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Molecular geochemistry of Cretaceous Dukul Formation, Yola Sub-basin, Northern Benue Trough, Nigeria: Origin, paleoredox condition, and thermal maturity

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ABSTRACT

Molecular geochemical characterization “biological markers” of Cretaceous sediments of Dukul Formation in Yola sub-basin of Northern Benue Trough, northeastern Nigeria was conducted with the an objective of determining the organic matter source inputs or origin, paleodepositional or paleoredox conditions, preservation stages and overall assessment of thermal maturity in relation to the effect of Tertiary volcanic plugs in the Northern Benue Trough. However, based on preliminary lithostratigraphic description, the sections revealed shelf or perhaps, shallow marine depositional environment for the sediments of Dukul Formation. The samples of Dukul Formation consist of a mixed terrestrially and aquatic or marine organic matter source origin. They were interpreted to be deposited under suboxic/dysoxic depositional condition to relatively anoxic marine conditions but with a dominance of the terrigeous organic matters. Biomarker maturity parameters suggest that the analyzed shale samples of Dukul Formation have reached the early to peak stage of maturity and this suggest peak-hydrocarbon generation. Hydrocarbon might have been generated and could be finding elsewhere in the basin. Thus, the Tertiary volcanic plugs in the Northern Benue Trough had enhanced thermal maturation of these samples.

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1. Introduction

Prior to a substantial commitment for petroleum oil and gas exploration in the Nigerian frontier inland sedimentary basins, a preliminary evaluation of a basins geochemical and petrological potential (e.g., organic matter source quality, quantity, and maturity) was carried out by some earlier workers particularly on Northern Benue Trough (Akande et al., 1998; Abubakar, 2014, and among many others). Most of the earlier studies help researchers to select best sedimentary formations for further sedimentological, geophysical, and geochemical investigations.

The Yola Sub-basin is a frontier inland sedimentary basin within Benue Trough, Nigeria. At the moment, there is no adequate data available for hydrocarbon potential and resource assessment of the basin. However, this current study focuses on the biomarker characterization

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of the Cretaceous sediments of the Dukul Formation (Figs. 1 and 2). This is with the aim of assessing the organic matter origin, paleodepositional condition, thermal maturation and perhaps, the effect of volcanic intrusives on the sediments. The study could provide data based needed for petroleum exploration activity.

Petroleum exploration activities in Northern Benue Trough were not conducted for many years although Nigerian National Petroleum Corporation (NNPC) is presently working in the basin by conducting aeromagnetic, aerogravity, and seismic data acquisition. Poor subsurface geology knowledge and tectonic evolution could have been responsible for unsuccessful petroleum exploration attempt for many decades. The outcome of this research could provide relevant information needed to answer questions on source origin, conditions of depositional environment, and thermal maturity. As such molecular geochemical evaluation using the biomarkers had been accepted widely to characterizes paleodepositional environments of deposition, organic matter source origin, and thermal maturation of sediments (e.g., Peters et al., 2005).

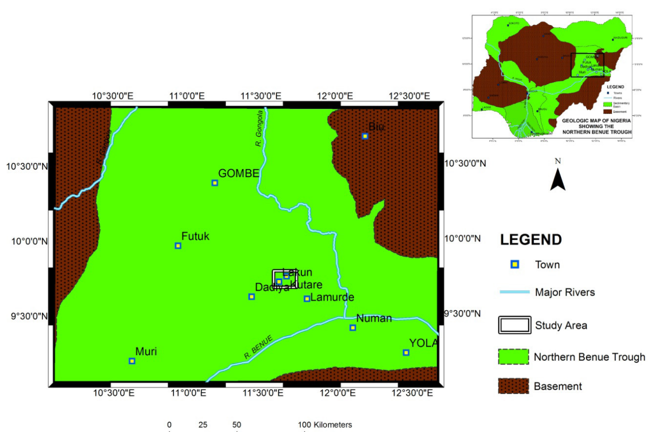

Figure 1. Geological map of Nigeria showing the study area represented as Open Square map and location of sedimentary sections (modified after Abubakar, 2014).

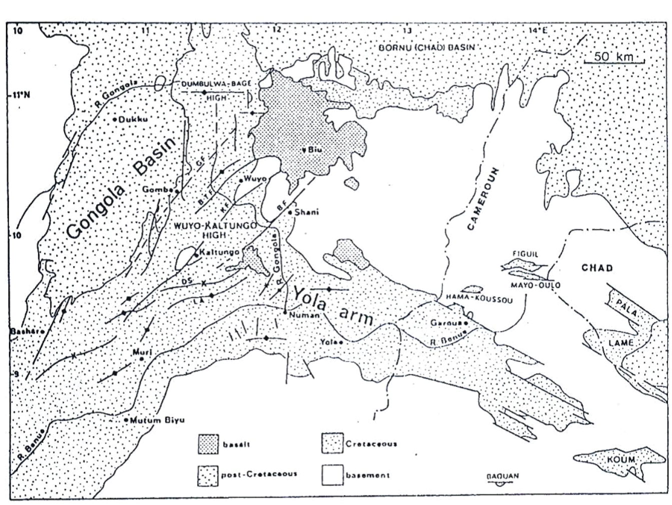

Figure 2. Outline geological map showing the main features of the Northern Benue Trough and study area (from Guiraud, 1990).

