GEOLOGY AND GEOCHEMISTRY OF TANTALUM - NIOBIUM MINERALISATION IN EGBE RARE - METAL ENRICHED PEGMATITES, PART OF ISANLU (SHEET 225) SOUTHWEST, NIGERIA

BY

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER OF SCIENCE DEGREE IN GEOLOGY

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DECLARATION

I declare that the work in this thesis "Geology and Geochemistry of Tantalum - Niobium Mineralisation in Egbe rare - metal enriched pegmatite, Part of Sheet 225 Southwest, Nigeria" has been carried out by me in the Department of Geology. The information derived from the literature has been duly acknowledged in the text and list of references provided. No part of this thesis was presented for another degree or diploma at this or any other institution.

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Name of student	(Signature)	Date

CERTIFICATION

This Thesis titled GEOLOGY AND GEOCHEMISTRY OF TANTALUM - NIOBIUM MINERALISATION IN EGBE RARE – METAL ENRICHED PEGMATITES, PART OF ISANLU (SHEET 225) SOUTHWEST; NIGERIA**,** by JOSE ADOZE USMAN meets the regulations governing the award of degree of Master of Science in Geology of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to my mother, USMAN KHADIJAT ONAYI, who was not opportuned to enjoy the fruit of her sweat before she departed.

ABSTRACT

The pegmatite of Egbe area which has been known to bear valuable economic minerals and associated with other rock types like banded gneiss, schist, amphibolite and granites were investigated with a view to elucidating their petrochemical and geochemical features that may be related to economic rare metal Ta-Nb mineralization in the area

Geological field mapping of the study area was carried out by collecting various rock types, observing their field occurrences, structural components and hand specimen observation.

Thin sections of ten representative rock samples were prepared and studied for petrographic analysis. Twenty whole rock (four pegmatites, five granites, one banded gneiss, one amphibolites, one Schist) samples, five muscovite samples extracted from the pegmatites, One albite and lepidolite were analyzed for major and trace elements including REES using the Inductively Coupled Plasma Mass Spectrometry(ICP-MS) analytical method, Boron- fusion – Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for Boron and Ion selective Electrode (ISE) for Fluorine at Acme Laboratory, Vancourva, Canada.

Geochemical studies indicated that the pegmatites and the other rock types in the study area are siliceous and peralkaline. The general structural trend in the study area is WNW – ESE direction and foliation with a N – S strike direction was observed in the banded gneiss and schist. Two types of folds, namely, asymmetric and isoclinals were recorded in the banded gneiss and schist respectively. Geochemical analysis revealed that the pegmatites are siliceous and of rare – metal type. The granites are peraluminous and of S – type. Albite, lepidolite and muscovites (extracted from the pegmatites) are significantly enriched in Li, Rb Cs, Nb and Ta compared to the granites, gneiss, schist and amphibolites. The granites showed strong affinity to the sncollisional and volcanic arc granites with an enrichment LREE and a depletion in HREE with a strong negative

Eu anomaly. the rare-metal pegmatites exhibits 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 low K/Rb ratio of the pegmatites indicates fraction accompanied by Rb enrichment and Ba depletion. In Egbe pegmatites, fractionation started from Mn- poor ferrocolumbite towards a slightly Mn- and Nb- enriched manganotantalite and finally to manganotantalite in the more evolved lepidolite. The economic mineral in Egbe area is tantalite.

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CHAPTER ONE

GENERAL INTRODUCTION

1.1 INTRODUCTION

Tantalum and niobium are the ore elements found together in the theoretical end-members of a solid solution series called tantalite (Ta_2O_5) - columbite (Nb_2O_5). These elements are geochemically associated and are found together in most rocks and minerals in which they occur. The principal reason for such coherency are the similarity in ionic radii and valency states of these elements (Ta^{+5}=0.68A and Nb^{+5}=0.69A), which are fundamental parameters controlling their entry into crystal structures of minerals. It has been recognized that economic deposits of tantalite - columbite are commonly associated with rare-metal pegmatites (Černý and Ercit, 2005). The rare-metal pegmatites, petrochemically belong to Li, Cs and Ta (L-C-T)-family (Černý 1991; Černý and Ercit, 2005) and are known to be derived from fertile granites (Breaks *et al*., 2003).

Pegmatite–forming melts with the potential for crystallizing tantalite - columbite originates mostly during the crystallization of a parental granitic melt or fertile granite. As the granitic melt initially crystallizes barren granite which is composed of common rock forming minerals (such as quartz, potassium feldspar, plagioclase, and mica), the residual melt is progressively enriched in incompatible (rare) elements such as Be, B, Li, Rb, Ta, Nb, Mn, Sn. H_2O and fluxing components such as B, P, Li and F also increase in late–stage granitic melt. The volatile components and the fluxes lower the viscosity and solidification temperature, inhibit crystal nucleation, and greatly enhance chemical diffusion within the melt. If the concentration of the volatiles, mainly H_2O, of the remaining residual melt exceeds its solubility limit, an aqueous fluid exsolves from the melt and promote 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 (Simmons *et al*., 2003; London, 2008).

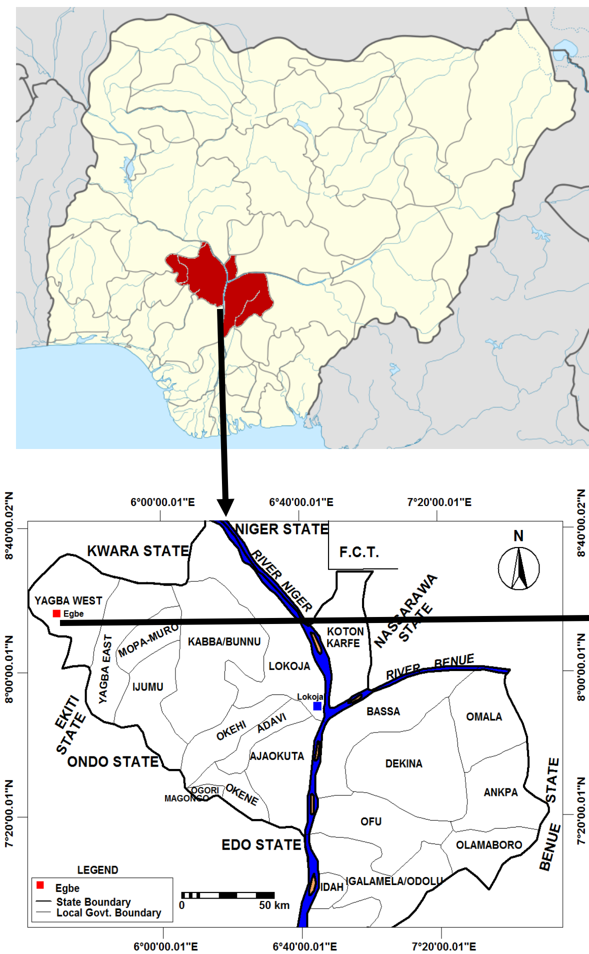
Two dominant styles of tantalite - columbite mineralization, namely, magmatic and metasomatic have been proposed by Černý P.(2005); Van Lichtervelde *et al*., (2007) and Linnen *et al*., (2012). The field indicators for tantalite - columbite minerals are crystal habit, streak, mineral association and specific gravity (Table 1.1).

Table 1.1: Properties of tantalite - columbite minerals

Colour	Luster	Crystal system	Cleavage	Mohs hadness value	Specific gravity	Streak
Iron black to dark brown	Sub-metallic to almost resinous	Orthorhombic	One direction with sub conchoidal fracture	6 – 6.5	8.0	Brownish to black

1.2 LOCATION AND ACCESSIBILITY

The study area is located in the western part of the present Kogi State (Egbe area). It is bounded by latitudes 8^{o} 09′ and 8^{o}19′ N and longitudes 5^{o} 30′ and 5^{o} 40′ E (Fig. 1.1). It covers an area of approximately 342.25 km^2. The area is fairly accessible by network of major, minor roads and footpaths. Accessibility is much better during the dry season when the grasses are usually dry or burnt.



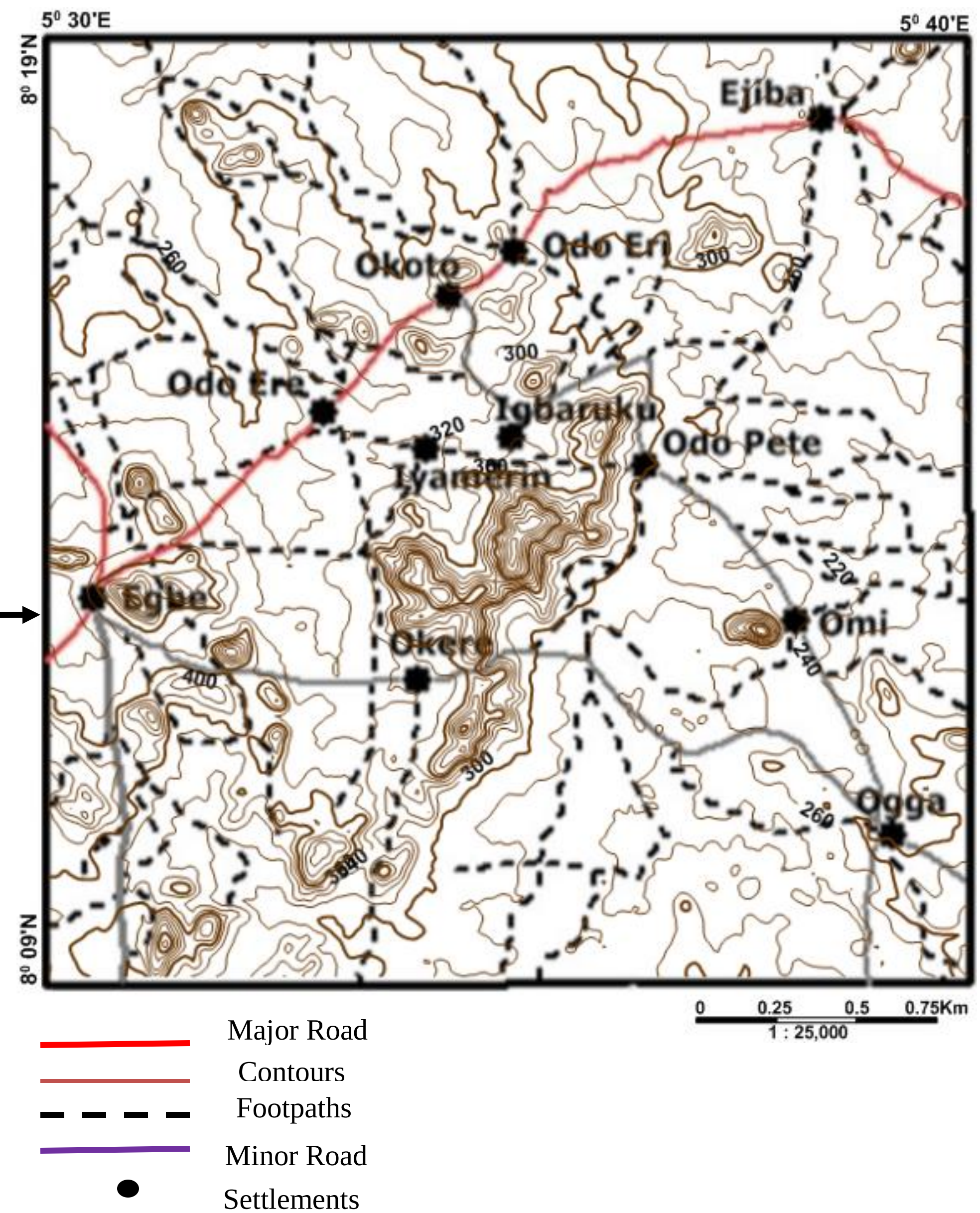


Figure 1.1: Location Map of the study Area

1.2 RELIEF AND DRAINAGE

Generally, the relief of the area is moderate with gentle rolling terrain and flat plains. Massifs and round topped hills are common with the highest peak being 1946 meters above the sea level in the central and southwestern parts of the study area. The south and northern part of the area are relatively low lying with average height of 750 metres above sea level. River Kampe, with its tributaries (River Oyi and River Origi) is the main river draining the area. Other rivers which drain the northwestern part of the area are River Ofili and River Ofe. Several stream channels cut across the terrain with most streams draining into River Kampe. In general the drainage pattern is dendritic.

1.4 PREVIOUS WORK

Earlier study of Pegmatites in Nigeria include the work of Jacobson and Webb, (1946) which identified that the pegmatites are of the complex category and also that the rare-metals pegmatites of Nigeria are confined to a 400 km long NW-SW trending belt stretching from Wamba area in central Nigeria to Ibadan area southwest Nigeria. This point of view was refuted by the work of Garba, (2003) and Okunlola, (2005). The occurrences in the Southeastern part of Nigeria, notably around Obudu hills were presumed to extend into Northeast Brazil (Garba, 2003, Ekwueme, 2004). The Nigerian pegmatites evolved during the time span of 600+530Ma, (Matheis and Caen Vachette, 1983), which indicates formation (Orogeny) during the periods of Pan African magmatism.

Ta – Nb (± Sn) pegmatites are hosted by rocks of the Pan – African basement complex. Many areas have been reported by Jacobson and Web (1946), Matheis and Caen – Vachette (1983), Kuster (1990), and Garba (2002) from central, northwest, southwest and southeast Nigeria.

Matheis, (1981), Matheis *et al.,(*1982)., Kuster, (1990)., Garba, (2003), Okunlola, (2005) classified the metallogeny of the rare metal Ta-Nb pegmatites of Nigeria, outlining 7 broad fields namely Kabba - Isanlu, ljero - Aramoko, Keffi- Nasarrawa, Lema -Ndeji, Oke Ogun, Ibadan -Osogbo and Kushaka - B/Gwari (Fig. 1.2). Akintola, *et al.,* (2011), in his work on the Petrographic and Geochemical Evaluations of Rare – Metal (Ta-Nb) Potentials of Precambrian Pegmatities of Awo Area Southwestern Nigeria, noted that the Precambrian pegmatites of Awo area which intruded the granite, banded gneiss, quartzite and quartz schist, are rare-metal pegmatites types. They are of the LCT petrogenetic family (Rb, Cs, Be, Li, Ga, Sn, Ta < > N (BPF) and of the Beryl sub type.

Omada., *et al*.,(2014), in his study of pegmatite bodies in parts of Lokoja, Central Nigeria, noted that the mineralogy and composition of the pegmatite bodies are indicative of post tectonic anorogenic acidic igneous protolith which underwent alkali metasomatism involving selective enrichment of trace elements and REE, fractionation and rock–fluid interactions.

In their study on the Post-collisional Pan-African granitoids and rare metal pegmatites in western Nigeria, Goodenough *et al*., (2014), were of the opinion that the LCT-type pegmatites were emplaced during the last magmatic event in western Nigeria. Some of these pegmatites, which evidently post-date the peraluminous granitoid plutons are enriched in tantalum and niobium and were, on the basis of current evidence, emplaced at c. 560–450 Ma.

Several studies had been carried out in Egbe area especially in the search for economic gold mineralization by many workers. There is need, however, for indepth investigation on tantalum – niobium mineralization in this area in order to determine the source of the metals, style and character of the mineralization and the associated rocks.

1.5 STATEMENT OF RESEARCH PROBLEM

The increase in the global demand for tantalum and niobium has led to a renewed interest in the search for economically viable deposits. Egbe area has been known to host a number of pegmatite bodies (Matheis. G., 1987) some of which are being mined for coltan. There are, apparently, both mineralized and barren pegmatites in the area and therefore discriminating between these types of pegmatites will assist exploration efforts in the search for rare – metal mineralization in the area. Similar pegmatites which occur in northcentral and northwestern Nigeria have been studied extensively by Kuster (1990), Garba, (2002; 2003), and in southwestern Nigeria by Okunlola and Oyedokun (2009); Akintola *et al*., (2012). It is therefore worthwhile to undertake detailed study of the geology and structural setting of the pegmatites in Egbe area with a view to constrain the origin of the niobium and tantalum mineralization which are associated with these pegmatites.

1.6 OBJECTIVES AND SCOPE OF THE PRESENT WORK

The objectives of the study are:

(i) To produce a detailed geological map of the study area.

(ii) To discriminate between rare – metal and barren pegmatites using major and trace elements distribution patterns.

(iii) To characterize and infer the origin of the Nb – Ta pegmatites in the Egbe area.

The scope of this work is to use both petrographic and geochemical (major and trace elements) characteristics of the pegmatites and host rocks in the area to achieve the above stated objectives

CHAPTER TWO

LITERATURE REVIEW

2 .0 REGIONAL GEOLOGICAL SETTING

2.1 INTRODUCTION

The study area is a part of the Precambrian Basement Complex of Southwestern Nigeria. The Basement Complex forms part of the Pan-African mobile belt which lies between the West- African and Northwest of Congo Craton. It is believed that the Pan-African belt evolved by plate tectonic activity which involved collision between the passive continental margin of West African Craton and the active continental margin of the Tuareg shield about 600 Ma ago (Black *et al*., 1979, Ajibade *et al*.1987). The collision led to the reactivation of the internal region of the belt especially at the plate margin.

