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# Geochemicko-mineralogické poměry polymetalických žil v rudním revíru Vrančice u Milína

# Geochemically-mineralogical Relations of Polymetallical Veins in the Ore District Vrančice near Milín (Bohemia)\*)

# (Došlo — presented 16. XII. 1960)

V rozmezí let 1958—1959 byl proveden komplexní geochemicko-mineralogický výzkum rudních žil v rudním revíru Vrančice zaujímající prostor asi 12 km jižně Příbrami. Během tohoto výzkumu byly petrograficky sledovány průvodní horniny vrančických žil, podrobně studovány minerální asociace jednotlivých rudních žil a řešeny jejich paragenetické a sukcesívní vztahy. Velmi podrobně byl proveden i geochemický výzkum rudních žil. Nejvýznamnější dosažené výsledky tohoto komplexního výzkumu je možno shrnout do následujících bodů:

1. Mezi průvodními horninami rudních žil, příslušejících širšímu komplexu středočeského plutonu, převažují granodiority (biotitický a biotiticko-amfibolický). Vzácnější jsou žuly (alkalické a normální) a žilná eruptiva (zejména lamprofyry-kersantity, pravděpod. i minety; vzácně žulový porfyr).

2. Geologická pozice lamprofyrů je často sblížena s pozicí rudních žil, které vyplňují tektonické struktury v plutonickém masivu sz.—jv. směru.

3. Přehled dosud zjištěných nerostů vrančického rudního revíru (více než 40), vznikajících v různých genetických stadiích, je uveden v tabulce č. 7. Převážná většina těchto nerostů se vyskytuje na hlavní, nejlépe prozkoumané, vrančické žíle Pošepný. Výzkům a identifikace nerostných paragenezí na ostatních současně otevřených rudních žilách revíru (Hofmannově, Slavíkově a Babánkově) je v tomto směru základní studií. Během mineralogického výzkumu byly identifikovány, vedle celé řady již známých nerostů z vrančických žil, také nové nerosty pro vrančický rudní revír-boulangerit, dolomit, markasit, nikelin, Ni-skutterudit (chloantit), pyrargyrit, stromeyerit a pravděpodobný argentit. Z topograficko-mineralogického hlediska je zejména významná první exaktní identifikace stromeyeritu na území ČSSR.

4. Vrančické rudní žíly jsou tvořeny typickou asociací polymetalických rud, z nichž ekonomický význam mají zejména dvě hlavní složky — sfalerit, který

\*) English text p. 3

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převládá nad galenitem. Významnou složkou rudiny jsou též Cu-rudy: chalkopyrit, tetraedrit, chalkosin, bornit, bournonit a Ag-rudy: hlavně ryzí stříbro, méně pyrargyrit, akcesoricky stromeyerit a argentit(?). Na Pošepného žíle se vyskytuje ve větším množství též další Zn nerost — willemit. Z nerudních složek převládají karbonáty nad křemenem, goethitem a lokálně se vyskytujícím barytem. Běžně rozšířenou složkou na vrančických rudních výskytech je hematit, který může být za určitých podmínek "koncentrátorem" vzácných prvků zejména india, kadmia apod. Ostatní zjištěné nerosty mají význam jen mineralogický, avšak jejich existence osvětluje zejména celkové geochemické pochody probíhající během minerogeneze. Na vrančických rudních žilách byly rozlišeny čtyři mineralizační etapy (oddělené tektonicky) a v jejich rámci ještě několik stadií:

l. etapa: křemen-sfaleritová — stadium alterace; stadium vylučování nerostů — Ni + SiO<sub>2</sub>; stadium vylučování ZnS + FeCO<sub>3</sub>

2. etapa: sulfidická — stadium vylučování nerostů Cu, Sb + SiO<sub>2</sub>; stadium vylučování nerostů Pb, Cu, Sb a  $BaSO_4 + Ca$ ,  $Mg/CO_{3/2}$ 

3. etapa: karbonátová I — zakončující tvorbu rudních paragenezí. Během této etapy došlo k vyloučení nerostů, jejichž původ není zcela jasný, zejména willemitu a sulfidických nerostů Cu-Ag

4. etapa: karbonátová II — ekonomicky bezrudní parageneze, způsobující místní znehodnocení rudních výskytů. Případný obsah pyritu a markasitu je vzhledem k ostatním rudním nerostům bezvýznamný, neboť jde o složky, které nejsou z hlediska ekonomického sledovány.

Později došlo ještě k místním tektonickým pohybům s průvodními projevy mylonitizace.

5. Na základě studia jednotlivých paragenezí a dílčích sukcesí hypogenních nerostů na jednotlivých vrančických žilách bylo sestaveno celkové schéma sukcese — viz tabulku č. 8.

6. Vznik willemitu není možno za současného rozsahu otevření ložiska jednoznačně vysvětlit. Jednou z možností jeho geneze je krystalizace z roztoků koloidní povahy při sekundárně hydrotermálních pochodech. Tyto pochody jsou diskutovány ve smyslu teorie H. S c h n e i d e r h ö h n a (1941), při čemž je předpokládáno, že probíhaly po oživených starých tektonických směrech. Vedle toho však nelze vyloučit v nejsvrchnějších partiích ložiska jeho ryze descendentní vznik.

Vývoj oxydačního a cementačního pásma je závislý i na místních změnách různých podmínek majících vliv na intenzitu oxydace a hloubku jejího pronikání. Jak se zdá, uplatňoval se v našem území v tomto směru zejména faktor strukturně geologický (morfologicko-tektonický) a petrografická povaha okolních hornin, čímž si lze vysvětlit různý vývoj oxydační či cementační zóny na vrančických žilách.

7. Velmi podrobné studium chemismu všech hlavních rudních i nerudních složek přineslo nové poznatky, které mají význam pro poznání geochemického vývoje rudních žil (viz kapitola VI) a způsob migrace některých rudních prvků při supergenních pochodech (viz kapitola VII).

# Geochemically-mineralogical relations of polymetallical veins in the ore district Vrančice near Milín

#### Introduction

In the years 1958—1959 a penetrating geochemically-mineralogical research of polymetallic ore veins has been carried out in the ore district Vrančice. The study of paragenetic and geochemical relations of the veins of Vrančice, which are a part of the metallogenetic zone of Central Bohemian pluton, has stated that these have a certain exceptional position regarding the other analogical deposits in this state. This is the reason why it is favourable for the specialists in general to know the results which have been attained during the study of ore deposits of Vrančice as far as it was possible to find the condition their opening by mine-works till 31st May 1959. Because of rapidly going mine research works it is not possible in the present time to keep this study as a final and perfect one, as it is very possible that in the future other new minerals can be found in the veins of Vrančice, and by these findings the knowledge of the total mineralogical paragenesis of ore deposits would be completed.

#### General part

#### I. The development of researches of the ore district Vrančice and present literature

The district of Příbram may be considered today as a classic region of occurrence of ore veins. For its economical significance and high repute, especially in the middle ages and younger centuries, the attention of investigators was drawn first at the veins of Příbram itself. On the contrary, the district of Vrančice, though its genetical continuity with the ore district of Příbram is, in a certain way, indisputable, escaped the specialists' attention and its value was not considered as a too great. As it comes out of the historically-montanic study of J. Bíle k (1954), no more considerable mine-works were opened on the ore veins of Vrančice in ancient times; this action was concentrated just in the period 1564-1580. The short extent of works may be explained by the fact that the ore district was evacuated after the exploitation of the richest parts of the cementation-zone, when Ag and Cu, occasionally even Pb was extracted; the exploitation of the primary deposit have been limited by technical difficulties. The reason why the mine-work was not reconstructed explains the negative report of A. Plamínek (in J. Bílek 1954) referring this district, dated 1890; the writer did not recommed further works for their high expenses. By this report a wrong idea was imputed to the literature for a long time, i.e. that most of the veins of Vrancice belong to the category of iron ores with a small hope in greater occurrences of polymetallic . ores. All this might be the reason of weaker interest of the specialists in the district Vrančice and we can state that the geological literature is incomparably poorer than the analogical one, dealing with Pribram itself; the literature concerning deposits of old times does not exist in practice, with the exception of short notices, relating the mine works in Příbram. From the historical aspect the district of Vrančice was evaluated in the informative report of J. Bilek (1954) in which the author concentrated all the archival sources, especcially those coming from the middle ages. The own development of researches of this zone is characterised by two periods. In the first one, lasting almost one hundred years (1850-1948), the research was directly influenced by the stopping, resp. by no reconstruction of mine works on the veins of Vrančice. From this time we can find sporadic informations concerning the deposit situations in the district of Vrančice in the works of investigators who made their researches in the surroudings of Příbram-J. Jok ély (1855), J. Grimm (1856), F. Babánek (1878), F. Pošepný (1895), B. Stočes (1918a), J. Diviš (1926), J. Barvíř (1929a, b; 1930). From the works with geological specialisation deal with this district beside the original

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report of J. Jok ély (1855) newer studies of J. Vachtl (1932a, b; 1935) who mainly solves the problems of petrography. Practical notices of some minerals occurring in the veins are to be found in above mentioned middle ages sources and also in the report of deposit commission headed by A. Plamínek (from the year 1890, in J. Bílek 1954) in the mineralogically-topographical compendiums J. K I vaňa (1886) and J. K ratoch víl (1943). Beside the cited reports there may be applicated even the knowledges of some authors dealing with the total problems of the district of Příbram, among whom we can mention A. E. Reuss (1836 and 1863), F. Babánek (1871), F. Pošepný (1872), A. Hofmann-F. Slavík (1910), F. Slavík (1916), B. Stočes (1918b), R. Kettner (1925, 1926, 1937), J. Kratochvíl-A. Orlov (1930), A. Orlov (1932, 1935, 1938), K. Urban (1933, 1937), in recent time V. Steinocher (1950).

A new period comes with the year 1948 when the reconstructed mine work was developed on the main vein Pošepný. After a short period (1948-49) of research work made by Jáchymov Mines, the Ore Mines of Central Bohemia in 1950 and after that the Geological Research Praha overtake the research since 1952; this research has enlarged the mineworks even on further veins of this ore district. Simultaneously with these research mineworks even a new exact mineralogical research begins; before this time the authors have not negociated with any systematic study of mineral composition of ore veins.

One of the first works of the new period is a short review made by J. Koutek (1950), recommending the following of Pošepný vein. Then there comes a series of works with a mineralogical and deposital direction, referring primarily this main vein of the ore district Vrančice; the authors of these are V. Hanuš (1953, 1955), A. A. Malachov (1955a, b; 1956, 1958), A. A. Malachov J. Kouřim-ský (1956), J. Kouřimský-A. A. Malachov (1956), K. Paděra (1956a, b), J. Kouřimský (1957) respectively. Together with the mineralogical research a new geological map-making was begun in the ore district. This was undertaken by a group of workers of Central Geological Institute O. Kodym jun. F. Sorf-J. Zikmund. New maps with the topographical report are deposited in the archive of Geofond Praha. Besides, a special geophysical research (S. Chudáček and J. Krs from Ores Research Institute Kutná Hora and Praha) and a metallometrical research (J. Pokorný-Ores Research Institute Kutná Hora) was made since 1955, directed at the following of ore veins. A series of minor mineralogical analyses of the ore with the identification of minerals of the Pošepný vein, as vell as the reports of calculation and the annual reports dealing with a detailed and general geological research of the ore veins Vrančice are deposited in the archives of Geofond Praha, Geological Research Praha and Institute of Mineral Raw Materials Kutná Hora.

#### II. A brief topographically-geological situation of the district Vrančice

The ore district Vrančice is situated in a territory approximately 12 km southward of Příbram. In the years 1955-56, the topographical situation of ore zones was stated by research work in this space, on the basis of which the whole district was divided into two parts, an internal and an external one. All the veins known from historical sources and followed simultaneously by mine research works were classified as the internal part. Our attention is drawn more to the internal part, which includes four ore veins, i. e. Pošepný (late Bescher Glück ), Hofmann (late Laurenti Gang), Slavík (late Gabe Gottes and probably Verklärung Christi) and Babánek (late Christophi Gang), which are situated among the villages Kojetín-Vrančice-Ostrov. From the external department, just for orientation, the specimen mined of the vein in Karel mine were identified. This mine takes place between the villages Milín and Slivice. The Pošepný vein is the main vein of the district. It was mined in the year 1948 in Alexandr Mine, which goes till 400 m of depth actually. The ore vein is directionally followed in 7 horizons. In the year 1957 the mining of the general crossheading directing to the W was begun in NW part of the 7. horizon. It was aimed to mine below the vein zones of Vrančice. In the time of terrain-works in spring 1959 the general cross-heading reached up to the Hofmann vein zone. The Hofmann vein was exploited in the year 1955 in Jan-mine; during this action three veins of small metallie value were mined. The mine was digged up to the second horizon and all mine works were stopped in July 1957 with regard to small results of research. In the time of our terrain-works the vein was mined southwards and northwards of the general crossheading about 400 m under the surface. The Slavík vein is situated on the eastern side of the village Vrančice. It was opened in the shaft Slavík, which gave a smaller apophysis rich on polymetallic ores. In the year 1958 the mine was digged up to the second horizon, from which the ore was followed up in direction. In present times the work goes on by further digging because the development of the vein needs to be verified. The Babánek vein was mined in the year 1955 in the shaft Václav, that is situated about 500 m NW of the village Vrančice. The shaft was directly digged to the niveau of the second horizon (about 100 m of depth) and affected the vein zone. In the time of terrain works in the year 1959 the ore vein was followed up in direction. on the fourth horizon mainly. The shaft itself was excavated to the niveau of the sixth horizon. The vein situated in the section Milín-Slivice was opened with the shaft Karel excavated to the niveau of the second horizon till 100 m of depth. It is situated near the road Milín-Příbram, NW from Milín. With regard to the fact that it reached only the zone of oxydation of the ore vein, the mine works were stopped at the end of the year 1957. In 1958 deep drilled holes were made here for verification, of the primary deposit. By these holes only the zone of oxydation was attained and the mine works in the shaft Karel were not reconstructed.



Map 1 The topographically-geologic situation of the district Vrančice and position of ore veins.

fields in use in historical times. Gold had to be washed out of the alluvium coming from the deposits situated near the hill Vraneč. In present time no such reports can be substantiated because the geochemical research gave negative results in this point (no gold could be identified in ore veins of Vrančice by qualitative spectral analysis).

# Petrographical part

### III. The petrographic character of rocks accompanying the ore veins of Vrančice

During the geochemically-mineralogical study of ore veins of Vrančice a great attention has been given to the rocks accompanying them. Specialized problems of genesis and the problem of special relations of different derivates, sometimes even complicated problems of inside tectonics of pluton formation are not included in this report. The mentioned problems have been studied by petrographs and geologists in the area of Central Bohemian pluton from the beginning of this century till these days, especially R. Kettner, A. Orlov, V. Rosický, F. Slavík, J. Vachtl, J. Kratochvíl, K. Urban, J. Svoboda, in present times V. Steinocher, O. Kodym jun., F. Šorf, J. Zikmund and others.

Identified rocks were ranged into four groups on the basis of macroscopic features and of microscopic study of thin sections as well. In these groups several rocktypes showing still facial differences were differentiated. The main groups represent: granites-granodiorites-diorites-vein eruptivities. Granodiorites anticipate in general dioritic types in rocks accompanying ore veins. Granites are rarer, similarly vein eruptivities do not reach to exceptional enlargement and mighty.

#### Granite

In the granite-group two different types can be distinguished-alkaline and normal granites. Alkaline granites are represented by middle or coarse grained rocks of meat-red colour. The structure of the rock is grained in all directions. The fracture is very irregular. K-feldspar is dominating as a constituent (orthoclase in great granophyric intergrowths with quartz) and quartz with a little plagioclases (acid oligoclase-extinction in symetrical  $zone = 10^\circ$ ; Ch<sub>m</sub> +; finer grains than quartz) and scaled biotite. As the accessory apatite could be currently stated (in quartz inclusions), muscovite and rare magnetite. A quite similar rock type is described in literature by J. Vachtl (1932, 1935) in a district in the area between Milín and Vrančice. These rocks are classified by Vachtl as aplitic granites. Normal granites differ in their macroscopic features from alkaline granites. One finds smaller grains and a higher content of plagioclase and mica. This type shows still facial differences so that one can distinguish binary granite and biotitic granite. The binary granite is macroscopically apparent by its fine-granulation. The colour of the rock is predominantly gray, sometimes even fairpink. The binary granite is microscopically analogue with the alkaline type. In composition however one can notice some quantitative changes. The rock is formed mainly by feldspars with quartz, in a smaller extent by mica. Feldspars are dominated by perthitic orthoclase (rarely even microcline) more than by lamellar plagioclases (oligoclase). The content of K-feldspars is smaller and in the contrary main components are formed by plagioclases. In considerable amount even dark brown biotite and small sheets of muscovite are present. In accessorial amounts zircon, titanite, pyrite, rarely tourmaline and orthite are present. The rock's texture hypidiomorphous grained. Fine-grained binary

granites are in the country Milín described in literature by J. V a c h t l (1932, 1935) who ranges them together with alkaline granites into a larger group of aplitic granites. Biotitic granites are clearly different from binary granites being variably grained; this granulation varies from finely grained to middle grained. The colour varies from light-gray to yellow-pink. Quartz often intergrowing perthitic orthoclase and zonar acid plagioclases (albite) belong to substantial components. Biotite is present in negligible amounts. The accessories are analogical with above described types.

# Granodiorite

In the granodiorite group two facies can be distinguished: biotitic granodiorite and biotite-amphibolic granodiorite (with strongly varying femic constituents). Biotitic granodiorite is a hard, regularly grained rock with middle-sized granulation. The colour is light-gray, influenced by a quantity of dark-brown biotite. In Alexandr mine even strongly biotitic derivates of dark-gray colour have been found; they form an interstage to more basic facies. Microscopically the rock is formed by plagioclases (composition oligoclase-andesine) with hypidiomorphous limitations. The spaces between the grains of feldspar are filled with allotriomorphous quartz. Another component is formed by very brown pleochroic biotite. K-feldspar is in general quite negligible and in more basic derivates, containing zonar more basic plagioclases (andesine-labradorite), beside a considerable amount of biotite, it is present just in exceptional cases. In accessorial amounts we can notice currently apatite and even zircon, rutile (often in form of sagenite in biotite), ore grains and pigment often included by biotite. Biotitic granodiorite is found, in accordance with all the authors making petrographic researches in the country Milín, as the most current rock type. Its great variability in composition as well as in texture is clear even from Biotite-amphibolic granodiorite has two significant macroscopic literary data. features - variable granulation and variable replacement of light and dark components. Finer grained melanocratic derivates form already direct transitions to dioritic types. Another stated derivate is formed by granodiorites of grav colour with porphyritic structure, fine and middle grained. Zonar lamelled plagioclases (andesine--labradorite) with a little more basic cores than the border zones belong primarily to substantial components of biotite-amphibolic granodiorite. Then one finds very brown pleochroic biotite and green pleochroic common amphibole, the mutual replacement of which is greatly varying. The amphibole often prevails the biotite. The space intervals between feldspars are filled with allotriomorphous quartz. The porphyritic variety of this facies of granodiorite has a composition quite similar to above cited rock; it differs only by its finely porphyritic texture. In porphyritic granodiorites, amphibole always prevails biotite. Biotite-amphibolic granodiorites contain very rarely potassium feldspar-orthoclase, with an exception of course, i. e. when a contamination of granodioritic material by a granitic one is in question. Contamined rocks were identified eg. in Alexandr mine. Apatite, zircon and magnetite, less titanite are current accessories.

