INTERNATIONAL JOURNAL NATURAL AND APPLIED SCIENCES (IJNAS), VOL. 2, NO. 2(2007);P. 81 – 86, 3 TABLES, 8 FIGS.

Dispersion of heavy metals in the stream sediments of eastern Oban massif, southeastern Nigeria

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ABSTRACT

A total of 110 stream sediments samples were collected from streams in the eastern part of Oban Massif. The samples were analysed for Pb, Zn, Cu, Sn, Ta and U using atomic absorption spectrophotometer VGP system, model 210. The mean concentration for the elements were Pb (4.0), Zn (42.0), Cu (9.0), Sn (3.0), Ta (0.45) and U (0.23) ppm. Element concentrations were generally low but uniform. Histogram plots reveal that the distribution of these elements were log-normal and showed positive skewness, implying that the distribution is influenced by only one factor, lithology. The geochemical data were also examined using correlation analysis to establish how the character and distribution of element associations relate to processes responsible for the overall data distribution.

INTRODUCTION

The Oban Massif is located between longitudes $4^0$30'N and $5^0$45'N and latitudes $8^0$30'E and $9^0$10'E. The area forms part of the South eastern Precambrian basement complex of Nigeria and is surrounded by Cretaceous and younger sedimentary rocks which constitute the Manfe Embayment in the north, Benue Trough in the west and the Calabar Flank in the south. The Massif is important because it lies between the West African Craton to the west and the Congo Craton to the south east forming part of the Precambrian to Paleozoic Mobile belt of Nigeria. Raeburn (1927) studied some tin fields in Calabar district. Rahman *et al* (1981, 1988) discussed the geology of parts of Oban Massif as well as geochemistry of some granitic intrusive rocks in the western section, while Ekwere and Ekwueme (1991) studied the geochemistry of the gneisses in the eastern part of the Oban Massif.

It is well drained area with dendritic and angular drainage patterns the later indicating the drainage to be partly structurally controlled. Radar imagery interpretation however indicates some rivers in the Massif to be tectonic in origin (Okonny, 1984). There are many active streams including Ackan, Akup, Eku, Ibe and Ikpan (Fig. 1). Run-off water from land transport particulates and dissolved humid substances into channels which are deposited at the bottom to form sediments. The detritus at the stream channel ranges from clay-size materials to boulders of various sizes.

The area is thickly forested with rugged topography. This restricts intra-land accessibility thereby hindering proper assessment of the economic potentials of the areas.

To overcome this, a reconnaissance steam sediment geochemical survey was undertaken to assess the distribution patterns of some selected metals and to evaluate the mineralization potential of the area. Nigeria is endowed with many base metal mineralizations which form the metallogenic provinces of the country. The need for development of the country has resulted in the various methods now being applied in the exploration and exploitation of mineral resources in Nigeria. The methods for exploration of minerals include geological, geophysical, geochemical and remote sensing. Geochemical exploration methods make use of the chemical properties of naturally occurring elements as aids in the search for economic mineral deposits. The choice of a particular geochemical method depends on the availability of sampling materials, convenience and what the survey is aimed at. Stream sediment geochemical survey is used in areas of poor accessibility, but with very good drainage net-work. It is used in the reconnaissance stage to delineate mineralization in relatively large areas so that attention could be focused on localized areas with high economic interest.

Geology

The geology of eastern Oban Massif differs substantially from that of the western section and characterized by a series of plutonic episodes during which calc-alkaline rocks were emplaced (Ekwueme and Ekwere, 1989). The rocks types in the eastern section of Oban Massif include metamorphic and intrusive rocks. The metamorphic rocks are gneisses and amphibolites whilst granite, syenites, diorites, and charnockitic rocks constitute the intrusive rocks (Fig. 1).

