

**PYROLYTIC AND SPECTROSCOPICAL IMPLICATIONS ON ORGANIC
MATTER CHARACTERIZATION FROM THE UPPER CRETACEOUS
SEDIMENTS IN THE ANAMBRA BASIN, NIGERIA**

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Abstract

Shale from basal Campanian to Maastrichtian strata of the Anambra Basin has been characterized by pyrolytical and spectroscopical techniques. The aims of this study were to assess the quality of its organic matter, evaluate its thermal evolution, highlight its potential as a source rock the source input and paleodepositional conditions of the organic matter. The TOC (1.18 wt. %) of the shale constitutes that of a good source rock with gas-prone kerogen indicated by Rock-Eval S_2/S_3 (4.16). The high OI (136.00 $\text{mgCO}_2\text{g}^{-1}\text{TOC}$) and Pr/Ph (1.53) suggest deposition in a shallow marine environment. The n-alkane distribution dominated by n-C₂₄ – n-C₃₁ and infrared spectrum dominated by aliphatic and aromatic functional groups are considered to be indicators of Type III kerogen. The CPI (1.49), Tmax (430°C), C₃₁(S/S+R) ratio (0.76) and R_o (0.56%) all indicate the onset maturity of this rock. This thermal evolution is thought to account for its current hydrogen index (174.00 $\text{mgHcG}^{-1}\text{TOC}$). The n-alkane distribution and predominance of low to medium molecular weight compounds (n-C₁₀ - n-C₂₀) with the significant waxy alkanes (+n-C₂₅), suggesting a significant high contribution of marine organic matter with minor terrigenous organic matter contribution. The kerogen is predominantly mixed Type II/III and Type III organic matter in all analyzed samples. This indicate that majority of the analyzed sediments are oil/gas prone and gas prone. The Tmax value 430 °C indicates that the organic matter is thermally immature to early mature for hydrocarbon generation. The Pr/Ph ratios of 1.53 suggest organic matter to be derived from source rock contains mixed organic facies and suboxic depositional conditions. The TS, Pr/n-C₁₇ and Ph/n-C₁₈ ratios systematically suggest the organic matter

in all the analyzed samples fall within mixed algal/aquatic and terrestrially derived and deposited under suboxic paleoenvironmental conditions.

Keyword: Geochemistry; Organic matter; Kerogen type; Maturity; Paleoenvironment; Cretaceous.

Introduction

The area of study is located between latitudes 5°55'N and 6°30'N and longitudes of 7°15'E and 7°40'E within the Anambra Basin (Fig. 1). Petroleum source rocks are the primary component of the petroleum system concept introduced by Magoon and Dow (1994). They constitute the precursors of petroleum which, under favourable conditions, may subsequently migrate to reservoirs and be sealed to form accumulation. Nigeria's current national petroleum reserves asset (proven), put at 32 billion bbl of oil and about 170 trillion standard ft³ of gas Nexant (2003), derives solely from the Niger Delta onshore and offshore. Some exploration campaigns have been undertaken in the inland basins with the aim of expanding the national exploration and production base and thereby add to the proven reserves asset (Obaje et al., 2004). The inland basins of Nigeria comprise the Anambra basin. The Anambra Basin is a big intra-continental basin that forms an arm of the lower Benue Trough (Obaje et al., 2004) with its NE-SW trending towards the Niger Delta (Fig. 1). Petroleum exploration in the Anambra basin was triggered by the occurrence of surface seeps and dates back to the early 1930s (Kulke, 1995). However, due to the Santonian inversion and the predominance of terrestrial sediments, as well as discoveries in the prolific Niger Delta in the south Ekweozor and Gormly (1983), the petroleum potential of this area has been under exploration and exploitation.

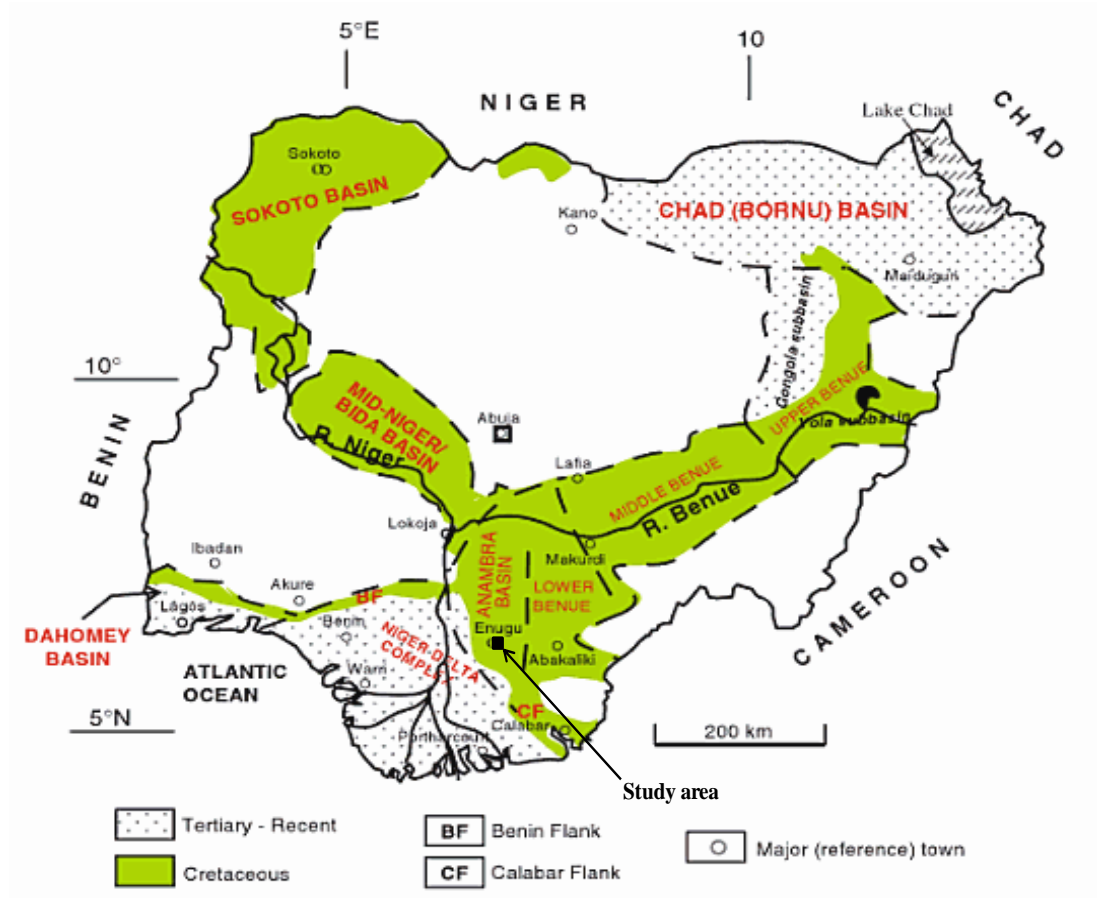


Fig. 1: Geological map of Nigeria showing the study location in the Lower Benue Trough (modified from Obaje et al., 2011).

Consequently on the exploration campaign, many wells have been drilled especially in the northeast to increase the national reserves but unfortunately most of these wells were reportedly dry. With this development, it has become necessary to adequately evaluate and characterize the petroleum source rocks in this basin by using well established geochemical techniques. At the core of any petroleum system is a good-quality source rock, total organic carbon (TOC) > 0.5%, hydrogen index (HI) > 150 mgHCg⁻¹TOC, liptinite content > 15%, Tmax ≥ 430°C, and R_o 0.5-1.2%, biomarker validation. However, other petroleum system elements must also include, apart from established source rocks, reservoir and seal lithologies, establishable trapping mechanisms, and favourable regional migration pathways (Obaje et al., 2004). The aims of this study were to characterize a shale sample from the basin using modern techniques of petroleum geochemistry in order to: (i) assess in detail the quality of its organic matter; (ii) evaluate its thermal evolution, and (iii) highlight its potential as a source and (iv) paleoenvironmental conditions. The

results of this study may stimulate further interest in petroleum exploration and exploitation in the Anambra basin.

