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Organic Geochemical Characterisation of the Campano-Maastrichtian Sediments in Anambra Basin, SE Nigeria: Implications for Paleodepositional Conditions, Provenance and Petroleum Generation Potential

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Abstract

A total of 24 rock samples comprising mainly shales, siltstones and shale heteroliths, collected from the Nkporo, Owelli and Mamu formations of Anambra Basin were subjected to bulk and molecular geochemical analyses (total organic carbon content determination, pyrolysis analysis, bitumen extraction and gas chromatography) to provide further insight on the quantity, quality and thermal maturity of organic matter within the sediments, the source input and paleodepositional conditions of the organic matter and the hydrocarbon generation potential. The total organic carbon (TOC) contents and hydrogen index (HI) of the analysed sediments from the Nkporo, Owelli and Mamu formations range from 0.60 to 2.02 wt.%, 0.25 to 2.75 wt.% and 0.52 to 4.78 wt.%, respectively, while the hydrogen index (HI) range between 07 and 359 mg HC/g TOC for the Nkporo samples, 39 and 408 mg HC/g TOC for the Owelli samples, and 10 and 226 mg HC/g TOC for the Mamu sediments. This indicate that the organic matter has fair to good hydrocarbon generation potential. The kerogen is predominantly Type II-III for the Nkporo shales and some of Owelli samples, while the organic matter in the Mamu Formation and the rest of Owelli samples is mainly Type III and Type IV kerogens. This indicate that majority of the analysed sediments from Nkporo Formation are oil and gas prone, while the others are mainly gas prone. Pyrolysis T_{max} values in the Nkporo, Owelli and Mamu samples are in the range of 418–437 ˚C, 415–430 ˚C and 424–430 ˚C, respectively, indicating that the sediments are thermally immature to early mature for hydrocarbon generation. This is supported by biomarker maturity parameters. Molecular geochemical data further suggested that the organic matter within the sediments was derived from mixed aquatic algae and land plant source input and was deposited under suboxic paleodepositional conditions.

Keywords: Paleoenvironment; Suboxic; Geochemistry; Organic matter; Nkporo Shale

1. Introduction

Geochemistry has been a veritable tool in hydrocarbon source rock assessment as well as in the reconstruction of environments of geological past (Peters et al. 2005; Peters and Fowler, 2002; Waples, 1985; Demaison and Moore, 1980). In the recent past, various geochemical techniques have become increasingly important for petroleum exploration, particularly for source identification and maturity assessment. Anambra Basin is one of the inland basins in Nigeria where exploration activities have been vigorously undertaken in the past. Unlike the prolific Niger Delta Basin, exploration campaign in the Anambra Basin was largely unsuccessful. The poor knowledge of the evolution of the subsurface rocks in the basin, especially with respect to the characteristics and the depositional conditions of the organic matter within the potential source rocks, may have been responsible for this failure.

The Cretaceous Anambra Basin, which contains thick sequences of clastic sediments (~6000 m), ranging from bituminous shales, lignites through sandstones and marl and strategically positioned as the proto-Niger Delta, provides an ideal ground for the geochemical evaluation of the source rocks (Nwajide and Reijers, 1995). The roughly triangular Anambra Basin (Fig 1) covers an area of about 40,000 sq.km and it is punctuated by super outcrops for comparative and/or correlative studies of the sedimentary units with their subsurface equivalents.

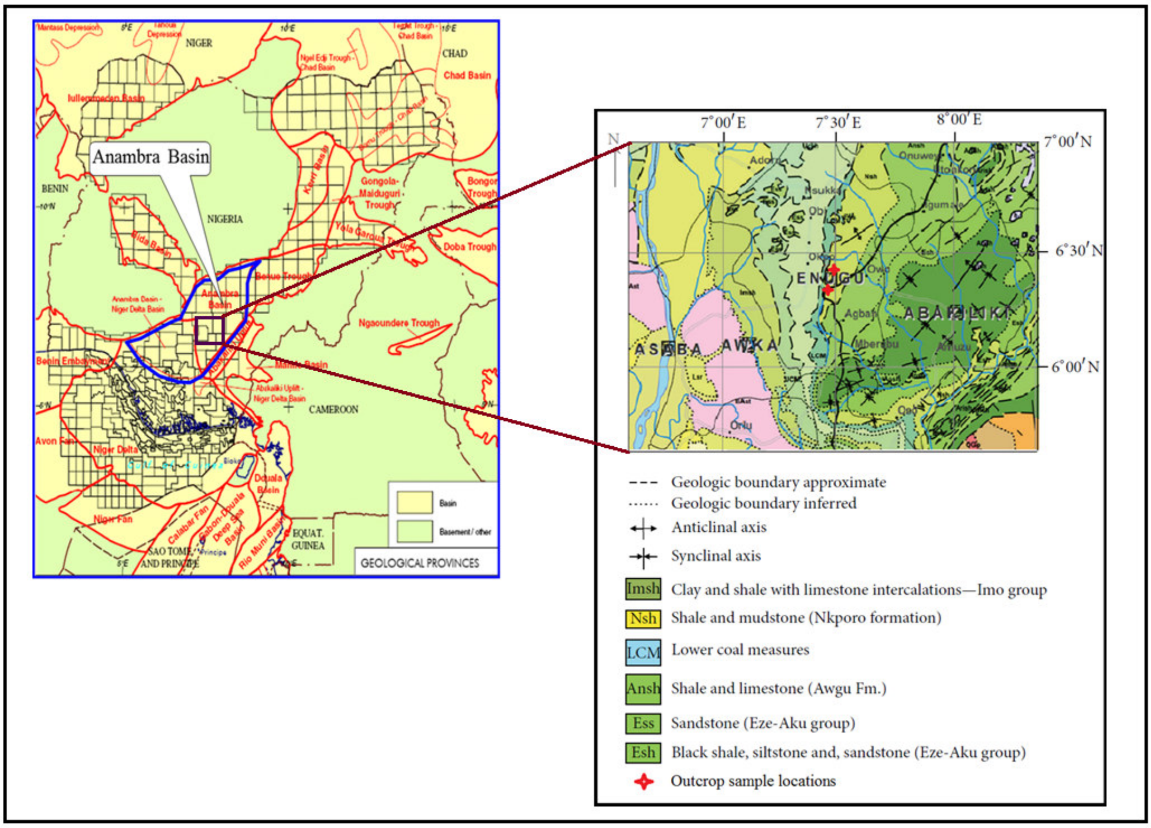

Figure 1. Geological map of Nigeria showing the Anambra Basin and the sampling locations (adapted from Odundun, 2015).

Although, some studies have been undertaken on this basin's source rock potential and organic matter (OM) maturity (Ehinola et al. 2005; Obaje et al. 2004; Akaegbobi and Schmitt, 1998; Unomah and Ekweozor, 1993; Ekweozor and Gormly, 1983; Agagu and Ekweozor, 1982; Petters and Ekweozor, 1982; Avbovbo and Ayoola, 1981; Agagu, 1978), detailed organic geochemical investigations and the assessment of the organic matter source input and depositional conditions are quite few. Numerous unpublished and published reports have shown that the Campano-Maastrichtian sequences of Anambra Basin exhibit characteristics of potential hydrocarbon source rocks (Ehinola et al. 2005; Obaje et al. 2004; Akaegbobi and Schmitt, 1998; Unomah and Ekweozor, 1993; Ekweozor and Gormly, 1983; Agagu and Ekweozor, 1982; Petters and Ekweozor, 1982; Avbovbo and Ayoola, 1981; Agagu, 1978).

In this study, attempts have been made to re-evaluate the hydrocarbon source rock potential of the Campano-Maastrichtian sequences of the Cretaceous Anambra Basin and to reconstruct the environment of deposition of the sediments, using several geochemical techniques. This study is aimed at giving an overview of the source input and conditions of depositional environment of the organic matter in the sediments, with a view to providing further insight into the geology of the basin and complement the existing database for the current and future petroleum exploration programme and resource assessment in the region.

2. Geological setting

The Anambra Basin, constituting the southern portion of the Benue Trough, is one of the intracratonic Cretaceous basins linked to the Benue Trough in central and west Africa and whose origin is related to the separation of Africa from South America and the opening of the South Atlantic Ocean (Obaje et al. 2004; Ofoegbu et al. 1990). It contains sediments of over 9km in thickness (Onuoha, 1986) and 250 miles long, extending in a NE-SW direction between Onitsha on the Niger River and Kwande on the Benue River (Whiteman, 1982). The Cretaceous Anambra depositional site reflects one mega-facies region, which received sediment load in two depositional cycles ranging from Campanian to Eocene (Obaje et al. 2004; Obaje et al. 1999; Murat, 1972; Reyment, 1965). The sediment is typical of continental fluvial-deltaic and shallow marine sedimentation millieux (Akaegbobi and Schmitt, 1998).

