Ore-forming processes and mineral parageneses of the Jáchymov ore district

**Rudotvorné procesy a minerální pragenze jáchymovského rudního okrsku**

(77 figs, 6 tabs)

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The contribution provides characteristics of the so-called five-element Ag–Ni–Co–Bi–U formation, points to differences in sources of the U formation and the Ag–Ni–Co–Bi–As formation, and presents a model of element fractionation in abyssal hydrothermal sources according to physical-chemical properties of the compounds. The role of arsenic (AsH₃) in the mobility of the triad Ni–Co–Fe is discussed. A new scheme of mineralization stages is proposed in relation to three sources, separated in space and time: 1. greisenization of granite: Sn–W sulpharsenide stage. 2. U formation: carbonato–uraninite stage. 3. Ag–Ni–Co–Bi–As formation: arsenide, arsenic–sulphide, and sulphide stages. A new geochemical and thermodynamic interpretation of hydrothermal processes of individual mineralization stages is presented, including a detailed discussion of thermodynamic conditions of U³⁺ mobility and uraninite precipitation. Redox potentials of hydrothermal environment after the carbonato–uraninite stage including crystallization of silver and bismuth dendrites, precipitation of Ni–Co–Fe polyarsenides and electrochemical dissolution of Ag and Bi dendrites are also discussed. Mechanisms of the precipitation of base metal sulphides and sulpharsenides are considered in relation to redox conditions and sulphur fugacity in the environment during individual stages of mineralization. Phase relations are used for the deduction of the conditions of formation of selected ore minerals. Diagrammatic interpretation of chemical analyses and substitution trends of selected minerals or mineral groups, and a paragenetic relation of primary and secondary minerals are used in the interpretation. A discussion of the dependence of weathering processes on mining activity is included. Data on fluid inclusions and stable isotopes are used for the interpretation of ore-forming processes.

Key words: Ag–Ni–Co–Bi–U formation, mineralization stages, redox potentials, uraninite precipitation, Ag, Bi precipitation and electrodissolution, Ni–Co–Fe polyarsenides, fluid inclusions, stable isotopes, Jáchymov.

**ELEMENT SOURCES AND FRACTIONATIONS**

**Mineralization sources**

V. Zoubek suggests Proterozoic sediments containing local accumulations of uranium minerals as a source of U; the uranium is assumed to be released during the recrystallization of rocks (Štěmprok 2003). Other hypothesis (Baumann et al. 2000) quote accessory minerals of granites as a uranium source; the release of uranium is associated with processes of metamorphism of the host rocks in this case. Recent studies date the U-mineralisation as late-Variscan (i.e., Upper Palaeozoic) – 300–240 Ma (Baumann et al. 2000), that means younger than greisens.

A connection of five-element mineralization to granites is assumed to be structural only instead of genetic (Baumann et al. 2000). Hence, the metals required were not released from granites but they came from unknown deep-seated sources and deposited in weakened structures that served also as feeder channels for granite intrusions. The feeder pathways for ore-forming solutions coincide with deep-seated faults of Gera-Jáchymov fault zone. The ore mineralisation resulted from post-Variscan tectonomagmatic re-activation which had a form of brittle tectonics. The mineralization is dated as post-Variscan (Mesozoic) with age 240–100 Ma.

**Abyssal hydrothermal sources – a model for separation of elements**

At least three independent thermal sources instrumental in the transport of ore-forming elements into the fractured crystalline complex and their accumulation are considered for the Jáchymov ore district.

1. The oldest thermal source is related to the intrusion of granite (Karlov Vary pluton), underlying the complex of metamorphic rocks. Greisenization related to younger granite resulted in the enrichment of the apical parts of granite in Sn, W, As, S, Fe, Cu, (Mo, Cd, In), a.o.

2. The second source in the time sequence is responsible for the transportation of uranium in the form of uranyl-carbonate complexes into fractures in older granite and in the metamorphic complex. Information on the source of uranium is not available.

3. The youngest thermal source is responsible for the introduction of Ag–Ni–Co–Bi–As into pre-existing and partly mineralized open fractures. Hydrothermal fluids penetrated along fault zones from a crustal domain below the granite massif. The ultimate source of these elements is again unknown.
Fractionation of elements of the Ag–Ni–Co–Bi–As formation

Ag–Ni–Co–Bi–As formation

The character of the individual periods of mineralization is interpreted as a consequence of the fractionation of Ag, Bi, Ni, Co, Fe and As compounds in a 3D domain of an evolving hydrothermal system. The process includes repeated crystallization and selective separation of elements controlled by differences in physical-chemical properties of their compounds with non-metallic elements: S, As, Cl, F, O (Fig. 1).

Silver and bismuth are the first fractionated elements due to the volatility of Ag and Bi chloro-complexes in hydrothermal environment under elevated temperatures. The subsequent fraction contains Ni, Co, Fe bound in volatile complexes of the MeX₄ or MeX₅ type (where X = Cl, OH, H₂O and AsH₃). With regard to new data [578], separation of these elements by the formation of pentacarbonyl-like phases with ligand AsH₃, or substitution of AsH₃ for CO (e.g. phase as P analogue of Fe(CO)₅(AsH₃)) with dissociation energy of ca. 40 kcal/mol [578]) is possible. Other possible ligands are: N₂, CCH₃, CH₃, H₂, NH₂, PH and many others. Evidence of the occurrence of Ni(CO)₅ in fermentation gases from a municipal sewage treatment plant was presented in [428].

This fraction is followed by a fraction containing only As(S) without significant metal concentration. In its final stages, these products were succeeded by the last fraction containing base metals (Pb, Cu, Zn, Fe) and S; arsenic content is insignificant.

The five-element association documented in the Jáchymov ore deposit with its succession of minerals corresponds to the outlined mechanism of element fractionation. The fact that certain minerals occur in several generations and in part in various oxidation states is interpreted as due to oscillating redox conditions and rejuvenations. For example, silver was primarily deposited as native metal, but was re-mobilized and deposited at other sites, under changed conditions, in the form of sulphides or sulphosalts.

PARAGENETIC RELATIONS OF THE ORE VEIN SYSTEM

Mineralization stages

Tectonic movements separated individual mineralization stages responsible for the deposition of the mineral contents of ore veins [374]. Deposition of vein minerals took place in several chemically specialized stages of mineralization. This development was accompanied by repeated opening of fractures and by fracturing of older vein minerals. Tectonization opened conduits for mineralizing solutions propagating along NW–SE-striking fault zones and lower-order faults. Tectonic effects accompanying the Tertiary volcanism included mainly movements on E–W-striking faults and the emplacement of basaltic breccia dykes. In places where ore veins were deformed by fault reactivation, their ore minerals were crushed and exposed.

Fig. 1. Estimated trends of variation with time in activities of major elements, Eh and temperature during the main mineralization stages.
to enhanced groundwater flow, resulting in a stronger secondary alteration. The existing mineral filling of ore veins is not significantly complicated by tectonics post-dating the mineralization [374].

The complicated mineralization succession can be partly reconstructed only on the basis of the preserved information and material. The value of this information is weakened by the profound effects of the younger stages of mineralization. Only the middle and lower parts of the veins have been preserved, while the upper parts were removed by erosion.

The above complications affected the interpretation of mineralization stages and of sources of ore-bearing solutions, presented by various studies of the problem: [386], [431], [435], [436], [437], [438]. The time succession of mineralization stages proposed by Mrha and Pavlu [351], [431], is presented here, modified with respect to the data of the present study.

Detailed characteristics of mineralization stages

Sn–W sulpharsenide stage

This stage is composed of several independent periods, which belong probably to high-temperature pneumatolytic and high-temperature hydrothermal mineralization stage known from Cinovec or from greisens of the Horni Slavkov–Krásno–Čistá area, also related to young granites. The authors of this study are convinced that this mineralization stage, or at least its younger period, is identical with the older sulphide stage defined by previous authors.

This stage of mineralization is probably the oldest one, with temperatures of ~300 °C (see Fluid inclusion study). The mineral paragenesis of Sn–W sulpharsenide mineralization is rare in the Jáchymov ore district. It was deposited on E–W structures, but the local characteristics of deposition are rather variable. It has been recorded in the Trojická vein, Svornost Shaft, Daniel level. In the Rovnost I mining field, minerals of this paragenesis are cut and displaced by about 0.5 m by veins of the five-element mineralization [431]. The Giftkies and No. 20 adits also encountered Sn–W sulpharsenide mineralization.

Minerals of this stage are not directly tied to the fracture system but represent accumulations in greisenized rocks. Rare and weak manifestations of this stage have been observed in some veins striking mainly NE–SW and E–W, e.g., Trojická vein. Principal minerals of this stage include quartz, pyrite, arsenopyrite, tourmaline, phlogopite, tungstenian rutile, cassiterite and molybdenite and younger sulphides: chalcopyrite, bornite, tennantite, argentofenantite, freibergite, aikinite, matildite, dark sphalerite, galena, stannite, kёsterite, mawsonite, and gersdorffite (Figs 2–4). These minerals occur in quartz veins or as impregnations in strongly altered greisens, in various combinations or isolated.

Interesting is the accessory occurrence of microscopic roquesite enclosed in mawsonite and stannite, which indicate increased contents of In in the solutions. This points to a relationship of the Jáchymov Sn–W sulpharsenide stage with the closely similar paragenesis at Cinovec [448].
Ore-free quartz stage

This stage is characterized by various varieties of quartz, carbonates and rare fluorite. The oldest mineral is quartz, including chalcedony-like, ferruginous, amethystine quartz and quartz of pectinate texture. The grey chalcedony-like quartz carries inclusions of microscopic pyrite and clay minerals. Ferruginous quartz is brown red due to the pigmentation by Fe oxides and is locally impregnated by fine-grained chalcopyrite. Both types of quartz constitute characteristic vein filling of lower parts of the N–S veins. Pectinate quartz also widespread is either colourless or pigmented occasionally at crystal tips. It is deposited on fracture walls, fragments of wall-rock or on the breccia of the two above mentioned types of quartz.

Significantly less abundant are light green fluorite and (Fe,Ca)-carbonates, affected by replacement. In the interpretation by Dymkov [436], this stage would correspond to quartz–fluorite paragenesis, positioned at the beginning of the carbonate–uraninite stage.

Carbonate–uraninite stage

Products of this stage are present in variable quantities in a large number of veins striking NW–SE and N–S. Hydrothermal solutions of this period were moderately tempered near 200 °C, mineral paragenesis crystallized under moderately oxidizing, neutral, and weakly alkaline conditions, which varied considerably. Sulphur fugacity was low, locally increased SiO₂ activity resulted in the coffinitization of uraninite.

The main mineral is colloform, botryoidal uraninite accompanied by pink dolomitic carbonate, sporadic dark violet fluorite, grey to black quartz and pyrite. Radioactivity around uraninite aggregates turned fluorite to nearly black in colour. Carbonate crystals near uraninite contain thin layers rich in Fe oxides, indicating growth zones.

Uranium deposited as uraninite was repeatedly remobilized and participates in mineral paragenesis of nearly all mineralization stages.

Detailed characteristics of uranium mineralization

Uranium mineralization cemented fragments of the older quartz gangue, penetrated it in thin veinlets and, in other instances, formed with associated carbonates the sole thin veinlets filling. Uraninite usually formed monomineralic massive botryoidal aggregates only several cm thick, but extending for meters along the vein less frequently as short veins showing a symmetric structure. The associated gangue was dolomite or dolomitic carbonate, coloured in proximity of uraninite to creamy, buff pink or red. Dolomite is usually coarsely crystalline, coloured by Fe oxides.

Less common gangue minerals are fluorite, dark violet to black near uraninite. Uraninite was locally accompanied by pyrite, especially where dolomitic gangue was absent and uraninite was deposited directly in crushed and hydrothermally altered wall rock.

Uraninite mineralization often developed in significant concentrations, with uraninite prevailing over minerals of younger stages of mineralization. The original extent of uranium mineralization was larger than encountered during mining, since some parts of uraninite were replaced by hydrothermal solutions of the arsenide stage. Uraninite at Jáchymov has relatively high contents of REE. In the course of younger evolution of veins, several events of mobilization and regeneration of uraninite took place as indicated by the range of radiometric age determinations (see Geology and hydrothermal vein system of the Jáchymov ore district).

Other ore minerals, mainly arsenides, sulphides (dominantly chalcopyrite and galena), localized mainly in fractures of uraninite aggregates or at their margins, are younger than uraninite and belong to the paragenesis of later mineralization stages. Dymkov [436] considered that calcite, later subject to dolomitization, originally accompanied uraninite.

Arsenide stage

By volume, mineralization of the arsenide stage represents the major part of the total mineralization of the Ag-Ni-Co-Bi-As formation.

Successive relations among minerals of this stage are discussed by Keil [440], Dymkov [436], Zückert [423], Mrha and Pavlú [351], [431] and others.

This stage is represented in a lower number of veins than uranium mineralization but is more varied and the most complicated in the district. It is characterized by low fugacity of sulphur and high fugacity of arsenic. Hydrothermal mineralizing solutions were medium- to low-temperature, up to 200–250 °C, mineral assemblages crystallized in a strongly reducing, neutral or weakly acid environment.

The main gangue mineral is semitransparent or strongly pigmented quartz with frequent fine and dark grey ore impregnation. Arsenide ores are occasionally localized in

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**Fig. 5. Alternating layers of nickeline (ni) and rammelsbergite (ra). Svornost shaft, Geschieber vein. Magnification 83 x. [524]**
dolomitic carbonates. However, it is uncertain whether these carbonates belong to the arsenide stage or represent re-mobilized material from older vein filling.

In some cases, ore accumulations of diarsenides and triarsenides show features of a rapid growth under conditions of oscillating Ni/Co/Fe ratio. The mineralizing solutions were probably rather concentrated. A change in p-T conditions probably triggered the deposition of gel-like amorphous precipitates. A subsequent crystallization of such materials resulted in the formation of aggregates with contraction fractures filled by quartz or younger generations of ore minerals.

Crystals, if developed, are nearly always zoned (nickel-skutterudite). Such changes are generally documented by repeated alternation of nickeline and rammelsbergite (Fig. 5) or by polynuclear arsenide rim around silver or bismuth.

Primary silver (bismuth) crystals served as crystallization (nucleation) sites for arsenides and diarsenides.

The main part of ore minerals consists of silver, bismuth, nickeline, Ni–Co–Fe diarsenides (safflorite, rammelsbergite, löllingite) and triarsenides (skutterudite, nickel-skutterudite). Minor aggregates of uraninite, remobilized from the uranium stage, represent a small heterogeneous component in the arsenide assemblage.

Arsenides are associated with alteration products of both native metals – regenerated bismuth, bismuthinite, argentite, sternbergite, argentopyrite, silver, a.o., less frequently alteration products of arsenides such as gersdorffite, glaukodot, alloclasite, pararammelsbergite, krutovite, a.o.

