GEOCHEMISTRY

The geochemistry of lignite from the Neogene Ogwashi-Asaba Formation, Niger Delta Basin, southern Nigeria

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ABSTRACT

Major and trace element compositions of lignite from the Tertiary Ogwashi-Asaba formation, Southern Nigeria, have been investigated to determine the prevailing environmental conditions which controlled their formation. Seven samples were obtained from outcrops along river valleys, streams and springs in seven localities; these samples were subsequently analysed using fusion combined with inductively-coupled plasma (FUS-ICP) and total digestion with inductively-coupled plasma (TD-ICP). Geochemical analysis revealed the following concentration range in weight percent (wt. %) for major oxides: SiO_2 (0.04-9.78); Al_2O_3 (0.56-6.40), Fe_2O_3 (0.05-1.22), MnO (0.001-0.004), MgO (0.02-0.11), CaO (0.05-0.15), K_2O (0.01 - 0.04), TiO_2 (0.016-0.299) and S (0.08-0.39). Trace elements indicated the following concentration range in parts per million (ppm): Be (2-5), Zr (4-63), Sr (5-22), Y (13-68), Ba (9-89), V (4-216), Zn (17-176), Ni (8-28), Co (5-13), Cr (2-31), Cu (1-22) and Ga (1-14). The low silica (<10 wt. %) and alumina contents (<7 wt. %) were explained by very limited detrital input during coal formation. Magnesium oxide and CaO content were relatively low thereby confirming the continental nature of the peat-forming environment. Redox-sensitive trace element ratios (Ni/Co, V/Cr and V/V+Ni) indicated predominantly oxic environments for coal deposition. The low trace element concentrations determined in the lignite samples did not point to any severe environmental impact from coal use.

RESUMEN

Las composiciones de elementos mayores y trazas de lignita de la formación terciaria Ogwashi-Asaba, en el sur de Nigeria, han sido investigadas para determinar las condiciones ambientales prevalecientes que controlaron su formación. Siete muestras fueron tomadas de afloramientos a lo largo de valles de ríos, arroyos y manantiales en siete localidades; estas muestras se analizaron posteriormente mediante fusión combinada (FUS-ICP) y la digestión total con plasma de acoplamiento inductivo (ICP-TD). El análisis geoquímico reveló el siguiente intervalo de concentración en porcentaje en peso (% en peso) para los óxidos mayores: SiO_2 (0,04 a 9,78); Al_2O_3 (0,56-6,40), Fe2O3 (0,05-1,22), MnO (0.001-0.004), MgO (0,02 -0,11), CaO (0.05-0.15), K_2O (0,01 - 0,04), TiO_2 (0.016-0,299) y S (0,08 a 0,39). Los elementos traza indican el siguiente rango de concentración en partes por millón (ppm): Be (2-5), Zr (4-63), Sr (5-22), Y (13-68), Ba (9-89), V (4-216), Zn (17-176), Ni (8-28), Co (5-13), Cr (2-31), Cu (1-22) y Ga (1-14). El bajo contenido de sílice (<10 en peso.%) y el contenido de aluminio (<7 wt.%) fueron explicados por la entrada muy limitado de detrítos durante la formación de carbón. El óxido de magnesio y el contenido de CaO son relativamente bajos, lo que confirma el carácter continental del entorno de formación de turba. La relación de elementos traza Redox-sensibles (Ni/Co, V/ Cr y V/V + Ni) indicó ambientes predominantemente óxicos para la deposición de carbón. Las bajas concentraciones de trazas de elementos hallados en las muestras de lignito no indican un impacto ambiental severo de la utilización del carbón.

Introduction

Coal accumulation in Nigeria took place mainly during upper Cretaceous and Tertiary times, resulting in the formation of extensive lignite, sub-bituminous and bituminous coal deposits in the Benue trough and Anambra basin (Simpson, 1954; Reyment, 1965; Akande *et al.*, 1992; Obaje and Ligouis, 1996; Obaje and Hamza, 2000; Obaje, 2009). The Ogwashi-Asaba formation occurs extensively within the Niger Delta basin

in southern Nigeria (Figure 1); it was first described by Wilson (1925) and named the "lignite group." Lithologically, it consists of a sequence of coarse-grained sandstones, light-coloured clays and carbonaceous shales, within which are continental lignite seam intercalations (Reyment, 1965; Kogbe, 1976; Jan du Chene *et al.*, 1978). Nigeria has the largest known lignite deposits in Africa, proven reserves exceeding 300 million tons (Orajaka *et al.*, 1990; MOMSD, 2007). Lignite is mined in open pits in Nigeria and is used mainly as a substitute for wood as fuel in domestic cooking. The pertinent literature on Nigerian lignite deposits' major and trace element composition is scarce (Adedosu *et al.*, 2007; Olobaniyi and Ogala, 2011).

Coal is heterogeneous sediment having both organic and inorganic fractions; it contains variable amounts of almost all the elements included in the periodic table (Christanis *et al.*, 1998; Orem and Finkelman, 2003). Most elements contained in coal usually show a close association with or-

ganic matter or with the coal's inorganic fraction. Changes in the elements' affinity with either the organic or inorganic fraction may also occur during coalification (Christanis *et al.*, 1998). Several researchers have attempted to study the geochemical features of trace elements contained in coal to understand and evaluate trace elements' mode of occurrence as well as their behaviour during combustion (Gluskoter *et al.*, 1977; Swaine, 1990; Finkelman, 1994; Meij, 1995; Spears and Zheng, 1999; Davidson, 2000; Vassilev *et al.*, 2001). Previous studies on trace elements in Nigerian coal have revealed their distribution (Olajire *et al.*, 2007; Ogala *et al.*, 2010a), composition (Ndiokwere *et al.*, 1983; Olabanji, 1991; Ewa *et al.*, 1996; Adedosu *et al.*, 2007; Ogala *et al.*, 2010b), characteristics (Nwadinigwe, 1992; Sonibare *et al.*, 2005) and association (Ewa, 2004; Ogala *et al.*, 2009).