Due to the great thickness of Post-Santonian sedimentary fill that occupies much of the basin, and lack of much subsurface information (Whiteman, 1982), much is not known about the Cretaceous and Pre-Santonian subsurface deposits in this basin. On the other hand, Cretaceous outcrops, from adjoining southern Benue Trough suggest what underlies the post-Santonian deposits in the Anambra Basin. The sedimentary sequences consist of the transgressive Albian Asu River Group, which is unconformably overlain by the Cenomanian-Early Santonian strata of the Cross River Group. This include shales, limestones and sandstones of the Nkalagu Formation, which consist of the Eze-Aku and Awgu Shales and their interfingering local facies equivalents (Amasiri, Makurdi, Agala, and Agbani Sandstones) (Petters and Ekweozor, 1982). In the Anambra Basin, post-Santonian sedimentary fill consist of the Nkporo Shale, Owelli Formation, Mamu Formation, Ajali Sandstones, Nsukka Formation, Imo Shale and Ameki/Nanka Formation (Mode, 2004; Akande and Erdtmann, 1998; Reijers, 1996; Whiteman, 1982).

3. Materials and methods

The area of study is located between latitudes 6°00’N and 6°30’N and longitudes of 7°20’E and 7°30’E within the Anambra Basin (Fig. 1). Accessibility is facilitated by the Enugu-Onitsha Expressway and other roads linking to this area. Location of outcrop sections and estimation of the distance from the nearest landmark or village were carried out using Global Positioning System (GPS) equipment. The outcrops in the study area are conspicuously exposed, especially the road cuts and the gullies, and were examined for detailed lithofacies variations, textural features, sedimentary structures, mode of occurrences, depositional cycles as well as other attributes.

For this study, a total of 24 outcrop samples comprising mainly carbonaceous shale, silty shale and marls were obtained from the Mamu Formation at the road cut section leading to Onyeama Mine, by the Enugu-Onitsha flyover and from the Owelli and Nkporo formations exposed along Enugu-Abakaliki Expressway, Enugu end (Fig. 2). The samples were subjected to geochemical analyses which include total organic carbon (TOC) and total sulphur (TS) measurements, bitumen extraction, Rock-Eval pyrolysis and gas chromatography (GC) analysis.

The samples were crushed and ground to less than 200 mesh. Total organic carbon and total sulphur contents were determined using a Multi EA 2000 Analyser. Pyrolysis was performed on approximately 80 mg of pulverised samples using a Rock Eval II instrument. The method and interpretative technique of Espitalié et al. (1977) was used. The samples were heated in the helium stream of the instrument under a programmed temperature pattern with characterisation of three peaks, which represent some of the parameters measured. S_1 (mg HC/g rock), which is the first peak, represents existing indigenous or migrated hydrocarbons in a rock, and is also referred to as the volatile hydrocarbon content. S_1 is mainly stripped at temperatures of about 300 ˚C. The second peak, S_2 (mg HC/g rock) represents hydrocarbons generated through thermal cracking of kerogen at temperatures in the range of 300–650 ˚C. It is also referred to as the remaining hydrocarbon generative potential. S_3 (mg CO_2/g rock) peak represents the CO2 which is generated from the kerogen at the same time the S2 hydrocarbons are being generated. Other parameter determined include temperature of maximum pyrolysis yield (T_{max}). Hydrogen index (HI, mg HC/g TOC), oxygen index (OI, mg CO_2/g TOC) and production index (PI) were calculated from the measured parameters.

Bitumen extraction were performed on the shale samples using a Soxhlet apparatus for 72 h using an azeotropic mixture of dichloromethane (DCM) and methanol (CH_3OH) (93:7). Long extraction time was necessary for exhaustive extraction of the bitumen from the powdered rock samples. The bitumen fractions were separated into the hydrocarbon fractions of saturated hydrocarbons, aromatic hydrocarbons and NSO (nitrogen, sulphur and oxygen) compounds by liquid column chromatography. Saturated fractions were dissolved in hexane and analysed by a GC instrument (HP-5MS column, temperature programmed from 40 to 300 ^{o}C at a rate of 4 ^{o}C/min, and then held for 30 min at 300 ^{o}C). These organic geochemical analyses were carried out at the ICG-4, ForschungsZentrum Julich, Germany.

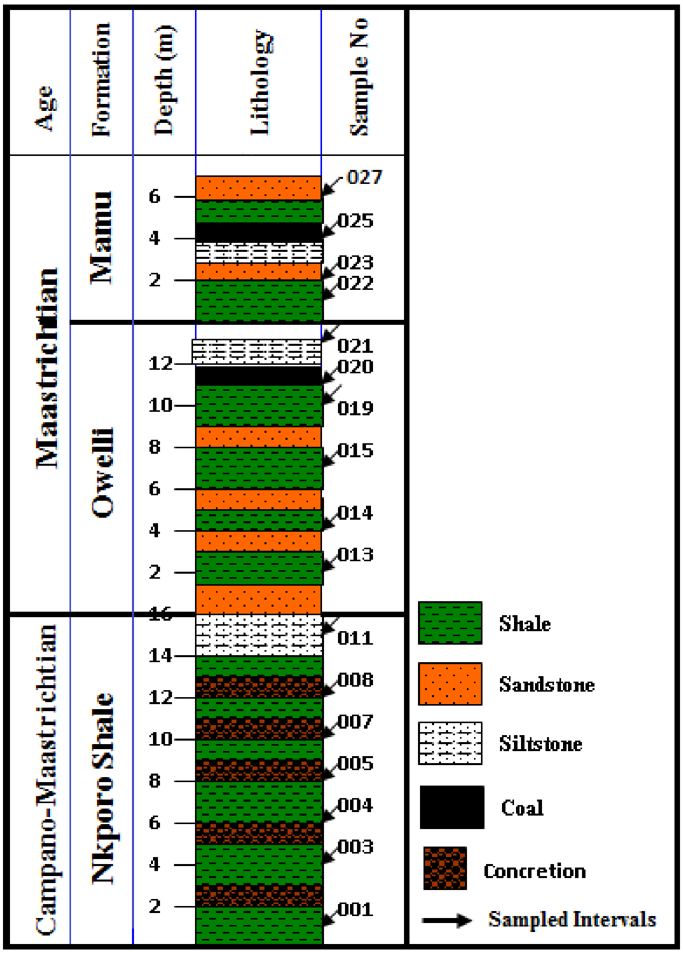

Figure 2. Stratigraphic sequence of the study area showing the sample positions.

4. Results

The results obtained from the organic geochemical investigations carried out in this research were presented.

4.1 Bulk geochemical characteristics

Bulk geochemical characterisation of sediments from Nkporo, Owelli and Mamu formations was carried out using Rock-Eval type pyrolysis analysis. The results are presented in Table 1. The total organic carbon (TOC) contents and pyrolysis data such as free hydrocarbons (S_1) in the rock, the amount of hydrocarbons (S_2) and CO_2 (S_3) expelled from pyrolysis of kerogen, hydrogen index (HI), oxygen index (OI), and T_{max} values were used to determine the amount of remaining organic matter and the present-day hydrocarbon generation potential from the sediments. The amount of hydrocarbon (S_2) expelled during pyrolysis is also a useful measurement to assess the generative potential of source rocks (Hakimi and Abdullah, 2014; Bordenave et al. 1993; Peters, 1986). The TOC values for the Nkporo, Owelli and Mamu formations range between 0.60 to 2.02 wt.%, 0.25 to 2.75 wt.% and 0.52 to 4.78 wt.%, respectively (Table 1; Fig. 3). The analysed samples from Nkporo, Owelli and Mamu formations also have S_2 pyrolysis yield values in the range of 0.14 – 3.98 mg HC/g rock, 0.30 – 3.70 mg HC/g rock and 0.35 – 1.47 mg HC/g rock, respectively (Table 1). The HI and

Table 1: TOC content and pyrolysis data with calculated parameters of the studied samples.

