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Dismembered ultramafic ophiolites from the Avren synform, Eastern Rhodopes

Dedicated to Prof. El. Aleksiev on his 80th anniversary

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Abstract. Dismembered ultramafic ophiolite bodies from the Avren synform have been investigated for understanding their petrological and geochemical properties and stratigraphic position in the general ophiolite section. The study of the textural and structural features of the ultramafic rocks, the variation in the chemistry of their relic minerals (spinels, olivines, orthopyroxenes, amphiboles), and the bulk chemical composition of the different rock types was conducted to determine the character of their protolith. The results indicate that most of these bodies are formed mainly by massive metamorphosed peridotites. Remarkable layered structures are characteristic of the remaining part. The massive and the thickly layered ultramafites are composed mainly of coarse-grained harzburgites with porphiroblastic tremolite or bastite and fine-grained to dense dunite. The mineralogical and chemical composition of the separate layers in most of the layered bodies is not considerably different. An exception is Avren-2 where the differentiation resulted in layers with dunite, harzburgite, lherzolite, and wehrlite composition. X_{Cr} in spinels of the massive and thickly layered ultramafites from Avren-2 has a lower value than in the thickly layered ones. This lower value together with the values of Fe³⁺ and the clear magmatic relations of the primary minerals is typical for the cumulates.

Harzburgites and dunites of the ophiolites that are included in the continental crust are almost completely serpentinized, while spinels in them are decomposed. These processes indicate that the ophiolites were retrogressively metamorphosed by several superimposed metamorphic stages, the last of which reached the conditions of green schist facies ($T < 500^{\circ}$ C).

Keywords: tectonized peridotite, ultramafic cumulates, East Rhodopes

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Резюме. Изследвани са разчленените ултрамафични офиолитови тела от Авренската синформа за изясняване техните петроложки и геохимични особености, както и тяхната позиция в обощения офиолитов разрез. Изучени са структурните и текстурни особености на тези скали, вариациите в химизма на техните реликтови минерали (шпинели, оливини, ортопироксени, амфиболи), както и геохимичните черти на различните типове скали с цел характеризиране на техния протолит.

Резултатите от изследванията сочат, че повечето от тези тела са изградени от масивни метаморфозирани перидотити (тектонити). Останалите тела се характеризират с ясни ивичести текстури. Масивните и дебелоивичестите ултрамафити са изградени предимно от едрозърнести харцбургити с порфиробластични тремолит или бастит и от дребнозърнести до плътни дунити. Отделните ивици в по-голямата част от ивичестите тела не се различават съществено по отношение на техните минераложки и геохимични особености. Изключение е ивичестото тяло Аврен-2, където в резултат на диференциация са се оформили ивици с дунитов, харцбургитов, лерцолитов и верлитов състав. Х_{ст} на шпинелите от масивните и дебелоивичестите харцбургити са със стойности, типични за значително обеднени тектонити. X_{Cr} на шпинелите от финноивичестите ултрамафити от Аврен-2 са с по-ниски стойности в сравнение с тези от дебелоивичестите. Тези по-ниски стойности на X_{Cr} и съответни по-високи на Fe³⁺, както и ясните магматични взаимоотношения на първичните минерали, са типични за кумулатите.

Харцбургитите и дунитите от включените в континенталната кора офиолити са почти изцяло серпентинизирани, а техните шпинели са разложени, в резултат на няколко наложени ретроградни метаморфни стадия, последния от които е достигнал условията на зеленошистния фациес ($T < 500^{\circ}$ C).

Ключови думи: тектонизирани перидотити, ултрамафични кумулати, Източни Родопи Адреси: К. Колчева - Катедра по минералогия, петрология и полезни изкопаеми, Софийски университет "Св. Кл. Охридски", 1000 София, България; И. Хайдутов, Л. Даиева - Геологически институт, Българска академия на науките, 1113 София, България

Introduction

1960; jazkova-Panajotova, 1966; Kozhoukharova, 1984).

However, other features of these ultramafites such as their age and their pristine location in the ophiolite section (tectonites vs. cumulates) are not well understood. The goal of the present paper is to evaluate the position of these ultramafic bodies in the ophiolite section (Penrose..., 1972).

Geological setting

The Eastern Rhodopes are characterized by complex geological structure. The most obvi-

Many Bulgarian geologists have investigated ous complexities are the established there two the ultramafic bodies in the Rhodopean meta- antiforms and two synforms. The Kesibir antimorphic complex. Kozhoukharova (1984) and form is a simple structure, elongated in ENE Kolcheva et al. (1984) have considered these direction. The Bela Reka antiform is an isometric ultramafic bodies as fragments of an oceanic structure of more complicated character. A dome crust. The petrologic and geochemical features structure (Karabunar, after Boyanov, 1995) and the associated mineral deposits of ultrama- which is limited by a circular outcrop of ophiofic bodies are relatively well-known (e.g. Zhel- lites forms the southern part of Bela Reka. The Zheljazkova- Avren synform is situated between both anti-Panajotova et al., 1978 a, b; Kozhoukharova, forms and also forms the northern limb of the 1984; Kolcheva, Eskenazy, 1988; Kozhouk- Bela Reka antiform. The Avren synform also has harova, Daieva, 1990), as are their geological complicated internal structure. A number of occurrence and their relationships with the sur- smaller folds have been established in this synrounding rocks (Dimitrov, 1958; Kožuharov, form (Kozhoukharov, 1992). The Snejina synform (Ivanov, 1961) crops out to the west of the Kesibir antiform.

The cores of the antiforms are composed of metagranites, orthogneisses, and orthoschists (Macheva, Kolcheva, 1992; Ovcharova, Sarov, 1995). The limbs of the antiforms and the cores of the synforms are formed by the so-called Variegated Formations (Kožuharov, 1966; Kozhoucharova, 1984). These formations consist of metasediments and metaigneous rocks. The metaigneous rocks comprise amphibolites and metagabbros of calk-alkaline (island-arc) affinity. The metasediments include marbles,

metapelites.

