

Research Article

Biomarker Geochemistry of Nkporo Shale from Ndi-Owerre in the Afikpo Basin, Southeast Nigeria

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Biomarker analysis was conducted on shale samples belonging to the Cretaceous Nkporo sediments of the Afikpo Basin in southeastern Nigeria to determine the distribution of n-alkanes, pristane and phytane ratios (Pr/Ph), odd-over-even preference (OEP), carbon preference index (CPI), transformation ratios. These parameters revealed the source, depositional conditions and maturity of the organic matter. Ts/Ts + Tm values of 0.9 to 0.12 and moretane/hopane ratio of 0.33 to 0.35 indicate shales are thermally immature to marginally mature. The presence of long-chain aliphatics (C₁₉₋₃₅) in the shale matrix suggests shale can at least generate oil and gas. Data show high Pristane/Phytane (Pr/Ph) values and preeminence of intermediate molecular weight n-alkanes (nC₁₂ - nC₃₃). The predominance of Pr against Ph suggests humic, toxic to dysaerobic organic matter origin. Distributed n-alkane patterns of gas chromatograms are non-unimodal with varying peaks. They show maximal between nC₁₂ - nC₃₃ with no remarkable protrusion, indicating slight or no organic matter alteration. The prevalence of OEP values (0.23 -2.10) and CPI values ranging from 1.09 and 1.61 with average oxygen indexes of 53.33mgHC/gTOC suggests donation from mostly terrestrial organic matter poor in hydroxyl groups.

Keywords: Biomarkers, Organic Matter, Transformation ratios, Shale, Nkporo, Afikpo Basin.

INTRODUCTION

The study area lies between latitude 5°40' to 6°00'N and longitudes 7°50' to 7°60'E (Figure 1). By all account, it is important to adequately study the petroleum source rocks in this basin by using well established geochemical techniques. A good quality source rock is an inestimable prerequisite for any petroleum system, (TOC-Total Organic Carbon >0.5%; HI-Hydrogen Index >150mgHCg⁻¹TOC; T_{max}-Pyrolysable Hydrocarbon Temperature ≥430°C and Liptinite Content>15%). Notwithstanding, typical petroleum systems must consist of matured source rocks, migration pathways, reservoir rocks, traps, seals or cap rock, provided the relative timing and geothermal temperature of generation is reached, (Obajeet *al.*, 2004). Likewise, biomarker analysis can reveal the source, depositional conditions and maturity of organic matter in sediments. The aim of this study is to identify organic geochemical characteristics of shale samples belonging to the Cretaceous Nkporo Formation through biomarker examination.

Geological Setting

The Campano-Maastrichtian Nkporo Shale with an approximate thickness of 150m has its type section exposed at Imilike Agu. Simpson (1954) and Reymont (1965) described the Nkporo Shale from its area in Asata and Obweeti stream valley within Enugu area. The Nkporo Shale which underlies the Mamu Formation in the Afikpo syncline on the mapped area covers about 40% of the area. It consists of predominantly soft, dark grey blue carbonaceous shales and sandy shale which alternate with siltstones and occasional bands of mudstones intercalation.

