

Full Length Research Paper

Geochemistry and mineralogy of Ogun phosphate rock

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Suitability of direct application of phosphate rock as low cost phosphorus fertilizer for crop production must be environmentally safe. Four pellets of Ogun phosphorites labeled OG1, OG2, OG3 and OG4 were randomly selected and subjected to petrographic, X-ray diffraction and X-ray fluorescence analyses. Petrographic results revealed two textural forms: nodular (OG1 and OG3) and granular (OG2 and OG4). Characteristic features like fine grains of phosphorites, geopetal texture with heavy iron staining were found in nodular form while presence of shell fragments and bioclastic materials with burrows were observed in granular form. The diffractogram of different pellets showed poorly crystalline mineral, fluorapatite was identified as the major apatite mineral. X-ray fluorescence results showed wide variations in elemental composition among the different forms of Ogun phosphorites. In nodular phosphorites (OG1 and OG3), apatite content were 31.28 and 30.20% P₂O₅ respectively, Granular phosphorites (OG2 and OG4) contain 19.73 and 11.12% P₂O₅. The alkali metals K₂O and Na₂O are variable and low showing its suitability as P source because minimal salt is added to the soil. Radionuclides present have low values (U 19 to 29 ppm; Th 5 to 13 ppm; Ni 41 to 80 ppm) indicating its environmental security.

Key words: Phosphorus, phosphorites, Ogun phosphate rock, x-ray fluorescence analysis, x-ray diffraction analysis, petrography analysis.

INTRODUCTION

Sustainability of human life on earth depends on sustainable agriculture (Fardeau, 1993). Phosphorus (P) is one of the major essential nutrients needed to ensure this sustainability. Superphosphates (single superphosphate (SSP) and triple superphosphate (TSP) are the most commonly used P fertilizer source on agricultural soils in Nigeria. But high cost, scarcity of these mineral P fertilizer coupled with the adverse effect of the use of chemical fertilizers on environmental quality (Carpenter et al., 1998; Sharpely et al., 1994) poses a great threat on food production. Therefore there is an urgent need for a suitable alternative.

Direct application of Phosphate rock as P fertilizer has been found to compete favorably well with mineral

fertilizers on acidic soils (Bolan et al., 1990; Chien et al., 1990; Akande et al., 1998; Adediran et al., 1998). In Ogun state of southwestern Nigeria are large deposits of Eocene Age phosphate rich sediments. Although the slightly older (Paleocene) phosphate deposits of Sokoto state have been extensively worked for agricultural material but Ogun phosphate rock received little attention (Adegoke et al., 1989; Akintokun et al., 2003). It is important to carry out characterization studies of Ogun phosphate rock to ascertain its suitability as P source to crops and its impact on the resource base.

The objective of the study presented in this paper was to determine the mineralogy of Ogun phosphate as a tool for accessing its suitability as phosphorus fertilizer for direct application in Agriculture.

MATERIALS AND METHODS

Ogun phosphate rock from Lower Eocene Sedimentary Phosphatic

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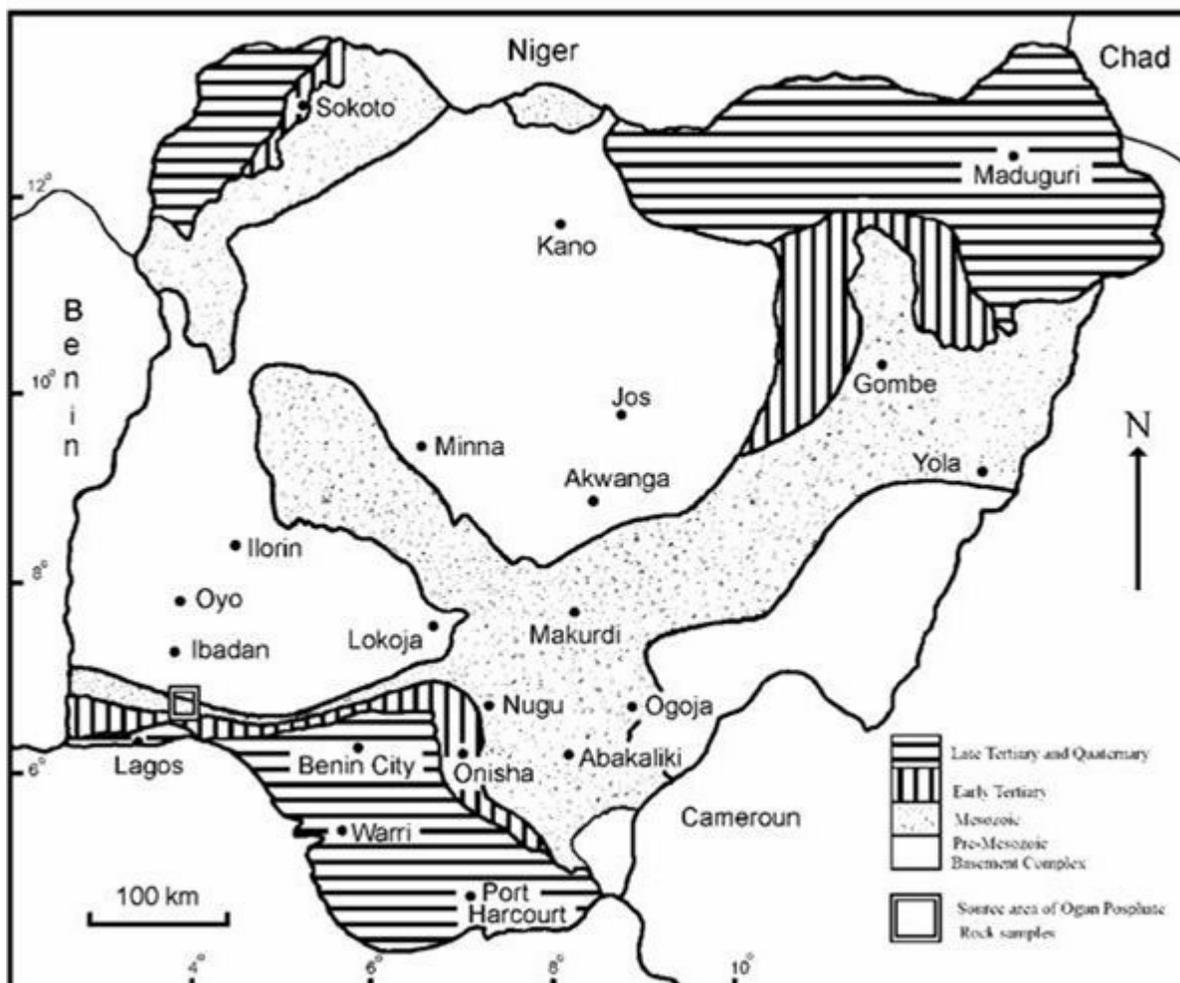


