Geochemical evaluation of the Pan-African pegmatites from parts of Oban massif, Southeast Nigeria

Geokemična preiskava panafriških pegmatitov iz delov Obanskega masiva v jugovzhodni Nigeriji

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Abstract

About 40 pegmatites exposures hosted by the metamorphic (schists and gneisses) and igneous rock unit (porphyritic and non-porphyritic granodiorites), which characterize the area were investigated and representative samples analyzed for geochemical characterization. Macroscopic study shows large crystals of schorls, albite, plagioclase and quartz. Geochemical analysis carried out at the Activation Laboratory -Canada, shows the pegmatites to be peraluminous from estimated Aluminium Saturation Index (ASI) which is greater than one (1). Variation plot of $Na_2O + K_2O$ vs. SiO₂ classifies the rocks as alkali to sub-alkalic types. SiO₂ and Al₂O₃ values which averages at 67.74 % and 14.49 % respectively are lower when compared to pegmatites from similar fields in other parts of the country. But they are richer in Fe_2O_2 with an average value of 4.16 %. Trace elements such as Ba, Sr, Zr, Rb, Ta, and Nb have average concentrations of (71.15, 27.50, 16.61, 344.70, 18.14, and 71.70) ppm respectively. While the ratios K/Ba, and K/Cs have very high average values of 430.43 and 1291.30 respectively. These extremely high values suggest that these pegmatites are barren and un-mineralized. Further discrimination using various standard ratios and variation plots for rare-metal mineralization indicates a poor level of mineralization for the Iwurupegmatites, while those of Igbofia and Akwa-Ibami shows very low degree of mineralization especially with respect to Ta-Nb.

Key words: Mineralization, Rare-metal, Southeastern Nigeria

Izvleček

Za geokemično opredelitev smo preiskali kakih 40 izdankov pegmatitov iz metamorfnih (kristalni skrilavci in gnajsi) in magmatskih (porfiritski in neporfiritski granodioriti) kamninskih enot, značilnih za to območje, in analizirali reprezentativne vzorce. Makroskopsko so opazni veliki kristali šorlitov, albita, plagioklaza in kremena. Geokemične analize, ki so jih opravili v Activation Laboratory v Kanadi, pričajo o peraluminjskem značaju pegmatitov, kar kaže ugotovljena vrednost indeksa nasičenosti aluminija (ASI), ki je večja od enote (1). Variacijski diagram Na₂O + K₂O glede na SiO₂ uvršča kamnine med alkalijske do subalkalijske tipe. Vsebnosti SiO, in Al₂O₂ s povprečjema 67,74 % in 14,49 % so nižje v primerjavi s tistimi za pegmatite podobnih območij iz drugih delov države. Vsebujejo pa več Fe₂O₂ s povprečjem 4,16 %. Sledne prvine kot Ba, Sr, Zr, Rb, Ta in Nb imajo po vrsti naslednje povprečne koncentracije: (7,15, 27,50, 16,61, 344,70, 18,14 in 70) ppm. Razmerji K/Ba in K/Cs imata zelo visoki povprečji, in sicer 430,43 in 1291,30. Te izjemno visoke vrednosti pričajo o tem, da so pegmatiti jalovi, neorudeni. Nadaljnje razvrščanje na osnovi raznih standardnih razmerij in variacijskih diagramov orudenja z redkimi kovinami nakazuje nizko raven orudenja za pegmatite območja Iwuru in zelo nizko raven orudenja za pegmatite območij Igbofia in Akwa-Ibami, zlasti kar zadeva Ta-Nb.

Ključne besede: orudenje, redke kovine, jugovzhodna Nigerija

Introduction

Pegmatites occur as dykes, veins, and lenses in the Nigerian basement complex and could be characterized by pneumatolitic ore deposits like tin, columbite, tantalite, and lepidolite. Pegmatites of Nigeria and the world at large are known to have generated great interest. This is because of the metals they host, which are of immense industrial concern. Examples include tantalum, niobium, columbite, tungsten amongst others (Garba, 2001). Based on macroscopic observation, two pegmatite types occur and prevail in the rare-metal granitic-pegmatites of west Africa which are: (1) those with biotite and black tourmaline: abundant graphic textures quartz feldspar; and quartz tourmaline (2) those with microcline, plagioclase, biotite and small amount of quartz (Varlamoff, 1972). And they could be hosted by the various rock types present in the Basement Complex rocks in Nigeria.

