

# Kerogen characterisation and petroleum potential of the Late Cretaceous sediments, Chad (Bornu) Basin, northeastern Nigeria

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**Abstract:** Detailed microscopic observations (palynofacies) and organic geochemical analyses were conducted on insoluble sedimentary organic matter (kerogens) from the Late Cretaceous sediments in the Chad (Bornu) Basin, northeastern Nigeria. This is to assess their origin, paleoenvironment and types, as well as their petroleum potential. The organic matter is mainly composed of mixed terrestrial plant and marine algae-derived AOMs. Phytoclasts are also present in significant amount in most of the samples, especially those obtained from the upper section of Fika Formation. However, most of the AOMs appears to be degraded and were not well preserved. The variations of relative abundances of marine and terrigenous organic matter may be controlled by terrestrial input in ocean and/or preservation rather than marine production. This organic matter was likely deposited in marine environment under environmental conditions that were mostly dysoxic. The intense degradation observed in most of the organic matter may be as a result of high thermal maturity. Further evidences in this study confirmed that most of the potential source rocks in Chad (Bornu) Basin contain Type III kerogens, but Type III/II kerogens were also present in some parts of the basin, especially at the upper section of Fika Formation. It was also revealed that most of the samples, especially those at the deeper sections of the basin display high aromatic character which suggest a dominant gas-prone nature of the organic matter. This study confirmed that a potential for gas generation exist in this basin.

**Keywords:** Fika Formation, Late Cretaceous, kerogen, palynofacies, aromatic, gas-prone

## 1. INTRODUCTION

Kerogen, the insoluble macromolecular organic matter (OM) dispersed in sedimentary rocks, is by far the most abundant form of OM on Earth (Vandenbroucke & Largeau, 2007). It can provide essential information on paleoenvironments, paleoclimates and ancient biological activities. The classification of kerogens according to their type is important for the definition of any kerogen assemblage and for the determination of the type of hydrocarbon it will likely generate. Also, because kerogen is immobile, it provides information on the type and source of organic matter in sediments and the conditions at original deposition with subsequent changes in the rocks. In contrast to kerogen, the extractable organic material is susceptible to migration. Optical microscopic method for kerogen typing has been widely used and can provide some relevant information. However, this has some shortcomings, such as in distinguishing between hydrogen-poor and hydrogen-rich amorphous kerogen and also in the interpretation of kerogen mixtures (Powell *et al.*, 1982; Dembicki, 2009). More so, they may not be able to interpret mixed kerogen assemblages and correctly determine the type(s) of hydrocarbon that may be generated by a source rock. Rock Eval kerogen typing too can be influenced by the mineral matrix effect of the source rock and may not be adequately resolved the issue of kerogen mixtures (Dembicki, 2009).

Studies have shown that most source rocks contain more than one type of kerogen, and this pose difficult

problem when interpreting Rock-Eval data on Van Krevelen diagrams. Therefore, Rock-Eval data alone are inadequate to determine what types of kerogen are present and what type of hydrocarbons they may generate. This is where pyrolysis-gas chromatography has proved to be a very reliable and rapid method of kerogen characterisation. It has provided a better solution to interpreting kerogen mixtures because it provides a direct indicator of the kerogen type and types of hydrocarbons that can be generated by the kerogen during maturation process (Giraud, 1970; Larter & Douglas, 1980; Dembicki *et al.*, 1983; Dembicki, 2009). However, this type of chemical method for typing kerogens is less developed when compared with the optical microscopic methods which are well established (Vandenbroucke & Largeau, 2007).

The characterisation of kerogens in the Chad (Bornu) Basin has not been reported to date in any detail in the literature. Recently, exploratory activities have picked up with the commencement of 3D seismic data acquisition, following the discovery of petroleum in other parts of the basin in neighbouring Chad and Niger. However, the exact kerogen type in Chad (Bornu) Basin is still a matter of debate. Olugbemiro *et al.* (1997), Obaje *et al.* (2004), Moumouni *et al.* (2007) have characterised the kerogen as gas-prone Type III based on modified van Krevelen plots of Rock-Eval HI versus  $T_{max}$  and HI versus OI, whereas Alalade & Tyson (2010) indicated that the Chad (Bornu) Basin kerogens are either Type III/IV based on Rock-Eval Hydrogen index or Type II and Type III based on elemental

and palynofacies analyses. The contradictory results from these studies indicate the need for the development of a reliable characterisation of Chad (Bornu) Basin kerogens by the combinations of geochemical, petrographic and spectroscopic approaches. However, it is not uncommon to record slight disagreement between the interpretation of source-rock potential based on optical methods (palynofacies), and that based on chemical methods, such as elemental analysis and pyrolysis of kerogen (Powell *et al.*, 1982). This study constitutes the first of its kind in Chad (Bornu) Basin. This work will attempt to characterise the kerogen type in the basin based on the integration of Rock-Eval pyrolysis parameters, elemental ratios, pyrolysis gas-chromatography and infrared spectroscopy in order to contribute to source rock characterisation in relation to maturity, conversion and volumetrics.

## 2. GEOLOGY OF STUDY AREA

According to Fairhead (1986), Chad (Bornu) Basin belongs to the genetically and physically related systems of faults and rifts termed the West and Central African Rift System (WCARS) (Figure 1). The origin is generally attributed to the Cretaceous breakup of Gondwana and the subsequent opening of the South Atlantic and Indian Ocean. The Benue – Chad axial trough is believed to be the third and failed arm of a triple junction rift system that preceded the opening of the South Atlantic during the Early Cretaceous and the subsequent separation of the African and South American continent (Carter *et al.*, 1963; Fairhead & Binks, 1991; Genik, 1992). The tectonic framework and evolution of the basin is divided into four phases, namely; Phase 1 – Pan African crustal consolidation (750 – 550 Ma) Phase 2 – Early rift stage (130 – 95 Ma) Phase 3 – Late rift stage (98 – 75 Ma) Phase 4 – Post rift stage (66 – 0 Ma)

The stratigraphic units represented in Bornu basin range from Albian to Recent age (Whiteman, 1982; Avbovbo *et al.*, 1986; Okusun, 1995). Deposition took place under various conditions, with each deposits representing one complete cycle of transgression and regression. It has been divided

into six units based on the nature of sedimentary deposits within the depression. The divisions are Bima, Gongila, Fika, Gombe, Kerri-Kerri and Chad Formation (Table 1). Structural features of the basin are mainly products of structural and tectonic events during Late Cretaceous times that shaped the basin. Odušina *et al.* (1983) pointed out that the geologic evolution of both the Bornu basin and the Upper Benue Trough are related. He identified four main structures, based on seismic line analysis and this includes; Intrusive features of either igneous or sedimentary origin; Mound structure growth faults and stratigraphic traps; Graben structures and growth faults and lastly, Onlap sequences. Avbovbo *et al.* (1986) also identified two major structural styles base on seismic line. They are: fold related structures with low fold frequency; and fault related structures which involve the basement and resulting horst and graben with preponderance of high angle normal faults and paucity of reverse faults, indicating dominance of tensional movement.

