

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 multivariate statistical approach to determine the major, trace and rare elements association with a view to determine the source of the terrestrial rocks, palaeoweathering/climatic conditions and tectonic setting. The dominant oxides such as SiO₂, Al₂O₃, Fe₂O₃, TiO₂ and CaO were identified in the coal to suggest terrigenous origin. The ratio of SiO₂/Al₂O₃ 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/K₂O + Na₂O ratios. The major oxides also revealed stable condition of deposition, low degree of tectonic setting but constant subsidence in the basin. The condition of deposition was acidic in nature as indicated by TiO₂/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 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 · Euclidean

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 (MacDonald et al. 2011; Raistrick 1974). 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 (Ogala et al. 2010). The Anambra Basin contains important coal measures in the Mamu and Nsukka Formations (Umeji 2005; Uzoegbu et al. 2014). The mining of this sub-

bituminous coal occurred in the Mamu Formation. Total coal reserves in the north–south trending coal belt were asessed to be about 1.5 billion tons (De Swardt and Cassey 1963). Lignite deposits occur in numerous seams in an east–west belt to the southwest (Simpson 1954; Uzoegbu et al. 2014). A number of studies (Obaje et al. 1999; Reyment 1965; Akande et al. 1992, 2007; Okorie and Egila 2014) 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 (Olajire et al. 2007; Ndiokwere et al. 1983; Sonibare et al. 2005; Ewa 2004; Ogala et al. 2009, 2010).

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 (Uzoegbu et al. 2014).

The objectives of this current study are to present the inorganic characteristics of Okaba coal using multivariate statistical approach with a view to determine the oxides/elements association, provenance of terrigenous

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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 (Fig. 1). Anambra basin, a near triangular basin is located in 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 north-west it directly overlies the Basement complex and inter fingers the Bida Basin (Adebayo et al. 2015; Osazuwa and Saka 2016). 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 (1998), Obaje et al. (1999) 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 (Reyment and Tait 1972). This rift model is supported by evidence from structural, geomorphic, stratigraphic and paleontological studies (Reyment 1969; Burk et al. 1972; Murat 1972). The evolution of Anambra Basin represents 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 (Murat 1972; Webber and Daukoru 1975; Adebayo et al. 2015).

The basin is a sedimentary succession that directly overlies the facies of the Lower Benue trough and consists of Campanian to early Palaeocenelithofacies (Adebayo et al. 2015). Several works on the Palaeoenvironment, palaeogeography, sedimentary tectonics, coal deposits and lithostratigraphy have been carried out (Nwajide and Reijers 1996; Akande et al. 2007; Ogala et al. 2009, 2010; Onyekuru and Iwuagwu 2010; Okorie and Egila 2014; Akinyemi et al. 2014; Uzoegbu et al. 2014; Adebayo et al. 2015). Sediments deposition within the Anambra Basin started during the Campanian, with Nkporo and Enugeshales constituting the basal beds of the Campanian period. The Campanian was a period of short marine transgression and regression, where the shallow-sea later became shallower due to subsidence (Akinyemi et al. 2014). 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 (Akinyemi et al. 2014).

2.1 Lithostratigraphy of study area

- (1) *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 (Odumoso et al. 2013). The formation is poorly exposed but has been described as coarsening upward deltaic sequence of shale and interbed of sands and shale with occasional thin beds of limestones (Odumoso et al. 2013).
- (2) *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 (Fig. 2). The bedding planes are poorly defined with early diagenetic minerals such as pyrite and siderites. The Enugu shale is assigned Campanian to Lower Maastrichtian (Odumoso et al. 2013).
- (3) *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 75 to over 100 m (Fig. 2). These deposits are estuarine flood plain, swamp and flat flood (Odumoso et al. 2013).
- (4) *Ajali Sandstones* This Formation (Middle Maastrichtian) overlies the Mamu Formation and has Middle to Upper Maastrichtian age (Fig. 2). It has thickness range of less than 300 m to over 1000 m

