

Stream Sediment Geochemistry As A Tool For Assessing Mineral Potentials In Arinta And Olumirin Waterfalls In Ekiti And Osun States, Southwestern Nigeria

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Abstract—The geochemical analysis were carried out on the stream sediments samples around Arinta (Ekiti State) and Olumirin (Osun State) waterfalls, Southwestern Nigeria, the study areas fall in the coordinates 7° 31' 00"N to 7° 34' 45"N and 4° 52' 45"E to 4° 54' 00"E. This investigation was carried out to determine the concentration and distribution of major and trace elements in the stream sediments with a view to reveal the mineral potentials of the study area. Twelve (12) stream sediments collected at the depth of 20 -25cm were analysed major, trace and rare earth elements using Multi-collector High Resolution Inductively Coupled Plasma-Mass Spectrometry (MC-ICPMS). Geological mapping of the study area on the scale of 1:50,000 reveal three rock types which are undifferentiated schists, gneisses and migmatites with pegmatites, schists and epidiorite complex, quartzite and quartz schist. The metal ratio of the selected trace elements is as follows : Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, Zn and Sr have values less than 1 in all locations, which means there is depletion of these elements in the study area. Nevertheless, there is a relative enrichment of Cd and Zr in the study area. The result of the correlation analysis of some selected elements shows that Cs, Nb, Sn, Ta, Cu, Mo, Ni, V, Zn, Co Ga, Hf, Cr, Nb, Ba, Nb, Sr, Pb and Rb has high positive correlation coefficients. The cluster groups are distinct at the first cluster stage. These are Ag, Cd, Cs, Mo, Lu, Tm, Tb, Co, Sc, As, Rb, Li, Tl, Pb, Ga, U, Eu, Ho, Sn, Cu, Ta, Cr, Pr, W, Er, Ni, Dy, Gd and Zn while the second group has Ba, Sr, Nb, V, Hf, Nd, Y, La, Ce and Zr. The first cluster is related to both mineralization and rock weathering processes of both mineralized and barren/unmineralized rocks from the study area. The second cluster group is significant in indicating the presence of barite and other minerals that are rich in Ba and also related to minerals which are rich in Zr. Relationships between various elements have been identified from multivariate analysis and reflect genetic associations. Multivariate analysis of the stream sediment data establishes Eigen values that

account for 92.69% of the total variance and separates elements into five components. Component I, an association of Nd, Pr, La, Ce, Gd, Eu, Tb, W, Nb, Sn, V, Dy, Ho, Cr, Ni, Y, Er, Tm, Lu, U, Zr, Hf, Ga, Sc, and Sr. Component II, an association of Zn, Cu and Co, Pb which suggest the occurrence of sulphide mineralization probably associated with the felsic or granitic rock. Component III, an association of Rb, Ba, Sr Co, Pb and Cd suggesting occurrence of mafic and ultramafic rocks within the study area. Component IV has an association of Tl and Ag. Component V has an association of Mo and Ag which suggest occurrence of sulphide mineralization.

Keywords—*Arinta; Olumirin; Stream sediments; Precambrian basement rock; multivariate statistical analysis.*

INTRODUCTION

A range of media including stream sediments, soils and waters have been used in many countries and across different scales for geochemical mapping (e.g. Darnley, 1990; BGS, 1990; Riemann *et al.*, 1998; Rice, 1999; Key *et al.*, 2004; and Johnson *et al.*, 2005). Stream sediment is a composite of the products of weathering and erosion derived from the catchment basin, and funnelled into and along the stream channels. Very fine grained sediments tend to have assemblages rich in zircon which is a result of weathering and sorting from source rock and not of the pressure of zircon-rich source rock. This implies that a regional distribution pattern of heavy minerals is due to various weathering process in source rock and not due to differences in the source. The stream sediments are generally composed of weathered products of basement rock. Lots of researches has been carried out using stream sediments as media for mineral exploration, such studies include Lapworth *et al.* (2012) who carried out regional geochemical mapping using stream sediments from central and south-western Nigeria. A total of 1569 stream sediment samples were collected and 54 major and trace element determined by ICP-MS and analysed

for Au, Pd and Pt by fire assay. The study revealed important new baseline/background geochemical values for common geological domains in Nigeria. Ayodele (2012a) worked on the stream sediments geochemistry of Okemesi area and concluded that there are high concentration of metallic, precious and base metals in the western part of Okemesi. Ayodele (2012b) also worked on the stream sediment samples from Ijero, seven samples were analysed for major, trace and rare earth elements in the area using ICP-MS analytical method. The results showed that most elements have their peak in northwestern part of the studied area and that the area is enriched in phosphate minerals, probably monazite or apatite. Emmanuel *et al.* (2011) carried out geochemical investigation of the southern part of Ilesha with the aim of clarifying the potential source of mineralization in the area. Geologic mapping of the area revealed that the area is made up of different lithologies such as undifferentiated schists, gneisses and migmatites with pegmatites, schists and epidiorite complex, quartzite and quartz schist. Sixty-one soil samples were collected and analyzed for elements such as Pb, Fe, Ni, Cd, Cr, Cu, Zn and Mn, using multivariate analysis to obtain the coefficient of principal components. The elemental association ratio revealed high metallic concentrations which led to the mineralization trend in southern Ilesha. Joshua and Oyebanji (2010) also worked on stream sediment samples from river Osun, south western Nigeria and revealed the presence of heavy minerals, opaque and non-opaque mineral assemblages such as zircon, tourmaline, rutile, silimanite, garnet and epidote in the sediments. Ajayi (1981) also carried out statistical geochemical exploration in Ife / Ilesha of 176 stream sediment samples from an area of 1800km² for copper, zinc, manganese, nickel and cobalt and found out that all the elements have density distribution closely approaching lognormal. The factor analysis for Cu-Co-Ni correlates spatially with area underlain by amphibolite complex, thus reflecting the parent rock as the influencing factor.

Aim

This research attempts to assess the mineral potentials in the stream sediments around Arinta and Olumirin Waterfalls in order to determine the type and nature of mineralization and to provide a baseline geological and geochemical data for further mineral prospecting and exploration in the studied areas.

Location, accessibility, topography and drainage

The study areas lie within latitudes 7° 31' 00"N to 7° 34' 45"N and longitudes 4° 52' 45"E to 4° 54' 00"E (Fig.1). The study localities comprising of two (2) distinct waterfalls which are Arinta waterfall in Ipole-Ekiti and olumirin waterfall in Erin Ijesa, Osun state (Figs.2&3). The neighboring towns to the study areas include Apapolu, Ikogosi, Irogbo, Erin-Oke and Erin Ijesa. The topography of the study areas is rugged with series of highlands, lowlands and massive rocks with steep sides. The major topographic landforms within the study areas are the quartzite ridge systems

which are usually formed by quartzite exposures that have undergone varying degrees of weathering. The drainage pattern of the study areas is indicated as both dendritic and trellis in nature and it has the form which looks like branching pattern of tree root, while majority of the rivers flow north- southwards and are structurally controlled (Figs 2&3). The rivers are found to occupy the valleys between the ridges and the gneissic terrains. The rivers found in the study area are perennial and the water falls have history of continuous supply of water throughout the year and are therefore targeted for hydrochemical assessment since they are used for domestic purposes especially during dry season when most surface water and shallow wells might have dried off.

