GEOCHEMICAL CHARACTERIZATION AND DEPOSITIONAL ENVIRONMENT OF ORGANIC MATTER FROM CRETACEOUS SEDIMENTS OF THE CALABAR FLANK, NIGERIA.

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ABSTACT

Twenty-eight shale and carbonaceous shale samples were collected from four outcrops in Nkporo, New Netim, Ekenkpon and Mfamosing Formations of the Calabar Flank, Nigeria. The source rock potential of the samples was determined using Rock-Eval analysis. The vitrinite reflectance measurements of the samples were taken using Zeiss standard universal reflected microscope. All the shales analyzed contained the minimum of 0.50wt.% and 2.00mg/g of Total Organic Carbon (TOC) and Petroleum Potential (PP) respectively of organic matter required to serve as good source rock for oil and gas. The petroleum potential of the Cretaceous units (Albian-Campanian Formations) of the Calabar Flank, Southeastern Nigeria was assessed by Rock-Eval pyrolysis. The TOC values range from 0.07 to 9.34 wt. % (averaging 2.41 wt. %). The PP and hydrogen index (HI) values range from 0.05 to 34.84 mg HC/g rock and 40.00 to 444.00 mg HC /g respectively. These values indicate that the sediments have gas and oil generating potential. The organic matter is predominantly gas prone (mostly type III and mixed type III/II). The level of thermal maturity deduced from the production index (0.04 to 0.63), calculated vitrinite reflectance of 0.10 to 0.66 %Ro and Tmax values between 338 and 439°C suggest that the shale and carbonaceous shale samples are thermally immature to marginally mature with respect to petroleum generation. Despite the source characteristics portraying moderate to high TOC values and immature to marginally mature; expulsion may have started or yet to get to more maturity stage before oil generation could be enough for expulsion.

Keywords: Production index; Shale; Petroleum; Rock-Eval pyrolysis; Expulsion, Vitrinite reflectance.

INTRODUCTION

The name Calabar Flank was first coined by Murat (1972) for the part of the continental margin of Nigeria characterized by block faults with NW-SE trending hoist and graben structures such as Ituk high and the Ikang trough. The study area lies between latitude 4°45ˈto 5°08ˈN and longitude 7°45ˈ to 8°35ˈE. Thus the Calabar Flank with a total thickness of over 3, 500m is related to the South Atlantic Cretaceous marginal basins which are characterized by similar horst structures (Reijers, 1996). The exposed Cretaceous sediments of the basin which is the major focus of this work appear rather unique in that the entire Upper Cretaceous sequence is exposed within a narrow stripe measuring about 8km (Fig. 1). A great deal of work has been carried out in this marginal sedimentary basin since the last three to four decades and these include works on biostratigraphy, depositional environment and diagenesis of Albian carbonate by Reijers and Petters (1987); the sedimentology of the Cretaceous sediments by Ebong (1989); petroleum source rock assessment of Nkporo shale (Unomah and Ekweozor, 1993), as well as Upper Cretaceous assemblage from Nkporo Shale by Kumaran and Ramanathan (1986) to mention but a few. This work is driven by the need to expand the frontier of search for hydrocarbon in the area because other geological provinces such as marginal basins of Equitorial Guinea, Angola and Gabon all in Africa, that show striking similarities in terms of stratigraphy and geological setting with the Calabar Flank are prolific oil fields. But despite long years of search no commercial accumulation of hydrocarbons has so far been discovered in the Calabar Flank. It is hoped that the data obtained in this study will further boost the research efforts in studying the sedimentary geochemistry of the Calabar Flank with the ultimate goal of ascertaining its hydrocarbon generative potentials, both in short and long terms.

The evaluation of petroleum prospect and plays in the Anambra and Afikpo Basins has been done and classified as having very good prospects for oil and gas (Whiteman, 1982). Hack et al. (2000), recognized a distinct hydrocarbon system that falls within the Anambra Basin, which features type II and type III oil prone kerogen, derived from Agwu and Imo formations. The geochemical analysis conducted shows that Eze-Aku shale, Agwu, Nkporo, Mamu and Enugu Shales are high in organic richness and ranges from immature to marginally mature source rocks while the Asu-River shale has condensate and dry gas.

The Cretaceous sediments of Calabar Flank have been classified as immature to early mature for hydrocarbon generation of type III and IV kerogen (Ekpo et al., 2013). In the Marginal Basins of Brazil and West Africa (Gabon, Angola and Congo), the Cretaceous Shale's are important source of hydrocarbons (Mello et al., 1988a,b; 1989;1991). Similar potential source rocks exist in the Calabar Flank, Anambra Basin and Afikpo Basin. In Lower Benue Trough of Nigeria (Ekweozor,1988; 1990; 1991), first described oil shale occurrence, followed by more regional research (Ehinola and Abimbola, 2002; Ehinola et al., 2003; 2004; 2005 and 2010). Unomah and Ekweozor,1993). Previous works on the Cretaceous outcrop sediment of Calabar Flank are limited to geological descriptions (Adeleye and fayose, 1978; Petters, 1982). Reyment, 1965), Preliminary Organic Geochemical appraisal (Essien et al., 2005), Geochemical studies of subsurface limestone (Ekwere, 1993), Geochemical and Organic Petrographic Studies (Ekpo et al., 2012) and Petroleum Geochemistry of the Cretaceous outcrop from Calabar Flank (Ekpo et al., 2013). Some of the mineralogical composition of shale affects the petrophysical properties and ability of the formation to be hydraulically fractured. These components and effects has been widely described in the United State of America (Sondergold et al. 2010; Peters et al., 2005; Bartis et al., 2005; Altun et al., 2006; Loucks et al., 2009; Jarvie et al., 2007; 2011; Kilmentidis et al. (2010) and in Estonia (Koel and Bunger, 2005).

This study identifies the potential source rocks in the Calabar Flank in order to determine the organic matter type, quantity and quality of organic matter, maturity, source of organic matter and hydrocarbon potential and the result compared with the existing geochemical data of the Calabar Flank. S_1 versus TOC will be use to discriminate the indigenous and non-indigenous organic matter from the source rocks.

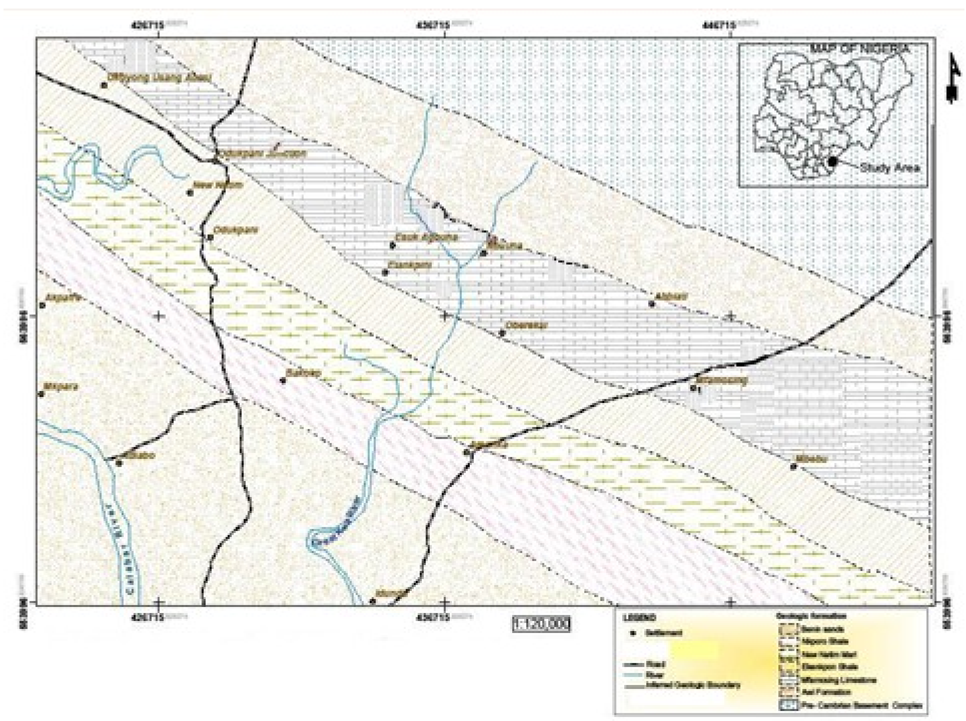

Fig. 1: Geological map of the Calabar Flank (after Essien and Ufot, 2010).

