

Petrochemical characteristics of the Precambrian rare metal pegmatite of Oke-Asa area, Southwestern Nigeria: implication for Ta-Nb mineralization

Petrološko-kemične značilnosti predkambrijskih pegmatitov z redkimi kovinami območja Oke-Asa, jugozahodna Nigerija: vpliv na Ta-Nb mineralizacijo

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Abstract: The Precambrian pegmatite of Oke-Asa area of Ijero Ekiti occurring as steeply dipping intrusives into the older rocks of migmatite gneiss complex and schistose rocks were investigated with a view to elucidating their petrochemical features that may be related to economic rare metal Ta-Nb mineralization.

Thin section petrographic study indicates that the pegmatite samples contain mainly quartz (37.0 %), muscovite (30.4 %), plagioclase (12.0 %) and microcline (7.0 %), with accessory biotite, hornblende and tourmaline.

Geochemical analysis of muscovite extracts from the pegmatite using (ICP-AES) analytical methods in Activation Laboratories, Ontario Canada; shows that the pegmatite is siliceous with average SiO₂ content of 71.79 %, Al₂O₃ (13.9 %), Fe₂O₃ 1.49 %, K₂O 8.77 %, Na₂O 2.08 % and CaO 1.11 % while other oxides MnO, MgO, TiO₂ and P₂O₅ are generally less than 0.3% in each case. Trace element analysis of the pegmatite shows a significant enhancement in Rb, Ba, Zr and Sr as against lower values for Ta, Sn, and Nb. Bulk chemistry, geochemical signatures and variation plot of Ta/(Ta+Nb) vs Mn/(Mn+Fe) indicate that the muscovite-quartz-microcline pegmatite of Oke-Asa area is of rare-element class, lepidolite subtype

and are essentially peraluminous in composition. Ta-Nb mineralization trend using variation plots of Ta vs Cs+Rb, Ta vs K/Cs, Ta/W vs Cs and Ta vs Cs plots shows that the pegmatites are relatively poorer than the mineralized Tanco deposits of Canada, and those of Igbeti, Nigeria but are similar to the marginally endowed Noumas pegmatites of South Africa.

Povzetek: Predkambrijske pegmatite območja Oke-Asa iz Ijero Ekitija, ki se pojavljajo kot strmo vpadajoče intruzije v starejših kamninah mignatitno gnajsnega kompleksa in v skrilavcih, smo raziskali, da bi ugotovili njihove petrološke in kemične značilnosti, ki morda kažejo na ekonomsko pomembno mineralizacijo s Ta in z Nb.

Mikroskopske petrografske raziskave kažejo, da so pegmatiti pretežno iz kremena (37.0 %), muskovita (30.4 %), plagioklaza (12.0 %) in mikrokлина (7.0 %), z akcesornim biotitom, rogovačo in turmalinom.

Geokemične analize muskovita z metodo ICP-AES, izvedene v Activation Laboratories, v Ontariju v Kanadi, so pokazale, da je v pegmatitu povprečna vsebnost SiO₂ 71.79 %, Al₂O₃ (13.9 %), Fe₂O₃ 1.49 %, K₂O 8.77 %, Na₂O 2.08 % in CaO 1.11 %, preostalih oksidov MnO, MgO, TiO₂ in P₂O₅ pa je navadno manj kot 0.3 %.

Analiza vsebnosti slednih prvin je pokazala precejšnje obogatitev z Rb, Ba, Zr in Sr v primerjavi z z majhno vsebnostjo Ta, Sn, in Nb. Glede na celotno kemijsko sestavo, geokemične značilnosti ter variacijske diagrame Ta/(Ta+Nb) z Mn/(Mn+Fe) se muskovitno-kremenovo-mikroklinov pegmatit Oke-Asa območja uvršča v razred pegmatiov, obogatenih z redkimi zemljami lapidolitnega podtipa in ima peraluminijski značaj. Ugotavljanje Ta-Nb mineralizacijske težnje na diagramih Ta s Cs+Rb, Ta s K/Cs, Ta/W s Cs in Ta s Cs kaže, da so pegmatiti relativno siromašnejši v primerjavi z mineraliziranimi iz Tanaca v Kanadi ter Igbeti v Nigeriji, a podobni nizko orudenim pegmentitom Noumas iz Južne Afrike.

