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Geochemical and Mineralogical Significance of Trace Metals in Benue Trough Coal, Nigeria

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Abstract: In the present study, sub-bituminous coals from Ribadu, Okaba, Okpara, Orukpa, Ogboyoga and Lignite from Asagba, all from Benue Trough, Nigeria were analyzed by energy dispersive x-ray fluorescence spectrophotometer (EDXRF). Different concentrations of trace metals present in the coal samples were recorded and subsequently used to determine the origin, organic matter input, maturity and mineralogical importance of the coals. There is closeness between Chromium (Cr) and Nickel (Ni) content as well as V/Ni ratio for the coals suggesting that the organic matter is derived from terrestrial/marine and are of low maturity. Also, the low V/V+Ni ratios for all the coals suggest that they are deposited under oxic condition, which is in agreement with earlier work done on these coals by other workers. Therefore, these ratios compliment with other geochemical parameters can be a useful tool in geochemical studies. Preliminary assessments of the mineral contents of the coal samples reveal that there is possible occurrence of iron bearing minerals like pyrite, siderite and ankerite and titanium rich minerals; ilmenite and rutile in the studied area. This is due to high abundance of iron (Fe) and titanium (Ti) in the samples. Also the level of some metals such as nickel, iron, titanium and copper in these samples indicate that the ash residue of these coals after burning could be a very good source of the metals. However, the presence of some trace elements like copper (Cu) and nickel (Ni) that causes corrosion of the turbines and also poison catalyst, in the coals, necessitate incorporation of the removal procedures of these metals before refining stage.

Key words: Coal, benue-trough, EDXRF, sub-bituminous, trace metals

INTRODUCTION

Trace metals such as Ti, V, Cr, Mn, Fe, Ni, Cu and Zn in various forms can be found in coal. They can be of economic interest and useful for geochemical studies. Occurrence of trace metals in soil (Wang and Qin, 2006), crude oil (Nwachukwu *et al*., 1995; Oluwole *et al*., 1993), bitumen (Ipinmoroti and Aiyesanmi, 2001), shale (Ehinola and Abimbola, 2002; Ehinola *et al*., 2005) and coal (Querol *et al*., 1997; Dill and Wehner, 1999; Querol *et al*., 2001; Ewa, 2004; Zhang *et al*., 2004a; Dangyu *et al*., 2007) have been properly documented.

For at least the first half of the first half of the 21st century, coal will continue to be a very important energy sources required to sustain the standard of living in the United States and many other developed countries. In many developing countries such as China and India, coal will be relied upon as the primary source of energy needed to fuel industrialization and to improve the standard of living of these large and growing population (Finkelman *et al*., 2002).

There is renewed interest in the coal deposits in Nigeria by the Federal government. This is aimed at diversifying the economy that has been solely dependent on crude oil and its refined products. Nigeria has one of the largest coal deposits in Africa. Nigeria's coal reserves are large, over 2 billion metric tons of which 650 million tons are proven. If fully revitalized, the coal industry could fetch up to 5 billion naira in export earnings. This could be achieved by exploring the minerals associated

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with these coal deposits. Coal production is from the Cretaceous Anambra basin, which extends to Bekina in the northern part of the Basin in Benue state and to Okigwe in the south. The coal in this basin is sub-bituminous and occurs principally at two levels, the lower coal measures (Mamu formation) and the upper coal measures (Nsukka formation) (Akande *et al*., 1992).

Nigerian sub bituminous coal has a high calorific value (5,000-6,000 cal g^{-1} or 5500-6500 air dried), low ash and low sulfur contents, with good storage characteristic. Nigeria has the largest Lignite deposits in Africa with reserves of about 50 million tones.

The Nigerian lignite belt, of mid-Tertiary age extends from Oriu in the southeast, through Urnuezeala, Umuahia, Nnewi, Oba, in a 20 to 40 km- wide belt across the Niger, to Ogwashi- Asagba, Mgbiigliba and Adiase-Uti in Delta State.

Trace metals are of great importance in ascertaining the depositional environment and maturity of geological samples within a basin.

Nature and quality of trace metals in coal depends on its location and geological history therefore quantitative study of the metal content can give information concerning the origin, depositional environment, organic matter content and maturation of the coal (Killops and Killops, 1993, 2005). The proportionality of Vanadium to Nickel is strongly influenced by the source rock depositional environment (Lewan, 1984; Nwachukwu *et al*., 1995), therefore V/Ni ratio can be useful in ascertaining the depositional environment of coal. Vanadium and nickel metals enter into the porphyrin structure by chelation during diagnosis (Peter *et al*., 2005). Although, porphyrins do undergo some changes with increasing maturity, the amounts of these metals in porphyrin are generally relatively minor and do not affect the overall interpretation of Ni:V ratios (Killops and Killops, 2005). Under normal oxic conditions, nickel reacts more readily than vanadium with free base porphyrins. Therefore, V/V+Ni can be related to redox conditions in source rock depositional environment. Low V/V+Ni porphyrin ratios in marine Toarcian rocks reflect oxic-sub-oxic conditions, while high ratios reflect anoxic sedimentation (Moldowan *et al*., 1986; Killops and Killops, 2005). The decreasing V/V+Ni ratios are thought to reflect increasing toxicity (Peter *et al*., 2005).

