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SUPERGENE MINERALS FROM HORNÍ SLAVKOV

This work is the first attempt of summary of supergene minerals from Horní Slavkov tin-tungsten ore deposit.

Using X-ray methods, spectral analysis and optical methods there were identified 14 minerals: *malachite*, *azurite*, *jarosite*, devilline-serpierite, brochantite, beraunite, wavellite, chalcosiderite, *pseudomalachite*, *libethenite*, *olivenite*, mixite, *scorodite* and *pharmacosiderite*. Lattice parameters were calculated in case of underlined minerals.

1. OUTLINE OF GEOLOGICAL SITUATION

1.1 Geological situation of a broad vicinity of the deposit

Geological situation and a description of the deposit were given by many previous authors (KRUSCH, 1915; FRIESER, 1916, 1920). The whole region was studied by FISCHER (1940) and later by FIALA (1957, 1962), ZOUBEK (1951) and JARCHOVSKÝ (1969). The complete description of the whole region of Slavkovský les Mts. was given by FIALA (1962). The rocks of the Slavkov gneiss block were studied by VONDROVÁ (1962). The outline of geological structure of Slavkovský les Mts. and its tectonic development with a summary of literature is given in ZOUBEK et al. (1963).

The vicinity of the deposit belongs to the northern part of Slavkovský les Mts. and from the geological point of view it is a part of Slavkov gneiss block, which is the mantle of Karlovy Vary granite pluton. Dominant rocks are here biotite paragneisses with a certain part of injecting migmatite component, which often change into migmatites. Bedded veins of amphibolites occur here and there in paragneisses. An occurrence of dioritic rocks is rarer. The whole complex is intruded by aplite and aplitic granite veins. The thickness of the mantle keeps within 200 and 500 meters. It is known from mining works that the rocks are intensively folded into a system of abrupt megafolds with axes in the E-W direction. In cores of their synclines remain to a certain extent original strongly deformed paragneiss bodies with thickness of several hundreds of meters. The cores of anticlines are granitized in the extensive complexes of migmatites or "orthogneisses" (VONDROVÁ, 1962).

Slavkov gneiss block is surrounded with granitic rocks of Karlovy Vary pluton, which embraces two groups of granites: the older granites to granodiorites dominate in the N-W rim of Slavkov gneiss block and younger ones protrude in its W rim as the Krudum massif. This massif is a complex intrusive body consisting of several varieties of biotite and two-mica granites (FIALA, 1962). In the neighbourhood of gneiss mantle and under it there is the most widespread rock: a topaz granite with lithium mica (Čistá type). Its shape under the gneiss mantle is not straight and granite forms here a lot of elevations. A widespread greisenization took place in the tops of those elevations and originated there large greisen bodies, which are at present the main source of tin-tungsten ores. The largest deposits of that type are the Huber stock and the Schnöd stock between Horní Slavkov and Krásno nad Teplou. A zone of quartz veins with tin-tungsten-molybdenum mineralization runs SE of those stocks and parallel with their connecting line. The main veins are Gellnauer and Marie ones. The veins incline in the direction to the stocks and their course is marked on the surface only by the rest of old dumps. Well arranged drawing of geological situation of this region is given by DŮRIŠOVÁ et al. (1968).

1.2 Geological situation of Horní Slavkov ore deposit

Previous authors are agreed that Horní Slavkov ore deposit consists of isolated granite bodies. However, as it follows from the results of a drilling exploration, this deposit consists of dome-shaped elevations of a continuous granite body in underlying rocks in this part of Slavkov gneiss block. The shape, the situation and the extent of the stocks were only prerequisite for occurrence of post-magmatic processes, to which belong both formation of greisens and their minerogenesis.

DROZEN (1969) distinguishes three types of the ore mineralization. The most economically important type of ore mineralization is a diffusive cassiterization of greisens and greisenized granites. The second type of ore mineralization is represented by so called "bonanzas". They are bodies of irregular shape with length below 1 meter and thickness below 50 centimeters. Their filling consists of scaly hydromica, cassiterite, sometimes well crystallized topaz. Last type of ore mineralization is represented by quartz veins with various accompanying minerals.

2. OUTLINE OF PREVIOUS MINERALOGICAL RESEARCH

Extensive previous literature, summarized by KRATOCHVÍL (1963) under items Krásno (Schönfeld) and Horní Slavkov (Schlaggenwald) describes about 100 mineral species. TUČEK (1970) who resumed Kratochvíl's work did not mention any new data for supergene minerals from that deposit. It is necessary to say that supergene minerals were in the periphery of the interest of previous authors. There exist only very few works with worthy and reliable data.

M. CH. GLÜCKSELIG (1854) belongs to the authors whose works are important for our topic. In his work there are descriptions of gypsum, scorodite, euchroite, malachite, chrysocolla, azurite (Kupferlasur), bismite and tungstite

(Wolframocker). A. M. GLÜCKSELIG (1864) mentioned euchroite, gypsum, azurite, malachite, molybdite (Molybdänocker), scorodite, bismite (Wismuthocker) and tungstite (Wolframocker). SCHRAUF (1873) mentioned questionable brochantite with an uncertainty whether it is from Horní Slavkov or from Jáchymov. HOFFMANN (1903) entered scorodite and recorded pharmacosiderite and psilomelane as new minerals from Horní Slavkov. SLAVÍK (1903) described newly alunite, jarosite, pitticite, wavellite and mentioned pharmacosiderite and scorodite. ROSICKÝ (1916) mentioned probable libethenite in his work of Slavkov topaz.

Recently they have worked in that field DROZEN (1967, 1969), TACL and BLÜML (1974), MACH (1979), MRÁZEK (1981) and KORBEL (1983). DROZEN recorded X-ray and spectral data of pharmacosiderite, olivenite, pseudomalachite, gypsum and scorodite. TACL and BLÜML described for the first time dioptase, libethenite and chalcosiderite and confirmed pharmacosiderite, malachite, pseudomalachite and scorodite. All these minerals were described using spectral and X-ray data. MACH (1979) described barium-pharmacosiderite as a new mineral from Horní Slavkov and recorded chalcosiderite. MRÁZEK (1981) described mixite from this deposit. KORBEL (1983) described for the first time devilline-serpierite, brochantite and beraunite.

3. CHARACTERISTICS OF THE MINERALS STUDIED

3.1 Recently nonverified minerals

3.1.1 Alunite

The first description of that mineral was given by SLAVÍK (1903). He described it as a new mineral for Bohemia. It was a druse coating on red grained quartz, consisting of tiny crystals below 0.25 milimeters. The colour was greenish white, the crystals were plates with predominating (001). This mineral has not recently been identified from Horní Slavkov.

3.1.2 Chrysocolla

This mineral is mentioned from Horní Slavkov by many authors as disseminated, massive or earthy mineral together with malachite. It was not verified either by DROZEN (1967, 1969) or by TACL and BLÜML (1974). This mineral is not present in author's material as well, but according to the macroscopic similarity with one type of pseudomalachite it is possible to deduce that it could happen to confusion of chrysocolla and pseudomalachite.

3.1.3 Euchroite

This mineral was described by M. CH. GLÜCKSELIG (1854) and A. M. GLÜCKSELIG (1864), but only with a remark that "it is said to have been found once in a druse". That mineral has not recently been identified.

3.1.4 Bismite

This mineral was recorded by M. CH. GLÜCKSELIG (1854) and A. M. GLÜCKSELIG (1864) as yellow coatings on wolframite, labelled as Wismuthocker. It has not recently been confirmed.

3.1.5 Tungstite

Tungstite was mentioned by M. CH. GLÜCKSELIG (1854) and A. M. GLÜCKSELIG (1864) as yellow coatings on wolframite, labelled as Wolframocker. In author's material has occurred a yellow pulverulent coating on wolframite but in spite of a careful separation, X-ray powder pattern showed only wolframite lines. No else method confirmed that mineral.

3.1.6 Dioptase

Dioptase was described by TACL and BLÜML (1974) from Horní Slavkov. It occurred in two types which differ in their colour and habit. The first type is a light green, very fine grained to massive aggregate; the second type is a mineral of nacrite or kaolinite habit, coloured by iron oxides to light brick red. In author's material dioptase did not occur.

3.1.7 Barium-pharmacosiderite

MACH (1979) mentioned in addition to chalcosiderite also barium-pharmacosiderite. It formed yellow to yellow-brown tiny crystals and crystalline crusts with vitreous luster. Crystals are cube similar rhombohedrons. The author did not find this mineral in the material available for this study.

