SULFIDE MINERALIZATION OF THE LEBEDINOE DEPOSIT, CENTRAL ALDAN

Svetlana N. Nenasheva, Vladimir Y. Karpenko, Leonid A. Pautov
IRAS Fersman Mineralogical Museum, RAS, Moscow, nenashevasn@mail.ru

The results of examination of minerals from the Lebedinoe deposit are discussed. In addition to previously described mineral species, digenite, anilite, spionkopite, yarrowite, pyrrohotite-5*c*, and minerals of the fahlore family (Zn-bearing tetrahedrite – sandbergerite, tetrahedrite-tennantite, and tennantite) were identified in the ore of the deposit. Anisotropic arsenosulvanite with well-formed polysynthetic twins has been found.
6 figures, 3 tables, 7 references.
Keywords: digenite, anilite, spionkopite, yarrowite, fahlores, Lebedinoe deposit.

Introduction

Margarita I. Novgorodova gave us for investigation the specimens from the Lebedinoe deposit (ore body Orochon, prospecting pit No 7 dumps) collected by A.I. Fastalovich in 1941 and stored in the collection by N.V. Petrovskaya.

The Lebedinoe deposit was described in detail in the article by Nenashava and Karpenko (this volume) according to Fastalovich and Petrovskaya (1940), and Petrovskaya (1973). Here, we give brief description only. The sequence of the Cambrian weakly metamorphosed dolomite overlapping eroded surface of granite plutons cutting ancient rocks is intruded by the Upper Jurassic-Lower Cretaceous numerous small bodies. These are predominantly stocks, laccoliths, and dykes of intermediate rocks of elevated alkalinity. The metasomatic sulfide-carbonate bodies occasionally as vein apophysises are hosted in dolomite along horizontal fractures (Petrovskaya, 1973). The primary ore minerals are dominated by pyrite; chalcopyrite occurs also; hematite is identified in some veins; galena, sphalerite, pyrrhotite, galenobismutite, tetrahedrite, native gold, bornite, cobaltite, and sulvanite are less frequent. Supergene minerals are iron hydroxides, jarosite, cuprite, chalcocite, covellite, malachite, azurite, cerussite, gypsum, and melanterite (Fastalovich and Petrovskaya, 1940).

Analytical techniques and results

The thin polished sections were studied with an OPTON microscope. The chemical composition was determined with a CamScan-4D scanning electron microscope equipped with a Link ISIS EDS operating at accelerated voltage 20 kV and beam current of 4 nA.

Microscopically, heterogeneous objects studied here are composed of ore minerals (pyrite, galena, and bornite are major minerals) enclosed in quartz-carbonate-arsenate matrix. The grains of fahlores, sulvanite, arsenosulvanite, and famatinite were found in galena. In addition, the segregations of pyrrhotite, covellite, digenite, anilite, spionkopite, yarrowite were determined with electron microprobe.

Fahlores are mainly antimonial. Tetrahedrite enriched in Zn, sandbergerite (Table 1, an. 1–24), was identified to be associated with galena, famatinite, arsenosulvanite, and anglesite (Fig. 1, 2). Content of Zn is variable (5.14–8.07 wt.% corresponding to 1.32–2.04 *apfu*). Concentration of Sb ranges from 23.53 to 28.16 wt.% that exceeds 3 *apfu* corresponding to 3.25 and 3.85 *apfu*. There is no clear correlation between Zn and As, but Sb and Zn+Ag are positively correlated. Such correlation was previously reported by Mozgova and Tsepin (1983) for fahlores. Anglesite $Pb[SO_4]$ occurs at the contact between sandbergerite and galena (Fig. 1, 2). Its composition is as follows, wt.%: 67.06 Pb, 10.82 S, 21.38 O, total is 99.26. Formula is: $Pb_{0.97}S_{1.01}O_{4.01}$.

The intermediate members of the tetrahedrite-tennantite series and tennantite (Table 1, an. 25–31) are associated with sulvanite, arsenosulvanite, and Cu-Ca arsenate (probably, tyrolite, $Ca_2Cu_5^{2+}(OH,O)_4(AsO_4)_2(CO_3)\cdot 6H_2O$, or clinotyrolite, $Ca_2Cu_9^{2+}(OH,O)_{10}[(AsO_4),(SO_4)]_4\cdot 10H_2O$) (Fig. 3).

