Petroleum and Coal

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GEOCHEMICAL ANALYSIS OF SHALE SAMPLES FROM EWEKORO FORMATION, BENIN BASIN (NIGERIA)

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Received January 17, 2018; Accepted April 23, 2018

Abstract

Utilizing four shale samples from a mine at Ibese, Southwest, Nigeria, this study evaluated the source rock potential of the shales of the Ewekoro Formation, Benin Basin. The four shale samples, Sample-1, Sample-2, Sample-3 and Sample-4, were analysed for their total organic carbon (TOC) content, elemental concentration of major, trace and transition elements as well as the type of organic matter they contain. Using the log (Fe_2O_3/K_2O) versus log (SiO_2/Al_2O_3) classification technique for terrigenous sediments, the samples were classified as iron-rich shales. The paleo-redox condition of deposition for the sediments was determined using the Vanadium-Chromium ratio (V/Cr). V/Cr ratios of 0.9, 1.3, 0.7 and 1.0 were estimated for Sample-1, Sample-2, Sample-3 and Sample-4 respectively. V/Cr ratio below 2.0 is indicative of sediment deposition in an oxic environment. The weight percentage of the total organic carbon of the samples ranged from 0.076 - 0.585 wt. %; this low values are indicative of poor to fair source rock potential. The kerogen extracts from Samples 1 through to 3 were interpreted as Type IV kerogen, while the extracts from Sample-4 were classified as Type III kerogen. The results of this study show that the shales of the Ewekoro Formation of the Benin Basin have poor to fair source rock potential. The constituent Type IV kerogen of Samples 1 - 3 are incapable of generating oil or gas, while the Type III kerogen of Sample-4 can generate gas and little oil.

Keywords*: Ewekoro Formation, Benin Basin, Source rock potential, Elemental analysis.*

1. Introduction

Benin Basin is an extensive coastal sedimentary basin at the margin of Gulf of Guinea. It is part of a system of West African Atlantic margin basins developed during the period of the rifting associated with the separation of South American and African plates and subsequent opening of Gulf of Guinea in the Late Jurassic to Early Cretaceous [2-3]. The basin stretches along the coast of Nigeria, Benin Republic, Togo and Ghana.

An Upper Cretaceous petroleum system, characterized by Type II-III kerogens with an average total organic carbon (TOC) content of 2.9 wt. %, has been established in the Basin Basin (e.g., Kaki *et al.* [45]. Oil is currently being produced in the Aje Field from Upper Cretaceous sandstone facies of the Abeokuta Group. With recent exploration data and geochemical evaluations of bituminous sand outcrops from onshore areas of the basin in southwest Nigeria suggesting the existence of a Lower Cretaceous petroleum system (e.g. Kaki *et al.* [45]), the Benin Basin is proofing to be a basin with significant hydrocarbon potential. This study is aimed at evaluating the source rock potential of shales of the post-Cretaceous Ewekoro Formation.

2. Geological setting

The study area is located within BENIN Basin, which is an extensive coastal sedimentary basin on the margin of Gulf of Guinea. It is part of a system of West African Atlantic margin basins developed during the period of the rifting associated with the separation of South American and African plates and subsequent opening of Gulf of Guinea in the late Jurassic to early Cretaceous [2-3].

The basin stretches along the coast of Nigeria, Benin Republic, Togo and Ghana in the margin of the Gulf of Guinea. Figure 1 shows the Nigerian section of the BENIN basin. It is separated from Niger Delta in the Eastern section by Benin Hinge Line and Okitipupa Ridge and marks the continental extension of the chain fracture zone [4-6]. It is bounded on the west by Ghana Ridge, and has been interpreted as the Romanche fracture zone [3,7]. The basin fill covers a broad arc–shaped profile, attaining about 13 km maximum width in the onshore at the basin axis along Nigerian and Republic of Benin boundary. This narrows westwards and eastwards to about 5 km [8-9].

