

Using aromatic biological markers as a tool for assessing thermal maturity of source rocks in the Campano-Maastrichtian Mamu Formation, southeastern Nigeria

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ABSTRACT

The concentration and distribution of aromatic biomarkers in coals and shales from five boreholes penetrating the Maastrichtian Mamu Formation of the Anambra Basin, southeastern Nigeria, were investigated by gas chromatography-mass spectrometry to assess the thermal maturity and organic matter input. The study focused on the variations of the relative abundances of naphthalenes, phenanthrenes, and monoaromatic and triaromatic steroids identified on the mass fragmentograms. Trimethylnaphthalene (TMN) is the most abundant member of the naphthalene family while methylphenanthrene (MP) is the most abundant phenanthrene family member. The total of phenanthrenes and their isomers was greater than that of naphthalenes. The distribution of these aromatic hydrocarbons and their alkyl derivatives was strongly controlled by a selective expulsion mechanism and thermal maturation of organic matter. The low dibenzothiophene/phenanthrene (DBT/PHEN) ratios (0.01-0.06), as well as the enhanced concentrations of 1,2,5-TMN relative to 1,2,7-TMN, indicates organic matter derived mainly from higher plants, and the extract ternary plot of C_{27} , C_{28} and C_{29} monoaromatic steroids suggests a Type III and mixed Type II/III kerogen. The calculated mean vitrinite reflectance (%R_m), determined from the distributions of the isomers of methyl dibenzothiophene ratio (MDR) in the rock extracts, ranged from 0.51 to 1.43. These maturity values indicate that the coal and shale extracts are marginally mature for hydrocarbon generation.

Key words: Aromatic biomarkers, Maturity, Mamu Formation, Anambra Basin

RESUMEN

La concentración y distribución de biomarcadores aromáticos en carbones y esquistos de cinco perforaciones en la formación Maastrichtian Mamu de la cuenca de Anambra, en el sureste de Nigeria, fueron analizados a través de un estudio de espectrometría cromatográfica y de masa del gas para medir la madurez termal y la entrada de material orgánico. El estudio está enfocado en las variaciones de la abundancia relativa de naftalinas y fenantrenos, y en los esteroides monoaromáticos y triaromáticos identificados en los fragmentogramas de masas. La trimetinaftalina (TMN) es la más abundante de la familia de las naftalinas mientras el metilfenantreno (MP) es el más abundante de los fenantrenos. El total de los fenantrenos y sus isómeros fue mayor que el de las naftalinas. La distribución de estos hidrocarburos aromáticos y sus alquilos derivados fue controlada ampliamente por un mecanismo de expulsión selectiva y de la maduración térmica de material orgánico. La baja proporción dibenzotiofeno/fenantreno (DBT/PHEN) (0.01-0.06), al igual que las concentraciones mejoradas de 1,2,5-TMN relativas de 1,2,7-TMN indican que la materia orgánica se deriva principalmente de plantas mayores, y del diagrama ternario de los esteroides monoaromáticos C_{27} , C_{28} y C_{29} sugiere un tipo III mezclado con tipos II/III de querógenos. El valor calculado de la reflectancia de vitrinita (%R_m) determinado de la proporción de isómeros de metildibenzotiofeno (MDR) en los extractos rocosos oscila de 0.51 a 1.43. Estos valores de madurez indican que los extractos de carbones y esquistos son marginalmente maduros para la generación de hidrocarburo.

Palabras clave: Biomarcadores aromáticos; Madurez geológica; Formación Mamu, cuenca de Anambra.

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INTRODUCTION

Aromatic biomarkers and their structural isomers have been found useful for the maturity assessment of oils, source rocks and coals (Radke *et al.*, 1982a; Radke and Welte, 1983; Alexander *et al.*, 1985; Radke *et al.*, 1986; Garrigues *et al.*, 1988; Strachan *et al.*, 1988; Akaegbobi *et al.*, 2000; Akinlua *et al.*, 2007; Sonibare *et al.*, 2008). Complex mixtures of aromatic hydrocarbons have been identified in crude oils (Cumbers *et al.*, 1986), organic extracts of coals (Radke *et al.*, 1982a, b; Puttman and Villar, 1987) and ancient sediments (Alexander *et al.*, 1985; Garrigues *et al.*, 1988, 1990). These complex mixtures of polyaromatic hydrocarbons (PAHs) are usually not generated through biosynthetic processes by living organisms in the sediments. However, some living organisms may synthesize benzoyl-derivatives in large quantities (Akaegbobi *et al.*, 2000).

Aromatic compounds found in crude oils and ancient sediments are believed to have been derived from modification through degradation of biologically produced compounds such as steroids and terpenoids (Hall *et al.*, 1984; Strachan *et al.*, 1988). They also observed that steroids give rise to substituted phenanthrenes, and terpenoids produce alkylnaphthalenes. Other potential sources of alkylnaphthalene include the thermal degradation of spores, coals, and sporopollenin (Allan and Larter, 1981), and of kerogens and cyclic sesquiterpenoids present in resinous components (Anderson *et al.*, 1992). For the alkylated phenanthrenes, the terpenoids derived from higher plant constituents such as resins and waxes seem to be one major source. Radke *et al.* (1982a) suggested that direct methylation of phenanthrene during catagenesis could be a substantial source of alkyl phenanthrene. Furthermore, the conversion of higher-plant triterpenoids in sediments into aromatic hydrocarbons is through the release of oxygen functional groups and subsequent aromatization of the rings (Johns, 1986; Radke, 1987; Rullkotter *et al.*, 1994; Akaegbobi *et al.*, 2000). The ultimate products of such processes are therefore tetracyclic and pentacyclic aromatic hydrocarbons. Through cleavages of bonds within the rings

coupled with photochemical and acid catalyzed processes during diagenesis/catagenesis, these tetracyclic and pentacyclic aromatic hydrocarbons could be broken into methyl-substituted naphthalenes and phenanthrenes, respectively. Therefore, relative variations in the concentrations of alkylnaphthalenes and alkyphenanthrenes in the sediments could supply information on the maturity of organic matter, organic facies input and depositional environment (Seifert and Moldowan, 1978, 1986; Radke *et al.*, 1982a, b; Radke, 1988).

The aim of this paper is to examine the ratios of aromatic compounds in coal and shale extracts from the Maastrichtian Mamu Formation in the Anambra Basin, southeastern Nigeria, and to assess the organic matter input and thermal maturity for the source rocks.

GEOLOGICAL SETTING

The Anambra Basin, constituting the southwestern portion of the Benue Trough (Fig. 1), is a roughly triangular-shaped sedimentary depression covering an area of approximately 40,000 km² (Akaegbobi *et al.*, 2000). The present study area lies within latitudes 6°20' to 7°55' N and longitudes 7°10' to 8°00' E (Fig. 2). The Anambra Basin was initiated in the Early Cretaceous with the formation of the Benue-Abakaliki Trough as a failed arm of a rift triple junction associated with the separation of the African and South American continents and the subsequent opening of the South Atlantic Ocean (Murat, 1972). The NE-SW trending Benue-Abakaliki Trough is believed to be the result of a pre-Albian rifting of the African Shield prior to the opening of the South Atlantic Ocean (Uzuakpunwa, 1974). The movements were reactivated by further plate activity in the Lower Tertiary soon after the intermittent Upper Cretaceous rifting (Petters, 1978). The Anambra Basin contains over 6 km thick Cretaceous/Tertiary sediments and provides a structural link between the Cretaceous Benue Trough and the Tertiary Niger Delta (Whiteman, 1982; Onuoha, 1986; Mohammed, 2005).