The Arinta waterfall at Ipole-Ekiti is about 6km southwest of Ikogosi, and could be reached through a secondary road from Ikogosi tourist centre. Olumirin waterfall in Erin Ijesa, Osun state is the most accessible of all the waterfalls in Nigeria. It beats Gurara in Niger State due to its relative proximity to the Ilesha- Abuja Expressway. Both Arinta and Olumirin water fall are tourist centres that generate revenue for Ekiti and Osun state governments respectively. Due to their tourist attractions, the towns have good road networks which link them with other states of the federation.

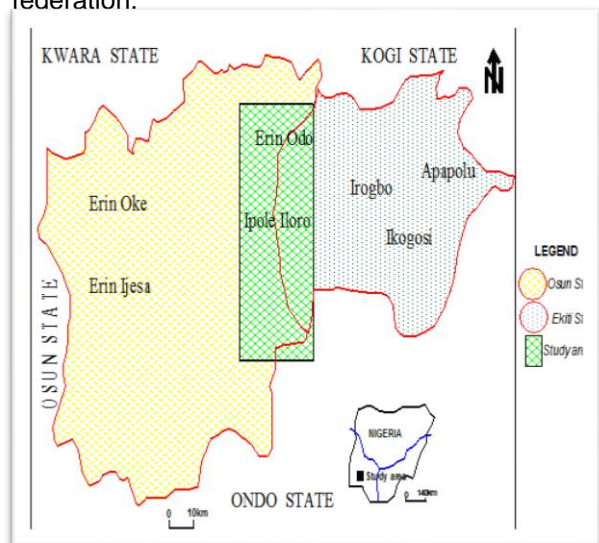


Fig. 1: Map of Erin-Ijesa and Ipole-Iloro (showing the location of study area).

Local geology of the study area

The study areas (Arinta and Olumirin) are parts of the basement complex of southwestern Nigeria. They are underlain by gneisses, migmatites and metasediments ranging from Precambrian to Paleozoic age in. However, the dominant rocks in the studied areas include quartzites and migmatites (Figs. 4&5). Quartzites

These tend to form good topographic features which rise up to about 400 meters above the surrounding terrain forming ridges. Around the studied areas, the varieties of quartzite encountered are massive, milky, smoky, sugary and schistose quartzites, however, schistose and smoky varieties are the prominent types

in the areas. The massive quartzite has been seriously affected by tectonism which resulted in fracturing and tilting thereby leaving the quartzites as shattered boulders in the water. The rocks have varying textures ranging from equigranular and medium to coarse grained. The varieties of quartzites are so closely related that, often, it is impossible to indicate them as separate units on the map. The quartzites consist of mainly quartz which is usually more than 90% with minor amounts of interlocking grains of muscovite and biotite. Structurally, the quartzites are highly jointed, with some having joint sets around Arinta and others are foliated by the presence of micaceous streaks. Dips ranging between $40^{\circ}E - 42^{\circ}E$ were measured around Ipole and Erin Ijesha areas.

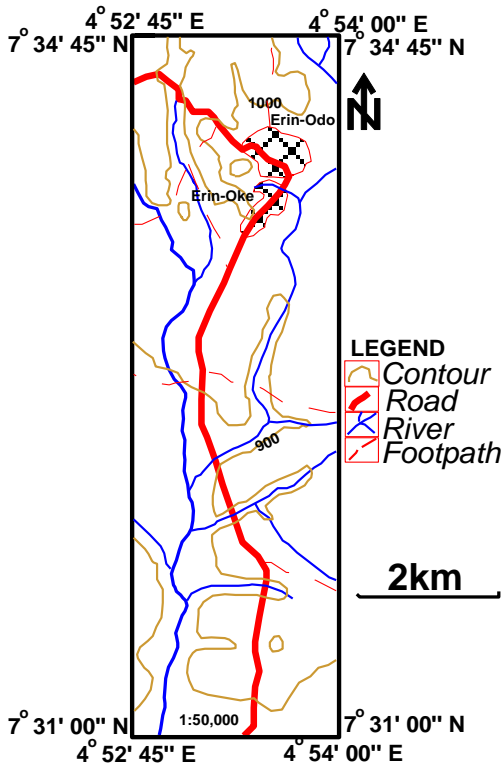


Fig.2: Drainage map of Arinta waterfall.

Migmatites

These are rocks that are mixtures of metamorphic and igneous rocks. They are formed when a metamorphic rock such as gneiss partially melts, and the melt recrystallizes into an igneous rock, creating a mixture of the unmelted metamorphic part with the recrystallized igneous part, they can also be known as diatexite. The migmatites in the study area are interbanded with the quartzites, only the Paleosome and the mesosome parts were visible. Migmatites also form under extreme temperature conditions during prograde metamorphism, where partial melting occurs in pre-existing rocks. Migmatite has a mineralogical composition of quartz, orthoclase, feldspar, hornblende and micas (muscovite or biotite). Commonly, migmatites occur within extremely deformed rocks that represent the base of eroded mountain chains, typically within Precambrian cratonic blocks.

Geology of Waterfalls

A waterfall is usually a geological formation resulting from water, often in the form of a stream flowing over erosion resistant rock formation that forms a nickpoint, or sudden break in elevation, they are the result of a specific set of conditions that allow water to maintain its vertical cascade. Waterfall develops in several ways; waterfalls can occur along

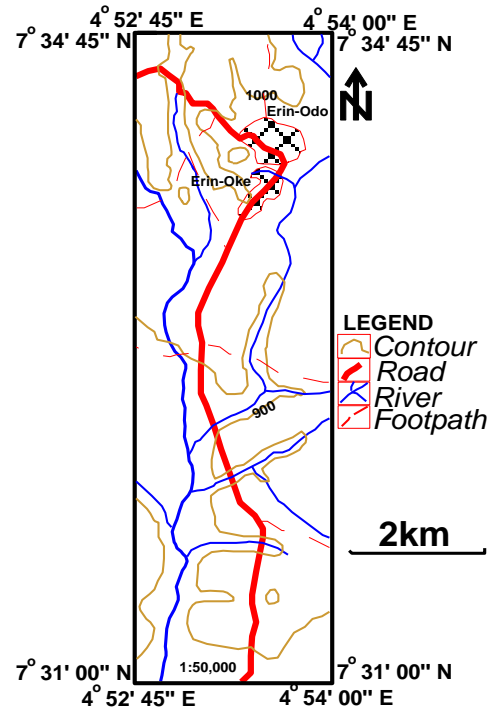


Fig. 3: Drainage map of Olumirin waterfall.

