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NEW DATA ON THE CENOZOIC VOLCANISM AND ORE MINERALIZATIONS IN THE PETROSHNITSA RIVER VALLEY, NW PART OF THE KRATOVO-ZLETOVO VOLCANIC AREA, REPUBLIC OF MACEDONIA

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Abstract

The studied district is situated in the northwestern periphery of the Kratovo-Zletovo paleovolcanic area at about 23 km NE from Kumanovo town. The recent study presents in brief the new data concerning the lithostratigraphy, petrology and ore mineralogy of the volcanic rocks exposed along the Petroshnitsa river valley. The deeply eroded volcanic section in the area mapped (ca. 30 km² in scale 1:10 000) is subdivided into five lithostratigraphic units having the following superposition from bottom to top: tuffite formation, tuff formation, formation of pyroclastic breccias, Petroshnitsa trachyte-latite body, lamprophyric bodies and dykes. The units are composed of intermediate volcanoclastic and massive rocks – products of two relatively huge volcanic-intrusive centers located in the northwestern part of Kratovo-Zletovo paleovolcanic area. The geochronologic ages obtained from volcanics exposed in the studied area pointed to Early Oligocene volcanic activity (ca. 33-29 Ma).

Paragenetically, with the products of the second volcanic center located in the valley of the Petroshnitsa river, at about 2 km southeast of Baylovtse, there appear complex sulfide mineralizations, associated with two stages of hydrothermal mineral formation. At the first stage there is carried out an area sericitization, kaolinitization, adularitization (± diaspore) of the latite-trachytes, on which is deposited a stockwork, at places a vein quartz-pyrite (± chalcopyrite with Au and Re) and quartz-galena-sphalerite mineralization. At the second stage there come acidic, slightly metalliferous solutions, from which are deposited disulfides of iron and monomineral quartz veins. They are located radially and aside from the center of the volcanic structure and in plan they form a ring zone. Some of the veins are associated with wide transit structures, draining carbonic acid with a deep source. On the sulfide mineralizations there is not a zone of oxidization. Only in some places are formed fissure hypergene mineralizations, represented by very complex composition of sulfates, phosphates, borates and hydrosilicates. By a set of criteria, direct and indirect evidence and data from detailed mineralogical, petrographic and geological, and geophysical studies there are determined in the area specific ore-likely sections, proposed for a further study.

Key words: Petroshnitsa trachyte-latite body**,** volcanic center, ring-like zone, mineral composition, hydrothermal stage

INTRODUCTION

The studied district is situated in the northwestern periphery of the Kratovo-Zletovo paleovolcanic area, approximately 23 km NE from the town of Kumanovo. According to the previous geological mapping [1, 2] the volcanic rocks within the district are Miocene-Early Pleistocene in age. They are subdivided into several "mapped units" with the following stratigraphic sequence: trachytes and "trachyandesitites", occupying at about ¾ of the area, are the oldest effusive varieties with a Miocene age; during Pliocene, they are covered by volcanic breccias; at the end of the Pliocene these breccias are intruded by "dacites" in the northwestern corner of the area mapped (the massif of Visoka summit).

Later on, mostly in relation to the exploration geology of the Kratovo-Zletovo ore district, a number of specialized studies on the volcanic activity, ore mineralizations, geochronology and geomorphology of the area have been carried out [4 - 10].

In this paper new results regarding the lithostratigraphy, petrology and ore mineralogy of the volcanites in the Petroshnitsa river valley are briefly discussed. A new model for the evolution of the Cenozoic volcanism and the genetic relation with two paleovolcanic centers localized in the northwestern part of the Kratovo-Zletovo volcanic area is suggested.

LITHOSTRATIGRAPHY AND PETROLOGY OF VOLCANITES

The deeply eroded volcanic section within the area mapped (30 km²) on the scale 1:10 000 (Fig. 1), is subdivided into five lithostratigraphic units, and namely (from bottom to top): tuffite formation, tuff formation, formation of pyroclastic breccias, Petroshnitsa trachyte-latite body, lamprophyric bodies and dykes.

The metamorphic basement rocks (gneisses, mica shists, amphibolites) belongs to the Lower complex of the Serbo-Macedonian Massif. On Bulgarian territory, the same rocks are distinguished as “Ograzhdenian Complex/Supercomplex” [3].

