Journal of Mining and Geology Vol. 40(1) 2004, pp. 29-40 © Nigerian Mining and Geosciences Society (NMGS) - Printed in Nigeria

Organic geochemical appraisal of limestones and shales in part of eastern Dahomey Basin, southwestern Nigeria

ANTHONY A. ELUEZE and MATTHEW E. NTON Department of Geology, University of Ibadan, Ibadan, Nigeria

Abstract

The major lithostratigraphic units of the eastern Dahomey Basin are the Araromi, Ewekoro and Akinbo Formations. Field studies show that the Araromi and Akinbo Formations contain shaly facies, while the Ewekoro Formation contains essentially fossiliferous limestones. The Araromi shales are dark and bituminous, while those of the Akinbo are fissile and concretionary. Selected subsurface and outcrop samples of these lithotypes were analysed to ascertain their palaeodepositional environments and hydrocarbon prospects.

Total organic carbon (TOC) of the limestones and shales range from 0.10 to 1.00 wt.% and 0.20 to 1.60wt% respectively. Bitumen yields are 896.20, 108.70 and 376.80ppm correspondingly for Araromi, Ewekoro and Akinbo Formations. Bitumen ratios are 68.70, 28.30 and 72.70mgext/g TOC respectively, for the three succeeding formations.

CPI values and pristane/phytane ratios are 1.29, 1.19, 0.99 and 1.53, 1.33, 1.17, respectively for Araromi, Ewekoro and Akinbo Formations. Cross-plots of isoprenoids/n-alkanes show that the organic matter falls within the terrestrial and transitional environments. However, the fossil assemblages of the limestones made up of coralline algae, pelecypods, echinoids, gastropods and few other skeletal debris, indicate a nearshore marine environment. Organic petrography reveals preponderance of vitrinites (Type III O.M.) with subordinate inertinites (Type IV) in all the three formations. The dominance of terrestrial O.M. indicates gas rather than oil proneness of the kerogen.

N-alkane profiles, plots of bitumen ratios with depth and the presence of unresolved complex mixture hydrocarbons in most gas chromatograms, indicate immature status for the kerogens. This suggests insufficient cooking of the sediments.

Introduction

The Dahomey Basin covers much of the continental margin of the Gulf of Guinea. It extends from the Volta delta in Ghana in the West, to the Okitipupa Ridge in Nigeria in the east (Fig. 1). It is a marginal pull-apart basin (Klemme, 1975) or marginal sag basin (Kingston et al, 1983) which developed in the Mesozoic as the African and South American lithospheric plates separated and the continental margin foundered (Burke et al., 1971; Whiteman, 1982). The basin contains extensive wedge of Cretaceous to Recent sediments up to 3,000m, which thicken from the onshore margin (where the predominantly clastic Cretaceous sediments rest on the basement) to the offshore. Within the offshore area, thick, fine-grained, Cenozoic



Fig. 1. East-west geological section showing position, extent and sediment thickness variations in the onshore Dahomey Basin and the upper part of the Niger Delta (after Whiteman', 1982)

sediments cover the basin (Whiteman 1982; Schlumberger, 1985). The axis of the basin and the thickest sediments occur slightly west of the border between Nigeria and the Republic of Benin (Slanky, 1962; Billman, 1992).

The geology, stratigraphy, sedimentology and organic geochemical studies of different parts of the basin have been reported in the literature (Jones and Hockey, 1964; Fayose, 1970; Adegoke, 1980; Omatsola and Adegoke, 1981; Coker et al; 1983; Nwachukwu and Adedayo, 1987; Ekweozor and Nwachukwu, 1989; Ekweozor, 1990; Mosunmolu Ltd, 1991; Idowu et al., 1993; Nton, 2001).

The eastern Dahomey basin has proved to be of great geological interest, particularly because of extensive occurrences of limestones and bitumen. Exploration activity commenced in this sector of the basin in 1908, near Okitipupa, east of Lagos, where bituminous sands outcrop. Such investigations were later abandoned and the wells termed "dry." With the discovery of oil in the Niger Delta in 1956, focus shifted from the eastern Dahomey basin to the Niger Delta. Recently due to increased government incentive to prospectors, and re-evaluation of data gathered from such unsuccessful attempts, there is a resurgence of interest in exploration activities in the eastern Dahomey basin.

Also, it is relevant to note that conventional hydrocarbons in commercial quantity, have been found offshore in the Republic of Benin (Billman, 1992). However, in comparison with the adjacent Niger Delta, few studies have been conducted in the eastern Dahomey basin in terms of hydrocarbon potential. For several years, attention has been focused on the black shales in the Agbabu area, associated with the tarsands of the Afowo and Araromi Formations (Enu, 1987). The present study, is a regional approach at evaluating the associated shales and limestones of Araromi, Ewekoro and Akinbo Formations in an attempt to highlight their palaeo-depositional environment as well as provide additional geochemical information on the source rocks. Such information would be useful to researchers and explorationists.

Stratigraphy of eastern Dahomey Basin

The study area lies between latitudes 6°45' to 7°00'N and longitudes 3°00' to 4°00'E and falls within the eastern Dahomey Basin (Fig. 2). The stratigraphic descriptions of sediments in the eastern Dahomey basin have been presented by Fayose (1970); Jones and Hockey (1964); Ogbe (1972); Omatsola and Adegoke (1981); Nwachukwu et al. (1992); and Nton (2001) among others. However, there are still controversies on age assignment and nomenclatures of the different lithounits.

