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Petrography, geochemistry, tectonic Setting and rare earth elements mineralization potentials of selected granitoids from southwestern Nigeria

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ABSTRACT

The demand for Rare Earth Elements (REEs) has necessitated the need to search for REEs from sources aside from carbonatites leading to granitoids currently being assessed globally as possible sources of REEs. Granitoids from parts of southwestern Nigeria were studied using field observations, textural features, and mineralogy. The dominant rock units observed were granitic gneisses, granites, diorites, and monzonites with minor intrusions of pegmatites and quartz veins. Petrogenesis and tectonic setting classification using geochemical data grouped the granitoids as calc-alkalic to alkalic, mostly metaluminous and emplaced mainly Within Plate Tectonic settings which may be related to post-collision settings. The REEs concentrations for the studied granitoids show higher concentrations of Light Rare Earth Elements (LREEs) compared to the Heavy Rare Earth Elements (HREEs) with a negative Eu anomaly indicating that these rocks have been formed from the crystallization of melted crustal materials with plagioclase fractionation. The ΣLREEs for the granites (ΣLREEs 13.10-1083.6 ppm, ΣHREEs 0.44-50.79 ppm) and monzonites (ΣLREEs 14.9-795ppm, ΣHREEs 0.34-33.86ppm), respectively were found to compare favorably with the Granites of China, (ΣLREEs 152-402ppm, ΣHREEs 16-53ppm) where REEs exploitation is ongoing. REE-bearing minerals in granitic gneisses, granites and monzonites include synchysites, allanites, monazites, apatites and tritomites from which the economic concentrations of REEs can be extracted. These granitoids are, therefore, rock units of interest in understanding the economic potential of REEs in Nigeria.

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Research Highlights

- Granite gneisses, granites and monzonites within the study areas were investigated for their REEs mineralization potentials and they showed higher REEs concentrations when compared with concentrations of granites from China and Indonesia where REEs mining is currently ongoing.
- REE-bearing minerals within these rock units include synchysites, allanites, monazites, apatites and tritomites from which REEs can be profitably extracted and areas of REEs mineralization within these study areas were delineated for further exploration by prospective investors.

Introduction

The use of fossil-fuel-driven engines and technologies has resulted in unintended environmental consequences including pollution and extreme climatic changes. These adverse effects have led to an increased awareness of the drastic global shift towards green technology. The application of this technology involves solar array production, reusable materials, wind generators and biogas production (Goodenough et al., 2016; Batapola et al., 2020) which has encouraged worldwide exploration of Rare Earth Elements (REEs) which are essential raw materials for these technologies.

REEs are a group of 17 elements grouped together on the periodic table because of their similar chemical properties and these include the fifteen Lanthanides (atomic numbers 57 - 71). They are generally subdivided into light (Sc, La, Ce, Pr, Nd and Pm), medium (Sm, Eu, and Gd), and heavy (Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) REEs (Balaram, 2019).

In the world today, REEs have been sourced primarily from Carbonatites which are igneous rocks that contain greater than 50% carbonate minerals alongside other silicate minerals such as pyroxenes, olivine, and amphiboles (Chakhmouradian and Wall, 2012). They exist in continental rift settings and, because of this peculiarity, are not widely distributed globally. However, other sources of REEs include alkaline igneous rocks, pegmatites, iron-oxide copper-gold deposits, skarn deposits, ion absorption clay deposits, and monazite-xenotime rich phosphate deposits (Chakhmouradian and Wall, 2012; Dushyantha et al., 2020). These sources have become sources of REES in various parts of the world, leading to increased production and greater flexibility in the global supply of REEs. The centralities of REEs to green technology and the fast momentum towards carbon -neutral society have made REEs one of the groups of critical minerals globally. It is therefore very important that the Nigerian nation is not left behind in this important task of looking for REEs deposits to be an REE-producing country.

Nigerian geologic endowments include large volumes of granitoids found as Pan African suits (Garba, 2003) and the Younger granites of north-central Nigeria (Adetunji et al., 2016; Umaru et al., 2023) making these rock units' potential hosts for REEs that need to be investigated. This study is thus devoted to investigate the REEs mineralization potentials of some Pan African granitoids in the southwestern Precambrian Basement Complex of Nigeria using petrographic analysis, Inductively Coupled Plasma Mass Spectrometry and Scanning Electron Microscopy (EDX).

Geological Setting

Generally, the geology of Nigeria consists of three major components; Precambrian basement complex, Jurassic Younger Granites and Cretaceous to recent sedimentary basins. In the Nigerian sector of West African region, the Precambrian complex domain comprises four main rock units; migmatite gneiss complex, metasedimentary and metavolcanic rocks, granitoid suite and undeformed acid and basic dykes (Carter et al., 1963; Burke and Dewey, 1972; Offodile, 1976; Black, 1980; Rahaman, 1988; Dada, 2006). This study focuses on areas within the Precambrian Basement Complex, which were reported to have been affected by the 600Ma Pan-African orogeny (Black, 1980; Burke and Dewey, 1972; Dada, 2006). The basement lithologies reported by different researchers include The Migmatite Gneiss Complex (MGC), Metasedimentary and Metavolcanic rocks (Schist Belts); the Pan African Granitoid Suite, and the undeformed acid and basic dykes (Russ, 1957; Klemm et al., 1984; Rahaman, 1988). The rock units within these lithologies include granite gneisses, granites, granodiorites, quartzites, and charnockites of different sizes and dimensions (Olarewaju, 2006; Fig. 1). Samples for this study were obtained from three areas, as shown in Table 1 and Fig. 2A-C;

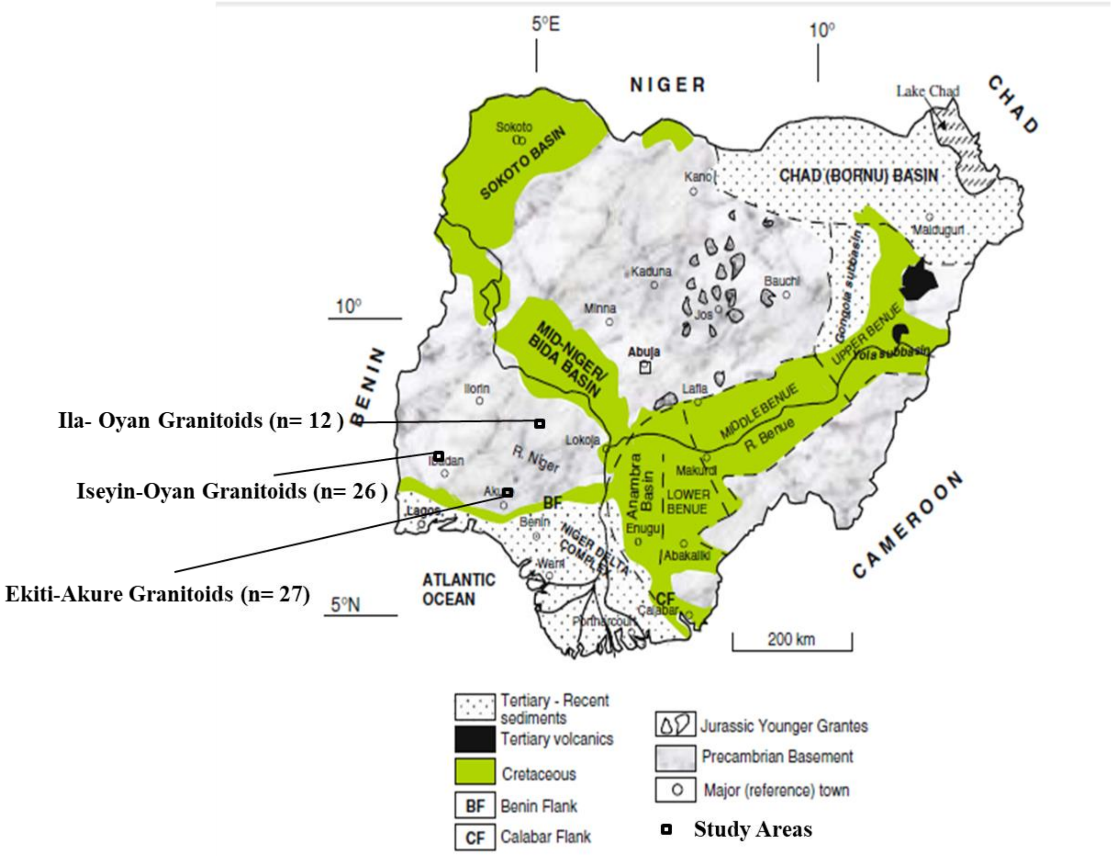

Fig. 1. Geological Map of Nigeria showing study areas and numbers of samples per area (modified after Obaje (2009))

Table 1. Coordinates of Ila Orangun, Iseyin-Oyan and Ekiti-Akure study areas

Study area	Lithologies	Northings	Eastings
Ila Orangun	granites and granite gneisses	08°00'00''N – 08°04'00N	04°45'00''E – 04°57'00''E
Iseyin-Oyan	granites, diorites and monzonites	08°00'00''N - 08°07'00''N	03°00'00''E – 03°08'00''E
Ekiti- Akure	diorites and monzonites	07°15'00''N – 07°50'00''N	05°00'00''E – 05°30'00''E

Methodology

Twelve (12) rock samples were collected along the Ila-Oyan axis; 26 rock samples from the Iseyin axis and 27 rock samples from the Ekiti-Akure axis. The collected rock samples were labeled, bagged, and taken to the Activation Laboratory Limited Laboratory, Canada for further analysis.

