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FEATURES OF BERILLIUM AND RARE METAL MINERALIZATION IN SYENITE OF THE PERGA DEPOSIT (UKRAINIAN SHIELD)

(Представлено членом редакційної колегії д-ром геол.-мінералог. наук, проф. В.М. Загнітком)

The results of the ore and accessory minerals study in the syenite of the Perga beryllium deposit are discussed. Phenakite and genthelvite are found among Be-bearing minerals. Genthelvite of this syenite, being compared to early published data on genthelvite of the Perga deposit, is distinguished by the highest ZnO content which is close to the theoretical maximum due to the alkaline nature of studied rock ($(Na + K)/Al = 1.09$). Genthelvite occurs as later mineral to phenakite or is formed by phenakite replacement at rising the alkalinity as a result of melt differentiation. Columbite with high-Mn content, Y-silicate (keiviite-(Y)?), rare-earth fluorocarbonate (bastnesite) are also found among other minerals of rare metals. The presence of fluorite and rare-earth fluorocarbonate in association with genthelvite or phenakite may indicate that Be and REE were transported in ore-bearing fluids as complex fluorine-carbonate compounds. Considering the geochemical characteristics of rocks (meta-aluminous, subalkaline and alkaline series, deep negative Eu-anomalies, low Sr, Ba, elevated – HFS elements) from the Sushcano-Perga region, enrichment of these rocks with rare metals and Be are related to intensive feldspar fractionation of the primary melts and due to alkaline oversaturation, volatile and rare metals (Be, Li, REE, Y, Nb, Ta) enrichment in the residual fractions of granitic or syenitic compositions. Postmagmatic alkaline solutions enriched in F and CO₂²⁻ promote of Be concentration in fluid phase with its following migration and crystallization as genthelvite.

Keywords: genthelvite, phenakite, subalkaline granites, alkaline syenites, columbite, Perga deposit, Ukrainian shield.

Problem statement. Minerals of the helvine series occur in rocks of different mineral composition and origin: helvine is more typical in skarns, granite – pegmatites, hydrothermal veins; danalite is mainly observed in skarns, (alkaline) granitoids and high-T metasomatites; genthelvite is associated with subalkaline and alkaline granites and syenitic rocks, alkaline pegmatites (Dunn, 1976).

The first publications about genthelvite find in siderophyllite greisen related to granites of the Sushcano-Perga area (SPA) are dated to the 60s of the last century (Gurvich et al., 1963). Despite the occurrence of genthelvite mineralization in SPA is known for a long time, however, there are no reliable explanations of the origin of ore-bearing rocks as well as processes resulted in formation of such specific beryllium mineralization.

Recent publications review. There are different concepts about possible origin of genthelvite-bearing rocks in SPA. Gurvich S.I. with co-authors (Gurvich et al., 1963) has described these rocks as altered and enriched in quartz (silicified syenites, which occur as small elongated or dike-like bodies in biotite granites. Based on the mineral composition – they include (%): 50–70 perthitic microcline, 10–30 albite, 10–15 quartz, 3–5 biotite and 2–3 magnetite – these rocks are interpreted to be microcline syenites similar to alkaline varieties. Superimposed hydrothermal-pneumatolithic alterations resulted in formation of quartz veins and silicified zones with associated genthelvite crystallization. Although the nature of such Be-enrichment of these fluids and Be concentration mainly in the genthelvite are still incompletely resolved problem.

In subsequent publications (Galetsky, 1966) the occurrence of genthelvite mineralization is mostly interpreted based on tectonic framework of the SPA that promote subalkaline granitoids formation and subsequent intensive auto- and metasomatic alterations with related rare metal mineralization. According to L.S. Galetskiy, Be mineralization itself should not be related to the specific syenitic (or granitic) rocks, but it occurs as confined to zones of intense metasomatic alteration formed in host granitoids by changing

their composition to quartz-K-feldspar, quartz-albite-K-feldspar, quartz-K-feldspar-albite, mica-K-feldspar and quartz-siderophyllite metasomatites. Increased concentrations of Ta, Sn, W, Ag, Li, Rb, Cs, REE, Y, Fe, Zn, Mo, Pb in beryllium-enriched rocks is interpreted to be a combined occurrence of two mineral associations: Sn-W-Be and polymetallic (Galetsky, 1966). According to this author, concentration of Be in genthelvite and formation of ore concentration of such unusual mineral association are treated to be a result of high enrichment of ore-bearing fluids in S, Si, as well as Zn and Fe, and depletion in Al. Nevertheless, the nature of such specific solutions and mineral association as well as the relation between genthelvite and phenakite (described by L.S. Galetskiy for the first time) and possible sequence of their appearance still remain uncertain.

