GEOLOGICAL, PETROLOGICAL AND GEOCHEMICAL CHARACTERISTICS OF THE PERLITES FROM THE "SCHUPENATA PLANINA'' DEPOSIT, EASTERN RHODOPES AND HOSTING VOLCANITES

Stanislav Stoykov[1], Anita Metodieva[1], Miloslav Katzarov[1], Milko Harizanov[1]

[1]University of Miningand Geology "St. Ivan Rilski", 1700 Sofia; ststst@abv.bg; mharizanov@mgu.bg;

ABSTRACT. Schupenata planina is the only perlite deposit in operation in Bulgaria. It is located in Kurdjali region, in the area of Djebel town and Vodenicharsko village. They are part of the Eastern Rhodope Paleogene depression. The perlite is hosted in the rhyolites of the Ustren volcanic region. They are part of the Oligocene III-th acid volcanism in the Eastern Rhodopes. The perlites are grey to white – grey, they show sub vertical prismatic joints 7 to 10 m long. The rocks are build up by quartz, sanidine, acid plagioclase and biotite. The rhyolites contain between 74.05 and 76.25 wt. % SiO_2 and the analyzed perlite products - between 73.85 and 74.79. The rhyolites are of high – K type. The volcanic glass content in the perlite is up to 90 %.

Keywords: perlite, rhyolites, Eastern Rhodopes, Schupenata planina deposit, implementation of perlite

ГЕОЛОЖКА, ПЕТРОЛОЖКА И ГЕОХИМИЧНА ХАРАКТЕРИСТИКА НА ПЕРЛИТНАТА СУРОВИНА ОТ НАХОДИЩЕ „СЧУПЕНАТА ПЛАНИНА", ДЖЕБЕЛСКО И ВМЕСТВАЩИТЕ Я ВУЛКАНИТИ

Станислав Стойков[1], Анита Методиева[1], Милослав Кацаров[1], Милко Харизанов[1]

[1]Минно-геоложки университет "Св. Иван Рилски", 1700София; ststst@abv.bg; mharizanov@mgu.bg;

РЕЗЮМЕ. Счупената планина е единственото находище на перлит в България, което се разработва. То се намира в Кърджалийска област, в близост до град Джебел и село Воденичерско. Районът на находището попада в Източнородопското Палеогенско понижение. Перлитната суровина се намира сред риолитите на Устренския вулкански район. Те са част от третия кисел вулканизъм на Олигоцена в пределите на Източните Родопи. Перлитите са сиви до сивобели, наблюдават се сред риолити, показващи субвертикална призматична напуканост с дължина на призмите от 7 до 10 метра. Вулканитите са изградени от кварц, санидин, кисел плагиоклаз, биотит и вулканско стъкло. Риолитите съдържат между 74,05 и 76,25 wt. % SiO_2, а изследваните перлитни продукти - между 73,85 и 74,79 wt. % SiO_2. Вулканитите са високо калиеви. Вулканското стъкло в перлитите достига до 90 %.

Ключови думи: перлит, риолити, Източни Родопи, находище Счупената планина, приложение на перлита

Introduction

Schupenata planina (The Broken Mountain) is the only perlite deposit in operation in Bulgaria. It is located in Kurdjali region, in the area of Djebel town and Vodenicharsko village. They are part of the Eastern Rhodope Paleogene Depression.

The perlite is hosted in the rhyolites of the Ustren volcanic region. They are part of the Oligocene III-th acid volcanism in the Eastern Rhodopes. The rhyolites are build up by quartz, sanidine, acid plagioclase and biotite. They contain between 74.05 and 76.25 wt. % SiO_2 and the analyzed perlite product - between 73.85 and 74.79. The water content of the volcanic rocks is between 2.26 and 3.11 wt. % and in the fractionated perlite between 5.55 and 4.70 (Table 1). The rhyolites are of high – K type. The volcanic glass content in the perlite is up to 90 %. The perlites are grey to white – grey, they show sub vertical prismatic joints 7 to 10 m long.

The perlites were described as petrographical variety at the end of XVIII century. Their mining and industrial application started in 1940 with the production of expanded perlite in USA.