Figure 1. Sketch map of the geology of Nigeria (Abimbola et al., 2002) indicating source of the Ogun Phosphate Rock samples.

sediments have been known from southern Nigeria since 1921 (Russ, 1924, quoted in McClellan and Notholt, 1986). Phosphatic sediments occur between the Ifo Junction and Ososum in southwestern Nigeria, approximately 43 km and 48 km north of Lagos (McClellan and Notholt, 1986). The resource estimate of this phosphate deposit is 40 million tonnes, but the reserve estimates need updating and confirmation (Ministry of Solid Minerals Development 2000) (Figure 1).

Phosphate rock samples were collected from two different pits (2 m deep) within the same location. The pellets having different shapes were mixed together, washed to remove sand and clay particles and sorted out based on visual examination by the help of a geologist into four parts, a representative sample (in duplicates) from each part was randomly selected and subjected to petrographic, x-Ray Diffraction (XRD) and x-Ray Fluorescence analyses. All analyses were carried out at School of Geological Sciences, University of KwaZulu-Natal, Westville Campus, Durban, South Africa.

Petrographic analysis

Thin section of the raw rock mineral was prepared cutting a section

of the rock followed by grinding and polishing of the rock sample before fixing on a petrographic slide. Thin section for the different pellets were later viewed and photographed under the microscope with magnification factor of 20 and 50.

X-ray diffraction (XRD)

Samples of different pellets were ground to powder and carefully packed into an aluminum holder, which is now placed in goniometer and bombarded with x-rays generated from a cobalt tube. The diffracted rays are collected by a detector and the information relayed to a computer. Diffractometer type used was Pw3710 BASED with Cobalt as tube anode. Powdered form of the ground mixture of different pellets used as fertilizer was also analyzed.

X-ray fluorescence (XRF)

Major element analysis of the Ogun phosphate rock was undertaken on powdered samples mixed with pure lithium metaborate, and ammonium nitrate as the oxidizing agent fused to a glass disc in a furnace at 1 000°C. Trace elements analysis was undertaken

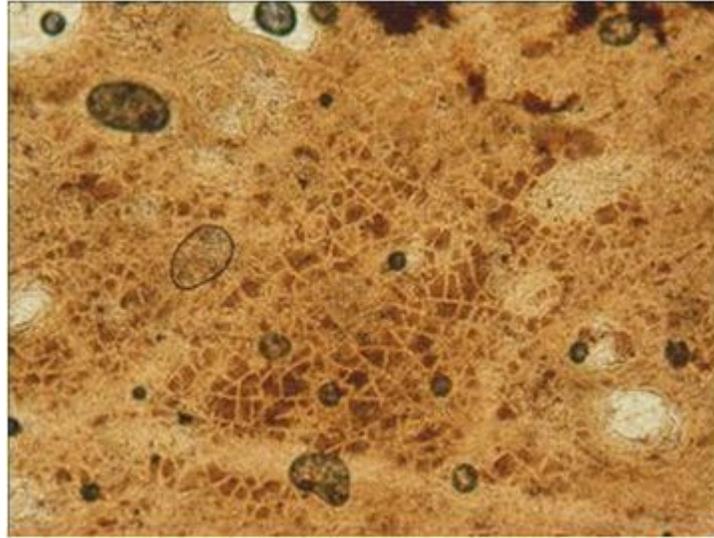


Figure 2. Thin section of nodular phosphorite (OG1 at x50).

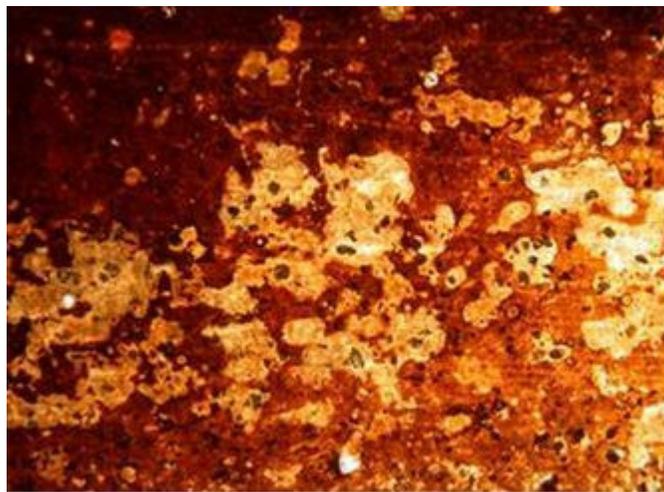


Figure 3. Thin section of Nodular Phosphorite OG 3 x 20 showing Geopedal texture with Fe staining.

on a 32 mm diameter 10 g pressed powder pellet (Norish and Hutton, 1969; Hutchison, 1974) using Philips X'Unique II and PW 1404 spectrometers at the University of KwaZulu-Natal. The Loss on Ignition was calculated from a weight loss of a sample heated to 1000°C (Hutchison, 1974).

