DISTRIBUTION PATTERNS OF TRACE METALS IN SOILS OF GBONGAN-ORILEOWU AREA, SOUTHWESTERN NIGERIA

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ABSTRACT

One hundred and eighty six (186) *in situ* soil samples of the B - horizon were collected around Gbongan-Orileowu area of Osun State, Southwestern Nigeria for a reconnaissance geochemical soil survey. The objective was to determine the distribution pattern of some trace metals in the area with a view to discovering any indication of metallic mineralization and possible correlation with the underlying bedrock. The samples were air-dried and sieved to obtain the minus 230 micron fractions which were split into two portions for hot aqua regia acid digestion and pH determinations. The solutions obtained from the digestion were analyzed for Ag, As, Au, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, and Zn using Atomic Absorption Spectrometric methods. The resulting data were used in preparing distribution maps of the elements in the study area, employing the location point symbol method. Simple statistical treatment was also carried out on the data to determine the mean and standard deviation for each element. With these, the spatial distributions of the trace elements in the area were discussed. The pH of the soils range from 4.70 to 7.59 and this reflects the geochemical distribution patterns of trace metals in the area. The spatial distribution maps of the elements showed similarity in the distributions of Co, Cr, Fe, Ni, Mn and Pb. This suggests close associations between these elements none of which showed any significant anomaly. The association might be due to the scavenging actions of Fe-Mn oxides on the other elements. Ag, Au and Sn on one hand and Zn on the other hand showed significant anomalies, which were thought to be due to mineralization and anthropogenic activities respectively. As, Co, Cu, Fe, Ni and Pb probably occur as sulphides within reported underlying ultramafic rocks or Au bearing quartz veins or both. It is probable that Au and Ag occur as disseminations within the ultramafic rocks, aside from their occurrence in the veins, while Sn is most probably from the pegmatites. The very high Zn in the area is probably due to contamination.

Keywords: Significant anomalies, Ultramafic, Anthropogenic, Mineralization

INTRODUCTION

The presence of high degree of weathering, which usually gives rise to formation of thick overburden, and widespread occurrence of dense vegetation cover in the tropical rain and equatorial forest areas, constitutes important obstacles to geological mapping. These features result in a low outcrop density, which hampers direct prospecting for minerals or preparation of an accurate geological map. Geochemical techniques have been shown to be capable of playing an important role in a regional reconnaissance survey of such areas (Freyssinet,1993; Key *et al.*, 2004; Adesiyan *et al.*, 2014 and Owoeye *et al.,* 2015). Key *et al.* (2004) and Owoeye (2012) emphasized the suitability of geochemical techniques for geological mapping and exploration in Nigeria, a tropical country, sometimes devoid of outcrops over wide areas owing to huge overburden.

Soil surveys are widely used in geochemical exploration and very successful results have been achieved especially with surveys conducted on residual soils. Their success is based on the fact that during the process of weathering and leaching, anomalous concentration of elements from underlying mineralization/rock may become incorporated in the soil, as well as in other weathering products and in groundwater (Morsy, 1995; Alexakis, 2008 and Knight *et al.*, 2011). Thus, the characteristic dispersion pattern in a soil is a reflection of the parent rock, the concealed ores and the effect of environmental factors. Adesiyan (2010) and Knight *et al.* (2011) concluded that the strength of residual anomalies over restricted areas might be directly related to the grade of mineralization in the underlying bedrock.

A reconnaissance geochemical soil survey of Gbongan-Odeyinka-Orileowu area of Osun State was carried out. The area is delineated by

longitude $4^{0}15^{'}$ and $4^{0}30^{'}$ E and latitude $7^{0}14^{'}$ and $7^{0}31^{'}$ N; a thickly forested tropical region (Fig. 1). Residual soil is the geochemical sample most often employed after stream sediment in geochemical surveys. It is more appropriately used in detailed study. However, because of its relatively high dependability, it can also be employed in reconnaissance survey. In this study, reconnaissance geochemical soil survey is applied

as a follow up of the reconnaissance geochemical stream sediment surveys earlier carried out in parts of the area (Alao, 2003; Adesiyan and Adekoya, 2008 and Adesiyan et al., 2014). The soil survey is aimed at defining more precisely and isolating areas of high metallic mineralization potential that can possibly be traced to the primary mineralization, if any, in the underlying bedrock.
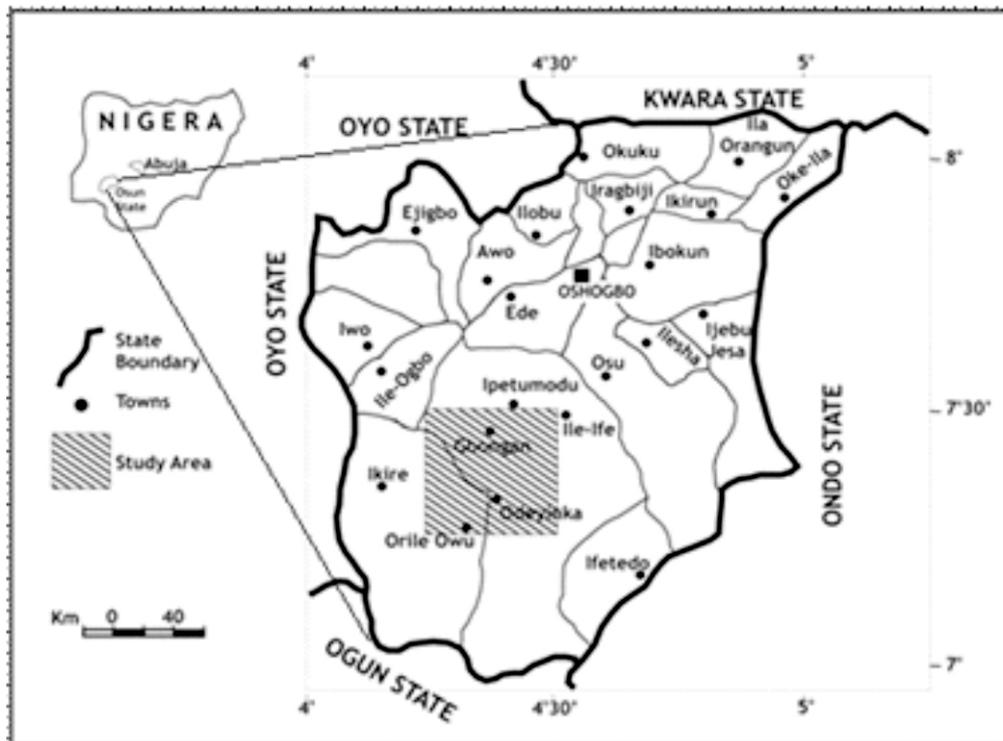

Figure 1: Map of Osun State showing Gbongan-Odeyinka-Orileowu Area.

GEOLOGICAL SETTING

The study area lies in the Precambrian crystalline Basement Complex of Southwestern Nigeria, which consists of a wide variety of metamorphic and igneous rocks and has been shown to be polycyclic, with isotopic ages ranging from 2800 Ma to 4500 Ma (Rahaman, 1988; Dada, 2006 and Adetunji et al., 2016). It forms part of the Pan-African mobile belt situated east of the West African Craton and west of the Congo Craton.

A number of workers have tried to group the wide varieties of rocks of the Nigerian Basement Complex into different divisions. Adekoya et al. (2003) gave a four – fold tectono-stratigraphic divisions and the main features of these rocks have been discussed in details. This seems to

explain best the field associations and age relationship among the lithologic units, namely (i) Migmatite-Gneiss-Complex of Archaean to Early Proterozoic; (ii) the Proterozoic Schist Belts; (iii) the Pan African Granites and associated granitoids; and (iv) late Neoproterozoic to Early Palaeozoic minor felsic and mafic intrusives.

However, the Basement Complex rocks underlying the area (Fig. 2) as shown on the geological map of Iwo region (de Swardt et al., 1965) consist of various rock types. Of the nine rock units, the pegmatitised schists cover the greater part of the area occurring around the central portion, the southwestern and southeastern portions and trending in the north-south direction. Following the pegmatitised

schists in area extent are both undifferentiated gneisses and migmatite and pegmatite, which appear to occur in almost equal proportions. The migmatite trends north - south in the western part of the study area with a portion occurring within the pegmatitised schists around the north central part while the pegmatite, which appears as intrusions within the pegmatitised schists underlies parts of the eastern and southern area of