Several researchers have studied trace element content in lignite and their behaviour during combustion (Foscolos *et al.*, 1989; Goodarzi *et al.*,
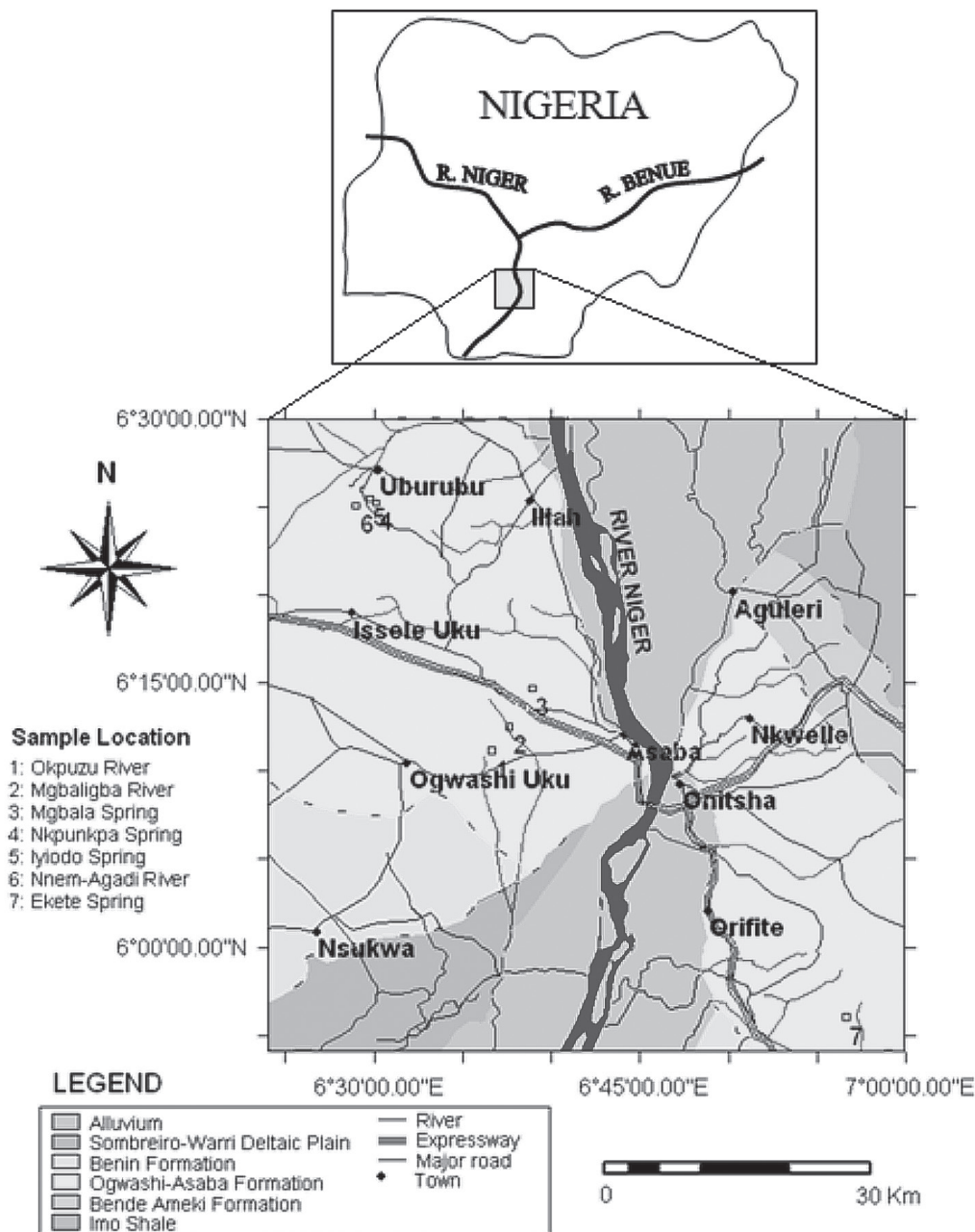

Figure 1. Map of Nigeria showing the location of Ogwashi-Asaba Formation and adjacent units.

AGE		FORMATION	LITHOLOGY	DEPOSITIONAL ENVIRONMENT	BASIN
Quaternary		Benin Formation	Sandstones, Clay, Shales	Continental	Niger Delta Basin
Tertiary	Pliocene				
	Miocene				
	Oligocene	Ogwashi Asaba Formation	Clay, Shales, Sandstones, Lignite	Continental	
	Eocene	Ameki Formation/Nanka Sand	Sandstones, Cl ay, Shales, Limestone	Estuarine, Shallow marine	
	Paleocene	Imo Formation	Clay, Shales, Limestone, Sandstone, Marl	Shallow Marine, deltaic	
Upper Cretaceous	Maastrichtian	Nsukka Formation	Sandstones, Clays, Shales, Coals, Limestone	Fluvio - deltaic	Anambra Basin
		Ajali Formation	Sandstones, Claystones	Fluvio – deltaic	
		Mamu Formation	Sandstones, Clays, Coals	Shallow Marine, deltaic	
	Campanian	Enugu/Nkporo/Owelli Formation	Shales, Sandstones, Clay, ironstones, Siltstones.	Shallow Marine, deltaic	
		MAJOR UNCONFORMITY			
	Santonian	Awgu Formation	Sandstones, Limestones, Clays, Coals, Siltstones	Shallow Marine, deltaic	Benue Trough
	Conician				
Middle Cret.	Turonian	Eze -Aku Formation	Shales, Limestones, Sandstones	Shallow Marine	
	Cenomanian	Odukpani Formation	Sandstones, Limestones, Shales	Shallow Marine	
Lower Cret.	Albian	Asu River Group	Shales, Limestones, Sandstones	Shal low Marine	
Aptian		MAJOR UNCONFORMITY			
		Basement complex	Granites, Gneisses, Schists, Migmatites	Igneous, Metamorphic	

Figure 2. Shows the stratigraphy of three basins in Southern Nigeria- Benue Trough, Anambra Basin and Niger Delta Basin (modified from Reyment, 1965).

1990; Georgakopoulos *et al.*, 1994; Filippidis *et al.*, 1996; Gentzis *et al.*, 1990; Gerouki *et al.*, 1996; Sakorafa *et al.*, 1996; Christanis *et al.*, 1998; Chatziapostolou *et al.*, 2006; Adamidou *et al.*, 2007). Trace elements are of great importance in ascertaining the depositional environment and maturity of geological samples within a particular basin (Adedosu *et al.*, 2007).

The present study was aimed at investigating the chemical composition (major and trace elements) of lignite samples from the Ogwashi-Asaba formation, southern Nigeria, to predict the prevailing geochemical environmental conditions as well as the processes responsible for their distribution.

The study area's geology and stratigraphy

The Ogwashi-Asaba formation (Reyment, 1965) occurs extensively within the Niger Delta basin in southern Nigeria, covering a 4,900 km² area (Fig. 1). The formation was originally referred to as a "lignite group" (Wilson, 1925; Wilson and Bain, 1928), "lignite series" (Simpson, 1949; 1954), and "lignite formation" (De Swardt and Casey, 1963). Lignite layers have also been encountered in the lowermost strata of the Ameki group (Fig. 1) and the uppermost strata of the Benin formation in drill holes, streams/river banks and road-cut outcrops (Okezie and Onuogu, 1985).

The southern Nigerian sedimentary basin's formation began during the early Cretaceous period (Albian) following basement subsidence along the Benue and Niger troughs (Nwachukwu, 1972; Olade, 1975). Folding and uplift occurred during the Santonian along a northeast-southwest axis

in the Abakaliki-Benue area. The Anambra platform, lying to the west and southwest of the Abakaliki folded belts, subsided to form the Anambra basin (Reyment, 1965; Short and Stauble, 1967; Murat, 1972; Benkhelil, 1989).

The upper Cretaceous stratigraphic succession in the Anambra basin began with the deposition of sediment from the marine Campanian-Maastrichtian Enugu/Nkporo shales and their lateral equivalent - deltaic Owelli sandstone (Fig. 2). These base units were successively overlain by the lower-middle Maastrichtian deltaic coal-bearing Mamu formation (lower coal measures) and middle Maastrichtian tidal Ajali sandstone (false-bedded sandstones) and overlain by the fluvial-deltaic Nsukka formation (upper coal measures) . The Imo and Nsukka formations marine shales were deposited during the Paleocene era and overlain by the regressive Ameki formation (Eocene); the paralic Ogwashi-Asaba formation (Oligocene-Miocene) was capped by the continental Benin formation (Miocene-recent) constituting the tertiary succession (Figures 1 and 2). The Ogwashi-Asaba formation consists of a succession of coarse-grained sandstone, clay and carbonaceous shale, containing continental lignite seam intercalations (Kogbe, 1976; Jan du Chene *et al.*, 1978). Reyment (1965) suggested an Oligocene-Miocene age for the Ogwashi-Asaba formation, but palynological study by Jan du Chene *et al.* (1978) proposed a late Eocene age for the base part. The lignite seams found within the Ogwashi-Asaba formation are usually brownish to black, varying in thickness from a few millimetres to a maximum of 6 meters. They are thinly laminated and fissile, having leaf and woody fragments on fresh cleats. The average overburden to
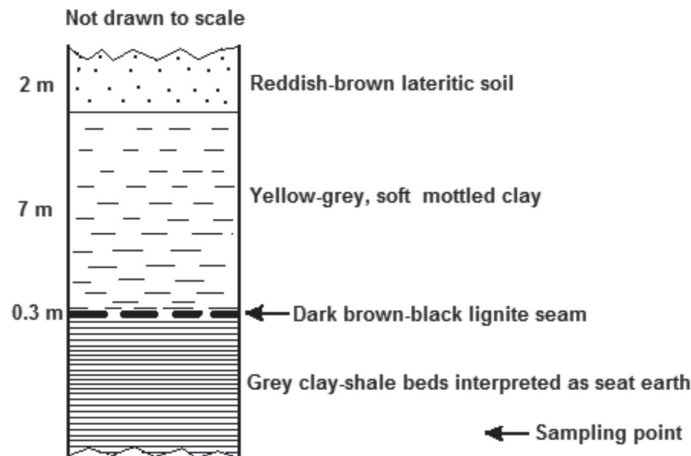
and Okpuzu Rivers in Ibusa and at the Mgbala and Ekete Springs in Okpa-nam and Nnewi, respectively. Lignite seams are also exposed along river valleys at the Nkpunkpa and Iyiodo Springs as well as Nnem-Agadi River, all occurring in Obomkpa. The lignite beds are brownish to black and vary in thickness from a few millimetres to a maximum of 2 meters. They are thinly laminated and fissile with leaf and woody fragments on fresh cleats. The lithological sequence of lignite seam outcropping along the Nnem-Agadi River was logged (Figure 3); seven lignite samples were collected: three samples from Obomkpa, two from Ibusa and one each from Okpanam and Nnewi.