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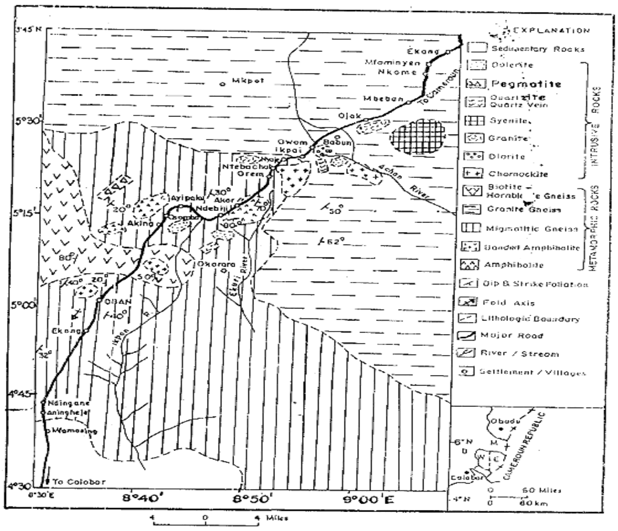

FIG. I : Geological Map of Eastern Oban Massif, Southeastern Nigeria (After Ekwere and Ekwueme, 1991.)

MATERIALS AND METHOD

A total of 110 stream sediments samples were collected during the field exercise. Active sediment samples were carefully taken from both banks and the middle of the stream channels and thoroughly mixed together to obtain a composite sample at each sample point. They were stored in calico bags already labelled against sample locations and taken to the laboratory. The samples were air dried, disaggregated and sieved through 100 Mesh bolting-sieve. 0.5g of each sample was digested using 10ml of HNO_3-HCl acid mixture of ratio 3:2. The samples were refluxed at 75^0C and then evaporated to dryness in about 24 hours. Leaching was done using 5ml of 6M HCl. The samples were analysed for Pb, Zn, Cu, Sn, Ta and U using Bulk Scientific AAS-VGP system model 210 Atomic Absorption Spectrophotometer at the Department of Soil Science, Federal University of Agriculture, Makurdi, Nigeria. The analytical precision for the analysed elements at 95% confidence level are Pb (93%), Cu (92%), Sn (86%), Zn (82%), Ta (80%) and U (77%).

RESULTS

The results of the trace elements are summarized in Table 1. The concentrations of zinc range from 0.24 to 122ppm with a mean value of 42±30ppm and a threshold value of 102ppm. Zinc distribution in the stream sediments is generally above the mean concentration with enhanced concentrations in sediment of river Acup near Nkame village, sediment of Agbor stream near old Ndebiji, Ikim stream sediment near Ntebachot village and Ikapn river sediment near Oban town. However these concentrations are generally lower than expected values for mineralization. It may be due to mechanical dispersion.

Table 1. Range, mean, standard deviation and threshold values for trace elements in stream sediments

Element	Range (ppm)	Mean (ppm)	Mean (log data)	STD. DEV (ppm)	STD. DEV. (log data)	COEF. Variation	Threshold (ppm)	Threshold (log data)
Zn	0.24-122	42	1.48	30.06	0.43	0.71	102	2.34
Cu	0-25	9	0.74	6.79	0.53	0.79	22	1.80
Pb	0-20	4	0.40	4.00	0.50	0.97	12	1.40
Sn	1-6	3	0.44	2.08	0.19	0.70	7	0.82
Ta	0.08-1	0.46	0.40	0.27	0.24	0.59	1	0.88
U	0-5	0.23	-0.77	0.56	0.34	2.44	1	-0.09

Number of samples analyzed for each element =110.