the map (Fig. 2). Granite gneiss occurs in the eastern part and around the pegmatite, giving the impression of being intruded by the latter. Other rock types occur in minor proportions and these include the undifferentiated schists with some gneiss in the northeastern part and granodiorite, biotite and biotite-muscovite granite, porphyritic granite and charnockitic meta-intrusives, all in the north western part.
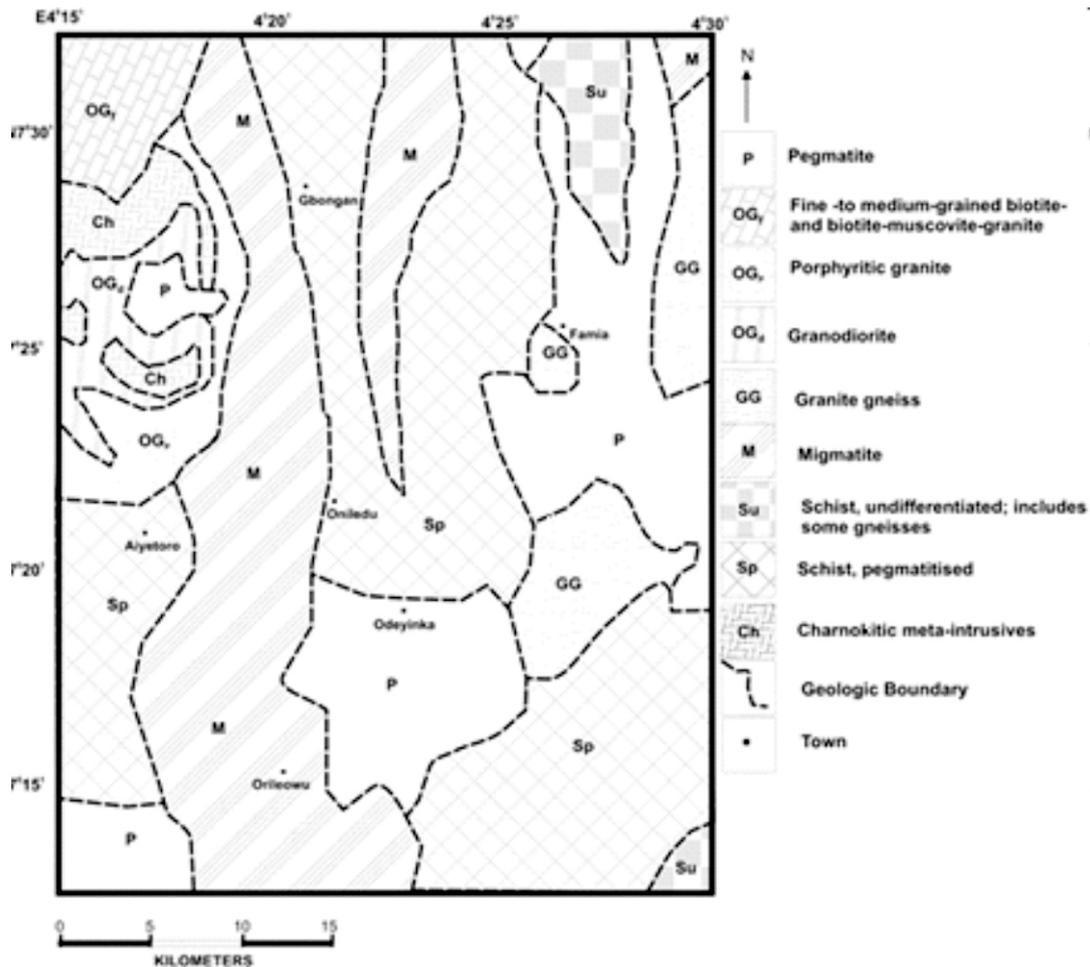

Figure 2: Geological Map of Gbongan–Odeyinka–Orileowu Area.

MATERIALS AND METHODS

In this study, 186 *in situ* soil samples of the B – horizon were collected from an area of approximately seven hundred and sixty square kilometers (Fig. 2). The B-Horizon of the soil profile was preferred for sampling because of the thickness of C-Horizon in the tropical region and a recent investigation by Arisekola *et al.* (2011) of the Nigeria Geological Survey Agency in a closer area also shows that B-Horizon can also give good results. The samples were taken at intervals of

between 500 m and 1000 m in such a way as to avoid rocky ground, areas close to river valleys, settlements, refuse dumps and other possible sources of contamination. The sampling was based on a 1:50,000 topographic map, sheet 262 (Apomu NE) and the actual sampling points were determined using the Global Positioning System (GPS).

The samples were air dried, disaggregated and sieved with a 230 micron nylon sieve. The

fractions passing the sieve were then reserved for digestion and determination of pH. Measurement of the pH of each of the samples was performed at room temperature in soil/water suspensions at soil to water ratio of 1:3 using ultra-pure deionized water. The soil/water suspensions were shaken with a Stuart Scientific SF1 Flask Shaker for 30 minutes and then allowed to equilibrate for another 30 minutes. The pH meter (Orion 420 A plus) was standardized at pH 4.0 and 7.0, and the meter electrode was inserted in the suspensions while the latter were being shaken. The measurements were taken when stable pH readings were obtained (modified after Mosetlha, 2007).

One gramme (1.0 g) of each of the samples was digested with 10 mL of aqua regia (mixture of HCl and HNO_3 in ratio 3:1) on hot plate (70 $^{\circ}$C $\pm$15 $^{\circ}$C) for 1 hour and filtered into 25 mL volumetric flask, which was made up to mark with ultra-pure deionized water. The resulting solutions from the digestion were analysed for Ag, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn using the Varian Spectra AA Flame Atomic Absorption Spectrometer and for As, Au and Cd using the Shimadzu AA-6800 platform type graphite furnace Atomic Absorption Spectrometer equipped with deuterium background corrector at the Department of Chemistry, University of Botswana, Gaborone, Botswana. Analytical precision and accuracy were determined by the analysis of duplicates, repeated analysis of some samples where necessary and insertion of standard solutions as checking standards at intervals of 50 samples. Both precision and accuracy were reasonable and satisfactory.

RESULTS AND DISCUSSION

The data obtained for the 13 trace elements determined in the 186 soil samples collected for this study, were subjected to simple statistical treatment to obtain some basic statistical parameters (see details in Adesiyan *et al.*, 2014). From these parameters, the threshold values for the elements were calculated (Table 1). Threshold, according to Levinson (1974), is the upper limit of normal background values, background itself being the normal range of concentrations for an element or elements in an area. In exploration geochemistry, the determination of threshold is

important because it is the value above which the concentration of any element is considered anomalous.

The analytical data were also used to prepare location point symbol map for each of the elements; to facilitate visual enhancement of the spatial distribution patterns of the elements in the study area.

pH of the Soils

The solubility of most elements and the stability of their compounds are extremely sensitive to the pH of the aqueous environment. Only a few elements are normally soluble throughout the entire pH range. Most metallic elements are soluble only in acid solutions and tend to precipitate as hydroxides (or basic salts) with increasing pH (Adesiyan, 2010 and Knight *et al.*, 2011).

In this study, the pH of the soil samples ranges between 4.70 in location 172 (underlain by granite gneiss) and 7.59 in location 28 (underlain by pegmatitised schists). However a pH of 6.00 - 6.99 recorded the highest frequency, covering 78.0 % of the values. About 92.5 % of the soil samples have pH values that range from 4.70 – 6.99 and the remaining 7.5 % reveals values of between 7.00 and 7.59. Thus, it can be inferred that the pH of soils of the study area is largely weakly acidic.

Various workers, notably, Kehinde-Philips and Tiez (1995), Knight *et al.* (2011) and Adesiyan *et al.* (2014) have reported the role of pH in controlling the solubility and precipitation of elements in an aqueous environment. For example, Cu, Pb, Zn, Ni and Ag go into solution under acidic conditions (low pH) but are precipitated under high pH. The analytical results of soils of the study area confirm this observation. For instance, Cu recorded a low concentration of 3.5 ppm at location 172 where the pH is 4.7 whereas it has a high concentration of 102.0 ppm at location 13 where the pH is 6.7. For Ni, a high concentration of 126.3 ppm was recorded at location 85 where the pH is 6.7 while a low concentration of 11.9 ppm was obtained at location 150 where the pH is 5.2. On the basis of the foregoing, it can be deduced that the geochemical distribution patterns of the elements in the soil of the study area reflects the prevailing pH conditions of the soils.

Table 1 :   Summary of basic statistical parameters for screened raw soil geochemical data of the study area

Elements	Range of Metal Concentrations in ppm	Arithmetic Mean Values $\overline{X}$	Median	Standard Deviation	Threshold =($\overline{X}$ + 2S)	Coefficient of Variation
Ag	0.02 - 7.36	2.41	2.24	1.50	5.41	62
*As	6.38 - 5795.17	1056.41	772.92	992.72	3041.85	94
*Au	0.17 - 162.64	18.40	9.65	24.63	67.66	137
*Cd	0.26 - 404.25	50.90	27.27	65.76	182.42	129
Co	2.06 - 352.45	44.00	25.82	52.16	148.32	119
Cr	0.33 - 246.71	29.36	17.11	36.86	103.08	126
Cu	2.38 -102.03	25.10	22.53	16.92	58.94	67
**Fe	0.79 -10.51	4.16	3.90	1.91	7.98	46
Mn	12.98 - 9460.63	1039.29	575.97	1539.54	4118.37	148
Ni	0.63 - 126.32	19.85	16.99	14.98	49.81	75
Pb	2.78 - 186.79	36.80	31.55	27.99	92.78	76
Sn	0.18 - 171.58	57.66	40.79	47.30	152.26	82
Zn	3.55 - 7085.36	510.75	242.37	897.46	2305.67	176

* – Given in ppb

** – Given in %

Distribution of Elements

Certain chemical elements show a marked affinity for rocks with a basic or ultra-basic character while others are relatively enriched in acid rocks (Key *et al., 2004;* and Reimann and Garrette, 2005*)*. Thus, one can infer that the trace element contents in superficial materials like soils are more or less directly linked to the composition of the underlying bedrock. Therefore, there is the possibility of utilizing the results of multi-element soil geochemical prospecting to define the geology of an area, apart from its usefulness in delineating areas of economic mineral prospect. The metal contents of the soils in the study area as it would be seen later show considerable variations from one area to the other. Despite this, certain broad characteristic distribution patterns of the elements can be observed. To this end, the distribution of trace elements in the study area is discussed using the location point symbol maps for illustrations. The maps are super-imposed on the geological map of the area to aid the description of elemental distribution. The mean value of each of the elements is compared with the average abundance of the element in the soil, earth crust and some rock types (Table 2) to consider the significance of the elements in the study area.

