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CHEMICAL-MINERALOGICAL INVESTIGATION OF CHALCOSTIBITE FROM THE NÍZKÉ TATRY MTS

CHEMICKO-MINERALOGICKÉ STUDIUM CHALKOSTIBITU Z NÍZKÝCH TATER

ХИМИКО-МИНЕРАЛОГИЧЕСКОЕ ИЗУЧЕНИЕ ХАЛЬКОСТИБИТА С НИЗКИХ ТАТРОВ

Abstract: The paper presents results of the detailed chemical-mineralogical investigation of chalcostibite from the Dve Vody and Dúbrava deposits in the Nízké Tatry Mts. Both deposits belong to the antimony paragenesis in which stibnite and quartz prevail over other minerals. Chalcostibite occurs as an accessory mineral only. In the Dve Vody deposit this mineral has been determined only microscopically in close association with zinckenite. In the Dúbrava deposit chalcostibite can be found in a far greater amount and is as a rule accompanied by tetrahedrite. In places it forms tabular crystals in cavities. Macroscopically steel-grey with bluish tinge chalcostibite can be clearly distinguished from tetrahedrite by its cleavage. The chemical analysis of the Dúbrava chalcostibite gave the following result: Cu — 25.13 %, Fe — 0.43 %, Sb — 48.99 %, S — 25.86 %, total — 100.41 %. Its crystallochemical formula is as follows: $(Cu_{0.9810}\,Fe_{0.0192})_{1.002}\,Sb_{0.9980}\,S_2$. $G_{meas.} = 4.99$. Z = 2. Of the elements established spectrally Ag, As, Bi, Hg, Fe, In, Pb and Zn can be taken for isomineral. Chalcostibite is characterized by the complex of lines: 3.09 (10), 3.01 (10), 1.825 (8) and 1.759 Å (8). The cell dimensions are as follows: $a_0 = 6.040$, $b_0 = 14.39$, $c_0 = 3.789$. Diagnostic etching: HNO_3 positive, other agents are negative. The presence of chalcostibite in the antimony deposits is conditioned by the presence of copper and particularly by a higher concentration of antimony and sulphur in ore-bearing solutions.

Introduction

During the detailed mineralogical-geochemical investigation of antimony deposits in the Nízké Tatry Mts. chalcostibite has been found in addition to rarer sulphosalts (boulangerite, zinckenite, jamesonite etc.); according to literature available this mineral has so far been identified only in the region of Czech Massif (Krásná Hora deposit — J. SOBOTKA

1958). In Slovakia chalcostibite has been not established up to this time. Chalcostibite is also very rare on a world scale and only few data can be gathered about it. The paper presented links with the preliminary report of J. HAK and Z. JOHAN (1959) and summarizes the results of the detailed chemical-mineralogical investigation of this mineral.

The Nízké Tatry ore district is characterized by the occurence of antimony ores with minute amounts of gold which are extensively distributed mainly in the centre of Ďumbier subzone in the western part of the Nízké Tary Mts. These deposits traditionally regarded as very simple (the s. c. Chinese type according to H. SCHNEIDERHÖHN, 1955) often display a considerably variegated mineral association in which in adddition to stibnite also berthierite, Pb-Sb sulphosalts and sulphides of Cu, Pb and Zn manifest themselves in a greater amount. Of non-ore components quartz strongly predominates over the carbonate of dolomite-ankerite chemism (cf. J. HAK, 1959).

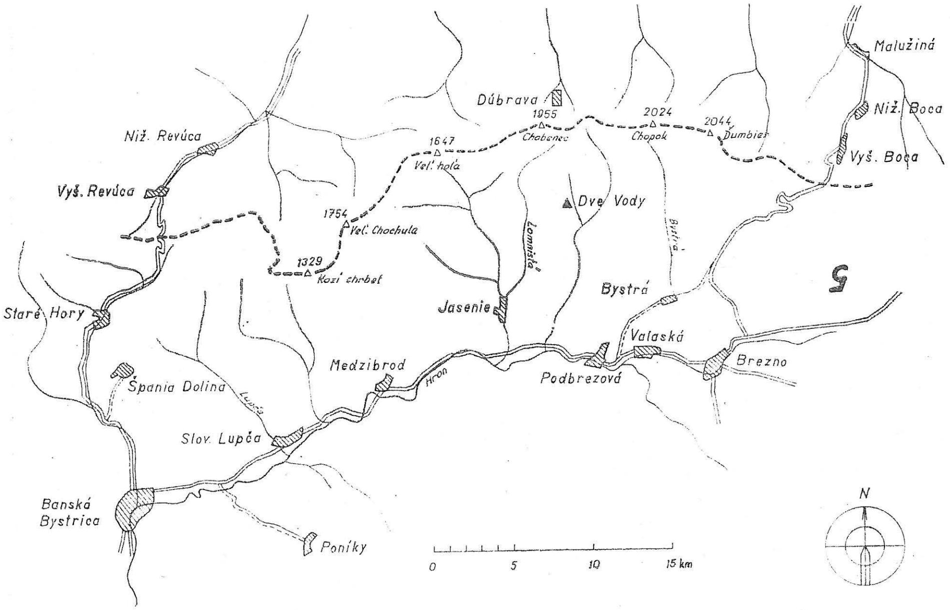
Chalcostibite has been established as a purely accessory mineral in two ore deposits only in the area under consideration, namely, in the localities of Dúbrava and Dve Vody. In an amount sufficient for the detailed mineralogical and chemical examination this mineral occurs in the Dúbrava deposit only, while in the Dve Vody locality it appears in microscopic dimensions and in an intimate intergrowth with zinckenite, so that it was impossible to gain pure material for further study.

Geological-mineralogical characterization of the deposits studied

The antimony deposits of the Nízké Tatry Mts. are situated throughout the crystalline complex composed of catazonally metamorphosed crystalline schists, migmatites and deep-seated intrusions of the granite group. The antimony deposits of this area follow two dominant tectonic lines trending E-W and N-S. The localization of the deposits with the occurrence of chalcostibite can be seen in fig. 1.