In later publications (Bezpal'ko, 1970) the genthelvite-bearing rocks were called as "perthosites" and considered as metasomatic rocks (perthositic association), in spite of the fact that "perthosite" (according to petrographic code) is used for description of leucocratic variety of alkali feldspar syenite that consists almost entirely of perthite. Thus this term might be appropriate only in case of magmatic origin of these rocks. So other researchers termed these rocks as K-feldspar metasomatites based on their metasomatic origin.

According to V.T. Shatska (Ginzburg et al., 1975) review that is based mainly on the results of V.M. Gorbunov, S.V. Metalidy, R.A. Slysh observations the ore sites are confined to the tectonic dislocation zones and adjacent fractures formed in quartz-feldspar granitoids (gneiss-like "granites"). Here granites are altered with formation of metasomatites of various compositions – quartz-biotite-microcline to quartz-siderophyllite.

Article aims. The authors hope that petrographic and mineralogical studies of ore-bearing rocks of the Perga beryllium deposit will promote clearer understanding of the nature of ore mineralization and help to distinguish the peculiarities of the geological processes that resulted in Be-concentration as quite rare mineral species.

Methods. Genthelvite was analyzed using a JCSA-733 (JEOL) electron microprobe, equipped with three vertical wavelength dispersive spectrometers, in the Institute of Geochemistry, Mineralogy and Ore Formation, NAS of Ukraine. Analytical conditions were as follows: beam acceleration voltage of 15 kV, beam current 20 nA, and beam diameter of 2 μm ; counting times per analysis of 30 s on peak positions and 10 s on two background positions. Chemical composition of rare metal minerals was determined using a JSM-6700F field emission scanning electron microscope equipped with a JED-2300 energy-dispersive spectrometer (JEOL) in the Institute of Geochemistry, Mineralogy and Ore Formation, NAS of Ukraine. Operating conditions were as follows: 20 kV accelerating voltage, 1,0 nA beam current, 2 μm beam size and a counting time of 90 seconds for one analysis. Pure metals, synthetic compounds and natural minerals were used for calibration. Raw counts were corrected for matrix effects with the ZAF algorithm implemented by JEOL.

Petrography. Set of samples collected from the waste dumps of the Perga mine is studied. Petrographic descriptions have shown the most interesting rock according to their mineralogy (almost completely consist of perthite and minor albite, lattice microcline and quartz (10–15 %)) and chemical composition (SiO_2 63,99, TiO_2 0,11, Al_2O_3 16,64, Fe_2O_3 1,07, FeO 1,86, MnO 0,04, MgO 0,38, CaO 0,71, Na_2O 5,23, K_2O 8,87, P_2O_5 0,04, Total 99,18) can be classified as quartz alkali-feldspar syenite. Geochemical investigation have shown the presence (in ppm): 5000 Ba, 200 La, 250 Ce, 100 Nb, 450 Zr, 500 Y, 60 La, 200 Ce, 100 Th. Large perthite grains which are found in the most samples are characterized by simple twinning that together with perthite have a "fir-like" shapes under crossed links (Carlsbad twinning), which are more typical for orthoclase. According to (Menert, 1971), such exsolution of primary K-Na-feldspars can occur at solvus temperatures (660–715°C), while crosshatched twinning of microcline formed as a result of rearrangement of earlier monoclinic orthoclase, at temperature not lower than 500°C. Based on the results of homogenization of gas-liquid inclusions ore metasomatites (with genthelvite and willemite) are formed at 400–500°C.

