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Pyrolysis analysis, organic petrology, and thermal effects of volcanics on Bima Formation shales, Yola Sub-basin, Northern Benue Trough, Nigeria

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ABSTRACT

The shale sediments of Bima Formation from the Yola Sub-basin of the Northern Benue Trough, northeastern Nigeria were studied based on pyrolysis analysis (rock-eval pyrolysis) and organic petrology (vitrinite reflectance and palynofacies) to determine the thermal effects of Tertiary (Neogene) volcanics on the organic matter thermal maturity. The study revealed that shale samples are of Type III and Type IV kerogens. This indicates high thermal maturity level and classified the samples as late-oil window to post-mature stage of hydrocarbon generation. This high thermal maturity could be attributed due to the Tertiary volcanic intrusion in most part of the basin. The samples, however, appeared as a good source of oil- and gas-prone hydrocarbons. This study, therefore, suggests that the initial oil and gas-prone of the Type II and II-III kerogens in the shales have been cracked into thermogenic gas probably due to the high thermal effects of Tertiary volcanic intrusion in the basin. This has yield the present-day Types III and IV kerogens. The volcanic plugs, however, intruded the Cretaceous sedimentary successions of the Northern Benue Trough during the Tertiary period and as such, they enhanced thermal maturity of the organic matters within the shale samples.

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1. Introduction

Sedimentary rocks contain some components of organic matter. Perhaps, on a few occurrences, hydrocarbons oil and gas may contain appreciable quantity of inorganic materials (e.g., Tissot and Welte, 1983). In principle, petroleum generation and accumulations generally originated from organic matter that is deposited *in situ* with sedimentary rocks. More so, almost all the occurrences of hydrocarbons either in igneous or metamorphic rocks are linked with sedimentary source rock beds. Thermal alteration of the organic matter at high temperatures in sedimentary environment after a long period of time leads to the formation of hydrocarbons (Perregard and Schiener, 1979; Rinna et al., 1996; Sweeney and Burnham, 1990).

A pyrolysis method is based on heating of rock samples in such a way that evolved hydrocarbons are monitored in relation to temperatures. It is also the thermally induced breaking up of large molecular compounds to give lower molecular weight products (e.g., Taylors et al., 1998). Hydrocarbons are naturally produced and stored in rock. They are released at temperatures lower than that one needed in breaking down of kerogen. Pyrolysis method of hydrocarbons

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by steadily increasing temperature provides a way in obtaining the total amount of generated hydrocarbons, maturation process relative to generation potential.

Organic petrology, on the other hand, is the evaluation of source origin, distribution, and composition through transmitted light, incident light, reflectance light, and fluorescence light microscopy approaches. Application of organic petrology is most useful for thermal maturity determination and delineation of hydrocarbon windows through measurement of vitrinite reflectance from macerals and all other organic matter, such as zooclasts or solid bitumen. Determination of organo-facies is not possible when the organic sample reached gas window of thermal maturity and in this case, fluorescence microscopy is not useful as most of the organic matter is no longer autofluorescent (Alalade and Tyson, 2013; Peters and Cassa, 1994).

Considerable source rock determination parameters are used to evaluate the possibility of hydrocarbons in any sedimentary basin (Sarki Yandoka, 2015). More so, it is not only type or quality of organic matter is important for accumulation and generation of hydrocarbons but also the thermal maturation level. Dry gas and heavy oil could be found in immature rock facies, while oil and wet gas in mature facies and only the dry gas within the metamorphosed facies. Temperatures, pressure, and duration of exposure to various heats are the most important factors in controlling the thermal maturation of organic matter in sediment (Taylors et al., 1998).

However, Tertiary volcanic rock of Neogene age was earlier reported (Carter et al., 1963) and are present in some localized areas within the Northern Benue Trough particularly in the Yola Sub-basin (Sarki Yandoka, 2015). The volcanic plugs, however, intruded the Cretaceous sedimentary successions (Fig. 1) and thereby, enhanced thermal maturity for the organic matters (e.g., Zhu et al., 2007). The current study attempt to integrate rock eval pyrolysis data (T_{max}, S1, S2, and HI) and organic petrology (vitrinite reflectance and thermal alteration index) to investigate the shale sediments of Bima Formation from Yola Sub-basin of the Northern Benue Trough. This is with a view to assess the effect of Tertiary volcanic plugs, relationship of sediments with volcanic rocks, the organic matter maturity vis-a-vis original hydrocarbon generation potential (before intrusions) and present-day generation potential (after intrusions).

2. Geological Setting

The Benue Trough was formed during the Early Cretaceous rifting and strike-slip faulting or movement of the Central West African Basement Complex (Abubakar, 2014; Benkhelil, 1982; 1989; Carter et al., 1963; Guiraud, 1990; Obaje et al., 2004; 2006). Authors such King (1950), Grant (1971), Kogbe (1976), Benkhelil (1989), and many others suggested rifting and strike-slip fault as the basis for the evolution of the Benue Trough. The most widely acceptable evolutionary model for Benue Trough is that of Grant, (1971). The Benue Trough trends northeast-southwest for about 1,000 km in length and about 150 km average in its width. It is bounded by Niger Delta Basin at the southern end of the trough and the Chad (Bornu) Basin in the northern end. The trough contains thick Cretaceous-Cenozoic sedimentary profile for up to 6,000 m associated with volcanics of Tertiary (Neogene) age (Wright, 1976).