The Dve Vody deposit is situated about 7 km N of the village Dolná Lehota on the eastern slope of the Ždiar Mt. — 1408 m, on the southern slope of the Nízké Tatry Mts. The surrounding rocks of the core crystalline massif are orthogneisses, in place migmatites and not very thick strips of amphibolites. According to the strike and dip two systems of veins striking NW-SE with different dip may be distinguished in the deposit. The principal veins dip steeply (65—80° towards NE). Mineral association is considerably variegated. The vein filling consists mostly of strongly crushed mylonite, sporadically with ore impregnations, carbonates and quartz which is in great excess. Of sulphides stibnite prevails. Zinckenite, galena, boulangerite, pyrite and sphalerite are present in a subordinate amount. Chalcostibite, arsenopyrite, bournonite, chalcopyrite and native antimony (?) appear as accessories. From the geochemical point of view antimony is the dominant element accompanied by lesser amounts of Pb, Fe, Zn, Cu and As. Of minor elements Bi, Cd and Hg are typical.

The Dúbrava deposit is situated about 5 km S of the village bearing the same name, on the northern slope of the Nízké Tatry Mts. The deposit represents an extensive ore district dissected by dells into several parts.



1— Geographical situation of antimony deposits with the occurrence of chalcostibite.
Geografická situace studovaných antimonových ložisek s výskytem chalkostibitu.
Географическое положение изученных сурмянных месторождений с нахождением халькостибита

J. MICHALENKO (1960) divides the Dúbrava deposit into several vein groups. The eastern group is composed of the veins of the Kamenisto and Pila localities which are only slightly metallized. The main group of veins consists of the ore localities Lubelská, Dechtárka, Vedro, Rakytová, Predpekelná, Matošovec and Ostredok. The western group is represented by the veins in the valley of Chabenec and Klačianka and shows a somewhat different strike. The veins of the principal and eastern group strike N-S with a dip towards the E and are situated in the so-called Prašivá granite accompanied rarely by some vein derivatives (pegmatites, aplites). Being one of the most extensive deposits of the area under consideration this locality has been studied by a number of authors, most recently by P. JAKEŠ (1963), who has summarized the earlier data. Of hypogene minerals in the deposit in addition to stibnite also arsenopyrite, bournonite, hematite, chalcopyrite, chalcostibite, pyrite, sphalerite, tetrahedrite, zinckenite and native gold are mentioned by P. Jakeš and have been verified by him. Other minerals introduced in literature are jamesonite, galena and marcasite, whose presence, however, has not been confirmed by P. Jakeš. The newly established hypogene senarmontite is being studied by a collective of authors (F. ČECH, J. MICHALENKO, Z. POUBA — cf. P. JAKEŠ 1963). The non-ore components involve barite, quartz and carbonates (ankerite and calcite), among them quartz is again dominant. The mineralogical composition of the individual veins frequently varies. The detailed description of mineral associations of different vein groups lies outside the scope of this paper.

Chalcostibite has so far only been found in the veins of the Predpekelná locality (J. HAK, Z. JOHAN 1959) and in the Nová Nadej vein from the Dechtárka locality (P. JAKEŠ 1963). From the geochemical point of view the deposit is characterized by a considerable predominance of antimony over iron, copper, lead, arsenic and zinc. Of subordinate elements Ag, Bi, Cd, and Hg occur, of characteristic trace elements Au, Co and Ni, which are mainly bound to the occurrence of sphalerite and tetrahedrite.

The chemism of some sulphide minerals from the Dúbrava deposit

Before dealing with the detailed examination of chalcostibite we shall mention some minerals which appear in close association with this mineral. As it has already been written chalcostibite could only be gained in a sufficient amount from the Dúbrava—Predpekelná locality. Therefore, attention will be paid only to the minerals and their chemism from this locality. The results of the qualitative spectrochemical analyses of more important minerals from the paragenesis studied are shown in table 1.

Pyrite belongs to fairly abundant minerals in the deposit and occurs in close association with chalcostibite. It forms chiefly euhedral crystals which are often cataclastic and are replaced by younger sulphides. According to J. H. BERNARD (1957) of the elements established by spectrochemical method As, Co, Cu, Ni and perhaps also Sb (minute amounts) can be taken for isomineral.

Sphalerite can be found only as an accesory forming irregular aggregates of red-brown colour in quartz gangue. Its chemism is interesting mainly by its increased concentration of Ag, Hg, Sb and by presence of trace elements Au, Co, Ga and Tl. The spectrochemical analysis indicated that this is the sphalerite poor in Fe and Mn with no Ge and In, while the concentration of Cd is large. Of the elements established in addition to the isomorphous admixtures (Cd, Fe, Mn) the authors regard As, Co, Ga, Hg and Tl and a part of the established contents of Ag, Cu, and Sb as isomineral. The presence of Au is ascribed to the occurrence of the native gold.

Tetrahedrite is the most abundant mineral in the material studied and is always most closely associated with chalcostibite. Tetrahedrite forms mostly irregular aggregates of up to several cm in size occurs in quartz and carbonate gangue. In practice all the chalcophile elements

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The qualitative spectrochemical analyses were carried out by the team of the spectrochemical laboratory at the Institute of Mineral Raw Materials in Kutná Hora under the following conditions: Spectrograph Zeiss Q—24, a. c. arc 8 A, gener. DG—1 or ABR 3, photoplate Foma s. o., exposure 30 sec. without pre-arcing, carbon electrodes ČKD Praha, analytical gap 3 mm, slid width 0.003 mm. The samples were mixed with the graphite buffer. The following elements have been evaluated: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cu, F, Fe, Ga, Ge, Hg, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Sb, Sc, Si, Sn, Sr, Ta, Te, Ti, Tl, U, V, W, Y, Yb, Zn, Zr.

Table 1.

Qualitative spectrochemical analyses of some minerals being in paragenesis with chalcostibite in the Dúbrava deposit.

Kvalitativní spektrální analýzy některých nerostů z ložiska Dúbrava, které se vyskytují v paragenezi s chalkostibitem.