Several separate parageneses can be distinguished in the arsenide stage. Depending on the presence or absence of one of the two native metals, Ag and Bi, Zückert [423] introduced the following division:

**Silver paragenesis**

- silver + Ni arsenides – dendritic crystals of silver overgrown by nickeline and rammelsbergite. Exsolved gersdorffite has been occasionally observed.
- silver + nickel-skutterudite – crystals of native metal are surrounded by nickel-skutterudite, followed by younger nickeline and rammelsbergite
- silver + rammelsbergite + safflorite – larger-size silver dendrites are overgrown by a broader rim of rammelsbergite, coated by a thin layer of safflorite

**Bismuth paragenesis**

- bismuth + safflorite – skeletal bismuth crystals surrounded by safflorite
- bismuth + skutterudite – bismuth shapes depend on mutual ratio of both components in solution
- bismuth + Ni arsenides
- bismuth + safflorite + rammelsbergite – skeletal bismuth crystals are surrounded by thin rammelsbergite with a broader rim of safflorite or safflorite–löllingite
- bismuth + safflorite + skutterudite – unlike the association with safflorite, simple dendrites of bismuth are surrounded by skutterudite with a thin rim of safflorite
- bismuth + löllingite – löllingite forms thin rims on bismuth

** Transitional paragenesis**

- native Bi, rammelsbergite, nickeline

**Arsenide paragenesis free of native metals**

- nickel-skutterudite, skutterudite, nickeline, löllingite

Minerals of the bismuth paragenesis are more common than minerals of the silver paragenesis [383]. Both the parageneses often occur in the same vein or fracture filling but are sharply separated and form independent lenses. Common occurrence of bismuth and silver is exceptional in the form of irregular bismuth aggregates around silver dendrite. Krause [424] described vertical zoning in the Jáhymov veins, with predominance of silver in upper levels, gradually replaced by bismuth towards deeper levels.

The period of mineralization was probably of weak tectonic activity, and the flow velocity of the mineralizing solutions must have been very low as indicated by the presence of delicate and brittle aggregates including dendrites, skeletal or quill-like crystals.

**Macroscopic description of mineral parageneses**

A common feature of the parageneses is the presence of white isomorphous diarsenides and triarsenides constituting two series:

- anisotropic series: rammelsbergite NiAs₂ – safflorite CoAs₃, löllingite FeAs₃
- isotropic series: nickel-skutterudite NiAs₃ – skutterudite CoAs₃

Ni–Co–Fe arsenides occur in the main paragenesis (i.e., silver and bismuth) as typical rims surrounding silver and bismuth (predominance of diarsenides), as well as independent grains and aggregates of variable shape. Most common are euhedral crystals – cubes of triarsenides, orthorhombic crystals of diarsenides, often in triplets having the shape of six-pointed stars.

The alternation of sharply defined layers is typical of polyarsenides (Fig. 5). The layers are often separated by a thin layer of remobilized uraninite of a younger generation.

The precipitation of polyarsenides took place in the succession:

arsenides ⇒ diarsenides ⇒ triarsenides,

and the oscillation in gradually increasing redox potential resulted in a partial repetition of the succession.
Silver paragenesis

This paragenesis includes ore minerals in dendrites forming mainly perimorphs after silver, which was largely dissolved during later hydrothermal processes. Resulting vugs and cavities were partly or completely filled with younger minerals, mainly ore-stage quartz, silver minerals (dominantly argentite) and sulphides. The main minerals of this paragenesis with Ni prevailing above Co are nickel-skutterudite, rammelsbergite, nickelene, rare safflorite, or löllingite.

Wire silver observed in occasional cavities does not belong to this paragenesis, since it was deposited later. Rather common is the alternation of thin botryoidal zones of nickelene with thicker layers of diarsenides and triarsenides. The precipitation of nickelene mainly occurred at an earlier time of the arsenide stage, with nickelene directly surrounding silver dendrites.

The analysis of minerals filling perimorphs of arsenides after silver indicates that silver was dissolved by solutions of the sulphide stage. The replacement of silver by diarsenides was not confirmed.

Dendrites with arsenide perimorphs after silver often reach the size of 5 cm and are hollow. The perimorphs were classified on morphological basis by Mrňa and Pavlí [383] as:
– dendrites with good crystal shape definition with branching corresponding to edges of cube (Fig. 6),
– dendrites well developed in one direction (Fig. 7),
– dendrites containing cavities which are imperfectly crystallographically defined (Fig. 8).

Bismuth paragenesis

Skeletal and quill-like bismuth crystals (Figs 9–10), often twinned, up to 2 cm long, are characteristic. Subhedral and irregular grains also occur. This paragenesis includes veinlets of younger bismuth, formed by the regeneration of primary bismuth and its deposition in fractures of gangue minerals. Owing to limited mobility of BiCl₆ complexes (liable to hydrolysis to BiOCl in slightly acid environment), the transport took place over the distance of several centimetres only.

Bismuth is common in paragenesis with arsenides containing increased Co and As, mainly skutterudite, safflorite, less frequently löllingite, rammelsbergite and bismuthinite. Such replacement is locally so intensive that perimorphs form. Galena and sphalerite are rimmed by a thin layer of diarsenides in the proximity of skeletal bismuth. Nickelene, typical of silver paragenesis, is rare in bismuth paragenesis. In a similar way as with silver dendrites, Ni–Co–Fe diarsenides form rims around skeletal bismuth crystals or fill cavities in bismuth. Unlike silver, bismuth may form lenses free of other ore minerals.

Analyses of ore lenses of bismuth paragenesis [351] show Ni:Co ratio up to 2:1, and cases of Co predominance occur. Notable is an increased As content in bis-
muth ores with Bi/As ratio of 1 : 2 to 1 : 2.8. In the silver paragenesis the Ag/As ratio is 1 : 1.5 to 1 : 2.3.

Mineral succession of the arsenide stage

The scheme of the precipitation succession of individual minerals of the arsenide stage is complicated by local physical and chemical conditions in a given part of the vein. The crystallization sequence is complicated by the superposition of a new generation of certain mineral and by the absence of some minerals in parts of the vein.

The compilation and evaluation of analytical and published data [351], [431] provided a basis for the scheme of mineralization succession in silver paragenesis of the arsenide stage:

ferruginous quartz ⇒ dendritic silver ⇒ spherulites of regenerated uraninite ⇒, nickel, nickel-skutterudite (larger aggregates) ⇒ rammelsbergite (less frequently safflorite), nickel ⇒ rammelsbergite (rimming nickel) ⇒ skutterudite (mainly isolated crystals) ⇒ ore quartz, rare carbonates.

Fig. 15. J117P. The oldest nickel-skutterudite is corroded and dissolved and it is rimmed by rammelsbergite. The arsenides are in turn enclosed in zonal nickel, which alternates with another generation of rammelsbergite. Border between monarsenide and diarsenide is sharp. Chalcopryite and proustite form minor inclusions near nickel-skutterudite. 1 – nickel, 2 – rammelsbergite, 3 – nickel-skutterudite, 4 – chalcopryite, nickel 5 – carbonate. Elišť mine, 2A vein. Reflected light. Magnification 100×.

a) single polarizer  b) crossed polarizers

Fig. 16. MP290C/H-5. 1 – löllingite, 2 – gersdörfite, 3 – nickel-skutterudite. Barbora shaft, 5th level, vein No. 32. BSE image. Magnification 20×.

Fig. 17. MP511C/B-2. 1 – nickeline-(NAP), 2 – uraninite, 3 – rammelsbergite, 4 – annabergite, 5 – dolomite. Rovnost II shaft, 6th level, vein No. 16. BSE image. Magnification 60×.

Fig. 18. J115P/B-1. 1 – arsenolite, 2 – matildite, 3 – nickel-skutterudite. Rovnost II shaft, 6th level, vein No. 16. BSE image. Magnification 800×.
Fig. 19. J117P/A-8. 1 – galena, 2 – nickeline a rammelsbergite. Eliáš mine, 2A vein. BSE image. Magnification 16×.

Fig. 20. J120P/B-1. 1 – bismuth, 2 – nickeline, 3 – rammelsbergite, 4 – S-rammelsbergite. Barbora shaft, 5th level, vein No. 32. BSE image. Magnification 130×.

Fig. 22. MP215. 1 – bismuth, 2 – uraninite, 3 – rammelsbergite, 4 – perimorphs after silver. Tomáš shaft. BSE image. Magnification 100×.

Fig. 23. MP215/1. 1 – bismuth, 2 – uraninite, 3 – rammelsbergite, 4 – nickel-skutterudite. Tomáš shaft. BSE image. Magnification 32×.

The succession of the bismuth paragenesis is similar: ferruginous quartz ⇒ bismuth ⇒ spherulites of regenerated uraninite ⇒ skutterudite (larger aggregates) ⇒ safflorite (or rare rammelsbergite) ⇒ löllingite, skutterudite (mostly colloform structures) ⇒ [galena, sphalerite] ⇒ ore quartz, rare carbonates.

Later or concurrently with the above-mentioned stages of arsenide mineralization, a number of other processes took place:

Native metals deposited as dendrites were partly or completely dissolved, nickeline was decomposed, secondary Bi and Ag minerals crystallized, precipitation of carbonates, quartz and copper minerals in vugs after leached native metals or among aggregates of arsenides took place.

The basic scheme is complicated by “rhythmic” crystallization of arsenides (mainly rammelsbergite, gersdorffite and nickeline; Fig. 11), by several generations of regen-
erated uraninite, by the presence of younger dendritic silver deposited in sheaf-like aggregates on arsenides, the existence of several generations of bismuth, a.o. Other typical and characteristic minerals of this period are: bismuthinite, anhedral bismuth, argentite (Figs 11–23).

**Arsenic–sulphide stage**

Besides arsenic, sulphur and to some extent also antimony participated in the hydrothermal process of this mineralization stage. Typical is an increase in redox potential of ore-bearing solutions, neutral or weakly acid conditions and crystallization temperature in the range of 180–200 °C in early stages and ca. 60 °C in its closing stage.

This paragenesis occurs in numerous veins, particularly in the central and southwestern part of the district. The paragenesis occurs in a vertical range in the Geschieber vein. Ores of this mineralization stage form either independent accumulations or associate with minerals of the arsenide stage, or with the youngest base metal sulphide mineralization stage.

The most common ore mineral is arsenic, accompanied by silver mineralization, sometimes with realgar, e.g., in the upper part of the Geschieber vein, and with löllingite. The main gangue mineral is dolomitic carbonate.

One of the oldest minerals of this stage is dendritic silver enclosed in lenses of arsenic. Leaching of silver or its substitution by proustite took place during this stage. Silver also occurs in globular aggregates directly in massive arsenic.

Silver paragenesis is represented by the following minerals: Sb–proustite, As–pyrrhotite, stephanite (important amounts in lower parts of the Geschieber vein), less frequent argentite, pyrrhotite (without proustite), polybasite, arsenopyrhotite, xanthoconite and small crystalline aggregates or isolated crystals of sternbergite and argentopyrite. Silver is not represented to such degree as in the arsenide stage. Silver minerals of this paragenesis are dominantly deposited on arsenic or fill vugs in arsenic.

The single arsenic observed in silver paragenesis is löllingite, which rims arsenic aggregates in the form of small crystals.

In some important veins (Geschieber, Hildebrand), the arsenic–sulphide mineralization stage shows increased Sb contents which resulted in the following association of Sb minerals: stibnite, pyrrhotite, antimony, dyscrasite, miargyrite, pyrrhotite, robinsonite, stibarsen, and AsSb and BiSb inter-metallic phases. Mráha and Pavlá [351] noted vertical zoning in Sb abundance in the Geschieber vein. It is demonstrated by the occurrence of Ag-sulphantimonates in lower levels, while in upper levels the content of Sb is lower, and Sb is contained mainly as equant admixture in proustite. Pyrite is also present in the above association of Sb minerals.

**Sb facies of mineralization**

Minerals containing Sb, or with prevalence of Sb above As, occur in the whole ore district, but are less numerous than minerals with prevailing As.

Sb is mainly contained in minerals of the proustite–pyrrhotite and tennantite–tetrahedrite series. It is impossible to identify crystallization sequence from the intergrowth of these minerals. In a similar way, relative succession cannot be determined from tennantites enriched in Sb. The presence of tetrahedrite filling fracture in quartz containing tennantite grains shows that tetrahedrite in the sample from Gifkies adit is younger than tennantite.

Sb content in gersdorffites is increased in late crystallization stages. In a similar way, Sb–bismuthinite crystallized in later stages.

The Hildebrand vein in the Svornost mine is known from historical records through the occurrence of Sb-bearing minerals. However, only a small number of precisely localized samples have been preserved from this fairly small vein, which occasionally yielded some good ores. The samples show that at least some parts of the vein reached notable enrichment in Sb, which enabled the origin of an anomalous mineral paragenesis for the Jáchymov deposit. Antimony was locally formed as inclusion in miargyrite, which is in equilibrium with Sb. Exceptionally, pyrrhotite occurs in this assemblage.

**Arsenic also occurs in the paragenesis with Sb minerals. Its younger parts contain increased Sb contents of max. 7 wt. % and inclusions of dyscrasite. This situation indicates approximately the time interval in which the As-dominated evolution was terminated and succeeded by a phase with increased Sb concentration. Tectonic effects coinciding with the onset of this change are indicated by veinlets of younger arsenic filling thin fractures in coarse-grained dolomite and calcite in the proximity of older arsenic.

Obviously one of the youngest (in the stage) minerals is radiating stibnite resting on a band of botryoidal pyrite and enclosed in whitish calcite. Terminal parts of stibnite crystals are partly replaced by spheres of light yellow sphalerite. This indicates that Sb largely remained in solutions during the crystallization of ore minerals and increased in concentration during later stages.

**Sulphide stage**

Minerals of this stage are distributed fairly extensively, but the accumulations are minor, developed independently of older mineralization or deposited on older ores. Minerals of this stage fill contraction fractures in uraninite (carbonate–uraninite stage) and marginal, fractured, or leached volumes in ores of arsenide stage.

The main minerals are galena with a low Ag content, sphalerite (light with low Fe, In, Cd), chalcopyrite, pyrite, marcasite and sometimes arsenopyrite. Isolated finds include bornite with exsolved chalcopyrite, boulangerite and tennantite, accompanied by accessory chalcopyrite, sphalerite and galena [351] (Figs 24–32).

Predominant gangue mineral is calcite, containing impregnations of sulphides or alternating with sulphides in banded structures.
Fig. 24. J059P. Concentric aggregates of chalcopyrite alternate with tennantite. Rammelsbergite preserved in relics. As-chalcopyrite forms pink brown layers. 1 – chalcopyrite, 2 – tennantite, 3 – As-chalcopyrite, 4 – rammelsbergite, Svornost shaft, 5th level, Prokop vein. Reflected light, single polarizer. Magnification 130x.

Fig. 25. Uraninite spherule enclosing rock fragment with relics of silver and fissure filled with chalcopyrite and bornite altered into covellite. Tennantite and silver in proximity. 1 – silver, 2 – chalcopyrite, 3 – bornite, 4 – tennantite, 5 – covellite. Svornost shaft, Daniel level, Trojická or Prokop vein. Reflected light, single polarizer. Magnification 260x.


Fig. 27. J183P/4. 1 – sphalerite, 2 – pyrite, 3 – smithite and pyrite, 4 – Fe-dolomite. Svornost shaft, 2nd level, Hildebrand vein. BSE image. Magnification 40x.

