

Organic and inorganic geochemistry of northwestern Niger Delta oils

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A detailed geochemical study of oil samples from an onshore field in the Niger Delta was carried out for their characterization and correlation. The samples were analyzed using Gas Chromatographic (GC), Gas Chromatographic-Mass Spectrometric (GC-MS) and Inductively Coupled Plasma-Mass Spectrometric (ICP-MS) analytical techniques. The results showed that CPI, Pr/Ph, Pr/nC₁₇, Ph/nC₁₈ and odd/even ratios ranged from 0.91 to 1.17, 3.07 to 6.04, 0.39 to 0.80, 0.14 to 3.30 and 1.33 to 1.39 respectively. The concentration levels of Co, Cr, Cu, Fe, Ni and V ranged from 0.9 to 32, 6.2 to 24, 3.31 to 19.4, 11.4 to 1241, 26.3 to 144 and 11.0 to 29.7 pbb respectively. The Pr/nC₁₇ vs. Ph/nC₁₈ plot revealed two oil types; non-degraded and minor degraded oils, which were derived from organic matter deposited in transitional environments. This suggests that both oil types have identical source rocks. Also, CPI values of 0.91 to 1.17 indicated that the oils are thermally mature. Biomarker data also discriminated the oils into two groups on the basis of biodegradation and revealed that the oils are mature and generated at almost the same thermal maturity level. The results of Ni vs. V, Co/Ni vs. V/Ni cross plots and cluster analysis similarly revealed identical two oil types. The similarity in the results of both organic and inorganic geochemistry of these oils shows that an integrated organic and inorganic geochemical data provide a reliable tool for the evaluation, characterization and correlation of crude oils.

Keywords: oil typing, biodegradation, Niger Delta, organic-inorganic geochemistry, maturity

INTRODUCTION

In petroleum exploration, organic geochemistry has been found to be an indispensable tool both at the initial and advanced stage in identifying source rocks and classifying crude oils into families (Ekweozor *et al.*, 1979; Doust and Omatsola, 1990). Classification of crude oils into families helps to locate hydrocarbons in explored areas and different stratigraphic units of the basin. It is now known that organic geochemistry is also very useful in petroleum production (Karlsen *et al.*, 1995; Larter and Aplin, 1995).

Organic geochemical methods of crude oil include biomarker fingerprints, stable isotope ratios, and hydrocarbon contents etc., which are fairly expensive. Trace elements data of crude oils have been reported to be equally effective in classifying and correlating crude oils and are relative to organic geochemical methods (Hitchon and Filby, 1984; Lewan, 1984; Curiale, 1987; Barwise, 1990; Udo *et al.*, 1992; Oluwole *et al.*, 1993).

The nature of occurrence of metals, their distribution patterns and concentrations in crude oils can give infor-

mation on the origin, migration, environment of deposition and maturation of petroleum (Elirich *et al.*, 1985; Barwise, 1990; Oluwole *et al.*, 1993). Trace metals are incorporated into oils in form of porphyrin complexes (species) in petroleum source rocks and may include direct incorporation from the biomass and formation during sedimentation. It may also involve diagenesis from organic molecules as well as metals derived from different biogenic (biomass) and abiogenic (weathering of minerals) sources. Lewan (1984) has shown that source rock, type of organic matter and depositional environment have profound effects on the concentration of trace elements in source rocks. There may be difficulty in correlating oils and/or source rocks using trace element contents. However, metals of proven association with organic matter may be used as reliable correlation tools. Nickel, Vanadium and Cobalt (usually referred to as biophile elements) are such examples.

Concentration of metals in crude oils can be used to classify oils into families. Low V/Ni ratios (<0.5) are expected for petroleum derived from marine organic matter, with high to moderate sulphur content, while V/Ni ratios (1–10) are expected for petroleum derived from lacustrine and terrestrial organic matter (Barwise, 1990). Oils from marine organic matter have high concentrations of metals (particularly Ni and V), this is expected since

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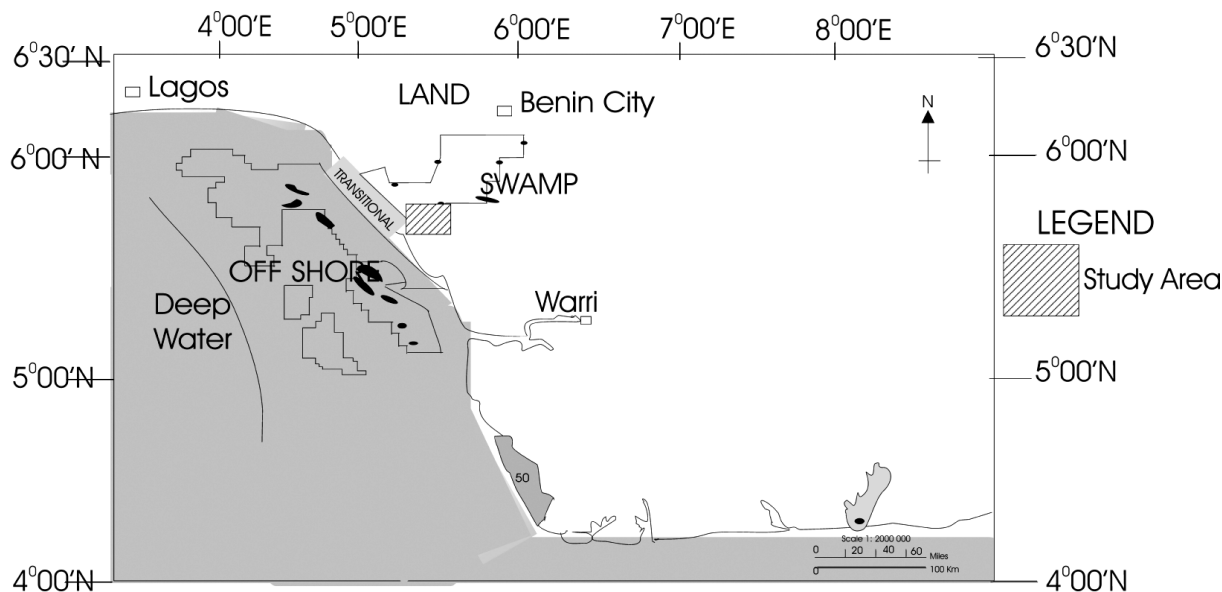