Regional Geological Setting

The tectonism in Southern Nigeria probably started in Early Cretaceous, with the separation of Africa from South America due to the opening of the Atlantic. This resulted in the development of the Benue Trough which stretched in a NE-SW direction (Fig. 1), resting unconformably upon the Pre-Cambrian basement complex. It extends from the Gulf of Guinea to the Chad Basin and is thought to have been formed by the Y-shaped (RRR) triple junction ridge system that initiated the breaking up and dispersion of the Afro-Brazilian plates in Early Cretaceous (Kogbe, 1989).

After the evolution of the Benue Trough, sediments started depositing in the Trough. Stages of sedimentations in the trough were in three cycles; the Pre-Cenomanian deposit of Asu River Group followed by the Cenomanian-Santonian sedimentation. According to Hogue (1977) the inversion tectonics of the Abakaliki anticlinoria which led to the evolution of both Afikpo Syncline and Anambra basin, represented the third cycle of sedimentation which produced the incipient Nkporo shale, Enugu shale and Owelli sandstone. The Nkporo group is overlain conformably by the Coal Group consisting of the Mamu, Ajali and Nsukka Formations that form the terminal units of the Cretaceous series.

Stratigraphic Setting

The sandstones which is about 330 m thick is an extensive stratigraphic unit conformably overlying the Lower Coal Measure (Mamu Formation) and Nkporo Formations that are 400 and 200 m thick, respectively and underlying the Upper Coal Measure (Nsukka Formation) in the Maastrichtian (Reyment, 1965 and Nwajide, 1990) (Fig. 2). The Ajali Formation is typically characterized by white coloured sandstone (Reyment, 1965) while the Mamu Formation is essentially composed of sandy shale and some coal seams; the Nkporo Formation consists mainly of grey - blue mudstone and shale with lenses of sandstone (Obaje, 2009). According to Reyment (1965), the prevailing unit of Ajali Formation consists of thick, friable, poorly sorted sandstone.

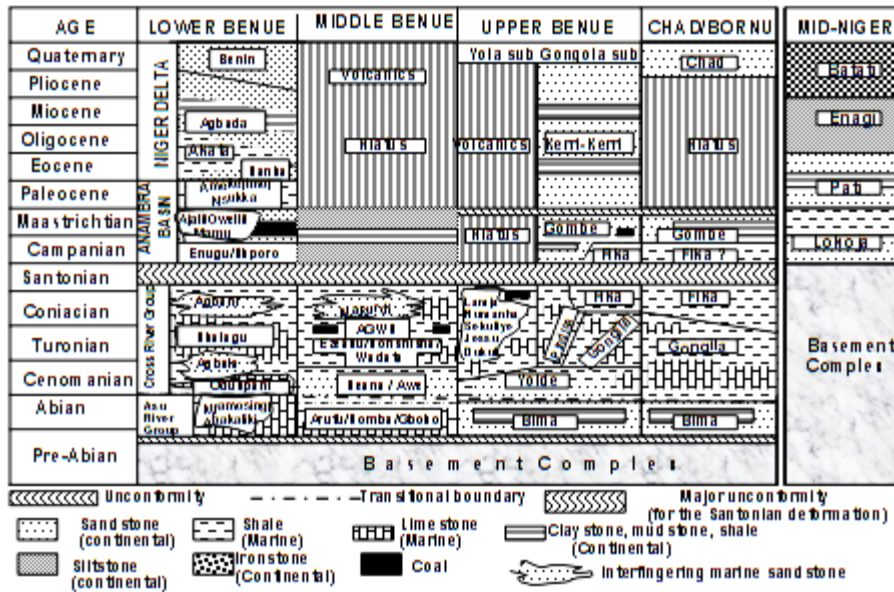


Fig. 2: Stratigraphic succession in the Benue trough, the Nigerian sector of the Chad Basin, the Mid-Niger Basin and relationship to the Niger delta (after Obaje et al., 2006).

Materials and Methods

The outcrop samples were obtained from the Nkporo shale at Leru 72 km south of Enugu along Enugu – PortHarcourt express road, the Enugu Shale at Enugu near the Onitsha-Road Flyover and the Mamu Formation exposed at Onyeama Mine section, along Enugu – Onitsha Express Road comprising mainly carbonaceous shale, silty shale and marls (Fig. 3). Care was taking to avoid weathered portions of the outcrop and to obtain material sufficient for various geochemical analyses. The samples were hard, thickly laminated but not fissile, with texture indicative of low permeability. This macro-structure suggests minimum risk of organic matter oxidation. The samples are attributed to the Campanian-Maastrichtian marine and paralic siliciclastics strata which are overlain by the coal measures of the Mamu Formation. The fluviodeltaic sandstones of the Ajali and Owelli Formations lie on the Mamu Formation. In the Paleocene, the marine shales of the Imo, and the continental/delta plain shale, mudstone, siltstones and sandstones of the Nsukka Formations were deposited, overlain by the tidal Nanka Sandstone of Eocene age which followed by lignitic Miocene-Oligocene Ogwashi-Asaba Formation.

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 105°C for 24 hours. Chips cut perpendicular to bedding were embedded in epoxy and polished following the procedures of Taylor et al. (1998) to yield polished

blocks for reflectance and fluorescence studies using scan electronic microscope. Another portion of the dried sample was pulverized in a rotating disc mill to yield about 50 g of sample for analytical geochemistry. The total organic carbon (TOC) and inorganic carbon (TIC) contents were determined using Leco CS 200 carbon analyzer by combustion of 100 mg of sample up to 1600°C, with a thermal gradient of 160°C min⁻¹; the resulting CO₂ 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 CO₂.

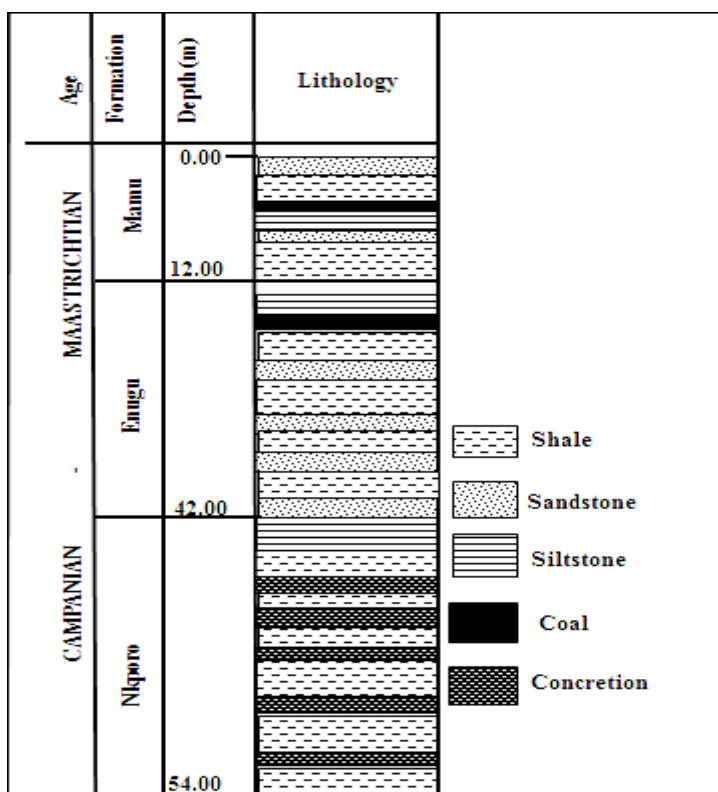


Fig. 3: Stratigraphic sequence of the studied area

One milligram of bulk powder sample was added to 200 mg of KBr and the mixture homogenized using a pestle in an agate mortar. Pressing the mixture using a load of 10 t yielded a pellet for Fourier Transform Infrared (FT-IR) Spectroscopy using a Nicolet Bench 505P Spectrometer, with sample absorbance monitored using 256 scans with resolution of 4 cm⁻¹ from a wave-number of 4000 – 400 cm⁻¹.

