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Full Length Article

n-Alkane bound biomarker fingerprints from asphaltenes in the bitumens of Eastern Dahomey Basin, Nigeria: Source and genetic implications

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ABSTRACT

The asphaltene fractions of the bitumens of Eastern Dahomey Basin in Nigeria, were analyzed by flash pyrolysis-gas chromatography (Py-GC) method in order to unravel its geochemical history and properties. The distributions of the initial biomarkers of the original oils from the pyrolysates are related to the assessment of organic matter source, paleo-redox conditions and source environment during deposition. Also, it effectively establishes the genetic relationship of the bitumens. The *n*-alkane distributions in the pyrolysates reveal nC_9-nC_{32} *n*-alkanes, maximizing at nC_{14}, isoprenoids-pristane (Pr) and phytane (Ph), and some *n*-alkene peaks. High peaks of low to medium-weight nC_9-nC_{20} *n*-alkanes and low peaks of nC_{21+} *n*-alkanes characterize the distributions. These reveal that abundant algal organic matter with some terrigenous inputs contributed to the source rock of the bitumens. The high concentration of marine organic matter inputs to the source rock is further confirmed by the nC_{17}/nC_{27} ratios which range from 5.39 to 19.82 and shows the predominance of nC_{17} alkanes. The general unimodal *n*-alkane distributions in the bitumens indicate derivation from similar organic matter types showing that they are genetically related. The anoxic to suboxic environmental conditions that prevailed during the deposition of the sediments is revealed by the isoprenoids, Pr/Ph ratios (0.72–1.28). Pristane/nC_{17} and Phytane/nC_{18} range from 0.16 to 0.33 and 0.22 to 0.56, revealing that the bitumens were from predominantly marine organic matter (type II kerogen) preserved in a reducing environment with no evidence of biodegradation. However, the Ph/nC_{18} ratio and the cross plot of Pr+Ph/nC_{17}+nC_{18} allow the classification of the bitumens into two subfamilies/groups (A and B). The bitumen samples have low wax content as indicated by the degree of waxiness ranging from 0.21 to 0.38 which confirms low terrigenous input. Based on the carbon preference index (CPI: 0.92 to 1.55) and odd-even predominance (OEP: 0.70 to 1.36), it is concluded that the bitumens are immature to marginally mature.

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1. Introduction

Genetic relationships of biodegraded oils are hindered by the depletion of the aliphatic and aromatic fractions commonly used in correlation due to severe biodegradation. The maltene fractions in such oils often lack original geochemical information if the analysis is based on the free biodegraded biomarkers (Peters et al., 2005). Abundant biomarkers (aliphatic and aromatic hydrocarbons) have been reported to be contained in the asphaltene fractions of such oils, and are covalently bound to the asphaltene (Ekweozor, 1986; del Rio et al., 1995; Sonibare et al., 2009). This asphaltene is very important in understanding the genetic history of hydrocarbons.

The macromolecular compounds (asphaltenes) with a structure very close to that of kerogen of the same sample are small in size and have less condensed aromatic nuclei which are often interpreted as kerogen moieties, resulting from its early evolution. Thermal evolution (pyrolysis) of asphaltenes can generate compounds; especially hydrocarbons, of the same type and distribution as kerogen (Behar et al., 1984). These bound biomarkers from asphaltenes have characteristics of the initial oils and are very useful in source or genetic research (Rubinstein et al., 1979; van Graas, 1986). Also, the products are found to be effective in correlation studies (oil-oil and oil-source rock correlation). However,

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conventional pyrolysis has been observed to result in the isomerization of biomarker skeleton and thermal cracking (Ekweozor and Strausz, 1983; Russell et al., 2004). Therefore, flash pyrolysis, an open system pyrolysis, which prevents the secondary cracking of the pyrolysates (allows the pyrolysates to avoid the high-temperature region) is a preferred and reliable modern method (Liao et al., 2015; Pan et al., 2017). To answer the genetic questions on the bituminous deposits of the Eastern Dahomey Basin, flash pyrolysis-gas chromatography (Py-GC) was used to produce *n*-alkane fingerprints from asphaltene pyrolysates to enable a reliable correlation of the bitumens in the basin.

2. Geological setting

The Dahomey Basin in Nigeria is one of the West African Pericratonic or margin sag basin.It developed during the rifting and the corresponding opening up of the Gulf of Guinea which occurred in the Late Jurassic to Early Cretaceous (Burke et al., 1971; Whiteman, 1982; Kingston et al., 1983). In the Mid-Late Cretaceous to Paleogene-Neogene times, thermally induced basin subsidence resulting from crustal separation (and the associated thinning) occurred in the basin as the South American and the African plates entered a drift phase. This created accommodation space for the emerging Atlantic Ocean. (Storey, 1995; Akinmosin et al., 2010). The Dahomey Basin is an extensive basin in West Africa starting from southeastern Ghana passing through Togo and Benin Republic to the western limit of the Niger Delta Basin in Nigeria. It consists of Cretaceous to Recent sequences (Nwachukwu and Ekweozor, 1989; Adekeye and Akande, 2010).

