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Organic Geochemical Characteristics of the Upper Cretaceous Shales from Gombe Formation, Gongola Basin, Upper Benue Trough, Nigeria

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Abstract

The shales from the Gombe formation were investigated by gas chromatography-flame ionization detector (GC-FID) for the n-alkanes and isoprenoids compositions, and gas chromatography-mass spectrometry (GC-MS) for the polycyclic aromatic hydrocarbons (PAHs) compositions within the context of the origin of organic matter, depositional environments and conditions, and thermal maturity. The n-alkane distribution in the samples indicated organic matter mainly derived from marine settings. All the samples studied relatively showed enriched amounts of PAHs. However, the relatively low abundance and lack of the 6-ring indeno[1,2,3-cd]pyrene and benzo[ghi]perylene in some samples suggested the absence of larger, high-temperature wildfires, either due to inadequate

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seasonality of the humid-arid climate, or limited terrigenous organic matter input. The geochemical ratios computed from the n-alkanes and isoprenoids in the shales indicated mixed inputs of terrigenous and marine organic matter but with higher contribution from marine and deposited under oxidizing and reducing conditions with low – marginal maturity status. Also, the geochemical ratios calculated from the PAHs indicated mixed inputs of petrogenic and pyrogenic sources for the shales but with major input from petrogenic sources. This study showed that biomarkers were effective in evaluating the origin, depositional conditions, and maturity of organic matter in the shales from Gombe formation, Gongola Basin, Nigeria.

Keywords: Shales, biomarkers, origin, depositional conditions, Gombe formation.

INTRODUCTION

Sediments from extinct organisms contain complex molecular fossils known as biomarkers (Mackenzie *et al*., 1984; Welte and Tissot, 1984; Peters *et al*., 2005; Ogbesejana *et al*., 2023). A biomarker is a material that preserves the structure of its biological precursor (Ogbesejana *et al*., 2023; Peters *et al*., 2005; Huc, 1997; Mackenzie *et al*., 1984). The use of biomarkers to infer paleoflora, paleoenvironments, and the origin of life on Earth, as well as to provide a zonation for diagenetic change, has been reported (Mackenzie *et al*., 1984; Brassell, 1992; Peters and Moldowan, 1993; Huc, 1997; Simoneit, 1998). Early investigations have indicated that the information contained within biomarker distribution can be effectively employed for the differentiation and evaluation of depositional settings (Brassell *et al*., 1978; Farrimond, 1987; Jiamo *et al*., 1990), particularly in the delineation and characterization of ancient marine and nonmarine petroleum source rocks (Moldowan *et al*., 1985; Brassell *et al*., 1986), or even in more specific subenvironments, such as lacustrine freshwater and hypersaline, marine carbonate and deltaic sediments (Palacas *et al*., 1984; Brassell *et al*., 1986; Philp and Gilbert, 1986; Fu, 1986; Mello et al., 1988). The constituents of sediment extracts and crude oils serve as indicators of both paleoenvironmental contexts and the precursor compounds present within the organisms that contributed organic matter (OM) during the sediment deposition phase, thereby offering critical insights regarding the organic matter input and the dominant depositional environment (Brassell *et al*., 1978; Jiamo *et al*., 1990). The source facies can be identified through the comparative analysis of structurally analogous chemicals found in sediments and crude oils alongside their probable biological precursors (Brassell *et al*., 1978; Jiamo *et al*., 1990; Ogbesejana *et al*., 2021a, 2021b). The thermal history of the sediments can be reconstructed by modifying the biomarker architecture (Peters et al., 2005; Ogbesejana *et al*., 2021a, 2021b). Certain biomarkers function as indicators of biochemical processes or environmental conditions.

The aromatic hydrocarbons sequestered within sedimentary deposits emerge from the biochemical transformations of biological precursors, which occur either via microbial mechanisms or as a consequence of thermal effects, pressure, and the catalytic influence of the mineral matrix throughout the diagenetic process (Albrecht and Ourisson, 1971). Aromatic hydrocarbons serve as a valuable source of information regarding both the provenance of the accumulated organic matter and the geochemical alterations that occur during the progression of thermal maturity (Ogbesejana *et al*., 2023). Polycyclic aromatic hydrocarbons (PAHs) identified within the geosphere predominantly originate from three distinct sources: those derived from combustion processes (commonly referred to as pyrolytic PAHs), those originating from higher plants, and those produced through diagenesis.