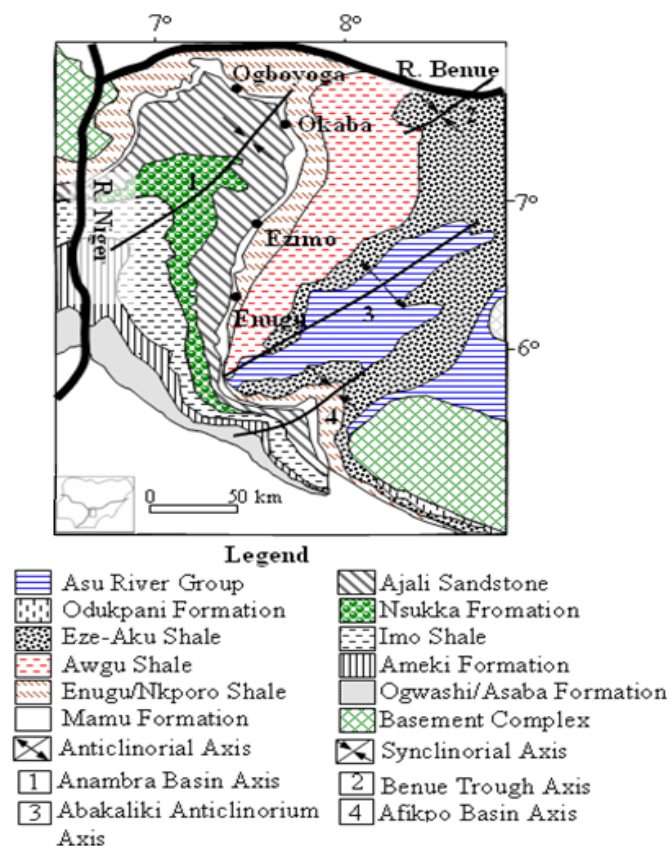


Figure 1: Geologic Map of the Anambra Basin and adjoining areas in southeastern Nigeria showing sample locations (modified from Akande *et al.*, 2007).

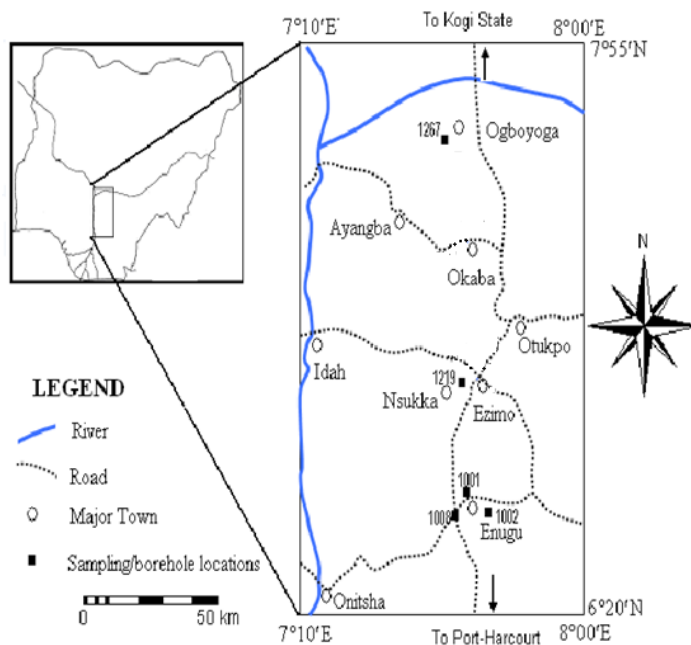


Figure 2: Location of study area with sampling sites.

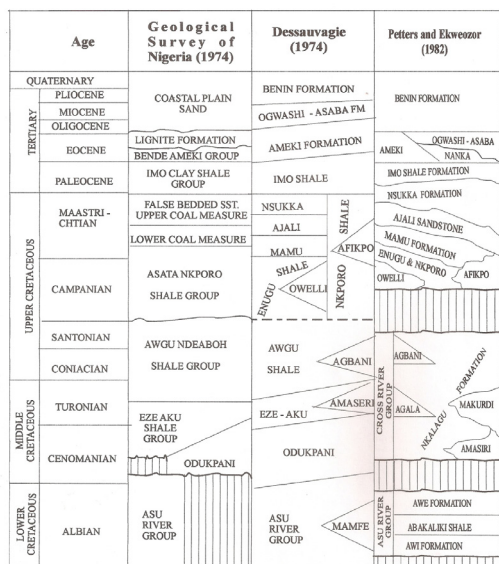


Figure 3: Stratigraphic subdivision of southern Benue Trough.

The stratigraphic succession ranges from Late Santonian to Eocene (Fig. 3), with sediments of fluvial, deltaic, pro-delta, and shelf facies origins. Accumulation of sediments in the Anambra Basin commenced with the Campanio-Maastrichtian marine and paralic shales of the Enugu and Nkporo Formations, along with the deltaic Owelli Sandstone equivalent. These basal units are overlain successively by the coal measures of the Mamu Formation (Lower Coal Measures), the Ajali Sandstone (Middle Coal Measures) and the Nsukka Formations (Upper Coal Measures). The Nsukka Formation, which overlies the Ajali Sandstone, begins with coarse- to medium-grained sandstones and passes upward into well-bedded blue clays, fine-grained sandstones, and carbonaceous shales with thin bands of limestone. The marine shales of the Imo Formation were deposited in the Paleocene, and overlain by the Ameki Formation (lateral equivalents of the tidal Nanka Sandstones) of Eocene age which constitutes the Tertiary succession (Petters and Ekweozor, 1982)(Fig. 3).

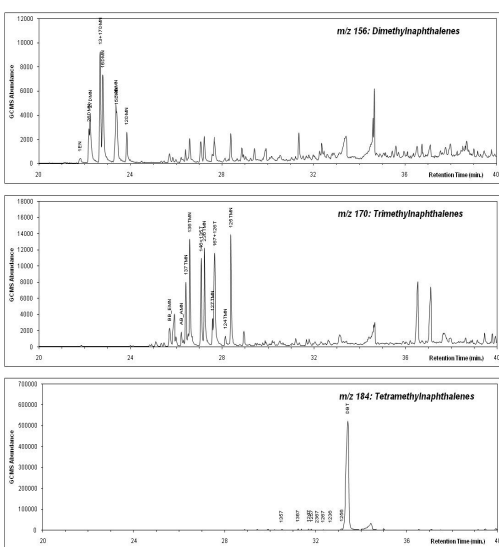


Figure 4a: m/z 156, m/z 170 and m/z 184 mass chromatograms showing the distributions of naphthalenes and its alkyl derivatives of representative coal sample (OG/1267/03) from the Anambra Basin

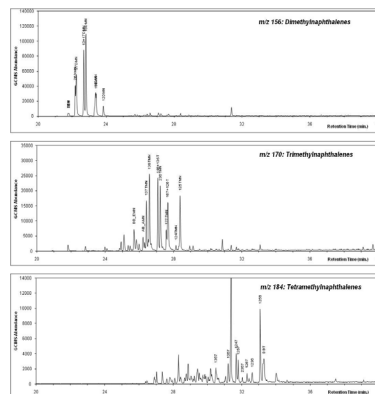


Figure 4b: m/z 156, m/z 170 and m/z 184 mass chromatograms showing the distributions of naphthalenes and its alkyl derivatives of representative shale sample (ENG/1001/02) from the Anambra Basin

MATERIALS AND METHODS

Seven core samples consisting of coal (4) and shale (3) having total organic carbon (TOC) values ranging from 3.35 to 55.07 wt.% were carefully selected at various depth intervals (75-221 m) from five boreholes penetrating the Mamu Formation in the Anambra Basin in three Coal fields at Enugu, Ezimo and Ogboyoga (Fig. 2). Pulverized samples were exhaustively extracted by Soxhlet extraction using dichloromethane as solvent. All samples were prepared according to standard organic geochemical sample preparation techniques (Radke *et al.*, 1980, 1984). Aliquots of the extracts were separated into saturated and aromatic hydrocarbons and heterocyclic compounds by liquid chromatography using a dual column system and a back-flushing technique as a preparatory step for biomarker analysis. The asphaltene fraction of the sample was recovered by precipitation in pentane overnight at room temperature. The pentane soluble portion of the sample (i.e., the maltenes) was further separated by liquid chromatography into saturated, aromatic and resin fractions using a large column containing silica gel with fractions quantified by gravimetric analysis. Aromatic hydrocarbons were eluted using 40 mL of 90:10 (v/v) pentane/dichloromethane mixtures. The aromatic fractions were diluted with 10 µl of carbon disulfide (CS₂) per mg of fraction and analyzed by Gas Chromatography-Mass Spectrometry using a Hewlett Packard 6890 GC/5973 MSD system (Agilent Technologies, California, U.S.A.) equipped with a high-resolution column (60 m, DB-1 phase, 0.2 mm i.d., 0.2 µm film). A constant flow of hydrogen carrier gas was used during the entire gas chromatographic run. The GC was temperature programmed from 80 °C (2 minutes hold) to 320°C at 3.5 °C/minute with a final hold time of 20 minutes. There was a 7.5-minute solvent delay on acquisition, and selected ion monitoring (SIM) was the standard method for analysis.