With increasing use of coal, the growing impact on the environment from the Potentially Hazardous Trace Elements (PHTEs) becomes a great concern; the information about the concentration, distribution and occurrence of the PHTEs in coal is of great importance (Zhang *et al*., 2004a). However, the trace metals of interest in the present study have been classified as of moderate to minor concern to our environment (Zhang *et al*., 2004a). Therefore, there is need to explore the distribution of these metals in coal in other useful areas.

Generally, most trace elements in coal are associated with the mineral matter (Gentzis and Goodarzi, 1997); therefore their analysis in coal can be used as tool of discriminating element mineral association (Dameng *et al*., 2001). For instance, the concentration of Iron is mainly controlled by the abundance of pyrite; other iron-bearing minerals are siderite and ankerite (Dameng *et al*., 2001). The mode of occurrence of Titanium is mainly titanium oxide (rutile) (Zhang *et al*., 2004b) but other minerals (e.g., ilmenite) can be associated with its presence. Major minerals present in Late Permian coals of China are quartz, kaolinite, illite, pyrite, calcite, smectite and marcasite while the presence of kaolinite, illite, pyrite, smectite and marcasite dominate in Late Triassic coal. Their abundance being controlled by distribution of metals in these coals.

In the present study, trace metal contents of Nigerian coal was investigated by EDXRF and, subsequently used for geochemical studies and preliminary investigation of minerals present in Nigerian coal.

MATERIALS AND METHODS

The coal samples used were collected from the Nigerian Coal Corporation Enugu, Nigeria. The samples were selected from seven locations in the Benue Trough, Nigeria. These include sub-bituminous coal from Ribadu, Okaba, Okpara, Orukpa, Ogboyoga, Onyeama and lignite from Ogwashi-Asagba (Fig. 1). The coal samples were packed in sealed envelopes prior to analysis.

The coal samples were pulverized using agate mortar. The powdered samples were then prepared and pressed into thick pellets of 13 mm diameter in spec-caps with binder. The elemental analysis of the coal samples were performed using energy dispersive X-ray spectrometer Fluorescence [EDXRF] Link Analytical system Model XR300 50 KV- Fundamental Parameter Model equipped with a multichannel analyzer at the center for Energy Research, Obafemi Awolowo University, Ile-Ife, Nigeria. The spectrometer composed of a Siemens FKO-04 tube with Mo anode, a cristalloflex 710 H X-ray Generator, a Canberra series 7300 Si (Li) detector (of resolution 165 eV at 5.9 KeV), with Canberra Model 1510 Integrated Signal Processor and a Canberra S100 MCA card interfaced to a 486 IBM/PC. This equipment operates under Quantitative X-ray Analysis System (QXAS) software (IAEA, 1996), which includes facilities for data acquisition, spectrum analysis and interpretation and quantitative analysis. Each sample pellet was irradiated for 20 min at fixed tube

