

Major Oxides and Trace Elements Composition of Phosphate Bearing Sedimentary Rocks from Sokoto, Northwest Nigeria

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Abstract Major and trace elements composition of phosphate rocks from phosphate bearing areas of Sokoto basin north-western Nigeria were investigated using PANalytical Minipal4 PW4025/45B energy dispersive x-ray fluorescence spectrometer (EDXRF). The results indicated that CaO, P₂O₅ and SiO₂ with mean concentration values ranging from 45.1±1.5 to 51.3±1.9 %, 19.9±1.0 to 21.6±2.2 % and 5.0±0.7 to 7.6±1.7 % respectively, are the most abundant species in Sokoto phosphate rocks (SPRs). Average concentrations of alkali metals were found to be less than 1wt % showing that very little salt will be added to agricultural soils via direct application of SPRs. The low concentration values recorded for alkali metals confirms the effectiveness of SPRs as good source of soil phosphorus. The estimated mean reactivity values varies from 2.2 to 2.4. These values underscore the suitability of SPRs as good raw material for fertilizer production. Cr, V, Cu and other studied trace elements were found to be enriched in the studied samples. Hence, direct application of SPRs can compete favourably with the conventional chemical fertilizers in enhancing the availability of soil nutrients for plant growth.

Keywords: phosphate rock, major oxides, x-ray fluorescence, CaO/P₂O₅ ratio, Sokoto

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1. Introduction

Attention has been focused in recent years, on the growing interest in direct application of phosphate rock (PR) to agricultural soils for enhance food production by local farmers in Nigeria. Scarcity and high cost of chemical fertilizers, coupled with adverse environmental effects associated with their use, compelled Nigerian farmers to seek alternative means of enhancing the growth and yield performance of their farm products. The natural abundance and relatively low cost of exploitation of PR coupled with its inherent capacity and effectiveness in supplying soil Phosphorus (P) for plants growth [1,2], makes it a readily available alternative for enhanced crop yield. PR is a vital component of agricultural environment and constitutes an indispensable, non-renewable nutrient source for plant growth [3]. It contains accessory minerals that are vital to the improvement of soil chemical and physical characteristics. This naturally occurring mineral assemblage with high concentration of apatite {Ca₅(PO₄)₃[F, OH, and Cl]} [4,5], has found good application in the agricultural sector and industrial processes as good supplements for animal feeds [6]. It is also a basic raw material for the production of phosphate fertilizers [7,8,9,10,11]. Phosphate ores occur in the

natural environment either as fluorapatite mainly in metamorphic and igneous environments, hydroxyl-apatite found, not only in igneous and metamorphic environments but also in biogenic (bone) deposits, or carbonate-hydroxy-apatite (guano-type deposits and bird and bat excrements) found mainly on islands and in caves [4,5,12]. The composition of phosphate rock which depends largely on its type and origin, exists in the earth's crust as sedimentary, igneous and metamorphic rock [13,14]. Sedimentary phosphates form the highest percentage of world's phosphate deposit and major raw material for phosphate fertilizer production. They contain varying concentrations of chemical and trace elements constituents some of which can be of environmental concern. Detail analysis of the major and trace elements geochemistry of this natural resource is therefore needed to determine their abundance and the interelement relationships within the phosphate bearing rocks with a view to interpreting their overall impact on phosphatic mineralization and the general environment.

Phosphate deposits occur in four states in Nigeria [15,16], which include Sokoto, Edo, Imo and Ogun states. Only Sokoto and Ogun deposits are however considered economically viable. The objective of this study is to investigate the major oxides and trace elements concentrations of Sokoto phosphate rocks (SPRs) and to ascertain its suitability for direct application to agricultural

soils for enhanced soil fertility and readily available supplementary source of plant nutrients.