One of the earliest workers of the Precambrian pegmatites of Nigeria was Raeburn, (1927) who explored and observed that the pegmatites of Calabararea were characterized by the presence of tinstone and tourmaline. Subsequently, Jacobson and Webb, (1946) carried out a more elaborate study of the pegmatites of Central Nigeria and concluded that they 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. But studies by Ekwueme and Schlag (1989), Ekwueme and Matheis (1995), Garba (2001), show that the Precambrian pegmatites of Nigeria are not restricted to the so called "Tin Province" or "Pegmatite belt of Nigeria", but occur also in the southeastern Nigeria. They are believed to extend into northeastern Brazil (Garba, 2001; Ekwueme and Matheis, 1995). Okunlola (2004) studied about 200 Precambrian pegmatite bod-



Figure 1: Geologic map of study area.

ies in Nigeria from which he recognized and defined 7 broad fields of the Precambrian raremetals pegmatites of Nigeria. This study aims at evaluating and classifying the pegmatites of the study area, and their economic importance based on geo-chemical characteristics.

The pegmatites found within the metamorphic terrain have undergone a high degree of weathering, but thegranodiorites and the pegmatitesintruding the metarmorphic rocks, which are the host rocks, were not deformed. The pegmatites of southeast Nigeria, which originate either from the cooling of the granodiorites or from the metamorphism and anatexis of country rocks, has been dated as rocks formed between 600 ma and 530 ma (Matheis and Caen-Vanchete, 1983). Ekwueme, (1989), further showed that they were emplaced as syn-collisional and volcanic arc granites. From hand specimen, the general mineralogy of the pegmatites can be summed up as quartz + feldspar (orthoclase and albite) + biotite + muscovite + tourmaline and other accessory minerals. Books of muscovite and graphic growth of quartz plus feldspar are mostly seen in samples of Iwuru area, while the Akwa-Ibami area is dominated by random crystals of schorls which could be as much as 30-40 % in the mode. Associated minerals such as tin, tourmaline, and beryl have been reported by the locals to have been mined in the past from both areas. Petrographic studies have been detailed in Raeburn, (1927), and Igonor, et al., (2010). Ekwueme and Matheis (1995) have shown with strong evidence that the pegmatites and older granites of southeast Nigeria are closely related, that in fact the pegmatites are derived from the cooling of the granodiorites and hence both rock types have a common petrogenetic origin. Similarly, the pegmatites of the metamorphic rock unit were suggested to have been formed from facies metamorphism and anatexis of country rock (Ekwueme, 1990).

Materials and methods

The area of study (Igbofia-Akwalbami-Iwuru) is located between latitudes 5°20' N to 5°27' N and longitudes 8°09' E to 8°18' E, in the western region of the Oban massif, southeastern Nigeria

(Figure 1). This area is characterized by thick forestation, highly undulating topography, with several stream channels. All these make accessibility remote and difficult.

Geologic mapping was undertaken to study the various lithological units of the study area (Oban massif) with special interest in the pegmatite veins occurring in the area. The structural orientation and physical characteristics of the veins were observed. These pegmatite occurrences, which cover an area extent of approximately 230 km² exceeds about 50 outcrop bodies, out of which about 40 were sampled and representative samples collected for further studies and geochemical analyses. 12 composite samples, which are representative of the pegmatites and their host rocks were taken for further geochemical analysis. Pulverized whole rock samples and extracted mineral content (muscovite flakes) were analyzed for major oxides and trace element contents at the Activation Laboratories, LTD., Canada using the ICP-MS analytical method. The method has a minimum detection limit of about 0.01 % for the major oxides and between 0.05-5 ppm in the trace and rare-earth elements. Acquired geochemical data were interpreted using simple computer software programme (Microsoft Excel 2007) based on established standard procedures by authors in pegmatite geochemistry.