Based on geographical view, the Benue Trough is divided into Southern (Lower), Central (Middle) and Northern (Upper) Benue basins (Nwajide, 2013; Sarki Yandoka, 2015; Sarki Yandoka et al., 2014; 2015a; 2015b; 2016; Zaborski et al., 1997) (Fig. 1). The Northern or Upper Benue Trough consists of the N-S trending Gongola Sub-basin and E-W trending Yola Sub-basin (Fig. 1). The geology and stratigraphy of the Northern Benue Trough were described in detail by earlier workers, such as Carter et al. (1963), Abubakar (2014), Sarki Yandoka et al. (2014), Ojo and Akande (2000), Sarki Yandoka (2015), and many others.

The stratigraphic succession of the Yola Sub-basin (Northern Benue Trough) comprises the Berremian-Aptian to Albian continental sediments of Bima Formation consisting of mainly cobbles, gravels, sandstones, and shales/clays. Recent authors (e.g., Sarki Yandoka, 2015) sub-divided into two members; Lower Bima (B1) and Upper Bima (B2) members. The Bima Formation is overlying by the Cenomanian transitional (coastal and shallow marine) sediments of Yolde Formation. The Cenomainan Yolde Formation consists of sandstones, clays and occasionally calcereous materials (Sarki Yandoka et al., 2015). The sediments were succeeded by the marine Late Cenomanina—Turonian—Coniacian sequences of the Dukul, Jessu and Sekuliye Formations and Numanha Shales (Sarki Yandoka et al., 2016).

These shallow marine sediments are the lateral equivalents of Pindiga and Gongila Formations in the Gongola Sub-basin. The Lamja Formation, a delta sequences overlies the Numanha Shales (Fig. 3). The Dukul Formation generally consists of bedded shales and fossiliferous limestone (Carter et al., 1963). Its type locality is at Dukul village and the formation is also exposed at Cham, Lakun and Kutari areas. The formation was dated as Early to basal Middle

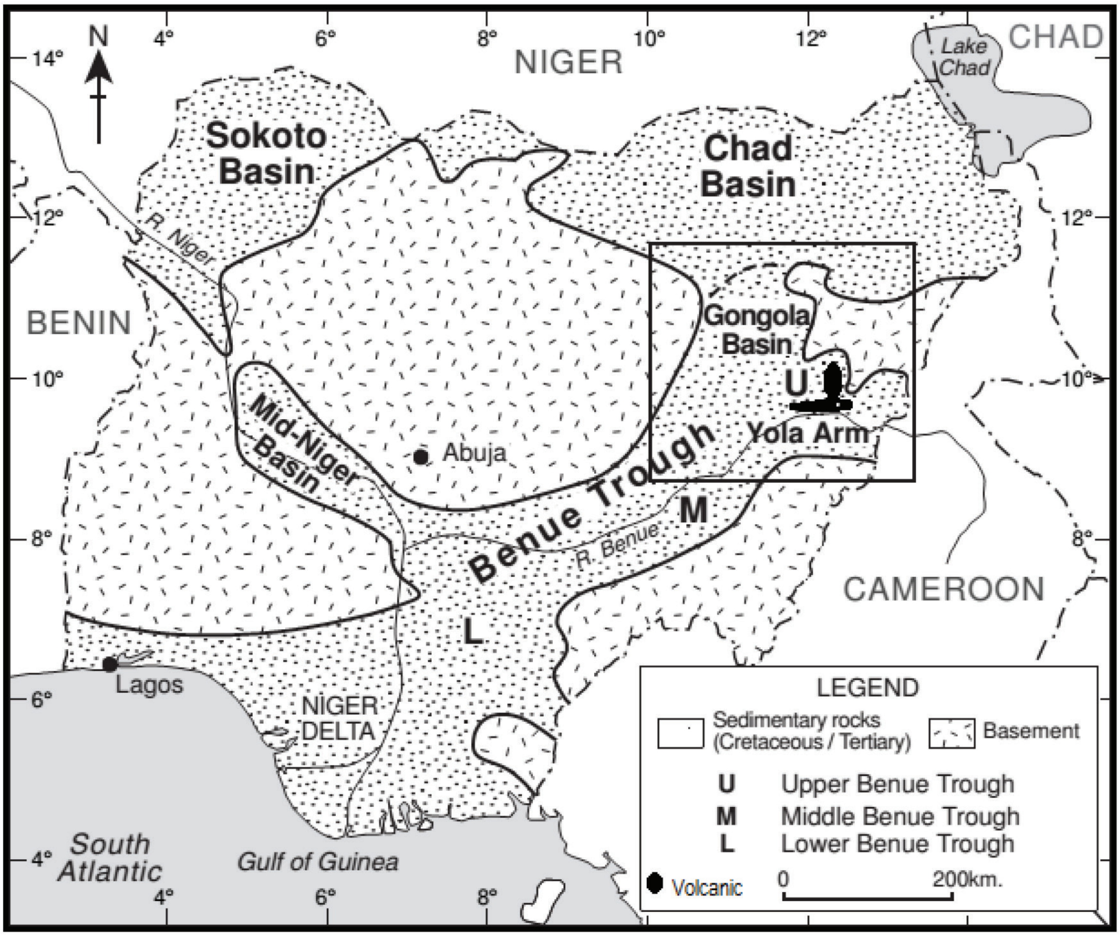

Figure 1. Generalized geological map of Nigeria showing volcanic and study area [modified after Abubakar et al. (2014)].

