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# Geochemistry of Pan-African Granitoids, Southwest Nigeria: Evidence of Magmatic Mixing

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# Authors' contributions

This work was carried out in collaboration between both authors. Author EEI designed the study, wrote the protocol, wrote the first draft of the manuscript, managed the literature searches and analyses of the study, while author AFA supervised the overall work from inception to completion. Both authors read and approved the final manuscript.

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# ABSTRACT

This study aimed to determine the major elemental oxides in the exposed rock types of the study area, classify these rocks on this basis and establish the relationships between the various elemental constituents and hence predict the mode of origin of the rocks. The study area falls within the south-western part of the reactivated Basement Complex of Nigeria. Field work to collect samples lasted about 21 days. About 13 fresh rock samples from the igneous suite, which range from fine to coarse grains, were collected. Thin sections were cut and petrographic studies carried out, also geochemical analysis of the samples was done at the Activation Laboratories, Ontario, Canada. Field investigation clearly revealed two distinct suite of rocks, which characterises the study area. These are the migmatite gneiss suite and the igneous suite. The migmatite gneiss suite, which consists of the migmatite gneiss and the banded gneiss, is the basement rock of the terrain. While the igneous suite, which is mainly the rocks of the older granitoids, intrude the older

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migmatite gneiss suite. Petrographic studies showed these igneous suites as having the major igneous rock forming minerals – that is quartz, biotite, plagioclase, orthoclase, and microcline. Also present was zircon and other accessory minerals. Geochemical studies of these rocks enabled their classification into granites, granodiorites, syenites, syenodiorites, and diorites using the plot of Na<sub>2</sub>O + K<sub>2</sub>O versus SiO<sub>2</sub>. Further geochemical evaluation revealed these felsic and intermediate rocks as peraluminous, non-oceanic in origin, ferroan and magnesian mixed, and alkali rich rocks. They were also grouped as within plate granites. A dual source of origin was finally proposed for the rocks based on their geochemical behaviour.

Keywords: Granitoids; fractional crystallization; magma mixing; geochemistry; igneous rock classification; Southwest Nigeria.

# **1. INTRODUCTION**

Igneous rocks have been classified in several ways, and though granitoids are the most abundant rock types in the continental crust, no single classification scheme has achieved wide spread use. Since geochemistry is vital in the evaluation and classification of igneous rocks, petrologists have relied upon geochemical evaluation schemes in the description, naming, and grouping of igneous rocks based solely on their chemical characteristics [1-5].

Some of the rocks "Older granites" of southwest Nigeria have been suggested to have been derived from a hybrid of sedimentary and igneous rocks, most probably in the form of a sedimentary geosynclinals pile (arkoses plus greywackes) interstratified with intermediate to silicic igneous intrusives and extrusives; [6,7]. These plutonic rocks (of Ado-Ekiti) southwest Nigeria crystallized at temperature range from 718°C to 950°C during the Pan-African thermotectonic event (600 ma), with pressure estimates of 4-6 kbars suggesting that these rocks represent the low-medium pressure types of granitoids.

This study aims to determine the major oxide composition in the granitoids, classify them, and further establish the relationships between the various elemental constituents and predict the mode of origin of the rocks. The study area lies between latitudes 5° 07'E and 5° 17'E, and longitude 7° 33'N and 7° 40'N and covers about 20 sq km in Ado-Ekiti (Fig. 1).

#### 1.1 Geologic Setting

The study area, Ado-Ekiti, lies within the southwestern part of the reactivated Basement Complex of Nigeria. The Nigeria Basement Complex forms a part of the Pan-African mobile belt, which lies to the east of the West African Craton and lies between the Dahomeyan of the Benin republic at the west and Cameroun at the east.

The Basement Complex of Nigeria consist of predominantly Archean polycyclic gray gneisses of granodioritic to tonalitic composition; remnants of unconformable Proterozoic cover now represented by variably migmatised metasediments which are preserved in syncollisional schist belts; and many syn-tectonic to late tectonic intrusions [8-10].