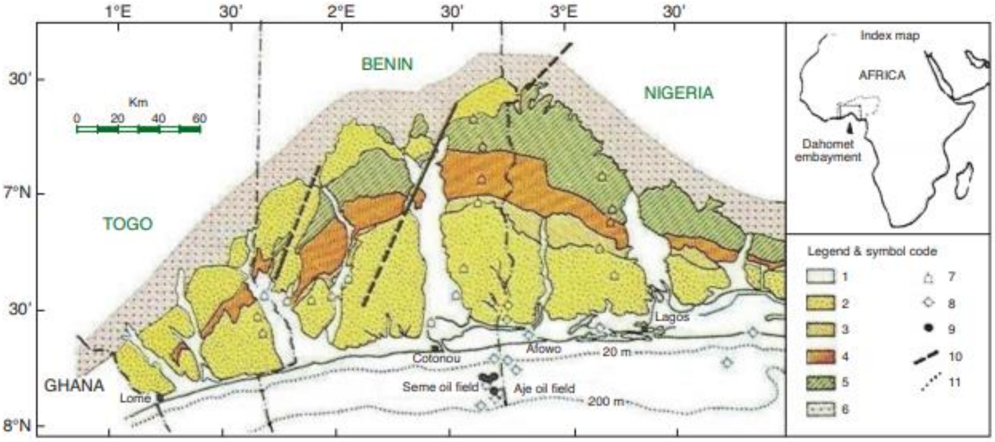

Figure 1. The Benin Basin within the "Dahomey Embayment"; 1-6 represent Formations; 1- Alluvium (Recent); 2- Benin-Ijebu (Pleistocene/Upper Miocene); 3- Oshoshun (Middle Eocene); 4- Imo shale (Lower Eocene/Paleocene); 5- Araromi shale and Turonian sandstone (Upper Cretaceous); 6- Pre-Cambrian crystalline basement; 7- Core hole or water well; 8- Dry well; 9- Oil well; 10- Faults; 11- Water depth contour (after Kaki *et al.* [45])

The tectonic framework along the continental margin of the BENIN basin is controlled by Cretaceous fracture zones expressed as trenches and ridges in the deep Atlantic, the basin is characterized by both block and transform faulting [10].

Adediran and Adegoke [11] proposed a four stage evolutionary model for the Gulf of Guinea Basin (BENIN Basin inclusive) as follows:

Stage 1 – The deposition of thick clastic sediments mostly immature sandstones and fresh water shales in the intracratonic basin.

Stage 2 – Reworked sands and silt intercalated with shales of fluviatile-lacustrine origin deposited within the grabens during a period of tectonic activity, erosion and sedimentation

Stage 3 – Paralic sequence (in the northern basins) and evaporitic deposits (in the southern basins) marking the beginning of marine incursion into the basin after the separation of South America from Africa.

Stage 4 –Marine sediments rich in fauna and flora marking the final stage of the development of the Gulf of Guinea Basins.

3. Lithostratigraphy of BENIN BASIN

The stratigraphic setting of the BENIN Basin has been described in detail in the works of Adegoke [12], Ogbe [13], Kogbe [14], Billman [15], Omatsola and Adegoke [16], Ako *et al.* [17], Okosun [41], Adekeye [19] and Adekeye *et al.* [20]. The recognized formations from the oldest to the youngest include: Abeokuta Group which comprises of Ise, Afowo and Araromi Formations (Cretaceous), Ewekoro Formation (Paleocene), Akinbo Formation (Late Paleocene – Early Eocene), Oshosun Formation (Eocene), Ameki Formation, Ogwashi-Asaba Formation and Benin Formation.

3.1. ISE FORMATION

This is the oldest formation in the BENIN Basin. It unconformably overlies the basement complex of southwestern Nigeria. It consists of conglomerates and grits at the base, and in turn overlain by coarse to medium grained sands with interbedded kaolinite. The Conglomerates are unimbricated and at some locations, ironstones occur [21]. The age is Neocomian to Albian based on the recovered Sporomorohs.

3.2. AFOWO FORMATION

This formation overlies the Ise Formation. It is composed of sandstones with interbeds of shales, siltstones and clay. The sandy facies are tar bearing while the shales are organic rich [22]. The lower part of this formation is transitional with mixed brackish to marginal horizons that alternate with well sorted, subrounded sands indicating a littoral or estuarine near shore environment of deposition [23]. Turonian to Maastritchtian age has been assigned to this formation on the basis of palynological assemblage.

3.3. ARAROMI FORMATION

This formation overlies the Afowo Formation and has been described as the youngest Cretaceous sediment in the eastern BENIN Basin [16]. It consists essentially of sand, overlain by dark-grey shales and interbedded limestone, marl and occasionally lignite bands. The formation is very similar in composition to the upper part of the Awgu Formation and the Nkporo Shale of the Anambra Basin [15], but their occurrence in separate basins with different geologic histories and lack of adequate outcrop sections necessitate a separate nomenclature. Observations made by Okosun [41] support the inclusion of thin interbeds of sandstone, shelly limestone and shale in the formation. A Maastrichtian to Paleocene age has been assigned to this formation [16].

