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Geochemical Characterization of Mineralized Pegmatites around Wowyen Areas, Akwanga, Northcentral Nigeria

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ABSTRACT
This study aims to account for the petrogenesis and mineralization of pegmatites around the Wowyen area, northcentral basement complex, Nigeria. Field studies, petrography and whole rock geochemistry (Major oxides were estimated by X-Ray Fluorescence while the trace elements were estimated by Inductively Coupled Plasma Mass Spectrometry) where the methods adopted. The pegmatites around Wowyen area are emplaced in the remobilized belt of the Nigerian Basement complex. They are predominantly complex pegmatites (rare-metal pegmatites) which are intruded in the biotite-muscovite gneiss while the simple pegmatites intruded more in the migmatitic banded gneiss. The major components of the complex pegmatites are quartz, albite and muscovite and tourmaline. The accessory constituents are garnet; ilmenites; cassiterite-columbite-tantalite oxides in contrast to quartz, microcline and biotite of the simple pegmatites. The complex pegmatites show higher peraluminous than the simple pegmatites, however, higher fractionation is observed in the complex pegmatites than the simple pegmatites. The complex pegmatites are rather enriched in rare elements such as Li, Rb, B, Cs, Sn, Nb, Be and Ta and show low ratios in Al/Ga and K/Rb than the simple pegmatites. The pegmatites are likely product of sedimentary origin and originated from post-collisional tectonic event.

Keywords: Rare-metal pegmatites
Geochemistry
Basement complex
Pan-African events
Wowyen

1. Introduction
Pegmatites are good host of rare metals which include Ta, Be, Nb, Sn, Li and Cs. The demand for the essential metals are in increase owing to the extraordinary values and uses in electronic facility for the assembly of capacitors used in microchips in handsets, cameras, laptops and automobiles, lubricants and batteries, Cs are used for high-pressure and temperature drilling in petroleum exploration [1-2]. Therefore, the explorations for the rare metal pegmatites are highly advocated among geoscientists to meet the global demand for these rare metals. The geological and structural framework of Nigeria makes it significant occurrences of these rocks of potential interest. There are several attempts at classifying

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pegmatites by notable authors, however, \cite{3,4} adopted the abyssal, Muscovite, Muscovite-rare element, rare element and miarolitic classes of \cite{5} based on their environment of formation and further developed subclasses as the lithium, Cesium and Tantalum (LCT) pegmatites and the Niobium, Yttrium and Fluorine (NYF) based on their geochemistry and tectonic settings.

The pegmatites in Wowyen areas of Akwanga, northcentral basement constitute integral components of the granitic and basaltic intrusions of late to post-tectonic Pan-African rocks which is about 600 ± 150 Ma \cite{6-8}. The pegmatites are accounted in linear belt spreading around Ago - Iwoye area in the southwest Nigeria along Jos, northcentral basement Nigeria (see Figure 1) \cite{9-15}. Some are also recorded around Zuru-Gusau, northwest \cite{11,16} and Obudu area southeastern Nigeria \cite{17}. Presently, no account of mining of rare metals from the pegmetites in the study location has been reported; but there are indications of alluvial panning by artisanal excavators along the stream channels. Age range of 580-530 Ma by Rb/Sr has been recorded for the pegmatites in the southwestern and part of Wamba area \cite{11}.

Earlier studies in Nasarawa, northcentral basements were mostly around Keffi and part of Wamba area. These workers include \cite{16,18,19,20} suggested that the pegmatites in Keffi area were emplaced along structures with high possibility for rare metals. \cite{9,12,19,20} advocated that the pegmatites in northern basement are associated to the Pan-African granitoids, but, wide isotopic age difference \cite{7} showed a different origin. This led to argue that the pegmatites around southwest Nigeria originated from remobilization of tectonism couple with partial melting \cite{11}. Therefore, earlier workers on the Nigerian pegmatites believed in the model formation by fractional crystallization from metal rich granites of \cite{21,22} even where there is no evidence of such batholith although the work of \cite{23} suggests a pegmatite conundrum. \cite{13-15} suggested partial melting rather than extended fractionation of granitic bodies between the pegmatites and host migmatitic gneisses. Detailed geochemistry accounts on the pegmatites in Wowyen area are very scanty despite the high potential for mineralization. This study applied studies from the fieldwork and whole rock geochemistry to characterize the elemental concentration of the pegmatites in Wowyen areas.