A total of forty-eight (48) rock samples were prepared as thin sections and viewed under an optical petrographic microscope to determine their mineral compositions. All 48 samples were then crushed, pulverized, and analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the major, trace, and rare earth elements (REEs) concentrations. Prior to ICP-MS analysis, pulverized samples were mixed with excess Lithium Borate, heated until the mixture formed a homogenous mass, and then dissolved in 5% HNO_3. Blank fusion solutions were provided so that calibration standards and blanks could be matched while quality assurance and quality control procedures were carried out using standard reference materials: OREAS101b, NCSDC86318, BCR-2, USZ42-2006, REE-1, and W-2b. Detection limits for MnO and TiO_2 were 0.001%; SiO_2, Al_2O_3, Fe_2O_3(T), MgO, CaO, Na_2O, K_2O, and P_2O_5 were 0.01%; Bi 0.4 mg/g; Ag, Sb, and Cs was 0.5 mg/g; Sc, Be, Y, Co, Ga, Ge, Nb, Sn, and W was 1mg/g; Ba, Sr, Zr, Rb, and Mo was 2 mg/g; V, As and Pb was 5 mg/g; Cu 10 mg/g: Cr and Ni were 20 mg/g while Zn was 30 mg/g. Duplicate and blank samples were collected throughout the experiment.

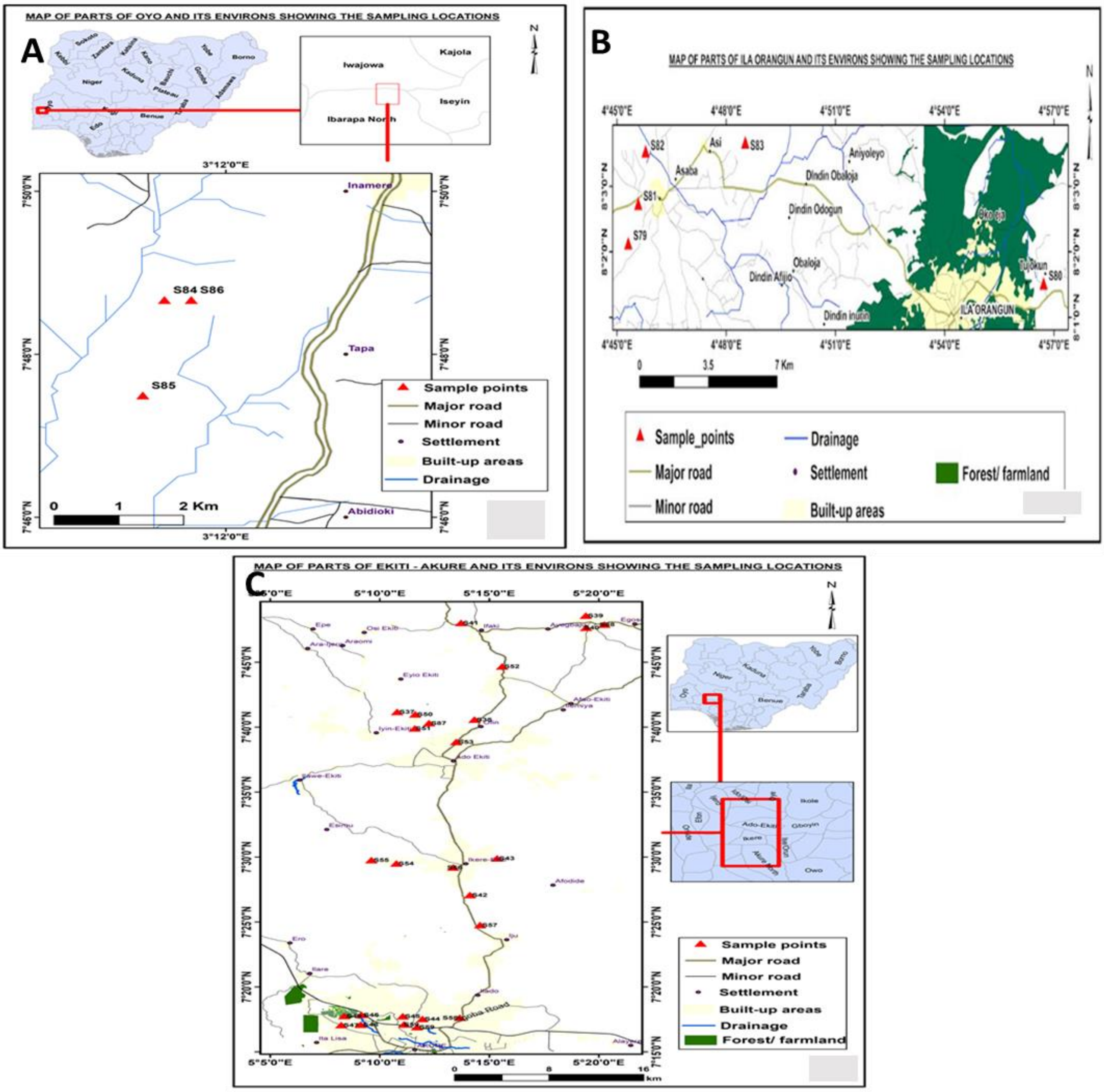

Fig. 2. A-C: Map of Iseyin-Oyan, Ila Oyan, and Ekiti-Akure showing sample locations

Five (5) pulverized samples of selected rock units were sent to the Department of Geology, University of the Free State, South Africa for SEM/EDX analysis to determine morphological and compositional characteristics of specific minerals such as apatite, monazite, xenotime, rutile and zircon that are notable host minerals for REEs. A portion of each of these five samples (1.5 x 1.5 x 1cm blocks) was prepared in epoxy, polished and analysed using a Jeol JXA-iSP100 Super Probe equipped with a Jeol EDS. To prevent charging of the samples, they were carbon-coated (the carbon in carbonates cannot be determined because of this) using a Quorum - Q150T sputter-coater. Analysis of the samples was completed by following the procedure to search for "bright" minerals (minerals with high atomic masses), as REEs have high atomic masses. All "bright" minerals were documented. The minerals documented here have different appearances, ranging from euhedral grains to inclusions within other minerals, to what could possibly be secondary minerals (Fig. 3).

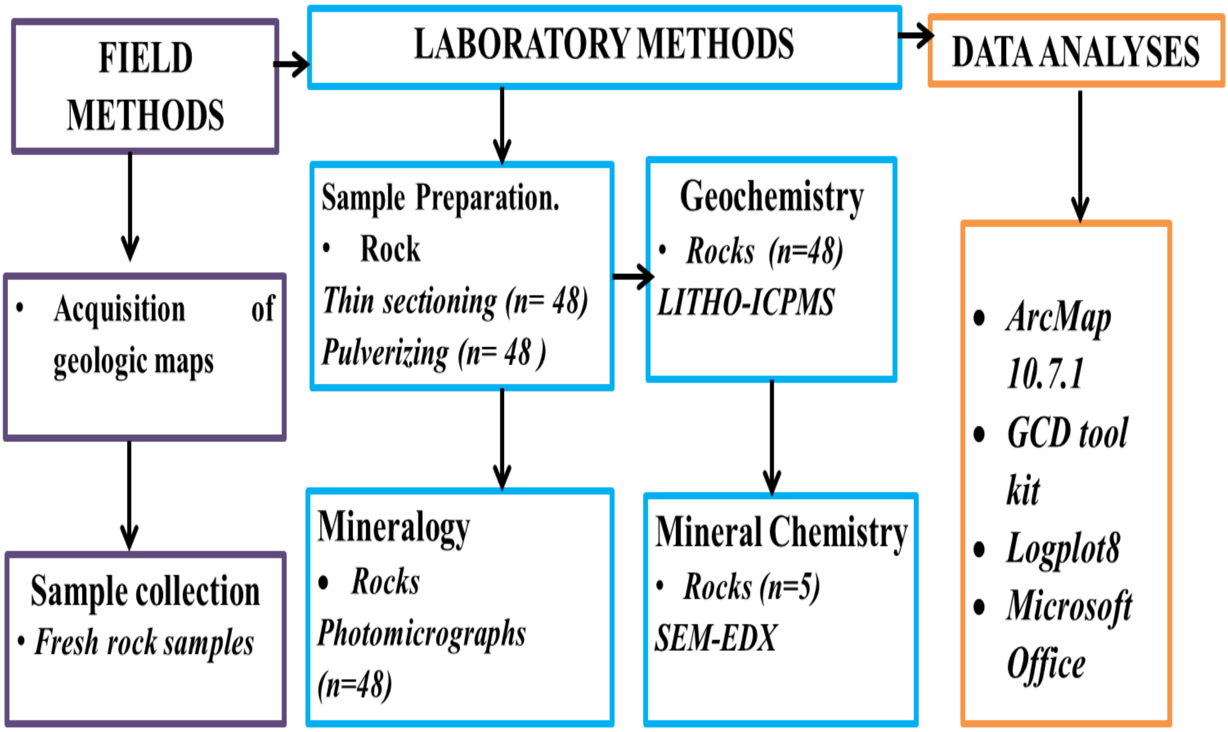

Fig. 3. Flowchart of the methodology for granitoids of the Ila-Oyan, Iseyin-Oyan, and Ekiti-Akure areas

Results and Discussions

Field Occurrences and Petrography

The granitoids observed within the study area were identified as porphyritic granites, granitic gneisses, diorites, and monzonites (Fig. 4A–F). The detailed modal compositions of these rock units are presented in Table 2 and typical photomicrographs of the rocks are presented in Fig. 5A–F.

The granitic gneiss outcrops were found in the northern part of Ila as highly weathered, low-lying, and extensive rock units trending in the NE-SW direction confirming the Pan-African Orogeny imprint with varying degrees of quartz veins and pegmatitic intrusions. They are generally leucocratic, medium - coarse-grained, and have varying degrees of foliation planes as well as mineral lineation of biotite and quartz minerals. Minerals identified through photomicrographs included Quartz (24-35%), alkali-feldspar (5-30%), plagioclase (6-22%), muscovite (4-6%), biotites (8-21%), garnet (2-5%) and opaque minerals (2-10%, Table 2).