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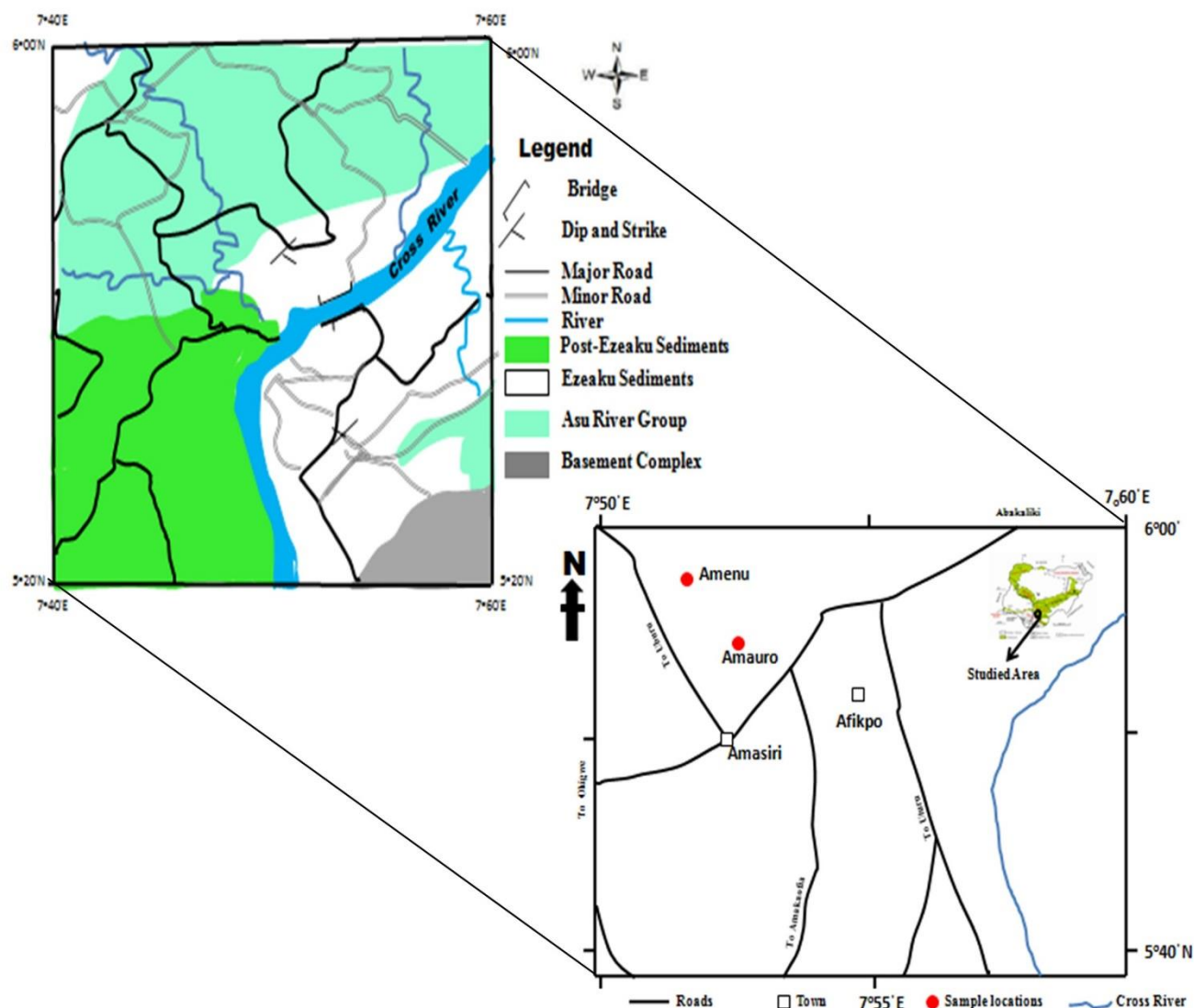


Fig. 1: Geological map of the Afikpo Basin showing the study area (modified from Microsoft Encarta, 2009).

The lithologic unit of the Nkporo Shale can be subdivided into three main subunits as (a) Sandy shale, (b) Grey shale and (c) Carbonaceous shale. An exposure of this subunit is recognized along the Abakaliki-Afikpo road and Amasiri. It comprises of dark soft carbonaceous shales which are thinly laminated. The shales are dark blue with nodular concretions and potholes at the base with intercalation of clay which alternate with siltstone (Akhirevbulu and Ogunbajo, 2011). At the top it is weathered to ferruginized sandstone. Along Amasiri – NdiOwerre road which is about 3km outside the studied area, a good exposure of this subunit was recognized. The type sections of this subunit in the study area were recognized along the channels of NdiOwerre and Umuyima streams at Afikpo and at Okposi along the channels of Omeme and Iyi-akwa streams. The grey shales alternate with mudstones and fine sandstones. The grey shale is commonly found overlying the carbonaceous shale in most of the outcrops studied, and also has nodular concretions. This shale gradually graded into sandy shale upwards and in some places it is weathered to reddish brown coarse sandstone or ferruginized sandstone and the top of which