2. Materials and Method

2.1. Sample Collection

Phosphate rocks of Paleocene sedimentary deposits occur within the southeast sector of extensive Iullmeden basin in Sokoto state (Figure 1). The deposits are identified to be of marine origin whose basic components are from vertebrate remains deposited during the Maastrichtian Paleocene trans-Saharan transgressions. SPRs, with high commercial prospects have been reported in six priority areas in Sokoto basin [17,18] which include Dillingu, Gada and Gidan-Bauchi (Figure 2). Additional commercial deposits could also be found in Illela and Kalambiana [8] in Sokoto state. SPRs occur generally as nodules on the surface with nodular beds measuring between 0.2-0.3 m. They are source of livelihood for the locals especially women and children who superficially mined and supplied them on contractual basis as major raw material to Crystal Talc Fertilizer Company in Niger state and Federal superphosphate Fertilizer Company in Kaduna, north central Nigeria.

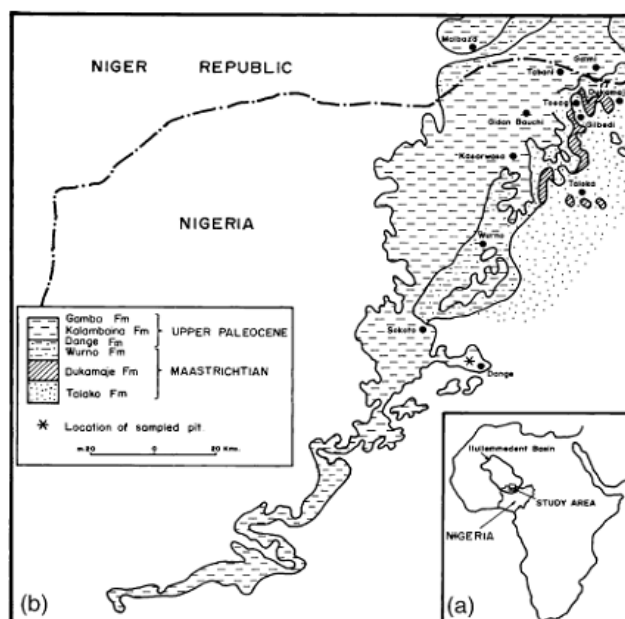


Figure 1. (a) Map of Africa, showing the Sokoto sub-basin, Northwest Nigeria in relation to the Iullemeden basin. Inset: Location of (b). (b) Simplified geological map of the southeastern sector marine and marginal facies of Illemeden basin, Sokoto sub-basin (Okosun, 1997)