REGIONAL STRATIGRAPHIC SETTING

The term Calabar Flank was first introduced by Murat (1972) as that part of the southern Nigerian sedimentary basin, which is bordered by the Precambrian Oban Massif in the north and the Recent Niger Delta in the south (Fig. 2). The Afikpo syncline marks the northwestern limit while the Cameroon volcanic ridge bounds it in the east. The origin of the Flank is associated with the break-up of South America from Africa during the opening of the Gulf of Guinea in the Mesozoic. Tectonically, the geologic history of southern Nigeria has been controlled by three major tectonic phases (Murat, 1972). These tectonisms, resulted in the displacement of the axis of the main basins giving rise to three successive basins in which Calabar Flank is one. The Calabar Flank is a hinge zone (Fig. 2) which consists structurally of NW-SE trending basement horsts (the Oban Massif and the Ituk high), separated by a graben-the Ikang Trough (Petters and Reijers, 1987). These basement horst and graben structures as well as eustatic sea-level changes controlled the Mid-Cretaceous sedimentation in the basin (Nyong and Ramanathan, 1985).

Sedimentary succession of southeastern Nigeria is marked by a series of marine transgressions and regressions. In the Calabar Flank, the Asu River Group begins with a medium to very coarse, often pebbly, poorly sorted, arkosic cross-stratified sandstone (Adeleye, 1975). This basal sandstone was later called the Awi Formation (Adeleye and Fayose, 1978), forming the basal sands of the Odukpani Formation of Reyment (1965). The Awi Formation unconformably overlies the weathered granites, schists, migmatites and gneisses of the Precambrian Basement Complex (Oban Massif). The Awi Formation is devoid of fauna but was assigned an Albian age based on its correlation with the Mamfe Formation in the Cameroons (Adeleye and Fayose, 1978). Overlying the Awi Formation is the carbonate sequence of the Mfamosing limestone with sandstones and shales that were deposited during the Cenomanian regression in the Calabar Flank (Nwachukwu, 1972). The lower Limestone beds of Odukpani Formation of Reyment (1965) and the Mfamosing Limestone described by Petters and Ekweozor (1982) are the same (Fig. 3). The limestone is sandy and has alternating shale beds at the top (Fayose, 1978) with type sections at Abini and Mfamosing quarries.

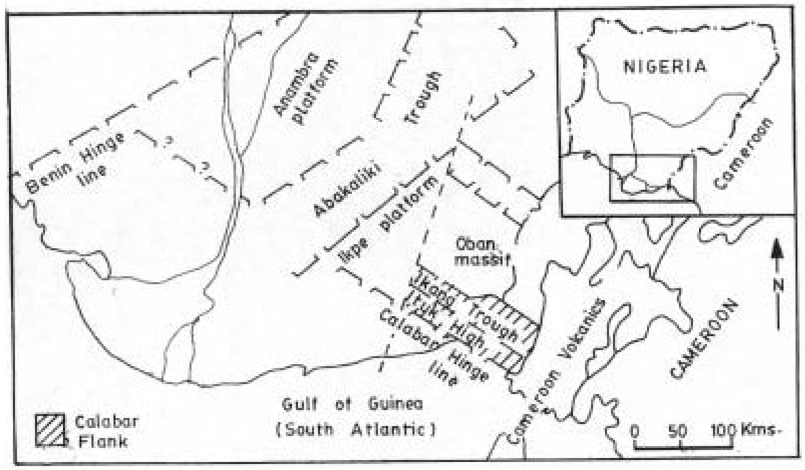

Fig. 2: Structural elements of the Calabar Flank and adjacent areas (after Nyong and Ramanathan, 1985)

Calcareous fissile dark grey to black shales of the Eze- Aku Formation lies on top of the Mfamosing limestone and was deposited during the extensive Turonian transgression (Nwachukwu, 1972). Reyment (1965) subdivided the Cenomanian-Santonian sediments into Odukpani, Eze-Aku and Awgu Shales. Petters (1980) also found that the Eze-Aku is Turonian and the Awgu Shales is Late Turonian-Coniacian on the Calabar Flank. He however noted that both the Eze-Aku and Awgu Shales are one continuous sequence of grey or black flaggy shales with limestone and sandstone interbed and spanning Turonian- Early Santonian. It was on this basis that Petters and Ekweozor (1982) proposed the name Nkalagu Formation to replace the upper shaly part of Odukpani, Eze-Aku and Awgu Shales (Fig. 3). According to them, all the limestones, shales and the inter-fingering regressive sandstones (Makurdi, Agala, Amasiri and Agbani Sandstones) of the Cenomanian-Early Santonian age belong to the Nkalagu Formation which is bounded at the bottom by the Early Cenomanian and at the top by the Late Santonian unconformities. Petters and Ekweozor (1982) proposed the Cross River Group for the Cenomanian-Early Santonian sequence while the Pre Albian – Albian sequences still belong to the Asu River Group of Reyment (1965).

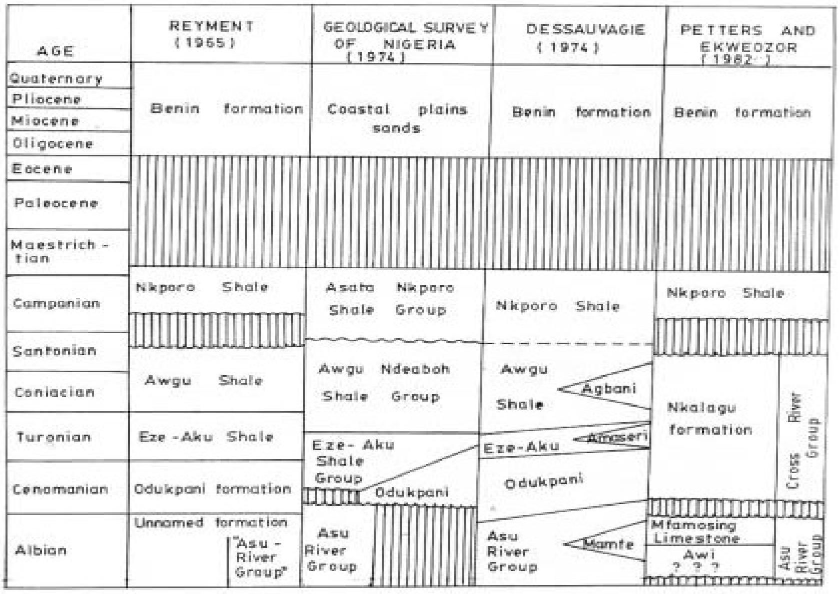

Fig. 3: Different views on the ages of Cretaceous sediments in the Calabar Flank (After Adegbie and Bassey, 2007).

