ZIBELINE INTERNATIONAL
PUBLISHING

ISSN: 2521-0920 (Print)

ISSN: 2521-0602 (Online)

CODEN: MJGAAN

Malaysian Journal of Geosciences

(MJG) DOI: <http://doi.org/10.26480/mjg.01.2020.13.18>

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RESEARCH ARTICLE

MINERAL CHEMISTRY AND GEOCHEMISTRY OF HYPERSTHENE-BEARING DIORITE FROM ERUSU AKOKO, SOUTHWESTERN NIGERIA

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ARTICLE DETAILS

Article History:

Received 05 December 2019

Accepted 12 January 2020

Available online 07 February 2020

ABSTRACT

Samples of mafic intrusive rock were analyzed for their mineralogical and chemical properties. The textural relationship was studied using the petrographic microscope, elemental composition of minerals was determined using the Electron Microprobe and the whole rock chemical analysis was done using the XRF and ICP-MS. The following minerals were observed in order of abundance; pyroxene, amphibole, plagioclase, biotite, opaque minerals, quartz and chlorite, with apatite and zircon occurring as accessory mineral. Two types of pyroxenes were observed; orthopyroxene (hypersthene) and clinopyroxene. Texturally, amphiboles have inclusions of plagioclase and pyroxene. The plagioclase has undergone sericitization. The chemical composition of the pyroxene is $\text{En}_{51.95}\text{Fs}_{44.53}\text{Wo}_{3.52}$, biotite has $\text{Fe}/(\text{Fe}+\text{Mg}):0.42$, $\text{Mg}/(\text{Fe}+\text{Mg}):0.59$, and plagioclase is $\text{Ab}_{63.5}\text{An}_{34.55}\text{Or}_{1.95}$. Whole rock chemistry shows a chemical composition; SiO_2 : 45.15 %, Al_2O_3 : 14.04 %, Fe_2O_3 : 16.01 %, MgO : 5.65 %, CaO : 7.58 % and TiO_2 : 3.59 %. There is an enrichment of LREE and a depletion of HREE. Based on the minerals, mineral chemistry and the geochemistry of the studied rock, the rock is mafic and hydrous minerals formed by hydration recrystallization of pyroxene. The rock has extensively retrogressed but has not been affected by any form of deformation.

KEYWORDS

Electron Microprobe, retrogressed, sericitization, inclusions.

1. INTRODUCTION

The Basement complex of Nigeria comprises some components of mafic to ultramafic in addition to other rock units which some believed to be remnants of mantle diapirs. The mafic intrusive rock (Hypersthene-Bearing diorite) under study is dark coloured, fine-medium grained and non-foliated (Figure 1). The other rock units in this area include: migmatite gneiss; which has both the grey and granitic gneisses. Erusu is a town in Akoko North West of Ondo State, which is part of the Basement Complex of Southwestern Nigeria. The Basement Complex of Nigeria is rocks of Precambrian age which underlay about half of the landmass of Nigeria (Haruna, 2017). The Basement Complex of Nigeria is divided into the Western and Eastern Provinces (Ajibade et al., 1979). The Basement Complex of Southwestern Nigeria is believed to have formed in a back-arc basin (Oyinloye and Odeyemi, 2001). Mafic intrusive were first mentioned in this area in a study, in which it was described as one of the rock units of Ikare area (Rahaman and Ocan, 1988). The petrography, mineral chemistry, and geochemistry (major, trace and REE elements) of samples collected from the mafic intrusive rock at Erusu Akoko is presented in this article.

2. MATERIALS AND METHOD

Petrographic studies were carried out both at the Department of Geology, Obafemi Awolowo University and Rhodes University, South Africa using

Petrographic Microscopes. Data acquisition for Electron Probe Micro-Analysis (BSE and Cathodo-luminescence imaging, major, minor and trace element analysis) was carried out using a JEOL JXA 8230 Superprobe, with 4 WD spectrometers at Rhodes University, South Africa. The Probe Machine was used under the following operating conditions: 15 kV acceleration voltage, 20 nA probe current 20 nA, beam size of ~1 micron, counting time 10 sec on peak and 5 sec. on each lower and upper background, respectively. The minerals grains selected were analyzed both at the core and at the rim.

Figure 1: Field photograph of a mafic intrusive rock at Erusu Akoko.

Major elemental analysis was carried out by XRF spectrometry on a PANalytical Axios Wave length Dispersive spectrometer at the Central Analytical Facilities (CAF), Stellenbosch University, South Africa. Laser Ablation ICPMS was used for the determination of trace and rare elements also at CAF Stellenbosch University.