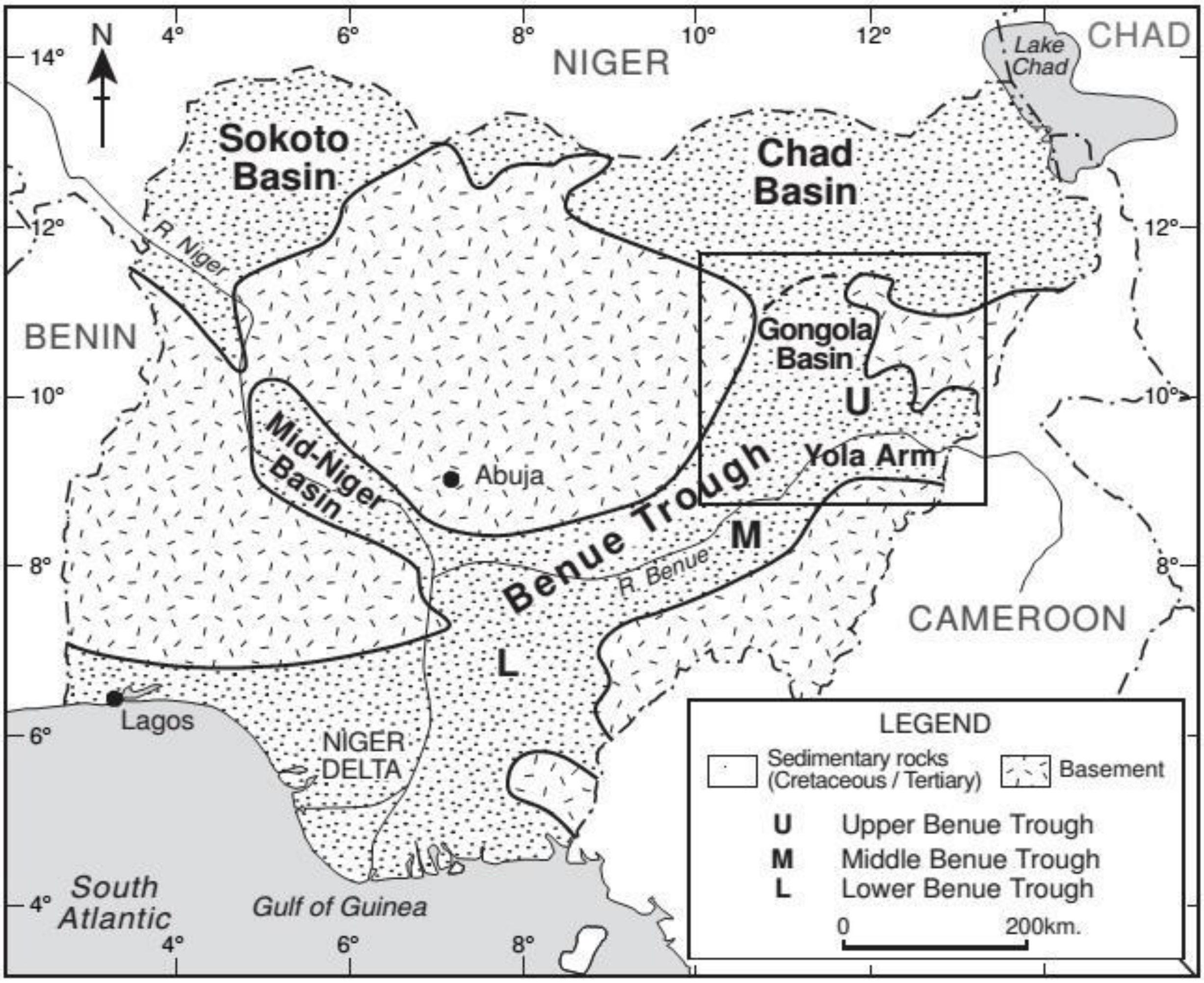

Fig. 1: Generalised geological map of Nigeria showing the location of the Gongola Basin (Abubakar, 2014).

The combustion-derived PAHs that predate deposition have been ascribed to the byproducts of ancient wildfires, signifying the incomplete combustion of biomass, solid fuels, or plant material (Laflamme and Hites, 1978; Wakeham *et al.*, 1979, 1980a; Prahl and Carpenter, 1983; Jiang *et al.*, 1998; Hasegawa, 2001; Yunker and Macdonald, 2003; Luo *et al.*, 2006; Grice *et al.*, 2007; Yunker *et al.*, 2011; Jiang and George, 2019; Xu *et al.*, 2019; Adedosu *et al.*, 2020). Typically, combustion-derived PAHs are characterized by the absence of substituents and possess three or more aromatic rings, encompassing compounds such as phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, benzo[b]anthracene, triphenylene, chrysene, benzo[e]pyrene, benzo[a]pyrene, benzo[b,j,k]fluoranthene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene, and coronene. The analysis of combustion-derived PAHs can facilitate the reconstruction of ancient environments and climatic conditions.

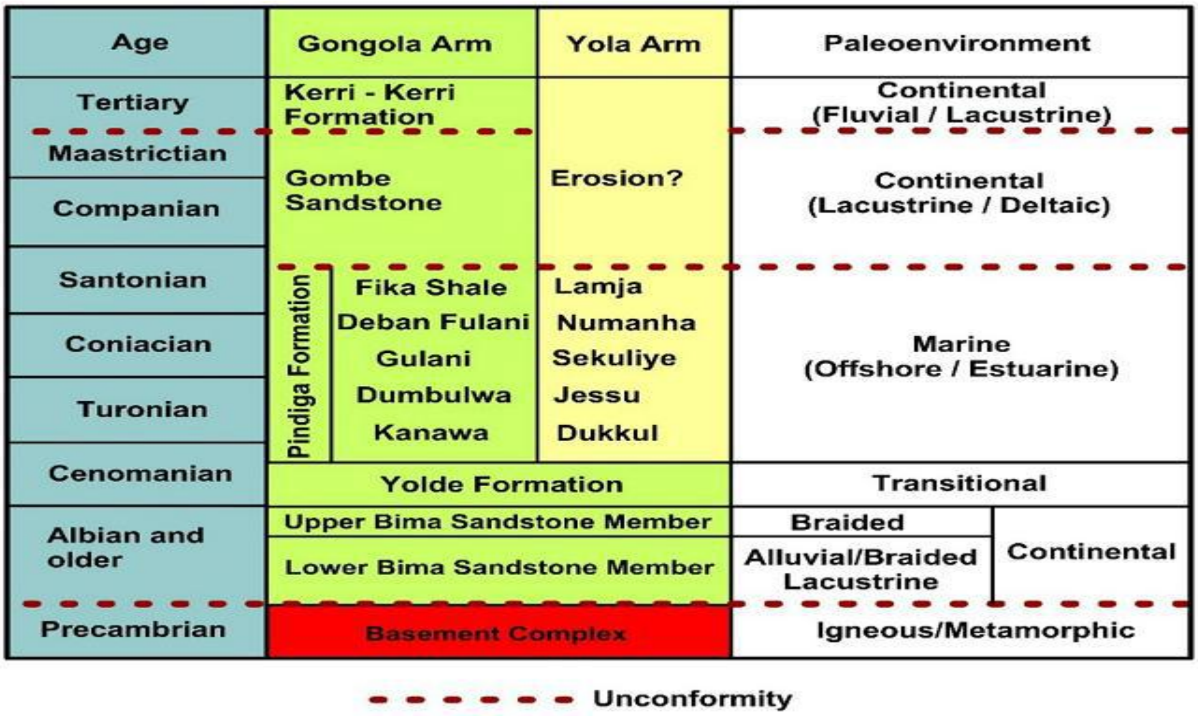

Fig. 2: Stratigraphic successions of Upper Benue Trough (Obaje *et al.*, 2006).

PAHs originating from natural biological precursors, particularly higher plants, are designated as higher-plant PAHs. This category includes compounds such as cadalene, retene, and simonellite, which may form during sedimentary diagenesis (Simoneit, 1977; Wakeham *et al.*, 1980b) or as a result of kerogen decomposition during catagenesis (Lu and Kaplan, 1992). Perylene and benzo[ghi]perylene are classified as diagenetic PAHs, which exhibit a sedimentary distribution that markedly differs from those of combustion-derived PAHs and higher-plant PAHs.

