

## GEOLOGICAL AND GEOCHEMICAL ANALYSES OF PEGMATITES IN EGBE, ISANLU (SHEET 225), SOUTHWESTERN NIGERIA

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### ABSTRACT

*The hitherto pegmatite of the Egbe area has been known to bear valuable economic minerals. They are associated with other rock types including banded gneiss, schist, amphibolite, and granites. These pegmatites and the host rocks were studied in detail to elucidate their petrochemical and geochemical features and also to assess the mineralization of Tantalum-Niobium and other minerals. Geological field mapping was done, thin section-petrographic analysis of ten representative rock samples was performed and nineteen whole-rock samples were analyzed for major and trace elements including REES aided by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Boron-Fusion-Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), and Ion-Selective Electrode (ISE) for Fluorine at Acme Laboratory, Vancouver, Canada. The general structural trend of the area under study is WNW-ESE and foliations of N-S strike were observed in the banded gneiss and schist which also exhibit asymmetric and isoclinal folding respectively. The tantalite-columbite mineralization is associated with the NE-SW trending pegmatite dykes. The mineralized pegmatites are genetically related to the peraluminous S-type granite. The minerals (i.e., Albite, lepidolite and muscovite) extracted from the pegmatites are well enriched in Li, Rb, Cs, Nb and Ta compared to the host rocks. The rare-metal pegmatites exhibit pronounced negative Ce and Eu anomalies and also show weak negative Yb anomalies while the barren pegmatites have positive Ce and weak negative Eu anomalies and exhibit weak positive Yb anomalies. The pegmatites are moderately evolved compared with other highly mineralized pegmatites. The pegmatites from Igaruku and one from the Okere area are of the rare-metal pegmatite and they are moderately fractionated while the barren pegmatite from Egbe and one from Okere are unfractionated. The economic mineral within the Egbe area is tantalite, with every possibility that the tantalite-columbite enrichment is ferrotantalite-columbite and manganotantalite columbite.*

**Keywords:** Egbe, Mineralized pegmatites, Economic mineral, S-type granite, Rare-earth metal.

### INTRODUCTION

Tantalum and niobium are the ore elements paired together in end members of a solid solution series called tantalite (Ta<sub>2</sub>O<sub>5</sub>) -

columbite (Nb<sub>2</sub>O<sub>5</sub>). These elements are geochemically associated as they usually occur together in rocks and minerals. However, the principal reason for such coherency is the similarity in these elements'

ionic radii and valency states ( $Ta^{+5}=0.68A$  and  $Nb^{+5}=0.69A$ ). The economic deposits of tantalite–columbite are usually associated with rare-metal pegmatites (Černý & Ercit, 1985). The rare-metal pegmatites belong to the Li, Cs and Ta (L-C-T)- family and are known to be derived from fertile granites (Černý, 1991; Černý & Ercit, 1985). As granitic melt crystallizes, barren granite composed of quartz, potassium, feldspar, plagioclase, and mica is formed, and the residual melt is progressively enriched in incompatible (rare) elements such as Be, B, Li, Rb, Ta, Nb, Mn, and Sn.  $H_2O$  and fluxing components such as B, P, Li and F also increase in the late-stage granitic melt. If the concentration of the volatiles, mainly  $H_2O$  (of the residual melt) exceeds its solubility limit, an aqueous fluid exsolves from the melt and promotes the formation of a miarole or primary pocket. Nearly pure, gem-quality crystals of Be-, Li-, B- and F- silicate minerals, tantalite - columbite along with other non-silicate minerals form in the miarole as the final products of crystallization (London, 1996, 2018).

Jacobson (1946) earlier stated that the rare-metal pegmatites of Nigeria are confined to a 400 km long NW-SW trending belt stretching from the Wamba area in central Nigeria to the Ibadan area in southwest Nigeria. This idea was refuted by the work of Garba, (2003b). The occurrences of the pegmatites in the southeastern part of Nigeria, especially around Obudu hills were presumed to extend into Northeast Brazil (Garba, 2003b). The Nigerian pegmatites evolved during the Pan-African Orogeny (Matheis, 1987). The Nb-Ta ( $\pm$  Sn) pegmatites are hosted by rocks of the Pan-African basement complex. Its occurrences in central, northwestern, southwestern, and southeastern Nigeria have been reported by some researchers (including Garba, 2003a; Jacobson, 1946; Matheis, 1987). Garba (2003b), Küster (1990) and Matheis (1987) classified the metallogeny of the rare metal Ta-Nb pegmatites of Nigeria, outlining seven broad fields namely Kabba - Isanlu, Ijero - Aramoko, Keffi- Nasarrawa,

Lema -Ndeji, Oke Ogun, Ibadan -Osogbo and Kushaka - B/Gwari.

Several geological research on Nigerian pegmatites has been done including Egbe (the study area), mostly in search of potential gold mineralization. The increase in the global demand for tantalum and niobium has led to the exploration of economically viable deposits. The study area has been known to host several pegmatite bodies (Matheis, 1987), some of which are being mined for coltan. There are both mineralized and barren pegmatites in the area. Thence, this work aims to ascertain and elucidate the composition and economic viability of the Egbe pegmatites as this will guide explorations in the search for tantalum-niobium and other mineral potential in the area.

#### **Location and Geology of the Study Area**

The study area is located within the western part of Kogi State (Egbe area) (Fig. 1). It covers an area of approximately 342.25 km<sup>2</sup>. The area is fairly accessible through major, and minor roads and footpaths, but it is much better during the dry season, as the grasses are usually dry and/or burnt.

The Basement Complex of Nigeria is one of the three major petrological components that forms the geology of Nigeria. This Basement Complex is believed to have evolved as a result of four cycles of orogeny (including the Liberian, the Eburnean, the Kibaran, and the Pan-African orogeny). The Pan-African orogeny was accompanied by regional magmatism, metamorphism, migmatization, extensive gneissification and granitization (Abaa, 1985). The complex is divided into five segments (Abubakar, 2024; Obaje, 2009). The study area forms part of the Southwestern Basement Complex of Nigeria. The Nigerian rare-metal pegmatite indicates the late stage of the Pan-African orogeny (Matheis & Caen-Vachette, 1983). The pegmatites are related to the Nigerian major lineament systems; on this basis, (Ekwueme & Matheis, 1995) speculated

that rare-metal mineralization may be as a result of late-stage fluids available at close to the Pan-African metamorphic cycle. Wright (1976) suggests that it may be as a result of sodium-rich hydrothermal solution from the mantle along ancient lineaments. However, Matheis & Caen-Vachette (1983) concluded that the pegmatites of southwestern Nigeria are products of the partial melting and leaching process of the basement units rather than the pegmatitic phase of the proximal Older Granite. Matheis (1987) also suggested that the rare-metal pegmatite mineralization of southwestern Nigeria was derived from the reactivation of deep-seated tectonic lineaments combined with partial melting and external fluid supply.

**Rare-element pegmatite.** The rare-elements pegmatites are examined and exploited around the world in numerous countries. Some of these countries include Brazil, Mozambique, Canada, India, Namibia and Australia. The Archean-aged pegmatites terrain tends to be the most economic (Galeschuk & Vanstone, 2007). All economically important types of primary tantalum mineralization are related to rare metal-enriched granitoid rocks. Ta mineralized granitoids are usually well fractionated and represent the latest stages of felsic magma evolution. A high degree of fractionation of volatile-enriched granitic magmas is a criterion for the formation of tantalum rare-metal deposits (Badanina et al., 2004; Černý et al., 2005, 2012; Kovalenko & Yarmolyuk, 1995; Lehman, 1994; Linnen & Cuney, 2005; Raimbault et al., 1995; Reyf et al., 2000; Salvi et al., 2005; Schmitt et al., 2002; Yin et al., 1995). Černý et al. (2005), Lehman (1994), and Linnen & Cuney (2005) also stated that the reaction between magmatic and/or meteoric fluids and host rocks in several deposits during rare-metal mineralization is not considered to be a

fundamental cause for the formation of Ta mineralization.