2. Regional Geology

The basement complex of Nigeria is flanked by the West African to the west, Congo Cratons to the east and Tuarreg Shield to the north (Figure 1). The Pan-African trans-Saharan mobile belt is developed by plate collision between Taureg shield and the West African craton about 600 Ma \cite{24,25,26} accounted that the subduction and subsequent collision at margin of the West African craton resulted to widespread downbucking which resulted to emplaced of calc-alkaline acid and basic rocks.

![Figure 1. Framework of the Nigerian basement complex visa-viz the West African, Congo Cratons and southern Tuarreg Shield. A is Pharusian belt; B is the central Tuarreg Shield; C is the eastern Tuarreg shield. Redrawn after \cite{8}.](image-url)

The rocks of the Basement Complex of Nigeria have experienced sequence of orogenic activities which are typified by metamorphism, deformation, reactivation and remobilization. These activities left imprints of the Liberian (2650 ± 150 Ma), the Eburnean (2000 ± 50 Ma), the Kibaran (1100 ± 200 Ma) and the Pan-African cycle (600 ± 150 Ma) in certain locations. The common rocks of the Nigerian basement from the oldest are the migmatite banded gneiss with rock types: biotite and biotite hornblende gneisses, quartzites and quartz schist; followed unconformably by schistose rocks such as mica-schist, amphibolite, quartzite, talcose rocks metaconglomerate, marble, iron-formations and calc-silicate rock and intruded by the pan-African granites which include granite, granodiorite and potassium rich syenite.

Geochronologically, the oldest rock is the migmatitic banded gneiss complex. They are characterized by wide compositional variation that shows variable protoliths and P-T conditions \cite{27}. The migmatite-gneisses are characterized by the leucosome, mesosome and paleosome components. The schist belt show predominantly N-S
orientation and believed to occur mostly around the western part of Nigerian Basement but; it has been found to occur in southeastern basement of Nigeria. The Pan-African granitoids occurred as the youngest of rocks of the basement complex. The rock types of the Pan-African granites are; porphyritic/porphyroblastic mica-granites, diorites, aplites, tonalities, syenites and chanockites \(^\text{(27)}\), \(^\text{(28)}\) classified the Pan-African granites to three phases: the early phase which are gabbros, diabase, granodiorites and quartz diorites; main phase which are coarse porphyritic hornblende granite, coarse porphyritic mica granite and syenites; late phase which are homogenous granite, pegmatite and aplite dykes. Furthermore, \(^\text{(29)}\) added that the intermediate rocks and pegmatites are classified as unmetamorphosed components of the Basement complex that represents the post-tectonic intrusion. The alkaline granites of Jos plateau intruded the basement complex.

3. Analytical Methods

The study was carried by detailed field work and rock sampling for laboratory analyses. Nine fresh samples of pegmatites (> 2-3 kg) were obtained for chemical analyses. They were sampled along traverse to represent average contents of the rocks. The samples were pulverized to grain size of less than 5 mm and grinded to 200 mesh. The geochemistry was done at Genalysis (Intertek) Laboratory Services Pty Ltd, Maddington, Australia. Major oxides were estimated by X-Ray Fluorescence (XRF) while the trace elements were estimated by sodium peroxide fusion Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Loss on ignition (LOI) was determined by robotic thermo gravimetric analyzer (TGA).

4. Geologic Setting and Petrography

The rocks in Wowyen area consist of largely migmatitic banded gneiss, interjected by biotite-muscovite gneiss and unconformable associated with subunit of amphibolite with polymetamorphic grades ranging from greenschist to amphibolite facies. The pegmatites occur as intrusion on mostly the biotite-muscovite gneiss. The migmatitic banded gneiss is a mesocratic coarse-grained, show foliation direction NNE-SSW. The foliation planes dip about 10° - 55° SE away from the horizontal. There are clear alternations of light and dark components. Whereas quartz, microcline and plagioclase constitute mainly the light components while biotite and hornblende constitutes the dark components. The migmatitic banded gneiss possesses thin quartzofeldspathic veins, mostly in same direction with the foliation trends. Furthermore, two phases of strike-slip faults have been observed in the study area. The migmatitic banded gneiss is cut by basaltic (Figure 2a), rhyolitic porphries and intruded by basic dykes, and pegmatitic dykes. A minor subunit of biotite rich gneiss which is concordant to the migmatitic banded gneiss is observed mostly around hilly areas having porphyroblastic structures that form augen like eyes. The plagioclase crystals are mostly sodic within the leucosome and more calcic around the melanocratic rich constituents. These are differentiated by the occurrences of obvious albite-carlsbad twinning. Microcline is shown by low relief, colourless, subhedral to euhedral that reflect cross-hatch twinning.