RESULTS

Biomarker Chemistry

The mass chromatograms of naphthalenes, phenanthrenes and akyl derivatives of representative coal and shale extracts from the Maastrichtian Mamu Formation in the Anambra Basin are shown in Figures 4a-b and 5a-b, respectively. The identification of the peaks labeled in Figures 4a-b and 5a-b are reported in Tables 1 and 2. Two methylnaphthalenes (MN), two ethylnaphthalenes (EN), nine dimethylnaphthalenes (DMN), ten trimethylnaphthalenes (TMN), eleven tetramethylnaphthalenes (TeMN) and two ethyl-methyl-naphthalenes (EMN) isomers were identified in the aromatic fractions of the coal and shale extracts (Figs. 4a-b). Among the tricyclic aromatic hydrocarbons, four methylphenanthrenes (MP), and fourteen dimethylphenanthrene isomers were identified (Figs. 5a-b). Dimethylnaphthalene was the most abundant among the naphthalene family (Fig. 6). All samples have similar distributions of phenanthrenes (*m/z* 178).

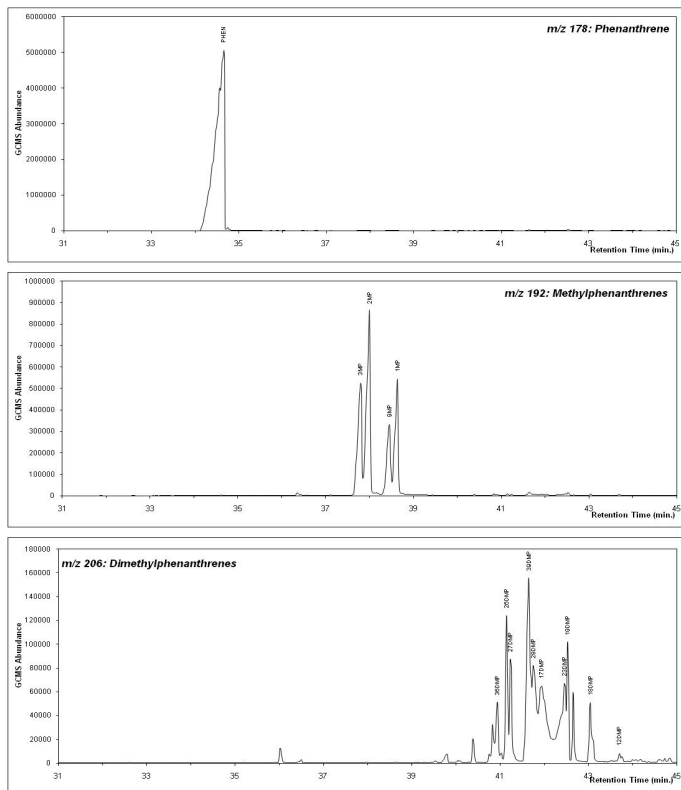


Figure 5a: m/z 178, m/z 192 and m/z 206 mass chromatograms showing the distributions of phenanthrene and its alkyl derivatives of coal sample (OG/1267/03) from the Anambra Basin.

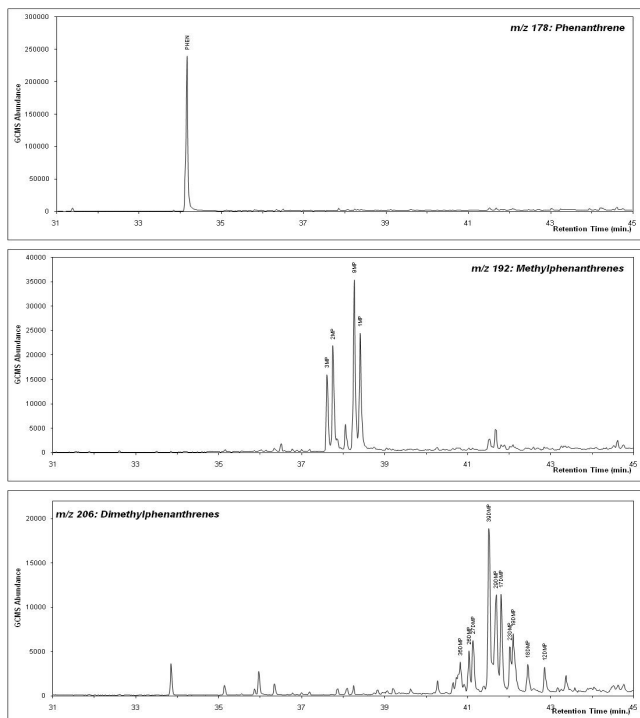


Figure 5b: m/z 178, m/z 192 and m/z 206 mass chromatograms showing the distributions of phenanthrene and its alkyl derivatives of shale sample (ENG/1001/02) from the Anambra Basin

Table 1: Peak identification in the m/z 156, 170, 184, 198, 154, 168, 178 and 192 mass chromatograms

Ion	Peak Label	Compound Name
128	NAPH	Naphthalene
142	2MN	2-Methylnaphthalene
142	1MN	1-Methylnaphthalene
156	2EN	2-Ethynaphthalene
156	1EN	1-Ethynaphthalene
156	26DMN	2,6-Dimethylnaphthalene
156	27DMN	2,7-Dimethylnaphthalene
156	13+17DMN	1,3 & 1,7-Dimethylnaphthalenes
156	16DMN	1,6-Dimethylnaphthalene
156	23DMN	2,3-Dimethylnaphthalene
156	14DMN	1,4-Dimethylnaphthalene
156	15DMN	1,5-Dimethylnaphthalene
156	12DMN	1,2-Dimethylnaphthalene
170	BB_EMN	Ethyl-methyl-Naphthalene
170	AB_EMN	Ethyl-methyl-Naphthalene
170	137TMN	1,3,7-Trimethylnaphthalene
170	136TMN	1,3,6-Trimethylnaphthalene
170	146+135T	(1,4,6+1,3,5)-Trimethylnaphthalenes
170	236TMN	2,3,6-Trimethylnaphthalene
170	127TMN	1,2,7-Trimethylnaphthalene
170	167+126T	(1,6,7+1,2,6)-Trimethylnaphthalenes
170	124TMN	1,2,4-Trimethylnaphthalene
170	125TMN	1,2,5-Trimethylnaphthalene
184	1357	1,3,5,7-Tetramethylnaphthalene
184	1367	1,3,6,7-Tetramethylnaphthalene
184	1247	(1,2,4,7+1,2,4,6+1,4,6,7)-TetraMNs
184	1257	1,2,5,7-Tetramethylnaphthalene
184	2367	2,3,6,7-Tetramethylnaphthalene
184	1267	1,2,6,7-Tetramethylnaphthalene
184	1237	1,2,3,7-Tetramethylnaphthalene
184	1236	1,2,3,6-Tetramethylnaphthalene
184	1256	1,2,5,6-Tetramethylnaphthalene
184	DBT	Dibenzothiophene
198	4MDBT	4 Methyl Dibenzothiophene
198	2+3MDBT	2 & 3 Methyl Dibenzothiophenes
198	1MDBT	1 Methyl Dibenzothiophene
154	BP	Biphenyl
168	2MBP	2-Methylbiphenyl
168	DPM	Diphenylmethane
168	3MBP	3-Methylbiphenyl
168	4MBP	4-Methylbiphenyl
168	DBF	Dibenzofuran
178	PHEN	Phenanthrene
192	3MP	3-Methylphenanthrene
192	2MP	2-Methylphenanthrene
192	9MP	9-Methylphenanthrene
192	1MP	1-Methylphenanthrene

Table 2: Peak identification in the m/z 206, m/z 191, m/z 231 and m/z 253 mass chromatograms

