



Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol

Origin and occurrence of crude oil in the Niger delta, Nigeria

Oluwadayo Sonibare ^{a,*}, H. Alimi ^b, Dan Jarvie ^b, O.A. Ehinola ^c^a Petroleum and Environmental Geochemistry Research Group, Chemistry Department, University of Ibadan, Nigeria^b Humble Geochemical Services, PO Box 789 Humble TX 77347, Texas, USA^c Department of Geology, University of Ibadan, Nigeria

ARTICLE INFO

Article history:

Received 28 February 2007

Accepted 19 May 2008

Keywords:

Niger delta

Gas chromatography–Mass spectrometry

kerogen

aromatic sulfur compounds

saturate biomarkers

aromatic biomarkers

ABSTRACT

Ten crude oils samples from onshore and offshore Niger delta were characterized based on their biomarkers and isotopic composition by Gas chromatography–Mass spectrometry and Isotope mass spectrometry. Abundance of pentacyclic triterpanes of hopane and oleanane skeletons and C₂₇–C₂₉ steranes in the oils indicates that they were formed from a mixed source (marine and terrestrial kerogen). The oleanane concentrations permit source grouping of the oils into three families.

Various maturity parameters computed for the oils, especially those of aromatic biomarkers and aromatic sulfur compounds (thiophenes) to some extent reveal an increasing thermal maturity with increasing reservoir depths. The carbon isotope values lacked sufficient variation to distinguish maturity differences in the oils. This observation is quite revealing in that oils whose associated gases had earlier revealed a consistent increase in maturity with increasing depths, also have similar maturity values.

The implication of this is that the oils and associated gases might have been formed at different levels of thermal maturity before being pooled together during migration into their present habitat.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The Niger delta is one of the major hydrocarbon provinces of the world, with an estimated reserve of about 23 billion barrels of oil and 183 trillion cubic feet of natural gas. Hydrocarbons within the basin occur at different productive horizons at very great depth apart. One of the questions these occurrences pose is whether the hydrocarbons are of the same origin. The migration processes that determined the pooling of the hydrocarbons at different depths are yet to be clearly understood. It has been revealed from previous studies on the molecular and isotopic composition of the natural gas from the Niger delta that the gases were stacked according to their respective degrees of thermal evolution and time of generation with the shallowest accumulation generally being the least mature (Ekweozor and Sonibare, 1998; Sonibare and Ekweozor, 2000). However, various maturity parameters computed from the aliphatic biomarker distributions in the associated oils lacked sufficient variation to differentiate the range of thermal maturities represented, unlike the corresponding indices in respect of gases (Sonibare and Ekweozor, 2001). The ratios are also lower than the values expected for highly matured oils. Up to now, it is not clear whether it is the aliphatic biomarker maturity parameters that are not sensitive enough to characterize the oil or whether the present molecular composition of

the oils resulted from the effect of migration – fractionation and migration-contamination. These two processes have been observed in some basins that are of similar geological setting as the Niger delta such as Mahakam delta in Indonesia (Jaffer et al., 1988b) and Gulf Coast in USA (Curiale and Bromley, 1996).

It has been reported that many of the aliphatic biomarker maturity parameters do reach equilibrium before the main stage of the oil window and in some cases show inversion at high maturity levels and as such are not effective maturity indicators (Farrimond et al., 1998). Aromatics hydrocarbon maturity parameters have been reported to be more sensitive to maturity differences in the mid to late parts of the oil generation window (Radke, 1988). Aromatic sulphur compounds have also been demonstrated to be very important in evaluating the maturity of crude oil and source rock (Radke et al., 1986; Radke, 1988; Chakhmakhchev and Suzuki, 1995a,b; Hegazi et al., 2003).

In the present study, we have looked at the isotopic composition and distribution of aliphatic and aromatic hydrocarbons including aromatic sulphur compounds (ASC) in the Niger delta oils. This is aimed at improving our present knowledge of the geology of the Niger delta within the context of the origin and occurrence of hydrocarbons found in the basin.

1.1. Geological setting and hydrocarbon habitat

The Niger delta basin covers an area of about 75,000 km² and consists of 9–12 km total thickness of regressive clastic sequences. The stratigraphy (Fig. 1) of the thick sedimentary sequence is divided into

* Corresponding author. Tel.: +234 802 327 8234; fax: +234 2 8103043.
E-mail address: sonibaredayo@yahoo.com (O. Sonibare).

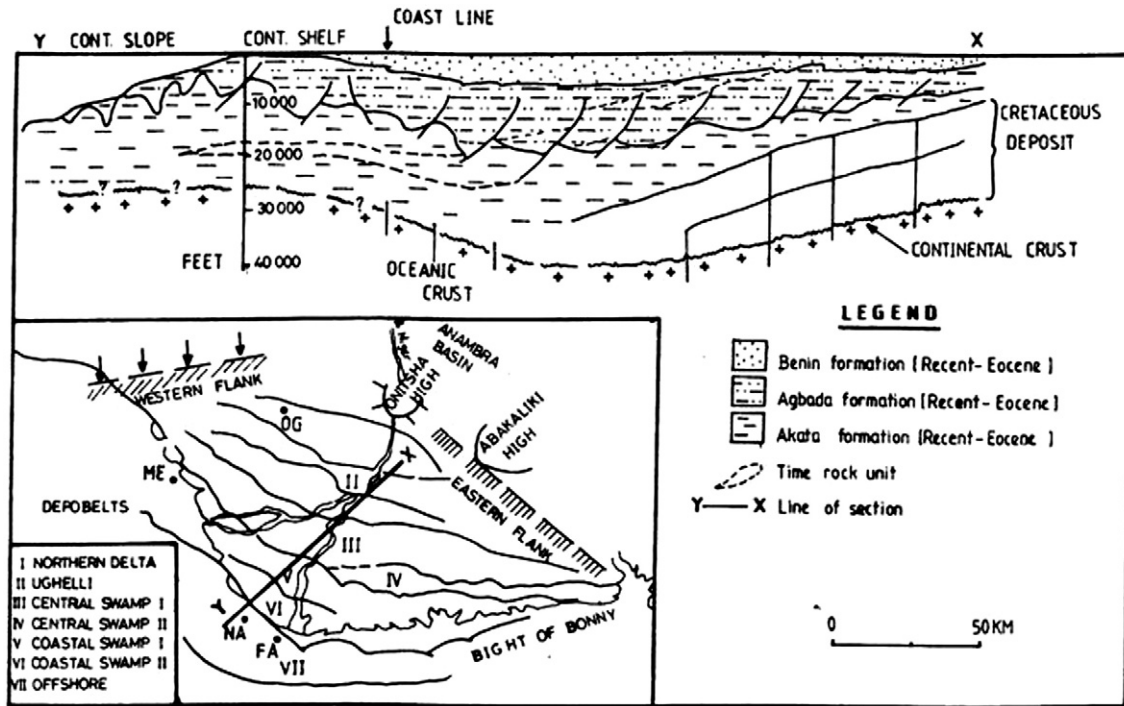


Fig. 1. Niger delta: stratigraphy, depobelts and samples locations (after Ekweozor and Daukoru, 1994).

three lithostratigraphic units, namely; the Akata, Agbada and Benin Formations (Short and Stauble, 1967). The Akata Formation, ranging in age from Paleocene to Recent, consists mainly of overpressure shale deposited under fully marine conditions. This Formation has not been drilled in most parts of the delta, except at the continental margin. Overlying the Akata Formation is the Agbada Formation (Eocene to Recent), which is composed of a paralic sequence consisting of interbedded sands and shales. It is about 4000 m thick in the central part, thinning seaward and towards the delta margin. The Benin

Formation, which is the youngest (Eocene to Recent), is composed of mainly fluvialite gravels and sands. It is up to 2000 m thick in the central onshore part and thins towards the delta margin.

