MAJOR OXIDES AND TRACE ELEMENT DISTRIBUTIONS IN COAL AND COALY SHALE SEAMS IN THE ENUGU ESCARPMENT OF SOUTH-EASTERN NIGERIA

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ABSTRACT

Elemental distributions in nine (9) sub-bituminous coal and four coaly shale samples from the Anambra Basin, south-eastern Nigeria were determined using FUS-ICP and TD-ICP spectrometry. Of the major oxides in these samples, SiO$_2$ and Al$_2$O$_3$ indicate the prevalence of quartz and clay minerals. The strong statistical correlation between SiO$_2$ and Al$_2$O$_3$ indicates a common source, likely detrital. The strong correlation between the other major oxides with both SiO$_2$ and Al$_2$O$_3$ indicates that all of these elements have a common detrital source. However, epigenetic carbonates and syngenetic or epigenetic sulphides may also be present. The concentrations of most trace elements in these coals are unremarkably, falling well within the range for U.S. and World coals. These data do not indicate any potential for economic by-product, potential technological problems or environmental or health concerns.

KEY WORDS: Nigerian sub-bituminous coal, coaly shale, trace elements, factor and, cluster analyses.

INTRODUCTION

Coal is a complex organic rock comprised mainly of decayed plants conditioned by syngenetic, diagenetic, epigenetic and detrital inorganic elements (Orem and Finkelman, 2003). Coal has been globally recognised as an important source of energy. Geological epoch favouring the formation of coal include the Carboniferous, Permian, and Jurassic to Tertiary. In southern Nigeria, the coal resources are found within the Mamu and Nsukka Formations of Campanian-Maastrichtian age (Reyment, 1965; Wright et al., 1985). These formations outcrop at intervals along the Enugu Escarpment over a distance of about 144 Kilometers from Enugu to Ogboyoga in Kogi State (Fig. 1). Coal occurs also in other sedimentary formation in Nigeria, such as in Lafia-Obi, Lamja, Gombe, Bauchi, Pindiga among others.

Most trace elements in coal are associated with mineral matter (Pollock et al., 2000). According to Orem and Finkelman (2003), most of the inorganic elements in coal are associated with detrital minerals but in some coals epigenetic mineralization is important. Trace elements in coal have been studied by a number of authors in different countries (Finkelman, 1982; Karayigit et al., 2000; Pollock et al., 2000; Ren et al., 1999; Song et al., 2007). Previous studies on trace elements in Nigerian coal revealed their occurrence (Olajire et al., 2007), composition (Ndik CWE et al., 1983), characteristics (Sonibare et al., 2005), and association (Ewa, 2004; Ewa and Adetunji, 1996).

The main objective of this study is to determine the concentrations, distribution and mode of occurrence of the major oxides and trace elements in coal and coaly shale samples from the Enugu escarpment, and to establish the relationship existing among the elements and their role in ash formation. This information may be useful in interpreting the geologic history of the coal deposits. Furthermore, information on the concentrations and modes of occurrence of the trace elements may be useful in anticipating economic by-product potential, technological behaviour, and environmental and human health impacts.

GEOLOGIC SETTING

The Anambra Basin is located in the southwestern end of the Benue Trough of Nigeria (Fig 1). The basin is bounded on the west by the Precambrian basement complex rocks of western Nigeria and on the east by the Abakaliki Anticlinorium. It extends northward to the lower Benue River and also forms a boundary with the Tertiary Niger Delta to the south.
The evolution of the Southern sedimentary basin began in the Early Cretaceous with the formation of the Benue – Abakaliki Trough as a failed arm of the rift triple junction associated with the separation of the African and South American continents and subsequent opening of the South Atlantic (Burke, 1996; Murat, 1972). The platform areas bordering the Benue Trough to the west (Anambra Platform) and to the east (Afikpo Platform) became downwarped due to the Santonian tectonism to form the Anambra Basin and Afikpo Syncline respectively (Benkhelil, 1989; Murat, 1972; Petters, 1978). The Anambra Basin contains about 6km thick Cretaceous/Tertiary sediments and is the structural link between the Cretaceous Benue Trough and the Tertiary Niger Delta (Mohammed, 2005).

