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ALABANDITE FROM THE METAMORPHOSED PYRRHOTITE-PYRITE DEPOSIT OF HEĽPA IN THE NÍZKE TATRY MTS.

(Fig. 1—6)

Abstract: Alabandite belongs to rare minerals in Czechoslovakia. The only indubitable occurrence are Litošice in the Železné hory Mts., Bohemian Massif. From the West Carpathian mountain system it has not been known so far.

In metamorphosed ores of the Heľpa deposit a ferrous variety with variable amounts of Fe occurs. The contents determined by microprobe are: Mn — 57,26, Fe — 9,67, S — 34,60 %. Formed during metamorphic processes. Its position is between high-temperature Fe-alabandites from Bühl near Kassel, from Fohberg in the FRG and common types of low-temperature, iron-poor alabandites.

Резюме: Алабандин относится к редким минералам в ЧССР. Единственное точное местонахождение находится в Железных горах, в Литошицах, Чешский массив. Из западно-карпатского района до сих пор не был известен.

В метаморфированных рудах месторождения Гелпа обнаружена железистая разновидность с колеблющимся количеством железа. Микрозондом были определены: Mn — 57,26, Fe — 9,67, S — 34,60 %.

Возникновение было при процессах метаморфизма. Минерал занимает положение в ряду высокотермальных Fe-алабандинов в районе Кассели, около Фогберга в ФРГ и с обычными типами, низкотемпературными алабандинами, с низким содержанием железа.

Introduction

In the West Carpathian system are known numerous occurrences of manganese minerals. Their accumulations attain dimensions of deposits: 1. in the Neogene with oxide Mn-ores in andesite pyroclastic rocks near Hriňová and Čelovce, 2. in the Paleogene with sedimentary oxide-carbonate ores in the inner basins (of Spiš, Brezno, Šariš and Rajec), where ore mineralization attains the highest intensity and was exploited in the area of Kišovce—Švábovce for many years, 3. in the Jurassic with pelocarbonate-oxide ores from Lednické Rovné near Považská Bystrica and Zázrivá in the Orava (Dogger) and in the Liassic of the Malé Karpaty Mts. from Borinka, Lozorno and Jabloňové, 4. in metamorphic rhodonite-rhodochrosite ores from the Silurian of the Spišsko-gemerské rudohorie Mts. from Betliar, Čučma and Bystrý Potok.

From sulphide compounds of manganese the rare mineral hauerite was described from Kalinka near Zvolen. It is found together with native sulphur in andesite tuffs. Another Mn sulphide alabandite has not been known from the West Carpathians so far. It has been found by one of the authors (J. Kantor) in metamorphosed pyrrhotite-pyrite ores from Heľpa in the Nízke Tatry Mts.

Alabandite belongs to rare minerals in Czechoslovakia. Its only indubitable occurrence was described from the area of Litošice in the Železné hory Mts. (Bohemian Massif) by L. Žák — J. Novotný (1954).

The Heľpa deposit is the second occurrence. It is also remarkable by the fact that a rare variety of ferrous alabandite has been identified here by aid of electron microprobe analysis (J. Krištín).

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Geological setting and mineralogy of the occurrence

The Heľpa pyrite deposit is situated at the southern slopes of the Nízke Tatry Mts., north of the community Heľpa. The area is formed by catazonally to mesozonally metamorphosed crystalline with granitoid intrusions.

The crystalline schists are represented by biotite-, biotite-muscovite gneisses, mica-schists, in which bodies of meta-gabbros and metamorphosed members of submarine diabase volcanism — metadiabases, amphibolites, actionalite schists etc. are found. In places an intense Alpine diaphthoresis is manifested (V. Zoubek — A. Gorek 1953, B. Cambel — J. Jarkovský 1967, 1969).

The crystalline is polymetamorphic: it underwent metamorphism during the Hercynian orogene when also intrusions of granitoids took place, and during Alpine movements. So far it has not been unambiguously proved which grade of metamorphism the complexes reached prior to the Hercynian folding and to what an extent are represented Lower Paleozoic rocks in the cata-mesozonally metamorphosed crystalline of this area.

There are remarkable analogies between the pyrite deposits and productive complexes in Heľpa and the Malé Karpaty Mts. (V. Zoubek — A. Gorek l. c., B. Cambel — J. Jarkovský l. c.). They have also been confirmed by one of the authors on the basis of isotope studies of sulphur (J. Kantor — M. Rybár — A. Klinec 1971). B. Cambel points to the Lower Paleozoic (Devonian) age of diabase volcanism, to which pyrite mineralization in the Malé Karpaty Mts. is bound.