Key words: precambrian, pegmatite, geochemical, rare metal, economic, mineralisation

Ključne besede: predkambrij, pegmentit, geokemija, redke kovine, ekonomično, mineralizacija

INTRODUCTION

The world economy at present is growing at a rate that necessitates an increasing demand for rare metals, with this trend likely to continue into the future (PATRICK DE ST. SIMMONS, 1999). In recent times, there has been a resurgence of interest in the study of rare metal pegmatite occurrences in Nigeria (GARBA, 2002, OKUNLOLA, 2005, 2008 OKUNLOLA & JIMBA 2006, OKUNLOLA & OYEDOKUN, 2009, ODEN, 2010,). Granite pegmatite is one of the classic sour-

ces of a broad spectrum of rare metals: Li, Rb, Cs, Be, Ga, Sc, Y and Rare Earth Elements: Sn, Nb, Ta, U and Th (CERNY, 1994). In Nigeria, Pan-African intrusive suites which comprise mainly granites, granodiorites and tonalities are intruded by numerous veins of pegmatites and aplites (OKUNLOLA, 2005). The pegmatite belongs to the terminal stage of Pan-African magmatism (RAHAMAN et al., 1988; ELUEZE, 2002). Rare metal pegmatite were hitherto thought to be known almost exclusively along the SW-NE striking belt covering about

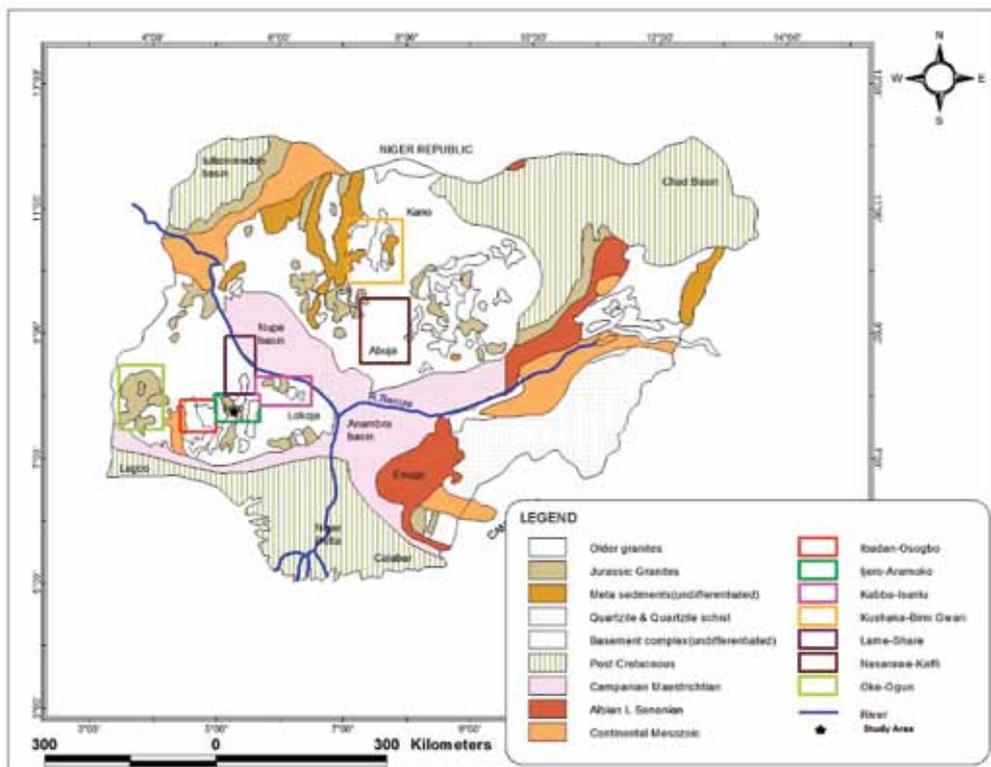


Figure 1. Geological map of Nigeria showing the study area located in the Ijero- Aramoko Pegmatite field (OKUNLOLA, 2005)

400 km long and terminating in the Jos plateau tin field (JACOBSON & WEBB, 1946, WRIGHT, 1970). However, recent studies (GARBA, 2003; OKUNLOLA, 2005) have shown that they are not restricted only to these confines. The Ta-Nb pegmatites of Nigeria are generally complex albitised muscovite-quartz-microcline pegmatites with indiscernible to distinct zonations (OKUNLOLA & JIMBA, 2006). Seven fields of these mineralized pegmatites as outlined by OKUNLOLA, (2005) include Kabba-Isanlu, Keffi-Nassarawa, Lema-Ndeji, Oke Ogun, Ibadan-Oshogbo, Kushaka-Birnin-Gwari and Ijero-Aramoko. In line with efforts to appraise into some details the petrography, geochemical features and economic potentials in relation to Ta-Nb mineralization of the pegmatites of these different fields, the Oke-Asa pegmatite veins which belong to the Ijero- Aramoko pegmatite field (Figure 1) are thus being studied. This is expected to add to the knowledge of composition, type and economic peculiarities of these suites of rocks.

