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Integrated Multi-Elemental Soil Geochemical Survey as a Tool in Geological Mapping in the Tropics: A Case Study of Songbe Area of Osun State, West Africa

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Abstract

Soil geochemical survey of Songbe area, a typical tropical environment of Nigeria was carried out to determine the concentrations and distribution patterns of trace elements in order to decipher the underlying geology in the area, as a complimentary tool to geological mapping, especially in areas with little or no rock exposure. The soil samples were collected by driving a 1-meter auger down to a depth of 50 - 80 cm into the ground after removing the top soil, to ensure adequate penetration into the "B-horizon". The samples were air-dried at room temperature for four weeks. Each sample was disaggregated gently with porcelain mortar and pestle. The pestle and mortar were washed and dried after each sample is processed to avoid inter-sample contamination. The samples were subjected to standard preparation and treatment prior to geochemical analyses determined by X-Ray Fluorescence (XRF) method on a PANalytical Axios Wavelength Dispersive spectrometer and LA-ICP-MS (Laser Ablaser Inductively coupled Plasma Mass Spectrometry) method at the Central Analytical Facility (CAF) of Stellenbosch University, South Africa. The point location maps were plotted using ArcView-Gis.The location point symbol map of each of the elements analysed revealed diverse patterns of distribution and showed considerable variations from one area to the other. Some of these distribution patterns did not perfectly correspond with the inferred geological boundaries, especially in areas with thick overburden. The point symbol maps of magnesium, iron, nickel and chromium (Mg, Fe, Ni and Cr) revealed anomalous and relatively high values in some areas underlain by quartzite, whereas anomalous and relatively high values of these ferromagnesian minerals are expected dominantly in areas underlain by mafic or ultramafic rocks. The symbol maps of tantalum and thorium showed dominantly low values for areas deduced to be underlain by charnockite with relatively high concentrations for pegmatitic bodies.The integration of the interpreted soil data with the point symbol maps of element concentrations superimposed on the produced geological map showed that most of the inferred rock boundaries were overestimated or underestimated and some mineral occurrences were yet to be accounted for. Hence, it was concluded that multielemental chemical analyses using soil as sampling media is a vital tool to delineate underlying geology in the tropics and is also an aid to geological mapping

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1. INTRODUCTION

Geological mapping is the preliminary study usually carried out to understand the geology of an area. The 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 (Matheis, 1976). These features result in a low outcrop density, which hampers direct prospecting for minerals and preparation of an accurate geological map of an area. There is, thus, the need for suitability of geochemical studies to compliment geological mapping and exploration in tropical zones, which often times are devoid of outcrops over wide areas owing to huge overburden.

Geochemical exploration methods involve the collection and analysis of various types of geological media, such as soils, stream sediments, rocks and certain biological materials (plant saps). Historically, these methods have proved to be more productive than any of the methods used in mineral exploration (Grunsky, 2010). For example, soil geochemical surveys are often employed to delineate mineral deposits at shallow depths where outcrops of bedrock are non-existent or minimal (Hawkes and Webb, 1962).

The popularity of residual soil survey as an exploration method is a simple reflection of the reliability of soil anomalies as ore guide. Residual soil surveys have been found particularly applicable in areas of deep residual cover and sparse outcrops, where other exploration methods either are too expensive or are technically ineffective (Bradshaw, 1975). In Ibogunde, a typical tropical environment characterized by thick overburden and poor rock exposures, soil survey was employed as an aid to geological mapping in order to delineate the nature of the underlying rock, hence, this study. The study will improve the understanding of the geology of the study area with an updated geological map and also provide a baseline geochemical map of the area.

Soil is a natural product of weathering which could be residual (insitu) or transported (Joffe, 1949). The samples collected for assay was from the B-horizon; fine silty or clayey surface materials that result from weathering of the underlying bedrock and may contain small fragments of bedrock (Hawkes, 1976). This is because it is the zone of accumulation where both clay minerals and Fe-Mn oxides have the capacity to absorb the elements in varying degrees.

Based on Global Reference Network (GRN) cells defined by Darnley *et al.* (1995), the study area falls within N05 E04 GRN cell (Fig. 1). It is defined by geographical coordinates of latitudes $7^{o} 42^{'}$ and $7^{o} 50^{'}$N and longitudes $4^{o} 18^{'}$ and $4^{o} 24^{'}$E which falls within the Iwo S. E. and N. E. standard topographic sheets number 242 (1:50,000) (Fig. 2).

2.1 PREVIOUS STUDIES

There is paucity of past geoscientific studies on the study area except for few works such as that of Adetunji (2012) and Adetunji *et al.* (2018). Some of the available publications on soil geochemical exploration include those of Onuogu and Ferrante (1965), Nichol *et al.* (1969), Ajayi (1988, 1995) and Adesiyan *et al.* (2014). Onuogu and Ferrante (1965) carried out geochemical orientation study for gold and nickel in the Ife-Ilesa area. The authors concluded that “in delineating potential gold areas, the values for Zn and Cu in the stream sediments were inconclusive, although both showed peaks in the soil profiles above gold-quartz lodes in Iperindo area. It was suggested that an alternative pathfinder for gold had to be found since arsenic was not detected in the soil”.

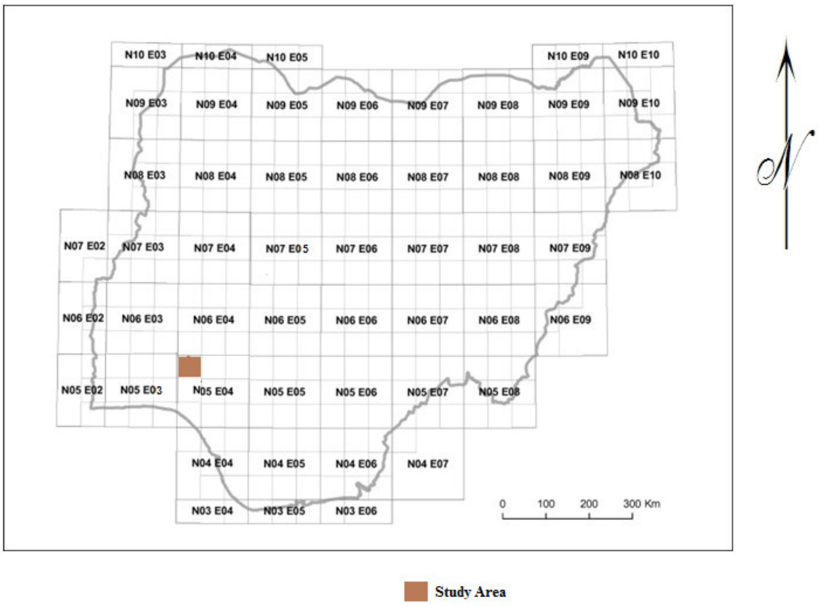

Figure 1: **The Distribution of Global Refernce Network (GRN) Cells in Nigeria (Darnley *et al.*, 1995).**

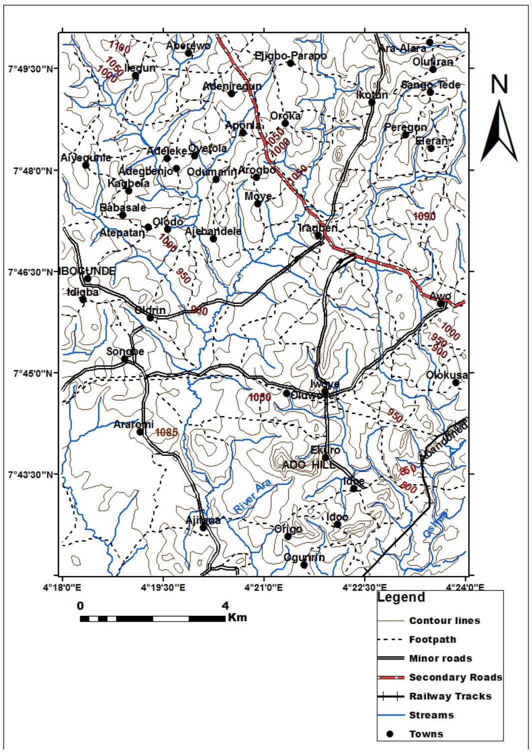

Figure 2: **Topographical Map of the Study Area (Culled from Iwo Sheets 242 S. E. and N. E., Federal Survey of Nigeria, 1965).**

Ajayi (1988) carried out a statistical analysis of soil samples from the Ife-Ilesha area and noted that both the simple statistical and R–mode factor multivariate analytical techniques were useful aids in interpretation of reconnaissance soil samples data. Ajayi (1995) later noted that the moving average and derivations from the trends using the moving average method reduced the effects of local variations in the regional geochemical data of the Ife-Ilesha gold field. The results demonstrated the effectiveness of these techniques as essential exploratory tool, particularly in areas where anomaly or background contrasts are generally low.

