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Geochemistry and K-Argeochronologyof Rare Metal Pegmatite, Osogbo-Okinni Area, Southwestern Nigeria: *Implications for Their Petrogenesis and Age of Emplacement*

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Abstract
Osogbo-Okinni pegmatite bodies intruded gneissic granite, quartzite, amphibolite, and granite as low-lying, thin, and massive dykes, sometimes up to 500mx150m in size. Quartz (25.0%), microcline (34.0%) and plagioclase (24.0%) were the main mineral constituents, with muscovite(5.0%), biotite (5.0%), and tourmaline (7.0%) as minor constituents. The mean concentration of SiO_2, Al_2O_3, Na_2O, K_2O and TiO_2 were 70.92, 15.95, 3.5, 4.23, and 0.02wt%, respectively. Average whole pegmatite trace elements contents (ppm) were 283.95, 101.94, and 70.35 for Ba, W, and Ta. LREE sum (18.92ppm) greater than HREE sum (2.22ppm), Low K/Rb (50.37-340.77) and Mg/Li (1.23-36.54) ratios indicated fractionated pegmatites.The mica extracts average trace elements contents (ppm) was 510.86, 104.86, 376.88, 1101.97, and 272.41 for Sn, Sc, Li, Rb, Nb, respectively. Na_2O+K_2O versus SiO_2, Al_2O_3/Na_2O+K_2O versus $Al_2O_3/CaO+Na_2O+K_2O$ and K/Rb versus Cs plots indicated an igneous origin, peraluminous nature and placement in the muscovite class of lithium-caesium-tantalum pegmatite family.The unspiked K-Ar dating, (Cassignol technique) yielded an absolute age of 774-692 Ma for the pegmatites, corresponding to evolution during the early Pan-African orogeny. This agrees with the early Brasiliano orogeny of South America (790Ma; 730-700Ma), both of which were created during the Gondwana formation between the Neoproterozoic and Cambrian evidenced by the presence of post-collisional granitoid plutons.

Keywords: *Osogbo-Okinni, pegmatites, Pan African Orogeny, Fractionation, Cassignol technique.*

Introduction

Nigeria possesses appreciable reserves of solid minerals, which include, precious stones, industrial and energy, base minerals, and metals. Pegmatite is an important source of a large range of these rare metals (Cerny, 1994). There is therefore a need to locate, delineate and constrain as many fertile pegmatite occurrences as possible in line with Nigeria's quest to diversify her economy. Nigeria falls withinthe Pan-African Orogenic belts generally made of rocks of Archean to Proterozoic age (4000-542Ma) modified during the Neoproterozoic to Cambrian (1000-488Ma) orogenicactivities resulting in plutons which are essentially post-collisional granitoids (Kuster and Harms, 1998). These orogenic belts spreads from the African continent to the Braziliano orogenic belt of Latin America (de Wit et al., 2008).

Generally, Nigerian pegmatites enriched in rare metals Ta-Nb-Sn are complex albitised muscovite-quartz-microcline with unrecognisable to well delineated zonation (Okunlola and Jimba, 2006). Several studies targeted at locating rare metal pegmatites have been undertaken in Nigerian precambrian basement complex which have led to the discovery and exploitation of rare metals. For example, Okunlola and Akinola (2010) examined the petrochemical characteristics of Oke-Asa area pegmatites for Ta-Nb mineralization implications, while the geochemistry and U-Pb zircon geochronology of pegmatites in Ede area,Southwestern Nigeria were studied by Adetunji et al., (2016) resulting in the new discovery of the oldest Pan African rock in Southwestern Nigeria. In other parts of Nigeria, studies were undertaken to identify rare metal mineralization such as in parts of Oban Massif, Southeastern Nigeria, (Ero and Ekwueme, 2009) and in Pan-African 600$\pm$150 basement of Northern Nigeria, (Garba,2003).

Osogbo-Okinni pegmatites are part of the Ibadan-Osogbo pegmatite field delineated by Okunlola, (2005), which intruded gneissic granite, quartzite, amphibolite, and granite as low-lying, thin, and massive dykes, up to 150mx500m. In line with the discovery of rare metals in Nigerian pegmatites and in continuation of the quest for more of these pegmatites, this study is aimed at the evaluation ofthe compositional features for mineralization potential and placement of the Osogbo-Okinnipegmatites in the geochronological sequence by absolute age derived from the Cassignol technique of K-Ar dating.

Study Area Description

Nigeria is underlain by three main litho-stratigraphic components, namely the basement complex, which is a part of the Pan-African mobile belt situated between Congo and West African cratons and south of the Tuareg shield (Black, 1980), it is polycyclic and bears the imprint of Liberian orogeny (2.9-2.5Ma), Eburnean tectonism (2080-2020Ma) and Pan-African orogeny (750-550Ma). The younger granites, which are Mesozoic calc-alkaline ring complexes, intrude into the basement complex at the Jos plateau area of Northern Nigeria and both are unconformably overlain by cretaceous and younger sediments.

Osogbo-Okinni area falls within the basement complex of Southwestern Nigeria, which occupies the reactivated region produced from plate collision between the inactive continental margin of the West African craton and the active Pharusian continental margin (Burke and Dewey, 1972; Dada, 2006). A regional metamorphism which produced migmatites, syntectonic granites and homogeneous gneisses accompanied the Pan-African orogeny (Abaa, 1983). Late tectonic emplacement of granites and granodiorites and associated contact metamorphism accompanied the end stages of this last deformation. The last part of the orogeny was characterised by faulting and fracturing (Gandu et al., 1986; Olayinka, 1992).

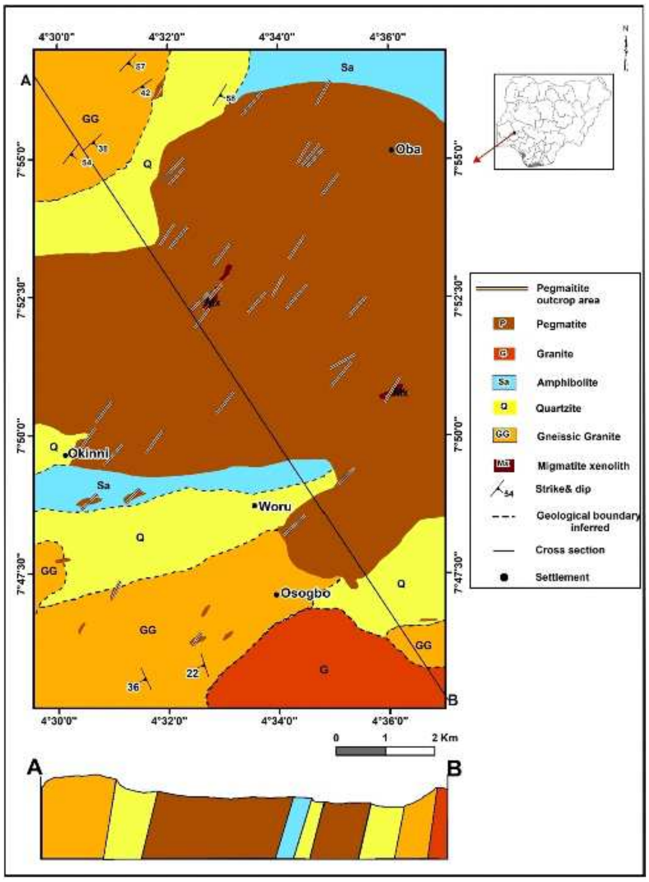
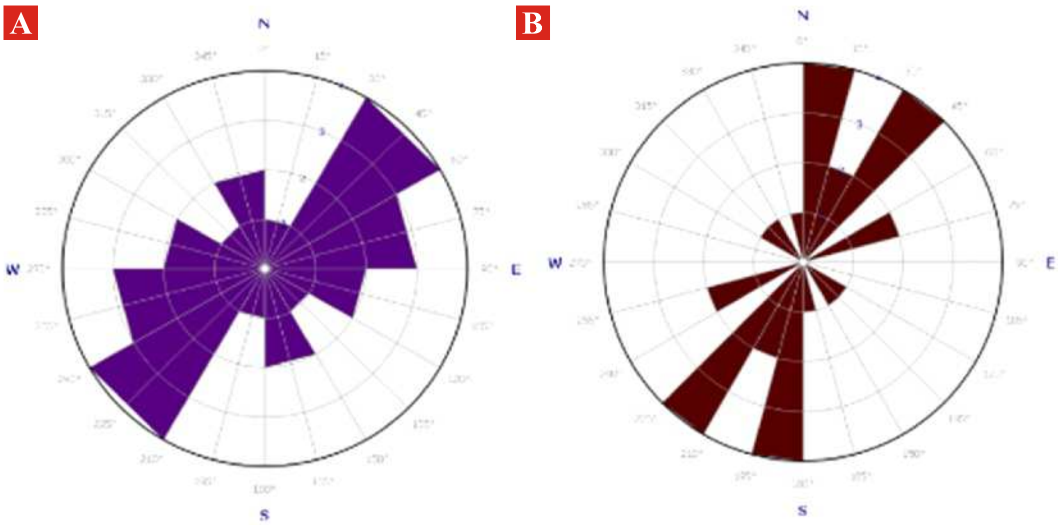


