Retrogression of Orthopyroxene-bearing Gneiss of Iboropa Akoko, Southwestern Nigeria

Retrogresija gnajsa z ortopiroksenom iz območja Iboropa Akoko, jugozahodna Nigerija

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Abstract

In this article, we report the mineral chemistry and petrographic features of charnockitic exposure of Iboropa within Precambrian Basement Complex of Nigeria. The mineral assemblages are pyroxene, plagioclase, biotite, hornblende, alkali feldspars, microperthite, quartz and ilmenite, with apatite occurring as accessory mineral. Apatite occurs in abundance as euhedral crystals. Orthopyroxene observed is strongly pleochroic and has numerous microfractures, and it is hypersthene ($\text{En}_{45}\text{Fs}_{54}\text{Wo}_1$) with low TiO_2 and MnO, having extremely low percentage of CaO. Hypersthene is mantled by a complex corona of amphibole, and the amphibole is hornblende with a chemical formula: $(\text{K,Na})(\text{Ca,Fe})_2(\text{Fe,Mg,Al,Ti})_5(\text{Al,Si})_8\text{O}_{22}(\text{OH})_2$. Plagioclase occurs as inclusions in both pyroxene and biotite. Biotite has high concentration of TiO_2 and extremely low CaO. The opaque mineral observed is ilmenite and it is concentrated around hypersthene and amphibole. Rare earth element (REE) displays negative Eu anomaly with enrichment of light REE over heavy REE. Amphiboles surrounding orthopyroxene are evidences of retrograde reactions and are formed at the expense of orthopyroxene reacting with plagioclase and quartz in the presence of fluid. The relationship between the mineral assemblages suggests the retrogression of the gneiss that might be as a result of rehydration process, and it is a transition from granulite facies to amphibolite facies during a retrogressive form of metamorphism.

Keywords: Hypersthene, microfractures, retrograde, microperthite, rehydration.

Povzetek

V tem članku predstavljamo mineraloško-kemične in petrografske značilnosti charnokita, ki se pojavlja na območju Iboropa znotraj predkambrijske podlage Nigerije. Opazovani minerali so: piroksen, plagioklaz, biotit, rogovača, alkalijski glinenec, mikropertit, kremen in ilmenit, z apatitom ki se pojavlja kot akcesorni mineral. Apatit je akcesorni mineral in se pojavlja v obilju kot evhedralni kristal. Opazovan ortopiroksen je močno pleokroičen in ima številne mikrorazpoke. Je hipersten ($\text{En}_{45}\text{Fs}_{54}\text{Wo}_1$) z nizkim TiO_2 in MnO in ima ekstremno nizek delež CaO. Hipersten je oploščen s kompleksno korono amfibola, ki je rogovača s kemijsko formulo $(\text{K,Na})(\text{Ca,Fe})_2(\text{Fe,Mg,Al,Ti})_5(\text{Al,Si})_8\text{O}_{22}(\text{OH})_2$. Plagioklaz se pojavlja kot inkluzije v piroksenu in biotitu. Biotit ima visoko koncentracijo TiO_2 in ekstremno nizko CaO. Opazovan nepreseven mineral je ilmenit in je koncentriran okoli hiperstena in amfibola. REE kaže na negativno Eu anomalijo z obogatitvijo LREE nad HREE. Amfiboli, ki obkrožajo ortopiroksene, so dokaz retrogradne reakcije in nastanejo pri reakciji ortopiroksena s plagioklazom in kremenom v prisotnosti fluida. Razmerje med mineralno sestavo predlaga retrogresijo gnajsa, ki bi lahko bila rezultat rehidracijskega procesa in je prehod granulitnega facies v amfibolitni facies med retrogresivno obliko metamorfizma.

Ključne besede: hipersten, mikro razpoke, retrogradno, mikropertit, rehidracija.