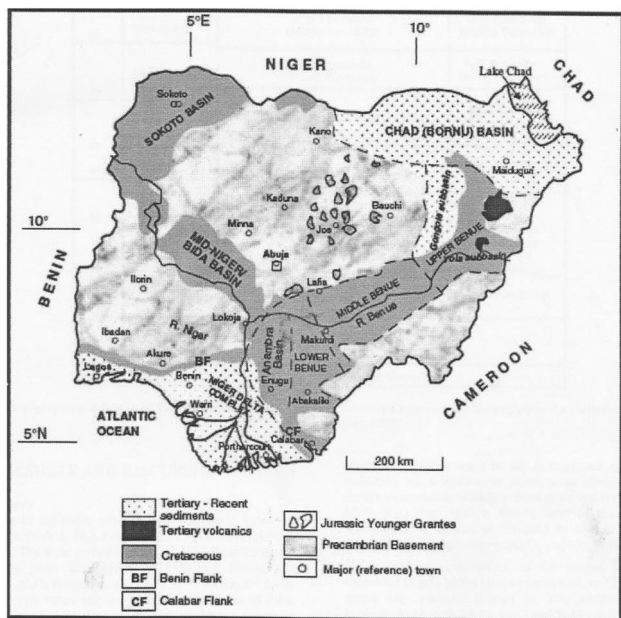


Fig. 1 General geology of Nigeria (after Obaje et al. 1994)

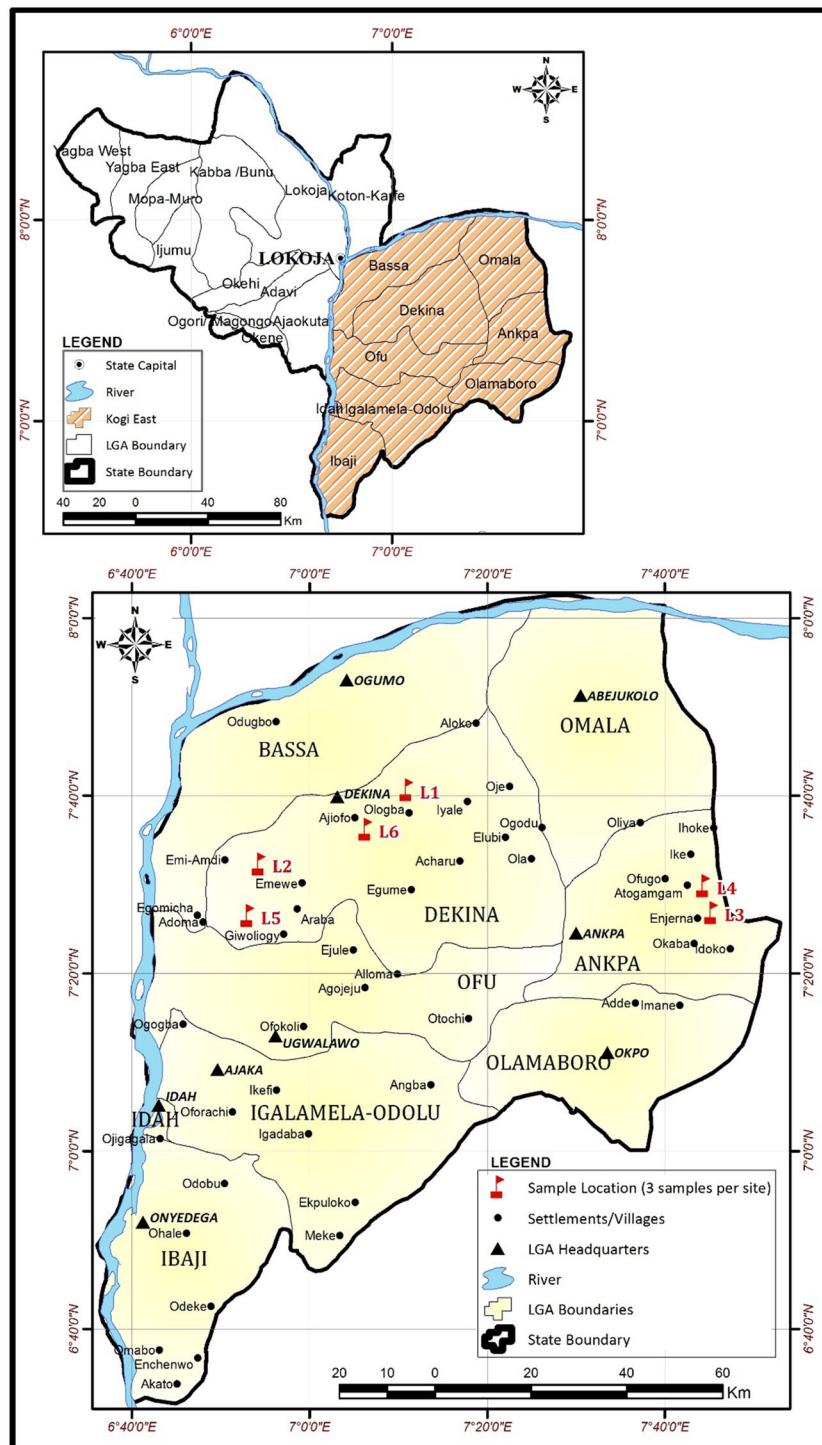


Fig. 3 Location map of Coal sample occurrences (Scale: 1:25,000)

and specific groups with respect to source and geochemical characteristics. Data for cluster analysis were standardized to equalize the influence of the geochemical variables.