In order to follow up some geochemical anomalies discovered in a regional stream sediment survey in parts of southwestern Nigeria, a medium density geochemical soil survey was carried out in Gbongan-Odeyinka area of Osun State, southwestern Nigeria by Adesiyan, *et al.* (2014). As a result, soil geochemical data of 13 elements (Ag, As, Au, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, and Zn) obtained from 186 samples from the study area were subjected to statistical analysis involving frequency distribution, Pearson correlation and R-mode varimax rotated factor analysis techniques. The Pearson correlation matrix and factor analysis enabled separation of the 13 elements into the following three factors or metal associations: Pb-Co-Ni-Fe-Cr-As-Mn-Cu; Sn-Ag-Au-Cd; and Zn-Cd, which were interpreted to reflect the influence of both environmental and mineralization factors on the soil of the study area. Of the three associations, only the Sn-Ag-Au-Cd was considered related to metallic mineralization based on the existing knowledge of Au and Sn mineralization in the adjacent Ife-Ilesa area. The gold is believed to be hosted by schists and the tin by pegmatites. The other metal associations are interpreted in terms of environmental factors. On the basis of the presence of Fe and Mn in the Pb-Co-Ni-Fe-Cr-As-Mn-Cu association, it was inferred that the scavenging action of iron and manganese oxides was at least partly responsible for forming such trace elements association in the soil. In the case of the Zn-Cd association, both metals are considered to be anthropogenic, being possibly introduced to the soil through the application of pesticides on cocoa and kolanut plantations of the study area, although the possibility of Zn being derived from other sources cannot be ruled out.

Owoeye *et al.* (2015) carried out reconnaissance stream sediment geochemical studies in Telemu-Awo-Ede areas of Osun State to determine the concentrations and distribution patterns of trace elements with a view to assessing the mineralization potential of the study area. The study concluded that this area has Sc-Sn-Ta and Th mineralization potentials related to the pegmatoids and also confirmed the heterogeneous nature of the underlying rocks. Areas underlain by pegmatites and pegmatised schist coincided spatially with zones of relatively high values for U, Th, La, Sc, Sn and Ta; and were suspected to be mineralized in tin, scandium, thorium and tantalum.

2.2 GEOLOGY OF THE AREA

The study area lies in the Basement Complex of Southwestern part of Nigeria and this forms part of the Pan African mobile belt. Several workers have compiled and reviewed the geology of the Basement Complex of Nigeria and of Southwestern part of Nigeria in particular. The crystalline Basement Complex consists of wide varieties of metamorphic and igneous rocks and has been shown to be polycyclic with isotopic ages ranging from 450 Ma to 3570 Ma (Rahaman, 1988; Kroner *et al.,* 2001; Dada, 2006; Okonkwo and Ganev, 2012; Adetunji *et al.,* 2018). Caby (1987) referred to the entire region east of West African craton as the Trans-Saharan fold belt.

The results from the geological mapping by Owoeye (2020) indicated that the area is underlain by three of the six rock groups of the crystalline Basement Complex of Nigeria (Fig. 3):

a. Migmatite-Gneiss-Quartzite Complex;
b. Charnockitic rocks (of various textural characteristics and composition) and diorite; and
c. Members of the Older Granite suite.

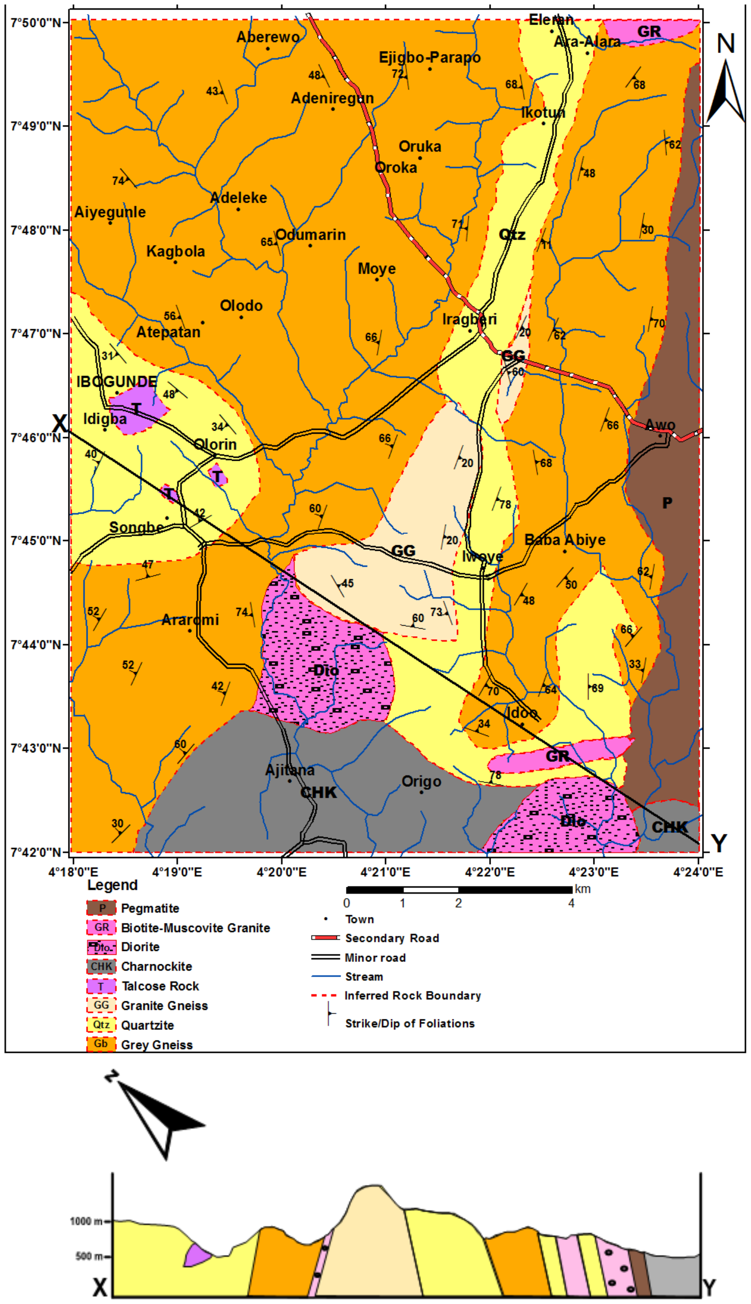

Figure 3: Geological Map and Cross Section of Ibogunde and its Environs (Owoeye, 2020).

Grey gneiss occupies the low topographical areas. It is found between Awo and Iwoye areas and eastern part of Awo along the Osogbo-Iwo road. It is the most dominant rock type constituting 60 % of the Migmatite-Gneiss-Quartzite Complex in the study area. Texturally, the rock is medium to coarse grained with individual mineral grain ranging from 1mm to 3mm with well-defined mineralogical banding (millimetric and centimetric).

The rock is highly migmatitic in few locations but mostly banded gneiss occurs in other locations.

Quartzite forms a narrow, slightly elevated topography that trend north-south in the eastern part of the study area. It occurs mainly as low-lying exposures. This is the structural marker in the study area with an antiformal fold which runs north-south and refolded at the base to give a synform. The granite gneiss occupies areas of relatively high elevations in the area which falls around Awo and Iwoye and major quarries in the study area. It occurs as low-lying outcrops in southeastern part of Iragberi. It is coarse grained with dominant quartzo-feldspathic minerals. The rock is strongly foliated (though less well defined than the grey gneiss). In terms of texture, the minerals in the rock are medium to coarse grained.

Charnockite is exposed generally in the southern part of the studied area and mostly low lying. It outcrops as small plutons in Osuntedo, Ajitenna and bouldery units in Awo. The charnockitic rocks have textural variations from fine to medium grained then to coarser grained around the southwestern part of the study area. The charnockitic rock is of igneous origin and it forms prominent topographical features around Ogunrin and Osuntedo.