3.2 Recently verified minerals

3.2.1 Malachite

The oldest malachite data were given by M. CH. GLÜCKSELIG (1854). He recorded malachite as radial spherules of emerald green colour. KRATOCHVÍL (1963) assumed his data and in addition to them he described malachite as acicular aggregates and coatings and as earthy aggregates with quartz. DROZEN (1969) did not verify that mineral, but TACL and BLÜML (1974) again described malachite as a fine grained to massive blue-green aggregate and thin coatings on rock fragments. The author has found this mineral in three various types. All the types are from the Huber quarry. The first type is formed by deep green crystalline aggregates, consisting of tiny crystals, covering pharmacosiderite. Green masses of a clay habit with well preserved radial structure form the second type. The massive thin coatings on greisen together with azurite are the third type. Azurite is younger than malachite and overgrows it.

Chemical composition was studied by means of spectral analysis, which gave the following results:

more than 1%	Cu, Fe, Si
0.X%	Mg
0.0X%	Bi, Ca, Mn, Li
less than 0.01%	Al, Ag, As, Co

Due to the impurities in the studied material are there high contents of iron and silicon. X-ray data agree well with the data for synthetic malachite in JCPDS tables (1974). From an accessible material it is possible to judge of the fact that malachite together with azurite belong to the youngest supergene minerals of Horní Slavkov deposit. The lattice parameters were calculated using BURNHAM (1962) computing program. The results and comparison with the data given by ŘÍDKOŠIL (1981) are in the table 1.

Table 1: X-Ray data of malachite (Guinier-de Wolff camera, CuK_α radiation)

Horní Slavkov			synthetic malachite (JCPDS, 1974)	
I	d (meas.)	hkl	I	d
3	7.406	110	12	7.410
6	5.985	020	55	5.993
8	5.039	120	75	5.055
3	4.695	200	14	4.699
10	3.693	220	85	3.693
3	3.028	310	18	3.028
4	2.988	040	18	2.988
9	2.862	$\bar{2}01$, 140	100	2.857
5	2.823	111	40	2.823
6	2.776	320, $\bar{2}11$	45	2.778
7	2.522	240	55	2.520
5	2.485	201	30	2.477
2	2.455	330	35	2.464
5	2.426	211	20	2.425
4	2.347	400, 131	14	2.349
4	2.312	$\bar{2}31$	18	2.316
4	2.287	221	18	2.289
3	2.186	041, 420	20	2.186
		$\bar{1}41$		
3	2.056	311	10	2.054
3	1.967	321	18	1.969
2	1.949	160	16	1.947
2	1.937	$\bar{4}21$	10	1.941
1	1.910	$\bar{1}51$, 241	18	1.911
1	1.895	350	14	1.899
2	1.688	161	25	1.691
1	1.678	450	14	1.678
2	1.642	$\bar{2}61$	12	1.640
3	1.614	431	18	1.616
3	1.588	012, 540	18	1.589
3	1.570	351	14	1.571
2	1.522	112	14	1.531
1	1.482	$\bar{3}22$	6	1.480
1	1.473	521	12	1.472
2	1.421	451, $\bar{3}32$	8	1.422
		531		
1	1.384	640	10	1.386

Lattice parameters:
a = 9.486(5) (10^{-10} m)
b = 11.997(9)
c = 3.241(1)
β = 98.75(4)°

Řídkošil (1981)
a = 9.494(8)
b = 11.985(9)
c = 3.243(3)
β = 98.68(7)°

3.2.2 Azurite

The descriptions of azurite given by the previous authors are summarized in KRATOCHVÍL (1963). This mineral has occurred as tiny blue crystals or massive aggregates, it has been rather rare. M. CH. GLÜCKSELIG (1854) described microscopic azure blue crystals and amorphous masses. DROZEN (1969) did not find it, BERNARD (1981) mentioned it without an exact description as products of chalcopyrite decomposition. The author of this work agrees with KRATOCHVÍL (1963) in evaluation of azurite rarity in Horní Slavkov. Azurite occured only in three specimens having been in two types. The small azure blue crystals overgrown olivenite are the first type. The second one is formed by coatings on greisen with malachite, in which azurite overgrows malachite. Both these minerals are probably the youngest supergene minerals of the deposit. Spectral analysis gave those results:

X0%	Cu
X%	Al, Ca, Si
0.X%	Ag
0.0X%	Fe, Mg
less than 0,01%	Mn, Ti

(figs. 12—23, pls V—IX)
(figs. 24—27, pls. X—XI)

High contents of aluminum, calcium and silicon are due to some admixture of rock material. X-ray powder pattern gave results in agreement with azurite data from Piesky near Banská Bystrica (ŘÍDKOŠIL, 1981). The lattice parameters were calculated from an indexed powder diffraction pattern using program of BURNHAM (1962) (table 2).

3.2.3 Jarosite

The first description of jarosite from Horní Slavkov was given by SLAVÍK (1903) at the same time as the first description of jarosite in Bohemia. Slavík characterized jarosite as crystalline coatings of red-brown colour with intensive to adamantine luster. Jarosite ocurred in form of small crystals to 0.7 milimeters which were shaped with a combination of rhombohedron and base. Unfortunately, Slavík's location of jarosite occurrence "greisen from Schönfeld station" is quite confused and nowadays unidentifiable. In Krásno (Schönfeld) railway had never led, so that we do not know what station was reported by SLAVÍK (1903). Next authors did not find any specimen of that mineral and they only repeated Slavík's description. Only now it has been discovered a mineral from greisen of Huber quarry which was determined to be jarosite. It occurred only in one specimen of greisen as ochre yellow earthy pellets up to 5 milimetres in diameter.

Spectral analysis was not able to do for the lack of material. X-ray data agree fairly well with the data of synthetic jarosite (JCPDS, 1974). The lattice parameters calculated by least-squares method using program of BURNHAM (1962) are presented in the table 3.

3.2.4 Devilline-serpierite

Devilline-serpierite is a new mineral for Horní Slavkov. Specimens with this mineral are from the 7th level of the Duriš mine, which exploited the Schnöd stock. Thin films have recently originated on the walls of galleries at that level. By means of X-ray methods a mineral from the devilline-serpierite group was discovered. Fresh films are deep blue-green, after drying the colour changes to light blue. The whole mass of the films is not homogeneous, mineral from the devilline group forms the main part of the mixture. Due to very fine integrowth

Table 2: X-Ray data of azurite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov			Piesky (Řídkošil, 1981)	
I	d (meas.)	hkl	I	d
8	5.170	002	7	5.159
5	5.111	011	6	5.080
4	5.011	100	5	5.001
1	3.868	012	1	3.872
3	3.795	110	4	3.803
9	3.670	102	8	3.667
10	3.527	$\bar{1}02$	10	3.535
1	2.964	013	3	2.969
3	2.917	020	1	2.925
2	2.810	021	3	2.815
3	2.595	$\bar{1}13$	4	2.598
6	2.539	022	5	2.547
3	2.522	120	4	2.527
6	2.512	113	4	2.517
4	2.335	$\bar{1}04$	3	2.340
1	2.298	210	1	2.304
4	2.284	$\bar{1}22$	4	2.290
5	2.262	$\bar{2}11$	6	2.269
5	2.232	211	9	2.231
2	2.173	114	3	2.172
1	2.108	114	2	2.109
1	2.018	123	3	2.019
7	1.945	$\bar{2}13$	5	1.952
2	1.901	220	5	1.904
1	1.877	$\bar{2}21$, 213	2	1.882
2	1.834	$\bar{2}04$	2	1.840
4	1.824	$\bar{1}24$	1	1.828
2	1.787	124	3	1.786
1	1.764	204	2	1.763
5	1.594	$\bar{3}11$	3	1.598

Lattice parameters (10^{-10} m)	Řídkošil (1981)
a = 5.010(3)	a = 5.020(1)
b = 5.836(4)	b = 5.853(1)
c = 10.375(1)	c = 10.356(2)
β = 92.22(7)°	β = 92.44(2)°

of mixture the author failed in separation of a pure material. The results of the spectral analysis are influenced by impurity of studied material.

more than 1%	Al, Cu, Fe, Si, Zn
0.X%	Ca, Mg, Mn
0.0X%	Ni, Sn
less than 0.01%	Be, Bi, Cd, Co, Pb, Mo, Ti

X-ray powder pattern from Guinier-de Wolff camera showed very few diffraction lines due to metacolloid state of the mineral (table 4). Nevertheless it is sufficient to the determination of that mineral. On the basis of the data discovered it is very difficult to determine exactly whether it is devilline or serpierite. For ser-

