



Geochemical Characterization and Economic Potential of Emure and Ijero Ekiti Pegmatites in Southwest Nigeria

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Abstract

Global demand increase for rare metals deposits has re-enacted the search for economically viable deposits. Precambrian pegmatites occurring as near dykes and massive types were studied for Emure-Ekiti and Ijero-Ekiti respectively, with the aim of characterizing them geochemically and determining their possible economic values. A total of twelve samples comprising seven from Emure-Ekiti, three whole rock muscovite extract for Ijero-Ekiti were analysed for major and trace elements using X-ray fluorescence method. Thin sections prepared for the Emure-Ekiti pegmatites show that quartz, microcline are major mineral constituents. The geochemical results reveals that the Emure-Ekiti and the whole rock samples of Ijero-Ekiti are considerably siliceous, with an average value of 68.72% and 68.6% respectively, while the muscovites extracts average 48.86%. Mean values of major oxides for the Emure, Ijero[whole rock, muscovite] are as follows; Al_2O_3 - 20.42%, [13.74%, 35.15%]; Fe_2O_3 - 1.83%, [1.24%, 2.19%]; MgO - 0.013%, [0.029%, 1.04%]; CaO - 0.02%, [0.34%, 2.4%]; Na_2O - 1.01%, [4.40%, 1.045%]; K_2O - 3.17%, [2.77%, 11.07%]. Trace and rare-earth elements result shows that the Emure-Ekiti pegmatites is “barren” – depleted in rare metals Ta, Nb, Cs, Sn, Rb, etc, and compare favourably with Apomu, Ago-Iwoye and Ijebu-Ife barren pegmatites. On the other hand, two of the whole rock samples are mineralized – fairly enriched in rare metals Ta, Nb, Rb while the remaining sample and the muscovite extract are barren; as depicted by the Rb vs Rb plot and when compared to the other rare metal pegmatites across the world.

Keywords: Emure-Ekiti, Ijero-Ekiti, pegmatites, characterization, geochemical, economic value

1. INTRODUCTION

Pegmatites are very coarse-grain igneous or metamorphic rocks, generally of granitic compositions. They are texturally distinct variants of more common and more voluminous plutonic igneous rocks, including gabbrous, syenites e.t.c. Pegmatites bodies vary greatly in size and shape i.e. they occur as segregations within granites and as sharp discordant dikes intruding igneous and metamorphic rocks. Other fabrics include systematic coarsening in crystal size from the margins to the centres of bodies; sharp mineralogical zonations from margin to centre; anisotropic fabrics and graphics intergrowth of quartz and feldspar termed “graphic granite” [1].

Pegmatites fields are widespread in south western Nigeria. The early workers [2, 3], on the pegmatites of south western Nigeria, while working on the Osu and Aramoko pegmatites recognized that the pegmatites of Osu area is emplaced into schistose and gneissic basement units which comprises microcline, sodic feldspar and quartz minerals with an average rock $Na/K=0.77$, while

pegmatites of Aramoko area is closely associated with the granodioritic main phase older granite, steeply tabular pegmatites which are composed mainly of microcline and quartz with an average rock $Na/K=0.16$. In a related study work on pegmatites source rocks related to the Pan-African Orogeny within and around Ijero-Ekiti found out that the degree of specialization of massive Ijero-Ekiti pegmatites are marked by albitization. Also, their work revealed that the Rb and Li concentrations are all within the range of barren pegmatites and other granitoids [4]. In another study [5, 6], studied the geochemical exploration for Sn-Nb-Ta in South western Nigerian, while [3] studied the pegmatites of Pan-African reactivation zones covering areas of Egbe-Ijero and Wamba, and also distinguished mainly between the barren and mineralized pegmatites. In a related study, [7] documented the metallogeny of the Nigeria basement complex rocks including the pegmatites. Similarly, [8] worked on the geochemical exploration guides of rare metal bearing pegmatites with case studies of Ijero and Wamba.