The Ta mineralized granitoids are grouped into peraluminous granitoids and peralkaline granitoid plutons. The peraluminous granitoids comprised granite plutons and pegmatitic dykes or sheets. The Ta-mineralized peraluminous granitoid is emplaced mainly at 2 to 4 kbar in upper greenschist to amphibolite facies (Černý, 1991). Rare-metal specialized peraluminous granites are late-orogenic to anorogenic and also post-date regional metamorphism and also their emplacement is controlled by deep-reaching crustal faults or shear zones (Černý, 1989; Pollard, 1989). According to (Černý, 1989, 1991), they crystallized from highly fractionated magmas derived from geochemically specialized rare-element enriched granites and the Ta mineralized peraluminous pegmatites are synonymous with the LCT (lithium cesium tantalum) pegmatite.

The peralkaline granites have A/NK (molar  $Al_2O_3/(Na_2O+K_2O) < 1$  and are characterized by the presence of sodic amphiboles and pyroxenes (arfvedsonite, riebeckite, aegirine). They also consist of very high concentrations of Zr, Hf, Y, REE, Nb, U and Th which clearly distinguishes them from the rare-element mineralized peraluminous variants. The rare-element enrichment is attributed to the very high solubilities of HFSE (high field strength elements) including Ta in peralkaline melts and retardation of crystallization of respective minerals until the volatile-rich end stages of magma evolution (Salvi et al., 2005). Ta-mineralization seems to be an essentially magmatic process with little contribution from meteoric fluids (Linnen & Cuney, 2005); however, hydrothermal processes probably play an important role in the formation of dominantly Zr, Nb, REE deposits (Salvi & Williams-Jones, 2006).

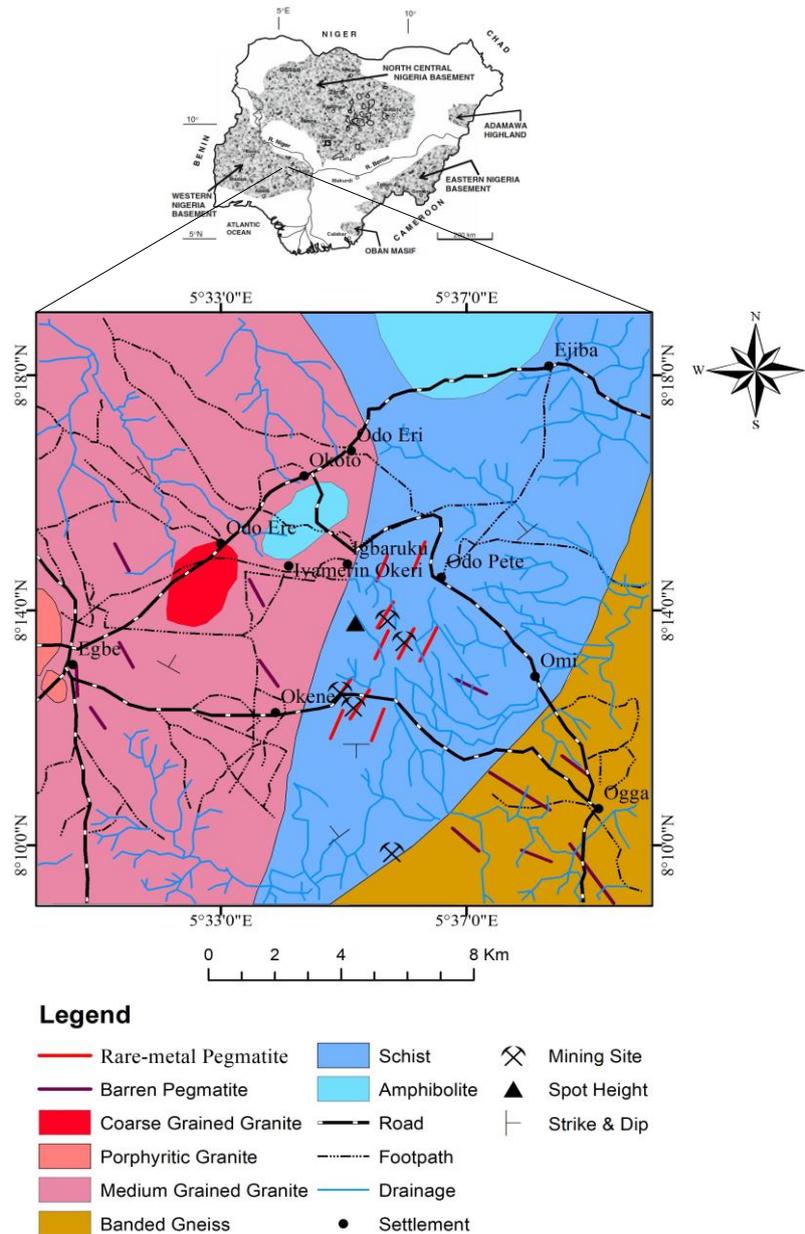


Figure 1: Geologic map of the study area showing the Egbe pegmatites and the mining sites

## MATERIALS AND METHODOLOGY

### Materials

The materials used in the geologic field mapping are hammer, compass-clinometer, recording materials, and GPS. In this section preparation and analysis, the following materials were used: thin slides, Canada balsam, Rock sample, mineralogical saw, Glass plate, source of heat, water, carborundum powder, and petrographic microscope. The Inductively Coupled

Plasma-Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Atomic-Emission Spectrometry (ICP-AES) and Ion-Selective Electrode (ISE) were used for elemental analysis.

### Methodology

Representative samples of rocks were collected for examination and laboratory analysis. Field measurements of strike and dip were carried out with the aid of a compass-clinometer and coordinates of

sampling points were recorded. Rose diagram was generated to determine the dominant direction of the lineaments, which was also checked using Landsat ETM+ imagery (aided with PCI geomatica line module).

Thin sections of ten representative rock samples were examined using a petrographic microscope at the Department of Geology, Ahmadu Bello University, Zaria. Nineteen samples of rocks and minerals (including twelve rock samples and seven mineral samples (extracted from pegmatites)) were pulverized in a carbide mill at the Multiuser Science Laboratory, Ahmadu Bello University, Zaria. Thereafter, the samples (pulverized) were shipped to Acme Laboratory, Vancouver, Canada, for analysis of major and trace elements by Acid-Digestion ICP-MS. Major and trace elements with rare-earth elements were analyzed with Boron-Fusion ICP-AES and ISE methods for Boron and fluorine respectively.

The procedure of the ICP-MS involved sample digestion using a mixture of (2:2:1:1) H<sub>2</sub>O –HF–HClO<sub>4</sub> – HNO<sub>3</sub> and 50% HCl. The solution was heated and allowed to cool. Upon cooling, the solutions were pumped into the sample introduction system, comprising a spray chamber and a nebulizer. The sample emerged as an aerosol. The excitation of the outer electrons produced photons of light with a specific wavelength from which the concentrations of the elements were then computed.

Fluorine was analysed using the Ion Selective Electrode method. The procedure involved the preparation of a standard solution of accurately known concentration. These solutions were then measured with the pH/millivoltmeter (mV). The mV reading of each solution was noted and a graph of concentration versus mV reading was plotted. Therefore the unknown solution was measured. The mV value of the unknown solution was then established and located on the graph and the corresponding solution concentration was determined.

The interpretation of the geochemical data was done using a geochemical tool kit (GCDkit). Descriptive statistics were used to discriminate between mineralized and non-mineralized rock samples. Results of petrographic studies and whole-rock geochemical analysis were used to evaluate the chemical characteristics of the rocks and the petrogenesis of the rock units and associated columbite-tantalite mineralization in the study area.

## RESULTS

### Petrography

The study area is underlain by granites, banded gneiss, metasediments, metavolcanic (schist and amphibolites) and pegmatites (Fig. 1). The banded gneiss occurs as massive, low-lying weathered outcrops. It is medium-grained, light-colored and strongly foliated with alternating bands of light minerals (plagioclase feldspar and quartz) and dark bands consisting of biotite and other opaque minerals. In the thin section, quartz, biotite and plagioclase feldspars form the bulk of the mineral composition (Plate 1Ia and Ib). The banded gneiss is composed of quartz (55%), biotite (30%) and plagioclase (15%). Quartz occurs as cloudy anhedral grains, with wavy extinction and low birefringence. The crystals of biotite are subhedral, brown, and of high relief. The biotite has perfect basal cleavage except for grains that are parallel to the crystallographic axis (biotite 2). The plagioclase feldspar is also colourless but cloudy and exhibits characteristic lamellar twinning (Plate 1 I and II). The banded gneiss is seen to have poikilitic inclusion of quartz in biotite under Plane polarized light (PPL) and observed in cross-polar (XPL) to occur with anhedral quartz, biotite and subhedral plagioclase crystals (Plate 1 II).