3.4. EWEKORO FORMATION

This formation overlies the Araromi Formation in the eastern BENIN Basin. It is one of the lithostratigraphic units under Imo Group. Elueze and Nton [24] has reported that the limestone is of shallow marine origin owing to abundance of coralline algae, gastropods, pelecypods, echinoids fragments and other skeletal debris.

3.5. AKINBO FORMATION

Overlying the Ewekoro Formation is the Akinbo Formation which is made up of shale and clayey sequence [13]. The claystone are concretionary and are predominantly kaolinite. Lenses of limestone from Ewekoro Formation grades into the Akinbo shale very close to the base. The base of the formation is defined by the presence of glauconitic band with lenses of limestone [13,21]. The formation is Paleocene to Eocene in age on the basis of the recovered microfossil assemblages.

3.6. OSHOSUN FORMATION

This formation overlies the Akinbo Formation. It consists of greenish-grey clay and shale with interbeds of sandstones. The shale is thickly laminated and glauconitic. The basal beds are thinly laminated, occasionally mottled with pockets of grits. According to Okosun [18], the basal beds consist of any of the following facies; Sandstones, Mudstones, Claystones, Clayey shale. The shales of the Oshosun Formation have highly variable colours, ranging from light grey, brownish grey, purple through green, bluish grey to dark grey and black. These dark coloured highly fossilferous shales pass upwards into a yellowish grey, faintly laminated, unfossilferous, slightly calcareous and glauconitic shales with thin phosphatic beds. The shales get sandier and show alternation of grey to green shales with brownish soft clayey sandstones towards the top of the formation. This formation is phosphate bearing [25]. The formation is dated Eocene based on the recovered fauna and microfossil assemblages.

3.7. AMEKI FORMATION

The Ilaro Formation of some workers [14,26] is assigned to this formation wholly or in part by Reyment [27], Antolini [28] and Adegoke [12]. This formation overlies conformably the Oshosun Formation and consists of massive, yellowish, poorly consolidated, cross-bedded sandstone. The formation is dated Middle Eocene based on the molluscs recovered from it.

3.8. OGWASHI-ASABA FORMATION

This formation consists of a sequence of coarse-grained sandstone, light coloured clays and carbonaceous shale within which are intercalations of lignite seams of Continental origin [29,40]. Reyment [27] suggested an Oligocene to Miocene age for the Ogwashi-Asaba Formation, but palynological study by Jan du Chene *et al.* [29] yielded a Middle Eocene age for the basal part. The lignite seams found within the Ogwashi-Asaba Formation are commonly brownish to black in colour and vary in thickness from few millimeters to a maximum of 6 m. They are thinly laminated and fissile with leaf and woody fragements.

3.9. BENIN FORMATION

This is the youngest sratigraphic sequence in the eastern BENIN Basin. It is also known as the Coastal Plain Sands [25]. It overlays the Ilaro Formation unconformably. 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. The stratigraphy of BENIN Basin is shown in Table 1.

Table 1. Stratigraphy of BENIN Basin

Period	Jones and Hockey [25]		Omatsola and Adegoke [16]		Agagu [46]	
	Age	Formation	Age	Formation	Age	Formation
Quaternary	Recent	Alluvium			Recent	Alluvium
Tertiary	Pleistocene	Coastal Plain Sand	Pleistocene	Coastal Plain Sand	Pleistocene	Coastal Plain Sand
	Oligocene-Eocene	Ilaro	Oligocene-Eocene	Ilaro	Oligocene-Eocene	Ilaro
	Paleocene	Ewekoro	Paleocene	Oshosun, Akinbo	Paleocene	Oshosun, Akinbo, Ewekoro
Cretaceous	Late Senonian	Abeokuta	Maastrichtian	Araromi, Afowo	Maastrichtian	Araromi, Afowo
			Neocomian	Ise	Neocomian	Ise
Precambrian Crystalline Basement Rocks						

4. Methodology

4.1. Samples

Four (4) samples were analysed in this study. The samples were sourced from Dangote Cement Mines at Ibese, Ogun State, sampling was done at vertical spacing interval of 1m. The samples are shales and are described in Table 2. The samples range in elevation of about 39m to 42m.