The Gombe Formation is the most recent lithostratigraphic unit of the Cretaceous period in the north-south trending Gongola sub-basin of the Northern Benue Trough (Popoff *et al.*, 1986; Nwajide, 2013). It is characterized by its unconformable relationship with the underlying Fika Shale and is later overlain by the Palaeocene Keri-Keri Formation. The lithological components of the Gombe Formation are systematically divided into three distinct units (Zaborski *et al.*, 1997): the basal interbedded unit, the middle bedded facies, and the upper red sandstone facies. The basal unit is composed of alternating thin layers of silty shales that contain plant detritus and fine to medium-grained sandstones that are interspersed with flaggy ironstones. Its center is composed of uniformly horizontally stratified fine to medium-grained quartz arenite with silts, silty clays, and ironstones; the upper part of the formation is primarily composed of brick-red sandstone, with grain sizes ranging from pebble-sized to medium-grained sandstones, such as trough, tabular, and planar cross-bedding configurations. The Gombe Formation is dated to the Maastrichtian period (Popoff *et al.* 1986).

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A comprehensive study of the organic geochemistry of n-alkanes, isoprenoids, and polycyclic aromatic hydrocarbons (PAHs) in the shales of the Gombe formation is conspicuously absent or insufficiently documented, despite the invaluable contributions of earlier researchers who have examined the organic geochemical characteristics of the shales from this formation (Adedosu *et al.*, 2020; Jimoh *et al.*, 2020; Ojo *et al.*, 2019; Onoduku *et al.*, 2013; Abubakar *et al.*, 2008; Akande *et al.*, 1998). The organic geochemistry of n-alkanes, isoprenoids, and PAHs in the Gombe formation's shales was investigated to close this gap; the majority of the PAHs were reported for the first time in Gombe shales in this work.

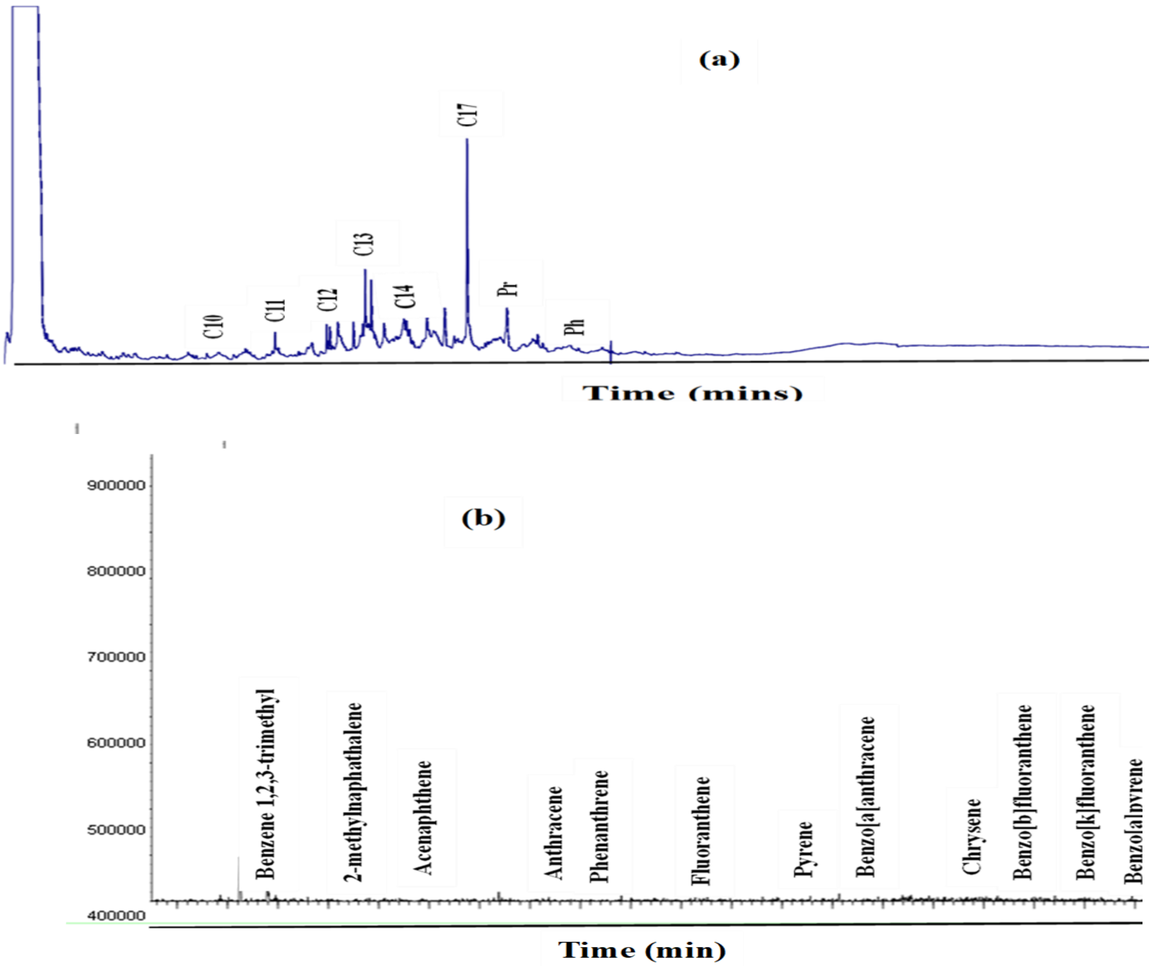


Fig. 3: Representatives of the total ion chromatograms of the (a) saturated fractions showing the distribution of n-alkanes and isoprenoids and (b) aromatic fractions showing the distribution of polycyclic aromatic hydrocarbons in the Gombe shales.

MATERIALS AND METHODS

Sampling

Due to the difficulties in obtaining subsurface samples and the limitations imposed by government regulations, outcrop samples were used for this investigation. Twenty outcrop samples were carefully selected from shaly sequences in the Gombe Formation in the Gongola Basin, which comprise a wide variety of sedimentary logs and facies. Since weathering is always a significant obstacle for inorganic geochemical analyses of outcrop sediments, weathered rock surfaces were carefully removed by excavating to a depth of about 0.5 m at each sampling location to obtain samples that were both fresh and unweathered. The geological map and stratigraphic column of the Benue trough are shown in the figures 1 and 2.

Extraction and Fractionation

Agate mortar was used to crush the shale samples into powder. A solvent extractor was used to extract the homogenized powdered samples using a solvent mixture of dichloromethane/methanol (9:1 v/v). Two-step silica gel column liquid chromatography was used to separate the extractable organic matter (EOM). The first column's total hydrocarbons were extracted by eluting it with n-hexane/dichloromethane (4:1 v/v). Aliphatic hydrocarbons (elution with n-hexane) and aromatic hydrocarbons (elution with n-hexane/dichloromethane (4:1 v/v)) were separated from the total hydrocarbons on a second column. To make sure there was no mixed elution of aliphatic and aromatic hydrocarbons, UV light monitoring was employed (Xu *et al.*, 2019).

