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New Pb–As-Bearing Eulytite from the Galechnoe Deposit, Eastern Yakutia

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Eulytite, $Bi_4(SiO_4)_3$, is a rare mineral. Since its discovery in Schneeberg and Johanngeorgenstadt (Saxony, Germany) by Breithaupt in 1827, this mineral has been reported from only a few other localities: Hechtsberg and the Clara Mine (Germany), Dognecea (Romania), Cornwall (England), Southwick Cliffs (Scotland), the Evans-Lou quarry (Canada), Pala pegmatites (United States), Smrkovec (Czech Republic), and Wombat Hill, Australia [1, 3, 4]. In all the deposits, the eulytite associates with Bi-bearing minerals: bismuthite, bismuthinite, and native bismuth. Eulytite from the Uralian deposits was studied in cathode and UV rays [2]. However, its exact locality, chemistry, physical properties, and relations with other minerals were not reported. Hence, the data reported below can be considered the description of the first reliable finding of eulytite in Russia.

There are limited data on the chemical composition of natural eulytite. The data on eulytite from the Schneeberg and Johanngeorgenstadt deposits reported in the reference books were based on wet chemical analysis [1]. Eulytite from these deposits contains Fe_2O_3 and P_2O_5 traces. Its cubic volume-centered structure is based on Si-tetrahedrons and Bi triangles linked by shared oxygens, with each Bi atom surrounded by six Si atoms [5]. Such an arrangement provides stability of the structure even in the case of partial substitution for larger atoms. It was shown experimentally that Si in SiO_4 tetrahedra is substituted for the elements of groups 5 and 6 (Cr, S, V, As, Ge, and P), if Bi is substituted for Pb^{2+} to balance the valence charge [1]. In addition, the isomorphic scheme of $Bi^{+3} + Si^{4+} \rightarrow Ba^{2+} + P^{5+}$ is also possible [6]. The Ge analogue of eulytite, $Bi_4(GeO_4)_3$, is applied in the electron industry [7, 8].

We found eulytite in the Galechnoe deposit located in the Tenkeli gold–tungsten–tin ore cluster in the central Derbek–Nel’gesin ore zone. The ore cluster is confined to the intersection of long-lived WE-trending Derbek–Nel’gesin and submeridional Khampinskii faults. The deposit is localized in the core of the Khospokh linear-box anticline, which is mainly composed of sandy rocks of the Middle Triassic Ladinskii Stage. The rocks were strongly hornfelsized by the Burgochan granitoid massif. The ore bodies restricted to the outer and inner contact zones of the massif dome consist of thin (5–60 cm) and short (up to 200 m) quartz–tourmaline–chlorite veins and veinlets with sulfide pockets and dissemination. The oldest metasomatic quartz–chlorite–tourmaline assemblage is developed around veins both after hornfels and granitoids. Metasomatites formed after granitoids are enriched in chlorite, while the metasomatites formed after hornfels are dominated by tourmaline. Ore veins are mainly composed of a wolframite–arsenopyrite–quartz assemblage, with arsenopyrite enriched As (As/S 1.05–1.10) and Co (up to 6 wt %) and inclusions of nickeline, rammelsbergite, and gersdorffite. A scheelite–gold–bismuth–sulfotelluride assemblage occurs sporadically as dissemination in quartz and fine pockets in quartz cavities. Bismuth minerals include sulfotellurides (tetradymite, joseite A, and joseite B), tellurides (tsumoite, hedleyite, and tellurobismuthite), maldonite, Au–Bi sulfide, and native bismuth, which are closely associated with native gold (fineness 690–940).

Eulytite was found in a heavy fraction of a crushed sample from ore veins and in one polished section of a sample taken from quartz-filled microcavities. It occurs mainly as individual spheroidal aggregates (Fig. 1a, *1*) less than 0.2 mm in size. More rarely, the mineral occurs as intergrowths of 2–5 microspheroids (Fig. 1a, *2*) and intergrowths of numerous hemispheric aggregates on different minerals. This morphology is consistent with previously described 48-hedral crystals, as well as with radial and hemispheric aggregates, from Schnee-