Fig. 1: Geological map of Osogbo-Okinni area

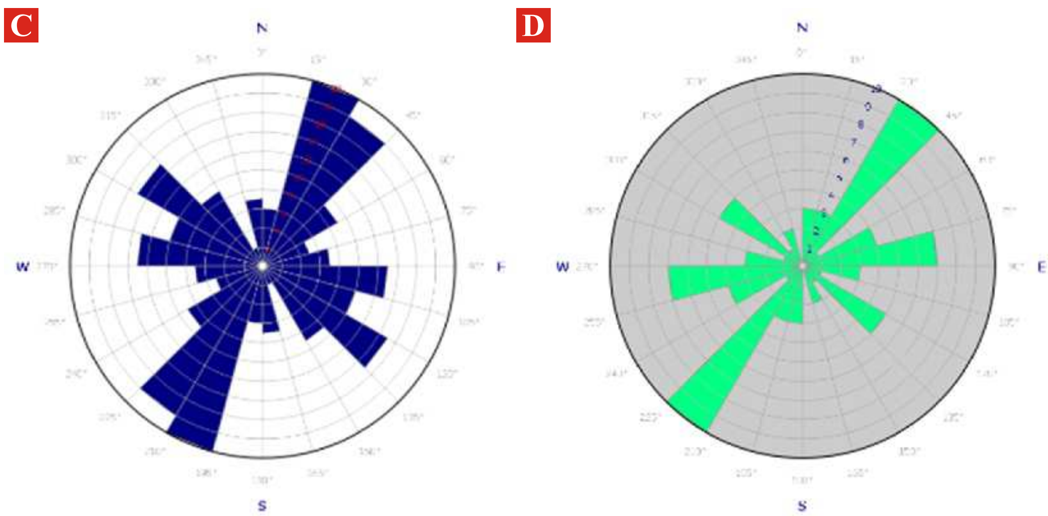
Rock types identified in Osogbo-Okinni area include migmatite which occur as xenoliths in pegmatites of the northcentral and eastern part of the study area, Fig. 1. Amphibolite which is part of the Proterozoic schist belts of southwestern Nigeria is found outcropping in the northeastern and central parts with large pegmatite vein intrusions in some parts.Granite gneiss which outcrops at four locations including the west of Osogbo, southwest, extreme northwest and eastern end of the study area, have indelible imprints of early to late Precambrian metamorphic episodes. Igneous reactivation of these suites of rocks has been attributed to the Pan-African thermotectonicevent. Granite outcrops mainly at the south to southeastern part of Osogbo.Quartzite occurs as massive ridges at the northwestern part and as hilly outcrops at the southern part of the study area. The pegmatites occur as thin distinct dykes of dimension ranging from about3.5m to 10m length and 1.2m to 5m breath intruding amphibolite and about 10m to 500mlength and 10m to 150m width massive mountainlike plutons in proximity without any regular pattern between the central to northern part of the area, they occupy about 60% of the land mass.Structural studies on the rock types of the area reveal foliations in the amphibolites and gneissic granites while all rock types display joints and quartzofeldspatic veins oriented in different directions. Rose diagrams plotted for the joints and veins show orientation in two major directions, NW-SE, and more prominent NE-SW, revealing deformation from the effect of Archean or pre-Pan-African orogeny and Pan African orogeny respectively. (Toteu et al., 1990; Egesi and Ukaegbu, 2010). (Fig. 2a-2f).

Methods/Techniques

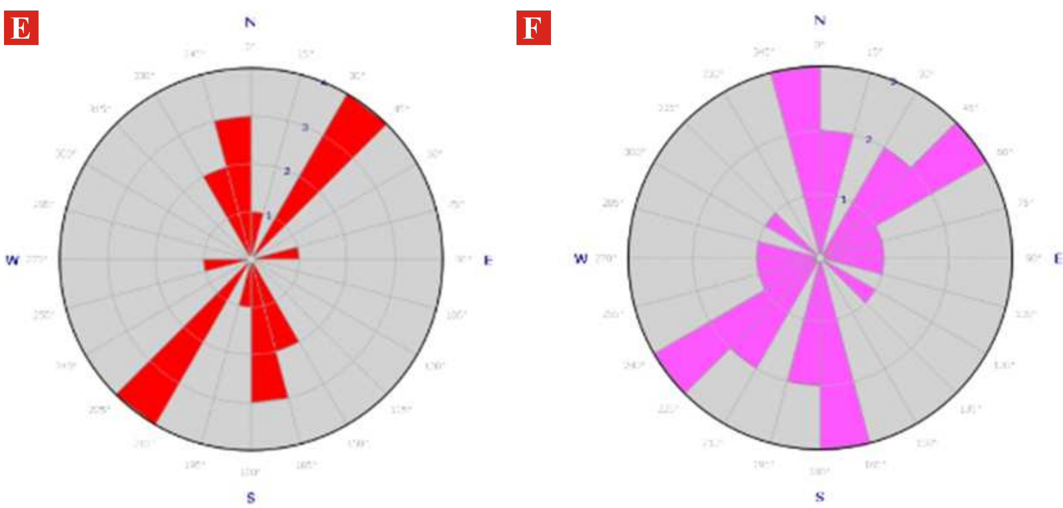
Field relationship between pegmatite and other rock types was established in terms of location, mineralogy-based identification, and structural features. Sixty-three samples of pegmatite and other rock types were taken for petrographic, geochemical analysis and dating, (Fig. 3). Selected samples which include 22 whole rock pegmatite, 22 feldspar and 17 mica extracts were prepared for laboratory analysis by crushing and grinding into powder using porcelain mortar and pestle. The geochemical analysis was undertaken using Inductively Coupled Plasma Emission Spectroscopy/Mass Spectroscopy (ICP-ES/MS) analytical technique, to give near accurate values for all elements, at Bureau Veritas Mineral Laboratories, Vancouver, Canada. Five muscovite samples extracted from the Osogbo-Okinni pegmatites were dated using the conventional K-Ar method modified by Cassignol and Gillot, 1982, called the Cassignol technique for potassium-argon dating. Analysis of the muscovite



Figs. 2(a & b): Rose diagram for the orientation of joints (a) and of veins (b) in Gneissic granite of Osogbo-Okinni area



Figs. 2(c & d): Rose diagram for the orientation of joints (c) and of veins (d) in Pegmatite of Osogbo-Okinni area



Figs. 2 (e & f): Rose diagram for the orientation of joints (e) and of veins (f) in Granite of Osogbo-Okinni area samples for potassium content was carried out using Inductively Coupled Plasma Emission Spectroscopy/Mass Spectrometry (ICP-ES/MS) analytical method at Bureau Veritas Mineral Laboratories, Vancouver and utilized at the Geochronological Research Center, Institute of Geosciences, University of Sao Paulo, Brazil, for application in the dating technique. Ar extraction from the muscovite samples, purification and Ar isotope measurement were carried out also at the above-named Institute in Brazil.

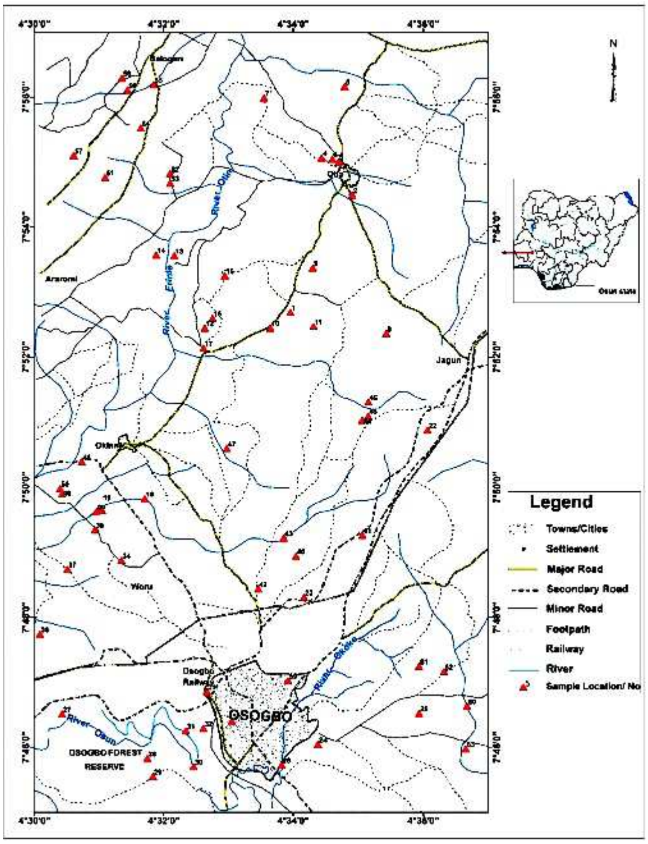


Fig 3: Map of Osogbo-Okinni area showing the sample locations.