As and Sb are negatively correlated in the intermediate members of the tetrahedrite-tennantite series and tennantite. Arsenate formed after arsenosulvanite occasionally fills veinlets, where grains of tennantite are

Table 1. **Electron microprobe data of tennantite-tetrahedrite, wt.%**

№ an.	Sample	Cu	Ag	Fe	Zn	Cd	Pb	Sb	As	S	Se	∑
1	242 (loc. 1)	34.90	2.83	0.40	6.91	1.10	0.71	25.70	1.68	23.75		97.98
2		35.80	1.72	0.26	6.41	1.05	0.78	25.54	1.64	24.13		97.33
3		35.77	1.58	0.33	6.44	0.82	0.87	26.62	0.59	24.17		97.34*
4		38.06	1.61	0.32	7.01	0.79	0.90	26.47	1.47	24.59		101.22
5		37.89	1.96	0.14	6.52	0.92	0.85	27.53	0.43	24.80		101.04
6		38.75	1.00	0.18	6.34	0.79	1.29	25.54	1.85	24.18		99.92
7		37.83	1.87	0.33	6.56	1.27	0.06	28.16	0.06	25.03		101.17
8		35.38	4.37	0.50	6.83	0.28	1.25	25.88	1.99	24.92	0.42	101.82
9		37.22	1.68	0.50	6.34	1.28	0.99	27.61	0.34	24.26	0.22	100.44
10		38.85	1.87	0.49	6.43	0.89	1.30	28.23	0.33	24.51	0.05	100.95
11	242 (loc. 4)	35.98	4.11	0.36	6.79	0.74	0.93	27.31	0.23	24.22		100.67
12	242 (loc. 2)	38.16	0.65	0.15	7.21	0.40	0.26	25.21	2.11	25.10		99.25
13		37.66	0.91	0.19	8.06	0.15	1.12	24.79	2.20	24.94	0.41	100.43
14		37.70	0.92	0.19	8.07	0.17	0.00	24.69	2.21	25.12	0.41	99.48
15	242 (loc. 3)	36.02	2.63	0.22	7.09	0.35	0.47	26.96	0.25	24.61	0.37	99.23
16		37.81	1.91	0.31	7.48	0.39	0.78	26.33	0.72	24.99	0.13	100.85
17	242 (loc. 6)	35.53	2.78	0.55	6.68	1.93	1.61	26.84	0.00	23.96		100.31
18		33.86	5.40	0.69	5.73	1.45	0.15	25.33	0.96	23.89		97.96
19		35.41	2.89	0.64	5.66	1.42	1.40	26.49	0.05	23.34	0.18	97.48
20		35.30	2.28	0.65	5.71	1.82	1.60	26.82		23.82		98.0
21		35.09	2.54	0.48	5.77	1.78	1.08	26.06	0.09	23.08	0.13	96.41
22		36.74	2.76	0.91	5.39	2.01	1.37	26.73	0.40	24.80		101.11
23	242 (loc. 5)	37.47	2.35	0.00	5.14	2.23	0.83	23.53	3.02	24.87		99.44
24		35.91	3.38	0.53	5.68	2.10	1.60	25.36	0.93	24.25		99.74
25	242/1 (loc. 1)	41.14	0.18	0.56	7.30	0.27	0.32	15.03	9.45	26.58		100.83
26		42.07	0.16	0.57	7.67	0.17	0.89	14.09	9.43	26.31		101.36
27	242/6 (loc. 1)	45.64		5.69	0.27			1.89	19.58	28.74		101.81
28		45.80		6.07				1.36	20.42	28.95		102.60
29		45.20		5.44				1.77	20.39	28.79		101.59
30	242/5 (loc. 1)	45.06		6.79	0.43			1.53	19.18	28.84		101.83
31		46.61		5.23	0.35			1.47	19.02	28.55		101.23