Turonian based on evidences of ammonites. Based on microfaunal assemblage, the formation was interpreted as deposition in littoral to open marine shelf environments.

The Dukul Formation composed of gray shales with thin limestone and siltstone beds. The thin limestone beds are evenly distributed with a thickness of 30 m. The lithofacies of the unit is composed of shales with thin interbedded of limestone. The limestones are grain supported and rich in bivalves and gastropods. The Jessu Formation (Fig. 2) consists of sandstones, mudstones, and shales. It was termed earlier as "Mudstone Shale Series" deposited by a brief regressive phase (Carter et al., 1963). Sandy mudstones are predominant in the lower part. It is considered to have being deposited during Upper Turonian and conformably overlies Dukul Formation (Nwajide, 2013).

The Sekuliye Formation is a sequence of shale and limestone with shale thicker than the limestone. The formation conformably overlies the Jessu Formation (Fig. 2). It consists of pale greenish—grey shale with bands of siliceous limestone (Offodile, 1976). Upper Turonian—Santonian age was assigned (e.g., Carter et al., 1963). The Numanha Shales composed of shale with bands of mudstone, sandstone, and limestone deposited in marine environment (Carter et al., 1963). The lower part consists of grey—black shale with occasional nodules and nodular beds of mudstones (Carter et al., 1963). It conformably overlies the Sekuliye Formation and was assigned to the Upper Coniacian (Akande et al., 1998; Carter et al., 1963; Nwajide, 2013).

The Lamja Formation (Fig. 2) consists of sandstone, shale, and coal. This formation was first described under the name "Carbonaceous Beds" and conformably overlies the Numanha Shales. It marks the end of sedimentation in the Yola Sub-basin during the Santonian (Carter et al., 1963; Nwajide, 2013). Tertiary volcanic plugs were reported and are localized at the boundary between the Gongola and Yola Sub-basins. They were believed to be unrelated to any specific tectonic control (e.g., Wright, 1976).