Diorite has a dome-like occurrence in the southeastern part of the study area; it occurs as a circular body around Origo station and southeast of Idoo village. The rock is light grey in colour and medium to coarse grained in texture. Pegmatite occurs as an intrusive igneous rock within the granite gneiss and grey gneiss. It covers the extreme eastern part of the study area and was also found at the Origo hill. The pegmatites occur as dykes and veins in gneiss and granite gneiss as seen in at Alabakan and Iwoye. Biotite-muscovite granite occurs in the study area as minor intrusives in form of tabular bodies and are mainly low lying. Talcose rocks occur in the study area as predominantly low lying exposures. The occurrence of talc is around Ibogunde as separate, mappable bodies.

3 METHODOLOGY

Fifty one (51) soil samples of the "B-horizon" were collected. The soil sampling was based on a 1: 12,500 topographic sheet and the actual sampling points were plotted using the Global Positioning System and later superimposed on the geological map of the area. The soil samples were taken by driving a 1-meter auger down to a depth of 50 - 80 cm into the ground after removing the top soil, to ensure adequate penetration into the "B-horizon" which is preferred in most soil surveys because it is a zone of metal accumulation. The samples were carefully hammered out of the auger into clean, pre-labelled sample bags in a way to avoid unnecessary loss and contamination. The samples collected were air-dried at room temperature for four weeks. Each sample was disaggregated gently with porcelain mortar and pestle. The pestle and mortar were washed and dried after each sample is processed to avoid inter-sample contamination. Each sample was quartered, using the coning and quartering method and a split fraction was reserved for reference. The remaining parts were passed through minus 80-mesh (177 micron) nylon sieve and the passing was reserved for geochemical analyses.

Analyses of major, trace and rare earth elements of all the soil samples were carried out using XRF and LA ICP-MS methods at the Central Analytical Facilities, Stellenbosch University, South Africa. About 10 g of each sample was crushed into a fine powder (particle size < 70 µm) with a jaw crusher and milled in a tungsten-carbide Zibb mill at the Department of Geology, Stellenbosch University prior to the preparation of a fused disc for major and trace elements analyses.

Glass disks were prepared for XRF analysis using 7 g of high purity trace element and Rare Earth Element-free flux ($LiBO_2$ = 32.83%, $Li_2B_4O_7$ = 66.67%, LiI = 0.50%) mixed with 0.7 g of the powdered sample. Mixtures of the sample and flux were fused in platinum crucibles with Claisse M4 gas fluxer at temperatures between 1100 °C - 1200 °C. The spectrometer was fitted with a Rhodium tube and with the following analyzing crystals: LIF200, LIF220, PE 002, Ge 111 and PX1. The instrument was fitted with a gas-flow proportional counter and a scintillation detector. The gas-flow proportional counter used a 90% Argon – 10% methane mixture of gases. Major elements were analyzed on a fused glass disk using a 2.4 kW Rhodium tube. Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured with the SuperQ PANalytical software. The concentration of the control standards that were used in the calibration procedures for major element analyses fit the range of concentration of the samples. Amongst these standards were NIM-G (Granite from the Council for Mineral Technology, South Africa) and BE-N (Basalt from the International Working Group).

For LA-ICP-MS, fusion disks prepared for XRF analysis by an automatic Claisse M4 Gas Fusion instrument and ultrapure Claisse Flux, using a ratio of 1:10 sample : flux, were coarsely crushed and a chip of sample mounted along with up to 12 other samples in a 2.4 cm round resin disk. The instrumental method set-up followed the guidelines from Eggins (2003). A Resolution 193 nm Excimer laser from ASI connected to an Agilent 7700 ICP-MS was used in the analysis of trace elements in bulk rock and soil samples. Ablation was performed in helium (He) gas at a flow rate of 0.35 L/min, then mixed with argon (0.9 L/min) and Nitrogen (0.004 L/min) just before introduction into the Inductively Coupled Plasma (ICP). A fusion control standard from certified basaltic reference material (BCR-2, and BHVO-1, values from Jochum *et al.*, 2016) was also analysed in the beginning of a sequence to verify the effective ablation of fused material. Data processing was done using the LA-ICP-MS data reduction software package Iolite v.3.2 (Paton *et al.,* 2011).

The methods of data analysis involved both qualitative and quantitative statistical analysis. The quantitative statistical treatment of geochemical data as a useful and a necessary technique in geochemical interpretation is widely accepted and practiced (Lepeltier, 1969, 1971, Rossiter, 1976; Chapman, 1976 and 1978; Garrett *et al.,* 1980; Ajayi, 1988; Filmoser *et al.,* 2005; Reimann *et al.,* 2008; Adesiyan *et al.,* 2014; Carranza and Laborte 2015a, b, c; Guo *et al.,* 2017; Xiong and Zuo, 2017; Fyzollahhi *et al.,* 2018; Zuo, 2018; Zuzolo *et al.,* 2018a; Wang *et al.,* 2019) since it is useful in simplifying and condensing data for easy comprehension of presentations. A qualitative examination of the analytical data was done to detect some excessively high values (if any) otherwise known as **outliers**. The data were treated statistically using both univariate and multivariate methods.

4 RESULTS AND INTERPRETATION

The results of the geochemical data (See Owoeye, 2020) were subjected to statistical treatment. The basic statistics of the raw and log transformed data are presented in tables 1a and 1b.

Table 1a: Summary of Basic Statistical Parameters of Raw Soil Geochemical Data of Ibogunde and its Environs, Southwestern Nigeria.

Elements	Range	Arithmetic Mean, X	Standard Deviation, (S)	Threshold = (X + 2S)
Fe	1.03 – 12.77	5.12	2.71	10.54
Mn	232.338 – 7125.03	1253.48	1285.76	3824.99
Mg	60.32 – 22860.14	2494.22	4280.69	11055.60
Sc	5.1 – 27.13	12.53	4.80	22.14
Cr	34.5 – 1145.2	191.32	237.84	667.01
Co	6.945 – 176.95	33.76	33.09	99.95
Ni	11.18 – 228.05	53.61	50.86	155.32
Cu	9.19 – 181.05	32.38	25.87	84.12
Zn	55.05 – 1283	334.4	268.02	870.44
Rb	24.67 – 196.75	79.72	39.75	159.22
Sr	21.68 – 665.6	162.62	155.07	472.75
Nb	13.12 – 56.13	27.29	9.23	45.75
Mo	0.60 – 15.10	2.08	2.08	6.23
Ba	134.1 – 2214.5	917.50	604.68	2126.85
La	13.44 – 218.2	55.03	37.37	129.78
Hf	10.10 – 100.6	33.31	14.96	63.22
Ta	1.12 – 7.28	2.36	1.25	4.87
Pb	16.70 – 135.70	41.60	23.84	89.29
Th	6.55 – 83.07	21.29	12.72	46.73
U	1.87 – 31.48	7.34	4.30	15.94

* All values are in ppm except Fe in %

Table 1b: Summary of Basic Statistical Parameters of Log Transformed (Log$_{10}$) Soil Geochemical Data of Ibogunde and its Environs, Southwestern Nigeria.

Elements	Range (Log$_{10}$)	Geometric Mean (Log$_{10}$)	Standard Deviation, (S)	Threshold =Antilog (X+ 2S.D)
Fe	0.01 – 1.11	0.64	0.26	7.91
Mn	2.37 – 3.85	2.95	0.34	899.69
Mg	1.78 – 4.36	3.07	0.53	1172.05
Sc	0.71 – 1.43	1.07	0.17	14.44
Cr	1.54 – 3.06	2.10	0.35	131.90
Co	0.84 – 2.25	1.39	0.32	29.05
Ni	1.05 – 2.36	1.61	0.30	44.39
Cu	0.96 – 2.26	1.43	0.26	30.22
Zn	1.74 – 3.11	2.40	0.33	256.75
Rb	1.39 – 2.29	1.85	0.22	73.86
Sr	1.34 – 2.82	2.03	0.42	112.32
Nb	1.12 – 1.75	1.41	0.13	28.55
Mo	-0.21 – 1.18	0.22	0.25	5.15
Ba	2.13 – 3.35	2.85	0.34	710.92
La	1.13 – 2.34	1.65	0.28	48.80
Hf	1.0 – 2.00	1.48	0.19	33.32
Ta	0.05 – 0.86	0.33	0.19	5.04
Pb	1.22 – 2.13	1.57	0.20	40.05
Th	0.82 – 1.92	1.27	0.22	21.77
U	0.27 – 1.50	0.82	0.19	9.54

* All values are in ppm except Fe in %.