RESULTS AND DISCUSSION

Petrographic analysis

The results of the petrographic analysis revealed that Ogun phosphate deposits were formed in shallow marine environment with isochous rim cement developed on many of the clasts indicating the influence of phreatic process thus confirming the earlier work done by Jones

and Hockey (1964) and Odigi and Brown-Awala (1992). The Ilaro formation contains the phosphorus rich horizons with presence of organic rich intraclastic and intrapellic phosphorites. The diffuse red brown iron staining present in all the samples and particularly strongly developed in OG4 (Figure 5) showed that primary sedimentary ferrous minerals (such as siderite, pyrite and glauconite) had undergone oxidation and alteration. Although glauconite is considered to have been the primary iron bearing mineral, oxidation and alteration has progressed to the stage where no glauconite could be identified as observed by Akande et al. (1999). Pellets labeled OG1 and OG3 are classified as nodular phosphorites (Figures 2 and 3) because of the presence of fine grains texture of the thin section. On the other hand OG2 and OG4 are granular

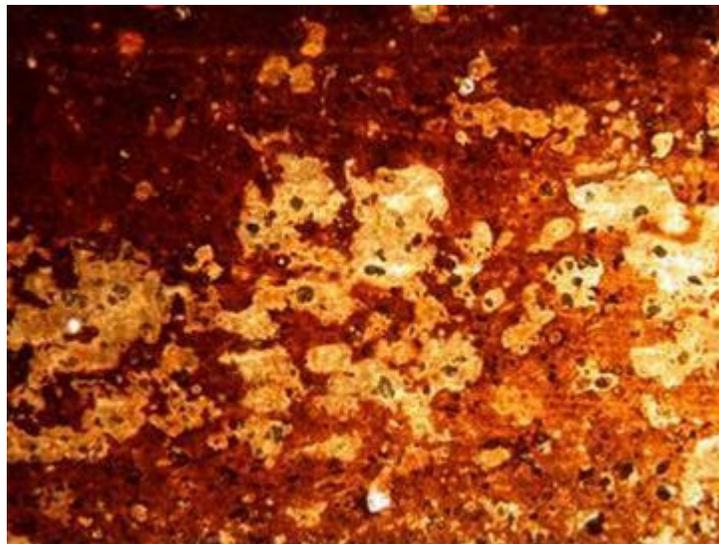


Figure 3. Thin section of Nodular Phosphorite OG 3 x 20 showing Geopedal texture with Fe staining.

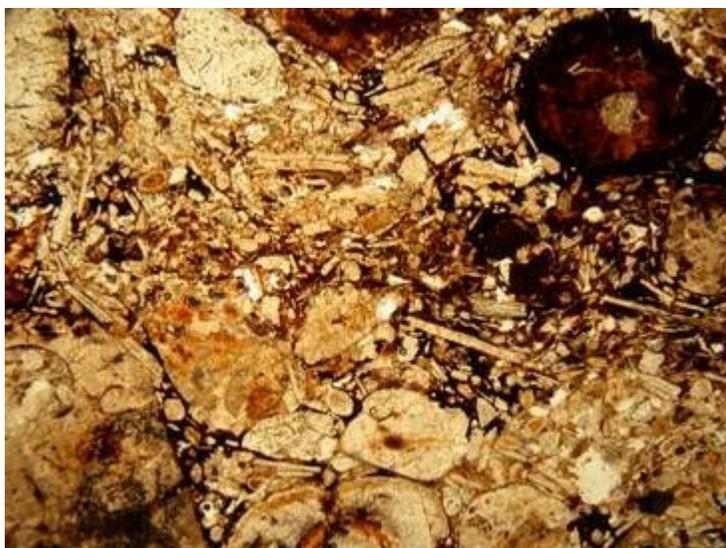


Figure 4. Thin section of OG2 at x20 (showing granular form with shell fragments)

phosphorite due to the presence shell fragments and bioclastic materials (Figures 4 and 5) Apatite mineral was more pronounced in nodular phosphorites (Figure 2) than granular. The results are in close agreement with X-ray diffraction and X-ray fluorescence analysis.

X-ray diffraction analysis

The diffractograms of different pellets of OPR when subjected to x-ray diffraction analysis revealed a poorly crystalline mineral (Figures 6 to 10). The XRD studies

showed the presence of significant quantities of an amorphous material, most probably of an organic nature. This could have been the reason for the poor crystalline patterns on the diffractogram of all the pellets analyzed. The diffractogram also revealed the presence of fluorapatite as the major apatite mineral in OPR in confirmation of earlier work done by BAT N° 4, (1995) and Abimbola et al. (2002). Pure apatite peaks had almost 100% peak intensity with value range between 2.78 to 2.79, peak intensities of the pellets within this range are OG1 (86%), OG3 (81%), OG2 (74%), OG4 (36%) and the mixture (41%). The peak intensities are directly