The name perlstein was given in XIXth century by a German petrologist naming certain rhyolotic glassy rock with concentric cracks, which looks similar to pearls. The most modern name perlite is now in use universally (Evans, 1993). The perlite is hydrated volcanic glass, composed mainly of amorphous silica with 12-18 wt. % Al_2O_3. Minor chemical components of the perlite are Na_2O, K_2O, Fe_2O_3, MgO, CaO, etc. This hydrated rocks carry between 2 and 5 wt. % water. Heating the perlite close to their melting temperature results, the contained water is converted into steam and the grains transform into light cellular particles. As a result, the weight of the material decreases 10 – 20 times. The product is with low thermal conductivity, high thermal, fire resistant, and high sound absorption.

The Schupenata planina deposit was in operation by Bentonite, S&B Industrial Minerals and now by Imerys minerals Bulgaria.

The Schupenata planina deposit is located in the Eastern Rhodopes, next to the Vodenicharsko village. It was discovered in 1955 and has been in operation since 1962. The perlite bodies outcrop on the area about 2 km^2.

The processing technology is crashing and fractionation. The fraction 0.5-2 mm is used for expansion and those below 0.5 mm for glass production. The average volume weight of the

expanded perlite from the Schupenata planina deposit is 100 - 150 kg/m3.

Production and use of perlite

The general technology of reworking of the perlite starts with crashing and fractioning of the material. The fraction from 0.5 to 2 mm is expanded. The fraction below 0.5 mm is used for glass production. The expanded perlite has the following properties:

- Specific gravity from 100 to 180 kg/m^3;
- One kg expanded perlite is produced from 135 kg fractionated perlite.

Over half of the world's production goes into the construction industry as aggregate for insulation boards, plasters and concrete in which weight reduction and special acoustic or thermal insulation properties are required (Evans, 1993). It is used for loose – fill insulation of cavity walls and for the thermal insulation of storage tanks for liquefied gases. The agricultural application of perlite includes use as a soil conditioner and as a carrier for herbicides and chemical fertilizers. The perlite is used for filtering water, other liquids, in food processing and as a filler in paints, plastics, etc.

The total world production of crude perlite in 2015 was 4.38 Mt, a slight increase from the revised value of 2014 (USGS, 2015). The world's leading producers of crude perlite in 2015 were, in descending order of production, China, Greece, Turkey, and the United States, accounting for 41%, 23%, 21% and 11%, respectively, of world production. Greece and Turkey remained the leading exporters of perlite. Although China was the leading producer, most crude perlite was believed to be consumed internally. S&B Industrial Minerals S.A. (Greece) was the primary supplier of processed crude perlite imports to the United States. Imerys completed its purchase of S&B Industrial Minerals in early 2015. The acquisition was one of the largest in the perlite industry since Imerys purchased World Minerals, a producer of perlite products with mines in Arizona and New Mexico, in 2010. Including the acquired S&B Industrial Minerals facilities, Imerys owns 6 perlite mines and 11 perlite plants located in 6 countries (O'Driscoll, 2015).

The expanded perlite consumed for construction-related uses, which accounted for about 53% of the market for expanded material, was about 260,000 t, a 6% increase compared to that of 2014. Construction uses of expanded perlite consisted of concrete aggregate, formed products, masonry- and cavity-fill insulation, and plaster aggregate. Expanded perlite consumption increased for fillers, filter aid, formed products, high-temperature insulation, masonry- and cavity-fill insulation, and plaster aggregate.

The main usage of perlite (about 50%) in 2015 is for formed products (including acoustic ceiling panels, pipe insulation, roof insulation board, and unspecified formed products). The second most important usage of perlite is as horticultural aggregate followed by filler and filter aids. Minor quantity of perlite is used as low-temperature insulation, plaster aggregate, etc. (USGS, 2015).

Bulgaria is in the first 15 world largest perlite producers with about 5 000 metric tons production for 2015 (USGS, 2015).

One of the important usages of expanded perlite is for extender design for well cement slurry. Neat cement slurries, when prepared from API Class A, C, G, or H cements using the amount of water recommended in API Spec. 10A (Bulgarian state standard (BDS) , EN ISO 10426-1:2010) will have slurry weights in excess of 15 lb/gal (1800 kg/m^3).

