Geochemistry and Mineralization Study of the Stream Sediments around Agunjin area Northeastern, Nigeria

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Abstract

Agunjin lies in the Northeastern part of Kwara State, Nigeria. The study area is largely underlain by the basement complex rocks of Northeastern Nigeria. Some parts of the area had been investigated in terms of mineral deposits but stream sediment mineral potentials of the area are unknown. Eight (8) stream sediment samples were selected for the study. The stream sediments were analyzed for major, and trace elemental concentration using the ICP-MS analytical method. The results of the geochemical analyses were later subjected to statistical analysis. The results revealed that Iron (Fe) has the highest concentration in major elements, Phosphorus (P), Antimony (Sb), Sulphide (S), and Rubidium (Rb) in trace elements. The conclusion drawn from the geochemical revealed that the mineralization of the underlying lithologies led to anomalous enrichment of Iron, Phosphorous, Rubidium, and Antimony rich minerals in the area. The high concentrations of Phosphorus (P), Sulphide (S), Antiomny (Sb), and Rubudium (Rb), indicate the possible mineralization of apatite, Platinum, Pyrite, Carnallite, Pollucite, and Stibnite respectively.

Keywords: Geochemistry, Mineralization, Stream Sediments, Agunjin

1. Introduction

Nigeria is blessed with numerous base metal mineralization that altogether forms the metallogenic provinces of the (Elueze and Olade, 1985). The quest for solid mineral development in the country has resulted in various methods now being applied in the exploration of mineral resources in Nigeria. Stream sediment survey is employed almost exclusively for reconnaissance studies in drainage basins. By determining the chemical composition of the stream sediments and/or the heavy minerals separated from them, it is possible to recognize geochemical or mineralogical anomalies within a catchment area and trace them to their sources (Levinson, 1974). Active stream sediments represent the fine to medium–grain solid (clayey-silty-sandy) material, which consists of fragments that are mostly derived from the erosion of weathered rocks and soil by a stream or river water (Ako, 1980; Allen, 1965). Depending on their particle size and stream water velocity, sediments are transported in solution, in suspension, or as bed load. Thus, stream sediments represent the best composite of materials from the catchment area of the stream drainage network (Ranasinghe *et al.,* 2009) and are commonly used as an exploration tool for regional geochemical surveys (Cohen *et al.,* 1999; Cannon *et al.,* 2004) as well as for provenance studies (Mange and Wright, 2007; Okon and Essien 2015). Stream sediments contain a group of minerals with high specific gravity, they include economically important minerals, these minerals occur in very low concentrations in a variety of igneous and metamorphic rocks, but are chemically and physically resistant to weathering and have a comparatively high specific gravity (Mange and Wright, 2007). A placer deposit is a result of flowing water like streams and rivers causing the accumulation of mechanically segregated minerals. The erosion of weathered rocks and minerals results in the concentration of the more resistant and higher specific gravity (density) minerals (Gandhi and Raja, 2014). Minerals having a density of more than 2.89 g/cm3 are seen as dense or heavy minerals. These minerals are both opaque and non-opaque in character (Singh, 2012; Akintola, 2013). Heavy minerals are defined as high-density minerals with specific gravities greater or equal to 2.9 g/cm3 (Muller, 1969; Suleiman, 2015). The heavy mineral assemblage in sediments reflects their parent rocks as well as their origin (Raiswell and Anderson, 2005). The study also attempted to delineate possible mineralized areas so that attention could be focused on localized areas with high economic interest.

