GEOCHEMISTRY AND PALEOENVIRONMENT OF THE PHOSPHORITES FROM THE AMEKI FORMATION, NIGER DELTA, NIGERIA

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ABSTRACT

The phosphorites of the Ameki Formation occur as nodules, pellets as well as primary phosphatic shales and siltstones. Geochemical analysis of the phosphate samples was carried out to determine its chemical composition as well as its depositional environment. The methodology applied include XRF, INAA, XRD and thin section petrography using Polarizing Microscope. The XRF result identified CaO- P_2O_5- F as the major mineral group, SiO_2, Al_2O_3, Fe_2O_3, MgO and TiO_2, which show minor occurrences and Cr, U, Pb, V, Cu, Zn, Se and Cd that occur in trace amounts. The nodules and pellets are of medium to high grade (25- 34wt% P_2O_5) whereas the primary phosphatic shales and siltstones are of low to medium grade (4.5– 22wt% P_2O_5). The phosphorites comprise mostly of francolites. The mean index of refraction estimated by Becke-line method using Standard Polarizing Microscope gave 1.634 and1.636.XRD analysis yielded an average values of9.243 (± 0.002) A° and 6.715 (± 0.002) A° for a and c crystallographic axes respectively with an axial ratio (c/a) of 0.726for unit cell parameter, suggestive of low degree of carbonate substitution. An increase in P_2O_5content is found to be accompanied by increase in CaO, CO_2 and F contents, but by a decrease in H_2O, organic carbon, SiO_2 and Fe contents indicative of amorphous solid phase of calcium phosphate. The phosphorite is interpreted to form under high biologic productive, shelf setting. High nutrient availability in the ancient sea is linked to upwelling along the West African Coastline during the Eocene.

KEYWORDS: Phosphorites; Geochemistry; Paleoenvironment; Ameki; Francolites; Nodules

INTRODUCTION

Sedimentary phosphorites are rocks that are significantly enriched in phosphorus over other types of rocks (Boggs, 2006). They contain 5 to 35% P_2O_5 and can be called by a variety of other names such as phosphate rock, rock phosphate and phosphates (Boggs, 2006; Nichol, 2009). Phosphorites are of special economic interest although their total volume in the geologic record is small (Boggs, 2006). Phosphorites occur in the low- latitude upwelling zones on the western shelves and continental margins of North and South America, Africa and India, as well as off the east coast of Australia (Baturin et al., 1972; Parker and Andseisser, 1972; Veeh et al., 1973; Burnett et al., 1980; Sheldon, 1981). They were also found on the floor of the Atlantic, Pacific and Indian Oceans (Baturin. 1982) and are recorded on the present ocean floor at shallow depths in the vicinity of coastlines. However, the largest phosphorite- bearing regions are situated along the west coasts of Africa and America, the east coast of the USA, off New Zealand and in the central part of the Northern Pacific (Baturin and Bezrukov, 1979). Formation of phosphate nodules in siliciclastic depositional systems is linked to upwelling, re- working and re- deposition (Föllmi, 1996; Tribovillard et al., 2006; Li et al., 2015). The process of phosphogenesis occur in two stages (Kolodny, 1980) viz; precipitation of apatite (CFA) or its metastable precursors by diagenetic process in a reducing basin by phosphorus mobilization in pore-waters and re- working and enrichment of the diagenetically formed phosphorite grains by mechanical concentration processes (Cook, 1976; Glenn et al., 1994; Föllmi, 1996; Filipelli, 2011) under oxidizing conditions (Kolodny, 1980). The concentration is considered to take place under high energy hydrodynamic regime (Föllmi, 1996; Trappe, 1998; Li et al., 2015). The prime genetic process in the formation of diagenetic phosphorites however, is believed to be the replacement of carbonate by phosphate (Ames, 1959; Simpson, 1964).

Depositional environments of ancient phosphorites and phosphatic sediments have been reconstructed using

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geochemical proxies (e.g., Galfati et al., 2010; Dumoulin et al., 2011; Khan et al., 2012; Dar and Khan, 2016; Garnit et al., 2017).

The Eocene Ameki Formation has been described asa clastic unit of about 1,550 m thick (Arua, 1982). Nwajide (2013) gave the maximum thickness of between 1,200 and 1,500 m for the formation. Lithologically, the formation is very heterogeneous and consists of alternating units of argillaceous, greenish- blue sandstones, clay stone, shale and white sandstone with thin limestone bands (Arua, 1982). 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. Two distinct subfacies recognized include; the lower fine to coarse sandstones with intercalations of shale and thin shelly (often coquinoid) limestone and the upper coarse, planar cross bedded sandstones, bands of fine, grey- green sandstone, and sandy clay (Nwajide, 2013).