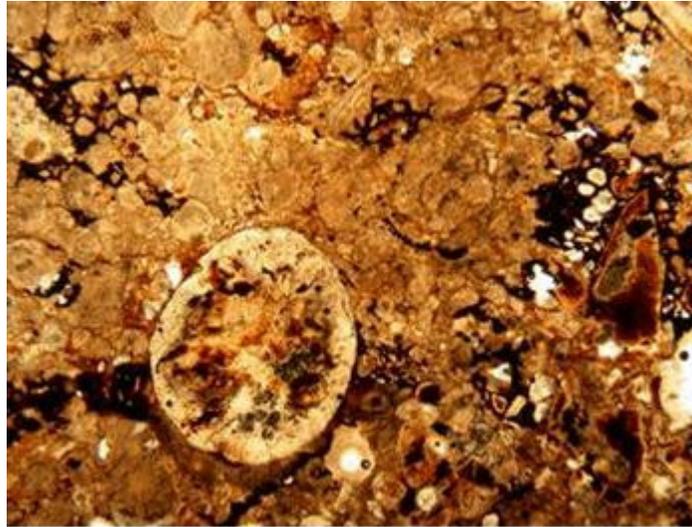


Figure 5. Thin sections of OG4 x 20 (showing granular form of Phosphorites with burrows)

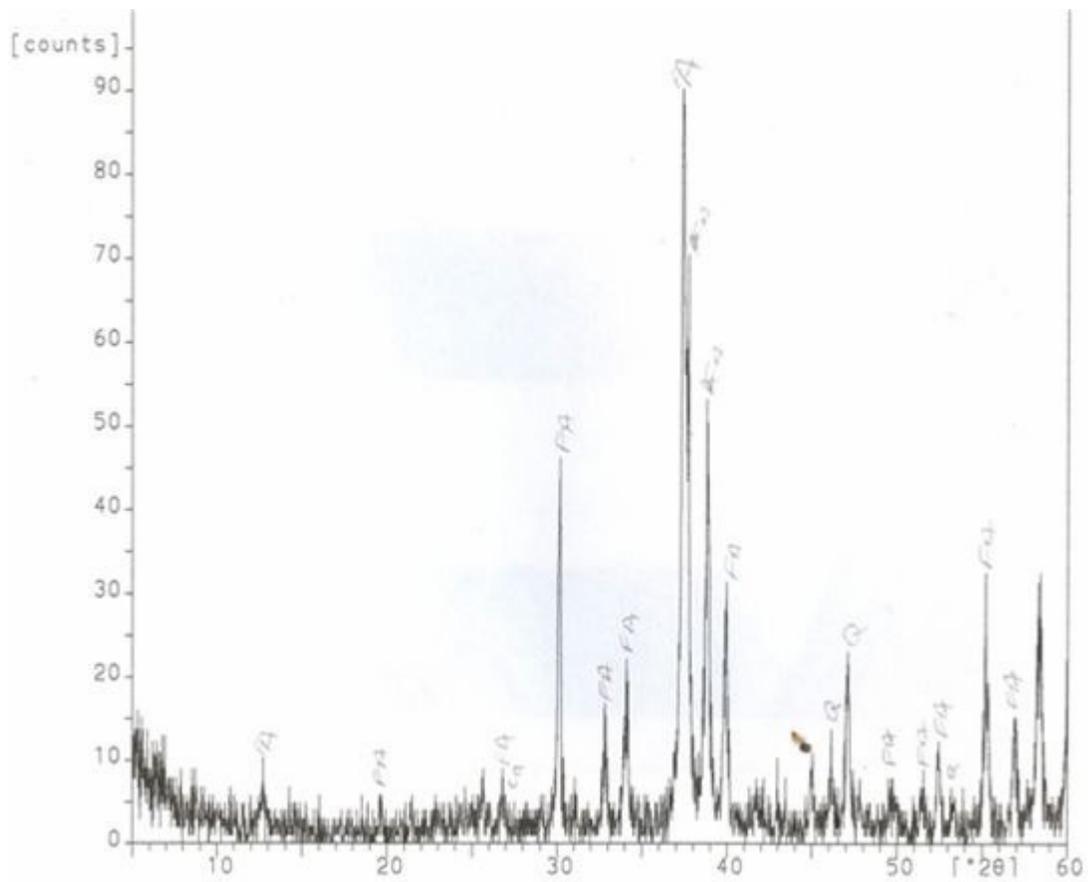


Figure 6. X – Ray diffractogram of OG1. FA = Flourapatite, Q = Quartz CA – Calcite.

related to the amount of apatite present therefore OG1 and OG3 had higher apatite content than OG2, OG4 and OGMIX. Differences in apatite content could easily be

seen from the peak intensities. The mixture used as fertilizer in this study contains more of OG2 and OG4 pellets. Quartz peaks with high peak intensities on