The basin is partitioned into six to seven east-west bound blocks corresponding to depositional belts or depobelts (Fig. 1). These depobelts correspond to discrete periods of the deltas evolutionary history starting from the oldest in the north, northern delta to the youngest, offshore in the south (Doust and Omatsola, 1990; Ekweozor and Daukoru, 1984). Each depobelt is believed to constitute a more or less independent unit

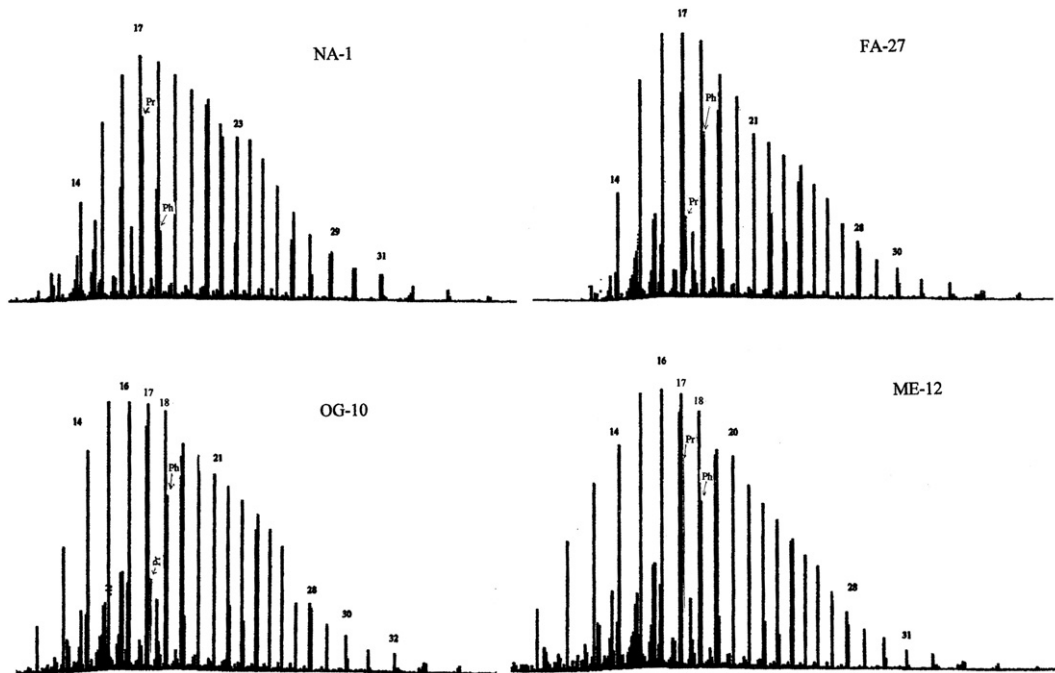


Fig. 2. Saturated hydrocarbons distributions of representative oils from the Niger delta.

Table 1
Source parameters from the saturated hydrocarbon and carbon isotope composition

Samples	Field	Depth (m)	Pr/ Py	Pr/ nC ₁₇	Ph/ nC ₁₈	DBT/ PH	$\delta^{13}\text{C}$ whole oil	$\delta^{13}\text{C}$ saturate	$\delta^{13}\text{C}$ aromatics
NA-1	A	4646–5000	2.7	0.9	0.3	0.08	-26.2	-26.3	-25.9
NA-21	A	6488–6500	3.7	0.8	0.2	0.10	-26.9	-27.1	-25.9
NA-29	A	9594–9604	2.5	0.9	0.4	0.11	-27.2	-27.7	-26.3
FA-6	B	5812–5820	3.9	5.7	1.8	0.07	-26.8	-27.2	-26.0
FA-27	B	6812–6822	3.1	0.7	0.3	0.10	-26.7	-27.0	-26.0
FA-14	B	7288–7298	3.1	1.4	0.3	0.10	-26.9	-27.3	-26.2
OG-3S	C	6085–6091	1.5	5.3	0.6	0.11	-28.3 (-50.2) ^a	-29.0	-27.4
OG-10	C	9418–9430	3.1	0.8	0.3	0.14	-28.6 (-44.4) ^a	-29.1	-27.4
ME-10	D	5379–5388	2.9	0.8	0.3	0.13	-26.6 (-47.4) ^a	-27.1	-26.1
ME12	D	9871–9877	3.1	0.8	0.3	0.12	-27.3 (-41.8) ^a	-27.8	-26.1

^a $\delta^{13}\text{C}$ of associated gas.

with respect to sedimentation, structural deformation and hydrocarbon generation and accumulation (Evamy et al., 1978).

Studies have shown that available source rocks in the basin exist mainly in the lower parts of the paralic sequence (Agbada Formation) and uppermost strata of the continuous marine shale (Akata Formation). The hydrocarbon habitat of the Niger delta is mostly within the sandstone reservoir of the Agbada Formation where oil and gas are usually trapped in rollover anticlines associated with growth faults. The thickness and age of the reservoir range from 10 to 20 m and Eocene to Pliocene respectively (Ejedawe, 1986). The reservoirs are widely spaced in depth in most of the fields.

2. Materials and methods

2.1. Samples

Ten crude oil samples were collected at stratigraphic depths ranging from 4646 to 9877 ft in four producing fields of the onshore and offshore Niger delta. The sample locations are shown in Fig. 1.

2.2. Oil fractionation and Gas chromatography–Mass spectrometry analyses

The oils were fractionated by column chromatography on silica gel. The saturated and aromatic hydrocarbons and polar compounds were eluted using n-hexane (20 ml), n-hexane/dichloromethane (90:10, v/v/ 40 ml) and DCM/methanol (50:50, 30 ml) respectively. Saturated and aromatic hydrocarbon fractions were analyzed by Gas chromatography–Mass spectrometry (GC–MS) using single ion monitoring (SIM) mode with an HP 5890 Series II gas chromatograph

fitted with a 30 m × 0.25 mm i.d fused silica capillary column coated with DB-5 coupled to a HP 5970 MSD. The oven temperature was held at 40 °C for 5 min and programmed from 40 °C to 300 °C at 4 °C/min. The mass spectrometer was operated at electron energy of 70 eV, an ion source temperature of 250 °C and separator temperature of 250 °C.

