TMPM Tschermaks Min. Petr. Mitt. 34, 167–182 (1985)

TMPM Tschermaks Mineralogische und Petrographische Mitteilungen

From the GIS BRGM-CNRS, Centre de Recherches sur la Synthèse et la Chimie des Minéraux, Orléans, France

The Černý Dûl Deposit (Czechoslovakia): An Example of Ni-, Fe-, Ag-, Cu-Arsenide Mineralization with Extremely High Activity of Arsenic; New Data on Paxite, Novakite and Kutinaite

Z. Johan

With 2 Figures

Received January 15, 1985;
accepted April 29, 1985

Summary

The Černý Dûl mineralization (Giant Mts., Czechoslovakia) consists of calcite veins crosscutting metamorphic rocks and exhibiting a complex paragenesis of Ni-, Fe-, (Co)- and Cu-, Ag-arsenides associated with native arsenic. Several new minerals belonging to Cu-As and Cu-Ag-As systems were described from this deposit (koutekite, novakite, paxite, kutinaite). New data on paxite, novakite and kutinaite were obtained. Paxite, $CuAs_2$, is monoclinic, $P2_1/c$, $a = 5.830$, $b = 5.111$, $c = 8.084$ Å, $\beta = 99.7°$, $Z = 4$, $D_{calc} = 5.97$ g/cm^3, polysynthetically twinned along (010). Novakite belongs to the Cu-Ag-As system. It is monoclinic, $C2/m$, Cm or $C2$, $a = 16.269$, $b = 11.711$, $c = 10.007$ Å, $\beta = 112.7°$, $Z = 4$, $D_{calc} = 8.01$ g/cm^3. The ideal formula is $Cu_{20+x}Ag_{1-x}As_{10}$, $x \simeq 0.16$. New microprobe analyses of kutinaite indicate a cell-content of 4 [$Cu_{14}Ag_6As_7$], $D_{calc} = 8.37$ g/cm^3.

Résumé

La minéralisation du gisement de Černý Dûl (Monts des Géants, Tchécoslovaquie) se distingue par une paragenèse complexe d'arséniures de Ni, Fe, (Co), Cu et Ag associés à l'arsenic natif, et apparaissant dans des filons de calcite qui recoupent une série de roches métamorphiques. Plusieurs minéraux nouveaux appartenant aux systèmes Cu-As et Cu-Ag-As ont été découverts dans ce gisement (koutekite, novakite, paxite, kutinaïte). De nouvelles données sur la paxite, la novakite et la kutinaïte ont été obtenues. La paxite, $CuAs_2$, est monoclinique, $P2_1/c$, $a = 5{,}830$, $b = 5{,}111$, $c = 8{,}084$ Å, $\beta = 99{,}7°$, $Z = 4$, $D_{calc} = 5{,}97$ g/cm^3; elle est polysythétiquement maclée suivant (010). La novakite est une phase du système Cu-Ag-As. Elle est monoclinique, $C2/m$, Cm ou $C2$, $a = 16{,}269$, $b = 11{,}711$, $c = 10{,}007$ Å, $\beta = 112{,}7°$, $Z = 4$, $D_{calc} = 8{,}01$ g/cm^3. Sa formule idéale s'écrit $Cu_{20+x}Ag_{1-x}As_{10}$, $x \simeq 0{,}16$. Des analyses de la kutinaïte conduisent à 4 [$Cu_{14}Ag_6As_7$] par maille, $D_{calc} = 8{,}37$ g/cm^3.

L'étude paragénétique a permis de voir que le système hydrothermal à Černý Důl couvre un interval de température large, s'étalant de $\simeq 500°$ à 100°C environ. Une très forte activité d'arsenic au cours des épisodes minéralisants tardifs a abouti à la cristallisation des arséniures de Cu riches en arsenic, stables à basse température. Cinq épisodes minéralisants ont été reconnus: le dépôt des arséniures de Ni, Fe, (Co) (löllingite, nickéline, pararammelsbergite, chloentite) était suivi de: kutinaïte, koutekite, arsenic natif et arséniures de cuivre riches en arsenic (novakite, Cu_2As, paxite). L'abondance des carbonates laisse entrevoir un rôle de composés ou de complexes de carbone dans l'évolution de ce système hydrothermal fortement réducteur.

The study of mineral associations showed that the Černý Důl hydrothermal system extended over a large temperature interval from $\sim 500°$ to 100°C. An extremely high arsenic activity during the late mineralization periods lead to the precipitation of low-temperature, As-rich copper arsenides. Five mineralization periods were distinguished: the precipitation of Ni-, Fe-, (Co)-arsenides (löllingite, nickeline, pararammelsbergite, chloanthite) was followed by kutinaite, koutekite, native arsenic and As-rich copper arsenides (novakite, Cu_2As, paxite). The abundance of carbonates suggests a possible role of carbon compounds or complexes in the evolution of this highly reducing hydrothermal system.

Introduction

The Černý Důl deposit, mined in late fifties for uranium, is situated 3.5 km north of Černý Důl village (Giant Mts., Czechoslovakia) in the Silver creek valley, near Berghaus.

The mineralization occurs in N-S calcite veins (with a low Mn-content), crosscutting diopside hornfels lenses concordant to the schistosity (N 90° to 120°) of strongly folded garnet-albite-muscovite gneisses forming an anticlinorium in the vicinity of the deposit. Several bodies of orthogneiss were observed in this area.

In tectonically affected hornfelses, trace Pb-Zn mineralization occurs locally (pyrite, chalcopyrite, sphalerite, galena). Its relationship with carbonate veins remains unknown. The maximum width of mineralized veins is approximately 20 cm. Several crystallization periods of calcite were recognized, separated by tectonic movements.

Carbonate veins contain local accumulations either of pitchblende and hematite (with rare selenides), or of copper arsenides associated with native arsenic and Fe-, Ni-, (Co)-arsenides. The mineralization was briefly described by *Johan* (1959). Several new minerals belonging to Cu-As and Cu-Ag-As systems were discovered in this deposit (*Johan*, 1958, 1960b and 1961; *Johan* and *Hak*, 1961; *Hak* et al., 1970).

The purpose of this paper is to provide detailed study of the mineral association determined previously but never examined using modern investigation methods, like the microprobe analysis.

It should be stressed that most of the samples studied came from mine dumps. Few specimens were collected in abandoned adits accessible in 1956 but only pitchblende and hematite mineralization were observed in the mine work.

Paragenesis

The evolution of the Černý Důl vein system is particularly complicated. Although this deposit was mined for uranium, the pitchblende + hematite association is practically never observed in samples containing arsenides. Indeed, the uranium-bearing period is distinctly separated from the arsenides precipitation. The relationship between these two paragenetical assemblages remains not well understood. Rarely, pitchblende is associated with tiemannite and clausthalite replacing it (*Johan*, 1960a).

