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BISMUTH MINERALIZATION OF Pb–Zn ORES AT THE DJIMIDON DEPOSIT (NORTH OSETIA)

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The Djimidon deposit is a new object in the Sadon ore district (Northern Osetia — Alania). Bismuth mineralization represented by a wide spectrum of Pb-Bi-Ag-S-bearing minerals has been found in the deposit and studied in detail. Its relationships with other mineral assemblages are shown in general sequence of consecution of ore deposition. The spatial regularities in distribution of bismuth mineralization in ores of the deposits are revealed.
1 table, 5 figures, 13 references.

The Djimidon deposit discovered in the end of the 1970s belongs to the group of the wide-known Pb-Zn deposits of the Sadon ore destrict (Northern Osetia — Alania). It is located in the Ardon River basin.

Deposits of lead and zinc in North Osetia are wide known. Their study and working began since 1853. Many geologists (Azhgirei, 1958; Vardanyants, 1935; Gurbanov, Zembatov, 1978; Davydov, Granovskii, 1985; Dobrovol'skaya, 1987, 1989; Nekrasov, 1980; Chernitsyn, 1985; Khetagurov, Katova, 1972; Konstantinov *et al.*, 2003, 2004, *etc.*) carried out the detailed studies of geological-structural position of the deposits, their mineral composition and geochemical peculiarities of ores, and also genesis conditions. The interest to these deposits has again arisen since the moment of discovery of the Djimidon deposit in the end of the 1970s and the following prospecting and working of its ores; it is represented by the Bozang and East Djimidon ore zones (Fig. 1).

Geological position of the deposit

The Sadon ore region is an area between horst-anticlinorium of the Main Caucasus Range and the Darial-Bogos uplift, which part is the Sadon-Unal horst-anticline controlling allocation of the main industrial deposits of the region. The Djimidon ore field is located within the bounds of the same name uplift, which is the eastern block-segment of the Sadon-Unal horst-anticline. Rock complexes with different age form the structure of the Djimidon deposit; they compose two structural stages divided by the regional unconformity. The lower structural stage is formed by the deep metamorphosed complex of rocks of the Buron suite (Upper Proterozoic — Lower Paleozoic), which are broken by the Upper Paleozoic granitoids. The Buron suite has the distinctly pronounced binary structure conditioned by the predominant distribution of hornblende amphibolites in its basis, which up-section are gradually changed by crystalline schists of different composition. On the rocks of the crystalline substratum with basal conglomerates in the sole the Lower Jurassic terrigenous sediments of the upper structural stage are superposed. Considerable role in the structure of deposit belongs to magmatic formations of the Jurassic volcano-plutonic assemblage represented by the consecutive series: from effusive facies of covering andesites (Osetinian volcanogene complex) to subvolcanic and hypabyssal facieses of diorites, granite-porphyries, and trachyandesites (Ardon-Nogkau complex).

In structural respect, the Djimidon ore field is confined to the Djimidon uplift represented by simple anticline structure, in which core the metamorphous rocks of basement are exposed, and on the limbs the formations of the upper structural stage are represented. Along the series of transversal dislocations, the uplift is divided into separate blocks.

The Djimidon deposit is a representative of the «blind» type of mineralization (Konstantinov *et al.*, 2003); main volume of its industrial ores is concentrated in ore bodies localized in the rocks of the Pre-Jurassic basement. The ores of metamorphic complex of the Buron suite are the most propitious (Fig. 1). At transition in rocks of the upper structural stage, the ore bodies are transformed to the zones of dispersed silicification and chloritization accompanied by dispersed sulphide mineralization. Detected vertical interval of mineralization is not less than 300-350 m. Morphology of ore bodies is determined by the composition of pre-ore structure and competence of host rocks. The veined platy ore bodies prevail; quite often they are accompanied by the aureole of vein-impregnated mineralization. Morphology of ore bodies is constant up the dip.