The granites around the Ila_Oyan and Iseyin areas mostly occur as high-rise plutons with characteristic porphyritic textures with intrusions. The granites were of two varieties, notably hornblende biotite granite and biotite granites, with a notable occurrence of partially digested xenoliths within the groundmass. Some of the granites intruded the older quartz-mica schists within the study area. Thin-section analysis showed the presence of quartz (20-36%), alkali feldspar (3-20%), biotite (8-34%), plagioclase (7-15%), muscovite (1-3%), hornblende (1-15%) and opaque minerals (2-10%) with porphyritic texture defined by phenocrysts of feldspars surrounded by quartz, biotite, and hornblende.

The diorites are intermediate igneous rocks that occur as plutons within the Iseyin-oyan and Ekiti-Akure areas, extending to approximately 20meters with porphyritic textures defined by large phenocrysts of plagioclase embedded in a matrix of biotite, feldspars, titanite, apatite, monazites and other accessory minerals. Lineation, defined by the parallel alignment of mafic minerals, was also observed. The modal compositions of minerals include quartz (8-9%), plagioclase (22-32%), alkali feldspar (2-7%), biotite (8-15%), hornblende (11-16%) and opaque minerals (1-4%).

The monzonites were abundant within the Ekiti-Akure areas occurring mostly as hills and high-rising plutons extending to more than 50meters on the surface with occasional occurrence as low-lying outcrops. They are generally coarse-grained and appear dark green, greenish-grey to greyish white with notable quartz vein intrusions. Mineral composition in hand specimens and photomicrographs includes; quartz (5-20%), biotite (10-25%), alkali feldspar typically Microcline and Orthoclase (7-23%), plagioclase (10-45%), hornblende (10-20%) and opaque minerals (5-20%).

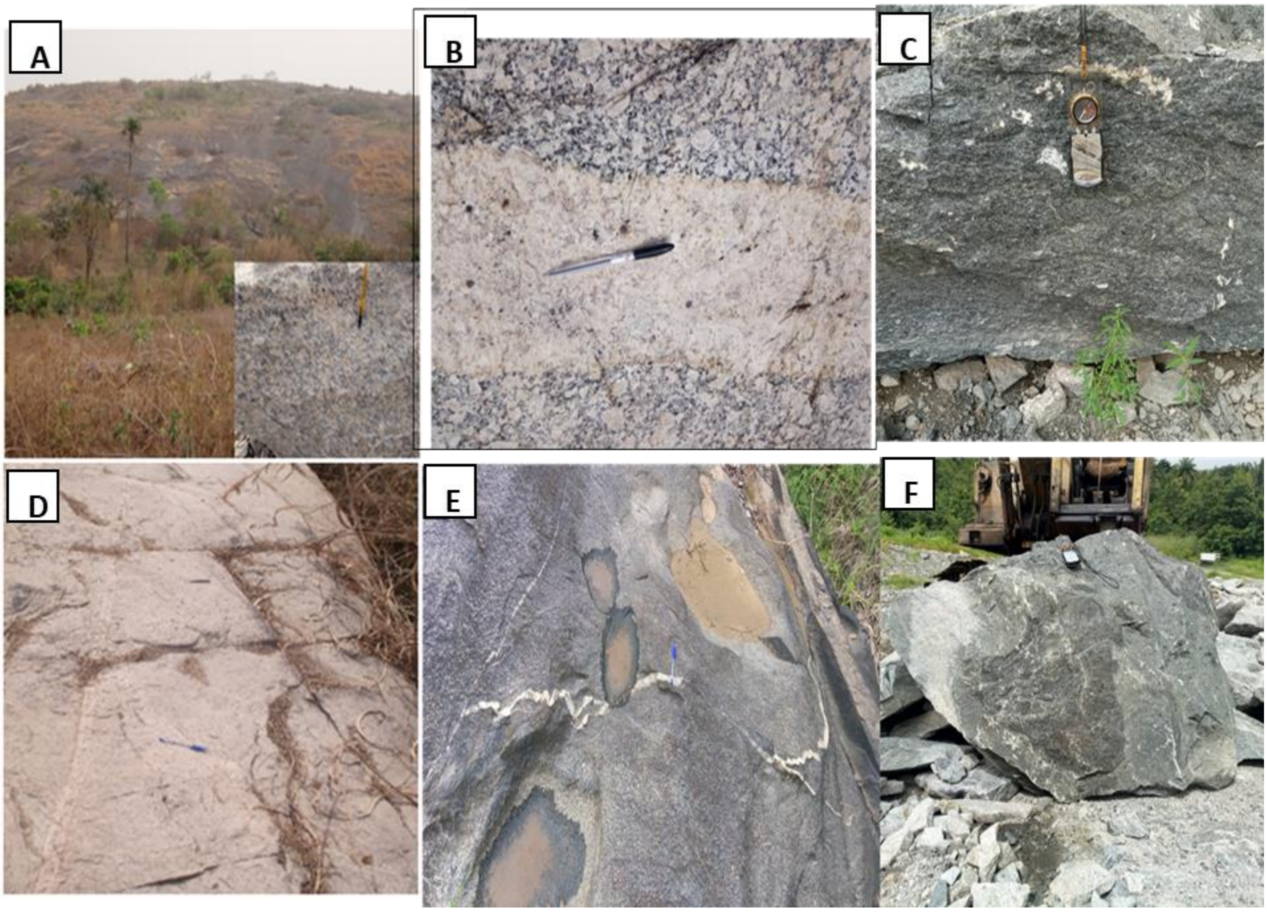

Fig. 4. Field photographs A and D: Ila-Oyan Porphyritic Granite and Granite Gneiss, B and E: Iseyin-Oyan Porphyritic Granite and Diorites, C and F: Ekiti-Akure Monzonites

Table 2. Modal composition of granitoids within Ila Oyan, Iseyin-Oyan and Ekiti-Akure areas

Minerals	Granitic Gneiss (n=9)	Granites (n=16)	Diorites (n=8)	Monzonites (n=15)
Quartz	24-35	20-36	8-9	5-20
Plagioclase	6-22	7-15	22-32	10-45
Microcline	5-15	8-20	2-5	10-20
Orthoclase	7-30	3-15	3-7	7-23
Muscovite	4-6	1-3	-	-
Biotite	8-21	8-34	8-15	10-25
Hornblende	-	1-15	11-16	10-20
Garnet	2-5	-	-	-
Opaque	2-10	2-10	1-4	5-20

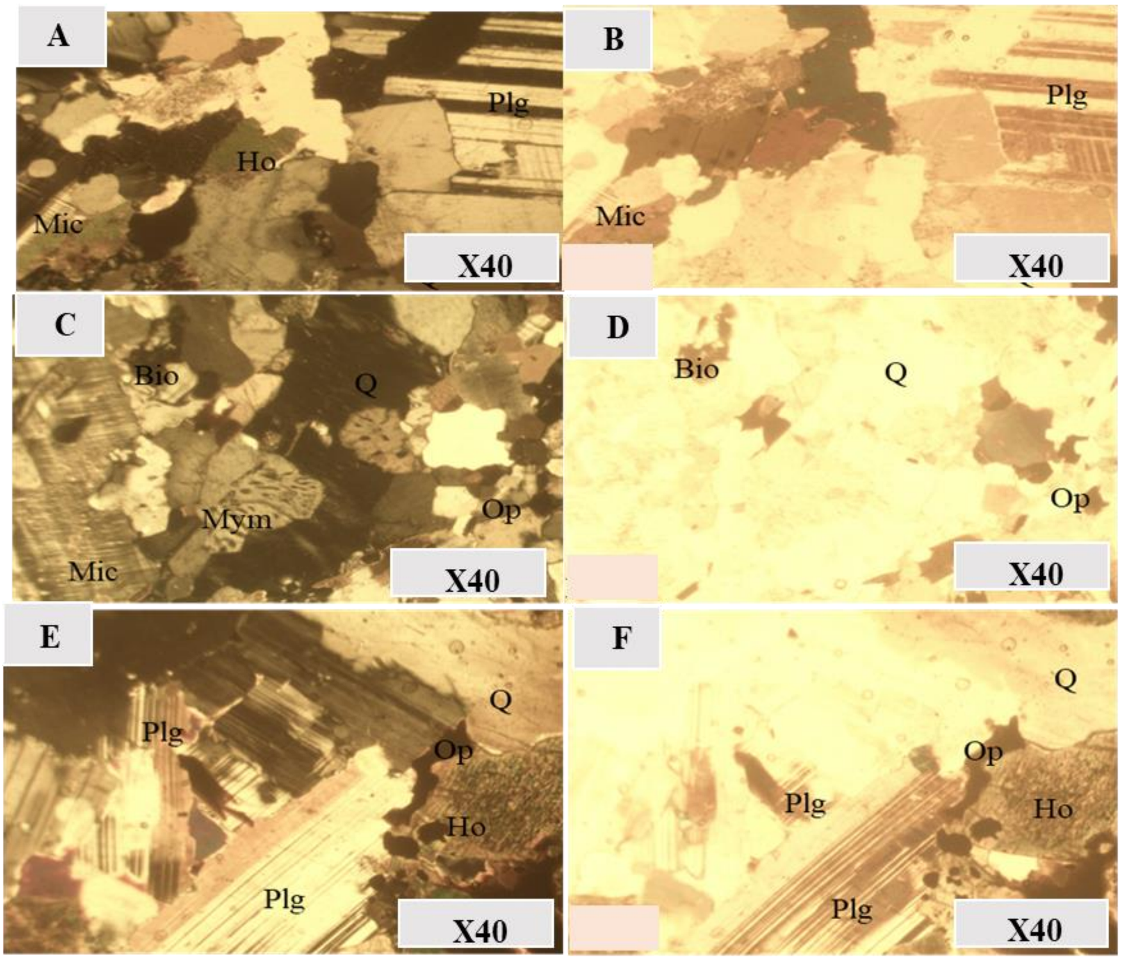

Fig. 5. Photomicrographs of primary and secondary minerals in Ila-Oyan, Iseyin-Oyan, and Ekiti-Akure areas (XPL and PPL (X40)). A to F: Plg: Plagioclase, Q: Quartz, Ho: Hornblende, Mic: Microcline, Bio: Biotite, Mym: Myrmekite and Op: Opaque. A-B: granites, C-D: diorites, E-F: monzonites