About 10 g of the sample was subjected to Soxhlet extraction using a solvent mixture of acetone, chloroform and methanol (47: 30: 23 v/v) at 60°C for 24 hours to extract the soluble organic matter. The extract was concentrated by evaporation to dryness using a

rotating vapour evaporator at 250 mb. The extract was transferred to an 8 ml vial using the same solvent mixture and allowed to evaporate to dryness in a vented hood. The dried extract was fractionated by silica gel column chromatography with a column prepared using 2 g of baker silica gel calcined at 200°C for 24 hours to yield six fractions ranging from saturate to polar.

The saturate fraction was subjected to urea adduction to separate isoprenoids from *n*-alkanes and subjected to gas chromatography-mass spectrometry (GC-MS) using a CE 5980 GC coupled to an HP Finnigan 8222 MS held at 80°C for three minutes and raised to 310°C at 3°C min⁻¹ and held isothermally for 10 minutes in order to assess some molecular parameters used in source rock characterization.

Results

Table 1 shows the results of 26 bulk and molecular geochemical parameters used in source rock quality and maturity evaluation. The shale is low in carbonate and its organic matter content within the threshold for petroleum source rocks.

The TOC values for the Nkporo, Enugu and Mamu formations range between 0.62 to 2.03 wt.%, 0.26 to 2.76 wt.% and 0.53 to 4.77 wt.%, respectively with a general mean value of 1.18 wt% (Table 1). S₁ ranges from 0.03 – 0.87 mg HC/g rock at Nkporo, 0.06 – 0.75 mg HC/g rock at Enugu and 0.06 – 1.12 mg HC/g rock at Mamu respectively. The analyzed samples from Nkporo, Enugu and Mamu formations also have S₂ 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. While S₃ values in Nkporo, Enugu and Mamu ranges from 0.08 – 1.13 mg HC/g rock, 0.49 – 2.25 mg HC/g rock and 1.13 – 2.66 mg HC/g rock respectively. The S₁, S₂ and S₃ mean values is within 0.26, 1.59 and 1.12 mg HC/g rock (Table 1). The HI and OI values range between 40 and 359 mg HC/g TOC and 07 and 187 mg CO₂/g TOC for the Nkporo samples, between 55 and 408 mg HC/g TOC and 17 and 418 mg CO₂/g TOC for the Enugu samples, and between 10 and 226 mg HC/g TOC and 67 and 356 mg CO₂/g TOC for the Mamu sediments, respectively with a general mean value of 174 mg HC/g TOC and 136 mg CO₂/g TOC. The Tmax values and PI in the Nkporo, Enugu and Mamu samples are in the range of 420 – 436 °C and 0.06 – 0.26, 417 – 432 °C and 0.07 – 0.24 and 426 – 431 °C and 0.06 – 0.16, respectively with a general mean values of 427 °C and 0.15. The TS values also range from 0.26 – 1.02 wt.%, 0.02 – 1.36 wt.% and 0.13 – 1.61 wt.% for the Nkporo, Enugu and Mamu samples, respectively with a general mean value of 0.58 wt.% (Table 1).

The EOM and HC for the Nkporo, Enugu and Mamu formations samples range from 305 to 2015 ppm and 264.20 to 1792.70 ppm; 231 to 3210 ppm and 201.70 to 2823.10 ppm

and 460 to 2270 ppm and 423.60 to 1423.30 ppm, respectively with a general mean values of 802 ppm and 645.89 ppm (Table 1). The highest amounts of EOM and HC are generally observed in all the formations (Nkporo, Enugu and Mamu).

The samples from the Nkporo Shale and Enugu Formation have fingerprints that display a typical unimodal nalkane 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 (Fig. 4; Table 1).

Pristane, generally occur in high relative concentrations in most of the analyzed samples, possessing Pr/Ph ratios in the range of 0.75 – 3.25 with a mean value of 1.53 (Table 1). The Pr/n- C_{17} and Ph/n- C_{18} ratios also range between 1.24 to 1.73 and 0.69 to 1.95 for Nkporo samples, 0.72 to 1.51 and 0.64 to 1.82 for Enugu samples and 0.76 to 1.48 and 0.52 to 0.95 for Mamu samples, respectively with a general mean value of 1.29 and 0.87. The CPI values for all the analyzed samples are greater than or less than 1.0 (Table 1), and range from 1.25 to 2.05 for the Nkporo samples, 0.96 to 1.71 for the Enugu samples and 1.25 to 1.95 for the Mamu samples.

Discussion

Organic richness and source rock quality

The TOC values for the Nkporo, Enugu and Mamu formations revealed that most of the analyzed 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).

Table 1: Bulk and molecular organic geochemical parameters for shale from the Anambra Basin.

Parameter	Result
TOC- Total Organic Carbon (wt%)	1.18
S_1 – Free bitumen determined by thermovaporation at 300°C (mgHCg ⁻¹ rock)	0.26
S_2 – Amount of kerogen that may be converted to petroleum (mgHCg ⁻¹ rock)	1.59
S_3 - Amount of carbon dioxide from carboxyl and carbonyl groups in kerogen (mgCO ₂ /g rock)	1.12
S_2/S_3 - To determine the quality of organic matter	4.16
Tmax – Temperature at which maximum decomposition of kerogen occurs (°C)	430.00
HI – S_2/TOC (mgHCg ⁻¹ TOC)	174.00
OI – S_3/TOC (mgHCg ⁻¹ TOC)	136.00
PI – Production Index ($S_1/(S_1+S_2)$)	0.15
S_1/TOC – Indices for generation of petroleum	0.31

R _o – Random vitrinite reflectance (%)	0.56
TSC - Total Sulphur content, wt. %	0.58
EOM - Extractable organic matter, %; ppm	0.08; 802.00
Sat - Saturated hydrocarbon fraction, ppm	540.78
Pr/ph – pristane/phytane ratio	1.53
Aro - Aromatic hydrocarbon fraction, ppm	137.11
CPI – Carbon Preference Index, $\sum(^n\text{C}_{23}\text{-C}_{31} + ^n\text{C}_{25}\text{-C}_{33}) / (2 * ^n\text{C}_{24}\text{-C}_{32})$	1.49
NSO - Nitrogen, Sulphur, Oxygen fraction, ppm	175.75
Pr/n-C ₁₇ – pritanne/ <i>n</i> -heptadecane ratio	1.29
Ph/n-C ₁₈ – phytane/ <i>n</i> -octadecane ratio	0.87
C ₃₁ (S/S+R) – homohopane ratio	0.76
Bit/TOC - Bitumen/TOC ratio	9.00
HC Yield - Hydrocarbon yield (Sat+Aro), ppm	645.89

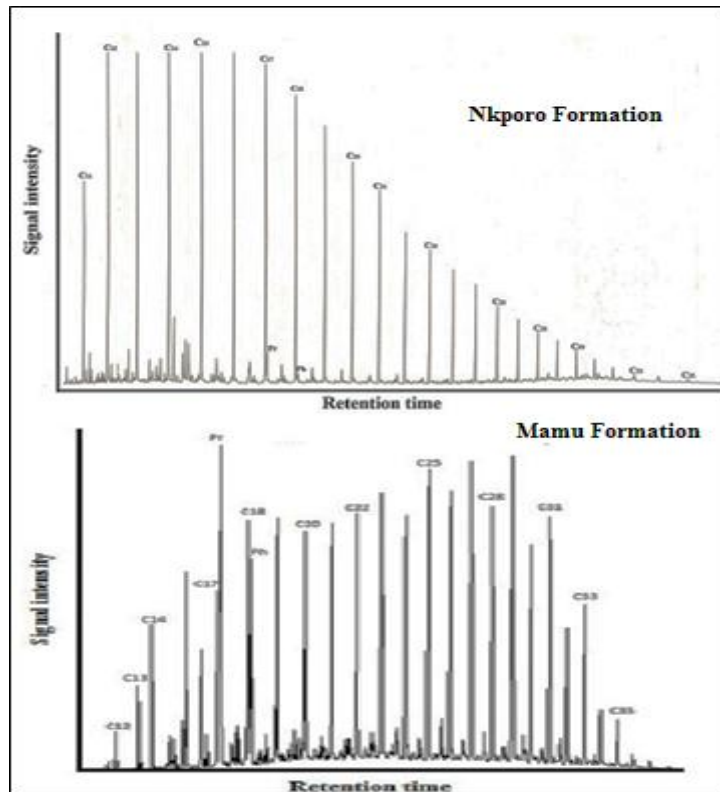


Figure 4: Gas chromatograms of representative samples from the Anambra Basin.

