ORIGINAL PAPER-EXPLORATION GEOLOGY

Organic geochemical evaluation of crude oils from some producing fields in the Niger Delta basin, Nigeria

Mudiaga Chukunedum Onojake[1,2] · Nsikan Edet Nkanta[1] · Joseph Onyekwelu Osakwe[3] ·
David Akpoebi Akpuluma[4] · Ikponmwosa Ohenhen[5] · Leo Chigbu Osuji[1,2]

Abstract

Geochemical and biomarker characteristics of representative crude oil samples from selected fields in southern Nigeria were evaluated to determine the organic matter input, origin of biological material, depositional environment, thermal maturity, and genetic relationship between the oils. Four crude oil samples were obtained from various oil producing fields from Delta, Bayelsa and Abia state in southern Nigeria and labeled Kwale (KW), Kolo creek (KLC), Owaza (OWA1 and OWA2). The crude oil samples were fractionated into saturates, aromatic hydrocarbons and polar compounds using column chromatography on silica gel thereafter, analyzed using Gas chromatography-mass spectrometry (GC–MS). The calculated ratios of normal alkanes, acyclic isoprenoids, carbon preference index (CPI), hopanes, and steranes showed the following results: Pr/Ph (0.34 to 0.89); C_{29}/C_{27} (0.78 to 1.25); $20S/(20S+20R)C_{29}$sterane (0.28 to 0.66); $22S/(22S+22R)$ C_{32} homohopane (0.17 to 0.23); CPI (0.96 to 0.98); $Ts/Ts+Tm$ (0.46 to 0.50); and sterane/hopane (0.16 to 0.87). The results obtained were used to correlate the crude oils with respect to depositional environment, thermal maturity, and organic matter source. The Pr/Ph ratios of KW and KLC were less than one, and the cross-plot of Pr/nC17 versus Ph/nC18 of KW and KLC suggested that the oils were deposited under anoxic environments, whereas OWA1 and OWA2 indicated oxic conditions with no biodegradation. From the calculated ratios of 22S $(22S+20R)C_{32}$ homohopane and CPI, the oils were mature and had entered the generating window. Sample OWA1 is the most mature, while KLC is the least mature. The calculated ratios also showed that the four oil samples were from a shale source rock with both terrestrial and marine inputs.

Keywords Biomarkers · Genetic · Families · Oxic · Hydrocarbons · Niger Delta

Introduction

The hydrocarbon-producing region of Nigeria is the Niger Delta, which is located on West Africa's Atlantic coast and comprises roughly 75,000 km^2 with a projected estimate of crude oil and natural gas volumes of 37 billion barrels and 256 trillion cubic feet. The area is predicted to be one of the most productive hydrocarbon-producing basins in the world (EIA 2015). The southern region is recognized for its wealth of hydrocarbon resources and is presently the only basin that houses commercial quantities of petroleum resources in Nigeria. It contains a siliciclastic fill with an average thickness of 9000–12,000 m and covers around 75,000 km^2. The region's main operational petroleum system is the tertiary Niger Delta. The Niger Delta basin's geology comprises principal geologic formations such as Agbada, Akata, and Benin (Abrakasa et al. 2016). The region's depobelt is the biggest regressive delta, comprising 300,000 km^2, with a sediment capacity of 500,000 km^3 and a sedimentary

✉ Mudiaga Chukunedum Onojake
    ononed@yahoo.com; mudiaga.onojake@uniport.edu.ng

1   Department of Pure and Industrial Chemistry, University
    of Port Harcourt, P.M.B 5323, Choba, Port Harcourt, Nigeria

2   World Bank Africa Centre of Excellence for Oilfield
    Chemicals Research, University of Port Harcourt, P.M.B
    5323, Choba, Port Harcourt, Nigeria

3   Quality Assurance/Quality Control Laboratory, Notore
    Chemical Industries PLC, Onne, Rivers State, Nigeria

4   School of Nuclear Science and Engineering, National
    Research Tomsk Polytechnic University, Tomsk, Russia

5   Department of Petroleum Engineering, University of Benin,
    Ugbowo, P.M.B. 1154, Benin City, Edo State, Nigeria

layer of more than ten kilometers in the basin's depocenter (Kaplan et al. 1994; Kulke and Zantop 1995). The research area's boundary is identical to that of southern Nigeria's geology and south-western Cameroon, with a boundary to the north similar to that of the Benin border. Outliers of the Cretaceous on the Abakaliki high are marked by the Cretaceous on the Calabar border, an axis line bordered by the Precambrian (Tuttle et al. 1999).

Benin, Agbada, and Akata are the three major formations composed of rivers, coastal sandstones, interbedded sandstones and shales deposited in a transitional to marine environment, with huge marine shales. The Niger Delta basin has six to seven depobelts, which correlate to different periods of the delta's evolutionary history, beginning in the north (northern delta) and ending offshore. Individually, the depobelt is a self-contained entity in terms of sedimentation, structural deformation, hydrocarbon production and accumulation (Evamy et al. 1978; Faboya et al. 2018).

The petroleum system research studies the production, movement, accumulation, and entrapment of hydrocarbons (Magoon and Schmoker 2000). The most common method for analyzing the petroleum system in a particular area is to estimate the quantity of accumulated hydrocarbons in the prospect, the composition of its source rock, and the degree of thermal maturity of all organic elements (Aladwani 2021). The Niger Delta's petroleum system remains unclear despite extensive oil exploration and production operations in the region. Hydrocarbons typically exist in many productive strata at various depths within the basin, raising the question of whether the hydrocarbons are from the same source. Several source rock organofacies are suggested based on the distributions of light hydrocarbons and biomarker characteristics such as the oleanane/hopane ratio (Eneogwe and Ekundayo 2003). Based on the existence of pentacyclic triterpane skeletons of hopane and oleanane, as well as C_{27}–C_{29} steranes in oil, the researchers revealed three unique families of Nigerian crude oil gathered from the Niger Delta depobelts. Sonibare et al. (2008) discovered that the oils were derived from both marine and terrestrial sources. Eneogwe and Ekundayo (2003) further determined the hydrocarbon route in the basin using maturity characteristics in the oils they analyzed. They concluded that as one proceeds from onshore to offshore, oil maturity decreases, indicating that either offshore oil was formed by younger source rocks or that first-generated oil from older sources moved largely to offshore areas.

Due to the possibility of investigating the diagenetic evolution pathways of chemical compounds, biomarkers can be used to describe organic matter's origin and maturity, as well as the paleoenvironmental conditions (Peters et al. 2005). Biomarkers were extensively used to describe the organic matter's origin and paleoenvironmental conditions within the lower and middle Jurassic strata from the epicontinental seas located in the Central European Basin System area (Ruebsam et al. 2020; Zakrzewski and Kosakowski 2021). Biomarkers are complex biological molecules formed from living organisms in oil that contain information about the oil. They are mostly derived from biological organisms that have been preserved over time (Hancok et al. 2013). These compounds are also known as genetic markers because they contain information on thermal history (maturity), the source of organic matter, and the paleoenvironmental deposition of the oils (Adedosu and Sonibare 2005).

This research was designed to examine and evaluate the distribution of biomarkers in selected crude oils from southern Nigerian producing fields in order to add to preceding research information on the organic matter origin, thermal maturity, and paleoenvironmental deposition of the crude oils based on information from geochemical evaluation from gas chromatography-mass spectrometry (GC–MS) analysis. The maturity status of oil from the southern region of the basin must be determined in order to gain a better understanding of the basin's petroleum system.

Geologic settings of study area

The geology of the research area, which is that of southern Nigeria, defines the Niger Delta basin's onshore regions and, in turn, the province's offshore boundaries to the eastern boundary of the Dahomey basin (Reijers 2011). It lies in the Gulf of Guinea (Fig. 1) and has three geologic formations: Benin, Agbada, and Akata (Haack et al. 2002).

The tertiary petroleum system, also known as the Akata-Agbada petroleum system, was established as the petroleum system of the Niger Delta (Fig. 2a, b). The Benin, Agbada, and Akata formations represent the three lithostratigraphic units, or formations, that make-up the basin of the region (Short and Stauble 1967; Doust and Omatsola 1990; Onojake et al. 2015). Benin (Oligocene), the youngest formation, is built of sandstone in a river and coastal environment, and under it is the Agbada (Eocene), which is made of interbedded sandstone and shale deposited in a transitional to marine environment. This formation's sandstone reservoir produces crude oil, and the Paleocene Akata formation is made up of a paralic sequence of interblended sands and large marine shales (Weber et al. 1978). The Agbada and Akata formations are prospective sources of crude oil in the Niger Delta region (Ekweozor and Daukoru 1994). The basin is categorized into 6–7 east–west bound units that correspond to depobelts.