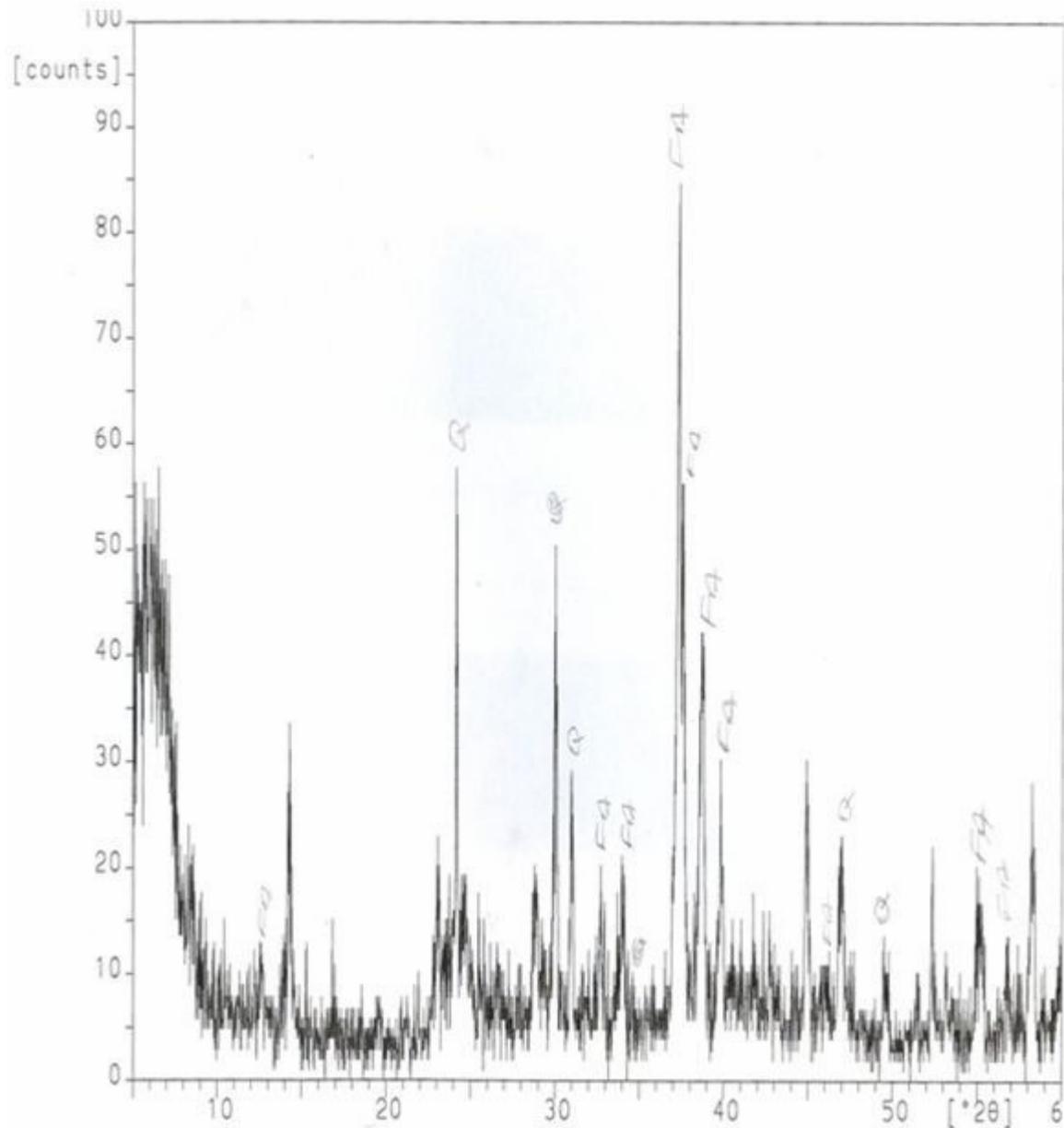


Figure 7. X – Ray diffractogram of OG2. FA = Fluorapatite, Q = Quartz CA – Calcite.

the diffractograms of OG2, OG4 and OGMIX closely agreed with XRF results on quartz content of the pellets. It is clear from the XRD results that diffractograms of OG1 and OG3 are identical while OG2, OG4 and OGMIX are also identical.

X-ray fluorescence analysis

X–ray fluorescence analysis data for the four different pellets of Ogun phosphate rock and the mixture used as fertilizers are presented in Tables 1 and 2. The elements have been classified into four groups based on their

relative abundance in nature as major, minor (Table 1) and trace constituents (Table 2).

The high P_2O_5 and CaO values (11.12 to 31.28 and 14.43 to 46.80 wt% respectively; (Table 1) are also indicative of the high apatite content, although the enhanced CaO content of OG1 suggests that calcite or gypsum is also present. The Al_2O_3 , SiO_2 , Fe_2O_3 and LOI values constitutes over 90% by weight of the rock material, this can be related to lower quantities of other minerals in the rock, particularly the detrital components as earlier observed by Abimbola et al. (2002). The iron content of the samples is highest (25.78 wt%) in the P_2O_5 poor phosphorite (OG4), however this value has been very