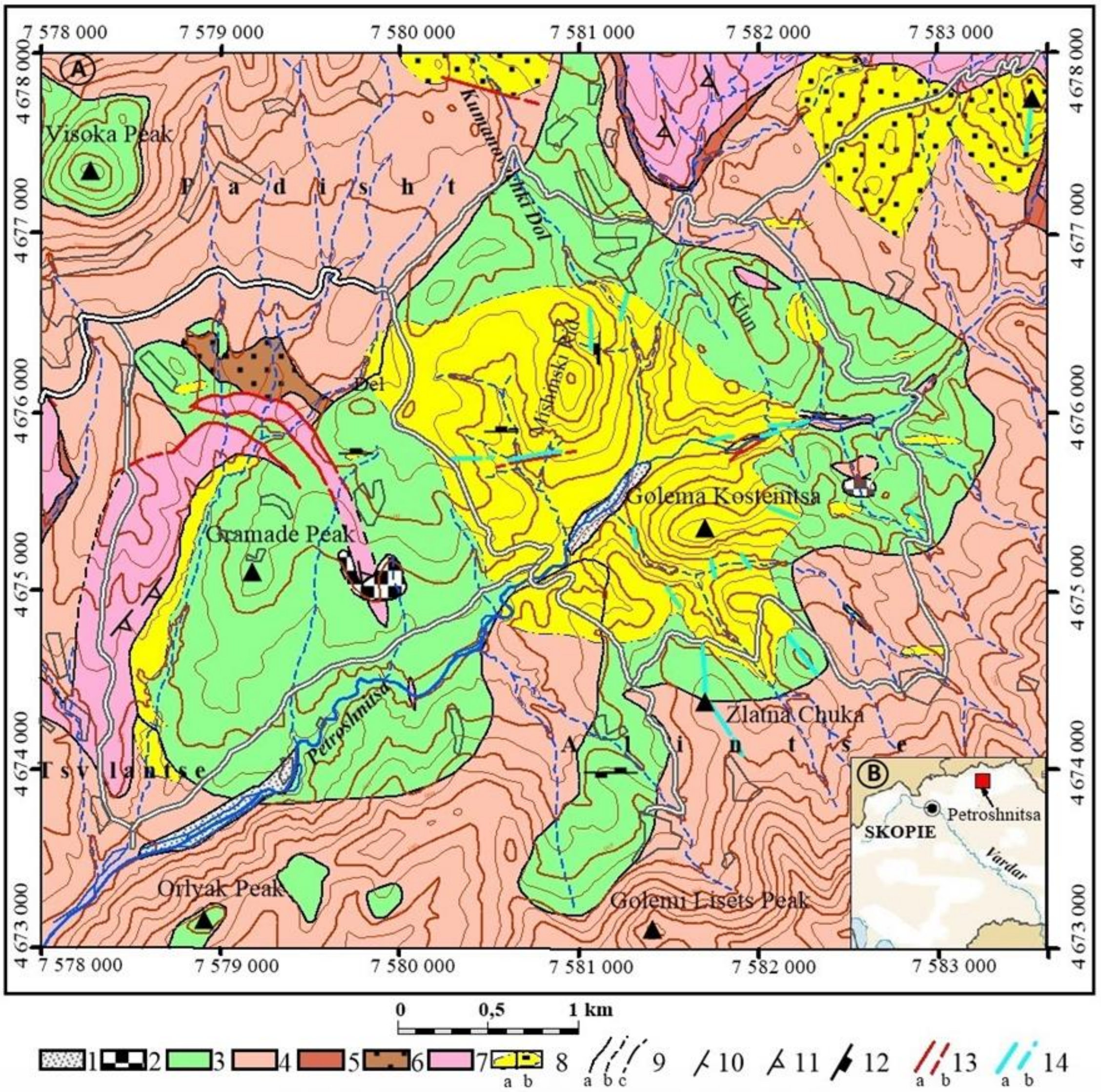

Fig. 1. Geological map of Petroshnitsa district

1 – Quaternary:Alluvial deposits – gravels, sands, clays; 2–6: Paleogene-Neogene: 2 – Lamprophyre bodies; 3 – Petroshnitsa trachyte-latite body; 4 – Formation of the pyroclastic volcanic breccias; 5 – Tuff formation; 6 – Tuffite formation; 7 – Neoproterozoic-Lower Paleozoic: Lower complex of the Serbo-Macedonian Massif; 8 – Hydrothermal alteration: a – in the Petroshnitsa trachyte-latite body; b – in the Formation of the pyroclastic volcanic breccias; 9 – Contact: a – proven; b – supposed; c – of the hydrothermal alteration; 10 – Strike and dip of bedding; 11 – Strike and dip of foliation; 12 – Strike and dip of joint set; 13 – Fault: a – proven; b – supposed; 14– Quartz and Quartz-sulfide vein: a– proven; b – supposed