Quick Response Code

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Website:
www.myjgeosc.com

DOI:
[10.26480/mjg.01.2020.13.18](https://doi.org/10.26480/mjg.01.2020.13.18)

3. RESULTS

3.1 Petrography

Under the microscope the mafic rock is generally granoblastic in texture and consists of the following minerals: pyroxene, amphiboles, plagioclase, biotite, chlorite, opaque minerals, and quartz with zircon and apatite occurring as accessory mineral. The two types of pyroxenes were observed, the orthopyroxene and the clinopyroxene (Figures 2 & 3). The orthopyroxene is highly pleochroic. The pyroxene is surrounded by amphiboles and with some occurring as inclusions in amphiboles. The pyroxene has opaque minerals occurring along its rims, especially where it (orthopyroxene) is in contact with amphiboles (Figures 4, 5, 6, 7 & 8). There is a recrystallization of the pyroxene to biotite (Figure 9).

The amphiboles are greenish brown in colour (Figures 2, 4, 6 & 10) and strongly pleochroic, with inclusions of plagioclase and pyroxene (Figures 10 & 11). Crystals of biotite show form of alteration to a greenish mineral which is chlorite (Figure 12). The biotite crystals are brownish in color and cuts across amphiboles and plagioclase (Figure 13 & 14). The plagioclase exhibit both albite and Carlsbad form of twinning and has inclusions of amphiboles. There is the alteration of some of the plagioclase crystals to sericite (Figure 15 & 16). Opaque minerals (Ilmenite) occur in close association with plagioclase. The Backscattered Electron (BSE) image show that there is no elemental zonation in any of the minerals (Figures 17 & 18).

Figure 2: Photomicrograph of diorite from Erusu Akoko showing Orthopyroxene and Clinopyroxene. PPL (Cpx, clinopyroxene; Opx, orthopyroxene; and PPL, plane polarized light)

Figure 3: Photomicrograph of diorite from Erusu Akoko showing orthopyroxene and clinopyroxene. XPL (Cpx, clinopyroxene; Opx, orthopyroxene; and XPL, cross-polarized light)

Figure 4: Photomicrograph of diorite from Erusu Akoko showing opaque mineral (dark mineral) surrounding orthopyroxene (Opx). PPL

Figure 5: Photomicrograph of diorite from Erusu Akoko showing opaque mineral (dark mineral) surrounding orthopyroxene (Opx). PPL

Figure 6: Photomicrograph of diorite from Erusu Akoko showing opaque mineral surrounding orthopyroxene (Opx). PPL

Figure 7: Photomicrograph of diorite from Erusu Akoko showing opaque mineral surrounding orthopyroxene (Opx). PPL

Figure 8: Photomicrograph of diorite from Erusu Akoko showing opaque mineral surrounding orthopyroxene (Opx). XPL

Figure 9: Photomicrograph of diorite from Erusu Akoko showing an alteration of orthopyroxene to (Opx) amphibole (Am). PPL

Figure 10: Photomicrograph of diorite from Erusu Akoko showing inclusions of plagioclase (Pl) in amphiboles (Am) and pyroxene (Px) in amphiboles. PPL

Figure 11: Photomicrograph of diorite from Erusu Akoko rock showing inclusions of plagioclase (Pl) in amphiboles (Am). XPL

Figure 12: Photomicrograph of diorite showing biotite (Bt) surrounded by chlorite. The blue arrows pointing towards chlorite. Chloritization of biotite. PPL

Figure 13: Photomicrograph of diorite from Erusu Akoko showing biotite (Bt) cutting across amphibole (Am). Opaque mineral (Opq) PPL

Figure 14: Photomicrograph of diorite from Erusu Akoko showing biotite (Bt) cutting across amphibole (Am) and plagioclase (Pl). XPL

Figure 15: Photomicrograph of diorite from Erusu Akoko showing alteration of feldspar to sericite. Biotite (Bt) occurring as inclusion in plagioclase (Pl). The blue arrow pointing towards sericite (XPL)

Figure 16: Photomicrograph of diorite from Erusu Akoko showing alteration of plagioclase feldspar (Pl) to sericite (XPL)

Figure 17: EPMA BSE image of diorite showing biotite, pyroxene, amphibole and plagioclase.

Figure 18: EPMA BSE image of diorite showing plagioclase, amphibole and pyroxene.

3.2 Mineral Chemistry

Biotite: The mineral chemistry of biotite for the mafic rock show the following: SiO₂; 36.64 wt %, Al₂O₃; 14.02 %, FeO; 16.76 %, MgO; 13.23 %, K₂O; 8.35 % while the total oxide is 92.53 wt % (Table 1).

