POLYMETAL PARAGENESES OF THE ORE OCCURRENCE IN THE CATCHMENT AREA OF THE SREBRENJAK BROOK SOUTH OF THE TOWN OF DVOR NA UNI IN CROATIA

With 1 Textfigure

The Srebrenjak Brook is one of the left tributaries of the Una River, into which it flows about 1.5 km. south-west of Bosanski Novi, i. e. a little south of the village of Matijevići (Fig. 1).

This brook received its name thanks to occurrences of silver-bearing galena, which were exploited in the Middle Ages as well as in the period of the so-called Military Province (Vojna Krajina). The first data on mining activities were furnished by B. Hacquet (1789, IV. p. 12). This author discovered remnants of mining activities in the area of the Srebrenjak Brook, which took place in 1771, but which were discontinued owing to Turkish invasions. In D. Stur's work (1863) it is mentioned that the ore belt of Trgovska Gora Mountain extends as far as Strgar and Tomašica. According to data furnished by F. v. Andrian (1868), in the Srebrenjak Brook are to be found copper ores containing less than 5% copper. F. Tućan (1908) made a quantitative chemical analysis of the siderite from the occurrence of Strgar. This siderite contained chalcopyrite, pyrite, galena and limonite. The results of the analysis were: 0.97% insoluble in HCl, 56.23% FeO, 1.31% MnO, 1.24% CaO, 2.18% MgO, S in traces, 38,25% CO₂, Al₂O₃ in traces, i. e. a total of 100.28%. By computation the author obtained: 90.51% FeCO₃, 2.12% MnCO₃, 2.21% CaCO₃, 4.52% MgCO₃. K. v. Reuter (1910) gives us data on the content of silver in the ores of the area of the Srebrenjak Brook:

	Eva		Srebrenjak	Strgar	Warda	
Pb in %	32.8	70.6	31.7	57.3	32,8	38.0
Ag/t ores in g.	160	268	150	280	_	-
Ag/t Pb in g.	488	380	483	492	93	180

K. v. Pap p (1919) gives us sketch and position of the ore fields of Haas, Camillo, Heliodor, Srebrenjak, Lazić, Adam and Eva in the catchment area of the Srebrenjak Brook. These ore fields were the property of the Belgian enterprise »A. G. Hauts fourneaux, mines et

forêts en Croatie«. In F. Tućan's (1941) work it is mentioned that in Strgar are to be found sidenite with impregnations of chalcopyrite,

galena and pyrite.

The Srebrenjak ore region is built of Upper Palaezoic clayey schists with intercalations of sandstones, less frequently limestones (D. Devidé-Neděla, 1953, manuscript), and it is situated within the Palaeozoic horst of Trgovska Gora Mountain.

Ore occurrences Srebrenjak(**) in Palaeozoic of Trgovska gora



Fig. 1

Jointly with Ing. A. Ferenčić the author inspected in 1951/52 this ore region and collected numerous ore samples from the remaining ore-dumping yards of the following old and filled-in mining sites: Adam, Eva, Srebrenjak, Strgar, Marijana. Microscopic examinations revealed in the otherwise very interesting parageneses for the first time also nickel-cobalt minerals (I. Jurković, 1959).

The ore occurrences of

1. Adam 2. Eva 3. Srebrenjak

In the source area of the Srebrenjak Brook are to be found the once most conspicuous prospecting works for silver-bearing galena. A few tens of metres below the mountain ridge are to be seen remnants of the old adits of Adam, Eva and Frohm. In the dumps are to be seen pieces of a coarse-grained siderite with a network of small veins, nests of quartz, impregnations of galena, and smaller quantities of pyrite and chalcopyrite. The siderite vein 1 m. thick was exposed at its outcrop by an open pit. In the adit of Frohm, which was 34 m. long, the vein possessed an 8 m. long thickening. In the ditches around this ore occurrence are to be observed occurrences of ochre. About 200 m. downstream, in a small right-hand tributary of the Srebrenjak Brook, is to be found the ore occurrence of Srebrenjak, which was earlier open by a smaller adit and trenches. In the ore-dumping yards were revealed blocks and large pieces of siderite with quartz, galena and chalcopyrite.

Paragenesis of the ore occurrences

Hypogene minerals: pyrite, arsenopyrite, gersdorffite, Ni-linnacite, millerite, siderite, quartz, sphalerite, chalcopyrite, tennantite, enargite, bournonite (seligmannite), boulangerite, mineral X, mineral Y, galena, marcasite, chalcedony, sericite.