The contributions of [9–15] have also contributed to the better understanding of south western and northern Nigeria pegmatites bodies and concluded that the pegmatites were not confirmed to earlier proposed 400km long NE-SW

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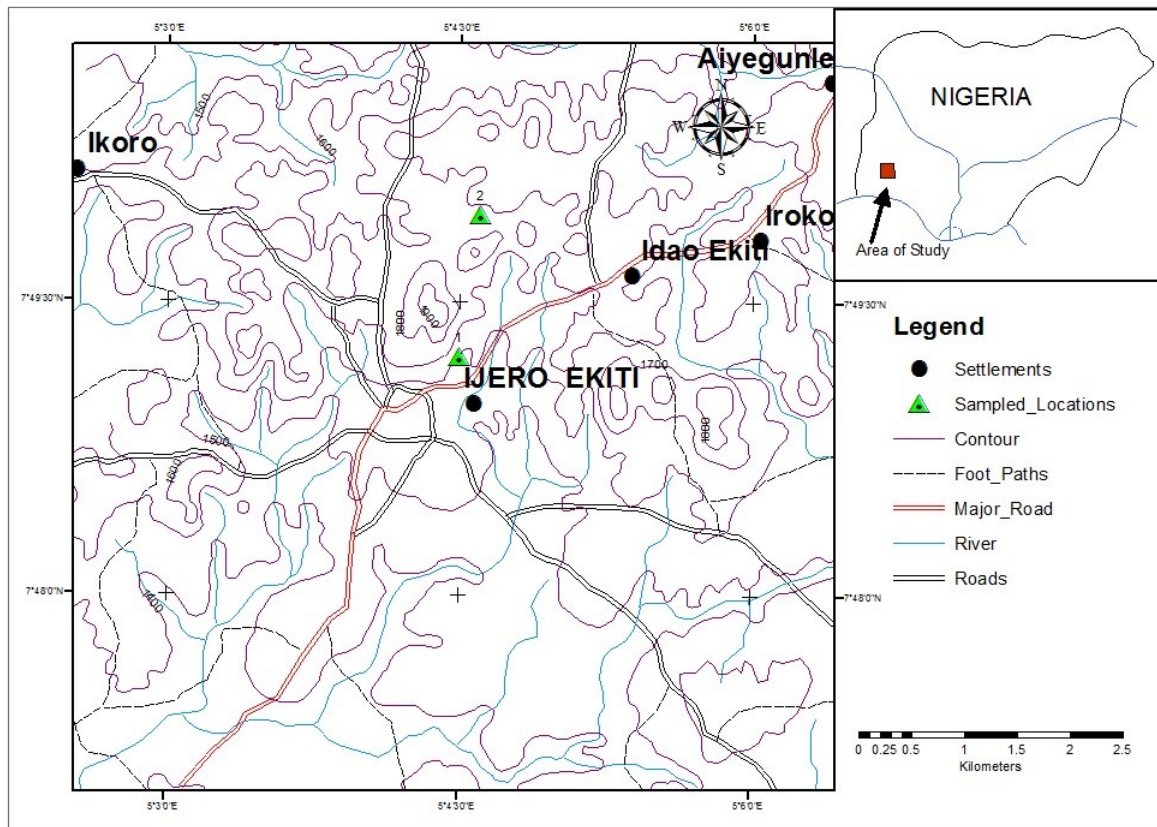


Figure 1: Location map of Ijero-Ekiti and Environs.

rending belt. Furthermore, [16, 17] worked on the pegmatites of Komu in Northern part of Oyo State and reported that these pegmatite which intrude semi discordantly older rock types, such as biotite gneiss, amphibolites, microcline, muscovite with accessories like Tourmaline, Tantalum, Niobium and Illmeno-Rutiles with the trace element analysis shows that the pegmatites contain rare metals with moderately high Ta, Nb, Sn, Rb, Li and Cs values and depleted in Ti, Ba and Zr. The Na/K versus Sn, Nb, Rb variation plots shows that the pegmatites of komu area are mineralized and compared favourably with those of other mineralized pegmatite area like Egbe and Ijero in south western Nigeria. Also, the variation plots of Ta versus K/Cs, and Ta/W versus Cs, also confirmed rare metal mineralization of komu pegmatites, which plot over the mineralized line of Beus and Gordiyenko with the plot of K/Rb versus Rb, Cs and Sn plots indicate low K/Rb ratios indicating moderate differentiation. Recently, [18] studied the geochemical features of the Precambrian Pan-African pegmatites of Ijebu-Ife area in south western Nigeria and concluded that the Ijebu-Ife pegmatites are fairly enriched in Rb, Sr, Zr but comparatively poor in the rare metals Ta, Nb, Cs and Sn. Rare metal mineralization enrichment indices mainly, Ta Vs Nb, Ta Vs K/Cs plots, shows it depletion in rare metal mineralization, suggesting this pegmatites To be barren in rare-metal mineralization when compared with other rare metal pegmatites cross the