4.1 Determination of Threshold Values

The threshold values in this study were obtained from computations of statistical techniques from both raw and log-transformed data as shown in tables 1a and 1b, respectively. It was observed that the thresholds computed from raw data are higher than those computed from log-transformed data except for tantalum. For selection of adequate thresholds, it was important to consider the fact that most of elements in the study area did all obey Ahrens' law of log-normality. Threshold of raw data were adopted.

4.2 Distribution of Elements

It can be inferred that trace element contents in superficial materials like stream sediment, soil, water, are more or less directly linked to the composition of the underlying bedrock (Haldar, 2018). Multi-element soil geochemistry can be used as a geological mapping tool in addition to its usefulness in delineating areas of economic mineral prospect.

The concentration of trace elements in soils of the study area shows considerable variations from one area to the other. Despite this, certain broad characteristic distribution relationship of the elements can be observed. The distribution of elements is discussed using the location point symbol maps for illustration (Figs. 4 to 12). The mean concentration of these trace elements in the study area is compared with the average abundance of elements in materials of earth's crust (Table 2). The location point symbol maps are super-imposed on the geological map of the area to aid the description of element distributions.

Table 2: Comparison of Average Abundance of Elements in Materials of the Earth's Crust (After Levinson, 1974; Rose *et al.*, 1979 and Mikelic *et al.*, 2013).

Elements	Earth's Crust	Ultra-mafic/Mafic	Granite	Granodiorite	Soil	This study-Background Value (50th Percentile)
Fe	4.65	9.4	1.42	–	0	5.11
Mn	950	1300	500	1200	850	1253.478
Co	25	150	1	10	1 – 40	33.76
Ni	75	2000	0.5	20	5 – 500	155.32
Cr	100	2000	4	20	5 – 1000	191.32
La	30	3.3	25	36	–	55.03
Ta	2	1	3.5	2	–	2.36
Th	10	0.003	17	10	13	21.29

*All values are in ppm except Fe in %.

4.2.1. Spatial Distribution of Elements

Iron – Fe

Iron showed relatively wide concentrations which range between 1.03 % and 12.77 % with a mean value of 5.12 %. With a threshold value of 10.55 %, there are seven anomalous values of iron predominantly concentrated in the southern part (Fig. 4). The underlying rocks in areas with these anomalous values are charnockite, diorite and grey gneiss. Other relatively high values which range from 7.38% – 10.55% occur in areas underlain by quartzite (western portion), talcose rock, grey gneiss (southwestern part) and pegmatite (southeast). Relatively low values (4.21 – 7.37) % and low values (1.03 – 3.32) % are underlain by pegmatite, grey gneiss, quartzite and pegmatite. With a background value (mean) of 5.12 %, the abundance of iron is relatively moderate in the study area when compared with its average abundance in the earth's crust (4.7 %), ultramafic rocks (9.46 %) and granite (1.42 %). The few anomalous concentrations may not be attributed to Fe mineralization in the area but rather a pointer to the precipitation of Fe-oxides in the soil (Clarke, 1966; Wedepohl, 1995).

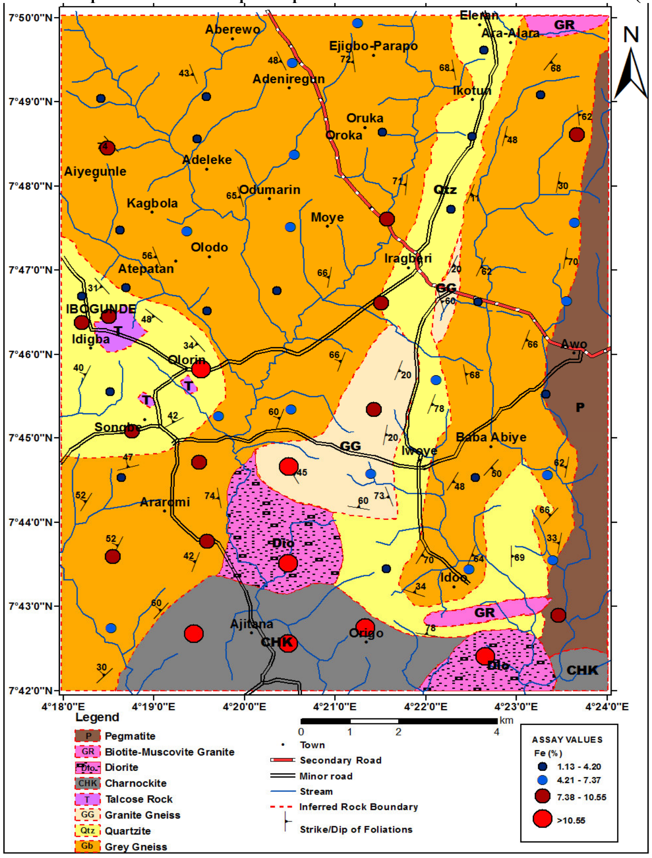

Figure 4: **Location Point Symbol Map of Iron Distribution in Soil Samples of Ibogunde and its Environs, Southwestern Nigeria.**

Manganese – Mn

Manganese shows wide concentrations which range from 232.34 ppm to 7125.03 ppm with a mean value of 125.48 ppm. The threshold value is 3824.99 ppm; which indicates that there are twelve anomalous values of Mn (Fig. 5).

The underlying rocks in areas with anomalous values are charnockite, diorite, talcose rock, quartzite (western portion), and pegmatite. An isolated anomalous value occurred in an area underlain by grey gneiss in the northwestern part. Other relatively high Mn values (2627.45 – 3824.99) ppm occurs mainly in the southwestern part which is underlain by grey gneiss; one isolated value occurred in the northwestern portion. The relatively low values and low values that ranged from 1429.90 ppm to 2627.44 ppm and 232.34 ppm to 1429.89 ppm, respectively are associated with areas underlain by quartzite (northeastern part), granite gneiss, pegmatite and grey gneiss (dominantly in the northern half).

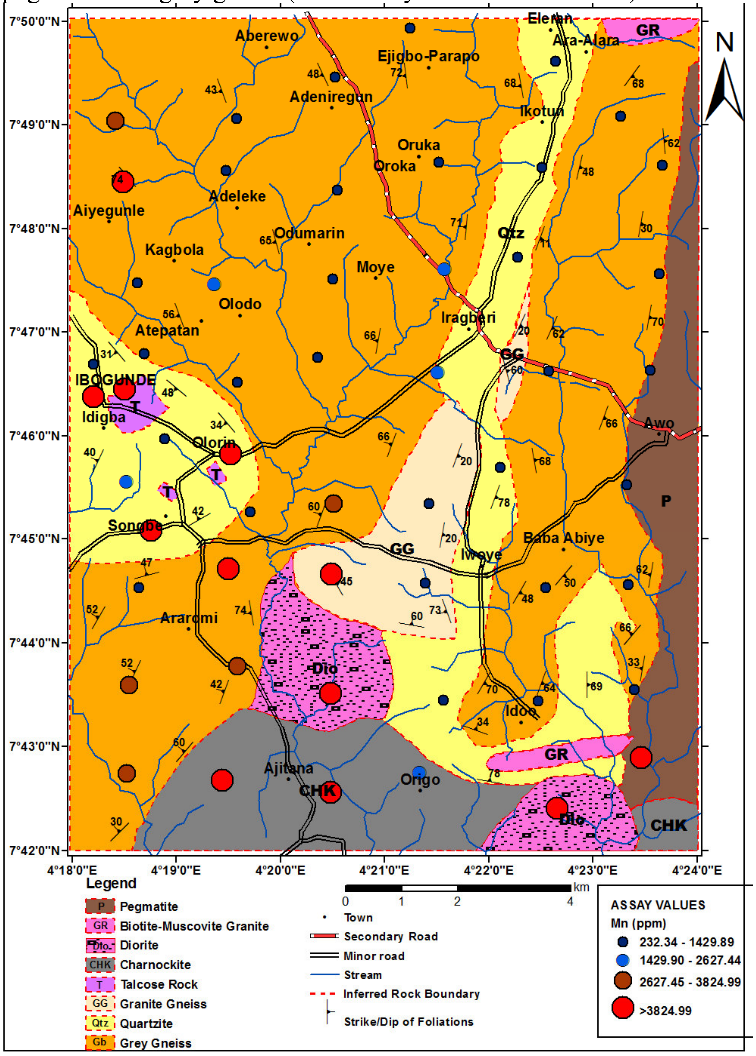

Figure 5: **Location Point Symbol Map of Manganese Distribution in Soil Samples of Ibogunde and its Environs, Southwestern Nigeria.**

The background value of 1253.49 ppm suggests relatively high abundance of manganese when compared with its average abundance in earth's crust (950 ppm), mafic/ultramafic rock (1300 ppm), granite (500 ppm) and soil (850 ppm). The detectable Mn in soils showed a very wide range of 38 ppm to 6290 ppm in Ife-Ilesha (Ajayi, 1988) while Adesiyan *et al.* (2018) reported a wider range between 12.98 and 9460.63 ppm in Gbongan with mean of 1039.29 ppm.