2.2 BASEMENT COMPLEX

The Basement Complex is one of the major litho-petrological components that make up the geology of Nigeria (Fig. 2.1). It is believed to have been affected by, atleast, three major tectonic cycles of deformation, metamorphism and remobilization corresponding to the Liberian (2700 Ma), the Eburnean (2000 Ma) and the Pan- African cycles (600 Ma).

These cycles were characterized by intense deformation and isoclinal folding accompanied by regional metamorphism which was followed by extensive migmatization. The Pan-African deformation was accompanied by a regional metamorphism, migmatization, extensive gneissification which produced syntectonic granite and homogenous gneisses (Abba, 1983). Late tectonic emplacement of granites and granodiorites and associated contact metamorphism accompanied the end stages of this last deformation. The end of the orogeny was marked by faulting and fracturing (Olayinka, 1992).

Three broad lithological groups are usually distinguished:

(i) A polymetamorphic migmatite-gneiss complex with ages ranging from Liberian (~2800 Ma) to Pan-African (~600Ma). Metamorphism is generally in the amphibolite facies grade.

(ii) The schist belts, which are mainly N–S to NNE–SSW trending belts of low grade (mainly greenschist facies) supracrustal (and minor volcanic) assemblages. They are considered to be Late Proterozoic cover infolded into the gneiss–migmatite complex. The schist belts are concentrated in the western half of Nigeria, and are seldom found east of 8°E longitude

(iii) Syntectonic to late-tectonic Pan-African granitoids which intrude both the schist belts and the gneiss–migmatite complex. They comprise gabbros, charnockites, diorites, granodiorites, granites and syenites.

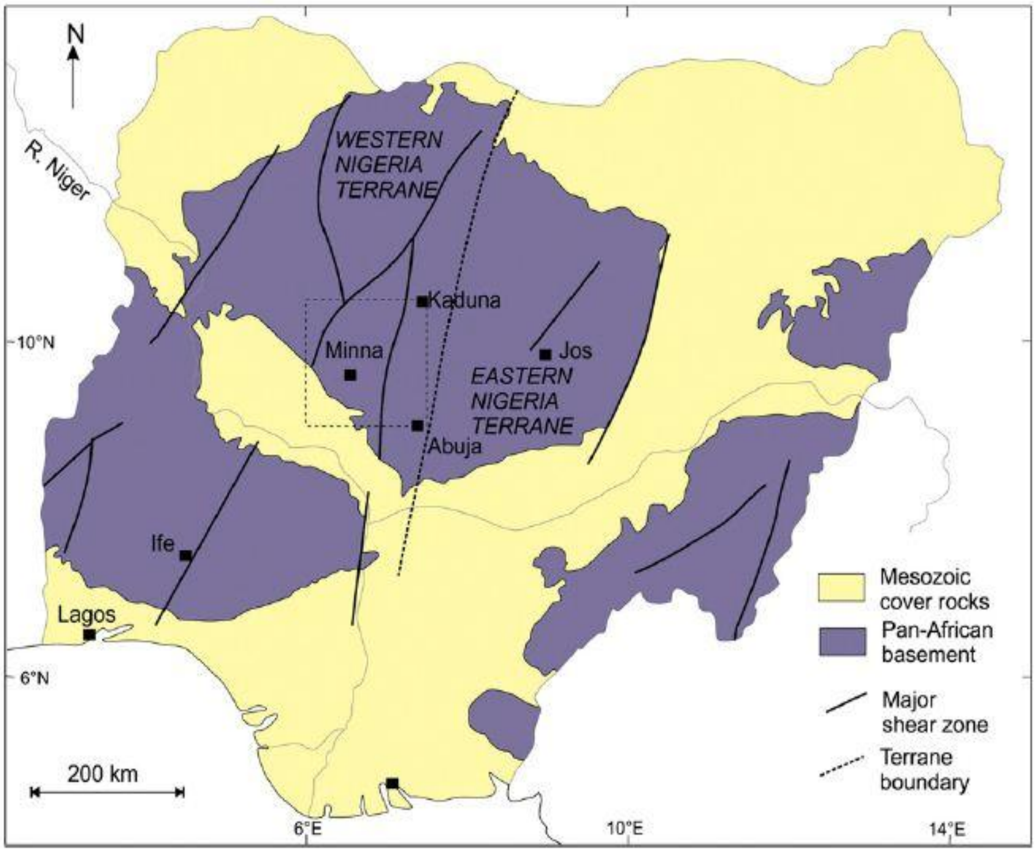


Figure 2.1: Simplified map of the geology of Nigeria, after Ferré *et al*. (1996) and Key *et al.* (2012). Box indicates the area shown in Fig. 2.

The Nigerian schist belts are thought to have been deposited in back-arc basins which developed after the onset of subduction at the West African cratonic margin at about 1000 Ma. Closure of the ocean at the cratonic margin at about 600 Ma led to deformation, metamorphism and emplacement of the Older Granites in Nigeria. Uplift, acid volcanism and development of faults and shear zones were the last manifestations of the Pan-African event. There is, however, increasing evidence to show that the Pan- African collision involved more of an aggregation of crustal blocks rather than between the West African craton and the Pan-African belt as a single entity. Two well-defined NE–SW (and NNE–SSW) trending fault systems (the Anka and Kalangai-Ifewara faults) cut and displace earlier N–S structures in the Nigerian Pan-African basement (Fig.2.1). The scale of movement and displacement and the occurrences of felsic–mafic–ultramafic rocks along these faults suggest that they might be crustal sutures of the Pan-African collision.

2.2.1 Migmatite–Gneiss Complex

The Polymetamorphic migmatite - gneiss complex with ages ranging from Eburnean to Pan–African is composed largely of gneisses and migmatites of various origin and compositions with a series of metamorphosed basic and ultrabasic rocks represented by amphibolites and talc-schist (Ajibade and Fitches, 1981).

The gneissic complex was considered by Russ (1957) to represent the oldest member of the Precambrian rocks of northwestern Nigeria which evolved by successive sedimentation, deformation, metamorphism and igneous intrusion over a vast period in the history of the basement. According to Ogezi (1988), banded gneiss and biotite gneiss are the principal rock types within the migmatite-gneiss complex. The biotite gneiss often grade into the generally, more complexly folded banded gneiss and migmatite in which there is a more complete break between the lighter quartz and feldspar rich bands and the darker mafic bands. Using rock age determinations from various parts of Nigeria, it is established that the gneissic complex has been through, at least, three major tectonic cycles of deformation, metamorphism, and remobilization in the Liberian 2,700 m.y. ago (Oversby, 1975), Eburnean, 2,000 m.y. ago (Grant, 1970) andPan-African, 600 m.y. ago (Ogezi 1977).

2.2.2 The Schist Belt (Metasedimentary and Metavolcanic Rocks)

The Nigerian schist belts consist dominantly of schists, phylites and quarzites with minor volcanic rocks, banded iron formations and conglomerates. It occurs in 300 to 400 km wide zone and predominantly west of longitude 8° E, which trends NNE, parallel to the boundary between the Pan-African province and the West African Craton (Turner, 1983; Fitches et al., 1985; Adekoya, 1986).

The schist belts are thought to have been deposited in back-arc basins which developed after the onset of subduction at the West African cratonic margin at about 1000 Ma. The schist belts are believed to be metasedimentary and metavolcanic, deformed low grade (greenschist facies) rocks that fall into two age groups. The earlier groups such as Maru and Kushaka belts contain assemblages of mafic igneous rocks, pelitic schist and phyllites, banded iron formations and locally coarse grained clastics and carbonate rocks. These are intruded by granitic plutons belonging to the Pan-African magmatic suite. They are dated to approximately 1,100 Ma and are thought to belong to the Kibaran ensialic process (Fitches *et al*., 1985).

The latter group of schist belts: Anka, Wonaka, and Kazaure, is characterized by coarse to fine grained clastic insignificant mafic igneous rock, and absence of central granite plutons. These schist belts are believed to belong to Pan-African marginal basin development (Turner, 1983; Fitches *et al*., 1985).

2.2.3 The Granites

The granitic rocks associated with the Pan-African orogeny in Nigeria have contrasting petrological and geochemical compositions and are collectively known as the Older Granite to distinguish them from Mesozoic anorogenic granite ring complexes (the Younger Granites).

They include (Syn- to late tectonic granitoids) suite of Pan-African age which intruded both the migmatite-gneiss complex and the schist belts, and comprise of a wide spectrum of rocks, which include monzonite, adamelite, granodiorite, syenite, chanokite and granite. To them, Ajibade et al., (1987) ascribed a mantle origin with minor crustal contribution. The gneissic of the rocks is reported to contain angular xenoliths of schist from adjacent belt. The plutons also exhibit a certain degree of foliation. This foliation in the Older Granite is regarded by Fitches *et al*. (1985) to be due to flow of magma tectonic-tectonic processes rather than deformation. However, Ajibade *et al*. (1987) used evidences from cross-cutting pegmatites and micro granites to show that the foliation is a result of post emplacement deformation. The Older Granites suites are mainly calc-alkaline except quartz syenites, Fitches *et al*. (1985). Available geochemical data shows that most of the bodies were emplaced within 700–500 Ma.

2.3 TANTALITE - COLUMBITE MINING AND TYPES OF DEPOSITS

Tantalite - Columbite deposits are most commonly associated with igneous rocks, including granites, pegmatites, syenites and carbonatites (Table 2.1). Other deposits may be concentrated by weathering and sedimentary processes. Global mining production of tantalite - columbite was around 1400 t (3.1 Mlbs) Ta_2O_5 (Papp, 2008). It is evident that tantalite mining production almost exclusively comes from pegmatite deposits. However, tantalite mining contributes only around 60% of the tantalite raw material supply, the rest originates from by- production of columbite-concentrates (with < 10% Ta_2O_5) and Sn-smelting (Ta- bearing slags with 25 - 15% Ta_2O_5). Global tantalite-columbite demand is estimated to grow by 7% (Paull, 2004).

Primary tantalite - columbite mineralization occurs together with concentrations of other rare- metals (Li, Cs, Rb, Be, Sn, W, U, Zr, REE) and is hosted by geochemically and mineralogically specialized magmatic rocks, mainly of the granitoid clan. Depending on the geological appearances and composition of the host rocks, tantalite - columbite deposits can be divided into four different types (Černý, 1989; Pollard, 1989; Fetherston, 2004), each of which also exhibits specific association of rare- metals, for instance

i. Peraluminous rare-element granitic pegmatite, mineralized with Ta, Li, Cs, (Be, Sn, Nb).
ii. Peraluminous rare-metal granites, also known as Li-mica albite granites, Li-F granites or apogranites, mineralized with Ta, Sn, (Be, Li, Nb).
iii. Peralkaline granites and quartz syenites mineralized with Zr, REE, Nb, (Ta, Sn, U, Th).
iv. Carbonatites and nepheline syenites, mineralized with Nb, REE, P, Zr, (Ta).
v. In deposits associated with peraluminous granites and pegmatites, tantalite is a major component whereas in deposits associated with peralkaline granites and carbonatites, columbite predominates

2.3.1 Peraluminous rare-elements granitic pegmatites

Rare-element granitic pegmatites are the classic source of tantalite because of its low Nb/Ta ratios (<1-2) and are suitably sized for simple gravity separation techniques. Most pegmatite–related columbite - tantalite deposits are small in size and usually occur in dyke- or sheet-like tabular bodies. This often restricts surface exposure and the possibility of cheap open pit mining. Instead underground mining needs to be employed to fully exploit most pegmatitic columbite - tantalite deposits.

Table 2.1: Major characteristics and examples of the major types of tantalite - columbite deposits (British Geological Survey, 2011)

Deposit type	Brief description	Typical grades and tonnage	Major examples
Carbonatite-hosted primary deposits	Niobium deposits found within carbonatitic igneous rocks in alkaline igneous provinces	Niobec, proven and probable reserves: 23.5 million tonnes at 0.59% Nb_2O_5	Niobec, Canada; Oka, Canada.
Carbonatite-Sourced secondary deposits	Zones of intense weathering or sedimentary successions above carbonatite intrusions in which niobium ore minerals are concentrated.	< 1000 million tons at up to 3% Nb_2O_5 in lateritic deposits. Up to 12% Nb_2O_5 in placer deposits at Tontor, tonnage not known	Araxa and Catalao, Brazil; Tontor, Russia; Lueshe, Democratic Republic of Congo.
Alkaline Granites and syenites	Niobium and lesser tantalum deposit associated with silicic alkaline igneous rock. Ore minerals may be concentrated by magmatic or hydrothermal processes	Generally less than 100 million tons, at grades of 0.1 to 1% Nb_2O_5 and less than 0.1% Ta_2O_5	Motzfeldt and limaussaq Greenland; Lovozero, Russia;Thor lake and strange lake, Canada; Pitinga, Brazil; Ghurayyah, Saudi Arabia; Kanyika, Malawi.
LCT- type granite	Tantalum and lesser niobium deposits associated with peraluminous leucogranitic plutons, which are often hydrothermally altered.	Generally < 100 million ton at grade of < 0.05% Ta_2O_5	Abu Dabab and Nuwebi Egypt; Yichun, China.
LCT-type pegmatites	Tantalum and lesser Niobium deposits associated with pegmatites of LCT (Li-(Cs-Ta-enriched)type	Generally < 100 million ton at grade of < 0.05% Ta_2O_5	Greenbushes and Wodgina, Australia; Tanco, Canada; Volta Grande, Brazil; Kenticha, Ethiopia; Morrua and Marropino, Mozambique.

2.3.2 Peraluminous rare-metal granites

Peraluminous rare-metal granites also have rather low Nb/Ta ratios (<1 – 2) with tantalite as the major ore mineral. On average, they show somewhat lower grades but contain greater tonnages than pegmatitic deposits. In addition, the disseminated occurrence of tantalite in circular to elongated stocks of several 100 m diameter enables mining by huge open pit operations. The ore minerals are typically fine grained and interstitially intergrown with the granitic gangue. Mining of this deposit style was therefore very limited in the past. If advanced gravity concentration technologies are applied (Burt, 2004), peraluminous rare-metal granites may constitute an important source of tantalite in the immediate future.

2.3.3 Peralkaline granites

Columbite - tantalite deposits associated with peralkaline granites have grades comparable to peraluminous rare-metal granites and even contain larger volumes of ore. However, Nb/Ta ratios are much higher (<10- 20) due to predominance of Nb–rich members of Ta-Nb solid solution (i.e pyrochlore-microlite and columbite-tantalite). In addition, pyrochlore needs floatation methods for effective recovery (Burt, 2004) and the higher natural radioactivity in these deposits requires further processing steps (smelting, chemical refining) before a marketable tantalite can be produced.

2.3.4 Carbonatites

Tantalite mining from carbonatite-hosted deposits basically faces the same problem as from peralkaline granites, due to similar occurrences of tantaliferous pyrochlore as the dominant ore mineral and the abundance of radioactive elements in the ore. Further technological development is therefore needed (Burt, 2004) to commercially exploit tantalum from carbonatite deposits.

2.4 ORIGIN OF NIGERIAN RARE–METAL PEGMATITES

The Nigerian rare–metal pegmatite formed over a time span of 562–534 Ma (Matheis and Caen Vachette, 1983) indicating the end of Pan–African magmatic activity. Since the pegmatites are related to the Nigerian major fault lineament systems, the albitization and rare–metal mineralization may have been due to late stage fluids available at the close of the Pan–African metamorphic cycle (Ekwueme and Matheis, 1995) or due to sodium rich hydrothermal solution from the mantle along ancient lineament (Wright , 1970). However, Matheis and Caen Vachette (1983) concluded that the rare–metal pegmatites of southwestern Nigeria are products of partial melting and leaching process of the basement units rather than the truly pegmatitic phase of the proximal Older Granite. It was also suggested by Matheis and Emofurieta (1987) that the rare-metal pegmatite mineralization of the southwestern Nigerian was derived from reactivation of deep seated tectonic lineaments combined with partial melting and external fluid supply.

2.5 Geology of Rare-element Pegmatites

Rare-element pegmatites are examined and exploited around the world in numerous countries and geological ages. Some of the countries include Canada, Brazil, Mozambique, Namibia, India and Australia. The pegmatites associated with Archean age granite terrains tend to be the most economic (Galeschuk and Vanstone, 2007)

The general geological characteristics of rare–element pegmatites include:

i. Dyke – like geometries.

ii. Propagation in horizontal and vertical directions.

iii. Association with deep-seated structures

iv. Fractionation away from the intrusive source (pegmatite granite, granite, e.t.c.) and the most distant pegmatite from the source contain economic concentrations of the less common minerals such as tantalite and pollucite.

v. Geochemical alteration of the surrounding host rock, especially with lithophile elements from metasomatic fluids.

vi. Mineralogical alteration by the addition of apatite, tourmaline, carbonate and micas (biotite).

vii. Varied economic deposits of Li-minerals (petalite, spodumene, etc), tantalite, pollucite (cesium mineral), beryl, quartz, feldspar and mica. As well as other minerals as marked by demands, including gemstones.