Качественные спектральные анализы некоторых минералов с месторождения Дубрава, которые встречаются в парагенезисе с халькостибитом

NEROST	Č.spektr. analýzy	Ag	Al	As	Au	B	Ba	Be	Bi	Ca	Cd	Co	Cu	Fe	Ga	Hg	K	Mg	Mn	Mo	Na	Ni	Pb	Sb	Si	Sn	Sr	Ti	Tl	Zn
Pyrit	79 341	•	•	●			?			•			•	■				•	•				•	●	▪					
	79 342		•	●			?			•			•	■				•	•				•	•	▪					
	9 416	•	●	▪		?		•	•	●	?	●	▪	■	•	●	●	•	?			•	●	▪	■	•		•		●
Sfalerit	98 980	●	•	•	•	?	•			▪	▪	•	●	▪	•	●		▪	•				●	▪	▪		•	•	•	■
	98 981	●	•	•	•		•			▪	▪	•	●	▪	•	●		▪	•				●	▪	▪	?	?	?	•	■
Tetraedrit	98 043	▪	•	▪					●	●	●	•	■	▪		●		•	•			•	•	■	▪			?		▪
	98 044	▪	•	▪	•				●	●	•	•	■	▪		▪		•	•			?	•	■	●			•		▪
	98 045	▪	•	▪	•				●	●	•	•	■	▪		▪		•	•			•	•	■	▪			•		▪
	98 046	▪	•	▪	•		●		▪	●	•	●	■	▪		▪		•	•	●		•	•	■	▪	•	•	•		▪
	79 343	▪	•	▪	•				•	▪	•	•	■	▪		●		▪	•				•	■	●			?		▪
	9 417	▪	●	▪	•			•	▪	●	•	●	■	■		■		•	•		?	•	•	■	▪	•		•		■
Zinkenit	79 356	●	•	●						▪	•		●	●				●	•				■	■	●	•		•		•
	79 357	●	•	●						●	?		●	▪				●	•				■	■	▪			•		•
	79 358	●	●	•						▪	•		●	●				●	•				■	■	▪			•		▪
	79 359	●	•	●					•	●	•		●	▪				•	•				■	■	●			?		•
Antimonit	79 344	•	●	•						●	•		•	●				●	•				•	■	▪			•		•
	79 345	•	•	•						▪			•	●				●	•				•	■	▪			•		•
	79 346	•	•	•						•			•	•				•	•				•	■	●					•
	79 347	?	•	•						•			•	●				•	•				•	■	•			?		?
	79 348.	•	•	•						●	•		•	●				●	•				•	■	●			•		•
	79 349	•	•	•						●			•	●				•	•				●	■	●			?		•
	79 350	•	•	•						▪			•	●				●	•				•	■	●			?		•
	79 360	•	•	•						●			•	●				•	•				•	■	●			?		•
	79 352	•	•	•						▪			•	●				●	•				•	■	●			•		•
	79 353	•	•	•						▪	•		●	●				●	•				•	■	●			?		●

■ množství podstatné /»1 %/

▪ množství podřadné />1 % - 0,1 %/

● množství vedlejší /0,1 % - 0,01 %/

• množství stopové /<0,01 % /

? problematická přítomnost prvku

ascertained, with the exception of sporadic Mo, belong to the tetrahedrite lattice and their concentration (except for Bi) is approximately constant. From the point of view of total chemism of the tetrahedrite mineral group the higher concentrations of Ag, Hg and Zn and in some samples also Bi are characteristic of the tetrahedrite studied. A very typical microelement is Au whose occurrence in native form cannot be excluded, but we can rather assume its bond in tetrahedrite lattice.

Zinckenite belongs to less common minerals and is associated especially with stibnite. Zinckenite forms irregular massif aggregates of steel-grey colour dispersed mostly in quartz and often intimately intergrown with stibnite. In these aggregates zinckenite can be distinguished from stibnite only microscopically by means of etching agents (KOH). Of the elements established Ag, As, Cd, Cu, Fe, and perhaps also the minute amounts of Bi and Zn can be taken for isomineral. The interpretation of isomineral form of elements presented is in accordance with the statistical evaluation of the microchemism of zinckenites from the whole area of the Nízké Tatry Mts. (cf. J. HAK 1958, 1963).

Stibnite is a characteristic and prevailing mineral in the deposit investigated. Although it does not appear as a rule in close association with chalcostibite, we describe its chemism in order to show the general geochemistry of the deposit. With respect to the chemism of stibnites from other deposits of this area the chemism of the stibnites cited does not display any anomalies. Ag and As and the minute amounts of Cu, Fe, Pb, and Zn can be regarded as isomineral.

Occurrence, Physical and Optical Properties of Chalcostibite from Dúbrava.

As already mentioned in the introduction, chalcostibite is an accessory mineral in the Dúbrava-Predpekelná deposit. Although this mineral has been found in macroscopic dimensions and monomineral aggregates, it usually occurs in microscopic form in close association with tetrahedrite. Macroscopically chalcostibite forms as a rule irregular aggregates of mm dimensions disseminated in quartz and carbonate gangue. Smaller crystals of chalcostibite showing a tabular development with characteristic striation on crystal faces (see Plate I, fig. 1.) were found rarely in cavities. Chalcostibite is steel-grey, with bluish tint, metallic luster and distinct cleavage. Sometimes variegated tinge colours can be observed. Streak black. Under the microscope we can observe tiny anhedral grains and irregular aggregates which usually metasomatic replace both the gangue and mainly tetrahedrite. Under less intensive metasomatism chalcostibite forms a network of veinlets and small grains impregnating the original tetrahedrite aggregate. Under more intensive metasomatism chalcostibite predominates over tetrahedrite, which remains preserved in the form of small isolated relics or a total metasomatic replacement of tetrahedrite by chalcostibite takes place. The typical forms of the replacement mentioned are given in photographic plates. (Pl. I, fig. 3, 4; Pl. II, fig. 1, 2).

In reflected light chalcostibite is white, showing a fairly high reflectivity (compared to tetrahedrite its reflectivity is distinctly higher). Reflection pleochroism in the air and in oil immersion is very weak, hardly visible. The anisotropy is strong. Chalcostibite can be easily polished, it is soft, and exhibits visible cleavage.

Diagnostic etching:

Etching agents according to M. N. SHORT (1940) have been used. Time of etching 1 min.

HNO_3 1 : 1 pos. — The mineral slowly takes iridescent colours and later becomes slightly brown. After the polished section has been wiped, the mineral remains slightly etched, slightly brown.

HCl 1 : 1 neg.
$FeCl_3$ 20 % neg.
$HgCl_2$ 5 % neg.
KCN 20 % neg.
KOH 40 % neg. pos. Chalcostibite from the Dúbrava deposit remains intact even after a 2-minute effect of etching agent. The chalcostibite from the Dve Vody deposit is intimately intergrown with zinckenite and takes intensive iridescent colours after one minute of etching; the film disappears after the polished section has been wiped. This fact distinguishes the chalcostibite from zinckenite which takes up iridescent colours almost immediately (see Plate II, fig. 3).

