

## Petrochemical Evaluations of the Pan African Pegmatites of Apomu Area, Southwestern Nigeria

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### Abstract

Pan African pegmatites occurring as near vertical dykes and striking mainly in the NNW-SSE direction have been studied in Apomu area with a view to evaluate their petrochemical features and possible economic potentials. These pegmatites intrude into the older lithology of granite around Apomu area Southwestern Nigeria. Petrographic determinations show they are composed of microcline, quartz and to a lesser extent plagioclase albite with interstitial muscovite, biotite and accessory minerals under transmitted light.

A total of eleven samples comprising whole rock pegmatites were analyzed for major and trace elements using Inductively Coupled Plasma-Atomic Emission Spectrometry analytical technique (ICP-AES).

From the geochemical results, the whole rock pegmatite is considerably siliceous, with an average value of 69.31%, while, MnO with a range of (0.01-0.23%), TiO<sub>2</sub> with a range of (0.01-0.69%), P<sub>2</sub>O<sub>5</sub> with a range of (0.02-0.23%) has values that are generally low. Mean contents of major oxides, Al<sub>2</sub>O<sub>3</sub> (14.34%), Na<sub>2</sub>O (3.31%), Fe<sub>2</sub>O<sub>3</sub> (2.61%), MgO (0.78%), CaO (1.63%), and K<sub>2</sub>O (4.80%) for the Apomu pegmatites compare favorably with the Ipetu Ijesha barren pegmatites, Kafin Maiyaki barren pegmatites and Ago-Iwoye barren pegmatites. Apomu pegmatites are fairly enriched in Rb, Sr, Zr but comparatively, poor in the rare metals Ta, Nb, Cs and Sn. Rare metal mineralization enrichment indices mainly, Ta vs Nb, Ta vs K/Cs, plots, suggests the Apomu pegmatites to be barren in rare-metal mineralization when compared with other rare-metal pegmatites across the world.

**Keywords:** granite, muscovite, pegmatite, mineralization, precambrian

### 1. Introduction

Pegmatites are known worldwide to host economically important mineral deposits such as gem stones and rare metals such as tantalum, niobium, tin and tungsten. Precambrian pegmatites of Nigeria occur mostly as dyke like intrusions which vary from few meters to several kilometers in length and few centimeters to meters in width and have been hitherto thought to be confined to a broad 400km long NW-SE trending belt stretching from Wamba area in central Nigeria to Abeokuta area south western Nigeria (Figure 1a). However, recent studies by (Garba, 2003; Okunlola, 2005), have shown that they are not restricted only to these confines. The south east Obudu hills occurrences are even thought to extend into north east Brazil (Garba, 2003; Ekwueme, 2004). The pegmatite evolved during the time span of 600 to 530 Ma, (Matheis & Caen-Vachete, 1983), which indicates formation during the latter periods of Pan African magmatism.

In recent times, there has been the resurgence of interest in the study of these pegmatites occurrences because of its associated economic rare metal and gem mineralization. This has led to concentration of study on discrimination of the pegmatites into the rare metal mineralized and barren ones in order to elucidate modes and features of mineralization (Matheis, 1981; Matheis et al., 1982; Kuster, 1990; Garba, 2003). Recently, Okunlola, (2005) defined the metallogeny of the rare metal Ta-Nb pegmatites of Nigeria outlining 7 broad fields namely Kabba-Isanlu, Ijero-Aramoko, Keffi-Nasarawa, Lema-Ndeji, Oke Ogun, Ibadan-Osogbo, Kushaka-Birnin Gwari. The Apomu pegmatites occurrences, which are members of the Ibadan-Osogbo fields, have therefore been studied with the aim of elucidating the Petrographic, and Petrochemical features with a view to understanding their genesis and economic potentials. The study area lies between latitude N7°11' and N7°13' and longitude

E4°18' and E4°21' within the basement complex of Southwestern Nigeria. The study area is easily accessible (Figure. 1b), because some of the outcrops are located within the villages while some are located within the dense vegetation; accessibility was made possible by minor roads and foot paths. Other settlements covered include Onkoko, Sango, Ita-marun, Agiri-elemu, Omirin, Akinremi, Idiroko, Alagbede, Ope, Ajebandele, Apaso among others.