Terpanes and steranes were identified using m/z 191 and 217 fragments, respectively. Dimethylnaphthalene, trimethylnaphthalene and tetramethylnaphthalene were identified by multiple ions m/z 156, 170 and 184, respectively. Identification of phenanthrene and methylphenanthrene was based on multiple ion fragmentograms m/z 178 and 192, respectively. Dibenzothiophene and methyl dibenzothiophene were identified on m/z 184 and 198 fragmentograms, respectively.

2.3. Isotopic analysis

The determination of carbon isotopic ratios for saturate and aromatic fractions was accomplished by converting the samples into carbon dioxide (CO₂) for mass-spectrometric analysis. The system employed is a standard elemental analyzer (Carlo Erba Elemental Analyzer) with carousel auto sampler, connected to an isotope ratio mass spectrometer (Finnigan Delta S Mass Spectrometer) through an interface supplied by the manufacturer. The MS measures the isotopic value of the sample CO₂.

3. Results and discussion

The origin of the oils in terms of organic matter source and thermal maturity was determined based on the distributions of saturate and aromatic biomarkers, aromatic sulfur compounds and stable carbon isotopic composition.

3.1. Normal alkanes and isoprenoids distribution

The gas chromatograms of the saturate fractions of representative oils from Niger delta are shown in Fig. 2. The chromatograms are dominated by n-alkanes in the range of nC₁₄–nC₂₈, maximizing at nC₁₆ or nC₁₇. The pristane/phytane (Pr/Py) ratios for the oils range from 1.5 to 3.9 (Table 1). The high Pr/Ph ratios suggest oils derived from source rock with a significant terrestrial contribution, deposited in an oxic paleoenvironment (Didyk et al., 1978; Mello and Maxwell, 1990). The ratio of dibenzothiophene to phenanthrene and the ratio of pristane to phytane have been used to infer crude oil source rock depositional environment and lithology (Hughes et al., 1995). A plot of dibenzothiophene/phenanthrene ratio (DBT/PHEN) versus Pr/Ph ratio is shown in Fig. 3. The oils plotted within the marine shale/lacustrine and fluvial/deltaic zone. The oils were further classified based on kerogen source by plotting the ratio of Pr/nC₁₇ against Ph/nC₁₈ in Fig. 4 (Connan and Cassou, 1980). The majority of the oils plotted in the

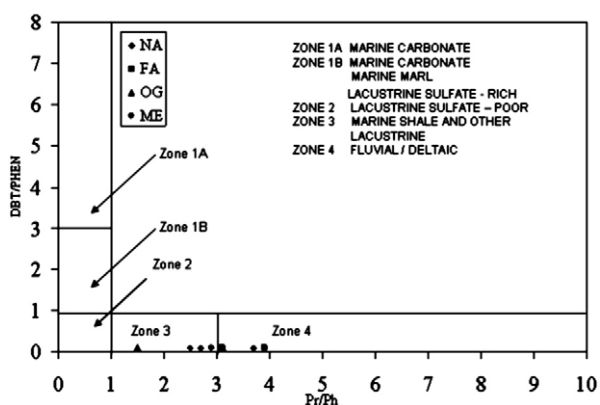


Fig. 3. A cross plot of dibenzothiophene/phenanthrene (DBT/PHEN) and pristane/phytane (Pr/Ph) ratios for oils from the Niger delta (after Hughes et al., 1995).

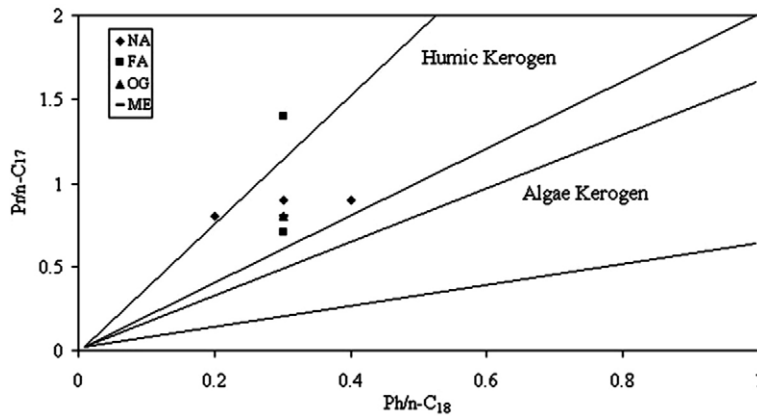


Fig. 4. Plot of Pr/n-C₁₇ versus Ph/n-C₁₈ of oils from Niger delta (after Connan and Cassou, 1980).

region of humic kerogen. This is in consistent with the terrestrial organic input already inferred from the high Pr/Ph ratios.

3.2. Stable carbon isotopic composition

Differences in isotopic composition of oils and source rock have been widely used in oil–oil correlation and oil–source rock correlation studies (Fuex, 1977; Stahl, 1977, 1978; Schoell, 1984; Sofer, 1984; Chung et al., 1992). The carbon isotopic composition of oil depends on the $\delta^{13}\text{C}$ values of the kerogen from which it is derived. The isotopic differences between the whole oils and the saturate and aromatic

fractions of the oils are generally lower than 1.44‰ (Table 1). The carbon isotope values lack sufficient variation to distinguish maturity differences in oils within the same field (Table 1). Oils whose associated gases revealed a consistent increase in maturity with increasing depth from our previous study also have similar isotope values within themselves (Ekweozor and Sonibare, 1998). For example, OG-3S (6085–6091 ft) and OG-10 (9418–9430 ft) oils have $\delta^{13}\text{C}$ values of –28.3 and –28.6 whereas the associated gases have $\delta^{13}\text{C}$ values of –50.2 and –44.4 respectively (Table 1). This observation suggests that the oils and associated gases might have been generated from different sources but subsequently mixed during migration.