Hypergene minerals: chalcocite, covellite, millerite, bravoite, psilo-

melane, lepidocrocite, goethite, Ag-mineral, pyrite, marcasite.

Siderite is the main mineral of these ore occurrences. Quartz is second in quantity after siderite. With the naked eye we were able yet to note galena, chalcopyrite, pyrite, tennantite and sphalerite. All the other minerals were discovered only under the microscope. Of sulphides PbS occurred in largest quantities.

Microphysiography of the minerals

Pyrite is present in several generations; it is much spread in the veins. Its quantities, however, are small. The pyrite of the first generation with some arsenopyrite is at the same time the oldest mineral of the paragenesis. It is preserved only in the form of smaller or larger relict masses in siderite, as well as in the form of single corroded or porous grains, while more rarely it comes as idiomorphically developed individuals in younger sulphides, sulphosalts and quartz. In places we noted various skeletons of pyrite in siderite and in galena as a relict of selective replacement. Pyrite I is as a rule coarse-grained, to a lesser or greater degree cataclased. The cataclases are filled with younger sulphides and sulphosalts, which gives rise to a replacement of pyrite, sometimes to the extent that there occur »island structures« of pyrite.

Locally, the pyrite is completely crushed, while its sharp-edged fragments are cemented with quartz or other younger minerals. At the edges of some small pyrite masses is to be noted myrmekite of byrite and tennantite, a phenomenon thus far not mentioned in literature. Still more interesting is the myrmekite of pyrite and an unknown Cu -mineral. The pyrite of the second generation is fine-grained and not infrequently ingrown with marcasite. There are also occurrences where marcasite replaces pyrite. This pyrite is to be noted along the cracks of siderite or quartz, or it occurs in the form of band-like series of grains in galena, tennantite etc. In one polish section was noted a larger mass of pyrite of radially-fibrous structure, probably a pseudomorphosis on marcasite. The pyrite of the youngest generation either envelops in the form of very fine films the grains of siderite, or it makes an irregular network of microscopically thin threads in the siderite mass (filiform replacement). This pyrite was surely deposited under the influence of vadose waters, maybe also descendingly. It is a characteristic of the pyrite of all generations that it is replaced to a smaller or greater extent by bravoite. This replacement is of descending character.

Siderite is the main mineral of the paragenesis. It occurs in two, maybe in three generations. The oldest generation is as a rule very coarse-grained. The structure is allotriomorphically granular, the texture compact, more rarely drusy. The younger generations is on the average fine-grained, while the texture is the so-called »Lagentextur«, where series of smaller and larger grains of siderite alternate. In addition, there are fan-like and subparallel aggregates of siderite grains. The rhombohedral cleavage of the siderite is very clearly developed. The cleavage planes are not infrequently bent, more rarely distorted. The siderite contains more or less strongly developed displacement zones, and these are in the main deposited with younger minerals. A characteristic feature is the fact that in places the siderite grains differ in reflectivity relief and resistance to replacement, and frequently we can note resistant rhombohedrons of siderite in the mass of sulphides and sulphosalts, or sieve-like structures of sulphides and siderite. The first (main) generation of siderite belongs to the principal phase of ore deposition, which took place after the crystallization of pyrite I, and it is older than quartz and the generation of sulphides and sulphosalts. Replacement of the siderite by the younger minerals was taking place either in the interstices of siderite grains - especially in the less compact masses of the siderite -, or where the siderite possesses drusy characteristics, or along cleavage fissures, or in crushed zones along cracks and fissures. Through replacement there occurred dendritic formations, more rarely net-like formations, in places also masses of younger minerals in frontal replacement. Siderite is less resistant to replacement than pyrite, so that in the sulphides there oftentimes remain corroded grains of pyrite. In the quartz there are almost no relicts of siderite. In parts of the veins near the surface the siderite undergoes oxidation into goethite. The oxidation follows as a rule the cleavage fissures, and in crushed zones the cracks and fissures.