A. Klinec (1966) recognizes two units in the area of Heľpa and the Vepor crystalline: 1. Hron unit — predominantly consisting of crystalline schists including the productive complex and 2. the Kráľova hoľa unit, granitoids and migmatites lying in tectonic position on the foregoing one. According to A. Klinec (l. c.) the Alpine rejuventation led even to formation of aplite and pegmatite veins.

The Heľpa pyrrhotite-pyrite deposit consisting of three lenses is situated in close proximity of granitoid intrusion. The ore mineralization occurs in amphibolites, actinolite schists; weaker impregnations also in paragneisses.

Genetic linking with basic rocks is obvious. In the past it made V. Zoubek — A. Gorek (l. c.) suppose the liquation origin of ores. B. Cambel — J. Jarkovský (l. c.) consider the deposit as exhalative-sedimentary, bound to submarine diabase volcanism. Isotope study has shown that sulphate-reducing bacteria played an important part in modification of isotopic composition of sulphur (J. Kantor — M. Rybár — A. Klinec 1971).

The deposit displays the same metamorphism as surrounding rocks metamorphosed into garnet — bearing — amphibolite facies.

The mineralogy of ores is relatively simple. The main mineral is pyrrhotite. Present is the hexagonal as well as the monoclinic modification. The original metamorphic product is hexagonal pyrrhotite; monoclinic is younger, lower-temperature one. It has formed by removal of Fe from the hexagonal one along fissures and from grain-boundaries (J. Kantor — J. Ďurkovičová, in press).

Pyrite is less abundant. It occurs in two generations: the older in the form of idioblasts, the younger in veinlets impregnations.

Chalcopyrite is always present, however, in insignificant amounts. This is also valid for the more rare sphalerite. Sporadically is found arsenopyrite. Pentlandite has not been observed in ores.

Marcasite, fine-grained pyrite-marcasite and pyrite aggregates are common products of supergene alteration of pyrrhotite.

Graphite is a common constituent of ores. Together with amphiboles and actinolites it testifies in favour of pyroclastic origin of a major part of mineralized layers (B. Cambel — J. Jarkovský l. c.). Its occurrence is also in accordance with isotope composition of sulphur ($\delta S^{34} = -15$ to -25 ‰, J. Kantor — M. Rybár — A. Klinec l. c.) and biogenic activity during formation of sulphides.

From nonmetallic minerals are frequent: quartz, amphiboles, garnets, feldspars, micas, carbonates, rutile, magnetite, ilmenite, etc.

Microscopic investigation has also revealed the presence of alabandite. It occurs sporadically: somewhere more abundant, elsewhere lacking totally. In the studied material the size of grains varied up to 0.2 mm.

In polished sections it acquires easily a good polish. Grinding hardness is relatively low, close to that of pyrrhotite and sphalerite, markedly lower than in chalcopyrite. In colouring and reflectance it may resemble sphalerite. However, alabandite is of somewhat lighter colour, approaching in appearance some Sb-rich tetrahedrites.

Between crossed nicols it is isotropic, usualy without internal reflections. The latter of brownish tint are abundant in sphalerites of this area.

In alabandite from Heľpa we have not observed any cleavage of triangular pits similar to those of galena as mentioned by P. Ramdohr (1952, 1957).

At the Heľpa deposit alabandite occurs in the form of irregular grains, usually in pyrrhotite or between pyrrhotite and silicates and/or pyrite. Remarkable is its common occurrence with chalcopyrite. In alabandite-chalcopyrite aggregates alabandite forms the central part, whilst chalcopyrite a relatively regular narrow rim. Formation of the latter is evidently connected with the ability of alabandite to coagulate from solutions the compounds of more precious metals (fig. 1, 2).

Distribution of Mn, Fe, Cu, S in alabandite-chalcopyrite aggregate is evident from fig. 3—6 prepared on electron-microprobe by one of the authors (J. Krištín).

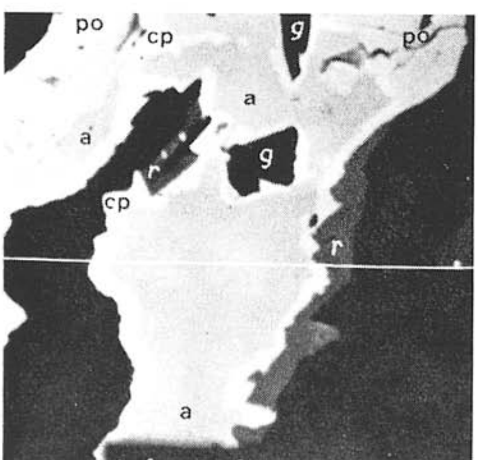

Fig. 1. Electron scanning photograph of minerals. Microprobe, 21 kV, 600 ×. a — alabandite, cp — chalcopyrite, po — pyrrhotite, g — graphite, r — rhodonite(?).

