>. Hydrocarbons and biomarkers results reveal a bimodal n-alkane envelope between (nC<sub>16</sub> and nC<sub>18</sub>) and (nC<sub>27</sub> and nC<sub>29</sub>) suggesting organic matter of mixed origin of algae and higher plant generally in the two well. The Significant contribution of marine algae in the deeper part of Gbekebo well was observed by the presence of C<sub>30</sub> 24-n-propyl cholestane (%C<sub>30</sub> sterane range from 0.45 to as high as 5.23%).

Integration of the Rock-Eval, organic petrology and biomarkers data reveal that the kerogen constituents of the source rocks in Araromi well are mainly Type II/III, III and IV with a high amount of inertinite constituents suggesting they have been reworked. Type II and II/III kerogen derived from marine algae are better preserved in the deeper part of Gbekebo well located more southerly in the basin than in the Araromi well. The source rocks are generally immature to marginally mature and hydrocarbon exploration effort should be targeted towards Gbekebo well area where we have more promising potential source rocks capable of generating more hydrocarbons essentially at a deeper depth.

# 1. Introduction

The Dahomey Basin is an extensive sedimentary basin, in the Gulf of Guinea which extends from southeastern Ghana through Togo and Benin Republic on the west side to the Okitipupa ridge/Benin Hinge line on the east side in the southern, part of Nigeria Brownfield and Charpentier (2006) Fig. 1. The basin evolution involved basement fragmentation, block faulting and subsidence of the Jurassic basement complex couple with wrench movements of the basement blocks Onuoha and Ofoegbu (1988), De Matos and Renato (2000), Arthur et al. (2003). The basin consists of sedimentary formations (Cretaceous —Tertiary) that outcrop in an arcuate belt roughly parallel to the coastline Omatsola and Adegoke (1981). This basin has attracted a lot of geoscientific interest, especially

in the recent years in view of the availability of the new boreholes and recent road cuts which have improved the knowledge of its geology and hydrocarbon potential assessment.

The analysis of sedimentary basins is of great geoscientific interest, in the world today particularly in areas where there are potentials for hydrocarbon occurrence. The Dahomey basin is generally a combination of inland, coastal, offshore basin that is located in the Gulf of Guinea (Fig. 1). It is separated from the Niger Delta, Nigeria by a subsurface basement high referred to as the Okitipupa Ridge (Omatsola and Adegoke, 1981) and its offshore extent is poorly defined. Sediment deposition in the basin follows an east-west trend with about Cretaceous strata thickness around 200 m thick in the onshore area where the studied wells are located (Okosun, 1990).

\* Corresponding author. *E-mail address:* jamesadejimi@gmail.com (J.A. Adeoye).

https://doi.org/10.1016/j.heliyon.2019.e01561

Received 1 October 2018; Received in revised form 10 March 2019; Accepted 18 April 2019

2405-8440/© 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).





Heliyon



Fig. 1. Major features of the Gulf of Guinea Province, West Africa: Dahomey, Keta, Saltpond, Tano, and Ivory Coast basin from the east to the west (After Brownfield and Chapentier, 2006).

In the recent time, hydrocarbon exploration in Lagos, eastern Dahomey Basin in Nigeria and Tano Basin in Ghana which is presently producing oil is becoming more attractive to investors and thereby increasing motivation for intense study of the basin. This study aimed at examining the hydrocarbon potentials of the sediments in the post Santonian successions penetrated by the Araromi and Gbekebo wells in the northern onshore area of the basin (Fig. 2). The drill core samples used in this study were collected from the Geological Survey of Nigeria Agency (GSNA), Kaduna main office.

## 1.1. Geology and stratigraphy of Dahomey Basin

The Dahomey Basin evolved in the Late Jurassic - Early Cretaceous as a result of the separation of the Africa and South America plates which led to the opening of South Atlantic Ocean. The Romanche, Chain, and Charcot fractures zone which develops during the drifting stages of South America away from Africa enhances the development of numerous horst and graben features in the Dahomey basin.