2.6 CHARACTERISTICS OF Ta - Nb MINERALIZED GRANITES AND PEGMATITES

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 (Lehmann, 1994; Kovalenko *et al*., 1995; Raimbault *et al*., 1995; Yin *et al.*, 1995; Reyf *et al*., 2000; Schmitt *et al*., 2002; Badanina *et al.*, 2004; Linnen and Cuney, 2005; Salvi and Williams-Jones, 2005; Černý *et al*., 2005). The reaction between magmatic and/or metereoric 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 (Lehmann, 1994; Linnen and Cuney, 2005; Černý *et al*., 2005). The Ta-mineralized granitoids can be grouped into two petrochemical categories based on their alumina saturation index. These are:

1) peraluminous granitoids, comprising granite plutons and pegmatitic dikes or sheets, and

2) peralkaline granitoid plutons.

2.6.1 Peraluminous granitic pegmatites

This type of Ta - mineralized granitoid is emplaced mainly at 2 to 4 kbar in upper greenschist to amphibolite facies (low P metamorphism) host rocks (Černý 1991). They crystallized from highly fractionated magmas derived from geochemically specialized, rare-element enriched granites (Černý, 1989, 1991). Rare-element pegmatites occur in aureoles usually at a distance of less than 5 km from their parental granite plutons.

Variations in mineralogical and geochemical evolution have lead to subdivision of rare-element pegmatites into several paragenetic-geochemical types (c.f. Černý, 1991). Ta-mineralized peraluminous pegmatites are synonymous with the LCT (for lithium, cesium, tantalum) pegmatite association of Černý (1991).

2.6.2 Peraluminous granites

Peraluminous rare-metal granites may form the most fractionated parts (usually muscovite- and albite-rich granites) of multiphase granitic intrusion sequences (commonly biotite granites and granodiorites). In other cases, precursor granites of the mineralized intrusions are not observed, at least not on surface. Rare-metal specialized peraluminous granites are late-orogenic to anorogenic and also post-date regional metamorphism (Černý, 1989; Pollard, 1989). Their emplacement is controlled by deep reaching crustal faults or shear zones.

2.6.3 Peralkaline granites

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 (arvfedsonite, riebeckite, aegirine). They are also characterized by very high concentrations of Zr, Hf, Y, REE, Nb, U and Th which clearly distinguishes them from the rare-element mineralized peraluminous variants. Enrichment of the rare-elements is caused by very high solubilities of HFSE (including Ta) in peralkaline melts and retardation of crystallization of respective minerals until the volatile-rich end stages of magma evolution (Salvi and Williams-Jones, 2005). In mineralized peralkaline granites usually Nb-rich minerals (pyrochlore, columbite) are the ore mineral of tantalum. Ta-mineralization seems to be an essentially magmatic process with little contribution from meteoric fluids (Linnen and Cuney, 2005); however, hydrothermal processes probably play an important role in the formation of dominantly Zr, Nb, REE deposits (Salvi and Williams-Jones, 2005).

2.6.4 Peraluminous granites

Tantalite - columbite mineralized rare-metal granites may be considered high-level analogues of the most evolved rare-metal pegmatites (albite- and complex Li-types), but are usually devoid of important lithium mineralization. Peraluminous rare-metal granites may form the fractionated parts (usually muscovite- and albite-rich granites) of multiphase granitic intrusion sequence (commonly biotite granites and granodiorites). In other cases, precursor granites of the mineralized intrusions are not observed, at least not on the surface. Rare-metal specialized peraluminous granites are late orogenic to anorogenic and also post-date regional metamorphism (Černý, 1989; Pollard, 1989). Their emplacement is controlled by deep crustal faults or shear zones.

Peraluminous rare-metal granites may be divided into high (<1.0wt % P_2O_5), intermediate (0.15 to 1.0 wt % P_2O_5) and low- (<0.15 wt % P_2O_5) P types (Linnen and Cuney, 2005). High P-type occur together with less fractionated S-type granites, while intermediate- and low P- types are commonly associated with less fractionated usually metaluminous I- type and A2-type granites.

2.7 EXPLORATION FOR TANTALITE – COULUMBITE DEPOSIT

Tantalum and niobium have high ratio of charge to ionic radius, i.e. they are high-field-strength elements (HFSEs); hence their partitioning behavior is very different from that of Li, Rb, and Cs. Tantalum and niobium are highly incompatible in quartz and feldspar; thus their bulk distribution coefficients are typically very small. However, they are compatible in muscovite and partition strongly into Ti-bearing minerals, notably rutile and titanite (Linnen and Cuney 2005). The Ta content of muscovite has been used as an exploration tool, and pegmatites that contain muscovite with greater than ~80 ppm Ta are considered to have economic potential for Ta (Černý 1989). Fluid–melt partition coefficients of Ta are very low, in contrast to the alkali rare elements. Therefore, Ta is not added to the wallrocks (Linnen and Cuney 2005); note also that most fluid inclusions lack Ta (e.g. Borisova *et al.* 2012).

CHAPTER THREE

MATERIALS AND METHOD

3.1 INTRODUCTION

The methodology adopted in the present research work includes literature review of relevant published and unpublished reports and systematic geological field mapping on a scale of 1:25,000. Representative rock samples were collected for hand specimen examination and laboratory studies. Preliminary observation and identification of constituent minerals of each rock sample were carried out using magnifying lens. Field mesurements of strike and dip were carried out with the aid of a compass - clinometer, while sampling points were recorded using a Global Position System (GPS). Remote sensing was applied in the generation of lineament of the study area which was automatically generated from Landsat ETM+ imagery using PCI geomatica line module. Generation of the lineaments was followed by construction of a rose diagram to determine their dominant direction in confirmation of field data.

Thin sections of ten representative rock samples were examined under the petrological microscope in the Department of Geology, Ahmadu Bello University, Zaria. Twenty selected rock and mineral samples (fifteen rocks, four muscovite and one feldspar samples) were pulverized in a tungston carbide mill at the Multiuser Science Laboratory, Ahmadu Bello University, Zaria. The pulverized samples were thereafter shipped to Acme Laboratory, Vancouver, Canada, for major and trace elements analysis by Acid-Digestion Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), for major and trace elements including rare–earth elements (REE), Boron–Fusion Inductively Coupled Plasma Atomic–

Emission Spectrometry (ICP–AES) and Ion Selective Electrode (ISE) methods for Boron and fluorine respectively.

Geochemical data interpretation were carried out with geochemical tool kit (GCDkit) through the use of various discrimination diagrams. 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 chemical characteristics of these rocks and established the petrogenesis of the rock units and associated columbite – tantalite mineralization in the study area.

3.2 FIELD MAPPING AND SAMPLE COLLECTION

Systematic geological mapping was carried out on a scale of 1 : 25,000. Representative rock samples were collected for hand specimen examination and laboratory studies. Preliminary observation and identification of constituent minerals of each rock sample were carried out using magnifying lens. Field mesurements of strike and dip were carried out with the aid of a compass - clinometer, while sampling points were recorded using a Global Position System (GPS). Remote sensing was applied in the generation of lineament of the study area which was automatically generated from Landsat ETM+ imagery using PCI geomatica line module and this was followed by construction of a rose diagram.

3.3 LABORATORY STUDIES

3.3.1 Petrographic studies

Thin sections of ten representative rock samples were examined under the petrological microscope in the microscope room of the Department of Geology, Ahmadu Bello University, Zaria.

3.3.2 Geochemical studies

Twenty selected rock and mineral samples (15 rock, four muscovite and one feldspar samples) were pulverized in a tungston carbide mill at the Multiuser Science Laboratory, Ahmadu Bello University, Zaria. The pulverized samples were thereafter shipped to Acme Laboratory, Vancouver, Canada, for major and trace elements analysis.

Major and trace elements including rare–earth elements (REE) were analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The procedure involved sample digestion using a mixture of (2:2:1:1) H_2O –HF–$HClO_4$ – HNO_3. 50% HCl. The solution was heated and allowed to cool . After 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 specific wavelength from which the concentrations of the elements were then computed.

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

CHAPTER FOUR

RESULTS

4.1 GEOLOGICAL SETTING AND PETROGRAPHY

The study area is underlain by banded gneiss, schist, amphibolites, granites and pegmatites. Other minor rocks include banded iron formation (BIF), laterite, and alluvium, marble and quartzite. Figure 4.1 is the geological map of the study area.

4.2 BANDED GNEISS

Banded gneiss occurs as low lying, massive, weathered outcrops in the southeastern part of the study area. This rock type constitutes about 10 % (34.2 km^2) of the study area. It is medium grained, light coloured and strongly foliated with alternating bands of felsic minerals (plagioclase feldspar and quartz) and dark bands consisting of biotite and other opaque minerals (Plate I).

In thin section, quartz, biotite and plagioclase feldspars form the bulk of the mineral composition. The rock is composed of quartz (55%), biotite (30%) and plagioclase (15%) (visual estimate). Quartz occurs as cloudy anhedral grains, with wavy extinction and a low birefringence. The crystals of biotite are subhedral, brown in colour and of high relief.

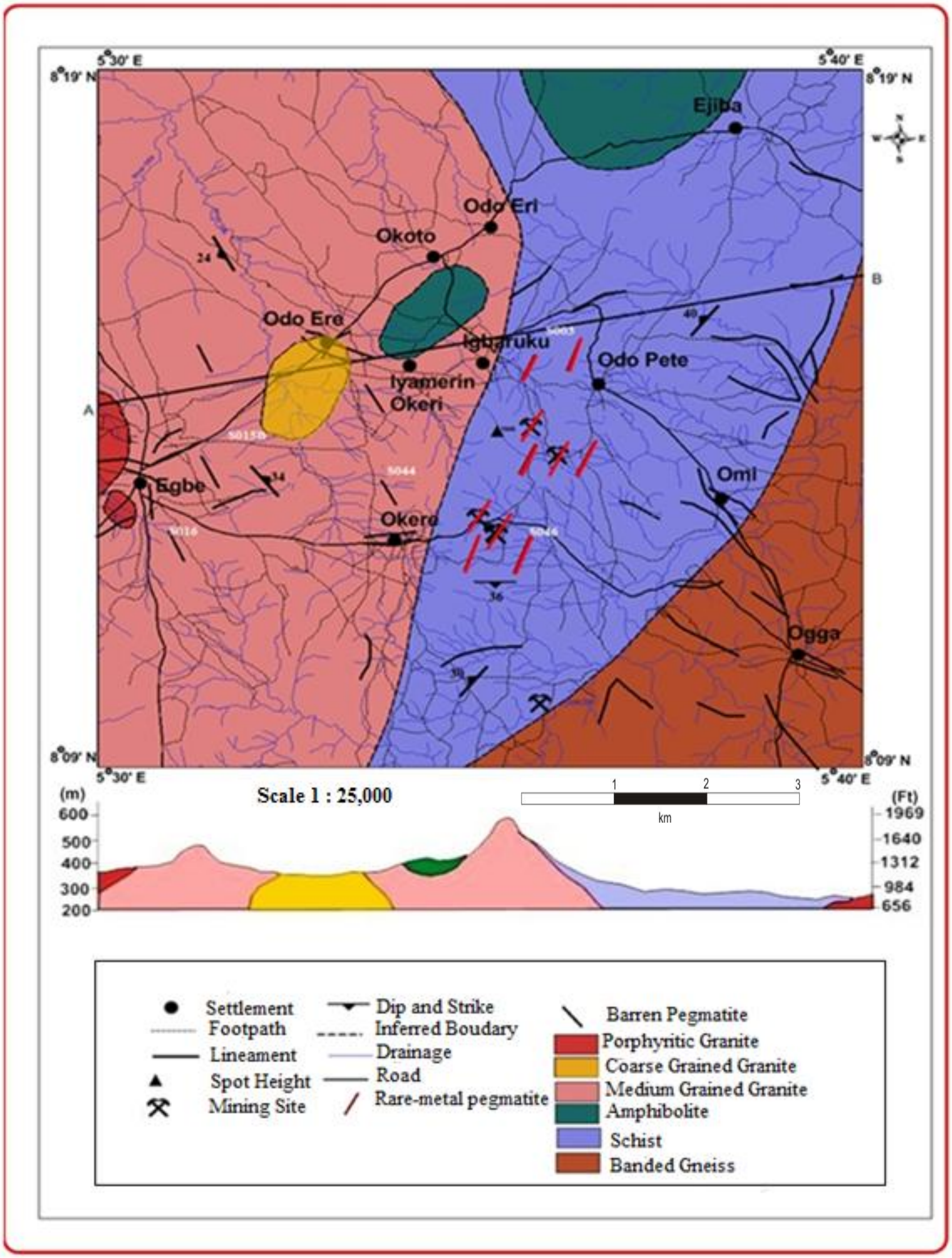


Figure 4.1: Geological map of Egbe area, part of Sheet 225 (Isanlu), SW Nigeria

The plagioclase feldspar is also colourless but cloudy and exhibits characteristic lamellar twinning (Plate II and III).

Plate I: Photograph of banded gneiss with alternating bands of felsic minerals (mainly quartz and feldspar) and mafic minerals (biotite) at Okere (08^{o} $13^{'}$ $21^{''}$ N, 05^{o} $33^{'}$ $10^{''}$ E).

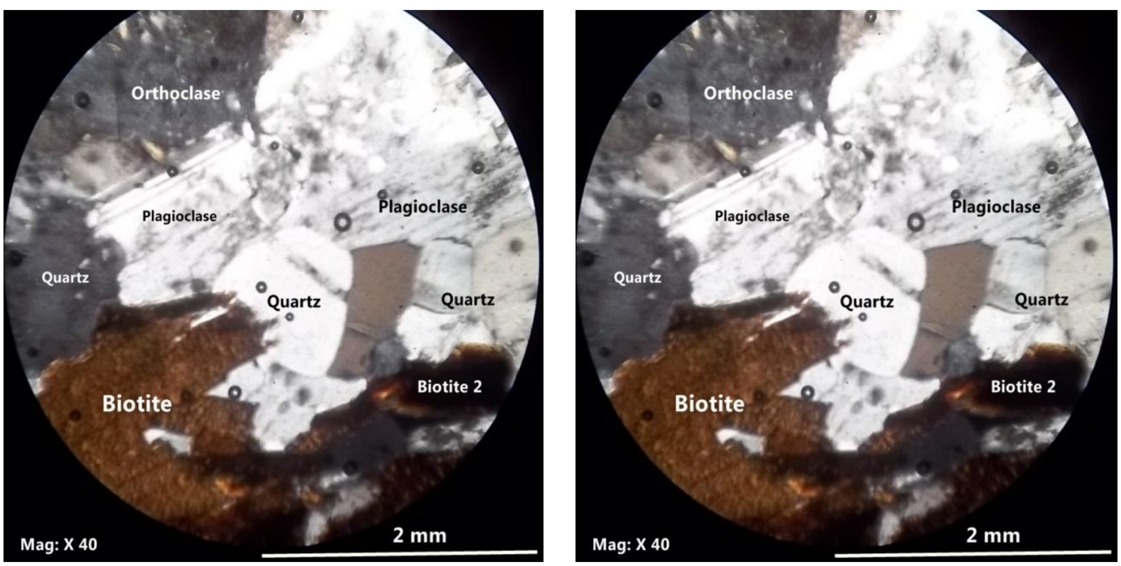


Plate II: Photomicrograph of banded gneiss under (a) (PPL) with quartz, biotite having perfect basal cleavage except grains that are parallel to crystallographic axis (Biotite 2), and (b) (XPL) biotite with brown polarization colour, grey feldspars (plagioclase and orthoclase).

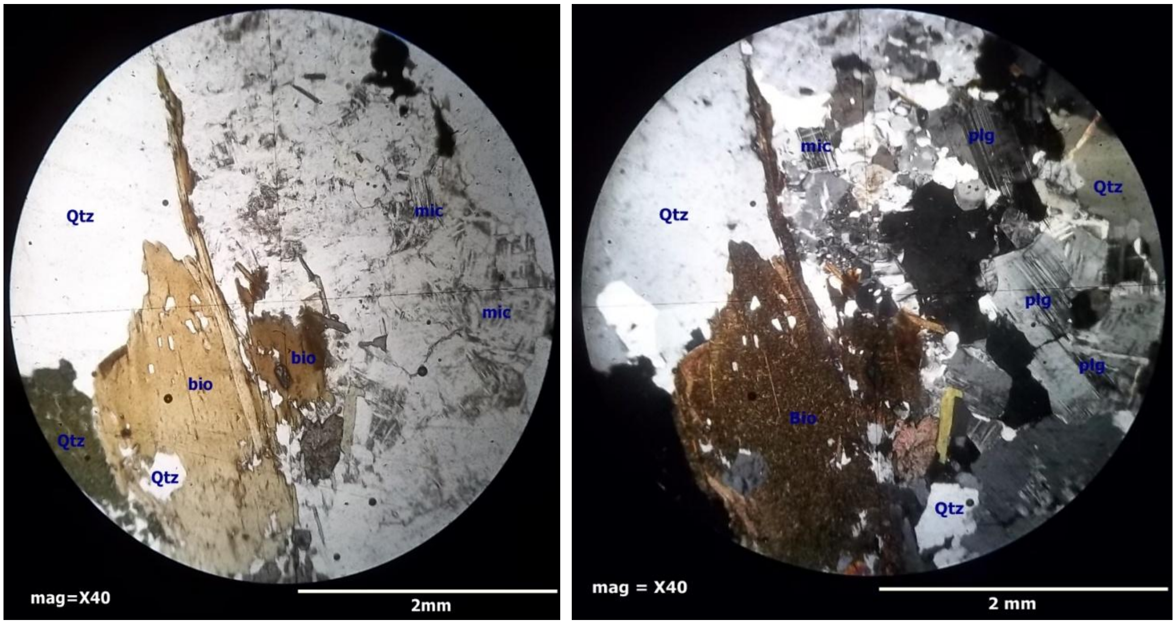


Plate III: Photomicrograph of banded gneiss with poikilitic inclusion of quartz (qtz) in biotite (bio), under (a) PPL, and (b) XPL with anhedral quartz, biotite and subhedral plagioclase crystals (Plag).