Omatsola and Adegoke (1981) proposed the Cretaceous stratigraphy of eastern Dahomey basin as beginning with the Ise Formation at the base, overlain by the Afowo and Araromi Formations successively. The Ise Formation overlies the basement complex of southwestern Nigeria and consists of conglomerates and grits at base and in turn overlain by coarse to medium grained loose sands with inter-bedded kaolinite. The conglomerates are unimbricated and at some locations, ironstones occur. Both the cross-bedding azimuths of the sandstones and the pebble alignments point to a NE – palaeo-current system (Nton, 2001). The age is Neocomian to Albian.

The Afowo Formation is composed of medium grained sandstones with inter-bedded shales, siltstones and claystones. The sandy facies are tar bearing around Okitipupa, while the shales are organic-rich (Enu, 1990). The lower part of this formation is transitional with mixed brackish to marginal horizons that alternate with well sorted, subrounded sands. These indicate a littoral or estuarine near-shore environment in which water level fluctuates. Billman (1992) assigned a Turonian age to this formation while the upper part ranges into the Maastrichtian.

The Araromi Formation is the youngest of the Cretaceous sediments in the eastern Dahomey Basin (Omatsola and Adegoke, 1981). It is composed of fine to medium grained sandstones at base, overlain by shales and siltstones with inter-bedded limestone, marl and lignite. The shales are light grey to black and organic-rich. The age is Maastrichtian to Palaeocene.

Overlying the Araromi Formation is a predominantly Inmestone sediments which constitutes the Ewekoro Formation. It is an extensive limestone body, which is traceable over a distance of about 320km continuously from Ghana eastward, towards the eastern margin of the Dahomey basin in Nigeria. The limestone is about 15m thick at the Ewekoro quarry while at Sagamu quarry, it is about 20m. It is thickly bedded and colour banded. Apart from the quarry exposures, outcrops are rare and are intercepted in several boreholes west of Ijebu Ode. It is Palaeocene in age and associated with shallow marine environment due to abundance of coralline algae, gastropods, pelecypods, echinoid fragments and other skeletal debris (Nton, 2001).

The Akinbo Formation (Ogbe, 1972) overlies the Ewekoro Formation and consists of shale, clayey sequence. The base of the formation is defined by the presence of a glauconitic band. The type locality is at the Ewekoro quarry. East of Ijebu Ode, the formation replaces the Ewekoro Formation, which thins-out here. Westward, the formation extends into the Republic of Benin and Togo (Slanky, 1962). In the field, the shales are grey, fissile, clayey and concretionary and dip gently (<5°SW) (Nton, 2001). The age of the formation is Palaeocene to Eocene age.

The Oshosun Formation overlies the Akinbo Formation and consists of greenish – grey or beige clay and shale with interbeds of sandstones. The shae is thickly laminated and glauconitic. According to Okosun (1998), the basal beds consist of any of the following facies; sandstones, mudstones, claystones, clay-shale or shale. This formation is phosphate- bearing and is compositionally phosphorite (Nton, 2001).

Overlying the Oshosun Formation is the Ilaro Formation which consists of massive, yellowish, poorly consolidated, cross- bedded sandstones. The youngest stratigraphic sequence in the eastern Dahomey basin is the Benin Formation. It consists of poorly sorted sands with lenses of clays. The sands are in parts cross-bedded and show transitional to continental characteristics. The age is from Oligocene to Recent.

Materials and methods

Both outcrop and core samples were used for this study. The outcrops were sampled at the West African Portland Cement Company PLC quarries at Ewekoro and Shagamu while the core samples are from wells drilled around Somo, near Shagamu and Itori 1583 (Fig. 2). Core samples from both wells were obtained from the Geological Survey Department, Federal Ministry of Solid Minerals Development, Abeokuta and Kaduna offices respectively.

The limestone outcrops are 15m and 20metres thick, respectively at the Ewekoro and Shagamu quarries.



Generally, they are grayish, thickly bedded, colour banded and fossiliferous. Other limestone units were encountered from the cores at Somo and Itori 1583 wells. Shales of the Akinbo Formation are also well exposed at both quarries. The shales are fissile, gently dipping, concretionary and clayey. In Somo well D, the thickness of the Akinbo Formation is over 20m. They were also sampled at Somo B, C and F wells. The shaly units of Araromi Formation were sampled only in Somo C and Itori 1583 wells. In Itori 1583 well, the colour is dark and carbonaceous. Details of the lithostratigraphy of both the outcrops and core samples are shown in Figs. 3 and 4.

Analytical methods

Total organic carbon

A total of 63 core and outcrop samples made up of 41 limestones from Ewekoro Formation, and 22 shale samples of Araromi and Akinbo Formations were pulverized (2gm each) and subjected to Total organic carbon (TOC) determination.







Fig. 4.Schematic representation of core samples used in this study. A-F (Somo wells) and Itori 1583

This analysis was done by chromic acid oxidation method of Wakley and Black (1934) at the Geological Laboratory, University of Ibadan.

