ISLAND ARC ORIGIN OF THE VARIEGATED FORMATIONS FROM THE EAST RHODOPE, BULGARIA - IMPLICATIONS FOR THE EVOLUTION OF THE RHODOPE MASSIF

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ABSTRACT

The Variegated Formations (VF) of the eastern Rhodope Mountains (SE Bulgaria) form part of the pre-Alpine basement of the region. They are composed of alternating sediments and igneous rocks with a high-grade metamorphic overprint. Numerous ophiolitic slivers are associated with the VF and include metamorphosed peridotites, ultramafic cumulates, and amphibolitized eclogites. The dismembered ophiolites usually form the base of the VF successions.

The metasedimentary rock types contain terrigenous materials (metapsammites and quartzites) that frequently alternate with metapelites and marbles. The nature of this sedimentary package, along with the field relations and sedimentary features, reflects its flysch character.

The metaigneous rocks of the VF occur either as layers interbedded with the metasediments, or as intrusive bodies that intersect the ultramafic rocks. The principal mineral phases in the metabasites are amphibole + plagioclase + quartz + epidote \pm garnet \pm chlorite. We calculate temperatures of 630°C to 520°C at 6-2 kbar pressures, indicating moderate amphibolite facies metamorphism. Major rock-forming minerals (amphibole, plagioclase, and garnet) exhibit zoning typical of retrograde P-T conditions.

When plotted on tectonic-setting discrimination diagrams, the metabasic rocks of the VF fall mainly in the fields of modern boninites and arc tholeiites. They show low Ti and Zr contents and key elemental ratios of CaO/TiO_2 , Al_2O_3/TiO_2 , Ti/Zr, Ti/Y and Zr/Y, all transitional between island arc tholeiites and boninites. Chondrite-normalized REE patterns reveal the existence of two different trends: U-shaped REE patterns (for the majority of samples) and LREE depleted patterns. Regardless of the existence of these two trends, the $[La/Sm]_N$ ratios of the metabasites perfectly coincide with the same ratios for many Cenozoic boninite series.

The flysch character of the sedimentary sequences, as well as the clear supra-subduction zone affinities of the igneous rocks, indicates that the VF formed in an oceanic island-arc setting. The boninitic affinities of the meta-igneous rocks indicate possible origin in an immature arc. The character of the VF and its association with the dismembered ophiolite slivers shows the presence of a suture zone. The East Rhodope suture zone distinguishes the VF from the rocks structurally below it, which consist of orthogneisses typical of continental crust. Existing U-Pb zircon data indicate that the orthogneisses are of Variscan age. New U-Pb zircon age data for the VF suggest Late Neoproterozoic ages for some protoliths.

Based on regional correlations, the interpretation of the VF as a fossil accretionary prism can be useful for elucidating the structure of the whole Rhodope composite terrane, and for tracing the suture itself to the Central and Western parts of the Massif.

INTRODUCTION

The Variegated Formations (VF) of the eastern Rhodope Mountains (SE Bulgaria) form part of the pre-Alpine basement of this region (Kozhoukharov et al., 1992). They are composed of alternating metamorphosed sedimentary and igneous rocks, including metagabbros and amphibolites, felsic orthogneisses, metapelites and metapsammites, and marbles. These units include rocks that experienced a high-temperature amphibolite facies metamorphic overprint. The total thickness of the VF in the studied area is 1800-2900 m. Numerous ophiolite bodies of the Rhodope Ophiolite Association (metaperidotites, metacumulates, and amphibolitized eclogites) occur, associated with the VF. The close spatial relationship between the dismembered Rhodope ophiolite bodies and the VF is well known, with the ophiolites forming the base of the VF (Kozhoukharova, 1996). This relationship suggests a possible genetic connection between these mafic rock sequences. However, little is known about the palaeogeographic origin of the VF (from the Rhodope Massif, South Bulgaria).

The goal of this paper is to clarify the origin and the significance of the rock assemblages that compose the VF. We also intend to determine if there is a connection with the adjacent remnants of oceanic crust recognized as the Rhodope Ophiolite Association. The relationship between these rock units has important implications for the geodynamic interpretation of the structure and evolution of the Rhodope Massif. We have selected rocks from the VF of the Avren Synform and the Bela Reka Antiform, close to the Bulgarian-Greek border, to carry out structural, petrographic, and geochemical studies on these assemblages.

The Rhodope Massif is part of the Thracian micro continent (after Bončev, 1986), although we regard it as a composite superterrane (Fig. 1) and we interpret it as an element of the Variscan belt of Europe. Its pertinence to the mentioned belt is evidenced by features such as the development of voluminous Variscan granitoid magmatism (~340-238 Ma, Zagorčev and Moorbath, 1986; ~331-250 Ma, Peytcheva and Quadt, 1995). The Thracian composite superterrane, together with the Balkan unit forms the Variscan orogen in Bulgaria. The Balkan unit is considered part of the Pennine - Austro-Alpine mobile belt, while the Thracian composite superterrane is related to the Moldanubian zone (von Raumer and Neubauer, 1993; Neubauer and von Raumer, 1993) which also includes the Massif Central, the Black Forest, and the Vosges. Von Raumer and Neubauer (1993) include in this zone portions of the Gondwana margin such as the Menderes Massif and the Montagne Noire. The Iberian Massif has been also cor-









Fig. 2 - Geological map of the East Rhodope, Bulgaria.

related to massifs of the Moldanubian zone by Casado et al. (2001).

