

UDC 549.322 (571.511)

MINERALS OF THE NICKELINE-BREITHAUPTITE SERIES FROM METAMORPHOGENIC-HYDROTHERMAL VEINS OF THE NORILSK ORE FIELD

Yulia D. Gritsenko, Ernst M. Spiridonov
Lomonosov Moscow State University, *mineral@geol.msu.ru*

The antimonide-arsenide mineralization of the Norilsk ore field, which was considered by previous researchers as a derivative of the P₂-T₁ trap formation, is connected with the post-trap regional metamorphism in conditions of zeolite facies with age 164-122 MA. The antimonide-arsenide mineralization is younger than a trap formation for more than 80 MA. Arsenides and antimonides of Ni (Co, Fe) occur among the metamorphosed Ni-Cu sulphide ores and in the nearest periphery of their deposit, mainly in the calcite and anhydrite-calcite veins. Parameters of vein formation are as follows: P = 0.9-0.1 kbar, T = 216-127°C, solutions NaCl-MgCl₂ of low salinity (0.2-1.4% equiv. NaCl). History of formation of metamorphogenic-hydrothermal aggregations is complicated. Three cycles of the antimonide-arsenide mineralization are revealed. The first cycle includes ten mineral complexes with significantly arsenide composition; presence of nickeline with high content of Co, diarsenides, and triarsenides of Ni-Co is characteristic. The second cycle includes two mineral complexes with significantly antimonide composition; presence of silver minerals is characteristic. The third cycle is represented by the sulphoarsenide-sulphoantimonide mineral complex.

The minerals of the nickeline-breithauptite continuous series form a considerable part of the antimonide-arsenide mineralization. The end-members of the series, nickeline and breithauptite, are the most widespread; antimony nickeline is quite wide distributed. The Norilsk nickeline contains up to 12 wt % of Co, up to 3 wt % of Fe and S. Breithauptite is poor by Co, Fe, S, Se. In concentrates of nickeline, Pd, Pt, and Au were not detected. The zones of geometrical selection are present in the aggregates of arsenides and antimonides; that is an evident of crystallization of arsenides and antimonides from the normal solutions in open space.

9 tables, 9 figures, 24 references.

Introduction

The arsenide mineralization is not characteristic for the magmatic Ni-Cu ores. Such mineralization occurs in the metamorphosed types of these ores (Schneiderhohn, 1953a; Yakovlev *et al.*, 1981; Leblanc *et al.*, 1990; Hytonen, 1999).

Nickeline, NiAs, and breithauptite, NiSb, are distributed in different types of hydrothermal deposits, especially they are characteristic for deposits of the five-element formation and close to them nickel-cobalt-arsenide deposits (Krutov, 1959; Ramdohr, 1962; Dymkov, 1985; Chvileva *et al.*, 1988). In these deposits, nickeline usually predominates (Bou-Azzer, Morocco; Khovu-Aksy, Tuva, etc.). Breithauptite prevails significantly rarely (Wittichen, German). In single deposits of the five-element formation (Belorechenskoe, Northern Caucasus), the intermediate members of the nickeline-breithauptite isomorphous series are also widespread (Pekov, 1993). Our observations have shown that minerals in the limits of a whole series of nickeline-breithauptite occur at the Norilsk ore field.

The Ni-Co-arsenide mineralization in the Norilsk sulphide Cu-Ni ores is known nearly 50 years (Godlevskii, 1959, etc.). Maucherite was exactly detected by E.A. Kulagov (Kulagov, 1968; Kulagov, Evstigneeva, 1971); nickeline, gersdorffite, and breithauptite were deter-

mined by L.N. Vyal'sov and V.M. Izoitko (Izoitko, Vyal'sov, 1973; Genkin *et al.*, 1981). V.V. Distler with co-authors characterized nickeline, maucherite, safflorite, loellingite, ramelsbergite, gersdorffite, breithauptite, and native arsenic (Distler *et al.*, 1975). A.I. Ponomarenko has found palladium-bearing breithauptite among nests of the initial Pt-Pd intermetallics of the Norilsk ores (Ponomarenko, Malov, 1991). Later, S.F. Sluzhenikin has described cobaltite in assemblage with the Ni arsenides, native bismuth, minerals of silver, and uraninite (Sluzhenikin, Mokhov, 2002). In the mentioned works are the single chemical analyses of arsenides and antimonides, images of distribution of elements in their aggregates.

Arsenide mineralization of the Norilsk ore field have been studied by us on materials of our expedition collections of 1998-2003 (Talnakhskoe and Oktyabr'skoe deposits), more earlier collections of E.A. Kulagov (Noril'skoe deposit), on collections of geologists of the Norilsk industrial complex, E.V. Sereda, S.N. Belyakov, A.N. Glotov, V.N. Serenko. Several hundreds samples have been studied, including the large lumps of ore. Size of most aggregations of arsenides and antimonides of Ni and Co is less than 3 mm. For their exposure the samples was cut up, including cutting up along the little-thick carbonate veins. Some details of

three-dimensional correlations of arsenides were studied with the X-ray microtomograph instrument VT50-1 DIATOM. In 60 polished sections and polished lumps of ore, nearly 700 microprobe analyses of ore and vein minerals, nearly 150 photos in reflected electrons and images of distribution of chemical elements in characteristic radiation were made (X-ray microprobe instrument CAMECA SX-50; electron microscope Link 10000, analyst N.N. Korotaeva). Contents of Pd, Pt, and Au in arsenides from the calcite veins were detected in the laboratory of G.M. Varshall in GEOKHI RAS under the guidance of I.Ya. Koshcheeva. Thermobarogeochemical study of fluid inclusions in carbonates of arsenide veins was made in IGEM RAS under the guidance of V.Yu. Prokof'ev.

Geological position and parameters of formation of the antimonide-arsenide mineralization of the Norilsk ore field

The Norilsk region is located in the zone of the edge dislocations on the northwest of the East-Siberian platform. This area has a maximal thickness of platform mantle, formed by several structural stages (Malich, 1975). The first stage consists of the V-C₁ sea deposits with thickness 3-8 km; these are terrigenous-carbonate rocks and evaporites, including anhydrite rocks with lenses of halite and aggregations of naphthides. The second stage is composed by the coal-bearing rocks of the C₂-P₁ Tungus series with thickness up to 1 km. The third stage is formed by the P₂-T₁ trap formation (245±5 MA). This is a lava series of basalts with subordinate tuffs and other volcano-sedimentary rocks with thickness up to 4 km, which is accompanied by numerous intrusions of dolerites and gabbro-dolerites, including ore-bearing ones. Terrigenous sediments of J, K, and KZ lie on the rocks of trap formation in the form of separate spots.

The ore-bearing ultrabasite-basite intrusions are the ribbon-shaped bodies with thickness up to 300 m, which are controlled by a zone of the Norilsk-Kharaelakh fault. They have crossed and metamorphized the sedimentary series of Silurian and Devonian, coal-bearing rocks of the Tungus series, the lower parts of trap formation. The magmatic sulphide Ni-Cu ores (compact deposits, lenses, veins, zones of impregnation) has age 245±3 MA (Zolotukhin, 1997, etc.). They lie at the near bottom parts of intrusions and below intrusions within the bounds of aureole of contact metamorphism

(Godlevskii, 1959; Stepanov, Turovtsev, 1988).

Formations of 1st, 2nd, and 3rd stages of platform mantle of northwest of the East-Siberian platform, including gabbroids of the ore-free and ore-bearing intrusions and magmatic sulphide ores, underwent post-trap regional metamorphism (Spiridonov *et al.*, 2000). Trend of metamorphism is as follows: the 1st stage in conditions of the low-temperature part of zeolite facies (232-196 MA); the 2nd stage in conditions of high-temperature part of zeolite facies to prehnite-pumpellyite facies (184-164 MA); and the 3rd stage in conditions from the high-temperature to the most low-temperature part of zeolite facies (164-122 MA) (Spiridonov *et al.*, 2000). The zeolite, agate, and datolite mineralizations are connected with the first stage; they were significantly changed during metamorphism of the second stage. The copper-zeolite formation, aggregations of the Zn, Pb, Cu, Mn, Cd sulphides, datolite, zeolite, arsenide mineralizations, deposits of Iceland spar are connected with the third stage of regional metamorphism. At that, magmatic sulphide and the low-sulphide Ni-Cu ores underwent visible, in separate parts considerable, changes. In these parts, the initial Fe-Cu-Ni sulphides are substituted by magnetite, valleriite, heazlewoodite, bornite, pyrite, marcasite, mackinawite, millerite, chalcocite, polydymite, tochilinite, Co-pentlandite, godlevskite, hematite in assemblage with anhydrite, carbonates, chlorite, serpentine, hydrogarnets, talc, prehnite, vermiculite, apophyllite, corrensite, xonotlite, muscovite, and quartz. At earlier stages of metamorphism the mineral assemblages enriched by chalcopyrite and millerite have appeared. The later formations are enriched by bornite, still more late formations – by chalcocite, and the latest formations are enriched by pyrite, marcasite, and the Ni-Fe-Co thiospinels.

Metamorphogenic-hydrothermal mineralization intensively occur in the zones of jointing, near any tectonic dislocations, especially in the zone of the Norilsk-Kharaelakh fault, and also among sedimentary rocks enriched by anhydrite and clay minerals. Combination of these two factors is characteristic for that part of the Talnakh deposit, which is worked by the Komsomol'skii mine. Arsenide mineralization of the same type occurs at all deposits of the Norilsk ore field and the most intensively in the mine Komsomol'skii.

The Rb-Sr age of apophyllite from arsenide-carbonate veins of the Norilsk ore field is 164 MA (Spiridonov *et al.*, 2001). Thus,

arsenide mineralization, which was considered as a derivative of the trap formation (Godlevskii, 1959, *etc.*), is younger than trap formation for more than 80 MA.