The amount of perthite intergrowths (30–50 %) in porphyry-like feldspar indicates high-temperature crystallization environment of this rock. It is widely known that at low temperature conditions albite and microcline that occur in hydrothermal rocks and low-temperature metasomatites are commonly crystallized as separate grains. Microcline grains with typical microcline twinning are smaller in size relative to grains of perthitic feldspar and can be found in crushing zones in association with fine grained quartz, that can indicate their formation at later stages. Besides rock-forming minerals and above mentioned genthelvite plus phenakite such ore and accessory minerals as columbite, monazite, rare earth carbonate, zircon,

magnetite, tungstenite (series tungstenite-gubnerite), as well as undiagnosed Y-silicate (keiviite-(Y)?) are found in this sample.

The studied rock is slightly oversaturated in alkalis and has increased agpaitic index ($(\text{Na}+\text{K})/\text{Al} = 1,09$), although the alkali minerals have not been found. At the same time early publications (Ginzburg et al., 1975; Myckevych et al., 1986) have presented analytical data on peralkaline "feldspar metasomatites" ($(\text{Na}+\text{K})/\text{Al} = 0,98\text{--}1,10$) found in SPA. Agpaitic nature of this rock might be a result of partial entering of Fe^{+3} into tetrahedral position of feldspar with associated decreasing in aluminum and resultant oversaturation in alkalis. Based on the obtained data the studied syenite might be considered as rock variety very similar to leucocratic syenites of the Yastrubetsky massif, which is also situated among granites of SPA. It should be noted that these syenites are also characterized by increased Be (up to 33 ppm in syenites and only up to 20 ppm in the Perga granites) (Dubyna et al., 2014), as well as by Zr, REE, Nb, Y. Data presented in this article taken together with results observations made by N.A. Bezpal'ko, make it possible to suppose that "perthosite" occurs as veins and might represent the dyke swarm or vein facies of the Yastrubetsky massif or syenites that are very similar to them.

Chemical composition of genthelvite. Earlier investigations carried out in SPA distinguished several generations of genthelvite from three (Ginzburg et al., 1975) to four (Galetsky, 1966) and up to seven (Metalydy and Nechaev, 1983). According to the early published data, genthelvite crystals commonly show zonal structure with various zones of different chemical composition (Tabl. 1). It is possible that these zones might be erroneously interpreted by early researchers as separate generations. In one of publication (Remeshilo et al., 1977) has discussed zonal crystal of genthelvite with up to 13 zones distinguished based on rather variable content of Zn and Fe (but without significant variations in Mn. Accordingly to (Metalid and Nechaev, 1983), have made an assumption about higher Zn and lower Fe contents in late generations but without presenting any detailed analytical results. The highest content of ZnO (53,3 %) was determined in the second generation of this mineral.

By early investigation genthelvite is crystallized in different rock varieties of SPA: syenites (perthosites), greisens and silicified varieties of these rocks. Among investigated samples leucocratic perthitic syenites characterized by the highest content of genthelvite. Our own results and their comparison with data of previous publication indicate that these varieties of genthelvite show maximum enrichment in zinc (ZnO up to 55,6 %) (Fig. 1). Separate genthelvite generation is not possible to be distinguished however in some cores of zonal crystals higher Zn contents are fixed in comparison to their rims.

Table 1

Chemical composition of genthelvite from syenites of the Perga deposit

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2	28,94	29,68	29,49	28,98	30,98	31,00	31,06	31,13	31,03	31,01	30,95	30,62	30,67	30,96	31,02	31,02
BeO_{calc}	12,74	12,66	12,45	12,43	12,89	12,90	12,92	12,95	12,91	12,90	12,88	12,74	12,76	12,88	12,91	12,91
ZnO	55,64	52,29	52,18	53,02	53,37	52,84	45,46	45,54	45,17	51,79	49,31	51,93	52,61	51,94	50,27	48,25
FeO	1,47	1,45	1,92	1,84	0,83	0,83	6,63	6,92	7,46	3,15	4,46	2,11	2,15	1,38	4,29	4,66
MnO	0,23	-	0,25	0,03	1,43	1,93	2,72	2,46	2,11	0,56	1,33	0,84	0,29	2,11	0,78	2,17
S	5,44	5,40	5,32	5,31	5,50	5,51	5,52	5,53	5,51	5,51	5,50	5,44	5,45	5,50	5,51	5,51
Total	104,46	102,96	101,61	101,60	105,00	105,00	104,30	104,53	104,19	104,91	104,42	103,67	103,94	104,76	104,78	104,51
-1/2S	101,74	100,26	98,95	98,95	102,25	102,24	101,55	101,77	101,44	102,16	101,68	100,95	101,21	102,01	102,02	101,76