Table 3: X-Ray data of jarosite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov			synthetic jarosite (JCPDS, 1974)	
I	d (meas.)	hkl	I	d
5	5.867	101	45	5.930
2	5.698	003	25	5.720
6	5.068	012	70	5.090
3	3.641	110	40	3.650
9	3.100	021	75	3.110
10	3.063	113	100	3.080
1	3.028	015	6	3.020
2	2.959	202	15	2.965
2	2.862	006	30	2.861
3	2.539	024	30	2.542
5	2.284	107	40	2.287
7	1.973	033	45	1.977
1	1.935	027	10	1.937
8	1.821	220	45	1.825
1	1.731	223	6	1.738
3	1.536	226	20	1.536
3	1.504	0.2.10	20	1.507
1	1.478	404	8	1.480

Lattice parameters (10^{-10} m)
a = 7.257(3)
c = 17.123(12)
γ = 120°

Strunz (1977)
a = 7.21
c = 17.03
γ = 120°

pierite a presence of relatively high contents of zinc, achieved by spectral analysis, gives the evidence. However, those data are only semiquantitative and X-ray powder pattern responds more to the powder pattern of devilline. Without chemical analysis it is impossible to draw any exact conclusion and chemical

Table 4: X-Ray data of devilline (Guinier-de Wolff camera, CuK$_\alpha$ radiation)

Horní Slavkov		Špania Dolina (Faraon et al., 1967)	
I	d (meas.)	I	d
10	10.163	100	10.17
7	5.068	80	5.075
6	3.395	80	3.389
4	3.159	40	3.178
3	2.867	5	2.871
2	2.512	60	2.507
3	2.389	40	2.381
1	1.708	5	1.705

analysis was out of the author's possibilities due to extremely fine intergrowth of material. The mineral from devilline group is described for the first time from Bohemia and Horní Slavkov is its third locality in Czechoslovakia.

3.2.5 Brochantite

Brochantite has been known up to this time from Slavkov deposit only by the questionable description of SCHRAUF (1873). This author recorded that mineral as parts of the thin green crust on lampadite (copper black) on trenched quartz columns. Location is not sure because SCHRAUF (1873) mentioned that the specimen is either from Horní Slavkov or Jáchymov. Confirmation of brochantite for Jáchymov was given by HLOUŠEK (1976) and this work is the first exact determination of brochantite from Horní Slavkov. Brochantite occurs as light blue-green crystalline crusts with botryoidal surface on the weathered tennantite. The specimens are from material of the Schnöd stock inbreak. Further type of occurrence there is a blue-green clay mass consisting of a mixture of brochantite and clay minerals. Chemical composition was studied by means of spectral analysis.

X0%	Cu, Al
X%	Ca, As
0.X%	Sb, Bi, Mg, Pb
0.0X%	Fe, Si, Sn, Mn, Be, Cd, In, Zn
less than 0.01%	Mo, Ag

X-ray data of Slavkov brochantite agree with the data of brochantite from Greece (SAPOUNTZIS, 1972) and other Czechoslovak localities, e.g. Borovec (ČECH, 1961), Ludvíkov (ČECH, 1954) and Piesky (ŘÍDKOŠIL, 1977) as well. X-ray powder pattern was indexed in accordance with the data of JCPDS tables (1974). Using program of BURNHAM (1962) crystal lattice parameters were calculated (table 5). In the same table there is also the comparison with the data of SAPOUNTZIS (1972). His data are a little bit different from our data; it is caused by the use of a different unit cell for our computing.

3.2.6 Beraunite

Beraunite from Horní Slavkov has already been known among mineral collectors, but there is no description of beraunite from this locality in scientific literature at all. Hemispherical aggregates with a radial structure occurred very rare in quartz vugs and they were determined to be beraunite. These aggregates are dirty green and their size reaches up to 3 milimeters in diameter. This habit of beraunite is quite unusual in our Czech localities. Beraunite from Hrbek and Zaječov forms hyacinth red acicular crystals on massive limonite (KRATOCHVÍL, 1958). Beraunite from Eleonora mine near Giessen (FRG) (FANFANI and ZANAZZI, 1967) occurs as monoclinic red-brown crystals, which are transparent and of columnar or tabular habit.

Spectral analysis showed the following element contents:

X0%	P
X%	Si, Fe
0.X%	Al, As, Zn
0.0X%	Ca, Ag, Cu
less than 0.01%	Mg

Table 5: X-Ray data of brochantite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov			Borovec (Čech, 1961)	
I	d (meas.)	hkl	I	d
2	7.830		2	7.86
5	6.394	200	7	6.38
6	5.356	210	7	5.37
2	4.934		1	4.96
9	3.909	220, 310	9	3.91
4	3.203	130, 400	6	3.19
3	2.917	230	4	2.92
1	2.805		1	2.80
8	2.679	420	7	2.67
3	2.600	330	2	2.60
10	2.515	122	10	2.52
2	2.458	302	3	2.46
3	2.380	331, 222	3	2.38
2	2.298		1	2.30
2	2.273		2	2.26
4	2.186	132, 402	4	2.18
3	2.134	431, 412	3	2.13
2	2.083	610	3	2.08
2	2.014		3	2.01
2	1.967	050, 332	2	1.967
1	1.947		2	1.943
2	1.881	042	1	1.877
2	1.822		3	1.821
8	1.737		7	1.734
2	1.710		2	1.711
2	1.677		3	1.674
2	1.630		3	1.634
4	1.596		3	1.593
5	1.560		4	1.558
5	1.536		4	1.536
2	1.520		1	1.520
4	1.503		4	1.502
1	1.462		2	1.463
1	1.448		1	1.446
2	1.431		3	1.431
1	1.400		2	1.405
2	1.373		1	1.372
1	1.338		2	1.336
1	1.312		4	1.314

Lattice parameters (10^{-10} m)
a = 12.778(8)
b = 9.845(8)
c = 6.034(8)
β = 90.4(1)°

Sapountzis (1972)
a = 13.087
b = 9.790
c = 6.022
β = 104.05°

X-ray data of beraunite are in good agreement with the data of JCPDS tables (1974) for beraunite from Rothlaufchen mine, Hessen, FRG (table 6).

Table 6: X-Ray data of beraunite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov		Rothlaufchen (JCPDS, 1974)	
I	d (meas.)	I	d
10	10.122	100	10.3
9	9.509	35	9.60
7	7.167	35	7.27
5	4.783	40	4.79
2	4.385	20	4.39
3	3.708	16	3.72
1	3.170	2	3.14
8	3.053	55	3.06
1	2.691	16	2.71
1	2.550	16	2.563
1	2.092	16	2.099
1	1.989	10	1.992

3.2.7 Wavellite

Wavellite was originally described from Horní Slavkov by SLAVÍK (1903). He mentioned three types of its occurrence. First type is formed by radial fibrous aggregates with the length of fibers up to 15 milimeters. Second type there are white botryoidal masses, macroscopically massive and of a chalky habit. Last type is formed by coatings of the small greyish mammilae on the fissures of greisen. Lately, wavellite was recorded by BERNARD (1981) as white or by various oxides coloured needles, radiating networks and spherules. Wavellite occured in two types in material from the Huber quarry. The first type is formed by white radial aggregates with the length of fibers up to 5 milimeters. The second type occurred as white-grey spherules of a radial structure up to 3 milimeters in diameter.

Chemical composition of wavellite was studied by means of spectral analysis, which gave the following results:

more than 1%	Fe, P, Al
0.X%	Si, Zn, As
0.0X%	Ca
less than 0.01%	Cu, Ag, Mg

X-ray powder data agree fairly well with the data of JCPDS table (1974) for wavellite from Sesceira, Portugal (table 7).