2. Geology

The Benue Trough is an intra-continental (Cretaceous to Paleogene) rift basin in Nigeria which formed in view of separation of the African and South American plates in Late Jurassic to Early Cretaceous (Nwajide, 2014). It extends up to 1,000 km in length and 50 km in width. Many authors presented tectonic models for the evolution of Benue Trough, e.g., King (1950) suggests movement by tension which results in rifting. Rift-Rift-Failed model was proposed by Grant (1971). Benkhelil (1989) and Guiraud (1990) suggests faulting as the tectonic process for the evolution and defined Benue Trough as a pull-apart basin.

The Benue Trough was seperated into Southern, (Lower) Central (Middle) and Northern (Upper)

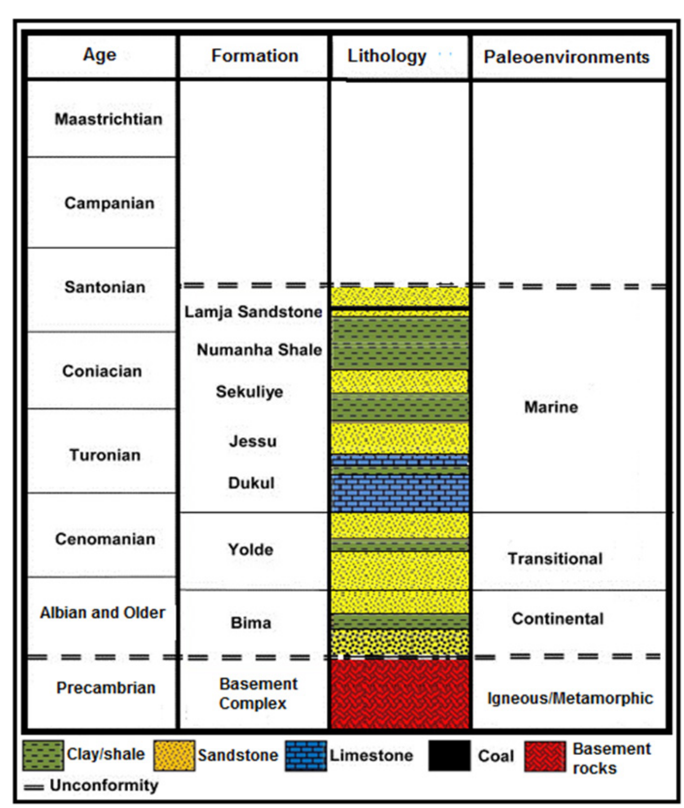

Figure 3. Stratigraphic sequence of the Yola Sub-basin (Sarki Yandoka et al., 2015).

Benue portions (Abubakar, 2014). The Northern Benue Trough consists of Gongola Sub-basin and Yola Sub-basin. The basins were earlier investigated by Falconer (1911) who mapped the area on a regional scale in his work geology and geography of Northern Nigeria. Moreover, the geology of Northern Benue Trough was systematically described by Carter et al. (1963) who defined it structural and stratigraphic framework and named most of the identified formation in the area which are currently in use with little modification. Stratigraphy of Yola Sub-basin (Fig. 3) comprises of the Aptian-Albian Bima Formation that was overlying conformably by the Cenomanian Yolde Formation. Sequences of shale and limestone of Dukul Formation, sandstone/mudstone of Jessu Formation, the Sekuliye Formation, Numanha (Shale), and the Lamja Formation were deposited in Yola Sub-basin.

According to Carter et al. (1963), Dukul Formation was deposited in an oxygen deficient sub-littoral marine environment. Mamman et al. (2007) suggested deposition in anoxic coastal to open marine (inner to middle-self) environment. Based on preliminary organic geochemical studies, Obaje et al (2000), Abubakar (2014), and Sarki Yandoka et al. (2015) interpreted the organic matter of the formation to be deposited in a sub-oxic environment with substantial terrigeneous source input. Based on ammonites (Vascoceras, Paravascoceras, Gombeceras, and Pseudotissotia), Carter et al. (1963) dated the Dukul Formation as lower Turonian. The early to basal middle Turonian shale with subordinate limestone and siltstone occurring between the Yolde and Jessu Formation in the Northern Benue Trough belongs to the Dukul Formation. The unit crops cut in the Dadiya, Reme, and Bobbin Syncline. The formation also occurs east of the Languda Plateau and in the Yola arm and south of the Benue River. The Formation corresponds to the lowest sub-division of the limestone—shale series of Falconer (1911).