4 Results and discussion

(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 (Ogala et al. 2010). The inorganic elements present in the coals suggest that these elements were sourced from terrigenous origin (Yandoka et al. 2015).

The result of the dominant coal major oxides shows average mean weight% of SiO₂ (16.36); Al₂O₃ (3.5); Fe₂O₃ (1.20); TiO₂ (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 Al₂O₃ could imply limited supply of detrital materials in peat and low level of weathering in source area and coal seams (Stanislav et al. 2010). On the basis of the concentrations of CaO; Na₂O 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 limited supply of Ti in peat and high in situ nature of inorganic matter (Stanislav et al. 2010).

(2) Coal oxides ratios

The SiO₂/Al₂O₃ ratio recorded is 4.58. The low SiO₂/Al₂O₃ ratio is an indication that the coal was formed under stable conditions of deposition, where subsidence was slow and steady and with low degree of tectonic activities (Yossifova et al. 2009; Zhao et al. 2015; Stanislav et al. 2010).

The CaO + MgO/K₂O + Na₂O and the ratio of CaO/MgO revealed values of 4.25 and 4.67 respectively. These ratios shows that the coals were probably associated with

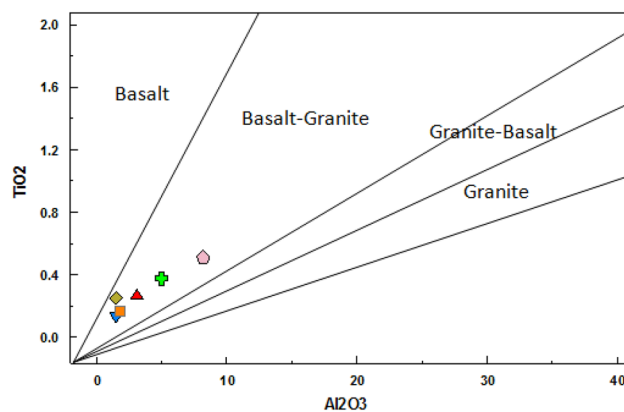


Fig. 4 Provenance diagram of Al₂O₃ versus TiO₂ in coal (after Amajor 1987)

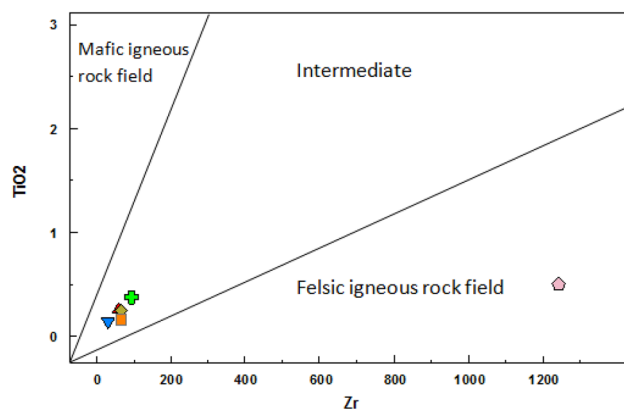


Fig. 5 Provenance diagram of TiO₂ versus Zr in study area (after Hayashi et al. 1997)

Table 1 Descriptive statistics of major oxides

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 ₂ O ₃	1.53	8.26	3.57	2.67	1.09	3.27	0.76	6.37
Fe ₂ O ₃	0.18	2.22	1.20	0.73	0.30	4.01	0.43	1.97
MgO	BDL	0.07	0.03	0.02	BDL	3.40	BDL	0.05
CaO	0.01	0.32	0.14	0.11	0.04	3.06	0.02	0.26
Na ₂ O	BDL	0.01	BDL	BDL	BDL	2.08	BDL	0.01
K ₂ O	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 ₂ O ₅	BDL	0.03	0.01	0.01	BDL	2.55	BDL	0.02
MnO	BDL	0.04	0.01	0.01	BDL	2.22	BDL	0.03
Cr ₂ O ₃	BDL	0.01	BDL	BDL	BDL	3.28	BDL	BDL
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