Table 2. Sample description

Sample number	Sampling elevation(m)	Rock Type	Colour	Grain Size	Structure	Minerals Observable In Hand Specimen
1	39	Shale	Dark Coloured	Fine	Fissility	Clay Minerals
2	40	Shale	Dark Coloured	Fine	Fissility	Clay Minerals
3	41	Shale	Dark Coloured	Fine	Fissility	Clay Minerals
4	42	Shale	Dark Coloured	Fine	Fissility	Clay Minerals

4.2. Elemental analysis

Major, minor and trace elements of the sample were determined by Proton-induced X-ray emission (PIXE) technique at the centre for Energy Research and Development (CERD) O.A.U, Ile-Ife. The samples were first oven dried at 45-50 degree Celsius. The dried samples were ground with a grinding machine at the workshop in the Department of Geology O.A.U and prepared into pellets of 11mm diameter without binder.

The PIXE experiments were performed using a 3.0 MeV proton beam obtained from the CERD ion beam analysis (IBA) facility. The facility is centered on a NEC 5SDH 1.7MV Pelletron Accelerator, equipped with a radiofrequency charge exchange ion source. The ion source is equipped to provide proton and helium ions. The end-station consists of an Aluminium chamber of about 150 cm diameter and 180 cm height. It has four ports and window. Port 1 at 165° is for the RBS detector, port 2 at 135° is for PIXE detector, port 3 at 30° is for the ERDA detector; the window at 0° is for observing the beam position and the size, while port 4 at 225° is for PIGME. The chamber has a sample ladder that can carry 11 (eleven) 13 mm diameter samples. The end-station has a turbo pump and a variable beam collimator to regulate beam size, and isolation value.

Shale standard (NIST) GRS5 was used for the determination of the element values which was subsequently used for analysing the shale samples and to assure the accuracy of the experimental procedure. The measurements were carried out with a beam spot of 4mm in diameter and a low beam current of 3-6 nA. The irradiation was for about 10-20 minutes. A Canberra Si(Li) detector Model ESLX 30-150, beryllium thickness of 25 μm, with full width half maximum (FWHM) of 150 eV at 5.9 KeV, with the associated pulse processing electronics, and a Canberra Genie 2000 (3.1) MCA card interfaced to a PC were used for the X-rays data acquisition. With respect to the beam director, the sample's normal was located at 0° and the Si (Li) detector at 45°. The PIXE set-up was calibrated using some pure element standards and NIST geological standard, NBS278.

4.3. Organic carbon determination

The organic carbon was determined in the Department of Soil science, Faculty of Agriculture, O.A.U, Ile-Ife. 0.5 g of the powdered samples was weighed on the balance and poured into a conical flask. 10ml of potassium dichromate ($K_2Cr_2O_7$) and 20 ml of concentrated H_2SO_4 was added and it was left for 30 minutes, after 200 ml of distilled water was added to the sample, then 10mL of H_2PO_4 was added to the sample and 0.2 g of Sodium Fluoride was equally added to the sample. It was then back titrated with ammonium ferrous sulphate to reach a greenish end point.

4.4. Kerogen isolation

The kerogen isolation was carried out in the Geochemistry laboratory of the Department of Geology, Obafemi Awolowo University, Ile-Ife.

Kerogen was isolated, using the standard technique of acid digestion with HCl/HF. The acid digestion procedures were carried out in the fume cupboard. About 5g of the powdered sample (dry) was placed in beaker, and distilled water added to wet the sample. It was then treated with conc. 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 con. HF (52%) to digest silica. This step was carried out in two stages. Conc. 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 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 sample left to stand in distilled water, overnight before washing. The samples were then centrifuged at 2000 rpm for two minutes each, three times in distilled water, then once in acetone and lastly, twice with distilled water. The kerogen concentrate was then placed in a dish and oven dried at 146°F (58°C) and stored in glass vials. No attempt was made to further demineralise the kerogen by a float-sink technique, using $ZnBr_2$ or other heavy liquid.

A small portion of kerogen was disaggregated and mounted on microscope glass slides. These slides were then examined under a petrographic microscope.

5. Results and discussions

The result of the elemental analysis is shown in tables 3 - 6. The elemental analysis is interpreted based on the major, trace and transition elements contents of the studied samples.