The TOC is a primary parameter in source rock appraisal, with a threshold of 0.5-1.0 wt% at the immature stage for potential source rocks (Tissot and Welte, 1984; Bordenave et al., 1993; Hunt, 1996). The value of 1.18 wt% of the shale studied exceeds this threshold (Table 1). High TOC of 4.45 wt% was obtained in Mamfe basin and this value exceeds

the threshold for oil generation (Eseme et al., 2006). However, high TOC is not a sufficient condition for oil generation. Coals usually have high TOCs that exceed 50 wt% but do not generate oil except when rich in liptinite, indicating the relevance of maceral composition. In contrast, deltaic sediments may have TOCs below 1.0 wt% but generate commercial accumulations of petroleum due to deposition of large volumes of sediments, as seen in the Niger Delta. High TOC content in shales indicates favorable conditions for preservation of organic matter produced during deposition. This may related to the redox condition, with high oxygen favoring organic matter oxidation, but also amount of organic matter produced. The high oxygen index of $136.00 \text{ mgCO}_2 \text{ g}^{-1}\text{TOC}$ suggests high contribution from terrestrial organic matter poor in hydroxyl groups (Tissot and Welte, 1984) and that the depositional environment was oxic.

The infrared spectrum (Fig. 5) shows a broad band from $1200\text{-}900 \text{ cm}^{-1}$, with a peak at 1030 cm^{-1} attributed to silicate minerals. Principal functional groups related to organic matter include the aliphatics ($2920\text{-}2850 \text{ cm}^{-1}$) and aromatics ($1700\text{-}1600 \text{ cm}^{-1}$, $850\text{-}700 \text{ cm}^{-1}$). The response at $350\text{-}3400 \text{ cm}^{-1}$, attributed the hydroxyl group, is also influenced by clay minerals and cannot be considered as wholly from organic matter (Eseme et al., 2006).

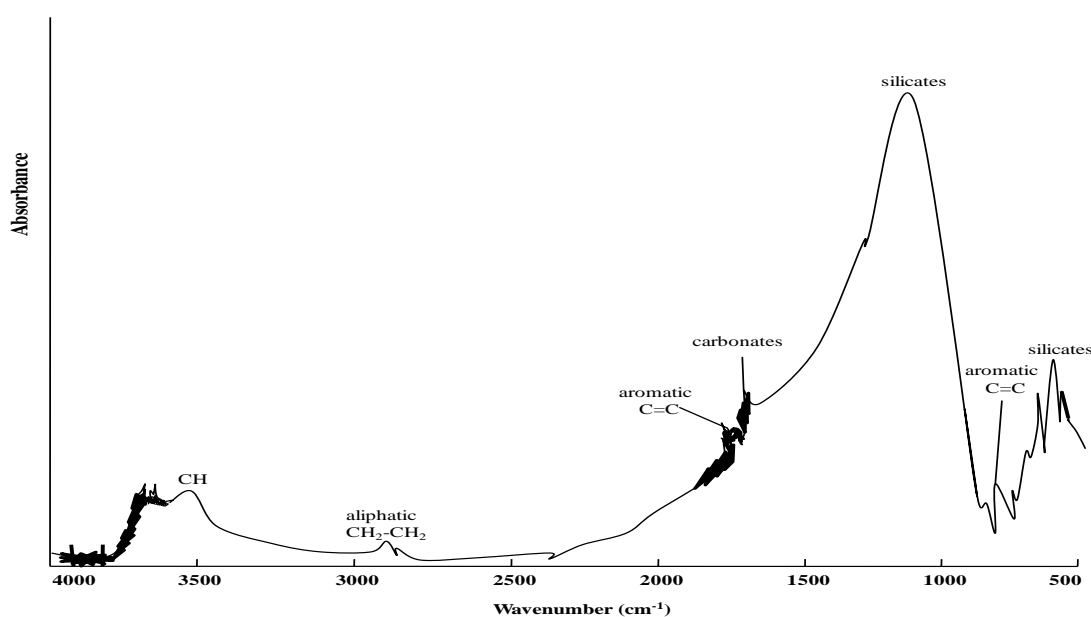


Fig. 5: FT-IR spectrum of shale from the Anambra Basin, showing the principal functional groups related to organic matter between 4000 cm^{-1} and 400 cm^{-1} , with the most prominent band that peaks at 1030 cm^{-1} attributed to silicate minerals in the bulk powder sample.

The principal application of infra-red spectroscopy is to evaluate the relative importance in organic matter of C=O and C-C functional groups (Tissot and Welte, 1984). Infrared spectrum shown in Fig. 5 is dominated by the prominent peak from 1200 cm^{-1} to 900 cm^{-1} , consisting of the response of silicate minerals in the rock. Prominent functional groups related to organic matter include the hydroxyl groups at 3500-3400 cm^{-1} , the aliphatic at 2950-2850 cm^{-1} and 1450-1350 cm^{-1} , as well as the aromatics at 1700-1600 cm^{-1} and 850-700 cm^{-1} . The C=O groups attributed to the spectral region of 1710-1700 cm^{-1} (Mongenot et al., 1999) are absent in Figure 3, but some, attributed to 1400-1040 cm^{-1} (Tissot and Welte, 1984), may be masked by the broad band attributed silicates. Both the fact that the C=O groups have a high molecular absorption coefficient that is well resolved by FT-IR, and the low intensity of the 1710-1700 cm^{-1} band relative to other functional groups with lower molecular absorption coefficient, indicate the presence of few carboxyl and carbonyl groups. Aliphatic and aromatic bands dominate the spectrum, with low C=O and OH functionally in agreement with the high OI of 136.00 $\text{mgCO}_2 \text{g}^{-1}\text{TOC}$ (Table 1).

Fluorescence observation showed a fairly well fluorescing liptodetrinite and alginate, with orange to yellow fluorescence. The kerogen content of 1.59 $\text{mgHC g}^{-1}\text{rock}$ is described as good, with an S_2/S_3 of 4.16 indicative of gas-prone organic matter. Random reflectance of 50 particles of vitrinite yielded a value of 0.56% R_o , consistent with its Tmax of 430°C, all indicative of early maturity. The extractable organic matter (EOM) of 802.00 ppm is less than the threshold (2000 ppm organic matter) thought to be necessarily below for expulsion, while the S_1/TOC of 0.31 indicates early generation of petroleum. The hydrogen index (HI = 174 mgHC/gTOC) is low compared with liptinite-rich rocks, with values slightly above 50 $\text{mg g}^{-1}\text{TOC}$ for Type III kerogen at the immature stage. The oxygen index (OI) is high, suggesting deposition in a high oxygen environment and high terrestrial higher plant contribution.

Rock-Eval prolysis yields parameters that are used to describe the generation potential of a source rock by providing information on organic matter quality, type and maturity, with the TOC, S_2 and HI as relevant parameters (Peters, 1986). The HI of 174.00 $\text{mgHC g}^{-1}\text{TOC}$ of this shale is low and results to a Type III kerogen at early maturity stage. The gas-prone nature of this rock rules out Type II kerogen, which usually shows S_2/S_3 greater than 5, while the maturity from vitrinite reflectance as well as Tmax suggest that the current HI results from thermal evolution of a Type III kerogen, with initial HI between 600 $\text{mgHC g}^{-1}\text{TOC}$ and 850 $\text{mgHC g}^{-1}\text{TOC}$ (Lafargue et al., 1998).