The density was determined in pycnometer on a carefully separated sample which was later used for further examination. G = 4.99 (an average of two determinations) is in accordance with the literature data (F. V. CHUKHROV 1960 gives the following values: G_{meas} = 4.8 — 5.0, $G_{calc.}$ = 5.010).

Table 2.

Qualitative spectrochemical analyses of chalcostibite from the Dúbrava deposit.
Kvalitativní spektrální analýzy chalkostibitu z ložiska Dúbrava.
Качественные спектральные анализы халькостибита с месторождения Дубрава.

Č. spektr. analýzy	Ag	Al	As	Ba	Bi	Ca	Cd	Cr	Cu	Fe	Hg	In	Mg	Mn	Pb	Sb	Si	Zn
97 817	•	•	●	•	•	●	?	•	█	•	•		•	•	•	█	■	•
9 142	●	•	●		●	●			█	●	●	•	•	?	•	█	●	•

Qualitative spectrochemical analysis

The results of qualitative spectrochemical analysis of two chalcostibite samples are given in Tab. 2. (The sample signed 9142 was also chemically analysed and is identical with the sample whose density was determined). In discussing the character of the bond of the elements established in chalcostibite it is necessary to note that the sporadic literature on chalcostibite contains only few informations on the occurrence and concentration of some elements, mostly without clearly pointing out whether these are the elements bound to the chalcostibite lattice or belong to heterogenous admixtures (cf. F. V. CHUKHROV 1960, H. V. WARREN and R. M. THOMPSON 1945, J. SOBOTKA 1958). Only the late of the authors mentioned has done, on the basis of one qualitative spectrochemical analysis, the interpretation of the presence of some minor elements in chalcostibite. This author assumes that Ag, As, Cd and Zn can be isomorphous in chalcostibite of Krásná Hora deposit. Of other chalcophil elements the folowing are present in chalcostibite from Krásná Hora: Au, Bi, Hg, Pb, Ni and Tl; of them Au belongs to native gold. Another difficulty is due to the fact, that in the material studied, chalcostibite is closely associated with tetrahedrite whose chemical qualitative composition is the same and whose complete separation from the material analyzed failed. Although the presence of tetrahedrite in the chalcostibite sample analyzed is very small (see further the result of quantitative chemical analysis and the calculation of crystallochemical formula), we cannot, however, entirely eliminate the effect of some elements on the microchemism of chalcostibite: these elements occur in tetrahedrite in higher concentrations (mainly Ag, As, Bi, Fe, Hg and Zn). Also a small number of spectrochemical analyses is insufficient for the statistical evaluation of the elements present. Nevertheless, correlating the basis of concentrations of the elements already mentioned in both the formulas of chalcostibite and of tetrahedrite, we can assume that all these elements may be (at least in small concentrations) regarded as isomineral. Also the trace contents of In and Pb are evidently isomineral. Mainly the presence of In in chalcostibite as the only mineral in the deposit is remarkable because neither sphalerite which, as a rule, is the main host mineral of this element nor tetrahedrite contain In. Other elements established which are of dominantly lithophile character are heterogenous.

Chemical analysis

The identification of chacostibite was confirmed by the chemical quantitative analysis of purely separated sample which was also spectrally analyzed (No. 9142, see table 2). Because there was insufficient material only the main components could be determined. 0.6 g of the sample was used and all the determinations were carried out twice (in table 3 an average of two determinations is given).

TABLE 3

Quantitative chemical analysis of chalcostibite from the Dúbrava deposit.
Kvantitativní chemická analýza chalkostibitu z ložiska Dúbrava.
Количественный химический анализ халькостибита с месторождения Дубрава

	1	2	3
Cu	25.13 %	25.03 %	0.3939
Fe	0.43	0.43	0.0077
Sb	48.99	48.79	0.4007
S	25.86	25.75	0.8030
Total	100.41	100.00	

1. Chemical analysis 2. Recalculated to 100 %. 3. Atomic quotients.

Crystallochemical formula:

$$(Cu_{0,9810}\ Fe_{0,0192})_{1,0002}\ Sb_{0,9980}S_2$$

The sample for the Cu, Sb and Fe determinations was decomposed in a mixture of nitric acid and hydrochloric acid. After the evaporation the residue was removed by a diluted hydrochloric acid and the copper and iron sulphides were precipitated by means of sodium sulphide. After the dissolution of these sulphides Fe was separated from Cu by ammonia. Cu was determined by complexometric titration with the use of glycinthymol blue as indicator. Fe was established by photometric method by means of complexon. Antimony was precipitated as sulphide by addition of diluted sulphuric acid to the filtrate after the separation of copper and iron sulphides. After dissolving antimony sulphide in concentrated sulphuric acid, antimony was determined by means of titration by potassium bromate. For the determination of sulphur the sample was decomposed by sintering with a mixture of soda and zinc oxide and the sulphur was determined gravimetrically as barium sulphate.

The crystallochemical formula calculated approaches considerably the theoretical formula usually given for chalcostibite — $CuSbS_2$. This fact confirms both the correctness of the chemical analysis and also the great purity of the material analyzed. With respect to the quantitatively largely different representation of these elements in tetrahedrite, which in the first place could represent a hetetrogenous admixture in the chalcostibite studied, this possibility cannot be taken into account, as follows from the crystallochemical formula. Although a small amount of pyrite was also present in the material from which chalcostibite was separated for the analysis, it is not probable that a small content of Fe established would be bound to the pyrite admixed. An illustration of the aforesaid is given by the crystallochemical formula of the analyzed chalcostibite on the assumption that the iron determined is heterogenously bound to pyrite: $Cu_{0.9998}\,Sb_{1.0172}\,S$. From the comparison of both the formulae it follows that the formula including Fe approaches more to the theoretical composition. This fact, however, does not justify us to regard the higher concentrations of Fe as reliably isomineral in chalcostibite.