GEOLOGICAL SETTING

Oke-Asa area within the Ijero pegmatite field lies within the Precambrian basement of southwestern Nigeria). The basement rocks of Nigeria form part of the extensive Pan-African Province of West Africa and are delimited in the west by the West Af-

rican Craton and east by the Congo Craton. Based on lithological associations and geochronological delineations, the Nigeria basement comprises the Migmatite-gneiss complex, the Schist belts and the Older Granites. The Migmatite Gneiss Complex is the oldest, most widespread and abundant rock type in the basement (OGEZI, 1988). It is of Achean-Proterozoic age and a product of long, protracted and possibly polycyclic evolutionary histories. The Nigerian Schist belts comprise of low-grade metasediments and metamorphosed pelitic and psammitic assemblages that outcrop in a series of N-S trending synformal troughs infolded into the crystalline complex of migmatite-gneiss. The Pan-African Granites referred to as Older Granites include rocks of wide range of composition varying from tonalite, granodiorite, granite and syenite. (RAHAMAN et al., 1988) The Oke-Asa pegmatite form an intrusion into the older lithology of biotite schist that occupies the central part of the area, covering about three quarter of the total land mass (Figure 2). The schistose rock is grayish, highly fissile and weathered. The topographical configurations are essentially low-lying discontinuous outcrops that have a westerly dip values ranging between 25° and 30°. Mineralogically, they are composed of quartz, biotite and hornblende, while accessory minerals include

apatite and opaques. Biotite gneiss occupies the north central area and extends towards the northwestern direction. Outcrops of the rock are low-lying, highly foliated with characteristic black tints imposed by the preponderance of biotite impregnations. Most of the mineral alignments are conformable with the foliation planes of the adjacent schistose rock.

The pegmatite comprises of quartz (37 %), albite (27 %), muscovite (14 %) and microcline (14 %) while biotite, (1.0 %) hornblende (2.8 %)

and tourmaline (3.2 %) minerals occur in subordinate amount. Quartz occurs as irregular masses of euhedral crystals. Microcline occurs as phenocrysts with characteristic strong crosshatched twinning and variable microperthitic intergrowth while Carlsbad-twinning and albite twinning characterizes the albite. Muscovite occurs as large platy grains. Accessory minerals include tourmaline and biotite. Tourmaline crystals exhibit long needle-like prismatic shapes with their long axis aligned parallel to each other.