Quartz also occurs in several generations. Its oldest generation is coarse, the dimensions of the grains exceeding several mm. Grains of this quartz are cracked or cataclased, while optically they are anomalous. Sometimes it is possible to note a strong internal strain of the quartz grains and a beginning of crystallization in the form of infrastructure, which is spatially oriented in a certain direction. An optical anomaly of the quartz manifests itself in a wave-like darkening or an irregular division of the quartz grain into optical fields, each of which shows an individually different darkening. In places the optical fields are without spatial orientation, in others they are oriented in a special direction. The quartz of the second generation is finer-grained, the grains being either isometric or elongated. Oftentimes it is possible to note that part of this quartz was formed through recrystallization from chalcedony, for we can still observe relicts of a chalcedony of radially -fibrous structure and fan-like forms. The quartz replaces pyrite I and the siderite. Very beautiful are the dendritic structures of replacement of the siderite. The younger quartz replaces pyrite II and other minerals. Relicts of quartz I in the form of corroded grains are to be seen in the mase of sulphides. Crystallization of the quartz preceded the sulphide generation.

Millerite is in the form of fine needles that lie embedded in other sulphides. The needles either occur singly or are arranged subparallel or radially, forming bundles. The needles are of various dimensions, from a few microns to 0.3 mm. in length. There are also smaller and larger masses of a fine-grained millerite. The most beautiful bundles of millerite needles are to be found in bournonite. One gets the impression that we are concerned with idioblasts of millerite. Gersdorffite oftentimes envelops the millerite masses or fills in the interstices of the needle-like bundles of millerite. Millerite is likewise associated with linnaeite, which is somewhat younger than the former. Millerite occurs also through exsolution of Ni-linnaeite in the form of crystallographically oriented lamellae into two systems. The lamellae are thin, shorter or longer. At interstices of the lamellae are formed disks and irregular masses of millerite. In places millerite replaces whole parts of Ni-linnaeite. Millerite is formed from Ni-linnaeite through wear in the transitory oxidation-cementation zone. Millerite, as are gersdorffite and Ni-linnaeite, is associated with sphalerite, tennantite, chalcopyrite, bournonite, enargite, galena and pyrite. Accordingly it belongs to the younger sulphide generation. The true relation of millerite to these sulphides is not clear, the only thing possible to conclude being that it is younger than pyrite and maybe sphalerite, but it is older than galena, bournonite and tennantite.

Ni-linnaeite is like the other Ni-minerals only locally developed in the siderite veins. It is bound to the generation of sulphides and sulphosalts, and its relations resemble those of millerite. Ni-linnaeite is not infrequently idiomorphically developed either in the form of single crystals or as intergrown crystals. There are also irregular small masses of linnaeite. By its rosy tint – particularly in oil – it is easily

differentiated from the cream-yellow colour of gersdorffite. The excess of nickel in the molecule of Ni-linnaeite is often deposited in the form of lamellae of millerite along (111) linnaeite. Ni-linnaeite contained also copper in the molecule, which manifests itself by the exsolution of chalcopyrite or covellite.

Gersdorffite (Korynite?) it to be found associated with Ni-linnaeite and millerite, while all three minerals are associated with pyrite, sphalerite, chalcopyrite, tennantite, bournonite, enargite and galena. It is in part idiomorphically developed and embedded in galena, bournonite and tennantite, partly in the form of masses in the interstices of bundles of crystals of millerite, partly as intergrown masses on pyrite and Ni-linnaeite. Its largest crystals were noted in bournonite. On some individuals of gersdorffite are to be seen numerous intergrown lamellae, which points to a submicroscopically oriented intergrowths of gersdorffite and chloantite. There are also zonary grains of gresdorrfite. The zones differ by their hardness and colour. The harder zones are yellower in tint, the softer ones possess a bluish-rosy tint when watched in oil. The hexahedral cleavage and triangular pits are visible on the larger grains of gersdorffite. Because of the microscopic dimensions of the grains and crystals of gersdorffite and the intimate intergrowths with other sulphides and sulphosalts it was impossible to carry out a qualitative analysis of this material in order to find out whether we were concerned with gersdorffite or korynite. In the same metallogenous district - in the ore deposits of Gradski potok - Z epharovich (1873) mentions the presence of gersdorffite on the basis of a quantitative chemical analysis by Escka.

Sphalerite is rarely visible with the naked eye, but quite frequently under the microscope. In most cases it occurs associated with galena, which as a younger mineral, replaces it, most particularly along the veins in siderite. It occurs frequently in the form of rounded masses in tennantite, and then almost as a rule with a thin rim of chalcopyrite. This sphalerite contains exsolutions of lamellae and drops of chalcopyrite, and it possesses dark red-brown internal reflections. On the other hand, the sphalerite that occurs alone with galena shows almost no exsolution of chalcopyrite, and it possesses lighter internal reflections. We are concerned here probably with two generations of sphalerite.