Introduction

Orthopyroxene-bearing gneiss is usually referred to as charnockitic gneiss or granulite, most especially if the orthopyroxene is hypersthene. In this article, the use of the term charnockitic gneiss will be adhered to. Charnockites are hypersthene-bearing rocks [1]. There has been an extensive study on charnockites and charnockitic rocks in India [2–5]. Charnockites are orthopyroxene-bearing anhydrous granitoids [1, 6], and they are of magmatic or metamorphic origin [7]. Charnockites are restricted to high-grade belt and those that are of metamorphic origin take their source either from igneous or from sedimentary protoliths during high-grade metamorphism under anhydrous conditions [8]. In some parts of south India and Sri Lanka, ‘patchy’ charnockites have been termed as ‘arrested growth’, ‘in situ’ charnockites or charnockitisation of amphibolite facies [9–15]. For the patchy charnockites of east Gondwana, metamorphic transformation from amphibolite facies gneiss occurred by two mechanisms: CO_2 ingress from deep level and a drop in the pressure of fluid [11, 16–18]. The process of charnockitisation is propagated by the influx of the CO_2 – H_2O fluid, which results in the migration of most basic elements from the initial rock towards the transition zones [19]. Touret and Huizenga [20] studied charnockite microstructures from magmatic to metamorphic and realised that microstructures alone cannot always provide solution to the igneous or metamorphic origin of charnockites due to high temperature of recrystallisation. In their study, further evidence for the presence of brine fluids includes the high-temperature fluid–mineral reactions at inter-grain boundaries (K-feldspar microveins and myrmekites) observed in both igneous and metamorphic charnockites. Yang et al. [21] gave the first report of Paleoproterozoic incipient charnockite from the North China Cratons. They documented centimetre- to decimetre-scale anhydrous zones of incipient charnockite within tonalite–trondhjemite–granodiorite (TTG) rocks that are adjacent to an intrusive charnockite. From their study, they concluded that the incipient charnockite formed at ultrahigh-temperature conditions of 890°C – 970°C .

Figure 1. Sketch geological map of the Hoggar-Air-Nigeria Province showing the Neoproterozoic Trans-Saharan belt, resulting from terrane amalgamation between the cratons of West Africa and Congo and the East Saharan block [26].

The study area for this research is part of the Neoproterozoic basement of Nigeria (Figure 1). Rocks of the Basement Complex of Nigeria are made up of predominantly migmatitic and granitic gneisses; quartzites; slightly migmatized to unmigmatized meta-sedimentary schists and meta-igneous rocks; charnockitic, gabbroic and dioritic rocks and members of the Older Granite suite mainly granites, granodiorites and syenites [22]. The migmatite gneisses of South-Western Nigeria are usually composed of three components, all of which sometimes may be present in a single outcrop [22]. These components are (a) early gneiss, (b) mafic–ultramafic bands and (c) granitic or felsic components. Iboropa Akoko is about 10 km from

Figure 2. Location map of the study area.

Figure 3. Field photograph of charnockitic gneiss with quartzo-feldspathic material at Iboropa Akoko.

Ikare (Figure 2), and Ikare area is dominated by migmatite gneiss-quartzite complex, making up 90% of the rock units [23]. The charnockitic gneiss of Iboropa is dark grey in colour (Figure 3), and it is poorly foliated. Other associated rocks in this area are grey gneiss, granitic gneiss, pelitic gneiss and pegmatite. Almost all granulite facies rocks described so far from the

Nigerian Basement Complex are of charnockitic affinity. Rocks of the granulite facies are found in all crystalline basement of the world [24]. Hubbard [25] suggested that these granulite facies rocks represent relicts of an earlier and more widespread granulite facies metamorphism of unspecified age, predating the Pan-African Orogeny.

However, Rahaman and Ocan [23] suggested that the charnockitic rocks were original igneous rocks that retained their anhydrous affinity during the Pan-African Orogeny. Most of the other rocks of the basement complex described so far range in metamorphic grades from greenschist to upper amphibolite facies. Metamorphic rocks that have attained higher grades of metamorphism are probably the cordierite-sillimanite gneisses at Bena village in northern Nigeria, which Sacchi [27] ascribed to the granulite facies. On the published 1:250,000 G.S.N. Sheets 61, Akure, some localities within the migmatite gneiss-quartzite complex were indicated by Dempster [28] as containing granulite facies mineral paragenesis. Petrographic evidence presented strongly suggests that the

granulite facies mineral paragenesis in Ikare area is a result of prograde metamorphism [29]. In this respect, rocks of the granulite facies mineralogy in Ikare area are different from others of similar mineralogy described so far [23], as original igneous rocks, because of composition, especially low water content, retained their original (igneous) granulite facies mineralogy. Data used for this work are from the PhD thesis of the first author.

Materials and Methods

Detailed petrography was carried out using Petrographic Microscopes, both at the Department of Geology, Obafemi Awolowo University and Department of Geology, Rhodes University, South Africa. Major elements and trace elements were determined at the Central Analytical Facility (CAF), Stellenbosch University, South Africa, using X-ray fluorescence (XRF) and laser ablation ICP-MS, respectively. The mineral chemistry of the minerals was done using electron microprobe analysis (EPMA) at the Department of Geology, Rhodes University South Africa by a JEOL JXA 8230 Superprobe, using 4 WD spectrometers. Equipment operating conditions employed for the EPMA were 15 kV acceleration voltage, 20 nA probe current, beam size of ~1 µm and counting time 10 s on peak and 5 s on each lower and upper background, respectively. Natural standards were used for measuring the characteristic X-rays, and the ZAF matrix correction method was employed for quantification.