Gas chromatography-flame ionization detector (GC-FID)

The Hewlett Packard 5890 Series II, which was outfitted with a Gerstel on-column injector, an electronic pressure control (EPC), a fused silica capillary column (HP Ultra I) of 50 m length, 0.2 mm inner diameter, and 0.33 m film thickness, as well as a standard flame ionization detector (FID), was used to analyze the aliphatic fractions by capillary gas chromatography for the characterization of the n-alkanes, pristane, and phytane Hydrogen gas was used as a carrier gas (pressure regulated) at a flow rate of 1 ml min1. The oven temperature was set to rise at a rate of 4 °C min−1 from 90 °C (hold time of 5 minutes) to 310 °C. Retention periods and peak areas were processed and stored using a Multichrom 2-online data system (Fisons).

Gas chromatography-mass spectrometry (GC-MS)

An Agilent GC (6890N) connected to an Agilent Mass Selective Detector (5975B) with a J&W DB-5MS fused silica column (length 60 m, inner diameter 0.25 mm, film thickness 0.25 m) was used to analyze the aromatic hydrocarbon fractions on gas chromatography-mass spectrometry (GC-MS). After three minutes of holding the inlet at 35 °C, it was designed to reach 310 °C (0.4 min isothermal) at a rate of 700 °C per minute. Splitless injection was used for the samples. The GC oven's temperature was first maintained at 35 °C for 4 minutes, then it was programmed to reach 310 °C at a rate of 4 °C per minute, and finally, it was maintained for 40 minutes. The carrier gas was helium (99.999%). The carrier gas flow rate (constant flow) was 1.5 mL/min. The ion source of the mass spectrometer was operated in EI mode at 70 eV. The MS data were acquired in full scan mode. The relative abundance of compounds was determined from peak areas (using selected mass chromatograms for the integration of the compounds) (Xu *et al.*, 2019).

RESULTS AND DISCUSSION

The source, depositional environment, and thermal maturity status of the organic matter contained in the shale samples were determined based on the distributions and abundance of aliphatic and PAH biomarkers in the shale extracts.

n-Alkanes and Isoprenoids

Most samples have an n-alkane distribution that varies from C_8 to C_{40}, with C_{17} being the maximum (Figs. 3 and 4). Organic matter primarily originating from marine environments is indicated by this distribution pattern (Ogbesejana *et al.*, 2021a; Adedosu *et al.*, 2020; Peters *et al.*, 2005). One of the most widely used geochemical parameters, the pristane/phytane (Pr/Ph) ratio has been used as an indicator of the depositional environment. However, because of the interferences of thermal maturity and the initial evaluation of organic matter source inputs, it has low specificity (Onojake *et al.*, 2015; Peters *et al.* 2005). It is also frequently employed as an indicator of the depositional environment's redox potential. Ten Haven (1996), for example, emphasized that low Pr/Ph (<0.8) implies anoxic/hypersaline or carbonate environments, while high Pr/Ph (>3.0) shows terrigenous input under oxic conditions. High Pr/Ph values (up to 10) are associated with peat swamp depositional settings (oxidizing conditions), while low values (<2) imply aquatic depositional environments, including fresh, brackish, and marine water (reducing conditions) (Roushdy *et al*. 2010). The Pr/Ph ratios for the examined samples range from 0.18 to 17.5 (Table 1), indicating mixed inputs of terrigenous and marine organic matter deposited under oxidizing and reducing conditions for the shales (Onojake et al., 2015; Peters et al., 2005). The amount of aquatic to terrigenous derived n-alkanes, or short-chain to long-chain n-alkanes, in geological samples is determined by the aquatic/terrigenous ratio (ATR) of hydrocarbons (Wilkes *et al*. 1999; Adedosu *et al*., 2020). While values above 0.5 suggest marine organic matter, values below 0.5 imply an increased inflow of long-chain n-alkanes or organic matter from terrestrial sources. Mixed contributions of marine and terrigenous organic matter in the samples are supported by the TAR and nC_{31}/nC_{19} values in the investigated shales, which vary from 0.08 to 0.84 and 0.11 to 27.32 (Table 1), respectively (Wilkes *et al*., 1999; Adedosu *et al*., 2020). A plot of Pr/nC_{17} vs Ph/nC_{18} has been used by many authors to categorize geological materials into various groups (Fig. 5). The samples' varied terrestrial and marine organic matter origins are further demonstrated by this figure (Peters *et al*., 2005). In geological samples, the Carbon Preference Index (CPI) has been used extensively as a maturity indicator (Peters *et al*. 2005; Muhammad *et al*. 2010). According to some researchers, the CPI values of immature rocks were frequently high (>1.5). The CPI values (Table 1) in this study fall between 0.01 and 11.38. Low-marginal maturity status of the samples is reflected in these values (Adedosu *et al*., 2020; Onojake *et al*., 2015; Peters *et al*., 2005).