The investigation of the origin and the age of the VF are necessary in order to clarify structure and geological evolution of the Rhodope Massif, as well as of the whole Moldanubian zone. The interpretation of the VF is particularly important due to the geographical position of the Rhodope Massif, located between the Arabian plate and Western Europe, and for the presence of ophiolite fragments in all blocks of the Moldanubian zone.

GEOLOGICAL SETTING OF EAST RHODOPE

Many of the characteristic geological features of East Rhodope are relevant for the purpose of this research. The larger bodies of the Rhodope Ophiolite Association, the highest concentrations of metabasic igneous rocks of the VF are located in the East Rhodope. Additionally, the eastern part of the Rhodope Massif has a comparatively lower degree of alpine metamorphism than the central and western parts, where anatexis and migmatization occur also in the felsic portions of the sequence. Moreover, the influence of the Upper Cretaceous and Tertiary large intrusive bodies in the Rila and Pirin Mountains (West Rhodope) is lacking, and the rocks from East Rhodope are not significantly affected by later thermal perturbations.

GEOLOGICAL FEATURES OF THE VARIEGATED FORMATIONS

Several types of sedimentary rocks are recognized among the components of the VF. Quartzites and metapsammites alternate with metapelites (Anguelova and Kolcheva, 2001); marbles, with layers up to 80 m thick, as well as calcschists, are also typical of the VF. According to Kozhoukharov (1987) the Variegated Formations have flysch characteristics.

Orthoamphibolites occur in as layers and slices interlay-

ered with metasediments (e.g., in the Avren Synform), or as intrusive bodies intersecting the ultramafic fragments of the ophiolitic units (mainly located in the Bela Reka Antiform; Fig. 2). The orthoamphibolites of the Avren Synform were studied in two localities. The first locality is a metagabbro body south of Bubino (Fig. 3), which is transformed into banded amphibolites in its outer parts. This elongated body has a total a thickness of ~200 m, alternates with biotite and two-mica gneisses and with marbles. The second study area is situated directly to the east of the large ultramafic body of Avren. At this locality, the orthoamphibolites alternate with marbles as shown on Fig. 3. Locally the thickness of the orthoamphibolite layer can attain 100 m.

The relationship between the orthoamphibolites and the ultramafic rocks was studied in the Bela Reka Antiform, where these rock types form the limbs of a dome structure (Carabunar Dome). This relationship was observed in Hambar Dere (1), west of the village of Boturche (2), and to the northeast of the village of Zalti Chal (3, see Fig. 2 for map locations). These metabasites cross-cut the ultramafic bodies, and contain xenoliths of the ultramafic rocks that are typically altered to actinolite-talc or talc-chlorite schists along their edges.

In some localities the metamafic rocks of the Bela Reka Antiform were metasomatically altered into tourmaline bearing metagabbro-pegmatites, or into clinozoisite-clinopyroxene rodingite-like rocks (Zalti Chal; Hambar Dere; Fig. 2).



Fig. 3 - Geological map of the Avren Synform (after Kozhoukharov et al., 1992) with additions.

Orthoamphibolites are widespread in the VF. They are fine- to medium-grained, mesocratic to melanocratic rocks showing variable amounts of post-magmatic shearing. They are massive in the internal parts of the bodies, and they are usually foliated in their outer parts, and rare relics of ophitic textures are also preserved. The igneous activity had multistage character as reflected by the crosscutting relations of compositionally and structurally different dikes and large, irregularly shaped bodies from the Bela Reka Antiform. Fine- to medium-grained melano- to mesocratic metagabbro to metagabbro-dioritic bodies crosscut serpentinized peridotites. The rocks of these bodies are not always homogeneous. For instance, we observed melanocratic and leucocratic nebulous portions showing rapid transitions between these textures. These bodies are intruded by fine- to medium-grained melanocratic metagabbro or metagabbro-dioritic dikes that also intrude the serpentinites. All rocks of the considered bodies are recrystallized but not intensively foliated. Some of the fine-grained amphibolites, occur interlayered with parametamorphites, and may represent preserved parts of metavolcanic sequence.

ANALYTICAL METHODS

We used a JEOL JXA-8800 SuperProbe at the Florida Center for Analytical Electron Microscopy at Florida International University, Miami, to determine the chemical composition of rock-forming minerals. Microprobe operating conditions for wavelength dispersive analyses included an accelerating voltage of 15 kV, a 20nA current, and a spot size of 1-2 micrometers. Counting times were 10 s for each element, with a background count of 5 s.

Analyses of whole rock major and trace elements were performed via several methods. Major elements were determined by wet chemical analyses; Cu, Zn, Pb, Ni, and Co were analysed with AAS using a Perkin-Elmer Spectrophotometer 3030, and Rb, Ba, Sr, Cr, V, Zr, and Y were analysed by XRF using a VRA-2 spectrometer. All the analyses were performed in the Research Geological Laboratory at the Geological Institute of the Bulgarian Academy of Sciences. Rare Earth Elements (REE) and Y abundances were measured via a HP 4500 plus Series 200 ICP-MS at the College of Marine Sciences, University of South Florida, St. Petersburg, FL, USA. Data were normalized to repeat analyses of the certified geochemical reference samples (USGS basalts: BIR - 1, UB-N; NBS688 and W-2), with reproducibility on the order of 5% to 10%. Results are reported in Tables 3 and 4, and represented graphically in Figs 5-10.