Geochemistry of the Granitoids

Geochemical results showed the major oxides concentrations ranged as follows (Table 3): For the granitic gneisses SiO_2 ranged from 65.2-72.2%, Al_2O_3, 13.05-15.21%, Fe_2O_3(t), 1.54-7.24%, MgO, 0.25-0.87%, CaO 0.79-2.77%, Na_2O 2.22-3.9%, K_2O 3.15-7.72%, TiO_2 0.26-0.91%, P_2O_5 0.11-0.67% and MnO, 0.03-0.1%;

The granites; revealed a range of 66.3-74.96% for SiO_2, 11.55-17.04% for Al_2O_3, 1.03-3.3% Fe_2O_3(t), 0.1-0.58% MgO, 0.55-2.7% CaO, 2.86-5.5% Na_2O, 4.16-6.93% K_2O, 0.15-0.35% TiO_2, 0.07-0.44% P_2O_5 and 0-0.17% MnO; diorites is characterized with 45.65-65.59% SiO_2, 13.73-19.15% Al_2O_3, 6.34-15.40% Fe_2O_3(t), 2.77-8.16% MgO, 3.44-10.44% CaO, 2.63-4.11% Na_2O, 0.91-3.29% K_2O, 0.62-3.13% TiO_2, 0.13-2.61% P_2O_5 and 0.10-0.17% MnO;

The composition of monzonites showed a range of 51.20-65.75% for SiO_2, 14.57-17.41 % for Al_2O_3, 3.31-11.81% for Fe_2O_3(t), 0.10-2.22% for MgO, 1.23-7.33% for CaO, 2.79-7.75% for Na_2O 2.99-6.98% for K_2O, 0.25-2.99% for TiO_2, 0.07-1.87% for P_2O_5 and 0.04-0.22% for MnO.

The Cao concentrations in all rock units were higher than the MgO concentrations, which may be an indication of the remobilization of pre-existing minerals within the igneous rocks or varying compositions of protoliths before metamorphism (Omotunde et al., 2020).

The Low Field Strength Elements (LFSE) including Cs, Rb, Ba, Pb, Sr, Th and U ranges between the rock units as follows: granite gneisses 1.3-6.3ppm Cs, 162.5-277.1ppm Rb, 326-1071ppm Ba, 1.1-5.7ppm Pb, 70.6-113.6ppm Sr, 3.7-71.7ppm Th, 1-5.4ppm U; granites 2.2-2.7ppm Cs, 99.9-242.6ppm Rb, 225.13-831.78ppm Ba, 6.3-32ppm Pb, 15.9-187.1ppm Sr, 19.23-65.4ppm Th, 6-8.8ppm U; diorites 0.5-1.9ppm Cs, 309-1029ppm Ba, 6.0-32.0ppm Pb, 155-680ppm Sr, 1.7-33.2ppm Th, 0.3-17.6ppm U; monzonites 0.50-1.70ppm Cs, 75.00-218.00ppm Rb, 988.00-2223.00ppm Ba, 18-46ppm Pb, 156.00-469.00ppm Sr, 5.60-93.90ppm Th, 1.50-5.70ppm U while the High Field Strength Elements (HFSE) including Zr, Hf, Nb, Ta and Ti have values in the range of: granite gneisses 7.3-35.5ppm Hf, 8.5-103.8ppm Nb, 1.9-3ppm Ta, 241.9-1298.1ppm Zr, 0.3-1.5ppm Ti; granites 17.1-35.3ppm Hf, 19.6-127.3ppm Nb, 1.9-3ppm Ta, 170.8-1175.6ppm Zr, 0.3-0.4ppm Ti; diorites 2.0-9.4ppm Hf, 11.3-146.0ppm Nb, 0.3-2.8ppm Ta, 76-316ppm Zr, 0.1-0.8ppm Ti; monzonites 6.50-31.50ppm Hf, 54.60-217.80ppm Nb, 0.70-2.70ppm Ta, 360-1279ppm Zr, 0.3-0.8ppm Ti.

Concentrations of Be and Ta were generally low in all granitoids studied whereas those of Pb, Ni and Co were higher in diorites and monzonites than in granite and granitic gneisses. These variations may be the result of the primary magma composition.

Petrogenesis and Tectonic Setting

The plot of TiO_2 against SiO_2 (Tarney, 1977) showed all Granite gneisses samples fall within the igneous field indicating igneous origin for the gneisses (Fig. 6A) while the plot of $Na_2O + K_2O$ Vs SiO_2 (Middlemost, 1994) described the lithologies of the granitoids to include granites, monzonites, diorites and grabbroic diorites (Fig. 6B).

Granite geochemical classification scheme by Frost et al. (2001) showed all granitoids plotted within the Calc-alkalic to Alkalic boundaries, while the Aluminum Saturated Index plot indicated that the Granites, Diorites, and Monzonites were all metaluminous and the Granite gneisses were peraluminous indicating their granitic protoliths may have suffered some level of magma contamination (Olanrewaju 2006; Fig. 6C, D and E).

On the Hacker plots, SiO_2 was correlated against all the other major oxides to determine their relationship (Fig. 7A–H). Only K_2O showed a positive correlation with SiO_2 as opposed to other oxides that showed negative correlations an indication of the fractional crystallization as the dominant mode of formation for the magmas that produced the rocks while the other oxides showed negative correlation with SiO_2. The moderate to high silica and alumina concentrations within the granitoids further explains the abundance of quartz, feldspars and biotite. The scattered correlation between Na_2O and SiO_2 may suggest contamination of the melt bringing about formation of heterogeneous granitic rocks (Ahmadi Khalaji et al., 2007).

Trace elements geotectonic discrimination plots (Pearce et al., 1984) of Nb Vs Y revealed Within Plate Granites classification for most of the granitoids implying enriched mantle sources and crustal materials inclusions while some Granitic gneisses fell within the Orogenic boundary indicating their metamorphic changes may have been as a result of the Pan African Orogeny (Fig. 8).

Table 3. Geochemical concentrations of Granitoids within Ila Oyan, Iseyin-Oyan and Ekiti-Akure areas (Major Oxides wt.%, Trace and Rare Earth Elements in ppm)

	Granite Gneisses	**Granites**	**Gabbro-diorites**	**Monzonites**
SiO_2	65.2-72.22	66.3-74.96	45.65-65.59	51.20-65.75
Al_2O_3	13.05-15.21	11.55-17.04	13.73-19.15	14.57-17.41
Fe_2O_3	1.54-7.24	1.03-3.3	6.34-15.40	3.31-11.81
MgO	0.25-0.87	0.1-0.58	2.77-8.16	0.10-2.22
CaO	0.79-2.77	0.55-2.7	3.44-10.44	1.23-7.33
Na_2O	2.22-3.9	2.86-5.5	2.63-4.11	2.79-7.75
K_2O	3.15-7.72	4.16-6.93	0.91-3.29	2.99-6.98
TiO_2	0.26-0.91	0.15-0.35	0.62-3.13	0.25-2.99
P_2O_5	0.11-0.67	0.07-0.44	0.13-2.61	0.07-1.87
MnO	0.03-0.1	0-0.17	0.10-0.17	0.04-0.22
Ba	326-1071	225.13-831.78	309-1029	988.00-2223.00
Be	1-10	1-5	1.00-4.00	2.00-3.00
Co	2.6-8.5	1.6-2.8	14.0-60.0	4.00-32.00
Cs	1.3-6.3	2.2-2.7	0.5-1.9	0.50-1.70
Ga	11.9-25.6	17.7-33.8	17.0-24.0	19.00-27.00
Hf	7.3-35.5	17.1-35.3	2.0-9.4	6.50-31.50
Nb	8.5-103.8	19.6-127.3	11.3-146.0	54.60-217.80
Rb	162.5-277.1	99.9-242.6	16.0-189.0	75.00-218.00
Sn	3-11	3.15-9	1.0-3.0	1.00-4.00
Sr	70.6-113.6	15.9-187.1	155-680	156.00-469.00
Ta	1.1-8.1	1.9-3	0.3-2.8	0.70-2.70
Th	3.7-71.7	19.23-65.4	1.7-33.2	5.60-93.90
U	1-5.4	6-8.8	0.3-17.6	1.50-5.70
V	9-43	0-28	55-291	0-204.00
W	0.6-5.1	<0.5	0-1	0-1
Zr	241.9-1298.1	170.8-1175.6	76-316	360-1279
Mo	0.1-2.9	0.8-1.5	2.0-3.0	3-13
Cu	0.4-15.7	3.8-22.12	19.7-160.0	10-30
Pb	1.1-5.7	6.3-32	6.0-32.0	18-46
Zn	18-171	20.4-177.9	50.0-170.0	50-180
Ni	1.6-5.8	1.3-26.21	20.0-310.0	22.79-35.38
As	0.6-8.7	0.04	2.1-4.4	0.82-15.69
Ti	0.3-1.5	0.3-0.4	0.1-0.8	0.30-0.80