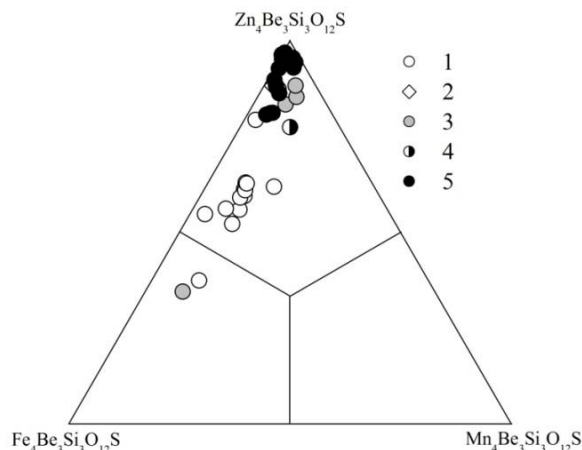


Fig. 1. Composition of genthelvite of the Perga deposit are plotted on triangle diagram of helvite-danalite-genthelvite coordinates. Legend:

1 – (Remeshilo et al., 1977); 2 – (Metalid, Nechaev, 1983);
3 – (Ginzburg et al., 1977); 4 – (Galetsky, 1966); 5 – author's data published in this paper (Tabl. 1)

In our opinion, another feature of the beryllium-bearing rocks of SPA, which is still obscure, concerns the interrelation between two beryllium minerals – genthelvite (abundant) and phenakite. Based on early publications about SPA it is widely known that phenakite is confined to the silicified zones of gneiss-like granites, greisens and syenites (Ginzburg et al., 1975, 1977).

According to these investigations phenakite commonly was found at the peripheral part of genthelvite enriched areas, and phenakite being crystallized later than genthelvite at lower temperature (180–250°C) during of metasomatic stage. As one of main of mentioned arguments is presence of phenakite on the margin of genthelvite grains. However, it should be mentioned that association of phenakite and helvite series minerals is commonly observed in metaluminous or peralkaline rocks, so alkaline Be-silicates is more typical for alkaline rocks unsaturated with silica. Phenakite is also observed (oral evidence from one of author of this paper) in Perga porphyry granite (biotite and oligoclase) i.e. without any presence of alkaline minerals.

The results of petrographic and mineralogical studies made on quartz-alkali-feldspar syenite do not prove early concept about crystallization sequence of beryllium minerals, or, at least, indicate the ambiguity of the supposed relation between genthelvite and phenakite. In addition, the above mentioned low-temperature conditions of phenakite crystallization disagree with experimental data on phenakite

and bertrandite stability at moderate pressures (0,5–3,5 kbar) and temperatures (up to ~ 350°C) where bertrandite is more stable in comparison with phenakite (Hsu, 1983).

In the studied samples (thin and polished sections) single crystals of genthelvite and phenakite are commonly found. Phenakite is generally larger in size and shows presence of fissures filled with iron phase (hematite?) and rarely rare-earth-fluorocarbonate. In thin sections, large phenakite crystals (Fig. 2) are common. Sometimes in cracks and on the edges of these crystals fine-grained (<0.1 mm) and tetrahedral (triangular in shape) crystals of genthelvite are developed. In addition, core parts of large triangular genthelvite crystals (by transparent light) are filled with brownish aggregate where small relics of phenakite are also discovered. Fine-grained (< 10 µm) genthelvite rim around smaller (~ 100 µm) phenakite crystals are found but they are more rare. It is possible to suppose that phenakite is earlier mineral, at least in the investigated syenite. At alkalinity increasing of granitoid melt or ore-bearing solutions phenakite became unstable and was replaced by genthelvite.

Other rare metal minerals. As mentioned above, granitoids and studied syenite sampled in the Perga mine are characterized by increased contents of LIL and HFS elements too. Among minerals that contain these elements columbite, ferropseudobrookite, monazite, bastnäsite and Y-silicate are studied (Tabl. 2).