Sample ID	Height (m)	Lithology	Formation	TOC (wt.%)	S1	S2	S3	S2/S3	T_{max}	HI	OI	PI
ANS/IT/001	0.8	Shale	Nkporo	0.95	0.04	0.38	0.61	0.62	432	40	64	0.10
ANS/IT/002	2.1	Siltstone	Nkporo	0.75	0.06	1.29	0.72	1.79	435	172	96	0.05
ANS/IT/003	2.5	Shale	Nkporo	0.77	0.21	2.66	0.48	5.54	437	346	62	0.07
ANS/IT/004	3.8	Shale	Nkporo	1.57	0.87	2.56	0.49	5.22	428	163	31	0.25
ANS/IT/005	5.4	Shale	Nkporo	1.03	0.26	2.43	0.64	3.80	418	236	62	0.10
ANS/IT/006	7.4	Shale	Nkporo	0.85	0.44	3.05	0.46	6.63	420	359	54	0.13
ANS/IT/007	8.6	Shale	Nkporo	2.02	0.31	1.64	0.52	3.15	426	82	26	0.16
ANS/IT/008	9.4	Shale	Nkporo	1.6	0.51	3.98	0.66	6.03	422	249	41	0.11
ANS/IT/009	11.4	S/Shale	Nkporo	0.96	0.26	2.4	0.07	34.29	430	250	7	0.10
ANS/IT/010	12.8	Shale	Nkporo	0.6	0.19	1.03	1.12	0.92	427	171	187	0.16
ANS/IT/011	14.4	Shale	Nkporo	1.23	0.21	1.54	0.12	12.83	435	125	10	0.12
OW/IT/013	3.8	Shale	Owelli	0.81	0.76	2.48	0.16	15.5	418	306	31	0.23
OW/IT/014	5.4	Shale	Owelli	0.72	0.07	0.46	2.24	0.21	425	63	311	0.13
OW/IT/015	7.1	Shale	Owelli	0.63	0.05	0.35	1.26	0.28	415	55	200	0.13
OW/IT/017	9.2	Shale	Owelli	0.34	0.08	0.37	1.42	0.26	421	109	418	0.18
OW/IT/019	11.8	Shale	Owelli	0.86	0.52	2.92	1.35	2.16	430	340	178	0.15
OW/IT/020	13.0	Shale	Owelli	2.75	0.33	3.7	0.48	7.71	425	135	17	0.08
OW/IT/021	13.6	Siltstone	Owelli	0.25	0.4	1.02	0.98	1.04	415	408	392	0.22
MF/IT/022	0.5	Shale	Mamu	1.19	0.08	0.94	1.55	0.61	424	79	130	0.08
MF/IT/023	1.6	Shale	Mamu	1.68	0.05	0.95	1.12	0.85	425	57	67	0.05
MF/IT/024	2.8	Shale	Mamu	0.85	0.15	1.47	1.37	1.07	430	173	161	0.09
MF/IT/025	3.2	Shale	Mamu	4.78	0.10	0.47	3.72	0.13	426	10	78	0.17
MF/IT/026	3.8	Shale	Mamu	1.16	0.05	0.35	2.65	0.13	428	30	228	0.13
MF/IT/027	5.6	Siltstone	Mamu	0.52	0.10	1.17	1.85	0.63	425	226	356	0.08

Notes

S1: Volatile hydrocarbon (HC) content, mg HC/ g rock
TOC: Total Organic Carbon, wt. %
S2: Remaining HC generative potential, mg HC/ g rock
T_{max}: Temperature at maximum of S_2 peak
S3: Carbon dioxide yield, mg CO2/ g rock
PI: Production Index = S1/ (S1+S2)
HI: Hydrogen Index = S2x 100 / TOC, mg HC/ g TOC
OI: Oxygen Index = S3x 100 / TOC, mg CO2/ g TOC

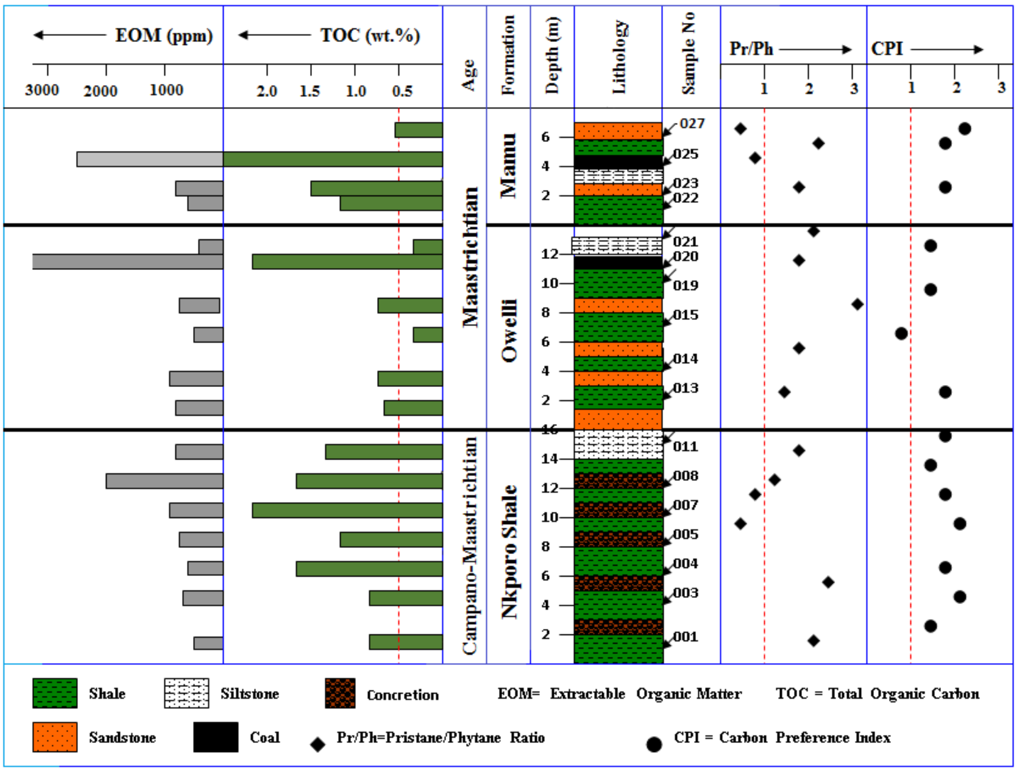

Figure 3. Geochemical log of the analysed samples.

OI values range between 07 and 359 mg HC/g TOC and 07 and 187 mg CO_2/g TOC for the Nkporo samples, between 39 and 408 mg HC/g TOC and 17 and 418 mg CO_2/g TOC for the Owelli samples, and between 10 and 226 mg HC/g TOC and 67 and 356 mg CO_2/g TOC for the Mamu sediments, respectively. The pyrolysis T_{max} values and production index (PI) in the Nkporo, Owelli and Mamu samples are in the range of 418 – 437 ˚C and 0.05 – 0.41, 415 – 430 ˚C and 0.08 – 0.63 and 424 – 430 ˚C and 0.05 – 0.17, respectively. The total sulphur content (TSC) values also range from 0.25 – 1.01 wt.%, 0.01 – 1.35 wt.% and 0.15 – 1.6 wt.% for the Nkporo, Owelli and Mamu samples, respectively (Table 1).

4.2 Extractable organic matter (EOM) and hydrocarbon yield (HC yield) contents

The amount of hydrocarbon isolated from the bitumen extracted from finely ground rock samples can provide a useful indication of whether any oil/gas potential exists (Adegoke, 2015; Mustapha and Abdullah, 2013; Peters and Cassa, 1994; Killops and Killops, 1993). Oil source rocks are generally considered to require a minimum extractable organic matter (EOM) and hydrocarbon content of 1000 ppm and 200-300 ppm, respectively, while gas source rocks require lower values (Peters and Cassa, 1994; Killops and Killops, 1993).

The results obtained from the bitumen extraction of the selected samples from Nkporo, Owelli and Mamu formations are presented in Table 2 and shown graphically in Figure 3. The EOM and hydrocarbon yield (HC yield) in all of the analysed samples are widely variable and range from 303 to 3200 ppm and 201.8 to 2832 ppm, respectively. EOM and HC yield for the Nkporo, Owelli and Mamu formations samples range from 303 to 2013 ppm and 265.1 to 1791.6 ppm; 225 to 3200 ppm and 201.8 to 2832 ppm and 620 to 2265 ppm and 467.7 to 1413.4 ppm, respectively (Table 2). Generally, highest amounts of EOM and HC Yield are found in three shale samples in Nkporo, Owelli and Mamu formations.

Table 2: TOC and TS contents, bitumen yield (EOM), hydrocarbon yield (HC Yield), Bitumen/TOC ratio and selected biomarker parameters in the studied samples.

