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DOWN-HOLE GEOCHEMISTRY OF THE CORE SEDIMENTS FROM PART OF THE NIGER DELTA BASIN, SOUTHERN NIGERIA.

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ABSTRACT

Sedimentary geochemistry is concerned with chemical investigation of geological processes and materials in low temperature and pressure environments at or relatively close to the Earth's surface. Eight core sediment samples from offshore exploratory well within part of the Niger Delta, southern Nigeria were investigated for major and trace elements abundances using Proton-Induced X-ray Emission (PIXE) spectroscopy analytical method as well as the determination of the organic matter types. The aims were to investigate the down-hole variation in depositional environment and organic matter type within the studied depth. Most major elements concentration showed high variations in the shale facies. Silicon (SiO_2) concentration varied from 20.05 to 40.01%. High Si content (~32-40%) were observed in the sandstones (litharenite, arkose and wacke) while the low concentration was found in the shales. The elemental contents of Aluminium (Al_2O_3) (9.01 to 11.82%) and Iron (Fe_2O_3) (0.01 to 4.53%) showed similar trend in the samples, as high Al and Fe content are observed in the shales. The low Sr content observed in all the samples showed diagenetic alteration due to meteoric water rock interaction. The result of the kerogen analysis indicated that the organic matters in the samples were essentially Type III and with few Type II/III organic matters. These are capable of generating mainly gas and waxy crude oil. The slight down-hole variations of the organic matter in the samples probably reflected slight differences in the depositional environments and the degree of organic matter preservation.

Keywords: Kerogen, organic matter, major elements, trace elements, Niger Delta.

INTRODUCTION

Geochemistry of sedimentary rocks is a valued tool to deduce factors that control sediment characteristics during and after their deposition and also to describe the relationship between specific units of both clastic and carbonate strata (Nagarajan *et al.*, 2007; Armstrong-Altrin *et al.*, 2009; Frimmel, 2009; Madhavaraju and Lee, 2009). The importance of geochemistry in defining the source area of sedimentary rocks, paleo-weathering conditions as well as tectonic evolutions of sedimentary basins is well known in many literatures (Cullers *et al.*, 1988; Nagarajan *et al.*, 2007). The concentration of

major and trace elements in clastic and carbonate rocks are useful indicators of depositional environment, facies and diagenetic changes in different sedimentary basins (Lewis and Bandera, 1981; Armstrong-Altrin *et al.*, 2003).

The Niger Delta is one of the world's largest delta complexes and major hydrocarbon provinces. It is situated in the Gulf of Guinea on the western coast of Africa between Latitudes $3^{\circ}50'$ and $6^{\circ}50'$ North and Longitudes $3^{\circ}25'$ and $8^{\circ}50'$ East (Figure 1). It covers an area which extends more than 300 km from its apex to its mouth. The delta is a high energy, wave and tide

dominated environment and is arcuate in shape (Short and Stauble, 1967; Whiteman, 1982; Doust and Omatsola, 1990). The sedimentary units of the Niger Delta Basin are very important due to its suitability in generating and storing hydrocarbon. The geochemistry of the sediments of the delta petroleum province have been fairly studied as most researches in this region focuses extensively on the source rocks, reservoir rocks and hydrocarbon occurrence within the basin (Ekweozor and Okoye, 1980; Nwachukwu and Chukwura, 1986). However, no detailed study

of geochemical constraints on provenance and depositional conditions has been carried out within this basin. Hence, this study focuses on the use of geochemical characteristics (including major, trace elements and organic matters analysis) to determine the down-hole variation in depositional environment and organic matter type within the specified depth.

