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GEOCHEMISTRY AND MULTIVARIATE STATISTICAL EVALUATION OF MAJOR OXIDES, TRACE AND RARE EARTH ELEMENTS IN COAL OCCURRENCES AND DEPOSITS AROUND KOGI EAST, NORTHERN ANAMBRA BASIN, NIGERIA

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Abstract

The Cretaceous Mamu Formation coal samples located within the Northern Anambra Basin were collected, analysed and interpreted using a multivariate statistical approach to determine the major, trace and rare elements association with a view to determining the source of the terrestrial rocks, palaeoweathering/climatic conditions and tectonic setting. The dominant oxides such as SiO_2, Al_2O_3, Fe_2O_3, TiO_2, and CaO were identified in the coal to suggest terrigenous origin. The ratio of SiO_2/Al_2O_3 of 4.8 suggests that the coal was formed from low land peat associated with freshwater continental marine or blackish water with low salinity as indicated by Sr/Ba and $CaO+MgO/K_2O+Na_2O$ ratios. The major oxides also revealed the stable condition of deposition, a low degree of tectonic setting but constant subsidence in the basin. The condition of deposition was acidic in nature as indicated by TiO_2/Zr plot. Based on the abundance of Zr, Zn, Ba, Ni, Co, Sr, V, and Y, moderate salinity, sub-oxic to oxic bottom water condition was prevalent and also an indication of marine influence. Based on the ratios of La/Yb; La/Sm and Gd/Yb, LREE has higher enrichment than HREE. Humid climatic conditions were observed at the coal formation stage while weak laterization to kaolinization was also evidence.

***Keywords**: Kogi East; Multivariate; Factor and Cluster; Varimax; Eucledean.*

1. Introduction

Coal is a carbon-rich, combustible, stratified organic sedimentary rock composed of altered and/or decomposed plant remains of non-marine origin combined with varying minor amount of inorganic materials [1]. The Anambra Basin, located in the Lower Benue trough is a major coal producing basin in Nigeria. Coal is a complex organic rock comprised of mainly decayed plants conditioned by syngenetic, diagenetic, epigenetic and detrital inorganic elements [2]. The Anambra Basin contains important coal measures in the Mamu and Nsukka Formations [3]. The mining of this sub-bituminous coal occurred in the Mamu Formation. Total coal reserves in the north-south trending coal belt were assed to be about 1.5billion tons. Lignite deposits occur in numerous seams in an east-west belt to the southwest [3]. A number of studies [4-8] have been conducted on the stratigraphic succession, organic and inorganic geochemistry of coal, distribution, and abundance of coal in Anambra Basin. Previous work has also been carried out on the trace elements in coal in the study area [2,9-13].

Nigeria is endowed with abundant coal reserves of the required quality suitable for power generation and other by products that are waiting to be tapped [3].

The objectives of this current study are to present the inorganic characteristics of Okaba coal using the multivariate statistical approach with a view to determining the oxides/elements association, the provenance of terrigenous components of coal deposits, palaeoclimate/weathering environments and tectonic settings.

2. Geological setting

Anambra basin, located in the Lower Benue Trough is a major coal producing basin in Nigeria (Figure 1). Anambra basin, a near triangular basin is located in the eastern part of Nigeria. The basin is bounded in the west by the Okitipupa ridge, in the south by the Niger Delta Basin, to the northwest, it directly overlies the Basement complex and inter fingers the Bida Basin [14]. Anambra basin lies between longitudes 6.3°E and 8.0°E and latitudes 5.0°N and 8.0°N. This basin is delimited in the north by the Basement complex, the Middle Benue Trough, and the Abakaliki Anticlinorium. Authors such as Akande and Erdtmann, [15]; Obaje *et al.* [4] have considered the basin as the lower Benue Trough, a NE-SW trending, folded, aborted rift basin that runs obliquely across Nigeria. Its origin was linked to the tectonic processes that accompanied the separation of the African and South American plates in the Early Cretaceous. This rift model is supported by evidence from structural, geomorphic, stratigraphic and paleontological studies [16-18]. The evolution of Anambra Basin represented the third cycle in the evolution of the trough and its associated basins when the Abakaliki Trough was uplifted to form the Abakaliki Anticlinorium while the Anambra platform was downwarped to form the Anambra Basin resulting in the westward displacement of the trough's depositional axis [18-20].

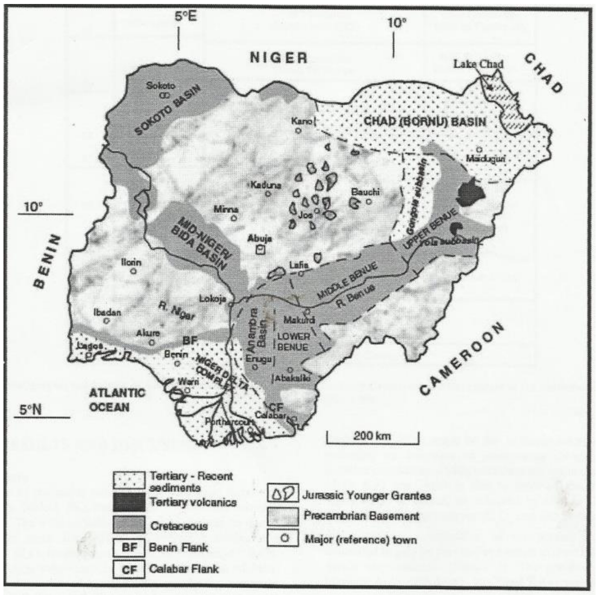

Figure 1. General geology of Nigeria *(after Obaje et al.* [24])

The basin is a sedimentary succession that directly overlies the facies of the Lower Benue trough and consists of Campanian to early Palaeocene lithofacies [20]. Several works on the Palaeoenvironment, palaeogeography, sedimentary tectonics, coal deposits and lithostratigraphy have been carried out ([2-3,7-8,13,20,23]). Sediments deposition within the Anambra Basin started during the Campanian, with Nkporo and Enuge shales constituting the basal beds of the Campanian period. The Campanion was a period of short marine transgression and regression, where the shallow-sea later became shallower due to subsidence [23]. This resulted in a regressive phase during the Maastrichtian which deposited the flood plain sediments and deltaic foresets of Mamu Formation regarded as the Lower coal measures. The Mamu Formation is overlain by the Ajali sandstones which also overlain by Nsukka Formation [23].