Results

Petrography

The charnockitic gneiss is granoblastic in texture. The minerals that are present in the charnockitic gneiss include pyroxenes, amphiboles, biotite, plagioclase feldspar, K-feldspar quartz, opaque minerals, while apatite occur as accessory mineral. Orthopyroxene occur as porphyroblasts, changing from colourless to grey, highly pleochroic and changing from grey to pinkish, a property indicative of hypersthene (Figure 4). Some of the porphyroblasts have

Figure 4. Photomicrographs showing (a) porphyroblast of pyroxene (Px) having numerous fractures. Pale biotite (Bt) along cleavage planes (PPL). (b) Plagioclase (Pl) occurring as inclusions in pyroxene (XPL). PPL, plane polarised light; XPL, crossed polarised light.

inclusions of plagioclase and biotite (Figure 4) which make them poikiloblastic in texture. There is rimming of pyroxene by amphibole (Figure 5a). Back scattered electron (BSE) image and elemental maps in Figure 5a are also presented (Figures 5b and 6). There are small patches of pale-coloured biotite along the cleavage planes of pyroxenes (Figure 4a). Amphibole occurs as large, xenoblastic, dark green crystals and it is strongly pleochroic with inclusions of pyroxene (Figure 7a and 7b). Also, amphiboles have close association with opaque minerals. Biotite observed is of two varieties, namely the light brown and the deep brown, and both are strongly pleochroic. The longer axes of biotite are slightly aligned in preferred orientations

Figure 5. (a) Photomicrograph showing pyroxene (Px) rimmed by amphibole (Am). The opaque mineral (Opq) (PPL). (b) Back-scattered electron image of minerals shown in (a). PPL, plane polarised light; XPL, crossed polarised light.

Figure 6. The compositional maps of minerals shown in Figure 5, showing elemental levels of Si, Mg, Na, Ca, Fe, Al, K, Mn and Ti.

Figure 7. Photomicrographs showing: (a) amphiboles (Am) with inclusions of pyroxene (Px) (PPL). (b) Amphiboles with inclusions of pyroxene, surrounded by plagioclase (Pl) (XPL). (c) Biotite having inclusions of plagioclase feldspar (XPL). (d) Biotite having inclusions of plagioclase feldspar (PPL). PPL, plane polarised light; XPL, crossed polarised light.

Figure 8. Photomicrographs showing: (a) pyroxene in close contact with areas occupied by transparent minerals: plagioclase and K-feldspar. Altered biotite (brownish mineral) surrounded by transparent mineral (PPL). (b) Pyroxene (Px), perthitic K-feldspar (Kfs) and plagioclase feldspar (Pl). The straight lamellae in the perthite (XPL). (c) Biotite (Bt) and apatite. The smaller needle-shaped apatite crystals (PPL). (d) K-feldspar (Kfs), quartz (Qtz), apatite (Ap) and plagioclase (Pl) (XPL). PPL, plane polarised light; XPL, crossed polarised light.

which thus defines the foliation. The biotite grains have inclusions of plagioclase and apatite (Figure 7c and 7d). Plagioclase occurs as porphyroblasts, and grains are almost equidimensional. Plagioclase crystals observed exhibit both albite and carlsbad twinning. There is a close association between plagioclase and pyroxene. Plagioclase occurs as inclusions in both pyroxene and biotite, and plagioclase crystals occur at the margins of amphiboles. K-feldspar has perthitic texture and is in close contact with pyroxene (Figure 8a and 8b). Apatite is needle-like and colourless, occurring as inclusions in feldspars (Figures 8c and 8d).

Mineral Chemistry

Pyroxene: The mineral composition of pyroxene in charnockitic gneiss shows a slight variation from core to rim (Table 1). The range in composition for both the core and rim is: SiO₂: 49.68–49.82%, MgO: 15.20–15.07%, FeO: 31.91–32.19% and CaO: 0.495–0.618%. This result confirms the orthopyroxene as hypersthene and the formula can be written as MgFeSi₂O₆ (Table 1). In terms of the pyroxene end members, the formula can be written as En₄₅Fs₅₄Wo₁ (Table 1). The BSE image shows no form of zoning (Figure 5b), while the compositional maps show the levels of element in the minerals (Figure 6). The compositional maps

show high levels of magnesium (Mg) and iron (Fe), but a very low level of calcium (Ca) in the pyroxene (Px).