Several workers have interpreted the environment of deposition based on its diverse and richly abundant assemblages of micro and macrofossils (Adegoke, 1969; Adegoke and Tevesz, 1974; Arua, 1982, 1988; Fayose and Ola, 1990; Nzekwe and Okoro, 2016). The paleoenvironment was variously interpreted as estuarine (White, 1926), shallow marine (Adegoke and Tevesz, 1974; Nzekwe and Okoro, 2016) and inshore sandy environment (Arua, 1982). Nwajide (2013) suggested the environment of deposition to be shallow marine with the presence of amber and lignite suggesting shallowing that marked establishment of swampy and in coaling conditions. The paleoenvironment of the phosphatic rocks of the Ameki Formation needs to be interpreted using the geochemical proxies.

The age of the Ameki Formation has been interpreted as Eocene (Berggren, 1960; Adegoke, 1969; Adegoke et al., 1980; Whiteman, 1982; Fayose and Ola, 1990).

This paper is aimed at determination of the chemical composition of the phosphatic rocks of the Ameki Formation, interpretation of its depositional environment and mode of formation of the phosphorites using geochemical proxies. Figure 1 is the geologic map of the study area.
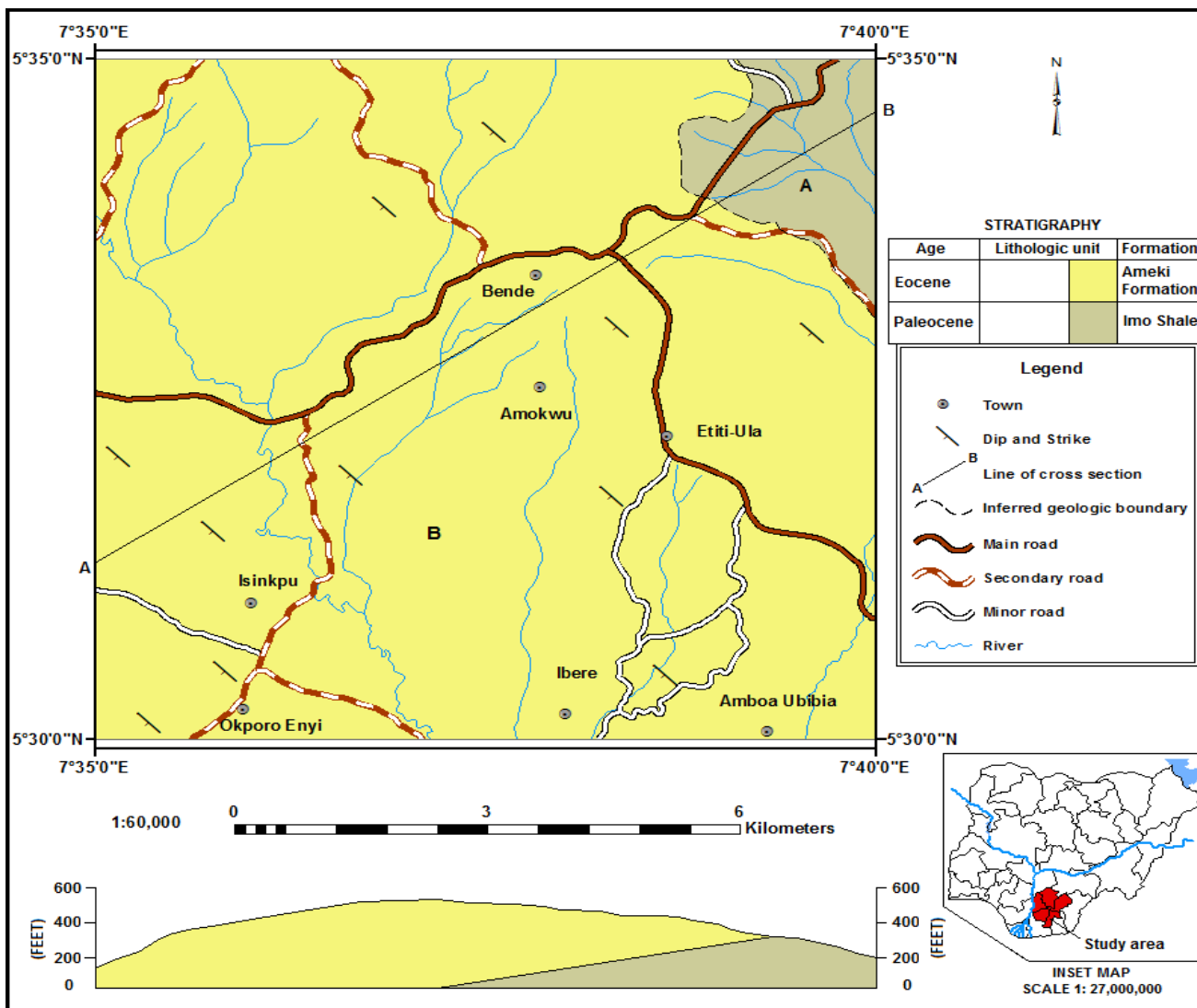