Stratigraphic column of the study area

The Niger Delta, which covers Southern Nigeria, is made up of three major strata that contribute petroleum habitat: the Akata, Agbada, and Benin formations. The
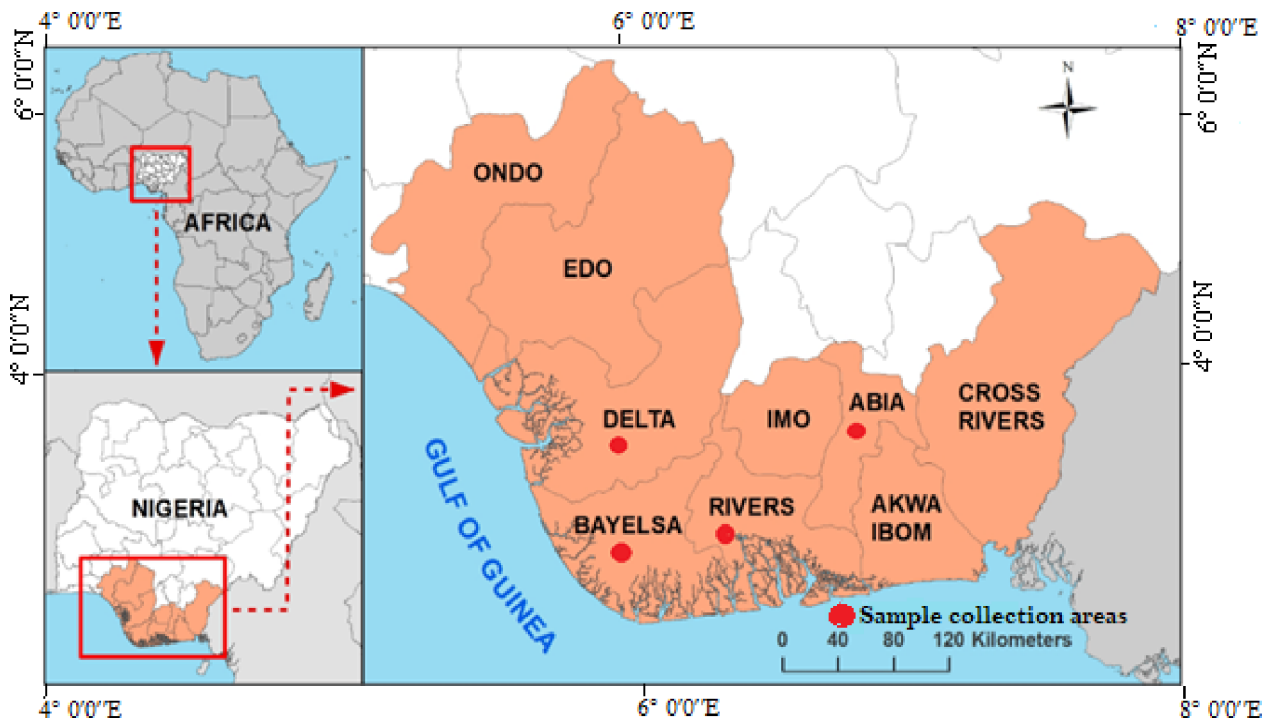
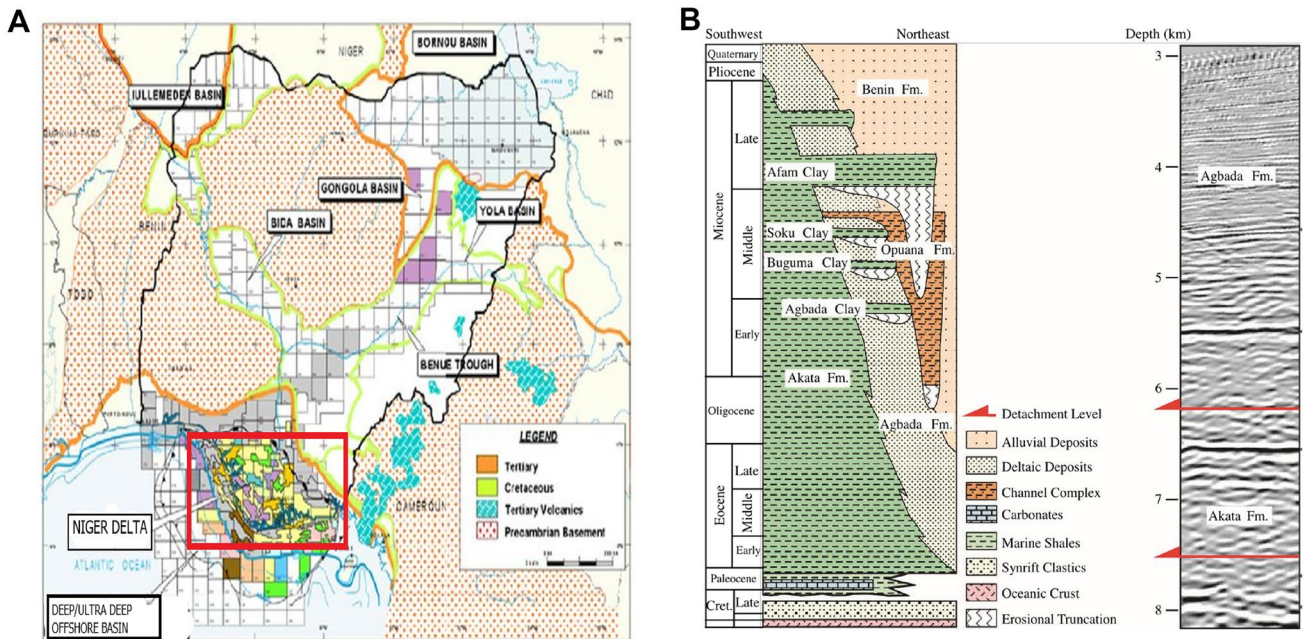**Fig. 1** Map of study area showing sample locations in the Niger Delta Nigeria

Fig. 2 **a** Geological map and sedimentary basins of Nigeria. **b** Description of the regional stratigraphy of the Niger Delta basin and the variable density-seismic display of the major stratigraphic sections (Corredor et al. 2005)

first formation (Akata) is a marine-derived structure found at the delta's base. Furthermore, it extends from the Paleocene to the Recent, has tremendous pressure, and is beneath the delta. It comprises thick shale structures:

prospective source rocks, marine sedimentary sand, deep water reservoirs, and a trace of clay and silt (Fig. 2a, b). Akata formation is associated with a low energy condition and a lack of oxygen, which were formed in low stands

when terrestrial organic matter compositions and clays were conveyed to deep water regions (Stacher 1995).

The projected thickness of the formation, according to Doust and Omotsola (1990), is about 7000 m. The second formation (Agbada) is the main petroleum-bearing block, which is composed of sand and shale and dates from the Eocene to the Recent. The formation comprises paralic siliciclastic that is almost 3700 m thick and constitutes the deltaic section of the series. Shale and sandstone layers were generated in almost equal amounts in the lower Agbada formation. The upper region, on the other hand, is mostly sand with occasional shale interbeds. The Benin formation, which follows the Agbada formation, is a late Eocene to recent continental deposit of sedimentary and high coastal plain sands up to 2000 miters thick (Avbovbo 1978). The upper Benin formations consist of freshwater-bearing, continental rocks. The upper Benin formations consist of freshwater-bearing, continental sand, and gravel stone. From the late Eocene to the recent, the formation is a continental deposit of sedimentary and upper littoral plain sands with a thickness of up to 2000 m (Smith-Rouch 2006). Tectonic traps created during the stratigraphic deformation of the Agbada formation and geological traps formed preferentially along the delta border are the most notable reservoir formations in the study region (Niger Delta) (Beka and Oti 1995).

Materials and method

Sample collection and preparation

Four crude oil samples were obtained from three different oil fields in three different southern states of Nigeria, namely: Delta, Bayelsa, and Abia, respectively, in Teflon-caped glass vials and labeled as Kwale (KW), Kolo creek (KLC), Owaza (OWA1 and OWA2). Figure 1 shows the sample collection areas.

Fractionation of crude oil samples by column chromatography

Each of the oil samples was fractionated using column chromatography with petroleum ether (70 mL) as an eluent for aliphatic constituents and dichloromethane (DCM) (70 mL) as an eluent for aromatic constituents, respectively. The aliphatic fraction was recovered by carefully evaporating the solvent in a sand bath, followed by removal of the excess solvent with nitrogen gas (Farrimond et al. 1996).