X-Ray Powder Data

The sample which was spectrally and chemically analyzed and whose density determination was carried out was also used for the X-ray investigation. The character of material made it possible to employ only the Debye-Scherrer method. The analysis was carried out in the physico-chemical laboratory of Institute of Mineral Raw Materials in Kutná Hora under the following conditions: Fe/Mn radiation, time of exposure 6 hours, calibration substance Al. Intensities were estimated visually. The values established were confronted with the values given for this mineral by L. G. BERRY and R. M. THOMPSON (1962). A good conformity follows from this comparison. Four week lines given by the authors mentioned were not ascertained. For the lattice constants calculation the following lines were used d = 2.12, 1.900 and 1.689 Å. Chalcostibite is characterized by a complex of lines with d = 3.09 (10), 3.01 (10), 1.825 (8), and 1.759 Å (8). The conformity between the measured and calculated d values is sufficient. The indexed powder pattern is given in table 4.

The position of chalcostibite in the system Cu-Sb-S

From the phase diagram of the Cu-Sb-S system (see fig. 2) it follows that chalcostibite will occur in paragenesis with tetrahedrite (or stibiolu-

TABLE 4

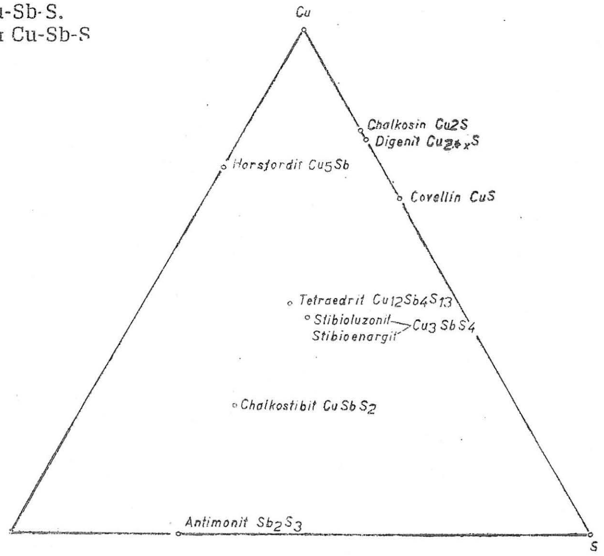
X-ray powder patttern of chalcostibite from the Dúbrava deposit.
Rentgenometrická data chalkostibitu z ložiska Dúbrava.
Рентгенометрические данные халькостибита с месторождения Дубрава
Fe/Mn radiation, λ = 1.9373 Å, camera 57.3 mm.

Chalcostibite Dúbrava			Chalcostibite — L. G. Berry and R. M. Thompson (1962)		
I	d (meas.)	d (calc.)	I	d	hkl
1	3.59 Å	3.60 Å	1	3.65	011, 040
10	3.09	3.09	10	3.13	111, 140
10	3.01	3.01	9	3.00	200, 031
0.5	2.79	2.78	0.5	2.79	220
			1	2.56	230
Al	2.34				
5	2.31	2.31	4	2.31	240, 051
2	2.25	2.24	2	2.24	160, 221
4	2.12	2.12	3	2.12	231
Al	2.02				
4	1.900	1.894	3	1.895	002
8b	1.825	1.832	4	1.831	022, 251
			0.5	1.817	071, 080
8	1.759	1.757	5	1.762	311, 340
			0.5	1.743	171
2	1.689	1.683	1	1.687	261
			2	1.621	142
4b	1.598	1.605	1	1.603	202
3	1.545	1.547	1	1.554	190, 271, 280
Al	1.432		3	1.441	191, 430

b = broad line
Al = internal standard
The cell dimensions are: a_0 = 6.040 Å, b_0 = 14.39 Å, c_0 = 3.789 Å
$a_0 : b_0 : c_0 = 0.4197 : 1 : 0.2633$, Z = 2.

zonite or stibioenargite) and stibnite. The investigation carried out also confirms this fact. In comparison with tetrahedrite, chalcostibite exhibits much larger content of antimony and sulphur with regard to copper. One of the principal factors influencing the formation of chalcostibite is without doubt a sufficiently high antimony content (in addition to sulphur) in ore-bearing solutions. This holds good primarily in the stibnite deposits, because antimony was the dominant element in ore-bearing solutions. The study of the conditions of succession in the Dúbrava deposit has shown that the formation of chalcostibite took place between the formation of tetrahedrite and that of stibnite which is in perfect accordance with the phase system. With regard to the replacement of tetrahedrite by chalcostibite even the simultaneous supply of copper with that of antimony is

2— Phase diagram of the system Cu-Sb-S.
Fázový diagram systému Cu-Sb-S.
Фазовая диаграмма системы Cu-Sb-S



not necessary for the formation of this mineral, because chalcostibite may originate by the reaction of tetrahedrite with stibnite according to the equation (the tetrahedrite formula is given in a simplified form):

$$Cu_3 Sb S_3 + Sb_2 S_3 = 3 Cu Sb S_2$$

The occurrence of chalcostibite intimately intergrown with zinckenite (Dve Vody deposit) indicates that with respect to different paragenetic conditions in this deposit the mechanism of the chalcostibite formation was somewhat different. Even there, however, the condition of increased antimony concentration in ore-bearing solutions was fulfilled while copper concentration was relatively low which caused the formation of bournonite and the absence of tetrahedrite. The following scheme shows the position of chalcostibite in the mineral succession in the Dve Vody deposit: galena-bournonite-chalcostibite-zinckenite-stibnite-native Sb. This succession is again in accordance with the phase diagram of the system Cu-Sb-S, or Cu-Sb-Pb-S. T. N. SHADLUN (1954) who studied chalcostibite from the Granitogorsk deposit in the USSR mentions this mineral in typical association with chalcopyrite and bornite. According to this author chalcostibite originated after the crystallization of sulphides richer in copper, after the decrease of copper amount and the increase of antimony concentration in ore-bearing solutions. Also the occurence of chalcostibite in association with tetrahedrite and aurostibite in the Krásná Hora deposit (of J. SOBOTKA 1958) indicates a higher content of antimony in ore-bearing solutions by the origin of the mineral.

In conclusion we can say that chalcostibite originates probably under very specific physico-chemical conditions which is evidenced by the rare occurrence of this mineral in sulphide deposits.

Acknowledgements

The authors want to thank the co-workers of the spectrochemical and physico-chemical laboratory of the Institute of Mineral Raw Materials in Kutná Hora who executed carefully the analyses applied.

The samples of chalcostibite studied from the Dúbrava locality are deposited in the collection of National Museum in Prague.