world. In the same vein, [19] studied the geochemical and compositional features of Precambrian pegmatites of Ago- Iwoye area- South western Nigeria and reported that though the samples are fairly enriched in Rb, Sr, Zr but are comparatively poor in the rare metals Ta, Nb, W, Cs and Sn; with the rare metal mineralization enrichment indices show its depletion in rare metal mineralization suggesting Ago-Iwoye Pegmatites to be barren in rare metal mineralization when compared with other rare metal pegmatites across the world. This study seeks to carry out a comprehensive geochemical study of the Pegmatite bodies in Emure Ekiti area and also to determine the mineralogy of the pegmatites using both visual and instrumental observations and to compare the mineralogy and geochemistry of the pegmatites and with those of the other parts of Nigeria and the world.

2. LOCATION AND ACCESSIBILITY

Ijero-Ekiti (Fig. 1) the second area of study lies between latitudes $7^{\circ}47'N$ and $7^{\circ}51'N$ and longitudes $5^{\circ}02'E$ and $5^{\circ}05'E$ on sheet 244 of the Federal Survey Sheet. It has a total area cover of about 170 Km. other towns around the area include Ikoro-Ekiti, Ara, Ido, Epe, Ayegunle, Ijuri, Ipoti and Iloro. While on the other hand; Emure Ekiti (Fig. 2) is a town located in the eastern part of Ekiti state. It is situated about 50km southwest of Ikere-Ekiti and it is one of the towns that constitute Emure local government area of