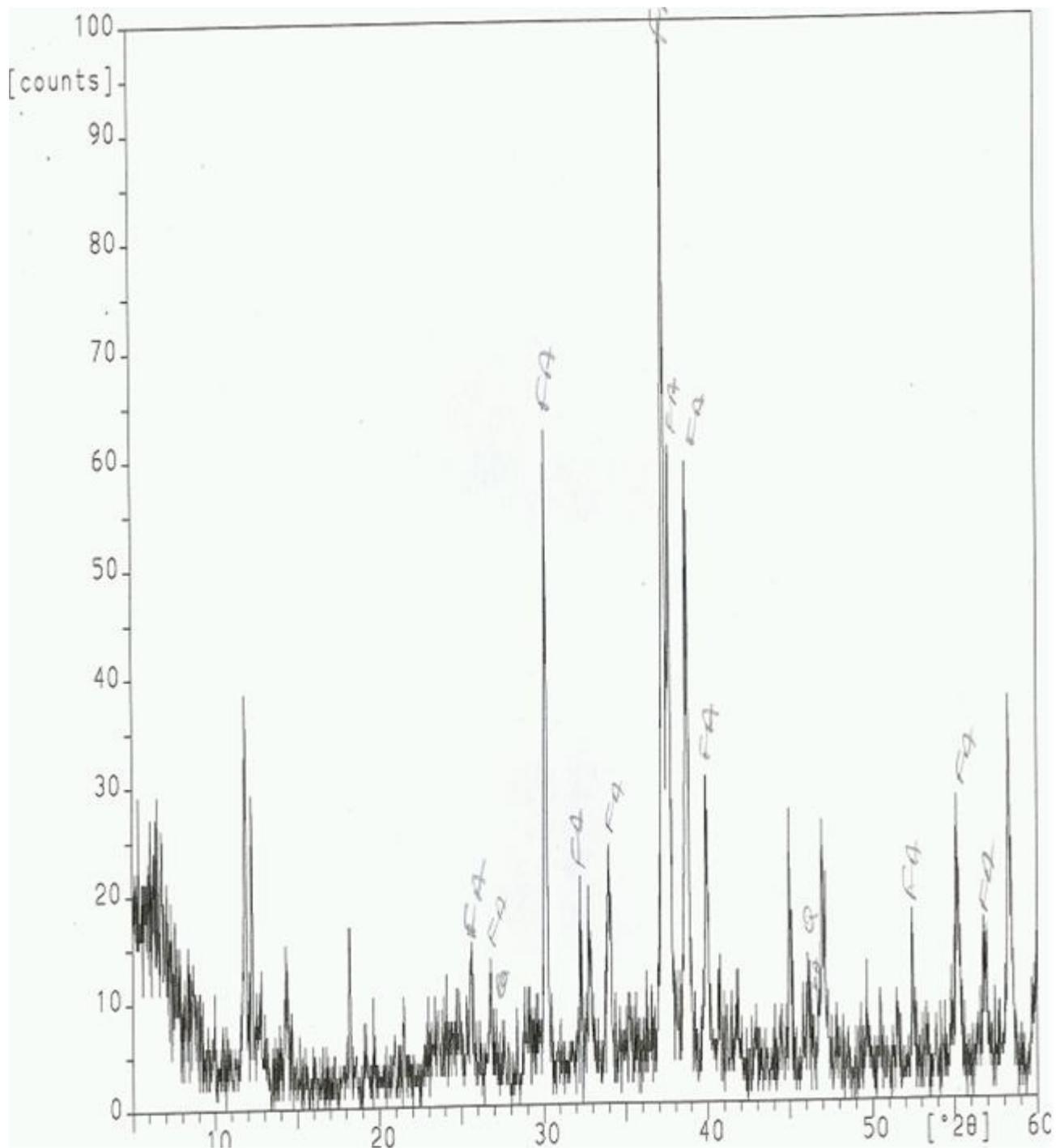


Figure 8. X – Ray diffractogram of OG3. FA = Flourapatite, Q = Quartz, CA= Calcite.

significantly effected by secondary iron mineral deposition related to the weathering and cannot be ascribed to the sedimentary environment. In the other relatively low P_2O_5 sample the Fe_2O_3 content is just less than 10 wt% (9.34 wt %), with the more P_2O_5 rich samples having Fe_2O_3 values of 6.28 and 4.74 wt% (Table 1). The Loss

on Ignition values (LOI) are relatively constant (Table 1), except for the slight decrease in sample OG1, which suggest that this sample may have a slightly lower organic material, calcite or gypsum content.

An inverse relationship was observed between quartz and apatite content (Figure 11). Similar trend was

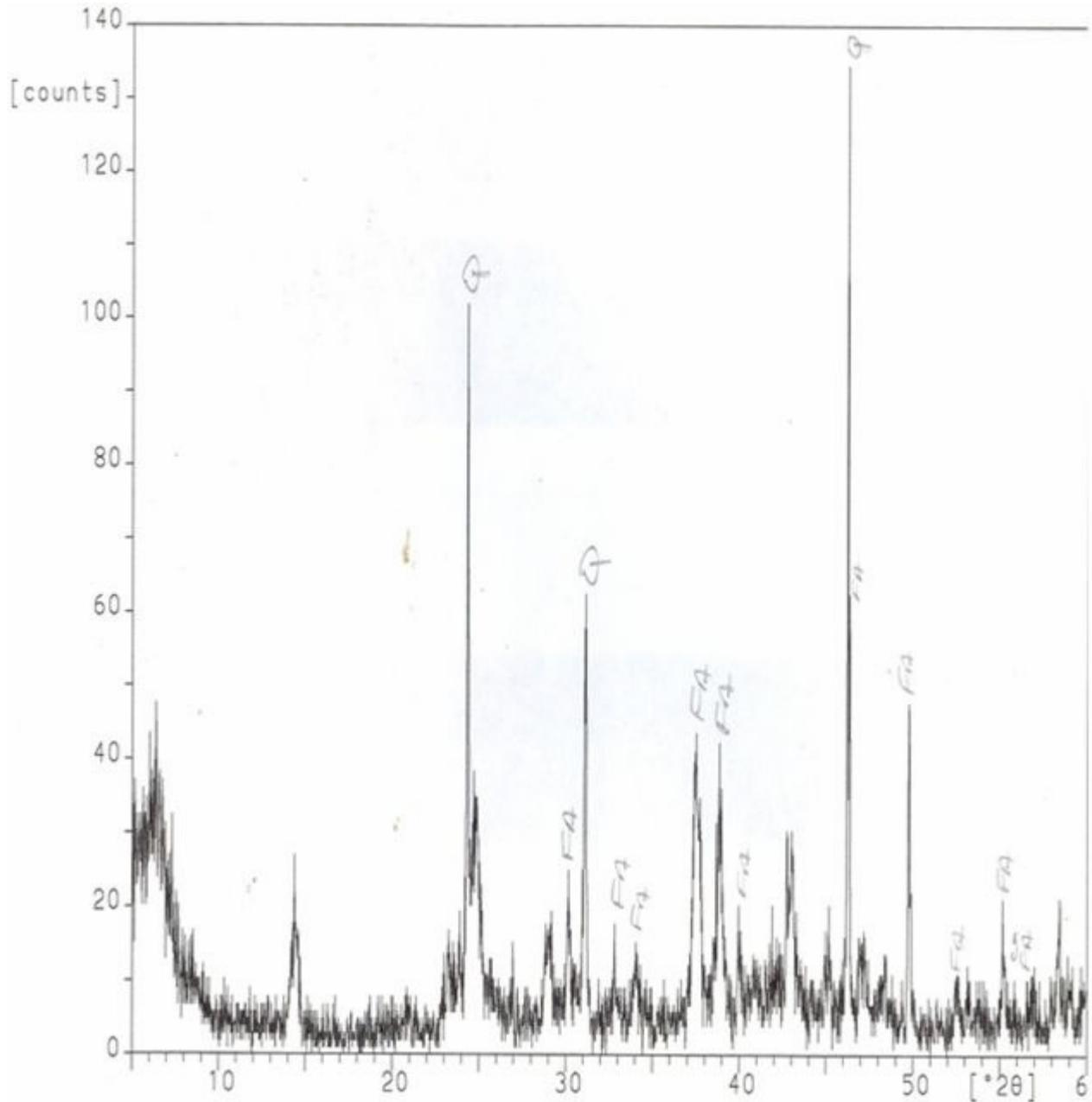


Figure 9. X – Ray diffractogram of OG4.