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Institute of Mineral Raw Materials Kutná Hora

Ore Research Institute Prague

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JAROSLAV HAK — MILAN KVAČEK — ZDENĚK JOHAN

CHEMICKO-MINERALOGICKÉ STUDIUM CHALKOSTIBITU Z NÍZKÝCH TATER

Při podrobném mineralogicko-geochemickém výzkumu antimonových ložisek Nízkých Tater byl mimo vzácnější sulfosoli (boulangerit, zinkenit, jamesonit aj.) zjištěn i chalkostibit, který podle dostupných literárních údajů byl na území ČSSR identifikován jen z oblasti Českého masivu (Krásná Hora — J. Sobotka 1958). V rámci studované oblasti je chalkostibit vzácným nerostem, který byl nalezen na dvou lokalitách (Dve Vody a Dúbrava). Detailní studium bylo provedeno pouze na materiálu z ložiska Dúbrava—Predpekelná. Na lokalitě Dve Vody se chalkostibit vyskytuje jen v mikroskopických rozměrech a v intimním srůstu se zinkenitem. Obě zmíněná ložiska patří k antimonové formaci Nízkých Tater a jejich lokalizace je patrná z obr. 1. Hlavními složkami žilné výplně těchto ložisek jsou antimonit a křemen, zatímco ostatní nerosty, jako např. pyrit, sfalerit, galenit, Pb—Sb sulfosoli (jamesonit, boulangerit, zinkenit), tetraedrit, chalkopyrit, bournonit a z nerudních karbonáty (především Fe-dolomit), jsou zastoupeny podřadně až akcesoricky. Kromě vlastního výzkumu chalkostibitu byl spektrálně sledován i chemizmus některých sulfidických nerostů z ložiska Dúbrava, které se vyskytují v asociaci s chalkostibitem. Kvalitativní spektrální analýzy těchto nerostů jsou uvedeny v tabulce 1.

I když byl chalkostibit na ložisku Dúbrava zjištěn ojediněle makroskopicky ve formě nepravidelných agregátů a vzácných tabulkovitých krystalů, vyskytuje se zpravidla v mikroskopické formě v těsné asociaci s tetraedritem, který často velmi intensivně zatlačuje. Jeho fyzikální a optické vlastnosti jsou v souladu s literárními údaji. Výsledky diagnostického leptání: HNO_3 1 : 1 pozit., HC1 1 : 1 neg., $HgCl_2$ 5 % neg., $FeCl_3$ 20 % neg., KCN 20 % neg., KOH 40 % neg. Pro detailní studium byl vyseparován čistý materiál, na němž byla stanovena hustota (D=4,99) a který byl rentgenometricky, spektrálně a chemicky analyzován. Kvalitativní spektrální analýzy dvou vzorků chalkostibitu jsou uvedeny v tabulce 2. Za izominerální prvky lze považovat Ag, As, Bi, Fe, Hg, In, Pb a Zn, alespoň pokud jde o stopové koncentrace těchto prvků. Výsledek kvantitativní chemické analýzy je uveden v tabulce 3. Vypočtený krystalochemický vzorec chalkostibitu: $(Cu_{0.9810}\,Fe_{0.0192})_{1\cdot0002}\,Sb_{0.9980}\,S_2$. Tento vzorec se velmi blíží teoretické formuli $CuSb_2$ a potvrzuje čistotu analyzovaného materiálu. Rentgenometrická data chalkostibitu jsou uvedena v tabulce 4. Pro chalkostibit je charakteristický komplex linií: 3,09 (10), 3,01 (10), 1,285 (8) a 1,759 Å (8); indexováním snímku byly vypočteny mřížkové konstanty:

$$a_0 = 6{,}040\ \text{Å},\ b_0 = 14{,}39\ \text{Å},\ c_0 = 3{,}789\ \text{Å} \quad a_0 : b_0 : c_0 = 0{,}4197 : 1 : 0{,}2633 \quad Z = 2$$

Zjištěné hodnoty jsou ve velmi dobré shodě s literárními údaji.

Jak vyplývá z fázového diagramu Cu—Sb—S (viz obr. 2), je vznik chalkostibitu podmíněn vysokým obsahem antimonu (vedle síry) v rudonosných roztocích. Tato podmínka je splněna především na ložiskách antimonu. Postavení chalkostibitu v sukcesi na ložisku Dúbrava je dáno schematem: tetraedrit-chalkostibit-antimonit, což je ve shodě s fázovým systémem. Vzhledem k často velmi intenzivnímu zatlačování tetraedritu chalkostibitem není nutný pro tvorbu tohoto nerostu ani současný přínos mědi s antimonem, neboť chalkostibit může vznikat reakcí tetraedritu s antimonitem podle rovnice (vzorec tetraedritu je uveden ve zjednodušené formě):

$$Cu_3\,Sb\,S_3 + Sb_2\,S_3 = 3\,Cu\,Sb\,S_2$$

Mechanizmus tvorby chalkostibitu na ložisku Dve Vody byl poněkud odchylný vzhledem k jiným paragenetickým poměrům (parageneze galenit-bournonit-chalkostibit-zinkenit-antimonit); i zde však byla splněna podmínka zvýšené koncentrace antimonu v rudonosných roztocích. Sukcese na tomto ložisku je opět v souladu s fázovým diagramem systému Cu-Sb-S, resp. Cu-Pb-Sb-S.

ЯРОСЛАВ ГАК — МИЛАН КВАЧЕК — ЗДЕНЕК ЙОГАН

ХИМИКО-МИНЕРАЛОГИЧЕСКОЕ ИЗУЧЕНИЕ ХАЛЬКОСТИБИТА С НИЗКИХ ТАТРОВ

При подробном минералогическо-геохимическом изучении сурьмяных месторождений Низких Татров кроме более редких сульфосолей (буланжерит, цинкенит, джемсонит и т. ц.) обнаружен в халькостибит, который по доступным литературным данным пока был идентифицирован только с месторождения Красна гора в Чехии (Ю. Соботка 1958). На территории Словакии пока не был обнаружен. В рамках изученной области халькостибит является редким минералом, найденным лишь на двух месторождениях (Две Воды и Дубрава). Детальное изучение было проведено только на материале с месторождения Дубрава-Предпекельна. На месторождении Две Воды халькостибит втсречается только в микроскопических размерах и в интимном срастании с цинкенитом. Оба упомянутых месторождения относятся к сурьмяной формации Низких Татров, а их локализация обозначена на рис. 1. Основными составляющими жильного заполнения этих месторождений являются антимонит и кварц, в то время как остальные минералы, как например, пирит, сфалерит, галенит, Pb-Sb-сульфосоли (джемсонит, буланжерит, цинкенит), тетраэдрит, халькопирит, бурнонит, а из жильных — карбонаты (пдежде всего Fe - доломит) представлены второстепенно или акцессорически. Кроме изучения халькостибита был спектрально исследован и химизм некоторых сульфидов с месторождения Дубрава, которые встречаются в ассоциации с халькостибитом. Качественные спектральные анализы этих минералов представлены в таблице 1.