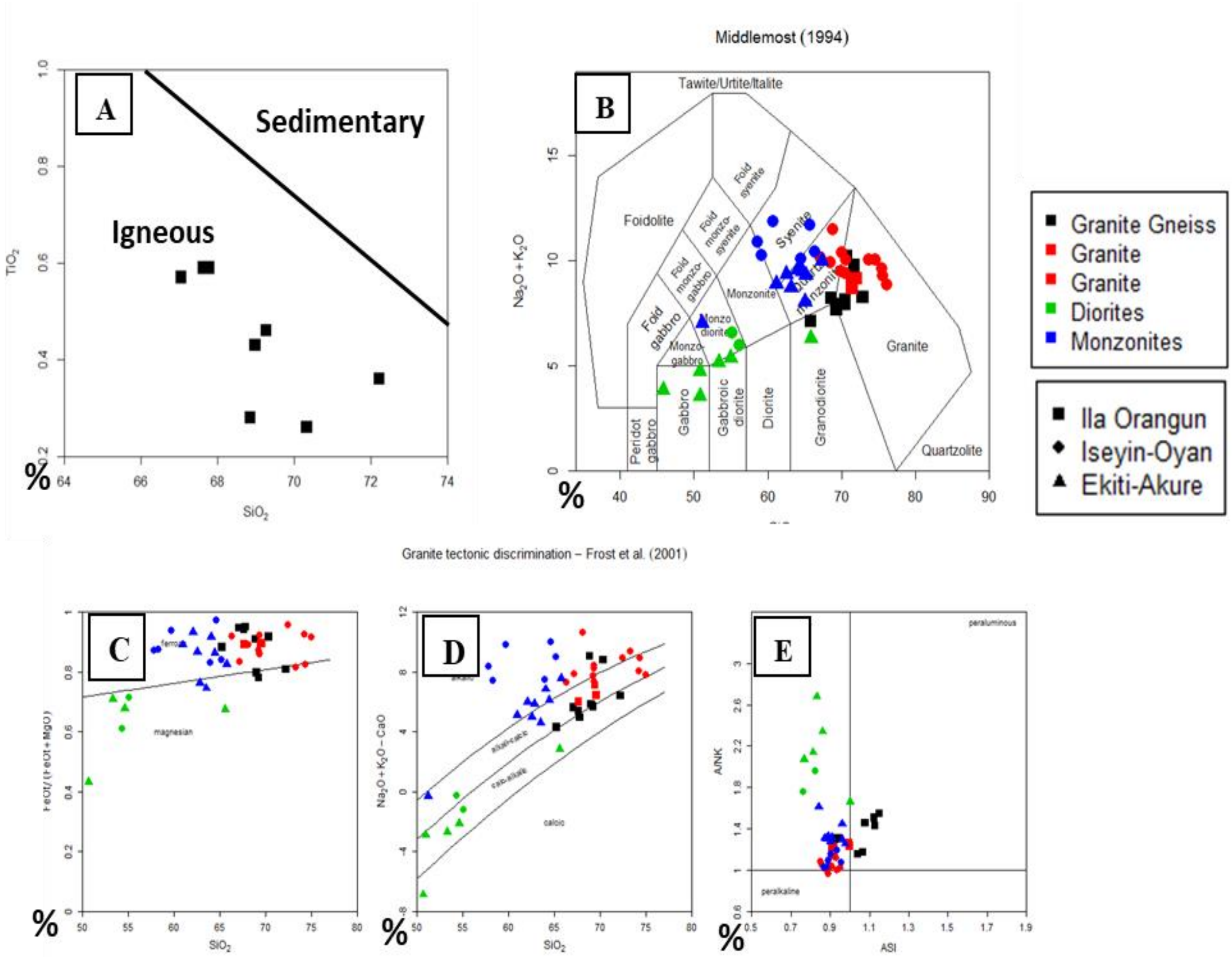

Fig. 6. Discrimination plots of Ila Oyan, Iseyin-Oyan and Ekiti-Akure areas. A: TiO_2 vs SiO_2 after Tarney, 1977, B: Na_2O+K_2O vs SiO_2 (Middlemost, 1994), C, D and E: Aluminum Saturation Index plots after Frost et al. (2001)

The REEs concentrations of all granitoids (granitic gneisses, granites, diorites, and monzonites) within the study area are presented in Table 4. Granites have the highest concentrations of REEs followed by monzonites, granitic gneisses, and diorites with the lowest concentrations. The LREEs in all granitoids have higher concentrations when compared with the HREEs (Sm-Lu). The general enrichment in LREEs and depletion in HREEs (displayed by ratio La/Yb_N which ranged between 2.67- 72.19) with a negative Eu anomaly (Eu/Eu* range 0.15-1.35) in the granitoids indicate the magma that produced these granitoids crystallized plagioclase and most of the Eu was incorporated in the minerals (Fig. 9). The values of ΣLREE, ΣHREE, and ΣREE for each rock unit were: Granitic gneisses 3947.55, 916.44, and 4863.99; Granites 15221.7, 1818.01, and 17039.7; Diorites 2903.5, 426.96 and 3330.46; Monzonites 11108.3, 1094.9 and 12203.2 which may point to origin of their magma being from upper continental crust. Both LREEs and HREEs are abundant in the rock units in the order Granites>Monzonites>Granitic gneisses>Diorites. Spider plot of REEs for all granitoids normalized using Chondrite values after Boynton (1984) showed values of REEs were greater than 1 indicating the formation of granitoids was from continental crust materials. These characteristics compare favorably with the geochemical properties of granites of Dingnan, Southern China (Ishihara et al., 2008).

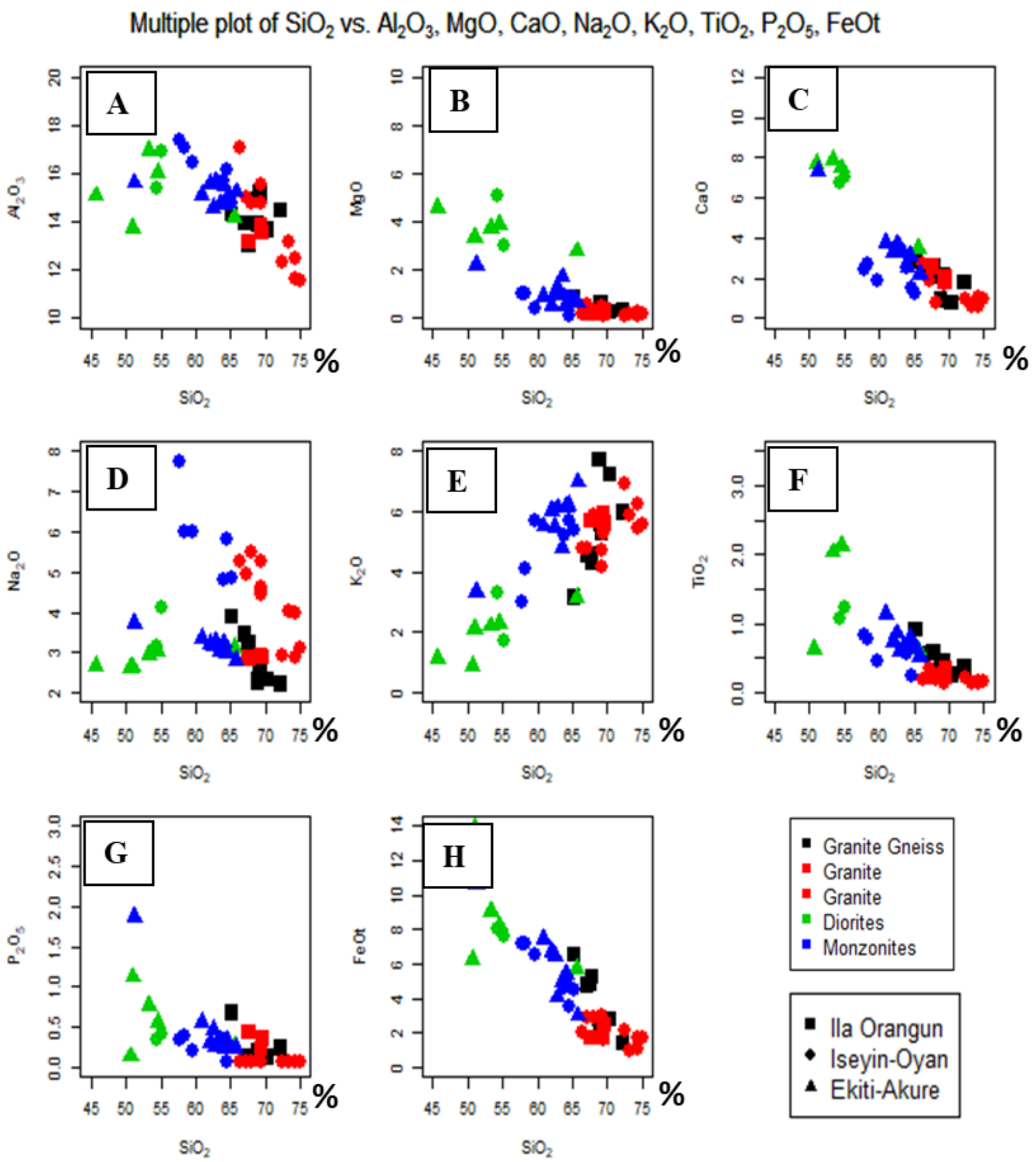

Fig. 7. A–H: Harker variation plots for the granitoids of Ila Oyan, Iseyin-Oyan and Ekiti-Akure areas

REE Mineralization Potentials

The concentrations of REEs in the different rock units within the granitoids were compared with concentrations of REEs in mineralized areas to determine the mineralization potentials (Table 3). The REEs concentrations of the granitoids studied when compared with those of granites of Masamba, South Sulawesi, Indonesia (Maulana et al., 2012) showed similarities with the granitic gneisses and diorites while the granites and monzonites had far higher REE concentrations, especially the LREEs. However, a comparison of the REEs concentrations with the granites of Dingnan, Southern China, where REEs exploration is ongoing, showed higher concentrations of LREEs in the granites and monzonites with lower HREEs concentrations in all the rock units. These might suggest that the granites and monzonites of the study areas are places of interest for further investigation in the search for potential sources of rare earth elements in Nigeria.

