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GEOCHEMISTRY, CLASSIFICATION CHARACTERISTICS OF PEGMATITES FROM IJERO-EKITI, EKITI-STATE, SOUTHWEST NIGERIA

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ABSTRACT: Geochemical analysis of ten (10) representative pegmatite samples reveal high silica (SiO₂) 66-78 wt % and alumina (Al_2O_3) 10.08-19.57 wt % contents. The alumina (Al_2O_3) is greater than the alkali $Na_2O + K_2O + CaO$ in all the rock samples by values ranging between 1.43 and 4.90 wt % implying that the rocks are peraluminous. MgO (0.02-1.60wt%), CaO (-0.01-1.39wt %) and Fe_2O_{3T} (0.77--6-99 wt %) have low contents. Rocks that are characterised by low Mg, Ca, and Fe as well as low ratio of Na_2O/K_2O are termed "fertile" and peraluminous. A plot of $Al_2O_3/(CaO + Na_2O + K2O)$ versus $Al_2O_3/Na_2O + K_2O$ shows and confirms the peraluminous character of the pegmatite from Ijero while the molecular $Al_2O_3/Cao+Na_2O+K_2O$ versus SiO₂ shows the plottings on the S-type granitoids. Rocks that are fertile and peraluminous are rich in albite (NaAlSi₃ O_8), potassium feldspar (KAlSi₃ O_8) and quartz (Si O_2). The abundance of feldspar and mica are geochemical indicators for Sn-Ta mineralisation. Industrial minerals (Kaolin, feldspar and gemstones (tourmaline, beryl and topaz)) occur in abundance considered significant and exploitable. The crossplots of MgO, Fe_2O_3 , Na_2O Al_2O_3 and TiO_2 against SiO_2 .respectively indicate negative correlation that suggest non association with SiO₂. However, some oxides like Fe_2O_3 , Na_2O_3 like Al_2O_3 trend negatively downward but cluster along the trend showing their relative abundance with silica. The plotting of samples in both the tholeiitic and calc-alkaline fields shows that the magma from which the pegmatite was formed was not totally restricted in occurrence only to subduction-related environment but also from the oceanic crust of calc-alkaline environments. Samples plottings on both the igneous, sedimentary and metasedimentary origins as seen in Na_2O/Al_2O_3 versus K_2O/Al_2O_3 support the derivation of materials that made up the rock from mixed sources. Further classification using various parameters show that pegmatite samples plot on the granodiorite, syenogranite, alkali granite and quartz syenite as well as granitic groups, all having the attributes of granites, and supporting the granitic character of pegmatites.

KEYWORDS: Geochemistry, peraluminous, S-type granitoid, mixed sources, continental/oceanic.

INTRODUCTION

Ijero-Ekiti lies between latitudes 7°46'N and 7°55'N and longitudes 5°00'E and 5°80'E. Ijero-Ekiti area is underlain by the rocks of the Basement Complex. Rahaman (1976) classified the

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major rocks into four distinct units namely; the migmatite-gneiss complex , the biotitehornblende gneiss, the metasediments (schists), and the Older granites .The pegmatites are coarse-grained and were emplaced during the late stage of the Pan-African Orogeny (600 ± 150 Ma)(Rahaman, (1988), Manier and Piccoli., 1989). Wright (1976) and Waokes et al., (1987) suggested that during this late phase the pegmatite intruded into the migmatite gneiss, schists, amphibolites and granites of the Pan-African Basement. The metasediments are the mica schists, the amphibolites schist and the quartzite. The mica schist is dark-coloured and composed of muscovite and biotite with quartz in variable amounts.At Ijeri-Ekiti , quartz+ muscovite and quartz + muscovite + biotite schists are exposed in places and are highly pegmatised.The Older granites are the porphyritic granites and the pegmatites. Varlamoff (1972) related the pegmatite with the Older granite body and reported that the massive oligaclase albite and tourmaline -rich pegmatite in Ijero-Ekiti represent the apical parts of a concealed granitoid (most likely Older granite) body. The field relationship shows that the pegmatite occurs as massive and tabular bodies as well as dykes and veins (Plates 1& 2).



