Stream Sediment Geochemistry of Telemu and its Environs: A

Tool in Baseline Assessment of Mineralization Potential

Adedamola Owoeye¹, Taiwo Ajayi², Taoreed Adesiyan¹,

1. Department of Geology, Obafemi Awolowo University, Ile -Ife, Osun State, Nigeria

2. The Premiere University of Sao Tome and Principe

* E-mail of the corresponding author: *dammybea@yahoo.co.uk

Abstract

Reconnaissance stream sediment geochemical studies were carried out in Telemu-Awo-Ede areas of Osun State to determine the concentrations and distribution patterns of trace elements. This was with a view to assessing the mineralization potential of the study area.

Ninety six active stream sediments were collected from stream channels in Telemu-Awo-Ede. The samples were air-dried and sieved. One gram each of the minus 177 micron fraction was subjected to hot acid extraction with aqua regia (3 HCl: 1 HNO₃) and perchloric acid (HClO₄) in ratio 2:1. The aliquots were analyzed for Mo, Co, Cd, Ta, Cr, Cu, Fe, U, Th, Sc, Zn, Sr, La, Mn, Ni, Pb, Sn and Zn using the Buck 205 Atomic Absorption Spectrometer (AAS) interfaced with Graphite Furnace. The geochemical data was interpreted using both univariate and multivariate statistical methods. The element distribution and smoothed contour maps were plotted using ArcView-GIS and Geosoft Oasis Montaj Software, respectively.

The results showed that only four (4) elements out of the eighteen (18) elements analyzed showed significant anomalous values. The anomalies of Sn, Sc, Ta, and Th were considered to be derived from primary mineralization of these elements. Those of Mn, Zn, Cd, and Fe are interpreted as being caused by secondary environmental controls, notably, precipitation of Mn-oxides in the soils and or anthropogenic contamination for Zn and Cd. Insignificant anomalies were observed from Ni, Cr, La, Mo, Pb, Cu Co, U, Sb and Sr.

The study concluded that this area has Sc-Sn-Ta and Th mineralization potentials related to the pegmatoids. The results obtained from the geochemical studies confirmed the heterogeneous nature of the underlying rocks. Areas underlain by pegmatites and pegmatised schist coincide spatially with zones of relatively high values for U, Th, La, Sc, Sn and Ta; and are suspected to be mineralized in tin, scandium, thorium and tantalum.

Keywords: Mineralisation potential, significant anomalies, insignificant anomalies, environmental controls.

1. Introduction

Modern exploration involves integrated approach that involves geophysical and geochemical studies. However, geophysical method is relatively more expensive in tropical environment where high rate of weathering has generated thick overburden and dense vegetation that is likely to conceal any obvious mineralization. The area chosen for this study is a typical tropical environment. Geochemical studies using stream sediment as sampling media in this area can help in the delineation of likely areas of mineralization for further exploration studies. Stream sediments are employed almost exclusively for reconnaissance studies in drainage basins (Hawkes, 1976) and if samples are properly collected, the samples represent the best composite of materials from the catchment areas upstream from the sampling site with potential of recognizing geochemical or mineralogical anomalies within the catchment areas for follow-up works (Adekeye, 1999, Lepeltier, 1971; Webb, 1971). Stream sediments are natural composite of all materials upstream from a sample site (Tooms, 1983).

The spatial framework for the stream sediment geochemical mapping of the study area is based on Global Reference Network (GRN) cells defined by Darney *et al.* (1995) and falls within N05 E04 GRN cell. The study area falls within the Iwo SE standard topographic sheet number 242 published by the Federal Survey of Nigeria in 1965 on a scale of 1:50000. The total area covered is about 26 x 55 km² defined by latitudes 7° 38¹ and 7⁰ 45¹ N and longitudes 4⁰ 15¹ and 4⁰ 30¹ E (Fig. 1).

Although, illegal mining for gemstones, tantalite, cassiterite and columbite, within the area underlain by pegmatitic schist, had been reported in Telemu-Awo-Ede area of Osun State, no systematic exploration programme had been carried out. Thus, the finds were limited to chance discoveries. This study intends to apply stream sediment geochemistry as a reconnaissance tool in the delineation of potential mineralization areas.



Figure 1: Topographical Map of the Study Area (Adapted from Iwo Sheet 242 S.E, Produced by Federal Survey of Nigeria, 1965)

2. Geology of the Area

The study area is underlain by rocks of the Nigerian Basement Complex, which are Precambrian to Cambrian in age (Federal Survey of Nigeria, 1966; and NGSA, 2009). The crystalline Basement Complex consists of a wide variety of metamorphic and igneous rocks (Fig. 2) and has been shown to be polycyclic with isotopic ages ranging from 2800 Ma to 4500 Ma (Rahaman, 1988).

A lot of work has been carried out on the Basement Complex of Nigeria by various researchers: Jones and Hockey (1964), Oyawoye (1964, 1972), Mc Curry (1976), Odeyemi (1981), Rahaman (1976, 1988, 2002a), Adekoya (1991) and Adekoya *et al.* (2003). The division adopted for the purpose of discussing the Nigeria Basement Complex in this study however followed the fourfold tectono-stratigraphic division given by Adekoya (1991) and Adekoya *et al.* (2003). This seems to explain best the field associations and age relationship among the lithologic units of the Basement Complex. These divisions are: Migmatite-Gneiss Complex, the Schist Belts; the Pan African Granites (Older Granites) and associated granitoids; and minor felsic and mafic intrusives.



Figure 2: Map of Osun State Showing the Study Area (Adapted from NGSA, 2011)

The Basement Complex rocks underlying the study area are as shown on the 1:250,000 Iwo sheet 60 and modified from Geological and mineral resources map of Osun State published by Authority of the Federal Republic of Nigeria (Fig. 3). These consist of pegmatite, fine to medium-grained biotite and biotite muscovite granite, quartz syenite, charnockitic rocks, pegmatised schist (biotite-muscovite schist), undifferentiated schist, quartz ite and quartz schist, porphyroblastic gneiss and migmatite (undifferentiated).

Adetunji (2012) carried out detailed geological mapping and petrographic descriptions of rocks that covered Telemu-Awo-Ede area and the various lithologic units in the study area were classified into three (3) groups: Older Granite (Pan-African Granitoids), Metasedimentary and metaigneous rocks (Schist Belt) and Migmatite-Gneiss-Complex.



Figure 3: Geological Map of the Study Area (Adapted from Iwo Sheet 60, 1966 and NGSA, 2009).