Fig. 2. Like fig. 1. Detail, 1200 ×.

Chemical composition of alabandite was determined with the electron microprobe JEOL JXA-5A. The measured data were corrected then and evaluated by the calculation programme SONDA 03.

From the measured values the following composition of alabandite has resulted:

Mn = 57.26 %
Fe = 9.67 %
S = 34.60 %
= 101.53 %

As a matter of fact, it is already apparent from the microscopic character of alabandite, that chemical composition is not quite uniform at the whole deposit but may vary in certain limits also at a relatively small distance. This is also indicated by distribution pattern for FeKα (fig. 4), according to which alabandite in the lower part of the photograph is richer in Fe than in the upper one.

Alabandite has formed during metamorphic mobilization, which is evident at the deposit, and according to the amounts available variable Fe contents were incorporated in the lattices.

Beside alabandite also rhodonite (or other Mn silicates) appears to be present sporadically at the Heľpa deposit as it is also evident from comparison of the electron scanning photographs (fig. 1, 2) as well as X-ray images for MnKα and SKα (fig. 3, 5).

S. Ďurovič (in B. Cambel — M. Böhmer 1955) studied the contents of Fe, Mn, Cu, Ni and Zn+Co in cut samples from the Heľpa ores using polarographic analyses. From 241 analyses the following average Mn concentrations result for the individual adits of the western deposit:

adit no. 1 (highest)	— 0.40 % Mn
adit no. 2	— 0.19 % Mn
adit no. 3	— 0.10 % Mn

A decrease of Mn in deeper parts of the deposit is evident.

For genetically very similar ores from the Malé Karpaty Mts. S. Ďurovič mentions variation of Mn within the range 0.01—0.08 % and an average value of 0.05 %, i. e. essentially less than for the Heľpa ores.

Comparison with other occurrences of alabandite

Alabandite is most often found at low-temperature, hydrothermal vein deposits, associated with rhodochrosite and rhodonite. It is usually accompanied by sphalerite, galena, chalcopyrite. Sometimes silver minerals or gold tellurides are present. Deposits of this type are known from Roumania, Mexico, USA, South America etc. Prevailingly ore mineralizations of Tertiary to Cretaceous age are concerned. Mutual relations between alabandite and other minerals were studied by D. F. Hewett — O. N. Rove (1930) and others.

A remarkable occurrence of alabandite was described from Litošice in the Železné Hory Mts. in the Bohemian Massif by L. Žák — J. Novotný (1954) and L. Žák (1956). The ore mineralization occurs in the Algonkian of eastern Bohemia known by the presence of bodies of syngenetic Mn-ores (Chvaletice).

From the shaft of Litošice (depth 41—48 m) vein parageneses with dialogite, green alabandite, opal, chalcedony, quartz, crystal, pyrite, pyrrhotite, neotokite, cronstedite are reported.

At the depth 110—140 m in the borehole near the shaft impregnation ores with graphite, pyrite, garnet, rhodonite, quartz, black alabandite, pyrrhotite, chalcopyrite

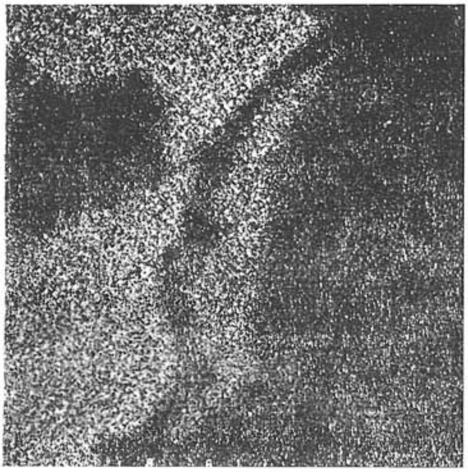

Fig. 3. MnKα, 1200 ×, 21 kV.

Fig. 4. FeKα, 1200 ×, 21 kV.

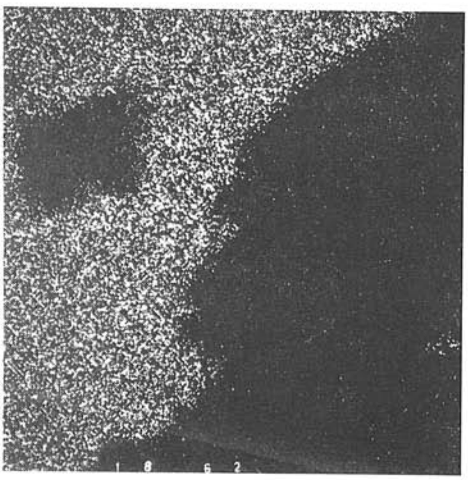

Fig. 5. SKα, 1200 ×, 21 kV.