3. Materials and Methods

Thorough fieldwork was conducted to study the sedimentary logs of the Cretaceous Dukul Formation from Yola Sub-basin, exposed at Kutare and Lakun areas. Ten (10) fresh outcrop shale and mudstones samples of the Dukul Formation were collected. The quality of rock might differ from one location to another. The samples were thick and hard, laminated but texturally feasible. The sedimentary logs were recorded using measuring tape and log sheet. Coordinate points and field photographs were recorded from outcrops using camera, compass and Global Positioning System (GPS).

The samples were crushed and about 30 g was selected for soxhlet extraction for 72 hours using organic solvents; dichloromethane and Methanol (93:7). The extractable bitumens were separated into aliphatic compounds, aromatic, and Nitrogen Sulfur and Oxygen (NSO). They were fractionated using column chromatographic method using 50 ml of petroleum either for saturated, 50 ml of DCM for aromatic, and 25 ml of menthol for NSO, respectively. The saturated fractions were dissolve in hexane and analyzed by Gas chromatography (Agilent 7890 model)-mass spectrometry (GC-MS). The oven temperature program has initial temperature of 600°C to hold for 2 minutes at 120°C/minutes and final temperature of 300°C to hold for 10 minutes. The fingerprints (fragmentograms) acquired were used for biomarker identification, which was quantified by measuring peak height in m/z 85, m/z 191 and m/z 217 mass fragmontograms.

4. Results and Discussion

4.1. Lithostratigraphic sections

In the study area, Dukul Formation in the study area composed of shales, limestone, and siltstone. The limestone beds are evenly distributed at Lakun. In most of the sections, the lithofacies composed of shales with interbedded limestone measures about 2.5 m. These limestones are grain-supported and consists of gastropods and bivales (Figs. 4–7). In some few instances, limestones occur as two facies; the shelly and crystalline limestone facies. Shelly limestone is highly fossiliferous with fossils and occurs frequently in both localities whilst siltstone beds occur in the middle and toward the top of the Kutari and Lakun sections.

4.2. Molecular geochemistry

4.2.1 n-alkanes and acyclic isoprenoids

The normal alkanes and acyclic isoprenoids shows saturates in m/z 85 between n-C_{12} – n-C_{33} n. The analyzed samples indicates bimodal n-alkane distribution with a dominance of long chain molecular weight HC compounds. Pristane and phytane occur in high amounts (see Fig. 8), with pristane/phytane ratio (1.20–2.68) (Table 1). Moreover, lower amount of acyclic isoprenoids compared to n-alkanes shows low pristane/n-C_{17} and phytane/n-C_{18} ratio ranging from 1.12 to 1.86 and 0.68 to 0.76, respectively (Table 1) and carbon preference index (CPI) values range from 1.45 to 0.79.

4.2.2. Terpanes and steranes

Figures 9 and 10 show hopane and steranes distributions for this study (Tables 2 and 3). The m/z 191

