A review of mineral associations and paragenetic groups of secondary minerals of the Jáchymov (Joachimsthal) ore district

Přehled minerálních asociací a paragenetických skupin sekundárních minerálů jáchymovského rudního revíru (Czech summary)

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This paper presents information on relations between physical-chemical properties and genetic features for two hundred and seven secondary minerals and thirty natural phases newly discovered in the Jáchymov ore district.
Eight distinct paragenetic groups are described and discussed with respect to formation conditions of the secondary minerals in the Jáchymov ore district.

Key words: mineral associations, paragenetic groups, secondary minerals, Jáchymov

Introduction

In the course of work on the project supported by the Grant Agency of the Czech Republic *Study of secondary minerals in the Jáchymov ore district* [299] we have described and in many cases closer characterised 207 secondary mineral species and discovered 30 new natural phases.

In view of this complexity, it proved necessary to characterise minerals not only on the basis of chemical compositions but also in the framework of paragenetic groups. Eight distinct paragenetic groups were defined and discussed in connection with conditions of formation of the secondary minerals.

Mineralogical observations or reported descriptions of sampling sites surroundings provided information on mineral paragenesis. As this information was sometimes incomplete, it was not possible to characterise the paragenetic position of all minerals. The names of the individual paragenesis were chosen with the aim to obtain a designation for a particular paragenesis, which would be sufficiently distinct from other parageneses.

In this study, paragenesis is understood as a common occurrence of minerals which formed at the same time, or in a sequence, during a single mineralization process. The term association is used to denote a common occurrence of minerals without genetic relations. Since all the minerals described formed during weathering processes, it is possible to understand the term association as indicating generally looser relations of jointly occurring minerals, in comparison to a paragenesis.

The paragenesis of secondary minerals of bismuth

The secondary minerals of bismuth are relatively scarce. From the paragenetic point of view, they can be described as two groups with the following succession:

a) bismite - preisingerite - bismutite - walpurgite - metatorbernite - eulytite - bismutoferrite - limonite
b) eulytite - bismutite - kettnerite - beyerite - pucherite - namibite

A complete sequence of these two paragenesis is rare.

The first paragenesis can be considered in two parts, including the following groups of minerals: walpurgite - metatorbernite - limonite and bismite - bismutite - kettnerite - eulytite - bismutoferrite - beyerite. The primary mineral in this case is native bismuth, occurring rarely as isolated grains to 3 mm, as remains of skeletal bismuth crystals in quartz of the Geister vein. The native bismuth was pseudomorphed by bismite**,** preisingerite, and bismutite in a microcrystalline mixture. These aggregates are dark grey in colour and have a greasy to adamantine lustre. Bismutite also occurs isolated in whitish earthy fill of vugs after crystals of native Bi or as a dusty coating. Other younger minerals of this paragenesis occur in vugs or along fractures of quartz veinlets.

Walpurgite occurs with ***metatorbernite***. The scarce eulytite forms minute yellowish and translucent smooth and lustrous spheres, deposited on walls of the vugs. Earthy to powdery bismutoferrite of grey-yellow colour, and limonite are the youngest minerals of this paragenesis.

Native ***bismuth*** served as the primary mineral also for a second paragenesis. Its remains up to 0.5 mm long are disseminated in massive eulytite, which was possibly in part also a primary mineral. This eulytite is dark grey, with a waxy lustre. It locally fills veinlets up to 2 cm wide and forms spherical aggregates up to 1 cm across, with a rough surface. A part of eulytite is altered to a massive grey-brown mixture of bismutite and kettnerite. These aggregates, as well as eulytite, are coated by a thin layer of yellow, powdery bismutite. Beyerite in tetragonal tablets of the order of 100 µm in size is deposited on, or intergrown with, bismutite.