Chalcopyrite occurs in several generations. To the oldest generation probably belong the tiny rounded masses in the siderite. The second generation of chalcopyrite was exsoluted in the form of drops and disks in marmatite. The third generation is most intimately intergrown with tennantite, oftentimes with mutual boundaries. Amounts of chalcopyrite are small; it is rarely seen with the naked eye, but it occurs very frequently in the samples examined.

Tetrahedrite is a very frequent mineral in the paragenesis, but its guantities are much smaller than those of galena. It is younger than sphalerite and the main mass of chalcopyrite, and older than bournonite

and galena. At the beginning of the crystallization tetrahedrite replaces sphalerite, during which action around the relict masses of sphalerite-there is deposited a reaction rim of chalcopyrite. This tetrahedrite is as a rule porous; it contains markedly resorbed small masses of chalcopyrite, corroded grains of pyrite, and siderite. Along with such larger masses of tetrahed rite we can note small masses of enargite and chalcopyrite. The colour of the tetrahedrite is olive-green, the internal reflections are rarely noticeable, and it is hard to ascertain whether we are concerned with tetrahedrite or tennantite. We established the presence of tennantite as a certainty in that tetrahedrite which associated with galena replaces siderite. This tetrahedrite shows in cedar oil numerous red-brown and red internal reflections, while typical of tennantite is its greenish colour. Tennantite, along with galena, cements and replaces crushed masses of pyrite. Through ascension of lead ions there occurs by reaction with tetrahedrite bournonite, which, for this very reason, is most intimately intergrown with tetrahedrite, while through replacement of such tetrahedrite along galena there remain in the latter relicts of bournonite. Characteristic is the occurrence of myrmekite of tetrahedrite and pyrite.

Enargite is of microscopic dimensions. We noted it only in some of the polish sections, and then it was rather frequent and occurred associated with marmatite, tetrahedrite and chalcopyrite. Its masses are extraordinarly fine-grained. In places are to be seen twinning lamellae.

Boulangerite was observed only here and there in the siderite in the form of small needles of rhombic cross sections. The needles are rarely scattered, while in places there are denser clusters. The reflection pleochroism is weakly expressed, the anisotropic effects are clear but not strong.

Bournonite is a frequent mineral, although of microscopic dimensions. It is most intimately intergrown with tetrahedrite, while smaller quantities are to be found also in galena. Between the tetrahedrite and galena we can note very frequently a reaction rim of bournonite. It is evidently younger than tetrahedrite, and older than galena. In cedar oil it differs clearly by its bluish tint from the greenish colour of tetrahedrite. It is distinctly anisotropic, especially with incompletely crossed nicols. Commonly polysinthetically twinned, sometimes the twinning lamellae intersect each other, producing parquet-like appearance. In one polish section it was possible to note how bournonite is forming a reaction rim between the oval formations of an unknown mineral in galena. Besides bournonite, the reaction rim is composed of tetrahedrite. This mineral X has a higher reflectivity than galena, but when observed in oil — in contradistinction to the rose-coloured tint of galena—it possesses a creamy tint.

In one polish section there was observed among the grains of pyrite and tetrahedrite a mass of a grey-violet mineral that in oil assumed a brown tint, and which was darker than tetrahedrite. Along (111) this mineral there were deposited lamellae of covellite and millerite. Lo-

cally, almost the whole mass of this mineral was transformed into covellite. This mineral Y is very frequently intergrown poikilitically or mirmekitically with pyrite. At time there can be noted in it lamellae of a much lighter component. When occurring in single crystals it is zonary, the zones being separated by a lighter component. We are concerned here probably with structures of deterioration of an unstable Cu-Ni mineral.