Results/Discussion.

Petrography

Petrographic studies reveal a mineral assemblage of mainly quartz, plagioclase (albite), microcline, muscovite, and biotite. Tourmaline, zircon, garnet, and opaque minerals are minor accessories (Table 1). Quartz exhibits anhedral to sub-euhedral shape, intergrowth with feldspar, colourless to cloudy with evidence of poikilitic inclusions of feldspar and other minerals. under crossed polars it displays low positive relief.Plagioclase which is mainly albite with characteristic albite twinning is present in most samples. The nature and type of twinning in plagioclase provides important clues about the origin of the rock,the C-type twins include Carlsbad, albite-Carlsbad and penetration twins which are abundant in plagioclases in the pegmatites of the study area may indicate their magmatic origin (Fig. 4a,b,d). Large crystals of microcline (Fig. 4b) which is a low-temperature polymorph of K-feldspar are abundant in the pegmatites of Osogbo-Okinni area. Current concepts have it that primary pegmatitic K-feldspar grows as a partial or fully disordered phase, with associated growth-twins of Baveno, Manebach or Carlsbad laws, and develops the albite-pericline (cross-hatched) twinning only upon inversion to microcline (Martin, 1988). Microcline shows perthitic texture resulting from the exsolving of albite crystals (Fig. 4d). Muscovite occurs as pink and yellow elongated platy crystals interstitial between other minerals like quartz and feldspar (Fig. 4a). Biotite is seen (Fig. 4b) as brownish platy minerals exhibiting perfect cleavage in one direction and strong birefringence colour. However, muscovite is more prevalent in the pegmatites of the study area, this may indicate the peraluminous nature of the pegmatite. The crystallization of muscovite from melt along with quartz, albite and k-feldspar constrains pegmatites to crystallize at pressures and temperatures within the stability range of this assemblage which is mostly below 650^{o}C to 700^{o}C at pressures of 200 to 400 Mpa H_2O (London, 2008).

The presence of muscovite primarily and tourmaline with garnet (Fig. 4c) as accessory minerals in the pegmatite of Osogbo-Okinni area suggest a peraluminous nature of the source magma for these pegmatites and the abundance of muscovite in most samples (Table 1), which is a veritable source of both lithium and caesiumis one of the pointers to the classification of these pegmatites as members of LCT family of pegmatites.

Geochemistry

Major Elements Characterisation of Whole Rock, Feldspar and Mica Extracts

The result of the geochemical analysis of the major element composition of whole rock samples as presented in Table 1, shows that the Osogbo-Okinni pegmatite are highly siliceous with SiO_2 values ranging from 59.12 to 79.01% and an average value of 70.92% and about 70% have SiO_2>70%. Some samples have SiO_2 content between 59.12 to 64.74% and plot in the

Table 1: Modal Composition of Pegmatites of Osogbo-Okinni area

Sample No.	Quartz	Microcline	Plagioclase	Biotite	Tourmaline	Muscovite	Opaque	Total
1	21	24	41	5	--	10	--	101
2	21	22	42	4	--	7	--	96
3	26	23	38	3	--	10	--	100
4	23	21	37	6	4	8	1	100
5	21	24	36	7	4	8	--	100
6	20	29	41	5	--	4	--	99
7	26	20	38	5	--	10	--	99
8	20	22	42	4	--	12	--	100
9	26	23	36	6	--	9	--	100
10	25	23	39	3	--	10	--	100
11	20	14	59	2	--	5	--	100
12	20	15	44	3	--	5	--	87
13	23	21	33	10	10	3	1	101
14	24	21	26	15	10	3	1	100
15	25	20	28	12	8	6	1	100

Fig. 4(a): Photomicrograph of a section of pegmatite of Osogbo-Okinni area in transmitted light, showing Albite (A), Muscovite (MUS) and Quartz (Q).

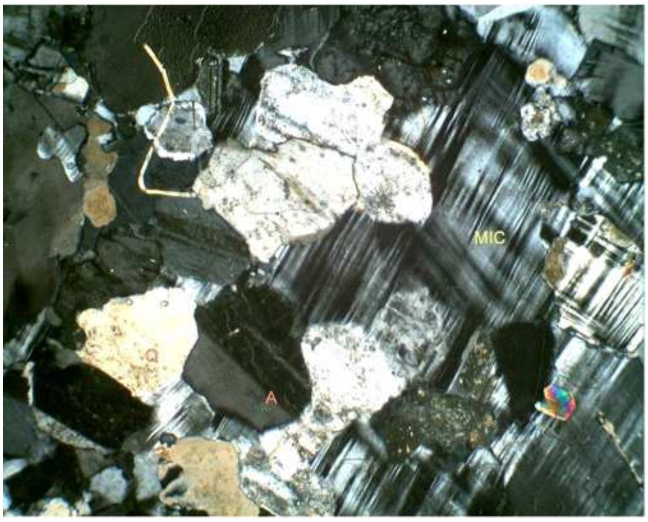


Fig. 4(b): Photomicrograph of a section of pegmatite in transmitted light showing Microcline (Mic) and Quartz(Q) and Albite (A) in Osogbo-Okinni pegmatite.

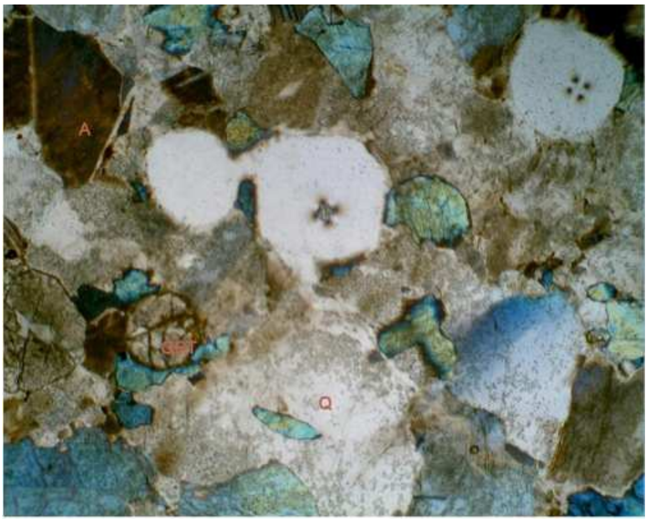


Fig. 4(c): Photomicrograph of Osogbo-Okinni Pegmatite in transmitted light showing Garnet (Grt), Albite (A) and Quartz (Q).

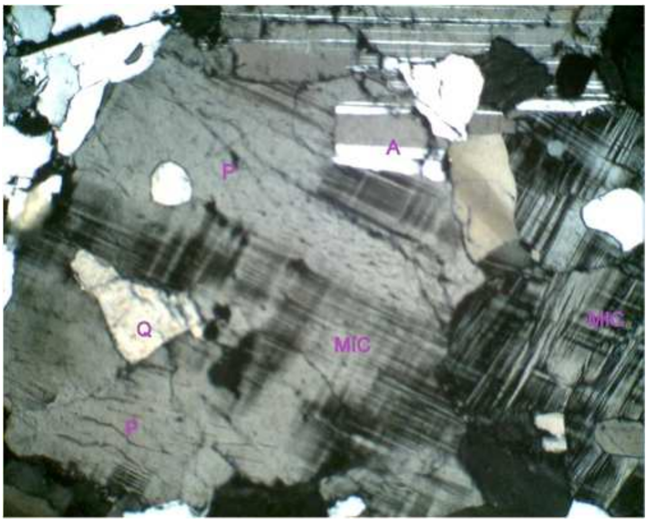


Fig. 4(d): Photomicrograph of Osogbo-Okinni Pegmatite in transmitted light showing Quartz (Q), Microcline (MIC), Albite (A) and perthitic texture in microcline (P).

Fig. 4(e): Photomicrograph of Osogbo-Okinni Pegmatite in transmitted light showing Biotite (B), Quartz (Q), Microcline (MIC)

granodiorite, syenite and monzonite fields of total alkali vs silica diagram of Gillespie and Styles, 1999 (Fig. 5). Al_2O_3 content ranges between 11.93% and 22.97% with an average of 15.95%. K_2O content is next in abundance with a range of 1.74% to 10.59% and an average of 4.23%. Na_2O content ranges between 2.05% and 4.53% with an average of 3.50%. The CaO content ranges from 0.17% to 0.33% and an average of 0.28%. Fe_2O_3 ranges from 0.62% to 1.40% with an average of 1.15%, P_2O_5 content ranges from 0.11% to 0.57% with an average of 0.19%, MgO content ranges from 0.03%-0.10% with an average 0.08%, TiO_2 content ranges from 0.02% to 0.03% with an average 0.02%, MnO content ranges from 0.01% to 0.06% with an average of 0.04%. The SiO_2 content of feldspar extracts is lower than that of whole rock of the pegmatites of Osogbo-Okinni area with a range of 54.51% to 64.76% and an average of 56.81%. However, the Al_2O_3 content is much higher than that of the whole rock with a range of 21.02% to 29.57% and an average of 27.03%. The K_2O content is slightly higher than the whole rock content with a range of 0.67% to 10.04% and an average of 4.70%, while all the other major element oxides have lower content than the whole rock, that is, Na_2O=0.46%-8.98%, 3.04%; Fe_2O_3=0.05%-1.09%, 0.55%; MgO=0.02%-0.05%, 0.03%; CaO=0.05%-0.22%, 0.10%; TiO_2=0.01%-0.02%, 0.01%; P_2O_5=0.11%-0.35%, 0.21%; MnO=0.03%-0.08%, 0.07%.