Numerous ophiolite bodies of different composition with high-pressure overprint associate with the considered formations. Metaophiolites occur as lenses with a length of 1 to 5 km and with a maximum thickness of 40 m to 1 km. They are usually tectonically included within the base of the Variegated Formations. Eclogites are characterized by MORB geochemistry.

Taking into consideration that the origin of the Variegated Formations is primitive island arc (Haydoutov et al., 2000) and that they are located over the metagranites, the geotectonic setting of both the metaophiolites and the primitive island arc could be considered as a suture zone. Burg et al. (1996) assign the Variegated Formations from the Avren complex synform to part of their upper terrane as defined by the authors.

At present, data regarding the age of the ophiolites and their enveloping metamorphics in the Eastern Rhodopes is scarce. However, there is data regarding the age of metagranites from the cores of the antiforms - U-Pb zircon age 305-320 Ma (Peytcheva, Quadt, 1995). Some authors (Kozhoukharova, 1984) consider the age of the ophiolites to be Precambrian without real evidence. Preliminary U-Pb data for metaeclogites from the Karabunar dome (Peytcheva, personal communication) shows zircons consisting of inherited cores with Proterozoic age and younger covers of Hercynian and possible even Alpine age. Involvement of older mantle and its crustal evolution during Hercynian and Alpine time could be assumed. Model Sm-Nd ages for metaeclogites (Quadt, Pevtcheva, 1998) confirm such a conclusion.

The metamorphic history of the considered rocks from the region of the Eastern Rhodopes is polyphase. Relics of high-pressure mineral assemblages are found in the metagranites and in the metapelites from the Bela Reka antiform (Macheva, 1998). Such assemblages exist also in the lenses of amphibolitized eclogites included in the section of the Variegated Formations (Kozhoukharova, 1984; Kolcheva, Eskenazy, 1988). High-pressure mineral assemblages are

biotitic and two-mica gneisses, as well as overprinted by widespread amphibolite facies metamorphism. The Variegated Formations are locally migmatized and cut by numerous pegmatite veins.

> Together with the surrounding metamorphic rocks the ophiolitic bodies are deformed and metamorphosed. In many cases, ultramafic bodies are found in the cores of isoclinal folds, the limbs of which are composed of metabasites and marbles of the Variegated Formations. An example of this setting is the ultramafic body Avren-1 (Fig. 1) which is situated in the core of a NE-SW antiform. Shear zones mark the contacts between ophiolitic bodies and the rocks of the Variegated Formations.

> Some of the larger ultramafic ophiolite fragments of variable dimensions in the region such as Bubino, Brusevtci, Tchernichino, Golyamo Kamenjane, Bostan Dere, and Avren are investigated (Fig. 1). The surface-outcrop area of the eastern Bubino body is 0.5 km²; of the Brusevtci body - also 0.5 km^2 ; of Bostan Dere body - 1 km^2 ; of the western Golyamo Kamenjane body - 1.4 km², and of the eastern one - 0.7 km^2 .



Fig. 1. Geological sketch of the Avren synform (after Kozhoukharov et al., 1992)

Фиг. 1. Схематична геоложка карта на Авренската синформа (по Кожухаров и др., 1992)

Avren-1 is the largest, with a surface-outcrop area of 9 km^2 .

The shape of the studied bodies is isometric (the eastern Bubino, Brusevtci) to elongated (Avren, Bostan Dere). The Avren-1 body is 9 km long (5 km of which are on Bulgarian territory) and approximately 1 km wide.

Internal structures of the ultramafic bodies

Most of the studied bodies are formed by massive ultramafites (Fig. 2, a). Some of these bodies are characterized by compositional layering. Two types of layering are recognized. Rhythmic layers of harzburgite and dunite form the first type. These layers differ in thickness, usually from 1 cm to 1 m. Most of the lavers are 20-35 cm thick. The contacts of the different layers are clear, but not sharp (Fig. 2, b). The second type of layering (Fig. 2, c and d) is characterized by very fine layers (2-3 mm to 1 cm) consisting of layers of partly serpentinized olivine, intercalated by layers of tremolite and chlorite (Fig. 3, c). The contacts between the different layers are not as clear as in the first type of layering. Both types of compositional layering are rhythmic. Not all bodies are characterized by equally clear layering. The clearest, best-expressed layering is observed in Avren-2, Bostan Dere, SE Bubino, and Tchernichino (Fig. 1). The layering in the Brusevtci body is also relatively well expressed - fifteen rhythmically alternating layers of dunites and harzburgites have been observed in an outcrop of this body. Marked layering is similarly observed in the eastern part of the larger Golyamo Kamenjane body. Defined lavering is not established in the eastern part of Brusevtci, the western part of the larger Golvamo Kamenjane, or Avren-1. Massive tectonized peridotites are observed in the latter bodies (Fig. 2, a). In addition, planar structures of different minerals are present in some of the massive bodies. In the dunite layers, large grains of chromium spinels form the planar structures. The planar structures in the harzburgites are composed of coarse-grained ortopyroxenes, which are transformed into bastites (serpentine or talc).

Chromium spinels and coarse-grained talc show some differences in their planar arrangements. Chromium spinels are evenly distributed, while the bastites are concentrated in relatively narrow zones.

Petrography

The rocks of the studied ultramafic bodies are almost entirely serpentinized. The main rock type of the massive and thickly layered ultramafites is harzburgite. This rock type is coarse-grained. Olivine in harzburgites is observed as small relics in the matrix of serpentine. Large grains of serpentine or talc, sometimes together with fine relics of orthopyroxene, usually stand out in harzburgite. The presence of large tremolite porphyroblasts, which are often situated in nests, is also characteristic for these rocks.