# Diorite

Diorites are in their composition and macroscopic appearance analogue to fine grained variants of biotite-amphibolic granodiorite. They have relatively fine grains, a structure with all directions and a dark-gray to black colour. Main components of the rock are formed by zonar band plagioclases (stretching even to labradorite) and often mutually intergrowing common amphibole with biotite. The amphibole always prevails the biotite. The amount of quartz which always fills remaining spaces between feldspars is in comparison with granodiorites considerably smaller. The presence of K-feldspar is very small. Apatite, magnetite, pyrite, rare zircon and epidote are present in accessorial amounts. The arrangement of components is suggestive of the textures gabbroid-rocks. The studied rock can be specified with respect to cited composition as quartzous biotite-amphibolic diorite. The occurrences of diorite-rocks are known from literary data of different investigators not only from this district but from the whole area of Central Bohemian pluton. They are in general described together with more basic derivates under a universal tittle gabbrodiorites, as they were originally called by J. K r a t o c h v í l - A. O r l o v (1930).

#### Vein eruptivities

First of all, lamprophyres which have certain relations to ore veins have been studied among vein eruptivities. In the Karel-mine one succeeded to find even a specimen of granite-porphyre that was strongly altered.

The granite-porphyre is a gray rock carrying pinkish parties. The rock has macroscopically aphanitic appearance and a little growth of pink feldspar can be distinguished. Under microscope a clearly porphyritic texture with a microgranitic or graphic texture of matrix is to be seen. The growth is created by "karlsbad" doubled orthoclases, in a smaller extent by plates of biotite. The matrix is formed by K-feldspars and plagioclases, often graphically penetrating the quartz. The development of myrmekites could be noticed. Apatite is present in accessorial amounts. Graniteporphyres are frequently represented in the whole Central Bohemian pluton. From this area, porphyric rocks are cited also by J. V a c h t 1 (1935) and in the mapreport as well (Central Geological Institute-1956).

The lamprophyres are rocks of graybrown to grayblack colour. The high content of biotite is striking. It was not possible to determine uniformly by microscope the existence of minettes or kersantites because the feldspars necessary for determination were highly decomposed. The samples taken correspond better with kersantite. They have a very typical porphyritic texture in which the growth forms hypo- or idiomorphous biotite showing zonar pleochroism. The centre of plates shows usually a weaker pleochroism in brown colours than the border areas. Finer grained matrix is composed of minute plates of biotite, by small columns of strongly chloritised pyroxene (conserved only in relics, probably diopsite), feldspars in which more acid plagioclases can be distinguished (highly sericitised) and rarely even some potassium feldspar. Very often apatite, less magnetite can be determined as accessories. It is nevertheless not excluded that there are rock-types having a considerable content of potassium feldspar which could be assigned as minettes. Both typeskersantites and minettes—are cited in this district in the map-report (Central Geological Institute-1956). In older literature, kersantites are cited in Milín-region by J. Vachtl (1935) and pyroxenic kersantites by V. Rosický (1921) from Kojetín near Milín. Even some studied samples of lamprophyre rocks could be assigned as pyroxenic kersantites.

The hydrothermal alteration of rocks is shown by decomposition of original rock-forming minerals and by formation of new minerals. For a correct and true evaluation of relations between the processes of alteration and ore-forming it is

necessary to mind, that the hydrothermal decomposition of rocks is influenced by a series of factors. One of the most important factors are tectonic structures in rock complexes (dimensions and shape of ruptures and fractures) and time during which hypogene solutions had leaked them. During the alteration of rocks, chemical processes ran between the rock components and ore-bearing solutions. From this fact, other factors come out, influencing the intensity and the extent of alteration. It is the chemism of accompanying rocks and of hypogene solutions. The chemism of ore-bearing solutions is further changed during the mineralisation processes so that younger minerals developed by alteration may be changed again, dissociated and replaced by other minerals. This case occurs most frequently in the places with favourable conditions for a long treatment of adjacent rocks by hypogene solutions. Even a reverse case can occur when a protecting crust of quartz defending further decomposition of rocks, develops on the borders of ore veins, so that the time looses its value. Also other factors must be, of course, taken in consideration, i.e. mechanical properties of rocks, pH of ore solutions etc. A series of combinations may occur in the processes of alteration itself when more or less singular factors may apply; but, it directly depends on the might, the degree of alteration and the mighty of ore-forming only in a small percent.

Similar conclusions may be made even by observing these dependences on ore veins of Vrančice, especially on the most exploited vein Pošepný in Alexandr mine. Here can be found either veins of certain might accompanied by a relatively few decomposited area or places with small might of ore-forming having very intensive and mighty alteration of border rocks. Till now, following processes developing during the alteration of rocks accompanying ore veins could be stated: the sericitisation of feldspars, the chloritisation and the baueritisation of biotite, the chloritisation of amphibole and pyroxene, the uralitisation of pyroxene, very rarely even epidotisation which can occur either at amphiboles and pyroxenes or at feldspars. In general, ores are affected besides the pyritisation by silicification and carbonatisation. Hydrothermal alterations reveal on different rocks in different ways. Potassium feldspars, affected most by alteration of the granite group, are more intensively sericited than plagioclases. Biotite is generally quite chloritised, sometimes even bauretised. The colour of altered granites is gray-green. The rocks are affected also by pressure. During the alteration of granodiorites and diorites, plagioclases which are sericitised, are mainly affected. The sericitisation proceeds along the cleavage cracks and along the directions of zonar growth of feldspars as well. The biotite is chloritised; on its cleavage planes fine exsolved scales of haematite and plates of leucoxenised ilmenite could be observed. Also sagenite, developed probably secondary during the processes of alteration of biotitic granodiorites was identified in strongly chloritised biotites. Amphibole is usually more intensively chloritised when biotite is baueritised. Epidote, originating probably by alteration of amphibole or more basic plagioclases, was also stated in diorites. In granite-porphyres, intensive changes of K-feldspar could be noticed; a microcrystalline mixture of clavey and micaceous minerals is resulting. The biotite is fully replaced by chlorites. The chloritisation, causing a change of colour of the ore from dark to green, is the most current change in alteration of lamprophyres. The chlorite has its origin in the alteration of biotite and diopsite. The pyroxene is also affected by uralitisation.

# Mineralogical part

#### IV. Minerals of the ore district Vrančice and their chemism

An exact mineralogic investigation of minerals of the district of Vrančice, as it was once discussed in the chapter concerning the development of investigations, begun practically with the beginning of new investigative works in the year 1948. Only the Pošepný vein has been more detailedly studied in mineralogical way during last ten years: other occurrences were followed just for orientation, mainly in dump Special data of results of mineralogic researches and of identifications material. of individual minerals of the ore district Vrančice made by single writers who worked there (V. Hanuš, A. A. Malachov, J. Kouřimský, K. Paděra etc.) are introduced together with the described minerals. A summary of found and exactly identified minerals of the ore district Vrančice is given by J. Kouřimský (1956) in collaboration with A. A. Malachov. The mineralogically-geochemical research of mineral associations made in the same time enlarged the exact studies of ore district Vrančice as a whole and illustrated new topographically-mineralogic and geochemical knowledges; from these new aspects of paragenetic and successive relations of the ore veins of Vrančice were drawn.

In this chapter all the identified minerals together with their description and occurrence. are introduced The microchemism of studied minerals was discussed on the basis of results of qualitative spectral analyses and of microscopic and mineralographic study as well. The isomineral or anisomineral form of occurrence was watched in individual determined elements on the basis of statistically evaluated spectral analyses made in analogous analytical conditions. The term "isomineral or anisomineral element" is used in accordance with the suggestion of J. H. B e r-n a r d (1957); the term "isomineral" is superior to the term diadoche and isomorphous replacement in mineral lattice for elements adsorbed or present in interatomic spaces of crystal lattices. An isomineral element belongs to heterogeneous admixtures of minerals.

Minerals are described in two groups: A-non-sulphidic minerals B-sulphidic minerals-in certain correlating units (eg. carbonates, Pb-Zn sulphides etc.).

#### 1. MINERAL ASSOCIATION

# A-Non-sulphidic minerals

#### Carbonates

Calcite—CaCO<sub>3</sub>—belongs to most current nonmetallic minerals of vein fillings. Macroscopically it forms middle- or finely grained, sometimes also coarse grained aggregates of different colour-milkwhite and pink, beside gray shades, sometimes red-brown. Some types of calcite contain up to 5 % MnO; these may be assigned Mn-calcites. Calcite (together with the Mn-type) belongs to youngest hypogene minerals. It is represented in two generations: I. generation is preponderately a middle-grained calcite; II. generation of calcite is formed mainly by coarse grained aggregate, filling the mighty veins. The calcite II forms sometimes even typical coloidal textures with macroscopically uniform appearance (e.g. Alexandr Mine), sometimes it is crystalised into holes in form of low rhombohedrons and scalenohedres. Calcite (Mn-calcite) I is present especially in Pošepný and Babánek vein. In zones of Hofmann ore area a mighty vein of calcite II, which was identified even in Alexandr mine, was opened.

As it was shown by qualitative analysis, the chemism of calcite is without considerable changes. The admixture of Mn is characteristic (it varies from 0.94 to 3.52 %); Mn is present in relatively higher quantities than Fe (it varies from 0.15 to 1.13 %) and Mg (it varies from traces to 0.45 %). Different colours of calcite originate in admixtures of oxidic or hydroxidic compounds of Fe and Mn.

The microchemism of calcite was observed by qualitative spectral analyses; the results are summarized in table 9, 10, 11, 12. Among other determined elements Pb, Zn, Cu, probably even Cd and Sr may be found as isomineral; from rare elements also Y. Chalcophile isomineral elements however are partially bound with heterogene



admixtures of a sulphides. Remaining elements may be considered as being anisomineral.

**Dolomite** —  $CaMg(CO_3)_2$ —was detected as a less current nonmetallic component only in Slavík vein. Dolomite creates middle to coarse grained aggregates (apparent by cleavable rhombohedrons) of milkwhite and pink colour. It was stated as one of older minerals of the second miner. stage, associated with siderite, bournonite and chalcopyrite.

The chemism of dolomite was followed by qualitative spectral analysis (table 11). Isomineral elements in dolomite are analogical with those in calcite. Its identification was moreover

- Fig. 1. Differential thermal curves of dolomites from the district Vrančice.<sup>1</sup>)
  - No. 1. Middle-grained, milk-white dolomite from the Slavík vein (Slavík mine).
  - No. 2. Middle-grained, clear-rose dolomite from the Slavík vein (Slavík mine).

<sup>1</sup>) All thermic records were made using a photoregistrating apparatus, from the input 0,2-0,3 gr of finely pulverised samples. The temperature of the oven and the differential temperature were verified by a Pt-Pt/Rh thermocouple. The weldment of the differential thermocouple which was mounted in a vessel for the sample was protected against the corrosion by a layer of powdered alumina. Alumina was also used as inert matter. The temperature of the oven was raised in a rate of  $10^{\circ}$  C/min. Original thermic records were drawed for comparison so that similar types of carbonates have the same scale. All the differential thermal analyses were made by the laboratory of Institute of Mineral Raw Materials Kutná Hora by Mr. M. Anděl and Miss J. Havránková.

verified by DTA (fig. 1). The shape differential thermal curves is not quite normal. It is true for the first endothermal nimimum, which is relatively markedly weaker than in characteristic curves of dolomite. But even so, two endothermal minimums ranging about 780—880°C, indicating dolomite, appeared. To exclude the doubtfulness that a heterogene mixture of two carbonates might occur, an X-ray identification of both samples was made; it showed clearly homogene material represented by dolomite.

Siderite—FeCO<sub>3</sub>—is represented in much smaller extent than calcite in ore-veins. J. K o u ř i m s k ý (1956) cites it without any more accurate identification in Pošepný and Babánek veins. The researches of my own verified its occurrence in both veins and in addition its presence was stated in Slavík vein. Siderite forms middle grained aggregates of very good cleavage. It has in most cases a light honeybrown colour which in weathered zones grows brown, sometimes even with a red tint.

Siderite is usually associated with quartz I and II, sphalerite, tetrahedrite, bourno-

nite and chalcopyrite, in a smaller extent with dolomite but very often with calcite I. The macrochemism of siderite was determined by the quantitative chemical analysis. It shows only a higher admixture of Mn (7,59 %), while the Mg (1,69 %) and Ca content is relatively very low. The Ca content (1,63 %) of the siderite of Vrančice does not overreach normal limits. Beside the main elements, even the microchemism of siderite from individual ore veins (table 9, 11, 12) was followed by qualitative spectral analysis. Isomineral elements with the exception of Ni are analogical with other carbonates.

The differential thermal analysis (fig. 2) absolutely univocally verified the identification of siderite since the differential thermal curves are marked by very characteristic endothermal

- Fig. 2 Differential thermal curves of siderite from the district Vrančice. No. 1. Honey-brown crystals of siderite from the Pošepný vein (Alexandr mine).
  - No. 2. Brown-colour, middle-grained siderite from the Babánek vein (Václav mine).
  - No. 3. Honey-brown, grained siderite from the Slavík vein (Slavík mine).



effects in the range of 550—580° C and by exothermal effects in the range of 600—620° C. Noteworthy are smaller maximums corresponding the temperature approximately 850° C, probably caused by reactins of forming complicated oxides of manganese, which is present in siderite in rather greater amounts.

Cerussite —  $PbCO_3$  — was locally detected by Geological investigation workers in the zone of oxidation of Slavík vein.

Malachite —  $Cu_2[(OH)_2/CO_3]$  — currently occurs in Pošepný vein in areas, affected by supergene processes. In the review of minerals of Vrančice, it is cited in this vein by J. Kouřim ský (1956) and V. Hanuš (1955); the former reported also further detected occurrences in old dump material of the Slavík vein, rarely in Hofmann vein and in an investigation groove near Životice. In Pošepný vein it is

#### TABLE 1

Roentgenometric identification of malachite from the Pošepný vein—Vrančice. Debye-Scherrer method, radiation FeK $\alpha_{1,2}$ , Mn-filter, 24kV, 22 mA, exposition 7 h, cell-diameter 57,3 mm, glass-hair, reference substance A1( $a_0 = 4,0483$  Å).

		Malachite Vrančice		Malac ASTM	hite I (1950)
No.	I	2 0	d	I	d
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18	5 6 8 1 10 2 dif. 4 1 dif. A1 2 dif. 2 dif. 2 dif. 1 0,5 dif. 1 dif. 1 dif. 3 dif. 1 dif.	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$5,90 \text{ \AA}$ $4,99$ $3,67$ $2,99$ $2,84$ $2,76$ $2,51$ $2,44$ $2,33$ $$ $2,18$ $2,18$ $2,13$ $2,06$ $1,952$ $1,900$ $1,798$ $1,681$ $1,610$	$\begin{array}{c c} & 40 \\ & 80 \\ & 100 \\ & \\ & 100 \\ & 80 \\ & 80 \\ & 80 \\ & 40 \\ & 40 \\ & 40 \\ & 40 \\ & 40 \\ & 40 \\ & 20 \\ & 60 \\ & 40 \\ & 60 \\ & 20 \\ & 40 \\ & 20 \\ & 80 \\ & 40 \\ & 40 \\ & 10 $	$5,90 \text{ Å}$ $5,00$ $3,67$ $$ $2,84$ $2,76$ $2,51$ $2,46$ $2,41$ $2,32$ $2,29^{1})$ $2,23$ $2,17$ $2,12$ $2,06$ $1,96$ $1,90$ $1,78$ $1,68$ $1,64$
$     19 \\     20 \\     21 \\     22 \\     23 \\     24 \\     25   $	1 dif. 1 dif. 1 dif. 3 A1 1 dif. 1 dif.	75,4 76,2 80,2 82,2 85,2 85,2 88,4 90,7	1,584 1,570 1,505 1,474 1,432 1,389 1,362		1,61 1,59 1,56 1,50 1,47 1,421) 1,38 1,35

<sup>1</sup>) Coincidence of Al-line

concentrated mainly in the I., II. and III. horizon generally together with chalcocite on which it forms fine film. It occurs only seldom in greater concentrations. Malachite was stated by older writers only visually; accurate determinations were not made. A sample was taken for more precise identification and for detecting its chemism; it was undergone to qualitative spectral analysis (table 9) and to X-ray analysis (table 1). Stated d-values of the malachite of Vrančice are in fairly good accordance compared with the values in A S T M tables (1950—53). Nevertheless low intensity and diffuse lines are apparent in many cases; this may probably be due to its very fine crystalinity. Even defects of crystal lattice are not impossible.

It is necessary to range to malachite even a blue-green carbonate found in the year 1955 by A. A. Malachov in a groove near Životice. It was an object of detailed study of J. K ou ř i m s k ý (1957). With the respect to its quite analogical optical properties with *rosasite*—(Cu, Zn)  $_2$ [(OH) $_2$ /CO<sub>3</sub>]—the author calls the mineral as "a mineral close to rosasite" since it contained practically no Zn, this phenomenon makes it approach more to malachite. In the contrary, it has a little more Pb as Cu, Pb-carbonates, but these show quite different optical properties than the above cited carbonate of Vrančice.

Azurite —  $Cu_3[OH/CO_3]_2$ —developed as a typically supergene mineral in surface zones of ore veins of Vrančice, is named without any identificative values in the mineral review by J. K o u ř i m s k ý (1956). It occured in small amounts associated with malachite, cuprite and remaining chalcocite in upper horizons of the Alexandr mine (Pošepný vein) and in old dumps of ore material of Pošepný and Slavík vein. It was not studied more detailed because of the lack of sufficient material.

Quartz is the second mineral component of all the veins of Vrančice. It does not occur in such amounts as the carbonates but its extensive distribution is very large. Five generations of quartz were distinguished; they belong to different stages of mineralisation. Mince, column-shaped fine crystals of quartz I are found very often in close association with specularite in cracks. Quartz II, III and V in most cases form middle to coarse grained aggregates, locally it occurs even crystaline in cavities in druses (riffled crystals, mostly diffuse). Quartz IV is formed as a low-temperature  $\alpha$ -modification with characteristic zonar growth. This quartz has many microscopic inclusions—needles of goethite, gas inclusions. It is possible to see also different shades of colour—from clear crystal to amethyst to smoky quartz. In association with this quartz, a fibrous variety of chalcedony-quartzine, was optically determined by A. A. Malachov-J. Kouřimský (1956).