The Proterozoic sediments have been classified into the older metasediments of early Proterozoic age, and the younger metasediments of the Pan-African age. Reactivated Archean Basement often referred to as the migmatite-gneisses of the Zinder in-lier in Niger Republic in the northeast; those of Obudu and Oban Massif in southwestern Nigeria [11]; and the migmatite gneisses in neighbouring Cameroon Republic. The migmatite-gneiss complex is dominated by quartzo-feldspathic biotite-hornblende bearing gneiss; schist and migmatite, in which minerals such as garnet, silimanite, kyanite and staurolite suggest high amphibolites facies metamorphism [10].

The evolution of the basement rocks in Nigeria is associated with the overall evolution of the African continent. And from available radiometric dating data, it is believed that the evolution of the Basement rocks in Nigeria took place during five main orogenic events, which corresponds to five major ages that punctuated the Pre-Cambrian history of Africa. These are:

- Pan-African Orogeny 600-450 ma
- Kiberian Orogeny 1600-900 ma
- Eburnean Orogeny 2400-1600 ma
- Liberian Orogeny 2900-2400 ma
- Leonean Orogeny 3500-2900 ma

Among all the Orogenic events, the Pan-African is the most significant. It brought about the evolution of the older granites and the subsequent reactivations, folding, deformation and metamorphism of the Basement. Thus a more modified description of the Basement [12] recognises three main rock units viz:

- > The Older granites and related rocks
- The Schist belts
- The Gneiss-migmatite complex

The study area is characterized by the gneissmigmatite complex suite of rocks and the Older granites suites of rocks (Figs. 2a and 2b).



Fig. 1. Location map of the study area, central Ado-Ekiti, showing sampling location points and drainage system



**Fig. 2a. Geologic map of Ekiti state showing the study area location (Ado-Ekiti)** Adapted and modified from the Nigerian Geological Survey Agency (NGSA – personal communication)

# 2. MATERIALS AND METHODS

The study area was investigated during a field mapping exercise which lasted for about 21days. Representative rock samples were collected from exposed outcrops, and divided into 2 sets of A and B. Set A was cut into small sizes with a rock cutting machine and the sliced surface was glued to a glass slide and mounted on a hot plate at 80°C and later put under the mounting jig for 20 minutes, removed and allowed to cool. The samples were then reduced on the micro-cutter to about 30 microns. The samples were later covered with a covering slip and heated on the hot plate together with the section on the slide. The resulting slides were examined on the rotating stage of model M5 polarizing microscope to identify the minerals in the section and the modal count was done using a "Point Counter". Set B samples were air-dried at 60°C, crushed to a nominal minus 10 mesh (1.7 mm), mechanically split (riffle) to obtain а representative sample and then pulverized to at least 95% minus 150 mesh (105 microns). About 0.5 g of the prepared sample were put in a platinum crucible and digested using 5mls of perchloric acid (HCLO<sub>3</sub>), Trioxonitrate (V) (HNO<sub>3</sub>) and 15 mils of hydrofluoric acid (HF). This solution is stirred slowly under low heat. On cooling, the solution was diluted to 50 mils with distilled water, which was then introduced into

the ICP torch as an aqueous aerosol. The ions emit some lights in the ICP and it is these emitted light that is converted to electric signal by a photomultiplier in the spectrometer.

Geochemical analyses for major, trace and rareelements was carried out at the Activation Laboratory, Ontario, Canada using the Inductively Coupled Plasma-Mass Spectometry (ICP-MS) analytical method. While the petrographic studies were done at the University of Ibadan, Ibadan-Nigeria.

#### 3. RESULTS

#### 3.1 Rock Occurrences and Textures

The study area is characterized by two distinct suites of rocks: the underlying migmatite gneiss suite and the intrusive granitoids (Fig. 2b).