The Cretaceous stratigraphy of the Eastern Dahomey Basin (Table 1) is made up of the Abeokuta Group which consists of the Ise, Afowo and Araromi Formations. The Paleogene-Neogene sedimentary sequences belong to Ewekoro, Akinbo, Oshosun, Ilaro and Benin (the coastal plain sands) Formations while the recent alluvium is of Quaternary age (Jones and Hockey, 1964; Omatsola and Adegoke, 1981; Obaje, 2009; Nton and Otoba, 2011). The tar sand occurs in the Afowo Formation which mainly comprises of coarse to medium-grained sandstone. Variable, but thick interbeded shale, siltstone and clay are also present, The Afowo Formation is deposited in transitional to marginal marine environments (Omatsola and Adegoke, 1981; Billman, 1992). The shale of the overlying Maastichtian Araromi Formation capped the tar sand (Enu, 1985).

3. Materials and methods

3.1. Sampling

Tar sand and solid bitumen samples were collected from various outcropping sections within the bitumen belt (Fig. 1) of south-western Nigeria. Additionally, core materials from shallow exploration wells were also sampled for this work. A total of 20 samples consisting of 16 tar sands (8 cores and 8 outcrops) and 4 bitumen samples (seepages) were used for the analyses. From each sample, 100g was collected for laboratory analyses.

3.2. Extraction of bitumen

Aliquots (approximately 25 g) of crushed tar sand samples were set in the cellulose thimbles that have been pre-extracted. These thimbles (containing the samples) were covered with cotton wool and inserted in the Soxtec apparatus. The extraction was done using an azeotropic mixture (125 mL) of distilled DCM/Methanol (93:7, v/v). The thimbles (containing the samples) were immersed in boiling solvent for 2 h and 10 min and at a heater temperature of 125 °C, they were rinsed for 2 h. At a temperature of 20 °C, the solvent was allowed to drain from the samples for 20 min with a total run time of 4 h 30 min. The extraction process was performed 3 times on each sample because of the high organic matter content. This ensures the total extraction of organic matter, with the total time per sample extraction being 13 h and 30 min.

3.3. Separation of bitumen extracts into maltenes and asphaltenes

The bitumen extract (~50 mg), was weighed into an Iatroscan vial, 9 mL of cold n-hexane was added and the vial was sealed with a crimping tool. The content of the vial was shaken before sonicating in a sonic bath for about 4 min. The vial was transferred into a refrigerator set at 4 °C for at least 15 h to allow the asphaltene to precipitate. After precipitation, the vial content was centrifuged at ca. 3000 rpm for 5 min and the seal was removed using the decrimping tool. The maltene fraction (the clear supernatant) was removed carefully with pipette pasture and added to a 100 mL round-bottomed flask. The asphaltenes were washed in 9 mL cold hexane until the supernatant appeared colorless. This is to ensure that the asphaltene is free from biodegraded biomarkers in the maltene fraction.

Table 1
The stratigraphic column of Eastern Dahomey Basin (Adapted and Modified from various authors).

Author	Jones and Hockey (1964)		Omatsola and Adegoke (1981)		Agagu (1985)		
Period	**Age**	**Formation**	**Age**	**Formation**	**Age**	**Formation**	
Quaternary	Recent	Alluvium			Recent	Alluvium	
Tertiary	Pleistocene- Oligocene	Coastal plain sand	Pleistocene- Oligocene	Coastal plain sand	Pleistocene- Oligocene	Coastal plain sand	
	Eocene	Ilaro	Eocene	Ilaro	Eocene	Ilaro	
	Paleocene	Ewekoro	Eocene	Oshosun	Eocene	Oshosun	
			Paleocene – Eocene	Akinbo	Paleocene – Eocene	Akinbo	
			Paleocene – Eocene	Ewekoro	Paleocene – Eocene	Ewekoro	
Cretaceous	Late Senonian	Abeokuta Formation	Maastrichtian - Paleocene	Araromi	Maastrichtian - Neocomian	Araromi	Abeokuta Group
			Turonian – Maastrichtian	Afowo		Afowo	
			Albian	Ise		Ise	
	Precambrian Crystalline Basement Rocks						