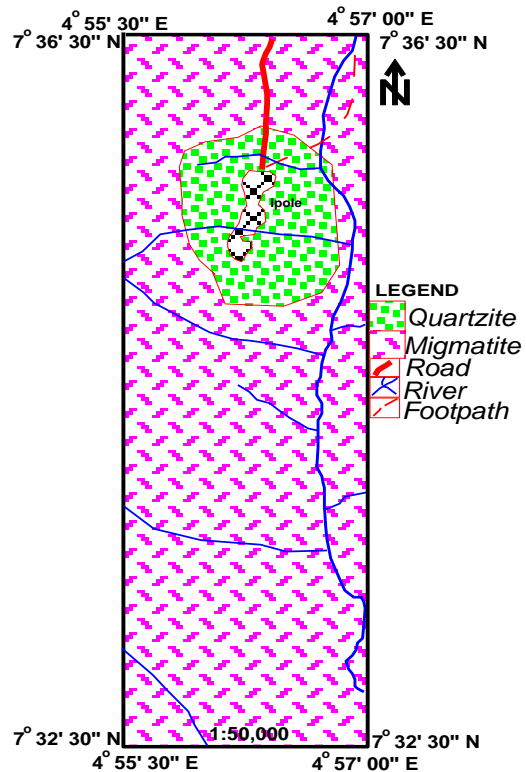


Fig.4: Geological Map of Ipole showing Arinta waterfall.

glacial troughs where by a stream or river flowing into a glacier has receded or melted. The large waterfalls in Yosemite Valley are examples of this phenomenon. Most waterfalls are the result of many years of the action of water on layers of rock composed of different degrees of hardness.

Hard layers are more resistant to erosion while soft layers are less resistant to erosion. Typically, a stream will flow across an area of formation and the more resistant rock strata will form shelves across the stream way, elevated above the further streambed when the less erosion resistant rock around it disappears. Over a period of years, the edges of this shelf will gradually break away and the water fall will steadily move upstream. Often, the rock strata just below the more resistant shelf will be of a softer type and will erode out to form a shallow cave like formation or plunge pool known as a rock shelter found beneath many waterfalls. Eventually, the outcropping more resistant cap rock will collapse under pressure to add blocks of rocks to the base of the water fall. These blocks of rocks are then broken down into smaller boulders by attrition as they collide with each other, and they also erode the base of the water falls by abrasion creating a deep plunge pool or gorge formed as a result of the kinetic energy of the water hitting the bottom (Fig. 6). Olumirin waterfalls, Arinta waterfalls (Figs. 7&8), Athabasca falls and Sunwapta falls are typical examples. Other waterfalls originate where a fault uplifts a mountain range or part of a range, creating a fault scarp over which streams drop steeply. Continued under cutting and erosion of the edge and of the rock bed above the falls move many waterfalls upstream; these ultimately diminish in size, dwindle to rapids, then disappear.

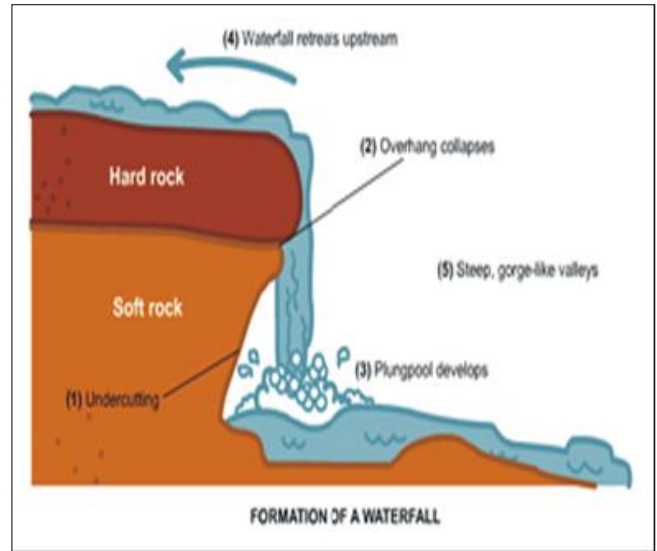


Fig.6: Schematic diagram showing different stages of formation of a waterfall (AfterHem, 1970)

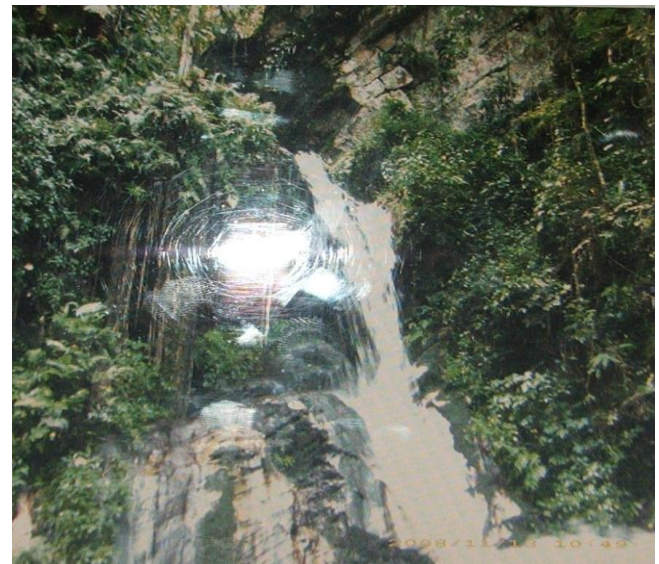


Fig.7: Arinta waterfall at Ipole Ekiti, Ekiti State.

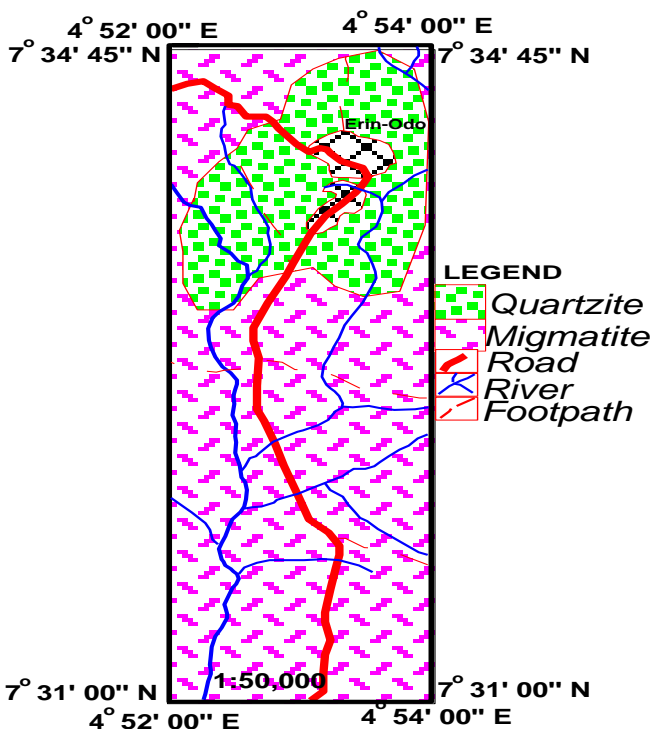


Fig. 5: Geological map of Erin Odo showing Olumirin waterfall.