After the Santonian-Campanian deformation, marine sedimentation resumed and the Nkporo shale was deposited as the first set of clastic sediments on the Flank. Its occurrence has been reported in the Ikang Trough, between the Oban Massif and the Ituk High (Whiteman, 1982). The Nkporo Shale consists of dark shales and sandstone and has been assigned a Campanian-Maestrichtian age by Reyment (1965). Cox (1952) used mollusks and fish remains from corehole samples to assign a Maestrichtian age to the Nkporo Shale, which is in line with the works of Nyong and Ramanathan (1985) and Kumaran and Ramanathan (1986). Nkporo Shale can therefore be said to cap the Cretaceous sequence of the Calabar Flank. Repeated periods of erosion and/or non-deposition occurred during Upper Maestrichtian – Lower Paleocene time, this led to the paucity of outcrops of Nkporo Shale on the Flank.

However, the Late Eocene witnessed a regressive phase which persisted in some parts of the Calabar Flank brought in the Tertiary-Recent continental sands of the Benin Formation (Reyment, 1965). From the above discussions, Calabar Flank is filled with Cretaceous to Recent sediments and there is no consensus of opinion amongst workers with regard to the nomenclature of the stratigraphy of this region (Fig. 3).

MATERIALS AND METHODS

A total of 28 outcrop carbonaceous shale and shale samples were obtained from the Nkporo (Shale), New Netim (Marl), Ekenkpon (Shale) and Mfamosing (Limestone) Formations at Akim Qua Junction, New Netim Community and Cave, Odukpani Junction and Akpabuyo localities all along Odikpani – Calabar Highway belonging to Albian-Campanian age of the Calabar Flank. Care was taking to avoid weathered portions of the outcrop and to obtain material sufficient for various geochemical analyses. In the laboratory, the samples were reshaped using a rotating steel cutter to eliminate surface that could be affected by alteration. Chips were cut from the samples and dried in an oven at 105ºC for 24 hours. The dried sample was pulverized in a rotating disc mill to yield about 50 g of sample for analytical geochemistry. The TOC and inorganic carbon (TIC) contents were determined using Leco CS 200 carbon analyzer by combustion of 100 mg of sample up to 1600ºC, with a thermal gradient of 160ºC min^{-1}; the resulting CO_2 was quantified by an Infrared detector. The sample with known TOC was analyzed using a Rock-Eval 6, yielding parameters commonly used in source rock characterization, flame ionization detection (FID) for hydrocarbons thermal conductivity detection (TCD) for CO_2. The Zeiss standard universal reflected microscope was used for vitrinite reflectance.

RESULTS AND DISCUSSIONS

Petroleum source potential (PP) represents the maximum quantity of hydrocarbon that a sufficiently matured source rock might generate; and is given as (S_1+S_2). It is a measure of genetic potential (Tissot and Welte, 1984) or the total amount of petroleum that might be generated from a rock. It therefore accounts for the quantity of hydrocarbons that the rock has already expelled (S_1) and hydrocarbon embedded in the kerogen (S_2).

Total organic carbon content (TOC) and Rock-Eval analysis were performed on 28 potential source rock samples (Table 1). Total organic carbon in a source rock comprises three basic components: (1) organic carbon in a retained hydrocarbons as received in the laboratory; (2) organic carbon that can be converted to hydrocarbons, called convertible carbon (Jarvie, 1991a) or reactive or labile carbon (Cooles et al., 1986); and (3) a carbonaceous organic residue that will not yield hydrocarbons because of insufficient hydrogen commonly referred to as inert carbon (Cooles et al., 1986; Jarvie, 1991a). Adequate amount of organic matter is a necessary prerequisite for sediment to generate oil or gas (Cornford, 1986).

The TOC content for the outcrop samples ranges from 0.71 to 2.36 wt. % (averaging 1.68 wt. %), 0.07 to 4.45 wt. % (averaging 1.89 wt. %), 0.10 to 1.68 wt.% (averaging 0.56) and 0.84 to 9.34wt. % (averaging 5.21 wt. %) respectively (Table 1). These TOC values show that the sediments have comparable average TOC contents, which are greater than the 0.5 wt. % threshold value required for a potential source rock to generate petroleum (Tissot and Welte, 1984).

The source rock quality of the shale and carbonaceous shale in the four outcrops is confirmed by the pyrolysis-derived petroleum potential (PP = S_1+S_2) of selected samples (Table1). The petroleum generative potential of outcrops Akim Quo Junction, New Netim, Odukpani Junction and Akpabuyo ranges from 0.61-3.80 mg/g rock, 0.05-10.53 mg/g rock, 0.08-2.56 mg/g rock and 0.96-34.83 mg/g rock respectively. Hydrogen index (HI) values for the studied samples ranges from 79 to 174 mgHC/g TOC for Akim Quo Junction, 43 to 220 mgHC/g TOC for New Netim, 40 to 181 mgHC/g TOC for Odukpani Junction and 104 to 444 mgHC/g TOC for Akpabuyo respectively. These values indicate a moderately good source rock with gas and oil generating potential (PP > 2 mg/g; [Peters and Cassa, 1994; Tissot and Welte, 1984]).

The type of organic matter in sediments penetrated by the three outcrops (Akim Quo Junction, New Netim, Odukpani Junction and Akpabuyo) was assessed by Rock-Eval pyrolysis (Table1).

Table 1: Total Organic Carbon and Rock-Eval Pyrolysis Data Sets.