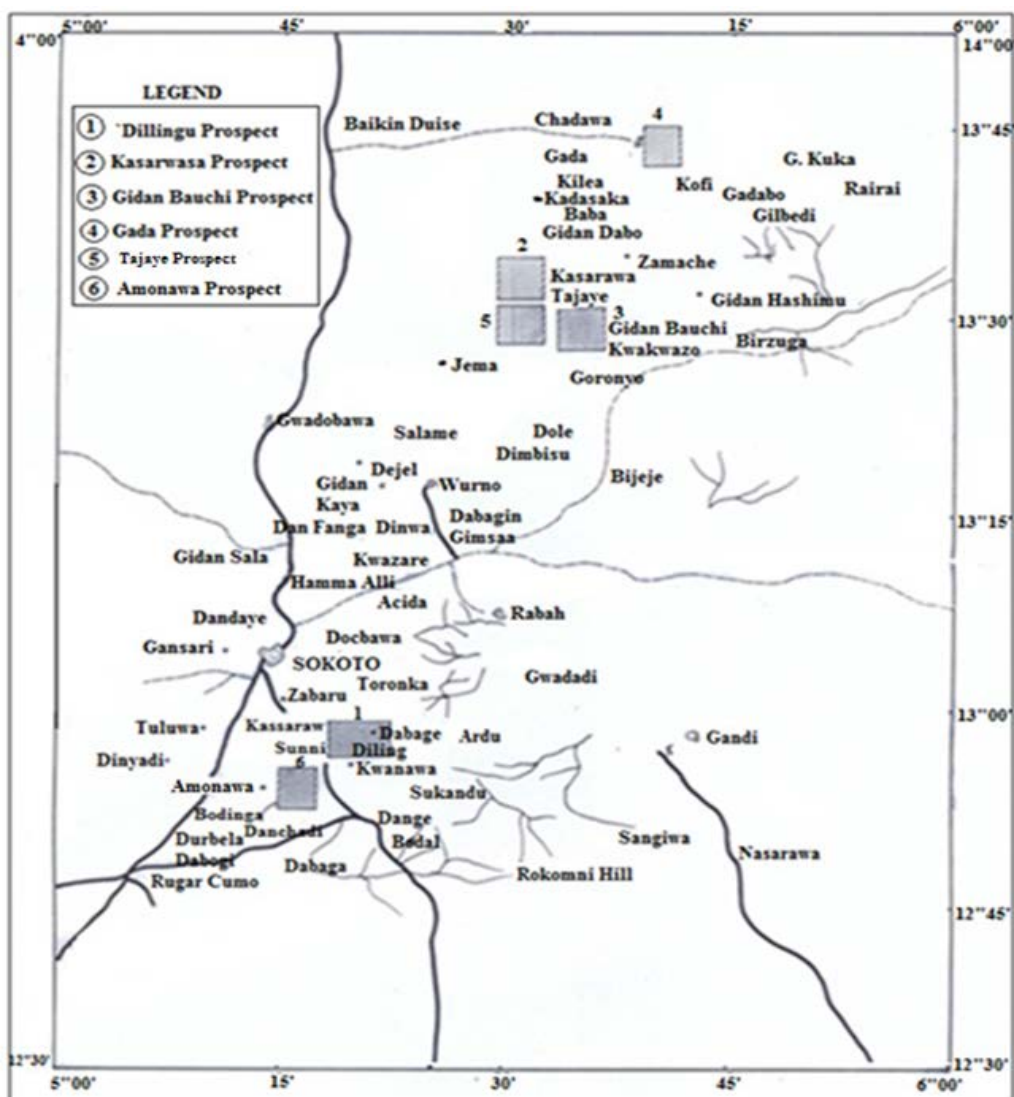


Figure 2. Location of phosphate deposit prospects in Sokoto State (GSN, 1986)

The nodules are also blended by local farmers for direct application to their agricultural farms as readily available substitute for the expensive and scarce commercial fertilizer products [19].

Five villages within the phosphate bearing areas in Sokoto basin were visited from which a total of 45 phosphate rock samples were collected for analysis. The villages are Dange (DNG), Dankilo (DKL), Wurno (WRN), Kindiru (KDR) and Dilingu (DLG). 9 samples were collected from each of the villages in a manner that 4 samples were randomly picked and mixed together to give a true representation of each sampling point. The collected samples which were cleared of all debris and foreign matters, were neatly packed in well labelled polythene bags, properly sealed and transported to the laboratory for analysis. The analysis was carried out at the National Metallurgical Development Centre (NMDC), Jos, Plateau State, Nigeria.

2.2. Sample Preparation and Analysis

In the laboratory, all the samples were sundried for 72 hours to near constant weight under ambient temperature. About 20 g of each dry rock sample was crushed thoroughly, homogenized and finely powdered using the agate mortar. Pressed pellets of the samples were prepared for analysis as follows: collapsible aluminium cups were half-filled with boric acid and 3 ± 1 g of the finely powdered samples were poured on the boric acid and finally pressed into sample pellets under 25 ton pressure using the hydraulic press. The resulting pellets have a diameter of 30 mm and average uniform mass of 9.8 ± 0.5 g. The sample pellets were analysed for their major oxides and trace elements concentrations using the PANalytical MiniPal4 model PW4025/45B energy dispersive x-ray fluorescence spectrometer (EDXRF).