3. Methodology

Ninety-six (96) stream sediment samples were collected from the first and second order streams at appropriate sampling interval. The actual sampling points were determined with the use of Global Positioning System (GPS) and later plotted on the topographical map of the study area (Fig. 4)

In the laboratory, the samples were air dried at room temperature for six weeks. The minus 80-mesh (177 micron) fraction size was used for instrumental (elemental) analysis. One gram of each of the retained minus 80 mesh sieve size samples was subjected to hot acid extraction with aqua regia (3 HCl: 1 HNO₃) and perchloric acid (HClO₄) in ratio 2:1 in a 1000 l volumetric flask. 500 ml of ultra-distilled water was also measured into another 1000 ml volumetric flask. About 30 ml of the acid mixture was dispensed and

left in a digester block for 3 hours at 250^oC. The aliquots were allowed to cool at room temperature. Sample digestions with these acids were desirable than fusion. The reasons for these are three (3) folds. First, sample decomposition by these acids is generally simpler and more rapid. Secondly, the blanks are usually lower. Lastly, lower determination limits are attained because of the lower amount of dissolved solid (Aruscavage and Crook., 1996; Balcerzak, 2002).



Figure 4: Drainage and Sample Location Map of the Study Area

The resulting aliquots were transferred to a set of vials for elemental determinations of Mo, Co, Cd, Ta, Sb, Sc, U, Th, Sr, Cr, Cu, Fe, La, Mn, Ni, Pb, Sn and Zn using the Buck-205 Scientific Model Atomic Absorption Spectrophotometer (AAS) compartmentalized with Graphite Furnace. This AAS has Zeeman background correction systems to eliminate various forms of interferences. Standard analytical conditions for Buck-205 AAS model such as wavelength, slit setting, correct lamp, right flame, linear range etc. were strictly adhered to. Analytical precision and accuracy were determined by the analysis of duplicates, repeated analyses of some samples where necessary, random insertions of standard samples and plotting quality control charts.

The geochemical data generated were interpreted using both univariate (frequency distribution plots, and cumulative probability plots) and multivariate statistical techniques (correlation coefficient, and factor analysis). In addition, the trace element distribution maps were produced using ArcView GIS and Geosoft Oasis Montaj software.

4. RESULTS AND INTERPRETATION

To identify regions favourable for mineralization, it is necessary to establish the background and threshold, the latter being the upper limit to background above which values were assumed to be anomalous. In this

reconnaissance surveys, thresholds were established by presenting the data in the form of frequency distribution plots (histograms), computing mean and standard deviation (Table 1).

The threshold values for the individual elements were then determined using the formula:

Median plus two times standard deviation

Threshold = Median $\times 2$ S.D

(1)

Where:

S.D = Standard deviation

Median values were used for estimating the average concentrations of elements as these proved to be better statistical parameter of average concentrations than mean.

Geochemical maps in general term have an important key element of location since the eye is well adapted to the recognition of patterns in spatial data. McCammon (1974) commented that the use of maps is perhaps the most powerful single tool in the interpretation of spatially distributed data. Figures 5A to 22A show the point location symbol maps produced with ArcView GIS (version 9.3) while Figures 5B- 22B show the contour maps plotted using the Geosoft Oasis Montaj software from the geochemical data.

Table 1: Summary of Basic Statistical Parameters of Raw Active Stream Sediment Geochemical Data, Telemu-Awo-Ede Area, Southwestern Nigeria

Elements	Range	Arithmetic Mean Values, X	Median, X _m	Standard Deviation, (S)	Threshold = $(X_m +$
					2S)
Cd (ppb)	3.17 - 385.15	99.91	59.89	82.24	224.37
Ni (ppm)	2.85 - 204.70	51.53	29.25	52.57	134.39
Zn (ppm)	12.76 - 3472.19	670.37	507.32	653.82	1814.96
Pb (ppm)	2.2 - 156.25	55.44	51.19	38.33	127.85
Cr (ppm)	0.62 - 273.90	77.66	57.60	70.63	198.86
Co (ppm)	1.32 - 361.32	62.96	21.00	93.02	207.04
Mo (ppm)	0.01 – 1.91	0.52	0.36	0.49	1.34
Sn (ppm)	0.58 - 276.58	80.48	62.34	59.22	180.78
La (ppm)	0.02 - 51.35	9.50	1.52	13.89	29.30
Sc (ppm)	2.5 – 194.10	37.82	11.45	45.79	103.03
U (ppm)	0.07 -10.20	0.96	0.73	0.84	2.41
Sb (ppm)	0.06 - 0.31	0.13	0.12	0.05	0.22
Ta (ppm)	0.7 10.2	1.50	4.61	1.76	8.11
	0.7 - 10.2	4.59	4.61	1.76	25.54
Th (ppm)	2.1 – 37.11	12.96	11.00	7.23	25.56
Sr (ppm)	0.05 - 2.30	0.86	0.87	0.47	1.79
Fe (%)	0. 7128 – 18.61	7.61	7.63	3.50	14.62
Cu (ppm)	2.1 - 142.28	44.66	44.67	36.84	118.328
Mn (ppm)	23.45 - 6976.45	2225.66	1193.76	2230.43	5654.81

4.1. Spatial Distribution of Elements

According to Rosler and Lange (1972), certain elements show a marked affinity for rocks with basic or ultrabasic character while others are relatively enriched in acidic rocks. It can be inferred that trace element contents in superficial materials like stream sediment, water, are more or less directly linked to the composition of the underlying bedrock. Multi-element stream sediment 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 stream sediments 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 and smoothed contour maps for illustration (Figs. 5A to 22B). The location point symbol maps are super-imposed on the geological map of the area to aid the description of element distributions.

Cadmium – Cd

Cadmium is widely distributed in the study area and range from 3.17 ppb - 385.15 ppb with a mean value of 99.91 ppb, threshold value of Cd is 224.37 ppb. There are six anomalous values of Cd. The underlying rocks in areas with anomalous values are migmatite, undifferentiated schist, and porphyroblastic gneiss. Generally, the low values that fall between 3.17 and 76.91 ppb are associated with areas underlain by pegmatite and migmatite

on the eastern and western parts of the study area, respectively (Fig. 5A).

Comparing the median value of Cd in stream sediments of the study area (59.89 ppb) with the average abundance of Cd in the earth's crust, ultramafic rocks, granite and soils 200 ppb, 2 ppb, 200 ppb and 100-200 ppb, respectively, it was observed that the relative abundance of Cd in this area is high. However, these anomalous concentrations may not be connected with Cd mineralization. The increasing use of Zn in fertilizers may lead to Cd contamination. Phosphate fertilizers contain between 5 and 100 ppb Cd and up to 300 ppb (Smith, 1999b; Pfeifer, 2000). The smoothed contour map of cadmium in (Fig. 5B) delineates more anomalous zones with contour values greater than 248.7 ppm around northeastern and north central parts in areas underlain by migmatite and pegmatised schist. The prominent N-S trending anomalous zone in the southeastern part is underlain by undifferentiated schist. Background values are shown in western part where the underlying rocks are migmatite, undifferentiated schist and charnockitic meta-intrusives.