is capped with laterites. The grey shales are characteristically fissile and split into thin flexible flakes of various sizes. The colours of dark carbonaceous shale and grey shale are due to the quantity of organic matter or oxidation state of iron in the rock (Pettijohn, 1975; Ojo and Akande, 2009, Valkarelo and Bhattacharya, 2009; Uchebo, 2010; Obaje *et al.*, 2011; Omali *et al.*, 2011; Uzoegbu *et al.*, 2013a).

MATERIALS AND METHODS

Three representative shale samples were obtained from Nkporo Shale in Ndi-Owerre of the Afikpo Basin and used for the analysis. 50g of each sample was washed, oven dried for 24 hours at 40°C, crushed with BB-200 jaw crusher. Crushed samples were divided into equal halves and one half pulverized by vibratory disc mill Model RS 100 to <50µm size. Analysis involving liquid chromatography, gas chromatography and gas-chromatography-mass spectrometry were conducted on each sample.

The GC-MS analyses of the fractions were performed on a Hewlett-Packard 6890N gas chromatograph interfaced to a Hewlett-Packard 5973N Mass spectrometer. The gas chromatograph was equipped with a DB-5 MS fused silica capillary column (30 m x 0.25 mm) and helium was used as carrier gas with a flow rate of 1ml/min. The Mass spectrometer was operated with electron impact energy of 70 eV and ion source temperature of 230 °C. The GC oven temperature was isothermal for 1min at 80 °C and then programmed from 80 to 280 °C at 3 °C/min and isothermal for 20 min at 280 °C. Individual saturated, aromatic and NSO- compounds were monitored by selected ion monitoring (SIM) at a cycle time of 1s. The GC-MS data were acquired and processed with a Hewlett-Packard Chemstation data system.

RESULTS AND DISCUSSION

Biomarker Fingerprints

Figures 2 and 3 show the relative concentrations of extracts obtained from the respective solvent extractions from shale samples. The shale samples from Nkporo have extract concentration ranging from 50 to 60ppm. Bitumen concentrations in the extracts range from 1.92 to 2.26%. The maltenes values range from 89.34% to 92.94% in the shale samples. The asphaltenes range from 6.74 to 8.52% (Table 1).

Table 1: Amount and percentage extracts (aliphatics, aromatics and heteropolar compound of shale samples from the Nkporo Formation.

Sample Name	Sample Type	Locality	Lithology	Formation	Extract (ppm)	Bitumen (%)	Maltene (%)	Aliphatic (%)	Aromatic (%)	Heteropolar (%)
NKPO-1	Outcrop	Afikpo	Shale	Enugu	50	1.92	92.94	0.07	38.03	61.56
NKPO-2	"	"	"	"	60	2.26	89.34	0.07	40.56	58.95
NKPO-3	"	"	"	"	50	1.92	90.14	0.03	46.69	52.20

Table 2: n-Alkanes and Isoprenoids distribution and ratios from GC-MS of the Nkporo shale samples. [CPI = $[(C_{25}+C_{27})/(C_{27}+C_{29})+(C_{29}+C_{31})/(C_{31}+C_{33})]/[2(C_{26}+C_{28}+C_{30}+C_{32})]$].

