Petrological and Geochemical Characteristics of Mafic Granulites Associated with Alkaline Rocks in the Pan-African Dahomeyide Suture Zone, Southeastern Ghana

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1. Introduction

Most alkaline complexes are characterized by the presence of a distinctive zone where alkaline emanations appear to affect the wall rocks and the contact zones with country rocks (Winter, 2001). Such alkaline solutions and magmas may be effective agents for transporting trace elements and modifying the compositions of the host rocks (Wallace & Green, 1988, Rudnick et al., 1993). As a result the primary minerals can be replaced by alkaline minerals such as nepheline and feldspar. In this way nepheline-bearing rocks and other metasomatic derivatives of variable compositions can arise (Dawson et al. 1990). In the Pan-African Dahomeyide suture zone in southeastern Ghana, variably deformed alkaline rocks, comprising nepheline syenite and carbonatitic rocks, referred to as the Kpong complex (KC), occur in tectonic contact with high-pressure (HP) mafic granulite rocks of garnet-pyroxene-amphibole composition (Nude et al., 2009). The Dahomeyide mafic granulites have been found to preserve geochemical imprints of island arc theoleiitic (IAT) basalts as well as rocks with N-MORB-like affinities (Agbossoumonde et al., 2001, Attah & Morgan 2004). Thus the mafic granulites possess distinct geochemical signatures that differ significantly from the alkaline rocks.

This paper presents petrological and geochemical data on the nepheline-bearing mafic rocks previously referred to as mafic nepheline gneiss (Holm, 1974) at the contact zone between the HP mafic granulites and the KC rocks. The data are used to evaluate the distinctive mineralogical and trace element contents of the nepheline-bearing mafic rocks, and also infer the interactions of the alkaline magma with the mafic granulites at the contact zone.

2. Regional geological setting

The Dahomeyide orogen in southeastern Ghana and adjoining parts of Togo and Benin is the southern segment of the Pan-African Trans-Saharan belt (TSB). The TSB defines the eastern margin of the West African craton (WAC) and extends for over 2500 km from the Sahara to the Gulf of Guinea (Caby, 1987). The Pan-African orogen resulted in the assembly of northwest Gondwana (Hoffman, 1991; Cordani et al., 2003; Tohver et al., 2006). In southeastern Ghana and adjoining parts of Togo and Benin the Dahomeyide is interpreted to have resulted from easterly subduction after resorption of oceanic lithosphere at rifted margin of WAC (Affatton et al., 1991; Agbosoumonde et al., 2004; Attoh & Nude, 2008) with a preserved suture. These rocks are also exposed in the Amalaoulaou complex to the north in the Gourma fold and thrust belt in Mali (Berger et al., 2011) and shares comparable geochemical, metamorphic and tectonic evolution to the rocks of the Dahomeyides to the south in Benin, Togo and Ghana.

Figure 1 is a geologic map of the Dahomeyide orogen in southeastern Ghana, and adjoining parts of southern Togo and Benin (Sylvain et al., 1986, Castaing et al., 1993; Attoh et al.,

Fig. 1. Tectonic map of the Dahomeyides in southeastern Ghana and its northern extension (After Attoh, 1998) showing the study area

1997) showing the principal lithologies of the orogen. From the west is the deformed margin of the WAC that include 2.1 Ga granitoids (Agyei et al., 1987; Agbossoumonde et al., 2007), known as Ho gneisses, now deformed into proto-mylonites, and its cover rocks (Atacora nappes) occurring on the rifted passive margin. These are bounded to the east by distinctive high-pressure (HP) mafic granulite and eclogite facies rocks known locally as the Shai-Hill gneisses that form the suture zone unit (Attah, 1998; Agbossoumonde et al., 2001; Attah & Morgan, 2004) and mark the zone of collision of WAC with presumed exotic blocks to the east. Granitoids to the east of the suture zone comprise migmatites and dioritic gneisses which represent the arc terrane that is postulated to have formed during the subduction and accompanying oceanic closure.