The S_2 values and HI also indicate that the analyzed 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. 6 and 7). However, the

TOC and S_2 values show that samples from Nkporo Formation are relatively richer organically than samples from Mamu and Enugu formations (Table 1; Fig. 3).

The van Krevelen diagram HI versus OI and plot of HI versus Tmax were used to identify the kerogen type in the analyzed samples (Figs. 8 & 9). These plots reflected the generation potential and indicate that majority of organic matter in the Nkporo Shales and in some Enugu Shale samples can be classified as predominantly Type II-III kerogen, while the organic matter in most of Mamu Formation samples and the rest of Enugu samples is majorly Type III and Type IV kerogens (Figs. 8 and 9).

Most of the analyzed samples have Hydrogen Indices (HI) below 200 mg HC/g TOC and are gas-prone (Fig. 7), while samples with HI below 50 mg HC/g TOC contain inert carbon (no hydrocarbon generation potential).

N-alkanes are used as a proxy for source contribution to organic matter, including algae, macrophytes and land plants (Meyers, 2003). Their distribution in algae is dominated by low molecular weight compounds, especially $n-C_{17}$, while high molecular weight *n*-alkanes dominated by $n-C_{29}$ or $n-C_{31}$ are assigned to terrestrial higher plants (Tissot and Welte, 1984; Hunt, 1996).

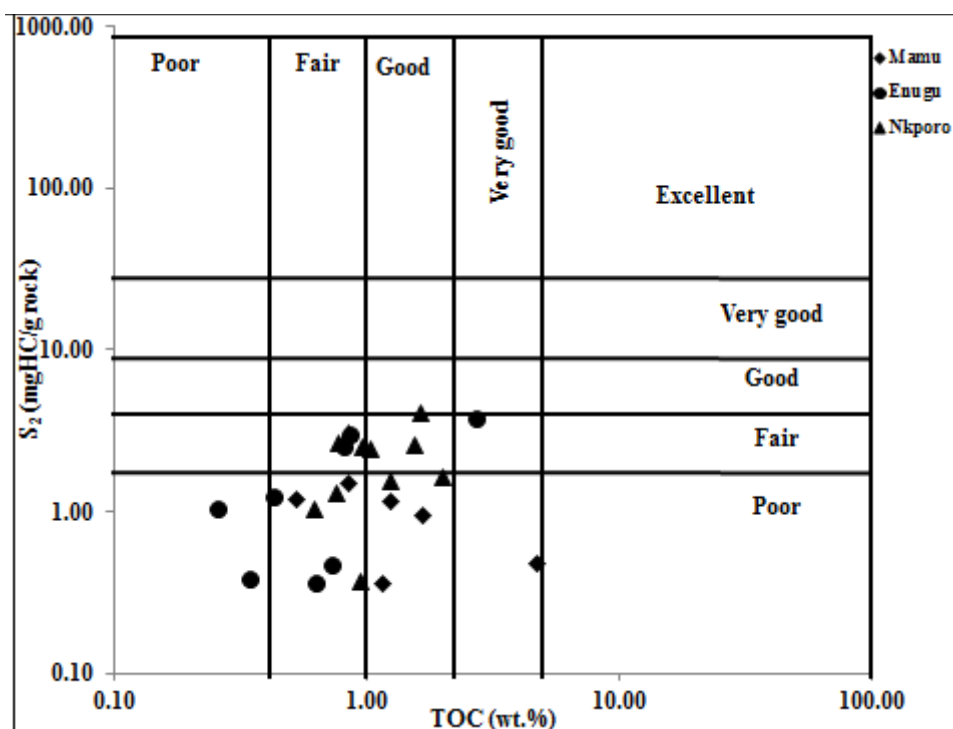


Fig. 6: Plot of S_2 versus TOC showing kerogen quality in the samples analyzed.

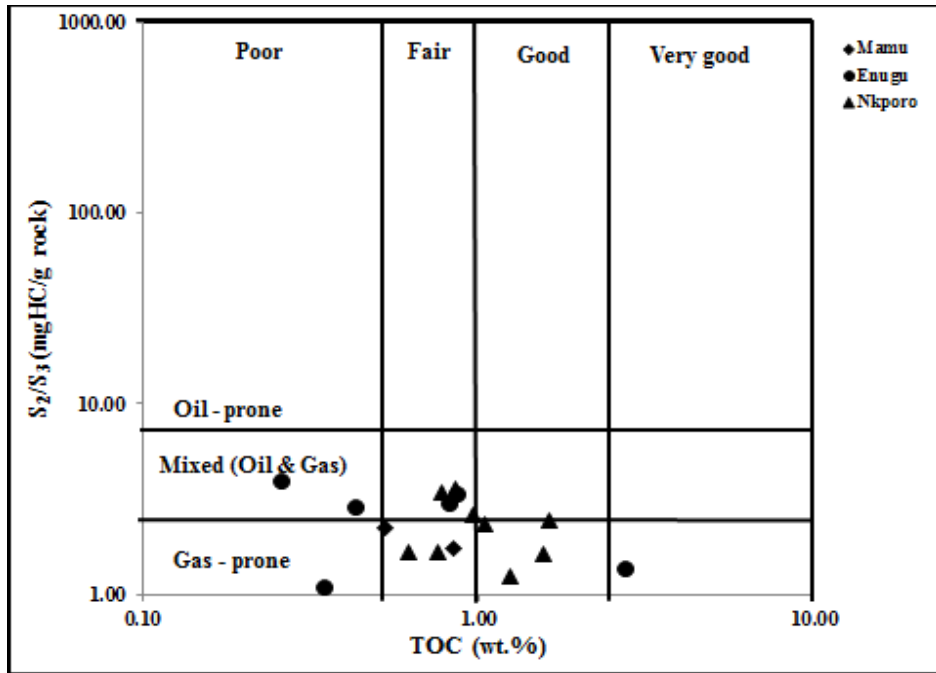


Fig. 7: Plot of S₂/S₃ versus TOC showing hydrocarbon generative potential in analyzed Anambra Basin sediments.

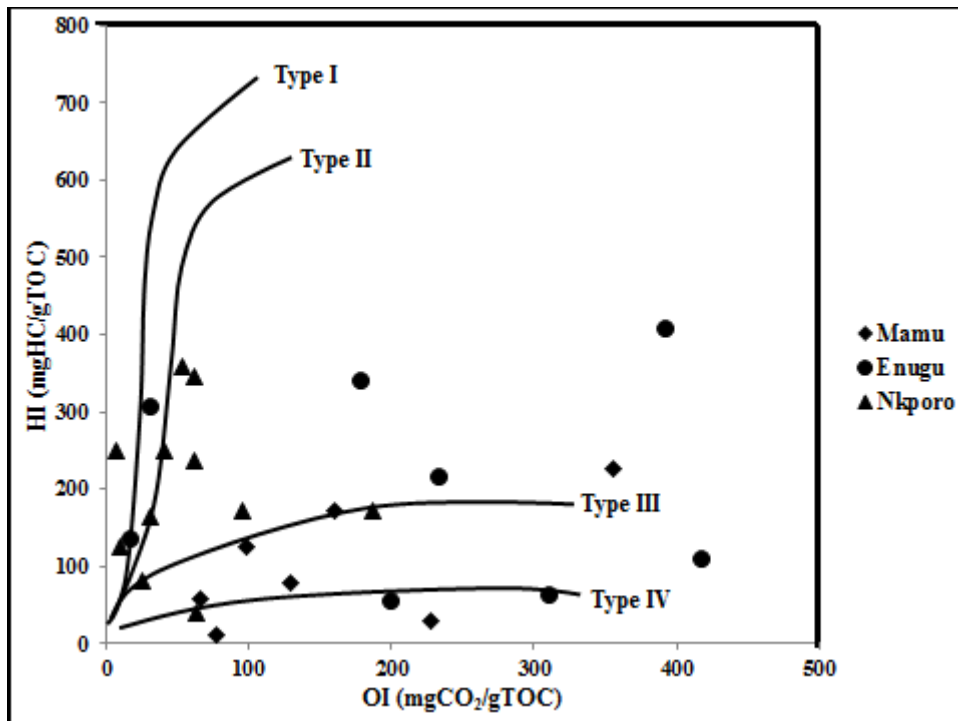


Fig. 8: The van Krevelen diagram of HI versus OI for the studied Nkporo, Enugu and Mamu formations samples showing kerogen type.