Gas chromatography-mass spectroscopy analysis of the aliphatic fraction

The gas chromatography-mass spectrometry (GC–MS) was used to analyze the aliphatic hydrocarbon fraction to observe fragment ions of specific biomarkers with a standard Hewlett-Packard 5890II GC coupled to a split or split-less inlet/injector of 280 °C connected to a HP 5972 MSD (mass spectrometry detector) using a 70 eV electron voltage, a 220 A filament current, and a 160 °C source temperature. The collection of data was monitored by the HP Vectra PC chem station computer in full scan mode (FSM) and selected ion mode (SIM). 1μL of diluted sample was injected into the inlet using the auto-sampler HP 7376 (290 °C) and split open after 1 min. Component separation was achieved on a capillary column (30 m × 0.25 mm ID DB-5) sintered with silica and coated with 0.25 m (film thickness) of 5% phenylmethyl silicone (HP-5). The GC was set to operate at a temperature of 40/50–300 °C at a count of 4 °C per minute and then held for 16.7–20 min. Helium served as the carrier gas, flowing at 1.0 mL/min at 500 Kpa with a slit at 30 mL/min. The data was recorded on a digital audio tape (DAT), and the peak was integrated using the RTE integrator. Figure 3 is a flow chart showing the methodology used in the analysis of crude oils.

Results and discussion

The results of the peak identities calculated from the selected ion modes of the m/z 85, 191, and 217 saturated fractions of KW, KLC, OWA1, and OWA2 are shown in Table 1, 2 and 3, respectively. The chromatograms obtained from the GC–MS revealed that n-alkanes, acyclic isoprenoids, steranes, and terpanes (hopanes) were distributed in the crude oil samples. The peaks were identified, and the areas of the respective peaks were used to obtain values for standard plots of Pr/nC_{17} against Ph/nC_{18} and other cross-plots used for geochemical evaluation of the crude oil.

Parameters calculated from the aliphatic fraction of the samples for area deposition, source, and thermal maturity are shown in Tables 4 and 5, respectively. The chromatograms of m/z 191 and 217 showing the distribution of hopanes and steranes for the oils are shown in Fig. 4A–F.

Thermal maturity

Thermal maturity emphasizes the effects of heat and time on sediment burial with the transformation of kerogen to petroleum due thermal exposure. Thermal maturity has been evaluated using a variety of variables and biomarkers, including vitrinite reflectance data (% Ro), carbon preference index (CPI), pentacyclic triterpenes, and regular
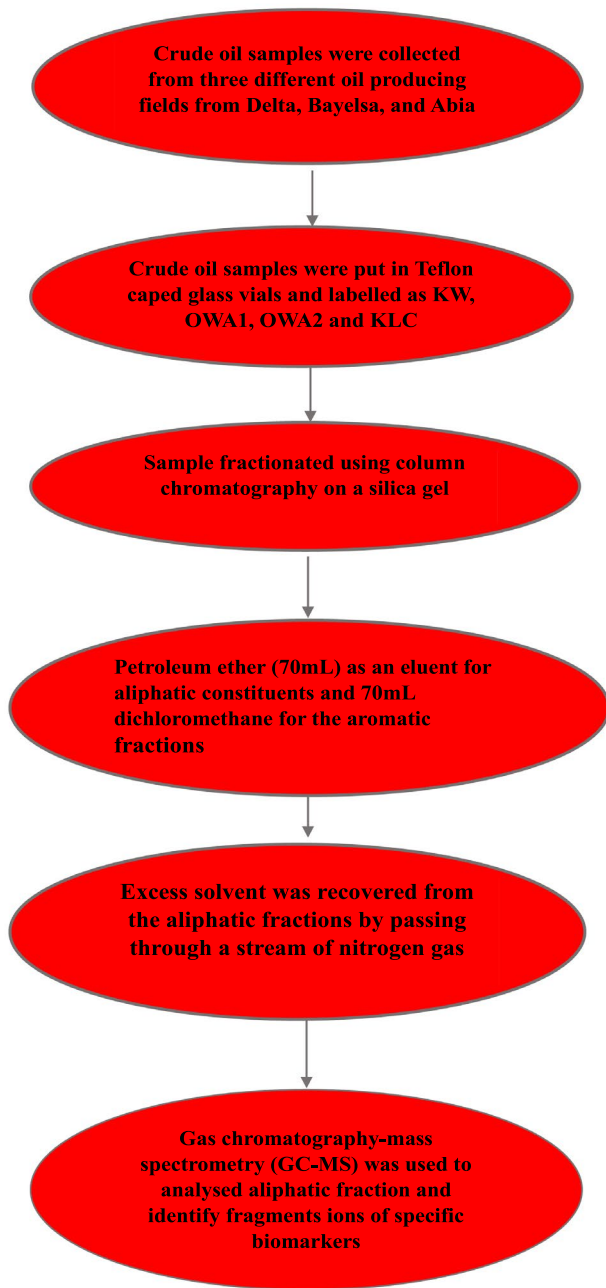
Table 1 Data obtained from GC–MS used in computing n-alkanes and isoprenoids ratios

Cn	KW	KLC	OWA1	OWA2
C3	1,670,666	110,069	–	–
C4	2,822,852	298,700	–	–
C5	3,122,747	341,885	–	–
C6	2,971,074	344,554	–	–
C7	2,889,889	45,110	–	–
C8	1,275,690	466,961	–	–
C9	1,673,797	549,247	–	–
C10	2,840,224	220,166	–	–
C11	2,689,531	613,442	–	147,883
C12	1,340,595	358,711	56,189	384,380
C13	2,997,658	617,991	135,525	470,463
C14	2,773,679	612,511	185,511	174,690
C15	1,697,593	253,321	53,215	391,544
C16	4,110,301	1,023,668	151,383	1,013,297
C17	2,463,408	602,628	178,333	512,007
Pristane	816,858	236,123	179,761	449,253
C18	244,655	77,602	50,247	137,193
Phytane	2,335,963	553,330	201,929	556,368
C19	2,365,921	537,270	223,376	624,727
C20	2,420,253	534,158	250,985	637,427
C21	2,477,457	521,845	54,197	623,817
C22	2,548,147	510,993	248,809	578,890
C23	2,676,416	456,106	238,249	588,881
C24	2,632,386	460,770	229,783	525,583
C25	2,721,862	404,243	198,775	514,883
C26	2,813,177	386,354	189,991	466,480
C27	2,619,060	330,544	168,188	477,634
C28	2,502,444	323,886	161,839	357,844
C29	1,927,895	228,463	121,893	388,470
C30	1,819,839	231,565	129,897	248,641
C31	NIL	137,543	75,375	246,329
C32	NIL	121,646	71,555	135,878
C33	NIL	70,286	38,397	103,738

Fig. 3 Flow chart showing the methodology used in the analysis of crude oils

Crude oil samples were collected from three different oil producing fields from Delta, Bayelsa, and Abia

Crude oil samples were put in Teflon caped glass vials and labelled as KW, OWA1, OWA2 and KLC

Sample fractionated using column chromatography on a silica gel

Petroleum ether (70mL) as an eluent for aliphatic constituents and 70mL dichloromethane for the aromatic fractions

Excess solvent was recovered from the aliphatic fractions by passing through a stream of nitrogen gas

Gas chromatography-mass spectrometry (GC-MS) was used to analysed aliphatic fraction and identify fragments ions of specific biomarkers

sterane isomerization ratios (Moldowan et al. 1985). The Ts/(Ts + Tm) ratio (also known as Ts/Tm) can be employed to evaluate thermal maturity of oils (Seifert and Moldowan 1980; Abdullah et al. 2021). This ratio increases with the oil's thermal maturity, but also may be affected by source lithology (Ekpo et al. 2012). In general, most oil samples have a ratio of diastereoisomers Ts less than Tm, and thus values of *Ts/(Ts + Tm)* are less than one. Table 5 shows the increasing trend of KW, KLC, OWA1 and OWA2 from 0.46

to 0.50 (Fig. 5), indicating incomplete isomerization of the compound, and the crude oils have reached the oil generating window inferring they are thermally mature (Peters and Moldowan 1993; Tissot and Welte 1984; Onojake et al. 2015; Fu et al. 2023).

