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Elemental Composition of the Phosphorites of the Ameki Formation around Bende-Ameke Area, Southeastern Nigeria: Potential for Environmental Pollution

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ABSTRACT

Geochemical analysis was carried out on the phosphorites of the Ameki Formation using XRF and INAA methods. This was done for the purpose of evaluation of the elemental composition of the phosphorites, determination of the elemental enrichments and their potential for environmental pollution. The elemental compositions of the phosphorites in the order of decreasing concentration is stated as; Ca > P > Fe > F > Ti > Si > Al > Mg > K > Ba > Na > Cl > Mn and S whereas Cd, Ba, Pb, Cu, Cr, Zn, U, V, Se and Hg occur in trace amounts. The concentrations of Ca, P, Fe, Mg, F, Cl, Ti and Ba exceed the world average shale values, thus, suggest enrichment whereas Na, K, Mn, Al, S and Si are depleted. Enrichment with Pb, U and Se were also indicated in some samples. The calculated Pollution Index (PI) indicated tendency of the surrounding environments (water and soil) to be polluted with Mg, P, F, Ca, U, Se, Fe, Ti, Cl, Ba and Pb due to weathering and quarrying of the rock. Geochemical analysis is recommended for the nearby soils and streams/river sediments and physicochemical analysis for surface and groundwater to determine their extent of pollution by these elements especially the toxic ones.

Key words: Elemental, geochemical, phosphorites, ameki, environment, pollution

INTRODUCTION

Phosphorites are mineralized rock. Studies on its geochemistry (e.g., in South Africa[1-3], North America[4], South America[5], West Africa[6-7] and Asia[8-9]) have shown them to have reasonable concentrations of elements such as metals and halogens. Nriagu[10] attributed mankind (anthropogenic sources) as the key element in the cycle of most of the trace metals. Mining is noted as one of the anthropogenic activities that introduces heavy metals into the environment[11]. Leaching of heavy metals from mineralized rocks[12] or leaching of the potentially toxic ones such as Cu, Pb and Zn from weathered rocks at closed mine sites[13] is a serious environmental problem because the mobilized toxic metals can cause soil and groundwater pollution. Raja *et al.*[14], noted heavy metal concentration in phosphate rock as well as the increase in environmental pollution with this heavy metals at the proximity of the mining area. Toxic metals and radioactive elements of significant human health problems such as Hg, Pb, As, U, Cd, Th and Rd are associated with phosphate mining[15]. Assessment of the fluoride distribution in different areas around the phosphorite mining carried out by Tanouayi *et al.*[16] shows that high level of fluoride can cause illness among people living close to the mining and processing sites. Nriagu[10] in their review on the environmental impact of phosphate mining and processing, emphasized on phosphate potential effects on water pollution, air pollution and human health. The impacts of active mining on the distribution of heavy metals in soils by Oyebamiji *et al.*[17] also indicated mining activities to have adverse effect on the soils. Heavy metals on soils in turn affects plants[18].

Flouride pollution of the air, surface and groundwater, soil and vegetables around phosphorite mining and processing sites as well as their environmental impacts are documented in literature (e.g., Toler[19], Ashley and Burley[20] and Carmargo[21]).

The Ameki Formation and its lateral equivalents (the Nanka and the Nsugbe Formations) are the outcropping lithostratigraphic units of the Niger Delta. Agbada Formation is noted as their subsurface equivalent[22-24]. The Ogwashi Asaba Formations conformably overlies the Ameki Formation (Table 1).

Lithologically, Ameki Formation consists of sandstone, claystone, shale, siltstone, thin bands of limestone[25], phosphate[26] and francolites[27]. The argillaceous sandstone member exposed along Umuahia-Bende road has been described as being highly distinctive in its micaceous and gypsiferous contents with chunks of amber, pockets of lignite and calcareous phosphatic nodules and bone beds. Carbonaceous and plant fragments are also common[24].

Studies have been carried out on the geochemistry of the phosphate rocks of the Ameki Formation which was employed in the delineation of its environment of deposition[26,27]. The mode of formation of the phosphorites was discussed by Onuigbo *et al.*[27].

The phosphorites of the Ameki Formation has since been exposed to weathering and erosion due to road construction and quarrying activities and the pollution potential of these exposed phosphorites to the surrounding environments (water and soil) to the best of our knowledge has not been evaluated. This paper was aimed at the evaluation of the elemental composition of the phosphorites and determination of the degree of enrichments of various elements especially heavy metals and halogen as well as their potentials for environmental pollution.