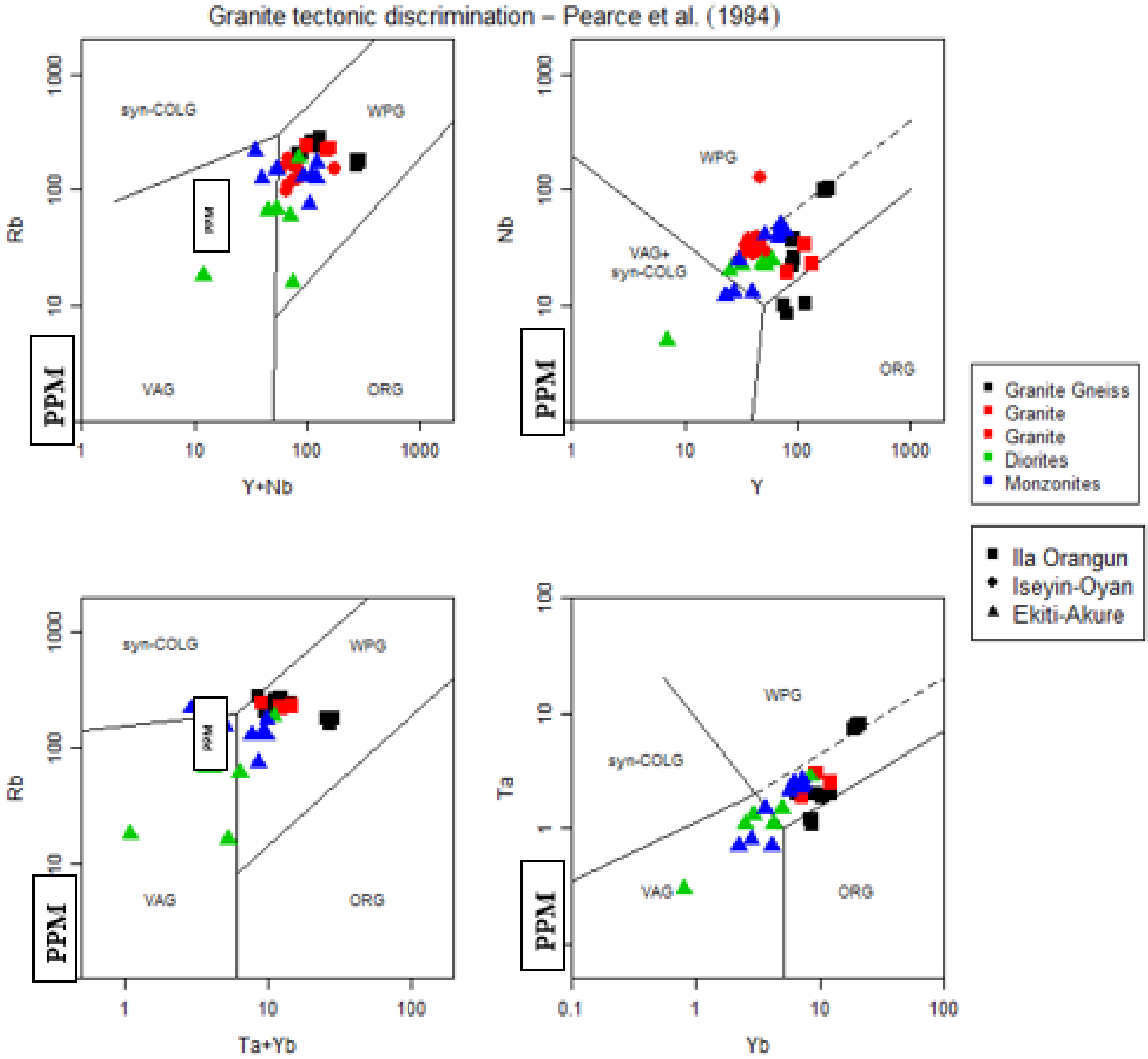

Fig. 8. Geotectonic discrimination plots of Ila Oyan, Iseyin-Oyan and Ekiti-Akure areas. (Pearce et al., 1984)

Mineral Chemistry

Representative samples of granitic gneisses (2), Older Granites (1) and monzonites (2) that have shown enrichment in REEs based on comparison with places where mining is currently ongoing were further studied using SEM-EDX back scattered electron images (BSE) to ascertain their REE-bearing accessory minerals with emphasis on the chemical composition of minerals with significant Rare Earth Elements concentrations within their structures (Table 5).

The REE- bearing accessory minerals found in the granitic gneiss samples in the order of abundance include: synchysite $Ca(Ce, La)(CO_3)_2F$ with range values of REE concentration of La 7.19-16.93%, Ce 17.27-24.83%, Nd 8.03-14.85% and Y 3.39-7.51%; tritomite $(Y,Ca,La,Fe)_5(Si,B,Al)_3(O,OH,F)_{13}$ with range values of La 7.72-10.46%, Ce 12.43-18.13%, Nd 4.98-8.7% and Y 8.47-10.28%; allanite $(Ce,Ca,Y,La)_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$ with range values of La 1.97-2.65%, Ce 4.71-8.96%, Nd 2.39-3% and Y 6.31-10.12%. The concentrations show the granite gneisses have higher LREEs concentrated in synchysites, tritomite (a member of apatite Supergroup) and allanites (a member of the epidote supergroup) minerals (Fig. 10).

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Table 4. REEs concentrations within Granitoids in the study area compared to other granitoids Ila Oyan, Iseyin-Oyan and Ekiti-Akure areas

(ppm)	1	2	3	4	5	6
La	67.8-204.5	70.31-944.39	12.6-136	79.20-629.59	7.6-75.1	33.4- 101.00
Ce	126-385.3	153.35-1083.6	24.0-301.0	145-795	16.6-157	73.2-196.00
Pr	13.72-40.07	13.10-103.02	2.7-35.3	14.9-70.9	2.11-17.2	8.11-20.00
Nd	49.5-136.6	47.07-326.69	11.3-146.0	54.6-217.8	8.9-53	30.4-71.30
Sm	10.18-27.65	7.79-50.79	2.3-26.0	9.5-33.86	2.3-7.18	6.49-13.60
Eu	1.24-4.92	1.41-3.51	1.0-5.8	2.04-5.68	0.10.92	0.22-1.65
Gd	11.16-29.69	8.29-45.91	2.0-18.6	6.90-22.96	2.41-5.98	5.71-15.00
Tb	2.07-5.23	3.01-4.92	0.3-2.4	1.0-3.5	0.5-0.86	0.89-2.62
Dy	13.75-33.34	6.91-43.59	1.8-17.0	5.4-21.79	2.23-5.88	4.48-15.2
Ho	2.97-7.21	2.94-5.18	0.3-2.3	1-3.4	0.39-1.31	0.76- 2.95
Er	9-21.8	4.74-34.70	0.9-9.4	2.6-17.35	1.22-4.21	1.94-7.98
Tm	1.17-3.12	0.68-4.96	0.1-1.2	0.35-2.48	N/A	0.28-1.19
Yb	6.64-20.71	4.54-32.58	0.8-8.3	2.20-16.29	N/A	1.72-7.45
Lu	0.92-2.99	0.44-4.76	0.1-1.4	0.34-2.38	0.03-0.21	0.24-1.05
LREE	13.72-385.3	13.10-1083.6	2.7-301.0	14.9-795	38-310	152-402
HREE	0.92-33.34	0.44-50.79	0.1-26.0	0.34-33.86	9-17	16-53

1.Granite gneisses of Ila Oyan area
2. Granites of Ila Oyan, Iseyin-Oyan areas
3. Gabbro-diorites of Iseyin-Oyan and Ekiti-Akure areas
4. Monzonites of Ekiti-Akure area
5. Masamba granitic rocks in South Sulawesi, Indonesia
6. Granites of Dingnan, Southern China

Accessory minerals found in the Older Granite samples enriched in REEs are as follows in the order of REEs abundance: apatite $Ca_{10}(PO_4)_6(OH,F,Cl)$ in the range of La 17.94-19.89% and Ce 32.39-33.97%; monazite $(Ce,La,Nd,Th)(PO_4,SiO_4)$ in the range of La 19.69-20.39% and Ce 29.23-32.69%; allanite $(Ce,Ca,Y,La)_2(Al,Fe^{3+})3(SiO_4)_3(OH)$ in the range of La 3.06% and Ce 3.21-8.87%. The results further confirmed earlier analysis which classified the Older Granites as rock units essentially enriched in LREEs which are hosted in apatite, monazite and allanites (Fig. 11).

The monzonite samples had essentially two REE-bearing minerals with dominantly Light Rare Earth Elements (La and Ce). synchysite minerals $Ca(Ce,La)(CO_3)2F$ had La concentration ranging from 13.65-25.65% and Ce concentration between 25.65-30.29% while allanite $(Ce,Ca,Y,La)_2(Al,Fe_3)_3(SiO_4)_3(OH)$ had La concentration between 1.64-5.64% and Ce concentrations of 4.39-11.77%. These monzonites also indicate enrichment in LREEs similar to the granitic gneisses with synchysites and allanites as their REE- bearing minerals but no tritomite (Fig. 12).