Table 3. Elements and their concentration in Sample 1

Z	Element	Concentration (ppm)	Concentration Error
11	Na	322.0	±63.92
12	Mg	35723.5	±146.47
13	Al	96030.3	±172.85
14	Si	297292.0	±267.56
15	P	717.7	±65.74
16	S	13866.7	±84.59
19	K	9875.9	±59.26
20	Ca	6544.6	±51.05
22	Ti	6652.7	±46.57
23	V	203.4	±35.41
24	Cr	214.7	±15.54
25	Mn	189.3	±15.83
26	Fe	40436.6	±133.44
29	Cu	328.7	±107.32
30	Zn	875.8	±187.77

Table 4. Elements and their concentration in Sample 2

Z	Element	Concentration (ppm)	Concentration Error
11	Na	270.9	±65.75
12	Mg	32628.1	±143.56
13	Al	101183.5	±182.13
14	Si	294344.6	±264.91
15	P	622.8	±66.76
16	S	13047.9	±83.51
17	Cl	606.0	±48.18
19	K	11073.7	±62.01
20	Ca	7022.4	±53.37
22	Ti	6670.6	±48.03
23	V	283.5	±35.58
24	Cr	217.6	±16.30
25	Mn	193.8	±15.95
26	Fe	40404.0	±133.33
30	Zn	1570.3	±194.25

Table 5. Elements and their concentration in Sample 3

Z	Element	Concentration (ppm)	Concentration Error
11	Na	221.1	±64.83
12	Mg	34139.6	±146.80
13	Al	97959.0	±176.33
14	Si	293816.2	±264.43
15	P	786.2	±62.90
16	S	12002.3	±79.22
17	Cl	496.9	±44.22
19	K	11100.9	±59.94
20	Ca	11003.5	±62.72
22	Ti	6839.4	±48.56
23	V	180.7	±36.30
24	Cr	265.0	±16.43
25	Mn	184.9	±15.46
26	Fe	41888.7	±138.23
29	Cu	203.7	±95.86
30	Zn	1133.7	±183.21
40	Zr	345.6	±160.36

Table 6. Elements and their concentration in Sample 4

Z	Element	Concentration (ppm)	Concentration Error
11	Na	317.1	±66.40
12	Mg	39986.7	±151.95
13	Al	92485.3	±175.72
14	Si	298332.2	±268.50
15	P	1203.8	±63.80
16	S	11635.0	±77.95
17	Cl	1111.9	±45.25
19	K	8879.5	±55.05
20	Ca	9926.5	±57.57
22	Ti	5941.7	±44.56
23	V	257.3	±33.35
24	Cr	239.4	±15.70
25	Mn	258.0	±15.33
26	Fe	38579.2	±131.17
28	Ni	123.4	±51.03
30	Zn	1212.4	±170.34

5.1. Sample classification

The four samples were classified on the basis of their iron, potassium, silicon and aluminium concentrations using the Heron [30] classification scheme for terrigenous sedimentary rocks. In the Heron [30] classification, the log (Fe_2O_3/K_2O) is plotted against log (SiO_2/Al_2O_3). The advantage of this classification is that it can be used to identify shales, sandstones, arkose and carbonate rocks in-situ from geochemical logs, using neutron activation and gamma-ray tools [31].

The classification of the samples is as follows;'
Sample 1 = Fe-Shale
Sample 2 = Fe-Shale
Sample 3 = Fe-Shale
Sample 4 = Fe-Shale

5.2. Major elements

The variation of the concentration of major elements across various sampling elevation are shown Table 7. For most silicate rocks, oxygen, silicon, aluminium, sodium, magnesium, calcium and iron are major elements [32], major elements are those elements whose crustal abundances are greater than 1%. The concentration of potassium, sodium, iron, magnesium, aluminium, calcium and silicon were determined.

Table 7. Correlation matrix of trace and transition elements in the samples

	Titanium	Vanadium	Chromium	Manganese	Iron	Zinc
Titanium	1.0000					
Vanadium	-0.4771	1.0000				
Chromium	0.0625	-0.5265	1.0000			
Manganese	-0.9902	0.4581	0.0616	1.0000		
Iron	0.9475	-0.6408	0.3754	-0.9018	1.0000	
Zinc	-0.0454	0.7859	-0.0899	0.0991	-0.1134	1.0000

Potassium (K): The concentration of potassium varies from 8879.50 – 11100.90 ppm in Samples 1, 2, 3 and 4. Sample 4 from the sampling elevation of 42 m has the least concentration of 8879.50 ppm, while Sample 3 from the sampling elevation of 41 m has the highest concentration of 11100.90 ppm. The average concentration in the samples is 10232.50 ppm; this value is attributed to the high abundance of clay minerals formed from K-feldspar.

Sodium (Na): The values of its concentration in Samples 1, 2, 3 and 4 vary from 221.10 - 322.00 ppm. Sample 3 from the sampling elevation of 41m has the least concentration of 221.10 ppm and Sample 1 from sampling elevation of 39m has the highest concentration of 322.00 ppm. The average concentration is 282.77 ppm. The average concentration of sodium in the samples is low, which may be as a result of substitution of Na^+ for K^+.