The concentration of lead is much lower in the stream sediments. Lead values range from 0 to 20ppm with a mean concentration of 4±4ppm and a threshold value of 12ppm. The highest concentration of lead (20ppm) was found in Nnem stream sediment near Mbeban village. Samples collected near Osomba, Camp 3 and Ibe river sediment have lead concentrations of about 14ppm each. The copper levels are very low in the stream sediments. The mean concentration for copper is 9±6.79ppm. The highest concentrations (25 ppm) are recorded for samples obtained from Menim stream near Mbeban and Ikim stream near Ntebachot village. Copper concentrations in the stream sediments are generally below the mean. Tin concentration range from 1 to 6ppm with a mean value of 3±2.08ppm. Most of the values are below the threshold value of 7ppm. Tantalum and Uranium concentrations are very low in the stream sediments. The values are generally below 1.0ppm. The highest Tantalum concentration (1.40ppm) was obtained at Acup near Ekong village. Samples obtained form Achan river near Mbeban and Mfamiyen villages have U concentrations of 4ppm and 5ppm respectfully.

DISCUSSION

The geochemical data obtained in this study demonstrate that the concentrations of the trace elements do not vary appreciably within the stream sediments but are generally below their threshold values. The element concentrations are very low especially when compared to those of British Columbia (Hoffman and Fletcher, 1979), Benue Trough (Olade *et al*, 1979), Muelha-Dungash (Soliman, 1981), Cross River Estuary (Azmatullah and Ekwere, 1984), Middle Gongola Basin (Ojo, 1984), Calabar River Estuary (Azmatullah and Ekwere, 1985), Qua Iboe Estuary and Associated Creeks (Ekwere *et al*, 1992), Bight of Bonny (Ntekim *et al*, 1992) and Calabar River (Ntekim *et al* , 1993) as shown in Table 2.

Table 2.Comparison of mean metal concentrations (ppm) in various stream sediments.

Location	Zn	Cu	Pb	Sn	Ta	U	References
Capoose Lake (British Columbia)	313.0	110.0	17.2	-	-	-	Hoffman and Fletcher (1976)
Benue Trough (Nigeria)	112.0	21.0	50.0	-	-	-	Olade ***et al*** (1979)
Muelha-Dungash (Egypt)	-	19.0	45.0	298.0	-	-	Soliman (1981)
Cross River Estuary (Nigeria)	58.3	28.1	25.2	-	-	-	Azmatullah and Ekwere (1984)
Middle Gongola Basin (Nigeria)	58.1	32.7	11.1	-	-	-	Ojo (1984)
Calabar River Estuary (Nigeria)	53.0	28.0	25.0	-	-	-	Azmatullah and Ekwere (1985)
Qua Iboe Estuary and Associated Creeks (Nigeria)	714.0	33.0	26.0	-	-	-	Ekwere *et al* (1992)
Bight of Bonny (Nigeria)	647.0	-	16.0	-	-	-	Ntekim *et al* (1992)
Calabar River (Nigeria)	184.0	64.0	20.0	-	-	-	Ntekim *et al* (1992)
Oban Massif (Nigeria)	42.0	9.0	4.0	3.0	0.46	0.23	This study

The relationships between the elements are examined by statistical analytical methods in order to promote a better interpretation of the results obtained. The geochemical data were examined and interpreted with the help of correlation and frequency distribution patterns. The frequency distribution plots (Fig. 2) reveal log-normal populations for the elements. This implies the influence of one factor, most probably, lithology on the overall distribution of the elements in the stream sediments.