2.1. Lithostratigraphy of study area

Nkporo Formation. This is the basal sedimentary unit deposited during the Santonian folding and inversion in south eastern Nigeria and indicates a late Campanian age [25]. The formation is poorly exposed but has been described as a coarsening upward deltaic sequence of shale and interbed of sands and shale with occasional thin beds of limestones [25].

Enugu shales. This consists of carbonaceous grey, black shales and coals with interbeds of very fine sandstones/siltstones deposited in lower flood plain and swampy environment. The bedding planes are poorly defined with early diagenetic minerals such as pyrite and siderites. The Enugu shale is assigned Campanian to Lower Maastrichtian [25].

Mamu Formation. This formation overlies the Enugu shales conformably and contains sandstones, shale, mudstone, sandy-shale with coal seams in various horizons. The sediment pile ranges from 75m to over 100m. These deposits are an estuarine flood plain, swamp and flat flood [25].

Ajali Sandstones. This Formation (Middle Maastrichtian) overlies the Mamu Formation and has Middle to Upper Maastrichtian age. It has a thickness range of less than 300m to over 1000m at the Centre of the basin. This formation is made up of texturally mature sand facies [25].

Nsukka Formation. The Nsukka Formation is Upper Maastrichtian to Danian in age. It consists of alternating sandstones, sandy shales, and mudstones with interbedded coal seams. The marine shales of the Nsukka Formation were deposited in the Palaeocene, overlain by the tidal Nanka sandstones of Eocene age which constitute the Tertiary succession [2].

3. Materials and methods

Eighteen samples were collected from six locations scattered around Kogi east, Northern Anambra Basin, Nigeria. These eighteen representative samples were pre-prepared by washing, cutting and bagging and sent to Acme Laboratory Canada for sample preparation and analysis. All samples were analyzed at the Acme Analytical Laboratories Ltd, Canada for major, minor and trace element geochemistry. The ICP-mass spectrometer (Perkin-Elmer, Elan 6000) and inductively coupled plasma-mass spectrograph were used for the analysis. The samples were digested by weighing 0.2g aliquot in a graphite crucible mixed with 1.5g lithium metaborate/tetraborate ($LiBO_2$/LiB_4O_7) to form flux. The crucibles were placed in an oven and heated up to 980oC for 30 minutes. The cooled bead was dissolved in 5% HNO_3 (ACS grade nitric acid diluted in demineralized water). Calibration standards and reagent blanks were added to sample sequences. The basic package that consists of thirty-four elements (Ba, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, Y, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Lu) was determined. A second 0.5g split sample was digested in Aqua Regia and analysed by ICP-MS to determine Au, Ag, As, Bi, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Se, and Zn. An ICP-emission spectrograph (Spectro Ciros Vision or Varian 735) was also used for determination of major oxides and some trace elements (SiO_2,Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, P_2O_5, Cr_2O_5, Ba, Nb, Ni, Sr, Sc, Y, and Zr). Loss on ignition (LOI) was determined by the weight loss upon heating 1g split sample at 95^{o}C for 90 minutes.

The multivariate technique was applied to reveal hidden affinities within the database and undetectable by other means [26]. This method helps in extracting information about the similarities or dissimilarities among parameters. Latent factors in data sets were identified, and variables responsible for the variations observed explained the structure of the data set [26]. This is the basis for factor and cluster analyses which themselves are based on correlation coefficient relationships.

Factor analysis through a linear dependence model constructed in an abstract space called factor score space was used. It searches for correlations among measured variables that characterized a set of geochemical data [27]. Factor analysis reduces space dimensionality to obtain a better grouping of variables and determine relations between major components and variables analysed [29]. Elements association obtained from factor analysis is mathematically independent. The factor solutions provide information on loadings; communalities and eigenvalues [30].

Cluster analysis was also performed to classify elements of different geochemical sources on the basis of similar chemical properties. Hierarchical cluster analysis was used to find the true group of data. Cluster analysis using dendograms was used to identify relatively homogeneous groups of variables with similar properties [28]. Each cluster group shows similar and specific groups with respect to the source and geochemical characteristics. Data for cluster analysis were standardized to equalize the influence of the geochemical variables.