Fig. 1: Geologic map of the study area

REGIONAL TECTONICS AND STRATIGRAPHIC SETTING

The evolution of the Niger Delta Basin is related to the opening of the southern Atlantic Ocean during the break- up of Gondwana Supercontinent and installation of the Benue Trough in the early Cretaceous (Burke et al., 1972; Benkhelil. 1982, 1989; Hoque and Nwajide, 1984; Fairhead, 1988). The Benue Trough is a rift within the West and Central African Rift System and represents a major tectonic structure in the Nigerian sedimentation history. The trough after its development, was filled with both continental and marine sediments ranging in age from early Cretaceous to Santonian in its southern part (Table 1). The Santonian thermotectonics event later folded and uplifted the sediments in the Southern Benue Trough into the Abakaliki- Benue Anticlinorium (Murat, 1972) and there was translocation of the depositional axis which involved a simultaneous subsidence of the Anambra Basin and the Afikpo Sub-Basins to the northwest and southeast of the folded axis respectively (Murat, 1972; Burke, 1972; Burke et al., 1972; Benkhelil, 1989). The Anambra Basin after its evolution was filled from late Campanian to Danian with the sediments of the Nkporo Group, Mamu, Ajali and Nsukka Formations which conformably and successively overlie each other. Establishment of the Niger Delta occurred due to further subsidence of the Southern Benue Trough after the Anambra Basin was filled and sediments compacted. This subsidence induced the major marine transgression of the early Paleocene and thus sedimentation began in the Niger Delta basin.

The Imo Formation which is the basal outcropping lithostratigraphic unit of the Niger Delta was deposited during the late Paleocene transgression. The formation is conformably and successively overlain by the Ameki Group (middle to late Eocene) and Ogwashi-Asaba and Benin Formations. The Ameki Formation was deposited north of the Niger Delta and south of Anambra Basin (Short and Stauble, 1967).

Though the Southern Benue Trough, the Anambra Basin and the Niger Delta Basin are vertically stacked in the southern reaches (Table 1), they are separate stratigraphic entities (Nwajide, 2013).

Table 1: Stratigraphic succession in the southern Benue Trough, Anambra Basin and Niger Delta (from Reyment, 1965; Short and Stauble, 1967; Maron, 1969, Murat, 1972; Whiteman, 1982; Nwajide, 2013)

TIME SCALE				SEDIMENTARY UNITS			
Cenozoic	Quaternary			Niger Delta	Benin Formation		
	Pliocene						
	Miocene						
	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				Unconformity		
	Coniacian				Awgu Formation		
	Turonian				Ezeaku Group		
	Cenomanian				Mfamosing Limestone		
	Albian				Abakaliki Formation		
	Aptian				Awi Formation		
	Preaptian				? ? ? ?		
Precambrian				Basement Complex			

MATERIALS AND METHODS

Ten selected fresh samples of nodules, pellets and phosphatic shales and siltstones were collected from the outcrop sections of the Ameki Formation exposed at Bende-Ameke area in southeastern Nigeria for laboratory analyses. The samples were carefully labelled to avoid mix up.

Geochemical analysis for major and trace elements was done using Standard X- Ray Fluorescence Spectrometry (XRF) technique. Each of the dried samples was crushed to powdered form (200 mesh size) using an agate mortar. Major element composition and trace elements 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 trace elements were checked for using Instrumental Neutron Activation Analysis (INAA). Wet chemical methods were used to determine CO_2 and F contents while weight loss methods were used to determine loss of water content (H_2O^-) (at 120°C), and the loss on fusion (with lithium borate flux) at 1000°C.

The unit cell parameter was determined by X-Ray Diffraction (XRD) using Electric XRD- 5 Diffractometer with CuKα radiation.

The refractive index of four selected samples were also estimated by the becke-line method using Standard Polarizing Microscope.

Concentrations of P, Fe (III), Al, Ca and Ba were re-calculated from their oxides using the molar weight method and the degree of pyritization (DOP) was estimated based on Raiswell et al. (1988). The results of the major and trace elements distributions, unit cell parameters and index of refraction formed the basis for the interpretations.

RESULT

The phosphorites were collected in the field as nodules, pellets, primary phosphatic shales and siltstones. The result of XRF analysis is shown in Table 2. CaO has the highest concentration among the major oxides followed by P_2O_5. Concentrations ofNa$_2$O, K$_2$O, BaO, S, Cl and H_2O is less than 1wt% (Table 2a). For the trace elements, concentration in decreasing order of abundance in the phosphorites is as follow; Cr, U, Pb, V, Cu, Zn, Se, Cd (Table 2b). Ranges of concentrations of the re- calculated major elements are shown in Table 2c.

Table 2a: Ranges of major elements, oxides and organic matter in the phosphorites of the Ameki Formation

Constituents	Concentration (wt%)
P_2O_5	25.00- 34.00 in nodules 4.50- 22.00 in phosphatic shales and siltstones
Fe	3.40- 8.00
Fe_2O_3	1.25- 4.80
Al_2O_3	1.60- 3.80
Cl	0.02- 0.06
MgO	0.95- 2.05
CaO	49.00- 56.00
S	0.01- 0.04
SiO_2	3.00- 5.50
BaO	0.12- 0.14
Na_2O	0.13- 0.16
K_2O	0.31- 0.66
Ti	1.0- 3.00
H_2O	0.35- 0.68
CO_2	1.86- 3.25
F	2.30- 4.80
MnO	0.02- 0.08
Mn	2.00- 8.00
Organic matter	Nil- 6.00