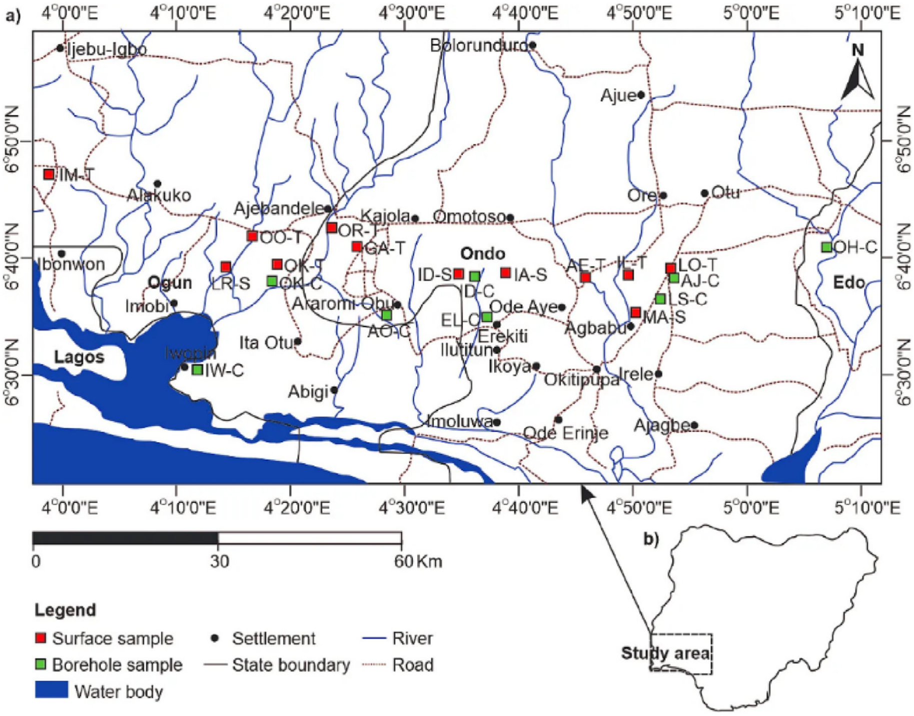

Fig. 1. a) Location map of the study area showing the drainage systems and road networks with marked sampling points. b) Inset map of Nigeria showing the location of the study area.

3.4. Pyrolysis-gas chromatography (Py-GC)

The sample aliquot (asphaltene: 1 mg) was put in the combustion cup and pyrolyzed using a Single Shot Frontier Pyrolizer (3030s) that is coupled to an Agilent gas chromatography (GC). The sample was pyrolyzed for 20 s in the furnace at a temperature of 610 °C while the interface temperature was set to 300 °C. The generated gas from the pyrolysis passed into the GC equipment (Agilent 7890A) where the analysis of the asphaltene pyrolysate was performed. The temperature of the GC equipment was programmed from 40 to-310 °C at 4 °C/min and was held at the final temperature for 20 min. The carrier gas (helium) was set to a flow rate of 1 ml/min and the inlet pressure was kept at 50 kPa and the rate of splitting was 30 ml/min. An Agilent fused silica capillary column (60 m × 0.25 mm i.d) coated with 0.25 μm of 5% phenylmethylpolysiloxane (HP-1MS) phase was used for the separation. AgilentChemStation software was used for data acquisition and processing.

4. Results and discussion

4.1. n-Alkane distributions

The representative gas chromatographic fingerprints of the asphaltene pyrolysates are presented in Fig. 2. The distributions are characterized by well-preserved *n*-alkane biomarkers and some *n*-alkenes, appearing with their corresponding *n*-alkanes from the asphaltene pyrolysates. They displayed *n*-alkanes between nC_9-nC_{32} and isoprenoids pristane (Pr) and phytane (Ph) peaks having maximum peaks ranging from nC_{12}-nC_{16}, maximizing at nC_{14}. They are predominantly low to medium molecular weight *n*-alkanes and a low concentration of high molecular weight *n*-alkanes. The *n*-alkane peaks generally show a sharp decline from nC_{21} to nC_{32}. This pattern of distribution suggests a limited contribution of higher plants to the source rock from which the bitumen was generated. However, the abundance of the low molecular weight *n*-alkanes is suggestive of marine organic matter with algae and planktonic inputs (El Nady et al., 2014; Pan et al., 2017). Generally, a similar unimodal hydrocarbon distribution was observed in all the samples. These unimodal *n*-alkane distributions which are dominated by *n*-alkanes with relatively low to moderate carbon numbers suggest that the bitumens were derived from similar types of organic matter and indicate an abundance of algal organic matter with some terrigenous input (Rodriguez and Philip, 2015). The observed uniformity in the distribution pattern suggests that the bitumens are genetically related (Peters et al., 2005). The relative abundance of microbial and algal against higher plants organic matter contributions (Esegbue et al., 2020) indicated by nC_{17}/nC_{27} ratios range from 5.39 to 19.82 showing the dominance of nC_{17} which supports a source rock that received a greater contribution of algal (marine) organic matter. However, one of the core samples (LS-C) has a significantly high nC_{17}/nC_{27} ratio of 19.82 which suggests that the concentration of marine organic matter received by its source rock is more than that received by the other samples.

