

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

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(Received 10 December 2009; Revision Accepted 07, April 2010)

## 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<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> indicate the prevalence of quartz and clay minerals. The strong statistical correlation between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> indicates a common source, likely detrital. The strong correlation between the other major oxides with both SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> 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 (Ndiokwere 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

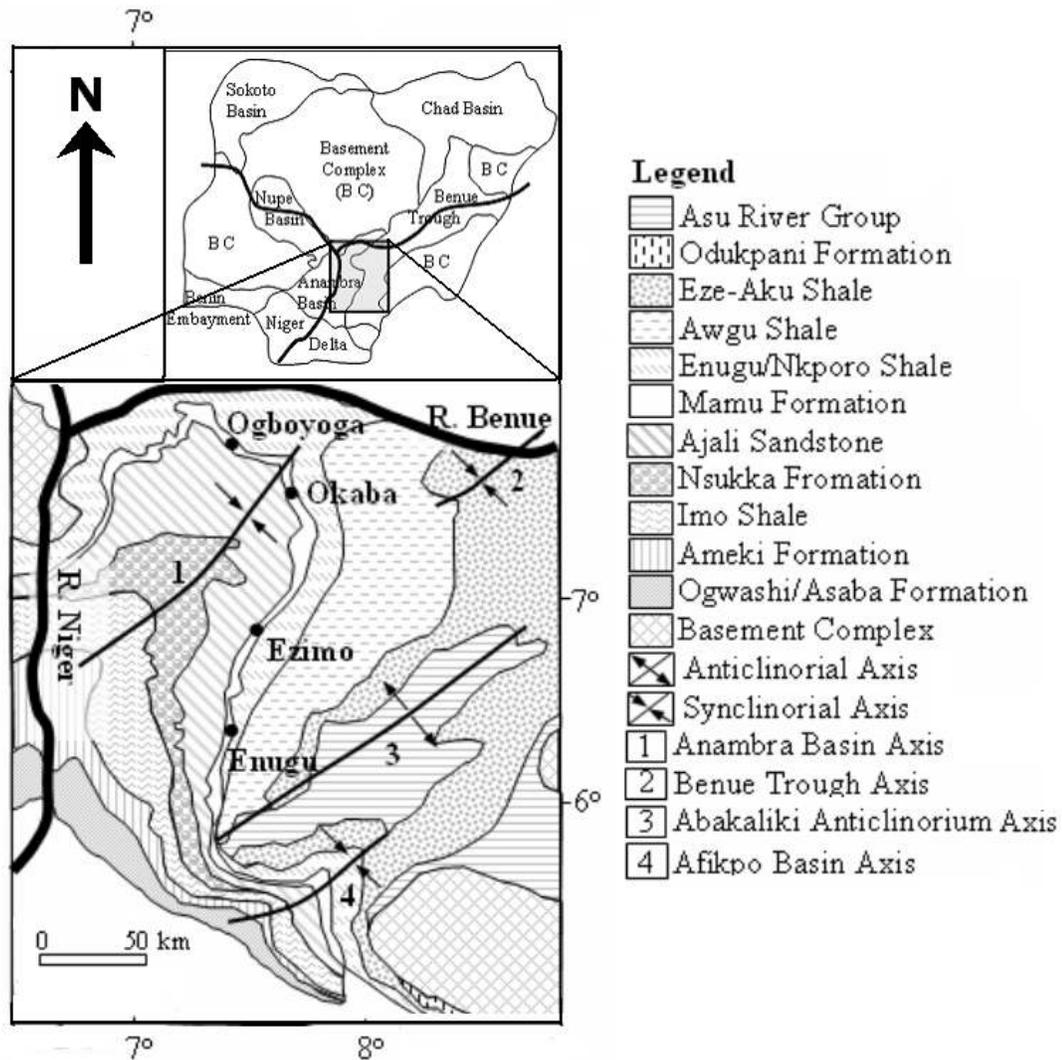
The Anambra Basin is located in the south-western end of the Benue Trough of Nigeria (Fig 1). The basin is bounded on the west by the Precambrian basement complex rocks of western Nigeria and on the east by the Abakaliki Anticlinorium. It extends northward to the lower Benue River and also forms a boundary with the Tertiary Niger Delta to the south.

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**Fig 1: Geologic maps of Nigeria (insert area) and south-eastern Nigeria showing the locations of the coal and coaly shale deposits**

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 Campano – 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).

| PERIOD/AGE |                           | FORMATION                         |
|------------|---------------------------|-----------------------------------|
| Tertiary   | Eocene                    | Bende/Ameki Formation             |
|            | Palaeocene                | Imo Shale Group                   |
|            | Maastrichian - Palaeocene | Nsukka Formation                  |
| Cretaceous | Maastrichian              | Ajali Formation<br>Mamu Formation |
|            | Campanian - Maastrichian  | Enugu/Nkporo /Owelli Formation    |
|            |                           | XXXXXXXXXX                        |
|            | Santonian                 |                                   |

XXXXXXXXXX Major Unconformity

Fig. 2. Stratigraphic sequence of the Anambra Basin

**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 (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>(T), MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>) 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° 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).

