FUOYE Journal of Pure and Applied Sciences

Available online at https://fjpas.fuoye.edu.ng

Geochemical Study of Precambrian Metavolcanic Rock Around Bunu Area, Part of Kabba-Lokoja-Igarra Schist Belt, SW Nigeria

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ARTICLE INFO

Received: Feb. 2023
Accepted: July 2023

Keywords:
Petrogenesis, amphibolites, tholeiitic, sub-alkaline, metavolcanics, Precambrian.

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DOI: 10.55518/fjpas.LDUQ2018

Abstract

In Bunu area, Precambrian meta-sedimentary rocks are extensively exposed and interbanded with amphibolitic rocks. These dark green foliated rocks, known as amphibolites, are mostly made of green hornblende, plagioclase, and quartz, with lesser amounts of pyroxene, quartz, and epidote. The amphibolitic rocks are calc-alkaline Island Arc tholeiites by nature, but their initial chemistry has been extensively altered both before and after their emplacement, according to a geochemical investigation. Geochemical analysis also revealed that Ba is enriched over Rb signifying that the rocks that were formed from K feldspar-rich protoliths and relatively high Cr and, occasionally, Ni concentrations suggest the existence of considerable amounts of mafic elements. Very low K_2O, high Al_2O_3, low TiO_2, Nb, and Y contents, and low Al_2O_3 concentration are all characteristics of back-arc or island-arc settings in Bunu amphibolites. The protoliths of the amphibolites were igneous tholeiitic basalts that were extruded in a back-arc tectonic setting, close to a subduction zone, according to geochemical characterization. The work supports the orogenic nature of the Pan-African event, which occurred in the region around 600 Ma and resulted in regional metamorphism and the origin of the amphibolites magmas from upper mantle melting. The original properties of the fabric of the parent basaltic rocks may have changed as a result of later metasomatic and metamorphic processes. The study also reveals similarities in petrological and geochemical properties between metavolcanic rocks studied in this area and those in Zuru Schist Belt to the north and the Ilesha Schist Belt to the west.

1.0 Introduction

The Nigerian Basement Complex forms the southern part of the Trans-Saharan mobile belt and situated between the West African craton in the west, the Congo craton in the southeast and the East Saharan block (Figure 1) in the northeast[1]. According to Rahaman [2] the rocks in Basement are grouped into four lithological units namely: migmatite-gniesses, with relics of ancient metasediments, younger low to medium grade metasediments/metavolcanic rocks, Older Granite suites including granodiorites, diorites, charnockites and unmetamorphosed felsic and basic dykes including quartz veins, pegmatite, aplite and dolerite.
According Dada [3], Okonkwo and Ganev [4], these Basement rocks have recorded at least four major tectonic cycles of deformation, metamorphism and remobilization in the Liberian, Eburnean, Kibarian and Pan-Africa and have evolved over a long period of time from Archean (> 2700 Ma) to the Neoproterozoic (< 600 Ma). Because of this long age variations, several geological settings evolved and characteristics of these rocks both mineralogical and geochemical also varied. To be able to unravel these variations, detailed geological mapping, petrological and geochemical fingerprinting are required.

Rahaman [2] believed that the mafic rock (amphibolites) of the schist belts were derived from two different magmatic sources; one with ocean floor affinities and the other with island arc (characteristic of ocean closure) into which the Pan-African granites intruded See Figure 1.

According to Ako [5], amphibolite parent rocks include basalt flows, tuffs, gabbroic rocks, and various combinations of shaly limestone or calcareous rocks. These rocks all have equivalent chemical compositions.

Viewpoints on the genesis of amphibolites, for instance, differ [6], [7]. Three primary formation mechanisms have thus far been put forth. They include altering existing rocks through metasomatic processes, metamorphosing sediments with the right composition, and metamorphosing basic igneous rocks [6, 8]; According to Leake [9] in Ako [5], para-amphibolites are decarbonated combinations of pelitic sediments and calcite or dolomite, while meta-igneous amphibolites are entirely re-crystallized dolerites, basalt, or basic tuffs. In order to distinguish between ortho- and para-amphibolites, Leake [9] presented a strategy based on geological nature, quantity of elements and their link to recognized igneous and sedimentary patterns. When comparing ortho-amphibolites and para-amphibolites,
this method is thought to be a more reliable basis for chemical criteria than the absolute concentration level. In ancient Precambrian terrains, amphibolites have been useful in illuminating the history of crustal evolution [10], [11]. The nature and genesis of the area where they occur are typically constrained by their petrochemistry [12].

The majority of research on amphibolites found in the Precambrian basement complex of southwest Nigeria tends to focus on their field relationships, petrological descriptions, mineralogical characteristics, and chemical compositions. As an illustration, Olade and Elueze [13] recognized and described four textural varieties of the Ilesa amphibolites as massive, banded, schistose, and strongly gneissic textural types, while Elueze [14] recognized various ore minerals in the Ilesa amphibolites and also described their metallographic characteristics. In contrast to Ajayi [15], who proposed a dual parentage for these amphibolites, Elueze [14] and Olade and Elueze [13] have suggested a tholeiitic basalt precursor and emplacement within the continental crust for the Ilesa amphibolites.

Various efforts to unravel the petrogenetic affinity of amphibolites in most regions of

Nigerian Basement Complex have been dogged with controversy [16]. Little to no detailed geochemical and petrogenetical work has been done on the eastern flank of the Kabba-Lokoja-Igarra schist belts. Therefore, this present investigation seeks to generate and utilize geochemical data to unravel the nature and origin of the amphibolites around Bunu area in the Kabba-Lokoja-Igarra schist belt, southwestern Nigeria.

1.1 Physical and Geologic Settings of the Study Area

The study area is within the southwestern Basement complex of Nigeria and located between latitude 8^0 $00'$ N to 8^0 15^l N and longitude 6^0 $00'$E to $6^0 15^l$ E (Fig 2a). Politically, the area is within the western senatorial district of Kogi State, north central Nigeria and covers part of three Local Government Areas of the State, namely Kabba/Bunu and Ijumu. The main study area around Bunu includes villages like Suku, Osomule, Iyah-Loke and Ayedero. It is covered by Sheet 226 Aiyegunle SW topographic map on a scale of 1:50,000 with an area of about 756.25 km^2. The Study areas are characterized by rugged and undulating topography with elevation about 700m to 1300m above sea level (Figure 2b).

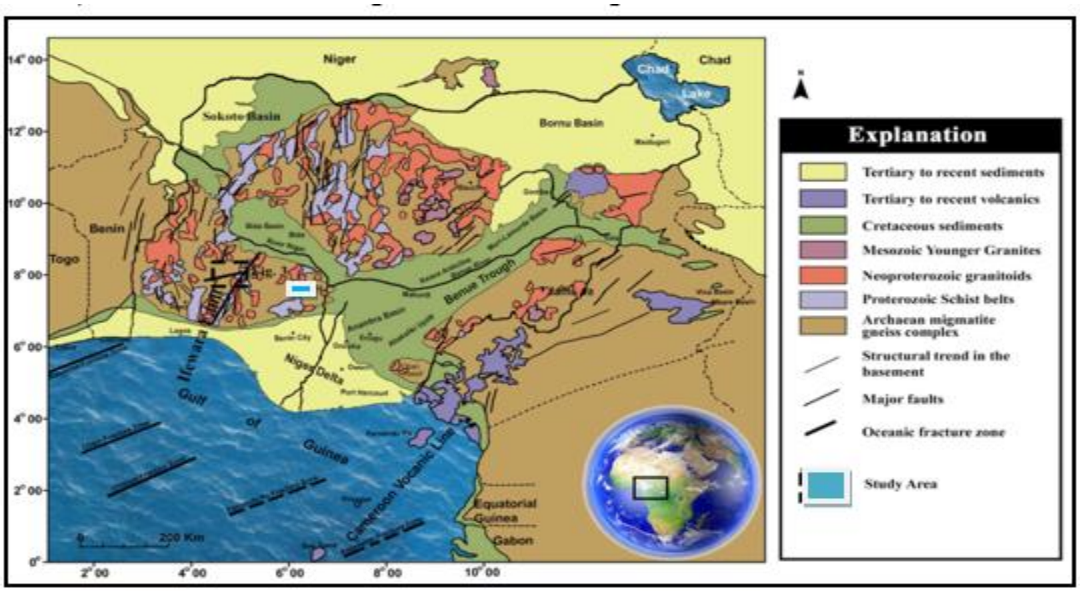

Figure 1: Simplified Geological map of Nigeria. Inset is the map of Africa showing the location of Nigeria. The blue square is the approximate location of Bunu area (after [1]).