Fig. 1. *Schematic geological map of the Djimidon ore field.(After K.V. Davydov with some changes).*
1 — limestones, dolomites (J_1ox); 2 — sandstones, aleurolites, clays, limestones (J_2); 3 — argillites, intercalations of sandstones (J_1t_{1-2}-J_2a); 4 — clay shales, aleurolites, intercalations of sandstones (J_1t_{1-2}); 5 — sandstones, aleurolites (J_1p_{2m}); 6 — conglomerates (J_1^1). The Buron suite: 7 — crystalline schists, amphibolites (PR_3 — PZ_1br); 8 — coarse-grained granites (γPZ_3). The Jurassic volcano-plutonic assemblage: 9 — lavas of andesites and their tuffs (νJ_1os); 10 — trachyandesites ($\tau\alpha J_2$); 11 — ore zones: 1 — Bozang, 2 — Zagarsar, 3 — East Djimidon; 12 — dislocations with a break in continuity: upthrow faults (a), faults (b), fractures (c): I — Fist transversal fault, II — Second transversal fault, III — East Djimidon fault, IV — West Djimidon fault, V — Agshartyrag upthrow fault, VI — Sadon-Unal fault, VII — Latitudinal fracture, VIII — Zamadon upthrow fault, IX — Zagadon fault, X — Dagom fault; 13 — supposed geological boundaries; 14 — thrusts

Post-ore dislocations significantly influence on position of ore bodies; their amplitude varies from 1 cm to 30-40 m.

Mineral assemblages and sequence of ore formation

The macroscopic and microscopic study of representative samples from the Djimidon deposit from the Bozang (adit 47, North, South, and Main drifts; adit 3, South drift; and adit 8) and East Djimidon (holes 045, 047, 061, 061A, *etc.*) ore zones allow to distinguish main mineral assemblages and make a scheme of mineral formation. Textural and structural features, variations of chemical composition of the mineral individual, in particular, sphalerite from different assemblages, and fluid regime of ore-forming system were the basis for detection of age correlations of mineral aggregates.

In the result of summarizing of obtained data, four stages of ore formation were distinguished: 1) quartz-pyrite-arsenopyrite; 2) quartz-carbonate-pyrite-pyrrhotite-chalcopyrite-sphalerite; 3) quartz-calcite-arsenopyrite-sphalerite-galena; 4) quartz-fluorite-calcite-barite. Each of these stages is represented by one or several mineral assemblages (Fig. 2).

The pre-ore stage preceded the ore deposition; quartz, potash feldspar, chlorite, sericite