The mica extract is enriched in the following major element oxides when compared to the whole rock and feldspar extracts, Al_2O_3 with a range of 26.99% to 29.71% and an average of 29.01%, K_2O with a range of 2.86% to 8.75% and an average of 8.10%, Fe_2O_3 with a range of 1.29% to 3.22% and an average of 2.88%, MgO

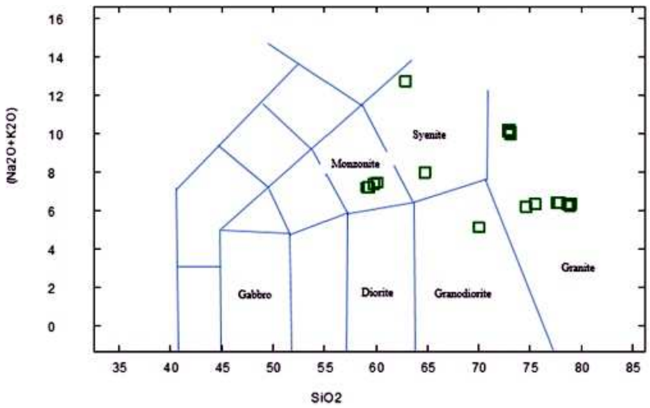


Fig. 5: Total alkali versus silica diagram for whole rock pegmatites of Osogbo-Okinni area (Gillespie and Styles, 1999.)

with a range of 0.08% to 0.52% and an average of 0.45%, TiO_2 with a range of 0.03% to 0.14% and an average of 0.12%. It is however depleted in SiO_2 with a range of 41.37% to 53.56% and an average of 43.55%, Na_2O with a range of 0.58%-3.05% and an average of 0.87% and P_2O_5 with a range of 0.11% to 0.15% and an average of 0.12%.

When compared with the major element oxides of other pegmatites of Nigeria, the SiO_2 content of Osogbo-Okinni area compares favourably with that of the pegmatites of Southern Obudu (A), Oban (B), Oke-Asa (C), Itakpe (D), but generally higher than that of Komu (E), Igbeti (F), Sepeteri (G), and Awo (H) while Oro (I) pegmatites have a higher content of SiO_2 (Table 2). G and H has a much higher Al_2O_3 content than that of Osogbo-Okinni pegmatites which however compares favourably with that of A, B, C, D, E and F. Fe_2O_3 content in pegmatites of the study area compares favourably with B,C and D but is enriched in E,F,G,H and I. Na_2O content of F is similar to that of the study area but depleted in the others. K_2O content of pegmatites of the study area compares with that of B, D and E but is depleted in the others. E and F has higher CaO content that the pegmatites of Osogbo-Okinni, while G and I compares with it, but CaO content is lower in the other pegmatites. Of significance is the TiO_2 content of the pegmatites of the study area which is very low compared to all the other pegmatites of Nigeria as given in Table 2.

The major element oxide content of Osogbo-Okinni pegmatites compares favourably with the same content of pegmatitic leucogranite and potassic pegmatite of Greer Lake, Manitoba, Canada and pegmatite from the Spruce Pine district, North Carolina, US, with some exceptions. The values SiO_2=70.92%,Al_2O_3=15.95%, Na_2O=3.50%, K_2O=4.23% for Osogbo-Okinni

Table 2: Major Element Oxide content of Whole Rock, Feldspar Extracts and Mica Extract of Osogbo-Okinni Pegmatite

	Whole Rock Pegmatite		Feldspar Extract		Mica Extract	
Oxides (wt%)	Range N=22	Average	Range N=22	Average	Range N-22	Average
SiO_2	59.12 - 79.01	70.9191	54.51 - 64.76	56.8145	41.37 - 53.56	43.5541
Al_2O_3	11.93 - 22.97	15.9541	21.02 - 29.57	27.0318	26.99 - 29.71	29.0082
Fe_2O_3	0.62 - 1.40	1.1464	0.05 - 1.09	0.5491	1.29 - 3.22	2.8847
MgO	0.03 - 0.10	0.0768	0.02 - 0.05	0.0318	0.08 - 0.52	0.4559
CaO	0.17 - 0.33	0.2768	0.05 - 0.22	0.0977	0.11 - 0.22	0.1935
Na_2O	2.05 - 4.53	3.4986	0.46 - 8.98	3.0441	0.58 - 3.05	0.8682
K_2O	1.74 - 10.59	4.2314	0.67 - 10.04	4.7036	2.86 - 8.75	8.1029
TiO_2	0.02 - 0.03	0.0219	0.01 - 0.02	0.0144	0.03 - 0.14	0.1241
P_2O_5	0.11 - 0.57	0.1945	0.11 - 0.35	0.2132	0.11 - 0.15	0.1200
MnO	0.01 - 0.06	0.0393	0.03 - 0.08	0.0662	0.03 - 0.07	0.0329

pegmatites agree with SiO_2=75.15%, Al_2O_3=14.55%, Na_2O=3.98%, K_2O=3.76% for pegmatitic leucogranite and SiO_2=76.13%, Al_2O_3=14.75%, Na_2O=3.43%, K_2O=3.52% for potassic pegmatite of Greer Lake, Manitoba (Cerny et al., 2005) and SiO_2=73.79%, Al_2O_3=15.11%, Na_2O=4.71%, K_2O=4.02% for pegmatite of the Spruce Pine district, North Carolina, US (Jahns & Burnham 1969). However, the Fe_2O_3 and MgO content of Osogbo-Okinni pegmatite at 1.15%; 0.8% are much higher than those of pegmatitic leucogranite, potassic pegmatite of Greer Lake and pegmatite of the Spruce Pine District at 0.54%; 0.03% and 0.58%; 0.06%; and 0.26%; 0.07% respectively.

Table 3: Major element oxide content of Osogbo-Okinni pegmatites compared to pegmatites of Nigeria

Oxides (wt%)	This Study	A	B	C	D	E	F	G	H	I
SiO2	70.92	71.90	71.02	71.46	70.17	68.26	63.02	66.17	54.95	86.43
Al2O3	15.95	15.44	15.99	13.90	15.68	14.02	15.03	25.51	25.77	6.86
Fe2O3	1.15	0.48	1.5	1.49	1.15	1.95	5.58	3.91	2.44	2.05
MgO	0.08	<0.01	0.056	0.12	-	0.16	0.18	0.19	1.61	0.23
CaO	0.28	0.12	0.063	0.03	0.13	1.49	2.75	0.37	0.06	0.22
Na2O	3.50	0.88	0.38	1.11	1.19	1.38	4.25	0.35	0.30	2.09
K2O	4.23	2.43	4.43	2.08	3.26	3.42	2.93	1.18	1.28	0.45
TiO2	0.02	7.42	4.83	8.77	6.05	4.64	4.10	1.16	3.74	0.30
P2O6	0.19	0.05	0.01	0.01	0.04	0.20	0.75	0.73	0.06	0.08
MnO	0.04	0.05	0.51	0.26	0.02	0.03	0.30	0.02	0.14	0.03

A = Southern Obudu pegmatites (Edem et al, 2015)
B = Oban pegmatites (Ero and Ekwueme, 2009)
C = Oke-Asa pegmatites (Okunlola and Akintola, 2010)
D = Itakpe pegmatites (Okunlola and Somorin, 2006)
E = Komu pegmatites (Okunlola and Udoudo, 2006)
F = Igbeti pegmatites (Okunlola and Oyedokun, 2009)
G = Sepeteri pegmatites (Okunlola and Akintola, 2007)
H = Awo pegmatites (Akintola et al, 2011)
I = Oro pegmatites (Oyebamiji, 2014)

The Osogbo-Okinni pegmatites are peraluminous in bulk composition. A/CNK>1; where A=Al_2O_3, CNK = $CaO+Na_2O+K_2O$ (Table 4). LCT family pegmatites have been observed to have a mild to extremely peraluminous granitic composition parent (Cerny, 1992). The higher the A/CNK ratio, the higher the alumina content, and the greater the abundance of Al-rich minerals, such as garnet and muscovite. Barren granites have a low A/CNK ratio, fertile granites have a moderate value while rare-element pegmatite have a high A/CNK value. The bivariant plot of Al_2O_3/Na_2O+K_2O against $Al_2O_3/CaO+Na_2O+K_2O$ (Fig. 6) also shows the peraluminous composition of the Osogbo-Okinni pegmatites.