The (22S/22)S + 22R) homohopane ratio is one of frequently utilized biomarker maturity indicator. During maturation, the C_{31} or C_{32} 22S/22S + 22R homohopane ratios increase from zero to approximately 0.6 at equilibrium. Some researchers determined the maturity of lower Jurassic strata based on the CPI, C_{29} ββ/(αα + ββ), C_{29} 20S/(S + R), C_{31} S/(S + R) (Ekpo et al. 2012; Zakrzewski et al. 2022). It is postulated that oil generation has just begun at values within the range of 0.50 to 0.54, but ratios between

Table 2 Shows the distribution of hopanes in the crude oil

Biomarker	KW	KLC	OWA1	OWA2
Ts	58,457	17,820	7906	30,418
Tm	67,986	19,742	7736	29,489
C28 Bisnorhopane	74,831	11,753	3273	15,746
C29 Nor-25 hopane	39,110	12,287	6249	14,698
C29 Norhopane	270,955	73,934	41,198	128,051
C29 Normoretane	42,907	1356	6913	20,894
C30 Oleanane	207,569	112,791	41,768	131,712
C30 Hopane	414,239	108,849	61,342	193,976
C30 Moretane	87,240	25,488	10,936	40,713
C31 Homohopane (22S)	96,302	29,653	15,659	55,296
C31 Homohopane (22R)	64,964	17,819	10,944	38,685
C32 Homohopane (22S)	52,815	14,483	8096	32,502
C32 Homohopane (22R)	35,842	13,519	5642	22,777
C33 Homohopane (22S)	24,816	11,937	4713	24,814
C33 Homohopane (22R)	21,427	7605	3467	13,540

Table 3 Data showing steranes distribution in the crude oil samples

Biomarker	KW	KLC	OWA1	OWA2
C27ααS	9186	26,140	5824	20,821
C27ββR	5153	8276	2474	5156
C27ββS	5053	4016	2000	5597
C27ααR	8571	10,441	8611	25,328
C28ααS	5049	4844	1865	12,897
C28ββR	6235	7368	1911	8944
C28ββS	15,519	6329	2295	13,162
C28ααR	12,967	6941	6005	20,051
C29ααS	NIL	4678	2730	9128
C29ββR	NIL	6589	2934	11,933
C29ββS	NIL	5451	1967	9880
C29ααR	NIL	7234	7189	26,140

Table 4 Shows the ratios of n-alkanes and isoprenoids

Sample ID	Pr/Ph	Pr/nC17	Ph/nC18	(Pr + Ph)/ (nC17 + nC18)	Pr + nC17/ Ph + nC18
KW	0.34	0.33	9.54	1.16	1.27
KLC	0.42	0.39	7.13	1.16	1.32
OWA1	0.89	1.00	4.01	1.66	1.42
OWA2	0.80	0.87	4.05	1.54	1.38

0.57 and 0.62 indicate that the oil generation window has been reached. In this research, apart from KLC with a C_{32} homohopane isomerization value of 0.51 (Table 5), signifying it just barely entered the oil generation window,

Table 5 Calculated parameters from saturate biomarkers used for source and thermal maturity

Biomarker ratio	KW	KLC	OWA1	OWA2
C_{31} 2S(22S + 22R)	0.59	0.51	0.58	0.58
$C_{29}\alpha\alpha\alpha$ 20S(20S + 20R)	0.12	0.28	0.66	0.61
C_{27} Sterane %	41.20	27.40	41.20	33.60
C_{28} Sterane %	58.70	38.00	26.30	32.50
C_{29} Sterane %	31.00	34.00	32.00	33.00
αββ/αββ + ααα	0.23	0.71	0.33	0.38
Moratane/Hopane	0.21	0.23	0.17	0.20
Sterane/Hopane	0.16	0.56	0.74	0.87
Oleanane Index	0.50	1.03	0.68	0.67
C_{29}/C_{27} Sterane	1.10	1.25	0.78	1.00
C_{29}/C_{30} Hopane	0.65	0.67	0.67	0.60
Ts/Tm	0.85	0.90	1.02	1.03
Ts(Ts + Tm)	0.46	0.47	0.50	0.50
Pr/nC$_{17}$	0.33	0.39	1.00	0.87
Ph/nC$_{18}$	9.54	7.13	4.01	4.05
CPI	0.98	0.96	0.97	0.98

values for OWA1, OWA2 and KW, were 0.58 for both OWA1 and OWA2 and 0.59 for KW, which showed that these oils have reached the oil generation window and are thermally mature. The 20S/(20S + 20R) and ββ/(ββ + αα) C_{29} sterane ratios suggest a comparable explanation, with the moretane/hopane ratios. Thermal maturity causes the moretane fraction of its comparable hopanes to decrease from around 0.8 in immature sediments to roughly 0.05 to 0.15 in mature source rocks and oils (Connan et al. 1986).

The moretane/hopane ratio for the studied crude oils ranged from 0.20 to 0.8 to 0.21 for KW, 0.23 for KLC, 0.20 for OWA1 and 0.17 for OWA1. From the values obtained, it was observed that all the oils have some level of maturity, with OWA1 being the most mature. This confirms what various authors have said as regards the use of this ratio as an indicator for thermal maturity. From the data shown (Table 5), the Moretane/Hopane ratios were 0.21, 0.23, 0.17, and 0.20 for KW, KLC, OWA1, and OWA2. From the values obtained, it was observed that the oils all have some level of maturity, with the most mature being OWA1. Further confirmation that the crude oils have reached the beginning of the oil generating window.