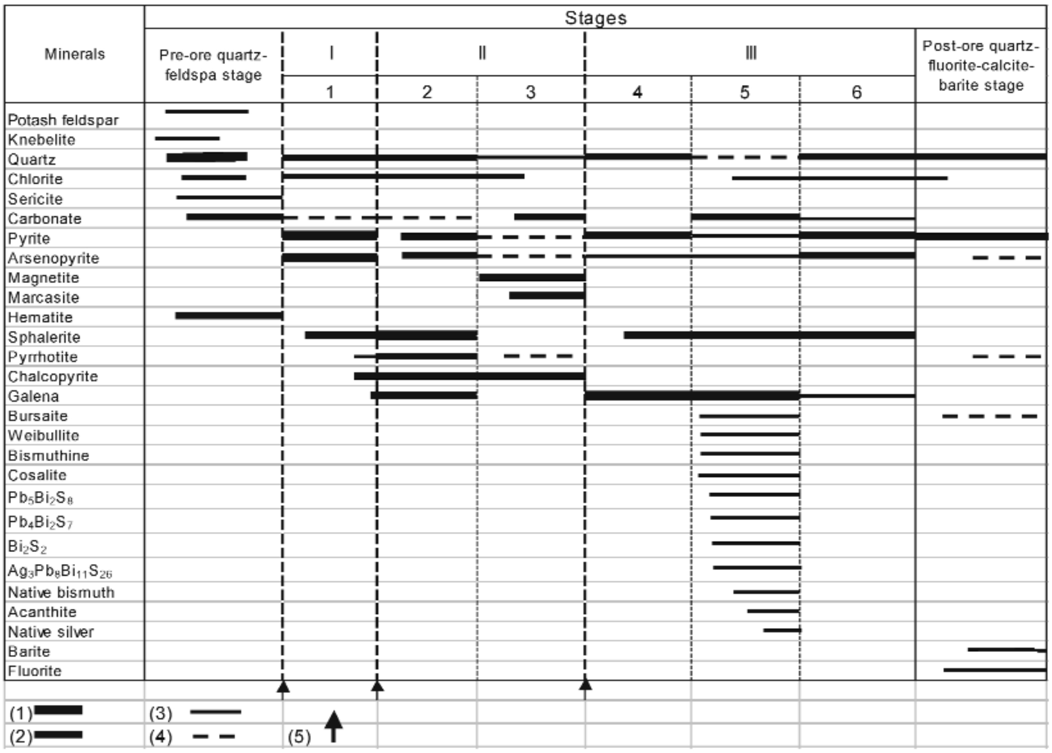


***Fig. 2**. Scheme of sequence of ore formation of the Djimidon deposit. Stages: I — quartz-pyrite-arsenopyrite; II — quartz-carbonate-pyrite-pyrrhotite-chalcopyrite-sphalerite; III — quartz-calcite-arsenopyrite-sphalerite-galena, assemblages: 1 — quartz-pyrite-arsenopyrite, 2 — quartz-galena-pyrrhotite-chalcopyrite-sphalerite, 3 — quartz-carbonate-pyrite-marcasite-magnetite, 4 — quartz-chalcopyrite-galena-sphalerite, 5 — acanthite-bismuthine-cosalite-galena, 6 — quartz-pyrite-arsenopyrite. Minerals: (1) — main, (2) — accessory, (3) — rare, (4) — redeposited; (5) — dislocations with a break in continuity*

were mainly deposited during pre-ore stage. Crystallization of knebelite, occurring in the form of xenoliths in ores, can also be related to this stage. Mineral aggregates of the pre-ore stage were here and there broken, brecciated as a result of tectonic movements that took place in the beginning of the ore deposition.

The quartz-pyrite-arsenopyrite assemblage, here and there with sphalerite I, was deposited during the fist stage in the disturbed tectonic conditions. The mineral aggregates of this assemblage form veinlets, spot-veinlet aggregations, rarely they occur in the form of compact ores. The quartz-pyrite-arsenopyrite assemblage with predominance of either pyrite or arsenopyrite occurs in the ore bodies irregularly, but its correlations with the later minerals are simple. Quartz, pyrite, and arsenopyrite are brecciated, broken down, fractured; the fractures are filled up by sphalerite, chalcopyrite, pyrrhotite, galena, and quartz, forming the next by time of deposition assemblage belonging to the second stage. The assemblage is not observed everywhere. In separate parts, the amounts of minerals forming it are changed. In some parts, pyrite and chalcopyrite prevail in the assemblage, they form intergrowths; in other parts are chalcopyrite and sphalerite, and also pyrite of the second generation. Sphalerite in this assemblage contains the abundant inclusions of chalcopyrite and pyrrhotite, which are characteristic for sphalerite II.

The quartz-galena-pyrrhotite-chalcopyrite-sphalerite assemblage of the second stage is the main assemblage in the ores. After its formation, the deformations in mineral aggregates of this assemblage (the local fragmentation and boudinage of aggregates, the curved and removed twins in pyrrhotite and sphalerite, etc.) have appeared as a result of the disturbed tectonic conditions. We should note galena was not undergone deformations; that indicates its later crystallization.