Figure 2. a: field photograph of the migmatitic banded gneiss cross cut by basic dyke at Wowyen hill, b: field photograph of complex pegmatite at Wogan showing mineralized (black) zone. 2c Photomicrograph of the simple pegmatite showing microcline. d complex pegmatite showing dominant albite.
are generally blocky and very coarse grain, showing euhedral quartz, biotite and microcline (Figure 2c). Minor constituents are plagioclase (albite), muscovite, few garnet and magnetite. Quartz is colourless while feldspar is pink coloured. Biotite is brownish and occurred predominantly as primary whereas muscovite occurred as secondary replacement. The biotite, plagioclase and microcline have similar characteristics as the migmatitic banded gneisses but larger grain sizes.

The complex pegmatites (albite-muscovite pegmatites) mostly intruded the biotite-muscovite gneiss. These pegmatites have no clear zones but there are traces of roughly developed zones of large crystals of quartz (about 20 cm), muscovite-cleavandite and random black tourmaline (Figure 2b) uneven interior and medium grain to aplitic muscovite-quartz and biotite surface zones. The pegmatites consist of colourless to unclear quartz, pink coloured and albite (Figure 2d). Other minerals are microcline and muscovites. Sporadic tourmaline (black) and garnets constitute accessory. There are intergrowth of albite-quartz as myrmekite and metasomatic albitization. Garnet, tourmaline and cassiterite-columbite-tantalite oxides are mostly in association with albitization.

Figure 3. Geological map of Wowyen area indicating position of the pegmatites

5. Geochemistry

The geochemical compositions of the pegmatites are presented in Tables 1 and 2. The complex pegmatites have high SiO$_2$ contents ranges from 63.88 to 74.8 wt%, while the simple pegmatites have SiO$_2$ values ranges from 66.0 to 78.8 wt% comparable to the complex pegmatites (Table 1). The complex pegmatites have Na$_2$O (2.64 to 9.51 wt%), K$_2$O (2.04 to 5.7 wt%) and Al$_2$O$_3$ (13.79 to 21.62 wt%) values relatively higher compared to the simple pegmatites Na$_2$O (3.37 to 7.12 wt%), K$_2$O (2.66 to 3.8 wt%) and Al$_2$O$_3$ (11.84 to 19.92 wt%). Na$_2$O concentrations dominate K$_2$O confirming albitization in the pegmatites, which is concordant to the modal composition with higher albite to k-feldspars ratio. Fe$_2$O$_3$ values range from 0.94 to 3.56 wt% in the complex pegmatites compared to 0.69 to 1.15 wt% in the simple pegmatites. The values of TiO$_2$, MgO and CaO are generally less than 1 wt % across the two pegmatites types. Furthermore, the values of Li (27 to 101 ppm), Cs (5.1 to 56.5 ppm), Ta (1.8 to 24.3 ppm), Nb (27 to 59 ppm), Sn (18 to 170 ppm), W (69 to 118 ppm) and B (21 to 4205 ppm) in the complex pegmatites are higher compared to the simple pegmatites which have of Li (5 to 40 ppm), Cs (4.3 to 32.1 ppm), Ta (0.8 to 10.7 ppm), Nb (7 to 15 ppm), Sn (3 to 35 ppm), W (61 to 438 ppm) and B (33 to 420 ppm). ∑REE in the complex pegmatites range from 4.95 to 16.29 ppm compared to 5.93 to 24.55 ppm in the simple pegmatites. The ratios of A/CNK, Al/Ga and K/Rb in the complex pegmatites range from 1.59 to 2.14, 1595.96 to 2159.63 and 57.14 to 107.59 respectively compared to the simple pegmatites which range from 1.47 to 1.73, 3686.07 to 4583.77 and 149.44 to 267.11.