The horst and graben structural features control deposition of

Cretaceous to Tertiary sediments in the basin Adegoke (1969), Ako et al. (1980), Omatsola and Adegoke (1981), Adediran and Adegoke (1987), Brownfield and Charpentier (2006). The stratigraphic setting of the Dahomey Basin has been described in detail in the works of Adegoke (1969), Ogbe (1970), Kogbe (1974), Billman (1976), Omatsola and Adegoke (1981), Ako et al. (1980), Okosun (1990), Idowu et al. (1993), Adekeye (2004) and Adekeye et al. (2006). These authors reported five lithostratigraphic formations covering the Cretaceous to Tertiary ages. The formation from the oldest to the youngest include: Abeokuta Group comprises Ise, Afowo and Araromi formations (Cretaceous), Ewekoro Formation (Paleocene), Akinbo Formation (Late Paleocene-Early Eocene), Oshosun Formation (Eocene) and Ilaro Formation (Middle-Late Eocene) Fig. 3.

#### 2. Materials and methods

#### 2.1. Hydrocarbon source rock potential

The core samples from the Araromi Formation penetrated by the



Fig. 2. A. Location of Dahomey Basin in the Gulf of Guinea area of West Africa, B. Geological map of Dahomey basin showing the location of the Araromi and Gbekebo wells (red box) on the eastern margin of Dahomey (west of the Niger Delta).

GEO	LOGIC TIME	FORMATION							
PERIOD	ЕРОСН	Ako et al., (1980)	Om Adeg	atsola and joke, (1981)	Billman (1976)				
QUARTERNARY	HOLOCENE PLEISTOCENE	Coastal Plain Sands	Ве	enin Fm	Benin Fm				
ιRY	EOCENE	Ilaro Fm	Ilaro Fm		Ijebu Fm				
TERTL		Oshosun Fm	Oshosun Fm		Oshosun Fm				
	PALEOCENE	Ewekoro Fm	Ewekoro Fm		Imo Shale				
CRETACEOUS	MAASTRICHTIAN	Abeokuta Fm		Araromi Fm					
	CAMPANIAN				Nkporo Shale				
	CONIACIAN		t Group	Afowo Fm	A				
	TURONIAN		eokuta		Awgu Fm				
	CENOMANIAN		Ab	Ice Em	Abeokuta Fm				
	BARREMIAN			Ise Fill	Folded Sediments				

Fig. 3. Generalised stratigraphic setting of the Dahomey Basin in the southwestern Nigeria.

Araromi and Gbekebo wells drilled on the eastern margin of the Dahomey Basin (Fig. 2) were analysed for their total organic carbon content (TOC) and hydrocarbon source quality by Rock-Eval Pyrolysis using standard experimental techniques. The Rock-Eval pyrolysis was carried out at the Organic Geochemistry Laboratory of the University of New Castle Upon Tyne following the standard procedure of Rock-Eval pyrolysis experimentation on Rock-Eval II machine. The Rock-Eval II analysis has the ability of measuring the total organic organic carbon (TOC) content on the pulverized samples at elevated temperatures of ca. 600 °C (Espitalie et al., 1977). Pyrolysis of 10–40mg of samples at 300 °C for 4 mins was followed by programmed pyrolysis at 25 °C/min to 550 °C in an atmosphere of helium. The parameters assessed from Rock-Eval Pyrolysis include Source Potential (SP), Genetic Potential (S<sub>1</sub> + S<sub>2</sub>), Thermal Maturity of the organic matter (T<sub>Max</sub>), Total Organic Carbon content (TOC), Hydrogen Indices (HI) and Productive Index (PI).

Bitumen extracts from selected organic-rich source rock samples were analysed for their biomarker and stable carbon isotope composition of *n*alkanes using the GC, GC-MS and GC-MS-MS techniques described below. Gas chromatography was performed on the saturated hydrocarbon fractions in order to obtain *n*-alkane and isoprenoid data as well as to determine sample concentration and complexity before GC-MS and gas chromatography-isotope ratio mass spectrometry (GC-IRMS) analyses. An HP 5890 series II gas chromatograph equipped with an HP-5 coated capillary column (60 m  $\times$  0.25 mm, 0.25µm film thickness) was used. The GC oven was initially set at 50 °C for 2 min and then the temperature was ramped from 50 °C at 4 °C/min to 300 °C and held at final temperature for 20 min with hydrogen as the carrier gas (flow rate approx 2 ml/min and initial pressure of 100 kPa).