In very few specimens, the early paragenesis of pitchblende with respect to nickeline + pararammelsbergite was established. It is then highly probable that the uranium-bearing period preceded the precipitation of arsenides. Moreover, the same order of crystallization was observed in several complex uranium deposits (*Kvaček*, 1965; *Johan* et al., 1982). *Tarkian* et al. (1983) met with difficulties, trying to establish the relationship between uranium-bearing and Co-, Ni-arsenides periods at Talmessi and Meskani deposits in Iran.

Five mineralization periods can be distinguished in the evolution of arsenide-bearing mineralization (Fig. 1). The first of them involves precipitation of löllingite I, whose composition is characterized by a high Co and Cu content and by a complete absence of Ni concentration (Table 1). Löllingite I occurs as fine-grained and frequently porous aggregates, replaced by younger phases. The first mineralization period ends with tectonic movements causing cataclasis of löllingite I and of associated calcite.

The second period starts with kongsbergite, containing up to 5.4 at.% Hg (Table 1). Its presence demonstrates a high activity of Ag and Hg in hydrothermal solutions from the earliest evolutionary stages of the Černý Důl mineralization, as shown also by the appearance of tiemannite, associated with pitchblende. Furthermore, kongsbergite is a precursor of kutinaite which precipitated at lower

Table 1. *Microprobe Analyses of Ore Minerals Belonging to the First and Second Mineralization Periods*

	LO I	LO I	KON	KON	NI	NI	PRA	PRA	PRA	CHL	PRA	LO II
Cu	4.48	5.77		0.13			0.77	1.58	0.09	3.68	0.17	0.43
Ag			88.86	88.88				0.09				
Hg	n.a.	n.a.	9.61	9.08								
Ni			1.18	0.50	42.75	41.68	25.79	25.03	27.52	16.19	20.72	6.81
Co	3.65	4.32	0.09	0.06	1.86	1.97	1.26	1.60	0.46	3.53	0.10	0.05
Fe	19.11	17.23							0.03	0.04	8.14	20.90
As	72.28	72.29	0.35	0.25	55.25	55.87	71.23	71.41	70.42	77.42	70.13	71.69
S	0.09	0.09					0.02			0.02	0.03	0.03
total	99.61	99.74	100.09	98.90	99.86	99.52	99.07	99.71	98.52	100.88	99.29	99.91
Cu *	0.146	0.188		0.002			0.025	0.052	0.003	0.147	0.006	0.014
Ag			0.927	0.938				0.002				
Hg			0.054	0.051								
Ni			0.019	0.008	0.987	0.952	0.923	0.891	0.997	0.699	0.753	0.242
Co	0.128	0.151			0.042	0.045	0.045	0.057	0.016	0.152	0.004	0.002
Fe	0.707	0.637							0.001	0.002	0.311	0.781
As	1.994	1.994			1.000	1.000	1.999	2.000	2.000	2.621	1.998	1.998
S	0.006	0.006					0.001			0.001	0.002	0.002

n.a. = not analyzed

LO I = löllingite I; KON = kongsbergite; NI = nickeline; PRA = pararammelsbergite; CHL = chloanthite; LO II = löllingite II.

* Number of atoms per formula unit calculated on 2(AS+S) for LO and PRA, 1 As for NI, 1(Ag+Hg+Ni) for KON (after substraction of (Ni,Co)As).

Analyses were performed on the BRGM-CNRS Camebax microprobe in Orléans. Analytical conditions: 20 kV, 10 nA, standards: pure Cu, Ag, Ni, Co; Cu_3As, FeS_2, HgS.

temperature. Taking into account a high activity of As in the hydrothermal system at the time of kongsbergite crystallization (association with NiAs and $NiAs_2$), one could expect the presence of the ϵ-phase known in the Ag-As system. Its absence can be explained by temperature constraints, because the stability of this phase is restricted to the temperature interval 582°—446°C (*Eade* and *Hume-Rothery*, 1959; *Makovicky* et al., 1979), definitely too high for the Černý Důl mineralization.

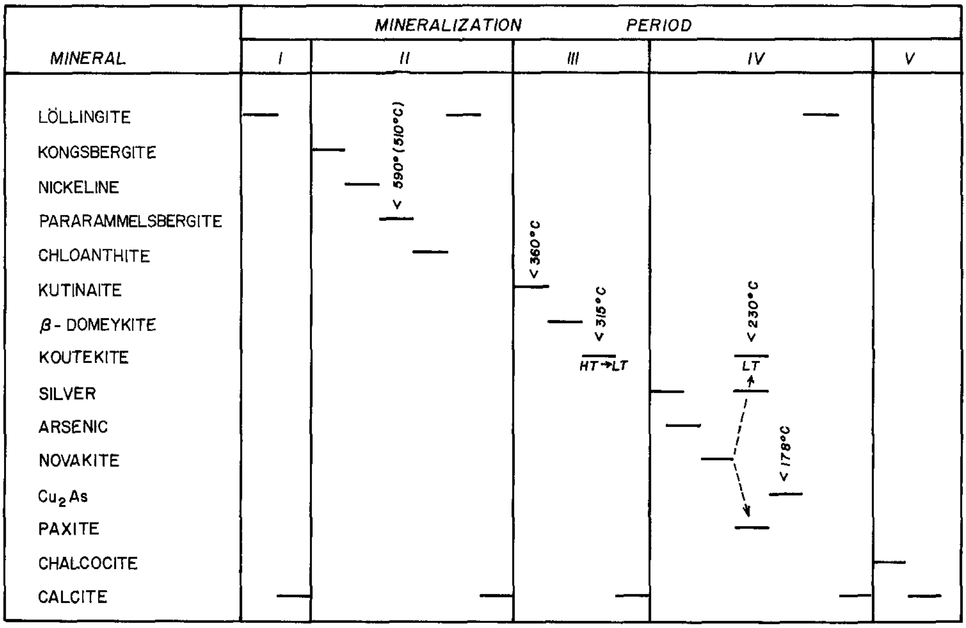

Fig. 1. Depositional succession of minerals in the Černý Důl carbonate veins. Uranium-bearing period is omitted. For some minerals, maximal precipitation temperatures estimated from equilibrium assemblages are indicated. See text for other explanations

Kongsbergite was followed by nickel arsenides whose succession: nickeline → pararammelsbergite → chloanthite, indicates a gradual increase in the arsenic activity of the hydrothermal milieu. Nickeline contains up to 2 wt.% Co (Table 1). This cobalt contents is similar to that found in nickeline associated with pararammelsbergite at the Silverfields deposit at Cobalt, Ontario (*Halls* and *Stumpfl*, 1969; *Petruk* et al., 1971). Nickeline grains are systematically surrounded by pararammelsbergite containing, unlike nickeline, copper in concentrations exceeding sometimes 1 wt.%, but its Co-content is lower and diminishes from the core to the periphery of botryoidal aggregates (Table 1). Chloanthite is the only triarsenide found in this deposit. Microprobe analyses gave a formula $(Ni_{0.699}Co_{0.152}Cu_{0.145})As_{2.621}$, indicating an important arsenic deficiency (*Roseboom*, 1962; *Petruk* et al., 1971) as well as a high copper content which corresponds to 14.7 mol.% $CuAs_{2.62}$ in solid solution.