Results and discussion

Pegmatites occur in several locations in the area of study. They outcrop mostly as veins or as giant outcrops reaching a height of more than 5 m. This is probably because the host rocks (most likely schist) have been weathered away leaving behind the more resistant pegmatite vein. The most preferred orientation trend for these veins is the NNW - SSE, which is between 140° and 170°. Also these pegmatites occur in high angle structures as over 94 % have dip values greater or equal to 50° (Oden, 2010). These rocks, which are either hydrothermal injections or formed from facies metamorphism and anatexis of country rock (Ekwueme, 1990) are distributed across the entire study area and are hosted by two main rock units. And these are the metamorphic (schists and gneisses) and the igneous (granodiorite) rocks. Detailed description of these host rocks have been described by Ekwueme, (1989); Theresa and Ekwueme, (1996); and Igonor et al., (2010) among others.

The pegmatite veins range in exposed length from about 1.5 m to 20 m and width of between 0.2 m and 8.4 m. The pegmatites are generally coarse grained with large crystal grains of representative minerals visible in hand specimen. Quartz grains range from about 1 cm × 2 cm to greater than 2 cm × 3 cm, while black tourmaline (schorl) of more than 4 cm in length is sometimes present. Variation in mineral composition of the pegmatite results in the various shades of colour observed in the pegmatites. Where orthoclase and/or albite is dominant, the colour is pinkish to white, while dense amount of schorl + biotite results in a dark-coloured rock type The Akwa-Ibami area is characterized by a higher degree of weathering and deformation of host rock, massive ridges (up to 200 m \times 20 m) and veins of pegmatitesare undeformedand generally trending in the NE-

SW direction. Undeformed veins and dykes that are not too extensive and protected by their host (granodiorites) from intensive weathering characterize the Igbofia area. Aplitic dykes are associated with the pegmatites of Igbofia and Iwuru area which is a common feature of granitic pegmatites. Similarly, the Igbofia and Iwurupegmatites run conformably with the general structural trend of the host rocks in the study area, that is, NE-SW. some of these pegmatite veins trend in the NW-SE direction.



Figure 2: Plot of $AI_2O_4/(Na_2O + K_2O)$ vs $AI_2O_4/(Na_2O + K_2O - CaO)$ showing the peraluminous nature of the pegmatites from study area (after Maniar and Piccoli, 1989).

Oxides Wt %	T1	Т2	Т3	T4	Τ5	Т6	Τ7	Т8	
	Igbofia pegmatites		AkwaIbami pegmatites			Iwuru pegmatites			
SiO ₂	73.01	71.58	69.10	67.60	69.50	72.89	73.01	53.05	
TiO ₂	0.04	0.18	0.04	0.07	0.19	0.06	0.07	1.66	
Al ₂ O ₃	16.01	15.00	14.00	15.50	14.50	12.01	12.00	16.89	
Fe ₂ O ₃	4.98	5.09	2.50	1.40	2.98	2.50	2.10	15.70	
Mn0	0.02	0.04	0.05	0.07	0.09	0.05	0.02	0.08	
MgO	1.53	1.10	1.65	0.17	1.04	0.19	2.11	2.10	
CaO	1.04	4.49	1.35	3.17	3.73	2.47	2.17	2.03	
Na ₂ 0	0.10	0.14	0.18	0.07	0.09	0.29	0.11	0.02	
K ₂ 0	3.01	0.65	10.04	11.12	5.57	6.28	5.89	6.32	
$P_{2}O_{5}$	ND	ND	ND	ND	ND	ND	ND	ND	
Total	100.27	99.81	99.86	99.61	99.99	98.70	99.04	99.94	
MALI	negative		positive			positive			

Table 1: Major oxides compositions of pegmatites of parts of Oban massif (south eastern Nigeria)

N.B: T1, T2 – average of samples from Igbofia area; T3, T4, T5 – average of samples from Akwa Ibami area; T6, T7, T8 – average of samples from Iwuru area. T5 and T8 are muscovite extracts. Average values are of five samples in each case; MALI = Modified-Alkali-Lime-Index. ND – not detected.