The selected shale samples were crushed to less than 2mm and impregnated in epoxy for qualitative reflected light microscopy. Where organic constituents are sparse, kerogen concentrates were prepared, mounted and polished. Organic petrology studies were carried out on a Reichert Jung Polyvar Photomicroscope equipped with halogen and HBO lamps, a photomultiplier and computer unit at the Zentraleinrichtung fur Elektronemikroskopie (ZELMI), Technische Universitat Berlin, Germany. Mean random reflectance of vitrinite in oil (R<sub>o</sub>%, cf. Bustin et al., 1983) was calculated from the reflectance of at least 30 grains of vitrinite measured in random orientation using monochromatic (546 nm) non-polarised light in conjunction with a x40 oil immersion objective. Calibration of the microscope photometer was achieved using standards of known reflectance (1.23 and 3.16 %). Measured Rom values of reflectance standards confirmed the photomultiplier to be consistently linear within the range of the measurements. Data collection and evaluation were done using the coal programme by Reichert Jung and macerals were identified through the use of white light and blue light excitation at 546 and 460 nm respectively. The mean reflectance as

compared to the median or modal reflectance appears to be an adequate measure of thermal maturity in this study (Tissot and Welte, 1984; Pollastro and Barker, 1986).

# 3. Results & discussions

## 3.1. Petroleum potential assessment of the source

The Rock-Eval pyrolysis result is presented in Tables 1 and 2. The various parameters for assessing the hydrocarbon, potential of a source bed are discussed here. The principal parameters discussed, below include: Source Potential (SP), Hydrogen 'Index (HI), Thermal maturity (Tmax), Kerogen Types and Total Organic Carbon' (TOC).

#### 3.2. Organic matter richness

High concentrations of organic matter tend to occur in sediments that accumulate in areas of high organic matter productivity. Environments of high productivity can include nutrient-rich coastal upwelling, swamps, shallow seas and lakes. The total organic matter (TOC) is a direct measurement of the organic matter richness of a given sedimentary rock. It is the measure of the quantity of organic matter (OM) present in a rock. According to North, 1985 the TOC values of any rock can be classified as poor, fair, good, very good and excellent. The analyzed Araromi shale samples from both Araromi and Gbekebo wells have a value range of 0.5-4.78 wt% (Tables 1 and 2), which indicates variable source rock organic carbon quality from poor to excellent. There is an overall trend of increasing TOC down the well (Fig. 4) suggesting better source rock quality in deeply buried intervals. Most of the shales have TOC values >0.5 wt%, the minimum threshold value for hydrocarbon generation in siliciclastic source rock (Peters and Cassa, 1994) suggesting they are fair to good quality source rocks capable of generating hydrocarbon (Tissot and Welte, 1978; Hedberg et al., 1979).

# 3.3. Hydrogen index (HI)

Hydrogen Index (HI) is proportional to the amount of hydrogen contained in the kerogen and higher HI indicates a good quality of a source rock to generate hydrocarbon. Peters and Cassa (1994) gave geochemical parameters describing kerogen types and the quality in their work. The hydrogen index values of Araromi shales in the two wells vary from 1 - 327mgHC/gTOC (Tables 1 and 2) thus, suggesting source rock quality that spans from poor to good. The HI values ranging from 1 -45mgHC/g TOC having kerogen Type IV in the upper part of the two wells indicate a highly reworked terrestrially derived OM perhaps in a highly oxic depositional environment. They form inert source which have no potential for hydrocarbon generation. The shales within the shallow upper to the middle part i.e. 200-400 m in Araromi well Fig. 4 and 800-885 m in Gbekebo well Fig. 5 are characterized with HI values of 45–132mgHC/g TOC with kerogen Type III suggest woody or herbaceous organic matter origin having gas prone characteristics. The deeper parts of Gbekebo well from the depth of 887 m have the best source rock quality with HI value ranging from 151 - 327mgHC/g TOC consisting of kerogen Type II and Type II/III oil and gas prone kerogen. The Type II and Type III kerogen apparently increases down-hole profile concomitant with TOC trend in the well logs (Figs. 4 and 5). The trend of increasing HI is also noticeable in Araromi well between 557 and 572 m to be 151 to 202 mgHC/gTOC respectively suggesting that the deeper section of the formation consists more organic-rich successions and thus presumably have greater potential to generate liquid hydrocarbon. Additionally, two organic-rich intervals (A and B) Fig. 5 contain HI values of 327mgHC/g TOC suggesting that more organic-rich strata in the deep offshore where we have the highest sediment thickness in the basin may have greater potential to generate liquid hydrocarbon.

#### 3.4. Thermal maturation

A good match exists between the thermal maturation ( $T_{max}$ ) measured from the Rock-Eval pyrolysis which varies from 398 °C to 437 °C and the vitrinite reflectance values varying from 0.50 to 0.68 %R<sub>o</sub>. These values suggest that the source rocks are thermally immature to marginally mature for hydrocarbon generation. The plots of Rock-Eval  $T_{max}$  against hydrogen index also show thermally immature to early mature source rocks with respect to hydrocarbon generation and dominance of a mixture of oil prone Type II and gas prone Type III kerogens (Fig. 6).