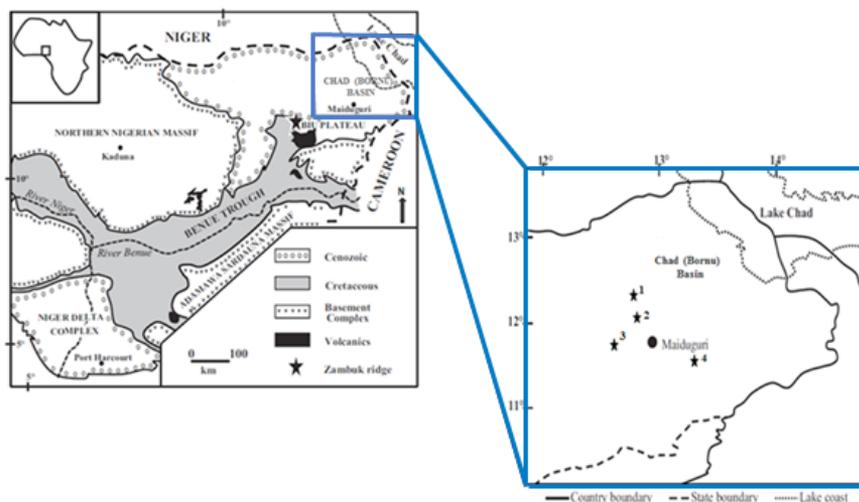
## 3. SAMPLES AND EXPERIMENTAL

### 3.1. Samples

Twenty eight ditch cuttings samples were selected from four exploration wells drilled in Chad (Bornu) Basin. The wells are Kamar-1, Kanadi-1, Kinsasar-1, and Tuma-1. The selected samples cut across Gongila and Fika Formation, which are regarded as the potential source rocks in the basin. The samples were sieve-washed using water to remove possible contaminations by drilling mud as oil-based mud were not detected. These samples were subsequently air-dried and subjected to the following analyses.

### 3.2. Bulk geochemical analysis

Twenty eight whole rock samples were pyrolysed using a *Weatherford* Source Rock Analyzer-TPH/TOC (SRA) instrument. The method and interpretative technique of Espitalié *et al.* (1977) was used. Approximately 60 mg of powdered rock were heated in the helium stream of the instrument. The parameters determined include total organic carbon (TOC); volatile hydrocarbon content, mg HC/g rock (S1), remaining hydrocarbon generative potential, mg



**Figure 1:** Geological Map of Nigeria, showing the Chad (Bornu) Basin including location of the studied exploratory wells: 1. Kanadi-1; 2. Kinsasar-1; 3. Tuma-1; 4. Kamar-1 (after Whiteman, 1982; Alalade & Tyson, 2010).

**Table 1:** Stratigraphic succession in the Chad (Bornu) Basin, northeastern Nigeria (after Carter *et al.*, 1963; Avbovbo *et al.*, 1986; Okosun, 1995).

Age	Thickness (m)** (from well logs)	Formation	Lithology	Depositional Environment
?Pliocene-Pleistocene	50 – 425	Chad	Clay, Sand	Continental (Lacustrine)
Paleocene	455 – 545	Kerri-Kerri	Sandstones, Claystones	Continental
Maastrichtian	301 – 402	Gombe Sandstone	Shale, Sandstone, Siltstone	Deltaic, Estuarine
Turonian-Santonian	606 – 2012	Fika Shale	Blue-black shale	Shallow marine
Turonian	226 – 1363	Gongila	Shale, Sandstone, Limestone	Marine, Estuarine (Transitional)
Albian-Cenomanian	408 – 1397	Bima	Sandstone, Shale	Continental
Pre-Cambrian		Crystalline Basement		

\*\* thickness in the studyarea ( obtained from well logs),  unconformity.

HC/g rock (S2), carbon dioxide yield, mg CO<sub>2</sub>/g rock (S3), temperature of maximum pyrolysis yield (T<sub>max</sub>) and their derivatives, which include hydrogen index (HI, mg HC/g TOC) and oxygen index (OI, mg CO<sub>2</sub>/g TOC).

### 3.3. Isolation of kerogen

The 28 whole rock samples were crushed to 2 – 5 mm diameter grain size in an agate mortar. Approximately 20 – 25 g of the crushed samples was extracted in a Soxhlet apparatus for 72 hours, using an azeotropic mixture of dichloromethane (DCM) and methanol (93:7). This is to remove soluble organic matter (bitumen). Thereafter, pre-extracted samples were treated with HCl and HF following the standard procedure outlined by Saxby (1970) and Durand (1980). After each treatment, the residue was washed with distilled water until the pH is 7. Hot 10% HCl was added after the removal of HF and subsequent rinsing, in order to dissolve any possible insoluble neo-fluorides and fluorosilicates formed during the HF–silicates reaction (Durand & Nicaise, 1980; Ercegovic *et al.*, 1997). The kerogen was separated from the remaining residue (containing organic matter, pyrite and other insoluble heavy minerals) by gravity separation, using zinc bromide (specific gravity ~ 2.2). The resulting kerogen concentrate was sequentially washed with distilled water (7×). Some of the residue was set aside for palynological slide preparation (palynofacies), while the remaining was oven dried at a temperature of 40°C and used for elemental analysis, pyrolysis-gas chromatography and ATR-FTIR spectroscopy.

### 3.4. Palynofacies analysis

Two palynofacies slides per samples were prepared for the 28 kerogen samples. Wet residue obtained after HCl/HF treatment were siphoned and dropped onto non-fluorescent cover slips. After drying, they were mounted

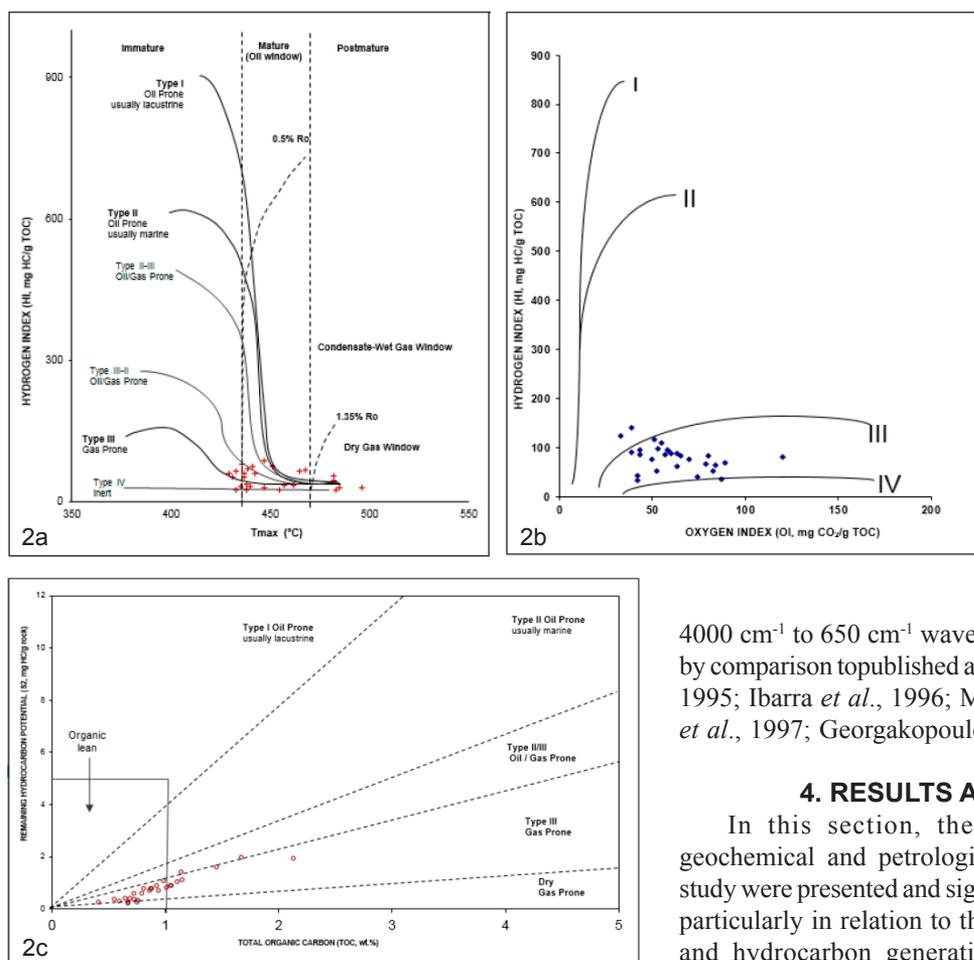
in permanent slides, using *Sigma Aldrich* Canada basalm, for microscopic examination. Counts of organic matter composition of kerogen were made using a *Leica DM 6000M* transmitted light microscope and a ×20 objective. An initial count was made using white light illumination to determine the relative percentages of the three main kerogen groups: amorphous organic matter (AOM), phytoclasts and palynomorphs (Tyson, 1995). The slides were then recounted using fluorescence light microscopic observation. Both the morphology of the AOM under transmitted light microscope and the incident blue light fluorescence were used to identify the types of amorphous particles in the samples (Tyson, 1995; Tribouvillard *et al.*, 2001; Ercegovic & Kostic, 2006). This is because the method of using only fluorescence light microscopic observation to differentiate between AOM may show some discrepancies, because overmature AOM may not fluoresce (Durand, 1980; Sawada *et al.*, 2012).