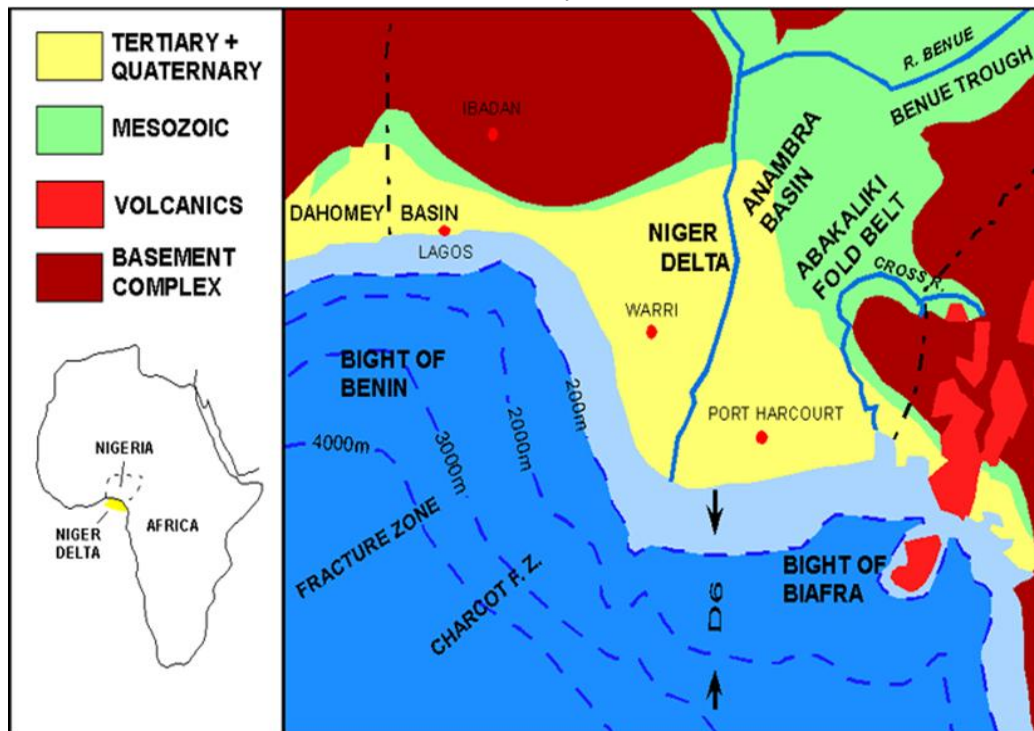


Figure 1: A geological Map of the Niger Delta Region (After Whiteman, 1982).

The Tertiary segment of the Niger Delta is divided into three formations, indicating prograding depositional facies that are distinguished mostly on the basis of sand-shale ratios. These formations are described in Short and Stäuble (1967) and summarized in a variety of papers (Doust and Omatola, 1990). The Akata Formation at the base of the delta is of marine origin and is composed of thick shale sequences (potential source rock), turbidite sand (potential reservoirs in deep water), and minor amounts of clay and silt. Beginning in the Paleocene and through the Recent, the Akata Formation formed

during lowstands when terrestrial organic matter and clays were transported to deep water areas characterized by low energy conditions and oxygen deficiency (Stacher, 1995). Little of the formation has been drilled till date. It is estimated that the formation is up to 7,000 meters thick (Doust and Omatsola, 1990). The formation underlies the entire delta, and is typically over-pressured. Turbidity currents likely deposited deep sea fan sands within the upper Akata Formation during development of the delta (Burke, 1972).

The deposition of the overlying Agbada

Formation, the major petroleum-bearing unit, began in the Eocene and continues into the Recent. The formation consists of paralic siliciclastics over 3700 meters thick and represents the actual deltaic portion of the sequence. The clastics accumulated in delta-front, delta-topset, and fluvio-deltaic environments. In the lower Agbada Formation, shale and sandstone beds were deposited in equal proportions, however, the upper portion is mostly sand with only minor shale interbeds. The Agbada Formation is overlain by the third formation, the Benin Formation, a continental latest Eocene to Recent deposit of alluvial and upper coastal plain sands that are up to 2000 m thick (Avbovo, 1978).