The antimonide-arsenide mineralization occurs within the bounds of the Ni-Cu ores deposit and outside it in the form of separate spots, nests, veins, impregnation, cement of breccias. The main mass of the Fe-Ni-Co arsenides and the Ni antimonides, native arsenic is in the carbonate, calcite-anhydrite, calcite-apophyllite veins and veinlets, often also containing sphalerite, wurtzite, chalcoprite, galena, pyrrhotite, magnetite, alabandite, greenockite. Morphology of the carbonate-arsenide veins is complicated, strike is predominantly NNW, bedding is usually steep to vertical, rarely flat; length is from share of meters to 30 m, thickness is to 60 cm. Size of the arsenides nests in the carbonate veins is to 20 cm. The calcite and calcite-anhydrite veins with native arsenic and loellingite occur within the limits of the sulphide ore deposits and beyond their bounds. Carbonate veins with the Ni-Co-Fe arsenides and the Ni antimonides occur among the sulphide Ni-Cu ores and in near periphery of their deposits. Impregnation of the Ni arsenides occurs in the metamorphosed Ni-Cu ores with the millerite-chalcoprite and pyrite-bornite-millerite composition. It is evidently, the surrounding sulphide Ni-Cu ores was a source of Ni and Co for antimonide-arsenide mineralization. Possibly, the Ni-Cu ores were also a source of As; in them, content of As is to 47 g/t (Czamanske *et al.*, 1992). In veins enriched by arsenides, calcite usually predominates, dolomite and anhydrite occur in a subordinate amount. Along contacts of these veins in the Ni-Cu ores, in the zone of 1-2 cm, pyrrhotite and chalcoprite are partly replaced by calcite and sphalerite.

Calcite in veins with arsenides and antimonides contains the initial nests of the gas-liquid inclusions with low salinity, 0.2-1.4% equiv. NaCl; NaCl and MgCl₂ are predominant components in the inclusions solution. Pressure, from 0.9-0.5 to 0.1 kbar, and temperature 216-203-181-175-172-147-127 °C were detected by these inclusions. Our estimations of temperatures are close to the results given in the work of V.V. Distler with co-authors (1975). The P and T parameters of arsenide mineralization correspond to parameters of formation of zeolite facies.

New actual data show that hydrothermal antimonide-arsenide mineralization of the Norilsk ore field is connected with the

post-trap regional metamorphism in conditions of zeolite facies.

Stages of antimonide-arsenide mineralization of the Norilsk ore field

Antimonide-arsenide mineralization of the Norilsk ore field has a number of stages. Occasionally, the crossings of the arsenide-carbonate veins with different mineral composition are observed. More often the brecciated early mineral aggregates are overgrown and/or partly replaced by the younger mineral complexes. Arsenide-carbonate veins are often zoned. Gouges of veins are usually composed by the earlier mineral assemblages; and central parts of veins consist of the later mineral assemblages. Taking into account these observations and the results of detailed mineral studies, three cycles of antimonide-arsenide mineralization were distinguished; each of them is represented by several mineral complexes. Mineral complex can include several generations of arsenides and antimonides. Mineral aggregates of arsenides and antimonides are often represented by spherocrystals and their intergrowths, which are usually named «pisolites», or «nodules», or «peas».

Antimonide-arsenide mineralization of the first cycle is closely associated with bornite-bearing ores. The general trend is from the Ni monoarsenide to diarsenides and triarsenides of Ni and Co. The first cycle is finished by the formation of native arsenic. Antimonide-arsenide mineralization of the second cycle is closely associated with chalcocite-bearing ores. The general trend is from diarsenides to antimonide and monoarsenide of Ni. The presence of native silver, silver sulphides, mercurial silver is characteristic. Mineralization of the third sulphoantimonide-sulphoarsenide cycle is associated with pyrite-bearing ores.

The first cycle includes nine mineral complexes of different age. The first complex is cobaltite-gersdorffite-maucherite-nickeline; it is represented by nodules in veins of white calcite and chlorite-calcite veins, by impregnation and nodules in the metamorphosed Ni-Cu ores. The second complex is maucherite-gersdorffite-nickeline; it is represented by the zoned nodules, which overgrow on aggregates of the first complex and partly substitute them. Combination of the low-antimony and high-antimony nickeline is characteristic. The third complex is represent-

ed by intergrowths of maucherite and breithauptite, which form separate aggregations and overgrow on aggregates of the second complex; they are edged by Sb-nickeline and rammelsbergite. Aggregates of the fourth, rammelsbergite-nickeline-breithauptite, complex overgrow on aggregates of the first and second complexes, partly substitute them. The fourth complex includes the members the whole nickeline-breithauptite series. The fifth complex is cobaltite-breithauptite-maucherite-nickeline; it is represented by the zoned nodules in veins of pink calcite; absence of intermediate members of the nickeline-breithauptite series is characteristic. Maucherite, breithauptite, and Co-nickeline of the sixth mineral complex overgrow on aggregates of the fifth complex. In seventh complex diarsenides (rammelsbergite, loellingite) alternating with nickeline prevail. Calcite-dolomite veins with the Ni-Co triarsenides of the eighth mineral complex cut arsenide-calcite veins. Triarsenides of the eighth complex overgrow on rammelsbergite of the seventh complex. Even more late and relatively widespread calcite-anhydrite and calcite-apophyllite veins with nests and spherulite aggregates of native arsenic and loellingite are distinguished as the ninth complex. Minerals of the ninth mineral complex often compose central parts of veins, which gouges are formed by aggregates of arsenides of the seventh complex.

The second cycle is characterized by predominance of the Ni antimonide, with trend from diarsenides to antimonide and monoarsenide of Ni; presence of parkerite, native silver, bismuth, and lead, mercurial silver, pyrrargyrite, clausthalite, uraninite is characteristic. The second cycle includes two mineral complexes. Nickeline, breithauptite, diarsenides of Ni and Fe, and maucherite of the tenth mineral complex compose the complex-zoned nodules. Sb-nickeline and breithauptite of the eleventh complex form intergrowths with native silver, mercurial silver, pyrrargyrite.

The third cycle includes only one, the twelfth, mineral complex, which is significantly sulphoarsenide-sulphoantimonide. Among arsenide nodules of the first two cycles the twelfth mineral complex is represented by the borders of substitution and the cutting veinlets of sulphoarsenides; among arsenide-antimonide nodules of the second cycle it is represented by the borders of substitution and the cutting veinlets of ullmannite.

Minerals of the nickeline-breithauptite series of the Norilsk ore field

It is represented expedient to give the description of these minerals separately for the concrete mineral complexes. The eighth, ninth, and twelfth mineral complexes do not contain the nickeline-breithauptite series minerals.

In the work, the through numeration of mineral analyses for all samples is used. The numbers of analyses in Tables and on Figures are the same.

The first mineral complex. The first mineral complex is represented by the large lamellar crystals of antimony-free nickeline, nodules composed by split crystals of nickeline, Sb-nickeline, maucherite overgrowing of sphalerite and wurtzite, by the Sb-nickeline borders on sphalerite and chalcopryrite, and by the maucherite borders on bornite and millerite.

The borders of Sb-nickeline around crystals of sphalerite and chalcopryrite (Fig. 1a) are the earliest from these formations. The content of antimony in this nickeline varies from 3 to 20 wt % (Tabl. 1, an. 443, 495). Central parts of nodules are composed by aggregates of high-antimony nickeline in intergrowth with separate nodules of maucherite (Fig. 1b); content of antimony in nickeline is to 22 wt % (an. 458, 556). Thin-split aggregates of the low-antimony and antimony-free nickeline overgrow on them, then are the long (1-15 mm) thin (0.01-0.05 mm) lamellar crystals of antimony-free nickeline (an. 544, 558). Typical formations of the first complex are the long lamellae of nickeline framed by the aggregate of Fe-Co-gersdorffite and Ni-cobaltite (Fig. 1c, d).

Content of antimony in nickeline I is from 1 to 22 wt%, it is reduced from the centre of nodules to the edge. Lamellar crystals of nickeline I is poor by antimony (an. 20, 544). Content of sulphur, cobalt, and iron in nickeline I is to 2 wt %.

The X-ray diffraction pattern of lamellar crystals of antimony-free nickeline is as follows: 2.65 Å(10) (101); 2.348 (2) (202); 1.960 (10) (102); 1.810 (5) (110); 1.479 (3) (103); the unit cell parameters, a_0 3.58 (1) Å and c_0 5.02 (6) Å, corresponds to standard nickeline.

The second mineral complex. The second complex includes aggregates of thin-split crystals of the low-antimony and Sb-nickeline, gersdorffite, maucherite, cobaltite, i.e. complex-zoned nodules with diameter 0.5-5 mm.