Plate 1: Photomicrograph of tabular pegmatite



Plate 2 Photomicrograph of tabular pegmatite

The use of geochemistry to study the tectonic setting, the provenance and chemical characteristics of pegmatite from Ijero has not received any desired attention, hence this paper.

Physiography

Ijero Ekiti is one of the local Government areas of Ekiti State, Nigeria. The climate reflects the general climate of Nigeria which is characterized by alternating rainy and dry seasons. The humid condition of the area encourages chemical weathering of he basement rocks and the formation of red earth called laterite. The landform comprises undulating lowlands separated by hillocks representing granite and pegmatite ridges. The pegmatite ridges rise between 10 meters and 35 meters above the general ground level. The hills are disserted by numerous streams and rivers such as Awo, Yaro and Oyi which again drain the Ijero Ekiti areas .

MATERIALS AND METHODS

Ten (10 representative pegmatite rock samples were collected from Ijero- Ekiti and environs. (Fig 2) The samples were cut into two, one half for thin section and the other for pulverization. The pulverized samples were sent to the Activation Laboratories Ltd Ontario, Canada for chemical analysis using the X- ray fluorescence spectrometer (XRF). The major oxides and minor elements were determined. 20 grams of the samples were put into the pellet cup containing 1 gram of stearic acid. The mixed samples were compressed into pellet in an aluminium crucible using machine (1-40 autopress). The pellets were then fed into the X-ray spectrometer Philip model 1450. Scintillation counts from the samples in the x-ray spectrometer were red from the curves as percentages of the selected major oxides. The analysed samples gives the iron (Fe) concentration only as total iron oxide. The loss on ignition (LOI) was determined by gravimetric method.

The rock samples for thin section were prepared into slides in the laboratory of the Department of Geology, Obafemi Awolowo University, Ile-Ife. The slides were studied under the petrographic microscope to determine the mineralogy and microstructures of the rocks.

RESULTS AND DISCUSSION

The geochemical composition of pegmatite from Ijero-Ekiti area is presented in Table 1.

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Sample	1	2	3	4	5	6	7	8	9	10
SiO ₂	74.29	64.47	73.85	78.61	74.13	69.51	74.07	72.54	77.06	76.47
Al_2O_3	12.27	16.02	13.87	13.65	14.82	16.95	13.11	14.50	11.32	11.92
Fe ₂ O3	4.03	6.99	1.68	1.59	0.77	0.91	6.55	4.19	5.62	3.94
MgO	0.16	1.60	0.26	0.08	0.08	0.02	0.02	0.15	0.24	0.03
CaO	0.72	1.39	1.10	-0.01	0.37	0.13	0.07	0.03	0.17	0.17
Na ₂ O	1.98	4.51	3.21	0.21	2.93	3.52	0.13	0.13	0.11	2.32
K ₂ O	1.84	2.76	5.41	3.74	6.07	8.14	3.44	5.20	2.03	2.58
SO2	0.08	-	-	-	-	-	0.06	0.06	0.07	0.06
TiO ₅	-	0.856	0.137	0.013	0.016	-0.001	-	-	-	-
MnO	-	0.085	0.038	0.026	0.010	0.02	-	-	-	-
P_2O_5	-	0.20	0.08	0.02	0.20	0.33	-	-	-	-
LOI	4.71	0.75	0.31	2.03	0.64	0.40	1.96	3.12	3.45	2.57
Total	100	99.64	99.95	99.97	100.02	100.02	100	100	100	100

Table 1: Geochemical composition of pegmatites from Ijero-Ekiti.

