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PRELIMINARY INVESTIGATION OF PEGMATITES IN OBUDU AREA, SOUTHEASTERN NIGERIA, USING STREAM SEDIMENTS GEOCHEMISTRY

GRACE O. EDEM, BARTH N. EKWUEME, BASSEY E. EPHRAIM AND EMMANUEL E. IGONOR

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ABSTRACT

Stream sediments of Obudu Plateau were investigated with a view to elucidating their geochemical features, mineralization potentials and element concentrations. Stream sediment samples were collected from Southern Obudu Plateau area and analyzed for 22 elements, comprising major and trace elements, using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The data obtained were statistically treated. Ba, Sr, Nb, Co, Pb, Ta and Na show moderate to high concentrations, when compared with threshold values of these elements. The concentrations of these elements in sediments of Southern Obudu show low mineralization potentials of pegmatites of the Obudu Plateau. The elements in Obudu stream sediments show perfect, strong, moderate and weak correlations among themselves, indicative of variations in their mobility.

KEYWORDS: Correlation matrix, Major and Trace Elements, Stream sediments, Threshold.

INTRODUCTION

Stream sediment samples from major streams and tributaries in Obudu area can be considered representative of upstream lithology. They play a significant role in exploration and environmental geochemistry. Since elements are not static but migrate within the geochemical environment, these sediments are considered to be important carriers of elements. However, sediment yield and the geochemistry of stream sediments are controlled not only by physical and chemical weathering of parent rocks, but also by factors such as climate, hydrology and morphology of the basin (Ranasinghe et al., 2009). Sufficiently intense rainfall can initiate bed load transport, bringing the 100µm fraction into suspension (Fletcher, 1996).Stream sediment samples were used to represent the mineral composition of the pegmatites through which the streams flow. Pegmatite host considerable rare metals such as Ta, Nb, Sn, Li and W mineralization

The study is to determine the extent of mineralization of pegmatites and to elucidate the concentration and distribution pattern of elements in the stream sediments around Southern Obudu Plateau.

GEOLOGIC SETTING OF THE AREA

Within the context of the geology of the Nigerian Basement Complex, three broad lithological units are distinguishable. These are the migmatite-gneiss complex, the schist belts and the Pan-African older granite series (Elueze,2000). The migmatite gneiss complex is a heterogeneous assemblage of predominantly amphibolite facies migmatites, orthogneisses, paragneisses and basic to ultrabasic rocks (Rahaman, 1988). The migmatite - gneiss is dominantly made up of guartzo - feldspathic gneiss that are predominantly biotite and / or hornblende - bearing and rarely pyroxene (Ekwueme and Kroener, 2005; Ukwang et al., 2003). The schist belts, believed to overlie the migmatite gneiss complex and consisting mainly of psammitic to politic metasediments with minor occurrences of banded iron formation, marbles and amphibolites with the latter being interpreted as metavolcanic (Turner, 1983; Elueze and Okunlola, 2003). And the older granite (syn-late tectonic Pan African granite) intrudes the schist belts and the gneiss migmatite complex, and composed mainly of granites, pegmatites, charnockites, diorites, gabbros and syenites. The pegmatites which are believed to be late Pan-African (600 ± 150Ma) host considerable rare metals such as Ta, Nb, Sn, Li and W mineralization (Okunlola and Solomon Jimba, 2006). Isotopic data have revealed that the Basement Complex has been involved in several tectonothermal events, which include from the oldest Liberian, Eburnean, and Pan African (Grant et al. 1972; Ekwueme, 1987; Rahaman, 1988; Ekwueme and Kroener 2005).

The study area Obudu Plateau, is composed of Precambrian rocks (Fig. 1), which include migmatites, gneisses, charnockites, granulites, amphibolites, schists and intruded by rocks of acidic, intermediate, basic and ultra-basic compositions (Ekwueme, 1985a). The area forms part of the Pan African mobile belt which lies between the West African and Congo Cratons and South of the Tuareg shield (Black, 1980).