The early formations of the second complex are the most widespread: a) nickeline II from metamorphic ingrowths in aggregates of nickeline I, cobaltite, and gersdorffite. Nickeline II cuts off their borders and a picture of their zoning (Fig. 1c); b) nickeline II of «caps» on lamel-

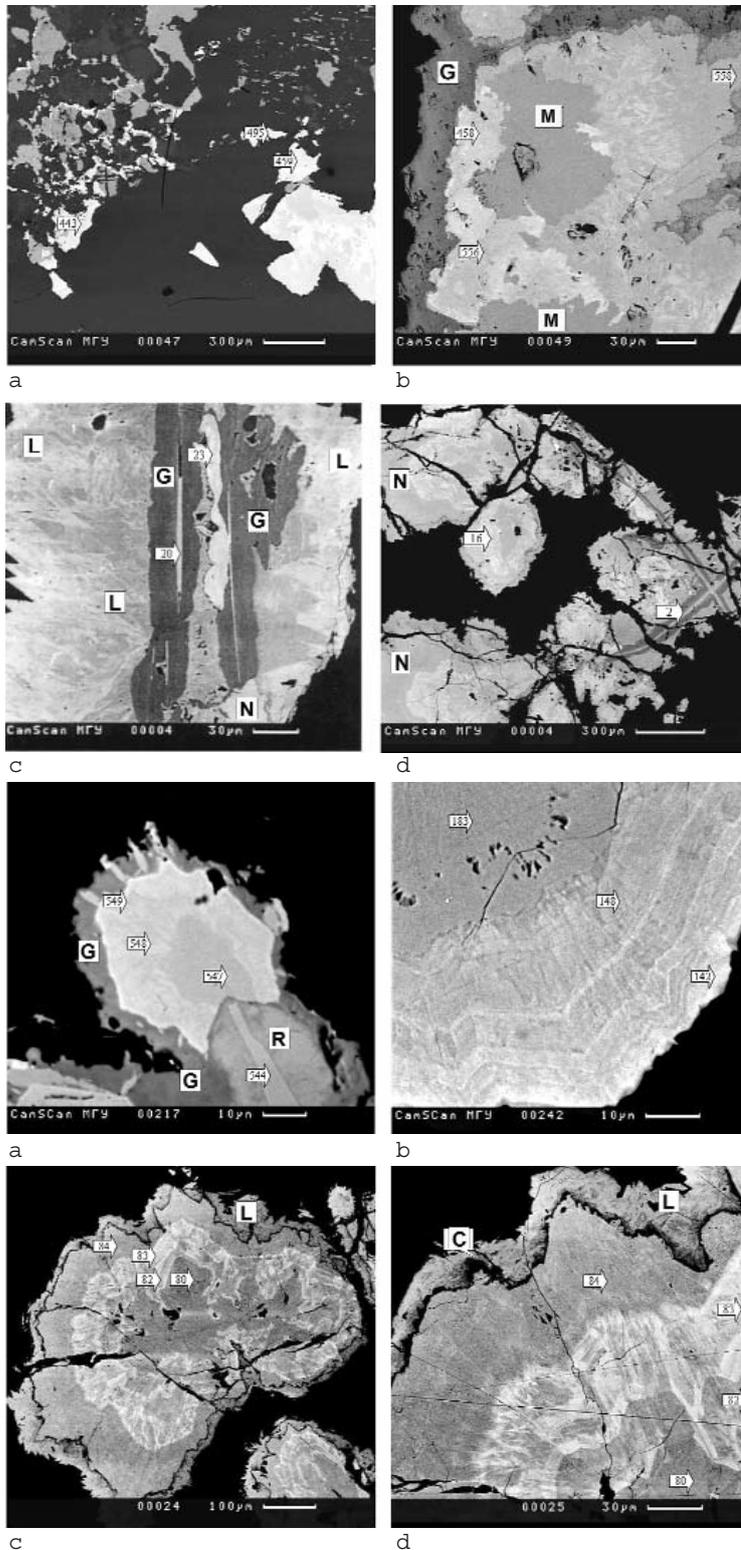


Fig. 1. Arsenides of the first and second mineral complexes. Matrix is calcite (black). Talnakh, the Komsomol'skii mine.

a – Sb-nickeline I (white, an. 443, 459, 495) overgrowing on chalcopyrite and sphalerite (grey);
 b – Aggregate of arsenides of the first mineral complex. Intergrowth of high-antimony nickeline (white, an. 458, 556) and maucherite (grey, «M»), overgrown by low-antimony and Sb-nickeline (light grey) with a picture of geometrical selection zone; then low-antimony nickeline (grey, an. 558); then rammelsbergite and gersdorffite (dark grey, «G»);
 c – Correlations of the first and second mineral complexes. The first mineral complex: lamellar crystals of antimony-free nickeline I (light grey, an. 20) surrounded by the aggregate of gersdorffite and cobaltite (dark grey, «G»), on which are split crystals of loellingite with a picture of geometrical selection zone (light grey to white, «L»); The second mineral complex: metasomes of Sb-nickeline II (white, an. 23, «N»). Nickeline II cuts off the borders of the first complex minerals.
 d – Cruciform intergrowth of lamellar crystals of antimony-free nickeline I (an. 2) bordered by gersdorffite and cobaltite (dark grey), loellingite (grey) of the first mineral complex. On them are zoned nodules of Sb-nickeline II («N», an. 16) of the second mineral complex.
 Photos in reflected electrons (BSE image).

Fig. 2. Nodules of arsenides of the second mineral complex. Matrix is calcite (black). Talnakh, the Komsomol'skii mine.

a – «Cap» of overgrowth, zoned nodule of nickeline II (an. 547) and Sb-nickeline II (an. 548, 549) on the lamellar crystal of nickeline I (an. 544) and on rammelsbergite («R»). Around «cap» is a border of gersdorffite («G»);
 b – Fragment of a «cap» of nickeline II: in the centre is low-antimony nickeline (an. 183), outside zone is the thin-zoned Sb-nickeline (an. 142, 148);
 c – Pisolite of nickeline II with a border of loellingite («L») and veinlets of calcite (black). Nickeline (an. 80, 84), Sb-nickeline (an. 82, 83);
 d – Fragment of the Figure 2c. Nickeline is bordered by cobaltite («C») and loellingite («L»).
 BSE image.

Table 1. Chemical composition of nickeline and Sb-nickeline of the first mineral complex (Fig. 1, 2a).

№	Element wt %										Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Cu	As	Sb	S	Se	Total		Ni	Co	Fe	Cu	Total	As	Sb	S	Se	Total
20	43.56	1.50	0.22	—	55.13	1.40	0.06	0.19	102.04	0.973	0.033	0.005	—	1.012	0.967	0.015	0.002	0.003	0.988	
544	41.12	1.64	1.67	—	53.58	1.96	1.45	—	101.22	0.913	0.036	0.039	—	0.988	0.932	0.021	0.059	—	1.012	
443	42.16	0.14	1.33	0.05	48.98	4.96	1.53	0.29	99.44	0.963	0.003	0.032	0.001	0.999	0.877	0.055	0.064	0.005	1.001	
558	41.24	1.19	0.01	—	51.76	6.88	0.18	—	101.26	0.952	0.027	—	—	0.979	0.936	0.077	0.008	—	1.021	
495	42.65	0.47	0.25	—	45.99	11.71	0.01	0.21	101.29	1.001	0.011	0.006	—	1.018	0.846	0.132	0.001	0.004	0.982	
556	40.93	0.35	0.22	—	43.57	14.71	1.13	—	100.91	0.965	0.008	0.006	—	0.979	0.805	0.167	0.049	—	1.021	
459	39.83	0.11	0.37	0.05	37.23	20.36	1.22	0.30	99.47	0.974	0.003	0.009	0.001	0.987	0.713	0.240	0.055	0.005	1.013	
458	39.17	0.14	0.19	—	35.79	22.26	0.14	0.29	98.18	0.997	0.003	0.005	—	1.006	0.710	0.272	0.007	0.005	0.994	

Note. In Tables 1-9 analyses are performed with X-ray microprobe instrument Cameca SX-50. Conditions: accelerating voltage 20 kV, electron current 20 nA. Analysts are N.N. Kononkova, I.A. Bryzgalov. Dash in table is the content of element is below detection limits and/or element is not detected. Numbers of analyses in the tables and on the figures are the same.

Table 2. Chemical composition of nickeline and Sb-nickeline of the second mineral complex (Fig. 1c, d, 2a, b, 3b).

№	Element wt %										Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Te	Total		Ni	Co	Fe	Total	As	Sb	S	Se	Te	Total
547	42.30	0.41	1.36	55.17	1.34	1.47	—	—	102.05	0.933	0.009	0.032	0.973	0.953	0.014	0.059	—	—	1.027	
183	43.56	1.50	0.22	55.13	1.40	0.06	—	—	101.87	0.971	0.033	0.005	1.009	0.974	0.015	0.002	—	—	0.991	
531	41.84	0.62	0.73	51.22	2.99	1.46	—	—	98.86	0.957	0.014	0.017	0.988	0.918	0.033	0.061	—	—	1.012	
548	43.02	0.38	1.51	49.26	5.05	1.79	—	—	101.01	0.964	0.009	0.035	1.008	0.865	0.055	0.073	—	—	0.992	
148	42.05	0.38	2.40	47.38	6.18	2.19	0.27	0.06	100.85	0.943	0.008	0.056	1.007	0.833	0.066	0.089	0.004	0.001	0.993	
532	41.02	0.53	1.16	47.08	8.80	2.16	—	—	100.74	0.934	0.012	0.028	0.974	0.84	0.097	0.09	—	—	1.026	
16	40.45	1.01	0.06	46.26	8.97	0.20	0.17	0.04	97.15	0.98	0.024	0.001	1.005	0.878	0.105	0.009	0.003	—	0.995	
549	41.25	0.13	1.25	47.14	10.87	1.41	—	—	102.06	0.943	0.003	0.03	0.976	0.845	0.12	0.059	—	—	1.024	
23	38.63	2.35	0.71	50.57	5.16	0.53	—	—	97.96	0.965	0.029	0.003	0.997	0.844	0.128	0.031	—	—	1.003	
142	42.81	0.11	0.02	41.47	17.30	0.17	0.19	0.11	102.07	1.015	0.003	—	1.018	0.773	0.198	0.007	0.003	0.001	0.982	

Table 3. Chemical composition of nickeline and Sb-nickeline of separate nodules of the second mineral complex (Fig. 2c, d).