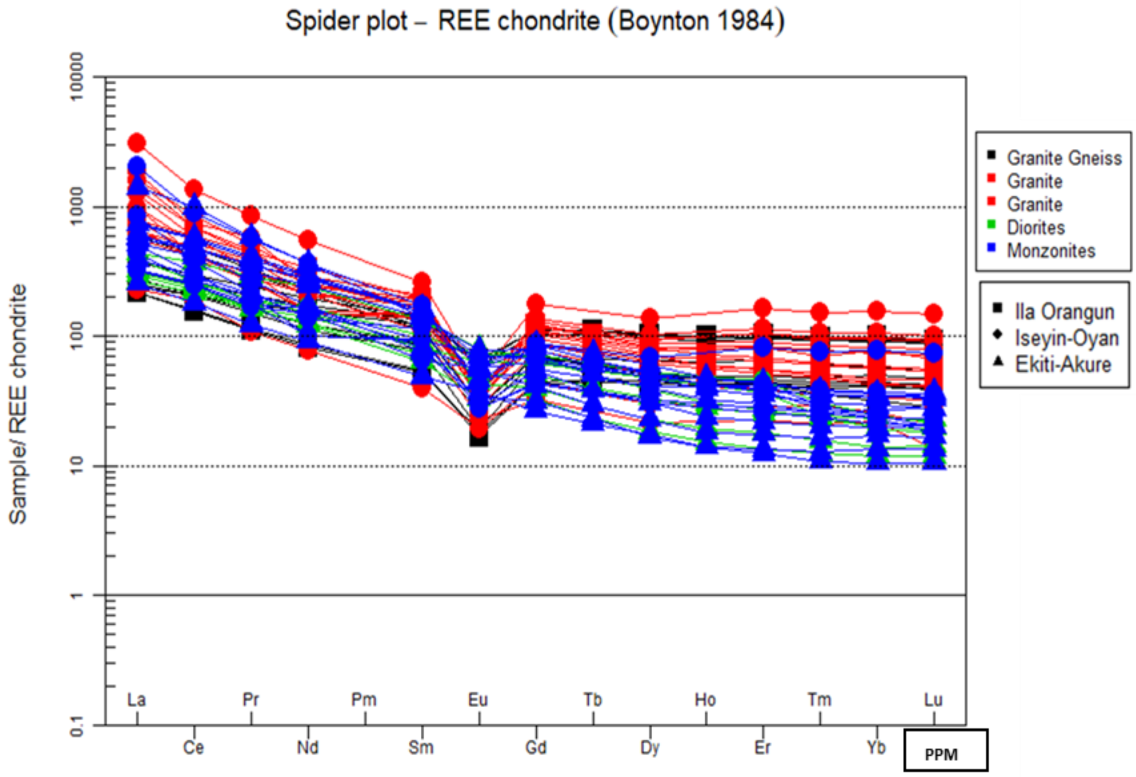

Fig. 9. Spider plot normalized by REE Chondrite (Boynton, 1984) for all granitoids within Ila Oyan, Iseyin-Oyan and Ekiti-Akure areas

Table 5. Summary of LREEs and HREEs concentrations in host minerals within the various rock types of Ila Oyan, Iseyin-Oyan and Ekiti-Akure areas

Rock type	REE minerals	LREEs (%)					HREEs (%)	
		La	Ce	Pr	Nd	Er	Y	Dy
Granitic gneisses	Synchysite	7.2-16.9	17.3-24.8	_	8.0-14.9	_	3.3-7.5	_
	Tritomite	7.7-10.5	12.4-18.1	_	4.9-8.7	_	8.5-10.3	_
	Allanite	1.9-2.7	4.7-8.9	_	2.4-3.0	_	6.3-10.2	_
Granites	Allanite	0.1-3.1	3.2-8.9	_	_	_	_	_
	Apatite	17.9-19.9	32.4-33.9	_	_	_	_	_
	Monazite	19.7-20.4	29.2-32.7	_	_	_	_	_
Monzonites	Synchysite	13.7-25.7	19.1-30.3	_	_	_	_	_
	Allanite	1.6-5.6	4.4-11.8	_	_	_	_	_

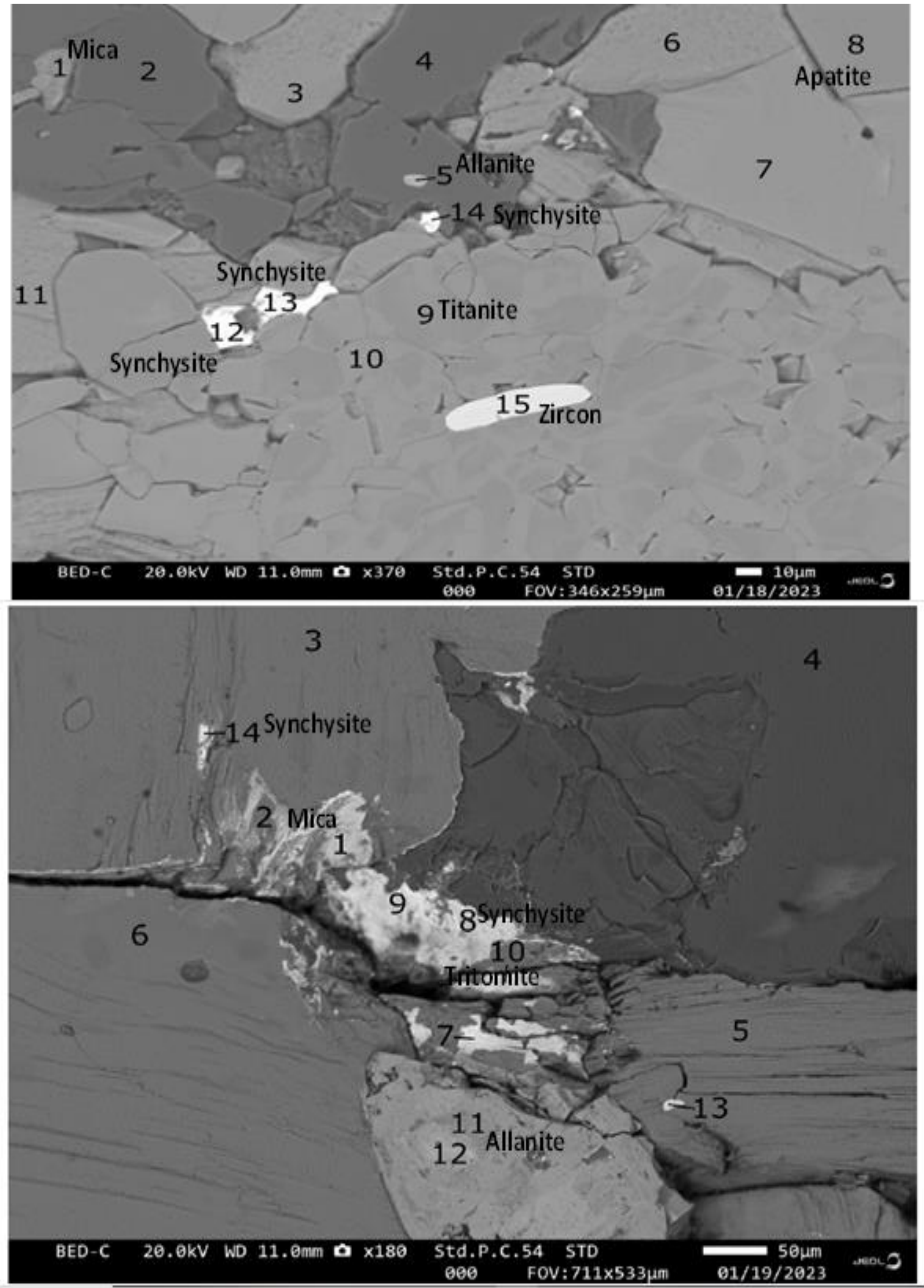

Fig. 10. Back-scattered electron (BSE) images of REE-bearing minerals synchysite, apatite, tritomite and allanite within the granite gneiss samples of Ila Oyan area

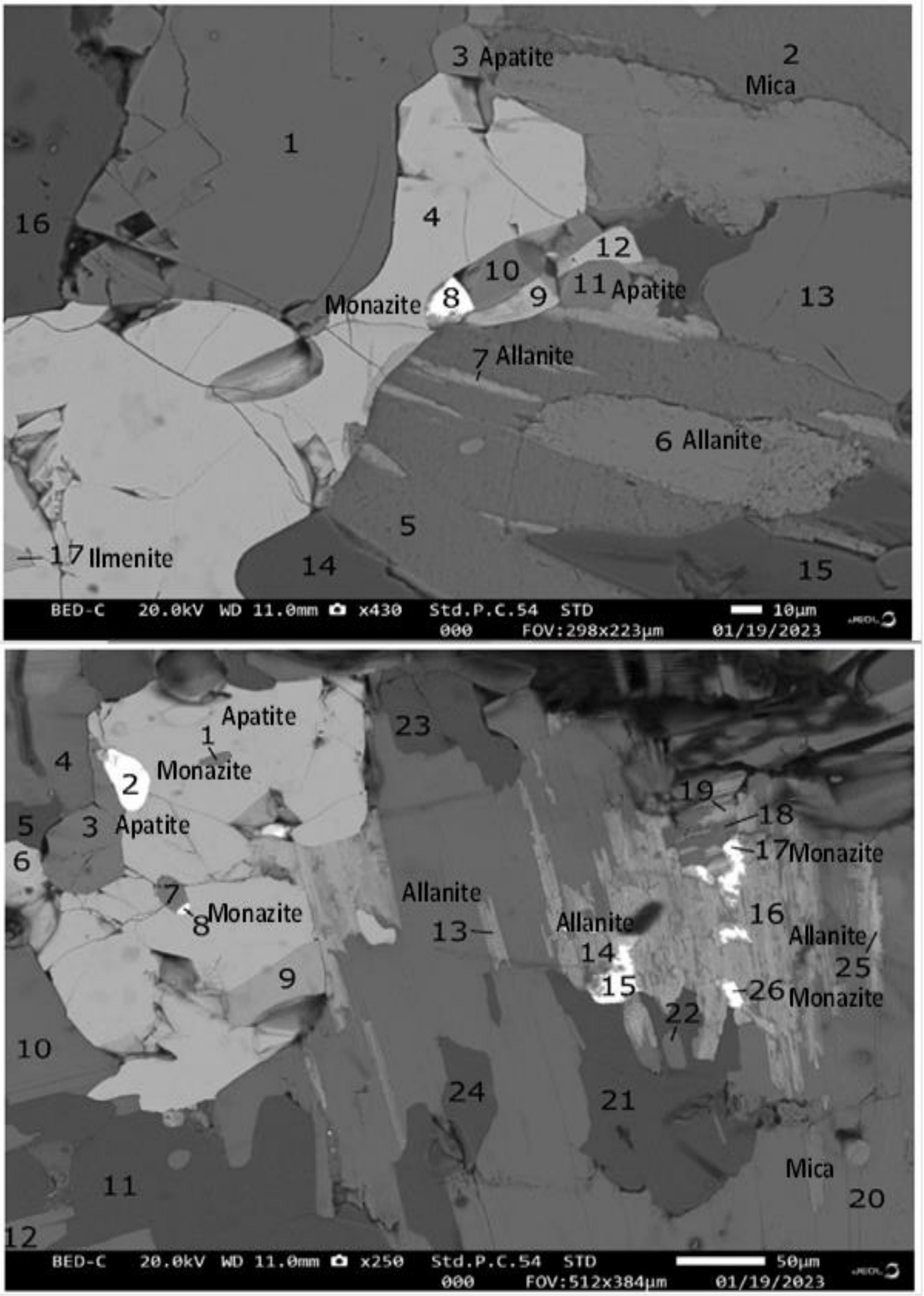

Fig. 11. Back-scattered electron (BSE) images of REE-bearing minerals allanite, monazite and apatite within the Older Granites samples of Ila oyan and Iseyin Oyan areas