Analytical procedure

Samples (0.25 g) were powdered in an agate mortar and determined by a combination of methods to investigate lignite chemical composition (major and trace elements), i.e. fusion with inductively-coupled plasma (FUS-ICP) and total digestion with inductively-coupled plasma (TD-ICP). Loss on ignition (LOI) caused by escaping volatiles was measured after heating to about 1,050°C. Limits of detectable measurement (LDM) for major elements were 0.01 for SiO_2, Al_2O_3, $Fe_2O_3(T)$, MgO, CaO, Na_2O, K_2O and P_2O_5, 0.001 for MnO and TiO_2 and 0.01% for S.

LDM for trace elements were 2 ppm for Ba, Sr, Zr, Bi, Te, 1 ppm for Y, Sc, Be, Co, Cr, Cu, Ga, Hg, Ni and Zn, 5 ppm for V, Sb, Tl and W, 0.3 ppm for Ag and Cd, 10 ppm for U, 3 ppm for As and Pb and 4 ppm for Sc

Coal data was calculated on an ash basis (value in ash = element value in coal × 100/ash yield, where ash yield = 100 – LOI).

Major oxides and selected trace elements were analysed by the fusion technique (Table 1). Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten melt was immediately poured into a 5% nitric acid solution containing an internal standard and mixed continuously until becoming completely dissolved (c. 30 minutes). The samples were run for major oxides and selected trace elements using a combination fusion technique (FUS-ICP) followed by inductively-coupled plasma-optical emission spectrometry (ICP-OES) analysis using simultaneous/sequential Thermo Jarrell-Ash Enviro II ICP.

A 0.25 g sample was digested with four acids for trace element analysis (Table 2), beginning with hydrofluoric acid (HF), followed by a mixture of nitric (HNO_3) and perchloric acid ($HClO_4$), heated using precise

Figure 3. Lithologic column of outcrop along Nnem-Agadi River at Obomkpa.

lignite ratio is 6:1, thereby appearing to rule out open-cast mining (Da Swardt and Piper, 1957).

Ogwashi-Asaba lignite outcrops along river valleys and streams/springs in Ibusa (Okpunzu and Mgbiligba River), Okpanam (Mgbala Spring), Obomkpa (Nnem-Agadi River, Iyiodo and Nkpunkpa Springs) and Nnewi (Ekete Spring) (Fig. 1).

Analysis methods

Field work and sampling

Field work for the present study took place in outcrops along river valleys, streams and springs in seven localities (Fig. 1). Lignite seams do not easily outcrop in the field but good exposure was found along the Mgbiligba

Table 1. Major element concentration in weight percent (wt. %) for lignites of the Ogwashi-Asaba Formation.

Element	Detection limit	Analysis method	Location 1	Location 2	Location 3	Location 4	Location 5	Location 6	Location 7
SiO_2	0.01	FUS-ICP	0.39	0.04	3.94	1.04	9.38	9.78	2.99
Al_2O_3	0.01	FUS-ICP	0.56	0.65	2.47	1.31	6.4	2.13	2.7
Fe_2O_3T	0.01	FUS-ICP	0.05	1.22	0.13	0.21	0.42	0.38	0.17
MnO	0.001	FUS-ICP	0.001	0.004	0.002	0.004	0.002	0.004	0.001
MgO	0.01	FUS-ICP	0.02	0.02	0.04	0.04	0.04	0.11	0.02
CaO	0.01	FUS-ICP	0.08	0.08	0.09	0.15	0.05	0.43	0.05
Na_2O	0.01	FUS-ICP	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K_2O	0.01	FUS-ICP	< 0.01	< 0.01	0.02	0.01	0.04	0.03	0.02
TiO_2	0.001	FUS-ICP	0.016	0.017	0.095	0.025	0.299	0.07	0.095
P_2O5	0.01	FUS-ICP	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01
LOI		FUS-ICP	97.45	96.84	91.02	95.92	82.8	87	92.8
Total	0.01	FUS-ICP	98.6	98.88	97.82	98.71	99.45	99.94	98.86
Ash Yield		FUS-ICP	2.55	3.16	8.98	4.08	17.2	13	7.2

Table 2. Trace elements and sulphur concentration for lignites of the Ogwashi-Asaba Formation (Values are in parts per million except for S which is in weight percent); 1: Low-rank coal world average after Seredin and Finkelman (2008).

Elements	Detection Limit	Analysis method	Location 1	Location 2	Location 3	Location 4	Location 5	Location 6	Location 7	LRCWA1
Ba	2	FUS-ICP	17	44	54	27	60	93	23	150.0
Sr	2	FUS-ICP	5	6	12	7	22	20	10	110.0
Y	1	FUS-ICP	34	68	57	42	33	18	13	8.6
Sc	1	FUS-ICP	< 1	< 1	4	2	7	6	4	4.1
Zr	2	FUS-ICP	4	6	31	10	63	32	24	36.0
Be	1	FUS-ICP	2	4	3	4	5	3	3	1.6
V	5	FUS-ICP	< 5	< 5	47	23	197	45	33	25.0
Ag	0.3	TD-ICP	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.1
As	3	TD-ICP	< 3	< 3	< 3	< 3	< 3	< 3	< 3	8.3
Bi	2	TD-ICP	< 2	< 2	< 2	< 2	< 2	< 2	< 2	
Cd	0.3	TD-ICP	0.4	< 0.3	< 0.3	0.3	< 0.3	< 0.3	< 0.3	0.2
Co	1	TD-ICP	7	5	13	8	9	6	6	5.1
Cr	1	TD-ICP	3	2	12	6	31	16	15	16.0
Cu	1	TD-ICP	1	1	21	3	22	12	5	16.0
Ga	1	TD-ICP	2	1	5	2	14	2	5	5.8
Hg	1	TD-ICP	< 1	< 1	< 1	< 1	< 1	< 1	< 1	0.10
Mo	1	TD-ICP	< 1	< 1	1	< 1	2	< 1	< 1	2.2
Ni	1	TD-ICP	17	8	28	22	21	17	10	13.0
Pb	3	TD-ICP	< 3	< 3	5	< 3	8	3	< 3	7.8
Sb	5	TD-ICP	< 5	< 5	< 5	< 5	< 5	< 5	< 5	0.84
S	0.01	TD-ICP	0.12	0.19	0.14	0.16	0.08	0.34	0.11	
Te	2	TD-ICP	< 2	< 2	< 2	< 2	< 2	< 2	< 2	
Tl	5	TD-ICP	< 5	< 5	< 5	< 5	< 5	< 5	< 5	0.68
U	10	TD-ICP	< 10	< 10	< 10	< 10	< 10	< 10	< 10	2.4
W	5	TD-ICP	< 5	< 5	< 5	< 5	< 5	< 5	< 5	1.1
Zn	1	TD-ICP	176	52	105	54	29	36	17	23.0
V/(V+Ni)			0.23	0.38	0.63	0.51	0.9	0.73	0.77	
Ni/Co			2.43	1.6	2.15	2.75	2.33	2.83	1.67	
V/Cr			1.66	2.5	3.92	3.83	6.36	2.81	2.2	

programmer-controlled heating in several ramping and holding cycles thus drying the samples. After dryness was attained, samples were brought back into solution using hydrochloric acid. The sample solution was then analysed for element concentration using Varian Vista Pro inductively-coupled plasma-optical emission spectrometry (ICP-OES). USGS and CANMET certified reference materials were used for calibration. The Activation Laboratories in Ancaster, Canada, performed the chemical analysis.