The ratio of A/CNK = 1.45 to 2.14 of the pegmatites in Wowyen area show strongly peraluminous where the complex pegmatites showing the highest value. On the R1 - R2 diagram of [26]; Figure 3) the pegmatites plot predominantly in the granite fields with sample (W9) of the simple pegmatite plotting in quartz syenite area.
Table 1. Major element oxides concentrations in wt %. of the pegmatites in Wowyen areas

|          | Complex pegmatite | Simple pegmatite |
|----------|-------------------|------------------|
|          | WO1   | WO2  | WO3  | WO4  | WO5  | WO6  | WO7  | WO8  | WO9  |
| SiO₂     | 74.75 | 74.43 | 74.83 | 74.71 | 63.88 | 68.74 | 78.81 | 75.19 | 66.06 |
| TiO₂     | 0.03  | 0.03  | 0.01  | 0.02  | 0.02  | 0.05  | 0.03  | 0.04  | 0.04  |
| Al₂O₃    | 14.69 | 13.79 | 14.5  | 14.75 | 21.62 | 17.49 | 11.84 | 14.21 | 19.92 |
| Fe₂O₄T   | 1.07  | 2.18  | 1.01  | 1.13  | 0.94  | 3.56  | 1.15  | 0.69  | 0.87  |
| MnO      | 0.02  | 0.03  | 0.05  | 0.02  | 0.04  | 0.02  | 0.02  | 0.02  | 0.04  |
| MgO      | 0.12  | 0.23  | 0.08  | 0.09  | 0.12  | 0.41  | 0.02  | 0.06  | 0.17  |
| CaO      | 0.31  | 0.11  | 0.17  | 0.35  | 0.53  | 0.12  | 0.87  | 0.64  | 1.73  |
| Na₂O     | 4.87  | 2.64  | 4.75  | 5.18  | 9.51  | 3.6   | 3.37  | 5.08  | 7.12  |
| K₂O      | 3.59  | 5.7   | 4.22  | 3.15  | 2.04  | 4.47  | 3.8   | 3.89  | 2.66  |
| P₂O₅     | 0.14  | 0.189 | 0.156 | 0.147 | 0.416 | 0.154 | 0.022 | 0.062 | 0.593 |
| LOI      | 0.47  | 0.38  | 0.47  | 0.53  | 0.8   | 0.76  | 0.23  | 0.2   | 0.65  |
| Total    | 100.1 | 99.79 | 100.31| 100.13| 99.97 | 99.57 | 100.23| 100.12| 100.02|
| Na₂O+K₂O | 8.46  | 8.34  | 8.97  | 8.33  | 11.55 | 8.07  | 7.17  | 8.97  | 9.78  |
| A/NK     | 1.74  | 1.65  | 1.62  | 1.77  | 1.87  | 2.17  | 1.65  | 1.58  | 2.04  |
| A/CNK    | 1.68  | 1.63  | 1.59  | 1.70  | 1.79  | 2.14  | 1.47  | 1.48  | 1.73  |
| K₂O+NaO-CaO | 8.15 | 8.23  | 8.8   | 7.98  | 11.02 | 7.95  | 6.3   | 8.33  | 8.05  |