№ an.	Sample	Formula calculated on the sum of 29 atoms	Valence balance Δ, %
1	242 (loc. 1)	$(Cu_{9.51}Ag_{0.45})_{9.96}(Zn_{1.83}Fe_{0.12}Cd_{0.17}Pb_{0.06})_{2.18}(Sb_{3.65}As_{0.39})_{4.04}S_{12.82}$	3.0
2		$(Cu_{9.73}Ag_{0.28})_{10.01}(Zn_{1.69}Cd_{0.16}Fe_{0.08}Pb_{0.06})_{1.99}(Sb_{3.62}As_{0.38})_{4.00}S_{12.99}$	0.1
3		$(Cu_{9.74}Ag_{0.26})_{10.00}(Zn_{1.71}Cd_{0.12}Fe_{0.10}Pb_{0.07})_{2.00}(Sb_{3.78}As_{0.14}Ge_{0.03})_{3.95}S_{13.04}$	0.8
4		$(Cu_{9.97}Ag_{0.25})_{10.22}(Zn_{1.79}Cd_{0.12}Fe_{0.10}Pb_{0.07})_{2.08}(Sb_{3.62}As_{0.33})_{3.95}S_{12.76}$	2.7
5		$(Cu_{9.97}Ag_{0.30})_{10.27}(Zn_{1.67}Cd_{0.14}Fe_{0.04}Pb_{0.07})_{1.92}(Sb_{3.78}As_{0.10})_{3.88}S_{12.93}$	0.3
6		$(Cu_{10.27}Ag_{0.16})_{10.43}(Zn_{1.64}Cd_{0.12}Fe_{0.06}Pb_{0.10})_{1.92}(Sb_{3.53}As_{0.41})_{3.94}S_{12.70}$	2.6
7		$(Cu_{9.90}Ag_{0.29})_{10.19}(Zn_{1.67}Cd_{0.19}Fe_{0.10})_{1.96}(Sb_{3.85}As_{0.01})_{3.86}S_{12.90}$	1.1
8		$(Cu_{9.27}Ag_{0.68})_{9.95}(Zn_{1.74}Fe_{0.15}Cd_{0.04}Pb_{0.10})_{2.03}(Sb_{3.54}As_{0.44})_{3.98}(S_{12.94}Se_{0.09})_{13.03}$	0.4
9		$(Cu_{9.91}Ag_{0.26})_{10.17}(Zn_{1.64}Cd_{0.19}Fe_{0.15}Pb_{0.08})_{2.06}(Sb_{3.84}As_{0.08})_{3.92}(S_{12.80}Se_{0.05})_{12.85}$	1.3
10		$(Cu_{9.78}Ag_{0.29})_{10.07}(Zn_{1.66}Cd_{0.13}Fe_{0.15}Pb_{0.11})_{2.05}(Sb_{3.91}As_{0.08})_{3.99}(S_{12.89}Se_{0.01})_{12.90}$	1.3
11	242 (loc. 4)	$(Cu_{9.61}Ag_{0.65})_{10.26}(Zn_{1.76}Cd_{0.11}Fe_{0.11}Pb_{0.08})_{2.06}(Sb_{3.81}As_{0.05})_{3.86}S_{12.82}$	1.2
12	242 (loc. 2)	$(Cu_{10.00}Ag_{0.10})_{10.10}(Zn_{1.84}Cd_{0.06}Fe_{0.05}Pb_{0.02})_{1.97}(Sb_{3.44}As_{0.47})_{3.91}S_{13.03}$	1.1
13		$(Cu_{9.82}Ag_{0.14})_{9.96}(Zn_{2.04}Fe_{0.06}Cd_{0.02}Pb_{0.09})_{2.21}(Sb_{3.37}As_{0.49})_{3.86}(S_{12.88}Se_{0.09})_{12.97}$	0.1
14		$(Cu_{9.82}Ag_{0.14})_{9.96}(Zn_{2.04}Fe_{0.06}Cd_{0.03})_{2.13}(Sb_{3.36}As_{0.49})_{3.85}(S_{12.97}Se_{0.09})_{13.06}$	1.0