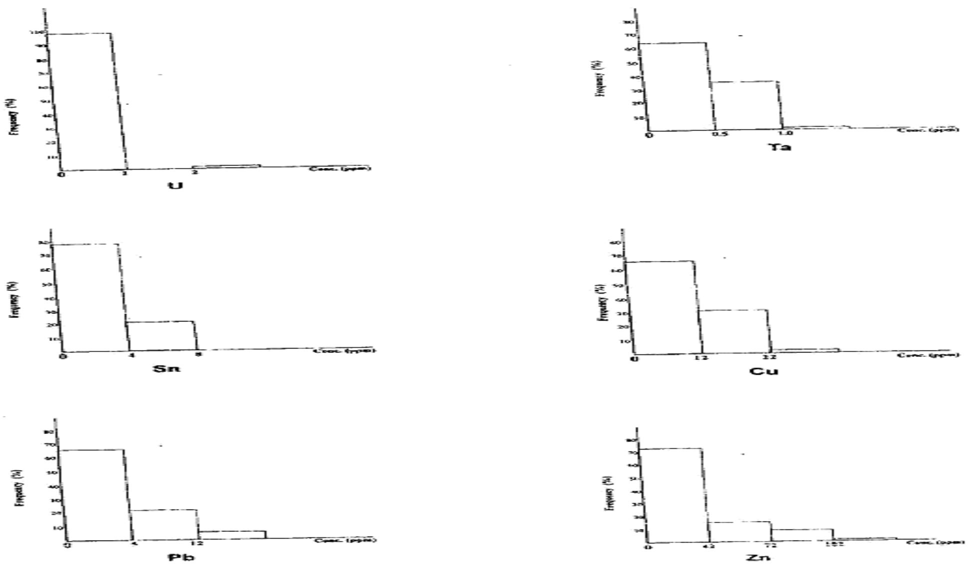

Fig. 2. Frequency distribution plots of trace elements in stream sediments

In order to establish the level of contrast between the background stream sediments and the few observed values above threshold (ppm), the pooled standard deviation (SP) and the geochemical contrast using the student t-test were calculated (Table 3). The observed results are low when compared to those obtained by Ukpong (1981) for stream sediments in the mineralized Pb-Zn belt of the Nigerian Benue Trough. Also, the contrast are generally less than expected 1.5 to 2 regional threshold for mineralization (Hoffman and Fletcher, 1976). Application of $\log_{10}$ transformation on the obtained data further reveal the concentration of these metals to belong to background populations only. The few observed values above their thresholds (ppm) may further suggest mechanical dispersion and not mineralization.

Despite problems associated with transport of metal values into stream and subsequent redistribution, the relationship between sediment geochemistry, geology and mineralization appear to be relatively direct (Hoffman and Fletcher, 1976). The geochemical maps presented (Fig. 3 to 8) are evaluation of regional geochemical stream sediment pattern of heavy metals. The trace element content of stream sediment in the study area reflects major geological units.

Table 3. Geochemical contrast (t-values) between enhanced concentration and background for trace elements in stream sediments

Element	Log Mean		Log Std. Dev.		Variance		Sp	Contrast
	A	B	A	B	A	B		T
Zn	2.06	1.60	0.70	1.68	0.490	2.822	1.661	0.5
Cu	1.40	0.92	0.00	0.81	0.000	0.656	0.806	0.8
Pb	1.16	0.54	0.32	0.48	0.102	0.230	0.472	3.4
Ta	0.16	-0.35	0.00	-0.59	0.000	0.350	0.350	1.5
U	0.63	-0.80	-0.72	-1.16	0.518	1.346	0.157	1.7

Sp = pooled standard deviation

A = above threshold

B = below threshold

Tin was not computed for because of not having any value above its threshold.

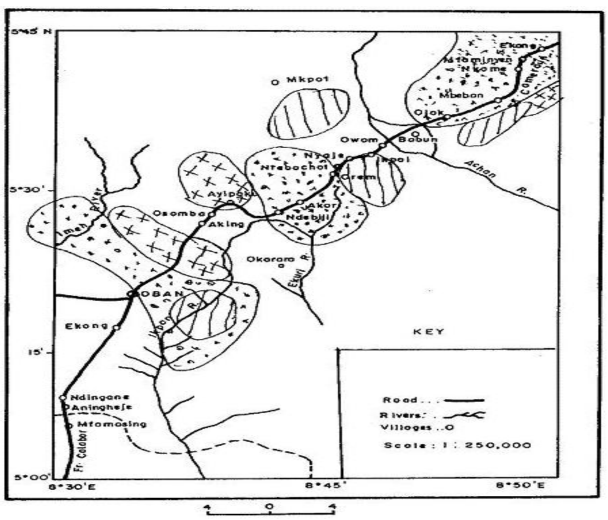

Fig. 3. Distribution of zinc in stream sediments, eastern Oban massif.