Fig.2. Structures in the ultramafic rocks from the Avren synform: a) massive metamorphosed (tectonized) peridotites, Avren-1; b) thickly layered ultramafic rocks of Bubino; c and d) finely layered ultramafic rocks of Avren-2

Фиг.2. Структури в ултрамафичните скали от Авренската синформа: а) масивни метаморфозирани перидотити (тектонити), Аврен-1; b) дебелоивичести ултрамафити от Бубино; с и d) финоивичести ултрамафити от Аврен-2



Fig. 3. a) Olivine with cleavage; serpentinized harzburgite, Brusevtci, sample 21a-1-96; b) deformed olivine; partly serpentinized harzburgite, Avren-1, s. 31a-1-96; c) monomineral layers of serpentinized olivine (ol) and layers of tremolite (tr), chlorite (chl) and decomposed spinel (spl); finely layered ultramafics, Avren-2, s. 54b-1-96; d) serpentinized euhedral olivine (ol) and subhedral orthopyroxene (opx); finely-layered ultramafics, Avren-2, s. 54a-1-96; e) euhedral olivine (ol) included in orthopyroxene (opx); finely layered ultramafics, Avren-2, s. 54a-1-96; f) olivine (ol) and spinel (spl), included in subhedral amphibole (hbl), peritectically replacing clinopyroxene (cpx?); finely layered ultramafics, Avren-2, s. 54b-1-96; a, b, d, e, f - N +; c - N ||; base of photo - a, d, e, f - 1.5 mm, b, c - 6 mm;

Фиг. 3. а) Оливин с цепителност; серпентинизиран харцбургит, Брусевци, обр. 21а-1-96; b) деформиран оливин; частично серпентинизиран харцбургит, Аврен-1, обр. 31а-1-96; c) мономинерални ивици от серпентинизиран оливин (ol) и ивици от тремолит (tr), хлорит (chl) и разложен шпинел (spl); финоивичести ултрамафити, Аврен-2, обр. 546-1-96; d) серпентинизиран автоморфен оливин (ol) и хипидиоморфен ортопироксен (орх); финоивичести ултрамафити, Аврен-2, обр. 54а-1-96; e) автоморфен оливин (ol), включен в ортопироксен (орх); финоивичисти ултрамафити, Аврен-2, обр. 54а-1-96; f) оливин (ol) и шпинел (spl), включени в ксеноморфен амфибол (hbl), перитектично заместващ клинопироксен (срх?); финоивичисти ултрамафити, Аврен-2, обр. 546-1-96; a, b, d, e, f - N +, c - N]; основа на снимките: a, d, e, f - 1.5 mm, b, c - 6 mm

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Lherzolite is presented very seldom in the cumstances of high mobility of the components. lherzolite in the thickly layered ultramafites.

served in finely layered ultramafites (Avren-2). tion of the flows in an open system. Therefore, Rhythmic layering of different in composition the described by Kozhoukharova mineral comand thickness layers is observed in these rocks. position, fabric and geological position of the According to the composition there are considered rocks probably reflect the formation monomineral layers of olivine (Fig. 3, c), of orthopyroxene, as well as layers of lherzolite, wehrlite, and harzburgite. Olivine, orthopyroxene, and amphiboles are partly altered but in the finely layered ultramafites the primary relationship between them is preserved. Olivine is euhedral, orthopyroxene is euhedral to subhedral and amphibole is subhedral to anhedral (Fig. 3, d, e, and f). There are poicilitic inclusions of fine-grained olivine or partly included euhedral coarse-grained olivine in orthopyroxene and intercumulus amphibole (Fig. 3, d, e, and f). These features indicate that the finely layered ultramafites are orthocumulates. For some polymineral layers heteradcumulate texture is characteristic. Microlayers of olivine or orthopyroxene with adcumulate texture occur also. In some layers the primary minerals are almost completely transformed into a mixture of fine-grained tremolite, chlorite and ore minerals (Fig. 3, c).

According to Kozhoukharova (1998) the peripheries of some serpentinized ultramafic bodies from the Avren synform are eclogitized. The concept of the author for metasomatic formation of eclogites in sheared serpentinites during the process of their folding is difficult to accept on the following grounds:

- the published chemical composition of clnopyroxene (diopside) and garnet (mostly grossulare) differ considerably from the typomorphic for eclogitic mineral assemblage of clinopyroxene (omphacite) and garnet (almandine);

- the profound transformation of the simple chemical MgO-SiO₂-H₂O system of the serpentinites into CaO-MgO-FeO-Al2O3 -SiO2 system of the eclogites is possible to occur in the cir-

thickly layered peridotites (Bostan Dere, Goly- The HP conditions, typical for the formation of amo Kamenjane, and Brusevtci). Layers of fine- eclogites, can not be considered as favorable for grained dunite alternate with harzburgite and such mobility. The described by the author symmetrical zonal fabric of the "eclogite" bands The primary igneous texture is best pre- is possible only in the conditions of free circulaof metasomatic skarn-like rocks, generated in shear zones cutting the ultramafic bodies. These rocks are developed in the layers with appropriate chemical composition of the characterized in this paper layered cumulates.

Analytical methods

The chemical composition of the ultramafic rocks from the Eastern Rhodopes was determined by the "Research geological laboratory" at the Geological Institute of the Bulgarian Academy of Sciences. The major elements were detected by wet chemical analyses; they were duplicated by XRF analyses on glass discs fused with lithium tetraborate. The trace elements (Rb, Sr, Ba, Cr, V, Zr and Y) were determined by XRF - analyses of rock powder on pressed discs and a polyvinyl alcohol binder. All XRFanalyses were carried out using VRA-2 spectrometer. The determination of Cu, Zn, Pb, Ni and Co was carried out by AAS using a Perkin-Elmer Spectrophotometer 3030. The accuracy of the data was controlled by regularly analyzing certified geochemical reference samples.

Quantitative analyses of mineral phases were made by electron-probe microanalyser JEOL Superprobe 733 with EDS ORTEC-5000 system at the Geological Institute. The operating conditions included accelerating voltage 15kV. Natural standards were used. Cations and Fe^{3}/Fe^{2} were estimated by charge balance criteria (Droop, 1987) assuming 3 cations and 4 O (oxygen anions) for olivine and spinel, 4 cations and 6 O for pyroxene, 4 cations and 23 O for amphibole, and 4 cations and 28 O for chlorite.

Mineralogy

The focus of our attention are the primary minerals. A large part of these minerals undoubtedly underwent a subsolidus recrystallization prior to the emplacement of the ophiolites into the upper crust.

