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Mineralogy and Rare Earth Elements Concentration in Granites around Ilaji-Ile, Southwestern Nigeria

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ABSTRACT **Technological advancement has led to an increase in exploration for Rare Earth Elements (REE) to meet the increasing demand. REE mineralization in Nigeria is largely undefined and there is paucity of data on possible REE bearing rocks, their concentration and distribution. This study was carried out to determine REE concentration and distribution in porphyritic granites around Ilaji-Ile, southwestern Nigeria. Samples of porphyritic granites were subjected to mineralogical characterization using petrography and Scanning Electron Microscope (SEM) while geochemical characterization was carried out using Inductively Couple Plasma Mass Spectrometry (ICPMS). Mineralogical characterization revealed major minerals present are feldspars of albite to andesine composition, quartz, biotite while accessory minerals are titanite, zircon and garnet. ICPMS result revealed La, Ce, Pr and Nd ranged 4-284 ppm, 7 – 610 ppm, 1 – 71 ppm and 4 – 255ppm respectively. ∑REE ranged 160 – 422ppm, with enrichment in Low Rare Earth Elements (LREE) relative to High Rare Earth Elements (HREE) ({La/Yb}N = 9.37-12.45), a weak to strong negative Eu anomaly (0.17-0.59) indicative of removal of plagioclase from the melt during fractional crystallisation and or the presence of plagioclase as a major fractionating phase. REE composition in the granitoids may be lower than the required concentration required for REE exploitation.**

Keywords: Accessory minerals, Europium anomaly, Mineralogy, Mineralization, Rare Earth Elements, Zircon

Introduction

Over the past 3 decades, technological and industrial advancement has led to an increase in the demand for Rare Earth Elements (REE) and their minerals due to their numerous applications. REE have found application in the production of environmental and military appliances, wind turbines, lasers, screens, superconductors, mobile phones, high strength magnets etc (Long et al, 2010).

REE are usually divided into Light Rare Earth Elements (LREE) characterized by lower atomic weight and elements from lanthanum to europium while Heavy Rare Earth Elements (HREE) includes elements from gadolinium to lutetium. REE are common in silicate minerals, phosphates, oxides, fluorocarbonates and they also occur in trace amounts in ferromagnesian minerals such as biotite and amphiboles.

Over the last decades, as the demand for REE and their minerals increased, there has been an increase in the price of these minerals and this has led to increase in exploration for the elements and minerals which contain them in abundance. REE occur in varieties of minerals as major or minor constituents and they are common in economic proportion in alkaline igneous rocks, placer deposits rich in monazite, ion adsorption clay deposits and carbonitites.

REE partition preferentially into certain minerals and partitioning into minerals such as monazite, apatite, zircon and plagioclase is influenced by substitution of trivalent REE for other cations. The trivalent REE show significant substitution for Ca^{2+}, Y^{3+}, Mn^{2+}, Th^{4+} and Zr^{4+} and this significantly affects REE composition in minerals (Henderson, 1984; Boynton, 1989; Rollinson, 1993; Randive, 2012). During melting or fractional crystallization of rocks, minute concentration of certain small accessory minerals may affect REE availability and enrichment (Rollinson, 1993). For example, apatite preferentially concentrates LREE while garnet preferentially substitutes HREE in their crystal structures.

The study was carried out to determine the mineralogy, trace elemental concentration and REE mineralization potential of granites around Ilaji-Ile, southwestern Nigeria to provide information for mineralization.

Materials and methods

Representative rock samples were collected; thin sections were made and viewed with the use of a petrological microscope at the Department of Earth Sciences, OlabisiOnabanjo University. Polished sections were prepared and analysed with a JEOL JSM6610 Scanning Electron Microscope (SEM) equipped with a Thermo Fisher Ultra dry Energy Dispersive Spectrometry (EDS) detector. Analysis of the polished sections was carried out at the Department of Geology, University of Free State, South Africa. 11 samples of porphyritic granite were analysed for their trace and rare elemental concentrations at the Bureau Veritas Minerals (BVM) Laboratories using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analytical method.