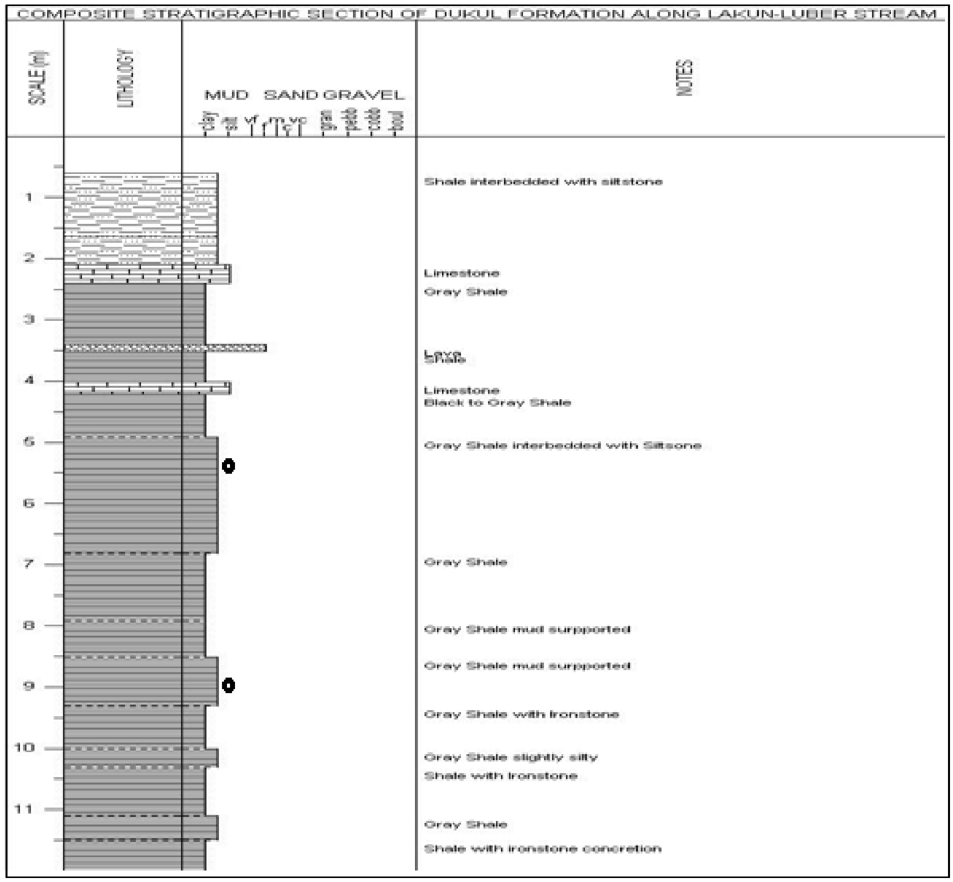

Figure 4. Lithostratigraphic section of Dukul Formation at Lakun-luber stream.

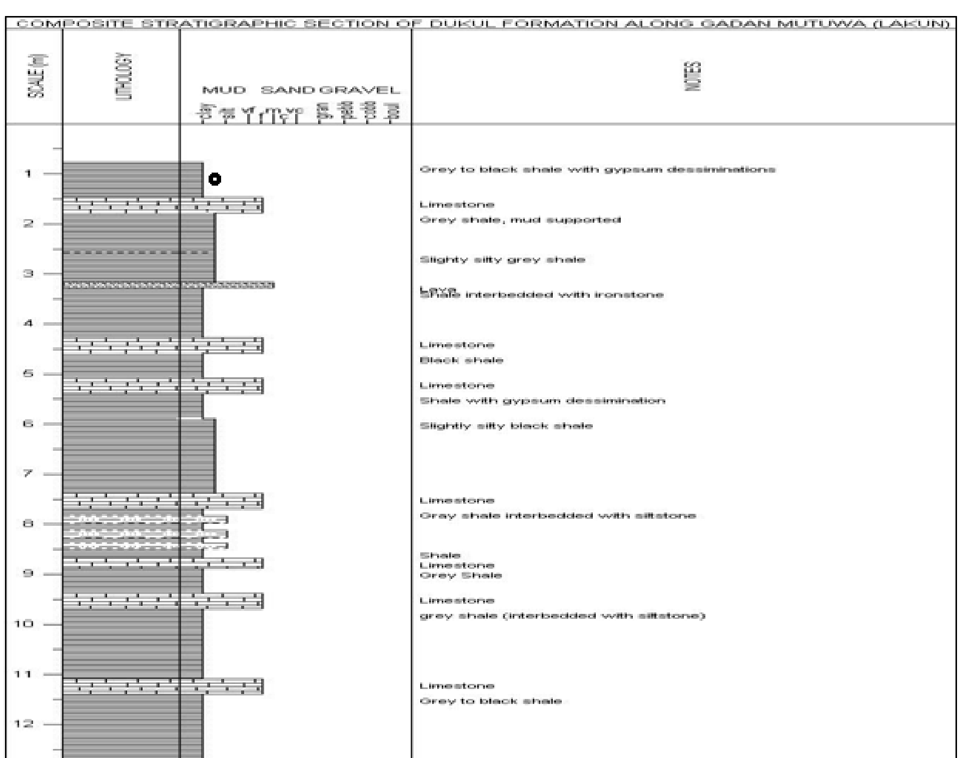

Figure 5. Lithostratigraphic section of Dukul Formation at Gadan mutuwa (Lakun).