Table 2. Trace elements concentration in ppm for the pegmatites in Wowyen areas

|          | Complex pegmatite | Simple pegmatite |
|----------|-------------------|------------------|
|          | WO1   | WO2  | WO3  | WO4  | WO5  | WO6  | WO7  | WO8  | WO9  |
| Li       | 101   | 27   | 30   | 42   | 29   | 66   | 5    | 31   | 40   |
| B        | 31    | 2191 | 73   | 21   | 35   | 4205 | 106  | 33   | 420  |
| Ba       | 14    | 19   | 31   | 28   | 21   | 11   | 112  | 10   | 571  |
| Be       | 4.4   | 20.3 | 4.2  | 4.6  | 6.2  | 197.5| 4.6  | 3.4  | 84.7 |
| Co       | 8.0   | 7.2  | 8.7  | 7.1  | 7.9  | 9.9  | 19.0 | 11.3 | 4.8  |
| Cr       | 2     | bl   | bl   | bl   | bl   | bl   | 1    | bl   | 1    |
| Cs       | 8.4   | 26.5 | 5.1  | 6.7  | 56.5 | 45   | 4.3  | 7.1  | 32.1 |
| Ga       | 36    | 33   | 37   | 37   | 59   | 58   | 17   | 20   | 23   |
| Hf       | 0.5   | 1.7  | 0.5  | 0.1  | 0.5  | 1.8  | 0.9  | 2.1  | 3.1  |
| Nb       | 27    | 33   | 43   | 30   | 41   | 59   | 8    | 7    | 15   |
| Pb       | 21    | 12.7 | 15   | 13   | 6    | 9    | 32   | 27   | 33   |
| Rb       | 277   | 500  | 438  | 249  | 296  | 534  | 118  | 216  | 127  |
| Sn       | 44    | 18   | 170  | 36   | 141  | 120  | 4    | 3    | 35   |
| Sr       | bl   | bl   | bl   | bl   | 35   | bl   | 79   | bl   | 234  |
| Ta       | 1.8   | 24.2 | 2.8  | 2.4  | 7.4  | 20.9 | 1.1  | 0.8  | 10.7 |
| Th       | 2.0   | 1.6  | 2.0  | 1.6  | 1.0  | 1.6  | 63.0 | 3.0  | 1.2  |
| Tl       | 1.4   | 3.0  | 2.1  | 1.2  | 1.2  | 2.7  | 0.6  | 1.2  | 0.7  |
| U        | 3.1   | 1.2  | 10.6 | 6.2  | 1.2  | 1.2  | 12   | 5    | 2.1  |
6. Discussion

The simple pegmatites are composed of predominantly of quartz, microcline and biotite while the complex pegmatites are dominated by quartz, albite and muscovite in addition to garnets, tourmaline and cassiterite-columbite-tantalite oxide patches. The highly peraluminous characteristics of the study pegmatites in Wowyen areas is obvious on the Shand index diagram (Figure 4a), $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ vs $\text{Al}_2\text{O}_3/(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$ of $^{[33]}$. The complex pegmatites indicate higher fractionation with higher peraluminous ($A/\text{CNK}=1.5 - 2.1$) when compared to the simple pegmatites ($A/\text{CNK}=1.4 - 1.7$). Samples of the pegmatites fall mostly within the field of high-K calc-alkaline of $^{[34]}$ (Figure 4b). On the $\text{SiO}_2$ vs $\text{Fe}^*$ of $^{[35]}$, the pegmatites fall predominantly in the ferroan field (Figure 4c). The ferroan similarity of the pegmatitic rocks is consistence with the occurrence of magnetites in the mode and norm of the rocks. Considering MALI diagram of $^{[35]}$, the pegmatites fall predominantly in alkalic-calcic field (Figure 4d).

In addition, the pegmatites in Wowyen area have geochemical and mineralogical characteristics of S-type granites of Lachlan Fold Belt derived from sedimentary material $^{[35]}$. These geochemical characteristics are in concordance to the outcomes of $^{[23,13,14]}$ in pegmatites within the northcentral basement Nigeria. Peraluminous nature of the pegmatites are consistence with the findings on pegmatites in other locations of Nigeria notably in southwestern Nigeria, Oke-Asa and Igbeti pegmatites $^{[36]}$; northcentral Nigeria, Sarkin Pawa-Minna Pegmatites $^{[23]}$ and Angwan Doka pegmatites $^{[20]}$; southeastern Nigeria, Oban and Bamenda massif pegmatites $^{[37]}$.