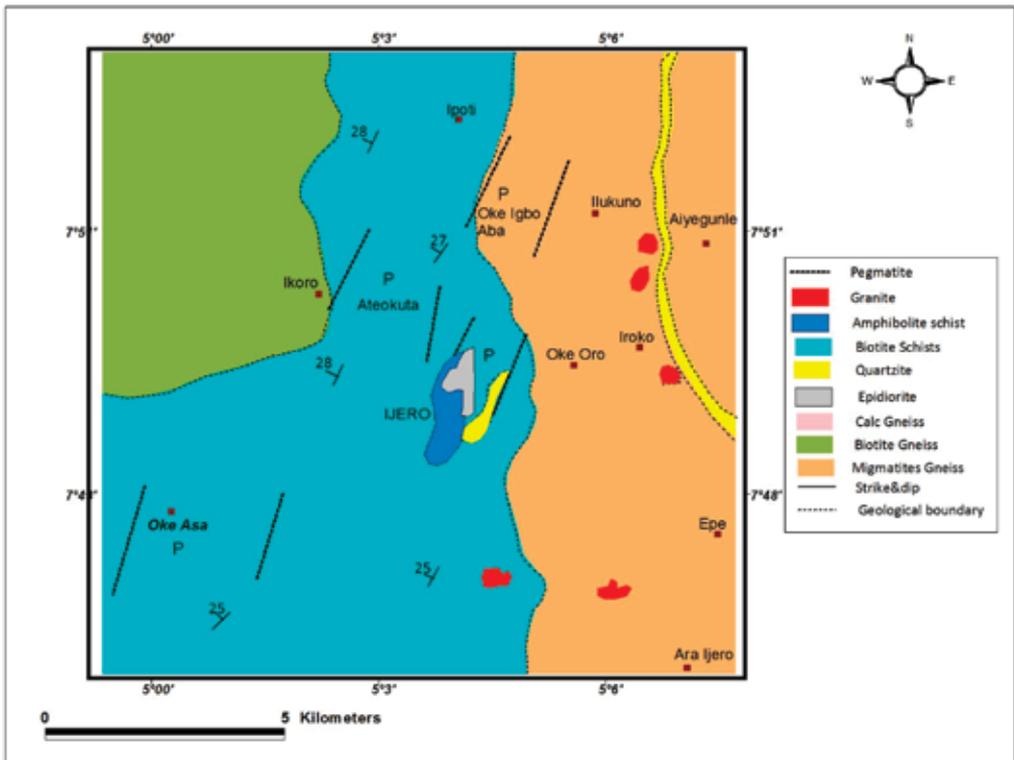


Figure 2. Geologic map of Ijero Ekiti area showing Oke-Asa pegmatite

MATERIALS AND METHODS

Systematic geological mapping was carried out on a scale of 1: 50 000 with grid controlled sampling of the pegmatite veins. Fifteen samples were initially obtained, while ten which were representative of the different veins, fresh and uncontaminated were eventually analyzed. Whole rock analysis of the pegmatite for major, trace and rare earth elements were carried out after they were duly pulverized and homogenized. Many authors including GAUPP et al., (1984) KUSTER, (1990), CERNY et al., (1995) and OKUNLOLA & OYEDOKUN (2009) had established that homogenized and fresh samples of the whole rock pegmatite could be used to establish their genetic features and rare metal potentials, even though the mineral extracts of muscovite, feldspar and tourmaline could also be used effectively. The analysis was carried out using Inductively Coupled Atomic Emission Spectrophotometry (ICP-AES) analytical method at the Activation Laboratories Ltd, Ontario Canada. Rock samples weighing 0.5 g pulverized to 75 μm was put in the platinum crucible. 5 mL perchloric acid, HNO_3 and 15 mL hydrofluoric acid were added. The resulting solution was stirred properly and allowed to evaporate to dryness after warming at low temperature for some hours. 4 mL hydrochloric acid was then added to the cooled solution and warmed to dissolve the salts.

On cooling, the solution was diluted to 50 mL with distilled water. The diluted solution was then introduced into the ICP torch as aqueous-aerosol. The light emitted by the ions in the ICP was converted to an electrical signal by a photo multiplier of the spectrometer. The intensity of the electrical signal produced by emitted light from the ions were compared to a standard, which is a previously measured intensity of a known concentration. The quality control incorporates a sample prep blank as the first sample and pulp duplicate to monitor analytical precision which is carried all through the stages of preparation to analysis, and the concentration computed. The chemical data are presented in Tables 1 and 2.

GEOCHEMICAL FEATURES IN RELATION TO TA-Nb MINERALIZATION.

The analytical results of major, trace and rare elements of pegmatite from Oke-Asa area are presented in Tables 1 and 2. Table 1 shows that the SiO_2 (ca. 71.46 %), Al_2O_3 (ca. 13.9 %), K_2O (ca. 8.77 %) constitute the bulk of the oxide composition. These values are within the range of values of other Ta-Nb pegmatites of Nigeria (OKUNLOLA, 2005). Other major oxides, Fe_2O_3 (ca. 1.49 %), CaO (ca. 1.11 %), Na_2O (ca. 2.08 %) are comparably low while TiO_2 (ca. 0.01 %), MnO (ca. 0.12 %), MgO (ca. 0.03 %) and P_2O_5 (ca. 0.26 %) are much lower.

Table 1. Chemical composition of Oke-Asa pegmatite compared with similar rocks from other locations