Galena is the most important and at the same time the youngest sulphide of the ore occurrence. It occurs either alone or associated with other minerals, especially tetrahedrite and sphalerite. When alone, it replaces siderite, filling the interstices of the siderite grains, or it widens them metasomatically, in which case are created dendritic forms of galena. In case there exists a resistance of the more resistant rhombohedrons of siderite, then are formed polygonal spaces filled with galena. Impregnations of tetrahedrite or sphalerite in siderite are replaced by galena frontally, during which action there remain smaller or larger masses or oval formations of these minerals in galena. If the tetrahedrite contained bournonite, then, by the tetrahedrite being replaced, there remain masses of bournonite in galena. Between galena and tetrahedrite we can note very frequently the reaction rims of bournonite. The galena contains relicts of older sulphides, as for instance corroded grains of pyrite, idiomorphic crystals or masses of gersdorffite, furthermore millerite, sphalerite etc. Some masses of galena are filled sieve -like with remaining masses of siderite. Myrmekite of tetrahedrite and galena was observed very rarely. Owing to inclusions of tetrahedrite in galena, the analyses of the galena from Srebrenjak showed marked amounts of silver.

Of hypergene minerals goethite is the most abundant. It is formed through the oxidation of siderite. Goethite and lepidocrocite are formed through the oxidation of pyrite. Manganese, which is contained in the molecule of siderite, leaves during the process of oxidation in the form of psilomelane. Through weathering of tetrahedrite and chalcopyrite, covellite and chalcocite are formed, more rarely malachite and azurite. The silver from tetrahedrite was deposited in the form of an Ag-mineral, which, owing to its small dimensions, could not be determined. Weathering of Ni-linnaeite gives rise to the formation of millerite and covellite. The most conspicuous mineral of the hypergene processes is bravoite. It is formed through the weathering of nickel hyporene minerals. Descending solutions, which contained a thus exsoluted nickel, deposit by way of cementation on the fresh pyrite of the primary zone bravoite. Bravoite replaces pyrite along microcracks or along boundaries of the grains. Thus is formed a very irregular network of bravoite in the pyrite masses. Where the pyrite is fine-grained it can be noted that the grains of pyrite are zonary, and that the external zones contain the bravoite component, i. e. that they contain nickel. This bravoite may have been formed ascendently at very low temperatures, but through the influence of vadose waters. In one polish section it was possible to observe marked zonary crystals of bravoite. The internal zone has a

higher relief. It is yellow in colour, and this core is of pyrite; the outer zone possesses a lower relief, it is separated into sectors, each of the sectors has another tint: yellowish-rosy, rose-coloured, brown, dark brown, which points to the varied contents of nickel in these sectors.

4. The ore occurrence of Marijana - 5. The ore occurrence of Strgar

The position of Marijana is circa 0.5 km. upstream in the Srebrenjak Brook, on its left bank. In the time of the Military Province it was open along a 10 rm. long adit. Beside the entrance to the filled-in adit there is an outcrop of limonitized siderite vein 0.2-0.4 m. thick. In addition to siderite as the main mineral, the vein contains some quartz and much less chalcopyrite and pyrite, and very rarely galena. The stretching of the vein is E-W, sloping northwards.

The position of Strgar is circa 0.5 km. south-west of Marijana, in a right-hand tributary of the Srebrenjak Brook. During the Military Province it was open owing to a shorter adit and several trenches. Above the filled-in adit it is possible to see an outcrop of limonitized siderite vein extending NW-SE.

A microscopic examination of ore samples collected in the dumps of the adits of Marijana and Strgar gave the following paragenesis:

Hypogene minerals: pyrite, gersdorffite, siderite, quartz, sphalerite, chalcopyrite, tetrahedrite, galena, sericite.

Hypergene minerals: covellite, chalcocite, malachite, azurite, lepidocrocite, goethite.

Pyrite is the old est mineral; it is to be found in relict forms embedded in siderite and in younger sulphides, especially in chalcopyrite.

Gersdorffite occurs frequently, but it is of microscopic dimensions. It was noted as impregnations in pyritized fragments of schists, furthermore in the form of idiomorphic crystals in chalcopyrite. Noted could be also intergrown crystals of gersdorffite on the boundaries of the quartz masses. There are also masses and crystals of gersdorffite in siderate. In the larger individuals is developed a clear hexahedral cleavage, while in places are visible both components of gersdorffite.

Siderite is the main mineral; it is coarse-grained, predomiantly compact in structure. A finer-grained siderite of a lighter colour can be observed where the metasomatosis of the siderite along the younger sulphides is more strongly developed. This younger siderite probably originated through recrystallization in the action of warmer sulphide thermae. Younger sulphides and quartz replace the siderite.