 Table 1

 Rock-Eval pyrolysis data of the shales from Araromi Formation in the Araromi Borehole.

Sample No	Depth	Location	Fm	$S_1$	$S_2$	SP	T <sub>max</sub>	PI	VRo	TOC	HI	Kerogen Type
Ar-91	405.38	Araromi	Araromi	0.02	0.01	0.03	403	1.00	0.51	0.65	1	IV
Ar-97	435.86	Araromi BH	Araromi FM	0.05	0.10	0.15	419	0.36	-	0.61	16	IV
Ar-100	454.46	Araromi BH	Araromi FM	0.05	0.10	0.15	412	0.36	-	0.75	13	IV
Ar-105	463.29	Araromi BH	Araromi FM	0.04	0.05	0.09	410	0.50	-	0.66	7	IV
Ar-110	475.49	Araromi BH	Araromi FM	0.17	0.95	1.12	424	0.15	-	1.69	56	III
Ar-114	487.68	Araromi BH	Araromi FM	0.11	0.57	0.68	428	0.16	-	1.05	54	III
Ar-119	495.30	Araromi BH	Araromi FM	0.15	0.75	0.87	422	0.17	-	1.77	40	IV
Ar-124	505.36	Araromi BH	Araromi FM	0.18	0.54	0.72	420	0.25	-	1.19	45	III
Ar-132	518.16	Araromi BH	Araromi FM	0.08	0.26	0.34	409	0.24	-	1.02	25	IV
Ar-139	539.49	Araromi BH	Araromi FM	0.08	0.18	0.26	411	0.31	0.51	1.01	17	IV
Ar-145	557.78	Araromi BH	Araromi FM	0.21	3.10	3.31	423	0.06	0.66	2.05	151	II-III
Ar-148	566.93	Araromi BH	Araromi FM	0.28	5.18	5.46	424	0.05	-	2.75	188	II-III
Ar-151	572.72	Araromi BH	Araromi FM	0.52	3.70	4.22	426	0.12	-	1.83	202	II-III

Depth-m, Formation-Fm, S1-(mgHC/grock), S2-(mgHC/grock), SP-(kg/t), Tmax - °C, VRo-%, TOC - wt%, HI-(mgHC/grock).

Table 2

Bulk geochemical and selected biomarker parameters for the analysed shales of Araromi Formation from Gbekebo well in Dahomey Basin.

Sample No	Depth	TOC	$S_1$	<b>S</b> <sub>2</sub>	T <sub>max</sub>	HI	PI	Pr/Ph	%C27	%C28	%C29	%C30	OL	C29 S/S + R
GB 304	834	0.50	0.00	0.01	430	2.00	0.00							
GB 305	835	0.63	0.12	0.36	425	57.14	0.25							
GB 306	841	1.02	0.14	0.51	425	50.00	0.22							
GB 307	845	1.01	0.13	0.48	432	47.52	0.21	1.06	36.94	25.55	37.06	0.45	0.00	0.23
GB 309	850	0.69	0.05	0.24	425	34.78	0.17							
GB 310	853	0.91	0.04	0.34	430	37.36	0.11	1.28	45.28	26.62	28.09	0.00	0.00	0.18
GB 311	854	0.99	0.06	0.55	430	55.56	0.10							
GB 312	859	0.95	0.08	0.41	425	43.16	0.16							
GB 313	861	1.00	0.28	0.42	432	42.00	0.40							
GB 314	862	0.68	0.12	0.44	435	64.71	0.21	0.78	24.10	41.81	32.77	1.32	0.00	0.25
GB 315	863	0.91	0.07	0.36	435	39.56	0.16	0.93	23.62	35.50	38.88	2.00	0.06	0.31
GB 316	864	0.76	0.06	0.21	437	27.63	0.22							
GB 318	865	0.82	0.06	0.30	431	36.59	0.17	1.18	22.16	39.74	36.59	1.51	0.00	0.26
GB 320	874	1.24	0.06	0.15	422	12.10	0.29							
GB 323	883	1.67	0.12	1.29	435	77.25	0.09							
GB 324	885	1.70	0.06	0.83	432	48.82	0.07	1.25	31.95	41.15	24.29	2.61	0.00	0.31
GB 325	887	1.87	0.27	3.01	427	160.96	0.08							
GB 326	889	2.13	0.18	5.25	430	246.48	0.03		38.20	38.47	20.83	2.50	0.00	0.26
GB 327	890	2.12	0.17	3.01	427	141.98	0.05							
GB 402	903	1.97	0.21	1.39	432	70.56	0.13		31.39	31.00	33.51	4.11		0.23
GB 421	959	1.66	0.28	0.42	415	25.30	0.40							
GB 450	1012	2.24	0.31	5.01	433	223.66	0.06	1.13	33.68	38.20	25.09	3.02	0.20	0.29
GB 451	1013	2.52	0.32	6.44	432	255.56	0.05							
GB 454	1016	4.78	0.81	13.75	434	287.66	0.06							
GB 455	1017	3.33	0.73	10.30	431	309.31	0.07	2.02	30.15	30.74	33.89	5.23	0.21	0.16
GB 456	1019	3.94	1.29	12.88	426	327.07	0.09	1.39	37.91	33.23	26.73	2.13	0.12	0.47
GB 460	1028	1.54	0.31	1.09	434	70.78	0.22	0.96	34.20	33.56	29.00	3.24	0.09	0.19