Sample No.	Height (m)	Lithology	Formation	TOC (wt%)	TSC (wt%)	EOM (%)	EOM (ppm)	Bit/TOC ratio	Sat (ppm)	Aro (ppm)	NSO (ppm)	HC Yield	Pr/Ph	Pr/nC17	Ph/nC18	CPI
ANS/IT/001	0.8	Shale	Nkporo	0.95	0.52	0.0543	543	0.057	348.6	46.7	147.7	395.3	2.05	1.64	0.71	1.4
ANS/IT/002	2.1	Siltstone	Nkporo	0.75	0.72	0.0303	303	0.040	217.9	47.3	37.9	265.1	2.15	1.73	0.69	2.05
ANS/IT/003	2.5	Shale	Nkporo	0.77	0.25	0.0633	633	0.082	403.2	89.3	140.5	492.5	2.62	1.65	1.95	1.6
ANS/IT/004	3.8	Shale	Nkporo	1.57	0.8	0.0530	530	0.034	360.4	100.7	68.9	461.1	-----	-----	-----	-----
ANS/IT/005	5.4	Shale	Nkporo	1.03	0.75	0.0788	788	0.077	543.7	108.7	135.5	652.5	0.88	1.24	0.72	1.56
ANS/IT/006	7.4	Shale	Nkporo	0.85	0.53	0.0650	650	0.076	459.6	91.7	98.8	551.2	-----	-----	-----	-----
ANS/IT/007	8.6	Shale	Nkporo	2.02	0.95	0.0983	983	0.049	668.4	186.8	127.8	855.2	0.95	1.55	0.75	1.4
ANS/IT/008	9.4	Shale	Nkporo	1.6	0.75	0.2013	2013	0.126	1389.0	402.6	221.4	1791.6	1.21	1.53	0.95	1.25
ANS/IT/009	11.4	S/Shale	Nkporo	0.96	0.55	0.0520	520	0.054	343.2	104.0	72.8	447.2	-----	-----	-----	-----
ANS/IT/010	12.8	Shale	Nkporo	0.6	0.32	0.0484	484	0.081	324.3	87.1	72.6	411.4	-----	-----	-----	-----
ANS/IT/011	14.4	Shale	Nkporo	1.23	1.01	0.0855	855	0.070	624.2	153.9	77.0	778.1	1.69	1.46	0.77	1.4
OW/IT/013	3.8	Shale	Owelli	0.51	0.3	0.0640	640	0.125	448.0	121.6	70.4	569.6	1.55	1.51	0.78	1.51
OW/IT/014	5.4	Shale	Owelli	0.72	0.21	0.0725	725	0.101	439.4	150.8	134.9	590.2	1.72	-----	-----	-----
OW/IT/015	7.1	Shale	Owelli	0.63	0.32	0.0340	340	0.054	238.3	45.6	56.1	283.9	3.25	1.25	1.3	0.98
OW/IT/017	9.2	Shale	Owelli	0.34	0.15	0.0225	225	0.066	159.1	42.8	23.2	201.8	-----	-----	-----	-----
OW/IT/019	11.8	Shale	Owelli	0.76	0.65	0.0540	540	0.071	388.3	102.1	49.7	490.3	-----	-----	-----	-----
OW/IT/020	13	Shale	Owelli	2.75	1.35	0.320	3200	0.116	2291.2	540.8	368.0	2832.0	1.07	1.32	1.82	1.33
OW/IT/021	13.6	Siltstone	Owelli	0.25	0.01	0.0245	245	0.098	183.8	35.0	26.2	218.8	2.33	0.96	0.93	1.27
MF/IT/026	3.8	Shale	Mamu	1.16	0.57	0.062	620	0.053	424.7	105.4	89.9	530.1	-----	-----	-----	-----
MF/IT/024	2.8	Shale	Mamu	0.85	0.65	0.072	720	0.085	341.3	139.0	239.8	480.2	-----	-----	-----	-----
MF/IT/022	0.5	Shale	Mamu	1.19	0.58	0.074	740	0.062	390.7	77.0	272.3	467.7	1.8	-----	-----	-----
MF/IT/023	1.6	Shale	Mamu	1.68	0.78	0.087	870	0.052	372.4	102.7	395.0	475.0	0.95	1.48	0.52	1.95
MF/IT/025	3.2	Shale	Mamu	4.78	1.6	0.2265	2265	0.047	1091.7	321.6	851.6	1413.4	0.88	1.35	0.95	1.75
MF/IT/027	5.6	Siltstone	Mamu	0.52	0.15		-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

Notes

TOC: Total Organic Carbon, wt. %
TSC: Total Sulphur content, wt. %
EOM: Extractable organic matter, %; ppm
Sat: Saturated hydrocarbon fraction, ppm
Aro: Aromatic hydrocarbon fraction, ppm
NSO: Nitrogen, Sulphur, Oxygen fraction, ppm
Bit/TOC: Bitumen/TOC ratio
HC Yield: Hydrocarbon yield (Sat+Aro), ppm
Pr/Ph: Pristane/Phytane
Pr/nC_{17}: $Pristane/nC_{17}$
Ph/nC_{18}: $Phytane/nC_{18}$
CPI: Carbon preference index (1): $\{2(C_{23} + C_{25} + C_{27} + C_{29}) / (C_{22} + 2[C_{24} + C_{26} + C_{28}] + C_{30})\}$

4.3 Straight chain alkanes and isoprenoids

Gas chromatograms of saturate fractions from two representative samples are shown in Figure 4a & 4b, representing samples from the Nkporo and Mamu formations, respectively. The distribution of *n*-alkanes may be indicative of source input of original organism(s). For example, algal-sourced organic matter is rich in short-chain *n*-alkanes $<C_{20}$, and land-plant derived organic matter is dominated by long-chain *n*-alkanes $>C_{27}$ with odd-over-even carbon number predominance (Eglinton and Hamilton, 1967; Cranwell, 1987). Generally, samples from the Nkporo Shale and Owelli Formation have fingerprints that displays a typical unimodal n-alkane distribution within the range of $C_{12} – C_{37}$, while the chromatograms from the Mamu Formation display a bimodal distribution of the n-alkanes within the range of $C_{14} – C_{36}$. Acyclic isoprenoids occur in significant amounts in all the studied samples (Figs. 4a; 4b; Table 2).

Pristane (Pr) and phytane (Ph) are usually the most important acyclic isoprenoids hydrocarbons in terms of concentration and reflect the palaeoenvironmental conditions of source rocks (Powell and McKirdy, 1973). Their ratios have been widely used to assess the redox conditions during sedimentation and diagenesis (Chandra et al. 1994; Didyk et al. 1978). The most common origin of pristane (C_{19}) and phytane (C_{20}) is the phytyl side chain of chlorophyll-a in phototrophic organisms. Other sources include chlorophyll-b and bacteriochlorophyll-a in purple sulphur bacteria (Powell and McKirdy, 1973; Brooks et al. 1969). It has been stated that the formation of pristane from phytol occurs in oxidizing environments, such as peat swamp or bogs, while phytane occurs in reducing type environments (Farhaduzzaman et al. 2012; Peters and Moldowan, 1993). For oils and rocks within the oil-generative window, pristane/phytane (Pr/Ph) ratios correlate with the depositional redox conditions (Large and Gize, 1996; Didyk et al. 1978; Powell and McKirdy, 1973). Low Pr/Ph ratio values (<0.8) indicate anoxic conditions, commonly carbonate or hypersaline environments and high values (>3.0) usually typify oxic conditions often associated with terrigenous organic matter input (Peters and Moldowan, 1993). However, Pr/Ph ratio can be influenced by other source materials than phytol from chlorophylls (Ten Haven et al. 1987) and by thermal maturity (Vu et al. 2009). Pristane, generally occur in high relative concentrations in most of the analysed samples, possessing pristane/phytane (Pr/Ph) ratios in the range of 0.88 – 3.25 (Table 2).

The Pr/n-C_{17} and Ph/n-C_{18} ratios also range between 0.88 to 2.62 and 0.69 to 1.95 for Nkporo samples, 0.96 to 1.51 and 0.78 to 1.82 for Owelli samples and 1.35 to 1.48 and 0.52 to 0.95 for Mamu samples, respectively. Carbon preference index (CPI) of n-alkanes between n-C_{22} and n-C_{30} was also calculated to provide some insights into the source input and depositional conditions of the organic matter. CPI value that is less than 1.0 would indicate reducing depositional conditions (Meyers and Snowdon, 1993). The value, which is greatly influenced by organic matter input, was calculated based on the formula proposed by Peters and Moldowan, 1993), that is $(2(C_{23}+C_{25}+C_{27}+C_{29})/[C_{22}+2(C_{24}+C_{26}+C_{28})+C_{30}])$. The CPI values for all the analysed samples are greater than or less than 1.0 (Table 2), and range from 1.25 to 2.05 for the Nkporo samples, 0.98 to 1.51 for the Owelli samples and 1.75 to 1.95 for the Mamu samples.

5. Discussion

5.1 Organic richness and source rock quality

The TOC values for the Nkporo, Owelli and Mamu formations revealed that most of the analysed samples meet the accepted standards of a source rock with fair to good generative potential (Killops and Killops, 2005; Hunt, 1996; Peters and Cassa, 1994; Killops and Killops, 1993; Tissot and Welte, 1984; Waples, 1985). The S_2 pyrolysis yield values and hydrogen index also indicate that the analysed samples have fair to good hydrocarbon generative potential (Peters and Cassa, 1994). This is supported by the plots of S_2 pyrolysis yield versus TOC and S_2/S_3 versus TOC (Figs. 5 & 6). However, the TOC and S_2 values show that samples from Nkporo Formation are relatively richer organically than samples from Mamu and Owelli formations (Table 1; Fig. 3).