Fig. 1. Map of Niger Delta showing location of study.

for marine source rocks, there is an abundant input of porphyrin-precursor chlorophylls to the organic matter derived from algae and bacteria (Barwise, 1990). Moderate quantities of metals are found in oils derived from lacustrine source rocks while little nickel and vanadium is found in land-plant derived oils. The V/Ni ratio tends to increase with increasing Pr/Ph and 18H-oleanane/17H, C30-hopane ratios, suggesting high terrigenous source input (Udo *et al.*, 1992). Lewan (1984) reported that V/(V + Ni) ratio is negatively correlated with the even predominance of *n*-alkanes and the Pr/Ph ratio, but it is positively correlated with the Ph/*n*C₁₈ ratio, which infers marine organic matter input. Nickel, Cobalt, Strontium, Silver and Bismuth have been found to correlate positively with the absolute amount of heavy *n*-alkanes in the petroleum, as these elements are relatively more abundant in parafinic petroleum (Karlsen *et al.*, 1995). Enriched V and Ni concentrations greater than 100 ppm are observed in bitumens that are associated with Type II and Type I kerogens. Bitumens associated with Type III kerogens contained V and Ni concentrations less than 100ppm (Lewan, 1984).

Lewan and Maynard (1982), Lewan (1984) reported that source rock type and depositional environment have a profound effect on the predicted levels of nickel and vanadium in the source rocks. Barwise (1990) also showed that there is a systematic variation in the nickel and vanadium content of crude oils which can be related to depositional environment and source rock types. This implies that the source rock depositional environment determines the proportion of vanadium to nickel in crude

oil. It has been proved that high V/Ni ratio is associated with anoxic paleoenvironment of deposition (Lewan, 1984) whilst both high V/Ni and Co/Ni ratios have been shown to be anoxic/oxic related parameters (Udo *et al.*, 1992).

An inverse proportional relationship exists between API gravity and the total transition metal contents. The API gravity is also inversely correlated with each of Cu, Ni, V, Se, Mn and Cr (Oluwole *et al.*, 1993). These infer that total transition metal content decreases with increase oil maturity. Many workers have used the V/Ni ratio as indicator of oil maturity (Barwise, 1990; Udo *et al.*, 1992). Udo *et al.* (1992) reported that V/Ni ratio decrease as Pr/*n*C₁₇ ratio decreases, and as depth and API gravity of oils increase, thus suggesting that V/Ni ratio decrease with increasing maturation. Barwise (1990) also reported that high concentrations of metals are only associated with oils of low to moderate API gravity. He further stressed that the highest concentrations of metal are found in low maturity crude oils.

Though, organic geochemical properties of Niger Delta crude oils have been fairly well reported, also few studies on trace element contents of Niger Delta oils have been carried out. However, there has been no study on combined/integrated organic and inorganic geochemical data of Niger Delta crude oils to evaluate whether these methods complement each other.

The present study is therefore an attempt to classify and correlate Niger Delta oils using integrated organic and inorganic geochemical data to evaluate the reliability of each of these methods.

Table 1. Gas chromatographic data of Northwestern Niger Delta oils

Sample	Pr/Ph	Pr/n-C ₁₇	Ph/n-C ₁₈	Odd/Even	CPI	nC ₇ /MCH	Tol/nC ₇	2MP/3MP
Non-degraded oils								
T1	6.05	0.68	0.14	1.30	1.17	0.31	0.61	2.10
T3	3.08	0.39	0.16	1.35	1.10	0.47	0.39	1.95
T6	3.18	0.47	0.19	1.39	1.02	0.14	0.04	1.55
T8	3.23	0.46	0.19	1.37	1.30	0.26	0.10	1.82
T9	3.23	0.46	0.19	1.38	1.05	0.24	0.08	1.80
T10	3.07	0.50	0.21	1.34	0.91	0.25	0.49	1.63
T12	3.63	0.53	0.21	1.37	1.09	0.19	0.18	1.76
Degraded oils								
T2	3.09	0.79	0.32	1.35	1.09	0.10	0.15	1.60
T4	3.12	0.74	0.31	1.36	1.11	0.11	0.14	1.85
T5	3.03	0.78	0.33	1.34	1.15	0.14	0.25	1.95
T7	3.10	0.80	0.33	1.34	1.16	0.12	10.72	1.66
T11	3.10	0.71	0.29	1.33	1.14	0.18	6.67	1.69

EXPERIMENTAL

Gas Chromatographic (GC) and Inductively Coupled Plasma-Mass Spectrometric (ICP-MS) methods were used for the analyses of oil samples collected from Northwestern Niger Delta (Fig. 1). This was done using the Hewlett Packard 5890 series II Plus GC equipped with a 50 m × 0.2 mm × 0.5 μm film thickness PONA (paraffins, olefins, naphthenes, and aromatics), cross-linked methyl siloxane capillary column. A flame ionization detector (FID) detected separated components. The carrier gas was hydrogen flowing at a rate of 300ml/sec and the oven was programmed from 30–305°C at 1°C/min. The final temperature was held for 20 minutes. The peak areas were electronically integrated and identification was based on retention times and comparison with standards. The peak integration was achieved using the HP chemstation software. The GC analysis was carried out at Humble Geochemical Services Laboratory, Humble, Texas, USA.

The oil samples were fractionated using silica gel column chromatography into saturates, aromatics and NSOs (nitrogen, sulphur, and oxygen containing compounds) using *n*-hexane, toluene and methanol as eluents respectively. Each fraction was concentrated by evaporating the solvent in a stream of nitrogen gas. Aromatic and saturated fractions were analysed by Gas Chromatography-Mass Spectrometry (GC-MS) on an Agilent 6890 GC-MS system. The carrier gas was hydrogen. The mass spectrometer was operated at electron energy of 70 eV, an ion source temperature of 250°C and MSD transfer line temperature of 300°C.

The crude oils were digested with concentrated sulphuric acid (H₂SO₄) and 50% hydrogen peroxide (H₂O₂) under thermal agitation. Blank was prepared under the same conditions. The elemental analysis of the digested

crude oils samples was performed using VG Plasma Quad-3 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). ICP settings operated at frequency of 27.12 MHz, with incident power of 1.35 KW and reflected power of <5 W. The auxiliary, Nebuliser, coolant/plasma flow rates were at 1.51 min⁻¹, 0.75 min⁻¹, 131 min⁻¹, 12.01 min⁻¹ respectively.