№	Element wt %										Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Te	Total		Ni	Co	Fe	Total	As	Sb	S	Se	Te	Total
80	42.37	1.69	0.15	51.58	2.01	0.49	0.22	0.07	98.51	0.954	0.040	0.004	0.997	0.955	0.023	0.021	0.004	0.001	1.003	
71	41.92	0.81	0.11	52.31	2.45	0.13	0.22	0.10	98.05	0.981	0.018	0.003	1.002	0.959	0.028	0.006	0.004	0.001	0.998	
63	47.94	1.50	0.11	46.39	3.51	0.55	—	—	100.00	0.959	0.030	0.002	0.991	0.928	0.070	0.011	—	—	1.009	
84	40.31	1.68	0.19	49.86	6.52	0.37	—	—	98.93	0.947	0.039	0.005	0.991	0.919	0.074	0.016	—	—	1.009	
82	40.58	1.04	—	46.13	9.32	0.32	0.15	0.06	97.54	0.978	0.025	—	1.003	0.871	0.108	0.014	0.003	0.001	0.997	
75	40.26	0.79	—	45.88	9.73	0.18	0.20	0.10	97.14	0.979	0.019	—	0.998	0.874	0.115	0.008	0.004	0.001	1.002	
83	41.56	1.00	—	44.05	12.60	0.60	0.23	0.11	100.04	0.971	0.024	—	0.995	0.825	0.148	0.027	0.004	0.001	1.005	
69	41.10	0.42	0.11	42.11	14.09	0.77	0.23	0.11	98.94	0.990	0.010	0.002	1.002	0.795	0.164	0.034	0.004	0.001	0.998	

lae of nickeline I with the cobaltite-gersdorffite border and without it (Fig. 1d, 2a, b, 3a). Nickeline of «caps» is thin-zoned by chemical composition. Content of antimony increases to 20 wt % to edges of «caps» (Tabl. 2, an. 142, 148, 183, 547-549); c) nickeline II of the isolated nodules: in the centre, nickeline is usually low-antimony (Tabl. 3, an. 63, 80), in other volume of nodules the content of antimony is from traces to 15 wt % (Tabl. 3, an. 69, 71, 75, 82, 83). The width of zones with different concentration of antimony is from 10 to 100 µm (Fig. 2c, d); number of such zones reaches 15. Some nodules are bordered by cobaltite.

The late formations of the second complex

are less widespread: the lamellae of nickeline in the gersdorffite mass (Fig. 3b) and maucherite with broken basis and thin border of Sb-nickeline III (Fig. 3b, c).

The concentration of cobalt in nickeline II is to 1.5 wt % and iron to 2.5 wt %. Coefficients of pair correlation of contents are as follows: Ni-Co = -0.95; Ni-Fe = -0.77 (selection contains 47 analyses) is an evidence of isomorphous substitution of nickel by cobalt and iron. The high-antimony nickeline is usually less cobaltous than low-antimony nickeline; a coefficient of pair correlation is Sb-Co = -0.45. In nickeline of lamellar crystals and separate nodules is Co > Fe, in nickeline of «caps» is Fe > Co.

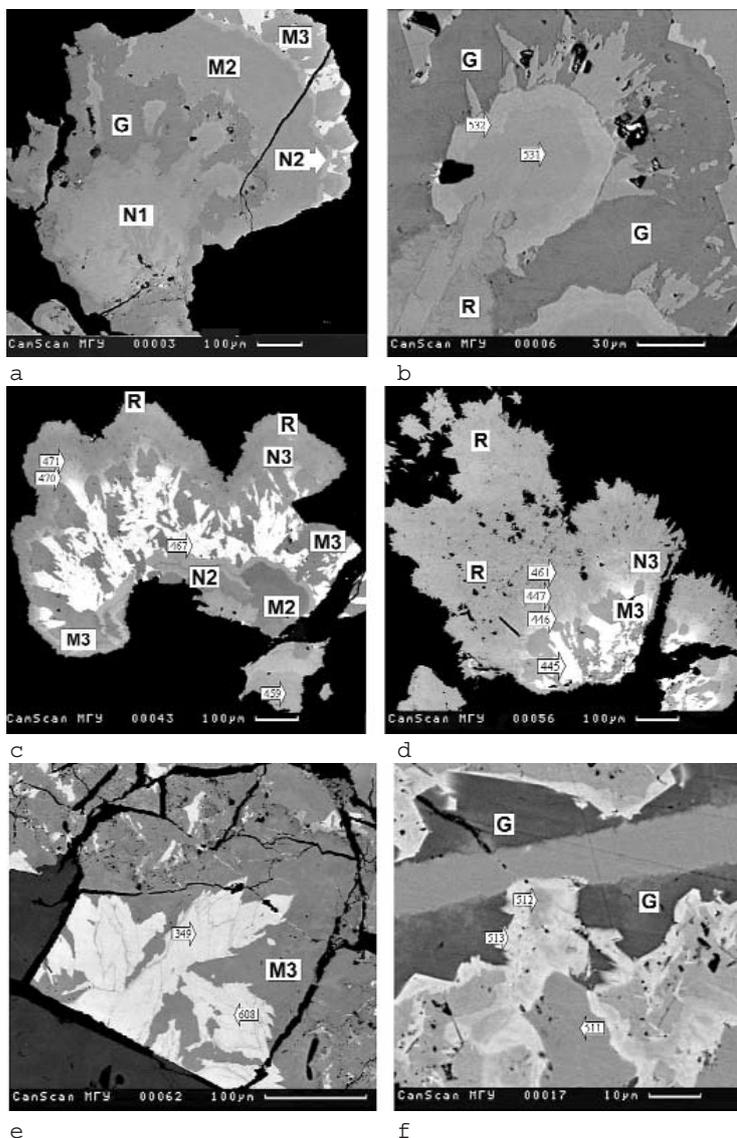


Fig. 3. Correlations of the first, second, third, and fourth mineral complexes. a-d, f – the Komsomol'skii mine, Talnakh. e – the Oktyabr'skii mine, Talnakh.

a – Pisolite of arsenides of the first, second, and third mineral complexes. The first complex: in the basis is the aggregate of low-antimony nickeline I («N1») with projecting crystals, on them is rammelsbergite (dark grey). The second complex: «caps» of nickeline II (on the basis of the first complex), then are the lamellae of nickeline on gersdorffite mass («G») (better seen on the Fig. 3b). The third complex: «caps» of nickeline II (an. 531, 532), Rammelsbergite («R»), gersdorffite («G»);

c – Pisolite of the second and third complexes. The second complex: aggregate of maucherite («M2»), nickeline, and Sb-nickeline («N2»). The third complex: intergrowth of breithauptite (white, an. 467) and maucherite («M3»), the border is Sb-nickeline («N3», an. 470, 471), the edge is rammelsbergite («R»);

d – Pisolite of the full-shown third complex. Early breithauptite (an. 445) and maucherite (dark grey, «M3»), later is Sb-nickeline («N3», an. 446, 447, 461), the latest is Fe-rammelsbergite («R»);

e – Isolated aggregation of early minerals of the third complex. Intergrowth of breithauptite (an. 349, 608) and maucherite («M») on the basis of wurtzite (dark grey);

f – Lamellar crystal of nickeline with a border of gersdorffite («G») of the first complex is partly substituted by arsenides of the fourth complex, low-antimony nickeline (an. 511) and Sb-nickeline (an. 512, 513); BSE image.

The third mineral complex. The early formations of the third complex, intergrowths of maucherite and breithauptite I, compose the complex-zoned nodules; they are overgrowing on the aggregates of the second complex; in their basis there is the zone of geometrical selection (Fig. 3a, c). Moreover, they form central parts of the isolated nodules of the third complex (Fig. 3d) and the isolated kidney-shaped aggregates overgrowing on wurtzite (Fig. 3e). Closer to the edge of nodules, breithauptite give place to As-breithauptite, then Sb-nickeline III, and then the antimony-free nickeline with border of Fe-rammelsbergite (Fig. 3d).

The third complex includes minerals of the

continuous breithauptite-nickeline series (Tabl. 4). In nickeline III and intermediate members of the nickeline-breithauptite series, the content of sulphur, cobalt, and iron is higher than in breithauptite I: S to 2.6 wt %, Co and Fe to 2.5-3 wt %.

The fourth mineral complex. The aggregates of the fourth complex minerals overgrow on the aggregates of the first and third complexes and partly substitute them (Fig. 3f). In the most cases, they form the isolated nodules (Fig. 4a, b). The intensively split crystals of the low-antimony nickeline (the first generation) form the central parts of nodules, which are surrounded by a narrow zone of nickeline with

Table 4. Chemical composition of the nickeline-breithauptite series minerals of the third mineral complex (Fig. 3c-e).

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Cu	As	Sb	S	Se	Total	Ni	Co	Fe	Cu	Total	As	Sb	S	Se	Total
461	42.65	0.09	2.69	0.09	46.89	5.27	2.64	0.27	100.59	0.948	0.002	0.063	0.002	1.015	0.817	0.056	0.108	0.005	0.985
471	38.96	0.87	0.88	0.07	49.85	9.70	0.21	0.26	100.78	0.915	0.020	0.022	0.001	0.959	0.918	0.110	0.009	0.005	1.041
470	40.96	0.53	0.10	0.03	44.54	14.31	—	0.29	100.75	0.979	0.013	0.003	0.001	0.995	0.835	0.165	—	0.005	1.005
460	42.38	0.11	0.29	—	37.41	17.53	2.45	0.31	100.47	0.994	0.002	0.007	—	1.004	0.688	0.198	0.105	0.005	0.996
447	40.58	0.48	0.17	0.04	41.46	17.47	0.06	0.22	100.47	0.984	0.011	0.004	0.001	1.001	0.788	0.204	0.003	0.004	0.999
446	40.43	0.15	0.03	0.08	32.87	27.37	0.02	0.19	101.14	1.013	0.004	0.001	0.002	1.019	0.645	0.331	0.001	0.004	0.981
349	33.10	—	—	—	5.27	63.81	0.31	0.16	102.66	0.964	—	—	—	0.964	0.120	0.896	0.016	0.003	1.036
467	33.31	—	0.04	—	2.21	64.00	0.61	0.17	100.35	0.991	—	0.001	—	0.993	0.052	0.919	0.033	0.004	1.007
608	32.92	—	—	0.26	2.61	64.52	0.53	0.16	100.95	0.980	—	—	0.007	0.987	0.061	0.921	0.029	0.002	1.013
445	32.45	—	—	0.18	2.62	64.19	0.38	0.26	100.07	0.976	—	—	0.005	0.981	0.062	0.931	0.021	0.006	1.019

Table 5. Chemical composition of the nickeline-breithauptite series minerals of the fourth mineral complex (Fig. 3f, 4).