The pegmatites in the Wowyen area indicate flexible concentrations of trace element and REEs patterns and show highly fractionation which is obvious in the complex pegmatites. These can be seen in the enrichment of Rb, B, Cs, Sn, Nb, Ta, K, Pb, Li and U however indicate depletions in Ba, La, Ce and Ti and REEs see Figure 5a. The pegmatites also indicate low values of REE (Figure 5b) with values lower than detectable limit in some samples. Even though the pegmatites show some

\[ \begin{align*}
\text{W} & \quad 94 & \quad 118 & \quad 93 & \quad 91 & \quad 69 & \quad 95 & \quad 438 & \quad 142 & \quad 61 \\
\text{Y} & \quad 8.0 & \quad 2.5 & \quad 2.7 & \quad 3.3 & \quad 1.7 & \quad 2.9 & \quad 2.5 & \quad 9.4 & \quad 6.5 \\
\text{Zn} & \quad 53 & \quad 125 & \quad 34 & \quad 40 & \quad 29 & \quad 240 & \quad 23 & \quad 25 & \quad 48 \\
\text{Zr} & \quad 15 & \quad 39 & \quad 11 & \quad 0 & \quad 8 & \quad 21 & \quad 26 & \quad 49 & \quad 77 \\
\text{La} & \quad 1.9 & \quad 1.3 & \quad 1 & \quad 1.2 & \quad 0.7 & \quad 2 & \quad 0.8 & \quad 3.1 & \quad 4.3 \\
\text{Ce} & \quad 4.6 & \quad 2.3 & \quad 2.4 & \quad 3.4 & \quad 1.5 & \quad 3.5 & \quad 1.5 & \quad 6.6 & \quad 8.9 \\
\text{Pr} & \quad 0.6 & \quad 0.3 & \quad 0.3 & \quad 0.4 & \quad 0.2 & \quad 0.5 & \quad 0.2 & \quad 0.8 & \quad 1 \\
\text{Nd} & \quad 2.6 & \quad 1.3 & \quad 1.1 & \quad 1.3 & \quad 0.6 & \quad 2 & \quad 0.9 & \quad 2.6 & \quad 4 \\
\text{Sm} & \quad 1.1 & \quad 0.6 & \quad 0.6 & \quad 0.6 & \quad 0.4 & \quad 0.8 & \quad 0.4 & \quad 0.5 & \quad 1.3 \\
\text{Eu} & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad 0.2 & \quad bl \\
\text{Gd} & \quad 1.3 & \quad 0.4 & \quad 0.5 & \quad 0.5 & \quad 0.4 & \quad 0.6 & \quad 0.5 & \quad 0.7 & \quad 1.5 \\
\text{Tb} & \quad 0.3 & \quad 0.1 & \quad 0.1 & \quad 0.2 & \quad 0.1 & \quad 0.1 & \quad 0.1 & \quad 0.2 & \quad 0.3 \\
\text{Dy} & \quad 1.8 & \quad 0.4 & \quad 0.6 & \quad 0.6 & \quad 0.5 & \quad 0.7 & \quad 0.5 & \quad 1.3 & \quad 1.4 \\
\text{Ho} & \quad 0.3 & \quad bl & \quad bl & \quad 0.1 & \quad bl & \quad 0.1 & \quad 0.1 & \quad 0.2 & \quad 0.2 \\
\text{Er} & \quad 0.7 & \quad 0.3 & \quad 0.2 & \quad 0.3 & \quad 0.1 & \quad 0.2 & \quad 0.3 & \quad 1 & \quad 0.5 \\
\text{Tm} & \quad 0.1 & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad 0.1 & \quad bl \\
\text{Yb} & \quad 0.8 & \quad 0.4 & \quad 0.2 & \quad 0.3 & \quad 0.2 & \quad 0.3 & \quad 0.3 & \quad 0.9 & \quad 0.5 \\
\text{Lu} & \quad 0.1 & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad 0.2 & \quad bl \\
\sum\text{REE} & \quad 16.29 & \quad 7.72 & \quad 7.31 & \quad 9.11 & \quad 4.95 & \quad 10.98 & \quad 5.93 & \quad 18.24 & \quad 24.55 \\
\sum\text{LREE} & \quad 10.8 & \quad 5.8 & \quad 5.4 & \quad 6.9 & \quad 3.4 & \quad 8.8 & \quad 3.8 & \quad 13.6 & \quad 19.5 \\
\sum\text{HREE} & \quad 5.4 & \quad 1.84 & \quad 1.83 & \quad 2.12 & \quad 1.5 & \quad 2.12 & \quad 1.93 & \quad 4.6 & \quad 4.55 \\
\sum\text{LR/HR} & \quad 2.00 & \quad 3.15 & \quad 2.95 & \quad 3.25 & \quad 2.27 & \quad 4.15 & \quad 1.97 & \quad 2.96 & \quad 4.29 \\
\text{La/Yb} & \quad 1.61 & \quad 2.21 & \quad 3.40 & \quad 2.72 & \quad 2.38 & \quad 4.53 & \quad 1.81 & \quad 2.34 & \quad 5.84 \\
\text{Eu/Eu}^* & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad bl & \quad 1.36 & \quad bl \\
\end{align*}\]
kind of strong LREE compared to the HREE \((\text{La}/\text{Yb})_n = 1.62 - 5.84\); Table 2 but the LREE and HREE values are very low (Figure 5b) since REEs values in pegmatites are easily apportioned into accessory phases of the minerals \[38\]. The Eu concentrations in most of the pegmatites are generally lower than detection limit of < 0.1 ppm with the exception of two samples of the simple pegmatites. The variant in patterns of the REEs in the pegmatites possibly reflect the behavior of separation of accessory mineral phases. The anomalies of Eu can be described as fractional crystallization of feldspars and to melt-fluid interface in the concluding part of magma crystallization \[39,40\]. The pegmatites from the study area plot predominantly in syn-collisional granites however accumulated towards post-collisional granites which suggest compressional tectonic setting (Figure 6a and 6b). This supports the findings of \[14\] that the pegmatites around northcentral basement complex of Nigeria are post-collisional granites and possibly postdates the Pan-African granites rather than being the concluding fraction of the Pan-African granites.