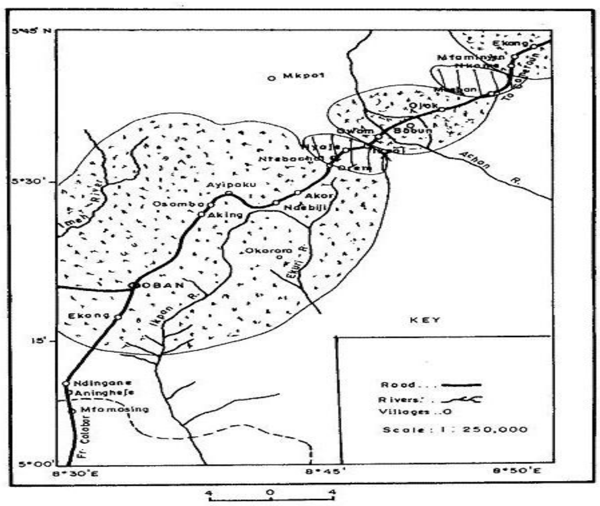

Fig. 4. Distribution of copper in stream sediments, eastern Oban massif

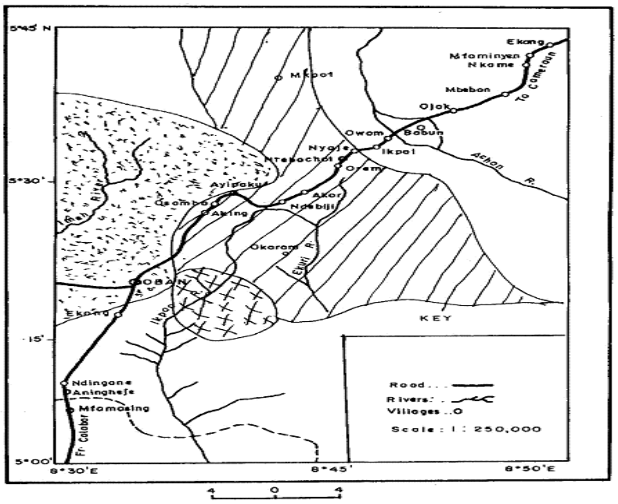

Fig. 5. Distribution of lead in stream sediments, eastern Oban massif

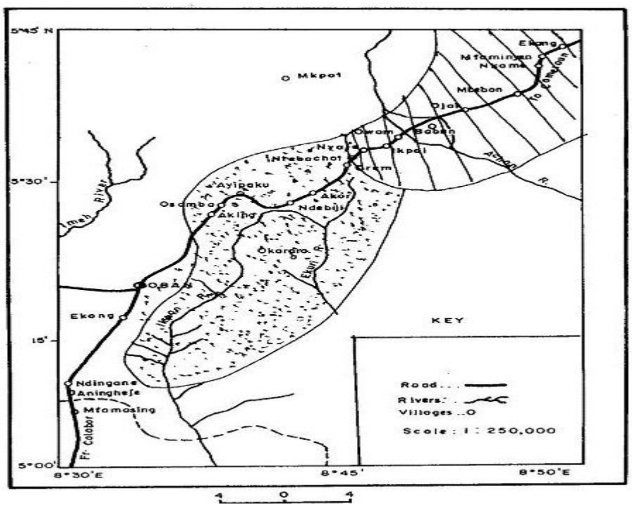

Fig. 6. Distribution of Tin in Stream Sediments, Eastern Oban Massif.