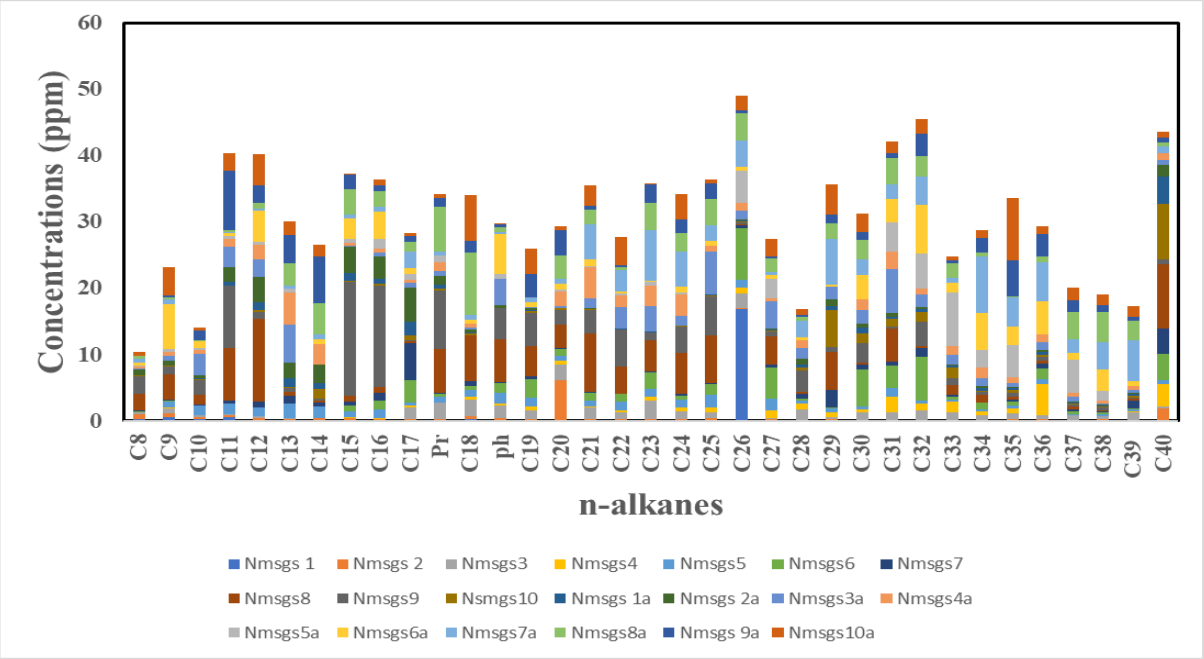


Fig. 4: The histogram showing the distribution of n-alkanes in Gombe shales

Table 1: Geochemical ratios computed from the n-alkanes and isoprenoids in the studied shales

Ratios	Nmsgs 1	Nmsgs 2	Nmsgs3	Nmsgs4	Nmsgs5	Nmsgs6	Nmsgs7	Nmsgs8	Nmsgs9	Nsmgs10
Pr/Ph	1.27	0.37	1.32	0.31	0.55	0.28	0.93	1	1.87	17.5
Pr/nC_{17}	1.08	0.55	1.48	0.29	1.82	0.12	0.03	26.04	80.09	0.49
Ph/nC_{18}	0.5	0.71	0.74	0.57	1.61	2.39	0.21	0.49	0	0.56
$Pr+nC_{17}/Ph +nC_{18}$	0.82	0.43	0.95	0.5	0.53	1.18	6.82	0.5	0.92	2.52
$Pr+Ph /Ph+C_{18}$	0.76	0.57	0.99	0.47	0.96	0.9	7.12	1.82	9.66	0.42
$C_{30}/Pr+Ph$	0.2	0.17	0.27	1.47	0.17	1.9	0.4	3.16	0.38	4
nC_{18}/Ph	2	1.4	1.35	1.77	0.26	0.42	4.6	1.07	0	18
CPI	0.01	1.96	2.84	1.12	1.07	0.71	0.14	1.2	1.03	2.8
ATR	0.69	0.5	0.68	0.22	0.43	0.47	0.63	0.47	0.84	0.15
nC_{31}/nC_{19}	0.34	1.40	0.86	3.71	0.84	1.05	1.02	0.95	1.60	5.54

Table 1: Contd

Ratios	Nmsgs 1a	Nmsgs 2a	Nmsgs3a	Nmsgs4a	Nmsgs5a	Nmsgs6a	Nmsgs7a	Nmsgs8a	Nmsgs 9a	Nmsgs10a
Pr/Ph	15.5	3.61	0.18	6.7	1.21	0	2.37	8.89	2.93	5.08
Pr/nC_{17}	0.3	0.26	0.92	3.94	1.06	0	0.26	4.63	1.59	1.25
Ph/nC_{18}	0.44	0.76	12.65	0.34	0	9.82	0.36	0.08	0.25	0.02
$Pr+nC_{17}/Ph +nC_{18}$	20.92	7.44	0.34	3.05	1.79	0.14	3.11	0.82	0.87	1.17
$Pr+Ph /Ph+C_{18}$	5.08	1.99	1.09	2.47	1.68	0.34	0.28	13.4	2.48	6.99
$C_{30}/Pr+Ph$	1.42	0.33	0.46	1.45	3.27	0.31	1.17	0.04	0.61	3.53
nC_{18}/Ph	2.25	1.32	0.08	26.5	0	0.1	2.78	12.25	2.82	52.77
CPI	1.07	0.93	2.09	2.03	0.6	1.5	11.38	1.2	1.2	1.13
ATR	0.72	0.8	0.08	0.55	0.26	0.37	0.47	0.3	0.68	0.45
nC_{31}/nC_{19}	27.32	0.92	0.13	0.34	0.00	1.10	0.11	0.68	0.19	0.41

***Pr= pristane; Ph= phytane; CPI= Carbon preference index; ATR= Aquatic-terrigenous ratio**

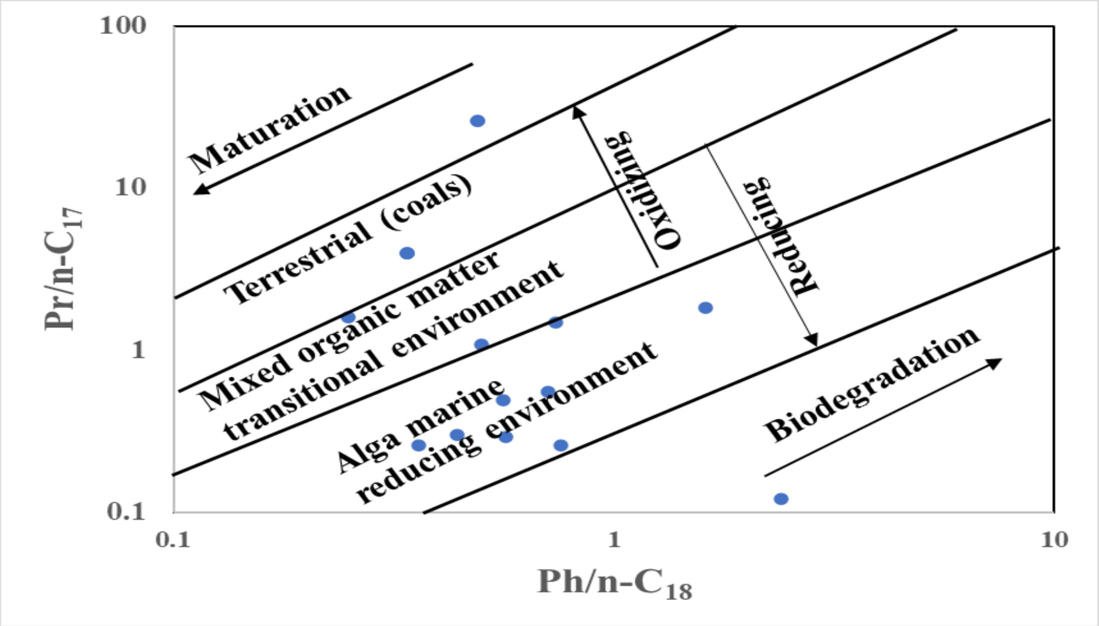


Fig. 5: Cross plot of Pr/nC_{17} against Ph/nC_{18} of shale samples from Gombe formation (Modified after Shanmugam, 1985)