### 3.5. Elemental analysis

A portion of each kerogen sample (approximately 1.5 mg) was analysed for elemental ratios, carbon (C), hydrogen (H), and nitrogen (N) on a *Perkin-Elmer 2400 Series II* CHNS/O Analyzer. The analysis was carried out in duplicate to confirm the reproducibility of the method of isolation and analysis. The average results were used for the interpretation.

### 3.6. Pyrolysis-gas chromatography (Py-GC) analysis

Pyrolysis-gas chromatography (Py-GC) analysis of the kerogen samples was performed using a *Double-Shot Pyrolyzer PY-2020iD* from Frontier Laboratories Ltd installed in the Department of Geology, University of Malaya. Approximately 4 – 5 mg of the kerogen sample (crushed powder) was weighed into a disposable eco-cup



**Figure 2:** Modified Van Krevelen diagrams—(a) HI versus  $T_{max}$  for Kerogen Type and Maturity; (b) HI versus OI for Kerogen Type determination; (c) S2 versus TOC for Kerogen quality.

4000  $cm^{-1}$  to 650  $cm^{-1}$  wave number. Bands were identified by comparison to published assignments (Mastalerz & Bustin, 1995; Ibarra *et al.*, 1996; Mastalerz & Bustin, 1996; Cloke *et al.*, 1997; Georgakopoulos *et al.*, 2003).

#### 4. RESULTS AND DISCUSSION

In this section, the results obtained from the geochemical and petrological methods performed in the study were presented and significant findings were discussed, particularly in relation to the type, depositional conditions and hydrocarbon generating potential of the insoluble sedimentary organic matter (kerogen).

##### 4.1. Bulk geochemistry

The Source Rock Analyzer-TPH/TOC results for the studied samples are presented in Table 2. The TOC values are between 0.64 and 2.13 wt.% in the Fika Formation, while in the underlying Gongila Formation, the TOC values are much lower (0.41 – 0.94 wt.%). For all the analysed samples, the HI values are below 150 mg HC/g TOC, but generally higher in the Fika Formation, especially in the upper intervals. This likely suggests a preponderance of both terrestrial and inert organic matter in the sediments. The predominance of inert organic matter may be due to either over maturity and/or poor preservation in the environment of deposition. However, the higher TOC, HI and S2 values at the upper part of Fika Formation as compared to the deeper sections of Fika and Gongila Formation suggests relatively more favourable depositional conditions for the organic matter within this upper intervals. Maturity of the organic matter may also account for this distinction. SRA  $T_{max}$  data show that samples within the upper Fika Formation are in the early to peak mature stage of hydrocarbon generation as compared to samples recovered from the deeper sections of Fika and Gongila Formations, which are mostly in the post mature stage. Based on the modified van Krevelen plots of HI versus  $T_{max}$ , HI versus OI and S2 versus TOC (Mukhopadhyay *et al.*, 1995), the studied samples contain

and placed in the sample probe, which was then lowered into the furnace. The initial temperature is 54°C, ramping to the pyrolysis temperature of 600°C at a rate of 20°C/min. A flow of helium flushes the pyrolysates into the column where components are separated. An ultra-alloy capillary column specified with 30 m length, 250  $\mu m$  nominal diameter and 0.25  $\mu m$  nominal film thickness was used. The initial flow is 1.2  $\mu L/min$ , with an initial pressure and average velocity of 13.3 psi and 29 cm/sec, respectively. The outlet of the splitter was connected to a flame ionisation detector (FID). The total run time for analysing a single sample is 95 minutes.

##### 3.7. Attenuated total reflection-fourier transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectra were collected using a Perkin Elmer Spectrum-100 FTIR Spectrometer equipped with a universal ATR unit. The measurement was performed on 10 powdered kerogen samples. The powdered sample was placed on a Diamond/ZnSe crystal plate and was compressed below 98%. ATR-FTIR measurements were performed at 25°C. Interferograms from 240 scans were averaged to obtain one spectrum by overlain on the background spectrum of air. The ATR accessory was purged with nitrogen prior to and during acquisition of spectra to minimize the effect of water vapour. The spectra were collected in the region between

**Table 2:** Data from the Source Rock Analyzer (equivalent to Rock-Eval), including TOC and pyrolysis parameters from the studied samples.

Sample	Depth (m)	Formation	TOC (wt.%)	S1	S2	S3	T <sub>max</sub>	HI	OI
<b>Kemar-1</b>									
KEM 755	755	Fika	1.14	0.06	1.42	0.29	437	124	33
KEM 950	950	Fika	0.92	0.05	0.89	0.4	438	96	43
KEM 1020	1020	Fika	0.98	0.04	0.25	1.07	433	109	55
KEM 1210	1210	Fika	0.86	0.04	0.72	0.45	435	83	80
KEM 1450	1450	Fika	0.81	0.07	0.78	0.47	440	96	58
KEM 1725	1725	Fika	0.72	0.07	0.59	0.27	447	81	120
<b>Kanadi-1</b>									
KAN 1150	1150	Fika	1.67	0.09	1.98	0.59	436	118	51
KAN 1205	1205	Fika	1.01	0.08	0.84	0.44	431	83	65
KAN 1665	1665	Fika	1.05	0.08	0.91	0.4	437	86	57
KAN 2155	2155	Fika	0.64	0.07	0.41	0.54	455	64	84
KAN 2325	2325	Fika	0.67	0.07	0.24	0.58	462	36	87
KAN 2565	2565	Gongila	0.69	0.06	0.43	0.31	496	62	63
KAN 2690	2690	Gongila	0.59	0.1	0.31	0.42	482	52	83
<b>Kinasar-1</b>									
KIN 970	970	Fika	0.88	0.08	0.78	0.43	429	88	63
KIN 1255	1255	Fika	1.1	0.10	1.04	0.4	439	94	59
KIN 1520	1520	Fika	1.15	0.12	1.14	0.4	442	99	53
KIN 1640	1640	Fika	1.45	0.25	1.62	0.52	447	140	39
KIN 1755	1755	Fika	0.87	0.11	0.78	0.47	451	89	60
KIN 2225	2225	Gongila	0.55	0.09	0.38	0.32	465	69	89
KIN 2855	2855	Gongila	0.41	0.17	0.27	0.32	468	67	79
<b>Tuma-1</b>									
TUM 1060	1060	Fika	2.13	0.06	1.96	0.82	433	92	39
TUM 1650	1650	Fika	1.04	0.06	0.91	0.32	447	87	43
TUM 1805	1805	Fika	0.79	0.05	0.61	0.41	457	77	70
TUM 2255	2255	Fika	0.76	0.07	0.33	0.32	485	43	42
TUM 2575	2575	Fika	0.72	0.11	0.39	0.38	483	54	52
TUM 2870	2870	Gongila	0.94	0.96	0.71	0.47	441	76	50
TUM 2920	2920	Gongila	0.75	0.11	0.25	0.17	482	33	42
TUM 3055	3055	Gongila	0.67	0.15	0.27	0.49	458	40	74