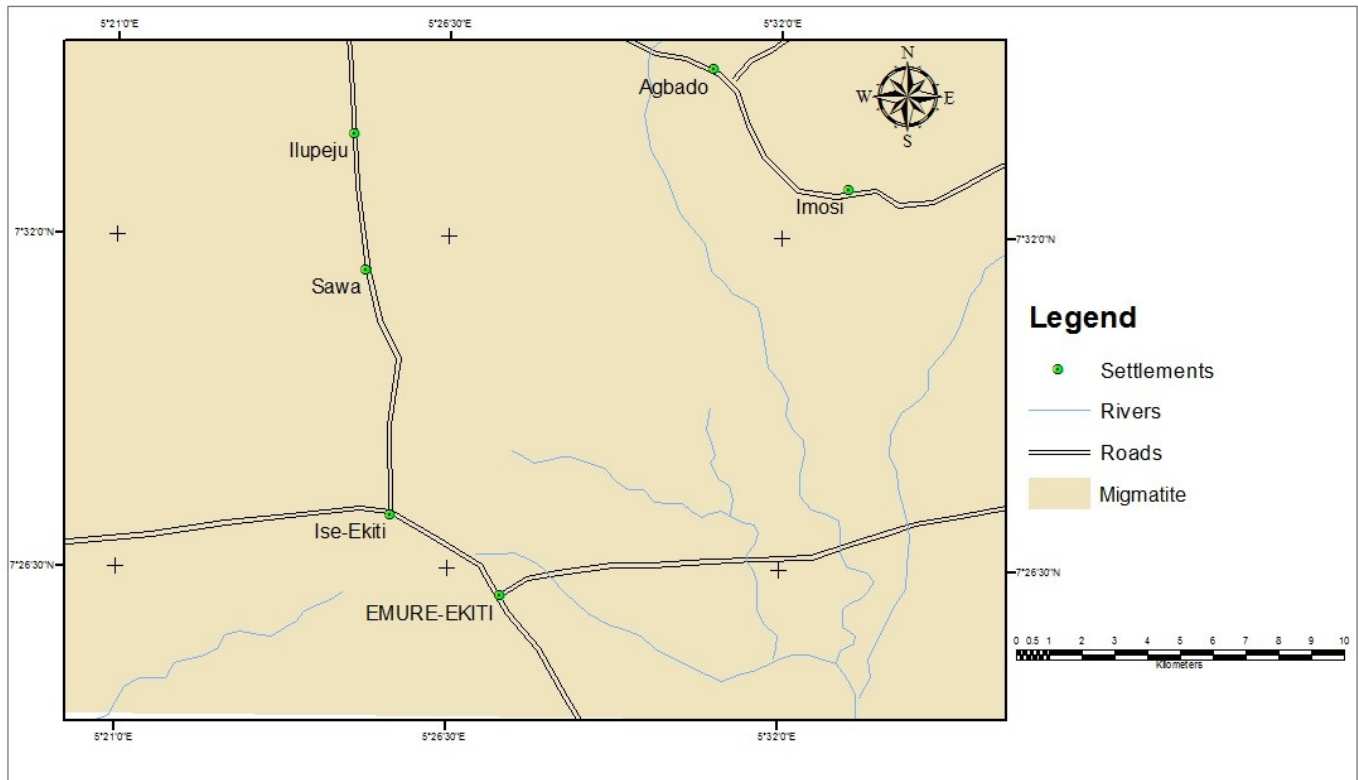


Figure 2: Location map of Emure–Ekiti and Environs.

Ekiti State. The study area is a part of the town that is situated between latitudes $70^{\circ}25'10''$ and $70^{\circ}25'30''$ and longitudes $50^{\circ}26'35''$ and $50^{\circ}25'40''$ and is easily accessible through the major, minor roads and footpaths.

3. METHODS

This research involved detailed mapping and sampling of the pegmatite bodies with accurate locations of each sampled points made by using the GPS. Single bead low-dilution fusion technique was adopted for the XRF analysis. The fresh chips of the sample are hand-picked and a standard volume of chips (approximately 28 g) is ground in a swing mill with tungsten carbide surfaces for 2 minutes. Three and a half grams (3.5 g) of the sample powder is weighed into a plastic mixing jar with 7.0 g of spec pure dilithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) and assisted by an enclosed plastic ball, mixed for ten minutes. The mixed powders are emptied into graphite crucibles with internal measurements of 34.9 mm diameter by 31.8 mm deep. Twenty four (24) filled crucibles are placed on a silica tray and loaded into a muffle furnace only large enough to contain the tray. Fusion takes 5 minutes from the time the preheated furnace returns to its normal 1000°C after loading. The silica plate and graphite crucibles are then removed from the oven and allowed to cool. Each bead is reground in the swing mill for 35 seconds, the glass powder then replaced in the graphite crucibles and refused for 5 minutes.

Following the second fusion, the cooled beads are labeled with an engraver, their lower flat surface is ground on 600 silicon carbide grit, finished briefly on a glass plate (600 grit with alcohol) to remove any metal from the grinding wheel, washed in an ultrasonic cleaner, rinsed in alcohol and wiped dry. The glass beads are then ready to be loaded into the XRF spectrometer. Preparation of a single bead takes, on average, 45 minutes.

4. RESULTS

This sub-section focuses on the sequential presentation of the geochemical analysis of the pegmatite in the study area for both major metallic oxides in percentages and the trace and rare earth metals in ppm see in Tables 1 and 2 and also a comparison of the geochemistry of the pegmatites in Emure and Ijero-Ekiti samples with selected pegmatites samples from other parts of Nigeria and the world presented in Table 3.

The weight percentage result of the samples, show that the Emure pegmatite is highly siliceous and aluminous with 65.80% – 72.76% for SiO_2 and 18.99% – 22.32% for Al_2O_3 wt %. The data also show that potash, K_2O ranges between 2.90 – 3.40 wt %, while Soda, Na_2O and quicklime, CaO ranges between 0.75 – 1.30 wt % and 0.02 – 0.04 wt % respectively. The high ratio of $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO}$ is the various samples imply that the pegmatite is peraluminous while the high ratio of $\text{K}_2\text{O}/\text{Na}_2\text{O} + \text{CaO}$ implies a pegmatite rich in orthoclase a potassium feldspar.

Table 1: Major and Trace elements Composition of Emure-Ekiti Pegmatites.