3.2.8 Chalcosiderite

This mineral was originally described from Horní Slavkov in an unpublished work of TACL and BLÜML (1974) and then by MACH (1979) as a new mineral for Czechoslovakia. According to these authors chalcosiderite forms fibreous, radial and spherical aggregates of blue-green and emerald green colour. It occurs in the quartz gangue with wolframite and iron hydroxides. On the specimen, kindly lent by dr. Mach from Karlovy Vary, this mineral forms green,

Table 7: X-Ray data of wavellite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov		Sesceira (JCPDS, 1974)	
I	d	I	d
8	8.346	100	8.39
7	5.626	60	5.64
3	4.809	50	4.82
1	4.322	20	4.30
3	4.040	40	4.03
1	3.834	40	3.79
10	3.414	80	3.44
9	3.215	80	3.20
5	3.063	40	3.05
3	2.950	60	2.95
4	2.797	60	2.78
6	2.571	80	2.56
3	2.356	40	2.37
3	2.268	20	2.25
1	2.189	20	2.19
4	2.094	60	2.09
2	2.032	20	2.03
3	1.957	60	1.95
2	1.881	40	1.88
1	1.822	40	1.82
3	1.743	50	1.75
2	1.705	40	1.70
2	1.665	20	1.66
2	1.586	50	1.60
2	1.567	40	1.56

rose shaped aggregates, consisting of thin slabs which overgrow wolframite. The size of one such rose is about 1.5 milimeters. Spectral analysis, carried out by dr. Mach, showed the following element contents:

X0%	Fe
X%	P, Cu
0.X%	Al
0.0X%	Be, Bi, Ca, Mg, Si, W
less than 0.01%	Ag, Cr, Mn, Sc, Sn, Ti, Zn

Relationships in the group turquoise-chalcosiderite were studied by BRAITHWAITE (1981). There are minerals of the general formula $CuX_6(PO_4)_4(OH)_8 \cdot 4\,H_2O$, where X is either Al or Fe. Turquoise is the end member with Al contents, chalcosiderite is the end member with Fe contents. The specimen of chalcosiderite from Cornwall studied in Braithwaite's work is formed by small green crystals of a short columnar habit with a tendency of forming of spherical aggregates. X-ray data of Slavkov chalcosiderite agree well with the data of GRAHAM (1948) for chalcosiderite from Cornwall (table 8).

Table 8: X-Ray data of chalcosiderite (diffractometer DRON, CuKα radiation)

Horní Slavkov		Cornwall (Graham, 1948)	
I	d	I	d
50	6.326	30	6.40
52	4.962	10	4.96
100	3.786	100	3.77
44	3.562	40	3.56
52	3.395	70	3.39
54	3.015	60	3.02
40	2.954	40	2.96
12	2.582	5	2.59
20	2.383	30	2.39
12	2.338	5	2.31
20	2.139	40	2.14
20	2.080	40	2.07
23	1.953	30	1.96
15	1.846	30	1.85
23	1.539	40	1.54
17	1.468	40	1.47

3.2.9 Pseudomalachite

Pseudomalachite was described from Horní Slavkov by DROZEN (1967) as a pulverulent, light blue-green mineral. It was confirmed by TACL and BLÜML (1974) as well in form of green aggregates of malachite-like habit. The author found this mineral in relatively high abundance in the material from the Huber quarry. It is possible to distinguish three various types of pseudomalachite ocurrence. The first type is represented by black-green botryoidal crusts on olivenite and wolframite. The second type are blue-green crystalline aggregates in the quartz vugs which overgrow pharmacosiderite. The last type is formed by blue-green fine grained to massive aggregates with azurite, azurite is younger than pseudomalachite. This type is macroscopically very similar to chrysocolla which has not recently been discovered. It is probable that chrysocolla of the previous authors could be pseudomalachite in many cases.

Spectral analysis gave the following results:

X0%	Cu
X%	P
0.X%	As, W, Zn
0.0X%	Ca, Bi, Fe, Si
less than 0.01%	Al, Ag, Be, Cd, Mg, Mn, Mo, Ti

X-ray data correspond well with the data of HUTTON (1959) who studied pseudomalachite from Safford, Arizona. Using program of BURNHAM (1962) there were calculated lattice parameters. Their comparison with the data of SHOEMAKER and KOSTINER (1981) brings the table 9. These authors have in their work inverse symbols *a* and *b*.

Table 9: X-Ray data of pseudomalachite (Guinier de Wolff camera, CuKα radiation)

Horní Slavkov			Safford (Hutton, 1959)	
I	d (meas.)	hkl	I	d
2	8.465	200	1	8.51
5	4.770	210	1	4.78
10	4.484	001	10	4.49
7	3.466	$\bar{1}11$, 410	5	3.46
9	3.116	$\bar{4}01$	4	3.11
7	3.058	401	3	3.05
3	3.018	$\bar{3}11$	1	3.02
6	2.998	311	4	2.98
5	2.931	510	3	2.92
3	2.880	020	1	2.867
4	2.730	$\bar{4}11$, 220	3	2.724
2	2.706	411	1	2.700
2	2.571	320, 610	2	2.561
6	2.465	$\bar{5}11$	3	2.468
8	2.442	511	6	2.443
7	2.411	$\bar{6}01$, 021	6	2.418
7	2.398	601, 121	7	2.386
3	2.327	$\bar{2}21$, 221	5	2.324
6	2.241	321, $\bar{6}11$	4	2.234
2	2.199	611, 520	1	2.196
2	2.125	$\bar{4}21$	1	2.129
3	2.099	421	2	2.094
1	2.014	620, $\bar{7}11$	1	2.018
1	1.991	521	1	1.993
1	1.967		1	1.961
1	1.949		1	1.945
2	1.857		3	1.855
1	1.816		1	1.816
1	1.791		1	1.791
3	1.766		4	1.765
2	1.734		5	1.730
2	1.707		1	1.703
1	1.691		1	1.692
1	1.671		2	1.670
1	1.627		2	1.624
3	1.594		3	1.595
2	1.573		1	1.575
3	1.562		4	1.560
2	1.531		3	1.527
2	1.506		2	1.505

Lattice parameters (10^{-10} m)

a = 17.087(16)
b = 5.758(3)
c = 4.482(6)
β = 90.94(4)°

Shoemaker and Kostiner (1981)

a = 4.473
b = 5.747
c = 17.032
β = 91.04°

3.2.10 Libethenite

Libethenite together with olivenite belongs to the most interesting supergene minerals from the Slavkov deposit. Its first description but not quite unambiguous was given by ROSICKÝ (1916). Further data, already undoubted, are from the work of TACL and BLÜML (1974). They mentioned libethenite as grass green tiny crystals of vitreous luster which accumulate into fine grained aggregates. Besides it, these authors mentioned greenish colour of the clay masses to be caused by libethenite. There are two types of libethenite in the material from the Huber quarry. The first type is formed by pseudocubic (octahedral) orthorombic crystals of green colour up to 1 milimeter. The second type is represented by black-green crystalline aggregates consisted of orthorombic crystals.

Spectral analysis showed the following element contents:

more than 1%	Cu, P
0.X%	Si, As
0.0X%	Be, Cd
less than 0.01%	Al, Ag, Bi, Ca, Fe, Mg, Mn, Pb, V

High contents of silicon are due to the presence of quartz in the studied sample. X-ray data of libethenite conform with the data of MORRIS et al. (1980) for synthetic libethenite (table 10). Using indexed powder diffraction pattern there were calculated lattice parameters (table 10). Optically, libethenite is biaxial negative with refraction indices $N_g = 1.788(2)$, $N_p = 1.703(3)$ and $N_m = 1.742(3)$. These indices correspond well with the data of WINCHELL and WINCHELL (1951) and SUMIN (1955).

Table 10: X-Ray data of libethenite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov			synthetic libethenite (Morris et al., 1980)	
I	d (meas.)	hkl	I	d
7	5.791	110	93	5.813
8	4.809	101	100	4.818
8	4.732	011	68	4.751
2	4.114	111	6	4.137
6	3.715	210	42	3.729
4	3.626		15	3.638
3	2.931	220	18	2.946
10	2.908		72	2.912
5	2.640	112	43	2.647
9	2.622	310	61	2.627
3	2.607		19	2.610
4	2.560	310	25	2.561
2	2.518		10	2.532
2	2.442		11	2.446
4	2.411	202	26	2.414
3	2.374		21	2.377
2	2.347		10	2.348
3	2.301	212	21	2.312
1	2.284		4	2.288
1	2.259		3	2.265
2	2.067		6	2.071

Table 10: continuation

Horní Slavkov			synthetic libethenite (Morris et al., 1980)	
I	d (maes.)	hkl	I	d
2	1.963		3	1.968
1	1.939		3	1.941
1	1.931		6	1.933
1	1.918	103, 013	6	1.924
2	1.903		5	1.908
2	1.859		5	1.861
1	1.834		2	1.820
1	1.811		2	1.814
1	1.791		2	1.796
1	1.735		2	1.737
4	1.705	042	11	1.711
3	1.663	430	7	1.664
1	1.642	340	3	1.646
3	1.618		10	1.620
1	1.594		4	1.595
3	1.584		9	1.585
2	1.573		7	1.577
1	1.554		4	1.559
2	1.547		9	1.547
1	1.529		3	1.530
1	1.504		3	1.506
4	1.453		6	1.455
1	1.425		3	1.428