The metasediments (schist) of Igbarukumake up about 35% of the rocks of the study area. They are light to dark coloured. The dominant strike direction is NE-SW, and generally dipping 40° NW. It is foliated with the trend parallel to the strike direction. The schist is

highly weathered. There is no sharp contact observed between the schist and other lithologies in the area of study. The schist is composed of quartz (52%), biotite (30%) and muscovite (10%) with few crystals of plagioclase feldspar (8%). The plagioclase has been altered to sericite in some places. The biotite has perfect cleavage with moderate relief (Plate 1 III). Under both the PPL and XPL, the lineated muscovite and biotite grains cut perpendicular to the c-axis. The biotite has a brown interference colour while the muscovite had a light blue interference colour.

Metavolcanics (amphibolite) outcrops at Iyameri over an area of about 17.1 km<sup>2</sup> and make up about 5% of rocks in the study area. They occur as boulders and cobbles, and no visible contact was observed with other rocks. The rock is dark green to black. Thin section analysis reveals that it is composed of amphibole (38%), quartz (30%), plagioclase (20%), microcline (1%) and accessory minerals. The hornblende displays different interference colours, including brown, green, blue, and pink with high relief. There is an intergrowth of quartz and biotite in the amphibolite grains. Plagioclase is euhedral to subhedral with a characteristic polysynthetic twinning (Plate 1 IV). Subhedral grains of hornblende with a shade of brown colour is common. The hornblende has two sets of cleavages intersecting at nearly 120°. Under XPL the plagioclase is subhedral and the quartz and biotite are anhedral.

The granites are of three varieties: (i) medium-grained biotite granite (ii) medium to coarse-grained biotite granite and (iii) porphyritic biotite granite have been recognized. The medium-grained biotite granite is the most dominant rock in the area, occurring as a hill (ranging from 350-557 m above sea level, especially in Egbe town). The coarse-grained granite is composed of quartz crystals with low relief, microcline and brown biotite (Plate 1 V). Microcline occurs as a large phenocryst, with its cross-hatch twinning characteristics. Modal analysis

shows that quartz constitute (50%), microcline (30%), biotite (15%) and accessory (5%). The pegmatites occur as dykes and pods in the gneisses, schist and granites. In the southern part of the study area, the pegmatites are weathered with conspicuous large muscovite crystals within banded gneiss and schist. Quartz, feldspar, and muscovite are the major minerals in the pegmatites (Plate 2). Lots of the mineralized pegmatites at Okere and Igbaruku are currently being mined for tantalite by artisanal miners. Although several weathered unmineralized pegmatite veins are ranging from 10 to 30 m in length.

### Structures

The lineament was automatically generated from Landsat ETM imagery using the PCI geomatica line module (Fig. 2a) to complement the field data. The lineaments map was followed by the construction of a rose diagram to determine their dominant direction. The lineaments were seen to have a dominant WNW-ESE trend (Fig. 2b). The biotite schist and the banded gneiss were observed to be foliated. In the gneisses, foliation is defined by the parallel alignment of alternating quartz and feldspathic mineral and biotite. The predominant foliation trend was observed to be NE-SW with an average dip of 40°NW. Schistosity is well developed in the schist and the trends are predominantly N-S. An asymmetric fold was observed on the quartz-biotite schist (Plate 2f) while the isoclinal fold was observed on the granite (Plate 2g).

### Geochemistry

The whole-rock geochemical analysis gives information on the elemental concentration. The concentration was used in establishing the geological, geochemical, and geotectonic processes that have taken place in the study area. The oxide concentration of the major element provides the basis for a comprehensive rock classification, while the trace elements including the rare-earth elements (REE) composition were used for

the determination of the petrogenetic and mineralization processes as well as the associated tectonic environment.

The elemental composition of the rocks and minerals in the study area is presented in Table 1a and 1b.

Table 1a: Elemental composition of granites, pegmatites, amphibolite, schist and gneiss of Egbe area

Major elements (All values are in wt. %)												
Sample	Granites					Pegmatites				Amph	Schist	Gn
	CG	P	MG	P	CG	CG	S003	S016	S044			
	S015B	S021	S031	S034	S074	S003	S016	S044	S046	S011	S061	S078
SiO <sub>2</sub>	74.55	70.1	70.09	72.04	70.64	72.60	73.67	74.12	76.50	46.15	71.0	70.04
Al <sub>2</sub> O <sub>3</sub>	13.76	14.7	13.18	14.02	16.40	15.4	15.41	14.25	12.14	12.39	16.0	11.03
Fe <sub>2</sub> O <sub>3</sub>	1.17	3.5	4.25	4.06	4.18	0.9	0.5	1.4	1.74	11.47	2.75	4.32
CaO	0.41	1.8	1.57	1.71	2.07	0.28	3.07	0.41	0.17	1.7	1.37	3.08
MgO	0.33	0.88	0.53	0.65	0.67	0.23	0.43	0.44	0.2	10.6	2.56	1.06
Na <sub>2</sub> O	5.93	2.6	4.73	2.78	2.02	5.47	5.43	7.1	6.5	2.65	2.75	2.54
K <sub>2</sub> O	2.45	2.02	1.44	0.48	0.5	4.53	0.44	1.15	2.21	2.69	2.23	3.34
MnO	0.15	2.08	0.07	0.05	0.07	0.15	0.01	0.23	0.1	0.08	0.05	0.11
TiO <sub>2</sub>	0.01	0.38	0.42	0.5	0.42	0.04	0.01	0.03	0.04	0.45	0.5	0.6
P <sub>2</sub> O <sub>5</sub>	0.16	0.07	0.01	0.10	0.08	0.19	0.11	0.11	0.1	0.11	0.06	0.12
FeO	1.05	1.79	3.7	3.61	3.04	0.22	0.45	0.65	0.3	11.7	2.63	3.76
Total	99.97	99.86	99.99	100	99.99	100.01	99.98	99.89	100	99.99	99.99	100
Trace Elements (all values in ppm except the ratio)												
U	4.7	6.8	6.3	9.1	6.4	0.6	0.9	0.9	0.8	5.9	8.5	10.9
Th	4.7	2.4	2.7	3.6	2.4	0.7	0.3	0.7	1.3	2	0.9	0.2
Sr	13	21.5	32.8	29.5	27.9	15	19	1	1	28.3	19.2	11.7
Bi	0.06	111	98	148	127	0.08	0.04	0.04	0.15	110	63	118
V	1	0.05	0.11	0.04	0.04	1	1	2	1	0.05	0.04	0.2
Cr	9	8	10	31	9	5	7	8	6	12	32	71
Ba	85	10	10	15	11	72	25	7	2	10	16	16
Sn	2.7	6.9	2.7	7.5	2.2	140.2	2.3	62.2	24	2.9	2.6	2
Be	8	2	2	5	3	36	1	6	5	3	2	1
Y	5.4	28.4	43	31	37.6	0.8	1.5	0.2	0.5	40.7	13.2	28.6
Hf	1.48	2	2.8	3.97	2.18	0.33	0.22	0.21	0.45	2.53	4.12	0.65
Li	10.2	52.6	32.8	95.1	32.1	52.1	4.4	173.6	223.1	52.9	14.6	85.2
Rb	675	1350	1046	20	126.1	820.5	36.5	75	1170	112.7	103.1	103.4
Ta	4.3	2.2	1.5	0.9	1.2	44.3	0.5	12.6	18.3	1.5	0.6	0.4
Nb	22.8	22.4	29.3	22	26.6	35.3	1.7	88.7	84.3	28.9	9.4	8.4
Cs	400	800	908	24	24	640	34	30	840	5.2	2.5	2.2
Ga	24.29	20.91	21.33	20	24.57	39.82	10.9	55.48	29.03	20.65	16.86	17.04
Ta/Nb	0.19	0.10	0.05	0.041	0.04	1.26	0.29	0.14	0.22	0.05	0.06	0.05
K	20332	16763	11950	912.9	4149	37593	3651	9544	18340	22324	18506	27884
K/Rb	30.12	12.42	11.42	45.64	32.91	45.82	100.03	127.2	15.68	198.1	179.5	269.7
Rare-earth elements (all values in ppm)												
La	1.3	88.6	137.4	94.5	124.8	6.84	17.2	15	3.20	126.7	24.5	27.4
Ce	2.9	162.8	250.9	140.8	241.8	0.16	81	70	0.3	247.6	50.9	73.5
Pr	0.4	17.8	28.3	20.2	25.5	0.5	0.4	0.3	0.1	26	6.2	8
Nd	1.6	64.7	92.1	69.3	90.3	0.6	13.8	44.7	0.8	94.8	21.1	26.2
Sm	0.8	10.4	17.5	13.1	14	3.2	2.5	5.4	2.3	15	4	5.8
Eu	0.1	1.8	1.8	1.4	2.2	0.02	0.5	0.8	0.02	2	0.7	1
Gd	0.6	7.3	12.5	10	10.5	4.2	2.4	5.2	5.2	11	3.7	5.8
Tb	0.2	1.1	1.6	1.2	1.4	0.1	0.4	0.9	0.1	1.5	0.5	1
Dy	1.1	6.2	9.4	6.7	8.1	0.1	0.5	0.4	0.2	9.2	2.8	5.5
Ho	0.2	1.1	1.6	1	1.5	0.1	0.7	0.3	0.3	1.7	0.5	1.2
Er	0.5	2.9	4.3	2.5	3.6	0.1	0.2	0.3	0.1	3.9	1.3	3.9
Tm	0.1	0.4	0.6	0.3	0.5	0.1	0.1	0.1	0.2	0.6	0.2	0.5
Yb	0.8	2.6	3.7	2.1	3.5	0.3	0.8	3.3	0.1	3.7	1.3	3.4
Lu	0.1	0.4	0.5	0.3	0.5	0.1	0.1	0.2	0.2	0.5	0.2	0.5