1.1 Geology of the Study Area

The study area (Agunjin) is located in the northeastern part of Kwara State, Nigeria within latitude 8^0 26' 28" N to $8^0$30' 00" N and longitude $4^0$57' 30" E to 5^0 00' 00" E (Fig. 1) Geologically, the study area falls within the region dominated by crystalline rocks including gneisses, migmatites, and metasediments of Precambrian age (Rahaman, 1976; Odewumi, 2015). The major rock units of the area include granite gneiss, migmatitic gneiss, and diorite. Others include granites and pegmatites (Haruna *et al.,* 2008; Ajibade, 1987). Migmatite gneiss is the major rock unit and mostly intruded by granitoids of the Older Granite suite (granodiorite, diorites) during the Pan-African orogeny (600±150 My). Rahaman (1976) recognized five petrological units within the Basement Complex of Nigeria, namely: (i) migmatite-gneiss complex; (ii) slightly migmatised para-schists; (iii) charnokite rocks, meta-gabbros, and diorites; (iv) Older Granites and (v) un-metamorphosed dolerite dykes and hypabyssal intrusive (Fig 2 and 3). Available age data (Ekwueme, 2005; Dada, 2006) indicate that Nigerian Basement Complex is mainly of Proterozoic age and has been involved in at least two orogenic events (Rahaman, 1988). During the first event, the Eburnean orogeny (1850±250Ma) pre-existing ancient sediments and volcanic were subjected to widespread migmatization and granitization. There was also local mobilization and intrusion of granites (Gandu, 1986). Rocks formed during this ancient granitic cycle are represented by gneisses, quartzites, schists, and amphibolites. These rocks constitute the bulk of the migmatite-gneiss complex. The second orogeny, known as the Pan African

Orogeny (600±150Ma) is characterized by local migmatization, mobilization, and intrusion of granites, known as Older Granites.

Figure 1 Map of the Study Area (Agunjin) Kwara State, Nigeria (Maphill, 2011).