The expanded perlite from Schupenata planina deposit was studied as a component of lightweight well cement slurry based on perlite extender and its parameters in accordance with BDS EN ISO 10426-2:2006 and BDS EN ISO 10426-1:2010 requirements as well as improvement of its formulation by neat and additives treatment cement slurries. Analysis of perlite - containing mixture providing the lowest density while maintaining other required parameters was conducted. As a cement base, cement API Class G HRS, cement CEM I 42,5 N SR 5 and perlite M100 and M150 were used. Perlite typical content varied from 1 ft^3 Perlite additive/1 ft^3 cement to 2 ft^3. Perlite additive/1 ft^3 cement; and water-to-cement-ratio ranged from 0.8 to 1.2. To sum up, despite the fact that lightweight cement slurry based on perlite satisfies BDS EN ISO 10426-2:2006 and BDS EN ISO 10426-1:2010 requirements under laboratory conditions, field studies are necessary in order to make a conclusion about applicability of this slurry for well cementing in field conditions.

There are several different types of materials that can be used as extenders by reducing the average specific gravity of the dry mix and cement slurry. These include:

- Physical extenders (clays and organics);
- Pozzolanic extenders;
- Chemical extenders;
- Gases.

These are particulate materials that function as cement extenders by increasing the water requirements or by reducing the average specific gravity of the dry mix. The most common low-specific-gravity solids used to reduce cement slurry specific weight are bentonite, diatomaceous earth, solid hydrocarbons, expanded perlite and pozzolan.

Perlite cement additive is a physical extender and light, granular material made from crushed volcanic rock. Expanded perlite is a siliceous volcanic glass that is heat-processed to form a porous particle that contains entrained air. The dry weight of perlite is only 8 lb/ft^3 (128 kg/m^3) as opposed to 25–100 lb/ft^3 (400–1600 kg/m^3) the dry weight of the other materials (William, 2010, Nelson, 1990).

Its primary use is to lower the density of cement slurries as low as 1.44 g/cm^3. It can be used at bottom hole temperatures (BHTs) between 4°C and 204°C. Typical concentrations are 1 ft^3 (28.32 Litr.) perlite additive/1 ft^3 (28.32 Litr.) cement or 2 ft^3 (56.64 Litr.) perlite additive/1 ft^3 (28.32 Litr.) cement (William, 2010, Nelson, 1990).

Geology of the perlite deposits

Perlite, like other glasses, devitrifies with time so that commercial deposits are mainly restricted to areas of Tertiary and Quaternary volcanism. Perlite occurs as lava flows, dykes, sills and circular or elongate volcanic domes. The domes are the largest and most commercially important bodies and they can be as much as 8 km across and 270 m in vertical extent. Many of these lava domes cooled quickly in their outer parts to obsidian but the interiors remained hot and formed fine-grained, crystalline rock. In certain instances, the obsidian has been hydrated as a result of penetration by ground water forming perlite. Remnants of unaltered obsidian may remain in the perlite, which may also contain phenocrysts of quartz, feldspar and other minerals (Evans, 1993).

Geology of the region of the Schupenata planina deposit

In the area of the deposit outcrop there are the following rock formations: Djhebel formation (DOl_1) overlies with erosional boundary various Paleogene sedimentary and volcanogenic-sedimentary units: Podrumche formation, terrigenous limestone formation from the volume of the carbonate-terrigenous complex, pyroclastic-limestone formation and Podkova formation from the volume of the Kardzhali Volcano-Sedimentary Group, limestone-pyroclastic formation from the volume of the Chiflik Volcanic Subcomplex (Nanovitsa Volcanic Complex), tuffite-tuffaceous formation (fig. 2). In eastern direction, near Sekirka village, the formation pinches out under rocks of the lower tuffaceous-tuffite epiclastic package of the Zvezdel Volcanic Complex. It is also intersected and covered concordantly by epiclastites, pyroclastites and lavas of the Zvezdel Volcanic Complex, Ustren and Pcheloyad Volcanic complexes, as well as by sediments of the limestone formation (Yordanov et al., 2008).

The sandstones are yellow-beige, loose, displaying coarsely horizontal and characteristic cross bedding. Their structure is massive. Their texture is inequigranular, predominantly psephitic-psammitic to aleuro-psammitic. The rocks are poorly sorted.

The clastic component reaches 75%. The sandstones are polymict, dominated by quartz and feldspar. Subordinately represented are coarse flakes of muscovite, biotite and chlorite, single grains of amphibole and tourmaline. The rock fragments were derived from acid and intermediate volcanics, massive rocks with granitoid composition, schists, etc. The matrix is monomineralic being composed of clay minerals or carbonate. Its type is contact-pore-filling, with limited occurrence of basal type. The matrix is pigmented by iron oxides.