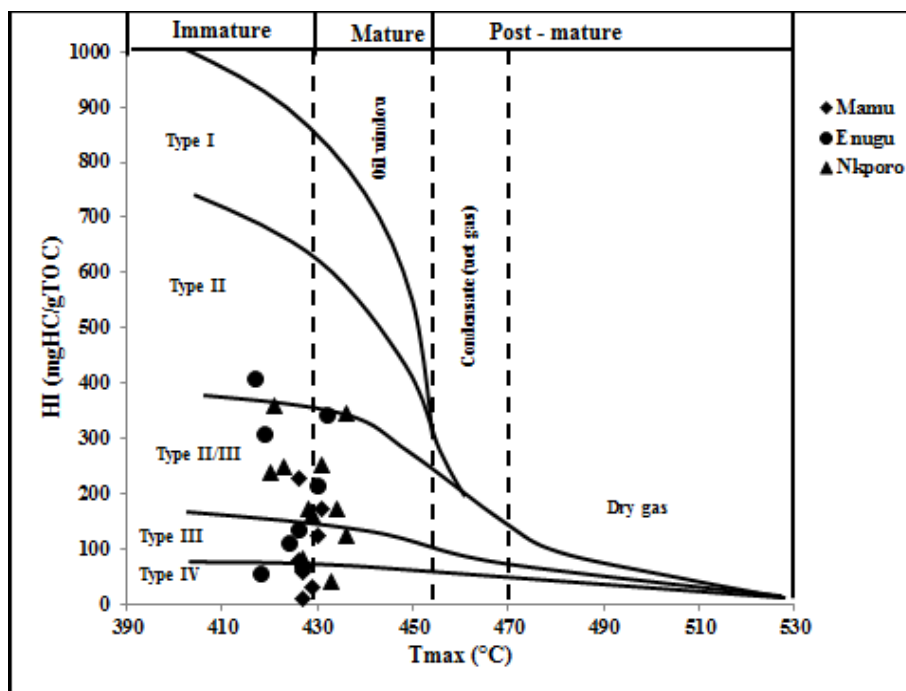


Fig.9: Plot of HI versus Tmax for the analyzed samples from the Anambra Basin.

The *n*-alkane distribution pattern support contribution from Type III kerogen because of the presence of high molecular weight *n*-alkanes considered as markers for terrestrial plant contribution (Uzoegbu, 2010; Uzoegbu et al., 2014). The *n*-alkanes that constitute the prominent peaks are dominated by *n*-C₂₉, with a pattern similar to the Scotian shale.

Fig. 4 shows the chromatogram of the saturate fraction of the shale. The *n*-alkane distribution is dominated by high molecular weight *n*-alkane, with maximum at *n*-C₂₉. Ratio calculated from the chromatogram includes a Pr/Ph ratio of 1.53. The common redox proxy (Pr/Ph) is affected by source organism but its value of 1.53 also indicates major contribution from terrestrial higher plants. Pr/Ph is commonly used as a redox proxy but it is influenced by source organisms and maturity (Peters and Moldowan, 1993). Its value of 1.53 in Table 1 is present in other marine source rocks, such as the Scotian shale (Powell, 1982). Gammacerane represents a marker for high salinity during deposition (Peters and Moldowan, 1993; Uzoegbu et al., 2014). Salinity increases in the water column favours stratification and preservation of organic matter due to a reduced oxygen, which is unfavourable to benthic organisms in the bottom water (Schreiber et al., 1986). Esemé et al. (2002) used geochemistry of brines from the Mamfe basin to suggest a genetic relation between evaporates and shales due to the correlation of sulphides found in the Mamfe basin shale by Le Fur (1965) with major ions that form the dominantly halite-evaporite. A signal for oxic conditions during deposition, such as low homohopane

index, was found. However, the consistency of different independent parameters, such as the high oxygen index and Pr/Ph ratio –though affected by source and maturity, together suggests deposition in an oxidizing environment.

Maturity indicators

The PI is used to assess the generation status of source rocks but is often useful when homogeneous source rocks of different rank are compared, in which case it is characterized as the transformation ratio (Bordenave et al., 1993). Hunt (1996) suggested that a PI from 0.08 to 0.4 is characteristic of source rocks in the oil window. The value of 0.15 of this shale is consistent with its vitrinite reflectance of 0.56% R_o . This maturity is also consistent with the fairly well fluorescing organic matter as well as Rock Eval Tmax of 430°C, reaching the 430-436°C for low sulphur immature source rocks containing Type III (Bordenave et al., 1993; Hunt, 1996). The PI is not affected by expulsion (Rullkötter et al., 1988) and this will not limit its use as an indicator of the organic matter transformation because generation may start for rocks with Type II at 0.55% R_o (Leythaeuser et al., 1980). Rullkötter et al. (1988) used a mass balance scheme to show that, at 0.68% R_o , the transformation ratio in the Posidonia shale from northern Germany had reached 30%.

The CPI of 1.49 supports the early maturity indices discussed above, though this parameter is usually high in marine source rocks that produce mostly high molecular weight hydrocarbons (Peters and Moldowan, 1993). Fig. 4 shows the distribution of hopanes investigated at m/z 191 of the non-adduct fraction. The $17\alpha\beta$ - C_{30} hopane is dominant, but also prominent is a step-like decrease in homohopanes up to C_{34} . The ratio 0.87 of the geo-epimer to the sum of the geo and bio-epimers of homohopane (C_{31} S/S+R) is indicative of equilibrium and support the early maturity of this shale. The ratio of the geo-epimer (C_{31} S) to the sum of the geo and bio-epimer (C_{31} R) reaches equilibrium around 0.76 (Radke et al., 1977), corresponding to the main stage of diagenesis (Peters and Moldowan, 1993). More mature samples will be revealed by drilling and the volume of source rocks will be crucial in the evaluation of their potential to generate commercial accumulations. Various maturity indicators suggest that this shale is at the onset of oil window and its current HI of 174.00mgHCg⁻¹TOC is thought to reflect thermal evolution due to labile kerogen from an initial HI between 600 mgHC g⁻¹TOC and 850 mgHCg⁻¹TOC, characteristics of Type III kerogens (Lafargue et al., 1998).

The Tmax values show that the organic matter within the analyzed sediments from Nkporo, Enugu and Mamu formations are predominantly immature to early mature, since more than 70% of the analyzed samples have Tmax 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 Tmax and PI versus Tmax (Figs. 9 and 10).

With increasing thermal maturation, the EOM 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 0.03 to 0.13, 0.05 to 0.13 and 0.05 to 0.09 for the Nkporo, Enugu and Mamu formations, respectively. These values indicate that the organic matter is essentially immature to early mature source rocks (Peters and Cassa, 1994; Demaison, 1984).

The CPI values for all the analyzed samples are significantly above 1.0 and there is a significant odd carbon number preference between $n\text{-C}_{22}$ and $n\text{-C}_{30}$. The CPI values for the analyzed sediments range from 0.95 to 2.05 putting the organic matter from immature to marginally mature (Peters et al. 2005; Peters and Moldowan, 1993; Bray and Evans, 1961). There is no specific trend between CPI and depth, probably because they are surface samples. The relationship between isoprenoids $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$ ratios further show that the analyzed samples are thermally immature to early mature for hydrocarbon generation (Fig. 11).