Method of study

The methods adopted for this research work is divided into two aspects namely field and laboratory operations. The field operation is essentially geologic mapping of the study area to determine the underlying lithologic units. The geologic mapping was carried out at a scale of 1:50,000 using grid-controlled sampling method at a sampling density of one sample per 4sqkm² for the collection of stream sediment samples. Nineteen samples were initially obtained while twelve which were representative of the different stream channels were eventually selected and analyzed. Sediment samples were taken at a depth of 20-25cm; they were bagged and labeled to avoid mix up before transportation to the laboratory. The geographical locations of each sample collected were noted and recorded in the field notebook. Also the characteristic features of the stream sediments collected were also recorded in the field notebook as well. The laboratory operations involve pulverization and homogenizing the

stream sediment samples using a pulverizer to allow to crush the coarse particles in the sediments after which the milling machine was used for further pulverization until the samples became very fine in size ($-15\mu\text{m}$). 30g of the homogenized sample was analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Samples were dissolved using Lithium Tetraborate fusion method followed by HCl and HF acid digestion (Watts and Johnson, 2010). This digestion method was chosen to provide a more aggressive dissolution of refractory minerals than a standard mixed-acid method. The sediment samples were placed in a sample container which was properly labeled. The twelve stream sediment samples from both areas were transferred to ACME Laboratories, East Vancouver, Canada for major, trace and rare earth elements using Multi-collector High Resolution Inductively Coupled Plasma-Mass Spectrometry (MC-ICPMS).



Fig.8: Olumirin waterfall at Erinodo, Osun State.

Data treatment and multivariate statistical methods
Multivariate statistical method was applied on the bulk chemical data obtained from the sediment samples using SPSS-17.0 statistical software. Varimax rotated factor analysis was performed on correlation matrix of the reorganized data of the samples. The variance, cumulative, and extraction sums of square loadings of the variables with Eigen-values were computed. Rotation of the axis defined by factor analysis produced a new set of factors, each one involving primarily a sub-set of the original variables with a little overlap as possible, so that the original variables were divided into groups. The factor analysis of these data set was further sorted by the contribution of the less significant variables (< 0.4 factor score). A varimax rotation (raw) of the different varifactors of eigen-value greater than 1, were further cleaned up by this technique and in varifactors original variables participated more clearly. Liu *et al.* (2003a) classified the factor loading as “strong”, “moderate”, and “weak”, corresponding to absolute loading values of > 0.75 ,

0.75–0.50, and 0.50–0.40, respectively. Factor and cluster analyses were combine to assess the degree of major component matrix dissolution and determination of chemical processes. Hierarchical agglomerative clustering was performed on data normalized to z scores and unit variance using squared Euclidean distances as the measure of similarity (Massart *et al.*, 1988). Wards method was selected because it possesses a small space distorting effect, uses more information on cluster contents than other methods (Helena *et al.*, 1999), and has been proven to be an extremely powerful grouping mechanism (Willett, 1987). The cluster analysis was represented by a dendrogram, in which the endpoints of the branches represent the samples, and the height at which the branches join corresponds to the sample similarity level for admission to pre-existing group. The higher the branches, the more similar are the samples (Morsy, 2000).

Results and discussion

Major element geochemistry

The analytical results for the major elements are presented in Tables (1a-b). Table 1a shows the major elements concentration and Table 1b shows the statistical summary of major elements with respect to their average shale content respectively. The concentration of Na_2O ranges from (0.02 - 0.06%) with a mean value of 0.04. It has an average shale content of 1.6% (Table 1b). Location code-named Erin Ijesa 4 has the highest concentration of Na_2O . Concentration of MgO ranges from (0.01 - 0.13%) with an average value of 0.08. It has an average shale content of 2.6% (Tables 1a and 1b). Location code-named Ipole 5 has highest concentration of MgO which may be attributed to Mg-rich micas present in the study area.

The mean values of Na_2O and MgO in the study area is lower when compared to stream sediments around Ede and its environs (Akintola *et al.*, 2013) with the average values of 0.141 and 0.135 respectively. The concentration of Al_2O_3 ranges from (1.27% - 5.11%) with an average value of 3.00. Concentration of Al_2O_3 in the average shale is 16.7%. Location code-named Ipole 5 has highest concentration of Al_2O_3 (Table 1a) which can be attributed to prevalence of clay minerals in the sample which may be derived from weathered feldspars from rocks. Average concentration of Al_2O_3 in the stream sediments from Ede and its environs (Akintola *et al.*, 2013) which is found to be lesser than, that of the study area. Concentration of K_2O ranges from (0.07 - 0.25%) (Table 1a), which has an average value of 0.16. It also has an average shale content of 3.6%. Locations code-named Erin Ijesa 1 & 4 has highest concentrations of K_2O which may be attributed to weathering of K-feldspar and micas. The concentration of CaO ranges from 0.01 - 0.21% with an average value of 0.08 (Tables 1a & b). The highest concentration is observed in Location code-named Ipole 5 with shale average content of 2.20%.

Table 1a. Major element concentration of stream sediments of the study area (%)

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Cr ₂ O ₃	TiO ₂	MnO	P ₂ O ₅	SrO	BaO	LOI	Total
Erin Ijesa 1	79.9	3.04	11.4	0.08	0.11	0.05	0.25	0.01	2.14	0.01	0.1	0.01	0.009	2.68	99.79
Erin Ijesa 2	80.1	3.44	9.97	0.13	0.11	0.03	0.2	0.009	1.91	0.02	0.1	0.009	0.01	4.41	100.45
Erin Ijesa 3	85.4	3.92	5.1	0.11	0.11	0.04	0.21	0.008	1.25	0.02	0.09	0.008	0.008	4.03	100.30
Erin Ijesa 4	83.5	3.64	7.11	0.14	0.1	0.06	0.25	0.009	1.31	0.01	0.08	0.007	0.01	4.49	100.72
Erin Ijesa 5	64.0	2.05	26.5	0.02	0.07	0.04	0.07	0.01	4.27	0.02	0.09	0.01	0.009	1.19	98.35
Erin Ijesa 6	72.3	2.81	20.4	0.06	0.08	0.02	0.15	0.009	3.05	0.01	0.1	0.009	0.01	2.28	101.29
Erin Ijesa 7	71.5	2.81	21.5	0.04	0.08	0.05	0.12	0.01	3.33	0.02	0.13	0.01	0.008	2.27	101.88
Ipole 1	88.9	3.79	1.34	0.05	0.08	0.02	0.15	0.008	1.16	0.01	0.06	0.008	0.01	4.27	99.86
Ipole 2	94.3	2.66	0.81	0.05	0.06	0.03	0.1	0.009	0.76	0.01	0.03	0.009	0.009	2.31	101.15
Ipole 3	99.2	1.27	0.28	0.009	0.01	0.05	0.09	0.01	0.06	0.009	0.01	0.007	0.008	0.76	101.77
Ipole 4	97.1	1.41	0.24	0.009	0.02	0.05	0.08	0.009	0.14	0.009	0.009	0.009	0.009	0.87	99.96
Ipole 5	81.7	5.11	1.67	0.21	0.13	0.04	0.19	0.008	1.09	0.03	0.08	0.008	0.01	10.75	101.03

Table 1b Summary of univariate statistics of major element concentration in stream sediments