BDL below detection limit

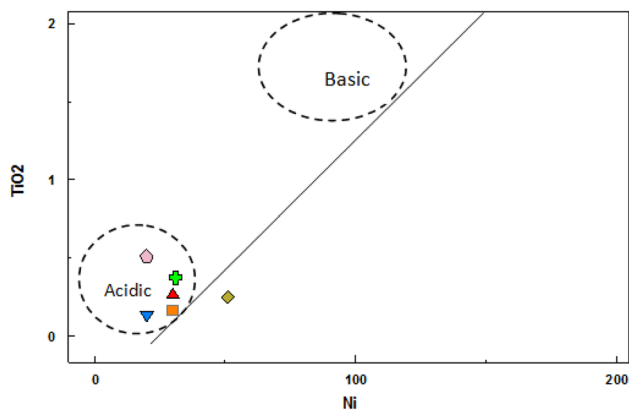


Fig. 6 Provenance diagram of TiO₂ versus Ni in coal samples (Floyd et al. 1989)

marine or brackish water influences, saline lakes or inorganic matter enriched in algal remains (Stanislav et al. 2010).

According to Chen et al. (2016), Al₂O₃ and TiO₂ in source rocks are preserved in the clastic sedimentary rocks

because Al and Ti are not readily mobilized by weathering processes. The ratio of Al₂O₃/TiO₂ in sandstones, mudstones and other sedimentary rocks changed insignificantly during weathering of source rocks and subsequent transportation, deposition and diagenesis of the sediments (Hayashi et al. 1997).

Based on the discriminating criterion used to distinguished different types of parent igneous rocks, the ratio of Al₂O₃/TiO₂ in the study coal ranged from 3 to 10 (Fig. 4). This reflects predominantly basalt to granite rocks as the source of the terrestrial sediments that form part of the coal (Amajor 1987; Chen et al. 2016).

(3) Evidence from major and trace elements

The plot of TiO₂ versus Zr can be compared with earlier defined source rock fields (Stone et al. 1987; Hayashi et al. 1997). From the TiO₂ versus Zr plot (Fig. 5), 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 were predominantly from intermediate igneous rocks.

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 ₂ O ₃ (0.907); P ₂ O ₅ (0.947); Cr ₂ O ₃ (0.958)
Al ₂ O ₃	TiO ₂ (0.921); Cr ₂ O ₃ (0.962); LOI (0.932)	Na ₂ O (0.887)
MgO		MnO (0.813)
CaO	MnO (0.927)	
TiO ₂	Cr ₂ O ₃ (0.964); LOI (- 0.999)	P ₂ O ₅ (0.956)
P ₂ O ₅		Cr ₂ O ₃ (0.958); LOI (- 0.948)
Cr ₂ O ₃	LOI (- 0.969)	

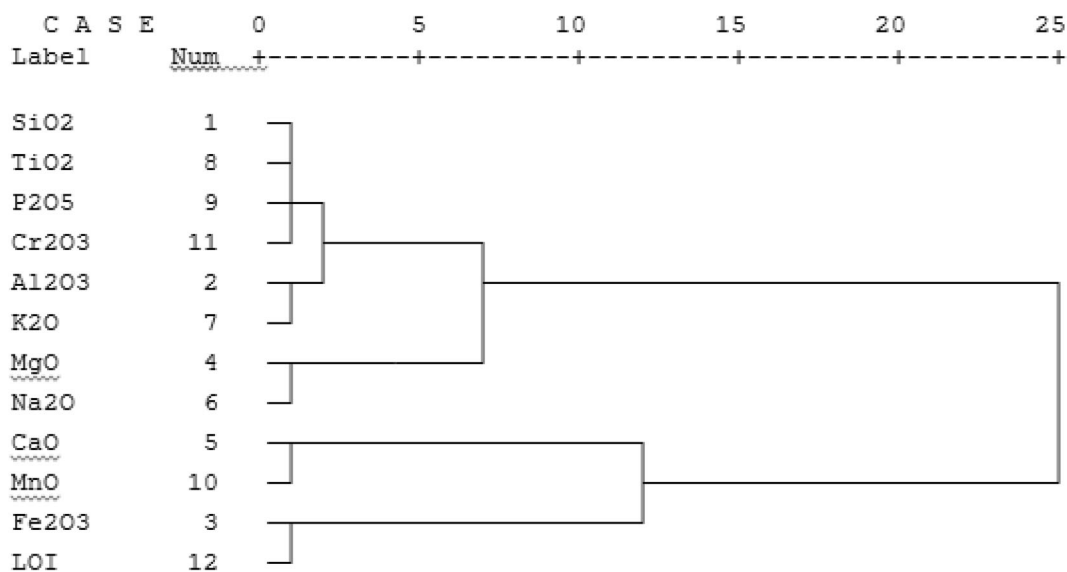


Fig. 7 Cluster yield of major oxides of coal

Table 3 Varimax rotated component of major oxides of coal

Component	Major oxides											Eigen values	Variance (%)	Cumulative (%)	
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cr ₂ O ₃				LOI
1	0.986	0.972	-0.999	0.538	-0.338	0.729	0.952	0.989	0.957	-0.228	1.000	-0.992	8.685	72.378	72.378
2	-0.165	0.236	-0.050	0.843	0.941	0.684	0.307	-0.148	-0.290	0.974	-0.013	0.128	3.315	27.622	100.00

The values in bold are the values that were statistically significant for this study

The provenance plot of TiO₂/Ni (Fig. 6) 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.