The migmatite suite was not analysed in the course of this study due to lack of exposed fresh outcrop but is believed to be mainly migmatite gneiss and banded gneiss [12].

The granitoids are the Older Granites and related intrusive rocks which intrude the underlying migmatite suite. The granites and granodiorites occur in the northwest and north central part of the study area (along Ikere-Ekiti road), extending to the eastern part. They are phaneritic in texture, leucocratic in colour, and are relatively less in abundance than other rock types. The Syenites/syenodiorites occur as extensive outcrops along the Oyin road of Ado-Ekiti at the central eastern portion of the study area, extending to the southern part. They are medium to coarse grained, mesocratic in colour, intermediate in silica saturation and more abundant than the granite/granodiorites of the study area. The diorites are found occurring as extensive outcrops scattered over the study area that is western, central, eastern, and southern portions of the study area (Fig. 2). The diorites from study area are generally of medium size grains and mesocratic in texture.



Fig. 2b. Geologic map of the study area (central Ado-Ekiti) showing the two distinct suites of rocks

Details of the modal analyses from petrographic studies and major oxides analyses of representative samples are given in Tables 1 and 2 respectively while Table 3 shows the range values of major oxides.

Average SiO<sub>2</sub> content varies from 58.61% wt in the diorites to 66.80% wt in the granites. Al<sub>2</sub>O<sub>3</sub> ranges narrowly from 14.14% wt in the granites to 16.35 % wt in the syenites and syenodiorites. The diorites have the highest average Fe<sub>2</sub>O<sub>3</sub> content of 7.91% wt, which is almost twice that of the granites (4.39% wt) that has the least value of all the rocks sampled. Again the diorites have the lowest average alkali (Na<sub>2</sub>O + K<sub>2</sub>O) value of 5.70% wt, while the syenites have the highest (9.56% wt). Average MgO content varies widely from 0.54%wt in the syenites to 3.44% wt in the diorites. In CaO content, the granites have the least average value (2.72% wt), while the diorites have the highest value of 6.11% wt.

# 3.2 Petrographic Analyses

Thin sections of the representative samples were studied under the microscope and results aided the identification of the various rock types.

#### 3.3 Geochemistry

#### 3.3.1 Major oxides

About 10 major oxides (as tabulated in Table 2) were analysed for and used to evaluate the rocks of the study area.

# 4. DISCUSSION

#### 4.1 Nomenclature of Rocks

A simplified form of the IUGS classification scheme for plutonic rocks using their average modal composition (Quartz - Alkai feldspar -Plagioclase feldspar) (Fig. 3), differentiated the granitoids from study area as granites, granodiorites, syenites, syenodiorites, and diorites. This classification was also supported by the plot of  $(Na_2O + K_2O)$  (Alkali-Lime-Index) against SiO<sub>2</sub> [13] (Fig. 4). (Granites=Fr1 and Fr2; Granodiorites = Fr3 and Fr13: Svenites/svenodiorites = Fr8, Fr9, Fr10 and Fr11; Diorites = Fr4, Fr5, Fr6 and Fr7). According to [14], these rocks are syn-tectonic to late tectonic rocks. They range from medium to coarse grained rocks and generally trend in the northeast - southwest direction. These granitoids are more dominant in the north-north and south-south portion of the study area thereby creating a form of valley in the central portion of the study area.

### 4.2 Classifications of the Rocks

From the plot of  $Fe_2O_3/(Fe_2O_3+MgO)$  (the Fenumber of the rocks) against  $SiO_2$  [15] (Fig. 5), the granites, syenites and syenodiorites from study area are ferroan (iron rich) while the granodiorites and diorites are magnesian (magnesium-rich).

The iron-enrichment also tends to increase with increase in silica until after 63%wt SiO<sub>2</sub> point where the value is noticed to begin to drop.