Baryte—BaSO<sub>4</sub>—is one of subsidiary hypogene components of the ore veins of Vrančice. It is named by J. K o u ř i m s k ý (1956) in Slavík vein (dump-pits), further in A. A. Malalchov's finding in Pošepný vein, where it was present in minor amounts only (this baryte was determined optically and following refraction indexes were prescribed:  $N\gamma = 1,646$ ,  $N\beta = 1,637$ ,  $N\alpha = 1,636$ ). But neither supergene origin of baryte in oxidation zones of ore vein can be excluded. Baryte was newly identified by the author in Babánek vein, where it is present in much smaller extent than in Slavík vein, but it is more abundant than in Pošepný vein. Baryte forms either massive, middle or coarse grained stalky aggregates of white, red to brown colour (esp. in Slavík vein) or accumulations of white or clear tabular crystals. Baryte occurs often associated with older minerals, i.e. with quartz, sphalerite, siderite, tetrahedrite, but mainly with younger minerals, i.e. with galena, chalcopyrite and calcite. To follow successive relations of baryte, decrepitation methods have been used to determine relative temperatures of formation of barytes, separated from the material of individual ore veins. From the enclosed figure (Pl. I., fig.1) of decrepitation records is evident that the decrepitation of barytes from individual veins ran in most cases with clean-cut effects and with starts in the range 220— 270°C. A common interval of crystallisation may be therefore considered. Barytes stated in individual veins were subjected also to qualitative spectral analyses and the identification was verified by X-ray measurements.

Anglesite—PbSO<sub>4</sub>—was detected by workers of Geologic Investigation in sporadic cases in the zone of oxidation of the Slavík vein.

**Haematite**—Fe<sub>2</sub>O<sub>3</sub>—is one of the most common components in ore deposits of Vrančice. It occurs in two forms—fine grained to earthy and in crystals with habitus of fine needles. Fine grained or earthy haematite forms films, kindney-shaped coatings and irregular accumulations of rust-brown, red-brown to reddish colour, namely in the cracks of ore vein. It often makes fillings of druse-cavities in quartz and in carbonates. Needle-shaped or scaled haematite-specularite, occurs generally associated with quartz and calcite. Macroscopically, the crystals of specularite are black coloured. It forms either crystaline accumulations or druse formations in cavities. In polished sections it is apparent by its expressive relief of a relatively bad polishability and a low reflection.

The genesis of specularite has been correctly discussed by V. H a n u š (1955); also from my own observations it is to be seen, that haematite originated in the supergene and in hypogene stage of mineralisation process as well. Nevertheless, distinguishing of individual generations of haematite is in a certain way subjective.

A noteworthy chemism was determined by spectral analyses of separated haematites from different veins of Vrančice (tables 9, 10, 12). Associated with haematite is to be found a series of elements forming an element association which is with respect to its general geochemical nature characteristic for polymetallic deposits. Regarding the up-to-date knowledges of geochemical character and behaviour of elements in certain conditions, following elements may be classified as being isomineral: Mn, Ti, In and Ge. There are contemporarily almost no discussions of replacement of iron by manganese, as this replacement is known in various intensities in various compounds. A certain part of Mn may be bound with the heterogene admixture of carbonates. Replacement of iron by titanium in form of limited mixibility with FeTiO<sub>3</sub> is introduced in literature similarly.

The bond of In and Ge in haematite is a much more complicated question. These elements occur in the same order of concentrations in haematite as in pure sphalerites, but the Zn-content appears to be smaller than if the bulk of In and Ge would be considered as bound with the sphalerite. A higher admixture of sphalerite is absolutely impossible and the detected contents of In and probably even those of Ge may be taken into account as isomineral.

The problem of geochemistry of In is especially in the last 20 years a subject of a series of works, but notes and discussions of the migration of indium in the supergene zone have begun to appear in literature only recently. Relatively great contents of In have been determined just in supergene haematite, as it is published in an informative work by A. S. V i š n e v s k i j (1958). The problemacy of geochemistry of In is solved by many works, e.g. by D. M. S h a w (1952, 1957) who considers on the basis of experimental results, that the distribution of indium in igneous rocks and minerals is in part ruled by iron. He speculates about  $In^{34}$ —Fe<sup>24</sup> replacement

with regard to their near ion radii and admits even the  $In^{3+}$ —Fe<sup>3+</sup> replacement in haematite and chlorite. The replacement of bivalent Fe by trivalent In in oreforming minerals is discussed in the same sense by L. R. Wager—J. van R. Smit—H. Irving (1958). The above cited work of A. S. Višnevskij (1958) verifies the possibility of mutual representation  $In^{3+}$ —Fe<sup>3+</sup>. The writer classifies the descendently formed haematite, goethite, limonite etc. as typical "concentrators" of indium, for these represent a slightly disperse metacolloidal mediums convenient to this phenomena. He explicates the In-concentration in these minerals by high adsorbtion capacities of gels of hydroxides of Fe, Sn and other compounds depending upon easy polarisation ability of In-compounds. Analogous cases are described by A. S. Višnevskij (1958) even in the ore veins of Vrančice.

Another open question is the bond of Ge in the haematites of Vrančice. Notices of small concentrations of Ge in haematite may be found in literature (e.g. S. A. El W a r d a n i—1957), but without any detailed discussion of its bond. Ge may apparently be concentrated in haematite in a similar way as In, i.e. that its coefficient of migration is rather small in comparison with other elements (e.g. Sb, As, Zn). It remains more or less in situ in conditions of supergene development of minerals, without any influence of its original hosts which can be either sulphidic minerals or mineralforming components. Experimental results of different investigators show a long time known fact that germanium has an extraordinary capacity of bouding with siderophile compounds; the question of its bond in haematite remains still disputable. In haematite it is not excluded that, Ge replaces Ti, which is considered as an isomineral element. A considerable physically-chemical analogy of oxidic compounds of germanium and titanium-GeO<sub>2</sub> with TiO<sub>2</sub> has been experimentally detected in the values of V. M. G o l d s c h m i d t (1958). This analogy has its source in close ion radii Ge<sup>44</sup> (0,52 Å) and Ti<sup>44</sup> (0,64 Å).

**Goethite**— $\alpha$ -FeOOH—is a very frequent mineral in Vrančice area. It occurs in greater accumulations esp. in the vein Pošepný and Hofmann, and is present currently even in Babánek vein. It is found also in old dump material from the Slavík vein and near the Karel-mine. Macroscopically, two general types of goethite can be distinguished: 1<sup>st</sup> type is middle- or coarse-radiating, of fair coffee-brown colour. It forms lumpy- or radiating-aggregates, sometimes with kindney-shaped surfaces. This type occurs currently in association with haematite and willemite and makes fillings of druse-cavities.

 $2^{nd}$  type is much more rare. It was detected only in Pošepný vein. It generally creates very fine needle-shaped aggregates of fair brown or yellow-brown colour. It fills up druse cavities and is very similar with the velvet iron ore of Příbram. The goethite of Vrančice, in analogy with haematite, has a capacity of adsorbing a serise of elements which are characteristic for an ore body of a certain chemism.

Microscopic identifications of goethite were verified by X-ray measurements.  $\alpha$ -FeOOH was detected in all cases.

Limonite is known in the district of Vrančice from ancient times already. It occurs in relatively small amounts in the surface zones of oxidation of ore veins of Vrančice. It forms powder coatings esp. in ruptures of ore associations. Limonite is in general of ochre colour and is formed by a mixture of hydrated oxides and iron hydroxides. The composition of limonite-coatings was not studied in details because of the lack of material; the main part of earthy ochre-brown or rusty masses belongs to haematite and goethite.

**Polianite**—the crystaline needle-shaped derivate of *pyrolusite* ( $\beta$ -MnO<sub>2</sub>). It is cited by J. K o u ř i m s k ý (1956) in Pošepný vein, where it was identified in collaboration of A. A. Malachov microscopically in polished section, associated with specularite. I did not succeed to find polianite again and therefore its existence in the district of Vrančice could not be proved exactly.

Cuprite— $Cu_2O$ —is described from the district of Vrančice by V. H a n u š (1955) who detected it macroscopically and microscopically in old dump material in association with earthy haematite. Its presence is apparently very rare, as during later dated mineralogic researches, no more important concentrations of this mineral could be detected. Its existence could therefore not be verified by other methods.

**Chrysocolla**—CuSiO<sub>3</sub>.**n**H<sub>2</sub>O—was detected in sporadic amounts in the material from investigation grooves in the area of Pošepný vein and near Životice. This amorphous greenish hydrosilicate is mentioned in the review of minerals of Vrančice without any data of identification by J. K o u ř i m s k ý (1956).

Vésigniéite—BaCu<sub>3</sub>  $[OH/VO_4]_2$ —is a very rare mineral. It occurs in the material of the zone of oxidation of Pošepný vein, where it formed powder or earthy coatings of greenish colour. It was exactly identified by K. P a d ě r a (1956a).

**Bindheimite**—Pb<sub>1-2</sub>Sb<sub>2-1</sub> (O, OH, H<sub>2</sub>O)<sub>6-7</sub>—was found as a more rare supergene mineral. It was identified optically and by X-ray measurements in the material from Pošepný vein by K. P a d ě r a (1956b). According to the author, it makes fillings of cracks in the veiny mass, esp. in form of greenyellow powder coatings of chalcocite and calcite.

**Apophyllite**—KCa<sub>4</sub> [F/(Si<sub>4</sub>O<sub>10</sub>)<sub>2</sub>].8H<sub>2</sub>O—was optically determined by J. Kouř i m s k ý (1956) and A. A. Malachov, who found it in the quartzy vein-mass in a investigative groove near Životice. It formed mince white crystals in druse cavities.

Magnetite—Fe<sub>3</sub>O<sub>4</sub>—and ilmenite—FeTiO<sub>3</sub>—were described in the district of Vrančice from a unicate occurrence in the mine Jan by J. Pokorný (1955) and A. A. Malachov (1956). These minerals occurred in association with molybdenite, pyrite, pyrrhotite and chalcopyrite.

B-Sulphidic minerals (+sulphosalts and native metals)

#### Zn-Pb minerals

Sphalerite—ZnS—is the principal ore mineral in all the veins of Vrančice which are researched actually. It was not found only in the material of the left mine Karel.

Macroscopically, it forms middle or coarse grained aggregates of light-brown colour. Different shades are noticeable under binocular microscope in the crushed sphalerite aggregate-from honey-yellow to redbrown or dark coffee-brown. Zonarly coloured parts of sphalerite were observed very rarely.

Microscopically, the sphalerite of Vrančice has a lower reflection and gray colour in reflected light; under crossed nichols it is still isotropic but shows often strong internal reflexes of yellowbrown or redbrown colour. Sphalerite with quartz I, specularite and rare Ni-minerals makes fillings of the oldest tectonic cracks. Sphalerite is accompanied by chalcopyrite and calcite in all the researched veins. Sphalerite occurs also in association with willemite (Pošepný vein); in the Alexandr mine, it f orms with the latter two principal technologic types of ore connected one with another by continuous transitions.

Macrochemism and microchemism of separated sphalerites of Vrančice was studied in detail. The macrochemism of sphalerite from different veins of Vrančice does not change considerably. It is evident from results of analyses and from calculate ed crystalochemical formulas that iron is the main isomineral element replacing zinc. The Fe-content of the sphalerites of Vrančice is in the range 0.14 - 1.17 %. The content slightly higher than 1% is more common. In comparison with sphalerites from other deposits in this country (e.g. Kutná Hora), the iron content is in its sum very low; this phenomenon contest in general a middle or lower temperature of development not only of this mineral but even of the ore veins themselves. Cd, Sn and Hg are outstanding in comparison with other isomineral elements. The range of Cd-contents is regularly in tenths of %, preponderately amounting to 0,3%; only fair sphalerites of Slavík vein contain up to 0.5% Cd. The Cd-contents of the sphalerites of Vrančice may be found in commercial aspect as middle-ranged, if compared with the values of cadmium-rich sphalerites of Sardinia, which contain in average 1% Cd (D a n a 1946). The Sn-contents of analysed sphalerites is in the order of 0.01-0.1%. V. M. Goldschmidt (1958) cites the Sn-contents of sphalerites from traces to 0.2% to be current. The Sn-contents detected by us (0.03-0.12%) does not overreach these limits. Mercury is nearly always present in small amounts in lowtemperature sphalerites. The contents detected by us range all in 0.01% - 0.08%.

Ga, Ge, In partly Mn and in trace amounts even Ag may be classified as isomineral in a series of detected microelements. The admixture of Ga, Ge and In in the sphalerites of Vrančice is noteworthy from commercial aspect. Whilst the Ga- and Gecontents of sphalerites are very low (as far as they may be evaluated from quantitative spectral analyses of ordinary mean ores) sometimes even negligible, indium forms their quite regular component. Its order of concentration is 0,005-0,02%(stated of quantitative spectral analysis).

Willemite— $Zn_2$  [SiO<sub>4</sub>]—is ranged among sulphidic minerals as an exception for the reason that it is, beside sphalerite, an important zinc ore mineral of the Alexandr mine.

Willemite is a generally rare mineral of ore deposit all over the world. Vrančice is its only occurrence in ČSSR, originally described by A. A. Malachov (1955). This mineral was later studied from many sides by J. Kouřimský who publicated a penetrating study of willemite in a collective work. A. A. Malachov—J. Kouř i m s ký (1956). Willemite was studied by the cited authors optically (constants), crystalographically (goniometrical measurements of crystal faces), by X-rays and chemically (quantitative chemical analyses and qualitative spectral analyses), so that it was not necessary to negotiate with willemite during this research. We therefore point to the above cited study.

Two or three types of willemite may be distinguished macroscopically. The above cited authors classify them as three generations of willemite. The first type, which is most current, forms mince crystallic, often even radiating aggregates of gray, greenish, brownish or slightly violet colour. The second type of willemite is formed by idiomorphous mostly long columnar crystals which crystalise in druses in the cavities. The third type is described as formed by little needle-shaped crystals. All the three types beam in ultraviolet light by different shades of colour.

The three types of willemite can be distinguished in extreme cases only from descriptive aspect, but it is a more complicated problem to prove that there are three real generations of different age. This question is connected with the total problem

2\*

of the genesis of willemite, which was not discussed in details by cited authors, even though J. Kouřímský made a careful partial study of its successive position against the associated minerals. This question of the genesis of willemite will be discussed in details in following parts.

The chemism of willemite of Vrančice was studied in detail by J. Kouřimský. For making the analytic conditions uniform, a qualitative spectral analysis of separated willemite from Pošepný vein has been run repeatedly (table 9). Isomineral elements of willemite of Vrančice, except of Zn and Si, are Mn, Fe, Mg, eventually small amounts of Ca. It is not excluded that to this group belong also trace elements Be, Ge and V. Their origin, however, may be various.

During the research, I observed namely the occurrence and distribution of willemite in the ore veins of Vrančice as this forms an economically important component of the ore mass of Vrančice. From the up-to-date made investigative works it was stated that the main concentrations of willemite are to be found in Alexandr mine (Pošepný vein), minor occurrences were noticed in the material from Hofmann vein band, sporadic occurrences in Babánek vein. In Slavík vein it was not stated at all. Its occurrence depends upon certain specific conditions and its identification upon actual degree of exploitation of the vein.

Galena—PbS—is another of the main ore minerals of the ore veins of Vrančice. Its existence is known from older times already, similarly as that of sphalerite.

Macroscopically, it forms fine grained or coarse grained aggregates. It is to be found mainly in Slavík vein in form of coarse crystallic formations (in symetric veins etc.), in a smaller extent in Babánek vein. It forms more massive fillings in Pošepný vein. Galena is, in the ore veins of Vrančice, mostly associated with older minerals like sphalerite and quartz I and II, with tetrahedrite, chalcocite and chalcopyrite (in general with the second generation) and bornite.

The chemism of galena of various ore veins of Vrančice was determined by quantitative chemical analyses and by spectral analyses. Ag, Bi, Cd, Sn, Tl and partly even Sb may be classified as isomineral elements of the galena of Vrančice. The content of Ag, which is bound with the lattice of galena varies from 0,03 to 0,32%. Sn-contents of galenas are rather varying—from traces to 0,01—0,1%. Cd and Bi contents are in general relatively small; slightly higher concentrations were found in the galena of Babánek vein (Bi = 0,008%, Cd = 0,1%). But even in these cases, real lattice bounds are in place in these higher concentrations, because the content of heterogene admixed sphalerite and tetrahedrite, which can similarly bind both elements, is quite negligible. V. M. Goldschmidt (1958) notices the Tlcontents of galenas. They are explicated by the author as a lead-thallium replacement.

### Cu-minerals

**Chalcopyrite**—CuFeS<sub>2</sub>—is quantitatively a more rare mineral than sphalerite and galena, but in comparison with other Cu-ore minerals it is distributed very extensively. Current presence of chalcopyrite in Pošepný vein (J. Kouřimský 1956) was verified by my own researches; even higher local concentrations of this mineral may be found in this vein. Chalcopyrite was stated as accessoric component in the ore material from the Hofmann vein band; its common occurrence was stated even in Slavík and Babánek veins.

Chalcopyrite forms in most cases massive fillings of fine or very fine cracks, esp. of those in sphalerite. It occurs currently associated with tetrahedrite, galena,

in a smaller extent with bournonite. It is very close bound to bornite. Microscopically, it shows a typical yellow colour in polished sections, under crossed nichols it shows always anisotrope effects of middle strength.

Two generations of chalcopyrite were successively distinguished. Whilst chalcopyrite I was stated in Pošepný vein only in close association with tetrahedrite, chalcopyrite II occurs either as veinlets and irregular formations, sometimes partly depressing older minerals, or in a close association with bornite, forming with this mineral typical concretional screen structures, originating in the decomposition of the solid solution by decreasing temperatures.

It is necessary to notice a kind of chalcopyrite, which is in paragenesis with pyrrhotite, magnetite, ilmenite, molybdenite and pyrite. This paragenesis, described originally by J. Pokorný (1955) and later by A. A. Malachov (1956) is apparently older than the development of the ore veins themselves, and in J. Pokorný's opinion, it is not directly dependent upon them.

The chemism of chalcopyrite of Vrančice was not studied in details by anybody till present time. The chemism of chalcopyrite from Pošepný vein is very simple according to the author's observations. Ag, partly Zn and Cd and rarely even Sn are considered as isomineral elements, what is in good agreement with literary data. It is not excluded however that even Sn belongs to this group. Zinc and cadmium are ranged among admixtures of sphalerite or tetrahedrite as it was stated by microscopic control of the homogenity of the material. Only minor amounts of Cd may be classified as isomineral. Similarly also As, a rare element in chalcopyrites, belongs in our formulas more to heterogene pyrite. The Sn-bound is not clear, as it can belong either to heterogene sphalerite, tetrahedrite and galena or to its lattice bound, if its structural relativity to the compounds CuFeS<sub>2</sub> and Cu<sub>2</sub>FeSnS<sub>4</sub> is taken into question. Ni-bound remains unclear regarding to other common trace elements. With respect to the character of heterogene minerals, it is more probable in this case that it is an isomineral element, belonging rather to pyrite.

**Bornite**—Cu<sub>5</sub>FeS<sub>4</sub>—is one of more rare ore minerals of the veins of Vrančice. J. K o u ř i m s k ý (1956) cites it in Pošepný vein. I myself verified its occurrence in this vein during my own researches and succeeded to identify it even in Babánek and Hofmann vein. Lump-shaped bornite is present in Pošepný and Babánek veins in macroscopically evident accumulations. In Hofmann vein, it was detected only microscopically in accessoric amounts.

