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Mineralization, geochemical signatures, and provenance of stream sediments on the Jos Plateau, Northcentral Nigeria

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Abstract

This study aimed at determination of mineralization, geochemical signatures and provenance of stream sediments on the Jos Plateau, northcentral Nigeria. Ten (10) stream sediments samples collected were air-dried and subjected to X-Ray Fluorescence analysis. The SiO₂ value of 49.79 to 77.03 wt%, Fe₂O₃ value of 1.30 to 28.84 wt%, Al₂O₃ value of 5.27 to 18.25 wt%, CaO value of 0.22 to 1.88 wt%, MgO value of 0.12 to 0.92 wt%, K₂O value of 0.44 to 2.00 wt% and Na₂O value of 0.02 to 0.65 wt%. The low values of CaO (0.22-1.88 wt %) and Na₂O (0.02-0.65 wt %) could be associated with the destruction of plagioclase feldspar while low K₂O composition (0.44-2.00 wt%) could be associated with the destruction of K-feldspar during weathering. The concentration of MnO $(0.06-0.12 \text{ wt%)}$ indicates manganite enrichment, the high TiO₂ value $(0.63-4.25 \text{ wt%)}$ shows rutile enrichment while ZrO_2 value (0.48-18.48 wt%) indicates zircon mineralization from the underlying lithologies. The high values of pathfinder elements (Y, Zn and Nb) could be attributed to the presence of Older and Younger Granites at the upstream of the study area. Samples 4, 5, 8 and 9 have Thorium (Th) concentrations >15 ppm threshold which point to areas favorable for Th mineralization. Enrichment Factor (EF) ranges from 3.03 to 42.42 indicating moderate, significant, very high enrichment and extremely high enrichment. The Contamination Factor (CF) of 1.27 to 201.03 indicates moderate and very high contamination possibly from geogenic sources. The provenance of stream sediments is associated with felsic and mafic sources.

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1. Introduction

Stream sediment materials are derived through the process of weathering of underlying rocks and transported along the drainage basin. Sediments represent the geochemical compositions of materials from the upstream drainage basin [\[1\]](#page-8-0) and mineralogical compositions of bedrock [\[2\]](#page-8-1). Geochemical studies based on the chemical analysis of active stream sediments are an effective tool with several applications [\[3\]](#page-8-2).

Major geochemical variations are controlled by source geology and provenance, as well as chemical weathering and winnowing processes, more subtle variations are a result of land use and contamination from anthropogenic activity [\[2\]](#page-8-1). Heavy metals are natural constituents of the earth's crust, but human activities have drastically altered their geochemical cycles [\[4\]](#page-8-3) and heavy metals are transported via erosion into streams and rivers [\[5\]](#page-8-4).

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Lapworth *et al*. [\[6\]](#page-8-5) provides an overview of regional geochemical mapping using stream sediments from central and south-western Nigeria in which major geochemical variations were controlled by geology, provenance, weathering and anthropogenic activities. The elemental compositions of vegetables grown along the bank of the river Delimi at village hostel, University of Jos was reported by Odewumi *et al*. [\[7\]](#page-8-6). The source, contamination assessment and risk evaluation of heavy metals in the stream sediments in Ibadan SW, Nigeria was reported by Okonkwo *et al*. [\[8\]](#page-8-7).

Several authors have used major element discrimination diagrams to discriminate the tectonic settings of stream sediments [\[9\]](#page-8-8). The indicator mineral chemistry has increased the contribution of stream sediments in understanding the Geology and mineral Prospectivity [\[10\]](#page-8-9). The present study aimed at determination of mineralization, geochemical signatures and provenance of stream sediments on Jos Plateau, northcentral Nigeria.

Lar *et al.* [\[11\]](#page-8-10) reported on heavy metals in the urban soils, stream sediments and vegetables in Jos metropolis with implications on children's health. Several researchers have also reported on heavy metals contaminations of soils in Jos [\[12,](#page-8-11) [13\]](#page-8-12). However, the researches on mineralization in Jos were centred on tin mineralization for over five decades and the focus was on cassiterite, sulphide mineralization and tin mining activities.

Ogunyele $\&$ Akingboye [\[14\]](#page-8-13) described the tin mineralization in Jos and suggested to be associated with late-stage peraluminous granites both as disseminations in veins and greisens. The zeolite mineralization within the basalts of Tim-Kwalla, Jos Plateau was reported by Mangdong *et al*. [\[15\]](#page-8-14) while Davou *et al*. [\[16\]](#page-8-15) reported on subsurface cavity produced by tin mining activities in Jos but less attention was given to other mineralization and enrichment in stream sediments on the Jos Plateau. Therefore, there is need to determine the mineralization, contamination, enrichment and provenance of stream sediments using major and trace geochemical compositions

2. Geology of the study area

An outline of Geology of the area is similar to that of Jos Plateau and Geological map of the study area is shown in Figure [1.](#page-1-0) The rock units constitute part of the Basement Complex in northcentral Nigeria and include: migmatite and aplopegmatitic granite gneisses that are Precambrian to Lower Paleozoic in age while hornblende biotite porphyry is Jurassic in age of Younger Granite Complexes. Basic dyke of younger age have been identified across-cutting the Migmatite and Aplopegmatitic granite gneiss (Figure [1\)](#page-1-0). The detailed geology of part of Jos-Plateau, northcentral Nigeria was reported by Odewumi *et al*. [\[17\]](#page-8-16).