Olivine. This is the main rock-forming mineral. In the massive harzburgites it is either coarse grained with a clear cleavage (Fig. 3, a), or strongly deformed (Fig. 3, b). Olivine is euhedral in the finely layered ultramafites. It is associated with other magmatic minerals and is often included in orthopyroxene or in amphibole (Fig. 3, e, f). In other cases, olivine forms monomineral microlayers (Fig. 3, c). It is highly

magnesian - X_{Mg} > 0.86 (Table 1 and 2). In the massive harzburgites X_{Mg} reaches 0.93. In the layered harzburgites X_{Mg} depends on the type of layering. In the finely layered ones X_{Mg} decreases to 0.86. In the harzburgite layers (Avren-2) however, X_{Mg} is still high, 0.92. NiO content in olivine varies from 0.03 to 0.73 wt%, without a clear relationship to the rock type. A tendency towards decreasing from the core to the rime has been outlined in some large grains. *Spinel*. The investigated rocks rarely contain primary spinels. Almost all spinels are metamorphosed and transformed into Cr-magnetites with a high degree of oxidation of iron, Fe³⁺/(Cr+Al+Fe³⁺)> 0.33.

Table 1. Representative electron-microprobe analyses of minerals from finely layered ultramafites (Avren-2) Таблица 1. Представителни микросондови анализи на минерали от финоивичести ултрамафити (Аврен-2)

	54b-1-96 harzburgite layer				55-1-96 lherzolite layer				55a-1-96 wehrlite layer				
wt%	Ol-1	Opx-1	Spl-2	Hb-2	Ol-2	Hb-16	Hb-3	Chl-22	Ol-19	Hb-26	Hb-29	Chl-15	Chl-10
SiO ₂	41.31	56.96		53.50	40.22	44.29	56.05	32.49	40.01	54.20	56.67	32.08	31.58
Al_2O_3		1.35	23.18	5.55	0.26	11.70	1.90	15.57		3.69	1.52	16.12	16.43
TiO ₂						0.50	0.04	0.13				0.12	0.05
FeO	8.17	5.64	28.38	2.39	12.18	5.41	2.71	4.14	12.30	3.09	2.30	4.54	4.26
MnO		0.04		0.00	0.19	0.08	0.01		0.23			0.09	
MgO	50.64	35.21	10.83	21.63	47.23	18.28	23.45	34.84	46.37	22.93	23.63	34.15	34.07
CaO		0.05		12.58		12.55	12.83	0.06		12.21	12.63		
Na ₂ O				1.06		2.46	0.44	0.44	0.33	1.22	0.45	0.75	0.70
K_2O						0.57	0.13	0.03		0.10	0.05		
Cr ₂ O ₃		0.07	38.10					0.96				0.64	0.14
NiO	0.40	0.11							0.73			0.23	0.33
Total	100.52	99.43	100.49	96.71	100.08	95.84	97.56	88.66	99.97	97.44	97.25	88.72	87.56
X _{Mg}	0.92	0.92	0.50	0.97	0.87	0.94	0.97	0.94	0.87	0.97	0.96	0.93	0.93
X _{Cr}			0.53										
Y _{Cr}			0.47										

 $X_{Mg}=Mg/(Mg+Fe^{2+}); X_{Cr}=Cr/(Cr+Al); Y_{Cr}=Cr/(Cr+Al+Fe^{3+})$

Mineral abreviations: Ol – olivine; Opx – orthopyroxene; Spl – spinel; Hb – amphibole; Chl - chlorite Blank – not detected; Празните полета – под чувствителността на анализа

The latter are non transparent, strongly corroded and decomposed, and replaced by chlorite (Fig. 3, c). The unaltered spinel grains are transparent with a brown-reddish color. A relatively high Cr/(Cr+Al) ratio is typical for spinels from the thickly layered harzburgites of Brusevtci - 0,69 to 0.67, decreasing from the core to the rime (Table 2). Spinels of the finely layered ultramafites from Avren-2 have a lower Cr/(Cr+Al) ratio, 0.52-0.46.

Orthopyroxene. Orthopyroxenes are almost entirely serpentinized in the massive and thickly layered peridotites and are frequently replaced by large serpentine or talc grains. Euhedral short-prismatic orthopyroxene grains, some of which are characterized by finelamellar structures, are preserved in the finely layered ultramafites of Avren-2. Their X_{Mg} is 0.92, Al₂O₃ is relatively low, 1.35-1.65 wt%, and CaO is very low, 0.03-0.05 wt%. Clinopvroxene (?). Small strongly corroded very rare grains were observed in the inner parts of some amphibole grains from the Avren-2 finely layered ultramafites (Fig. 3, f). Together with amphiboles which peritectically replace them, they form a typical intracumulus phase. These grains are considered to be possible clinopyroxene because their chemical composition is not stoichiometric.

Amphibole. All investigated rock types except the dunites contain amphiboles. Amphiboles are irregularly distributed. They are of two types according to their relationship with the other minerals. The first type appears to be of the magmatic intercumulus phase, which is found in the finely layered ultramafites (Avren-2). The second type is clearly metamorphic and is presented as large porphyroblasts in the harzburgites or as fine grains in the mixture of chlorite and ore minerals (Fig. 3, c). The analyzed amphiboles are calcic with a high X_{Mg} 0.97-0.99. According to Leake et al. (1997) these amphiboles are magnesiohornblendes to tremolites (Table 1 and 2).

Chemistry of the ultramafic rocks

The chemical composition of 18 ultramafic samples from the Avren region together with their normative minerals Ol, Opx and Cpx is included in Table 3.