S/N	Elements %	Em ₁	Em ₂	Em ₃	Em ₄	Em ₅	Em ₆	Em ₇
1	SiO ₂	70.78	65.60	72.76	66.54	67.67	71.78	65.68
2	Al ₂ O ₂	19.01	22.10	20.14	19.10	21.09	18.99	22.32
3	Fe ₂ O ₂	1.85	1.33	2.97	1.90	1.38	1.99	1.40
4	MgO	0.03	ND	0.01	0.02	ND	ND	0.03
5	CaO	0.02	0.03	0.03	ND	0.02	ND	0.04
6	Na ₂ O	1.30	1.09	1.04	0.99	0.99	0.75	0.98
7	R ₂ O	3.33	3.09	2.97	3.00	3.00	3.40	2.90
8	MnO	0.08	0.06	0.02	0.07	0.06	0.09	0.08
9	TiO	0.25	0.09	0.10	0.23	0.11	0.33	0.08
10	P ₂ Os	ND	ND	ND	ND	ND	ND	ND
Values in ppm								
11	Cr	60	200	600	ND	ND	60	ND
12	V	100	60	56	170	60	110	ND
13	Ti	5700	ND	80	10600	80	2900	700
14	Ba	5200	4700	80	4900	4200	5200	4600
15	Nd	1200	400	5200	1500	600	1600	500
16	Sm	600	1300	1100	900	1500	800	1030
17	Bi	9	360	360	180	700	90	700
18	Y	160	80	200	80	0.0	200	80
19	Co	80	300	240	80	240	160	80
20	Rb	92	71	96	111	88	96	24
21	Zr	26	ND	27	ND	90	19	ND
22	U	140	ND	90	ND	ND	50	140

Em₂ – Em₂ = Samples from Emure – Ekiti pegmatite

Table 2: Major and trace elements composition of Ijero-Ekiti Pegmatites.

S/N	Elements %	Whole Rock			Muscovite	
		J ₁	J ₂	J ₃	J ₄	J ₅
1	SiO ₂	71.00	68.20	66.6	44.05	43.66
2	Al ₂ O ₂	14.40	14.22	12.60	35.92	34.37
3	Fe ₂ O ₂	0.91	1.12	1.7	1.72	2.66
4	MgO	0.20	0.19	0.46	0.90	1.18
5	CaO	0.46	0.44	0.12	1.89	2.86
6	Na ₂ O	4.28	6.45	2.45	1.87	1.22
7	K ₂ O	1.82	1.69	4.80	8.72	8.99
8	MnO	0.08	0.09	0.07	0.07	0.05
9	TiO	0.05	0.18	0.05	0.08	0.07
10	P ₂ Os	0.04	0.03	0.01	0.07	0.02
Values in ppm						
11	V	100	60	ND	60	60
12	Cr	ND	70	ND	ND	70
13	Ba	80	40	30	90	90
14	Ta	77	74	60	40	40
15	Nb	108	79	74	47	67
16	Sn	28	21	52	61	70
17	Rb	345	640	460	180	300
18	Y	80	ND	80	160	80
19	U	46	47	60	110	102
20	Zr	47	45	57	60	60
21	Sr	40	47	46	45	45

J₁ – J₃ = whole rock crushed samplesJ₄ – J₅ = crushed samples from Muscovite mineral only

Table 3: Comparison of chemical composition of Emure and Ijero-Ekiti pegmatites with some selected pegmatites from other parts of Nigeria and the World.

S/N	Elements %	A	B	C	D	E	F	G	
1	SiO ₂	65.90	69.31	73.74	60.35	46.65	68.72	68.60	
2	Al ₂ O ₃	7.71	14.34	14.68	19.80	36.83	20.42	13.7	
3	Fe ₂ O ₃	19.28	2.61	1.49	3.43	1.34	1.83	1.27	
4	MgO	0.049	0.78	0.18	0.26	0.21	0.013	0.28	
5	CaO	0.3	1.63	0.78	0.02	0.05	0.02	0.9	
6	Na ₂ O	1.89	3.31	4.46	0.70	0.82	1.83	1.27	
7	K ₂ O	1.86	4.80	3.52	10.33	9.49	3.17	3.39	
8	TiO ₂	2.77	0.18	0.08	0.2	0.2	0.17	0.09	
9	MnO	0.056	0.05	0.4	0.16		0.06		
10	P ₂ O ₅	0.12	0.08	0.202	0.11				
		Values in ppm							
11	Be	16.9	2.73	4.5	21.00	21.00			
12	Co	1.69			1.00	1.00			
13	Cs	9.01	5.07	4.57	195.00	195.00			
14	Ga	16.20	19.01	19.01	283.00	283.00			
15	Hf	13.00	2.25	3.82					
16	Nb	50.60	9.46	21.88	381.00	358.00		87.00	
17	Rb	183.99	212.96	106.85	1000.00	1479.00	83.00	482.00	
18	Sn	15.50		3.90	78.00	2.31		34	
19	Sr	63.18	198.15	89.43	7.00	21.00	26.00	44.00	
20	Ta	8.64	1.35	6.54	76.20			70.00	
21	Th	5.26	9.50	2.98	0.20				
22	W	1.15		1.56	14.00	102.00			
23	Zr	440.39	68.61	102.66	3.00	10.00	23.00	50.00	
24	K/Rb	183.92	187.11	273.48	85.75	53.00	317.05	56.43	
25	Na/k	0.91	0.61	1.13	0.06	0.07	0.08	1.92	