Table 1. **Cont.**

№ an.	Sample	Formula calculated on the sum of 29 atoms	Valence balance Δ, %
15	242 (loc. 3)	$(Cu_{9.62}Ag_{0.41})_{10.03}(Zn_{1.84}Fe_{0.07}Cd_{0.05}Pb_{0.04})_{2.00}(Sb_{3.76}As_{0.06}Te^{4+}_{0.03})_{3.83}(S_{13.03}Se_{0.07})_{13.10}$	2.2
16		$(Cu_{9.88}Ag_{0.30})_{10.18}(Zn_{1.90}Fe_{0.09}Cd_{0.06}Pb_{0.06})_{2.11}(Sb_{3.59}As_{0.16})_{3.75}(S_{12.94}Se_{0.03})_{12.97}$	1.0
17	242 (loc. 6)	$(Cu_{9.58}Ag_{0.44})_{10.02}(Zn_{1.75}Fe_{0.17}Cd_{0.29})_{2.21}(Sb_{3.78}Te_{0.06})_{3.84}S_{12.80}$	1.6
18		$(Cu_{9.28}Ag_{0.87})_{10.15}(Zn_{1.52}Cd_{0.23}Fe_{021}Pb_{0.01})_{1.97}(Sb_{3.62}As_{0.22}Bi_{0.14})_{3.98}S_{12.98}$	0.3
19		$(Cu_{9.80}Ag_{0.47})_{10.27}(Zn_{1.52}Cd_{0.22}Fe_{0.20}Pb_{0.12})_{2.06}(Sb_{3.82}As_{0.01})_{3.83}(S_{12.79}Se_{0.04})_{12.81}$	1.0
20		$(Cu_{9.69}Ag_{0.37})_{10.06}(Zn_{1.52}Cd_{0.28}Fe_{0.20}Pb_{0.14})_{2.06}Sb_{3.84}S_{12.95}$	0.2
21		$(Cu_{9.81}Ag_{0.42})_{10.23}(Zn_{1.57}Cd_{0.28}Fe_{0.15}Pb_{0.09})_{2.09}(Sb_{3.80}As_{0.02}Bi_{0.02}Te^{4+}_{0.02})_{3.86}(S_{12.79}Se_{0.03})_{12.82}$	1.4
22		$(Cu_{9.72}Ag_{0.43})_{10.15}(Zn_{1.39}Fe_{0.28}Cd_{0.30}Pb_{0.11})_{2.08}(Sb_{3.69}As_{0.09})_{3.78}S_{13.00}$	1.3
23	242 (loc. 5)	$(Cu_{9.92}Ag_{0.37})_{10.29}(Zn_{1.32}Cd_{0.33}Pb_{0.07})_{1.72}(Sb_{3.25}As_{0.68})_{3.93}S_{13.05}$	2.2
24		$(Cu_{9.66}Ag_{0.54})_{10.20}(Zn_{1.49}Cd_{0.32}Fe_{0.16}Pb_{0.13})_{2.10}(Sb_{3.56}As_{0.21})_{3.77}S_{12.93}$	0.6
25	242/1	$(Cu_{10.13}Ag_{0.03})_{10.16}(Zn_{1.74}Fe_{0.16}Cd_{0.04}Pb_{0.02})_{1.96}(As_{1.97}Sb_{1.93})_{3.90}S_{12.97}$	0.6
26		$(Cu_{10.33}Ag_{0.02})_{10.35}(Zn_{1.83}Fe_{0.16}Cd_{0.02}Pb_{0.07})_{2.08}(As_{1.96}Sb_{1.81})_{3.77}S_{12.80}$	0.8
27	242/6 (loc. 1)	$Cu_{10.00}(Cu^{2+}_{0.43}Fe_{1.48}Zn_{0.06})_{1.97}(As_{3.79}Sb_{0.23})_{4.02}S_{13.01}$	0.8
28		$Cu_{10.00}(Cu^{2+}_{0.37}Fe_{1.56})_{1.93}(As_{3.92}Sb_{0.16})_{4.02}S_{12.99}$	0.5
29		$Cu_{10.00}(Cu^{2+}_{0.35}Fe_{1.42})_{1.77}(As_{3.96}Sb_{0.21})_{4.17}S_{13.06}$	0.3
30	242/5 (loc. 1)	$Cu_{10.00}(Cu^{2+}_{0.25}Fe_{1.76}Zn_{0.10})_{2.11}(As_{3.70}Sb_{0.18})_{3.88}S_{13.01}$	0.6
31		$Cu_{10.00}(Cu^{2+}_{0.70}Fe_{1.36}Zn_{0.08})_{2.14}(As_{3.70}Sb_{0.18})_{3.88}S_{12.98}$	0.2