Table 2: Average abundance of elements in the earth's crust, ultramafic rocks, soil, granite and granodiorite.
(After Levinson, 1974 and Rose, et al., 1979)

(All values in ppm except for As, Au and Cd which are in ppb and Fe in Percentage)

Element	Earth's Crust	Ultramafic/Mafic	Granite	Granodiorite	Soil	Mean values
Ag	0.07	0.06	0.04	0.07	0.1	2.41
As	1800	1000	1500	2000	1000-50000	1056.41
Au	4	5	4	4	2	18.40
Cd	200	200	200	200	100-500	50.90
Co	25	150	1	10	1-40	44.00
Cr	100	2000	4	20	5-1000	29.36
Cu	55	10	10	30	2-100	25.10
Fe	4.65%	9.40%	1.42%	-	2.10%	4.16
Mn	950	1300	500	1200	850	1039.29
Ni	75	2000	0.5	20	5-500	19.85
Pb	12.5	0.1	20	15	2-200	36.80
Sn	2	0.5	3	2	10	57.66
Zn	70	50	40	60	10-300	510.75

Silver

Silver is a chalcophile metal which can occur in nature in the native form, although it is most commonly found as a sulphide or sulphosalt, or as a minor element in a sulphide (Kabata-Pendias and Pendias, 2001).

The element was detected in 151 samples out of the 186 samples analysed. It has a concentration range of 0.02 ppm to 7.36 ppm and a mean value of 2.41 ± 1.5 ppm (Table 1). This mean value is relatively high when compared with the average abundance of Ag in soil, ultramafic rocks and granite which are 0.1 ppm, 0.06 ppm and 0.04 ppm, respectively (Table 2). The location point symbol map (Fig. 3A) shows an even distribution of Ag over the study area without indicating lithologic influence. However, with a threshold value of 5.41 ppm, there are seven anomalous values of between 5.63 ppm and 7.36 ppm forming a NE – SW trend at the southeastern part of the area where pegmatite and granite gneiss are the underlying rocks. Apart from these, there are a few relatively high values (3.61 – 5.42) ppm scattered over the area with a cluster also around the southeastern portion, in an area underlain by pegmatite and pegmatitised schists.
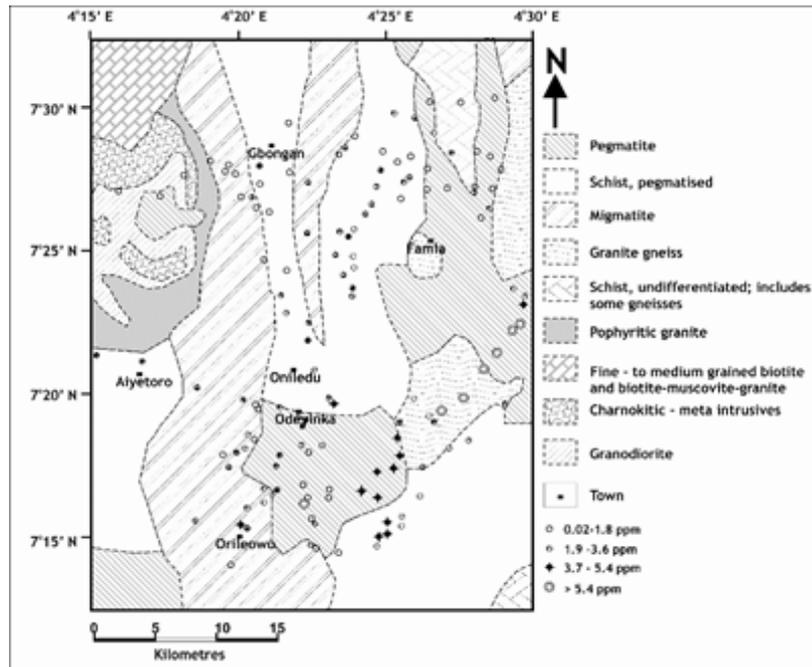
Figure 3A: Location Point Symbol Map of Silver Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Since the mean value of silver (2.41 ppm) in soils of the study area is greater than its average abundance in soil and the rocks underlying the area (Table 2), the abundance of silver in this area may be considered high. Consequently, the anomalous values of silver in the area are significant and may be related to the occurrence of primary sulphide mineralization probably in quartz veins occurring within the rocks of the area.

Arsenic
Arsenic is a chalcophile element which shows strong coherence with Au in practically all types of Au deposits, except the Witwatersrand (Kabata-Pendias and Pendias, 2001). It can be found in minor amount in sphalerite and trace in pyrite while its most abundant ore mineral is arsenopyrite (Plant *et al.*, 2001 and Alexakis, 2008). Arsenic was detected in 180 samples (Table 1). It has a very wide concentration range of 6.4 ppb to 5795.2 ppb with a mean value of 1056.4 $\pm$ 992.72 ppb and coefficient of variation of 94 %. The threshold value for arsenic in this area is 3041.9 ppb, thus there are eight anomalous sites scattered around the north central and the south central portions, in areas underlain by pegmatitised schists and pegmatite, respectively, as shown by the location point symbol map (Fig. 3B). Apart from this, one anomalous value occurs to the

western portion where the underlying rock is pegmatitised schists and there are a number of fairly high values scattered all over the area. It is noteworthy that the portions underlain by migmatite in the study area record very low concentration of As except in few places where this rock has contact with pegmatitised schists.

When the mean value of arsenic in this area, which is 1056.4 ppb, is compared with the average abundance of As in soil and the earth crust which are 1000-50,000 ppb and 1800 ppb respectively (Table 2), the abundance of arsenic in the study area is low. Consequently, the few anomalous values recorded are insignificant and may not be related to occurrence of As deposit, rather they may indicate the presence of some sulphide minerals in which arsenic is present in trace amounts. Elueze (1977) reported that the areas around Itagumodi and between Iyere and Amuta in Ife-Ilesa Schist Belt are characterized by relatively high density of anomalous arsenic values. He inferred that this is related to the occurrence of sulphide bearing amphibolites which occur in the area. Adesiyan *et al.* (2014) also reported the common pathfinder for gold (Arsenic) is not associated with the precious metal in the study area and the weak correlation between As and Au buttress the fact that As could not serve as a pathfinder element for Au in the locality.
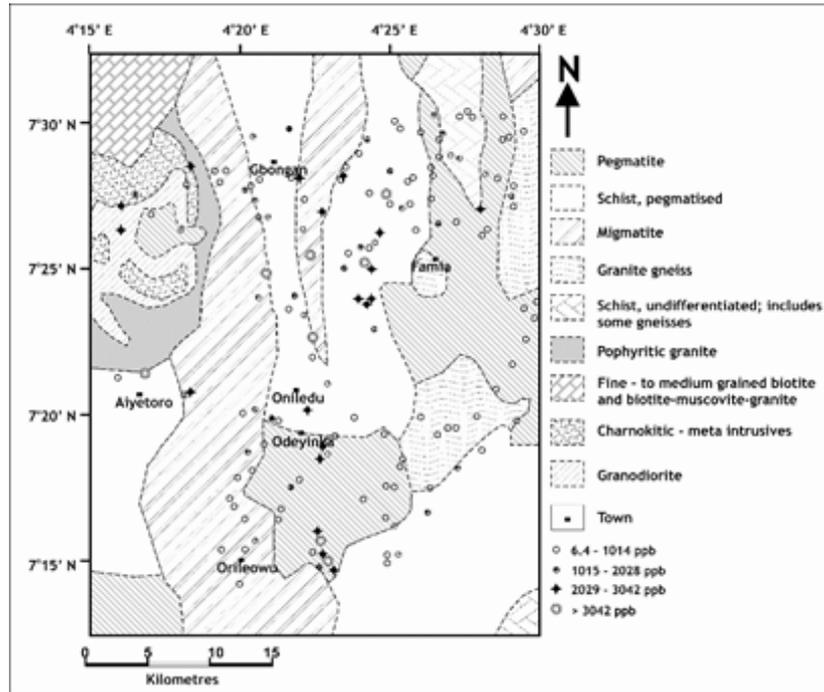
Figure 3B: Location Point Symbol Map of Arsenic Distribution in Soils of Gbongan Odeyinka-Orileowu Area.

Gold

Gold (Au) is a precious metal which commonly occurs in the native form. It also associates with Ag, As, Sb, Hg, Se, and Te in precious metal deposits and with Fe, Zn and Cu in many sulphide deposits (Kabata-Pendias and Pendias, 2001; Swiecki, 2005).

Au was detected in 154 out of the 186 samples analysed. Its concentration range is from 0.17 ppb to 162.4 ppb and it has a mean value of 18.4 ppb. The threshold value is 67.7 ppb and given this value there are only six anomalous values scattered in the northeastern, north central, south central and western portions of the area, which are underlain by undifferentiated schists, pegmatitised schist, pegmatite and undifferentiated gneiss and migmatite (Fig. 3C). Also, there are a few other fairly high values sandwiched between the anomalous and low values in the same area.