Table 2b: Trace elements in the phosphorites of the Ameki Formation

Element	Concentration (ppm)
Zn	3.00- 5.00
Cu	2.00- 10.00
V	Nil- 30.00
Hg	Nil- trace
Pb	2.00- 38.00
Se	Nil- 5.00
Cr	Nil- 60.00
As	Not detected
Cd	Nil- 2.60
U	Nil- 50.00

Table 2c: Ranges of concentrations of the re- calculated major elements

Element	Concentration (wt%)
Fe (III)	0.87- 3.36
Ca	35.02- 40.08
Al	0.85- 2.01
P	1.96- 14.84
Ba	0.11- 0.13

The nodules and the pellets are of medium to high grades (25- 34wt% P_2O_5) whereas the primary phosphatic shales and siltstones are of low to medium grades (4.5 and 22wt% P_2O_5). The major mineral in the phosphorites is the Carbonate hydroxyl fluorapatites, consisting of CaO, P_2O_5 and F, and are referred to as francolites. Francolites have been described as the principal mineral in sedimentary phosphorites which exhibit several systematic isomorphous substitutions. These substitutions result in measurable variations of the crystallographic properties including unit- cell parameters (McClellan, 1980). The variability in chemical composition can be represented by $(Ca, Mg, Sr, Na)_{10}(PO_4, SO_4^{2-}, CO_3^-)_6 F_{2-3}$(Benmore et al., 1983).

The mean index of refraction (n_ε and n_ω) measured for the selected samples gave values of 1.634 and 1.636 respectively. Carbonate fluorapatite have been documented to have the refractive index (n) which ranges from 1.614 to 1.633 for n_ε and 1.622 to 1.640 for n_ω (Hand book of mineralogy, 2001- 2005 data publishing version 1). XRD analysis carried out on selected samples gave the values of 9.243 (± 0.002) A° and 6.715 (± 0.002) A° for a and c crystallographic axes respectively with an axial ratio (c/a) of 0.726 for unit cell parameters. The values are also not far from that of fluorapatite given as a = 9.36A°, c= 6.88A°, and c/a = 0.7350 (Gruner et al., 1937). This reflects the hexagonal crystal system (a= 9.34A°, c = 6.88 A° and a/c = 0.737) and thus suggests a low degree of carbonate substitution by phosphates.

SiO_2, Al_2O_3, Fe_2O_3, MgO and TiO_2 are minimal. Millisite and Wavellite, which have been referred to as the principal aluminum phosphate minerals occur in small quantities and constitute the accessory minerals. Goethite which is also present is associated with the primary phosphates whereas quartz is the only crystalline gangue which was identified.

The result of XRF analysis also revealed that the primary phosphatic shales and siltstones which have the P_2O_5 value ranges of between 4.5 and 22wt% contain between 49 and 50wt% CaO, 1.86 and 2.5wt% CO_2 and 2.3 and 2.5wt% F. On the other hand, nodules which have the P_2O_5 value up to 34wt% contain between 50 and 56wt% CaO, 2.6 and 3.25wt% CO_2 and 3.2 and 4.8wt% F (Table 3). These suggest the amount of P_2O_5 in the phosphorites to increase with increasing proportions of CaO, CO_2 and F. This is in agreement with the strong positive correlations which exist between them (Figs. 3a- c).

Furthermore, the values of H_2O, SiO_2, Fe and organic matter contents in the nodules are between 0.35 and 0.38wt%, 3 and 3.5wt%, 3.4 and 4wt% and 0 and 0.95wt% respectively, but in the primary phosphatic shales and siltstones, their values range from 0.48 to 0.62wt%, 4 to 5.5wt%, 5 to 8wt% and 3.2 to 6wt%, respectively (Table 3). This suggests decrease in their proportions with increasing P_2O_5 which is in agreement with the strong negative correlations which exist between them (Figs. 3d- g).

Table 3: Relationships between the proportions of P_2O_5 and other constituents of the phosphorites