Nickel – Ni

Nickel was detected in all samples and showed relatively wide concentrations which range between 2.85 ppm and 204.7 ppm with a mean value of 51.33 ppm. The threshold value of nickel is 134.39 ppm and this value indicates that there are eleven isolated anomalous nickel values occurring in areas underlain by migmatite, porphyroblastic gneiss, charnockitic meta-intrusives, pegmatised schist and undifferentiated schist. The area underlain by pegmatites is characterized by relatively low (46.71-90.56) ppm and very low values in (2.85-46.70) ppm are scattered throughout the area underlain by pegmatised schist and pegmatite (Fig. 6A).

With a background value (median) of 29.25 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).



Figure 5A: Location Point Symbol Map of Cadmium Distribution in Stream Sediments of Telemu-Awo-Ede Area



Figure 5B: Contour Map of Cadmium Distribution in Active Stream Sediments of Telemu-Awo-Ede Area.



Figure 6A: Location Point Symbol Map of Nickel Distribution in Stream Sediments of Telemu-Awo-Ede Area

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. Taylor (1965), Wedepohl (1978) and Ure and Burrow (1982) concluded that since Ni²⁺ substitutes readily for Mg^{2+} , a high background concentration of the element in mafic or ultramafic rocks must be expected.

The distribution of nickel in the study area as revealed by its smoothed contour map (Fig. 6B) is similar to that of the location point map (Fig. 6A). The prominent N-S trending anomalous zone in the central part is underlain by

the charnockitic meta-intrusives whilst the southeastern and northeastern zones are underlain by undifferentiated schist and pegmatised schist. The general low background areas are underlain by the felsic rocks (fine-medium grained biotite-muscovite granite and porphyroblastic gneiss).

Zinc – Zn

Zinc is widely distributed in the area and the values range from 12.76 ppm - 3472.19 ppm with a mean value of 670.37 ppm. With a threshold of 1814.96 ppm, there are six anomalous values of zinc concentrated in the eastern part (Fig. 7A). The underlying rocks in areas with anomalous values are migmatite, pegmatised schist and undifferentiated schist. The very low zinc values (12.76-613.49) ppm dominantly characterizes areas underlain by pegmatite.

Comparing the median value of zinc in the study area (507.32 ppm) with the average abundance of zinc in earth's crust (70 ppm), ultramafic/mafic rocks (50 ppm) and granite (40 ppm), the abundance of zinc in the study area is relatively higher.



Figure 6B: Contour Map of Nickel Distribution in Stream Sediments of Telemu-Awo-Ede Area



Figure 7A: Location Point Symbol Map of Zinc Distribution in Stream Sediments of Telemu-Awo-Ede Area

The distribution map of zinc and cadmium showed some simi the ratio of the mean values of Zn and Cd is 6704.1:1 compared to 500:1 of Rose *et al.* (1979). The highest proportion of zinc in the study area is likely from anthropogenic sources, since cadmium with which its associate is a typical anthropogenic element (Pfeifer *et al.*, 2000). It can therefore be concluded that use of fertilizers or pesticides that contain zinc in spraying cocoa plantation, zinc released from decayed leaves (Goldschmidt, 1954; Fyfe, 1999) in the study area might be the source of high zinc values rather than mineralization.

The smoothed contour map of zinc shown in Figure 7B reveals areas of relatively high concentrations in the eastern part. The areas of high concentration levels in the southwestern and central part with smaller closures scattered defined a N-S trend. Areas underlain by pegmatite, pegmatised schist, and migmatite show low background values.



Figure 7B: Contour Map of Zinc distribution in Stream Sediments of Telemu-Awo-Ede Area

Lead - Pb

Lead concentrations range between 2.2 ppm and 156.25 ppm with a mean value of 55.44 ppm. The threshold is 127.85 ppm and this indicates only four anomalous lead values (Fig. 8A). The underlying rocks in these areas with anomalous values are undifferentiated schist, migmatite and porphyroblastic gneiss. The area underlain by pegmatite is characterized by very low values (2.2-44.08) ppm and moderately low Pb values (44.09-85.93) ppm.



Figure 8A: Location Point Symbol Map of Lead Distribution in Stream Sediments of Telemu-Awo-Ede Area

However, the anomalous lead may not be attributed to mineralization, since the origin of lead in the area is not very clear. These high values may also be due to feldspars within the pegmatised schist or the micas in migmatites and or gneisses. Wedepohl (1970) reported the primary occurrence of lead in K-feldspars structure in which the element diadochically replaces potassium. Cech *et al.* (1971) has also observed the accumulation of lead in pegmatitic bodies in which it occurs in amanzonite feldspars while Hinnawi *et al.* (1969) noted the enrichment of lead in acid igneous rock.

The smoothed contour map for the distribution of lead in the study area (Fig. 8B) shows anomalous concentrations in the eastern and southeastern parts. These areas with anomalous and relatively high values show a N-S trending pattern; underlain by charnockitic meta-intrusives, pegmatised schist, migmatite and undifferentiated schist. The general low background values are underlain by the felsic rocks (fine-medium grained biotite-muscovite granite and porphyroblastic gneiss, pegmatite).



Figure 8B: Contour Map of Lead distribution in Stream Sediments of Telemu-Awo-Ede Area

Chromium – Cr

Chromium was detected in all samples and showed concentrations from 0.62 ppm - 273.9 ppm with a mean value of 77.66 ppm (Fig. 9A). The threshold value is 198.86 ppm and this indicates that there are eight anomalous values of chromium. The underlying rocks in these areas with anomalous values are migmatite, charnockitic meta-intrusives and porphyroblastic gneiss. Area underlain by pegmatites is generally associated with low chromium values (0.62-66.70) ppm.

When the background value (median) of chromium in stream sediments of the study area (0.63 ppm) is compared with the average abundance of the element in the earth's crust, ultramafic rocks and soils which is 100, 200 and 5-1000 ppm, respectively, the abundance of chromium is relatively lower. 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). The origin of the element in Telemu-Awo-Ede areas, Osun State may be due to the underlying mafic or ultramafic rocks.

The smoothed contour map of chromium (Fig. 9B) reveals anomalous concentrations in the western and northeastern parts with other smaller closures. These anomalous zones are underlain by migmatite, charnockitic meta-intrusives and porphyroblastic gneiss. The general low background areas are underlain by pegmatite, quartzite, migmatite and pegmatised schist.