Macroscopically, it is noticeable by its darker brownish copper colour which is to be seen in fresh breaks and in fresh polished sections. This colour turns quickly in air to various but preponderately blue shades. Microscopically, bornite has in reflected light a strong pink colour, under crossed nichols it is isotropic.

Hypogene bornite occurs in a close association with chalcopyrite II and forms together typical screen structures, originating in decomposition of solid solution by the decrease of temperature; this phenomenon is a sufficient proof of its ascendental origin. Probably even bornite of cementational origin, associated with massive concentrations of chalcocite, which in these surface parties are considered by the writer as cementational as well, may be found in the ore veins of Vrančice.

The identification and chemism of this bornite of Vrančice was verified by quantitative chemical analyses and by spectral analyses as well. Only Ag, in small amounts of course, may be classified as isomineral in bornite. The bound of other elements in question however remains always unclear. This is true especially for the elements detected in all analysed samples which need not be univocally anisomineral: Bi, Ga, Ge, Sn. There are no perfect informations of Bi and Ga in literature; they may be, in this case, explicated by the above cited heterogene admixtures, but this explication is not univocal. K. R a n k a m a—T. G. S a h a m a (1952) write that Ge, Sn and Ni (which was detected sporadically) form current admixtures in sulphides and Cu-sulphosalts. The quantitatively detected tin-content in the bornite of Vrančice is to be mentioned. Its quantity (0,07%) is clearly higher than it ought to be in occasion of its exclusive bound with heterogene sulphides. Another mineral with Sn as main construction component may be present or this element is really bound in the lattice of bornite.

A structural modification of bornite of Vrančice (Pošepný and Babánek veins) was identified by X-ray measurements on the basis of comparison of following strongest lines with tabellar values of this mineral in the compendium of A. G. Torre—J. Garrido (1953):

Bornite-Vrančice—3,31 Å(5); 3,12 Å(5); 2,71 Å(5d); 1,925 Å(10). Bornite-Torre, Garrido—3,29 Å(6); 3,15 Å(6); 2,73 Å(6); 1,925 Å(10).

X-ray researches proved a cubic  $\beta$ -modification of bornite.

**Chalcocite**— $Cu_2S$ —is a generally rare mineral in the ore district of Vrančice; but in Pošepný vein, it is rather current and in some horizons of Alexandr mine is to be found even in extraordinary accumulations. As it results from the works of older writers, its presence was known only in Pošepný vein, where I collected the bulk of material esp. for the study of its chemism. In addition, I was successful in identifying it in Babánek vein.

Chalcocite is macroscopically observed only in Pošepný vein, where it forms irregular lump-shaped accumulations of various sizes, rarely even larger lentils in form of splitted veins. It is of darker gray colour, often with blueish films and a rather bright metallic luster. In Babánek vein, it was observed only microscopically, whereas it was not detected in other veins till now. Microscopically, it is of graywhite colour with a blueish shade in fresh-made polished section. V. Hanuš (1955) studied it in details and points to the fact that the chalcocite of Vrančice shows only a weak anisotropy and it is not possible to determine univocally in many cases that the element is isotropic or anisotropic. The question of the occurrence of modifications of chalcocite at Vrančice is connected with this phenomenon. One of the first exact identifications of chalcocite was according to J. Kouřimský (1956) the X-ray identification of F. Vrabka, dated 1952, who stated two modifications—a rhombic and a cubic one—in mixture. This identification was during the research of V. Hanuš newly verified by X-ray measurements; the author stated only the existence of rhombic modification of chalcocite. I similarly viewed this question and identified only the rhombic  $\alpha$ -modification of chalcocite, in a perfect accordance with V. Hanuš (1955), in Pošepný and in Babánek veins the classification of H. Strunz (1957). The existence of a cubic form in minerals of the veins of Vrančice remains to be an open problem; this form designated in literature by lastest researches by P. Ramdohr (1955) and H. Strunz (1957) as neodigenite, which, however, has another Cu: S relation than chalcocite, so that its formula is by cited authors written  $Cu_9S_5$ . The presence of neodigenite at Vrančice is stated by J. Kouřimský (1956) and A. A. Malachov-J. Kouřimský (1956). It is described as forming microscopic veinlets in sphalerite, of intensive blue colour, but without any exact proof of its existence.

I did not succeed to identify it univocally during my mineragraphic study, though several parts of chalcocite (especially those which grow through galena) are not always markedly anisotropic. Preponderate pseudomorphoses of rhombic chalcocite in cubic neodigenite can occur actually.

The chalcocite of the ore veins of Vrančice is quite correctly held by V. H a n u š (1955) and A. A. M a l a c h o v - J. K o u ř i m s k ý (1956) as hypogene. Nevertheless, I concluded on the basis of the study of many samples containing chalcocite that beside the above cited hypogene chalcocite even a descendent-cementation chalcocite is present in Pošepný vein, presumably in lump-shaped aggregates together with native metals, noble silver ores and the paragenesis of Cu-ores. Chalcocite is often associated with galena, tetrahedrite, chalcopyrite and willemite as one of the youngest minerals.

The chalcocite of Vrančice was also analysed by quantitative chemical and spectral analyses. Ag is in literature generally characterised as an isomineral element of chalcocite (in a series of elements detected). In this case, silver (content 0.36 %) has the nature of a primary anisomineral element, as it is in its native form represented in chalcocite currently. Other elements characterised as isomineral are Fe and Cu, which can replace Cu in the lattice of chalcocite (in this case are ranged to anisomineral elements again). The presence of elements Bi, Cd, Ga, Hg, In and Sn is remarkable from geochemical point of view. Bi is the most expressive (beside Sn) in the series of cited elements; its quantitatively determined amount (0.01 %) is higher than the content of heterogene minerals able to bind it. On the basis of this fact, Bi is taken partly as anisomineral. In the sum, the cited elements are characteristic for sphalerite and tetrahedrite, but analysed chalcocite contains only negligible amounts of heterogene elements. Their bond is not quite clear. The Sn-content is remarkable and there are no literary data of its presence in chalcocites. The question of the Sn-bond was discussed by V. Hanuš (1955) who concluded its admixture as caused by submicroscopic minerals containing Sn in considerable amounts. This is not excluded in fact, because a similar case was stated in bornite, where the bond is similarly not clear. The presence of indium in the cement chalcocite from Pošepný vein is the most significant phenomenon among the cited elements from the genetic point of view as far as it can be considered from the data of J. S. Anderson (1953); he writes that it is just the presence of In which is current and as shown by analyses from different world's deposits even characteristic for chalcocites developed by cementation. The form of Ga- and Hg-bond is also unclear and there are no exact notices in literature of their presence in chalcocite. It is not exluded however that their occurrence could be motivated in a similar way as that of indium.

**Covellite**—CuS—is very rare in the ore veins of Vrančice; it is found only in form of films originating as a product of alteration of Cu-minerals, esp. of chalcocite. In polished sections, covellite shows a very strong anisotrophy with characteristic bright colours.

Native copper is another very rare mineral of Vrančice. According to J. K ou -  $\check{r}$  i m s k ý (1956) it was found for the first time in Pošepný vein by Ing Schmidt. A notice of native copper is also in the work of V. H a n u š (1955). It occurs in form of fine grains, plates or wires which make fillings of fine cracks of calcite and quartz, in analogy with native silver. Native copper is also present in association with chalcocite and native silver.

It has a high reflection under microscope in polished sections, but the surface has many scratches. The colour in reflected light is slightly pink.

#### Cu, Pb, Sb-minerals

#### Minerals of the group tetrahedrite-tennantite

According to J. K o u ř i m s k ý (1956), the occurrence of tetrahedrite is known in the district of Vrančice in older times already. The author draws the reader's attention to the fact that it was mostly mistaked for chalcocite. Recently, a subordinate occurrence of tetrahedrite is cited by V. H a n u š (1955) and a probable occurrence of tennantite by J. K o u ř i m s k ý (1956) in Pošepný vein. No appropriate attention however has been paid to the exact determination of this mineral. That is why an extraordinary attention was paid to the minerals of isomorphous series tetrahedrite-tennantite during latest mineralogic studies of the ore veins of Vrančice. Their detailed compilation from the mineralogically-chemical and structural point of view is in the separate work of J. K o u ř i m s k ý-V. H o f f m a n (1961) to which I draw the reader's detailed attention.

The occurrence of Zn-rich tetrahedrite was detected in the veins of Vrančice; it is ranged to more rare minerals but its extensive distribution is very considerable. It is currently present in Pošepný vein, in a smaller extent in Babánek vein and it was detected in accessory amounts even in the Hofmann vein zone. Its local accumulations are exclusively in Slavík vein. A rare presence of tennantite was identified in Pošepný vein.

Minerals of the tetrahedrite-tennantite group occur most often in association with chalcopyrite, bournonite and galena, in a smaller extent with sphalerite, bornite and chalcocite.

**Bournonite**—2 PbS. Cu<sub>2</sub>S. Sb<sub>2</sub>S<sub>3</sub>—was originally identified by J. Kouřímský and A. A. Malachov (J. K o u ř i m s k ý 1956) in the district of Vrančice by optical and X-ray measurements of the material from Pošepný vein. I succeeded to find this mineral even in Slavík and Babánek vein besides. Bournonite is in its sum a rare mineral in the district of Vrančice, but sometimes its local greater accumulations was ascertained.

It is very difficult to distinguish bournonite from tetrahedrite macroscopically. It forms in general fine grained, lump-shaped accumulations, in exceptional cases also crystal units of tabullar habitus (Slavík vein). Its colour is gray, with metallic luster. For its similar appearance with galena, it is easy to overlook it in the polished section; its colour is olive-green. It is slightly anisotropic under crossed nichols; its parquet-like lamellating is typical.

Bournonite is in most cases associated with tetrahedrite, with which it has a very similar crystalinity, and with chalcopyrite and galena. The chemism of bournonite from the district of Vrančice (Slavík vein) was determined by quantitative chemical and spectral analyses (table 9, 11). Determined contents of principal components Cu, Pb, Sb and S are rather concordant with its theoretic values. Isomineral arsenic amounting 0.24 %, which replaces diadochally antimony, belongs also to macro-components. J. D. D a n a (1946) writes that the relation Sb : As can reach in bournonite to 4:1. The Sn-bond remains unclear as it is in other minerals. The amount is slightly higher (0.03 %) than it would correspond to the amount of heterogene admixed sphalerite able to bind it. It is therefore not excluded that even tin is an isomineral element, at least partly. I suppose Ag and Bi as isomineral. Other identified microelements are isomineral because they belong to heterogene admixtures of sulphides, quartz, carbonates or rock constituents.

The occurrence of seligmannite at Vrančice remains open. F. Kupka identified in 1955 by X-rays in the samples of A. A. Malachov minerals with nearly the same chemism as is that of seligmannite. This mineral forms together with bournonite, according to latest researches of G. Leineweber (1956) an isostructural series, analogical to the series tetrahedrite-tennantite. The two minerals form continuous isomorphous mixtures with a differently related replacement of antimony by arsenic. The resolution of whether the mineral is nearer to one or another member of the series bournonite-seligmannite is possible just on the basis of quantitative determinations of As and Sb content, which was not available to univocal identification of F. K u p k a (1955). It is not possible, however, to exclude the occurrence of seligmannite at Vrančice for similar reasons as that of tennantite. I can confirm from my own researches merely the identification of bournonite verified beside the quantitative determination of individual components also by X-ray measurements,

**Boulangerite**— $5PbS : 2Sb_2S_3$ —is a new mineral of the ore district of Vrančice. A specimen of typical "felt-like" mineral crystalised in a druse cavity was found in 1958 by A. Kollert in Pošepný vein (Alexandr mine) and was kindly given me for identification.

Boulangerite forms macroscopic fibrous aggregates of dark gray colour. It is associated with quartz, calcite, sphalerite, bournonite and galena. It forms druseshaped fillings of sphalerite. The discovery of boulangerite may be classified as individual in the veins of Vrančice, as I was no more successful to find it even in many samples from different places of particular veins (even not by microscope). This unicate occurrence is figured by the enclosed photograph (Pl. II-fig. 1).

Boulangerite was exactly identified first by X-ray measurements and its chemism was verified by qualitative spectral analysis (table 9). The considerable amount of Pb and Sb confirmed the incidence of the researched mineral to the group of Pb-Sb sulphosalts. Considering that the analysed material was very pure following elements may be classified in accordance with literary data as isomineral: Cu, Ag, Cd, Fe and Co. Quartz and calcite with incident elements Si and Ca form a negligible heterogene admixture. It is necessary to notice that only a very small volume of the material was used for analyses, as it was a risk that the specimen could be destroyed. For that reason all present trace elements had not to be detected and the analysis may be a little erratic. X-ray identification (the complete evaluation is in the table 2) confirmed univocally that the studied mineral is boulangerite. There appeared very distinctly a characteristic complex of lines which separates boulangerite from other minerals of the group of Pb-Sb-sulphosalts.

Antimonite—Sb<sub>2</sub>S<sub>3</sub>—is a very rare mineral of the district of Vrančice. It occured isolated just in Pošepný vein where it was found by A. A. Machalov in an ore specimen; it filled up the cavities in form of druses (see J. K o u ř i m s k ý 1956). Antimonite formed here long fine needles or short needle-shaped crystals. V. H a n u š (1956) cites the occurrence of antimonite in the ore material from the Alexandr mine as well. An exact identification of antimonite by spectral and X-ray analyses was made by F. K u p k a - J. P o k o r n ý (1954). As it results from the spectral analysis of antimonite of Vrančice, following elements of isomineral character are present: Sb (the main component of construction), As, Cu and Fe. Even a trace content of mercury was detected in the antimonite of Vrančice but its origin is not quite clear. Hg is in most cases absent in antimonite but on the basis of the purity of analysed material it may be assumed that this phenomenon is a certain geochemical speciality of this antimonite.

#### TABLE 2

Roentgenometric identification of boulangerite from the Pošepný vein—Vrančice. Debye-Scherrer method, radiation CuK $\alpha_{1,2}$ , Ni-filter, 28 kV, 24 mA, exposition 2 h, cell-diameter 57,3 mm, glass-hair, reference substance A1 ( $a_0 = 4,0483$  Å).

	5	Boulangerite Vrančice		Boulang Torre-Garri	gerite ido (1953)
No.	I	2 0	d	ÌI	d
$1\\2\\3\\4\\5\\6\\7\\8\\9\\10\\11\\12\\13\\14\\15\\16\\17\\18\\19\\20\\21\\22\\23\\24\\25\\26\\27$		$\begin{array}{c}$	$\begin{array}{c}$	$     \begin{array}{c}       1 \\       2 \\       1 \\       1 \\       2 \\       3 \\       10 \\       2 \\       4 \\       6 \\       5 \\       9 \\       4 \\       2 \\       1 \\       2 \\       6 \\       1 \\       1 \\       5 \\       3 \\       2 \\       3 \\       8 \\       1 \\       7 \\       7     \end{array} $	6,74 Å 6,13 5,20 4,86 4,61 4,36 3,89 3,71 3,43 3,32 3,21 3,02 2,815 2,691 2,578 2,515 2,435 $2,337^1$ ) 2,303 2,226 2,145 $2,056^1$ ) 1,967 1,920 1,861 1,829 1,757 etc.

<sup>1</sup>) Coincidence of Al-line

#### Ag-minerals

**Pyrargyrite**—Ag<sub>3</sub>SbS<sub>3</sub>—is a new mineral of the ore district of Vrančice. It occurred in ore specimens of Pošepný vein in macroscopically observable amount in recent times. Its occurrence in Alexandr mine is reported in a geologic investigation report of the year 1958 by A. Kollert. During my own researches, I was successful to identify exactly pyrargyrite from Pošepný vein and microscopically from Slavík vein.

Pyrargyrite forms macroscopically well observable fillings of mince cracks of ore veins, especially in the places of dominating paragenesis of Cu-ores. It is of gray colour with a slightly reddish shade. Under microscope in reflected light, it has a lighter gray colour with a fine blueish shade. Even a double reflexion is relative-

#### TABLE 3

		Pyrargyrite Vrančice		Pyrarg Michee	gyrite v (1957)
No.	I	2 0	d	I	d
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0,5 dif. 4 7 10 8 dif. A1 3 1 A1 4 5 dif. 2 dif. 2 dif. 2 dif. 2 dif. 1 dif. 1 dif. 1 dif. 2 dif. 2 dif.	$\begin{array}{c} 22,4\\ 26,7\\ 27,8\\ 32,2\\ 35,1\\ 38,5\\ 39,8\\ 42,6\\ 43,4\\ 44,8\\ 46,3\\ 48,9\\ 52,2\\ 54,5\\ 57,7\\ 60,5\\ 64,1\\ 65,2\\ 66,3\\ 67,5\\ 69,5\\ \end{array}$	$\begin{array}{c} 3,96\ \text{\AA}\\ 3,34\\ 3,21\\ 2,78\\ 2,56\\ 2,34\\ 2,26\\ 2,12\\ 2,08\\ 2,02\\ 1,96\\ 1,863\\ 1,753\\ 1,683\\ 1,753\\ 1,683\\ 1,598\\ 1,530\\ 1,453\\ 1,431\\ 1,409\\ 1,387\\ 1.352\end{array}$	$     \begin{array}{r}             7 \\             9 \\           $	$\begin{array}{c} & \overline{}\\ 3,35 \text{ kX}\\ 3,20\\ 2,79\\ 2,55\\ &\\ 2,26\\ 2,12\\ &\\ 2,00^1)\\ 1,96\\ 1,865\\ 1,750\\ 1,680\\ 1,865\\ 1,750\\ 1,680\\ 1,600\\ 1,530\\ 1,458\\ &\\ 1,402\\ &\\ 1,350\\ \end{array}$

Roentgenometric identification of pyrargyrite from the Pošepný vein—Vrančice. Debye-Scherrer method, radiation  $CuK\alpha_{1,2}$ , Ni-filter, 28 kV, 24 mA, exposition 4 h, cell-diameter 57,3 mm, glass-hair, reference substance A1 ( $a_0 = 4.0483$  Å).

1) Coincidence of Al-line

ly well observable. Pyrargyrite shows a very strong anisotropy and very characteristic reflexes of crimson-red colour under crossed nichols.

It was possible to detect the chemism of pyrargyrite only by spectral qualitative analyses (table 9). Ag and Sb are the main elements of construction. Ag may be with safety classified as isomineral. All the other determined elements are to be ranged with respect to their admixtures of heterogene ore minerals, for the most part to anisomineral elements. An isomineral form of bond may be supposed merely in the case of mercury (if the analyses of pyrargyrite from other deposits are compared).

Pyrargyrite was quite univocally identified by X-ray analysis (table 3) as the complex of lines is in the good accordance with the tabellar values given for this mineral by V. I. Micheev (1958).

Stromeyerite—Cu<sub>2</sub>S . Ag<sub>2</sub>S—is another of newly identified minerals of the ore district of Vrančice. It occupies a prominent position in a series of local rare minerals for the fact that its finding and exact identification is the first safely detected occurrence of this mineral in ČSSR.