Tectonics and geologic setting: Niger Delta Basin is a Tertiary sedimentary basin in the southern part of Nigeria. Its origin is associated with the break-up of Gondwana Supercontinent and installation of the Benue Trough as a rift basin within the West and Central African Rift System[28-32]. The event which took place during the Jurassic, later folding and uplift of the sediments of the Benue Trough by Santonian Thermotectonic events led to simultaneous subsidence of the Anambra Basin and Afikpo sub-basin in the southern Benue Trough[33,34,28,30]. The Anambra Basin was filled between late Campanian and Danian, after which further subsidence during the Paleocene shifted the depositional axis to the Niger Delta. Vertical stacking of the Benue Trough, Anambra and the Niger Delta Basins in the southern reaches (Table 1) does not entail that they are not separate basins[24].

Deposition began in the Niger Delta during early Paleocene with marine sediments (Imo Formation and its subsurface equivalent; the Akata Shale) which constitute the basal lithostratigraphic unit of the basin. The formation is successively and conformably overlain by the Ameki Group (the Ameki, Nanka and Nsugbe Formations), the Ogwashi Asaba Formation and the Benin Formation[33-35]. Ameki Formation was deposited north of the Niger Delta and south of the Anambra Basin. The geologic map of the study area is shown in Fig. 1.

Table 1: Stratigraphic succession in the southern Benue Trough, Anambra Basin and Niger Delta([36,35,22,33,37,24])

Time scale			Sedimentary units				
Cenozoic	Quaternary		Niger delta	Benin formation			
	Plicoene						
	Micoene						
	Oligocene			Ogwashi-asaba formation			
	Eocene			Nanka formation	Ameki formation		
	Paleocene	Thanetian		Imo formation			
		Danian					
Late cretaceous	Maastrichtian		Anambra basin	Nsukka formation			
				Ajali formation			
				Mamu formation			
	Campanian			Nkporo Fm	Enugu Fm	Afikpo Sst	Otobi Sst
Early cretaceous	Santonian		Southern benue trough	Unconformity			
	Coniacian			Awgu formation			
	Turonian			Ezeaku group			
	Cenomanian			Mfamosing limestone			
	Albian			Abakaliki formation			
	Aptian			Awi formation			
	Preaptian			?	?	?	?
Precam brian				Basement complex			

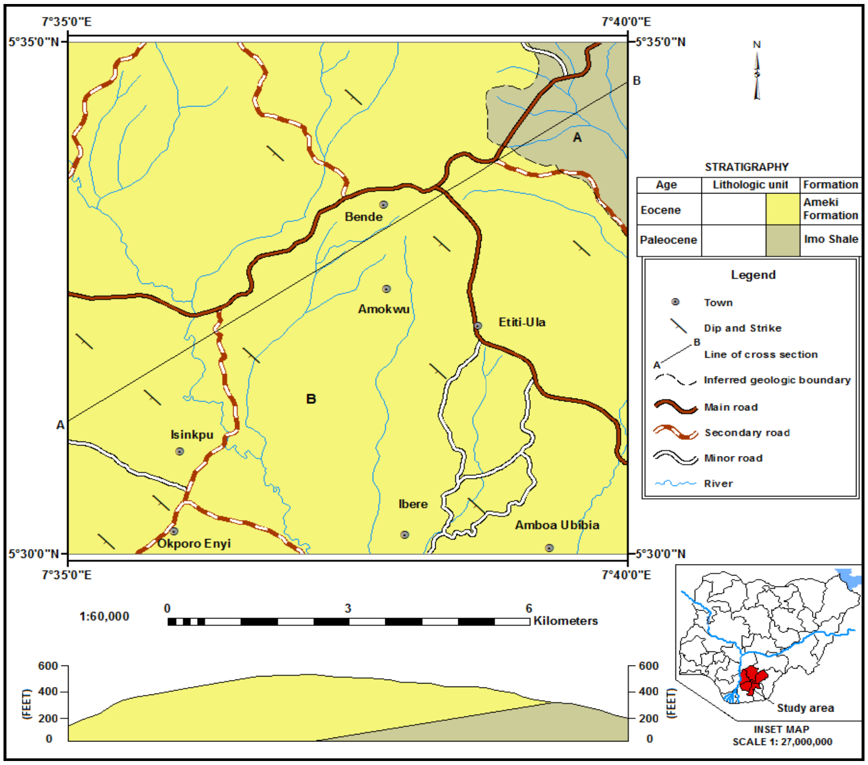

Fig. 1: Geologic map of the study area

MATERIALS AND METHODS

Ten representative samples of the phosphorites consisting of nodules, pellets, shale and siltstones were carefully collected with the aid of a geologic hammer from the outcrop sections of the Ameki Formation at Bende-Ameke in southeastern Nigeria. The samples were collected in nylon bags, well labelled and properly handled to avoid mixed up.