Figure 9A: Location Point Symbol Map of Chromium Distribution in Stream Sediments of Telemu-Awo-Ede Area



Figure 9B: Contour Map of Chromium Distribution in Active Stream Sediments of Telemu-Awo-Ede Area.

Cobalt - Co

Cobalt was detected in all the samples analyzed and showed concentrations which range between 1.32 ppm and 361.32 ppm with a mean value of 62.96 ppm. The threshold of cobalt is 207.04 ppm and this value indicates that there are thirteen anomalous cobalt values (Fig. 10A). These anomalous areas are underlain by schist undifferentiated, pegmatised schist, porphyroblastic gneiss and migmatite. The area underlain by pegmatites is characterized by low values between 1.32 ppm and 69.89 ppm.



Figure 10A: Location Point Symbol Map of Cobalt Distribution in Stream Sediments of Telemu-Awo-Ede Area

When the background value (median) of cobalt in the study area (21.00 ppm) is compared with the average abundance of cobalt in mafic/ultramafic rocks (150 ppm) such as meta-ultramafites, migmatite, or charnockitic meta-intrusives which may be the source of cobalt in the study area, the abundance of cobalt can be said to be low. These anomalous values are thus insignificant and may be due to co precipitation of cobalt with Mn- and or Fe-oxides.

The smoothed contour map of cobalt distribution (Fig. 10B) shows anomalous zone. The areas with relatively high values show a N-S trending pattern; underlain by migmatite, undifferentiated schist and pegmatised schist.

Molybdenum – Mo

The concentration of molybdenum range from 0.01 ppm to 1.91 ppm with a mean value of 0.52 ppm. With a threshold of 1.34 ppm, there are seven anomalous values of molybdenum. The underlying rocks in areas with anomalous values are undifferentiated schist, migmatite and porphyroblastic gneiss and charnockitic meta-intrusives (Fig. 11A).



Figure 10B: Contour Map of Cobalt Distribution in Active Stream Sediments of Telemu-Awo-Ede Area



Figure 11A: Location Point Symbol Map of Molybdenum Distribution in Stream Sediments of Telemu-Awo-Ede

Area

A comparison of the background value (0.34 ppm) for molybdenum in the study area with its average abundance of molybdenum in earth materials shows that the concentration of molybdenum in the former is low. A possible source of these anomalous values of molybdenum could result from the use of fertilizers containing molybdenum (Ure and Berrow, 1982; Bostick *et al.*, 2003) and or domestic contamination (Morrison *et al.*, 2006).

The smoothed contour map of molybdenum in this study area is shown in Fig. 11B. The areas with relatively high values show prominent N-S trending anomalous underlain by undifferentiated schist and pegmatised schist, charnockitic meta-intrusives, migmatite and porphyroblastic gneiss. The areas underlain by the felsic rocks (fine-medium grained biotite-muscovite granite and porphyroblastic gneiss) show low background values.



Figure 11B: Contour Map of Molybdenum Distribution in Active Stream Sediments of Telemu-Awo-Ede Area

Tin – Sn

The concentration of tin range between 0.58 ppm and 276.58 ppm with a mean value of 80.48 ppm and threshold of 180.78 ppm. Eight anomalous values occur in the eastern area underlain by pegmatised schist, charnockitic meta-intrusives and pegmatite (Fig. 12A). The area underlain by charnockitic meta-intrusives with anomalous concentration is close to the old mine in Awo. In the area underlain by the pegmatised schist, these ranges of values define a general NW-SE trend which probably indicates pegmatitic bodies. Generally, the moderately low values between 60.66 ppm and 120.73 ppm and very low values (0.58-60.65) ppm are associated with areas underlain by migmatite in the western part.

A comparison of the background value for tin (62.34 ppm) in the study area with its average abundance in granite, granodiorite shows that tin is relatively in high abundance. The anomalous and relatively high tin values are significant and may be attributed to tin mineralization related to pegmatoids in the area.



Figure 12A: Location Point Symbol Map of Tin Distribution in Stream Sediments of Telemu-Awo-Ede Area

The smoothed contour map of tin distribution in the study area (Fig. 12B) shows a prominent NE-SW trending anomalous zone; underlain by pegmatised schist and pegmatites. The southeastern corner and northwestern part of the study area is generally marked as low concentration zone of tin, which is also correspond with portion explained to have low concentration in the location point symbol map of tin in the study area (Fig. 12A).

Tantalum - Ta

Tantalum was detected in all samples analyzed and shows wide range of concentrations which fall between 0.7 ppm and 10.2 ppm with a mean of 4.59 ppm. The threshold value of Ta is 8.11 ppm and this value indicates that there are eight anomalous values occurring mainly in the eastern part (Fig. 13A). These anomalous sites are underlain by pegmatite, pegmatised schist, charnockitic meta-intrusive and quartzite/quartz schist. The area underlain by charnockitic meta-intrusives with anomalous and high Ta concentration is close to the old mine in Awo. Areas underlain by undifferentiated schist, migmatite and quartz syenite in the western portion are characterized by relatively low (3.18-5.64 ppm) and low values (3.18 ppm). Similar to tin, the anomalous values and string of tantalum values in the range (3.2-5.0) ppm also define a NW-SE trend in the pegmatised schist. This indicates pegmatitic bodies enriched in tin and tantalum, but with tin being dominant.





Figure 12B: Contour Map of Tin Distribution in Active Stream Sediments of Telemu-Awo-Ede Area



Figure 13A: Location Point Symbol Map of Tantalum Distribution in Stream Sediments of Telemu-Awo-Ede Area

The background value of 4.61 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.

The smoothed contour map of tantalum distribution (Fig. 13B) shows almost similar pattern to its location point symbol map. Figure 13B shows a NE-SW trending zone of high values in the north-central and eastern part.

Other relatively high concentration zones of tantalum were revealed by the smoothed contour map in the western part underlain by charnockitic meta-intrusives, migmatite and pegmatised schist.



Figure 13B: Contour Map of Tantalum Distribution in Active Stream Sediments of Telemu-Awo-Ede Area

Scandium – Sc

The concentration of scandium range between 2.5 ppm and 94.1 ppm with a mean value of 37.82 ppm and threshold of 103.03 ppm. Fourteen anomalous values occur in areas underlain by undifferentiated schist, migmatite (where these two rocks in contact with pegmatised schist), pegmatised schist, pegmatites and charnockitic meta-intrusives (Fig. 14A).