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Cu	As	Sb	S	Se	Total	Ni	Co	Fe	Cu	Total	As	Sb	S	Se	Total
496	44.08	0.56	0.58	0.03	52.72	0.96	1.16	0.23	100.32	0.987	0.012	0.014	0.001	1.014	0.925	0.010	0.047	0.004	0.986
511	44.70	0.47	0.08	0.13	52.62	2.85	0.41	0.35	101.61	1.005	0.011	0.002	0.003	1.019	0.927	0.031	0.017	0.006	0.981
512	43.69	0.86	0.01	0.05	52.89	3.08	0.09	0.37	101.04	0.993	0.019	—	0.001	1.014	0.942	0.034	0.004	0.006	0.986
497	42.08	0.75	0.74	0.11	46.83	6.54	2.42	0.31	99.79	0.954	0.017	0.018	0.002	0.991	0.832	0.071	0.101	0.005	1.009
503	42.06	0.52	0.21	—	47.91	8.66	0.01	0.24	99.60	0.993	0.012	0.005	—	1.010	0.886	0.099	—	0.004	0.990
513	41.92	0.08	0.12	0.08	39.38	19.60	0.14	0.26	101.58	1.011	0.002	0.003	0.002	1.017	0.744	0.228	0.006	0.005	0.983
502	39.69	0.20	0.06	0.07	33.82	26.85	0.03	0.21	100.93	0.996	0.005	0.002	0.002	1.004	0.665	0.325	0.001	0.004	0.996
500	37.16	0.05	0.01	0.02	21.99	41.06	0.02	0.19	100.51	0.998	0.001	—	0.001	1.000	0.463	0.532	0.001	0.004	1.000
499	36.82	0.14	0.03	—	16.14	49.73	0.03	0.12	103.00	0.998	0.004	0.001	—	1.003	0.343	0.650	0.002	0.002	0.997
501	34.28	0.05	—	0.08	9.15	57.34	0.05	0.16	101.11	0.987	0.002	—	0.002	0.991	0.207	0.796	0.003	0.003	1.009
498	33.59	0.07	0.05	0.05	4.41	63.25	0.14	0.23	101.78	0.986	0.002	0.001	0.001	0.991	0.101	0.895	0.007	0.005	1.009

Table 6. Chemical composition of breithauptite and nickeline of the fifth mineral complex (Fig. 6).

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Cu	As	Sb	S	Se	Total	Ni	Co	Fe	Cu	Total	As	Sb	S	Se	Total
226	33.28	0.02	0.01	0.03	2.52	65.24	0.02	0.13	101.24	0.995	0.001	—	0.001	0.997	0.059	0.941	0.001	0.002	1.003
230	33.39	0.04	0.06	0.08	2.10	65.93	0.05	0.15	101.80	0.994	0.001	0.002	0.002	0.999	0.049	0.946	0.003	0.003	1.001
243	33.26	0.08	0.00	0.16	1.79	67.05	0.08	0.31	102.73	0.985	0.002	—	0.004	0.991	0.042	0.957	0.004	0.005	1.009
242	34.54	9.99	0.22	—	50.74	3.87	0.07	0.29	99.72	0.797	0.230	0.005	—	1.032	0.918	0.043	0.003	0.005	0.968
239	40.79	2.96	0.11	0.05	52.21	3.39	0.03	0.42	99.96	0.940	0.068	0.003	0.001	1.012	0.943	0.038	0.001	0.007	0.988
225	42.75	2.21	0.04	0.10	52.50	3.93	0.03	0.28	101.80	0.968	0.050	0.001	0.002	1.020	0.931	0.043	0.001	0.005	0.980

5-7 wt % of Sb (Tabl. 5, an. 497) (the second generation). The thin-alternating As-breithauptite and Sb-nickeline (the third generation), rammelsbergite overgrow on nickeline of the second generation. The content of cobalt and iron in nickeline IV and breithauptite II is less than 1 wt %. The content of sulphur in nickeline of the first generation is 1-2.5 wt %. Nickeline of the second and third generations and breithauptite contain less than 0.5 wt % of sulphur.

The fifth mineral complex. The fifth mineral complex is represented by complex-zoned nodules of the antimony-free, cobalt-free and Co-nickeline V, breithauptite III, maucherite, cobaltite (Fig. 5, 6). Central parts of the nodules are usually composed by intergrowths of small crystals of breithauptite and

Co-nickeline (Tabl. 6, an. 239) with borders of cobaltite (Fig. 6a, b). On them there are aggregates of the Co-nickeline crystals (an. 242), which growth zones are marked by Ni-cobaltite (Fig. 6a, b). They are surrounded by nickeline with ingrowths of breithauptite and with a border of microcrystalline breithauptite (Fig. 6b). The latter form the central parts of some nodules (Fig. 6c), where the aggregates of maucherite with small inclusions of breithauptite and with a border of the fine-grained breithauptite overgrow on them (Fig. 6c).

Minerals of the nickeline-breithauptite series of the fifth complex are represented by the end-members. The content of cobalt in nickeline V is to 10 wt %, sulphur is <0.1 wt %.

The sixth mineral complex. The sixth complex is formed by maucherite, breithauptite IV,

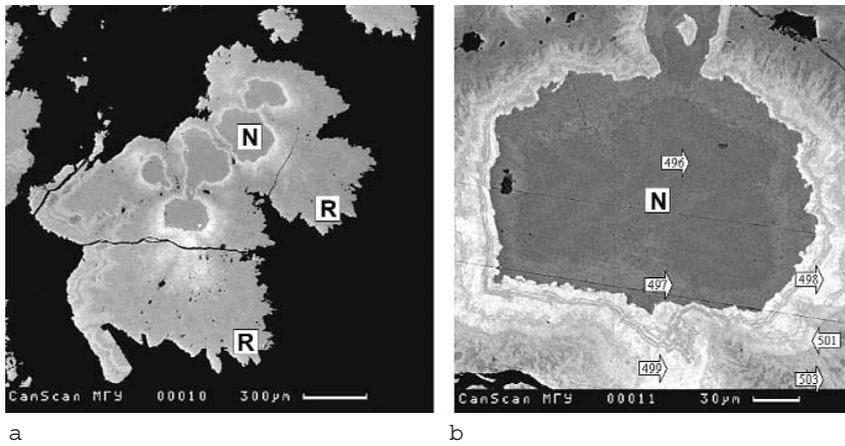


Fig. 4. Nodules of the fourth mineral complex in calcite (black). Talnakh, the Komsomol'skii mine. On low-antimony nickeline («N», an. 496, 497) are breithauptite (an. 498-500), Sb-nickeline (an. 501, 503), rammelsbergite (grey, «R»). BSE image.

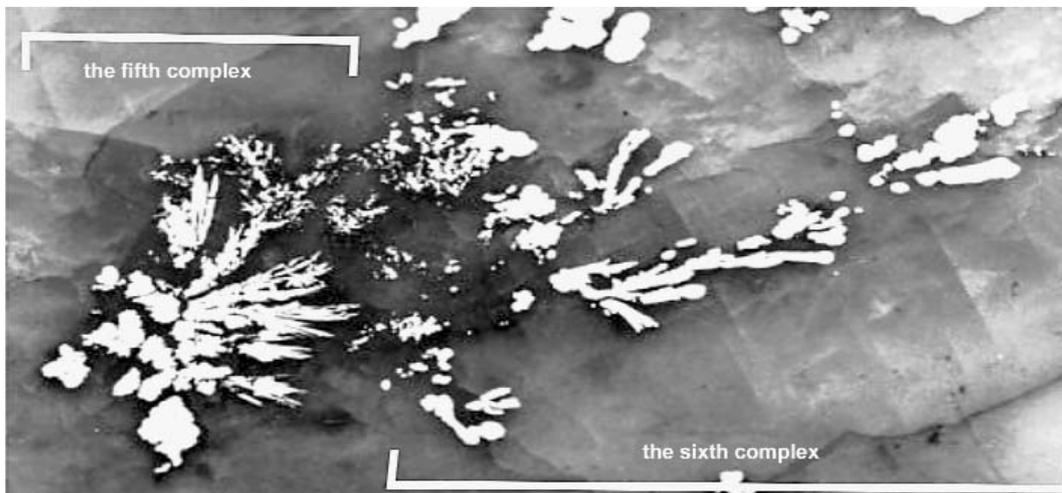


Fig. 5. Arsenides (white) of the fifth and sixth mineral complexes in carbonate vein. The Oktyabr'skii mine, Talnakh. Polished section. Width of image is 35 mm.