Pucherite and ***namibite*** are the youngest minerals. Pucherite in crystals up to 1.5 mm long are deposited on powdery bismutite. Green namibite occurs as minor aggregates and coating on fractures in eulytite as well as in the local country rock, i.e., quartz porphyry and biotite gneiss. Thin offshoots of quartz veinlet in the gneiss carry minute tetrahedral crystals of yellow eulytite, in part altered to bismutite, and exceptional radiating aggregates of namibite crystals.

The paragenesis of secondary minerals in native arsenic-quartz veins

The absence of carbonates of Ca, Mg, and Fe, and arsenides of Fe, Co, Ni, i.e. absence of cations for crystallisation of the erythrite group arsenates or Ca, Mg arsenates, is essential for this paragenesis. Marcasite and pyrite, disseminated in these veins, provide Fe as the important cation and serve as a trigger and accelerator of oxidation process. Instable marcasite yields concentrated sulphuric acid, which accelerates oxidation of native arsenic to As_2O_3 and further to arsenic acid, which reacts with Fe ions and precipitates arsenates of Fe.

This results in crystallisation of arsenolite, whose crystals up to 3 mm long coat all free surfaces of native arsenic. ***Arsenolite*** octahedra to 6 mm long developed under soft coating of dickite deposited on native arsenic. However, no increase in size of arsenolite crystals took place under massive accumulations of hard dickite, which apparently had poor permeability for solutions.

Scorodite in aggregates of radiating acicular crystals or compact spheres is a common member in the succession. It is not deposited on native arsenic, but on adjacent vein quartz or intergrown in clay. Kaatilaite also occurs in this paragenesis in isolated soft aggregates of acicular crystals or rather compact greenish aggregates; it does not occur in intergrowth with scorodite.

Geminite, ***sulphur***, and possibly also the unnamed phase $\boldsymbol{[(MoO_2)_2As_2O_5(H_2O)_2]\ .\ H_2O}$, probably belong to this paragenesis. Geminite was prepared as a synthetic phase by reaction of As_2O_5 with malachite. In Jáchymov, the mineral probably formed in a similar way, by reaction of weathering products of native arsenic with solution carrying Cu. Geminite occurs as aggregates of tabular crystals deposited on arsenolite; no additional secondary minerals were observed on these specimens.

Sulphur constituting minute prismatic pseudomorphs, possibly after argentopyrite, occurs but exceptionally. The phase $[(MoO_2)_2As_2O_5(H_2O)_2]\ .\ H_2O$ - is very scarse, being limited to matrix coating adjacent to a strongly corroded veinlet. Laterally, it gives way to spheroidal and botryoidal aggregates of scorodite.

The paragenesis of secondary minerals of lead

This paragenesis occurs on specimens from the Geister vein or from its proximity. The primary mineral preserved in small amounts is galena and exceptionally uraninite. The oldest minerals in this paragenesis are ***limonite***, ***Mn-oxide***, and ***mottramite-duftite***, deposited in this sequence on quartz matrix. Mottramite-duftite is overgrown by disseminated thin crystals of ***torbernite***, which on their turn may be overgrown by yellow prismatic and acicular crystals of ***parsonsite. Ca-pyromorphite*** as a light yellow fill of some vugs and in minute acicular crystals is younger than parsonsite.

Parsonsite also occurs as radiating aggregates of acicular crystals, light yellow to green yellow, in vuggy samples of vein quartz. It is accompanied by minute white or rusty spheres of ***churchite-(Y)*** with intergrown tabular crystals of ***zeunerite***. The specimens also carry yellow tabular ***autunite***, largely replaced by amorphous oxi-hydroxides of Fe, designated incorrectly in some reports as bassetite. Small yellow brown spheres deposited on these pseudomorphs could not be safely identified due to small amount of material; the major elements would correspond to ***corkite***. Minute transparent or rusty crystals of anglesite occur in fractures of vein material, in weathered uraninite, and in a mixture with ***bismutoferrite*** around galena.