3. Materials and methods

3.1. Sample collection

The study area is located on Jos Plateau, northcentral Nigeria on latitudes 9.968° to 9.890° N and longitudes 8.884° to 8.900° E (Figure [2\)](#page-1-1). A Global Positioning System (GPS)

Figure 1: Geological map of the study area [\[18\]](#page-8-17).

Figure 2: Location map of the study area with sampling points (after Odewumi *et al*. [\[17\]](#page-8-16).

GARMIN 78SC Model was used to appropriately locate the sampling points on the topographical map, the longitude and latitude readings were recorded in the field note. The stream sediments were taken through systematic sampling of active streams along the drainage system in the study area. Ten (10) stream sediments were collected at the centre of the stream courses to obtain more recent and active stream sediments using the natural drainage system at an interval of about 500 m (Figure [2\)](#page-1-1).

The stream sediments were collected at depth of about 30cm and labeled with appropriate sample number while the top 20-25 cm of sediment is discarded to avoid spurious high

contents of Fe and Mn in oxide coatings. Hand trowels were utilized to collect at each sampling point where the flow velocity was low. The organic materials, winnowed sediments, deposits of well-sorted gravel and sources of contamination from roads and habitation were strictly avoided.

3.2. Geochemical analysis

Ten (10) stream sediments samples were air-dried and subjected to X-Ray Fluorescence (XRF) for major elements and trace elements compositions of stream sediments at Nigerian Geological Survey Agency Kaduna with sample preparations, procedures and analyses [\[19\]](#page-8-18). The values of heavy metals from the stream sediments were compared with standards from regulatory bodies such as background reference value of UNEP [\[20\]](#page-8-19) and permissible limit of WHO [\[21\]](#page-8-20). The trace elements compositions were compared with the background values of Clarke [\[22\]](#page-8-21).

3.3. Statistical analysis

The results of major and trace elements compositions of stream sediments obtained from XRF analysis were subjected to ANOVA analysis using SPSS software. The spatial distribution diagrams were plotted using ArcGIS software

3.4. Single-element pollution indices

Single pollution indices are employed in the assessment of metal contamination because they show how concentrated an element is in a certain location in comparison to a background. As an example:

Contamination factor (CF) is a quantitative evaluation of the contaminant's level and sources. The following is how CF is assessed: $CF = Cm_{Sample}/Cm_{Background}$

where $\text{Cm}_{Sample} = \text{concentration of a given metal in the sed-}$ iment, $Cm_{\text{Background}} = \text{Background}$ value of the metal of interest at a site [\[23,](#page-8-22) [24\]](#page-8-23). The following four classes were established. The contamination factor (CF) with level of contamination was classified by Hakanson $[25]$ into four (4) groups namely: low contamination (CF < 1), moderate contamination ($1 \leq CF < 3$), considerable contamination ($3 \leq CF < 6$) and very high contamination ($CF > 6$).

Enrichment Factors (EF) are useful indicator of contamination status and level in the research environment [\[4\]](#page-8-3). As seen below, the EF computation compares each value to a certain (control sample) background level in order to identify possible sources:

$$
EF = (Me/Fe)_{\text{Sample}} / (Me/Fe)_{\text{background}},
$$
\n(1)

where Me/Fe)sample = the metal to Fe ratio in the sample under study; (Me/Fe)background is the natural background value of metal to Fe ratio. We used metal background values from roughly 4.5 kilometers away for this study. Iron was chosen as a normalization factor since its natural sources (1.5 percent) have a significant influence on its input [\[26\]](#page-8-25).

The Enrichment Factor (EF) was classified according to Mmolawa et al. [\[27\]](#page-9-0) into five (5) categories namely: deficiency to minimal enrichment ($EF < 2$), moderate enrichment ($2 \le EF$ $<$ 5), significant enrichment (5 \leq EF $<$ 20), very high enrichment (20 \leq EF $<$ 40) and extremely high enrichment (EF \geq 40).

4. Results

The major oxides composition of stream sediments is presented in Table [1](#page-3-0) and trace elements composition of stream sediments is presented in Table [2.](#page-3-1) The Clarke values [\[22\]](#page-8-21) for the indicator elements in stream sediments and range of trace elements values in present study is presented in Table 3 . The TiO₂ (wt%) vs Al₂O₃ (wt%) binary plot of stream sediments [\[28\]](#page-9-1) is shown in Figure [3.](#page-5-0) Table [4](#page-5-1) shows the minimum, maximum, mean, the metal to Fe ratio in the sample under study (Me/Fe) sample, the metal to Fe ratio in the natural background value (Me/Fe) background, the background value [\[20\]](#page-8-19) and WHO standards [\[21\]](#page-8-20).