Bitumen extraction

Based on TOC threshold values of 0.30 and 0.50 wt %, for limestone and shale respectively (Tissot and Welte, 1984), which provided a preliminary screening method, 23 samples, made up of 13 limestones and 10 shales were pulverized, sieved and extracted for soluble organic matter. About 30 - 55gm of each sample was taken into cellulose timbles and extracted in a standard Soxhlet apparatus using dichloromethane in 250m1 round bottom flask containing activated copper in a set of four (4) extractors, for 24 hours. The soluble organic matter (bitumen) was evaporated and concentrations computed in parts per million for each sample.

Gas chromatography

Gas chromatography of the extracts was performed with an HP 5890A SERIES 2^{TM} gas chromatograph, equipped with a flame ionization detector. The gas chromatograph was fitted with a 50m x 0.2mm x 0.5mm film thickness PONA (Paraffins, Olefins, Napthanes and Aromatics) cross linked methyl siloxane capillary column. Hydrogen was used as carrier gas. The column oven temperature was programmed from 30 to 40°C at 1°C/mm., 2°C/mm. to 75°C; 4°C/min. to 305°C and held isothermally for 20 minutes. The injection port temperature was set at 300°C with a split ratio of 400:1. The carrier gas flow rate was 0.5m1/min.

The bitumen extract was diluted with a drop of dichloromethane and 0.2µl of the extract was rapidly injected into the gas chromatograph in split mode, using a graduated Hp injection syringe. Chromatographic data were acquired using an HP Vectra XM series 3 computer. Peak integration and associated data processing were accomplished using HP Chemstation software. For a single run, the complete retention time is 107. 5mins. Peak identification was accomplished by matching chromatographic peaks and profiles using HP Naptha standards. The pristane and phytane peaks were also used to confirm the isoprenoids and the n-alkane distribution. Both the bitumen extraction and the gas chromatography were conducted at Chevron Geochemical Laboratory, Lekki, Lagos.

Organic petrography

Organic petrographic analysis was conducted on selected, pulverized samples based on TOC adequacy. The procedure for the determination of maceral composition involves the preparation of polished section as done by coal petrologists. A reflected light microscope, fitted with x 32 oil immersion objective (Leitz orthoplan polarising microscope) was used for the study of the macerals The relative quantities were estimated statistically based on point counting method of Powell et al. (1982). The major maceral and submaceral groups were estimated as percentages. The analysis was conducted at the Geological Laboratory, University of Ilorin.

Thin section petrography

Selected limestone chips were smoothened and mounted on glass strip by means of canada balsam. The mounted chips were then grounded down to the required thickness with carborundum. The prepared slides were examined under the flat stage of a petrographic microscope. Point count method was used for studying the allochems, sparites and micrites. The slide preparation was done at Geological Laboratory, Obafemi Awolowo University, Ile-Ife, while the petrographic study was undertaken at the Geological Laboratory, University of Ibadan. Details of all the analytical procedures are documented in Nton (2001).

Discussions of results

Organic matter quantity

Total organic carbon data for the samples are presented in Table 1. Adequate amount of organic matter measured as percentage total organic carbon (TOC) is necessary prerequisite for sediment to generate oil or gas (Cornford, 1986). The limestones from the Ewekoro Formation have values that range from 0.10 to 1.00 wt%, while the shales from Araromi and Akinbo Formations are from 0.10 to 1.60wt % Total organic carbon. Average values of TOC are 1.29wt %, 0.41 wt%, and 0.53wt% for Araromi, Ewekoro and Akinbo Formations respectively. These values indicate that the sediments have satisfied the required threshold values of 0.30wt% and 0.50wt% for non clastic and clastic rocks respectively to generate petroleum (Tissot and Welte, 1984).

The soluble organic matter (SOM) content of the sediments ranges from 30.90 to 1583. 20 ppm (Table 2). The respective average values for the different formations are 896.20ppm, 108.70ppm and 376.80ppm for Araromi, Ewekoro and Akinbo. Based on the quality definition concept of Hunt and Meinert (1954); Baker (1972), the organic matter is adequate, particulariy from the shales of Araromi and Akinbo Formations for the generation of hydrocarbon.

	% T.O.C	0.50	0.30	0.20	0.20	0.10	0.20	0.10	0.20	0.20	0.30	0.60	0.30	1.00	1.60	1.04	1.40	1.60	1.60						
	Rock type	Shale	Shale	Limestone	Shale	Shale	Shale	Shale	Shale																
	Formation	Akinbo	Akinbo	Ewekoro	Ewekoro	Ewekoro	Ewekoro	Ewkoro	Ewkoro	Ewekoro	Ewekoro	Ewkoro	Ewkoro	Ewkoro	Araromi	Araromi	Aroromi	Araromi	Araromi						
mestones	Sample No	SQI	SQ2	SQ3	SQ4	SQ5	SQ6	SQ7	SQ8	SQ9	SQ10	SQN	IT6	IT8	IT12	IT13A	IT13B	IT14	IT17	(a					
nales and li	% T.O.C	0.40	0.50	0.50	0.50	0.40	0.40		0.30	0.20	0.20	0.40	0.30	0.20	0.10	0.20	0.20	0.20	0.30	0.30	0.20	0.20	0.10	0.10	0.10
(T.O.C) for sl	Rock Type	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone		Shale	Shale	Shale	Limestone													
rganic carbor	Formation	Ewekoro	Ewekoro	Ewekoro	Ewekoro .	Ewekoro	Ewekoro		Akinbo	Akinbo	Akinbo	Ewekoro	Ewekoro	Ewekoro	Ewekoro	Ewkoro	Ewekoro								
ble 1. Total or	Sample No	Somo E17	Somo E16	Somo E23	Somo E24	Somo E29	Somo E30		Somo F10	Somo F11	Somo F12	Somo F16	EQ3	EQ4	EQ5	EQ6	EQ7	EQ8	EQ9	EQ10	EQ11	EQ12	EQ13	EQ14	EQ15
T	% T.O.C	0.50	0.30	0.40	0.30	0.40	0.30			0.40	0.30	0.30	0.30	0.20	0.40	0.40	0.50	0.60	0.30	0.20	0.20	0.50	0.30	0.50	0.20
	Rock Type	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone			Shale	Shale	Limestone	Limestone	Limestone	Limestone	Shale									
	Formation	Ewekoro	Ewekoro	Ewekoro	Ewekoro	Ewekoro	Ewekoro			Akinbo	Akinbo	Ewekoro	Ewekoro	Ewekoro	Ewekoro	Araromo	Araromi	Akinbo							
	Sample No	Somo A11	Somo A12	Somo A13	Somo A15	Somo A18	Somo A22			Somo B8	Somo B12	Somo B15	Somo B17	Somo B19	Somo C9	Somo C20	Somo C22	Somo D3	Somo D5	Somo D8	Somo D12	Somo D20	Somo D23	Somo D25	Somo D7