4.2. Pristane/Phytane ratio

The redox conditions of depositional environments are usually determined by the relative abundance of acyclic isoprenoids, pristane and phytane (Al-Khafaji et al., 2017). Phytane occurs in a relatively higher concentration in most of the studied samples than pristane resulting in Pr/Ph ratios that varies from 0.72 to 1.28 (Table 2). This suggests that the source rocks were deposited under anoxic to suboxic conditions (Njoku et al., 2021), and the organic matter sources are marine and terrigenous. Pr/Ph ratios < 1 are indicative of anoxic (or hypersaline) depositional environment conditions (Anyanwu et al., 2021) while values between 1 and 3 is common in sediments deposited under suboxic conditions (Akinlua et al., 2020). Pr/Ph ratios also reflect the nature of the contributing organic matter. However, this ratio increases with thermal

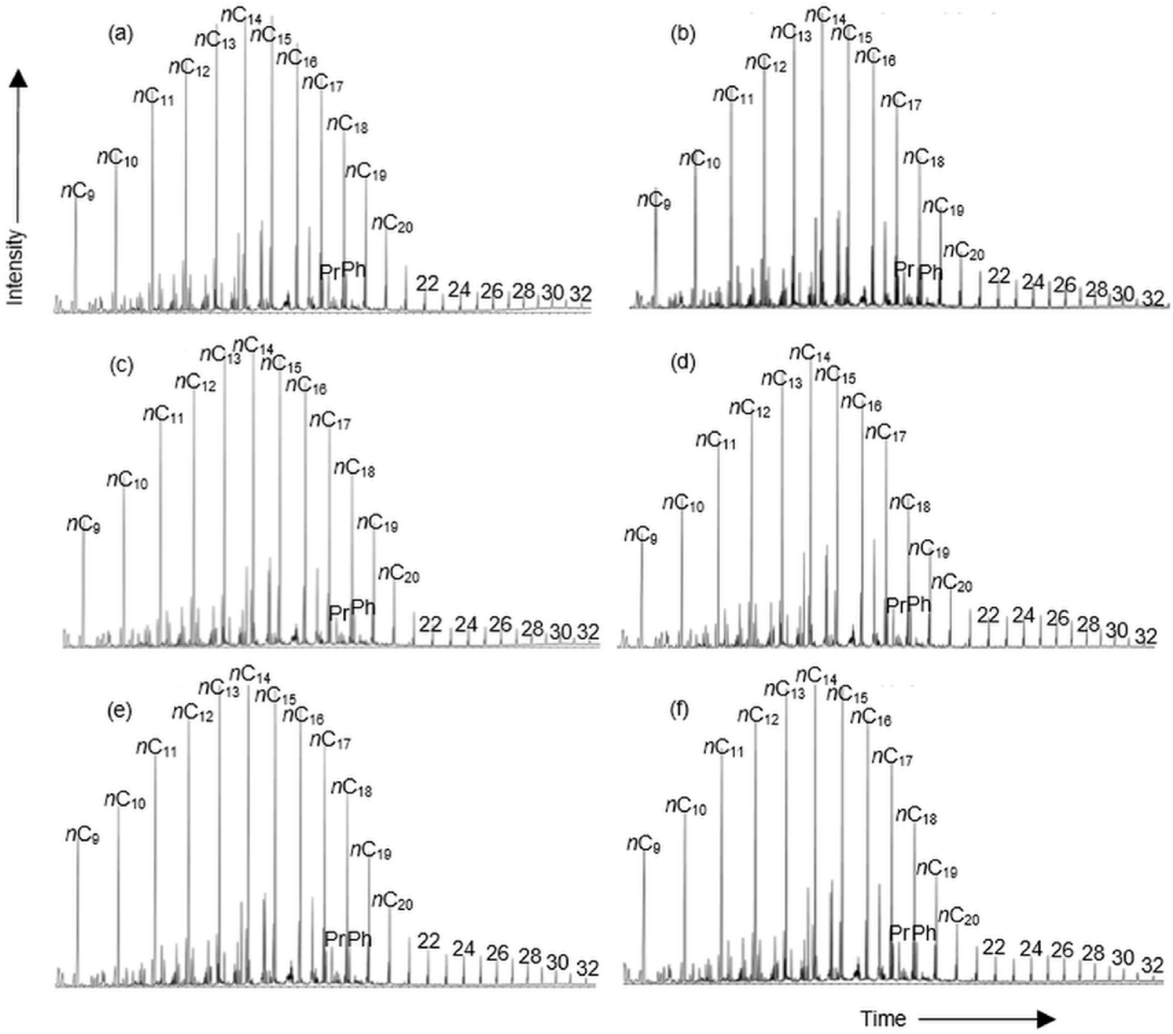

Fig. 2. Representative gas chromatographic fingerprints (m/z 85) of the bitumen asphaltene pyrolysates showing similarity in distribution patterns in the outcrop samples (a, b; sample numbers LO-T and IL-T), core samples (c, d; sample numbers LS-C and ID-C), and seepage samples (e, f; sample numbers MA-S and IA-S). Note: Numbers 9, 10, 11 etc represents nC_9, nC_{10}, nC_{11} etc; Pr = Pristane; Ph = Phytane.

Table 2

n-Alkane and isoprenoid parameters obtained from asphaltene pyrolysates. Pr/Ph is the ratio of Pristane to Phytane; Pr/nC_{17} is the ratio of Pristane to nC_{17}; Ph/nC_{18} is the ratio of Phytane to nC_{18}; the degree of waxiness was calculated as $\sum(nC_{21}\text{-}nC_{31})/\sum(nC_{15}\text{-}nC_{20})$; the carbon preference index (CPI) = $[2(nC_{23}+nC_{25}+nC_{27}+nC_{29})/(nC_{22}+2(nC_{24}+nC_{26}+nC_{28})+nC_{30})]$; improved odd-even predominance (OEP) = $nC_{27}+6nC_{29}+nC_{31}/\ 4nC_{28}+4nC_{30}$.

