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An Assessment of the Major Elemental Composition and Concentration in Limestones Samples from Yandev and Odukpani Areas of Nigeria Using Nuclear Techniques

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ABSTRACT
Limestone samples from Yandev and Odukpani limestone deposits in Nigeria were subjected to elemental analysis by Proton Induced X-ray Emission (PIXE) technique with the aim of broadening any database information on their elemental composition and concentration and accessing the extent of their environmental friendliness. The analysis was carried out with a 1.7 MV Tandem accelerator at the Center for Energy Research and Development (CERD), Ile Ife, Nigeria. In house calibration results involving the analysis of a NIST standard NBS 278 sample was used for quality assurance and control. Altogether fifteen different elements were observed in both locations. Fourteen elements that include Ca, Si, Al, Fe, K, Mg, Ti, S, Rb, P, Mn, Sr, Cl and Zn were observed in the Yandev deposit while ten elements including Ca, Si, Al, Fe, Na, Mg, K, Ti, Mn and Sr were observed in the Odukpani deposit. Some harmful rare earth elements (Ti, S, Rb, P, Mn, Cl, Sr and Zn) were observed only in the Yandev samples (except for Sr and Mn). These observations suggest that all particulate emissions and wastes from the Yandev deposit should be closely monitored to reduce its effects on the environment and health. The average Ca/Si ratio of the Yandev deposit is 4.32 while that of Odukpani deposit is 8.64. The observed low Ca/Si ratio in Yandev Limestone was attributed to the comparatively high Si content of the limestones. Thus the Odukpani limestone deposit appears to be more friendly to health and the environment.

Key words: Odukpani, Yandev, limestone, PIXE, elemental composition, environment

INTRODUCTION
The Federal Government of Nigeria has recently formulated policies that have encouraged investments in the solid mineral sector in order to reduce her over dependence on revenues from oil and gas. Nigeria is endowed with several solid mineral resources which are alternative sources of revenue. Such revenues can only be harnessed after the mineral resource has passed through exploration, mining and processing stages. Each of these stages has both health and environmental implications (Aigbedion and Iyayi, 2007).

The solid mineral deposits that investors are jostling for in the country have been listed by Adetunji *et al.* (2005) to include coal, columbite, cassiterite, marble, limestone, clay, bitumen and tantalite. Others include granite, lead, zinc, gold and barite. The history of mining of some of these minerals dates back to the colonial days and they have generated substantial revenue to the government and contributed immensely to the socioeconomic developments of their host communities (Adetunji *et al*., 2005). These desirable effects are overshadowed by the adverse effects that have been listed by Olaleye and Oluyemi (2010), Aigbedion and Iyayi (2007), Mokobia *et al*. (2006) and Mokobia and Balogun (2004) to include ecological disturbance, destruction of natural flora and fauna, pollution of air, land and water, instability of soil and rock masses, landscape degradation and radiation hazards. A plan of action to ameliorate some of these effects can only be effective if there is information on the elemental composition of the mineral deposit that is being mined. Such information can be generated by highly technical procedures. Amodu (2010) have listed some of these techniques to include the Atomic Absorption Spectrometer (AAS), X-Ray Fluorescence (XRF), Particle Induced Gamma Ray Emission (PIGE), Instrumental Neutron Activation Analysis (INAA) and Particle Induced X-ray Emission (PIXE).

Limestones occur extensively in all the sedimentary basins in Nigeria and are being mined daily for various purposes. Many investors are mindless of the environmental consequences of their mining activities so long as it does not disrupt production at their factories. This study is an attempt to generate information on the elemental composition of some limestone samples that will be useful in planning some remedial measures to cushion some of the effects of mining limestone in Nigeria. Some limestone samples were collected from Yandev limestone deposit near Gboko in Benue State where active mining has been going on and the other samples were collected from Odukpani limestone deposit in Cross River State (Fig. 1).