The tuffite formation is restricted only in an outcrop area of 0,2 km^2 west-northwest of Del summit. It occupies the lowermost part of the volcanic complex as its boundary with the metamorphic basement is not exposed on the surface. Upwards the formation is unconformably covered by pyroclastic volcanic breccias. It has tectonic contacts with the two-mica gneisses of the Lower complex and intrusive relationships with the Petroshnitsa trachyte-latite body.

The formation is composed of thin- to medium-layered lapilli, psammitic and aleuritic, brownish or yellow tuffites. They include both pyroclastics and clastic component (quartz, muscovite, rock fragments from muscovite schists, gneisses and micro-granular, unevenly recrystallized limestones).

The apparent thickness of the formation is 200-220 m. An Early Oligocene age is supposed for the unit.

The tuff formation unconformably covers the metamorphic basement and grades or has a sharp contact with the formation of pyroclastic volcanic breccias. It is composed of red, pink and gray lapilli tuffs alternating with thin layers of ash (psammitic and aleuritic) tuffs as well as lenticular layers of small-grained volcanic breccias and single angular blocks. The pyroclastic component predominates and is presented by crystalloclasts, lithoclasts and vitroclasts. The clastic component is of mineral grains (quartz, plagioclase, muscovite) as well as rock fragments of gneisses and mica schists.

The thickness of the tuff formation varies from 0 to 30 m. An Early Oligocene age is supposed.

The formation of pyroclastic volcanic breccias occupies over ⅓ of the mapped area. It has fast or gradual transitions with the underlaying tuff formation or unconformably covers either metamorphic basement or tuffite formation. The pyroclastic breccias are intruded by the Petroshnitsa trachyte-latite body and several smaller bodies of similar composition as well as a single lamprophyre dyke. The intrusive contacts are steep to subvertical. The rocks of the unit are plenty of clasts thus from lapillis to blocks and bombs reaching up to 1-2 m in diameter. Breccias are heterogeneous in texture. Gradations in granulometry or preferred orientation of the clasts have not been observed. They are composed mainly of latite and trachyte pyroclasts. Locally, near to the lower boundary with the gneiss basement, they contain up to 15-20 % lithoclasts of gneisses, mica schists, amphibolites and metamorphic quartz. The pyroclastic matrix consists of intermediate in composition (trachytes and latites) volcanoclastics. The thickness of the formation of pyroclastic volcanic breccias probably exceeds 800 m. U-Pb zircon age (31,01 ± 0,19 Ma) was obtained from a sample of trachyte volcanoclast collected in the vicinity of Baylovtse village [10]. The geochronological and field data well constrain the Early Oligocene age of the formation.

The Petroshnitsa trachyte-latite body occupies an area of ca. 10 km^2 in the central part of the map. It is irregular-shaped and SW-NE elongated, reaching up to 5 km in length and 1.5-3 km in width. The smaller bodies reach up to 1 km in diameter and form the summits of Visoka, Vitlich and Orlyak. The contact of the Petroshnitsa body with the host rocks is steep and easily observed in a number of outcrops.

The results of the petrographic analysis of samples of trachyte-latites and lamprophyries from the Petroshnitsa district are shown in Table 1. They are plotted on the TAS classification diagram [11] on Figure 2.

Latites are light gray, gray or gray-green rocks, locally with a violet shade. These are massive in structure and porphyritic in texture (by plagioclase and more rarely by mafic minerals) rocks. Trachytes are gray to gray-green dense rocks, massive in structure, and porphyritic, glomeroporphyritic, microlitic and trachytic in texture. Internal contacts between the latites and trachytes composing the Petroshnitsa body have not been observed in the field. Both rock types are indistinguishable in meso-scale.

The obtained U-Pb zircon age of a porphyritic trachyte from the northern part of the Petroshnitsa body is 29,58 ± 0,23 Ma [10] i.e. is Early Oligocene. The received isotopic ages at this analysis for large-porphyry trachyte (**PSR-1/2016**) **- 32.56 ± 0.25 Ma**, also for tiny-porphyry latite along a plagioclase (**PSR-50/2016**) **- 32.26 ± 0.25 Ma**, are from samples east of Gramade Peak (Fig. 3 and Fig. 4).