Galena, pyrrhotite, chalcopyrite, and sphalerite form intergrowths, sometimes with features of earlier deposition of sphalerite. A peculiarity of this assemblage is in unsteady ratios of quartz and sulphides; sometimes, it is represented only by quartz with rosettes of chlorite and by sphalerite II without other sulphides. The quartz-sphalerite aggregates form veinlets or aggregations in the gouges of ore bodies.

In the end of the second stage, the conditions were strongly changed; the sulphur and oxygen activity has increased, as a result, the disulphidization of pyrrhotite and formation of carbonate-pyrite-marcasite-magnetite assemblage has happened; this assemblage is probably reactionary, arising at the border of two stages of ore deposition. Pyrite and marcasite intensively substituted pyrrhotite, sometimes together with magnetite and siderite. In the separate parts magnetite (muschketowite) replaced hematite.

The third stage, quartz-calcite-arsenopyrite-sphalerite-galena, is represented by three mineral assemblages: quartz-chalcopyrite-galena-sphalerite, here and there with pyrrhotite; acanthite-bismuthine-cosalite-galena; and quartz-pyrite-arsenopyrite. The quartz-chalcopyrite-galena-sphalerite assemblage, sometimes with calcite and pyrrhotite, occurs everywhere and mainly in the central parts of ore bodies. In contrast to early assemblage with the similar name, pyrrhotite in the late assemblage is not disulphidized. Sphalerite III, dominating in the assemblage, contains the irregularly distributed inclusions of chalcopyrite, but in significantly smaller amounts. Crystallization of low-iron sphalerite associated with galena, quartz, and calcite is connected with the third stage.

The acanthite-bismuthine-cosalite-galena assemblage occurs in the ores locally. It was found in the adit 47 and in a number of holes: 045, 047, 061, 061A, 076. The facies distinctions are typical for it. In some parts, the Ag-Pb-Bi assemblage with galena, native bismuth, sulphides, and sulphosalts of Pb and Bi occurs; in other parts are native silver, acanthite, and galena. Bismuth minerals substitute earlier sulphides: pyrite, arsenopyrite, pyrrhotite, chalcopyrite, sphalerite; they are associated with quartz and calcite.

Mineral aggregates of the quartz-pyrite-arsenopyrite assemblage of the third stage fill up the veinlets; minerals of this assemblage form metacrystals. Pyrite and arsenopyrite overgrow quartz in the form of cockades, cut up mineral aggregates of earlier stages, form metacrystals in sphalerite, chalcopyrite, and galena. Quartz metacrystals are often observed among sulphides.

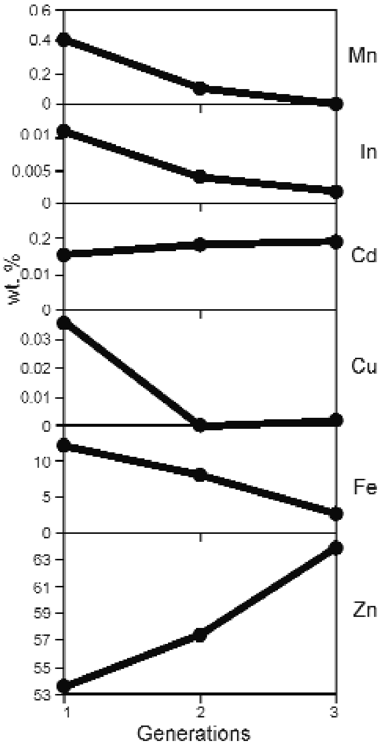


Fig. 3. *Graphs showing average contents of elements-admixtures in sphalerite of different generations. Generation I (24 analyses), generation II (9 analyses), genera-*

The fourth stage, quartz-fluorite-calcite-barite, finishes a process of minerogenesis. In this stage, the quartz-calcite veinlets were deposited, which cut the mineral aggregates of earlier stages. In some veinlets, quartz prevails, in other ones, calcite does so; sometimes there are barite and fluorite. These minerals form also individual veins with thickness of 20-30 cm, beyond the bounds of main ore bodies. Some veins are composed by microcline and calcite.