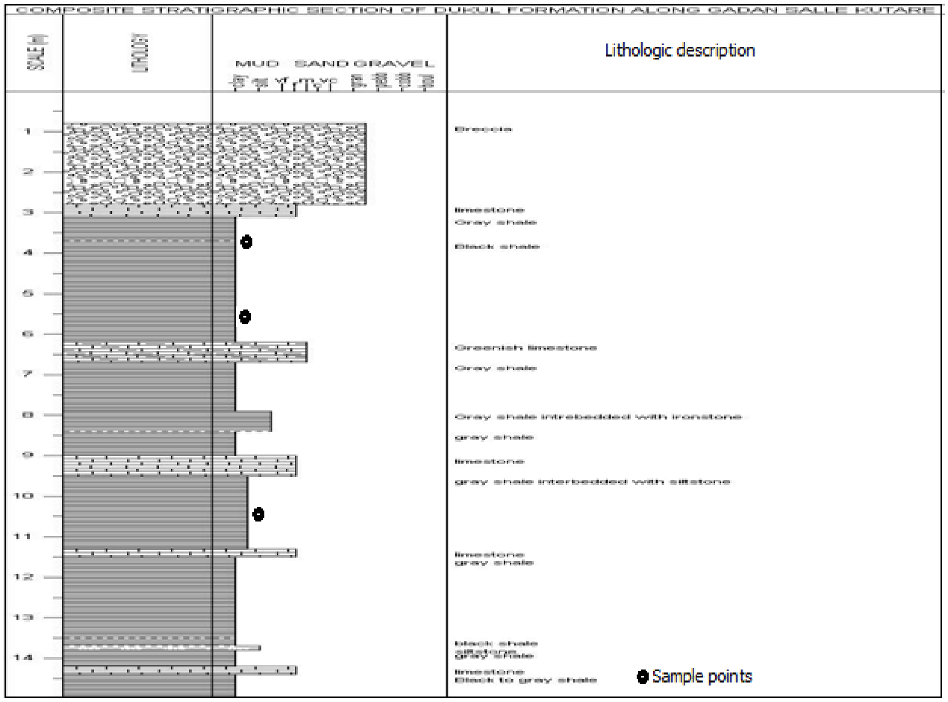

Figure 6. Lithostratigraphic section of Dukul Formation at Gadan tsalle Kutare.

Figure 7. Field photo of shale beds of Dukul Formation in the study areas.

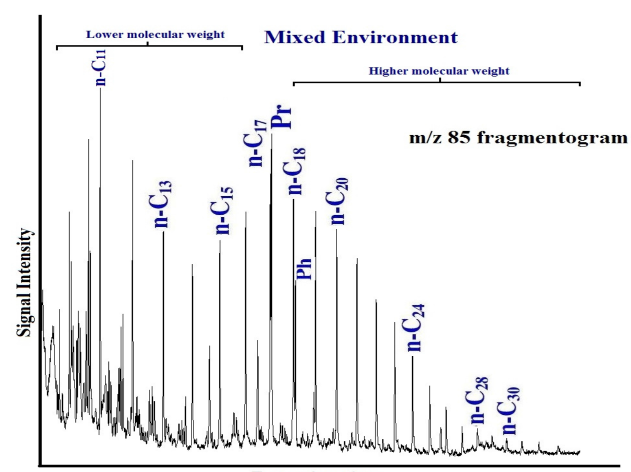

Figure 8. Representative of a saturated hydrocarbon fraction (m/z 85).

mass fragmontograms show that T_m is higher than T_s in with T_m/T_s ratios 0.90 (0.33–1.80) and (T_s/T_s + T_m) ratios 0.63 (0.5–0.75). Concentration of tricyclic terpanes is higher than tetracyclics (Table 2) with high C_{24}/C_{26} lower to moderate C_{24}/C_{23} and C_{22}/C_{21} and high C_{26}/C_{25} tricyclic terpane ratios (Table 2). Steranes and diasteranes are present in with relative proportions of regular steranes (C_{27}, C_{28}, and C_{29}) varying greatly; C_{29} (53.36–27.44) C_{27} (25.48–41.20) and compare to C_{28} (21.15–31.33).

4.2.3. Organic matter source input/origin

The source origin of organic matter shows that long chain n alkenes (>$^{n\text{-}}C_{25}$) are characteristics biomarkers

Table 1. n-alkanes and isoprenoid ratio of studied samples.

Sample ID	Foramtion	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	C P I	n-alkanes maximum
L_2 G/Matuwa	Dukul	2.68	1.86	0.72	1.10	C_{17}
L_3 G/Matuwa	Dukul	1.20	1.12	0.71	1.48	C_{19}
Lakun L_1	Dukul	1.97	1.44	0.70	1.01	-
L_1 Kutare	Dukul	1.84	1.13	0.68	1.03	C_{17}
L_2 kutare	Dukul	2.16	1.74	0.76	0.79	C_{17}
Average		1.97	1.45	0.71	1.08	
Range		(1.20–2.68)	(1.12–1.86)	(0.68–0.76)	(1.48–0.79)	

CPI—Carbon Preference Index (1): $\{2(C_{23} + C_{25} + C_{27} + C_{29}) / (C_{22} + 2[C_{24} + C_{26} + C_{28}] + C_{30})$.

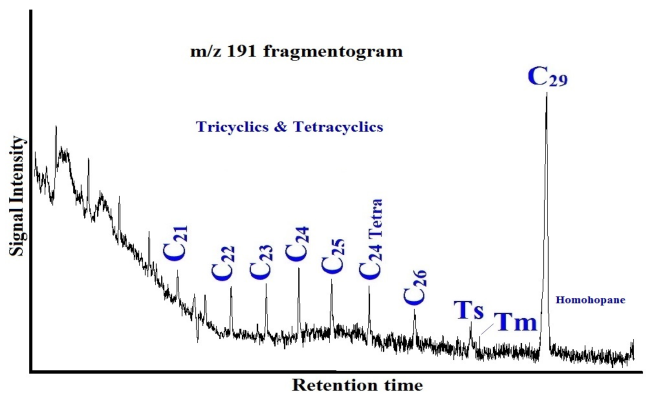

Figure 9. A typical mass fragmentogram (m/z 191) of terpenoids.