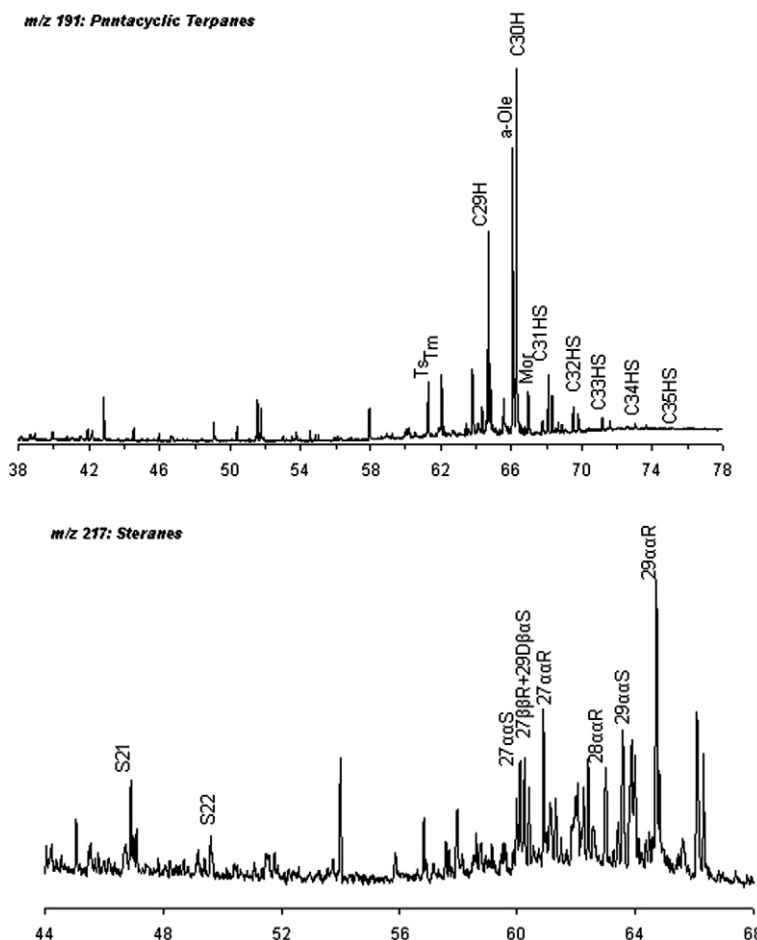


Fig. 5. Mass chromatogram of m/z 191(terpanes) and 217 (steranes) of NA-21 oil from the Niger delta.

Table 2
Peak identification on m/z 191 and 217 mass chromatogram of Niger delta oils

Peak	Compound
Ts	18 α (H)-trisnorhopane
Tm	17 α (H)-trisnorhopane
C29H	C29 Tm 17a(H)21b(H)-norhopane
C30DiaH	C3017 α (H)-diahopane
α -Ole	α -oleanane
C30H	C3017 α (H)-hopane
Mor	C30 moretane
C31HS	C31 22S 17 α (H) homohopane
C31HR	C31 22R 17 α (H) homohopane
C32HS	C32 22S 17 α (H) bishomohopane
C32HR	C32 22R 17 α (H) bishomohopane
C33HS	C33 22S 17 α (H) trishomohopane
C33HR	C33 22R 17 α (H) trishomohopane
C34HS	C34 22S 17 α (H) extended hopane
C34HR	C34 22R 17 α (H) extended hopane
C35HS	C35 22S 17 α (H) extended hopane
C35HR	C35 22R 17 α (H) extended hopane
S21	C21 sterane
S22	C22 sterane
27 $\alpha\alpha$ S	C27 $\alpha\alpha$ 20S cholestane
27 $\beta\beta$ R	C27 $\beta\beta$ 20R cholestane
27 $\alpha\alpha$ R	C27 $\alpha\alpha$ 20R cholestane
28 $\alpha\alpha$ R	C28 $\alpha\alpha$ 20R ergostane
29 $\alpha\alpha$ S	C29 $\alpha\alpha$ 20S stigmastane
29 $\alpha\alpha$ R	C29 $\alpha\alpha$ 20R stigmastane

3.3. Saturated biomarker distributions

The mass chromatograms m/z 191 (terpanes) and 217 (steranes) of a representative samples are shown in Fig. 5. The assignments of the peaks labeled in Fig. 5 are listed in Table 2. Source and thermal maturity parameters computed from the terpanes and sterane distributions are listed in Table 3. The terpanes are dominated by pentacyclic triterpanes of hopane (17 α (H), 21 β (H)-hopane and 17 α (H), 21 β (H)-norhopane) and oleanane skeleton. A very low homohopane index (0.02 to 0.04) indicates an oxic deposition environment of the oil source rock (Sinninghe Damste et al., 1995). The presence of oleanane is a good indicator of terrestrial input into the oil-prone source rocks deposited in a deltaic environment (Whitehead, 1974; Ekweozor et al., 1979; Philip and Gilbert, 1986). The oleanane concentrations permit source grouping of the oils into three families. Samples from field A and B have Oleanane Indices ranging from 0.84 to 1.06 (Table 3). Field C and D oils have Oleanane index that range from 0.37 to 0.47 and 2.27 to 2.91 respectively (Table 3). These groupings probably reflect the extent of higher plants contribution to the source rock that generated the oils.

Table 3
Source and thermal maturity parameters computed from the saturate biomarkers distributions in Niger delta oils

Samples	Field	Depth (ft)	Oleanane index	Homohopane index	Sterane (%)			$\beta\alpha/\beta\alpha+\alpha\beta$	22S/ 22S +22R	20S/ 20S +20R	$\beta\beta/\beta\beta+\alpha\alpha$
					C ₂₇	C ₂₈	C ₂₉	C ₃₀	C ₃₂	C ₂₉	C ₂₉
NA-1	A	4646–5000	1.06	0.04	22.8	28.8	48.4	0.70	0.56	0.38	0.36
NA-21	A	6488–6500	1.06	0.04	22.0	26.8	51.2	0.80	0.52	0.39	0.38
NA-29	A	9594–9604	0.84	0.03	24.2	29.6	46.2	0.84	0.53	0.44	0.45
FA-6	B	5812–5820	1.04	0.03	21.0	26.7	52.3	0.73	0.57	0.36	0.37
FA-27	B	6812–6822	1.02	0.03	23.1	30.0	46.9	0.79	0.56	0.41	0.37
FA-14	B	7288–7298	1.04	0.03	24.5	25.0	50.5	0.78	0.56	0.41	0.37
OG-3S	C	6085–6091	0.47	0.03	15.1	27.8	57.1	0.72	0.53	0.39	0.4
OG-10	C	9418–9430	0.37	0.04	20.4	25.8	53.7	0.75	0.55	0.44	0.37
ME-10	D	5379–5388	2.91	0.02	16.6	21.5	61.9	0.94	0.52	0.42	0.29
ME12	D	9871–9877	2.27	0.02	16.5	31.5	52.0	0.92	0.50	0.39	0.38

Oleanane index (OI) = 18 α (H)-Oleanane/17 α (H), 21 β (H)-Hopane.

Homohopane index (HI) = $\alpha\beta$ C₃₅homohopane (22S+22R)/ \sum C₃₁–C₃₅ $\alpha\beta$ homohopane (22S+22R).

The abundance of C₂₇–C₂₉ sterane in the oil (Table 3) indicates an origin of the oils from source rock of mixed kerogen types (terrestrial and marine). However, the abundance of C₂₉ sterane suggests greater contributions from terrestrial materials (Huang and Meischein, 1979).