On the diagram Ol-Opx-Cpx (Fig. 4, a) ultramafites are concentrated in and dunites which is typical for many ophiolite complexes

Table 2. Representative electron-microprobe mineral analyses from the thickly layered (Brusevtc, 21^{a} -1-96) and the massive (Avren-1, 31^{a} -1-96) ultramafites

Таблица 2. Представителни микросондови анализи на минерали от дебелоивичестите (Брусевци, 21 ^а -
1-96) и масивните (Аврен-1, 31 ^a -1-96) ултрамафити

	La	yered harzbu	rgite (21 ^a -1-9	Massive harzburgite (31 ^a -1-96)				
wt %	Ol-10	Ol-13 ^a	Spl-7 c	Spl-8 ^a r	Ol-3 r	Ol-4 c	Hbl-5	
SiO ₂	40.82	41.17			41.68	41.55	58.87	
Al_2O_3			15.42	15.49			0.42	
FeO	10.89	10.32	22.98	25.58	6.55	6.08	1.17	
MgO	47.72	47.40	9.30	7.12	51.30	51.76	24.51	
CaO							12.91	
Na ₂ O							0.46	
Cr_2O_3			50.52	49.07				
NiO	0.46	0.29			0.03	0.13		
Total	99.89	99.16	98.13	97.26	99.56	99.52	98.34	
X _{Mg}	0.89	0.89	0.46	0.36	0.93	0.94	0.97	
X _{Cr}			0.69	0.68				
Y _{Cr}			0.66	0.65				

The notes are the same as in Table 1; c - core; r - rim.

Бележките са както в Таблица 1; с - център; г – периферия

(Coleman, 1977). One sample falls in the field of the tectonized lherzolites (s. 39a). The samples from the dark (s. 55) and the light (s. 55a) layers (Table 3) of the finely layered ultramafites fall respectively in the fields of lherzolites and wehrlites. The compositional uniformity of all investigated rocks is also reflected in relatively constant proportions of the calculated normative Ol-Opx-Cpx. As mentioned above, ultramafites from the studied region are considerably serpentinized (LOI - from 10.27 to 16.69%). After correcting the weight percent to reflect ignition loss, the proportions of the calculated normative minerals remain almost unchanged while the main petrogenic oxides vary. Volatile free major element abundance's of peridotites studied vary as follows: for the harzburgites SiO₂ is from 42.50 to 45.93%; FeOt is from 6.37 to 10.33%; and MgO is from 41.75 to 46.48%; for the dunites SiO_2 is from 38.44 to 40.28%; FeO_t is from 8.60 to 11.40%; and MgO is from 46.64 to 48.78%. The low content of TiO₂ which is less than 0.01% in almost all analyzed harzburgites and lherzolites stands out. Values of TiO₂ lower than 0.1% are characteristic of mantle rocks. According to earlier research on the Rhodopean ultramafites (Zheljazkova-Panajotova et al., 1978 b) TiO₂ content varies from 0.05 to 0.07% and the 100TiO₂/FeO_t ratio varies from 0.56 to 1.08. In most of the investigated harzburgites and dunites this ratio is less than 0.14 and only in the data from Tchernichino (s.s. 42 and 42a) and Avren-2 (s. 54b) it is respectively 0.56 and 0.72. Values of this ratio lower than 2.00 are typical for mantle rocks (Zheljazkova-Panajotova et al., 1978 b). TiO₂ content in lherzolites (s. 39a and 55) and wehrlite (s. 55a) is higher, as is the 100TiO₂/FeO_t ratio, which reaches 2.98 in wehrlite. These values are typical for cumulates. It is interesting to mention that the samples 55 and 55a reflect the finely layered ultramafites of Avren-2 A clear tendency towards the decrease in Fe, Ti, Al, and Ca contents (Table 3) is observed in the transition from lherzolites (s. 39a and 55) to harzburgites (s.s. 39, 54b) from the localities Bostan Dere and Avren-2. Depending on their chemical composition the investigated rocks are very close to other primitive peridotites (Frey et al., 1985, Bazylev et al., 1993). This can be observed in the diagram MgO/SiO_2 vs. Al₂O₃/SiO₂ (Fig. 4, b), where most of harzburgites and the only lherzolite (s. 39a) fall close to or in the field of the fresh mantle harzburgites and lherzolites from the Lanzo and Ronda massifs (Frey et al., 1985) and the Mamonia complex (Bazylev et al., 1993). Comparison of the FeO_t/SiO₂ ratio - 0.18 of the investigated harzburgites and respectively 0.18 of those from the Mamonia complex, shows a close resemblance of these rock types. The low value of this ratio in harzburgites from Avren-1 (s. 31a), 0.14, indicate a clear depletion of these rocks (Bazylev et al., 1999), and should be especially noted. An analysis of Cr, Ni, and Co content which is characteristic for the ultramafic rocks also indicates that the rocks are alike. Cr₂O₃ varies from 0.21 to>0.39%, NiO from 0.23 to 0.33%, CoO from 0.009 to 0.013% for harzburgites and Cr₂O₃ from 0.35 to>0.39%, NiO from 0.25 to 0.33%; CoO from 0.012 to 0.015% for dunites. These contents, with the exception of Cr₂O₃ which is very high in the investigated rocks, are correlative to the values established by Zheljazkova-Panajotova (1978 b) for the Rhodopean ultramafites and to the ultramafic rocks from Ronda massif (Frey et al., 1985). These values are typical for mantle rocks.

Metamorphism of the ultramafic rocks

The highest-temperature-relic mineral assemblages *forsterite+enstatite+spinel* in harzburgites and dunites, which were found at Brusevtci, Bubino, Golyamo Kamenjane, and Avren-1, show that the studied ophiolites could be assigned to the so-called spinel lherzolites. The later are stable in $T>850^{\circ}$ C and P>6 kbar, but lower than 16 kbar (Bucher, Frey, 1994). The nearly complete serpentinization of harzburgites and dunites and the decomposition of spinels show that ophiolites which are included in the continental crust suffered several overprinted metamorphic processes.