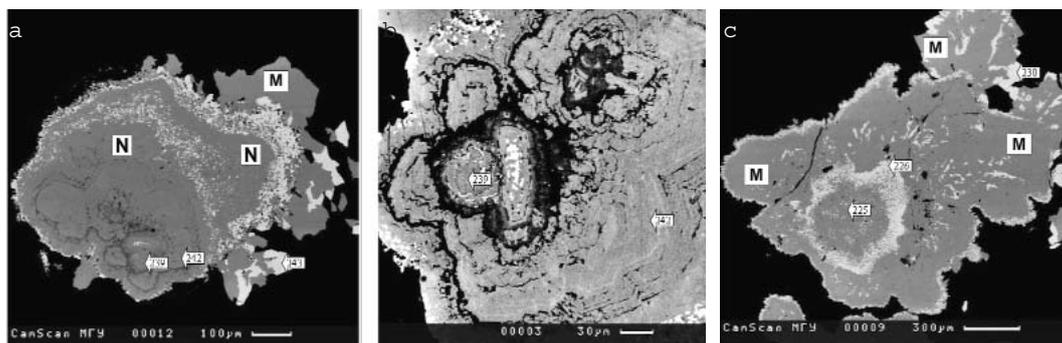


Fig. 6. Fragments of the Figure 5. The fifth and sixth mineral complexes. a – The fifth complex: early breithauptite (white) and Co-nickeline (an. 239) with a border of cobaltite (black); later Co-nickeline (an. 242) with thin zones of cobaltite (black); even more later nickeline («N») with ingrowths of breithauptite (white); the latest small crystals of breithauptite. The sixth complex: intergrowth of large crystals of maucherite («M») and breithauptite (an. 243), a border around arsenides of the fifth complex; b – The detail of the Figure 6a; c – The fifth complex: nickeline (an. 225) surrounded by the small-grained breithauptite (an. 226). The sixth complex: maucherite («M») with inclusions of breithauptite (white) and surrounded by a border of breithauptite (an. 230). BSE image.

Table 7. Chemical composition of Co-nickeline and breithauptite of the sixth mineral complex (Fig. 7).

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Te	Total	Ni	Co	Fe	Total	As	Sb	S	Se	Te	Total
305	36.40	2.00	0.10	32.28	29.83	0.06	0.14	—	100.80	0.974	0.028	0.002	1.004	0.855	0.134	0.002	0.004	0.001	0.996
309	40.92	1.17	0.06	45.89	11.64	0.04	0.22	0.05	99.97	0.928	0.051	0.003	0.981	0.646	0.367	0.003	0.003	—	1.019
213	41.49	2.79	0.07	52.85	2.58	0.02	0.22	0.06	100.07	0.951	0.064	0.002	1.017	0.949	0.028	0.001	0.004	0.001	0.983
222	38.43	4.81	0.06	51.31	6.45	0.02	0.27	0.07	101.40	0.885	0.11	0.001	0.996	0.925	0.072	0.001	0.005	0.001	1.004
248	37.55	6.62	0.19	50.33	5.96	0.10	0.15	0.03	100.92	0.863	0.152	0.005	1.020	0.907	0.066	0.004	0.003	—	0.98
223	34.95	9.35	0.25	51.66	4.85	0.04	0.20	0.01	101.30	0.798	0.213	0.006	1.017	0.925	0.053	0.002	0.003	—	0.983
242	34.54	9.99	0.22	50.74	3.87	0.07	0.24	0.05	99.72	0.797	0.23	0.005	1.032	0.917	0.043	0.003	0.004	0.001	0.968
249	33.36	10.04	0.32	50.95	3.40	0.99	0.30	0.05	99.40	0.764	0.229	0.008	1.001	0.913	0.038	0.042	0.005	0.001	0.999
214	30.74	12.98	0.29	52.76	2.44	0.06	0.26	—	99.52	0.708	0.298	0.007	1.013	0.954	0.027	0.002	0.004	—	0.987
220	33.35	0.27	0.03	5.21	62.08	0.03	0.12	0.08	101.17	0.983	0.008	0.001	0.992	0.120	0.882	0.002	0.003	0.001	1.008
304	32.21	0.12	0.10	0.63	67.85	0.08	0.12	—	101.10	0.977	0.004	0.003	0.984	0.015	0.994	0.004	0.003	—	1.016

Table 8. Chemical composition of the nickeline-breithauptite series minerals of the tenth mineral complex (Fig. 8a-c).

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Te	Total	Ni	Co	Fe	Total	As	Sb	S	Se	Te	Total
679	44.02	0.09	1.71	50.02	1.54	2.16	0.19	0.01	99.75	0.979	0.002	0.040	1.021	0.871	0.017	0.088	0.003	—	0.979
677	42.77	0.13	—	51.44	6.78	0.02	0.21	0.04	101.40	0.987	0.003	—	0.990	0.930	0.075	0.001	0.004	—	1.010
639	41.33	0.31	0.34	44.42	15.54	0.00	0.13	0.03	102.09	0.979	0.007	0.009	0.995	0.825	0.178	—	0.002	—	1.005
644	40.54	0.06	0.32	36.13	24.23	0.08	0.18	0.08	101.61	0.998	0.001	0.008	1.008	0.697	0.288	0.003	0.003	0.001	0.992
641	38.90	0.09	0.10	28.64	31.91	0.05	0.10	—	99.79	1.009	0.002	0.003	1.014	0.582	0.399	0.002	0.002	—	0.986
661	37.36	0.08	0.03	29.06	35.45	0.05	0.12	0.04	102.18	0.964	0.002	0.001	0.966	0.588	0.441	0.003	0.002	—	1.034
633	37.28	0.17	0.05	27.07	36.43	0.11	0.17	0.01	101.29	0.973	0.004	0.001	0.979	0.554	0.459	0.005	0.003	—	1.021
634	32.77	0.19	—	3.30	65.24	0.29	0.16	—	101.95	0.969	0.006	—	0.974	0.076	0.930	0.016	0.004	—	1.026
678	33.02	—	—	3.86	65.51	0.22	0.08	0.04	102.74	0.969	—	—	0.969	0.089	0.928	0.012	0.002	0.001	1.031
675	31.66	—	0.08	2.68	65.82	0.24	0.18	—	100.66	0.957	—	0.003	0.960	0.063	0.960	0.013	0.004	—	1.040
638	33.31	—	0.02	3.19	65.91	0.01	0.11	0.09	102.63	0.983	—	0.001	0.984	0.074	0.938	—	0.002	0.001	1.016
630	32.85	—	—	2.10	66.81	0.76	0.17	—	102.69	0.963	—	—	0.963	0.048	0.944	0.041	0.004	—	1.037

Table 9. Chemical composition of the nickeline-breithauptite series minerals of the eleventh mineral complex (Fig. 8d).

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Hg	As	Sb	S	Se	Total	Ni	Co	Fe	Hg	Total	As	Sb	S	Se	Total
575	45.00	0.25	0.04	—	49.00	6.82	1.19	0.19	102.49	1.007	0.006	0.001	—	1.014	0.860	0.074	0.049	0.003	0.986
576	44.44	0.32	—	—	50.02	3.87	2.08	0.23	100.96	0.991	0.007	—	—	0.998	0.871	0.042	0.085	0.004	1.002
579	43.50	0.20	0.06	1.01	42.47	14.30	1.27	0.18	102.99	1.005	0.004	0.001	0.007	1.017	0.768	0.159	0.053	0.003	0.983
580	35.18	0.03	0.03	0.15	11.65	52.00	0.68	0.10	99.82	0.995	0.001	0.001	0.001	0.998	0.257	0.708	0.035	0.002	1.002
581	34.30	0.11	—	0.50	7.81	59.38	0.38	0.08	102.56	0.979	0.003	—	0.004	0.986	0.175	0.817	0.020	0.002	1.014
582	41.26	0.05	0.06	0.32	34.20	24.25	1.45	0.16	101.75	0.998	0.001	0.002	0.002	1.003	0.647	0.283	0.064	0.003	0.997
583	40.62	0.08	—	—	32.99	27.27	1.01	0.20	102.17	0.994	0.002	—	—	0.996	0.633	0.322	0.045	0.004	1.004
584	33.10	—	—	2.09	1.02	67.16	0.15	0.02	103.54	0.987	—	—	0.018	1.005	0.024	0.963	0.008	—	0.995
585	34.16	—	—	—	5.01	60.43	0.42	0.08	100.10	1.004	—	—	—	1.004	0.115	0.857	0.022	0.002	0.996
586	38.59	0.12	0.01	—	24.46	38.89	0.24	0.11	102.42	1.000	0.003	—	—	1.003	0.498	0.486	0.011	0.002	0.997
587	33.23	0.03	—	—	1.90	66.93	0.27	—	102.36	0.985	0.001	—	—	0.986	0.044	0.956	0.014	—	1.014