Results and discussion

Field occurrence and mineralogy

The study area falls within the Iseyin-Oyan River Schist Belt, and lithologies in the areas include migmatite gneisses, granite gneisses, metasedimentary rocks and amphibolites as well as porphyritic granites, granodiorite, leucogranite and biotite granites. Porphyritic granites occur in different shapes and sizes ranging from massive to low lying outcrops of porphyritic granite with well-developed crystals of orthoclase in a groundmass which contains quartz, feldspars, muscovite and low percentage of biotite (Figure 1a and b). In thin section, plagioclase feldspar appears as euhedral to subhedral grains with polysynthetic twinning and low relief; biotite occurs as brown to black, elongated pleochroic crystals with low to moderate relief; quartz is colourless to white, purple, yellow, brown, pink and blue while cross hatched microcline is anhedral and forms the majority of the phenocrysts. Petrographic study of the polished section revealed potassium feldspar, plagioclase feldspar, garnet, zircon, titanite, quartz and biotite are minerals present in the granites (Figure 1 c and d).

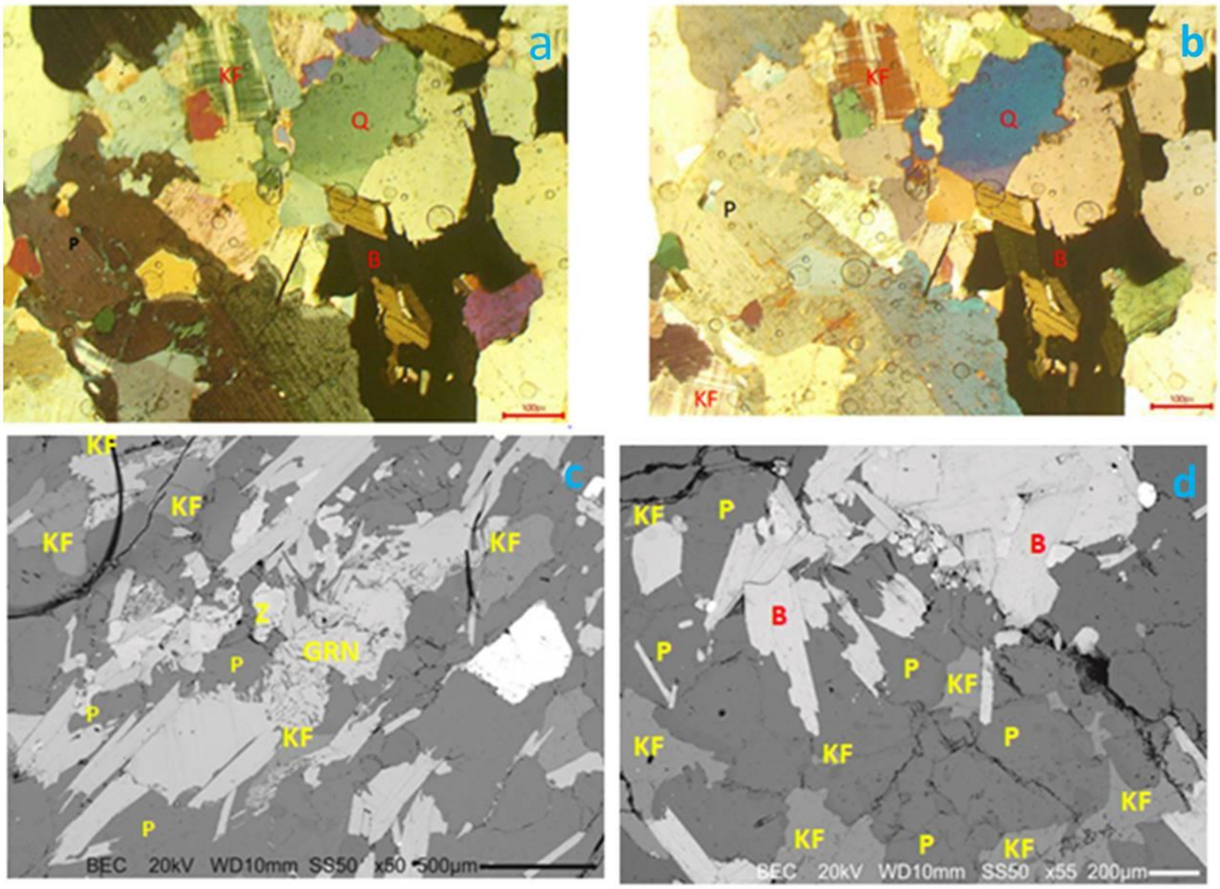

Figure 1: (a and b): Photomicrograph of a section of granite under transmitted light showing large polysynthetic twinned microcline around a central quartz (c and d) Backscatter electron image of a section of porphyritic granite showing plagioclase feldspar, alkali feldspar, titanite, biotite and quartz (P – Plagioclase feldspar, KF – Potassium feldspar, T –B – Biotite, Q – Quartz, GRN – Garnet, Z – Zircon, Mu- microcline)

SEM-EDS results indicate feldspar composition (%) varies as follows: 62.92 – 69.45, 17.08 – 21.38, 1.85 – 4.88, 0.53 – 11.04 and 0.9 - 18.79 for SiO_2, Al_2O_3, CaO, Na_2O and K_2O respectively while mean concentrations (%) are 64.93, 19.28, 3.09, 6.35, 15.34 for SiO_2, Al_2O_3, CaO, Na_2O and K_2O respectively (Table 1).