A comparison of the mean value of Au (18.4 ppb) in the soil of the study area with its average abundance in some earth materials including soil (Table 2), suggests that the Au concentration in the anomalous sites of the area is relatively high

and is considered significant. This might indicate the presence of primary gold mineralization around these locations, which may occur within quartz veins or as disseminations within some rocks, particularly the schists. Woakes and Bafor (1983) have reported that regionally, primary gold deposits are associated with some Schist Belts (example, Ilesa, Maru, Anka and Kushaka) and that they are often spatially related to amphibolites and regional NE–SW to N–S fault or shear zones, with no specific relationship to Older Granites or BIF. Wright et al. (1985) noted that the primary gold of the Nigerian Basement Complex occurs in form of veins, lenses, stringers, reefs and similar bodies in quartz and quartz-feldspar-tourmaline rocks. Moreover, Oyinloye (1997) reported that the quartz veins which host the Iperindo primary gold deposits are pure massive quartz, occupying fractures in the host biotite granite gneiss where they form a stock work structure. According to him, the quartz veins contain gold, sulphides, K-feldspar and minor chlorites. Adesiyan and Adekoya (2008) and Adesiyan et al. (2014) established that gold occur in this study area and is hosted by schists and granite gneiss.
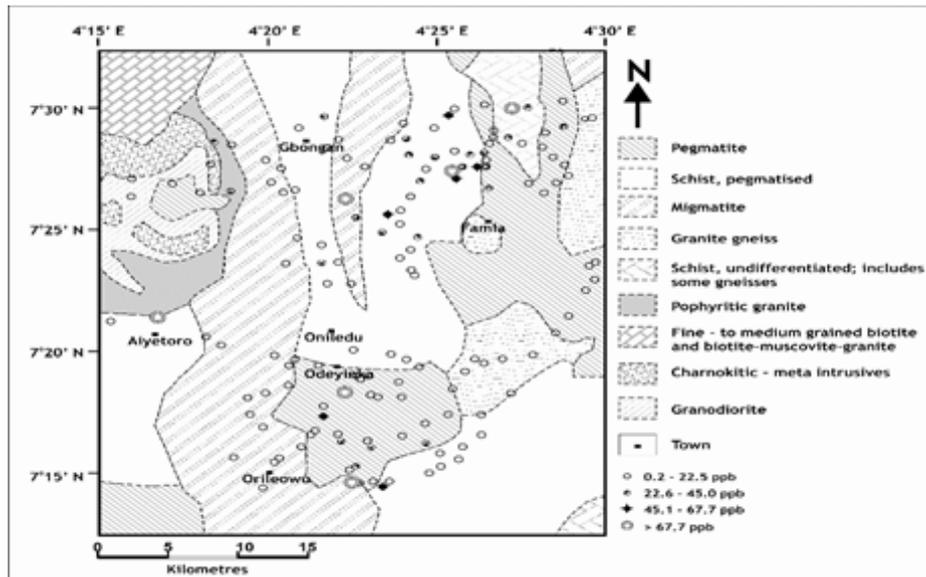
Figure 3C: Location Point Symbol Map of Gold Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Cadmium (Cd)

Cadmium is a chalcophile element which shows an almost universal association with Zn (Kabata-Pendias and Pendias, 2001). The main Cd mineral is greenockite (CdS) but Cd also occur in some other minerals notably sphalerite, galena, boulangerite and bournonite. The highest concentration of Cd is found in sphalerite (Smith, 1999).

Cadmium is widely distributed in the study area as it was detected in 185 out of the 186 samples analysed. It has a concentration range of 0.3 ppb to 404.3 ppb and a mean value of 50.9 ppb. The threshold value of Cd is 182.4 ppb and consequently, there are twelve anomalous Cd values as seen in its location point symbol map (Fig. 3D). Apart from these, there are a few other fairly high values (121.7 ppb to 182.4 ppb) and together with the anomalous values they concentrate at the north-eastern and south-central portions of the study area, in parts underlain by schists and pegmatite. Only one anomalous value each occurs in the northwestern and western portions of the area underlain by migmatite.

When the mean value of Cd (50.9 ppb) in this area is compared with the average abundance of Cd in some earth materials, which include soil (Table 2), it was observed that the relative abundance of Cd in the area is low. Thus, the few anomalous concentrations are insignificant and may not be connected with Cd mineralization but rather serve as a pointer to the occurrence of sulphides and possibly vein-type Au mineralization in which the Cd occurs as traces in minerals like galena. According to Adesiyan et al. (2014), gold bearing quartz veins typically carry some sulphides; galena and pyrite being the most common.

Moreover, the location point symbol map of Cd in the study area (Fig. 3D) has a fairly similar feature to that of Au (Fig. 3C). This reflects the possibility of an association between Cd and Au in this area, similar to what Ajayi (1988), Elueze (1977) and Oyinloye (1997) reported in the Ife-Ilesha area. According to them, the spatial relationship of anomalous Cd areas with those of known gold deposits in Ife-Ilesha area could make Cd a possible pathfinder element for Au in the area. The occurrence of Au with Cd in factor of the R-mode varimax rotated factor analysis suggested that Cd could be a possible pathfinder for gold in the study area (Adesiyan et al., 2014).
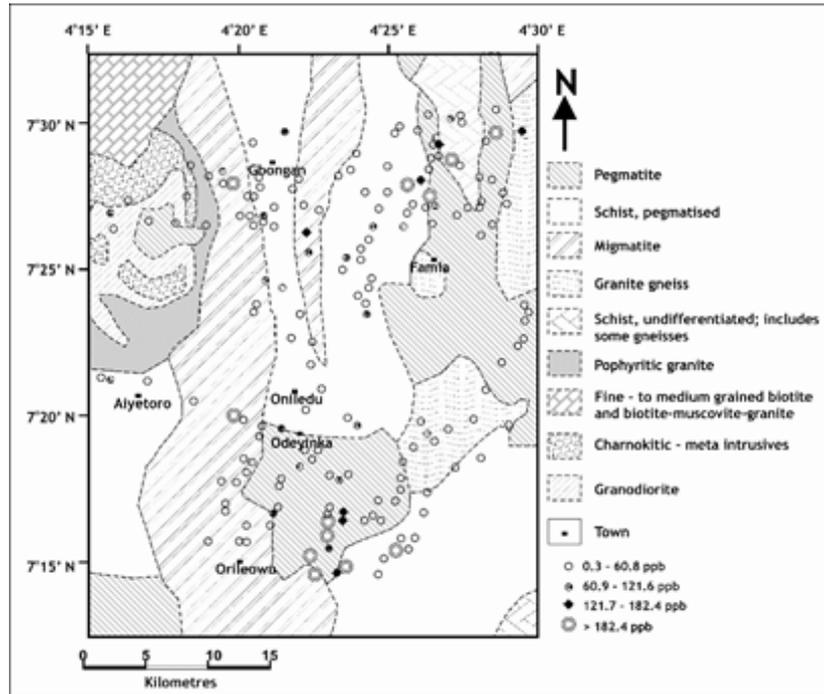
Figure 3D: Location Point Symbol Map of Cadmium Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Cobalt

Cobalt is mainly a chalcophile element and it associates with Mg and Ni in mafic and ultramafic rocks (Kabata-Pendias and Pendias, 2001). It is present in trace amounts in some major rock forming minerals such as olivine, amphibole, pyroxene and biotite as well as in magnetite. In hydrothermal deposits, cobalt readily enters as an isomorphous impurity of Fe in sulphide and arsenide ores and for this reason pyrite and arsenopyrite often contain Co in workable concentrations (Plant *et al.*, 2001).

The distribution of cobalt in the study area is very wide as it was detected in all the samples analysed. It shows a wide variation of concentration with values ranging between 2.1 ppm and 352 ppm and it has a mean value of 44 ppm. The threshold value of Co is 148.3 ppm and thus there are only nine anomalous values, some of which are scattered around the north central portion of the study area while three of them form a N–S trend at the southern portion (Fig.3E). Apart from these anomalous values, there are other fairly high values (98.9 ppm – 148 ppm) which occur around the anomalous sites, with only one in the northwestern portion of the area. Both the anomalous values and the fairly high concentration values of Co occur in portions mostly underlain by pegmatite and pegmatitised schists, and to a lesser extent migmatite and granodiorite.

When we compare the mean value of Co in the study area (44 ppm) with the average abundance of Co in soil and mafic/ultramafic rocks, which are 40 ppm and 150 ppm respectively (Table 2), the abundance of Co in the area is low. Thus, the few anomalous values are insignificant and probably result from co-precipitation of Co with Mn oxide. This is observable with the striking similarity in the distribution patterns of Co and Mn, as revealed by the elements distribution maps. The cobalt might have its origin in some underlying mafic/ultramafic rocks and or sulphide bearing quartz veins.
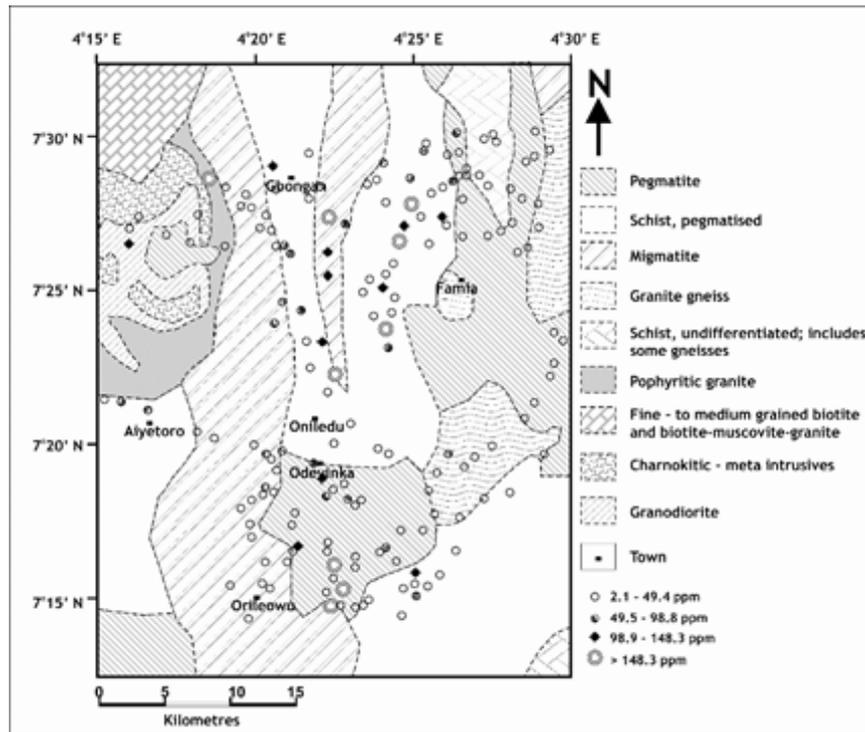
Figure 3E: Location Point Symbol Map of Cobalt Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Chromium