The data show a wide compositional range of the pegmatites with high silica ,SiO₂ (64.46 - 77.54 wt %) and alumina AL₂O₃ (11.92 - 16.95 wt %) contents while the loss on ignition(LOI) ranges from 0.31 to 4.71 wt %. The data reveal also that soda, Na₂O varies between 0.21 and 4.51 wt % while potash, K₂O ranges between 1.84 and 8.14 wt %. These compositional values are typical of pegmatites. Iron content (Fe₂O₃) is relatively moderate ranging between 0.91 wt % and 6.99 wt %. The TiO₂ values are generally less than unity (< 1). Major oxides are used to obtain cross plots to determine their compatibility or relationships. Figure 1 shows the plots of MgO, Fe₂O₃, Na₂O Al₂O₃ and TiO₂ against SiO₂ respectively.These oxides correlate negatively with SiO₂ but the trends in some of them like MgO, and TiO₂ show that the samples cluster around the silica, SiO₂ an indication of its abundance. The negatively correlated oxides have downward linear trend suggesting non association with SiO₂. Though, some oxides like Fe₂O₃, Na₂O Al₂O₃ trend negatively downward they cluster along the trend showing the their relative abundance .





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Figure 1: Cross Plots of major oxide

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Sample	1	2	3	4	5	6	7	8	9	10
SiO ₂	74.29	64.47	73.85	78.61	74.13	69.51	74.07	72.54	77.06	76.47
Al ₂ O ₃	12.27	16.02	13.87	13.65	14.82	16.95	13.11	14.50	11.32	11.92
Fe ₂ O3	4.03	6.99	1.68	1.59	0.77	0.91	6.55	4.19	5.62	3.94
MgO	0.16	1.60	0.26	0.08	0.08	0.02	0.02	0.15	0.24	0.03
CaO	0.72	1.39	1.10	-0.01	0.37	0.13	0.07	0.03	0.17	0.17
Na ₂ O	1.98	4.51	3.21	0.21	2.93	3.52	0.13	0.13	0.11	2.32
K ₂ O	1.84	2.76	5.41	3.74	6.07	8.14	3.44	5.20	2.03	2.58
SO2	0.08	-	-	-	-	-	0.06	0.06	0.07	0.06
TiO ₅	-	0.856	0.137	0.013	0.016	-0.001	-	-	-	-
MnO	-	0.085	0.038	0.026	0.010	0.02	-	-	-	-
P ₂ O ₅	-	0.20	0.08	0.02	0.20	0.33	-	-	-	-
LOI	4.71	0.75	0.31	2.03	0.64	0.40	1.96	3.12	3.45	2.57
Total	100	99.64	99.95	99.97	100.02	100.02	100	100	100	100
Na ₂ O/ K ₂ O	1.08	1.63	0.59	0.06	0.48	0.43	0.04	0.05	0.05	0.89
Al ₂ O ₃ / Na ₂ O+	2.70	2.41	1.43	3.46	1.58	3.29	3.60	2.64	4.90	2.35
$CaO+K_2O$										
Excess of	7.73	7.36	4.15	9.71	5.45	5.15	9.47	9.00	9.01	6.85
Al ₂ O _{3 over}										
Na ₂ O+ CaO+										
K ₂ O										
Na ₂ O+ CaO+	0.37	0.54	0.70	0.29	0.63	0.69	0.28	0.38	0.20	0.42
K_2O/Al_2O_3										

Table 2:	Major	Oxides	with	some ratios
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The geochemical data displaying the ratios of Na₂O/K₂O and Al₂O₃/Na₂O +K₂O +CaO for the various samples are shown in Table 2. The ratio of Na₂O/K₂O in the rocks is low. It ranges from 0.05 to 63wt %. The alumina (Al₂O₃) is greater than the alkali Na₂O + K₂O +CaO in all the rock samples by values ranging between 1.43 and 4.90 wt % implying that the rocks are peraluminous. MgO (0.02-1.60wt%), CaO (-0.01-1.39wt %) and Fe₂O_{3 T} (0.77--6-99 wt %) have low contents. Rocks that are characterised by low Mg, Ca, and Fe as well as low ratio of Na₂O/K₂O are termed "fertile" and peraluminous (Cerny, et al;1981 and Longstaff, 1982). Corollary, the ratio of $Na_2O + K_2O + CaO/Al_2O_3$ is less than unity (0.20-0.70) and according to Pearce et al., (1984) such a ratio confirms the peraluminous character of the rock. Rocks with these characteristics and similar to the Ijero-Ekiti pegmatites are rich in albite (NaAlSi₃ O_8), potassium feldspar (KAlSi₃O₈) and quartz (SiO₂). A plot of $Al_2O_3/(CaO + Na_2O + K2O)$ versus Al₂O₃/Na₂O + K₂O in Figure 2 shows and confirms the peraluminous character of the pegmatite from Ijero while the molecular Al₂O₃/Cao+Na₂O+K₂O versus SiO₂ shows the plottings on the S-type granitoids . (Figure 3). Wilson (1991) stated that peraluminuos granites contain crustal or sedimentary materials in their original magma. Also a plot of rock in the Stype field implies that the original magma from which the pegmatite was formed contained great amount of sedimentary or crustal materials. Chappell & White, (1974) in their geochemical schemes for classification of granitic rocks recognized two distinct granitoid 6