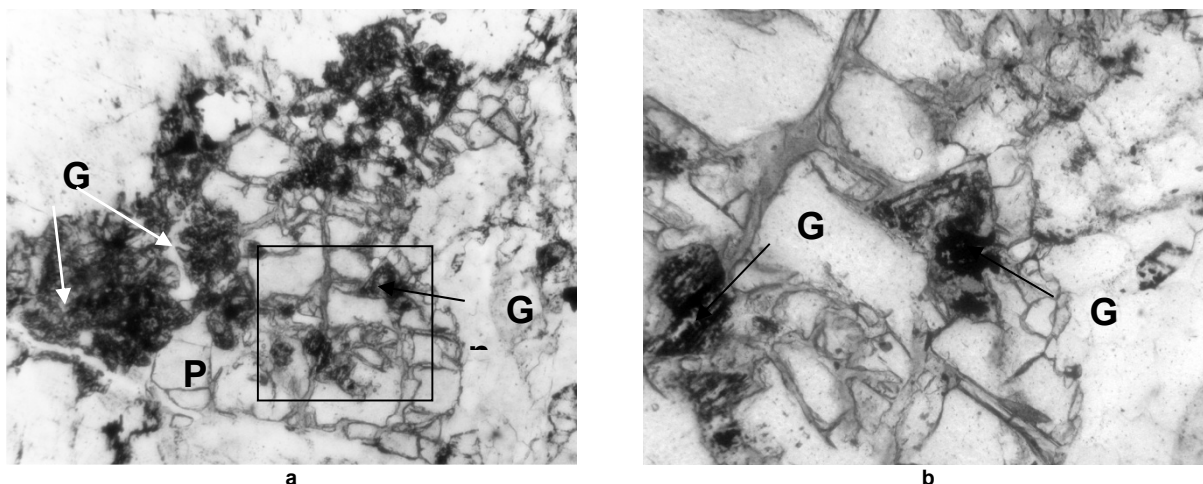


Fig. 2. a – the large (~3 mm) grain of phenakite (Phe) with small (usually <100 µm, commonly triangle in shape) grains of genthelvite (Gn) (magnification 40×) in fractures; b – genthelvite grains of (magnified part of A) image, magnification 100×). Photos in transparent light

Table 2

Chemical composition of rare metal minerals from syenites of the Perga deposit

	1	2	3	4	5	6	7	8*	9	10*	11*	12	13	14	15*	16*
	Columbite						Ferropseudobrookite			Ilmenorutile		Monazite	Keiviite-(Y)		REE-F-carbonate	
SiO ₂	2,06	1,63	2,58				2,12			3,22	4,17	1,69	40,98	39,12	2,49	0,34
TiO ₂	3,65	2,38	2,93	3,09	2,44	2,18	69,78	58,27	70,26	65,69	67,22				0,13	0,01
FeO	15,21	13,75	14,34	15,41	16,64	13,71	26,9	26,03	27,25	25,72	19,12		2,34	3,05	18,1	1,34
MnO	5,55	6,03	5,88	3,89	2,59	6,22	1,2	12,63	2,49	1,04	0,2				0,05	0,04
CaO													5,01	4,46	2,05	0,67
F															2,67	11,02
Nb ₂ O ₅	73,52	76,2	74,27	72,41	75,94	76,33					2,99					
Ta ₂ O ₅				5,21	2,39	1,56										
P ₂ O ₅												29,75			0,01	
Y ₂ O ₃													51,67	53,38	14,13	1,45
La ₂ O ₃												16,06			4,14	19,65
Ce ₂ O ₃												39,59			8,54	28,8
Nd ₂ O ₃															4,27	9,35
REE ₂ O ₃ ^{tot}															32,41	62,11
ThO ₂												12,92			0,54	0,25
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	63,05	78,15

* Following elements are also determined in presented analysis are: 8 – 3,07 ZnO; 10 – 4,34 ZrO₂; 11 – 6,3 ZrO₂; 15 – 3,02 Al₂O₃; 0,17 MgO; 0,66 SrO; 0,09 Na₂O; 0,6 PbO₂; 0,05 UO₂; 0,91 Pr₂O₃; 0,28 Eu₂O₃; 0,14 Sm₂O₃; 16 – 0,89 SrO; 2,77 Pr₂O₃; 0,73 Eu₂O₃; 0,61 Sm₂O₃; 0,2 Tb₂O₃.

