



## Application of Tetracyclic Polyprenoid Biomarkers in Yola Basin of the Northern Benue Trough, Northeast Nigeria: Implications for Source Origin and Paleoenvironment



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### ABSTRACT

Tetracyclic polyprenoids biomarkers (TPP) were investigated on the Cretaceous sediments of Yola Sub-basin based on gas chromatography-doublet mass spectrometry. This is with an objective to re-examine the organic source input and paleodepositional environment of the sediments. The study revealed that the Bima shales were deposited in the lacustrine environment under suboxic to relatively anoxic depositional condition while the analysed Yolde, Dukul, Jessu, Sekuliye and Numanha shale sediments were deposited within the marine environment under suboxic depositional condition. More so, the analysed Lamja coal and shale samples were deposited in a delta environment under oxic to suboxic depositional condition. The study therefore, suggest that the paleodepositional environments of the studied shale sediments within the Yola Sub-basin remain as continental (lacustrine), transitional (marine and delta) and could have the potential to generate appreciable quantity of oil and gas.

### Keywords:

Sediments,  
Tetracyclic,  
Biomarkers,  
Cretaceous,  
Yola Basin.

### INTRODUCTION

Sedimentary biomarkers that are generally related to algal input but of a non-specific nature were earlier studied by the petroleum geochemist (Peters and Moldowan, 1991, 1993). Biomarker characterization of the lacustrine and marine depositional systems is more complex, because they have a wider range of paleoredox conditions (Peters et al. 2005). There are biomarker indicators that are specific to fresh and brackish water; algal organic matter input of tetracyclic polyprenoid (TPP) compounds. These compounds had become available as provided by Holba et al. (1999, 2000). It was previously observed that the C<sub>30</sub> tetracyclic polyprenoid (C<sub>30</sub> TPP) isomers are in elevated concentrations relative to the algal steranes. The TPP compounds (C<sub>30</sub>) were also observed in Early Cretaceous lacustrine oils from West Africa and far eastern lacustrine oils (Holba et al. 2003).

In general, tetracyclic polyprenoids (TPP) are mostly observed in samples that are derived from low-salinity (e.g. fresh to brackish lacustrine environments) but they are generally present in low levels in samples that are derived from saline environments. The TPP ratios, together with other environmental indicators such as 4-methyl steranes or hopane/sterane ratio are used to

distinguish between marine and non-marine source rocks (Holba et al. 2003; Adegoke et al. 2015). However, biomarker characterisation using Gas chromatography-Mass spectrometry (GC-MS) of the saturated hydrocarbon extracts of Cretaceous formations within the Yola Sub-basin was conducted by Akande et al. (1998) and Sarki Yandoka et al. (2015).

Biomarkers were previously studied on the sediments of Northern Benue Trough (Obaje et al. 2004; Abubakar et al. 2008; Sarki Yandoka et al. 2015) using normal alkanes, isoprenoids, terpanes and steranes. However, there is no reported work on biomarkers based on tetracyclic polyprenoids. This study therefore, present the tetracyclic polyprenoids (C<sub>30</sub> TPP) biomarkers analysed using Gas-chromatography-Doublet Mass Spectrometry (GC-MS/MS) of the shale extracts within the Yola Sub-basin. This is aimed to re-examine the organic source inputs or origin and paleodepositional environment of the sediments. It is expected that this study will help in petroleum source rock assessment of the Northern Benue Trough.

### Geologic and Location of Study Area

The Benue Trough is an intra-continental (Cretaceous to Paleogene) rift basin in Nigeria which formed due to separation of the African and South American plates in Late Jurassic to Early Cretaceous (Nwajide, 2013). It extends up to 1000 km in length and 50 km in width. Many authors presented tectonic models for the evolution of Benue Trough. King, (1950) suggests movement by tension which results in rifting. Rift-Rift-Failed (RRF) 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 separated into

Southern, (Lower) Central (Middle) and Northern (Upper) Benue portions.