(4) Major oxides correlation

Given $P < 0.01$ (Table 2), analysis of major oxides of coal revealed strong correlation between SiO₂ and TiO₂ (0.999); SiO₂ and LOI (0.998); Al₂O₃ and TiO₂ (0.921); Al₂O₃ and Cr₂O₃ (0.962); Al₂O₃ and LOI (0.932); CaO and MnO (0.927); TiO₂ and Cr₂O₃ (0.964); TiO₂ and LOI (-0.999); Cr₂O₃ and LOI (-0.969). At $P < 0.05$, significant correlations were also observed between SiO₂ and Al₂O₃ (0.907); SiO₂ and P₂O₅ (0.956); SiO₂ and Cr₂O₃ (0.958); Al₂O₃ and Na₂O (0.887); MgO and MnO (0.813); TiO₂ and P₂O₅ (0.956); P₂O₅ and Cr₂O₃ (0.958); P₂O₅ and LOI (-0.948).

The dominant major oxides were SiO₂; Al₂O₃ and Fe₂O₃. The likely carriers of these elements were quartz; clay minerals and pyrites (Zhao et al. 2015). The relatively high presence of TiO₂ is an indication that Ti was incorporated into the aluminosilicates structure. It could also implied that kaolinite and TiO₂ co-precipitated or that the TiO₂ content could be as a result of the following: that the Ti was incorporated into the aluminosilicates structure; that kaolinite and TiO₂ co-precipitated or that the Ti content from the intermediate rocks were probably high (Zhao et al. 2015). 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, TiO₂; Cr₂O₃; LOI and Na₂O, all showed positive correlation with Al₂O₃. This suggests that these oxides in coal were associated with aluminosilicates such as clay minerals and probably from the same source (Zhao et al. 2015). The Cr₂O₃ and LOI showed positive relationship with P₂O₅. This affinity implies aluminophosphates minerals (Zhao et al. 2015).

Two clusters were extracted from the oxides of coal analysis. Cluster one consist of SiO₂, TiO₂, P₂O₅, Cr₂O₃, Al₂O₃, K₂O, MgO and Na₂O. Within this cluster, strongest similarities were observed between SiO₂, TiO₂, Cr₂O₃, K₂O and Na₂O. A lesser degree of similarities were observed within same cluster between P₂O₅ and Al₂O₃. Cluster two includes: CaO, MnO, Fe₂O₃, and LOI. Most significant similarity was however observed between MnO and LOI (Fig. 7).

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 (Stanislav et al. 2010; Taghipour and Marshk 2015).

Table 4 Descriptive statistics of trace elements in coal

Trace elements	Minimum	Maximum	Mean	SD	t-square	95% confidence interval of the difference	
						Lower	Upper
Ni	BDL	51.00	14.20	19.28	2.89	2.67	44.66
Sc	BDL	11.00	2.53	3.66	3.78	1.76	9.23
Ba	BDL	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	BDL	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	0.80	32.40	6.71	12.59	1.30	- 6.49	19.93
Nb	BDL	23.50	5.24	7.35	2.45	- 0.38	16.12
Rb	0.20	3.30	1.46	1.18	3.03	0.22	2.70
Sn	2.00	2.00	2.00	BDL	1.00	- 0.52	1.19
Sr	BDL	28.40	12.12	11.13	5.47	9.63	26.72
Ta	0.10	1.60	0.55	0.54	2.48	- 0.02	1.12
Th	1.50	17.40	5.26	6.11	2.11	- 1.15	11.68
U	BDL	4.50	1.16	1.49	2.44	- 0.07	3.17
V	10.00	49.00	28.00	14.11	4.85	13.18	42.81
W	0.50	1.40	0.95	0.63	1.36	- 0.27	0.91
Zr	34.40	1242.50	261.20	481.13	1.33	- 243.71	766.11
Y	BDL	118.00	19.78	33.43	2.71	2.27	83.45
Mo	0.20	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	BDL	BDL	BDL	BDL	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	BDL	5.54	0.74	2.02
Ag	BDL	2.60	1.03	0.82	2.84	0.01	0.37
Au	0.05	0.43	0.19	0.170	2.07	- 0.01	0.18
Hg	BDL	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

BDL below detection limit

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 SiO₂ (0.986); Al₂O₃ (0.972); Fe₂O₃ (-0.999); MgO (0.538); Na₂O (0.729); K₂O (0.929); TiO₂ (0.989); P₂O₅ (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); Na₂O (0.684); MnO (0.974). Eigenvalue of 3.315 and % variance of 27.622 was recorded.