Lattice parameters (10^{-10} m)	Cordsen (1978)
a = 8.229(10)	a = 8.062(5)
b = 8.445(20)	b = 8.384(4)
c = 5.896(2)	c = 5.881(2)

3.2.11 Olivenite

This mineral together with libethenite belongs to the most interesting supergene minerals from Horní Slavkov. BREITHAUPT (1849) originally described olivenite in the paragenesis with quartz and feldspar but without any further details. References to olivenite were missing at many later authors, only DROZEN (1967) mentioned it. According to him olivenite forms short stalky, bunch-shaped and fan-shaped aggregates of pale green to yellow-green colour in a greisen vug with pseudomalachite. That specimen came from the 4th level of Slavkov mine, while most of the author's specimens are from the Huber quarry. It is possible to distinguish in this material three various types of olivenite. The first type is formed by black-green spherical aggregates of a radial structure with younger pseudomalachite. The further type occurs in a shape of green scaly aggregates with mixite, mixite is younger. The last type is a green clay mass with preserved radial structure. This clay mass fills the space between quartz crystals.

Chemical composition of olivenite was studied by means of spectral analysis which gave the following results:

more than 1%	Cu, Si, Zn
0.X%	Al, As, Fe, P
0.0X%	Pb, Sn
less than 0.01%	Ag, Be, Bi, Ca, Cd, Mn, V

High contents of silicon and aluminum are due to an inhomogeneity of the material available. It is possible to conclude that in case of Slavkov olivenite there is a variety labelled zinc-olivenite, with zinc contents. This variety is a member of the olivenite-adamite isomorphous series. The first description of that variety was given by DUNIN-BARKOVSKAJA (1960) together with the data of zinc-olivenite from Lačin-Chana in Uzbekistan. The detailed study of zinc-olivenite from Zapačica, Bulgaria is presented in the work of MINČEVA-STEFANOVA (1964). This authoress does not give only the full data, but the features in which differ olivenite and zinc-olivenite according to their X-ray powder data as well. It is necessary to say, that a lot of these features do not correspond with the data obtained for the Slavkov mineral. Nevertheless, it is possible to consider the Slavkov mineral to be zinc-olivenite because in case of zinc-olivenite from Poniky (RIEDER and POVONDRA, 1961), which was exactly determined by means of chemical analysis, many features of Minčeva-Stefanova (1964) do not correspond as well. According to the author's experience with a lot of natural olivenites it is possible to say that the data of MINČEVA-STEFANOVA (1964) are acceptable only for synthetic olivenites, but they are not applicable for the natural ones.

X-ray data of the Slavkov mineral agree well with the data of BERRY (1951) for olivenite from Cornwall. Using computing program of BURNHAM (1962) there were calculated lattice parameters from the indexed powder pattern. The results and the comparison with the data of WALITZI (1963) are in the table 11. This authoress had in her work inverse symbols of parameters *a* and *b*.

Table 11: X-Ray data of olivenite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov			Cornwall (Berry, 1951)	
I	d (meas.)	hkl	I	d
6	5.926	110	70	5.92
10	4.822	011, 101	90	4.82
4	4.201	111	60	4.19
5	3.794	120	40	3.80
8	2.983	220, 002	100	2.98
3	2.694	130	40	2.70
9	2.648	221, 112	60	2.65
2	2.596	310, 031	10	2.59
6	2.449	301, 131, 022	70	2.47
7	2.408	202, 311	70	2.39
4	2.330	122, 212	10	2.33
1	1.985	330, 141, 312	10	1.97
1	1.920	013, 103	5	1.93
2	1.884	411, 331, 113	20	1.88
3	1.731	213, 042	10	1.74
2	1.649	332, 223	20	1.65
1	1.622	151, 510	10	1.62
2	1.609	242, 303, 133	30	1.60
4	1.578	313, 422	60	1.58
1	1.562	511	5	1.56
5	1.479	440, 004	50	1.49

Lattice parameters (10^{-10} m)	Walitzi (1963)
a = 8.191(12)	a = 5.94(1)
b = 8.560(6)	b = 8.59(2)
c = 5.904(9)	c = 8.21(2)

3.2.12 Mixite

This mineral was described from Horní Slavkov for the first time by MRÁZEK (1981). Mixite occurred in the specimens of quartz gangue from the dumps. There were two types of mixite there. It formed fibreous to felt-like bunches in the quartz vugs, sometimes individual acicular crystals overgrown on the crystalline crust of olivenite.

Chemical composition was determined by means of spectral analysis, which gave the following results:

X0%	Cu, Si
X%	As, Bi, Ca, Al, Fe
0.X%	K, Mg, Sn, Zn
0.0X%	Mo
less than 0.01%	Be, Cr, Mn, Pb, V

High contents of silicon, iron and aluminum are due to heterogeneous impurities. WALENTA (1970) presents the general formula A_2Cu_{12} $(AsO_4)_6(OH)_{12} . H_2O$ for the minerals of the mixite-agardite-(Y) group. The symbol A is either bismuth or calcium or REE. Mixite is a member with bismuth and without REE, agardite-(Y) does not contain bismuth. Agardite-(Y) is now the only one permitted name for the mineral previously named chlorotile. X-ray data of the Slavkov mineral correspond with the data published for the minerals of the mixite-agardite-(Y) group (WALENTA, 1960) (table 12). X-ray data of both these minerals are nearly identical but with respect to contents of bismuth there is mixite in Horní Slavkov. The values of refraction indices $N_o = 1.745(3)$ and N_e = more than 1.780 agree with the data of WALENTA (1960) and

Table 12: X-Ray data of mixite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov		Heubachtal (Walenta, 1960)	
I	d (meas.)	I	d
10	11.632	10	12.03
2	6.006	3	6.91
1	5.626	0.5	5.26
3	4.439	5	4.47
2	4.201	5	4.18
1	3.909	4	3.93
9	3.555	8	3.57
2	3.261	5	3.27
6	2.945	7	2.95
2	2.849	6	2.86
7	2.694	6	2.70
5	2.637	2	2.64
3	2.564	6	2.57
8	2.455	9	2.46
2	2.201	3	2.19
1	1.886	0.5	1.887
2	1.833	3	1.840
1	1.791	5	1.797
2	1.774	5	1.777
2	1.688	3	1.683
1	1.633	5	1.634

TIMOFEJEVA (1965). Horní Slavkov is the third locality for mixite in Czechoslovakia after Jáchymov (SCHRAUF, 1879) and Moldava (FENGL et al., 1981).

3.2.13 Scorodite

Scorodite is a very frequent mineral in the descriptions of the previous authors. The first description was given by SOMMER in 1847 (in SLAVÍK, 1903). Further references and descriptions are almost in all the authors who studied supergene minerals from Horní Slavkov (M. CH. GLÜCKSELIG, 1854; A. M. GLÜCKSELIG, 1864; HOFFMANN, 1903; SLAVÍK, 1903 and others). They described scorodite in form of coatings and crystals of olive green-grey colour. New descriptions are given by DROZEN (1967, 1969) and BERNARD (1981). They characterize scorodite as tiny olive green crystals or radial crusts with limonite. Most types of scorodite occurrences are described by TACL and BLÜML (1974). There are transparent green crystals in the vugs of grey quartz with a habit similar to topaz crystals; nontransparent orthorombic crystals, green to brown, with vitreous to greasy luster, in parts fan-shaped aggregates; nontransparent green aggregates with greasy luster, which have a very fine grained structure and an apatite-like habit; blue-green transparent orthorombic crystals similar to libethenite; very thin, pointed to acicular grey-white crystals and thin crusts, in parts pale greenish; spherical and clustery light green aggregates; green clay masses.

In the author's material there were only few specimens with scorodite. All the specimens are from the Huber quarry and scorodite forms in these specimens porous crystalline mass of yellow-green, green and rusty colour on quartz.

Chemical composition was studied using spectral analysis:

more than 1%	Fe
0.X%	As, Cu, Sn
0.0X%	Bi, W, P
less than 0.01%	Al, Ag, Ca, Cd, Mg, Mn, Ni, Si, Mo, Zn

X-ray data agree well with the data recorded by DROZEN (1967) for scorodite from the same locality and correspond with the data of JCPDS tables (1974) for scorodite from Bhilivara District, India as well (table 13). From an indexed X-ray powder pattern there were calculated lattice parameters using program of BURNHAM (1962). The results agree with the data published by KITAHAMA et al. (1975).