Statistical analysis

The elements were subjected to univariate (minimum, maximum, mean and standard deviation, correlation coefficient) and multivariate sta-

tistical analysis (factor and principal component) using statistical package for social sciences (SPSS) software (version 16.0). Since most parameters measured here were not normally distributed, Spearman's rank correlation was used to examine the correlation between elements (the correlation coefficient matrix measures how well each constituent's variance can be explained by its relationship to the others). Factor analysis (FA)/principal component analysis (PCA) was applied to the experimental data standardised through z-scale transformation to avoid misclassification due to differences in the units of measurement. Standardisation tends to increase the influence of variables whose variance is small and reduce the influence of variables whose variance is large (Liu *et al.*, 2003). Factor analysis was applied to the data set to study the association of the trace elements and
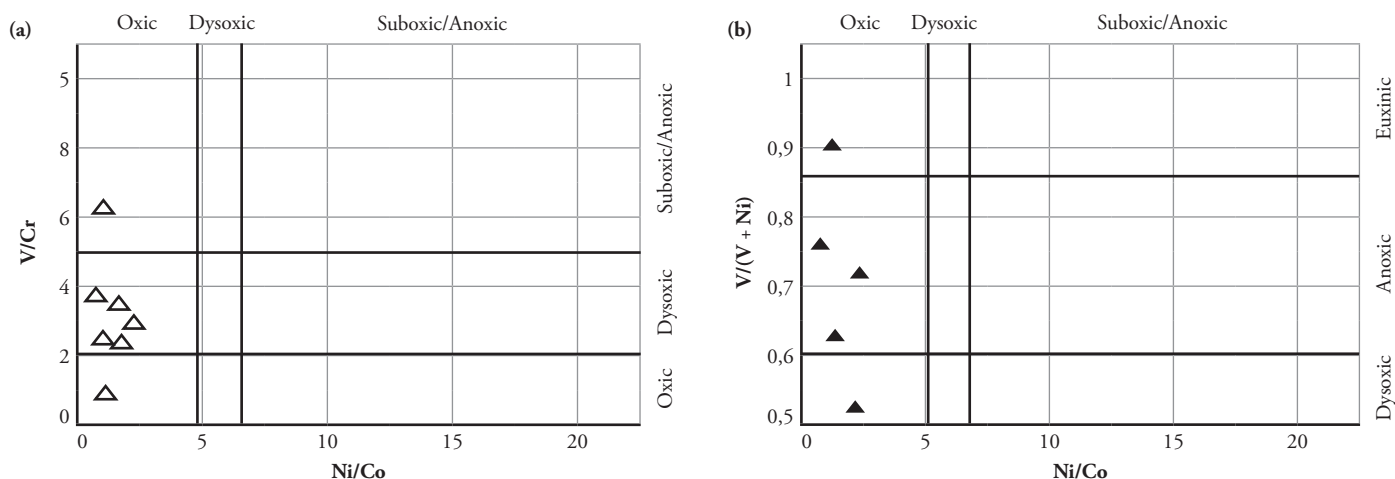
Figure 4. Cross plots of redox-sensitive trace metal ratios (a) V/Cr *vs.* Ni/Co; (b) V/(V+Ni) *vs.* Ni/Co.
Ranges for V/Cr and Ni/Co are from Jones and Manning (1994); ranges for V/(V+Ni) are from Hatch and Leventhal (1992).

extract the principal factors governing trace element distribution (Lu *et al.*, 1995). Components having > 1 eigenvalue were selected to explain association amongst the measured variables.

Cluster analysis (CA) established site segregation and desegregation; such analysis is an unsupervised pattern recognition technique which uncovers a data set's intrinsic structure or underlying pattern without previous knowledge concerning the data being available. This is to enable classification being made based on measured objects' nearness or similarity, thereby helping to establish relationships among sites in the form of a dendrogram. Hierarchical agglomerative CA involved normalising the data set by means of Ward's method (i.e. using Euclidean distances as a measurement of similarity). CA was applied to the data set to group similar sampling sites (spatial variation) spread over the region.

Results and discussion

The chemical composition of lignite

The chemical composition of the lignite samples is presented in Tables 1 and 2. Thirty-seven parameters were measured, consisting of ten major elements, loss on ignition (LOI) and 26 trace elements. SiO_2 (0.04-9.78%), Al_2O_3 (0.56-6.40%) and Fe_2O_3 (0.05-1.22%) were the dominant oxides in most lignite samples; Mgo, MnO, CaO, TiO_2,

Na_2O, K_2O and P_2O_5 all occurred in traces. LOI had high values (82.80-97.45%). The low to moderate SiO_2, Al_2O_3 and Fe_2O_3 concentration was due to quartz, feldspar and pyrite constituting the lignite samples' main mineral phase (Adamidou *et al.,* 2007; Kalaitzidis *et al.,* 2010). The low SiO_2 (< 10%) and Al_2O_3 content (< 7%) suggested very limited detrital input during coal formation. The relatively low CaO (0.05-0.43%) and MgO content (0.02-0.11%) implied a continental origin for the lignite (Olobaniyi and Ogala, 2011); this agreed with the Ogwashi-Asaba formation's continental setting (Reyment, 1965; Kogbe, 1976; Jan du Chene *et al.,* 1978).

The most abundant trace element was Zn (average 67 ppm), followed by V, Ba, Y and Zr (50.71 ppm, 45.43 ppm, 37.86 ppm and 24.29 ppm average values, respectively) (Tables 2 and 6). The average mean values for Sr, Sc, Be, Cd, Co, Cr, Cu, Ga, Mo, Ni and Pb ranged from 0.2 ppm to 18 ppm, Ag, As, Bi, Hg, Sb, Te, Tl, U and W concentration being below the detection limit in all samples. Compared to average worldwide coal concentration (Seredin and Finkelman, 2008), most trace element content was lower than world average values for low-ranking coal due to low ash yield (Table 2). Y, Be, V, Co and Zn were the only trace elements having relatively higher concentrations in the coal samples used here than the world coal average.

Redox-sensitive trace element ratios (Ni/Co, V/Cr and V/V+Ni) are usually considered powerful geochemical indicators for environmental dis-

Table 3. Compositional average and standard deviation of major oxides for lignites of the Ogwashi-Asaba Formation.