Concurrently with the paragenesis of phosphates a paragenesis of arsenates occurs, however, their mutual relations could not be clarified and succession relations were not found. In this paragenesis, ***bayldonite*** takes the place of ***mottramite-duftite***. It is succeeded by thick tabular to equant crystals of dark green, opaque ***zeunerite***, rarely coated by botryoidal aggregates of hidalgoite. Soft, incoherent aggregates of ***mimetite***, filling small vugs, represent the last member of this partial paragenesis. ***Mixite***, found in the vein material or deposited on bayldonite, also belongs here.

Walpurgite, ***vandendriesscheite***, ***kasolite***, and ***wulfenite*** do not show clear relations to other minerals, though they also belong to this paragenesis. Walpurgite, occasionally in parallel growth, forms isolated crystals in vugs. Vandendriesscheite occurs as coating on fractured and weathered uraninite. Kasolite was identified as yellow grains up to 5 mm across in vein quartz and as powdery coating on vandendriesscheite. Wulfenite formed in a single case pseudo-hexahedral crystals to 2 mm long, overgrowing quartz in a drusy quartz veinlet. Both the minerals are coated by limonite and scarce, minute ***pyromorphite***.

The paragenesis of uranyl-carbonates

Minerals of this paragenesis occur in proximity of primary uraninite veinlets, or uraninite dust settled on wall rock during mining or ore transportation in the mine. Only a minor content of pyrite or marcasite in the ore, resulting in pH = 5 to 8 and a relatively dry environment are important conditions for this paragenesis. The secondary uranium minerals, showing a close association with uraninite, may serve as indicator of inconspicuous uraninite veinlets. Older ***gypsum*** is a common associate of these minerals. Similar rules controlled formation of uranyl-carbonates from fine fraction of uraninite lost during exploitation in transportation adits; uranyl-carbonates thus formed on pieces of rock submerged in water in some watercourses in the mine. It is possible that mine water served as a source of Na. The absence of gypsum is characteristic of the last type of occurrence.

The uranyl cation forms with carbonate anion rather stable uranyl-carbonate complexes. Their existence is controlled by a relatively narrow range of pH values. The anion $[UO_2(CO_3)_2(H_2O)_2]^{2-}$ is stable in the range pH = 4.5 to 6.5, anion $[UO_2(CO_3)_3]^{4-}$ in the range 6.5 to 11.5 [220]. This indicates that minerals containing the complex $[UO_2(CO_3)_2(H_2O)_2]^{2-}$ (zellerite, metazellerite) will be more stable in an acid environment in comparison to liebigite, rabbittite, and ***znucalite***, containing the complex $[UO_2(CO_3)_3]^{4-}$.

Schröckingerite, forming soft scaly aggregates, is the oldest mineral in this paragenesis. It is closely accompanied by liebigite, which impregnates some schröckingerite aggregates. ***Liebigite*** coatings show voids, with limonite coating only, where pyrite or marcasite is present in the matrix.

Zellerite and ***metazellerite*** in yellow to brown-yellow aggregates also belong to this paragenesis. ***Rabbittite*** in acicular, bent or otherwise malformed crystals, occurs jointly with schröckingerite, liebigite and zellerite. These rare minerals are preferentially associated with, or deposited on gypsum matrix. Liebigite shows a similar tendency. It appears that the stronger affinity of sulphate ions to calcium than to uranyl resulted in separation of sulphates from carbonates. Predominance of primary carbonates over sulphides in the vein material was an important condition for this paragenesis. ***Gypsum***, even if present in two generations, avoids carbonate matrix; its transparent larger crystals of the older generation crystallised on wall rock and the younger powdery gypsum deposited on older gypsum.

The unnamed ***phase*** $Na_4(UO_2)(CO_3)_3$ forms granular aggregates some 100 μm long. It is not deposited on wall rock but on dust coating resulting from mining activity. It was found in the same place as ***andersonite*** or ***schröckingerite*** but in sites free of additional secondary minerals.