RESULTS AND DISCUSSION

Geochemical data of twelve selected oils are presented in Tables 1, 2 and 3. Figures 2(a) and (b) show typical gas chromatograms of the selected oils.

Organic geochemical data

Inspection of the chromatograms (Figs. 2(a) and (b) and Appendices 1 and 2)—representative chromatograms of the selected oils) reveals that some of the oils are slightly degraded while some are normal. Out of the twelve oil samples, seven (T1, T3, T6, T8, T9, T10 and T12) were found to be non-degraded while five also were found to be slightly degraded (T2, T4, T5, T7, and T11) (Table 1, Fig. 3). All the oils have unique geochemical signatures by having a recognizable C₈+ fingerprint (Figs. 2(a) and (b)) characterized by odd carbon preference mostly in C₁₇–C₂₇ as well as the decreased hydrocarbon yield in the C₂₇+

Based on the GC data a number of cross plots were generated to correlate and examine the relationship between the oils. On the basis of cross plot of Pr/nC₁₇ versus Pr/nC₁₈, two distinct groups of oils were identified. The two groups are classified as types A and B (Fig. 3), which confirms our inference based on visual examination of the chromatograms.

Table 2. Biomarker data of Northwestern Niger Delta oils

Samples	Ole./C30H	Ts/(Ts + Tm)	%C2720R	%C2820R	%C2920R	Rc	TAS/(TAS + MAS)	MPI-1	MPI-2	2MP + 3MP	1MP + 9MP
T1	0.45	0.49	14.10	24.40	61.60	0.99	0.78	1.03	1.11	1385.80	1603.70
T2	0.38	0.50	26.70	29.90	43.30	0.95	0.88	0.97	1.05	572.70	712.70
T3	0.59	0.63	27.80	29.50	42.70	0.90	0.87	0.89	0.96	1569.20	2108.70
T4	0.41	0.49	30.10	28.70	41.20	0.95	0.88	0.97	1.04	636.60	777.80
T5	0.40	0.49	29.80	29.00	41.20	0.91	0.88	0.89	0.94	750.10	886.00
T6	0.44	0.52	29.30	27.80	42.90	0.89	0.89	0.87	0.87	806.70	1026.40
T7	0.40	0.49	30.10	28.50	41.40	0.90	0.85	0.89	0.94	799.90	932.80
T8	0.46	0.51	29.20	28.00	42.80	0.91	0.97	0.90	0.93	1237.60	1487.50
T9	0.46	0.51	28.50	28.90	42.60	0.90	0.97	0.88	0.92	1301.30	1561.30
T10	0.47	0.53	29.90	29.60	40.40	0.93	0.96	0.94	1.00	1707.70	1709.90
T11	0.40	0.49	29.60	29.50	40.90	0.93	0.90	0.94	0.99	897.40	1064.40
T12	0.46	0.49	26.60	27.20	46.20	0.88	0.87	0.85	0.90	548.40	696.40

The abbreviations represent: Rc = 0.6(MPI-1) + 0.37 (for Ro < 1.3), 0.6(MPI-1) + 2.3 (for Ro > 1.3), TAS = triaromatic steroid, MAS = monoaromatic steroid, MPI-1 = 1.5(2MP + 3MP)/(Phen + 1-MP + 9-MP), MPI-2 = 3(2MP)/(Phen + 1-MP + 9-MP), Ole = Oleanane, C30H = C30 hoapane, Ts = 22, 29, 30-trisor-18-(H) hopane, Tm = 22, 29, 30-trisor-17-(H) hopane.

Table 3. Trace metal data of Northwestern Niger Delta oils and comparison of trace metal data of Niger Delta oils

Samples	Co	Cr	Cu	Fe	Ni	V	
Non-degraded oils (ppb)							
T1	0.89 ± 0.02	9.60 ± 0.16	5.84 ± 0.09	21.00 ± 0.30	26.30 ± 0.40	17.30 ± 0.20	
T3	1.78 ± 0.04	23.70 ± 0.40	6.03 ± 0.10	636.00 ± 9.52	51.30 ± 0.80	25.20 ± 0.35	
T6	12.70 ± 0.30	13.40 ± 0.22	9.24 ± 0.15	24.00 ± 0.40	94.20 ± 1.50	19.20 ± 0.32	
T8	10.52 ± 0.23	9.90 ± 0.16	8.25 ± 0.10	22.08 ± 0.35	75.70 ± 1.20	14.90 ± 0.25	
T9	7.49 ± 0.16	9.60 ± 0.10	4.28 ± 0.07	17.77 ± 0.30	62.50 ± 1.05	11.20 ± 0.10	
T10	10.42 ± 0.20	7.50 ± 0.13	8.99 ± 0.15	12.78 ± 0.21	61.00 ± 1.00	12.30 ± 0.20	
T12	3.55 ± 0.07	9.60 ± 0.15	6.71 ± 0.10	17.97 ± 0.30	38.50 ± 0.65	11.20 ± 0.18	
Range	0.89–12.70	7.50–23.70	4.28–9.24	12.78–636.00	26.30–94.20	11.20–25.20	
Degraded Oils (ppb)							
T2	27.72 ± 0.60	6.20 ± 0.10	4.34 ± 0.07	14.17 ± 0.20	130.20 ± 2.20	26.20 ± 0.44	
T4	23.29 ± 0.52	8.10 ± 0.13	3.31 ± 0.05	17.74 ± 0.29	121.40 ± 2.05	26.80 ± 0.40	
T5	21.43 ± 0.48	10.20 ± 0.10	19.40 ± 0.30	20.46 ± 0.34	114.00 ± 1.90	29.70 ± 0.50	
T7	32.44 ± 0.70	11.70 ± 0.20	13.76 ± 0.23	1241.00 ± 19.50	144.10 ± 2.40	28.00 ± 0.47	
T11	22.44 ± 0.50	8.40 ± .14	6.56 ± 0.11	11.39 ± 0.19	85.40 ± 1.40	17.60 ± 0.20	
Range	21.43–32.44	6.20–11.70	3.31–19.40	11.39–241.00	85.40–144.10	17.60–29.70	
This study (ppb)	Range	0.89–32.44	6.2–23.7	3.31–19.4	11.4–1241	26.3–144.1	11.2–29.2
Nwachukwu <i>et al.</i> , 1995 (ppm)	Range	0.003–1.174	0.021–0.219	0.54–42.308	0.006–25.073	0.351–11.282	0.009–1.832
Udo <i>et al.</i> , 1992 (ppm)	Range	0.46–3.54	0.30–0.70	0.03–0.07	0.06–0.36	4.4–6.9	3.70–40.0
Oluwole <i>et al.</i> , 1993 (ppm)	Range	0.008–0.993	0.031–0.129	1.86–18.9	3.40–9.54	0.54–5.03	0.54–1.195
Ndiokwere, 1983 (ppm)	Range	1.42–1.57	—	—	—	2.2–5.6	0.1–0.642

Note: n = 3.