The distinguished mineral assemblages, textural and structural analysis of ores indicate the interrupted-continuous process of coming of hydrothermal solution, that resulted in crystallization of identical minerals (quartz, pyrite, arsenopyrite, sphalerite, pyrrhotite, chalcopyrite, galena) in mineral assemblages, differing by time of formation, and within the limits of different stages. The periodicity in formation of early and late assemblages, in particular, quartz-pyrite-arsenopyrite assemblage, is an

Table 1. **Chemical composition of bismuth minerals from ores of the Djimidon deposit (wt %)**

№ п/п	№ sample	Occurrence	Pb	Bi	S	Fe	Ag	Sb	Se	Zn	Cu	Total	Mineral
1	3-8a	Bozang, adit 3	84.43	1.35	13.37	–	0.46	0.00	0.47	–	0.02	100.10	galena
2	1.8	East Djimidon, hole 061A-220.5	70.24	14.09	13.91	0.06	0.30	0.00	0.28	0.00	0.07	98.95	Bi-galena
3	3-8a	East Djimidon, hole 061A-220.5	68.42	15.10	14.80	–	0.48	0.04	0.57	–	0.11	99.52	Bi-galena
4	1.3	East Djimidon, hole 061A-219.6	63.60	21.03	13.50	1.02	0.25	0.00	0.26	0.03	0.08	99.77	beegerite
5	1.3	East Djimidon, hole 061A-219.6	59.06	26.89	11.05	0.34	2.00	0.09	0.26	0.05	0.00	99.74	hoongarrite
6	1.1	East Djimidon, hole 061A-220.5	50.86	34.84	13.50	0.09	0.43	0.00	0.23	0.04	0.00	99.99	lillianite
7	3-8a	Bozang, adit 3	44.19	37.36	15.78	–	1.48	0.01	0.50	–	0.11	99.43	bursaite
8	3-8a	Bozang, adit 3	39.33	42.22	16.60	–	0.62	0.00	0.23	–	0.81	99.81	cosalite
9	1.6	East Djimidon, hole 061A-219.6	37.86	44.91	15.42	0.09	0.25	0.04	0.20	0.04	0.00	98.81	cosalite
10	47-43	Bozang, adit 47	37.58	44.74	15.28	–	2.63	–	–	–	–	100.24	cosalite
11	47-43	Bozang, adit 47	34.68	47.61	15.58	–	1.90	0.00	0.10	–	0.30	99.35	weibullite
12	47-43	Bozang, adit 47	33.78	48.04	16.70	–	1.30	0.00	0.10	–	0.00	100.16	weibullite
13	47-43	Bozang, adit 47	32.31	47.76	15.97	–	5.60	0.00	0.10	–	0.40	98.24	$Ag_3Pb_8Bi_{11}S_{26}$
14	1.9	East Djimidon, hole 061A-220.5	22.18	61.14	15.75	0.03	0.18	0.10	0.11	0.04	0.04	99.57	galenobismutite
15	5	East Djimidon, hole 061A-220.5	5.56	75.72	18.26	0.20	0.02	0.10	0.00	0.04	0.00	99.96	bismuthine
16	8.2	East Djimidon, hole 061A-219.6	0.00	81.06	18.51	0.11	0.00	0.00	0.11	0.00	0.00	99.81	bismuthine
17	1.7	East Djimidon, hole 061A-219.6	7.93	89.19	1.43	1.11	0.02	0.00	0.07	0.04	0.06	99.89	native Bi
18	47-43	Bozang, adit 47	0.86	96.08	0.15	–	0.00	0.00	0.00	–	0.80	98.49	native Bi
19	2.4	East Djimidon, hole 061A-219.6	0.00	99.56	0.07	0.03	0.00	0.00	0.00	0.02	0.03	99.71	native Bi
20	47-43	Bozang, adit 47	0.70	83.24	12.81	–	0.10	0.00	0.10	–	0.60	98.96	Bi_2S_2