Depth-ft, Formation-Fm, S<sub>1</sub>-(mgHC/grock), S<sub>2</sub>-(mgHC/grock), SP-(kg/t), Tmax -  $^{\circ}$ C, VRo-%, TOC - wt%, HI-(mgHC/grock), Pr/Ph = pristane/phytane. % C27-C30 = % individual C27-C30 ααα sterane to sum of C27-29 ααα regular steranes. OL =  $18\alpha(H) + 18\beta(H)$  oleanane/C<sub>30</sub>  $17\alpha(H)$ ,  $21\beta(H)$ - Hopane. C29 S/S + R = ratio of  $5\alpha(H)$ ,  $14\alpha(H)$ ,  $21\alpha(H)$  - steranes (20S/S + R) thermal maturity parameter.



Fig. 4. Geochemical log of the Araromi well showing the distribution of organic matter as it increases down the well.

A high S<sub>1</sub> values commonly result from either potential or effective source rocks or rocks containing migrated oil or contaminated by drilling additives. Similarly, samples with migrated oil or drilling additives are readily distinguished from source rocks by anomalously high production indices (PI) for their level of thermal maturity (Espitalie et al., 1985; Huizinga et al., 1988). Source rocks having  $T_{max}$  ranging 390–435 °C with PI  $\leq$  0.1,  $T_{max}$  ranging 436°-445 °C, with PI  $\leq$  0.3 and  $T_{max}$  ranging 445–460 °C, with PI  $\leq$  0.4 are categorized as samples not contaminated by drilling additives or migrated oil (Espitalie et al., 1985; Huizinga et al., 1988). The production indices of the source rocks in Gbekebo indicate that the potential source rock intervals (A and B) are immature (Figs. 4 and 5). The shales in the entire shallow intervals of Gbekebo and Araromi wells which are immature but have high production indices that

commonly suggest a significant hydrocarbon potential are interpreted as being stained or impregnated with migrated oil (Figs. 4 and 5).

#### 3.5. Source potential (SP)

The source potential is calculated from the addition of  $S_1 + S_2$  values and is a measure of the genetic potential of the rock. This is regarded as the total amount of petroleum that might be generated from a rack. This potential usually depends on the nature and abundance of kerogen, which in turn are related to the original organic input at the time of sediment deposition and to the conditions of microbial degradation and rearrangement of the organic matter in the young sediments. Dymann et al. (1996) gave a standard for SP qualities.



Fig. 5. Geochemical log of the Gbekebo well showing the two organic-rich intervals (A and B).



Fig. 6. Plot of Rock-Eval HI against Tmax indicating the kerogen types and their respective hydrocarbon potentials in the analysed Araromi Formation sediments.

The Source Potential (SP) value ranges from 0.01 - 14.56kgHC/ton of rock (Tables 1 and 2). The SP values are generally lower than the 2kgHC/ ton of rock expected for good source rock (Dymann et al., 1996), suggesting little or no oil source rock potential but some potential for gas. Samples with higher SP values; Ar 145 (3.31 kgHC/ton), Ar148 (5.46 kgHC/ton), Ar151 (4.22 kgHC/ton), GB455 (11.03 kgHC/ton) and GB456 (14.17 kgHC/ton) of rock suggest a moderate source rock with good oil potential. These source potentials in the Araromi and Gbekebo wells are consistent with the total organic contents and hydrogen index at that basal part indicating zones of the best and highest potential in the study area. Tissot and Welte (1984) also proposed a genetic potential (SP = S<sub>1</sub> +S<sub>2</sub>) for the classification of source rocks. According to their classification scheme, rocks having SP of less than 2mgHC/g rock correspond to gas-prone rocks or non-generative ones, rocks with SP between 2mgHC/g and 6 mgHC/g rock are moderate source rocks, and those with SP greater than 6mgHC/g rocks are good source rocks.