Fig. 28. MP41/D-4. 1 – rammelsbergite, 2 – matildite and mimetite. Svornost shaft, 10th level, Gesieber vein. BSE image. Magnification 600x.

Fig. 29. MP41/D-5. 1 – matildite and Bi-arsenate. Svornost shaft, 10th level, Gesieber vein. BSE image. Magnification 500x.
Post-ore stage

This stage was divided in the literature [351], [423] into several periods, such as Mn-rich calcite, fluorite–barite, or opal–quartz, with variable manifestations in various parts of the deposit. In general, the post-ore stage is indistinct in the Jáchymov ore district.

Dominant mineral of this stage is Mn-rich calcite, filling offshoots branching from the major NW–SE-striking fault zones. Minerals deposited in this stage show limited effects of younger tectonic deformation. The mineralization of the fluorite–barite stage is poorly defined; some fluorite occurrences belong to older mineralization stages, and barite is too rare. For these reasons, relations of post-ore stage to the general succession of the deposit are not sufficiently clarified.

Gangue minerals of individual mineralization stages

Important gangue minerals include carbonates mostly of the dolomite–ankerite series, quartz in several generations, minor fluorite, and exceptionally barite and siderite. Dolomite and Fe-rich dolomite were observed in majority of veins, but pure calcite was fairly rare, its separate veinlets formed in later stages of mineralization, partly by the recrystallization of dolomitic carbonates.

Although carbonates represent the main gangue minerals, the total volumes of carbonates are quite low. This situation is responsible for strongly acidic conditions at the deposit. The relatively low carbonate buffering capacity could not neutralize the aggressive arsenate- and sulphate-rich solutions. The solutions circulated through large volumes of the deposit and produced a wide range of secondary minerals.

Quartz of the oldest generation was described as grey, hornstone quartz. Drusy quartz of the second generation is widespread in the district. It occurs as early deposition in open fractures, later filled by uranium and complex ores. Its deposition marked the beginning of ore mineralization. Quartz of the third generation is white, grey and brown, sometimes rather fine-grained. This generation occurs mainly in the parts of veins with carbonates.

Carbonates filled many vein offshoots, especially in sections where the main vein was filled by mylonite. Carbonate formation is represented by dolomite, Mg-rich calcite or Fe-rich dolomite and ankerite. Yellow and pink colours prevail but dispersed hematite turns carbonates to brown colour. In the proximity of uranium accumulations the carbonates are typically brick red. Calcite crystallized after the deposition of the dolomite–ankerite carbonates and occurs only in small amounts. Its typical colour is white. The least common carbonate is siderite.

Fluorite is relatively rare. It was deposited on drusy quartz, before the crystallization of carbonates, and either before or after the deposition of uraninite.
GEOCHEMICAL AND THERMODYNAMIC INTERPRETATION OF HYDROTHERMAL PROCESSES OF INDIVIDUAL MINERALIZATION STAGES

Carbonate–uraninite stage

Modelling of conditions (pH, Eh and concentration) during the formation and remobilization of uraninite

The dissolution or precipitation of solid uranium phases can be modelled using a calculation based on known thermochemical and electrochemical parameters. Unfortunately, natural processes are extremely complicated in the Jáckymov ore district, influenced mainly by the following quantities: U activity, pH, Eh, p, T, activities of O, S, CO₂, HS⁻, H₂S, and AsH₃, the ionic strength of solution, type of crystal structure, the size of crystallites, a.o. In order to estimate the values of important variables (pH, Eh, T and U activity), it is necessary to introduce dramatic simplifications and assume limited effects of individual factors.

Chemical analyses of the Jáckymov uraninite confirm a composition close to UO₂, with a low component of U⁴⁺. General assumptions for a proposed model: reaction in hydrothermal environment in the temperature range of 150–200 °C, moderately oxidizing, neutral or weakly basic conditions; solution contains CO₂, HCO₃⁻, Cl⁻, SO₄²⁻, uranium as dominantly U⁴⁺ carbonate complexes.

On the basis of these assumptions, Eh, pH diagram (Fig. 33) was designed using tabular data [457]. The diagram shows conditions for uraninite precipitation, based on the calculation with amorphous UO₂. The graph shows that UO₂ can coexist at a range of pH–Eh conditions with the following ions: U(OH)₂⁺, U(OH)₃⁺, UO₂²⁺. Activities of these ions are also influenced (in equilibrium) under conditions of the above defined environment, with a variable of pH–Eh conditions, by ions: U⁴⁺, U(OH)₅⁻, UO₂²⁺, [UO₂(CO₃)₃]⁴⁺, [UO₂(CO₃)₂]²⁻, UO₂CO₃⁻.

![Fig. 33. pH-Eh diagram of equilibria of products of a reaction of uraninite with hydrothermal environment in the system: amorphous uraninite – O₂ – CO₂ – H₂O at 100 °C.](image-url)
Table 1. Equilibrium concentrations in hydrothermal environment in the system: amorphous UO₂–O₂–CO₂–H₂O at 100 °C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant</th>
<th>Standard Free Gibbs Energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂ + 2H⁺ ↔ U(OH)₂⁺⁺</td>
<td>α₁ = 1.32</td>
<td>ΔG° = -1031.8</td>
</tr>
<tr>
<td>pH = (log [U(OH)₂⁺⁺] = 1.32)²</td>
<td></td>
<td>K = -992.4</td>
</tr>
<tr>
<td>UO₂ + 3H₂O ↔ U(OH)₇⁻ + H⁺</td>
<td>α₂ = 12.2</td>
<td>ΔG° = -237.1</td>
</tr>
<tr>
<td>pH = log [U(OH)₇⁻] + 12.2</td>
<td></td>
<td>K = -1641.8</td>
</tr>
<tr>
<td>UO₂ ↔ UO₂⁺² + e⁻</td>
<td>E° = 0.325 V</td>
<td>ΔG° = -968.6</td>
</tr>
<tr>
<td>Eh = E° + 0.059 log [UO₂⁺²]</td>
<td></td>
<td>K = -952.7</td>
</tr>
<tr>
<td>UO₂⁺² ↔ UO₂²⁺⁺ + e⁻</td>
<td>E° = 0.165 V</td>
<td>ΔG° = -2658.5</td>
</tr>
<tr>
<td>Eh = E° + 0.059 log ([UO₂²⁺⁺]/[UO₂⁺²])</td>
<td></td>
<td>K = -2106.8</td>
</tr>
<tr>
<td>UO₂⁺²⁺ + H₂O + CO₂ ↔ UO₂CO₃ + 2H⁺</td>
<td>ΔG° = -46.2</td>
<td>ΔG° (CO₂) = -394.4</td>
</tr>
<tr>
<td>pH = (log ([UO₂CO₃]/[UO₂⁺²⁺]) = -8.095</td>
<td>K = -1538.0</td>
<td></td>
</tr>
<tr>
<td>UO₂CO₃ + H₂O + CO₂ ↔ UO₂(CO₃)²⁻ + 2H⁺</td>
<td>ΔG° = -62.7</td>
<td>ΔG° (UO₂(CO₃)²⁻) = -2106.8</td>
</tr>
<tr>
<td>pH = (log ([UO₂(CO₃)²⁻]/[UO₂CO₃]) = -11.25</td>
<td>K = -2658.5</td>
<td></td>
</tr>
<tr>
<td>UO₂(CO₃)²⁻ + H₂O + CO₂ ↔ UO₂(CO₃)⁴⁺ + 2H⁻</td>
<td>ΔG° = -79.8</td>
<td>ΔG° (UO₂(CO₃)⁴⁺) = -2658.5</td>
</tr>
<tr>
<td>pH = (log ([UO₂(CO₃)⁴⁺]/[UO₂(CO₃)²⁻]) = -13.74</td>
<td>K = -2658.5</td>
<td></td>
</tr>
</tbody>
</table>

ΔG° = standard free Gibbs energy at 25 °C [457], pCO₂ = partial pressure of CO₂ (atm)

The overlap area of horizontal and vertical belts in the pH–Eh diagram indicates the most probable range of conditions for the formation of the carbonate–uraninite stage of mineralization. A detailed analysis of the overlap area yields the set of equations shown in Table 1.

Based on thermodynamic relations obtained, concentrations of the individual above mentioned ions were calculated under equilibrium conditions such as to correspond to conditions at corners and the centre of the quadrilateral defined in Fig. 33. Inspection of data in Table 2 shows that the role of some ions in the interaction of amorphous UO₂ in hydrothermal environment containing O₂–CO₂–H₂O under variable redox and pH conditions is not significant. This group of ions includes U(OH)₃⁻, U(OH)⁵⁻, UO₂⁻. Some of the reactions are independent of redox conditions, some of variation in pH (see Table 1 with equilibrium reactions).

The review also shows that a combination of a slightly acid environment (pH = 5) with reducing conditions (Eh = −0.2 V) is in favour of the transport of uranium. Neutral conditions (Eh = 0.0 V, pH = 7) do not represent optimum conditions for U transport either. In acid and oxidizing environment, uranium is mobile in the form of UO₂⁻ ions, or as undissociated dissolved UO₂CO₃.

Analyses of pH of hydrothermal quartz powdered in suspension [351] yielded values in the range of 7.0–8.4. This indicates that hydrothermal environment during the main mineralization stages was probably moderately basic, with pH ~ 8. Based on these assumptions, the combination of Eh = 0.2 V, pH = 5 can be eliminated. A fun-

Table 2. Equilibrium reactions, thermochemical and electrochemical interpretation of products in the system: amorphous UO₂–O₂–CO₂–H₂O at 100 °C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ion</th>
<th>Log (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(OH)₃⁻</td>
<td>7.20</td>
<td>UO₂⁻⁺⁻</td>
</tr>
<tr>
<td>U(OH)⁵⁻</td>
<td>8.68</td>
<td>UO₂⁻⁺⁺</td>
</tr>
<tr>
<td>UO₂⁺⁺</td>
<td>9.00</td>
<td>UO₂⁻⁺⁺</td>
</tr>
<tr>
<td>UO₂⁻</td>
<td>10.08</td>
<td>UO₂⁻⁺⁺</td>
</tr>
<tr>
<td>UO₂⁻⁺⁻</td>
<td>11.18</td>
<td>UO₂⁻⁺⁻</td>
</tr>
<tr>
<td>UO₂(OH)²⁻</td>
<td>13.43</td>
<td>UO₂(OH)²⁻</td>
</tr>
<tr>
<td>UO₂(OH)⁴⁻</td>
<td>14.27</td>
<td>UO₂(OH)⁴⁻</td>
</tr>
</tbody>
</table>

αᵢ – calculated equilibria activity of the i-th ion for given pH-Eh conditions and temperature of 100 °C and pressure of 0.1 MPa.
dential condition for hydrothermal uranium formation is the deposition of U in the form of precipitated and eventually recrystallized gels to phases of a general composition \( (U^{4+}, U^{6+}, REE^{3+}, M^{2+}, D)_{(OH)} \) [459] through the reduction of mobile ions \( U^{6+} [458] \). Although the existence of \( U^{6+} \) is possible in slightly basic reducing environment (on the basis of the above calculations), we suppose, due to the redox potential change, that the environment was slightly oxidizing.

**Precipitation of \( UO_2 \) and conditions of uraninite formation**

The above discussed calculations, analyses and assumptions indicate that uraninite in the Jáchymov ore district formed from gels, later partly recrystallized, precipitated from slightly basic solutions (pH = 8) carrying ions of \( UO_2(CO_3)^{2+} \) and \( UO_2(CO_3)^{4+} \). These ions play the most important role during the hydrothermal environment and in the precipitation of \( UO_2 \) gels. The trigger in \( UO_2 \) precipitation was a change in pH and Eh caused by the reaction of hydrothermal solutions with materials in the vein or the neighbouring wall-rock, which possibly created sufficient reaction potential and provided for a change in pH, the concentration of \( UO_2(CO_3)^{4+} \) and \( UO_2(CO_3)^{2+} \) ions is not directly dependent on Eh. The equations for precipitation of \( UO_2 \) can be generally formulated as follows:

\[
UO_2(CO_3)^{2+} + 2H^+ + 2e^- \rightleftharpoons UO_2 + 2HCO_3^- \\
E^0(U^{6+}/U^{4+}) = 0.2 \text{ V, estimation from } [460] \\
UO_2(CO_3)^{4+} + 3H^+ + 2e^- \rightleftharpoons UO_2 + 3HCO_3^- \\
E^0(U^{4+}/U^{2+}) = 0.2 \text{ V, estimation from } [460]
\]

A quantitative course of these reactions depends on the fulfillment of the following conditions:
- reducing condition of sufficient capacity
- change in pH value allowing decomposition of uranyl-carbonate complexes
- environment providing for pressure decrease and release of \( CO_3 \)
- environment containing sufficient Ca and Mg for the crystallization of carbonates

Reducing conditions in the Jáchymov veins resulted from Fe\(^{2+}\), contained in country rocks, vein carbonates or sulphides; reduction of organic matter played a negligible role owing to its low concentration. The oxidation of sulphides and Fe\(^{2+}\) phases allowed a sufficient increase in acidity:

\[
2Fe(OH)\_2 \rightleftharpoons Fe_2O_3 + H_2O + 2H^+ + 2e^- \\
E^0(Fe^{3+}/Fe^{2+}) = -0.86 \text{ V } [457] \\
HS^- \rightleftharpoons S^{\text{aq}}(aq) + 2e^- + H^+ \\
E^0(S^{\text{aq}}/S^\text{aq}) = -0.133 \text{ V } [403] \\
2S_2^{\text{aq}} \rightleftharpoons 4S^{\text{aq}}(aq) + 4e^- \\
E^0(S^{\text{aq}}/S^\text{aq}) = -0.30 \text{ V } [461] \\
S^2^- \rightleftharpoons S^{\text{aq}}(aq) + 2e^- \\
E^0(S^{\text{aq}}/S^\text{aq}) = -0.48 \text{ V } [403]
\]

In the second step, oxidation continued with the participation of \( H_2O \):

\[
S^{\text{aq}}(aq) + 3H_2O \rightleftharpoons SO_4^{2-}(OH) \_2 + 5H^+ + 4e^- \\
E^0(S^{2+}/S^{aq}) = -0.66 \text{ V } [403] \\
SO_4^{2-}(OH) \_2 + H_2O \rightleftharpoons SO_4^{2-} + 3H^+ + 2e^- \\
E^0(SO_4^{2-}/SO_4^{2+}) = -0.94 \text{ V } [403]
\]

And finally, a shift in the redox equation \( U^{VI} \rightleftharpoons U^{IV} \), caused by the consumption of \( HCO_3^- \) ions via precipitation of \( Ca^{2+} \) and \( Mg^{2+} \), in favour of the final products – calcite and dolomite:

\[
2HCO_3^- + 2Ca^{2+} \rightleftharpoons 2CaCO_3 + H_2O \\
4HCO_3^- + 2Mg^{2+} + 2Ca^{2+} \rightleftharpoons 2CaMg(CO_3)_2 + H_2O.
\]

It is probable that the redox mechanisms discussed will vary and oscillate, which may result in local reversal of reactions toward the initial components. Thus with the onset of the arsenic-sulphide stage, with an increase in redox potential and acidity, mechanisms started to operate, facilitating transition of U in solution via oxidation \( U^{IV} \rightleftharpoons U^{VI} \):

\[
UO_2 \downarrow + 2H_2O \rightleftharpoons UO_2 + 4H^+ + 4e^- \\
E^0(U^{4+}/U^{2+}) = 0.278 \text{ V (crystalline) } [460] \\
E^0(U^{4+}/U^{2+}) = 0.031 \text{ V (amorphous) } [460] \\
U_3O_8 + H_2O + H^+ \rightleftharpoons 3 UO_2(OH)^+ + 2e^- \\
E^0(U^{VI}/U^{IV}) = 0.707 \text{ V } [460] \\
UO_2 \rightleftharpoons UO_2^{2+} + 2e^- \\
E^0(U^{IV}/U^{2+}) = 0.221 \text{ V } [460]
\]

The ions \( UO_2^{2+} \) and \( UO_2(OH)^+ \) are very mobile, which resulted in frequent rejuvenation (remobilization) of the original uraninite.