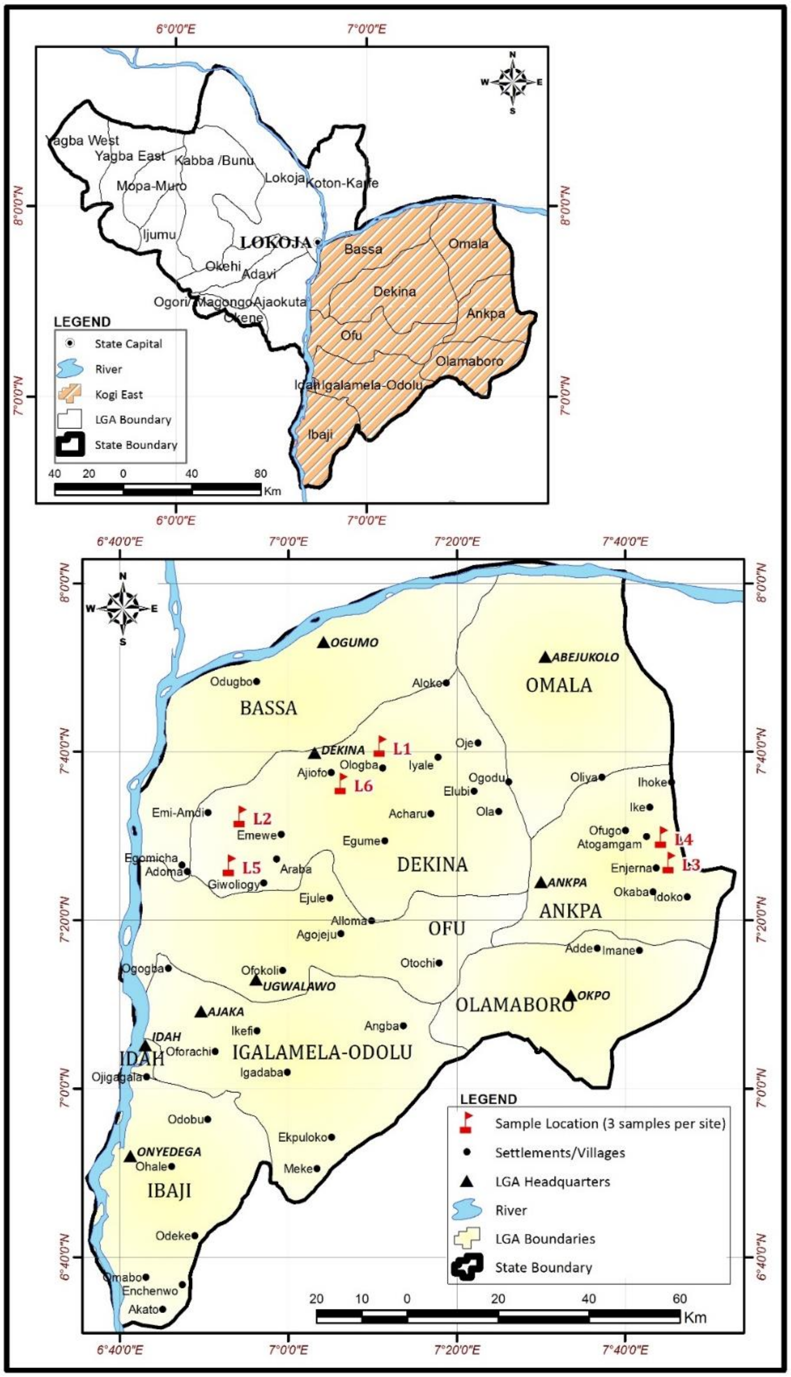

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Figure 2. Sample location map of the study area (*modified after Ameh, 2019)*

4. Results and discussion

4.1. Evidence from major oxides

The oxides, trace and rare elements are present in coals in inorganic forms. Many elements in coal are derived from the detrital inputs to the precursor swamp and many chalcophile elements associated with sulphide minerals [2]. The inorganic elements present in the coals suggest that these elements were sourced from terrigenous origin [31].

The result of the dominant coal major oxides shows average mean weight% of SiO_2 (16.36); Al_2O_3 (3.5); Fe_2O_3 (1.20); TiO_2 (0.44) and CaO (0.14) respectively. The rest oxides have significantly low mean weight percentages. The percentage weight of LOI is 78.06 (Table 1). The low Al_2O_3 could imply limited supply of detrital materials in peat and low level of weathering in the source area and coal seams [32]. On the basis of the concentrations of CaO; Na_2O and MgO, this coal may have been formed under continental freshwater conditions and low salinity environment. The major source of K in coal could be detrital, from coal intrusive and volcanic rocks which were clearly absent here. Also, the low Ti concentration observed may be due to the limited supply of Ti in peat and high in situ nature of inorganic matter [32].

Table 1. Descriptive statistics of major oxides in shale

Major oxides	Minimum	Maximum	Mean	SD	Std. error Mean	t-square	95% Confidence interval of the difference	
							Lower	Upper
SiO_2	3.94	62.00	16.36	22.55	9.20	1.77	-7.30	40.02
Al_2O_3	1.53	8.26	3.57	2.67	1.09	3.27	0.76	6.37
Fe_2O_3	0.18	2.22	1.20	0.73	0.30	4.01	0.43	1.97
MgO	0.00	0.07	0.03	0.02	0.00	3.40	0.00	0.05
CaO	0.01	0.32	0.14	0.11	0.04	3.06	0.02	0.26
Na_2O	0.00	0.01	0.00	0.00	0.00	2.08	0.00	0.01
K_2O	0.01	0.08	0.04	0.02	0.012	3.80	0.01	0.07
TiO_2	0.12	1.51	0.44	0.52	0.21	2.07	0.10	1.00
P_2O_5	0.00	0.03	0.01	0.01	0.00	2.55	0.00	0.02
MnO	0.00	0.04	0.01	0.01	0.00	2.22	0.00	0.03
Cr_2O_3	0.00	0.01	0.00	0.00	0.00	3.28	0.00	0.00
LOI	26.70	92.80	78.06	25.55	10.43	7.48	51.25	104.88
Total	32.49	167.35	99.86	52.19	21.28	38.99	44.31	154.68

4.2. Coal oxides ratios

The SiO_2/Al_2O_3 ratio recorded is 4.58. This low ratio shows that the coal results from low land peat. It also suggests a stable condition of deposition, a low degree of tectonic movement and slow but constant subsidence in the basin [32]. The $CaO+MgO/K_2O+Na_2O$ and the ratio of CaO/MgO revealed values of 4.25 and 4.67 respectively. These ratios show that the coals were probably associated with marine or brackish water influences, saline lakes or inorganic matter enriched in algal remains [32].