A - Ijebu Ife Pegmatite = Barren (2012); B - Apomu (2012) = Barren; C - Ago Iwoye (2011) = Barren; D - Komu = Mineralized; E - Cape de creus, Catalonia Spain = Mineralized; F - Emure Ekiti and G - Ijero Ekiti.

The weight percentage show that the whole rock samples J₁ – J₃ is more siliceous with 66.6-71.00 wt % then the muscovite samples J₄ - J₅ with 43.66-44.05 wt % and also contain lower alumina 12.60-14.40 wt % compared with the muscovite samples 34.37-35.92 wt %. This reflects the differences in the mineralogy of the samples. The high ratio of Al₂O₃/Na₂O + K₂O+CaO in the samples indicate peraluminous pegmatites with a probably plagioclase Na-Ca feldspar mineralogy for the whole rock samples.

The result shows the comparison of the Emure and Ijero-Ekiti whole rock with the other highly siliceous and aluminous pegmatites in Nigeria and other parts of the world. The trace of Sn-Ta elements in Ijero-pegmatites; which were not detected in the Emure-Ekiti show that the Ijero pegmatites samples are more mineralized than the Emure pegmatites.

5. DISCUSSION

The analytical results presented in Table 1 show that the Emure pegmatites are highly siliceous; ranging from 65.68% – 72.76% with an average value of 68.72%. While on the other hand the Ijero pegmatites as seen in Table 2, ranges from 66.6% – 71.00% for whole rock and 43.66% – 44.05% for the muscovite samples. This high silica content in the Emure-Ekiti pegmatites are comparable with the ‘barren’ Ijebu-Ife pegmatites. Al₂O₃ ranges from 18.99% – 22.32% with an average value of 20.42% for Emure-Ekiti pegmatites and 12.6% – 14.40%, 34.37 – 35.92% for

the Ijero-Ekiti whole rock and muscovites respectively. Mean values for the major oxides are; K₂O 3.17%, 6.09% for Emure and Ijero-Ekiti, respectively. Also, average values for CaO 0.02%, 1.15%, Fe₂O₃ 1.83%, 1.16%, TiO₂ 0.17%, 0.086%, MgO 0.013%, 0.58%, Na₂O 1.01%, 3.06% for Emure and Ijero-Ekiti pegmatites respectively. Statistical summary for trace and rare elements (Tables 1 and 2) shows some of the following averages values Ta 70 ppm, 40 ppm, Nb 87 ppm, 57 ppm, Sn 34 ppm, 66 ppm respectively for the Ijero-Ekiti pegmatites whole rocks and the muscovite samples respectively. While the averages for Emure-Ekiti pegmatites for both trace and rare elements are Ba 146 ppm, 90 ppm, Rb 482 ppm, 240 ppm, Y 53 ppm, 120 ppm, Zr 50 ppm, 60 ppm, Li 51 ppm, 106 ppm respectively. The remaining trace elements and rare earth elements have relatively high values and are exclusive to the Emure-Ekiti pegmatites.