The SiO₂ value ranges from 49.79 to 77.03 wt%, $Fe₂O₃$ value ranges from 1.30 to 28.84 wt%, Al_2O_3 value ranges from 5.27 to 18.25 wt%, CaO value varies from 0.22 to 1.88 wt%, MgO value ranges from 0.12 to 0.92 wt%, K_2O value ranges from 0.44 to 2.00 wt%, $Na₂O$ value ranges from 0.02 to 0.65 wt%, TiO₂ value ranges from 0.63 to 4.25 wt%, MnO value ranges from 0.06 to 0.12 wt% and $ZrO₂$ value varies from 0.48 to 18.48 wt% (Table [1\)](#page-3-0). Statistically, the percentage compositions of stream sediments analyzed ranges from 77.02 wt% of SiO_2 to 0.02 wt% of Na₂O in location 2 and the difference was significant ($p < 0.05$). The Coefficient of Variability (CV) ranges from 0.57 to 1.80 %.

V varies from 230.00 to 754.00 ppm, Cr (800.00 - 2700.00 ppm), Cu (220.00 - 650.00 ppm), Sr (5.00 - 800.00 ppm), Ba (3.25 - 67.00 ppm), Zn (233.00 - 1100.00 ppm), Ga (17.55 - 86.00 ppm), Y (80 - 800 ppm), Mo (824.00 - 5900.00 ppm), Ta (22.50 - 885.00 ppm), W (9.80 - 40.00 ppm), Hf (2.00 - 9000.00 ppm), Th (1.77 - 44.60 ppm) and Sn (199.00 - 433.50 ppm) among others (Table [2\)](#page-3-1).

Trace element composition from the analysis of variance was higher (9000 ppm) for Hf as present in sample 4 and lowest (0.001 ppm) in Ce, Eu, Nd, Rb and Th across all stream sediments. Generally, sample 5 had abundance composition of trace element compared to other stream sediments with a mean composition of 547 ppm. Meanwhile, Mo had the highest abundance with a mean composition of 2596.82 ppm as evaluated across all the stream sediments.

5. Discussion

The low values of CaO and $Na₂O$ may be associated with the destruction of plagioclase feldspar during weathering while low K_2O composition could be associated with the destruction of K-feldspar during weathering $[29]$. The high values of $ZrO₂$ (0.48 - 18.48 wt%) and Hf (2.00 - 9000.00 ppm) indicate stream sediments that lack of clayness [\[30\]](#page-9-3). The high concentration of MnO (0.06 - 0.12 wt%) in the stream sediments indicates possibility of manganite enrichment in the underlying lithologies. The high TiO₂ value (0.63 - 4.25 wt%) shows the possibility of rutile enrichment in underlying lithologies while $ZrO₂$ value $(0.48 - 18.48 \text{ wt\%)}$ indicates zircon enrichment in the underlying lithologies [\[31,](#page-9-4) [32\]](#page-9-5).

The mineralizations in the stream sediments samples were derived through the weathering of minerals hosted in the under-

Table 1: Major oxide compositions (wt%) of stream sediments.

| Major Oxide | | 2 | 3 | $\overline{4}$ | 5 | 6 | 7 | 8 | 9 | 10 |
|--------------------------------|--------|-------------------|-------------------|-------------------|--------|-------------------|--------|----------|-------------------|-------------------|
| SiO ₂ | 49.79a | 77.02a | 71.80a | 59.32a | 73.04a | 65.19a | 70.90a | 62.56a | 70.99a | 50.37a |
| Fe ₂ O ₃ | 16.64c | 1.30e | 3.47c | 2.64e | 2.18e | 16.42c | 4.00d | 16.00b | 3.34c | 28.84b |
| Al_2O_3 | 18.25b | 8.78b | 14.00b | 15.44c | 13.00b | 17.19b | 8.87b | 6.89c | 6.53 _b | 5.27c |
| CaO | 0.25h | 0.22h | 0.40 _h | 1.00 _g | 1.44g | 0.66f | 1.88f | 0.97f | 1.56f | 0.60 _g |
| MgO | 0.44g | 0.31 _g | 0.37i | 0.12i | 0.56h | 0.81d | 0.92g | 0.72g | 0.87 _g | 0.37i |
| K_2O | 1.02e | 0.56f | 2.00e | 1.23f | 1.80f | 0.67e | 0.54h | 0.44h | 0.56h | 2.00 _d |
| Na ₂ O | 0.04i | 0.02i | 0.61 _g | 0.43h | 0.55i | 0.04 j | 0.11j | 0.20i | 0.08j | 0.65f |
| TiO ₂ | 1.15d | 2.18d | 1.71f | 4.25d | 2.60d | 0.63 _g | 2.53e | 1.32d | 1.80e | 1.24e |
| MnO | 0.11i | 0.06i | 0.06 j | 0.07 j | 0.09j | 0.11i | 0.12i | 0.09 i | 0.10i | 0.10k |
| P_2O_5 | ND | ND | ND | ND | ND | ND | ND | ND | ND | 0.36 i |
| ZrO ₂ | 0.91f | 5.16c | 3.27d | 18.48b | 5.41c | 0.12h | 6.20c | 1.08e | 2.75d | 0.48h |
| LSD _(0.05) | 0.06 | 0.03 | 0.13 | 0.04 | 0.01 | 0.01 | 0.01 | 0.08 | 0.22 | 0.04 |
| CV(%) | 0.58 | 0.97 | 1.63 | 0.58 | 0.57 | 0.32 | 1.80 | 0.70 | 0.65 | 1.68 |

Note: Means followed by the same letter (s) within a column are not statistically significant at 5% level of Probability; ND-Not Detected; LSD- Least Significant Difference; CV- Coefficient of Variability.