3.2.14 Pharmacosiderite

The first description of Slavkov pharmacosiderite was given by HOFFMANN (1903). He described that mineral in form of blue-green crystals with faces of the cube and two tetrahedrons. This mineral was recorded by many authors summarized in KRATOCHVÍL (1963). New descriptions are given by DROZEN (1967, 1969) and mainly by TACL and BLÜML (1974). They distinguished three various types of pharmacosiderite occurrences. The first type is formed by small, grass green crystals in greisen vugs with quartz, wolframite and sulphides. Another type was light green crusty coatings of almost clay character. The last type forms lustreous crystalline aggregates of emerald green colour which are attended by dissociated wolframite. BERNARD (1981) recorded pharmacosiderite in the form of green, cube-like crystals with blunted edges. In the author's material from the Huber quarry it is possible to distinguish five various types. There are green cubic crystals, either only cubes (100) or a combination of cube

Table 13: X-Ray data of scorodite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov			Bhilivara District (JCPDS, 1974)	
I	d (meas.)	hkl	I	d
9	5.609	111	80	5.65
6	5.025	020	40	5.05
8	4.484	002	100	4.50
5	4.105	211	40	4.11
4	3.794	112	40	3.82
10	3.175	122	80	3.20
5	3.058	311	60	3.07
5	3.003	131	60	3.01
4	2.687	032	40	2.695
4	2.600	400	60	2.601
3	2.508	040	40	2.511
2	2.315	331	20	2.324
2	2.191	412	5	2.190
1	2.151	114	5	2.145
1	2.118		5	2.118
2	2.006		5	2.011
1	1.985		5	1.954
1	1.829		5	1.833
1	1.802		5	1.805
1	1.757		5	1.760

Lattice parameters (10^{-10} m)	Kitahama et al. (1975)
a = 10.329(14)	a = 10.325(6)
b = 10.028(9)	b = 8.953(3)
c = 8.961(8)	c = 10.038(2)

(100) and octahedron (111) up to two milimeters in greisen vugs; crystalline aggregates consisting of accumulated tiny crystals (under 0.1 milimeter) in quartz vugs; crystalline crusts of green and rusty brown colour, consisting of strongly corroded crystals; fine grained to massive coatings of a pappilate surface; light green clay masses. Pharmacosiderite is one of the most abundant supergene minerals in Horní Slavkov. Spectral analysis showed the following element contents:

more than 1%	Fe
0.X%	Al, As, Bi, Cu, Si, Sn
0.0X%	Ag, Na, P
less than 0.01%	Be, Ca, Cd, Mg, Mn, Sb, Zn

The powder diffraction pattern agree well with the data published by WALENTA (1966) for pharmacosiderite from Cornwall (table 14). Refraction index value is 1.683 measured using spindle stage method and it corresponds well with the value 1.687 (RÖSLER, 1979). Using programme of BURNHAM (1962) there were calculated lattice parameters.

Table 14: X-Ray data of pharmacosiderite (Guinier-de Wolff camera, CuKα radiation)

Horní Slavkov			Cornwall (Walenta, 1966)	
I	d (meas.)	hkl	I	d
10	7.935	100	10	8.00
6	4.611	111	5	4.60
6	3.978	200	5	3.98
3	3.562	210	2	3.56
9	3.249	211	8	3.25
8	2.818	220	7	2.806
4	2.656	300, 221	4	2.647
7	2.515	310	6	2.508
7	2.401	311	6	2.394
4	2.298	222	3	2.290
3	2.129	321	2	2.125
2	1.989	400	1	1.987
3	1.931	410	2	1.925
4	1.879	411, 330	3	1.871
2	1.828	331	1	1.823
5	1.783	420	4	1.774
3	1.740	421	2	1.735
3	1.623	422	4	1.620
4	1.594	500, 430	4	1.586
3	1.533	511, 333	4	1.528
2	1.454	521	3	1.449
3	1.407	440	5	1.403

Lattice parameters (10^{-10} m)
a = 7.965(1)

Walenta (1966)
a = 7.937

4. CONCLUSIONS

By means of mineralogical methods there were determined 14 supergene minerals from Horní Slavkov tin-tungsten deposit. The origin of most of the supergene minerals is controlled by the change of chalcopyrite, tennantite and arsenopyrite under the conditions of the oxidation zone. The origin of azurite and malachite is conditional on the presence of $(HCO_3)^-$ ions. The oxidation zone in Horní Slavkov ore deposit reaches to the depth of 200 meters. Documentary material is deposited in the mineral collection of the Department of Mineralogy and Petrology of the National Museum in Prague and in the mineral collection of the Department of Mineralogy at the Charles University in Prague.

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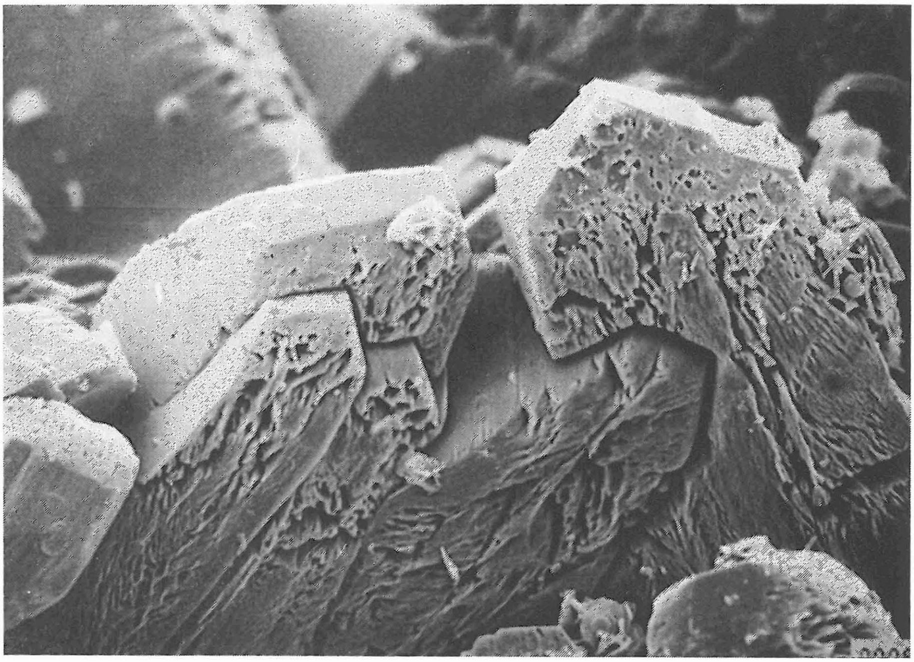

Figure 1: Brochantite, enlarged 500 ×, Z. Mach SEM photo.

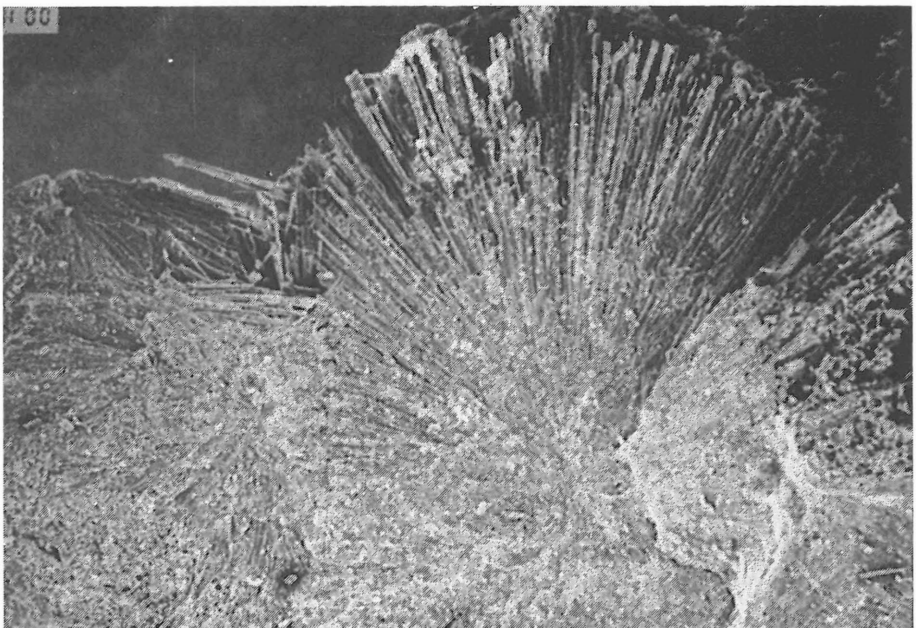

Figure 2: Wavellite, enlarged 50 ×, Z. Mach SEM photo.