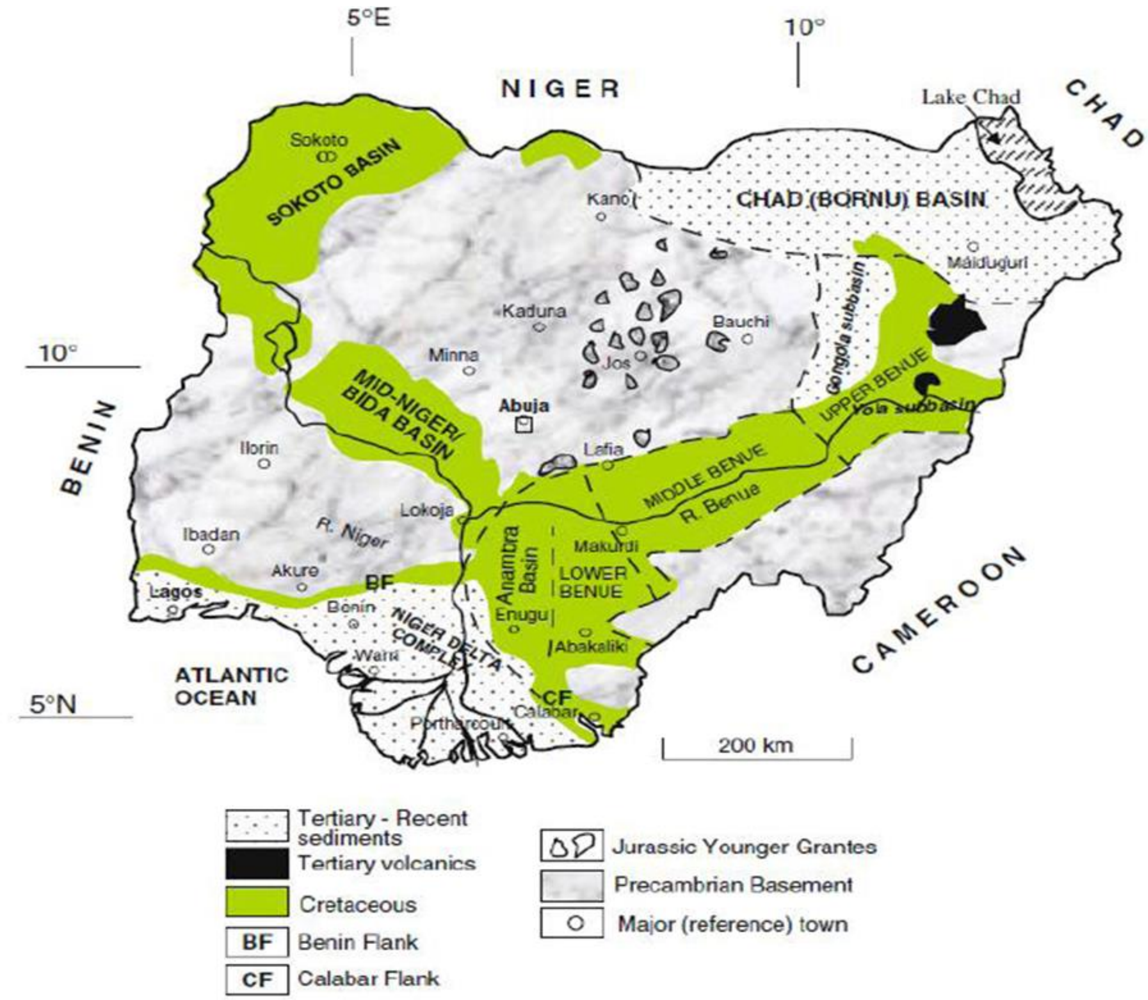

Figure 2. Geological map of Nigeria showing major lithological units (Obaje, 2009).