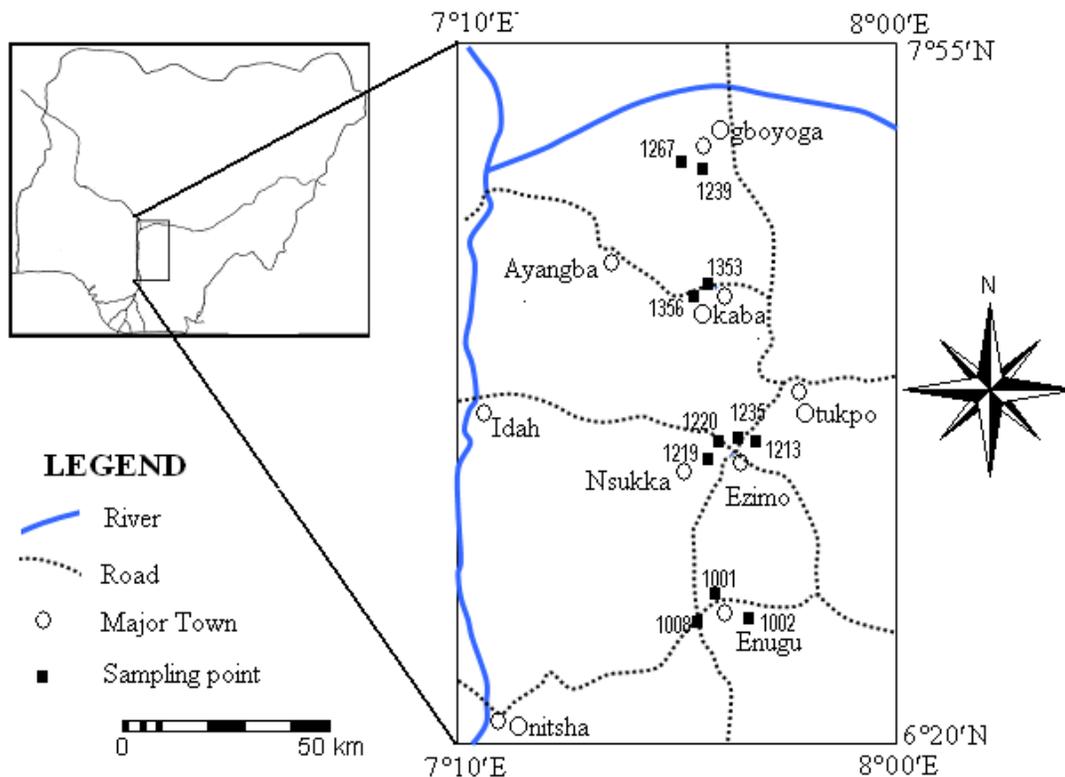


Fig. 3. Location map of study area showing sample locations

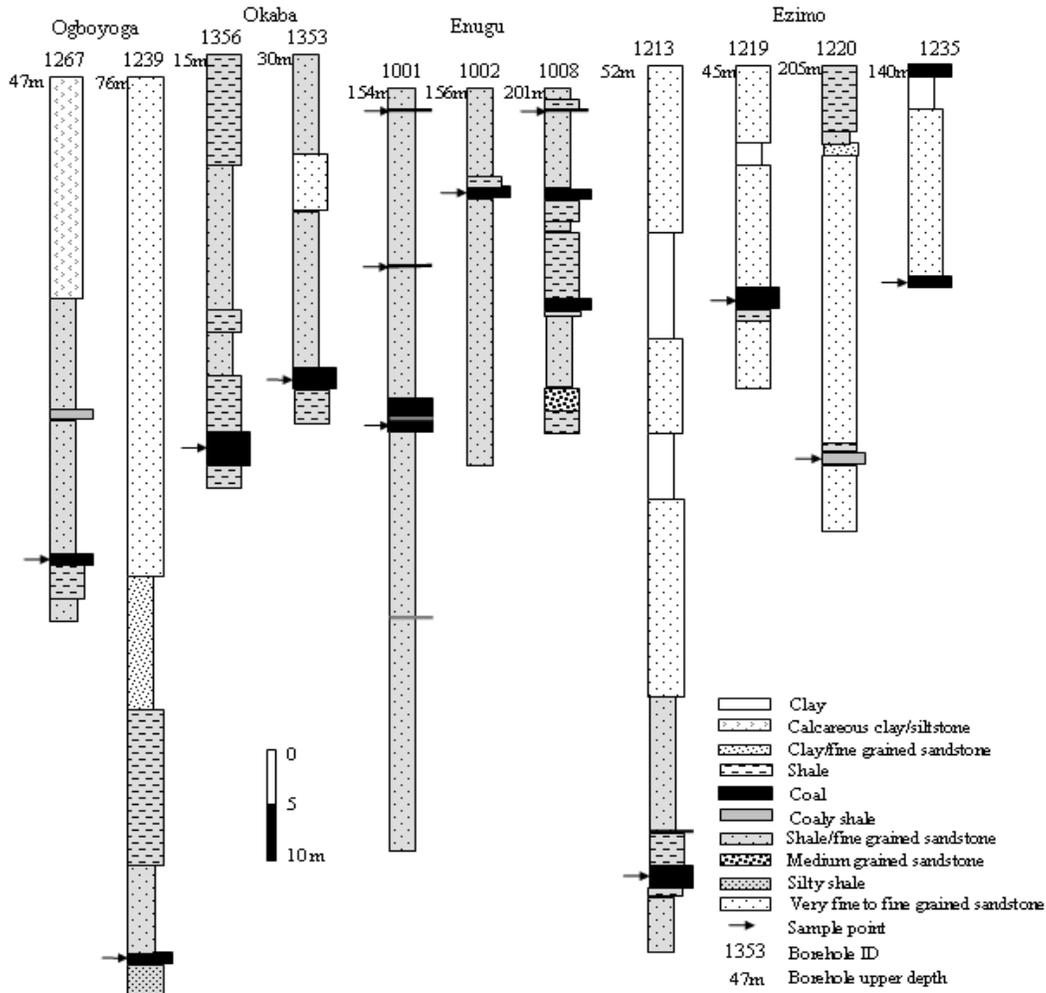


Fig. 4. Lithologic sections of sampled boreholes

**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 dendrograms. 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<sub>3</sub><sup>-</sup> 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      | Borehole ID | Element<br>Detection Limit<br>Sample No. | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> (T) | MnO     | MgO    | CaO    | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | LOI   |
|---------------|-------------|--|------------------|--------------------------------|------------------------------------|---------|--------|--------|-------------------|------------------|------------------|-------------------------------|-------|
|               |             |  | 0.01             | 0.01                           | 0.01                               | 0.001   | 0.01   | 0.01   | 0.01              | 0.01             | 0.01             | 0.001                         | 0.01  |
| Ogboyoga (OG) | 1267        | 12                                       | 5.74             | 2.19                           | 2.01                               | 0.011   | 0.02   | 0.07   | 0.06              | 0.05             | 0.093            | < 0.01                        | 88.42 |
|               | 1239        | 13                                       | 4.72             | 1.79                           | 0.91                               | 0.024   | 0.03   | 0.11   | 0.05              | < 0.01           | 0.141            | < 0.01                        | 90.90 |
| Okaba (OK)    | 1356        | 9  | 15.35            | 7.86                           | 1.08                               | 0.009   | 0.15   | 0.23   | 0.08              | 0.23             | 0.416            | 0.03                          | 73.16 |
|               | 1353        | 7  | 3.28             | 1.61                           | 0.49                               | 0.009   | 0.03   | 0.09   | 0.09              | 0.03             | 0.087            | < 0.01                        | 93.87 |
| Ezimo (EZ)    | 1213        | 14                                       | 1.98             | 1.18                           | 0.2                                | 0.005   | < 0.01 | 0.02   | 0.05              | 0.03             | 0.022            | < 0.01                        | 95.36 |
|               | 1219        | 8  | 7.25             | 4.14                           | 0.26                               | 0.003   | 0.02   | 0.02   | 0.03              | 0.06             | 0.326            | 0.01                          | 86.56 |
|               | 1220        | 10                                       | 49.65            | 20.69                          | 1.36                               | 0.009   | 0.16   | 0.02   | 0.1               | 0.45             | 1.919            | 0.10                          | 24.59 |
|               | 1235        | 6  | 1.02             | 0.66                           | 0.04                               | < 0.001 | < 0.01 | < 0.01 | 0.06              | < 0.01           | 0.011            | < 0.01                        | 97.30 |
| Emugu (EN)    | 1001        | 3  | 52.77            | 19.6                           | 1.24                               | 0.007   | 0.25   | 0.08   | 0.13              | 1.36             | 2.142            | 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              | < 0.01           | 0.020            | < 0.01                        | 93.63 |
|               | 1008        | 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            | 18.58                          | 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      | Borehole ID | Element<br>Detection Limit<br>Sample No. | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> (T) | MnO   | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | Total  | Ash Yield |
|---------------|-------------|--|------------------|--------------------------------|------------------------------------|-------|------|------|-------------------|------------------|------------------|-------------------------------|--------|-----------|
|               |             |  | 0.01             | 0.01                           | 0.01                               | 0.001 | 0.01 | 0.01 | 0.01              | 0.01             | 0.01             | 0.001                         | 0.01   |           |
| Ogboyoga (OG) | 1267        | 12                                       | 49.57            | 18.91                          | 17.36                              | 0.09  | 0.17 | 0.60 | 0.52              | 0.43             | 0.80             | 0.04                          | 88.51  | 11.58     |
|               | 1239        | 13                                       | 51.87            | 19.67                          | 10.00                              | 0.26  | 0.33 | 1.21 | 0.55              | 0.05             | 1.55             | 0.05                          | 85.55  | 9.10      |
| Okaba (OK)    | 1356        | 9  | 57.19            | 29.28                          | 4.02                               | 0.03  | 0.56 | 0.86 | 0.30              | 0.86             | 1.55             | 0.11                          | 94.77  | 26.84     |
|               | 1353        | 7  | 53.51            | 26.26                          | 7.99                               | 0.15  | 0.49 | 1.47 | 1.47              | 0.49             | 1.42             | 0.08                          | 93.33  | 6.13      |
| Ezimo (EZ)    | 1213        | 14                                       | 65.84            | 27.44                          | 1.80                               | 0.01  | 0.21 | 0.03 | 0.13              | 0.60             | 2.54             | 0.13                          | 98.74  | 75.41     |
|               | 1219        | 8  | 37.78            | 24.44                          | 1.48                               | 0.02  | 0.19 | 0.19 | 2.22              | 0.19             | 0.41             | 0.19                          | 67.09  | 2.70      |
|               | 1220        | 10                                       | 42.67            | 25.43                          | 4.31                               | 0.11  | 0.11 | 0.43 | 1.08              | 0.65             | 0.47             | 0.11                          | 75.37  | 4.64      |
|               | 1235        | 6  | 53.94            | 30.80                          | 1.93                               | 0.02  | 0.15 | 0.15 | 0.22              | 0.45             | 2.43             | 0.07                          | 90.17  | 13.44     |