Ion	Peak Label	Compound Name
206	36DMP	3,6-Dimethylphenanthrene
206	26DMP	2,6-Dimethylphenanthrene
206	27DMP	2,7-Dimethylphenanthrene
206	39DMP	(3,9+3,10+2,10+1,3)-Dimethylphenanthrenes
206	29DMP	(2,9+1,6)-Dimethylphenanthrenes
206	17DMP	1,7-Dimethylphenanthrene
206	23DMP	2,3-Dimethylphenanthrene
206	19DMP	1,9-Dimethylphenanthrene
206	18DMP	1,8-Dimethylphenanthrene
206	12DMP	1,2-Dimethylphenanthrene
191	BH32	C ₃₂ Benzohopane
191	BH33	C ₃₃ Benzohopane
191	BH34	C ₃₄ Benzohopane
191	BH35	C ₃₅ Benzohopane
231	1TA20	C ₂₀ Triaromatic Steroid
231	2TA21	C ₂₁ Triaromatic
231	3TA26	C ₂₆ 20S Triaromatic
231	4TA26+27	C ₂₇ 20S & C ₂₆ 20R Triaromatic
231	5TA28	C ₂₈ 20S Triaromatic
231	6TA27	C ₂₇ 20R Triaromatic
231	7TA28	C ₂₈ 20R Triaromatic
231	8TA29	C ₂₉ 20R Triaromatic (24 n-propyl)
253	1MA21	C ₂₁ Ring-C Monoaromatic Steroid
253	2MA22	C ₂₂ Monoaromatic steroid
253	3MA27	C ₂₇ Reg 5b(H),10b(CH ₃) 20S
253	4MA27	C ₂₇ Dia 10b(H),5b(CH ₃) 20S
253	5MA27	C ₂₇ Dia10bH,5bCH ₃ 20R+Reg5bH,10bCH ₃ 20R
253	6MA27	C ₂₇ Reg 5a(H),10b(CH ₃) 20S
253	7MA28	C ₂₈ Dia 10aH,5aCH ₃ 20s+Reg5bH,10bCH ₃ 20S
253	8MA27	C ₂₇ Reg 5a(H),10b(CH ₃) 20R
253	9MA28	C ₂₈ Reg 5a(H),10b(CH ₃) 20S
253	10MA28	C ₂₈ Dia 10aH,5aCH ₃ 20R+Reg5bH,10bCH ₃ 20R
253	11MA29	C ₂₉ Dia 10bH,5bCH ₃ 20S+Reg5bH,10bCH ₃ 20S
253	12MA29	C ₂₉ Reg 5a(H),10b(CH ₃) 20S
253	13MA28	C ₂₈ Reg 5a(H),10b(CH ₃) 20R
253	14MA29	C ₂₉ Dia 10bH,5bCH ₃ 20R+Reg5bH,10bCH ₃ 20R
253	15MA29	C ₂₉ Reg 5a(H),10b(CH ₃) 20R

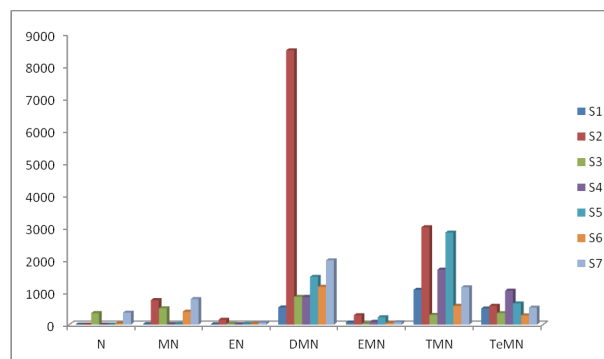


Figure 6: Relative distribution (concentration) of naphthalene homologues in rock extracts from the Anambra Basin. See Table 3 caption for abbreviations.

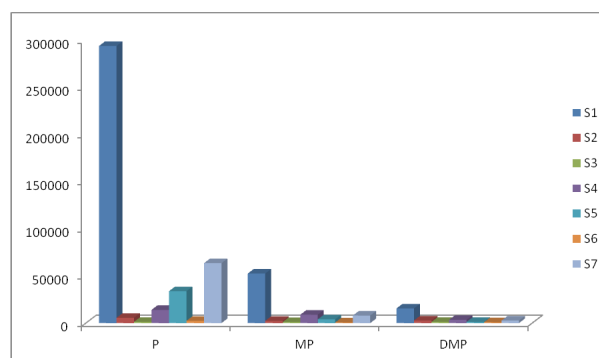


Figure 7: Relative distribution (concentration) of phenanthrene homologues in rock extracts from the Anambra Basin. See Table 3 caption for abbreviations.

Dimethylphenanthrene was the least abundant of the phenanthrene homologues (Fig. 7). The distribution of total naphthalenes and phenanthrenes in the coal and shale extracts from the Mamu Formation indicates that the total sum of the phenanthrenes and their isomers was greater than that of the naphthalenes in all the samples analyzed (Fig.8). The distribution of these aromatic hydrocarbons and their alkyl derivatives was strongly controlled by a selective expulsion mechanism and thermal maturation of organic matter (Akaegbobi *et al.*, 2000). In the present study, the relative abundance of the phenanthrenes and their alkyl derivatives was greater than that of the naphthalenes. Radke *et al.* (1982a) suggested that a substantial source of alkyl phenanthrene could be the direct methylation of phenanthrene during catagenesis. The results obtained in this study corroborate with those reported by Akinlua *et al.* (2007). These isomers were applied in the calculation of temperature-sensitive maturity parameters such as methylphenanthrene indices (MPI-1 and MPI-2), methylidibenzothiophene ratio (MDR), dimethylnaphthalene ratios (DNR-1 and DNR-2) and trimethylnaphthalene ratio (TNR-1).

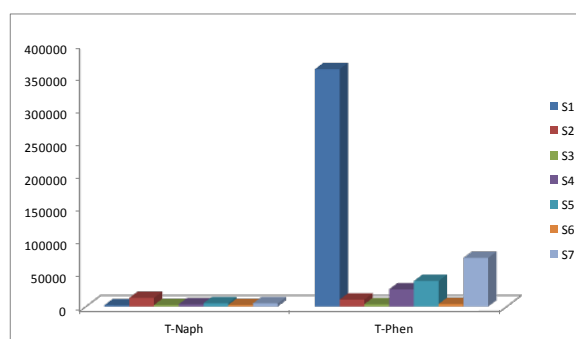


Figure 8: Relative concentrations of the sum total of naphthalenes (T-naph) and phenanthrenes (T-phen) in rock extracts from the Anambra Basin. See Table 3 caption for abbreviations.

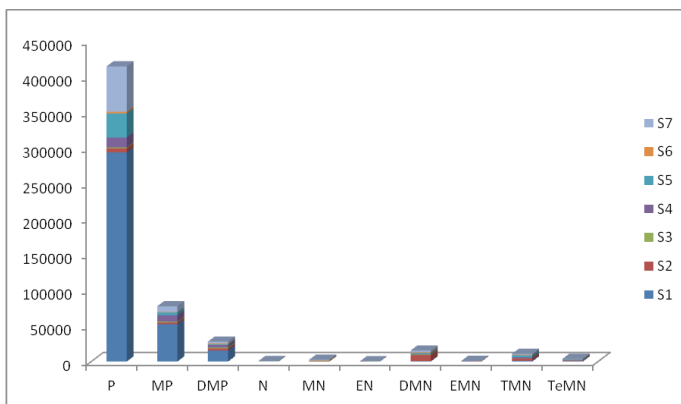


Figure 9: Relative distribution (concentration) of aromatic hydrocarbons in rock extracts from the Anambra Basin. See Table 3 caption for abbreviations.

DISCUSSION

Thermal maturity

The concentration of aromatic compounds, such as naphthalenes, phenanthrenes, dibenzothiophenes and their structural isomers are at present attracting increasing attention as maturity indicators for coals and shale source rocks. These indicators rely either on an increase in maturity with the degree of alkylation of a given parent compound, or a shift in the isomer distribution of alkyl-aromatic homologues increasing towards isomers with greater thermal stability (Radke, 1988). The aromatic isomer ratios and indexes (DNR-1, DNR-2, TNR-1, TDE-1, TDE-2, MPI-1, MPI-2, and MDR) used in this study are reported in Table 5.