The paragenesis of uranyl-sulphates

Development of this paragenesis requires absence or only a minor occurrence of primary carbonates and significant amounts of pyrite and marcasite in the veins, resulting in pH values near 3, and the presence of uraninite. A surplus of sulphate ions may thus result in crystallisation of uranyl-sulphates - uranopilite and sodium-zippeite. The matrix of the specimens is often coated by ***limonite*** and ***gypsum*** crystals. ***Uranopilite*** and ***sodium-zippeite***, although occurring together, do not show clear succession relations. Both the minerals form minute coating of gypsum. Uranopilite is well indicated by its colour, but orange or red brown ***zippeite*** may be less conspicuous. Uranyl sulphates may be also deposited in fractures of country rock, where especially zippeites may have crystallised as somewhat larger single crystals or radiating aggregates. Owing to variability in appearance of zippeite, some unidentified phases escaped attention. These include ***jáchymovite*** and the new phases ***"pseudo-zippeite(Mg)"***, ***magnesium-zippeite***, ***"ferro-zippeite"***, and ***zippeite***. The phases "pseudo-zippeite(Mg)" and zippeites (K, Mg, Fe, Ni) accompanies ***sodium-zippeite*** and form intergrowth with this mineral, so that it rarely occurs as a pure phase. Its aggregates are usually more porous and less coherent than those of zippeite.

Nesquehonite, ***sklodowskite***, and ***metaschoepite*** occur in this paragenesis. Nesquehonite together with ***sodium-zippeite*** covers altered wall rock. Earthy, light buff coloured minor nodules of sklodowskite scarcely occur in samples with ***gypsum*** and sodium-zippeite. Metaschoepite, in distinction to sklodowskite, has a bright light yellow colour.

Johannite, a rare but well-known mineral in Jáchymov, belongs to this paragenesis. It occurs with ***gypsum*** and often with ***uranopilite***. Johannite is easily recognised by its striking bright apple green colour. The ***"pseudo-johannite"*** in small nodules of grey olive green colour, composed of minute acicular crystals, accompanies johannite in some specimens. These two minerals derive from uraninite-pyrite (marcasite) vein material. Minor chalcopyrite served as a source of Cu.

Frondel [24] and Brindley [205] observed in their experiments with uranyl-sulphate precipitation that a slow decrease in the pH values is necessary for crystallisation of zippeite. If this condition is not fulfilled, a spontaneous precipitation of phases of the type $Me^{+}_{2}(UO_2)_6O_4(OH)_6 \,.\, 8\, H_2O$ (becquerelite, compreignacite a.o.) or $Me^{+}_{2}(UO_2)_6(OH)_{14} \,.\, 4\, H_2O$ follows [205]. As some uraninite-bearing veins with sulphides were characterised by a relatively steep pH gradient during weathering, it is possible that such processes took place concurrently with precipitation of sodium-zippeite. This could mean, that some minerals of the schoepite or metaschoepite type may be represented mainly by sodium-dominant members, as is the case with sodium-zippeite or natrojarosite.

According to Čejka [229], phases of the general type $(UO_2)_6(SO_4)_{1-x}(OH)_{10+2x} \,.\, n\, H_2O$ (for $x = 0$, $n = 13$ to 14, for $x > 0$, $n = 10-x$) may exist in the system UO_3-SO_3-H_2O.

The paragenesis of secondary minerals of copper

Minerals of this paragenesis occur on veins with a low content of carbonates. These are quartz veins, often vuggy and fractured, with sulphides, sulpharsenides or arsenides. Chalcopyrite, bornite with chalcocite and tennantite are the most common primary minerals. Although this paragenesis is not widespread, some of the minerals are typical for Jáchymov, i.e., ***lavendulan*** and ***lindackerite***.

The copper secondary minerals can be divided in two groups. One group includes copper sulphates: ***langite***, ***posnjakite***, ***brochantite***, and devilline. These minerals occur separately but in proximity, except langite and posnjakite. They are all deposited on tennantite in vein quartz or next the vein.