Oxides in %	1	2	3	4	5	6	7	8	9	10	Average	A*	B**	C***
SiO ₂	72.29	72.0	72.46	73.44	72.23	71.58	71.12	71.23	71.62	71.77	71.46	70.17	68.26	66.17
Al ₂ O ₃	14.16	13.76	13.79	14.07	13.72	14.21	13.69	13.87	13.87	13.83	13.90	15.68	14.02	25.51
Fe ₂ O ₃	1.25	1.58	1.54	1.35	1.69	1.61	1.41	1.49	1.50	1.46	1.49	1.15	1.95	3.91
MnO	0.11	0.12	0.13	0.12	0.12	0.13	0.12	0.12	0.12	0.12	0.12	-	0.16	0.19
MgO	0.03	0.02	0.03	0.01	0.04	0.04	0.02	0.03	0.03	0.01	0.03	0.13	1.49	0.37
CaO	1.30	1.17	1.23	0.72	1.02	1.16	1.41	1.07	1.35	0.75	1.11	1.19	1.38	0.35
Na ₂ O	2.12	2.04	2.04	2.11	2.02	2.14	2.09	2.07	2.13	2.08	2.08	3.26	3.42	1.18
K ₂ O	9.02	8.97	8.86	8.88	8.66	8.64	8.71	8.61	8.78	8.61	8.77	6.05	4.64	1.16
TiO ₂	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.02	0.01	0.01	0.01	0.04	0.20	0.73
P ₂ O ₅	0.30	0.26	0.26	0.25	0.26	0.25	0.25	0.24	0.25	0.26	0.26	0.02	0.03	0.20
LOI	0.15	0.14	0.07	0.04	0.12	0.65	0.36	0.20	0.21	0.24	0.22	-	-	-
Total	100.7	100.1	100.4	100.9	99.89	99.12	99.18	98.94	99.87	98.66				
Trace Elements in µg/g														
Ta	27.5	30.3	33.9	33.9	51.8	17.7	17.5	22.9	21.2	24.3	28.1	4.64	170.5	33.08
Cs	20.2	20.6	19.9	23.3	25	19.7	22	21.4	22.1	22.7	21.69	1.34	105.8	72.29
Rb	576	590	544	600	594	536	571	553	562	580	570.6	115.6	1791	547.7
Sn	14.0	6.0	7	6	13	5	7	9.0	7.0	9.0	8.3	1.18	202.3	50.41
Nb	23.0	29.0	30	53	39	18	18	27.0	23.0	24.0	28.4	1.28	157.5	36.73
Sr	72.0	69.0	54	56	69	90	82	86	78	81	73.7		111.9	87.52
Y	31.0	36.0	39	37	43	28	31	37	33	33	34.8	2.55	26.31	6.52
Ba	206	203	213	221	216	205	213	206	213	212	210.8	986.2	21.3	237.1
Hf	3.5	3.8	3.3	2.2	2.9	2.4	2.3	2.4	2.6	2.2	2.76	0.47		
Th	4.0	4.2	4.4	4.8	5	3.8	2.9	3.3	3.7	0.2	3.63	1.93	8.28	
W	1.0	2.0	4.0	5	5	4	4.0	4.0	5.0	4.0	3.8	0.65	174.3	3.25
Be	13.0	12	12	12	11	11	12	12.0	11.0	11	11.8	138.4	14.8	16.56
Zr	46.0	56	76	39	69	50	51	51.0	52.0	47.0	53.7		23.8	41.98
Ga	22.0	22	22	24	24	22	23	21.0	22.0	23.0	22.5	18.88	75.45	30.15
Zn	25	25	25	25	25	25	25	25	25	25	25	15.27	111.7	
U	25.6	27.2	34.8	41.9	50.6	45.5	25.2	31.1	28.5	26.5	33.6	0.56	9.96	
K	19400	20000	6100	4200	6900	4700	19300	20000	19500	5100	12520			
Na	960	1050	620	520	350	650	1010	1020	1040	490	771			
Ratios	1	2	3	4	5	6	7	8	9	10				
K/Rb	33.7	33.90	11.21	7.0	11.62	8.77	33.8	36.17	34.69	8.79	18.3			
Rb/Sr	8.0	8.55	10.07	10.71	8.61	5.96	6.96	6.43	7.21	7.16	7.97			
Na/K	0.05	0.053	0.102	0.124	0.05	0.14	0.05	0.05	0.05	0.096				
Ba/Rb	0.36	0.34	0.39	0.37	0.36	0.38	0.37	0.37	0.38	0.366				
Zr/Hf	13.1	14.74	23.03	17.73	23.79	20.8	22.2	21.3	20.0	21.36				
Sr/Rb	0.13	0.116	0.099	0.093	0.116	0.17	0.14	0.155	0.139	0.14				
Rb/Cs	28.5	28.6	27.34	25.75	23.76	27.2	26.0	25.8	25.43	25.55	26.39			
Ta/W	27.5	15.15	8.48	6.78	10.36	4.43	4.38	4.58	5.3	6.08	9.31			
K/Cs	960	971	306.5	180.3	276	239	877	934.6	882.4	224.7	585.2			

A= Itakpe pegmatite (Okunlola & Somorin, 2006); B= Komu pegmatite (Okunlola & Ofonime, 2006); C= Sepeteri pegmatite (Okunlola & Akintola, 2007). *Average of 11 representative samples.