3. Lithological distributions and previous geochronological work

3.1 Lithological distribution

The lithological distributions of the alkaline rocks in relation to the mafic granulite gneiss and other lithological units have been described by several workers including Holm (1974), Attah et al. (2007), Nude et al. (2009), and the geology is shown in Figure 2. The alkaline rocks comprise alternating layers and interfolded units of nepheline syenite gneiss and carbonatite along the inferred sole thrust of the suture that separates the mafic granulite

Fig. 2. Geological map of the study area showing the lithological relationships and the metasomatic zone where the samples were taken.

gneiss from rocks of the deformed edge of the WAC. The nepheline-bearing mafic granulite which forms the basis of this study is a garnet-bearing rock that is restricted to the contact zone with the alkaline rocks and the Shai Hills gneisses. It occurs in isolated outcrops in the northeast of the area (Fig. 2) where it is typically folded with steep axial surfaces, subvertical hinge zones and asymmetrical limbs. Atttoh et al. (1997) interpreted the structure of the suture zone to have resulted from early east-west compression, which produced the north-south imbricate thrust slices followed by NNW-directed thrusting.

3.2 Previous geochronological work

Geochronological studies of the suture zone mafic granulite gneisses (Shai Hill gneisses) and the alkaline rocks provide constraints on the chronology of the tectonic record of the area. U-Pb zircon ages determined from the mafic granulites from the suture zone in Ghana by Atttoh et al. (1991) and interpreted as peak metamorphic age was 610 ± 2 Ma. Also Hirdes and Davis (2002) reported U-Pb zircon ages of 603 ± 5 Ma from the mafic granulites from the Shai Hills area which confirm the timing of peak metamorphism in the suture zone. Similar age of 613 ± 1 Ma from zircon evaporation ($^{207}\text{Pb}/^{206}\text{Pb}$) was reported by Affaton et al. (2000) for the suture zone rocks in northern Togo. Hornblende separates from the mafic granulites yielded $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 587 and 567 Ma, interpreted as the time of exhumation of the nappes (Atttoh et al., 1997). Thus taken together high pressure metamorphism of the suture zone rocks occurred around 603-613 Ma and exhumation through the hornblende ages around 580-570 Ma (Atttoh et al., 2007). U-Pb ages on zircon separates determined by Bernard-Griffiths et al. (1991) from eclogite facies rocks from the suture zone in southern Togo had a discordant lower intercept of $\sim 640 \pm 53$ Ma and Nd model ages (T_{DM}) of 1150 Ma (Bernard-Griffiths et al., 1991). Nd model age of 940 Ma was obtained by Atttoh and Schmitz (1991) in the HP mafic granulites from the Shai Hills area in Ghana. The model ages suggest that the mantle derivation of the protoliths of these rocks may have occurred earlier. In the Amalaoulaou arc in Mali, the magmatic activity was found to have occurred at least c. 793 - 660 Ma followed by UHP metamorphism at c. 623 Ma (Berger et al., 2011).

Analyses of zircons separates from the carbonatite and the nepheline syenite gneiss samples yielded ages of $592\text{-}594 \pm 4$ Ma interpreted as the time of intrusion of the alkaline rocks (Nude et al., 2006). So the available age data suggest the emplacement of the alkaline rocks during syn-orogenic rifting, but this occurred after peak granulite metamorphism (Atttoh et al., 2007). Overall therefore the alkaline rocks appear to have been emplaced later than the mafic granulites.

4. Petrographic and geochemical characteristics of the mafic granulites in the suture zone

The mafic granulites (Shai Hills gneiss) are variably sheared and deformed, and have a streaky appearance. The rocks are characterized by prominent modal layering consisting of alternating but discontinuous garnet-rich and hornblende-rich zones that are cut by veins of all sizes and orientations. The microstructural features of the Shai Hills gneisses have been described by Atttoh and Nude (2008). Generally the rocks are composed of variable proportions of garnet, diopside pyroxene and scapolite. The following petrographic types have been identified by Atttoh (1998): a) hornblende-rich granulite with typical modal compositions of 42% hornblende, 38 % plagioclase, 9 % garnet, 4% diopside and 5% quartz,

and b) garnet-rich granulites that have similar mineral assemblage but with different mineral proportions of 29% garnet, 26% plagioclase, 20% diopside, 9% hornblende, 10% quartz and 2% scapolite. Geochemical features determined by Attoh and Morgan (2004) suggest that the mafic granulites have predominantly island arc tholeiite imprints with subordinate N-MORB signatures and trace element patterns that are very similar to lower crust compositions.

