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KUTINAITE; A NEW COPPER-SILVER ARSENIDE MINERAL FROM ČERNÝ DŮL, CZECHOSLOVAKIA

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ABSTRACT

Kutinaite, a new copper-silver arsenide, occurs with novakite, koutekite, paxite, arsenolamprite and löllingite, in the carbonate-rich veins of the Černý Důl ore deposit. Microprobe analyses gave: Cu, 45.3%; Ag, 21.5%; As, 25.6%; total 102.4 wt.%. The synthetic compound, prepared from the pure elements at 400°C, gave: Cu, 44.1%; Ag, 30.8%; As, 25.1 wt.%, indicating a formula of $Cu_{2.07}Ag_{0.84}As$.

Kutinaite is cubic, with $a = 11.76 \pm 0.01$ Å, $Z = 28$, specific gravity 8.38. The strongest X-ray lines are 2.259 (10), 2.078 (10), 2.702 (9), 2.398 (8), 1.991 (7), 1.959 (7), 1.776 (7), 1.387 (7), 1.182 (7). In polished sections it is isotropic, color grey-white to grey-blue, reflectivity 47.2% (4200 Å) to 39.3% (6200 Å).

INTRODUCTION

In specimens containing the rare copper arsenides (koutekite, novákite and paxite) (Johan, 1960, 1961; Johan and Hak, 1961) from the ore deposit at Černý Důl in the Giant Mountains of Northern Bohemia, we noticed in isotropic mineral, reminding us by its color and reflectivity of koutekite. Further investigation has proved it to be a new mineral. We have named it kutinaite in honor of Dr. J. Kutina, Lecturer at the Charles University in Prague. The name has been approved by the Commission on New Minerals and Mineral Names, IMA.

Type material of kutinaite is deposited in the collections of the Mineralogical Department, Charles University, Prague, specimen number 14427, with a polished section prepared from the type material deposited in the Brush Mineral Collection, Yale University, New Haven, Connecticut, specimen number 1254.

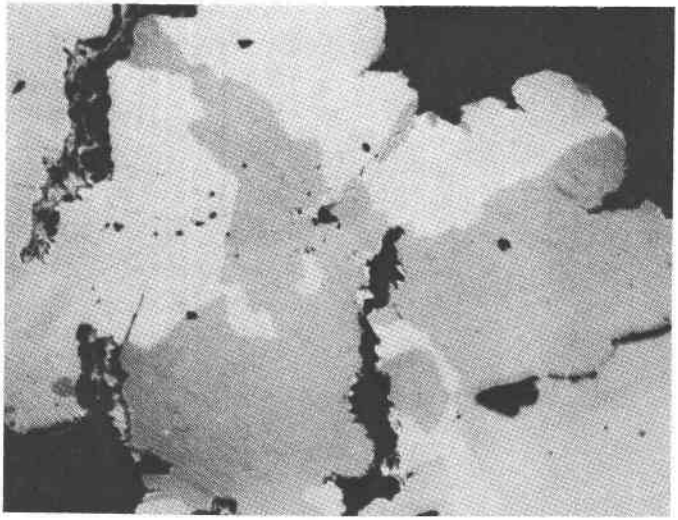

Fig. 1 Polished surface of kutinaite (grey) intergrown with novákite (white) and calcite (black). A selvedge of löllingite occurs along the boundaries between calcite and both kutinaite and novákite. 150x.

Kutinaite is a rare mineral in the Černý Důl ores. So far it has only been observed in a few polished sections, where it occurs intergrown with novákite (Fig. 1). The specimens containing kutinaite were found in carbonate-rich veins, up to 20 cm wide, exposed during recent mining operations. The ore mineral characteristically occur in complex intergrowths, making mineral separations and sometimes identification difficult. To the present time, silver, arsenic, arsenolamprite, koutekite, novákite, paxite löllingite, skutterudite, chalcocite, tiemannite, clausthalite, niccolite, chalcopyrite, bornite, and pitchblende have been identified.

Physical Properties

Kutinaite has a silvery-grey color, a distinctly metallic luster, and is malleable. It is opaque and in reflected light a polished surface appears greyish-white to light blue-grey in color. In oil immersion kutinaite is bluish-grey and similar to, but slightly less blue, than koutekite.

Kutinaite is isotropic in reflected light and lacks internal reflection, but it has a fairly high reflectivity (Table 1). The Vickers microhardness under a load of 7.6 grams is 387 kg/mm^2, and under a load of 15.2 grams is 398 kg/mm^2. Etching characteristics are given in Table 2.

The extremely fine intergrowths of kutinaite and novákite precluded any opportunity to measure the specific gravity of the natural material.

TABLE 1. REFLECTIVITY OF KUTINAITE, OBTAINED AS AN AVERAGE OF FOUR SEPARATE MEASUREMENTS AT EACH WAVELENGTH[a]

λ(Å)	R(%)	λ(Å)	R(%)
4200	47.2	5400	42.8
4400	46.9	5600	42.2
4600	46.5	5800	41.4
4800	45.8	6000	41.7
5000	44.2	6200	39.3
5200	43.3		

[a] Measurements by P. Picot and R. Caye.

On a synthetic kutinaite, with the composition $Cu_{2.07}Ag_{0.84}As$, however, a specific gravity of 8.38 ± 0.07 was determined by means of a Berman microbalance and toluene as an immersion fluid.