S/N	Sample Identity	Location	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	nC_{17}/nC_{27}	Pr+Ph/$nC_{17}+nC_{18}$	Degree of waxiness	CPI	OEP
1	LO-T	Loda	0.93	0.21	0.29	7.51	0.25	0.24	1.10	0.98
2	IL-T	Ilubinrin	0.95	0.21	0.31	9.99	0.25	0.29	1.05	1.02
3	AE-T	Akindolu Emaye	1.20	0.25	0.32	8.31	0.28	0.32	1.01	1.10
4	GA-T	Gbegude Akinola	0.81	0.32	0.56	5.75	0.42	0.32	0.92	0.71
5	OK-T	Onikitibi	0.96	0.30	0.36	6.05	0.33	0.28	1.11	1.03
6	OR-T	Orisunbare	0.94	0.28	0.44	5.56	0.35	0.35	1.02	0.80
7	OO-T	Oke Oyinbo	1.02	0.33	0.48	7.60	0.39	0.28	1.12	1.12
8	IM-T	Imeri	0.99	0.25	0.31	9.88	0.28	0.25	0.94	0.97
9	LS-C	Ludasa	1.28	0.23	0.25	19.82	0.24	0.23	0.94	1.09
10	AO-C	Araromi Obu	0.93	0.29	0.46	6.50	0.35	0.30	1.21	0.95
11	ID-C	Idobilayo	0.90	0.27	0.44	5.45	0.34	0.35	1.55	1.34
12	IW-C	Iwopin	0.81	0.25	0.52	5.36	0.35	0.38	1.29	1.15
13	OK-C	Onikitibi	1.02	0.33	0.47	6.27	0.39	0.29	1.12	1.26
14	EL-C	Erekiti Luwoye	0.96	0.22	0.34	10.88	0.27	0.21	1.16	0.89
15	AJ-C	Ajana Ejidokun	0.77	0.16	0.28	7.96	0.21	0.25	0.96	0.92
16	OH—C	Ohosu	1.12	0.16	0.22	6.65	0.18	0.27	1.07	1.16
17	MA-S	Mile 2 Agbabu	0.90	0.19	0.28	5.74	0.23	0.28	0.96	1.12
18	IA-S	Ijoke Ago-Titun	1.07	0.23	0.29	6.24	0.25	0.32	1.10	1.36
19	ID-S	Idobilayo	0.72	0.16	0.30	6.16	0.22	0.29	1.07	1.11
20	LR-S	Loore	0.87	0.26	0.44	6.81	0.33	0.31	1.05	0.97

maturation (Peters et al., 2005). A high Pr/Ph ratio (>3) reflects oxic conditions often associated with terrigenous organic matter input, while low values (<0.8) commonly indicate anoxic in hypersaline or carbonate environments (El Diasty and Moldowan, 2012). Samples having Pr/Ph ratios < 1are derived from strongly reducing (anoxic) conditions while those with ratios > 1 are deposited in less reducing (suboxic) conditions. No significant trend occurs in the Pr/Ph ratios across the bitumen belt. However, the low variations in Pr/Ph ratios of these samples also suggest a genetic relationship between the bitumens.