5. Petrographic and geochemical characteristics of the alkaline rocks

The alkaline rocks consist of nepheline syenite gneiss and carbonatite, and their petrographic features have been described by Holm (1974), Nude et al. (2009). The nepheline syenite gneiss is composed of nepheline (20–30%) which sometimes shows replacement by cancrinite. Other major phases are sodic feldspar (An₀–An₄, 30–50%), perthitic microcline and/or orthoclase (15–30%), annitic biotite (5–15%). Titanite is a widespread accessory constituent. Minor accessories include fine grained calcite, zircon, apatite, and muscovite. More syenitic varieties occur locally consisting essentially of albite, microcline, accessory biotite and nepheline. Modally, the carbonatite consists of coarse-grained mosaics of subhedral to euhedral equant calcite (35–50%) and annitic biotite (25–40%), with feldspar (albite and microcline/orthoclase, 5–20%) and nepheline (2–20%) and rare zircon.

Common mineral phases such as calcite, nepheline, feldspar and biotite in the nepheline syenite gneiss and the carbonatite have similar compositions (Attoh & Nude, 2008; Nude et al., 2009). The calcites show homogeneous compositions; CaO concentrations fall within 49.07–57.36 wt% and they are enriched in Sr with SrO values up to 1.4 wt%. Nepheline in both rock suites is generally similar in composition; it is relatively sodium rich, and compositions fall within Na_{6.0–8.1}K_{0.4–1.7}Al_{7.3–7.9}Si_{8.0–8.2}O₃₂. K-feldspar in the rocks is almost pure orthoclase with over 94 mol% Or in the nepheline syenite. Plagioclase is essentially albite, and common in almost all samples with compositions from 78 to 99 mol% Ab in the carbonatite, 94–98 mol% Ab in some nepheline syenite gneiss samples, confirming the compositional similarities in both rock suites. Biotite from the rocks is generally annitic with the composition falling within K_{1.8–1.9}Fe_{3.1–3.5}Mg_{1.2–1.4}Si_{5.2–5.3}Al_{3.1–3.4}O₂₀(OH,F_{0.1–0.4}). Geochemically the alkaline rocks are characteristically enriched in alkalis (Na₂O + K₂O is up to 16.4 wt %), Ba (3389–4665 ppm), Sr (3891–5481 ppm), Nb (78–135 ppm). The rocks show strong LREE fractionations and large deletions of Zr and Hf relative to primitive mantle (Nude et al., 2009). Most carbonatite and related rocks worldwide are known to have these geochemical features (Potter, 1996; Nelson et al., 1988; Woolley & Kemp, 1989; Hornig-Kjarsgaard, 1998; Bell & Tilton, 2001; Thompson et al., 2002; Chakhmouradian et al., 2007).

6. Petrography of the mafic granulites in the metasomatic zone

Representative samples of the mafic granulites analyzed in this study were taken from the metasomatic zone (Fig. 2). Generally these rocks which were previously mapped as mafic nepheline gneiss (Holm, 1974, Kesse, 1985) are found in isolated outcrops as a dense, foliated rock close to the alkaline rocks. The dark colour, coarse texture and significant modal content of garnet and pyriboles make the mafic granulite gneiss conspicuous in the bluish-gray nepheline gneiss and the dark-grey carbonatite. The rock contains feldspar and nepheline rich veinlets in the shear zone. Major modal compositions are variable and are composed of garnet (10–25 vol. %), sodic plagioclase (~30 vol. %), microcline (~15 vol. %),

nepheline (~20 vol. %), aegirine-augite (~35 vol. %), ferro-pargasite amphibole (10-30 vol. %), coarse titanite (~5 vol. %). The feldspars are generally coarse but in some of the crystals they occur as equigranular, granoblastic and interstitial grains. Accessory constituents include calcite, mostly found in cleavage cracks, zircon and rare kaersutite.

6.1 Composition of common mineral phases in the mafic granulites from the metasomatic zone and the alkaline rocks

The common mineral phases in the mafic granulites from the metasomatic zone and the alkaline rocks are calcite, nepheline, and feldspar. The compositions of these mineral phases were determined from representative samples of the mafic granulites with the objective of comparing their chemical contents with those from the alkaline rocks determined from previous studies by Attoh and Nude (2008) and then Nude et al. (2009). This will provide an insight into the extent of similarities in these common phases in the adjacent rocks. Two representative samples PN32A and PN56 which represent the variability of the compositional phases were selected for phase chemistry analysis. The mineral chemistry analysis was done using a Cameca SX-50 electron microprobe at the University of Utah. The minerals were tentatively identified using energy dispersive spectrometry (EDS). Table 1 lists the results of the microprobe analysis.