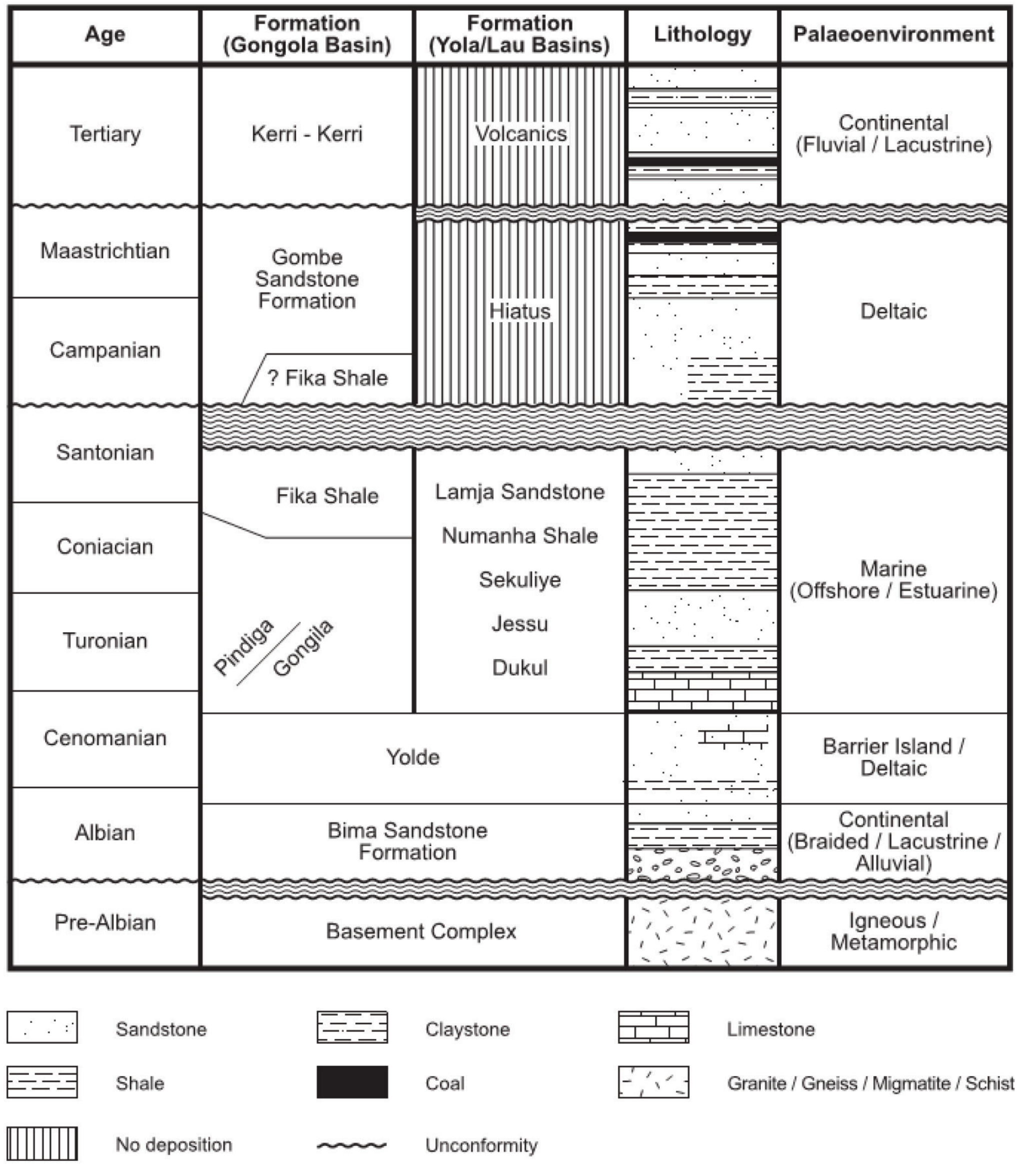

Figure 2. Stratigraphic succession of the Northern (Upper) Benue Trough [modified after Abubakar (2014).

3. Materials and Methods

The outcrop shale samples of the Bima Formation were collected during field studies at the core of Lamurde Anticline (Figs. 3 and 4). The Lamurde Anticline was formed during the Santonian tectonic inversion that affected the whole of Benue Trough. The collected samples were subjected to laboratory analyses. Pyrolysis method of analysis for a whole rock sample could be used to describe the hydrocarbon generation potential of prospective source rocks. At least, 50 g of each of the samples were crushed to powder. The crushed samples were analyzed at temperature of 600°C.

Some of the samples were crushed into pieces using pastel and mortar. The pieces samples were embedded in 30 mm moulds using epoxy resin and perhaps, hardened for some hours. Samples were ground with 350 (coarse), 550 (intermediate), 800 (fine), and 1,200 (very fine) silicon carbide powder and finally polished with 1 µm and 0.30 µm alumina powders and 0.04 µm OP-S suspension solution for final polishing. The polished samples were studied for vitrinite reflectance (%Ro) measurements and macerals identifications.

Few of the samples were treated with HCl and HF acids. The samples residues were washed with distilled or pure water up to the level where the pH is 7. The kerogen was separated from the remaining residue using heavy liquid gravity separation by applying zinc bromide ($ZnBr_2$). The remaining residue of collected kerogen was sequentially washed and set aside

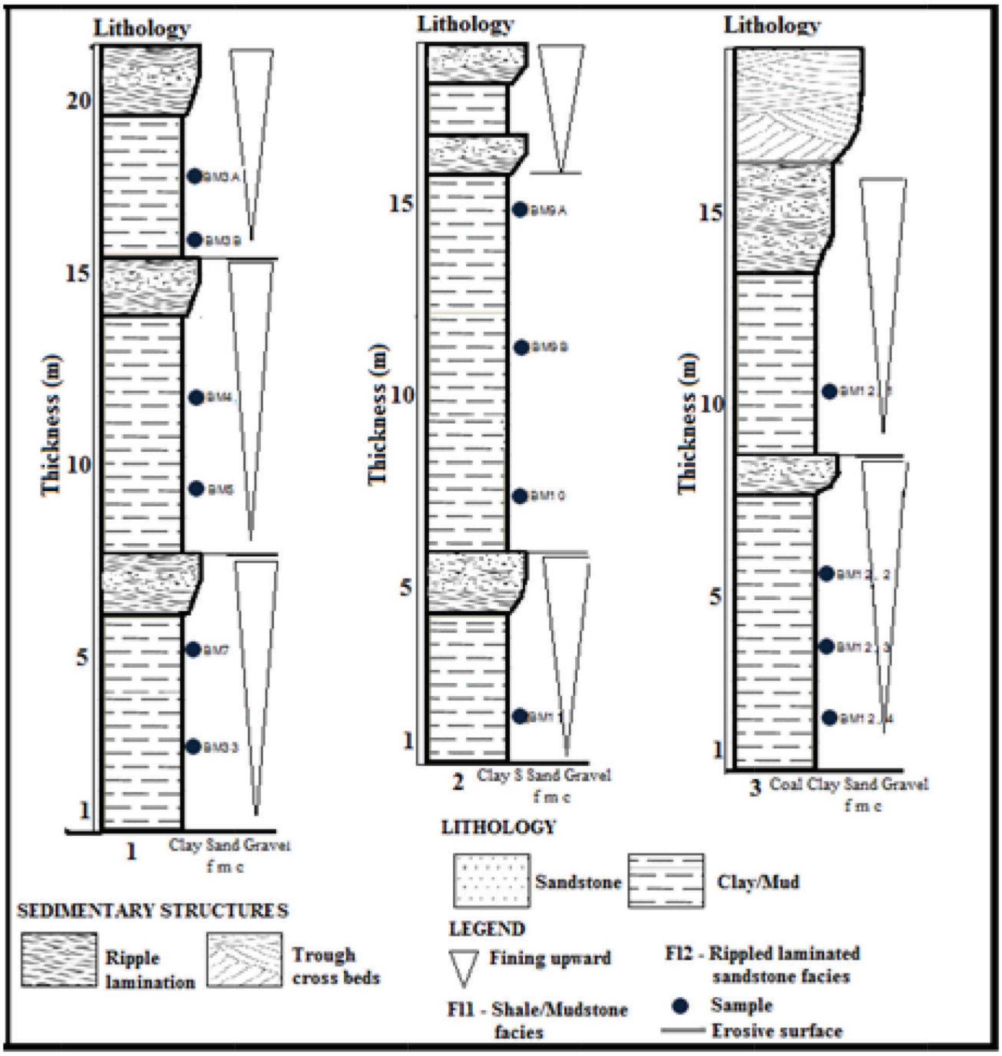

Figure 3. Sedimentary log sections showing the sampling horizon.

for palynofacies slide preparation while the remaining residue isolated kerogen was dried in oven at 30°C and used for pyrolysis gas chromatography (Py-GC) analysis.