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), Sarki Yandoka et al. (2014) and many others, who defined its structural and stratigraphic framework. Carter et al. (1963) named most of the identified formations in the area which are currently in use with little modification.

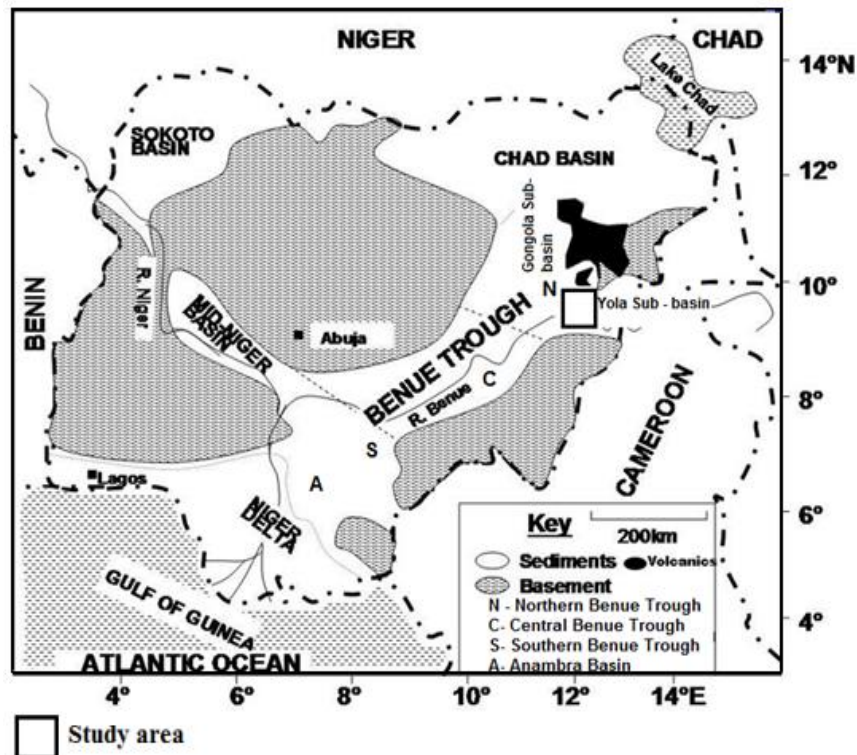


Figure 1: Geological map of Nigeria showing the study area (after Abubakar, 2006)

The sediments of the Yola Sub-basin are associated with Tertiary volcanics (Sarki Yandoka et al., 2014; Sarki Yandoka, et al. 2015). The oldest lithostratigraphic unit in the basin (Fig. 2) is the Aptian–Albian thick continental Bima Formation that unconformably overlies the Precambrian crystalline basement rocks. The Bima Formation was overlain by the transitional Yolde

Formation followed by the coastal-shallow marine sequences of Dukul, Jessu and Sekuliye Formations, Numanha Shales (Formation) and deltaic Lamja Formation in the Yola Sub-basin (Carter et al., 1963; Zarborski et al., 1997). The Lamja Formation marked the end of sedimentation in Yola Sub-basin.