Type A oils

Type A oils include T1, T3, T6, T8, T9, T10 and T12, which are non-degraded (normal) oils. Although T1 plots separately, it is classified as Type A because its GC fingerprinting shows no obvious degradation, which is a characteristic of Type A oils and also plots close to Type A oils. Type A oils have pristane/phytane ratio of 3.08–6.05 with an average of 3.64. The Pr/nC₁₇ ratios range from 0.39 to 0.53 averaging 0.5 while Pr/nC₁₈ ratio ranges

from 0.16 to 0.21 with an average of 0.18. The CPI values range from 0.91 to 1.30 with an average of 1.09 while the odd/even ratio ranges between 1.34 and 1.39 with an average of 1.36.

Meyers and Snowdon (1993) showed that Pr/Ph > 1 indicates oxygenated depositional environments. The Pr/Ph values > 3.0 for these oils are thus suggesting oxidizing depositional environment for the source rocks. Averaged Pr/nC₁₇ ratio of 0.5 and Ph/nC₁₈ ratio of 0.18 is sug-

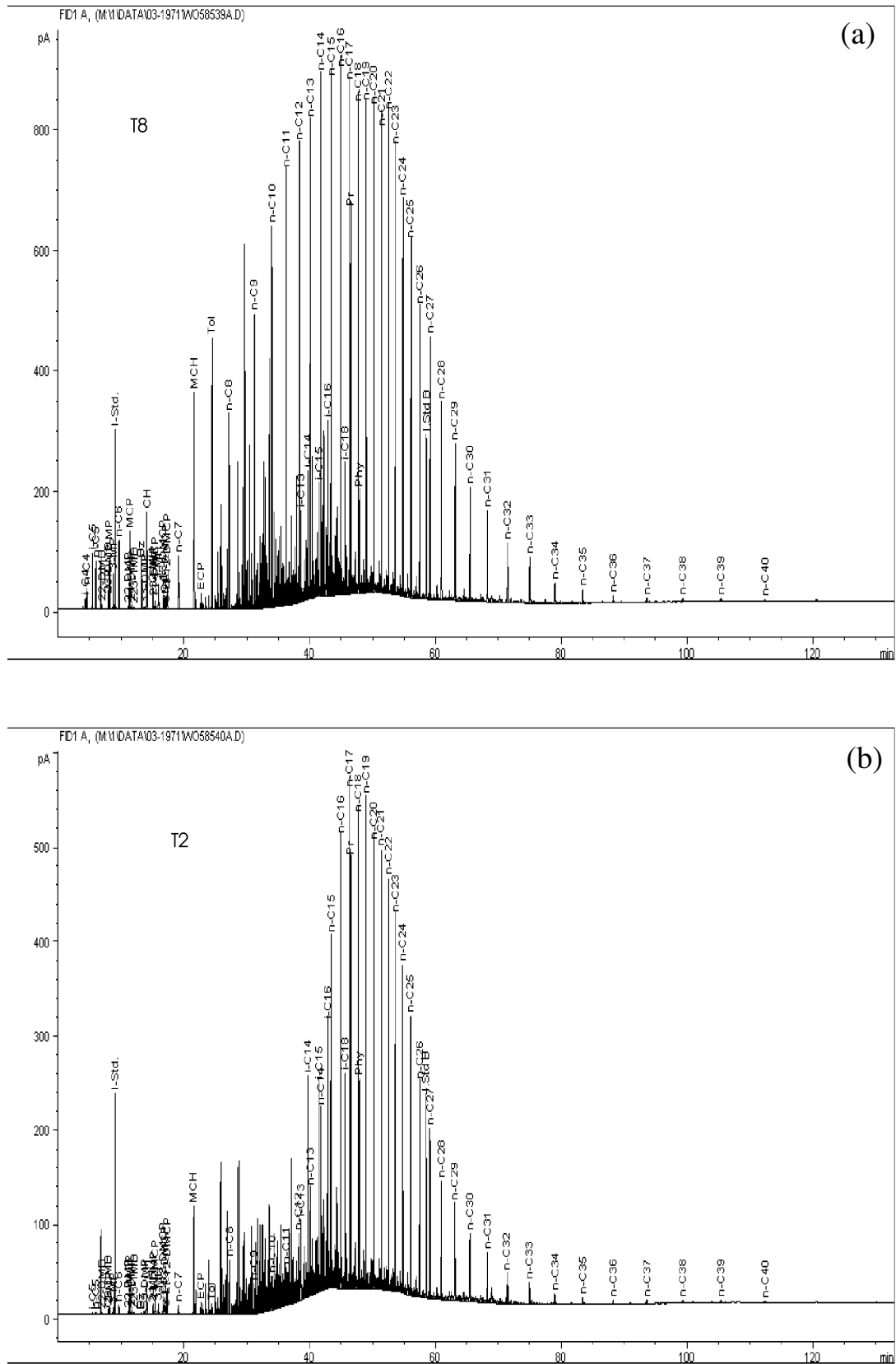


Fig. 2. (a) Representative gas chromatogram of normal oil. (b) Representative gas chromatogram of slightly degraded oil.