The total concentration of naphthalene and its isomers is greater than that of the phenanthrenes. The higher abundances of naphthalenes relative to phenanthrenes can be attributed to selective expulsion mechanisms and direct methylation during diagenesis/catagenesis (Akaegbobi *et al.*, 2000; Radke *et al.*, 1982a). The increase in the concentrations of naphthalenes along with an increase in the number of alkyl substitutes indicates that the oils are mature. This increase in the number of methyl substituents of naphthalene in mature oils occurs because of the thermal rearrangement of methyl-naphthalene with

Table 3: Abundance of aromatic hydrocarbons in rock extracts (concentrations are in ppm)

Sample Number	Lithology	N	MN	EN	DMN	EMN	TMN	TeMN	P	MP	DMP	T-Naph	T-Phen
OG/1267/03	Shale	ND	16.70	9.40	532.90	65.60	1077.30	499.80	293865.20	52542.10	15581.00	2201.70	361988.30
ENG/1001/02	Shale	ND	759.50	153.10	8496.00	292.60	3016.60	583.70	5554.50	2403.90	2799.50	13301.50	10757.90
ENG/1001/12	Coal	358.50	505.00	20.90	859.60	27.40	301.00	357.30	1280.10	1157.40	1275.00	2429.70	3712.50
ENG/1001/16	Coal	ND	14.80	11.10	858.20	86.80	1703.10	1053.80	14007.80	8875.70	3444.00	3727.80	26327.50
ENG/1002/06	Shale	ND	21.30	22.5.00	1479.40	230.90	2852.50	657.60	33841.70	3946.90	1240.40	5264.20	39029.00
ENG/1008/13	Coal	39.50	402.20	25.00	1175.80	49.30	581.90	287.20	2397.80	686.10	889.70	2560.90	3973.60
EZ/1219/08	Coal	372.50	793.00	62.20	1991.50	76.30	1157.80	526.30	63560.40	7983.40	2703.20	4979.60	74247.00

Abbreviations: N – naphthalene, MN – methyl-naphthalene, EN – ethyl-naphthalene, DMN – dimethyl-naphthalene, EMN – ethylmethyl-naphthalene, TMN – trimethyl-naphthalene, TeMN – tetramethyl-naphthalene, P – Phenanthrene, MP – methylphenanthrene, DMP – dimethylphenanthrene, T-Naph – total naphthalene, T-Phen – total phenanthrene, ND – not detected

Table 4: Abundance of isomers of trimethyl-naphthalenes and methylphenanthrenes in rock extracts (concentrations are in ppm)

Sample Number	Depth (m)	Lithology	2-MP	3-MP	1-MP	9-MP	125TMN	127TMN
OG/1267/03	75-76	Shale	19203.20	13913.70	10818.90	8606.30	173.50	44.20
ENG/1001/02	157	Shale	519.90	369.80	595.40	918.80	389.90	159.40
ENG/1001/12	186-187	Coal	144.90	184.80	179.00	648.70	34.90	16.50
ENG/1001/16	205	Coal	1797.30	1065.80	2640.50	3372.10	418.20	144.80
ENG/1002/06	167-178	Shale	1446.70	1079.20	701.20	719.80	325.90	176.50
ENG/1008/13	220-221	Coal	144.50	120.40	108.90	312.30	62.50	30.60
EZ/1219/08	80-82	Coal	2567.10	1784.30	2113.60	1518.40	166.80	50.20

Abbreviations: 1-MP – 1-methylphenanthrene, 2-MP – 2-methylphenanthrene, 3-MP – 3-methylphenanthrene, 9-MP – 9-methylphenanthrene, 125TMN – 1, 2, 5-trimethyl-naphthalene, 127TMN – 1, 2, 7-trimethyl-naphthalene

increasing thermal stress (Akaegbobi *et al.*, 2000). Furthermore, the coal and shale extracts contain enhanced concentrations of 1, 2, 5-trimethylnaphthalene relative to 1, 2, 7-trimethylnaphthalene (Table 4). This is typical of mature oils (Strachan *et al.*, 1988; Akinlua *et al.*, 2007). However, in the present study, the relative abundance of the total of phenanthrene and its isomers was greater than that of naphthalenes (Table 3, Fig.9). The abundance of phenanthrenes relative to naphthalenes suggests that the rock extracts are mature (Akinlua *et al.*, 2007).

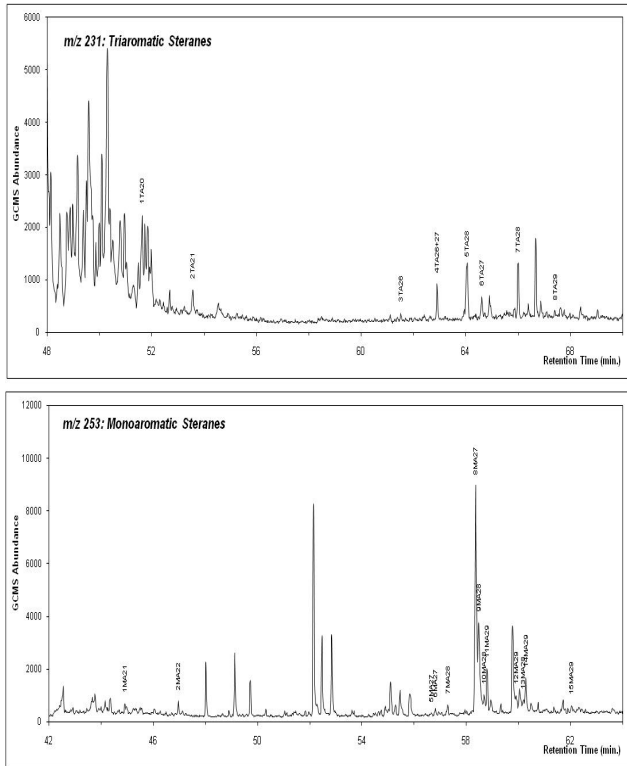


Figure 10a: m/z 231 and 253 mass chromatograms showing the distributions of triaromatic steranes and monoaromatic steranes in representative shale sample OG/1267/03 from the Anambra Basin.

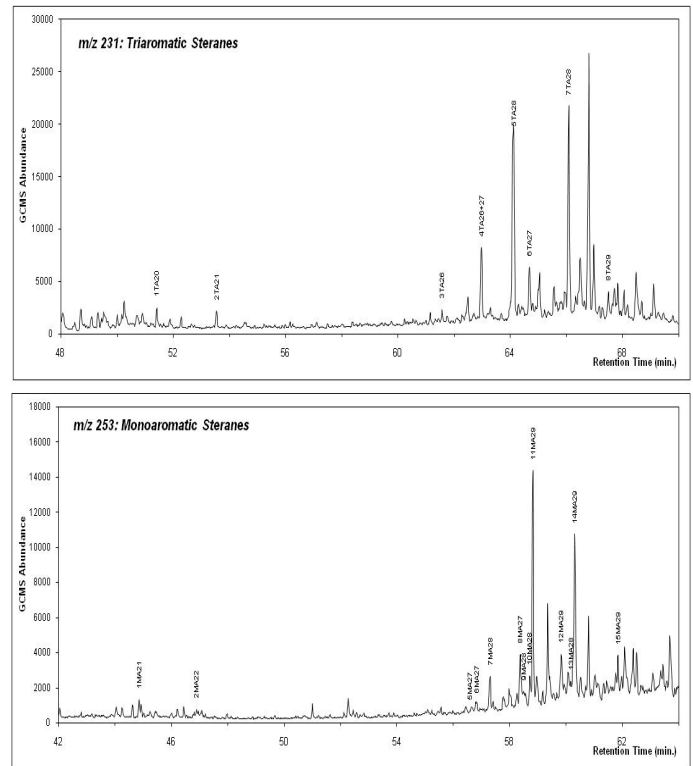


Figure 10b: m/z 231 and 253 mass chromatograms showing the distributions of triaromatic steranes and monoaromatic steranes in representative coal sample ENG/1001/12 from the Anambra Basin.