Table 1b: Elemental composition of muscovite, albite, and lepidolite from Egbe pegmatites

Major elements (wt. %)							
Sample	Muscovite					Albite	Lepidolite
	S001	S002	S070	S071	S077C	S077E	S077G
SiO <sub>2</sub>	64.95	61.71	63.2	64.58	63.04	72.47	63.98
Al <sub>2</sub> O <sub>3</sub>	18.98	24.14	18.52	21.67	14.06	17.93	20.14
Fe <sub>2</sub> O <sub>3</sub>	7.62	5.85	6.9	5.59	8.07	4.12	5.33
CaO	0.03	0.04	0.03	0.03	1.03	0.03	0.03
MgO	0.28	0.41	0.2	0.12	0.03	0.25	0.03
Na <sub>2</sub> O	0.35	0.85	0.68	0.52	2.53	0.42	0.55
K <sub>2</sub> O	4.63	3.9	5.63	5.44	5.34	3.96	6.58
MnO	0.13	0.11	0.06	0.05	0.01	0.21	0.35
TiO <sub>2</sub>	0.01	0.12	0.05	0.03	0.12	0.6	0.07
P <sub>2</sub> O <sub>5</sub>	0.02	0.04	0.03	0.03	0.08	0.01	0.02
FeO	5.34	3.66	4.7	3.42	5.64	3.69	3.29
Total	99.69	99.82	99.93	99.4	99.95	99.76	99.96
Trace elements (all values in ppm)							
Mo	0.05	0.05	0.05	0.08	0.05	0.05	0.12
Cu	1.13	0.71	3.18	0.53	0.02	0.78	2.23
Ni	4.5	10.8	3.9	2.8	0.8	913.7	95.3
Sr	2	4	2	1	3	0.1	0.1
Cr	3	19	9	4	3	5	2
Ba	51	43	21	11	11	4	2
Sn	493.5	514.5	424.7	555	2.9	866.9	114.2
Be	19	19	18	20	3	19	34
Sc	1.5	2.4	0.9	0.3	0.4	2.5	0.2
Y	0.1	0.1	0.1	0.1	0.2	0.1	0.1
Hf	0.24	1	0.4	0.15	0.05	0.23	0.18
Li	3200	1344	551.2	452.6	182.7	3600	3100
Rb	4000	2700	3800	3600	1392.3	3900	3900
Ta	125.4	155.8	61.4	123.1	0.8	337.6	123.6
Nb	107.1	80.6	153.9	88	1.5	45.8	28.7
Cs	345.7	309.2	149.7	371.1	148.3	81.4	2700
B	-	18	15	25	16	29	-
F	-	8290	3190	3800	210	10000	-

All the rocks and minerals exhibit high SiO<sub>2</sub> content, but considerably lower in the amphibolite. There is significant variation in the trace elements concentration amongst the rocks and minerals. Albite, lepidolite, and muscovite show significant enrichment in Li, Rb, and Cs (especially in lepidolite) compared to other rock types. The enrichment of Li in albite, lepidolite, muscovite, and pegmatite is attributed to the fact that Li would preferentially enter into the late crystallizing minerals due to the greater ease of maintaining charge balance – electrostatic attraction. Muscovites are relatively enriched in F, but albite has the highest concentration of F and B. This indicates that Ta- mineralization was associated with highly fluxed melt. A lower concentration of B may be due to its removal to form schorl.

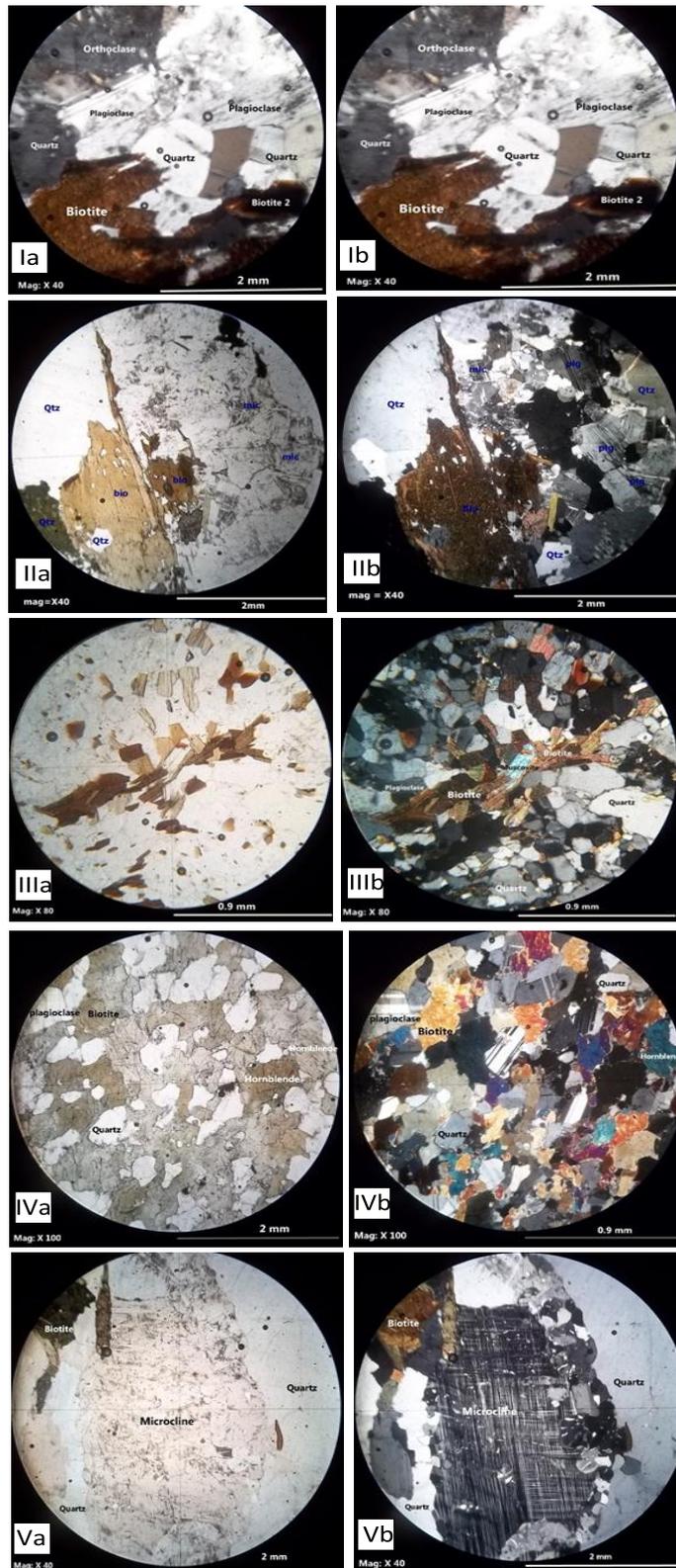


Plate 1: Representative photomicrographs.