4.3. Isoprenoids/n-alkane ratios

The *n*-alkane distributions showed lower amounts of acyclic isoprenoids compared to *n*-alkanes (Fig. 2) resulting in significantly low Pristane/nC_{17} (0.16–0.33) and Phytane/nC_{18} (0.22–0.56) ratios. Marine organic matter sources (mainly algae) deposited under reducing environments are interpreted based on the low Pristane/nC_{17} and Phytane/nC_{18} ratios in the samples (El Nady et al., 2014). These ratios also expressed a close genetic relationship between the studied bitumen. The cross plot of Ph/nC_{18} and Pr/nC_{17} shows that all the studied bitumen asphaltene pyrolysates are derived from marine source rocks with dominantly type II kerogen (Wu et al., 2020) preserved in a reducing environment with low maturity levels (Fig. 3). This is consistent with anoxic to suboxic depositional environment conditions inferred from Pr/Ph ratios.

4.4. Oil family/group

Isoprenoids and isoprenoid/*n*-alkane ratios are effective parameters used for the genetic classification of oils into families (El Diasty and Moldowan, 2012). The cross plot of Pr/nC_{17} and Ph/nC_{18} classified the bitumens as one genetic family, being derived from a similar organic matter type (marine algal Type II) in reducing environmental condition (Fig. 3). However, with the Ph/nC_{18} ratio the bitumen samples have been grouped into two subfamilies. The samples in subfamily A have Ph/nC_{18} ratios varying from 0.22 to 0.34 reflecting higher thermal maturity while the bitumen samples in subfamily B reflect lower thermal maturity with Ph/nC_{18} ratios varying from 0.36 to 0.56. Similarly, the cross plot of Pr/Ph and Pr+Ph/nC_{17}+nC_{18} also classified the bitumens into two groups based on low and moderate Pr+Ph/nC_{17}+nC_{18} ratio values (Fig. 4).

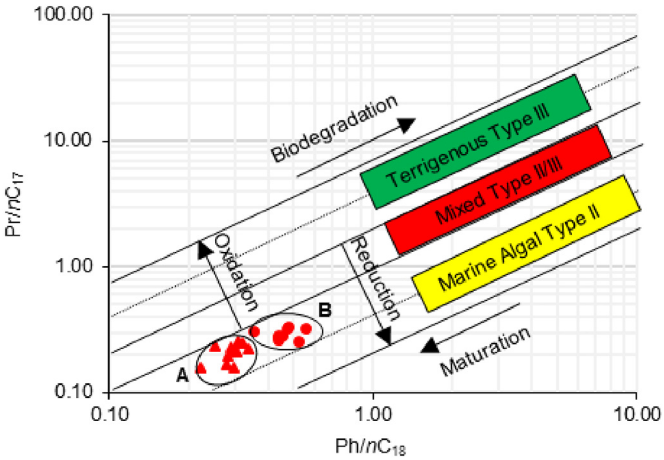

Fig. 3. Cross-plot of Ph/nC_{18} versus Pr/nC_{17} ratios showing depositional environment conditions, type of organic matter inputs, maturation and biodegradation alterations for the asphaltene pyrolysate. Subfamily A have Ph/nC_{18} ratios (0.22–0.34) and higher maturity while subfamily B have Ph/nC_{18} ratios (0.36–0.56) and lower maturiry (After Anyanwu et al., 2021).

4.5. Biodegradation

The distribution of the biomarkers from gas chromatograms revealed well-preserved *n*-alkanes and isoprenoids (Fig. 2). Based on Peters and Moldowan (1993) biodegradation model, this indicates low degrees of biodegradation. Biodegraded oils are recognized by their Pr/nC_{17} and Ph/nC_{18} ratios. These ratios for all samples (<1) indicate no or low levels of biodegradation (Barakat et al., 2018). Also, the cross plot of Pr/nC_{17} and Ph/nC_{18} ratios show no evidence of biodegradation (Fig. 3). Thus, the biomarkers in asphaltenes extracted from the bitumen samples are interpreted as the remnants of the original oils locked up in the asphaltene aromatic rings by covalent bonds before the beginning of biodegradation (Sonibare et al., 2009; Pan et al., 2017).

4.6. Degree of waxiness

The degree of waxiness of the bitumen samples ranges from 0.21 to 0.38 suggesting low wax content (Table 2). A high abundance of nC_9 to nC_{20} n-alkanes was observed in the samples compared to nC_{21+} n-alkanes (Fig. 2). This supports the low waxy contributions in the samples. In recent studies, the classification of oil by source input is largely dependent on the degree of waxiness as an environmental source input parameter (Barakat et al., 2018). The cross plot of the degree of waxiness versus Pr/Ph ratios (Fig. 5) revealed that the bitumens were generated from marine organic matter under a reducing condition in a marine setting.