Table 2. Results of extraction of soluble organic matter

Sample No	Formation	Lithology	S.O.M (ppm)	T.O.C (wt %)	S.O.M/ T.O.C (mgextr/g TOC)
SomoA11 SomoA12	Ewekoro Ewekoro	Limestone Limestone	90 70.9	0.5 0.3	18 24
SomoA13	Ewekoro	Limestone	30.9	0.4	7.7
SomoA15	Ewekoro	Limestone	187.5	0.3	62.5
SomoC9	Ewekoro	Limestone	67.5	0.4	16.9
SomoC22	Araromi	Shale	375	0.5	75
SomoD3	Akinbo	Shale	325.7	0.6	54.3
SomoD20	Akinbo	Shale	423.3	0.5	84.7
SomoC25	Akinbo	Shale	706.7	0.5	141.3
SomoF16	Ewekoro	Limestone	40	0.4	10.0
SQ1	Akinbo	Shale	51.4	0.5	10.3
SQ10	Ewekoro	Limestone	42.2	0.3	14.1
SQ11	Ewekoro	Limestone	78.2	0.6	13.0
EQ3	Ewekoro	Limestone	198	0.3	66.0
EQ4	Ewekoro	Limestone	60	0.3	20.0
EQ9	Ewekoro	Limestone	98	0.3	32.7
IT6	Ewekoro	Limestone	163.3	0.3	54.4
IT8	Ewekoro	Limestone	285.7	1.0	28.6
IT12	Araromi	Shale	1538	1.6	96.1
IT13A	Araromi	Shale	402	1.04	38.7
IT13B	Araromi	Shale	1222.0	1.4	87.3
IT14	Araromi	Shale	257.1	1.6	16.1
JT17	Araromi	Shale	1583.3	1.6	99.0

Zx103 SOMISSMI

TOC (#1%) 1=103 2=103 SOM [ppm] TOCIWI WI 1x10³ 2x10³ SOM (spm) 1.0 2.0 Depth im! Depthtm 10 D 1=103 2 = 103 SOM Lasm TOC INT VA 1+10³ 3=10³ SOM (9 pm TO C (#1%) 1.0 2.0 Depth 1m1 11

Variations of soluble organic matter with depth for some of the different wells and outcrop samples are shown in Fig. 5. In Somo well A (Fig.5a), the TOC and the SOM decrease with depth for the limited data. In Somo well C (Fig. 5c), there is increase in TOC and SOM with depth. In Somo well (Fig. 5d), the soluble organic matter increases from 16.80 to 21m. There is also higher SOM value at shallow depth, which slightly correlates with the TOC. This may be due to additives of the drilling fluids. In Itori 1583, (Fig. 5 IT), the SOM shows an increase at 58m and decreases at 64m with a rather sharp increase at 72m. TOC values also show similar trends with depth. This interval (72m) may point to the organic - rich facies of the Araromi Formation with high bitumen yield. At Sagamu quarry (Fig. 5 SQ), TOC is relatively high at shallow depth while SOM values tend to increase. Since the yield increases with depth, it may be argued that the lower unit may be close to Araromi Formation in the subsurface which has been reported to be tar-bearing (Ekweozor 1990, Ekweozor and Nwachukwu, 1989). On the other hard, samples from the Ewekoro quarry (Fig. 5 EQ) show TOC decrease with depth. Clastic influx resulting in dilution may be associated with these low values. This corroborates the findings of Idowu et al., (1993).

Organic matter type

TOC / w1 %)

The application of organic petrography to the generation of oil and gas from organic matter in sedimentary rocks and coals, has been demonstrated and widely documented (Murchison, 1987; Bordenave, 1993). It is obvious that the



50 M WELL C 50 MO 5040 WELL D EQ = EWELORO QUAREY SHAGAMU QUARRY ITORI ISES WELL

Fig. 5. Variations of soluble organic matter and total organic carbon with depth

generation of oil and gas is related to the rank, quality and type of organic matter or macerals. Kerogen, which is a complex material, which vary in composition depending on its source, can be correlated with macerals in organic petrography (Murchison, 1987). formations is shown in Table 3. The average vitrinite, liptinite, inertinite and mineral matter are respectively 53.30%, 7.60%, 35.60% and 1.80% (Araromi Formation); 29.10%, 6.60%, 29.40% and 39.90% (Ewekoro Formation); and 42.60%, 8.20%, 36.40% and 12.80% (Akinbo Formation).