Variables	Average shale (wt. %)	Minimum	Maximum	Mean	Std. Dev.	Skewness	Kurtosis
SiO ₂	58.9	64	99.2	83.16	10.69	-0.14	-0.56
Al ₂ O ₃	16.7	1.27	5.11	3.00	1.09	0.09	0.09
Fe ₂ O ₃	6.90	0.24	26.5	8.86	9.29	0.87	-0.62
CaO	2.20	0.01	0.21	0.08	0.06	0.97	0.52
MgO	2.6	0.01	0.13	0.08	0.04	-0.80	0.08
Na ₂ O	1.6	0.02	0.06	0.04	0.01	-0.31	-0.86
K ₂ O	3.6	0.07	0.25	0.16	0.06	0.20	-1.39
Cr ₂ O ₃	n.d	0.01	0.01	0.01	0.00	-0.16	-1.26
TiO ₂	0.78	0.06	4.27	1.71	1.29	0.71	-0.19
MnO	-	0.01	0.03	0.01	0.01	1.03	0.23
P ₂ O ₅	-	0.01	0.13	0.07	0.04	-0.68	-0.50
SrO	-	0.01	0.01	0.01	0.00	-0.26	-1.00
BaO	-	0.01	0.01	0.01	0.00	-0.35	-1.45
LOI	-	0.76	10.75	3.36	2.69	2.01	5.23

Table 2a. Trace and rare elements concentration (ppm) of stream sediments of the study area

Sample	Ag	As	Ba	Cd	Co	Cr	Cu	Cs	Ga	Hf	Li	Mo	Nb	Nd	Ni	Pb	Rb	Sc	Sn	Sr
Erin Ijesa 1	0.48	4.0	92.9	0.39	2.0	40.0	2.0	0.29	7.0	81.2	8.0	0.8	64.1	138	13.0	7.0	9.1	2.0	7.0	82.8
Erin Ijesa 2	0.47	4.5	75.1	0.37	3.0	40.0	4.0	0.4	7.4	75.1	7.9	0.7	69.7	106.5	14.0	10.0	7.9	2.0	5.0	79.8
Erin Ijesa 3	0.49	4.9	72.9	0.38	2.9	20.0	3.0	0.43	6.0	56.1	7.6	0.9	40.2	89.2	8.0	9.0	8.5	2.0	4.0	82.4
Erin Ijesa 4	0.47	4.7	71.6	0.39	3.0	30.0	4.0	0.38	5.9	31.7	7.9	0.7	35.6	68.8	8.0	7.0	8.3	2.0	4.0	74.1
Erin Ijesa 5	0.49	4.9	30.1	0.37	2.8	70.0	6.0	0.15	10.2	130	7.8	0.6	111.5	242	25.0	4.0	2.6	3.0	10.0	79.5
Erin Ijesa 6	0.48	4.7	49.0	0.37	2.7	50.0	15.0	0.25	8.8	72.1	8.0	0.7	71.6	149	17.0	10.0	4.5	2.0	8.0	66.9
Erin Ijesa 7	0.47	4.9	37.8	0.38	2.9	60.0	4.0	0.27	8.9	87.2	7.9	0.8	77.5	180	23.0	11.0	4.9	3.0	8.0	58.8
Ipole 1	0.49	4.8	49.4	0.37	3.0	20.0	6.0	0.57	5.0	71.6	8.0	0.9	44.4	41.7	5.0	11.0	7.1	2.0	3.0	28.8
Ipole 2	0.48	4.7	42.1	0.39	2.0	10.0	4.0	0.55	3.6	44.4	7.6	0.6	30.3	27.7	5.0	8.0	7.3	1.0	2.0	22.8
Ipole 3	0.49	4.9	17.3	0.39	0.9	9.0	2.0	0.49	1.4	4.3	7.8	0.8	7.8	4.7	2.0	3.0	5.6	0.9	1.0	5.9
Ipole 4	0.47	4.9	19.1	0.38	1.0	9.0	1.0	0.4	1.5	6.7	8.0	0.7	13.9	5.0	2.0	3.0	4.9	0.8	1.0	7.6
Ipole 5	0.47	4.6	80.3	0.39	5.0	20.0	8.0	0.63	6.3	53.5	7.9	0.6	30.3	41.8	8.0	10.0	8.4	2.0	2.0	41.6
Sample	Ta	Tl	U	V	W	Y	Zn	Zr	Ce	Dy	Er	Eu	Gd	Ho	La	Lu	Pr	Tb	Tm	
Erin Ijesa 1	6.3	9.0	9.57	48.0	15.0	132.5	11.0	3260	347.0	20.0	14.3	4.92	19.4	4.75	180.0	2.57	37.8	3.12	2.43	
Erin Ijesa 2	7.9	8.0	8.56	47.0	15.0	125.5	19.0	3020	274.0	19.1	14.05	3.81	15.9	4.36	143.5	2.62	29.4	2.85	2.35	
Erin Ijesa 3	4.4	10.0	6.31	26.0	9.0	92.1	20.0	2210	227.0	14.1	9.5	3.29	13.3	3.16	118.5	1.78	24.3	2.17	1.63	
Erin Ijesa 4	3.4	8.0	4.61	28.0	7.0	69.3	16.0	1280	170.5	10.5	7.52	2.42	9.7	2.45	90.6	1.2	18.8	1.65	1.22	
Erin Ijesa 5	31.2	9.0	16.95	90.0	24.0	252	15.0	5290	598.0	37.9	26.4	8.43	35.0	8.67	322.0	4.94	66.8	5.80	4.51	
Erin Ijesa 6	7.7	6.0	11.85	67.0	17.0	183.5	47.0	2880	391.0	26.6	20.0	5.77	22.7	6.27	200.0	3.68	41	3.91	3.43	
Erin Ijesa 7	8.2	9.0	11.8	68.0	19.0	188	17.0	3550	448.0	28.0	19.4	6.27	25.7	6.58	233.0	3.44	48.8	4.39	3.25	
Ipole 1	12.9	8.0	7.42	29.0	9.0	106	21.0	2890	108.0	14.6	11.0	2.08	9.64	3.46	51.3	2.19	11.0	2.00	1.93	
Ipole 2	25.4	9.0	3.75	16.0	3.0	42.3	12.0	1790	66.8	6.1	4.27	1.11	4.88	1.4	34.4	0.83	7.46	0.93	0.72	
Ipole 3	9.4	10.0	0.65	4.0	1.0	4.4	3.0	177	11.6	0.7	0.48	0.24	0.72	0.17	6.0	0.09	1.26	0.12	0.07	
Ipole 4	18.7	8.0	1.01	4.0	1.0	6.8	4.0	277	12.7	1.1	0.7	0.3	0.94	0.23	6.5	0.13	1.38	0.16	0.12	
Ipole 5	2.9	8.0	8.26	25.0	5.0	92	33.0	2110	98.0	12.5	9.89	1.89	8.85	3.09	51.0	2.01	11.15	1.84	1.78	

Table 2b. Summary of univariate statistics of trace element concentration in stream sediments