Table 1. Location (latitude / longitude, WGS 84) and mineral composition of trachytes, latites and lamptophyres from Petroshitsa district

Sample №	Coordinates	Rock	Mineral Composition (primary/secondary)*
4	42,223524/21,995212	phenolatite	Pl+Kfs+Bt+Hbl+Ap+Zr/Qtz+Ca+M
56	42,233454/21,974831	phenolatite	Pl+Kfs+Bt+Hbl?+Ap/Ca+Qtz+M+Chl
106	42,216063/21,990225	phenotrachyte	Pl+Kfs+Bt+Ap/Ca+M+Qtz+Chl
112	42,215576/21,984239	phenotrachyte	Pl+Sa+Bt+Hbl+Py+Ap/Ca+Ep+Chl+Al+Qtz
125	42,210748/21,979319	phenolatite	Pl+Kfs+Bt+Hbl+Ap+Zr/Ca+Kfs+Bt+Ep+Chl+Qtz
147	42,223472/21,996255	phenolatite	Pl+Kfs+Bt+Hbl+Ap+Zr/Ca+M+Qtz
243	42,241787/21,976528	phenotrachyte	Pl+Kfs+Bt+Ap+Zr/M+Qtz
250	42,227902/21,968531	phenolatite	Pl+Kfs+Bt+Cpx+Ap+Ti/Ca+Chl+Ep+Al+Qtz
266	42,225042/21,990278	phenotrachyte	Pl+Kfs+Bt+Hbl+Cpx+Ap/M+Qtz+Bt+Chl
303	42,218865/21,967978	phenolatite	Pl+Kfs+Bt+Ap/M+Ca+ Chl+Ep+Al+ Qtz
331	42,212723/21,96939	phenolatite	Pl+Sa+Bt+Hbl+Py+Ap/Bt+Kfs+Qtz+Chl+Ep+M+Ca
457	42,225207/21,951893	phenotrachyte	Pl+Kfs+Bt+Cpx +Ap/Ca+M+ Bt
478	42,205605/21,977372	phenolatite	Pl+Kfs+Bt+Cpx +Ap/Chl+Ca+Qtz
504	42,207417/21,962611	phenolatite	Pl+Kfs+Bt+Hbl+Cpx +Ap/Chl+Ca+M+Qtz
526	42,203541/21,955125	phenotrachyte	Pl+Kfs+Bt+Hbl+Ap+Ti/Ca+Qtz
787A	42,2223055/21,9935555	phenolatite	Pl+Kfs+Qtz +Bt+Ap/Chl+Ca+M
878	42,2192222/21,9948056	phenotrachyte	Pl+Sa+Bt+Hbl?+ Py +Ap/Chl+Ca+Qtz +M
7	42,222955/21,99316	lamprophyre	Pl+Bt+Cpx+Hbl+Ap+Ti/Ca+Chl +Qtz+M+Bt
652	42,215638/21,961277	lamprophyre	Bt+Cpx+Pl+Hbl+Ap/Ca+Bt+Chl+Qtz+M
876	42,2201945/21,9946945	lamprophyre	Pl+Bt+Hbl+Ap/Ca+Qtz+Chl+M

*Abbreviations:
Pl – plagioclase; Kfs - potassium feldspar; Bt - biotite; Sa – sanidine; Hbl – amphibole; Qtz – quartz; Py – pyroxene; Cpx – clinopyroxene; Ap – apatite; Ti – titanite; Chl – chlorite; M – mica; Ep – epidote; Al – albite; Ca – carbonate

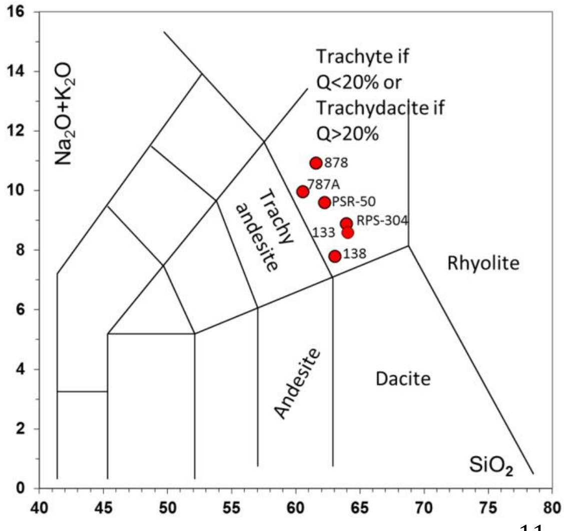

Fig. 2. TAS classification diagram [11] **with the locations of the analyzed samples. Petroshnitsa.**