Sample N0.	Lithology	Formation	Locality	S1 (mgHC /g rock)	S2 (mgHC /g rock)	S3 ($mgCO_2$ /g rock)	TOC (wt.%)	HI (mgHC /g TOC)	OI ($mgCO_2$ /g TOC)	Tmax (^{o}C)	PP S1 + S2	S2/S3	SI/TOC (mgHC/ g TOC)	PI [S1/S1+S2]	Net Expulsion (%)	HI/OI	TS (%)	%Ro	TOC/TS (%)
NKP-1	Shale	Nkporo	Akim Qua JN.	0.42	3.05	0.32	1.75	174.00	18.00	430.00	3.47	10.00	24.00	0.12	148.14	9.67	5.70	0.57	64.81
NKP-2	"	"	"	0.17	1.47	0.19	1.05	140.00	18.00	436.00	1.64	8.00	16.00	0.10	119.00	7.78	5.50	0.64	23.33
NKP-3	"	"	"	0.15	1.53	0.26	1.07	143.00	24.00	432.00	1.68	6.00	14.00	0.09	121.54	5.96	5.21	0.62	20.54
NKP-4	"	"	"	0.05	0.56	0.25	0.71	79.00	35.00	436.00	0.61	2.00	7.00	0.08	67.04	2.26	5.05	0.64	1.75
NKP-5	"	"	"	0.11	1.70	0.34	1.25	136.00	27.00	432.00	1.81	5.00	9.00	0.06	115.60	5.04	5.30	0.62	23.58
NKP-6	"	"	"	0.19	3.00	0.53	1.87	160.00	28.00	432.00	3.19	6.00	10.00	0.06	136.36	5.71	5.20	0.62	44.52
NKP-7	"	"	"	0.15	3.65	0.46	2.17	168.00	21.00	431.00	3.80	8.00	7.00	0.04	142.97	8.00	5.20	0.58	41.73
NKP-8	"	"	"	0.15	3.00	0.62	2.24	134.00	28.00	439.00	3.15	5.00	7.00	0.05	113.84	4.79	5.50	0.66	64.00
NKP-9	"	"	"	0.17	3.32	0.57	2.36	141.00	24.00	434.00	3.49	6.00	7.00	0.05	119.58	5.88	5.23	0.65	45.12
NKP-10	"	"	"	0.15	3.12	0.55	2.28	137.00	24.00	431.00	3.27	6.00	7.00	0.05	116.32	5.71	5.23	0.61	53.90
NNT-1	"	New Netim	New Netim	0.12	1.77	0.60	2.96	60.00	20.00	424.00	1.89	3.00	4.00	0.06	50.83	3.00	5.40	0.47	87.06
NNT-2	"	"	"	0.03	0.32	4.91	0.27	44.00	6.82	431.00	0.35	0.00	4.00	0.09	100.74	6.45	6.30	0.60	6.28
NNT-3	"	"	"	0.23	4.51	0.48	3.29	137.00	15.00	432.00	4.74	9.00	7.00	0.05	116.52	9.13	5.90	0.59	67.14
NNT-4	"	"	"	0.75	9.78	0.76	4.45	220.00	17.00	430.00	10.53	13.00	17.00	0.07	186.81	12.94	6.00	0.57	148.33
NNT-5	"	"	"	0.64	0.37	0.54	0.31	119.00	17.40	338.00	1.01	1.00	20.60	0.63	101.45	6.84	5.60	0.10	6.74
NNT-6	"	"	"	0.02	0.03	0.07	0.07	43.00	10.00	392.00	0.05	0.00	29.00	0.40	36.43	4.30	6.50	0.10	1.56
EKE-1	"	Ekenkpon	Odukpani JN.	0.04	0.04	0.08	0.10	40.00	8.00	425.00	0.08	1.00	40.00	0.50	34.00	5.00	5.90	0.49	2.56
EKE-2	"	"	"	0.09	0.58	0.24	0.32	181.00	75.00	439.00	0.67	2.00	28.00	0.13	154.06	2.41	5.12	0.66	6.25
EKE-3	"	"	"	0.12	2.44	0.39	1.68	145.00	23.00	432.00	2.56	6.00	7.00	0.05	123.45	6.30	6.20	0.62	52.50
EKE-4	"	"	"	0.03	0.13	0.34	0.22	59.00	15.50	439.00	0.16	0.00	14.00	0.19	50.23	3.81	5.56	0.66	4.82
EKE-5	Shale	"	"	0.07	0.37	0.26	0.48	77.00	54.00	436.00	0.44	1.00	15.00	0.16	65.52	1.43	5.16	0.64	11.54
MFA-1	Carb-shale	Mfamosing	Akpabuyo	1.88	30.53	1.79	9.34	327.00	19.00	437.00	32.41	17.00	20.00	0.06	277.84	17.21	6.27	0.65	177.23
MFA-2	"	"	"	1.04	22.53	1.73	9.32	242.00	19.00	430.00	23.57	13.00	11.00	0.04	205.48	12.74	5.34	0.58	214.75
MFA-3	"	"	"	1.19	13.35	1.11	5.54	241.00	20.00	436.00	14.54	12.00	21.00	0.08	204.83	12.05	5.60	0.64	120.43
MFA-4	"	"	"	0.20	3.79	0.68	2.01	139.00	34.00	436.00	3.99	6.00	10.00	0.05	160.27	4.09	5.82	0.64	52.62
MFA-5	"	"	"	0.18	2.81	0.82	1.95	144.00	42.00	431.00	2.99	3.00	9.00	0.06	122.49	3.43	5.86	0.58	40.12
MFA-6	"	"	"	1.68	33.16	2.92	7.47	444.00	39.00	432.00	34.84	11.00	22.00	0.05	377.32	11.38	5.20	0.62	233.44
MFA-7	Shale	"	"	0.09	0.87	0.20	0.84	104.00	24.00	439.00	0.96	4.00	11.00	0.09	88.04	4.33	5.30	0.66	19.53

Most of the studied rock units from the four outcrops are mainly of type III with subordinate type II-III. The plots Rock-Eval S_2 versus TOC (Fig. 4) are useful to compare the petroleum-generative potential of source rocks (Langford and Blanc-Valleron, 1990; Peters, 1986). The slopes of lines radiating from the origin in Figure 4 are directly related to hydrogen index (HI= $S_2 \times 100/TOC$, mg HC/g TOC).

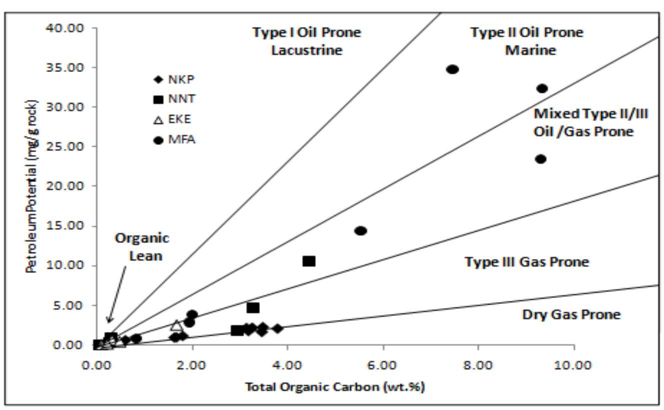

Fig. 4: Plots of Rock-Eval S2 versus TOC (Langford and Blanc-Valleron, 1990).

Hydrogen index values of greater 600, 300-600, 200-300, 50-200 and less than 50 mg HC/g TOC classifies organic matter as type I (very oil prone), type II (oil prone), type III (gas prone) and type IV (inert) respectively (Peters, 1986). The relationship between the hydrogen index (HI) versus oxygen index (OI) (Fig. 5), reveals kerogen of type III and mixed type II-III organic matter which are predominantly gas prone. Plots of HI versus Tmax (the maximum temperature of pyrolysis) (Fig. 6) and HI versus calculated %Ro (Fig. 7), also shows that the organic matter in the samples is mainly type III with subordinate type II/III. The above results are in agreement with the data obtained by earlier workers (Akaegbobi and Schmitt,1998; Akande et al., 2007; Shanmugam, 1985).

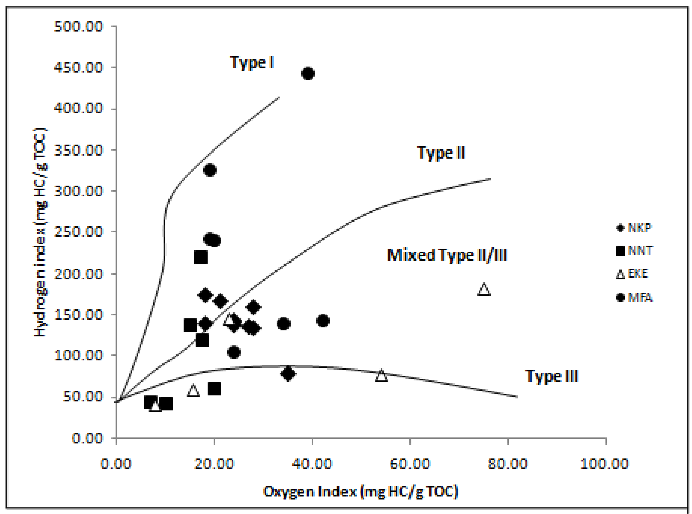

Fig.5: Plot of hydrogen index (HI) versus oxygen index (OI) for the shale units from Cretaceous sediments of the Calabar Flank.