1–3 – analysis from different part of single grain; 4, 5 – fine-grained (about 60 μm) irregularly shaped columbite; 6 – similar to previous neighboring grain; 7–10 – analysis from different part of single elongated (about 0.6 mm) grain; 11 – single grain in association with columbite; 12 – core (unaltered) part of small (about 140 μm) elongated grain; 13, 14 – the most large (up to 15 μm) grain in fine-grained segregation around magnetite; 15 – small (up to 50 μm) inclusion in core part of genthelvite; 16 – single grain (up to 250 μm) next to zircon.

Columbite occurs as small (0,1 mm) crystals of irregular shape with corroded faces. Locally at grain edges a thin rim of secondary ferruginous phase (hematite?) is formed, though some intergrowths between columbite, isometric magnetite (?) and ilmenorutile are also found. The contents and ratio of main components are consistent with columbite analyses that were published earlier (Buchinskaya and Nechaev, 1992) and point out to increased of Mn content. The similar Mn-rich columbites are described by these authors in the aegirine-biotite and siderophyllite granites of SPA.

Ferropseudobrookite forms elongated (0.6×0.15 mm) crystal which sometimes shows presence of idiomorphic faces. On back-scattered electron image, crystal looks like homogeneous grains, with one single point showing significant increase of MnO and ZnO (Tabl. 2, an. 8).

Keiviite-(Y) (?) is a secondary mineral which is most commonly observed in cracks of quartz and fluorite from "amazonite" pegmatite's. The minerals that might be preliminarily diagnosed (by the ratios of main elements (Y:Si = 1:1)) as keiviite-(Y) occur only as fine aggregates (<5 μm) that surround large magnetite grain. These aggregates include larger grains (up to 15 μm) of irregular shape, among which one single grain was analyzed. But more detailed investigation is needed, because in analyzed grain only Y is presented, whereas typical keiviite-(Y) should also be enriched in HREE.

Bastnäsite might be found as small inclusions in genthelvite, in cracks of phenakite and single small grains. The presence of rare-earth-fluorocarbonate and obvious secondary (or late) nature of their occurrence as confined to beryllium minerals as well as constant presence of fluorite prove the conclusions of experimental studies. These results testify that the main agents of postmagmatic or hydrothermal fluids, which are responsible for the transfer and concentration of Be, are not purely fluorine but F-CO₃²⁻ is in composition that is more typical for alkaline conditions.

Conclusions. It is known that subalkaline and peralkaline magmas can concentrate Be in different rocks ranging in composition from subalkaline biotite granites and syenites to riebeckite-aegirine varieties. As a rule, magmatic rocks similar to alkaline granites and quartz syenites show rather high Be contents (Khaldzan-Buregtey, Mongolia),

although ore mineralization are mainly associated with alkaline pegmatites (Strange Lake, Thor Lake, Canada) formed at the final stages of granitoid melts differentiation.

According to published data (Esypchuk et al., 1993; Dubyna and Kryvdik, 2014), chondrite-normalized REE patterns of the Perga granites and syenites of the Yastrubetsky massif are characterized by large negative Eu-anomalies (Eu/Eu* = 0,05–0,11) and significant enrichment in HREE ((La/Yb)_n = 0,3–20). Such REE distribution patterns and other geochemical features (low Sr and Ba, high HFSE) give us a reason to assert that at least the alkaline varieties of the Perga granites and associated syenites, i.e. syenites of the Yastrubetsky massif, are formed as a result of intensive crystalline fractionation of granitic or syenitic melts. Apparently, these processes of differentiation could be responsible for formation of residual melts enriched in volatile and alkaline elements with associated increasing of fluorine and rare metal (Be, Li, REE, Y, Nb, Ta) contents.

