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Petrology of Golobradovo perlite deposit, Eastern Rhodopes

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Abstract. The Golobradovo perlite deposit is related to the Studen-Kladenetz volcano referred to the 2nd Lower Oligocene acid phase of the Eastern Rhodopes volcanic area. It consists of a dozen of small domes (up to 240 × 150 m in diameter) with reddish-brown trachyrhyolite cores rimmed by black to dark-gray perlite envelopes, and one perlite sill (ca. 350 × 350 m in size and thickness varying from 20 to 80 m). Compared with crystallized varieties, the perlites have lower contents of SiO_2, Na_2O, Li, and Ba, higher of Al_2O_3, K_2O, Ti, Zr, Mn, Y, Cs and Rb, and much higher K_2O/Na_2O ratio (up to 2.3). The transition between the crystallized and glass varieties is represented by linearly arranged trachyrhyolite spheruloids "growing" on trachyrhyolite layers and "cemented" by perlite. The petrologic and chemical data suggest that water in perlites is of magmatic origin and that the trachyrhyolite spheruloids and layers have an immiscibility genesis.

The nanostructure of the glass of Golobradovo perlite (distances between network-forming ions, valence state and type of Fe occurring in the glass and its distribution, types of water and average hydrogen bond distance) was studied by X-ray and spectroscopic methods. Mössbauer study shows that Fe in the perlites occurs essentially as magnetite microlites (<30 nm in size), hematite and wüstite nanoaggregates (<15 nm). These black particles, disseminated in the glass matrix, determine the black color of the perlite.

Key words: Paleogene volcanism, perlite deposits, perlite/rhyolite transition, spheruloids, immiscibility, glass nanostructure.

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Резюме. Перлитовото находище Голобрадово е свързано с вулкана Студен кладенец, принадлежащ на втората долноолигоценска кисела фаза на Източнородопската вулканска област. Находището е съставено от десетина малки вулкански купола (размери до 240 × 150 m), изградени от червенокафяви трахириолитови ядра и периферия от черни до тъмносиви перлити, както и от един перлитов сил (размери около 350 × 350 m и дебелина 20 - 80 m). Перлитите, сравнени с кристализиралите разновидности (преизчислени към 100% сухо вещество) имат по-ниско SiO_2, Na_2O, Li и Ba, по-високо Al_2O_3, K_2O, Ti, Zr, Mn, Y, Cs и Rb съдържание, както и много по-високо K_2O/Na_2O отношение (до 2,3). Преходът между кристализиралите и стъклените скални разновидности представлява скала, изградена от линейно подредени трахириолитови сферолоиди, "нараснали" върху трахириолитови "слоеве" всред перлитов матрикс. Петроложките и химически данни позволяват да се предположи, че перлитовата вода е с магмен произход и че трахириолитовите сферолоиди и слоеве имат ликвационнен генезис.

Наноструктурата на стъклото на перлитите в Голобрадовското находище (разстоянията между стъклообразуващите катиони, формите на желязото в стъклото и разпределението им, формата на водата и разстоянията между съставящите я йони) е изяснена с рентгенови и спектроскопски изследвания. Мьосбауеровите спектри показват, че желязото в стъклото е съсредоточено основно в магнетитовите микролити (размери <30 nm), в хематитови и вюститови наноагрегати (размери <15 nm). Тези черни наночастици, разпръснати в стъклото определят черния цвят на перлитите.

Introduction

The Golobradovo deposit of water-bearing volcanic glasses (perlites) is located 25 km to the east of Kardjali in the valley of Arda River. The deposit is related to the Lower Oligocene volcano Studen-Kladenetz (Fig. 1) which belongs to 2nd acid volcanic phase of the Eastern Rhodopes Paleogene volcanic activity (Yanev, 1970, 1998). First Bonchev (1906) noted the presence of perlite in the volcano but the deposit was discovered much later by Goranov et al. (1960). This is one of the few perlite deposits in Bulgaria that had been object of drilling exploration during the 70s and the beginning of the 80s. Due to the relatively high density of expanded perlite and its high Fe-content, the deposit has not been exploited.

The aims of this paper are to report new results and to summarize all available data on the geology of the deposit and the glass nano-structure in order to provide comprehensive information on the deposit. The new data concern the petrography and petrochemistry of volcanic rocks, the distribution of alkalies, the mineral chemistry, the geology and structure

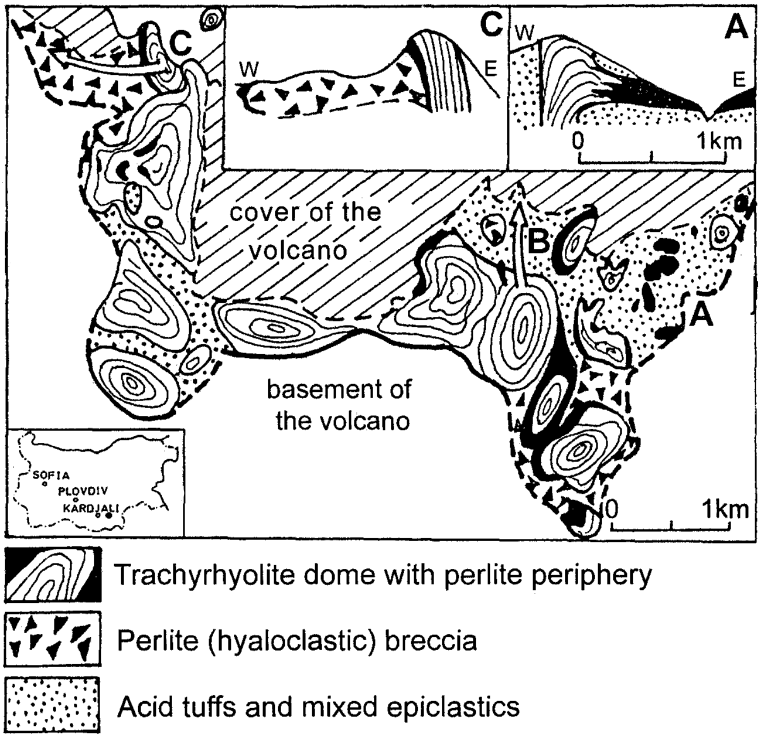

Fig. 1. Geological sketch map of the Oligocene Studen-Kladenetz volcano (modified from Yanev, 1987, 1998): A - Golobradovo, B - Svetoslav and C - Konevo perlite deposits. In the right corner: schematic cross sections of A and C deposits. Note: white arrows indicate the hyaloclastic flows

Фиг. 1. Схематична геоложка карта на олигоценския вулкан Студен кладенец (Yanev, 1987, 1998, с допълнения). Перлитови находища: А - Голобрадово, В - Светослав, С - Конево (в десния ъгъл – схематични разрези през две от находищата). Заб.: белите стрелки обозначават хиалокластични потоци of the volcano and the perlite deposit, and the perlite/trachyrhyolite transition. These data can shed new light on the origin of perlites and in particular on the origin of perlite water and the transition between glassy (perlites) and crystallized (trachyrhyolites) rocks.

Geology of Studen-Kladenetz volcano

The volcano is situated to the north of Arda River (Fig. 1), on the northern slope of Studen-Kladenetz Dam Lake. It is elongated in an E-W direction parallel to a system of E-W trending faults.

The volcano basement is composed of sediments, latite pyro- and epiclastic rocks that cover the frontal parts of two latite flows of the large St. Ilya stratovolcano (2nd intermediate phase), located to the south of the Studen-Kladenetz volcano.

The products of the volcano interfinger with explosive products of the 2nd acid phase (pumice and perlite tuffs 50-70 m thick) and epiclastic rocks (70 m thick). They are overlain by 130-m thick limestones with acid tuff intercalations. The epiclastic rocks are of acid composition, silty, sandy to granular. In the central and western parts of the volcano, they are of mixed composition and contain rounded perlite, trachyrhyolite, latite and gneiss clasts up to 20-30 cm in size. The epiclastic rocks are poorly sorted to chaotic and cemented by an ash-pumice matrix.