Sample no/elements	Quartz	Plagioclase feldspar	Alkali feldspar	Biotite	Opaques	Total %
Fr 1 (Granite)	43	14	30	10	3	100
Fr2 (Granite)	44	13	30	10	3	100
Fr3 (Granodiorite)	41	30	17	9	3	100
Fr4 (Diorite)	8	62	14	11	5	100
Fr5 (Diorite)	10	66	12	9	3	100
Fr6 (Diorite)	5	65	16	10	4	100
Fr7 (Diorite)	6	68	13	8	5	100
Fr8 (Syenite)	5	19	63	8	5	100
Fr9 (Syenite)	6	20	61	9	4	100
Fr10 (Syenite)	9	23	52	10	6	100
Fr11 (Syenite)	6	25	55	9	5	100
Fr13 (Granodiorite)	40	31	16	11	2	100

Table 1. Modal analyses of the granitoids from study area

#### Igonor and Abimbola; JGEESI, 5(4): 1-17, 2016; Article no.JGEESI.19041

Oxide	Fr1	Fr2	Fr3	Fr4	Fr5	Fr6	Fr7	Fr8	Fr9	Fr10	Fr11	Fr12	Fr13
<u>(//)</u> SiO	67.02	66 57	64.25	57 61	50 50	59.40	59 76	60.62	60.29	62.05	61.20	46.06	65 59
3102	07.02	00.57	04.25	57.01	59.59	56.49	56.70	00.05	00.38	03.05	01.20	40.90	05.56
$IIO_2$	0.82	0.45	0.77	1.39	1.36	1.47	1.27	0.70	0.97	0.68	0.81	3.50	2.10
$AI_2O_3$	14.25	14.03	15.01	14.84	15.18	15.35	15.93	15.53	16.68	15.76	17.43	14.90	14.92
$Fe_2O_3$	4.01	4.76	5.47	8.19	7.82	8.32	7.30	8.66	7.21	7.43	5.53	15.09	12.77
MnO	0.03	0.03	0.14	0.19	0.17	0.19	0.12	0.16	0.14	0.14	0.09	0.17	0.16
MgO	0.65	0.78	2.07	3.53	3.07	3.51	3.66	0.68	0.58	0.37	0.53	5.37	4.83
CaO	3.06	2.88	4.19	6.57	6.24	6.10	6.03	2.64	3.15	2.36	3.52	7.44	6.97
Na <sub>2</sub> O	2.82	2.71	3.06	3.57	3.34	3.21	3.78	3.06	4.01	3.44	4.41	3.03	2.78
K <sub>2</sub> O	5.87	5.71	3.96	2.29	2.59	2.35	2.17	6.09	5.49	6.12	5.63	1.86	2.93
$P_2O_5$	0.50	0.84	0.40	0.47	0.68	0.47	0.44	0.25	0.28	0.21	0.27	0.93	0.66
LOI	1.11	1.14	0.87	0.85	0.59	0.83	0.80	1.62	1.21	0.57	0.72	0.49	1.00
Total	100.10	99.88	100.20	99.49	100.60	100.30	100.30	100.00	100.10	100.10	100.10	99.73	99.69

Table 2. Results of major element geochemistry of granitoids from study area

Fr1 and Fr2=Granites; Fr3 and Fr13 = Granodiorites; Fr8, Fr9, Fr10 and Fr11 = Syenites/syeno-diorites; while Fr4, Fr5, Fr6 and Fr7 = Diorites. Fr12 plotted in the region of gabbro, but was discarded as error probably due to man or machine. So it is not included in the results analysis and discussion

Oxides	Ranges (in percentage)
SiO <sub>2</sub>	46.96 - 67.02
$AI_2O_3$	13.92 – 17.43
Fe <sub>2</sub> O <sub>3</sub>	4.01 - 15.09
MgO	0.37 – 5.37
CaO	2.36 - 7.44
Na₂O	2.71 – 4.41
K <sub>2</sub> O	1.86 – 6.12
MnO	0.032193
$P_2O_5$	0.21 – 0.68
TiO <sub>2</sub>	0.45 – 1.21
LOI	0.49 – 1.21