| Emugu (EN)    | 1001        | 3  | 68.34            | 25.38                          | 1.61                               | 0.01  | 0.32 | 0.10 | 0.17              | 1.76             | 2.77             | 0.12                          | 100.58 | 77.22     |
|               | 1001        | 7  | 70.52            | 23.25                          | 1.23                               | 0.01  | 0.20 | 0.04 | 0.10              | 0.81             | 2.00             | 0.07                          | 98.25  | 68.90     |
|               | 1001        | 10                                       | 46.15            | 32.18                          | 0.78                               | 0.01  | 0.08 | 0.16 | 1.10              | 0.08             | 0.31             | 0.08                          | 80.93  | 6.37      |
|               | 1008        | 3  | 53.02            | 22.22                          | 0.79                               | 0.01  | 0.08 | 0.08 | 1.11              | 1.11             | 0.75             | 0.08                          | 79.25  | 6.30      |
|               | 1002        | 5  | 65.86            | 28.88                          | 1.79                               | 0.01  | 0.30 | 0.05 | 0.12              | 0.95             | 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        | Oghoyoga (OG)   |       | Okaba (OK) |       | Ezimo (EZ) |       |       |       | Enugu (EN) |      |      |       |       |      |
|-----------------|-----------------|-------|------------|-------|------------|-------|-------|-------|------------|------|------|-------|-------|------|
|                 | 1267            | 1239  | 1356       | 1353  | 1213       | 1219  | 1220  | 1235  | 1001       | 1001 | 1001 | 1008  | 1002  |      |
| Borehole ID     |                 |       |            |       |            |       |       |       |            |      |      |       |       |      |
| Sample No.      | 12              | 13    | 9          | 7     | 14         | 8     | 10    | 6     | 3          | 7    | 10   | 3     | 5     |      |
| Upper depth (m) | 100             | 162   | 50         | 55    | 132        | 80    | 241   | 159   | 157        | 172  | 184  | 203   | 166   |      |
| Element         | Detection Limit |       |            |       |            |       |       |       |            |      |      |       |       |      |
| Ba              | 2               | 161   | 227        | 255   | 147        | 20    | 64    | < 2   | 452        | 388  | 218  | 12    | 12    | 733  |
| Sr              | 2               | 15    | 19         | 46    | 15         | 4     | 15    | < 2   | 66         | 83   | 54   | 3     | 2     | 130  |
| Y               | 1               | 4     | 2          | 7     | 3          | < 1   | 4     | < 1   | 30         | 54   | 28   | < 1   | < 1   | 48   |
| Sc              | 1               | 1     | 1          | 5     | 2          | < 1   | 2     | < 1   | 14         | 17   | 11   | < 1   | < 1   | 15   |
| Zr              | 2               | 22    | 21         | 56    | 22         | 2     | 28    | 2     | 335        | 739  | 486  | 5     | 6     | 319  |
| Be              | 1               | 1     | 2          | 2     | < 1        | 2     | 3     | < 1   | 2          | 4    | 3    | < 1   | < 1   | 5    |
| V               | 5               | 14    | 10         | 49    | 17         | < 5   | 27    | < 5   | 99         | 138  | 89   | < 5   | < 5   | 96   |
| Ag              | 0.3             | < 0.3 | < 0.3      | 0.3   | < 0.3      | < 0.3 | < 0.3 | < 0.3 | 1.1        | 0.8  | 1.1  | < 0.3 | < 0.3 | 0.4  |
| As              | 3               | < 3   | < 3        | < 3   | 5          | < 3   | < 3   | < 3   | < 3        | 4    | 4    | 3     | 4     | 3    |
| B               | 1               | < 1   | < 1        | < 1   | < 1        | 1     | 2     | 3     | 1          | 1    | 1    | 2     | 2     | 3    |
| Bi              | 2               | < 2   | < 2        | < 2   | < 2        | < 2   | < 2   | < 2   | < 2        | < 2  | < 2  | < 2   | < 2   | < 2  |
| Cd              | 0.3             | < 0.3 | < 0.3      | < 0.3 | < 0.3      | < 0.3 | < 0.3 | 0.3   | 0.6        | 0.5  | 0.4  | < 0.3 | < 0.3 | 0.5  |
| Co              | 1               | 15    | < 1        | 6     | 2          | 3     | 3     | 3     | 21         | 22   | 20   | 2     | 3     | 13   |
| Cr              | 1               | 46    | 8          | 58    | 29         | 5     | 37    | 4     | 96         | 107  | 81   | 8     | 10    | 89   |
| Cu              | 1               | 12    | 1          | 21    | 14         | 2     | 22    | 4     | 27         | 36   | 25   | 6     | 5     | 30   |
| Ga              | 1               | 11    | 1          | 14    | 3          | 1     | 10    | 2     | 17         | 16   | 16   | 4     | 3     | 21   |
| Hg              | 1               | 3     | < 1        | < 1   | < 1        | < 1   | < 1   | < 1   | < 1        | 1    | 2    | < 1   | < 1   | 3    |
| Mo              | 1               | 1     | < 1        | < 1   | < 1        | < 1   | 1     | < 1   | 2          | 2    | 1    | < 1   | < 1   | 1    |
| Ni              | 1               | 27    | 1          | 18    | 5          | 5     | 8     | 9     | 30         | 39   | 40   | 4     | 4     | 29   |
| Pb              | 3               | 10    | < 3        | 23    | 9          | < 3   | 12    | 4     | 32         | 31   | 22   | 3     | 7     | 31   |
| Sb              | 5               | 7     | < 5        | 6     | < 5        | 5     | < 5   | < 5   | < 5        | < 5  | < 5  | < 5   | < 5   | < 5  |
| S (%)           | 0.01            | 2.29  | 0.09       | 0.59  | 0.62       | 0.14  | 0.45  | 0.19  | 0.1        | 0.97 | 0.16 | 0.42  | 0.19  | 0.15 |
| Te              | 2               | < 2   | < 2        | < 2   | < 2        | < 2   | < 2   | < 2   | 2          | 4    | 3    | < 2   | < 2   | < 2  |
| Tl              | 5               | < 5   | < 5        | < 5   | < 5        | < 5   | < 5   | < 5   | < 5        | < 5  | < 5  | < 5   | < 5   | < 5  |
| U               | 10              | < 10  | < 10       | < 10  | < 10       | < 10  | < 10  | < 10  | 10         | < 10 | < 10 | < 10  | < 10  | < 10 |
| W               | 5               | < 5   | < 5        | < 5   | < 5        | < 5   | < 5   | < 5   | < 5        | < 5  | < 5  | < 5   | < 5   | < 5  |
| Zn              | 1               | 20    | 5          | 17    | 6          | 9     | 14    | 17    | 58         | 69   | 67   | 6     | 8     | 115  |