Thermal maturity provides an indication of the maximum paleotemperature reached by a source rock. The thermal maturity of the shale and carbonaceous shales of the Anambra Basin, Afikpo Basin and Calabar Flank have been discussed by several authors (Akaegbobi and Schmitt,1998; Akaegbobi and Nwachukwu, 2000; Unoma and Ekweozor, 1993). The degree of thermal maturity of the shale and carbonaceous shales of Cretaceous sediments of the Calabar Flank was assessed by pyrolysis-derived indices, such as Rock-Eval Tmax, production index and calculated %Ro (Table 1). According to (Peters, 1986), PI and Tmax values less than about 0.1 and 430°C respectively, indicate immature organic matter while Tmax greater than 470°C points to the wet-gas zone. The Tmax values of the shale and carbonaceous shale samples in outcrops Akim Qua Junction, New Netim, Odukpani Junction and Akpabuyo ranges from 430 to 439°C (averaging

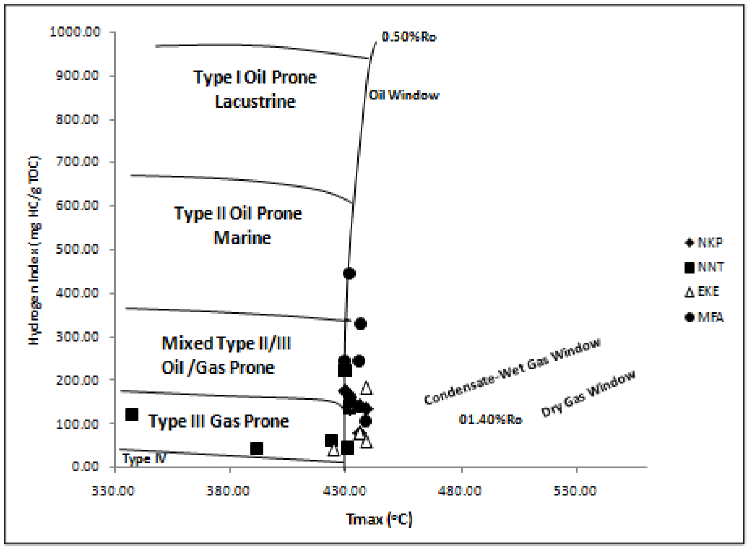

Fig. 6: Plot of HI versus Tmax for characterization of the organic matter for outcrop sediments from Calabar Flank.

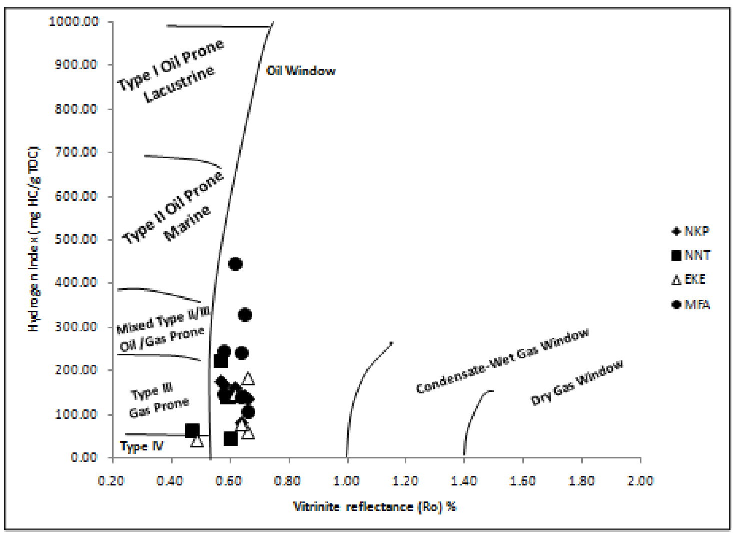

Fig. 7: Plot of HI versus calculated vitrinite reflectance (Calc.%Ro).

433ºC), 338 to 432ºC (averaging 408ºC), 425 to 439ºC (averaging 434ºC) and 430 to 439ºC (averaging 435ºC) respectively. The calculated vitrinite reflectance values range between 0.58 to 0.66 %Ro (Akim Qua Junction), 0.10 to 0.60 %Ro (New Netim), (Odukpani Junction), 0.49 to 0.61 %Ro and 0.58 to 0.66 %Ro (Akpabuyo). Both values indicate that the samples are thermally immature to marginally mature with respect to petroleum generation. Plots of PI versus Tmax (Fig. 8), PI versus calculated vitrinite reflectance (Fig. 9) also show that the coal and shale sediments are partly within the oil window.

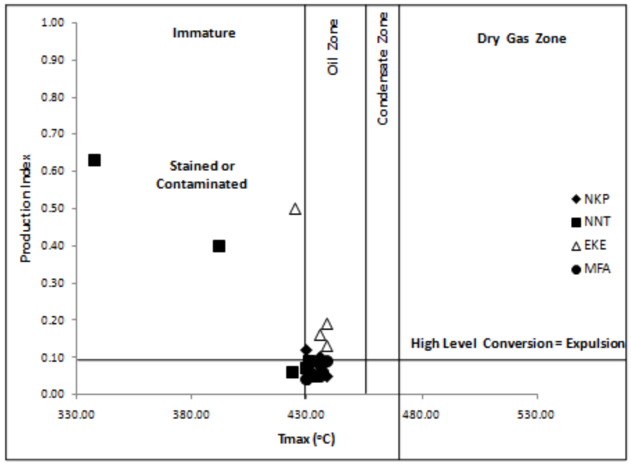

Fig. 8: Plot of production index (PI) against Tmax of the studied rock samples from the Calabar Flank.

The production index ($PI=S_1/S_1+S_2$) values > 0.1 (Table 1) observed on few outcrop samples indicate possible impregnation by migrated bitumen or contamination by mud additives (Clementz, 1979). Other samples with PI-values ranging from 0.02 to 0.09 correspond to the expected results.

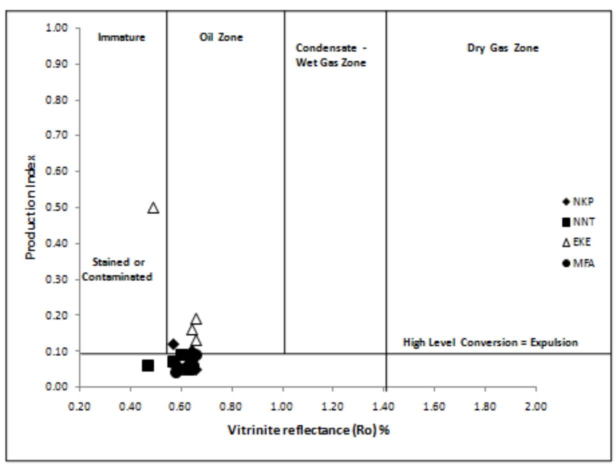

Fig. 9: Plot of production index (PI) versus calculated vitrinite reflectance (Calc. %Ro).

Regionally, there is a progressive increase of TOC towards the deeper part (Akim Qua Junction to Akpabuyo) of the Calabar Flank. This suggests that, with increasing organic matter content, the prospectivity of the studied area in terms of hydrocarbons increases in this direction.

On the selected samples for Rock-Eval S_1 ranges from 0.02 in New Netim to 1.68mgHC/g rock in Akpabuyo while S_2 ranges from 0.03 in New Netim to 33.16mgHC/g rock in Akpabuyo.

These parameters [S1, S2, HI and (S1+S2)/gTOC] when plotted relative to %Ro will show the peaks to plateaus exhibited in these plots for S_1, S_2, HI and $(S_1 + S_2)$/gTOC at 0.58%Ro for HI, and between 0.53, 0.56 and 0.60%Ro for S_1, S_2 and $(S_1 + S_2)$/gTOC indicating the level of maturity and area of hydrocarbon generation potential.