**Notes:**

TOC – Total Organic Carbon, wt.%

S1 – Volatile hydrocarbon (HC) content, mg HC/g rock

S2 – Remaining HC generative potential, mg HC/g rock

T<sub>max</sub> – pyrolysis temperature (°C) at the maximum rate of kerogen conversionS3 – Carbon dioxide content, mg CO<sub>2</sub>/g rockOI – Oxygen index = S3 x 100/TOC, mg CO<sub>2</sub>/g/TOC

HI – Hydrogen index = S2 x 100/TOC, mg HC/g TOC

Type III/II, Type III and Type IV kerogen (Figures 2a, 2b, 2c). The kerogen is typically gas prone, but limited oil may be generated also from the Type III/II kerogen.

#### 4.2. Palynofacies data of kerogen

One of the main objectives of studying palynofacies is to establish the kerogen type and hence the type of generated hydrocarbon and also to assist in subsequent environmental interpretations. Three main kerogen groups were recognised in the investigated samples, namely amorphous organic matter (AOM), phytoclasts and palynomorphs (Table 3).

The analysis indicate a strong predominance of amorphous organic matter (more than 80%) in the kerogen assemblages of all the 28 samples investigated under transmitted white light. The AOM is light to dark brown. Phytoclasts (woody tissue and cuticles) are also predominant in most of the samples whereas palynomorphs (spores, pollens and algae) are found to be present in low quantities. Minute fluorescent “liptodetrinitic” inclusions were also seen in some of the samples, especially those at the upper part of Fika Formation. The AOM recognised can be classified into two major groups. They are the fluorescent uniformly

**Table 3:** Description of insoluble organic matter (kerogen) identified in the studied samples under transmitted and fluorescent microscope. Classification is based on Tyson (1995), Ercegovac & Kostic (2006), Sawada (2006), Sawada *et al.* (2012).

Kerogen	Possible origins	Characteristics in transmitted microscope	Characteristics in fluorescent microscope
<i>Amorphous organic matter (AOM)</i>			
Brown weakly-fluorescent amorphous organic matter (BWFA)	Marine algae	Brown to dark brown amorphous organic matter	Weak white fluorescence
Non-fluorescent amorphous organic matter (NFA)	Terrestrial plant	Opaque dark brown to black minute particles and amorphous organic matter	Non-fluorescence
<i>Structured organic matter (SOM)</i>			
<i>Phytoclast</i>			
Wood	Terrestrial plant woody tissue	Opaque and semi-transparent dark brown to black particles with sharp angular outlines	Non-fluorescence
Cuticle	Terrestrial plant cuticle tissues	Transparent filter-like light yellow to dark brown fragment	Strongly white to yellow fluorescence
<i>Palynomorphs (PAL)</i>			
Sporomorphs	Terrestrial plant spore and pollen fossils	Transparent light yellow to yellow granular particle	Strongly white to yellow fluorescence
Dinoflagellates	Fully marine conditions. Also found in marginal marine settings.	Transparent light yellow to brownish	Weak yellow fluorescence

granular AOM and the non-fluorescent AOM. In all the samples, the non-fluorescent AOM is more abundant than the fluorescent AOM.

Generally, the percentage of the non-fluorescent AOM increased with depth, probably in response to increasing thermal maturation of the organic matter. The non-fluorescent AOM is probably formed by high degradation and fragmentation of woody tissues of higher plant and vitrinite and/or inertinite maceral groups (Tyson 1995; Ercegovac & Kostic, 2006; Sawada 2006). They may also form from degradation of marine algae deposited in aerobic environment (Tyson, 1995). The two main types of phytoclasts recognised in this study are woody debris (wood) and cuticle. The woody debris is structured opaque black to brown, poorly to moderately preserved fragments with sharp angular edges under transmitted microscope (Figure 3). Some are elongated and lath-shaped, while others are small and semi-transparent. Some are also unstructured. This group of organic matter did not fluoresce at all under UV light. Most of the cuticles recognised are dark brown and not well preserved, which suggests that partial oxidation has taken place and their oil generating capability is low (Tyson, 1995). The nature of the phytoclasts in the samples probably indicates the environmental conditions in which they were preserved, which is mainly dyoxic. Also, the presence of abundant non-fluorescent AOM and phytoclasts suggests significant input from terrestrial plants. Sporomorphs and some dinoflagellate cysts are the main palynomorphs recognised in some of the samples. The dinoflagellate cysts might be an indication of marine deposition, but perhaps in conditions of lower than normal marine salinity (Batten & Stead, 2005).

However, the samples from the upper part of Fika Formation are characterised by a fairly richer, but poorly to moderately preserved mixed kerogen assemblage with

relatively high percentages of fluorescent AOM and low to intermediate percentages of phytoclasts than samples from the lower part of Fika Formation and the rest of Gongila Formation. More marine algae cysts were also recognised (Table 4). This suggests that these assemblages were deposited in a marginally marine, proximal setting with a strong influx of terrestrial plant matter under environmental condition that was probably mainly dyoxic (Tyson, 1995). By “marginally marine” we refer to subnormal or hypo-salinity as resulting from e.g. high river discharge. Unlike the Fika Formation, samples from the deeper Gongila Formation possess more non-fluorescence AOM with the phytoclasts also more degraded. This probably suggests an environmental condition that is even relatively less dyoxic and more input from terrestrial sources. They could also reflect the overall effect of increased thermal maturity. It is noteworthy that due to the presence of some moderately preserved kerogen assemblages especially at the upper part of the Fika Formation, it is possible that more dyoxic environmental conditions occur within those intervals. But, this could not be confirmed due to small sample population size and the random nature of the analysed samples. Finally, from these palynofacies data, it can be inferred that most of the studied samples are of Type III kerogen, but the upper Fika Formation samples probably possess some amounts of Type II kerogen in addition to the more common Type III kerogen assemblages.