Two small lamprophyric bodies and a single dyke crosscut the rocks of the Petroshnitsa body as well as the xenoliths of gneisses and volcanic breccias (Fig. 1). Lamprophyres are dark-gray to black, dense rocks, porphyritic by biotite. They are massive in structure and porphyritic, serial porphyritic, microlitic or trachytic in texture. The results from the petrography of the lamprophyries are presented in brief in Table 1. The concordant age in 4 of the youngest zircons in the sample (**PSR-4$_1$/2016**) from the biggest body south of Gramade Peak is **31.24 ± 0.36 Ma** (Fig. 3 and Fig. 4).

Rocks in the central part of the Petroshnitsa body (occupying an area of ca. 3,74 km²) as well as in a number of smaller outcrops are affected by an intense hydrothermal alteration.

EVOLUTION OF THE VOLCANIC COMPLEX

The results from the recent detail mapping as well as the petrographic analyzes show that the distinguished lithostratigraphic units, composed of intermediate in composition volcanoclastic and massive rocks, are products of two relatively huge volcano-intrusive centers located in the northwestern part of the Kratovo-Zletovo paleovolcanic province.

The obtained geochronological data (Zircon La-ICP-MS) evidence the volcanic activity during the Early Oligocene (ranging between 32-29 Ma) in the studied area. Similar data (about 31 Ma) are reported for the volcanic rocks, situated to the north in the vicinity of Kokino village [12].

Earliest product of the subaerial volcanism in the area was the tuffite formation, composed of re-worked lapillis and ash tuffs, where the clastic component (ca. 30-35%) is of quartz, muscovite and rocks fragments of schists, gneisses and microgranular limestones. The presence of limestone fragments indicates that this epiclastic suite is related to a relatively remote eruptive center situated in an area with a preserved sedimentary cover of the crystalline basement. After a short break and deformation, the pyroclastic formations (the tuff formation and the formation of pyroclastic volcanic breccias) are formed due to extensive eruptions of a volcanic center located in the mapped area. They uncomfortably covered both the exhumed metamorphic basement and the subvertical layers on the tuffite suite.

Probably, a successive effusive volcanism was revealed, followed by the emplacement of the Petroshnitsa trachyte-latite body in the root zone of the volcanic edifice and subsequent alteration and ore mineralization.

The following evidences indicate that the main eruptive center was located in the Petroshnitsa river valley between Mishinski ridge, Sadovnitsa and Golema Kostenitsa: the positions of both the Petroshnitsa body and zone of an intense hydrothermal alteration; the radial orientation of the dominant fracture groups controlling the position of quarzitization zones and the concentration of huge blocks of volcanic breccias are ca. 500 m southwest of M. Kostenitsa. They are in accordans with the assumption of [8].

Small sub-isometric bodies occupying the Visoka and Vitlich summits in the northwestern and southeastern corner of the map as well as the neck located northeast of Kokino village most probably were the conductive channels of the local volcanic centers, operating simultaneously with the main center Baylovtse and were genetically related to a common magma source.

CHARACTERISTICS OF ORE MINERALIZATIONS

Complex sulfide mineralizations are genetically related with the latite-trachytes from the second volcanic center southeast of Baylovtse village. The particular ore minerals are generated during a two-stage mineralization process.

During the first stage, the host latite-trachytes were affected by both general and linear kaolinitization, sericitization, adulari-zation (with diaspore) as the mineralization is of stockwork type and locally of vein type – quartz-pyrite (± chalcopyrite and molybdenite) and quartz-sphalerite-galena.

Fe-disulfides and monomineral quartz veins were formed **during the second stage**. They are located outside the eruptive center or radially surround them forming a ring-shape zone in a plan view (Fig. 3). An extrapolation of the trajectories of the quartz veins strike directions from the ring-shaped zone towards the center outlines a “quartz star” which center coincides with the eruptive center.

The position of the eruptive center (besides from the quartz veins) is additionally fixed by the configuration of Petroshnitsa volcanic body and related zone of hydrothermal alteration (as pseudomorphic grow of chlorite, carbonate, epidote and sulfide after feldspar have taken place as these structures are rather similar to the sulfide pseudomorphoses described in [13] in some ore fields) as well as by the main fracture groups which strike directions are mutually intersected in the Petroshnitsa river valley (Fig. 3).