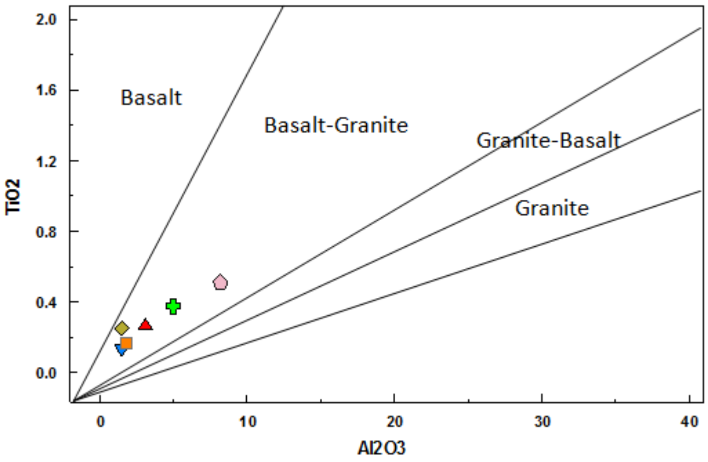

Figure 3. Provenance diagram of Al_2O_3 vs TiO_2 in coal *(after Amajor [35])*

According to Chen *et al.* [34], Al_2O_3 and TiO_2 in source rocks are preserved in the clastic sedimentary rocks because Al and Ti are not readily mobilized by weathering processes. The ratio of Al_2O_3/TiO_2 in sandstones, mudstones, and other sedimentary rocks changed insignificantly during weathering of source rocks and subsequent transportation, deposition, and diagenesis of the sediments [35].

Based on the discriminating criterion used to distinguished different types of parent igneous rocks, the ratio of Al_2O_3 /TiO_2 in the study coal ranged from 3-10 (Figure 3). This reflects predominantly mafic igneous rocks to intermediate rocks as the source of the terrestrial sediments that form part of the coal [33,35].

4.3. Evidence from major and trace elements

The plot of TiO_2 vs Zr can be compared with earlier defined source rock fields [34,36]. From the TiO_2 vs Zr plot (Figure 4), the inorganic components of the coal around the study area falls completely in the intermediate igneous rocks. This plot, like the earlier one, showed that the terrestrial source of sediments was predominantly from intermediate igneous rocks.

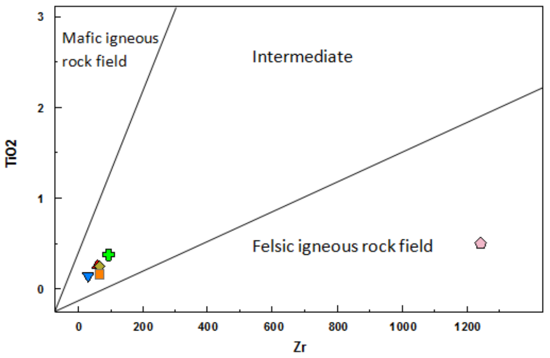

Figure 4. Provenance diagram of TiO_2 vs Zr in the study area *(after Hayashi et al. [34])*

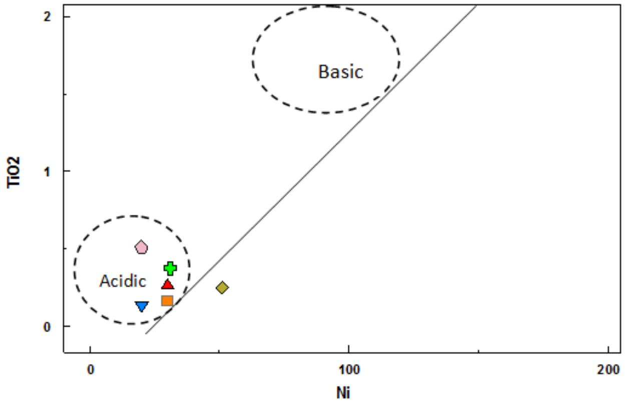

Figure 5. Provenance diagram of TiO_2 Vs Ni in coal samples *(Floyd et al. [37])*

The provenance plot of TiO_2/Ni (Figure 5) revealed that most samples plotted within the acidic field while only three samples plotted around the sandstones sedimentary trend. This is consistent with earlier plots that were predominantly basalt-granite source for the sediments.

Table 2. Correlation matrix of major oxides in coal

Major oxides	Correlation @ p= 0.01	Correlations @ P= 0.05
SiO_2	TiO_2 (0.999), LOI(0.998)	Al_2O_3 (0.907); P_2O_5(0.947; Cr_2O_3(0.958)
Al_2O_3	TiO_2(0.921); Cr_2O_3 (0.962); LOI(0.932)	Na_2O(0.887)
MgO		MnO(0.813)
CaO	MnO(0.927)	
TiO_2	Cr_2O_3(0.964); LOI(-0.999)	P_2O_5(0.956)
P_2O_5		Cr_2O_3(0.958); LOI(-0.948)
Cr_2O_3	LOI(-0.969)	

** Correlation is significant at the 0.05 level. ** Correlation is significant at the 0.01 level.*

4.4. Major oxides correlation

Given $P < 0.01$ (Table 2), analysis of major oxides of coal revealed strong correlation between SiO_2 and TiO_2 (0.999); SiO_2 and LOI (0.998); Al_2O_3 and TiO_2 (0.921); Al_2O_3 and Cr_2O_3 (0.962); Al_2O_3 and LOI (0.932); CaO and MnO (0.927); TiO_2 and Cr_2O_3 (0.964); TiO_2 and LOI(-0.999); Cr_2O_3 and LOI(-0.969). At $P < 0.05$, significant correlations were also observed between SiO_2 and Al_2O_3 (0.907); SiO_2 and P_2O_5 (0.956); SiO_2 and Cr_2O_3 (0.958); Al_2O_3 and Na_2O (0.887); MgO and MnO (0.813); TiO_2 and P_2O_5 (.956); P_2O_5 and Cr_2O_3 (0.958); P_2O_5 and LOI (-0.948).