The volcano is composed of several large domes of complex structure (up to 3 × 1 km in diameter), numerous smaller domes (diameters from tens to several hundred meters), sills, and necks some of them producing hyaloclastic flows up to 1 km long. All these bodies are emplaced on an area of about 20 km^2, i.e. the volcano morphology is transitional between that of a dome-volcano and a dome-cluster (Yanev, 1998). One of the domes (trachyrhyolite and perlite exposed at Cholderen Summit) is dated at 32-33 Ma (Lilov et al., 1987; Georgiev et al., 2003).

The domes are emplaced at different levels: in the eastern part of the volcano in its basement (Fig. 2), in the central and western parts - in the acid tuffs and mixed epiclastic rocks, and in the limestones. The structure of the domes is zonal: the cores are built up of flow-banded reddish-brown trachyrhyolites, and the peripheries – of black to gray perlites forming lense-, crescent-shaped or ring-like bodies. Two types of transitions between trachyrhyolites and perlites are recognized (Yanev, 1987): 1) alternation of trachyrhyolite and perlite layers or lenses; 2) domains of trachyrhyolite spheruloids, enclosed by a perlite matrix. In the first case (Fig. 3), the trachyrhyolite layers gradually decrease in thickness towards the perlite periphery, from 10-15 cm to a few mm, and finally disappear. Alternatively, the perlite layers thin towards the trachyrhyolite core. Along their strike the trachyrhyolite and perlite layers grade into wedges and disappear, i.e. the both varieties interfinger laterally with one another. The trachyrhyolite spheruloids*, in the second type of transition, are up to 10-15 cm in diameter, have a sharp phase boundary with the perlite matrix, and spherulite structure (Yanev, 1970). Towards the trachyrhyolite core, the spheruloids coalesce and the glass in between decreases to complete disappearance. In contrast, toward the perlite periphery, the spheruloids gradually decrease in number and size, and finally, they also disappear.

The hyaloclastic flows consist of gray perlitic breccias (the Svetoslav and Konevo deposits – Fig. 1) formed in a marine environment as indicated by coral reefs that have grown on their top. Trachyrhyolite bodies, tens of meters in size, are also present within the flows, "enveloped" by the alternation of perlie and trachyrhyolite layers. The flows grade into massive perlites towards the necks. Here the trachyrhyolite/perlite transition is an alternation of layers (the Konevo deposit), or interfingering between perlite and trachyrhyolite wedges (the Svetoslav deposit).

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*Spheruloid after Bryan (1954): a spherical, semispherical, ellipsoidal, or pillow-like silicic body, a few mm to 1 m in size with spherulitic, felsitic or other texture (pyromerides in French literature).

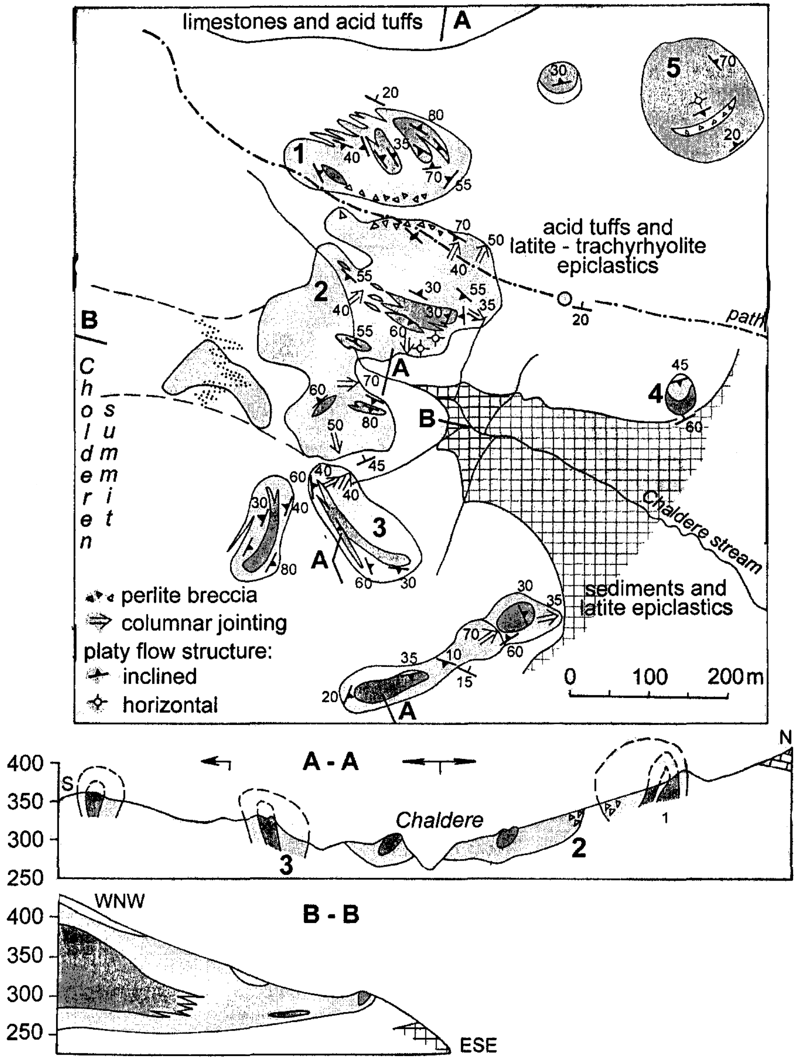

Fig. 2. Geological map of the Golobradovo perlite deposit (mapped by Y. Yanev in 1975 on scale 1:10 000). The gray areas are perlites and the black ones are trachyrhyolites. Key: (1) Odjak-Kaya dome, (2) sill (dashed line - not exposed part of the sill and dotted line - schematic position of the perlite/trachyrhyolite transition zone), (3) Central dome, (4) Little dome and (5) North-eastern dome. A-A and B-B – cross sections shown at the bottom

Фиг. 2. Геоложка карта на перлитовото находище Голобрадово (съставена от Й. Янев през 1975 г. в М 1:10 000). Сивите полета – перлити, черните – трахириолити. Легенда: 1-купол Оджаккая, 2-сил (пунктирната линия е границата на неразкрита част от сила, а точковата – преходът перлит/трахириолит), 3-централен купол, 4-малкият купол и 5-североизточен купол. А-А и В-В – линии на напречните разрези

Geology of the Golobradovo deposit

The deposit is located in the eastern part of the Studen-Kladenetz volcano (Fig. 1). It includes (Fig. 2) a dozen of small trachyrhyolite domes (the larger three ones are 240 × 150, 220 × 80 and 160 × 60 m in size), having black to dark-gray perlite peripheries (the trachyrhyolite/perlite ratio varies from 1:5 to 4:1), as well as one thick perlite sill.

The domes are emplaced into sediments, epi- and pyroclastic rocks from the basement, about 50-60 m below the base of the volcano, i.e. they cooled at shallow subvolcanic level and are practically cryptodomes. Dome-rounding colluvial breccias (talus), normally developing around subaerially erupted domes, are absent. The pumiceous cap, typical of subaerially erupted perlitic domes (Nassedkin, 1975), is also missing. The perlites exhibit columnar jointing with hexagonal or pentagonal columns (20-25 cm in diameter) that are oriented perpendicular to the cooling surfaces, i.e. most commonly horizontal. This type of jointing results from very rapidly cooling lava that intrudes water-rich and probably unconsolidated sediments and tuffs (Yanev, 1987). At the contact with perlites, the hosting tuffs are silicified and zeolitized (platy clinoptilolite crystals within a chalcedony matrix), and have a glassy appearance. The trachyrhyolites from the core of the dome show distinct flow banding and parallel jointing. The transition zone between the trachyrhyolite core and the perlite periphery is an alternation of trachyrhyolite and perlite layers (Fig. 3) or a combination of the two above described types: linearly-arranged trachyrhyolite spheruloids "growing" upon trachyrhyolite layers (Fig. 4). Vesicles (from several mm up to 10-15 cm in size) are observed only in the trachyrhyolite spheruloids and layers. Some of them are partly filled with opal-chalcedony aggregates. The small crescent-shaped vesicles are parallel to the surface of the spheruloids (Yanev, 1970).