SAMPLING AND ANALYTICAL PROCEDURES

Rocks in the study area have undergone

Grace O. Edem, Department of Geology, University of Calabar, Calabar, Cross River State, Nigeria. Barth N. Ekwueme, Department of Geology, University of Calabar, Calabar, Cross River State, Nigeria. Bassey E. Ephraim, Department of Geology, University of Calabar, Calabar, Cross River State, Nigeria. Emmanuel E. Igonor, Department of Geology, Federal University of Technology, Akure, Nigeria. considerable weathering and some have formed alluvial deposits, which are in many cases associated with pegmatites. Seven stream sediments from Abeb, Sumo, Akak, Abeku, Urie, Metu and Attia streams in Southern Obudu (Fig. 2) were collected for geochemical analyses. Stream sediment samples were used to represent the mineral composition of the pegmatites through which the streams flow. Samples of the most organic-free sediments available were collected from channels of

active streams and rivers. The collections of these samples were mainly along the stream banks and the centre of the stream. Areas where sediments were composed predominantly of coarse-grained material were avoided to ensure that sufficient fine-grained and meaningful amount of material would be contained in the sample. A total of fifteen (15) stream sediment samples were collected, of which seven (7) were analysed geochemically.



FIG. 1: Geological map of Southern Obudu Plateau, Southeastern Nigeria. (After Ekwueme and Kroener, 1997).



FIG. 2: Sample Location Map of Obudu – Obanliku Area of Southern Obudu Plateau

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The collected samples were air-dried to allow for the moisture to be removed naturally. All materials were passed through an 80mesh stainless steel screen to remove pebbles and cobbles before further processing. The air-dried samples were then sieved through a 60mesh stainless steel screen. The -60mesh fraction was pulverised and homogenised to -300mesh in a pulveriser with ceramic plates, and a split of this material was saved in already labelled brown envelopes and sealed with masking tape for easy identification and to avoid contamination. Pulverisation of the samples was done in the Workshop of the Department of Geology, University of Calabar, Calabar, Nigeria. All the samples were analysed for major and trace elements using the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique at the Acme Analytical Laboratories Vancouver, Canada.

The geochemical analytical procedure involved addition of 5ml of perchloric acid (HClO₄), Trioxonitrate (v) (HNO₃) and 15ml Hydroflouric acid (HF) to 0.5gm of

sample. The solution was stirred properly and allowed to evaporate to dryness after which it was warmed at a low some hours. Thereafter, temperature for 4ml hydrochloric acid (HCL) was added to the cooled solution and warmed to dissolve the salts. The solution was cooled, and diluted to 50ml with distilled water. The solution was then introduced into ICP torch as aqueousaerosol. The emitted light by the ions in the ICP was converted to an electrical signal by a photo multiplier in the spectrometer, the intensity of the electrical signal produced by the emitted light was compared to a standard (a previously measured intensity of a known concentration of the elements) and the concentration then computed.

RESULT OF STREAM SEDIMENTS ANALYSIS

The result of geochemical analysis of the stream sediment samples in southern Obudu Plateau are presented in Table 1.

Table 1: Major and trace elements concentrations in stream sediments around Southern Obudu area, Southeastern

										N	ligeri	а										
	Majo	Major Elements Trace Elements																				
	Al	Ca	Fe	Κ	Mg	Na	Mn	Р	Ti	Cu	Pb	Zn	U	Та	Cs	Co	Ва	Nb	Sn	Zr	W	Sr
S/N					(%)											(ppm)					
1	4.4	0.8	3.1	0.9	0.3	0.8	0.1	0	0.7	10	7	15	4	1	1	15	482	13	<1	1583	65	119
2	4.1	0.4	3.6	1.3	0.2	0.5	0.1	0.1	0.6	12	12	29	9	1	1	15	689	9	<1	1205	52	104
3	4.2	0.4	1.8	3.3	0.4	0.7	0	0	0.1	6	3	17	1	1	1	35	973	6	<1	233	349	133
4	4.2	0.4	3.1	1.4	0.3	0.5	0	0	0.4	15	10	36	7	1	1	19	712	8	<1	1002	99	108
5	7	1.2	5.1	4	0.2	1.6	0.1	0.1	0.7	11	4	45	1	2	1	18	2523	43	<1	186	107	341
6	5.1	0.6	2.4	2.2	0.3	0.8	0	0	0.3	7	4	18	2	1	0	17	918	9	<1	518	97	160
7	5.9	0.7	2.9	2.3	0.4	0.9	0.1	0	0.6	8	5	29	5	1	1	16	1033	15	<1	865	65	171