The second period terminated in the crystallization of iron-rich pararammelsbergite, poor in Co and Cu (Table 1, Fig. 1) which was followed by nickeliferous, copper-bearing (and cobalt-free) löllingite II. The sequence of crystallization of this period indicates a successive appearance of Co → Ni → Fe in arsenides, but with restricted Co concentration. On the other hand, exceptionally high copper concentrations in di- and triarsenides give evidence of a substantial copper activity in hydrothermal solutions since the earliest mineralization stages.

The absence of rammelsbergite in the mineral assemblage described above suggests that the Ni-, Fe-arsenides were deposited at a temperature lower than the rammelsbergite-pararammelsbergite inversion temperature (*Yund*, 1961).

Copper arsenides appear during the third mineralization period (Fig. 1). Kutinaite is the earliest phase occurring either as rims of botryoidal pararammelsbergite aggregates or as veinlets in löllingite I. In the latter case, it is often associated with β-domeykite which extensively replaces löllingite I. Rarely, the association of β-domeykite with polysynthetically twinned koutekite originating from the transition of high-temperature (HT) to low-temperature (LT) modification, was found. It should be emphasized that kutinaite is never associated with koutekite. This observation is in perfect agreement with experimental results at 400°C (*Makovicky* et al., 1979), where kutinaite and koutekite are separated by a two-phase field of β-domeykite and arsenic.

In contrast with the third mineralization period which is only weakly developed, the fourth appears to be the most important. It began by deposition of native arsenic forming coarse-grained aggregates replacing the older calcite gangue. Microprobe analyses systematically revealed copper contents varying from 0.1 to 0.3 wt.% Cu in native arsenic; sometimes, Hg concentrations (as high as 0.3 wt.% Hg) were measured. Arsenic aggregates contain minute inclusions of native silver*.

Novakite crystallized after native arsenic. It forms irregular veinlets crosscutting arsenic, or coarse botryoidal aggregates frequently found at the löllingite I – arsenic contact. The extensive replacement of arsenic by novakite gave rise to an intimate intergrowth of these two phases in which novakite grains display remarkable optical continuity. Thus, novakite seems to form huge megacrysts included in native arsenic. Novakite is followed by koutekite (LT) and paxite. These two copper arsenides are always associated and their texture suggests a reaction-like relationship. It also appears that koutekite (LT) grains are never in direct contact with native arsenic from which they are separated by a fringe of paxite. In contrast, isolated koutekite (LT) grains, rimmed by löllingite III were observed as inclusions in calcite gangue.

On the other hand, novakite and koutekite (LT) are incompatible. A detailed study of polished sections at high magnification revealed the presence of minute grains of native silver in the assemblage koutekite (LT) + paxite, as well as the incipient transformation of koutekite (LT) into Cu_2As.

All these observations suggest that the assemblage koutekite (LT) + paxite

---

* The position of arsenolamprite (*Johan*, 1959) in the precipitation sequence is not yet elucidated. Arsenolamprite occurs as lamellar crystals in calcite gangue, associated with native silver and löllingite. In other deposits (Jáchymov, Kapnik), arsenolamprite is older than native arsenic (*Picot* and *Johan*, 1982). The structure of arsenolamprite might be stabilized by the presence of impurities.

results from a reaction of novakite with arsenic. The estimation of respective volumes of coexisting phases leads to the following reaction:

$$2\ Cu_2Ag_{0.1}As + 2\ As \rightarrow Cu_{2.5}As + 3\ Cu_{0.5}As + 0.2\ Ag$$

novakite arsenic koutekite paxite silver

The fourth mineralization period ends in precipitation of löllingite III which is Co- and Ni-free but shows high Cu concentrations (Table 2). Finally, chalcocite which is the only sulphide directly associated with arsenides, terminates the deposition of metallic minerals. Its composition varies from $Cu_{1.99}S$ to $Cu_{1.96}S$. Microprobe analyses showed low, but persistent, iron content (0.02 to 0.08 wt.%) and sometimes, the presence of arsenic (as high as 1.8 wt.%).

Table 2. *Microprobe Analyses of Löllingite III*

Cu	3.86	4.25	2.88	3.75	3.16	2.04
Hg	0.08					
Ni	0.03					
Co			0.01			
Fe	24.03	23.95	25.04	24.60	24.65	26.39
As	72.28	73.18	71.23	71.09	71.52	72.72
S			0.01			0.06
Total	100.28	101.38	99.17	99.44	99.33	101.21
Cu*	0.126	0.137	0.095	0.124	0.104	0.066
Hg						
Ni						
Co						
Fe	0.892	0.878	0.943	0.928	0.925	0.972
As	2.000	2.000	1.999	2.000	2.000	1.996
S			0.001			0.004

*number of atoms per formula unit calculated on 2(As+S)

All mineralization periods drew to a close in the precipitation of calcite. Generally, younger carbonates replace the older ones, as well as the associated metallic minerals.

Copper Arsenides

β-Domeykite

Because its properties in reflected light are very similar to those of novakite and its intimate intergrowth with other arsenides, the recognition of β-domeykite in the Černý Důl deposit is rather late (*Johan*, 1963). β-domeykite is associated with kutinaite and löllingite I, or with polysynthetically twinned koutekite (HT → LT).

Microprobe analyses of β-domeykite (Table 3) indicate that its silver content is very low even if it coexists with kutinaite, confirming the experimental results of *Makovicky* et al. (1979). The composition of β-domeykite associated with kutinaite is $Cu_{2.820}As$ near the arsenic-rich side; β-domeykite from the assemblage with koutekite (HT → LT) shows a greater copper deficiency: $Cu_{2.737}As$. These compositions lie within the homogeneity field established by *Naud* and *Priest* (1972, 1974) and agree also with data published by *Heyding* and *Despault* (1960), *Makovicky* et al. (1979).

Other known occurrences of β-domeykite are restricted to assemblages of higher copper arsenides: α-domeykite and algodonite (*Paděra*, 1951; *Skinner* et al., 1963; *Picot* and *Vernet*, 1967; *Skinner* and *Luce*, 1971; *Moore*, 1971; *Pierrot* et al., 1972; *Tarkian* et al., 1983). In them, the presence of β-domeykite was interpreted as a result of the α-domeykite decomposition (*Skinner* and *Luce*, 1971; *Tarkian* et al., 1983).