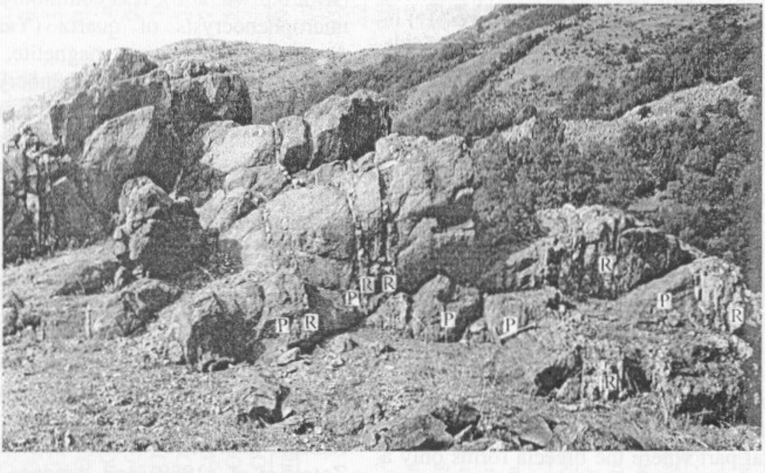

Fig. 3. Trachyrhyolite/perlite transition zone in the Little dome (Golobradovo deposit): R, trachyrhyolite and P, perlite layers (to the right – trachyrhyolite core of the dome, to the left – perlite periphery)

Фиг. 3. Трахириолит/перлитова преходна зона в Малкия купол (находище Голобрадово): R-трахириолитови и P-перлитови слоеве (в дясно – трахириолитово ядро на купола, в ляво – перлитова периферия)

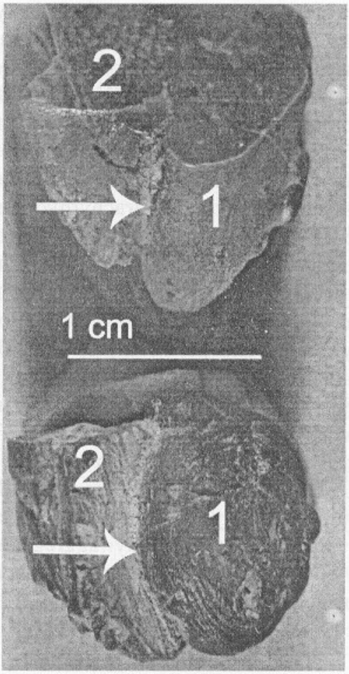

Fig. 4. Trachyrhyolite spheruloids (1) with meniscus (arrows) located on the trachyrhyolite "layer" (2) in the perlite/trachyrhyolite transition zone (Little dome). The perlite matrix is eroded. (Collection No MR.1.03.9.12 of the Geological Institute)
Фиг. 4. Трахириолитови сферолоиди (1) с менискуси (стрелки), лежащи върху трахириолитови "слоеве" (2) в перлит/трахириолитовата преходна зона (Малкият купол). Перлитовият матрикс е изнесен. (Колекционен № MR.1.03.9.12, Геологически институт)

The sill is L-shaped in plan view. In previous papers it has been described as perlite flow (Yanev, 1987; Popov et al., 1989) but its emplacement between numerous cryptodomes and its massive internal structure (except for the frontal part where the breccia forms only a 1 m wide zone – Fig. 2) indicate that this body is a sill. It is probably connected to a neck located about 200 m to the WNW of the sill outcrop (Cholderen Summit). Close to the neck, the perlites interfinger with trachyrhyolites. There, the sill is 150 m wide, about 20-30 m thick, and includes two large "lenses", tens of meters in size, of hosting sedimentary and epiclastic rocks. The exposed eastern part of the sill, elongated in SW-NE direction, is 350 × 200 m in size and 80 to 25 m thick, i.e. this is the largest perlite body in the deposit. It is almost entirely exposed on both banks of the Chaldere Stream. Here, the perlites exhibit vertical columnar jointing with column diameter 12-20 cm. Due to the uneven lower surface of the sill, the columns are often not vertical but inclined (along the Chaldere Stream). The internal structure of the sill is complicated by numerous small trachyrhyolite "lenses", especially in its lower parts, and two trachyrhyolite subvertical "bodies" 20 × 50 and 40 × 130 m in size, displaying combined perlite/trachyrhyolite transition – spheruloids "grown" on trachyrhyolite layers.

Petrographic description

The perlites consist of phenocrysts up to 1-2 mm in length and matrix. The phenocrysts (Table 1) are of sanidine, plagioclase, biotite (with 0.3 wt. % F), less commonly augite, and microphenocrysts of quartz (Yanev, 1998). Accessory minerals are magnetite, apatite, and zircon. The plagioclase phenocrysts contain melt inclusions reflecting the primary composition of the magma. The sum of oxides in them is far below 100%, which is caused by the presence of fluid phase in the glass (probably water mainly), as well as to partial loss of Na_2O during the microprobe analyses.

Magma temperature calculated using the two-feldspar geothermometer of Fuhrman and Lindsley (1988) is 776°C.

The matrix consists of black or banded (black and gray) volcanic glass with perlitic cracks. The glass contains numerous, mainly feldspar microlites (about 1 wt. % according to Zotov et al., 1989) and dendrite-like crystallites. They form flow bands that are disturbed around phenocrysts and small spheruloids (Fig. 5b). The volcanic glass is fresh (Fig. 6), without zeolites, clays or other alteration products. Parallel to the perlite cracks there are micro-vesicles in the gray perlite indicating

Table 1. *Chemical composition of phenocrysts and their melt inclusions*

Таблица 1. *Състав на порфирни минерали и стъклени включения в тях*

Mineral	Sanidine		Plagioclase (Pl)			Biotite		Pyroxene	Melt inclusions in Pl		
SiO_2	64.61	65.69	62.94	62.69	61.62	33.34	33.58	49.74	71.97	72.55	72.66
TiO_2	n.d.	n.d.	n.d.	0.08	0.10	5.63	5.51	0.11	0.23	0.18	0.18
Al_2O_3	18.09	18.81	23.13	23.55	23.44	12.72	13.01	0.50	12.93	13.17	13.14
FeO_{tot}	0.09	0.08	0.22	0.32	0.24	22.02	22.48	21.22	0.82	0.65	0.75
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	0.62	0.03	1.38	n.d.	n.d.	n.d.
MgO	0.01	n.d.	0.05	0.01	0.02	7.86	7.78	8.05	0.09	0.09	0.08
BaO	0.27	n.d.	n.d.	n.d.	n.d.	0.31	n.d.	n.d.	n.d.	n.d.	n.d.
CaO	0.29	0.29	5.10	4.79	5.37	0.02	0.09	18.11	0.63	0.60	0.68
Na_2O	3.98	4.14	9.07	8.37	7.99	0.64	0.70	0.15	1.11	1.97	1.38
K_2O	10.63	10.75	1.32	1.14	1.07	7.78	7.82	Cr_2O_3=0.1	3.62	4.58	4.19
H_2O	-	-	-	-	-	3.65	3.67	-	n.d.	n.d.	n.d.
Total	97.97	99.75	101.83	101.07	99.91	94.75	94.70	99.37	91.40	93.79	92.33
Si	2.999	2.988	2.765	2.765	2.750	5.471	5.486	1.968			
Ti	n.d.	n.d.	n.d.	0.003	0.003	0.695	0.678	0.004			
Al	0.989	1.008	1.197	1.224	1.233	2.460	2.505	0.023			
Fe^{2+}	0.004	0.003	0.008	0.012	0.009	3.023	3.072	0.657			
Mn	n.d.	n.d.	n.d.	n.d.	n.d.	0.086	0.005	0.046			
Mg	0.001	n.d.	0.003	n.d.	0.002	1.923	1.896	0.477			
Ba	0.005	n.d.	n.d.	n.d.	n.d.	0.020	n.d.	Fe^{3+}=0.042			
Ca	0.014	0.014	0.240	0.226	0.257	0.004	0.015	0.768			
Na	0.358	0.365	0.772	0.716	0.692	0.204	0.222	0.011			
K	0.629	0.624	0.074	0.064	0.061	1.628	1.629	Cr=0.003			
Total	5.000	5.002	5.059	5.010	5.006	15.515	15.510	3.999			
Or	62.80	62.20	6.81	6.3	6.1	^{VI}Al =	^{VI}Al =	Wo=39.5			
Ab	35.76	36.38	71.10	71.2	68.5	2.529	2.514	En=24.5			
An	1.44	1.42	22.09	22.5	25.4	-	-	Fs =36.0			
Mg#	-	-	-	-	-	0.38	0.38	0.42			