Hopanes and steranes include the biomarkers most commonly used for maturity assessment (Seifert and Moldowan, 1978, 1981; Peters and Moldowan, 1993). Hopane (C₃₀) $\beta\alpha/\beta\alpha+\alpha\beta$ and homohopane (C₃₂) 22S/22S+SSR ratios for the oils range from 0.72 to 0.94 and 0.50 to 0.57 respectively (Table 3). These values are consistent with generation from early mature source rocks (Seifert and Moldowan, 1986; Peters and Moldowan, 1993). Steranes (C₂₉) 20S/20S+20R and $\beta\beta/\beta\beta+\alpha\alpha$ values range from 0.36 to 0.44 and 0.29 to 0.45 respectively (Table 3). These values further support the low maturity status of the oils (Grantham, 1986b; Seifert and Moldowan, 1986). These maturity parameters have narrow ranges and lack any particular trend with increasing depths in each of the fields. The negative correlation between the C₂₉ 20S/20S+20R and C₂₉ $\beta\beta/\beta\beta+\alpha\alpha$ sterane ratios (Fig. 6) suggests that their variation is not related to differences in thermal maturity of the oils.

3.4. Aromatic hydrocarbons distributions

The abundances and distributions of polycyclic aromatic hydrocarbons and their structural isomers have been found useful in maturity assessment of oils, source rock and coal (Radke et al., 1985; Radke, 1988). It has been established that aromatic hydrocarbons do change in a regular fashion with increasing maturity, thus a number of maturity parameters have been developed based on the distributions of alkyl naphthalene and phenanthrene (Alexander et al., 1985; Radke, 1988; van Aarssen et al., 1999). Aromatic hydrocarbons have in some cases been found to be more reliable than the aliphatic biomarkers (Farrimond et al., 1998; Radke, 1988). The mass chromatograms appropriate to naphthalene and phenanthrene and their alkyl derivatives in the Niger delta oils are shown in Figs. 7–9. The assignments of the peaks labeled in Figs. 7–9 are listed in Table 4.

The presence and abundance of 1,2,5 and 1,2,7 Trimethylnaphthalene (TMN) in the oils further support higher plants input into the oil source rock. The presences of 1,2,5 and 1,2,7TMN have been attributed to the contribution of angiosperms to sediments and petroleum by Strachan et al. (1988) who further proposed 1,2,7 TMN to be derived directly from the structural degradation of oleanane-type triterpenoids present in angiosperms.

Maturity parameters computed from the aromatic hydrocarbon compounds in the oils are listed in Table 5. The DNR-1 and DNR-2 ratios derived from the alkyl naphthalene distributions in the oils

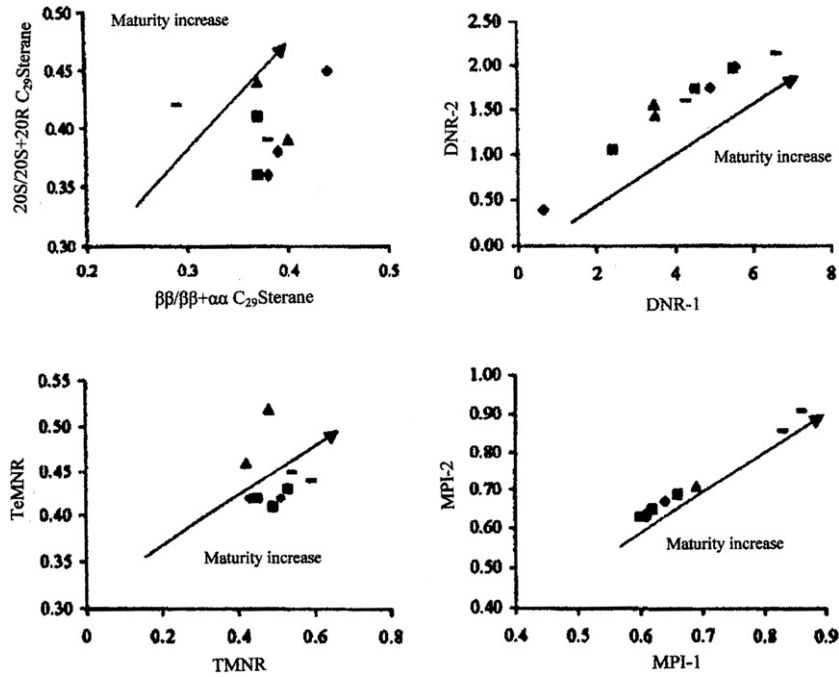


Fig. 6. Cross plot of various maturity parameters computed from the saturate and aromatic hydrocarbons for oils from the Niger delta.

range from 2.42 to 6.58 and 1.06 to 2.15 respectively (Table 5). NA-1U sample from Field A, shows abnormally low values for these two parameters. A positive correlation exists between the DNR-1 and DNR-

2 ratios (Fig. 6). The TMNr and TeMNR ratio in the oil range from 0.43 to 0.59 and 0.41 to 0.52 respectively. Again, the NA-1U sample has abnormally low values. Fig. 6 shows the cross plot of the TMNr against

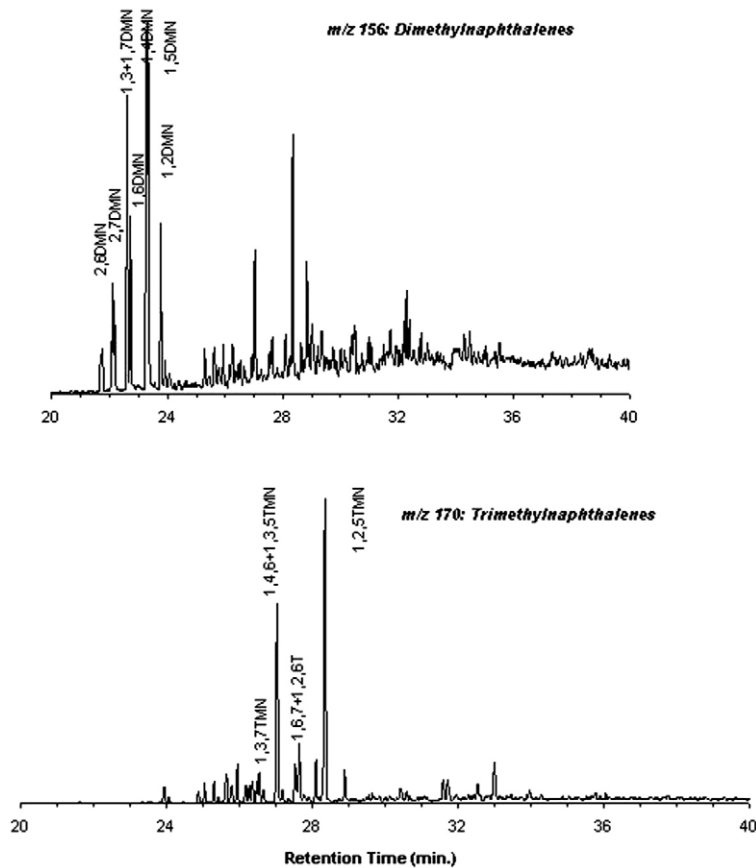


Fig. 7. Mass chromatogram of m/z 156 (Dimethylnaphthalene) and m/z 170 (Trimethylnaphthalene) of NA-1 oil from the Niger delta.