Major oxide composition was used to calculate the feldspar composition which revealed albite composition varies from 0.00 – 91.52, anorthite composition varies from 0.00 – 16.98 and orthoclase composition varies from 0.00 – 100.00 (Table 2). The porphyritic granitic rock around Ilaji-Ile, this result shows types of feldspar composition which varies as follows: anorthite composition ranges from 0.00 – 16.98, albite composition ranges from 0.00 – 91.52, orthoclase composition ranges from 0.00 – 100.00 and mean values are 7.26, 45.44 and 47.30 for anorthite, albite andorthoclase respectively. AbAnOr ternary diagrams revealed plagioclase composition in the porphyritic granite varies from albite to andesine (Figure 2).

Table 1: Representative elemental composition of feldspars in granite around Ilaji-Ile

	1	2	3	4	5	6	7	8	9	10	11	12	13	Range
SiO_2	65.82	66.14	63.99	63.64	66.38	65.9	64.64	63.94	64.28	63.32	63.71	63.53	65.75	62.92 – 69.45
Al_2O_3	20.83	20.36	17.94	18.06	20.85	21.38	17.95	17.08	17.38	18.08	17.76	17.82	20.92	17.08 – 21.38
CaO	3.38	3.21	-	-	2.61	2.83	-	-	-	-	-	-	3.18	1.85 – 4.88
Na_2O	9.98	10.28	0.63	0.94	10.17	9.89		0.92		0.9	0.67	1.06	10.15	0.53 – 11.04
K_2O	-	-	17.45	17.36	-	-	17.41	18.06	18.34	17.7	17.86	17.6	-	0.39 – 18.79
Si	11.59	11.65	11.94	11.89	11.65	11.57	12.02	12	12.03	11.87	11.93	11.9	11.58	5.79 – 12.07
Ti	0	0	0	0	0	0	0	0	0	0	0	0	0	0.00 – 0.00
Al	4.32	4.23	3.94	3.98	4.31	4.42	3.93	3.78	3.83	3.99	3.92	3.93	4.34	2.88 – 4.45
Fe(II)	0	0	0	0	0	0	0	0	0	0	0	0	0	0.00 – 0.00
Ca	0.64	0.61	0	0	0.49	0.53	0	0	0	0	0	0	0.6	0.00 – 0.71
Na	3.41	3.51	0.23	0.34	3.46	3.37	0	0.33	0	0.33	0.24	0.38	3.47	0.00 – 7.15
K	0	0	4.15	4.14	0	0	4.13	4.32	4.38	4.23	4.27	4.21	0	0.00 – 4.59
An	15.76	14.72	0	0	12.42	13.65	0	0	0	0	0	0	14.76	0.00 – 16.98
Ab	84.24	85.28	5.2	7.6	87.58	86.35	0	7.19	0	7.17	5.39	8.39	85.24	0.00 – 91.52
Or	0	0	94.8	92.4	0	0	100	92.81	100	92.83	94.61	91.61	0	0.00 – 100.00