WDS analyses made on Camebax and CX-50 (melt inclusions) in the Universities Paris-11 (Orsay) and Paris-6 respectively; n.d. – not determined; Mg# = $Mg/Mg+Fe_{tot}$ (for pyroxene $Mg/Mg+Fe^{2+}$)

Анализите са WDS и са извършени на Camebax и CX-50 (на стъклените включения) съответно в Университетите на Париж-11 (Орсе) и Париж-6; n.d. – не е определяно; Mg# = $Mg/Mg+Fe_{tot}$ (за пироксена $Mg/Mg+Fe^{2+}$)

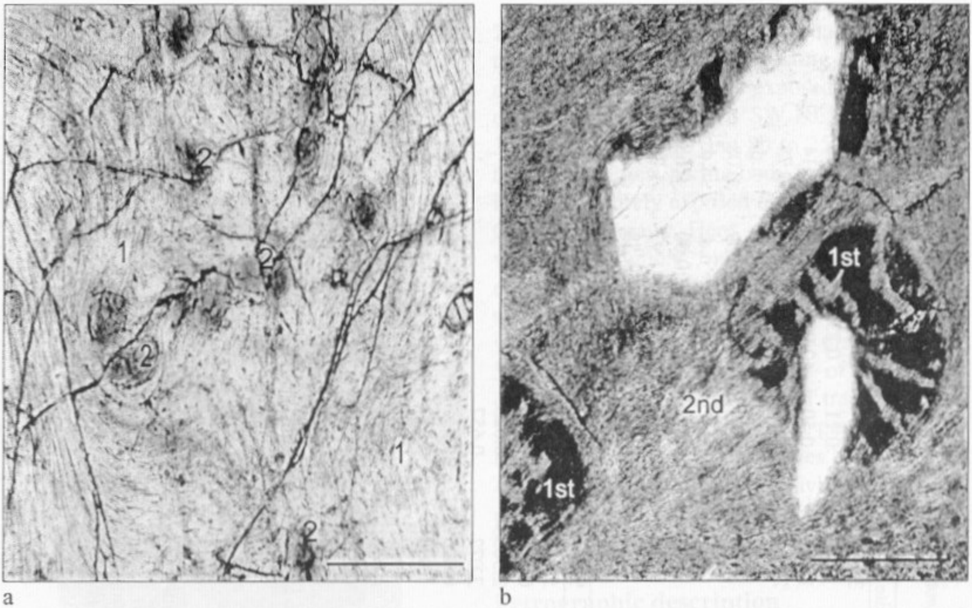

Fig. 5a – Deformation of flow bands of Fe-oxide microlites in the glassy matrix (1) by the trahyrhyolitic spheruloids (2); b - two generations spherulites (1st and 2nd) in trachyrhyolite spheruloid with diameter 10 cm from the perlite/trachyrhyolite transition zone. Bar 0.25 cm; plain light

Фиг. 5a – Деформация на Fe-оксидни микролитни потоци в стъклення матрикс (1) от трахириолитови сферолоиди (2); b – две генерации сферолити (1st and 2nd) в трахириолитов сферолоид с диаметър 10 cm от перлит/трахириолитовата преходна зона. Скала - 0,25 cm; || N

an initial stage of pumice formation (Fig. 6).

The trachyrhyolites contain the same phenocrysts as the perlites, but the texture of their matrix is felsitic or locally axiolitic, and consists of feldspar and tridymite microcrystals (Dimitrov et al., 1984). Their color is reddish-brown (at a depth of several tens of meters below the surface – gray), caused by the superficial oxidation of magnetite microlites dispersed in the matrix.

The texture of the spheruloids is spherulitic. According to X-ray data they consist of cryptocrystalline K-Na feldspar and tridymite (crystals <1 μm) with magnetite dendrites. The centres of spherulite crystallization are often situated on the phenocryst surfaces or in the centres of the spheruloids or, if vesicles are present, on their surfaces (Yanev, 1970). Some of the spheruloids enclose an earlier generation of spherulites (Fig. 5a). The spheruloids that lay on the trachyrhyolite layers have a meniscus (Fig. 4) and deformed bottom surfaces like pillow-lava (Fig. 7). Some large spheruloids contain latitic enclaves with diffuse outlines composed of glassy matrix with microlithic plagioclase and pyroxene, indicative of a magma-mingling process (Yanev, 1998).

Chemical composition

The trachyrhyolites are rich in alkalis (Table 2, Fig. 8) with K_2O/Na_2O ratio 1.5 – a value typical of most Eastern Rhodopes acid volcanic rocks (Yanev et al., 1983). The perlites are also rich in alkalis. Their normative composition is: quartz 29%, K-feldspar 44%, and albite 27% (Yanev, Zotov, 1995). Compared with trachyrhyolites (water-free base - Table 2), perlites contain lower amounts of SiO_2, Na_2O, and higher of K_2O, and Al_2O_3. Similar data are

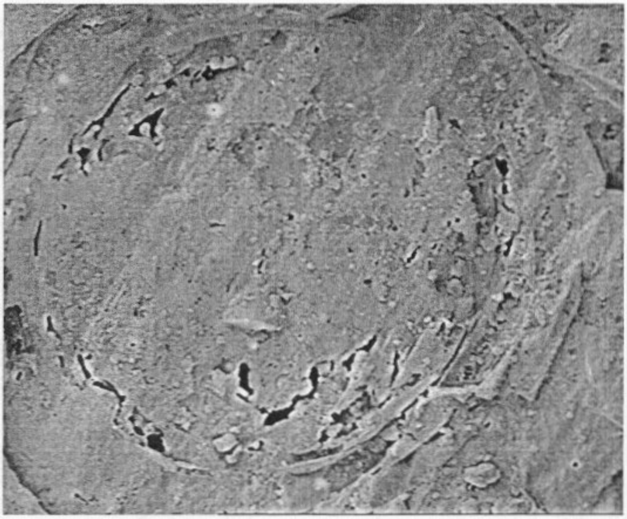

Fig. 6. SEM image of the glassy matrix from gray perlite (beginning of the foaming) without any alteration products; × 350. JEOL JSM T-300 (operator S. Danev, Geological Institute)

Фиг. 6. Електронмикроскопска снимка на стъкления матрикс на сив перлит (начало на пемзуване), в който отсъстват продукти на промяна на стъклото; × 350, сканиращ електронен микроскоп (оператор С. Данев, Геологически институт)

published by Ewart (1971), Salova et al. (1990) for obsidians and in "Perlite genesis" (1992). Consequently, the K_2O/Na_2O ratio in Golobradovo perlites is much higher (up to 2.3), positively correlating with the H_2O content (Fig. 9).

The alkali content in the transitional trachyrhyolite/perlite zone changes gradually from the trachyrhyolite core to the perlite periphery (Fig. 10): in trachyrhyolite layers, Na_2O, K_2O, and Rb gradually decrease; in the perlite ones, Na_2O increases, K_2O does not change significantly, and Rb decreases. Thus, Na_2O and Rb contents in the perlite periphery and in the neighboring trachyrhyolite layers become equal.