### Geochemical characteristics of coal

The coal and coaly shale of the Anambra basin have SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>(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

SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with the ratio of Al<sub>2</sub>O<sub>3</sub> to SiO<sub>2</sub> ranging from 1.43 to 3.03. This indicates the prevalence of quartz and clay minerals.

The strong correlation between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> indicates a common source, likely detrital (Table 3).

Table 3

Correlation coefficient matrix for major elements and ash yield

|                                  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> T | MnO  | MgO  | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | Ash Yield |
|----------------------------------|------------------|--------------------------------|----------------------------------|------|------|-------|-------------------|------------------|------------------|-------------------------------|-----------|
| SiO <sub>2</sub>                 | 1.00             |                                |                                  |      |      |       |                   |                  |                  |                               |           |
| Al <sub>2</sub> O <sub>3</sub>   | 0.99             | 1.00                           |                                  |      |      |       |                   |                  |                  |                               |           |
| Fe <sub>2</sub> O <sub>3</sub> T | 0.52             | 0.53                           | 1.00                             |      |      |       |                   |                  |                  |                               |           |
| MnO                              | 0.09             | 0.08                           | 0.57                             | 1.00 |      |       |                   |                  |                  |                               |           |
| MgO                              | 0.92             | 0.93                           | 0.57                             | 0.17 | 1.00 |       |                   |                  |                  |                               |           |
| CaO                              | -0.01            | 0.01                           | 0.42                             | 0.54 | 0.31 | 1.00  |                   |                  |                  |                               |           |
| Na <sub>2</sub> O                | 0.66             | 0.66                           | 0.38                             | 0.00 | 0.75 | 0.21  | 1.00              |                  |                  |                               |           |
| K <sub>2</sub> O                 | 0.88             | 0.85                           | 0.44                             | 0.02 | 0.91 | 0.08  | 0.77              | 1.00             |                  |                               |           |
| TiO <sub>2</sub>                 | 0.98             | 0.98                           | 0.51                             | 0.09 | 0.92 | -0.02 | 0.71              | 0.90             | 1.00             |                               |           |
| P <sub>2</sub> O <sub>5</sub>    | 0.89             | 0.94                           | 0.48                             | 0.05 | 0.88 | -0.04 | 0.60              | 0.77             | 0.89             | 1.00                          |           |
| Ash Yield                        | 1.00             | 0.99                           | 0.54                             | 0.10 | 0.93 | 0.01  | 0.66              | 0.87             | 0.99             | 0.90                          | 1.00      |