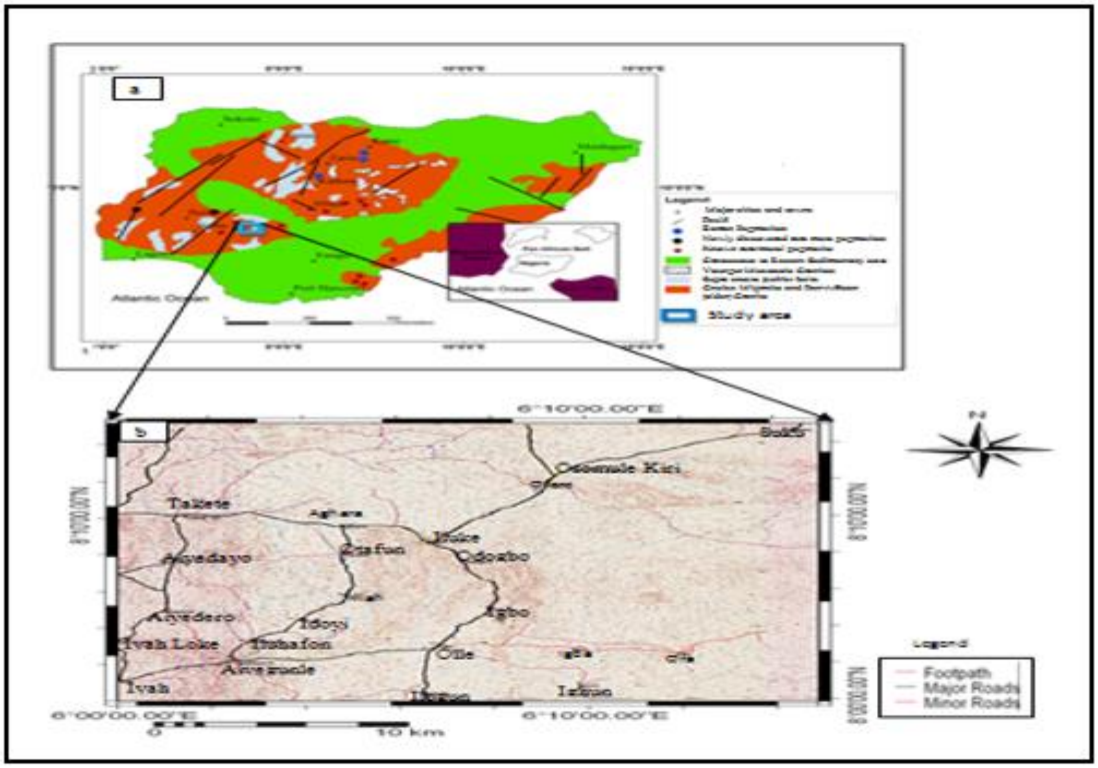

Figure 2: (a) Geological map of Nigeria showing Bunu area within the SW basement (Inset: Location of Basement Complex of Nigeria between the West African and Congo Cratons) and (b) sheet 226, Aiyegunle SW topographic map covering the study area (Modified from [17, 18].

2.0 Materials and methods

Systematic field mapping was carried using Aiyegunle SW sheet 226 as base topographic map. Traverses were planned along motorable tracks, footpaths and cattle tracks using motor bike to gain access, measurement taken using GPS, Compass clinometer etc. In areas of good exposure, especially across geological and structural contacts traverses were also taken on foot and along stream channel; fresh samples were collected for laboratory test

Fresh representative rock samples were selected for petrographic study that involved cutting the rock samples into thin flat size, dried and grinded to about 3mm and further reduced to 0.3 mm (30 microns) after which they were mounted on a glass slide to become clear under the microscope.

Some selected amphibolite samples were sent to the Geosciences Laboratories (Geo Labs), Ontario Canada for geochemical analysis. At Geo Labs, proper samples preparation conducted include washing, crushing, pulverizing and mineral separation where applicable before sample preparation.

Closed Vessel Multi-Acid Digest was used which is best for ICP-MS and XRF analyzes and it is designed for the thorough dissolution of silicate rock samples.

2.1 X-Ray Fluorescence (XRF)

This method was chosen because it may be used to identify and quantify the elements present in solid, powdered, and liquid samples without causing any damage to the materials themselves. It is the most popular analytical method for figuring out the chemistry of the major and trace elements in rock samples [19]. XRF was only employed for significant parts in this study. The first step in the process is to select your target audience. The second step is to identify your target audience and then develop a strategy to reach them. The XRF method is based on the fluorescence that results from the release of quantum energy when an atom is freed after being exposed to X-rays. The X-ray beam, produced by the Molybdenum tube, is reflected on a multilayer monochromator resulting in a monochromatic X-ray beam. This method was employed to determine the major oxides in the metavolcanic rocks in the study area.

2.2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) is developed for the measurement of minor and trace elements in prepared non-mineralized geological samples using either a closed or open vessel multi-acid digestion process. For elements found in acid-resistant phases (such as garnet, zircon, monazite, xenotime, and/or chromite), data acquired using the IMC-100 method are thought to be more accurate due to the closed vessel digestion's increased efficiency [20]. Following preparation, the sample powder was mixed and dried for 12 hours at 110 degrees Celsius. ICP-MS was used to measure trace and REE contents, and 0.25 g of powdered rock and 2 g of Na_2O were properly weighed into a graphite crucible. The mixture was heated for nearly an hour at 700^oC, followed by water extraction and leaching. HNO_3 was used to dissolve the hydrated oxide precipitate, and ICP-MS was used to analyze the results [20].

For all elements examined, precision and accuracy based on duplicate analyses of an internal basalt standard [21] and USGS standard G-2 are 5%. The geochemical data were processed and analyzed using PETROGRAPH version 1.0.2 created by M. Perelli, Department of Earth Sciences, University of Perugia, and then plotted on several discrimination diagrams (Italy).

For spider diagrams for all the samples, the primordial mantle normalization of [22] and [23] was employed. The variables proposed by [42] for normalizing samples to chondrite were also employed for all samples.

3.0 Results

3.1 Field Relations.

According to Kolawole [25], the rocks that outcrop in the area are; the migmatite-gneiss and migmatized schist, foliated and massive quartzite, quartz schist, and mica schist, as well as inter-banding amphibolitic schist that make up the gneiss-metasedimentary/metaigneous rock units. Large amphibolites are mainly found in the Osomule-Suku and IyahLoke-Ayedero regions. He opines [25] that granitic plutons in the northernmost part of the study area are composed of fine-medium grained granites, a porphyritic and medium-coarse grained granodiorite, and fine-medium grained granite-gneiss with local garnetiferous variants. These Older Granite series rocks are largely seen in the area as low whale backs and pavements, phyllites, quartz-mica schist, and amphibolite are found in comparatively lowlands while migmatite-gneiss and

quartzite mostly form highlands in the area. Both felsic quartzo-feldsphatic veins, pegmatites, aplites and mafic dykes have gradational or acute contact relationships with country rocks and intrude all these rock groups (Figure 3).