Sample Name	Sample Type	Locality	Lithology	Formation	CPI	Pr/Ph Ratio	ng/Sh Ratio	OEP	Pr/n-C17	Ph/n-C18	C31/C32
NKPO-1	Outcrop	Afikpo	Shale	Enugu	1.65	8.50	11.00	2.00	n.d	0.90	0.50
NKPO-2	"	"	"	"	1.67	7.70	10.80	1.00	n.d	0.93	0.40
NKPO-3	"	"	"	"	1.68	7.50	11.40	2.10	n.d	0.94	0.40

n.d = not determined

Table 3: Triterpanes indices from GC-MS of the studied shale samples from the Afikpo Basin. [qS and rS represent 22S/(22S+22R)αβ-Homohopanes and (22S/22S+22R)αβ-Bishomohopanes respectively].

Sample Name	Sample Type	Locality	Lithology	Formation	Ts/(Ts+Tm)	Moretane/Hopane	qS/qS+qR	rS/rS+rR	qS/qS+rS
NKPO-1	Outcrop	Afikpo	Shale	Enugu	0.12	0.33	0.53	0.47	0.75
NKPO-2	"	"	"	"	0.09	0.34	0.55	0.46	0.76
NKPO-3	"	"	"	"	0.09	0.35	0.55	0.44	0.77

n.d = not determined

Isoprenoids Distribution

After the integration of $m/z71$ in the fingerprints indicate hydrocarbon fractions dominated by a homologous series of C_{16} - C_{35} n-alkanes with predominance of the odd-numbered homologues. The C_{31} and C_{29} n-alkanes are the most abundant compared to other n-alkanes obtained in these samples from the Afikpo Basin (Table 2). The ratio (C_{31}/C_{29}) of these two n-alkanes (C_{31} and C_{29}) is higher in the sample number NKPO-1 with value 0.50. The carbon preference index (CPI) of the n-alkanes also varies with values ranging from 1.65 to 1.68 (Table 2). There is generally a high pristane/phytane (Pr/Ph) ratio ranging from 7.50 to 8.50.

Pr/ C_{17} values could not be determined in the shale samples while Ph/ C_{18} is between 0.90 and 0.94. There is predominance of long chain over short chain n-alkanes as their value varies from 10.80 to 11.40. This is in consonance with the values from gas chromatograph (FID) where Pr/Ph ranges from 4.60 to 6.10, OEP values between 0.74 and 1.40 respectively. While long and short chain ratio ranges from 2.07 to 8.90, the values of Ph/ C_{18} and Pr/ C_{17} vary from 0.10 to 0.20 and 6.10 to 7.20 respectively. Comparing results obtained from GC-MS and FID based on their sensitivities, GC-MS peaks n-alkanes from C_{15} to C_{35} while FID peaks from C_{19} to C_{32} . There is greater long chain n-alkanes produced from GC-MS as compared to FID, while GC-MS values indicate more sensitivity.

Triterpanes

The hopanes have a comparable distribution in all the samples with 17 α (H),21 β (H) homohopanes (C₃₁hopane) being predominant occur exclusively with the 22R configuration. All the samples recorded high concentrations of 17 α (H)-27,29,30-trinorhopane (Tm). The ratio of 17 β , 21 α (H)-moretane and 17 α ,21 β (H)-hopane [i.e $\beta\alpha/(\beta\alpha + \alpha\beta)$ - C₃₀hopane] ratios in the samples were grouped according to their localities (Table 3). The evident of ($\beta\alpha/\beta\alpha + \alpha\beta$)- C₃₀ hopane ratios in the shale samples from Nkporo values range from 0.33 to 0.40. The ratio of 22S to (22S and 22R) (q_s/q_s+r_s) epimers of 17 α (H),21 β (H) C₃₁-hopanes [22S/(22S + 22R)- C₃₁ $\alpha\beta$ hopanes] and that of 22S to (22S and 22R) (r_s/r_s+r_r) epimers of 17 α (H),21 β (H) C₃₂-hopanes [22S/(22S + 22R)- C₃₂ $\alpha\beta$ hopanes] were determined. The ratios of C₃₁-hopanes and C₃₂-hopanes (q_s/q_s+r_s) are shown in Table 3. The values of C₃₁-hopanes (q_s/q_s+r_s) range from 0.53 to 0.55.