Iron (Fe): The values of its concentration in Samples 1, 2, 3 and 4 vary from 38579.20 - 41888.70 ppm. Sample 4 has the lowest concentration with a value of 38579.20 ppm while Sample 3 has the highest concentration with a value of 41888.70 ppm The average concentration is of iron in the samples is 40327.13 ppm; this supports the classification of the studied samples as Iron rich shales using the Herron classification scheme.

Magnesium (Mg): The concentration of Mg in Samples 1, 2, 3 and 4 vary from 32628.10 – 39986.70 ppm. Sample 2 has the least concentration with a value of 32628.10 ppm, while Sample 4 has the highest concentration with a value of 39986.70 ppm. The average concentration of the element in the samples is 35619.48 ppm; this is probably due to the infiltration of Mg^{2+} into the shales from the surrounding carbonate rocks that are rich in Mg^{2+}.

Aluminium (Al): The concentration of Al in Samples 1, 2, 3 and 4 ranges from 101183.50 – 92485.30 ppm. Sample 4 has the least value of 101183.50 ppm, while Sample 2 has the highest value of 92485.30 ppm. The average concentration is of the element is 96914.53 ppm; this significantly low value is interpreted as indicating that some aluminium ions had been substituted for magnesium ions.

Silicon (Si): The concentration of Si in Samples 1, 2, 3 and 4 ranges from 293816.20 – 298332.20 ppm. Sample 3 has the least concentration with a value of 293816.20 ppm while Sample 4 has the highest concentration with a value of 298332.20 ppm. The average concentration of the element is 295946.30 ppm; this is expected because silicon is the second most abundant element in the Earth crust.

Calcium (Ca): The concentration of Ca in the Samples ranges from 6544.60 – 11003.50 ppm. Sample 1 from sampling elevation of 39m has the least concentration with a value of 6544.60 ppm while Sample 3 has the greatest concentration with a value of 11003.50 ppm. The average concentration of the element is 8624.25 ppm; this value is rather high for a terrigenous sedimentary rock. It is interpreted that the calcium ions must have been sourced from the surrounding limestone and gypsum.

Silicon has the highest average abundance of 295946.30 ppm followed by aluminium with a value of 96914.50 ppm, while calcium and sodium have the least abundances with values of 8624.25 ppm and 282.77 ppm respectively.

5.3. Trace and transition metals

An element that occurs in minute but detectable quantities in minerals and rocks, much less than 1% is a trace element, all elements except the most common rock forming elements (O, Si, Al, Fe, Ca, Na, K, Mg, and Ti) generally occur as trace elements, except where locally concentrated in their ores.

The International Union for Pure and Applied Chemistry (IUPAC) defines a transition element as an element that has an incomplete d-subshell in either the neutral atom or its ions. The trace and transition elements analysed in the samples are: titanium, vanadium, chromium, manganese, iron and zinc, their concentration (in ppm) at different sampling elevations are shown in Table 8.

Table 7 shows the correlation coefficients of the transition elements in samples. The following pairs have strong positive correlation; iron and titanium (0.9475), zinc and chromium (0.7859). While titanium and manganese (-0.9902), iron and manganese (-0.9018) have strong negative correlation.

Table 8. Some trace element ratios to evaluate paleoredox condition according to Jones and Manning [37]; Hatch and Levantal [42]; Kimura and Watanabe [43]

Element ratios	Oxic	Dysoxic	Suboxic to Anoxic	Euxinic
Ni/Co	< 5	5 to 7	> 7	
V/Cr	< 2	2 to 4.25	> 4.25	
U/Th	< 0.75	0.75 - 1.25	> 1.25	
V/(Ni +V)	< 0.46	0.46 - 0.60	0.54 - 0.82	> 0.84
V/Sc	< 9.1			

5.4. Paleo-redox condition

A number of authors have used V/Cr ratio as an index of paleooxygenation [33-35]. Bjorlykke [35] reported the incorporation of Cr in the detrital fraction of sediments and its possible substitution for Al in the clay structure. Vanadium may be bound to organic matter by the incorporation of V^{4+} into porphyrins, and is generally found in sediments deposited in reducing environments [36]. According to Jones and Manning [37], the V/Cr ratios above 2 indicate anoxic conditions.

The V/Cr ratio was determined for the samples, Sample 1 has a ratio of 0.9, Sample 2 has 1.3, Sample 3 has a ratio of 0.7 and Sample 4 has a ratio of 1.0. All samples have ratios that are below 2 which indicate that they were deposited in oxic environments.