MATERIALS AND METHOD

Samples were collected from one exploratory drill core (W43) from part of the Niger Delta area, southern Nigeria. The core samples were picked within depth interval of 2764.3 to 2785.6 m. The whole-rock chemical analysis for major and trace elements concentration in eight core samples were determined using Proton-Induced X-ray Emission (PIXE) spectroscopy. The selected samples were first air dried and powdered in an agate mortar. 5 g of each measured sample was placed in well labelled white cellophane bags and sent for geochemical analysis in Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile Ife. At the centre, the samples were then mixed with 20% ultra-pure carbon in the mixer and pressed into thick pellets of 13 mm diameter. These samples after experimental process performed using 2.5 MeV proton beam issued from the Ion Beam Analysis (IBA) facility were then prepared based on preparation of shales in the National Institute of Standard and Technology (NIST) shale standard GSR5 PIX K8 (Pearce *et al.*, 2007). This was pressed into duplicate pellets and was used for quality assurance. The NIST standard was measured just before and immediately after measuring the samples.

The organic carbon was determined by weighing 0.5 g of the powdered samples into a beaker containing 10 ml of potassium dichromate ($K_2Cr_2O_7$). 20 ml of concentrated sulphuric acid (H_2SO_4) was then added and left for 30 minutes. After 30 minutes, 200 ml of distilled water was added to the sample; followed by 10 ml of phosphate (H_2PO_4) and then 0.2 g of sodium fluoride. It was then back titrated with ammonium ferrous sulphate to reach a greenish end point. The percentage carbon was calculated assuming that the milli-equivalent of organic matter oxidized was equivalent to oxidation of 77 % of the organic carbon from a valence of zero to +4 (Nwachukwu *et al.*, 2000). Mathematically,

$$\begin{aligned} \% \text{ Carbon} &= \frac{MeqOX}{g} * \frac{12}{4000} * \frac{1}{0.77} * 100 \quad (1) \\ &= \frac{MeqOX}{g} * 0.390 \end{aligned}$$

Where,

$\frac{MeqOX}{g}$ = milli-equivalent of organic matter

oxidized in grams

$\frac{12}{4000}$ = milli-equivalent weight of carbon in grams

$\frac{1}{0.77}$ = factor of converting the carbon actually oxidized to total carbon and

100 = factor to change from decimal fraction to percent.

The percentage organic matter was obtained by assuming that the percentage carbon was correct and that the organic matter contains 58 % carbon (Schumacher, 2002).

$$\begin{aligned} \%OM &= \%C * \frac{1}{0.58} \quad (2) \\ &= \%C * 1.72 \% \end{aligned}$$

Where,

%OM = percentage organic matter

$\frac{1}{0.58}$ = factor for converting carbon to organic matter.

Kerogen was isolated, using the standard

technique of acid digestion with hydrochloric acid (HCl) and hydrofluoric acid (HF). 5 g of the powdered sample (dry) was placed in an ordinary laboratory beaker, and distilled water added to wet the sample for palynological studies. It was then treated with concentrated HCl (40 %) to remove carbonates, washed three times with distilled water in order to remove all traces of acid. The sample was then treated with concentrated HF (52 %) to digest silica. This step was carried out in two stages; concentrated HF was slowly poured on the sample, until the beaker was 2/3 full. It was left for three hours, after which the HF was carefully poured off into a waste plastic reagent bottle. HF was added a second time and the sample left to stand for two hours. The HF was also poured off and the samples left to stand in distilled water, overnight before washing. The samples were then centrifuged at 2000 r.p.m. for two minutes each, three times in 100 ml of distilled water, then once in acetone and lastly, twice with 100 ml of distilled water. The kerogen concentrate was then placed in a dish and oven dried at 146° F (58° C) and stored in glass vials. For palynological studies, a small portion of the kerogen was disaggregated and mounted on microscope glass slides with depex. These slides were then examined under a palynological microscope.

RESULTS AND DISCUSSION

Major and Trace Elements Geochemistry

The analysed samples were classified into sandstone and shale (Fig. 2) based on the concentrations of the major elements (Table 1) using Herron, 1988 graph. The classification showed that the analysed samples were mainly shales while others sandstone (litharenite, arkose and wacke) based on the Herron, (1988) metal oxides classification (Fig. 2). The concentrations

of the major and trace elements are presented in Tables 1 and 2 respectively. High variations were observed in the major elements contents in the samples.