The summary of maceral counts for the different

Table 3. Summary of major maceral groups in study area

ANINGO FORMATION												
Maceral group	Sample No.	SQ1	Somo D3	Somo D20	Somo D25	Average						
Vitrinite Liptinite Inertinite		43.5 6.0 41.6	28.2 10.4 20.6	50.8 6.9 42.0	47.9 9.7 41.2	42.6 8.2 36.4						
Mineral Matter		8.9	40.8	0.3	1.2	12.8						

EWEKORO FORMATION

Maceral group	Sample No.	EQ3	EQ9	EQ11	SomoA11	SomoA13	SomoA15	SomoC9	Somo	IT6	IT8	Average
Vitrinite			46.3	23.3	31.5	36.2	37.4	14.5	33.3	15.3	54.9	29.1
Liptinite			4.4	7.9	4.6	7.9	10.4	5.3	10.2		14.9	6.6
Inertinite		10.6	34.2	24.2	30.6	29.1	30.3	22.0	33.2	1.0	29.3	24.4
Mineral Matter		89.4	15.1	45.6	33.3	26.8	21.9	58.2	24.4	83.7	0.9	39.9

Maceral group Sample No. SomoC22 IT12 **IT13A** IT13B IT14 IT17 Average -> Vitrinite 58.9 54.4 57.0 47.9 56.6 55.3 Liptinite 5.8 10.5 5.2 5.7 13.3 5.1 7.6 Inertinite 53.0 34.1 34.3 35.8 38.4 33.9 35.3 Mineral Matter 2.1 1.0 1.6 1.5 0.4 4.4 1.8

ARAROMI FORMATION

It had earlier been pointed out from few studied wells, that the preponderance of vitrinite with subordinate inertinite in eastern Dahomey basin indicates prospects for generation of gas (Nton and Elueze, 1999). In this study, incorporation of more data based on regional studies within the basin, strongly indicate terrestrial organic matter (Type III). These further confirm that the sediments therefore have prospects to generate gas rather than oil in the basin.

Maturity of organic matter

Thermal maturity describes the extent of heat-driven reactions, which convert sedimentary organic matter into petroleum (Peters and Moldowan, 1993). In general terms, organic matter can be described as immature, mature or postmature, depending on its relation to the oil generative window (Tissot and Welte 1984). In this study, the level of maturity of the organic matter is determined on the basis of the following parameters.

N - alkane profiles

The normalized GC data for the n-alkanes are documented in Nton (2001). A typical n-alkane profile from gas chromatogram for the sediments is shown in Fig. 6 and their CPI values arising from the profiles are shown in Table 4. The average CPI values determined from the gas chromatograms for Araromi, Ewekoro and Akinbo Formations are 1.21, 1.19 and 0.99 respectively (Table 4). Hunt (1979) has pointed out that sediments with CPI of 1 at the surface and at all depth, indicate marine source, while CPI considerably >1 shows contribution from continental plants and also immature. Mosunmolu Ltd. (1991) has reported CPI values of 1.24 and 1.26 for sediments of Benin West -1 and Baba - 1 wells from the same basin and associated these with immature sediments and presence of terrestrial organic matter. In this study, >60% of the sediments have CPI >1 (Table 4) and point to immature sediments with terrestrial organic input.



Table 4. Gas chromatographic data showing values of isoprenoids, isoprenoids/N-alkane ratios and their carbon preference indices

Sample No	Fomation	Pr/Ph	Pr/nc17	Ph/nc18	CPI		
SQ1	Akinbo	2.38	5.35	0.27	1.11		
SomoD20	Akinbo	0.46	3.70	1.51	0.95		
Somo D25	Akinbo	0.66	1.47	0.59	0.91		
Somo F16	Ewekoro	3.87	0.66	0.08	1.04		
EQ3	Ewekoro	0.23	2.83	1.97	1.84		
EQ9	Ewekoro	1.92	1.30	0.36	1.02		
SQ10	Ewekoro	2.30	0.07	0.10	1.17		
SQII	Ewekoro	1.00	0.88	1.29	0.64		
SomoA11	Ewekoro	0.54	0.35	1.95	1.41		
SomoA13	Ewekoro	0.14	3.42	6.02	1.11		
SomoA15	Ewekoro	0.84	0.27	0.59	1.09		
IT6	Ewekoro	1.82	1.41	0.71	1.81		
IT8	Ewekoro	0.47	1.04	1.39	0.76		
IT12	Araromi	5.26	0.88	0.10	1.43		
IT13A	Araromi	0.35	0.15	0.21	0.97		
IT13B	Araromi	1.10	0.26	0.05	0.55		
IT14	Araromi	0.64	0.45	0.25	1.44		
IT17	Araromi	1.05	0.46	0.19	1.79		
SomoC22	Araromi	0.79	0.39	0.44	1.10		

Maxwell et al. (1971) have shown that strong odd / even bias of heavy n-alkanes is indicative of sediment immaturity. Earlier, Nton (2001) reported that most of the sediments (Somo A₁₁, EQ₃, EQ₉, IT₆, IT₁₂, IT₁₄) show strong odd/even bias, indicative that the sediments are immature. A typical gas chromatogram of one of the samples has a hump of unresolved complex mixture (ucm) (Fig. 6). Mosunmolu Ltd. (1991) has reported similar chromatograms from some wells in eastern Dahomey basin, which were explained as typical of immature sediments. Killops and A1-Juboori, (1990) associated such hump with biodegraded petroleum. The aspect of biodegradation may not be ruled out in this study since such had been reported (Ekweozor and Nwachukwu 1989). However, other indicators strongly support immaturity of the sediments of the eastern Dahomey basin.