Chromium is a lithophile element, which possesses a strong association with Ni and Mg in ultramafic rocks. Cr^{+3} have identical size with Fe^{+3} and Al^{+3} and will readily concentrate in minerals, which will accommodate these trivalent ions, such as pyroxene (Mc Lennan and Taylor, 1991). However, Cr occurs in varying quantities in other rock-forming minerals such as olivine, amphibole, biotite, sphene, apatite, muscovite and tourmaline (Kabata-Pendias and Pendias, 2001).

Chromium was detected in 176 out of the 186 samples analysed. The elemental contents in the samples show a wide variation, with values ranging between 0.3 ppm and 246.7 ppm. Cr has a mean value of 29.4 ppm and a threshold value of 103.1 ppm. With this threshold value, there are only eight anomalous values scattered in the northern half of the area in parts underlain largely by pegmatitised schists and to a lesser extent by charnockitic meta-intrusives and migmatites.

This can be seen in the location point symbol map of Cr in the study area (Fig. 3F). There are also a few other fairly high values occurring without any discernable pattern. Generally, low values of Cr in this area are associated with pegmatite except in areas where the rock is in contact with pegmatitised schists.

When the mean value of Cr in the study area (29.4 ppm) is compared with the average abundance of the element in soil which is 5-1000 ppm (Table 2), the abundance of Cr in the study area is very low. The few anomalous concentrations of Cr in the area are therefore insignificant and may result from co-precipitation of the element with Fe - Mn oxides. This is reflected in the fairly close similarity in the distribution patterns of Cr, Ni, Pb, Fe, Mn and Co as shown by their distribution maps. The primary source of Cr in this area may be the mafic or ultramafic rocks present in the underlying bedrock.
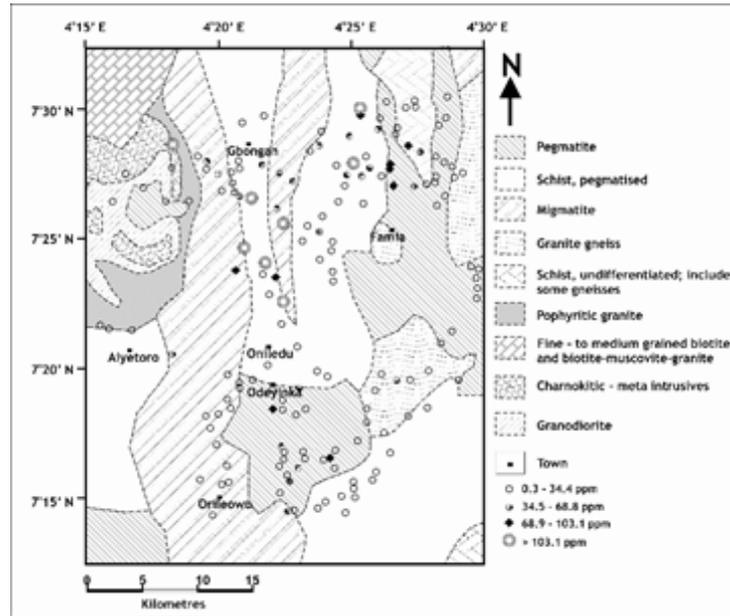
Figure 3F: Location Point Symbol Map of Chromium Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Copper

Copper is a chalcophile element which sometimes occurs in the native form. It is found in most rock forming minerals, since Cu will enter plagioclase and apatite, substituting for Na^+ and Ca^+ during magma crystallization. It will also enter minerals containing Fe^{2+}. Therefore, most ferromagnesian minerals will house copper. However, it prefers the sulphide phase to the silicate phase (Reimann and de Caritat, 1998). Cu has intermediate mobility, which is controlled by adsorption to Fe–Mn oxides and organic matter and precipitation by hydrolysis at pH >5.0 (Kabata-Pendias and Pendias, 2001).

The location point symbol map showing distribution of copper in the study area (Fig. 3G) revealed that the element is widely distributed in the area. It was detected in 185 out of the 186 samples analysed, and its concentration ranges from 2.4 to 102 ppm. This is consistent with the work of Ajayi (1988) who obtained a concentration range of between 6 and 196 ppm for Cu in the soils of part of Ife – Ilesha Schist Belt. The mean value of Cu is 25.1 ppm and the threshold value is 58.9 ppm. With this threshold, there are only six anomalous values, apart from a few other relatively high values of between 39.3 and 58.9 ppm. The anomalous concentrations together with the relatively high values of Cu occur at the north central and south central portions of the area in parts underlain by pegmatite and pegmatitised schists and, to a lesser extent, migmatite.

Comparing the mean value of Cu (25.1 ppm) in this area with the average abundance of copper in soil (2 – 100ppm) (Table 2), the abundance of Cu in the area can be said to low. In this connection, the few anomalous values are insignificant and may not be related to occurrence of Cu ore. However, since most rock forming minerals will house copper, occurrence of the anomalous concentrations may be a pointer to the co-precipitation of Cu with Fe-Mn oxides in the area underlain by heterogeneous rock types. Also, the association of Cu with the inferred sulphide bearing quartz veins may not be ruled out.
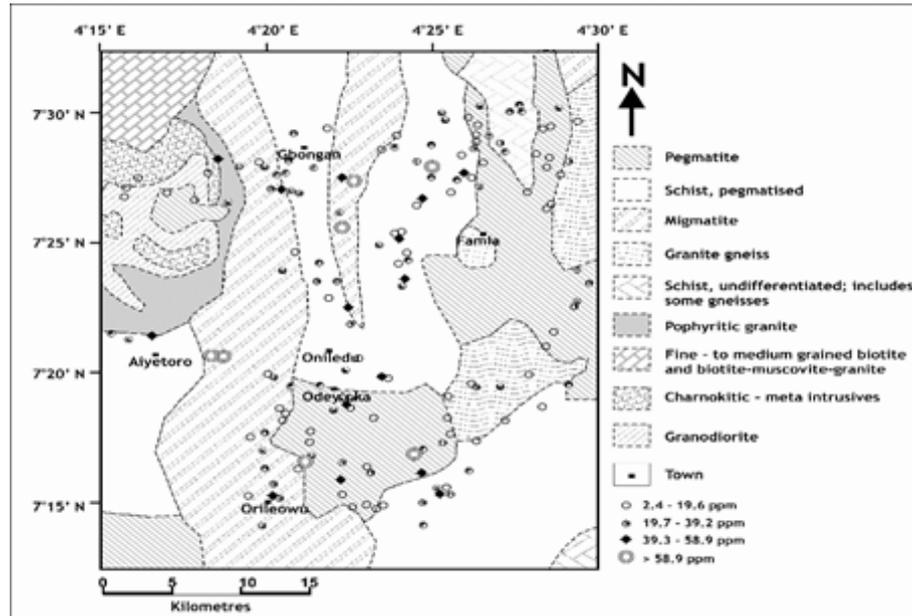
Figure 3G: Location Point Symbol Map of Copper Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Iron

Iron is a siderophile element, which occurs in deposits of different genetic types, with sedimentary and metamorphic deposits being the most important industrially (Kabata-Pendias and Pendias, 2001). Iron, together with Mg, plays an important role in the formation of a number of rock forming silicates like olivine, pyroxene, amphibole and mica, although it's major ore minerals are hematite and magnetite.

It is important to note that in soils overlying sulphide ores and in the beds of streams draining them, some of the ore metals are co-precipitated with Fe-oxides. Thus, the metal content of the resulting limonitic material may be a useful ore guide (Kabata-Pendias and Pendias, 2001).

Iron has a wide distribution in the study area, as it can be seen in its location point symbol map (Fig. 3H). It was detected in all the samples analysed with a concentration range of 0.8%-10.5% and a mean value of 4.2 %. The coefficient of variation

is 46 % and there is a threshold value of 8.0 %. With this value, there are only six anomalous concentrations of Fe in the study area, although we have a number of relatively high values. The anomalous values and the relatively high values together have a uniform distribution over the area without showing any lithologic influence. However, there are three clusters of high values in the area, with one around the central portion and the remaining two at the south central and southwestern portions of the area.