Similar to Sn and Ta, the anomalous and strings of relatively high values occur in the area underlain by pegmatite and pegmatised schist. These anomalous and relatively high values define a general N-S trend which probably indicates pegmatitic bodies enriched with Ta, Sc and Sn, but with Sn being dominant. Generally, low Sc values (2.5-36.01) ppm are associated with areas underlain by undifferentiated schist, migmatite and charnockitic meta-intrusives in western part.

The background value of 11.45 ppm for scandium in this study in relation to its average abundance in earth's crust indicates that scandium is relatively abundant. This might reflect presence of scandium mineralization. Sc can occur with tin, rare Sc minerals, such as thortveitite $(Sc, Y)_2Si_2O_7$ in pegmatites (Dorokhin *et al.*, 1969).



Figure 14A: Location Point Symbol Map of Scan Suspected Trend of Peginatolds ediments of Telemu-Awo- Ede Area

The smoothed contour map of scandium (Fig. 14B) shows a NE-SW trending zone of high values in the eastern part in areas underlain by undifferentiated schist, migmatite (where these two rocks are in contact with pegmatised schist), pegmatite, and pegmatised schist. The southeastern corner and western part are generally marked as low concentration zones of scandium.

Thorium – Th

Thorium shows range of concentrations between 2.13 ppm and 7.11 ppm with a mean value of 12.96 ppm. The threshold is 27.48 ppm; indicating thirteen anomalous values (Fig. 15A). The anomalous sites are underlain by pegmatite, charnockitic meta-intrusives and pegmatised schist in the eastern part. The areas underlain by migmatite, fine-medium grained biotite-muscovite granite and undifferentiated schist in the western part are characterized by low values (2.1-10.56) ppm. Similar to tin and tantalum, the anomalous values and string of thorium values in the range (19.03-27.48) ppm also define a NW-SE trend in the pegmatised schist. The anomalous locations common to U, Th and La 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. These anomalous and relatively high Th concentrations are significant and may be related to suspected tin mineralization.



Figure 14B: Contour Map of Scandium Distribution in Active Stream Sediments of Telemu-Awo-Ede Area.



Figure 15A: Location Point Symbol Map of 1 norium Listribution in Stream Sediments of Telemu-Awo-Ede Area.

The smoothed contour map of thorium distribution in the study area (Fig. 15B) shows a NE-SW trending zone of high values in the eastern and north-central part (underlain by pegmatised schist charnockitic meta-intrusives and pegmatite). The general low background areas are underlain by undifferentiated schist and migmatite.



Figure 15B: Contour Map of Thorium Distribution in Active Stream Sediments of Telemu-Awo-Ede Area

Uranium – U

The concentration of uranium range between 0.07 ppm and 4.46 ppm with a mean value of 0.96 ppm and threshold of 2.41 ppm. Twelve anomalous values occur in the eastern area; underlain by pegmatite, charnockitic meta-intrusives and pegmatised schist (Fig. 16A). This location point symbol map (Fig. 16A) to some extent shows a pattern, which is similar to distribution patterns in La, Sn, Th, U because these elements have some common anomalous and relatively high concentrations in the eastern part of the study area. In the area underlain by the pegmatised schist, anomalous values define a N-S trend which probably indicates pegmatitic bodies

The background value (median) of uranium in the area is 0.73 ppm. A comparison of median value of U obtained in this study with its average abundance in earth's crust (2.7 ppm) and granite (4.8 ppm) shows that uranium is relatively lower.

The distribution of uranium in the study area from the smoothed contour map (Fig. 16B) shows a similar pattern with that of its location point symbol map. The prominent N-S trending anomalous zones in the southeastern, north-central and northeastern parts are underlain by pegmatised schist, pegmatite and charnockitic meta-intrusives. The general low background areas in the western part are underlain by migmatite, quartz syenite, undifferentiated schist and charnockitic meta-intrusives.



Figure 16A: Location Point Symbol Map of Uranium Distribution in Stream Sediments of Telemu-Awo-Ede Area.



Figure 16B: Contour Map of Uranium Distribution in Active Stream Sediments of Telemu-Awo-Ede Area.

Lanthanum – La

Lanthanum was detected in all samples analyzed and shows range of concentrations between 0.02 ppm and 51.35 ppm with a mean value of 9.50 ppm. The threshold value of lanthanum is 29.30 ppm and this value indicates that there are fourteen anomalous values in the eastern part (Fig. 17A). These anomalous sites are underlain by charnockitic meta-intrusives, pegmatised schist and pegmatite.



Figure 17A: Location Point Symbol Map of Lanthanum Distribution in Stream Sediments of Telemu-Awo-Ede Area

The background value (median) of 1.52 ppm suggests the abundance of lanthanum is relatively lower when compared with its average abundance in granite and earth's crust. This could also be attributed to low mobility of lanthanum in secondary environment (Moermond *et al.*, 2001).

The smoothed contour map of lanthanum distribution (Fig. 17B) shows a NE-SW trending zone in the northcentral and eastern part. The N-S trending patterns in these anomalous zones are underlain by pegmatite, pegmatised schist and charnockitic meta-intrusives.. The low concentration zones are the background areas and are underlain by undifferentiated schist, migmatite, charnockitic meta-intrusives and quartz syenite.



Figure 17B: Contour Map of Lanthanum Distribution in Active Stream Sediments of Telemu-Awo- Ede Area

Antimony - Sb

The concentration of antimony range between 0.6 ppm and 0.31 ppm with a mean value of 0.13 ppm and threshold of 0.25 ppm; indicating seven isolated anomalous values. The underlying rocks in areas with

anomalous concentrations are undifferentiated schist, porphyroblastic gneiss and migmatite (Fig. 18A).

With a background value (median) of 0.12 ppm, the abundance of antimony is moderate when compared with that of the earth's crust (0.2 ppm), ultramafic rocks (0.1 ppm) and granite (0.2 ppm). This is not indicative of any mineralization because only high concentration of antimony in stream sediment is a positive indication of a sulphide deposit in the immediate vicinity (Polikavpochin *et al.*, 1958; Lueth, 1999b).

The smoothed contour map for the distribution of antimony is shown in Fig. 18B. The prominent N-S trending anomalous zones are underlain by pegmatised schist, undifferentiated schist migmatite and charnockitic metaintrusives. The general low background values are underlain by fine-medium grained biotite-muscovite granite, pegmatised schist porphyroblastic gneiss and pegmatite.

Strontium – Sr

Strontium shows a range of concentrations which fall between 0.05 ppm and 2.3 ppm with a mean value of 0.86 ppm. The threshold value of strontium is 1.760 ppm and this value indicates that there are nine isolated anomalous Sr values which occur in areas underlain by undifferentiated schist, porphyroblastic gneiss and migmatite (Fig. 19A).



