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NOVÁKITE, $(Cu,Ag)_4As_3$, A NEW MINERAL*

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ABSTRACT

Novákite is a new copper arsenide with the formula $(Cu, Ag)_4As_3$. It forms steel-gray granular aggregates in carbonate veins found in Černý Důl, in the Giant Mts., northern Bohemia. Density 6.7. Hardness 3–3.5. It shows medium strong anisotropism. Diagnostic etching: HNO_3 1:1 positive; NCl 1:1 positive; $FeCl_3$ 20% positive; HgCl 5% negative (film); KOH 40% negative; KCN 20% negative. The indexed x-ray powder photograph gives $a_0=9.99$, $c_0=14.03$Å, $c/a=1.405$. The cell is pseudocubic ($a_0\sqrt{2}=14.12$). $G_{calc}=6.75$. $Z=12$. It is associated with arsenic, arsenolamprite, koutekite, silver, löllingite, mineral X, chalcocite, smaltite, chalcopyrite, bornite and pitchblende.

INTRODUCTION

A new mineral was found during an investigation of the waste dumps of deserted mine-works in Černý Důl in the Giant Mountains. It is a copper arsenide, and was named in honor of Dr. Jiří Novák, Professor of Mineralogy at the Charles University in Prague.

The locality is about 3.5 km. north of the village of Černý Důl, in the valley of Stříbrný potok (Silver Creek), near Berghaus. The novákite was found associated with arsenic, arsenolamprite, koutekite (Johan, 1958), silver, löllingite, mineral X,† chalcocite, smaltite, chalcopyrite, bornite and pitchblende. All these minerals occur as inclusions in the carbonate gangue, fragments of which can be found on the dumps.

The Černý Důl locality is in a region of mica schists and gneisses (Máška, 1954; Svoboda and Kodym, 1948). The schists are garnetiferous in places, and contain abundant albite porphyroblasts. In them there lies an elongated erlan (pyroxene gneiss) body, tens of meters thick. The mica schists also contain bodies of conformable synkinematic orthogneisses. The crystalline body is highly folded, and forms an anticline near the deposit.

Carbonate veins containing the ore minerals run through the erlans, and less often through the mica schists. The veins are up to 20 cm. thick. The formation of the carbonate took place in several stages, separated by tectonic movements of the vein. The ore minerals are closely intergrown, and enclosed in the carbonate gangue. All of the ore minerals are metasomatically replaced by younger slightly manganous calcite.

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† A new copper arsenide mineral, which is still being studied.

THE NEW MINERAL

Novákite forms irregular aggregates with grains up to 3 cm. in size. It is steel-gray on a fresh surface, but soon turns iridescent and later becomes black. It weathers easily to secondary copper arsenates. Hardness 3–3.5; streak black; cleavage none. Since the novákite is intergrown with löllingite and chalcocite, the value of G = 6.7 is only approximate.

In reflected light novákite appears white with a light cream tint, which is distinct from arsenic. The anisotropy is medium, with dark blue-gray and light brown ocher color effects in marginal positions. No reflection pleochroism could be observed. The reflectivity is a little higher than that of arsenic. Small grains of novákite embedded in arsenic cannot be distinguished microscopically without etching. No internal reflections could be observed, even in oil immersions. On account of its low hardness, the mineral can be easily polished.

Diagnostic etching:

Etching agents according to M. N. Short (1940) were used. Time of etching was 1 min.

HNO_3	1:1	pos.	—The mineral changes color to dark-grey with a brown tint, later varied iridescent colors appear.
HCl	1:1	pos.	—The color changes to light gray-green with a brown and bluish tint. This distinguishes novákite from arsenic.
$FeCl_3$	20%	pos.	—The reaction is the same as with HCl 1:1.
$HgCl_2$	5%	neg. (pos.)	—The etching is not distinct. The mineral is covered with a yellow-brown film, which can be washed away easily. After the film removal the polished section is intact.
KOH	40%	neg.	
KCN	20%	neg.	

SPECTROCHEMICAL ANALYSIS

Semi-quantitative spectrochemical analyses were carried out by J. Litomiský in the Institute for Ore Research in Kutná Hora.

	I	II
>10%	As, Cu	As, Cu
10–1%	Ag	Ag, Ca, Fe
1–0.1%	Ca, Si	Co
0.1–0.01%	Al, Co, Fe, Sb	Sb, Ni, Si
0.01–0.001%	Mg, Pb	Al, Cd, Mg, Mn, Y
<0.001%	Mn, Zn, Ni	Be, Pb, Yb, Zn
?	Ti	Bi

Technical conditions: Spectrograph Zeiss Q 24, a.c. arc 4 A (gener. DG 1), exposure 30 sec. without pre-arcing, photoplate Foma super-ortho, slit-width 0.003 mm., carbon electrodes ČKD Prague, analytical gap 3 mm.