Table 2: Trace elements compositions (ppm) of stream sediments.

| Trace | Stream sediments | | | | | | | | | |
|-------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|----------------------------|-----------------------------|
| elements | | $\overline{2}$ | $\overline{3}$ | $\overline{4}$ | $\overline{5}$ | 6 | 7 | $\overline{8}$ | $\overline{9}$ | 10 |
| $\overline{\mathbf{v}}$ | 700.60 ^{Imnopq} | 564.00 ^{Imnopq} | 366.00^{nopq} | 754.00 Imnopq | 298.00^{opq} | 230.00 ^{opq} | 330.00^{nopq} | 323.00 ^{opq} | 334.00^{10} | 300.00^{opq} |
| Cr | 2000.00 ^{fghij} | 800.00 ^{klmnopq} | 1000.00 jklmnop | 1011.00 jklmnop | 1500.00 ^{ghijkl} | 1500.00 ^{ghijkl} | 1400.0 hijklm | 2050.00 ^{fghi} | 2700.00^{def} | 1800.00 ^{fghijk} |
| Cu | 500.50 ^{Imnopq} | 420.00^{nopq} | 300.50 ^{opq} | 350.00^{nopq} | 650.00 ^{Imnopq} | 405.00^{nopq} | 220.00^{opq} | 400.00^{nopq} | 420.00^{nopq} | 305.00 ^{opq} |
| Sr | 5.009 | 800.00 ^{klmnopq} | 366.00 | 55.00 ^{pq} | 233.00 ^{opq} | 12.00 ^q | 500.00 ^{Imnopq} | 54.00 ^{pq} | 48.509 | 510.00 ^{Imnopq} |
| Ba | 16.90 ^q | 9.50 ^q | 4.55 9 | 6.00 ^q | 12.55 ^q | 20.55 ^q | 4.55 ^q | 3.25 ^q | 67.00 ^{pq} | 32.50 ^q |
| Zn | 501.00 ^{Imnopq} | 233.00^{opq} | 600.00 ^{Imnopq} | 600.00 ^{Imnopq} | 700.00 ^{Imnopq} | 1100.00 ^{jklmno} | 500.00 ^{Imnopq} | 540.00 ^{Imnopq} | 1000.0 jklmnop | 605.00 ^{Imnopq} |
| Ce | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q |
| Pb | 2200.00fghi | 30.86 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 2500.00 defg | 0.001 ^q | 0.001 ^q | 0.001 ^q | 1300.0 ijklmn |
| Bi | 12.00 ^q | 220.00 ^{opq} | 200.00 ^{opq} | 205.50^{opq} | 250.00^{opq} | 0.001 ^q | 270.00 ^{opq} | 0.001 ^q | 0.001 ^q | 32.55 ^q |
| Ga | 35.50 ^q | 86.00 ^{pq} | 49.00 9 | 17.55 ^q | 22.50 ^q | 70.00 ^{pq} | 65.50 ^{pq} | 22.85 9 | 34.00 ^q | 40.00 ^q |
| As | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.006 ^q | 0.001 ^q | 0.02 ^q | 0.001 ^q | 0.065 ^q |
| Nd | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q |
| Y | 100.00^{pq} | 170.00^{opq} | 150.00 ^{pq} | 158.85 ^{pq} | 200.50^{opq} | 120.00 ^{pq} | 190.00^{opq} | 80.009 | 240.00 ^{opq} | 800.00 ^{klmnopq} |
| Ni | 0.001 ^q | 0.001 ^q | 0.001 ^q | 300.00 ^{opq} | 200.00^{opq} | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q |
| Rb | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q |
| Mo | 1100.00 ^{jklmno} | 5900.00 ^b | 2100.00 ^{fghi} | 2230.00efghi | 3400.00 ^{cd} | 2500.00^{defg} | 4200.0° | 1300.0 ijklmn | 2500.0 defg | 824.00 ^{klmnopq} |
| Tl | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.0019 | 0.001 ^q | 0.001 ^q | 0.001 ^q |
| Cd | 0.06 ^q | 0.001 ^q | 0.0859 | 0.001 ^q | 0.0559 | 0.001 ^q | 0.556 ^q | 0.001 ^q | 0.08 ^q | 0.055 ^q |
| Ru | 0.81 ^q | 1.59 ^q | 1.60 ^q | 1.09 ^q | 1.41 ^q | 1.43 ^q | 1.62 ^q | 1.02 ^q | 1.19 ^q | 0.71 ^q |
| Eu | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q |
| Re | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.001 ^q |
| Nb | 700.00 ^{Imnopq} | 1800.00 ^{fghijk} | 1100.00 jklmno | 2800.00^{def} | 1800.00 ^{fghijk} | 800.80 ^{klmnopq} | 2400.00defgh | 54.00 ^{pq} | 2300.00 ^{efghi} | 400.00^{nopq} |
| Ta | 580.00 ^{lmnopq} | 452.00 ^{mnopq} | 788.00 ^{klmnopq} | 685.00 lmnopq | 885.00 ^{klmnopq} | 435.00 ^{nopq} | 452.00 ^{mnopq} | 22.50 ^q | 588.90 ^{lmnopq} | 340.00^{nopq} |
| W | 12.00 ^q | 9.80 ^q | 40.00 ^q | 33.50 ^q | 38.00 ^q | 20.50 ^q | 31.00 ^q | 40.00 ^q | 22.55 ^q | 13.50 ^q |
| Hf | 3261.00 ^{cde} | 900.00 ^{klmnopq} | 600.50 ^{Imnopq} | 9000.00 ^a | 8700.00 ^a | 38.80 ^q | 22.54 ^q | 2.00 ^q | 588.00 ^{lmnopq} | 12.00 ^q |
| Yb | 0.879 | 0.0019 | 0.089 | 0.0549 | 0.0019 | 0.0019 | 0.0019 | 0.0019 | 0.0229 | 0.0019 |
| Se | 0.0019 | 0.0019 | 0.0559 | 0.0019 | 0.0019 | 0.089 | 0.0019 | 0.0629 | 0.0019 | 0.0019 |
| U | 0.001 ^q | 0.001 ^q | 0.001 ^q | 0.40 ^q | 2.55 ^q | 0.329 | 1.02 ^q | 0.001 ^q | 0.0019 | 0.0019 |
| Th | 2.889 | 2.709 | 12.009 | 44.609 | 43.009 | 1.779 | 3.009 | 22.509 | 32.00 ^q | 0.0019 |
| Sb | 0.559 | 0.0019 | 0.0019 | 0.769 | 0.0019 | 0.0019 | 0.5509 | 0.0019 | 0.0019 | 0.0759 |
| Ge | 1.059 | 4.00 ^q | 3.559 | 6.229 | 7.709 | 52.00 ^{pq} | 11.00 ^q | 30.50 ^q | 28.50 ^q | 12.009 |
| Sn | 355.00^{nopq} | 275.00^{opq} | 857.00 ^{klmnopq} | 199.00^{opq} | 221.00^{opq} | 433.50^{nopq} | 275.00^{opq} | 654.00 ^{Imnopq} | 231.00^{opq} | 422.00^{nopq} |
| Pd | 0.429 | 0.489 | 0.789 | 0.559 | 0.889 | 1.10 ^q | 0.529 | 0.0019 | 1.399 | 0.259 |
| La | 0.0019 | 0.001 | 0.0019 | 0.0019 | 0.0059 | 0.0079 | 0.0019 | 0.0019 | 0.0019 | 0.0059 |
| Co | 20.009 | 7.50 ^q | 0.0019 | 0.0019 | 0.0019 | 120.00 ^{pq} | 0.0019 | 17.00 ^q | 0.5669 | 310.00 ^{opq} |
| LSD _(0.05) | 863 | | | | | | | | | |
| SE_{\pm} | 363.72 | | | | | | | | | |
| $CV(\%)$ | 109.82 | | | | | | | | | |