Хотя и были халькостибит на месторождении Дубрава обнаружен отдельно макроскопически в форме неправильных агрегатов и редких таблитчатых кристаллов, как правило он встречается в микроскопической форме в тесной ассоциации с тетраэдритом, который часто очень интенсивно замещает. Его физические и оптические свойства совпадают с литературными данными. Результаты диагностического травления: HNO_3 1 : 1 — положительные, HC 1 : 1 – отрицательные, $HgCl_2$ 5% – отриц., $FeCl_3$ 20% – отриц., KCN 20%. – отриц. KOH 40% – отриц. Для подробного изучения был высепарирован чистый материал, у которого был определен удельный вес (= 4,99) и который был рентгенометрически, спектрально и химически анализирован. Качественные спектральные анализы двух образцов халькостибита представлены в табл. 2. Ag, As, Bi, Fe, Hg, In, Pb и Zn можно принимать за изоминеральные элементы, хотя в тех случаях, когда они встречаются в следах. Результат количественного химического анлиза представлен в табл. 3. Рассчитанная кристаллохимическая формула хакькостибита:

$$(Cu_{0{,}9810}\,Fe_{0{,}0192})_{10002}\,Sb_{0{,}9980}\,S_2$$

Эта формула сильно приближается к теоретической формуле $CuSbS_2$ и подтверждает чистоту анализированного материала. Рентгенометрические данные халькостибита представлены в табл. 4. Для халькостибита характерен комплекс линий: 3,09 (10), 3,01 (10), 1,825 (8) и 1,759 Å (8) и рассчитанные константы решетки: a_0 = 6,04 Å, b_0 = 14,39 Å, c_0 = 3,789 Å. Найденные результаты очень хорошо совпадают с литературными данными.

Как вытекает из фазовой диаграммы Cu – Sb – S (см. рис. 2) возникновение халькостибита обусловлено высоким содержанием в рудоносных растворах сурьмы (вместе с серой). Это условие соблюдается прежде всего на месторождениях сурьмы. Положение халькостибита в последовательности выделения минералов на месторождении Дубрава обусловлено схемой: тетраэдрит — халькостибит — антимонит, что совпадает с фазовой системой. Учитывая частое очень интенсивное замещение тетраэдрита халькостибитом, для образования этого минерала необязателен одновременный принос меди с сурьмой, т. к. халькостибит может образовываться при взаимодействии тетраэдрита с антимонитом по уравнению (образец тетраэдрита приведен в упрощенной форме): $Cu_3SbS_3 + Sb_2S_3 = 3\,CuSbS_2$

Механизм образования халькостибита на месторождении Две Воды был несколько иной с учетом иных парагенетических соотношений (парагенезис галенит — бурнонит — халькостибит — цинкенит — антимонит, однако и здесь было выполнено условие повышенной концентрации сурьмы в рудоносных растворах. Сукцессия на этом месторождении опять совпадает с фазовой диаграммой системы Cu-Sb-S или Cu- Pb- Sb- S.

PLATE I.

Fig. 1. Tabular crystal of chalcostibite with typical striation on the cavity. The Dúbrava deposit. Macrophotograph. Magn. 10×.

Tabulkovitý krystal chalkostibitu s typickým rýhováním v dutině. Ložisko Dúbrava Makrofoto. Zvětš. 10×.

Таблитчатый кристалл халькостибита с типичной штриховкой в полости. Месторождение Дубрава. Макрофотография. Увелич. 10×.

Fig. 2. Old Fe-dolomite is penetrated and replaced by tetrahedrite (white). The Dúbrava deposit. Polished section. 280×.

Starší Fe-dolomit je pronikán a zatlačován tetraedritem (světlý). Ložisko Dúbrava Mikrofoto nábrusu. Zvětš. 280×.

Старший Fe-доломит пронизан и замещен тетраэдритом (светлый). Месторождение Дубрава. Полированный шлиф. Увелич. 280×.

Fig. 3. Tetrahedrite (grey) is penetrated and replaced by younger chalcostibite (white). Initial stage of metasomatism. The Dúbrava deposit. Polished section. 120×.

Tetraedrit (šedý) je pronikán a zatlačován mladším chalkostibitem (bílý). Počáteční stadium metasomatozy. Ložisko Dúbrava. Mikrofoto nábrusu. Zvětš. 120×.

Тетраэдрит (серый) пронизан и замещен младшим халькостибитом (белый). Начальная стадиа замещения. Месторождение Дубрава. Полированный шлиф. Увелич. 120×.

Fig. 4. Advanced stage of the replacement of older tetrahedrite (grey) by chalcostibite (white). The Dúbrava deposit. Polished section. 120×.

Pokročilejší stadium zatlačování staršího tetraedritu (šedý) chalkostibitem (bílý). Ložisko Dúbrava. Mikrofoto nábrusu. Zvětš. 120×.

Более прогрессивная стадия замещения старшего тетраэдрита (серый) халькостибитом (белый). Месторождение Дубрава. Полированный шлиф. Увелич. 120×.

PLATE II.

Fig. 1. Only minute relics of tetrahedrite (grey) are preserved in chalcostibite (white). The contact of chalcostibite with carbonate (dark gray) represents the fossil boundary of 1st stage according to J. Kutina (1956). The Dúbrava deposit. Polished section. 120×.

V chalkostibitu (bílý) jsou zachovány pouze nepatrné relikty tetraedritu (šedý). Styk chalkostibitu s karbonátem (tmavě šedý) představuje fosilní hranici 1. stupně ve smyslu J. Kutiny (1956). Ložisko Dúbrava. Mikrofoto nábrusu. Zvětš. 120×.