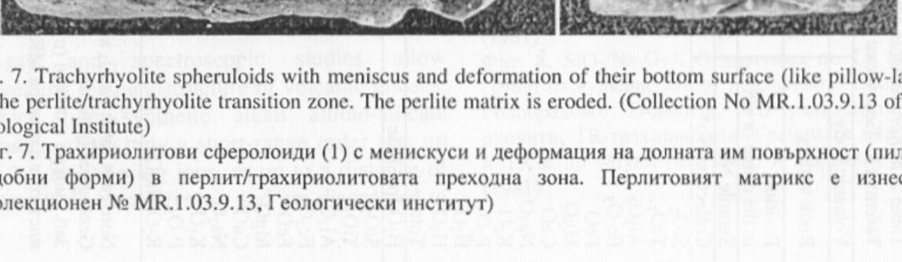

Fig. 7. Trachyrhyolite spheruloids with meniscus and deformation of their bottom surface (like pillow-lava) in the perlite/trachyrhyolite transition zone. The perlite matrix is eroded. (Collection No MR.1.03.9.13 of the Geological Institute)

Фиг. 7. Трахириолитови сферолоиди (1) с менискуси и деформация на долната им повърхност (пилоуподобни форми) в перлит/трахириолитовата преходна зона. Перлитовият матрикс е изнесен. (Колекционен № MR.1.03.9.13, Геологически институт)

Table 2. *Major elements content in the trachyrhyolites and perlites, wt. %*
Таблица 2. *Химически състав на трахириолити и перлити, тегл.%*

Volcanic body	Sill					Central dome				NE dome	Little dome
Rock variety	trachy-rhyolite	perlite	perlite	trachy-rhyolite	perlite	trachy-rhyolite	perlite	trachy-rhyolite	perlite	trachy-rhyolite	trachy-rhyolite
Position in the dome or sill	core	periphery	periphery	transition zone		core	periphery	transition zone		core	(spheru-loid)
Sample No	SK-333	1165	G-73	769	768	SK-337	SK-796	794	793	SK-327	SK-325
Collection No*	1	2	3	4	5	6	7	8	9	10	11
SiO_2	73.62	71.07	70.14	74.70	70.13	74.73	70.33	75.30	69.75	74.18	74.47
TiO_2	0.12	0.14	0.14	0.12	0.13	0.13	0.14	0.12	0.15	0.11	0.11
Al_2O_3	12.58	13.04	13.49	12.88	13.06	11.78	12.89	11.37	13.13	12.50	12.24
Fe_2O_3	1.33_{tot}	1.67_{tot}	1.15	0.76	1.23	1.03	2.00_{tot}	0.75	1.01	1.03	0.94
FeO	n.d.	n.d.	0.50	0.72	1.08	0.36	n.d.	0.58	0.90	0.46	0.86
MgO	2.52	n.d.	0.23	0.80	0.30	0.15	n.d.	0.05	0.06	0.25	0.27
CaO	0.56	0.72	0.60	0.52	0.61	1.08	0.74	1.32	0.93	0.46	0.96
Na_2O	3.23	3.40	2.86	3.64	2.80	3.60	3.06	2.45	2.74	3.70	3.60
K_2O	4.95	5.69	6.62	5.46	6.10	5.21	5.88	4.50	6.00	5.30	5.10
P_2O_5	n.d.	n.d.	0.03	0.01	0.03	0.02	n.d.	0.01	0.01	0.02	0.03
H_2O^-	n.d.	n.d	0.40	0.26	0.45	0.55	n.d.	1.64	0.88	0.39	0.50
H_2O^+	0.75_{tot}	4.2_{tot}	3.60	0.07	3.64	0.84	4.45_{tot}	2.18	4.11	0.57	0.63
Total	99.68	99.93	99.76	99.94	99.56	99.48	99.49	100.27	99.67	98.97	99.71
H_2O free base											
SiO_2	74.42	74.25	73.24	75.01	73.46	76.19	74.00	78.07	73.67	75.68	75.56
TiO_2	0.12	0.15	0.15	0.12	0.14	0.13	0.15	0.12	0.16	0.11	0.11
Al_2O_3	12.72	13.62	14.09	12.93	13.68	12.01	13.56	11.79	13.87	12.75	12.42
Fe_2O_3	1.34_{tot}	1.74_{tot}	1.20	0.76	1.29	1.05	2.10_{tot}	0.78	1.07	1.05	0.95
FeO	n.d.	n.d.	0.52	0.72	1.13	0.37	n.d.	0.60	0.95	0.47	0.87
MgO	2.55	n.d.	0.24	0.80	0.31	0.15	n.d.	0.05	0.06	0.26	0.27
CaO	0.56	0.75	0.63	0.52	0.64	1.10	0.78	1.37	0.98	0.47	0.97
Na_2O	3.29	3.55	2.99	3.65	2.93	3.67	3.22	2.54	2.89	3.78	3.65
K_2O	5.00	5.94	6.91	5.48	6.39	5.31	6.19	4.67	6.34	5.41	5.17
P_2O_5	n.d.	n.d.	0.03	0.01	0.03	0.02	n.d.	0.01	0.01	0.02	0.03
K_2O/Na_2O	1.53	1.67	2.31	1.50	2.18	1.45	1.92	1.84	2.19	1.43	1.42

Note: wet (with Fe_2O_3 and FeO) and X-ray fluorescence (with total Fe as Fe_2O_3) analyses *The samples are in the collection MR.1.03.9.1 to 11 of the Geological Institute

Заб.: мокри анализи (с Fe_2O_3 и FeO) и рентгено-флуоресцентни анализи (с общо Fe като Fe_2O_3) *Образците са в колекцията на Геологическия институт с номера MR.1.03.9.1 до 11

In the earlier generation of spherulites within the large spheruloids (Fig. 5b), the contents of Na_2O and K_2O are nearly equal (Na_2O 4.35, K_2O 4.69 wt. %), while the spheruloid hosts (2nd generation spherulites) show the significant predominance of K_2O (Na_2O 3.39, K_2O 6.62 wt. % - Yanev, 1970).

Trace element contents of the Golobradovo volcanic rocks (Table 3, 4) are typical of the younger phases of the Eastern Rhodopes acid volcanism (Yanev et al., 1990; Yanev, 1998): lower Sr and Ba contents, higher Rb, Ta, Nb, Ce, Hf, Zr, Sm, and Y contents (Fig. 5 and 7 in Yanev, 1998) and a well expressed Eu anomaly (Fig. 11). Their ORG-normalized patterns show positive anomalies of Rb, Th, and in lesser degree of Ce, negative ones of Ba and Nb. Most of these anomalies are typical of suprasubduction volcanic rocks (Pearce et al., 1984), but they are enriched in Rb, Th, and depleted in Ba as compared to the acid subduction-related volcanic rocks, especially from active continental margins of Andean type. Including the rocks studied, all Eastern Rhodopes Paleogene magmatic rocks are considered to be collision-related (Yanev, 1998).

Due to their crystallochemical properties with respect to glass formation, the contents of most trace elements in the perlite are higher than those in the trachyrhyolite (Table 3 and 4): Zr^{4+} is a network-forming cation; Ti^{4+}, Th^{4+}, Zn^{2+}, and Pb^{2+} are intermediate cations; Cs^{+}, Rb^{+}, Mn^{2+}, Y^{3+}, and REE^{3+} are modifier cations in the glass structure due to their favorable metal-oxygen bonds (Zarzycki, 1982). Only Li (stimulating crystallization of alumo-silicate malts according to Appen, 1974) and Ba are prevailing in the trachyrhyolites.

Perlite nanostructure

X-ray and spectroscopic studies allow revealing the nanostructure of volcanic glasses, which like synthetic alkali alumo-silicate glasses, show only a short-range order (i.e. up to 2-3 neighboring ions, or up to a distance of about 8 Å, respectively), and are disordered in medium- and long-range distances. Using X-ray radial distribution function analysis (Zotov et al., 1989), the following distances between network-forming ions, arranged in 6-membered rings, have been measured (in Å): $(Si,Al)_1$-O_1 1.62, O_1-O_1 2.68, $(Si,Al)_1$-$(Si,Al)_1$ 3.15, $(Si,Al)_2$-O_2 4.12, $(Si,Al)_2$-$(Si,Al)_2$ and O_2-O_2 5.265; Si,Al-O-Si,Al angle is 153°. The nanostructure of the Golobradovo perlite is similar to that of the feldspar glasses (Taylor, Brown, 1979), but the angle in volcanic glasses is 10° larger probably due to the tetrahedral rings expansion that might have resulted of presence of water molecules (Zotov et al., 1989).