Bitumen ratio

The ratio of extractable bitumen to total organic carbon (Bitumen/TOC), sometimes called Transformation Ratio, can be used in determining sediment maturity (Peters and Moldowan, 1993). It has been pointed out that such values range from near zero in shallow sediments to about 250mg/g TOC at the peak of oil generation. In this study, the bitumen ratio is from 7.7 to 141.3mg/g TOC (Table 2). This range indicates immature sediments. It has been demonstrated that at greater depths, these values decrease as a result of conversion of bitumen to gas (Peters and Moldowan, 1993).

From the plots of bitumen ratio with depth, (Figs. 7a & b), it can be observed that in Itori 1583 well, sustained increase occur at depth of 68m while in Somo well D, there is continuous increase of bitumen ratio with depth. However, since the ratio of 141.3mg/g TOC (at depth 21m in Fig.7a or sample Somo D 25 in Table 2) does not correlate with the low TOC value of 0.5wt% this value may be

36

associated with migrated oil. In Somo well A, with few sampling points, there is likelihood of sustained increase at 8m. At the Ewekoro quarry (Fig.7b), there is sustained

2

4

increase (though with few sampling points) at 7m while the Shagamu quarry has no distinct trend for reasonable interpretation.





Top of mature zone or "oil kitchen" Cannon (1974) proposed the threshold of intense hydrocarbon generation (TIGH) or the top of "oil kitchen" as the point of inflexion arising from a consistent variation of CPI with depth. In this study, such consistent pattern is not quite observable, however in Itori 1583 well (Fig. 7a), the possible points of inflexion are 35 and 62m, but the 35m depth does not correlate with high bitumen ratio (Fig. 7a). The TIGH may therefore be placed at 62m in this well. In Somo A, the data is not sufficient to allow for reasonable deductions while no meaningful trends can be obtained from other wells and outcrops (Figs. 7a and b). From the study, TIGH of 62m is very shallow when compared with the top of the "oil kitchen" of 1818m and 2727m reported respectively for B-1 and Benin West - 1 wells within the eastern Dahomey basin (Mosunmolu Ltd, 1991).

The mature bed in B-1 well, is associated with Ise Formation, while that of Benin West – 1 well is from the Araromi Formation. The vitrinite reflectance (R) for the mature intervals is 0.6%, while estimated generating capacity of 123 x 10 bbls/cm has been reported for B -1 well. The organic matter also shows vitrinite and inertinite, which characterize them as humic (Mosunmolu Ltd. 1991)

It can therefore be deduced that the sediments of eastern Dahomey basin have adequate organic matter, from terrestrial biota; which is immature. It is however likely that mature strata may be intercepted at greater depths, most probably from the deep offshore within the Araromi Formation. These views have been expressed by Ekweozor and Nwachukwu (1989); Ekweozor (1990); Mosunmolu Ltd (1991), Nton (2001).

Depositional environment

Petrographic studies of the associated limestones show the presence of gastropods, coralline algae, pelecypods, echinoid fragments and other skeletal debris (Figs. 8 and 9). Such an assemblage points to a shallow marine environment (Black, 1970). Didyke et al. (1978) have indicated that the pristane/phytane (Pr/Ph) ratio of sediments can indicate the environment of deposition. According to them, Pr/Ph ratios <1 indicate anoxic deposition while oxic conditions are indicated by ratios >1. The accuracy of these generalization has been challenged often times. Pratt (1984) has therefore suggested that for accurate environmental interpretation, geological data should be incorporated since the ratio decreases with catagenesis. In this study, the Pr/Ph ratio for the samples ranges from 0.14 – 5.26 (Table 4). The average Pr/Ph ratios for Araromi, Ewekoro and Akinbo Formations are respectively 1.53, 1.31 and 1.17 which indicate oxidizing environment for the sediments (Lijmbach, 1975; Didyke et al. 1978).



Fig. 8. Photomicrograph under crossed nicols of algal mat (am) encrusting micrite in sample EQ 13 X 40



Fig. 9. Photomicrograph under crossed meols of biomicrite showing gastropod (g) in longitudinal section in sample SQ11 X40

The prevalence of terrestrial organic matter in the sediments (Types III and IV kerogens) favour a continental environment where oxic conditions prevail. In addition, the relative higher concentrations of high molecular weight n-alkanes from the gas chromatograms further indicate organic input form terrestrial plants (Hunt, 1979).

Cross plots of isoprenoids /n-alkanes (Fig. 10) reveal that the majority of the sediments were deposited in oxidizing environments. Average ratios from the plots of Pr/nCl7 versus Ph/nCl8 for the Araromi and Ewekoro sediments fall within the transitional environment, while the Akinbo shales indicate terrestrial organic matter source.