4.7. Carbon preference index (CPI)

The calculated carbon preference index (CPI) values of the asphaltene pyrolysates based on the expression of Peters and Moldowan (1993) range from 0.92 to 1.55 and odd-even predominance (OEP) based on Scalan and Smith (1970) ranges from 0.70 to 1.36 (Table 2). This range of values suggests immature to marginally mature. While high CPI values (above 1.5) always refer to relatively immature samples, low CPI values could either indicate higher maturity or a lack of higher n-alkanes stemming from terrestrial input (Tissot and Welte, 1984). The depositional condition is said to be reducing if the CPI value is less than 1.0 (Meyers and Snowdon, 1993).

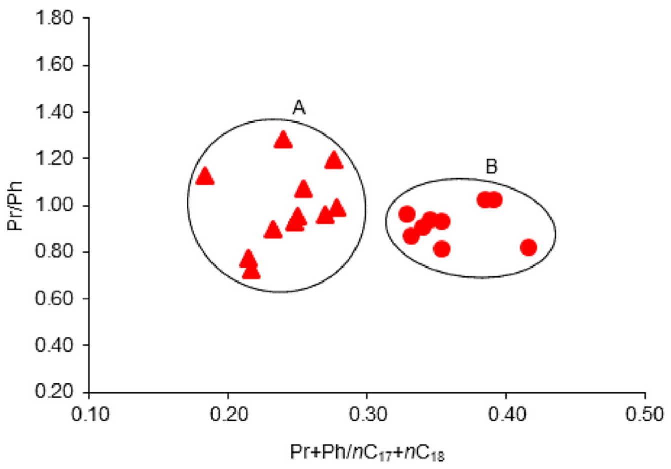

Fig. 4. Cross plot of Pr/Ph versus Pr+Ph/nC_{17}+ nC_{18} ratios separates the bitumen samples into two distinct groups, A and B (After Ndukwe et al., 2015).

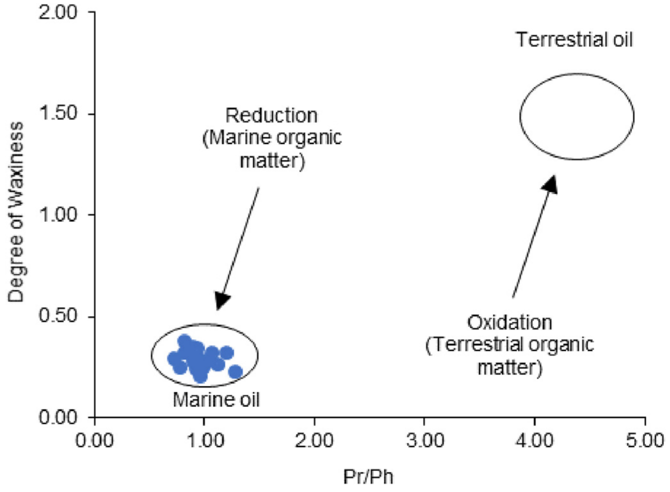

Fig. 5. Cross plot of pristane/phytane(Pr/Ph) versus degree of waxiness of the *n*-alkane from the asphaltene pyrolysates showing the depositional conditions and the organic matter source input (After El Nady et al., 2014).

The thermally immature sample is indicated by CPI or OEP values significantly above or below 1.0. Values of 1.0 suggest, but do not establish that a sample is thermally mature (Peters and Moldowan, 1993). The cross-plot of CPI versus Pr/Ph ratios (Fig. 6) generally indicates that the bitumens are at different levels of thermal maturation (immature to marginally mature) and were generated from organic matter in reducing anoxic to suboxic conditions.

4.8. Depositional environment of source rock

The source rock characteristics commonly used to distinguish the depositional environments are the type of organic matter input, the redox conditions, rock type, and age. Though the bitumen belongs to one family, yet, the oil grouping revealed some variations with few overlaps that characterizes the depositional environment of the source rocks in the identified group A and B. Despite the fact that marine organic matter constitutes the dominant input in all samples (Fig. 5), the nC_{17}/nC_{27} ratios and degree of waxiness revealed that subfamily A with nC_{17}/nC_{27} ratios of 5.74–19.82 and degree of waxiness values of 0.21–0.32 has higher marine organic matter inputs and lower terrigenous organic matter inputs. On the other hand, subfamily B with nC_{17}/nC_{27} ratios of 5.36–6.81 and degree of waxiness between 0.28 and 0.38 has lower marine organic matter inputs and higher terrigenous organic matter inputs. The redox condition indicators, Pr/Ph values of subfamily A range from 0.72 to 1.28 while that of subfamily B range from 0.81 to 1.02. This suggests that the depositional condition of subfamily B is more strongly reducing than subfamily A. The presence of plant-derived organic matter indicates that the sediments that generated the initial oils are of Cretaceous or younger age Moldowan et al. (1994); El Diasty and Moldowan (2012).