Table 5: Thermal maturity parameters computed from the aromatic biomarkers and aromatic sulphur compounds in the coal and shale extracts

	Interpretative Ratios	OG/1267/03	ENG/1001/02	ENG/1001/12	ENG/1001/16	ENG/1002/06	ENG/1008/13	EZ/1219/08
Naphthalenes	DNR-1=(2,6+2,7)/(1,5)DMN	2.08	3.93	4.13	2.04	2.71	6.03	4.93
	DNR-2=(2,6+2,7)/(1,4+2,3)DMN	1.21	2.52	3.37	1.35	1.72	2.93	1.91
	TNR1=(2,3,6)/(1,4,6+1,3,5)TMN	1.12	0.86	0.73	0.75	0.95	0.87	1.22
	TDE-1=1,2,5-TMN/1,2,4-TMN	10.43	10.81	4.41	15.21	7.22	7.22	11.51
	TDE-2=1,2,7-TMN/1,2,6-TMN	0.20	0.30	0.33	0.53	0.33	0.31	0.20
	1,2,7-TMN/1,3,7-TMN	0.45	0.46	0.44	1.07	0.54	0.39	0.41
Phenanthrenes	MPI-2=3(2MP)/(PHEN+1MP+9MP)	0.18	0.22	0.21	0.27	0.12	0.15	0.11
	MPI-1=1.5(2MP+3MP)/(PHEN+1MP+9MP)	0.16	0.19	0.23	0.21	0.11	0.14	0.10
	Rc(a)=0.6(MPI-1)+0.37 (for Ro<1.3)	0.47	0.48	0.51	0.50	0.43	0.45	0.43
	Rc(b)=0.6(MPI-1)+2.3 (for Ro>1.3)	2.40	2.41	2.44	2.43	2.36	2.38	2.36
	MDR=4MDBT/1MDBT	6.56	1.69	0.40	0.72	3.13	0.88	0.62
	Rm=0.40+0.30(MDR)-0.094(MDR) ² +0.011(MDR) ³	1.43	0.69	0.51	0.57	0.76	0.60	0.55
	MDR23=23MDBT/DBT	0.42	0.31	0.65	0.32	0.21	0.75	0.06
	MDR1=1MDBT/DBT	0.07	0.23	0.66	0.75	0.13	0.67	0.14
	DBT/Phenanthrene	0.06	0.02	0.04	0.01	0.01	0.02	0.01
	Triaromatic Steroids	TAS C ₂₀ +C ₂₁ /all TAS (20R and 20S)	0.52	0.13	0.06	0.11	0.21	0.09
TAS C ₂₀ /C ₂₀ +C ₂₇		0.70	0.22	0.12	0.19	0.31	0.20	0.20
TAS C ₂₀ /C ₂₀ +C ₂₈ (20R)		0.72	0.26	0.08	0.20	0.42	0.17	0.35
TAS C ₂₁ /C ₂₁ +C ₂₈		0.15	0.08	0.04	0.07	0.13	0.05	0.10
TAS C ₂₈ /C ₂₆ (20S)		3.62	3.89	12.71	4.04	2.09	17.11	5.6
TAS C ₂₈ /C ₂₇ (20R)		2.12	2.16	3.96	2.92	2.27	2.87	1.33
% C ₂₆ TAS		5.30	5.70	2.30	6.70	8.20	2.30	4.70
% C ₂₇ TAS		36.70	35.90	23.70	32.20	40.5	23.9	35.80
% C ₂₈ TAS		52.80	50.70	68.90	57.70	42.70	70.10	43.70
% C ₂₉ TAS	5.20	7.60	5.10	3.40	8.60	3.60	15.70	
Monoaromatic Steroids	MAS Dia/Reg C ₂₇	0.00	0.69	0.00	1.21	0.91	1.17	2.19
	MAS C ₂₁ +C ₂₂ /all MAS	0.05	0.04	0.04	0.04	0.05	0.04	0.06
	% C ₂₇ MA	50.10	43.00	11.00	26.50	46.30	14.20	11.60
	% C ₂₈ MA	29.30	21.70	14.50	21.80	21.00	20.90	22.60
	% C ₂₉ MA	20.60	35.20	74.50	51.70	32.70	65.00	65.70
	TAS/(TAS+MAS)	0.22	0.38	0.59	0.46	0.28	0.57	0.23
	TAS C ₂₈ /(TAS C ₂₈ +MA C ₂₉)	0.58	0.79	0.87	0.87	0.69	0.88	0.39

A number of aromatic maturity parameters based on the distribution of naphthalene, phenanthrene and alkyl isomers were calculated for the study samples after Radke *et al.* (1982a), Radke *et al.* (1986) and Alexander *et al.* (1985, 1986). Radke (1988) observed that aromatic hydrocarbons do change in a regular fashion with increasing maturity and thus developed maturity parameters based on the distributions of alkylnaphthalene and alkylphenanthrene. The maturity parameters computed from the aromatic biomarker distributions in the coal and shale extracts are listed in Table 5. The maturity parameters computed from naphthalene and its isomers, the dimethylnaphthalene ratios (DNR-1 and DNR-2) and trimethylnaphthalene ratio (TNR-1) ranged from 2.04 to 6.03, 1.21 to 3.37 and 0.73 to 1.22, respectively (Table 5).

The methylphenanthrene index (MPI-1) is one of the most widely used maturity parameters based on aromatic hydrocarbons (Radke *et al.*, 1982a, 1982b; Radke, 1988). The parameter relies on a shift with maturity in the methylphenanthrene distribution towards a preponderance of β -type isomers. The methylphenanthrene indices (MPI-1 and MPI-2) were computed based on the relative concentrations of the 1-MP, 2-MP, 3-MP, 9-MP and phenanthrene (P). This was based on the assumption that the 2-MP and 3-MP are derived from the rearrangement of the 1-MP and 9-MP, and from phenanthrene (P) through methylation reactions. The relative abundances of the alkyl homologs of the aromatic hydrocarbons (phenanthrenes) were used to calculate the vitrinite reflectance (% R_v) after the method of Radke *et al.*, (1982a, b) and Radke (1988). The MPI-1 is often used for estimating the equivalent vitrinite reflectance values (% R_v) for crude oils and source rocks. The MPI-1 and % R_v values calculated for the coal and shale extracts range from 0.10 to 0.23 and 0.43 to 0.51, respectively (Table 5). MPI-1 calculated reflectance (% R_c) was carried out because of insufficient and good reflecting vitrinite in the samples.

Maturity parameters based on the isomers of the methylidibenzothiophene (MDBT) were calculated (Radke *et al.*, 1986). This ratio (MDR) generally increases with increasing maturity and correlates well with vitrinite reflectance and the Rock-Eval T_{max} of source rock (Radke, 1988). The ratio is also useful in calculating mean vitrinite reflectance (% R_m). The methylidibenzothiophene ratio (MDR) and mean vitrinite reflectance (% R_m) for the coal and shale extracts ranged from 0.40 to 6.56 and 0.51 to 1.43, respectively (Table 5). The high MDR exhibited by some of the samples may be a result of the effect of heating rates or thermal stress (Akaegbobi *et al.*, 2000). The % R_m values show that the coal and shale extracts range from immature to mature (Table 5).

Monoaromatic and triaromatic steroids were detected in all samples in the m/z 253 and m/z 231 fragmentograms (Figs. 10a-b). Both 20R and 20S homologues of C_{26} - C_{28} , C_{20} and C_{21} triaromatic compounds are present (Figs. 10a-b).

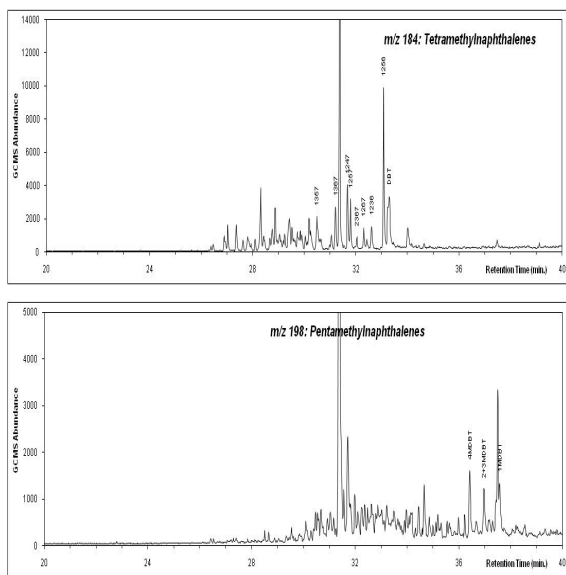


Figure 12a: m/z 184 and 198 mass chromatograms showing the distributions of aromatic sulfur compounds of representative shale sample in well ENG/1001/02 from the Anambra Basin.