Furthermore, thermal maturity was obtained from the ratios of cholestane ($C_{29}\alpha\alpha\alpha$ 20S/(20S + 20R) and ββ/(ββ + αα) C_{29} sterane, which ranged from 0.28 to 0.66 and 0.33 to 0.71 signifying an oil generating window including a high level of maturity (Peters and Moldowan 1993; Seifert and Moldowan 1980; Tissot and Welte 1984; Huang et al. 2022).
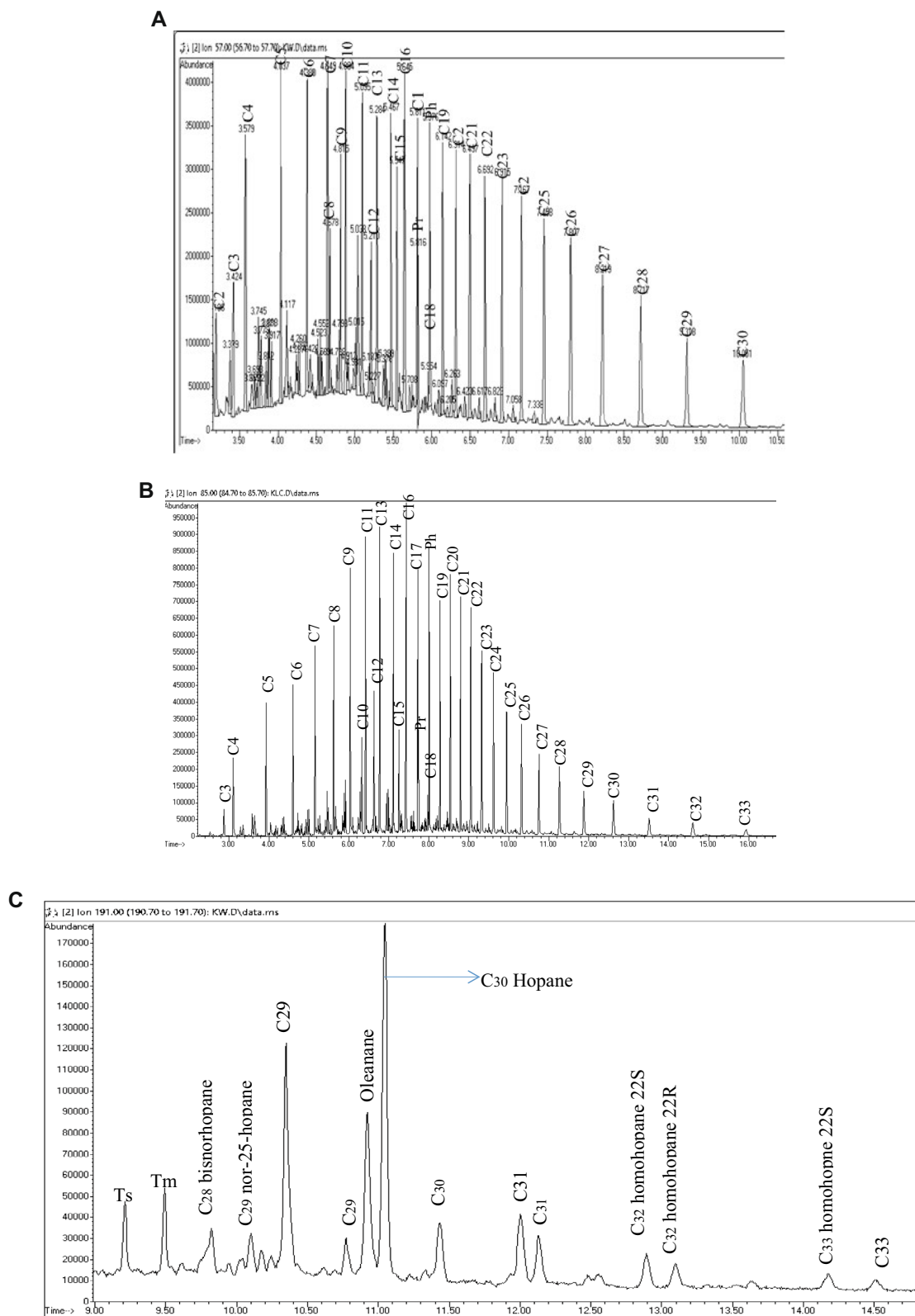
Fig. 4 **A** GC–MS chromatogram of m/z 85 of n-alkanes and isoprenoids distribution for crude oil sample KW. **B** GC–MS chromatogram of m/z 85 of n-alkanes and isoprenoids distribution of crude oil sample KLC. **C** GC–MS chromatogram of m/z 191 of hopanes for crude oil sample KW. **D** GC–MS chromatogram of *m/z* 191 of hopanes for crude oil sample OWA1. **E** GC–MS chr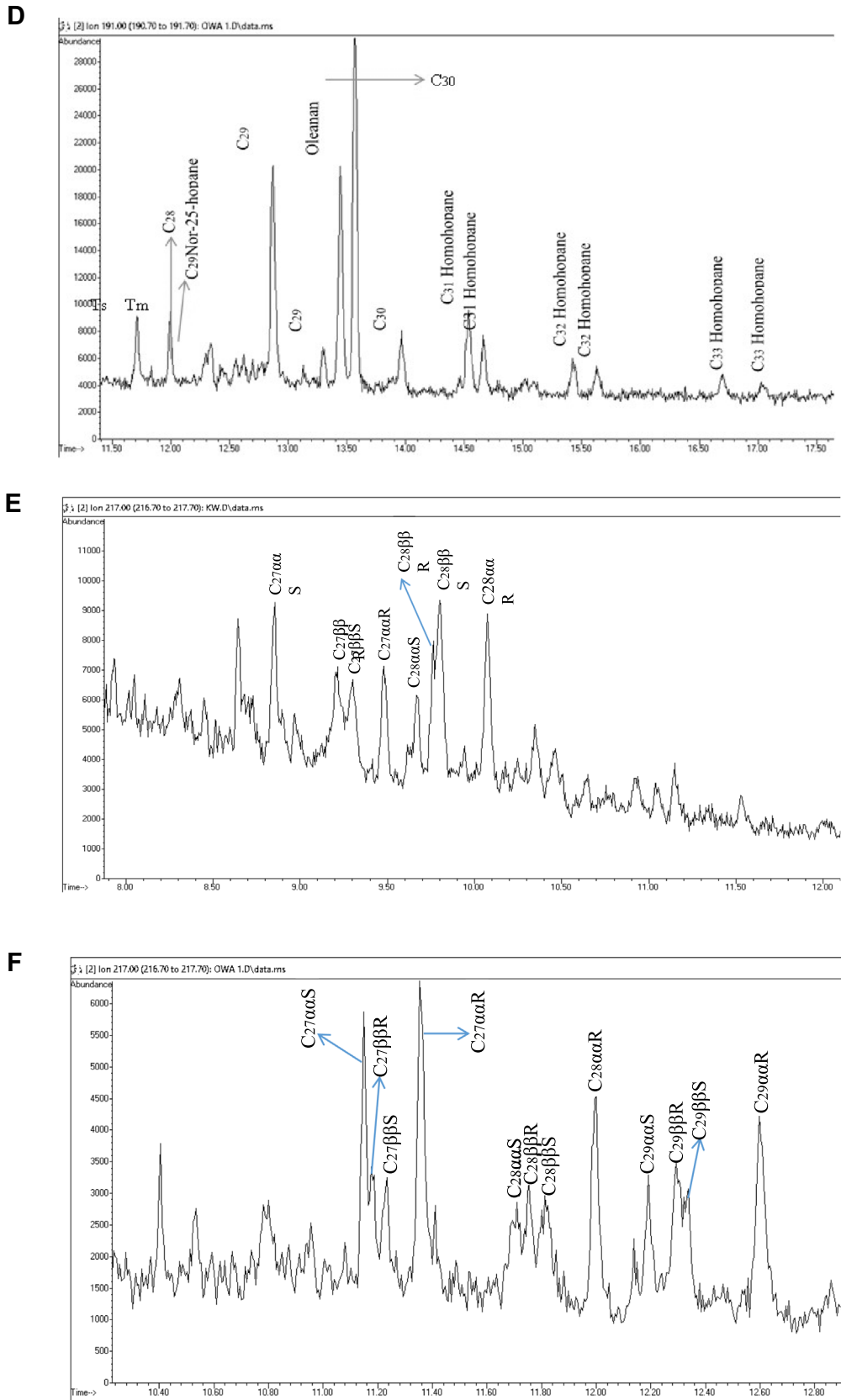omatogram of m/z 217 of the steranes for crude oil sample KW. **F** GC–MS chromatogram of *m/z* 217 of the steranes for crude oil sample OWA1

Fig. 4 (continued)
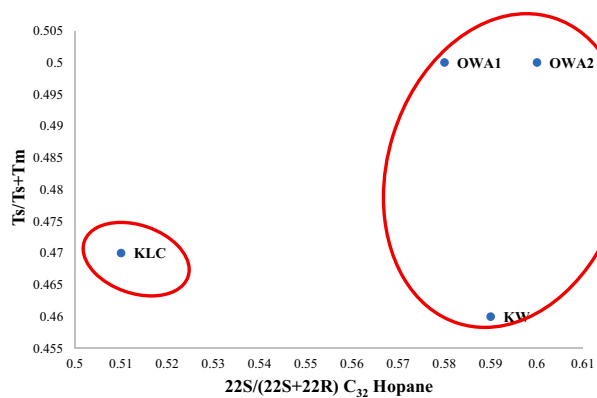
Fig. 5 Cross-plot of Ts/Ts + Tm vs 22S/(22S + 22R) C$_{32}$ Hopane

Fig. 6 Cross-plot of Pr/nC$_{17}$ vs Ph/nC$_{18}$ showing kerogen type

Source of organic matter

The organic richness and composition of the organic matter input are the key parameters establishing the amount and type of petroleum formation in the source rocks (Aziz et al. 2020; Sohail et al. 2022). Once, thermal maturity is reached, the presence of adequate quantity of organic matter in the source rocks is crucial for managing the hydrocarbon generative potential (Aziz et al. 2020). The distribution pattern of steranes in oil can give information on the source of organic matter in the crude oil (Walples and Machihara 1991; Ahmad et al. 2022). Regular steranes/hopanes values are commonly employed to indicate eukaryote (mostly algae and advanced plants) and prokaryote (bacteria) inputs in crude oil parent materials. The high Σregular steranes/Σ hopanes (≥ 1) value represents the marine organic characteristics of algae; the low regular steranes/hopanes ratio, on the other hand, shows the characteristics of terrigenous organic matter or organic matter altered by bacteria (Ekpo et al. 2012; Younes 2001). The calculated sterane/hopane ratios (Table 5) ranged from 0.16 to 0.87, which is less than unity. The low ratio is a characteristic of terrigenous organic matter, or organic matter that must have undergone some modification by microorganisms (Connan et al. 1986).