Pyroxene: The mineral composition of pyroxene has the composition: SiO₂; 50.79 %, FeO; 27.13 %, MgO; 17.59 % and CaO; 1.08 % (Table 2). The average of 52.48 % enstatite and 45.09 % ferrosilite. This composition confirms that the pyroxene present is hypersthene. The formula of the pyroxene from this result can be written as MgFeSi₂O₆ (Table 2).

Plagioclase: The mineral composition of plagioclase show; albite - 63.5 %, anorthite - 34.55 % and orthoclase - 1.95 % (Table 3).

Amphiboles: The mineral composition of amphiboles shows that it is edenite-hornblende (Table 4).

Ilmenite: the mineral composition of ilmenite in the mafic rock has a composition of, SiO₂: 1.01 %, TiO₂: 52.52 % and FeO: 33.62 % (Table 5).

3.3 Major Element Chemistry of Diorite

The whole rock chemistry (Table 6) show compositions of the oxides as: SiO₂ (45.15 wt %), Al₂O₃ (14.04 wt %), CaO (7.58 wt %), Fe₂O₃ (16.01 wt %), MgO (5.65 wt %), K₂O (1.94 wt %), MnO (0.21 wt %), Na₂O (2.45 wt %), TiO₂ (3.59 wt %), P₂O₅ (0.51 wt %) and Cr₂O₃ (0.02 wt %).

3.4 Trace Element Composition of Diorite

The trace elements composition of the mafic rock show high level of composition of V, Cr, Zn, Cu, Co, Ni and Ba as, V: 312.6 ppm, Cr: 89.86 ppm, Zn: 136.5 ppm, Cu: 39.92 ppm, Co: 74.7 ppm, Ni: 71.59 ppm and Ba: 483.1 ppm, respectively (Table 7).

Table 1: Chemical Composition of Biotite in Diorite

Sample	17
SiO ₂	36.64
TiO ₂	3.18
Al ₂ O ₃	14.02
Cr ₂ O ₃	0.09
FeO	16.76
MnO	0.08
MgO	13.23
CaO	0.02
Na ₂ O	0.09
K ₂ O	8.35
Cl	0.1
H ² +O	1.83
Total	92.53
Si	5.93
Al ^{IV}	2.07
Al ^{VI}	0.60
Ti	0.39
Fe ²⁺	2.27
Cr	0.01
Mn	0.01
Mg	3.19
Ca	0.00
Na	0.03
K	1.72
Cations	16.22
CCl	0.06
OH	1.97
O	24
Fe/(Fe+Mg)	0.42
Mg/(Fe+Mg)	0.59

(Al^{IV}: aluminium in tetrahedral site, Al^{VI}: aluminium in octahedral site)

Table 2: Mineral Composition of Pyroxene in Diorite

Sample	17c	17r	mean
SiO ₂	50.809	50.772	50.7905
TiO ₂	0.026	0.04	0.033
Al ₂ O ₃	0.406	0.441	0.4235
FeO	26.073	28.189	27.131
Cr ₂ O ₃	0.065	0.043	0.054

MnO	0.537	0.499	0.518
MgO	17.418	17.754	17.586
CaO	1.642	0.517	1.0795
Na ₂ O	0.002	0	0.001
K ₂ O	0.034	0.041	0.0375
Total	97.01	98.3	97.655
TSi	2.004	1.983	1.9935
TAl	0	0.017	0.0085
TFe ³⁺	0	0	0
M1Al	0.019	0.003	0.011
M1Ti	0.001	0.001	0.001
M1Fe ³⁺	0	0.012	0.006
M1Fe ²⁺	0	0	0
M1Cr	0.002	0.001	0.0015
M1Mg	0.978	0.982	0.98
M2Mg	0.046	0.052	0.049
M2Fe ²	0.86	0.908	0.884
M2Mn	0.018	0.017	0.0175
M2Ca	0.069	0.022	0.0455
M2Na	0	0	0
M2K	0.002	0.002	0.002
Sum_cat	3.998	3.998	3.998
Ca	3.52	1.093	2.3065
Mg	51.948	52.204	52.076
Fe2_Mn	44.533	46.703	45.618
JD1	0.095	0.104	0.0995
AE1	0	0	0
CFTS1	0.104	0.701	0.4025
CTTS1	0	0.06	0.03
CATS1	0	0.052	0.026
WO1	3.445	0.288	1.8665
EN1	52.375	52.588	52.4815
FS1	43.981	46.207	45.094
Q	1.954	1.963	1.9585
J	0	0	0
WO	3.52	1.086	2.303
EN	51.948	51.878	51.913
FS	44.533	47.036	45.7845
WEF	99.984	100	99.992
JD	0.016	0	0.008
AE	0	0	0

(M1: Y octahedral site, M2: X octahedral site, JD: jadeite, AE: aegirine, WO: wollastonite, EN: enstatite, FS: ferrosilite, CAT: cation)

Strontium is high and Rb is very high in sample. Barium is high (483.06 ppm), Zr is also high but Hf and Th are both low in values.