Analysis No. I was carried out on practically pure novákite. Analysis No. II was on material analyzed quantitatively by chemical methods. It represents a mixture of novákite, löllingite, chalcocite and gangue carbonate.

It is assumed that the Ag replaces Cu, and the Sb replaces As. The heterogeneous, carbonate-rich gangue contains the Ca, Si, Al, Mg and Mn. The presence of löllingite in analysis II is indicated by the increased content of Fe, Co and Ni.

CHEMICAL ANALYSIS

The sample used for the determination of density was analyzed. The mineral was separated from a polished section, in which novákite was intergrown with calcite, löllingite and chalcocite. A 0.4 gm. sample was used for the analysis. All determinations were carried out in duplicate with the exception of S and CaO. The CO_2 content was calculated.

After dissolving the finely powdered mineral in concentrated H_2SO_4 and after adding dilute HCl, arsenic was determined directly by titrating with 0.05-N $KBrO_3$. After a suitable adjustment, the same sample was used for separating silver as AgCl, which was then dissolved in ammonia; silver was determined electroanalytically from an ammoniacal complex. After reduction and removal of arsenic by means of hydroxylamine and hydrochloric acid, iron was determined manganometrically (0.05 N $KMnO_4$) following several reprecipitations and separation as hydroxide. Copper was estimated electroanalytically from an ammoniacal solution of the filtrate, which was then used after a suitable adjustment for an electroanalytical determination of cobalt. After removal of R_2O_3 and ammonium salts and after separation of cobalt the solution was used for a complexometric estimation of calcium (0.01 N versene) with fluorexone as indicator. Sulfur was determined on a portion of the original sample as barium sulfate, after fusion of the mineral with a mixture of sodium carbonate and sodium peroxide.

The results of the chemical analysis are as follows:

As	43.30%	43.23%
Cu	41.39	41.32
Fe	5.13	5.12
Ag	1.96	1.96
Co	0.79	0.79
S	2.73	2.73
CaO	2.72	2.72
CO_2 (calc.)	2.13	2.13
	100.15%	100.00%

Percentage composition after subtraction of $CaCO_3$, (Fe, Co)As_2 and Cu_2S:

		atomic quotients	
As	45.82%	0.6117	
Ag	3.27	0.0303	0.8316
Cu	50.91	0.8013	
	100.00%		

The ratio of atomic quotients corresponds to the formula $(Cu, Ag)_{1.36}As_1$, or in integers $(Cu, Ag)_4As_3$.

X-RAY POWDER DATA

The character of the material allowed only the powder method to be used. Patterns were obtained on both 57.3 and 114.59. mm. cameras, with $CuK\alpha$ radiation. Intensities were estimated visually. Before indexing was undertaken, isostructural or chemically analogous compounds were looked for, but without success. Then the analogy between the tetragonal structure of Cd_3Sb_2 with a pseudocubic cell was used. The Hull-Davy charts were used. When the coincidence of some of the diffraction lines with a cubic pattern was noticed, an axial ratio $c/a=\sqrt{2}$ was tried, and all of the lines could be indexed. The agreement between the theoretical and measured *d*-values is satisfactory. The cell dimensions are

$$a_0 = 9.99, \quad c_0 = 14.03\text{Å}; \quad c/a = 1.405; \quad Z = 12.$$
$$a_0\sqrt{2} = 14.12$$

The indexed powder pattern is given in Table I.

SYNTHESIS AND STABILITY OF Cu_4As_3

Synthesis of the compound Cu_4As_3 was attempted by fusing a mixture of copper and arsenic in an evacuated glass tube. After fusion the material was examined microscopically, chemically and by *x*-rays. A primary phase consists of crystals of Cu_2As, which are embedded in a eutectic of Cu_2As and an unidentified white phase.

Since the Cu_4As_3 phase could not be prepared by direct union of the elements, a stability investigation of novákite was carried out. A sample was heated in an evacuated tube to 500° C. The mineral did not melt, but a microscopic investigation revealed that the original mineral was no longer present. It decomposed below its melting point to Cu_2As and the unidentifed white phase mentioned above.

RELATION OF NOVÁKITE TO OTHER MINERALS

Novákite is found most frequently intergrown with native arsenic. As shown in Fig. 1, it forms metasomatic veinlets in arsenic. Löllingite of younger origin occurs in the center of the veinlets. On account of atmospheric oxidation of the polished section, a reaction zone between novákite

TABLE I. *X*-RAY POWDER PATTERN OF NOVÁKITE—$(Cu, Ag)_4As_3$
Locality: Černý Důl
Cu/Ni, $\lambda = 1.5418$ Å, camera 114.59 mm.