5.5. Total organic carbon (TOC)

The guidelines for assessing the source rock potential of shales [38], shown in Table 9 was used to characterize the source rock potential of the samples, Sample 1 has a percentage carbon of 0.076 which is less than 0.5 and it is indicative that the source rock potential is poor. Sample 2 has a percentage carbon of 0.232 which is less than 0.5; this is indicatives a poor source rock potential.

Table 9. Guidelines for assessing the source rock potential of shales [38]

Source rock potential	TOC (wt. %)
Poor	0.0 - 0.5
Fair	0.5 - 1.0
Good	1.0 - 2.0
Very Good	2.0 - 5.0
Excellent	>5.0

Sample 3 has a percentage carbon of 0.195 which is less than 0.5 this indicates that the source rock potential of the rock is poor. Sample 4 has a percentage carbon of 0.585 which is between 0.5 and 1.0 this value indicates that the source rock potential of the rock is fair.

Table 10 shows the total organic carbon of the studied sample while Fig. 3 shows the plot of the percentage carbon of the samples against their respective sampling elevation.

Table 10. The total organic carbon (TOC) of studied samples

Sample number	Sampling elevation (m)	(TOC) (wt. %)	Source rock potential
1	39	0.076	Poor
2	40	0.232	Poor
3	41	0.195	Poor
4	42	0.585	Fair

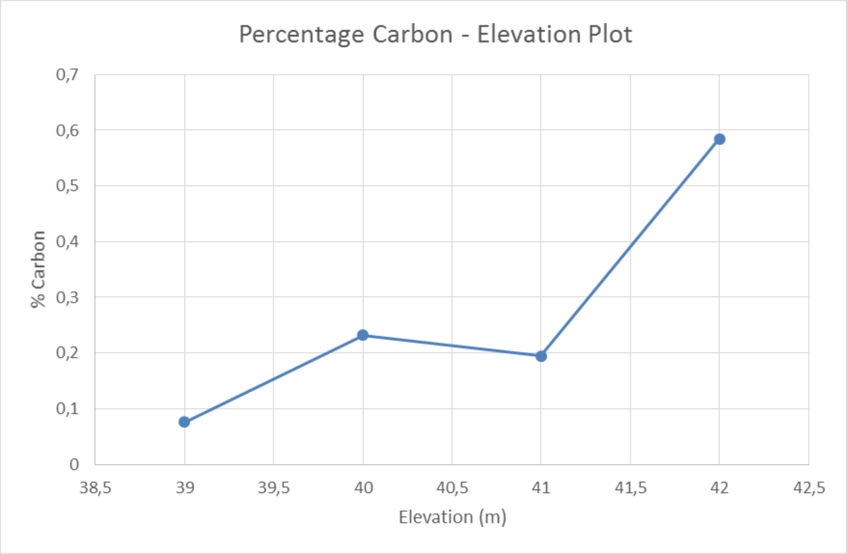

Figure 3. Plot of percentage Carbon of samples (1-4) versus elevation

5.6. Organic matter types

The accumulation of organic matter in sediments is controlled by a limited number of geological conditions [39]. The main factors that control the accumulation of organic matter include the production of the biomass and the degradation processes and transport of the organic matter.

The quantity and quality of the organic matter accumulated in sediment are basically the result of the combined influence of the biomass productivity, biochemical degradation and of the organic matter depositional processes. The accumulation is practically restricted to sediment deposited in aquatic environments, which must receive a certain minimum amount of organic matter.

In subaerial sediments, organic matter is easily destroyed by chemical or microbial oxidation. It is necessary balanced conditions between the energy level in a body of water and rate sedimentation to preserve and concentrate organic matter in sediments. This organic matter can be supplied on the form of particulate organic matter (in particles) or as dissolved organic matter (dissolved organic components).

Organic matter in sedimentary rocks mainly exists as kerogen, kerogen are types of disseminated organic matter that exist in impermeable sediments, it is insoluble in normal petroleum solvents e.g. Carbon bisulphide, this characteristic distinguishes kerogen from bitumen. There are four types of kerogen; Type I, Type II, Type III and Type IV.

The kerogen isolated from Samples 1, 2, 3 and 4 were studied under a petrographic microscope, the kerogen extracts from samples 1, 2 and 3 are black in colour, composed of recycled organic matter and are therefore classified as type IV which is incapable of generating oil or gas. The kerogen extract in sample 4 is brown in colour and it is composed of recycled organic matter and amorphous matter, subsequently it is classified as kerogen type III which is gas prone and generates little oil. Figures 4–7 shows photomicrographs of the kerogen contained in the studied samples.