Polycyclic Aromatic Hydrocarbons

The concentrations (ppm) and geochemical ratios of the eighteen (18) PAHs found in the shale samples in this study are shown in Tables 2 and 3, respectively. All of the samples examined exhibit relatively enriched amounts of PAHs (Table 2, Figs. 6); however, the relatively low abundance and absence of the 6-ring indeno[1,2,3-cd]pyrene and benzo[ghi]perylene in some samples suggests that there were no larger, high-temperature wildfires, either because of the humid-arid climate's insufficient seasonality or the limited input of terrigenous organic matter (Xu *et al*., 2019) (Table 2). The PAH ratios of Fla/(Fla + Py), BaA/(BaA + Chy), InPy/(InPy + B*ghi*P), and A/(A+P) have been proposed for assessing origins from fossil fuel/petroleum (petrogenic sources: thermal alteration of natural biolipids due to normal burial processes during diagenesis and catagenesis in sedimentary basins) or the combustion of biomass/solid fuel (pyrogenic sources) (Grice *et al*., 2007; Quiroz *et al*., 2011; Zakir Hossain *et al*., 2013; Fang *et al*., 2015; Huang *et al*., 2015; Yunker *et al*., 2015; Jiang and George, 2019; Xu *et al*., 2019). Relatively low values for these ratios (Fla/(Fla + Py) < 0.4; InPy/(InPy + B*ghi*P) < 0.2; BaA(BaA + Chy) < 0.2) collectively indicate petrogenic inputs, whereas high ratios (Fla/(Fla + Py) > 0.5; InPy/(InPy + B*ghi*P) >0.5; and BaA/(BaA + Chy) > 0.35) indicate pyrogenic sources (Jiang and George, 2019; Xu *et al*., 2019). Ratios of A/(A+P) >0.1 are typical of combustion-related sources, whereas ratios <0.1 are regarded as typical of petrogenic sources (Fang *et al*, 2015; Huang *et al*., 2015). The studied samples from the Gombe formation have values of Fla/(Fla + Py), BaA/(BaA + Chy), InPy/(InPy + B*ghi*P), and A/(A + P) range from 0.09 to 0.88, 0.08 to 0.97, 1.3 to 1.76, 0.09 to 1.0, respectfully (Table 3), indicating mixed inputs of petrogenic and pyrogenic sources in the shales. The samples analyzed fall within the range of fossil fuel/petroleum (petrogenic) origin and biomass/solid fuel combustion origin (Xu *et al*., 2019; Yunker *et al*., 2015), indicating that extensive wildfires did not occur in the studied area during the deposition of the Gombe Formation (Fig. 9). These parameters suggest a dominant petrogenic source for the PAHs, and in some samples a mixed fossil fuel/petroleum (petrogenic) and combustion (pyrogenic) source.