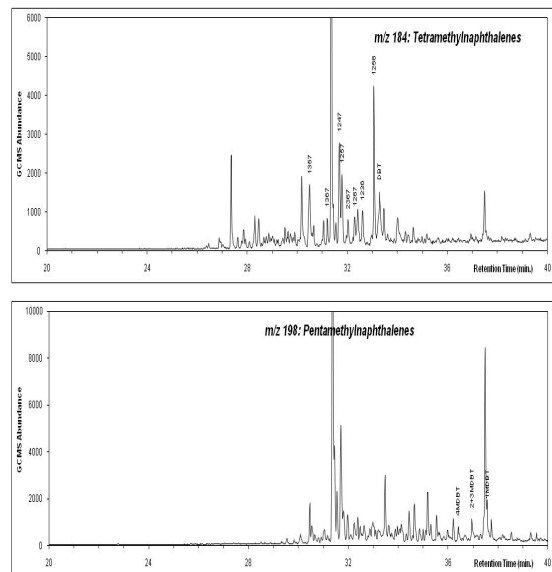


Figure 12b: Mass chromatograms showing the distributions of aromatic sulfur compounds of representative coal sample in well ENG/1001/12 from the Anambra Basin.

Peters and Moldowan (1993) and El-Gayar (2005) suggested that the extent of cracking in the side chains of triaromatic steroids can be used to provide information about petroleum maturity. The triaromatic steroid maturity parameters $C_{20}/C_{20}+C_{28}$ (20R) and $(C_{20}+C_{21})/(C_{20}+C_{21}+C_{26}+C_{28})$ (20R and 20S) were used to evaluate the thermal maturity of the coal and shale extracts in this study (Peters and Moldowan, 1993; Peters *et al.*, 2005). The maturity parameters computed from the peak areas of the m/z 231 ranged from 0.08 to 0.72 and 0.09 to 0.52, respectively (Table 5). These values indicate an immature to marginally mature status of the source rock.

The monoaromatic steroid ratios (MAS Dia/Reg C_{27} and MAS $C_{21}+C_{22}$ /all MAS) were measured from the m/z 253 fragmentograms (Table 5) and used to evaluate the source-rock depositional environment and thermal maturity (Peters and Moldowan, 1993). Both of these ratios increase with higher thermal maturity (Mackenzi *et al.*, 1981; Moldowan and Fago, 1986). The MAS Dia/Reg C_{27} sterane ratio ranges from 0.69 to 2.19 (Table 5). The coal and shale extracts in the Mamu Formation contain significant amounts of diasteranes, which appear to form through the interaction of steranes with clay mineral surfaces in source rocks (Rubinstein *et al.*, 1975; Sieskind *et al.*, 1979). Thus, the presence of significant amounts of diasteranes relative to regular steranes in oils has been used as evidence of petroleum generation from argillaceous source rocks, whereas low concentrations are considered an indication of a source rock lacking in clay minerals (Hughes, 1984; Mello *et al.*, 1988a, 1988b; Hill *et al.*, 2007). The calculated monoaromatic maturity ratio (MAS $C_{21}+C_{22}$ /all MAS) ranges from 0.04 to 0.05 (Table 5).

Thermal maturity was also evaluated on the basis of monoaromatic and triaromatic steroids because they are more resistant to the effects of biodegradation than alkane-type biological markers (Volkman *et al.*, 1983). According to Tissot and Welte (1984), aromatization of C-ring steroid hydrocarbons occurs in mature oils. With an increase in thermal maturation, there is a conversion of C-ring monoaromatic steroid hydrocarbons to ABC-ring triaromatic steroid hydrocarbons (Akinlua and Ajayi, 2009). The TAS/(TAS+MAS) and TAS 28/(TAS 28+MAS 29) ratios ranged from 0.22 to 0.59 and 0.39 to 0.88, respectively (Table 5), indicating an immature to marginally mature status of the rock extracts.

Source of organic matter

The trimethylnaphthalene is dominated by 1, 2, 5- TMN in all the samples analyzed (Figs. 4a-b and Table 4). The high abundance of the naphthalenes, especially the dimethyl- and trimethyl-isomers, indicates organic matter derived

mainly from higher plants (Strachan *et al.*, 1988). High concentrations of 1, 2, 5- and 1, 2, 7- trimethylnaphthalene (TMN) in oils have been attributed to aromatization and cleavage of the ring-C of β -amyrin in angiosperms (Strachan *et al.*, 1988). 1, 2, 5- and 1, 2, 7- trimethylnaphthalenes can form as diagenetic products of oleanane-type triterpenoids (Chaffee and Johns, 1983; Chaffee *et al.*, 1984; Sonibare *et al.*, 2008). The presence of 1, 2, 5-TMN in the studied samples could be linked to aromatization of oleanane, as indicated by the absence of appreciable amounts of oleanane in the m/z 191 fragmentograms. This compound can also be formed from gymnosperm resins (van Aarssen *et al.*, 1999) or from hopanoid precursors (Villar *et al.*, 1988). Among the tetramethylnaphthalene family, 1, 2, 5, 6- tetramethylnaphthalene is the most abundant (Figs. 4a-b).

Strachan *et al.* (1986) used two related ratios (TDE-1 and TDE-2) of trimethylnaphthalenes to differentiate coal swamps from marine, lacustrine, and deltaic environments. 1, 2, 7- trimethylnaphthalene (TMN) has been used as a marker of angiosperm input. 1, 2, 5-trimethylnaphthalene and 1, 2, 7- trimethylnaphthalene can form as diagenetic products of oleanane-type triterpenoids (Chaffee and Johns, 1983; Chaffee *et al.*, 1984). Strachan *et al.* (1988) compared the relative abundance of trimethylnaphthalene isomers in Southeast Asian samples ranging in age from Permian to Tertiary. They found that the relative concentrations of the 1, 2, 7-trimethylnaphthalenes were appreciably higher in most oils derived from post-Cretaceous source rocks dominated by the input of higher-plants, and in extracts from Cretaceous and younger samples, than in samples of older age or with little or no terrigenous plant input. Oils of this type yielded ratios of 1, 2, 7-*I*, 3, 7-trimethylnaphthalenes from 0.46 to 1.36, while oils from older source rocks containing higher-plant material yielded ratios from 0.34 to 0.16, and oils from marine source rocks yielded ratios from 0.15 to 0.32. In this study, the rock extracts yielded ratios of 1, 2, 7-*I*, 3, 7-trimethylnaphthalenes ranging from 0.40 to 1.07 (Table 5). The computed TDE-1 and TDE-2 ratios for the study samples range from 4.41 - 15.21 and 0.20 - 0.53, respectively (Table 5). The presence of 1, 2, 5- and 1, 2, 7-TMN in the rock extracts (Figs. 4a-b; Table 4) indicate both angiosperm and gymnosperm material contribution to the organic matter that formed the coals and shales (Killops and Killops, 2005; Adedosu *et al.*, 2012). Furthermore, the occurrence of appreciable amounts of 1, 6- and 2, 6-DMNs in all the samples indicate terrestrial organic matter input (Achari *et al.*, 1973). Additionally, the occurrence of 1, 7-DMP in the analyzed samples (Figs. 5a-b) is attributed to terrestrial organic matter (Simoneit *et al.*, 1986), while plots of C_{27} , C_{28} and C_{29} monoaromatic steranes (Fig. 11) indicate that the kerogens were derived from mixed terrestrial and marine organic matter.

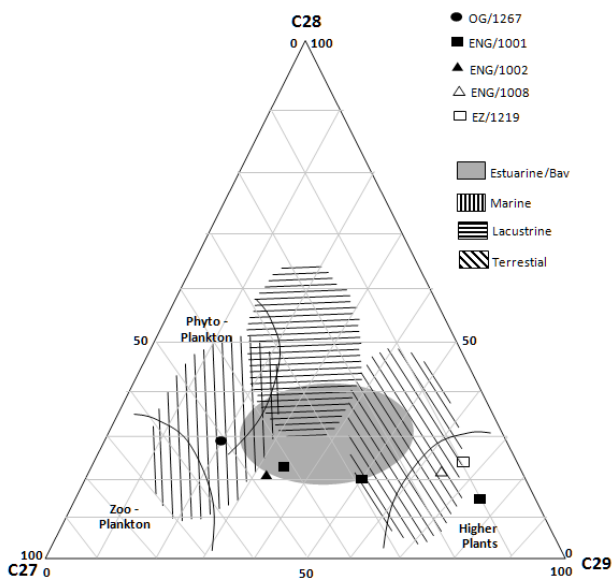


Figure 11: Ternary diagram showing the relative contributions of C27, C28 and C29 monoaromatic steranes for rock extracts from the Anambra Basin.