3. Results and Discussion

The results of the major oxides and trace elements concentrations of SPR samples are presented in Table 1. SPRs are composed mainly of CaO, P_2O_5 , SiO_2 , Al_2O_3 and Fe_2O_3 , with CaO, P_2O_5 and SiO_2 being the most abundant

species. This results follow the normal trend observed in most phosphate deposits around the world. The mean concentration of CaO, which recorded the highest among the major oxides in the studied samples vary from 45.1 ± 1.5 % for KDR samples to 51.3 ± 1.9 % for DNG samples, while the mean concentration of P_2O_5 range between 19.9 ± 1.0 % for KDR samples and 21.6 ± 2.2 % for DNG samples. The lowest mean concentration of 5.0 ± 0.7 % for SiO_2 was recorded in DNG samples while DKL samples recorded the highest mean concentration value of 7.6 ± 1.7 %. WRN samples (6.7 ± 0.5 %), KDR samples (6.4 ± 0.4 %) and DLG samples (5.4 ± 0.2 %) showed higher mean concentration values for SiO_2 in comparison with DNG samples. The appreciable concentration of SiO_2 content in SPRs could be attributable to ore silification that occurred during the shallow marine conditions of the sedimentary basin [9]. The highest mean concentration value of 10.6 ± 1.7 % was recorded for Fe_2O_3 in DLG samples while KDR and DKL samples registered the highest mean value of 3.1 ± 0.3 % and 3.1 ± 0.6 % respectively for Al_2O_3 . The mean concentration values for MnO, TiO_2 and K_2O were very low, being less than 1wt % in all the studied samples. A careful observation of the results presented in Table 1 showed that CaO and P_2O_5 have appreciably higher mean concentration values suggesting SPRs to have high apatite content [9,10,20]. Phosphate ores have been classified based on their P_2O_5 concentration value as low-grade ores (12-16 % P_2O_5), intermediate- grade ores (17-25 % P_2O_5) and high-grade ores (26-35 % P_2O_5) [6,21]. Based on this classification therefore, SPRs are intermediate- grade phosphate ores which make the deposits viable aggregate for fertilizer production. Relatively low mean concentration values for MnO (0.8 ± 0.2 % - 0.9 ± 0.1 %) recorded for all the studied samples give an indication of non-dolomitization in the studied SPRs. Furthermore, the process of deposition may have allowed the entrapment of marine water in the sediments which could be responsible for the low mean concentration values (0.1 – 0.2 %) recorded for K_2O in all the studied samples. This is however advantageous to local farmers since very little salt will be added to the soil when SPRs is considered for direct application as a good source of P_2O_5 [20,22].

Table 1. major oxides (wt. %) and trace elements (ppm) composition of Sokoto phosphate rock samples