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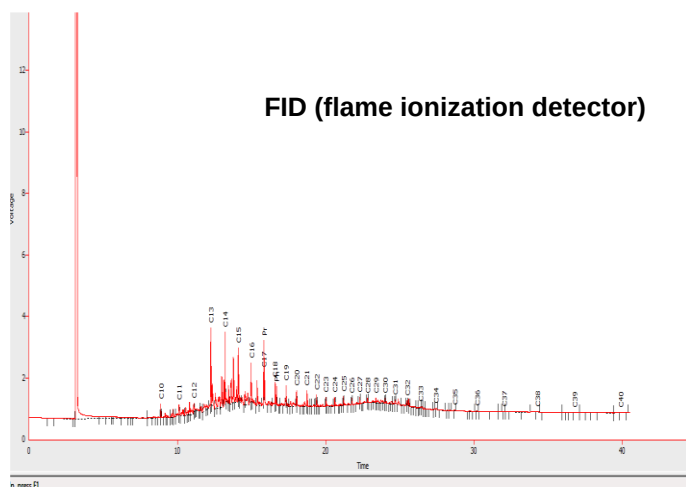


Fig. 2: Mass Chromatograms (FID) of NKPO peaks identification

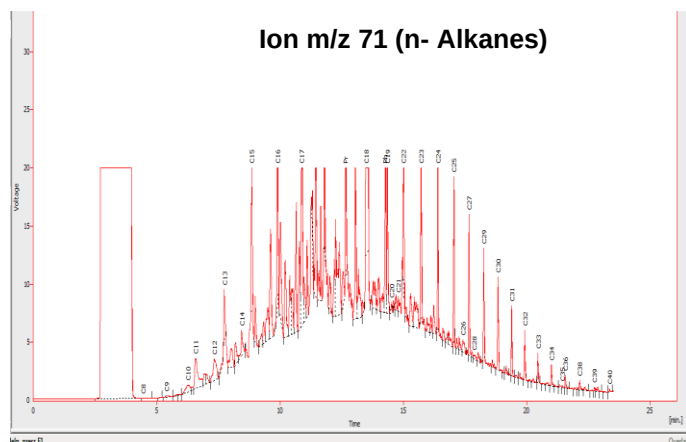


Fig. 3: Mass Chromatograms (Ions 71) of NKPO peaks identification

For C₃₂-hopanes (r_s/r_s+r_r) the values range from 0.40 to 0.50. The ratio of q_s/q_s+r_s varies from 0.76 to 0.77. The ratios and peaks of Ts/(Ts + Tm) C₂₇-hopanes are shown in Table 3 and the value range from 0.09 and 0.12. These analyses are in consonance with previous research of Akaegbobi and Schmitt, 1998; Akande *et al.*, 2007; Shanmugam, 1985).

The concentration of extracts from shale samples expressed in parts per million (ppm) is low in shale samples (Table 1). Powell (1978) and Snowdon (1987) are of the opinion that figures obtained for extracts can lead to erroneous conclusion in view of undissolving OM accommodating dissolving hydrocarbons, a prerequisite for initial migration. For proper understanding, extract yield was given in ppm and bitumen in percentage of organic carbon as shown in Table 1. The plot shows that the concentration of maltenes is directly proportional to concentration of the bitumen. The maltenes are made up of aliphatics, aromatics and nitrogen, oxygen and sulphur containing compounds, together referred to as the NSO (Speight, 2004). The variability in extract concentration amongst samples could also be due to maturity, source factor and/or biodegradation (Peters *et al.*, 2005). The amount of aliphatics 0.03 to 0.07 in the Nkporo samples may be caused by the maturity of the OM in the samples. Geometrically, vitrinite reflectance increase with thermal maturity as well as increase in the length of aliphatic chain (Petersen and Nytoft, 2006). All these therefore factor-out the paleo-temperature. These factors combined with the pronounced effects of tectonics at southern part of the lower Benue Trough may explain how Afikpo Basin is elevationally lower than the Anambra Basin.