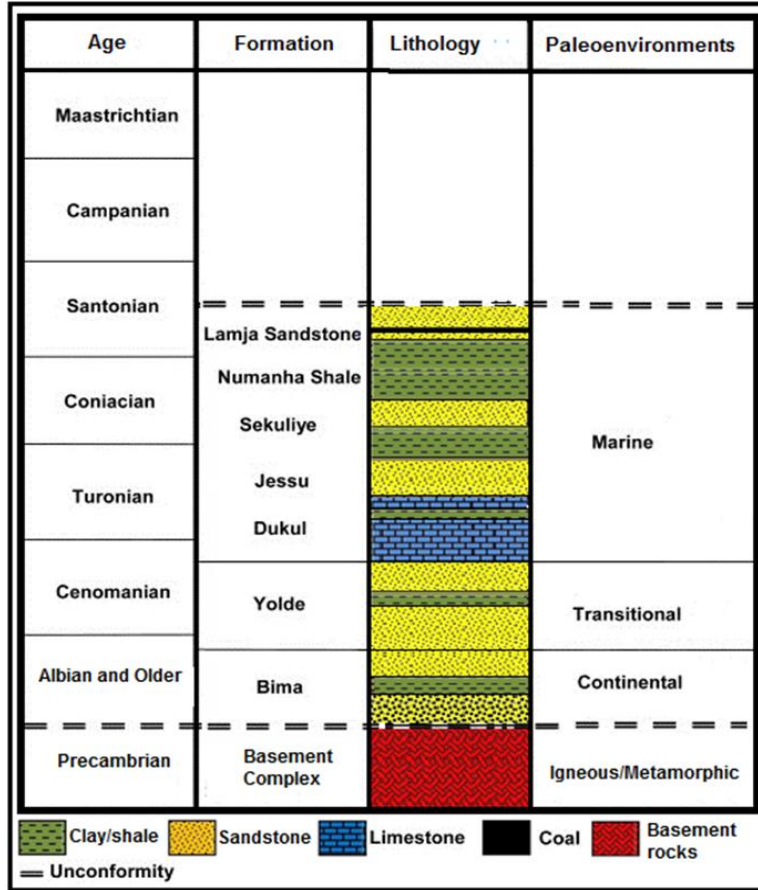


Figure 2: Stratigraphic sequence of the Yola Sub-basin (Sarki Yandoka et al., 2015)