Note: *Desh – element was not detected. Analyses were performed in the laboratory of IGEM RAS, electron microprobe instrument SX-50, analyst A.I. Tsepin.*

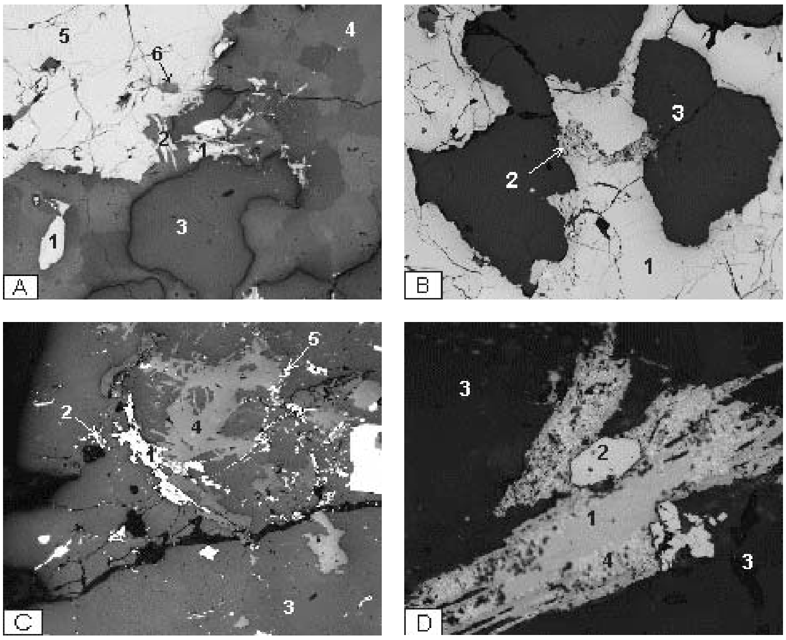
indication of the stage formation of ore bodies (Dobrovol'skaya, 1989). The consecution of ore deposition is also confirmed by the change of chemical composition of sphalerite. The analytical data has shown that sphalerite I is enriched by iron (9.55-15.48 wt %) and manganese, in sphalerite II, the content of iron varies from 5.8 to 9.96 wt %, the third generation of sphalerite is represented by the low-iron (0.73-3.88 wt %) cleiophane with content of cadmium up to 0.3 wt % (Fig. 3).

The results of the thermo-cryometric study of fluid inclusions in sphalerite, quartz, and carbonate from ore bodies also allow realizing the main features of fluid regime of formation of mineral assemblages of the Djimidon deposit. Ores were deposited from hydrothermal solutions with predominantly sodium-chloride composition with admixtures of other components in a wide range of concentrations from 18 to 0.5 wt % equiv. NaCl under the pressure not less than 400-300 bar. In each ore stage, the process of minerogenesis began from higher temperatures (250-350 °C); to the end, the temperature has reduced to 120-150 °C. This data also emphasizes the pulsatile character of the process.

Chemical composition of the Bi-minerals

The bismuth mineralization is represented by a wide spectrum of Bi-bearing minerals (Tabl. 1).

tion III (14 analyses)



The analytical data allowed identifying bismuthine (Bi_2S_3), bursaite ($Pb_3Bi_4S_{11}$), weibullite ($Pb_3Bi_4S_9$), cosalite ($Pb_2Bi_2S_5$). In the same assemblage, the phases $Pb_5Bi_2S_8$ and $Pb_4Bi_2S_7$ were found, and also there are a phase, containing silver ($Ag_3\ Pb_8Bi_{11}S_{26}$), acanthite (Ag_2S) and native silver and bismuth. Chemical composition of Bi-bearing minerals is studied quite minutely, 94 phases were analysed; in Table 1 are the analyses, which are correctly calculated on mineral formulas and correspond by chemical composition to sulphosalts of lead and bismuth described by N.N. Mozgova (1985).