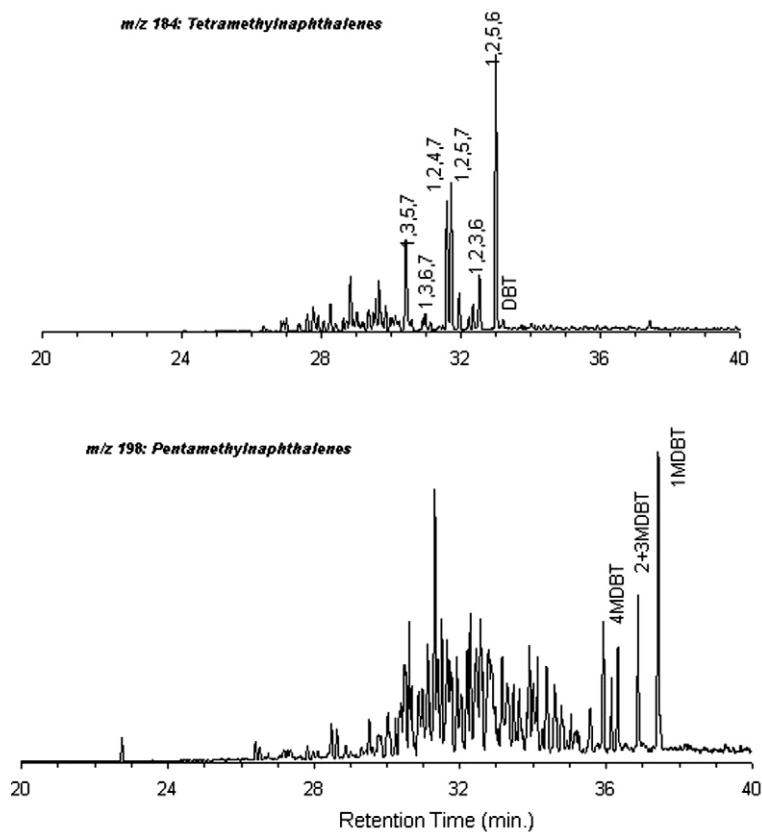


Fig. 8. Mass chromatogram of m/z 184 (Tetramethylnaphthalene) and m/z 198 (Aromatic sulfur Compounds) of NA-1 oil from Niger delta.

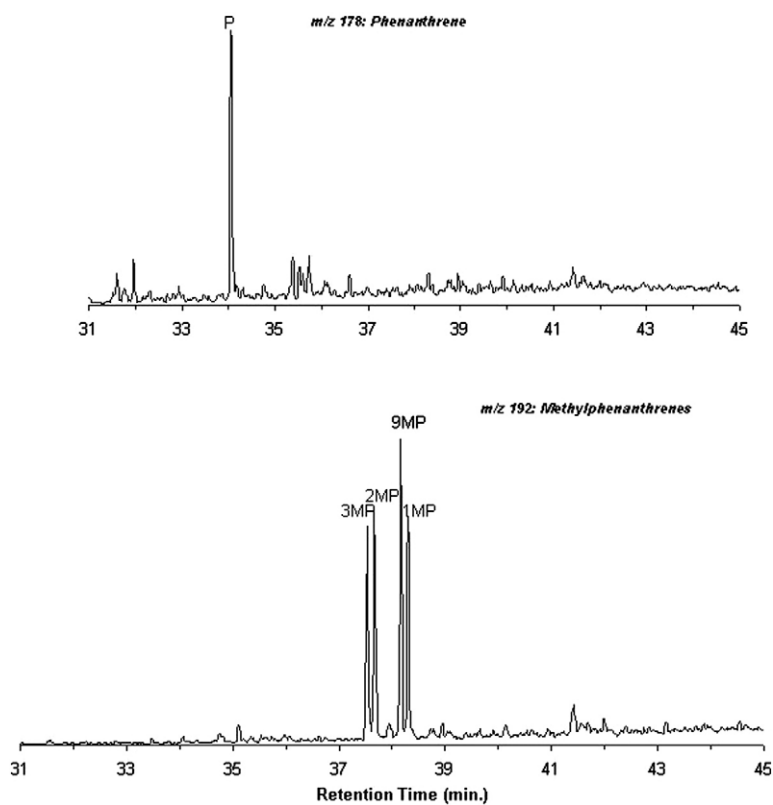


Fig. 9. Mass chromatogram of m/z 178 (Phenanthrene) and m/z 192 (Methylphenanthrene) of NA-1 oil from the Niger delta.

Table 4
Peak identification of aromatic biomarkers and aromatic sulfur compounds (thiophenes) in the Niger delta oils

Peak	Compound
26DMN	2,6-Dimethylnaphthalene
27DMN	2,7-Dimethylnaphthalene
13+17DMN	1,3 & 1,7-Dimethylnaphthalenes
16DMN	1,6-Dimethylnaphthalene
14DMN	1,4-Dimethylnaphthalene
15DMN	1,5-Dimethylnaphthalene
12DMN	1,2-Dimethylnaphthalene
137TMN	1,3,7-Trimethylnaphthalene
146+135T	(1,4,6+1,3,5)-Trimethylnaphthalenes
167+126T	(1,6,7+1,2,6)-Trimethylnaphthalenes
125TMN	1,2,5-Trimethylnaphthalene
1357	1,3,5,7-Tetramethylnaphthalene
1367	1,3,6,7-Tetramethylnaphthalene
1247	(1,2,4,7+1,2,4,6+1,4,6,7)-TetraMNs
1257	1,2,5,7-Tetramethylnaphthalene
1236	1,2,3,6-Tetramethylnaphthalene
1256	1,2,5,6-Tetramethylnaphthalene
DBT	Dibenzothiophene
4MDBT	4 Methyl Dibenzothiophene
2+3MDBT	2 & 3 Methyl Dibenzothiophenes
1MDBT	1 Methyl Dibenzothiophene
PHEN	Phenanthrene
3MP	3-Methylphenanthrene
2MP	2-Methylphenanthrene
9MP	9-Methylphenanthrene
1MP	1-Methylphenanthrene

TeMNR. It appears that there is no positive correlation between these two values.