Table 4: Elemental ratios of some Major Element Oxides of whole rock of Osogbo-Okinni pegmatites

E/R	Range	Average n=22
K_2O/Na_2O	0.40-4.93	1.61
Na_2O/Al_2O_3	0.11-0.38	0.23
K_2O/Al_2O_3	0.10-0.61	0.28
CaO/Na2O	2.37-4.85	3.78
$CaO+Na_2O+K_2O$	5.39-13.02	8.01
Al/CNK	1.26-3.15	2.08
Na_2O+K_2O	5.14-12.74	5.90

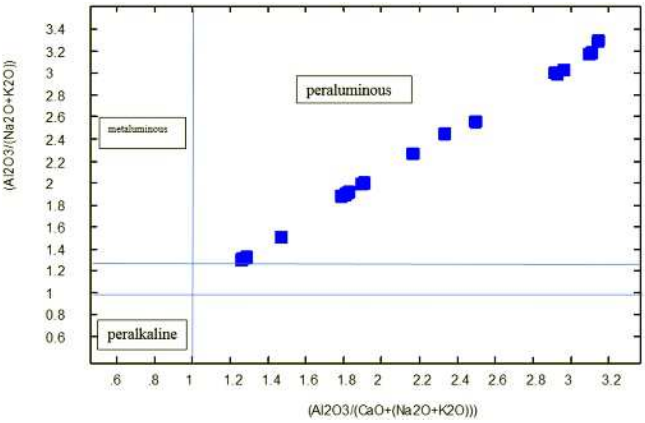


Fig. 6: Plot of Al_2O_3/Na_2O+K_2O against $Al_2O_3/CaO+Na_2O+K_2O$ (Maniar and Piccoli 1989).

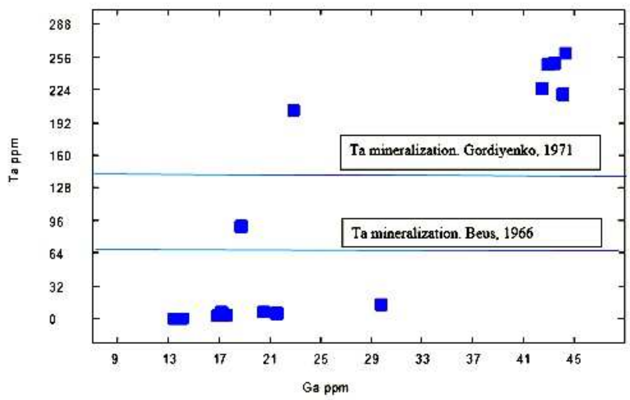
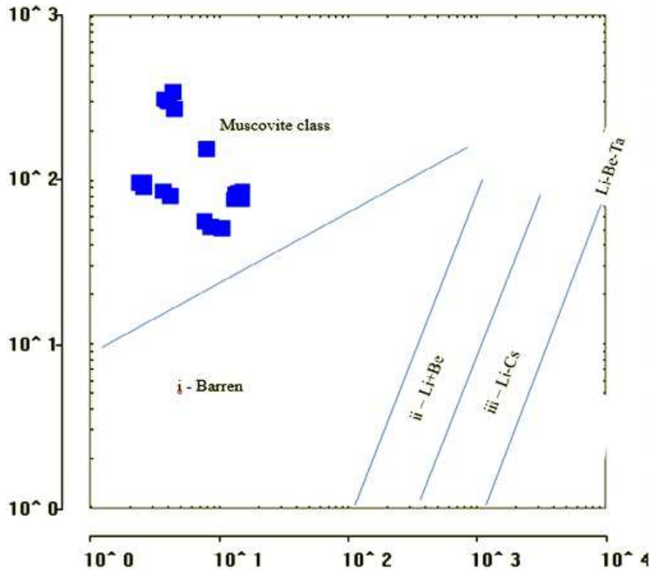


Fig. 7: Plot of Ta vs Ga for Osogbo-Okinni pegmatites after Moller and Morteani, 1987.

Trace Elements Characterization of Whole Rock, Feldspar, and Mica Extracts

Comparison of trace element concentrations in whole rock with feldspar and mica extracts reveal enrichment of whole rock in Be, Sr, Ba, W and Ta. Normal fractionation tends to induce higher silica content in the melt, and the ratio Nb/Ta reduces. This trend enriches the residual melt in Ta over Nb which results in oxides richer in Ta, this is consistent with chemical variations



X = Cs ppm, Y = K/Rb.

Fig. 8: Plot of K/Rb vs Cs for whole rock of Osogbo-Okinni Pegmatites showing classification of the pegmatites. (After Cerny, 1982

Table 5: Range of some trace elements ratios in whole rock of fertile granites and average value for Upper Continental Crust compared to that of Osogbo-Okinni pegmatites.

Elemental Ratio	Fertile Granite	Osogbo-Okinni pegmatites	Average Upper Continental Crust
K/Rb	42-270	50.37-340.77	252
K/Cs	1,600-15,400	1375.22-17,645.77	7,630
K/Ba	48-18,200	77.98-1171.78	
Rb/Sr	1.6-185	2.13-43.03	
Mg/Li	1.7-50	1.23-32.33	
Al/Ga	1,180-3,100		
Zr/Hf	14-64	5.23-30.00	
Nb/Ta		0.58-10.46	11.4

Fertile granite – Cerny, 1989a
Average upper continental crust – Taylor and McLennan, 1985

observed in granites and their pegmatites, (London, 2008) this probably explains the enrichment of whole rock in Ta. For Be, Sr and Ba the trend in enrichment is whole rock > Feldspar > mica. Zn, Sn, Sc, Li, Rb and Nb are enriched in mica and Zn, Li, Rb and Nb enrichment trend is mica > feldspar > whole rock, (Table 6). Mica enrichment over feldspar and whole rock in these elements may be dueto their compatibility in mica and incongruent melting of mica at source and recrystallization and accumulation of the elements in pegmatite. Ce is enriched in feldspar probably because feldspar is a principal reservoir for Ce, (London, 2005b).

Table 6: Trace element content of Whole rock, Feldspar and Mica extracts of Osogbo-Okinni area pegmatite

Trace Elements	Whole Rock Pegmatite (ppm)		Feldspar Extracts (ppm)		Mica Extracts (ppm)	
	Range (N=22)	*Mean*	*Range (N=22)*	*Mean*	*Range (N=17)*	*Mean*
Mo	0.29 - 0.93	0.66	0.05 - 0.20	0.08	0.19 - 0.43	0.34
Cu	6.70 - 22.80	13.09	1.40 - 10.40	5.17	4.70 - 11.90	6.17
Pb	13.72 - 67.14	31.77	8.05 - 56.34	32.22	4.97 - 37.76	12.01
Zn	6.50 - 57.90	34.29	9.10 - 106.60	51.13	129.10 - 286.60	239.17
Ag	33.00 - 77.00	52.12	-	-	-	-
U	1.40 - 6.70	3.76	0.80 - 12.80	4.52	0.20 - 4.60	0.81
Th	0.50 - 2.60	1.14	0.20 - 2.10	0.60	0.50 - 1.10	0.67
Sr	7.00 - 97.00	34.50	2.00 - 17.00	9.18	5.00 - 14.00	7.18
Cr	3.00 - 13.00	7.04	1.00 - 6.00	3.31	3.00 - 10.00	6.76
Ba	30.00 - 861.00	283.95	14.00 - 102.00	53.45	16.00 - 93.00	29.29
W	73.50 - 178.00	101.94	0.20 - 6.60	2.24	9.20 - 58.70	27.16
Zr	4.10 - 81.80	25.85	0.90 - 131.80	28.41	4.30 - 19.10	6.83
Sn	5.40 - 89.40	25.78	4.50 - 20.70	11.63	123.80 - 615.80	510.86
Be	3.00 - 737.00	40.64	5.00 - 386.00	34.41	10.00 - 25.00	13.71
Sc	0.40 - 12.10	3.65	0.30 - 0.80	0.47	19.80 - 133.40	104.86
Y	1.20 - 9.80	5.66	0.60 - 9.90	3.83	0.90 - 7.30	1.59
Hf	0.15 - 10.04	2.75	0.09 - 8.95	2.01	0.42 - 1.91	0.76
Li	15.40 - 202.40	59.61	53.90 - 121.40	74.15	138.70 - 448.30	376.88
Rb	161.40 - 387.20	257.42	67.90 - 1998.30	528.46	473.80 - 1601.60	1101.97
Ta	0.20 - 259.00	70.35	6.50 - 72.40	28.59	20.00 - 123.90	38.20
Nb	1.83 - 202.96	63.00	3.86 - 164.71	77.30	136.65 - 313.06	272.41
Cs	2.40 - 20.80	7.65	1.90 - 117.90	48.78	14.80 - 54.20	35.53
Ga	13.45 - 44.33	23.64	21.23 - 47.13	33.48	68.16 - 68.16	68.16
Tl	0.77 - 16.41	2.21	0.32 - 26.29	11.03	2.84 - 10.61	5.06

K/Rb, K/Cs, and Nb/Ta are elemental ratios which are excellent fractionation indicators. The lower the values of these ratios the greater the mineralization potential of pegmatites. In the plot of K/Rb v Cs (Fig. 9) all samples plot in the muscovite class. This put Osogbo-Okinni pegmatites in the muscovite class of pegmatites. The values for the elemental ratios stated above for some samples of Osogbo-Okinni pegmatites compare favourably with the values for fertile granite (Cerny, 1989a), (Table 5).