observed with Fe content in nodular compared with granular forms Calcium content increases proportionally as P_2O_5 content increases (Table1) with CaO/P_2O_5 ratio ranging from 1.18 to 1.59., highest ratio was recorded for OG1 The value was lower than values derived for the most reactive phosphate rock (3.5: 5.0) (McClellan and Gremillion, 1980) This show the extent of carbonate substitution, in OPR. A reaction that will remove CO_3^{2-} will improve agronomic efficiency of OPR.

The values of TiO_2 , MnO , MgO , K_2O , and Na_2O (Table1) are all less than 0.60 wt%. TiO_2 is in the sedimentary environment normally introduced as a detrital

heavy mineral confirms the same trend of decreasing detrital sediment input with increased P_2O_5 content as indicated by the SiO_2 and Al_2O_3 data. MnO content interestingly did not reflect the Fe_2O_3 pattern confirming the deduction that the remobilization of iron has occurred. The MgO values are very low (0.30 to 0.41 wt %) and relatively consistent. This is an indication that very little, if any, dolomitization has occurred. The alkali metals K_2O and Na_2O are rather variable (0.08 to 0.17 wt% and 0.10 to 0.53 wt% respectively); however, at these levels (Table 1) they can be considered to be traces of the marine water trapped in the sediments during deposition. The

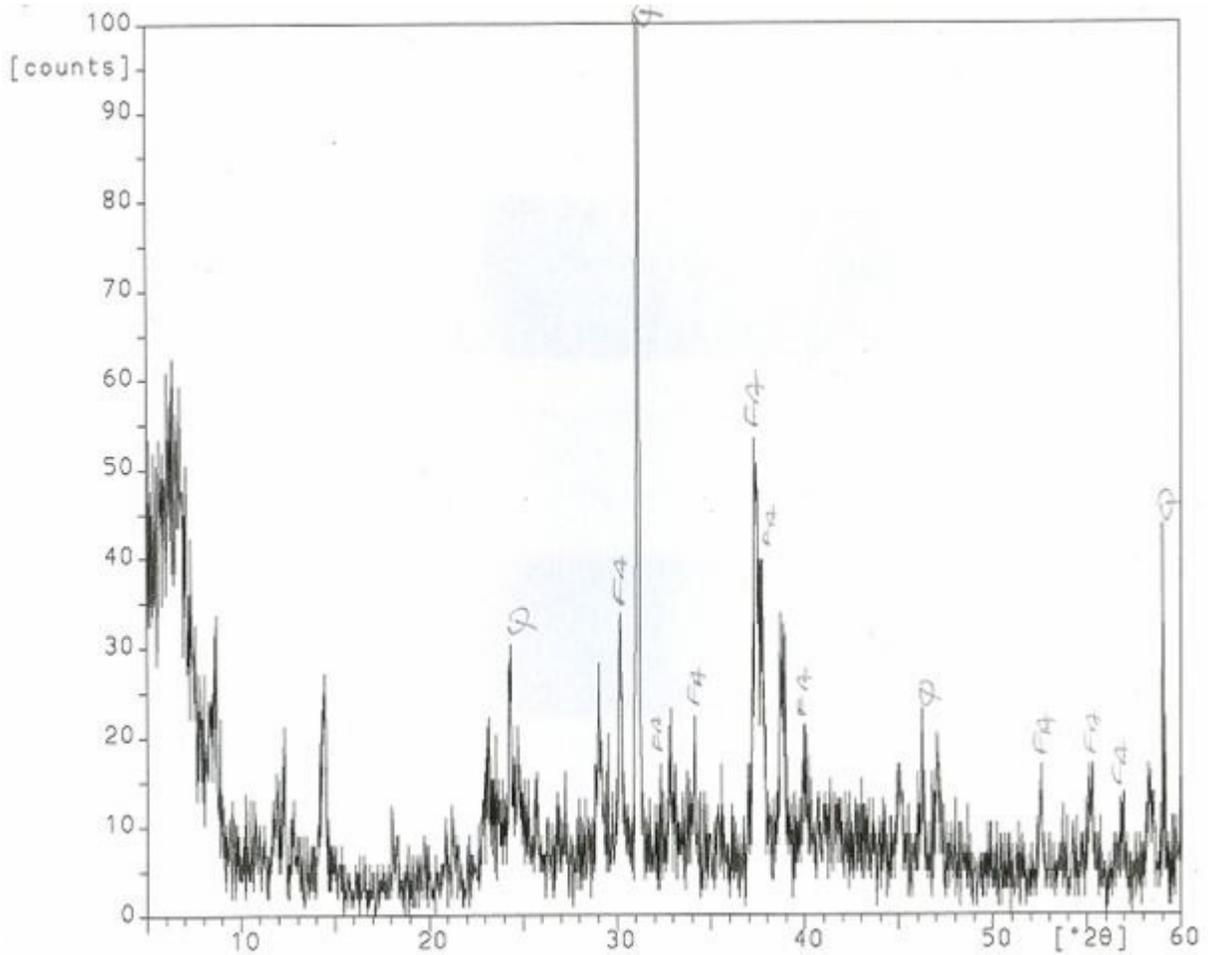


Figure 10. X – Ray diffractogram of OGMIX. FA = Flourapatite, Q = Quartz, CA - Calcite