4.3 METASEDIMENTS (SCHISTS)

The metasediments consist essentially of schists and quartzite. The schist occurs as light to dark coloured rock at Igbaruku, constituting about 35 % of the rocks in the area. The dominant strike direction is NE-SW, and generally dipping 40^o NW. It is generally foliated with the trend parallel to the strike direction (Plate IV a and b). The schist has been affected to a varying degree by weathering. There is no sharp contact observed between the schist and other lithologies in the study area.

In hand specimen, 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 places. The biotite has perfect cleavage with moderate relief (Plate V).

Plate IV (a): Photographs of quartz schists at Igbaruku with quartzo- feldsparthic Vein and (b): biotite schists at Igbaruku (08^{o} 10' 11" N, 05^{o} 38' 13" E)

Plate V: Photomicrograph of schist (a) under PPL and (b) under XPL, both with lineated muscovite and biotite grains cut perpendicular to c-axis. In (b), biotite has brown interference colour while the muscovite had light blue interference colour.

4.4 METAVOLCANICS (AMPHIBOLITE)

Amphibolite outcrops at Iyameri over an area of about 17.1 km^2 and constitute about 5% of the rocks in the study area. The rock occurs as cobbles and boulders and nowhere was its contact with other rocks seen. In hand specimen, the rock is massive, dark green to black.

Under the microscope, the rock is composed of amphibole (38%), quartz (30%) plagioclase (20%), biotite (10%), and microcline (1%) and accessory minerals. The hornblende display different interference colours, brown, blue and pink with high relief. There are intergrowth of quartz and biotite in amphibolites grains. Plagioclase is euhedral to subhedral with a characteristic polysynthetic twinning (Plate VI). Also subhedral grains of hornblende with shade of brown colour are common. The hornblende has two sets of cleavages intersecting at nearly 120^{o}. In plane polarized light, biotite is brown in colour.

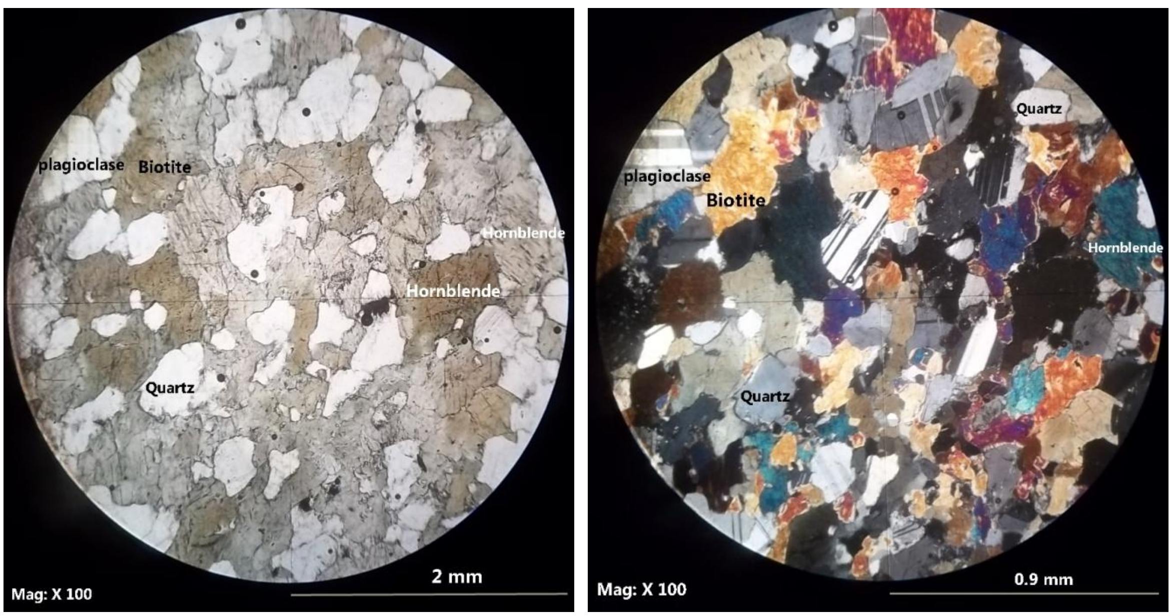


Plate VI: Photomicrograph of amphibolite with hornblende displaying two sets of cleavages at approximately 120^{o} to one another under (a) PPL, and (b) XPL with subhedral plagioclase, anhedral quartz, and biotite.

4.5 GRANITES

Granite occupies about 40% of the total area of study. There are three varieties: (i) medium grained biotite granite, (ii) medium to coarse grained biotite granite and (iii) porphyritic biotite granite have been recognized. Outcrops of this rock types are found around Egbe town.

4.5.1 The medium grained biotite granite

The medium grained biotite granite is the most widespread rock in the study area, occurring as hill (ranging from 350 – 557 m above sea level, especially in Egbe town). Some outcrops of this rock are several meters across in the form of whale back outcrops, and as flat lying bodies (Plate VII). The rock varies from light to dark coloured and fine to medium grained. It is composed of microcline, quartz, biotite and plagioclase feldspar as the major minerals.

Plate VII: (a) Photograph of medium grained biotite granite and (b) flat lying outcrop of medium grained biotite granite along Egbe - Okere road (08^{o} $12^{'}$ $15^{''}$ N, 05^{o} $33^{'}$ $51^{''}$ E)

4.5.2 Coarse grained granite

Outcrops of coarse grained biotite granites are found in Egbe town and in the south western part of the study area (Plate VIII). It is light coloured, coarse grained and composed of quartz, microcline and biotite. Microcline occurs as large phenocryst of microcline with its cross hatch twinning characteristic. Modal analysis shows that quartz constitute (50%), microcline (30%), biotite (15%) and accessory (5%) (visual estimate) (Plate IX)

Plate VIII: Coarse grained granites at Egbe with crystals of quartz, k – feldspar and biotite (08^{o} 12$^{'}$ 3.2$^{''}$ N, 08^{o} 31$^{'}$ 02$^{''}$ E)

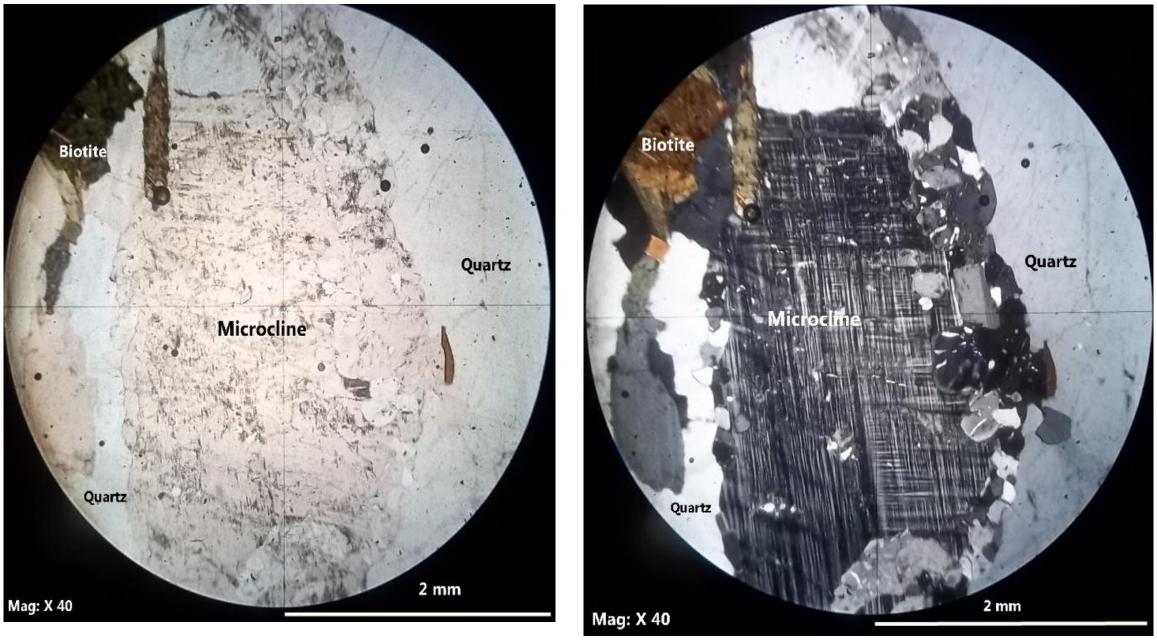


Plate IX: Photomicrograph of coarse grained granite under (a) PPL and (b) XPL, with large crystal of microcline showing characteristic cross hatched twinning, quartz crystals with low relief and brown biotite.

4.5.3 Porphyritic Granite

Porphyritic granite outcrops at Odoeri, Egbe town and in the southwestern part of the area along Egbe-Ilorin highway. In hand specimen, it is composed of quartz, biotite, microcline and biotite. In places, quartz and feldspar occur as phenocrysts (Plate XI).

Plate X: Porphyritic granite at Oderi with phenocryst of quartz in a groundmass of biotite, feldspar and quartz (08^o 18' 20'' N, 05^o 35' 10'' E)

4.6 BANDED IRON FORMATION (BIF)

Banded iron formation (BIF) outcrops in an area 4 km south of Iyameri and constitute 0.1 % (0.34 km^2) of the sudy area. It is dark coloured, fine grained, deeply weathered and highly fractured.

4.7 PEGMATITES

Pegmatites in the study area occur as vertically dipping 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. According to Matheis and Caen Vachet (1983), the tantalite – columbite mineralization is associated with these pegmatites which are generally linked to the late orogenic Pan – African (600 ±150 Ma) orogeny. Quartz, feldspar, and muscovite are the major minerals in the pegmatites (Plate XI and XII). A lot of the mineralized pegmatites at Okere and Igbaruku are currently being mined for tantalite by artisanal miners (Plate XIII). On a hill at Egbe, are several weathered unmineralized pegmatite veins ranging from 10 to 30 meters in length.

Plate XI: Photograph of (a), abandoned pegmatite field from which tantalite was mined and (b), Pegmatite with large crystals of quartz and feldspar and crudely zoned (08^{o} $12^{'}$ 38.1“ N, 05^{o} $35.1^{'}$ 08.5“ E)

Plate XII: Photograph of a 10 cm wide pegmatite vein in medium to coarsed grained granite at Okere (08^{o} $10^{'}37.6^{''}$N, 05^{o} $30^{'}38.1$“ E)

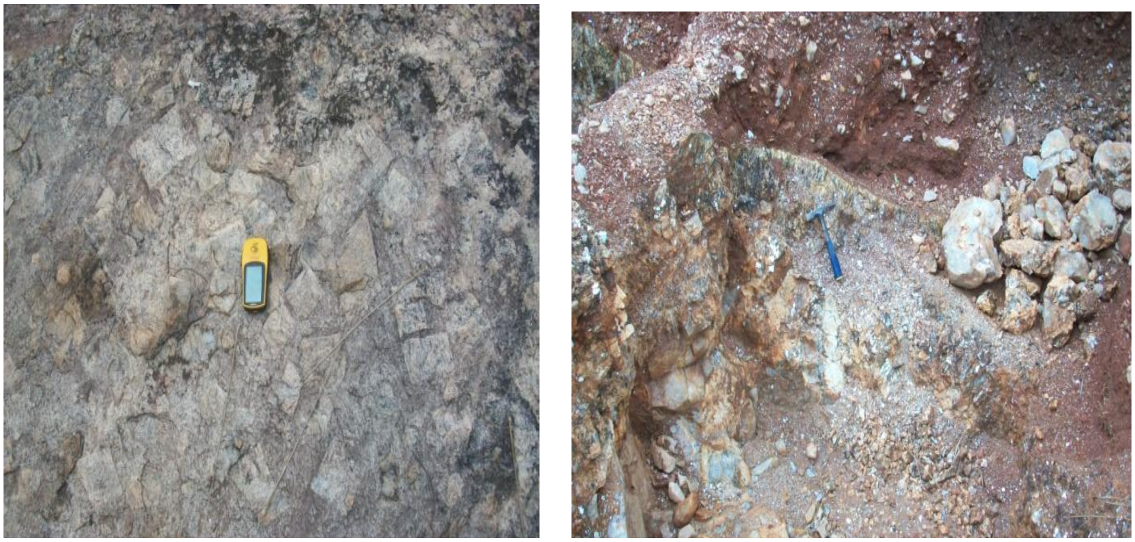


Plate XIII: Photograph of (a), a complex Pegmatite with phenocryst of plagioclase feldspar at Iyameri, (b) Pegmatite vein being exploited for tantalite at Igbaruku (08^{o} 16' 10.2" N, 05^{o} 37' 03" E)

4.8 STRUCTURES

4.8.1 Lineament Analysis

A linearment is a mappable linear or curvilinear feature of a surface whose part aligned in a straight or slightly curving relationship. They may be expressed as a fault or other line of weakness. The surface features making up lineaments may be geomorphological that is caused by relief or tonal caused by contrast differences.

Lineament within the study area was automatically generated from Landsat ETM imagery using PCI geomatica line module (Fig.4.2) to complement field data. The generation of the lineament map was carried out under the default paremeter of the software as presented in (Table 4.1)

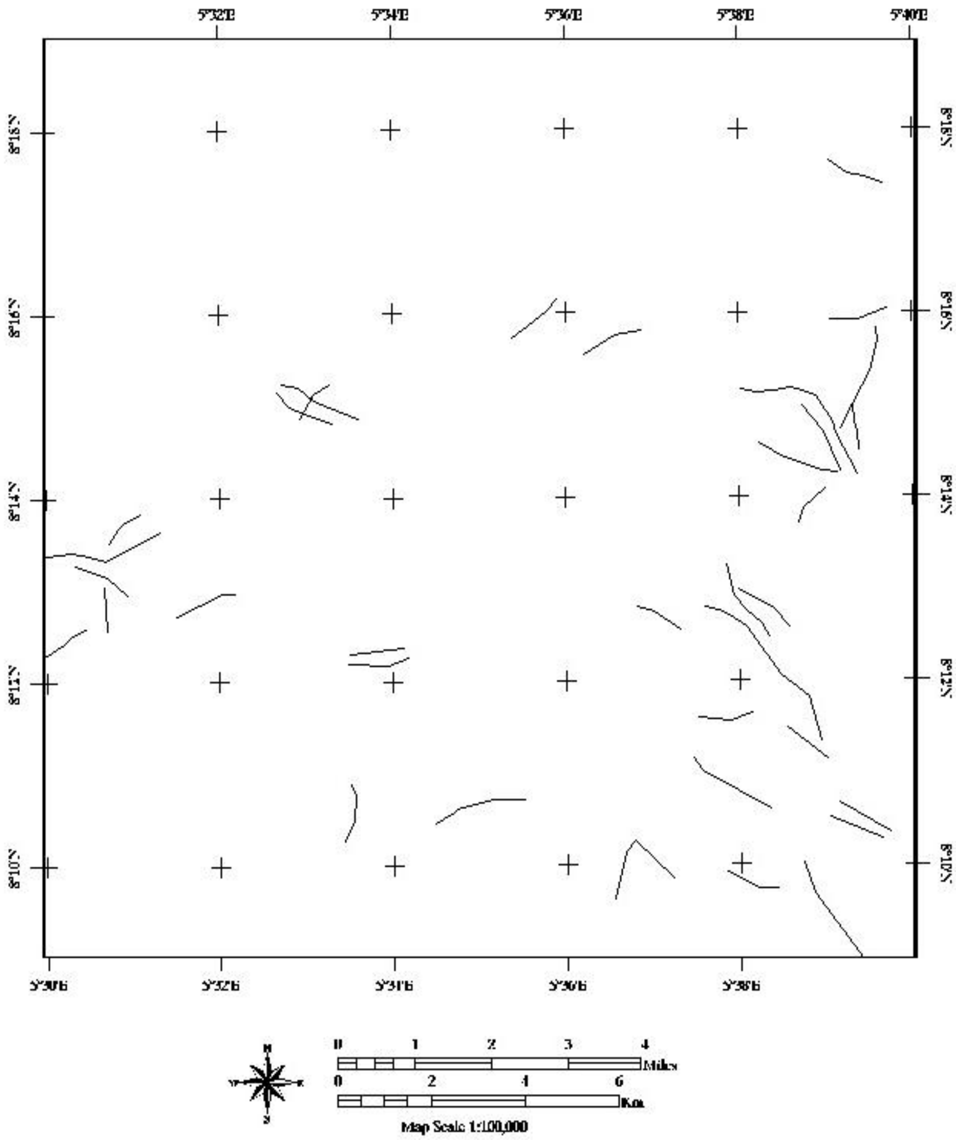


Figure 4.2: Lineaments Map of the Study Area.