Researchers such as Younes (2001) reported that Ph/nC$_{18}$ > 0.30 is typical of shale source rocks, while oils of carbonate source rocks have Ph/nC$_{18}$ < 0.30. Pr/nC$_{17}$ ratio > 0.60 signifies terrestrial input to source rock. Also Pr/nC$_{17}$ < 0.50 indicates marine matter input to source rock. Figure 6 shows that all oil samples have a Ph/nC$_{18}$ greater than 0.30, typifying shale source rock, while the Pr/nC$_{17}$ of oil samples OWA1 and OWA2 have Pr/nC$_{17}$ ratios exceeding 0.60, signifying terrestrial input to source rock, while KW and KLC have Pr/nC$_{17}$ ratios less than 0.50, which is characteristic of marine input to source rock (Uzoegbu et al. 2023).
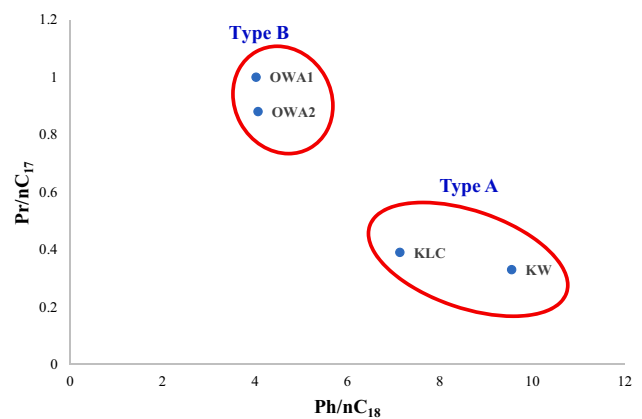
Phytoplankton, bryophytes, and aquatic plants can all be associated with n-alkanes that are predominately mid-chain C$_{21}$–C$_{25}$ homologues (Volkman et al. 1998). Although, the high abundances of long-chain C$_{27}$ homologues can be predominantly attributed to input from terrestrial plants (Zakrzewski et al. 2023). The ratio of isoprenoids to n-alkanes easily distinguishes oil families into marine organic matter contribution and suboxic-anoxic (Type II/III kerogens) depositional conditions for Family-A, which is mostly indicated by low pristane/phytane ratios and pristane/n-C$_{17}$ ratios that are greater than or equal to phystane/n-C$_{18}$ ratios. Pristane/phytane ratios that are slightly high and a correlation between pristane/n-C$_{17}$ and phytane/n-C$_{18}$ for Family-C point to the presence of mixed organic facies and suboxic depositional conditions. A Type II/III source rock with considerable terrestrial organic facies and dysoxicoxic depositional conditions can be determined by high pristane/phytane ratios and the pristane/n-C$_{17}$ against phytane/n-C$_{18}$ relationship for Family-B (Fig. 6) (Uzoegbu et al. 2023). The bituminite shale rocks contain Type II/III kerogen, which is both gas- and oil-prone and has a high potential for oil production (Hakimi et al. 2023).

Philip (2003) showed that ratios of C$_{29}$/C$_{30}$ hopanes are mostly high (> 1) in crude oils produced from organic-rich carbonates and evaporates and less than unity for oils from shale or carbonaceous source rocks. The oil samples under study have C$_{29}$/C$_{30}$ hopanes ranging from 0.60 to 0.67, which are all less than unity. Signifying that the oils might have come from carbonaceous organic matter-rich shale source rocks.

The presence of C$_{29}$ moretane, gammacerance, oleananes, and a slight high concentration of C$_{28}$ bisnorhopanes supports this proposition and designates an age range for the crude oils from cretaceous or younger and higher in tertiary sediments, which coincide with the evolution of angiosperms and are indicative of both source rock age and terrestrial

input (Fazeelat et al. 2009; Peters et al. 2005; Onojake and Abrakasa 2021). The crude oil came from a shale source rock with terrigenous and marine inputs, according to the results of the various ratios used in this study.

Depositional environments

Since, some compounds are related to organisms or plants that thrive in specific forms of depositional environments, biomarkers can be used to indicate depositional paleoenvironments (Powel and Mckirdy 1973). Consequently, Powel and Mckirdy (1973) postulated a process for the synthesis of a very high ratio of pristane under oxic conditions and moderately high concentrations of phytane under reducing conditions. Crude oil and coal extract contain isoprenoids such as pristane (Pr) and phytane (Ph), and the ratio of pristane/phytane (Pr/Ph) is extensively utilized to evaluate depositional environments (Ten Haven et al. 1987). Values greater than one indicate oxic conditions, and values less than one (< 1) indicate anoxic paleodepositional environments (Ten Haven and Rullkötter 1988; Pandey et al. 2012). Consequently, the Pr/Ph ratio has evolved into an indicator of the toxicity of the depositional environment. Both pristane and phytane are generated from the phytol substituent of chlorophyll, either under reducing or oxidizing conditions. The pristane-to-phytane ratio is used to determine the redox state of sediments during diagenesis (Osuji and Anita 2005).

The pristane/phytane ratio is one of the most commonly used correlation parameters and has been utilized as an indication of the depositional environment (Eneogwe and Ekundayo 2003; Sletten 2003; Uzoegbu et al. 2023). A pristane/phytane ratio higher than 3.0 is thought to be associated with a terrigenous bed with oxidizing conditions (Lijmbach 1975). Ten Haven and Rullkötter (1988) stated that Pr/Ph ratios (> 3.0) suggest terrigenous input under oxic conditions, whereas low Pr/Ph (0.8) represents an anoxic, hypersaline, or carbonate environment. Terrestrial sediments often have high pr/ph ratios (greater than 3). Pr/ph ratios of 1 to 3 suggest an oxidizing depositional (Ekpo et al. 2018). According to Lijmbach (1975), low values (Pr/Ph < 2) indicate marine depositional environments such as marine, fresh, and brackish water (reducing conditions), values between two and four (2–4) indicate fluvio-marine and coastal swamp depositional environments, and high ratios up to ten (10) describe oxidizing conditions and peat/swamp depositional environments. The chromatogram of the samples showed a predominance of phytane over pristane, indicating an anoxic paleoenvironment, as phytane is formed by the reduction of the phytol side chain of the chlorophyll molecule (Powel and Mckirdy 1973). The Pr/Ph ratio of the four crude oil samples is shown in Table 4. KW and KLC had values of 0.34 and 0.42, respectively,

suggesting anoxic, hypersaline, or carbonate environments, while the values for OWA1 and OWA2 were 0.89 and 0.80, respectively, which also point towards anoxic depositional environments. Though without corroborating data, Pr/Ph ratios of 0.8 to 3.00 are thought to designate certain paleoenvironmental conditions. The ratio of Pr/nC17 can be applied to distinguish organic matter generated in swamp environments (more than 0.1) from organic matter formed in marine environments (less than 0.5), although the ratio is influenced by maturity in addition to biodegradation (Osuji and Anita 2005). The calculated values for crude oil samples KW and KLC have values of 0.34 and 0.39 (< 0.5), while OWA1 and OWA2 have values of 0.87 and 1.0. The obtained results are typical of type II organic matter from shale in the marine environment, where values should be between 0.6 and 1.6 (Ekpo et al. 2012).

The cross-plot of Pr/nC_{17} vs. Ph/nC_{18}, as shown in Fig. 6, is supportive evidence that the studied crude oils are classified into two types (A and B), produced from mixed organic matter with KW and KLC in the anoxic environment while OWA1 and OWA2 are in the oxic depositional environment (Huang and Meinschein 1979).

The computed relative abundance of C_{27}, C_{28}, and C_{29} steranes represents the percentage distributions of C_{27}, C_{28}, and C_{29} steranes for all samples (Table 5). C_{27} sterane of 41.2% and 33.6% for OWA1 and OWA2 predominated over C_{28} and C_{29}, which is typical of organic origin with a marine input. KLC and KW, with dominant C_{28} and C_{29} of 58% and 38%, clearly show a mixed origin of marine and terrigenous plants owing to the high presence of oleanane in the chromatograms of both samples (Onojake and Abrakasa 2021).

The relative abundance of C_{27}, C_{28}, and C_{29} steranes, which ranged from 27.4 to 41.2, 26.3 to 58.7, and 32.0 to 34.0 percent, respectively (Table 5), indicates crude oil from

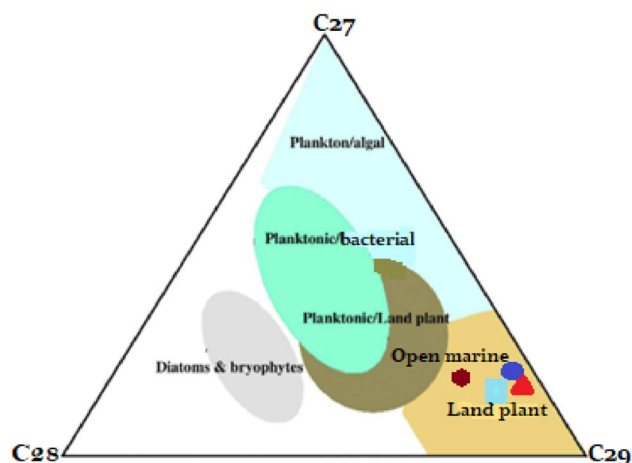**Fig. 7** Ternary diagram of regular $C_{27} - C_{29}$ steranes indicating the relationship between the organic matter input and depositional environment (modified after Huang and Meinschein 1979)

source rock with mixed origins (terrestrial and marine) as shown in Fig. 7 (Su and Jiang 2022; Yu et al. 2022). Furthermore, the higher abundance of C_{27} steranes over C_{29} steranes suggests that more algal constituents were deposited into the source rock (Peters and Moldowan 1993; Hanson et al. 2000; Duan et al. 2008).