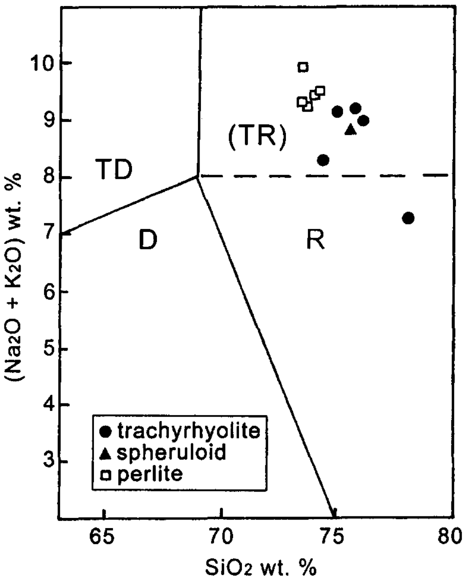

Fig. 8. TAS diagram (after Le Maitre, 1989) of the volcanic rocks from the Golobradovo perlite deposit: D, dacite; TD, trachydacite; R, rhyolite; TR, trachyrhyolite. The limit between R and TR is according to Miyashyro (1978) and Bogatikov et al. (1981)

Фиг. 8. SiO_2/Na_2O+K_2O диаграма по Le Maitre (1989) на вулканитите от перлитовото находище Голобрадово: D-дацити, TD-трахидацити, R-риолити, TR-трахириолити. Границата между R и TR е по Miyashyro (1978) и Bogatikov et al. (1981)

Fe is a specific modifier cation since its valence state defines the colour of perlites and, consecutively, the possibilities for their use in glass industry. It was found by EPR spectroscopy (Calas et al., 1988) that the Golobradovo perlites contain Fe^{3+}, mainly in nanocrystals (signal at g 3.2), and much less as ion in the glass structure (signal at g 4.3). The ratio between these two signals is 90. Mössbauer measurements (Dormann et al., 1989) performed at room temperature, 77K and 4.2K (Fig. 12), show the following distribution of Fe in the Golobradovo perlites: magnetite microlites (>30 nm in size) 32%, hematite nanoaggregates (15-30 nm) 17%, wüstite nanoagreggates (<15 nm) 25%, Fe^{2+} and Fe^{3+} ions in the glass structure 17 and 9%, respectively. The high contents of black nano- and microcrystals, the high mineral phases/structural Fe ratio (2.85), and the high Fe_{total} content in perlite (1.65 wt. %), define its black colour. Thus, the perlite colouring is of colloid type (the coloured compounds have colloidal size - Kocik et al., 1983). The presence of Fe^{2+} ions in the glass structure is responsible for its bluish shade and the existence of FeO nanoaggregates in the glass structure indicates the reduction conditions during the perlite cooling at T_g. The gray perlites contain less black nano- and microcrystals, and the main part of the Fe is in the form of cations bonded to the glass structure. They also include very small expanding bubbles (Fig. 6).

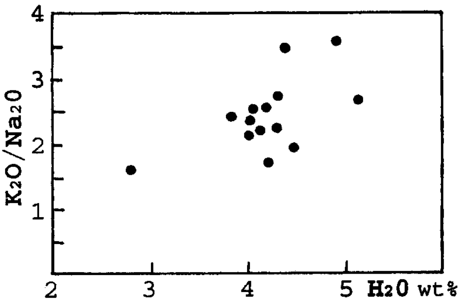

Fig. 9. K_2O/Na_2O vs. H_2O diagram for the perlites of the Golobradovo deposit

Фиг. 9. Диаграма K_2O/Na_2O към H_2O на перлитите от находище Голобрадово

Table 3. *Trace element contents in volcanic rocks, ppm*

Таблица 3. *Съдържание на редки елементи във вулканити, ppm*

Sample	793	794
Rock variety	perlite	trachy-rhyolite
Li	2.65	3.66
Rb	235	107
Cs	29.25	7.75
Sr	49	32
Ba	74	<70
Zr	234	201
Ti	845	714
Mn	507	181
Pb	38	32
Zn	34	25
Cu	8	11
Ni	35	19
La	70.8	64.0
Ce	155	131
Sm	8.4	7.7
Eu	0.30	0.30
Tb	1.22	1.03
Yb	5.8	4.8
Lu	0.85	0.70
Th	62.2	49.5
U	11.5	9.8
Sc	4.1	3.4
Hf	6.3	5.2
Co	0.7	0.7
V	0.5	0.5
Ta	5.8	4.2
Y	45	37
Nb	18.4	18.2

Analytical methods: Li, Pb, Zn, Cu, Ni - atomic absorption; Rb, Sr, Ba, Zr, Ti, Mn, Y - X-ray fluorescence; *REE*, Cs, Th, U,Sc, Hf, Co, V, Ta – neutron activation; Nb – colourimetric (Geological Institute)

Presence of water in perlites is the main cause for their expansion. It is known (Scholze, 1959) that water in glasses occurs as molecular water and hydroxyl groups bonded to the glass structure. Infrared studies of the Golobradovo perlites showed the presence of OH-groups and two groups of molecular water (Dimitrov et al., 1984; Yanev, Zotov, 1996). The perlite spectrum is characterized by bands at 3588,

Table 4. *Contents of some trace elements in trachyrhyolites and perlites, ppm*
Таблица 4. *Съдържание на някои редки елементи в трахириолити и перлити, ppm*

Samples	337	325	327	331	768	808	Average	
Rock variety	trachy-rhyolite	trachy-rhyolite	trachy-rhyolite	spheru-loid	perlite	trachy-rhyolite	trachy-rhyolite (6)	perlite (2)
Sr	35	37	61	23	<20	<20	<33	<35
Rb	283	282	272	313	364	276	256	300
Zr	197	191	201	217	210	211	203	222
Ti	758	785	850	729	756	766	767	800
Ba	144	<70	317	<70	<70	<70	<124	<72
Mn	<40	<40	112	70	476	93	<89	492

Analytical methods: X-ray fluorescence (Geological Institute). The average contents include also samples 793 and 794 from Table 3; in the brackets – numbers of analyzed samples
Аналитичен метод – рентгено-флуоресцентен (Геологически институт). Средното съдържание включва също образци № 793 и 794 от табл. 3; в скоба – брой анализирани проби

3233 cm^{-1} (combined bands of the two groups of molecular water) and 3450 cm^{-1} (band of the OH-groups), and in NIR (Fig. 13) – 5260, 5155-5025 cm^{-1} (of the molecular water), and 4535 cm^{-1} (of the OH-groups), respectively. The absorption band in the 3000-3600 cm^{-1} interval permits the average hydrogen bond distance R (O...O) of the OH groups and of the molecular water to be determined (Yanev, Zotov, 1996). The results are: about 2.9 Å for OH groups, 2.8 Å (ice type H-bond), and 3.1 Å for molecular water. The O-H distance of all water species is 0.94-0.97Å.