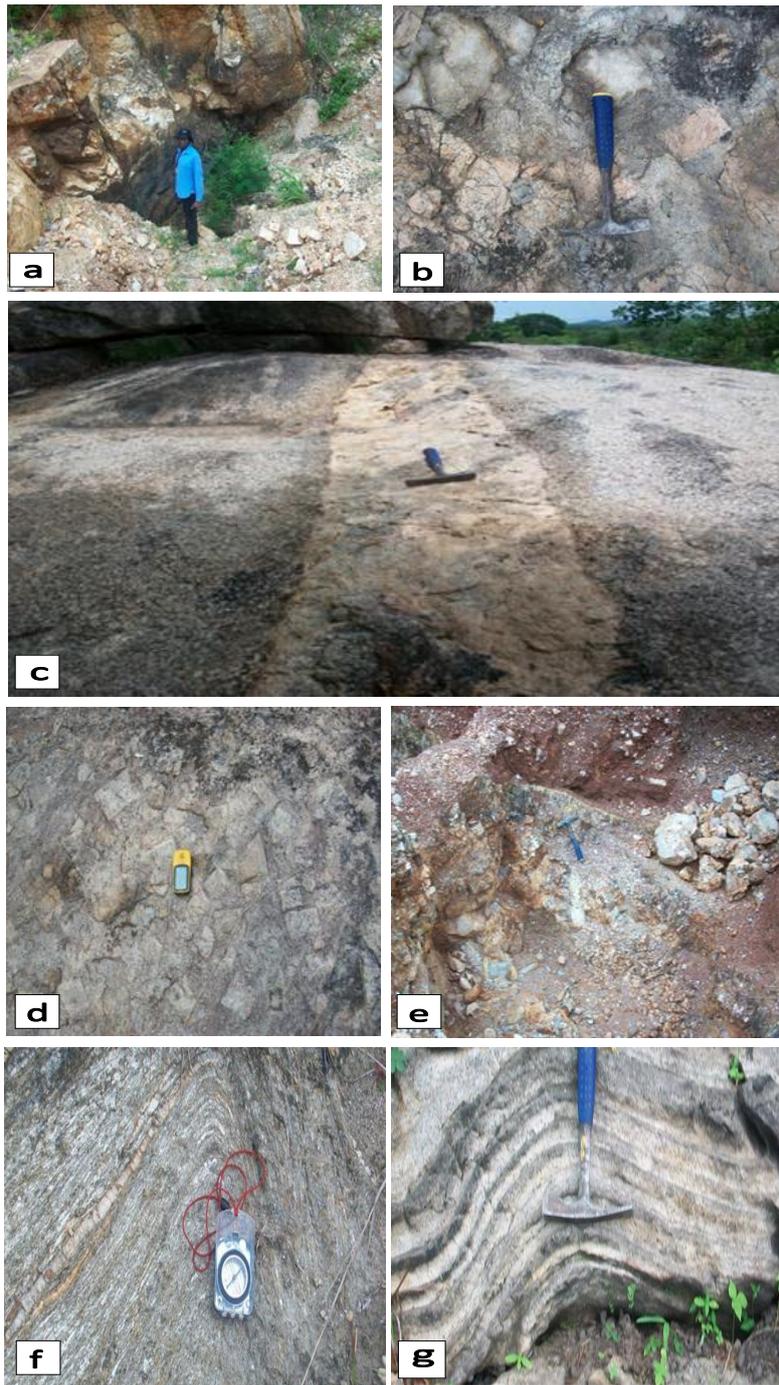


Plate 2: Photograph of pegmatite zones. (a) Abandoned pegmatite field from which tantalite was mined (b) Pegmatite with large quartz and feldspar (a and b are located at  $08^{\circ} 12' 38.1''\text{N}$ ,  $05^{\circ} 35.1' 08.5''\text{E}$ ). (c) Pegmatite vein of 10 cm width in medium to coarse grained granite at Okere ( $08^{\circ} 10' 37.6''\text{N}$ ,  $05^{\circ} 30' 38.1''\text{E}$ ). (d) A complex pegmatite with phenocryst of plagioclase feldspar at Iyameri (e) Pegmatite vein being exploited for tantalite at Igbaruku ( $08^{\circ} 12' 38.1''\text{N}$ ,  $05^{\circ} 35.1' 08.5''\text{E}$ ). (f) Asymmetrical fold in weathered schist at Igbaruku ( $08^{\circ} 14' 48''\text{N}$ ,  $05^{\circ} 34' 0''\text{E}$ ). (g) Isoclinal fold in banded gneiss at Okere ( $08^{\circ} 10' 45.3''\text{N}$ ,  $05^{\circ} 33' 34.4''\text{E}$ ).

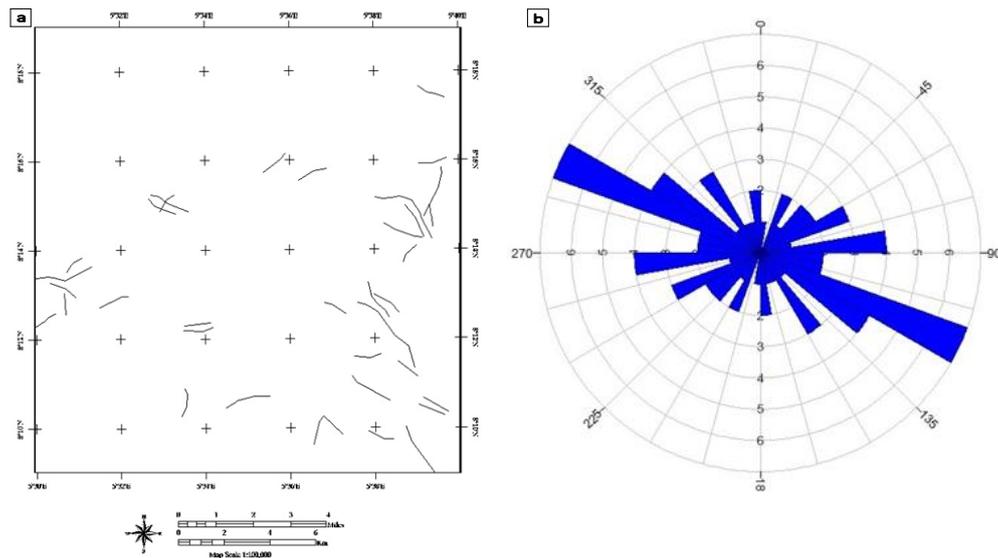


Figure 2: Structural trend of the study area (a) Lineament map (b) Rose diagram for the dominant structural trend.

The granites are metaluminous to peraluminous (Fig. 3). The granites plot largely in the fields of volcanic arc and syn-collisional granites (Fig. 4). They mostly plot on the field of S-type granitoids (Fig. 5), which suggests that the granites probably stem from the anatexis of schist or aluminous gneisses of sedimentary origin and could be parental to the rare-metal pegmatite in the Egbe area.

The REE pattern for amphibolites, schist, gneiss, porphyritic granite displayed enrichment in light rare-earth elements and depletion in heavy rare-earth elements with a negative Eu anomaly (Fig. 6). Enrichment of LREE relative to HREE in samples is probably caused by the presence of hornblende in the felsic melt (Rollinson, 1993) while negative Eu anomaly is due to fractionation of plagioclase in the melt.

The chondrite normalized plot for pegmatite (Fig. 7) reveals that the rare-metal pegmatites exhibit pronounced negative Ce and Eu anomalies while the barren pegmatites have positive Ce and weak negative Eu anomalies. Rare-metal pegmatites also show weak negative Yb anomaly and the barren ones exhibit weak positive Yb anomaly.