PETROGRAPHY AND MINERAL CHEMISTRY OF THE METABASITES

The rock-forming minerals in the investigated samples of orthoamphibolites are amphibole + plagioclase + quartz + epidote \pm garnet \pm chlorite. Accessory phases include titanite, apatite, rutile, magnetite, and zircon. Amphiboles are the dominant minerals in most of analysed rock samples. They are sub- to idioblastic green nematoblasts, coarse-grained in Bubino and Avren rocks and medium-grained in the rocks from Bela Reka Antiform. Large S₁-amphibole porphyroblasts (0.2-0.5 cm) occur in the Bubino metagabbro. The porphyroblasts are surrounded by S₂-prismatic amphiboles, defining clear foliation in the outer parts of the body.

larger amphibole porphyroblasts contain numerous rounded quartz inclusions. Very rare garnet grains are also included in the periphery of some porphyroblasts. Amphiboles show a tschermakite to magnesio-hornblende composition, and can be classified as Ca-amphiboles according to the classification of Leake et al. (1997) (Table 1, Fig. 4a). Amphiboles from the Bubino area are mainly tschermakites. The finergrained amphiboles and the rims of some larger grains are magnesio-hornblendes. Amphiboles from all other studied localities are Mg-rich hornblende, with exception of one mineral analysis from Hambar Dere.

Plagioclase crystals from the Boturche and Hambar Dere samples are completely recrystallized into fine-grained aggregates. In contrast, the plagioclase from the Avren samples is generally coarse-grained and prismatic. At places, magmatic, euhedral grains are partly preserved in all these localities. An-content ranges from 33.2 to 18.3 mol percent (Table 2) for most samples, but high An-contents in the range of 55.9 to 92.3 mol percent occur only in samples of metagabbros from Bubino. In this body, coarse plagioclase prismatic grains are intensively deformed and recrystallized into subhedral grains with fine polysynthetic deformational lamellae or micro-grained aggregates. The recrystallized



Fig. 4 - **a.** Amphibole classification diagram after Leake et al. (1997); **b.** Graphical geothermobarometer of Plyusnina (1982).

Sample	817-2a	817-2e	1005-1b	1005-2d	46b-2c	46b-3a	1009-11a	1009-10a	1009-10b	1009-3c
								core	rim	
Location	Botu	ırche	Hamba	r Dere	Avren		Bubino	Bubino	Bubino	Bubino
Nomenclature	Mg-Hbl	Mg-Hbl	Mg-Hbl	Mg-Hbl	Mg-Hbl	Mg-Hbl	Tsch	Tsch	Mg-Hbl	Tsch
SiO ₂	50.59	50.94	49.50	47.70	47.50	47.61	44.64	42.87	44.71	43.37
TiO ₂	0.15	0.15	0.21	0.28	0.37	0.37	0.21	0.39	0.41	0.41
Al ₂ O ₃	8.15	7.68	10.06	10.85	11.24	11.06	13.90	15.60	11.67	11.83
FeO	12.24	12.08	13.84	14.36	9.71	8.85	14.13	17.29	17.93	17.39
Cr ₂ O ₃	0.15	0.13	0.02	0.01	0.19	0.13	n.d.	0.02	n.d.	0.08
MnO	0.21	0.22	0.29	0.31	0.14	0.17	0.19	0.26	0.23	0.23
MgO	14.33	14.27	13.12	12.74	14.22	14.46	11.04	9.18	9.36	9.95
CaO	9.64	9.45	10.09	9.49	11.89	11.50	10.01	11.41	11.59	11.43
Na ₂ O	1.63	1.57	1.18	1.61	1.44	1.61	0.92	1.04	0.94	0.89
K ₂ O	0.22	0.16	0.03	0.11	0.3	0.3	0.27	0.31	0.25	0.22
Total	97.31	96.65	98.34	97.46	97.00	96.00	95.00	98.00	97.09	95.80
T Si	7.134	7.217	6.927	6.743	6.815	6.868	6.477	6.198	6.612	6.463
T Al	0.866	0.783	1.073	1.257	1.185	1.132	1.523	1.802	1.388	1.537
Sum T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
C 41	0 407	0.400	0.595	0.540	0.715	0 7 4 7	0.953	0.054	0 (15	0.520
C AI	0.48/	0.498	0.585	0.549	0.715	0./4/	0.852	0.854	0.645	0.539
C Cr	0.010	0.014	0.002	0.001	0.022	0.015	0.000	0.002	0.000	0.009
Cre	0.954	0.909	1.092	1.512	0.238	0.23	1.203	0.970	0.002	0.931
C Ma	0.010	0.010	0.022	0.03	0.039	0.04	0.023	0.043	0.040	0.045
C Mg $C \text{ Fe}^{2+}$	5.012	5.014	2.737	2.005	5.042	0.837	2.588	1.9/9	2.004	2.21
C re	0.010	0.322	0.328	0.385	0.907	0.037	0.012	0.022	0.028	0.02
C MII Sum C	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5,000
BCa	1 456	1 434	1 513	1 437	1 828	1 777	1 556	1 768	1 837	1 825
B Na	0.446	0 4 3 1	0.319	0 441	0.172	0 223	0.260	0.232	0.163	0.175
Sum B	1 902	1 866	1 832	1 879	2,000	2 000	1 816	2 000	2 000	2,000
A Na	0.000	0.000	0.000	0.000	0.228	0.228	0.000	0.059	0.106	0.081
AK	0.039	0.03	0.005	0.019	0.055	0.056	0.050	0.057	0.047	0.041
Sum A	0.039	0.03	0.005	0.019	0.284	0.283	0.050	0.116	0.153	0.123
Sum cat.	14.941	14.895	14.837	14.898	15.284	15.283	14.866	15.116	15.153	15.123
X_{Mg}	0.86	0.85	0.84	0.87	0.77	0.79	0.82	0.64	0.57	0.65
-					-		•			

Table 1 - Chemical composition of selected amphiboles from the metabasic rocks, VF, East Rhodope

Note: n.d. - not detected; Structural formulae were calculated on the basis of 23 oxygenes -13 CNK, using RECAMP software (Spear, Kimbal, 1984).