#### 4.3. Elemental analysis

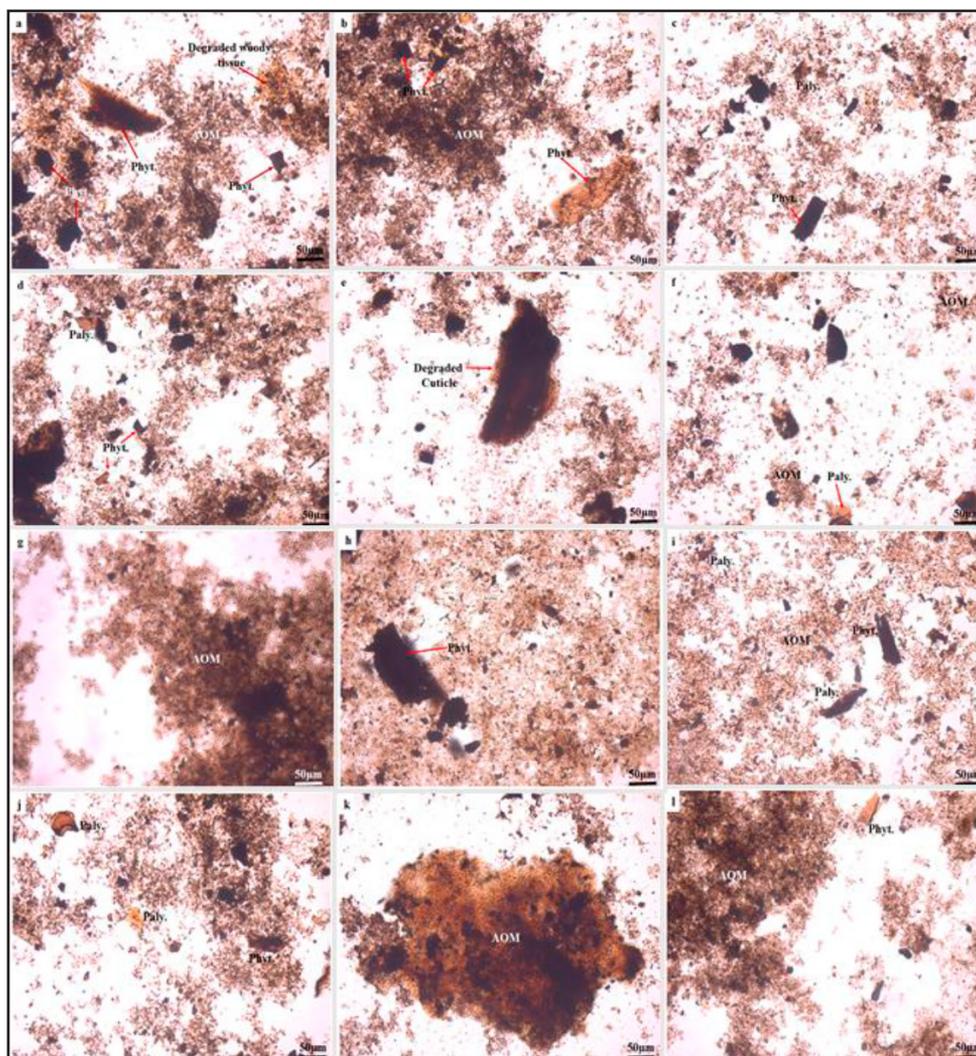
The results of the elemental analysis of the kerogen samples are presented in Table 5. The carbon (C) contents recorded for the 20 isolated kerogen samples are fairly high (55.3% to 69.9%), whereas the hydrogen (H) and the nitrogen (N) are present in low abundance (2.05% to 4.69% and 1.17% to 2.08%, respectively). The low hydrogen and

nitrogen contents is probably related with the amorphous organic matter, as examined by optical microscopic method, whereby most are degraded non-fluorescent herbaceous materials. In addition, more nitrogen may have been lost during the early diagenesis when they are hydrolysable (Meyers, 1997, Vandenbroucke & Largeau, 2007). Therefore, the low hydrogen and nitrogen content in the analysed kerogen samples probably reflects in part, the state of preservation of the organic matter during early diagenesis.

The H/C atomic ratios of the kerogen samples range from 0.41 to 0.96 (Table 5). The upper part of the Fika Formation exhibit obviously higher H/C atomic ratios (0.76 – 0.96) than the lower part of Fika Formation and the rest of Gongila Formation (0.41 – 0.69). Baskin (1997) noted that kerogen atomic H/C ratios better define original organic matter quality and are good indicators of thermal maturity for end-member kerogen types. The changes in the atomic H/C ratios from 0.96 to 0.41 may be due to increase in thermal maturity as a result of depth of burial. This is consistent with the thermal maturity as measured by the SRA  $T_{max}$ . The lower H/C ratios found mostly at lower depth intervals suggest that the samples may have

been more thermally altered. The H/C atomic ratio is also consistent with the aromatic character of the samples, in which the samples with low H/C ratios possess significant amount of aromatic, as observed from the Py-GC data. However, Powell (1988) and Hunt (1991) proposed that H/C ratio of 0.8 – 0.9 can be used as the cut-off limit for liquid hydrocarbon potential in terrigenous sequences. Thus, the studied samples from the upper section of Fika Formation appear to be slightly liquid prone relative to the lower part of Fika Formation and the rest of Gongila Formation. This interpretation is in good agreement with the Py-GC data, which show that limited liquid hydrocarbon may be generated by the kerogen (Figure 4). This interpretation also support the palynofacies data.

Atomic C/N ratios have been widely used as a proxy to identify changes in the proportions of sedimentary organic matter input from algal and land-plant origins (e.g. Meyers *et al.*, 1996; Silliman *et al.*, 1996; Meyers, 1997). Vandenbroucke & Largeau (2007) reported that the atomic N/C ratio in terrigenous higher plants is usually below 0.05, whereas that in planktonic organisms is higher than 0.08. Emerson & Hedges (1988) and Meyers (1994) also reported



**Figure 3:** Photomicrographs of the various organic matter types recognized in the analysed samples.

**Table 4:** Insoluble organic matter composition (%) of the analysed samples by palynofacies analysis.

Sample	Depth (m)	Formation	BWFA	NFA	Wood	Cuticle	PAL	Total AOM	AOM Colour
<b>Kemar-1</b>									
KEM 755	755	Fika	5	73	16	4	2	78	Brown
KEM 950	950	Fika	4	79	13	3	1	83	Brown
KEM 1020	1020	Fika	4	79	13	3	1	83	Brown
KEM 1210	1210	Fika	4	80	12	3	1	84	Dark brown
KEM 1450	1450	Fika	3	82	12	3	tr	85	Dark brown
KEM 1725	1725	Fika	3	88	8	1	tr	91	Dark brown
<b>Kanadi-1</b>									
KAN 1150	1150	Fika	7	73	16	5	2	80	Brown
KAN 1205	1205	Fika	5	80	12	3	tr	85	Light brown
KAN 1665	1665	Fika	3	85	10	2	tr	88	Brown
KAN 2155	2155	Fika	1	93	5	1	tr	94	Brown
KAN 2325	2325	Fika	1	94	4	1	tr	95	Dark brown
KAN 2565	2565	Gongila	1	94	4	1	tr	95	Dark brown
KAN 2690	2690	Gongila	1	93	4	1	tr	94	Dark brown
<b>Kinasar-1</b>									
KIN 970	970	Fika	8	74	14	3	1	82	Brown
KIN 1255	1255	Fika	7	76	15	2	tr	83	Brown
KIN 1520	1520	Fika	6	78	12	3	1	84	Brown
KIN 1640	1640	Fika	7	73	15	4	1	80	Brown
KIN 1755	1755	Fika	5	80	13	1	tr	85	Dark brown
KIN 2225	2225	Gongila	2	89	5	2	tr	91	Dark brown
KIN 2855	2855	Gongila	2	89	5	2	tr	91	Dark brown
<b>Tuma-1</b>									
TUM 1060	1060	Fika	7	75	14	3	1	82	Brown
TUM 1650	1650	Fika	5	83	10	1	1	88	Brown
TUM 1805	1805	Fika	5	81	11	2	1	86	Brown
TUM 2255	2255	Fika	2	92	5	1	tr	94	Brown
TUM 2575	2575	Fika	3	87	8	2	tr	90	Dark brown
TUM 2870	2870	Gongila	3	89	8	1	tr	91	Dark brown
TUM 2920	2920	Gongila	1	96	3	tr	tr	97	Dark brown
TUM 3055	3055	Gongila	1	96	3	tr	tr	97	Dark brown

**Notes:** BWFA – Brown or weakly fluorescent AOM, NFA – Non-fluorescent AOM, PAL – Palynomorph, Total AOM – Sum of BWFA and NFA, tr – trace (<0.5%)

that algae typically have atomic C/N ratios between 4 and 10, whereas organic matter from vascular land plants has C/N ratios of 20 and greater. This fundamental difference in elemental compositions arises principally from (1) the dearth of cellulose in algae and its abundance in vascular plants, and (2) the protein richness of algal organic matter (Vandenbroucke & Largeau, 2007). The atomic N/C and C/N ratios of the kerogens range from 0.016 to 0.032 and 31.5 to 62.7, respectively. Thus, the low N concentration in these kerogens is consistent with their predominantly terrigenous organic source. The C/N ratios of all the analysed samples are greater than 20, also reflecting a significant input from vascular land plant. This interpretation is in good agreement with the palynofacies data, in which the kerogen is dominated by degraded non-fluorescent AOM and phytoclasts as discussed in Section 4.2.