Variables	Average shale	Metal ratio	Minimum	Maximum	Mean	Std. Dev.	Skewnes	Kurtosis	Variables	Average shale	Metal ratio	Minimum	Maximum	Mean	Std. Dev.	Skewnes	Kurtosis
Ag	-		0.47	0.49	0.48	0.01	0.19	-1.87	U	3.7	2.04	0.65	16.95	7.56	4.72	0.31	0.03
As	-		4.00	4.90	4.71	0.26	-2.02	4.82	V	130	0.29	4.00	90.00	37.67	26.82	0.60	-0.39
Ba	650	0.08	17.30	92.90	53.13	25.04	0.03	-1.27	W	-	-	1.00	24.00	10.42	7.51	0.34	-0.97
Cd	0.3	1.27	0.37	0.39	0.38	0.01	-0.19	-1.87	Y	-	-	4.40	252.00	107.87	74.49	0.39	-0.22
Co	19	0.14	0.9	5	2.6	1.07	0.41	1.75	Zn	95	0.2	3.00	47.00	18.17	12.06	1.26	2.20
Cr	90	0.35	9.00	70.00	31.50	20.57	0.63	-0.72	Zr	160	15.0	177.00	5290.00	2394.50	1429.06	0.18	0.46
Cu	45	0.11	1.00	15.00	4.92	3.73	1.97	4.80	Ce	-	-	11.60	598.00	229.38	186.33	0.63	-0.46
Cs	-	-	0.15	0.63	0.40	0.14	-0.07	-0.70	Dy	-	-	0.73	37.90	15.92	11.14	0.45	-0.14
Ga	-	-	1.40	10.20	6.00	2.78	-0.40	-0.51	Er	-	-	0.48	26.40	11.46	7.89	0.33	-0.36
Hf	-	-	4.30	130.00	59.49	35.21	0.12	0.41	Eu	-	-	0.24	8.43	3.38	2.55	0.61	-0.37
Mn	850	0.17	200.00	300.00	148.00	68.90	1.03	0.23	Gd	-	-	0.72	35.00	13.89	10.36	0.63	-0.05
Li	-	-	7.60	8.00	7.87	0.14	-1.07	0.21	Ho	-	-	0.17	8.67	3.72	2.58	0.39	-0.30
Mo	1.3	0.56	0.60	0.90	0.73	0.11	0.26	-1.00	La	-	-	6.00	322.00	119.73	98.94	0.71	-0.21
Nb	-	-	7.80	111.50	49.74	29.83	0.58	0.08	Lu	-	-	0.09	4.94	2.12	1.46	0.33	-0.23
Nd	-	-	4.70	242.00	91.20	74.30	0.70	-0.23	Pr	-	-	1.26	66.80	24.93	20.47	0.72	-0.19
Ni	68	0.16	2.00	25.00	10.83	7.69	0.74	-0.49	Tb	-	-	0.12	5.80	2.41	1.71	0.51	-0.10
Pb	22	0.35	3	11	7.75	2.99	-0.67	-1.03	Tm	-	-	0.07	4.51	1.95	1.34	0.32	-0.33
Rb	140	0.05	2.60	9.10	6.59	2.04	-0.61	-0.68	Sr	300	0.18	5.90	82.80	52.58	29.77	-0.53	-1.44
Sc	-	-	0.80	3.00	1.89	0.71	-0.08	-0.24	Ta	-	-	2.90	31.20	11.53	9.02	1.31	0.80
Sn	-	-	1.00	10.00	4.58	3.03	0.48	-1.05	Tl	-	-	6.00	10.00	8.50	1.09	-0.76	1.58

The elevated concentration can be attributed to the presence of Ca-rich feldspars. The average concentration is found to be lower than stream sediments of Ede and its environs area (Akintola et al., 2013). Concentration of TiO_2 ranges from 0.06 - 4.27% with the mean value of 1.71 (Table 3b), with the average shale content of 0.78%. Concentration is found to be higher when compared to those of Ede and its environs with mean value of 0.0435 (Akintola et al., 2013). The highest value is recorded at Location code-named Erin Ijesa 5(4.27%). It is usually linked to Ti-bearing minerals like ilmenite. Concentration of Fe_2O_3 ranges from 0.24 – 26.5% with mean value of 8.86. It has an average shale content of 6.90% (Tables 1a and 1b). Location code-named Erin Ijesa 7 has highest concentration of Fe_2O_3 which may be attributed to oxidation/weathering process in the study area. Concentration of SiO_2 ranges from 66 – 99.2% with mean value of 83.16. It has an average shale content of 58.9% (Tables 1a and 1b). Location code-named Ipole 3 has highest concentration of SiO_2 which may be attributed to siliceous stream sediments in the study area. The concentration of MnO ranges from 0.01 – 0.03% with an average value of 0.01. Location code-named Ipole 5 has highest concentration of MnO (Table 1a) which may be ascribed to prevalence of clay minerals in the sample which may be derived from weathered feldspars from rocks.

Trace element geochemistry

The results of trace element geochemical analysis of the studied samples and the univariate statistical summary of the concentration of the element in the study area are shown in Tables 2a and 2b respectively. Vanadium has minimum and maximum values of 9.00ppm and 90ppm respectively with an average value of 37.67. The highest concentration of vanadium was recorded in the location code named Erin Ijesa 7. It has skewness and kurtosis values of 0.60 and -0.39 respectively. Nickel has minimum and maximum values of 2.00ppm and 25.00ppm respectively with an average value of 10.83. Highest concentration of nickel was observed in the location code named Erin Ijesa 5. The skewness and kurtosis values are 0.74 and -0.49 respectively. Cobalt has minimum and maximum values of 0.9ppm and 5ppm respectively with an average value of 2.6. The highest concentration of cobalt was obtained in the location code named Ipole 5. The cobalt has skewness and kurtosis values of 0.41 and 1.75 respectively. Copper has minimum and maximum values of 1.00ppm and 15ppm respectively with an average value of 4.92ppm. The highest concentration of copper was obtained in the location code named Erin Ijesa 6. Copper has skewness and kurtosis values of 1.97 and 4.80 respectively. Chromium has minimum and maximum values of 9.0ppm and 70ppm respectively with an average value of 3.15ppm. The highest concentration of chromium was recorded in the location code named Erin Ijesa

5. Chromium has skewness and kurtosis values of 0.63 and -0.72 respectively. Zinc has minimum and maximum values of 3.00ppm and 47ppm respectively with an average value of 18.17ppm. Highest concentration of zinc was observed in the location code named Erin Ijesa 6. Copper has skewness and kurtosis values of 1.26 and 2.20 respectively. Silver has minimum and maximum values of 0.47ppm and 0.49ppm respectively with an average value of 0.48ppm. The highest concentration of silver was recorded in the locations code named Ipole 1&3 and Erin Ijesa 3&5. Silver has skewness and kurtosis values of 0.19 and -1.87 respectively. Lead has minimum and maximum values of 3ppm and 11ppm respectively with an average value of 7.75ppm. The highest concentration of lead was obtained in the locations code named Ipole 1 and Erin Ijesa 7. Lead has skewness and kurtosis values of -0.67 and -1.03 respectively. Molybdenum has minimum and maximum values of 0.60ppm and 0.90ppm respectively with an average value of 0.73ppm. The highest concentration of molybdenum was observed in the locations code named Ipole 1 and Erin Ijesa 3. Molybdenum has skewness and kurtosis values of 0.26 and -1.00 respectively. Arsenic has minimum and maximum values of 4.00ppm and 4.90ppm respectively with an average value of 4.71ppm. The highest concentration of arsenic was observed in the locations code named Ipole 3 &4 and Erin Ijesa 3, 5 & 7. Arsenic has skewness and kurtosis values of -2.02 and 4.82

Table 3: Correlation Coefficient of Some Selected Elements From the Result of Geochemical Analysis of Some Stream Sediment Samples From Arinta and Olumirin and Its Environs.