Therefore, the main reason of increased concentration of Be in SPA is likely to be explained by geochemical characteristics of highly differentiated melts, namely, reduced in aluminum content (metalluminous) and increased alkalinity. It can be also proved by the fact of enrichment in Be and rising of Zr, Nb, REE concentrations, which is typical for the similar types of alkaline or subalkaline magmas. In addition, low or reduced aluminum content and high alkalinity can promote formation of phenakite instead of beryl that is more typical for peraluminous granites. At entering of these melts into hypabyssal environment and their subsequent crystallization, volatile enriched solutions could be separated, that adduce to increasing of Be solubility and its accumulation in the fluid phase. Low activity of SiO₂ in the syenite rocks could also enhance this effect. The presence of fluids enriched in Be and other rare metals, that are genetically associated with subalkaline or alkaline granites and syenites, high oxygen fugacity and low sulfur content, are favorable for transportation and subsequent concentration of Be in genthelvite. Genthelvite can be crystallized together with phenakite or by its replacement. At the same time, genthelvite of alkaline syenites is characterized by the ZnO content that is very similar to the

theoretically calculated composition, which is related with alkaline conditions of this mineral crystallization.

In our opinion, significant Zn enrichment of genthelvite found in studied sample is caused by its elevated alkalinity. As is known, genthelvite is the member of sodalite-danalite series, which is characterized by entering of S (or SO_4^{2-}) in additional anions, that is caused, on the one hand, by reduced sulfur and elevated oxygen fugacity, and on the other hand, by increased alkalinity of the melt where Fe and Mn comprise oxides and other silicates (Burt, 1988). Therefore, at crystallization of alkaline melts occurrence of hydrothermal and sulfide mineralization is not typical, and S, SO_4^{2-} and H_2O , together with Na, enter into silicate minerals (sodalite, cancrinite, haüyne, nosean).

Experimentally studied relation between FeO and ZnO solubility and pH of solution is also indicates that in range of pH from 9 to 11, their solubility is practically the same. At these condition Be and Zn migrate as similar complexes: $\text{Be}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$, $\text{Be}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_3^-$, which determines their occurrence in the same minerals (Khodakovskiy, 1975). In addition, the geochemical feature of Be is formation of stable complexes with fluorine ($[\text{BeF}_4]^{2-}$, $[\text{BeF}_3]^{2-}$, $[\text{BeF}_2]$, $[\text{BeF}]^+$), which prevail at low pH (2–5), while mixed F-CO_3^{2-} complexes (such as BeCO_3F^-) are predominant at higher pH (5–7) (Wood, 1992). According to experimental data (Kogarko et al., 1968), the fluorine separation in the fluid phase rise with increased acidity of the silicate melt and sharply decreases with increasing alkalinity. Therefore, in agpaite melts, F is not separated into gas phase at all, subsequently silicate melt gradually passes into the fluid-melt from which pegmatites with various minerals (including soluble in water NaF, sodium phosphates, soda and another rare earth minerals) are crystallized. These pegmatites might be treated to certain extent as similar to coarse-grained "perthosite".

Such crystallization enriched in Zn (and Mn) minerals might be found in highly differentiated (residual) melts represented by alkaline rocks. For example, Zn-kupletskite (up to 7,86 % ZnO) and hendricksite (21,5–25,8 % ZnO) were discovered in agpaite phonolites of the Oktyabrsky massif (Azov area), and high-Mn (up to 8,7 % MnO) amphibole and biotite (up to 3,52 ZnO and up to 14,3 % MnO) are also known in dike aegirine microphoyaites of this massif.

Possible influence of hydrothermal processes on the ore-ability of Be deposits that are associated with granite intrusions is still controversial, because sometimes both primary magmatic (Miller, 1996) and hydrothermal enrichments (Salvi and Williams-Jones, 1996) are treated to be important even for the same deposits. The reviews of published data show in spite of high Be content in pegmatoid alkaline rocks, the highest Be concentrations are still associated with later hydrothermal processes. Based on the type of mineralization of the beryllium-bearing rocks of SPA they are quite similar to fluorite-phenakite-helvite mineralization of the Verhnee Espe district (Kazakhstan), which occurs at the marginal zones of hydrothermally altered porphyry alkaline (riebeckite) granites.