High Mn values in association with Cr, Ni, Fe, etc. are indicative of mafic rocks (McLennan and Taylor, 1999). The anomalous values may however be related to the precipitation of manganese as oxides in soils probably derived from the underlying mafic/magnesium and iron rich silicate rocks (Bloss and Steiner, 1960). Rose *et al.* (1979) noted that Mn could cause false anomalies as a result of co-precipitation or adsorption on other elements on its oxides.

Like iron, the element manganese is extremely important in geochemical exploration because of the very large number of trace elements that may be co-precipitated with or adsorbed on Mn-oxide minerals (Chao and Theobald, 1976; Nowlan, 1976; Jenne, 1968). Mn allows the screening of false anomalies of other elements (Dorokhin *et al.,* 1969; Rose *et al.,* 1979; Yang and Sanudo–Wilhelmy, 1998). The few anomalous concentrations may not be attributed to Mn mineralization in the area but rather a pointer to the precipitation of Mn-oxides in the soil (Kabatas-Pendias and Pendias, 2001).

Chromium – Cr

Chromium was detected in all samples and showed concentrations from 34.5 ppm to 1145.2 ppm with a mean value of 191.32 ppm (Fig. 6). The threshold value is 667.01 ppm and this indicates that there are six anomalous values of chromium which are more concentrated in the western part. The underlying rocks in these areas with anomalous values are talc and quartzite. Two (2) isolated anomalous values occur in areas underlain by grey gneiss (northwestern part) and charnockite (southeastern portion). Other relatively high values (456.18 ppm – 667.01 ppm) occur in the southern part of the map and these areas are underlain by grey gneiss, charnockite and diorite. Area underlain by grey gneiss (mainly in the northern half), quartzite (northern portion), granite gneiss and pegmatite are associated with very low chromium values (34.50 – 245.33) ppm.

When the background value of chromium in soil samples of the study area (191.32 ppm) is compared with the average abundance of the element in the earth's crust, ultramafic rocks and soils which is 100, 2000 and 5 – 1000 ppm, respectively, the abundance of chromium is low. Chromium mineralization is very unlikely in this area; the few anomalous values of Cr may be due to co-precipitation of Cr with manganese hydroxide or Fe-oxide (Whalley *et al.,* 1999). Adesiyan *et al.* (2018) also interpreted the only anomalous value associated with migmatite in Gbongan area, Osun state as due to co-precipitation of Cr with Mn or Fe oxide. The origin of the element in Ibogunde area, Osun State may be due to the underlying mafic or ultramafic rocks.

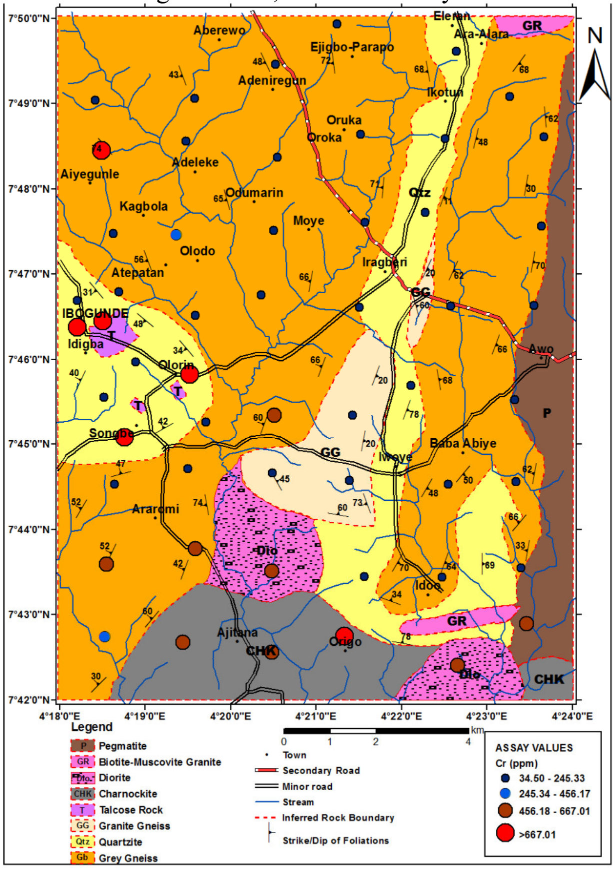

Figure 6: **Location Point Symbol Map of Chromium Distribution in Soil Samples of Ibogunde and its Environs, Southwestern Nigeria.**

Cobalt – Co

Cobalt was detected in all the samples analyzed and showed concentrations which range between 6.945 ppm and 176.95 ppm with a mean value of 33.76 ppm. The threshold value of cobalt is 99.95 ppm and this indicates that there are fourteen anomalous cobalt values (Fig. 7). These anomalous values are in areas where the underlying rocks are: grey gneiss (western portion), talcose rock, quartzite (western portion), charnockite and diorite. The remaining anomalous value is located in the southeastern part and is underlain by pegmatite. Other fairly high

Co values (68.96 ppm – 99.95 ppm) occur in areas underlain strictly by grey gneiss (southwestern part). The areas underlain by grey gneiss (predominantly in the northern half), quartzite (eastern portion), granite gneiss and pegmatite are characterized by low values between 2.13 ppm and 37.94 ppm.

When the background value of cobalt in the study area (33.76 ppm) is compared with the average abundance of cobalt in mafic/ultramafic rocks (150 ppm) such as talcose or charnockitic rock which may be the source of cobalt in the study area, the abundance of cobalt can be said to be low (Table 2). This is further buttressed by the association of Co with other elements in Factor 1 earlier interpreted in terms of underlying mafic to ultramafic lithologies and environmental influence. These anomalous values are thus insignificant and may be due to co-precipitation of cobalt with Mn- and or Fe-oxides.

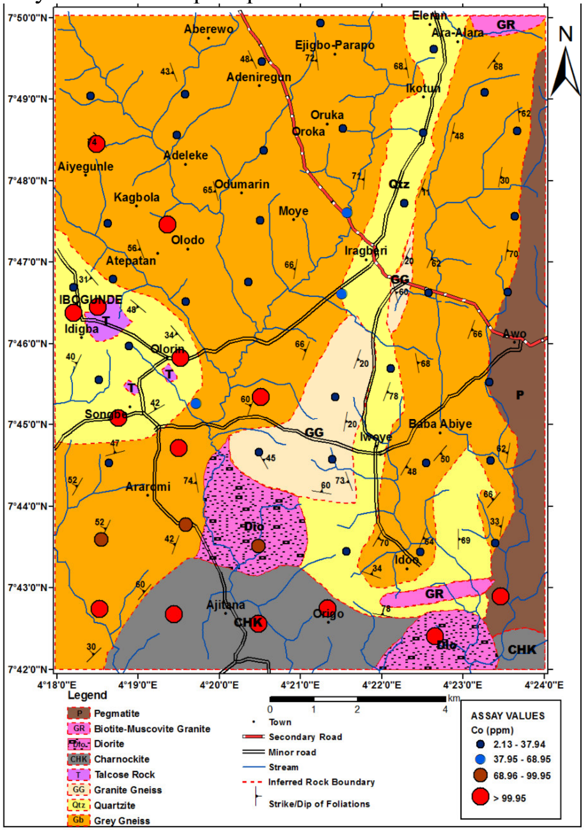

Figure 7: **Location Point Symbol Map of Cobalt Distribution in Soil Samples of Ibogunde and its Environs, Southwestern Nigeria.**

Other workers like Ajayi (1988), Adesiyan and Adekoya (2008) and Adesiyan *et al.* (2014; 2018) have recognized the association of cobalt with manganese oxides in the secondary environment. This association may result from adsorption on the Mn-oxide surfaces and a structural substitution of Co for Mn as suggested by Loganathan and Burau (1973) and Burns (1976).