Silicon (SiO₂) concentration varied from 20.05 to 40.01%. High Si content (~32-40%) were observed in the sandstones ((litharenite, arkose and wacke) while the low concentration was found in the shales. The elemental contents of Aluminium (Al₂O₃) (9.01 to 11.82%) and Iron (Fe₂O₃) (0.01 to 4.53%) showed similar trend in the samples, as high Al and Fe content are observed in the shales. The elemental content of Mg, K, Ti and P are low in all the analysed samples (Table 1). Ca showed distinctive negative correlation with other major elements (very low concentration) which probably suggested that the elemental Ca exhibits different mode of origin. The positive correlations of Fe and Cu, Fe and Mn and Cu and Mn (r= 0.693, 0.621 and 0.598 respectively) indicated that these elements were associated with detrital phase (Nagarajan *et al.*, 2007).

The trace elements concentrations showed significant variations in the samples (Table 2). The concentration of Sr, Zr, Ti and Cr are significantly enriched in the samples as compared to the National Institute of Standard and Technology (NIST) shale standard of 90.0, 96.0, 3991.8 and 74.5 ppm respectively. The Sr (~ 102 -175 ppm) was lower than the average value of the lithospheric sedimentary rock (610 ppm). The low Sr content showed diagenetic alteration due to meteoric water rock interaction (Turekian and Wedepohl, 1961).

The plot of TTM with depth showed the down-hole variation of the total concentration of the trace metals with increase in depth in the well (Figure. 3). The TTM concentrations decreased with increasing depth; this could be a biodegradation effect in the rock samples at greater depths (Dreyer *et. al*, 2005).

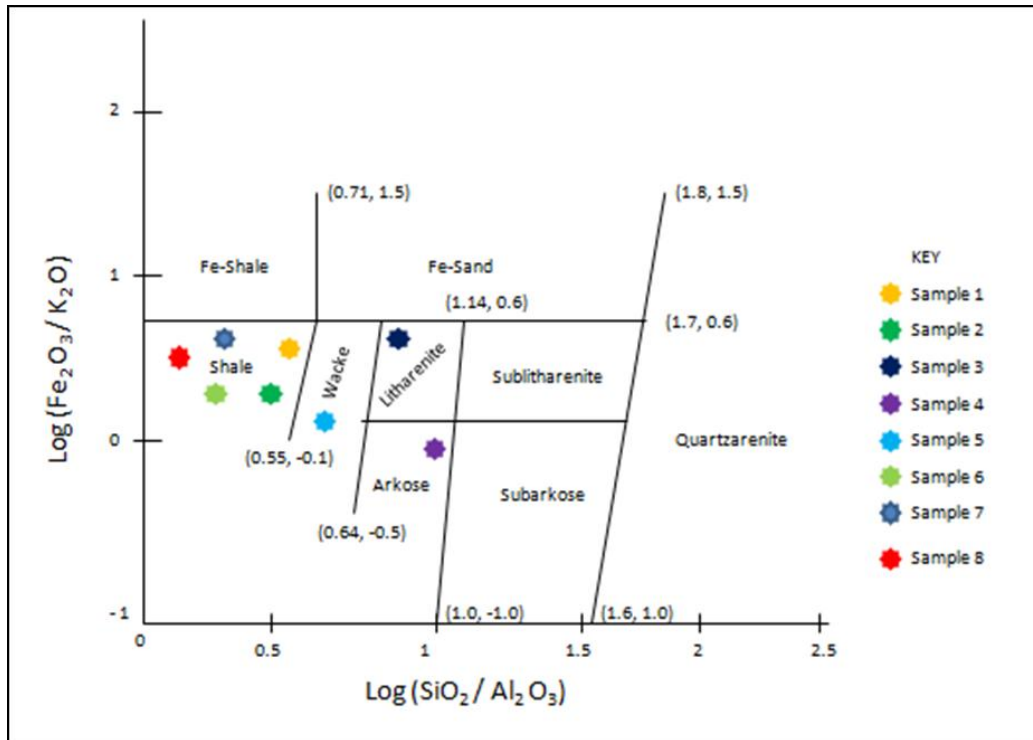


Figure 2: The classification of samples into shale and sandstone using Herron (1988) graph.