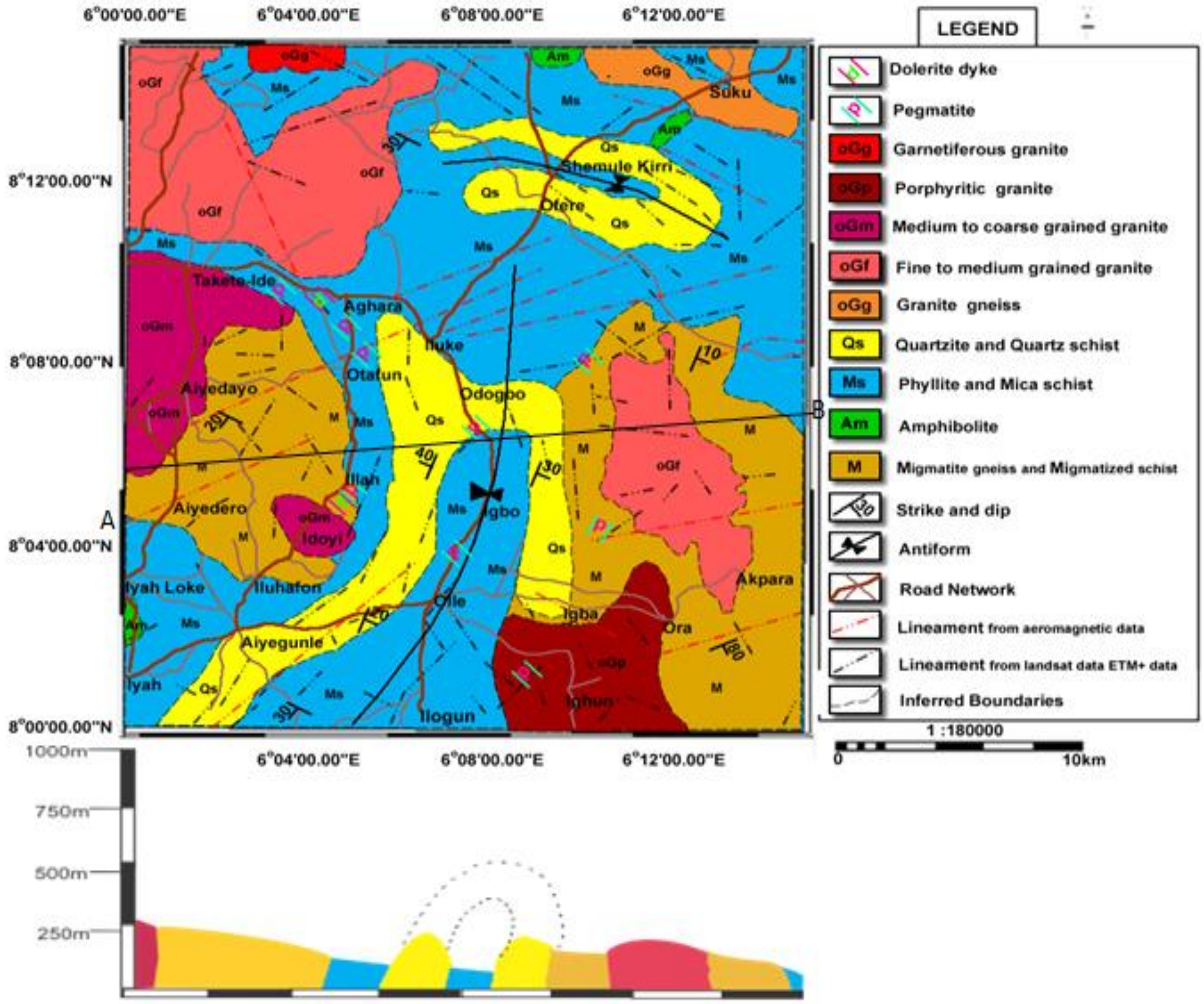

Figure 3: (a) Geological map and (b) cross section of Bunu area, Aiyegunle SW Sheet 226 [25].

3.2 Petrography

At Osomule and to the north of Ofere, small, narrow metabasic dykes and lenses of amphibolite interband the gneiss-schist suite. The amphibolite is a dark green color, with nearly glossy black hornblende crystals on newly formed surfaces and brown crusts on aged surfaces (Figure 4). The well-foliated, fine- to medium-grained amphibolites is composed primarily of green hornblende, plagioclase, and quartz. It is distinguished by the presence of quartz and epidote, as well. The planar orientation of tabular hornblende phenocrysts embedded in a finer-grained matrix of tiny subhedral plagioclase crystals and the calcium-rich environment are what cause the foliation. Plagioclase and hornblende are the two main mineral components of amphibolites. Additional subordinate minerals include opaque typically makes up less than 5% of the modal composition, quartz, chlorite, biotite, pyroxene, and biotite [26]. The rock is characterized by narrow, quartz- and feldspar-containing felsic veinlets that range in width from 2 to 4 mm and run parallel to the foliation trend. Some of the alteration minerals found in the samples include green hornblende, chlorite, and epidote (Figure 5).

The modal proportion of the minerals that make up amphibolite. The mineral assemblage of the rock is composed of hornblende, plagioclase, quartz, actinolite-tremolite, biotite, garnet, and calcite. The majority of amphibolite contains pyroxenes, while the felsic variation has well-developed epidote and microcline [15] (Table 1).

Table 1: Modal Composition of Metaigneous Rock from Bunu area

Mineral	Amphibolite (%)
Plagioclase	10
Biotite	15
Quartz	13
Hornblende	52
Pyroxene	8
Opaque minerals	2
Total	100

Figure 4: Field photograph of outcrop of amphibolitic schist with narrow felsic veinlets parallel to the general foliation trend along Ofere-Suku road (Location: 08° 13' 04.9'N; 006° 10' 30.1"E).

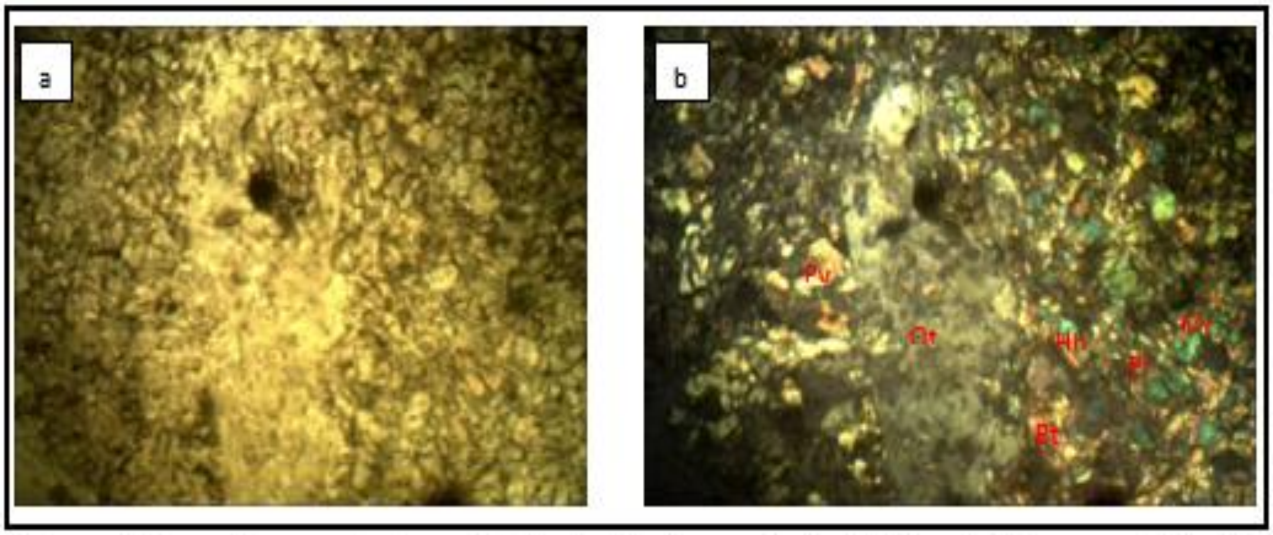

Figure 5: Photomicrograph of amphibolite in (a) plane polarized light and (b) cross polarized light. Qt=Quartz, Bt=biotite, Hb=Hornblende, Py=Pyroxene, Pl=Plagioclase, Mc=Muscovite (Mag. X 50).

3.3 Geochemistry

Bulk chemical analysis of all the major rock units that outcrop in the study area was carried out in order to quantify the chemical composition of the rocks and consequently infer the petrogenetic affinities and tectonic setting of the rocks.

A straightforward statistical method called discriminant analysis is used to divide samples into new groups based on a number of different criteria. In this study, many different factors are looked at in order to find the one that best categorizes the data. On bivariate and triangular diagrams, the axes are defined using the strongest discriminants. The boundaries between the various groups of samples are drawn, and the separate groups of samples are shown as either elemental concentrations or derived discriminant functions depending on the elemental concentration. Unknown samples are then categorized in accordance with the stated field. This has been successfully used to look into the relationship between the tectonic setting of the rocks in the Bunu area and the chemistry of the major and trace elements.

3.3.1 Major Oxides, Trace and Rare Earth Element Concentrations in Metaigneous Rocks

Five unaltered and fresh samples of metaigneous rocks collected from the study area were analyzed for major oxides, trace elements and rare earth element (REE) compositions summary of the whole rock geochemistry is presented in Tables 2a, b, c and for major oxides, trace, REE and comparison with others respectively below.

Table 2a: Major Oxides concentrations (wt%) of Bunu Amphibolites [25]

	Amphibolites								
Sample Nos	KAB175A	KAB179B	KAB166I	KAB179C	KAB167	**RANGE**			**AVERAGE**
SiO_2	57.22	53.73	51.23	53.48	48.52	**48.52**	-	**57.22**	**52.84**
Al_2O_3	12.02	11.43	15.58	12.51	15.07	**11.43**	-	**15.58**	**13.32**
CaO	11.907	17.718	17.793	17.048	19.116	**11.91**	-	**19.12**	**16.72**
Fe_2O_3	6.92	5.73	6.71	5.72	7.59	**5.72**	-	**7.59**	**6.53**
K_2O	0.17	0.12	0.25	0.12	0.23	**0.12**	-	**0.25**	**0.18**
MgO	7.3	7.64	5.29	6.93	5.85	**5.29**	-	**7.64**	**6.60**
MnO	0.265	0.104	0.123	0.114	0.136	**0.10**	-	**0.27**	**0.15**
Na_2O	0.56	2.65	0.57	2.76	0.38	**0.38**	-	**2.76**	**1.38**
P_2O_5	0.144	0.16	0.261	0.104	1.023	**0.10**	-	**1.02**	**0.34**
TiO_2	0.48	0.82	0.58	0.91	0.64	**0.48**	-	**0.91**	**0.69**
LOI	1.45	0.45	1.34	0.66	1.56	**0.45**	-	**1.56**	**1.09**
Total	**100.27**	**100.57**	**99.74**	**100.37**	**100.12**	**99.74**	-	**100.57**	**100.21**
Ap	0.34	0.38	0.62	0.25	2.42	**0.25**	-	**2.42**	**0.80**
Il	0.57	0.22	0.26	0.24	0.29	**0.22**	-	**0.57**	**0.32**
Sp	0.54	1.73	1.08	1.92	1.20	**0.54**	-	**1.92**	**1.29**
Or	1.00	0.71	1.48	0.71	1.36	**0.71**	-	**1.48**	**1.05**
Ab	4.74	22.42	4.82	23.35	3.22	**3.22**	-	**23.35**	**11.71**
An	29.78	18.94	39.21	21.39	38.74	**18.94**	-	**39.21**	**29.61**
Hm	6.92	5.73	6.71	5.72	7.59	**5.72**	-	**7.59**	**6.53**
Di	21.57	41.04	28.42	39.23	31.43	**21.57**	-	**41.04**	**32.34**
Q	23.44	3.62	11.91	3.90	9.31	**3.62**	-	**23.44**	**10.44**
Hy	8.18	0.00	0.00	0.00	0.00	**0.00**	-	**8.18**	**1.64**
Wo	0.00	5.32	3.88	4.99	3.07	**0.00**	-	**5.32**	**3.45**
Total	**97.00**	**100.00**	**98.40**	**99.70**	**98.60**	**97.00**	-	**100.00**	**99.18**
CIA	48.75	35.81	45.56	38.57	43.31	**35.81**	-	**48.75**	**42.40**
ICV	2.27	3.03	2.00	2.68	2.24	**2.00**	-	**3.03**	**2.45**
DF	-3.49	3.51	3.10	4.06	3.28	**-3.49**	-	**4.06**	**2.09**
CIW	49.09	35.95	45.90	38.71	43.60	**35.95**	-	**49.09**	**42.65**
PIA	0.49	0.36	0.45	0.38	0.43	**0.36**	-	**0.49**	**0.42**