Larger data sets have been used by Sykes and Snowdon (2002) and Petersen (2002). These same similar peaks on Rock-Eval 6 parameters relative to T_{max} or vitrinite %Ro have been noted previously by various authors (Table 2). The implication for peaks in these coals studied is that hydrocarbon generation potential increases with increasing rank.

Table 2: Peaks for petroleum generation on Rock-Eval parameters relative to Tmax or Vitrinite %Ro

Authors	Peaks on Rock-Eval parameters relative to Tmax or vitrinite %Ro
Pittion and Gouadain (1985)	S1/TOC peak~1.0 %Ro, Tmax~450°C
Suggate and Boudou (1993)	HI peak, Tmax~440°C and 0.80 %Ro
Boreham et al. (1999)	HI peak, Tmax~440°C and 0.80 %Ro
Petersen (2002)	S_1 and S_2, 0.85%Ro; HI at 0.90%Ro
Staisuki et al. (2006)	HI peak at 0.90%Ro, between 0.90 and 1.0%Ro for S_2 and $(S_1 + S_2)$TOC

A Plot of the SOM (extract yield) against TOC as proposed by Landis and Connan (1980) in Jovancicevic et al. (2002) for the shale samples when plotted will indicates that no migration of oil will take place. This is supported by the diagram of $S_1 + S_2$ vs TOC (Fig. 4) characterizing the shale samples from the Calabar Flank as good to excellent source rocks with TOC and $S_1 + S_2$ above 1.0wt% and 5.0mg/g respectively. Twenty-one samples with TOC greater than 0.6wt% were derived from shaly carbonaceous samples. This is also supported by the report of Beka et al. (2007) from their investigations on shaly facies of gas prone sequences in the Afikpo Basin based on the values of TOC (1.09-18.24wt%) and soluble organic matter (SOM) (190-2900ppm) which are indicative of good to excellent and adequate source potential. This will also supported by a diagram of Hydrocarbon (ppm) versus TOC (wt. %) when plotted will show that all the samples contains oil and oil with some gases.

The content of sulphur (S) in the Cretaceous sediments from the Calabar Flank ranges from 2.70 to 5.30% with an average of 4.29%. The overall tendency towards lower S with increasing TOC, as well as the TOC/S ratios for shale samples between 1.75 to 68.81% (averaging 38.33%) in Akim Qua Junction, 1.56 to 148.33% (averaging 52.85%) in New Netim, 2.56 to 52.50% (averaging 15.53%) and 19.53 to 233.44% (averaging 122.59%) in Odukpani Junction and Akpabuyo respectively indicated depositional environment of organic matter. The result of TOC/S from the shale samples argue for a marine environment during deposition as observed from the sulphur content (Berner, 1984).

Oxygen index (OI) ranges from 6.82wt.% in New Netim to 75.00wt.% in Odukpani Junction. The OI is relatively moderate, suggesting deposition in a low oxic environment and high terrestrial higher plant contribution as source of organic matter. All these parameters S, TOC/S and OI are supported by the content of HI/OI. In the shale samples, HI/OI ranges from 1.43 in Odukpani to 17.21 in Akpabuyo. The organic matter from the shale samples is distinguishable by their very low HI/OI ratio despite a terrestrial origin of the OM (Galimov, 2004).

Expulsion of Petroleum

The proportion of oil expelled from the source rock expressed as a percentage of total oil generated is called expulsion efficiency. Expulsion efficiency increases with the maturation process, that is, the more oil generated in the source rock, the more that can be effectively expelled from it (Ameh et al., 2016). Expulsion efficiency is intimately related to the degree of hydrocarbon saturation of the pore system. The expulsion efficiencies are higher for a rich, oil prone source rock unit compared to a poorer quality source rock, which may not have rich organic matter and very much dependent on S_2. Net Expulsion efficiencies range from 34.00% to 377.32% of the samples studied. Expulsion should be about 60% for good source rocks (Cools et al*.,* 1985).

Net Expulsion is S_1 expressed as carbon, relative to the TOC. The productive index depends on S_1, and both parameters are affected by the expulsion (Rullkotter et al*.,* 1988). From the plot of Net Expulsion Efficiency vs. Tmax, (Fig. 10) the studied samples showed high expulsion rates (above 20% for all samples). McKenzie et al*.,* (1987) proposed that a good quality source rock at its peak generation potential reaches Expulsion Efficiency between 50-70%, and the studied samples showed a high percentage above 20%. Despite the source characteristics portraying moderate to high TOC values and immature to marginally mature; expulsion may have started or yet to get to more maturity stage before oil generation could be enough for expulsion.

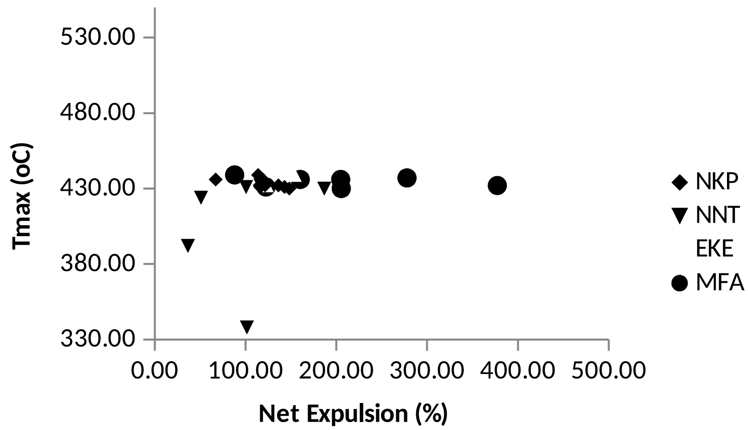

Fig. 10: A graph of Tmax vs Net Expulsion

CONCLUSION

This study has shown that the shales of the Cretaceous sediments in the Calabar Falnk, SE Nigeria has TOC contents of up to 75.00wt. %. The hydrogen index (HI) and petroleum potential (PP) of the shale samples in this study are above the minimum values required for a potential source rock, suggesting that the sediments have gas and oil generating potential. The organic matter is predominantly gas prone (mostly Type III and some mixed Type II/III). The level of thermal maturation derived from the Rock-Eval data show that the shale sediments are partly within the oil window. Net Expulsion Efficiency vs. Tmax, the studied samples showed high expulsion rates (above 20% for all samples). The S, TOC/S, OI and HI/OI indicated that the organic matter from the shale samples are terrestrially source and deposited on shallow marine environment.

REFERENCES

Adeleye, D.R., 1975. Nigerian Late Cretaceous Stratigraphy and paleogeography. Bulleting of American Association of Petroleum Geologists, 29(12), pp. 2302-2313.

Adeleye, D. R. and E. A. Fayose, 1978, Stratigraphy of the type section of Awi Formation, Odukpani Area, South-Eastern Nigeria, *Nigeria Journal of Mining Geology*.15 (1) 35-37.

Akaegbobi, I.M., and Schmitt, M.: (1998), Organic facies, hydrocarbon source potential and the reconstruction of depositional paleoenvironment of Campano-Maastrichtian Nkporo shale in the Cretaceous Anambra Basin, Nigeria NAPE Bull., 13(1), 1-19.

Akaegbobi, I.M., Nwachukwu, J.I., and Schmitt, M.: (2000), Aromatic hydrocarbon distribution and calculation of oil and gas volumes in post-Santonian shale and coal, Anambra Basin, Nigeria. In: Mello, M.R., and Katz, B.J., (eds.), Petroleum systems of south Atlantic margins. AAPG Memoir, 73, 233-245.