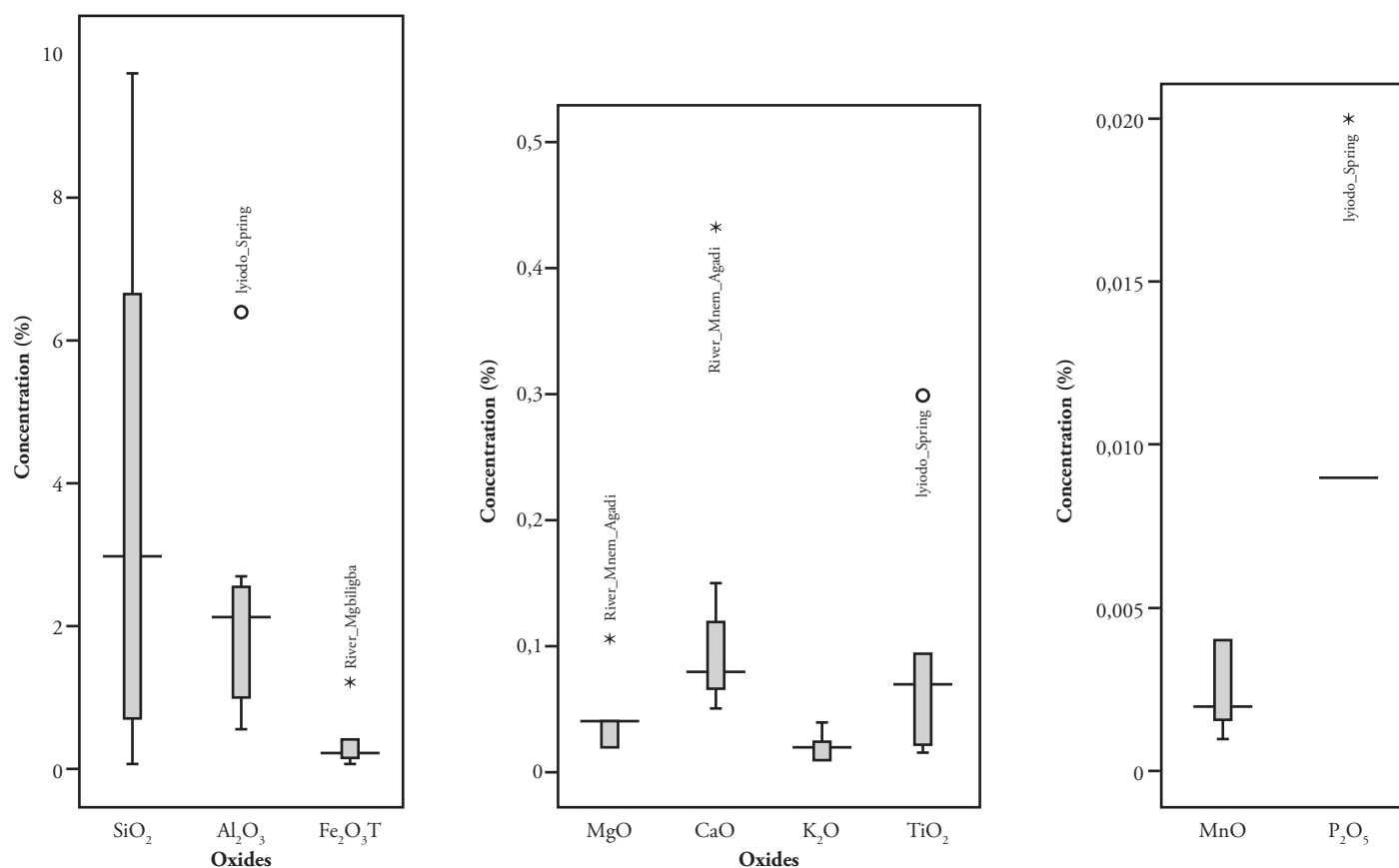| Element N=7	Range	Minimum	Maximum	Mean	Standard Deviation
SiO_2	9.74	.04	9.78	3.937	4.099
Al_2O_3	5.84	.56	6.40	2.317	1.990
Fe_2O_3T	1.17	.05	1.22	.369	.398
MnO	.003	.001	.004	.003	.001
MgO	.09	.02	.11	.041	.032
CaO	.38	.05	.43	.133	.135
Na_2O	.000	< 0.01	< 0.01	< 0.01	.000
K_2O	.031	< 0.01	.040	.020	.012
LOI	14.65	82.80	97.45	91.976	5.473

Figure 5. Box plots showing the distributions of major elements.

crimination (Lewan, 1984; Hatch and Leventhal, 1992; Jones and Manning, 1994; Hoffman *et al.*, 1998; Rimmer, 2004; Rimmer *et al.*, 2004; Algeo and Maynard, 2004; Johnson *et al.*, 2010; Saez *et al.*, 2011). Jones and Manning (1994) suggested that < 5 Ni/Co ratios inferred oxic conditions, 5-7 dysoxic conditions and > 7 suboxic to anoxic conditions. They also used < 2 V/Cr ratios to infer oxic conditions, 2-4.25 for dysoxic conditions and > 4.25 for suboxic to anoxic conditions. Lewan (1984) showed that V/V+Ni should be greater than 0.5 for organic matter accumulated in euxinic conditions.

Hatch and Leventhal (1992) compared V/V+Ni ratios to other geochemical redox indicators, including degree of pyritisation, and suggested that ratios greater than 0.84 showed euxinic conditions, 0.54-0.82 anoxic water and 0.46-0.60 for dysoxic conditions. According to Calvert and Pedersen (1993), Jones and Manning (1994), Hoffman *et al* (1998) and Algeo and Maynard (2004) anoxic environments are characterised by high V/Cr ratios and V/V+Ni values lying between 0.5 and 0.9 because of the disparate behaviour of V, Ni and Cr during redox processes in marine environments characterised by fine-grained detritic sedimentation.

All the samples analysed and shown on the V/Cr *cf* Ni/Co and V/V+Ni *cf* Ni/Co diagram (Figure 4) plotted within the oxic ranges for the four redox-sensitive trace element ratios proposed by Jones and Manning (1994).

Table 4. Correlation coefficients between the major elements in lignite samples from Ogwashi-Asaba Formation

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$T	MnO	MgO	CaO	K2O	TiO$_2$	P$_2$O$_5$	Ash_Yield
SiO$_2$	1.000									
Al$_2$O$_3$	.744	1.000								
Fe$_2$O$_3$(T)	-.122	-.127	1.000							
MnO	.075	-.261	.577	1.000						
MgO	.736	.126	-.077	.503	1.000					
CaO	.513	-.166	-.016	.581	.951	1.000				
K$_2$O	.955	.902	-.111	-.099	.505	.240	1.000			
TiO$_2$	.717	.993	-.084	-.288	.077	-.214	.885	1.000		
P$_2$O$_5$	.585	.905	.057	-.180	-.020	-.270	.755	.937	1.000	
Ash_Yield	.963	.889	-.100	-.030	.547	.276	.994	.870	.739	1.000

Table 5. Unrotated component matrix from loadings of 9 major elements and LOI on three significant factors.

Elements	Factor 1	Factor 2	Factor 3
SiO_2	0.929	0.341	-0.105
Al_2O_3	0.935	-0.316	0.080
Fe2O3T	-0.127	0.193	0.932
MnO	-0.103	0.764	0.544
MgO	0.451	0.868	-0.203
CaO	0.175	0.956	-0.204
K_2O	0.991	0.063	-0.028
TiO_2	0.923	-0.361	0.123
P_2O_5	0.823	-0.386	0.301
LOI	-0.988	-0.114	0.011
Eigen values	5.485	2.801	1.372
% of Variance	54.847	28.008	13.716
Cumulative %	54.847	82.855	96.571

Figure 6. Principal component analysis for the first 3 components for oxides.

Major element geochemistry-correlation matrix

Table 3 shows the composition average and standard deviation for the lignite samples from the Ogwashi-Asaba formation analysed here.

The data set was screened to identify outliers (Figure 5). The other elements were not normally distributed, except for SiO_2, K_2O and MnO; a non-parametric Spearman test was thus used which applies variables' ranking order in determining the correlation coefficient. Table 4 shows major elements' correlation coefficients. There was a strong positive relationship between MgO, K_2O, TiO_2 and P_2O_5 with SiO_2, Al_2O_3 and ash yield, suggesting a common detrital source for these elements; the strong positive statistical correlation between Al_2O_3 and TiO_2 (r= 0.993) was typical of elements which probably came from clastic rocks.