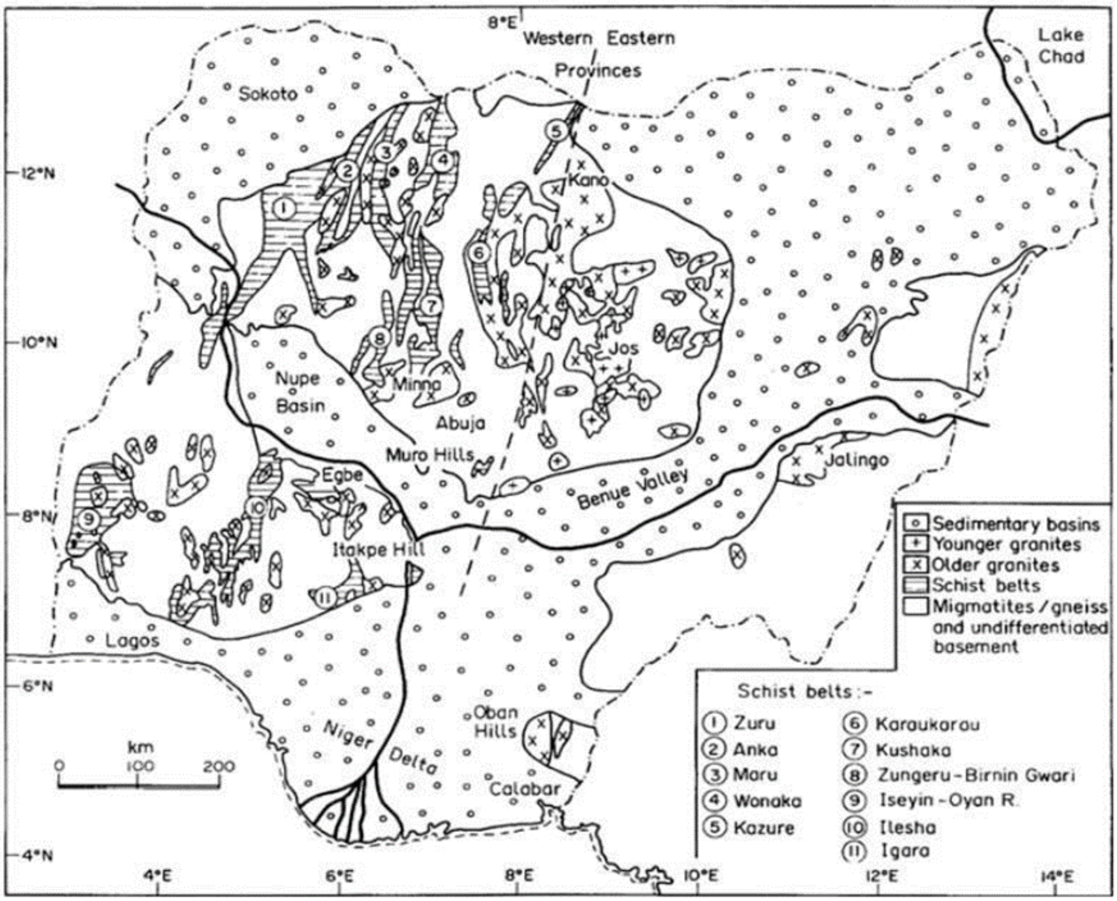

Figure 3. Schist belt localities within the context of the Geology of Nigeria (Woakes *et al.,* 1993)

2. Materials and Methods

Transverse were made through the bush to locate more of the exposures, clinometers compass was used to take strike and dip of foliated rocks, bearing, measure the trend of the geological structures like joints, and faults, and measure the trend of intrusions and lineation, hand specimen of the rocks were used to analysis the mineralogy and texture. GPS (Geographic Positioning System) was used to know coordinates and elevations. Fresh samples were taken with the use of a geological hammer and chisel into the sample bags, stream sediments samples were also taken by digging the channel of the stream and then taking the samples which were wet. Outcrops and geological structural feature photographs were taken with the aid of a camera. Proper labeling of the samples was done on the field with the use of marker and masking tape. All descriptions and necessary parameters were documented inside the field note. A total of eight (8) samples were collected from the study area for analysis which were put in a sample bag for onward transmission to the laboratory.

2.1 Geochemical Analysis

A total of Eight (8) samples were collected in Agunjin which is located in the northeastern part of Kwara State, Nigeria. The samples collected were laid out in pre-numbered evaporating dishes to dry and then placed in a low-temperature oven and maintained at 105°C for 12 hours. Each sample was disaggregated and homogenized by the use of an agate pestle and mortar. A 100 mesh screen was used. This is because in environmental research with the purpose of assessment of total elemental concentration, it is necessary to use a broader screen value compared to that needed in mineral exploration. The homogenized samples were passed through a 100-mesh nylon screen. This helped extract metals from the <100 mesh fractions which are considered highly adsorptive fractions. The nylon screen was used to avoid contamination. The samples were digested by the use of aqua regia based on standard methods described in Fletcher (1981). 0.5 g of the screened samples were weighed out and placed in a 20 ml beaker. 10 ml of aqua regia was added and stirred and was gently boiled on a hot plate to a volume of 25 ml. 10 ml of deionized water was added and gently boiled to a volume of 5 ml. This was kept to cool and thereafter filtered into a 50 ml measuring cylinder. Beaker and filter paper was washed into the cylinder to a level of 12.5 ml. Deionized water was added to make up to 25 ml. The samples were analyzed for major and trace elements using the Inductive Coupled Plasma Optical Emission Spectrometer (ICPMS) technique in Acme Laboratory Ltd Vancouver, Canada.

3. Results and Discussion

3.1 Geochemical Analysis

The concentration of the major elements SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O, TiO_2, and MnO (wt%) and trace elements Co, Cu, No, Pb, Rb, S, Sb, Sn, Ni, As, Mo, Zn, P, Cr, Mn, and Cd (ppm) are presented in (Table 1).