	Brusevci			Tchern	ichino	Bubino			Gol. Kamenjane	
	21	23	21a	42	42a	8	10a	10	35	34b
wt%	D	Н	Н	Н	Н	Н	Н	Н	D	D
SiO ₂	33.63	37.20	37.50	38.98	39.17	38.33	38.57	39.15	33.28	33.66
TiO ₂	< 0.01	< 0.01	< 0.01	0.04	0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Al_2O_3	1.04	1.23	1.14	1.59	1.28	1.24	1.42	2.70	1.70	1.49
Fe_2O_3	5.89	5.28	5.19	5.60	8.34	6.85	5.83	5.01	5.97	6.90
FeO	1.88	2.00	1.93	1.97	1.43	1.35	1.93	2.40	1.90	2.49
MnO	0.22	0.20	0.21	0.21	0.21	0.18	0.20	0.15	0.21	0.20
MgO	40.72	38.56	38.56	36.13	35.75	37.03	36.90	35.25	41.06	39.20
CaO	0.08	0.11	0.06	0.50	0.17	0.04	0.10	1.47	< 0.01	0.06
Na ₂ O	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.07	0.03	< 0.01
K_2O	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.03	0.03	< 0.01
P_2O_5	0.02	0.02	0.04	0.03	0.02	0.01	0.02	0.04	0.02	0.04
H_2O^-	1.43	1.53	1.38	2.07	1.91	1.85	1.47	1.03	1.07	1.11
H_2O^+							13.40	12.40		
CO_2							0.38	0.49		
LOI	15.26	13.70	13.76	12.80	11.76	13.33			14.86	14.65
Total	100.17	99.83	99.77	99.92	100.09	100.21	100.22	100.19	100.13	99.80
ppm										
V	20	29	29	48	34	22	33	49	17	36
Cr	2414	>2700	>2700	>2700	1442	1544	2653	>2700	>2700	>2700
Co	98	94	95	103	84	103	96	78	109	108
Ni	2100	1900	2000	2600	1800	2200	2100	1900	2000	2100
Cu	2	3	1	10	8	21	4	12	2	9
Zn	19	18	20	23	46	27	30	46	31	24
Срх	0.5	0.5	0.5	2.1	0.9		0.5	6.3		0.5
Opx		18.4	19.8	28.7	29.9	26.8	27.8	23.4		
Ol	100	81.4	79.7	69.2	69.2	73.2	71.7	70.3	100.4	100.8

Table 3. Chemical composition of ultramafites from Avren synform Таблица 3. Химичен състав на ултрамафити от Авренската синформа

D-dunite; H-harzburgite; L-lherzolite; W-wehrlite

Ophiolites reached ultimately the metamorphic conditions of green schist facies ($T < 500^{\circ}$ C).

of the mineral assemblages during and after the accretion of the ophiolite fragments onto the continental crust indicate high- to mediumtemperature stage of metamorphism. This metamorphism is characterized by replacement of clinopyroxene by tremolite and Mg-chlorite in lherzolite and wehrlite layers, as well as by the coexistence of forsterite and enstatite.

The decomposition of clinopyroxene in a CMASH (CaO-MgO-Al₂O₃-SiO₂-H₂O) system under the conditions of medium pressure (Kyisoterm) starts at 825°C. Clinopyroxene is entirely replaced by the reaction: *Senstatite* + *2diopside* + $H_2O \rightarrow$ *tremolite* + *forsterite* at The summarized data on the transformation

800°C. The formation of chlorite under the same conditions can be described by the reaction: *forsterite* + *2enstatite* + *spinel* \rightarrow *chlorite*. The talc pseudomorphs of orthopyroxene and its overgrowths on olivine and tremolite (Avren-1) are indicative for temperature of about 680°C. This means that the lower temperature limit of stability of enstatite has been reached. The formation of serpentine and the mass destruction of all high temperature minerals begin at temperatures lower than 550°C in the conditions of Ky-isotherm. The forsterite-tremoliteantigorite- talk assemblage is preserved up to 400°C. Almost complete serpentinization occurs at temperatures lower than 400°C.

Table 3: Continued

Таблица 3. Продължение

	Bostar	n dere		Avren-1		Avren-2			
	39	39a	31	25	31a	55	55a	54b	
wt%	Н	L	D	Н	Н	L	W	Н	
SiO ₂	38.77	39.70	31.40	36.60	37.70	37.23	38.75	39.81	
TiO ₂	< 0.01	0.17	< 0.01	< 0.01	0.01	0.14	0.21	0.05	
Al_2O_3	1.64	3.75	1.15	1.58	1.26	2.81	5.74	1.72	
Fe_2O_3	6.68	6.60	7.85	5.88	3.47	5.76	3.66	4.14	
FeO	1.18	2.70	2.24	2.89	2.40	4.14	3.74	3.23	
MnO	0.21	0.12	0.24	0.21	0.13	0.24	0.20	0.24	
MgO	36.52	31.80	38.70	38.88	40.29	34.14	28.92	38.70	
CaO	0.04	1.90	0.06	0.04	1.28	2.38	6.31	0.58	
Na ₂ O	< 0.01	0.50	< 0.01	< 0.01	0.07	0.04	0.09	< 0.01	
K_2O	< 0.01	0.03	< 0.01	< 0.01	0.03	< 0.01	0.05	< 0.01	
P_2O_5	0.02	0.03	0.04	0.03	0.05	0.05	0.03	0.03	
H_2O^-	2.03	0.90	2.29	1.15	1.08	1.48	1.55	1.22	
H_2O^+		11.65	14.99		11.82				
CO_2		0.35	1.24		0.59				
LOI	12.98			12.54		11.34	10.50	10.27	
Total	100.07	100.23	100.20	99.80	100.18	99.75	99.75	99.99	
ppm									
V	35	30	34	39	86	80	143	32	
Cr	>2700	>2700	>2700	>2700	>2700	2571	2389	2169	
Со	95	74	115	100	71	90	65	87	
Ni	1900	2100	2600	1800	1800	1600	1200	2000	
Cu	3	4	13	1	14	25	35	6	
Zn	28	31	30	31	37	53	40	29	
Срх		8.1		0.5	5.2	10.4	26.5	2.5	
Opx	29.8	28.4		11.4	9.4	9.3	4	22.6	
OÎ	70.2	63.5	100.9	88.1	85.4	80.3	69.5	74.9	

Results and conclusion

The following important general features of the studied ultramafites have been established:

1. Harzburgite is the most widespread rock type.

2. Remarkable layering characterizes some of the bodies. The mineralogical and chemical compositions of the separate layers of thickly layered ultramafites do not differ considerably for most of the bodies. An exception is Avren-2, where fine layers with dunite, harzburgite, lherzolite, and wehrlite composition and monomineral microlayers of olivine and orthopyroxene exist. 3. The relics of olivine, orthopyroxene, and porphyroblastic amphibole were subjects of ductile deformation for almost all of the investigated bodies. In the finely layered ultramafites of Avren-2 olivine, orthopyroxene and amphibole are not so intensively deformed. Hyipidiomorphic-granular and locally panidiomorphic-granular texture of the finely layered rocks is often preserved which is indicative of their origin as cumulates.