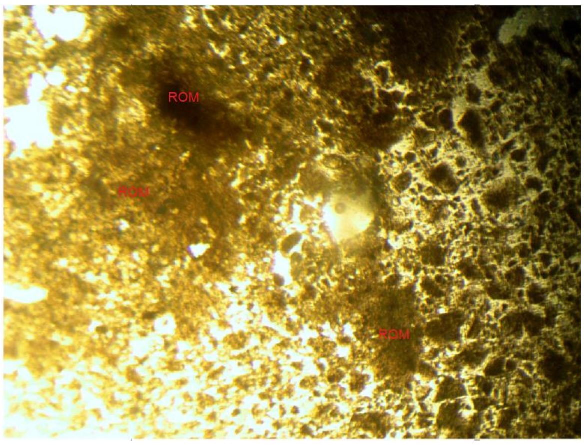

Figure 4 Photomicrograph of Sample 1 (39m) (magnification: x40) ROM –recycled organic matter

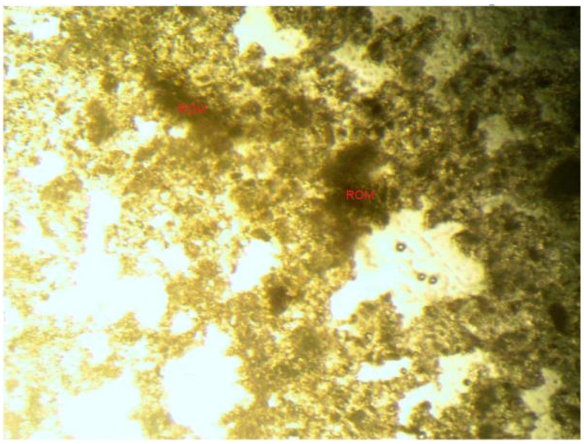

Figure 5. Photomicrograph of Sample 2 (40m) (magnification: x40)

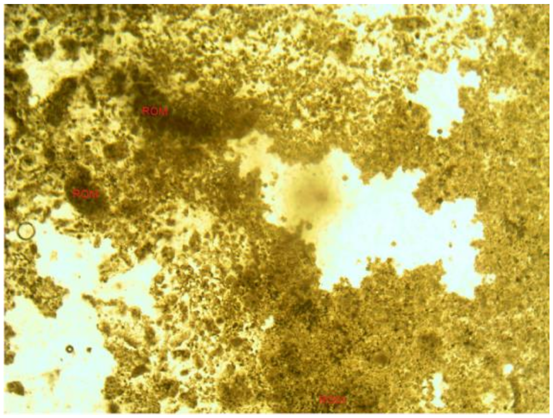

Figure 6. Photomicrograph of Sample 3 (41m) (magnification: x40), ROM –recycled organic matter

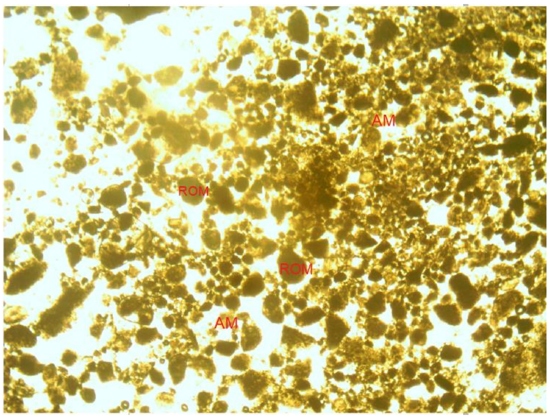

Figure 7. Photomicrograph of sample 4 (42m) (magnification: x40), ROM –recycled organic matter, AM-amorphous matter

6. Conclusion

This study used organic and inorganic geochemical techniques to evaluate the variations of major and trace elements, and organic matter type in the analysis of four samples from Dangote Cement Mines located at Ibese, Ogun State.

Using the Herron classification scheme, this study shows that the four studied samples are all iron-rich shales. The similarities in the distribution pattern of the element concentration in the samples indicated that the samples have the same provenance, which is a felsic plutonic rock.

The V/Cr ratio determined for the samples indicate that the paleo-redox condition in which the sediments were deposited was oxic; this is responsible for the low total organic carbon (TOC) of the samples which ranges from 0.076 – 0.585, indicating that the source rock potential of the rocks range from poor to fair.

The organic matter contained in samples 1 – 3 is Type IV kerogen which is incapable of yielding hydrocarbon, while sample 4 contains Type III kerogen which yields gas and little oil.

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