The second groups includes proper arsenates, which occur close to the first group of minerals, however, the two groups do not intermix. Formation of Cu-arsenates is strongly dependent on pH of the environment, which is influenced by the primary minerals (tennantite, chalcopyrite, bornite a.o.) and on their chemical stability. ***Lindackerite*** crystallisation on primary minerals, in absence of lavendulan, is preferred under very low pH conditions. More frequently, ***lindackerite*** occurs in the centre of flat radiating aggregate of ***lavendulan***, which is accompanied by younger minerals including ***köttigite*** in pink radiating aggregates, ***picropharmacolite***, ***Cu-AsO_4-H_2O(1)***, ***Cu-AsO_4-H_2O(2)***, ***Cu-AsO_4-H_2O(3)***, ***geminite***, and ***"pseudo-lindackerite"***. The presence of the latter minerals also depend on pH conditions. For this reason, specimens with abundant picropharmacolite contain but rare lindackerite. This limitation is not valid for lavendulan. ***Strashimirite*** in small botryoidal aggregates is younger than lindackerite. Small radiating spheres of olivenite crystallised on strashimirite.

The paragenesis of uranium-free sulphates

This paragenesis can be divided into several partial paragenesis, which include different minerals, although sites of their occurrence are not far apart. This paragenesis near the Geschieber vein is characterised by crystallisation of minerals on strongly porous altered country rock. Strong porosity was instrumental in an efficient circulation of fluids. No clear connection with some primary minerals was observed.

One partial paragenesis includes ***picropharmacolite***, unnamed ***phase*** $Mg\text{-}AsO_4\text{-}H_2O$, ***gypsum***, and ***thenardite***. The specimens represent a crust up to 1 cm thick of vitreous prismatic crystals, oriented perpendicular on matrix of altered wall rock located next to the ore vein. The base of the crust grown on matrix consists of milky radiating acicular picropharmacolite. The central and prevalent part of crust contains prisms and acicular crystals of an unknown Mg-arsenate, intergrown with ***gypsum*** and ***thenardite***. The latter mineral forms milky dusting as the upper part of the crust.

Crystallisation of such massive crusts was probably connected with a significant material transport and distribution of elements. Assuming that S and As were derived from arsenides and sulphides in the vein, a substantial content of Fe would be expected in the secondary minerals. Surprisingly, no Fe was detected. The unusual paragenesis thenardite - gypsum - Mg-(Ca)-arsenates is rather common near the Geschieber vein. It is suggested that anions and cations for these minerals were transported by mineral waters circulation through the fractured rocks. Active mineral springs were confirmed within several metres of the occurrence of the arsenate-sulphate paragenesis.

Another partial paragenesis includes the sulphates morenosite and ***nickelhexahydrite***, yellow-green to bluish green in colour. The skeletal crystals are twisted. Skeletal white crystals of an unknown manganese sulphate are deposited on morenosite and nickelhexahydrite. Powdery coating of ***krautite*** occurs next to the above sulphates. Krautite is most abundant in places adjacent to fractures in rock matrix. Krautite also forms light pink to light buff earthy aggregates deposited on coarse milky ***gypsum***.

The place and character of occurrence suggests that two unnamed hydrous arsenates of iron ($Fe\text{-}AsO_4\text{-}H_2O(1)$, $Fe\text{-}AsO_4\text{-}H_2O(2)$) also belong to this paragenesis. The two rather similar minerals are deposited on gypsum as irregular aggregates of minute crystals. As the two minerals were found in samples collected at different times separated by decades, it is possible that $Fe\text{-}AsO_4\text{-}H_2O(2)$ is an unstable phase which transformed to the $Fe\text{-}AsO_4\text{-}H_2O(1)$, while kept in the collection.

The paragenesis of Ca-Mg arsenates

This represents the most populous and widespread paragenesis of the secondary minerals in the Jáchymov ore district. It occurs on all veins carrying carbonates with native arsenic, any of arsenides of Ni, Co, Fe or even single tennantite.