4. The magmatic relationships of euhedral olivine and orthopyroxene from the layered cumulate of Avren-2 are preserved and show that these rocks are cumulates. Amphibole



Fig. 4. Diagrams displaying the composition of investigated rocks from the Avren synform: a) normative proportions of major mineral phases of ultramafic rocks from the region (fields after Coleman, 1977); b) comparison of ultramafic rocks composition from Avren synform with that of Lanzo (Boudier, 1976) and Ronda (Frey et al., 1985) massifs

Фиг. 4. Диаграми отразяващи състава на изследваните скали от Авренската синформа: а) нормативни съотношения на главните минерални фази на ултрамафичните скали от района (полета по Coleman, 1977); б) сравнение на състава на ултрамафичните скали от района с тези от масивите Ланцо (Boudier, 1976) и Ронда (Frey et al., 1985)

grains locally are euhedral too, but in other domains they form subhedral grains or peritectically replace clinopyroxene (?).

5. Olivine from the massive and thickly-layered (first morphological type) peridotites shows a high Mg content, characteristic for tectonites. Olivine with low Mg content which is typical for cumulates is observed in the finely layered rocks. According to Ozawa (1988) and Hebert et al. (1989) X_{Mg} of olivine is 0.88-0.93 for tectonized peridotites, while for cumulates it is 0.82-0.89. The high Mg content and the considerably lower NiO content (0.03-0.21 wt%) of olivine from Avren-1 is characteristic of a secondary olivine which is formed in connection with deserpentinization.

6. $X_{Cr} > 0.4$ in unaltered spinels indicates that most of the investigated rocks belong to the separated by Ozawa (1988) Cr spinel peridotites (CSPP). In the massive and thickly layered harzburgites X_{Cr} of spinels has values typical for considerably depleted tectonites. This is also supported by the low content of Fe³⁺ (Fe³⁺ 0.08 cations per formula unit p.f.u.). Spinels of the finely layered ultramafites from Avren-2 are with a lower X_{Cr} , and the content of Fe³⁺ reaches 0.23 p.f.u., characteristic for cumulates (Ozawa, 1983). The variations of X_{Cr} in spinels over and below 0.60 in the investigated ultramafites assign them to the type of peridotites formed in complicated tectonic setting (Dick, Bullen, 1984) such as of island-arc over older ocean crust (Miyashiro, 1973), or transitional zone between arc and ocean lithosphere (Menzies et al., 1980).

7. The chemical composition of the massive and thickly layered ultramafites characterizes them as primitive peridotites. The relatively low value of the FeO_t/SiO_2 ratio indicate that these peridotites are depleted.

In conclusion, the present study indicates that most of the ultramafic bodies of the region are formed by tectonized peridotites. Part of the layered bodies such as Bubino and Bostan dere are also composed of tectonized peridotites. Tectonized peridotites with remarkable layering are well known (Coleman, 1977; Ozawa, 1988). The only layered body assigned to the lower part of the cumulate unit is Avren-2.

References

- Bazylev, B. A., R. Magakian, S. A. Silantiev, K. I. Ignatenko, K. Xenofontis. 1993. Petrology of the ultramafic Mamonia complex, southwestern Cyprus. - *Petrology*, 1, 4, 348-378 (in Russian).
- Bazylev, B. A., G. S. Zakariadze, M. D. Zhel-

jazkova-Panajotova, K. Kolcheva, R. E. Oberhansli, N. V. Soloveva. 1999. Petrology of ultramafic rocks from the ophiolite association in the crystalline basement of the Rhodope Massif. - *Petrology*, 7, 2, 191-212 (in Russian).

- Boudier, F., 1976. Le massif lherzolitique de Lanzo, etude structurale et petrologique. - *Ph.D. Thesis, Univ. Nantes*, 163 pp.
- Boyanov, I. 1995. Tectonics. In: Goranov, A., D. Kozhoukharov, I. Boyanov, E. Kozhoukharova. Geological map of R. Bulgaria, M 1:100 000, *Explanatory Note, Sheet Krumovgrad and Sape* Sofia, Com. of Geology, 69-79 (in Bulgarian).
- Bucher, K., M. Frey. 1994. Petrogenesis of Metamorphic Rocks. Berlin, Springer Verlag, 318 p.
- Burg, J.-P., L.-E. Ricou, Z. Ivanov, I. Godfriaux, D. Dimov, L. Klain. 1996. Syn-metamorphic nappe complex in the Rhodope Massif. Structure and kinematics. - *Terra Nova*, 8, 1, 6-15.
- Coleman, R. 1977. *Ophiolites*. Berlin-Heidelberg-New York, Springer-Verlag, 261 p.
- Dick, H. J. B., T. Bullen. 1984. Chromian spinel as a petrogenetic indicator in abyssal and alpine-type peridotites and spatially associated lavas. – *Contrib. Mineral. Petrol.*, **86**, 1, 54-76.
- Dimitrov, S. 1958. Über die alpidische Regionalmetamorphose und ihre Beziehungen zu der Tektonik und dem Magmatismus in Südostbul-garien. -*Geologie*, 7, 3-6, 560-568.
- Droop, G. T. R. 1987. A general equation for estimating Fe³⁺concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. - *Mineral. Mag.*, **51**, 3, 431-435.
- Frey, F. A., C. J. Suen, H. W. Stockman. 1985. The Ronda high temperature peridotite: Geochemistry and petrogenesis. - *Geochim. Cosmochim. Acta*, 49, 11, 2469-2491.
- Haydoutov, I., K. Kolcheva, L. Daieva, I. Savov. 2000. Origin of the Variageted Formations from the East Rhodopes (Avren synform and Bela Reka antiform). - Book of Abstracts, Geol. Conf., Bulg. Geol. Soc., 143-144.
- Hebert, R., G. Serri, R. Hekinian. 1989. Mineral chemistry of ultramafic tectonites and ultramafic to gabbroic cumulates from the major oceanic basins and Northern Apenninic ophiolites, Italy: A comparison. - *Chem. Geol.*, **77**, 183-207.
- Ivanov, R. 1961. Stratigraphie und Struktur des Grundgebirges in den Ostrhodopen. - Trav. Geol. Bulg., Serie Geochim. et Gites Metallif., 2, 69-119.
- Kolcheva, K., M. Zheljazkova-Panajotova, N. Dobrecov. 1984. Fragments of ancient ophiolite as-

sociation in the region of Ardino (Central Rhodopes, Bulgaria). – C. R. Acad. bulg. Sci., **37**, 2, 187-190 (in Russian).