COMPOSITION

The fine-grained state of the natural material made the use of the electron microprobe essential. Following qualitative analyses, which established that Cu, Ag, and As were the only major elements present, quantitative determinations of Cu and As were made on the first order $K\alpha_1$ lines and of Ag on the first order $L\alpha_1$ line. Pure Cu, Ag, and As were used as analytical standards, with corrections for absorption and atomic number effect following Theisen and fluorescence of the K-series after Castaing. Microprobe analyses were performed on two different instru-

TABLE 2. ETCH REACTIONS OF KUTINAITE WITH A ONE-MINUTE ETCHING TIME

Etchant	Strength (volume %)	Reaction
HNO_3	50	Positive. Reaction is immediate and intense, with the evolution of gas. The surface becomes blue, then brown, and finally black.
HCl	50	Negative.
$FeCl_3$	20	Positive. The surface darkens, turns grey, and develops an iridescent sheen.
$HgCl_2$	5	Negative.
KOH	40	Negative.
KCN	20	Negative.

TABLE 3. ELECTRON-MICROPROBE ANALYSES OF KUTINAITE FROM ČERNÝ DUL, CZECHOSLOVAKIA[a]

Element	Geoscan II[b]	Cameca[c]
Cu	45.3 wt %	44.6 wt %
Ag	31.5	31.6
As	25.6	25.7
	102.4	101.9
Indicated formula	$Cu_{2.08}Ag_{0.85}As$	$Cu_{2.05}Ag_{.85}As$

[a] Two different instruments were used to analyze the material, but identical corrections were made in each case.
[b] Measurements by Z. Johan
[c] Measurements by R. Giraud and R. Pierrot

ments—A geoscan II and a Cameca—and yielded results that agree very closely (Table 3).

In order to verify the composition, kutinaite was synthesized from spectrographically pure elements by suitable reactions in sealed, evacuated, silica-glass tubes. A coarsely crystalline, monomineralic and homogenous phase was prepared on the composition Cu, 44.1, Ag, 30.8, and As, 25.1 weight percent ($Cu_{2.07}Ag_{0.24}As$) by first melting the components for 15 minutes at 750°C, then heating the quenched charge at 400°C for 2 days. When charges with the compositions $Cu_{2.08}Ag_{0.85}As$, corresponding to the compositions computed from the microprobe analyses (Table 3), were similarly treated, mixtures of phases resulted. Compositions slightly more silver-rich yielded mixtures of β-domeykite and arsenic and kutinaite. The results indicate that, at any temperature, the composition of kutinaite can vary within exceedingly narrow limits only. The slight differences between the microprobe analyses and the composition found for the synthetic phase lie within the limits of error of the analyses, and we believe that $Cu_{2.07}Ag_{0.84}$ As must be accepted as an exact formula.

The valency charges for the compound $Cu_{2.07}Ag_{0.84}As$ can only be balanced if some of the As is pentavalent rather than trivalent. There is no evidence to support this possibility, however, and in view of the distinctly metallic properties described above it is more reasonable to suggest that kutinaite is an alloy.

X-RAY DIFFRACTION DATA

Powder data, for both natural and synthetic kutinaite, are presented in Table 4. The pattern is distinctly different from those of other arsenides and can be completely indexed on the basis of a cubic cell with $a = 11.76 \pm 0.01$ Å. Using the measured specific gravity of 8.38, and com-

TABLE 4. X-RAY POWDER DATA FOR NATURAL AND SYNTHETIC KUTINAITE. ($\lambda CuK_\alpha = 1.518$ Å). CAMERA DIAMETER 114.59 mm. INTENSITIES (I) ESTIMATED VISUALLY. VB = VERY BROAD. $a = 11.76 \pm 0.01$ Å

hkl	Kutinaite			Synthetic	
	I	*d* (meas.)	*d* (calc.)	*I*	*d* (meas.)
111	3	6.76 Å	6.79 Å	4	6.90 Å
200	1	5.85	5.88	1	5.85
210	1	5.26	5.26	1	5.28
300, 221	1	3.908	3.918	—	—
321	2	3.137	3.143	2	3.153
400	3	2.940	2.940	4	2.940
331	9	2.702	2.698	9	2.695
421	1	2.564	2.567	1	2.567
422	8	2.398	2.401	8	2.405
511, 333	10	2.259	2.263	10	2.268
440	10	2.078	2.079	10	2.080
531	7	1.991	1.988	6	1.993
600, 442	7	1.959	1.960	7	1.961
622	7	1.776	1.773	7	1.778
711, 551	2, vb	1.640	1.647	2, vb	1.638
731, 553	1	1.531	1.531	2	1.534
800	4	1.469	1.470	4	1.472
733	3	1.438	1.437	3	1.441
822, 660	7	1.387	1.386	6	1.389
662	5, vb	1.351	1.349	4, vb	1.357
911, 753	5, vb	1.287	1.291	4, vb	1.288
844	2	1.202	1.200	2	1.203
933, 711, 755	7	1.182	1.182	6	1.184

position $Cu_{2.07}Ag_{0.84}As$, we compute the number *Z* of formula units in the cell to be 28. The density calculated for this content is 8.45 g/cm^3. Lacking suitable crystals for further X-ray studies, we have been unable to determine the structure or space group.

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