Results of the major oxide geochemistry of the pegmatites from study area are as shown in Table 1. The results show that Igbofiapegmatites are the most siliceous and aluminous, while Iwurupegmatites are the poorest in SiO₂ and Cabut richer in Fe. Generally, the pegmatites are high in aluminous content and are seen to be peraluminous (Figure 2). But Iwuru pegmatite is relatively slightly depleted in alumina content. Based on the high silica and alkali plus low CaO content, the pegmatites of AkwaIbami and Iwuru area, are more granitic in composition, while the Igbofia area tends towards granodioritic composition because of their high silica, CaO, MgO, and low alkali content. The areas have a reasonably high Fe-number ranging between 0.66 and 0.77. The calculated Modified-Alkali-Lime-Index (MALI) shows positive values for both AkwaIbami and Iwuru areas, while it is negative for the Igbofia group with a narrow range.



Figure 4: Plot of Rb vs Sr showing the likely depth of origin for the pegmatites of study area (after Brown et. al., 1979).



Figure 5: Plots of Ta vs K/Cs of pegmatites from study area (after Beus, 1966 and Gordiyenko, 1971).

Table 2 shows values of trace elements and elemental ratios for the pegmatites from study area. This shows selected trace elements such as Ba, Sr, Zr, Rb, Ta, Nb and Cs having average concentrations of 71.15 ppm, 27.5 ppm, 16.61 ppm, 344.7 ppm, 18.14 ppm, 71.7 ppm and 24.5 ppm respectively. Trace element ratios of K/Ba and K/Cs have very high average values of 430.43 and 1291.30 while Ta:Cs ratio is far below 10 for all samples.

According to Frost et al., (2001), a reason these rocks are peraluminous could be as a result of the parent melt having another aluminous phase present, which could be aluminous biotite or muscovite, garnet or an Al_2O_5 polymorph. Also Miller, (1985) believes that such rocks could have formed from strongly peraluminous melt which was derived from the melting of biotite bearing metaluminous felsic rocks.

According to Ekwueme and Matheis, (1995) it is inferred that the magma which produced these pegmatites must have been alkaline in nature hence the high alkali content of these pegmatites.

The high Fe-number of the pegmatites probably reflects a high modal proportion of a ferromagnesian mineral e.gbiotite (Frost et at., 2001). And the narrow range in the Fe-number values signifies similarity in source rock composition and or nearness in degree of melting undergone by rocks (Patino and Beard, 1996; Nabelek et al., 1991). Similarly, the narrow range in MALI supports the theory of similar parent source for the pegmatites of the study area (Frost et al., 2001).

The moderately high values of Cs indicate moderately high alkali metal fractionation (Cerny, 1982, 1989). Ta:Nb ratio ranges between 0.1 to 0.41. This suggests a preference for possible Nb enrichment. But Ta and Nb values are obviously too low for any profitable mineralization in tantalum and or niobium. Also since residual fluids, which form Ta rich pegmatites, are enriched in Ga (Cerny, 1982), the low level of Ga in the pegmatites of study area indicates a near impossibility of Ta mineralization. The higher than normal content of Rb (150 ppm - Taylor, 1965) is indicative that the melts which formed these rocks, have undergone high degree of partial melting of source material. It can be said that the pegmatites of study area, originate from average depth intrusions (20-30 km) since pegmatites originating from deeper intrusions have been shown to have similar low values of

Elements (ppm)	T1	Т2	Т3	T4	Т5	Т6	T7	Т8
Ва	84	23	54	51	168	84	51	118
Rb	212	23	563	914	288	265	337	156
Sr	11	38	13	17	61	18	18	44
Y	1	1	1	4	3	1	1	5
Zr	26	39	3	18	21	8	9	9
Nb	131	259	33	53	38	14	13	32
Th	6	1	1	2	2	5	2	2
Pb	5	12	18	29	14	13	18	16
Ga	37	34	27	42	23	19	23	16
Zn	533	2133	2236	1246	5247	2851	3385	3280
Cu	11	14	18	20	25	20	15	47
Ni	1	5	6	4	8	7	14	15
V	2	4	3	3	17	7	6	18
Cr	7	28	36	20	44	39	36	104
Hf	3	4	0.3	2	2	1	1	0.4
Cs	15	27	13	62	22	9	29	18
Sc	0.3	2	0.4	1	2	0.3	1	2
Та	53	429	14	15	1	4	7	
Со	1	1	1	1	2	1	3	4
Li	11	56	5	7	73	43	15	118
Ве	124	580	5	49	59	11	6	331
K/Ba	500	104	856	847	174	289	575	98
Na/K	7	22	0.8	1	0.27	0.1	1	0.4
Rb/Sr	19	0.6	43	54	5	15	19	4
K/Rb	47	105	82	47	83	92	90	74
K/Cs	667	89	3527	700	1077	2641	997	634
Th/U	2	0.4	0.4	0.3	0.1	1	0.3	1