- Kolcheva, K., G. Eskenazy. 1988. Geochemistry of metaeclogites from Central and Eastern Rhodope Mnts. (Bulgaria). - *Geologica Balc.*, 18, 5, 61-78.
- Kožuharov, D. 1966. Vorkambrische metamorphosierte ultrabasische und basische Magmatite in den Zentralrhodopen. - *Rev. Bulg. Geol. Soc.*, 27, 1, 51-62 (in Bulgarian).
- Kozhoukharov, D. 1992. Lithostratigraphic features and structure of the Precambrian of the Rhodopian Supergroup in the Ivaylovgrad and Krumovgrad areas, East Rhodope Mountains. -*Geologica Balc.*, **22**, 3, 3-31.
- Kozhoukharov, D., I. Boianov, A. Goranov, E. Kozhoukharova. 1991. Geological map of R. Bulgaria, M 1:100 000, Sheet Ivailovgrad. Sofia, Com. of Geology.
- Kozhoukharov, D., I. Boianov, A. Goranov, E. Kozhukharova. 1992. Geological map of R. Bulgaria, M 1:100 000, Sheet Krumovgrad and Sape. Sofia, Com. of Geology.
- Kozhoukharova, E. 1984. Origin and structural position of the serpentinized ultrabasic rocks of the Precambrian ophiolite association in the Rhodope Massif. I. Geologic position and composition of the ophiolite association. - *Geologica Balc.*, 14, 4, 9-36 (in Russian).
- Kozhoukharova, E. 1998. Eclogitization of serpentinites into narrow shear zones from the Avren syncline, Eastern Rhodopes. - *Geochem., Mineral., Petrol.*, **35**, 29-46 (in Bulgarian).
- Kozhoukharova, E., L. Daieva. 1990. Petrochemical characteristics of Precambrian amphibolites from the northern parts of the Central Rhodopes. *Geologica Balc.*, 20, 4, 19-35.
- Leake, B. E. et al. 1997. Nomenclature of amphiboles; report of the Subcommittee on amphiboles of the IMA CNMMN. - *Eur. J. Mineral.*, 9, 623-651.
- Macheva, L. A. 1998. 3T-phengites in the rocks from Byala Reka metamorphic group: An indicator of high pressure metamorphism. -*Geochem., Mineral., Petrol.*, **35**, 17-28 (in Bulgarian).
- Macheva, L., K. Kolcheva. 1992. Metagranitoids from East Rhodopes - occurrences and main features. – C. R. Acad. bulg. Sci., 45, 6, 63-66.
- Menzies, M., D. Blanchard, C. Xenophontos. 1980. Genesis of the Smartville Arc-ophiolite, Sierra Nevada foothills, California. - Am. J. Sci., 280A, 329-344.

- Miyashiro, A. 1973. The Troodos ophiolitic complex was probably formed in an island arc. -*Earth Planet. Sci. Lett.*, **19**, 218-224.
- Ovtcharova, M., St. Sarov. 1995. Petrology and tectonic setting of the metagranitoids from Kesebir Reka region in the Eastern Rhodopes.
 - XV Congress CBGA, Geol. Soc. Greece, Spec. Public., 4/2, 613-618.
- Ozawa, K. 1983. Evaluation of olivine-spinel geo-thermometry as an indicator of thermal history for peridotites. - *Contrib. Mineral. Petrol.*, **82**, 52-65.
- Ozawa, K. 1988. Ultramafic tectonite of the Miyamori ophiolitic complex in the Kitakami Mountains, northeast Japan: Hydrous upper mantle in an island arc. - *Contrib. Mineral. Pet-rol.*, **99**, 159-175.
- Penrose field conference on ophiolites. 1972. *Geo-times*, **17**, 24-25.
- Peytcheva, I., A. v. Quadt. 1995. U-Pb zircon dating of metagranites from the Bela-reka region in the Eastern Rhodopes, Bulgaria. -*Proc. XV Congr. CBGA, Geol. Soc. Greece, Spec. Publ.*, 4/2, 627-631.
- Quadt, A., I. Peytcheva. 1998. Multi-element approach for the Variscan orogen within the

Rho-dopean Massif (Bulgaria). - *Abstracts, XVI Congress CBGA*, Geol. Survey Austria, p.503.

- Zeljazkova-Panajotova, M. 1960. The Golyamo Kamenyane group of ultrabasic massives and their chromite content. – *Ann.Univ. Sofia*, *Fac. de Biol., Geol. et Geogr.*, **53**, 2, 59-142 (in Bul-garian).
- Zheljazkova-Panajotova, M., K. Kolcheva, S. Boy-adziev, L. Ivchinova, V. Vuchev, P. Petrov. 1978a. Study of ultrabasic rocks in Bulgaria by means of mathematical methods. III Petrochemi-cal characteristics. - *Geologica Balc.*, 8, 3, 9-14 (in Russian).
- Zheljazkova-Panajotova, M., L. Ivchinova, K. Kol-cheva, S. Boyadziev, V. Vuchev, P. Petrov. 1978b. Study of ultrabasic rocks in Bulgaria by means of mathematical methods. IV. Petroge-netic indicators. - *Geologica Balc.*, 8, 4, 27-48 (in Russian).

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