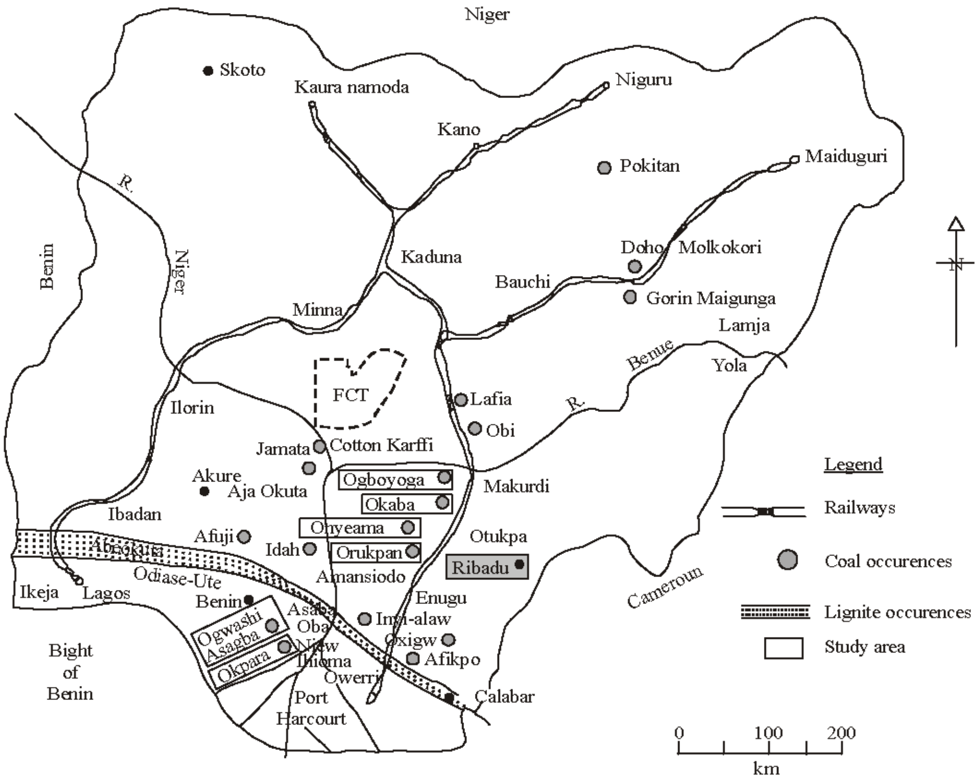

Fig. 1: Coal/Lignite occurrences in Nigeria (modified from Ehinola *et al*., 2002)

conditions of 30 KV and 10 mA. All data are the results of an average of three measurements on each sample.

RESULTS AND DISCUSSION

Geochemical studies: Distribution of elements in coal seams represents factors in geochemical environments during coal formation (Liu *et al*., 2001). Also reflects the changes of pH of coal-accumulating peat swamp environments and differences in floral populations of the swamps (i.e., factor of depositional environments (Liu *et al*., 2001; Song *et al*., 2007).

The distribution of metals, especially, Nickel (Ni) and Vanadium (V) in geological samples can provide information on depositional environments and maturity. Both Nickel and Vanadium appears to be strongly associated with asphaltene and ratio of Nickel to Vanadium appears not to be affected by post diagenetic processes (Killops and Killops, 1993, 2005).

The presence of the trace metals-Ti, V, Cr, Mn, Fe, Ni, Cu and Zn (Table 1) and its subsequent use as geochemical parameters are investigated. The moderately low vanadium contents of the coal (9.54-31.08 mg kg^{-1}) suggest a low mature and marine/terrestrial sourced coal. The value of V/Ni ranges from 0.2 to 1.4 (Table 2). The source rock depositional environment determines the proportionality of vanadium to Nickel. The closeness in the Cr and Ni contents as well as V/Ni ratios for all the coal samples suggest the same depositional environment V/V+Ni ratio can be related to redox condition in source rock and low ratio reflects oxicity while high ratio ($\geq$0.9) reflects anoxic condition in the depositional environment of coal (Peters *et al*., 2005; Killops and Killops, 2005). The low V/V+Ni ratio (0.2-0.6) shows that the coals are deposited under oxic condition. This is typical of coal depositional environment and also in agreement with earlier work done on these coals (Akande *et al*., 1992) using other geochemical parameters like organic petrography.

Mineralogical contents: Concentrations of the trace element present in each samples varies (Table 1). It can be shown from the results that the mineral content of Okaba coal is the highest.

The concentration of iron ranges from 829.99 to 6029.46 mg kg^{-1} with the average of 3034.97 mg kg^{-1}. Since iron is the most abundant metal in the coal samples, its high concentration indicates the presence of iron bearing minerals such as iron pyrite (FeS_2), siderinite and ankerinite (Liu *et al*., 2001). After iron, the next abundant

Table 1: Concentration of trace metals in Nigerian coal

Samples	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn
	mg kg^{-1}							
Ribadu	151.19±3.60	9.54±2.70	ND	34.97±4.01	829.99±8.680	42.06±4.48	64.83±2.86	65.43±2.31
Okaba	474.08±5.12	31.08±5.23	10.39±2.04	97.24±3.40	4142.21±35.80	22.92±4.58	83.51±3.16	37.34±2.78
Okpara	157.28±3.49	12.24±2.62	9.81±2.85	12.11±2.87	966.02±8.460	18.26±5.45	60.33±3.10	28.20±2.54
Orukpa	225.23±6.85	11.59±3.49	9.60±2.32	206.74±6.41	6029.46±54.40	26.63±5.32	64.27±3.28	29.74±2.40
Ogboyoga	299.24±6.46	15.20±3.97	7.05±1.40	169.57±5.28	4480.36±33.91	23.04±4.60	82.52±4.14	37.25±2.76
Ogwashi-Asagba	80.05±6.24	20.66±3.10	13.53±2.61	28.82±3.56	2403.45±15.90	18.36±5.79	64.37±3.15	60.63±2.45
Onyeama	247.78±5.55	14.73±2.78	9.01±1.80	14.35±3.10	2393.30±22.35	24.61±5.92	83.20±4.65	32.77±2.41
Mean	233.55	16.43	8.48	80.54	3034.97	25.13	71.86	41.62
Range	80.05-474.09	9.54-31.08	0.00-13.53	12.11-206.74	829.99-6029.46	18.26-42.06	60.33-83.51	28.20-65.43
CV	0.54	0.49	0.28	0.99	0.63	0.32	0.2	0.45