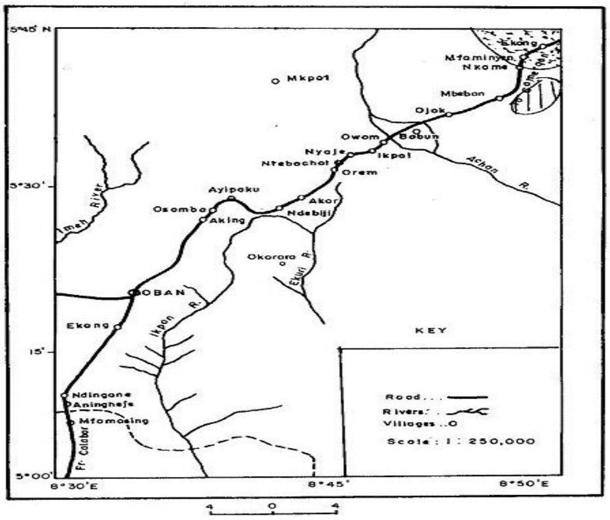

Fig. 7. Distribution of Tantalum in Stream Sediments, Eastern Oban Massif.

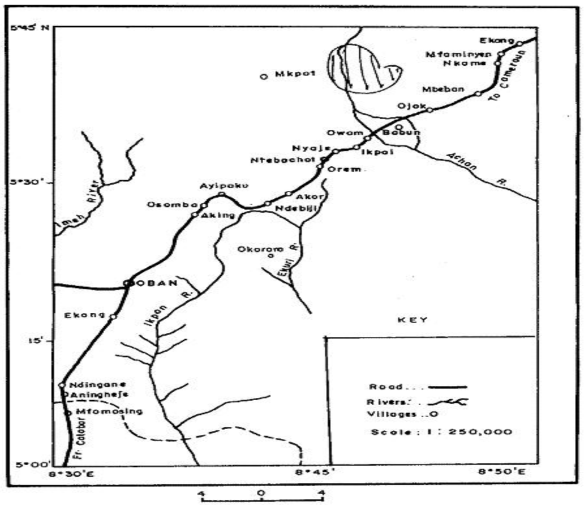

Fig. 8. Distribution of uranium in stream sediments, eastern Oban massif.

Zinc values in excess of 102 ppm were obtained where intrusive rocks like charnockite, syenite and quartz vein were found (fig. 1). The concentration of 72-102 ppm were obtained in areas underlain by amphibolite and granite gneiss. Work on the mineral composition of these rocks does not reflect the presence of accessory minerals like sphalerite, chalcopyrite, molybdenite, galena (Ekwere and Ekwueme, 1991). This may account for the low value of Zn obtained. Copper values above 22ppm were found where charnockite intrude migmatitic gneiss and where syenite intrude granite gneiss. A lower value of 12-22 ppm was obtained in areas underlain by amphibolite and biotite-hornblend gneiss and also where intrusive granite and pegmatite occur. Geochemically, high copper values are associated with granite and amphibolites and Cu-Zn mineralization is common where metamorphic complex have been intruded by granite. The regional patter of Cu coincide with that of Zn as expected. The concentrations of these metals are low for mineralization and may suggest the absence of accessory minerals like cordierite, staurolite, andalusite and tourmaline in the host rocks.

Lead concentration of 3-6ppm were generally found in area where acid volcanic rocks intrude migmatitic gneiss. Values less than these were found in areas underlain by granite gneiss. Tin values of 4-6ppm were found where syenite and charnockite intrude granite gneiss while a concentration of 2-4ppm were obtained where dolerite and amphibolite intrude migmatitic gneiss. The Ta concentrations were very low with only 1.44ppm obtained in granite gneiss environment. This rock had been reported to be depleted in accessory minerals like sphene, Zircon and apalite (Ekwueme and Ekwere, 1991). This support the low concentration of U obtained generally. However, the highest U content of 5ppm observed in the stream sediments in this area may be due to mechanical dispersion. The spatial distribution maps correlate the regional patterns of metals with the regional lithology and leads to a better understanding of the metalogeny of the area. The igneous intrusion of metamorphic rocks did not favour trace element mobilization and mineralization in the area. Thus, the area is depleted of high concentration of trace element as reflected in this study.