Nickel – Ni

Nickel was detected in all samples with concentrations which ranged between 11.18 ppm and 228.05 ppm with a mean value of 53.61 ppm. The threshold value of nickel is 155.32 ppm and this value indicates that there are twelve anomalous nickel values in all; occurring in areas dominantly underlain by grey gneiss (southwestern portion), charnockite, diorite, talcose rock, quartzite (western portion) and one isolated value in area underlain by pegmatite (Fig. 8) . Other fairly high values in the range of 107.28 ppm – 155.32 ppm occur in areas underlain by diorite, charnockite and grey gneiss (southwestern part). Areas underlain by quartzite (in the eastern portion), grey gneiss (northern portion) and pegmatite are characterized by relatively low (59.15 ppm – 107.27 ppm) and very low values in (2.30 ppm – 59.14 ppm).

With a background value (mean) of 53.61 ppm, the abundance of nickel is very low in the study area when compared with the average abundance in the earth's crust (75 ppm), ultramafic rocks (2000 ppm), granite (0.5 ppm) and soils (5 – 500 ppm) (Table 2).

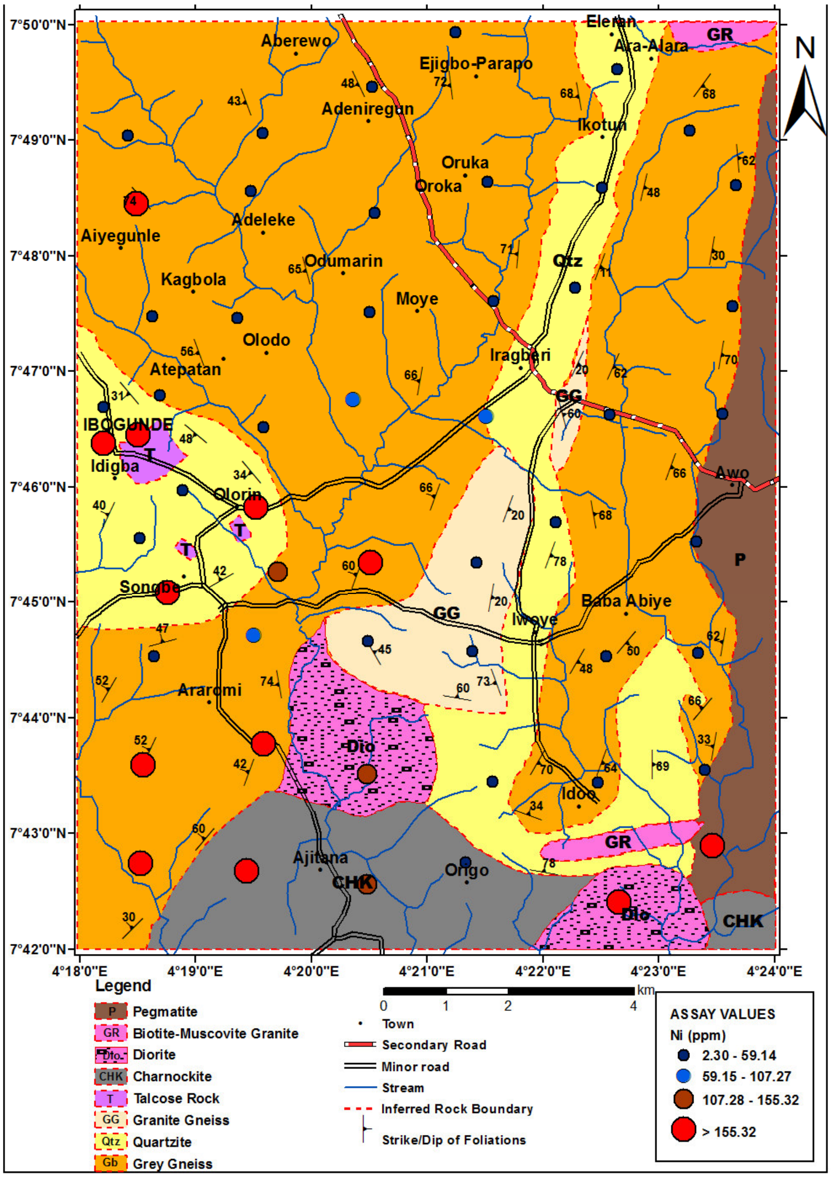

Figure 8: **Location Point Symbol Map of Nickel Distribution in Soil Samples of Ibogunde and its Environs, Southwestern Nigeria.**

Anomalous values of Ni occur dominantly in areas underlain by mafic or ultramafic rocks (Onag and Sevillano, 1975; Adesiyan *et al.,* 2014). Adetunji (2012) reported the occurrence of meta-ultramafites and amphibolites in parts of the study area. Nickel can occur with chromium, copper and cobalt in ultramafic and mafic rocks (Wedepohl, 1978). Ure and Burrow (1982) concluded that since Ni $^{2+}$ substitutes readily for Mg^{2+}, a high background concentration of the element in mafic or ultramafic rocks is expected. Ajayi (1988) obtained values of Ni between 30 and 40 ppm from soils predominantly within the area underlain by amphibolite in Ife-Ilesha Schist Belt.

Copper – Cu

The concentration values of copper ranged from 9.19 ppm to 181.05 ppm with a mean value of 32.38 ppm. The threshold is 84.12 ppm and this value indicates that there are twelve anomalous values though with clusters in the southern portion (Fig. 9). The concentration range (between 6.0 ppm and 196 ppm) of copper was obtained by Ajayi (1988). The underlying rocks in the study area with anomalous values of Cu are charnockite, diorite, talcose rock and quartzite (western portion); two (2) isolated anomalous values occur in areas underlain by grey gneiss. Relatively high Cu values between 59.16 ppm and 84.12 ppm occur in areas underlain by grey gneiss and granite gneiss.

A comparison of the background value (32.38 ppm) to its average abundance in earth's crust (55 ppm), ultramafic rocks (10 ppm), granite (10 ppm) and soil (2 ppm – 100 ppm) shows moderate abundance of copper in soil samples of the study area (Table 2).

The point symbol map of copper shows fairly similar distribution pattern to those of Fe, Mn, Ni and Co. Most ferromagnesian minerals will house copper (showing a greater affinity for mafic than for felsic igneous rocks), though copper prefers the sulphide phase to the silicate phase (Kabatas-Pendias and Pendias, 2001).

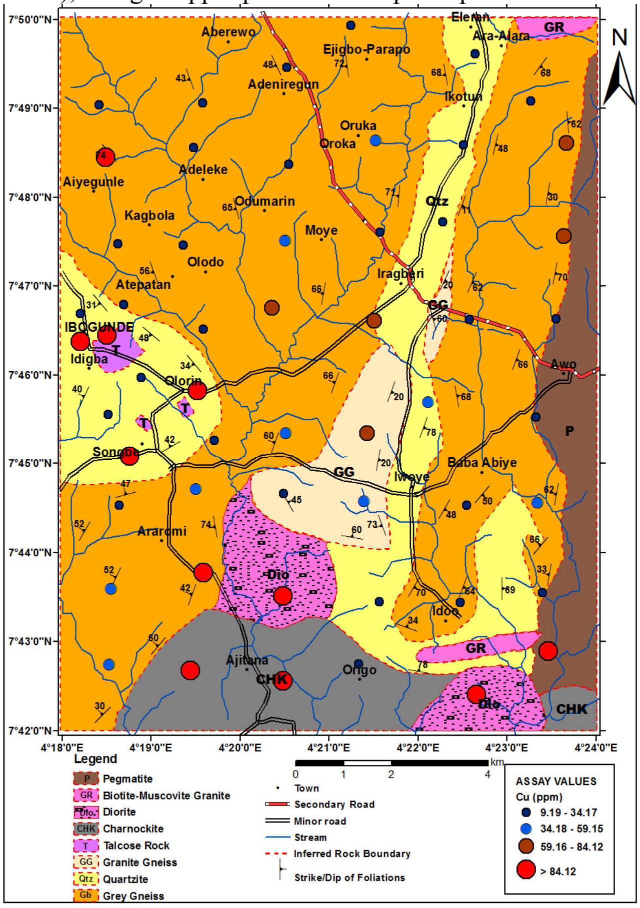

Figure 9: **Location Point Symbol Map of Copper Distribution in Soil Samples of Ibogunde and its Environs, Southwestern Nigeria.**