### The mineralization potential of the pegmatites

The pegmatites are fractionated, and the barren class is differentiated from the rare-metal class (Fig. 8), the Okere and Igaruku pegmatites plot within the rare-metal pegmatites while the pegmatites in Egbe and a few others in Igaruku are barren pegmatite. Based on the proposition of (Beus, 1966), one muscovite sample plotted below the mineralization line, while four muscovite and feldspar fell above the mineralization line (Fig. 11). But, based on the (Gordiyenko, 1971) mineralization line, two muscovite samples plotted below the mineralized line. However, the three muscovite and the feldspar samples (extracted from the Okere and Igaruku pegmatites) plot above the mineralization line which is indicative of rare-metal mineralization in the pegmatites. The mineralized Okere and Igaruku pegmatites show similar geochemical trends to their host granite. The fractionation trend from the granites to the pegmatites reveals Rb enrichment increases from granites to pegmatites while the Barium decreases from granites to pegmatites (Fig. 9). According to (London, 2018) substantial chemical fractionation accompanies evolution from granite to pegmatites, as this can be seen in

the Nb/Ta versus Ta discrimination diagram (Fig. 10).

The composition of the tantalite-columbite is generally controlled by Fe-Mn substitution during fractional crystallization, progressing from ferrocolumbite ( $\text{FeNb}_2\text{O}_6$ ) to manganotantalite ( $\text{MnTa}_2\text{O}_6$ ) (Černý et al., 1986). The Nb-Ta content of columbite group minerals can be related to that of micas that coexist with them (Van Lichtenvelde et al., 2007). The Egbe pegmatites fractionation started from Mn-poor ferrocolumbite towards slightly Mn- and Nb-enriched

manganotantalite and finally to manganotantalite in the more evolved lepidolite (Fig. 12). The solubility of Fe-rich member of the columbite group mineral in a melt is higher than that of Mn-rich, thus the Fe-rich group will be enriched over that of Mn-rich (Linnen & Cuney, 2005). However, the enrichment of the Fe-rich group is controlled by the presence of other Fe-bearing minerals such as tourmaline and biotite evolution (London, 2018). According to (Černý & Ercit, 1985), Ta-dominant species are restricted to the most highly fractionated complex type of rare-element pegmatite.

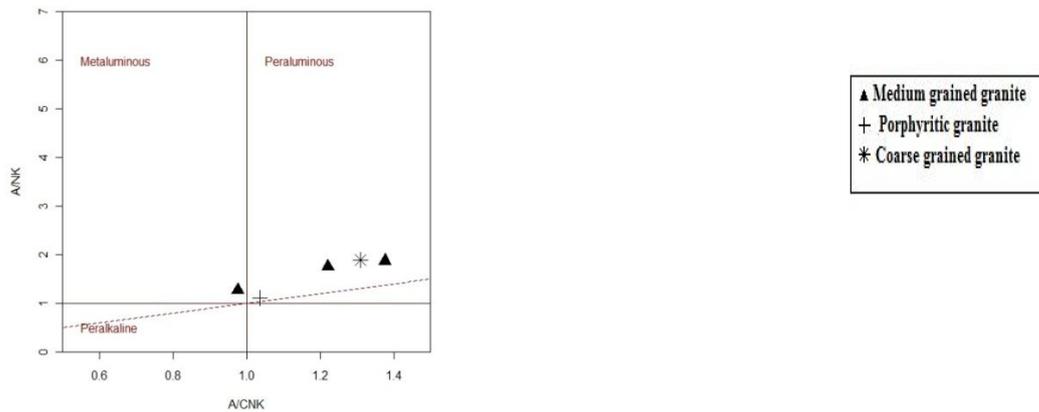


Figure 3: Chemical classification of the granitic rocks using the molecular ratio of alumina to alkalis  $[\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{K}_2\text{O})]$  versus alumina to lime and alkalis  $\text{Al}_2\text{O}_3/(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$  discrimination diagram (after (Shand, 1947)

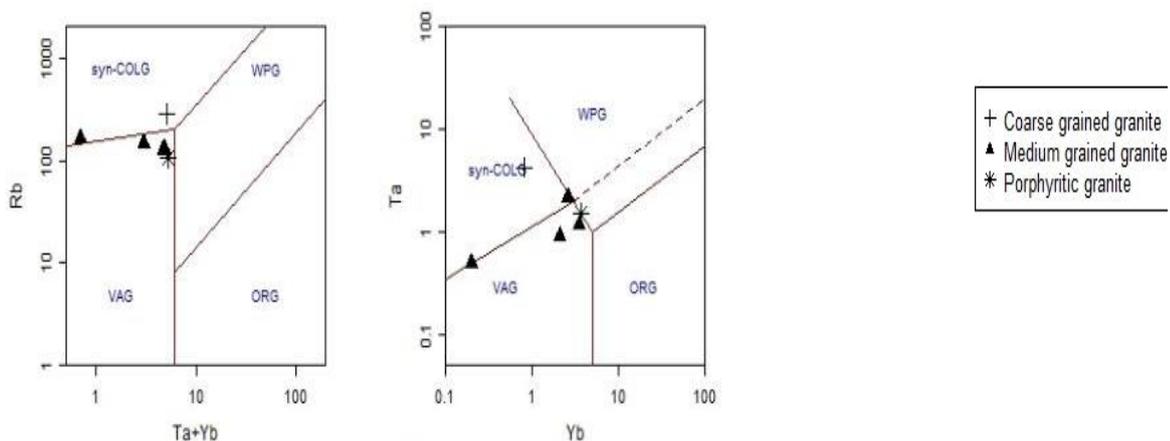


Figure 4: Plots of granites on tectonic discrimination diagrams of (Pearce et al., 1984). Abbreviations: ORG - oceanic ridge granites; COLG - collision granites; VAG - volcanic arc granites and WPG - within plate granites

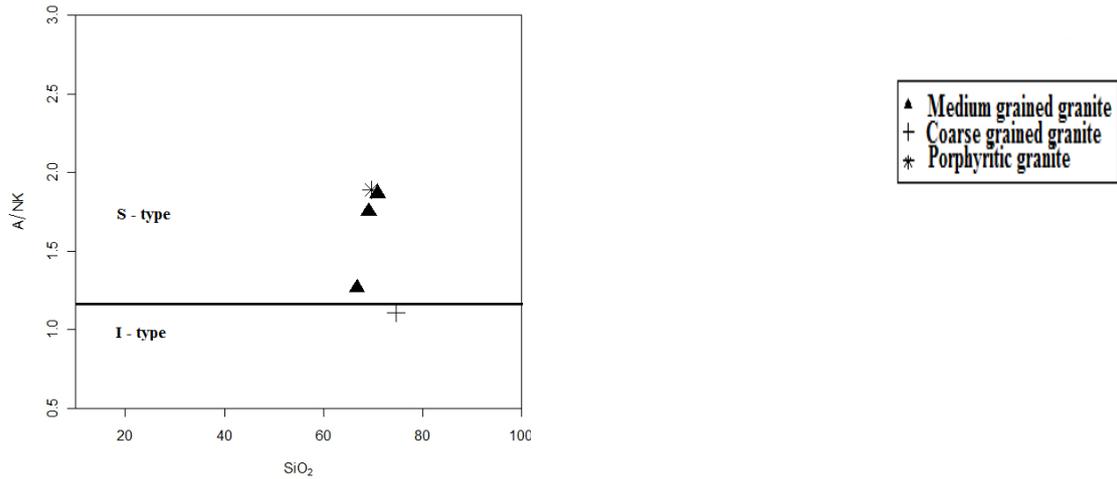


Figure 5: Molecular  $Al_2O_3/CaO+Na_2O+K_2O$  versus  $SiO_2$  diagram showing the classification of the granite into S-type and I-type granitoids (after (White & Chappell, 1977).