#### 4.4. Pyrolysis – GC data of kerogen

The characterisation of kerogen is enabled through pyrolysis-gas chromatographic technique. In this method, parts of the material making up the remaining hydrocarbon generative potential (S<sub>2</sub>) peaks are collected and analysed by gas chromatography. This gives information on the kerogen type and the hydrocarbons likely to be generated by the kerogen during maturation process (Larter & Douglas, 1980; Dembicki *et al.*, 1983; Dembicki, 2009). According to Larter & Douglas (1980), this can be achieved in terms of the chromatographic “fingerprint” and also the production of a numerical “type index” (R) determined as the peak height ratio of m(+p)-xylene and n-octene (n-C<sub>8</sub>) in the pyrogram. The “type index” is closely related to kerogen type. Type I kerogens have low type index (<0.4), Type II kerogens have values between 0.4 and 1.3, while Type III kerogens have

**Table 5:** Atomic ratios of hydrogen to carbon (H/C), nitrogen to carbon (N/C) and carbon to nitrogen (C/N) determined from the elemental analysis of studied kerogen samples and the peak height ratios of some compounds calculated from Py-GC pyrograms.

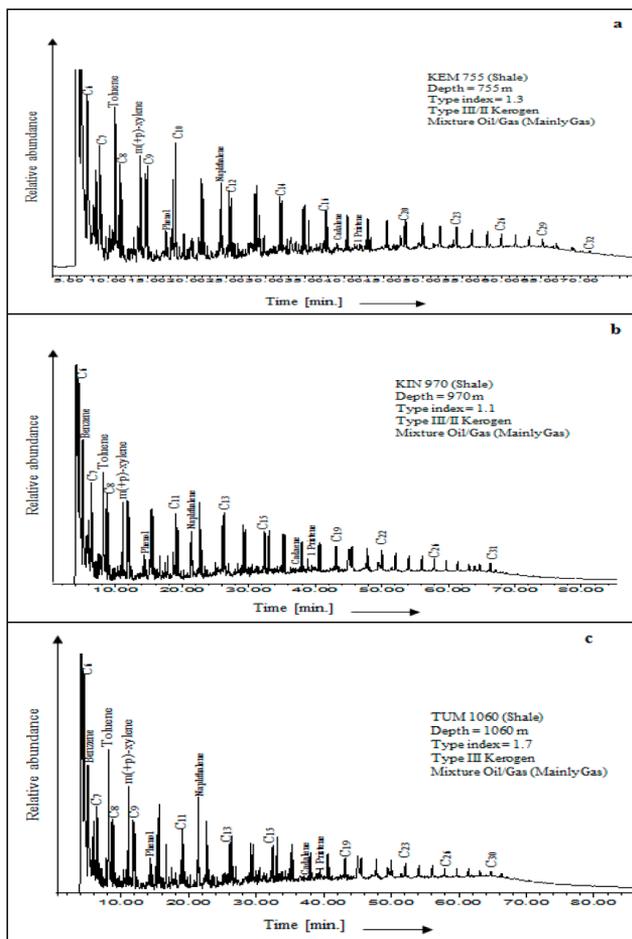
Sample	Depth (m)	Formation	Atomic ratios			Py-GC ratios		
			H/C	N/C	C/N	Type index	C <sub>8</sub> /xy	cd/xy
<b>Kemar-1</b>								
KEM 755	755	Fika	0.76	0.026	40.6	1.3	0.78	0.08
KEM 1020	1020	Fika	0.80	0.027	37.2	1.1	0.92	0.04
KEM 1210	1210	Fika	0.49	0.023	43.2	1.5	0.65	0.08
KEM 1450	1450	Fika	0.57	0.023	44.3	1.7	0.6	0.08
KEM 1725	1725	Fika	0.48	0.018	56.2	1.8	0.56	0.06
<b>Kanadi-1</b>								
KAN 1150	1150	Fika	0.96	0.029	34.5	0.9	1.1	0.06
KAN 1665	1665	Fika	0.44	0.021	48.1	1.6	0.61	0.11
KAN 2155	2155	Fika	0.43	0.018	55.8	3.1	0.32	0.14
KAN 2325	2325	Fika	0.45	0.017	58.1	3.0	0.33	0.04
KAN 2565	2565	Gongila	0.45	0.016	61.4	4.4	0.23	0.09
KAN 2690	2690	Gongila	0.41	0.016	62.7	3.5	0.28	0.13
<b>Kinasar-1</b>								
KIN 970	970	Fika	nd	nd	nd	1.1	0.87	0.08
KIN 1255	1255	Fika	0.81	0.032	31.5	1.1	0.93	0.04
KIN 1520	1520	Fika	0.82	0.029	34.3	1.1	0.94	0.08
KIN 1640	1640	Fika	0.69	0.022	45.9	1.6	0.61	0.07
KIN 2225	2225	Gongila	0.56	0.023	44.3	1.6	0.63	0.06
<b>Tuma-1</b>								
TUM 1060	1060	Fika	0.77	0.022	44.6	1.7	0.6	0.05
TUM 1650	1650	Fika	0.67	0.023	44	1.7	0.59	0.07
TUM 2255	2255	Fika	0.44	0.020	50.2	2.4	0.42	0.09
TUM 2575	2575	Fika	0.50	0.018	56.6	2.6	0.38	0.18
TUM 2780	2780	Gongila	nd	nd	nd	2.0	0.5	0.14
TUM 2920	2920	Gongila	0.45	0.021	47.8	1.7	0.6	0.2

**Notes:** H/C – Hydrogen/Carbon Atomic ratio, N/C – Nitrogen/Carbon Atomic ratio, C/N – Carbon/Nitrogen Atomic ratio, Type index (R) – m(+p)-xylene/n-octene, C<sub>8</sub>/xy – n-octene/m+(p)-xylene, cd/xy – cadalene/m+(p)-xylene, nd – not determined