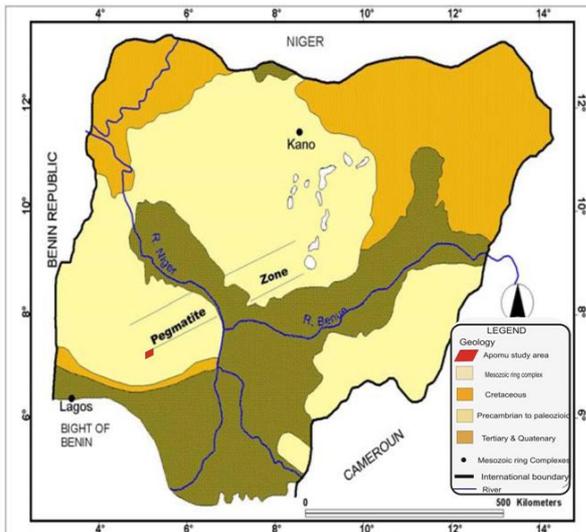


Figure 1a. General geology of Nigeria showing the location of the pegmatite zone (after Kinnaird 1984)

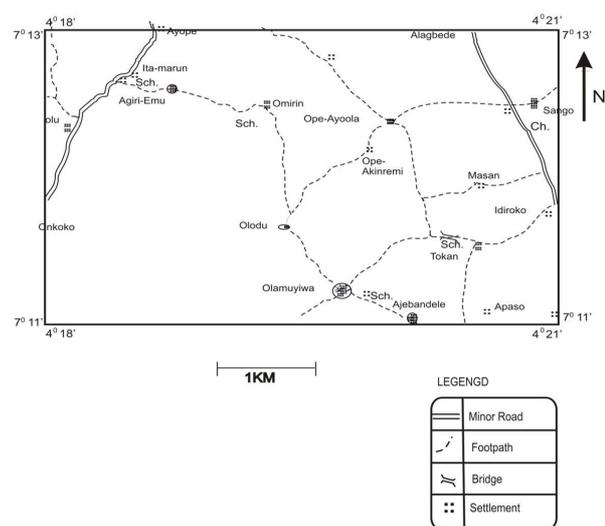


Figure 1b. Showing the location and accessibility map of the study area

## 2. Regional Geological Setting

Rocks of the Precambrian basement complex of Nigeria underlie the project area. The Precambrian basement of African can be divided into three large cratons, these are the Kalahari craton, Congo and West African cratons, separated from each other by a number of mobile belts active in late Proterozoic times. The Nigerian basement complex lies north-east of the Congo Craton in a mobile belt affected by the Pan African Orogeny. These rocks outcrop in two large areas (viz the south-western and north-central parts of the country) and in smaller areas in the northeastern parts and the southeastern parts notably around the Oban massif and Obudu areas (Ekwueme, 2000)

Three main lithologic groups are usually distinguished in the Nigerian basement. These are (i) a gneiss migmatite complex with evidences of polycyclic metamorphism mainly of amphibolites facies grade with Archean and Pan African ages (ii) A N-S trending schist belts of low grade subcrustal rocks with minor volcanic assemblages. They are concentrated in the western half of Nigeria although minor occurrences have been noted in the northern eastern and southern eastern parts (iii) Syn-late tectonic Pan African granite, which are collectively termed Older Granites and intrude the schist belts and the gneiss migmatite complex. They comprise mainly granites pegmatites, gabbros, charnockites, diorites and syenites.

The schist belts, despite paucity of agreements in terms of their nomenclature, geographic delimitation and geodynamic setting are composed largely of metamorphosed pelitic and psammitic assemblages. Secondary lithologies such as ferruginous rocks (Banded Iron Formation), carbonate, and metal ultramafic bodies are often used to discriminate them.