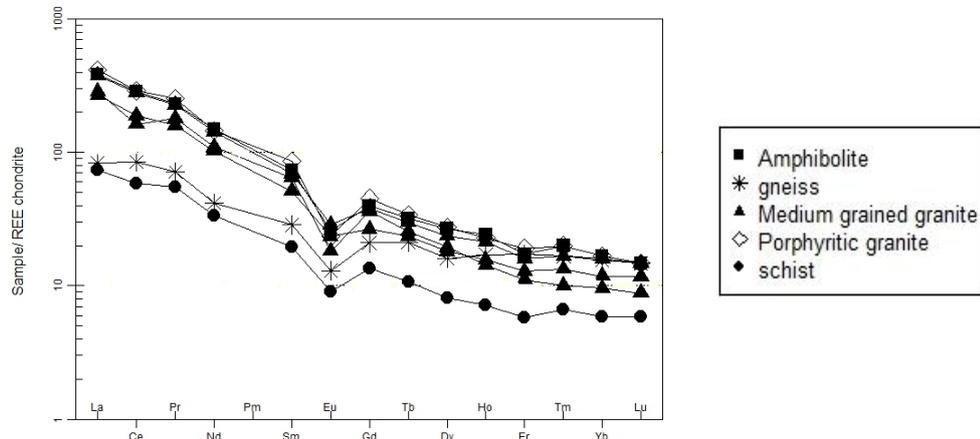


Figure 6: Chondrite normalized plot of the rare-earth elements (after(Nakamura, 1974)

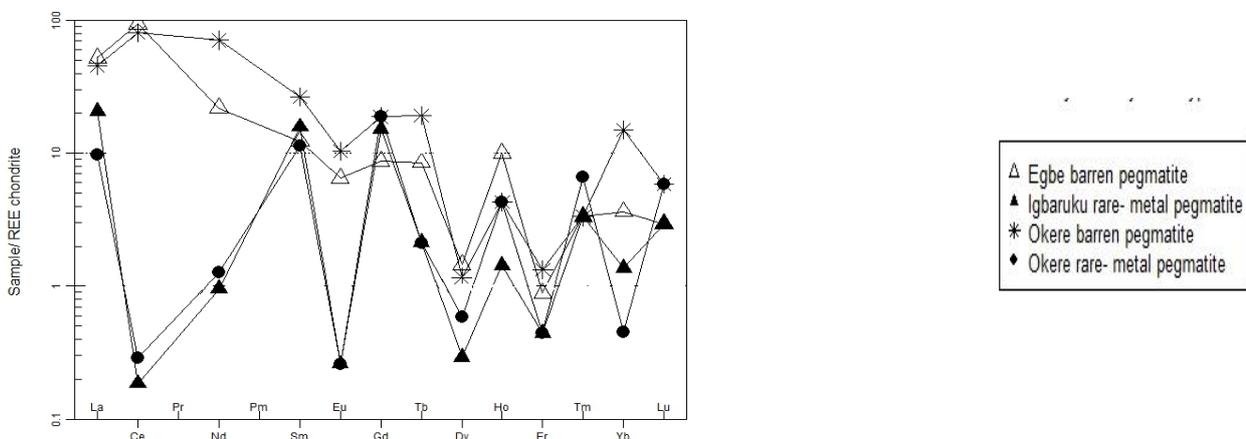


Figure 7: Chondrite normalized plot of the rare–earth elements (REE) for the pegmatites (after (Nakamura, 1974).

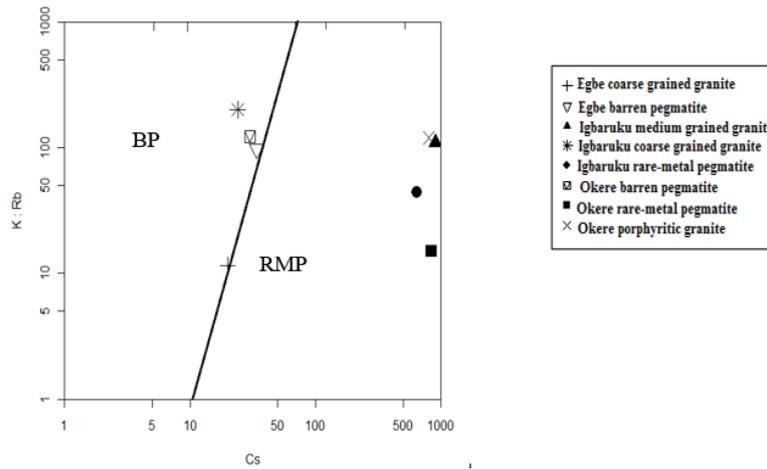


Figure 8: K/Rb versus Cs discrimination diagram showing the degree of fractionation and mineralization of the pegmatites. The discrimination line separates the field of rare-metal pegmatites (RMP) from the barren class (BP), (adapted from(Cerny & Burt, 1984).

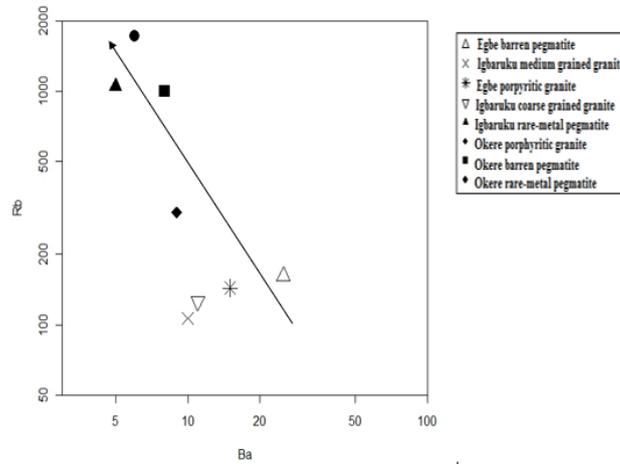


Figure 9: Rb versus Ba plot in granites and pegmatites from the study area (Adapted from(Taylor & Heier, 1960).

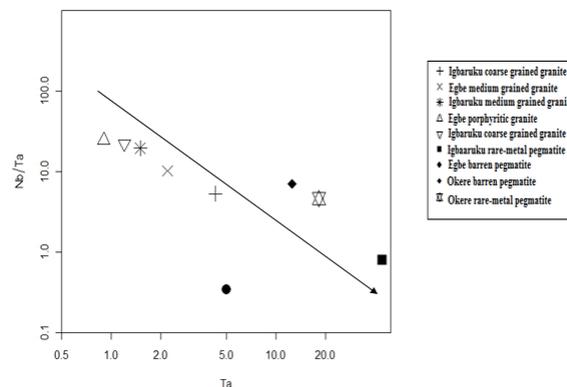


Figure 10: Nb/ Ta versus Ta showing fractionation trend from granites to pegmatites in the study area (adapted from(London, 2018).

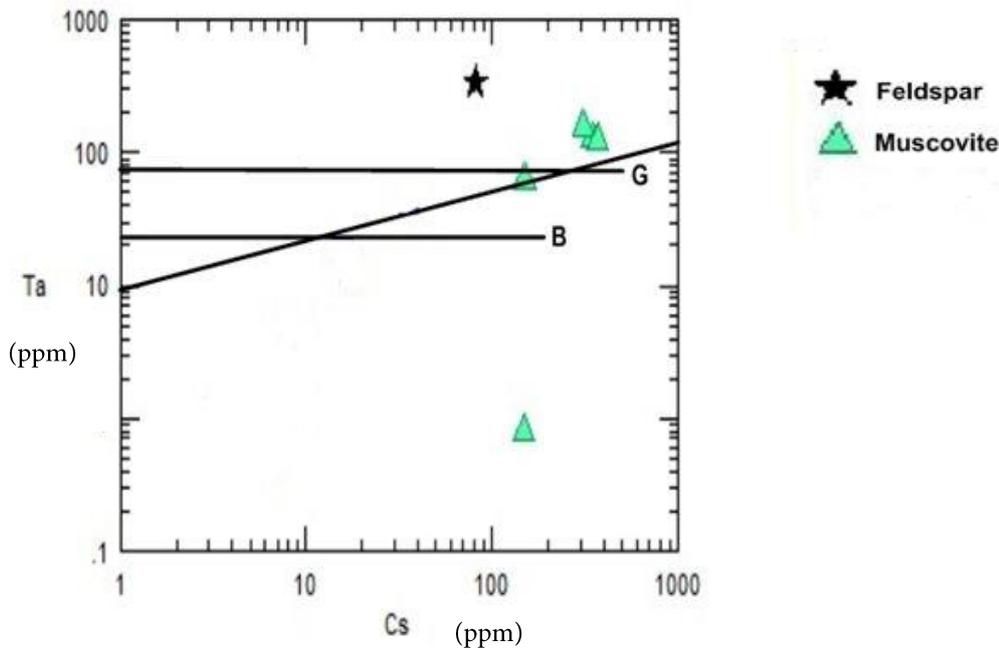


Figure 11: Plot of Ta versus Cs in feldspar and muscovite (in mineralized pegmatites) from the study area [adapted after (Beus, 1966; Gordiyenko, 1971) Beus, 1966 (B) and Gordiyenko, 1971 (G)]