From the rotated result (Table 3), component two revealed high factor loadings for all variables except K₂O (0.684). Theses high factor loadings suggest lignites while the relatively low K₂O could imply a higher ranking coal (Stanislav et al. 2010). Component one ranged from factors such as aluminosilicates, aluminophosphates and basalts as possible sources for the variables (Zhao et al. 2015).

(5) Trace Elements

The geochemical behavior of trace and rare elements in modern, organic rich sedimentary rocks such as coal has

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)	

been documented and used to determine the terrestrial sediments source component of the organic rocks (Adebayo et al. 2015).

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 transitional boundary from oxic to suboxic and anoxic depositional environment (Taghipour and Marshk 2015).

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

The trace element yielded four clusters (Fig. 8). 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 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).

(6) Rare Earth Elements

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 an evidence that fractionation occurred in the LREE and HREE. The average ratio (La/Sm) n value of 2.82 indicate that some degree of fractionation also occurred among the LREE (Taghipour and Marshk 2015).

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 La and Ce that may suggests dominantly phosphatic affinity with organic origin.

Cluster analysis of rare earth elements yielded two clusters (Fig. 9). 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.

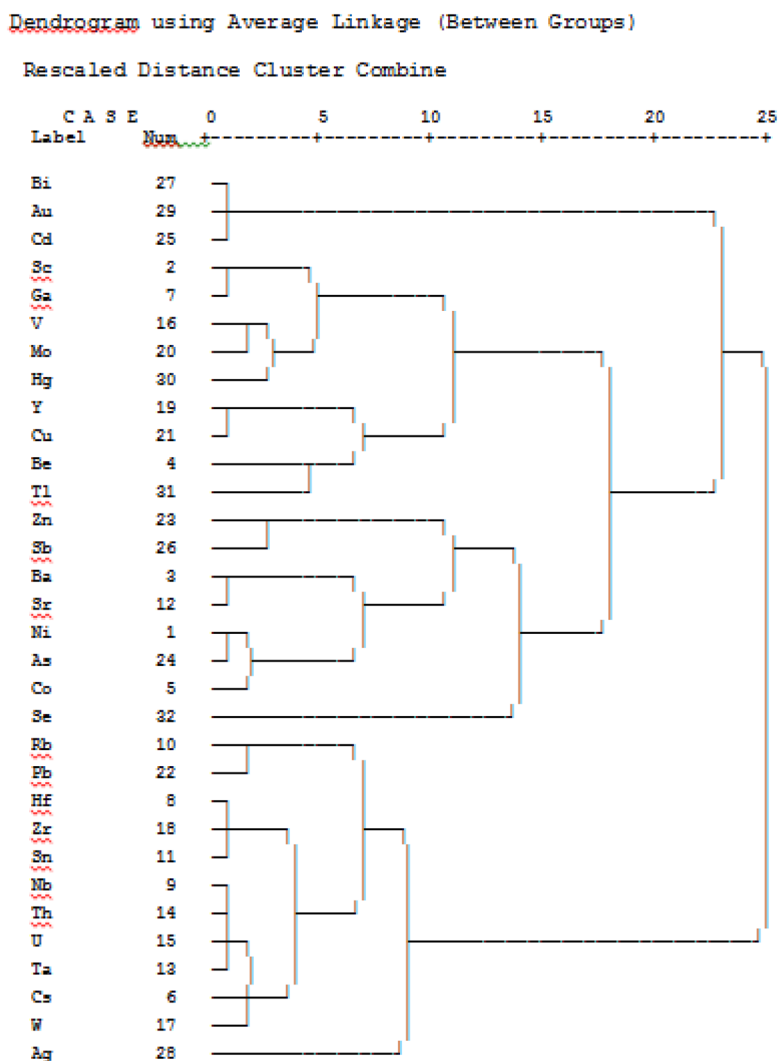


Fig. 8 Cluster result of trace elements in coal

Cluster two consists of La and Ce. These two elements showed the most significant similarity (Fig. 9).