В халькостибите (белый) сохранены лишь незначительные остатки тетраэдрита (серый). Стык халькостибита с карбонатом (темносерый) представляет первычные границы первой степени по Кутиным (1956). Месторождение Дубрава. Полированный шлиф. Увелич. 120×.

Fig. 2. Final stage of metasomatic replacement of tetrahedrite by chalcostibite. An indication of cleavage may be observed on chalcostibite aggregate (white). The Dúbrava deposit. Polished section. 120×.

Konečné stadium metasomatozy tetraedritu chalkostibitem. Na agregátu chalkostibitu (bílý) možno pozorovat náznak štěpnosti. Ložisko Dúbrava. Mikrofoto nábrusu. Zvětš. 120×.

Окончательная стадия замещения тетраэдрита халькостибитом. На агрегате халькостибита (белый) можно наблюдать намек спайности. Месторождение Дубрава. Полированный шлиф. Увелич. 120×.

Fig. 3. Chalcostibite (white) characteristically intergrown with zinckenite (grey). Zinckenite is etched by 40 % KOH. The Dve Vody deposit. Polished section. 100×.

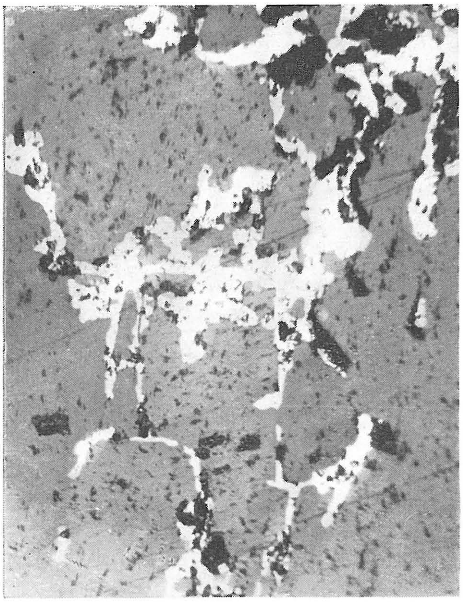
Charakter prorůstání chalkostibitu (bílý) se zinkenitem (šedý). Zinkenit je naleptán 40 % KOH. Ložisko Dve Vody. Mikrofoto nábrusu. Zvětš. 100×.

Характер сростания халькостибита (белый) с цинкенитом (серый). Цинкенит травлен 40% KOH. Месторождение Две Воды. Полированный шлиф. Увелич. 100×.

Fig. 4. Symmetrical veinlet of stibnite with various grain size. The Dúbrava deposit. Polished section. Crossed nicols. 180×.

Symetrická žilka antimonitu o různé zrnitosti. Ložisko Dúbrava. Mikrofoto nábrusu. Nikoly X. Zvětš. 180×.

Симметрическая жилка антимонита с различной зернитостью. Месторождение Дубрава. Полированный шлиф. Николи X. Увелич. 180×.



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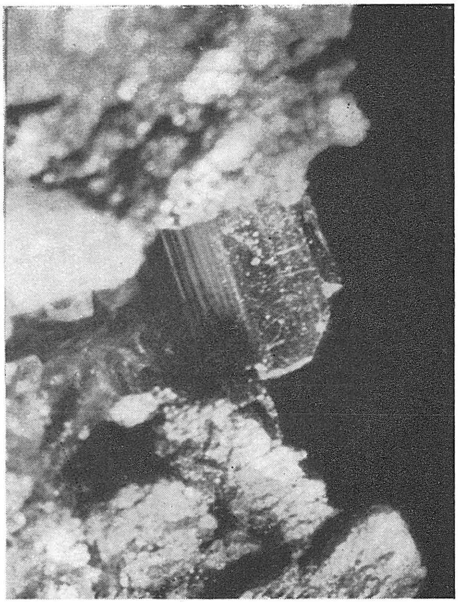

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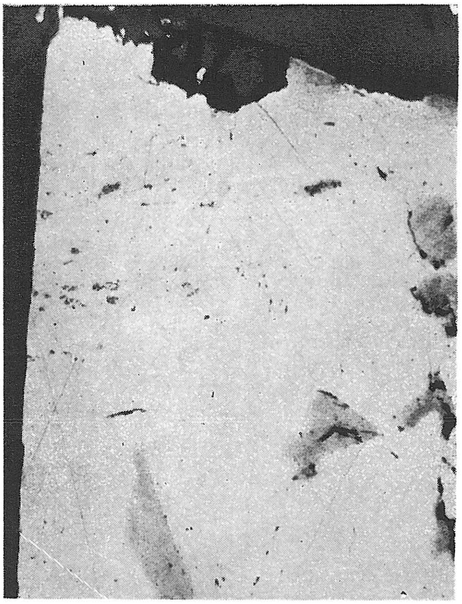

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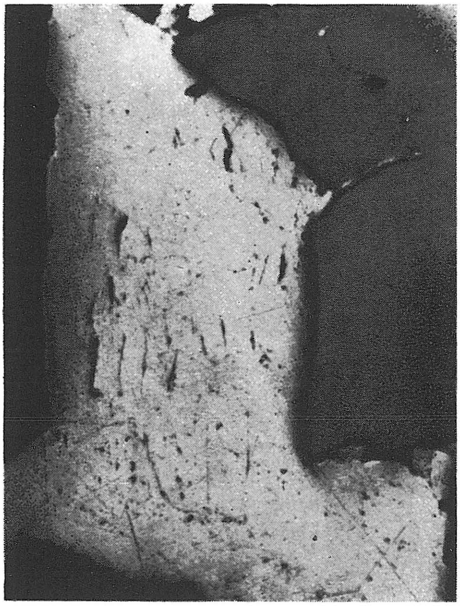

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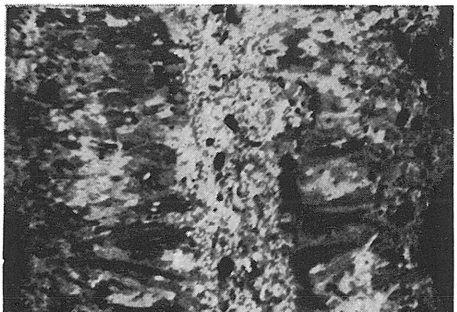

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