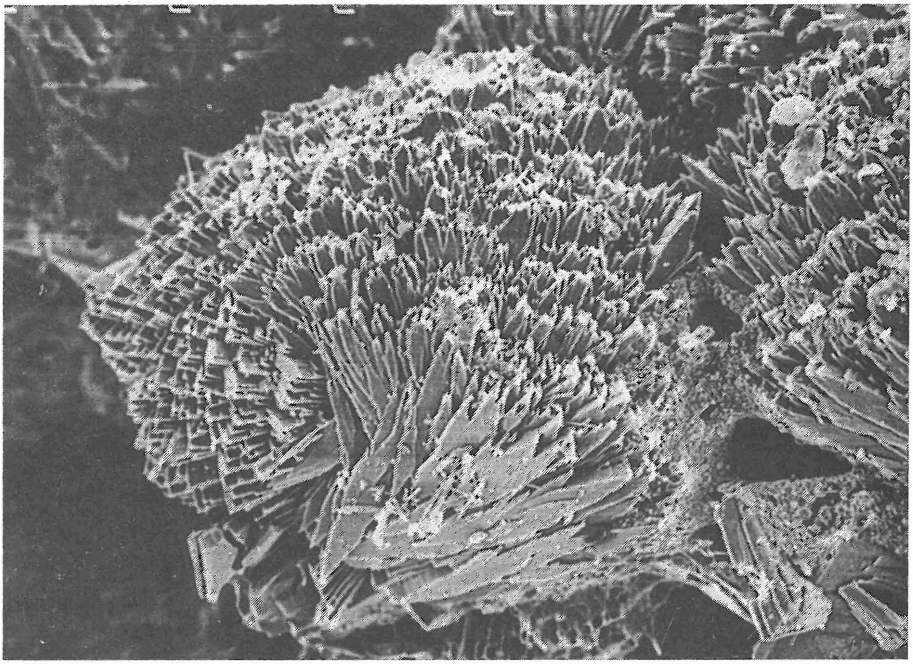

Figure 3: Chalcosiderite, enlarged 200×, Z. Mach SEM photo.

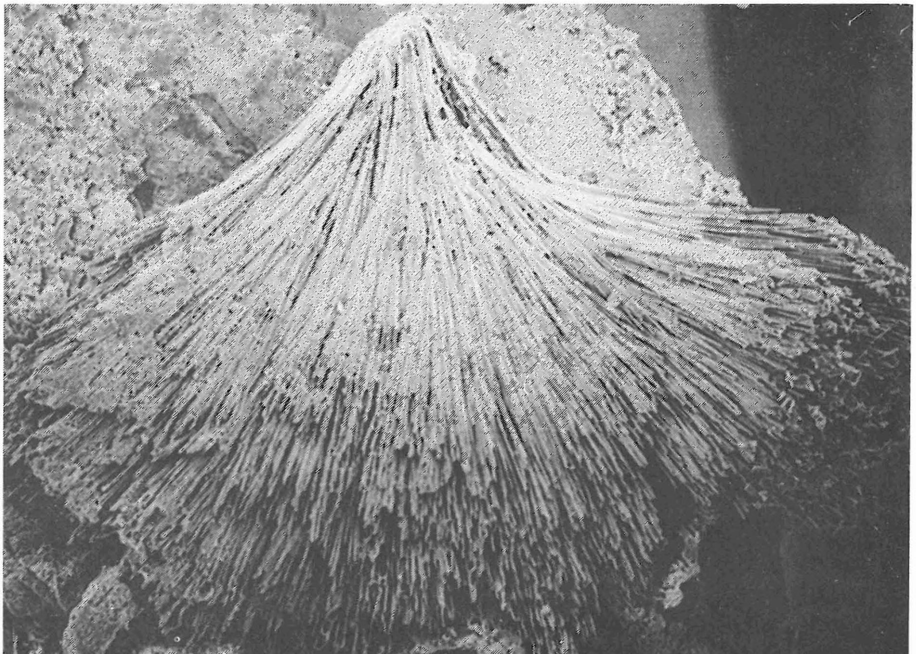

Figure 4: Pseudomalachite, enlarged 50×, Z. Mach SEM photo.

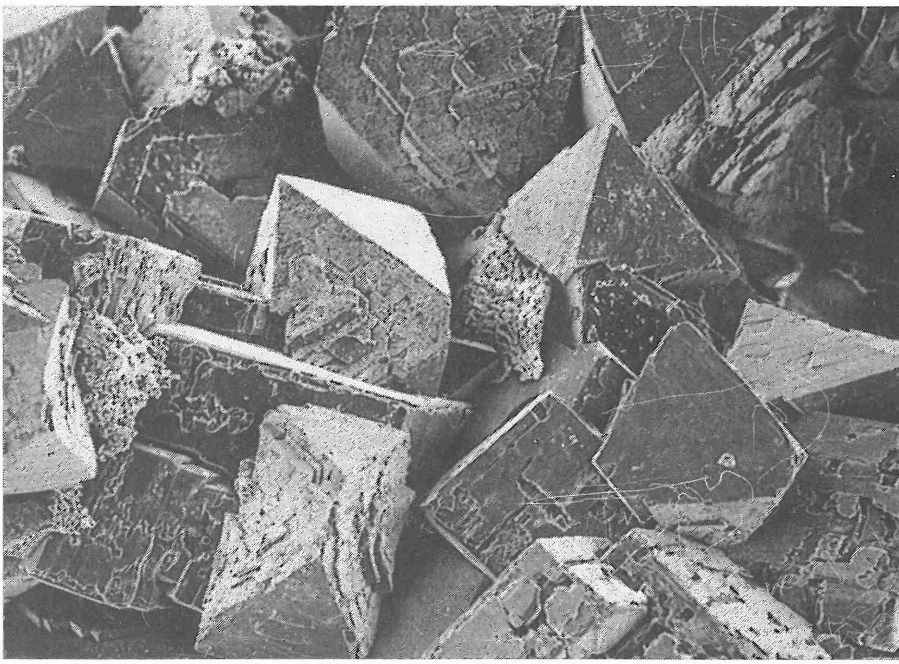

Figure 5: Libethenite, enlarged 75×, Z. Mach SEM photo.

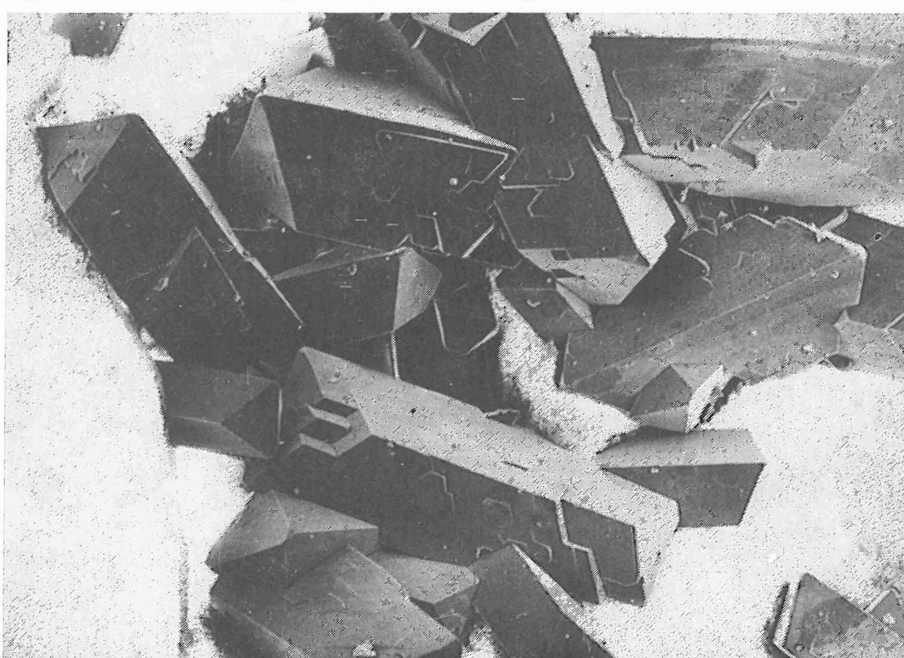

Figure 6: Libethenite, enlarged 200×, Z. Mach SEM photo.