types, the I-type metaluminuos formed from a mafic metaigneous source and the S-type peraluminuous formed from the melting of metasedimentary rocks. (Miller, (1985)) however, stated that similar granitic compositions can be produced by partial melting of a variety of sources. John and Wooden, 1990; Miller et al., 1990.were of the opinion that granitoids rarely come from single sources, but instead are mixtures of mantle-derived mafic melts and melts of crustal rocks that may or may not contain metasedimentary components This has recently been demonstrated for the 'type' S- and I-type granitoids of the Lachlan Belt (Collins, 1996)



Figure 2 : Al2O3/(CaO + Na2O + K2O) versus Al2O3/Na2O + K2O plot showing the dominantly Paraluminus nature of the rocks (after Maniar and Piccoli, 1989)



Figure 3: Molecular Al2O3/Cao+Na2O+K2O versus SiO2 diagram showing the classification of the rocks into the fields of I-type and S-type granitoids (after White and Chappell (1977).

The low ratio value of N_2O/K_2O indicates that the rocks are highly chemically mature. Pettijohn, et al; 1987 attribute low Na_2O/K_2O ratio to the dominance of K-feldspar and K- mica over albite plagioclase. The abundance of feldspar and mica are geochemical indicators of Sn-Ta mineralization (Cerny, et al; 1981). High potash content in any rock is an indication that generation of the magma is plutonic. An AFM diagram in terms of the alkalies ($Na_2O + K_2O$), Fe_2O_3 , and MgO shows that the samples plotted in both the tholeiitic and calc-alkaline fields (Figure 4). The dashed line separates the tholeiitic fields from the calc-alkaline fields.



Figure 4: AFM diagram for rocks in the study area discriminating calc-alkaline field from tholeiitic (Ivine and Baragar, 1971).

The tholeiitic rocks normally shows stronger Fe -enrichment relative to Mg than do the calcalkaline while the calc-alkaline shows enrichment in silica and alkalies (Miyashiro, 1974). The plotting of the samples in both the tholeiitic and calc-alkaline fields shows that the magma from International Research Journal of Natural Sciences Vol.4, No.4, pp.1-18, December 2016

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which the rock was formed was not totally restricted in occurrence only to subduction-related environment. This suggests that the pegmatite may have been derived not only from subduction-tectonic environment but also from the oceanic crust of calc-alkaline environments. Figure 6 shows a plot of K_2O versus SiO₂ where the plots cut across low K-tholeiitic series and high -K calc-alkaline series. Meanwhile, the plot of TiO₂-K₂O-P₂O₅ in Figure 5 indicates that substantial samples plotted in the continental crust.



Figure 5 : TiO2-K20-P205 plot of the rocks (Pearce et al., 1975)

High potash content (alkalies) with relative Fe-enrichment and silica suggest the plutonic generation of magma. and the development of the rocks in both the oceanic and continental crusts.

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Figure 6: Plot of K2O vs. SiO2 for the Ijero samples (after Le Maitre et al., 1989)

Geochemical classification

Figure 7 shows that the pegmatite samples plotted on both the igneous, sedimentary and metasedimentary origins as seen in a plot of Na_2O/Al_2O_3 versus K_2O/Al_2O_3 (After Garrels and Mackenzie, 1971), supporting the derivation of materials that made up the rock from mixed sources.