Table 2 - Chemical composition of selected plagioclases from the metabasic rocks, VF, East Rhodope

Sample	817-2b	817-2d	1005-1a	1005-	46b-2b	46b-3b	1009-4c	1009-10c	1009-	1009-3b	1009-1b
-				4 b				core	10d		
									rim		
Location	Boturche		Hambar Dere		Avren				Bubino		
SiO ₂	64.04	63.36	60.04	62.31	61.92	62.01	45.49	47.36	52.91	47.18	53.83
TiO ₂	n.d.	n.d.	0.01	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al_2O_3	21.64	22.37	24.59	23.03	23.42	22.98	33.80	32.71	29.31	32.39	28.42
FeO	0.11	16.00	6.00	0.14	1.00	0.02	0.15	0.37	0.44	0.21	0.35
MnO	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05
MgO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.
CaO	3.95	4.59	6.98	5.18	5.65	4.71	18.42	16.49	12.20	16.76	11.69
Na ₂ O	9.70	9.39	7.75	9.03	8.19	8.56	0.83	1.84	4.44	1.57	5.07
K ₂ O	0.05	0.06	0.02	0.06	0.14	0.16	0.03	0.03	0.05	0.03	0.03
Total	99.49	99.96	99.45	99.76	99.42	98.44	98.72	98.8	99.37	98.14	99.44
Mol. proportions											
Ab	81.4	78.5	66.7	75.7	71.8	76.0	7.5	16.8	39.6	14.5	43.9
An	18.3	21.2	33.2	24.0	27.4	23.1	92.3	83.0	60.1	85.4	55.9
Or	0.3	0.3	0.1	0.3	0.8	0.9	0.2	0.2	0.3	0.2	0.2

Note: n.d.- not detected.

outer portions of large plagioclase grains show low An-contents (55.9-66.1 %) while the cores of the grains display higher An-contents.

Granoblastic quartz occurs as single grains, or associated with plagioclase in leucocratic bands in the foliated outer parts of some bodies. Euhedral, coarse-grained or anhedral fine-grained epidote and zoisite crystals are commonly formed at the expense of the plagioclases. Garnet occurs very rarely, and is concentrated in the more leucocratic portions of the metabasic bodies from Hambar Dere and Boturche. In the Bubino metagabbro, garnet is found in the outer, banded parts of the body. The composition is Alm 61.2-56.3; Gross 20.5-17.4; Prp 20.1-19.3; Spess 3.8-2.1. Pyrope and almandine components decrease slightly from core to rim, while the spessartine component increases slightly.

METAMORPHIC PRESSURE-TEMPERATURE CONDITIONS

The near absence of relics of igneous minerals and the observed microstructural relations indicate that the protoliths of the studied metamorphic rocks are completely recrystallized and mineral assemblages are re-equilibrated. In some of the studied localities, however, traces of magmatic gabbro-ophitic or porphyritic textures are still preserved, especially in the Bubino gabbro.

The chemical zonation from core to rim in both plagioclase, amphibole, and garnet reveals the retrograde character (simultaneous decompression and cooling) of the metamorphic evolution of the investigated rocks. P-T estimates are based on mineral phases in equilibrium. Generally, the pressure and temperature determinations of the orthoamphibolites from the localities of Boturche, Hambar Dere, and Avren indicate moderate amphibolite facies metamorphism. The temperatures estimated using the Holland and Blundy (1994) geothermometer would range from 630° C to 525°C, while they would range from 550° to 520° using the Pluysnina (1982) geothermometer (Fig. 4b). These data confirm similar results that have previously reported by Nasir and Okrusch, (1997) and John et al. (1999), which show that the geothermometer of Holland and Blundy (1994) produces higher temperatures for metabasites.

Pressure determinations using the Al-in-hornblende geobarometers and the calibrations of Hammarstrom and Zen (1986), Hollister et al. (1987), and Schmidt (1992), yield mutually comparable pressure values for most samples. For the Boturche locality, the estimated pressures are 4-2 kbar; for Hambar Dere pressures are - 5.5-4 kbar; and they are 6-5 kbar for Avren. The pressures after applying the geobarometer of Plyusnina (1982) are generally in accordance with the pressure-estimates obtained by the Al-in-hornblende geobarometers (Fig. 4b).

Pressure and temperature determinations for the Bubino metagabbro yield somewhat different results. The estimated high pressures (from 11 to 5 kbar), very high An-content in plagioclase $(An_{92}-An_{83})$ and the high tschermakite substitution in the inner parts of the large amphibole grains show high-grade metamorphic conditions at the amphibolite - granulite facies boundary (see also Bucher and Frey, 1994). The clear foliation in the periphery of the metagabbro body is well marked by S₂ amphibole-garnet-epidote assemblages and plagioclase-quartz bands. Relics of S₁ high An plagioclase are re-oriented along S₂. The temperatures estimated

by the Hbl-Pl thermometer of Holland and Blundy (1994) are 780° to 680°C.