### 2.1 Lithological Association and Petrography

The pegmatites which occur as near vertical dykes strike mainly in the NNW-SSE direction, and intrude into the older lithology of granite. (Figure 2a) The *granite* covers almost the whole portion of the map; the granites which are often coarse grained to porphyritic in texture are mainly composed of biotite, microcline and quartz. The *pegmatite* occurs as coarse inequigranular veins, milky white in appearance; with interstitial mica plates; intruding the older lithology of granite. The main mineral assemblages include quartz, microcline and biotite. From the study of structural features and rosette diagrams plotted, the general trend of the veins and the joints

lies in the NNW-SSE direction which implies that the orientation of joints and veins of the study area are in the same direction and the tectonic forces that led to the fracturing of the outcrops were more pronounced in the NNW-SSE direction which was also shown and demonstrated by the direction of flow of the river and that of the intruding pegmatite (Figure 2b). The petrography of Apomu pegmatite under the thin section study shows that the predominant constituents include microcline, quartz, biotite, plagioclase, and opaque minerals. The modal proportions of the dominant mineralogical composition of some of the studied samples are presented in (Table.1). Quartz exhibits euhedral shape with wavy extinction. The plagioclase feldspar exhibits polysynthetic twinning with microperthite development which is exsolution growth while microcline displays cross-hatch twinning or pericline twinning and is often graphically intergrown with quartz; biotite generally occurs as dark brown platy grains within the samples. (Figure 3)

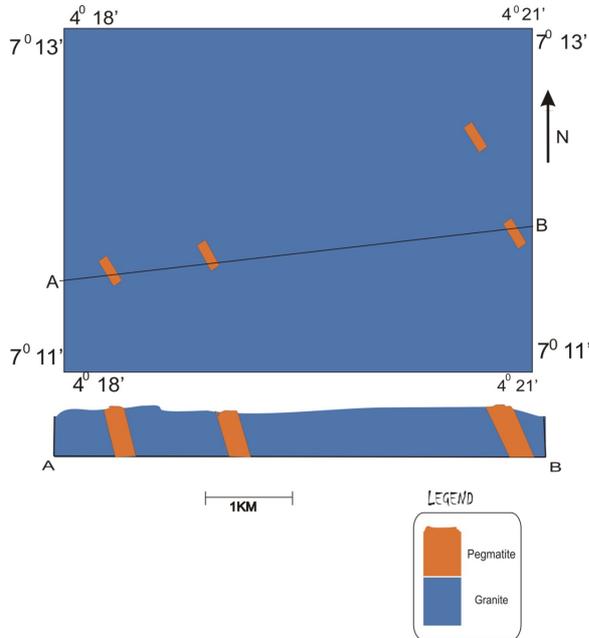


Figure 2a. The geological map of apomu study area

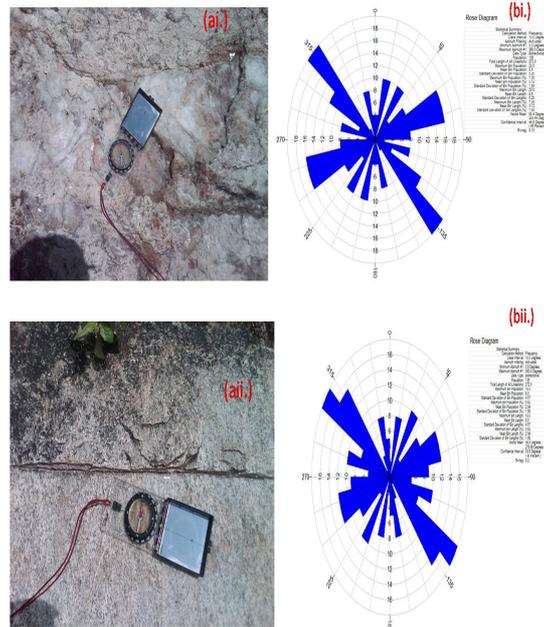
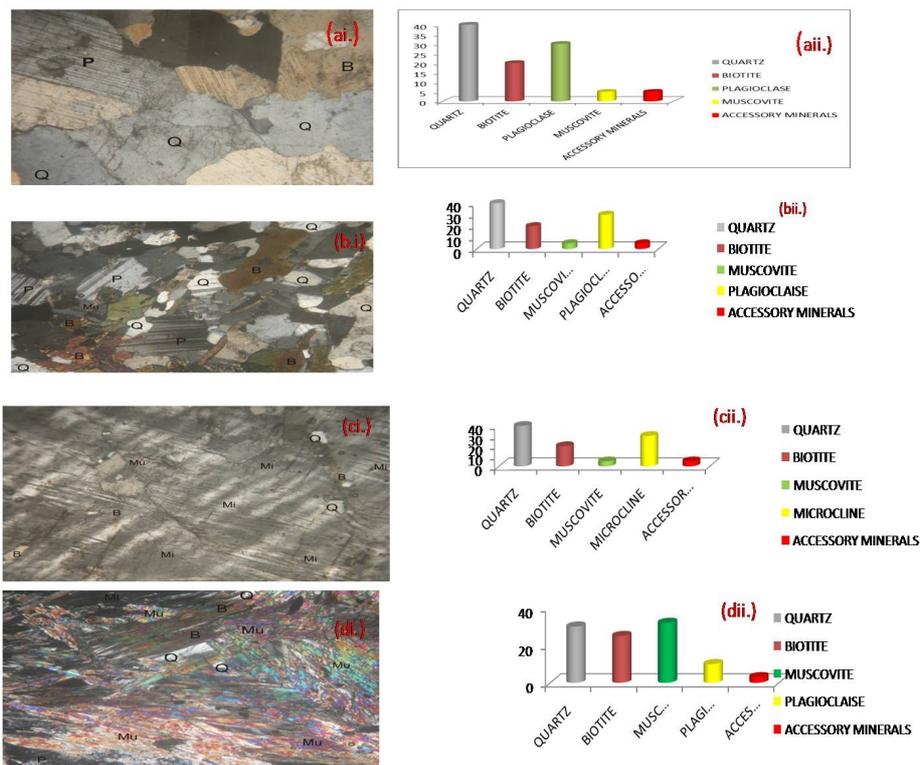