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ОСОБЛИВОСТІ БЕРИЛІЄВОЇ ТА РІДКІСНОМЕТАЛЕВОЇ МІНЕРАЛІЗАЦІЇ В СІЄНІТІ ПЕРЖАНСЬКОГО РОДОВИЩА (УКРАЇНСЬКИЙ ЩИТ)

Наведено результати дослідження рудних та акцесорних мінералів із сієніту Пержанського родовища берилію. Серед Be-вмісних мінералів діагностовано фенакіт і гентгельвін. Останній вирізняється максимальним, порівняно з опублікованими в літературі аналізами гентгельвіну Пержанського родовища, і близьким до максимального теоретичного вмістом ZnO, що зумовлено лужним характером досліджуваної породи ((Na+K)/Al=1,09). Гентгельвін є більш пізнім мінералом відносно фенакіту або утворюється за рахунок його заміщення в результаті підвищення лужності розплаву в процесі диференціації. З інших мінералів рідкісних металів виявлено колумбіт з підвищеним вмістом Mn, Y-силікат (кейвіїт-(Y)?), рідкісноземельний фторкарбонат (бастнезит). Наявність флюориту та рідкісноземельних карбонатів, агрегати яких часто приурочені до гентгельвіну або фенакіту, може свідчити, що в рудоносних флюїдах Be і REE переносилися у вигляді комплексних фтор-карбонатних сполук. Ураховуючи геохімічні характеристики порід (метаглиноземисті, сублужного і лужного ряду, глибокі негативні Eu-аномалії, низький вміст Sr, Ba, підвищений – HFS елементів) Суцано-Пержанського району, причини збагачення на рідкісні метали і Be пов'язані з інтенсивним польовошпатовим фракціонуванням вихідних розплавів, що зумовлювало пересичення лугами, збагачення леткими компонентами і рідкісними металами (Be, Li, REE, Y, Nb, Ta) залишкових порцій магматичних розплавів гранітоїдного або сієнітового складу. Постмагматичні лужні розчини, збагачені F і CO₃²⁻, сприяли концентруванню Be у флюїдній фазі з подальшою його міграцією і кристалізацією гентгельвіну.

Ключові слова: гентгельвін, фенакіт, сублужні граніти, лужні сієніти, колумбіт, Пержанське родовище, Український щит.

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ОСОБЕННОСТИ БЕРИЛЛИЕВОЙ И РЕДКОМЕТАЛЛИЧЕСКОЙ МИНЕРАЛИЗАЦИИ В СИЕНИТЕ ПЕРЖАНСКОГО МЕСТОРОЖДЕНИЯ (УКРАИНСКИЙ ЩИТ)

Приведены результаты исследования рудных и акцессорных минералов из сиенита Пержанской месторождения бериллия. Среди Be-содержащих минералов диагностирован фенакит и гентгельвин. Последний отличается максимальным, по сравнению с опубликованным в литературе, анализами гентгельвина Пержанского месторождения, и близким к максимальному теоретическому содержанию ZnO, что обусловлено щелочным характером исследуемой породы ((Na+K)/Al=1,09). Гентгельвин более поздний минерал относительно фенакита или образуется за счет его замещения в результате повышения щелочности расплава в процессе его дифференциации. Из других минералов редких металлов обнаружен колумбит с повышенным содержанием Mn, Y-силікат (кейвиит-(Y)?), редкоземельный фторкарбонат (бастнезит). Наличие флюорита и редкоземельных карбонатов, агрегаты которых часто приурочены к гентгельвину или фенакиту, может свидетельствовать о том, что в рудоносных флюидах Be и REE переносились в виде комплексных фтор-карбонатных соединений. Учитывая геохимические характеристики гранитов и сиенитов (метаглиноземистые, субщелочного и щелочного ряда, глубокие негативные Eu-аномалии, низкое содержание Sr, Ba, повышенное – HFS элементов) Суцано-Пержанского района, причины обогащения этих пород на редкие металлы (REE, Y, Nb, Ta) и Be связаны с интенсивным полевошпатовым фракционированием исходных расплавов, что вызывало пресыщение щелочами, обогащение летучими компонентами и редкими металлами остаточных порций магматических расплавов гранитоидного или сиенитового состава. Постмагматические щелочные растворы, обогащенные F и CO₃²⁻, способствовали концентрированию Be во флюидной фазе с последующей его миграцией и кристаллизацией гентгельвина.

Ключевые слова: гентгельвин, фенакит, субщелочные граниты, щелочные сиениты, колумбит, Пержанское месторождение, Украинский щит.