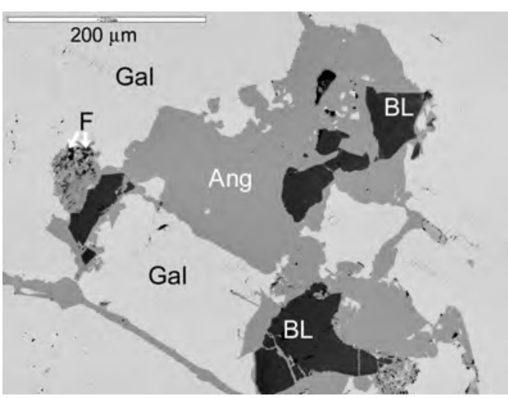
Notes: (1–24) Zn-bearing tetrahedrite (sandbergerite), (25, 26) tennantite-tetrhedrite, (27–31) tennantite. Including, wt. % : 0.15 Ge (an. 3), 0.26 Te (an. 15), 0.43 Te (an. 17), 0.12 Te (an. 21), 0.50 Bi (an. 18), and 0.19 Bi (an. 21).

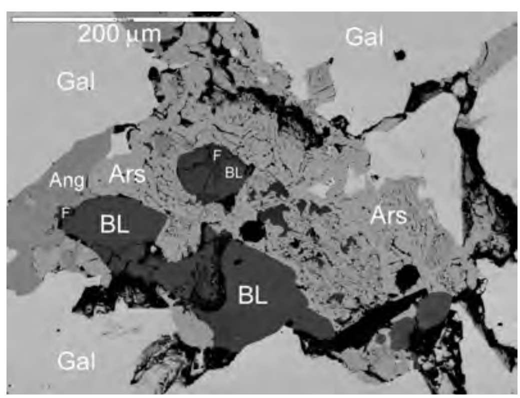
Table 2. **Electron microprobe data of famatinite, wt.%**

№ an.	Sample	Cu	Ag	Zn	Cd	Sb	Pb	S	Σ
1	242 (loc. 1)	42.71	0.58		0.42	26.26	0.88	28.65	99.56*
2	242 (loc. 6)	42.56	0.28	0.10	0.02	24.95	2.39	29.10	99.65**
3		41.00	0.38	0.11		24.56	3.78	28.21	98.04
№ an.	Sample	Formula calculated on the sum of 64 atoms							Valence balance Δ, %
1	242 (loc. 1)	$(Cu^{+}_{7.81}Ag_{0.19})_{8.00}(Cu^{2+}_{16.15}Fe_{0.04}Cd_{0.13}Pb_{0.15})_{16.47}Sb_{7.68}S_{31.85}$							0.4
2	242 (loc. 6)	$(Cu^{+}_{7.91}Ag_{0.09})_{8.00}(Cu^{2+}_{15.89}Zn_{0.06}Cd_{0.01}Pb_{0.41})_{16.37}Sb_{7.28}S_{32.25}Se_{0.10}$							3.3
3		$(Cu^{+}_{7.87}Ag_{0.13})_{8.00}(Cu^{2+}_{15.73}Zn_{0.06}Pb_{0.66})_{16.45}Sb_{7.37}S_{32.17}$							2.1

*Notes: Including * Fe – 0.06, ** Se – 0.25.*

Fig. 1. Segregations of sandbergerite (BL) and famatinite (F) enclosed in galena (Gal) and anglesite (Ang). BSE image.
Fig. 2. Grains of sandbergerite (BL), famatinite (F), and anglesite (Ang) enclosed in matrix of galena (Gal) and arsenosulvanite (Ars). BSE image.