During the first hydrothermal stage, the stepwise ore-generating process followed the next succession: a general hydrothermal alteration of the latite-trachytes (kaolinization and sericitization); biotitization stage (the first potassium metasomatic alteration). Spheroidal metasomatic biotite aggregates with radial habit have been formed around numerous centers (nucleous); stage of a K-feldsparization (the second potassium metasomatic alteration). Due to this metasomatic process all femic minerals in the latites were replaced by feldspars and the rocks became paler; patches or veins of secondary quartzites appeared as they intersect the hydrothermally altered volcanics; first quartz-sulfide stage (generation of quartz-pyrite±chalcopyrite and molybdenite with enhanced Re and Au contents). Zones with vein-nest sulfide mineralizations have been formed which intersect the linear quartz-adular-diaspore zones; a quartz-wavellite stage is recognized in the eastern flank of the curved ore-prospecting area (Fig. 3). Quartz-wavellite or wavellite veins and aggregates filled variously oriented cracks within intensively

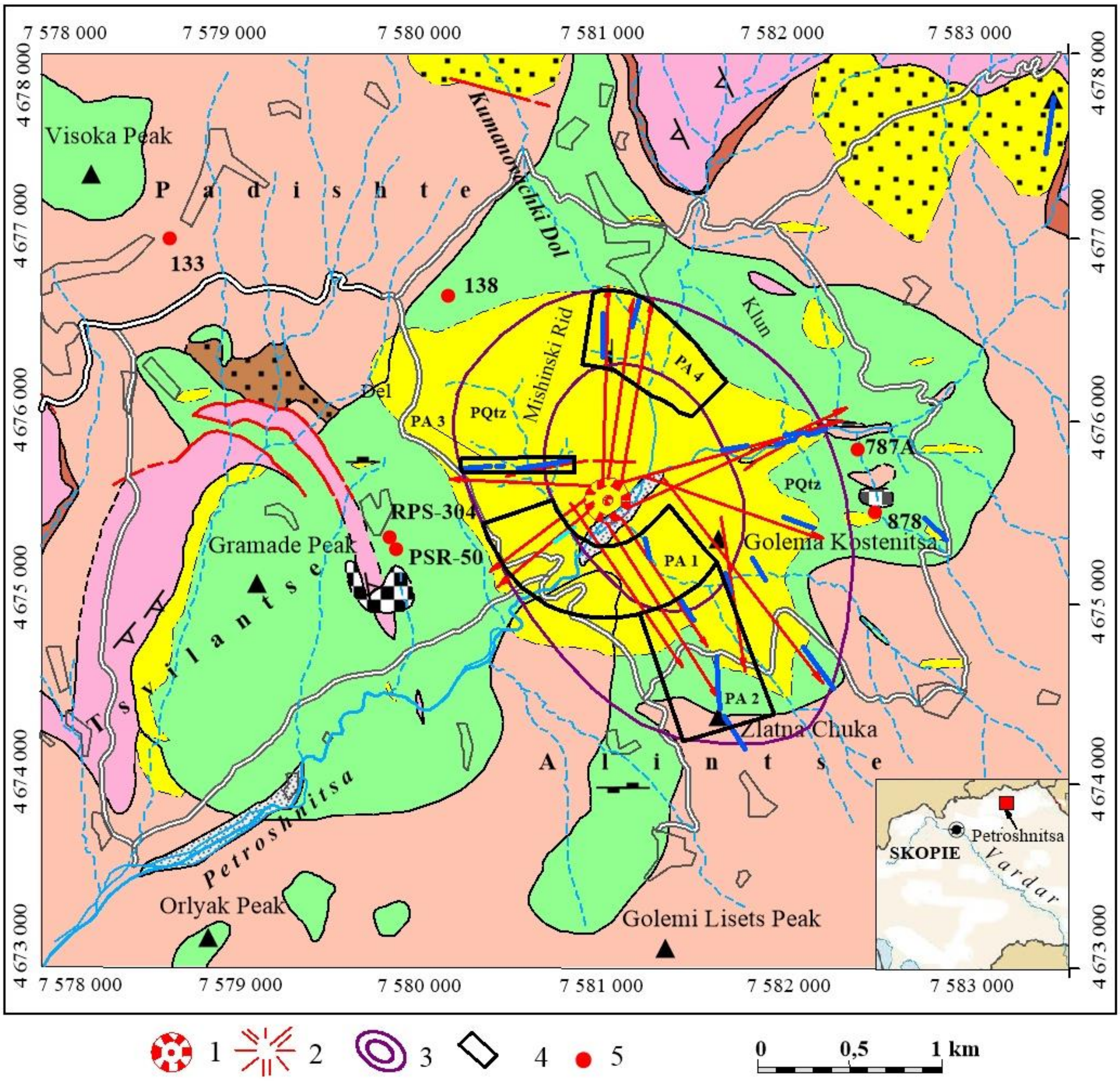

Fig. 3. Ore-structural map of Petroshnitsa district (the geological basis and structural symbols are same as in Fig. 1)

1 – eruptive center; 2 –"quartz star"; 3 – ring-like zone of radial monomineral quartz veins; 4 – ore-likely area (PA 1, PA 2, PA 3, PA 4); 5 – location and number of sample for silicate and geochronological Zircon LA-ICP-MS analysis (133, 138, RPS-304, PSR-50) and for silicate analysis (787A, 878)

quartzified latite-trachytes (Fig. 5b); mordenite-heulandite stage – generation of spheroidal and vein-shaped aggregates of mordenite and heulandite with radial habit of the grains; a second quartz-sulfide stage (quartz-polymetal) – quartz, pyrite, sphalerite, chalcopyrite, galena, tennantite and calcite. This stage is revealed north of the eruptive center and is controlled by an E-W to W-NW faults.

During the second hydrothermal stage, Fe-disulfides (pyrite and marcasite) and monomineral quartz veins were generated as they surround radially the eruptive center (Fig. 3).

All mineral phases formed during both hydrothermal stages and limited hypergenic processes are shown in Table 2. Specific and peculiar are hypergenic minerals presented by complex aluminum silicates, aluminum phosphates, hydrosilicates to hydroborates (Fig. 6). Some of these minerals are especially rare in nature. The complex in composition hypergenic minerals were genetically related with the oxidation of Cu-bearing (massive and vein-nest type) and Pb-Zn mineralizations as well as with the intense hydrothermal alteration of latite-trachytes.