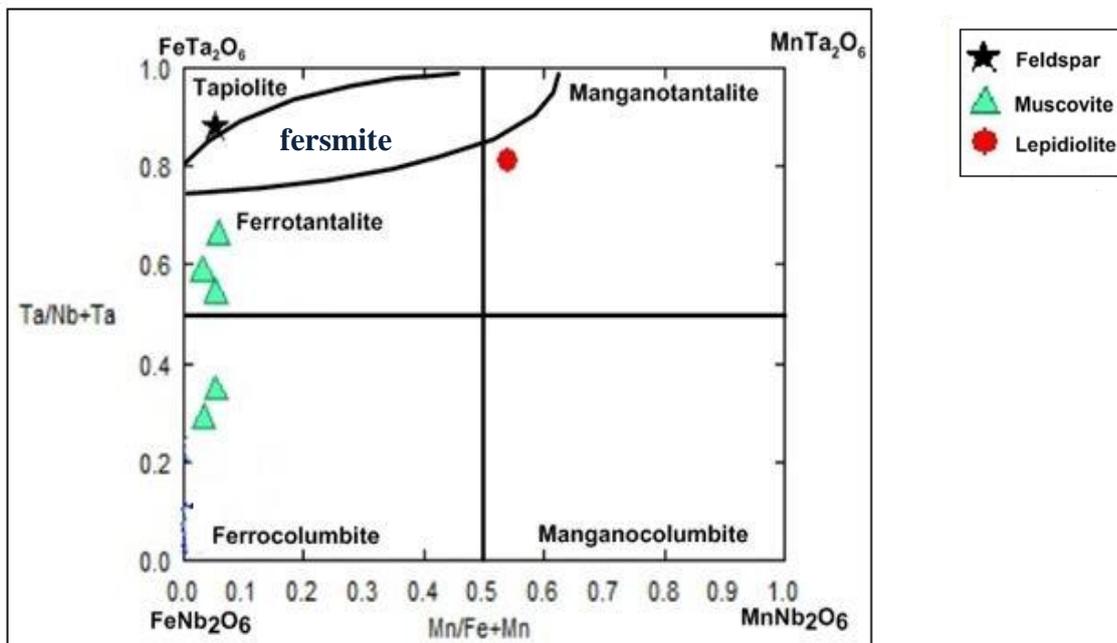


Figure 12: Chemical composition of  $FeTa_2O_6 - FeNb_2O_6$  in feldspar, muscovite, lepidolite, and lepidolite (adapted from (Černý & Ercit, 1985)).

**DISCUSSION**

The geochemical study revealed that the granites are metaluminous to peraluminous and are mainly S-type granites formed from the anatexis of schist or aluminous gneisses

of sedimentary origin. In addition to the major and minor element compositional features, consistent negative Eu signature of chondrite normalized REE plots suggest the possibility of pegmatites being derived from anatexis of undepleted upper to middle crustal

protoliths or supracrustals with possible later metasomatic alteration. The original sedimentary rock probably comprises mostly of clay-rich material produced by extensive chemical weathering of continental rocks (Chappell & White, 2001). These sedimentary rocks could therefore be the source of the fertile granites from which the rare-metal pegmatite hosting columbite-tantalite mineralization in the study area was derived.

REE distribution pattern revealed enrichment in light rare-earth elements (LREE) with negative Eu anomaly in amphibolite, schist, and porphyritic granites, while the medium-grained granites and coarse-grained granite display an almost equal enrichment of light and heavy REEs with negative Eu anomaly. Enrichment of LREE can be attributed to the presence of hornblende in felsic melt while a negative Eu anomaly is due to fractionation of plagioclase in melts. The granites also show a strong affinity to the volcanic arc and syn-collisional tectonic setting. This feature appears to be the hallmark of all the Nigerian Pan-African granites which formed as a result of the convergence of lithospheric blocks during the Pan-African orogeny.

The mineralized and barren pegmatite bodies are associated with the granite suites in the study area. The barren pegmatites are characterized by low Rb, Cs, Ta, and Nb but high Ba, Sr, and K/Rb. This suggests that the pegmatite formed from less fractionated/primitive granitic melt. The rare-metal pegmatites on the other hand are chemically enriched in Rb, Cs, and Ta. These pegmatites are however depleted in Ba and Sr, thus indicating that the pegmatite is a product of progressive fractionation. Late-stage progressive fractional crystallization leads to enrichment in Rb and depletion of Ba in these pegmatites. The negative Europium (Eu) anomaly suggests fractionation and indicates a late metasomatic effect, while the negative Ce anomaly observed in the pegmatites may also suggest they are rare metal mineralization (Taylor et al., 1986).

Similarly, (Garba, 2003b; Piper, 1974) believe that the Negative Ce anomaly of the rare metal pegmatite is taken to indicate oxidizing conditions during mineralization and interaction between magmatic fluids and host rocks over a long distance. The pegmatites are fractionated, and the K/Rb versus Cs discrimination diagram revealed that pegmatites from Egbe and few pegmatites from Okere area plot in the field of barren pegmatite, while the pegmatites from Igaruku area and few others from Okere plot within the field of rare-metal pegmatite. The plot of the mineralized pegmatites on the commonly used (Gordiyenko, 1971) discrimination diagram revealed that the mineralized pegmatites in the study area have a high potential for tantalite since most of the muscovite extracted from the pegmatites plot above the minimum cut-off point of tantalite mineralized pegmatites. The enrichment of Ta, Cs in these pegmatites and their association with some peraluminous S-type granite suggest that they have affinities with the Lithium-cesium-tantalum (LCT) pegmatite family which is typically considered to comprise the most highly fractionated part of S-type or peraluminous granitic suites formed during crustal thickening (Černý et al., 2012). Geochemical data obtained from the muscovite and lepidolite indicate that they are enriched in Li, Rb, Ta, F, Sn, and Cs.

The geochemical characteristics of the rare-metal pegmatites of the Okere and Igaruku areas which are hosted by the schist and gneiss are unlike those of metamorphic origin, such as the barren pegmatites of the Egbe areas. Rather, they appear to be highly fractionated granitic pegmatites. Of great importance is the distinct enrichment of Rb, Cs and in many, in the rare-metal pegmatites relative to the barren types and the Pan African granitoids. The most enriched sample in Nb and Ta from the study area is Lepidolite from Okere and the economic mineral is tantalite. The systematic fractionation trends from granites to pegmatite (Fig. 8) and the peraluminous

nature of these pegmatites and the surrounding granites suggest that both the pegmatites and the surrounding granites were sourced from the melting of a strongly peraluminous sedimentary/metasedimentary protolith.

## CONCLUSION

The Egbe area is underlain mainly by rocks of the basement complex, comprising banded gneiss, schist, amphibolites, granites, and pegmatite. The foliation trend varies between NW-SE and NE-SW. The structures within the area indicate evidence of the Pan-African thermo-tectonic effect.

The study area has a high potential for columbite-tantalite mineralization. The tantalite-columbite mineralization is associated with the NE-SW trending pegmatite dykes. The Ta and Nb contents of Egbe pegmatites are low compared to Tanco pegmatite in Canada but are comparable to those of Nassarawa-Keffi (Wamba) pegmatite field of Nigeria, Wodgina pegmatite of Australia, Hergendorf pegmatite of Western Germany, and Noumas pegmatite of South Africa. The Egbe pegmatite is more enriched in Ta than the Jemaa (Kaduna) and Ijero (Ekiti) pegmatite fields of Nigeria. Based on the field relationship and geochemical study, these mineralized pegmatites are genetically linked to the peraluminous S-type granite. The geochemical studies of the muscovite (extracted from the pegmatites) indicate that the pegmatites are siliceous with a peraluminous composition. The pegmatites are moderately evolved compared with other highly mineralized pegmatites. Low Cs and K/Rb are indications of low-moderate enrichment. The Chondrite normalized plot of the rare-earth element (REE) for amphibolites, schist, gneiss, and porphyritic granite shows a negative Eu signature suggesting fractionation of plagioclase in the melt.

The pegmatites from Igaruku and one from the Okere plot in the field of rare-metal pegmatite are moderately fractionated. While the pegmatite from Egbe and one from Okere

plot in the field of barren pegmatites and are unfractionated. The chondrite normalized plot of REE of the barren pegmatites showed positive Ce and weak positive Yb anomaly and pronounced negative Eu anomaly. The possibility of tantalite-columbite enrichment in the study area is ferrotantalite-columbite and mangano-tantalite columbite.

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