Table 4.1: Default Parameters For Lineaments

Parameter	Number
Filter radius (pixel)	10
Edge gradient threshold	100
Curve length threshold (pixel)	30
Line fitting error threshold (pixel)	3
Angular difference threshold (degree)	30
Linking distance threshold (pixel)	20

Generation of lineament was followed by construction of a rose diagram to determine their dominant direction. From the rose diagram, the lineaments are seen to have a dominant WNW – ESE trend (Fig. 4.3).

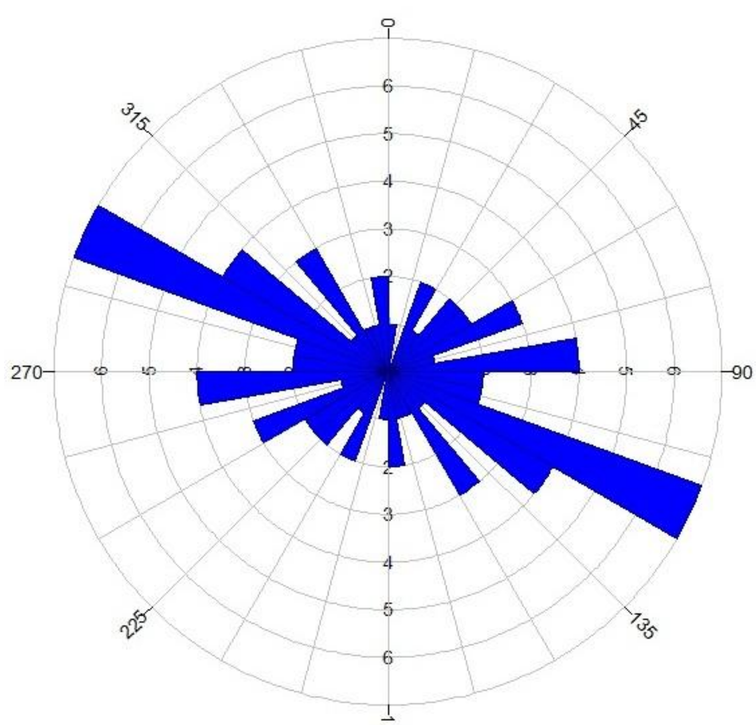


Figure 4.3 : Rose diagram for the dominant structural trend in the Study Area

4.2.2 Foliation

Rahaman (1976) reported that the regional strike direction of foliation within the schist belts in the southwestern region of Nigeria is roughly constant in a N-S direction with variations between NW-SE and NE-SW directions (007, 015, 020, 045,355,175). The srike of foliation in the study area is accordance with this trend(Fig. 4.4)

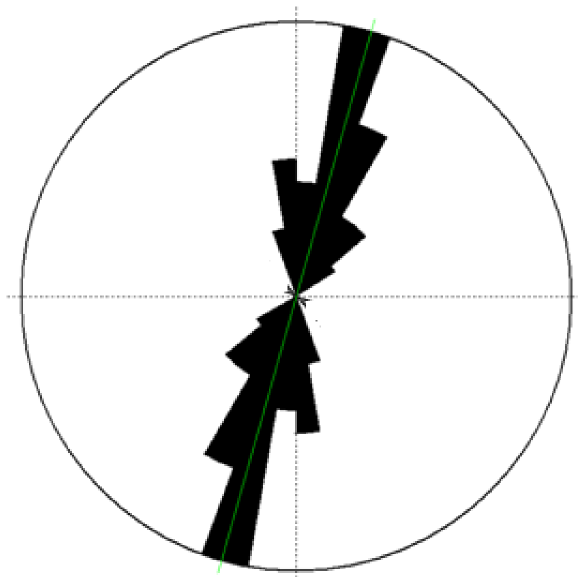


Figure 4.4: Rose diagram for the general trend of foliation in the study area

The rock types in which foliation has been recorded are the biotite schist and banded gneiss. In the gneisses, foliation is defined by parallel alignment of alternating quartzofeldspathic material and biotite (Plate IV). The predominant foliation trend observed is NE- SW with an average dip of 40^{o} NW. In the schist, schistocity is well developed and trends predominantly N-S.

4.2.3 Fold

Two types of folds were observed in the study area. These are: asymmetric fold (plate XVI) and isoclinal fold (Plate XVII). The asymmetric fold is associated with the quartz-biotite schist while the others are associated with the granites.

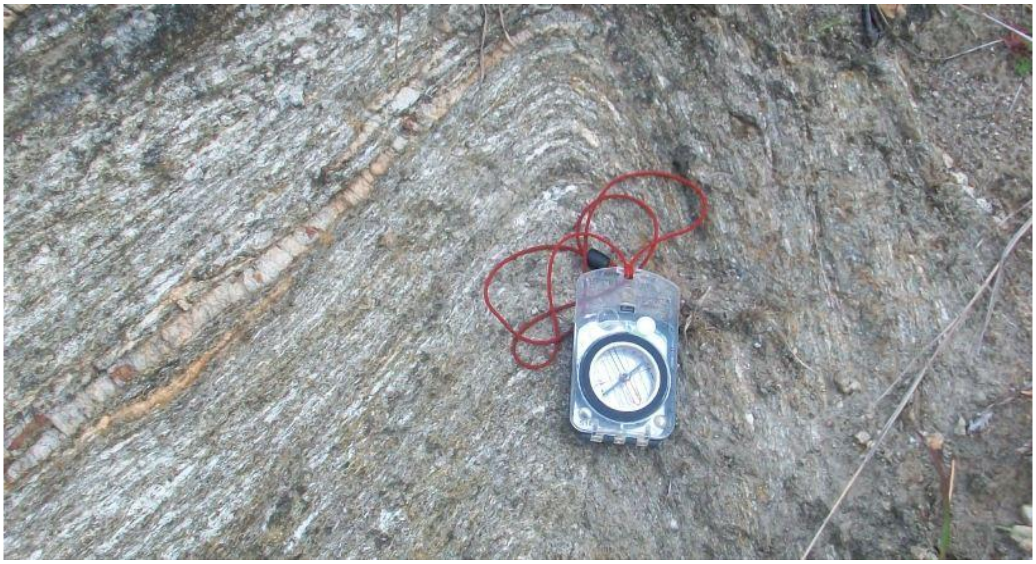


Plate XIV: Photograph of asymmetrical fold in weathered schist at Igbaruku (08° 14′ 48″ N, 05° 34′ 0″ E)

Plate XV: Photograph of isoclinal fold in banded gneiss at Okere (08° 10′ 45.3″ N, 05° 33′ 34.4″ E)

4.3 GEOCHEMISTRY

4.3.1 Introduction

Whole rock geochemical analysis provided information on the elemental concentration for use in establishing the geological, geochemical and the geotectonic processes that have taken place in the study area. Oxides of the major elements concentration provided basis for a comprehensive rock classification while 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.

4.3.2 Whole rock composition and characterisation

The major oxides composition of the rocks in the study area is presented in Table 2a and Table 2b.

Granites

The geochemical data shows that SiO_2 content in the granite ranges from 70.09 – 74.55 wt. %, Al_2O_3 ranges from 13.18 – 16.40 wt. % while Fe_2O_3 varies from 01.17 – 4.25 wt. %. The CaO content ranges from 0.41 – 2.07 wt %, MgO from 0.33 – 0.88 wt. % and Na_2O from 2.02 – 5.93 wt. % while K_2O content ranges from 0.48 – 2.45 wt. %, MnO ranges from 0.05 – 2.08 wt.% and TiO_2, from 0.01 – 0.5 wt. %, P_2O_5 ranges from 0.01 – 0.16 wt.% while FeO varies from 1.05 – 3.61 wt.%. The high content of SiO_2 in granites is an indication of acidic nature and enrichment in common rock forming minerals such as quartz and feldspar. This is higher than in amphibolites.

Pegmatite

In pegmatite, SiO_2 content ranges from 72.60 – 76.50 wt%, Al_2O_3 ranges from 12.39 – 15.41 wt % while Fe_2O_3 varies from 0.5 – 1.74 wt %. The CaO content ranges from

0.17 – 3.07 wt.%, MgO from 0.2 – 0.44 wt.% and Na_2O from 5.43 – 7.1 wt.% while K_2O content ranges from 0.15 – 4.53 wt.% , MnO ranges from 0.01 – 0.23 wt.% and TiO_2, from 0.01 – 0.04 wt.%, P_2O_5 ranged from 0.10 – 0.19 wt.% while FeO varies from 0.22 – 0.65 wt %. The high silica content in granites is due to the high contents of alumino-silicate minerals such as quartz, muscovite and feldspars. Although the SiO_2 content in gneiss and schist is high, it is slightly lower than in granites and pegmatites.

Amphibolite

In this study, it is observed that the SiO_2 content in amphibolite is 46.75 wt. %, Al_2O_3 is 12.39 wt % , Fe_2O_3 is 12.48 wt. %, FeO content is 11.47 wt %, MgO is 10.6 wt %, CaO 1.7 wt % %. The high concentration of Fe and Mg in the amphibolite reflects the abundance of titanomagnetite and mafic nature. The low CaO content is an indication of the absence of Ca-rich pyroxene. The total alkaline concentration is very low reflecting the subalkaline nature of this rock. Na_2O is 2.65 wt % while K_2O in this rock is 2.69 wt %. The contents of TiO_2, MnO and P_2O_5 are very low in this rock.

Muscovites

The SiO_2 content of muscovite ranges from 61.71 – 64.95 wt. % and Al_2O_3 ranges from 14.06 – 24.14 wt. % while Fe_2O_3 varies from 5.59 – 8.07 wt. %. The CaO content ranges from 0.03 – 1.03 wt. %, MgO from 0.03 – 0.41 wt % and Na_2O from 0.35 – 2.53 wt %. K_2O content ranges from 3.9 – 5.63 wt. % and FeO varies from 3.42 – 5.64 wt. %

Schist

The SiO_2 content in schist is 71.0 wt %, Al_2O_3 is 16.0 wt % and Fe_2O_3 is 2.75 wt %, while FeO is 2.63 wt %. The K_2O content is 2.23 wt %, Na_2O is 2.75 wt % and CaO is 1.37 wt %, while others (MnO, TiO_2, and P_2O_5) are low.

Gneiss

The SiO_2 content in gneiss is 70.04 wt %, Al_2O_3 is 11.03 wt % and Fe_2O_3 is 4.32 wt %, while FeO is 3.76 wt %. The K_2O content is 3.34 wt %, Na_2O is 2.54 wt % and CaO is 3.08 wt %, while others (MnO, TiO_2, and P_2O_5) are low.

Albite

The SiO_2 content in albite is 72.47 wt %, Al_2O_3 is 17.93 wt % and Fe_2O_3 is 4.12 wt %, while FeO is 3.69 wt %. The K_2O content is 3.96 wt %, Na_2O is 0.42 wt % and others (MnO, CaO, TiO_2, and P_2O_5) are low.

Lepidolite

The SiO_2 content lepidolite is 63.98 wt %, Al_2O_3 is 20.14 wt % and Fe_2O_3 is 5.33 wt %, while FeO is 3.29 wt %. The K_2O content is 6.58 wt %, Na_2O is 0.55 wt % and others (CaO, MnO, TiO_2, and P_2O_5) are low.

Trace elements are useful fingerprints of the origin of igneous rocks and igneous processes because they exhibit a range in concentration far greater than major elements (Frost and Frost, 1999). The trace element composition of the gneiss, schist, amphibolites and granites are presented in Table, 4.2. There is significant variation in trace elements concentration among the various rock units. Albite, lepidolite and muscovites (extracted from pegmatites) show significant enrichment in Li, Rb,and Cs compared to the granites and amphibolite. However, these minerals (albite, lepidolite and muscovites) are slightly depleted in Ba and Sr than the amphibolite and granites.

Enrichment of Li in albite, lepidolite, muscovite and pegmatite is attributed to the fact that Li would preferrentially enter into the late crystallizing minerals due to the greater ease of maintaining charge balance – electrostatic attraction. Muscovite, albite and lepidolite are depleted in Be, this could be due to crystallization in Beryl ($Be_3Al_2Si_6O_{18}$) from the melt. Muscovites is relatively enriched in F, but albite has the highest concentration of F and B. This indicate that Ta- mineralization was associated with highly fluxed melt. Lower concentration of B may be due to its removal to form schorl.

Table 4.2: Element composition of major rock types in the area (wt. %)

	Granites					Pegmatites				Amphibolite	Schist	Gneiss
	Coarse grained	Porphyritic	Medium grained	Porphyritic	Coarse grained							
Sample	S015B	S021	S031	S034	S074	S003	S016	S044	S046	S011	S061	S078
SiO_2	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_2O_3	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_2O_3	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_2O	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_2O	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_2	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_2O_5	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 ratios)											
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 4.3: Major element (wt. %) and trace element composition of muscovite, albite and lepidolite from the study area

	Muscovite					Albite	Lepidolite
Sample	S001	S002	S070	S071	S077C	S077E	S077G
SiO_2	64.95	61.71	63.2	64.58	63.04	72.47	63.98
Al_2O_3	18.98	24.14	18.52	21.67	14.06	17.93	20.14
Fe_2O_3	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_2O	0.35	0.85	0.68	0.52	2.53	0.42	0.55
K_2O	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_2	0.01	0.12	0.05	0.03	0.12	0.6	0.07
P_2O_5	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	-

The granites are metaluminous to peraluminous in character as shown on the (Al_2O_3/ (Na_2O + K_2O)) versus (Al_2O_3/ (CaO + Na_2O + K_2O)) discrimination diagram after Shand (1943) (Fig. 4.5)

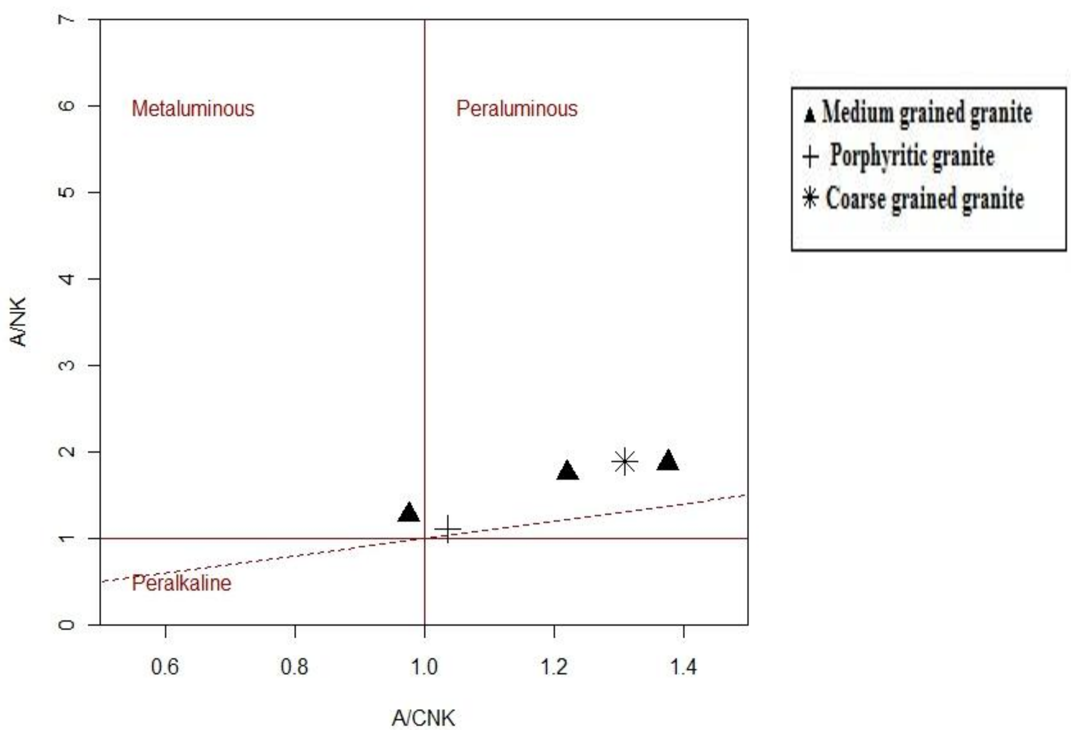


Figure 4.5: Chemical classification of the granitic rocks using the molecular ratio of alumina to alkalis [$Al_2O_3/(Na_2O+K_2O)$] versus alumina to lime and alkalis $Al_2O_3/(CaO+Na_2O+K_2O)$]

On the Rb versus Ta + Yb plot and Ta versus Yb plot after Pearce *et al*., (1984) the granitic rocks plot largely in the fields of Volcanic Arc and Syn-collisional Granites (Fig. 4.6).