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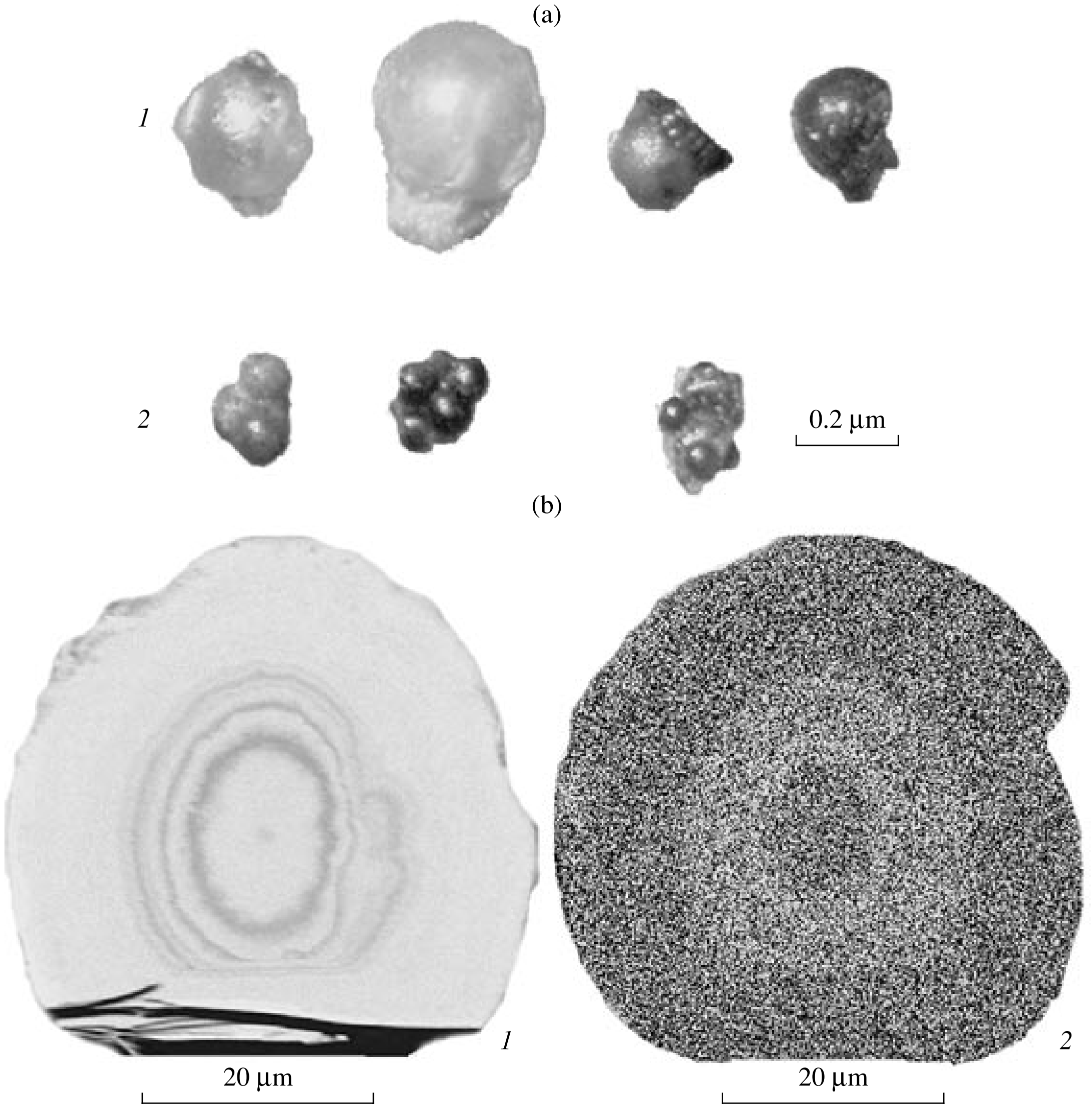

Fig. 1. Morphology and internal structure of eulytite aggregates. (a) Individual spherical grains (*1*) and intergrowths of several microspherules (*2*); (b) zoned structure of spherical eulytite: (*1*) heterogeneity revealed in BSE image, (*2*) heterogeneous As distribution found in its characteristic radiation.