Conclusions

Organic geochemical studies of the shaley facies, belonging to Araromi and Akinbo Formations, as well as the fossiliferous limestone of Ewekoro Formation, within the eastern Dahomey Basin were carried out to ascertain their depositional environment and hydrocarbon potential.

Results show that the organic richness is adequate (particularly with the shales of Araromi and Akinbo Formations), with mainly Type III and subordinate Type IV organic matter. These indicate dominance of terrestrial organic matter, having gas rather than oil proneness of the kerogens. Fossil assemblages associated with the limestone are made of coralline algae, pelecypods, echinoids, gastropods and other skeletal debris and deduced nearshore marine environment for the sediments. The N-alkane profiles, plots of bitumen ratios with depth and presence of unresolved complex mixture hydrocarbon in the gas chromatograms indicate low maturity status for the sediments arising from insufficient cooking time.

It is necessary to examine deeper cores, with increased sampling density, for a thorogh understanding of the

- ADEGOKE, 0. S., 1980. Relevant Geosciences. Discuss, Nigeria Academy of Science. pp. 31-33.
- BAKER, D.R. 1972. Organic geochemistry and geological interpretations. J. Geol. Ed.; 20(5) pp. 221-234.
- BLACK, R. M., 1970. The Elements of Palaeontology. Cambridge University Press; 339p.
- BILLMAN, H.G; 1992. Offshore stratigraphy and Paleontology of the Dahomey Embayment, West African. Nigerian Association of Petroleum Exploration Bulletin, Vol. 7 (2), pp. 121-139.
- BORDENAVE, M.L., 1993. The vitrinite reflectance as a geological interpretation tool. In J. Bordenave (ed). Applied Petroleum Geochemistry. Edition technip, Paris. pp. 290-314.
- BURKE, K.C.B., DESSAUVAGIE, T. F. J.; WHITEMAN A.J., 1971. The opening of the Gulf of Guinea and the Geological History of the Benue Depression and Niger Delta. Nature, Physical Science, 233 (38), pp. 51-55.
- COKER, S.J., EJEDAWE, J.E. and OSHIORIENUA, J.A., 1983. Hydrocarbon source potentials of Cretaceous rocks of Okitipupa Uplift, Nigeria. Journal of Mining and Geology. Vol. 2, pp.163-169.
- CONFORD, C., 1986. Source rocks and hydrocarbons of the North sea. In: K.W. Glennie (ed.) Introduction to the Petroleum Geology of the North sea, Oxford U.K. pp. 197-236.
- CONNAN, J., 1974 Time Temperature relationship in oil genesis. American Association of Petroleum Geologist Bulletin, Vol. 58, pp. 2516-2521.
- DIDYK, B.M., SLMONEIT, B.R.T., BRASSELL, S.C. and EGLINTON, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. Nature 72, pp. 216-222.
- EKWEOZOR, C.M. 1990. Geochemistry of oil sands of southwestern Nigeria. In: B. D. Ako and E. I. Enu (eds). Occurrence, utilization and economics of Nigeria tarsands. Nigerian Mining and Geosciences Society publication on tarsands workshop, Ago-Iwoye, pp. 50-62.
- EKWEOZOR, C.M. and NWACHUKWU J.I., 1989. The origin of tar sands of southwestern Nigeria. Nigerian Association of

 stratigraphy and other relevant information pertaining to source rock potential. These may probably show reliable trends for useful deductions.

Further geochemical characterization may require more information through biomarker analysis or studies. This will allow for better understanding of the source rock potentials, maturity, depositional environment and correlations. Also integrating vitrinite reflectance information on the maceral studies will be useful in determining the maturity of the sediments particularly v...en used along side the enumerated parameters.

Acknowledgements

The authors are grateful to the Geological Survey Department of Nigeria, for supplying well samples for this study. Much gratitude also goes to Chevron Nigeria Limited, Lagos, for permission granted the second author to use its laboratory facilities for some aspects of this work; while Professors M. Nwachukwu and O. Omole are thanked for their useful suggestions and criticisms.

References

Petroleum Exploration Bulletin, Vol 4, pp. 82-94.

- ENULEI. 1987. The palaeoenvironment of deposition of Late Maestrichtian to Paleocene black shales in the eastern Dahomey Basin, Nigeria. Geologie Mijnbouw, 66, pp. 15-20.
- NU, E.I., 1990. Nature and occurrence of tar sands in Nigeria. In: B.D. Ako and E. I Enu (eds). Occurrence, Utilization and Economics of Nigeria tar sands. Nigerian Mining and Geosciences Society Publication on Tarsands workshop, Ago-Iwoye, pp.11-16.
- FAYOSE, E.A., 1970. Stratigraphical paleontology of Afowo -I Well, southwestern Nigeria - Journal of Mining and Geology, 5 (1 & 2), pp. 1-99.
- HUNT, J.M., 1979. Petroleum Geochemistry and Geology W.H. Freeman and Company, 617p.
- HUNT, J. M. and MEINERT, R.N., 1954. Petroleum prospective. U.S. Patent 2, 854, 396. Patent Trademark Office, Washington D.C. 20231.
- IDOWU, J.O., AJIBOYE, S.A., IIESANMI, M. A and TANIMOLA, A., 1993. Origin and significance of organic matter of Oshosun Formation, southeastern Dahomey basin. Nigeria. Journal of Mining and Geology, Vol. 29, No. 1, pp. 9-17.
- JONES, H.A. and HOCKEY R.D., 1964. The Geology of part of southwestern Nigeria. Geological Survey of Nigeria Bulletin 31, 87p.
- KILLOPS, S.D., and AL-JUBOORI, M.A.H.A. 1990. Characterisation of the unresolved complex mixture (UCM) in the gas chromatograms of biodegraded petroleums. Organic Geochemistry, Vol. 15, pp. 147-160.
- KINGSTON, D.R., DISHROON, C.P. and WILLIAMS, P.A., 1983. Global basin classification system. American Association of Petroleum Geologists Bulletin, Vol. 67, pp. 2175-2193.
- KLEMME, H.D., 1975. Geothermal gradient, heat flow and hydrocarbon recovery. In: A.G. Fischer and S. Judson (eds). Petroleum and global tectonics. Princeton University Press. pp. 251-304.
- LIJMBACK, G. W. M., 1975. On the origin of petroleum. Proceedings 9th World Petroleum Congress, Vol. 2, Applied Science