Figure 2b. The rosette diagram plot and orientations of veins in the Apomu pegmatite field, as shown by (ai.) and (bi.). The Rosette diagram plot and orientation of Joints in the Apomu pegmatite field, as shown by (a ii.) and (b ii.)

Table 1. Average modal composition (%) of minerals of Representative samples in Apomu pegmatites

Minerals	P1 (%)	P2 (%)	P3 (%)	P4 (%)
Microcline (M)	30	30	35	10
Muscovite (Mu)	05	05	-	32
Quartz (Q)	40	40	40	30
Biotite (B)	20	20	20	25
Plagioclase (Pl)	-	-	1	-
Accessories (A)	05	5	4	03
Total	100	100	100	100

P1-P4 represent photomicrographs of pegmatites from apomu study area.



Bar scale =20mm, (Resolution: 150dpi)

Figure 3a (i.). Photomicrograph of Pegmatite in transmitted light showing Quartz (Q), Biotite (B), and plagioclase (P); b (i.): Photomicrograph of Pegmatite in transmitted light showing Quartz (Q), Biotite (B), Plagioclase (P), Muscovite (Mu). C (i.): Photomicrograph of Pegmatite in transmitted light showing Microcline (Mi), Biotite (B), Quartz (Q) and Muscovite (Mu). D (i.): Photomicrograph of Pegmatite in transmitted light showing Plagioclase (P), Quartz (Q), Biotite (B), and Muscovite (Mu). 3a (ii.), b (ii.), c(ii.) and d(ii.) Modal distributions of estimated minerals in Apomu pegmatites

### 2.1.1 Petrochemical Features

Eleven samples of whole rock pegmatites were analyzed for major, trace and rare earth elements using inductively-coupled plasma atomic emission spectrophotometry (ICP-AES), at Activation Laboratories Ltd. (ACTLAB) Ancaster, Ontario Canada. The geochemical analytical procedure involves addition of 5ml of Perchloric acid (HClO<sub>4</sub>), Trioxonitrate (V) HNO<sub>3</sub> and 15ml Hydrofluoric acid (Hf) to 0.5gm of sample.

The solution was stirred properly and allowed to evaporate to dryness after it was warmed at a low temperature for some hours. 4ml hydrochloric acid (HCl) was then added to the cooled solution and warmed to dissolve the salts. The solution was cooled; and then diluted to 50ml with distilled water. The solution is then introduced into the ICP torch as aqueous - aerosol. The emitted light by the ions in the ICP was converted to an electrical signal by a photo multiplier in the spectrometer, the intensity of the electrical signal produced by emitted light from the ions were compared to a standard (a previously measured intensity of a known concentration of the elements) and the concentration then computed.