Factor analysis of the major elements studied here gained statistical information on the grouping and hence the processes responsible for their formation. The variance/covariance and factor loadings of the variables having eigenvalues were computed; factor analysis results are summarized in a factor matrix (Table 5). A 3-factor model was adopted, covering
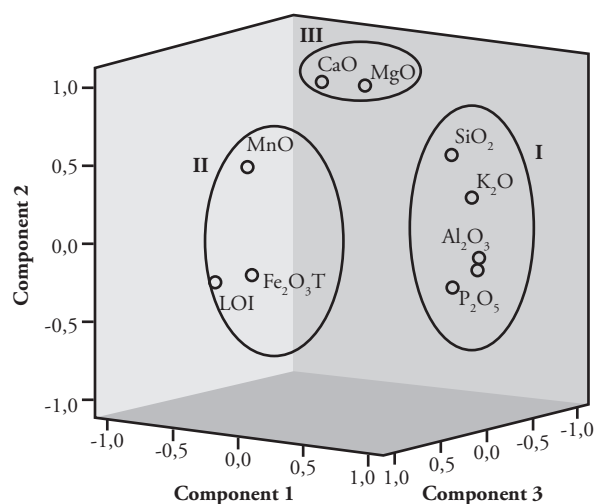
96.6% of total variance.

The first factor expresses 54.9% of the total data variance and showed high positive loading for elements SiO_2, Al_2O_3, K_2O, TiO_2, and P_2O_5 and negative loading for LOI (Table 6). The strong positive correlations between SiO_2, Al_2O_3, and TiO_2 were typical of clay minerals. The loadings in factor 1 reflected sediments believed to have their source probably in the mafic basement complex (Oban Massif) on the north-eastern flank of the Niger Delta basin (Edet *et al.*, 2003; Elueze *et al.*, 2009). The presence of TiO_2 and P_2O_5 was indicative of basaltic rocks of oceanic environment (Ogala *et al.*, 2009); such interpretation is supported by the strong positive correlation between TiO_2 and P_2O_5 (r= 0.937). The second factor expressed 28% of the total variance and showed high positive loadings with MnO, MgO and CaO. The grouping in factor 2 suggests a lithogeochemical input representative of weathering and composition of carbonate sediments. The close proximity of the limestone bands/nodules in the Ameki Formation within the Niger Delta basin in close proximity may be the possible source. The strong positive correlation between CaO and MgO
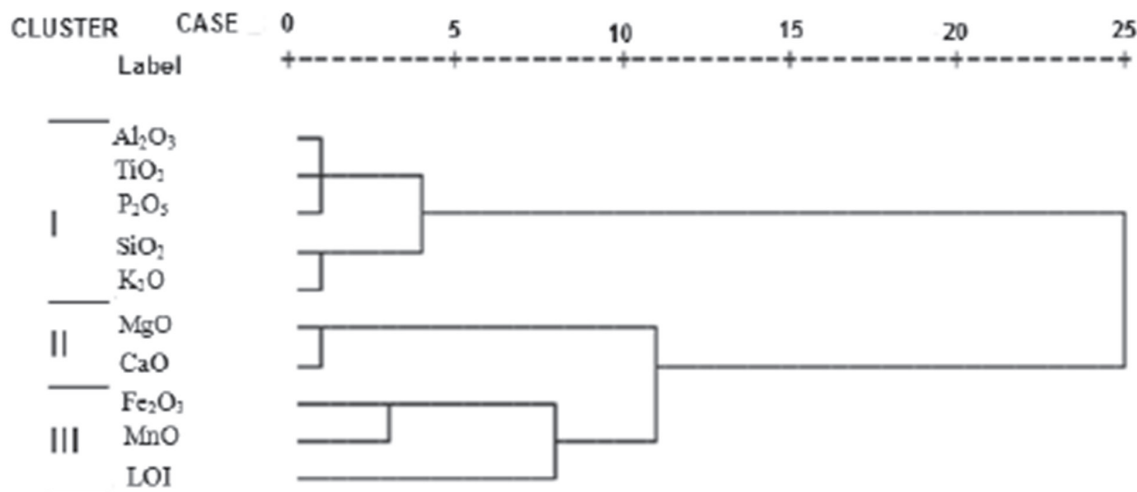

Figure 7. The results of cluster analyses on the major elements contained in the lignite samples from Ogwashi-Asaba Formation.

Table 6. Compositional average and standard deviation of trace elements for lignites of the Ogwashi-Asaba Formation.

| Element N=7	Range	Minimum	Maximum	Mean	S.D.
Ba	76.00	17.00	93.00	45.43	26.46
Sr	17.00	5.00	22.00	11.71	6.80
Y	55.00	13.00	68.00	37.86	19.76
Sc	6.01	.99	7.00	3.57	2.37
Zr	59.00	4.00	63.00	24.29	20.63
Be	3.00	2.00	5.00	3.43	.98
V	192.01	< 5	197.00	50.71	66.72
Ag	.00	< 0.3	< 0.3	< 0.3	.00
As	.00	< 3	< 3	< 3	.00
Bi	.00	< 2	< 2	< 2	.00
Cd	.11	.29	.40	.31	.04
Co	8.00	5.00	13.00	7.71	2.69
Cr	29.00	2.00	31.00	12.14	10.02
Cu	21.00	1.00	22.00	9.29	9.14
Ga	13.00	1.00	14.00	4.43	4.50
Hg	.00	< 1	< 1	< 1	.00
Mo	1.01	< 1	2.00	1.14	.38
Ni	20.00	8.00	28.00	17.57	6.95
Pb	5.01	< 3	8.00	3.99	1.92
Sb	.00	< 5	< 5	< 5	.00
S	.26	.08	.34	.16	.09
Te	.00	< 2	< 2	< 2	.00
Tl	.00	< 5	< 5	< 5	.00
U	.00	< 10	< 10	< 10	.00
W	.00	< 5	< 5	< 5	.00
Zn	159.00	17.00	176.00	67.00	55.71
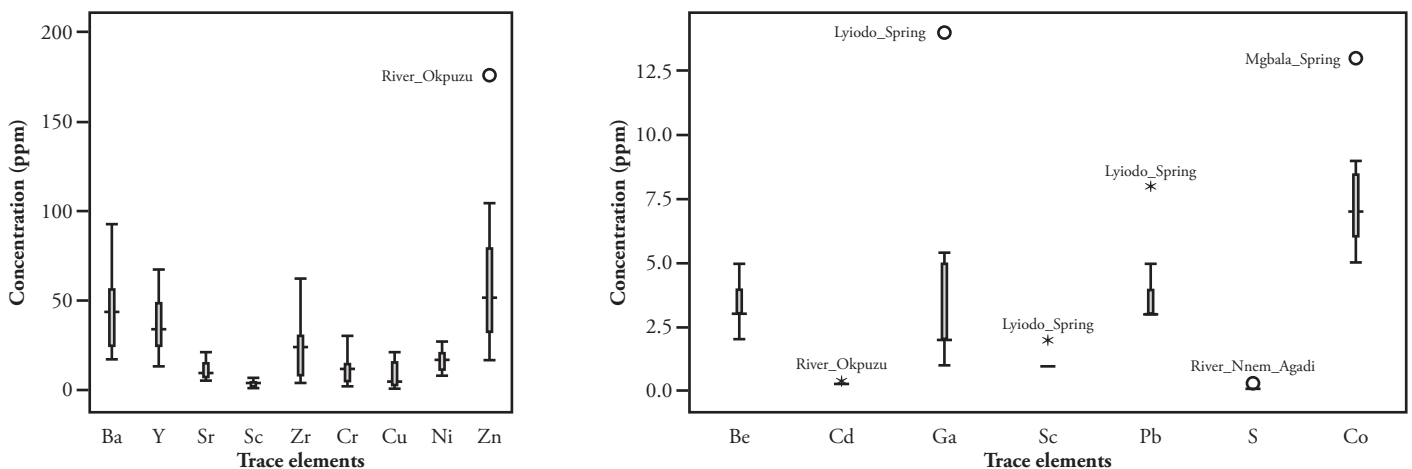
Figure 8. Box plots showing the distribution of trace elements.