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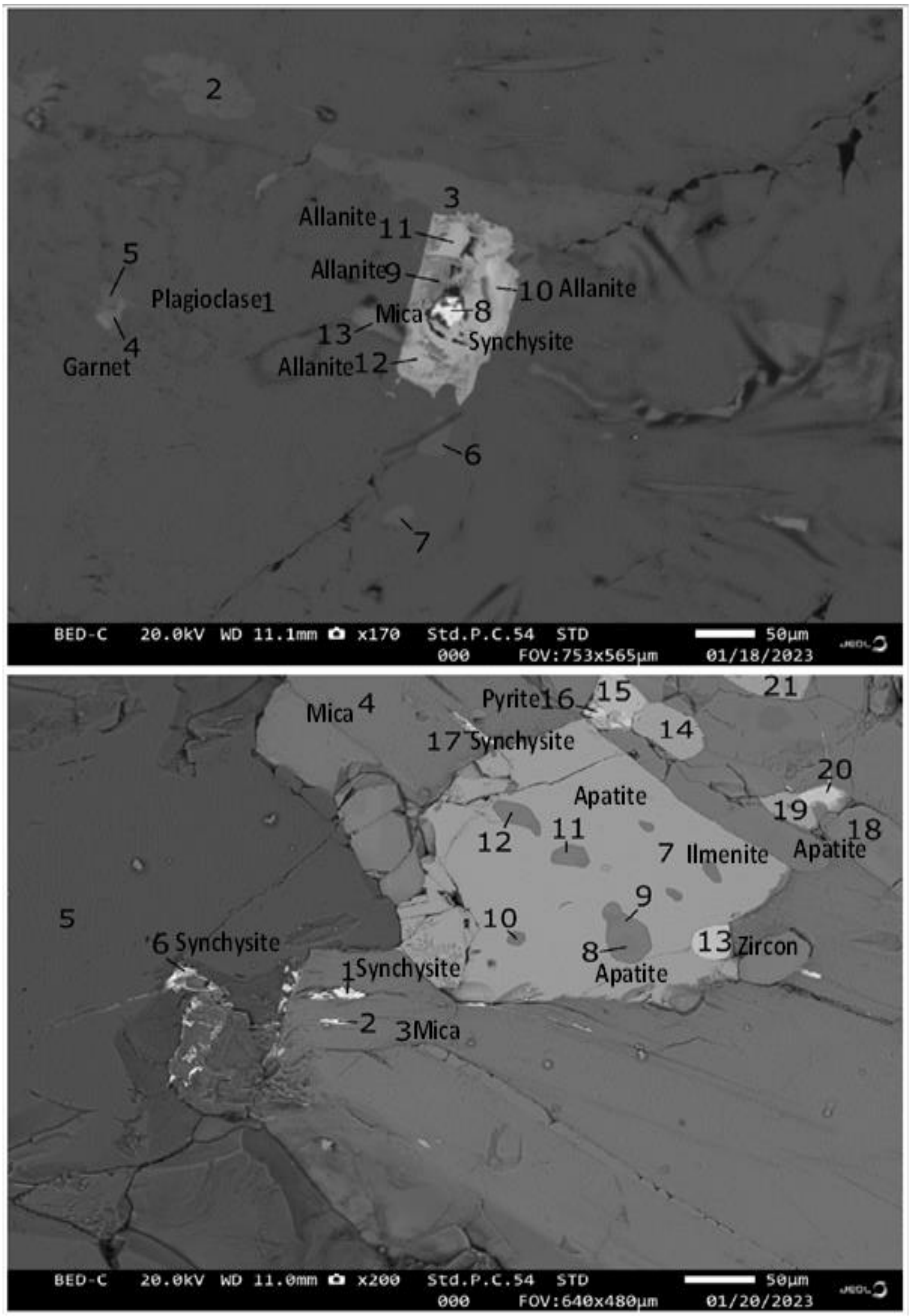

Fig. 12. Back-scattered electron (BSE) images of REE-bearing minerals allanite and synchysite within the monzonite samples of Ekiti-Akure area

Conclusion

The Nigerian Granitoids within the study areas were observed to consist of granitic gneisses, granites, diorites, and monzonites generally occurring as high rising plutons with occasional low-lying features with a general foliation trend of NE-SW directions which is typical of outcrops that have experienced Pan African Orogeny. Petrographic studies showed the presence of minerals such as quartz, plagioclase, microcline, orthoclase, muscovites, biotite, hornblende, and opaque minerals in varying proportions.

Geochemical classification indicated that the granitoids are calc-alkalic to alkalic, mostly metaluminous except for the granitic gneisses that showed peraluminous implying they are linked to areas of post continental collisions events. Tectonic discrimination plots showed granitoids were mostly associated with WPG indicating formation within plates while the Granite gneisses fell within the ORG (Orogenic events), further confirming they had experienced some level of Orogeny. All Granitoids were enriched in LREEs, depleted in HREEs, and had negative Eu anomaly similar to the granites of Dingnan and indicating moderate fractionation and preservation of alkali and plagioclase feldspars.

Mineral chemistry analysis of selected samples of granite gneisses, granites and monzonites showed the important REE-bearing minerals within these samples include synchysites, allanites, monazites, apatites and tritomites. A comparison of REEs concentrations with concentrations from Masamba, Indonesia, and Dingnan, Souther China indicated higher REEs especially the LREEs in the granites and monzonites investigated. Thus, this suggests that the granites and monzonites investigated are potential REEs mineralization zones hosted in synchysites, apatites, monazites and allanite minerals and these prospects can be further be explored.

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Author Contributions

All authors contributed to the conception and design of this research work. Materials preparation, data collection and analysis were performed by Mustapha S.O, Olatunji A.S., Abdus-salam M.O., Omotunde V.B. and Emecho-Ted O.S. The first draft of the manuscript was written by Mustapha S.O. and all authors commented on previous versions of the manuscript. All authors have read and approved the final manuscript.

Declaration of Interest

The authors declare that there are no conflicting interests.

Data Availability Statement

The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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چکیده

تقاضا برای عناصر خاکی کمیاب، جستجو برای یافتن این عناصر را از منابعی غیر از کربناتیت‌ها ضروری ساخته است و به همین دلیل، گرانیتوئیدها در حال حاضر به عنوان منابع بالقوه عناصر خاکی کمیاب در سطح جهان مورد ارزیابی قرار می‌گیرند. بخش‌هایی از گرانیتوئیدهای جنوب‌غربی نیجریه با استفاده از مشاهدات صحرایی، ویژگی‌های بافتی و کانی‌شناسی مورد بررسی قرار گرفتند. واحدهای سنگی غالب مشاهده‌شده، عبارت بودند از گنیس‌های گرانیتی، گرانیت‌ها، دیوریت‌ها و مونزونیت‌ها به همراه تزریق‌های فرعی پگماتیت‌ها و رگه‌های کوارتز. طبقه‌بندی سنگ‌زایی و جایگاه زمین‌ساختی با استفاده از داده‌های زمین‌شیمیایی، گرانیتوئیدها را در گروه کالک‌قلیایی تا قلیایی، اغلب متاآلومین و بیشتر جای‌گیری‌شده در محیط‌های درون‌صفحه‌ای که ممکن است مربوط به محیط‌های پس از برخورد باشند، قرار داد. غلظت عناصر خاکی کمیاب در گرانیتوئیدهای مورد بررسی، غلظت بالاتری از عناصر خاکی کمیاب سبک را در مقایسه با عناصر خاکی کمیاب سنگین همراه با یک بی‌هنجاری منفی Eu نشان می‌دهد که بیانگر آن است که این سنگ‌ها از تبلور مواد پوسته‌ای ذوب‌شده همراه با تبلور تفریقی پلاژیوکلاز تشکیل شده‌اند. مقادیر مجموع عناصر خاکی کمیاب سبک برای گرانیت‌ها (ΣLREEs معادل ۱۳/۱۰ تا ۱۰۸۳/۶ گرم در تن و ΣHREEs معادل ۰/۴۴ تا ۵۰/۷۹ گرم در تن) و مونزونیت‌ها (ΣLREEs معادل ۱۴/۹ تا ۷۹۵ گرم در تن و ΣHREEs معادل ۰/۳۴ تا ۳۳/۸۶ گرم در تن) به طور مطلوبی با گرانیت‌های چین (ΣLREEs معادل ۱۵۲ تا ۴۰۲ گرم در تن و ΣHREEs معادل ۱۶ تا ۵۳ گرم در تن) که استخراج REEs در آنها در حال انجام است، قابل مقایسه است. کانی‌های حاوی عناصر خاکی کمیاب در گنیس‌های گرانیتی، گرانیت‌ها و مونزونیت‌ها شامل سینکیسیت، آلانیت، مونازیت، آپاتیت و تریتومیت هستند که می‌توان غلظت اقتصادی REEs را از آنها استخراج کرد. بنابراین، این گرانیتوئیدها واحدهای سنگی بااهمیتی برای درک پتانسیل اقتصادی عناصر خاکی کمیاب در نیجریه محسوب می‌شوند.

استناد به این مقاله

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