Tantalum - Ta

Tantalum was detected in all samples analyzed and shows wide range of concentrations which fall between 1.12 ppm and 7.28 ppm with a mean of 2.36 ppm. The threshold value of Ta is 4.87 ppm and this value indicates that there are four anomalous values (Fig. 10). These anomalous sites are underlain by pegmatite largely and granite gneiss to a very small extent. The isolated anomalous value in the area underlain by granite gneiss is a suspected outlier. Low values between 2.38 ppm and 3.62 ppm occur in areas underlain by pegmatite and grey gneiss. Areas underlain by talcose rock, quartzite, charnockite, diorite and grey gneiss are characterized by very low values (0.33 ppm – 2.37 ppm). The background value of 2.36 ppm suggests relatively high abundance of tantalum when compared with its average abundance in earth's crust (2 ppm), ultramafic (1 ppm), and granite (3.5 ppm).

However, the source of tantalum in this area is thought to be the intrusive pegmatite. According to Woakes *et al.* (1987); Fyfe (1999), mineralized pegmatites consist of quartz, k-feldspars, albite, muscovite and less commonly biotite and a range of accessory minerals including tourmaline, and economically important cassiterite and columbite, tantalite.

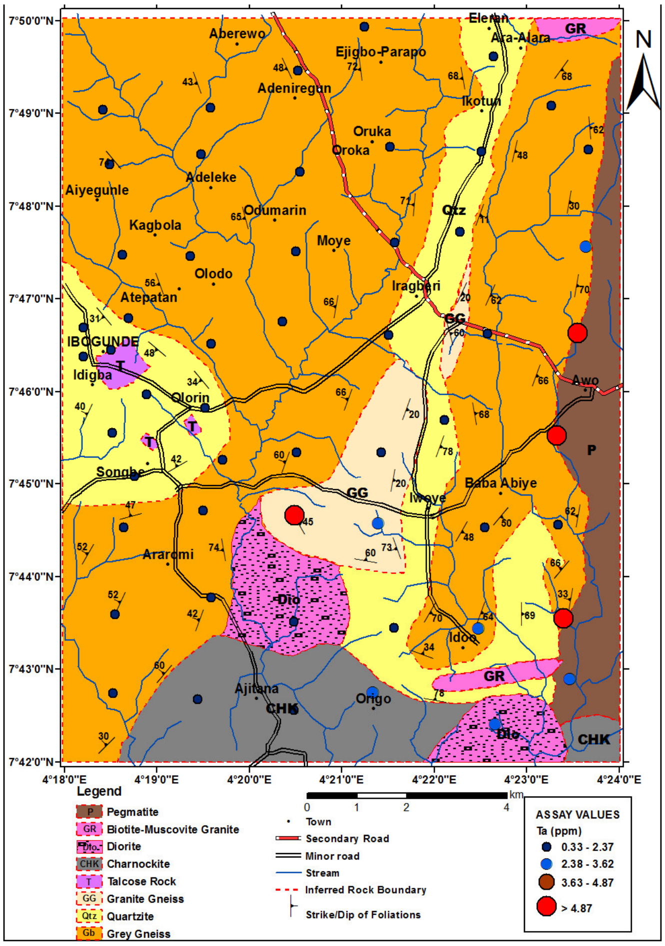

Figure 10: **Location Point Symbol Map of Tantalum Distribution in Soil Samples of Ibogunde and its Environs, Southwestern Nigeria.**

Thorium –Th

Thorium shows range of concentrations between 6.55 ppm and 83.07 ppm with a mean value of 21.72 ppm. The threshold is 46.73 ppm; indicating three anomalous values (Fig. 11). The anomalous sites are underlain by pegmatite in the eastern part except for an area with relatively low Th value.

The areas underlain by quartzite (western portion), talcose rock, grey gneiss, charnockite and diorite are characterized by low values (19.95 – 33.53) ppm and very low values (0.44 – 19.94) ppm. Similar to tantalum, the anomalous values and string of thorium values greater than 46.733 ppm – 27.48 ppm also define a similar trend in the pegmatite. This indicates pegmatitic bodies enriched in tantalum and thorium. The anomalous locations common to La, Th and Ta support their possible occurrence in the same rock type, mostly pegmatitic bodies.

A comparison of the background value (11.00 ppm) for thorium in the study area with its average abundance in earth's crust (10 ppm) shows that thorium is relatively high. This work is consistent with the work of Adepoju (2018) who obtained a mean of 10.70 ppm in the soils of Orle district. These anomalous and relatively high Th concentrations are significant and may be related to suspected tin mineralization. Thorium associates with tantalum and lanthanum in pegmatites (Wedepohl, 1978 and 1995).

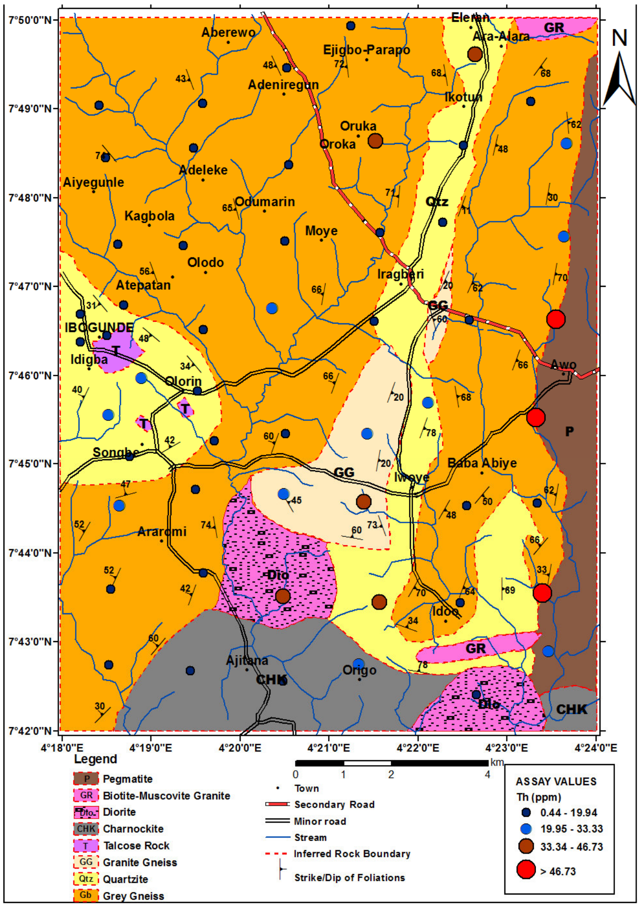

Figure 11: **Location Point Symbol Map of Thorium Distribution in Soil Samples of Ibogunde and its Environs, Southwestern Nigeria.**

Magnesium – Mg

Magnesium is widely distributed in the study area and range from 60.32 ppm – 22860.14 ppm with a mean value of 2494.22 ppm. The threshold value of Mg is 1172.05 ppm. There are twelve anomalous values of Mg; the underlying rocks in areas with anomalous values are quartzite (western portion), charnockite, grey gneiss, diorite and talcose rock. An isolated anomalous value occurs in area underlain by pegmatite. Other relatively high values (7370.41 – 110505.60) ppm occurs mainly in area underlain by grey gneiss and diorite (Fig. 12).

The relatively low concentrations that range between 3685.21 ppm and 7370.40 ppm are more scattered in areas underlain by granite gneiss, grey gneiss (mainly in the northern half), quartzite (eastern portion) and pegmatite. Generally, the low values that fall between 60.32 ppm and 3685.20 ppm are associated with areas underlain by grey gneiss. There is fair similarity in the point symbol maps of Mg, Fe and Ni.