The geologic strata of the Anambra Basin were deposited in a syncline initiated by the major folding episode in the Benue trough during Late Cretaceous times. During the Maastrichtian, the Anambra Basin became silted up and extensive thickly vegetated swamps developed near sea level, on top of a broad delta fan built up by rivers bringing sediments from the hinterland (Wright et al., 1985). Sedimentation in the Anambra Basin commenced with the Campanian–Maastrichtian marine and paralic shales of the Enugu and Nkporo Formations. These basal units are overlain successively by the coal measures of the Mamu Formation (Lower Coal Measures), the Ajali Sandstone (Middle Coal Measures), and the Nsukka Formation (Upper Coal Measures). The marine shales of the Imo and Nsukka Formations were deposited in the Paleocene, overlain by the tidal Nanka Sandstones (lateral equivalents the Ameki Formation) of Eocene age which constitute the Tertiary succession (Fig. 2).
Sampling and analytical techniques
Nine coal and four coaly shale samples were collected from eleven different borehole logs from four localities in the study area (Figs. 3 and 4). Ten oxides ($\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3(T)$, $\text{MnO}$, $\text{MgO}$, $\text{CaO}$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{TiO}_2$, $\text{P}_2\text{O}_5$) were analysed using the fusion technique (FUS) followed by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis using a Thermo Jarrel Ash Enviro II simultaneous/sequential ICP. Loss on ignition (LOI) was determined by weighing a 2 g sample and igniting at $1050^\circ$ C for 2 hours. The sample is weighed again and the weight loss is computed as LOI.

The trace elements Ba, Sr, Y, Sc, Zr, Be and V were determined using FUS-ICP-OES, while the Ag, As, B, Bi, Cd, Co, Cr, Cu, Ga, Hg, Mo, Ni, Pb, Sb, Te, Ti, U, W including S and Zn were determined with the aid of Total Digestion-ICP (TD-ICP-OES).
Data processing

The original data sets were subjected to statistical analysis using the SPSS (Statistical Package for Social Sciences) version 16.0. Elements Ag, As, Bi, Cd, Hg, Mo, Sb, Te, Tl, U and W were excluded from further data processing as they either recorded zero variance or had more than 50 percent qualified values. Factor analysis was applied on the remaining variables (i.e. B, Ba, Be, Cr, Cu, Ga, Ni, Pb, S, Sc, Sr, V, Y, Zn, and Zr) to study the association of the trace elements and extract the principal factors that govern the distribution of these trace elements (Lu et al., 1995). Components having Eigenvalue >1 were selected to explain the association among the measured variables.

Cluster analysis (CA) was performed to establish the site segregation and desegregation. Cluster analysis is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behaviour of a data set without previous knowledge concerning the data. This is to enable classification be made based on nearness or similarity of measured objects. It helps to establish the relationships among the sites and this is presented as dendograms. Hierarchical agglomerative CA was achieved by normalizing the data set by means of the Ward's method. This method uses the euclidean distances as a measure of similarity. Cluster analysis was applied to the data set with a view to grouping the similar sampling sites (spatial variation) spread over the region. According to Horner and Krissek (1992), CA 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.

RESULTS AND DISCUSSION

The results of the analyses on coal/coaly shale and ash basis for major elements are presented in Tables 1a and b respectively. The sum of the major oxides is between 67.1 and 100.6 percent, averaging 88.7 percent. The difference between the sum of the oxides and 100 percent is likely due to the presence of $SO_3^-$ in the ash combining with Fe, Ca, Mg, Na, etc. For example, if these elements in Sample 12 were present as sulphates the oxide sum would be greater than 92 percent.
Table 1a
Major oxides concentration in the coal and coaly shale samples of the study area. (Values in weight percent (Wt%) coal basis).