Table 2: Trace element and elemental ratio composition of pegmatites of parts of Oban massif, SE Nigeria

N.B: T1, T2 – average of samples from Igbofia area; T3, T4, T5 – average of samples from Akwa Ibami area; T6, T7, T8 – average of samples from Iwuru area. T5 and T8 are muscovite extracts. Average values are of five samples in each case.

Zr and aplite area less commonly found in association with them (Cerny, 1992). This fact is further buttressed by the graph of Rb vs Sr (Figure 4). Also the low Zr content is indicative of an almost no crustal derivation. Since these pegmatites have, Ta:Cs ratio far below 10, they conveniently group in the lack to low mineralized pegmatites of the world. (Moller and Mortteani, 1989; Cerny, 1992.)

Low values of K/Ba and K/Cs are believed to be indicative of mineralized pegmatites (Garba, 2001). Thus the extremely high values in pegmatites of study area suggest that these pegmatites are barren and unmineralised. Further economic mineralization of these pegmatites from Oban massif was evaluated using variation plots of Ta vs K/Cs (Figure 5), Ta vs Ga (Figure 6), K/Rb vs Rb (Figure 7), and K/Rb vs Cs (Figure 8). As any rock falling below the defining line of mineralization of Beus, (1966) and Gordiyenko, (1971) is considered barren, while those plotting above the lines are considered mineralized, the pegmatrites from Iwuru are barren as they plot far below both mineralization boundaries. But the pegmatites of Igbofia and Akwa-Ibami have a very low mineralization potential as they are seen to plot above the defining line of Beus, (1966), but below that of Gordiyenko, (1971). On the contratry, in the work of Kingsley and Ekwueme (2009), these same pegmatite seem to be high in mineralization. A scrutiny of the work showed a mistake in the calculation of the K/Rb and K/Cs data, which is pertinent in inferring the mineralization of pegmatite. Pegmatites from the Igbofia-Akwaibami-Iwuru area when compared with pegmatite from other parts of the country (the seven (7) fileds of Okunlola, 2004) are depleted in silica but more enriched in Fe_2O_3 , though has a lesser Fe-number except in comparism to those of BirniWari-Kushakafield. This lesser Fe-number is due to a relatively higher MgO content of the pegmatites from study area. Average alumina content is only silmilar to those of the Nassarawa-Keffi field but more depleted than pegmatites from the other six fields. Comparing alkali content, those of the study area is greater than those of Nassarawa-Keffi, Lema-Share, and BirniWari-Kushakabut less than those of the other four fields. According to Bateman and Chappell, (1979), rocks with SiO, less than 70 % and Fe-number less than 0.6 are usually magnesian. This agrees with the pegmatites of study area. Further, Frost and Frost (1997), posits that such magnesian rocks are related to magmas which follow relatively oxidizing differentiation trends.

Conclusion

The Igbofia-Akwalbami-Iwurupegmatites are members of the Precambrian pegmatites of Nigeria formed in the Pan-African Orogeny. They are hosted by Precambrian rocks of Oban Basement Complex comprised of mainly schist and granodiorites. They are peraluminous, alkali rich, and tend towards granitic composition. These pegmatites from all reasonable indications and variation diagrams discriminations, are barren and unmineralised and thus have little or no economic potential as it pertains to rare-metals especially Ta-Nb minerals. This is in disagreement with Kingsley and Ekwueme, (2009). This disagreement stems from the wrong calculation of K/Rb and K/Cs ratios in their work, which invariably led to a wrong interpretation of mineralization potential as these ratios are important in pegmatite mineralization evaluation.



Figure 6: Plot of Ta vs Ga for pegmatites of study area.



Figure 7: Plot of K/Rb vs Rb for pegmatites of study area (after Straurov et. al., 1966).



Figure 8: Plot of K/Rb vs Cs for pegmatites of study area (after Moller and Morteani, 1987).

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