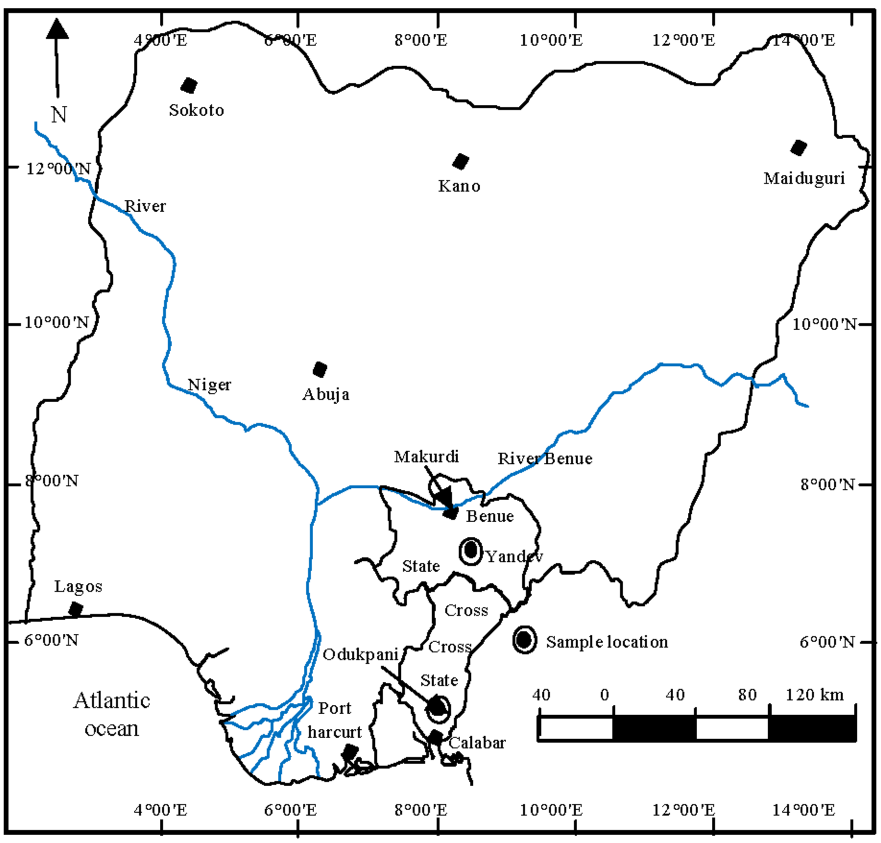

Fig. 1: Political map of Nigeria showing sample locations

This research is our contribution to the understanding of the elemental composition of the Yandev and Odukpani Limestone deposits and also to broadening of the existing database. It is our hope relevant government agencies and investors will find any information generated in this study useful in planning and formulating policies that will ameliorate the effects of mining limestones from these two deposits.

MATERIALS AND METHODS

Sample collection and preparation: Three representative samples were collected from Yandev Limestone deposit near Gboko in Benue State of Nigeria between February and June, 2008. Pseudo names (S for the sample from the southern side of the deposit, PQ for the sample from the northern end of the deposit and DE for samples from the eastern side of the deposit) were assigned to the samples for proper identification. The separation between the points in the field that each representative sample was collected was 100 m. The Odukpani Limestone samples were coded A, B and C samples and were collected at distances of about 50 m from each other since this deposit is not very extensive.

The samples were taken to the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile Ife in Nigeria for analysis. At CERD, the samples were broken into pieces and crushed into powdery form using a small porcelain mortar and piston. They were then made into pellets of about 500 mg and 13 mm diameter by using pellet making set which consists of a speck, cop, dice and hydraulic press (Obiajunwa *et al.*, 2002; Obiajunwa and Nwachukwu, 2000).

Pixe analysis: The PIXE analysis was carried out using proton beams produced by Ion Beam Analysis (IBA) facility of the 1.7 MeV Tandem accelerator located at the CERD, Nigeria. The PIXE system was calibrated using an in-house calibration system and the National Institute of Standards and Technology (NIST) geological standard NBS 278, Obsidian rock, was used for quality assurance and control of results (Obiajunwa and Nwachukwu, 2000).

The IBA facility used in this analysis consists of a 5SDH modeled NEC Tandem Pelletron accelerator complete with an end station made up of aluminum chamber of about 150 cm in diameter and 180 cm high. The samples were irradiated by a 4 mm diameter beam of protons with energy of 2.5 MeV and beam current of 0.2 nA for 900 sec. The chamber of the accelerator has four ports and a window. Port 2 that is inclined at 135° to the horizontal is used for PIXE detector. This detector is an ESL X 30-150 model of a Cambera Si (Li) detector (resolution 175 eV at 5.9 KeV), coupled to a Canberra Inspector-2000 Digital Signal Processor. Canberra Genie-3.1 software was used for acquisition of the PIXE data (Obiajunwa, 2001; Obiajunwa *et al.*, 2005; Alhassan *et al.*, 2010) while the Gupxwin computer code was used for fitting the experimentally generated PIXE spectrum prior to quantitative analysis (Campbell *et al.*, 2002). A funny filter placed between the detector and the samples cuts off unwanted signal frequencies. The analysis of the samples ended in September, 2009.