Organic Matter Source

Aliphatics

Higher weight molecules of n-alkanes housing odd carbon numbers (C₂₇, C₂₉ and C₃₁) have been attributed to cuticula waxes of higher plant. Generally, in all the shale samples n-C₂₉ dominates probably due to high influence of terrestrial OM (Fig. 4). More especially n-alkanes having long chains comprise 50% and above n-alkanes in minimally ranked shaly sediments, typically in terrestrial sources (Amajiya *et al.*, 2006). Suggestively, resins very high in hydrogen content at an appropriate temperature will decompose into oily/gaseous materials, and can also take the form of cyclic redissolving remain. From Hunt (1996) suggestion, the value of 0.04 for the samples from Nkporo aligns to strong flourishing organic materials. Tmax (429°C) is less compared to sulphuric non-matured type III sources at 430-435°C. Average Carbon Preference Index (1.67) was obtained from the Nkporo samples (Table 3), although this can be little for marine sources (Cooley *et al.*, 1986; Esemé, 2006). CPI range (C₂₅-C₃₁) for samples from the Afikpo Basin is generally high (>1), indicating immaturity and indicating influx and inclusion of waxy n-alkanes which form bitumen at the end of diagenesis (Hunt, 1979).

Terpanes

There is appreciable quantum of bacteria-derived markers like hopane in relation to other continental types. Practically, the decomposition of OM by bacteria-assembly produces hopanoids inclusions but reservation with respect to some terrestrial types. The low $18\alpha(\text{H})$ -trisneonorhopanes/ $17\alpha(\text{H})$ -trisnorhopanes [Ts/(Ts + Tm)]

0.01 to 0.12 and appreciably higher moretanes/ $17\alpha(\text{H})21\beta(\text{H})$ -hopanes (m/ $\alpha\beta\text{H}$) ratios (0.33 to 0.79) deduce maturation beneath normal beginning of hydrocarbon production. $17\alpha(\text{H})$ -trisnorhopanes (Tm) normally transformed to [Ts] $18\alpha(\text{H})$ -trisneonorhopanes and moretanes to $[\alpha\beta\text{H}]$ $17\alpha(\text{H})21\beta(\text{H})$ -hopanes as maturation progresses (Meyer *et al.*, 1993).