Figure 18A: Location Point Symbol Map of Antimony Distribution in Stream Sediments of Telemu-Awo-Ede Area



Figure 18B: Contour Map of Antimony Distribution in Active Stream Sediments of Telemu-Awo-Ede Area



Figure 19A: Location Point Symbol Map of Strontium Distribution in Stream Sediments of Telemu-Awo- Ede Area

A comparison of the background value for strontium (0.87 ppm) in the area with its average abundance in earth's crust (300 ppm), ultramafic rocks (1 ppm) and granite (5000 ppm) shows the abundance of strontium is relatively lower. Consequently, the anomalous and the many relatively high concentrations are not likely to be related to Sr mineralization in the area.

The smoothed contour map of strontium distribution is shown in Fig. 19B. It reveals areas of relatively high concentrations defined by a N-S trend; underlain by migmatite, undifferentiated schist, porphyroblastic gneiss and charnockitic meta-intrusives. The areas underlain by pegmatised schist and pegmatite show low background values.

Iron – Fe

Iron showed relatively wide concentrations which range between 0.71 % and 18.61 % with a mean value of

7.61 %. With a threshold value of 16.61 %, there are only three anomalous values of iron concentrated in the southwestern part (Fig. 20A). The underlying rock in areas with these anomalous values is migmatite. Areas underlain by pegmatites and pegmatised schist are characterized by relatively low (5.35-9.98) % and low values (0.71-5.34) %.

With a background value (median) of 7.63 %, 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 sediments (Clarke, 1966; Wedepohl, 1995). The anomalous and other relatively high values occur dominantly in area underlain by mafic or ultramafic rocks reported earlier by Adetunji (2012).



Figure 19B: Contour Map of Strontium Distribution in Active Stream Sediments of Telemu-Awo-Ede Area



Figure 20A: Location Point Symbol Map of Iron Distribution in Stream Sediments of Telemu-Awo-Ede Area

The smoothed contour map of iron distribution (Fig. 20B) reveals areas with relatively high values in areas underlain by migmatite and charnocitic meta-instrusives. However, the zone of relatively high values in the northwestern part is more pronounced in the smoothed contour map than in location point symbol map of iron (Fig. 20A). The eastern part underlain by pegmatite and pegmatised schist is generally marked with low background values concentrations.



Figure 20B: Contour Map of Iron Distribution in Active Stream Sediments of Telemu-Awo-Ede Area

Copper – Cu

Copper was detected in all samples analyzed and the values range from 2.10 ppm to 142.28 ppm with a mean value of 44.66 ppm. The threshold is 118.33 ppm and this value indicates that there are seven isolated anomalous values. The underlying rocks in areas with anomalous values are migmatite, charnockitic meta-intrusive and porphyroblastic gneiss (Fig. 21A). The areas underlain by pegmatites and pegmatised schist are characterized by relatively low (40.85- 79.58) ppm and very low values (2.1-40.85) ppm, and a few of these low values form cluster in areas underlain by pegmatised schist.

A comparison of the background value (44.67 ppm) to its average abundance in earth's crust, ultramafic rocks and granite shows moderate abundance of copper in stream sediment of the study area. The anomalous and relatively high values occur dominantly in areas underlain by mafic or ultramafic rocks. 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 (Anozie, 1978).

The smoothed contour map of copper distribution (Fig. 21B) reveals relatively high values in areas underlain by charnockitic meta-intrusive, schist undifferentiated and migmatite. The eastern part of the study area underlain by pegmatite and pegmatised schist is marked as low concentration zone of copper.



Figure 21A: Location Point Symbol Map of Copper Distribution in Stream Sediments of Telemu-Awo-Ede Area



Figure 21B: Contour Map of Copper Distribution in Active Stream Sediments of Telemu-Awo-Ede Area

Manganese – Mn

Manganese shows wide concentrations which range from 23.45 ppm to 6976.46 ppm with a mean value of 2225.66 ppm. The threshold value is 5654.81 ppm; which indicates that there are nine isolated anomalous values of Mn located in the eastern and western parts (Fig. 22A). The underlying rocks in areas with anomalous values are migmatite, undifferentiated schist, charnockitic meta-intrusives and porphyroblastic gneiss. Generally, the low values that range between 23.45 ppm and 1900.57 ppm are associated with areas underlain by felsic rocks (pegmatites, fine-medium grained biotite-muscovite granite and quartzite).



Figure 22A: Location Point Symbol Map of Manganese Distribution in Stream Sediments of Telemu-Awo- Ede Area

The background value (median) of 1193.76 ppm suggests relatively high abundance of manganese when compared with its average abundance in earth's crust (950 ppm), mafic/ultramafic rock (1300 ppm), and granite (500 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 stream sediments probably derived from the underlying mafic/magnesium and iron rich silicate rocks (Ahrens *et al.*, 1957; Bloss and Steiner, 1960). The anomalous and other relatively high values occur dominantly in area underlain by mafic or ultramafic rocks.

The distribution of manganese in the study area as revealed by its smoothed contour map (Fig. 23A) is similar to that of the location point map (Fig. 22A). The prominent N-S trending anomalous zones are underlain by undifferentiated schist, charnockitic meta-intrusives and migmatite. The general low background areas are underlain by felsic rocks (fine-medium grained biotite-muscovite granite and quartzite).



Figure 22B: Contour Map of Manganese Distribution in Active Stream Sediments of Telemu-Awo-Ede Area

4.2 Discussion

The use of drainage geochemistry in mineral exploration had been found to be effective (Elueze, 1977; Ajayi, 1988; Gordana et al., 2004; Adesiyan and Adekoya, 2008; Bamigboye and Adekeye, 2011; and Lapworth et al., 2012). The complexity of stream sediment compositions is a major problem in delineating the source of the elemental enrichment particularly where the catchment area include various lithological units (Aryafar, 2004). 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. The geochemical distribution maps (location point symbol map and contour maps) of each element determined in the stream sediments of the study area give a quick pictorial view of the distribution patterns (Figs. 5A to 22B). It also facilitated comparison between the distribution patterns and the geology, as well as possible geochemical associations. Certain elements such as U, Th and La showed similarity in their geochemical distribution map. Some of these elements have common sites of anomalous concentrations. Zones of relatively high values for U, Th, La, Sc, Sn ad Ta coincide spatially with areas underlain by pegmatites and pegmatised schist. Also, the anomalous element patterns reflect metal associations characteristic of felsic rocks.