berg and Johanngeorgenstadt. Eulytite also occasionally occurs as rims around mica, scheelite, tellurides, and native gold. Spheroids usually have a smooth surface with nacreous luster. However, high magnification investigation under a scanning electron microscope showed that their surface is uneven and covered by micrograins of other minerals, in particular, fine-lamellar mica aggregates. The spheroidal eulytite aggregates vary in color from transparent, colorless, and pale yellowish (or brownish) to gray or dark gray and opaque. Some aggregates are uniformly colored, while others are contrasting in color. Some spheroids reveal distinct concentric zoning, which is expressed in alternation of zones with the different tints mentioned above. The central parts of the grains often are darker, whereas the remaining part is transparent. Wide zones (30–100 µm) are alternated with less polished narrow zones (1–5 µm) containing tiny dark inclusions. It will be shown below that color heterogeneity and zoning of the eulytite aggregates is related to variations in its chemical composition.

The chemical composition of eulytite was studied on a Camebax-Micro microprobe. Table 1 demonstrates the typical chemical compositions of homogenous spheroids (analysis 1), analyses with the lowest and highest contents of components in the weakly zoned grains (2, 3), analyses with the lowest Pb and As contents (4, 5), and their average composition (analysis 6). We also analyzed the differently colored zones from the most contrasting zoned grain (7–9). Scanning of the latter grain revealed domains no more than 10 µm in size with the maximum Pb and As contents. The data in

Table 1. Microprobe analysis of eulytite from the Galechnoe deposit

Ordinal no.	Analyzed areas		Content of components, wt %					Total	Formula
			Bi_2O_3	PbO	As_2O_3	SiO_2	P_2O_5		
1	Homogenous grain (7)		78.69	1.80	2.82	14.36	0.07	97.74	$(Bi_{3.91}Pb_{0.09})_{4.00}(Si_{2.76}As_{0.33}P_{0.01})_{3.10}O_{12}$
2	Weakly zoned grain (5)		78.44	2.40	3.16	14.17	0.06	98.23	$(Bi_{3.89}Pb_{0.12})_{4.01}(Si_{2.73}As_{0.37}P_{0.01})_{3.11}O_{12}$
3	Weakly zoned grain (6)		76.96	4.15	3.65	13.11	0.10	97.97	$(Bi_{3.92}Pb_{0.22})_{4.14}(Si_{2.59}As_{0.44}P_{0.02})_{3.05}O_{12}$
4	Grain with the minimum Pb content		79.74	1.14	3.32	13.74	0.04	97.98	$(Bi_{4.00}Pb_{0.06})_{4.06}(Si_{2.67}As_{0.39}P_{0.01})_{3.07}O_{12}$
5	Grain with the minimum As content		77.82	1.99	2.08	15.61	0.05	97.55	$(Bi_{3.77}Pb_{0.10})_{3.87}(Si_{2.94}As_{0.24}P_{0.01})_{3.19}O_{12}$
6	Average content over 24 points		78.55	2.88	3.22	13.86	0.08	98.59	$(Bi_{3.92}Pb_{0.15})_{4.07}(Si_{2.68}As_{0.38}P_{0.01})_{3.07}O_{12}$
7	Zoned grain	core	77.63	1.72	2.43	14.97	0.05	96.80	$(Bi_{3.83}Pb_{0.09})_{3.92}(Si_{2.86}As_{0.28}P_{0.01})_{3.15}O_{12}$
8		intermediate zone	79.20	3.46	4.27	12.99	0.16	100.08	$(Bi_{3.97}Pb_{0.18})_{4.15}(Si_{2.52}As_{0.50}P_{0.03})_{3.05}O_{12}$
9		rim	75.25	5.74	3.59	13.16	0.11	97.85	$(Bi_{3.85}Pb_{0.31})_{4.16}(Si_{2.61}As_{0.43}P_{0.02})_{3.06}O_{12}$
10	Local point		62.54	17.46	7.25	10.96	0.13	98.34	$(Bi_{3.36}Pb_{0.98})_{4.34}(Si_{2.28}As_{0.92}P_{0.02})_{3.22}O_{12}$
11			43.85	33.85	11.4	8.44	0.12	97.66	$(Bi_{2.53}Pb_{2.04})_{4.57}(Si_{1.89}As_{1.55}P_{0.02})_{3.46}O_{12}$

Note: Analyses were performed on a Camebax-Micro microprobe (accelerating voltage 15 kV, standards: Bi_2O_3, PbO, As, diopside, and apatite). *The number in parentheses is the number of analyses.