Table 2b: Trace Elements Concentrations (ppm) of Bunu Amphibolites [25]

	Amphibolites							
Sample Nos	KAB175A	KAB179B	KAB166I	KAB179C	KAB167	**RANGE**		**AVERAGE**
Ba	1740	87.9	60.2	118.4	43.2	**43.20**	**- 1740.0**	**409.94**
Be	7.76	2.48	5.36	2.55	3.72	**2.48**	**- 7.76**	**4.37**
Cd	0.179	0.341	0.637	0.302	0.657	**0.18**	**- 0.66**	**0.42**
Co	17.52	26.39	17.44	25.23	19.27	**17.44**	**- 26.39**	**21.17**
Cr	59	171	47	111	51	**47.00**	**- 171.00**	**87.80**
Cs	0.406	0.51	1.832	0.526	0.774	**0.41**	**- 1.83**	**0.81**
Cu	1.5	1.7	<1.4	2	<1.4	**1.50**	**- 2.00**	**1.73**
Ga	10.58	13.77	26.47	15.4	27.48	**10.58**	**- 27.48**	**18.74**
Hf	4.75	2.2	3.47	2.62	4.43	**2.20**	**- 4.75**	**3.49**
Li	2.5	18.6	3.4	16.4	2.6	**2.50**	**- 18.60**	**8.70**
Mo	0.43	0.36	0.12	0.51	0.14	**0.12**	**- 0.51**	**0.31**
Nb	11.405	3.657	9.101	4.118	10.026	**3.66**	**- 11.41**	**7.66**
Ni	37.6	118.5	31	103.4	35.7	**31.00**	**- 118.50**	**65.24**
Pb	9.9	10.8	43.1	11.2	46.1	**9.90**	**- 46.10**	**24.22**
Rb	4.1	2.16	14.66	3.02	12.09	**2.16**	**- 14.66**	**7.21**
Sb	0.15	0.06	0.38	0.04	0.62	**0.04**	**- 0.62**	**0.25**
Sc	12.9	19.2	12.1	18.6	12.4	**12.10**	**- 19.20**	**15.04**
Sn	2.28	2.8	6.94	2.97	7.93	**2.28**	**- 7.93**	**4.58**
Sr	261.2	638.1	597.8	648.8	637.8	**261.20**	**- 648.80**	**556.74**
Ta	1.109	0.265	0.726	0.336	0.824	**0.27**	**- 1.11**	**0.65**
Th	14.236	1.94	8.457	2.342	9.528	**1.94**	**- 14.24**	**7.30**
Ti	3695.0	4978.0	3555.0	5468.0	3775.0	**3555.0**	**- 5468.0**	**4294.2**
Tl	0.019	0.007	0.039	0.009	0.044	**0.01**	**- 0.04**	**0.02**
U	3.237	0.891	4.895	0.837	4.374	**0.84**	**- 4.90**	**2.85**
V	91.3	91.6	106.7	104.7	115.2	**91.30**	**- 115.20**	**101.90**
W	0.4	1.33	0.76	1.51	1.22	**0.40**	**- 1.51**	**1.04**
Y	33.26	7.65	32.92	9.43	32.28	**7.65**	**- 33.26**	**23.11**
Zn	169	86	408	76	375	**76.00**	**- 408.00**	**222.80**
Zr	167	62	124	78	162	**62.00**	**- 167.00**	**118.60**

Table 2c: Rare Earth Elements (REE) Concentrations (ppm) of Bunu Amphibolites [25]

		Amphibolites							
Sample Nos	KAB175 A	KAB179 B	KAB166 I	KAB179 C	KAB16 7	**RANG E**			**AVERAG E**
La	41.95	11.23	34.24	10.10	35.72	**10.10**	-	**41.95**	**26.65**
Ce	87.84	19.11	66.13	24.34	71.08	**19.11**	-	**87.84**	**53.70**
Pr	10.82	2.87	8.27	2.98	9.34	**2.87**	-	**10.82**	**6.85**
Nd	41.81	11.31	30.67	11.74	34.36	**11.31**	-	**41.81**	**25.98**
Sm	8.05	2.26	6.01	2.43	6.61	**2.26**	-	**8.05**	**5.07**
Eu	0.96	0.61	1.22	0.65	1.30	**0.61**	-	**1.30**	**0.95**
Gd	6.70	1.85	5.48	2.11	5.78	**1.85**	-	**6.70**	**4.38**
Tb	1.01	0.27	0.87	0.31	0.91	**0.27**	-	**1.01**	**0.67**
Dy	6.13	1.61	5.47	1.91	5.63	**1.61**	-	**6.13**	**4.15**
Ho	1.18	0.28	1.09	0.36	1.10	**0.28**	-	**1.18**	**0.80**
Er	3.39	0.78	3.13	0.95	3.22	**0.78**	-	**3.39**	**2.29**
Tm	0.48	0.12	0.43	0.14	0.45	**0.12**	-	**0.48**	**0.32**
Yb	3.05	0.72	2.58	0.93	2.73	**0.72**	-	**3.05**	**2.00**
Lu	0.43	0.11	0.34	0.14	0.38	**0.11**	-	**0.43**	**0.28**
Sum LREE	198.13	49.23	152.02	54.34	164.20	**49.23**	-	**198.13**	**123.58**
Sum HREE	15.66	3.88	13.91	4.73	14.41	**3.88**	-	**15.66**	**10.52**
Sum REE	213.79	53.12	165.93	59.07	178.61	**53.12**	-	**213.79**	**134.10**
LREE/HRE E	12.65	12.68	10.93	11.49	11.39	**10.93**	-	**12.68**	**11.83**

Table 2d: Major Oxides Concentration (wt%) comparison of Bunu Amphibolites with others in Nigeria

	4a	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**	**4h**	**PAS**	**AVG**
SiO_2	**52.84**	59.00	53.99	48.91	53.92	49.03	47.11	51.11	62.80	66.70
Al_2O_3	**13.32**	14.16	12.22	15.91	13.21	22.84	16.57	13.52	18.90	13.50
CaO	**16.72**	7.62	12.89	9.33	10.78	7.83	1.08	8.75	1.30	2.50
Fe_2O_3	**6.53**	7.82	9.74	13.31	9.06	11.48	13.31	14.51	6.50	3.54
K_2O	**0.18**	1.24	0.42	0.73	0.26	0.02	0.28	1.13	3.70	2.00
MgO	**6.60**	5.82	7.03	9.84	9.14	6.63	6.59	5.04	2.20	2.10
MnO	**0.15**	0.13	0.18	0.13	0.01	0.04	0.26	0.22	0.11	0.10
Na_2O	**1.38**	2.62	2.16	1.52	2.0	1.55	1.65	2.79	1.20	2.90
P_2O_5	**0.34**	0.12	0.06	0.03	1.6	0.01	0.52	0.39	0.16	0.20
TiO_2	**0.69**	0.65	0.26	0.05	0.09	-	2.05	2.42	1.00	0.60
LOI	**1.09**	1.13	1.28	0.31	0.3	-	-	-	6.00	-

4a= Average of Sampled Amphibolitic rocks from Bunu area (Present Work)
4b= Average of 7 sampled Amphibolite rocks from Lokoja-Okene area [28]
4c= Average of Amphibole Schist from Ibadan area [6]
4d= Average of amphibolites from Wonu-Apomu (Iseyin) area [27]
4e= Average of amphibolites from Lema-Ndeji [6]
4f= Average of amphibolites from Zuru area [12]
4g Average of amphibolites from Ilesha area, SW Nigeria [13]
4h= Average of amphibolites from Jebba area, SW Nigeria [29]
PAS= Post-Archean terrigenous shale
AVG= Average of greywackes composition of [30]

The concentrations of Al_2O_3, CaO, Fe_2O_3 and MgO in the amphibolites are 13.32, 16.72, 6.53 and 6.60 wt % respectively. The presence of plagioclase feldspar in the gniesses and hornblende and plagioclase in amphibolites may explain the high Al_2O_3 and CaO values. The higher value of Fe_2O_3 and MgO in metaigneous rocks is due to the presence of pyroxene and amphibole. There are low concentrations of TiO_2 and MnO of 0.69 and 0.15 in amphibolites respectively. The low value of these oxides especially in amphibolites is typical of basalts erupted at convergence plate boundaries [31].