Amphibole: The composition of the various oxides is (Table 1): SiO₂: 42.45%, TiO₂: 2.038%, FeO: 18.10%, Al₂O₃: 10.39%, MgO: 9.16%, CaO: 11.30%, Na₂O: 1.53%, K₂O: 1.41% and Cl: 0.071%. The compositional maps (Figure 6) show amphibole with an appreciable amount of Fe, Ca and Mg but very low Na content. The formula of the amphibole is (K,Na)(Ca,Fe)₂(Mg,Fe,Ti,Al)₅(Al,Si)₈O₂₂(OH)₂ that is named as hornblende (Table 1).

Biotite: The chemical composition of biotite crystals is (Table 2): SiO₂: 34.71–35.95%, FeO: 19.97–20.97%, MgO: 9.64–10.15%, Al₂O₃: 13.35–14.14%, TiO₂: 4.84–5.23%, CaO: 0–0.07% and K₂O: 8.54–9.74%. The elemental composition of the biotite shows that it is annite.

Plagioclase: The chemical composition of 14 crystals of plagioclase shows the following range of values: SiO₂: 58.14–60.19%, Al₂O₃: 24.06–25.77%, CaO: 7.18–8.58%, Na₂O: 5.99–7.35% and K₂O: 0.34–0.49%, and in terms of anorthite content it can be written as Ab₅₉An₃₉Or₂ that is known as andesine (Figure 9). The chemical formula of the plagioclase based on cations is (Na,Ca)AlSi₃O₈ (Table 3).

Table 1. The chemical composition of pyroxene and amphibole

Pyroxene				Amphibole					
Sample	1c	1r	Crystal	1	2	3	4	5	6
SiO ₂	49.680	49.830	SiO ₂	42.453	41.804	43.680	42.904	43.139	42.786
TiO ₂	0.037	0.114	TiO ₂	2.038	1.450	1.505	1.669	1.826	1.993
Al ₂ O ₃	0.618	0.682	Al ₂ O ₃	10.389	10.342	9.819	10.039	10.174	10.186
FeO	32.470	31.910	FeO	18.095	17.894	17.156	18.178	18.975	18.580
Cr ₂ O ₃	0.000	0.010	Cr ₂ O ₃	0.000	0.000	0.043	0.132	0.053	0.101
MnO	0.585	0.712	MnO	0.058	0.016	0.111	0.132	0.049	0.054
MgO	15.200	15.070	MgO	9.163	9.361	9.943	9.474	9.399	9.622
CaO	0.618	0.495	CaO	11.305	11.394	11.575	11.465	11.431	11.455
Na ₂ O	0.014	0.055	Na ₂ O	1.533	1.338	1.108	1.386	1.406	1.443
K ₂ O	0.057	0.030	K ₂ O	1.409	1.430	1.215	1.411	1.347	1.349
Total	99.290	98.900	Cl	0.071	0.085	0.063	0.077	0.043	0.140
TSi	1.958	1.970	Total	96.510	95.110	96.180	96.740	97.79	97.610

Table 1. *The chemical composition of pyroxene and amphibole (continue)*

Pyroxene			Amphibole						
Sample	1c	1r	Crystal	1	2	3	4	5	6
TAl	0.029	0.030	O_Cl	0.020	0.020	0.010	0.020	0.010	0.030
TFe ³⁺	0.014	0.000	TSi	6.553	6.517	6.681	6.580	6.556	6.512
M1Al	0.000	0.002	TAl	1.447	1.483	1.319	1.420	1.444	1.488
M1Ti	0.001	0.003	Sum_T	8	8	8	8	8	8
M1Fe ³⁺	0.044	0.026	CAI	0.442	0.416	0.449	0.393	0.377	0.337
M1Fe ²⁺	0.062	0.080	CFe ⁺³	0.000	0.038	0	0	0	0
M1Cr	0.000	0.000	CTi	0.237	0.170	0.173	0.193	0.209	0.228
M1Mg	0.893	0.888	CMg	2.109	2.176	2.267	2.166	2.129	2.183
M2Mg	0.000	0.000	CFe ⁺²	2.213	2.201	2.106	2.232	2.279	2.240
M2Fe ²	0.950	0.949	Sum_C	5	5	5	5	5	5
M2Mn	0.020	0.024	BFe ⁺²	0.123	0.095	0.089	0.099	0.132	0.125
M2Ca	0.026	0.021	BMn	0.008	0.002	0.014	0.017	0.006	0.007
M2Na	0.001	0.004	BCa	1.870	1.903	1.897	1.884	1.861	1.868
M2K	0.003	0.002	Sum_B	2	2	2	2	2	2
Sum (cat)	3.997	3.998	ANa	0.459	0.404	0.329	0.412	0.414	0.426
Ca	1.337	1.069	AK	0.277	0.284	0.237	0.276	0.261	0.262
Mg	45.770	45.260	Sum_A	0.736	0.689	0.566	0.688	0.675	0.688
Fe2_Mn	52.890	53.670	Sum_cat	15.736	15.689	15.566	15.688	15.675	15.688
JD1	0.000	0.108	CCl	0.019	0.022	0.016	0.020	0.011	0.036
AE1	0.202	0.186	Sum_oxy	23.102	23.000	23.023	23.031	23.016	23.002
CFTS1	2.056	1.168							
CTTS1	0.056	0.174							
CATS1	0.000	0.000							
WO1	0.000	0.000							
EN1	45.780	45.560							
FS1	51.902	52.800							
Q	1.931	1.939							
J	0.002	0.008							
WO	1.299	1.055							
EN	44.460	44.670							
FS	54.240	54.280							
WEF	99.890	99.570							
JD	0.000	0.032							
AE	0.100	0.396							