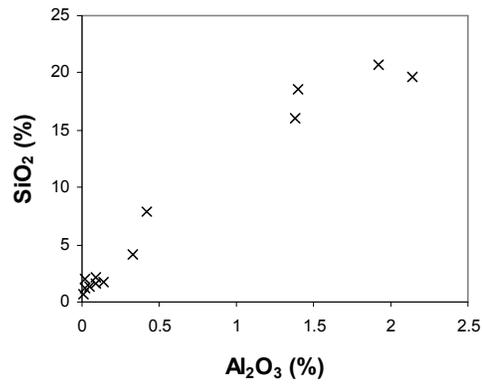
The strong correlation between MgO, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub> with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and ash yield also indicates that all of these elements have a common detrital source. The weak correlation among these elements with Na<sub>2</sub>O is most likely due to leaching of the coal by water or to the organic components of the coal. One of the sources accounted for by epigenetic carbonates demonstrate a poor correlation of CaO with the other elements and ash yield. This carbonate likely contains some of the manganese and iron, resulting also

in their poor correlation with the ash yield. Some of the

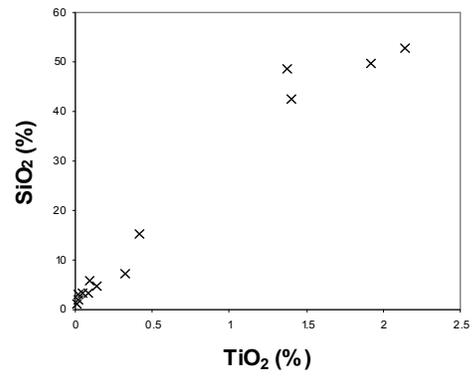
### MAJOR OXIDES AND TRACE ELEMENT DISTRIBUTIONS IN COAL

with SiO<sub>2</sub> and ash yield.

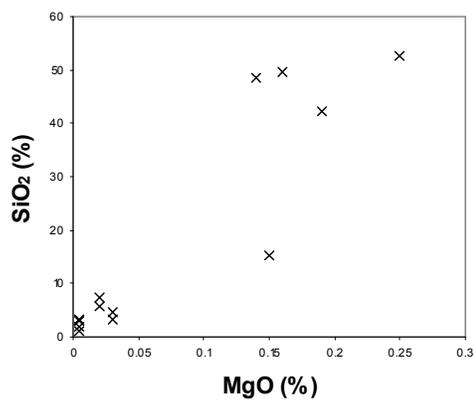
The relationships between selected major oxides with each other and with ash yield are illustrated in Figs. 5 and 6, while those that exist between trace elements and ash yield are represented in Fig. 7. The bimodal distribution of CaO displayed in Fig. 6 is a further indication of multiple sources for this element.



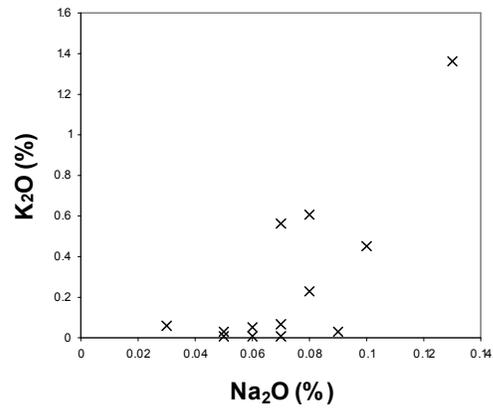
(i)



(ii)

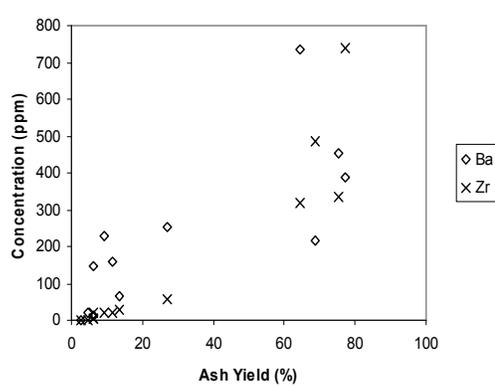


(iii)

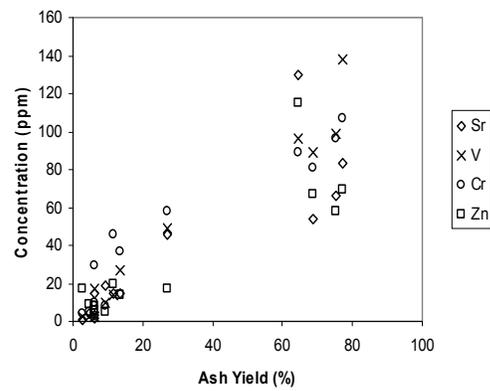


(iv)

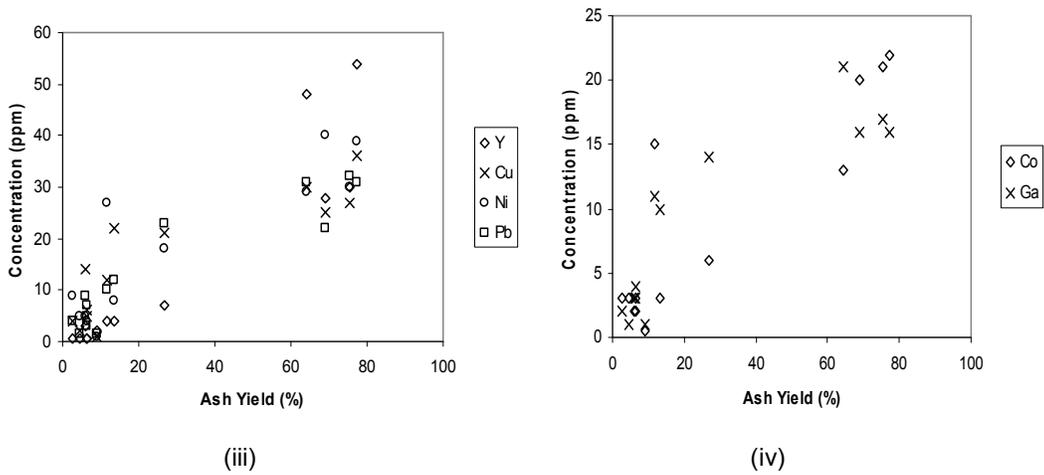
Fig. 5. Relationship among major elements in coal and coaly shale samples (i)  $\text{SiO}_2$  vs  $\text{Al}_2\text{O}_3$  (ii)  $\text{SiO}_2$  vs  $\text{TiO}_2$ , (iii)  $\text{SiO}_2$  vs  $\text{MgO}$ , (iv)  $\text{K}_2\text{O}$  vs  $\text{Na}_2\text{O}$