The Methyphenanthrene Index (MPI 1) is one of the most widely used molecular maturity parameters (Radke and Welte, 1983; Radke, 1988). This parameter relies on a shift with maturity in the methylphenanthrene distribution towards a preponderance of β -type isomers. The inclusion of phenanthrene (parent compound) in the ratio is intended to compensate for facies-dependent variations in the degree of phenanthrene alkylation (Radke et al., 1982). MPI 1 may be used to estimate the equivalent vitrinite reflectance value (%Rc) for crude oils because of its linear relationship with vitrinite reflectance throughout the conventional oil window (Radke and Welte, 1983). The MPI-1 and MPI-2 values for the oils range from 0.60 to 0.86 and 0.63 to 0.91 respectively (Table 5). The two parameters show a consistent increase with increasing depth in most of the fields. A cross plots of these two values give an excellent correlation (Fig. 6).

Table 5
Thermal maturity parameters computed from the aromatic biomarkers and aromatic sulfur compounds in the Niger delta oils

Samples	Field	Depth (ft)	DNR-1	DNR-2	TMNr	TeMNR	MPI-1	MPI-2	MDR	MDR-1	Rc	Rm
NA-1	A	4646–5000	0.65	0.40	0.07	0.03	0.61	0.64	3.96	0.31	0.74	0.80
NA-21	A	6488–6500	4.90	1.75	0.51	0.42	0.64	0.67	3.74	0.19	0.75	0.78
NA-29	A	9594–9604	5.54	1.99	0.43	0.42	0.61	0.63	3.50	0.17	0.74	0.77
FA-6	B	5812–5820	2.42	1.06	0.45	0.42	0.60	0.63	4.35	0.25	0.73	0.83
FA-27	B	6812–6822	5.48	1.97	0.53	0.43	0.66	0.69	5.05	0.16	0.77	0.93
FA-14	B	7288–7298	4.51	1.74	0.49	0.41	0.62	0.65	6.38	0.12	0.74	0.77
OG-3S	C	6085–6091	3.47	1.56	0.48	0.52	0.62	0.65	4.97	0.21	0.74	0.92
OG-10	C	9418–9430	3.49	1.43	0.42	0.46	0.69	0.71	3.85	0.21	0.79	0.79
ME-10	D	5379–5388	6.58	2.15	0.59	0.44	0.83	0.86	6.84	0.15	0.87	2.37
ME12	D	9871–9877	4.28	1.60	0.54	0.45	0.86	0.91	7.94	0.12	0.88	1.57

DNR-1=(2,6+2,7)/(1,5) DMN; DNR-2=(2,6+2,7)/(1,4+2,3)DMN.
 TMNr=(1,3,7) TMN/(1,3,7)+1,2,5) TMN; TeMNR=(1,3,6,7) TeMNR/(1,3,6,7+1,2,5,6) TeMNR.
 MPI-1=1.5(2MP+3MP)/(P+1MP+9MP); MPI-2=3(2MP)/(P+1MP+9MP).
 MDR=4MDBT/1MDBT; MDR-1=1MDBT/DBT.
 $Rc=0.6(MPI-1)+0.37$; $Rm=0.40+0.30(MDR)-0.094(MDR)^2+0.011(MDR)^3$.

3.5. Aromatic sulfur compounds distributions

Aromatic sulfur compounds are common constituents of sediments and crude oils. They have been found very useful in paleoenvironmental and maturation assessments (Hughes et al., 1995; Radke et al., 1986; Chakhmakhev and Suzuki, 1995a,b, 1997). 1MDBT has been reported to show the lowest thermal stability among the four-methyldibenzothiophene isomers (Hughes, 1984). The 4-/1-MDBT ratio (MDR) has been proposed as a maturity parameter (Radke et al., 1986; Chakhmakhev and Suzuki, 1995a,b, 1997). The ratio generally increases with increasing maturity in oil and source rock. The ratio can be used to give equivalent vitrinite reflectance (%Rm) for oils.

The distributions of the dibenzothiophenes in the representative oil are shown in Fig. 8. 1-methyldibenzothiophene (1MDBT), 2+3-methyldibenzothiophene (2+3-MDBT) and 4-methyldibenzothiophene (4-MDBT) were identified in all the oils. This distribution suggests that the oils are of low thermal maturity. The MDR and %Rm values for the oils range from 3.50 to 7.94 and 0.77 to 2.37 respectively (Table 5). The ratios increase with increasing reservoir depths in some of the fields.

4. Conclusions

Saturated hydrocarbon molecular composition of Niger delta oils revealed that the oils were formed in source rocks containing mixed kerogen (marine and terrestrial) deposited in a deltaic depositional environment. The aliphatic biomarkers maturity parameters show that the oils were formed from early mature source rocks but lacked any maturity trends.

Maturity parameters based on aromatic hydrocarbons and sulfur-containing aromatic compounds were generally well-correlated and allowed maturity trends to be established. Aromatic biomarkers and aromatic sulfur compounds (thiophenes) to some extent reveal an increasing thermal maturity with increasing reservoir depths in most of the fields. This study shows that a full integration of oil–source rock correlations and the study of biomarkers that are migration indicators are necessary for better understanding of petroleum generation, migration and accumulation in the Niger delta.

References

Alexander, R., Kagi, R.I., Rowland, S.J., Sheppard, P.N., Chirila, T.V., 1985. The effects of thermal maturity on distributions of dimethylnaphthalenes and trimethylnaphthalene in some ancient sediments and petroleum. *Geochim. Cosmochim. Acta* 49, 385–395.
 Chakhmakhev, A., Suzuki, N., 1995a. Saturate biomarkers and aromatic sulfur compounds in oils and condensate from different source rock lithologies of Kazakhstan, Japan and Russia. *Org. Geochem.* 23 (4), 289–299.