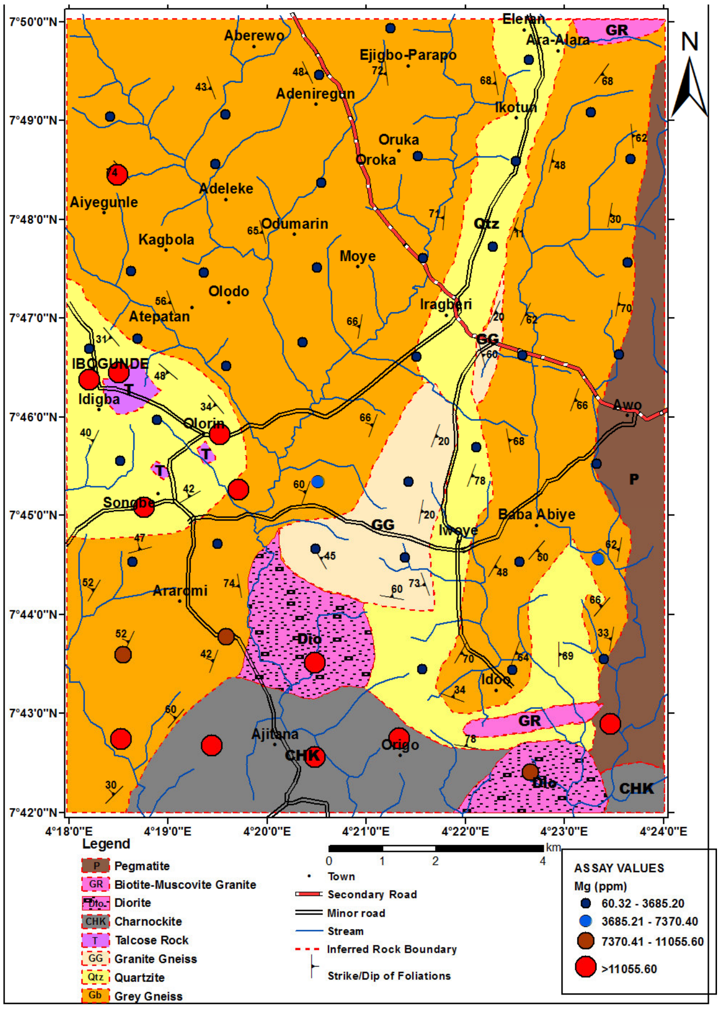

Figure 12: **Location Point Symbol Map of Magnesium Distribution in Soil Samples of Ibogunde and its Environs, Southwestern Nigeria.**

4.3 Discussions

The use of soil geochemistry in geological mapping and mineral exploration had been found to be effective (Cohen *et al.,* 2008; Ajayi, 1988; Zuo and Wang, 2016 and Adesiyan, 2018; Thiombane *et al.,* 2018). This study is another way of demonstrating the suitability of soil geochemical survey in investigating the mineral potential of the study area and as a means to unravel the underlying bedrock being an aid to geological mapping in such area. The multiple approaches to interpretation of the analytical data were found to be excellent as this provided basis of comparison with works carried out by some authors in different areas. Various workers have also applied various statistical methods in the interpretation of data (Shiva, 2004; Adesiyan *et al.,* 2014; Adepoju *et al.,* 2018).

The general concept in the interpretation of exploration oriented geochemical data relies on the recognition of anomalous patterns with a high degree of confidence. These are considered more useful than anomalous values. Variation in trends within a region, district, or an area is considered to be of greater practical value than geochemical deviations from normal. The ability of these techniques to delimit spatially significant anomalous patterns therefore make them potential and useful interpretational tools, particularly in an area where geochemical responses are weak (Reimann *et al.,* 2010; Caers, 2011). The geochemical distribution maps (location point symbol map and contour maps) of each element determined in the soils of the study area gave a quick pictorial view of the distribution patterns (Figs. 4 to 12). It also facilitated comparison between the distribution patterns and the geology, as well as possible geochemical associations.

It is a well established fact that the characteristic dispersion pattern in soil is a reflection of the parent rock, concealed ores and the effect of environmental factors (Levinson, 1974; Adesiyan *et al.,* 2018). The point symbol map of each of the elements analysed in soils of Ibogunde and its environment revealed diverse pattern of distribution. Some of these did not perfectly correspond with the inferred geological boundaries especially in areas with thick overburden. In addition, integrating the interpreted statistical soil data with the point symbol map of element concentration superimposed on the produced geological map shows that most of the inferred rock boundaries were over or underestimated and some mineral occurrences were yet to be accounted for.

The anomalous and relatively high values of ferromagnesian minerals (Fe, Cr, Ni and Mg) are expected dominantly in areas underlain by mafic or ultramafic rocks but the point symbol maps revealed anomalous and relatively high values in some areas underlain by quartzite in some location (Figs. 4, 6,7 and 12). Considering the almost flat topography of the study area and lack of movement either thrust, soil creep, nappe in the environment, most soils in the study area can be said to be in situ and these are representative of the underlying geologic material. The tropical nature of the environment which gave rise to thick overburden made rock exposure to be poor in such place and the rock boundaries were inferred. There are still missing talcose bodies within the quartzite in Ibogunde considering the consistently anomalous and relatively high values of ferromagnesian minerals. Thus, the area extent of the talcose rock was extended. A close view at the point symbol maps of tantalum and thorium (Figs. 10 and 11) show dominantly low values for areas deduced to be underlain by charnockite with relatively high concentrations for pegmatitic bodies. However, the width and length of the pegmatitic body in the eastern portion was overestimated. The soil geochemical data showed that some of the areas with poor exposure are underlain by charnockite and not by pegmatite as inferred. Charnockites are characterized by spheroidal weathering and are weathers from the outer to the inner core. The point symbol maps which revealed high concentrations of Fe and Mg and could be linked to the mineralogy of the rock as charnockite as opposed to the earlier inferred pegmatite (Figs. 4 and 12). After inferences and careful interpretation of all data, the produced geological map was thereafter improved by the soil geochemical data as some of the areas have paucity of outcrops or poor exposures (Fig. 13).

4.4 Conclusions

Only three (3) elements out of the nine (9) elements plotted showed significant anomalous values. The anomalies of La, Ta, and Th were considered to be derived from primary mineralization of these elements. Those of Mn, Co and Fe are interpreted as being caused by secondary environmental controls, notably, precipitation of Mn-oxides in the soils. Insignificant anomalies were observed from other elements. The location point symbol maps aided in properly delineating the underlying geology of the study area. The correlations of these geochemical maps allowed for the adjustment of the geological boundaries where rock exposures were not found.

The study concluded that multi-element soil geochemistry can be used as a geological mapping tool especially in areas devoid of rock exposures due to thick overburden, in addition to its usefulness in delineating areas of economic mineral potential.

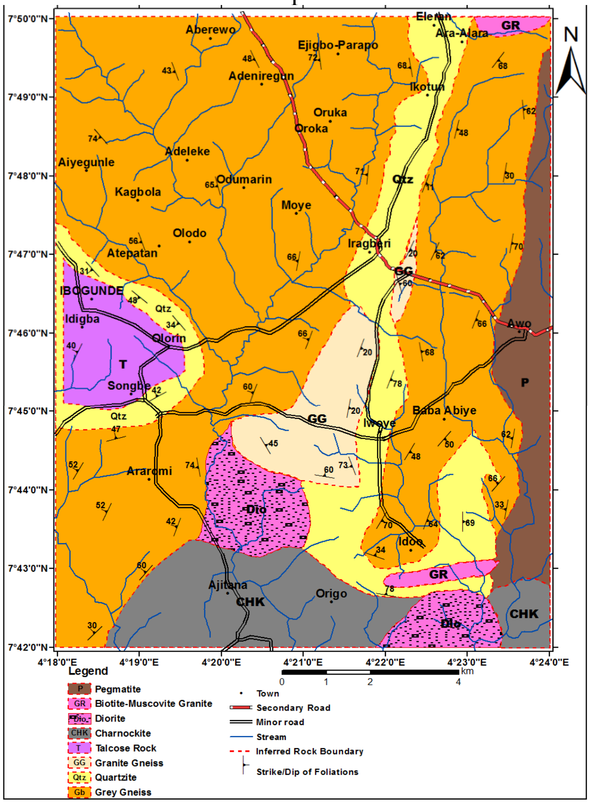

Figure 13: **Integrated and Updated Geological Map of Ibogunde and its Environs on the Basis of Soil Geochemistry.**

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