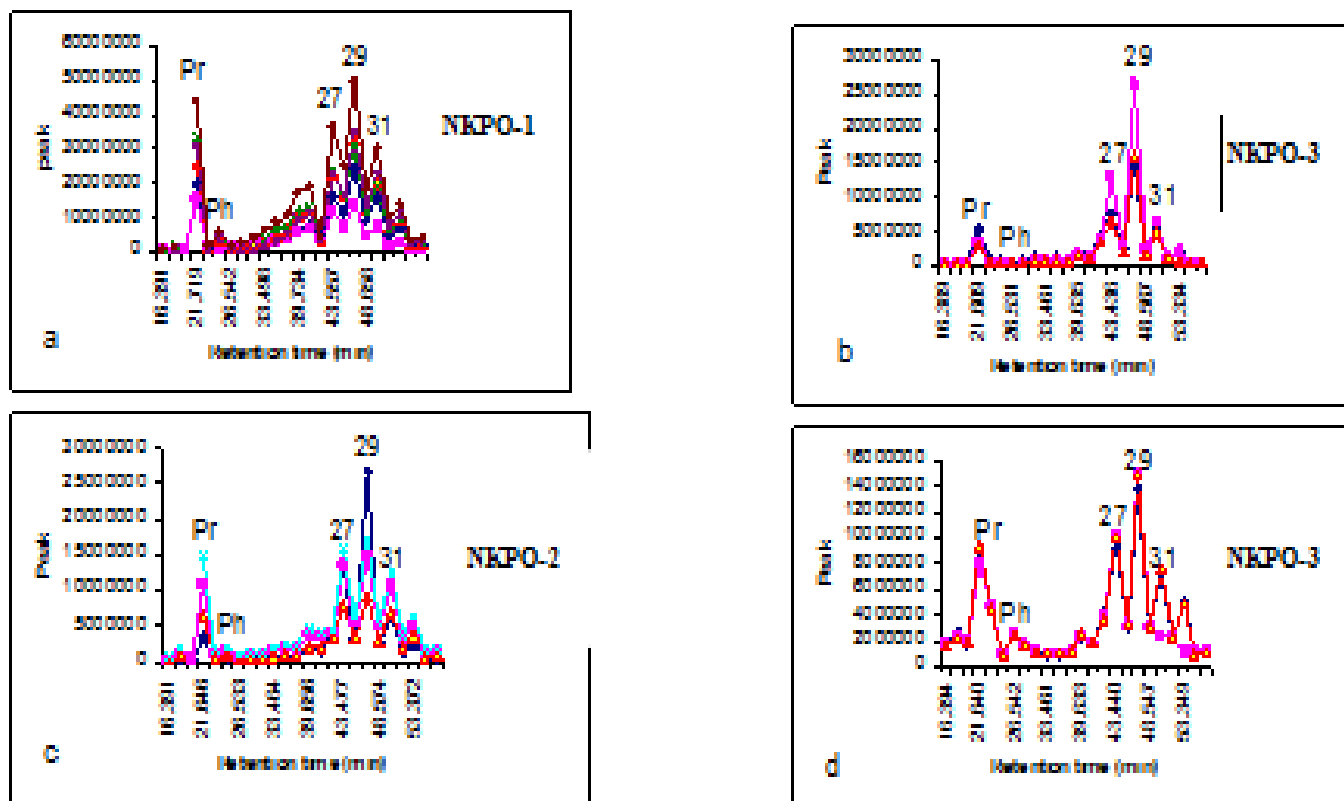


Fig. 4(a-d): n-alkane distributions from three localities of shale samples in Afikpo Basin.

Practically, Tm (17α -22, 29, 30-trisnorhopanes) possess more instability than Ts (18α -22, 29, 30-trisneonorhopanes), however it's unlikely to deduce transformation from Tm to Ts (Peters *et al.*, 2005). In my data, the low Ts/(Ts+Tm) ratio (Table 3) immaturely tells incapacitated transformation of Tm to Ts and unfathomably ratio by non-presence of Fe-rich clayey materials. Ts/(Ts + Tm) ratio gives consistent result at temperature of 430-436°C and stabilizes at temperature 436-444°C, but decreases at temperature >456°C (Marzi *et al.*, 1993; Farrimond *et al.*, 1998). Maturity parameters such as Ts/(Ts + Tm) ratio (0.09 - 0.12) and (22S/22S + 22R) $\alpha\beta$ -homohopanes ratio (0.16 to 0.58) all indicate immaturity for the shale samples from the Afikpo Basin. The ratio of $q_s/(q_s+r_s)$ in the shale samples range from 0.75 to 0.77. This also shows the immaturity of OM for the Nkporo Shale.

CONCLUSION

Biomarker analysis has shown that potential source rocks in the Afikpo Basin will produce more gas than oil, varying the source, maturity and depositional conditions of the organic materials. Therefore, the petroleum potential of shale sediments is marginally matured. This further suggests that source rocks of Afikpo Basin are gas-oriented with more of type III kerogen (Omontese *et al.*, 2019). Furthermore, it is suggestive to indicate that potential reservoir unit may occur in the marginal marine and flood plain sandstones of the Mamu Formation which directly overlies the Nkporo Shale.

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