found. Betekhtin (1941), who described arsenosulvanite for the first time, denoted probable occurrence of tyrolite in the ore of the Lebedinoe deposit. He suggested that bright green powder crusts, which are oxidizing products of arsenosulvanite, are certain intermediate variety between copper vanadates, turanite, $Cu_5(VO_4)_2(OH)_4$, or volborthite, $(Cu,Zn,Ni)_3V_2O_7(OH)_2 \cdot 2H_2O$), and copper arsenate, tyrolite, $CaCu_5^{2+}(AsO_4)_2(CO_3)(OH)_4 \cdot 6H_2O$, or erythrine, $Co_3(AsO_4)_2 \cdot 8H_2O$.

As aforementioned, famatinite is associated with sandbergerite and galena. It occurs as small grains up to 10 microns in size. In reflected light, this mineral has weak pink tint in comparison with sandbergite and is anisotropic (Fig. 1, 2; Table 2).

Sulvanite and arsenosulvanite are discussed in this volume in the article by Nenasheva and Karpenko.

The composition of galena (Fig. 1, 2) close to theoretical is as follows, wt.%: 87.44 and 86.30 Pb and 13.82 and 13.46 S, total is 101.26 and 99.76. Valence balance is 2.0 and 0.9%, respectively. Formula is as follows: $PbS_{1.02}$ and $PbS_{1.01}$.

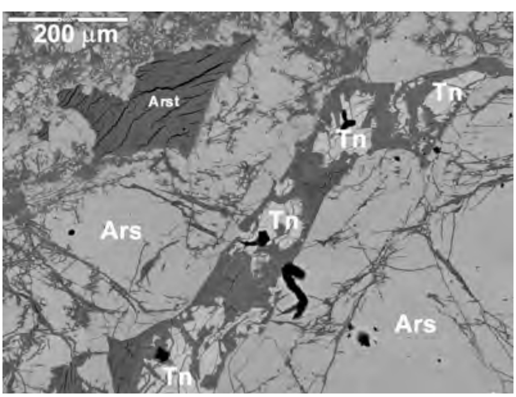
Four compositions of pyrite (Fig. 4 – 6; Table 3, an. 1 – 4) are not different from each other, exceptionally compositions 2 and 3, where small content of Cu was detected 0.87 and 0.71 wt.%, respectively that correspond to 0.02 and 0.1 *apfu*. Ramdohr (1962) noted that copper admixture in pyrite is caused most likely by mechanical contamination, but in our cases it is microimpurity.

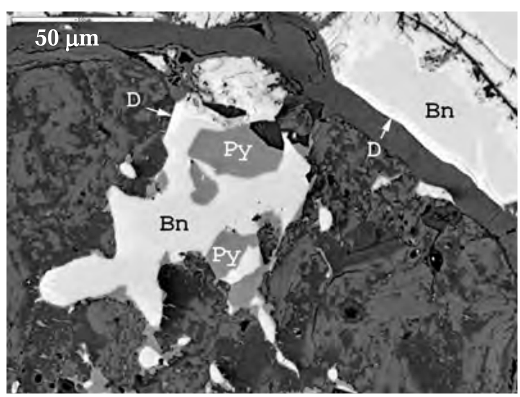
The grain of pyrrhotite-5*C* $Fe_7^{2+}Fe_2^{3+}S_{10}$ (Table 3, an. 5) containing Cu impurity was identified in association with arsenosulvanite, pyrite, chalcopyrite, and copper arsenate, probably tyrolite. The calculated formula of this pyrrhotite is $Fe_{8.67}Cu_{0.31}S_{10.01}$ or $(Fe_{6.67}Cu_{0.31})^{2+}_{6.98}Fe^{3+}_{2.00}S_{10.01}$ that corresponds ideally to theoretical composition.