Constituents	Nodules composition (wt%)	Primary phosphates (shales and siltstones composition (wt%)
P_2O_5	34.00	4.50- 22.00
CaO	50.00- 56.00	49.00- 50.00
CO_2	2.60- 3.25	1.86- 2.50
F	3.20- 4.80	2.30- 2.50
H_2O	0.35- 0.38	0.48- 0.62
SiO_2	3.00- 3.50	4.00- 5.50
Fe	3.40- 4.00	5.00- 8.00
Organic matter	Nil- 0.95	3.20- 6.00
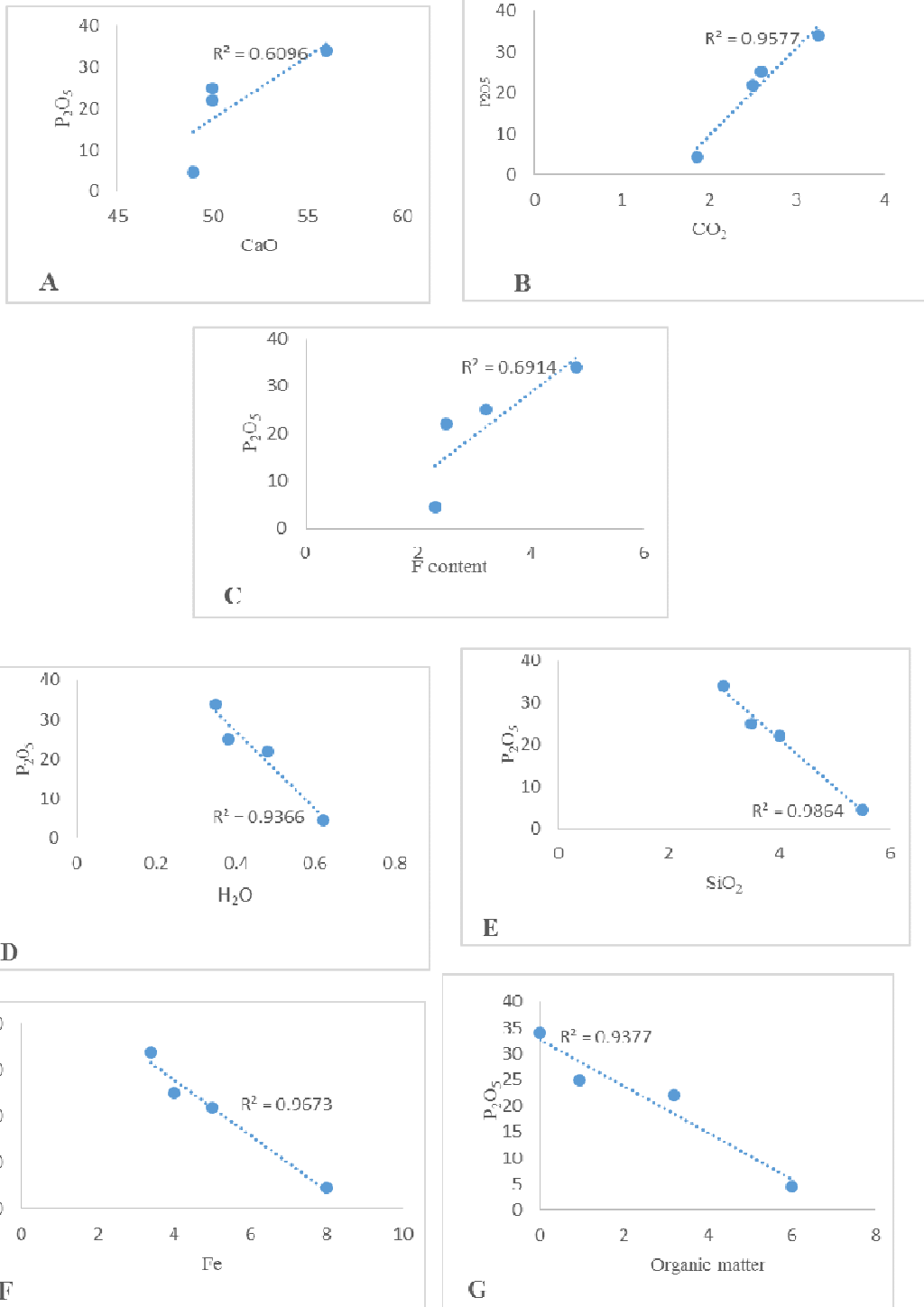
Fig 2: Relationships between P_2O_5 and (a) CaO (b) CO_2 (c) F (d) H_2O (e) SiO_2 (f) Fe (g) Organic matter

DISCUSSION

Sedimentary phosphorites are composed of calcium phosphate minerals, which are varieties of apatite with the principal types consisting of fluorapatite (CFA), given as $[Ca_5(PO_4)F]$ typically in cryptocrystalline masses (grain sizes <1μm) and are referred to as cellophane, the chlorapatite $[Ca_5(PO_4)Cl]$, and the hydroxyapatite $[Ca_5(PO_4)_3OH]$ (Glenn et al., 1994; Boggs, 2006). The fluorapatites have been reported as originating from hydrothermal veins (Glenn et al., 1994) and hydroxyapatite from vertebrate bones and teeth. Most phosphorites are said to be carbonate hydroxyl fluorapatites in which up to 10% of the carbonate ions can be substituted for phosphate ions in order to yield the general formula $Ca_{10}(PO_4.CO_3)_6F_{2-3}$ and are commonly called francolites. Detrital quartz, authigenicchert, opal- CT, calcite and dolomite are other common constituents of many phosphorites (Boggs, 2006). Clay minerals such as glauconite, illite, montmorillonite, and zeolite may also be present in some phosphorite deposits. Moderate abundance of organic matter is a characteristic of many phosphorites (Nathan, 1984).