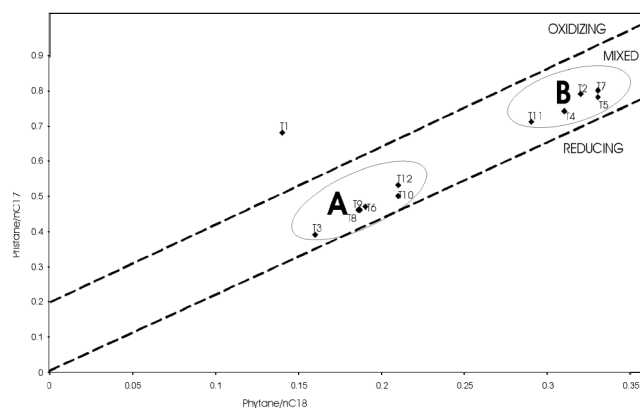


Fig. 3. Cross plot of Pr/nC_{17} versus Ph/nC_{18} .

gestive that Type A oils are generated from organic matter deposited in mixed/transitional depositional environments as indicated in Fig. 3. The average CPI value of 1.09 indicates that the oils are thermally mature.

Type B oils

Type B oils include T2, T4, T5, T7 and T11 which show minor degradation. The pristane/phytane ratios for these oils range from 3.03–3.12 with an average of 3.09. Pr/nC_{17} ratios range from 0.710–0.796 with an average of 0.76 while Ph/nC_{18} ratios range from 0.29–0.33 with an average of 0.32. The CPI values range between 1.09 and 1.16 with an average of 1.13 while the odd/even ratios range from 1.33–1.36 averaging 1.34 (Table 1).

The average Pr/nC_{17} ratio of 0.76 and Ph/nC_{18} ratio of 0.32 indicate that the oils were generated from mixed Type II/III organic matter (Nwachukwu and Chukwura, 1986; Okoh and Nwachukwu, 1997). This shows similarity in source rocks with Type A oils. The average odd/even ratio of 1.34 is similar to that of Type A (1.36), which also suggests derivation from identical source rocks. The average CPI value of 1.13 is relatively higher than that of Type A oils, indicates that Type B oils are thermally more mature than Type A oils. The higher thermal maturity may probably be responsible for the slight degradation of Type B oils. The average Pr/Ph ratio of 3.09 for Type B oils also suggests that they were generated from organic matter deposited in transitional oxidizing environments (Nwachukwu *et al.*, 1995; Obaje, 2000). The relatively high Pr/Ph ratio for both Types A and B oils are attributable to their high maturation levels and the significant contribution of humic organic matter in the source rocks from which these oils were generated (Obaje, 2000), though there were also measurable contributions from marine source. Also the high Pr/Ph ratios which are greater than 3 for all the oils means that the oils were generated from organic matter at maturation levels corresponding

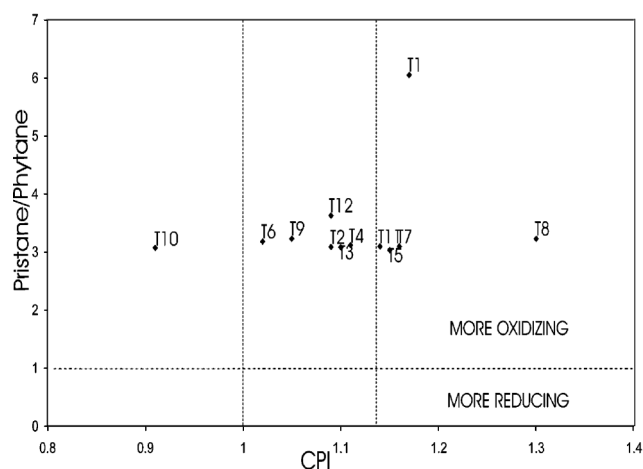


Fig. 4. Cross plot of Pr/Ph versus CPI of Niger Delta oils.

to the main phase of oil generation as proposed by Diessel (1992).

Types A and B oils correspond to Bonny light stream of Evamy *et al.* (1978) and Doust and Omatsola (1990), which are paraffinic and waxy.

Depositional environments

The results of the bulk geochemical parameters especially C_8+ hydrocarbons (both isoprenoid biomarkers and paraffin) indicate that the oils are grouped into Type A and Type B oils which were generated from mixed organic matter deposited in transitional environments (which are more oxidizing). The cross plot of Pr/nC_{17} versus Ph/nC_{18} (Fig. 3) indicated mixed/transitional environments for all the oils.

The cross plot of Pr/Ph versus CPI (Fig. 4) show that most of the oils fall into the field of more oxidizing. This indicates that these oils have identical source rocks but they were at various levels of thermal maturation.

Biomarker chemistry

Biomarkers are useful for establishing the origin and thermal maturity of crude oils. Biomarker data are presented in Table 2. The ratio of oleanane/hopane, a source indicator showed that these oils are of mixed marine/terrestrial origin. This inference is made apparent with the abundances of C_{27} , C_{28} and C_{29} steranes (Table 2). The sterane contents of these oils indicate mixed organic matter source input with higher contribution of terrestrial organic matter. Thermal maturity dependent parameters calculated from the terpanes and steranes distributions; $Ts/(Ts + Tm)$ ratio (Table 2) and cross plot of $C_{29}\alpha\beta\beta 20/(\alpha\alpha\alpha + \alpha\beta\beta)$ versus $C_{29}\alpha\alpha\alpha 20S/(S + R)$ steranes (Fig. 5) indicate that these oils are mature and are at almost the same thermal maturity.

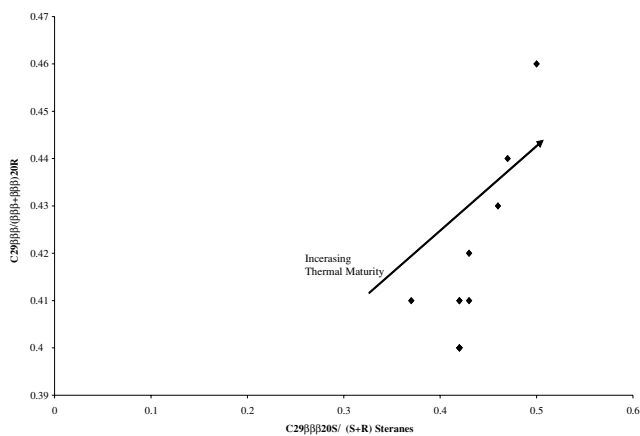


Fig. 5. Cross plot of $C_{29}\alpha\beta\beta_{20}/(\alpha\alpha\alpha + \alpha\beta\beta)$ versus $C_{29}\alpha\alpha\alpha_{20}S/(S + R)$ steranes showing thermal maturity of the oils.