Published by European Centre for Research Training and Development UK (www.eajournals.org) Figure 7: Na₂O/Al₂O₃ vs. K₂O/Al₂O₃ plot for pegmatites at Ijero (After Garrels and Mackenzie,

However, a discrimination diagram of TiO_2 versus SiO_2 as proposed by Tarney (1977) shows that the samples plotted within the igneous field only (Figure 8) an implication that substantial materials may have been generated from igneous sources.

1971).



Figure 8 : TiO₂ versus SiO₂ Discrimination Diagram (after Tarney, 1977



Figure 9 : $SiO_2 - Na_2O + K_2O$ diagram showing the granitic protolith of the pegmatites in the study area (after Cox et al., 1979)

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Figure 9 indicates a plot of SiO₂ against Na₂O + K₂O showing the granitic protolith of the pegmatite. The plots are within the granodiorite and granitic groups supporting the granitic character of pegmatites. Further classification of the plutonic rock using the parameters R1 and R2 (after de la Roche et al., 1980), calculated from millications proportions. R1 = 4Si - 1(Na + K) - 2(Fe + Ti); R2 = 6Ca + 2Mg + Al. reveals that some samples plotted on the syenogranite, alkali granite and quartz syenite respectively, all having the attributes of granites. (Figure 10)



Figure 10: Classification of plutonic rocks using the parameters R1 and R2 (after de la Roche et al., 1980), calculated from millications proportions. R1 = 4Si - 1(Na + K) - 2(Fe + Ti); R2 = 6Ca + 2Mg + Al.



Figure 11 : $Na_2O + K_2O$ -CaO versus SiO₂ diagram after Peacock (1931) showing the classification of the major rocks into Alkaline, A-C (alkali-calcic), C-A (calcic-alkali) and Calcic groups.

Published by European Centre for Research Training and Development UK (www.eajournals.org) The samples in figure 11 plotted in the calcic class after Peacock (1931 just like



Figure 12: $Na_2O + K_2O$ -CaO versus SiO₂ diagram after Frost et al. (2001) showing the classification of the major rocks into Alkalic, Alkali-calcic, Calcic-alkali and Calcic groups

in Na₂O+K₂O-CaO versus SiO₂ diagram (Figure 12) after Frost, et al., (2001), where the pegmatites plotted in the calcic to calcic-alkali fields and only one of the pegmatite samples plotted in the alkalic field pointing to the fact of mixed sources of materials in the magma that formed the rock.



Figure 13: $(Al_2O_3+CaO)+(Na_2O+K_2O)/(Al_2O_3+CaO)-(Na_2O+K_2O)$ versus SiO₂ (after Wright, 1969)

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A plot of $(Al_2O_3+CaO)+(Na_2O+K_2O)/(Al_2O_3+CaO)-(Na_2O+K_2O)$ versus SiO₂ (after Wright, 1969) reveals that all the pegmatite samples plotted on the peralkaline rocks. Using the aluminum saturation index (ASI) proposed by Zen,(1988), that rocks which have ASI > 1.0are corundum-normative and are termed peraluminous, meaning that they have more Al than can be accommodated in feldspars and that they must have another aluminous phase present. Futhermore, if ASI < 1.0 and Na + K > AI, the rock is peralkaline. In these rocks there are more alkalis than are necessary to produce feldspar, which means that some alkali, particularly Na, must be accommodated in the ferromagnesian silicates. Going by the plots in figures 2,3 and 13 the pegmatite samples are aluminous as well as peralkaline. The diagnostic minerals in strongly peralkaline rocks are the sodic amphiboles and pyroxenes. In strongly peraluminous granites the phase can be muscovite, cordierite, garnet or an Al₂SiO₅ polymorph, but they are commonly taken to have formed from a sedimentary source (Chappell & White, 1974), again strongly peraluminous melts may form by melting of biotite-bearing metaluminous felsic rocks (Miller, 1985) or even by water-excess melting of mafic rocks (Ellis & Thompson, 1986). All these come to indicate that the pegmatite from Ijero may have formed from mixed plutonic sources.