The wall-rock alteration affected mainly Mg and Fe minerals, Ca was probably transported by mineralizing solutions. The oxidized forms of Fe were deposited mainly in the abundant hematite pigment in vein fillings as well as in altered wall-rock.

**Precipitation of Fe oxides**

Carbonate crystals near uraninite contain thin layers rich in Fe oxides, indicating growth zones. Formation of such growth zones can be explained by the mechanism of redox reactions. Due to the oscillation in \( Ca^{2+}/Fe^{2+} \) ratio and varying Eh and pH, the successive growth zones contain a variable Fe\(^{2+}\) component. During the episode with lower pH and increased oxidizing capacity of the solution, U in uraninite was dissolved at the formation of mobile \( UO_2^{2+} \):

\[
UO_2 \downarrow \rightleftharpoons UO_2^{2+} + 2e^- \\
\]

Over a short distance, \( UO_2^{2+} \) ions were reduced back to UO, through reaction with Fe\(^{3+}\), bound in a thin layer of ankeritic carbonate:

\[
UO_2^{2+} + 2FeCO_3 \rightleftharpoons 2Fe^{3+} + 2CO_3^{2-} + UO_2 \downarrow
\]
The released Fe^{2+} ions were precipitated in a neutral or slightly basic environment, buffered by carbonates, following the reaction:

$$2\text{Fe}^{3+} + 6\text{(OH)}^- \leftrightarrow 3\text{H}_2\text{O} + \text{Fe}_2\text{O}_3$$

$$\text{Fe}^{3+} + 3\text{(OH)}^- \leftrightarrow \text{H}_2\text{O} + \text{Fe(OH)}_3$$

In contrast to the precipitated and relatively stable Fe$_2$O$_3$, the newly precipitated UO$_2$ was easily soluble and re-mobilized over longer distances.

**Redox potential of hydrothermal environment after the carbonate–uraninite stage**

The following model is proposed for the interpretation and prediction of the deposition of ore components in hydrothermal veins (arsenide and arsenic–sulphide stages) based on a change of redox conditions controlling mineral crystallization.

Estimates of Gibbs free energy were calculated for the oxidation of the anionic part of minerals as a basis for estimates of reducing capacity or stability/instability under changing redox properties of the environment in dependence of Eh on hydrothermal solutions. The following equation was employed:

$$\Delta G_{\text{AN}} = n \cdot \text{E}^\circ,$$

where AN represents anionic part of an arsenide, sulpharsenide or sulphide molecule.

In a formal way, Gibbs free energy is assigned to mean the value of valence of atoms in anionic part of each molecule ($n$), based on the relation between the exchange of free energy and electromotoric strength (EMS) given by the relation:

$$\Delta G_{\text{AN}} = -n \cdot \text{E}^\circ,$$

where F is Faraday constant and E$^\circ$ is standard reduction potential of the equations below. The following reactions hold for a neutral or slightly basic environment:

$$2\text{S}^8 + 2e^- \leftrightarrow (\text{S}_2)^2-$$

$$\text{E}^\circ(\text{S}^8/\text{S}^2^-) = -0.25 \text{ V} \ [403]$$

$$2\text{As}^5 + 2e^- \leftrightarrow (\text{As}_2)^2^-$$

$$\text{E}^\circ(\text{As}^5/\text{As}^3^-) = -0.50 \text{ V}$$

(estimated value from [403])

$$3\text{As} + 2e^- \leftrightarrow (\text{As}_3)^2^-$$

$$\text{E}^\circ(\text{As}^3/\text{As}^3^-) = -0.33 \text{ V}$$

(estimated value from [403])

![Fig. 34. Sulphur vs. nickel content in selected arsenides of the arsenide mineralization stage.](image)

**Table 3.** Oxidation state and modified Gibbs free energies ($\Delta G^o$) for selected arsenides, sulpharsenides and sulphides of Ni, Co, Fe.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>As</th>
<th>S</th>
<th>Me</th>
<th>results</th>
</tr>
</thead>
<tbody>
<tr>
<td>OS</td>
<td>n</td>
<td>E$^\circ$</td>
<td>$\Delta G^o$</td>
<td>OS</td>
</tr>
<tr>
<td>nickeline</td>
<td>−3.0</td>
<td>1</td>
<td>−1.37</td>
<td>132</td>
</tr>
<tr>
<td>löllingite</td>
<td>−1.0</td>
<td>2</td>
<td>−0.50</td>
<td>97</td>
</tr>
<tr>
<td>chinosafflorite</td>
<td>−1.0</td>
<td>2</td>
<td>−0.50</td>
<td>97</td>
</tr>
<tr>
<td>sallforite</td>
<td>−1.0</td>
<td>2</td>
<td>−0.50</td>
<td>97</td>
</tr>
<tr>
<td>rammelsbergite</td>
<td>−1.0</td>
<td>2</td>
<td>−0.50</td>
<td>97</td>
</tr>
<tr>
<td>skutterudite</td>
<td>−0.7</td>
<td>3</td>
<td>−0.33</td>
<td>96</td>
</tr>
<tr>
<td>nickel-skutterudite</td>
<td>−0.7</td>
<td>3</td>
<td>−0.33</td>
<td>96</td>
</tr>
<tr>
<td>arsenepryite</td>
<td>−1.0</td>
<td>1</td>
<td>−0.50</td>
<td>48</td>
</tr>
<tr>
<td>akloskas</td>
<td>−1.0</td>
<td>1</td>
<td>−0.50</td>
<td>48</td>
</tr>
<tr>
<td>gersdorfite</td>
<td>−1.0</td>
<td>1</td>
<td>−0.50</td>
<td>48</td>
</tr>
<tr>
<td>pyrrhotite</td>
<td>0</td>
<td>−2.0</td>
<td>−0.48</td>
<td>371</td>
</tr>
<tr>
<td>marazite</td>
<td>0</td>
<td>−1.0</td>
<td>2</td>
<td>−0.25</td>
</tr>
<tr>
<td>pyrite</td>
<td>0</td>
<td>−1.0</td>
<td>2</td>
<td>−0.25</td>
</tr>
<tr>
<td>sternbergite</td>
<td>0</td>
<td>−2.0</td>
<td>3</td>
<td>−0.48</td>
</tr>
<tr>
<td>sphalerite</td>
<td>0</td>
<td>−2.0</td>
<td>1</td>
<td>−0.48</td>
</tr>
<tr>
<td>chloropyrite</td>
<td>0</td>
<td>−2.0</td>
<td>2</td>
<td>−0.48</td>
</tr>
<tr>
<td>acanthite</td>
<td>0</td>
<td>−2.0</td>
<td>1</td>
<td>−0.48</td>
</tr>
<tr>
<td>proustite</td>
<td>3.0</td>
<td>1</td>
<td>0.68</td>
<td>−66</td>
</tr>
<tr>
<td>arsenic</td>
<td>0.0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

OS – oxidation states ([592], [593], [594]),
n, (n$_k$) – anion (or cation) atoms per formula unit,
E$^\circ$ (V) – estimated standard reduction potential,
$\Delta G^o$ (kJ/mol) – free Gibbs energy (calculated from estimated standard reduction potentials).
The $\Delta G^\circ$ values express the ability of atoms to accept electrons and increase their oxidation state. Minerals with a higher $\Delta G^\circ$ value would precipitate more readily in reducing conditions, and minerals with a lower value or corresponding to zero would preferentially crystallize in environment with a higher oxidation potential.

Mean values of valence (oxidation state) of all atoms in anionic part of the arsenides molecule are generally lower than in sulpharsenides and sulphides (see Table 3).

Application of the above calculations to the interpretation of crystallization succession of the five-element assemblage in the Jáchymov ore district shows (Table 3) that the oxidation potential of the arsenide stage was very low, probably the lowest among all the mineralization stages. An important role during the arsenide stage was played by the pH of the environment.

Also important is the role of sulphur [447], which did not take part in mineral crystallization due to its low fugacity (or high fugacity of As) at the beginning of the arsenide stage. Later, when S fugacity increased, sulphur partially participated in the mineralization process. Interesting are significant sulphur contents (Fig. 34) in the arsenides (rammelsbergite, skutterudite) of the arsenide stage. On the other hand, some sulpharsenides are deficient in S, due to the high As fugacity. This is seen in gersdorffite with As/S ratio varying from the normal value $1:1$ to extreme values of $1.85:0.15$. Minerals of such composition still retain gersdorffite structure and isotropic optical behaviour (see figures for gersdorffite).

Arsenide stage

Crystallization of silver and bismuth dendrites

Ag and Bi are delivered in the form of Cl complexes, mainly AgCl$_2^-$ and BiCl$_4^-$. The absence of Ag,S in the primary silver accumulations indicates a deficiency in HS$^-$ ions, which would preferentially precipitate sulphides [see below $\beta$(AgHS) $\gg \beta$(AgCl$_2^-$)], in comparison with the chlorides. Besides this, free HS$^-$ ions in coexistence with AgCl$_2^-$ complexes spontaneously oxidize to SO$_4^{2-}$ ions:

$$\text{HS}^- + 4\text{H}_2\text{O} + 8\text{AgCl}_2^- \leftrightarrow \text{SO}_4^{2-} + 8\text{Ag} + 16\text{Cl}^- + 9\text{H}^+$$

Hydrothermal solutions were strongly saline (ca. 20 % CaCl$_2$, NaCl), weakly acid (pH $\sim 6$–7), and S fugacity was probably low.

Mercury shows similar chemical properties of chloride complexes as those characteristic of Ag, resulting in joint precipitation of the two metals. This is indicated by the occurrence of mercurian silver with up to 2 wt. % Hg in rims of the old silver dendrites.

Estimate of concentration of mobile Ag or Bi ions:

Silver: For the reaction

$$\text{Ag}^+ + 2\text{Cl}^- \leftrightarrow \text{AgCl}_2^-$$

it is at $20^\circ\text{C}$ $\log(\beta_s) = 5.14$ [463], log $(K_{(\text{AgCl})}) = \log(\beta_{(\text{AgCl})}) = -9.75$ [463].

This gives equilibrium concentration $[\text{AgCl}_2^-] = \beta\text{K}_{(\text{Cl})} = 2.45 \times 10^{-4}$ [Cl$^-$] mol/l. The concentration of dissolved AgCl$_2^-$ ions in the presence of 20 % and 0.1 % NaCl at $20^\circ\text{C}$ is $8.6 \times 10^{-5}$ mol/l and $4.9 \times 10^{-7}$ mol/l, respectively, of free Ag.

In case of a parallel existence of two hydrothermal solutions with comparable contents of HS$^-$ a Cl$^-$ ions at a given time, the HS$^-$ ion will be preferentially instrumental in Ag transport. For the reaction

$$\text{Ag}^+ + 2\text{HS}^- \leftrightarrow \text{Ag(HS)}_2^-$$

is $\log(\beta_s) = 17.43$ [463], and for argentite (acanthite) dissociation:

$$\text{Ag}_2\text{S} \leftrightarrow 2\text{Ag}^+ + \text{S}^{2-}$$

is $K = -48.8$ [463]. From this follows that $[\text{Ag(HS)}_2^-] = \beta\text{K}_{(\text{HS})} = \beta\text{K}_{(\text{Ag})} = 3\sqrt{2}K$. For $[\text{HS}^-]$ concentration of, e.g., 0.001 mol/l, $[\text{Ag(HS)}_2^-] = 0.014$ mol/l.

Bismuth: For the reaction

$$\text{Bi}^{3+} + 4\text{Cl}^- \leftrightarrow \text{BiCl}_4^-$$

at $20^\circ\text{C}$, $\log(\beta_s) = 5.52$ is obtained [463]. This shows that Bi in chloride solution will behave in a similar way as Ag. Nevertheless, stability of the complex BiCl$_4^-$ is strongly influenced by Cl$^-$ concentration and the value of pH:

$$\text{BiCl}_4^- + \text{H}_2\text{O} \leftrightarrow \text{BiOCl(s)} + 2\text{H}^+ + 3\text{Cl}^-, \text{where} \log K = -1.20$$ [463].

Growth of native Ag and Bi dendrites

As noted above, spontaneous precipitation of native Ag or Bi in the form of dendrites proceeded by the reduction of Ag or Bi chloro-complexes:

$$\text{AgCl}_2^- + \text{e}^- \leftrightarrow \text{Ag} + 2\text{Cl}^-$$

$$\text{BiCl}_4^- + 3\text{e}^- \leftrightarrow \text{Bi} + 4\text{Cl}^-$$

The rapid growth of skeletal crystals was caused by increased concentration of $[\text{Ag}] \sim 10^{-2}$ mol/l (a similar situation applies to Bi), and the existence of reducing environment. The latter was represented in this mineralization stage mainly by biotite-bearing rocks with increased Fe$^{3+}$ and by rocks with finely dispersed pyrite.

The released Fe$^{3+}$ in neutral or slightly basic environment is readily oxidized to Fe$_2$O$_3$. In an oxidation environment, the oxidation of pyrite readily takes place following the equation:

$$\text{FeS}_2 + 8\text{H}_2\text{O} \leftrightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 14\text{e}^-.$$
Dendritic silver and bismuth crystals precipitated rapidly at separated sites. The following factors are considered important for their separated precipitation:

- difference in standard electrochemical potential $E^\circ(\text{Bi}^{3+}/\text{Bi}) = 0.320$ V, $E^\circ(\text{Ag}^+/\text{Ag}) = 0.799$ V,
- differences in the stability of $\text{AgCl}_2^-$ and $\text{BiCl}_2^-$ complexes in hydrothermal environment. The anion $\text{BiCl}_2^-$ readily changes to $\text{BiOCl}$ with a low solubility.

**Precipitation of Ni–Co–Fe polyarsenides**

Precipitation of polyarsenides took place under increasingly reducing conditions imposed by high arsenic (AsH$_3$) contents. Arsenic is dissolved in brine fluids; dissociation to ions AsH$_2^-$ (log(K) = −155 [425]) is negligible.