4. Results and Discussion

4.1. Pyrolysis analysis

The bulk pyrolysis analysis of the shale samples was conducted (see Table 1). The results were used to determine the amount of the remaining organic matter before and after thermal cracking as well as the present-day hydrocarbon or oil-generation potential. However, minimum TOC accepted for a source rock facies should be more than 1% for any sediments (e.g., Peters and Cassa, 1994). As such, the analyzed shale samples are regarded as "poor to fair" source rocks based on high thermal maturities (T_{max}) and the Total Organic Carbon (TOC) values of 0.38 to 0.86 wt% and hydrocarbon yield (S2) in the range 0.17 to 0.69 mg/g (Table 1).

The pyrolysis hydrogen index plotted against temperature (T_{max}) data are used in classifying kerogen typing and source generative potential. In this study, the data generally reflects the present-day generation potential and it indicated that the organic matter within the shale samples are of Type III and Type IV kerogens (Fig. 5). This agrees and consistent with hydrogen index (HI) values range from 24 to 127 mg HC/g TOC. The samples are expected to generate major gas, and inert carbon as indicated by high level of thermal maturity indicated based on temperature T_{max} and PI values (Ebukanson and Kinghorn, 1986).

4.2. Organic petrology

Organic petrological parameter, such as vitrinite reflectance (%Ro) measurement, is widely accepted and

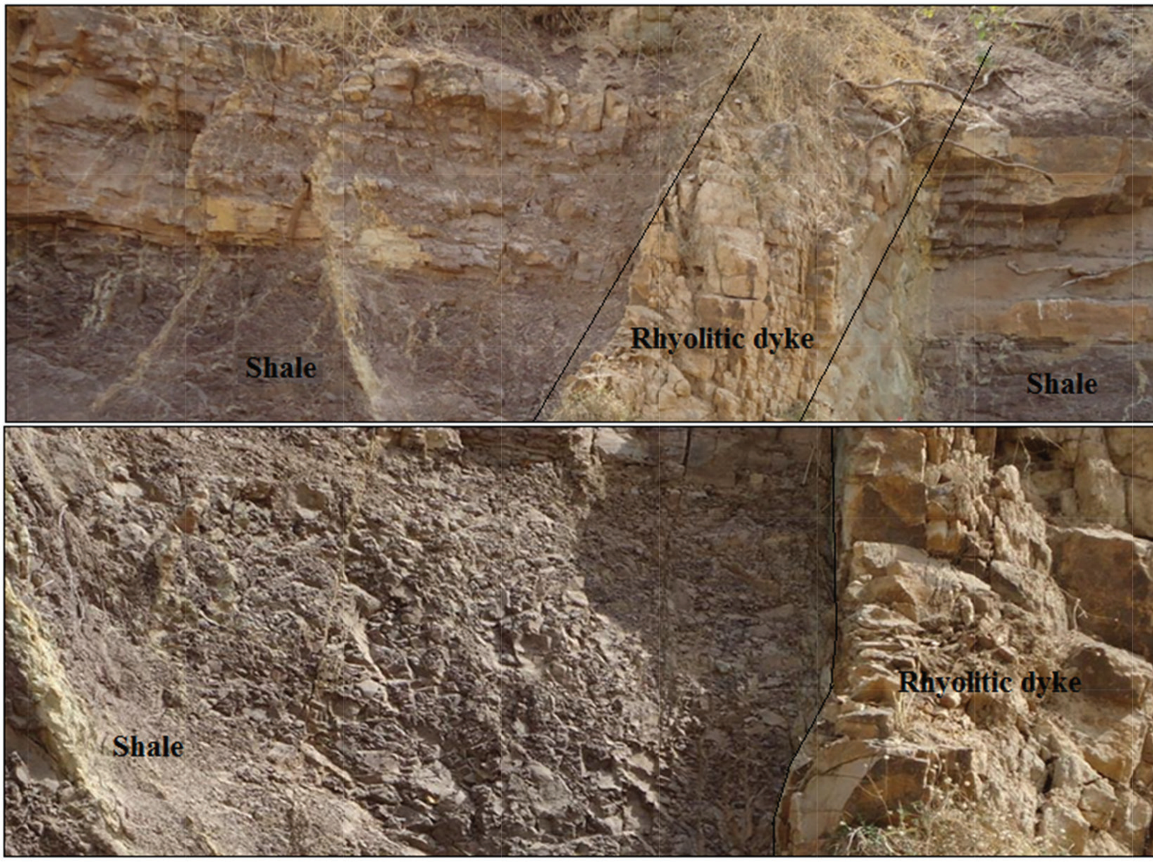

Figure 4. Field photograph showing the Bima shale samples and rhyolite-volcanic dyke.