DF= 10.44 - 0.21 SiO_2 - 0.32 Fe_2O_3 (Total Fe) -0.98 MgO + 0.55 CaO + 1.46 Na_2O + 0.54 K_2O

Positive DF values suggest an igneous origin while negative DF values point to sedimentary. The DF value of av. 2.09 for Bunu metaigneous samples indicates an igneous protolith (Table 2a).

For trace element concentrations, Ni and Sr with average values of 65.24 and 556.75 ppm respectively are more enriched in metaigneous rocks than in metasedimentary rocks. Average Ba and Rb values of 77.43 and 7.21 ppm respectively, have been recorded in the amphibolites from the study area. The high content of MgO and Ni in metaigneous rocks probably indicates the presence of olivine in the more primitive magmas of the suite while high content of Sr and Ba suggest the presence of plagioclase and K-feldspar in the protoliths.

4.0 Discussion

4.1 Classification of the protolith

On the MgO-CaO-Al_2O_3 ternary diagram after Leyreloup *et al* [31] in Kolawole [25], the metaigneous samples plot within magmatic field (Figure 6a). On the plot of Na_2O/Al_2O_3 versus K_2O/Al_2O_3 after [32 in 25] (Figure 6b), the amphibolites samples plot in both the igneous and sedimentary fields indicating that though it has magmatic origin, the rock has been sufficiently contaminated by continental materials. The volcanic rocks (in particular basalt) exhibit specific chemical features for specific tectonic environment [25]. Therefore, basalt with similar chemistry may be produced in different tectonic regimes such that their composition may reflect the nature of the particular mantle and the melting processes in operation during their formation (Odigi, 2002). The nature of the parent magma for the metaigneous rocks is revealed in the total alkali versus silica (TAS) plot of Le Bas *et al*. [33] in Kolawole [25]. As shown in Figure 7 the amphibolites in Bunu area sandwiching in the basaltic, basaltic andesite and andesite fields which confirms it intermediate statues.

The plot SiO_2 Vs K_2O (Fig 8a) exhibits that Bunu Amphibolite occupied the calc-alkaline and low-K theolitic series. This is corroborated by AFM diagram of Irvine and Baragar [34] (Figure 8b). However, the plots of Fe_2O_3 + Ti_2O - Al_2O_3 - MgO and Na_2O + K_2O vs SiO_2 is useful for discriminating between these two fields as seen in Figures 9a and b that show all samples within the tholetiic field indicating tholeiitic basalt affinity for the Bunu amphibolite

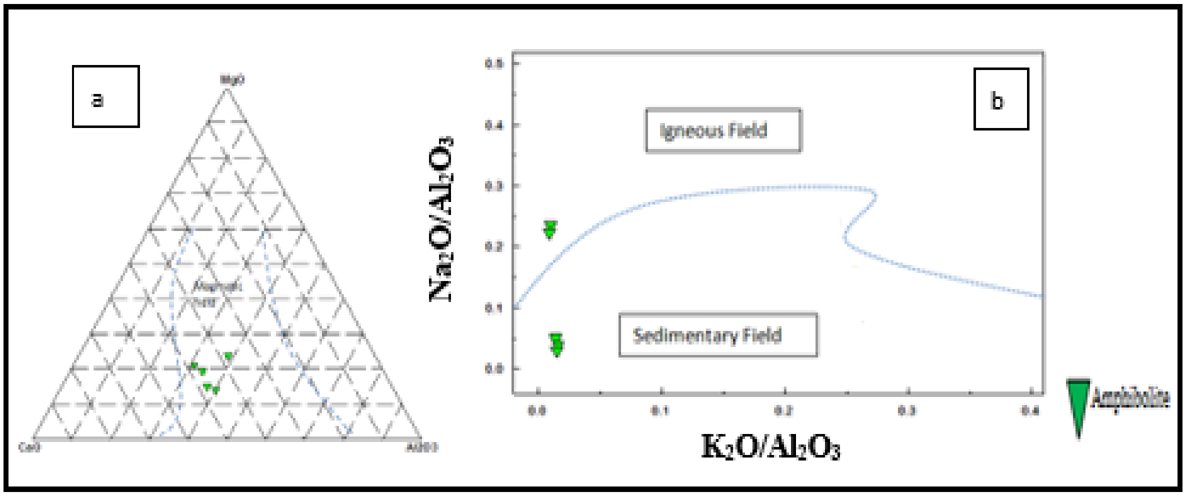

Figure 6: (a) Plot of MgO-CaO-Al_2O_3 on ternary diagram after [31 **in** 25] and (b) plot of Na_2O/Al_2O_3 against K_2O/Al_2O_3 after [32 **in** 25] of the metaigneous rocks of the study area.

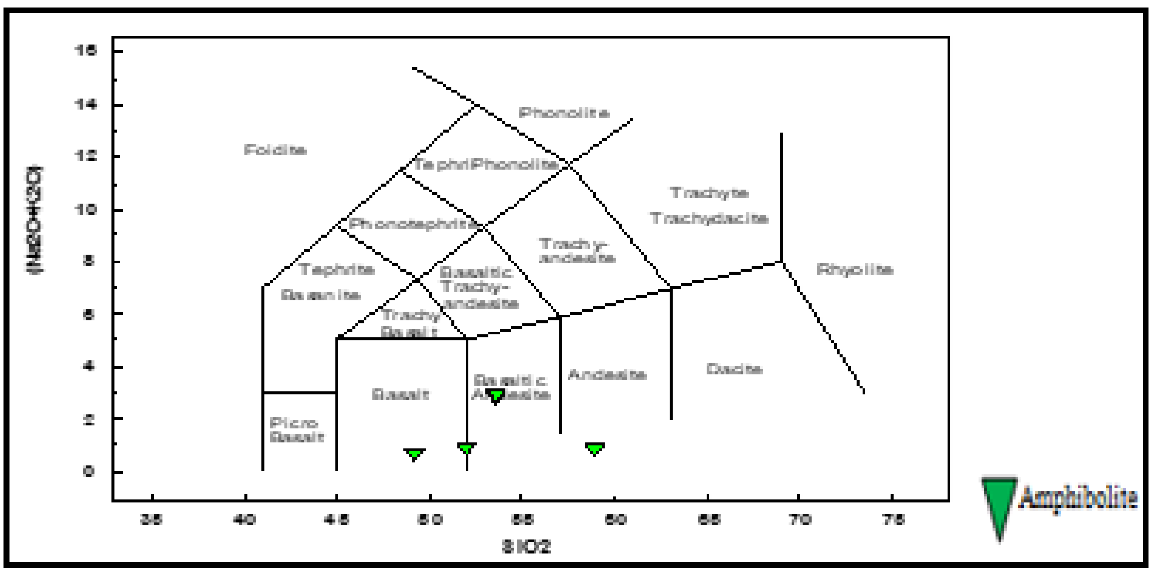

Figure 7: Total Alkali versus Silica plot of Bunu amphibolites on [33 **in** 25] diagram.