Conclusions

Biomarkers or genetic markers were used to investigate the geochemical characteristics (maturity, source of organic matter, depositional environment and genetic relationship) of crude oils from some fields in the Niger Delta basin, Nigeria using column chromatography and Gas chromatographic—mass spectroscopic (GC–MS) techniques. The conclusions from this study are summarized below:

1. Organic geochemical evaluation of representative crude oils from southern Nigeria was carried out and the biomarker ratios and the different cross-plots served as tools for appraising the different oil samples geochemically.
2. Each crude oil assay from different producing fields has its own distinct characteristics, ranging from barely reaching the oil generating window for some to actual thermal maturity for others.
3. The distribution patterns of normal alkanes, hopanes, and steranes, as well as source-specific maturity and of biomarker diagnostic ratios, such as Pr/Ph, Pr/nC_{17}, Ph/nC_{18}, C_{29}: $(20S/(20S + 20R)$ and $Ts/(Ts + Tm)$, revealed a high level of genetic similarity across the three producing fields. These information identified two genetically related crude oil families.
4. This research also revealed that the origin of the crude oils was shale source rock containing mixed organic matter from terrigenous and marine input, showing hypersaline and anoxic environments of deposition.
5. The biomarker maturity ratios revealed that the oils have reached the oil generation window and are thermally mature, with no clear evidence of biodegradation.

Author Contributions MCO: Conceived, designed, supervised and was involved in the writing of the manuscript.NEN: Collected samples, analyzed interpreted result and wrote part of the manuscript. JOO: Collected samples, contributed reagents, analyzed and interpreted results. DAA: Contributed reagents, provided analysis tools and offered special advice. IO: Performed the experiments and interpreted part of the results. LCO: Provided expert advice and corrected the technical aspects of the article.

Declarations

References

Abdullah ES, Ebiad MA, Rashad AM, El Nady MM, El-Sabbagh SM (2021) Thermal maturity assessment of some Egyptian crude oils as implication from naphthalene, phenanthrene and alkyl substituents. Egypt J Petrol 30(1):17–24. https://doi.org/10.1016/j.ejpe.2020.12.004

Abrakasa S, Ukaegbu V, Onojake M (2016) The source kitchen of the Niger Delta oils: case study on Nembe Creek E1.0 and the Kolo Creek E2.0 Reservoirs. J Petrol Expl Prod Technol 6(3):331–341. https://doi.org/10.1007/s13202-015-0211-9

Adedosu TA, Sonibare OO (2005) Characterization of Niger delta crude oil by infrared spectroscopy. J Appl Sci 5(5):906–909. https://doi.org/10.3923/jas.2005.906.909

Ahmed A, Khan T, Jahandad S, Hakimi MH, Gharib AF, Kahal AY, Khan MA, Munir MN (2022) Organic matter characteristics of the Datta Shale formation and their contribution to conventional oil generation resources in the Upper Indus Basin, Northern Pakistan. Asian J Earth Sci 224:104975. https://doi.org/10.1016/j.jseaes.2021.104975

Aladwani NS (2021) Assessment of petroleum system of Arabian Iranian Basin in Kuwait. All Earth 33(1):108–123. https://doi.org/10.1080/27669645.2021.1976930

Avbovbo AA (1978) Tertiary lithostratigraphy of Niger delta. AAPG Bull 62(2):295–300. https://doi.org/10.1306/c1ea482e-16c9-11d7-8645000102c1865d

Aziz H, Ehsan M, Ali A, Khan HK, Khan A (2020) Hydrocarbon source rock evaluation and quantification of organic richness from correlation of well logs and geochemical data: a case study from the Sembar formation, Southern Indus Basin, Pakistan. J Nat Gas Sci Eng 81:103433. https://doi.org/10.1016/j.jngse.2020.103433

Beka FT, Oti MN (1995) The distal offshore Niger Delta: frontier prospects of a mature petroleum province. In: Geol of deltas, pp 237–241. https://doi.org/10.4236/ajcm.2014.42010

Connan J, Bouroullec J, Dessort D, Albrecht P (1986) The microbial input in carbonate-anhydrite facies of a sabkha palaeoenvironment from Guatemala: a molecular approach. Org Geochem 10(1–3):29–50. https://doi.org/10.1016/0146-6380(86)90007-0

Corredor F, Shaw JH, Bilotti F (2005) Structural styles in the deepwater fold and thrust belts of the Niger Delta. AAPG Bull 89(6):753–780. https://doi.org/10.1306/02170504074

Doust H, Omatsola E (1990) Niger delta divergent/passive margin basins. AAPG Bull 45:201–238. https://doi.org/10.1306/m48508c4

Duan Y, Wang CY, Zheng CY, Wu BX, Zheng GD (2008) Geochemical study of crude oils from the Xifeng oilfield of the Ordos basin, China. J Asian Earth Sci 31(4–6):341–356. https://doi.org/10.1016/j.jseaes.2007.05.003

Ekpo BO, Ibok UJ, Essien N, Wehner H (2012) Geochemistry and organic petrography of Cretaceous sediments of the Calabar Flank, Southeastern Nigeria. Mar Petrol Geol 35(1):252–268. https://doi.org/10.1016/j.marpetgeo.2012.03.010

Ekpo BO, Essien N, Neji PA, Etsenake RO (2018) Geochemical fingerprinting of western offshore Niger Delta oils. J Petrol Sci Eng 160:452–464. https://doi.org/10.1016/j.petrol.2017.10.041

Ekweozor CM, Daukoru EM (1994) Northern Delta Depobelt Portion of the Akata-Agbada (!) Petroleum System, Niger Delta, Nigeria: Chapter 36: Part VI. Case Studie—*Eastern* AAPG Memoir Hemisphere 60:599–614. https://doi.org/10.1306/m60585c36

Eneogwe C, Ekundayo O (2003) Geochemical correlation of crude oils in the NW Niger Delta, Nigeria. J Petrol Geol 26(1):95–10. https://doi.org/10.1111/j.1747-5457.2003.tb00019.x

Energy Information Administration (EIA) (2015).Country analysis brief: Nigeria. http://www.eia.gov/beta/international/analysis_includes/countries_long/Nigeria/nigeria

Evamy BD, Haremboure J, Kamerling P, Knaap WA, Molloy FA, Rowlands PH (1978) Hydrocarbon habitat of Tertiary Niger delta. AAPG Bull 62(1):1–39. https://doi.org/10.1306/c1ea47ed-16c9-11d7-8645000102c1865d

Faboya OL, Ojo AA, Bello H, Osasona I (2018) Geochemical investigation of trace elements in crude oils from two different depobelts in the Niger Delta basin, Nigeria. Petrol Sci Technol 36(2):130–135. https://doi.org/10.1080/10916466.2017.1410557

Farrimond P, Bevan JC, Bishop AN (1996) Hopanoid hydrocarbon maturation by an igneous intrusion. Org Geoch 25(3–4):149–164. https://doi.org/10.1016/s0146-6380(96)00128-3

Fazeelat T, Asif M, Saleem A, Zulfiqar MA, Nadeem S (2009) Geochemical investigation of crude oils from different oils fields of the Potwar Basin. J Chem Soc Pak 31(6):863–870

Fu J, Li M, Sun Y, Li Y, Yang Y, Lu X, Lai GT (2023) Thermal maturity of crude oils in the Baiyun sag, Pearl River Mouth basin, South China Sea: insights from biomarkers, aromatic hydrocarbon and adamantane compounds. Mar Petrol Geol. https://doi.org/10.1016/j.marpetgeo.2023.106353

Haack RC, Sundararaman P, Diedjomahor JO, Gant NJ (2002) Niger delta petroleum systems: regional geology, organic facies and thermal maturity. In: AAPG annual meeting. https://doi.org/10.1306/61eeea0c-173e-11d7-8645000102c1865d

Hakimi MH, Kumar A, Singh AK, Lashin A, Rahim A, Varfolomeev MA, Mustapha KA (2023) Geochemistry and organic petrology of the bituminite shales from the Kapurdi mine, Rajasthan of NW India: implications for waxy oil generation potential. J Petrol Expl Prod Technol 13(2):505–521. https://doi.org/10.1007/s13202-022-01597-9

Hanson AD, Zhang SC, Moldowan JM, Liang DG, Zhang BM (2000) Molecular organic geochemistry of the Tarim Basin, northwest China. AAPG Bull 84(6):1109–1128. https://doi.org/10.1306/a9673c52-1738-11d7-8645000102c1865d