The dominant major oxides were SiO_2; Al_2O_3 and Fe_2O_3. The likely carriers of these elements were quartz; clay minerals and pyrites [38]. The relatively high presence of TiO_2 is an indication that Ti was incorporated into the aluminosilicates structure. It could also be implied that kaolinite and TiO_2 co-precipitated or that the Ti content in sediment input to the original peat swamp from mafic basaltic rocks was probably high [38]. The high correlation between CaO-MnO (0.927) and MgO-MnO (0.813) shows that the CaO and MgO in the coals maybe associated with carbonates (calcite, dolomite, and ankerite). From Table 2, TiO_2; Cr_2O_3; LOI and Na_2O, all showed a positive correlation with Al_2O_3. This suggests that these oxides in coal were associated with aluminosilicates such as clay minerals and probably from the same source [38]. The Cr_2O_3 and LOI showed a positive relationship with P_2O_5. This affinity implies aluminophosphates minerals [38].

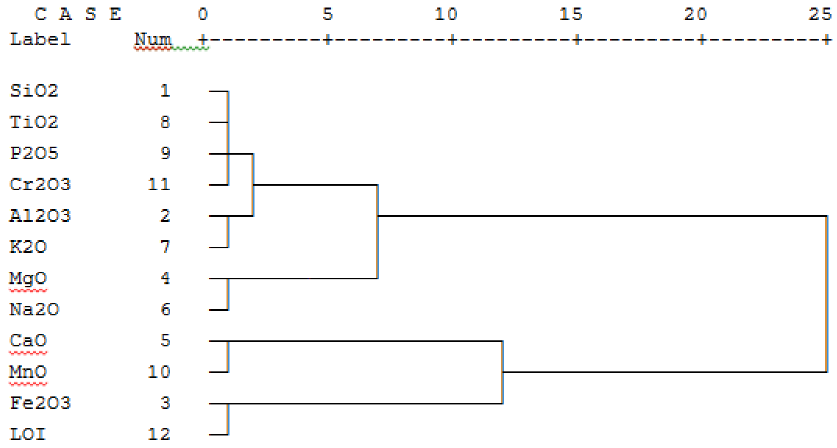

Figure 6. Cluster yield of major oxides of coal

Two clusters were extracted from the oxides of coal analysis. Cluster one consist of SiO_2, TiO_2, P_2O_5, Cr_2O_3, Al_2O_3, K_2O, MgO and Na_2O. Within this cluster, strongest similarities were observed between SiO_2, TiO_2, Cr_2O_3, K_2O, and Na_2O. A lesser degree of similarities was observed within the same cluster between P_2O_5 and Al_2O_3. Cluster two includes CaO, MnO, Fe_2O_3, and LOI. Most significant similarity was however observed between MnO and LOI (Figure 6).

While cluster one indicates mixtures of origin such as detrital quartz, clay minerals, basaltic salts of oceanic environment and some degree of carbonate affinity, cluster two suggests carbonate affinity and Fe bearing montmorillonite, chlorite and oxyhydroxides sources [32,39].

Table 3. Varimax rotated a component of major oxides of coal

Major oxides	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
Component 1	**0.986**	**0.972**	**-0. 999**	**0.538**	-0.338	**0.729**	**0.952**	**0.989**	**0.957**
Component 2	-0.165	0.236	-0.050	**0.843**	**0.941**	**0.684**	0.307	-0.148	-0.290

Major oxides	MnO	Cr_2O_3	LOI	Eigen values	% variance	% cumulative
Component 1	-0.228	**1.000**	**-0.992**	8.685	72.378	72.378
Component 2	**0.974**	-0.013	0.128	3.315	27.622	100.00

Varimax rotated analysis extracted two factors as responsible for the 100% cumulative variance observed in the data (Table 3). Factor one consist of high factor loadings for SiO_2 (0.986); Al_2O_3 (0.972); Fe_2O_3 (-0.999); MgO (0.538); Na_2O (0.729); K_2O (0.929); TiO_2 (0.989); P_2O_5 (0.957); and LOI (-0.992). This factor has eigenvalue of 8.685 and % variance of 72.378. Factor two include high factor loadings of MgO (0.843); CaO (0.941); Na_2O (0.684); MnO (0.974). Eigenvalue of 3.315 and % variance of 27.622 was recorded.

Table 4. Descriptive statistics of trace elements in coal.