6.1.1 Calcite

Calcite is the only carbonate in the rocks; CaO contents range from 51.0 – 53.8 wt %. The totals of the major element concentrations are limited and fall within 55-58 wt % excluding volatiles and. The mineral is characteristically Sr-rich, with values within 1.3- 1.5 wt %.

6.1.2 Nepheline

Nepheline compositions in the rocks are variable, but a key feature is that it is Na-rich, and the variable compositions fall within $\text{Na}_{2.9-6.0}\text{K}_{0.0-1.7}\text{Al}_{4.2-8.2}\text{Si}_{8.0-11.8}\text{O}_{32}$. Two varieties of the nepheline have been recognized from the samples (Table 1b). The first variety is relatively SiO_2 -rich and Al_2O_3 -poor. This type is also relatively low in alkalis especially K_2O . The second type is relatively poor in SiO_2 , but has high contents of Al_2O_3 and Na (Table 1b).

6.1.3 Feldspar

Feldspar compositions are also variable within the samples. The mineral is present as two-feldspar components, comprising albite and orthoclase in some samples (PN 32A, Table 1c), with representative compositions of 21-32 mol% Ab and 67-78 mol% Or, or as single

Sample:	PN 32A		PN 56	
Analyses no:	1	2	3	4
<i>(a) Calcite</i>				
FeO	0.23	0.26	0.21	0.28
MnO	0.39	0.3	0.45	4.58
MgO	0.02	0.06	0.03	0.01
CaO	53.82	53.3	53.3	51.96
SrO	1.28	1.5	1.33	1.39
Total	55.74	55.42	55.32	58.22
Mg#	15.5	28.3	20.9	4.8

Sample:	PN 32A		PN 56		
Analyses no:	1	2	1	2	3
<i>(b) Nepheline</i>					
SiO ₂	67.9	65.33	42.69	42.17	42.31
Al ₂ O ₃	20.77	20.37	34.94	34.75	35.17
FeO	0	0.02	0.15	0.04	0.18
CaO	0.54	0.41	0.46	0.69	0.61
Na ₂ O	11.33	8.5	15.7	15.5	16.06
K ₂ O	0.08	3.26	6.76	6.51	6.41
Total	100.62	97.89	100.7	99.66	100.74
Si	11.8	11.782	8.165	8.143	8.095
Al	4.255	4.329	7.878	7.908	7.93
Fe	0	0.003	0.024	0.007	0.028
Ca	0.101	0.079	0.094	0.142	0.125
Na	3.819	2.973	5.821	5.801	5.958
K	0.017	0.749	1.65	1.603	1.564
Total	19.992	19.915	23.632	23.604	23.7
Sample:	PN 32A		PN 56		
Analyses no:	1	2	1	2	
<i>(c) Feldspar</i>					
SiO ₂	67.07	68.05	62.16	61.29	
Al ₂ O ₃	20.92	20.23	20.38	20.42	
FeO	0	0.21	0	0.16	
CaO	0.61	0.15	0.1	0.05	
Na ₂ O	11.35	11.79	3.24	2.18	
K ₂ O	0.12	0.07	10.43	12.12	
BaO	0	0	3.51	3.87	
Total	100.07	100.5	99.82	100.09	
Si	2.934	2.964	2.897	2.88	
Al	1.079	1.039	1.119	1.131	
Fe	0	0.008	0	0.006	
Ca	0.029	0.007	0.005	0.003	
Na	0.963	0.995	0.293	0.199	
K	0.006	0.004	0.62	0.727	
Ba	0	0	0.064	0.071	
Total	5.011	5.017	4.998	5.017	
Mol% An	2.9058	0.6958	0.5447	0.3229	
Mol% Ab	96.493	98.9066	31.9172	21.4209	
Mol% Or	0.6012	0.3976	67.5381	78.2562	

Total Fe as FeO

Table 1. Representative compositions of calcite, nepheline and feldspar in the mafic granulites from the metasomatic zone.

feldspar comprising almost pure albite with composition of 96-99 mol% Ab (PN 56, Table 1c). A notable feature in the mafic granulites from this study is that calcite, nepheline and feldspars are similar in their compositions to those from the alkaline rocks, with nepheline and feldspars showing similar variability as in the alkaline rocks (Nude et al., 2009). These comparable features suggest mineralogical influence of the alkaline rocks on the mafic granulites.