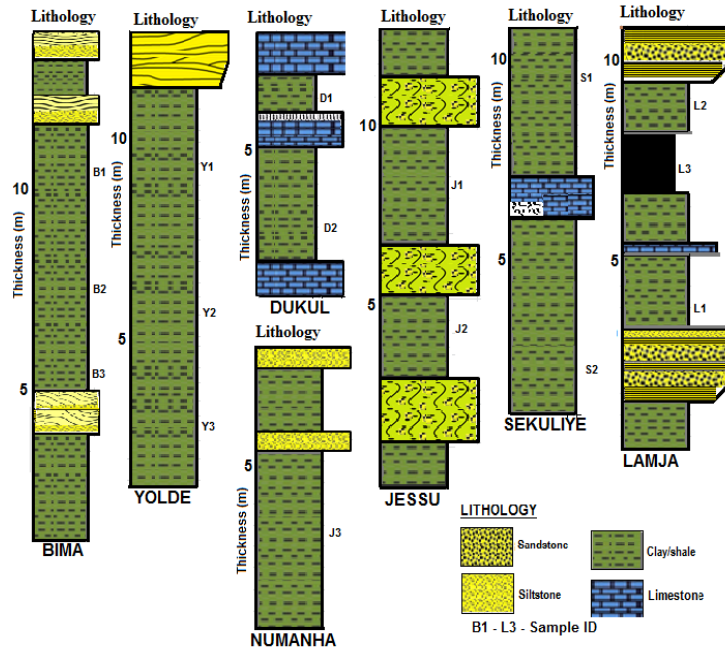


Figure 3: Lithostratigraphic sections showing the sampling areas

## MATERIALS AND METHODS

Standard fieldwork was conducted on the sediments of Yola Sub-basin from Upper Benue Trough. Twelve (12) shale samples were collected and crushed to fine powder. The crushed samples were subjected to soxhlet extraction in a Soxhlet apparatus for 72 hours, using an azeotropic mixture of dichloromethane (DCM) and methanol (93:7). The extracts were fractionated using liquid-column chromatography, into aliphatic, aromatic and NSO (nitrogen, sulfur and oxygen) compound. Gas chromatography mass spectrometry/mass spectrometry (GC-MS-MS) analysis of the aliphatic hydrocarbon fractions were performed on an Agilent 7890A gas chromatograph equipped with a split/splitless injector (280°C) and fitted with fused silica capillary column (60 m × 0.25 mm i.d) coated with 0.25 μm film thickness. This was linked to an Agilent7000B Triple Quadrupole mass spectrometer (electron voltage 70 eV, filament current 50uA, source temperature 230 °C, quad temperature 40 °C, multiplier voltage 1400 V, and interface temperature 300 °C). The following parent-to-daughter ion transitions were undertaken for the following compounds: m/z 372 → 217 (C<sub>27</sub> steranes), m/z 386 → 217 (C<sub>28</sub> steranes), m/z 400 → 217 (C<sub>29</sub> steranes), m/z 414 → 217 (C<sub>30</sub> steranes), m/z 414 → 259 (C<sub>30</sub> tetracyclic polyprenoid), m/z 358 → 217 (C<sub>26</sub> 27-norcholestanes). The GC-MS/MS analysis was carried out at the Department of Geology, University of Malaya, Malaysia.

## RESULTS AND DISCUSSIONS

### C<sub>30</sub> tetracyclic polyprenoid (TPP)

The C<sub>30</sub> tetracyclic polyprenoid biomarkers are most prominently observed in samples derived from low salinity, i.e. fresh to brackish lacustrine environments, and are generally present in low levels in samples derived from saline, i.e., marine and saline lacustrine, environments. The C<sub>26</sub> 27-norcholestanes as the most consistent parameter representing fresh/brackish water organic input and are derived from diagenetic processes upon C<sub>27</sub> steroids. They are low in lacustrine samples and prominent in marine samples (Holba et al., 1999, 2000, 2003).

The C<sub>30</sub> tetracyclic polyprenoids (TPP) compounds were calculated as follows: [TPP Ratio = (2 x peak Ta) / (2 x peak Ta) + Σ20R steranes)] (Σ20R are from C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub> regular steranes). Sterane data, especially regular steranes, can also be acquired from the GC-MS-MS using appropriate parent to daughter transitional ions. These include m/z 372 → 217 (C<sub>27</sub> steranes), m/z 386 → 217 (C<sub>28</sub> steranes), m/z 400 → 217 (C<sub>29</sub> steranes) and m/z 414 → 217 (C<sub>30</sub> steranes). Other compounds that can be measured are C<sub>30</sub> tetracyclic polyprenoid (m/z 414 → 259) and C<sub>26</sub> 27-norcholestanes (m/z 358 → 217). Based upon the mass spectrum of the C<sub>30</sub> TPP compounds, a tetracyclic polyprenoid structure was anticipated and subsequently confirmed by mass spectral comparison with two authentic synthesized reference compounds (2a, b) as described by Holba et al., (2003).