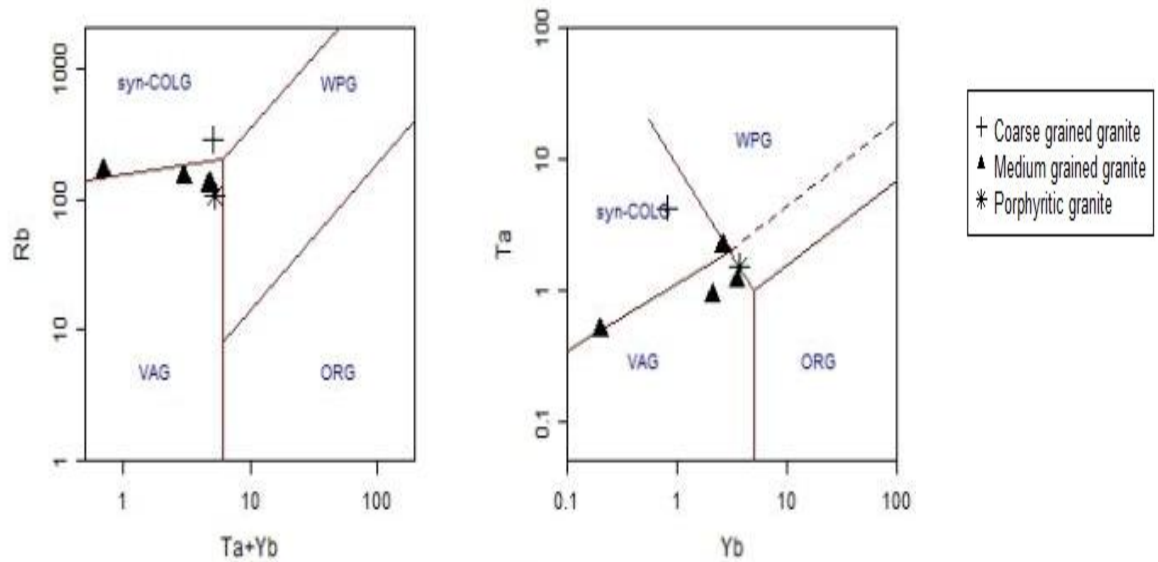


Figure 4.6: Plots of the granitoids from the Egbe area on tectonic discrimination diagrams of Pearce *et al*., (1984). Abbreviations: ORG - oceanic ridge granites; COLG – collision granites; VAG – volcanic arc granites and WPG – within plate granites

Molecular Al_2O_3/CaO+Na_2O+K_2O versus SiO_2 were used to classify the rocks into their magmatic origin. On this diagram, the granites plot largely within the field of S – type granitoids (Fig. 4.7). This 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 Egbe area.

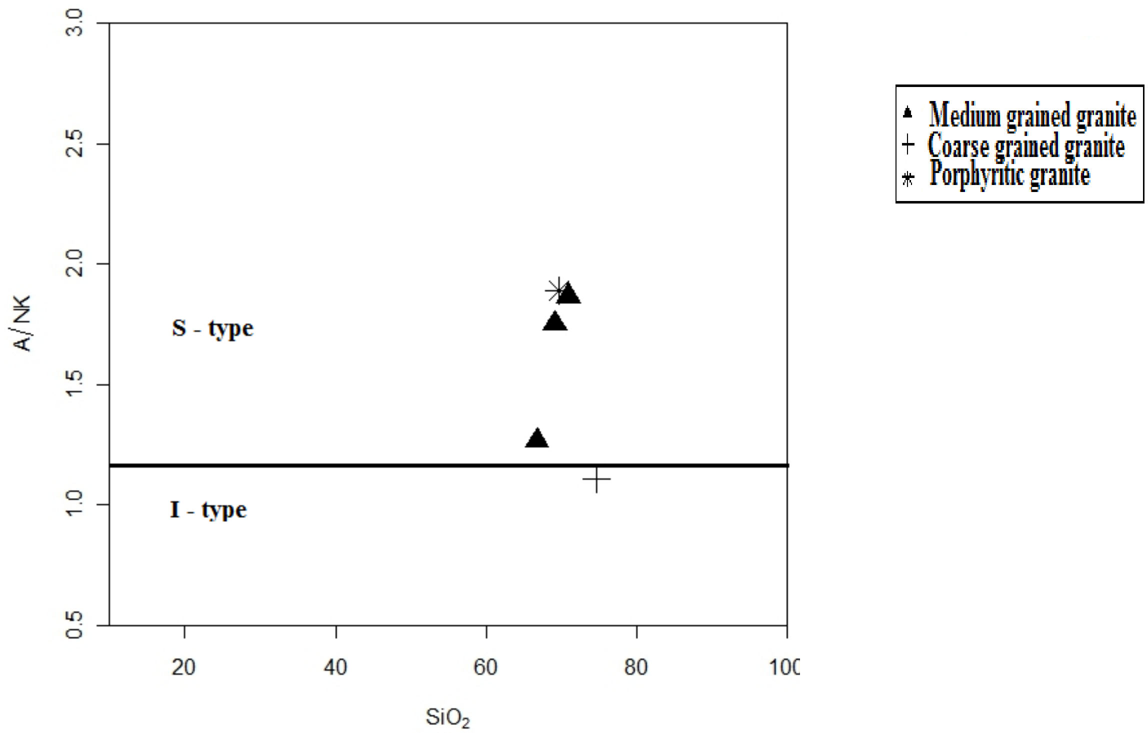


Figure 4.7: Molecular $Al_2O_3/CaO+Na_2O+K_2O$ versus SiO_2 diagram showing the classification of the granites as S-type and I-type

Trace elements are useful guides to the origin of igneous rocks and igneous processes because they exhibit a range in concentration far greater than major elements (Frost and Frost, 1999). The trace element composition of the gneiss, schist, amphibolites and granites are presented in Table 4.2. There is significant variation in trace elements concentration among the various rock units. Albite, lepidolite and muscovites (extracted from pegmatites) show significant enrichment in Li, Rb and Cs compared to the granites and amphibolite. However, these minerals (albite, lepidolite and muscovites) are slightly depleted in Ba and Sr than the amphibolite and granites.

Enrichment of Li in albite, lepidolite, muscovite and pegmatite is attributed to the fact that Li would preferrentially enter into the late crystallizing minerals due to the greater ease of maintaining charge balance – electrostatic attraction. Muscovite, albite and lepidolite are depleted in Be, this could be due to crystallization in Beryl ($Be_3Al_2Si_6O_{18}$) from the melt. Muscovite is relatively enriched in F, but albite has the highest concentration of F and B. This indicate that Ta- mineralization was associated with highly fluxed melt. Lower concentration of B may be due to its removal to form schorl.

The REE pattern for amphibolites, schist, gneiss, porphyritic granite displayed enrichment in light rare - earth element and a depletion in heavy rare earth element with a negative Eu anomaly (Fig. 4.8). Enrichment of LREE relative to HREE in samples is probably caused by the presence of hornblende in felsic melt (Rollinson, 1993) while negative Eu anomaly is due to fractionation of plagioclase in melt.

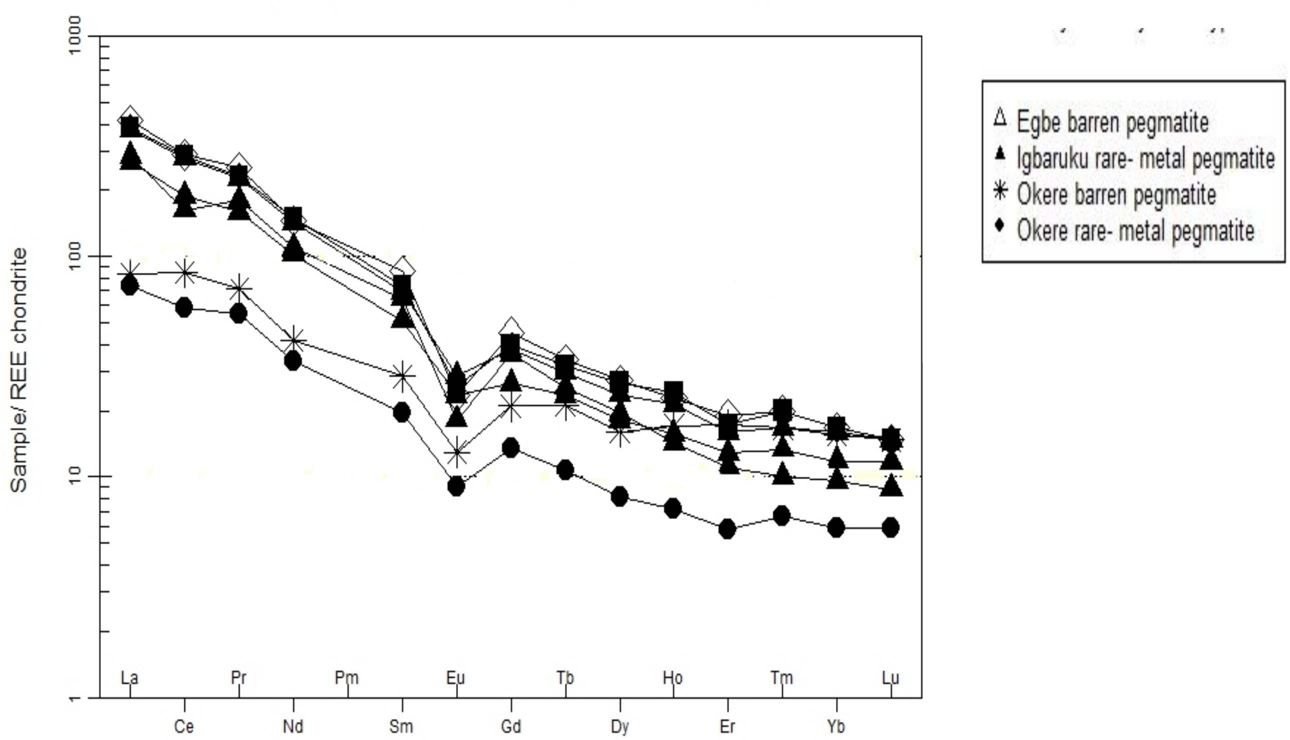


Figure 4.8: Chondrite normalized plot of the rare-earth elements (REE) for the rocks from the study area. Normalizing values are those of Nakamura (1974).

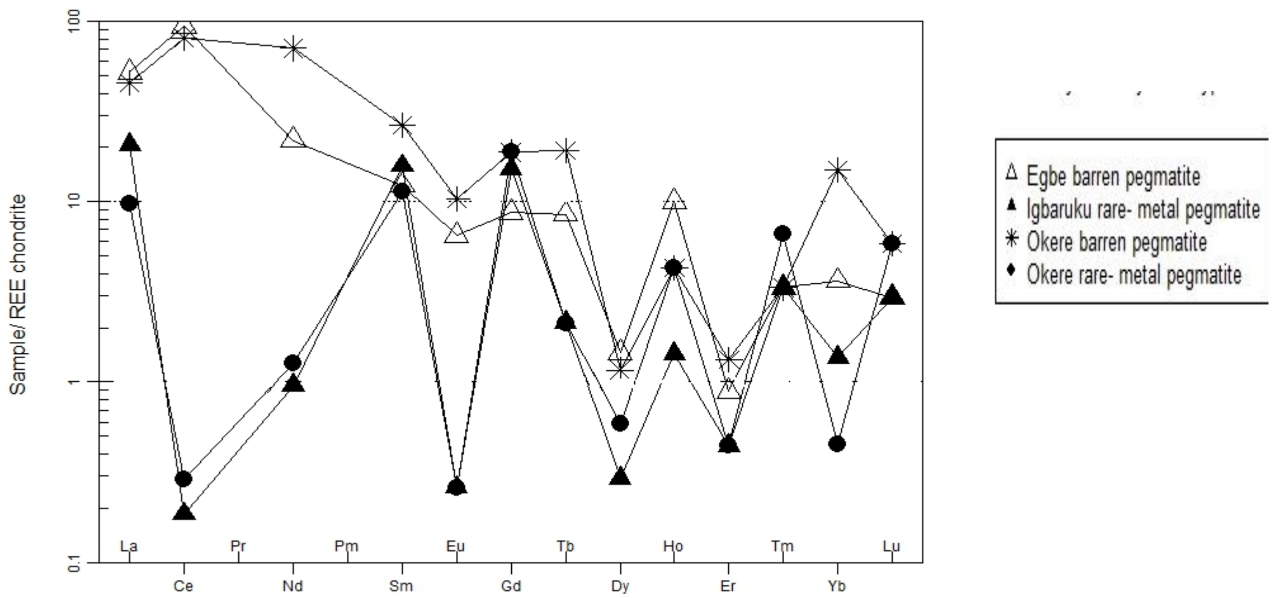


Figure 4.9: Chondrite normalized plot of the rare–earth elements (REE) for the pegmatites from the study area. Normalizing values are those of Nakamura (1974).

From the Chondrite normalized plot of the rear–earth elements (REE) for the pegmatites in the study area (Fig. 4.9), the rare-metal pegmatites exhibit pronounced negative Ce and Eu anomalies while the barren pegmatites has 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.

4.3.3 Geochemical features and mineralization potential of the pegmatites

The pegmatites are fractionated as shown on the K/Rb versus Rb discrimination diagram (Fig. 4.10). K/Rb versus Cs plot was used to determine the mineralisation potential in pegmatites. Here, a discrimination line was used to separate the rare - metal class from the barren class (Fig: 4.11). From this plot it was observed that two of the pegmatites (Okere and Igbaruku pegmatites) plot within the field of rare metal pegmatites, while the pegmatites in Egbe and few others in Igbaruku plot within the field of barren pegmatite. It is important to note that the mineralised Okere and Igbaruku pegmatites show similar geochemical trends to their host granite.

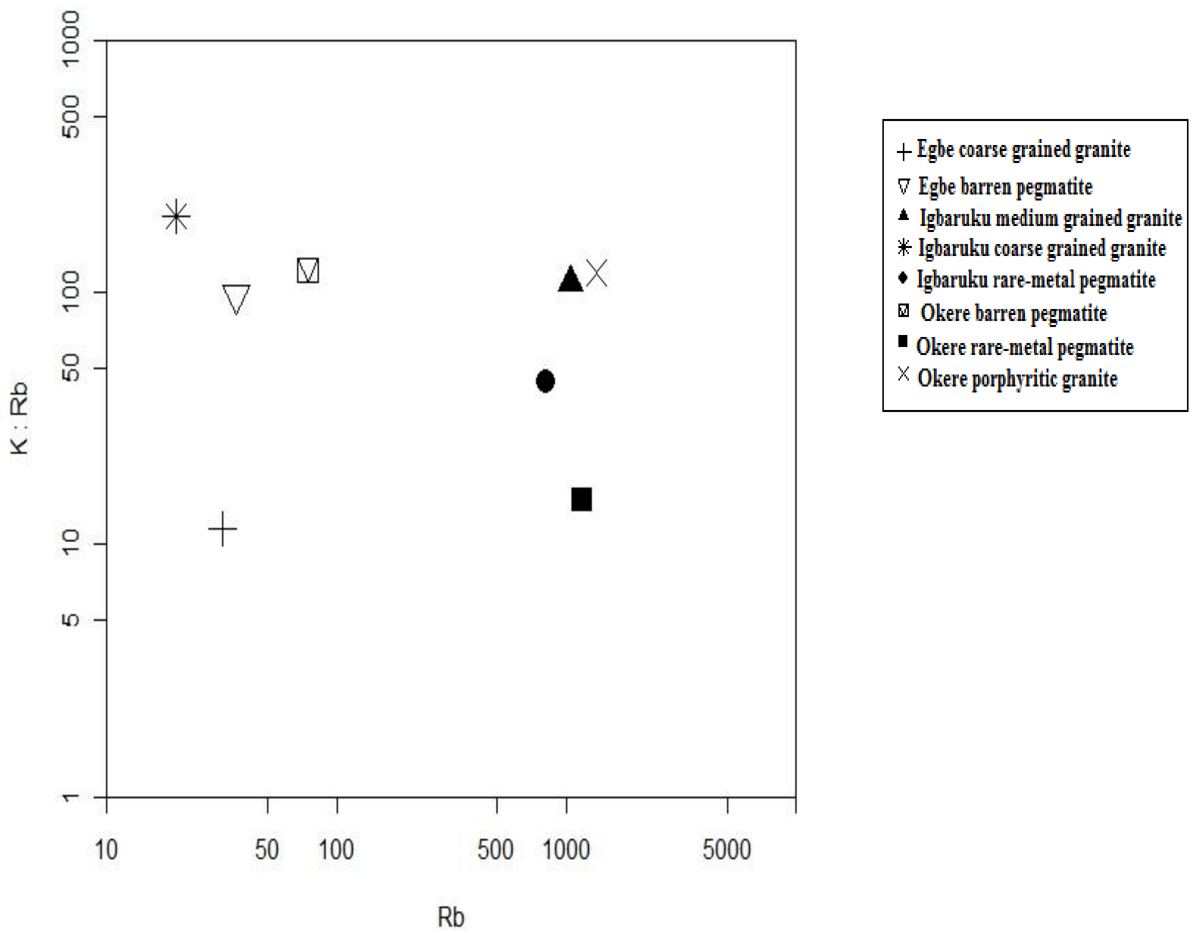


Figure 4.10: K/Rb versus Rb discrimination diagram showing the degree of fractionation and mineralization of the pegmatites (adapted from Morteani *et al*., 2000).