** Average of 10 representative samples; *** Average of 25 representative samples

Table 2. REE/ Chondrite data for Oke-Asa Pegmatite

REE	1	2	3	4	5	6	7	8	9	10	Range
La	1.4	1.7	1.8	2.5	2.2	1.8	2.3	1.8	1.9	3.7	1.4–3.7
Ce	3.3	2.7	3.9	3.0	3.1	2.8	3.3	2.7	2.9	2.9	2.7–3.9
Nd	3.1	2.6	3.5	2.8	3.1	2.8	3.3	2.7	2.7	2.9	2.6–3.5
Sm	1.1	1.0	1.3	1.0	1.2	1.1	1.3	1.1	1.2	1.4	1.0–1.4
Eu	0.13	0.11	0.14	0.12	0.13	0.11	0.14	0.13	0.13	0.13	0.11–0.14
Gd	2.0	1.3	2.3	1.4	1.7	1.6	1.8	1.5	1.6	2.0	1.3–2.3
Tb	0.4	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.4–0.5
Dy	2.8	2.7	3.3	2.8	3.4	3.1	3.5	3.0	3.3	4.1	2.7–4.1
Ho	0.7	0.6	0.8	0.6	0.8	0.7	0.8	0.7	0.8	1.0	0.6–1.0
Er	2.4	2.1	2.7	2.1	2.7	2.5	2.9	2.4	2.8	3.2	2.1–3.2
Tm	0.45	0.39	0.49	0.38	0.48	0.44	0.51	0.43	0.49	0.53	0.38–0.51
Yb	3.4	0.45	0.56	0.43	0.53	0.48	3.8	3.1	3.5	3.8	0.43–3.8
Lu	0.55	0.45	0.56	0.43	0.53	0.48	0.55	0.47	0.54	0.57	0.43–0.57

Trace element data (Table 2) shows a pronounced enrichment in trace elements like Rb (570.6 $\mu\text{g/g}$), Ba (209.8 $\mu\text{g/g}$) and Li (1285 $\mu\text{g/g}$). However, fairly lower values are recorded for Ta (ca. 28.1 $\mu\text{g/g}$), Nb (ca. 28.3 $\mu\text{g/g}$) and Sn (ca. 83 $\mu\text{g/g}$). These values are significantly lower compared to those for rare metal pegmatites of Nasarawa-Keffi (OKUNLOLA, 2005). Following the classification system of pegmatites based on bulk chemistry and geochemical signatures (CERNY, 1991) and Ta/(Ta+Nb) versus Mn/(Mn+Fe) plot, (Figure 3), The Oke-Asa pegmatites are of rare element complex pegmatite type, LCT petrogenetic (Li, Rb, Cs, Be, Ga, Sn, Ta > N(B, P, F)) family, and of the lepidolite sub type. The pegmatite are of peraluminous bulk composition ($\text{Al}_2\text{O}_3 > \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$) (Figure 4). CERNY (1992), states that the LCT family has a mildly to extremely peraluminous parent granitic composition.

Based on this, there is a strong possibility that the Oke-Asa pegmatites are derived from the anatexis of crustal protoliths or supracrustal rocks with evidence of sodic metasomatic alteration. Using the K/Rb versus Rb plots (Figure 5) shows the pegmatite of Oke-Asa area are rare metal bearing. (MATHEIS, 1987; CERNY, 1994) Also, the relatively low Mg and Ti with attendant high Rb, Li, Cs composition indicate a high level of fractionation, as is usual with such pegmatites, While the level of mineralization may be comparable to those for some Nigerian pegmatite fields such as Egbe (MATHEIS, 1987), it is lower when compared to that of highly mineralized Tanco Pegmatite of Canada (CERNY, 1982, MOLLER & MORTEANI, 1987). The Ta vs Ga (Figure 6) plot also show the Oke-Asa pegmatite plotting above the BEUS (1966) mineralization line but below the GORDIYENKO (1971) line. The Na/K vs Ta diagram (Figure 7) also in-

dicates that the pegmatite of Oke Asa area are moderately albitised and compares with other mineralized pegmatite of Egbe-Isanlu area (MATHEIS, 1987) and Komu pegmatite Nigeria (OKUNLOLA & OFONIME, 2006) but lower than those of Tanco and Noumas pegmatites. Chondrite normalized plot of the rare earth element (REE) reveals high light REE (LREE) (La, Ce, Pr) values and lower heavy (HREE) (Er, Lu, Yb). There is a marked negative Europium (Eu) anomaly (Figure 8) which according to Taylor et al., (1986) suggests fractionation and intense late metasomatic effect.

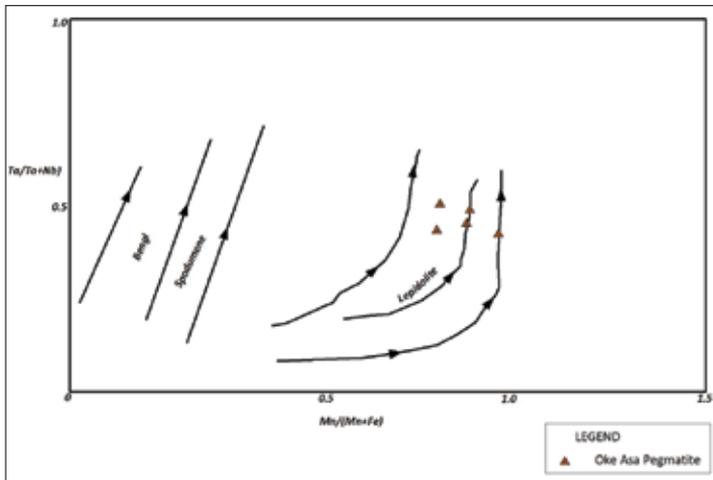


Figure 3. Ta/(Ta+Nb) vs Mn/ (Mn+Fe) plot of Oke Asa pegmatite indicating Lepidolite subtype