From Fig. 9 and Table 7, La and Ce appeared in the same cluster, factor component and also showed very strong correlation (0.987). This is an indication that these elements were from same source and are controlled by factor (s) different from other rare earth elements appeared in the same cluster and factor component. Other REEs such as Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu maybe associated with the inorganic component of the coal (Zhao et al. 2015).

The rare earth element analysis recorded two factor components (Table 8). Factor one consists of high factor loadings of 0.8–0.9 for all rare earth elements analysed except La and Ce. This factor has 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 8).

(7) Palaeoweathering/climatic conditions of deposition
According to Suttner and Dutta (1986), binary plot of SiO₂ versus (Al₂O₃ + K₂O + Na₂O) 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 (Fig. 10). This indicates that both weathering of source rocks/materials and conditions surrounding the coal formations occurred in humid climatic environments (Chen et al. 2016; Schellmann 1981).

The Si becomes unstable in rocks due to removal of silica rocks as weathering progresses. According to Chen et al. 2016, the SiO₂–Al₂O₃–TFe₂O₃ (SAF) ternary diagram proposed by Schellmann (1986) can be used to quantify the degree of laterization. On the basis of the SAF

Table 6 Descriptive statistics of rare earth elements in coal

Rare elements	Minimum	Maximum	Mean	SD	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	0.78	18.19	7.45	5.82	2.37	3.13	1.34	13.55
Eu	0.15	4.40	1.72	1.42	0.57	2.97	0.23	3.21
Gd	0.82	23.69	8.49	7.81	3.19	2.66	0.29	16.70
Tb	0.13	3.71	1.35	1.22	0.49	2.70	0.06	2.63
Dy	0.78	21.00	7.67	6.93	2.83	2.71	0.40	14.95
Ho	0.15	4.05	1.52	1.32	0.53	2.81	0.13	2.90
Er	0.50	10.44	4.11	3.34	1.36	3.01	0.60	7.62
Tm	0.05	1.38	0.57	0.44	0.18	3.16	0.10	1.03
Yb	0.43	8.06	3.64	2.61	1.06	3.42	0.90	6.38
Lu	0.06	1.15	0.53	0.37	0.15	3.50	0.14	0.92
Total	18.25	239.37	100.41	80.16	32.68	36.32	16.24	369.12

Table 7 Correlation matrix of rare earth elements in coal

Rare earth elements	Correlation @ $P = 0.01^{**}$
La	Ce (0.987);
Sm	Eu (0.983); Gd (0.982); Tb (0.985); Dy (1.988); Ho (1.994); Er (1.997); Lu (1.975); Tm (0.999); Yb (1.983)
Eu	Gd (0.994); Tb (0.997); Dy (0.996); Ho (1.994); Er (0.991); Lu (0.922); Tm (1.982); Yb (1.941)
Gd	Tb (0.999); Dy (0.997); Ho (0.997); Er (1.993); Lu (1.918); Tm (0.978); Yb (1.933)
Tb	Dy (0.999); Ho (0.998); Er (0.995); Lu (1.924); Tm (0.983); Yb (0.942)
Dy	Ho (0.998); Er (0.996); Lu (0.931); Tm (1.986); 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 (1.996)
Tm	Yb (0.987)

ternary diagram above, the coal samples from the study area may have suffered weak laterization to kaolinisation (Fig. 11).

5 Conclusion

- (1) The coal was formed from low land peat environment associated with marine or blackish water influence.
- (2) Stable condition of deposition, low degree of tectonic movement but constant subsidence in the basin was observed.
- (3) Transitional boundary of oxic to sub-oxic and anoxic environments were observed with acidic and humid climate.
- (4) Weak laterization to kaolinization were also observed.