Batches of fluids containing Ni, Co, Fe were closely tied to AsH$_3$, at fairly low S fugacity, in a neutral or weakly acid environment. Under these conditions Ni, Co, Fe aqua chloro-complexes formed, facilitating the transport of these elements. Complexes with ligand AsH$_2^-$ were probably also formed: $[\text{Ni(H}_2\text{O)}_n(\text{AsH}_3)_mX_n]^z−$, where $n+v+w = 4$ or 6, $X = \text{OH}$, $\text{Cl}$; co-ordination of the central atoms (Ni,Co,Fe) of the above group of complexes is 4 or 6, with co-ordination 6 being the most common.

The disintegration of these complexes, caused mainly by a change in pressure and temperature, resulted in the precipitation of arsenides (polyarsenides in general). The appearance, chemical composition and physical properties of some arsenide aggregates suggest a rapid precipitation, which indicates high concentrations of the complexes.

The formation of arsenides–diarsenides–triarsenides is closely related to the redox potential of the environment. Based on the redox model (see Redox potential of hydrothermal environment after carbonate-uraninite stage above), it is possible to say that the redox potential values play a leading role in the precipitation, and control the type of arsenide to be precipitated. Our observations of several generations of individual arsenides indicate repeated changes in redox environment. Local variation in available oxidants, such as $\text{UO}_2^{2+}$, $\text{Fe}^{3+}$, O a.o., may have caused these changes.

Arsine oxidation in acid environment can proceed easily through the reaction with wall-rocks ($\text{Fe}^{3+}$, $\text{Mn}^{4+}$) and with components brought by the mineralizing solutions ($\text{UO}_2^{2+}$, O a.o.). Small interposed layers of uraninite separating some arsenide layers serve as evidence of the participation of $\text{UO}_2^{2+}$ ions in the deposition of polyarsenides.

The chemical analyses of arsenides (in particular triarsenides) reveal a variable composition (Ni, Co, Fe) of successive growth zones. Hydrothermal solutions of the first stage show the highest contents of metal in the order of $\text{Ni} > \text{Co} \geq \text{Fe}$, and, at the same time, the lowest values of Eh potential, thus providing for the crystallization of nickeline, with the highest content of metals and with the lowest valency state of As:

\[
[N\text{H}_2\text{O}_n(\text{AsH}_3)_mX_n]^z− \leftrightarrow \text{NiAs} + 3\text{H}^− + \text{wCl}^− + \text{uH}_2\text{O} + (\text{w−1})\text{AsH}_3^− + \text{e}^−
\]

or in a simplified form (mild oxidation):

\[
\text{Ni}^{2+} + \text{AsH}_3 \leftrightarrow \text{Ni}^{3+}\text{As}^{4+} + 3\text{H}^− + \text{e}^−
\]

The deposition of diarsenides and triarsenides proceeded in a similar manner only in the environment with an increased Eh potential. The following equations express multistage redox processes:

\[
\text{Ni}^{2+} + \text{AsH}_3 + \text{H}_2\text{S} \leftrightarrow \text{Ni}^{3+}\text{As}^{4+} + \text{5H}^− + 3\text{e}^−
\]

\[
\text{Ni}^{2+} + 2\text{AsH}_3 \leftrightarrow \text{Ni}^{3+}\text{As}^{4+} + 6\text{H}^− + 4\text{e}^−
\]

\[
\text{Ni}^{2+} + 3\text{AsH}_3 \leftrightarrow \text{Ni}^{3+}\text{As}^{4+} + 9\text{H}^− + 7\text{e}^−
\]

Oxidation states of As and Ni are adopted from [592], [593], and [594].

Variation in As fugacity and other parameters in the course of the arsenide stage is shown in Fig. 1. Increasing acidity, not significantly buffered by carbonates, is characteristic of these processes. The increased acidity of solutions resulted in the alteration of wall-rocks and brec- cias, characterized by the formation of clay minerals (see figure for kaolinite in the encyclopaedia section).

In a general way, the experimentally confirmed trend in the precipitation of arsenides corresponds to a gradually increasing oxidation potential of the whole fracture system, following the succession:

arsenides \( \Rightarrow \) diarsenides \( \Rightarrow \) triarsenides,

Oscillations in the redox potential resulted in a partial repetition of this succession. The above equations of arsenide precipitation indicate increasing acidity in the process.

Antimony was probably transported in the form of stibine (SbH$_3$), in a similar way as arsenic in the form of AsH$_3$. In the final stage of polyaneside precipitation, the fugacity of Sb increased due to the supply of additional Sb.

**Dissolution of Ag and Bi dendrites**

Dendritic crystals of Ag and Bi were quantitatively overgrown by Ni, Co, Fe polyarsenides and some other minerals. After the deposition of polyarsenides, the dendritic aggregates of native Ag and Bi were nearly quantitatively dissolved.

It appears that the dissolution of Ag and Bi was not accomplished purely by chemical dissolution (metals were surrounded by polyarsenides), but rather through electrochemical dissolution. Metallic Ag or Bi enclosed in non-conducting polyarsenides behaved as an electro-
chemical half-cell in solutions with a high content of Cl\(^{-}\) ions. The potential of such half-cell is:

\[\text{Ag(s) + Cl}^- \leftrightarrow \text{AgCl(s) + e}^- \quad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.222 \text{ V.}\]

Released AgCl in such environment is dissolved:

\[\text{AgCl(s) + Cl}^- \leftrightarrow \text{AgCl}_2^-(\text{aq})\]

To achieve electrolysis resulting in the dissolution of Ag, the second part of the electrochemical cell must represent a redox half-cell with a potential higher than 0.222 V. With regard to ions available in the hydrothermal environment at Jáchymov, the following reaction is considered:

\[\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \quad E^\circ_2(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.771 \text{ V}\]

\[\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \quad E^\circ_2(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.771 \text{ V}\]

\[O_2 + 4\text{H}^+ + 4e^- \leftrightarrow 2\text{H}_2\text{O} \quad E^\circ_2(\text{O}_2^-/\text{O}_2^-) = 1.229 \text{ V}\]

This redox reaction applies only to a slightly acid environment. The oxidation ability of UO\(^2\)\(^{-}\) is insufficient for the dissolution of Ag: \(E^\circ(U^\text{VI}/U^\text{V}) = 0.221 \text{ V}\).

The resulting electrochemical cell:

\[\text{Ag(s) + Cl}^- + \text{Fe}^{3+} \leftrightarrow \text{AgCl(s) + Fe}^{2+}\]

will generate under standard conditions potential of \(\Delta E^\circ = E^\circ_2(\text{Fe}^{3+}/\text{Fe}^{2+}) - E^\circ_2(\text{Ag}^+/\text{Ag}) = 0.549 \text{ V (see Fig. 35). Assuming that the cell will operate under connection of the "electrodes" by salt solution, Ag will be dissolved and } \Delta E^\circ \text{ value will be negative: } \Delta G^\circ = -nF\Delta E^\circ = -52.9 \text{ kJ/mol. To obtain activity relation } [\text{Fe}^{3+}]/[\text{Fe}^{2+}]. \]

\[\Delta G^\circ = 0 = \Delta G^\circ + RT \ln(K) \text{, resulting in } \Delta G^\circ = -RT \ln(K) = -RT \ln([\text{Fe}^{3+}]/[\text{Fe}^{2+}]). \]

For the reaction to proceed \(\Delta G^\circ < 0\), it is necessary to have \([\text{Fe}^{3+}]/[\text{Fe}^{2+}] = \exp(-\Delta G^\circ/RT) = 3.5 \times 10^3\). This condition will be satisfied under hydrothermal conditions in a certain range of pH values. Hydrolysis of Fe\(^{3+}\) ions is proceeding following the reaction:

\[\text{Fe}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}^{2+} + \text{H}^+ \quad \log(K) = -2.20, \log(K) = -36.5 [463];\]

this implies that approximately \([\text{Fe}^{3+}] = ([\text{H}^+]c\text{Fe})/K\), where cFe is the total content of dissolved Fe. For example, for pH = 6, cFe = 10\(^{-3}\) mol/l will be \([\text{Fe}^{3+}] = 1.6 \times 10^{-3} \text{ mol/l}.\)

In the course of Ag dendrite dissolution, Ag is mobilized and deposited in other parts of the ore veins. It becomes bound mainly in sulphides and sulpharsenides, only to a limited degree it is precipitated as native Ag. In the transport of Ag from dissolved dendrites, HS\(^{-}\) ions played probably a much more important role in the formation of stable complexes AgHS and Ag(HS\(^{-}\))\(^2\), where \(\log(\beta) = 13.48\) and \(\log(\beta) = 17.43 [589]\)

\[\text{Ag} + \text{H}^- \leftrightarrow \text{AgH}\]

\[\text{Ag} + 2\text{HS}^- \leftrightarrow \text{Ag(HS)}^-\]

Increased acidity results in the precipitation of Ag\(_2\)S (argentite):

\[2\text{Ag(HS)}^- + 2\text{H}^+ \leftrightarrow \text{Ag}_2\text{S} + 3\text{H}_2\text{S}.\]

Precipitation of Ag\(_2\)S is also triggered by an increased redox potential:

\[4\text{H}_2\text{O} + \text{Ag(HS)}^- \leftrightarrow \text{Ag}_2\text{S} + \text{SO}_4^{\text{2-}} + 10\text{H}^+ + 8\text{e}^- .\]

Precipitation of silver sulphosalts (prousite, xanthoconite) proceeds through the reaction of Ag with complex ions \(\text{H}_2\text{AsS}_3^-\) or \(\text{H}_2\text{AsS}_4^- [590] ;\)

\[9\text{AgHS} + \text{H}^+ + \text{H}_2\text{AsS}_3^- \leftrightarrow 3\text{Ag}_2\text{AsS}_4^- + 6\text{H}_2\text{S}\]

These reactions take place owing to increasing S fugacity, redox potential and acidity of the hydrothermal environment.

Dissolution of Bi was accomplished by similar electrochemical processes as in the case of Ag.

\[\text{Fig. 35. Schematic image of electrodissolution of native silver.}\]

**Arsenic–sulphide stage**

**Precipitation of arsenic**

Arsenic-rich solutions, after removal of metallic ions (Ni, Co, Fe), quantitatively precipitated native As under moderately acid conditions (pH ~ 6) in an oxidizing environment. Sulphur fugacity was insufficient for the production of As–S phases. Realgar was observed only as insignificant accumulations in the association with arsenic.
The following relation applies in an acid environment:

$$\ce{AsH_3} \leftrightarrow \ce{As^0} + 3\ce{H^+} + 3\ce{e^-}$$

$$E^\circ (\ce{As^0/As^III}) = -0.225 \text{ V}$$ [403].

The reaction can take place spontaneously, if under standard conditions $\Delta G^\circ$ of the whole reaction is negative, i.e. $\Delta E^\circ > 0$. If $\Delta E^\circ = E^\circ_2 - E^\circ_1$, where $E^\circ_2$ represents redox reaction, where $E^\circ_2 > E^\circ_1$, i.e., for $E^\circ_2 > -0.225 \text{ V}$, oxidation of arsine to As will take place. In other words, arsine oxidation in acid environment will proceed easily [591], in particular with $\ce{Fe^{3+}}, \ce{UO_2^{2+}}, \ce{O_2}$ and other oxidants characterized by a positive standard redox potential.

**Precipitation of base metal sulphides and sulpharsenides**

Arsenic fugacity abruptly decreased during this period but S fugacity was gradually increasing. Redox poten-
tial and acidity were increased in fractures of the vein system.

Minerals containing metallic elements (Cu, Ag, Pb, Zn, Fe) crystallized. The first generation precipitated from chloride or hydrosulphide complexes of hydrothermal solutions. Crystallization was triggered by temperature decrease, for example:

\[ \text{PbCl}_2^+ + \text{H}_2\text{S} \leftrightarrow \text{PbS} + 3\text{Cl}^- + 2\text{H}^+ \]

\[ \text{ZnCl}_2^2- + \text{H}_2\text{S} \leftrightarrow \text{ZnS} + 4\text{Cl}^- + 2\text{H}^+ \]

\[ 2\text{AgHS} \leftrightarrow \text{Ag}_2\text{S} + \text{H}_2\text{S} \]

precipitation was positively influenced by increasing acidity, for example:

\[ 2\text{Ag(HS)}_2^2- + 2\text{H}^+ \leftrightarrow \text{Ag}_2\text{S} + 3\text{H}_2\text{S} \]

9\text{Me}^3\text{HS} + \text{H}^+ + \text{H}_2\text{AsS}_3 \leftrightarrow 3\text{Me}^3\text{AsS}_3 + 6\text{H}_2\text{S}

**Redox potential of the arsenic–sulphide mineralization stage:**

**oxidation states of arsenic, sulpharsenides and Ag, Cu sulphides**

The majority of elements in minerals of this paragenesis have a higher oxidation state compared to the arsenide stage. A significant participation of sulphur, and to a lesser extent antimony, is observed in this mineralization stage.

The oxidation state of As changed from −III or −1 to 0 and in part to +III,
resulting in accumulations of native arsenic, Ag, Cu sulphosalts with the anion \([\text{As}^{\text{III}}\text{S}^2]^\cdot\) or of realgar. At the end of the arsenic–sulphide stage, the activity of AsH\(_3\) significantly decreased (see Fig. 1, 36–43).

Hydrothermal solution supplied some Sb jointly with dominant As, resulting in the crystallization of Ag, Pb, and Cu sulphosalts with the anions \([\text{Sb}^{\text{III}}\text{S}^2]^\cdot\), \([\text{Sb}^{\text{VI}}\text{S}^2]^\cdot\), \([\text{Sb}_2\text{S}_3]^\cdot\), \([\text{SbS}_2]^\cdot\), a.o. The fairly increased Sb content in the Hildebrand vein is responsible for the formation of Sb paragenesis: antimony, stibnite, arsenic, dyscrasite, miargyrite, pyrargyrite, robinsonite, stibarsen, and intermetallic phases AsSb and BiSb.

Manifestations of increased oxidation potential are seen also in the deposition of silver. The main part of silver is bound as Ag\(^+\) cation in the above named sulphosalts, or as acanthite, argentopyrite or sternbergite.

This chapter gives interpretation of chemical analyses (for source data see Primary minerals – encyclopaedic part) of the most common ore minerals of the Jáchymov district.

Attention is focused mainly on minerals of the arsenic stage. Repeated variations in the composition and Eh potential of the mineralizing solutions during the deposition of minerals of this stage resulted in the crystallization of minerals with highly variable composition. Ni/Co/Fe and S/As ratios show isomorphous substitutions in mineral structures [490]. Owing to the high fugacities of As, minerals with extremely high contents of As crystallized. This concerns mainly pyrite containing nearly 11 wt. % As and gersdorffite containing over 62 mol. % As. In spite of these chemical differences, the minerals retain their crystal structure and optical properties (isotropic behaviour).

Oxidizing environment is also indicated by hematite pigmentation in dolomitic carbonate, which is the main gangue mineral of the arsenic–sulphide stage.

**Role of sulphur in the hydrothermal process**

Nearly all stages of mineralization include some sulphides, mainly pyrite and sphalerite. This shows that sulphur fugacities in the hydrothermal solutions were slightly above zero.