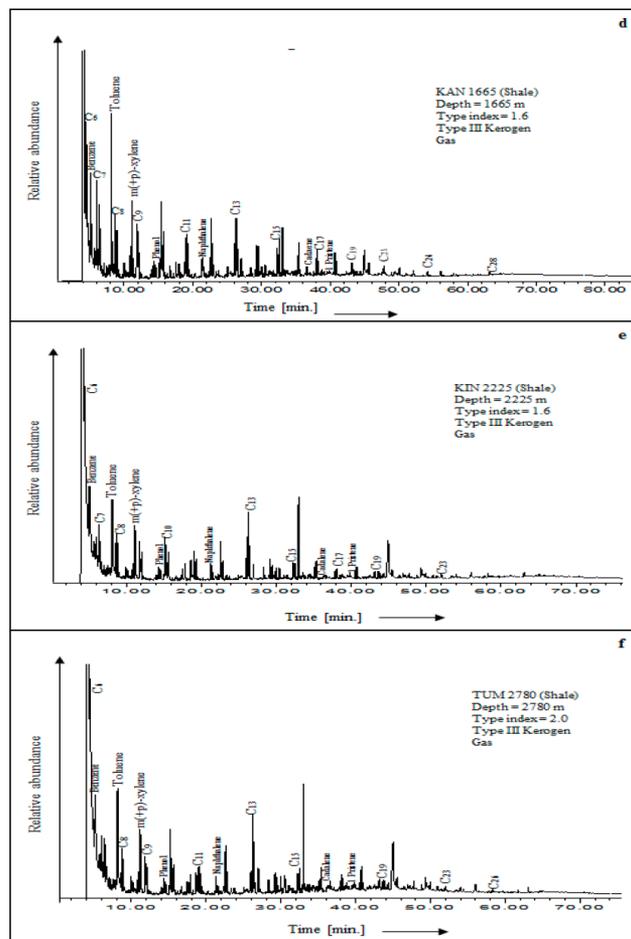
ratios ranging from 1.3 to more than 20. Giraud (1970) also revealed that kerogens (Type I) containing algal/microbial (marine) organic source material gave more “aliphatic” pyrolysates whereas kerogens (Type III) with higher plant (terrestrial) organic source material gave more “aromatic” pyrolysates. Dembicki (2009) also suggested that Type I kerogens display abundant long-chained *n*-alkanes/*n*-alkenes (>*n*-C<sub>15</sub>) and short-chained *n*-alkanes/*n*-alkenes (<*n*-C<sub>10</sub>) in their Py-GC traces whereas Type III gas-prone kerogens show the bulk of the pyrolysis products restricted to the low molecular weight end (< *n*-C<sub>10</sub>) of the pyrograms. An intermediate situation is typical of Type II kerogens, while Type IV kerogens are mostly inert and give little or no signal.

The “type index” calculated from the Py-GC traces of the studied kerogen samples range between 0.9 and 4.4, which indicates a mixture of Type II and Type III kerogens (Table 5). Samples recovered from the upper part of Fika Formation (shallow depth) are mostly Type III/II kerogen [mixture of 75% Type III and 25% Type II kerogens, according to Dembicki, 2009], based on their type index

(0.9 – 1.3) and their characteristic Py-GC pyrograms that extend beyond *n*-C<sub>30</sub>. The Py-GC pyrograms of this set of samples (Figure 4) also display prominent *n*-alkane/*n*-alkene doublets in the low molecular weight end (< *n*-C<sub>10</sub>) with some specific abundant aromatic compounds (especially benzene, toluene, m(+p)-xylene and naphthalene). These are indicative of aromatic-rich with significant aliphatic compounds, and suggest a mixture of oil and gas generation, but mainly gas. On the other hand, kerogen pyrolysates from analysed samples recovered from deeper depth intervals in the Fika Formation and the rest of Gongila Formation yielded gas chromatograms with fewer *n*-alkane/*n*-alkene doublets, but abundant specific aromatic compounds when compared to the kerogen pyrolysates of samples recovered from shallow depth in Fika Formation (Figure 5). Although, the *n*-alkane/*n*-alkene doublets in the low molecular weight end (< *n*-C<sub>10</sub>) are prominent, they did not extend beyond *n*-C<sub>26</sub>. There are very low concentrations of the >*n*-C<sub>15</sub> compounds, and this is characteristic of Type III kerogen, as confirmed by their type index (> 1.3). This interpretation is in agreement



**Figure 4:** Py-GC pyrograms of three kerogen samples from the upper part of Fika Formation which display mainly Kerogen Type III/II. The generation products are mixture of oil and gas, but mainly gas. The *n*-alkanes and *n*-alkenes doublets are represented by  $C_n$  (*n* is numeral and represents the carbon numbers).



**Figure 5:** Py-GC pyrograms of three kerogen samples from the lower part of Fika Formation and the rest of Gongila Formation which display Kerogen Type III. The generation product is gas. The *n*-alkanes and *n*-alkenes doublets are represented by  $C_n$  (*n* is numeral and represents the carbon numbers).

with the atomic H/C ratio and the palynofacies data. The classification of kerogen of the analysed samples was also done using the relative abundance of *n*-octene, *m*(+*p*)-xylene and phenol (Larter, 1984). The ternary plot shows that all the samples are kerogen Type III (Figure 6). Some samples that are very close to Type II kerogen in the plot may be regarded as Type III/II, since the plot does not provide for mixture of kerogen.

Generally, the concentrations of both aliphatic and aromatic compounds in the Py-GC pyrograms of samples from deeper section of Fika Formation and the rest of Gongila Formation are lower than those in the samples recovered from the shallower depth intervals of Fika Formation. This may be as a result of the  $S_2$  depletion as hydrocarbon is being generated due to increase in thermal maturity with depth. As source rock generates and hydrocarbon migrates off, the amount of organic matter in the source rock will decrease, with a corresponding decrease in the amount of hydrogen and reactive kerogen. And this result in a decrease in the amount of hydrocarbon ( $S_2$ ) formed during the thermal decomposition of the kerogen (Jarvie & Lundell, 1991; Dembicki, 2009). Most of the analysed samples in

the upper Fika Formation are in the early mature stage of hydrocarbon generation, based on the  $SRA T_{max}$  values. This interpretation is consistent with the atomic H/C ratios, which decrease with increasing depth.

Semi quantitative and qualitative analysis of the kerogen samples was also carried out based on the ratio of *n*-octene/*m*(+*p*)-xylene ( $n-C_8/xy$ ) and cadalene/*m*(+*p*)-xylene ( $cd/xy$ ). The  $n-C_8/xy$  ratio has been used as a measure of the comparative abundance of aliphatic to aromatic hydrocarbons and also to determine hydrocarbon generating potential (van Aarssen *et al.*, 1992; Wan Hasiah, 1999). High  $n-C_8/xy$  ratio of more than 1.0 is interpreted as possessing good hydrocarbon generating potential, whereas ratio below 1.0 is interpreted as being less oil prone and more gas prone. The analysed kerogen samples display a wide variation of  $n-C_8/xy$  ratio, which range from 0.23 to 1.1. In the Fika Formation samples, the calculated  $n-C_8/xy$  ratio range from 0.32 to 1.1, whereas the ratio is generally low (0.23–0.63) in the deeper and highly matured Gongila Formation. Since almost all the samples possess ratios lower than 1.0, they are interpreted as being less oil prone. However, the samples with  $n-C_8/xy$  values between 0.78

and 1.1 in the upper part of Fika Formation are regarded as capable of a mixture of mainly gas with limited oil generation. The samples which show lower ratio (less than 0.65) were inferred to be gas prone.

Almost all the analysed samples show higher concentration of specific aromatic compounds (especially benzene, toluene and m(+p)-xylene) relative to the n-alkanes/alkenes (aliphatic) in the pyrograms. This is characteristic of Type III kerogen. However, based on the  $n-C_8/xy$  ratio, there seems to be higher concentrations of aromatic compounds in the Gongila Formation samples than in the Fika Formation samples. This suggests that the samples from Gongila Formation are more mature than the Fika Formation. The calculated cadalene to xylene (cd/xy) ratios in the samples which range from 0.04 to 0.14, also imply a significant input from land-derived plants (Solli *et al.*, 1984).