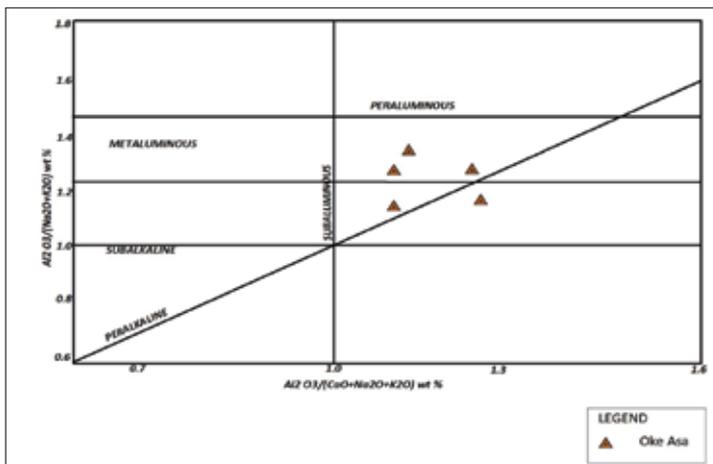


Figure 4. Al₂O₃/(Na₂O+K₂O) vs Al₂O₃/ (CaO+Na₂O+ K₂O) plot of Oke-Asa pegmatite showing it as having Peraluminous composition

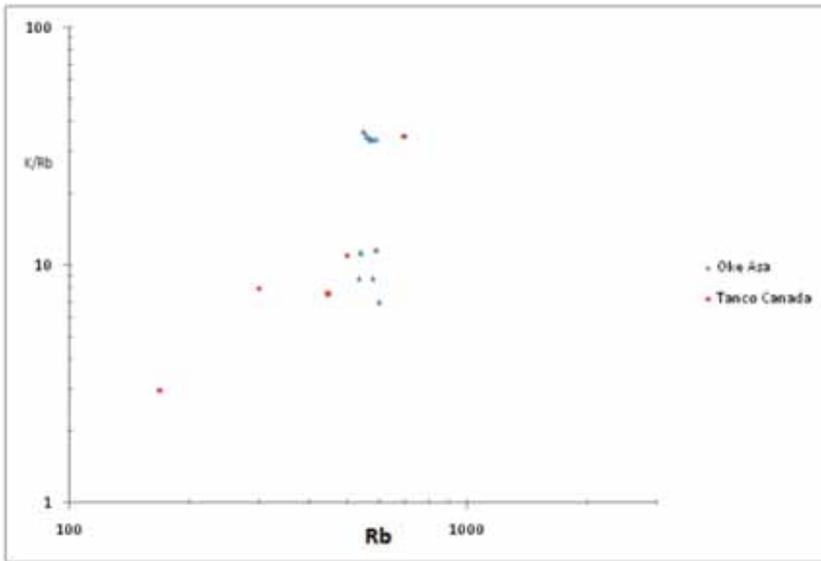


Figure 5. K/Rb/Rb plot of the Oke Asa pegmatite

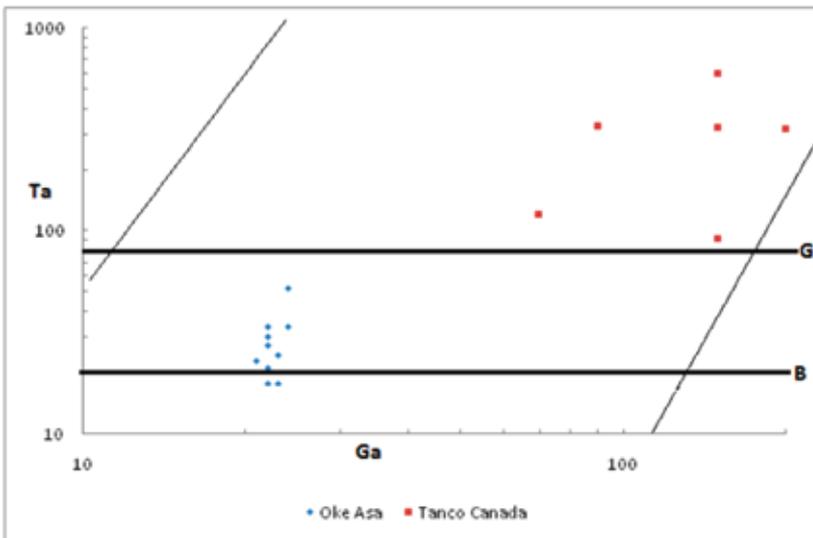


Figure 6. Ta/Ga plot of the Oke Asa pegmatite.
B=BEUS (1966) line , G=GORDIYENKO (1971) line