It is assumed that sulphur was transported in solutions as HS\(^-\), H\(_2\)S or in anionic complexes with metallic elements \([\text{Me}(\text{HS})_n]^n\) or \([\text{Me}((\text{HS})_n)^n\) \(2\). Relations between these components were influenced by many factors, including p–T, pH, Eh, contents of metallic elements, oxygen, etc., and regulated the dissolution or precipitation of sulphides, sulpharsenides and sulphosalts. A major factor triggering crystallization of these species was sulphur fugacity \((f_{\text{S}})\). Table 4 presents S fugacities for common sulphur-bearing minerals of all mineralization stages. The relations are documented in Fig. 44. The reference temperature of 160 °C represents average temperature of all mineralization stages. The succession of minerals from bottom to top (Table 4) generally corresponds to the formation of S-minerals in the Jáchymov ore district. The first minerals to crystallize were sphalerite, pyrhostite and galena, the late minerals include sulphosalts and Bi-, Ag-sulphides.

**GRAPHIC INTERPRETATION OF CHEMICAL ANALYSES – SUBSTITUTION TRENDS**

![Fig. 44. Sulphur fugacity (log \(f_{\text{S}}\)) vs. temperature for selected minerals of the Jáchymov district.](image-url)
Group of diarsenides and triarsenides of Ni–Co–Fe

Fig. 45. Ni–Co–Fe ratio (atomic values) in selected diarsenides of the arsenide mineralization stage.

Fig. 46. Ni–Co–Fe ratio (atomic values) in selected triarsenides of the arsenide mineralization stage.

Fig. 47. Me (Me=Ni,Co,Fe) (apfu) vs. S (apfu) for nickel-skutterudite. Regression lines express correlation trends of analytical data.

Fig. 48. Me (Me=Ni,Co,Fe) (apfu) vs. As (apfu) for nickel-skutterudite.

Fig. 49. Me (Me=Ni,Co,Fe) (apfu) vs. S (apfu) for skutterudite.

Fig. 50. Me (Me=Ni,Co,Fe) (apfu) vs. As (apfu) for skutterudite.
Correlation of chemical composition and structural parameters of diarsenides

From the mineralogical point of view, crystal shapes of Ni-löllingite (sample J171P) and Fe-safflorite (Fig. 57) similar to six-pointed stars are very interesting. The crystals are triplets with twinning on plane (101) [348]. This type of twinning is limited by the condition \( a/c = \tan(60) \), where \( a, c \) are unit-cell parameters. This condition is shown in Fig. 56 by a grey band. The \( a/c \) ratio is a function of chemical composition – substitution of Ni, Co, Fe, so that the condition for the formation of a hexagram (Fig. 58) is met only for particular compositions, with löllingite containing substantial Ni or safflorite containing Fe. These conditions are often met in Jáchymov (see Ni-Co-Fe ternary diagrams for safflorite and löllingite – Fig. 45). Triplets do not occur with rammelsbergite, since its \( a/c \) ratio (near 1.33) is
far from the value of tan(60). Triangular symbols in the diagram below, plotting outside the grey belt, correspond to relatively pure löllingite without triplets.

**Variation of Ni, Co, Fe against As in selected polyarsenides and sulpharsenides**

Fig. 56. \(a/c\) ratio of unit-cell parameters vs. Ni (in löllingite) and Fe (safflorite) (apfu). Grey belt shows range of \(a/c\) values compatible with formation of six-pointed star triplets.

Fig. 57. J171P. Ni-löllingite triplets on (101) plane in the shape of six-pointed star. Zimni Eliáš mine. SE image. Magnification 1450×. Photo A. Gabašová.

Fig. 58. Computer model of löllingite triplet with twinning plane (101), in projection on \(ac\) plane. Unit-cell parameter ratio \(a/c = 1.732\).

Fig. 59. As (at%) vs. atomic ratio Ni/(Ni+Co+Fe) for selected minerals of the arsenide mineralization stage.

Fig. 60. As (at%) vs. atomic ratio Co/(Ni+Co+Fe) for selected minerals of the arsenide mineralization stage.

Fig. 61. As (at%) vs. atomic ratio Fe/(Ni+Co+Fe) for selected minerals of the arsenide mineralization stage.
Group of sulphasenides (*gersdorffite, arsenopyrite, alloclasite*)

Fig. 62. S vs. As (apfu) in selected sulphasenides of the arsenide mineralization stage.

Fig. 63. Ni–Co–Fe ratio (atomic values) in selected sulphasenides of the arsenide mineralization stage.

Fig. 64. S–As–Ni ratio (atomic values) in gersdorffite.

Fig. 65. Me (Me= Ni, Co, Fe) (at.%) vs. As (at.%) for gersdorffite.

Fig. 66. Gersdorffite. Me (Me= Ni, Co, Fe) (apfu) is correlated with atomic ratio As/(As+S).

Group of disulphides (*pyrite, marcasite, vaesite*)

Fig. 67. Me (Ni, Co, Fe) (at.%) vs. As (at.%) for pyrite.
Group of tetrahedrite–tennantite (tennantite, tetrahedrite, argentotennantite, freibergite)

Fig. 68. As (apfu) vs. S (apfu) for pyrite.

Fig. 69. Ni–Co–Fe ratio (atomic values) in pyrite of selected mineralization stages

Fig. 70. Fe–Ni–As ratio (atomic values) in pyrite, marcasite, and vaesite.

Fig. 71. Sb (apfu) vs. As (apfu) diagram for tetrahedrite group minerals.

Fig. 72. Zn (apfu) vs. Fe (apfu) diagram for tetrahedrite group minerals. Argentotennantite and freibergite are Fe dominant members; two types (Fe and Zn dominant) of tetrahedrite are observed and Fe–Zn solid solution in tennantite was found.

Fig. 73. Ag (apfu) vs. As (apfu) diagram for tetrahedrite group minerals. The minerals are separated into two group – Ag-free and Ag-rich; no intermediate member was found.
DEDICATING THE CONDITIONS OF FORMATION OF SELECTED SULPHIDES

The Jáchymov ore veins represent a multicomponent natural ore system. Individual stages of its development differ in their age, chemistry and p–T conditions. Furthermore, the p–T conditions varied within the individual mineralization stages, and the mineralizations formed during different stages overlap in space. Consequently, it is often difficult to assign individual minerals to a specific mineralization stage. In the ore assemblages studied, disequilibria are very common, as is manifested by the occurrence of zoned crystals, reaction rims, colloform structures and the presence of various metastable assemblages. A low-temperature re-equilibration of higher-temperature ore assemblages is visible in exsolution intergrowths. Likewise, a change in the chemistry of ore-bearing fluids is preserved in the form of replacement textures. All of these effects make the estimation of the p–T conditions of formation a difficult task.

Sn–W sulpharsenide stage

This is a high-temperature stage related to the processes of greisenization of the granite that underlies the Jáchymov ore district. Chalcopyrite, stannite, sphalerite, késiterie, and roquesite formed broad solid solutions under the (high) temperatures that prevailed during their primary crystallization that, in turn, gave rise to typical breakdown textures formed during a subsequent period of cooling. Unfortunately, low-temperature solvi in the corresponding synthetic systems have not been studied. Nevertheless, the presence of mawsonite in this mineralization stage indicates that the temperature of formation could not have exceeded 390 °C. Considering also other evidence, the temperature of formation of minerals in this stage can be estimated at ~300 °C. Frequent intergrowths of stannite with mawsonite demonstrate that these minerals form a stable association. This is in agreement with [514] but it is difficult to reconcile with the observation of [510] who described the association of stannoidite with stannite as a stable one. The occurrence of cassiterite in this mineral assemblage indicates a higher activity of O₂ during this stage.

Arsenide stage

This stage is characterized by the presence of native Ag, Bi (Hg) and of Co–Ni(Fe) arsenides and sulpharsenides. According to the presence of either silver or bismuth, this stage is further subdivided into silver and bismuth parageneses. The presence of native metals proves a very low activity of sulphur, certainly below that of the univariant sulphidation curves of Ag/Ag₂S, Bi/Bi₂S and Hg/HgS. The observed succession of Co–Ni(Fe) arsenides → diarsenides → triarsenides corresponds to a gradually increasing activity of arsenic during this stage. The appearance of bismuthinite and bornite in the late phases of the arsenide stage documents an increasing sulphur activity, above that of the univariant curves bismuthinite/bismuth and bornite/pyrite/chalcopyrite. Also, the presence of younger sulpharsenides with elevated contents of sulphur indicate a higher activity of sulphur in the later phases of this stage. For example, sulphur contents in the studied rammelsbergite are higher than the maximum content (1 wt. %) determined experimentally by [490], and vary within the range of 0.02–19 wt. % whereas in pararammelsbergite, the sulphur contents reach only 0.08–2 wt. %. The analyses also point out the unexpected existence of a rammelsbergite–gersdorffite isomorphous series. The existence of the same solid solution has recently been reported by Fanlo et al. [587] from the San Juan de Plan deposits in Spain. The variation in the As/S ratio in gersdorffite and rammelsbergite, also echoed in arsenopyrite, reflects the variation in sulphur activity during their formation. Unfortunately, no experimental data are available and therefore it is not possible to use the As/S ratio of gersdorffite and rammelsbergite (and arsenopyrite, [503]) as a geothermometer. Fortunately, the occurrence of skeletal aggregates of bismuth crystals can be used as a fixed-point geothermometer; the crystals must have grown below the melting point of Bi (271 °C). Likewise, the occurrence of argentite indicates a temperature above 179 °C. Rammelsbergite is an interesting mineral, because it is stable above 590 °C and inverts to pararammelsbergite at lower temperatures. However, any temperatures near 590 °C appear unacceptably high, but it should not be forgotten that the possible effect of the activity of sulphur on the temperature of this phase transition remains unknown. Still, this disqualifies rammelsbergite from the arsenic stage as a fixed-point geothermometer. Karup-Moller and Makovicky [395] pointed out a topotactic influence of the matrix on the
crystallization of rammelsbergite. Consequently, we can only roughly estimate the temperature of formation as being below 300 °C. Roseboom [512] studied the pseudoternary system of NiAsS₂-CoAsS₂-FeAsS₂ and reported a wide solid solution with a miscibility gap between NiAsS₂ and FeAsS₂. This miscibility gap corresponds to the analyses of diarsenides from Jáchymov. Again, no experimental data exist on the low-temperature solvus in this system that would allow us to narrow down the possible range of temperature.

Arsenic–sulphide stage

In this stage, the sulphur activity varied very widely. Native metals are represented by arsenic, dendritic aggregates of silver, native antimony, and intermetallic alloys dacyrasite, AsSb and BiSb. Native silver and antimony indicate a sulphur fugacity below that of the argentite/silver and stibnite/antimony univariant curves (Fig. 44). On the contrary, minerals such as realgar (stable below 265 °C [507]), proustite and rossonite together with a sulphur-rich rammelsbegite and safflorite indicate that the sulphur activity must have been above that of the pyrite/pyrrhotite univariant curve (Fig. 44). Also, several sulphides are present that have a limited field of thermal stability and thus could be used as fixed-point geothermometers. Xanthocconite is stable at up to 191 °C, and transforms to the high-temperature phase of proustite above this temperature. Stromeyerite is stable at temperatures below 93 °C, whereas the presence of argentite and pyrrargyrite indicates temperatures of formation above 197 °C [506] and 192 °C, respectively [444]. In addition to that, stenberget is a narrow field of thermal stability and breaks down at 152 °C to argentite, pyrite and pyrrhotite [445, 508]. Proustite and pyrrargyrite form a complete solid solution at above 300 °C, but have a miscibility gap at lower temperatures [513, 347]. The lamellar intergrowths of pyrrargyrite and proustite thus indicate temperatures of formation below this temperature, even though the relevant solvi remain unknown. All these fixed-point geothermometers indicate low temperatures of formation, probably in the range of 100–200 °C.

Sulphide stage

In the sulphide stage, the main minerals are simple sulphides: chalcopyrite, sphalerite, galena, pyrite, accompanied by sulphosalt rossonite. Löfflingite, tennantite and arsenian pyrite are the principal bearers of arsenic in the stage. The broad stability fields of these minerals do not permit to use these minerals as fixed-point geothermometers. Only the presence of bornite with exsolution intergrowths of chalcopyrite indicates a higher temperature of formation which, unfortunately, cannot be quantified any closer. Low-temperature Cu (Fe) sulphides with narrow fields of thermal stability represent late phases of the sulphide stage. These minerals indicate temperatures of formation below 100 °C. Djuurleite breaks down at 93 °C, anilite at 87 °C [507], and smithite is reported to be stable below 75 °C [554]. The presence of sulphosalt represents a consequence of a higher sulphur activity in this stage (Fig. 44). A very low iron content of sphalerite furnishes evidence of the high activity of sulphur during the crystallization (assuming a low pressure of formation and the presence of iron in the system).

Conclusions

The hydrothermal vein systems at Jáchymov were formed under a relatively low sulphur activity and at low temperatures – otherwise the mineral assemblages would contain no native metals and sulphides with a low thermal stability. During the late phases of individual mineralization stages, the sulphur activity increased and the temperature decreased. Sulphosalt and sulphasenides started to crystallize in these late phases.

A feature common to all mineral assemblages is the low activity of oxygen: with the exception of cassiterite (in the Sn–W sulphasenide stage), no metal oxides are present in the studied ore assemblages.

PARAGENETIC RELATION OF PRIMARY AND SECONDARY MINERALS

Compared to secondary minerals of the Jáchymov ore district, its primary mineralization is fairly simple in its ore minerals as well as gangue minerals. Combinations of major primary minerals occur practically in the whole vertical range of the veins. However, this is not exactly valid for all veins and in the whole district [475, 476, 477].

A typical scheme of a vein deposit with a leached oxidation zone, enriched oxidation zone, and cementation zone above unchanged primary zone, is seen only on Geister and Geschieber veins and partly also on the Červené veins, which reach up to the surface. Majority of accessible surface outcrops of other veins show a relatively small zone of nearly complete leaching of ore components, with only sporadic occurrences of secondary uranium minerals (particularly torbernite, autunite and also uranophane and kasolite), bismuth minerals (bismuttite, bismutoferrite), copper (malachite, mixite) and lead minerals (anglesite, pyromorphite). Even the relatively limited accumulations of secondary minerals may be leached, as indicated by limonite pseudomorphs after uranium micas. Majority of the veins do not crop out on the surface. Upper parts of veins were removed by erosion and only middle and lower parts of veins remained.

The enriched cementation zone exploited in 16th century contained mainly silver, acanthite and chlorargyrite. As noted by Mathesius [308], the richest accumulations of ores were located at a depth of 60–80 m. The fact that uraninite reputedly occurred mainly at lower levels may be due to its better solubility in the descending meteoric water during supergene evolution.
A weak limonitization was limited to parts of veins immediately reaching the land surface. The richest secondary mineral assemblage formed under the recent or historically imposed conditions. The occurrence of the same or similar secondary minerals depends mainly on the content of the ore vein. This trend is seen nearly in the whole vertical range of the veins. The quantity of circulating “fracture” water and the mode of exposure of the ore vein by mining play the main role. Subrecent minerals formed as a result of long-lasting mining activity.