(i)



(ii)



**Fig. 6. Relationship between major elements and ash yield in coal and coaly shale samples (i) SiO<sub>2</sub> vs Ash Yield (ii) Al<sub>2</sub>O<sub>3</sub> vs Ash Yield (iii) MgO vs Ash Yield (iv) CaO vs Ash Yield**

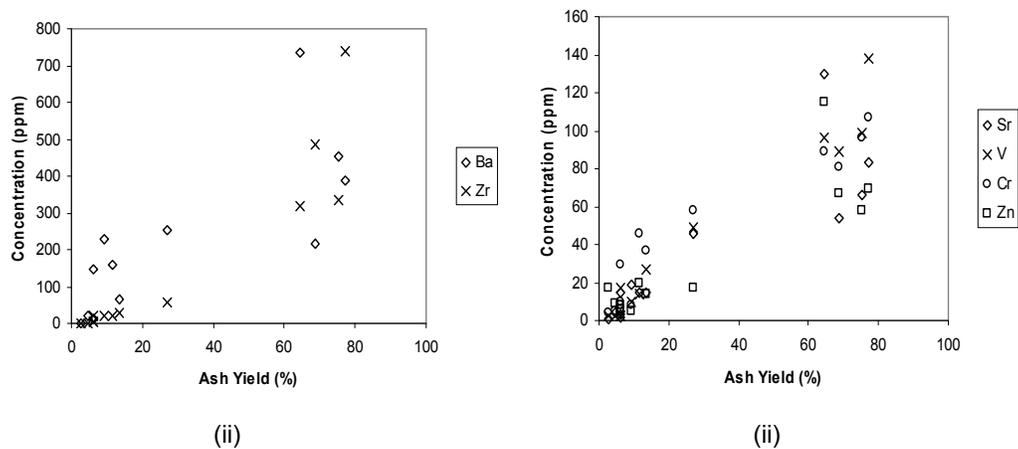
**Mode of occurrence of trace element and concentrations**

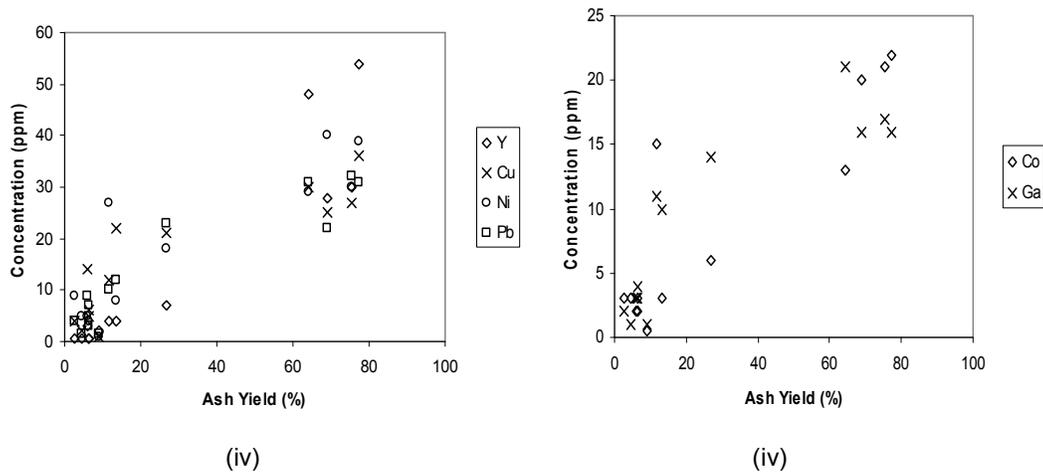
The concentrations of most trace elements in these coals are unremarkable, falling well within the range of U.S. (Orem and Finkelman, 2003) and World coals (Swaine, 1990). As expected, the concentrations of the most elements in the coaly shales are considerably higher than that of the coal (Table 2). 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**





**Fig. 7. Relationship between trace elements and ash yield in coal and coaly shale samples (i) Ba, Zr vs Ash Yield (ii) Sr, V, Cr, Zn vs Ash Yield (iii) Y, Cu, Ni, Pb vs Ash Yield (iv) Co, Ga vs Ash Yield**

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).

Table 4

Correlation coefficient matrix for trace elements and S from Nigerian coal and coaly shale samples