		Descriptive statistics	Major elements distribution (wt. %)										Trace elements distribution (ppm)						
SAMPLE ID	No of Samples		CaO	P ₂ O ₅	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO	TiO ₂	K ₂ O	Cr	V	Cu	Ni	Sr	Ba	Zr	Ce	
DNG	9	Min	47.4	18.7	4.2	3.6	1.5	0.7	0.1	0.1	68.4	56.0	239.7	ND	2283.1	53.7	85.1	732.7	
		Max	54.0	24.8	5.9	8.1	2.4	1.1	0.3	0.2	205.3	168.0	319.5	ND	3467.0	358.3	170.2	1139.7	
		Mean	51.3	21.6	5.0	4.8	1.9	0.8	0.2	0.2	146.6	104.0	275.2	ND	2687.1	276.4	113.4	904.5	
		SD	1.9	2.2	0.7	1.4	0.3	0.2	0.1	0.1	43.7	35.8	39.7	ND	349.3	272.3	40.1	135.4	
KDR	9	Min	42.8	18.5	5.7	7.6	2.7	0.8	0.2	0.1	136.8	168.0	239.7	22.1	2198.6	268.7	85.1	895.5	
		Max	47.2	20.9	6.8	11.9	3.6	1.1	0.3	0.2	273.7	224.1	319.5	368.2	3551.5	1612.1	255.2	2035.2	
		Mean	45.1	19.9	6.4	10.0	3.1	0.9	0.2	0.1	197.7	201.7	292.9	131.8	2696.5	639.7	170.2	1438.2	
		SD	1.5	1.0	0.4	1.8	0.3	0.1	0.0	0.0	38.8	27.4	37.7	101.6	450.0	418.5	40.1	332.3	
DLG	9	Min	43.5	19.9	5.1	8.4	2.3	0.7	0.2	0.1	136.8	56.0	239.7	44.2	1944.9	179.1	85.1	814.1	
		Max	51.7	21.1	5.8	12.4	2.5	0.8	0.2	0.1	273.7	224.1	319.5	58.9	2283.1	358.3	255.2	976.9	
		Mean	46.2	20.6	5.4	10.6	2.4	0.7	0.2	0.1	220.5	168.0	284.0	53.7	2095.2	268.7	170.2	862.9	
		SD	2.3	0.5	0.2	1.7	0.1	0.1	0.0	0.0	43.0	59.0	39.7	4.9	103.8	89.6	40.1	65.1	
WRN	9	Min	47.0	19.8	6.0	2.6	1.9	0.7	0.2	0.1	136.8	56.0	239.7	29.4	2705.9	895.6	85.1	814.1	
		Max	52.6	21.1	7.5	7.3	2.6	1.0	0.3	0.2	205.3	224.1	319.5	29.7	3128.7	1522.6	170.2	1221.1	
		Mean	50.0	20.5	6.7	4.7	2.2	0.9	0.2	0.1	166.2	112.0	284.0	29.5	2846.8	925.5	132.3	936.2	
		SD	2.1	0.4	0.5	1.8	0.2	0.1	0.0	0.0	33.9	52.8	39.7	0.0	182.7	263.7	42.3	146.8	
DKL	9	Min	44.2	19.3	6.0	4.2	2.4	0.8	0.2	0.1	136.8	56.0	239.7	73.7	2621.4	89.6	170.2	814.1	
		Max	52.8	21.0	10.0	5.5	3.8	1.0	0.4	0.2	205.3	168.0	559.2	441.9	3044.2	1343.4	425.4	895.5	
		Mean	48.6	20.4	7.6	5.0	3.1	0.9	0.3	0.1	167.2	124.5	301.8	191.5	2818.7	796.1	283.6	841.2	
		SD	3.0	0.7	1.7	0.4	0.6	0.1	0.1	0.1	34.0	35.2	98.0	128.4	143.7	467.2	106.1	38.4	

SD = standard deviation.

The CaO/P₂O₅ ratio for SPRs presented in Table 2 range between 2.2 to 2.4. This suggests a high carbonate enrichment which make SPRs high limiting materials for acid soils. Although these values were found to be lower than the values reported for most reactive phosphate ores [23], the reactivity of SPRs is still very significant, thus making SPRs indispensable raw materials for fertilizer production. Furthermore, SPRs by virtue of their reactivity, need no further modification other than fine grinding for direct application to soils as a good nutrient source for high crop yield.

There is a wide variation in trace elements concentrations among the studied samples as seen in Table 1, which of course is expected of sedimentary phosphates.

The mean concentration value for Cr varies between 146.6±43.7 mgkg⁻¹ for DNG samples and 220.5±43.0 mgkg⁻¹ for DLG samples, while that for V is between 104.0±35.8 mgkg⁻¹ for DNG samples and 201.7±27.4 mgkg⁻¹ for KDR samples. The variation in the average concentration of Cu look averagely uniform across all the samples, ranging from 275.2±39.7 mgkg⁻¹ obtained in DNG samples to 301.8±98.1 mgkg⁻¹ for DKL samples, while Ba recorded the highest mean concentration of 925.5 mgkg⁻¹ in WRN samples. The appreciable concentrations of Ba and Cu follow the same trend as the phosphorites from Peru margins which might have originated in the organic matter from marine plankton [24].