Quartz is bound to a new phase of mineralization. There predominate dendritic formations of metasomatosis that originated either through filling in the system of cracks in siderite or through replacement along cleavage fissures or along interstices in siderite.

Sphalerite is very rare, and it is observed only under the microscope associated with chalcopyrite. It shows exsolutions of drops of chalcopyrite as well as dark internal reflections.

Chalcopyrite is the most important sulphide of the paragenesis. It is visible also with the naked eye in the form of masses and nests in siderite, oftentimes along with more strongly silicified zones, filling cavities and pores in the quartz. Its structure is granular, its grains are locally twinned. It is replaced by galena.

Tetrahedrite is rare. Whenever it occurs it is as a rule intergrown with masses of chalcopyrite, but also younger veins of tetrahedrite were observed in chalcopyrite.

Galena is the youngest mineral; it replaces all other minerals, particularly siderite and chalcopyrite.

Sericite forms locally foliated clusters in the cavities of siderite.

Sequence of crystallization

After opening of the first cracks and fissures, which, in our opinion, are the so-called »Zerrungsspalten«, the pyrite of the first generation was deposited, and probably also smaller amounts of arsenopyrite.

The main phase of ore deposition commenced with the crystallization of siderite, which filled up the open fissures, the siderite veins thus being formed. During the crystallization siderite was dissolving the earlier crystallized pyrite masses, of which only relicts have remained in the siderite. Along with siderite very small quantities of chalcopyrite were deposited.

By a revival of the already filled fissures as well as by the formation of new satellite cracks there were opened paths for the ascension of silicic acid and the crystallization of the older generation of quartz. Thermae ascended besides along cracks also along cleavage fissures and boundaries between grains of siderite, and in them quartz was deposited by the process of metasomatosis. Owing to such a manner of deposition quartz formed in the siderite irregular nests, networks of small veins as well as fine impregnations.

After the crystallization of quartz from younger high-temperature thermae there was deposited through replacement of the siderite, quartz and pyrite the younger generation of sulphides and sulphosalts. This phase of ore deposition commenced with the crystallization of small amounts of Fe-sphalerite (marmatite), chalcopyrite, tetrahedrite and enargite, while through the ascension of lead ions there crystallized boulangerite, bournonite and, as the youngest mineral, galena. Some of these minerals crystallized in two generations, as for example sphalerite and tetrahedrite.

In the course of this high-temperature sulphide phase by the local recrystallization of the siderite there was formed a fine-grained siderite, while at the end of the process also chalcedony was deposited.

The situation of the nickel-cobalt minerals is not quite clear. The tendency of these minerals towards idiomorphic development makes any conclusion hard. It is difficult to establish whether we are concerned with original idiomorphic forms or whether they came about subsequently as idioblasts. Microscopic investigations in the ore occurrences of Srebrenjak show that these minerals are older than galena and bournonite, but younger than pyrite. Some of them can be found idiomorphically developed also in tetrahedrite. In view of the fact that almost always they are to be found associated with other sulphides and sulphosalts, we are in favour of the belief that they belong to the sulphide phase of ore deposition. In the hypergene phase were deposited also the nickel minerals millerite and bravoite. The nickel in these minerals originates from hypogene nickel minerals. Part of the bravoite could well be of ascending origin – deposited in the presence of vadose waters.

The paragenesis of the siderite veins of Srebrenjak resembles in no small measure the paragenesis of the siderite veins at Siegerland in Germany (H. Schneiderhöhn, 1923; P. Hennig, 1926; Rückert, H. 1926; Hüttenhain, J. M., 1932). Also the sequence of deposition is almost identical, the opinions being at variance only in respect of the position in the sequence of nickel-cobalt minerals. While P. Hennig (1926) is of the opinion that the cobalt-nickel minerals with the exception of sichnodimite were deposited in the oldest phase of ore deposition along with pyrite I, H. Schneiderhöhn (1941) holds the view that only cobaltite was deposited in the first generation, and that sichnodimite, hauchecornite and millerite were deposited in the third rejuvenation phase, which caused the hematitization of siderite.

In the forthcoming papers on the ore occurrences of Trgovska Gora special attention will be paid to the problem of nickel-cobalt minerals.

The ore veins are folded together with country rocks.