The aromatic biomarker data are evaluated for thermal maturity and biodegradation. The relatively high values of MPI-1 (0.85–1.03) and MPI-2 (0.87–1.11) indicate that these oils are mature (Table 2). The calculated vitrinite reflectance values for the oils are within narrow range of 0.88–0.99% (Table 2), which supports the earlier inference that the oils are mature and suggests that the oils were generated at almost the same level of thermal maturity. The ratio of TAS/(TAS+MAS) that ranged from 0.78–0.97 (Table 2) for these oils also indicates that the oil samples are mature.

The effect of biodegradation on the distribution of aromatic hydrocarbons of these oils was evaluated using 1-MP + 9-MP versus 2-MP + 3-MP (Fig. 6), which discriminated the oils into two distinct groups as did the cross plot of Pr/nC₁₇ versus Pr/nC₁₈. The discrimination is clearly on the basis of biodegradation.

Trace element geochemistry

The transition metals have been found to be very useful in crude oil characterization, especially in oil-oil correlation studies (Curiale, 1987; Barwise, 1990; Udo *et al.*, 1992; Oluwole *et al.*, 1993; Nwachukwu *et al.*, 1995). In this study, special attention is paid on the following transition metals: Co, Cr, Cu, Fe, Ni, and V.

Cobalt ranges from 0.9–32 ppb with average of 14.56 ± 10.6 ppb in the oils. These values are lower than those of Ndiokwere (1983), Udo *et al.* (1992), Oluwole *et al.* (1993) and Nwachukwu *et al.* (1995) (Table 3).

Chromium concentration ranges from 6.2–24 ppb with an average of 10.65 ± 4.52 ppb. These values are lower than the values given in Table 2 obtained by Udo *et al.* (1992), Oluwole *et al.* (1993) and Nwachukwu *et al.* (1995). These values further confirm Hitchon and Filby's (1984) assertion that most oils show no detectable chro-

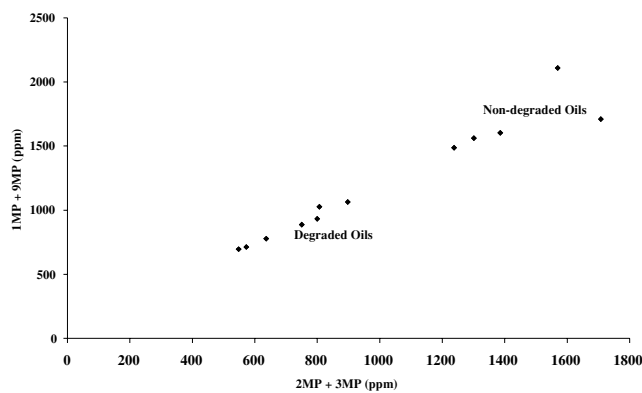


Fig. 6. Cross plot of 1MP + 9MP versus 2MP + 3MP showing that the oils are discriminated on basis of biodegradation.

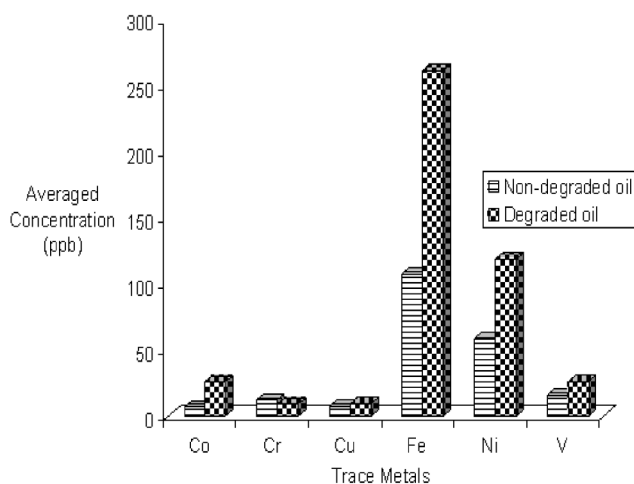


Fig. 7. A chart comparing the trace metal contents of degraded and non-degraded oils from Northwestern Niger Delta, Nigeria.

mium and where it is detectable; it is useful in classifying crude oils (Table 3).

Copper ranges from 3.31–19.4 ppb with an average of 8.06 ± 4.54 ppb. These values are also lower than the values obtained by Udo *et al.* (1992), Oluwole *et al.* (1993), Nwachukwu *et al.* (1995) (Table 3).

Iron concentrations range from 11.4–1241 ppb, averaging 177.36 ppb in the oils (Tables 2(a) and (b)). The values are lower than those of Oluwole *et al.* (1993), Nwachukwu *et al.* (1995) but higher than that of Udo *et al.* (1992) (Table 2).

Nickel concentrations range from 26.3–144.1 ppb with an average of 83.72 ± 37.8 ppb. These values are lower than the values obtained by Ndiokwere (1983), Udo *et al.* (1992), Oluwole *et al.* (1993), and Nwachukwu *et al.* (1995) (Table 2).

The values of vanadium range from 11.0–29.7 ppb

with an average of 19.97 ± 6.90 ppb. These values are also lower than those obtained by Ndiokwere (1983) (Table 3).

Figure 7 is a chart comparing the abundance (averaged concentration) of degraded oils with non-degraded oils. The concentrations of the metals were more in degraded oils than non-degraded oils except Cr. This agreed with the fact that biodegraded oils have more metal contents than non-degraded oils (Udo *et al.*, 1992).

The ratios of transition metals in crude oil are useful in the determination of source rock type, depositional environment and maturation because they remain unchanged irrespective of diagenetic and in-reservoir alteration effects (Lewan, 1984; Barwise, 1990; Udo *et al.*, 1992).