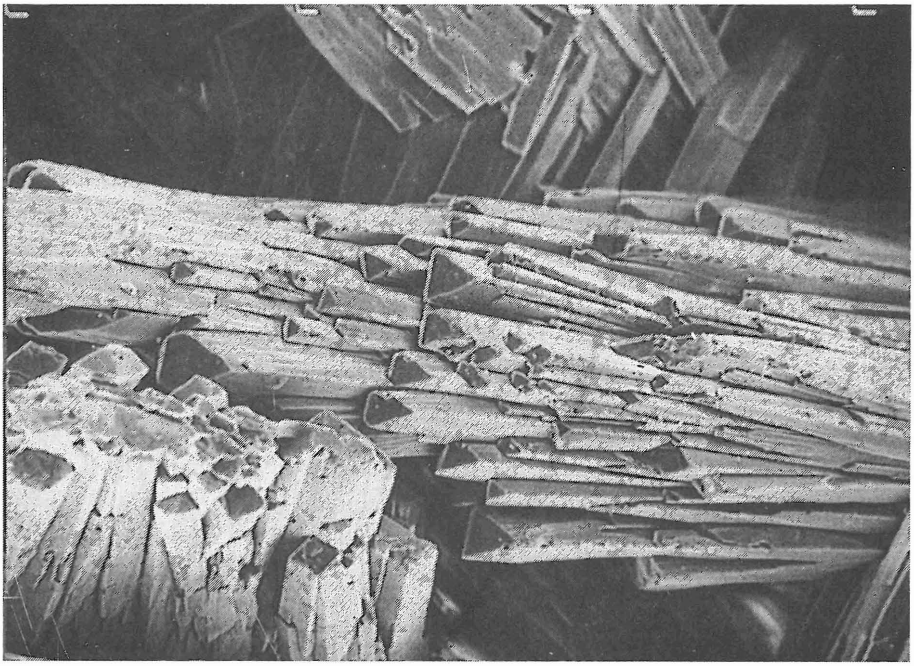

Figure 7: Olivenite, enlarged 350×, Z. Mach SEM photo.

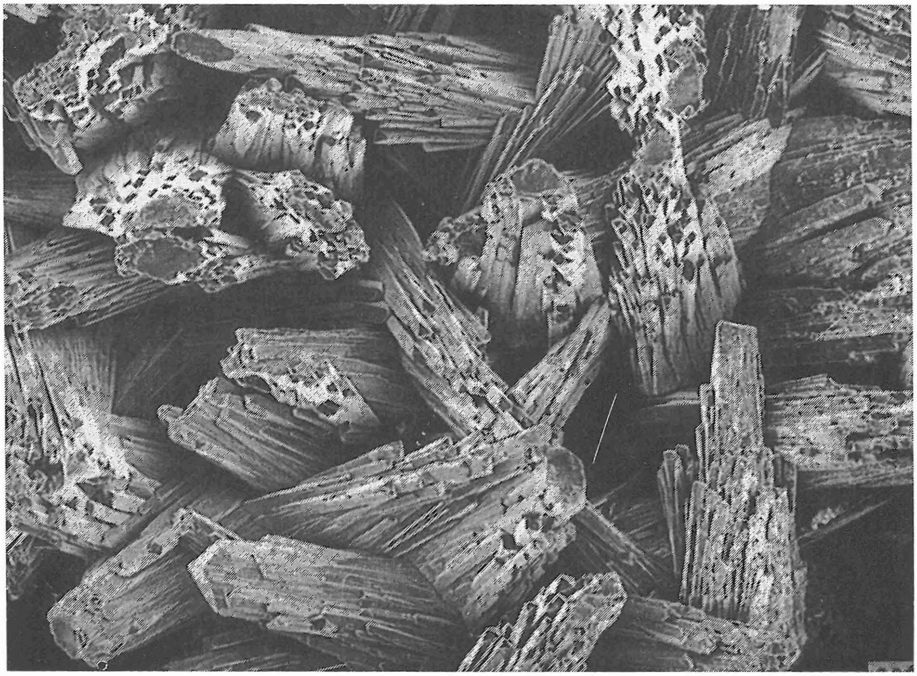

Figure 8: Olivenite, enlarged 100×, Z. Mach SEM photo.

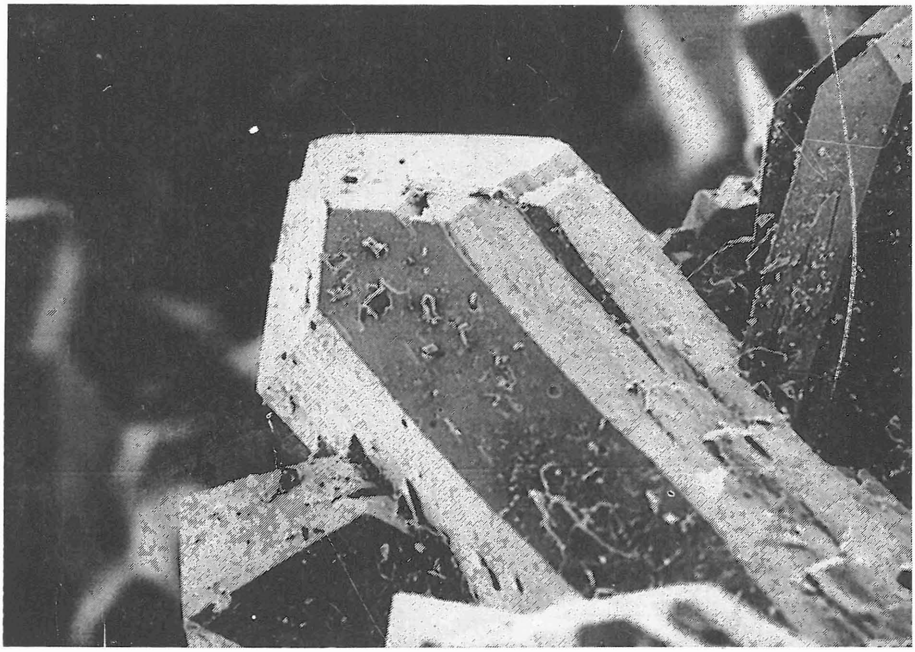

Figure 9: Scorodite, enlarged 100×, Z. Mach SEM photo.

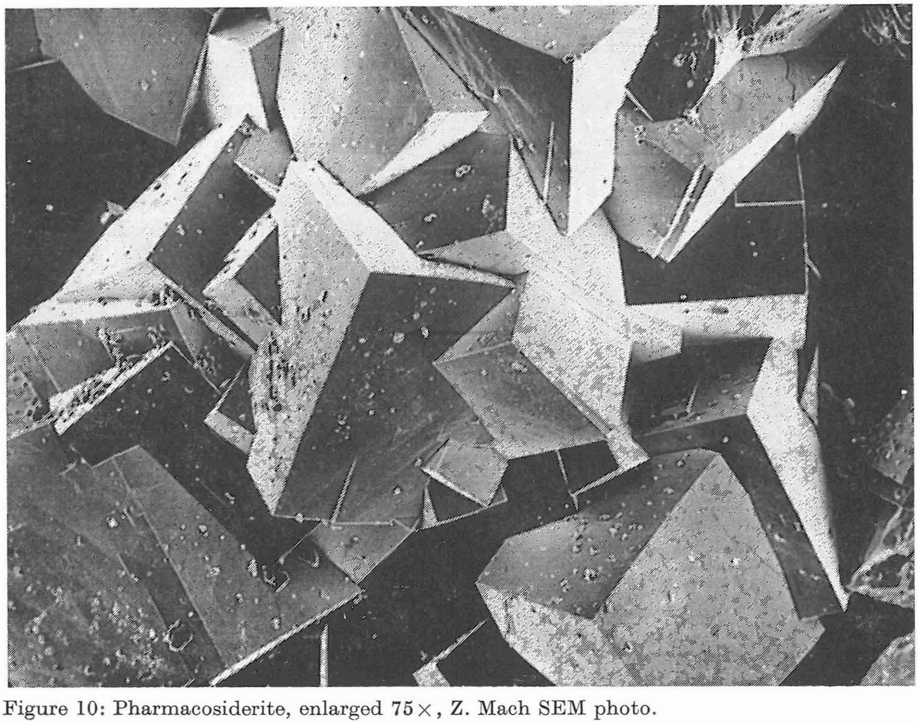

Figure 10: Pharmacosiderite, enlarged 75×, Z. Mach SEM photo.