Weathering processes induced by mining activity

Underground exposures of massive ores (including bismuth, nickel-skutterudite, pyrite, arsenic and uraninite) carry minor coating of powdery secondary minerals. Rich occurrences of recently formed secondary minerals were found in places where the ore was widely dispersed by explosions. Rich accumulations of secondary minerals were found in parts of ore-free adits, where fine-grained part of ore from overturned tub was spilled on the floor (e.g., lindackerite, geminitite at the 7th (Werner) level of the Rovnost I shaft). Rich accumulations of zykaitite were found on disintegrating mica schist containing arsenopyrite. Generally, occurrences of secondary uranium minerals are common in the proximity of water drainage “ditches” as coatings on barren rocks in adits, including minerals like â€œjkaite [473], [479], a.o.

Special objects include waste rock fill of exploited sections and pillars. Carbonate-rich gangue is easily dissolved, resulting in calcite and aragonite stalactite decorations in adits. The stalactites are often coloured in blue (Cu), violet to brown pink (Co), rusty (Fe), and most frequently yellow (U). In the Geschieber vein, calcite drapes 0.75 m long formed during the 20 years after mining was terminated. Besides calcite stalactites, stalactites of pure zmacalite up to 3 cm long formed in the Evangelist vein. Up to 1 m long stalactites of muddy “glockerite” were observed at places with rich pyrite. Brown, rope-like accumulations of algae proliferating on rotting wood supports are impregnated and laphidified by infiltration of calcite.

Alteration of bismuth minerals

Secondary bismuth minerals do not accompany rich native bismuth accumulations associated with Ni and Co arsenides; their formation in historical times has not been observed. On the other hand, secondary Bi minerals formed where bismuth was dispersed as a minor component in the ores and particularly where bismuth was partly replaced by bismuthinite. Exceptionally, bismuthinite needles protruding to vugs in porous gangue are coated by a thin layer of bismuthite, usually without other mineralization.

Alteration of arsenic

Massive arsenic aggregates are less susceptible to weathering than complex ores. Arsenic accumulations are locally covered by powdery arsenolite coatings and small pharmacolite crystals. Rather different behaviour has been noted with porous arsenic from the Geschieber vein. In addition to relatively abundant arsenolite and claudite crystals, aggregates of strongly acidic kaaitialante occur here, with compact crusts of scorodite in their proximity. This type of arsenic contains disseminated pyrite, which on weathering accelerates the dissolution of arsenic. Some specimens of this type of arsenic, without scorodite, carry droplets of a strongly acidic liquid, which persists on these specimens for years, when stored in a dry environment. It is assumed that the drops are formed by hygroscopic arsenic acid. Other specimens of porous arsenic carry prisms filled inside with powdery sulphur and crust of pyrite or acanthite. These pseudomorphs are clearly after argentopyrite.

In the Geschieber vein, a vertical chimney penetrating lenses of native arsenic was used for draining water from an adit. In areas where water flowed on arsenic, dendritic silver precipitated. As the place is no more accessible, it is uncertain whether silver precipitated from flowing mine water containing Ag⁺ ions or from leaching minor proustite disseminated in arsenic. Silver dendrites were up to 1 cm long, they precipitated within 10 years after this place was mined in 1962 (samples were collected here in 1972–1973).
Alteration of arsenides, sulpharsenides and sulphides

The 12th level of the Svornost mine exposed strongly crushed and weathered Geschieber vein without noticeable mineralization with rich water supply, accompanied by recent growth of köttigite crystals, almost on day-to-day basis.

In the proximity of borehole HG-1, near the contact of granite with metamorphic mantle, the discharge of the Běhounek radioactive spring, in places with massive ores, is accompanied by a rich assemblage of secondary minerals, mainly sulphates. It includes nickelhexahydrite, morenosite, jarosite, arsenolite, kaatalaita, švenekite, crusts of magnesian annabergite, and extremely rare minerals vajdakite [472] and cobalkoritnigite. Highly acidic minerals such as kaatalaita and švenekite, acidic as well as basic minerals (jarosites, copiapite) occur here in close proximity. Sulphates of vitriol type co-occur with arsenates krautite, rösslerite, a.o. Cations include nearly all ore components (Ni, Co, Zn, Fe), as well as cations derived from carbonate gangue and from wall-rocks: Ca, Mg, Mn, and Al, and cations brought by the radioactive thermal spring (Na, K). The ultimate source of molybdenum contained in vajdakite has not been identified, and possibly comes from the altered younger granite. Surprisingly, the deepest levels in the mine thus abound with minerals of oxidation zone, including native copper. So far, no secondary minerals of silver and lead have been encountered. Jarosite formed in the proximity of strongly corroded proustite crystals, but argentojarosite or native silver are absent. It is possible that silver was removed in the form of soluble silver sulphate or arsenate.

Alteration of pyrite and marcasite

Marcasite weathers more readily than pyrite. Marcasite decomposition, accompanied by the formation of sulphuric acid, acts as a catalyst, as it triggers and accelerates pyrite decomposition. In the absence of other components, alteration of marcasite and pyrite started by reaction of FeS\textsubscript{2} with oxygen from air in the presence of water (even air humidity). Sulphur changed its oxidation state. Where the alteration proceeded slowly, some powdery sulphur may coat corroded sulphides. In case of spontaneous reactions, sulphur quantitatively acquires oxidation state VI. This process is accompanied by an increase in the volume of sulphide aggregates, fracturing and coating by rusty films of amorphous ferric sulphates. If hydrolysis of these products sets in, and if pH of the solution increases above 4.5, ferric iron is precipitated in the form of complex hydro-sulphates. Sulphuric acid released by this reaction accelerates weathering of additional FeS\textsubscript{2} and carbonates. Large volumes of FeS\textsubscript{2} resulted in Fe\textsuperscript{2+} and SO\textsuperscript{4\textsuperscript{2-}} concentrations exceeding solubility, and skeletal aggregates of vitriols – sulphates crystallized on the surface of the sulphides. The presence of gypsum also serves as an indicator of conditions suitable for the crystallization of secondary sulphates.

Alteration of Cu minerals

Interesting is also the occurrence of copper minerals at the Daniel level, at the intersection of the Trojická vein and Geschieber vein. A quartz lens penetrated by carbonate veinlets contains primary pyrite, bornite and tennantite. Copper arsenates lindackerite, geminitke, laven-dulan, strashimirite and other unknown Cu-arsenate species [474] formed in the proximity of primary copper minerals. Nearby porous arsenic was accompanied by common arsenates of Ca and Mg. However, fragments of arsenic, mixed with relics of Cu minerals possibly in the process of mining, yielded copper arsenates (geminitke, lindackerite).

The Geister vein between the 3rd and 7th levels (Albrecht) of the Rovnost I mine yielded accumulations of newly formed cementation copper. A chimney between the levels, functioning as a water channel, exposed coatings of hydrated iron oxides and arborescent and flaky copper aggregates on all iron and wooden constructions.

Alteration of U minerals

As a general rule, the least developed secondary mineralization occurs in the proximity of carbonate veins. Prima-ry minerals including uraninite are nearly unaffected by the alteration. Minor coatings of Ca and Mg arsenates and local coatings of uranium carbonates (liebigite, schröckingerite, zellerite) were formed. Vein carbonates with ura-ninite found in dumps are usually preserved rather fresh. In the presence of significant pyrite, the surface of the samples was corroded but secondary mineralization was limited to an amorphous glassy yellow coating in the proximity of uraninite. Massive uraninite in quartz veins or uraninite veins in the country rock is weakly weathered to zipeite or uranopilite, depending on the amount of pyrite. If arsenide was present in the vein, the most common weathering product was (meta)ceumerite. In the presence of very abundant pyrite, uraninite was coated by a thick limonitic crust and no secondary minerals were formed.

A different situation exists in the wet environment in the mine. Uraninite accompanied by pyrite is strongly weathered, coated by zipeite and uranopilite. A different situation occurs with the carbonates. Secondary uranium minerals are sometimes deposited at a distance from uraninite without obvious reason or relation to any other mineralization. Dusty walls of adits, representing surfaces with efficient evaporation, represent a favourite site for the crystallization of secondary uranium minerals. A similar role is played by pieces of rock lying on the floor, particularly in the proximity of drainage ditches. Walls of adits may be covered with small aggregates of schröckingerite on areas of several square meters.

Weathering of uraninite is critically dependent on the character of the environment. It is nearly insoluble under reducing conditions or alters to coffinite [150], but is unstable under oxidation conditions; the efficiency of alteration is notably increased in the presence of water.
In dry environment, uraninite is subject to oxidation by oxygen diffusion into interstitial structural sites. Owing to the presence of other elements than uranium, an ideal UO₂ cubic structure of the fluorite type is not materialized. Limits for oxidation occur with the value x = 0.25, characterized by a shift in unit-cell parameters, while cubic structure is retained UO₂‡, i.e., U₂O₇ and at x = 0.33, resulting in a distortion of cubic structure to body-centred distorted tetragonal structure UO₂₃₉ (U₂O₇) [471]. These changes may result in weakly coherency of granular aggregates, formation of microfractures and increase in the reactive surface of the material.

Progressive oxidation toward U₃O₈ (UO₂⁶⁺) is accompanied by the transformation of tetragonal structure to orthorhombic, which is associated with a significant volume change. However, this transformation takes place only at temperatures above 150 °C [458].

In the presence of water (or wet air), changes in uranium oxidation do not exceed UO₂⁺, since dissolution sets in under these slightly oxidative conditions. Oxidation of uraninite in water-rich environment is characterized by more efficient kinetics compared to the alteration in air. Its alteration and dissolution leads to the formation of phases containing U⁶⁺ in the form of very stable UO₂⁺.

Factors controlling uraninite destruction include temperature, pH, oxygen fugacity, and concentration of ions such as SiO₂⁺, HCO₃⁻, HSO₄⁻, H₂AsO₄⁻, and Ca²⁺ admixtures, grain size, presence of other minerals, especially pyrite, and others.

Interesting information on underground weathering of ore components was revealed in the historic Gifftkiesstollen. These old workings were penetrated during the 1950s by new works in the course of uranium mining (Jächymovské doly enterprise). The breccia resulting from old historic mining, comprising fragments of uraninite, pyrite, chalcopyrite and gange minerals (quartz, dolomite, calcite), was cemented by gypsum, jarosite, plumbojarosite and a number of uranium minerals (oxyhydroxides, silicates, carbonates, phosphates).

Newly formed products resulting from uraninite decomposition show a certain sequence of precipitation. This was made possible by the fact that large amounts of finely crushed ore fragments remained on the spot after a blast in the course of mining operation. Crushed ore included abundant uraninite in grains 2–5 mm in size. The effective surface of this material was large and contributed to effective weathering. This material was not drained by water and was exposed to air with certain moisture. Uraninite in this artificial breccia was grey to bluish grey, with matt powdery to porous surface, free of secondary uranium minerals, although they were present in the proximity. Secondary minerals concentrated mainly in the proximity of gypsum.

The observed succession of crystallization of secondary minerals is as follows:

uraninite \(\rightarrow\) metaschoepite (UO₂)O₆(OH)₆(H₂O)₁₀
schoepite (UO₂)O₆(OH)₆(H₂O)₁₁ \(\rightarrow\) becquerelite Ca(UO₂)O₆(OH)₆(H₂O)₆
compreignacite K₄(UO₂)O₆(OH)₆(H₂O)₆ \(\rightarrow\) massyite Pb(UO₂)O₆(OH)₆(H₂O)₆
vandendriesscheite Pb₄(UO₂)O₆(OH)₆(H₂O)₆ \(\rightarrow\) uranophane Ca(UO₂)₃(SiO₄)O₆(H₂O)₆
sklodowskite Mg(UO₂)₂(SiO₄)O₆(H₂O)₆
cuprosklodowskite Cu(UO₂)₂(SiO₄)O₆(H₂O)₆

The interpreted precipitation of oxyhydroxides before silicates is supported by the observation of oxyhydroxides in some samples covered by silicates, mainly small spheres of cuprosklodowskite; a reversed sequence was not observed. Otherwise, the two groups of minerals tend to occur separately.

pyrite \(\rightarrow\) melanite + gypsum:

FeS₂ + 3.5O₂ + H₂O \(\rightarrow\) Fe²⁺ + 2SO₄²⁻ + 2H⁺

typical way of uraninite oxidation:

UO₂ + 2H⁺ + 1.5O₂ \(\rightarrow\) UO₂²⁺ + H₂O

and examples of hydrolysis of UO₂²⁺ ions and formation of basic uranium oxyhydroxides:

formation of metaschoepite:

8UO₂²⁺ + 16OH⁻ + 8H₂O \(\rightarrow\) (UO₂)₈O₆(OH)₁₂(H₂O)₁₀
formation of schoepite:

8UO₂²⁺ + 16OH⁻ + 10H₂O \(\rightarrow\) (UO₂)₈O₆(OH)₁₂(H₂O)₁₂
formation of becquerelite:

6UO₂²⁺ + Ca²⁺ + 14OH⁻ + 4H₂O \(\rightarrow\) Ca(UO₂)₆O₆(OH)₆(H₂O)₆
formation of compreignacite:

6UO₂²⁺ + 2K⁺ + 14OH⁻ + 3H₂O \(\rightarrow\) K₄(UO₂)₆O₆(OH)₆(H₂O)₆
becquerelite \(\rightarrow\) uranophane:

Ca(UO₂)₂O₆(OH)₆(H₂O)₆ + 6SiO₂ + 2Ca²⁺ + 4OH⁻ + 5H₂O \(\rightarrow\) 3Ca(UO₂)₂(SiO₄)O₆(OH)₆(H₂O)₆

The strongest representation among newly formed minerals have oxyhydroxides of unanyl, forming spheroideal glassy aggregates or highly lustrous minute crystals. Uranium silicates are less abundant, occur in a powdery form, such as uranophane and sklodowskite, or form coatings and small radiating spheroideal aggregates.
(cuprosklodowskite). These minerals constituted cement of the described "breccia".

The presence of other uranyl minerals was sporadic. They include phases which occur largely in the proximity of fragments representing the source of the respective ions. The carbonates *metazellerite* Ca(UO$_2$)(CO$_3$)$_2$(H$_2$O)$_2$ and *zellerite* Ca(UO$_2$)(CO$_3$)$_2$(H$_2$O)$_2$ concentrated always in the proximity of *dolomite* fragments, *metazellerite* Cu(UO$_2$)$_2$(AsO$_4$)$_2$(H$_2$O)$_2$ near *chalcopyrite*. Sulphides do not show such dependence on the source. *Uranopilite* (UO$_2$)$_2$(SO$_4$)(OH)$_3$(H$_2$O)$_3$ is generally associated with gypsum. *Rabejacie* Ca(UO$_2$)$_2$(SO$_4$)$_2$(OH)$_4$(H$_2$O)$_6$ was found on earthy coating of larger rock fragments or around uranyl oxyhydroxides together with gypsum. The originally present *pyrite* fragments were probably completely decomposed. Other types of uranium minerals were not recorded in this particular assemblage, e.g., minerals of the *zippeite* group, common in other places, or other uranyl carbonates. The respective ore batch was obviously poor in carbonate gangue, and the relatively small amount of *pyrite* was consumed in *jarosite*- and *gypsum*-producing reactions. The lead contained in *plumbojarosite* is almost certainly of radiogenic origin, since no primary lead minerals were found.