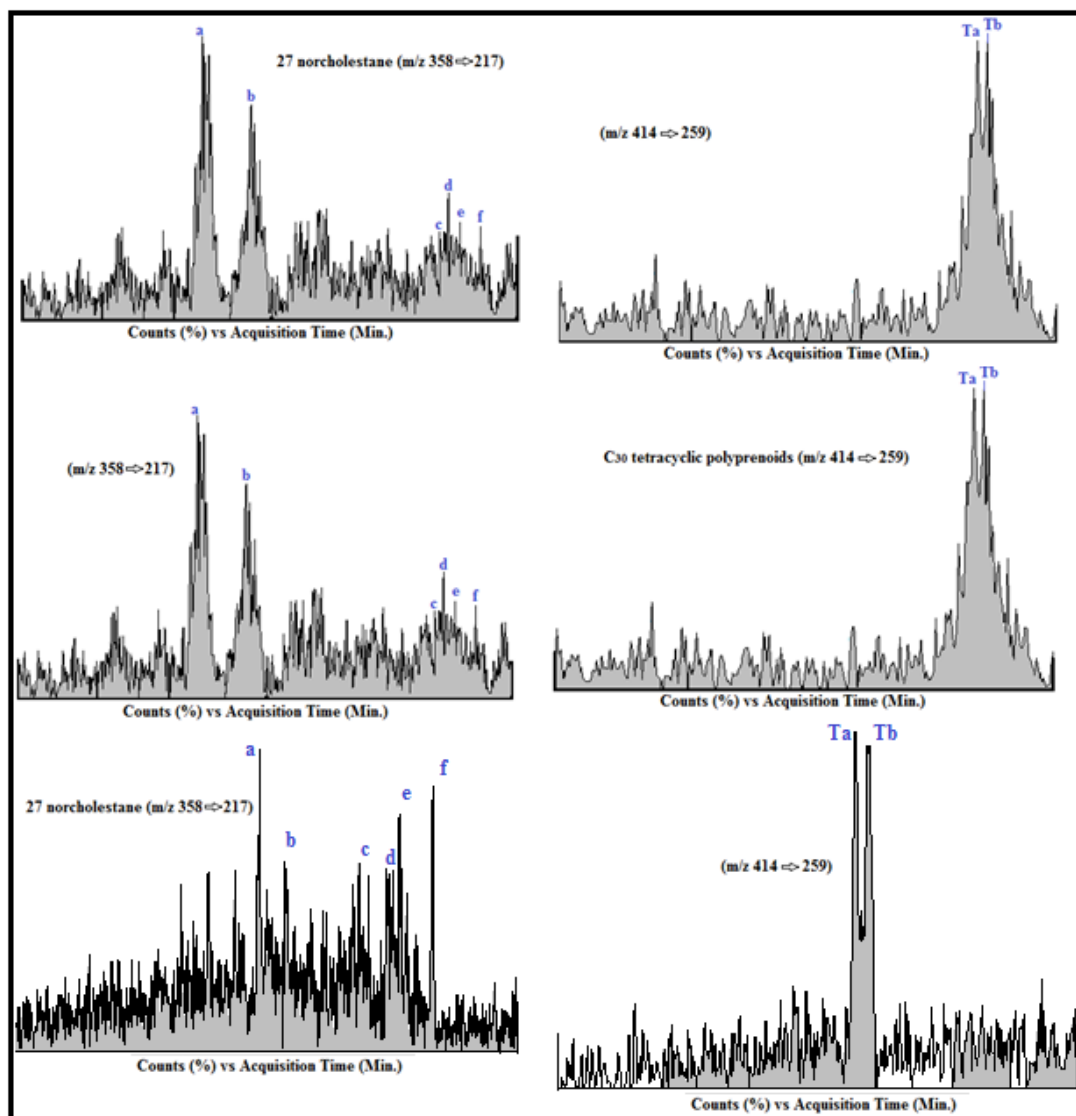


Figure 4: Selected biomarker fingerprints of the C<sub>30</sub> tetracyclics and 27 – norcholestanes of the studied shale extracts

Oils derived from source rocks deposited in fresh/brackish water depositional environments shows elevated C<sub>30</sub> TPP compounds relative to steranes. In this study, the C<sub>30</sub> tetracyclic polyprenoids 21R (Ta) and 21S (Tb) isomers were determined on m/z 414 - 259 and 27-norcholestanes and on m/z 358 - 217 from GC-MS/MS transitions performed on selected samples (Fig. 4). A TPP ratio > 4.0 indicates lacustrine oils whilst marine and

deltaica oils displayed values < 0.4 (Holba et al., 2003). The TPP ratios of the Bima shale samples ranges from 0.41–0.48 while they are present in analysed shale samples of Yolde, Dukul, Jessu, Sekuliye and Numanha, they range from 0.23-0.32 (Table 1). In the Lamja shales and coals, the TPP ratios are generally present in low concentration ranging from 0.23-0.27.