Table 3. *Microprobe Analyses of β-Domeykite and Koutekite*

	β-domeykite						koutekite				
	1	2	3	4	5	6	7	8	9	10	11
Cu	69.89	70.18	70.36	70.14	69.77	70.21	67.91	68.09	66.31	66.45	66.51
Ag		0.16							0.03	0.03	0.10
Fe			0.38		0.61				0.13	0.07	0.05
As	28.52	29.34	29.26	29.32	29.68	30.24	32.48	32.20	33.85	33.73	33.86
Total	98.41	99.68	100.00	99.46	100.06	100.45	100.39	100.29	100.32	100.28	100.52
Cu*	2.890	2.820	2.835	2.820	2.772	2.737	2.465	2.495	2.310	2.323	2.316
Ag		0.004									0.002
Fe			0.017		0.027				0.005	0.003	0.002
As(at.%)	25.71	26.15	25.96	26.18	26.32	26.76	28.86	28.61	30.16	30.07	30.12

* cell content on 1 As

1,2: associated with kutinaite; 3-6:associated with koutekite(HT→LT)

7,8: koutekite(HT→LT); 9-11: koutekite(LT) associated with paxite

It is clear that this hypothesis is not relevant to the explanation of the presence of β-domeykite in the Černý Důl deposit. Here, its stabilization is due to a relatively high temperature during the precipitation of the earliest copper arsenides. The association of β-domeykite with As-rich arsenides (koutekite, löllingite) permits the estimation of the extension of $Cu_{3-x}As$ stability field to the arsenic-rich side.

Koutekite

Discovered in the Černý Důl deposit (*Johan*, 1958, 1960b), koutekite was later described from several occurrences in France (*Picot* and *Vernet*, 1967; *Pierrot* et al., 1972; *Picot* and *Ruhlmann*, 1978), and very recently from the Talmessi-Meskani deposit in Iran (*Tarkian* et al., 1983).

The phase $Cu_{5-x}As_2$ is known in two modifications. The high-temperature cubic form decomposes peritectically to β-domeykite and arsenic between 360° and 340°C. If quenched, the high-temperature phase transforms at 315°C into a low-temperature, orthorhombic modification identical with koutekite (*Juza* and *von Benda*, 1968; *Liebisch* and *Schubert*, 1971).

The composition of koutekite is temperature dependent but despite numerous studies, its composition field is still not well determined. *Heyding* and *Despault* (1960) reported composition limits $Cu_{2.5}As$ and $Cu_{2.45}As$. *Juza* and *von Benda* (1968) established that the formula of both $Cu_{5-x}As_2$ modifications is the same, $Cu_{9.5}As_4$ ($Cu_{2.375}As$). *Liebisch* and *Schubert* (1971) performed the crystal structure determination of the low-temperature form of koutekite with a composition of Cu_5As_2. *Naud* and *Priest* (1972) indicated $Cu_{2.40}As$ as a composition limit on the arsenic-rich side for the low-temperature form of koutekite. *Makovicky* et al. (1979) suggested that the compositional range of the high-temperature form coincides with that of the low-temperature form, and gave the formula $Cu_{2.47}As$.

In the Černý Důl deposit, koutekite appears in two different assemblages:

- high-temperature assemblage of koutekite (HT → LT) and β-domeykite
- low-temperature association of koutekite + paxite.

Microprobe analyses (Table 3) indicate a different chemical composition of koutekite in these two assemblages. Koutekite (HT → LT) has an average composition of $Cu_{2.467(0.032)}As$ (standard deviation in parentheses), in good agreement with data of *Heyding* and *Despault* (1960) and of *Makovicky* et al. (1979). The results obtained by *Naud* and *Priest* (1972) suggest an increase in metal vacancies at a low-temperature. This conclusion is confirmed by the average composition of koutekite associated with paxite: $Cu_{2.345(0.042)}As$. The low-temperature koutekite contains Ag and Fe as minor elements.

Paxite

It was described, as a new mineral, from Černý Důl by *Johan* (1961) who ascribed to it a formula Cu_2As_3 (based on a microanalysis of paxite + arsenic intergrowth coupled with a volume estimation of these two phases) and indexed its powder diffraction pattern (Ito's method) on a orthorhombic unit-cell by analogy with Sb_2S_3. *Picot* and *Johan* (1982) completed data on the optical properties of paxite.

Microprobe analyses showed, without any doubt, that the formula given by *Johan* (1961) was erroneous. As indicated in Table 4, the Cu/As ratio is close to 1/2, all analyses falling into the range limited by $Cu_{1.022}As_2$ and $Cu_{1.090}As_2$. According to these results, the ideal formula of paxite may be written as $CuAs_2$.

It appears then, that the paxite content in the sample analyzed by *Johan* (1961) was actually 60.95 wt.% instead of 50.7 wt.% calculated from modal analysis. Using this new value, the corrected measured density of paxite is 5.4 g/cm^3. Measurements of Vickers microhardness (load = 25 g) yielded 146 kg/mm^2 (average of 7 determinations). The indentations are very irregular with cleavage traces along (010) (twin lamellae direction).

The Weissenberg photographs (Ni filtered Cu radiation) showed a monoclinic symmetry. The unit-cell parameters obtained by least-squares refinement from the X-ray powder diagram are

$$a = 5.839(2)\ \text{Å}$$
$$b = 5.111(2) \qquad \beta = 99.7°$$
$$c = 8.084(3)$$
$$a:b:c = 1.1407:1:1.5817$$
$$V = 237.4\ \text{Å}^3;\ Z = 4;\ D_{calc} = 5.97\ \text{g/cm}^3$$

Observed systematic extinctions correspond to the space group $P2_1/c$. The large discrepancy between the calculated and the measured density can be explained by the low accuracy of measured values due to a considerable porosity of paxite

+ arsenic aggregates. An indexed X-ray powder pattern published by *Johan* (1961) exhibits all strong diffraction lines of rhombohedral arsenic. Furthermore, the lines at $d(I)$ 7.56(2), 6.42(4) could not be attributed; the line 4.00(1) corresponds to hkl (002), d_{calc} 3.990 Å.

According to the Weissenberg photographs, paxite crystals are polysynthetically twinned along (010). The compound $CuAs_2$ has not yet been synthesized (*Naud* and *Priest*, 1972). Among chemically similar phases, $ZnAs_2$ and CuP_2 possess monoclinic unit-cells belonging to the $P2_1/c$ space group (*Senko* et al., 1959).