When the mean value of extractable Fe in the study area (4.2 %) is compared with the average abundance of Fe in soil (2.1 %), the earth crust (4.7 %) and mafic/ultramafic rocks (9.4 %) (Table 2), the abundance of Fe in the area is relatively moderate. Therefore, the few anomalous concentrations are insignificant and may not be attributed to Fe mineralization in the area but rather to the precipitation of Fe as oxides in the soils.
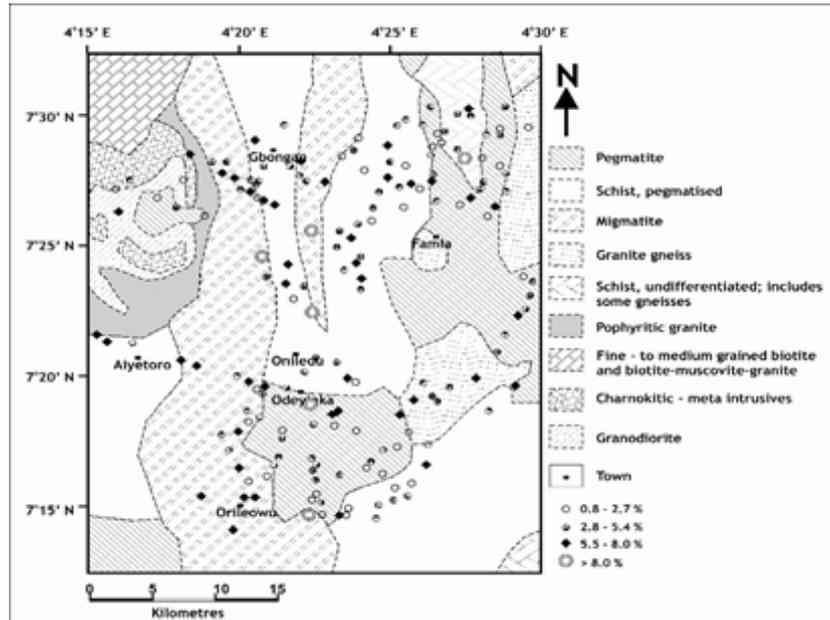
Figure 3H: Location Point Symbol Map of Iron Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Manganese

Manganese is a lithophile element which is associated mostly with mafic igneous rocks; a common associate of Mg and Fe in silicates (Kabata-Pendias and Pendias, 2001). Chemically, Mn stands closest to iron and it forms more than a hundred minerals, only few of which are widespread and rich. The principal ore mineral of Mn is pyrolusite, although it occurs in most mafic minerals. Manganese has intermediate to low mobility, except in the acid, reducing environment of organic swamps and bogs where it can move very readily (Kabata-Pendias and Pendias, 2001). Like Fe, the element Mn is extremely important in geochemical exploration because of the very large number of trace elements that may co-precipitate with or adsorb on Mn oxides (Reimann and de Caritat, 1998).

The distribution of Mn in soils of the study area is very wide as it was detected in all the samples analysed (Fig. 3I). Its concentration shows a wide variation with values ranging from 13.0 ppm to 9460.6 ppm. The mean concentration for Mn is 1039.3 ppm and it has a threshold value of 4118.4 ppm. With this threshold, there are only nine anomalous values which together with the other relatively high values are randomly distributed over the area. These anomalous and relatively high concentrations are distributed without much

lithologic control although there seems to be preference for high concentrations in the soils in areas underlain by pegmatitised schists and pegmatites.

When the mean value of Mn in the study area (1039.3 ppm) is compared with its average abundance in soil (850 ppm), mafic/ultramafic rocks (1300 ppm) and granodiorite (1200 ppm) (Table 2), the abundance of Mn in the area is somewhat moderate and thus insignificant. The few anomalous values and the other relatively high values may therefore be related to the precipitation of Mn as oxides in soils possibly derived from mafic/Mg and Fe rich silicate rocks in the study area. Ajayi (1988) obtained a concentration range of 80 – 4480 ppm for Mn in soils of part of Ife – Ilesa Schist Belt.

Moreover, there is a fair similarity in the distribution patterns of Mn and Fe in the study area, as revealed by their location point symbol maps. This is probably as a result of the scavenging effects of oxides of both metals on the same set of elements in the area, notably, Co and Pb. A closer look at the distribution maps of Co and Pb shows a striking similarity, which also suggests a similar distribution pattern for these elements. On the whole one can conclude that the distribution patterns of Mn, Fe, Co and Pb in the study area are similar.
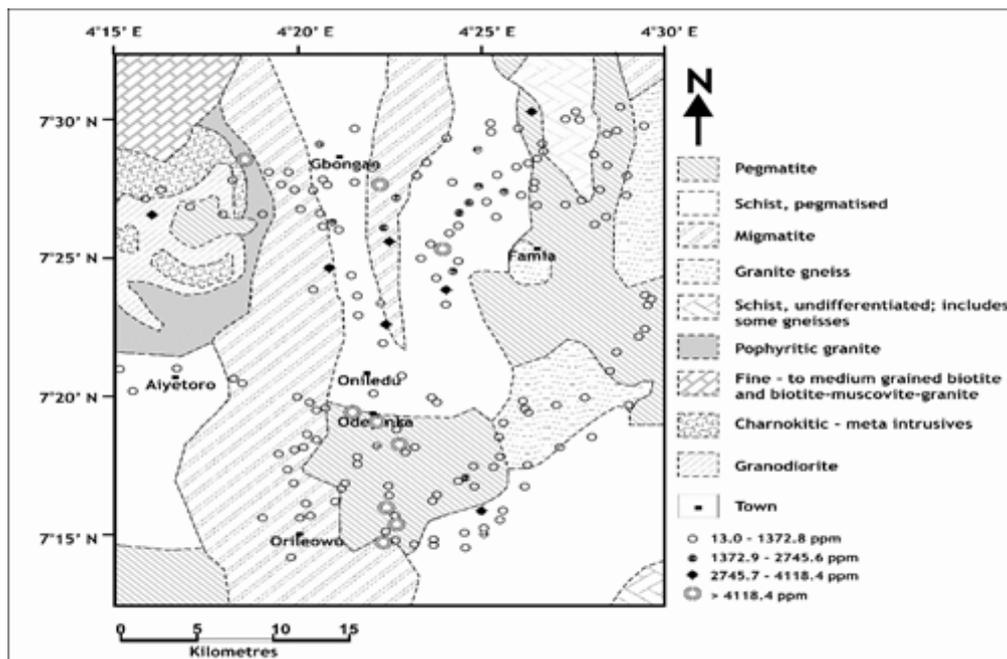
Figure 3I: Location Point Symbol Map of Manganese Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Nickel

Nickel is a siderophile and to a lesser degree, chalcophile element, which is chemically related to cobalt. It normally associates with Mg and Co in ultramafic and mafic rocks and with Co, Cu and Pt in sulphide deposits. It is found in rock forming minerals such as olivine, pyroxene, biotite and plagioclase and in magnetite. Mobility of Ni is relatively low and it is limited by co-precipitation with limonite and hydrolysis, where pH is greater than 6.5 (Kabata-Pendias and Pendias, 2001). The tendency of Ni to hydrolyse at pH above 6.5 is reflected in this work, as most of the samples with anomalous values of Ni have pH above 6.5.

Nickel was detected in 174 out of the 186 samples analysed. Its distribution in the study areas is relatively wide (Fig. 3J) and it has a concentration range of 0.62 ppm to 126.6 ppm with a mean value of 19.9 ppm and coefficient of variation of 75 %. This is consistent with the work of Ajayi (1988) who obtained a Ni concentration in the range of 6 to 100 ppm for soils from some parts of Ife–Ilesa Schist Belt. The threshold value of Ni in the study area is 49.8 ppm and based on this value, there are only seven anomalous Ni values. A part from these, there are a few other relatively high values, which together with the anomalous values are distributed randomly at the north central portion

of the area with only three occurring at the south central portion. The anomalous values and the relatively high values concentrate in area underlain mostly by pegmatitised schist at the north central part, while at the south central portion a few are found on soils overlying pegmatite and pegmatitised schists.

A comparison of the mean value of nickel (19.9 ppm) with the average abundance of nickel in soil (5 – 500 ppm) (Table 2) reveals that the abundance of Ni in the study area is low. Hence, the few anomalous values are insignificant and may not be related to any Ni mineralisation in the area. Rather, they may be attributed to the co-precipitation of Ni with Fe-oxide in the vicinity of mafic/ultramafic suites, more so that the distribution of Ni in the study area, as revealed by its distribution map (Fig. 3J) is similar to those of Co, Cr, Fe, Mn and Pb. Babafemi (1983) reported the occurrence of amphibolites and talc-tremolite-actinolite schists in Akinlalu, a part of the study area. Adesiyan (2010) concluded that, since Ni^{2+} substitutes readily for Mg^{2+} and Fe^{2+}, a high background concentration of the element in amphibolite must be expected. He obtained relatively high values of Ni (> 100 ppm) from some stream sediments predominantly within amphibolite zone of Ife–Ilesa Schist Belt. He also