**Table 1: Sterane biomarkers calculated from the GC –MS-MS fragmentograms**

Sample ID	Formation	Lithology	Steranes	
			Hopanes/ (Hopanes + ? 20R steranes)	TPP ratios
B1	Bima	Shale	1.09	0.46
B2	Bima	Shale	1.16	0.43
B4	Bima	Shale	1.04	0.42
Y1	Yolde	Shale	0.57	0.26
Y2	Yolde	Shale	0.56	0.30
D1	Dukul	Shale	0.54	0.27
D3	Dukul	Shale	0.55	0.32
J1	Jessu	Shale	0.58	0.28
J4	Jessu	Shale	0.59	0.26
S1	Sekuliye	Shale	0.59	0.25
S3	Sekuliye	Shale	0.54	0.27
N1	Numanha	Shale	0.57	0.26
N2	Numanha	Shale	0.56	0.24
L1	Lamja	Shale	0.72	0.24
L2	Lamja	Shale	0.71	0.26
L3	Lamja	Coal	0.78	0.25

Diasterane/sterane ratio: C29 diasteranes/C29 regular steranes

TPP ratio:  $2 \times \text{peak Ta} / (2 \times \text{peak Ta} + ? 20\text{R steranes})$

#### Source inputs and paleoenvironment

TPP ratios of the Bima shale sediments are relatively high, ranging from 0.41–0.48 with an average value of 0.44% indicating that the samples were deposited in freshwater lacustrine environment. This is supported by high hopane/sterane ratios which indicate fresh/brackish water conditions (Holba et al., 2003) and the plot of TPP ratios against Hopanes/Hopanes+ $\Sigma$ 20R steranes (Fig. 5) which indicates a lacustrine depositional environment. Moreover, the high ratios of hopane/sterane (2.73-28.40)

in the analysed Yolde, Dukul, Jessu, Sekuliye and Numanha shale sediments also support a marine depositional environment. This also concurs with the finding based on C<sub>30</sub> tetracyclic polyprenoids (TPP) ratios indicating that the shale samples were deposited in a marine environment. C<sub>30</sub> tetracyclic polyprenoids (TPP) ratios plotted against hopane/(hopane+ $\Sigma$ 20R steranes) of the analysed Lamja coal and shale samples indicates deposition in a deltaic environment.