GEOCHEMISTRY

Fifteen orthoamphibolite samples from the Avren Synform and the Bela Reka Antiform were analysed for major, trace, and rare earth elements (REE). The metamorphic overprint upon these rocks has obscured their original minerals and textures, and causes problems for their classification. Nonetheless, evidence for widespread metasomatic alteration is lacking, and the geochemistry of these rocks is expected to mimic the original bulk rock chemistry, especially for relatively immobile elements. Special attention was therefore given to track the behavior of the immobile HFSE (High Field Strength Elements) and of the REE, and the analysed patterns were compared to similar suites. The most striking features of the rocks studied are their low Ti and Zr contents. When plotted on the TiO₂ vs. Zr discrimination diagram (Pearce, 1980), they fall in the field of volcanic arc basalts (Fig. 5). Three data points lie out of this diagram because of their very low TiO₂ and Zr content (see samples 15, 15b, and 75, Table 3). Characteristics such as CaO/TiO₂, Al₂O₂/TiO₂, Ti/Zr, Ti/Y, and Zr/Y ratios also support an island arc affinity. All are resulted of transitional origin between island arc tholeiites and boninites. The samples fall predominantly into the low-Ca boninite group (with $CaO/Al_2O_3 < 0.75$) according to the classification by Crawford et al. (1989). When plotted in the CaO vs. SiO₂ classification diagram, they distribute in the fields for high-Ca boninite, intermediate-Ca boninite, low-Ca boninite, intermediate-Ca andesite, and andesite (Fig. 6, after Spadea et al., 1998). One sample (1004c) falls within the dacite field. The investigated orthoamphibolites have variable MgO contents (from 9.9 to 5.5 wt%), but most of the Mg-number values range from ~75 to ~60 for most of them (Table 3), and are close to that of primitive mantle derived magmas (Bloomer and Hawkins, 1987). Elemental characteristics of these samples are similar to Tertiary boninites of Bonin Island, DSDP Site 458, and boninites from Cyprus (Fig. 7a,



Fig. 5 - TiO_2 - Zr discrimination diagram for orthoamphibolite rocks from Avren Synform and Bela Reka Antiform; VAB - volcanic arc basalts; WPB - within plate basalts; MORB - mid ocean ridge basalts (after Pearce, 1980). Symbols are valid for Figs. 6, 7 and 8.



Fig. 6 - CaO - SiO₂ diagram for the orthoamphibolite rocks from the VF. Fields after Spadea et al.(1998).

except samples 1004c and 15b). The geochemical features of the orthoamphibolites from Avren Synform and Bela Reka Antiform can be seen on the Mg-number vs. TiO_2 diagram (Fig. 7b) after Pearce et al. (1992), modified by Wyman (1999). The composition of some of the orthoamphibolites falls in the fields of DSDP Site 458 and Zambales ophiolite boninites, and only one in the Birch Lake tholeiite field. The most primitive samples (46a, 46b and 75) fall in the MORB field. It should be noted, however, that rocks from both the Avren Synform and the Bela Reka Antiform regions fall in the boninitic, tholeiitic and MORB fields (Fig. 7b). Because of their low TiO₂ and low Mg-number, samples 15, 15b, 75 and 1004c are out of the fields of the diagram. Taylor et al. (1992) used Zr/Y ratios to distinguish between arc (Zr/Y <2) and either fore- or back-arc setting (Zr/Y >2). On this basis, the investigated orthoamphibolites from Avren Synform fall in the first group, and the ones from Bela Reka Antiform in the second group. The rocks from the first group also have higher Ti/Zr and Ti/Y ratios in comparison with those from the second group. Finally, on the MnOx10-TiO₂-P₂O₅x10 discrimination diagram of Mullen (1983), our rock samples cluster between the islandarc tholeiite (IAT) and the boninite (BON) fields (Fig. 8).

A characteristic signature of boninite and boninite-like rocks is their chondrite-normalized REE patterns. Many authors observed that the U-shaped REE pattern is characteristic of boninites (Hickey and Frey, 1982; Hawkins et al., 1984; Coish, 1989). However, there are also examples of boninitic rocks with LREE depleted patterns (Marianas, New Caledonia, Lau Basin; Crawford et al., 1989; Cameron, 1989; Hawkins, 1995). The investigated rocks exhibit two distinct patterns (Fig. 9). The first pattern (samples 46a and 46b) shows LREE depletions (avg. $[La/Sm]_N = 0.49$) and flat to slightly depleted HREE patterns (avg. $[La/Yb]_N = 0.44$), with distinctive positive Eu anomalies (Eu/Eu* = 1.42