#### 3.6. Maceral analysis

The organic petrological study of the disseminated organic matter in the shale samples was carried out using the techniques in studying optical characteristics of finely dispersed organic matter particles in coals, coaly shales, and carbonaceous shales. Terminologies of Stach et al. (1982) modified in Teichmuller (1987) were used here. Selected shale samples were polished and observed under organic petrological microspcope. The different macerals of vitrinite, liptinite, and inertinite were observed. Photomicrographs of representative macerals are shown in Fig. 7. In general, the maceral composition includes liptinite (av. 26.0 %), vitrinite (av. 38.1 %) and inertinite (av. 35.9 %) in all the samples investigated. The dominance of vitrinite and inertinite macerals suggests terrestrially derived, reworked and oxidized organic matter in the shale sediments. There is no particular maceral variation pattern or zonation down deep in all the wells.



Fig. 7. Photomicrographs of the macerals Araromi shale bar scale 50 µm. (1. White light observation of large huminite grain within mineral matter matrix in Ar-140. and 2. Blue light excitation of the same field in 1 showing threads of sporinites and resinites with yellowish fluorescence intensity, sandwiched within the huminite cell structure; 3. White light observation of discrete euhedral to subhedral grains of pyrite distributed within mineral matter and clouds of amorphous organic matter in Ar-145, and 4. Blue light excitation of the same field in 3 showing thin-walled sporinite with yellow fluorescence in the clouds of organic matter and the non-fluorescensing pyrite grains in black colour, 5. White light observation of irregular grains of huminite within mineral matter matrix in Ar-146, 6. Blue light excitation of the same field in 5 showing non-fluorescensing huminites in black colour associated with threads of sporinite in the lower bottom and yellowish fluorescensing pollen grain ? in the upper sector of the huminite grain).



Fig. 8. A bimodal peaks n-alkane envelope of sample Ar-149 maximizing at nC16 and nC29 typical of source rock whose organic matters have been derived from a variable mixture of algal and terrigenous higher plant materials. Note 13,15, e.t.c represent the n-alkane carbon numbers and Pr; Pristane, and Ph; Phytane.

## 3.7. Biomarker compositions of the shales

Drilled core samples analysed by Gas Chromatography (GC) display a bimodal n-alkane GC fingerprint envelope with maxima between  $nC_{16} - nC_{18}$  and  $nC_{27} - nC_{29}$  (Fig. 8), suggesting variable inputs from both terrigenous and non-terrigeneous (probably marine algal) organic matter. However, some samples display a unimodal n-alkane GC fingerprint typical of dominantly normal marine algal contribution (maximizing between  $nC_{16}$  and  $nC_{18}$ ). There is a relatively high input from algabacterial precursors indicated by the abundance of the low molecular weight relative to high molecular weight n-alkane derived from

terrigeneous higher plants (Bray and Evans, 1961). Additionally, Pr/Ph ratios vary from 0.78 - 2.02 reflecting anoxic to sub-oxic source rock depositional environment (Didyk et al., 1978; Volkman and Maxwell, 1986).

Steranes in the saturated hydrocarbon fractions of the bitumen extracts of the Araromi shale samples analyse by GC-MS and GC-MS-MS show the C<sub>27</sub> - C<sub>29</sub> distributions to be nearing a ratio of 1.1:0.9:1.0, with higher C<sub>27</sub> and C<sub>28</sub> compounds on occasions relative to the C<sub>29</sub> sterane homologues for the 5α(H),14α(H),17α(H) 20R configuration isomers. Figs. 9 and 10 show the sterane distributions of the bitumen extracts from the Araromi shales. The above observation suggests a



Fig. 9. Gas chromatograms of representative saturated hydrocarbon fractions of the Araromi shale (samples GB314 and GB 307) extracts showing how n-alkane and isoprenoid distributions in the Araromi shale. m/z 217 mass chromatograms.