	Ag	As	Ba	Cd	Co	Cr	Cu	Cs	Ga	Hf	Li	Mo	Nb
Ag	1	0.235	-0.246	-0.215	-0.254	-0.042	0.025	-0.027	-0.051	0.193	-0.375	0.408	0.09
As	0.235	1	-.738**	-0.274	-0.117	-0.094	0.029	0.046	-0.189	-0.189	-0.332	0.054	-0.142
Ba	-0.246	-.738**	1	0.191	.591*	0.072	0.082	0.125	0.355	0.233	0.077	0.093	0.128
Cd	-0.215	-0.274	0.191	1	-0.113	-0.503	-0.431	0.399	-0.479	-0.554	-0.258	-0.125	-.605*
Co	-0.254	-0.117	.591*	-0.113	1	0.277	0.478	0.2	0.57	0.44	0.041	-0.205	0.299
Cr	-0.042	-0.094	0.072	-0.503	0.277	1	0.378	-.836**	.923**	.856**	0.234	-0.152	.955**
Cu	0.025	0.029	0.082	-0.431	0.478	0.378	1	-0.151	0.518	0.352	0.249	-0.265	0.366
Cs	-0.027	0.046	0.125	0.399	0.2	-.836**	-0.151	1	-.643*	-0.567	-0.205	0.069	-.762**
Ga	-0.051	-0.189	0.355	-0.479	0.57	.923**	0.518	-.643*	1	.902**	0.134	-0.146	.926**
Hf	0.193	-0.189	0.233	-0.554	0.44	.856**	0.352	-0.567	.902**	1	0.061	-0.091	.952**
Li	-0.375	-0.332	0.077	-0.258	0.041	0.234	0.249	-0.205	0.134	0.061	1	0.079	0.132
Mo	0.408	0.054	0.093	-0.125	-0.205	-0.152	-0.265	0.069	-0.146	-0.091	0.079	1	-0.149
Nb	0.09	-0.142	0.128	-.605*	0.299	.955**	0.366	-.762**	.926**	.952**	0.132	-0.149	1
Nd	0.091	-0.107	0.11	-0.475	0.246	.974**	0.322	-.848**	.922**	.892**	0.086	-0.105	.965**
Ni	-0.055	-0.058	0.064	-0.471	0.316	.984**	0.368	-.792**	.928**	.869**	0.118	-0.191	.950**
Pb	-0.211	-0.184	0.53	-0.262	.684*	0.199	0.463	0.21	0.465	0.367	0.085	0.227	0.249
Rb	-0.199	-.588*	.815**	0.496	0.303	-0.465	-0.271	0.558	-0.206	-0.26	-0.113	0.255	-0.402
Sc	-0.001	-0.024	0.272	-0.427	.586*	.876**	0.31	-0.561	.922**	.866**	0.131	0.04	.853**
Sn	0.086	-0.168	0.127	-0.486	0.204	.971**	0.391	-.867**	.916**	.869**	0.174	-0.065	.954**
Sr	-0.043	-0.393	.651*	-0.273	0.434	.697*	0.211	-.590*	.819**	.677*	-0.01	0.045	.719**
Ta	0.317	0.318	-.614*	-0.267	-0.353	0.138	-0.093	-0.228	-0.025	0.265	-0.269	-0.443	0.269
Tl	0.418	0.144	-0.112	0.418	-0.289	-0.207	-.751**	0.113	-0.274	-0.089	-.641*	0.312	-0.175

respectively. Strontium has minimum and maximum values of 5.90ppm and 82.80ppm respectively with an average value of 52.58ppm. The highest concentration of strontium was observed in the location code named Erin Ijesa 1. Strontium has skewness and kurtosis values of -0.53 and -1.44 respectively. Zircon has minimum and maximum values of 177ppm and 5290ppm respectively with an average value of 2394.5ppm. The highest concentration of zircon was observed in the location code named Erin Ijesa 5. Zircon has skewness and kurtosis values of 0.18 and 0.46 respectively. Gallium has minimum and maximum values of 1.40ppm and 10.20ppm respectively with an average value of 6.00ppm. The utmost concentration of gallium was recorded in the location code named Erin Ijesa 5. Gallium has skewness and kurtosis values of -0.40 and -0.51 respectively. Uranium has minimum and maximum values of 0.65ppm and 16.95ppm respectively with an average value of 7.56ppm. Highest concentration of uranium was observed in the location code named Erin Ijesa 5. Uranium has skewness and kurtosis values of 0.31 and 0.03 respectively. Yttrium has minimum and maximum values of 4.40ppm and 252ppm respectively with an average value of 107.87. The observed maximum concentration of yttrium was recorded in the location code named Erin Ijesa 6. Yttrium has skewness and kurtosis values of 0.39 and -0.22 respectively.

Metal ratio and correlation analysis

Metal ratio is usually expressed with respect to average shale content to qualify the degree of pollution (Forstner and Wittman, 1983). Table 1a; shows the computed values of metal ratio of trace element in the study area.

It is calculated thus; C_n/C_b Where C_n —obtained concentration in ppm.

C_b – Average shale concentration in ppm.

The metal ratio of the selected trace elements is as follows : Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, Zn and Sr have values less than 1 in all locations, which means there is depletion of these elements in the study area. Nevertheless, there is a relative enrichment of Cd and Zr in the study area. The result of the correlation analysis of some selected elements (Table 3) shows that Cs, Nb, Sn, Ta, Cu, Mo, Ni, V, Zn, Co Ga, Hf, Cr, Nb, Ba, Nb, Sr, Pb and Rb has high positive correlation coefficients. Negative correlation coefficient was observed between Ag and Ba, Cd, Co, Cr, Cs, Ga, Li, Ni, Rb, Sc and Sr. There is also negative correlation coefficient between As and Ba, Cd, Co, Cr, Ga, Hf, Li, Nb, Nd, Ni, Pb, Rb, Sc, Sn and Sr while Cu has negative coefficient of correlation with Cd, Cs, Mo, Rb, Ta and Tl. Nevertheless, Co showed negative correlation coefficient with Ag, As, Cd, Mo and Ta. Similarly, Cr has a negative correlation coefficient with Ag, As, Cd, Cs, Tl and Rb. Barium also has a negative correlation coefficient with Ag, As, Ta and Tl.