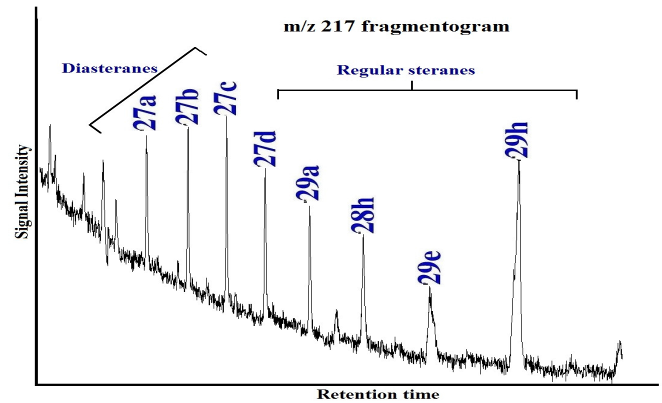

Figure 10. A typical mass fragmentogram (m/z 217) of steranes.

Table 2. Hopane biomaker parameters calculated from m/z 191 chromatograms.

Sample ID	Formation	Thermal maturity		Source input and paleodeposition condition							
		Tm/Ts	Ts/Ts + Tm	*C19T/C23T*	*C21T/C23T*	*C22T/C21T*	*C24T/C23T*	*C26T/C25T*	*C24TEt/C26T*	*C23T/C24T*	*C23T/C24TEt*
L_2 G/Matuwa	Dukul	0.33	0.75	0.89	5.15	0.15	1.1	0.66	1.25	0.90	1.33
L_3 G/Matuwa	Dukul	1.0	0.5	0.72	3.07	0.13	0.62	0.55	1.36	1.6	2.66
Lakun L_1	Dukul	1.8	0.64	-	0.25	1.83	1.04	0.66	1.16	0.96	0.75
L_1 Kutare	Dukul	-	-	-	-	-	-	-	-	-	-
L_2 Kutare	Dukul	0.5	0.66	0.9	0.65	1.88	1.25	0.59	1.58	0.8	1.00
Average		0.90	0.63	0.83	2.28	0.99	1.00	0.61	1.33	1.06	1.45

of higher terrestrial plant (Sarki Yandoka et al., 2015), while the short-chain n-alkanes (>n-20) are predominantly found in algae and microorganisms (Peters et al., 2005). The n-alkanes of the study samples shows a mixed organic matter with appreciable input of terrigineous source material as further backed by moderate CPI ratio (>1.08). T_m/T_s ratios of 0.90 (0.33–180) in the analysed sample further indicate samples contain a mixed of aquatic organic matter and terrestrial plant.

Peters et al. (2005) shows that tricyclic terpanes are normally associated with marine sources. The Dukul extracts have relatively high tricyclic tarpanes compare to tetracyclic which is consistent with a mixed contribution of aquatic and terreginous organic matter source inputs (Adegoke et al., 2015). It is agreed that the relative amounts of C_{27}–C_{29} steranes can be used to give indication of source difference (Fig. 11). The predominance of C_{29} and C_{27} in the analyzed samples

Table 3. Sterane biomaker parameters calculate from m/z 217 fragmetograms.

Sample ID	Formation	Thermal maturity		Source input and paleo deposition condition				
		Ster C2920s (20*s* + 20*R*)	*Ster C29ββ* ββ + αα	*C27 Ster %*	*C28 Ster %*	*C29 Ster %*	*C27 Ster/* C_{27} + C_{29}	$^{Ster}C_{29}/_{Ster}C_{27}$
L_2 G/Matuwa	Dukul	0.19	0.54	25.48	21.15	53.36	0.32	2.09
L_3 G/Matuwa	Dukul	0.73	0.55	26.96	22.47	50.56	0.34	1.87
Lakun L_1	Dukul	0.41	0.54	41.20	31.31	27.47	0.6	0.6
L_1 Kutare	Dukul	0.25	0.48	27.46	25.90	46.63	0.37	1.69
L_2 Kutare	Dukul	0.73	0.55	26.96	22.47	50.56	0.34	1.87
Average		0.46	0.53	29.61	24.65	45.71	0.39	1.62
Range		**(0.19–0.73)**	**(0.48–0.55)**	**(25.48–41.20)**	**(21.15–31.33)**	**(53.36–27.44)**	**(0.32–0.6)**	**(0.6–2.09)**