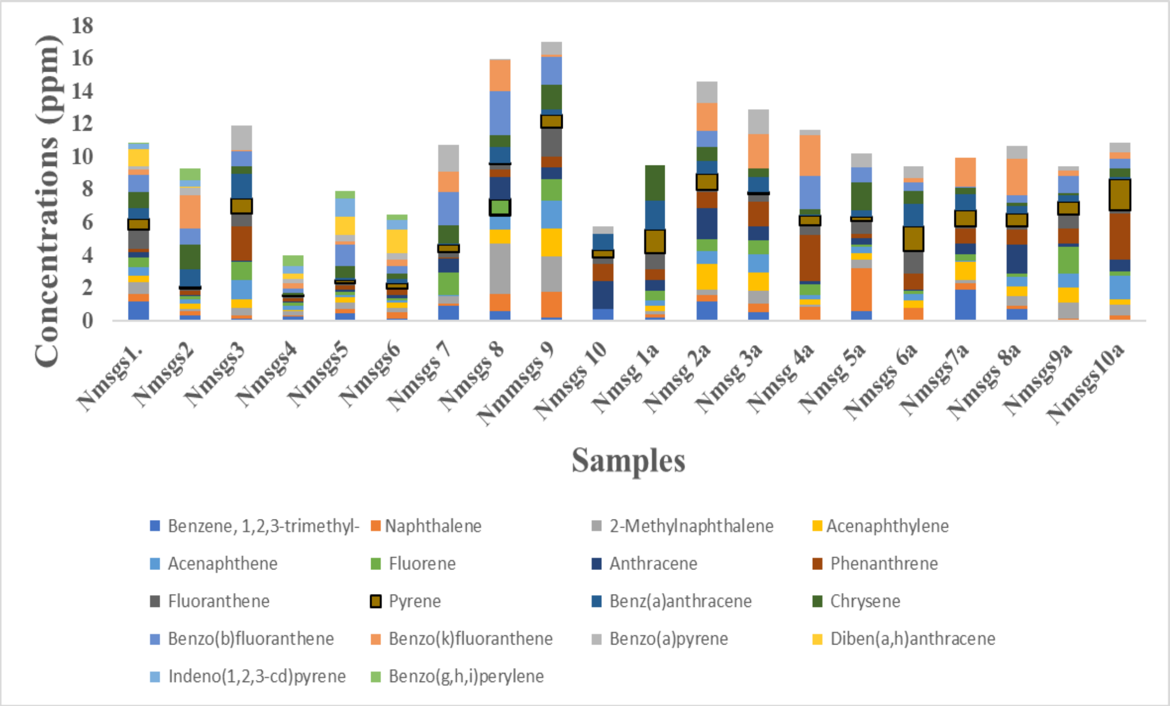


Fig. 6: The histogram showing the distribution of PAHs in Gombe shales

Table 2: Concentrations (ppm) of PAHs in the studied shales

Compounds	Nmsgs1.	Nmsgs2	Nmsgs3	Nmsgs4	Nmsgs5	Nmsgs6	Nmsgs7	Nmsgs8	Nmmsgs 9	Nmsgs10
Benzene, 1,2,3-trimethyl-	1.2	0.3	0.14	0.24	0.44	0.15	0.9	0.61	0.21	0.74
Naphthalene	0.4	0.28	0.15	0.11	0.25	0.39	0.12	1	1.52	N.D.
2-Methylnaphthalene	0.73	0.15	0.52	0.21	0.42	0.22	0.47	3.09	2.18	N.D.
Acenaphthylene	0.44	0.31	0.52	0.12	0.32	0.32	0	0.86	1.72	N.D.
Acenaphthene	0.52	0.25	1.14	0.22	0.13	0.15	0.05	0.86	1.72	N.D.
Fluorene	0.54	0.18	1.14	0.22	0.21	0.13	1.41	0.97	1.29	N.D.
Anthracene	0.32	0.11	0.02	0.02	0.11	0.23	0.87	1.36	0.7	1.66
Phenanthrene	0.25	0.22	2.13	0.21	0.28	0.32	0.03	0.49	0.7	1.06
Fluoranthene	1.16	0.17	0.8	0.12	0.13	0.03	0.36	0.32	1.72	0.37
Pyrene	0.65	0.12	0.87	0.08	0.22	0.32	0.4	0.06	0.82	0.49
Benz(a)anthracene	0.65	1.06	1.54	0.02	0.1	0.28	0.09	0.96	0.3	0.96
Chrysene	0.97	1.46	0.45	0.14	0.73	0.35	1.12	0.72	1.52	N.D.
Benzo(b)fluoranthene	1.05	1.01	0.92	0.22	1.33	0.41	2.04	2.69	1.67	N.D.
Benzo(k)fluoranthene	0.33	2.01	0.08	0.37	0.16	0.4	1.2	1.94	0.13	N.D.
Benzo(a)pyrene	0.18	0.49	1.49	0.23	0.4	0.4	1.66	0.06	0.82	0.49
Diben(a,h)anthracene	1.05	0.05	N.D	0.33	1.12	1.44	N.D.	N.D.	N.D.	N.D.
Indeno(1,2,3-cd)pyrene	0.33	0.37	N.D	0.44	1.12	0.58	N.D.	N.D.	N.D.	N.D.
Benzo(g,h,i)perylene	0.03	0.76	N.D	0.66	0.45	0.36	N.D.	N.D.	N.D.	N.D.

* N.D = Not determined

Table 2: Contd

Compounds	Nmsg1a	Nmsg2a	Nmsg3a	Nmsg4a	Nmsg5a	Nmsgs6a	Nmsgs7a	Nmsgs8a	Nmsgs9a	Nmsgs10a
Benzene, 1,2,3-trimethyl-	0.21	1.17	0.49	0.05	0.57	0.06	1.91	0.7	N.D.	0.02
Naphthalene	0.15	0.41	0.52	0.77	2.6	0.76	0.4	0.19	0.14	0.29
2-Methylnaphthalene	0.21	0.3	0.79	0.14	0.57	0.04	0.18	0.59	0.98	0.69
Acenaphthylene	0.33	1.6	1.14	0.31	0.37	0.41	1.09	0.59	0.88	0.32
Acenaphthene	0.33	0.75	1.14	0.31	0.37	0.41	0.09	0.59	0.88	1.41
Fluorene	0.61	0.71	0.8	0.63	0.19	0.18	0.35	0.19	1.6	0.29
Anthracene	0.65	1.95	0.87	0.19	0.36	0.1	0.69	1.77	0.21	0.68
Phenanthrene	0.65	0.95	1.54	2.8	0.28	0.97	0.9	0.91	0.96	2.82
Fluoranthene	0.97	0.15	0.45	0.6	0.74	1.38	0.14	0.23	0.85	0.19
Pyrene	1.45	0.94	0.08	0.64	0.31	1.53	0.99	0.78	0.73	1.94
Benz(a)anthracene	1.76	0.84	0.92	0.06	0.35	1.35	0.99	0.46	0.4	0.13
Chrysene	2.15	0.82	0.52	0.32	1.74	0.76	0.4	0.19	0.14	0.49
Benzo(b)fluoranthene	N.D.	0.97	0.02	1.99	0.88	0.56	0.04	0.48	1.09	0.59

Benzo(k)fluoranthene	N.D.	1.74	2.13	2.5	0.02	0.28	1.75	2.21	0.32	0.39
Benzo(a)pyrene	N.D.	1.28	1.49	0.36	0.85	0.69	N.D.	0.78	0.27	0.59
Diben(a,h)anthracene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Indeno(1,2,3-cd)pyrene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo(g,h,i)perylene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

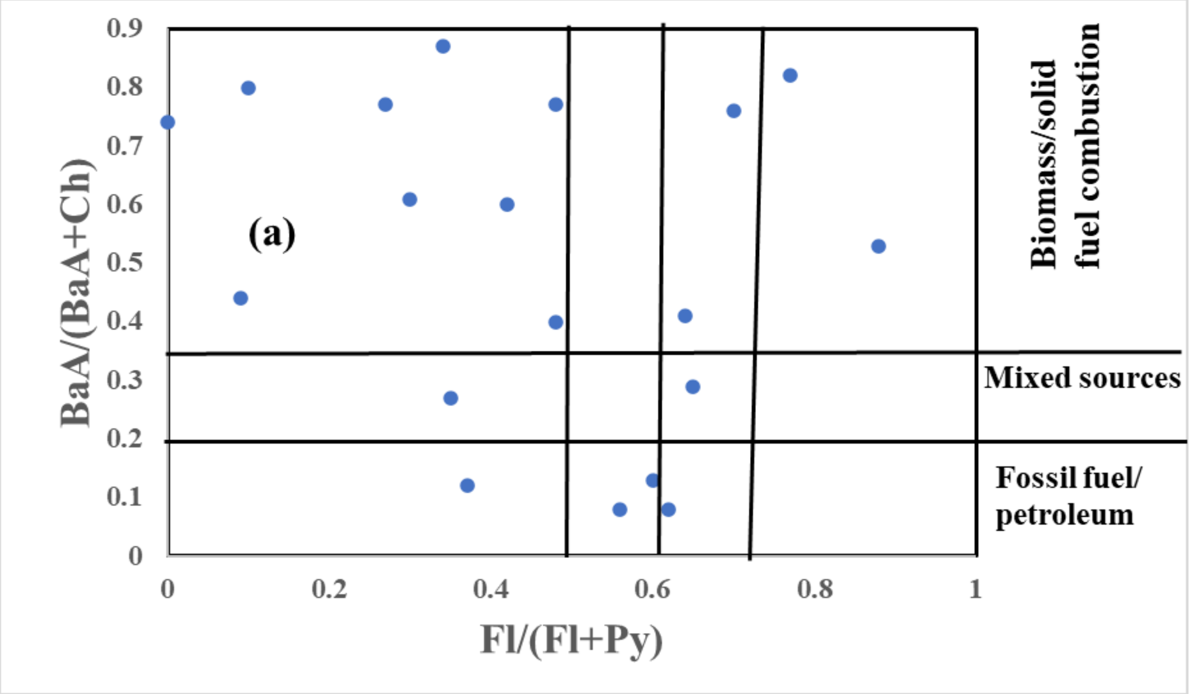
Table 3: Geochemical ratios computed PAHs in the studied shales