Table 1. Pyrolysis and vitrinite reflectance data of Bima shale sediments.

Sample ID	%Ro	Pyrolysis data (SRA)					
		S_1 (mg/g)	S_2 (mg/g)	T_{max} (°C)	HI	PI	TOC wt. %
BM3A	1.84	0.08	0.28	469	44	0.22	0.63
BM3B	2.32	0.05	0.23	496	45	0.11	0.51
BM4	1.22	0.09	0.26	452	63	0.26	0.41
BM5	1.46	0.13	0.19	455	35	0.41	0.55
BM6	-	0.03	0.17	501	42	0.15	0.41
BM7	1.97	0.07	0.28	482	57	0.10	0.49
BM33	-	0.04	0.31	451	52	0.12	0.60
BM8	-	0.15	0.32	467	70	0.32	0.46
BM8B	1.12	0.04	0.24	448	63	0.14	0.38
BM9A	1.34	0.03	0.42	452	96	0.07	0.49
BM9B	1.32	0.07	0.68	450	127	0.04	0.55
BM10	1.78	0.06	0.26	468	30	0.19	0.86
BM11	-	0.12	0.16	458	24	0.43	0.68
BM12.1	1.31	0.40	0.18	459	28	0.68	0.65
BM12.2	1.98	0.14	0.25	478	33	0.34	0.77
BM12.3	2.11	0.02	0.18	489	32	0.11	0.56
BM12.4	-	0.03	0.29	469	50	0.09	0.58

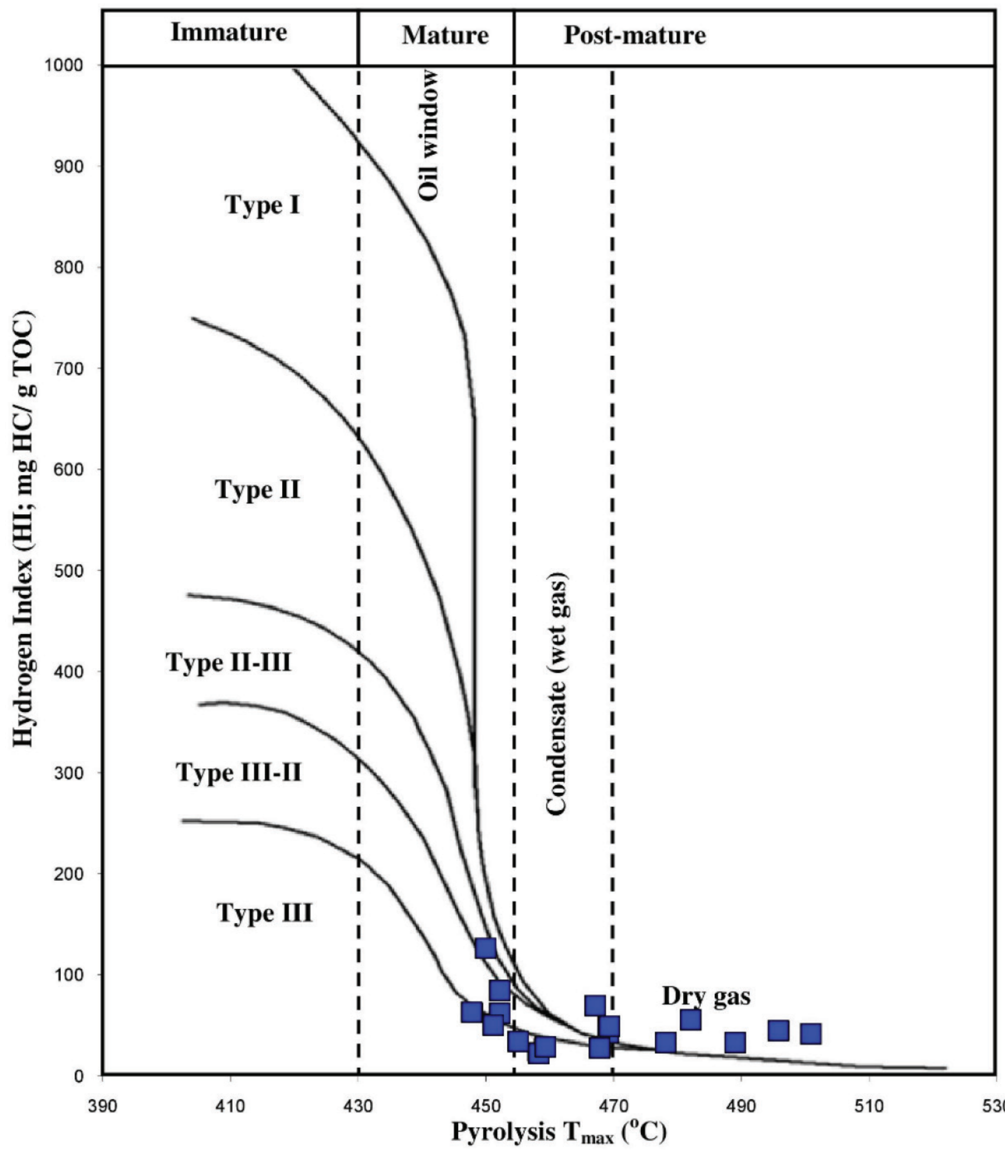

Figure 5. Plot of HI values against temperature T_{max} showing the kerogen typing and type of hydrocarbon generated.

used by exploration geologists as a strong technique in determination of thermal maturities of source rocks (Tissot and Welte, 1984). Vitrinite reflectance is occasionally affected by environment of deposition and lithology. Thermogenic oil is generated from lacustrine or marine source rocks at vitrinite reflectance values of 0.5% to 1.3% oil window maturity (Tissot and Welte, 1984), while vitrinite reflectance that is greater than 1.3 % indicates gas window maturity (Tissot and Welte 1984).