STATISTICAL TREATMENT OF DATA

A better interpretation of results obtained from geochemical analysis is by statistical methods which allow examination of relationship among elements. The data obtained were statistically treated. The mean, standard deviation and threshold analyses were calculated and presented in Table 2.Relative abundance of selected elements in the different stream sediment samples analysed from Southern Obudu area is presented in Table 1.

DISCUSSION

The essence of any geochemical exploration programme whether at reconnaissance or detailed level is to establish the trend of elemental distribution and possible mineralization. For these to be achieved, baseline information (threshold) for comparison must be obtained. Below the threshold values are regarded as background, depicted as the normal range of concentrations for elements in an area. Values higher than threshold are considered anomalous.

The patterns of major and trace elements distribution in the stream sediments of Southern Obudu Plateau show that in all locations, Cu concentration is lower than threshold value (15.93ppm) (Table 2). Cu values are lower than expected for mineralization (Ojo, 1984). This is understandable since Cu being a

chalcophile element is not expected to be high in granitic rocks, to the extent of forming ores, Cu is also highly mobile under weathering condition and this could also contribute to the observed low values. Elements such as Pb, Ba, Co, Ta, Sr, Nb and Na have anomalous concentrations (Fig. 2) in the stream sediments of the area. The implication is that, the source of these elements in the stream sediments are not far from the sample locations or the sources could be from weathered basement rocks and dissolution of these elements in stream sediments. This may be also as a result of the chemical composition of the rocks which include granitic gneisses, metabasites, syenitic gneisses and monzonitic gneisses which show enrichment of these elements (Ranasinghe et al, 2009). The source could be from the Bed load which is the sediment transported by a combination of rolling and skipping of particles along the bed of the stream channel. And also sediment transported by suspended load which is the particles that remain floating within the water column by turbulence. All these could be the sources of these elements.

Zn has very low concentration in all the samples of the study area when compared to that obtained by Ukpong (1981) for the mineralized Pb-Zn belt of the Nigerian Benue Trough. 170

TABLE 2: Descriptive statistics of major and trace elements analysed

The Range, Mean (\overline{X}) , Standard Deviation (SD), Threshold (TH), values of Trace and Major Elements analysed.

Elements	Range	Mean (iola (T) x)	Standard Deviation (SD)	Threshold (TH)
Cu (ppm)	6.3-14.7	9.79	3.07	15.93
Pb (ppm)	3.2-11.6	6.19	3.28	2.75
Zn (ppm)	15-45	27	11.09	49.18
U(ppm)	1.0-9.0	4.06	2.95	9.96
Ta (ppm)	0.5-2.3	0.97	0.61	2.19
Cs (ppm)	0.4-0.7	0.57	0.11	0.79
Co (ppm)	14.7-34.8	19.13	7.01	33.26
Ba (ppm)	689-2523	1047.14	678.29	2403.74
Nb (ppm)	5.9-42.8	14.53	12.83	40.19
Sn (ppm)	<1 -1	<1	<1	<1
Zr (ppm)	185.7-1583	798.81	516.52	1831.85
W (ppm)	51.5-349.3	118.97	103.66	362.33
Sr (ppm)	104.1-340.7	162.27	82.60	327.46
AI (%)	4.13-6.98	5.00	1.03	7.18
Ca (%)	0.38-1.19	0.62	0.29	1.21
Fe (%)	1.77-5.11	3.14	1.04	5.23
K(%)	0.90-3.98	2.19	1.13	4.45
Mg (%)	0.23-0.43	0.29	0.08	0.44
Na (%)	0.45-1.58	0.81	0.38	1.51
Mn (%)	0.02-0.06	0.4	0.01	0.07
P (%)	0.03-0.08	0.04	0.02	0.08
Ti (%)	0.14-0.74	0.49	0.22	0.92

Mean (\overline{X}) : This is the sum total of values observation over the number of locations.