\textbf{Figure 4.} Plots of the Wowyen pegmatites in (a) Shand index; A/NK = \(\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{K}_2\text{O})\) and A/CNK = \(\text{Al}_2\text{O}_3/(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})\) after \[33\]. (b) \(\text{K}_2\text{O} \text{ versus SiO}_2\) of \[34\]; (c) \(\text{FeO}/(\text{FeO}+\text{MgO}) \text{ versus SiO}_2\) after \[35\]; (d) modified alkali-Lime Index (MALI) versus SiO\(_2\) after \[35\]. Symbols are as in Figure 3.
The observations in the spidergrams (Figure 5a) is concordance to that of the Shand index plot (Figure 4a) where the complex pegmatites show presence of Nb -Ta, Sn and B bearing minerals (columbite, tantalite, cassiterite and tourmaline respectively) compared to the simple pegmatites.

Based on the mineralogical and geochemical characteristics of the Wowyen pegmatites, they are classified as Li-Cs-Ta rare metal mineralized pegmatites of [7,8,43]. The complex pegmatites show higher concentrations of Rb, Cs, Sn, B, Nb, Ta, Li and less concentration in Ba and Ti whereas the simple pegmatites show relative reduction in Nb, Ta and enhancement in REEs. The mineralization of the pegmatites can be seen in Figure 7a and 7b of [44] where the complex pegmatites predominantly plot in mineralized field. There are other rare metal pegmatites found in highly metamorphic terrains having comparable geochemical signatures that are accounted for in areas with related tectonic setting and magmatism. Analogous examples are found in Altai mountains of China [45] and Gneiss Complex of Lewisian in north-west Scotland [46].

The degrees of fractionation in pegmatites concentrate valuable elements which can serve as a pathfinder for advance assessment for rare metals. Such as granitic rocks with intensely peraluminous (A/CNK > 1.2) is a good index for evaluation of grade of fractionation in fertile granite [1]. A/CNK ratios of the albite-muscovite pegmatites (1.5 - 2.1) which are highly peraluminous show that the study pegmatites are fractionated and rich in Al bearing minerals like garnet and muscovite. [32] has shown that rare element compositions in fertile granites/pegmatites tend to increase with rise in fractionation of Rb, B, Be, Li, F, P, Rb, Ga, Y, Cs, Sn, Nb and Ta and reduction in Sr, Ti, Zr and Ba. The fractionation in the pegmatites is obvious in Figure 7c and 7d.