Trace elements	Minimum	Maximum	Mean	Std. Deviation	T-square	95% confidence interval of the difference	
						Lower	Upper
Ni	.00	51.00	14.20	19.28	2.89	2.67	44.66
Sc	.00	11.00	2.53	3.66	3.78	1.76	9.23
Ba	.00	122.00	69.00	43.43	5.80	44.86	116.13
Be	2.00	16.00	8.66	5.78	3.67	2.59	14.73
Co	2.50	30.50	13.75	10.62	3.17	2.60	24.89
Cs	0.00	0.30	0.06	0.10	1.74	-0.03	0.20
Ga	2.80	24.20	10.90	7.59	3.51	2.93	18.86
Hf	.80	32.40	6.71	12.59	1.30	-6.49	19.93
Nb	.00	23.50	5.24	7.35	2.45	-.38	16.12
Rb	.20	3.30	1.46	1.18	3.03	.22	2.70
Sn	2.00	2.00	2.00		1.00	-.52	1.19
Sr	.00	28.40	12.12	11.13	5.47	9.63	26.72
Ta	.10	1.60	.55	.54	2.48	-.02	1.12
Th	1.50	17.40	5.26	6.11	2.11	-1.15	11.68
U	.00	4.50	1.16	1.49	2.44	-.07	3.17
V	10.00	49.00	28.00	14.11	4.85	13.18	42.81
W	.50	1.40	.95	.63	1.36	-.27	.91
Zr	34.40	1242.50	261.20	481.13	1.33	-243.71	766.11
Y	.00	118.00	19.78	33.43	2.71	2.27	83.45
Mo	.20	0.40	0.31	0.09	7.88	0.21	0.41
Cu	7.10	30.50	14.71	8.19	4.39	6.11	23.31
Pb	2.00	10.30	5.48	3.18	4.21	2.13	8.82
Zn	7.00	504.00	118.50	192.52	1.50	-83.54	320.54
As	3.80	54.20	25.43	17.73	3.51	6.82	44.04
Cd	0.00	0.00	0.00	0.00	1.85	-0.18	1.15
Sb	0.30	1.70	0.72	0.66	1.58	-0.02	0.08
Bi	0.10	0.10	0.10	0.00	5.54	0.74	2.02
Ag	0.00	2.60	1.03	0.82	2.84	0.01	0.37
Au	0.05	0.43	0.19	0.170	2.07	-.01	0.18
Hg	0.00	0.20	0.10	0.10	2.23	0.02	0.08
Tl	0.10	0.20	0.21	0.32	1.35	0.26	0.91
Se	0.20	0.40	0.01	0.11	3.15	0.18	0.26
Total	**77.65**	**2384.03**	**630.32**	**884.96**	**97.19**	**435.49**	**1606.78**

From the rotated result (Table 3), component two is clearly a carbonate source factor while component one range from factors such as aluminosilicates, aluminophosphates, and basalts as possible sources for the variables [38].

4.5. Trace elements

The geochemical behavior of trace and rare elements in modern, organic rich sedimentary rocks such as coal has been documented and used to determine the terrestrial sediments source component of the organic rocks [20].

The trace element analysis (Table 4) indicates abundance order of: Zr>Zn>Ba>V>As>Y>Cu>Ni>Co>Sr>Ga>Be>Hf>Pb>Th>Nb>Sc>Sn. The ratio Sr/Ba of 0.176 showed that these coal occurrences were deposited on the continent. The V/(V+Ni) ratio of 0.66 is also considered as a transitional boundary from oxic to sub oxic and anoxic depositional environment [39].

The correlation (Table 5) revealed that the likely source of the trace elements was lithophilic at P=0.01.While the significant relationship was recorded between the lithophiles and the chalcophiles from trace elements such as Nb to W, it is worthy to state that this relationship occurred at P=0.005. At P=0.001 and P=0.05, from trace element Y to Sb, the chalcophile dominated the association (Table 5).

Table 5. Correlation of trace elements in coal

Trace elements	Correlation @ p= 0.01	Correlations @ P= 0.05
Ni	Z(0.993); As(0.994)	Sb (0.999); Se (0.916)
Sc	Cs(0.993); Ga (0.956); W(1.00)	V(0.819)
Ba	Sr(0.993); W(-1.00)	
Be	W(-1.00)	
Co	W(1.00); As(0.926)	Zn(0.886)
Cs	Nb(0.993); U(0.985); W(1.00); Sb(1.00); Hg(-1.00)	Hf(1.00); Zr(1.00)
Ga	W(1.00)	
Hf	Nb(0.981); Ta(0.958);Th(0.987);U(0.942); W(1.00); Zr(1.00)	
Nb	Ta(0.976); Th(0.996); U(0.988); W(1.00); Zr(0.982)	Rb(0.842); Pb(0.958)
Sr	W(1.00)	
Ta	Th(0.976); U(0.976); W(1.00); Zr(0.956)	Pb(0.812)
Th	U(0.990); W(1.00); Zr(0.943)	Pb(0.849)
U	W(1.00); Zr(0.943)	Pb(0.879); Se(-0.998)
V	W(1.00)	Mo(0.879)
W	Zr(1.00); Y(1.00); Cu(1.00); Pb(1.00); Zn(1.00); As(1.00); Sb(1.00);Hg(1.00); Tl(1.00)	
Y	Cu(0.986)	Se(-0.999)
Zn		As(0.867)
Sb	Se(1.00)	