Trace elements composition

Table 3 shows the characteristics of the few trace elements analysed from the pegmatite. Sr ranges between 6 and 150 ppm and is relatively high due to substitution of Sr for Ca in the pegmatite. Ca is strongly depleted. Zr values are between 4 and 274 ppm as Ba ranges from 6 to 562 ppm. The compatible elements ,Ni (7-26.80) and Cr (0.01-57.23) have low concentrations . The low concentrations of these two compatible elements suggest that the materials that formed the pegmatite are derieved from a depleted or metasomatised mantle. K has high concentrations (1465-. 10471) ppm. These high values are obvious due to the presence of K-feldspar.

Ni	-	-	-	-	-	26.80 7.00	0 7.69	7.26	7.13
Ba	510	562	6	180	16	-	-	-	-
Sr	150	147	3	29	8		-	-	-
Y	27	21	2	8	2		-	-	-
Sc	16	3	2	-1	24		-	-	-
Zr	274	117	4	6	7		-	-	-
Be	5	7	3	5	2		-	-	-
V	98	6	-5	-5	-5		-	-	-
Cr	-	-	-	-		57.23 0	.01 1.85	0.01	0.01
Κ	-	-	-	-		10471 5	957 1406	2574	1465
Ca	-	-	-	-	-	0.01 0	.01 0.01	0.01	0.01

 Table 3: Trace elements composition (ppm)

The Ijero-Ekiti pegmatite was formed during the late phase of Pan-African plutonism 600 ± 150 Ma (Rahaman, 1988). This plutonic activities resulted in deformation and creation of fractures in the Basement Complex rocks of Southwest, Nigeria. During this episode, hydrothermal fluids came into contact with the basement complex rocks. The Na and K contents of the fluids caused a change or metasomatism of the host rock leading to the formation of minerals of the

feldspar family namely; orthoclase, $KAlSi_3O_8$ and albite $NaAlSi_3O_8$. Late phase tectonic granite plutons are often marked by minerals with volatile components (OH, F, B) and a wide range of accessory minerals containing rare lithophile elements. (Evan, 1993) The abundance of quartz (SiO₂), potash (K₂O), Soda (Na₂O), alumina (Al₂O₃) and loss on ignition (LOI) give evidence of volatile contents in the pegmatites from Ijero-Ekiti. The pegmatites are source rocks for gemstones, (tournaline, topaz and beryl) industrial and metallic minerals.

CONCLUSION

Geochemical analysis reveals that the pegmatites from Ijero-Ekiti have high SiO₂ content 66-78wt%, low Na₂O/k₂O ratio and are strongly peraluminous and peralkaline. The diagnostic minerals in strongly peralkaline rocks are the sodic amphiboles and pyroxenes. In strongly peraluminous granites the phase can be muscovite, cordierite, garnet or an Al₂SiO₅ polymorph, but they are commonly taken to have formed from a sedimentary source .Strongly peraluminous melts may form by melting of biotite-bearing metaluminous felsic rocks or even by waterexcess melting of mafic rocks. All these come to indicate that the pegmatite from Ijero may have formed from mixed plutonic sources. Low ratio of Na₂O/k₂O with high Al₂O₃ content are consistent with kaolin/feldspar formation as well as tourmaline enrichment in the Ikoro area. The plots of MgO, Fe₂O₃, Na₂O Al₂O₃ and TiO₂ against SiO₂.respectively show negative correlation with SiO₂ but the trends in some of them like MgO, and TiO₂ show that the samples cluster around the silica, SiO₂ an indication of its abundance. The negatively correlated oxides have downward linear trend that suggest non association with SiO₂. The plottings of the pegmatite samples in both the tholeiitic and calc-alkaline fields show that the magma from which the rock was formed was not totally restricted in occurrence only to subduction-related environment but also from the oceanic crust of calc-alkaline environments.

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