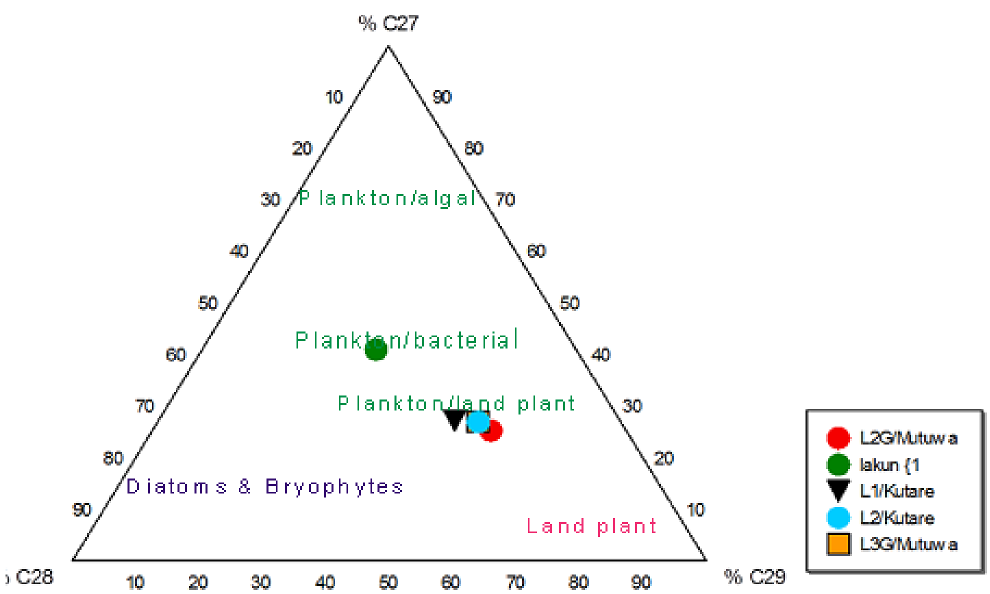

Figure 11. Ternary plot showing the relationship between regular sterane composition and source input [modified after Peters et al. (2005)].

clearly show organic source mainly from mixed terrestrial and marine organic source. This is in agreement by low to moderate C_{29}/C_{27} Steranes ratios (Table 3) and also supported with a significant amount of land plant as indicated by the regular steranes ratio in the turnery diagram (Adegoke et al., 2014; Peters et al., 2005; Sarki Yandoka et al., 2015).

4.2.4. Paleodepositional condition

The pristane/phytane (Pr/ph) ratio is one of the important correlation parameters used to indicate or define redox condition which is believed to be sensitive to diagenetic condition (Peters et al., 2005). Pr/ph ratios below unity (1) indicate highly reducing depositional condition (anoxic), between 1 and 3 sub-oxic condition and high pr/ph ratios <3 as associated with oxidizing depositional condition (oxic) (Hunt, 1996; Sarki Yandoka et al., 2015). In this regards, the pr/ph ratios (1.20–2.68) average 1.92 (Table 1) of the analyzed Dukul Formation indicate sub-oxic deposition condition. The pr/n-C_{17} and ph/n-C_{18} ratio (Fig. 12) also suggest sub-oxic condition, hence supported by plot of pristane/n-C_{17} versus phythane/n-C_{18}, pr/ph Vs CPI and plot of $C_{23}T/C_{24}T$ against C_{24} + or/$C_{26}T$ (Figs. 13 and 14). Cross-plot of C_{29}/C_{27} regular steranes versus pristane/phytane ratios also supported suboxic condition (Fig. 15).

4.2.5. Maturity of organic matter

Biomarker maturity indicators used to evaluate the level of thermal maturity of the organic matter of the studied shale of Dukul Formation are C_{29} sterane ββ

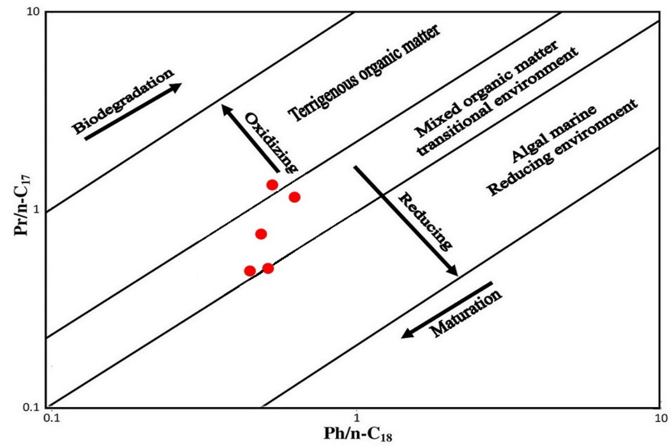

Figure 12. A plot of pristane/n-C17 versus phytane/n-C18 for the investigated samples [modified after Adegoke et al. (2015)].