The first mineral in the succession is ***picropharmacolite***. It typically forms milky white radiating aggregates. In places with abundant water supply, picropharmacolite occurs in clusters of randomly oriented needles. It is then similar to the unnamed ***phase*** $Ca\text{-}Mg\text{-}AsO_4\text{-}H_2O$, which forms in an early stage of weathering of arsenide ores. This phase was unnoticed for a long time owing to its similarity to picropharmacolite, with which it is often mixed. In contrast to the latter mineral, the phase Ca-Mg-AsO_4-H_2O forms shorter crystals. Additional discoveries of the Ca-Mg-AsO_4-H_2O are probable in Jáchymov and elsewhere. It was identified by authors of this study in one specimen from Příbram (private comm. P. Černý) as well, which contains a fan-shaped aggregates of long acicular crystals.

Pharmacolite follows in the sequence. It occurs in vitreous transparent acicular crystals, but rare examples of white crystals represent a mixture of ***weillite*** and ***pharmacolite***. It is probable that weillite formed by dehydration of pharmacolite. Weillite was never identified in freshly collected specimens. It is not clear what stabilises or destabilises pharmacolite; unaltered pharmacolite was preserved even in museum specimens collected over a century ago.

Rösslerite follows after ***pharmacolite*** and it is always accompanied by pharmacolite, however, the latter mineral is not always accompanied by rösslerite. It is common only over a certain depth range and in higher or lower levels it becomes rare. It is an unstable mineral, which looses water soon after collecting, turns white and alters to ***brassite***. The alteration starts from certain point centres, distributed randomly through the crystal. Some rösslerite crystals resist alteration even when kept in collection for time longer than 20 years. It is possible that small amounts of sulphuric or arsenic acid present in the specimen stabilise this mineral. The total amount of rösslerite is less than the amount of all Ca-arsenates combined, which corresponds to the prevalence of Ca over Mg in carbonates.

The sequence of pharmacolite and rösslerite crystallisation can be inverted. It is uncertain if such cases indicated inverted succession or result from more than a single generation of minerals. A similar behaviour was observed with ***picropharmacolite***.

Haidingerite in small vitreous spheres with radiating internal structure is accompanying pharmacolite and rösslerite and sometimes deposited on these minerals. Haidingerite can be easily overlooked, except for specimens in which vitreous rösslerite was altered to milky brassite.

Sainfeldite follows in the succession. It occurs in isolated white or light buff spheres and crusts. An increased content of Mn correlates with pink colour of sainfeldite.

The same relation is valid for pink fluckite, which occurs next to strongly corroded products of weathered arsenates. Weathering products include yellow-brown to green amorphous material, which is bordered externally by incoherent vuggy carbonates, decorated in places by pink spheres of ***fluckite***. Mn originates from vein carbonates.

Villyaellenite or ***Ca-villyaellenite*** has the same place in succession as sainfeldite. These isostructural minerals are recognised by their habits; villyaellenite occurs in isolated scaly crystals, not in spherical aggregates as ***sainfeldite***. Colour of these minerals is a poor guide: ***fluckite*** and sainfeldite with a low Mn content are pink, while villyaellenite with major Mn content is light buff in colour.

Several specimens carried another Ca-Mg-arsenate, ***talmesite***. It occurs in fan-shaped aggregates or spheres of acicular crystals, light dirty yellow in colour. One example of acicular crystals of gypsum deposited on spheres of talmesite was observed.

Minerals of the erythrite group are relatively abundant in this paragenesis. ***Annabergite*** and ***köttigite*** are the most common species, followed by parasymplesite, erythrite and ***hörnesite***. Annabergite precipitated on all Ni-bearing ore minerals, most notably gersdorffite and skutterudite, and least frequently on millerite and nickeline. Köttigite is represented by a pink, Co-bearing variety. Zinc for köttigite is supplied from sphalerite, one of the most common sulphides in Jáchymov.