| Location | Bombhole ID | Sample No. | SiO₂ | Al₂O₃ | Fe₂O₃(T) | MnO | MgO | CaO | Na₂O | K₂O | TiO₂ | P₂O₅ | LOI |
|----------|-------------|------------|------|------|---------|-----|-----|-----|------|-----|------|------|-----|
| Ubungo (ug) | 1267 | 12 | 3.74 | 2.19 | 2.01 | 0.011 | 0.02 | 0.07 | 0.06 | 0.05 | 0.083 | < 0.01 | 88.42 |
| 1266 | 13 | 4.72 | 1.79 | 0.91 | 0.024 | 0.03 | 0.11 | 0.05 | < 0.01 | 0.141 | < 0.01 | 90.90 |
| Chaka (ek) | 1356 | 9 | 15.35 | 7.96 | 1.08 | 0.009 | 0.15 | 0.23 | 0.08 | 0.23 | 0.416 | 0.03 | 73.16 |
| 1355 | 7 | 3.28 | 1.61 | 0.49 | 0.009 | 0.03 | 0.09 | 0.09 | 0.03 | 0.087 | < 0.01 | 93.87 |
| Ezaas (zz) | 1213 | 14 | 1.98 | 1.18 | 0.2 | 0.035 | < 0.01 | 0.02 | 0.05 | 0.03 | 0.022 | < 0.01 | 95.26 |
| 1219 | 8 | 7.25 | 4.14 | 0.26 | 0.035 | 0.02 | 0.02 | 0.03 | 0.05 | 0.036 | 0.01 | 86.86 |
| 1220 | 10 | 46.65 | 20.99 | 1.36 | 0.099 | 0.16 | 0.02 | 0.1 | 0.45 | 1.919 | 0.10 | 24.59 |
| 1225 | 6 | 1.02 | 0.66 | 0.04 | < 0.001 | < 0.01 | < 0.01 | 0.06 | 0.11 | 0.011 | < 0.01 | 97.30 |
| Enege (zi) | 1001 | 3 | 52.77 | 19.96 | 1.24 | 0.007 | 0.25 | 0.08 | 0.13 | 1.96 | 2.42 | 0.09 | 22.78 |
| 1001 | 7 | 48.59 | 16.02 | 0.85 | 0.007 | 0.14 | 0.03 | 0.07 | 0.56 | 1.376 | 0.05 | 31.10 |
| 1001 | 10 | 2.94 | 2.05 | 0.05 | < 0.001 | < 0.01 | < 0.01 | 0.07 | 0.07 | 0.047 | < 0.01 | 93.63 |
| 1006 | 3 | 3.34 | 1.40 | 0.05 | < 0.001 | < 0.01 | < 0.01 | 0.07 | 0.07 | 0.047 | < 0.01 | 93.7 |
| 1002 | 5 | 42.37 | 18.98 | 1.15 | 0.007 | 0.19 | 0.03 | 0.08 | 0.61 | 1.404 | 0.14 | 35.67 |

Table 1b
Major oxides concentration in the coal and coaly shale samples of the study area. (Values in weight percent (Wt%) ash basis).

| Location | Bombhole ID | Sample No. | SiO₂ | Al₂O₃ | Fe₂O₃(T) | MnO | MgO | CaO | Na₂O | K₂O | TiO₂ | P₂O₅ | Total | Ash Yield |
|----------|-------------|------------|------|------|---------|-----|-----|-----|------|-----|------|------|-------|---------|
| Ubungo (ug) | 1267 | 12 | 49.37 | 18.91 | 17.16 | 0.09 | 0.17 | 0.60 | 0.02 | 0.43 | 0.81 | 0.04 | 88.31 | 11.38 |
| 1266 | 13 | 51.87 | 19.67 | 10.00 | 0.26 | 0.33 | 1.21 | 0.35 | 0.55 | 0.55 | 0.05 | 85.35 | 9.10 |
| Chaka (ek) | 1356 | 9 | 59.19 | 28.25 | 4.02 | 0.03 | 0.56 | 0.86 | 0.30 | 0.56 | 1.55 | 0.11 | 94.77 | 26.84 |
| 1355 | 7 | 53.54 | 25.38 | 7.99 | 0.05 | 0.49 | 1.47 | 1.47 | 0.89 | 1.42 | 0.08 | 93.36 | 61.13 |
| Ezaas (zz) | 1213 | 14 | 65.84 | 27.84 | 1.80 | 0.01 | 0.05 | 0.05 | 0.00 | 0.00 | 2.54 | 0.13 | 98.94 | 75.41 |
| 1219 | 8 | 57.38 | 24.44 | 1.80 | 0.02 | 0.10 | 0.19 | 2.02 | 0.10 | 0.10 | 1.76 | 0.12 | 76.09 | 2.70 |
| 1220 | 10 | 42.97 | 25.43 | 4.21 | 0.11 | 0.45 | 1.06 | 0.65 | 0.47 | 0.11 | 75.27 | 4.64 |
| 1225 | 6 | 53.94 | 30.00 | 1.93 | 0.02 | 0.15 | 0.15 | 0.22 | 0.45 | 2.43 | 0.07 | 90.17 | 13.44 |
| Enege (zi) | 1001 | 3 | 69.34 | 25.38 | 1.61 | 0.01 | 0.32 | 0.10 | 0.17 | 1.76 | 2.77 | 0.12 | 100.38 | 77.22 |
| 1001 | 7 | 70.71 | 23.25 | 1.23 | 0.01 | 0.04 | 0.10 | 0.51 | 1.00 | 0.07 | 98.25 | 62.90 |
| 1001 | 10 | 46.15 | 32.18 | 0.78 | 0.01 | 0.08 | 0.16 | 1.10 | 0.08 | 0.31 | 0.08 | 80.95 | 63.37 |
| 1008 | 3 | 53.02 | 22.22 | 0.79 | 0.01 | 0.08 | 0.08 | 1.11 | 1.11 | 0.75 | 0.08 | 79.25 | 63.0 |
| 1002 | 5 | 65.86 | 28.88 | 1.79 | 0.01 | 0.30 | 0.05 | 0.12 | 0.55 | 2.18 | 0.22 | 100.36 | 64.33 |