### 3. Results and Interpretation

The analytical results are presented in Tables 2, 3, 4, 5 and 6. Major element distribution show that the pegmatites are siliceous; with SiO<sub>2</sub> content ranging between 46.03% and 73.54% with an average value of 69.31%; this is marginally lower than average values of rare metal Ta-Nb pegmatite of Nigeria (Okunlola, 2005) but comparable to the Ipetu ijsha barren pegmatites (Elueze, 1982), and Ago-Iwoye barren pegmatites (Akintola et al., 2011). From the analytical result of major element concentration, SiO<sub>2</sub> has the highest percentages in the pegmatite samples while P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, CaO and MnO are relatively low, in the same vein MnO

(0.01-0.23%), TiO<sub>2</sub> (0.01-0.69%), P<sub>2</sub>O<sub>5</sub> (0.02-0.23%) values are generally low (Tables 2 and 4). Mean contents of major oxides, Al<sub>2</sub>O<sub>3</sub> (14.34%), Na<sub>2</sub>O (3.31%), Fe<sub>2</sub>O<sub>3</sub> (2.61%), CaO (1.63%), and K<sub>2</sub>O (4.80%) for the Apomu pegmatites compare favorably with the Ipetu Ijesha barren pegmatites, Kafin Maiyaki barren pegmatites and Ago-Iwoye barren pegmatites (Elueze, 1982; Garba, 2003; Okunlola, 2005; Akintola et al., 2011).

Table 2. Major element oxide composition of Apomu Pegmatites (Wt %)

SAMPLE	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Cr <sub>2</sub> O <sub>3</sub>
	%	%	%	%	%	%	%	%	%	%	%
1	73.51	14.32	0.55	0.15	1.34	3.14	6.21	0.06	0.05	0.01	<0.002
2	66.01	15.79	4.40	1.80	3.09	4.06	3.00	0.69	0.23	0.07	0.008
3	72.05	15.43	0.26	0.03	0.57	2.88	8.24	0.03	0.04	<0.01	<0.002
4	72.19	15.37	0.44	0.07	0.89	3.50	6.81	0.05	0.04	<0.01	<0.002
5	75.54	13.52	0.65	0.11	0.71	3.13	5.91	0.06	0.02	0.01	<0.002
6	73.25	14.53	1.60	0.25	1.17	4.42	4.03	0.15	0.05	0.04	<0.002
7	72.60	14.66	0.55	0.61	0.25	2.69	7.86	0.02	0.10	<0.01	0.009
8	74.63	14.31	0.29	0.03	0.19	4.52	5.45	<0.01	0.09	0.04	<0.002
9	46.03	7.84	13.67	3.47	2.54	0.14	0.05	0.32	0.03	0.23	0.339
10	68.35	16.25	3.15	1.37	5.12	4.26	0.48	0.20	0.04	0.05	<0.002
11	68.23	15.77	3.16	0.67	2.08	3.65	4.73	0.39	0.20	0.06	<0.002

Table 3. Trace and rare earth element data of apomu pegmatites (ppm)

ELEMENT	V	Zr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm
	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
1	<8	56.8	6.7	13.7	24.9	2.77	9	1.96	0.45	1.52	0.26	1.23	0.26	0.74	0.12
2	53	291.2	23.8	38.4	86.2	9.7	36.1	6.36	1.53	5.05	0.82	4.58	0.88	2.56	0.38
3	<8	31.6	90.2	27.5	55.9	6.52	23.4	6.49	0.58	8	1.92	12.46	2.89	8.77	1.41
4	<8	39.6	108.9	21.6	44.8	5.12	19	5.4	0.55	7.93	2.12	15.06	3.56	11.26	1.73
5	<8	23	9.7	29.4	60.6	6.92	24.1	4.89	0.3	3.38	0.49	1.99	0.37	0.94	0.14
6	<8	41.3	13.6	35.3	71.5	8.28	26.7	5.77	0.32	4.34	0.64	2.87	0.51	1.29	0.19
7	<8	4.6	4	0.7	1.4	0.19	0.6	0.3	0.05	0.38	0.11	0.6	0.11	0.45	0.07
8	<8	3.3	4.2	0.8	1.6	0.19	0.8	0.37	<0.02	0.38	0.12	0.75	0.13	0.43	0.08
9	127	28.1	13.7	4.5	6.9	1.63	8.2	2.03	0.44	2.44	0.43	2.28	0.48	1.48	0.23
10	58	25.3	2.5	8.2	14.5	1.46	4.7	0.69	0.49	0.56	0.09	0.56	0.1	0.24	0.04
11	19	209.9	16.7	50.2	97	10.64	35.2	5.99	1.18	4.28	0.64	3.03	0.61	1.73	0.26