Table 3 - Chemical composition of the metabasic rocks from the VF, East Rhodope

	Avren Synform						Bela Reka Antiform								
-	Avre	n		Bubino			Hamba	r Dere		Boti	ırche		Zhalti	Chal	
wt%	46a	46b	15	15b	1009d	1004c	1005c	831	1006	817	817-1	74	75	76a	76b
SiO ₂	48.22	47.55	51.63	57.67	52.11	67.30	60.58	57.01	54.86	55.11	53.91	45.73	47.12	53.37	50.50
TiO ₂	0.47	0.36	0.01	0.45	0.45	0.68	0.45	0.50	0.36	0.76	0.65	0.48	0.01	0.61	0.40
Al ₂ O ₃	16.55	17.60	17.11	15.31	17.19	11.48	14.01	12.16	15.40	14.35	14.16	20.65	20.91	15.08	17.07
Fe ₂ O ₃	2.20	1.90	3.20	4.90	4.03	6.69	1.81	3.46	1.80	3.56	4.34	3.24	2.34	3.27	3.61
FeO	4,73	4.20	5.47	6.60	6.65	3.36	4.46	4.61	6.92	5.08	4.79	6.16	3.43	4.76	4.74
MnO	0.11	0.11	0.13	0.18	0.19	0.09	0.12	0.13	0.13	0.15	0.19	0.07	0.05	0.12	0.09
MgO	9.07	9.80	7.15	3.05	5.51	1.58	6.21	8.81	7.54	5.94	6.65	5.87	7.14	7.78	7.70
CaO	12.69	12.98	11.12	7.42	10.9	5.04	7.53	7.84	5.65	9.36	9.95	12.34	13.66	7.40	8.58
Na ₂ O	2.61	2.26	1.36	1.77	1.35	2.76	3.65	3.39	4.39	3.58	3.63	2.18	1.95	4.94	4.44
K ₂ O	0.30	0.30	0.24	0.33	0.21	0.10	0.10	0.38	0.13	0.16	0.12	0.20	0.13	0.08	0.15
P_2O_5	0.04	0.03	0.03	0.08	0.08	0.11	0.08	n.a.	0.11	0.35	n.a.	0.02	0.02	0.09	0.03
LOI	2.76	2.70	2.43	2.46	1.17	1.40	0.96	0.28	1.96	0.81	1.00	2.82	2.99	2.48	2.50
Total	99.75	99.79	99.88	100.22	99.84	100.59	99.96	98.57	99.25	99.21	99.39	99.76	99.75	99.98	99.81
Mg#	70.71	74.70	60.40	33.00	48.91	23.10	64.49	67.00	61.10	56.10	57.70	53.50	69.70	64.30	63.21
ppm		•													
Cu	18	54	145	75	72	17	15	27	10	4	5	7	4	6	41
Zn	30	25	59	86	89	159	56	69	232	63	73	15	9	39	39
Pb	7	6	4	4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	7	8	8	6
Ni	80	120	47	3	15	10	85	143	125	<5	11	14	40	142	80
Co	27	29	40	23	38	<10	26	28	38	31	30	36	26	27	26
Zr	26	16	<7	<7	45	170	100	52	83	185	185	19	17	59	32
Y	12.8*	10.4*	5.9*	15.9*	10	32	42	17	18	28	25	3.3*	6	14.1*	8.8*
Sr	361	273	53	62	120	320	215	140	150	440	370	175	177	115	174
Rb	7	3	27	13	9	3	3	15	3	4	20	3	7	5	3
Ва	86	73	30	79	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	88	56	137	128
Cr	470	557	57	15	13	6	212	373	170	66	75	31	11	256	57
V	172	140	156	200	190	60	130	240	200	210	170	904	259	193	226

Note: n.a.- not analyzed; * - determined by ICP-MS; Mg# =100 x Mg/(Mg+Fe²⁺) - atomic ratios.

Classification of the rocks:

Avren: s. 46a and 46b - mesocratic coarse- to medium-grained metagabbro; Bubino body: s. 15 - porphyritic coarse-grained metagabbro from

the central part; s. 15b - partly foliated metagabbro; s. 1009d - foliated and banded metagabbro from the outer part;

Hambar Dere: s. 1004c, 1005c and 831 - fine- to medium-grained metagabbrodioritic irregular body, cross-cutting serpentinized peridotite;

s. 1006 - melanocratic fine-grained metagabbrodiorite dike, cross-cutting the metagabbrodiorite body;

Boturche: s. 817 and 817-1 - melanocratic fine- to medium-grained metagabbrodiorite;

Zalti Chal: s. 74 - metagabbroic dike, cross-cutting serpentinized peridotite; s. 75 - metagabbroic irregular body, cross-cutting serpentinized peridotite; s. 76a - fine-grained metagabbroic dike, cross-cutting metagabbroic irregular body (s. 76b), which intersects serpentinized peridotite.



Fig. 7 - **a**. CaO/Al₂O₃ - Mg# diagram (fields after Beccaluva and Serri, 1988); **b**. Mg# - TiO₂ diagram (fields after Pearce et al., 1992 and Wyman, 1999).



Fig. 8 - MnOx10-TiO₂-P₂O₅x10 discrimination diagram of Mullen (1983). Fields as follows: IAT- island-arc tholeiite; BON- boninite; CAB- calc-alkaline basalt; OIT- ocean island tholeiite; OIA- ocean island alkali basalt.

and 1.76; Fig. 9a). The second group shows characteristic U-shaped boninite-like REE patterns (high avg. $[La/Sm]_N = 1.34$), moderately elevated compared to group one but on the whole low (avg. $[La/Yb]_N = 0.87$) indicative of both LREE and HREE enrichment. For this group, varying Eu anomalies from 0.80 to 1.93 were observed (Fig. 9b). The



Fig.9 - Chondrite-normalized REE pattern for orthoamphibolite rocks studied: **a**. LREE depleted pattern in samples from Avren Synform; **b**. Ushaped REE pattern in samples from Avren Synform and Bela Reka Antiform (exept s.s. 76a and 76b); **c**. fields for ODP Leg 125 boninites after Pearce et al. (1992) and for Bonin Island boninites after Shimizu et al. (1992). Data are normalized to C1 chondrite of Sun and McDonough (1989).

positive Eu anomaly in most of the metabasites suggests plagioclase accumulation. These data suggest that the analysed rocks, although metamorphosed to $T = 630-525^{\circ}C$ and P = 6-2 kbar, reflect the REE abundances of the protoliths (as shown by Sun and Nesbitt, 1978). Earlier investigations of Sorensen and Grossman (1989) and Berger et al. (2001 and references therein) indicate that REE remain immobile under relatively high-grade metamorphic conditions. On the basis of their REE patterns, we interpret samples 15 and 15b, which often fall out of the fields of other diagrams, as boninites. Despite the differences in the REE patterns in the studied rocks, the comparison with the Tertiary West Pacific boninites (Fig. 9c) shows that our data overlap the fields of ODP Leg 125 (Pearce et al., 1992) and Bonin Island boninites (Shimizu et al., 1992). Similar diverse REE patterns were reported for Nepoui and Koh boninite sequences from New Caledonia (Cameron, 1989).