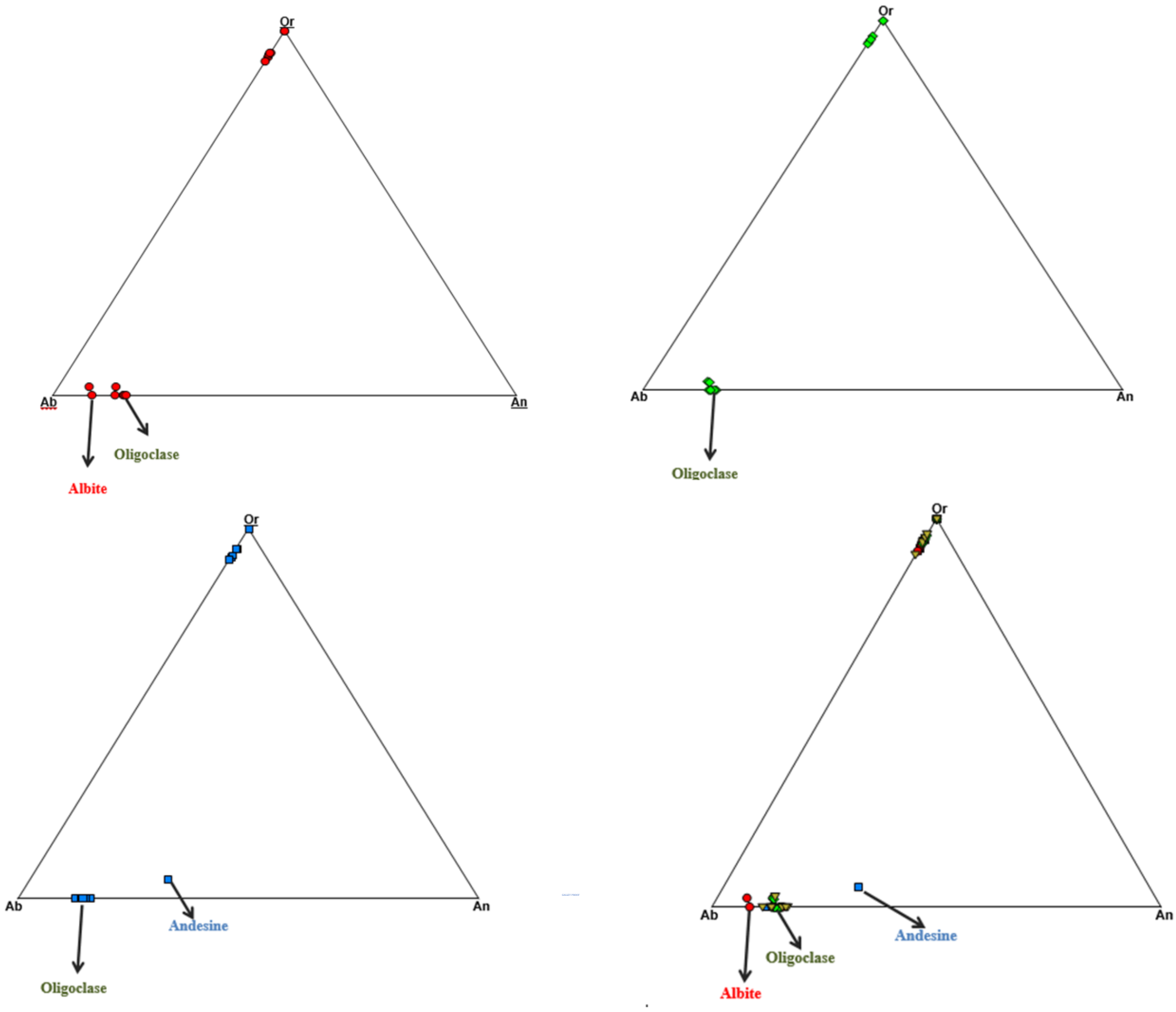

Figure 2: Ternary diagram showing composition of feldspar in porphyritic granite of Ilaji-Ile;Plagioclase feldspar: plagioclase composition is mainly oligoclase, $Ab_{85-91}An_{9-15}$ and potassium feldspar comprising mostly microcline and orthoclase.