The distribution of the aromatic sulfur compounds including dibenzothiophenes (DBTs) and their methyl homologues in the coal and shale extracts are reported in Figures 12a-b. The dibenzothiophene/phenanthrene (DBT/PHEN) ratio together with the Pr/Ph ratio can be used to infer source rock depositional environments and lithologies (Hughes *et al.*, 1995). High DBT/PHEN ratios are found in oils from marine carbonates, and low ratios are found in oils from marine shales and most lacustrine rocks (Petersen *et al.*, 2007). The coal and shale extracts (Table 5) have low DBT/PHEN ratios (0.01 – 0.06), indicating a strong input of terrigenous Type III organic matter. However, DBT/PHEN (Table 5) and Pr/Ph ratios only reflect the Eh and pH irrespective of depositional environment, and a cross-plot of the two ratios by itself cannot be used to distinguish lacustrine from marine oils (Petersen *et al.*, 2007). The presence of organic sulfur compounds and sulfur-containing aromatics in rock extracts and crude oils indicates an anoxic depositional environment (Sinninghe Damste *et al.*, 1988, 1989a, 1989b; Hughes *et al.*, 1995). 1-methyldibenzothiophene (1-MDBT), 2+3-methyldibenzothiophene (2+3-MDBT) and 4-methyldibenzothiophene (4-MDBT) were detected in all the samples analyzed (Figs. 12a-b; Table 6). The high relative abundance of dibenzothiophenes (DBTs) in all of the samples is indicative of probable oxic/anoxic conditions prevailing during deposition (Table 6). The distribution of DBTs has been proposed as an indicator of crude oils derived from carbonate versus siliciclastic sources (Hughes, 1984; Hegazi and El-Gayar, 2009). The presence of a definite V pattern (4-methyl > 2+3-methyl < 1-methyl) in the methyldibenzothiophenes is generally associated with oils from predominantly carbonate source rocks, while a stair-step pattern (4-methyl > 2+3-methyl > 1-methyl) is associated with predominantly siliciclastic source rocks, or oils of advanced maturity (late- to post-oil window) from carbonate sources (Hegazi and El-Gayar, 2009). Furthermore, oils from carbonate sources are characterized by an abundance of benzothiophenes (BTs) and a fairly equal distribution of substituted DBTs, while siliciclastic oils exhibit low concentrations of BTs and decreasing amounts of dimethyldibenzothiophenes and trimethyldibenzothiophenes relative to methyldibenzothiophenes (Hughes, 1984; Hegazi and El-Gayar, 2009). The results obtained in this study indicate that the 4-methyldibenzothiophenes (24.0%) are more abundant than the 2+3-methyldibenzothiophenes (20.4%) and 1-methyldibenzothiophenes (4.4%) (Table 6), indicating a siliciclastic source rock input for the organic matter (Hegazi and El-Gayar, 2009).

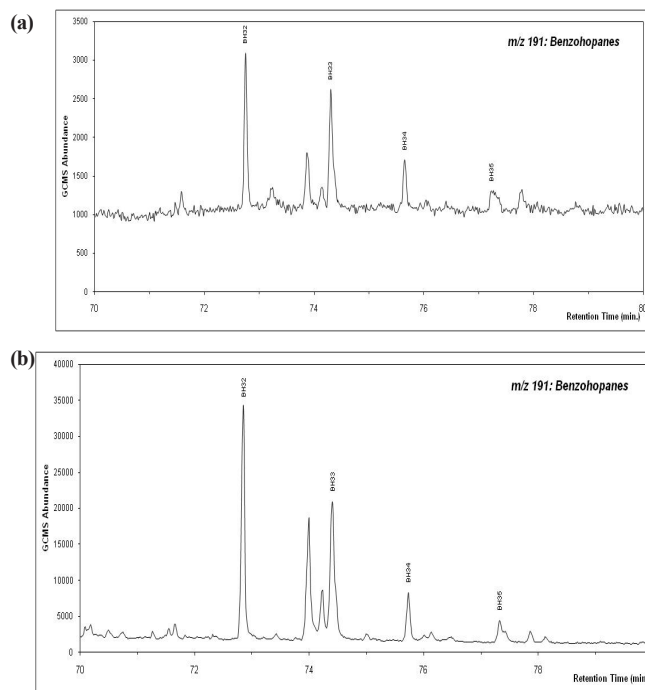


Figure 13a-b: m/z 191 mass chromatogram showing the distributions of benzohopanes in representative shale (a) OG/1267/03 and coal (b) ENG/1001/12 from the Anambra Basin.

Table 6: Abundance of dibenzothiophenes and their alkyl homologues in rock extracts (concentrations are in ppm)

Sample Number	Lithology	DBT	4MDBT	2+3MDBT	1MDBT
OG/1267/03	Shale	17410.70	8454.20	7230.60	1287.90
ENG/1001/02	Shale	106.20	40.80	32.60	24.10
ENG/1001/12	Coal	48.80	13.10	32.00	32.40
ENG/1001/16	Coal	137.00	74.40	43.80	103.40
ENG/1002/06	Shale	281.80	116.50	59.00	37.20
ENG/1008/13	Coal	49.00	28.80	37.00	32.80
EZ/1219/08	Coal	726.40	63.50	41.60	102.90

Abbreviations: DBT – dibenzothiophene, 4MDBT – 4-methyl dibenzothiophene, 2+3MDBT – 2, 3- methyl dibenzothiophene, 1 - methyl dibenzothiophene

The mass chromatograms (m/z 184 and m/z 198) of the extracts representing the DBTs in this study show a high concentration of DBTs (51.2%) and decreasing amounts of dimethyl dibenzothiophenes (24.0%) and trimethyl dibenzothiophene (20.4%) relative to methyl dibenzothiophenes (4.4%) (Figs. 12a-b and Table 6). These results are consistent with previous analyses that indicate that the coal and shale extracts in this study were generated by a siliciclastic source rock (Hegazi and El-Gayar, 2009).

Benzohopanes are formed by the cyclization of extended hopanoid side chains followed by aromatization (Hussler *et al.*, 1984a, 1984b). Benzohopanes range in carbon number from C_{32} to C_{35} . He and Lu (1990) observed that oils and bitumens from evaporitic and carbonate source rocks have the highest concentrations of benzohopanes, which occur in trace amounts in most source rocks and crude oils. Benzohopanes were identified in all the rock extracts, but concentrations are low (Figs. 13a-b). All samples have similar distributions of benzohopanes (m/z 191). The distribution of benzohopanes (Figs. 13a-b) shows that C_{32} benzohopane is the most abundant member of the bezohopane family. The relative concentrations of the various members of the aromatic hopane series seem to follow that of the regular hopanes in the saturated hydrocarbon fraction, and like the saturated hopanes, they most likely have a bacterial origin (Petersen *et al.*, 2007).

CONCLUSION

The results of this study indicated that the aromatic hydrocarbons contained in the coal and shale samples from the Campano-Maastrichtian Mamu Formation of the Anambra Basin are marginally mature. The kerogens were formed from organic matter of mixed origin (terrestrial and marine). The distributions/concentrations of naphthalenes and phenanthrenes show that trimethylnaphthalene is the most abundant member of the naphthalene family and methylphenanthrene is the most abundant phenanthrene family member. All samples have similar distributions of phenanthrenes. The relative abundance of the total of phenanthrene and its isomers was greater than that of the naphthalenes. Thus, the distributions of aromatic hydrocarbons in the rock extracts are influenced by methylation reactions at elevated maturity. The slightly higher concentrations of C_{29} monoaromatic steranes (49%), compared with C_{28} (22%) and C_{27} (29%) monoaromatic steranes, suggests a mixed input of terrestrial and marine organic matter.

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