Similar conditions of hydration-oxidation weathering of *uraninite* were recorded in upper levels of the Evangelista vein. The identified secondary minerals include oxyhydroxides (metaschoepite, becquerelite, compregnacite), silicates (uranophane, sklodowskite) as well as carbonates (*liebigite*, *schröckingerite*). Somewhat more common are uranyl-sulphates (*uranopilite*, *zippeite*, *jo-hannite*) and *plumbojarosite* containing radiogenic lead. Common *jarosite* and *gypsum* also occur.

**FLUID INCLUSION STUDY**

Fluid inclusions in *barren* quartz, *fluorite* and carbonates of the *Sn–W sulpharsenide, arsenide, arsenic–sulphide* and *sulphide* stages of the vein Ni–Co–Bi–Ag+U mineralization were studied at Jáchymov. The results also comprise the data of Benešová (in [359]) on dark violet *fluorite* of the *carbonate–uraninite* stage.

### Table 5. Results of fluid inclusions measurement from Jáchymov deposit.

<table>
<thead>
<tr>
<th>sample</th>
<th>mineral</th>
<th>FI type</th>
<th>LVR</th>
<th>Th (°C)</th>
<th>Tm (°C)</th>
<th>salinity (% wt.)</th>
<th>Tm</th>
<th>Ts (°C)</th>
<th>Tm CO$_2$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mineralization stages)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Sn–W sulpharsenide stage</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>J066P</td>
<td>quartz</td>
<td>prim</td>
<td>0.6</td>
<td>294–306</td>
<td>−19.6</td>
<td>20</td>
<td>−52.5</td>
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<td></td>
</tr>
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<td>quartz</td>
<td>prim</td>
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<td>2.4</td>
<td>−56.5</td>
<td></td>
<td></td>
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<tr>
<td>Trojcká vein</td>
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<td>210–218</td>
<td>−8.2</td>
<td>7.6–9.5</td>
<td></td>
<td>240–246</td>
<td></td>
</tr>
<tr>
<td><strong>Carbonate–uraninite stage</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>dark violet fluorite [359]</td>
<td>fluorite</td>
<td>prim</td>
<td>0.9</td>
<td>246–262</td>
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<td>7.3–7.9</td>
<td>−34</td>
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<td></td>
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<td>J00512</td>
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<td>96–112</td>
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<td>23.5–24</td>
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<tr>
<td>J0061</td>
<td>ankerite</td>
<td>prim</td>
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<td>118–142</td>
<td>−22.4 to −25</td>
<td>22–23</td>
<td>−55.8</td>
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<td></td>
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<td>prim</td>
<td>variable</td>
<td>22–24</td>
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<td>−54</td>
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<tr>
<td>J00812</td>
<td>dolomite</td>
<td>prim</td>
<td>0.9</td>
<td>126–144</td>
<td>−22.6 to −30</td>
<td>22–24.5</td>
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<td>J019P</td>
<td>carbonate</td>
<td>prim</td>
<td>variable</td>
<td>−38</td>
<td></td>
<td>?</td>
<td></td>
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<tr>
<td>J119P</td>
<td>carbonate</td>
<td>prim</td>
<td>0.95</td>
<td>112.114</td>
<td>−8.9</td>
<td>12.7</td>
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<tr>
<td>MP271D</td>
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<td>prim</td>
<td>variable</td>
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<td>0.4–0.9</td>
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<td><strong>Arsenic–sulphide stage</strong></td>
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<td>NM9527</td>
<td>Mg-calcite</td>
<td>prim</td>
<td>0.95</td>
<td>112–123</td>
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<td>prim</td>
<td>0.95</td>
<td>112–138</td>
<td>−24.5 to −25.7</td>
<td>23–23.5</td>
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<td>prim</td>
<td>variable</td>
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<tr>
<td><strong>Sulphide stage</strong></td>
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<td>calcite</td>
<td>sec</td>
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<td>70–80</td>
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<td>3.6–4.0</td>
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<td>prim</td>
<td>L-only</td>
<td>&lt;100</td>
<td>−0.1 to −0.3</td>
<td>0.2–0.5</td>
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</table>

*Table includes the temperature of homogenization (Th), temperature of the first melting (Tlm), temperature of melting of the last crystal of ice (Tm), temperature of melting of CO$_2$ (Tm CO$_2$), temperature of solid phase dissolution (Ts), L – liquid phase, V – gaseous phase, S – solid phase, FI type: prim – primary inclusions, sec – secondary inclusions.*
Methods

A microthermometric study of the fluid inclusions was undertaken on doubly polished sections 300 mm thick and on cleaved carbonate chips. Fluid inclusions were analysed on a Chaixmeca heating-cooling stage [484], which was calibrated between 100 °C and 400 °C by Merck chemical standards, the solidification point of distilled water, and phase transitions in natural pure CO₂ inclusions. Homogenization and cryometric data show reproducibility of ±0.2 °C at temperatures below 0 °C and ±3 °C at temperatures to 400 °C.

Homogenization temperature (Th), temperature of first melting (Tfm) and of the final melting of ice (Tm), and temperature of melting of solid CO₂ (Tm CO₂) and temperature of dissolution of solid phase (Ts) were measured.

The salinity of the fluids was calculated according to Bodnar and Vitik [481] and the composition of the salt systems was determined according to Borisenko [482].

As calcite, dolomite and ankerite arecleavable minerals, fluid inclusions may change during subsequent events and even during the preparation of the wafers and the microthermometric measurements ([480], [483]). Metastability, leakage, stretching and decrepitation of inclusions in these minerals can occur and have to be recognized and taken into account in the interpretation of the microthermometric data.

Results

Sn–W sulpharsenide stage

Primary aqueous inclusions in quartz of the J066P and J107P samples have a variable liquid-to-vapour ratio (LVR). Vapour-rich inclusions with LVR = 0.2 and liquid–vapour inclusions with LVR = 0.6 can be found. Moreover, L+V+S inclusions with NaCl daughter crystal and vapour bubble of about 30 vol. % were observed. Very small amount of CO₂ was identified in vapour-rich inclusions. The temperature of melting of solid CO₂ was measured at −56.5 °C, which corresponds to the temperature of the triple point of pure CO₂. The salinity of vapour-rich inclusions is low, of about 2.5 wt. % NaCl equiv.

Homogenization temperatures of inclusions with LVR = 0.6 were measured between 294 and 306 °C. The salinity of these inclusions varies between 7.6 and 20 wt. % NaCl equiv., the salt system of the solution is formed by CaCl₂, NaCl, KCl, and probably MgCl₂ (Tfm = −52.5 °C).

The dissolution of sodium daughter crystal in L+V+S inclusions was observed between 240 and 264 °C. The bulk salinity, estimated using Ts, is from 33 to 35 wt. %.

The relationships of these three fluid inclusion types are complicated; the preliminary data suggest that the inclusions represent a relatively high temperature–high salinity post-magmatic fluid.

Carbonate–uraninite stage

Benešová (in [359]) studied fluid inclusions in dark violet fluorite, which was sampled from U-rich mineralization. Primary aqueous fluid inclusions homogenized at temperatures between 190 and 198 °C. Pseudosecondary and secondary inclusions homogenized in the interval from 105 to 158 °C.

Arsenide stage

Fluid inclusions were studied in several carbonates of dolomite–ankerite composition (J00512, J0061, J00811, J00812, J019P, J119P, and 217D). Primary inclusions of aqueous fluid have variable shape, size of max. 80 µm, and a variable liquid-to-vapour ratio. L-only, V-only, V<>L and L+V (LVR = 0.9 to 0.95) inclusions were found in 3D distribution. Variable LVR is believed to be caused by the long-term maturation of inclusions and nucleation of vapour phase under relatively low temperature [581]. Homogenization temperatures were measured in groups of the inclusions with LVR = 0.9 to 0.95 and ranged from 96 to 144 °C. Tm of ice was observed between −22.4 and −30 °C, and the bulk salinity of inclusions is between 22 and 24.5 wt. % (for H₂O–CaCl₂ salt system). Tfm was measured in the range from −54 to −55.8 °C and indicates a CaCl₂–NaCl–KCl±MgCl₂ salt system in the solution. Lower salinity was observed in the J119P sample, of about 13 wt. % NaCl equiv. and especially in the 217D sample, where the salinity of fluid in carbonate adjacent to proustite is very low, from 0.4 to 0.9 wt. % NaCl equiv.

Arsenic–sulphide stage

Primary H₂O inclusions in Mg-rich calcite of the NM 9527 sample show a consistent LVR = 0.95. The inclusions homogenized at temperatures between 112 and 123 °C. The shape of vapour bubble was deformed during cooling experiments, and the bubble obtained the original shape at temperatures of about +10 °C. This phenomenon is supposed to be caused by the formation and melting of clathrates of hydrocarbons. Thus, the vapour bubble probably contains a very small amount of hydrocarbons.

Primary H₂O inclusions with variable LVR (L-only, V<>L, L+V inclusions) were found in Fe-rich dolomite (sample J00912). Homogenization temperatures were measured in L+V inclusions with LVR = 0.95 between 112 and 138 °C. The salinity of inclusions is high, of about 23 wt. %. Tfm = −60 °C and indicates the dominant portion of CaCl₂ in the solution.

The later dolomite of the J00911 sample forms the hem on the older dolomite. Primary H₂O inclusions in this dolomite show a variable LVR and, in contrast, very low salinity, of about 0.4 wt. % NaCl equiv.
**Sulphide stage**

*Calcite* of the J004I sample contains primary H₂O inclusions. The inclusions are liquid-only and indicate low temperature of trapping of the inclusions, below 100 °C. The salinity of primary inclusions is very low, from 0.2 to 0.5 wt. % NaCl equiv.

Secondary H₂O inclusions along healed microfractures showed a consistent LVR = 0.95 and homogenized at temperatures between 70 and 80 °C. The salinity of secondary inclusions is low, from 3.6 to 4 wt. % NaCl equiv.

**Discussion**

The character of fluid inclusions in minerals of various paragenetic stages of the Jáchymov deposit indicates a long-term evolution of the hydrothermal system. The first generation of veins connected with the *Sn–W sulphar senide* mineralization opened during early post-magmatic stage. *Carbonate–uraninite, arsenide, arsenic–sulphide, and sulphide* mineralization stages can be recognized during periodical opening of the veins under lower pT conditions. The high salinity of fluids suggests a deep circulation of ore-bearing fluids. The latest vein minerals formed under temperatures below 100 °C, from low salinity fluids.

Speaking about U-bearing mineralization, the obtained data can be compared with the results of fluid inclusion study from the Příbram and Rožná uranium deposits. Water-rich fluid inclusions from K3 and K5 calcite of the Příbram U deposit [582] showed Th between 62 and 131 °C and a low salinity, which does not reach 5 wt. % NaCl equiv.

Carbonates K4 of the U-bearing stage from the Rožná uranium deposit [583] have Th from 150 to 180 °C and the salinity of fluids up to 15 wt. % NaCl equiv.

The introduced temperature intervals of the formation of U mineralization correspond very well to the data of Poty and Pagel [584]. They suggested that most U-bearing mineralizations throughout the world formed under temperatures in the interval of 90 to 250 °C.

**STABLE ISOTOPES**

Nine samples of carbonate [343] were analysed (see Table 6 and Fig. 76). Isotope data of oxygen and carbon are in most cases homogeneous, which indicates relatively uniform source of carbon and water in the hydrothermal process and also stable physical-chemical conditions during the formation of carbonates, especially a limited variation in temperature.

Carbon of hydrothermal solution had calculated isotopic composition of about –6 to –8 ‰ PDB. According to Robinson [486], the supposed temperature of the formation of carbonates is 150 °C. Carbon with such isotopic composition may be mantle-derived or may represent the so-called homogenized carbon of the Earth’s crust. Carbon of sample J009I1 originated probably from marbles which occur around the deposit, and from which the carbon was mobilized during the hydrothermal processes. Carbonate J009I1 forms white thin rhombobedral crystals in vugs. It is the youngest carbonate on the sample, i.e., it is younger than carbonate J009I2.

Calculated isotopic composition of oxygen of water in the hydrothermal solution was about +5 to +6 ‰ SMOW (according O’Neill et al. [588]; supposed temperature of the formation of carbonates is 150 °C). Such water may

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**Table 6.** Isotopic composition of O and C (‰) in carbonates of different mineralization stages of hydrothermal veins in the Jáchymov ore district.

<table>
<thead>
<tr>
<th>sample</th>
<th>pt.</th>
<th>mineral</th>
<th>δ¹³C PDB</th>
<th>δ¹⁸O PDB</th>
<th>δ¹⁸O SMOW</th>
<th>stage</th>
</tr>
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<tbody>
<tr>
<td>J004I</td>
<td>1</td>
<td>calcite</td>
<td>–6.3</td>
<td>–11.1</td>
<td>19.4</td>
<td>sulphide</td>
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<tr>
<td>J005I</td>
<td>1</td>
<td>calcite</td>
<td>–6.2</td>
<td>–12.6</td>
<td>17.8</td>
<td>arsenide</td>
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<td>J005I</td>
<td>2</td>
<td>Fe-dolomite</td>
<td>–4.0</td>
<td>–10.3</td>
<td>20.2</td>
<td>arsenic-sulphide</td>
</tr>
<tr>
<td>J006I</td>
<td>1</td>
<td>ankerite</td>
<td>–7.0</td>
<td>–11.9</td>
<td>18.6</td>
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<tr>
<td>J007I</td>
<td>1</td>
<td>dolomite</td>
<td>–4.0</td>
<td>–9.5</td>
<td>21.1</td>
<td>arsenide</td>
</tr>
<tr>
<td>J008I</td>
<td>1</td>
<td>dolomite</td>
<td>–6.1</td>
<td>–9.1</td>
<td>21.5</td>
<td>arsenide</td>
</tr>
<tr>
<td>J008I</td>
<td>2</td>
<td>dolomite</td>
<td>–6.0</td>
<td>–9.1</td>
<td>21.5</td>
<td>arsenide</td>
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<tr>
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<td>–5.8</td>
<td>–12.1</td>
<td>18.4</td>
<td>arsenic-sulphide</td>
</tr>
</tbody>
</table>
be most probably either magmatic or metamorphic water, i.e., water isotopically equilibrated with metamorphic or igneous rocks at high temperature.

According to the data in [342], $\delta^{14}$S values range from ca. $-21$ to $+17$ $\%$ CDT – see Fig. 77. The lack of information on mineral species and mineralization stage of the respective samples analysed for S isotopes precludes a detailed interpretation.

Significant fluctuation in $\delta^{14}$S values indicates changes in the source of sulphur of hydrothermal solution and/or (more probably) indicates changes in the physical-chemical conditions during the crystallization of sulphides (mainly pH, Eh, oxygen fugacity, sulphur fugacity).

As isotopic equilibrium among sulphides was not attained, the $\delta^{14}$S values cannot be used for thermometric calculations.

**Rudotvorné procesy a minerální pragenze jáchymovského rudního okrsku**