Geochemistry

Trace element composition can be used to delineate the degree of magma differentiation as the trace elemental concentration in igneous rocks is a reflection of magma source, extent of partial melting and processes involved in magma evolution (Hollings and Wyman, 2005).

Geochemical analysis results mean concentration (ppm) of Ni, Th, U, Cr, Zr, Y, Hf, Ta and Nb are 55, 40, 6, 79, 120, 34, 4, 13 and 42 respectively (Table 2). Tectonic discrimination diagram of Pearce, (1984) revealed the granites were emplaced in a within plate granite/volcanic arc granite (WPG/VAG) setting (Figure 3a and b). Rb varies from 122-309ppm with an average of 183ppm in the granites which signifies low level enrichment as the values are above the values of 150ppm quoted by Taylor, (1965) for granites suggesting the rocks either represent late stage differentiates of granitic melts or derived from small degrees of partial melting of the source material. Sr concentration varies from 35- 285ppm with mean value of 127ppm, values which also exceed the average content of 100ppm for granites (Wright, 1971); with variation in Sr content due to crustal contamination. van Breemen et al., (1977) reported Rb/Sr values of 0.8-2.0 for Pan African granites from north-central Nigeria and Rb/Sr values ranged 0.8-8.8 in this study, and samples with higher Rb/Sr values are characterized by depletion in Sr. Concentration and variation in Sr is related to progressive differentiation and depletion of the melt in Sr due to the early crystallisation of Sr in K rich minerals. Ba/Sr ranges from 2-6.

There is no consistent trend for individual Th and U concentrations but average Th/U varies 1.52- 8.59ppm with an outlier with Th/U value of 33 observed in a sample with anomalous Th concentration of 159ppm. Th/U ratio generally decrease with fractionation (e.g.

Rogers and Ragland, 1961; Heier and Rogers, 1963) due to the oxidation of U. Strongly fractionated rocks are characterized by Low Th/U values which are typical of rocks formed under non-oxidizing conditions or fractionated rocks in which the vapor phase is incorporated upon crystallisation (Heier and Brooks 1966). Th/U values in the granites indicate low level of fractionation.

Table 2: Trace and rare earth elemental concentrations (in ppm) of Ilaji-Ile granites

	1	2	3	4	5	6	7	8	9	10	11
Mo	0.63	0.19	0.95	0.28	0.81	0.05	2.01	1.32	0.36	20.62	0.66
Cu	17.4	3.1	17.4	3.9	4.6	2.8	12.6	24.6	16.2	4.5	3.9
Pb	18.87	28.83	22.5	38.71	19.15	60.16	19.36	26.08	51.83	22.96	32.11
Zn	78.5	7.9	90.9	48.7	111.5	59.4	119.9	222.7	29.3	85.6	52.1
Ag	31	<20	32	86	29	61	160	260	55	20	61
Ni	322.9	1.7	266.7	1.8	1.3	0.7	1.2	3.3	1	1.3	0.5
Co	25.5	0.3	24.3	2.3	3.9	1	4.9	6.8	1.7	3.6	2
As	1	1	0.9	<0.2	2.4	<0.2	1.2	<0.2	0.7	1	0.6
U	2.7	1.6	4.7	3.2	7.3	15.9	7.9	4.9	4	8.3	3.7
Th	5.7	2.5	25	27.5	40.7	42	50	159.4	18.3	31.7	32.2
Zr	37	3	53.8	89.7	198.1	95	221.7	209.7	95.6	177.3	137.5
V	40	2	44	12	9	2	12	30	4	8	2
Cr	451	5	378	4	4	4	5	14	1	2	1
Ti	0.185	0.008	0.206	0.129	0.356	0.055	0.431	0.564	0.1	0.304	0.086
Cs	8.9	35	8.1	2.1	4.4	1.3	6.5	2.3	2.2	5.5	1.5
Ga	20.02	25.92	19.7	25.07	30.07	35.47	30.43	40.35	23.87	24.66	24.65
Sr	72	35	85	167	144	88	171	151	235	137	113
Rb	129.7	309.4	121.5	194.9	153	293.4	143.2	174.5	194	150.4	154
Rb/Sr	1.8	8.8	1.4	1.2	1.1	3.3	0.8	1.2	0.8	1.1	1.4
Pb/Sr	0.3	0.8	0.3	0.2	0.1	0.7	0.1	0.2	0.2	0.2	0.3
Nb/Ta	1.66	0.98	0.83	7.22	11.3	42.08	12.97	24.7	6.1	12.17	19.31