RESULTS AND DISCUSSION

The fitted spectrum and the experimentally derived continuous background shown in Fig. 2 are typical of any PIXE spectrum. According to Obiajunwa and Nwachukwu (2000) and Mokobia *et al.* (2006), the observed continuous background is an inherent property of all PIXE spectra. The Gupxwin code extracts peak intensities from the filtered signals and converts them to concentration using the H-value standardization method. The strength of the detector signals which are

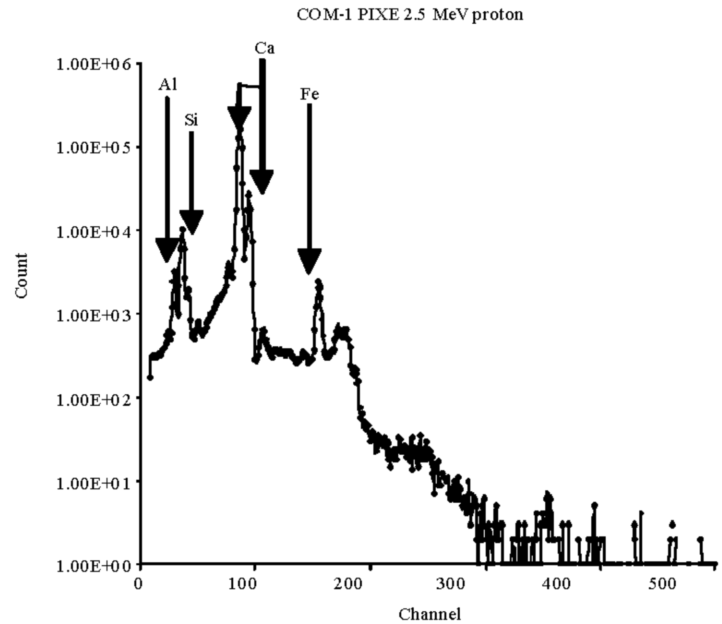

Fig. 2: A typical PIXE spectrum from the samples

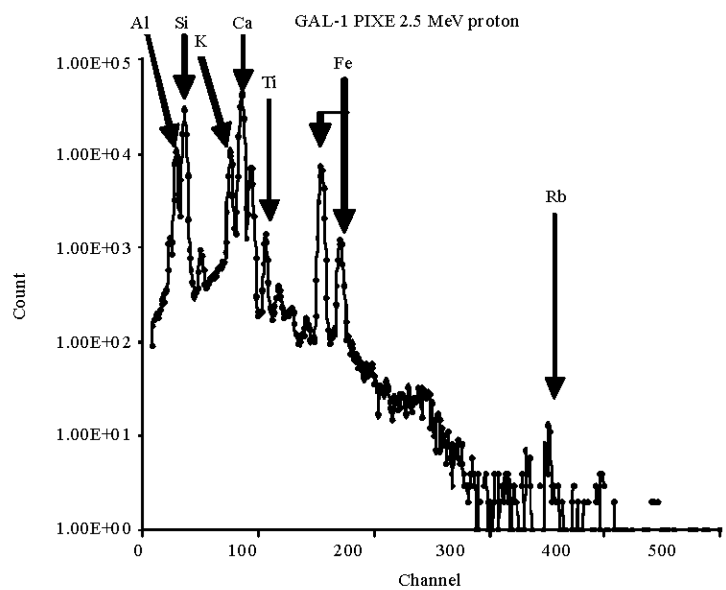

Fig. 3: A PIXE spectrum of S-bench sample from Yandev deposit

proportional to x-ray energies were processed and converted to digital form for storage in a multi channel analyser at the end of the measurements. Spectral stripping was performed to obtain a least fit to several peaks plus background.