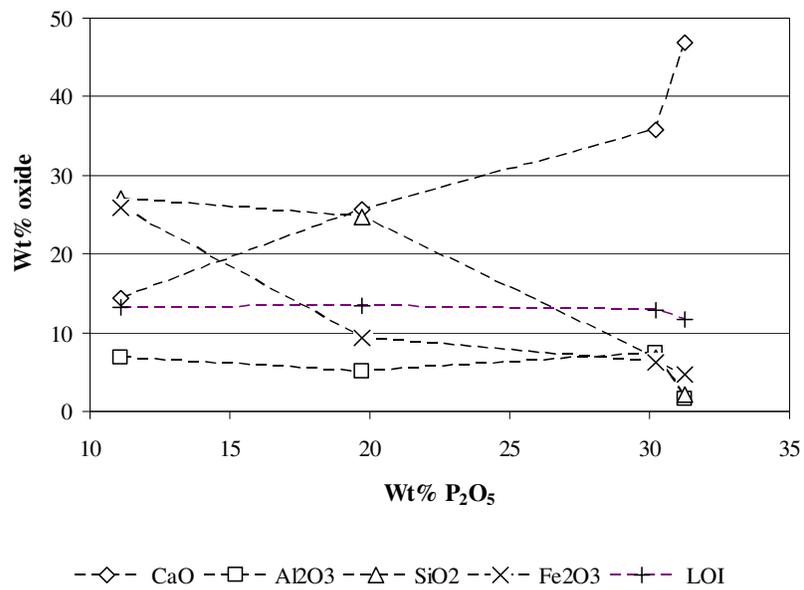


Figure 11. Variations in major elements CaO, Al₂O₃, SiO₂, Fe₂O₃ and LOI (Loss on Ignition) concentrations relative to P₂O₅ contents in the different forms of Ogun Phosphate Rock.

Table 1. Major and Minor Element in different forms of the Ogun Phosphate Rock

	OG1	OG2	OG3	OG4
SiO ₂	2.21	24.67	6.77	26.98
Al ₂ O ₃	1.55	5.07	7.47	6.84
Fe ₂ O ₃	4.74	9.34	6.28	25.78
CaO	46.80	25.66	35.72	14.43
P ₂ O ₅	31.28	19.73	30.20	11.12
K ₂ O	0.08	0.10	0.17	0.10
LOI	11.67	13.37	12.77	13.29
Total	99.48	98.95	100.37	99.39

The LOI represents the combined moisture and CO₂ loss.

Table 2. Trace constituents (ppm) in the Ogun phosphate rock.

		OG1	OG2	OG3	OG4
Cr	M	298	390	1365	402
V	M	121	368	309	524
Sr	M	1413	695	678	502
Ba	M	136	337	525	313
Y	M	205	161	79	107
V	M	121	368	309	524
S	M	3742	1513	1113	1132
Ni	m	50	50	41	80
Rb	m	3	6	5	6
U	m	20	19	22	29
Th	m	5	12	13	7
Sc	m	10	13	8	17
Zn	m	130	114	104	156
Nb	m	<1	7	6	10
Zr	m	40	115	44	160

The elements are characterized as main (M) and minor (m) of their abundance with 200ppm being taken as the division.

low K₂O and Na₂O levels in the phosphorite rock are considered highly desirable in material to be used as a source of P₂O₅ because minimal salt is added to the soil with the fertilizer.

The relatively wide variations in chemical composition was observed among the different forms of Ogun Phosphate Rock is typical of sedimentary phosphorites as these rocks are renown for their lateral and vertical variability. The main trace elements values varied widely and often by a factor of over 4 times, (Cr 298 ppm to 1365 ppm; V 121 to 524 ppm; Sr 501 to 1 413 ppm. The analysis of sulphur did not distinguish between sulphate and organic sulphur, and although in all cases <0.40 wt% could contribute to soil acidification. Gypsum rich horizons are known within the Ogun phosphorite beds and development of the phosphate resources must take account of their presence. The minor trace elements Zr and Nb also show wide variation this was considered to be largely due to their very low concentration (Nb < 11

ppm and Zr 40 to 160 ppm) and the fact that element like titanium, concentrated in heavy mineral grains. Other minor trace elements showed only limited variation, Zn was present at higher concentration (104 to 156 ppm) while the other elements, notably the radionuclides present have low values (U 19 to 29 ppm; Th 5 to 13 ppm; Ni 41 to 80 ppm). The low values of alkalis, radio-enic elements and undesirable heavy metals indicates that direct use of OPR as phosphorus fertilizer can be considered environmentally safe.

Conclusion

Though Ogun phosphorite has potential as a low cost phosphorus fertilizer for sustainable crop production but the significant variations in the mineralogy and chemistry of the deposit was observed. Pellets of the same form still have significant variation in mineralogy and the final

product used as fertilizer in this experiment contains more of OG2 and OG4 (granular form) than OG1 and OG3 (the nodular form). The fertilizer value (P_2O_5 content) of Ogun phosphorite depends solely on the proportion of each of the form present in the mixture collected from the mining site thus making it extremely difficult to get a fixed value to quantify P_2O_5 content in Ogun phosphate rock.

The chemical variability of the major elements, particularly the phosphate content, may present difficulties to producing a consistent commercial product.

However, the differences on the other hand may provide be a good opportunity of having different grades of Ogun phosphate fertilizer by varying the ratio of nodular and granular phosphorite. Therefore careful geological and chemical studies will be required at the specific mining site to establish the lithological sequence, phosphorus content and availability of each horizon in the sequence.

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