Table 3. Showing range of major oxides of rocks from study area

According to [16], this plot suggests that iron enriched melts derived from reduced source (either tholeiitic or mildly alkali) make important contributions to ferroan granitoids, while the magnesian granitoids in contrast are probably related to island arc magmas which follow relatively oxidizing trends. [17], suggested that a

wide range in the Fe-number of rocks is probably related to differences in the source rock composition, while [18,19], suggest it is also related to the degree of melting undergone by the rocks.

By means of the plot of  $Na_2O + K_2O - CaO$ (Modified-Alkali-Lime-Index MALI) versus SiO<sub>2</sub>, (Fig. 6) the alkali character or otherwise of the rocks were ascertained [15]. This plot shows the diorites plotting as cal-alkalic rocks; the granites and granodiorites fall within the field of alkalicalcic rocks, while the rest of the rock samples syenites and syenodiorites, display the most enrichment in alkali content as they fall within the field of alkali rocks. It is observed that the diorite samples all display a negative MALI value and they plot on the negative axis of the MALI vs SiO<sub>2</sub> plot. According to [15], one explanation for a suite of rocks that crosses the trend line would be that it involves mixing of more than one magma series. Though it is possible however, that differentiation can cause a suite of rocks to become more alkali.



Fig. 3. A simplified form of the IUGS classification scheme for plutonic rocks using the modal composition of the rocks from the study area [20]



Fig. 4. Plot of Na<sub>2</sub>O + K<sub>2</sub>O vs SiO<sub>2</sub> showing the rocks from study area differentiated into their different names (13)



Fig. 5. Plot of Fe<sub>2</sub>O<sub>3</sub>/(Fe<sub>2</sub>O<sub>3</sub> + MgO) vs SiO<sub>2</sub> differentiate rocks into ferroan or magnesian granitoids

Rocks from study area (the granites and syenites) plot as ferroan and (the granodiorites and diorites) magnesian granitoids [15]

On the plot of  $Al_2O_3/Na_2O + K_2O$  versus  $Al_2O_3/CaO + Na_2O + K_2O$  (Fig. 7), all the rocks of Ado-Ekiti area plotted as peraluminous rocks. The diorites plot as the strongest peraluminous rocks, while the granites and syenites/syenodiorites are the weakest peraluminous.

For the strongly peraluminous rocks, this could be as a result of the parent melt having more aluminium than can be accommodated in feldspar.It is also like that they have another aluminous phase present, which could be aluminous biotite for the weakly peraluminous, or muscovite, garnet, or an Al<sub>2</sub>SiO<sub>5</sub> polymorph for the strongly peraluminous [15]. According to [21] granitoids which are strongly aluminous and of high silica content, are S-type granitoids. Or that they were formed from the melting of metasedimentary rocks [22], or by the melting of

mafic rocks in water-excess saturation [23]. [24] also believes that partial melting of a variety of other sources can produce rocks of similar granitic composition. From the foregoing, it can be deduced that none of all the rocks studied shows any positive evidence of sedimentary origin moreso as their mineral assemblages are generally that of quartz + feldspar + biotite  $\pm$  zircon  $\pm$  hornblende. Hence they are taken to be of magmatic origin. In the ternary plot  $Fe_2O_3 - (Na_2O+K_2O) - MgO$ (Fig. 8) [25], the granites and granodiorites plotted as felsic while the syenites, syenodiorites, and diorites all plotted as mesocratic. From the ternary plot of MgO-CaO-Al<sub>2</sub>O<sub>3</sub> (Fig. 9), there is an indication that the rocks of study area have been formed from the differentiation and fractionation of an originally magmatic melt [26]. These rocks have equally been formed in a continental environment as shown by ternary plot of TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O (Fig. 10) [27].