- Chakhmakhchev, A., Suzuki, N., 1995b. Aromatic sulfur compounds as maturity indicators for petroleum from the Buzuluk depression, Russia. *Org. Geochem.* 23 (7), 617–625.
- Chakhmakhchev, A., Suzuki, N., 1997. Distribution of alkylated dibenzothiophenes in petroleum as a tool for maturity assessments. *Org. Geochem.* 26, 483–490.
- Chung, H.M., Rooney, M.A., Toon, M.B., Claypool, G.E., 1992. Carbon isotope composition of marine crude oils. *AAPG Bull.* 76, 1000–1007.
- Connan, J., Cassou, A.M., 1980. Properties of gases and petroleum liquids derived from terrestrial kerogen at various maturation levels. *Geochim. Cosmochim. Acta* 44, 1–23.
- Curiale, J.A., Bromley, B.W., 1996. Migration of petroleum into Vermilion 14 field, Gulf Coast, USA – molecular evidence. *Org. Geochem.* 24, 563–579.
- Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature* 272, 216–222.
- Doust, H., Omatsola, E., 1990. Niger Delta divergent/passive margin basins. *AAPG Bull. Mem.* 45, 201–238.
- Ejedawe, J.E., 1986. The expulsion in the evaluation of the petroleum source beds of the Tertiary Niger Delta. *J. Pet. Geol.* 9, 439–450.
- Ekweozor, C.M., Daukoru, E.M., 1984. Petroleum source-bed evaluation of the Tertiary Niger Delta reply. *AAPG Bull.* 68, 390–394.
- Ekweozor, C.M., Daukoru, C.M., 1994. Northern delta depobelt portion of the Akata-Agbada(!) petroleum system, Niger Delta, Nigeria, in *The Petroleum system—from source to trap*. AAPG Memoir 60, 599–613.
- Ekweozor, C.M., Sonibare, O.O., 1998. Molecular and stable isotope composition of hydrocarbon natural gases from Niger Delta. In: Mpanju, F., Kilembe, E., Kagya, M. (Eds.), *Proceedings of the 4th Conference of the Afro Asia Association of Petroleum Geochemists*, pp. 170–181.
- Ekweozor, C.M., Okogun, J.I., Ekong, D.E.U., Maxwell, J.M., 1979. Preliminary organic geochemical study of samples from the Niger Delta (Nigeria). *Chem. Geol.* 27, 29–37.
- Evamy, B.D., Haremboure, J., Kamerling, P., Knaap, F.A., Molley, P., Rowland, P.H., 1978. Hydrocarbon habitat of Tertiary Niger Delta. *AAPG Bull.* 62, 1–39.
- Farrimond, P., Taylor, A., Telnaes, N., 1998. Biomarker maturity parameters: the role of generation and thermal degradation. *Org. Geochem.* 29, 1181–1197.
- Fuex, A.N., 1977. The use of stable carbon isotopes in hydrocarbon exploration. *J. Geochem. Explor.* 7, 155–188.
- Grantham, P.J., 1986b. Sterane isomerization and moretane/hopane ratios in crude oils derived from Tertiary source rocks. *Org. Geochem.* 9, 293–304.
- Hegazi, A.H., Andersson, J.T., El-gayar, M.S., 2003. Application of gas chromatography with atomic emission detection to the geochemical investigation of polycyclic aromatic sulfur heterocycles in Egyptian crude oils. *Fuel Process. Technol.* 85, 1–19.
- Huang, W.Y., Meischein, W.G., 1979. Sterols as ecological indicators. *Geochim. Cosmochim. Acta* 43, 739–745.
- Hughes, W.B., 1984. Use of thiophenic organosulfur compounds in characterizing crude oils derived from carbonate versus siliclastic source. In: Palacas, J.B. (Ed.), *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks*. American Association of Petroleum Geologists Study Geology, vol. 18, pp. 181–196.
- Hughes, W.B., Holba, A.G., Dzou, I.P., 1995. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. *Geochim. Cosmochim. Acta* 59, 3581–3598.
- Jaffer, R., Albrecht, P., Quadri, J.L., 1988b. Carboxylic acid as indicator of oil migration II. Case of Mahakam Delta, Indonesia. *Geochim. Cosmochim. Acta* 52, 2599–2607.
- Mello, M.R., Maxwell, J.R., 1990. Organic geochemical and biological marker characterization of source rocks and oils from lacustrine environments in the Brazilian continental margin. In: Katz, B.J. (Ed.), *Lacustrine Basin Exploration*. AAPG Mem., vol. 50, pp. 77–97.
- Peters, K.E., Moldowan, J.M., 1993. The biomarker guide: interpreting molecular fossils in petroleum and ancient sediments. Prentice Hall, Englewood Cliffs, NJ.
- Philip, R.P., Gilbert, T.D., 1986. Biomarker distributions in Australian oils predominantly derived from terrigenous source material. *Org. Geochem.* 10, 73–84.
- Radke, M., 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Mar. Pet. Geol.* 5, 224–236.
- Radke, M., Welte, D.H., 1983. The methylphenanthrene index (MPI): a maturity parameters based on aromatic hydrocarbons. In: Bjoroy, M. (Ed.), *Advances in Organic Geochemistry 1981*. Wiley, Chichester, pp. 504–512.
- Radke, M., Welte, D.H., Willsch, H., 1982. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochim. Cosmochim. Acta* 46, 1–10.
- Radke, M., Welte, D.H., Willsch, H., 1985. Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. *Adv. Org. Geochem.* 10, 51–63.
- Radke, M., Welte, D.H., Willsch, H., 1986. Maturity parameters based on aromatic hydrocarbons: influence of organic matter type. *Org. Geochem.* 10, 51–63.
- Schoell, M., 1984. Recent advances in petroleum isotope geochemistry. *Org. Geochem.* 6, 645–663.
- Seifert, W.K., Moldowan, J.M., 1978. Application of steranes, terpanes and monoaromatics to the maturation, migration, and source of crude oils. *Geochim. Cosmochim. Acta* 42, 77–95.
- Seifert, W.K., Moldowan, J.M., 1981. Palaeoreconstruction by biological markers. *Geochim. Cosmochim. Acta* 45, 783–794.
- Seifert, W.K., Moldowan, J.M., 1986. Use of biological markers in petroleum exploration. In: Johns, R.B. (Ed.), *Biological Markers in the Sedimentary Record*. Methods in Geochemistry and Geophysics, vol. 24. Elsevier, pp. 261–290.
- Short, K.C., Stauble, A.J., 1967. Outline of geology of Niger Delta. *AAPG* 51, 761–779.
- Sinninghe Damste, J.S., Kenig, F., Koopmans, F.M.P., Koster, J., Schouten, S., Hayes, J.M., de Leeuw, J.W., 1995. Evidence for gammacerane as an indicator of water column stratification. *Geochim. Cosmochim. Acta* 59, 1895–1900.
- Sofer, Z., 1984. Stable carbon isotope composition of crude oils: application to source depositional environments and petroleum alteration. *AAPG* 68 (1), 31–49.
- Sonibare, O.O., Ekweozor, C.M., 2000. Migration pattern of hydrocarbon natural gas in the Niger Delta: isotopic evidence. *Niger. Assoc. Pet. Explor. Bull.* 15, 72–80.
- Sonibare, O.O., Ekweozor, C.M., 2001. Distribution of pentacyclic triterpanes and steranes, in relation to the origin and thermal maturity of crudes from the Niger Delta, Nigeria. *J. Min. Geol.* 37, 37–43.
- Stahl, W.J., 1977. Carbon and nitrogen isotopes in hydrocarbon research and exploration. *Chemistry* 20, 121–149.
- Stahl, W.J., 1978. Source rock–crude oil correlation by isotopic type-curves. *Geochim. Cosmochim. Acta* 42, 1573–1577.
- Strachan, M.G., Alexander, R., Kagi, R., 1988. Trimethylnaphthalenes in crude oils and sediments: effect of source and maturity. *Geochim. Cosmochim. Acta* 52, 1255–1264.
- van Aarssen, B.G.K., Bastow, T.P., Alexander, R., Kagi, R.I., 1999. Distribution of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. *Org. Geochem.* 30, 1213–1227.
- Whitehead, E.V., 1974. The structure of petroleum pentacycles. In: Tissot, B., Biener, F. (Eds.), *Advances in Organic Geochemistry*. Editions techniq, vol. 1973, pp. 225–243.