Means that follow the same letter (s) within a column are not statistically significant at 5% level of probability.

CV: Coefficient of Variability; SE± : Standard Error of Means; LSD (0.05): Least Significant Difference at 5% level of probability.

lying granitic rocks upstream of the study area that have been dispersed along the stream. This is similar to the report of Lapworth *et al*. [\[6\]](#page-8-5) on geochemical mapping using stream sediments in west-central Nigeria where high stream sediment Zr concentrations (mean >0.2%), from proximal zircons derived from weathering of basement rocks.

Table 3: Clarke [\[22\]](#page-8-21) values for the indicator elements in stream sediments and range of elements' values in present study.

| | Range of elements |
|-----|--------------------|
| 200 | 888.00-136,808.00 |
| 10 | 54.00 -2800.00 |
| 25 | $233.00 - 1100.00$ |
| 18 | $80 - 800$ ppm |
| | |

The mineralizations in the study area are similar to the report of Ayodele [\[5\]](#page-8-4) on Stream Sediment of Ara, Epe and Ijero Area, South Western Nigeria that was mineralized in phosphate minerals such as monazite, turquoise, or apatite; ferruginous minerals which could be hematite and manganese-bearing minerals such as manganite or mica rich manganese. These mineralizations in Ara, Epe and Ijero Area are hosted by the pegmatites that intrude the country rocks in the northwestern part of the area.