3.1.1 Major elements

From (Table 1), the concentration of Na_2O ranges from (0.00 - 0.00%) which indicated the depletion of sodium-rich feldspar while the concentration of MgO ranges from (0.00 - 0.00%) which showed that Mg-rich micas has depleted in the study area. The concentration of Al_2O_3 ranges from (4.20% - 7.03 wt%). Al_2O_3 is high in FG37 and AG18, which can be attributed to the prevalence of clay minerals in the sample which may be derived from weathered feldspars from rocks. The concentration of K_2O ranges from (3.85– 5.88 wt%) and it is high in AG18 and AG-30 which may be attributed to weathering of K-feldspar and micas while the concentration of CaO ranges from (9.66 – 15.74 wt%) and it is high in AG 02 and AG 18, the elevated concentration can be attributed to the presence of Ca-rich feldspars. Meanwhile, the concentration of TiO_2 ranges from (0.25 – 0.78 wt%), and Its highest values are recorded FG 31, FG 37, AG 16, and AG18 which indicate the low presence of Ti-bearing minerals. The concentration of Fe_2O_3 ranges from (15.81 – 28.19 wt%). The concentration of Fe_2O_3 is high in all the samples except in AG 02 and AG 30, this is an indication of high ferruginized minerals. The concentration of SiO_2 ranges from (37.07-49.54 wt%). Almost all Samples have a high concentration of SiO_2 which may be attributed to the presence of quartz in the study area. A Positive correlation exists between Al_2O_3 and SiO_2 (0.87), K_2O and SiO_2; Al_2O_3 (0.91, 0.96), TiO_2 and Fe_2O_3 (0.94) and MnO_2 and Al_2O_3; Fe_2O_3 (0.87, 0.90) (Table 2). The positive correlation that exists between these elements shows they are from the same bedrock source. The highest value of SiO_2 was discovered in the samples collected from the Agunjin location. The results of geochemical analysis of the stream sediments in the study area revealed a high concentration of major oxides such as Fe_2O_3, CaO, and SiO_2 in stream sediments which could be attributed to the fact that the area is underlain by rocks that are rich in olivine, pyroxene, and amphibole.

3.1.2 Trace Element

The results of trace element geochemical analysis of the studied samples of the concentration of the element in the study area are shown in (Table 1). Cobalt values range from 21ppm to 40ppm, Phosphorus values range from 41ppm to 91ppm. Zinc values range from 23ppm to 30ppm. Molybdenum values range from 25ppm to 49ppm. Tin values range from 31ppm to 38ppm. Sulfur values range from 40ppm to 70ppm. Rubidium values range from 33ppm to 63ppm. A positive correlation exists between Pb and Co (0.85), S and Nb (0.96), Sb and Cu (0.92), Ni and Cu, Sb (0.81, 0.87), Mo and Nb, S (0.88, 0.91), V and Pb, Co (0.87, 0.75), P and Nb, S, Mo (0.86, 0.89, 0.99), Cr and Nb, S, Mo, P (0.91, 0.85, 0.98, 0.98) and Mn and Co, Zn (0.73, 0.97). The positive correlation between these elements suggests they are derived from the same bedrock source (Table 3).

The high concentrations of Phosphorus (P), Sulphide (S), Antimony (Sb), and Rubidium (Rb), indicate the possible mineralization of Apatite, Monazite Platinum, Pyrite, Carnallite, Pollucite, and Stibnite respectively.

Table 1

Major and Trace elements.

Samples		FG31	FG36	FG37	AG17	A6G16	AG18	AG02	AG30
Element	Units								
SiO_2	wt%	41.91	38.30	42.31	37.07	41.11	44.73	26.60	49.54
Al_2O_3	wt%	6.93	6.35	7.03	6.16	6.82	7.43	4.20	6.71
Fe_2O_3	wt%	26.42	24.13	26.67	23.37	25.92	28.19	17.87	15.81
CaO	wt%	10.78	9.85	10.88	9.54	10.57	11.52	15.74	9.66
K_2O	wt%	5.52	5.04	5.56	4.87	5.41	5.87	3.85	5.88
TiO_2	wt%	0.73	0.67	0.73	0.65	0.71	0.78	0.52	0.25
MnO_2	wt%	0.25	0.21	0.24	0.22	0.23	0.26	0.14	0.18
MgO	wt%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	wt%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P_2O_5	wt%	1.08	0.98	1.07	0.93	1.05	1.15	2.09	1.35
Co	ppm	37	34	38	33	37	40	31	35
Cu	ppm	18	16	18	16	17	19	16	18
Nb	ppm	2	2	2	2	2	2	11	3
Pb	ppm	2	2	2	2	2	3	2	2
Rb	ppm	37	34	38	33	37	40	43	42
S	ppm	46	42	46	40	45	49	70	52
Sb	ppm	48	44	48	42	47	51	46	43
Sn	ppm	35	32	36	31	35	38	33	32
Ni	ppm	8	8	8	7	8	9	7	8
As	ppm	2	2	2	2	2	2	2	2
Mn	ppm	19	17	19	17	18	20	11	16
Mo	ppm	28	26	28	25	28	30	49	34
Zn	ppm	30	28	30	27	30	32	23	25
V	ppm	5	5	5	5	5	6	6	5
P	ppm	47	43	47	41	46	50	91	68
Cr	ppm	2	2	2	2	2	2	11	6