CV = Coefficient of Variation

Table 2: Trace metals ratios in Nigerian coal

Samples	Ni (mg kg^{-1})	V (mg kg^{-1})	V/Ni	V/(V+Ni)
Ribadu	42.06	9.54	0.2	0.2
Okaba	22.92	31.08	1.4	0.6
Okpara	18.26	12.24	0.7	0.4
Orukpa	26.63	11.59	0.4	0.3
Ogboyoga	23.04	15.20	0.7	0.4
Ogwashi-Azagba	18.36	20.66	1.1	0.5
Onyeama	24.61	14.73	0.6	0.4

Table 3: Trace element concentrations in selected individual coal samples from Beypazari Basin, Turkey with worldwide averages (modified from Querol *et al.*, 1997)

Elements	Btv	Btv7	Btv10	World-wide mean values (Max) mg kg^{-1}	World–wide mean values (Min) mg kg^{-1}
		(mg kg^{-1})			
Cr	30	25	13	30	10
Cu	12	2	2	35	15
Mn	4	35	251	90	30
Ni	90	54	51	20	15
V	7	25	3	100	2
Zn	33	9	6	60	10

abundant metal is titanium with its concentration ranging from 80.05 to 474.09 mg kg^{-1} with an average of 233.55 mg kg^{-1}. The highest concentration of Titanium is recorded in Okaba coal sample.

The waste during oil extraction from Okaba coal sample could be considered as a source of Titanium. Also abundance of this metal with the co-existence of a high concentration of Iron indicates the occurrence of the Titanium rich minerals e.g., ilmenite, $FeTiO_3$ (Ipinmoroti and Ayesanmi, 2001) and Rutile, TiO_2 (Zhang *et al.*, 2004b). Vanadium's concentration ranges from 9.54 to 20.66 mg kg^{-1} with an average of 16.43 mg kg^{-1} (Table 1). Chromium has its concentration ranging from 7.05 to 13.53 mg kg^{-1} with an average of 9.90 mg kg^{-1} but chromium is below detection limit in Ribadu coal. The concentration of manganese ranges between 12.11 to 206.74 mg kg^{-1} with the average of 80.54 mg kg^{-1} and the highest concentration was found in Orukpa coal while the lowest concentration was recorded in Okpara coal. Concentration of nickel ranges from 18.26 to 42.07 mg kg^{-1} with the average of 27.13 mg kg^{-1}; highest concentration of nickel was recorded in Ribadu coal and the least in Okpara coal. The concentration of zinc ranges between 28.20 to 65.43 mg kg^{-1} with the average of 41.62 mg kg^{-1} (Table 2). Meanwhile the values of V, Cr, Mn and Zn are within the worldwide mean value. With the level of nickel, the ash from the coal residue with vast deposit of coal beds could be considered as a good source of nickel (Ipinmoroti and Aiyesanmi, 2001). Coppers concentration ranges from 64.27 to 83.51 mg kg^{-1} with the average of 71.86 mg kg^{-1} (Table 3). High abundance of copper (>40 mg kg^{-1}) (Ehinola and Abimbola, 2002) in this coal may suggest viable deposit of this metal close to the coal beds. The abundance of metals like nickel, copper, titanium and iron with their high concentrations indicates that these coal samples coupled with their coal beds could be a good source of these metals.

CONCLUSIONS

The study of trace element content needs to be considered and studied for the interest of the geochemical studies and the economic interest.

It is interesting to know that from our studies, the level of trace metals in Nigerian coal shows that all the coal samples are low matured and marine/terrestrial sourced coal. Also, all the coal samples have common origin deposited under oxic condition. Trace metal distributions compliment with other geochemical parameters (e.g., biomarker ratios, organic petrography) can be a viable tool in geochemical studies.

From the mineralogy point of view, it was discovered that the concentration of iron and titanium are the most abundant metals in all the coal sample which indicate that the possibility of occurrence of iron bearing minerals like pyrite, siderite, ankerite and titanium rich mineral; illmenite and rutile in the studied area. Although the presence of these minerals still need confirmation by crystallographic analysis (SEM-EDX and XRD) in our subsequent studies.

It was also revealed from this work that coal beds are very rich source of some metals such as nickel, iron, titanium and copper. These indicate that the ash residue of this coal after burning could be a very good source of these metals and they can also be used to manufacture some other chemicals.

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