M1, third octahedral site; M2, second octahedral site; M3, first octahedral site; T, tetrahedral site; JD, jadeite; AE, aegirine; WO, wollastonite; EN, enstatite; FS, ferrosilite; CAT, cation.

Table 2. Chemical composition of biotite crystals

Crystal	1	2	3	4	5	6	7	8
SiO ₂	35.20	35.10	35.19	34.71	35.52	35.34	35.95	35.42
TiO ₂	5.23	5.15	4.97	4.84	4.84	4.97	5.09	5.00
Al ₂ O ₃	13.63	13.79	14.14	13.75	13.92	13.35	13.82	13.83
Cr ₂ O ₃	0.04	0.06	0.00	0.03	0.02	0.05	0.03	0.00
FeO	21.02	20.48	20.75	20.96	19.97	20.59	20.41	20.72
MnO	0.00	0.04	0.03	0.03	0.00	0.01	0.00	0.02
MgO	9.88	9.95	10.15	9.93	10.00	10.07	9.99	9.64
CaO	0.01	0.07	0.00	0.04	0.02	0.00	0.00	0.04
Na ₂ O	0.13	0.11	0.09	0.14	0.09	0.08	0.14	0.11
K ₂ O	9.74	9.71	9.57	9.62	9.56	8.54	9.63	9.74
Cl	0.15	0.11	0.12	0.15	0.09	0.09	0.10	0.10
H ₂ O	1.80	1.81	1.81	1.78	1.81	1.80	1.83	1.81
Total	95.03	94.57	95.01	94.2	94.03	93.09	95.16	94.62
Si	5.739	5.735	5.717	5.714	5.803	5.823	5.812	5.782
AlIV	2.261	2.265	2.283	2.286	2.197	2.177	2.188	2.218
AlVI	0.356	0.388	0.423	0.380	0.481	0.414	0.443	0.441
Ti	0.641	0.633	0.607	0.599	0.595	0.616	0.619	0.614
Fe ²⁺	2.866	2.798	2.819	2.885	2.729	2.837	2.759	2.829
Cr	0.005	0.008	0.000	0.004	0.003	0.007	0.004	0.000
Mn	0.000	0.006	0.004	0.004	0.000	0.001	0.000	0.003
Mg	2.401	2.423	2.458	2.437	2.436	2.474	2.408	2.346
Ca	0.002	0.012	0.000	0.007	0.004	0.000	0.000	0.007
Na	0.041	0.035	0.028	0.045	0.029	0.026	0.044	0.035
K	2.026	2.024	1.984	2.020	1.993	1.795	1.986	2.028
Cations	16.338	16.327	16.323	16.381	16.270	16.170	16.263	16.303
CCl	0.083	0.061	0.066	0.084	0.050	0.050	0.055	0.055
OH	1.959	1.970	1.967	1.958	1.975	1.975	1.973	1.972
O	24	24	24	24	24	24	24	24
Fe/(Fe + Mg)	0.5400	0.54	0.530	0.540	0.530	0.530	0.530	0.550
Mg/(Fe + Mg)	0.460	0.460	0.470	0.460	0.470	0.470	0.470	0.450

AlIV, aluminium in tetrahedral site; AlVI, aluminium in octahedral site.