7. Geochemistry

7.1 Analytical methods

Whole rock samples were analyzed from representative samples for 10 major elements (SiO_2 , TiO_2 , Al_2O_3 , total Fe as Fe_2O_3^* , MnO, MgO, CaO, Na_2O , K_2O , P_2O_5) and 12 trace elements (Nb, Zr, Y, Sr, Rb, Zn, Cu, Ni, Cr, Sc, V, Ba) at Utah State University, and the analytical techniques have been described by Nude et al. (2009). The analysis was carried on Philips 2400 X-ray fluorescence spectrometer using pressed powders for both major and trace elements, with selected U.S.G.S. and international standards prepared identically to the samples. Accepted concentrations were taken from the compilation of Potts et al. (1992). Matrix corrections were carried out within the Philips SuperX software package, which uses the fundamental parameters approach (Rousseau, 1989) to calculate theoretical alpha coefficients for the range of standards. Replicate analyses of selected standards as unknowns suggest percent relative errors $\approx 1\%$ for silica, $\approx 2-4\%$ for less abundant major elements, and $\approx 1-6\%$ for trace elements.

The concentrations of rare earth elements (REE) and other trace elements in whole rock samples were determined using Perkin-Elmer 6000 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) at Centenary College, Shreveport, Louisiana, with acid digestion techniques. Standard reference samples were used in the quantitative analyses of the elements. Table 2 shows the major and trace elements concentrations in the representative samples.

7.2 Major elements

The representative samples of the mafic granulites have SiO_2 contents in the range of 35.0 and 52.0 wt% while CaO contents are from 8.0 to 24.0 wt%. Al_2O_3 contents range from 12.9 to 17.2 wt%; Fe_2O_3 total values range from 7.9 to 10.5 wt% whereas TiO_2 and P_2O_5 are from 1.2 to 1.8 and 0.5 to 0.7 wt% respectively. The total alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) contents are relatively high, with values ranging from 9.7 to 14.1 wt%. Figure 3 are Harker plots in which selected major elements concentrations and total alkalis compositions in the metasomatic mafic granulites are compared to that of the alkaline rocks. The data for the alkaline rocks are from Nude et al. (2009). Apart from K_2O the other major elements from the mafic granulites display linear trends with those from the alkaline rocks. The deviation of K_2O from this trend is not surprising because it is much more mobile and susceptible to alteration. From the present data the linear trends suggest mechanical mixing of the rocks rather than fractional crystallization which can also show linear trend.

Attoh and Morgan (2004) carried out geochemical investigations of the mafic granulites which they sampled from nearby the areas where the present study was carried out, but outside the metasomatic zone, specifically to the east and south of the zone. The following major element ranges (wt %) were reported by these authors: $\text{SiO}_2 = 42.4-52.0$, $\text{TiO}_2 = 0.9-3.4$, $\text{Al}_2\text{O}_3 = 8.6-18.9$, Fe_2O_3 total = 6.3- 6.8, MgO = 4.4-11.6, CaO = 7.7-11.1, $\text{Na}_2\text{O} = 1.52- 4.36$ + and $\text{K}_2\text{O} = 0.01- 0.57$. Their major element results appear similar to those obtained in the present study; exceptions are Fe_2O_3 total, CaO, the alkalis, Na_2O and K_2O , which are relatively