Geochemistry of the phosphorites of the Ameki Formation studied are similar to that reported for South West Africa (Parker, 1971; Parker and Siesser, 1972; Dingle, 1975) and Midcontinent, USA (Ece, 1990). However, the P_2O_5 contents of the nodules from the Ameki Formation appears to be higher than that of phosphorites from South West Africa. The silica concentration is higher in the phosphorites of both South West Africa and Midcontinent, USA. Cronan (1980) observed that P values increase with lithification in South West Africa. The P_2O_5 content reaches 8% or more in the lumps of phosphatized mud, 25% in unconsolidated nodules, 27- 29% in brittle fine grained nodules and 31- 33% in compact concretions. Higher value of some constituents such as CaO (49- 56 wt%) was recorded in the phosphorites of the Ameki Formation. The maximum value for SiO_2 in the phosphorites of the Ameki Formation is 5.5wt% which is quite low compared to that of South West Africa and Midcontinent, USA. Variations in the average whole-rock geochemical composition of phosphatic materials has been attributed to varying degree of dilution of the phosphatic materials by non-phosphatic components (Burnett, 1977; Birch, 1990). The minimal concentrations of SiO_2, K_2O and Fe_2O_3 in the phosphorites of the Ameki compared to that of South West Africa suggest lower quartz and glauconite contents in the deposit. Ameki Phosphorites also recorded an increase in CaO, CO_2 and F with increasing P_2O_5 whereas H_2O, SiO_2, Fe and organic matter concentrations decreased with increasing P_2O_5. This situation is suggestive of amorphous solid phase of calcium phosphate (Baturin, 1971; Robert and Vercoutere, 1986). The strong positive correlations between P_2O_5 and CaO, P_2O_5 and CO_2 as well as P_2O_5 and F (Figs. 3a- c) indicate association in the crystal structure of the francolites whereas, the strong negative correlations which exist between P_2O_5 and SiO_2, P_2O_5 and H_2O, P_2O_5 and Fe as well as P_2O_5 and organic matter show association with alumnosilicate group. Chen et al. (1996) outlined the sources of terrigenous alumnosilicates (clay minerals and fine grained rock- forming minerals)in the marine environment to include; discharge from the atmosphere in the form of air bone dusts and rivers as suspended matter.

DEPOSITIONAL ENVIRONMENT
Paleo-redox Condition

Trace element abundances in sediments and sedimentary rocks are very important tool in the reconstruction of paleodepositional conditions (Lyons et al., 2003; Algeo, 2004; Tribovillard et al., 2006). The response of some of the trace elements/metals such as V, Mo, Cr, Co and U to redox variations (i.e under oxic and anoxic conditions) in the ambient sea has been employed as useful parameters in the reconstruction of the redox conditions in both recent and ancient sedimentary basins, especially in relationship to extensive organic matter deposition and sulfide formation in O_2- depleted environment (e.g Jones and Manning, 1994; Algeo and Magnard, 2004; Tribovillard et al., 2006; Rimmer, 2004; Rimmer et al., 2004; Nameroff et al., 2004; Pattan and Pearce, 2009). The V/Cr and Ni/Co ratios are very useful paleoredox tools also (Hatch and Leventhal, 1992; Jones et al., 1994; Morford and Emerson, 1999; Tribovillard et al., 2006; Pattan and Pearce, 2009; Yao et al., 2017). The threshold value for the Mo content of terrigenous detrital matter is 1 ppm (Dean et al., 1997) and 10 ppm for black shale (Vine and Tourtelot, 1970). Rare occurrence of Mo, Co and Ni with depletion of V and Cr (0- 30 ppm and 0- 60 ppm respectively) compared to the threshold for black shale (Vine and Tourtelot, 1970) are typical attribute of the Ameki Formation. These are suggestive of deposition under oxic condition. Scott and Lyons (2012) noted the adsorption of Mo to Mn- oxides and little Mo enrichment below sediment- water interface in a fully oxic condition. Also Mn is an element generally depleted under anoxic conditions, whereas elements such as Cu, Ni, Mo, V, Zn and Cd are enriched due to formation of organometallic complexes of sulfide minerals (Calvert and Pedersen, 1993; Tribolvillard et al., 2006; Wignall et al., 2007; Zhou et al., 2012). Mnvalue ranges of 2- 8 wt%, depletion of Zn, Cu and Cd and complete absence of Mo and Ni in the Ameki Formation is in agreement with an oxygenated water condition. Minor enrichment of U has also been reported for oxic-suboxic environments (Yao et al., 2017). Based on the redox classification of the depositional environment of Jones and Manning (1994), V/Cr ratio of <2 and Ni/Co ratio of <5 suggest oxic conditions. The average V/Cr ratio for the Ameki Formation is 0.48 whereas Ni and Co are lacking. These are also in agreement with oxygenated water condition. However, Neubert et al. (2008) is of the opinion that V/Cr ratio as well as U and V enrichment could not be used as indicators of depositional conditions in phosphatic rocks owing to the disturbances of the system by the substitutions of V and U into apatite.