Table 4. Range and average values of major elements in the whole rock of Apomu pegmatites in mass fraction (Wt %)

WHOLE ROCK PEGMATITE		
N=11		
ELEMENTS	RANGE	AVR (%)
SiO <sub>2</sub>	46.03 – 75.54	69.31
Al <sub>2</sub> O <sub>3</sub>	7.84 – 16.25	14.34
Fe <sub>2</sub> O <sub>3</sub>	0.26 – 13.67	2.61
MgO	0.03 – 3.47	0.78
CaO	0.19 – 5.12	1.63
Na <sub>2</sub> O	0.14 – 4.52	3.31
K <sub>2</sub> O	0.05 – 8.24	4.8
TiO <sub>2</sub>	0.01 – 0.69	0.18
P <sub>2</sub> O <sub>5</sub>	0.02 – 0.23	0.08
MnO	0.01 – 0.23	0.05
Cr <sub>2</sub> O <sub>3</sub>	0.002 – 0.339	0.03

Table 5. Range and averages of some of the trace elements in the whole rock of Apomu pegmatites (ppm)

WHOLE ROCK PEGMATITE		
N=11		
ELEMENTS	RANGE (ppm)	AVR (ppm)
Ta	0.2 – 3.8	1.35
Cs	0.2 - 11.3	5.07
Rb	2.3 – 540.1	212.96
Sn	1 – 9	3.36
Nb	1.6 – 26.6	9.46
Sr	3.6 – 531.7	198.15
Y	2.5 – 108.9	26.73
Hf	0.2 -8.3	2.25
Ba	9 – 1443	433.45
Th	0.2 – 19.9	9.5
Be	1 – 6	2.73
Zr	3.3 – 291.2	68.61
Ga	10.9 - 25.0	19.08
Zn	5-59	24.18
Ti	0.1-0.9	0.24

Trace and rare earth element data (Tables 3, 5 and 6) show that the following trace element Rb (540.1ppm), Cs (11.3ppm), Nb (26.6ppm), Ta (3.8ppm), Be (6.0ppm), Th (19.9ppm), Hf (8.3ppm), Y(108.9ppm), Sn (9.0ppm), Sr (531.7ppm) for the whole rock pegmatite samples of Apomu area has values that are significantly lower than the averages for the rare metal pegmatites of Ijero-Aramoko-Ara, Kushaka-Birni Gwari, Oke- Ogun, Isanlu-Egbe and Share but are comparable to the Ilesha barren pegmatites (Elueze, 1982; Okunlola, 2005) , Nasarawa-Kafin-Maiyaki barren pegmatites (Garba, 2003) and Ago-Iwoye barren Pegmatites (Akintola et al., 2011). The Rb/Sr ratio is low when compared to other rare metal mineralized pegmatites of Nigeria (Matheis &

Emofurieta, 1987; Okunlola & Ocan, 2002; Okunlola, 2005, Elueze, 1980; 1981) but compares with the barren Nasarawa pegmatites (Garba, 2003). The K/Rb ratio have values that are significantly higher than those of the rare metal pegmatites of Nigeria but are comparable with values of the barren pegmatites and granitoids (Kuster, 1990; Garba, 2003).

From the plot of K/Rb versus Cs (Figure 4); for the whole rock pegmatites of Apomu which separates barren fractionation sequence and mineralized pegmatites; show the Apomu pegmatite samples as plotting in the barren field, confirming the low degree of fractionation. From the works of Garba, (2003), it is believed that extreme fractionation of lithophile elements such as Rb and Cs is a common geochemical feature of granitic pegmatites, especially the rare-metal bearing types. Late – stage progressive fractionation crystallization leads to decrease in K: Rb ratio suggesting metasomatism and invariably mineralization. However this assertion is not in consonance with values obtained for the Apomu pegmatites in which the K/Rb ratio was on the higher side due to no late-stage progressive fractionation crystallization, hence, no mineralization. Further, from the plot of K/Rb versus Cs (Figure 4); it can be inferred that, the Apomu pegmatites are relatively unfractionated (\*primitive\*) when compared with the rare-metal pegmatites. While Rb is an indicator of the degree of fractionation in the granitic pegmatites, Cs appears to be the most important discriminator of the rare-metal pegmatites.