Another indicator of fractionation of granites and pegmatites is Mg/Li ratio for whole rock. Mg/Li ratio <30 is evidence of high level of fractionation, (Beus, et al., 1968 and Cerny, 1989a). Mg/Li ratio =/>50 means abundance of Mg in a barren granite, while Mg/Li ratio <10 points to high Li content in an evolved rock. Li-rich rocks have high economic potential because of their association with Ta mineralization. Appling the Mg/Li ratio as indicated by Beus, et al. (1968) and Cerny, (1989a), 3 out of 22 pegmatites of Osogbo-Okinni outcrop samples can be termed barren, while 12 have high degree of fractionation but not necessarily fertile and 7 can be said to have Ta mineralization. This points to the fact that Osogbo-Okinni pegmatites can be grouped into mineralized and unmineralized or barren in Ta mineralization, plots of Ta vs Ga and Ta vs Rb+Cs (Figures 8 and10).

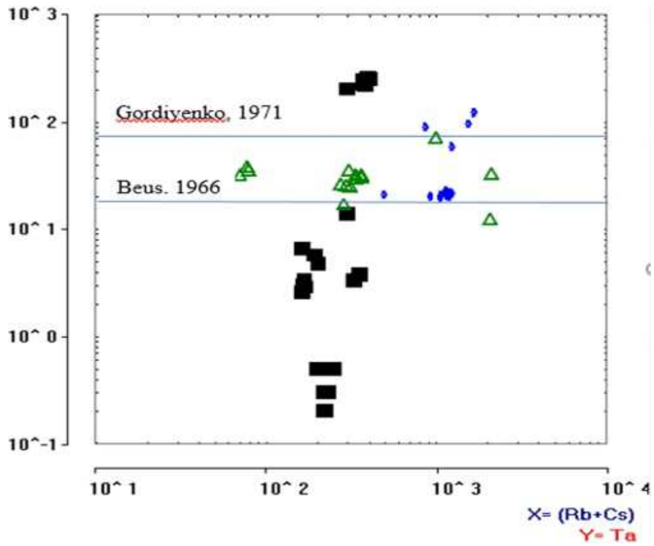


Fig. 9: Plot of Ta vs Rb+Cs for whole rock, feldspar and mica extracts of Osogbo-Okinni pegmatites showing Ta mineralization after Beus, 1966 and Gordiyenko 1971.

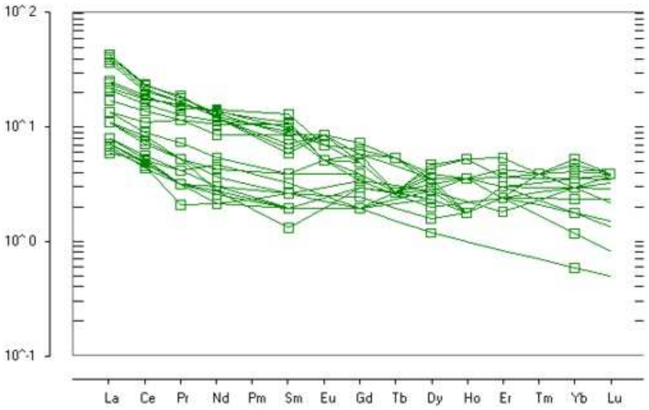


Fig. 10: REE pattern of Osogbo-Okinni pegmatite

Some elemental ratios such as K/Rb, K/Cs, Nb/Ta and Mg/Li are excellent fractionation indicators, and pegmatites with the highest economic potential for Li-Cs-Ta (LCT) will have very low values of these ratios. The values for the elemental ratios stated above for some samples of Osogbo-Okinni area pegmatites compare favourably with the values of fertile granite (Cerny 1989a), Table 5.

The relatively high content of Zn, 129.10-286.60ppm range and 239.17ppm average; Sn, 123.80-615.80ppm range and 510.86ppm average; Li, 138.70-448.30ppm range and 376.88ppm average; Nb, 136.65-313.06ppm range and 272.41ppm average, (Table 6), may indicate Zn, Sn, Li and Nb mineralization in mica extracts of Osogbo-Okinni area pegmatites.

Whole rock content of Li, 15.40-202.40ppm range and 59.61ppm average and Nb, 1.83-202.96ppm and 63ppm average though lower than mica extract content is a pointer to mineralization in these elements. Tantalum mineralization in whole rock is also indicated by Ta content of 0.20-259ppm range and 70.35ppm average (Table 6).

The whole rock samples plot mainly into the field ofWPG,in the diagram of Rb vs Y+Nb,(Pearce et. al., 1984), suggesting they have a high component related to an extensional tectonic setting which was inherited from a stage of basin formation. In the diagram of Nb vs Y (Pearce et. al.,1984), the samples fall in the field of VAG and Syn-COLG suggesting that their syn-collisional geochemical signatures were inherited from their protolith, which may be granites associated to island arc or to continental arc, (Silva Filho, et al., 2014),(Figs. 11 and 12). The results of these tectonic discrimination plots indicate the intrusion of the Osogbo-Okinni pegmatites during the transition between active margin and within-plate tectonic setting similar to that of the Brasiliano orogeny. This commonly occur at the final stages of an orogeny, (Silva Filho, et al., 2014). The plot of Sr vs Rb indicating the depth of emplacement of the Osogbo-Okinni pegmatite at between 20-30km attest to the near surface low temperature zone of intrusion, (Fig. 13).

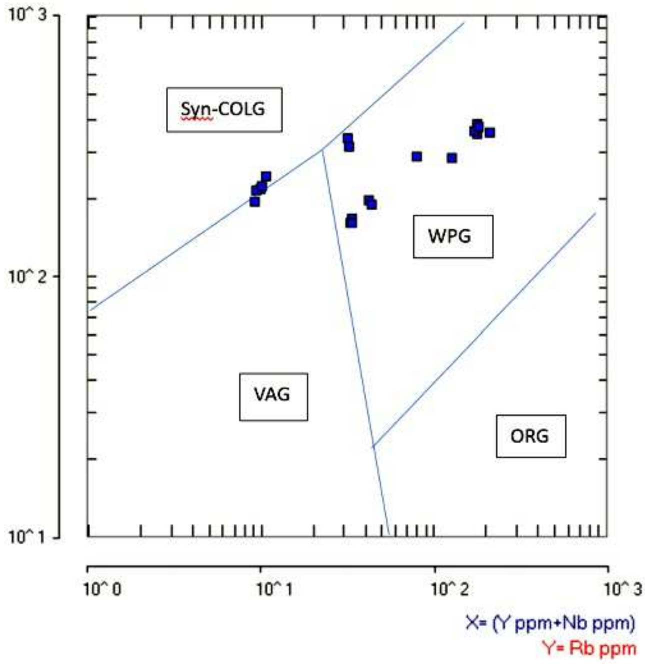


Fig. 11: Plot of Rb vs Y+Nb for whole rock pegmatite, tectonic discrimination after Pearce et al. (1984).