Table 7. Correlation coefficients between trace elements and ash yield in lignite samples from Ogwashi-Asaba Formation.

	Ba	Sr	Y	Sc	Zr	Be	V	Cd	Co	Cr	Cu	Ga	Mo	Ni	Pb	S	Zn	Ash_Yield
Ba	1.000																	
Sr	.807	1.000																
Y	-.097	-.412	1.000															
Sc	.705	-973	-.503	1.000														
Zr	.568	.918	-.302	.940	1.000													
Be	.243	.423	.246	.381	.539	1.000												
V	.387	.803	-.195	.798	.940	.678	1.000											
Cd	-.507	-.468	-.079	-.511	-.467	-.629	-.322	1.000										
Co	.093	.204	.294	.266	.398	.054	.332	-.114	1.000									
Cr	.490	.903	-.453	.943	.981	.521	.932	-.432	.274	1.000								
Cu	.602	.795	-.026	.814	.886	.358	.767	-.432	.729	.791	1.000							
Ga	.188	.679	-.198	.722	.901	.596	.963	-.262	.397	.903	.741	1.000						
Mo	.245	.668	-.104	.639	.830	.709	.968	-.186	.220	.831	.620	.939	1.000					
Ni	.209	.297	.139	.311	.377	.056	.338	-.011	.902	.274	.663	.316	.224	1.000				
Pb	.298	.667	.061	.662	.874	.624	.945	.255	.551	.817	.829	.947	.925	.477	1.000			
S	.293	.242	-.125	.130	-.147	-.196	-.330	-.224	-.350	-.173	-.099	-.539	-.428	-.132	-.465	1.000		
Zn	-.386	-.500	.279	-.546	-.463	-.653	-.384	.863	.278	-.522	-.198	-.317	-.298	.295	-.178	-.196	1.000	
Ash_Yield	.728	.987	-.380	.981	.969	.469	.870	-.475	.291	.952	.851	.780	.741	.338	.761	.091	-.491	1.000

Table 8. Unrotated component matrix from loadings of 17 trace elements on four significant factors.

Elements	Factor 1	Factor 2	Factor 3	Factor 4
Ba	.557	-.536	.536	.114
Sr	.897	-.323	.218	-.172
Y	-.216	.395	.060	.817
Sc	.909	-.288	.182	-.219
Zr	.990	-.026	.028	-.105
Be	.636	-.089	-.453	.548
V	.957	.130	-.197	-.075
Cd	-.508	.498	.007	-.596
Co	.421	.660	.511	.217
Cr	.963	-.091	-.087	-.224
Cu	.882	.185	.390	.073
Ga	.907	.277	-.286	-.123
Mo	.858	.209	-.363	-.068
Ni	.412	.547	.618	.094
Pb	.900	.384	-.106	.063
S	-.165	-.763	.557	.057
Zn	-.487	.686	.342	-.276
Eigen values	9.230	3.002	2.071	1.644
% of Variance	54.295	17.660	12.183	9.669
Cumulative %	54.295	71.954	84.138	93.806

Table 9. Varimax rotated component loadings of 17 trace elements on four significant components explaining 93.80% of the total variance.

Elements	Component 1	Component 2	Component 3	Component 4
Ba	0.276	0.872	0.164	0.185
Sr	0.779	0.606	0.084	0.070
Y	-0.437	-0.316	0.500	0.577
Sc	0.818	0.560	0.072	0.035
Zr	0.920	0.292	0.195	0.152
Be	0.507	-0.070	-0.040	0.809
V	0.954	0.025	0.151	0.209
Cd	-0.220	-0.478	0.028	-0.764
Co	0.242	-0.048	0.928	0.008
Cr	0.958	0.260	0.034	0.088
Cu	0.691	0.340	0.600	0.129
Ga	0.961	-0.151	0.162	0.152
Mo	0.913	-0.164	0.074	0.226
Ni	0.235	0.102	0.883	-0.114
Pb	0.859	-0.117	0.406	0.239
S	-0.386	0.866	-0.152	-0.009
Zn	-0.374	-0.399	0.474	-0.614
Eigen values	7.898	3.028	2.798	2.223
% of Variance	46.46	17.81	16.45	13.07
Cumulative %	46.46	64.27	80.72	93.80

(r= 0.951) indicates the presence of dolomite in the lignite samples (Yazdi and Shiravani, 2004). Finally, the third factor expresses 13.7% of the total variance and shows high positive loadings with Fe_2O_3. The high positive loading of Fe_2O_3 in factor 3 confirms the presence of iron bearing minerals such as pyrite. Also the moderate positive correlation between Fe_2O_3 and MnO (r= 0.577) indicates that the element is present in carbonates, probably siderite.

Principal component analysis extraction method was further applied to characterize the geochemistry of major elements. The elements were plotted in rotated space yielding three components (Fig. 6) which explained 97% of the total data variance. The chemical compositions were categorized to three groups (Fig. 7) by cluster analysis. According to Horner and Krissek (1992), cluster analysis is a powerful tool that helps in the identification of groups with similar samples, while principal component analysis aids in the identification of elements (variables) that are responsible for the similarities or differences between groups of samples. The three components derived from factor analysis (Fig. 6) correspond to the three cluster groups of major elements (Fig. 7). Cluster I comprises of Al_2O_3, TiO_2, P_2O_5, SiO_2, and K_2O, indicating that the majority of these elements were mainly of terrigenous origin. Cluster II comprises of MgO and CaO, indicating sediments of carbonate origin, while cluster III comprises of Fe_2O_3, MnO and LOI indicating affiliation to epigenetic minerals such as pyrite and siderite.

Trace element geochemistry-correlation matrix

Table 6 shows the average composition and standard deviation of the trace elements in the lignite sample. The data set was screened to identify outliers (Figure 8). Among the trace elements analysed, Zn, Cd, Ga, Mo, Pb, S and Co were not normally distributed. Spearman's rank correlation determined the correlation coefficient between trace elements and ash yield (Table 8). Most trace elements had strong positive correlation coefficients with ash yield and with each other (Table 7); this indicated a common detrital source for most of these elements. Y, Be, Cd, Co, Ni, S and Zn poorly correlated with ash yield (- 0.380 < r < 0.469) which could be explained by organic affinity and these elements' association with sulphide
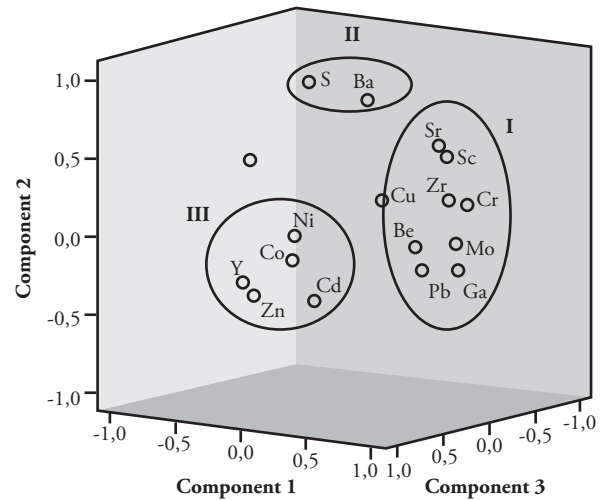

Figure 9. Principal component analysis for the first 3 components for trace elements.

phases. The poor correlation of S with Cu (r = - 0.099), Zn (r = - 0.196), Cd (r = - 0.224), Ga (r = - 0.539), Pb (r = - 0.465), Sr (r = 0.242), Sc (r = 0.130), Y (r = -0.125), Zr (r = - 0.147), Be (r = - 0.196), V (r = - 0.330), Co (r = - 0.350), Cr (r = - 0.173), Ni (r = - 0.132) and Mo (r = - 0.428) indicated that sulphur was not only present in its sulphide form but also as an organic form (Finkelman, 1995).