Mean,	X	=	<u>2X</u> N
Where	Ν	=	Total number of samples
	Х	=	value of each element
		=	Summation symbol

Standard Deviation (SD): Sum of the square deviation from the mean over the number of locations.

$$SD = \sqrt{\frac{\Sigma(x-\overline{x})^2}{N}}$$

Threshold (TH) value: Is a reference point at which the concentration of the element is measured, and is the concentration value above anomaly.

Threshold (TH) $=\overline{X} + 2$ (SD).

The mean Zn content of 27ppm is also very low when compared to those obtained from stream sediments from Qua Iboe estuary and associated Creek (Ekwere, *et al.*, 1992) and Calabar River estuary (Ntekim *et al.*, 1993). There was no enrichment of Sn in the study area. This could be due to the weathering process in the area that appears to have a moderate transporting effect on the element.

There was no observed enrichment of Cs, U, Al, Ca, Fe, Mg, Mn, P and Ti above their threshold. The

weathering process in the area appears to have a moderate transporting effect on the elements. The low level of U concentrations is however due to sediment in shallow water not usually having high U content because of aeration and absence of H_2S contamination in such shallow beds (Chung and Chang, 1996). It may also be due to the low radioactive materials in the area. However, it is observed that most of these elements that have higher concentrations are from samples from Akak stream sediments (Location 05) Fig.2.



FIG. 2: Graphical distribution of trace and major elements at sample locations

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Elements occurring in high concentrations in Southern Obudu stream sediments could play important role in economy of Nigeria. Barite for instance, could be mined and used in the production of wallpapers and asbestos goods, and in the production of white paint, especially to give weight to paper. It can also be used in fireworks to give green colouration. Additionally, barium can also be used in glassmaking, production of magnets, containers for the storage of radioactive materials. It can also be used as a hardener for lead, (Buzzle, 2010).

Element such as Lead (Pb) has values above its threshold and show higher concentrations in all locations. This element is a metal employed in the construction of accumulators as the oxide, for the Lead sheeting and piping, cable - covers, ammunition, foils. Other elements such as Nb, Ta occurring in high concentration in stream sediments are rare and soft transition metals. Primarily, Nb is used in the production of high grade steel and in super alloys for items such as jet engine, while Ta is primarily used in electrical and aerospace. The Sr occurring in the study area may be used for the production of glass (cathode ray tubes) for colour television, used in systems for nuclear auxiliary power devices. Also used in the fire that is flares and in producing ferrite ceramic.

Correlation Matrix

Statistical correlation reflects the degree of similarity between all possible pairs of as many variables

with the correlation matrix lying between -1.0 and 1.0. An absolute value of 1.0 indicates perfect correlation while a value approaching zero represents no correlation. According to Ekwere, (1981) correlation matrix helps to assess inter-element relationship and how good one variable can serve as a pathfinder to another. Fig. 3 shows the following correlations: Perfect correlation (r) = \pm (0.9 to 1.00); Strong correlation (r) = \pm (0.6to 0.9); Moderate Correlation (r) = \pm (0.5to 0.6); weak or no correlation = \pm (0 to 0.5)

Correlation matrix is the concentration value of one particular element with the concentration value of another element.

 $Correlation matrix, r = \frac{n \sum XY - \sum X \sum Y}{\sqrt{[n \sum X^2 - (\sum X^2)]} [n \sum Y^2 - (\sum Y)^2]}$

The correlation matrices of both major and trace elements in the stream sediment samples are presented in Table 3 and Fig. 3.

The geochemical data of stream sediments were examined using correlation matrix to establish the character and distribution of elemental associations related to processes responsible for the overall data distribution. The results show perfect, strong, moderate and weak correlations among these elements, and these are indicative of various factors, notably, composition of the source rocks, variations in mobility of elements, variation through uptake by plants, etc..