Table 1: Major Oxide concentration (%) for the core samples

Well ID/Sample No	Depth (m)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	TiO ₂	P ₄ O ₆
W43/1	2764.3	30.08	9.75	3.98	0.93	0.29	1.37	1.09	0.08
W43/2	2768.8	28.90	9.90	2.50	0.47	0.14	1.60	0.79	0.07
W43/3	2770.8	35.47	9.45	3.05	0.84	0.34	1.31	0.66	0.17
W43/4	2771.2	40.01	9.01	0.98	0.19	0.15	1.43	0.35	0.11
W43/5	2771.6	32.34	9.43	1.52	0.48	0.16	BDL	0.71	0.12
W43/6	2780.0	27.83	10.20	3.17	0.49	0.10	1.53	0.79	0.05
W43/7	2782.5	24.67	10.71	0.01	0.60	0.18	1.58	0.56	0.09
W43/8	2785.6	20.05	11.82	4.53	0.69	0.24	1.54	0.81	0.06
NIST STD		27.60	10.30	5.30	1.30	0.40	3.40	0.40	0.08

Note: ppm= % *10,000

BDL - Below Detection Limit

Table 2: Trace elements concentrations (ppm) for the core samples

Well ID/Sample No	Depth (m)	Sr	Zr	Cu	Ti	Cl	Rb	Cr	Mn	TTM
W43/1	2764.3	175.2	1877.8	94.7	10930.4	2172.4	56.7	130.6	135.7	15573.5
W43/2	2768.8	102.3	847.8	42.2	7903.2	1923.4	75.9	174.4	148.0	11217.2
W43/3	2770.8	116.1	1185.0	71.1	6610.7	3012.2	BDL	69.1	554.4	11618.6
W43/4	2771.2	157.9	1312.8	35.6	3521.9	1501.2	BDL	51.3	114.4	6695.1
W43/5	2771.6	BDL	1398.6	32.0	7070.2	2814.6	BDL	BDL	100.0	11415.4
W43/6	2780.0	118.4	673.6	58.3	7914.0	1037	86.6	113.8	182.8	10184.5
W43/7	2782.5	148.1	1593.4	47.8	5634.5	1610.5	46.7	258.4	221.2	9560.6
W43/8	2785.6	144.0	971.4	65.7	8057.6	1713.6	109.1	91.7	391.6	11544.7
NIST STD		90.0	96.0	101.0	3991.8	219.9	205.6	74.5	201.8	

TTM – Total Trace Metals Note: ppm= % *10,000

Table 3: Transition metals in samples from Well-43

Well ID/ Sample No	Depth (m)	V	Fe	Cu	Cr	Mn	TTM
W43/1	2764.3	NA	39840.8	94.7	130.6	135.7	40201.8
W43/2	2768.8	NA	24963.5	42.2	174.4	148.0	25707.9
W43/3	2770.8	NA	30474.3	71.1	69.1	554.4	31168.9
W43/4	2771.2	NA	9804.0	35.6	51.3	114.4	10005.3
W43/5	2771.6	NA	15226.9	32.0	NA	100.0	15358.9
W43/6	2780.0	122.6	31694.4	58.3	113.8	182.8	32188.1
W43/7	2782.5	133.6	37346.6	47.8	258.4	221.2	38007.6
W43/8	2785.6	NA	45276.3	65.7	91.7	391.6	45825.3