In the past, pink köttigite was misidentified for erythrite, in view of its colour. Erythrite is very rare in Jáchymov, much the same as hörnesite, which remained unnoticed for a long time owing to its similarity to ***picropharmacolite***. ***Parasymplesite***, nearly always in a mixture with symplesite, formed during weathering of arsenides and sulphides, mainly skutterudite, löllingite, sphalerite, and pyrite.

Succession relations among minerals of the erythrite group are not quite clear; the same holds true with respect to arsenates of Ca and Mg. It is probable that Co-bearing phases are among the youngest, as indicated by zoned köttigite aggregates, which are darker pink towards periphery. Some aggregates dark green in centre and pink at margins were observed. One of rare specimens of erythrite shows this violet-red mineral as a crust, clearly separated from the matrix of spheroidal-radiating red-orange ***Fe-erythrite***. Generally, pink Co-bearing arsenates are more abundant on vein material carrying native bismuth, which correlates with the observation that skutterudite in this type of veins contains more cobalt than in veins without native bismuth.

The following succession is proposed: talmesite - erythrite group - picropharmacolite - rösslerite - pharmacolite - haidingerite - sainfeldite + villyaellenite + fluckite - picropharmacolite; in a few cases the sequence pharmacolite - rösslerite was observed. In addition to the minerals listed, a number of additional species belongs to this paragenesis. However, they can not be classified in the succession in view of their rarity.

Adamine is confined to a single type of specimens from the Geschieber vein. It occurs with ***köttigite*** showing a striking buff white-light grey brown colour banding. At a small scale, adamine associates only with white köttigite. Köttigite crystallised on wall rock matrix in larger free vugs, while adamine deposited in minor fractures in wall rock. Adamine is a basic arsenate, while other arsenates in the paragenesis are acid. In absence of carbonates in the vein, a complete neutralisation of solutions is improbable. In one specimen, adamine is deposited directly on partly weathered pyrite, where surplus of free sulphuric acid seems to be evident. This suggest that another mechanism was responsible for adamine crystallisation.

Guerinite is the most rare Ca-arsenate in Jáchymov. It was found in the Kryštof vein in several crystal clusters, together with ***picropharmacolite*** and ***köttigite*** on carbonate with rare skutterudite. Guerinite deposited next to small vitreous coatings of aragonite.

Monohydrocalcite was found only in several specimens as small lustrous spheres with ***talmesite***.

Ca-Mg-Fe-Zn-Mn-arsenates belonging to this paragenesis can be characterized with respect to their chemical properties (acidity) in the following way:

	Me	**H**	**H_2O**	**A**	**B**	**A . B**
$Ca(H_2AsO_4)_2$ (***CAS***)	2	4	0	0.67	1.00	0.67
Kaatialaite	3	6	5.3	0.67	0.73	0.49
Weilite	2	1	0	0.33	1.00	0.33
Haidingerite	2	1	1	0.33	0.80	0.26
Fluckite	4	2	2	0.33	0.80	0.26
Pharmacolite	2	1	2	0.33	0.71	0.23
Brassite	2	1	4	0.33	0.64	0.21
Rösslerite	2	1	7	0.33	0.59	0.19
Villyaellenite	10	2	4	0.17	0.80	0.14
Sainfeldite	10	2	4	0.17	0.80	0.14
Irhtemite	10	2	4	0.17	0.80	0.14
Picropharmacolite	10	2	11	0.17	0.68	0.12
Guerinite	10	2	9	0.17	0.70	0.12
Adamite	4	-1	0	0	1	0
Talmesite	6	-	2	0	0.80	0
Scorodite	3	0	2	0	0.71	0
Erythrite group	6	-	8	0	0.64	0

Me - *number of metal atoms (Ca,Mg,Mn,Zn,Fe) multiplied by their charge number*
H - *charge of all H^+ ions, which can dissociate*
H_2O - *number of structurally bound H_2O molecules in the formula*

Where :

$$A = H/(Me + H)$$

$$B = 1/[1 + H_2O/(Me + H + H_2O)]$$

The symbol "A.B" indicates "acidity" trend in Ca-Mg-Fe-Zn-Mn-arsenates, i.e., the property to crystallise and persist under certain pH conditions. The "A.B" value is directly proportional to probability of arsenate occurrence in an acid environment.