Depositional Environments

The source input and depositional environments of the analyzed shales were determined based on plot of TOC versus TS (Fig. 13) and biomarker distribution ratios (Pr/Ph , $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$). The distribution of n-alkanes in the gas chromatograms of most of the analyzed 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. 4). The isoprenoids and n-alkanes data also provide valuable information on source rock facies of petroleum samples (Peters et al. 2005; Peters and Moldowan, 1993). The $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$ ratios of between 0.72 to 1.74 and 0.52 to 1.95 with mean values of 1.29 and 0.87 respectively indicate that the organic matter in all the analyzed sediments is in a mixed algal/aquatic and terrestrially derived and deposited under suboxic paleoenvironmental conditions. The cross plot of $\text{Pr}/n\text{-C}_{17}$ versus $\text{Ph}/n\text{-C}_{18}$ was also used to interpret the source rock depositional environment condition and organic matter type (Van Kreverden 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. 11). 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.

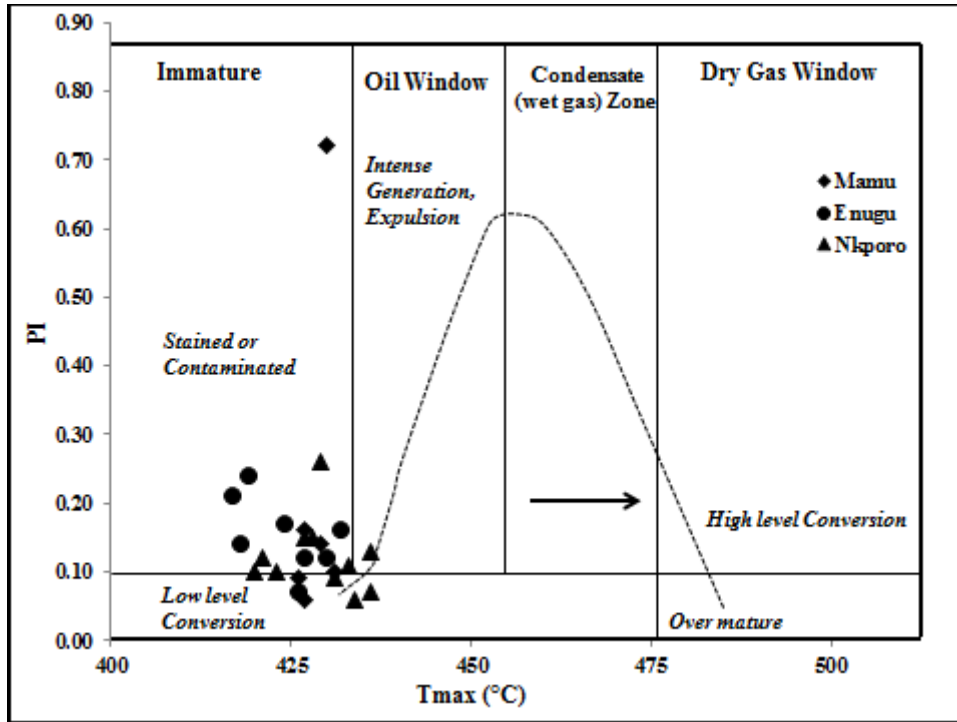


Fig. 10: Plot of PI versus Tmax showing kerogen conversion and maturity of the analyzed sediments in the Anambra Basin (after Hakimi et al. 2011).

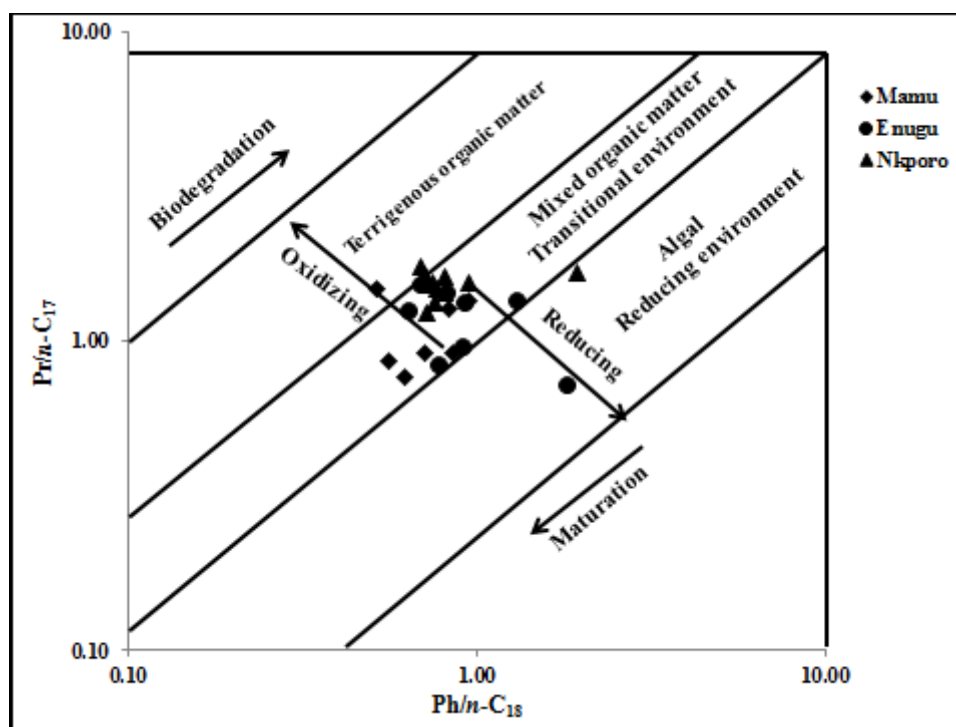


Fig. 11: The plot of $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ showing depositional conditions of organic matter from Nkporo, Enugu and Mamu extracts (after Peters and Moldowan, 1993).

Pr/Ph ratios 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 1; Adegoke et al. 2014; Didyk et al. 1978). Furthermore, carbon preference index (CPI) of *n*-alkanes between *n*-C₂₂ and *n*-C₃₀ 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 analyzed samples are greater than or less than 1.0 (Table 1). 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. 12) further supports this interpretation (Akinlua et al. 2007; Meyers and Snowdon, 1993). The plot of the TOC versus TSC of the analyzed samples also indicates deposition under normal marine environment, with samples from Mamu Formation tending towards freshwater depositional region (Fig. 13).

Hydrocarbon Potential

The TOC and pyrolysable data information, bitumen extraction and biomarker characteristics, enabled the characterization of the organic matter in the Nkporo, Enugu and Mamu formations. The kerogen type was derived from the pyrolysable data. The relationships between the HI, OI and Tmax revealed kerogen of mixed type II/III and type III for most of the samples and few of the samples for type II and type IV organic matter, which suggests that the organic matter inputs are both of marine and terrestrial sources with contribution predominantly of terrestrial plants (Figs. 8 and 9; Akaegbobi, 1995; Ekweozor and Gormly, 1983).

The plots of S_2 versus TOC and S_2/S_3 versus TOC equally revealed that most of the analyzed samples can be regarded to possess a fair to good source generative potential and is essentially gas-prone (Figs. 6 and 7). However, majority of samples from Nkporo Shale and a few of Enugu samples are richer organically than other samples from Enugu 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 Enugu and Mamu formations (Table 1; Figs. 9 and 10). According to Tissot and Welte (1984), the EOM is that portion of the organic matter representing what has been generated but not expelled. The quantity of 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 Table 1, Figs. 6 and 7, the extract yields show that most of the samples fall within the range of fairly to very good source rocks (Hunt, 1996; Killips and Killips, 1993; Philippi, 1957). This is supported by the plot of EOM versus TOC (Fig. 14), indicating that almost the entire samples fell within the range of improved oil source rock of 10 to 50%. Based on observations, the Nkporo Shale is likely to have the highest generative potential as obtained from the pyrolysable data of the analyzed samples. This is in agreement with previous work by Akaegbobi and Schmitt (1998), Unomah and Ekweozor (1993) and Akaegbobi et al. (2017), who have variously identified the Nkporo Shale as the hydrocarbon source rock within the Cretaceous Anambra Basin.