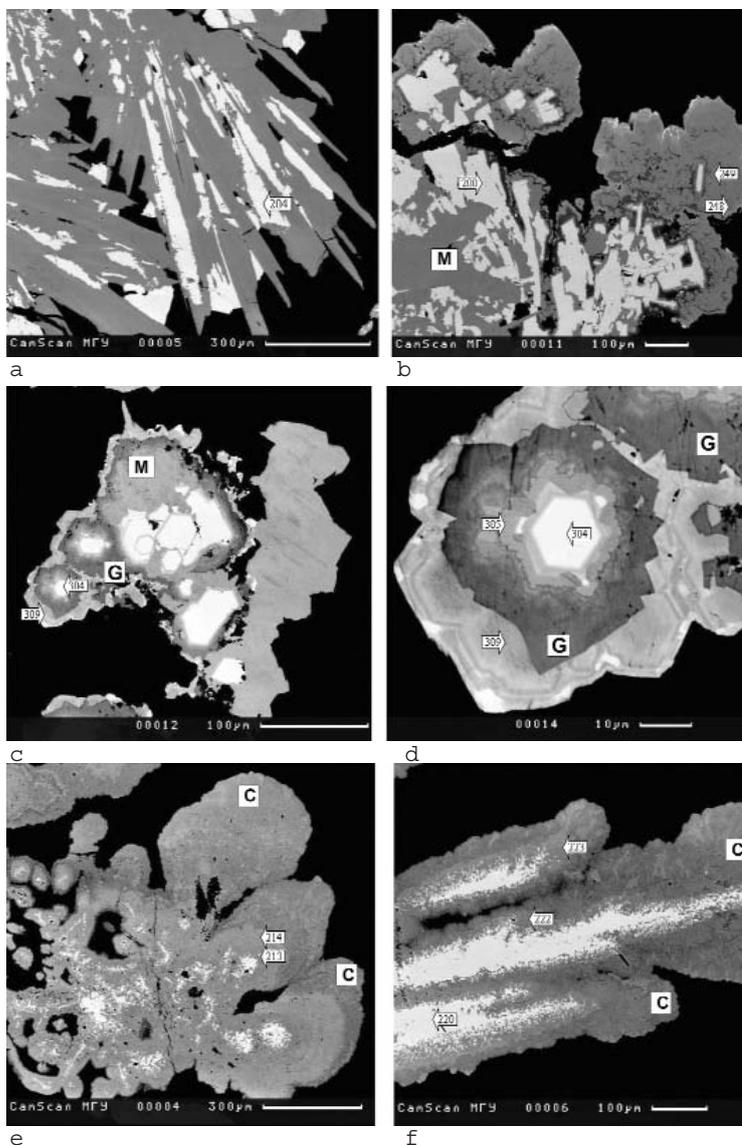


Fig. 7. Fragments of the Figure 5. Aggregates of the sixth mineral complex. Talnakh, the Oktyabr'skii mine. *a* – Lamellar crystals of maucherite, interstices between them are filled up by breithauptite (an. 204); *b* – Intergrowths of tabular crystals of breithauptite (an. 200) and maucherite («M»), on them is Co-nickeline (an. 248, 249); *c* – Crystals of breithauptite (an. 304) and Sb-nickeline are surrounded and partly substituted by maucherite («M»). On them is a border of Co-gersdorffite (dark grey, «G»). Around are Sb-nickeline (an. 309), maucherite, and breithauptite; *d* – In the centre is breithauptite crystal (an. 304) with a border of Sb-nickeline (an. 305). Around is Co-gersdorffite («G»), then is zoned aggregations of Sb-nickeline (an. 309); *e* – Zoned nodules of Co-nickeline (an. 213, 214) with inclusions of breithauptite (white). Border is sulphur safflorite; *f* – Intergrowths of the split crystals of breithauptite (an. 220) and Co-nickeline (an. 222, 223). Border is high-sulphur safflorite («C»). BSE image.

nickeline VI; split crystals of nickeline enriched by cobalt are typical. The early formations are intergrowths of maucherite and breithauptite (Fig. 7a, b), sometimes with a border of Sb-nickeline. They are surrounded by maucherite with a border of Co-gersdorffite. On the described aggregations are Sb-nickeline (Tabl. 7, an. 309) and breithauptite (Fig. 7c, d). In a number of cases, these minerals form the central parts of nodules (Fig. 7e, f), which outside are formed by the split crystals of Co-nickeline surrounded by aggregates of the split crystals of the high-sulphur Fe-safflorite (Fig. 7e, f).

The content of cobalt in nickeline VI increases from the centre of nodules to out-

sides to 15 wt%. Nickeline VI contains to 30 wt% of Sb, breithauptite does not practically contain As (Tabl. 7, an. 243, 304). The X-ray diffraction pattern of breithauptite IV is as follows: 2.83 Å (8) (101); 2.565 (2) (002); 2.047 (7) (102); 1.965 (10) (110); 1.537 (6) (103). The unit cell parameters are as follows: a_0 3.926(6) Å; c_0 5.143(6) Å.

The seventh mineral complex. Nodules of the seventh complex are composed by diarsenides of the rammelsbergite-loellingite series with the separate thin (10–30 m) zones of nickeline VII. This nickeline contains 2–5 wt % of Sb.

The tenth mineral complex. The tenth mineral complex is represented by the com-

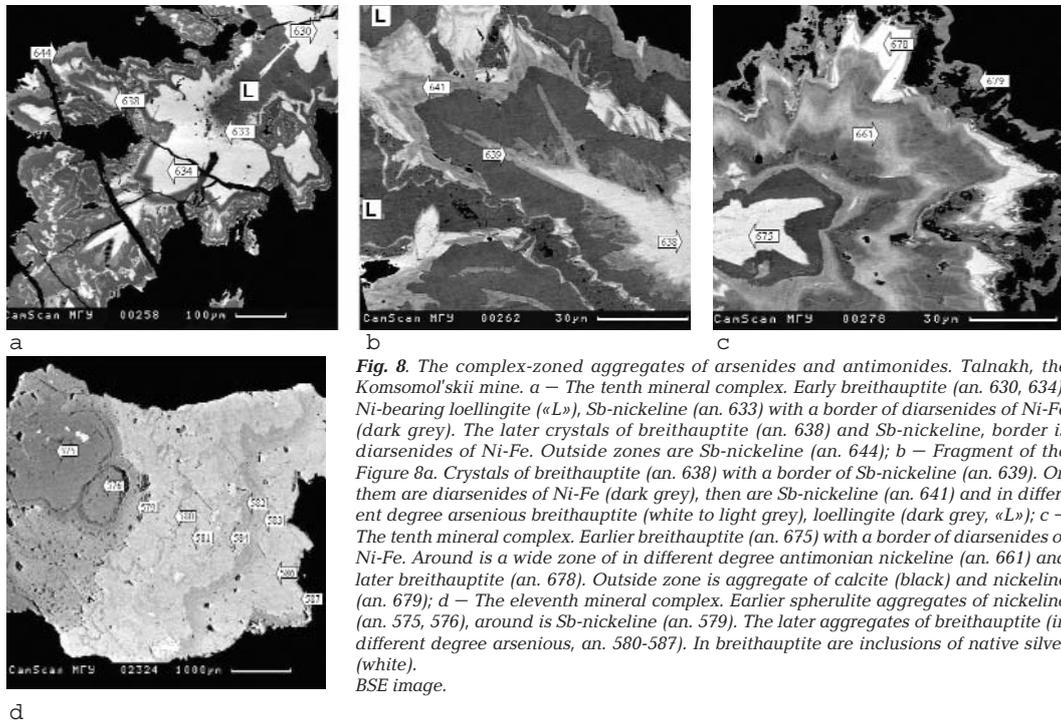


Fig. 8. The complex-zoned aggregates of arsenides and antimonides. Talnakh, the Komsomol'skii mine. a – The tenth mineral complex. Early breithauptite (an. 630, 634), Ni-bearing loellingite («L»), Sb-nickeline (an. 633) with a border of diarsenides of Ni-Fe (dark grey). The later crystals of breithauptite (an. 638) and Sb-nickeline, border is diarsenides of Ni-Fe. Outside zones are Sb-nickeline (an. 644); b – Fragment of the Figure 8a. Crystals of breithauptite (an. 638) with a border of Sb-nickeline (an. 639). On them are diarsenides of Ni-Fe (dark grey), then are Sb-nickeline (an. 641) and in different degree arsenious breithauptite (white to light grey), loellingite (dark grey, «L»); c – The tenth mineral complex. Earlier breithauptite (an. 675) with a border of diarsenides of Ni-Fe. Around is a wide zone of in different degree antimonian nickeline (an. 661) and later breithauptite (an. 678). Outside zone is aggregate of calcite (black) and nickeline (an. 679); d – The eleventh mineral complex. Earlier spherulite aggregates of nickeline (an. 575, 576), around is Sb-nickeline (an. 579). The later aggregates of breithauptite (in different degree arsenious, an. 580-587). In breithauptite are inclusions of native silver (white). BSE image.

plex-zoned nodules from a great number of generations of breithauptite V, nickeline VIII, rammelsbergite, and loellingite.

The lamellar crystals of arsenic-free breithauptite V of the first generation and their cruciform intergrowths frame the aggregate of Ni-bearing loellingite, on which the high-antimony nickeline VIII of the first generation overgrows (Fig. 8a). On that nickeline are the large short-prismatic crystals of low-arsenic breithauptite V of the second generation (Tabl. 8) with a thin border of diarsenides of Ni and Fe (Fig. 8a).

These formations are a basis for the aggregates of long-prismatic crystals of low-arsenic breithauptite V of the third generation with a picture of the geometrical selection zone (Fig. 8a) and high-antimony nickeline VIII of the second generation with a border of diarsenides of Ni and Fe (Fig. 8b).

On them are the complex-zoned aggregates of the split crystals of the high-antimony, antimony-free, Sb-nickeline VIII of the third generation and breithauptite V of the fourth generation (Fig. 8b, c). In a number of cases, these aggregates are surrounded by a border of nickeline VIII of the fourth generation with calcite (Fig. 8c) or loellingite. On them are Sb-nickeline VIII of the fifth generation (Tabl. 8,

an. 644) and breithauptite V of the fifth generation; the breithauptite crystals are to 1 mm in size. Some nodules of the tenth complex are surrounded by a border (10-20 μm) of maucherite.

The eleventh mineral complex. The eleventh complex is represented by the zoned thin-split nodules of antimonides and arsenides with inclusions of native silver, mercurial silver, pyrargyrite (Fig. 8d).

Central parts of the nodules are composed by the thin-split aggregates of Sb-nickeline IX with inclusions of silver. This nickeline contains 5-7 wt % of Sb (Tabl. 9, an. 575, 576). Nickeline containing 15 wt % of Sb (an. 579) overgrows on it; then there is As-breithauptite with inclusions of pyrargyrite. The content of As in breithauptite wavy changes from 1 to 15 wt % (an. 580, 581). The outside zone of nodules is composed by the intermediate members of the nickeline-breithauptite isomorphous series and breithauptite (an. 582-587).

Nodules of the eleventh mineral complex are surrounded by the substitution border and/or cut by the veinlets of ullmannite of the twelfth mineral complex.