Table 4. *Selected Microprobe Analyses of Novakite and Paxite*

						novakite						
											$\bar{x}$	σ
Cu	60.32	60.22	60.08	60.15	60.47	60.20	60.49	60.29	60.30	60.48	60.30	0.143
Ag	4.24	4.45	4.20	4.16	4.45	4.48	4.43	4.20	4.14	4.55	4.33	0.155
As	34.80	35.05	35.53	35.32	35.66	36.04	35.54	35.25	35.14	34.72	35.30	0.403
Total	99.36	99.72	99.81	99.63	100.58	100.72	100.46	99.74	99.58	99.75	99.93	
Cu*	2.044	2.025	1.993	2.008	1.999	1.990	2.007	2.017	2.023	2.054	2.016	0.021
Ag	0.085	0.088	0.082	0.082	0.086	0.086	0.087	0.083	0.082	0.091	0.085	0.003
						paxite						
											$\bar{x}$	σ
Cu	30.75	30.75	30.71	31.13	31.09	30.67	31.56	30.64	30.66	29.76	30.35	0.933
As	68.95	70.94	69.93	69.36	68.84	68.40	68.89	69.64	70.52	69.81	69.91	1.041
Total	99.70	101.69	100.64	100.49	99.93	99.07	100.45	100.28	101.18	99.57	100.26	
Cu*	1.046	1.015	1.030	1.061	1.061	1.061	1.077	1.030	1.030	1.005	1.024	0.043

*cell content on 1 As for novakite and 2 As for paxite

$\bar{x}$,σ : average and standard deviation

Novakite

Novakite was described as a new mineral from the Černý Důl deposit by *Johan* and *Hak* (1959, 1961). The wet chemical analysis performed on an intimate intergrowth of novakite, löllingite, chalcocite and calcite separated from polished sections, gave the formula $(Cu, Ag)_4As_3$. The X-ray powder pattern was tentatively indexed on a tetragonal cell (Ito's method).

Later, a detailed study of polished sections showed that in addition to the minerals mentioned above, native arsenic was also present in the analyzed sample. This implies a more copper-rich composition of novakite, confirmed by microprobe analyses done in 1966 by *Skinner* and *Hey* (pers. comm.). *Makovicky* et al. (1979) published new analytical data on copper arsenides from Černý Důl. According to them, the formula of novakite is $Cu_{2.01}Ag_{0.07}As$.

Selected microprobe analyses of novakite are given in Table 4. The silver content is remarkably constant. Despite a large number of analyses (n = 28) performed on several polished sections, no replacement of Cu by Ag is apparent. This suggests that novakite actually belongs to the Cu-Ag-As system. The average formula calculated from microprobe analyses (Table 4) is $Cu_{2.016}Ag_{0.085}As$, very close to that proposed by *Makovicky* et al. (1979). Among other elements analyzed (Co, Ni, Fe, Hg, S), none was systematically found in concentrations higher than the detection limit 1.10^{-2} wt.%.

A fragment of novakite was examined by Weissenberg zero, first and second level photographs (Ni filtered Cu radiation) about [010] and [001] axes. The unit-cell parameters, refined by least-squares from X-ray powder pattern (Table 5) are

$$a = 16.269(3)\ \text{Å}$$
$$b = 11.711(2) \qquad \beta = 112.7^{\circ}_{4}$$
$$c = 10.007(2)$$
$$a{:}b{:}c = 1.3892{:}1{:}0.8545$$
$$V = 1758.5\ \text{Å}^3; Z = 4$$

Systematic extinctions: $hkl : h + k = 2n; h0l : h = 2n; 0k0 : k = 2n$, reveal a C-centred unit-cell with $C2/m$, $C2$ or Cm as possible space groups.

Taking into account the chemical composition deduced from microprobe analyses, the density originally measured (6.7 g/cm^3, *Johan* and *Hak*, 1961) must be corrected by subtraction of the following impurities: (Fe,Co)As$_2$, Cu$_2$S, As and CaCO$_3$. The recalculated value is 8.1 g/cm^3.

The low accuracy of the measured density makes difficult the determination of the unit-cell content. For $Z = 38$, the calculated density is 7.61 g/cm^3 and the cell contains $Cu_{76.6}Ag_{3.23}As_{38}$; for $Z = 40$, D_{calc} is 8.01 g/cm^3 and the cell content is $Cu_{80.64}Ag_{3.40}As_{40}$. The latter value is more plausible if densities of chemically similar compounds in the system Cu-As are taken into consideration, such as $Cu_{5-x}As_2$ (D_{calc} = 7.84 g/cm^3; *Juza* and *von Benda*, 1968) or Cu_2As (D_{calc} = 7.88 g/cm^3; *Naud* and *Priest*, 1972).

It is interesting to note that for $Z = 40$, the unit-cell contains 84 (Cu + Ag) atoms. Furthermore, on the basis of microprobe analyses, it can be assumed that silver and copper occupy different sites in the novakite structure. In that case, the formula may be written as $4\,[Cu_{20.16}Ag_{0.85}As_{10}]$ or ideally $Cu_{20+x}Ag_{1-x}As_{10}$, with $x \simeq 0.16$.

Makovicky et al. (1979) reported the similarity between unit-cells of the high-temperature form of koutekite (a = 5.81 Å; *Juza* and *von Benda*, 1968) and kutinaite (a = 11.76 Å, *Hak* et al., 1970; a = 11.782 Å, *Makovicky* et al., 1979): $a_{\text{KUT}} \simeq 2a_{\text{KOUT(HT)}}$. It is noteworthy that b_{NOV} is very close to a_{KUT}. This indicates that the unit-cell of novakite might be derived from a distorted cubic cell with a lattice constant close to that of kutinaite. Considering the vectorial plane $<\vec{a}_{\text{NOV}}, \vec{c}_{\text{NOV}}>$, it can be shown that $\vec{a}_{\text{NOV}}/\sqrt{2} = 11.50\ \text{Å} = \vec{A}$, to compare with a_{KUT} and $a_{\text{KOUT(HT)}}$. Taking $\vec{A}$ as an orthogonal vectorial base, $\vec{C} = {}^4/_5\,\vec{A} + {}^1/_3\,\vec{A} = 9.965\ \text{Å} \simeq c_{\text{NOV}}$. The calculated angle between $\vec{A} \cdot \sqrt{2}$ and $\vec{C}$ is 112.4° (β_{NOV} = 112.7°).

Kutinaite

Kutinaite was described from Černý Důl by *Hak* et al. (1970). *Picot* and *Ruhlmann* (1978) found it associated with allargentum and koutekite (HT) at Wasserfall (Vosges, France), and recently, *Tarkian* et al. (1983) observed this mineral in the Meskani deposit (Iran).

New microprobe analyses of kutinaite from Černý Důl (Table 6) yielded an average formula $Cu_{2.081}Ag_{0.884}As$ which is in good agreement with results previously published (*Hak* et al., 1970; *Makovicky* et al., 1979; *Tarkian* et al., 1983). The Me/As ratio is very close to 3/1.