Conclusions

The present publication contains results of four year project of detailed study of secondary minerals and their genetic relations in the Jáchymov ore district.

Paragenetic groups are reviewed in the following text.

The paragenesis of secondary minerals of bismuth

The secondary minerals of bismuth are relatively rare. From the paragenetic point of view, they can be described as two groups with the following succession:

a) bismite - preisingerite - bismutite - walpurgite - metatorbernite - eulytite - bismutoferrite - limonite
b) eulytite - bismutite - kettnerite - beyerite - pucherite - namibite

The paragenesis of secondary minerals in native arsenic-quartz veins

The absence of carbonates of Ca, Mg, and Fe, and arsenides of Fe, Co, Ni, i.e., absence of cations for crystallisation of the erythrite group arsenates or Ca, Mg arsenates, is essential for this paragenesis. Marcasite and pyrite, disseminated in these veins, provide Fe as the important cation, and serve as a trigger and accelerator of oxidation process. Unstable marcasite yields concentrated sulphuric acid, which accelerates oxidation of native arsenic to As_2O_3 and further to arsenic acid, which reacts with Fe ions and precipitates Fe-arsenates.

The paragenesis of secondary minerals of lead

This paragenesis occurs on specimens from the Geschieber vein or from its proximity. Galena and exceptionally uraninite are the primary minerals preserved in small amounts.

The paragenesis of uranyl-carbonates

Minerals of this paragenesis, uranyl-carbonates of Ca, Mg (or Na), show a close association with uraninite. Absence or only minor content of pyrite and marcasite in ore, i.e., pH = 5 to 8, and relatively dry environment are limiting this paragenesis. Minerals of this paragenesis only rarely occur with uranyl-sulphates.

The paragenesis of uranyl-sulphates

Development of this paragenesis requires absence or only a minor occurrence of primary carbonates and significant amounts of pyrite and marcasite in the veins, resulting in pH values near 3, and the presence of uraninite. The succession relations are not clearly defined. Uranyl-sulphates occur only exceptionally with uranyl-carbonates.

The paragenesis of copper arsenates

Minerals of this paragenesis occur on veins with a low content of carbonates. These are quartz veins, often vuggy and fractured, with sulphides, sulpharsenides or arsenides. Chalcopyrite, bornite with chalcocite and tennantite are the most common primary minerals. Although this paragenesis is not widespread, some of the minerals are typical for Jáchymov, i.e., lavendulan and lindackerite.

The paragenesis of uranium-free sulphates

This paragenesis can be divided into several partial paragenesis, which include different minerals, although sites of their occurrence are not far apart. Paragenesis near the Geschieber vein is characterised by crystallisation of minerals on strongly porous weathered country rock. The strong porosity was instrumental in an efficient circulation of fluids. The unusual association thenardite-gypsum-Mg-(Ca) -arsenates formed by reaction of percolating mineral waters with acidic arsenate-sulphate solutions.

The paragenesis of Ca-Mg arsenates

This represents the most populous and widespread paragenesis of the secondary minerals in the Jáchymov district. It occurs on all veins carrying carbonates with native arsenic, any of arsenides of Ni, Co, Fe or even single tennantite.

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Přehled minerálních asociací a paragenetických skupin sekundárních minerálů jáchymovského rudního revíru

V této práci jsou shrnuty poznatky o vztazích mezi fyzikálně chemickými vlastnostmi a genetickými rysy 207 sekundárních minerálů a 30 novými přírodními minerálními fázemi, které jsou popsány z Jáchymova.
Je zde definováno a popsáno 8 typů paragenezí s ohledem na podmínky vzniku sekundárních minerálů.