Ustren Volcanic subcomplex - (Ustren Rhyolitic Complex). It includes the acid pyroclastics exposed in the vicinity of Stomantsi village and the rhyolite dome near Zlivrah summit. The complex is exposed in the vicinity of Vodenicharsko village as well as over vast areas between Zlivrah summit and the villages Stomantsi, Rastnik, and Muglene. In structural aspect the rocks belong to the Ustren subzone of the Galenit Tensional Zone. Rock fall blocks are commonly encountered along the periphery of the acid domes (Yordanov et al., 2008).

The rocks intersect or overlie concordantly the Chiflik Volcanic Subcomplex and the Dzhebel Formation. They are respectively intersected by subvolcanic bodies from the volume of the Zvezdel Volcanic Subcomplex. Mainly acid volcanics (rhyolites and dacites) and associated perlites and acid pyroclastics comprise the volume of the complex. “Multiple reopening of fractures and filling with new portions of the same lava and its pyroclastics” was observed in some of the larger rhyolitic bodies. They build relatively uniform sectors with specific features, the Ustren Volcanic complex is subdivided into the following units:

- rhyolites and pyroclastics – Stomantsi volcano;
- and rhyolites – Ustren volcano.

Analytical technics

Volcanic rocks from the quarry and from Ustren volcanic complex west from the deposit were sampled. The major element of 5 samples rhyolites and 2 of fractionated perlite were analyzed by OES – ICP in the laboratories of the University of Mining and Geology ‘St. Ivan Rilski’. Chemical analyses were performed on samples from rhyolites, contact zone of inclusion in rhyolite and fractionated perlite.

Petrological and geochemical characteristics of rhyolites and perlite

The perlite deposits in the Eastern Rhodopes are related to the Oligocene acid volcanism. The Schupenata planina deposit is located in the Ustra volcanic region, part of the volcanism developed in the eastern Rhodope Paleogene Depression. The Ustra volcanic region is located west of town of Djebel and is around the top of Ustra between the villages of Lebed, Ustren and Vodenicharsko.

The volcanics are rhyolitic extrusions, necks, dykes and flows, they contain numerous perlitic bodies. They cut the Djebel sandstone formation of Oligocene age. The Schupenata planina deposit is built up by rhyolitic dome and flows which cover Oligocene sandstones and clays (Yanev, 1985). This results into rock falls and landslides forming the present relief. The base of the rhyolitic dome and flows (sandstone and clay sediments) and the earthquake result in subsiding of the Schupenata planina perlite deposit at the beginning of XIXth century. The perlite deposits are of effusive, extrusive and dyke type. The magmatic rocks are presented by extrusions, necks and lava flows. They are high - K rhyolites. The porphyry generation is represented by quartz, sanidine, acid plagioclase and biotite. The ground mass is glassy.

Rhyolites contain between 74.05 and 76.25 SiO_2, Na_2O from 2.14 to 2.67, K_2O from 4.99 to 5.91 wt. %, the water content of the volcanic rocks is between 2.26 and 3.11 wt. %. The chemical properties of the fractionated perlite are between 73.85 and 74.79 SiO_2, Na_2O from 2.32 to 2.39, K_2O from 4.52

to 5.99 wt. %, the water content is between 5.55 and 4.70 wt. % (Table 1). The rhyolites have higher SiO_2, K_2O, Fe_2O_3 and TiO_2 content and lower water content compared to fractionated perlite.

Fig. 1. Panorama to the Schupenata planina perlite deposit

Table 1.
Chemical composition (wt. %) of rhyolite from the Ustren volcanic region and fractionated perlite from the Schupenata planina deposit

Sample	Description	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	LOI	Water
Y1	White volcanic rock	75.16	0.13	12.65	0.68	0.03	0.10	0.29	2.14	5.41	2.94	0.35
Y2	Grey volcanic rock	75.05	0.10	12.36	0.62	0.05	0.07	0.42	2.66	5.12	3.11	0.29
Y3	Pinkish volcanic rock	75.10	0.11	12.68	0.64	0.04	0.07	0.35	2.58	5.00	3.00	0.21
Y4	Dark pink volcanic rock	75.80	0.11	12.61	0.68	0.05	0.07	0.36	2.67	4.93	2.26	0.27
Y5	Contact zone in the volcanics	76.25	0.10	11.66	0.60	0.03	0.07	0.44	2.71	5.32	2.32	2.26
Y6	Darkpink – to black volcanic rock – contact zone	82.99	0.05	9.03	0.37	0.06	0.05	0.29	2.09	3.45	1.13	1.18
E	Fractionated perlite	73.85	0.06	12.50	0.55	0.11	0.06	0.39	2.39	4.99	4.70	0.30
P2	Fractionated perlite	74.79	0.06	11.65	0.48	0.10	0.06	0.38	2.33	4.52	4.55	0.28