Table 3. The chemical composition of plagioclase crystals

Crystal	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO ₂	58.96	59.05	59.39	59.47	58.84	58.19	58.45	59.22	59.23	58.7	59.76	60.19	58.14	58.57
TiO ₂	0.02	0	0	0	0.04	0	0.37	0.01	0	0	0.04	0	0.03	0
Al ₂ O ₃	25.53	25.59	25.55	25.03	25.72	25.77	25.8	25.65	25.34	25.26	24.06	24.78	25.24	25.49
FeO	0.12	0.07	0.05	0.15	0.02	0.07	0.24	0.07	0.11	0.17	0	0.08	0.01	0.01
MnO	0.01	0.01	0.05	0.02	0.01	0.04	0	0.03	0	0.04	0.02	0	0	0
MgO	0	0.01	0	0	0.01	0	0	0	0.02	0	0	0.01	0	0
BaO	0.01	0.04	0.08	0.05	0.07	0	0.07	0.03	0.09	0	0.06	0.01	0.08	0.03
CaO	8.05	8.04	7.98	7.82	8.13	8.58	8.49	8.21	7.78	7.88	7.18	7.3	8.34	8.15
Na ₂ O	6.87	6.88	5.99	7.04	6.75	6.7	6.26	6.62	6.93	7.01	7.35	7.35	6.07	6.53
K ₂ O	0.38	0.37	0.39	0.39	0.34	0.37	0.36	0.34	0.37	0.36	0.49	0.41	0.37	0.39
Total	99.95	100.06	99.48	99.97	99.93	99.72	100.04	100.18	99.87	99.42	98.96	100.13	98.28	99.17
Si	2.639	2.64	2.659	2.661	2.633	2.616	2.617	2.642	2.651	2.642	2.697	2.683	2.642	2.639
Al	1.346	1.347	1.347	1.319	1.356	1.364	1.36	1.347	1.336	1.339	1.279	1.301	1.351	1.353
Fe ³⁺	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ti	0.001	0	0	0	0.001	0	0.012	0	0	0	0.001	0	0.001	0
Fe ²⁺	0.004	0.003	0.002	0.006	0.001	0.003	0.009	0.003	0.004	0.006	0	0.003	0	0
Mn	0	0	0.002	0.001	0	0.002	0	0.001	0	0.002	0.001	0	0	0
Mg	0	0.001	0	0	0.001	0	0	0	0.001	0	0	0.001	0	0
Ba	0	0.001	0.001	0.001	0.001	0	0.001	0.001	0.002	0	0.001	0	0.001	0.001
Ca	0.386	0.385	0.383	0.375	0.39	0.413	0.407	0.392	0.373	0.38	0.347	0.349	0.406	0.393
Na	0.596	0.596	0.52	0.611	0.586	0.584	0.543	0.573	0.602	0.612	0.643	0.635	0.535	0.571
K	0.022	0.021	0.022	0.022	0.019	0.021	0.021	0.019	0.021	0.021	0.028	0.023	0.021	0.022
Cations	4.994	4.995	4.937	4.997	4.989	5.003	4.971	4.979	4.992	5.002	4.998	4.995	4.958	4.98
X	3.986	3.987	4.006	3.98	3.99	3.98	3.989	3.989	3.987	3.981	3.977	3.984	3.994	3.992
Z	1.008	1.007	0.93	1.016	0.998	1.023	0.981	0.989	1.003	1.021	1.02	1.011	0.963	0.987
Ab	59.4	59.5	56.2	60.6	58.9	57.4	55.9	58.2	60.4	60.4	63.2	63.1	55.6	57.9
An	38.4	38.4	41.4	37.2	39.2	40.6	41.9	39.8	37.4	37.5	34.1	34.7	42.2	39.9
Or	2.2	2.1	2.4	2.2	1.9	2.1	2.2	1.9	2.1	2.1	2.8	2.3	2.2	2.2

Ab, albite; An, anorthite; Or, orthoclase.

Figure 9. Ternary diagram showing feldspar solid solution.

Ilmenite: The result of the chemical composition of ilmenite for charnockitic gneiss shows the following values (Table 4): TiO_2 : 50.79%, FeO : 46.37% and SiO_2 : 0.046%.

Major Element Geochemistry

The composition of the major oxides is as follows (Table 5): SiO_2 (50.93 wt%), Al_2O_3 (15.51 wt%), CaO (7.79 wt%), Fe_2O_3 (12.3 wt%), MgO (5.14 wt%), K_2O (1.01 wt%), MnO (0.15 wt%), Na_2O (3.33 wt%), TiO_2 (2.15 wt%), P_2O_5 (0.65 wt%), and Cr_2O_3 (0.02 wt%).