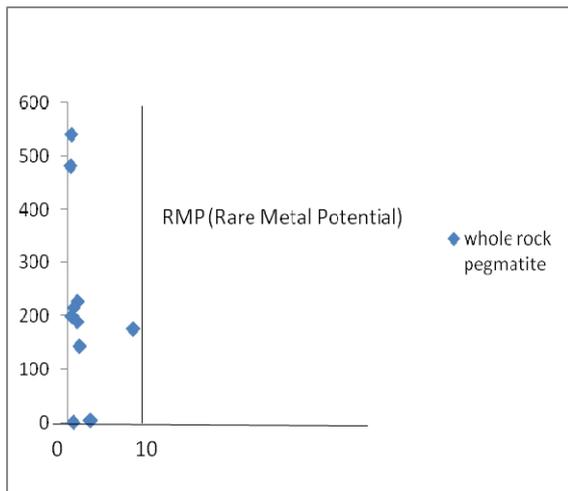


Figure 4. Plot of K/Rb versus Cs for Apomu Pegmatites. Discrimination line separates the field of rare metal pegmatites from the barren class ( adapted from Cerny, 1982)

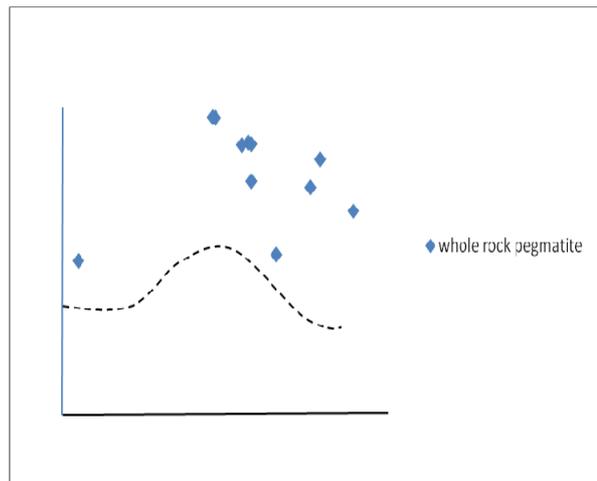


Figure 5. Plot of  $Na_2O/Al_2O_3$  vs  $K_2O/Al_2O_3$  (Wt%) showing variation diagram for the field of Igneous and Meta sedimentary rocks of Apomu Pegmatites (After Garrels & Mackenzie, 1971)

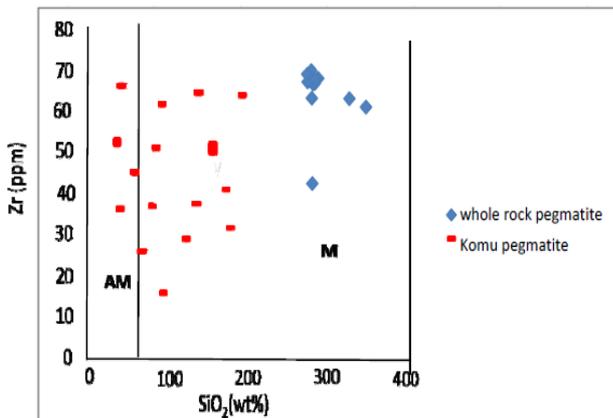


Figure 6. Zr-SiO<sub>2</sub> Plots of the Apomu whole rock pegmatites compared to those of the Komu pegmatites

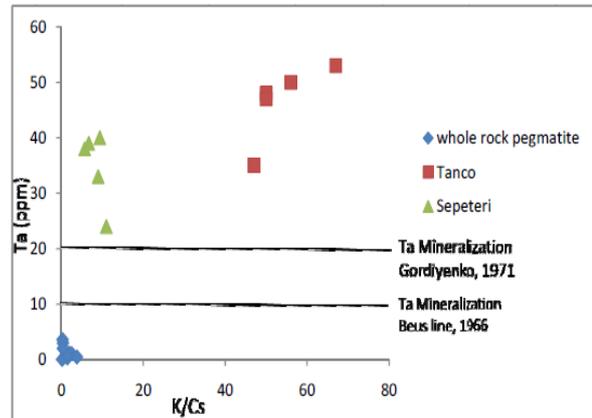


Figure 7. Plot of Ta vs K/Cs ratio for the pegmatites of Apomu study area (After Gordiyenko, 1971; Beus, 1966).