I	$d_{meas.}$	$d_{calc.}$	*hkl*
2	9.98 Å	9.99 Å	100
5	6.41	6.32	111
2	4.08	4.08	202
1	3.80	3.77	212
1 B	3.35	3.33	300
4	3.164	3.163	310
1	3.089	3.086	311
2–3	3.018	3.013	302
2	2.903	2.886	312
2 B	2.806	2.806	005
1	2.698	2.704	105
1	2.622	2.621	313
2	2.508	2.500	400
3	2.449	2.449	205
4	2.386	2.389	411
1	2.322	2.324	331
3 B	2.281	2.279	106
2	2.206	2.208	421
2	2.171	2.176	324
1	2.133	2.131	422
1	2.108	2.100	315
4	2.072	2.073	216
8	1.998	2.000	500
9	1.959	1.960	510
5	1.913	1.915	306
10	1.877	1.881	316
1	1.844	1.841	520
3	1.787	1.789	326
1 B	1.730	1.729	108
2	1.670	1.667	600
2	1.655	1.655	601
1	1.598	1.600	612
1	1.566	1.565	407
1	1.546	1.544	109
2	1.500	1.498	623
3–4	1.443	1.442	624
3	1.407	1.407	711, 551
6	1.351	1.353	713, 553
1	1.336	1.338	2.1.10
4	1.312	1.313	730
2	1.293	1.294	3.0.10
4	1.268	1.267	1.1.11
2	1.251	1.253	3.2.10
6	1.225	1.227	530
1	1.200	1.200	618
9	1.180	1.178	660
5	1.157	1.158	751

B—broad line.

and arsenic is visible. The arsenic may be very extensively replaced metasomatically by novákite (Fig. 2). When rarely found without arsenic, it forms irregular aggregates partly replaced by carbonate, and

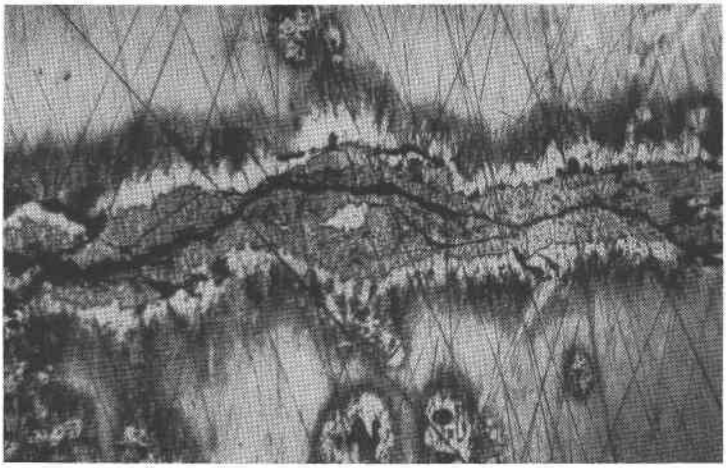

Fig. 1. A metasomatic veinlet of novákite in native arsenic. On account of atmospheric oxidation, a reaction zone occurs between novákite and arsenic. Löllingite (white) appears in the center of the novákite veinlets. Polished section, etched by 1:1 HCl. Magnification about 160×.

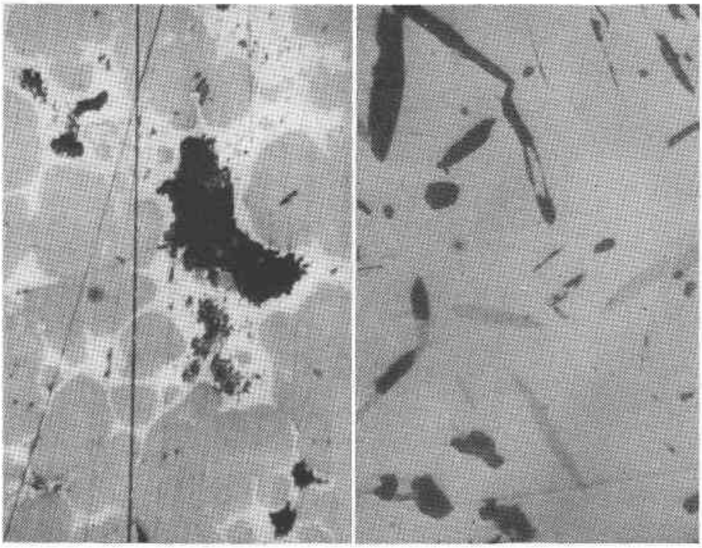

FIG. 2. (Left) Arsenic (white) is very extensively replaced by novákite (gray); uneven areas appear black. Polished section, etched by 1:1 HCl. 100×.

FIG. 3. (Right) The "oleanderblätter" texture in novákite (light gray groundmass). The original mineral forming the "oleanderblätter" was replaced by carbonate (black), which is in turn partly or completely replaced by relatively younger chalcocite (gray). Polished section without etching. 500×.

surrounded by löllingite fringes. These aggregates occasionally show a texture (Fig. 3) caused by unmixing of the solid solution, called "oleanderblätter" by Ramdohr (1955).

The genesis of novákite in the Černý Důl locality was characterized by the presence of much arsenic in the hydrothermal solutions, resulting in the formation of copper arsenides with higher arsenic content than previously known.

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