obtained some isolated high values (>100 ppm) within the micaceous Schist Belt. Similarly, Ajayi (1988) reported that the distribution map of nickel in soils of Ife–Ilesa Schist Belt reveals that the greater percentage of high concentrations falls within the area underlain by amphibolite. Also, Zhai *et al.* (2003) concluded that the concentrations of heavy metals in Gaborone (capital city of Botswana) rural soils are strongly influenced by the bedrock above which they are found. It is thus possible to infer that the origin of Ni in the study area is the underlying mafic/ultramafic rocks.
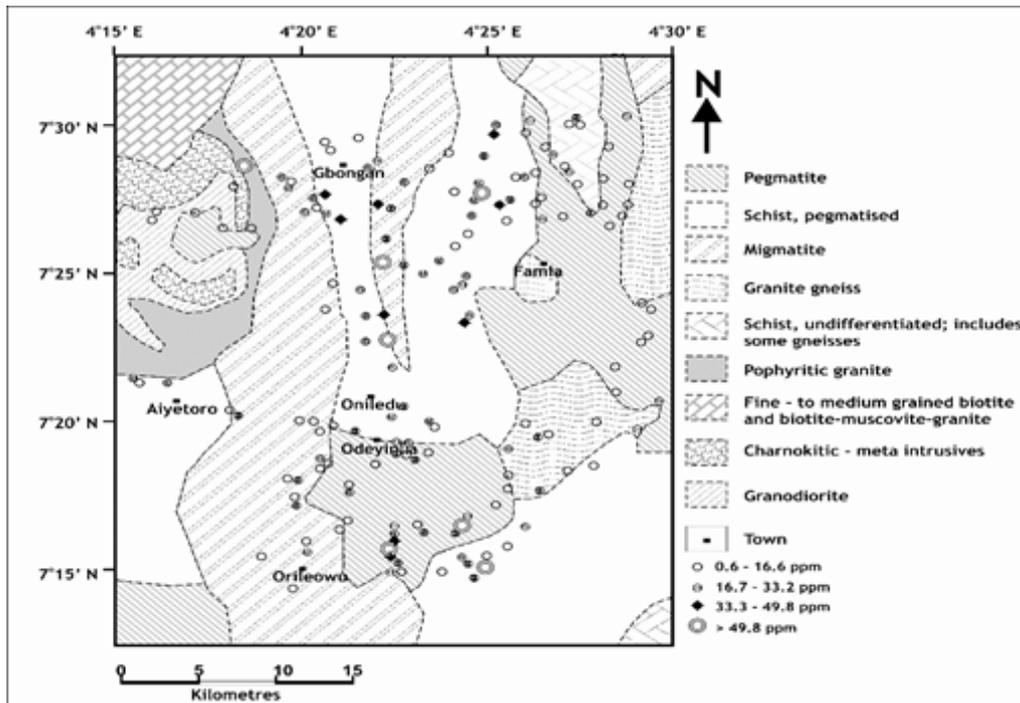

Figure 3J: Location Point Symbol Map of Nickel Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Lead

Lead is a chalcophile element which commonly associates with Ag in precious metal deposits and with Fe, Zn, Cu and Sb in many sulphide deposits (Kabata-Pendias and Pendias, 2001). It is more often found as Pb^{2+} and occurs in trace amounts in major rock forming minerals like amphibole, micas and K-feldspars. Mobility of lead is relatively low as it is restricted by its tendency for adsorption to Mn – Fe oxides and insoluble organic matter.

The distribution of Pb in the study area is very wide as it was detected in 183 out of the 186 samples analysed (Fig. 3K). It has a concentration range of 2.8 to 186.8 ppm, with a mean value of 36.8 ppm and coefficient of variation of 76 %. The threshold value of lead in this area is 92.8 ppm and thus there are only five anomalous values randomly distributed at the northern half of the area. Apart from these, there are other relatively high values (61.9 – 92.8 ppm), some of which are also randomly distributed at the northern half, while others are concentrated at the central portion of the southern half of the area. The anomalous values together with the relatively high values at the northern half of the study area occur predominantly in soils overlying pegmatitised schists, with a few in soils developed on other rock types. In contrast, the high values at the southern half of the area are restricted to soils underlain by pegmatite.

When the mean value of Pb in the study area (36.8 ppm) is compared with its average abundance in soil (2 – 200 ppm) (Table 2), the abundance of Pb in this area is rather low and thus insignificant. The few anomalous concentrations may result from accumulation of Pb in soils of the area due to co-precipitation of the element with Fe – Mn oxides

or from a possible occurrence of sulphide bearing Au quartz veins. Woakes *et al.* (1987) have reported that gold bearing quartz veins in Nigeria often contain some sulphides, galena and pyrite being the most common. Moreover, the abundance of feldspar in the pegmatites of the study area and mica in the gneisses and migmatite may be a source of the available Pb that co-precipitates with Fe – Mn oxides. The fact that Pb occurs in trace amounts in major rock forming

minerals (Kabata-Pendias and Pendias, 2001) is buttressed by this study which reveals that high Pb values are likely to be favoured by the high feldspar content of the underlying pegmatite bedrock. This is consistent with the observation of Adesiyan and Adekoya (2008) on the accumulation of Pb in pegmatite in which it occurs in amazonite feldspar. Also Smith *et al.* (1996) reported the enrichment of lead in acid igneous rocks.
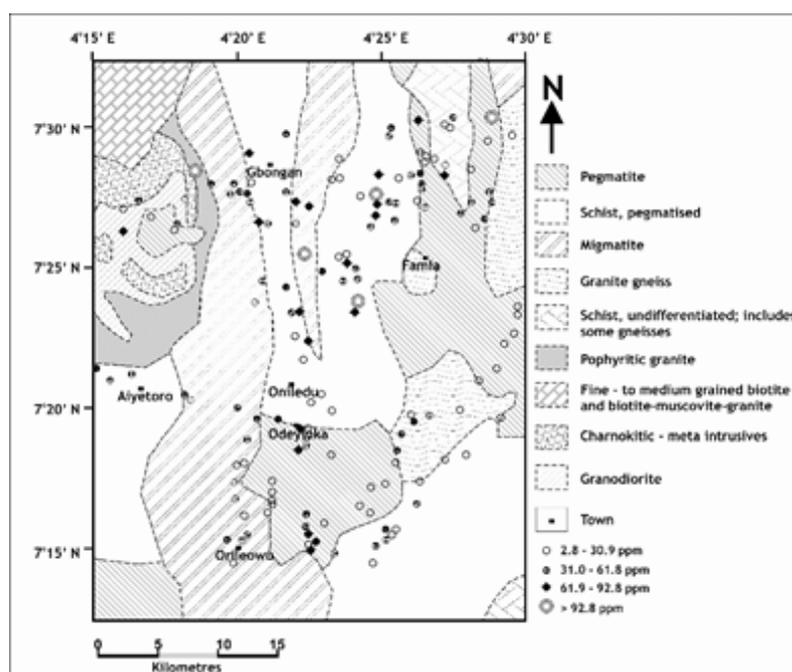

Figure 3K: Location Point Symbol Map of Lead Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Tin

Tin is a siderophile and, to a lesser extent, lithophile element. It commonly associates with B, F, Li and Rb in late-stage differentiates of granites and with Be, Li, Nb-Ta, W and rare earth elements in pegmatites (Kabata-Pendias and Pendias, 2001). The principal ore mineral of Sn is cassiterite (78.6 % Sn) while the metal is found in trace amounts in some rock forming minerals (e.g. biotite).

Tin does not have a widespread distribution in soils of the study area (Fig.3L). It was detected in only 112 out of the 186 samples analysed and it has a wide concentration range of 0.2 ppm to 171.6 ppm with a mean value of 57.7 ppm and coefficient of variation of 82 %. Okunlola (2006) obtained a concentration range of 16 – 200 ppm

and 15 – 100 ppm for Sn in pegmatites of Ijero – Aramoko and Ibadan – Osogbo areas, respectively in SW Nigeria. The threshold value obtained for Sn in soils of the study area is 152.3 ppm. Consequently, there are only three anomalous concentrations, one of which occurs in a portion underlain by pegmatite at the northeastern part of the area, while the other two are at the northwestern and north central portions underlain by porphyritic granite and pegmatitised schists, respectively. Besides these anomalous concentrations there are a number of other relatively high values (101.7 – 152.3 ppm) scattered about the northeastern, northwestern and southwestern portions of the area. In totality, it appears the largest proportion of the high Sn concentration in soils of this area falls in the western half of the map apparently without much

lithologic control.

A comparison of the mean value of Sn in soils of the study area (57.7 ppm) with the average abundance of tin in soil (10.0 ppm) indicates that the abundance of Sn in the area is comparatively high. Consequently, the anomalous and the relatively high Sn values may be attributed to primary tin mineralization in the area. The source of the tin is likely to be the pegmatites in the area. Adesiyan *et al.* (2014) established that Sn is hosted by pegmatites and pegmatised schists (that is, schists massively invaded by pegmatites) and is contained in the residual soils derived from this underlying rock type. Adesiyan and Adekoya (2003) reported anomalous concentrations of Sn in stream sediments derived from the area underlain by pegmatitised schists and undifferentiated schists in the northern half of the study area. Ako (1980) documented the presence of Sn in pegmatites of the adjacent area to the study area. Ajayi (1988) reported that cassiterite and columbite together with alluvial gold have been won in Iregun, a village in Ife-Ilesa area. According to him both minerals are derived from the weathered pegmatites intruded into the gneisses, migmatites and schists of the Basement Complex. Owoeye *et al.* (2015) attributed anomalous tin values recorded (with mean of 80.48 ppm) in stream sediments of Telemu-Ede area to tin mineralization in areas underlain by pegmatites.
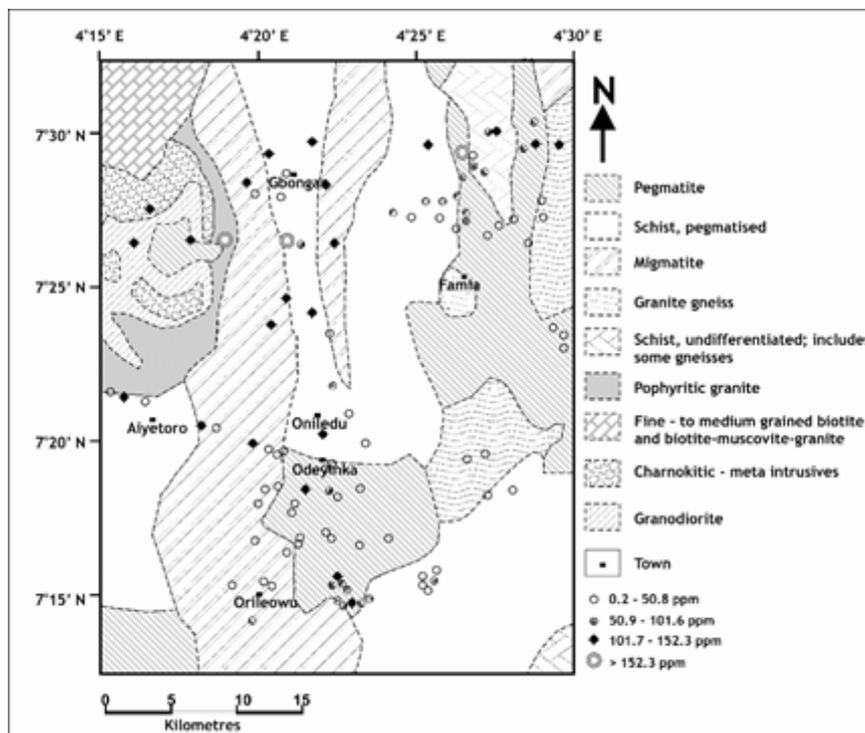