Table 2. Mean composition of major oxides (wt. %), CaO/P₂O₅ ratio and trace elements (mgkg⁻¹) in Sokoto phosphate rock samples

Table 2: Mean composition of major oxides (wt. %) and trace elements (ppm) in control phosphate rock samples																	
Major elements distribution (wt. %)										Trace elements distribution (ppm)							
SAMPLE ID	CaO	P ₂ O ₅	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO	TiO ₂	K ₂ O	CaO:P ₂ O ₅	Cr	V	Cu	Ni	Sr	Ba	Zr	Ce
DNG	51.3	21.6	5.0	4.8	1.9	0.8	0.2	0.2	2.4	146.6	104.0	275.2	ND	2687.1	276.4	113.4	904.5
KDR	45.1	19.9	6.4	10.0	3.1	0.9	0.2	0.1	2.3	197.7	201.7	292.9	131.8	2696.5	639.7	170.2	1438.2
DLG	46.2	20.6	5.4	10.6	2.4	0.7	0.2	0.1	2.2	220.5	168.0	284.0	53.7	2095.2	268.7	170.2	862.9
WRN	50.0	20.5	6.7	4.7	2.2	0.9	0.2	0.1	2.4	166.2	112.0	284.0	29.5	2846.8	925.5	132.3	936.2
DKL	48.6	20.4	7.6	5.0	3.1	0.9	0.3	0.1	2.4	167.2	124.5	301.8	191.5	2818.7	796.1	283.6	841.2

Ni was not detected in DNG samples but witnessed the highest mean concentration of 131.8±106.8 mgkg⁻¹ in KDR samples. Other minor trace elements like Zr (113.4-283.6 mgkg⁻¹) and Ce (841.2-1438.2 mgkg⁻¹) showed wide variations in their concentration within the studied rocks.

3.1. Correlation Matrix

The relationships and degree of association that may exist among the major oxides and trace elements in the studied rocks were assessed by Pearson's correlation analysis using statistical program for social science (SPSS 22.0). The calculated linear Pearson's correlation coefficients among the variables for the studied SPRs are given in Table 3. A very strong positive correlation was observed between P₂O₅ and CaO ($r^2 = 0.783$). This may be

due to the diagenetic phosphatization which might have occurred before the precipitation of phosphorites whereby PO₄ eliminated CO₂. Al₂O₃ however, showed negative relationship with P₂O₅ ($r^2 = -0.783$) which may be attributed to the adsorption of Al₂O₃ in hydrous aluminium-silicates and clay minerals with high P₂O₅ contents. Weak negative correlation witnessed between Fe₂O₃ and P₂O₅ ($r^2 = -0.492$) points to the possibility that Fe₂O₃ was not deposited together with P₂O₅ during phosphatization. Sympathetic weathering and leaching of Fe from ores in highly oxidizing marine environment and its possible re-precipitation with P₂O₅ in cavities and pore spaces may be another reason for the negative relationship between the pair [22].