CONCLUSION

The geochemical data obtained in this study demonstrate that stream sediments from eastern Oban Massif are characterized by low concentrations of Pb, Zn, Cu, Sn, Ta and U. These elements are uniformly distributed. Geo-statistical analysis indicate lithology as the only factor influencing the distribution of elements in the stream sediments. The element distribution pattern implies that the rocks of eastern Oban do not contain concentration of the elements that can constitute mineralization. This is consistent with the observation that mineralization in rocks are characterized by considerable variation in the trace elements concentrations of stream sediments.

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REFERENCES

Azmatullah, M. and Ekwere, S. J. (1984). Heavy metal distribution in sediments from Cross River Estuary, South Eastern Nigeria. Nig. *Jour. Min. Geol.* 21 (1 and 2): 165-169.

Chung, Y. and Chang, W. C. (1996). Uranium and thorium isotopes in marine sediments of North Eastern Taiwan. *Marine Geol.* 133: 89-102.

Ekwere, S. J and Ekwueme, B. N. (1991) Geochemistry of Precambrian gneisses in the eastern part of Oban Massif, South eastern Nigeria. *Geologie en Mijnbouw* 70: 105-114.

Ekwere, S. J., Akpan, E. B. and Ntekim, E. E. U. (1992) Geochemical studies of sediments in Qua Iboe Estuary and Associated Creeks, South Eastern Nigeria. *Trop. Jour. Appl. Sci.* 2:90-94.

Ekwueme, B. N and Ekwere, S. J. (1989). The geology of the eastern section of Oban Massif, South-Eastern Nigeria. jour. min. geol. 25(1 and 2): 317-329.

Hoffman, S. J and Fletcher, W. K. (1976). Reconnaissance geochemistry of the Nechako Plateau, British Columbia, using lake sediment. *Jour. Geochem. Explor.* 5: 101-114.

Ntekim, E. E. U., Ekwere, S. J and Ukpong, E. E. (1993). Heavy metal distribution in sediments from Calabar River, South eastern Nigeria *Environ. Geol.* 21:237-241.

Ntekim, E. E. U., Ekwere, S. J. and Okon, G. A. (1992). Trace metal distribution in the sediments of the Bight of Bonny, South Eastern Nigeria. *Trop. Jour. Appl.* Sci. 2:8-13.

Ojo, O. M. (1984). Pre-Turonian structural control of basement Mineralization in Middle Gongola Basin. *Jour. Min. Geol.* 21 (1 and 2): 13-17.

Okonny, T. P. (1984). Tectonic analysis of Oban Massif Area using radar imagery *Jour. Min. Geol.* 21 (1 and 2): 157-163.

Olade, M. A., Van De Kraats, A. H. and Ukpong, E. E. (1979). Effects of environmental parameters on metal dispersion patterns in stream sediment from lead-zinc belt, Benue Trough, Nigeria: Using Factor Analysis. *Geologic En Mijn bouw.* 58(3): 341-351.

Raeburn, C. (1927). The tin stone of the Calabar district. *Geol. Surv. Nigeria Bull*. 11:72-88.

Rahman, A. M. S., Ekwere, S. J., Azmatullah, M. A. and Ukpong, E. E. (1988). Petrology and geochemistry of granitic intrusive rocks from the western part of the Oban Massif, South Eastern Nigeria. *Jour. Afri. Earth Sci.* 7(1): 149-157.

Rahman, A. M. S., Ukpong, E. E. and Azmatullah, M. (1981). Geology of parts of the Oban Massif, Southeastern Nigeria. *Jour. Min. Geol.* 18(1): 60-65.

Soliman, M. M. (1981). Geochemical surveys for Sn, Nb, Cu and Au-mineralization, Muelha-Dungash area, Southeastern Desert, Egypt. *Geol. Mag.* 118(5): 545-549.

Ukpong, E. E. (1981) Total and partial extractable metals in anomalous and background stream sediment samples from lead-zinc belt of Benue Trough, Nigeria: a Comparative analysis of extraction techniques. *Jour. Min. Geol.* 18(1): 209-215.