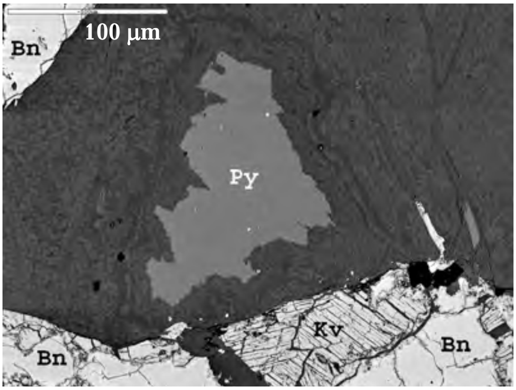
Compositions of bornite are close to theoretical $Cu_{5+x}FeS_{4-x}$, Cu_5FeS_4 or $Cu_{5-x}FeS_{4+x}$ (Table 3, an. 6 – 8; Fig. 4 – 6).

The results of the examination of the material that looks like covellite in reflected light are of interest. Large areas (up to 300×200 microns) are broken down by cleavage in plates up to 10 – 15 microns wide (Fig. 5, 6). In reflected light, the mineral is light blue; bireflectance ranges from light gray with bluish tint to bright light blue; anisotropy varies from light gray to pink, bright blue, and orange. Compositions of different plates are recalculated to formulas corresponding to different minerals of the Cu-S system: compositions 13 and 14 (Table 3) are recalculated to the formula corresponding to anilite, $Cu_7S_4 \rightarrow Cu_6^{+}Cu^{2+}S_4$; composition 15 (Table 3) corresponds to the mixture of spionkopite $Cu_{39}S_{28} \rightarrow Cu_{22}^{+}Cu_{17}^{2+}S_{28}$ and yarrowite $Cu_9S_8 \rightarrow Cu_2^{+}Cu_7^{2+}S_8$; and compositions 9 and 10 (Table 3) corresponds to covellite CuS or $3CuS \rightarrow Cu_2^{+}S \cdot Cu^{2+}[S_2]$ (Fig. 5, 6). It is easy to note that amount of bivalent copper increases toward covellite indicating increasing of mineralizing fluid acidity during mineral formation. According to the experimental data, sulfides containing lesser Cu (Cu^{+} and Cu^{2+}) are more stable with pH decreasing. They are uncharged because of partial oxidation of Cu to bivalent state. Rickard (1973) synthesized djurleite $Cu_{31}S_{16} \rightarrow Cu_{30}^{+}Cu^{2+}S_{16}$ (pH > 7.5) and covellite (pH < 7) at low temperature close to oxidative zone as a result of interaction of Na_2S and Cu_2O. Experimental data (Whiteside and Goble, 1986) of copper leaching from synthetic chalcocite and digenite

Fig. 3. Tennantite (Tn) in veinlet of Cu-Ca arsenate (Arst), (probable tyrolite) enclosed in arsenosulvanite (Ars). BSE image.
Fig. 4. Bornite (Bn), pyrite (Py), and digenite (D) enclosed in Cu carbonates and Cu-Ca arsenates. BSE image.







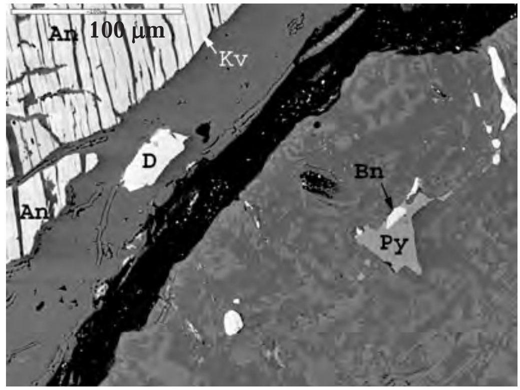


Fig. 5. Pyrite (Py), covellite (Kv), bornite (Bn) enclosed in intergrown Cu carbonates and Cu-Ca arsenates. BSE image.
Fig. 6. Covellite (Kv), annilite (An), bornite (Bn), digenite (D), and pyrite (Py) in matrix of supergene minerals. BSE image.