DEGREE OF PYRITIZATION (DOP)

The intensity of pyrite formation in a sedimentary rock is an important paleoenvironmental tool which needs to be integrated with other environmental parameters (Taylor and Maquaker, 2011). DOP is defined as the ratio of pyrite- bound Fe (II) to pyrite- bound Fe (II) plus HCl-extractable Fe (III) (Raiswell et al., 1988). Values of DOP close to 1 indicates that nearly all of the originally deposited reducible Fe (III) is now in the form of Fe (II)

in pyrite, and are regarded as indicating the presence of euxinic conditions in which abundant sulfide was available (Lysons and Severman, 2006; Taylor and Macquaker, 2011). DOP values that are less than 0.8 indicate the availability of sulfide as the limiting factor controlling pyrite formation and thus suggestive of normal open- marine conditions. It is worth noting that DOP should be employed alongside other indicators because a high DOP value close to 1 may not always indicate oxygen- free conditions (Schieber, 2009). The calculated DOP for the Ameki Formation varies from 0.70- 0.80 with sulfur contents of between 0.01 and 0.04 wt%. The paleoenvironment is interpreted as normal-open marine. The interpretation is in line with Arua (1988) that proposed normal to near normal marine for the Ameki Formation. Taylor and Maquaker (2011) summarized the processes which occur in three contrasting shallow- marine settings as follow; firstly, a situation where the reduction of detrital iron oxides is coupled to, or takes place in pore- waters that contain high concentrations of sulfide generated by sulfate reduction. This type of condition is obtainable in a shallow marine shelf sediment. Secondly, the case where abundant iron oxides susceptible to bacterial iron reduction are available, but the sulfide contents in the pore-water is low. Thirdly, system starved of reducible Fe (III) but containing abundant, dissolved reduced- sulfur species. Canfield (1989) noted that when iron oxides are present in relatively high concentrations, dissolved sulfide is nearly absent from sediment pore waters (with concomitant high concentrations of dissolved Fe), even in the presence of active sulfide production by sulfate reduction. A combination of experimental result and diagenetic modelling have shown that bacterial reduction of Fe oxides may be the source of pore-water Fe, and greater amounts of Fe are reduced by reaction of sulfides with iron oxides (Canfield, 1989). It is important to note that the concentration of Fe (III) in sediments is important but, its bioavailability is of more important (Canifield, 1989), because not all Fe (III) minerals are equally bioavailable (i.e can be readily reduced by bacterial processes at surface temperature). However, goethite and hematite which are Fe oxide minerals recorded in this study have been noted to be reducible and react to some extent with sulfide (Canifield, 1989).The Ameki Formation is deposited in a shallow marine shelf setting in which pore- water sulfide concentration is relatively lower than the bioavailable Fe (III) concentration.

PALEOPRODUCTIVITY
The amount of organic matter produced in per unit area and per unit time is referred to as paleoproductivity (Dong and Wang, 1996). Paleoproductivity proxies include; P, Ba and organic carbon or organic matter (Filippelli and Delaney, 1994; Murray and Leinen, 1996; Dymond and Collier, 1996; Chen et al., 1998; Pujol et al., 2006; Paytan and Griffith, 2007; Algeo et al., 2011; Yong et al., 2012). P/Al or P/Ti and Ba/Al or Ba/Ti are also useful proxies for paleoproductivity (Dean et al., 1997; Latimmer and Filippelli, 2002; Algeo et al., 2011). These ratios are preferable proxies than absolute P and Ba because they mitigate the dilution effects of organic matter and authigenic minerals on the absolute P and Ba contents in terrigenous organic matter (Algeo et al., 2011; Latimmer and Filippelli, 2012). P is a major

constituents of skeletal material. Its sources in the world oceans were outlined to include; the composition of atmospheric precipitation and dust, river, underground and glacial run off, abrasion of the shores, volcanic and hydrothermal activities as well as the composition of cosmic materials (Baturin (1982). Ba are formed in oceanic particles as a result of decomposition/uptake in microenvironments and Al and Ti are sourced from terrigenous detrital matter (Dymond et al., 1992; Calvert and Pedersen, 1993; Algeo and Maynard, 2004; Yong et al., 2012). The P/Al or P/Ti and Ba/Al or Ba/Ti can represent the nutrient conditions and the amount of organisms in the ancient sea respectively (Yong et al., 2012). For the Ameki Formation, the P/Al and P/Ti range from 2.30 to 7.40 and 1.96 to 4.95 respectively. These suggest high paleoproductivity (Ageo et al., 2011; Yong et al., 2012). Ba/Al and Ba/Ti values that vary from 647 to 1294 and from 433 to 1100 respectively, also agree with high paleoproductivity (Dean et al., 1997; Yong et al., 2012). These indicate Ameki Sea (shallow marine) to have supported large number of organisms on the water surface above the shelf. This interpretation is in agreement with shallow marinemacro and microfossils such as pelecypods, gastropods, nautiloids, echinoids, radiolarians, remains of whales, foraminifera and ostracodes recovered from the formation by previous workers (e.g. Newton, 1922; Eames, 1957; Berggren, 1960; Adegoke, 1969; Adegoke and Tevesz, 1974; Adegoke et al., 1980; Whiteman, 1982; Arua, 1982, 1988; Arua and Rao, 1987; Fayose and Ola, 1990; Nzekwe and Okoro, 2016). It also supported the interpreted depth ranges of occurrence of the faunal assemblages stated to range from 10- 65m (Jones, 1951; Buchanam, 1958) and did not exceed 80 m (Arua, 1988). Studies have related high biologic productivity to phosphorites formed in upwelling systems along coastlines (Brookfield et al., 2009; Dumoulin et al., 2004, 2008, 2011). Dumoulin et al. (2011) employed paleontologic and sedimentologic data as upwelling evidences of phosphorite formation and noted that abundance of radiolarians may be analogous to modern plankton accumulations in high- productivity upwelling zones whereas accumulation of organic- rich shale and multiple beds of granular phosphorites is indicative of a setting with high productivity. Ameki Formation is affected by upwelling oceanic hydrothermal fluid. Arua and Rao (1987) emphasized the influence of Benguela current on the water temperature of the Ameki Sea.
Organic carbon content of the Ameki Formation varies from 0 to 6 wt%. The variation is attributed to redox conditions of deposition. Oxic condition destroys organic matter whereas its preservation is enhanced by a reducing (anoxic) condition (Yong et al., 2012). The organic carbon does not represent the content of the original organic matter in the formation, thus, there is possibility of underestimation of paleoproductivity. In spite of this limitation, high paleoproductivity remains the attribute of the Ameki depositional condition.
Strong upwelling currents, high biological productivity, plankton blooms and large amount of organic matter production and subsequent accumulation trigger phosphate genesis in the shelf margin environment (Brookfield et al., 2009). Other controlling factors include; changes in sea level, rates of sedimentation, depth of impingement of the oxygen- minimum zone on the shelf and slope, concentration of various elements