Stromeyerite was found in very small amounts in the ore material of Pošepný vein. It was macroscopically observable only in a polished section under binocular microscope where it is apparent by its very small hardness (a sinking relief) and darkgray colour. Optical properties agree on the whole with microscopic values of P. R a m d o h r (1955) for stromeyerite. It is gray-white in reflected light, and in immersion it receives a creamy shade. The reflexion is slightly higher than that of tetrahedrite. Stromeyerite has a middle double-reflexion noticeable in immersion especially in the grain-boundaries with a change of colours from graywhite to gray with a fair pinkish shade. It shows a very strong anisotropy with colour effects from olive-green to bright violet under crossed nichols. Diagnostic etchings made for one minute resulted as follows:

HCl 1:1—negative; just after a longer interval irised tarnish of weak blue colour FeCl<sub>3</sub> 20 %—etches immediately and coats with manycoloured tarnish (brown colour predominates)

KCN 20 %-etches intensively, the colour turns to brown or black

HgCl<sub>2</sub> 5 %—a brown manycoloured tarnish

KOH 40 %—negative

HNO<sub>3</sub> 1 : 1 — negative

Stromeyerite occurs mainly associated with chalcocite, bornite, chalcopyrite, tetrahedrite, argentite (?), pyrargyrite and native silver. It is evident from the association that it is bound to such ore-parties where the filling of the ore vein is formed principally by the paragenesis of Cu-ores, whereas the content of Zn-Pb minerals is of smaller importance. Stromeyerite, in analogy to other Ag-ores, makes fillings of very fine and minute cracks of these vein parties. It is evident that it belongs to the youngest minerals and may be considered as descendent as other Ag-ores, concentrating in the zone of cementation of Pošepný vein.

An exact identification of stromeyerite was inabled by its careful separation with the needle directly from the polished section. The powdered sample gained in this way was used to qualitative spectral analysis and to X-ray analysis as well. Qualitative spectral analysis of stromeyerite from Pošepný vein:

Substantial amount (»1 %): Ag, Cu

Subsidiary amount (>1-0,1 %): Ca, Cr, Fe, Sb, Si

Accessory amount (0,1-0,01 %): As, Zn

Trace amount (<0,01 %): Al, Ba, Bi, Cd, Co, Ge, Mg, Mn, Ni, Pb, Sn

The result of the analysis verified main components of stromeyerite; considering that the mineral was separated in very difficult conditions from the polished section, the homogenity of the mineral could not be guaranteed. As we can see from the series of detected elements, there is an admixture of other elements in the analysed sample, i.e. calcite, quartz and of ore minerals tetrahedrite, chalcopyrite and chalcocite. This heterogene admixture of minerals is small in its total, because it did not influence the X-ray analysis, but all the same, it makes possible a discussion of the chemism of stromeyerite from the point of view of the presence of microelements. All the trace elements may mainly belong to the above cited heterogene admixtures. The X-ray pattern (table 4) of stromeyerite shows strong lines of identification. It was ascertained by comparison of stated d-values with the values published in different compendiums, that the values distinctly differ one from another. It is not excluded that the values of tables belong to non-homogeneous samples. It was therefore necessary to apply to the original literature of the latest years. H. S u h r (1955) pursued

#### TABLE 4

	S	tromeyerite Vrančice		Strome	eyerite (1955)
No.	I	$2 \Theta$	d	I	d
$     \begin{array}{r}       1 \\       2 \\       3 \\       4 \\       5 \\       6 \\       7 \\       8 \\       9 \\       10 \\       11 \\       12 \\       13 \\       14 \\       15 \\       16 \\       17 \\       18 \\       19 \\       20 \\       21 \\       22 \\     \end{array} $	2 dif. 4 0,5 2 10 2 1 dif. A1 0,5 dif. 1 dif. A1 3 5 2 dif. 0,5 dif. 2 dif. 0,5 dif. 1 0,5 dif. 1 1 0,5 dif. 2 1 0,5 dif. 4 1 1 1 1 1 1 1 1 1 1 1 1 1	$\begin{array}{c}\\ 25,5\\ 26,9\\ 28,3\\ 29,2\\ 34,3\\ 35,3\\ 37,3\\ 37,3\\ 37,3\\ 37,3\\ 37,3\\ 38,5\\ 40,9\\ 43,8\\ 44,8\\ 45,8\\ 48,4\\ 52,6\\ 54,1\\ 52,6\\ 54,1\\ 55,7\\ 58,1\\ 59,1\\ 60,6\\ 64,2\\ 65,2\\ \end{array}$	 3,49 3,31 3,15 3,06 2,61 2,54 2,41 2,34 2,23 2,07 2,02 1,982 1,880 1,741 1,695 1,649 1,588 1,563 1,528 1,451 1,431	$ \begin{array}{c} 1 \\ 7 \\ 8 \\ -6 \\ 10 \\ 6 \\ \\ -2 \\ 8 \\ 7 \\ 6 \\ 5 \\ 4 \\ 3 \\ 1 \\ 3 \\ 1 \\ -2 \\ \\ \\ \\ \\ 2 \\ 8 \\ \\ \\ \\ \\ \\ \\ $	$\begin{array}{c} 3,98\\ 3,46\\ 3,33\\ &\\ 3,07\\ 2,61\\ 2,55\\ &\\ &-\\ 2,10\\ 2,07\\ &-\\ &-\\ 2,10\\ 2,07\\ &-\\ &-\\ 1,99\\ 1,89\\ 1,75\\ 1,73\\ 1,70\\ 1,69\\ 1,63\\ 1,58\\ 1,58\\ 1,57\\ &-\\ &-\\ 1,45\\ &-\\ &-\\ \end{array}$
23	3	65,6	1,423	6	1,42

Roentgenometric identification of stromeyerite from the Pošepný vein—Vrančice. Debye-Scherrer method, radiation  $CuK\alpha_{1\cdot 2}$ , Ni-filter, 28 kV, 24 mA, exposition 4 h, cell-diameter 57,3 mm, glass-hair, reference substance A1 ( $a_0 = 4,0483$  Å).

especially the research of the system  $Ag_2S - Cu_2S$  and published d-values of pure stromeyerite, which correspond very exactly with the our opinion. The identification of stromeyerite of Vrančice may be therefore considered as adequately verified.

Argentite (?)—Ag<sub>2</sub>S—is another newly detected mineral of the ore district of Vrančice; its identification however is not exact. I succeeded to detect it in minimal amount only by microscope in the ore material from Pošepný vein, where it occurs together with other Ag-ores in an association mainly with the paragenesis of Cu-ores. Also this mineral makes fillings of fine cracks and, analogically with other noble silver ores, it is considered as descendent.

The studied mineral belongs indisputably to the group of Ag-ores as it is contested by its characteristic behaviour to diagnostic etchings. By its reaction to etchingreagents and by optical properties, it approaches mostly to argentite. This identification and its chemism could not be verified using other exact methods for the lack of available material. The properties of the Ag-mineral:

The mineral is not very hard. Its colour is galenawhite in reflected light (with a slight pink shade), fairly pink in immersion. The reflexion is lower than that of galena, but higher than that of tetrahedrite. The double-reflexion is negligible, but the anisotropy is of middle-size with light colour effects between green-blue to light violet. Internal reflexion was not observed. Results of diagnostic etchings (1 minute):

HCl 1:1 —negative HNO<sub>3</sub> 1:1—negative KOH 40 %—negative HgCl<sub>2</sub> 5 %—positive, turns brown, irised tarnish FeCl<sub>3</sub> 20 %—positive, etches intensively, turns brown KCN 20 %—positive, turns black immediately

Native silver is in general a rare mineral of the ore veins of Vrančice; it is cited by V. H a n u š (1955) and J. K o u ř i m s k ý (1956) from Pošepný vein. According to latest researches, its rather current occurrence in this vein, was stated accesoric amounts even in Slavík vein and Babánek vein. Silver forms wireshaped and platy formations which make fillings of fine cracks in the ore material. It occurs together with other Ag-ores in an association with chalcocite, calcite and quartz. It is of typical silver-white colour and gets manycoloured in the polished section very quickly. According to the form of occurrence I consider its origine to be more or less descendent.

Fine platy coatings of native silver were separated from the cracks in quartz for detecting the chemism by qualitative spectral analysis (table 9). Following elements are introduced as isomineral constituents in literature: Au, Hg, Cu, rarely As, Bi, Sb. By our analysis the presence of Cu, Hg, As and Sb was detected; these may be even in this case classified as isomineral elements. Other detected elements are anisomineral, because they belong to small heterogene admixtures of quartz, calcite or sulphidic minerals.

#### Ni-minerals

Nickeline—NiAs—is a new safely identified mineral of the ore district of Vrančice. Its occurrence is rare. It was found only in the ore-material from Slavík vein, where it forms minute accumulations included primarily in sphalerite. It is macroscopically characteristic by its reddish-copper colour.

It has a high reflexion and a yellow-pink colour under the microscope in reflected light. Also a double-reflexion with colour effects between light yellow-pink and light brown-pink is very distinct. The intensity of the colour changes of nickeline is extraordinary striking in revolving the desk of the microscope using the oil-immersion. Fine grains of nickeline which form accumulations are allotriomorphous. Nickeline is strongly anisotropic between crossed nichols, with colour effects shaded from gray to yellow (in immersion it is better noticeable again).

Nickeline was found in the ore-samples associated with Ni-skutterudite (chloantite), sphalerite, tetrahedrite, galena, chalcopyrite, native silver, quartz, baryte, siderite and calcite.

The microscopic identification of nickeline was exactly verified by a qualitative spectral analysis (table 11). Fe, S, Sb and Co are cited by literature as isomineral elements of nickeline, beside the substantial components of construction, i.e. Ni and As. All these elements were detected also by our spectral analysis, with the exception of sulphur. It is not sure whether they may be at least partly considered as isomineral, as it was very difficult to separate the analysed nickeline and so it was not possible to avoid heterogene admixtures of the above named associated minerals which contain these elements as well. The content of Mo is interesting; this element is almost absent in the ore minerals of Vrančice.

The identification of nickeline was univocally proved also by X-rays (table 5). The analysed sample contained an admixture of galena, which showed a higher amount of lines belonging to this heterogene mineral.

#### TABLE 5

Roentgenometric identification of nickeline from the Slavík vein —Vrančice. Debye-Scherrer method, radiation  $CuK\alpha_{1,2}$ , Ni-filter, 28 kV, 24 mA, exposition 4 h, cell-diameter 57,3 mm, glass-hair, reference substance A1 ( $a_0 = 4,0483$ Å).

		Nickeline ( +galena) Vrančice		[	Nickeline Micl	G heev (1957)	alena
No.	I	2 0	dÅ	I	d kX	I	d kX
$\begin{array}{c}1\\1\\2\\3\\4\\5\\6\\7\\8\\9\\9\\10\\11\\12\\13\\14\\15\\16\\17\\18\\19\\20\\21\\22\\23\\24\\25\\26\end{array}$	2 dif. 0,5 dif. 1 dif. 2 1 dif. 9 dif. 0,5 dif. 2 dif. A1 0,5 dif. 2 dif. A1 10 8 0,5 dif. 5 5 A1 0,5 dif. 6 2 A1 0,5 dif. 4 1 0,5 dif. 3 5 A1 0,5 dif. 3 5 A1 0,5 dif. 3 5 A1 0,5 dif. 3 2 2 A1 0,5 dif. 3 2 2 4 3 4 3 2 2	$\begin{array}{c} 25,9\\ 26,7\\ 28,4\\ 30,1\\ 31,4\\ 33,7\\ 35,1\\ 38,5\\ 39,7\\ 43,3\\ 44,8\\ 46,3\\ 50,4\\ 51,3\\ 53,7\\ 62,0\\ 62,8\\ 65,2\\ 69,0\\ 70,7\\ 75,5\\ 78,3\\ 79,3\\ 82,5\\ 83,8\\ 84,7\\ \end{array}$	3,440 3,339 3,143 2,968 2,849 2,639 2,557 2,338 2,270 2,090 2,022 1,961 1,810 1,780 1,707 1,497 1,480 1,431 1,361 1,322 1,259 1,220 1,209 1,154 1,144	$ \begin{array}{c}$		$ \begin{array}{c} 9\\\\ 10\\\\\\ 10\\\\\\\\\\\\\\\\\\\\ -$	3,442  2,963  2,093  2,093  1,780 1,780 1,707  1,480 1,359 1,324  1,209  1,141

Ni-skutterudite (chloantite)—NiAs<sub>3-2</sub>—CoAs<sub>3-2</sub>—is another of newly identified minerals of the ore district of Vrančice. It occurs always in a paragenesis with nickeline. Its occurrence is very rare. As it was told above, it was found in the same ore material from Slavík vein as nickeline, i.e. it is associated with the same minerals.

#### TABLE 6

Roentgenometric identification of Ni-skutterudite (chloanthite) from the Slavík vein— Vrančice. Debye-Scherrer method, radiation  $FeK\alpha_{1,2}$ , Mn-filter, 24 kV, 22 mA, exposition 7 h, cell-diameter 57,3 mm, glass-hair, reference substance A1 ( $a_0 = 4,0483$  Å).

	Ni-skutteru +	dite (chloant - sphalerite Vrančice	hite)	Chlosr	oanthite- naltite Michee	Spha ev (1957)	lerite
No.	I	$2 \Theta$	dÅ	I	d kX.	I	dkX
$\begin{array}{c}1\\2\\3\\4\\5\\6\\7\\8\\9\\10\\11\\12\\13\\14\\15\\16\\17\\18\\19\\20\\21\\22\\23\\24\\25\\26\\27\\28\\29\\30\\31\\22\\23\\33\\34\\35\\36\\37\\8\\39\end{array}$		$\begin{array}{c}$	$\begin{array}{c}$	$ \begin{array}{c} 5\\6\\5\\-\\-\\-\\6\\-\\-\\-\\-\\-\\8\\3\\-\\-\\-\\-\\8\\-\\-\\-\\-\\-\\-\\-\\-$	$\begin{array}{c} 6,0\\ 4,2\\ 3,4\\\\ 2,9\\\\ 2,64\\\\\\ 2,22\\ 2,07\\\\\\ 2,22\\ 2,07\\\\\\ 1,95\\\\ 1,95\\\\ 1,95\\\\ 1,95\\\\ 1,69\\\\ 1,63\\\\\\ 1,69\\\\ 1,63\\\\ 1,43\\ 1,38\\\\ 1,43\\ 1,38\\\\ 1,43\\ 1,38\\\\ 1,20\\ 1,20\\ 1,17^1)\\ 1,15\\ 1,13\\\\ 1,09\\ 1,05\\ \end{array}$	$ \begin{array}{c}                                     $	$\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$

<sup>1</sup>) Coincidence of Al-line

It is macroscopically observable only by binocular microscope. It is of whitish colour and has a relatively high metallic luster. Microscopically, it is possible to observe in fine grains of this mineral a strong tendency to idiomorphous limitations and to a zonar construction. In reflected light, it is of white colour and has a high reflexion, higher than that of galena. It is isotropic under crossed nichols, but several parts are also distinctly anisotropic; it results from the fact that they are in general very complicated mixtures of Ni (Co) -minerals, called by P. R a m d o h r (1955) with a common title "Weissnickelkies". This mixture is formed by rammelsbergite, skutterudite (=smaltite) and chloantite (designated also Ni-skutterudite, if the Co-component portion has to be expressed, because the skutterudite- and chloantite-components are mixed together in different ratios). The named mineral mixture is in general dominated by one mineral. It was stated by our X-ray researches(table 6) that the so called "Weissnickelkies" of Vrančice is formed preponderately by a mineral of the skutterudite group. The d-values of strongest lines approach most to the d-values of V. I. Micheev (1957) for the mineral group chloantite-smaltite. The X-ray pattern of the Ni-mineral contains also lines which belong to the heterogene admixture of sphalerite. The lines did not show the presence of rammelsbergite in the mixture of Ni-minerals, but its existence may be presumed from certain parties showed as anisotropic by the microscope.

The qualitative spectral analysis showed also (table 11) that the studied mineral constains main constituents of construction Ni, As and Co. Other stated elements cannot be discussed for the fact that the separation would be more difficult than that of nickeline; so it would not be possible to replace heterogene admixtures of ore minerals.

#### Fe-minerals and other

**Pyrite**— $\text{FeS}_2$ —belongs to less abundant minerals of the ore veins of Vrančice. Its occurrence in Pošepný vein is noticed by V. Hanuš (1955) and A. A. Malachov-J. Kouřímský (1956). J. Pokorný (1955) and A. A. Malachov (1956) mention it also together with minerals of Mo-paragenesis in Jan mine. I detected it during my new mineralogic researches in all the studied veins. It is most current and abundant in Babánek vein. Pvrite forms fine grains often of idiomorphous nature concentrated as smaller exclusions of original accompanying rocks of the ore veins. Pyrite forming greater local concentrations, often in form of lens, has another form of occurrence; it is associated with other minerals of the veins, especially marcasite and quartz with calcite. It forms also fine-grained veinlets in Babánek vein. This younger pyrite forms very often aggregates apparent by their concentric and platy construction, similar with that of marcasite. It was stated by X-ray controls that it is in most cases pure pyrite with a normal internal structure. This pyrite was identified, beside concentric aggregates, even in form of porous kidney-shaped aggregates (Alexandr mine). Pyrite was also identified very rarely crystalised in fine grains of druse-cavities of calcite.

It was stated microscopically that some parties of concentric or collomorphous construction are very similar to melnikovitpyrite described by P. Ramdohr (1955).

From the results of quantitative chemical analysis and qualitative spectral analysis and in accordance with the literary data it is evident that beside the main components of construction following isomineral elements in the pyrite of Vran-

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čice are present: Ag, As, Co, Ni, Sb, Tl. Arsenic (2,52 %) and antimony (0,06 %) are the most represented of the series of the cited elements. The two elements can replace the double ion  $[S_2]^2$ - in pyrite. The Co- and Ni-contents are common. A regular presence of nickel is observable in the occurrences of Vrančice; the presence of cobalt was identified only in pyrite from Slavík vein. Also Tl- and Ag-contents are often cited in the analyses of pyrites; their bond however is not quite clear.

Marcasite—a rhombic form of  $FeS_2$ —is much less quantitatively represented than pyrite in the vein of Vrančice. This mineral is not cited by older authors from the ore district. During my own researches I was successful to identify it microscopically in the ore material from the veins Pošepný, Slavík (in accessoric amounts) and Babánek. The optical identification was verified also by X-rays.

Marcasite is always present in an association with pyrite in aggregates which overgrow one another. It is mostly fine-grained, rarely it forms even short columnal crystals. It is microscopically distinguishable from pyrite (in polished sections) by its mat luster of polished surfaces; under crossed nichols it is rather strongly anisotropic with colour effects of red-blue-greenish.

The chemism of marcasite is in practice analogical to that of pyrite. Ag, As, Co, Ni, Sb are classified as isomineral elements. It is very probable that all these elements detected even by our spectral analyses may be at least partly considered as isomineral. A more extensive discussion, especially that of the presence of trace elements, is in practice impossible by the fact that the samples were very impure by components of ore veins which could not be replaced. The only difference between marcasite and pyrite is the absence of Tl in marcasite.