3.5 Rare Earth Element of Diorite

The REE abundances are given in Table 8 and the chondrite-normalized REE plot display a negative Eu anomaly. In calculated terms, the europium anomaly is 0.832 while the cerium anomaly is 1.087 (Table 8). The ratio of lanthanum to ytterbium is 5.344 (Table 8), which shows an enrichment of light rare earth elements (LREE) and a depletion of heavy rare earth elements (HREE) in these rocks.

4. DISCUSSION

Based on the petrographic studies the mafic intrusive rock can be given the name two-pyroxene diorite because of the presence of orthopyroxene and clinopyroxene. The strong pleochroic nature of the pyroxene suggests hypersthene which has been confirmed by the mineral chemistry (Table 2). The relationship between the pyroxene and the amphibole suggests that the pyroxene (anhydrous mineral) reacts with the hydrous melt in the presence of plagioclase to give amphiboles (hydrous mineral), this can be represented as ; $\text{Opx} + \text{Plagioclase 1} + \text{H}_2\text{O} = \text{Amphibole} + \text{Plagioclase 2}$. Plagioclase 1 will be Ca-rich (anorthite) while plagioclase 2 will be Ca-poor. The mineral chemistry confirms the Plagioclase 2 as Ca-poor (Table 3). The presence of opaque minerals (ilmenite) around pyroxene in close association with amphiboles an indication that these reaction gives off titanium (Ti^{4+}). The pyroxene-biotite relationship can be due to the reaction of orthopyroxene with alumina in the presence of potassium ions to give biotite and can be represented as; $\text{Opx} + \text{plagioclase} + \text{K}^+ + \text{H}_2\text{O} = \text{Biotite}$. The biotite is rimmed by a greenish mineral and indication that it is reacting to form chlorite.

Table 3: Chemical Composition of Plagioclase Feldspar in Diorite	
Sample	17
SiO ₂	59.15
TiO ₂	0.035
Al ₂ O ₃	24.775
FeO	0.04
MnO	0.015
MgO	0.005
CaO	7.195
Na ₂ O	7.31
K ₂ O	0.345
Total	98.9
Si	2.67
Al	1.317
Fe ³⁺	0
Ti	0.0015
Fe ²⁺	0.0015
Mn	0.0005
Mg	0.0005
Ba	0.0005
Ca	0.348
Na	0.64
K	0.0195
Cations	4.9995
X	3.9885

(Ab: Albite, An: anorthite, Or: orthoclase)

Table 4: Chemical Composition of Amphibole in Diorite			
Sample	17c	17r	Average
SiO ₂	43.81	44.28	44.05
TiO ₂	1.096	1.010	1.053
Al ₂ O ₃	9.825	10.02	9.920
FeO	15.41	15.02	15.21
Cr ₂ O ₃	0.057	0.204	0.130
MnO	0.150	0.084	0.117

MgO	11.76	11.70	11.73
CaO	11.74	11.43	11.58
Na ₂ O	1.459	1.334	1.396
K ₂ O	1.278	1.211	1.245
Cl	0.078	0.074	0.076
Total	96.61	96.16	96.39
O_Cl	0.020	0.020	0.020
TSi	6.613	6.689	6.651
TAI	1.387	1.311	1.349
Sum(T)	8.000	8.000	8.000
CAI	0.359	0.471	0.415
CCr	0.007	0.024	0.016
CFe ³⁺	0.099	0.00	0.050
CTi	0.124	0.115	0.120
CMg	2.647	2.633	2.640
CFe ²⁺	1.763	1.757	1.760
Sum(C)	5.000	5.000	5.000
BFe ²⁺	0.083	0.140	0.1115
BMn	0.019	0.011	0.015
BCa	1.898	1.850	1.874
Sum(B)	2.000	2.000	2.000
ANa	0.427	0.391	0.409
AK	0.246	0.233	0.240
Sum(A)	0.673	0.624	0.649
Sum_cat	15.67	15.624	15.65
CCI	0.020	0.019	0.019
Sum_oxy	23.00	23.02	23.01