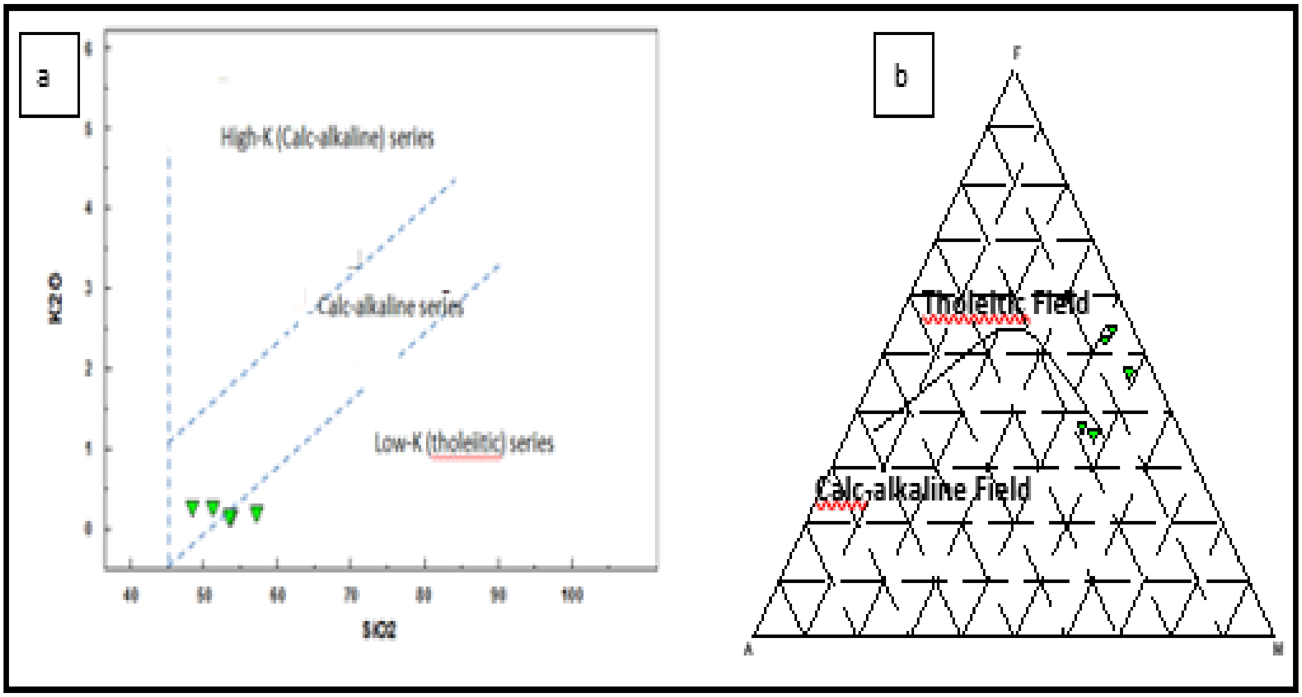

Figure 8: (a) The relationship between silica and alkalis shows calc-alkalic and tholeiitic nature of Bunu amphibolite corroborated by (b) AFM diagram of [34 **in** 25].

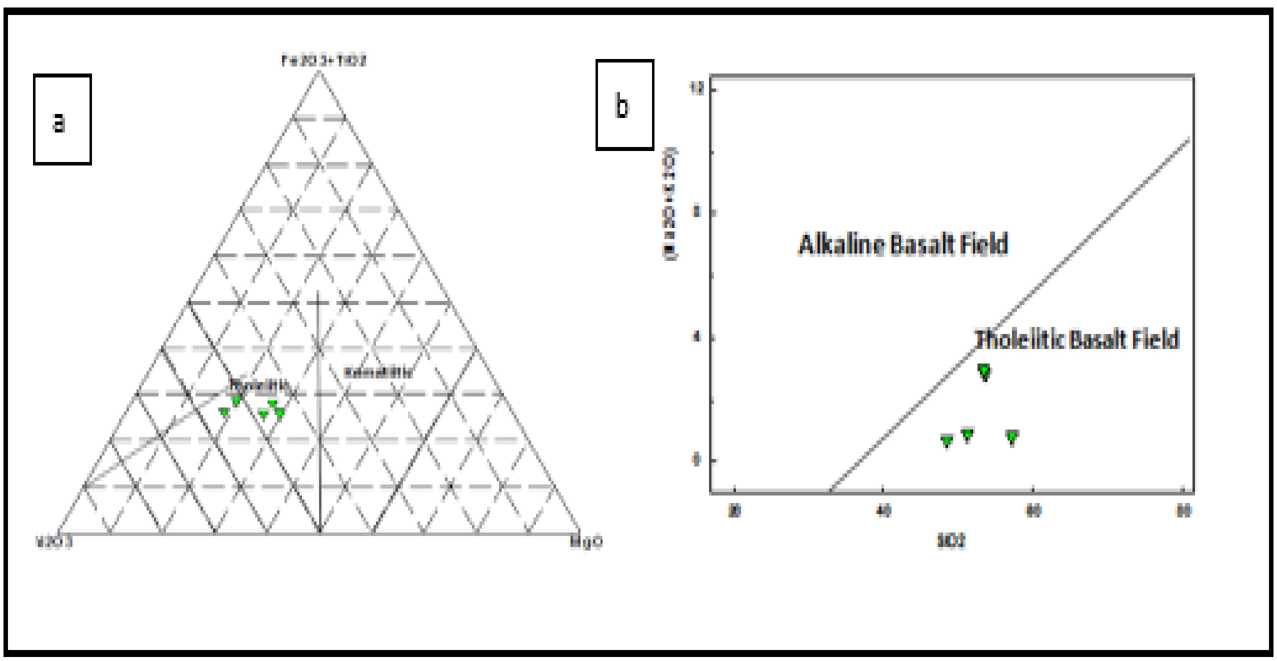

Figure 9: Plots of (a) Fe_2O_3+Ti_2O-Al_2O_3-MgO and (b) Na_2O+K_2O vs SiO_2 for Bunu amphibolite

4.2 Provenance tectonic setting

The Chemical Index of Alteration (CIA) proposed by Nesbitt and Young [35], Chemical Index of Weathering (CIW) proposed by Harnois (1988), Plagioclase Index of Alteration (PIA) proposed by Fedo et al. [36], and Index of Compositional Variability (ICV) of Cox and Lowe were used to estimate the degree of weathering and sediment maturity of the protolith.

They are defined as: CIA= $[Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O)]*100$.

CIW= $[Al_2O_3/(Al_2O_3+CaO+Na_2O)]*100$

PIA= $[(Al_2O_3-K_2O)/Al_2O_3+CaO+Na_2O-K_2O)]$

ICV= $(Fe_2O_3+K_2O+Na_2O+CaO+MgO+TiO_2)/Al_2O_3$.

The degree of weathering and sediment maturity of the protolith were estimated using the Chemical Index of Alteration (CIA) proposed by Nesbitt and Young [35], Chemical Index of Weathering (CIW) proposed by Harnois [37], Plagioclase Index of Alteration (PIA) proposed by Fedo et al. [36], and Index of Compositional Variability (ICV) of Cox and Lowe [38].

TiO_2-K_2O-P_2O_5 ternary plot after Pearce [39] was used to discriminate the rocks formed from oceanic and continental tectonic environments. This plot showed samples in both oceanic and non-oceanic continental environments (Figure 11a). This may imply emplacement of the metaigneous rocks in both fields confirming that the rock is a product of both environments. On the MgO-Fe_2O_3-Al_2O_3 ternary diagram [39] all amphibolite samples plot in island arc tholeiitic (IAT) field (Figure 11b) this confirming that their protoliths are probably arc related tholeiitic basalts erupted at a converging centre. Furthermore, trace elements characterization for the tectonic setting of the metaigneous rocks can be obtained using Zr/Y versus Zr of Pearce and Norry [41] further confirmed that the rock has island-arc basalt protolith (Figure 11c) while Zr/Y versus Zr of Pearce [42] further separated the fields of continental and oceanic-arc basalts on the basis of a Zr/Y value of 3 (Figure 11d). The occurrence of the amphibolite in this field indicates that these rocks were probably erupted at a converging center [12].

According to Taylor and McLennan [43] and Nyakairu and Koeberl [44], immobile elements such as La and Th are more abundant in felsic protoliths than in basic rocks whereas Sc and Co are more concentrated in basic rocks than in felsic ones. On a plot after Roser and Korsch [45] using discriminant functions 1 and 2 (Figure 12a) and that of Bhatia [46] using discriminant functions 11 and 22 (Figure 12b) the amphibolite schists of Bunu area plot mostly within mafic igneous provenance field and emplaced in an oceanic island arc tectonic setting.

The discriminant functions used after Roser and Korsch [45] in Figure 12a are:

Discrimination function 1= $-1.773\,TiO_2+0.06Al_2O_3+0.76\,FeO(t)-1.5MgO+0.616CaO+0.509Na_2O-1.224K_2O-9.09$

Discrimination function 2= $0.445TiO_2+0.07Al_2O_3+0.25\,FeO(t)-1.142MgO+0.438CaO+1.47Na_2O-1.426K_2O-6.861$.