	PN-32A	PN-36	PN-39	PN-42	PN-46	PN-55	PN-56	PN-61	PN-63
SiO ₂	35.98	50.03	49.2	38.2	39.33	43.7	42.46	38.4	50.48
TiO ₂	1.47	1.37	1.32	1.2	1.31	1.88	1.83	1.32	1.22
Al ₂ O ₃	12.94	17.07	17.11	14.08	14.93	17.23	18.53	14.34	17.21
Fe ₂ O ₃	10.86	8.2	9.41	9.54	9.42	12.34	10.52	9.93	7.92
MnO	0.30	0.28	0.35	0.29	0.29	0.36	0.36	0.31	0.27
MgO	3.05	1.01	1.52	3.71	2.43	1.82	1.48	2.49	0.96
CaO	23.85	8.48	8.01	19.59	17.8	10.25	9.55	19.38	8.36
Na ₂ O	4.32	8.53	8.95	6.62	7.49	8.24	10.13	6.94	8.64
K ₂ O	5.25	3.89	2.95	5.14	5.32	2.92	3.97	5.22	3.82
P ₂ O ₅	0.77	0.55	0.64	0.66	0.64	0.58	0.50	0.63	0.56
Total	98.79	99.41	99.46	99.03	98.96	99.32	99.33	98.96	99.44
Mg#	35.8	19.7	24.2	43.5	33.8	22.6	21.8	33.2	19.3
ppm									
Nb	90	256	261	124	146	157	216	144	245
Zr	339	398	365	295	324	266	257	267	352
Y	37	34	36	28	32	46	40	30	36
Sr	3815	2045	1574	3562	3366	1585	1007	3433	1996
Rb	139	82	53	157	139	77	117	137	83
Sc	38	17	16	32	24	16	13	31	14
V	158	60	115	162	191	155	126	199	53
Cr	57	31	21	46	27	33	1	27	44
Ni	12	3	1	23	6	1	1	7	2
Cu	23	4	5	8	17	4	1	16	6
Zn	96	105	111	101	86	87	77	92	106
Ba	3783	1623	1786	2769	2899	2812	2789	2924	1647
La	141.26	124.45	112.01	140.33	114.2	153.2	138.07	146.92	149.81
Ce	258.3	256.77	230.63	222.26	203.32	290.48	275.09	233.75	280.12
Pr	26.46	29.49	25.35	24.28	18.79	31.57	25.17	22.33	34.11
Nd	84.44	99.03	82.34	76.93	59.1	98.99	75.28	68.09	113.59
Eu	3.93	5.03	3.97	3.41	2.84	4.07	2.71	3.32	5.7
Sm	13.33	15.63	12.81	11.59	9.11	13.78	9.63	10.08	17.44
Gd	10.56	11.46	9.53	8.46	6.83	10.01	7	7.42	13.4
Tb	1.26	1.48	1.23	1	0.82	1.29	0.82	0.92	1.72
Dy	6.65	7.35	6.36	4.86	4.15	6.96	4.23	4.42	8.36
Ho	1.25	1.32	1.2	0.89	0.73	1.35	0.87	0.86	1.5
Er	3.2	3.29	2.95	2.25	1.72	3.71	2.37	2.13	3.84
Tm	0.43	0.43	0.41	0.3	0.25	0.53	0.32	0.3	0.54
Yb	2.57	2.49	2.48	1.77	1.4	3.4	1.88	1.74	3.06
Lu	0.38	0.39	0.41	0.26	0.21	0.51	0.29	0.24	0.47
Hf	3.21	3.2	3.37	1.82	1.89	4.25	4.34	1.81	3.32
Ta	4.48	21.4	16.86	6.98	10.44	12.54	18.16	8.64	20.11
Pb	10.43	0.45	0.59	0.35	6.13	-0.76	-1.35	7.08	0.24
Th	4.17	10.99	6.89	4.88	3.77	13.45	12.11	3.62	12.73
U	1.75	4.45	1.55	1.38	2.07	2.13	2.45	1.54	4.2
Zr/Hf	105.6	124.4	108.3	162.19	171.4	62.6	59.2	147.5	106.0
Nb/Ta	20.1	11.0	15.5	17.8	13.0	12.5	11.9	16.7	12.2

 Table 2. Major and trace element concentrations in the mafic granulites from the
 metasomatic zone.

Fig. 3. Harker plots comparing selected major element concentrations in the metasomatic mafic granulite rocks with the alkaline rocks (carbonatite and nepheline syenite). Data for the alkaline rocks are from Nude et al. (2009).

enriched in the rocks from the metasomatic zone compared to those obtained by Atttoh and Morgan (2004). For example K_2O contents in the metasomatic rocks are several folds enriched (concentrations range from 2.95 to 5.25 wt %, Table 2) compared to the

concentrations in the non-metasomatic varieties (0.01 – 0.57 wt %) determined by Atttoh and Morgan (2004). Na_2O also shows similar enrichment in the metasomatic rocks (4.32-10.13 wt %) compared to the non-metasomatic varieties (1.52- 4.36 wt %). The overall major element contents show that the mafic granulites in the metasomatic zone are particularly alkaline, presumably from the addition of Na- and K-rich fluids from the adjacent alkaline rocks. The rocks are also evolved and contain variable amounts of CaO.