5. Conclusion

Only four (4) elements out of the eighteen (18) elements analyzed showed significant anomalous values. The anomalies of Sn, Sc, Ta, and Th were considered to be derived from primary mineralization of these elements. Those of Mn, Zn, Cd, and Fe are interpreted as being caused by secondary environmental controls, notably, precipitation of Mn-oxides in the soils and or anthropogenic contamination for Zn and Cd. Insignificant anomalies were observed from Ni, Cr, La, Mo, Pb, Cu Co, U, Sb and Sr.

The point location symbol maps for tin, tantalum, scandium and thorium show NE-SW trends within the pegmatised schist and schist in the eastern portion that probably shows the trend of pegmatoids within these rock types. It therefore delineates these areas for follow-up studies. The smoothed contour maps of Cd, Zn, Ni, Sc, Sn, Ta, U, Th, La and Fe strongly reflect the underlying rocks. These observed trends underscore the usefulness of this technique as a geological mapping tool for producing improved geological map of the area.

The study area has been shown to be one of the seven mineralized pegmatite fields in Nigeria earlier outlined by Okunlola (2005) which refuted earlier confinement to occurrence along the SW-NE striking belt covering about 400 km and terminating in the Jos Plateau (Wright, 1970). Rare metal pegmatites occur within Telemu-Awo-Ede area of Southwestern Nigeria and are among the numerous bodies emplaced towards the end of Pan African magmatism within the region from the Jos Plateau in Central Nigeria to Abeokuta, Southwestern Nigeria.

Finally, the study concluded that factors controlling dispersion in the surficial environment of the study area are lithology, environmental influence, and primary mineralization. The results obtained from the statistical analyses and geochemical studies confirm the heterogeneous nature of the underlying rocks. Areas underlain by pegmatitic rocks (pegmatite and pegmatised schist) are suspected to be mineralized in tin, scandium, thorium and tantalum. The zones of relatively high values for U, Th, La, Sc, Sn and Ta coincide spatially with areas underlain by pegmatites and pegmatised schist. Stream sediments are therefore useful tool in the geochemical mapping of the study area. It serves as a pointer to possible occurrence of mineralization.

This study is another way of demonstrating the suitability or otherwise of stream sediment geochemical survey in investigating the mineral potential of the study area.

References

Adekeye, J. I. D. (1999), Heavy Minerals in stream sediments and their relationship to bedrock types and mineralization in Oro Area Southwestern Nigeria. *Nigeria Journal of Pure and Applied Sciences* 14, 906-914.

Adekoya, J. A. (1991), The geology of the banded iron-formations in the Precambrian Basement Complex of Northern Nigeria. Unpublished Ph.D. Thesis. University of Ibadan, Nigeria, 392-395.

Adekoya, J. A., Kehinde-Phillips, O. O. and Odukoya, A. M. (2003), Geological distribution of mineral resources in Southwestern Nigeria. In: Prospects for investment in mineral resources of Southwestern Nigeria, A. A. Elueze (editor.), 1-13.

Adesiyan, T. A. and Adekoya, J. A. (2008), Prospect of metallic mineralization in Gbongan area of Southwestern Nigeria. *Ife Journal of Science*, 10 (1), 151 – 170.

Adetunji, A. (2012), Geochemical and petrogenetic studies of pegmatites in some parts of Osun State. Unpublished Ph.D. Thesis, Obafemi Awolowo University, Ile-Ife, 28-67.

Ahrens, A., Willis, J. P. and Oosthuizen, C. O. (1967), Further observations on the composition of manganese nodules with particular reference to some of the rarer elements. *Geochimica et Cosmochimica Acta*, 31, 2169-2174.

Ajayi, T. R. (1988), Integrated exploration and statistical studies of geochemical data of amphibolites in Ife-Ilesha gold field. Unpublished Ph.D. Thesis, Obafemi Awolowo University, Ile-Ife, Nigeria, 139-210.

Anozie, J.O. (1978), Geochemical stream sediment exploration in Tin-mining area near Egbe, Kwara State, Nigeria. Unpublished M.Sc. Thesis, Obafemi Awolowo University, Ile-Ife, 67-69.

Aruscavage, P. J. and Crook, J. G. (1996), An improved method for the determination of trcae levels in geologic materials by Atomic Absorption Spectroscopy: *Analytical Chemica Acta*, Vol. 144, 223-227.

Aryafar, A. (2004), The analysis of the geochemical data in order to recognize the promising area in Khusf 1:50000 sheets, M.Sc. Thesis, University of Shahrood, Shahrood, Iran.

Balcerzak, M. (2002), Sample digestion methods for determination of traces of metals by spectrometric techniques. *The Japan Society of Analytical Sciences*, 18, 737-742.

Bamigboye, O. S. and Adekeye, J. I .D. (2011), Stream sediment survey of Eruku and its environs, Central Nigeria: implication for exploration. *International Journal of Research and Reviews in Applied Sciences*, 7 (2), 160-168.

Bloss, F. D. and Steiner, R. (1960), Biogeochemical prospecting for manganese in Northeast Tennessee. *Geological Society America Bulletin*, 71, 1053-1066.

Bostick, B. C., Fendorf, S., and Helz, G. R. (2003), Differential adsorption of molybdate and tetrathiomolybdate on pyrite (FeS₂). *Environmental Science and Technology*, 37, 285-291.

Cech, F., Misaf, F. and Povondra, P. (1971), A green lead-containing Orthoclase. Schweizerische Mineralogische und Petrogrphische Mitteilungen, 15 (3), 213 - 231.

Clarke, S. P. (1966), "Handbook of physical constants". Geological Society of America Memoir, 97, 11-18.

Darnley, A. G., Bjorklund, A., Bolviken, B., Gustavsson, N., Koval, P. V., Plant, J. A., Steenfelt, A., Tauchid, M., Xuejing, X., Garrett, R. G. and Hall, G. E. (1995), A global geochemical database for environmental and resource management. *Earth Science Report* 19, UNESCO Publishing, Paris, 22-23.

Dorokhin, I. V. and Bogacheva, E. N., Druzhinin, A. U, Sobolevsky, V. I. and Gorbunov, E. Z. (1969), Economic mineral deposits. Higher School Publishing Company, 99-105, 214-256.

Elueze, A. A. (1977), Geological and geochemical studies in the Ilesha Schist Belt in relation to gold mineralization, unpublished M. Phil. Thesis, University of Ibadan, Nigeria, 281-282.

Federal Survey of Nigeria (1965), 1:50,000 Topographical map of Iwo region, sheet 242 S.E. Complied by De Swardt, A. M. J., Van Coppenhagen, J. D., Ogbukagu, I. K. and Hubbard, F. H.

Federal Survey of Nigeria (1966), 1:250,000 Geological map of Iwo region: Iwo Sheet 60. Complied by complied by de Swardt, A. M. J., Van Coppenhagen, J. D., Ogbukagu, I. K. and Hubbard, F. H.