5.2 Organic matter type

The derivation of originally deposited organic matter affects both the quantity and quality of hydrocarbons generated. This is as a result of the concentration of originally deposited organic matter, its chemical

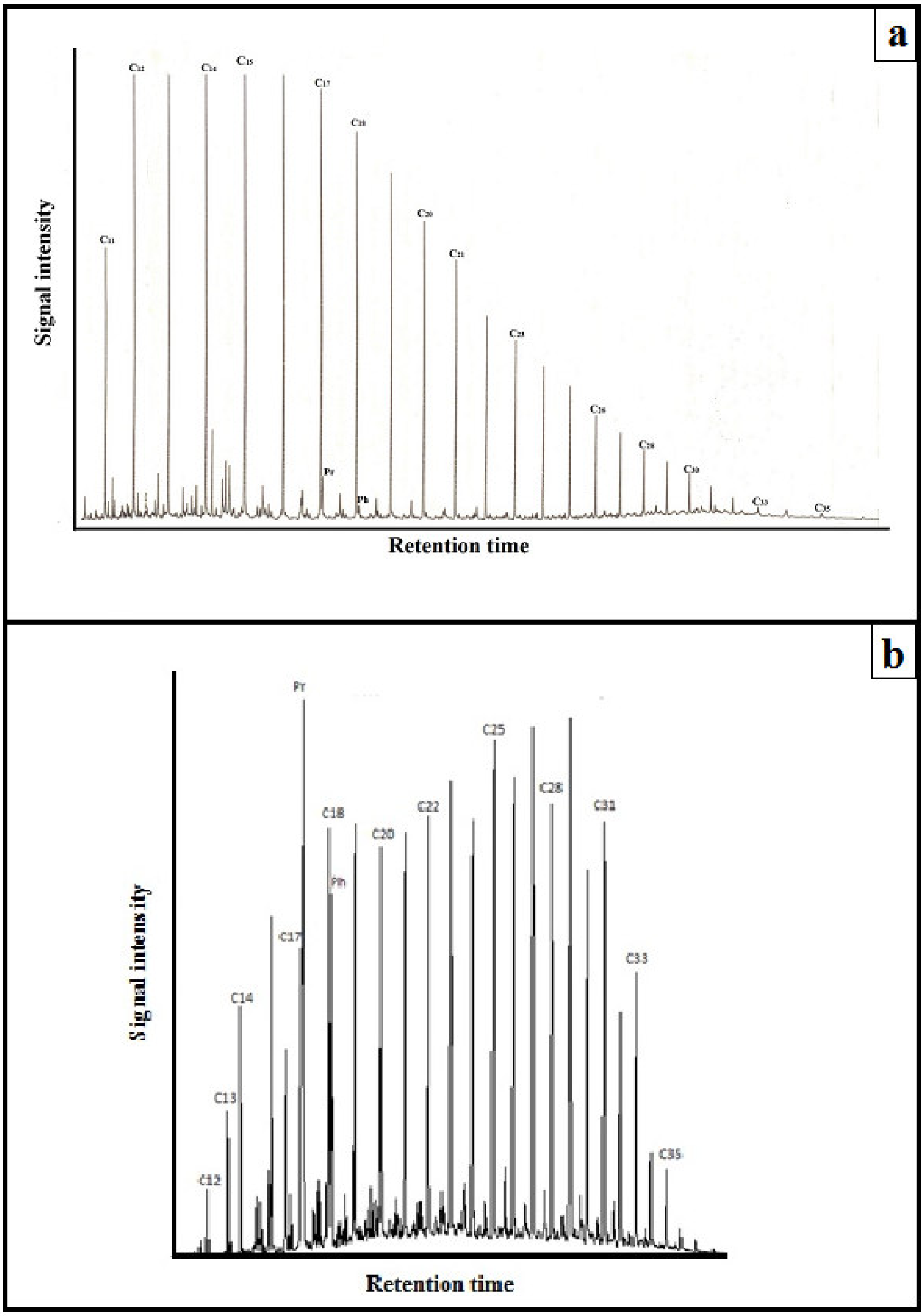

Figure 4. Gas chromatograms of representative samples from (a) Nkporo Formation and (b) Mamu Formation.

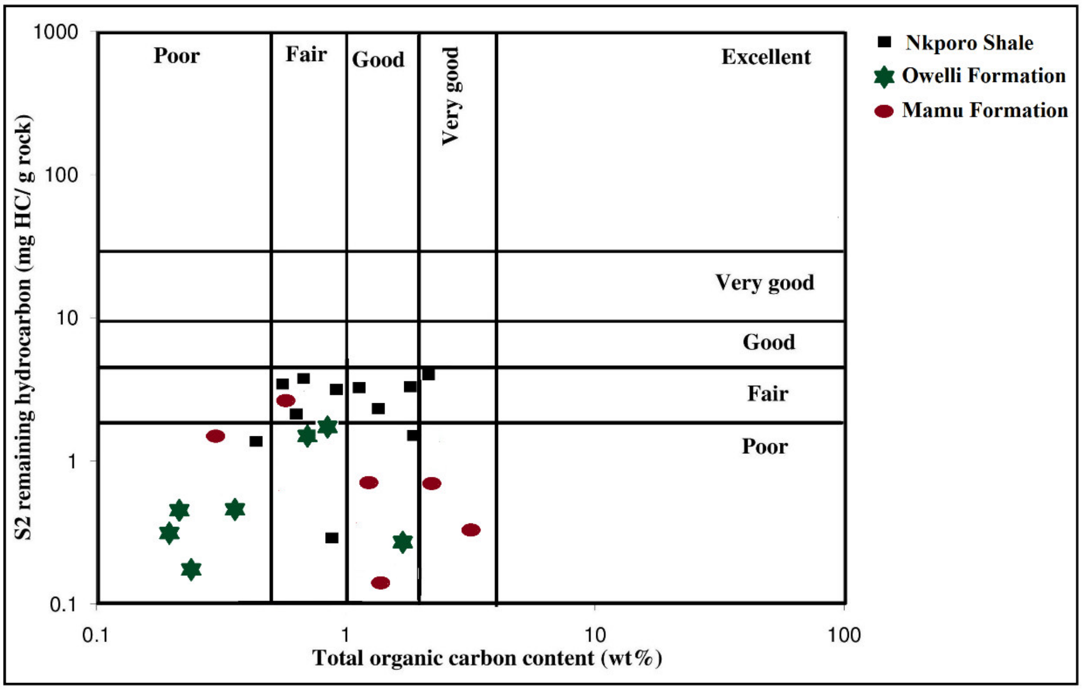

Figure 5. Plot of S2 pyrolysis yield versus TOC showing kerogen quality in the samples analysed.

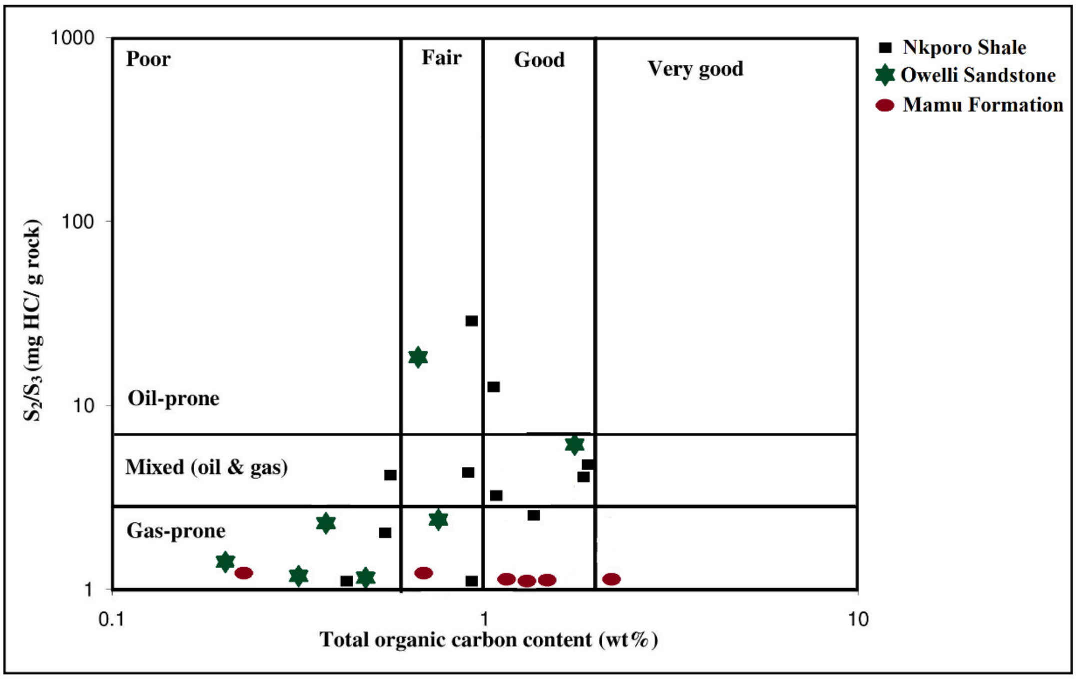

Figure 6. Plot of S2/S3 versus TOC showing hydrocarbon generative potential in analysed Anambra Basin sediments.