7.3 Trace element contents and variations

The trace element contents of the metasomatic zone mafic granulites show high absolute values of Sr (1574-3815 ppm), Ba (1623-3783 ppm), Nb (90-256 ppm). The rocks also have Nb/Ta values ranging from 11-20 and very high Zr/Hf values of 59-171. The Nb/Ta values from the analysed samples compares with chondritic values of 17.6, but the Zr/Hf values are far higher than chondritic values of approximately 36 determined in most reservoirs of the silicate earth (Weyer et al., 2003; Potter, 1996). In Figure 4, Sr and Ba concentrations in the metasomatic mafic granulites are compared with those in the alkaline rocks determined by Nude et al. (2009). From the figure, Sr displays linear trend as is Ba, although 2 samples of the nepheline syenite and a sample of the metasomatic mafic granulites show anomalously high Ba values and deviate from the linear trend. The linear trend has also been shown in the selected major elements in Figure 3, confirming the possible mechanical mixing of those rocks.

Fig. 4. Ba and Sr concentrations in the metasomatic mafic granulite rocks compared with the alkaline rocks (carbonatite and nepheline syenite). Data for the alkaline rocks are from Nude et al. (2009).

Figure 5 is a primitive mantle-normalized incompatible elements plot of the metasomatic zone mafic granulites compared with alkaline rocks. The similarities of the alkaline rocks to the analyzed samples are shown especially in the relative depletions of the HREE, Rb, Hf, Ti, Y and enrichment of K, Eu and Sm relative to Primitive Mantle. The analyzed rocks also differ from the alkaline rocks in elevated U, Ta, Nb, and Zr. Another difference is the prominent troughs at Th, U and Hf, Zr shown in the alkaline rocks; a feature not shown in the mafic granulites. Of particular interest is the relative fractionation of Zr from Hf in the analyzed samples.

Fig. 5. Primitive mantle-normalized concentrations in the mafic granulites from the metasomatic zone compared with the alkaline rocks (nepheline syenite and carbonatite). Data of the alkaline rocks are from Nude et al. (2009). Normalizing values are from McDonough et al. (1991).

In the REE plot (Fig. 6) the rocks show LREE enrichment, slight positive Eu anomaly and spread at the HREE end. However, the slight positive Eu anomaly is not shown in the carbonatite samples. Overall, the REE patterns of the metasomatic mafic granulites are similar to those of the alkaline rocks, particularly the nepheline syenite. Compared to the suture zone mafic granulites analyzed by Attoh and Morgan (2004) the trace element patterns shown by the rocks from the present study differ markedly. First is the LREE fractionation and steep REE pattern, second is the slight positive Eu anomaly and, third is the overall incompatible trace elements enrichments in the metasomatic granulites.

Fig. 6. Primitive mantle-normalized REE plot for the mafic granulites from the suture zone compared with the alkaline rocks (nepheline syenite and carbonatite). Data of the alkaline rocks are from Nude et al. (2009). Normalizing values are from McDonough et al. (1991).

8. Discussion

The new data presented in the present study on the modal contents, mineral chemistry and geochemical compositions of the mafic granulite gneiss at the contact zone between the alkaline rocks and the Shai Hills gneiss show that the rocks possess unique compositions which are suggestive of metasomatic transformation of the mafic granulites and hence the modification of the petrography and geochemistry of the original rocks. For example the ubiquitous presence of modal nepheline, feldspar and to a lesser quantity calcite in the mafic granulites is reflective of the mineralogy of the alkaline rocks. Additionally, the common mineral phases such as calcite, nepheline and feldspars in both rock suites have similar mineral chemistry. Partly, the Ca- Na- and K-rich fluids which formed these phases most likely emanated from the alkaline rocks. This evidence is supported by the comparable high CaO, Na₂O and K₂O contents in the mafic granulites under study to the alkaline rocks nearby, and suggests carbonate-alkali fluid interaction.

As shown from the present results the metasomatic mafic granulites are also enriched in Sr, Ba, Nb and show strong REE fractionation; these features are characteristic of carbonatitic melts. Most incompatible trace element concentration and patterns and the REE plots on the mantle-normalized diagrams also show similarities with the alkaline rocks. The observed very high Zr/Hf values in the rocks from the present study which is indicative of Hf fractionation is often associated with carbonate metasomatism (Dupuy et al., 1992) as the element pairs are expected to behave congruently in both fluids and melts (Jochum et al., 1986). Taken together, the major element compositions, the trace element contents and patterns constitute strong evidences to suggest the influence of the alkaline rocks on the overall modal compositions and bulk rock chemistry of the mafic granulites. The linear trends shown in the Harker plots and the spread at the HREE end of the mantle-normalized plots are indicative of mechanical mixing of the rocks, although this requires further evidence to confirm.