Akande, S.O., Ogunmoyero, I.B., Petersen, H.I., and Nytoft, H.P.: (2007), Source rock evaluation of coals from the lower Maastrichtian Mamu Formation, SE Nigeria. Journ. Petroleum Geology, 30(4), 303-324.

Altun,N.E, Hicyilmaz., Hwaang,J.Y.,Bagci,M.V. 2006.oil shales in the world and turkey reserves, current situation and future prospects; A Review.

Ameh, C., Aina, O., Ogbuwa, K., Abrakasa, S. and Ideozu, R. (2016), Source Rock Geochemistry of the Nsukka Formation in Arochukwu Area of Afikpo Basin, South–Eastern Nigeria. IOSR Journal of Applied Geology and Geophysics, 4(5), pp. 24-28.

Bartis, J.T., LaTourette,T.,Dixon.L.,Peterson,D.J.,Cecchine,G. 2005. Oil shale development in the United States, prospects and policy issues MG-414,-NETL

Beka, F., Ukaegbu, V., Oluwajana, O., Oledinma, N., Njoku, I., Beka, J., Amaechi, L. and Udoh, M. (2007), Spatial profiling of shaly facies and palaeoenvironment reconstruction of gas prone sequences in the Anambra Basin, Nigeria. Nig. Assoc. Petrol. Expl. 25th Annual Conf., Abuja, Nigeria, 2007. Abs. Vol., 25p.

Boreham, C. J., Horsfield, B. and Schenk, H. J. (1999), Predicting quantities of oil and gas generated from Australian Permian coals, Bowen basin using pyrolytic techniques. *Mar. Petrol. Geol*., **16**, 165-188.

Clementz, D.M.: (1979), Effect of oil and bitumen saturation on source-rock pyrolysis. AAPG Bull., 63, 2227-2232.

Cooles, G.P., Mackenzie, A.S., and Quigley, T.M.: (1986), Calculation of petroleum masses generated and expelled from source rocks. In: Leythaeuser, D., and Rullkötter, J., (eds.), Advances in organic Geochemistry, Oxford, Pergamon, Organic Geochemistry, 10, 235-245

Cornford, C.: (1986), Source rocks and hydrocarbons of the North Sea. In: Glennie, K.W., (ed.), Introduction to the Petroleum Geology of the North Sea, Oxford, U.K., 197-236.

Cox, L.R., 1952. Cretaceous and Eocene fossils from the Gold Coast. Bull. Gold Coast Geol. Surv., Vol. 17, 57p.

Ebong, U. E., 1989, The Sedimentology of the Cretaceous highway transect from the Calabar Flank across the Mamfe Embarment. Unpublished M.Sc. Thesis, University of Calabar.

Ehinola,O.A., Abimbola,A.F. 2002. Preliminary aspects of major and trace elements content in The middle cretaceous black shales of the Abakaliki fold belt, Southeastern Nigeria/Nafta vol53, No9,Pg 323-326.

Ehinola,O.A., Bassy,C.E., Ekweozor,C.M. 2003. Preliminary studies of the lithostratigraphy and Depositional environment of oil shale deposit of Abakaliki anticlinorium Southeastern Journal of mining and geology, vol.39.No2 Pg85-94.

Ehinola,O.A., Badejoko,T.A.,Ekweozor,C.M,Adebowale,K.O .2004. Organic facies variations in the middle cretaceous black shales of Abakaliki fold belt,Southeastern Nigeria/Nafta vol.55,No12,Pg505-515.

Ehinola,O.A., Sonibare,O.O., Akanbi,O.A. 2005. Economic evaluation, recovery techniques and Environmental implications of the oil shale deposits in the Abakaliki Anticlinorium,Southeastern Nigeria//oil shale.2005. Vol22 No.1, Pg5-19.

Ehinola,O.A.2010. Biostratigraphy and depositional Environment of the oil shale deposits in the Abakaliki fold belt , Southeastern Nigeria, Vol27, No2, Pg99-125..

Ekpo, B.O., Ibok, U.J., Wehner, H., (2013). Petroleum Geochemistry of Cretaceous outcrop sediments from the Calabar Flank, S.E. Nigeria

Ekpo, B.O., Ibok, U.J., Essien, N.E., Wehner, H., 2012. Geochemistry and organic petro graphic studies of the Calabar Flank, Southeastern Nigeria. Marine Pet. Geol. 35, 252-268.http://dx.doi.org/10.1016/j.marpetgeo.2012.03.010.

Ekwere, S.J., 1993. Geochemistry of subsurface limestone samples from Etankpini, Calabar Flank, southeastern Nigeria. Trop. J. Appl. Sci. 3, 9-17.

Ekweozor, C.M., Unomah, G.I. 1990. First discovery of oil shale in the Benue trough Nigeria. Fuel.Vol.69. p. 502-508.

Ekweozor, C.M., Udo, O.T., 1988. The oleananes: origin, maturation and limits of occurrence in southern Nigeria sedimentary basins. In: Mattavelli, L., Novelli, L. (Eds.), Advances in Organic Geochemistry 1987. Org. Geochem. vol. 13 (1-3),131-140

Essien, N. U. and Ufot, D. O. (2010), Age of the Mfamosing Limestone, Calabar Flank, South Eastern, Nigeria. International Journal of Basic & Applied Sciences IJBAS-IJENS, 10(5), pp. 8 – 19.

Essien, N., Ukpabio, E.J., Nyong, E., Ibe, K.A., 2005. Preliminary organic geochemical appraisal of Cretaceous rock units in the Calabar Flank, southeastern Nigeria. J. Mining Geol. 41 (2), 185-19

Fayose, E.A., 1978. Depositional environments of carbonates, Calabar Flank, southeastern Nigeria. Journal of Mining and Geology, Vol. 15, pp. 1-13.

Galimov, E. M. (2004), The pattern of $\delta^{13}C$ versus HI/OI relation in recent sediments as an indicator of geochemical regime in marine basins: comparison of the Black Sea, Kara Sea and Cariaco Trench. *Chem. Geol*., **204**, 287-301.

Haack, R.C., Sundaraman, P., Diedjomahor, J.O., Xiao, H., Gant, N.J., May, E.D., Kelsch, K., 2000. The Niger Delta petroleum systems, Nigeria. In: Mello, M.R., Katz, B.J. (Eds.), Petroleum Systems of South Atlantic Margins. American Association of Petroleum Geologists Memoir, vol. 73, pp. 213–231. Haq, B.U., Hardenbol, J., Vail, P.R., 1987. Chronology

Jarvie, D.M.: (1991a), Total organic carbon (TOC) analysis. In: Merril, R.K., (ed.), Treatise of petroleum geology: Handbook of petroleum geology, source and migration processes and evaluation techniques. AAPG, 113-118.

Jarvie, D.M., Hill, R.J., Ruble, T.E., Pollastro, R., (2007) unconventional shale gas systems, the Mississipian Barnett shale of North central Texas as one model for thermogenic shale-gas Assessment, AAPG BULL. 91Pp 475-499.

Jarvie,D.M., 2011, Shale resources systems for oil and gas in J.Breyer,ed,shale reservoirs,giant resources for the 21st century, AAPG Memoir 97 Pg 1-3.