La	18.8	4.6	54.1	63.1	81	30	62.7	283.9	38.2	85.7	60.9
Ce	32.99	6.54	108.84	111.58	169.24	71.01	188.26	610.33	72.86	165.03	108.7
Pr	4	1	13.7	13.8	20	8.2	15.9	71.3	8	18.8	12.1
Nd	15.2	3.8	49.6	49.2	74.6	30.2	57	255.2	27.6	66.5	40.3
Sm	3.2	1	10.5	9.7	17.5	8.3	14.6	49.7	4.4	12.3	6.4
Eu	0.6	0.2	0.6	1	2.6	0.5	2.3	2.3	0.9	2.1	0.9
Gd	2.9	1	8.6	6.8	14.7	6	12.7	29.9	3	10.8	4.5
Tb	0.4	0.2	1	1.2	2.7	0.7	2.4	4.1	0.3	1.7	0.5
Dy	2.6	0.9	5.9	6.1	15.2	3.1	15.2	17.3	2.3	10.4	2.6
Ho	0.5	0.09	0.8	0.9	3.3	0.4	2.8	2.1	0.3	2.2	0.4
Er	1.7	0.3	2.4	2	10	0.9	8.7	5.4	0.8	6.4	1
Tm	0.2	0.09	0.4	0.2	1.4	0.09	1.2	0.5	0.09	1	0.1
Yb	1.6	0.3	2.6	1.5	8.9	0.6	8.5	3.7	0.7	6.4	0.7
Lu	0.3	0.09	0.4	0.2	1.3	0.09	1.1	0.3	0.09	1	0.09
Eu/Eu*	0.59	0.61	0.19	0.36	0.48	0.21	0.51	0.17	0.72	0.55	0.49
(La/Sm)N	3.22	2.52	2.83	3.57	2.54	1.98	2.36	3.13	4.76	3.82	5.22
(La/Yb)N	7.12	9.29	12.61	25.49	5.52	30.3	4.47	46.5	33.07	8.12	52.73
(Tb/Yb)N	1.06	2.84	1.64	3.4	1.29	4.96	1.2	4.72	1.82	1.13	3.04
TotREE	85	20	259	267	422	160	393	1336	160	390	239