Table 5. *X-Ray Powder Data for Paxite and Novakite*

paxite				novakite			
I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl
1	5.72	5.75	100	3	9.34	9.23	110
3	4.32	4.30	011			9.23	001
4	3.822	3.819	110	3	4.06	4.066	$\bar{4}01$
7	3.604	3.605	$\bar{1}11$			4.058	$\bar{3}12$
5	3.295	3.302	111	2	3.785	3.784	221
10	3.144	3.142	012			3.783	112
1	3.039	3.042	102	2	3.631	3.633	311
3	2.874	2.873	200	1 B	3.359	3.340	$\bar{4}21$
10	2.616	2.614	112	6	3.153	3.158	420
2	2.546	2.543	$\bar{2}02$	3	3.089	3.084	401
9	2.495	2.497	$\bar{2}11$	4	3.020	3.019	$\bar{4}03$
2	2.426	2.434	021	3	2.936	2.933	222
3	2.349	2.357	013	3	2.898	2.898	$\bar{3}32$
1	2.307	2.305	$\bar{1}13$			2.898	$\bar{2}23$
2	2.201	2.200	121	1	2.798	2.798	312
3	2.156	2.151	022	3	2.670	2.670	$\bar{5}13$
1 B	2.079	2.078	$\bar{1}22$	7	2.520	2.521	241
4	1.993	1.992	004	4	2.441	2.441	$\bar{5}32$
4	1.958	1.957	122	5	2.380	2.379	530
3	1.915	1.915	300	2	2.315	2.318	332
5 B	1.855	1.856	014			2.314	150
4	1.815	1.817	$\bar{1}23$	3	2.280	2.283	422
		1.812	$\bar{3}11$			2.279	133
7	1.795	1.794	$\bar{3}10$	2	2.206	2.214	151
6	1.687	1.685	$\bar{2}14$			2.208	601
2	1.642	1.640	$\bar{2}23$	1	2.162	2.163	$\bar{6}04$
1	1.617	1.615	$\bar{1}31$	1	2.129	2.126	512
				2	2.106	2.108	710
				3	2.063	2.066	621
				9	1.998	1.999	204
				8	1.957	1.955	333
				7	1.910	1.911	602
				10	1.876	1.875	800
				1	1.849	1.846	550
						1.846	005
				5	1.783	1.786	820
						1.781	$\bar{6}25$
				2	1.732	1.733	551
						1.732	115
				1	1.672	1.667	$\bar{4}06$
				3	1.652	1.653	533
				1	1.588	1.589	552
				2	1.564	1.561	045
				3 B	1.348		
				2	1.309		
				1	1.293		
				2	1.265		
				1	1.248		
				8	1.178		
				4	1.158		

Cu/Ni, 240mm circumference camera, intensities estimated visually

B= broad line

Considering density values measured on synthetic kutinaite by *Hak* et al. (1970) of 8.38 g/cm^3 and *Makovicky* et al. (1979) of 8.36 g/cm^3, the estimated number of atoms per cell is equal to $Cu_{56}Ag_{24}As_{28}$, or respectively to 4 $[Cu_{14}Ag_6As_7]$. This formula gives D_{calc} = 8.37 g/cm^3 (calculated for the refined unit-cell parameter of *Makovicky* et al., 1979), a value in good agreement with D_{meas} and it corresponds well to the result of microprobe analyses, the theoretical composition being $Cu_2Ag_{0.857}As$.

On the other hand, the formula $Cu_5Ag_2As_3$ proposed by *Makovicky* et al. (1979) as the most probable one, although it yields a calculated density of 8.46 g/cm^3 ($Z = 11$) compatible with measured values, is rather far from the real composition of kutinaite, because the theoretical composition $Cu_{1.66}Ag_{0.66}As$ does not fit with analytical results (Table 6).

Table 6. *Microprobe Analysis of Kutinaite*

Cu	43.77	43.10	44.15	43.98	43.97	43.68	43.87
Ag	31.17	31.79	31.42	32.31	31.55	31.63	31.39
Co			0.08		0.08		
As	24.28	24.78	24.82	25.21	24.75	25.16	24.71
Total	99.22	99.67	100.47	101.49	100.35	100.47	99.97
Cu*	2.125	2.051	2.097	2.057	2.095	2.047	2.093
Ag	0.891	0.891	0.879	0.890	0.885	0.873	0.882
Co			0.003		0.004		

*cell content on 1 As

Conditions of Deposition

The assemblage of Ni-, Fe-, (Co)-arsenides, characteristic of early stages of the Černý Důl mineralization, was deposited at a temperature lower than the transition temperature 590°C of rammelsbergite-pararammelsbergite (*Yund*, 1961) which is probably as low as 510°C in the presence of impurities (*Moore*, 1971). The temperature range between 478° and 230°C in which kutinaite is stable (*Makovicky* et al., 1979) allows an estimate of the maximum temperature of the third mineralization period (Fig. 1). The exclusive association of kutinaite with β-domeykite (in spite of the existence of koutekite (HT → LT) + β-domeykite assemblage) indicates a crystallization temperature of kutinaite lower than 360° (*Juza* and *von Benda*, 1968; *Makovicky* et al., 1979) at which koutekite undergoes a peritectoid decomposition to β-domeykite and arsenic. *Heyding* and *Despault* (1960) located this reaction at 300°C.

Taking into consideration these constraints, the deposition of kutinaite and β-domeykite occurred between 360° and 230°C. Rare associations of koutekite (HT → LT) + β-domeykite indicate a temperature higher than the transition temperature 315°C of koutekite (HT) → koutekite (LT) (*Juza* and *von Benda*, 1968), and provide evidence of a quenching phenomenon which happened at the end of the third mineralization period and could be related to a pressure release due to tectonic movements.