Huang WY, Meinschein WG (1979) Sterols as ecological indicators. Geochim Cosmochim Acta 43(5):739–745. https://doi.org/10.1016/0016-7037(79)90257-6

Huang H, di Primio R, Pedersen JH, Silva R, Algeer R, Ma J, Larter S (2022) On the determination of oil charge history and the practical application of molecular maturity markers. Mar Petrol Geol 139:105586. https://doi.org/10.1016/j.marpetgeo.2022.105586

Kaplan A, Lusser CU, Norton IO (1994) Tectonic map of the world, panel 10". American Association of Petroleum Geologists, AAPG Tulsa. OCLC Number/Unique Identifier: 223027395

Kulke H, Zantop H (1995) Regional petroleum geology of the world. Part I: Europe and Asia. Part II: Africa, America, Australia and Antarctica. Econ Geol Bull Soc Econ Geol 90(5):1354. https://doi.org/10.4236/jhepgc.2021.71014

Lijmbach WM (1975) SP (1) On the Origin of Petroleum. In: 9th world petroleum congress. Onepetro. WPC-16134

Magoon LB, Schmoker JW (2000) The total petroleum system–the natural fluid network that constrains the assessment unit. US Geol Surv World Petrol Assess. https://doi.org/10.3133/ds60

Moldowan JM, Seifert WK, Gallegos EJ (1985) Relationship between petroleum composition and depositional environment of petroleum source rocks. AAPG Bull 69(8):1255–1268. https://doi.org/10.1306/ad462bc8-16f7-11d7-8645000102c1865d

Onojake MC, Abrakasa S (2021) The occurrence and distribution of Oleanane biomarkers in crude oils as an index. J Petrol Sci Technol 11(1):43–50. https://doi.org/10.22078/jpst.2021.4248.1690

Onojake MC, Osuji LC, Abrakasa S (2015) Source, depositional environment and maturity levels of some crude oils in Southwest Niger Delta, Nigeria. Chin J Geochem 34:224–232

Osuji LC, Antia BS (2005) Geochemical implication of some chemical fossils as indicators of petroleum source rocks. J Sci Environ Mgt 9(1):45–49

Pandey IP, Joshi HC, Tyagi A, Tiwari S, Garg N (2012) Study of the parameters and biomarkers of crude oils. Adv Pure Appl Chem 1(3):49–52

Peters KE, Moldowan JM (1993) The biomarker guide: interpreting molecular fossils in petroleum and ancient sediments. Prentice-Hall, Englewood Cliffs, pp 103–114

Peters KE, Peters P, Walters CC, Moldowan JM (2005) The biomarker guide, vol 1. Cambridge University Press, Cambridge. https://doi.org/10.1017/S0016756806212056

Philp RP (2003) Formation and geochemistry of oil and gas. In: Holland HD, Turekian KK (eds) Treatise on geochemistry sediments, diagenesis and sedimentary rocks, vol 17. Elsevier, Amsterdam. https://doi.org/10.1016/B0-08-043751-6/07135-8

Powell TG, McKirdy DM (1973) Relationship between ratio of pristane to phytane, crude oil composition and geological environment in Australia. Nat Phys Sci 243(124):37–39. https://doi.org/10.1038/physci243037a0

Reijers TJA (2011) Stratigraphy and sedimentology of the Niger Delta. Geologos 17(3):133–162. https://doi.org/10.2478/v10118-011-0008-3

Ruebsam W, Pieńkowski G, Schwark L (2020) Toarcian climate and carbon cycle perturbations its impact on sea-level changes, enhanced mobilization and oxidation of fossil organic matter. Earth Planet Sci Lett 546:116417. https://doi.org/10.1016/j.epsl.2020.116417

Seifert WK, Moldowan JM (1980) The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. Phys Chem Earth 12:229–237. https://doi.org/10.1016/0079-1946(79)90107-1

Short KC, Stauble AJ (1967) Outline of geology of Niger delta. AAPG Bull 51:761–779

Sletten EB (2003) A Comparison of petroleum from reservoirs and petroleum inclusions in Authigenic mineral Cements-Halten-banken (Master's Thesis). University of Oslo, Department of Geology, pp 80–107. http://hdl.handle.net/10852/12344

Smith-Rouch LS (2006) Oligocene–Miocene Maykop/Diatom Total Petroleum System of the South Caspian Basin Province, Azerbaijan, Iran, and Turkmenistan. US Geol Surv Bull 2201:1–27

Sohail GM, Radwan AE, Mahmoud M (2022) A review of Pakistani shales for shale gas exploration and comparison to North American shale plays. Energy Rep 8:6423–6442. https://doi.org/10.1016/j.egyr.2022.04.074

Sonibare O, Alimi H, Jarvie D, Ehinola OA (2008) Origin and occurrence of crude oil in the Niger delta, Nigeria. J Petrol Sci Eng 61(2–4):99–107. https://doi.org/10.1016/j.petrol.2008.05.002

Stacher P (1995) Present understanding of the Niger Delta hydrocarbon habitat. In: Geology of deltas, pp 257–267. https://www.researchgate.net/publication/281508240

Su S, Jiang Y (2022) Biomarker geochemistry of paleogene crude oils and source rocks from the Raoyang Sag, Bohai Bay Basin, NE China: an oil-source rock correlation study. J Petrol Geol 45(1):57–77

Ten Haven HL, Rullkötter J (1988) The diagenetic fate of taraxer-14-ene and oleanene isomers. Geochim Cosmochim Acta 52(10):2543–2548. https://doi.org/10.1016/0016-7037(88)90312-2

Ten Haven HL, De Leeuw JW, Rullkötter J, Damsté JS (1987) Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. Nature 330(6149):641–643. https://doi.org/10.1038/330641a0

Tissot BP, Welte DH (1984) Petroleum formation and occurrence, 2nd edn. Springer, Berlin

Tuttle ML, Charpentier RR, Brownfield ME (1999) The Niger delta petroleum system: Niger delta province, Nigeria, Cameroon, and equatorial guinea, Africa, US Department of the Interior, US Geol Surv 50-99

Uzoegbu U, Madu AJ, Ugwueze U, Omang O (2023) API gravities and geochemical evaluation of crude oils from sapele, niger–delta, nigeria. Global J Geol Sci 21(1):69–89. https://doi.org/10.4314/gjgs.v21i1.6

Volkman JK, Barrett SM, Blackburn SI, Mansour MP, Sikes EL, Gelin F (1998) Microalgal biomarkers: a review of recent research developments. Org Geochem 29(5–7):1163–1179

Walples DW, Machihara T (1991) Biomarkers for geologists, american association of petroleum geologist's methods. In: Exploration series, vol 9, 91pp. https://doi.org/10.1017/S0016756800008529

Weber KJ, Mandl GJ, Pilaar WF, Lehner BVF, Precious RG (1978) The role of faults in hydrocarbon migration and trapping in Nigerian growth fault structures. In Offshore Technol Conf. OnePetro, Houston. OTC-3356-MS. https://doi.org/10.4043/3356-MS

Younes MA (2001) Application of biomarkers and stable carbon isotopes to assess the depositional environment of source rocks and the maturation of crude oils, East Zeit Field, southern Gulf of Suez. Egypt Petrol Sci Technol 19(9–10):1039–1061. https://doi.org/10.1081/LFT-100108293

Yu Y, Peng W, Shi S, Sun H, Lu M, Shang P, Lu Y (2022) Geochemical characterizations of source and depositional environment of hydrocarbons in the Lake Albert Rift Basin. Acta Geol Sin Eng Ed 96(1):261–272. https://doi.org/10.1111/1755-6724.14862

Zakrzewski A, Kosakowski P (2021) Impact of palaeo-wildfires on higher plant parameter revealed by new biomarker indicator. Palaeogeogr Palaeoclimatol Palaeoecol 579:110606. https://doi.org/10.1016/j.palaeo.2021.110606

Zakrzewski A, Waliczek M, Kosakowski P, Pańczak J (2022) Lower Jurassic in the central part of the Polish Basin-Geochemical and petrological approach. Mar Pet Geol 146:105922. https://doi.org/10.1016/j.marpetgeo.2022.105922

Zakrzewski A, Krajewski M, Kosakowski P (2023) Geochemical fingerprint—inter-basin chemostratigraphic correlation allowed for a more detailed stratigraphic subdivision of the Pliensbachian-Bathonian strata from the Carpathian Foredeep basement (Ukraine). Int J Earth Sci 112(5):1389–1412. https://doi.org/10.1007/s00531-023-02311-8