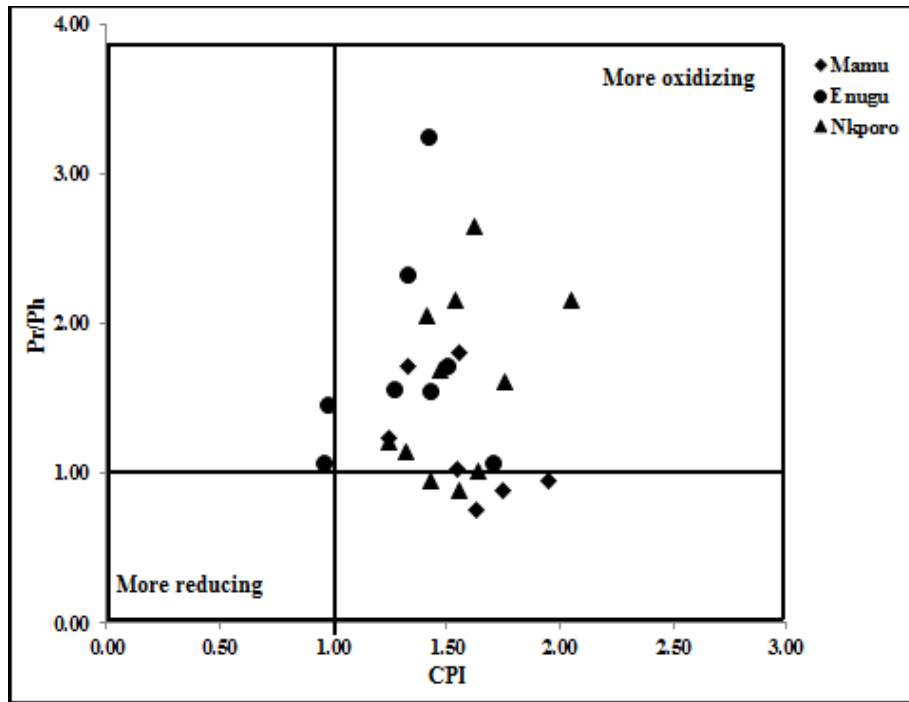


Fig. 12: The cross-plot of Pr/Ph ratios versus CPI showing the depositional conditions of the organic matter (After Akinlua et al. 2007; El-Diasty and Moldowan, 2012).

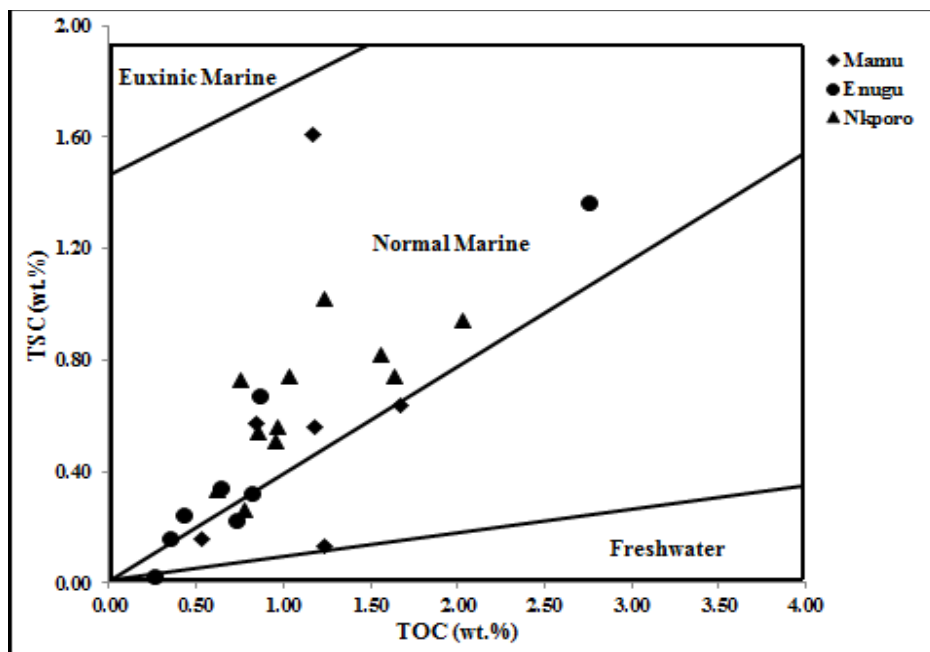


Fig. 13: The plot of TOC versus TS showing depositional environment of the organic matter.

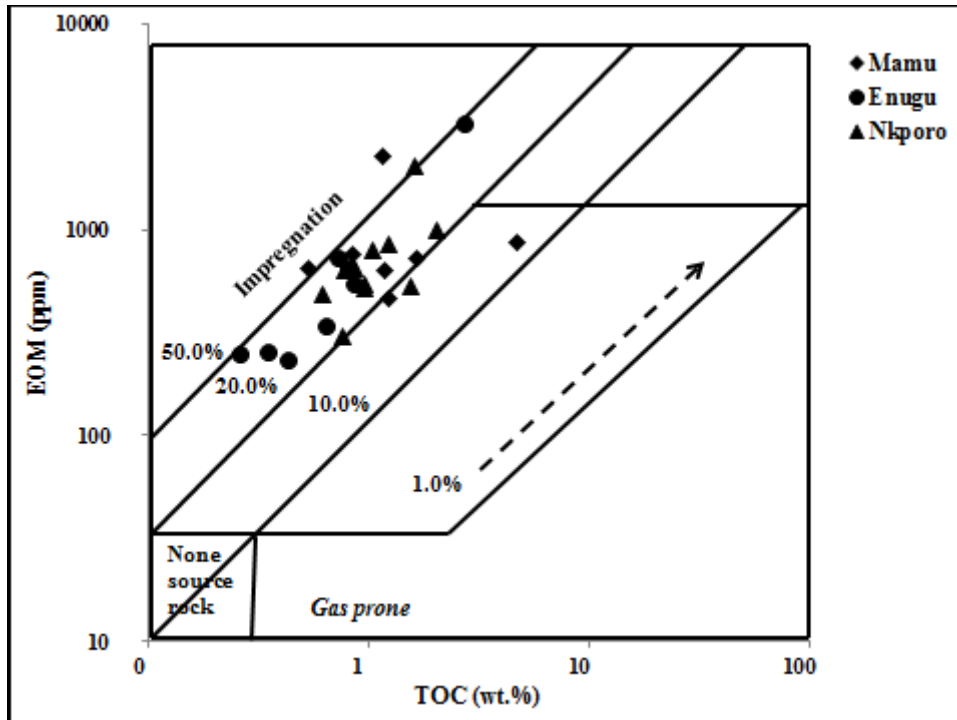


Fig. 14: The plot of EOM versus TOC showing the hydrocarbon generative potential of the organic matter (after Hunt, 1979).

Conclusion

Shale from the Anambra basin has been characterized for its source potential using bulk and molecular geochemistry. The shale is a good quality source rock, with gas-prone kerogen. The high OI, high Pr/Ph, Pr/*n*-C₁₇ and Ph/*n*-C₁₈, as well as distribution of organic matter-related functional groups on its infrared spectrum, suggest deposition in an oxidizing environment. In addition to the functional group distribution on the infrared spectrum, the *n*-alkane distribution, dominated by high molecular weight compounds, together with the HI, is considered to be characteristic of Type III kerogen. Multiple indicators, including %R_o, CPI, Tmax and C₃₁ homohopane ratio, consistently indicate immature to early mature source rock. Based on observations, the Nkporo Shale is likely to have the highest generative potential as obtained from the pyrolysable data of the analyzed samples. The plot of TOC versus TS, Pr/*n*-C₁₇ and Ph/*n*-C₁₈ ratios systematically indicate that the organic matter in all the analyzed samples is in a mixed algal/aquatic and terrestrially derived and deposited under suboxic paleoenvironmental conditions.

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