TTM* = Total Transition Metals; NA = Not Available

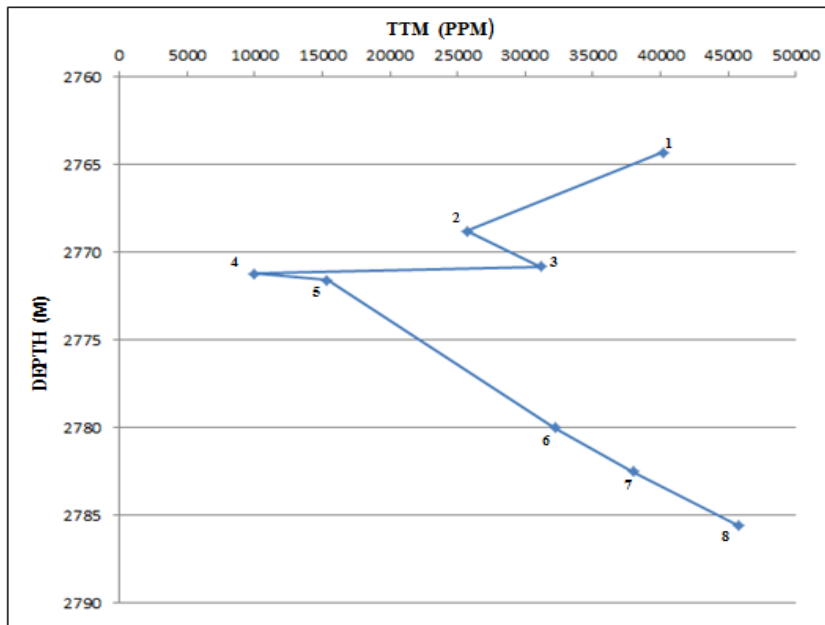


Figure 3: Plot of TTM concentrations with depth (m) in the well.

Organic geochemistry and Petrography

Organic geochemistry

Shales containing an average of 1.2 wt % organic matter are sufficient to generate petroleum provided there was enough heat and depth of burial more than 2 km. The minimum total organic carbon (TOC) value for shale source rock is 0.5.wt % (Adekoya *et al.*, 2014). The Niger Delta source rocks contained an average of 1.2 % TOC (Nwachukwu *et al.*, 2000).

with depth in the studied samples. The weight percent TOC ranges from 0.8 to 3.0 % with the shale with TOC greater than 1.2 %; these showed that the shale of this part of the Niger Delta are good source rocks. The values in Table 4 indicated that the shales have moderate to high amount of organic matter. The range of TOC values obtained (0.8 - 3.2 %) compares reasonably well with the 0.4 - 4.4 % reported by Ekweozor and Okoye (1980) for the Tertiary Niger Delta.

Table 4 showed the percentage organic carbon

Table 4: Percentage Total Organic Carbon (TOC) of the samples

Well ID/ Sample No	Depth (m)	% TOC
W43/1	2764.3	1.3
W43/2	2768.8	1.6
W43/3	2770.8	3.0
W43/4	2771.2	0.8
W43/5	2771.6	3.2
W43/6	2780.0	1.5
W43/7	2782.5	1.6
W43/8	2785.6	1.1

Petrography

The organic matter types were deduced from visual kerogen analysis. Table 5 showed the relative abundance of organic matter (kerogen) in the samples which were characterized by organic petrography (Figure 4). The photomicrograph revealed that the kerogen in the shale samples include recycled organic matter, cuticle material, wood fragment and amorphous material.

$$\% \text{ Kerogen} = (W + C)/(H + A) * 100 \% \quad (3)$$

Where;

C = Recycled or coaly organic matter

W = Woody remains

H = Herbaceous materials

A = Amorphous organic matter

The result of the calculation of percentage kerogen showed that the organic matters in the samples are essentially Type III and with few Type II/III organic matters. These are capable of generating mainly gas and waxy crude oil. Type II kerogen corresponds to aquatic organic matter and is hydrogen rich and oxygen poor while Type III kerogen corresponds to terrestrial organic matter and is hydrogen poor and oxygen rich. The slight down-hole variations of the organic matter probably reflect slight differences in the depositional environments and the degree of organic matter preservation.