Standard X-Ray Fluorescence Spectrometry (XRF) technique was employed in the analysis to determine the elemental composition of the rocks. Each of the dried samples was crushed to powdered form (200 mesh size) using an agate mortar. The compositions of the alkali and alkali earth and heavy metals such as Zn, Cu, V, U and Cr were determined by X-Ray Fluorescence (XRF) in fused $LiBO_2/Li_2B_4O_7$ (lithium metaborate/lithium tetraborate) disc using a Siemens SRS-3000 wavelength-dispersive X-Ray Fluorescence Spectrometer with Rh-anode X-Ray tube as a radiation source. Other heavy metals were checked for, using Instrumental Neutron Activation Analysis (INAA).

Elemental compositions of the phosphorites were deduced from their oxides by applying the online conversion factor method stated as Eq. 1. The conversion factors for the elemental oxides recovered from this work are shown in Table 2.

Table 2: Conversion factors for the metallic oxides

Oxides	Conversion factor	Oxides	Conversion factor
Al_2O_3	0.529251	MgO	0.603036
Fe_2O_3	0.699433	MnO	0.774457
CaO_3	0.714701	Na_2O	0.741857
K_2O	0.830147	SiO_2	0.467439
BaO	0.895660	P_2O_5	0.436421

$$\text{Elemental percent} = \text{Oxide percent} \times \text{Conversion factor} \qquad (1)$$

The Pollution Index (PI) for each of the elements was estimated using the method of Yang *et al.*[38] and given as:

$$PI = C_i/S_i \qquad (2)$$

where, C_i is the measured concentration of each metal of the study and S_i is the background value. The world average shale value[39] was taken as the geochemical background value (Table 3). Based on Yang *et al.*[38], PI is classified as follows; PI < 1, indicates non- pollution; 1 < PI < 2, low level of pollution; 2 ≤ PI < 3, moderate level of pollution; 3 < PI ≤ 5, strong level of pollution whereas PI > 5 suggests strong level of pollution. This standard was set for water and soil pollution. The reasoning behind using the Pollution Index in this work was that high values of PI far above the limit which has been specified to pose a threat when found in an environment (water and soil), may be a pointer to rock potential for environmental pollution.

RESULTS AND DISCUSSION

The concentrations of the various elements in the phosphorites and world average shale values for the elements are shown in Table 3. In the order of decreasing concentrations, the elemental composition of the phosphorites can be stated as; Ca > P > Fe > F > Ti > Si > Al > Mg > K > Ba > Na > Cl > Mn and S. However, Cd, Pb, Cu, Cr, Zn, U, V, Se and Hg occur in trace amounts.

Comparison of the concentrations of the elements in the phosphorites with the world average shale values shows that Ca, P, Fe, Mg, F, Cl, Ti and Ba exceed their values in the world average shale. This suggests very high to high enrichment of the phosphorites with these elements. However, the concentrations of Na, K, Mn, Al, S and Si are below the world average shale values. For the trace elements, Pb, U and Se indicated enrichment in some samples and depletion in others whereas Cu, Cr, Zn, V and Hg are depleted.

Pollution Index (PI): Further evaluation of the potential of the phosphorites for environmental pollution using the pollution index indicated very high values for Mg and P. These elements are classed as elements with very strong potentials. F with high value is grouped as strong potential element whereas moderate potentials are assigned to Ca, U and Se. Elements such as Fe, Ti, Cl, Pb and Ba are classified as having low potentials while others have no potentials for environmental pollution (Table 4).

The result of elemental enrichment in the phosphorites correlates with that of pollution index. This indicates that elements with high enrichment in the mineralized rock have strong potential for environmental pollution whereas the depleted ones have no potential.

The average concentrations of Cr, Pb, Hg, V and Cd in this work is compared with their average values in the phosphate deposits around the world documented in Kongshaug *et al.*[40]. Apart from South Africa, the average concentration of Pb in Ameki phosphorites is higher than that obtainable in phosphate rocks of USA, Morocco, North Africa and Middle East Africa, but average concentration of the other trace elements are lower in Ameki phosphorites. The average U concentration in Ameki phosphate is comparable with that of USA and Algeria[41,42].