Table 3. Correlation coefficient matrix for Sokoto phosphate rock samples

	CaO	P ₂ O ₅	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO	TiO ₂	K ₂ O	Cr	V	Cu	Sr	Ba	Zr	Ce
CaO	1														
P ₂ O ₅	0.783	1													
SiO ₂	-0.120	-0.647	1												
Fe ₂ O ₃	-0.912	-0.492	-0.287	1											
Al ₂ O ₃	-0.685	-0.826	0.713	0.345	1										
MnO	0.111	-0.450	0.769	-0.460	0.475	1									
TiO ₂	0.078	-0.180	0.742	-0.376	0.578	0.375	1								
K ₂ O	0.663	0.901	-0.656	-0.413	-0.661	-0.250	-0.250	1							
Cr	-0.892	-0.576	-0.111	0.938	0.365	-0.465	-0.238	-0.631	1						
V	-0.971	-0.711	-0.016	0.923	0.607	-0.093	-0.236	-0.512	0.827	1					
Cu	-0.464	-0.740	0.877	0.083	0.940	0.540	0.786	-0.684	0.194	0.330	1				
Sr	0.476	-0.064	0.584	-0.740	0.162	0.920	0.346	0.106	-0.775	-0.430	0.279	1			
Ba	0.066	-0.569	0.883	-0.417	0.424	0.868	0.401	-0.569	-0.255	-0.144	0.580	0.732	1		
Zr	-0.293	-0.462	0.755	-0.019	0.788	0.288	0.928	-0.512	0.126	0.119	0.917	0.123	0.362	1	
Ce	-0.605	-0.588	0.056	0.499	0.478	0.403	-0.348	-0.206	0.284	0.746	0.196	0.174	0.139	-0.153	1

The possibility of SiO₂ existing in phosphate rocks as quartz, along with Al₂O₃ [5], may have accounted for the high positive correlation ($r^2 = 0.713$) seen between the two oxides as seen in Table 3. This is however not the case

with the apatite content where an inverse relationship is observed. The poor negative correlation observed between SiO₂ and P₂O₅ ($r^2 = -0.647$) may not be unconnected with the existing diadochic relationship between the two oxides

[9] and a mutual substitution of Si^{+4} ions for P^{+5} in apatite (due to their close ionic radii 0.39Å and 0.35Å respectively) before the final precipitation of phosphorites. The antipathetic relationship between MnO and P_2O_5 demonstrated by their negative correlation coefficient ($r^2 = -0.450$), rule out the possibility of Mn occurring in apatite structure or having any direct affinity with phosphates. TiO_2 is normally introduced into sedimentary environments as a detrital heavy metal, and in a decreasing manner with increasing P_2O_5 content. This may be the reason for the weak negative correlation ($r^2 = -0.18$) between TiO_2 and P_2O_5 as seen in Table 3. Furthermore, negative correlation was observed between Cr and P_2O_5 ($r^2 = -0.576$) which may be due to chemical affinity of Cr to clay minerals. There is also the possibility of P^{+5} replacing Cr^{+6} in the sedimentary basin during diagenesis. Negative relationship was also observed between P_2O_5 and Cu ($r^2 = -0.740$) which may be due to the leaching of the ore during diagenesis which might have led to loss of Cu.

Sr showed very weak negative relationship ($r^2 = -0.064$) with P_2O_5 and a moderately positive relationship with CaO ($r^2 = 0.476$), which suggests that Sr is associated with calcite that with apatite. This study general reveals that although SPRs are enriched in major and trace elements which suggests a good source of soil nutrients for plant growth, direct application of SPRs to agricultural soil can be considered environmentally safe.

4. Conclusion

Phosphate rock samples from phosphate bearing formations in Sokoto state were analysed for their major oxides and trace elements concentrations using the energy dispersive x-ray fluorescence (EDXRF) spectrometer. The chemistry of the phosphate bearing sedimentary rocks showed very low concentrations for alkali oxides and appreciably high concentrations for P_2O_5 which makes SPRs good source of soil phosphorus and a readily available alternative to highly expensive chemical fertilizers. The significantly high CaO/ P_2O_5 ratio (2.2-2.4), typical for carbonate apatite, demonstrate the relative reactivity of SPRs which suggests its suitability as raw material for fertilizer production. Although SPRs are considered as agriculturally advantageous, its direct application must be environmentally safe. Possible environmental and health risk due to accumulation of toxic metals in soil and plants as a result of its direct application cannot be overlooked. Constant routine investigation of this valuable raw material is therefore proposed to check any negative metal impact and to keep the effects thereof as low as reasonably achievable considering the economic and the social factors. Detailed quantitative and qualitative assessment of these pollutants relative to their nutrient values will be an added tool in designing environmentally safe processes for fertilizer industry.

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