Figure 3L: Location Point Symbol Map of Tin Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

Zinc

Zinc is a chalcophile element which associates with Cu, Pb, Ag, Au, Sb, As and Se in base metal and precious metal deposits. It also associates with Mg in some silicates, and is found in trace amount in ferromagnesian minerals, plagioclase, epidote, K-feldspar, muscovite and quartz. The primary and major ore mineral of Zn is sphalerite while its secondary minerals include smithsonite and hemimorphite. The mobility of Zn is moderately high but it is limited by its tendency to be adsorbed by MnO_2 and insoluble organic matter (Mihaljevic, 1999b).

The distribution of Zn in soils of the study area as shown by the location point symbol map (Fig. 3M) is very wide as it was detected in all the 186 samples analysed. It has a wide concentration range of 3.6 ppm–7085.4 ppm, with a mean value of 510.8 ppm and coefficient of variation of 176 %. The threshold value for Zn is 2305.7 ppm and as such there are only seven anomalous values, five

of which are randomly distributed around the northwestern portion of the area while the remaining two are situated at the south central portion in an area underlain by pegmatite. Apart from these anomalous concentrations, there are other three relatively high values (1573.3 – 2305.7 ppm) at the south central portion which is underlain by pegmatite.
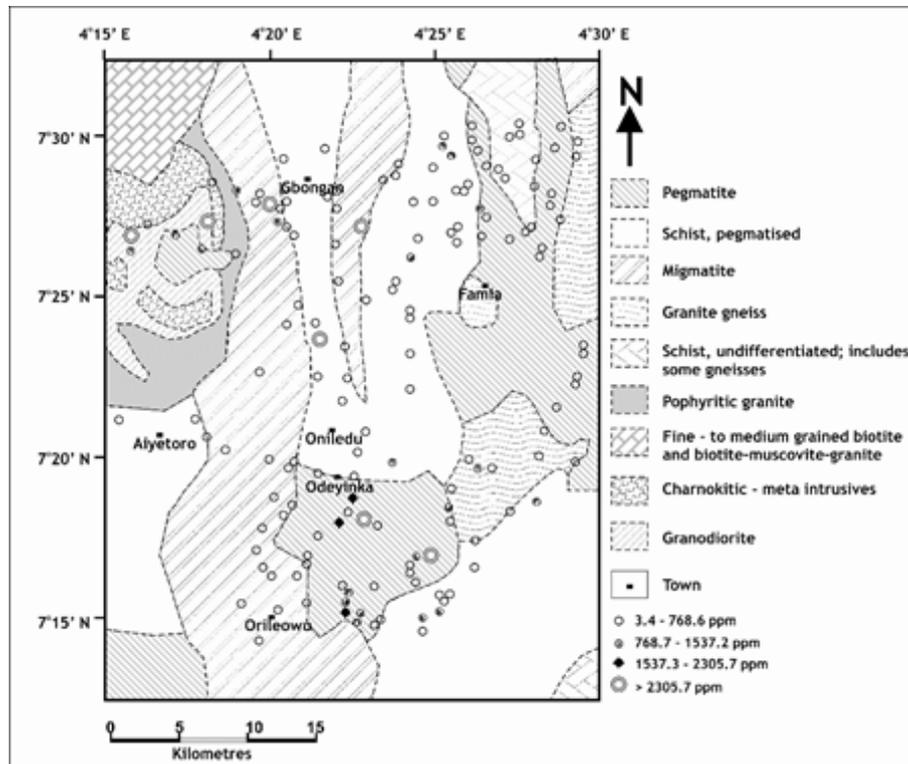

Figure 3M: Location Point Symbol Map of Zinc Distribution in Soils of Gbongan-Odeyinka-Orileowu Area.

When the average abundance of Zn in soil (10 – 200) ppm, ultramafic rocks (50 ppm), granite (40 ppm) and granodiorite (60 ppm) is compared with the mean value of Zn concentrations (510.8 ppm) in soils of the study area, the abundance of Zn in this area is very high. Thus, the few anomalous and relatively high values are significant. However these significant Zn concentrations are not considered to be related to primary Zn mineralization. This is because the spatial distribution pattern of Zn in this study is completely different from those of elements like Pb, Cu and Ag with which Zn is expected to associate in either the base metal or precious metal deposits as mentioned earlier. This is revealed by their location point symbol maps. Consequently, one can infer that the highest proportion of Zn in the area might have been derived from anthropogenic sources or from a high accumulation of leaves (Adesiyan, 2010) or both. Derivation of Zn from leaves is not surprising as

Zn is an essential nutrient for almost all plants. A possible anthropogenic source of Zn in the study area is the pesticides which could have been used in spraying cocoa plantation, which is a common preoccupation of farmers in the study area (Fyfe, 1999 and Pfeifer et al., 2000).

In addition, a consideration of Zn/Cd association and the ratio of the two elements in the study area tend to support the theory of anthropogenic contamination of Zn in the area. Normally Cd is associated with Zn in geological occurrences and the Zn/Cd ratio is, on average, 500 to 1, which does not deviate by more than a factor of 2 (Reimann and de Caritat, 1998; Kabata-Pendias and Pendias, 2001). However, in the study area, the Zn/Cd ratio is 10,016 to 1 (computed from the mean values of 510.8 ppm of Zn and 0.051 ppm of Cd). Such a great disparity in the Zn/Cd ratio from the normal average (500 to 1) is not likely to be natural; hence the support for anthropogenic

source of Zn in the area. Lastly, the dissimilarity between the location point symbol maps of both Zn and Cd is another possible indicator of anthropogenic source for Zn in the study area.

CONCLUSION

From the geochemical distribution map (the location point symbol map) of each of the elements determined in soils of the study area, diverse distribution patterns are revealed. These do not correspond perfectly with the lithological boundaries of the area as shown in the geological map 1:250,000 GSN Iwo Sheet 60 (Fig. 2). For example, the occurrence of high concentrations of Ag, Cd, Co, Cu and Ni (at the south-central portion) in areas presumably underlain by pegmatite negate the fact that high concentration of these elements are normally associated with mafic/ultramafic lithology. This may mean that the boundaries between pegmatite and the pegmatitised schists in this area were inaccurate. The sporadic mafic schists and ultramafites reported in this area by Adesiyan (2010) could be the primary sources for elements like Ni, Cr, Co and As in the soil. There is also the possibility that the underlying rock of this part was intruded by veins containing primary mineralization of complex sulphides. Adesiyan and Adekoya (2008) reported the occurrence of similar metal dispersion patterns in the northern portion of the study area from a stream sediment survey. However, the values obtained for the concentrations of most of the elements in the present study are consistently higher. This shows the tendency of trace elements to concentrate more in soils than in stream sediments as a result of progressive dilution of elements concentration in stream sediments.

Looking at the distribution patterns of the studied trace metals, it can be inferred that the factors controlling metal dispersion in the surficial environment of the study area, are lithology, environmental influence and primary mineralization. There is the possibility of occurrence of primary Au mineralization in form of disseminations within some underlying rocks and or Au bearing quartz veins with associated complex sulphides in the area. Based on observed distribution of anomalous values of both Sn and Au on the pegmatised schists and pegmatites areas

of the study area, the Sn is hosted by pegmatites and the Au by the schists and granite gneiss (Adesiyan, 2010 and Adesiyan *et al.,* 2014).

As stated by some previous authors, primary gold mineralization in the Nigerian Schist Belts commonly occurs as quartz veins within several types of lithologies. At Bin Yauri, these veins commonly contain pyrite, pyrrhotite, arsenopyrite, magnetite, ilmenite, chalcopyrite, marcasite, sphalerite and galena (Akande *et al.,* 1988, Garba and Akande, 1992; Garba, 2002). Also at Iperindo, the primary gold deposit is associated with pyrite, pyrrhotite, chalcopyrite, sphalerite and arsenopyrite (Oyinloye, 1997). Furthermore, the occurrence of primary Sn mineralization may not be ruled out. The Sn is probably hosted in the pegmatites of the area. There is a significant level of zinc pollution in the area probably due to the use of insecticides by farmers.

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