Fig. 10. m/z 217 mass chromatograms showing the distribution of C27-C29 steranes in representative intervals within the Araromi. Note the downhole variation in the sterane distributions within the Araromi shale extracts.

relatively higher input from the marine red algae and a low level of land plant contribution to the source organic matter (Goodwin, 1973). Additionally, the presence of the C<sub>30</sub> 24-*n*-propyl cholestane (detected by GC-MS-MS m/z 414-217 parent to daughter ion transition), confirms the relatively high marine algal contribution to the organic matter in the Araromi shales, as values of  $%C_{30}$  sterane range from 0.45 to as high as 5.23%, even in oleanane rich intervals in "Zone B" (Fig. 5).

## 4. Conclusion

The Late Cretaceous Araromi Formation in the Dahomey Basin, southwestern Nigeria has dominant of Type III and reworked organic matter in the shallow part of the studied wells probably as a result of the contribution of more of terrigenous components into the basin. The basal or deeper part of the wells indicate sterane distributions in the shale extracts dominated by  $C_{27}$  relative to  $C_{28}$  and  $C_{29}$  carbon homologues and significant  $C_{30}$  24-*n*- propyl cholestane concentrations diagnostic of marine algal inputs. The organic constituents suggest more contributions from marine settings at the base of the well than the terrigenous higher plant. They were probably deposited under anoxic to sub-oxic conditions as reflected by Pr/Ph ratios ranging from 0.78 - 2.02. The source rocks are predominantly immature to marginally mature at shallow levels particularly in this northern fringe of the basin where Gbekebo and Araromi

are located but reaching proven maturity in the subsurface in the southerly coastal and offshore areas.

There are indications of migrated hydrocarbons in some parts of the Araromi Formation even though its potential source rocks are immature. The Araromi shales have predominantly gas resources and exploration efforts should be targeted toward where the more promising potential source rocks capable of generating hydrocarbons are deeply buried.

# Declarations

# Author contribution statement

Olabisi A. Adekeye: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Samuel O. Akande: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

James A. Adeoye: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

#### Funding statement

This research did not receive any specific grant from funding agencies

in the public, commercial, or not-for-profit sectors.

#### Competing interest statement

The authors declare no conflict of interest.

#### Additional information

No additional information is available for this paper.

#### Acknowledgments

The authors wish to thank the Nigeria Geological Survey Agency (NGSA) for providing the drilled core samples. We thank the laboratory for the analysis and we also thank the reviewers for their time. We acknowledge the Department of Geology and Mineral Sciences, University of Ilorin, for the support towards the completion of this work.

#### References

- Adediran, S.A., Adegoke, O.S., 1987. Evolution of the sedimentary basins of the Gulf of Guinea. In: Current Research in Africa Earth Sciences, Matheis and Schandeimeier. Balkema, Rotterdam, pp. 283–286.
- Adegoke, O.S., 1969. Eocene stratigraphy of southern Nigeria. Mem. Bur. Rech. Geol. Mins. 23–46.
- 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, 202p.
- Adekeye, O.A., Akande, S.O., Erdtman, B.D., Samuel, O.J., Hetenyi, M., 2006. Hydrocarbon potential assessment of the upper Cretaceous-Lower Tertiary sequence
- in the Dahomey basin South-western Nigeria. NAPE Bulletin 19 (1), 50–60. Ako, B.D., Adegoke, O.S., Petters, S.W., 1980. Stratigraphy of the Oshosun Formation in
- South-western Nigeria. J. Min. Geol. 17, 97–106. Arthur, T.J., MacGregor, D.S., Cameron, N.R., 2003. Petroleum Geology of Africa—New
- Themes and Developing Technologies. Geological Society, London. Special Publication p. 207, 289.
- Billman, H.G., 1976. Offshore stratigraphy and paleontology of the Dahomey embayment. Proc. 7th Afri. Micropal. Coll. Ile-Ife 27–42.
- Bray, E.E., Evans, E.D., 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. Geochem. Cosmochim. Acta 22, 2–5.
- Brownfield, M.E., Charpentier, R.R., 2006. Geology and Total Petroleum Systems of the Gulf of Guinea Province of West Africa: U.S Geological Survey Bulletin 2207-C, 32p.
- Bustin, R.M., Cameron, A.R., Grieve, D.A., Kalkreuth, W.D., 1983. Coal petrology: its principles, methods and applications. Geol. Assoc. Canada Short Course Notes 3, 230p.