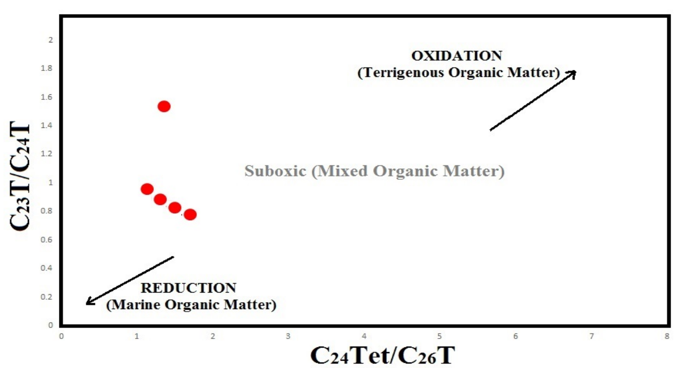

Figure 13. Cross-plot of C23T/C24T versus C24Tet/C26T, also showing increasing terrigenous input in the study samples [modified after Sarki Yandoka et al. (2015)].

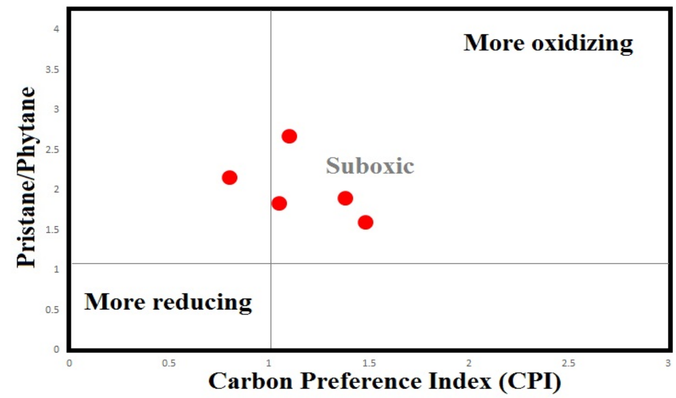

Figure 14. A plot of Pristane/phytane versus CPI, indicating the depositional environment conditions of the studied samples [modified after Adegoke et al. (2015)].

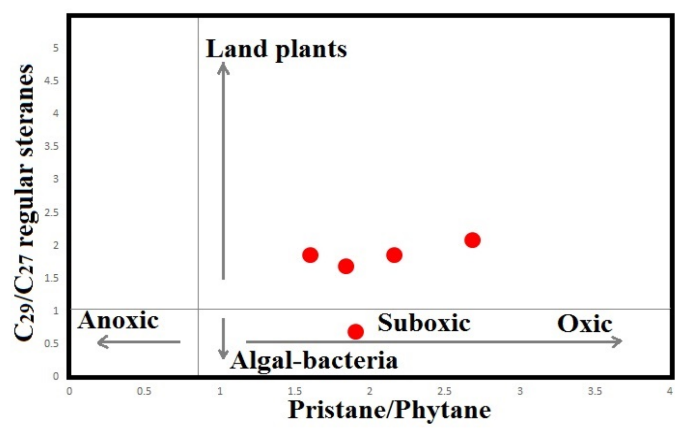

Figure 15. Cross-plot of C_{29}/C_{27}) regular steranes versus pristane/phytane ratios showing depositional environment conditions and source input.

(ββ + αα) (Table 3) which increase with increasing maturity (Peters and Moldwan, 1993; Sarki Yandoka et al., 2015). The analyzed sample of Dukul Formation have (ββ / ββ + αα) C_{29} ratio in the range of (0.48–0.55) average of 0.53 and T_s (T_s + T_m), 20S/20S + 20R) ratios also suggested that the organic matter is thermally mature and also supported by CPI values of the studied sample are close to one ranging from 0.79 to 1.4 with average of 1.08 indicating maturity. The analyzed shale samples are thermally mature and have already reached oil window and the shales samples reached high thermal maturity level.

5. Conclusions

The biomarker characterization of the Cretaceous Dukul Formation from the Yola sub-basin, Northern Benue Trough, NE Nigeria was performed in order to determine the organic matter source inputs, paleodepositional condition, and the thermal maturity and has consequently revealed the following findings:

- Sedimentological (lithologic description) of the studied sedimentary sections indicate that Dukul Formation was deposited in a shelf "shallow marine" environment under low-oxygen levels as strongly supported by the biomarker chracterization,
- The composition and distribution of the biomarkers indicates that the analyzed shale samples have mixed terrestrially-derived and aquatic/marine organic matter source inputs deposited under suboxic to relatively anoxic marine conditions. Thus, the samples were relatively preserved under oxygen free condition,
- The biomarker maturity parameters also suggested that the analyzed samples have reached early to peak stages of hydrocarbon generation.

It is, therefore, suggested that the samples had undergoes high level of thermal maturity probably due to Tertiary volcanic intrusions known to be present in the basin.

- However, biomarkers are only commonly presence within oil window and occur in very low amount or virtually absence in gas window. In the Dukul samples, the tricyclic terpanes and diasteranes/steranes increases at high levels (late oil window) whilst moretane/hopane relatively decreases (late oil window) and homohapones are depleted. This is due to high thermal maturity experienced by the samples.

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