The trace elements on a coal basis for the samples are presented in Table 2. All results for trace elements are reported in ppm by weight unless otherwise stated. For elements that had recorded values below the detectable limit, half of the value of the respective limit of detection was substituted for further statistical analysis.
Table 2
Trace elements and S concentration in the coal and coaly shale samples. (Values are in parts-per-million (ppm) of the coal except for S which is in percent).

| Location | Osogbo (OC) | Okehi (OK) | Prime (PF) | Enugu (EN) |
|----------|-------------|------------|------------|------------|
| Sample No. | 12 | 13 | 19 | 20 | 10 | 11 | 12 | 13 |
| Upper depth (m) | 100 | 162 | 58 | 55 | 132 | 20 | 241 | 159 | 257 | 129 |
| Pr | 1.09 | 1.00 | 0.97 | 0.94 | 0.92 | 0.91 | 0.89 | 0.87 | 0.85 | 0.83 |
| Fe | 0.87 | 0.84 | 0.81 | 0.79 | 0.77 | 0.75 | 0.73 | 0.71 | 0.70 | 0.68 |
| Mg | 0.65 | 0.62 | 0.59 | 0.57 | 0.55 | 0.53 | 0.51 | 0.49 | 0.47 | 0.45 |
| Ca | 0.44 | 0.42 | 0.40 | 0.38 | 0.36 | 0.34 | 0.32 | 0.30 | 0.28 | 0.26 |
| SiO₂ | 0.10 | 0.09 | 0.08 | 0.07 | 0.06 | 0.05 | 0.04 | 0.03 | 0.02 | 0.01 |

Geochemical characteristics of coal
The coal and coaly shale of the Anambra basin have SiO₂, Al₂O₃, and Fe₂O₃(T) ranging from 1.02% to 52.77%, 0.66% to 19.60% and 0.04% to 2.10% respectively. The major oxides in these samples are SiO₂ and Al₂O₃ with the ratio of Al₂O₃ to SiO₂ ranging from 1.43 to 3.03. This indicates the prevalence of quartz and clay minerals.

The strong correlation between SiO₂ and Al₂O₃ indicates a common source, likely detrital (Table 3).

Table 3
Correlation coefficient matrix for major elements and ash yield

| Major Oxides | SiO₂ | Al₂O₃ | Fe₂O₃(T) | MnO | MgO | CaO | Na₂O | K₂O | TiO₂ | P₂O₅ | Ash Yield |
|--------------|------|-------|---------|-----|-----|-----|------|-----|------|------|-----------|
| SiO₂         | 0.99 | 1.00  | 0.52    | 0.53 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| Al₂O₃        | 0.52 | 0.53  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| Fe₂O₃(T)     | 0.33 | 0.57  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| MnO          | 0.52 | 0.53  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| MgO          | 0.33 | 0.57  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| CaO          | 0.33 | 0.57  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| Na₂O         | 0.33 | 0.57  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| K₂O          | 0.33 | 0.57  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| TiO₂         | 0.33 | 0.57  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| P₂O₅         | 0.33 | 0.57  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |
| Ash Yield    | 0.33 | 0.57  | 1.00    | 0.57 | 1.00| 0.92| 0.33 | 0.30| 0.35| 0.32| 0.30 |

The relationships between selected major oxides with each other and with ash yield are illustrated in Figs. 5 and 6, while those that exist between trace elements and ash yield are represented in Fig. 7. The bimodal distribution of CaO displayed in Fig. 6 is a further indication of multiple sources for this element.
Fig. 5. Relationship among major elements in coal and coaly shale samples (i) SiO\textsubscript{2} vs Al\textsubscript{2}O\textsubscript{3} (ii) SiO\textsubscript{2} vs TiO\textsubscript{2}, (iii) SiO\textsubscript{2} vs MgO, (iv) K\textsubscript{2}O vs Na\textsubscript{2}O.
Mode of occurrence of trace element and concentrations