Figure 3 is the PIXE spectrum of the S-bench sample which appears different from Fig. 2. The difference was suspected to be caused by the high clay contents in the samples. In these figures, the fitted spectrum and the evaluated continuous backgrounds are superimposed on the

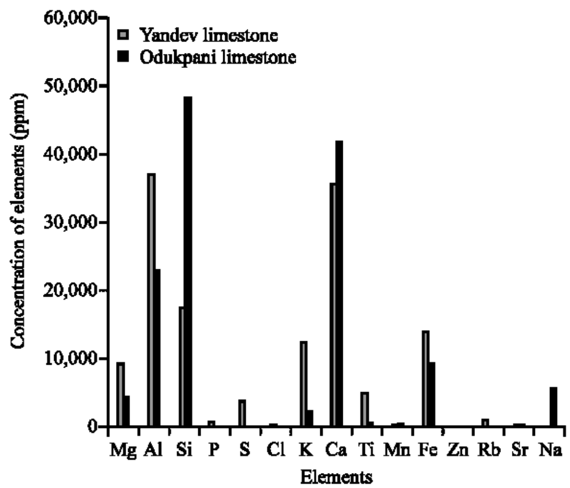

Fig. 4: A bar chart showing distribution of elements and their mean concentrations (10^2 ppm for Calcium only)

Table 1: Mean results from PIXE analysis of standard sample*

Elements	Certified values (ppm)	Concentration (ppm)	Standard error
Na	28,700.00	28,813.30	1,527.13
Al	60,290.00	60,373.20	507.13
Si	272,850.00	272,700.40	681.75
Cl	496.00	627.50	97.00
K	2,764.00	27,626.40	185.10
Ca	5,620.80	5,661.60	135.69
Ti	1,175.20	1,178.90	44.80
Mn	322.40	319.60	30.55
Fe	11,416.00	11,418.00	111.90
Zn	44.00	44.40	34.77
Rb	102.00	101.80	35.00
Sr	50.80	70.10	40.47
Zr	236.00	236.00	152.48
Ba	912.00	911.40	492.43
Ce	49.76	51.40	49.81

*The standard errors are due to counting statistics

experimental data. In regions below 10 KeV, it comes from secondary electron Bremsstralung and at higher energies it is due to incident proton Bremsstralung and also from Compton scattered gamma induced nuclear reactions (Read, 1970; Obiajunwa, 2001). Figure 4 is a bar chart showing the concentration of elements in sample from both locations.

The results of analysis of the NIST geological standard NBS 278 sample are shown in Table 1. These results are in good agreement with the certified values. The results of PIXE analysis of both the Yandev and Odukpani deposits are shown in Tables 2 and 3, respectively.

The results of the elemental analysis of the six samples are tabulated in Tables 2 and 3 for Yandev and Odukpani samples respectively. The average concentrations of all the elements at the two locations differ appreciably except for Mn and Sr (Fig. 4). Fourteen elements were detected in the Yandev sample while 10 elements were detected in the Odukpani sample. In order of

Table 2: Mean results from PIXE analysis of Yandev samples*

Observed elements	Concentration of element (ppm) in S-bench sample	Concentration of element (ppm) in PQ-bench sample	Concentration of element (ppm) in DE-bench sample	Mean concentration of elements (ppm)
Ca	141,073.00±409.11	446,274.10±490.90	477,963.80±525.76	35,5103.63±827.51
Si	211,458.50±740.10	11,449.90±267.93	23,706.70±312.93	82,205.03±847.03
Al	94,834.60±663.84	4,274.40±339.39	11,886.10±379.17	36,998.37±836.10
Fe	36,406.90±214.80	1,864.10±131.42	4,099.40±151.27	14,123.47±293.76
K	33,897.20±223.72	521.50±126.67	2,681.40±141.31	12,366.70±293.37
Mg	19,342.40±727.27	3,397.00±706.24	5,207.20±711.82	9,315.40±1238.70
Ti	5,069.30±92.26	**	**	5,069.30±92.26
S	3,846.30±161.16	**	**	3,846.30±161.16
Rb	156.20±44.08	1,864.10±131.42	**	1,010.15±138.62
P	699.70±289.19	**	**	699.70±289.19
Mn	353.40±50.54	633.90±108.14	386.30±109.40	457.87±161.92
Sr	362.90±93.48	**	409.40±75.73	386.15±120.34
Cl	278.20±125.13	**	**	278.20±125.13
Zn	92.60±50.87	**	**	92.60±50.87