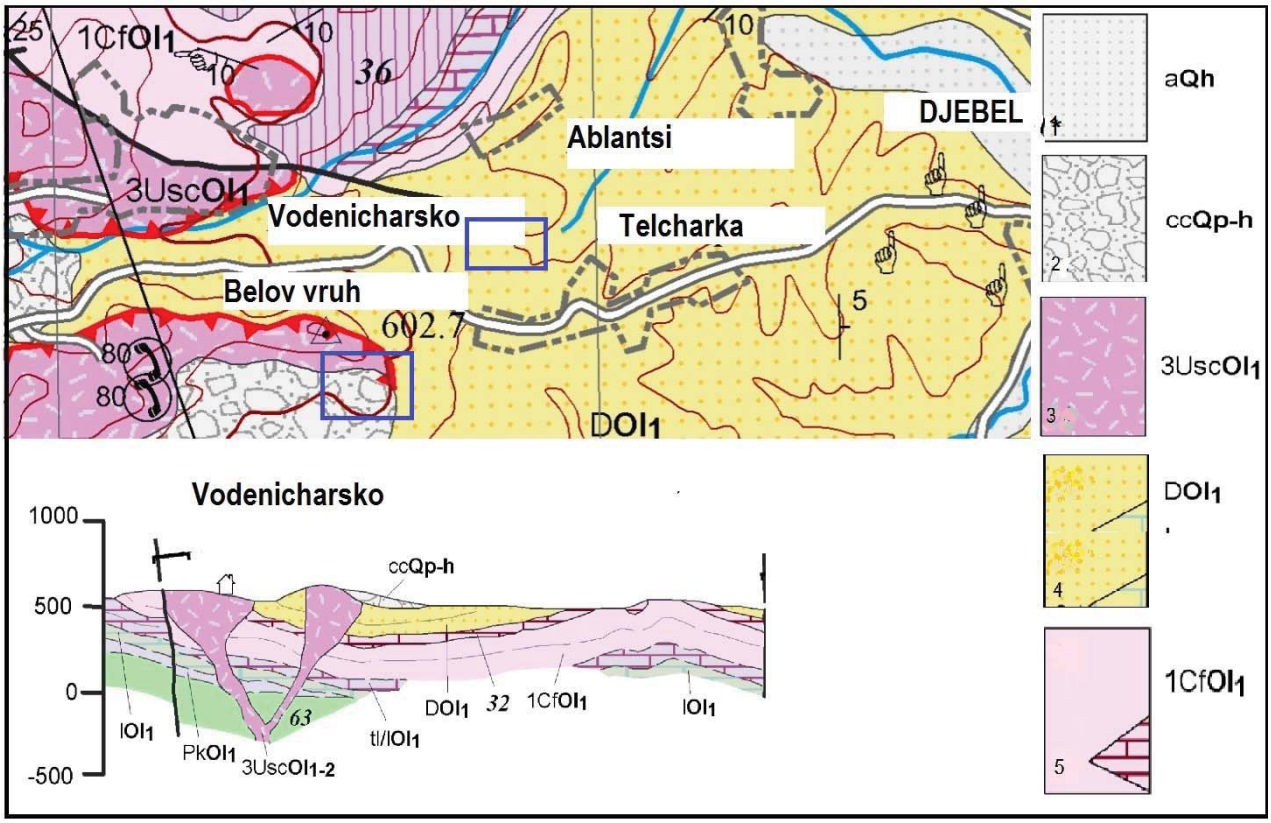

Fig. 2. Geological map of the region of the Schupenata planina perlite deposit (after the Geological map of Bulgaria 1:50 000 scale Map Sheet Djebel and Kirkovo (Yordanov et al., 2008) with addition. Blue squares – schematic location of the perlite bodies. 1 - Quaternary alluvial sediments; 2 - Quaternary proluvial sediments, rock falls and landslides; 3 – Rhyolites of Ustren volcanic complex; 4 – Sediments of Djebel Formation; 5 – Limestone and tuff formation