Ore mineralizations distinguished in the upper reaches of Petroshnitsa river are

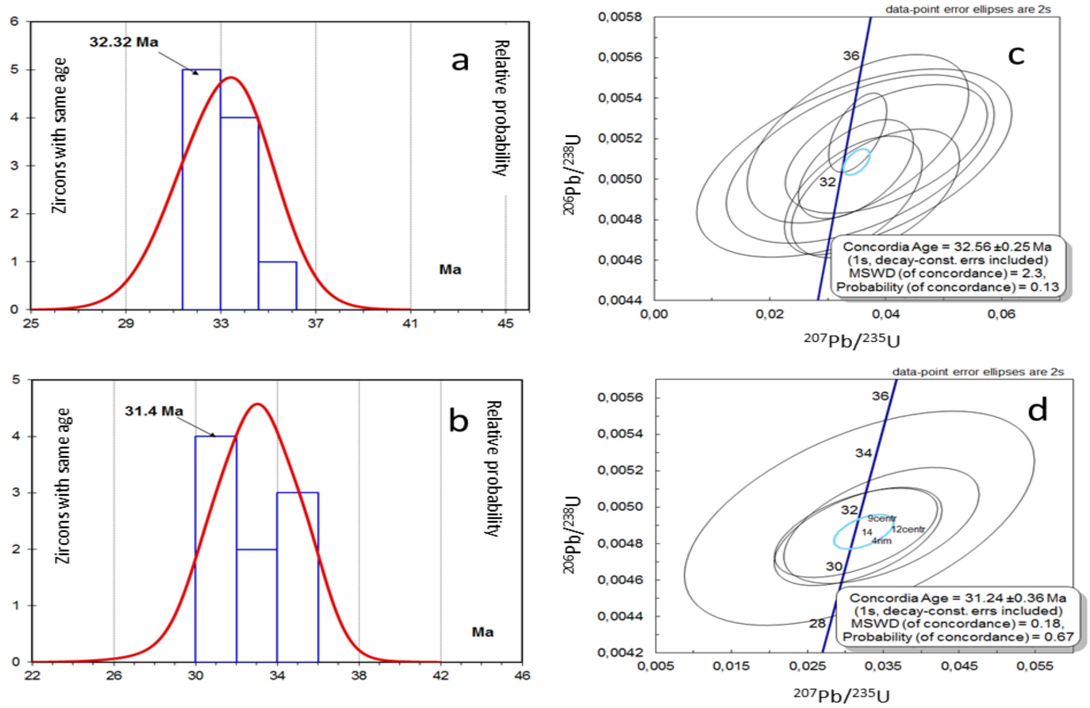

Fig.4. Age densities (a – PSR-1/2016, b –PSR-4₁/2016) and Concordia Age along the two lead isotopic relations $^{207}Pb/^{235}U$ and $^{206}Pb/^{238}U$ (c –PSR-1/2016, d –PSR-4₁/2016)

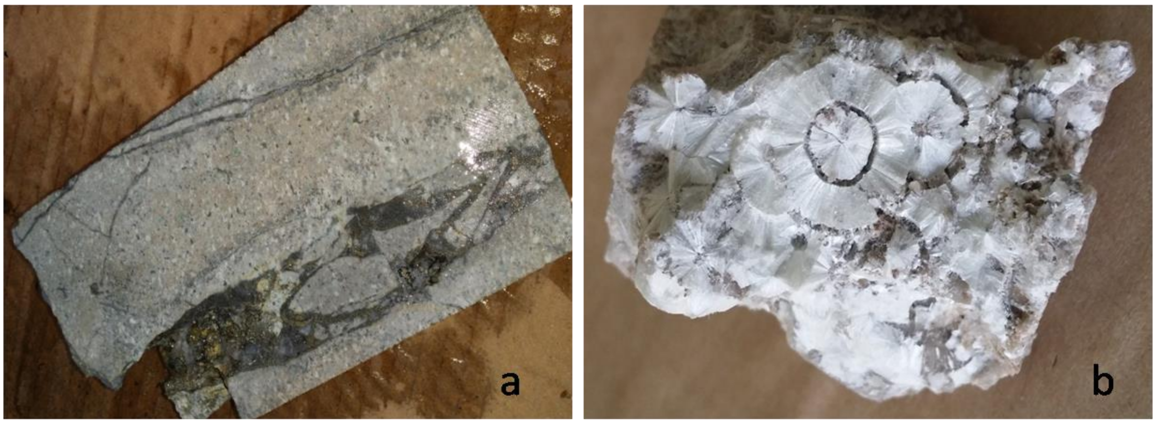

Fig. 5. Strongly quartzitized, kaolinitized and sericitizated volcanites with disseminations of diaspore, crossed by a stockwork pyrite mineralization (a) and spheroidal wavellite aggregates with a radial-like-ray structure along cracks in quartzitized volcanites (b). Size 1:1. Petroshnitsa.

Fig. 6. Mixture of kidney-like fibroferrite–langite–woodwardite aggregates with a ray-like structure (a) and oblong-kidney-like, brown-red aggregates of svanbergite, goyazite, basaluminite, koninckite (b) along cracks in strongly kaolinized and sericitized volcanites. Size of “a” 1:1, size of “b” 1:2. Petroshnitsa.

Table 2. Integral mineral composition of the ore mineralizations related to trachyte-latite volcanism in Petroshnitsa district

Primary minerals	Clinochlore	Pyrite
	Uvite	Marcasite
	Diaspore	Chalcopyrite
	Spinel	Sphalerite
	Adular	Galena
	Quartz	Tennantite
	Tridymite	-tetrahedrite
	Rutile	Siderite
	K-feldspar	Calcite
	Alunite	Mordenite
	Kaolinite	Heulandite
	Illite	Wavellite
	Montmorillonite	Corundum
	Sericite	Pyrophyllite
	Biotite	Chlorite
	Molybdenite	Epidote
Secondary minerals	Hematite	Goyazite
	Maghemite	Langite
	Lepidocrocite	Woodwardite
	Jarosite	Koninckite
	Plumbogumite	Basaluminite
	Plumbojarosite	Chalcocite
	Native Sulphur	Hydroxylapatite
	Fibroferrite	Copiapite
	Svanbergite	Alunogen

subdivided into the following mineralogical-geochemical types: Au-Cu-Mo with Re; Au-Cu-polymetal; Au-polymetal; pyrite-markasite and silicon (monomineral quartz veins). According to a number of direct and indirect criteria as well as data from detailed mineralogical-petrographic and geological-geophysical studies, specific ore-prospecting districts have been distinguished in the studied area as they are proposed for the further study.

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