However, the metasomatic mafic granulites from the present study preserve some textural, modal and geochemical features which are similar to the Shai Hill gneisses and which also make them different from the alkaline rocks in the area. These features are their coarse texture and presence of garnet, and pyriboles. On geochemistry the mafic granulites again differ in their relative enrichment of Th and U, and depletion of Hf relative to Zr in the spider plots. Importantly the slight positive Eu anomaly in the mantled-normalized plots is absent in the carbonatite. These features provide compelling evidence to suggest that the mafic granulites are alkaline facies of the Shai hills rocks; the trace element budget are likely to have resulted from alkaline fluid interactions.

Available age data show that the emplacement of the alkaline rocks postdates the formation of the mafic granulites (Attoh et al., 2007), so the alkaline rocks are strong candidates for the source of the trace elements and particularly LREE enrichment in the mafic granulites. Although the mechanism of the interaction of the alkaline fluids is not clear, it is possible that it could have resulted from deformation associated with the emplacement of the alkaline rocks through percolation of alkaline fluids and/or mechanical mixing of the rock suites. This hypothesis requires further testing using isotopic data. However, carbonatitic melts have been shown from experiments to be of low viscosity, and capable of separating from their source at low degree melt fractions, and can percolate wall rocks by low angle dihedral flow (Hunter and Mackenzie, 1989; Hammouda and Laporte, 2000). Thus the alkaline fluids are likely to have emanated from the carbonatite and the nepheline syenite into the mafic granulites.

8.1 Tectonic and petrological implications

The new geochemical data from this study also provide further constraints on the evolution of the alkaline rocks and associated mafic granulites exposed along the suture zone of the Pan African Dahomeyide orogen in West Africa. Evidence for the Pan African suture and high pressure metamorphism have been provided in the literature by several workers including Berger et al., (2011), Agbossoumonde, et al. (2001, 2004), Attoh (1998) and Caby, (1987). These data, together with geochemical data on the Shai Hills granulites (Attoh & Morgan, 2004) infer a lower crust chemical composition for the rocks. The latter authors argued that the Dahomeyide mafic granulites preserve chemical imprints of basaltic rocks with trace element compositions similar to those of lower continental crust. The postulation is that the suture zone mafic granulites represent the roots of Pan African volcanic arc that formed from subduction to great depths, followed by HP granulite facies metamorphism accompanied by partial melting and later thrusting along ductile shear zones to produce crystalline nappes along the margin of the West African craton (Attoh, 1998).

The new geochemical data from this study shows a slight positive Eu anomaly in the mantle-normalized trace element patterns in the metasomatic rocks along the suture zone. This feature is interesting because positive Eu anomaly in the Shai Hills rocks has not been previously reported. But evidence of positive Eu anomaly in mafic granulite terrains that formed from basaltic lower crust has been shown by Rudnick (1992). It therefore appears that the mafic granulites from this study preserve a geochemical characteristic that may be of lower crustal affinity, a feature consistent with the findings of Attoh and Morgan (2004). So its tectonic association with the alkaline rocks along the sole thrust of the suture could be partly responsible for the unique alkalic and trace element compositions, as from available age data the alkaline rocks formed possibly after peak granulite metamorphism related to the Pan African orogeny (Attoh et al., 2007).

9. Conclusions

We have provided petrological and geochemical data on the mafic granulites exposed at the contact zone with alkaline rocks of the Kpong complex in the Pan African Dahomeyide suture zone southeastern Ghana. The mafic granulites have been found to have distinct modal and geochemical compositions which are in many ways similar to the alkaline rocks and different from the other mafic granulites outside the contact zone. Some of these are the presence of nepheline-rich veinlets and calcite along cleavage cracks in the mafic granulites. Together with other features such as compositions of modal phases, namely, calcite, nepheline, and feldspar, enrichment of alkalis, Ba, Sr, Nb and LREE, very high Zr/Hf values and overall steep REE patterns observed in the mafic granulites provide compelling evidences which suggest interaction of the alkaline fluids with the mafic granulites at the contact zone.

From the present data the mafic granulites from this study which seem to have a precursor texture and mineralogy identical to the Shai Hill mafic granulite gneisses (Attoh, 1998, Attoh and Morgan 2004), and described by Holms (1974) and Kesse (1985) as mafic nepheline gneiss, is an alkaline facies of the Shai Hills gneisses. The unique composition resulted from alkali fluid interaction from the carbonatitic and nepheline syenite along the tectonized zone. The degree and style of the alkali metasomatism may have varied because of the variable compositions of some the common mineral phases.

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