Table 5: Organic matter types in studied samples

Well ID/Sample No	Depth (m)	W	C	H	A	% Kerogen	Organic Matter Type
W43/1	2764.3	7	4	16	16	34.4	II/III
W43/2	2768.8	12	3	5	12	88.2	III
W43/3	2770.8	6	16	28	7	62.9	III
W43/4	2771.2	5	5	3	14	58.8	III
W43/5	2771.6	2	8	12	10	45.5	II/III
W43/6	2780.0	13	12	3	26	86.2	III
W43/7	2782.5	0	11	0	18	61.1	III
W43/8	2785.6	7	9	0	20	80	III

Where;

C = Recycled or coaly organic matter

W = Woody remains

H = Herbaceous materials

A = Amorphous organic matter

C, W, H and A are estimated and recorded during organic petrographic analysis to determine the percentage kerogen.

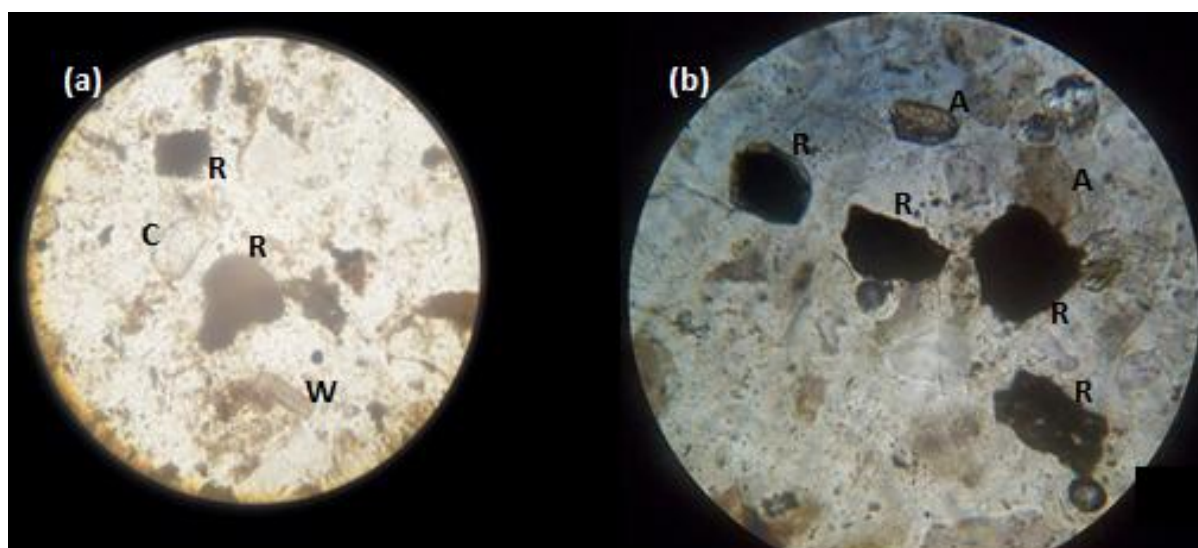


Figure 4: Photomicrographs of (a) Sample W43/1 (2764.3 m) and (b) Sample W43/4 (2771.2 m). Where R is Recycled Organic Matter, C is Cuticle Material, W is Wood Fragment and A is Amorphous Material.

CONCLUSION

This study showed the use of organic and inorganic geochemical data to evaluate the down-hole variations of major oxides and trace elements and organic matter type in the Niger Delta. The dark grey shales studied are similar to those reported by Adeleye and Fayose (1978) which concluded that the shales of the Niger Delta are mainly dark grey to black, organic rich, fluvial to deltaic and bathyal deposit. The shales are believed to be possible source rocks and the variations in their trace elements content have profound effects on the organic matter types (Lewan, 1984). Similarly, the inorganic and organic classification of the core sediments revealed significant variations in the major and trace elements concentrations and slight variation in the organic matter types. These probably reflected the slight differences in the depositional environment, the degree of organic matter preservation, and the proximity to organic matter source.

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