Peculiarities of the nicke-

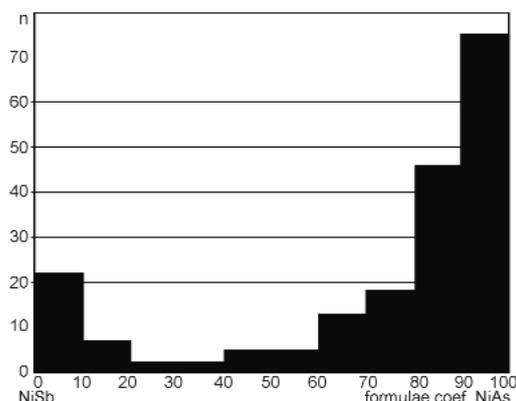


Fig. 9. Frequency of encountering of the nickeline-breithauptite series minerals in the Norilsk ore field.

line-breithauptite series minerals of the Norilsk ore field

Minerals of the whole nickeline-breithauptite series occur in the veins of the first and second cycles of the antimonide-arsenide mineralization of the Norilsk ore field. Nickeline and breithauptite are the most widespread; Sb-nickeline spread quite wide. The Sb-bearing nickeline is more widespread than As-bearing breithauptite (Fig. 9). The coefficient of pair correlation of contents is $As-Sb = -1.00$ for all selection of analyses of the nickeline-breithauptite series minerals ($n = 189$ analyses). The Sb-nickeline and As-breithauptite are the most typical for the first four mineral complexes of the first cycle and in the second cycle. The high-cobalt nickeline is characteristic for the arsenide veins of the first cycle. To the end of the first cycle, the content of Fe, S, and Se in nickeline decreases, the content of Co increases up to 12 wt %.

The intermediate members of the nickeline-breithauptite series is usually contain fewer admixtures than low-antimony nickeline. Breithauptite is poor by Co, Fe, S, and Se. For all selection of analyses of the nickeline-breithauptite series minerals ($n = 189$), the coefficients of pair correlation of contents are as follows: $Ni-Co = -0.80$, $Ni-Fe = -0.40$, $Sb-Co = -0.40$, $Sb-Fe = -0.30$, $Sb-S = -0.30$. The coefficients of correlation express the above-mentioned peculiarities of the mineral chemical composition and are an evidence of isomorphous substitutions of nickel by cobalt and iron.

In three concentrates of nickeline from carbonate veins, Pd, Pt, Au were not found (sensitivity of method for Pt and Au is 100 mg/t, for Pd is 30 mg/t; analyst I.Ya. Koshcheeva).

The split and thin-split crystals of nickeline and breithauptite forming nodules are widespread. The split aggregations are the most characteristic for Sb-nickeline and As-breithauptite. The bad-split and non-split crystals are typical for «pure» nickeline and breithauptite.

Conclusions

The antimonide-arsenide mineralization of the Norilsk ore field, which was considered by the previous researchers as a derivative of the P_2-T_1 trap formation, is connected with the post-trap regional metamorphism in conditions of zeolite facies. It is younger than the trap formation for more than 80 MA. At that, the partial mobilization of Ni, Co, As, Sb, and Ag, but not Pd, Pt, and Au, from initial ores took place. The Described Co-Ni antimonide-arsenide mineralization can be considered as the regenerated mineralization, in the interpretation of H. Schneiderhohn (1953b).

Three cycles of antimonide-arsenide mineralization occur. The first cycle is significantly arsenide, the presence of high-cobalt nickeline is characteristic. The second cycle is considerably antimonide. The third cycle is sulphoantimonide-sulphoarsenide.

The minerals of the continuous nickeline-breithauptite series form the significant part of antimonide-arsenide mineralization of the first and second cycles. Nickeline and breithauptite are the most widespread; Sb-nickeline is spread quite wide. The Norilsk nickeline contains up to 12 wt % of Co, to 3 wt % of Fe and S. In nickeline from carbonate veins, Pd, Pt, and Au were not detected. Breithauptite is poor by Co, Fe, and S.

In aggregates of arsenides and antimonides are the geometrical selection zones; that is an evident of crystallization of arsenides and antimonides from the normal solutions in open space.

Acknowledgements

The authors are grateful to geologists of the Norilsk industrial complex, E.A. Kulagov, S.N. Belyakov, A.N. Glotov, E.V. Sereda, and V.N. Stasenko, for help in collection of samples of arsenides and to the collaborators of laboratory of microprobe analysis of the Geological department of the Lomonosov MSU, N.N. Kononkova, N.N. Korotaeva, E.V. Guseva, and I.A. Bryzgalov, for help in the carrying out of

analyses.

The work was supported by a grant of the Russian Foundation for Basic Research (No. 04-05-64162).

References

- Chvileva T.N., Bezsmertnaya M.S., Spiridonov E.M., Vinogradova R.A.* Handbook-Determiner of Ore Minerals in Reflected Light. (Spravochnik-Opredelitel' Rudnykh Mineralov v Otrazhennom Svette). M.: Nedra. **1988**. 504 p. (Rus.).
- Czarnianska G.K., Kunilov V.E., Zientek M.L., Cardi L.J., Likhachev A.P.* A proton-microprobe study of magmatic sulfide ores from the Noril'sk-Talnakh district, Siberia // *Canad. Mineral.* **1992**. V. 30. P. 249-287.
- Distler V.V., Laputina I.P., Smirnov A.V., Balbin A.S.* Arsenides, sulphoarsenides of nickel, cobalt, and iron of the Talnakh ore field // In book: *Mineraly i Paragenезisy Mineralov Endogennykh Mestorozhdenii*. L.: Nauka. **1975**. P. 61-74. (Rus.).
- Dymkov Yu.M.* Paragenesis of Minerals of Uranium-Bearing Veins. (Paragenезis Mineralov Uranonosnykh Zhil). M.: Nedra. **1985**. 100 p. (Rus.).
- Genkin A.D., Distler V.V., Filimonova A.A., Evstigneeva T.L.* Sulphide Copper-Nickel Ores of Norilsk Deposits. (Sul'fidnye Medno-Nikelevye Rudy Noril'skikh Mestorozhdenii). M.: Nauka. **1981**. 234 p. (Rus.).
- Godlevskii M.N.* Traps and Ore-Bearing Intrusions of the Norilsk Region. (Trappy i Rudnosnye Intruzii Noril'skogo Raiona). M.: Gosgeoltekhizdat. **1959**. 68 p. (Rus.).
- Hytonen K.* Suomen Mineraalit. Geologian tutkimuskeskus. Erillisoukaisu: **1999**. 399 s.
- Izotko V.M., Vyal'sov L.N.* About assemblage of arsenides and antimonides of nickel in ores of the Talnakh deposit // In book: *Mineraly i Paragenезisy Mineralov Rudnykh Mestorozhdenii*. L.: Nauka. **1973**. P. 31-38. (Rus.).
- Krutov G.A.* Deposits of Cobalt. (Mestorozhdeniya Kobal'ta). M.: Gosgeoltekhizdat. **1959**. 232 p. (Rus.).
- Kulagov E.A.* Peculiarities of Mineral Composition of Ores of the Norilsk-I Deposit. (Osobennosti Mineral'nogo Sostava Rud Mestorozhdeniya Noril'sk-I). PhD Thesis. M.: MGU. **1968**. 239 p. (Rus.).
- Kulagov E.A., Evstigneeva T.N.* New nickel minerals in ores of the Norilsk and Talnakh deposits // In book: *Materialy Konferentsii Noril'skikh Geologov*. Norilsk: . **1971**. P. 157-158. (Rus.).
- Leblanc M., Cervilla F., Jedwab J.* Noble metals aggregation and fractionation in magmatic ores Rond and Beni Bousera lherzolite massifs (Spain, Morocco) // *Mineral. Petrol.* **1990**. V. 42. P. 233-248.
- Malich N.S.* Tectonic Development of Mantle of the Siberian Platform. (Tektonicheskoe Razvitiye Chekhla Sibirskoi Platformy). M.: Nedra. **1975**. 202 p. (Rus.).
- Pekov I.V.* Mineral of nickeline-breithauptite series from the Belorechenskoe deposit (North Caucasus) // *ZVMO*. **1993**. P. 122. N. 3. P. 44-49. (Rus.).
- Ponomarenko A.I., Malov V.S.* First finding of palladium breithauptite // *DAN SSSR*. **1991**. V. 320. N. 4. P. 967-970. (Rus.).
- Ramdohr P.* Ore Minerals. (Rudnye Mineraly). M.: IL. **1962**. 1136 p. (Rus.).
- Schneiderhohn H.* Fortschritte in der Erkenntnis sekundar-hydrothermalen und regenerierter Lagerstätten // *Neues Jahrb. Mineral. Monat.* **1953a**. H. 9/10. S. 65-89.
- Schneiderhohn H.* Ore Deposits. (Rudnye Mestorozhdeniya). M.: IL. **1953b**. 501 p. (Rus.).
- Sluzhenikina S.F., Mokhov F.V.* Minerals of gold and silver in deposits of the Norilsk region // In book: *Geologiya, Genezis i Voprosy Osvoeniya Kompleksnykh Mestorozhdenii Blagorodnykh Metallov*. M.: IGEM RAN. **2002**. P. 326-330. (Rus.).
- Spiridonov E.M., Ladygin V.M., Kulagov E.A., Stepanov V.K., Sereda E.V., Gritsenko Yu.D.* Mineralogy of rock metamorphosed at low-temperature and ores of trap formation of the Siberian platform // In book: *Mineralogiya – Osnova Ispol'zovaniya Kompleksnykh Rud*. SPb.: VMO RAN. **2001**. P. 97-99. (Rus.).
- Spiridonov E.M., Ladygin V.M., Simonov O.N., Kulagov E.A., Sereda E.V., Stepanov V.K.* Metavolcanites of Zeolite and Prehnite-Pumpellyite Facies of Trap Formation of the Norilsk Region of the Siberian Platform. (Metavulkanity Tseolitovoi i Prenit-Pumpellyitovoi Fatsii Trappovoi Formatsii Noril'skogo Raiona Sibirskoi Platformy). M.: MGU. **2000**. 212 p. (Rus.).
- Stepanov V.K., Turovtsev D.M.* Multifactor models of copper-nickel deposits of the Norilsk type // *Trudy TsNIGRI*. **1988**. N. 223. P. 86-94. (Rus.).
- Yakovlev Yu.N., Yakovleva A.K., Neradovskii Yu.N.*