|           | Ba    | Sr    | Y     | Sc    | Zr    | Be    | V     | Ag    | As    | B     | Cd    | Co   | Cr    | Cu    | Ga   | Hg   | Mo    | Ni   | Pb    | Sb    | S     | Te   | Zn   | Ash Yield |  |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|-------|-------|------|------|-------|------|-------|-------|-------|------|------|-----------|--|
| Ba        | 1.00  |       |       |       |       |       |       |       |       |       |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| Sr        | 0.96  | 1.00  |       |       |       |       |       |       |       |       |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| Y         | 0.84  | 0.93  | 1.00  |       |       |       |       |       |       |       |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| Sc        | 0.85  | 0.92  | 0.98  | 1.00  |       |       |       |       |       |       |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| Zr        | 0.62  | 0.75  | 0.93  | 0.92  | 1.00  |       |       |       |       |       |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| Be        | 0.76  | 0.85  | 0.82  | 0.77  | 0.70  | 1.00  |       |       |       |       |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| V         | 0.79  | 0.88  | 0.96  | 0.99  | 0.95  | 0.77  | 1.00  |       |       |       |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| Ag        | 0.52  | 0.60  | 0.72  | 0.83  | 0.84  | 0.47  | 0.84  | 1.00  |       |       |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| As        | 0.08  | 0.18  | 0.31  | 0.26  | 0.39  | 0.03  | 0.26  | 0.21  | 1.00  |       |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| B         | 0.05  | 0.14  | 0.11  | 0.04  | -0.06 | 0.14  | -0.05 | -0.17 | -0.01 | 1.00  |       |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| Cd        | 0.75  | 0.80  | 0.88  | 0.92  | 0.82  | 0.60  | 0.87  | 0.83  | 0.13  | 0.22  | 1.00  |      |       |       |      |      |       |      |       |       |       |      |      |           |  |
| Co        | 0.62  | 0.68  | 0.81  | 0.85  | 0.86  | 0.53  | 0.86  | 0.87  | 0.15  | -0.17 | 0.81  | 1.00 |       |       |      |      |       |      |       |       |       |      |      |           |  |
| Cr        | 0.81  | 0.87  | 0.90  | 0.95  | 0.87  | 0.72  | 0.96  | 0.81  | 0.20  | -0.12 | 0.82  | 0.90 | 1.00  |       |      |      |       |      |       |       |       |      |      |           |  |
| Cu        | 0.74  | 0.83  | 0.87  | 0.90  | 0.82  | 0.75  | 0.93  | 0.71  | 0.26  | -0.01 | 0.73  | 0.78 | 0.96  | 1.00  |      |      |       |      |       |       |       |      |      |           |  |
| Ga        | 0.81  | 0.88  | 0.83  | 0.87  | 0.72  | 0.75  | 0.87  | 0.70  | 0.07  | 0.03  | 0.74  | 0.82 | 0.94  | 0.92  | 1.00 |      |       |      |       |       |       |      |      |           |  |
| Hg        | 0.53  | 0.53  | 0.45  | 0.37  | 0.31  | 0.45  | 0.33  | 0.18  | 0.08  | 0.10  | 0.30  | 0.52 | 0.46  | 0.37  | 0.58 | 1.00 |       |      |       |       |       |      |      |           |  |
| Mo        | 0.58  | 0.61  | 0.78  | 0.81  | 0.80  | 0.53  | 0.84  | 0.77  | 0.04  | -0.11 | 0.81  | 0.86 | 0.84  | 0.78  | 0.70 | 0.21 | 1.00  |      |       |       |       |      |      |           |  |
| Ni        | 0.65  | 0.74  | 0.83  | 0.85  | 0.86  | 0.62  | 0.88  | 0.82  | 0.17  | -0.11 | 0.77  | 0.97 | 0.92  | 0.83  | 0.88 | 0.61 | 0.76  | 1.00 |       |       |       |      |      |           |  |
| Pb        | 0.84  | 0.89  | 0.88  | 0.94  | 0.80  | 0.71  | 0.94  | 0.77  | 0.17  | -0.01 | 0.83  | 0.82 | 0.97  | 0.95  | 0.94 | 0.37 | 0.78  | 0.84 | 1.00  |       |       |      |      |           |  |
| Sb        | -0.12 | -0.17 | -0.28 | -0.27 | -0.30 | -0.16 | -0.23 | -0.26 | -0.45 | -0.46 | -0.39 | 0.03 | -0.06 | -0.15 | 0.04 | 0.30 | -0.17 | 0.07 | -0.10 | 1.00  |       |      |      |           |  |
| S         | -0.05 | -0.09 | -0.03 | -0.10 | 0.00  | -0.14 | -0.03 | -0.16 | -0.06 | -0.38 | -0.21 | 0.27 | 0.14  | 0.10  | 0.14 | 0.49 | 0.17  | 0.28 | 0.01  | 0.66  | 1.00  |      |      |           |  |
| Te        | 0.33  | 0.47  | 0.73  | 0.74  | 0.93  | 0.48  | 0.80  | 0.80  | 0.40  | -0.22 | 0.65  | 0.78 | 0.71  | 0.66  | 0.51 | 0.11 | 0.74  | 0.76 | 0.60  | -0.26 | 0.06  | 1.00 |      |           |  |
| Zn        | 0.88  | 0.95  | 0.93  | 0.91  | 0.78  | 0.82  | 0.86  | 0.66  | 0.22  | 0.29  | 0.86  | 0.75 | 0.84  | 0.79  | 0.86 | 0.63 | 0.62  | 0.81 | 0.84  | -0.24 | -0.10 | 0.52 | 1.00 |           |  |
| Ash Yield | 0.79  | 0.86  | 0.93  | 0.98  | 0.92  | 0.73  | 0.98  | 0.91  | 0.23  | -0.30 | 0.91  | 0.90 | 0.95  | 0.88  | 0.88 | 0.37 | 0.83  | 0.89 | -0.93 | -0.25 | 0.97  | 0.77 | 0.88 | 1.00      |  |

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            | 2            |
| Ba                   | .863         | .181         |
| Sr                   | .938         | .220         |
| Y                    | .966         | .109         |
| Sc                   | .981         | .075         |
| Zr                   | .895         | -.081        |
| Be                   | .814         | .276         |
| V                    | .977         | -.029        |
| B                    | .020         | .781         |
| Co                   | .871         | -.347        |
| Cr                   | .976         | -.171        |
| Cu                   | .933         | -.078        |
| Ga                   | .935         | -.066        |
| Ni                   | .903         | -.297        |
| Pb                   | .957         | -.026        |
| S                    | .034         | -.808        |
| Zn                   | .927         | .262         |
| <b>Total</b>         | <b>11.98</b> | <b>1.76</b>  |
| <b>% of Variance</b> | <b>74.90</b> | <b>11.03</b> |
| <b>Cumulative %</b>  | <b>74.90</b> | <b>85.93</b> |

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).