Table 2

Correlation co-efficients for major element oxides

	SiO_2	*Al_2O_3*	*Fe_2O_3*	*CaO*	*K_2O*	*TiO_2*	*MnO_2*	*MgO*	*Na_2O*
SiO_2	1								
Al_2O_3	0.87	1							
Fe_2O_3	0.18	0.63	1						
CaO	-0.73	-0.73	-0.26	1					
K_2O	0.91	0.96	0.48	-0.87	1				
TiO_2	-0.13	0.35	0.94	-0.03	0.19	1			
MnO_2	0.54	0.87	0.90	-0.54	0.77	0.74	1		
MgO	00.0	00.0	00.0	00.0	00.0	00.0	00.0	1	
Na_2O	00.0	00.0	00.0	00.0	00.0	00.0	00.0	00.0	1

Table 3

Correlation Co-efficients for Trace elements

	Co	*Cu*	*Nb*	*Pb*	*Rb*	*S*	*Sb*	*Ni*	*As*	*Mo*	*Zn*	*V*
Co	1											
Cu	0.21	1										
Nb	00.0	-0.47	1									
Pb	0.85	0.23	0.16	1								
Rb	-0.81	0.34	-0.1	-0.64	1							
S	0.07	-0.21	0.96	0.25	00.0	1						
Sb	-0.07	0.92	-0.36	00.0	0.62	-00.1	1					
Ni	-0.09	0.81	-0.62	00.0	0.53	-0.41	0.87	1				
As	00.0	00.0	00.0	00.0	00.0	00.0	00.0	00.0	1			
Mo	-0.34	-00.2	0.88	-00.1	0.38	0.91	0.02	-0.27	00.0	1		
Zn	0.79	00.6	-0.57	0.62	-0.47	-0.43	0.35	0.44	00.0	-0.69	1	
V	0.75	-0.13	00.6	0.87	-0.69	0.62	-0.29	-0.41	00.0	0.26	0.26	1

4. Conclusion

The result of a geochemical investigation carried out on the stream sediments of Agunjin and its environs show that Iron oxide (Fe_2O_3) has the highest major oxide composition. It is likely that the parent rock from which iron materials are leached into the surrounding stream as sediments are highly ferruginized or contained Iron-bearing minerals next to the abundance of Aluminium oxide (Al_2O_3) which is an indication of the prevalence of clay minerals in the stream sediments. Positives correlation exists between (Al_2O_3 and SiO_2), (K_2O and SiO_2; Al_2O_3), (TiO_2 and Fe_2O_3) and (MnO_2 and Al_2O_3; Fe_2O_3) which shows they are from the same source. However, the Negative correlation of CaO_2 with the other elements indicated it from another bedrock source. The analytical results for trace element geochemistry of the Agunjin show that Rubidium (Rb) Phosphorus (P), Antimony (Sb), and Sulfide (S) have concentrations that are higher than other trace elements content suggesting significant enrichment of these elements in the study area.

Acknowledgment

We really want to thank the University of Ilorin and the department of geology and mineral resources for the privilege to carry out this research work.

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