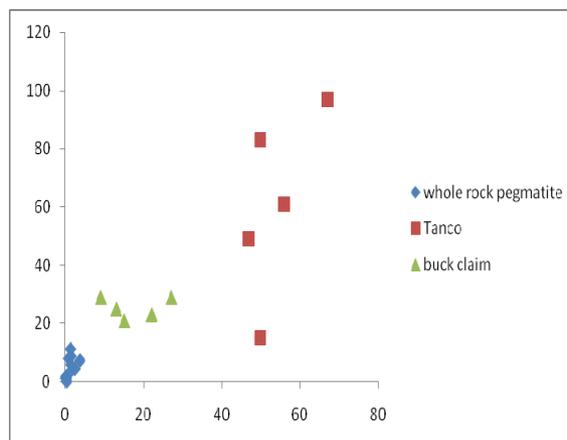


Figure 8. Plot of Ta vs Cs for the pegmatites of Apomu study area (After Moller & Morteani, 1987)

The variation diagram plot (Figure 5) of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  versus  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  reveals the igneous ancestry of the pegmatite which plot in the granite-igneous field of Garrells and Mackenzie, thus indicating and suggesting a granitic-igneous ancestry for the Apomu pegmatites. The plots of  $\text{Zr}/\text{SiO}_2$  (Figure 6) reveal samples plotting completely in the magmatic “M” field suggesting pegmatite outcrops around Apomu area to be genetically magmatic with no post magmatic metasomatism and poorly differentiated. This further confirms minimal or lack of metasomatic alterations or extensive post magmatic differentiation in their emplacement. This might also mean a close proximity of emplacement to their parent melt sources, which is “*insitu*”.

The Ta-Nb mineralization potential trend as shown from plot of Ta versus K/Cs (Figure 7) shows the whole rock samples of Apomu pegmatites plotting far below the boundary of mineralization Beus, (1966) line suggesting the pegmatites of this study area to be barren. In comparing with the global Ta-Nb endowments, from variation plots of Ta versus Cs (Figure 8), Apomu pegmatites compare favorably with the barren pegmatites of Pullerstreuth (Moller & Morteani, 1987).

They compare favorably with the barren pegmatites and granitoids of Nasarawa and Kafin Maiyaki Northern Nigeria (Garba, 2003), Itakpe Area Central Nigeria (Okunlola & Somorin, 2005), and plot far below the highly endowed Tanco pegmatites. In the same vein,

The Apomu pegmatites plot far below the marginally endowed White City, Cross Lake, Buckclaim, pegmatites all of Canada, Noumas South Africa (Moller & Morteani, 1987) and Sepeteri Nigeria (Okunlola & Akintola, 2007).

These plots confirm the barren nature of the Apomu Pegmatites. In the same vein they show the Apomu samples plotting far below the boundary of mineralization lines of Beus, (1966) and Gordiyenko, (1971), and also far below other rare metal pegmatites from across the world. Following after the classification criteria of pegmatites based on bulk chemistry signatures (Cerny, 1991), The Apomu pegmatites are of the simple non-mineralized class.

#### 4. Summary and Conclusion

The pegmatite which occur as near vertical dyke and strike mainly in the NNW-SSE direction, intrude into the older lithology of granite around Apomu area Southwestern Nigeria. Petrographic determinations show they are enriched in microcline, quartz and to a lesser extent in plagioclase albite with interstitial muscovite, biotite and accessory minerals. Geochemical studies reveal that they are poorly fractionated this shows nearness, to their parental melt sources. Rare metal indicative elements Ta, Nb, Rb, Cs, Sn are depleted in the rock unit while elemental ratio, K/Rb, Ba/Rb suggest low index of differentiation, poor fractionation and barren mineralization. Poor albitization is demonstrated in low Na/K ratio, while Ta vs Cs, Ta vs Rb and Ta vs K/Cs confirms its apparently poor or barren mineralization compared to other pegmatites bodies in Nigeria and around the world.

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