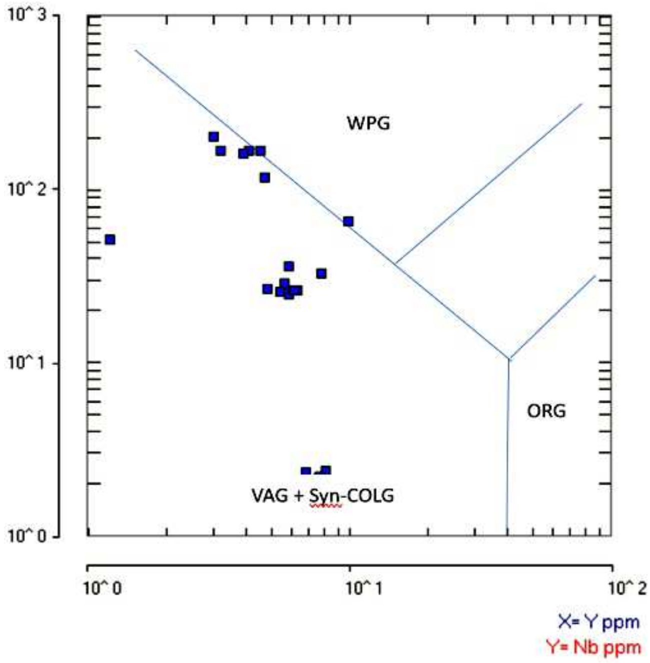


Fig. 12: Plot of Nb vs Y for whole rock pegmatite, tectonic discrimination after Pearce et al. (1984)

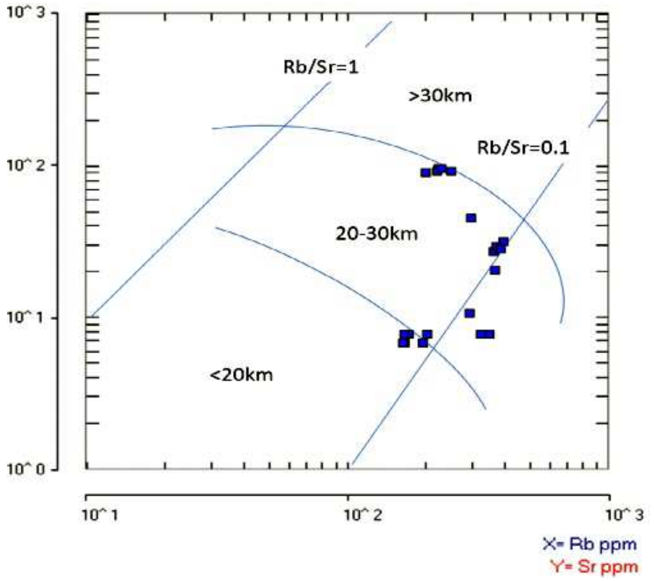


Fig. 13: Plot of Sr vs Rb for whole rock pegmatite showing depth of emplacement after Condie (1973)

In the normative mineral composition of Osogbo-Okinni pegmatites, quartz is the dominant mineral, orthoclase is the k-feldspar present while the plagioclase is albite (Table 7). The presence of corundum confirms the peraluminosity of the pegmatites. Fe minerals present are magnetite, and hematite and ilmenite, the last two in very low concentrations. Phosphate is present as apatite. Diopside is host to calcium and magnesium silicate, while wollastonite and rutile are present in low concentrations.

Rare Earth Elements Characterization of Whole Rock, Feldspar, and Mica Extracts

Generally, in igneous rocks, REE have preferential

Table 7: Normativeminerals of Osogbo-Okinni Pegmatites

Mineral	Range	Average
Apatite	0.26-1.35	0.44
Orthoclase	10.28-62.58	25.0
Ilmenite	0.04-0.04	0.04
Albite	17.35-38.33	29.60
Corundum	0.04-0.56	0.21
Magnetite	0.84-12.94	5.58
Hematite	0.01-0.14	0.08
Diopside	0.6-1.4	1.11
Wollastonite	0.07-0.25	0.19
Quartz	10.86-45.98	34.22
Rutile	0.02-0.03	0.03

accumulation in ultrabasic and basic rocks formed early as compared to intermediate and acidic rocks which are formed later, (Randive et al., 2014). Acidic rocks like granites have low to moderate REE content ($\sum$REE = 8-1977ppm) and low to moderate LREE/HREE ratio ($(La/Lu)_{cn}$= 0.54-137). Positive Eu anomalies are not common (Henderson, 1984).

The whole rock of Osogbo-Okinni pegmatites has $\sum$ REE = 7.3-41.22ppm, La/Lu = 14-104 (Table 8) and positive Eu anomalies (Eu/E u*=0.61-1.52) and this agrees with Henderson, (1984). These pegmatites have abundant light rare earth elements (LREE), ($\sum$LREE = 6.2-37.52ppm) when compared with their heavy rare earth elements (HREE) content, ($\sum$ HREE = 1.1-3.7ppm). This points to high fractionation of the pegmatites ($(La/Yb)_n$=2.06-9.00), while the wide REE pattern envelop suggest that the REE were fractionated during the magma evolution, (Silva Filho, et al., 2014), (Fig. 10).

The ratio of $\sum$REE in whole rock compared to feldspar and mica extracts is whole rock $\sum$ REE (7.33-41.22ppm) > mica $\sum$REE (5.17-16.99ppm) > feldspar $\sum$REE (2.01-9.73ppm), this trend is same for $\sum$LREE where whole rock $\sum$LREE (6.2-37.52ppm) > mica $\sum$ LREE (4.27-14.09ppm) > feldspar $\sum$ LREE (1.31-6.33ppm) but different for $\sum$HREE, where whole rock $\sum$ HREE (1.1-3.7ppm) > feldspar $\sum$ HREE (0.7-3.4ppm) > mica $\sum$HREE (0.9-2.9ppm). The trend for $\sum$ REE where whole rock $\sum$REE > mica $\sum$REE > feldspar $\sum$ REE may be because mica probably concentrates more of the REE and thus control the REE content during melting or crystallization, (Rollinson, 1993).Weak Eu anomalies are indicated in the REE pattern for whole rock, these may be used to distinguish presence or otherwise of mineralization in the pegmatites.

The proximity and probable genetic relationship of presumed parental granite and gneiss to the pegmatite bodies of Osogbo-Okinni area (Fig. 1) may suggest the formation of the pegmatites by fractionation of the older rocks. Alternatively, Harris et al., (1986), suggested a model where syn-collisional granites containing muscovite form during crustal-thickening periods. It was proposed that fluids enriched in volatiles rising into the crustal pile during tectonic movement may initiate partial melting by interacting with the over-riding sheet. Melts enriched in Rb, Ta, B and F are likely to result, and these elements are then moved by the gaseous phase.

Therefore, in an area of formation of partially melted

Table 8: Rare earth element content (ppm) of whole rock, feldspar extracts, mica extracts

Rare Earth Elements	Whole Rock Pegmatite (ppm)		Feldspar (ppm)		Mica (ppm)	
	Range (N=22)	*Mean*	*Range (N=22)*	*Mean*	*Range (N=17)*	*Mean*
La	1.40 - 10.40	4.59	0.20 - 0.90	0.47	0.70 - 2.70	1.58
Ce	2.70 - 14.62	7.67	0.41 - 1.93	1.03	1.57 - 5.39	3.38
Pr	0.20 - 1.80	0.94	0.10 - 0.30	0.23	0.30 - 0.70	0.42
Nd	1.00 - 6.70	3.61	0.20 - 2.00	1.14	1.20 - 3.50	1.99
Sm	0.20 - 2.00	0.89	0.10 - 0.60	0.40	0.30 - 1.00	0.46
Eu	0.30 - 0.50	0.39	0.10 - 0.10	0.10	0.10 - 0.20	0.17
Gd	0.40 - 1.50	0.83	0.20 - 0.50	0.35	0.10 - 0.60	0.33
Tb	0.10 - 0.20	0.13			0.20 - 0.20	0.20
Dy	0.30 - 1.20	0.75	0.10 - 1.00	0.51	0.10 - 0.70	0.30
Ho	0.10 - 0.30	0.16	0.20 - 0.20	0.20	0.20 - 0.20	0.20
Er	0.30 - 0.90	0.50	0.10 - 0.90	0.40	0.10 - 0.60	0.16
Tm	0.10 - 0.10	0.10	0.10 - 0.10	0.10	0.10 - 0.10	0.10
Yb	0.10 - 0.90	0.48	0.10 - 1.00	0.53	0.10 - 1.00	0.20
Lu	0.10 - 0.10	0.10	0.10 - 0.20	0.12	0.10 - 0.10	0.10
∑REE	7.3 - 41.22	21.14	2.01- 9.73	5. 58	5.17-16.99	9.59
∑LREE	6.2 – 37.52	18.92	1.31 – 6.33	3.72	4.27 – 14.09	8.33
∑HREE	1.1 – 3.7	2.22	0.7 – 3.4	1.86	0.9 – 2.9	1.26

Table 9: Unspike K-Ar ages of Osogbo-Okinni pegmatites

Sample No.	% atm-40Ar	Error	% K content	rad_40Ar (ppb)	Error	36Ar/38Ar	Error	Unspiked Age	Error
1	2.7	0.3	6.69	442	6	10	30	760	10
2	0.6	0.2	6.89	403	5	2	6	692	8
3	0.2	0.3	7.26	478	7	0	100	760	10
4	1.2	0.3	5.45	336	5	2	4	720	10
5	0.3	0.3	7.2	483	5	0	300	774	8

granites and pegmatites in a large compression zone and thick crust, the source materials available for melting may control the composition of pegmatite rather than magmatic processes like fractional crystallization. Similarity in major oxide concentrations and some trace element concentrations in granites and pegmatites of Osogbo-Okinni area seems to indicate formation by anatexis of source materials and some amount of fractional crystallization, Table 10.

k-Ar Geochronology

Dating of five samples of pegmatite of Osogbo-Okinni area was undertaken using the K-Ar methodology known as Cassignol dating technique. Duplicate analyses were made for each sample using muscovite extracts from the pegmatites. All analyses yielded 0.3-2.7% atmospheric ^{40}Ar content. This means the whole ^{40}Ar signal is potentially from radiogenic ^{40}Ar or may be a combination of radiogenic and inherited ^{40}Ar from the source of the pegmatite. K content is 5.45-7.26%, radiogenic ^{40}Ar, 336-483ppm and ^{36}Ar/^{38}Ar, 0-10. All samples gave Neoproterozoic ages between Ediacaran and Tonian, 774-692$\pm$10Ma (Table 8).