The distribution of bismuth mineralization in ores has some peculiarities. One of them is in occurrence of the bismuth minerals containing up to 5.6 wt % of silver in the upper parts of the ore bodies. In the lower parts, the amount of silver in them is reduced up to 1.7 wt %. The other peculiarity is the change of mineral composition according to depth of the ore body uncovering. Bismuthine is the most widespread mineral in the deep parts; above is cosalite. It is evidence that amount of bismuth increases with depth. The third peculiarity is in regular occurrence of bismuth mineralization only in determined parts, in particular, within the interval of depths of 180-220 m and only where pyrite, arsenopyrite, and pyrrhotite are present in ores; pyrrhotite was partly or sometimes entirely disulphidized. The single findings of the bismuth minerals were made at a depth of 100 m.

Native bismuth, sulphides, and the bismuth sulphosalts have been found in the adit 47 and in the holes 045, 047, and 061A. These minerals are mainly associated with quartz (Fig. 4). Their occurrence among calcite is explained by that quartz in alkaline conditions were dissolved and partly redeposited in the form of metacrystals; the bismuth minerals associating with quartz were kept in calcite (Fig. 4a). In a number of cases, the bismuth minerals occur among sulphides: pyrrhotite (Fig. 4b), arsenopyrite, sphalerite, and chalcopyrite. The sizes of single grains of the Bi minerals and their intergrowths are units of microns, sometimes up to 30 μm. The forms of aggregations are diverse: irregular, lamellar, needle-shaped, aggregated (Fig. 4).

Galena, presenting in the composition of Bi-bearing assemblage, differs by chemical composition according to depth of its occurrence. In 9 samples collected at the Djimidon deposit, galena contains a small amount of silver (0.09-0.48 wt %) and bismuth (0.24-15.1 wt %). At a depth of 186-220 m (holes 047, 061A), galena is enriched by bismuth (Tabl. 1, an. 3).

Native bismuth is distributed considerably wide than other Bi minerals. Especially often it occurs in samples from the holes of underground drilling, 045, 047, 061A, in the intervals of depths of 180-220 m. Native bismuth usually substitutes Bi-bearing minerals and also forms separate small aggregations among quartz (Fig. 4c). Chemical composition of 8 grains of native bismuth has shown the significant contents of admixtures of iron, copper,

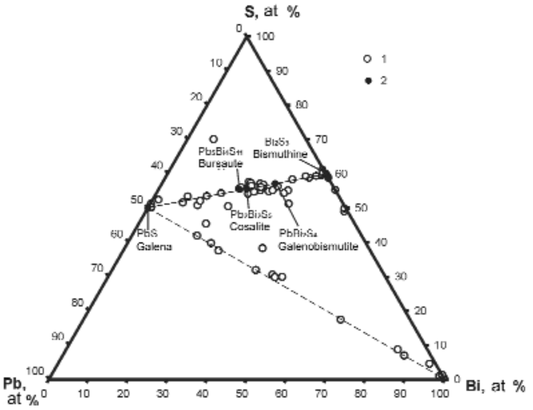


Fig. 4. *Forms of aggregations of Bi-bearing minerals. Polished sections. Magnification 160 (a, c), 200 (b), 250 (d).*
a — thin-lamellar aggregates of bismuthine (1) (Tabl. 1, an. 15), galenobismutite (2) (Tabl. 1, an. 14) in quartz (3) and calcite (4)

and sulphur in it. In one of analyses are silver (0.28 wt %) and lead (1.58 wt %). These admixtures are probably connected with surrounding sulphides, since grains of native bismuth are extremely small. The most representative analyses (an. 17 — 19) are given in Table 1.