The crystallization temperatures of β-domeykite and koutekite may also be estimated using experimental data on the composition of these phases (*Van Bin-Nan* et al., 1965; *Naud* and *Priest*, 1972, 1974; *Makovicky*, 1976) becoming progressively more and more copper deficient at lower temperatures. A plot of β-domeykite analyses from Černý Důl on composition range curves constructed from the experimental data (Fig. 2), indicates a temperature between 360° and 250°C (for the average composition), in agreement with values estimated above. The temperature deduced from the average composition of koutekite (HT → LT) is 290°C, just below the transition temperature; however,

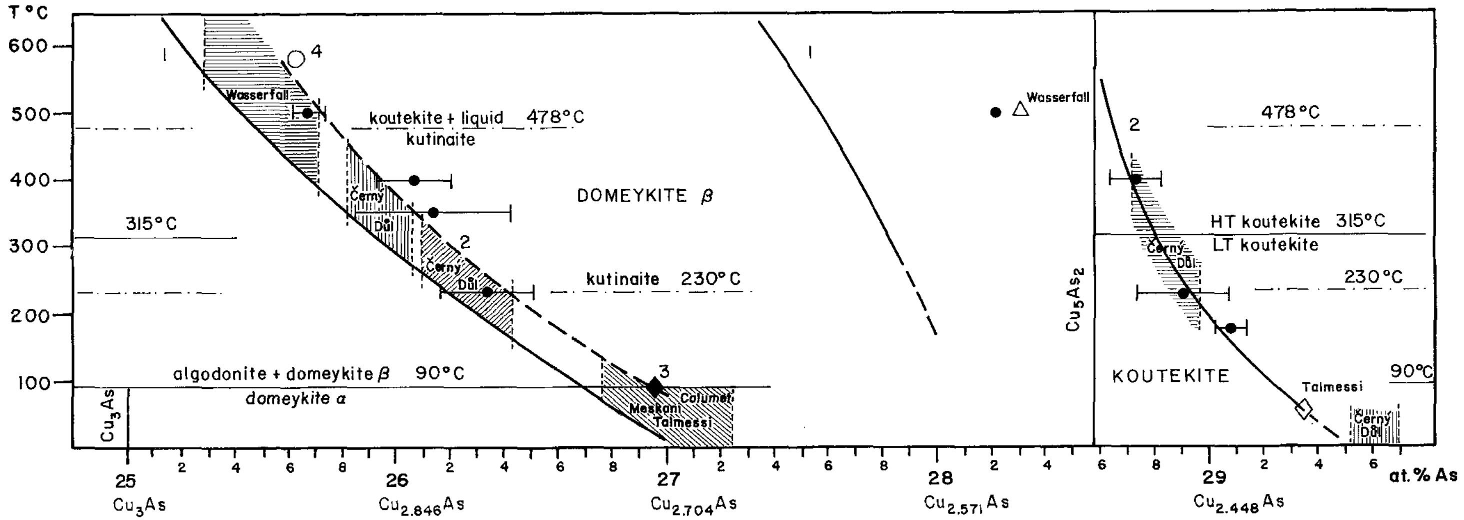

Fig. 2. Variation of β-domeykite and koutekite chemical compositions with temperature. Composition-range curves were constructed using experimental data of *Naud* and *Priest* (1974) (1), *Makovicky* (1976) (2, ├─●─┤, standard deviations indicated), *Skinner* and *Luce* (1971) (3, ♦), *Van Bin-Nan* et al. (1965) (4, ○). The Cu-rich portion of the Cu-As system is from *Skinner* and *Luce* (1971).
The stability field of kutinaite (*Makovicky* et al., 1979) and the transition temperature of koutekite (HT → LT) (*Juza* and *von Benda*, 1968) are plotted on the figure. Compositions of β-domeykite and koutekite from Černý Důl are compared with data from Wasserfall (*Picot* and *Ruhlmann*, 1978), Meskani-Talmessi (*Tarkian* et al., 1983) and Calumet (*Skinner* and *Luce*, 1971)

the standard deviation covers a large field extending from 400° to 210°C (Fig. 2) which is nearly the same as for β-domeykite.

Concerning the fourth mineralization period characterized by an extensive deposition of native arsenic preceding low-temperature copper (and Ag) arsenides (novakite, koutekite (LT), Cu_2As, paxite), the average composition of koutekite (LT), $Cu_{2.345}As$, indicates a temperature of ~ 100°C (Fig. 2). This low temperature is confirmed by the coexistence of koutekite (LT) with Cu_2As, stable only below 178°C (*Naud* and *Priest*, 1972). This phase was recently discovered in the Talmessi deposit (*Tarkian* et al., 1983). Low deposition temperatures of copper arsenides belonging to the fourth period explain why different attempts to synthesize them failed (*Skinner* et al., 1963; *Moore*, 1971). *Makovicky* et al. (1979) demonstrated that the stability fields of novakite and paxite must be situated below 150° and 130°C respectively. This study indicates even lower temperatures for the precipitation of these phases. One could expect α-domeykite to appear at these conditions (*Skinner* and *Luce*, 1971) but it cannot coexist with native arsenic (*Hansen* and *Anderko*, 1958; *Ugai* et al., 1972).

In conclusion, the Černý Důl mineralization extends over a large temperature interval, from about 500° to 100°C. Thus, it differs from those copper arsenide-bearing occurrences which are undeniably of high-temperature origin, as for example, Wasserfall in France (*Picot* and *Ruhlmann*, 1978). The paragenesis, as well as the plot of β-domeykite and koutekite analyses (Fig. 2) confirm this conclusion. The composition of koutekite from Wasserfall approaches that obtained by *Makovicky* (1976) at 500°C; β-domeykite analyses cover a field from 600°C up to the upper stability limit of kutinaite at 478°C. The high copper content (3.20 wt.%, *Picot* and *Ruhlmann*, 1978) in löllingite included in β-domeykite from Wasserfall indicates a very large temperature stability field of $FeAs_2$, also corroborated by results from the Černý Důl deposit.

On the other hand, the mineralization studied differs from occurrences where copper arsenides appear at very low temperatures (~ 100°C), such as the Keweenaw deposit in Michigan (*Skinner* et al., 1963; *Skinner* and *Luce*, 1971; *Moore*, 1971) or the Talmessi-Meskani deposit in Iran (*Paděra*, 1951; *Tarkian* et al., 1983). These parageneses are characterized by an extremely high copper activity leading to the precipitation of native copper and Cu-rich copper arsenides only (algodonite, α-domeykite, β-domeykite, and exceptionally koutekite).

The peculiarity of the Černý Důl deposit is its extremely high activity of arsenic during the late mineralization periods, responsible for the precipitation of novakite and paxite at low temperatures approaching 100 °C. No other deposit of this type is known in the world. Thus, the Černý Důl mineralization represents an exceptional target for studies on the low-temperature evolution of a highly reducing hydrothermal system.

The abundance of carbonates whose precipitation ends systematically every mineralization period suggests that carbon compounds or complexes played a substantial role in the evolution of this hydrothermal system. Because a high hydrogen fugacity is expected (due to the precipitation of native arsenic), the possible occurrence of methane in fluid inclusions is of great importance and this aspect of the research should be developed in the future.

Acknowledgements

I thank Dr. *M. Makovicky* and Prof. *E. Makovicky* (University of Copenhagen) for valuable discussion during the course of this work. The writer is indebted to Prof. *D. Watkinson* (Carleton University) who improved the English of the manuscript and to Dr. *J. Chisholm* (British Museum of Natural History) for critical comments.

References

Eade, G. A., Hume-Rothery, W., 1959: The constitution of silver-rich, silver-arsenic alloys. Z. Metallkunde *50*, 123–126.