*All errors are due to counting statistics. **Not detected

Table 3: Mean results from PIXE analysis of Odukpani samples*

Observed elements	Concentration of element (ppm) in A sample	Concentration of element (ppm) in B-bench sample	Concentration of element (ppm) in C-bench sample	Mean concentration of elements (ppm)
Ca	412,209.30±535.87	366,997.20±440.40	472,801.90±567.36	417,336.13±896.11
Si	73,704.60±456.97	42,540.00±314.80	28,572.20±328.58	48,272.27±644.89
Al	31,236.90 ±459.18	21,166.10±353.47	16,941.50±401.51	23,114.83±704.98
Fe	13,531.90±194.86	7907.10±149.44	6,653.90±166.35	9,364.30±296.61
Na	**	**	5,574.60±2654.07	5,574.60±2,654.07
Mg	5,015.70±694.17	**	3,953.60±712.04	4,484.65±994.42
K	3,859.00±153.59	1,934.50±123.61	1,286.70±141.41	2,360.07±242.62
Ti	1,477.90±141.44	421.90±106.95	428.3±130.93	776.03±220.42
Mn	500.90±109.30	311.40±94.70	931.40±110.56	581.23±182.04
Sr	162.50±78.21	408.70±93.80	365.20±88.93	312.13±151.08

*All errors are due to counting statistics and **Not detected

concentration, the elements detected in the Yandev sample were Ca, Si, Al, Fe, K, Mg, Ti, S, Rb, P, Mn, Sr, Cl and Zn while the ten elements observed in the Odukpani deposit were Ca, Si, Al, Fe, Na, Mg, K, Ti, Mn and Sr. These results show that the elements Ca, Si, Al and Fe are preferentially enriched. The high concentration of Ca in the two deposits suggests that the limestones are suitable for cement production (Adejumo *et al*., 1994; Olaleye and Oluyemi, 2010). Cakir *et al*. (2009) adopted similar analytical technique to analyse gold lira. Some elements that are harmful to health and the environment like Pb were not detected in any of the deposits but others including Ti, S, Rb, P, Cl and Zn were detected in the Yandev deposit only. Sr and Mn were observed in both deposits. This is not healthy because some rare earth elements like Zn though are essential for good health and development, are also dangerous to health and the environment if their concentration exceeds some limit (Hambidge *et al*., 1987; Wang *et al*., 1985; Adejumo *et al*., 1994). According to Akeredolu *et al*. (1994), Adejumo *et al*. (1994) and Olaleye and Oluyemi (2010), in the neighbourhood of cement plants, concentration of Ca in the air decreases exponentially with increasing distance from the plant while the toxic elements are usually enriched. Olaleye and Oluyemi (2010) pointed out that the extent of contamination depends on location and distances from the cement factory as well as the wind direction. Particulate emission from any industry mining these limestones must be closely monitored by all agencies concerned.

The average concentration of Si at the Yandev deposit was almost twice the observed concentration of Si in the Odukpani deposit. The high Si content of the Yandev deposit was suspected to be due to the high clay contents of the samples (Audu, 2009). Clay consists of finely divided rock materials whose mineral composition comprises various silicates mainly of Aluminum and Magnesium (Uvarov *et al.*, 1979). This observation corroborates with the observed high concentration of Si, Al and Mg in that sample. The average Ca/Si ratio for the Yandev samples is 4.32 while that of Odukpani deposit is 8.65. The high Silicon content observed in the S-bench sample from the Yandev sample is responsible for the low Ca/Si ratio.

CONCLUSION

The elemental composition of Yandev and Odukpani limestone deposits has been determined using the PIXE technique. Accuracy and quality assurance was controlled by the results obtained from the analysis of the 'NBS 278' standard sample. Altogether fifteen elements were detected from both samples. Fourteen elements including Ca, Si, Al, Fe, K, Mg, Ti, S, Rb, P, Mn, Sr, Cl and Zn and ten elements (Ca, Si, Al, Fe, Na, Mg, K, Ti, Mn and Sr) were observed in the Odukpani deposit. Na was not observed in the Yandev deposit. Some harmful rare earth elements (Ti, S, Rb, P, Mn, Sr, Cl and Zn) were observed only in the Yandev samples (except for Sr and Mn) where mining is ongoing. The Odukpani limestone is a more enriched limestone deposits with less concentration of harmful elements. Thus all wastes and particulate emissions from industries mining the limestones (Yandev deposit in particular) should be closely monitored to reduce their adverse effects on health and the environment. The Calcium–Silicon ratio is higher at the Odukpani deposit than the Yandev deposit as a result of the high silicon content of the Yandev deposit.

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