Arsenopyrite—FeAsS—is a very rare mineral of the ore district of Vrančice. It was not detected directly in the veins, but only in altered accompanying rocks. Its presence in the Václav pit is cited also by J. K o u říms k ý (1956). Beside this, I found it in altered rocks of Alexandr mine (Pošepný vein) and Slavík mine (Slavík vein).

Arsenopyrite forms very small idiomorphous crystals, observable just under microscope. It has a considerable reflexion and a white colour in reflected light, under crossed nichols it is apparently anisotropic with the effects of red-blue colour.

**Pyrrhotite**—FeS—was not at all detected in polymetallic veins at Vrančice. Its solitary occurrence in the district of Vrančice is recorded by J. P o k o r n ý (1955) and A. A. M a l a c h o v (1956) from the ore paragenesis, which is probably in no coherence with the polymetallic veins. It occurs in a paragenesis with molybdenite, Ti-magnetite (with off-mixed ilmenite) and chalcopyrite, with which it is associated very closely. J. Pokorný detected a beginning alteration in fine-grained mixture of pyrite and marcasite in fine cracks.

Molybdenite—MoS<sub>2</sub>—was not detected in polymetallic veins of Vrančice; its interesting, but quite solitary occurrence was recorded by J. Pokorný (1955) and A. A. Malachov (1956) in a paragenesis in plutonium-rocks, which was found during the dipping of the Jan mine.

Molybdenite formed here big leaves having a might of several mm, of a gray colour and a metallic luster. It forms an independent paragenesis together with magnetite (ilmenite), pyrrhotite, pyrite and chalcopyrite.

It is necessary to bring out at the end of this chapter that the mineral association at Vrančice is very coloured and rich in a number of minerals; this does not mean anyhow that the review would be perfect. Discoveries of other minerals which will

throw more light to total geochemically-mineralogical relations of this ore district are always to be presumed. It depends upon further exploitation of the ore veins in vertical and horizontal direction, which may result in many mineralogical discoveries of great value.

#### V. Paragenetic and successive conditions in the Vrančice ore veins.

The paragenetic and successive conditions in the Vrančice ore veins show a great variety which renders them highly complicated. At the present state of investigations the different evolutionary phases or mineralisation stages are sometimes difficult to be explained univocally from the genetic point of view. This chapter therefore summarizes all knowledge obtained by an exhaustive study of the Vrančice ore veins and on its basis the proper opinion of the paragenetic and successive conditions is given or discussed.

In the Vrančice ore veins several parageneses may be distinguished the origin of which was primarily conditioned by certain PT conditions varying during the evolution of the ore veins. There are also cases where the mineral association is constituted by different parageneses having had a different genesis. A general illustration of the mineral parageneses in the Vrančice ore veins is given in table 7.

TABLE 7

Mineral Paragenesis of the Veins in the Ore-	District Vrančice
Determined Minerals	Character of the Mineral Paragenesis
Ti-magnetite, ilmenite, molybdenite, pyrrhotite, chalco- pyrite	Intramagmatic stage (altered rocks)
Arsenopyrite, pyrite, quartz, carbonate	Alteration of rocks
Quartz I, haematite-specularite, nickeline, Ni-skut- terudite (chloanthite), sphalerite, siderite, quartz II, bournonite, tetrahedrite (tennantite), chalcopyrite I, dolomite, baryte, quartz III, boulangerite, galena, chalcocite, bornite, chalcopyrite II, antimonite, quartz IV, haematite, calcite I, quartz V, pyrite, marcasite, calcite II	$\operatorname{Hydrothermal}$ stage
Willemite*, quartz, chalcocite*, bornite*, argentite?*, pyrargyrite*, stromeyerite*, native silver, native cop- per, goethite	Supergene stage a) Zone of cementation
Malachite, azurite, rosasite, cuprite, chrysocolla, haema- tite, covellite, limonite, powdered calcite, bindheimite, apophyllite, anglesite, polianite	b) Zone of oxidation
Limonites (hydrox. Fe, Mn), vésigniéite, quartz	c) Iron-hat

#### Notice:

\*) Minerals of uncertain origin mainly cementation

3\*

The individual parageneses can represent on one hand a certain stage of mineralisation, i. e. they approximately correspond to the time periods of the evolution of the ore veins and on the other hand they partially coincide.

One of the oldest ore parageneses in the Vrančice ore district is the mineral association described by J. P o k o r n  $\circ$  (1955) and immediately thereafter also by A. A. Malachov (1956). It occured in the form of accumulations in the grandiorite body during the deepening of the Jan pit. Its constituents are coarse-grained amphibole, biotite and ore minerals such as Ti-magnetite with mixed-off ilmenite, pyrite, molybdenite, pyrrhotite, chalcopyrite and pyrite with marcasite produced from pyrrhotite. From the mode of occurrence J. Pokorn $\circ$  concludes that the origin of this paragenesis may be in connection with analogous conditions present at the genesis of minerals in skarns. This single mineralogical occurrence, however, did not permit the finding of closer relations to the proper ore veins. Nevertheless it is very probable that no direct genetic connection exists in this case.

A number of minerals produced during the hydrothermal stage of the formation of the ore veins constitute certain paragenetic wholes. The group of minerals the genesis of which cannot be explained univocally as hypogene has been included in the general succession scheme, however with the remark: "obscure origin". To express the different periods of the evolution of the veins the terms "mineralisation stage" and "mineralisation phase" are used and on their basis the probable general scheme of succession has been worked out.

The term mineralisation stage is employed in the sense of D. N  $\check{e}$  m e c (1958) and represents the period of mineralisation processes which took place in the interval between the tectonic movements (so called intermineralisation movements). This term corresponds to the "tectonic evolutionary stage" proposed by Z. Pouba-Z. Ve j n a r (1955). By its meaning it is very close to the "inlet-period" of J. Kutina (1955). The conception of the latter presumes however the determination of common uninterrupted material-inlets for which I had not always firm criteria and for this reason I did not employ this narrow genetic term. I adopted the term proposed by D. Němec (1958) which deals rather with the descriptive side of the matter. The mineralisation phase means the period when the crystallization of paragenetically related minerals took place. This phase was conditioned by the existing PT conditions and the chemism of solutions, partial small tectonic movements not being excluded. This conception was applied by J. Hak (1959). In this respect the term "mineralisation phase" corresponds to a certain extent to the "evolutionary stage" of J. Kutina (1955), and partially coincide with the term "paragenetic evolutionary stage" and "crystallization period" employed by Z. Pouba-Z. Vejnar (1955).

When working out the succession I proceeded first of all from the minerographic study of the polished sections of the ore samples and as far as the character of the vein filling allowed it also from the study of the macrotextures. Banded symmetric textures are relatively rare, more frequently sections with asymmetrically developed texture may be encountered. Nevertheless, the study of macrotextures is usually complicated by the massiveness and the brecciated character of the vein filling. A further complication making the recognition of the structural and textural features difficult is a frequent, very intense repulsion of older vein minerals by younger ones. This process goes so far as to obscure the features important for the distinction of tectonic factors playing a part during the evolution of veins (opening and closing of

fractures, crushing etc.). In the Vrančice veins there are, in fact, frequent cases of so called "fossil frontier" of first and exceptionally second degree in the sense of J. K u t i n a (1956). This refers especially to quartz I and II, to sphalerite and galena, eventually to tetrahedrite and chalcopyrite. The difficulty in working out the succession consisted also in irregular occurrence of ore minerals (sometimes only in accessory amounts). From this standpoint, the graphic representation of succession is to be understood as a scheme corresponding more or less in certain phases or stages to the presumed reality. From the general analogy in the paragenetic character of veins as well as from the successive uniformity and geological position it can be gathered that a common long-duration minerogenetic process conditioned by certain characteristic geochemical processes took place in the ore district. Eventual differences in paragenetic or successive conditions in individual veins are due to different factors, the most important being local changes in the chemism of solu-

				MAI	N STAGES OF MINERALISATION		
MINERAL	1/1	1.	1/3	11/1	//. ///2		IV.
Quartz .	<u> </u>	-toroneronarco				Contraction of the second s	
Pyrite	1-					5	-2-
Arsenopyrite	1 -	1					
Carbonate /ankerite/	1	4					
Haematite /specularite /	12-						-
Nickeline		-					
NI-skutterudite-chloanthite	1	1 · · -					
Sphalerite	1				l .		
Siderite	1	1	Concerns of the local data				
Bournonite		1 -					
Tetrahedrite		1		(1000000		1	
Chalcopyrite	1	1					
Dolomite	1	1					
Baryte	1	1	a		ferrel and and		1
Galena		İ.		1	deter S and	1.11.16	1
Boulangerite	1	1				410.00000000000000000000000000000000000	
Chalcocite		1				108	1.1
Bornite	1	1	1			.*.	
Antimonite	1	1				<u>-</u>	1
Willemite	1	1					
Calcite		1				LESIGN	1.5.5
Argentite ?		1					and the second second
Pyrargyrite	1						
Stromeyerite .		1	l l				
Silver native	-			2		-	
Copper netive		1					
Goethite	1	1				····*	
Marcasile	1		1				5
STAGES	Altero tion	Ni-min+SiD exsolution	ZnS + FeCOs exsolution	Gu,Sb min.+SiO exsolution	Pb,Cu,Sb min., BaSO4+Ca,Mg /CO3/2 exsolution	Cementation	Fe-min.+OaCo exsolution
ETAPES	QUA	RTZ-SPHA	LERITE		SULPHIDE	CARBONATE I.	CARBONATE
	E	Ni	(Zn) Fe, Mn	Cu Fe Pb	(PD) CUFE	(Mn) Fe	Mn, Fe
Subsignital elements /ore/	S,	As	s	S, Sb,As	S,Sb	ZeGaAg S	O, OH, S
Rare and trace elements	Bi.C	Co,Cu Sn	Ag.As,Bi,Cd Ço,Çu,Ga,Ga	Ag,Bi, Cd,Hg Mn,Ni, Sn,Zn	Ag, As, Bi, Ni	And Carto Pb	

Table 8 The possible design of succession of ore veins of Vrančice.

#### NOTICES:

definite or possible position of the mineral in the succession

- possible position of the mineral in the succession undefinite position of the mineral in the succession
- minerals of uncertain origin mainly comentation and correlating elements

leading elements

tions, in the concentration of elements and in the regime of opening and closing of the fractures. In the Vrančice ore veins four mineralisation stages have been distinguished and these stages are subdivided in several phases.

The begin of the "quartz-sphalerite" stage is connected with the alteration of tectonicaly affected rocks, the solutions being probably rather sterile. During these attacks of rocks by hot solutions, typical alteration phenomena of rock-building constituents were caused and some lithophile eventually siderophile elements were set free and mobilised to react with thermal solutions. The result of these chemical reactions was the crystallization of pyrite, event. arsenopyrite, quartz (silification) and carbonate (carbonatisation). In the accompanying rocks a certain relation between the products of alteration (sericite, chlorite etc.) and the concentration of quartz (carbonate) as well as pyrite (arsenopyrite) in rocks may be followed. From this may be concluded that the above mentioned processes coincided as shown in the scheme (tab. 8). Pyrite and arsenopyrite are concentrated mainly in altered rocks without being, however, associated with the druse-quartz I and with specularite. Intensified impregnations near the ore vein may be considered as pyrite I, because cases of even older pyrite the genesis of which is connected with the crystallization of magmatic rocks cannot be excluded. During the further phase of mineralisation the bulk of the quartz I crystallized in the form of short crystals which together with specularite in the form of druses fill the fractures of rocks. The question of the mutual relation of both minerals has been discussed correctly by V. H a n u š (1955) and a mutual partial coinciding of crystallization intervals may be presumed. During this phase an insignificant amount of Ni-minerals was separated and grows sharply, without any transition, on quartz I with specularite. The close of this mineralisation stage is marked by the crystallization of the chief mineral in the Vrančice veins which is sphalerite. This mineral filled in mostly mechanically the existing open fractures being not yet completely filled with quartz I and specularite. Sphalerite grows sharply on this quartz, without any transition, only in exceptional cases a weak corrosion of quartz may be observed. At the close of the mineralisation stage siderite which is in succession younger than sphalerite crystallized. Its relation to quartz II, however, is usually considerably obscured and it is not out of question that the crystallization interval persists until the second stage. The Ni-minerals are older in succession than sphalerite which repulses them selectively.

The crystallization of minerals of the first mineralisation stage was followed by relatively intense tectonic movements. During this period the crushing of the existing vein filling and the opening of new (and possibly also closing of old) fractures took place. The second mineralisation stage, called sulphidic, begins also with the crystallization of quartz followed by Cu, Fe, Pb, Sb-sulphides as well as by sulphosalts with baryte and dolomite. In this stage two phases, a younger and an older one, may be distinguished. They differ somewhat in concentration of chief ore elements in solutions and are also separated by local tectonic movements.

During the older phase of this stage considerable masses of quartz II, bournonite tetrahedrite and chalcopyrite I crystallized. Bournonite grows sharply, without any transition, on quartz II. Its crystallization interval coincides partially with that of tetrahedrite, sometimes being difficult to decide which mineral is older or younger. Most frequently tetrahedrite is somewhat younger. In the ore material from the Pošepný vein minerographically rare parts were encountered, where tetrahedrite is intensively intruded by chalcopyrite I. From the structural forms produced in such a way I conclude that this is due to a partial coinciding of crystallization intervals. During the younger phase a small amount of dolomite, baryte and locally in the Babánek vein also of small crystals of quartz III (growing on tabular baryte) was separated. Furthermore it was 'galena, boulangerite, chalcocite, bornite, chalcopyrite II and antimonite. Certain minerals of the second phase repulse rather intensively those of the first phase and send veinlets in them. Above all it is a strong repulsion of tetrahedrite, eventually of bournonite by galena which is widely distributed in all the Vrančice veins. Sometimes the galena intrudes the tetrahedrite veinlets-like, but more often it swallows the whole tetrahedrite masses whereby irregular relic forms of different size are left in galena. Chalcopyrite II penetrates older minerals of the first stage mostly veinlets-like. The intrusion of galena and chalcopyrite was frequently observed at the contact frontiers of quartz II—tetrahedrite or of sphalerite — tetrahedrite. The crystallization of dolomite, baryte, quartz III and galena went on progressively as expressed graphically in the scheme. It cannot be excluded that the quartz began to crystallize still at the close of the separation of the baryte.

The question concerned with the relation of galena to chalcocite and bornite has been correctly discussed already by V. Hanuš (1955) and A. A. Malachov-J. Kouřimský (1956). As regards succession, galena is older than chalcocite and bornite. The galena is sometimes very intensively repulsed by chalcocite which results microscopically in the formation of graphic intergrowths. These intergrowths are usually considered as decomposition structures produced by the separation from a solid solution at a decrease in temperature. In the case of the Vrančice occurrences of galena with chalcocite and their graphic intergrowths it may be proved that it is a metasomatic repulsion as shown and discussed in detail by V. H a n u š (1955). Chalcocite as a younger mineral often penetrates along the limit of sphalerite—galena. After galena and chalcosine the youngest minerals of this stage, namely bornite with chalcopyrite II crystallized. Both minerals are very closely connected as regards crystallinity and form typical lattice structures originating by the decomposition of a solid solution at the decrease in temperature. Bornite and chalcopyrite II repulse commonly veinlets-like nearly all ore minerals older in succession, especially sphalerite and galena. It is obvious that the crystallization interval of chalcopyrite II is considerably large and very probably coincides with that of galena and chalcocite and eventually of antimonite.

During the second mineralisation stage a negligible amount of boulangerite and antimonite crystallized. Their position in succession could not be determined univocally because of the lack of material. In the case of boulangerite it is certain that it crystallized during the second mineralisation stage, that it is younger than sphalerite, quartz II and bournonite and that a mutual coincidence with the crystallization interval of galena might have occurred. The position of galena in the succession is not guaranteed to be correct, nevertheless it may be considered as one of the youngest ore minerals of the Vrančice ore veins.

Most minerals of the second stage refill the cracks and directly repulse the cataclastic minerals of the first mineralisation stage, especially sphalerite. The crystallization of minerals of the second and third mineralisation stage was separated anew by tectonic movements which, however, did not reach by far the intensity which occurred between the first and second mineralisation stage.

The third mineralisation stage—that of carbonates I—is marked by the crystallization of non-ore constituents, mainly of quartz IV, haematite, goethite and calcite. During this stage which means the waning phase of the principal mineralisation process and which took place at very low temperatures, the separation of some minerals occurred. To these minerals the genesis of which has not been explained satisfactorily so far, belong willemite and the group of sulphidic minerals as well as pure metals such as chalcocite, bornite, paragyrite, argentite(?), stromeyerite and native Ag and Cu (with the exception of willemite they may be considered as products of the cementation processes). The mutual position of willemite and of the minerals included in the third mineralisation stage was dealt with in detail by J. Kouřimský in the paper A. A. M a l a c h o v - J. K o u ř i m s k ý (1956). His partial observations are correct and have been adopted in a simplified form in the general scheme.

The crystallization intervals of minerals of the third mineralisation stage very probably coincide. The largest one is probably that of calcite. The appartenance to the third stage of a small amount of pyrite ascertained in the cavities of calcite I is not out of question. The ore minerogenesis has been practically closed by the third mineralisation stage. It was followed again by a period of very intense tectonic movements which in some places brought about the crushing of the vein filling. This is especially conspicuous in the Pošepný vein. The old channels of supply were closed and new fractures originated, filled later by the minerals of the fourth mineralisation stage—that of carbonates II.

The characters (geological position, character of paragenesis etc.) of this youngest mineralisation stage hitherto stated provide evidence that this stage is not immediately connected with the ore parageneses of the first three mineralisation stages. It may be supposed that the crystallization of minerals of this last stage, namely of quartz, haematite, calcite, goethite and pyrite with marcasite took place in a period which was separated by a considerable time interval from the third stage. Striking are also textural and structural features (frequent colomorphic structure of calcite and goethite, radiated concentric structures of goethite and pyrite with marcasite) which suggest the origin from very low temperature solutions, probably of colloidal nature. As no other criteria have been found so far I suppose that the crystallization intervals of the minerals of the fourth etape coincided. The problem of classification of pyrite with marcasite the accumulations of which were encountered mostly in association with calcite, remains obscure. More signs pointed to the youngest stage and for this reason pyrite with marcasite have been assigned to the beginning of this stage, their position being however indicated as not guaranteed.

From the actual knowledge of the mining conditions in the Vrančice ore district and from the present state of investigations it may be concluded that the fourth mineralisation stage means the end of the minerogenesis in this region. In later phases further tectonic movements, accompanied by the processes of mylonitisation, occurred.

Former authors did not deal in detail with the question of the genesis of willemite. V. H a n u š (1955) includes it among hypogene minerals without giving further proofs of this classification. A. A. M a l a c h o v - J. K o u ř i m s k ý (1956) indicate that its origin is conditioned by a certain local migration of Zn. His hypothesis is however not supported by any proofs which could be discussed. As willemite cannot be considered as an absolutely hypogene mineral (according to the analogy of the mode of occurrence in different world deposits), its genesis in the Vrančice region should be considered.