Fig. 6. Plot of Na<sub>2</sub>O + K<sub>2</sub>O – CaO vs SiO<sub>2</sub>, the rocks from study area range widely from alkali to calcic granitoids [15]





Fig. 7. The plot of Al<sub>2</sub>O<sub>3</sub>/(Na<sub>2</sub>O+K<sub>2</sub>O) vs Al2O3/(Na<sub>2</sub>O+K<sub>2</sub>O+CaO)which differentiates the rocks from study area as peraluminous rocks [28]

Igonor and Abimbola; JGEESI, 5(4): 1-17, 2016; Article no.JGEESI.19041





(The plot show the granites and granodiorites are felsic, while the rest of the samples are mesocratic)



Fig. 9. Plot of CaO – MgO – Al<sub>2</sub>O<sub>3</sub> showing the rocks from study area plotting in the magmatic field and displaying richness in alumina [26] M=magmatic field, S=sedimentary field

#### 4.3 Differentiation Index and Rock Evolution

Selected major oxides and trace elements were plotted against silica in order to deduce their differentiation pattern (Figs. 11a-11j). It is observed in the rocks of Ado-Ekiti area that with increase in silica, there is a corresponding decrease in CaO, TiO<sub>2</sub>, MgO, MnO, P<sub>2</sub>O<sub>5</sub>, Sr, and Fe<sub>2</sub>O<sub>3</sub>, but K<sub>2</sub>O and Rb increases with increase in silica content. Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and Y, initially increases with increase in silica until the 60 %wt point of SiO<sub>2</sub> when an inflection point is noticed, i.e. a decrease in value of Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O<sub>3</sub>

and Yittrium begins to set in. According to [29] the (inflection point) observed in (Figs. 11c and 11g), reflects multiple magma series. contamination of magma, or possibly the onset of significant plagioclase fractionation. It is also taken to indicate either the entry of a new phase during crystal fractionation or the loss of a phase during partial melting [30], while the scattering in Ba, Nb and Ta vs SiO<sub>2</sub> (Figs. 11c and 11g) show non-compatibility of the elements with enrichment of silica during formation and signifies a changing fractionation assemblage during fractional crystallization or that the rocks are not from a single magma.



Fig. 10. Plot of  $P_2O_5 - TiO_2 - K_2O$  showing the rocks from study area plotting as continental rocks [27]



Igonor and Abimbola; JGEESI, 5(4): 1-17, 2016; Article no.JGEESI.19041







Igonor and Abimbola; JGEESI, 5(4): 1-17, 2016; Article no.JGEESI.19041











Plot B,C,G, I and J show positive reflections when  $SiO_2$  content reaches between 62% and 65%, while plot D, E, F and H registers negative reflections at similar points

# 5. CONCLUSION

To infer that a large scale direct fractional crystallization of a single parent basic magma was responsible for the formation of all the rocks of Ado-Ekiti area is impossible considering that: inflection points in the plot of Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and Yttrium vs SiO<sub>2</sub> all points to multiple source origin for the rocks; wide range in Fe-number; and negative MALI signature which supports the theory of mixing of more than one magma series or partial melting and contamination of source; and also the ternary plot of MgO-CaO-Al<sub>2</sub>O<sub>3</sub> indicates rocks derived from fractionation and differentiation of a granitic or basaltic melt.

Thus considering all these contrasting points, it could be suggested that a model involving dual mode of formation, that is, partial melting and probably augmented by an earlier crystallization is adopted for these rocks. It would also further be proposed that a basic magma (cal-alkaline source), which was the parent magma of these rocks, underwent fractional crystallization during emplacement to produce the initial diorites. As the residual melt phase ascended, it caused a partial melting of the crustal rocks to form an acidic magma, which eventually intruded and crystallized as syenites, syenodiorites, granodiorites, and granites, which are the major rock types found in the study area.

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# COMPETING INTERESTS

Authors have declared that no competing interests exist.

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