composition, and preservation, which is the result of sedimentation rates and environmental conditions during deposition (Demaison, 1984; Tissot and Welte, 1984). The kerogen characterisation was conducted based on pyrolysis data (Table 1). The analysed samples from the Nkporo, Owelli and Mamu formations have varied HI and OI values (Table 1). Pseudo-van Krevelen diagram (HI versus OI) and plot of HI versus T_{max} were used to identify the kerogen type in the analysed samples (Figs. 7 & 8). These plots reflected the present-day generation potential and indicate that majority of organic matter in the Nkporo Shales and in some Owelli Formation samples can be classified as predominantly Type II-III kerogen, while the organic matter in most of Mamu Formation samples and the rest of Owelli samples is majorly Type III and Type IV kerogens (Figs. 7 & 8). Most of the analysed samples have Hydrogen Indices (HI) below 200 mg HC/g TOC and are gas-prone (Fig. 6), while samples with HI below 50 mg HC/g TOC contain inert carbon (no hydrocarbon generation potential).

5.3 Organic maturation

The assessment of thermal evolution of the analyzed samples from the Anambra Basin is based on a number of data from bulk geochemistry and gas chromatography. The maturity data include pyrolysis T_{max} values and biomarker maturity ratios (Tables 1 & 2). Pyrolysis T_{max} values show that the organic matter within the analysed sediments from Nkporo, Owelli and Mamu formations are predominantly immature to early mature, since more than 70% of the analysed samples have T_{max} values that are essentially below the threshold value of 430°C required to be qualified as a mature source rock (Killops and Killops, 2005; Tissot and Welte, 1984). This is supported by the plots of HI versus pyrolysis T_{max} and production index (PI) versus pyrolysis T_{max} (Figs. 8 & 9). Although the T_{max} values generally show no specific trend unlike what is obtainable with their subsurface equivalents, which increases with burial depths (Akaegbobi and Schmitt, 1998; Unomah and Ekweozor, 1993), sediments from the Nkporo Formation are however generally more mature than those from the Owelli and Mamu formations. Bitumen/TOC ratios may also be used to assess the level of thermal maturity of organic matter within the sediments (Peters and Moldowan, 1993). With increasing thermal maturation, the free hydrocarbons content (EOM carbon) increases while the kerogen (convertible carbon) content decreases due to conversion to oil or gas. If the rock has a very high potential (high TOC content and oil prone), but is immature, little hydrocarbon will be generated, non-expelled, and no commercial reserves accumulated. The bitumen ratios range from 0.034 to 0.126, 0.054 to 0.125 and 0.047 to 0.085 for the Nkporo, Owelli and Mamu formations, respectively. These values indicate that the analyzed rock samples are essentially immature to early mature source rocks (Peters and Cassa, 1994; Demaison, 1984).

The proportion of odd versus even carbon numbered *n*-alkanes may be used to obtain a rough estimate of organic maturation level sediments (Peters et al. 2005; Peters and Moldowan, 1993; Bray and Evans, 1961). This measurement includes the carbon preference index (CPI), based on the formula proposed by (Peters and Moldowan, 1993). According to Peters and Moldowan, (1993), CPI values significantly above 1.0 (odd preference) or below 1.0 (even preference) indicate thermal immaturity, while values of 1.0 suggest that the organic matter is thermally mature. They however noted that CPI values are greatly influenced by organic matter input, and as a result, the maturity interpretation obtained from these values should be complemented with other maturity data. The CPI values for all the analysed samples are significantly above 1.0 and there is a significant odd carbon number preference between n-C_{22} and n-C_{30}. The CPI values for the analysed sediments range from 1.25 to 2.05, qualifying them as immature and marginally mature (Peters et al. 2005; Peters and Moldowan, 1993; Bray and Evans, 1961). The plot of CPI against depth also show no specific trend, probably because they are surface samples (Fig. 3). The relationship between isoprenoids Pr/n-C_{17} and Ph/n-C_{18} ratios further show that the analysed samples are thermally immature to early mature for hydrocarbon generation (Fig. 10).

5.4 Organic matter input and depositional environments

The organic matter source input and depositional paleoenvironments of the analysed Post-Santonian shales were determined based on the bulk geochemical parameters (TOC versus TSC; Fig. 12) and biomarker distribution ratios (Pr/Ph, Pr/n-C_{17} and Ph/n-C_{18}). The distribution of n-alkanes in the gas chromatograms of most of the analysed samples suggest organic matter input from both marine and terrestrial sources (Peters et al. 2005). However, some of the chromatograms from the Mamu Formation, which display a bimodal distribution of the n-alkanes and the presence of a relatively high concentration of high molecular weight alkanes suggest organic matter contribution from predominantly terrestrial plants (Fig. 4b). The isoprenoids

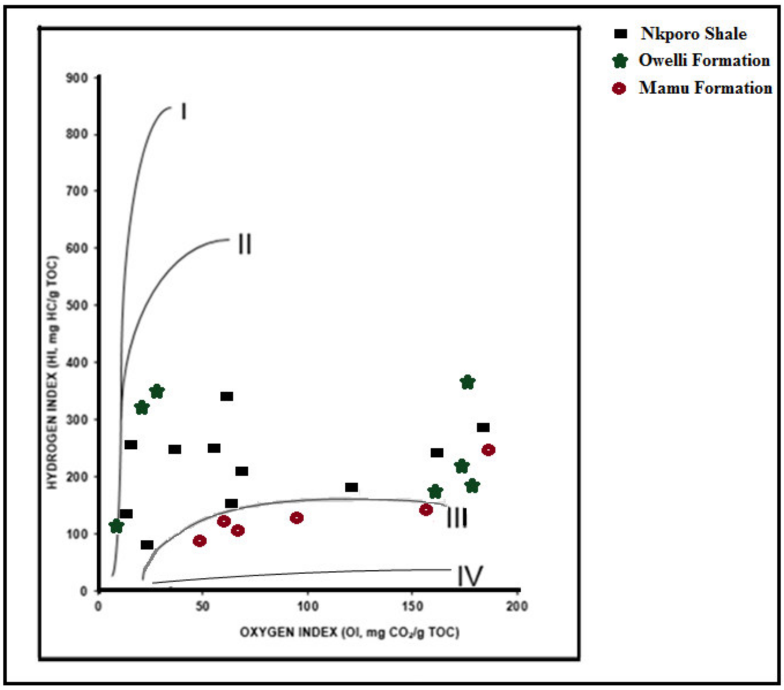

Figure 7. Pseudo-van Krevelen diagram (HI versus OI) for the studied Nkporo, Owelli and Mamu formations samples showing kerogen type.

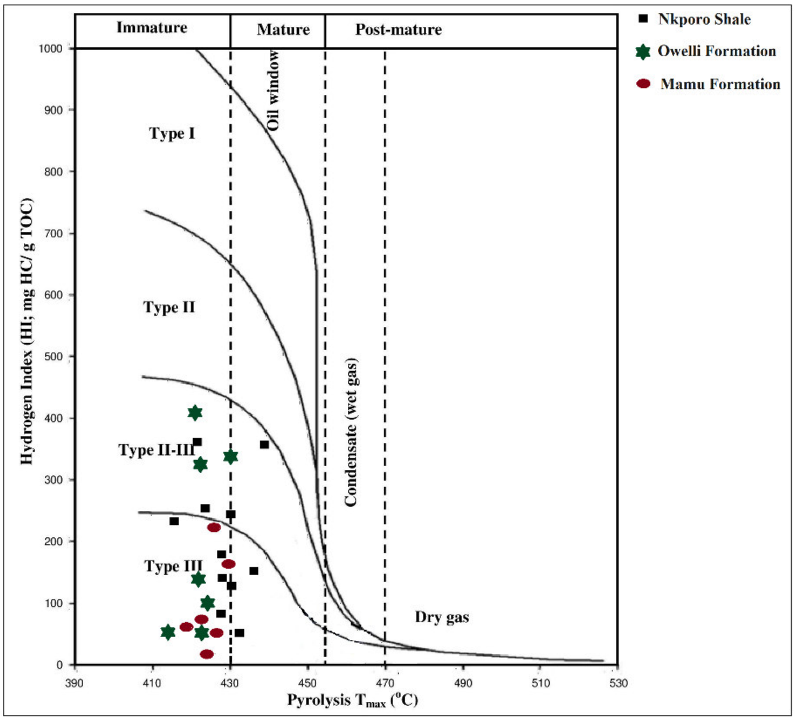

Figure 8. Plot of hydrogen index (HI) versus pyrolysis Tmax for the analysed samples from Nkporo, Owelli and Mamu formations, showing kerogen quality and thermal maturity stages.