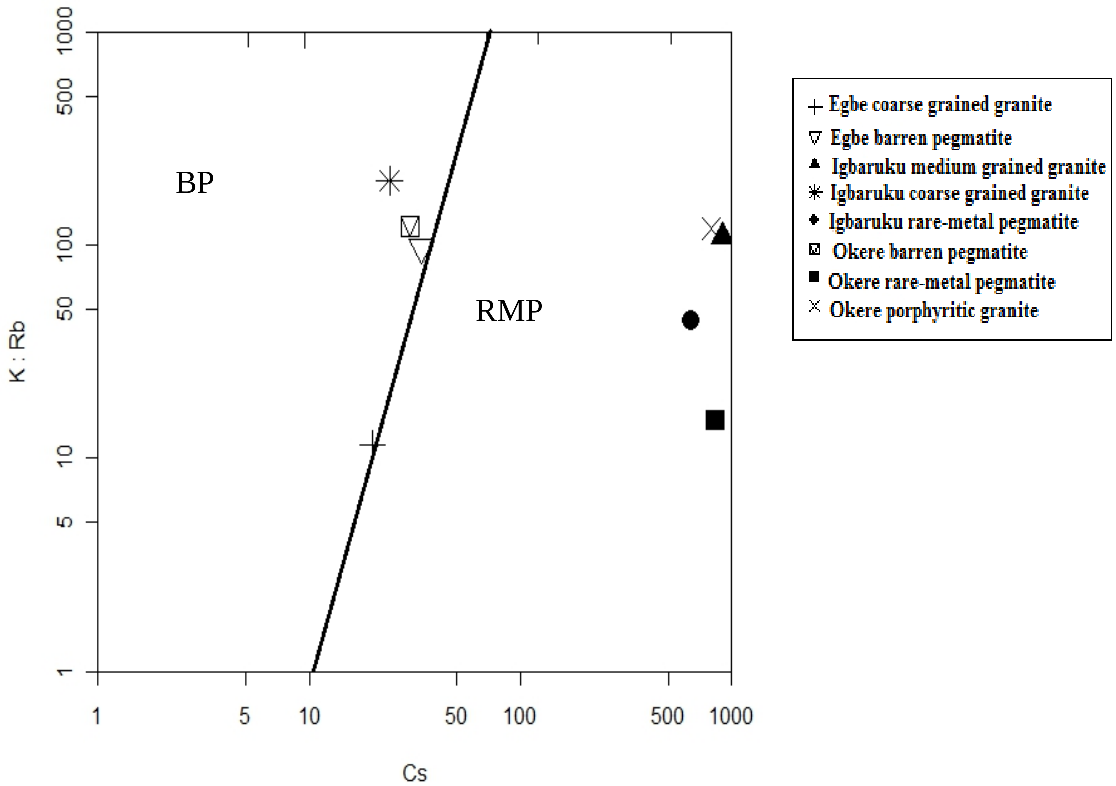


Figure 4.11: K/Rb versus Cs discrimination diagram showing the dgree of fractionation and mineralisation of the pegmatites. The discrimination line separates the field of rare-metal pegmatites (RMP) from the barren class (BP), (adapted from Morteani *et al.*, 2000)

Similarly, the Egbe and Igbaruku barren pegmatites also show similar geochemical trends to their host granite.

Rb versus Ba plot was used to indicate a fractionation trend from granites to pegmatites in the study area. Rb enricment is accompanied by Ba depletion with fractionation (Fig. 12).

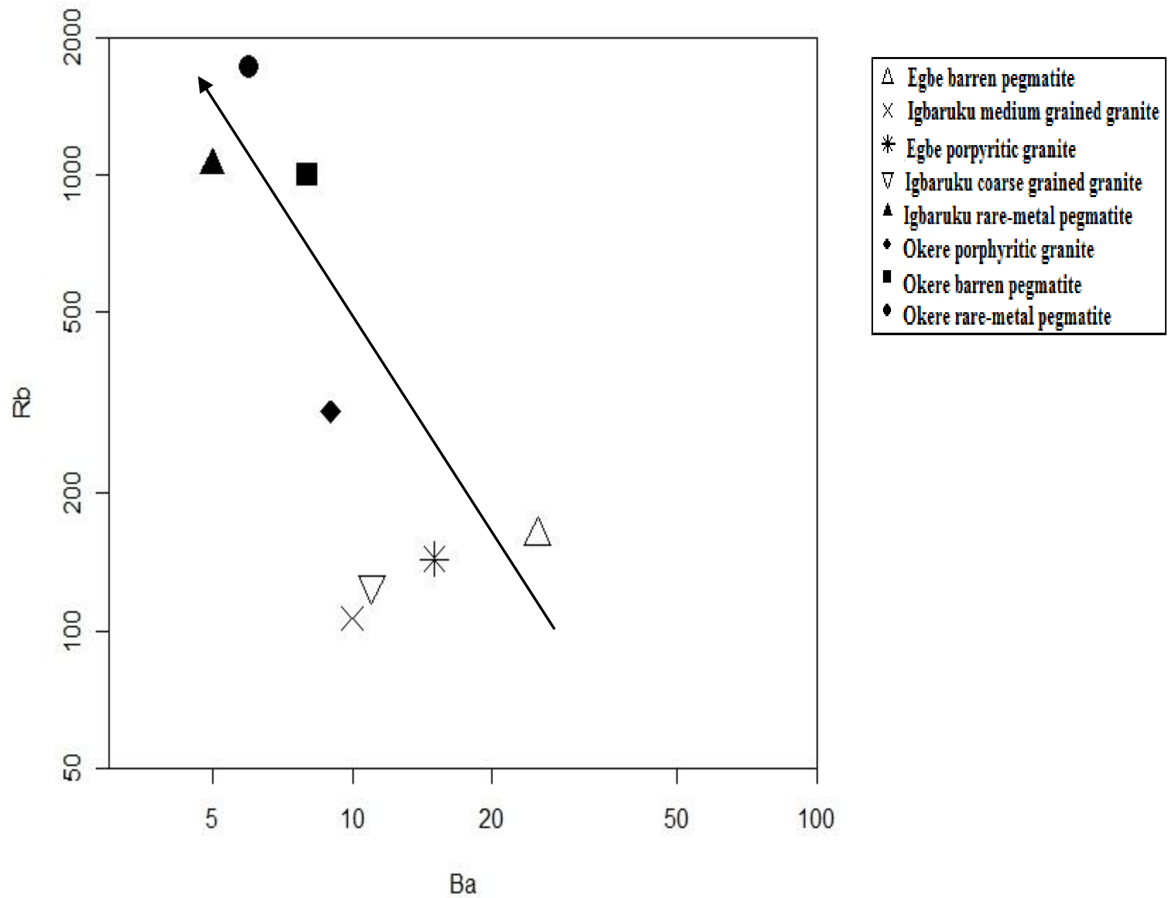


Figure 4.12: Rb versus Ba plot in granites and pegmatites from the study area (Adapted from Taylor and Heier, 1960)

Barium decreases with fractionation from granites to pegmatites while Rb increases from granites to pegmatites.

4.3.4 Relationship between the granites and pegmatite

Table 4.2: shows that K/Rb ratio decrease from 30.12 to 11.42 in granite and from 45.82 to 15.68 in rare metal pegmatites. This systematic decrease in K/Rb ratios from granite to pegmatite is an indication that the granites crystallized earlier than the pegmatites. According to London, (2008) substantial chemical fractionation accompanies

the evolution from granite to pegmatites. Plot of K/Rb Versus Cs shows that the Igbaruku and Okere granites and pegmatites plot within the field of mineralized pegmatites. The systematic fractionation trends from granites to pegmatite as shown in the Nb/Ta versus Ta discrimination diagram (Fig. 4.13) also support the earlier observation. The Nb and Ta ratio is presented in Table 4.2.

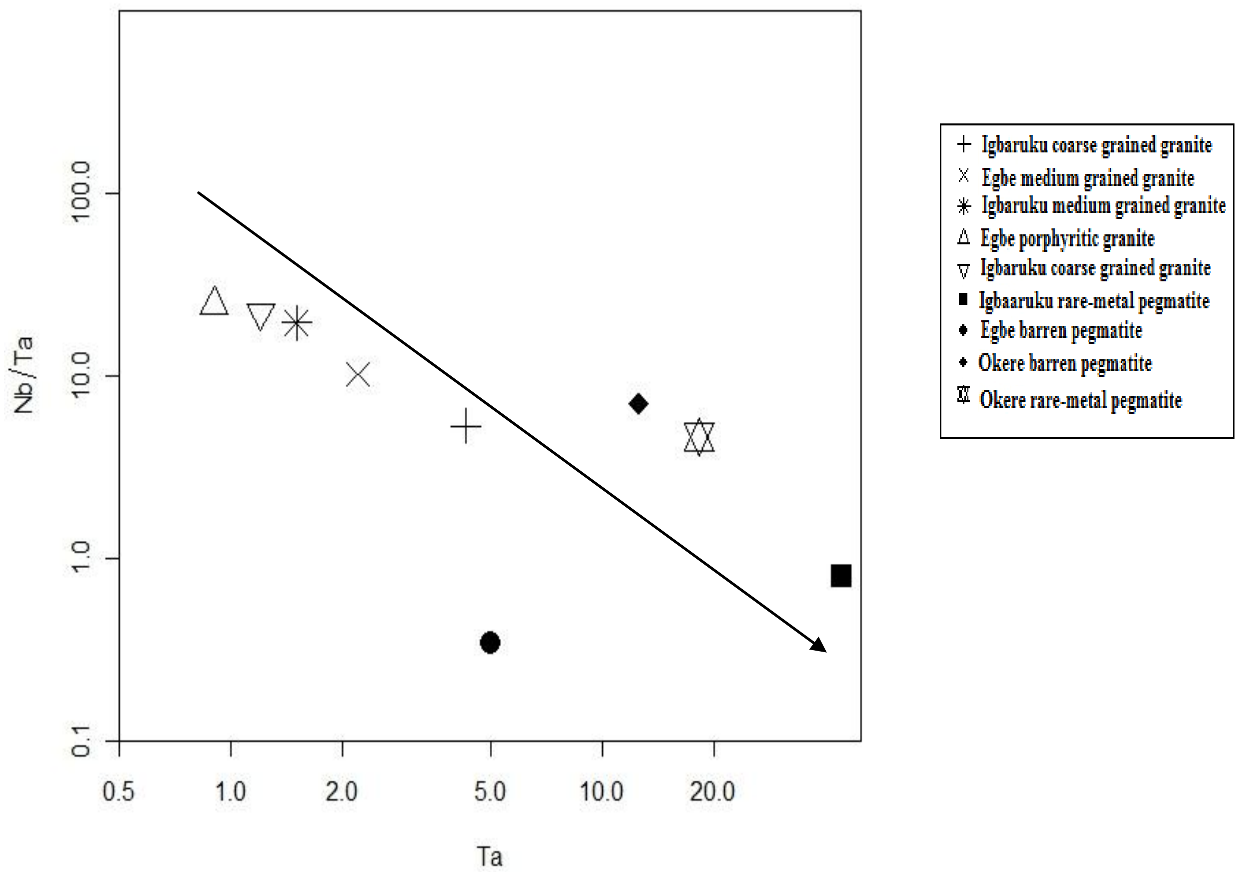


Figure 4.13: Nb/ Ta versus Ta showing fractionation trend from granites to pegmatites in the study area (adapted from London, 2008)

Ta versus Cs plot was used to discriminate mineralised rocks from non mineralised ones on Beus (1966) line and Gordiyenko (1971) line (Fig. 4.14). On the basis of Beus (1966) proposition, one muscovite sample plot below the mineralised line, while four muscovite and feldspar fell above the mineralised line. Using the Gordiyenko (1971) line, two muscovite samples plot below the mineralised line. Three muscovite (extracted from the pegmatite in Okere and Igbaruku) and feldspar plot above the mineralised line

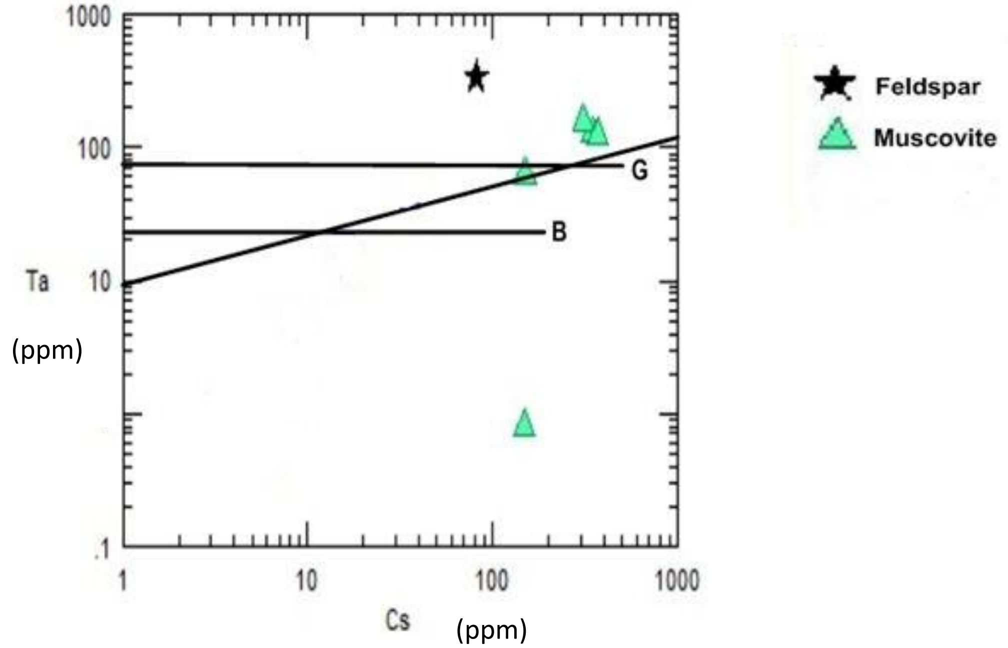


Figure 4.14: Plot of Ta versus Cs in feldspar and muscovite (in mineralized pegmatites) from the study area [adapted after Beus, 1966 (B) and Gordiyenko, 1971(G)]

4.3.5 Tantalum - Niobium Mineralization

Tantalum and niobium are elements with high charge to ionic radius ratios (HFSE) that do not substitute into lattice site in common rock forming minerals and thus behave incompatibly during crystallization of silicate melt (Linnen and Cuney, 2005). These elements are concentrated mainly by high degree of fractional crystallization of peraluminous granitic melt enriched in fluxing agent like F, B, P, Li and water under increasing alkalinity of the melt, commonly associated with pegmatite of the LCT class (Černý, 1991: London, 2008). Thus, the solubility of Ta- and Nb- oxides increases with temperature, increasing alkalinity of the melt and abundance of the fluxing elements in the melt (Linnen, 1998; Linnen and Cuney, 2005). With evolution of granitic melt, Mn is generally enriched relative to Fe during the fractionation of a pegmatitic melt in a closed system (Cerny and Ercit, 1985). The enrichment of Mn in the melt is enhanced by the high activity of Fluorine (Černý *et al*., 1986). Fractional crystallization causes the evolution of tantalite – columbite from ferrocolumbite ($FeNb_2O_6$) to manganotantalite ($MnTa_2O_6$). Therefore columbite should precipitate from the melt earlier than tantalite (Černý *et al*., 1986). As illustrated in the plot of Ta/(Ta + Nb) versus Mn/(Mn + Fe) (Fig 4.15), the composition of the tantalite - columbite is generally controlled by Fe-Mn substitution during fractional crystallization, progressing from ferrocolumbite ($FeNb_2O_6$) to manganotantalite ($MnTa_2O_6$) (Černý *et al*., 1986). The Ta - Nb content of columbite group mineral can be related to that of micas that coexist with them (Van Lichtervelde *et al*., 2007). In Egbe pegmatites, fractionation started from Mn- poor ferrocolumbite towards a slightly Mn- and Nb- enriched manganotantalite and finally to manganotantalite in the more evolved lepidolite. According to Linen and Cuney, (2005), 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 Mn-rich group but the enrichment of Fe- rich group is controlled by the presence of other Fe-bearing mineral such as tourmaline and biotite evolution (London, 2008). According to Černý and Ercit, (1985), Ta-dominant species are restricted to the most highly fractionated complex type of rare-element pegmatite.