In Southwestern Nigeria, Pan African events have been divided into three age intervals by Rahaman, et al., (1988), as pre 600Ma, 560 $\pm$ 40Ma and 500Ma. Also, Caby, (1989), divided Pan-African tectono-metamorphic events in Northern Nigeria into threefold time interval, 750-700Ma – early Pan African orogenic event, 630-580Ma – main Pan-African episode and 580-520Ma – Late Pan-African orogenic event. These Pan-African events resulted in orogenic belts created during

Table 10: Derived absolute age of Osogbo-Okinni pegmatites compared to other Neoproterozoic rocks of Nigeria, Africa, and South America

	Rock Type and Location	Dating Method	Age	Reference
1	Muscovite extract in Osogbo-Okinni pegmatite	UnspikeK-Ar (Cassignol Technique)	774-692±10 Ma	This study
2	Pegmatite of Wamba, Central Nigeria		750 Ma	Matheis and Caen Vachette, 1983
3	Osu pegmatite, Southwestern Nigeria		700 Ma	=ditto=
4	Ede pegmatite, Southwestern Nigeria	U-Pb Zircon	709+27/-19 Ma	Adetunji et. al., 2016
5	Komu pegmatite, Southwestern Nigeria	K/Ar	515-503±13 Ma	Okunlola and Udo udo, 2006
6	Hornblende in Coarse Porphyritic granite of Southern Kano, Nigeria	K/Ar	780±40 Ma	Snelling, 1966
7	Whole rock granite of Panyam area, Northcentral, Nigeria	Rb/Sr	677±161 Ma	Van Breemen et al., 1977
8	Whole rock hornblende granite and granodiorite around Maiinci, Northern Nigeria	Rb/Sr	665+65 Ma	Ogezi, 1977
9	Early phase magmatism in older granite of Minna, Northwestern Nigeria		790-760 Ma	Goodenough, 2014
10	Biotite granite of Morocco	U-Pb Zircon	705+2/-3 Ma	D'Lemos et al., 2006
11	Volcano-sedimentary rock of Borborema Province, Brazil		780-770 Ma	Fetters et al., 2003; Arthaud et al., 2008

the Gondwana formation between the Neoproterozoic and Cambrian. These belts span the African continent to the Brasiliano orogen of South America (Stern, 1994; Jacob and Thomas, 2004). The Brasiliano orogeny of South America occur in three age intervals of Brasiliano I – 790Ma and 730-700Ma; Brasiliano II – 640-620Ma and 600Ma; Brasiliano III – 595-560Ma and 520-500Ma (Da Silva, et al., 2005).

The derived age of between Ediacaran and Tonian, 774-692±10Ma, place the Osogbo-Okinni pegmatites in the early Pan-African orogenic event time interval as reported by Caby, (1989) and in line with the Brasiliano 1 orogeny time interval, (Da Silva, et al., 2005).

The Pan-African orogenic belts consist of rocks of Archaean and Proterozoic age which have gone through Neoproterozoic to Cambrian orogenesis, plus a mixed portion of young materials. These belts are made up of extensive post-collisional granitoid plutons. The plutons are potassic and of magmatic protolith resulting from mixed materials of mantle and crust which form major content of the upper crust during Gondwana formation (Kuster and Harm, 1998).

The ages derived for the Osogbo-Okinni pegmatite samples by unspike K-Ar dating technique which is 774-692 Ma compare favourably with ages of early Pan African rocks identified in the basement complex of Nigeria (Table 9). Some examples include, Snelling, (1966), with a K/Ar age of 780± 40Ma on hornblende derived from coarse porphyritic granite of Southern Kano, a part of the older granites identified in Northern Nigeria. Whole rock granite with foliations in Panyam area of Northcentral Nigeria was dated 677±161Ma by Rb/Sr method (Van Breemen et al., 1977). A whole rock isochron Rb/Sr age of 665+65Ma was reported by Ogezi, (1977), on hornblende granite and granodiorite around Maiinci. Pegmatites of Wamba, central Nigeria and pegmatites of Osu, southwestern Nigeria were dated 750Ma and 700Ma respectively by Matheis and Caen-Vachete, 1983.

Old Pan African rocks, 730Ma, were reported by Ferre et al., (2002), in Eastern Nigeria and were correlated with the Eastern Hoggar using the U-Pb zircon dating technique. Signature of an early phase of magmatism at 790-760Ma was recorded in Batholith of older granite in Minna, Northwestern Nigeria (Goodenough, 2014). U-Pb zircon dating of pegmatites of Ede area, Southwestern Nigeria, gave 709+27/-19Ma (Adetunji et al., 2016).

This Neoproterozoic Pan-African suite of rocks are present in Pan-African province of Madagascar as syntectonic (750-600Ma) and post tectonic (500Ma) pegmatites (Petters, 1991). Also, the Tazigzaout complex within BouAzzer inlier of Anti-Atlas orogenic belt of Morocco consist of metagabbro, augen granite gneiss, syn-tectonic leucogranite, closely banded granite gneiss with sheeted muscovite-biotite granite crosscutting the meta-igneous rocks. The muscovite-biotite granite gave 705 +2/-3Ma age (D'Lemos et al., 2006). Stratigraphic sequence derived from volcanic and sedimentary events in Borborema province of Brazil has signatures of Neoproterozoic magmatism with age at 780-770Ma. This is believed to be associated with break apart through faulting due to plate tectonics around continental margins (Fetter et al., 2003; Arthaud et al., 2008).

Table 11: Major oxides and some trace element concentration of granite compared with those of the pegmatites of Osogbo-Okinni area.

Major oxides (wt%)	Granite	Pegmatite
SiO	72.04	70.91
Al_2O_3	13.82	15.95
Fe_2O_3	3.03	1.14
MgO	0.61	0.07
CaO	1.65	0.27
Na2O	3.28	3.49
K2O	3.98	4.23
TiO	0.27	0.02
Trace elements (ppm)		
Mo	0.80	0.66
Cu	9.70	13.09
Pb	25	31.77
Zn	25.48	34.29
Th	52.1	1.14
Sr	166.75	34.50
Ba	904.5	283.95
W	49.35	101.94
Zr	53.65	25.85
Sn	4.5	25.78
Y	14.75	5.66
Hf	1.60	2.75
Li	77.23	59.61
Rb	192.33	257.42
Ta	2.55	70.35
Nb	13.87	63
Cs	5.55	7.65

Conclusions

Osogbo-Okinni pegmatites trending mainly NE-SW, occur as massive to mountainous plutons intruding quartzite, amphibolite, gneissic granites, and granites. Petrographic studies reveal the presence of quartz, albite, microcline, mica, mainly muscovite as major minerals with tourmaline, biotite and garnet as minor minerals.

Major elements oxide content of whole rock, feldspar, and mica extracts of Osogbo-Okinni pegmatites characterizes the pegmatites as silicic, with potassium as the dominant alkali, peraluminous and of granitic protolith. Trace elements content classify the Osogbo-Okinni pegmatites as fertile granite with respect to tantalum mineralisation (Cerny, 1989a) using some elemental ratios like K/Rb, K/Cs, Mg/Li, Zr/Hf as indicators. These ratios point to enrichment of pegmatites in Zn, Sn, Li and Nb and this is more pronounced in the mica extracts samples.Tectonic discrimination plots place these pegmatites in the fields of WPG, VAG and Syn-COLG.

The pegmatitesare enriched in Al_2O_3, Cu, Pb, Zn, Cs W, Ta, Sn, Rb, Nb, and Ga and is depleted in Fe_2O_3, MgO, TiO, Ba, Zr, Sr, Y and REE, which are left in the melt residue, when compared to granite which may indicate fractionation of the granite.

The derived ages for the Osogbo-Okinni pegmatite samples by unspike K-Ar dating technique which is 774-692 Ma is I n line with early Pan-African tectonic-metamorphic event (750-700 Ma) as delineated by Caby (1989), and the Brasiliano I (between 790 Ma and 730-700 Ma). Supracrustal sequences in the Borborema province, in the South American continent and paragneisses and schists from Cameroon in the African continent gave some U-Pb zircon ages indicating that their protoliths were deposited during the age interval 1000-700 Ma. (Toteu et al., 2001). These sequences are probably metamorphosed equivalent of extensive sedimentary units covering a substantial part of Sao Francisco and West African cratons, deposited in epicontinental and platformal environments during the Neoproterozoic. (Villeneuve and Cornee, 1994; Sial et al., 2000).

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Pictorial view of the new NMGS House under construction at Abuja.