Fyfe, W. S. (1999), Geochemistry. In: C. P. Marshall and R. W. Fairbridge (Editors), Encyclopedia of Geochemistry. Kluwer Academic Publishers, Dordrecht, Germany, 277-279.

Gordana, P., Prohic E., and Tibljas-Darkos, D. (2004), Statistical assessment of geochemical pattern in overbank sediments of the river Sava, Croatia. *Journal of Environmental Geology*, 2, 10-12.

Hawkes, A.E. (1976), The early days of exploration geochemistry. Journal of Geochemical Exploration, 6: 1-12.

Howarth, R.J. and Thompson, M. (1978), A new approach to the estimation of analytical precision. *Journal of Geochemical Exploration*, 23-30.

Lapworth, D.J., Knight, K.V, Key, R.M., Johnson, J.C., Ayodele, E.A., Adekanmi, M.A., Arisekola, M.T., Okunlola O.A., Backman, B., Eklund, M., Everett P. A., Lister R.T., Ridgway, J., Watts, M.J., Kemp, J.S. and Pitfield E. J. (2012), Geochemical implication mapping using stream sediments in West-Central Nigeria: implication for environmental studies and mineral exploration in West Africa. *NERC open research archive. Applied Geochemistry*, 27 (6), 1035-1052.

Lepeltier, C. (1971), Geochemical Exploration in the United Nations Development Programme. *Geochemical Exploration CIM Special*, 11, 24-27.

Lueth, V. W. (1999b), Antimony: Element and geochemistry. In: C. P. Marshall & R. W. Fairbridge (Eds.), Encyclopedia of Geochemistry. Kluwer Academic Publishers, Dordrecht, Germany, 15-16.

Mc Curry, P. (1976), The geology of the Precambrian to Lower Paleozoic rocks of Northern Nigeria-a review. In: C. A. Kogbe (Editor), Geology of Nigeria (1st Edition). Elizabethan Publishing Company, Lagos, 15-39.

McLennan, S. M. and Taylor, S. R. (1999), Earth's continental crust. In: C. P. Marshall & R. W. Fairbridge (Editors), Encyclopedia of Geochemistry. Kluwer Academic Publishers, Dordrecht, Germany, 145-150.

Moermond, C. T., Tijink, J., Van Wezel, A. P. and Koelmans, A. A. (2001), Distribution speciation and bioavailability of lanthanides in the Rhine- Meuse estuary, *The Netherlands Environmental Toxicology and Chemistry*, 20 (9), 1916-1926.

Morrison, S. J., Mushovic, P. S., and Niesen P. L. (2006), Early breakthrough of molybdenum and uranium in a permeable reactive barrier. *Environmental Science and Technology*, 40, 2018-2024.

Nigeria Geological Survey Agency (2009), Geological and mineral resources map of Osun State, complied by Authority of the Federal Republic of Nigeria.

Nigeria Geological Survey Agency (2011), Pegmatite potential of Osun State. Occasional report, compiled by Authority of the Federal Republic of Nigeria, 1-51.

Okunlola, A. O. (2005), Metallogeny of Na-Nb Mineralization of Precambrian pegmatite of *Nigeria*. *Mineral Wealth*; 137, 2005, 38-50.

Oyawoye, M. O. (1964), The Geology of the Nigeria Basement Complex. *Journal of Mining, Geological and Metallurgical Society*, 1, 82-102.

Oyawoye, M. O. (1972): The Basement Complex of Nigeria. In: T.F.J. Dessauvagie and A.J. Whiteman (Editors), African Geology, University of Ibadan, 67-99.

Pfeifer, H. R., Derron, M. H., Rey, D., Schlegel, C., Dalla Piazza, R., Dubois, J.D. and Mandia, Y. (2000), Natural trace element input to the soil-water-plant system, examples of background and contaminated situations in Switzerland, Eastern France and Northern Italy. In: Markert, B. and Friese, K. (editors), Trace metals- Their distribution and effects in the environment, pp. 33 - 86.

Polikavpochin, V. V., Kasyanova, V. I., Utgof, A. A. and Cherbyanova, L. F. (1958), Geochemical prospecting for poly-metallic ore deposits in the Eastern Transbaikal by means of the muds and waters of the drainage system (translation from Russia): *Int. Geol. Rev.*, 2: 247-254.

Rahaman, M. A. (1976), Review of the Basement Geology of Southwestern Nigeria. In: Geology of Nigeria, C.A. Kogbe (Editor). Elizabethan Publishing Company, Lagos, 41-58.

Rahaman, M. A. (1988), Recent advances in the study of the Basement Complex of Nigeria: In Oluyide, P. O., Mbonu, W. C., Ogezi, A. E., Egbuniwe, I. G., Ajibade, A. C. and Umeji, A. C. (editors): Precambrian Geology of Nigeria. Geological Survey of Nigeria, 11-41.

Rahaman, M. A. (2002a), Mineral resources endowment of Osun State. Paper delivered at Investment Opportunities in Osun State Forum, Ada, 1-3.

Rose, A. W., Hawkes, H. E. and Webb, J. S. (1979), Geochemistry in Mineral Exploration. 2nd Edition, Academic Press; London, 1-21, 234-322.

Rösler, H. J. and Lange, H. (1972), Geochemical tables. Elsevier, Amsterdam, 466-468.

Smith, K. S. (1999b), Cadmium. In: C. P. Marshall & R. W. Fairbridge (Editors), Encyclopedia of geochemistry. Kluwer Academic Publishers, Dordrecht, Germany, 50-54.

Taylor, S. R. (1965), The application of trace element data to problems in petrology. *Physics and Chemistry of the Earth*, 6, (2), 133-213.

Ure, A. M. and Berrow, M. L. (1982), The elemental constituents of soils. In: H.J.M. Bowen (Editor), Environmental chemistry. *Royal Society of London*, Special Report Series, 2, 94-204.

Webb, J. S. (1971), Research in Applied Geochemistry at Imperial College, London. *Geochemical Exploration*. CIM Special, 11, 40-45.

Wedepohl, K. H. (1978), Handbook of Geochemistry (Springer-Verlag, Berlin etc., 1969 - 1978), 2 and 3.

Wedepohl, K. H. (1995), The composition of the continental crust. *Geochim. Cosmochim. Acta* 59, 1217-1232. Whalley, C., Hursthouse, A., Rowlatt, S., Iqbal-Zahid, P., Vaughan, H. and Durant, R. (1999), Chromium speciation in natural waters draining contaminated land, Glasgow, U.K. *Journal of Water Air and Soil Pollution*, 112, 389-405.