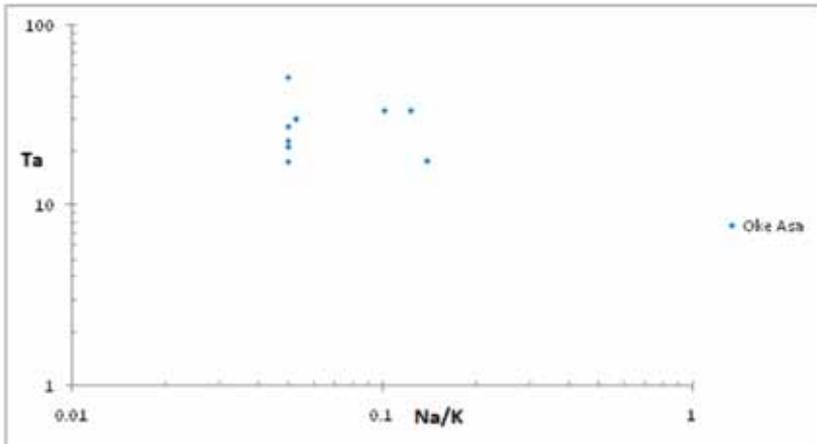


Figure 7. Ta vs Na/K plot for Oke-Asa pegmatite (OKUNLOLA, 2008).

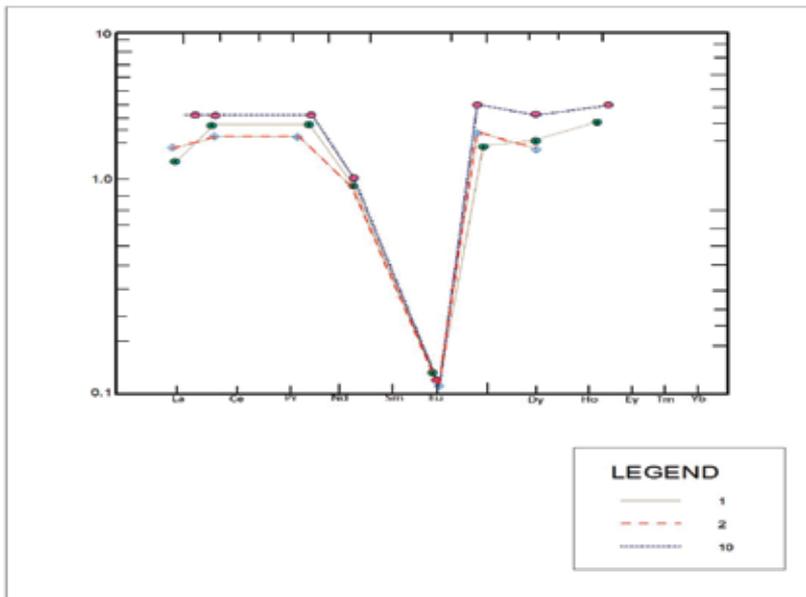


Figure 8. REE /chondrite plot for Oke Asa pegmatite

CONCLUSIONS

Systematic field mapping reveals that the the Precambrian pegmatite of Oke-Asa area are hosted by biotite gneiss and biotite schist. Petrographic analysis also shows that they contain mainly quartz, plagioclase, microcline and muscovite with accessory biotite, hornblende, tourmaline and opaque. From geochemical studies of the muscovite extracts, the pegmatite are siliceous, with a peraluminous composition, while trace elements analysis indicate that the pegmatite are variably enriched in rare metals Ta, Nb including Li, Rb and Sr. Variation plots for Ta versus K/Cs, Ta/W versus Cs, Ta versus Ga, Na/K versus Sn, Nb, Ta of the samples indicate a lower mineralization potentials when compared to Tanco pegmatite (Canada), Nassarswa-Keffi pegmatite field of Nigeria, but are comparable to those of Wodgina pegmatite (Australia), Hergendorf pegmatite (Western Germany) and Noumas pegmatite (South Africa). In addition to the major and minor element compositional features, consistent negative Eu signature of the chondrite normalized REE plots suggest the possibility of Oke-Asa pegmatites being derived from anatexis of undepleted upper to middle crustal protoliths or supracrustals with possible later metasomatic alterations.

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