Measurements of vitrinite reflectance (Ro) were performed and results are shown in Table 1. The samples have high vitrinite reflectance values 1.12–2.32 VRo% (Table 1). This, however, suggest a late oil window to post maturity stages of hydrocarbon generation. Organic petrological features show a predominance of inertinitic micrinites embedded on the vitrinitic macerals (Fig. 6). Therefore, based on high thermal maturity as indicated by vitrinite reflectance values, the shales samples show weak fluorescence under ultra-violet light.

Palynofacies is used to determine kerogen types and to extend, the hydrocarbon generation, thermal maturities and could also assist in paleodepositional environment interpretation (Alalade and Tyson, 2013; Tissot and Welte, 1984). The shale samples consist of high amorphous organic matter that is light to dark brown in color within the kerogen assemblages under transmitted white light (Fig. 6). The phytoclasts are also present in less than 20%, while palynomorphs

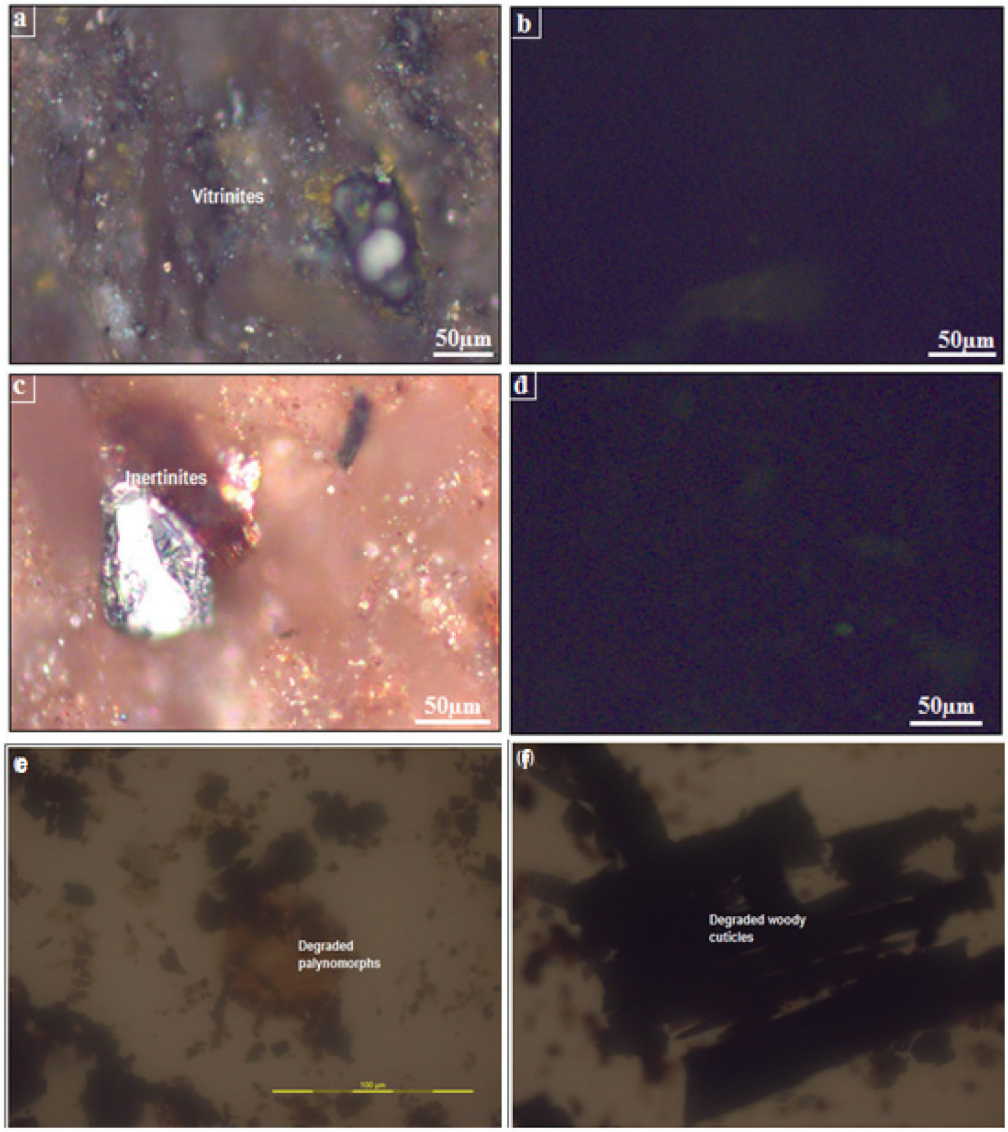

Figure 6. Photomicrographs of (a-d) vitrinites, inertinites under reflected and fluorescence light and (e-f) degreded palynomorphs and woody cuticles under white light.