The Fe₂O_{3T} value ranges from 1.30 to 28.84 wt% (Table [1\)](#page-3-0). Some stream sediments samples like sample 1 (16.64 wt %), sample 6 (16.42 wt%), sample 8 (16.00 wt%) and sample 10 (28.84 wt%) have Fe₂O_{3T} > 15 % and can be classified as Fe-rich sediments which could have been mineralized by the underlying Fe-rich mineralized rocks and veins. Low grade ore is a term applied to iron-rich rocks with cut-off grades in the range of 15-25% Fe₂O_{3T}. According to Levinson [\[33\]](#page-9-6), hematite mineralization can be associated with circulating hydrothermal fluids during late stages of cooling of molten magma. This is similar to the report of Ayodele [\[5\]](#page-8-4) on stream sediments from Ara, Epe and Ijero Area, South Western Nigeria where ferruginous minerals were reported.

The Sn value ranges from 199.00 to 654.00 ppm and could be linked to cassiterite mineralization possibly from Younger Granitic rocks upstream of the study area. The high concentrations of pathfinder elements such as Y (80.00 - 800.00 ppm), Zn (233.00 -1100.00ppm) and Nb (54.00 -2800.00 ppm) were obtained from the study area (Table [2\)](#page-3-1) and could be attributed to the presence of Older and Younger granitic rock at the upstream of the study area. This is similar to the report of Mira *et al*. [\[2\]](#page-8-1) on Stream Sediments Geochemical Exploration ofWadi El Reddah area, Northeastern Desert, Egypt where high contents of pathfinder elements (REE, Y, Zn, Nb and As) were discovered and attributed to the presence of alkali feldspar granite at Gabal Gattar area upstream of Wadi El Reddah in Egypt.

The Th value ranges from ≤ 0.001 to 44.60 ppm (Table [2\)](#page-3-1) and Samples 4, 5, 8 and 9 have Th values greater than threshold value of 15 ppm. This point to some of the areas favorable for Th mineralization and can be linked to remobilization and dispersion of Thorite within the stream sediments while U value ranges from <0.001 to 2.55 ppm (Table [2\)](#page-3-1) indicating lack of U mineralization in the area $[22]$. This is in contrast to the report of Mira *et al*. [\[2\]](#page-8-1) on Stream Sediments from Egypt where >5 ppm U and >15 ppm Th as threshold were reported and pointed to areas favorable for U mineralization that was linked to deformation-induced radioelement remobilization and subsequent precipitation in veins forms.

Table [3](#page-4-0) shows anomalous concentrations of pathfinder elements compared with the published background values of [\[20\]](#page-8-19). Higher value of Zr $(0.48 - 18.48 \text{ wt\%)}$ in the stream sediments of the study area than the Zr value for indicator element of 200ppm [\[22\]](#page-8-21) suggests zircon mineralization. Higher values of Y (80 - 800 ppm) in the stream sediments of the study area than the Y indicator element value of 18 ppm [\[22\]](#page-8-21) point to xenotime mineralization in the area while higher values of Nb (54.00 - 2800.00ppm) in the stream sediment than Nb indicator value of 10ppm [\[22\]](#page-8-21) point to columbite mineralization (Table [3\)](#page-4-0). The stream sediments have high values of Ta ranging from 22.50 to 885.00 ppm (Table [2\)](#page-3-1) which point to enrichment of tantalite in the study area.

The study area is enriched in resisting minerals such as zircon, rutile, xenotime, thorite, cassiterite, and columbitetantalite that could be attributed to the underlying mineralization hosted within the Older and Younger Granitic rocks in the area that were dispersed along the drainage basin. This is similar to the report of Mira *et al*. [\[2\]](#page-8-1) on Stream Sediments from Egypt where zircon, xenotime, thorite, and columbite-tantalite mineralizations were reported and hosted by alkali feldspar granite

The research of Lapworth *et al*. [\[6\]](#page-8-5) on geochemical mapping of stream sediments in west-central Nigeria identified placer deposits of potential economic importance for Au, REE, Ta, Nb, U and Pt, as well as other primary metal deposits. The values As $(<0.001 - 0.065$ ppm) and Cr $(800 - 2000$ ppm) obtained in the study area (Table [2\)](#page-3-1) were possibly derived from Jurassic Younger Granites of Jos Plateau. This is similar to the report of Lapworth *et al*. [\[6\]](#page-8-5) where higher As (>2 ppm) and Cr (>70 ppm) *we*re associated with Mesozoic and younger coastal stream sediments of west-central Nigeria.

Enrichment Factor (EF) ranges from 3.03 to 42.42, this indicates moderate enrichment ($2 \le EF < 5$), significant enrichment ($5 \le EF < 20$), very high enrichment ($20 \le EF < 40$) and extremely high enrichment ($EF \ge 40$) according to enrichment categories of Mmolawa *et al*. [\[27\]](#page-9-0). The higher average values of Cu (397.10 ppm) than the WHO $[21]$ standard (25 ppm) indicates contamination. Similarly, higher average values of Zn, Ni and Cr than the WHO standards [\[21\]](#page-8-20) attest to contamination in the study area (Table [4\)](#page-5-1). Contamination Factor (CF) ranges from 1.27 to 201.03 which indicate moderate contamination (1 \leq CF < 3) and very high contamination (CF > 6) according to contamination level of Hakanson [\[25\]](#page-8-24). The contamination could be attributed to geogenic sources

The presence and distribution of heavy metals in soils are influenced mainly by the parent material, the chemical and physical soil properties, the metal speciation, and the climatic conditions. The mineral content of the parent material is one of the most important factors for the amount of trace elements in soils, irrespective of classification or the amount of weathering [\[34\]](#page-9-7). This was observed in the present study where heavy metals in the stream sediments were suggested to be derived from geogenic sources.