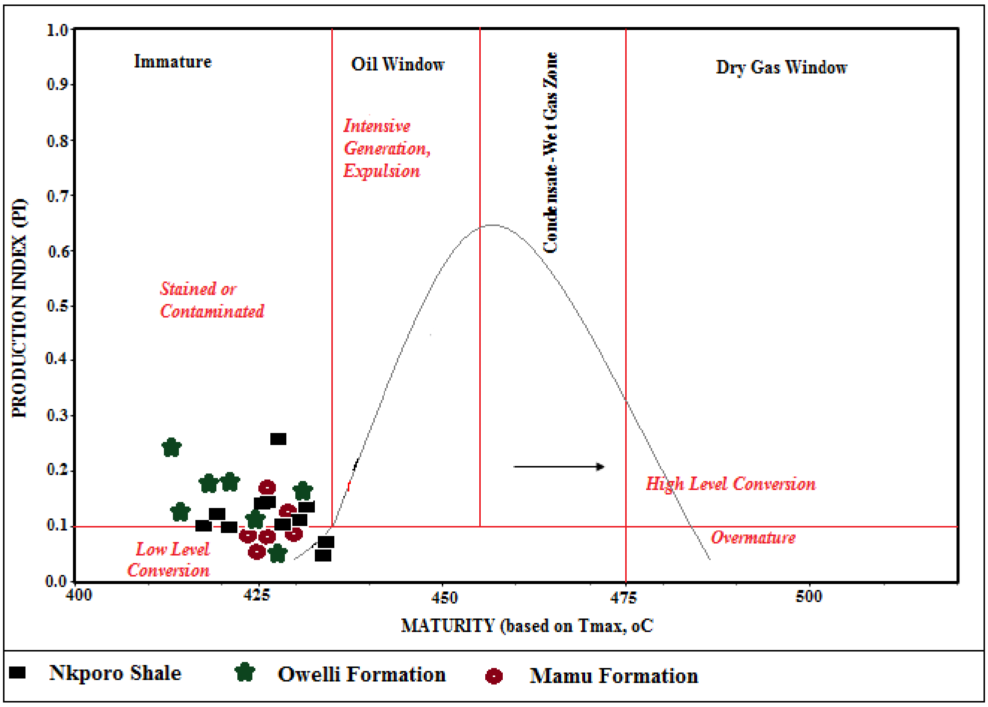

Figure 9. Plot of production index (PI) versus Tmax showing kerogen conversion and maturity of the analysed sediments in Anambra Basin (adapted from Hakimi et al. 2011).

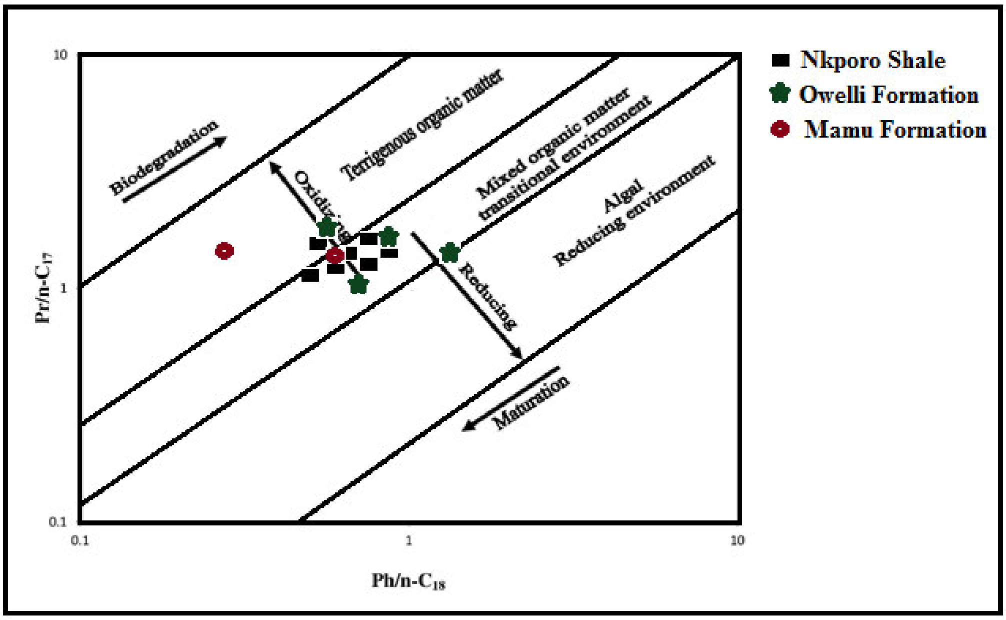

Figure 10. Phytane to n-C_{18} alkane (Ph/n-C_{18}) versus Pristane to n-C_{17} alkane (Pr/n-C_{17}) showing depositional conditions and type of organic matter of Nkporo, Owelli and Mamu extracts (adapted from Peters and Moldowan, 1993).

and n-alkanes data also provide valuable information on source rock facies of petroleum samples (Peters et al. 2005; Peters and Moldowan, 1993). The pristane/n-C_{17} and phytane/n-C_{18} ratios of between 0.88 to 2.62 and 0.52 to 1.95, respectively indicate that the organic matter in the many of the analysed sediments is mixed algal/aquatic and terrestrially derived and deposited under suboxic paleoenvironmental conditions. The cross-plot of pristane/n-C_{17} versus phytane/n-C_{18} was also used to interpret the source rock depositional environment condition and organic matter type (Van Koeverden et al. 2011; Peters et al. 2005). This plot suggests that the organic matter in the investigated samples was derived mainly from mixed marine and terrigenous materials deposited under suboxic conditions (Fig. 6). The cross-plot also shows that the organic matter in one of Mamu Formation samples was terrestrially derived and deposited under more oxidizing depositional environments.

Pristane/Phytane (Pr/Ph) ratios of source rock extracts have been used to indicate the redox potential of sediments (Didyk et al. 1978). The Pr/Ph ratios for the analyzed samples suggest that the redox conditions during the deposition of the sediments were suboxic (Table 2; Adegoke et al. 2014; Didyk et al. 1978). Furthermore, carbon preference index (CPI) of *n*-alkanes between *n*-C_{22} and *n*-C_{30} was calculated to provide some insights into the source input and depositional conditions of the organic matter. CPI value that is less than 1.0 would indicate reducing depositional conditions (Meyers and Snowdon, 1993). The CPI values for all the analysed samples are greater than or less than 1.0 (Table 2). This indicates a mixed input of marine and terrigenous organic matter deposited under relatively reducing (suboxic) conditions. The cross-plot of CPI against Pr/Ph (Fig. 11) further supports this interpretation (Akinlua et al. 2007; Meyers and Snowdon, 1993). The plot of the TOC versus TSC of the sample sets also indicate deposition under normal marine environment, with samples from Mamu Formation tending towards freshwater depositional millieux (Fig. 12).

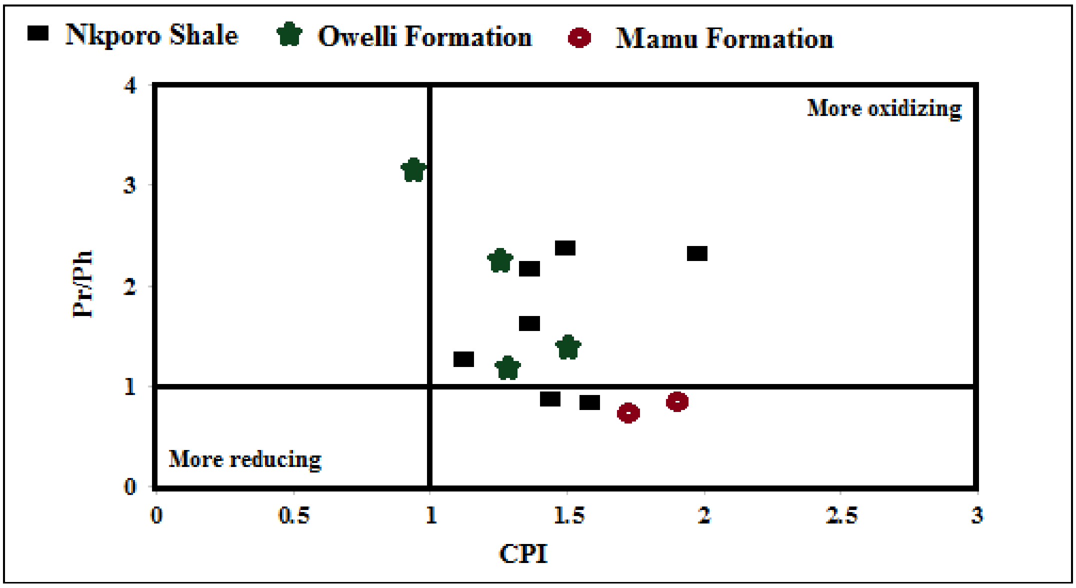

Figure 11. Cross-plot of pristane/phytane ratios versus CPI indicating the depositional environment conditions of the studied samples (Adapted from Akinlua et al. 2007; El Diasty and Moldowan, 2012).