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REFERENCES

- Andrian, v. F. (1868): Die Erzlagerstätten bei Tergove in der croat. Mikitärgrenze. Verhandl. k. k. geol. Reichsanst., Wien,
- Hacquet, B. (1789): Oryctographia carniolica, oder physikalische Ercheschreibung des Herzogthums Krain, Istrien und zum Theil der benachbarten Länder, Theil IV. Leinzig.
- Hennig, P. (1926): Chalkographische Untersuchungen an Siegerländer Erzen. N. Jb. Min. 55., Abt. A. Stuttgart.
- Hüttenhain, J. M. (1932): Die Elemente Gold und Wismut als Gangkomponenten der Siegerländer Spateisengänge. Min. petr. Mitteil. 42., Wien.
- Jurković, I. (1959): Pojave nikaljno-kobaltnih minerala u rudnim pojavama Trgovske gore. Predavanje održano dne 13. II. 1959. u Mineraloškopetro grafskoj sekciji Hrv. geol. društva u Zagrebu.
- Jurković, I. & Neděla-Devidé, D. (1953): Rudno područje Bešlinac. Manuskript. Zagreb.
- Kišpatić, M. (1901): Rude u Hrvatskoj. Rad Jugoslavenske akademije 147, Zagreb. Papp, v. K. (1919): Die Eisenerz- und Kohlenvorräte des Ungarischen Reiches, Budapest.
- Ramdohr, P. (1955): Die Erzmineralien und ihre Verwachsungen. Berlin.
- Reuter, v. K. (1910): Die Bešlinacer Bergbauverhältnisse. In Papp's » Die Eisenerzund Kohlenvorräte des Ungar. Reiches. Budapest.
- Rückert, H. (1926): Mikroskopisch-mineralogische Untersuchungen an sulphidischen Kupfererzen der Siegerländer Spateisensteingänge. N. Jb. für Min. Beilage-Bd., Abt. A., Stuttgart.
- Schneiderhöhn, H. (1923): Vorläufige Mitteilung über pyrometamorphe Paragenesen in der Siegerländer Spateisensteingängen. Zt. Kristallogr. 58, Festband P. v. Groth, Leipzig.
- Schneiderhöhn, H. (1941): Die Erzlagerstättenlehre, Jena.
- Stur, D. (1863): Bericht über die geol. Übersichtsaufnahme im mittleren Theile Croatiens. Jb. k. k. geol. Reichsanst., Wien.
- Thienhaus, R. (1954): Das Problem der Entstehung und Altersstellung der Siegerländer Spateisengänge. Geol. Rundschau, 42, Stuttgart.
- Tućan, F. (1908): Sideriti iz Samoborske, Petrove i Trgovske gore. Nastavni vjesnik 17, Zagreb.
- Tućan, F. (1941): Mineraloško-petrografsko istraživanje Trgovske gore. Ljetopis Jugosl. akad. 53, Zagreb.
- Zepharovich, v. V. R. (1873): Mineralogisches Lexicon, II, Wien.

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POLIMETALNE RUDNE POJAVE U SLIVU POTOKA SREBRENJAK JUŽNO OD DVORA NA UNI U HRVATSKOJ

U području potoka Srebrenjak južno od Dvora na Uni rudarilo se u Srednjem vijeku i u doba Vojne Krajine na srebronosne galenite. Poznate su grudne pojave Narda, Adam, Srebrenjak, Strgar i Marijana. Rudno područje je izgrađeno od glinenih škriljavaca s alternacijama pješčenjaka i rjeđe vapnenaca. Stijeme su gornjopaleozojske starosti i pripadaju paleozojskom horstu Trgovske gore, koja se nastavlja i s druge strane rijeke Une u sliv rijeke Sane. Rudne pojave su sideritske slojne žice s nešto kvarca, sulfida i sufosoli i borane su zajedno s okolnim sedimentima.

Mikroskopskim ispitivanjem rudnih uzoraka utvrdili smo ovu paragernezu:

a) Hipogeni minerali

pirit, arsenopirit, siderit, kvarc, gersdofit, Ni-lineit, milerit, sfalerit, halkopirit, tetraedrit (tenantit), enargit, bulanžerit, burnonit, galenit, kalcedon, minerali X i U. sericit.

b) Hipergeni minerali

getit, lepidokrokit, halkozin, kovelin, malahit, azurit, psilomelan, pirit, markazit,

Ag-mineral, bravoit, milerit.