The concentrations of most trace elements in these coals are unremarkable, falling well within the range of U.S. (Orem and Finkelman, 2003) and World coals (Swaine, 1990). As expected, the concentrations of the most elements in the coaly shales are considerably higher that that of the coal (Table 2). The data do not indicate any potential for economic by-product recovery, technological problems or environmental or health concerns as mercury, lead, concentrations are low and arsenic and boron concentrations are exceptionally low.

Trace elements are present in coal in either organic or inorganic forms, and probably most of them occur in both forms (Gürdal, 2008). Two methods may be used to determine the mode of occurrence of elements in coal; sequential leaching (Dai et al., 2003) and statistical methods (Song et al., 2007). Factor and cluster analyses were applied to establish the association of trace elements in coal and among sampled locations.

MAJOR OXIDES AND TRACE ELEMENT DISTRIBUTIONS IN COAL AND COALY SHALE SEAMS
Many elements in most coals are derived from the detrital input to the precursor swamp and many chalcophile elements are associated with sulphide minerals that may have formed syngenetically or epigenetically (Finkelman, 1995). These relationships appear to hold for these Nigerian coal samples. In these samples Sr, Y, Sc, Zr, Be, V, Cr, Ga, Ni, Te, and Zn have moderate to strong correlation coefficients (0.86, 0.93, 0.98, 0.73, 0.98, 0.91, 0.95, 0.88, 0.89, 0.77 and 0.88 respectively) with ash yield and with each other (Table 4).
This indicates a common detrital source for the bulk of these elements. Ag, As, Cd, Co, Cu, Hg, Mo, Pb, Sb, and S have weak to very weak correlations with ash yield. These elements are likely associated with sulphide phases. The poor correlation of many of these chalcophile elements with sulphur is an indication that the sulphur is present not only in the sulphide form but also as organic and sulphate sulphur. Boron and some antimony are likely associated with the organic components (Finkelman, 1995; Swaine, 1990). Barium is likely present in carbonates, phosphates, or sulphates.

Factor analysis aids in the identification of factors that can be meaningful. The Principal Component Analysis extraction method was applied yielding two components, which together explained 86% of the total variance (Table 5).

### Table 5
Output of Factor Analysis for trace elements

| Elements | Component 1 | Component 2 |
|----------|-------------|-------------|
| Ba       | .863        | .181        |
| Sr       | .938        | .220        |
| Y        | .966        | .109        |
| Sc       | .981        | .075        |
| Zr       | .895        | .051        |
| Ba       | .814        | .276        |
| B        | .977        | .029        |
| Co       | .871        | .347        |
| Cr       | .976        | .171        |
| Cu       | .933        | .078        |
| Zn       | .938        | .056        |
| Ba       | .903        | .297        |
| Pb       | .957        | .026        |
| S        | .034        | .808        |
| Zn       | .927        | .262        |
| **Total** | **11.98**    | **1.76**     |
| % of Variance | **74.90** | **11.03**     |
| Cumulative % | **74.90** | **85.93**     |

Majority of the trace elements (with the exception of B and S) correlated positively with Component 1. Component 1 is responsible for 74% of the total variance and is ascribed to the detrital input that includes quartz, clays, and accessory minerals such as zircon and rutile that commonly dominate the inorganic constituents in coal (Finkelman, 1995). Component 2 accounts for 11% of the total variance and consists of strong component loading of S and B. As indicated above, these two elements commonly have a strong organic association (Finkelman, 1995).

Cluster Analysis was applied to establish the association of eleven coal samples using trace element content. The two Components derived from Factor Analysis correspond to the two cluster classes of the sampled locations (Fig. 8).
CONCLUSION

The chemical analysis of coal and coaly shale samples from the Enugu escarpment of south-eastern Nigeria indicates that the major oxides in these samples are $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$, indicating the prevalence of quartz and clay minerals likely derived from a detrital source. However, epigenetic carbonates and syngenetic and/or epigenetic sulphides may also be present in these samples. The concentrations of most trace elements in these coals are unremarkable, falling well within the range of U.S. and World coals. The data do not indicate any potential for economic by-product, potential technological problems or environmental or health concerns.

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