There were highly significant correlations (r ≥ 0.90) between the elements in the following couples: Sr and Sc, Sr and Zr, Sr and Cr, Sc and Zr, Sc and Cr, Zr and V, Zr and Cr, Zr and Ga, V and Cr, V and Ga, V and Mo, V and Pb, Co and Ni, Cr and Ga, Ga and Mo, Ga and Pb and Mo and Pb (Table 7). This result was consistent with that recorded by Spears and Zheng (1999) and was interpreted as being essentially associated with detrital minerals and clay minerals.

FA applied to the correlation matrix initially produced overlaps in Ba, Be, Co, Ni and Cd (Table 8), thereby necessitating further analysis.
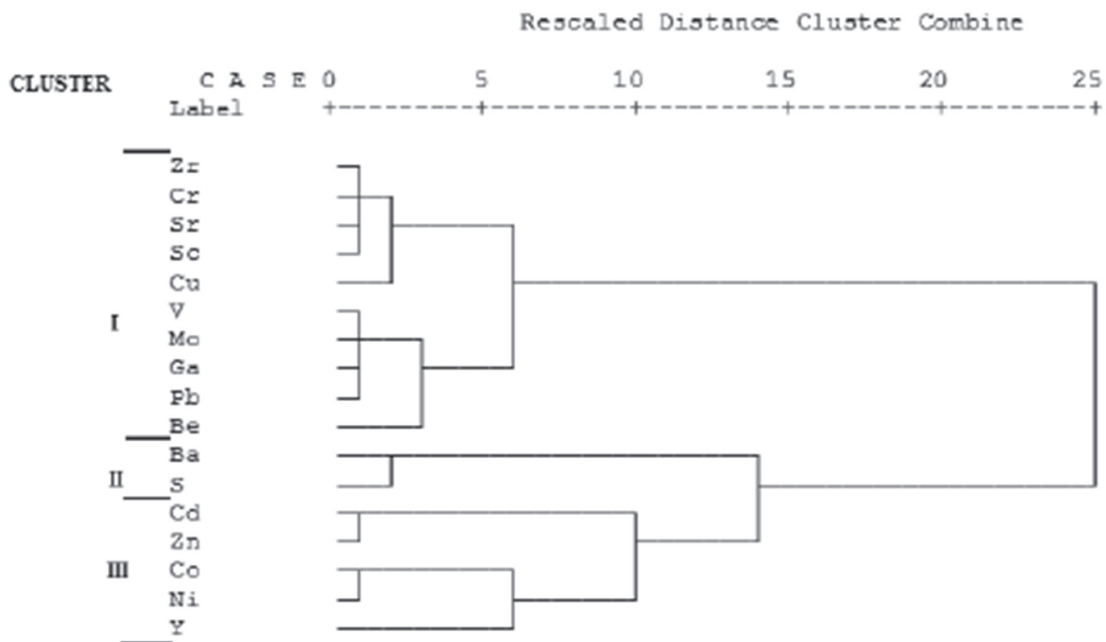

Figure 10. The results of cluster analyses on the trace elements contained in the lignite samples from Ogwashi-Asaba Formation.

This was achieved by rotating the axis, thereby producing a new set of factors; this was attained after 11 iterations (Table 9). Each factor involved a sub-set of the original variables with as much minimal overlap as possible (Table 9). Since the differences between the unrotated and rotated components were significantly different, the rotated option was used for further analysis. A 4-factor model having 93.8% total cumulative variance was obtained (Table 9). Principal component 1 (PC1) expressed 46.5% of total data variance and showed high positive loadings with Sr, Sc, Zr, V, Cr, Cu, Ga, Mo and Pb (Table 9). The inferred host phases for PC1 were a mixture of lithophile (Sr, Sc, Zr, V and Cr; $r = 0.803$-0.973) and chalcophile (Cu, Ga, Mo and Pb; $r = 0.620$-0.829). The high positive loading of Pb in PC1 may have resulted from processes which led to the emplacement of Pb-Zn mineralisation in the Lower Benue trough (Akande and Erdtmann, 1998; Ogala *et al.*, 2010b). The positive loading of Cu in both PC1 and PC3 indicated dual sources contributing to the presence of Cu. Further analysis using CA (Figure 10) confirmed that Cu belonged to PC1. PC1 had a high positive loading with Zr (Table 9), indicating a concentration of resistant heavy minerals, such as zircon.

Principal component 2 (PC2) expressed 17.8% of total data variance and had the highest loadings with Ba, Sr and S. According to Finkelman (1995) and Christanis *et al.*, (1998), Ba and S have a strong organic affiliation, while Sr indicates a carbonate origin.

Principal component 3 (PC3) expressed 16.5% of total data variance and showed positive loading with Co, Cu and Ni. It could be inferred from the data obtained that this group of elements was associated with Fe-sulphide (pyrite). The reported occurrence of chalcopyrite ($CuFeS_2$) in the Abakaliki area of the Lower Benue trough cannot be ruled out due to the presence of Cu (Elueze *et al.*, 2009).

Principal component 4 (PC4) expressed 13% of total variance and showed positive loading with Y and Be and negative loading for Cd and Zn. PC4 was made up of a mixture of lithophile (Be and Y) and chalcophile (Cd and Zn), suggesting that the elements were associated with silicates and sulphides, respectively.

The trace elements were plotted in rotated space yielding three components (Fig. 9). CA established trace element association and origin (Fig. 10); this clustering (Fig. 10) coincided with the results obtained from studying the correlation coefficient matrix (Table 7) and PCA (Fig. 9).

Cluster 1 consisted of elements associated with detrital input (i.e. Zr, Cr, Sr, Sc, Cu, V, Mo, Ga, Pb and Be) including quartz, clay and accessory minerals such as zircon and rutile commonly representing inorganic constituents (Finkelman, 1995). These elements' strong positive correlation with each other (Table 7) and with ash yield indicated a common terrigenous origin.

Cluster 2 was made up of Ba and S, suggesting a strong organic association. The positive statistical correlation between Ba and S ($r = 0.693$) also supported an organic association for these elements. Cluster 3 consisting of Cd, Zn, Co, Ni and Y, indicated a strong association with sulphides such as pyrite (FeS_2), sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and galena (PbS). The occurrence of polymetallic sulphide lodes of PbS, ZnS and $CuFeS_2$ within the Lower Benue trough cannot be ruled out for these elements (Elueze *et al.*, 2009).

Conclusion

The geochemical characteristics of the ignite seams within the Ogwashi-Asaba formation were investigated; the main mineral phases contained in the lignite were quartz, feldspar and pyrite. The relatively low silica (SiO_2) and alumina (Al_2O_3) content suggested very limited detrital input during coal formation.

The elements' geochemical association was examined through statistical correlation and principal component analysis (PCA) and cluster analysis (CA) of major and trace elements. The three components derived from FA corresponded to the three major elements' cluster groups. The first group consisted of clastic rock-derived elements, whilst the second and third groups consisted of elements having carbonate and sulphide affinity, respectively. The concentrations for most trace elements were lower than world average values for low-rank coals. This study has also shown that silicate and sulphide minerals were responsible for the occurrence and distribution of most trace elements in the lignite samples studied here.

Acknowledgement

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