Primitive mantle normalized plots (Fig. 10) summarize many of the common distinctive features shared by the boninites and the rocks of the VF.

Regardless of some minor differences in the chemical composition of the rocks from the Avren Synform and the Bela Reka Antiform, they both preserve evidence for protoliths with island arc tholeiite and boninite character. According to Bazylev et al. (1999), parts of the ultramafic bodies and metatholeiites were formed in a supra-subduction zone (SSZ) setting.

DISCUSSION

The comparison of the petrological and geochemical characteristics of the investigated rock assemblages with those of specific geodynamic oceanic settings (i.e. islandarc, fore-arc, back-arc, mid-ocean ridge) can be an important tool for the identification of their genetic identities. The characterization of the Avren Synform sediments as metamorphosed flysch containing a greywacke level (Kozhoukharov, 1987) is an important feature, because such sedimentary deposits are characteristic mainly of island-arc environments. Examples of similar flysch successions are exposed on the Mentawai Islands and Barbados Island (Mitchell and Reading, 1971). The Mentawai Islands Eocene-Miocene flysch deposits are over 5000 m thick and are also intensely deformed. Similarly, the Eocene flysch succession from Barbados Island has a thickness of about 4-500 m. These thick stratigraphic sequences consist largely of marine volcanoclastic turbidites, tuffs, and ash deposits overlying ophiolite blocks. The above successions were deposited in trench settings. Limestones, associate with flysch, are also typical of island arc-related successions, especially those in proximity to the island arcs. One example is the Eocene-Pleistocene sedimentary-volcanic sequence formed in the collision zone between the North d'Entrecasteaux Ridge and the New Hebrides (Vanuatu) Island Arc (ODP Site 829; Reid et al., 1994; Underwood et al., 1995; Cortesogno et al., 2001). Other examples are the carbonates from the marginal Japan Sea (ODP Site 799), Celebes Sea (ODP Site 767), Sulu Sea (ODP Site 768; see Torres et al., 1995 and references therein) and Lau Backarc Basin carbonates (ODP Sites 834-839; Marsaglia et al., 1995). The association of the considered sedimentary rock types with boninitic and tholeiitic magmatites is typical for the successions of island-arc settings. Such igneous rocks are exposed, for example, in the Bonin trench (Taylor et al., 1994). They are also found in ancient island arcs - e.g. those connected with the Koh (Meffre et al., 1996) and Betts Cove (Coish, 1989) ophiolites, the Cambrian island-arc in Tasmania (Brown and Jenner, 1989), as well as the Lower Proterozoic Trans-Hudson orogen (Wyman, 1999).

We interpret the formation of the VF and of parts of the associated Rhodope Ophiolite Association (ROA) as an ensimatic island arc (Haydoutov et al., 2000; 2001). Boninite generation is observed during the initial stages of the subduction (Crawford et al., 1989; Pearce et al., 1992). Our model fits well with the widely accepted early-arc development and the associated rock types found in the Izu-Bonin-Mariana subduction system (Bloomer et al., 1995). Some facts indicate the presence of different types of oceanic crust that are identified as ROA: **a**- The island-arc igneous boninites and tholeiites do not cut the eclogites; **b**- Some of the ultramafic rocks of the ROA were formed in a SSZ set-





		Avren Synfor	m		Bela Reka Antiform				
	46a	46b	15	15b	74	76a	76b		
La	0.88	0.55	0.64	0.94	0.62	3.11	1.66		
Ce	2.38	1.75	1.60	2.35	1.34	7.55	4.02		
Pr	0.46	0.31	0.20	0.34	0.15	1.12	0.60		
Nd	2.68	1.92	0.85	1.73	0.64	5.35	2.95		
Sm	1.12	0.85	0.28	0.72	0.18	1.60	0.93		
Eu	0.63	0.61	0.14	0.25	0.14	0.54	0.36		
Gd	1.69	1.34	0.45	1.32	0.27	2.01	1.20		
Tb	0.31	0.25	0.09	0.27	0.05	0.34	0.21		
Dy	2.13	1.73	0.74	2.15	0.45	2.26	1.44		
Но	0.45	0.37	0.18	0.52	0.11	0.48	0.31		
Er	1.31	1.10	0.60	1.75	0.39	1.46	0.95		
Tm	0.18	0.15	0.09	0.28	0.06	0.21	0.14		
Yb	1.18	0.98	0.72	2.02	0.48	1.45	0.97		
Lu	0.18	0.14	0.12	0.33	0.08	0.22	0.15		

Table 4 - REE content (ppm) in the metabaic rocks from the VF, East Rhodope

ting (Bazylev et al., 1999); **c**- The eclogites from the Rhodope massif have affinities similar to typical MORB (Kolcheva and Escenazi, 1988). The eclogite/ophiolite/boninite ensemble could be a tectonic association of two types of ocean crust, the first formed at a mid-ocean ridge and underwent eclogite facies metamorphism, and the second formed in a SSZ setting and underwent later (Variscan?) amphibolite facies metamorphism. A scenario of repeated subduction episodes or subduction polarity reversal could further support our model.