Jovancicevic, B., Wehner, H., Scheeder, G., Stojanovic, K., Sainovic, A., Cvetkovic, O., Ercegovac, M. and Vitorovic, D. (2002), Search for source rocks of the crude oils of the Drmno deposition (southern part of the Pannonian Basin, Serbia). *Jour. Serbian Chem. Soc.*, **67**, 553 – 566.

Kilmentidis,R., Lazar,O.R., Bohaus,K.M., Esch,W.L., Pedersen,P., 2010, integrated petrography of mudstones AAPG 2010. Annual convention, New Orleans, Louisiana, April 11-14

Koel, M., Bunger, J. 2005.over view of program on US-Estonia science and technology Cooperation on oil shale research and utilization(stratigraphy importanceof oil shale Studies for Estonia and USA).

Kumaran, K.P.N. and Ramanathan, R.M., 1986. An upper Cretaceous assemblage from the Nkporo shale of the Calabar Flank. Journal of Paleontological Society of India, Vol. 31, pp 9-15.

Langford, F.F. and Blanc-Valleron, M.-M.: (1990), Interpreting Rock-Eval pyrolysis data using graphs of pyrolizable hydrocarbons versus total organic carbon. AAPG Bull., 74, 799-804.

Loucks, R.G., Reed,R.M.,Ruppel,S.C.,Javie,D.M.,2009. Morphology,Genesis and distribution of nanometer scale pores in siliceous mudstones of Mississippian Barnett shale,Jour. Sedimentary Research 79, Pg 848-861.

McKenzie A.S. et al. (1987), The expulsion of petroleum from Kimmeridge Clay source-rocks in the area of the Brae oilfield, UK continental shelf, in: Petroleum geology of North West Europe. Proceedings of the 3rd conference on petroleum geology of North West Europe, London, 26-29 October, 865-877.

Mello, M.R., Gaglianone, P.C., Brassel, S.C., Maxwell, J.R., 1988a. Geochemical and biological marker assessment of depositional environments using Brazilian offshore oils. Marine Pet. Geol. 5, 205-223.

Mello, M.R., Telnaes, N., Gaglianone, P.C., Chicarelli, M., Brassell, S.C., Maxwell, J.R.,1988b. Organic geochemical characterisation of depositional paleoenvironments of source rocks and oils on Brazilian marginal basins. In: Mattavelli, L., Novelli, L.(Eds.)Advances in Organic Geochemistry 1987. Pergamon Press, pp. 31-45.

Mello, M.R., Koutsoukos, E.A.M., Hart, M.B., Brassel, S.C., Maxwell, J.R., 1989. Late Cretaceous anoxic events in the Brazilian continental margin. Org. Geochem.14(5), 529-542.

Mello, M.R., Mohriak, W.U., Koutsoukos, E.A.M., Figueira, J.C.A., 1991. Brazilian and west African oils. Generation, migration, accummulation and correlation. In: Proceeedings of the 13th World Petroleum Congress. John Wiley & Sons, New York, pp. 153-164

Murat, R.C.: (1972), Stratigraphy and paleogeography of the Cretaceous and Lower Tertiary in Southern Nigeria. In: Dessauvagie, T.F.J. and Whiteman, A.J (eds.), African Geology, University of Ibadan Press, 251-266.

Nwachukwu, S.O., 1972. The tectonic evolution of the southern portion of the Benue Trough, Nigeria. Geol. Mag., Vol. 109, pp. 411-419.

Nyong, E.E. and Ramanathan, R.M., 1985. A record of oxygen-deficient paleoenvironments in the Cretaceous of the Calabar Flank, SE Nigeria. Journal of African Earth Sciences, 3(4), pp. 455-460.

Peters, K.E.: (1986), Guidelines for evaluating petroleum source rock using programmed pyrolysis, AAPG Bull., 70(3), 318-329.

Peters, K. E., Cliford, C. E. and Moldowan, J. M. (2005), **The biomarker guide**. 2nd Edition Prentice –Hall, New Jersey.

Petersen, H. I. (2002), A reconsideration of the “oil window” for humic coal and kerogen Type III. *Jour. Petrol. Geol.*, **25**, 407-432.

Petters, S.W., 1980. Biostratigraphy of Upper Cretaceous foraminifera of the Benue Trough, Nigeria. Journal of Foraminiferal Research, Vol. 10, pp. 191-204.

Petters, S.W and Ekweozor, C.M.: (1982), Petroleum Geology of Benue Trough and southeastern Chad Basin, Nigeria. AAPG Bull., 66, 1141-1149.

Petters, S.W.: (1977), Mid -Cretaceous paleoenvironments and biostratigraphy of the Benue Trough, Nigeria. Geol. Surv. America Bull., 89, 151-154.

Pittion, J. L. and Gouadain, J. (1985), Maturity studies of the Jurassic’coal unit’ in three wells from the Haltenbanken area. Petroleum Geochemistry in Exploration of the Norwegian Shelf. Graham and Totman, London, 205-211.

Reijers, T. J. A., 1996, Selected Chapters on Geology-sedimentary Geology and Sequence Stratigraphy in Nigeria. SPDC Course Handbook (Field Guide) 121p

Reijers, T.J.A and S.W. Petters, (1987). Depositional environment and diagenesis of Albian carbonates in Calabar Flank, S. E. Nigeria: *Journal of Petroleum Geology*. (10), 283-294.

Reyment, R.A.: (1965), Aspects of geology of Nigeria. University of Ibadan press. 145.

Rullkötter, J., Leythaeuser, D., Horsfield, B., Littke, R., Mann, U., Müller, P. J., Radke, M., Schaefer, R. G., Schenk, H. J., Schwochau, K., Witte, E. G. And Welte, D. H. (1988), Organic matter maturation under the influence of a deep intrusive heat source: A natural experiement for quatitation of hydrocarbon generation and expulsion from a petroleum source rock (Toarcia Shale, northern Germany. In: Mattsvelli, L and Novelli, E (Eds.): Advances in Organic Geochemistry, 1987. Org. Geochem., **13**, 847-856.

Shanmugam, G.: (1985), Significance of corniferous rain forests and related organic matter in generating commercial quantities of oil, Gippsland Basin, Australia. AAPG Bull., 69, 1241-1254.

Sondergold,C.H,Ambrose,R.J., Rai,C.S., Moncreff,J.,2010a, Microstructural studies of gas shales, SPE 131771,SPE unconventional Gas conference,Pittsburgh,23-25 february,2010.

Stasiuk, L.D., Galarza, F. and Bagheri-Sadeghi, H. (2006), Petrology, rank and evidence for petroleum generation, upper Triassic to Middle Jurassic coals, central Alborz Region, Northern Iran. *Intern. Jour. Coal Geol.*, **67**, 249-258.

Suggate, R. P. and Boudou, J. P. (1993), Coal rank and type variations I Rock-Eval assessment of New Zealand coals. *Jour. Petrol. Geol*., **16**, 73-88.

Sykes, R., Snowdon, L.R., 2002. Guidelines for assessing the petroleum potential of coaly source rocks using Rock–Eval pyrolysis. Org. Geochem. 33, 1441–1455.

Tissot, B.P., and Welte, D.H.: (1984), Petroleum Formation and occurrence. 2nd ed., Berlin, Springer Verlag, 699.

Unomah, G.I., and Ekweozor, C.M.: (1993), Petroleum source-rock assessment of the Campanian Nkporo shale lower Benue Trough, Nigeria. NAPE Bull., 8(02), 172-186.

Whiteman, A.J., 1982. Nigeria: Its Petroleum Geology, Resources and Potential, 1. Graham and Trotman Ltd., Sterling House, London, SW1 V1DE, 166.