		PI	RELIMIN	ARY INV	ESTIGA	TION O	F PEGM	ATITES	IN OBU	DU ARE	EA, SOU	THEAS	TERN N	IGERIA		173					
			TABLE	3: Corre	lation M	atrix (r) v	alues of	element	ts from s	tream se	ediments	around	Southe	rn Obud	u area, S	South-Ea	astern Ni	geria			
	Cu	Pb	Zn	U	Та	Cs	Со	Ba	Nb	Zr	W	Sr	Al	Ca	Fe	K	Mg	Na	Mn	Р	Ti
Cu	1																				
Pb	0.83	1																			
Zn	0.58	0.22	1																		
U	0.66	0.93	0.18	1																	
Та	0.04	-0.38	0.66	-0.52	1																
Cs	0.73	0.7	0.53	0.55	0.13	1															
Со	-0.44	-0.44	-0.26	-0.5	0.11	0.15	1														
Ba	-0.06	-0.44	0.7	-0.51	0.94	0.03	0.06	1													
Nb	0.11	-0.29	0.7	-0.39	0.94	0.01	-0.22	0.93	1												
Zr	0.47	0.69	-0.28	0.67	-0.55	0.09	-0.59	-0.71	-0.4	1											
W	-0.48	-0.48	-0.31	-0.56	0.12	0.09	0.99	0.07	-0.2	-0.6	1										
Sr	-0.11	-0.5	0.63	-0.56	0.93	-0.13	-0.06	0.98	0.96	-0.63	-0.04	1									
Al	-0.2	-0.53	0.58	-0.47	0.78	-0.31	-0.23	0.87	0.88	-0.51	-0.22	0.93	1								
Ca	-0.05	-0.43	0.46	-0.52	0.84	-0.29	-0.3	0.79	0.93	-0.26	-0.27	0.89	0.87	1							
Fe	0.52	0.22	0.8	0.09	0.73	0.3	-0.52	0.7	0.87	-0.03	-0.52	0.71	0.63	0.74	1						
K	-0.46	-0.72	0.36	-0.73	0.77	-0.08	0.53	0.85	0.63	-0.94	0.54	0.79	0.67	0.5	0.23	1					
Mg	-0.54	-0.46	-0.34	-0.33	-0.14	-0.05	0.81	-0.17	-0.39	-0.36	0.77	-0.24	0.38	-0.39	-0.71	0.32	1				
Na	-0.2	-0.58	0.46	-0.65	0.89	-0.31	-0.12	0.89	0.94	-0.49	-0.08	0.96	0.92	0.97	0.66	0.7	-0.24	1			
Mn	0.45	0.32	0.62	0.29	0.49	0.17	-0.73	0.41	0.68	0.34	-0.74	0.47	0.54	0.66	0.88	-0.08	-0.65	0.5	1		
Р	0.41	0.2	0.85	0.11	0.74	0.46	-0.28	0.77	0.81	-0.27	-0.29	0.71	0.6	0.58	0.91	0.42	-0.51	0.58	0.71	1	
Ti	0.45	0.36	0.35	0.28	0.32	0.06	-0.74	0.18	0.52	0.56	-0.74	0.28	0.35	0.59	0.74	-0.29	-0.65	0.38	0.94	0.46	1



FIG. 3: Correlation matrix of trace and major element concentrations of stream sediments analyzed around Obudu area, Southeastern Nigeria, (a) showing all relationships (b) showing only significant relationships (* = trace elements)

CONCLUSION

Since elements are not static but migrate within geochemical environment, stream sediments the geochemistry is extensively used in mineral exploration and environmental studies. Major and trace elements concentration were measured from stream sediment samples collected from seven streams in southern Obudu Plateau. The result shows that Ba, Sr, Nb, Co, Pb, Ta and Na have high concentration in Southern sediments. Obudu stream The anomalous concentrations of these elements in Obudu area may be linked primarily to the lithology of the area. The elements that have high concentrations were obtained in stream sediments in Akak stream making the area an exploration target for rare-metals mineralisation.

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