On the whole, more than 30 occurrences of willemite from different world deposits are known. Among European countries: Germany, Belgium, Portugal, Norway, Italy and Czechoslovakia (the only deposit hitherto known is in Vrančice), furthermore Central Asia, Indochine, Africa, Rhodesia, Mexico and USA. In nearly all cases the genesis of willemite is explained by supergene processes occuring in zinc deposits. Only exceptionaly (for example in the case of the deposit in Franklin-Fournace USA) it is indicated that willemite was produced at high temperatures in a contact metasomatic type of deposit.

How to explain the genesis of willemite in Vrančice? The genesis at high temperatures is excluded in advance as in no case minerogenetic conditions analogous to those present at the origin of such ore parageneses as for example in the Franklin deposit, could be ascertained. Another possibility is the supergene origin. This hypothesis is supported mainly by the common occurence with the typical minerals of the oxidation zone of sulphidic deposits.

In the case of the Vrančice occurrence of willemite it may by stated that it occurs frequently in association with haematite, goethite, quartz (mainly with zonary quartz; chalcedone-quartzine), thus with minerals which may also point to its As further proof for supergene origin the concentration of descendance origin. willemite in places of considerably altered adjacent rocks and in leached parts of the sphalerite vein could be considered. Also its common occurrence with sphalerite when it is frequently concentrated in the ore in the form of fine-grained to powder fillings is suggestive for this genesis. On the other hand, the general localisation of the deposits of willemite is in contradiction with the descendance origin. Mineralogical and phase chemical determination would permit us to indicate sectors with willemite occuring both in upper horizons with typical minerals of an oxidation zone and in a transition zone where it is encountered with cementation and primary minerals. Nevertheless, when descending downwards, willemite continues to be found with dominantly primary ores. As regards the space, the concentrations of willemite form a kind of mantle on the principal ore body which is dominantly of sphalerite. Higher concentrations are met with both in nothern parts (in southern parts willemite disappears) and in the zone where the occurrence of cementation minerals may not be expected. Even though a certain decrease in the willemite quantity with the depth may be recorded, it cannot be said that it is confined exclusively to the cementation zone.

At the present state of things the probable genesis of willemite in the Pošepný vein could be best explained by the theory of H. Schneiderhőhn (1941) concerned with so called secondary hydrothermal processes which are conditioned by the revival of old tectonic structures. It may be supposed that the solutions from which willemite crystallized were produced by the mixture of juvenile non-ore therms (having brought about the setting free of zinc from sphalerite ore portions) with vadose solutions containing especially SiO<sub>2</sub>-mass (set free from rocks). This hypothesis is not in contradiction with the Schneiderhőhn theory. It is very probable that these solutions were of colloidal character. This assumption is supported by the structural forms of the occurrence of willemite as well as of the minerals of zonary quartz, namely of chalcedone-quartzine and goethite which presumably have had common genesis with willemite. For the time being it remains to elucidate what was the tectonic structure which influenced the presumed secondary hydrothermal processes in the Vrančice region. According to the space distribution of the ore parageneses and to certain difference, for example in quality and in the might of ore-forming, the ore district may be divided into two parts, namely the north-western and south-eastern. It is presumed that this limit would roughly correspond to some old tectonic structure of Variscian direction (NE-SW) renewed, at least partly, by later tectonic movements.

Another question discussed is the existence of cementation zones in the Vrančice ore veins. On the basis of my last studies I reached the conclusion that the cementation processes really took place in the Vrančice ore veins. The most convenient for these studies is the Pošepný vein, both by the greatest depth of exploitation and by its unique zonality (in comparison with other veins). Here may be followed a continuity from the uppermost zones of oxidation through the cementation zone to the primary deposit. I consider the following minerals as cementation minerals: chalcocite (though there is also hypogene chalcocite in the Vrančice veins), covelline and perhaps also bornite (the bulk of bornite being however hypogene), Ag-ores, pyrargyrite, stromeyerite, argentite(?), and finally native metals Ag and Cu.

I consider as cementation chalcocite especially its lump-fillings in the upper parts of the south-east part of the Pošepný vein, where the paragenesis of Cu-ores concentrates also in increased quantities. Thus, in their original positions the accumulation of lump-chalcocite occurs. In addition to the facts already cited, geochemical reasons point to the existence of descendance chalcocite. The descendance origin of covellite which forms mostly coatings on chalcocite is indiscutable. The cementation bornite could not be always recognized unequivocally. The native metals Ag and Cu along with Ag-ores such as pyrargyrite, stromeyerite and argentite(?) occur mostly in association with lump-chalcosine and fill most frequently fine fissures and cavities in the ore. This is suggestive of their descendance origin. On the other hand it is true that the Ag-minerals are disseminated also in other places of the ore and also in its deeper portions where the cementation processes cannot be presumed with certainty.

It is also important to mention the distribution of certain mineral parageneses or associations in the Vrančice ore district. The most widely distributed is the paragenesis of the quartz-sphalerite stage which in all ore veins studied for mining purposes was ascertained. The content of sphalerite as chief mineral of this paragenesis increases with the depth. The might of sphalerite ore-forming principally occupies the middle to northern sections of the above mentioned SE part of the ore district. The ore parageneses of Cu-ores (first phase of the second mineralisation stade) and of Pb-ores (second phase of the second mineralisation stage), younger in succession, are distributed on the one hand in tectonic fractures already filled with older minerals (dominantly with sphalerite) and on the other hand they form independent fillings of newly opened cracks. In the present state of the opening of the ore veins it may be supposed that the parageneses with Cu-ores are situated especially in the southern sections of the SE part of the ore district and that their concentration increases with the depth.

In the northwestern part of the ore district a decrease in the extent of ore-forming may be noted sometimes to the disappearance. In the northwestern parts of the Pošepný vein willemite accumulations also occur and in some places the paragenesis with prevailing galena plays an important part.

The non-ore paragenesis belonging to the youngest mineralisation etape mostly fills the newest fractures in independent veins. In certain sections it penetrates even along the vein fillings of older mineralisation stages (cementing the crushed portions).

The Vrančice ore veins thus represent typical polymetallic deposits which occupy an exceptional position in the metallogenetic province as has already been shown by V.  $\mathbf{H}$  an  $\mathbf{u}$  š (1955). Apart from the chief ores Zn-Pb the ore deposits are, in fact, constituted by a considerable amount of Cu-ores which is uncommon for this province. Also the regular predominance of sphalerite over galena distinguishes in general the Vrančice veins from for example the Příbram veins where galena is dominant.

# Geochemical part

# VI. Geochemical evolution of ore veins of the Vrančice district

During the geochemically-mineralogical research almost hundred spectral analyses of minerals separated from the Vrančice ore veins have been effected. The general illustration as to the geochemical character of individual veins is given in tables 9, 10, 11, 12 where the mineral constituents of the veins are indicated together with their chemism determined by the qualitative spectral analysis. There are, however, several minerals which could not be analysed because of the lack of material.

From these tables it may be gathered that the dominant ore elements are Zn, Pb, Cu, Fe. In addition, Ag, Sb, As and Cd play a part as macroelements. The above mentioned elements appear also as microelements in some minerals, namely in the cases where in a certain evolutionary stage their concentration in solutions was low or the existing PT conditions were unfavourable to crystallization of certain minerals permitting these elements to play a part as rock-building components.

Among the other ore elements identified in Vrančice some preserve the character of microelements during the whole evolution of vein, or their concentration increases only in local cases.

One of these elements is Sn. Its presence in the Vrančice vein minerals is characteristic, an increase in concentration being sometimes recorded in such minerals as for example sphalerite and galena. In spite of that, Sn could not be ascertained as self-mineral. Very characteristic, almost common element in the minerals of the Vrančice ore district is Cd the concentration of which varies in the range from traces to the tenths of percent. Its chief bearer is sphalerite. In certain cases the isomineral form of occurrence in tetrahedrite, boulangerite and probably also in chalcocite may also be considered. Among other elements of this category Bi should be cited. It occurs in Cu-minerals such as tetrahedrite, bornite, bournonite and also galena. In this connection it is interesting to note that it has not been ascertained in chalco-Further microelements are Ga, Ge and In the chief bearer of which are pvrite. sphalerites but also haematite, bornite (Ga, Ge), tetrahedrite (Ge, In), chalcocite (Ga, In), willemite (Ge), goethite (Ge). A relatively characteristic element is also Hg occuring mainly in sphalerite and tetrahedrite. The mercury has also been found in all minerals where relatively low to very low temperatures of genesis are presumable (pyrite, native silver, pyrargyrite and possibly also chalcosine).

Rare singly occuring microelements are Co, Ni, Mo, Tl and Y. Cobalt was ascertained as isomineral element in boulangerite, tetrahedrite, pyrite and marcasite. As a building component it plays a part only exceptionally in nickeline and Ni-skutterudite (chloantite) which, however, occurred only in accessory amounts. In addition, cobalt was found in sulphidic minerals from the molybdenite paragenesis from the Jan pit where it appears as isomineral only in pyrrhotite. Nickel is bound to pyrite, marcasite and tetrahedrite. The regular presence of Ni in the chalcopyrites of the Vrančice veins remains unexplained. As a building component nickel played a part exceptionally in nickeline and Ni-skutterudite which, however, occur only sporadically and in accessory amounts in the ore district. Molybden is a non-characteristic element of the Vrančice ore veins. In case of marcasite, galena and nickeline the

isomineral bound may be considered. As chief building constituent Mo occurred singly in the paragenesis in the Jan pit. A very rare element of the Vrančice veins is thallium of irregular occurrence in pyrite and galena. In three cases trace occurrence of yttrium—calcite, siderite and pyrargyrite was ascertained in the analysed minerals. Yttrium may be found in carbonates. In pyrargyrite it appears rather as anisomineral element.

Table 9 Qualitative spectral analysis of minerals from the Pošepný vein-Vrančice.<sup>2</sup>)

MINERAL	Ag	AI	As	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	Ga	Ge	Hg	in	Mg	Mn	Мо	Na	Ni	РЬ	56	si	Sn	Sr	Ti	TI	v	Y	Zn
Baryîe		0	+	空間		1.		-	1	1	•	•	+	1	-		•	•			-	•	-	0	•		ş	-	-		•
Bornite		•	•				0	0			1 TE		•	•			•	•	•			•	0		0			1			
Boulangerite	0								•			•										100 in 17 in 19	*	0							
Bournonite	•	•					6	0			14.6	•			0		0	•			Ģ			0	0						
Calcite	٥	0		•		1		•									•						•	0			0				•
Mn-calcite								0			•										8	۲		0	1	0	•	-			•
Galenite		0			1.	1		•	.r.						•		•	•							0			•			•
Goethite					٥						•						0	•	•		•	•									
Haematite			0	•	•			0			•	ALC: N				٥	•	0	0		0	•	0		•	•	•				
Chalcocite	10	•						•					) •		•	•	•	•					•	0	0		8	1			0
Chalcopyrite	0	0	•					0						ŝ	•		0	•			•	•	0		0		0				
Malachite	6		0				0					6	)		۲								0				2				0
Marcasite	8	•				•	0	0	•		-				•		e	0	6	S	0						1.1.1		1.54		
Pyrargyrite	1		0			•		•							9		۰				•			1.	•					0	
Pyrite	0						0				0				۰		•				•	•	0				ş				6
Quartz	•	0					•	8			0		)				0				•	•	•	2.4			2	1			
Siderite	0	•									•	44				•					•	•			1						•
Silver native											0	•			0		•	•				•	•	0							•
Sphalerite	•	•					0	No.				腰	•		0	0	•	•					0		0						
Stromeyerite		•	0	•		•		•	•	0				•			•	•					1		•						
Tetrahedrite		0					0		•						0		•	0			•	0			•		1				
Willemite		•	۰					•			•											•		1			•		•		

<sup>2</sup>) All qualitative spectral analyses were made by a collective of the spectral laboratory headed by Dr. J. L i t o m i s k  $\pm$  under following conditions: A Zeiss-Jena Q 24 spectrograph with alternating arc 8 A with a DG 1 or ABR 3 generator. The spectra of pulverised samples were obtained in an arc of carbon electrodes (cylindric, thin sides) ČKD Stalingrad, distance 3 mm, the screen T 10-5, diaphragma 3, 2, the cell-screen 1 : 15, slot 0,003 mm, time of exposition 30 sec, without pres-cintillation. A "Foma super ortho" was used as the photographic material. For obtaining a regular combustion, samples were mixed with carbon powder. Cited conditions are found optimal for complete qualitative spectral analysis and were carefully realised during the operation of all samples. The presence of following elements was searched for by the spectral qualitative analysis: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, F, Fe, Ga, Ge, Hg, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Sb, Sc, Si, Sn, Sr, Ta, Ti, TI, U, V, W, Y, Yb, Zn, Zr.

Semiquantitative amount of positively detected elements is represented in the tables 9-12 by following symbols:

Substantial amount (»1%)	• •	
Subsidiary amount $(>1-0,1\%)$		
Accessory amount $(0, 1-0, 01\%)$	• •	0
Trace amount $(<0,01\%)$		•
Problematic amount		?

MINERAL	Ag	AI	As	Ba	Be	Bi	Ca	Cd	Co	Cr	Си	Fe	Ga	Ge	Hg	In	Mg	Mn	Мо	Na	Ni	Рb	ѕь	Si	Sn	Sr	Ti	тι	Zn
Calcite	0	0						0			•							1		ŝ	2	0		۲	0		Ś		•
Goethite	•	0			S		0	ŝ			•			0			•	•			0	•		٦,	0		•		•
Haematite			0	6	0		0	•			•		•	0		0			•	3		۲		1	•	ş			0
Pvrite	•	0						ş	\$		0	197		1	•		۲	•			8	۲	۲		•		8	•	•
Quartz		•		•			0	•			•	0					•	•				•	0				0		•
Sphalerite		•	•	•		s					0			9	0	•	0	0		2		۲	۲		0	0		0	
Chalcopyrite *		0	•				0	•	•			به ب					0	۰			•	•					۲		۲
Molybdenite *	0		•			0	2.00		•	•	•	1.1	•					0	1		e	•							•
Pyrrhotite *	•		.0	0		•	0	•	•		•		•.				0	0		0	•	0					•		٥

Table 10 Qualitative spectral analysis of minerals from the Hofmann vein-Vrančice.

\*)Local mineral paragenesis in the grandiorite massif-Jan mine (J. Pokorný 1955; A. A. Malachov 1956).

Table 11 Qualitative spectral analysis of minerals from the Slavík vein-Vrančice.

MINERAL	Ag	AI	As	Ba	Bi	Ca	Cal	Co	Cr	Cu	Fe	Ga	Ge	Hg	In	Mg	Mn	Мо	Na	Ni	РЬ	56	Si	Sn	Sr	Ti	Zn
Baryte	•	•	S				0			•	0			•		•	0			•	•		0				0
Bournonite	•				•	۲	0									•	•				15		0	•			.41
Dolomite				•															0		•		0		9		•
Galenite				0	•	0	•			0	0			ŝ		•		•			and the second	0	0	•	•		0
Chalcopyrite		•				0	0		•							•	0			•			۲				0
Nickeline		•			0	77			×		۲					•	•	•							0		
Ni-skutterudite						N 22	12					2	2			0			2		0			•	۲		
Pyrite		•	0				•	•		0		1			4	•		i		•						3	0
Siderite	•	•															1.5			. 0	•			e		•	
Sphalerite	0			•	•			•		0			•		0	•	.0		5	0		۲					
Quartz	0	•					•			•	0					•	•				•	٥	1944 1844				
Tetrahedrite		•			0	•		•		1			•		•	0	•		ŝ	•	9			•		•	

Table 12 Qualitative spectral analysis of minerals from the Babánek vein-Vrančice.

MINERAL												0	-										0.	0					-	1
	Ag	AI	AS	Ba	Be	BI	Ca	Ca	Ce	00	0	00	re	Ga	Ge	ng	In	1	Mg	nivin	10	IV/	PD	30	51	Sn	Sr	11	11	2
Baryte	•	•				1	0		-		-	•	•		1				•	0	1		•		0	2		-	t	
Bornite		•		•	s	•	0	•			0	14		•	3	Ś			•	0						•				6
Calcite	•	0						0				•											•	•			0	•		
Mn-calcite	•					1		•						1					۲				•		•			0		
Galenite	•	•				•	1		1.	Θ.	0				1.3	12			0	•	.3.7	0		0	0		1			
Goethite	•		•		•	•	0	0				0	0		0					0	•	•	•	0	0	•				
Haematite			0		•		*	0					() at		•		•		1.2			•	0			•	Ś			
Chalcocite						•	0	•	-										•	. 0	191		1.4.4		0					
Chalcopyrite	0	0		•			2	•					1 .01						0	0		•	•	0	1.2	•	0		1	0
Marcasite	0	•					i.												•	•		•								0
Pyrite		•	200	0	1.40	*: + ·	•		S			0	1.54	4.5	1.00	•			•	•		•	0	0			2		•	C
Quartz	•			•				•				•							•	0			•		100					
Siderite		•	-				1.1	•					20					8			4		•		۲					•
Sphalerite			•	•		•									•	0	•		4	0	3	•	14	•	0	0				E alte

The chief ore elements, namely Ag, As, Cu, Fe, Pb, Sb, Zn occur also as microelements in some minerals of the Vrančice veins.

The silver was found in the lattices of a number of minerals such as sphalerite, galena, chalcopyrite, bornite, chalcocite, tetrahedrite, bournonite, boulangerite, pyrite and marcasite.

Arsenic is present in antimonite, pyrargyrite, native silver and sporadically also in chalcopyrite. Furthermore, it constitutes a more important isomorphic admixture in tetrahedrite, bournonite, pyrite and marcasite.

Mercury is considered as isomineral in calcite, dolomite, siderite, boulangerite, antimonite and native silver.

As microelement the iron is relatively rare. It occurs only in boulangerite, antimonite and nickeline. In sphalerite it is present as a major isomorphic admixture.

The plumb was always found in calcite, dolomite, siderite, baryte and tetrahedrite.

Antimony was ascertained as isomineral element in galena, native Ag, nickeline, pyrite and marcasite.

Zinc appears as microelement in carbonates, namely in calcite, dolomite and siderite as well as in chalcopyrite. As isomineral element it was also found in tetrahedrite, nevertheless the Vrančice occurrences are so rich in zinc that it appears there as macroelement.

The remaining commonly occuring lithophile and siderophile elements namely Al, Ba, Be, Ca, Cr, Hg, Mn, Na, Si, Sr, Ti, V, appear mostly as building components of non-ore constituents of the Vrančice veins such as carbonates (calcite, siderite, dolomite), baryte and quartz. The most of the above cited elements occur also as anisomineral in the analysed hypogene minerals which is due to the admixture of minute ore components. Manganese appears also as isomineral microelement in baryte, haematite, goethite, sphalerie and willemite.

Let us mention also the eventuality of the occurence of Au and U in the Vrančice veins as certain mineral parageneses of the metallogenetic region of Příbram (a part of which is also the Vrančice ore district) contain these elements. It is not excluded that further investigations will reveal minerals the building components of which will be Au eventually U.