Hak, J., Johan, Z., Skinner, B. J., 1970: Kutinaite; a new copper-silver arsenide mineral from Černý Důl, Czechoslovakia. Amer. Min. *55*, 1083–1087.

Halls, C., Stumpfl, E. F., 1969: Geology and ore deposition, Western Kerr Lake Arch, Cobalt, Ontario. Proc. 9th Commonwealth Mining and Metallurg. Congr. 1969, Mining and Petroleum Geol. Section, Paper 18, 1–44.

Hansen, M., Anderko, K., 1958: Constitution of binary alloys, 1305 p. New York: McGraw-Hill Book Co.

Heyding, R. D., Despault, J. G., 1960: The copper-arsenic system and the copper arsenide minerals. Can. J. Sci. *38*, 2477–2481.

Johan, Z., 1958: Koutekite: a new mineral. Nature *181*, 1553.

– 1959: Arsenolamprit – die rhombische Modifikation des Arsens aus Černý Důl (Schwarzenthal) im Riesengebirge. Chem. der Erde *20*, 71–80.

– 1960a: Preliminary data on the occurrence of tiemannite – HgSe, at Černý Důl, Krkonoše. Čas. Min. Geol. *5*, 65–66.

– 1960b: Koutekit – Cu_2As, ein neues Mineral. Chem. der Erde *20*, 217–226.

– 1961: Paxite – Cu_2As_3, a new copper arsenide from Černý Důl in the Giant. Mts. (Krkonoše). Acta Univ. Carolinae, Geologica, No. 2, 77–86.

– 1963: Die Applikation einiger Beziehungen des Cu-As-Phasensystems zur Genesis des Kupferarseniden von der Lagerstätte Černý Důl. Proc. Symp. on "Problems of magmatic ore deposition", Czech. Acad. Publ. House *1*, 420–424.

– *Hak, J.*, 1959: Novakit – $(Cu,Ag)_4As_3$, ein neues Mineral. Chem. der Erde *20*, 49–50.

– – 1961: Novakite, $(Cu,Ag)_4As_3$, a new mineral. Amer. Min. *46*, 885–891.

– *Picot, P., Ruhlmann, F.*, 1982: Evolution paragénétique de la minéralisation uranifère de Chaméane (Puy-de-Dôme), France: chaméanite, geffroyite et giraudite, trois séléniures nouveaux de Cu, Fe, Ag, et As. Tschermaks Min. Petr. Mitt. *29*, 151–167.

Juza, R., von Benda, K., 1968: Zur Kenntnis des Cu_5As_2. Z. anorg. allg. Chem. *357*, 238–246.

Kvaček, M., 1965: Beitrag zur Geochemie der Selenidvererzung im Českomoravská vrchovina-Gebiet, ČSSR: Sbor. 1. Geoch. Konf., Ostrava, 393–402.

Liebisch, W., Schubert, K., 1971: Zur Struktur der Mischung Kupfer-Arsen. J. Less-Common Met. *23*, 231–236.

Makovicky, M., 1976: Phase and phase relations in the system Cu-Ag-As at 500°C, 400°C and 350°C. Unpubl. M.Sc. Thesis, Univ. of Copenhagen, 67 p.

– *Rose-Hansen, J., Skinner, B.*, 1979: Phase and phase relations in the system Cu-Ag-As at 500°C, 400°C and 350°C. N. Jb. Min. Abh. *135*, 221–269.

Moore, P. B., 1971: Copper-nickel arsenides of the Mohawk, Keweenaw Co., Michigan. Amer. Min. *56*, 1319–1331.

Naud, J., Priest, P., 1972: Contribution à l'étude du système cuivre-arsenic. Mat. Res. Bull. *7*, 783–792.

– *Priest, P.*, 1974: Étude des arséniures de cuivre précipités par l'hydrogène arsénié. Mat. Res. Bull. *9*, 337–344.

Paděra, K., 1951: Revision of the domeykite-algodonite group. Bull. Acad. tchèque Sci. *4*, 9–16.

Petruk, W., Harris, D. C., Stewart, J. M., 1971: Characteristics of the arsenides, sulpharsenides and antimonides, in the silver-arsenide deposits of the Cobalt-Gowganda region, Ontario. Canad. Min. *11*, 150–186.

Picot, P., Johan, Z., 1982: Atlas of ore minerals: BRGM-Elsevier ed., 458 p.

– *Vernet, J.*, 1967: Un nouveau gisement de koutekite: le dôme du Barrot (Alpes-Maritimes). Bull. Soc. franç. Min. Crist. *90*, 82–89.

– *Ruhlmann, F.*, 1978: Présence d'arséniures de cuivre de haute température dans le granite des Ballons (Vosges méridionales). Bull. Min. *101*, 563–569.

Pierrot, R., Picot, P., Poulain, P. A., 1972: Inventaire minéralogique de la France; Département Hautes-Alpes 05. Orléans, BRGM, 184 p.

Roseboom, E. H., 1962: Skutterudites (Co,Ni,Fe)As_{3-x}: compositions and cell dimensions. Amer. Min. *47*, 310–327.

Senko, M. E., Dunn, H. M., Weidenborner, J., Cole, H., 1959: Lattice parameters of $ZnAs_2$. Acta Cryst. *12*, 76.

Skinner, B. J., Adler, I., Mead, C. W., 1963: Phase relations among the copper arsenides and their application to geologic thermometry. Econ. Geol. *58*, 1188.

– *Luce, F. D.*, 1971: Stabilities and compositions of α-domeykite and algodonite. Econ. Geol. *66*, 131–139.

Tarkian, M., Bock, W.-D., Neumann, M., 1983: Geology and mineralogy of the Cu-Ni-Co-U ore deposits at Talmessi and Meskani, Central Iran. Tschermaks Min. Petr. Mitt. *32*, 111–133.

Ugai, Ya. A., Pshestanchik, V. R., Gukov, O. Ya., Anokhin, V. Z., 1972: Phase diagram of the system Cu-As and properties of Cu_5As_2. Izv. Akad. Nauk SSSR, Neorg. Mater. *8*, 1734–1737.

Van Bin-Nan, Nikolskaya, G. F., Luzhnaya, N. P., Evfimovskii, I. V., Babitsyana, A. A., 1965: Study of the copper-arsenic system in the region of the compound Cu_3As. Izv. Akad. Nauk SSSR, Neorg. Mater. *1*, 1476–1483.

Yund, R. A., 1961: Phase relations in the system Ni-As. Econ. Geol. *56*, 1273–1296.

Author's address: Dr. *Z. Johan*, CRSCM, GIS BRGM-CNRS, 1A, rue de la Férollerie, F-45045 Orléans, Cedex, France.