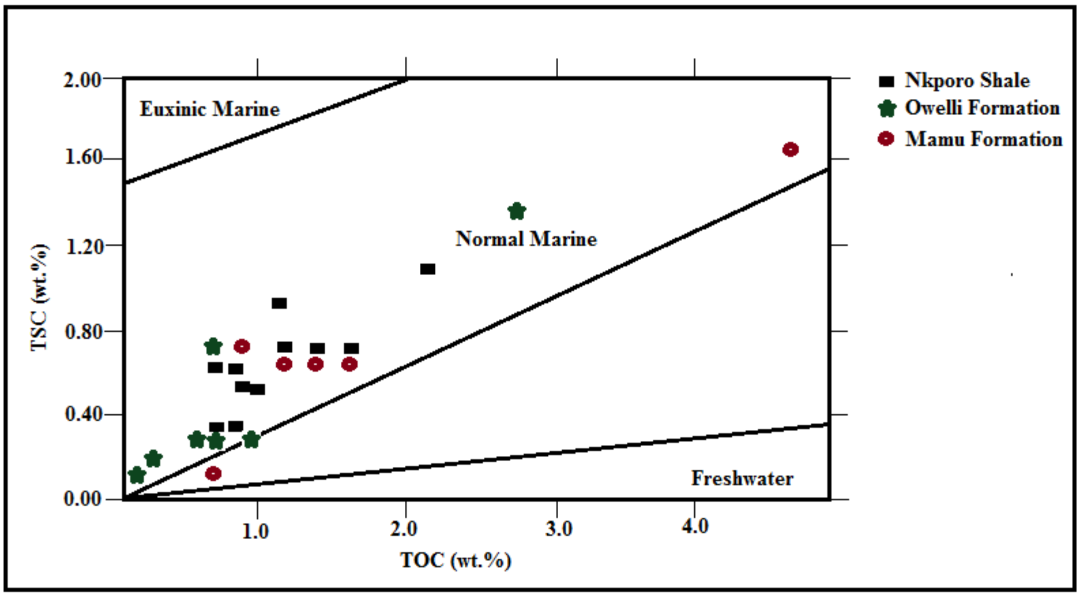

Figure 12. Plot of TOC versus TSC showing depositional environment of the analysed samples.

5.5 Hydrocarbon generation potential

The analytical program, which includes TOC and pyrolysis analyses, bitumen extraction and biomarker characteristics enabled the characterisation of the organic matter in the Nkporo, Owelli and Mamu formations samples. The organic matter type (kerogen type) was derived from the Rock-Eval pyrolysis data. The relationships between the HI, OI and T_{max} reveal kerogen of mixed type III/II for most of Nkporo samples and few of Owelli samples and type III and type IV organic matter for the rest of Owelli and Mamu formation samples, which suggests that the organic matter inputs are both of marine and terrestrial sources with contribution predominantly of terrestrial plants (Figs. 7 & 8; Akaegbobi, 1995; Ekweozor and Gormly, 1983). The plots of S2 versus TOC and S2/S3 versus TOC equally reveal that most of the analysed sediments can be regarded to possess a fair to good source generative potential and is essentially gas-prone (Figs. 5 & 6). However, majority of samples from Nkporo Shale and a few of Owelli samples are richer organically than other samples from Owelli and Mamu formations and are oil and gas prone. The thermal evolution of these formations was deduced from pyrolysis and biomarker distribution data. The maturity data show that organic matter in the sediments from the three studied formations is predominantly immature to early mature for hydrocarbon generation and that samples from Nkporo Shale are generally more mature than samples from the Owelli and Mamu formations (Table 1; 2; Figs. 9 & 10). The extractable organic matter (EOM) is that portion of the organic matter representing what has been generated but not expelled (Tissot and Welte, 1984). The quantity of extractable organic matter (EOM) or bitumen from a source rock does not only depend on the quantity and maturity levels of the kerogens, but also on the extent of hydrocarbon expulsion (Tissot and Welte, 1984). From the results presented in Table 2, the extract yields show that many of Nkporo and Mamu formation samples fall within the range of fairly good source rocks (Hunt, 1996; Killops and Killops, 1993; Philippi, 1957). This is supported by the plot of EOM versus TOC (Fig. 13), which shows that many of the sample sets plot within the range of improved oil source rock i.e. between 10 – 50% EOM/TOC ratio. Comparing the three formations, the Nkporo Shale seem to have the highest generative potential as could be seen from the pyrolysis data of the analyzed samples. This agrees with previous work by Akaegbobi and Schmitt (1998) and Unomah and Ekweozor (1993), who have variously identified the Nkporo Shale as the hydrocarbon source rock within the Cretaceous Anambra Basin.

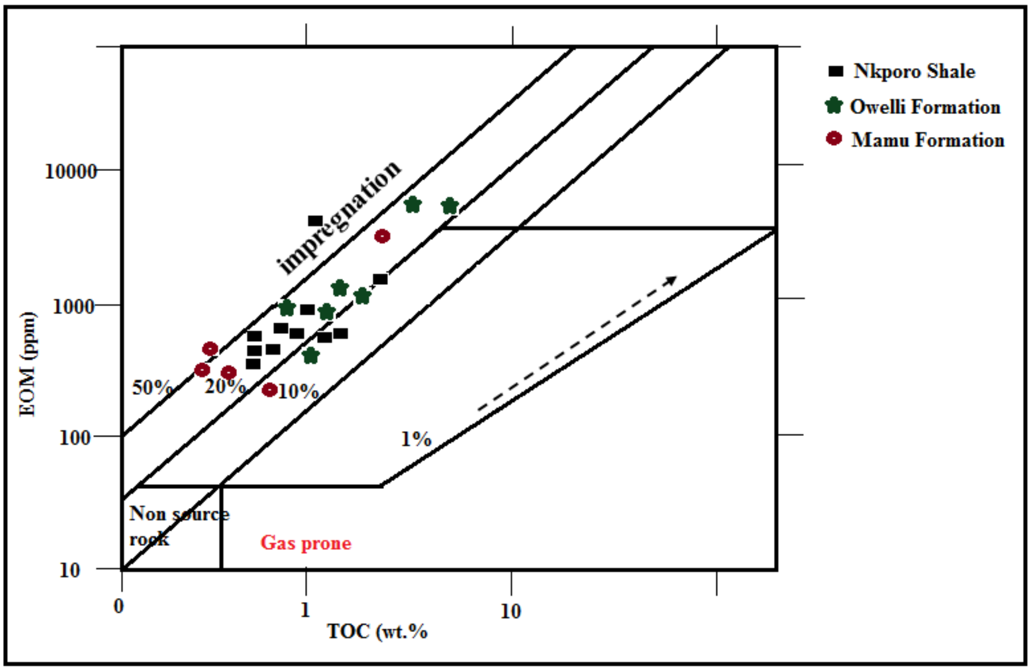

Figure 13. Plot of EOM versus TOC showing the hydrocarbon generative potential of the analysed samples (modified from Hunt, 1979).

6. Conclusion

The organic geochemical analyses of selected samples from the Nkporo Shale, Owelli and Mamu formations in Anambra Basin show that most of the analysed samples meet the accepted standards of a source rock with fair to good hydrocarbon generative potential and are essentially gas prone. However, few samples from the Nkporo and Owelli formations are oil and gas prone. More so, pyrolysis data indicate that the organic matter in majority of Nkporo samples and few of Owelli samples can be classified as predominantly Type II-III kerogen, while the organic matter in the rest of Owelli and Mamu formation samples is majorly Type III and Type IV kerogens. The samples are also immature to early mature in term of hydrocarbon generation. The organic matter in the investigated samples was derived mainly from mixed aquatic algae and terrigenous materials and was deposited under suboxic conditions. It was further revealed that the analysed samples were deposited in normal marine environment with samples from Mamu Formation tending towards freshwater depositional millieux.

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