The discriminant functions used after Bhatia [46] in Figure 12b are:

Discriminant function 11= $-0.0447\,SiO_2-0.972\,TiO_2+0.008\,Al_2O_3-0.267\,Fe_2O_3+0.208\,FeO-3.083\,MnO+0.14\,MgO+0.195\,CaO+0.719\,Na_2O-0.032\,K_2O+7.51\,P_2O_5+0.303$

Discriminant function 22= $-0.421\,SiO_2+1.988\,TiO_2-0.526\,Al_2O_3-0.551\,Fe_2O_3-1.610\,FeO+2.720\,MnO+0.881MgO-0.907\,CaO-0.177\,Na_2O-1.84\,K_2O+7.244\,P_2O_5+43.57$

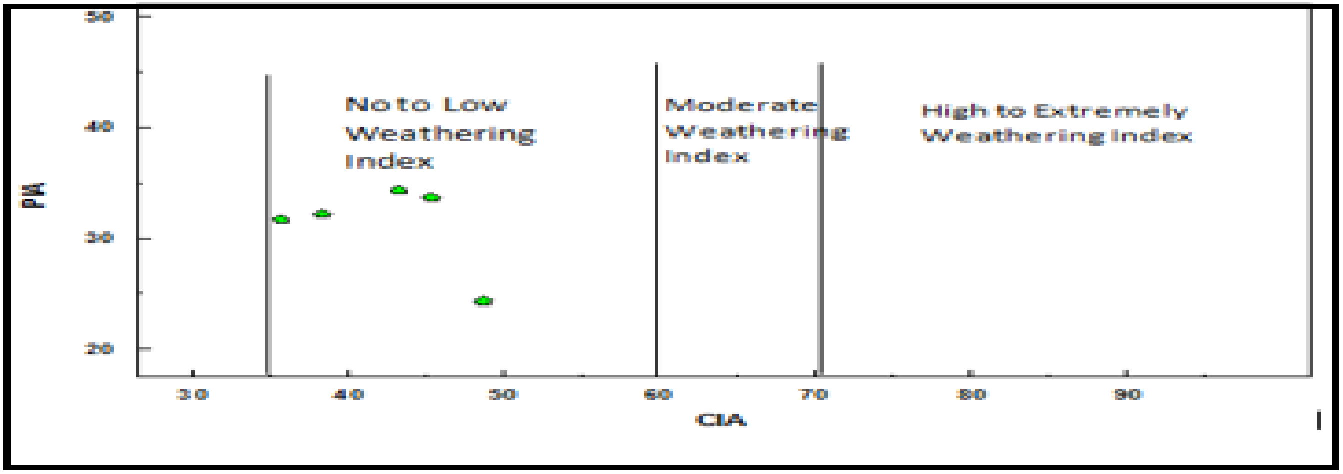

Figure 10: Plot of PIA against CIA for Amphibolitic rocks in the study area indicating that all the rocks in the area plot in the Low CIA inference field (CIA=80) [35

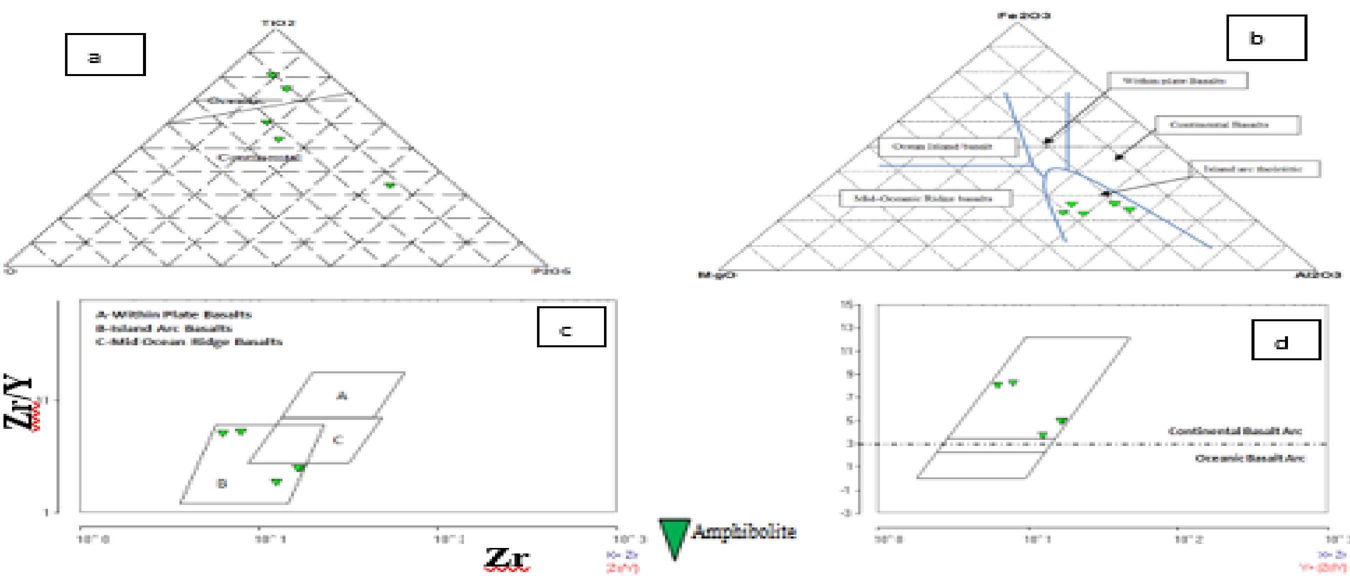

Figure 11: (a) TiO_2-K_2O-P_2O_5 diagram [39 **in** 25], (b) ternary discrimination diagram of Fe_2O_3-MgO-Al_2O_3 [40 **in** 25], (c) discrimination diagram of Zr/Y vs Zr [41 **in** 25] and (d) fields of continental and oceanic-arc basalts separated on the basis of a Zr/Y value of 3 [43 **in** 25] for the metaigneous rocks of Bunu are

These show that the amphibolites of the Bunu area have the same petrogenetic characteristic with most of the amphibolites of the basement complex of Nigeria with Archean metabasalt affinity [6], [8], [12], [28], [47] but slightly different from the amphibolites of Ibadan area and Katar Rash

Volcanic Group (KRVG), NE Iraq that mostly have calc-alkaline affinity [6], [48].

The amphibolites of Lafiagi/Osi area, SW Nigeria Basement Complex also show similar oceanic-continental affinities and sufficient continental contributions [47]. However, amphibolites of Okene-Lokoja area entirely plotted in the continental field pointing to a non-oceanic origin for the rocks [49]. The extensional back-arc tectonic setting with ocean floor affinity indicated by amphibolites from this area is similar to those of the Ife-Ilesha [50], Jebba [29], Anka [51] and Zuru [12]

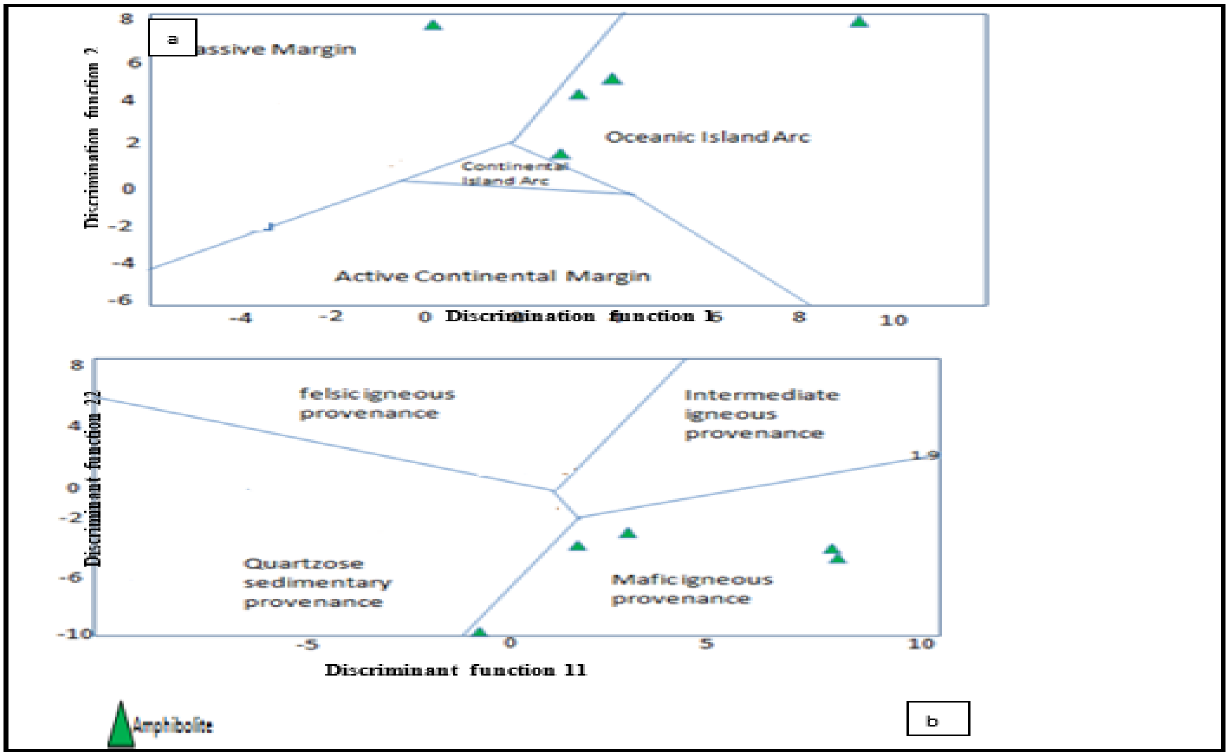

Figure 12: Discrimination function diagrams for (a) the provenance signature [45] and (b) the depositional fields [46] of the rocks in Bunu area using major elements.