The V/Ni ratios ranged from 0.179 to 0.658 with an

average of 0.32 ± 0.19 for Type A oils (i.e., T1, T3, T6, T8, T9, T10, and T12). The values for Type B ranged from 0.201–0.261 with an average of 0.24 ± 0.03 . The ratios are lower than the values of 0.60–6.60 obtained by Udo *et al.* (1992), for some Niger Delta oils, but slightly higher than average values, 0.15 and 0.16 reported by Nwachukwu *et al.* (1995). This suggests that Type B oils are more mature than Type A oils, because maturity increases with decrease in V/Ni ratio (Barwise, 1990; Udo *et al.*, 1992). However, since the average values are quite close, it suggests similar source rocks for the oils. It also suggests that the source rocks of the oils were deposited where nickelous and vanadyl cation are available but the presence of sulphide and hydroxide ions may hinder their availability for bonding (Lewan, 1984). Barwise (1992) concluded that such low ratios are typical of terrestrially derived source rocks. The values of V/(V + Ni) obtained for the oils range from 0.152–0.397. This is consistent with the values of 0.01–0.69 reported by Nwachukwu (1995), which is indicative of oils derived from terrestrial organic matter.

The Co/Ni ratios are also generally low. They vary from 0.034 to 0.26 (Table 4). Type A oils have averaged Co/Ni ratio of 0.09 ± 0.05 (i.e., <0.1) while Type B oils have averaged Co/Ni ratio of 0.24 ± 0.03 (i.e., >0.1). These values are within the range of 0.09–0.53 and 0.01–0.41 reported by Udo *et al.* (1992) and Nwachukwu *et al.* (1995) respectively. Udo *et al.* (1992) interpreted Co/Ni values greater than 0.1 as indicative of oil source rocks with more marine source input. Type B oils thus show more marine input than Type A oils.

Table 5 shows the Pearson correlation matrix of transition metals and hydrocarbon ratios for the oils. There is a significant and positive correlation between cobalt and nickel ($r = 0.95$), and between cobalt and vanadium ($r = 0.64$).

Table 4. Ratios of selected transition metals in North-western Niger Delta oils

Sample	TTM	V/Ni	Co/Ni	Fe/V	V/V + Ni
Non-degraded oils					
T1	80.93	0.66	0.03	1.22	0.40
T3	744.01	0.49	0.04	25.24	0.33
T6	172.74	0.20	0.14	1.25	0.17
T8	141.35	0.20	0.14	1.48	0.17
T9	112.84	0.18	0.12	1.59	0.15
T10	112.99	0.20	0.17	1.04	0.17
T12	87.53	0.29	0.09	1.61	0.23
Degrade oils					
T2	208.83	0.201	0.21	0.55	0.17
T4	200.64	0.221	0.19	0.66	0.18
T5	215.19	0.261	0.19	0.69	0.21
T7	1471.00	0.194	0.23	44.32	0.16
T11	151.79	0.206	0.26	0.65	0.17

Table 5. Pearson correlation matrix for transition elements, ratios and hydrocarbon ratios of northwestern Niger Delta Oils

	Co	Cr	Cu	Fe	Ni	V	TTM	V/Ni	Co/Ni	Fe/V	Pr/Ph	CPI	Tol/nC ₇
Co	1												
Cr	-0.39	1											
Cu	0.32	0.06	1										
Fe	0.31	0.50	0.30	1									
Ni	0.95	-0.24	0.35	0.34	1								
V	0.64	0.23	0.39	0.48	0.73	1							
TTM	0.15	0.08	-0.02	-0.13	0.30	0.18	1						
V/Ni	-0.6	0.43	-0.15	0.05	-0.61	0.03	-0.18	1					
Co/Ni	0.91	-0.54	0.28	0.08	0.79	0.33	0.07	-0.76	1				
Fe/V	0.27	0.53	0.28	0.99	0.30	0.44	-0.14	0.08	0.04	1			
Pr/Ph	-0.48	-0.09	-0.20	-0.16	-0.56	-0.23	-0.12	0.80	-0.57	-0.16	1		
CPI	0.12	0.04	0.14	0.16	0.12	0.24	-0.29	0.19	-0.231	0.15	0.22	1	
Tol/nC ₇	0.58	-0.01	0.30	0.72	0.43	0.27	-0.2	-0.2	0.56	0.70	-0.13	0.21	1

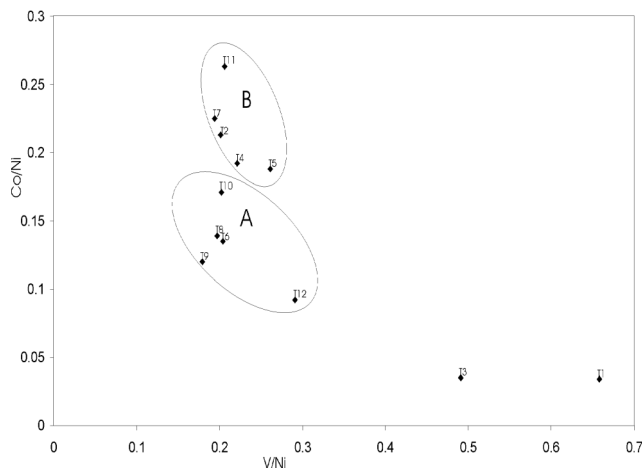


Fig. 8. Cross plot of Co/Ni versus V/Ni.

Vanadium and Nickel also show significant positive correlation ($r = 0.73$), which confirms their genetic association and their close association with organic matter. This suggests Co/Ni and V/Ni ratios can be used as oil classification or correlation tools. It is worth to note that Co/Ni has strong negative correlation ($r = -0.76$) with V/Ni. This suggests that cross plot of these ratios will segregate oils into families Pr/Ph ratio correlates negatively with Ni and V and total transition metal (TTM). This means that concentration of Ni, V, and metals decrease with increase terrestrial input. Pr/Ph ratio correlates strongly with V/Ni ratio. Co, Fe, Fe/V correlate significantly with Toluene/ nC_7 ratio. This indicates that Co, Fe, Fe/V are migration indicators.

Cross plot of Co/Ni versus V/Ni

Similar grouping of the oils as discussed above is also obtained from the plot of Co/Ni versus V/Ni (Fig. 8). It shows that Type A oils are distinct from Type B oils. This is in a good agreement with that of cross plot Pr/ nC_{17} versus Ph/ nC_{18} (Fig. 3).

Type B oils have higher Co/Ni values, indicating more marine input than Type A oils. The V/Ni values for the two groups of oils are about the same and are generally low (0.19–0.65). Such low V/Ni ratios are typical of terrestrially derived source rocks (Barwise, 1990; Udo *et al.*, 1992; Nwachukwu *et al.*, 1995).