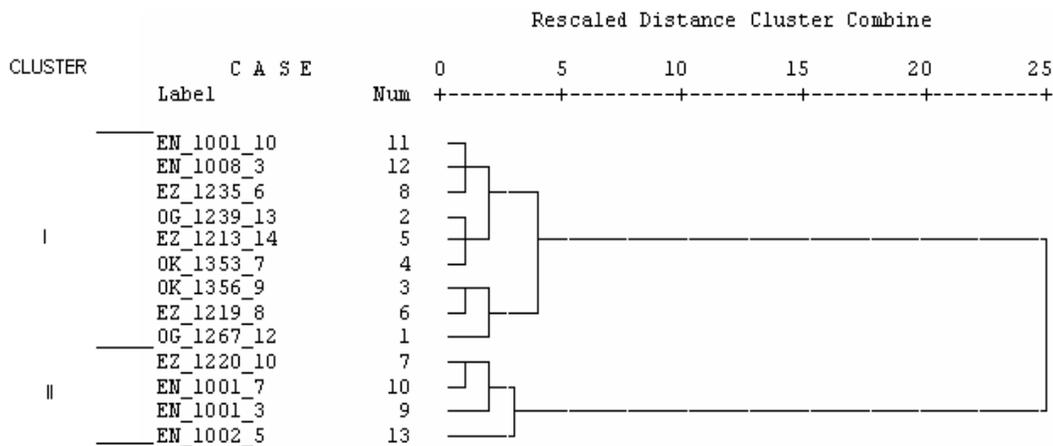


Fig. 8. Dendrogram for the classification of coal and coaly shale samples by location (sample code\*)  
 \*Sample code (e.g. EN\_1001\_10 = Location\_Borehole ID\_Sample\_no)

Cluster I comprises of coal from nine boreholes with pronounced detrital source with majority of the trace elements which could be indicative of the quality of coal in these localities. Cluster II is made up of coal from three boreholes, containing trace elements with a high positive loading of B and negative loading of S, highlighting strong organic associations.

**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 SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> 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.

**ACKNOWLEDGEMENTS**

The authors thank the Geological Survey Agency of Nigeria, Kaduna, for providing core samples used in this research. The Activation Laboratories, Ontario, Canada are also gratefully acknowledged for the analysis of the entire samples.

**REFERENCES**

Benkhelil, J., 1989. The evolution of the Cretaceous Benue Trough. Nigeria. *Journal of African Earth Sciences*, 8: 251-282.

Burke, K.C., 1996. The African Plate. *South African Journal of Geology*, 99: 341-409.

Dai, S., Ren, D., Zhang, J. and Hou, X., 2003. Concentrations and origins of platinum group elements in Late Paleozoic coals of China. *International Journal of Coal Geology*, 55(1): 59-70.

Ewa, I.O.B., 2004. Data evaluation of trace elements determined in Nigerian coal using cluster procedures. *Applied Radiation and Isotopes*, 60(5): 751-758.

Ewa, I.O.B. and Adetunji, J., 1996. Determination of trace elements in Nigerian coal ash by Instrumental Neutron Activation Analysis. *J. of Environmental Science and Health, Part A*, 31(5): 1089-1101.

Finkelman, R.B., 1982. Modes of occurrence of trace elements and minerals in coal: an analytical approach. *Atomic and Nuclear Methods in Fossil Energy Research*. Plenum, New York, 141-149 pp.

Finkelman, R.B., 1995. Modes of occurrence of environmentally sensitive trace elements of coal. *Environmental aspects of trace elements of coal*. Kluwer Academic Publishers, The Netherlands, 24-50 pp.

Gürdal, G., 2008. Geochemistry of trace elements in Çan coal (Miocene), Çanakkale, Turkey. *International Journal of Coal Geology*, 74: 28-40.

Horner, T.C. and Krissek, L.A., 1992. Statistical analysis of geochemical patterns in fine-grained Permian clastics from the Beardmore Glacier region, Antarctica. *Recent Progress in Antarctic Earth Science*. TERRAPUB, Tokyo, Japan, 241-248 pp.

Karayigit, A.I., Spears, D.A. and Booth, C.A., 2000. Distribution of environmental sensitive trace elements in the Eocene Sorgun coals, Turkey. *International Journal of Coal Geology*, 42(4): 297-314.

Lu, X., Zeng, H., Xu, T. and Yan, R., 1995. Chemometric

- Whiteman (Editors), *African Geology*. University of Ibadan press, pp. 251-266.
- Ndiokwere, C.L., Guinn, V.P. and Burtner, D., 1983. Trace elemental composition of Nigerian coal measured by neutron activation analysis. *J. Radioanalytical and Nuclear Chemistry*, 79(1): 123-128.
- Olajire, A.A., Ameen, A.B., Abdul-Hammed, M. and Adekola, F.A., 2007. Occurrence and distribution of metals and porphyrins in Nigerian coal minerals. *Journal of Fuel Chemistry and Technology*, 35(6): 641-647.
- Orem, W.H. and Finkelman, R.B. (Editors), 2003. Coal formation and geochemistry. *Sediments, Diagenesis, and Sedimentary Rocks*, 7. Elsevier-Pergamon, Oxford, 191-222 pp.
- Petters, S.W., 1978. Stratigraphic evolution of the Benue Trough and its implication for Upper Cretaceous paleogeography.
- Pollock, S.M., Goodarzi, F. and Riediger, C.L., 2000. Mineralogical and elemental variation of coal from Alberta, Canada: an example from the No. 2 seam, Genesee Mine. *International Journal of Coal Geology*, 43(1-4): 259-286.
- Ren, D., Zhao, F., Wang, Y. and Yang, S., 1999. Distributions of minor and trace elements in Chinese coals. *International Journal of Coal Geology*, 40(2-3): 109-118.
- Reyment, R.A., 1965. In: *Aspects of the Geology of Nigeria*. University of Ibadan Press, Ibadan, 145 pp.
- Song, D., Qin, Y., Zhang, J., Wang, W. and Zheng, C., 2007. Concentration and distribution of trace elements in some coals from Northern China. *International Journal of Coal Geology*, 69(3): 179-191.
- Sonibare, O.O., Ehinola, O.A., Egashira, R. and Lim, K., 2005. An investigation into the thermal decomposition of Nigerian coal. *Journal of Applied Science*, 5(1): 104-107.
- Swaine, D.J., 1990. *Trace Elements in Coal*. Butterworths, London, 278 pp.
- Wright, J.B., Hastings, D.A., Jones, W.B. and Williams, H.R., 1985. *Geology and mineral resources of West Africa*. Allen and Unwin, London, 187 pp.