The role played by the chief and secondary ore elements during the minerogenesis is shown in the table 8 (chapter V.). The evolution and the nature of ore solutions is determined by many agents the most important being physico-chemical properties of elements, their concentration in solutions, the oxidation-reduction potential, pH and the temperature of solutions. No less important is also the pressure. The oxidation-reduction potential is one of the most important factors if we proceed from the hypothesis of A. G. Betechtin (1955) according to which the formation of minerals is influenced above all by the concentration of sulphur and oxygen in solutions.

The beginning of the first mineralisation stage marked by the separation of quartz and haematite took place in an oxidation medium which, during further mineralisation and especially towards the end of this stage, was converted into the reduction medium. Under these circumstances sphalerite and siderite were separated.

The beginning of the second mineralisation stage when the quartz II was separated may be related to a transitory change of the oxidation-reduction potential. This change was probably due to relatively intense tectonic movements which occurred in the interval between the first and second etape and resulted in an increase of oxygen concentration in solutions. During the second mineralisation etape the reduction medium was dominant and the saturation of the  $H_2S$  solutions probably was produced as all remaining Pb, Cu, Sb, Fe-sulphides and sulphosols crystallized.

The incipient phases of the third and fourth mineralisation stages were accompanied again by an increased oxygen concentration and at the same time, quartz and haematite and under specific circumstances also goethite were separated. Under these circumstances older minerals of bivalent Fe were unstable which resulted in a strong resorption of siderite by haematite. During the further evolution the reduction medium again became dominant in both stages as the crystallization of the chief vein mineral calcite was effected. The separation of oxides eventually hydroxides of Fe which took place commonly with carbonate in a certain evolutionary phase may indicate that during these stages the oxidation potential was high enough as to permit the formation of these minerals.

Generally it may be stated that the intermineralisation tectonic movements are probably followed by a change of the oxidation-reduction potential the reduction medium being replaced by an oxidation one during a certain period. These changes are not necessarily due only to the tectonics, other factors may have played their part as well.

Among other agents influencing the mineralisation the solutions are to be considered. The incipient inlet of hydrothermal solutions was marked by their relative These relatively active solutions brought about a more or less intense acidity. alteration of adjacent rocks and at the same time quartz, pyrite, eventually haematite were produced. The alteration of rock-building constituents, especially of plagioclases very probably involved the setting free of alkali and their migration. This might have produced the neutralisation of originaly acid solutions which became even weakly alcalic during the further evolution. Towards the end of the first minerallisation stage the chief ore mineral sphalerite, in fact, crystallized and according to experimental indications of A. G. Betechtin (1955) its formation requires weakly alcalic solutions. After stronger tectonic movements occured at the limit of the first and second mineralisation stage the inlet of new solutions may by presumed which became still more acid at the beginning of the second stage. In view of the fact that immediately thereafter a progressive crystallization of polymetallic ores such as Pb, Cu, Sb, Fe and of dolomite with baryte was effected, it may be concluded that the pH of solutions changed. In this stage two phases differing somewhat in their chemism and separated by insignificant tectonic movements may also be recognized:

1st phase—paragenesis of Cu-ores; 2nd phase—paragenesis of Pb-ores. Whilst during the first phase the solutions most probably were neutral, during the second stage the basic solutions began to play a part along with the neutral ones at the crystallization of baryte and dolomite. The next two stages—those of carbonates —are characterized by probably prevailing weakly acid to neutral solutions.

Though the consideration of pH solutions is based on experimental data of A. G. B e t e c h t i n (1955) their application need not always correspond to the reality because these data do not necessarily correspond to the pressures and temperature present at the minerogenesis of the Vrančice veins.

The geochemical evolution of the veins depends also of the nature of solutions by which certain elements were transported. In the world literature this question is actually discussed from the theoretic standpoint. From the results given in works of different authors (for example Betechtin and alii 1955) it may be concluded that beside the true solutions the colloids are considered as having played a part which would facilitate the explanation of certain textural, structural and paragenetic features. I give below some examples showing that these new views may also be applied to the minerogenesis of the Vrančice ore veins:

The alteration of accompanying rocks obviously produced by considerably active solutions as well as the minerals newly formed point almost undoubtedly to true solutions which surely traversed more readily tectonically affected rocks than if they were of colloidal character. A positive identification as to the nature of neutral to alcalic solutions cannot be given because of the lack of criteria. Nevertheless it is not excluded that the solutions from which the polymetallic ores were produced were, at least partly, of a colloidal character. This assumption is supported by interesting macrotextures found in the 6th and 7th horizon of the Pošepný vein. In the first case galena forms colomorphic linings on tetrahedrite-bournonite massive accumulations, these linings showing a pronounced radial structure. Another interesting case as regards the texture was observed in the place where the vein filling consists dominantly of sphalerite. This sphalerite is fair (yellow-brown) with faint zonary colouring and the individual zones have a distinct colomorphic structure.

Also during the youngest mineralisation phases the minerals with concentric to radial structure (pyrite-marcasite) and with colomorphic texture made more distinct by colour shades (calcite) crystallized. These minerals may also be supposed to have been produced from very low temperated solutions of colloidal character. An interesting question is furthermore the nature of solutions from which willemite together with zonary quartzs, chalcedony-quartzine etc. were produced. In this case the genesis from solutions of colloidal character may also be considered as one of the possibilities.

Another question of highest interest from the theoretical point of view are the temperated solutions. In the recent specialized literature this problem is dealt with, among others, on the basis of relations between the macrochemism and microchemism of certain specific minerals and the conditions (i. e. also thermal) of their genesis. Among the minerals which proved convenient in this respect the most important are sphalerite and tetrahedrite. In the case of the Vrančice veins we dispose of very few criteria permitting us to determine the probable temperature of solutions. Tetrahedrite is a quite rare mineral and its distribution in the veins is irregular so that it cannot be used as geochemical indicator (in the sense of J. H. B e r n a r d 1957) when studying the horizontal and vertical changes in the chemism applicable also to the study of the temperated solutions. Instead of tetrahedrite sphalerite was used for those purposes. It was separated from the ore samples of the Pošepný and Babánek veins for qualitative spectral analyses so that the eventual horizontal and vertical changes be included.

In view of the fact that in the Vrančice veins sphalerite belongs to the oldest minerals, its temperatrue of genesis cold be considered also as approximate temperature of the ore solutions at the beginning of the minerogenesis. In the last years the problem of determining more exactly the thermal limit of the crystallization of sphalerite was studied experimentally by G. Kullerud (1953). This author employs sphalerite with varying content of Fe as geological thermometer. This method may, however, be applied with success only in the cases where the FeS-phase, can be proved microscopically, for example in the form of the off-mixtures of pyrrhotite. Such a case does not exist in Vrančice and for this reason only the presence of certain elements (Fe, Mn, Cd, Hg, In, Ga, Ge, Sn,) may serve as indicator of the temperature of solutions from which these sphalerites were produced. Generally it may be stated that these are middle to low temperated "fair" sphalerites which is proved especially by relatively low contents of Fe and Mn. Also the middle contents of Cd and mostly low contents of indium (in average by a range lower than for example in higher temperated "dark" sphalerites of Kutná Hora), the regular presence of Ge eventually Ga and a higher concentration of Hg (mostly higher than a trace concentration) lend full support to the hypothesis of the average to lower temperated sphalerites and thereby also of ore solutions. The regular presence of Sn points also to middle temperatures of genesis. To determine the relative temperature of genesis some authors (for example R. Stoiber 1940) study the presence of As, Co and Ni in sphalerites. In the Vrančice sphalerites these elements have been ascertained, nevertheless I believe that they are rather of anisomineral character, so that a reliable discussion cannot be engaged on this subject. From the comparison of results obtained by the analysis of sphalerites from both Vrančice veins the uniformity in their chemism follows. This chemism does not show any vertical changes (as far as we may conclude from the present state of the vertical opening of the veins). For the time being we can thus state that zonal phenomena as regards the temperated solutions did not take place.

On the whole it may be resumed that at the beginning of the minerogenesis the temperature of solutions most probably corresponded to the mesothermal degree. The proof of it is not only the chemism of sphalerite as discussed above but also the occurrence of finely scaled haematite-sphalerite the genesis of which is characteristic for middle to lower temperatures. In the course of further geochemical evolution of ore veins a progressive decrease in temperature (for example the presence of Tl in galena provides evidence of relatively low temperatures etc.) may be presumed even to the values which are characteristic for epithermal ore parageneses (crystallization of antimonite). Also the last mineralisations stages of the Vrančice veins are very probably marked by relatively low temperatures of solutions from which calcite, pyrite with marcasite and goethite crystallized. For the genesis at low temperatures the above discussed colomorphic textures of the vein filling are characteristic.

#### VII. Migration of some ore elements during supergene processes

During the geochemically-mineralogical study certain data concerning the migration of some more important elements were obtained. This migration was conditioned by supergene processes in the Vrančice veins.

The zinc the principal bearer of which is sphalerite dissolves very easily during supergene processes and zinc-sulphate stable in solutions is produced. For this reason we do not generally encounter the oxidation minerals of Zn in the deposit. In our case the dissemination of Zn is to a certain extent limited owing to the fixation by carbonates and probably also on account of the adsorption by highly disperse components. In the oxidation zone a part of Zn is bound to silicates.

The plumb is an element of a very low migration coefficient because it forms hardly soluble compounds in the oxidation zone. In spite of that we have hitherto not encountered any extraordinary accumulations of supergene Pb-minerals in the upper portions of the ore veins save single occurrences of cerrusite and anglesite. The plumb was also involved in the genesis of bindheimite. The copper is a very characteristic ore element of the Vrančice veins. The main oxidation product of the Cu-ores is copper-sulphate which is well soluble in water and relatively stable. This fact determines the considerable migration capacity of copper. In the Vrančice region a stronger leaching of copper is, however, limited as the produced CuSO<sub>4</sub> easily reacts with primary sulphides and thus the cementation sulphides, namely chalcocite, covellite, bornite as well as native copper originate. A very common vein constituent of the Vrančice veins are the carbonates which show a neutralization effect upon acid waters and form basic carbonates malachite and azurite with CuSO<sub>4</sub>. In addition, they facilitate the formation of further minerals being normally unstable in an acid medium. Such minerals are for example the hydrosilicate chrysocolla and the vanadate vésigniéite ascertained in the Vrančice region.

During the oxidation of minerals containing Ag a relatively well soluble Ag-sulphate is produced. From its solution which is relatively unstable native silver may easily be reduced. The reduction of native silver from weakly acid to neutral solutions is supported by the presence of some ore minerals the most important being arsenides and Cu-sulphides. Such cases occurred also in the Vrančice veins where the native silver is encountered mainly in association with chalcocite and covellite in the Pošepný vein. In the Slavík vein native Ag was ascertained in ore samples with nickeline and Ni-skutterudite (chloantite). The reactions of Ag<sub>2</sub>SO<sub>4</sub> with sulphides give also rise to supergene sulphides of silver among which pyrargyrite, stromeyerite and probably also argentite were ascertained in the Vrančice veins.

The cadmium constitutes a common admixture in the Vrančice primary ore minerals. The originating cadmium-sulphate is soluble in supergene conditions which determines a good migration ability of Cd. In the Vrančice region cadmium is partially fixed by carbonates and absorbed by disperse compounds.

Iron and manganese are commonly occuring elements in the Vrančice primary minerals, namely in sulphides and carbonates. The behaviour of both elements in the oxidation zone is analogous. The produced Fe- and Mn-sulphates are relatively well soluble. The hydrolysis and oxidation of sulphates give rise to oxicompounds (hydroxicompounds) which precipitated as gels namely haematite, goethite, pyrolusite. Owing to their adsorption capacity these gels can fix a number of elements such as Cu, Pb, Zn, Cd, In, Ge and others.

# Conclusion

The geochemically-mineralogical study of the ore veins in the Vrančice ore district (12 km southward from Příbram—Central Bohemia) was undertaken during 1958—1959. The most important results obtained can be resumed as follows:

(1) Among the accompanying rocks of the ore veins belonging to larger complex of Central Bohemian pluton granodiorites (biotitic and biotitic-amhibolic) are dominant. More rare are granits (alkaline and normal) and vein eruptivities (especially lamprophyres kersantites, probably also minettes, rarely granit-porphyry). The geological position of lamprophyres is often associated with that of the ore veins filling the tectonic structures in the plutonic massiv in NW-SE direction. The petrographic study of the accompanying rocks proved that they were more or less affected by alteration and that at the same time the following processes took place: sericitisation, chloritisation, baueritisation, uralitisation, epidotisation, silicification, carbonatisation and pyritisation. The alteration phenomena are related to the hydrothermal activity, nevertheless a direct relationship between the degree of alteration and the might of ore-forming could not be ascertained.

(2) The review of minerals hitherto identified in the Vrančice ore veins (more than 40) and produced in different genetic stages is given in the table 7. The great majority of these minerals occurs in chief Vrančice vein, that of Pošepný. The research and identification of the mineral parageneses from the remaining opened ore veins (Hofmann, Slavík, Babánek) has the character of a basic study. In addition to a number of minerals already known in the Vrančice veins several new such as boulangerite, dolomite, marcasite, nickeline, Ni-skutterudite (chloantite), pyrargyrite, stromeyerite and argentite(?) have been identified in the Vrančice ore district. From the topographic-mineralogical standpoint the first exact identification of stromeyerite on the territory of Czechoslovakia is of a special importance.

(3) The research into the individual vein parageneses and partial successions of hypogene minerals from the Vrančice veins revealed that a common long-protracted minerogenetic process conditioned by certain geochemical processes took place in the ore region. In the Vrančice ore veins four mineralisation stages subdivided in several phases were distinguished. The minerogenetic processes which gave rise to the ore veins were followed by local tectonic movements with accompanying phenomena of mylonitisation.

(4) During the research into the paragenetic conditions of the Vrančice ore veins the existence of the cementation zones was also studied. The most convenient for the study of these processes is the Pošepný vein both by its depth of exploitation and by its unique zonality (in comparison with other veins) where a continuity from the uppermost oxidation zone through the cementation zone to the primary deposit may be followed. In my opinion the following minerals may be considered as cementation minerals in the Vrančice veins: chalcocite (occuring however also as hypogene), covellite, probably also bornite (its bulk is however of hypogene character), Ag-ores such as pyrargyrite, stromeyerite, argentite(?) and native metals—Ag and Cu. The evolution of the oxidation and cementation zones depends on local changes in the structural geological factor and in the petrographic character of the rocks.

(5) The Vrančice ore veins are a part of the metallogenetic province of the Centra Bohemian pluton. Owing to their mineral character they occupy a special position. They are constituted by a typical association of polymetallic ores two constituents of which are of economic importance: sphalerite and galena, sphalerite being more abundant. Important ore-constituents are also the Cu-ores, namely chalcopyrite, tetrahedrite, chalcocite, bornite, bournonite as well as the Ag-ores: in the first place it is silver, then pyrargite and finally stromeverite and argentite(?) occuring in accessory amounts. In the Pošepný vein willemite as a further Zn-mineral occurs also economically important amounts. Among the non-ore components the carbonates prevail over quartz, goethite and locally occuring baryte. A commonly distributed constituent in the Vrančice ore occurrences is haematite which under certain circumstances may become "concentrator" of rare elements, especially of indium, cadmium etc. The remaining recognized minerals are of mineralogical importance only, nevertheless their existence enlightens the general geochemical processes which took place during the minerogenesis.

The documentation and study material on the basis of which the present account is given is deposited in the mineralogical collections of National Museum in Prague.

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#### EXPLANATIONS OF THE PLATES

Pl. I.

Fig. 1. Patterns of decrepitation-baryte of Vrančice.<sup>1</sup>)

- No. 1. Platy aggregate of baryte, gray-white colour, glassy luster-Babánek vein (Václav mine).
- No. 2. Middle grained stalky aggregate of baryte, meat-red colour-Slavík vein (Slavík mine).
- No. 3. Middle grained stalky aggregate of baryte, concentric construction, brown colour-Slavík vein (Slavík mine).
- No. 4. Platy aggregate of baryte, milkwhite colour-Pošepný vein (Alexandr mine).

Pl. II.

- Fig. 1. "Felt-like" aggregate of boulangerite, druse-fillings of the cavity of sphalerite -Pošepný vein. Macrophoto-approx. enlargement 7x.
- Fig. 2. A symetric vein formed from outside to the centre by baryte, galena and calcite-Slavík vein. Macrophoto-approx. enlargement 1/2 of the real.

Pl. III.

- Fig. 1. A part of the symetric ore-vein. The crack in the rock filled by quartz, idio morphous crystals of bournonite included by coarse-grained dolomite-Slavík vein. Macrophoto-approx. 1/2 of the real. Fig. 2. The intensive repulsion of sphalerite (gray) by galena (white) along the contact-
- line sphalerite-quartz (black). Pošepný vein. Polished section No. 1842, paralell nichols, linear enlargement  $45 \times$ .

Pl. IV.

- Fig. 1. Mutual intensive growth of tetrahedrite through chalcopyrite -Pošepný vein.
- Fig. 2. A graphic overgrowing of galena (white) with chalcocite (gray), repulsing the crushed sphalerite (S). All the cited minerals included by bornite (B). Pošepný vein. Polished section No. 1827, paralell nichols, linear enlargement  $45 \times$ .

Pl. V.

- Fig. 1. Screen concretions of bornite (gray) with chalcopyrite (light gray), repulsion galena (G). Pošepný vein. Polished section No. 1802, paralell nichols, linear enlargement  $45 \times$ .
- Fig. 2. Nickeline (N) with cavities filled by pyrargyrite (P) and native silver (Ag). Slavík vein. Polished section No. 1850, paralell nichols, linear enlargement  $45 \times .$

Pl. VI.

- Fig. 1. Zonar Ni-skutterudite (chloanthite), selectively replaced by veiny minerals (black). The figure demonstrates also sphalerite (S). Slavik vein. Polished section No. 1851, paralell nichols, linear enlargement  $45 \times$ .
- Fig. 2. Chalcocite (CH), lobe-like overgrowing with stromeyerite (S) and native silver (Ag). Pošepný vein. Polished section No. 1805, paralell nichols, linear enlargement  $15 \times$ .

#### All photographs made by L. Pilař.

<sup>1</sup>) The decrepitation analyses were made in the laboratory of Institute of Mineral Raw Materials Kutná Hora by an automatic register developed by Dr. Ing. F. K u pk a. The heat-increase was 30° C/min, measurements were made by a Pt-Pt/Rh thermocouple and registered photographically by an optical kymograph. Grained aggregates of the mineral in question were crushed, separated and the fraction with grains of 2,00-2,50 mesh was analysed. The input of aprox. 0,5 gr was placed in a Ag-crucible in an oven and the explosions passed through a pipeline to the microphone and were strengthened by an amplifier. The effects of decrepitation were galvanometrically registered and the variations registered photographically on a "Polaro" paper placed in a polarographic box.

V. Hoffman: Geochemically-mineralogical relations of polymetallical veins in the ore district Vrančice near Milín.















Pl. VI.