Table 5: Chemical Composition of Ilmenite in Diorite	
Sample	17
SiO ₂	1.012
TiO ₂	52.52
Al ₂ O ₃	0.162
FeO	33.62
Cr ₂ O ₃	0.010
MnO	9.079
MgO	0.001
CaO	0.885
Na ₂ O	0.000
Total	97.29
Si	0.026
Al	0.005
Ti	1.004
Fe ²⁺	0.714
Cr	0.000
Mn	0.195
Mg	00.00
Ca	0.024
Na	00.00
Cations	1.968

Table 6: Bulk Rock Composition of Diorite (%)

Sample	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	K ₂ O	MnO	Na ₂ O	TiO ₂	P ₂ O ₅	Cr ₂ O ₃	LOI	Total
17	45.15	14.04	7.58	16.01	5.65	1.94	0.21	2.45	3.59	0.51	0.02	2.05	99.2

Table 7: Trace Element Composition of Diorite (ppm)

Sample	V	Cr	Co	Ni	Cu	Zn	Rb	Sr	Zr	Nb	Mo	Cs	Ba	Hf	Ta	Pb	Th	U
17	312.6	89.86	74.7	71.59	39.92	136.5	100.5	326	281.4	24.72	1.86	4.02	483.1	7.18	1.52	10.5	3.38	0.7

Table 8: Rare Earth Element of Diorite (ppm)

Sample	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
17	27.45	43.46	32.38	73.01	9.5	41.22	8.97	2.495	9.38	1.399	8.32	1.675	4.745	0.6	4.35	0.676

La _N /Yb _N	Gd _N /Yb _N	Eu _N /Eu _N *	Ce _N /Ce _N *
5.344	1.79	0.832	1.087

Eu/Eu* = Eu_N/(Sm_N x Gd_N)^{0.5} ; Ce/Ce* = Ce_N/(La_N x Nd_N)^{0.5}. Subscript N denotes Chondrite normalized values. Normalized factors are from (Sun and McDonough, 1989).

Therefore, amphiboles and biotite can be said to have formed by hydration crystallization, the evidence of which is the resorbed pyroxene and oxide mineral (ilmenite) mantled by amphiboles and biotite (Figures 4-7) (Beard et al., 2004; Beard et al., 2005). The association of these minerals suggest that pyroxene is the earliest, because it occurs as inclusions in amphiboles and biotite. The amphiboles is quite earlier than biotite because the biotite cuts across the amphibole and plagioclase (Figures 13 and 14), this represents the normal crystallization of minerals in igneous rocks (Bowen, 1928). The plagioclase feldspar exhibit both albite and Carlsbad twinning an indication that it is of igneous origin. The petrographic study show the plagioclase alteration to sericite through a process called sericitization, common phenomenon in igneous rocks.

This could have resulted from the hydrothermal fluids reacting with the pores in the plagioclase a process which is usually associated with chloritization of biotite (Figure 12) (Que and Allen, 1996). The photomicrographs, BSE images and result from the mineral chemistry shows no zoning in any of the minerals. The Al₂O₃ in the pyroxene is extremely low (0.4 %). The aluminium content in the amphibole is high while TiO₂ is very low. The amphibole shows an Edenite-hornblende type which is calcium rich. The plagioclase in the mafic intrusive is oligoclase, an indication that it was formed at lower temperature in the later stage of crystallization and thus have inclusions of earlier crystallized minerals such as pyroxene.

The percentage of silica present (45.15 %) in the whole rock is an indication that the rock is basic or mafic in composition (Hafferen and O'Brien, 2010; Haldar, 2013). It is an indication that the rock evolved from MgO - FeO rich component which is typical of tholeiitic cumulates. The low Nd and high Sr isotopic ratios is characteristic of continental crust, whereas the upper mantle has high Nd and low Sr isotopic ratios (Best and Christiansen, 2001). The photomicrographs and BSE images of the minerals show no form of zoning an indication that the minerals were in equilibrium with the melt during crystallization.

5. CONCLUSION

Based on the mineral chemistry and the geochemistry of the studied rock, this mafic intrusive rock can be named as hypersthene-diorite. The presence of amphibole is an indication that the magma from which the rock was formed was hydrous in nature. The rock has not been affected by any form metamorphism and deformation based on texture. There is an enrichment of LREE and a depletion of HREE. The fact that the rock contains hypersthene, which is a high temperature mineral with amphibole and biotite forming from hydration crystallization, the hypersthene-bearing diorite can be said to have extensively retrogressed.

ACKNOWLEDGEMENTS

The use of JEOL JXA 8230 Superprobe, instrument sponsored by NRF/NEP grant 40113 (UID 74464) at Rhodes University, Grahamstown South

Africa is kindly acknowledged and the financial support from Tertiary Education Trust Fund (TETFUND) is recognized.

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