The TGA-curves (Fig. 14, Bagdassarov et al., 1999) show that the most significant molecular water evaporation occurs at 320°C, and the total water loss takes place at about

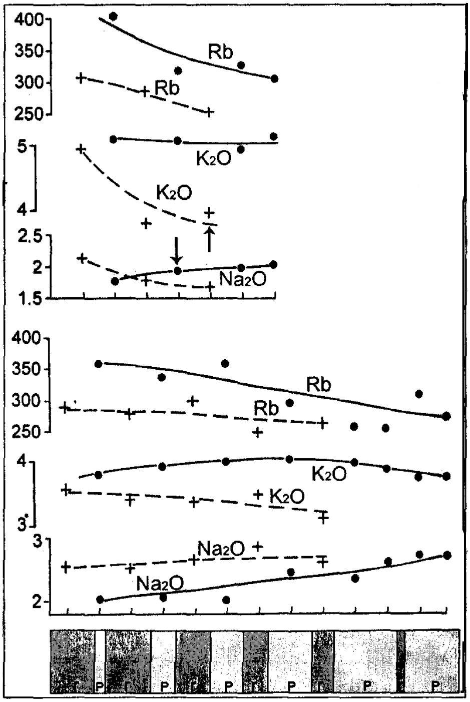

Fig. 10. Na_2O, K_2O (wt. %), and Rb (ppm) contents (flame photometry, analyzed by B. Karadjova) of the perlite (solid circles and solid lines) and trachyrhyolite (crosses and dashed lines) layers in the transition zone along two profiles across the Central dome periphery (left, towards the trachyrhyolite core; right, towards the perlite periphery). Bottom, schematic cross section of the perlite/trachyrhyolite transition zone (p, perlite and r, trachyrhyolite). The arrows indicate location of the samples analyzed for trace elements (Table 3)

Фиг. 10. Съдържание на Na_2O, K_2O (тегл. %) и Rb (ppm) (пламъчна фотометрия, анализатор Б. Караджова) на перлитови (кръгчета и плътните линии) и трахириолитови (кръстчета и пунктирните линии) "слоеве" в преходната зона по два профила в периферията на централния купол (ляво – към трахириолитовото ядро, дясно – към перлитовата периферия). Долу – схематичен разрез през перлит/трахириолитовата преходна зона (p-перлит, r-трахириолит). Стрелките означават посочените в табл. 3 проби

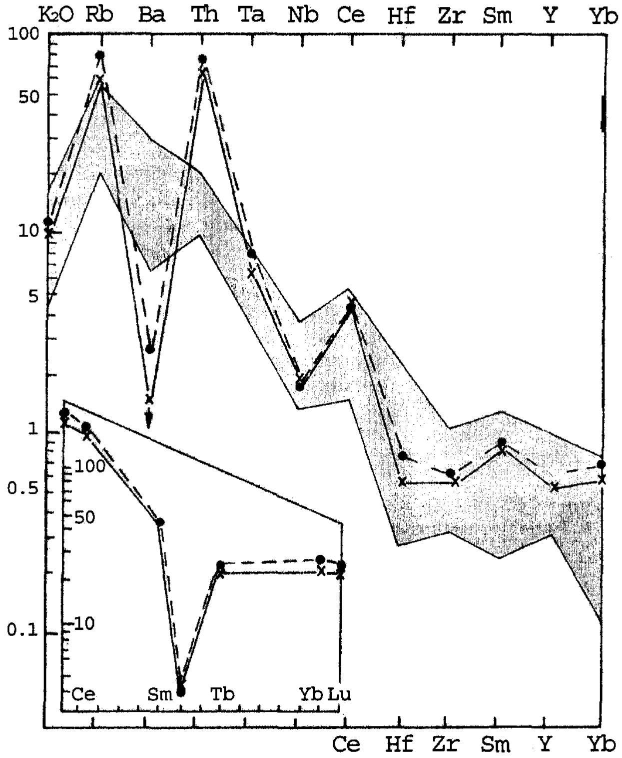

Fig. 11. ORG-normalized multi-element spidergram and hondrite-normalized *REE* diagram (in the left corner) of the Golobradovo perlite (points and dashed line) and trachyrhyolite (crosses and solid lines); the gray field is of the acid volcanic rocks from the active continental margin Andean type (Yanev et al., 1990 with references therein). The values of K_2O, Rb, Ba, and Zr are average according to Table 2, 3 and 4; other values are according to Table 3. ORG values – after Pearce et al. (1984) with Yb normalizing value of 8
Фиг. 11. ORG-нормирана многоелементна и хондрит-нормирана (в левия долен ъгъл) диаграма на перлит (черните точки и пунктира) и трахириолит (кръстчетата и плътната линия) от находище Голобродово; сивото поле е на киселите вулканити от активните континентални окрайнини Андийски тип (Yanev et al., 1990 с цитираните източници). Стойностите на K_2O, Rb, Ba и Zr са средни от табл. 2, 3 и 4, останалите – от табл. 3. ORG – по Pearce et al. (1984) с нормираща стойност за Yb 8

600°C. It is supposed that during dehydration, a part of the molecular water dissociates, and additional OH-groups enter the glass structure. The OH-groups do not escape totally (Fig. 13), even during heating at temperatures, corresponding to the perlite expansion (about 1200-1300°C). Hence, the expansion of perlite results from the rapid evaporation of the little H_2O remaining after 300-350°C preheating of the perlite from the softened glass (viscosity 10^8-10^7 Pa) heated above T_g (Bagdassarov, Dingwill, 1994).

Technical characteristics

Expanded perlite obtained from the Golobradovo deposit has a high density - 144 kg/m^3 of the 0.2-2.5 mm fraction (Popov et al., 1989). For comparison, the perlite breccia from the Svetoslav deposit produce expanded perlites with lower density - 102 kg/m^3.

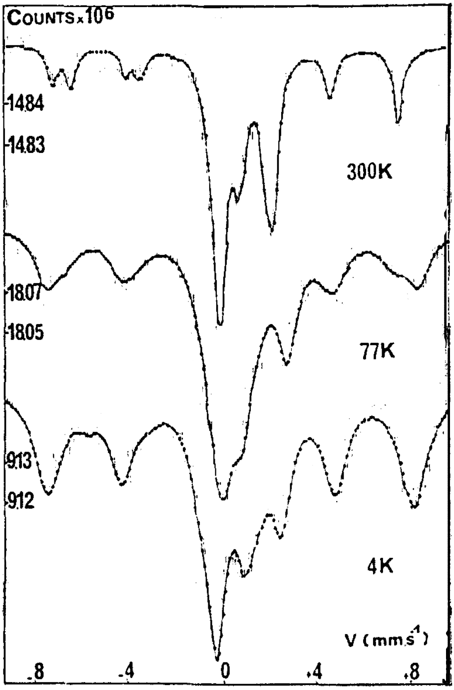

Fig. 12. Mössbauer spectra of Golobradovo perlite (sample G73) at three different temperatures (in K) according to Dormann et al. (1989)

Фиг. 12. Мьосбауеров спектър на перлит от Голобрадово (обр. G73) при три различни температури (в K) по Dormann et al. (1989)

However, the Golobradovo perlites can be used as a filler in concrete: a 2.5-5.0 mm fraction has a high compressive strength of 16.8 Mpa and density of 490 kg/m^3 after 30 sec expanding, or 27.0 MPa and 470 kg/m^3, respectively, after 60 sec expanding.

Discussion and conclusions

One of the most important questions raised by the present description of the Golobradovo perlite deposit is the genesis of the trachyrhyolite layers and spheruloids in the transitional zone. In the geological literature there are three hypotheses concerning the genesis of spheruloids (Yanev, 1987, 2000):

- products of suppressed crystallization, due to the fast increase of the cooling rate towards the dome periphery;
- products of partial crystallization of already solidified glass (partial devitrification);
- products of subliquidus immiscibility, in which the super-cooled water-containing lava splits into two immiscible liquids. One of them is rich in water, and after cooling, produces perlites; the other is a dry melt that crystallizes, and generates trachyrhyolite layers or spheruloids. Available petrologic data from the Eastern Rhodopes perlites are in agreement with this hypothesis (see below).