- De Matos, D., Renato, M., 2000. Tectonic evolution of the equatorial South Atlantic. In: Atlantic Rifts and Continental Margins. American Geophysical Union. Geophys. Monogr. Ser., v. 115, p. 331 - 354.
- Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G., 1978. Organic geochemical indicator of paleoenvironmental conditions of sedimentation. Nature 272, 216–222.
- Dymann, T.S., Palacos, J.G., Tysdal, R.G., Perry, W.J., Pawlewicz, M.J., 1996. Source rock potential of middle Cretaceous rocks in southwestern Montana. AAPG (Am. Assoc. Pet. Geol.) Bull. 80, 1177–1184.
- Espitalie, J., Deroo, G., Marquis, F., 1985. La pyrolyse Rock-Eval et ses applications (deuxieme partie). Revue Institut Francais du Petrole 40, 755–784.
- Espitalie, J., Madec, M., Tissot, B.P., Menning, J.J., Leplat, P., 1977. Source rocks characterization method for exploration. In: Offshore Technology Conf. Paper 2935, 11th Annual OTC, Houston, 3, pp. 439–444.
- Goodwin, T.W., 1973. Comparative biochemistry of sterols in eukaryotic microorganisms. In: Erwin, J.A. (Ed.), Lipids and Biomembranes of Eukaryotic Microorganisms. Academic Press, New York, pp. 1–40.
- Hedberg, H.D., Moody, J.O., Hedberg, R.M., 1979. Petroleum prospects of deep offshore. AAPG Bull. 63, 286–300.
- Huizinga, B.J., Aizenshtat, Z.A., Peters, K.E., 1988. Programmed pyrolysis-gas chromatography of artificially matured Green River kerogen. J. Energy Fuel. 74, 74–81.
- Idowu, J.O., Ajiboye, S.A., Ilesanmi, M.A., Tanimola, A., 1993. Origin and significance of organic matter of Oshosun Formation south-western Dahomey basin Nigeria. J. Min. Geol. 29, 9–17.
- Kogbe, C.A., 1974. Paleo-ecologic significance of vertebrate fossil in the Dukamaje and Dange formations (Maastrichtian and Paleocene) of northwestern Nigeria. J. Min. Geol. (Nigeria) 8, 49–55.
- Ogbe, F.A.G., 1970. In: Dessauvagie, T.F.J., Whiteman, A.J. (Eds.), Stratigraphy of strata exposed in the Ewekoro quarry western Nigeria. African Geology University of Ibadan Press, Nigeria, pp. 305–324.
- Okosun, E.A., 1990. A review of the Cretaceous stratigraphy of the Dahomey embayment, West Africa. Cretac. Res. 11, 17–27.
- Omatsola, M.E., Adegoke, O.S., 1981. Tectonic evolution and Cretaceous stratigraphy of the Dahomey basin. J. Min. Geol. 8, 30–137.
- Onuoha, K.M., Ofoegbu, C.O., 1988. Subsidence and evolution of Nigeria's continental margin: implications of data from Afowo-1 well. Mar. Petrol. Geol. 5, 175–181.
- Peters, K.E., Cassa, M.R., 1994. Applied source rock geochemistry. In: Magoon, L.B., Dow, W.G. (Eds.), The Petroleum System From Source to Trap. AAPG Memoir, vol. 60, pp. 93–117.
- Pollastro, R.M., Barker, C.E., 1986. Application of Clay Mineral, Vitrinite Reflectance and Fluid Inclusion Studies to the Thermal and Burial History of the Pinedale Anticline, Green River basin, Wyoming, 28. SEPM Special Publication, pp. 73–83.
- Stach, E.M., Mackowsky, T.H., Teichmuller, M., Taylor, G., Chandra, D., Teichmuller, R., 1982. Stach's Text Book of Coal Petrology. Gerbruder Borntaege, Berlin, 535p.
- Teichmuller, M., 1987. Organic material and very low grade metamorphism. In: Frey, M. (Ed.), Low Temperature Metamorphism. Blackie and Sons Pub, London, pp. 114–161. Tissot, B.P., Welte, D.H., 1978. Petroleum Formation and Occurrence. Springer-Verlag,
- New York, 538p.
  Tissot, B.P., Welte, D.H., 1984. Petroleum Formation and Occurrence, second ed. Spinger Verlag, Berlin, 699p.
- Volkman, J.K., Maxwell, J.R., 1986. Acyclic isoprenoids as biological markers. In: Johns, R.B. (Ed.), Biological Markers in Sedimentary Record. Elsevier, New York, pp. 1–42.