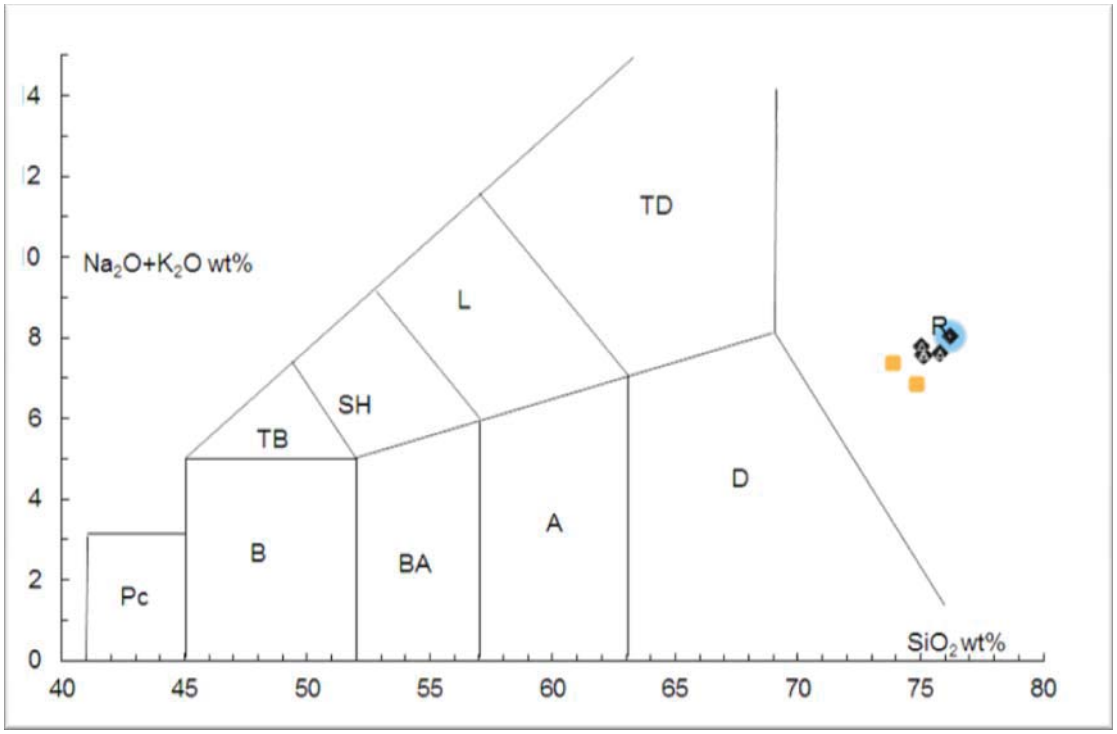

Fig. 3. TAS diagram Le Maitre (1989) for representative magmatic rocks from the studied region (B—basalt; BA—basaltic andesite; A—andesite; D—dacite; SH—shoshonite; L—latite; TD—trachydacite). Diamonds – rhyolites; squares – fractionated perlite from the Schupenata planina perlite deposit