Beginning from Greig (1928), many authors explain the spheres in acid lavas with the crystallization hypotheses since there are no spheres with glass textures observed (Zavaritzkii, Sobolev, 1961) and because their spherical shape is easily explained as resulting from spherulitic crystallization (Greig, 1928; Volyaniuk, 1972; Nassedkin, 1975; Perlite genesis, 1992). Spherulite nuclei are not located at the eventual phase boundary (the walls of the spheres) but in their centre (Grigor'ev, 1966). The difference in the chemical composition of the glass and spherulites (the perlites are enriched in K, trachyrhyolite

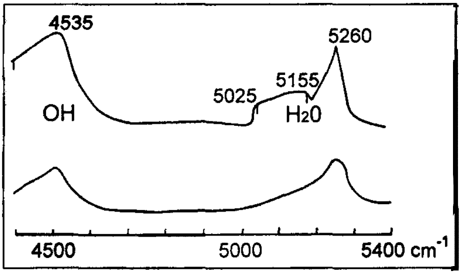

Fig. 13. Near infra-red spectra of Golobradovo perlite (sample G73) before (top, according to Yanev and Zotov, 1996) and after expanding at 1300°C (bottom)

Фиг. 13. Спектър на перлит от Голобрадово (обр. G73) в близката инфрачервена област преди (горе – по Yanev, Zotov, 1996) и след набъбване при 1300°C (долу)

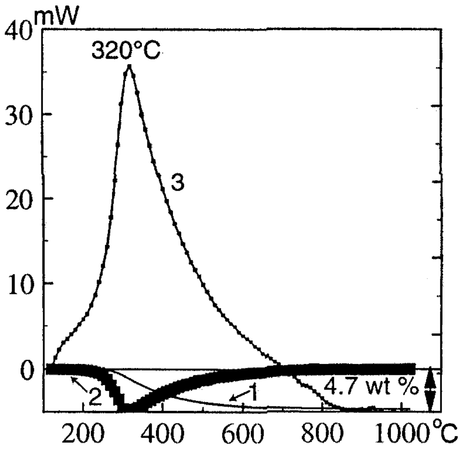

Fig. 14. Results of TGA (1, in wt. %), DTG (2, in 0.1mg/min) and DSC (3, in mW) of Golobradovo perlite (sample G73) obtained by a thermal gravitational balance with heating rate of 5 C°/min (according to Bagdassarov et al., 1999)

Фиг. 14. TGA (1, тегл. %), DTG (2, 0,1mg/min) и DSC (3, mW) диаграма на перлит от Голобрадово (обр. G73); скорост на нагряване 5 C°/min (по Bagdassarov et al., 1999)

layers and spherulites – in Na nevertheless that the Studen-Kladenetz volcanic rocks are potassic) can be explained either with crystallization at conditions of supercooling, when the chemical fractionation is not controled by the normal equilibrium crystal/melt (Ewart, 1971), or with authometasomatism of the glass and spherulites at which the alkalies have different behaviour in the two phases (Salova et al., 1990).

Whereas the immiscibility occuring in mafic and alkaline melts is proven (Roedder, 1979 and references therein; Sørensen et al., 2003), regarding acid ones it is rejected because of the absence of experimental evidence supporting the existence of immiscibility field in melts having water and/or fluorine contents corresponding to naturally observed. Hence, such a field has been recently registered in the system Na_2O-Al_2O_3-SiO_2-H_2O (V. N. Anfilogov, Inst. of Miner., Miass, Russia - pers. comm.). Starting with Tanton (1925) there are many authors (Petrographic Criteria..., 1963 and references therein; Yanev, 1970; Koronovskii, Fromberg, 1979; Marakushev, Yakovleva, 1980) presenting numerous petrographic and petrochemical evidence of the immiscibility origin of the spheruloids. These are: presence of obvious phase boundary in contrast to the uneven surface of the spherulites resulting from devitrification (Lofgren, 1971), coalescence of the immiscibility spheruloids and their deformation in the lower parts of the flows (Volovikova, 1955), presence of spheruloids with felsic and other textures giving no explanation of their spherical shape (Petrographic Criteria..., 1963). The distribution of the alkalis between the spherulites and hosting glasses can not be explained neither with crystallization (experimentally yelded spherulites have compositions similar to this of the parent melt - Bailey, Wenk, 1982), nor with metasomatic alteration sinse being much more reactive the glass should alter much more faster.

The following data presented in this paper suggest the immiscibility genesis of the trachyrhyolite spheruloids in the perlites:

1. The deformation of the flow bands around the spheruloids (Fig. 5a). According to Roedder (1979) this is an irrefutable indicator of the immiscibility origin of the spheruloids;
2. The meniscus on the base of the spheruloids that lay on the trachyrhyolite layers (Fig. 4) is also an “unequivocal evidence for immiscibility” (Hanski, 1993);
3. The deformation of their bottom surfaces (Fig. 7) indicating the liquid state of the spheruloids in the moment of their formation;
4. The crescent-shaped vesicles parallel to the spheruloid surface and growth of the spherulite fibers on the vesicle walls (Yanev, 1970);
5. The distribution of alkalies and trace elements between perlites and trachyrhyolite spheruloids.

The presence of two spherulite generations (Fig. 5b) with different alkali contents argues for a two-stage immiscibility in the large spheruloids (Yanev, 2000) like that occurring in synthetic glasses (Vogel, 1992). In “Perlite genesis” (1992) this is explained with siccessive crystalization at different degree of supercooling in the interval between T_f and T_g.

The second important question concerns the origin of water in perlites. It is believed that all volcanic glasses cool as obsidians (having H_2O<1wt. %) since the water escapes from the melts during their ascent to the surface, or it is explosively released producing pumice and tephra. Later the obcidians hydrate to form perlites under the influence of meteoric water or hydrotherms (that is why the perlite water is called secondary - Ross, Smith, 1955) in still hot (Nassedkin, 1963, 1975) or already cooled state. The hydration rate in cold state is too low (1 mm per 1 MA at 50°C - Friedman, Long, 1984) to be of any geological significance. Indeed, the hydrogen and oxigen isotope data for some american perlites indicate meteoric origin of the perlite water (Friedman, Smith, 1958; Steward, 1979). According to oxigen isotope data from Neogene perlites of the Transcaucasus area (Perlite genesis, 1992) the water in these perlites has not of meteoric origin (P. Petrov, Geol. Inst. of Bulg. Acad. of Sci. - pers. comm.). On the other hand, it is difficult to imagine that one so easily reacting phase, as volcanic glass, would not alter to low-temperature minerals (clays, zeolites) during the hydrothermal hydration. That is why, a hypothesis presuming hydration by fluids occurring at magmatic temperature 600-700°C was arisen (Nassedkin in Perlite genesis, 1992). The positive correlation of K_2O/Na_2O ratio and water content is also widely considered as evidence supporting the later glass hydration (Noble, 1967; Steward, 1979). Due to the smaller size of Na compared with potassium, Na cations hydrate easily and are leached more easily. However, as it was fairly noticed by Boyer-Guihaumaud (1974), it seems unprobable that K, emited from unknown source, is able to compensate exactly the same quantity of the leached Na.

On the contrary Marakushev et al. (1988, 1989) presented experimental evidence supporting their idea (Marakushev, Yakovleva, 1980) that perlites result from immiscibility and are quenched water-bearing magmas. On the basis of the different ratio between the molecular water and OH groups Epel'baum et al. (1991, 1994) divide perlites into magmatic (with water below 4-5 wt. % and H_2O/OH ratio corresponding to the diagram of Stolper) and additionaly hydrated - having higher water contents (up to 7-8 wt. %) and hydrothermally altered (with zeolites, clays). Such subdivision (of primary and secondary perlites) is also presented in "Perlite genesis" (1992). Indeed, there is no any doubt that acid magma contains water since the melt inclusions, entrapped by phenocrysts, are water-bearing (Hervig et al., 1989 and this study) and because of the crystalization of water-containing minerals from it (Naney, 1983). The possibility of preventing the water escape in superficial conditions is the main problem. Eichelberger (1989) stated "that to quench wet melt exceptional cooling rate is required. If the magma is emplaced in a cold, low-pressure environment it will cool by conduction long before can degas by diffusion". Moreover, degasing depents on the permeability of the medium as well.

The following facts from our study suggest the magmatic genesis of the perlite water:

1. The presence of wüstite nanophases and structurally bonded Fe^{2+} ions in the black perlites (Dormann et al., 1989); during hydration of glass Fe would oxidize (Noble, 1967);
2. The regular changes in the alkali contents of the perlite and trachyrhyolite layers in the transitional zone (Fig. 10) that cannot be explained with the hydration of the low-water-bearing volcanic glasses (obsidians) with loss of Na;
3. The total lack of any alteration minerals (Fig. 6) that would be formed during a long glass hydration;
4. The absence of residual not hydrated obsidian both in tens of perlite bodies of Studen-Kladenetz volcano and in all the rest of the several hundred perlite bodies in the Eastern Rhodopes (Yanev, 1987).

The emplacement of the Studen-Kladenetz domes and the sill at certain depth under the sea level did not allow the rapid loss of the water and respectively, the pumice formation.

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