High fractionation of the pegmatites are also observed in Table 2. The concentrations of Rb are high in complex pegmatite (277 ppm - 534 ppm) and simple pegmatite (126.5 ppm - 216.1 ppm; Table 2). On the contrary, the values of Ba and Sr in the pegmatites are lower than average crustal abundances reported by [31]. Sr concentrations in the pegmatites are generally below 10 ppm detection limit. The values of Sn, Nb and Ta which are up to 170 ppm, 59 ppm and 24.2 ppm respectively in the complex pegmatites are high compare to average concentrations in metal rich pegmatitic leucogranite of Superior Province [32,8]. Sn (4 to 35 ppm), Nb (7 - 15 ppm) and Ta (0.8 - 10.7 ppm) values in simple pegmatites are lower. The concentrations of REEs and Co, Ag, Cr, Cu, Zn and Pb are generally depleted in the pegmatites while the values of B, Cs and Ga are enriched especially in the complex pegmatites with values up to 4205 ppm, 56.5 ppm and 59 ppm respectively across the study area. The concentration of Li in the simple and complex pegmatites ranges from 5 ppm to 101 ppm respectively. These differences in concentrations show higher degrees of fractionation similar to concentration in fertile granites [32].

They have high possibility for rare metals (Sn, Nb and possibly Ta) mineralization in opposite to the earlier stand of [31] who was in doubt of mineralization in pegmatite around Nasarawa area.

Furthermore, some trace-element ratios (Mg/Li, K/Rb, Nb/Ta, K/Cs, and Al/Ga) are good pointer of fractionation in metal rich granites/pegmatites. These ratios are predictably and expressively lower than average upper continental crust [47], and are analogous to bulk trace element contents ratios of [48] in fertile granite/pegmatites [1]. The average ratios of K/Cs, K/Rb, Mg/Li, Nb/Ta and Al/Ga in the complex pegmatites are 2871.68, 85.66, 24, 8.76 and 2015 ppm while the average ratios in the simple pegmatites are 4190, 196.0, 20.5, 5.81 and 4009 respectively. This indicates strongly fractionation and strong possibility for rare metals in the complex pegmatites compared the simple pegmatites (see Table 3). These ratios are consistent with other studies on mineralized pegmatites from other parts of Nigerian Basement Complex [48,16,36,49,13,14].

**Table 3.** Ratios of trace elements in the Wowyen pegmatites compared with productive granites

| Complex pegmatites | Simple pegmatites | UCC | Fertile Granite. |
|--------------------|-------------------|-----|------------------|
| Range              | Average           | Range | Average  |
| K/Rb               | 57.14-107.59      | 85.66 | 149.44-267.11   |
| K/Cs               | 299.74-6869.17    | 2871.68 | 687.92-7336.30  |
| Mg/Li              | 5.97-51.38        | 24.80 | 11.67-25.63     |
| Al/Ga              | 1595.96-2159.63   | 2015.09 | 3686.07-4583.77 |
| Nb/Ta              | 1.36-15.36        | 8.76  | 1.40-8.75       |

*Data for fertile peg. from [49]  
*UCC is average upper-continental crust after [47]
Figure 5. (a) Primitive mantle-normalized spider diagrams (b) Chondrite-normalized trace elements pattern for the pegmatites. Normalizing factors from [41]. Symbols are as shown in Figure 3.

Figure 6. (a). Plot of Rb vs Y + Nb (b) Ta vs Yb of [42] of the pegmatites showing their tectonic setting.

Figure 7. (a). Plot of K/Rb vs Cs of [44] (b) K/Rb vs Rb for discriminating of barren and mineralized pegmatites (c) Ta vs Nb (d) Ta vs Rb for fractionation trends of the pegmatites.
7. Conclusions

This work indicates that the granitic pegmatites in the migmatitic banded gneiss basement complex in Wowyen areas are dominated by complex pegmatites. The complex pegmatites are fractionated with high possibility of hosting substantial quantity of rare elements than the simple pegmatites. This can be seen from the relatively high concentration of Li, Rb, B, Cs, Sn, Nb and Ta, low ratios of K/Rb and variation diagrams as indicated. The notable minerals in the pegmatites are albite, muscovite and quartz. Others are garnets, tourmaline and cassiterite-columbite oxides. The mineralogical and chemical signatures of the granitic pegmatites indicate peraluminous rich source of sedimentary origin that is saturated in LILE and HFSE. The complex pegmatites are evolved from the simple types indicating common source accompanied by internal fractionation. The pegmatites are generated in post-collisional tectonic settings of Pan-African events.

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