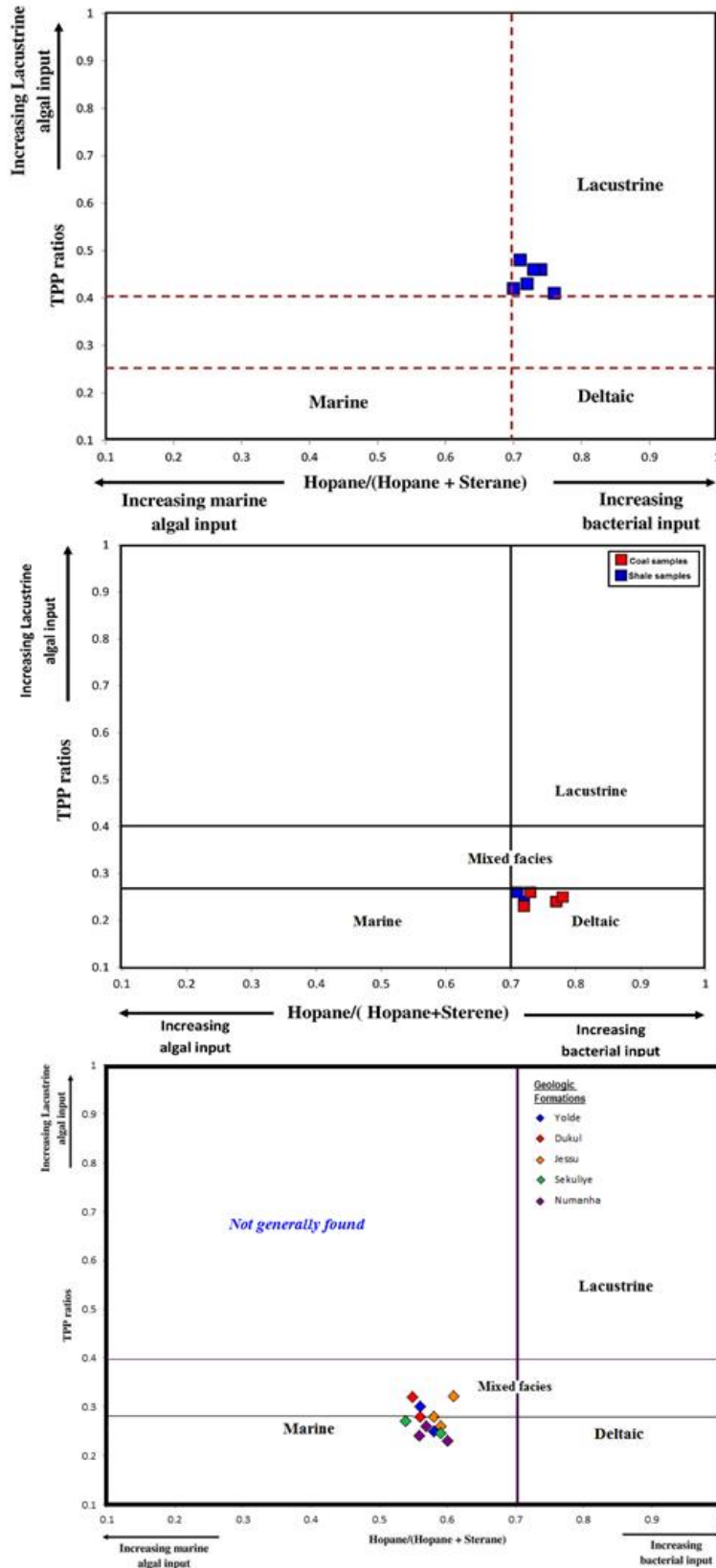


Figure 5: Cross plots of TPP ratios versus hopane/(hopane+Σ20R steranes) indicating lacustrine, marine and delta depositional environments of the studied shale sediments (as slightly modified after Holba et al. 2003)

The fresh water algae that contribute TPP compounds could have evolved and adapted to shallow transitional marine environments and become tolerant of salinities ranging from marine to brackish conditions. These adapted organisms might also contribute the TPP compounds in the near-shore marine to transitional facies. Low values of TPP ratio may occur in some lacustrine source rocks and oils when the algal source of the TPP compounds is sufficiently diluted by other organic inputs (e.g., terrigenous plant matter), or if the environment is not conducive to the growth of the algae responsible for biosynthesizing the TPP compounds (saline to hypersaline conditions). Marine source rocks and their derived oils from around the world typically have low values of TPP ratio.

### CONCLUSION

Tetracyclic polyprenoids biomarkers (TPP) analysis is a powerful tool for recognition of fresh/brackish water algal input into the depositional setting of oil source rocks, especially when used in conjunction with other geochemical indicators. The Bima shale sediments were deposited in freshwater lacustrine environment under low salinity stratified column and suboxic paleodepositional condition as supported by high hopane and sterane concentrations. The TPP ratios of the analysed Yolde, Dukul, Jessu, Sekuliye and Numanha shale sediments indicate deposition in marine environment under suboxic paleodepositional condition whilst the analysed Lamja coal and shale samples were deposited in a delta environment under oxic-suboxic paleodepositional condition. This shows that, the C<sub>30</sub> tetracyclic polyprenoids reaffirm the paleodepositional environment of the Cretaceous sediments in Yola Sub-basin as continental (lacustrine), transitional (marine and delta) and could have the potential to generate appreciable quantity of oil and gas.

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