Table 1 show that the Pb-rich samples are depleted in Bi. The same correlation is observed for the As–Si pair. The eulytite from the Galechnoe deposit contains subordinate amount of P_2O_5, which has a negative correlation with SiO_2 (analyses 7–9).

Zoning of eulytite spheroids is distinctly observed in BSE images and in the characteristic radiation images of As, Si, and Bi taken with an analytical low-vacuum scanning electron microscope JSM-6510LV + JED2300 (Fig. 1b, *1*, *2*). The As distribution over the grain correlates with the BSE image in which the darker zones are characterized by elevated As contents.

Table 2. Reflections of Pb–As eulytite of different compositions from the Galechnoe deposit

Wavelength, λ, nm	Reflection, *R*, %		
	bright zone	intermediate zone	dark zone
500	8.1	7.1	8.5
520	7.1	7.9	8.8
540	9.7	8.3	9.4
560	10.2	8.7	9.6
580	9.9	8.7	9.6
600	10.1	8.4	9.0
620	10.3	8.6	8.9
640	9.9	7.8	8.7
660	10.0	8.0	8.4
680	9.5	7.1	8.2
As, wt %	1.92	2.47	3.06

The correlations plotted on the basis of the obtained analytical data for the substitution As → Si (Si = –1.2238 As + 3.0717) and Pb → Bi (Bi = –1.07686Pb + 4.3056) indicate that simultaneous isomorphic substitutions of Si and Bi for As and Pb, respectively, in eulytite, which were demonstrated in previous experiments [1], are widespread in natural conditions.

The IR spectrum of eulytite in the region 4000–650 cm^{-1} was obtained on an IR Fourier Protégé-460 (Nicolet) spectrometer (resolution 4 cm^{-1}) using an InspectIR microscope (beam size ~150 μm). The results are quite consistent with previously published data [9]. The spectrum exhibits antisymmetric stretching vibrations of isolated $[SiO_4]^{3-}$ tetrahedra.

An X-ray powder diffraction study was made on a RKD chamber (57.3 mm across) with Si as the internal standard. The obtained interplanar spacings of the studied eulytite [*d*(*I*), Å 4.23(100); 3.275(85); 2.765(95); 2.110(55); 2.030(55); 1.680(40)] are more than those of reference eulytite [d(*I*) 4.18(8); 3.273(10); 2.742(10); 2.100(9); 2.011(9); 1.667(9) (1)]. The unit cell parameter a_0 calculated by the LSM over all reflections of the studied eulytite is 10.336(5) Å, which is more than the values of a_0 = 10.278 Å (1) and a_0 = 10.291 Å for the reference sample (JCPDS, No. 33-215). An increase in unit cell parameters of the studied eulytite is caused by its chemical specifics: Bi^{3+} (ionic radius 1.20 Å) and Si^{4+} (0.39 Å) are substituted for Pb^{2+} (1.26 Å) and As^{5+} (0.47 Å), which have larger ionic radii. Given the variable composition and significant difference in ionic radii of Si^{4+} and As^{5+}, eulytite with significant Si substitution for As can have an even higher a_0.

The reflection spectra were obtained for three differently colored zones with different chemical compositions (Table 2). The lightest zone is characterized by the maximum values of reflections, while the darkest zone with the highest As contents shows the lowest values. The isomorphic substitution of Bi and Si for Pb and As, respectively, shows no effect on the reflection curves. They are always subparallel, with the maximum peak of the mineral within 560–620 nm.

Thus, we found a new natural Pb–As variety of eulytite, in which substitution is described by compensation isomorphism according to the following scheme: $Pb^{2+} + As^{5+} \rightarrow Bi^{3+} + Si^{4+}$. This suggests a wider abundance of this mechanism (for example, incorporation of Ba and P) by analogy with similar synthetic compounds [6]. The distribution of the components in spherical sectors is zoned and distinct. Compositional variations lead to an increase in the unit cell parameters of eulytite. The reflecting properties of this mineral also depend on its composition.

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