Ratios	Nmsgs 1	Nmsgs 2	Nmsgs 3	Nmsgs 4	Nmsgs 5	Nmsgs 6	Nmsgs 7	Nmsgs 8	Nmsgs 9	Nsmgs10
FL/FL+PY	0.7	0.3	0.56	0.6	0.37	0.09	0.62	0.42	0.65	0
BaA/BaA+Ch	0.76	0.61	0.08	0.13	0.12	0.44	0.08	0.6	0.29	0.74
A/A+P	0.58	0.6	0.95	0.09	0.31	0.42	0.63	0.58	0.93	0
Inpy/Inpy+BghiP	1.3	1.76	N.D	1.66	1.45	1.36	N.D	N.D	N.D	N.D

*N.D= Not determineD; FL= Fluoranthene; PY= Pyrene; BaA= Benz[a]anthracene; Ch= Chrysene; A= Anthracene; P= Phenanthrene; Inpy= Indeno[1,2,3-cd]pyrene; BghiP= Benzo[ghi]perylene.

Table 3: Contd

Ratios	Nmsgs 1a	Nmsgs 2a	Nmsgs 3a	Nmsgs 4a	Nmsgs 5a	Nmsgs 6a	Nmsgs 7a	Nmsgs 8a	Nmsgs 9a	Nmsgs10a
FL/FL+PY	0.48	0.27	0.48	0.77	0.35	0.64	0.34	0.1	0.88	0.3
BaA/BaA+Ch	0.4	0.77	0.77	0.82	0.27	0.41	0.87	0.8	0.53	0.97
A/A+P	1	0.36	0.01	0.8	0.98	0.67	0.02	0.18	0.77	0.6
Inpy/Inpy+BghiP	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D



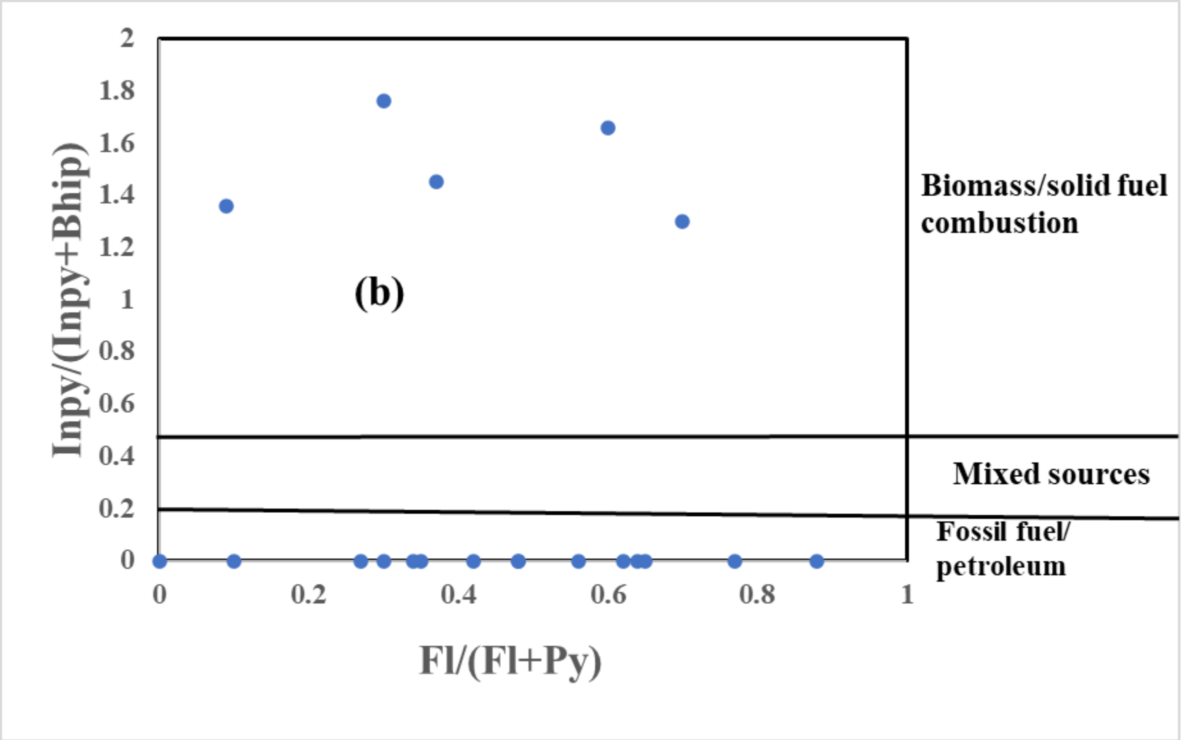


Fig. 7: PAHs ratio cross-plots for the Gombe shale samples, characterizing the origins of the PAHs (a) Fla/(Fla + Py) versus BaA/(BaA + Chy) and (b) Fla/(Fla + Py) versus InPy/(InPy + B*ghi*P) (after Xu *et al.*, 2019; Yunker *et al.*, 2015).

CONCLUSION

The n-alkane distribution in the samples ranges from C_8-C_{40} in most samples maximizing at C_{17}. This pattern of distribution indicates organic matter mainly derived from marine settings All the samples studied relatively showed enriched amounts of PAHs. However, the relatively low abundance and lack of the 6-ring indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene in some samples suggested the absence of larger, high-temperature wildfires, either due to inadequate seasonality of the humid-arid climate, or limited terrigenous organic matter input. The geochemical ratios computed from the n-alkanes and isoprenoids in the shales indicated mixed inputs of terrigenous and marine organic matter but with higher contribution from marine and deposited under oxidizing and reducing conditions with low – marginal maturity status. The geochemical ratios calculated from the PAHs indicated mixed inputs of petrogenic and pyrogenic sources for the shales but with major input from petrogenic sources. This study showed that biomarkers were effective in evaluating the origin, depositional conditions, and maturity of organic matter in the shales from the Gombe formation, Gongola Basin, Nigeria.

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