Bismuthine occurs in the form of prismatic and needle-shaped crystals, sometimes thin-crystal intergrowths among quartz (Fig. 4a). Chemical composition of bismuthine is relatively constant. Content of bismuth fluctuates from 75.7 to 83.2 wt %, sulphur — from 15.8 to 18.4 wt %. Some decrease of the bismuth content is caused by the lead admixtures. Results of analyses are well calculated on the bismuthine formula (Tabl. 1).

Cosalite is similar to bismuthine by forms of aggregations (Fig. 4c, d). The thin needle-shaped crystals, sometimes intergrowths and small-grained aggregates are also typical for it. Cosalite is optically heterogeneous; it forms intergrowths with other Bi-bearing minerals. The most constant by chemical composition cosalite was found in samples from the adit 47. The bismuth content in it increases with depth. 17 phases of cosalite were analysed; selected analyses calculated on mineral formula (an. 8-10) are given in Table 1. The summarized data has shown the fluctuations of Bi from 41.5 to 50.8 wt %, lead — from 36.6 to 41.2 wt %, sulphur — from 15.1 to 16.7 wt %.

Galenobismutite is not practically distinguished from cosalite by the optical properties. By chemical composition, these minerals are close to each other; in the single analyses of galenobismutite (Tabl. 1, an. 14), the higher, in comparison with cosalite, contents of bismuth and smaller amounts of lead, 61.14 and 22.18 wt % respectively, were obtained.

Weibullite, bursaite, Pb–Bi phases, and Ag–Pb–Bi–bearing phases occur usually in thin intergrowths with each other, these minerals and mineral phases are relatively rare in ores; their description is difficult because of sub-microscopic sizes of their grains. They were detected only on the basis of chemical analyses, distinguishing from analyses of cosalite and bismuthine (Tabl. 1), and calculated mineral formulas.

The variations in the chemical composition of the Pb-Bi-S minerals are shown on the diagram of phase correlations in the system (Fig. 5), which shows the regular continuous series of mineral phases, PbS — Bi_2S_3 (Minerals, 1974). The diagram is made on the basis of cosalite, experimentally grown as a stable phase at the temperature 400 °C (Craig, 1967), and chemical compositions of minerals from the Djimidon deposit. On the diagram, the filled circles correspond to theoretical chemical compositions of galena, bursaite, galenobismutite; the unfilled circles correspond to Bi-bearing minerals from the deposit. Some fluctuations of chemical compositions from the PbS-Bi_2S_3 system (Fig. 5) are probably connected with formation of phases in the same series at lower temperatures (Craig, 1967). Once more series, PbS-Bi, corresponding to the analysed samples, was found during the diagram making. This series, galena — native bismuth, corresponds to the unsteady ratios of lead, bismuth, and sulphur in the studied phases; it is apparently connected with their heterogeneity because of small-grained intergrowths.

By data of microthermometry of fluid inclusions (by quartz and carbonate from acanthite-bismuthine-cosalite-galena assemblage), it is obvious that solutions had both sodium-chloride and magnesium-chloride chemical composition and high concentrations up to 17 wt % equiv. NaCl; the highest temperatures of minerogenesis to 300-350°C were here.

Conclusion

Mineral composition of ore bodies of the Djimidon deposit is quite simple and similar to ore composition of other lead-zinc deposits of the Sadon ore region. The quite wide occurrence of arsenopyrite and presence of the diverse Pb-Bi-Ag-S mineralization found at the deposit for the first time are the distinctive peculiarity of ores of the Djimidon deposit.

Ores of the Djimidon deposit are characterized by the presence of facies distinctions in the mineral composition of main assemblages, local distribution of the Pb-Bi-Ag-S mineralization, and presence of two to three-four generations of main ore-forming minerals.

Geochemical peculiarities of ores, in particular typomorphism of sphalerite and galena, have shown the increased concentrations of indium in early stages of mineralization and cadmium, silver, and bismuth in later stages.

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