The low V/Ni ratios is because of a relatively lower chlorophyll input to such organic matter and a poor level of preservation of any algal derived chlorophylls under the more oxidizing conditions experienced by land-plant organic matter (Barwise, 1990).

Distribution patterns of transition metals

Figure 9(a) shows the transition metals distribution patterns of non-degraded oils to evaluate their similarity

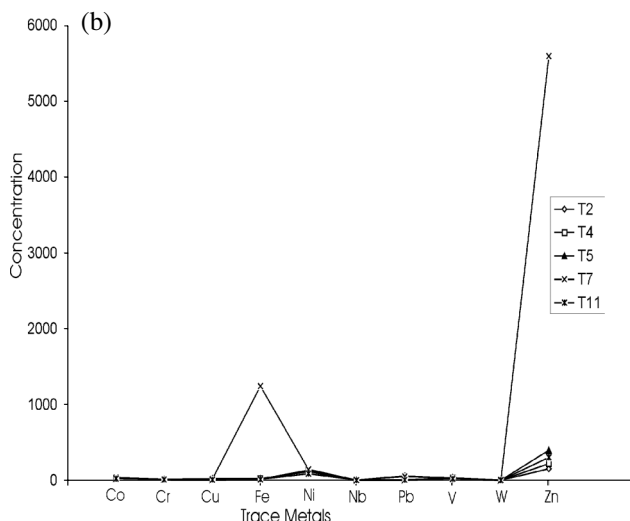
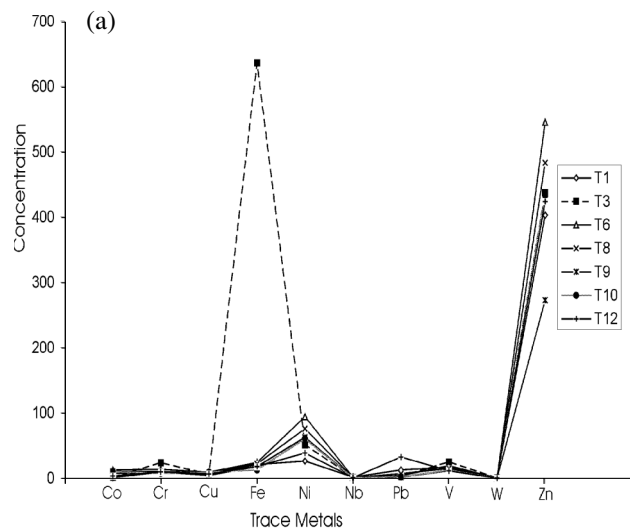


Fig. 9. (a) Transition metals distribution patterns of normal Niger Delta oils. (b) Transition metals distribution patterns of degraded Niger Delta oils.

or otherwise. The non-degraded oils (Type A) show similar and consistent TTM patterns except T3 oil, which has significant high Fe, content. This suggests that these oils were from identical source rocks. Type B (degraded) oils also have similar and consistent TTM patterns except for which T7 oil has relatively higher Fe and Zn contents (Fig. 9(b)). The similarity in the patterns indicates that Type B oils have identical source rocks. There is also similarity in the distribution pattern of transition metals of both Type A (normal) and Type B (degraded) oils. This further confirms that the two oil groups are genetically related, only that Type B oils are biodegraded equivalents of Type A oils.

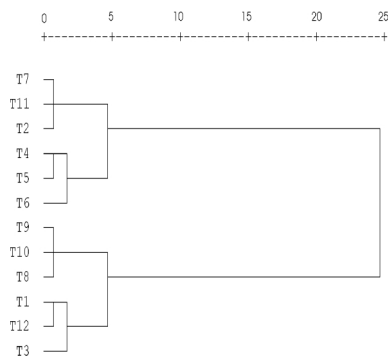


Fig. 10. Dendrogram for Niger Delta oils using Co, Ni, V as variables.

Oil typing using transition metals

Statistical evaluation of these oils on the basis trace metals was done to determine their similarity or otherwise using cluster analysis. Cluster analysis is very useful in establishing different families within a given suite of oils. On the *x*-axis of dendrogram are the samples indicated by their numbers while on the *y*-axis is the similarity matrix using euclidean distance. Figure 10 shows dendrogram cluster analysis of the oils analyzed using Co, Ni and V as variables (i.e., metals of proven association with organic matter). Two groups are evident. Non-degraded oils form one group with the exception of T6, which was wrongly misclassified while degraded oils form another group. This probably suggests that subtle biodegradation process is already being initiated in this oil sample. Cluster analysis of the oils using trace metals has been able to discriminate the oils on the basis of biodegradation. Thus, indicates that trace metals are useful in oil classification. This also indicates that the trace metal data compliment well with the organic geochemical data.

CONCLUSIONS

Organic geochemical data revealed that there are two main families of oils in this part of Niger Delta—Type A oils that are non-degraded oils and Type B oils which are slightly degraded oils. These oils are derived from organic matter deposited in less reducing transitional environments. All the organic geochemical data considered indicated that the two oil families are genetically related. The abundance of paraffin and isoprenoid hydrocarbons revealed that these oils are derived from organic matter of mixed terrestrial/marine input but with a preponderance of terrestrial organic matter. The results of biomarker analysis also indicate that the oils have mixed origin with higher terrestrial organic matter input, and revealed that the oils are mature. Classification on the basis of biomarkers also shows two groups of oils; degraded oils

and non-degraded oils.

The transition metal data particularly the cross plot of Co/Ni versus V/Ni also revealed two main oil groups (normal—Type A and degraded—Type B). This is in a good agreement with the results of organic geochemical data. Transition metal geochemistry also showed that these oils are derived from organic matter deposited in more oxidizing transitional environments. Transition metals distribution patterns indicated that both Type A (normal) and Type B (degraded) these oils are genetically related. Generally low concentrations of transition elements suggested strong terrestrial input.

In this study, we have successfully used organic and inorganic geochemical data to evaluate the petroleum system of northwestern Niger Delta, which forms a basis for application in the Niger Delta Basin or elsewhere. Generally, integrated organic and inorganic geochemistry approach provides a reliable and thorough evaluation of this field.

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