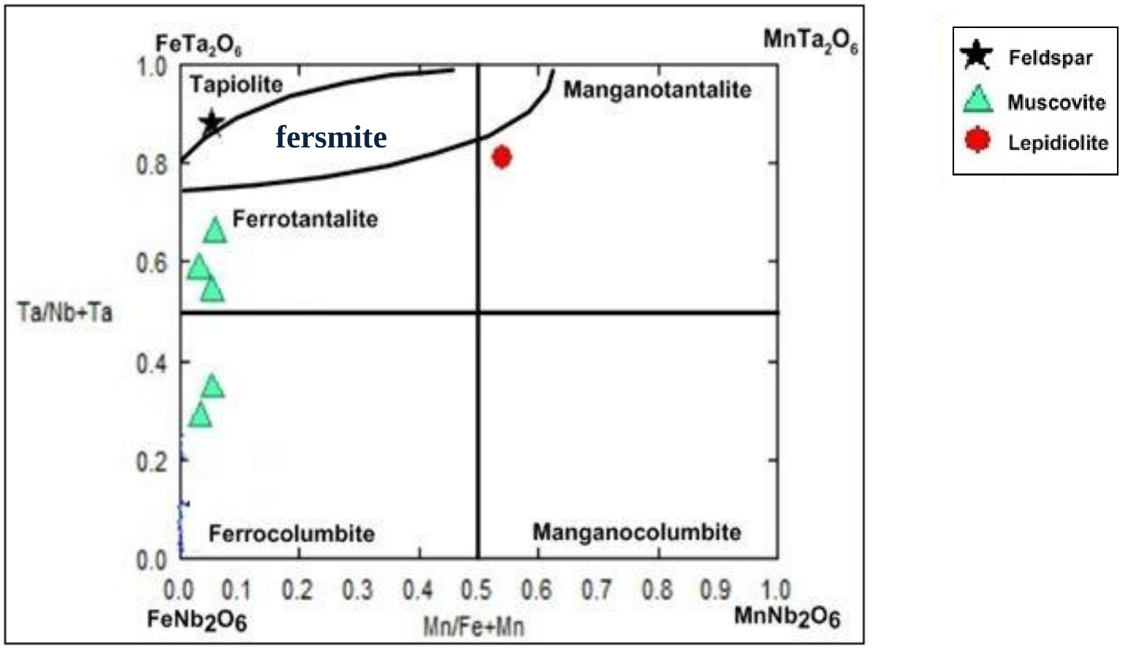


Figure 4.15: Chemical composition of $FeTa_2O_6$ – $FeNb_2O_6$ in feldspar, muscovite and lepidolite and lepidolite (adapted from Černý & Ercit, 1985).

CHAPTER FIVE

5.1 DISCUSSION

The study area is underlain by banded gneiss, metasediments which consist essentially of schist and quartzite, metavolcanics (amphibolite), granites and pegmatite. The banded gneiss is coarse grained in texture and is characterized by alternating light and dark bands. The metasediments are light to dark in colour, foliated and are medium to coarse grain in texture. The foliation strikes in NE–SW direction. Metavolcanic outcrops as minor bodies and plugs in the schists and gneisses. They are massive and dark green in hand specimen. The granite varies in texture and composition and comprises of three textural variants, namely, medium grained granite, coarse grained and porphyritic granites. These granites cover about 60% of the study area. They occur as dykes and veins in the granites, schists and gneisses. The pegmatites are crudely zoned with conspicuous books of mica in places and generally trending in WNW – ESE. The pegmatites consist of large phenocryst of quartz and feldspar suggesting a slow rate of cooling.

Foliation is the most prevalent linear structure in the eastern and southeastern parts of the study area. Rose diagram constructed for these lineaments revealed a WNW – ESE dominant trend which is concordant with the pattern of Pan- African event. Other structural features mapped in the study area include asymmetric and isoclinal folds within the schist and gneiss respectively. These fold types are evidently the records of tectonic activities to which the rocks were subjected to probably during the Pan–African orogeny.

Geochemical study revealed that the granites are metaluminous to peraluminous and are mainly S-type granites. This suggests that the granites formed from the anatexis of schist or aluminous gneisses of sedimentary origin. The original sedimentary rock probably consists mostly of clay - rich material produced by extensive chemical weathering of continental rocks (Chappell and White, 2001). These sedimentary rocks could therefore be the source of the fertile granites from which the rare – metal pegmatite hosting tantalite - columbite mineralization in the study area was derived.

REE distribution pattern reveals 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 (Fig. 4.8). 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 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 convergence of lithospheric blocks during the Pan African orogeny.

Barren and mineralized 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 a depletion of Ba in these pegmatites. The negative Europium (Eu) anomaly, according to Taylor *et al.,* (1986) suggests fractionation and indicates a late metasomatic effect. The negative Ce anomaly observed in the pegmatites may also suggest their rare metal mineralization. Taylor *et al.,* (1986) had also suggested that where there is a negative Ce anomaly and a negative Eu anomaly as in the case of these pegmatite samples it is an evidence of considerable fractionation and metasomatism. Similarly, Piper, (1974) and Garba, (2003) believe that Negative Ce anomaly of rare metal pegmatite is taken to indicate oxidizing condition during mineralization and interaction between, melt fluids and host rocks sometimes over long distance

They also exhibit negative Ce anomaly which is taken to be an indication of oxidizing conditions during rare-metal mineralisation, which possibly involved interaction between magmatic melt-fluids and host rocks over great distances (Garba , 2003)

The pegmatites are fractionated and 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 Igbaruku area and few others from Okere plot within the field of rare-metal pegmatite (Fig. 4.11). Plot of the mineralized pegmatites on the commonly used Godiyenko (1971) discrimination diagram revealed that the mineralized pegmatites in the study area have high potential for tantalite since most of the muscovite extracted from the pegmatites plot above the minimum cut-off point for 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 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 from the study area indicate that the muscovite and lepidolite are enriched in Ta and REE and that they are the possible sites for these rare elements that are associated with the pegmatite.

The geochemical characteristics of the rare-metal pegmatites of the Okere and Igbaruku areas which are hosted by gneisses and schist are unlike those of metamorphic origin, such as the barren pegmatites of the Egbe areas (Table 4.2) 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 low K/Rb ratios of the rare-metal pegmatites attest to their granitic origin.

The most enriched rock in Ta and Nb in the study area is Lepidolite from Okere and the economic mineral in the study area is tantalite.

5.2 From Granite to Pegmatite: A Proposed Petrogenetic Model

Once volatile-rich melts were recognised as the parent magma of individual rare-metal pegmatite, the anatectic or igneous provenance of these melts became a crutial question (Černý, 1991). In the light of the avalaible geochemical evidence such as systematic decrease in K/Rb from granite to pegmatites as well as the systematic fractionation trends from granites to pegmatite as shown in the Nb/Ta versus Ta discrimination diagram (Fig. 11),. The peraluminous nature of these pegmatites and the surrounding granites suggest that both the pegmatites and the sorrounding granites were sourced from the melting of a strongly peraluminous sedimentary / metasedimentary protolith.

5.3 ECONOMIC GEOLOGY

5.3.1 Economically Important Minerals in the study area

Egbe is an old mining area in southwestern Nigeria, well known for its high tantalite mining activities being carried out by artisanal miners at Igbaruku and Okere (Plates XVI - XX).

Tantalite is the main ore mineral from which tantalum is extracted. The primary use of Ta is in capacitors, particularly for wireless devices and touch screen technologies. It is also added to super alloys, because of its resistance to high temperature and corrosion, and is used in high-temperature turbines. Tantalum is biocompatible with human tissue and thus is used in prosthetic joints and pacemakers. Other uses are in surface acoustic wave filters and in carbides for cutting tools.

Gemstones such as beryl and tourmaline are also found in association with the rare – metal pegmatite hosting the tantalite in Egbe area. Feldspars and Quartz abounds in the pegmatites of Egbe.

Plate XVI: Photograph of active artisanal mining pit for tantalite at Okere (08^{o} 12' 24" N, 05^{o} 39' 12.2" E)

Plate XVII: Photograph of tantalite mining pit at Okere (08^o 10$^‘$ 30$^“$ N, 05^o 35$^“$ E)

Plate XVIII: Photograph of exploited tantalite for beneficiation at Okere (08^o 10$^‘$ 32$^“$ N, 05^o 34$^“$ E)

Plate XIX : Photograph of tantalite beneficiation field at Igbaruku (08^{o} $14.2^{'}$ $10^{''}$ N, 05^{o} $37^{'}$ $13.2^{''}$ E)

Plate XX: Photograph of tantalite mine pit at Igbaruku (08^{o} $14.2^{'}$ $10^{''}$ N, 05^{o} $37^{'}$ $13.4^{''}$ E)

5.3.2 Marble

An occurrence of marble was recorded in the study area on a hill 1 km from Okere (Plate: XXI and XXII). Marble has many industrial uses both as mined and processed into a wide variety of products. It is the raw material for a large variety of construction, agricultural, environmental, and industrial products. Marble as one of the purest of natural limestones has been the decorative stone of choice in government buildings and public statues. Marble is used to produce dangote cement at Obajana in Kogi state and in other places, as aggregate in concrete and asphalt. Marble is also the raw material for making lime (CaO) that is used to treat soils, purify water, and smelt copper.

Plate XXI: Photograph of Marble deposit at Okere (08^{o} $11^{'}$ $50.8^{''}$ N, 05^{o} $34^{'}$ $38.9^{''}$ E)

Plate XXII: Photograph of outcrops of Marble at Okere (08^{o} 11$^{'}$ 50.7$^{''}$ N, 05^{o} 34$^{'}$ 38.9$^{''}$ E)

5.3.3 Muscovite

Muscovite is another economic mineral deposit currently being exploited by artisanal miners in Egbe area (Plate: XXIII). It occurs in close association with the tantalite – columbite mineralized pegmatite in the study area. The single, perfect cleavage of micas enables them to be separated into thin, perfectly flat, flexible, strong, and tough flakes. Muscovite is transparent in thin sheets, with colors described as “rum” to light brown. World production of industrial mica in 2009 was estimated at about 348,000 tons (Hedrick, 2010). Muscovite has an outstanding combination of properties: good dielectric constant and electrical resistivity, low thermal conductivity, chemical resistance, high melting temperature, UV resistance, inertness, barrier properties (to sound and moisture), reinforcement properties, and a low coefficient of thermal expansion.

Plate XXIII: Photograph of muscovite being bagged for sale at Okere (08^o 09$^‘$ 57.8$^“$ N, 05^o 35$^‘$ 46.4$^“$ E)

Muscovite has a wide range of applications because of its properties. Transparent sheets of muscovite, known as “isinglass,” were employed as an early form of window material, and the thermal resistance of muscovite led to its usage as windows in cooking and heating ovens. Native Americans used muscovite as an ornament for grave decoration, and they traded it extensively In the U.S., muscovite has been called “the mineral that won World War II.” It served as the first high-temperature, inert, electrically insulating material that could be easily manufactured into thin sheets for use in electrical condensers and vacuum tubes industry.

Other importantant uses of muscovite are:

Fillers

In tape – joints that bond the edges of wallboards, where it reduces shrinkage during drying, of taped joints, thereby reinforcing the joints and making them smooth and crack free. Mica is the optimum mineral filler for maximizing the flexural modulus of engineering resins. In automotive plastic parts, which constitute the largest market for mica-filled parts, mica is found in bumpers, fenders, wheel covers, windshield components, selected interior parts, and under hood components.

Coatings

The durability of mica lends itself to widespread application in paints, stucco, and cements. Mica acts as a barrier to moisture and adds durability to all of these materials. Mica is used in many types of coatings as a performance additive. Mica's shape is perfect for reinforcing the resin system, thus reducing shrinkage and cracking of paint film, creating a barrier layer that minimizes moisture travel through the coating, and resisting UV penetration and damage, all of which add longevity and durability to the coating. Mica's thermal stability also allows its use in foundry coatings and molds. Mica strengthens the coating and provides it with the proper permeability so that gases can escape at the correct time, thus minimizing surface defects. (Alexander *et al*., 2012).

Lubricants

Mica has been used as a coating in roofing materials, paper, marine products, fabrics, seeds, industrial powder coatings, automotive surfaces, tires, wood finishes, furniture, concrete, and machinery. In these applications, the shape and smoothness of ground mica make it useful as a surface lubricant, especially in high-temperatures applications (e.g. tires). In oil well drilling, mica is used as a component of drilling mud lubricant. To prevent the escape of the drilling mud into cracks surrounding the wellbore, the mica flows into the cracks with the escaping mud and seals them, thereby maintaining the pressure of the drilling mud in the wellbore and also reducing loss of drilling fluid.

Premium quality, wet-ground mica is used in cosmetics. Muscovite adds sheen, cohesion, and moisture resistance to nail polish, eye shadow, lipstick, barrier creams, and other products of personal hygiene. In the agricultural market, mica has been used as a dusting agent on fruit trees because the reflection of light off the mica cleavage surfaces repels aphids. Mica flakes also repel insect pests from crops by lodging in their exoskeleton, causing irritation and discomfort.

CHAPTER SIX

6 SUMMARY AND CONCLUSIONS

6.1 SUMMARY

Egbe area is underlain mainly by rocks of the basement complex comprising banded gneiss, biotite schist, amphibolites, granites and pegmatites. The trend of foliation in the study area is a N-S direction with variation between NW-SE and NE-SW. The presence of foliation and folds in the rocks of Egbe area is an evidence of thermotectonic effect which the area have been subjected to probably during the Pan African event. The main evidence of lineation in the study area is the alignment and orientation of biotite, muscovite and quartz.

This research work has established that the area has high potential for columbite – tantalite mineralization. The tantalite-columbite mineralization is associated with the NE-SW trending pegmatite dykes. These mineralized pegmatites are closely associated with peralumimous S-type granite.

The geochemical studies of the muscovite extracted from the pegmatites indicated that the pegmatites are siliceous with a peraluminous composition. Field relationship and geochemical study has established that the mineralized pegmatites are genetically linked to the peraluminous S-type granites. The pegmatites are moderately evolved compared with other highly mineralized pegmatites. Low Cs, low K/Rb are indications of low-moderate enrichment. Chondrite normalized plot of the rare-earth element (REE) for amphibolites, schist, gneiss, porphyritic granite shows negative Europium (Eu) signature suggesting fractionation of plagioclase in melt

The Ta and Nb contents of Egbe pegmatites is low compared to Tanco pegmatite (Canada), but are comparable to those of Nassarswa- Keffi (Wamba) pegmatite field of Nigeria, Wodgina pegmatite (Australia), Hergendorf pegmatite (Western Germany) and Noumas pegmatite (South Africa). Egbe pegmatite is more enriched in Ta than the Jemaa (Kaduna) pegmatite and Ijero (Ekiti) pegmatite fields of Nigeria. In addition to the major and minor element compositional features, consistent negative Eu signature of the 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 alterations.

The study have shown that the pegmatites from Igbaruku and one from Okere plot in the field of rare-metal pegmatite on the K/RB versus Cs plot and are moderately fractionated. The Chondrite normalized plot of REE of these pegmatites exhibited a pronounced negative Ce, Eu and Yb anomalies while the pegmatite from Egbe and one from Okere plot in the field of barren pegmatites. The Chondrite normalized plot of REE of the barren pegmatites showed a positive Ce and Yb anomalies. From the Chondrite normalized plot of REE for the pegmatites in the study area, the rare - metal pegmatites exhibit pronounced negative Ce anomaly, an indication of oxidizing conditions of formation, while the barren pegmatites has positive Ce anomaly, indicating a reducing environment of formation. Rare- metal pegmatites also show weak negative Yb anomaly and the barren ones exhibit weak positive Yb anomaly. The possibility of the tantalite - columbite enrichment in the study area is basically ferro-tantalite - columbite and mangano-tantalite – columbite.

6.2 CONCLUSIONS

The main rock types present in the study area are banded gneiss, schist, amphibolites, granites and pegmatite. Foliation, folds and fractures are the commonly found structures in Egbe area. The general structural trends in the area are NWN – ESE, NE – SW and N – S.

From geochemical study, the granites are metaluminous to peraluminous and are mainly S-type, the granites probably formed from the anatexis of schist or aluminous gneisses of sedimentary origin.

REE distribution pattern generally revealed enrichment in light rare earth elements (LREE) 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 barren pegmatites are characterized by low Rb, Cs, Ta and Nb but high Ba, Sr and K/Rb, while the rare-metal pegmatites are chemically enriched in Rb, Cs and Ta. The depletion of Ba and Sr in the pegmatite indicated that the pegmatite is a product of progressive fractionation. The negative Europium (Eu) and Ce anomalies observed in the pegmatites suggest their fractionation and rare metal mineralization respectively.

The mineralized Egbe pegmatites have high potential for tantalite since most of the muscovite extracted from the pegmatites plot above the minimum cut-off point for tantalite mineralized pegmatites on the Beus and Godiyenko discrimination diagram.

The muscovite and lepidolite are the most enriched in Ta and REE and are therefore the possible sites for the rare - elements associated with the pegmatite. . The low K/Rb ratios of the rare-metal pegmatites attest to their granitic origin.

Igbaruku and Okere are the areas with the highest economic potentials for tantalite – columbite mineralization in Egbe. Other economic mineral deposits in the study area are marble and muscovite.

6.3 CONTRIBUTIONS OF THE WORK TO KNOWLEDGE

The following are the major contributions of this research work to knowledge:

i. A geological map of the study area on a scale of 1:25,000 have been produced

ii. The differences between rare – metal and barren pegmatites in the area have been established

iii. Lepidolite is the most closely associated mica with tantalite in Egbe area

iv. The mineralized and barren pegmatites in the study area show similar geochemical trends to their host granites.

v. This research work has established that the area has high potential for tantalite - columbite mineralization.

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