The results from Table 3 indicates the SiO₂ (%) of Ijebu Ife, Apomu and Ago-Iwoye, Emure-Ekiti and Ijero-Ekiti are approximately the same at (65.9, 69.3 and 73.7%) respectively with Cape de creus with concentration of SiO₂ been 46.65%. The case is however different for Al₂O₃ concentration of the pegmatite. Cape de creus has the highest concentration of the metallic oxide at 36.8% while Ijebu has the least concentration at 13.7% Al₂O₃. The Concentration K₂O for Komu and Cape de creus concentrations at (10.3 and 9.5)% respectively and only 1.86% concentration

at Ifebu-Ife as the least concentration. For the trace and rare metals, Komu and Cape de creus have Nb has peak concentration of about 360 ppm and 340 ppm respectively. While the others is insignificantly low with concentration less than 50 ppm except for the Nb concentration at Ijero Ekiti which is 87.0 ppm. Komu has the high Ta Concentration at 77 ppm, closely followed by Ijero-Ekiti with 70 ppm Ta concentration, with Ta being near 0 ppm at the other locations.

Chemical characterisation of the Emure-Ekiti and Ijero-Ekiti Pegmatites from Tables 2, Ijero Ekiti (whole rock) indicates that K/Rb ratio of the sample is very low (in the rare class zone) thereby indicating progressive fractionation and possible mineralization. The other samples of the whole rock from Ijero have values that are consistent with the barren zone while the muscovite extracts are mineralized [3].

The Zr/SiO₂ ratio (Table 3) is a geochemical variation used for determining or characterizing sample as magmatic or after magmatic. The values reveal that Emure-Ekiti Pegmatites are completely magmatic suggesting pegmatites to be genetically magmatic [7]. The Ijero-Ekiti sample also reveals magmatic field except the muscovite sample which have values that are consistent with the "AM" after magmatic field which connotes that the samples have been subjected in post magmatic alteration. The geochemical characterisations of the Pegmatites are determined using various geochemical variation ratios. The ratio, K/Rb vs Rb, Zr vs SiO₂, and K/Rb vs Rb were used as indices. This ratio is a geochemical variation for determining the degree of fractionation in pegmatite and then very useful tool for economic evaluation and chemical characterization of pegmatites for rare metals. In another study, they opined that extreme fractionation of lithophile elements such as Rb and Cs is a common geochemical feature of granitic pegmatites, especially the rare metal bearing types. Hence, late state progressive fractionation crystallization leads to decrease in K : Rb ratio, this suggesting metasomatism and invariably mineralization [11].

6. CONCLUSION

In the light of the analyses, results and interpretation given so far, this research work can be said to have achieved its aim and objectives: to carry out a comprehensive geochemical study of the Ekiti and Ijero-Ekiti Pegmatite and to compare the mineralogy and geochemistry of the pegmatites with those of the other parts of Nigeria and the world. The geochemical study carried out on these pegmatites revealed the Emure-Ekiti pegmatites belongs to the magmatics field and are "barren" - poorly fractionated and mineralized, as the rare metals indicative elements Ta, Nb, Rb, Cs and Sn are either absent or very low in values. This Emure-Ekiti pegmatites also compare favourably with other barren pegmatites bodies in South-western Nigeria like the Apomu, Ago-Iwoye and Ijebu-Ife pegmatites and other part

of the world. Studied from the Ijero-Ekiti pegmatites on the other hand, showed that two of the whole rock samples were plotted in the mineralized zone-highly differentiated, but the other whole rock sample and the muscovite samples plot in the "barren" zone, this may result as either low degree of fractionation of the samples. The depletion in Sr, Zr and Ba coupled with fairly enrichment in Nb, Ta in the Ijero-sample whole rock are comparably to some of the "rare metal" bearing pegmatites in the south western Nigeria e.g. Egbe, Komu and others from the Northern part of the country and the world. Rb, Sn, Li values of the Ijero pegmatites are fairly high but not up to the concentration level of most mineralized pegmatites.

Given the increase in demand for rare earth mineral globally, this research work serves as the quest for detecting and discovering more explored pegmatite bodies in Nigeria, its geochemical characterization and economical evaluation for its rare metal potentials.

7. RECOMMENDATION

From the result of the analysis, their seems to be high concentration values for some rare earth elements in the likes of Ti, Nd and Sm, with this, irrespective of whether the pegmatite is barren or mineralized, these rare earth elements can be of great economics potential as the advancement in technology highly demand these elements e.g. Sm - Nd as component of aerospace magnet and communication devices. A more thorough investigation is needed in the search and probably any exploration potentials of these rare earth elements in the area.

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