Table 3: Ranges of elemental composition and geochemical abundance index of the phosphate rocks

S/N	Element	World average shale value (ppm)	Elemental concentration (ppm)	Average (ppm)
1	Calcium (Ca)	22,100	350,203.0-400,233	375,230
2	Phosphorus (P)	700	19,639-148,383	84,120
3	Iron (Fe)	47,200	42,700.0-113,600.0	78,200
4	Magnessium (Mg)	1.5	5,729.0-12,362.0	9,049
5	Sodium (Na)	9600	964.0-1,187.0	1,082
6	Potassium (K)	26,600	2,573.0-5,479.0	4,029
7	Manganese (Mn)	850	155.0-620.0	390
8	Fluorine (F)	740	23000-48000	35,510
9	Sulfur (S)	2400	100-400	254
10	Aluminum (Al)	80,000	8,468.0-20,111.0	14,288
11	Chlorine (Cl)	180	200-600	410
12	Titanium (Ti)	4600	10,000.0-30,000.0	20,015
13	Silicon (Si)	73000	14,023.0-25,709.0	19,868
14	Barium (Ba)	580	1,074-1,254	1,167
15	Lead (Pb)	20	2.0-38.0	22
16	Copper (Cu)	45	2.0-10.0	6.4
17	Chromium (Cr)	90	Nil-60.0	31
18	Zinc (Zn)	95	3.0-5.0	4.2
19	Uranium (U)	3.5	Nil-50.0	27
20	Vanadium (V)	130	Nil-30.0	16.3
21	Selenium (Se)	0.6	Nil-5.0	2.4
22	Cadmium (Cd)	-	Nil-2.6	1.5
23	Mercury (Hg)	0.4	Nil-0.1	0.08

Table 4: Evaluation of the potentials of the elements for environmental pollution

S/N	Element	Pollution Index (PI)	Pollution potential
1	Ca	15.85-18.11	Moderate potential
2	P	28.06-211.98	Very strong potential
3	Fe	0.90-2.41	Low potential
4	Mg	3819.33-8241.33	Very strong potential
5	Na	0.10-0.12	No potential
6	K	0.10-0.21	No potential
7	Mn	0.18-0.73	No potential
8	F	31.08-64.86	Strong potential
9	S	0.04-0.17	No potential
10	Al	0.11-0.25	No potential
11	Cl	1.11-3.33	Low potential
12	Ti	2.17-6.52	Low potential
13	Si	0.19-0.35	No potential
14	Ba	1.85-2.16	Low potential
15	Pb	0.10-1.90	Low potential
16	Cu	0.04-0.22	No potential
17	Cr	0.0-0.67	No potential
18	Zn	0.03-0.05	No potential
19	U	0.0-14.29	Moderate potential
20	V	0.0-0.23	No potential
21	Se	0.0-8.33	Moderate potential
22	Hg	0.0-0.25	No potential

Tanouayi *et al.*[16] analyzed the fluoride in phosphate rocks of Togo which yielded an average concentration of 2.24%. They however, evaluated the impact of this fluoride on the surrounding environment (groundwater and soils) and noted a reasonable enrichment of the element in the groundwater and contamination of soils around the processing plant. Ameki phosphorites with 35,510 ppm (3.55%) fluoride had potential to affect its surrounding with the element.

The degree of toxicity of Ca, Fe and Mg with high enrichments in the Ameki phosphorites has been rated low to negligible[43]. Thus, they may not pose a threat to the surrounding environment. However, the degree of toxicity of F, Pb and Se which are also enriched in the phosphorites has been rated high whereas U and Ba are rated moderate[43,44]. Enrichment of these elements in the environment is detrital to health. Recent findings have also shown that Ti may cause harmful reactions in humans[45].

CONCLUSION

The elemental composition of the phosphorites of the Ameki Formation studied indicated an enrichment with elements such as Ca, P, Fe, Mg, F, Cl, Ti, Ba, U, Se and Pb and depletion of Na, K, Mn, Al, S, Si, Cu, Cr, Zn, V and Hg. Elements such as Pb, Se, F, U and Ba which are enriched in the phosphorites are toxic and can be a threat to the surrounding environments.

Geochemical analysis is recommended for the nearby soils and streams/river sediments and physicochemical analysis for surface and groundwater.

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