Publishers, London, pp. 357-369.

- MAXWELL, J. R., PILLINGER, C. and EGLINTON, G., 1971. Organic Geochemistry Quart. Rev. 25, 571p.
- MOSUNMOLU LTD; 1991. A petroleum geochemical evaluation of the Dahomey basin sediments, 116p.
- MURCHISON, D.G., 1987. Recent advances in Organic petrology and organic geochemistry: an overview with some references to oil from coal. In: A. C. Scott (ed). Coal and Coal bearing strata. Geological Society Special publication, Vol. 32, pp. 257-302.
- NTON, M. E.,2001. Sedimentological and geochemical studies of rock units in the eastern Dahomey Basin, southwestern Nigeria. Ph.D. Thesis, University of Ibadan, Ibadan, 315p.
- NTON, M.E. and ELUEZE A.A., 1999. Aspects of Sedimentology and Organic Petrographic studies of Somo Well sediments, Dahomey basin, southwestern Nigeria. 17th Annual International Conference, Nigerian Association of Petroleum Explorationist, 15th-19th Nov., Lagos Book of Abstract, 53p.
- NWACHUKWU, J.I. and ADEDAYO, B.A.; 1987. Source rock potential of Cretaceous shales associated with Nigerian tar sands. Nigerian Association of Petroleum Explorationist Bulletin, 87, pp. 56-62.
- NWACHUKWU, J.I; ADEGOKE, O.S. and SALAMI, M.B. 1992. Micropalaeontology of the Upper Cretaceous and Lower Tertiary of Bodashe - 1 and Ileppaw - 1 wells, southwestern Nigeria. Journal of Mining and Geology, Vol. 29(2) pp. 163-170.
- OGBE, F.G.A., 1972. Stratigraphy of strata exposed in the Ewekoro quarry, Western Nigeria. In:T.F.J Dessauvagie and A.J.Whiteman (eds). African Geology, Ibadan University Press, pp. 305-322.
- OKOSUN, E. A., 1998. Review of the Early Tertiary stratigraphy of southwestern Nigeria. Journal of Mining and Geology, Vol.

34, No.1 pp. 27-35.

- OMATSOLA. M.E. and ADEGOKE O.S. 1981. Tectonic Evolution and Cretaceous stratigraphy of the Dahomey basin. Journal of Mining and Geology, Vol. 18 (1) pp. 130-137.
- PETERS, K. E. and MOLDOWAN, J.M., 1993. The Biomarker Guide Interpreting molecular fossils in petroleum and ancient sediments. Englewood Cliffs, New Jersey 07632, Prentice Hall. 363p.
- POWELL, T. G. CREANEY, S. and SNOWDON, I. R., 1982. Limitations of the use of organic petrographic techniques for identification of petroleum source rocks. American Association of Petroleum Geologist Bulletin, 66, pp. 430-435.
- PRATT, L. M., 1984. Influence of palaeoenvironmental factors on preservation of organic matter in Middle Cretaceous Greenhorn Formation, Pueblo, Colorado. American Association of Petroleum Geologist Bulletin, Vol. 66, pp.1146-1159.
- SCHLUMBERGER., 1985. Well evaluation Conference, Nigeria, Paris: Sclumberger, 290p.
- SHANMUGAM, G., 1985. Significance of coniferous rain forests and related organic matter in generating commercial quantities of oil, Gippsland basin, Australia. American Association of Petroleum Geologists Bulletin, Vol. 69, pp 1241-1254.
- SLANKY, M., 1962. Contribution a a'etude geologique du basin sedimentaire cotier au Dahomey at du Togo. Bureau du Recherches geologiques of minieres, Memoir 11, 270p.
- TISSOT, B.P. and WELTE, D.H., 1984. Petroleum Formation and Occurrence. 2nd Edition, New York, Springer Verlag, 538 pp.
- WALKLEY, A. and BLACK, T.A., 1934. An examination of the Deginareft method for determining soil organic matter and a proposed modification of the chromic acid titration methods. Soil science 37, pp. 29-38.
- WHITEMAN, A.J., 1982. Nigeria: Its petroleum geology, resources and potential, Grahman and Trottan, London, 394p.

Received 14 April, 2003; Revision accepted 16 February, 2004