Table 3. **Electron microprobe data of sulfides, wt.%**

№ an.	Sample	Fe	Cu	S	∑	Formula	Valence balance Δ, %
1	245/1 (loc. 1)	45.92		51.87	97.79	$FeS_{1.97}$	
2	245/1 (loc. 3)	45.72	0.87	52.08	98.67	$FeCu_{0.02}S_{1.98}$	
3		44.91	0.71	52.23	97.85	$FeCu_{0.01}S_{2.02}$	
4	245/1 (loc. 5)	46.38		52.41	98.79	$FeS_{1.97}$	
5	242/6 (loc. 3)	57.41	2.32	38.04	97.77	$Fe_{8.67}Cu_{0.31}S_{10.01}$ or	
						$(Fe_{6.67}Cu_{0.31})^{2+}_{6.98}Fe^{3+}_{2.00}S_{10.01}$	0.2
6	245/1 (loc. 3)	12.63	60.27	25.75	98.65	$Cu_{4.80}Fe_{1.14}S_{4.06}$	1.2
7	245/1 (loc. 5)	11.00	63.80	25.45	100.25	$Cu_{5.03}Fe_{0.98}S_{3.98}$	0.4
8		11.28	62.48	25.46	99.22	$Cu_{4.97}Fe_{1.02}S_{4.01}$	0.1
9	245/1 (loc. 5)		71.22	29.79	101.01	$Cu_{1.09}S_{0.91}$	
10			71.91	28.47	100.38	$Cu_{1.12}S_{0.88}$	
11	245/1 (loc. 1)	0.76	78.35	21.79	100.90	$Cu^{+}_{7.96}Cu^{2+}_{1.00}Fe_{0.10}S_{4.94}$	2.8
12		0.66	78.21	22.20	101.07	$Cu^{+}_{7.90}Cu^{2+}_{1.00}Fe_{0.08}S_{5.01}$	0.4
13	245/1 (loc. 1)		77.37	22.29	99.66	$Cu^{+}_{6.00}Cu^{2+}_{1.00}S_{4.00}$	0.0
14			77.50	23.18	100.68	$Cu^{+}_{5.91}Cu^{2+}_{1.00}S_{4.09}$	3.0
15			72.27	27.78	100.05	$Cu^{+}_{12.00}Cu^{2+}_{11.84}S_{18.16}$*	1.8

*Notes: (1–4) Pyrite, (5) pyrrhotite-5C, (6–8) bornite, (9, 10) covellite, (11, 12) digenite, (13, 14) anilite, and (15) intermediate composition between spioncopite $Cu_{39}S_{28} \rightarrow Cu^{+}_{22}Cu^{2+}_{17}S_{28}$ and yarrowite $Cu_9S_8 \rightarrow Cu^{+}_{2}Cu^{2+}_{7}S_8$ (15). *This formula calculated for intermediate composition between spionkopite and yarrowite.*

with iron sulfate acidic solution testify that action of this reagent upon digenite results in the formation of anilite followed by spionkopite, yarrowite, and covellite. The conclusion of decreasing pH with temperature decreasing is supported by relicts of digenite as small euhedral grains up to 20–30 microns in size enclosed in supergene minerals, carbonates, copper arsenates, iron sulfates (Fig. 6; Table 3, an. 11, 12). Occasionally bornite is rimmed by digenite (Fig. 4). In compositions 10 and 11, 0.76 and 0.66 wt.% Fe were detected, respectively, corresponding to 0.10 and 0.08 *apfu*. Digenite is stable in alkaline environment.

Conclusions

Previously unknown minerals were found at the Lebedinoe deposit. These are minerals of the chalcocite polysomatic series depleted in copper in comparison with chalcocite: digenite, anilite, and mixture (probably fine intergrowths) of spionkopite and yarrowite. In addition anisotropic arsenosulvanite and anglesite are described.

Digenite, anilite, spinonkopite, and yarrowite indicate changing acidity of fluid during mineralizing process. Digenite is stable within wide range of temperature and alkaline environment, whereas anilite and spionkopite and yarrowite are stable within narrow range of temperature from 0 to 30°C and from 0 to 157°C, respectively are formed in acidic environment. Covellite is stable at 0—507°C and acidic environment.

Fahlores of the Lebedinoe deposit are Zn-bearing tetrahedrite — sandbergerite associated with galena, anglesite, arsenosulvanite, and famatinite and tetrahedrite-tennantite and tennantite associated with sulvanite, arsenosulvanite, and Cu-Ca arsenate (probably, tyrolite or clinotyrolite).

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