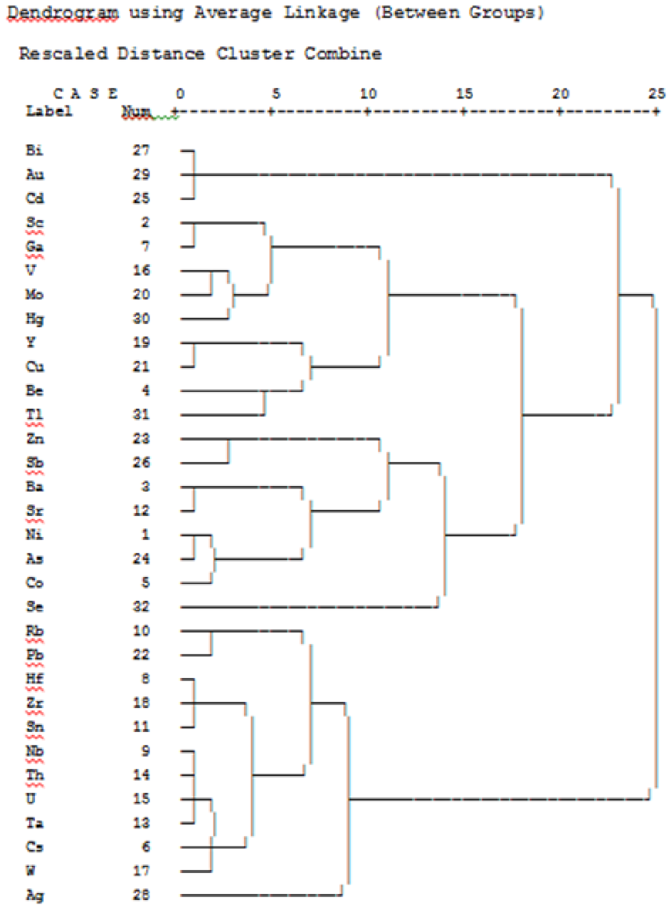

Figure 7. Cluster result of trace elements in coal

The trace element yielded four clusters (Figure 7). Cluster one (Bi, Au, and Cd) shows that all the elements were lithophilic. Cluster two is a mixture of sources. From dominantly lithophilic (Sc, V,Y,Cu, and Be) to chalcophilic (Ga,Hg and Tl) and finally the siderophile (Mo). Cluster three suggests three sources for the elements – the siderophile (Zn, Sb, Ni, Co, and Se), the lithophiles (Ba, Sr) and the chalcophiles (As). The last cluster is a mixture of two sources. These are lithophilic (Rb, Hf, Zr, Nb, Th, U, Ta, Cs and W) and the Chalcophile (Pb, Sn, and Ag).

From the above analysis, it is clear that the dominant sources for the trace elements were the lithophiles (clusters 4 and 2); Siderophile (clusters 3 and 2) and the chalcophile (clusters 1, 2, 4 and 3).

4.6. Rare earth elements

Table 6. Descriptive statistics of rare earth elements in coal

Rare Elements	Minimum	Maximum	Mean	Std. Deviation	Std. Error Mean	t-square	95% Confidence interval of the difference	
							Lower	Upper
La	4.50	48.90	21.01	17.28	7.05	2.97	2.88	39.15
Ce	9.90	94.40	42.35	31.60	12.90	3.28	9.17	75.52
Sm	.78	18.19	7.45	5.82	2.37	3.13	1.34	13.55
Eu	.15	4.40	1.72	1.42	.57	2.97	.23	3.21
Gd	.82	23.69	8.49	7.81	3.19	2.66	.29	16.70
Tb	.13	3.71	1.35	1.22	.49	2.70	.06	2.63
Dy	.78	21.00	7.67	6.93	2.83	2.71	.40	14.95
Ho	.15	4.05	1.52	1.32	.53	2.81	.13	2.90
Er	.50	10.44	4.11	3.34	1.36	3.01	.60	7.62
Tm	.05	1.38	.57	.44	.18	3.16	.10	1.03
Yb	.43	8.06	3.64	2.61	1.06	3.42	.90	6.38
Lu	.06	1.15	.53	.37	.15	3.50	.14	.92
Total	**18.25**	**239.37**	**100.41**	**80.16**	**32.68**	**36.32**	**16.24**	**369.12**

The LREE generally have higher mean concentration compared to the HREE (Table 6). The ratios of La/Yb (5.77); La/Sm (2.82) and Gd/Yb(2.33) showed that the degree of enrichment of LREE is higher than HREE. This is evidence that fractionation occurred in the LREE and HREE. The average ratio (La/Sm) n value of 2.82 indicates that some degree of fractionation also occurred among the LREE [39].

Table 7. Correlation matrix of rare earth elements in coal

Rare earth elements	Correlation @ p= 0.01	Correlations @ P= 0.05
La	Ce(0.987);	
Sm	Eu(0.983); Gd(0.982); Tb(0.985); Dy(0.988); Ho(0.994); Er(0.997); Lu(0.975);Tm(0,999); Yb(0.983)	
Eu	Gd(0.994); Tb(0.997); Dy(0.996);Ho(.994); Er(0.991); Lu(0.922);Tm(0.982); Yb(0.941)	
Gd	Tb(0.999); Dy(0.997); Ho(0.997); Er(0.993); Lu(0.918); Tm(0.978); Yb(0.933)	
Tb	Dy(0.999); Ho(0.998); Er(0.995); Lu(0.924); Tm(0.983); Yb(0.942)	
Dy	Ho(0.998); Er(0.996); Lu(0.931); Tm(0.986); Yb(0.950)	
Ho	Er(0.999); Lu(0.945); Tm(0.991); Yb(0.958)	
Er	Lu(0.958); Tm(0.996); Yb(0.969)	
Lu	Tm(0.978); Yb(0.996)	
Tm	Yb(0.987)	

*** Correlation is significant at the 0.01 level.*

At $P<0.01$, all the correlations recorded between Sm-Eu-Gd-Tb-Dy-Ho-Er-Lu-Tm-Yb were significant (Table 7) in both directions. Ce showed no significant relationship with any element. La also showed no significant relationship with all the elements except La and Ce (0.897). From Table 7, the REEs appeared to be generally related to primarily clay minerals and phosphates except for La and Ce that may suggest a dominantly phosphatic affinity with an organic origin.

Cluster analysis of rare earth elements yielded two clusters (Figure 8). Cluster one consists of Tb, Dy, Gd, Ho, Er, Eu, Sm, Tm, Yb, and Lu. Most significant similarities exist between Tb-Dy-Gd-Ho-Eu- Sm-Tm and Lu. Between Er and Yb was a lesser degree of similarity. Cluster two consists of La and Ce. These two elements showed the most significant similarity (Figure 8).