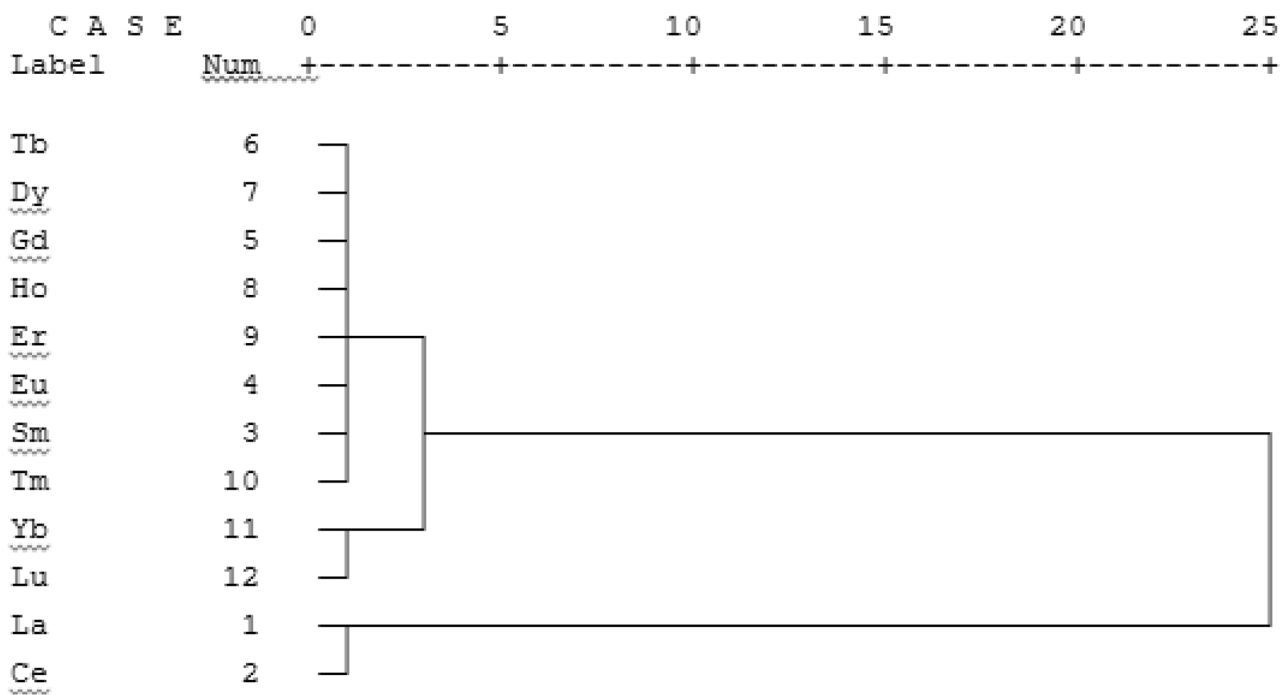


Fig. 9 Rare earth element cluster analysis

Table 8 Varimax rotated component matrix of rare earth elements

Component	Rare earth elements												Eigen values	Variance (%)	Cumulative (%)
	La	Ce	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
1	0.244	0.144	0.961	0.990	0.982	0.988	0.989	0.979	0.974	0.960	0.914	0.885	9.350	77.920	77.920
2	0.967	0.986	0.273	0.121	0.149	0.136	0.139	0.197	0.227	0.274	0.367	0.440	2.550	21.247	99.167

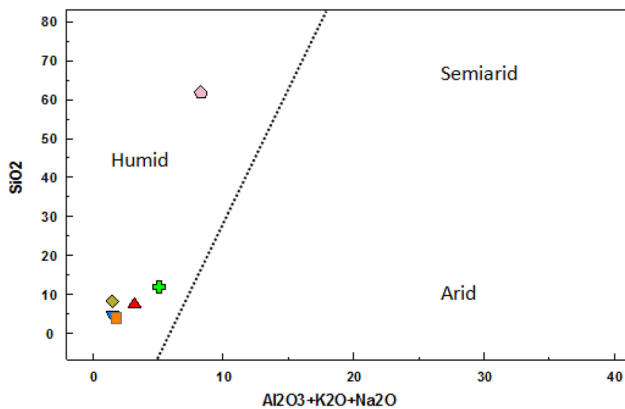


Fig. 10 Paleoclimatic diagram of SiO₂ versus Al₂O₃ + K₂O + Na₂O (AFTER Suttner and Dutta 1986)

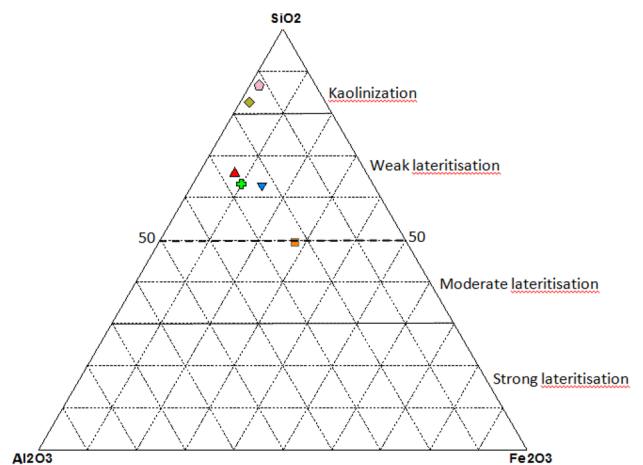


Fig. 11 Triangular diagram of SiO₂-Al₂O₃-Fe₂O₃ (after Chen et al. 2016)

Compliance with ethical standards

Conflict of interest The author declares that they have no conflict of interest.

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