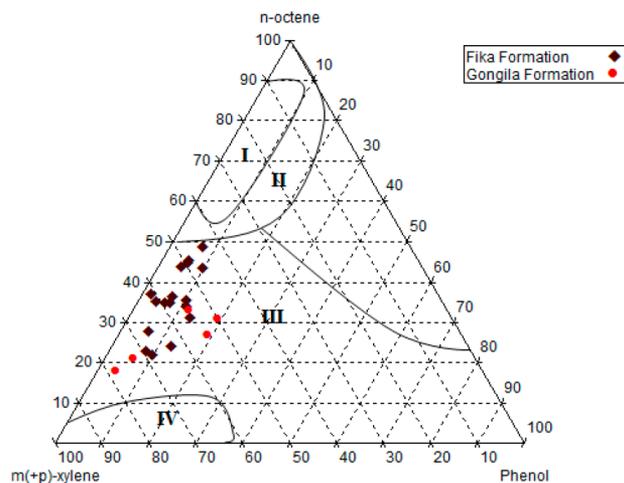
#### 4.5. Attenuated total reflection-fourier transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectroscopy was used to assess the quality of kerogen in the samples and also assisted in the elucidation of the molecular structure of kerogen by identifying the types of bonding present. These include the various aliphatic and aromatic carbon-carbon and carbon-hydrogen bonds and oxygen-containing functional groups (Mastalerz & Bustin, 1995; Ibarra *et al.*, 1996; Mastalerz & Bustin, 1996; Georgakopoulos *et al.*, 2003). In this study, the estimated proportion is obtained by visual comparison of the peaks measured from 3000 to 2750  $cm^{-1}$  for aliphatic (C-H stretching region) and from 1750 to 1550  $cm^{-1}$  for oxygenated groups and aromatic/olefinic region. Peaks were also observed from 700 to 900  $cm^{-1}$  for aromatic out of plane region. All spectra except one (KIN 1640) display low aliphatic C-H stretching band peaks in the 3200–2750  $cm^{-1}$  region (Figure 7). However, the samples obtained from the upper part of Fika Formation possess relatively higher and more distinct aliphatic stretching C-H band peaks than the other samples obtained from the lower part of Fika Formation and the rest of Gongila Formation. On the other hand, most of the samples show high aromatic ring stretching

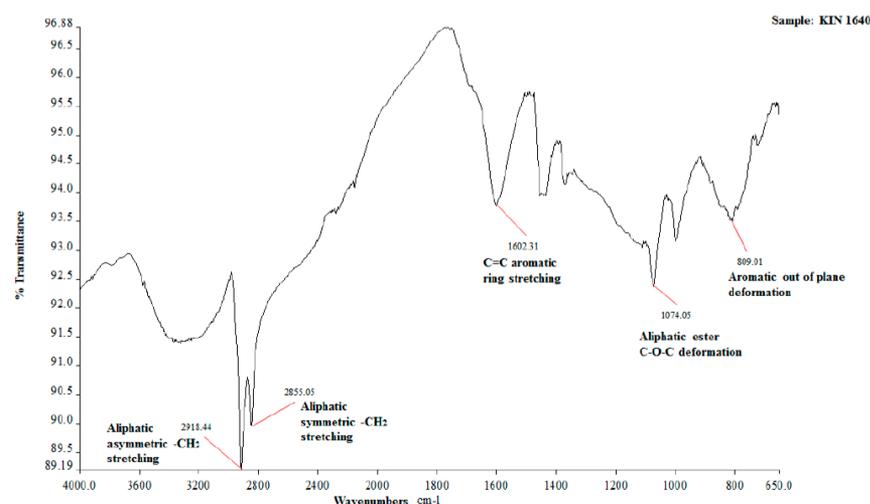
bands peaks C=C in the 1600  $cm^{-1}$  region. Furthermore, it is noteworthy that responses at region 700 to 900  $cm^{-1}$  for aromatic out of plane deformation bands are also high in most of the analysed samples (Figure 8). The high aromatic stretching bands of the samples are in good agreement with the Py-GC data and the low H/C ratios which demonstrate higher aromatic compound.

#### 4.6. Petroleum generation potential

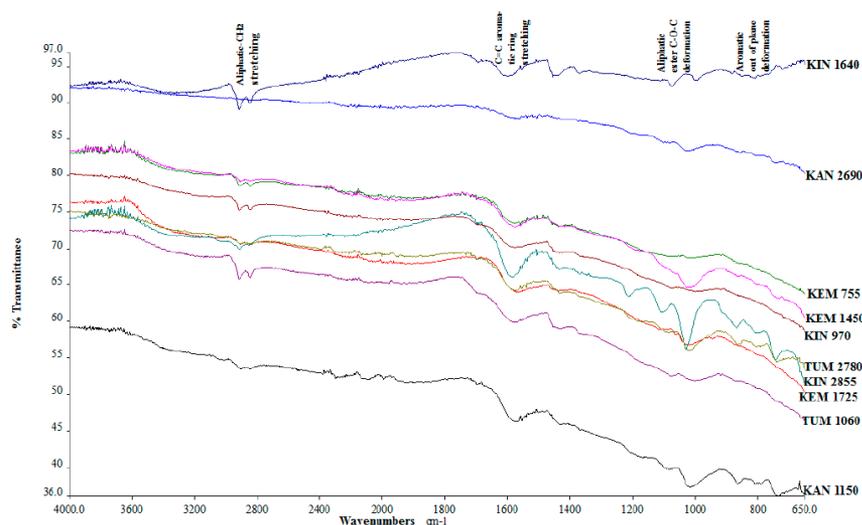
Kerogen is regarded as the source of oil and gas. The classification of kerogens according to their type is important for the definition of any kerogen assemblage and for the determination of the type of hydrocarbon it will likely generate. Assessment of the hydrocarbon source rock potential of the Late Cretaceous sediments in the Chad (Bornu) Basin has been carried out by some past workers such as Olugbemiro *et al.* (1997), Obaje *et al.* (2004) and Alalade & Tyson (2010). This study has confirmed their reports that the sediments are lean organically and are essentially gas prone. Though, the kerogen is predominantly Type III, and is expected to generate gas, the presence



**Figure 6:** Classification of kerogen of the analysed samples by using the relative abundance of n-octene, m(+p)-xylene and phenol (modified after Larter, 1984).



**Figure 7:** FTIR spectrum of a representative sample (KIN 1640).



**Figure 8:** FTIR spectra of all the analysed samples.

of slightly abundant  $> C_{15}$  mode in the Py-GC programs of some analysed samples coupled with the evidence of fluorescent amorphous organic matter, indicate that the organic matter in the sediments may also produce oil, albeit in limited quantity. This is further supported by the atomic H/C ratios interpretations.

In addition, Source Rock Analyzer  $T_{max}$  and the atomic H/C ratios show that the samples from the Late Cretaceous sediments are early mature at the upper section of Fika Formation to late mature at the lower part of Fika Formation and the rest of Gongila Formation. Consequently, the Late Cretaceous sediments of the Chad (Bornu) Basin can be regarded as potential source rock for gas and limited oil generation.

## 5. CONCLUSIONS

The origin, paleoenvironment and types of organic matter (kerogen) in the Fika and Gongila Formation of Chad (Bornu) Basin were assessed by means of organic geochemical characteristics and from palynofacies compositions. The organic matter is mainly composed of mixed terrestrial plant and marine algae-derived AOMs. Phytoclasts are also present in significant amount in most of the samples, especially those obtained from the upper section of Fika Formation. However, most of the AOMs appear to be degraded and were not well preserved. The variations of relative abundances of marine and terrigenous organic matter may be controlled by terrestrial input in ocean and/or preservation rather than marine production. This organic matter was likely deposited in marine environment under environmental conditions that were mostly dysoxic. The intense degradation observed in most of the organic matter may be as a result of high thermal maturity.

In this study, further evidences added to the insights of previous reports on the kerogen type in the basin. It was confirmed that most of the potential source rocks in Chad (Bornu) Basin contain Type III kerogens, but Type III/II kerogens are also present in some parts of the basin, especially at the upper section of Fika Formation. This study

also revealed that most of the samples, especially those at the deeper sections of the basin display high aromatic character which suggest a dominant gas-prone nature of the organic matter. Consequently, a potential for gas generation exist in this basin.

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