Siderit je glavni mineral svih navedenih rudnih pojava. Znatno manje, ali ipak u značajnim količinama ima kvarca. Sulfida i sulfosoli ima tek nekoliko postotaka i količine su im vrlo promjenljive na pojedinim rudnim pojavama. Na pojavama Marijana i Strgar glavni sulfidni mineral je halkopirit, a znatno manje ima pirita i galenita. Pojave Srebrenjak, Adam i Eva sadrže najviše galenita, a uz njega se golim okom vidi malo halkopirita, pirita, sfalenita i tetraedrita. Svi ostali minerali otkriveni su mikroskopom. Na izdancima su rudne pojave djelomično ili potpuno limonitizirane.

Nakon otvaranja prvih prelina i pukotina izlučio se pirit prve generacije i manje

količine arsenopirita.

Glavna faza orudnjenja počela je kristalizacijom siderita, koji je ispunio otvorene pukotine i time su formirane sideritske žice. Pri kristalizaciji siderita terme su ota-

pale iskristalizirane mase pirita od kojih su zaostali samo relikti u sideritu.

Oživljavanjem već ispunjenih pukotina, kao i stvaranjem novih satelitskih prslina otvorili su se putevi za ascenziju kremične kiseline. Osim sistemom prslina terme su ascendirale i pukotinama kalavosti te intersticijama zrnja siderita te je procesima metasomatoze kristalizirao kvarc starije generacije. Zbog takvog načina odlaganja vidimo u sideritu gnijezda, spletove nepravilnih žilica i sitne masice kvarca.

Nakon kristalizacije kvarca odlaže se potiskivanjem siderita, kvarca i pirita iz više temperiranih termi mlada generacija sulfida i sulfosoli cinka, bakra, olova, niklja i kobalta. Ta faza orudnjenja započela je kristalizacijom Fe-sfalerita (marmatita), zatim halkopirita, tetraedrita i enargita, a ascenzijom olovnog iona kristalizirani su bulanžerit, burnonit i kao najmladi mineral galenit. Neki od tih minerala, kao na pr. sfalerit i tetraedrit javljaju se i u dvije generacije. Tokom te višetemperirane hidro-termalne djelatnosti nastao je mjestimičnom prekristalizacijom siderita sitnozrnati siderit, a na kraju te faze izlučio se i kalcedon.

Položaj nikaljno-kobaltnih minerala u redosljedu izlučivanja nije posve jasan. Sklonost tih minerala idiomorfnom razviću otežavala nam je zaključke, jer je bilo teško utvrditi radi li se o prvobitnim idiomorfnim oblicima ili su ti nastali kasnijom idioblastezom. Mikroskopskim ispitivanjem rudnih pojava u Srebrenjaku zapazili smo da su idiomorfno razvijeni Ni-Co-minerali stariji od galenita i burnonita, a lokalno i tetraedrita, a mladi od pirita. Odnos prema sideritu i sfaleritu nije jasan. Obzirom na činjenicu da se nikaljni minerali gotovo redovito nalaze u društvu ostalih sulfida i sulfosoli skloni smo mišljenju da pripadaju sulfidnoj fazi orudnjenja. U našim budućim radovima o rudnim pojavama Trgovske gore posvetit ćemo naročitu paźnju problemu nikaljno-kobaltnih minerala.

U hipergenoj fazi nastali su procesom cementacije iz niklja hipogenih minerala, koji su bili zahvaćeni trošenjem, hipergeni milenit i bravoit. Ovaj posljednji mogao je nastati i iz vrlo nisko temperiranih termi uz sudjelovanje vadoznih voda.

Parageneza sideritskih žica Srebrenjaka vrlo je slična paragenezama sideritskih žica u Njemačkoj (H. Schneiderhöhn, 1923; P. Hennig, 1926; J. M. Hüttenhain, 1932). Što se tiče redoslijeda izlučivanja i taj je uglavnom isti. I kod njemačkih autora postoji razilaženje o problemu položaja nikaljno-kobaltnih minerala. Dok P. Hennig (1926) smatra da su ti minerali izuzev sihnodimita izlučeni u naj-starijoj generaciji zajedno s piritom, to H. Schneiderhöhn, 1941 misli da je jedino kobaltin izlučen u prvoj fazi orudnjenja, dok su se sihnodimit, hočkornit i milerit izlučili u trećoj rejuvenativnoj fazi, koja je uzrokovala hematitizaciju jednog dijela siderita.

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