Multivariate analytical results

Dendrogram is the hierarchic classification represented by a two-dimensional diagram. This illustrates the fusions or divisions made at each successive stage of the analysis (Brian, 1993). The dendrogram of the cluster analysis is shown in Fig.9. From the dendrogram (Fig. 9), 2 cluster groups are distinct at the first cluster stage. These are Ag, Cd, Cs, Mo, Lu, Tm, Tb, Co, Sc, As, Rb, Li, Tl, Pb, Ga, U, Eu, Ho, Sn, Cu, Ta, Cr, Pr, W, Er, Ni, Dy, Gd and Zn while the second group has Ba, Sr, Nb, V, Hf, Nd, Y, La, Ce and Zr. At the first cluster stage of the dendrogram, the first group consists of elements which are related to both mineralization and rock weathering processes of both mineralized and barren/unmineralized rocks that are present in the study area (Bottrill, 2008; Bamgboye and Adekeye, 2011). The second cluster group is significant in indicating the presence of barite and other minerals that are rich in Ba and also related to minerals which are rich in Zr. In recent years many geochemical studies have used factor analysis for reconnaissance and exploration work in southwestern Nigeria (Bamigboye and Adekeye, 2011; Odokuma-Alonge and Adekoya, 2013).

Table 2 shows the results of this factor, which is concerned with interrelations of among variables, each variable attributes a certain loading to each of the extracted factors, which is expressed in the matrix of factor loading. The variance indicates the amount of total information contained in each factor. The cumulative variance or total explained variance of the five-factors in the area is 92.69%. The communality for each element expresses the proportion of the total variability of that element that is contained in the factors. In the present study, factor analysis has shown the existence of five important factors that can broadly explain the observed variations and distribution of elements in the stream sediments of Ilesha and Ipole areas. The first component has total variance of 62.56% and strong loadings of Nd, Pr, La, Ce, Gd, Eu, Tb, W, Nb, Sn, V, Dy, Ho, Cr, Ni, Y, Er, Tm, Lu, U, Zr, Hf, Ga, Sc, and Sr. Rare element associations including Sn-Tb-Nb indicate resistate heavy minerals in the stream sediments derived from potentially economic deposits of minerals in the area. Rare element association such as La, Ce, Nd, Pr and U commonly characterise stream sediments derived from metasedimentary and metavolcanic lithologies and migmatitic gneisses. Thus it is fundamentally a Sc factor. The Sc-Ga-V-W and Hf association suggests a complex pegmatite lithology with veins and dykes being the source of these trace elements (Odokuma-Alonge and Adekoya, 2013). In addition, the association of V, Sc, Ni and Cr is almost certainly indicative of the occurrence of mafic and ultramafic rocks within the study areas. The second component accounts for 10.55% of total variance with strong loadings Zn, Cu and Co but moderate loadings of Pb could suggest the occurrence of sulphide mineralization probably associated with the felsic or granitic rock.

The third component has total variance of 9.73% and strong loadings of Rb and Ba but moderate loadings

of Sr and weak loadings of Co, Pb and Cd suggesting occurrence of mafic and ultramafic rocks within the study area. The fourth component show total variance of 5.50% with moderate loadings of Tl and weak loadings of Ag. The fifth component exhibit total variance of 4.35% with strong loadings of Mo and moderate loadings of Ag which suggest occurrence of sulphide mineralization.

Conclusions

A stream sediment geochemical survey was carried out in Ipole (Arinta waterfalls) and Erin Ijesa (Olumirin waterfalls). Considering the geochemical analysis of the stream sediments

as well as its interpretation, the following conclusions can be drawn.

1. Si, Fe and Al are the dominant major elements in the stream sediments. Si indicates the possible occurrence of siliclastic minerals, Fe indicates the possible occurrence of ferromagnesian minerals while Al indicates that the stream sediments are enriched in aluminosilicate minerals such as feldspars and micas.

Table 2. Varimax Rotated Factor Loadings Matrix and Communalities Obtained from Principal Component Analysis for the Studied Major, Trace and Rare earth Elements in the sediment samples

CASE Label	Variables	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Communalities
	Nd	0.99					
	Pr	0.99					
Ag	La	0.99					
Cd	Ce	0.99					
Cs	Gd	0.99					
Mo	Eu	0.99					
La	Tb	0.98					
Ta	W	0.98					
Tb	Nb	0.98					
Co	Sn	0.98					
Sr	V	0.98					
As	Dy	0.98					
Rb	Ho	0.97					
Li	Cr	0.97					
Tl	Ni	0.97					
Pb	Y	0.96					
Ga	Er	0.96					
U	Tm	0.95					
Eu	Lu	0.95					
Ni	U	0.94					
Dy	Zr	0.93					
Gd	Hf	0.93					
Zn	Ga	0.92					
Ba	Sc	0.88					
Sr	Cs	-0.82					
Mo	Sr	0.75		0.51			
V	Cd	-0.50		0.44			
HE	Zn		0.88				
Nd	Cu		0.79				
Y	Co		0.75	0.41			
La	Pb		0.74	0.41			
Ce	Ba			0.93			
Zr	Rb			0.87			
	As			-0.76			
	Ta			-0.70			
	Li				-0.88		
	Tl		-0.60		0.72		
	Mo					0.97	
	Ag				0.46	0.56	
	EV	25.32	4.55	2.84	1.91	1.53	
	VAR (%)	62.56	10.55	9.73	5.50	4.35	
	CVAR (%)	62.56	73.11	82.84	88.34	92.69	

Figure 9. Average linkage (Between groups)

2. High concentrations of zirconium probably indicative of resistant heavy minerals. Zirconium is predominantly found in detrital zircons grains. The

rock present within the study area is migmatite and quartzites which are rich in zirconium, therefore the enrichment in the stream sediment must be due to surficial processes. The weathering has formed quartz rich stream sediments enriched in resistant heavy minerals, including zircon. Zircons appears to be a good pathfinder element for placer deposits of heavy mineral and are used to make lamp filaments, surgical instruments. Zirconium alloys are used to make concrete drill bits. Cerium and Lanthanum concentrations are indicators of monazite mineralization.

3. The multivariate analysis applied to the data explained 92.69 % of the total variance through five components. Component 1, accommodated elements are Nd, Pr, La, Ce, Gd, Eu, Tb, W, Nb, Sn, V, Dy, Ho, Cr, Ni, Y, Er, Tm, Lu, U, Zr, Hf, Ga, Sc, and Sr which suggest the occurrence of heavy mineral phases such as garnet, zircon and monazite in the concentrates. Rare element associations including Sn-Tb-Nb indicate resistant heavy minerals in the stream sediments derived from potentially economic deposits of minerals in the area. Rare element association such as La, Ce, Nd, Pr and U commonly characterise stream sediments derived from metasedimentary and metavolcanic lithologies and migmatitic gneisses. Component 2 (Zn - Cu - Co - Pb) is probably associated sulphide mineralization probably associated with the felsic or granitic rock. Component 3, an association of Rb, Ba, Sr Co, Pb and Cd suggesting occurrence of mafic and ultramafic rocks within the study area. Component 4 is an association of Tl and Ag whereas Component 5 contains Mo and Ag which suggest occurrence of sulphide mineralisation.

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