Anthropogenic sources of contaminations from industrial, mining and domestic activities [\[35,](#page-9-8) [36\]](#page-9-9) could not be ascertained in the study area along the stream sediments since an-

Table 4: Minimum, maximum, mean, the metal to Fe ratio in the sample under study $(Me/Fe)_{(s)}$ the metal to Fe ratio in the natural background value (Me/Fe)_{brd}, Enrichment Factor (EF), Contamination Factor (CF), background value [\[20\]](#page-8-19) and WHO standard [\[21\]](#page-8-20).

| Elements | Min. | Max. | Mean | $\overline{\text{Me}}/\text{Fe}_{(s)}$ | $/Me/Fe$ _(brd) | ER | CF | Background value | WHO |
|-------------|---------|--------|----------|--|---------------------------|-------|--------|------------------|------------|
| Cu | 220.0 | 650.00 | 397.10 | 41.89 | 6.91 | 6.06 | 198.55 | $\overline{2}$ | 25 |
| Pb | < 0.001 | 2500 | 603.09 | 63.61 | 6.9 | 9.09 | 201.03 | 3 | ---- |
| Zn | 233 | 1100 | 637.90 | 67.19 | 3.17 | 21.21 | 91.13 | 7 | 123 |
| Ni | 0.001 | 300 | 50.00 | 5.27 | 1.74 | 3.03 | 50 | | 20 |
| Co | 0.001 | 310 | 47.51 | 5.01 | 0.82 | 6.06 | 23.76 | 2 | $---$ |
| Sr | 5.00 | 800.00 | 258.35 | 27.25 | 3.00 | 9.09 | 86.12 | 3 | |
| V | 230.00 | 754.00 | 419.90 | 44.29 | 1.62 | 27.27 | 46.66 | 9 | ---- |
| Cr | 800 | 2700 | 1,511.10 | 159.40 | 5.26 | 30.30 | 151.11 | 10 | 25 |
| Ba | 3.25 | 67.00 | 17.74 | 1.87 | 0.044 | 42.42 | 1.27 | 14 | |
| Fe $(wt\%)$ | 1.30 | 28.84 | 9.48 | | | | | 0.33 | |

Figure 3: TiO₂ (wt%) vs Al₂O₃ (wt%) binary plot of stream sediments [\[28\]](#page-9-1).

thropogenic sources are usually referred to as "Punctual" contamination with an identified source often close to the contaminated soil [\[37\]](#page-9-10). This is in contrast to the reports of Odewumi *et al*. [\[38\]](#page-9-11) and Momoh *et al*. [\[39\]](#page-9-12) on soils and vegetables from Jos where anthropogenic and/or geogenic sources of contamination were suggested. Okonkwo *et al*. [\[8\]](#page-8-7) reported on stream of Rivers around Olode Area SW, Nigeria where anthropogenic sources of contamination from mining activities which had negative impact on the study area have been indicated.

On the TiO₂ (wt%) versus Al_2O_3 (wt%) binary plot [\[28\]](#page-9-1) as shown in Figure [3](#page-5-0), the stream sediments plot in the basalt, basalt+granite/rhyolite, granite/rhyolite+basalt and granite/rhyolite fields. This indicates that the provenance could be from felsic and mafic sources.

The stream sediments have low percentages of MgO, CaO, K_2O and Na_2O and may be attributed to intense weathering and alteration of K-feldspar, plagioclase feldspar and unstable mafic minerals [\[40,](#page-9-13) [41\]](#page-9-14). The relatively high values of the ratio of K_2O/Na_2O could be attributed to the presence of albitic plagioclase, K-feldspar, mica and illite [\[42\]](#page-9-15) which is a major characteristic of felsic sources. The low value of $Na₂O$ (0.02 to 0.65 wt%) in the stream sediments point to the relatively small amount of Na-rich plagioclase in the protoliths of the stream sediments [\[43\]](#page-9-16).

Figure 4: Spatial distribution plot of $ZrO₂$ (wt%).

Figure 5: Spatial distribution plot of MnO (wt%).

The geochemical signature in stream sediments is strongly

influenced by the geological setting and local lithologies in

Figure 6: Spatial distribution diagram of TiO₂ (wt %).

Figure 7: Spatial distribution diagram of Fe₂O₃ (wt %).

Brazil [\[44\]](#page-9-17). This is similar to the present study where the geochemical signature of stream sediments is influenced by underlying mineralization and lithologies. The positive correlation between Al_2O_3 and Fe₂O₃, MnO, and MgO, indicates multiple sources for sediment and these oxides are associated with clay minerals of Eastern Ghats Mobile Belt in India [\[45\]](#page-9-18). The present findings also show multiples sources of stream sediments on the Jos Plateau which could be attributed to felsic and mafic sources.