and ions and Eh, pH and alkalinity of the pore fluids (Robert and Vercoutere, 1986). Marine phosphorites have also been linked to formation under anoxic bottom settings (Ece, 1990; Brookfield et al., 2009). The phosphorites formed may occur as primary phosphorite mud (microphorite), concretions or nodules, microconcretions in muds (pellets in mudstones), and as lenses and layers in encasing sediments (e.g Kennedy and Garrison, 1975; Birch, 1980; Glenn and Arthur, 1988; Föllmi and Garrison, 1991; Glenn et al., 1994).This supported the formation of Ameki Phosphorites under anoxic bottom setting. Ameki phosphorites are dominantly francolites, which have been described as the most abundant authigenic phosphate phase in marine sediments (McConnell, 1973; Jahnke, 1984). Formation of Ameki phosphoritesis explained using the model of Baturin (1982) which consists of biogenic- diagenetic processes of phosphate formation in fine grained sediments and subsequent reworking of the sediments to concentrate the apatite. The Ameki phosphorites is associated with sediments which accumulated beneath the West African coastal upwelling zones during the Eocene and were influenced by warm Benguela Oceanic Current from the Southern Atlantic Ocean. The nutrient- rich waters with phosphorus upwelling in this zone stimulated high primary productivity by phytoplankton and thus supported large number and diversity of species (e.g. pelecypods, gastropods, nautiloids, whales, radiolarians, echinoides, foraminifera, ostracodes etc) in the water surface above the shelf setting. Downward flux of phytodetritus was likely situation, and accumulation of much in the sediments due to high organic flux, high biological oxygen demand, as well as short sinking transit time on the shallow shelf (Crosby and Bailey, 2012). The calcareous parts/exoskeleton of the organisms which were abundant and diverse sourced the calcium carbonate (Birch, 1990). This is evidenced from the high concentration of Ca in the phosphorites. Body tissues of the organisms when dead, with time decayed gradually after burial i.e the microbial processes that mediate phosphorus cycling by creating sinks for the marine phosphorus acted upon the dead tissues of the organisms buried in the sediments (Schulz and Schulz, 2005; Aming et al., 2008, 2009; Goldhammer et al., 2010) and thus, led to phosphate pumping into the pore- waters of the sediments. Super saturation of the pore water with respect to apatite resulted in the precipitation of the phosphate. Brookfield et al. (2009) noted an increase in dissolved phosphate level under anoxic conditions and microbial activity. Phosphorite nodules thus, formed within the sediments by diagenetic reactions between the organic- rich sediments and their phosphate- enriched pore- waters. The low carbonate substitution by phosphate recorded by the phosphorites suggest minimal re-working typical of early stage of diagenesis. Eocene sea level fluctuations controlled the phosphate formation and re-working (Baturin, 1971; Glenn and Arthur, 1988, 1990; Grimm, 1992).

6. CONCLUSION

The geochemistry of the phosphorites of the Ameki Formation reveals that most of the phosphorites are francolites and have similar in composition to the phosphorites of South West African and Midcontinent, USA, except for minor variations. The variation in abundance of the elements and oxides is attributed to varying degrees of dilution from non phosphatic components. The Ameki phosphorite is interpreted to form in a shallow marine (shelf) setting. Paleoenvironment is characterized by high biologic productivity at the water surface and relatively higher reducible Fe (III) and lower sulfur concentrations in the pore- water. Upwelling by Benguela Current along West African Coast and sediment re- working were the possible mechanisms of formation and concentration of the phosphorites. Transgression and regression played a vital role.

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