On a plot on the Primodal mantle-McDonough and Sun [22], the trace elements in the rock units show rather flat distribution patterns with depleted Ba and Rb (Figures 13a and b) relative to significant enrichment of Ba and Rb in metasedimentary rocks. This suggests derivation of the metaigneous rocks of the study area from differentiated basic precursor.

It is also possible to distinguish between felsic and mafic source components using ratios of incompatible and compatible elements. Since basic rocks typically have low LREE/HREE ratios and no Eu anomalies but more silicic rocks typically have higher LREE/HREE ratios and negative Eu anomalies, the REE patterns have also been utilized to determine the origins of sedimentary rock [44]. The slightly gentler nature and lack of negative Eu exhibited by some of the metavolcanic rocks may reflect basic source region, reaffirming that the amphibolites in the area, though of basic magma origin but were sufficiently contaminated with continental materials. This compared and correlated well with PASS, NASC and ES standards (Figure 14).

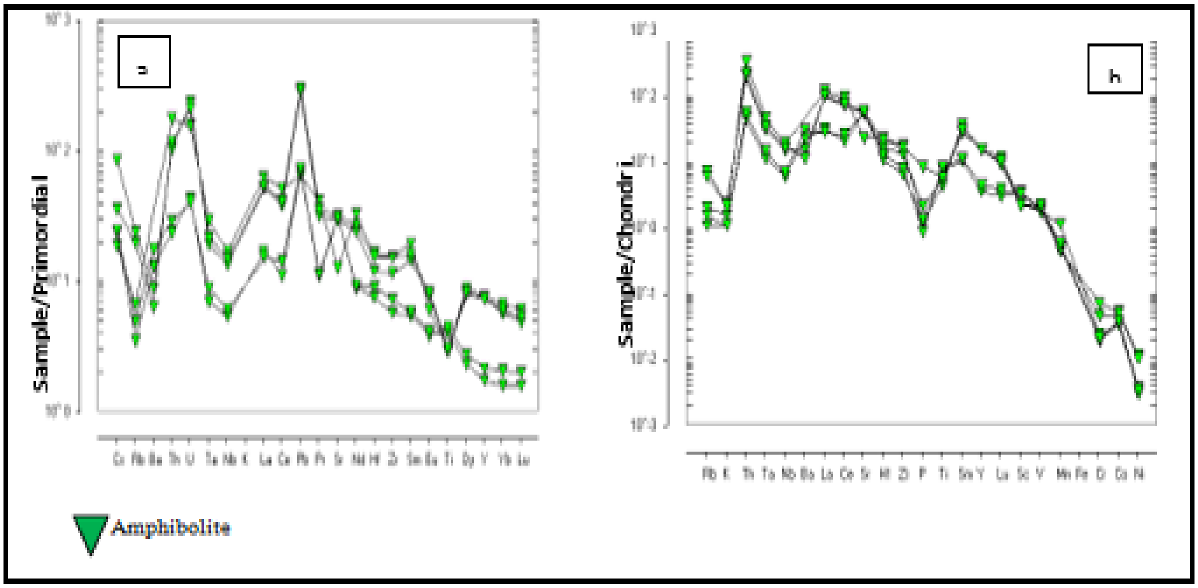

Figure 13: (a) Premordial mantle-normalized incompatible element pattern and (b) chondrite normalized pattern of metaigneous rocks in Bunu area Normalizing values are those from McDonough and Sun [22] and Wood *et al*. [23].

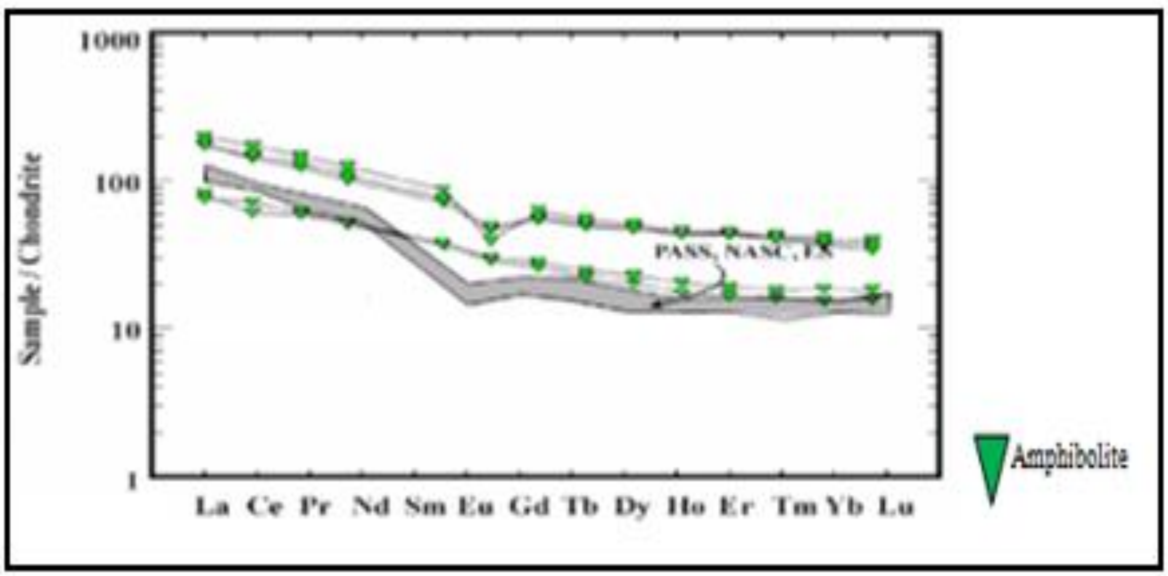

Figure 14: REE patterns for metavolcanic rocks from Bunu area on PASS (post-Archean average Australian sedimentary rock), NASC (North American shale composite), and ES (European shale) [52]. Normalizing values are those of Sun and McDonough [24 **in** 25].

According to classification scheme for basic volcanic rocks based on tectonic setting [53], there are oceanic floor basalts (divergent plate margins), volcanic arc basalts (converging plate margins), oceanic island basalts (within plate-oceanic crust) and continental basalt (within plate-continental crust) (Figure 15). In accordance with this classification, these amphibolites are classified as calc-alkaline basalt of volcanic arc setting.

5.0 Conclusion

Amphibolitic rocks of Bunu area occur as interbanding bodies within gniess-metasedimentary rocks units that comprise of migmatite-gniess and migmatized schist, foliated and massive quartzite and quartz-mica schist. Petrographic study of the amphibolites showed the dominance of hornblende, plagioclase feldspar and chlorite. Other minerals present are biotite, quartz, pyroxene and opaque minerals. Discrimination plots of amphibolites samples in the area confirmed that they have no to low weathering indices. Geochemical data also showed that they are essentially calc-alkaline island arc tholeiites in nature and continental basaltic igneous precursors that are emplaced in extensional back-arc tectonic setting with ocean floor affinity that were probably contaminated by crustal materials developed near the eastern edge of West African cratonic plate margin. This is consistent with the orogenic nature of the Pan-African event in the region, which occurred around 600 Ma and resulted in local metamorphism and the origin of the amphibolites' magmas from upper mantle melting.

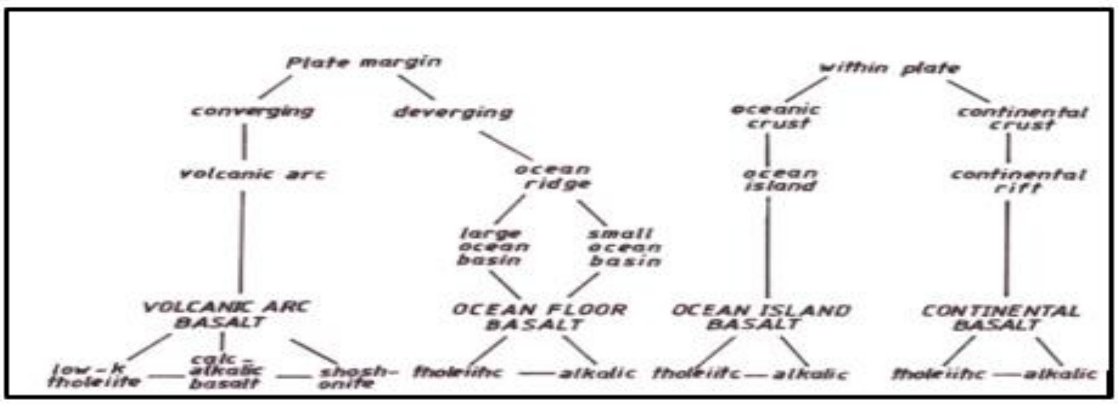

Figure 15: Classification scheme for basic volcanic rocks based on tectonic Setting [53 **in** 25].

Declarations:

Ethics approval: Not applicable

Consent for publication: Not applicable

Competing interests: The authors declare that there are no competing interests on the manuscript.

Funding: The work is self-funded.

Authors contributions: MSK conceptualized this work as part of his PhD work which was supervised by SBO. CAO and AAA went through the manuscript and all authors read and approved the final manuscript.

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