The problem of the age of the VF is important, but the ages of the protoliths of these rocks are poorly constrained. The considerations discussed above, indicating a possible correlation of the Rhodope metamorphics with the comparable rocks of the Moldanubian zone, where Neoproterozoic ages are reported (Pin, 1991), should be taken into account. Some evidences for the metamorphic rocks of the Thracian Superterrane itself are in accordance with these considerations as, for example:

- rocks metamorphosed in amphibolite facies, comparable with the VF, from Sredna Gora terrane, and associated with ultramafics and eclogites, are intruded by Variscan granites and covered by Lower Triassic sediments;
- U-Pb zircon dating of these metamorphic rocks indicate an old Paleozoic (480±30 Ma) metamorphism (Arnaudov et al., 1989);
- U-Pb zircon dating of the eclogites from C. Rhodope (600 Ma; Arkadakskiy et al., 2003) shows that they crystallized during the late Neoproterozoic.

The U-Pb zircon dating (572±5 Ma; Carrigan et al., 2003), suggests that the orthoampibolites of the VF crystallized in the late Neoproterozoic. The young ages established in the Rhodope metamorphics (e.g. Liati and Gebauer, 1999; Wawrenitz and Mposkos, 1997) are the result of the more recent Alpine metamorphic overprint.

CONCLUSIONS

Features of the VF such as the depleted geochemical characteristics of the igneous rocks, the flysch characteristics of the sedimentary protoliths, the presence of considerable amount of carbonates, and, finally, the association with eclogites and ultramafic rocks, suggest that the VF were formed as an ensimatic island arc. The cross-cutting relationships between of the orthoamphibolites with the ultramafic rocks of ROA and the evidence of the origin for the ultramafic rocks in a SSZ setting, indicate a genetic connection between the VF and the relics of the oceanic crust.

The eastern part of the Rhodope Massif consists of large-scale antiformal structures (Bela Reka and Kesebir) built up by metagranites, orthogneisses and gneiss-schists (Kozhoukharova et al., 1988; Macheva and Kolcheva, 1992) interpreted as Variscan continental crust domain (Fig. 2; Ricou et al., 1998). This continental crust forms the Prerhodopean (pre-Rhodope) Supergroup. The gneissic protoliths are Variscan in age (U-Pb zircon data ~305-320 Ma; Peytcheva and Quadt, 1995). The Variscan continental crust domain is overlain by the double-layered assemblage cropping out in the Avren and Snejina synforms. The lower layer consists of fragments of oceanic crust (intensely dismembered Kolcheva et al., 2000) overlain by the orthoamphibolites and the sedimentary components of the VF. As previously stated, the protolith ages for these rocks are almost totally unknown with exception of some new U-Pb zircon dating suggesting that the orthoampibolites of the VF crystallized in the late Neoproterozoic (572±5Ma, Carrigan et al., 2003). The relationships between the Variscan continetal crust and the VF is tectonic, according to the interpretation of VF as allochthon complex. This conclusion is supported by the lacking of evidences of contact metamorphism in the VF and the ROA. In some localities, ultramafics and eclogites are in direct tectonic contact with orthogneisses, and shearing in the orthogneisses becomes mylonitic close to the contact. In addition, a zone of intensively sheared granitoids from 100 to 300 m thick exists along the contacts. In most of the studied localities, the contact shows the features of a deep tectonic structure with internal tectonic imbrication. Rock slices from both types of crust in the zone of tectonic imbrication form an assemblage thick from 100 to 400 m.

These observations suggest that the East Rhodope suture corresponds to the location of the VF. Along this suture, the oceanic crust of probable Neoproterozoic age is emplaced over the Variscan continental crust. Therefore, the suture zone separates the Rhodope terrane thrust by the VF (Rhodopean Supergroup) from the Bela Reka terrane formed by the Prerhodopean Supergroup. The suture was formed probably in late Variscan time. The surface of the suture zone is an intensely folded, sub-horizontal plane in the East Rhodope block. We therefore consider the Rhodope massif as a composite terrane, and the Thracian micro continent of Bončev (1986) as a composite superterrane.

The ophiolite fragments from the Rhodope massif have been considered as obducted ocean crust according to Kozhoukharova, (1985) and Kolcheva and Eskenazi, (1988). Prior to obduction, the two types of oceanic crust were tectonically associated. Ricou et al. (1998) distinguished continental and mixed units within the Rhodope massif, the latter containing ophiolites. The close genetic and spatial relationships of the ophiolites and the VF indicate the latter as element of the same suture zone. The configuration of the suture, mentioned by Burg et al. (1996) for the East Rhodope, coincides with our interpretation of this structure. However, Burg et al. (1996) describe an upper terrane with "mafic-ultramafic-gneiss sequence" as well as intermediate thrust sheets with several sequences including "eclogite-metabasic-gneiss sequence", and they do not distinguish between the suture and their "syn-metamorphic nappe complex".

We suggest that the original association of the ophiolites with the VF provide important insights to clarify the origin and structure of the whole Rhodopean composite terrane. In addition, the data presented in this paper provide an important clue for the correlation of the VF with the arc tholeiites and boninites from the Central Rhodope identified by Daieva and Pristavova (1998).

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