The discrimination function diagram suggests a felsic igneous as well as quartzo-sedimentary provenance for stream sediments in India whereas the ratio of Al_2O_3/TiO_2 and concentration of V-Ni-Th suggest a felsic igneous source rock [\[45\]](#page-9-18). Similarly, the relatively high values of the ratio of K_2O/Na_2O obtained in the present study could be attributed to felsic

Figure 8: Spatial distribution diagram of Sn (ppm).

Figure 9: Spatial distribution diagram of Y (ppm).

sources. The low concentrations of MgO (mean 0.03%), Na2O (mean 0.008%), and K_2O (mean 0.04%) were reported from sandstone sediments of the Ilaro formation, Dahomey Basin, Southwestern Nigeria and suggested chemical destruction in an oxidizing environment [\[46\]](#page-9-19). In the present study, the low values of CaO (0.22-1.88 wt %) and Na₂O (0.02-0.65 wt %) could be associated with the destruction of plagioclase feldspar while low K_2O composition (0.44-2.00 wt%) could be associated with the destruction of K-feldspar during weathering

According to Seydi *et al*. [\[47\]](#page-9-20), the stream sediments in East Iran were reported to be favorable for copper and gold mineralization using concentration number. This is in contrast to the present study where stream sediments on the Jos Plateau were found to be favorable for Mn, Zr, Y, Nb, Th, Sn, Ta and

Figure 10: Spatial distribution diagram of Th (ppm).

Figure 11: Spatial distribution diagram of Nb (ppm).

Ti mineralization. Osei *et al*. [\[48\]](#page-9-21) suggested a stronger positive correlation of gold with Iron, Chromium and Vanadium using multivariate analysis of the geochemical data using Pearson product-moment of correlation and indicated gold mineralization in Ghana. The present study also show positive correlation of major oxides as presented in Table [1.](#page-3-0)

The enrichments of heavy metals of sediments in Mexico were identified through the accumulation and indicated that the contamination of Cd and Pb is mainly of anthropogenic origin of stream sediments in Mexico [\[49\]](#page-9-22) while high values of Fe $(>0.4 \text{ wt\%})$, and Mn $(>2000 \text{ ppm})$ were reported by Kelley *et al*. [\[50\]](#page-9-23) on stream-sediment from eastern Alaska, USA and suggested geogenic sources This is in contrast to the cur-

Figure 12: Spatial distribution diagram of Ta (ppm).

rent findings where contamination of heavy metals in the stream sediment was predominantly from geogenic sources

According to Ajaha *et al*. [\[51\]](#page-9-24), the concentration of the metals in the soil of Ebonyl State Nigeria such as Zn (7.28- 11.33), Cu (3.40 - 4.64), Fe (803.04 - 735.47) and Cd (1.14) were within FEPA and FAO/WHO limits. This is in contrast to the present findings where the value of Zn, Cu, Fe and Cd in the stream sediments exceeded the FAO/WHO limits. According to Olutona [\[52\]](#page-9-25), the As and Sr, values were below the background values for typical soil while the present study shows that the values of As and Sr exceeded the background values

The spatial distribution plot of $ZrO₂$ is shown in Figure [4,](#page-5-2) the spatial distribution plot of MnO is shown in Figure [5,](#page-5-3) the spatial distribution plot of $Fe₂O₃$ is shown in Figure [6](#page-6-0) while Figure [7](#page-6-1) shows the spatial distribution diagram of $TiO₂$ which are favorable for zircon, manganite, hematite and rutile mineralizations respectively. The spatial distribution plot of Sn is shown in Figure [8,](#page-6-2) the spatial distribution plot of Y is shown in Figure [9,](#page-6-3) the spatial distribution plot of Th is shown in Figure [10,](#page-7-0) the spatial distribution diagram of Nb is shown in Figure [11](#page-7-1) while Figure [12](#page-7-2) shows the spatial distribution diagram of Ta which are favorable for cassiterite, xenotime, thorite, columbite and tantalite mineralizations, respectively.

6. Conclusion

The stream sediment is enriched in resisting minerals such as zircon, rutile, xenotime, thorite, cassiterite, and columbitetantalite which could be attributed to the mineralization hosted in the underlying rocks. These mineralizations in the stream sediments were derived through the weathering of minerals hosted in the underlying Older and Younger Granitic rocks upstream of the study area which have been dispersed along the

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drainage basin. The provenance of stream sediments from the study area could be associated with felsic and mafic sources. The relatively high values of the ratio of K_2O/Na_2O could be attributed to felsic sources. The Enrichment Factor indicates moderate enrichment, significant enrichment, very high enrichment and extremely high enrichment. The higher average values of Cu, Zn, Ni and Cr in the stream sediments samples than the WHO standards attest to contamination in the study area. The Contamination Factor (CF) indicates moderate contamination and very high contamination possibly from geogenic sources

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