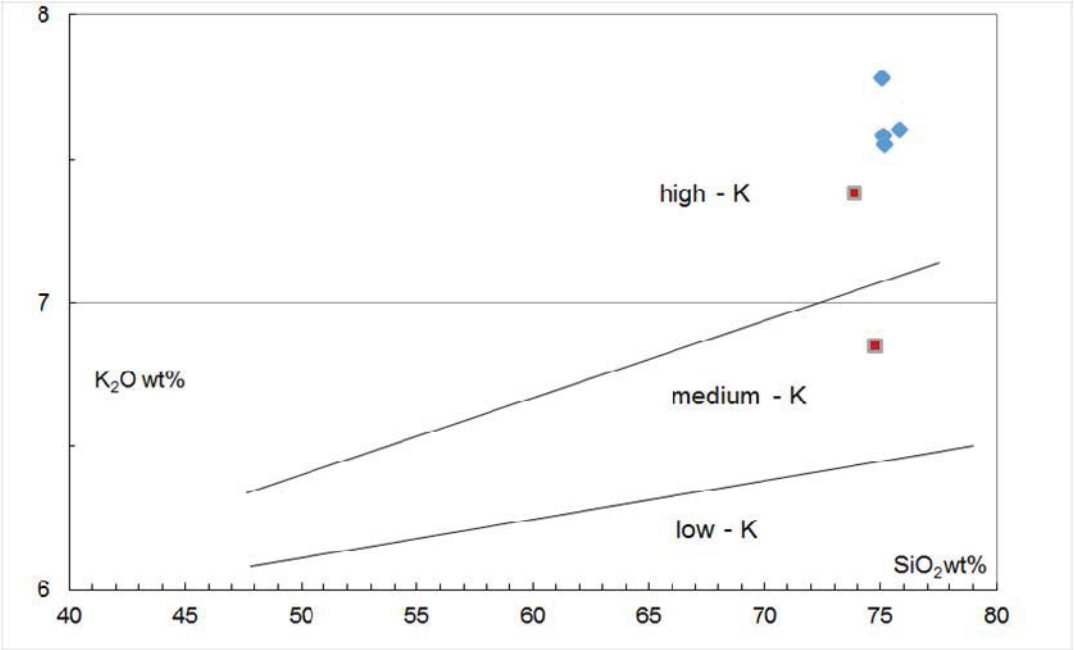

Fig. 4. SiO_2 – K_2O diagram Le Maitre (1989) for representative magmatic rocks from the studied region. Diamonds – rhyolites; squares – fractionated perlite from the Schupenata planina perlite deposit

Conclusions

The Schupenata planina is the only perlite deposit in operation in Bulgaria. It is located in Kurdjali region, in the area of Djebel town and Vodenicharsko village. They are part of the Eastern Rhodope Paleogene depression. The perlite is hosted in the rhyolites of the Ustren volcanic complex. They are part of the Oligocene III-th acid volcanism in the Eastern Rhodopes. The perlites are grey to white – grey, they show sub vertical prismatic joints 7 to 10 m long. The rocks are built up by quartz, sanidine, acid plagioclase and biotite.

Fig. 5. Columnar jointing in rhyolite and perlite bodies in the deposit.

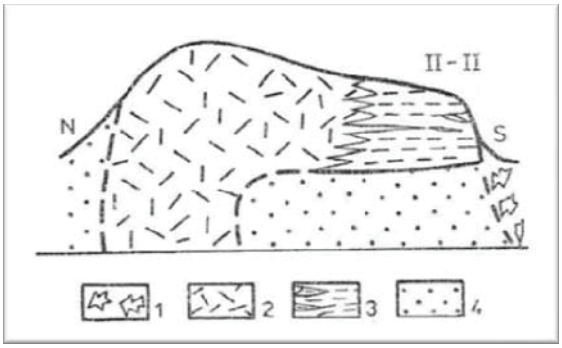

Fig. 6. Geological section of the Schupenata planina deposit after Yanev, (1985). 1. Landslide body; 2. Rhyolite; 3. Perlite and rhyolite lenses; 4. Sands and clays

They are classified as high – K rhyolites and contain between 74.05 and 76.25 SiO_2, Na_2O from 2.14 to 2.67, K_2O from 4.99 to 5.91 wt. %, the water content of the volcanic rocks is between 2.26 and 3.11 wt. %. The chemical properties of the fractionated perlite are between 73.85 and 74.79 SiO_2, Na_2O from 2.32 to 2.39, K_2O from 4.52 to 5.99 wt. %, the water content is between 5.55 and 4.70 wt. %. The rhyolites have higher SiO_2, K_2O, Fe_2O_3 and TiO_2 content and lower water content compared to fractionated perlite.

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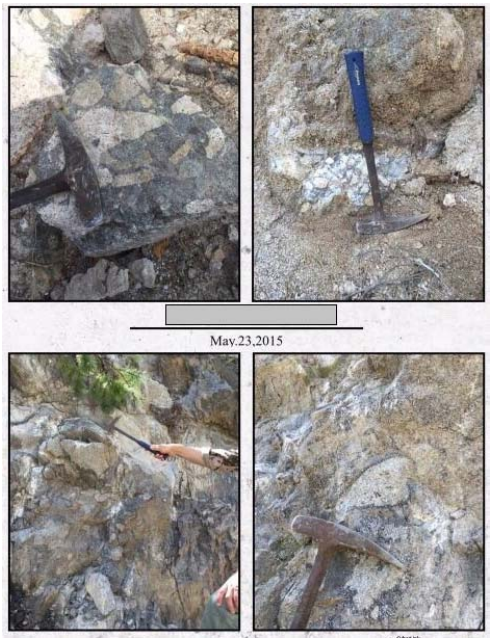

Fig. 7. Brecciation in the volcnanics from the volcanic complex

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