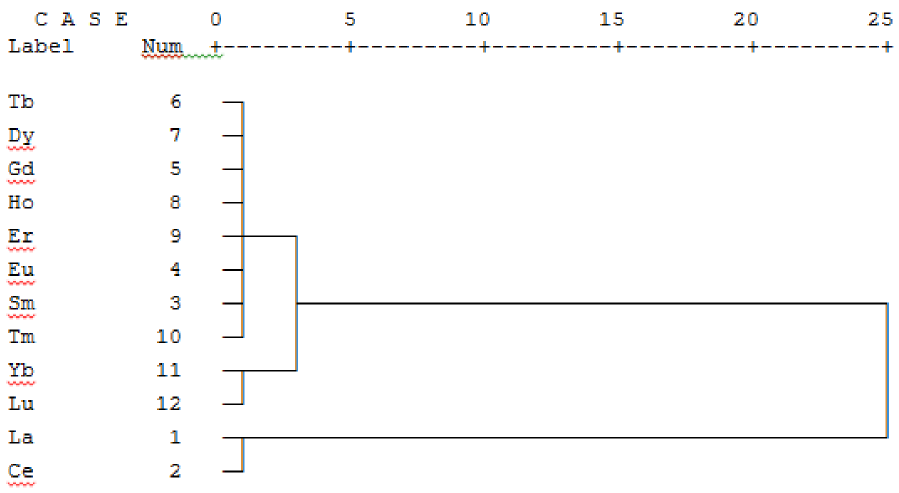

Figure 8. Rare earth element cluster analysis

From figure 8 and table 7, La and Ce appeared in the same cluster and factor component. This is an indication that these elements were from a different source and are controlled by a factor(s) different from other rare earth elements. While other REEs such as Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu maybe associated with the inorganic component of the coal, the La and Ce suggests organic origin such as phosphates [38].

Table 7. Varimax rotated component matrix of rare earth elements

Rare Earth Elements	La	Ce	Sm	Eu	Gd	Tb	Dy	Ho
Component 1	0.244	0.144	**0.961**	**0.990**	**0.982**	**0.988**	**0.989**	**0.979**
Component 2	**0.967**	**0.986**	0.273	0.121	0.149	0.136	0.139	0.197

Rare Earth Elements	Er	Tm	Yb	Lu	Eigen values	% variance	% cumulative
Component 1	**0.974**	**0.960**	**0.914**	**0.885**	9.350	77.920	77.920
Component 2	0.227	0.274	0.367	0.440	2.550	21.247	99.167

The rare earth element analysis recorded two factor components (Table 7). Factor one consists of high factor loadings of .8 to .9 for all rare earth elements analysed except La and Ce. This factor has an eigenvalue of 9.350 and % variance of 77.920. Factor two consists of high factor loadings of La (0.967) and Ce (0.986) only. The % cumulative of 99.167 was enough for the variations observed (Table 7).

4.7. Palaeoweathering/climatic conditions of deposition

According to Suttner and Dutta [40], the binary plot of SiO_2 Vs (Al_2O_3 + K_2O+ Na_2O) has been used to reconstruct the climatic conditions of the source area. Based on this plot, the coal samples from the study area plotted within the humid field (Figure 9). This indicates that both weathering of source rocks/materials and conditions surrounding the coal formations occurred in humid climatic environments [33].

The Si becomes unstable in rocks due to the removal of silica rocks as weathering progresses. According to Chen *et al.* [33], the SiO_2-Al_2O_3-TFe_2O_3 (SAF) ternary diagram proposed by Schellmann [41] can be used to quantify the degree of laterization. On the basis of the SAF ternary diagram above, the coal samples from the study area may have suffered weak laterization to kaolinisation (Figure 10).

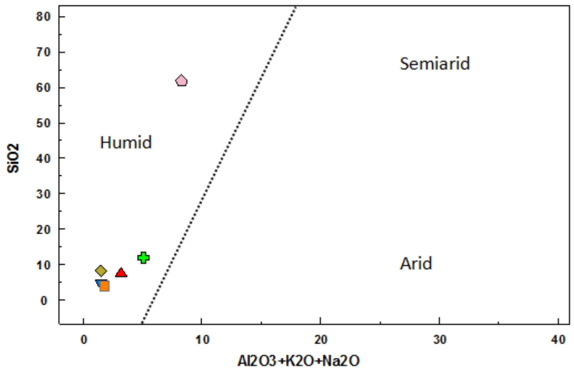

Figure 9. Paleoclimatic diagram of SiO_2 Vs Al_2O_3 +K_2O+ Na_2O *(After Suttner and Dutta, [40])*

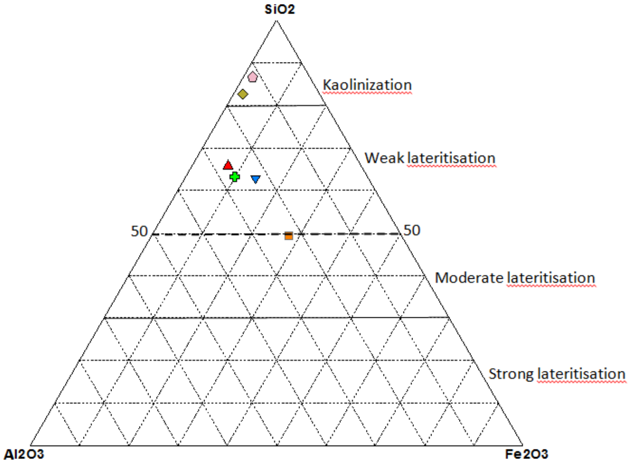

Figure 10. Triangular diagram of SiO_2-Al_2O_3-Fe_2O_3 *(after Chen et al. [33])*

5. Conclusion

From work carried out on the coal within the Northern Anambra basin, the following observations were revealed:

(a) The coal was formed from low land peat environment associated with marine or blackish water influence

(b) Stable condition of deposition, a low degree of tectonic movement but constant subsidence in the basin was observed.

(c) The transitional boundary of oxic to sub-oxic and anoxic environments was observed with an acidic and humid climate

(d) Weak laterization to kaolinization were also observed.

Conflict of interest

No conflict of interest as far as this manuscript is a concern.

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