(spores, pollens, and algae) are found in very low concentration of about 7%. More so, the non-fluorescent amorphous organic matter are more abundant than the fluorescence one. The samples have higher degraded cuticles and woody tissues as an indication of late oil window and high thermal maturities. This concurs with pyrolysis analysis where samples indicates dry gas stage and high thermal maturity level.

4.3. Thermal maturity and effect of volcanic

Integrated organic geochemical and petrological methods were used in the assessment of thermal maturity of organic matter in sediments. In the current study, several data types were used to assess the thermal maturity level for decompose and degraded organic matter within the shale samples of Bima Formation. The maturity data include the vitrinite reflectance (%Ro), palynofacies data, and the pyrolysis T_{max} values (Tables 1).

The shale samples have Ro values of 1.12%–2.32% (Table 1) and this corresponds to the late-oil window to post-maturity stage. Palynofacies of the kerogen indicates black to dark amorphous organic matters and very low concentration of pollen and woody fragments (Alalade and Tyson, 2013). This, however, supports the Type III and IV kerogens and supporting the high thermal maturity. T_{max} values of 448°C and 501°C is in good agreement with the vitrinite reflectance data indicating very high thermal maturity for the studied samples (Gurgey, 1999).

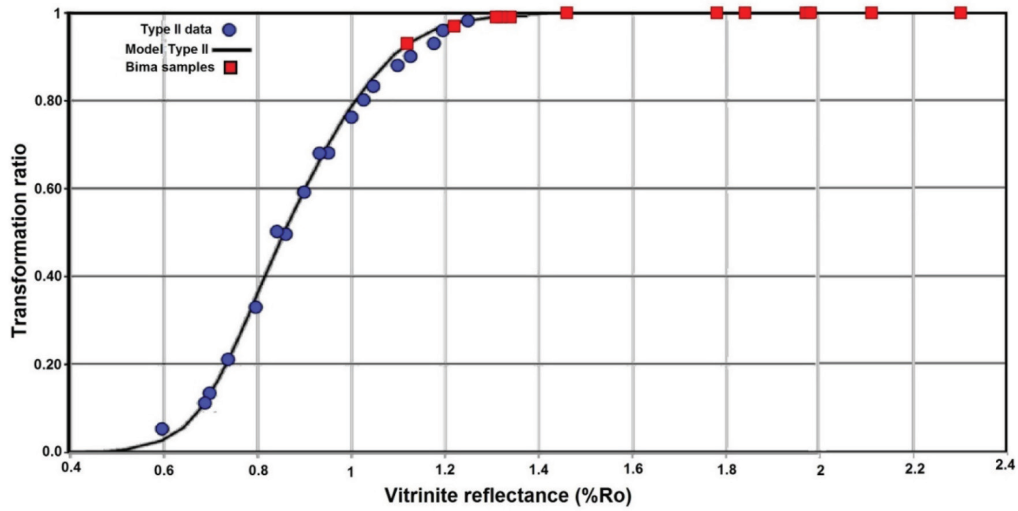

Figure 7. Model of transformation ratios against vitrinite reflectance showing the original kerogen typing of the studied samples.

The high prospect for gas-generation potential in the studied shales is due to high thermal maturity not by the original nature of the organic matters. This is suggested based on Van Krevelen diagram (Fig. 4) and organic petrography (Fig. 5), which reflects the present-day kerogen types III and IV. The high heat flow introduced by the Tertiary volcanics may have significantly influenced on the source rocks through prompting maturity and accelerating hydrocarbon generation. The oil and gas might have been cracked down and instead, thermogenetic and dry gas are only present. Considering the present-day kerogen types III and IV, based on pyrolysis analysis and organic petrography, and the original kerogen types II and II–III (Fig. 7), the shale sediments earlier appeared as a good source of oil- and gas-prone in the Yola Sub-basin of the Northern Benue Trough. Consequently, the oils have been cracked into thermogenic gas as a result of high thermal maturity experienced by the shale sediments, probably due to the Tertiary volcanic intrusion known to be present in the basin.

5. Conclusions

Pyrolysis analysis (rock-eval pyrolysis) and organic petrology (vitrinite reflectance and palynofacies) investigation of shale samples from Bima Formation in the Yola Sub-basin, to determine the organic matter thermal maturity associated with Tertiary volcanic intrusion and their relationship to hydrocarbon generation potential indicates that the studied shale sediments contain less than 0.90% TOC and are classified as poor to fair source rocks. The organic matter is of Type III and IV kerogens with mainly gas generation potential. Thermal maturities data such as pyrolysis T_{max} (448°C–501°C), vitrinite reflectance (1.14–2.33 %R), palynofacies of kerogen suggests high maturity level as late-oil window to post-mature stage of hydrocarbon generation. This high thermal maturity could be attributed to the Tertiary volcanic intrusion in the basin. This study, therefore, suggests that, the initial oil and gas-prone of the Type II and II-III kerogens have been cracked into thermogenic gas probably due to the high thermal effects of Tertiary volcanic intrusion in the basin that yield the present-day Types III and IV kerogens.

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