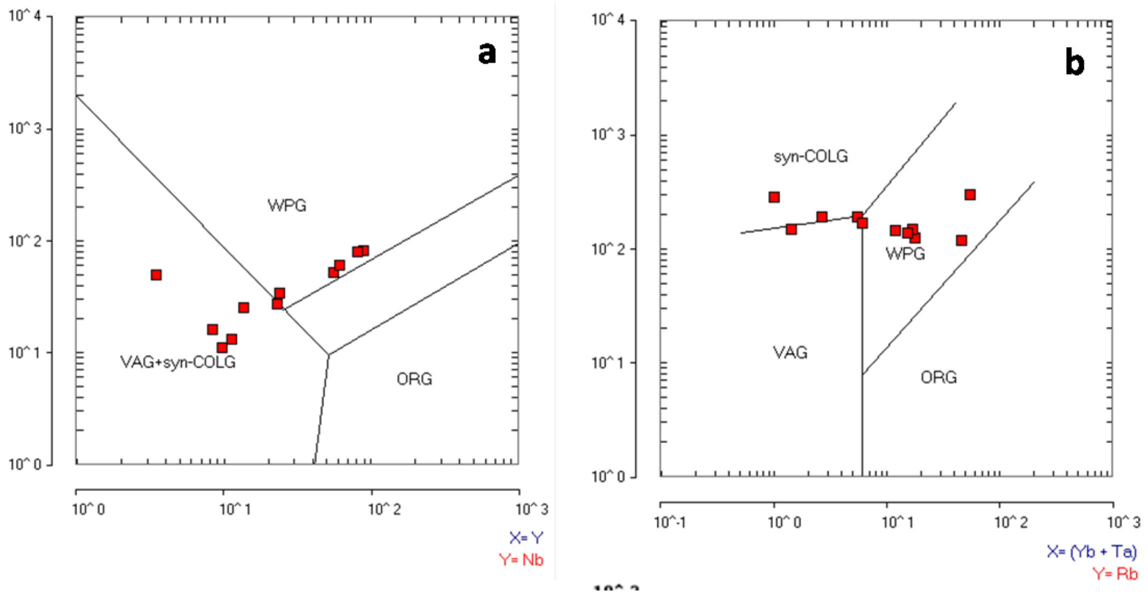

Figure 3: a) Discrimination diagrams show granitoids are syn to post collisional with majority falling within the VAG-syn collisional field - WPG field, (b) Plot of Rb vs Yb+ Ta for granitoids in the Ilaji area (after Pearce 1984).

Concentration of La, Ce, Pr and Nd ranged 4-284, 7 – 610, 1 – 71 and 4 – 255ppm; Sm, Eu, Gd and Tb varied from 1- 50, 0.2 – 2.6, 1 – 30 and 0.2 – 4.1ppm respectively while Dy, Ho, Er, Tm, Yb and Lu varied from 0.9 – 17.3, 0.09- 3.3, 0.3 – 10, 0.09 – 1.4, 0.3 – 8.9 and 0.09 -1.3 respectively (Table 2). Total REE ranged 160 – 422ppm with outliers of 20ppm, 85ppm and1336 ppm. They are enriched in LREE relative to HREE with a weak to strong negative Eu anomaly (Eu/Eu*= 0.25-0.41), with most samples having steep REE patterns ({La/Yb}N = 9.37-12.45) indicative of removal of plagioclase from the melt during fractional crystallisation and or plagioclase as a major fractionating phase (Mark, 1999). Negative Eu are possibly as a result of early crystallisation of plagioclase from the melt by fractional crystallisation, or retention of these elements in feldspars at the source during partial melting (Rollinson, 1993).

Variable REE content in the granitoids are due to the variable proportion of minor mineral phases such as apatite, monazite, epidote and zircon (Kedebe et al., 1999) while unfractionated HREE suggests magmas were produced outside the garnet stability field and plagioclase was stable in the source based on negative Eu and Sr anomalies.

The concentration of the REE within the granite was compared with values from other areas. The total REE concentration in the Ilaji-Ile granite was observed to be similar to concentration in granites from the Idofin-Osi-Eruku, Ila, Lanlate and Komu. However, compared to related granitoids within the Igangan area of southwestern Nigeria, the Ilaji-Ile granites are enriched in REE compared to the Idiko-Ile biotite granite, leucogranite and the Iwere-Ile granodiorite (Table 3)

Table 3: Comparison of Ilaji-Ile granite REE composition with other granitoids

ELEMENT	A	B	C	D	E	F	G
La	71	97	86	73	47	5	33
Ce	150	127	128	148	93	6	63
Pr	17	26	18	16	11	1	8
Nd	61	107	73	63	38	4	28
Sm	13	13	13	13	8	1	6
Eu	1	0	0	1	1	-	1

Gd	9	7	9	13	7	1	5
Tb	1	3	1	1	1	-	1
Dy	7	4	5	15	5	1	4
Ho	1	0	1	3	1	-	1
Er	4	1	2	12	3	-	2
Tm	0	0	0	1	0	-	-
Yb	3	1	2	10	3	0	2
Lu	0	0	0	0	1	-	-
∑REE	339	386	338	354	220	19	154

A: This study
B: Lanlate porphyritic granite (Omoniyi, 2021)
C: The Idofin-Osi-Eruku granite (Odewumi and Olarewaju, 2012)
D: Ilagranitoids (Omotunde et al., 2020)
E: Idiko-Ile biotite granite (Olisa, 2018)
F: Idiko-Ile leucogranite (Olisa, 2018)
G: Iwere-Ile granodiorite (Olisa, 2018)

Conclusion

The porphyritic granites of Ilaji-Ile and environs are composed of quartz, feldspar, biotite with zircon, titanite and garnet as the accessory minerals. The feldspars are of the oligoclase to andesine varieties and the granites are unmineralised with respect to selected rare metals and REE.

Conflict of interest

Authors declare there is no applicable conflict of interest in the study.

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