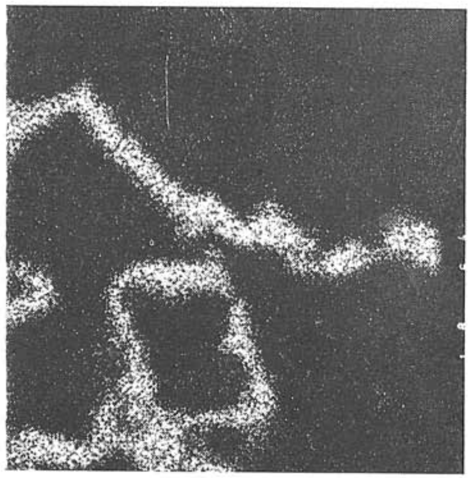

Fig. 6. CuKα, 1200 ×, 21 kV.

and neotokite have been found in graphite schists. Alabandite is intergrown with pyrrhotite or penetrates and replaces idiomorphic pyrite I.

Whilst the vein parageneses are quite different, several analogies may be found between impregnation ores from Litošice and the Heľpa associations. It cannot be excluded that the vein mineralization formed by remobilization of impregnation ores under the action of low-temperature solutions.

H. F. Huttenlocher (1936) established an interesting occurrence of alabandite in the Alps of Switzerland in an area made up of polymetamorphosed crystalline schists (chlorite-sericite schists, biotite and garnet gneisses) in proximity of granitoid intrusions. The crystalline — similarly as at Heľpa — was also affected by Alpine retrograde metomorphism near occurrences of ore. Concerned are lenticular quartz-carbonate veins containing alabandite, pyrrhotite, sphalerite, rhodonite, a little stannite and galena. Nonmetallic minerals are mainly represented by amphiboles and garnets.

Beside them veinlets with galena, chalcopyrite, sphalerite, pyrite and pyrrhotite are found in this area, associated with some stannite and argyrodite.

In pyroxenite-amphibolite rocks a pyrrhotite-chalcopyrite mineralization, not accompanied by other sulphides, has been found.

H. F. Huttenlocher supposes that the latter, pyrrhotite-chalcopyrite mineralization is genetically linked with old, basic magmatism. Formation of other ores he deduces from the intrusion of the Aar granite, emphasizing also the importance of metamorphic processes for final formation of the paragenetic associations.

Formation of alabandite by hydrothermal processes in the Oligocene sedimentary deposit with Mn carbonates, hydrosilicates from Obročište in Bulgaria is mentioned by B. Alexiev — L. Nacheva (1969).

At the Chiaturi (Čiaturi) manganese ore deposit in the URSS alabandite is found in places, where the deposit is intersected by basalt and effected by contact metamorphism (A. G. Betechtin 1946).

By microscopic study of parageneses with native iron from the known locality of Bühl in the FRG P. Ramdohr (1953) established a cubic mineral with similar reflectance and colour as Sb-tetrahedrite and supposed (MnFe) S with high Fe content to be present.

This assumption was later confirmed after analogous material from phonolite of Fohberg near Oberschaffhausen (P. Ramdohr 1957) was obtained. In the phonolite are found xenolithic inclusions of pyrrhotite attaining the size of fist. They also contain chalcopyrite, sphalerite, traces of arsenopyrite, valeriite as well as variable amounts of alabandite. According to X-ray data and the absence of exsolved FeS he supposes Fe-alabandite with a small excess of MnS over FeS to be concerned.

At Fohberg pyrrhotite is found in inclusion of crystalline schists, mainly amphibolites and is considered by P. Ramdohr (l. c.) partly as primary, in most cases, however, as a product of metamorphic alteration of original pyrite impregnations.

Larger xenoliths of sulphide minerals with pyrrhotite, alabandite etc. he supposes to represent relics of vein mineralization with pyrite, chalcopyrite, sphalerite, Mn-calcite, which has been destroyed, reworked and metamorphosed by the ascending phonolite magma.

Alabandite from Hefpa, according to chemical composition (10 % Fe) is an intermediate member between Fe-alabandites from Bühl and Fohberg described by P. Ramdohr ((l. c.) and common types from hydrothermal deposits, which are characterized by low Fe contents.

When we suppose that the solutions from which alabandite has formed were characterized by sufficient and comparable Fe concentrations, then alabandite from Hefpa may take up such a position also with regard to thermality in accordance with the investigations of Zen-Ichi-Shibata (in P. Ramdohr 1957).

The problem of entering of Fe into the alabandite lattice, however, no due attention has been paid so far to. Mn contents are probably variable and sometimes also higher than often supposed, a fact to which already P. Ramdohr (l.c.) called attention.

Translated by J. PEVNÝ.

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Review by B. CAMBEL.