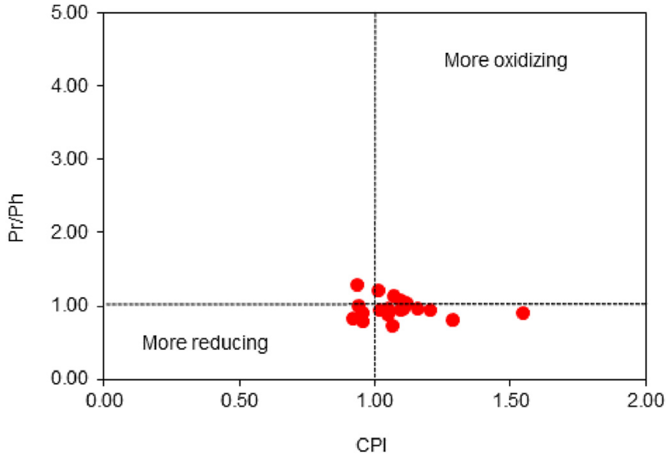

Fig. 6. The cross-plot of CPI versus Pr/Ph ratios shows maturity relative to the environment of deposition conditions of the studied bitumen (After Adegoke et al., 2014).

4.9. Oil-Source rock correlation

The biomarker parameters from the analysis of the asphaltene pyrolysates (subsections 4.1 to 4.7) indicate that the bitumens were generated from marine source rocks with predominantly marine organic matter deposited in anoxic to suboxic reducing conditions. The thermal maturity has been interpreted to be immature to marginally mature. Based on the organic matter type, paleo-redox and paleoenvironmental interpretations, and thermal maturity of the studied samples, it is therefore believed that the bitumen was sourced from the underlying Cenomanian-Turonian shales in the basin. The Cenomanian-Turonian sediments have been reported to contain a significant amount of total organic carbon (TOC) and hydrogen index (HI) of up to 1.9 wt% and 560 mgHC/gTOC respectively with type II and type III organic matter (Adeoye et al., 2020). Also, the thermal maturity indices of Adeoye et al. (2020) (with present-day thermal maturity of 0.95%VR_o) indicates that the Cenomanian source rock represents the most matured bed in the basin while the Turonian shales are a little less matured. Predominantly, the Cenomanian-Turonian source rock in the onshore section of the basin has been reported to be immature to marginally matured while the deeper parts and the offshore sections of the basin host matured source rocks with predominantly marine Type II kerogen. The Tertiary source rocks in the basin are also predominantly immature to marginally matured and hold low potential for hydrocarbon generation at present (Adekeye and Akande, 2010; Nton and Otoba, 2011; Ogala et al., 2019; Adeoye et al., 2020).

5. Conclusions

The distributions of bound *n*-alkane biomarkers obtained from the flash pyrolysis of asphaltene fractions in the bitumen of Eastern Dahomey Basin revealed a predominance of *n*-alkanes with low to medium molecular weight and a low concentration of high molecular weight *n*-alkanes suggesting an abundance of marine organic matter contribution to the source rocks. The general unimodal pattern of distributions suggests genetic relationship and derivation from similar organic matter types. Isoprenoid ratios (Pr/Ph ratios) suggest deposition under anoxic to suboxic conditions while isoprenoids/*n*-alkane ratios (Pr/nC_{17} and Ph/nC_{18} ratios) indicate derivation from marine organic matter (type II kerogen) in a reducing environment. Ph/nC_{18} ratio and the cross plot of $Pr+Ph/nC_{17}+nC_{18}$ classified the bitumens into two subfamilies/groups, A and B. Low wax content is interpreted from the degree of waxiness of the bitumens which supports low terrigenous inputs. Maturity deductions from the carbon preference index and odd-even predominance indicate that the bitumens are immature to marginally mature and derived from varying reducing conditions. All *n*-alkane and isoprenoid parameters from the studied bitumens support predominantly marine organic matter and source rock-derived oils. The study has proven that bound biomarkers released from asphaltenes by flash-pyrolysis are reliable sources of geochemical information for understanding the genetic relationship of biodegraded bitumens.

Declaration of interest

The authors declare that they have no known conflict of financial interests or personal relationships that could have appeared to influence the work reported in this article.

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