Trace Element Geochemistry

For the compatible elements Zn, Cr and V, the value ranges are as follows (Table 5): Zn (124.1 ppm), Cr (95.31 ppm) and V (188.28 ppm). The immobile transition elements Co and Ni have values of 107.09 and 52.36 ppm, respectively. The incompatible elements show a wide variation, and the large ion lithophile elements (LILE) have the values of Cs (0.31 ppm), Sr (583.8 ppm), Rb (18.36 ppm) and Ba (479.77 ppm).

Rare Earth Elements Geochemistry

The rare earth elemental (REE) composition of the charnockitic gneiss shows light REE (LREE) enrichment and depletion of heavy REE (HREE) (Table 5). The samples display a pattern of negative Eu anomaly.

Discussion

The orthopyroxene found in the charnockitic gneiss of Iboropa is hypersthene, that is Fe-Mg-rich (Table 1) and it is associated with amphibole (hornblende) and plagioclase. Pyroxene analysed is a solid solution between enstatite and ferrosilite ($\text{En}_{45}\text{Fs}_{54}\text{Wo}_1$), and because of the high Fe content it can be referred to as ferrohypersthene. Orthopyroxene is an essential mineral for all rocks in the charnockite suite.

Table 4. The composition of ilmenite in a charnockitic gneiss

Sample	1
SiO_2	0.046
TiO_2	50.787
Al_2O_3	0.02
FeO	46.372
Cr_2O_3	0.075
MnO	0.477
MgO	0.267
CaO	0
Na_2O	0.061
Total	98.11
Si	0.001
Al	0.001
Ti	0.986
Fe^{2+}	1.001
Cr	0.002
Mn	0.01
Mg	0.01
Ca	0
Na	0.003
Cations	2.014

The percentage of CaO in the analysed pyroxene is very low (0.5–0.6%), a value which is less than 1.0 and is consistent with the fact that Ca atoms per formula does not exceed 1.0, which occurs only in the M2 site [30]. The aluminium oxide content of the pyroxene is also low. Orthopyroxene can be found to be metamorphic because the weight percentage of $\text{MgO} + \text{FeO}_T$ is greater than 44.00% [31]. Orthopyroxene present could have formed during increase in grade of metamorphism from either hornblende or biotite. In Northern Nigeria, charnockite has been derived from the transformation of biotite by the addition of ferrous iron-rich juvenile

Table 5. Bulk rock composition of charnockitic gneiss; major elements (%), trace elements (ppm), REE (ppm)

Major element	1	Trace element	1	REE	1
Wt%		ppm		ppm	
SiO ₂	50.93	V	188.28	La	57.71
Al ₂ O ₃	15.51	Cr	95.31	Ce	119.2
CaO	7.79	Co	107.09	Pr	14.13
Fe ₂ O ₃	12.3	Ni	52.36	Nd	54.64
MgO	5.14	Cu	41.17	Sm	9.05
K ₂ O	1.01	Zn	124.1	Eu	2.27
MnO	0.15	Rb	18.36	Gd	7.325
Na ₂ O	3.33	Sr	583.8	Tb	0.856
TiO ₂	2.15	Zr	294.09	Dy	4.365
P ₂ O ₅	0.65	Nb	20.61	Ho	0.8
Cr ₂ O ₃	0.02	Mo	1.54	Er	2.02
LOI	0.34	Cs	0.31	Tm	0.251
Total	99.32	Ba	479.77	Yb	1.63
		Hf	6.49	Lu	0.22
		Ta	1.08	Total	274.4
		Pb	8.51	La _N /Yb _N	25.39
		Th	2.89	Gd _N /Yb _N	3.72
		U	0.45	Eu _N /Eu _N *	0.852
				Ce/Ce*	1.153

solution [32]. Orthopyroxene could be formed by any of the following reactions:

The earlier reactions are dehydration reactions resulting in a decrease in the activity of water and an increase in alkali activity [19]. Mineral assemblage show altered form of biotite (first-generation biotite) in close association with K-feldspar (Figure 8a). This process is a high-grade dehydration of rocks of the amphibolite facies to granulite facies and it can involve partial melting and in some cases fluid solid-state dehydration [33–35]. Orthopyroxene mantled by amphibole is an indication of retrogressive metamorphic event (Figure 5). The

retrogression of the charnockite could be due to various dehydration processes [36]. Retrogression involving the breakdown of orthopyroxene is quite common in granulite complexes [37, 38]. Orthopyroxene replaced by amphibole has been described in the granulite facies of gneiss in the granite Falls-Montevideo [39]. The hypersthene observed has numerous microfractures that may serve as a pathway for the movement of fluids (Figure 4a). The development of biotite along cleavage planes (Figure 4a) is also an indication of retrogression [40]. Amphibole could have been formed by a process in which orthopyroxene reacts with plagioclase (anorthite-rich) and quartz in the presence of water, and this can be represented by the following equation:

In this process, amphibole replaces orthopyroxene in a rehydration reaction. Biotite (second-generation biotite) that is in close contact with orthopyroxene (Figure 4a) could have been a product of a reaction in which K-feldspar is consumed by a rehydration process, and thus it can be represented by the following equation:

The biotite is annite-rich, an iron end member of biotite as indicated by the mineral chemistry (Table 2). Such retrogressive reactions have been found to result from fluid (CO_2 and H_2O) activity and oxygen fugacity in the later stages of dehydration zone [41]. Based on the BSE image and elemental maps (Figures 5b and 6), there is no evidence of zoning in the pyroxene crystals. Hornblende and biotite in charnockites have been found to be due to retrogressive metamorphism of pyroxene granulite facies rocks [42, 43], and retrograde form of metamorphism has been found to obliterate the mineralogy of the granulite facies [24]. Plagioclase occurring as inclusions in pyroxene and biotite is an indication that it was formed very early enough as primary minerals. Opaque minerals that are concentrated along the cleavage planes of amphiboles crystals are evidences of metamorphic alteration. The Al_2O_3 content of the amphibole is fairly high, and charnockitic rocks usually have Al_2O_3 higher than that of the normal igneous rocks. Hornblende has less magnesium than the coexisting orthopyroxene and a moderate composition of TiO_2 (2.04%). Hornblende has high TiO_2 (>2) which some authors have linked to the increase in the grade of metamorphism, and this link between temperature and Ti content of amphibole has been reported [44, 45]. There is a high value of TiO_2 (4.84–5.23%) in biotite, an indication that it is uniformly rich in Ti, and a higher value of X_{Fe} to X_{Mg} . Biotite could have reacted with quartz to give the Fe-Ti ilmenite. There has been suggestion that increasing Ti content leads to increase in the stability field of biotite [46]. The crystals of biotite have MgO of nearly the same range of composition as that of amphiboles but far less than that of orthopyroxene. Plagioclase is the dominant feldspar observed and it is al-

bite-enriched ($\text{Ab}_{55.9}\text{An}_{41.9}\text{Or}_{2.2}-\text{Ab}_{63.2}\text{An}_{34.1}\text{Or}_{2.8}$) that is andesine and is indicative of amphibolite zone. The K-feldspar has perthitic texture (Figure 8b). Perthite is an intergrowth of one feldspar within another, albite in orthoclase [47], and it is common in high-grade metamorphic rocks [48] due to the high temperature involved. The perthite observed has straight lamellae (Figure 7b), an indication of granulite facies. Based on the association of orthopyroxene and plagioclase, the granulite can be said to be of intermediate pressure [24], and one of the feature of this facies is the depletion of Th and U. The values of Cs have also been found to be depleted in high-grade metamorphosed rocks [24]. There is a depletion in the values of K, Rb, Th and U, and pyroxene gneiss with values of this nature has been suggested as a residue of partial melting in which there has been the removal of these elements from the original rocks [49]. The elements Th, U, Rb and Cs are usually present in the lattices of micas of the amphibolite facies but there is breaking down of micas to K-feldspar in the granulite facies, and K-feldspar do not concentrate Rb and Cs [24]. The Sr value in this rock is high, which might compound the low value of Rb, thus giving rise to low Rb/Sr ratio. REE patterns show LREE enrichment, and HREE-depleted patterns with negative Eu anomaly (Table 5), suggesting that this charnockitic gneiss of Iboropa could have been formed by partial melting and crystallisation. The enrichment of LREE and negative Eu anomaly are similar to the charnockitic rocks of Ado-Ekiti area of Nigeria [50]. The negative Eu anomaly reflects an intracrustal form of differentiation of the original igneous parent rock [51].

Conclusion

The detailed petrographic observation and the mineral assemblage suggest a retrograde metamorphic reaction. There are two generations each for biotite and plagioclase feldspar. The first-generation biotite is altered and it is concentrated in and around plagioclase as well as K-feldspar, while the second-generation biotite surrounds orthopyroxene. The high-grade minerals such as hypersthene and plagioclase gave

rise to hydrous minerals amphiboles and biotite. Fluids responsible for the hydration reaction could have been transported along the numerous microfractures within the hypersthene grains. The presence of straight lamellae in the perthite is an evidence of granulite facies. The charnockitic gneiss could have been resulted from a partial melting process.

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. The financial support from Tertiary Education Trust Fund (TETFUND) is recognised.

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