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A NEW COPPER-IRON SULFIDE

L. J. CABRI

MINERAL SCIENCES DIVISION

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L. J. CABRI

ABSTRACT

A copper-iron sulfide mineral from Noril'sk, Western Siberia, discovered and described as cubic chalcopyrite by Bud'ko and Kulagov (4), is shown to be a discrete mineral entity and not to be confused with cubic chalcopyrite. The term cubic chalcopyrite does, in fact, refer to a valid phase, which is the face-centered cubic high-temperature polymorph of chalcopyrite.

The new sulfide mineral tarnishes very rapidly in air, changing from the chalcopyrite color to hues of pink and brown, and eventually becoming iridescent. Electron-probe microanalyses of several grains using synthetic standards gave Cu = 36.1, Fe = 31.6, S = 31.9, Ni = 0.7 total = 100.3%. The strongest of the X-ray powder diffraction lines (in Å) are 3.04(10), 2.656(5), 1.879(9), 1.598(7), 1.210(5), 1.079(6), and 1.0193(5). The (110) reflection at 7.52 Å(3) clearly differentiates it from cubic chalcopyrite. Single-crystal X-ray diffraction indicates that it has a large cubic cell with $a = 10.64_8$ Å, possible space group $I\bar{4}3m$, and a probable composition of $Cu_{18}(Fe,Ni)_{18}S_{32}$. This composition gives a calculated specific gravity of 4.36 (measured value 4.24). High-temperature X-ray diffraction, D.T.A., and quench experiments indicate that on heating to about 80° C the mineral breaks down to "tetragonal" cubanite and minor bornite. On slow cooling the original mineral is reformed.

Since this new mineral closely resembles the qualitative descriptions for chalcopyrrhotite in the literature, attempts to find it in specimens from the type chalcopyrrhotite locality were made, but none was found.

INTRODUCTION

SOME years ago, Hiller and Probsthain (1956) synthesized a Cu-Fe sulfide which they called β -phase. They gave it the formula $Cu_{17+x}Fe_{17+x}S_{32}$ ($x = \sim 0.6$), and obtained space group $I\bar{4}3m$ and cell parameter $a_0 = 10.60$ Å by single crystal X-ray diffraction. They described it as brownish yellow on a fresh break, but with rapid tarnish forming so that it soon resembles pyrrhotite, and then bornite. It was produced on cooling after heating in nitrogen either natural tetragonal chalcopyrite (allowing sulfur to escape) or a synthetic mixture between 550° and 720° C. Hiller and Probsthain suggested that the β -phase has some similarity to the $Cu_3Fe_4S_6$ phase of Merwin and Lombard (12), or the chalcopyrite b of Schlegel and Schüller (14), and assumed it to be identical to the disordered "high-temperature modification" of chalcopyrite found by Buerger and Buerger (6).

In their recent work, Yund and Kullerud (18) did not discuss Hiller and

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Probsthain's reports in the light of their own investigations, which left open the question of the stability of the β -phase.

Genkin et al. (10) have shown that in certain ores, such as those found at Noril'sk, there exist both cubic cubanite and cubic chalcopyrite.* They indexed the cubic "chalcopyrite" on the basis of a large cell of about 10.6 Å, although their X-ray data are also consistent with a small (5.3 Å) cell. They also related this cubic "chalcopyrite" to the β -phase of Hiller and Probsthain and suggested that it is intermediate between the completely ordered tetragonal chalcopyrite and the synthetic cubic chalcopyrite with a small cell ($a = 5.29$ Å) obtained by Donnay and Kullerud (8) and Frueh (9).

It will be shown that the so-called cubic "chalcopyrite" from Noril'sk, not to be confused with the f.c.c. high-temperature polymorph of chalcopyrite, has, in fact, a large cubic cell with $a = 10.64_8$ Å, possible space group $I\bar{4}3m$, a structure related to that of tetrahedrite (16), or binnite (17), and a composition close to $Cu_{18}(Fe,Ni)_{18}S_{32}$. Data will also be given showing that its thermal properties are unique and that it cannot be considered a cubic form of chalcopyrite but rather a separate mineral entity.

A new name had been proposed for this mineral to the Commission on New Minerals and Mineral Names, I.M.A., after Professor J. E. Hiller who appears to have been the first to synthesize the compound and to provide a recognizable characterization of it (11). The data establishing the compound as a new mineral were accepted by a majority vote, but the name was voted unacceptable by a vote of 8 to 9 with a suggestion that Bud'ko and Kulagov (4) be asked to name it. There were no objections to the name itself. Since there is no precedent or rule that permits the discoverer of a new mineral to retain the privilege of proposing a new name regardless of later, more definitive, work, and in view of Bud'ko and Kulagov's failure to give it a name other than the ambiguous one of "cubic chalcopyrite," I felt quite justified in proposing a new name. However, in view of the IMA Commission's suggestion, I have asked the USSR Representative to the Commission to try to get Bud'ko and Kulagov to propose a name for this mineral.¹ This manuscript has been re-written without reference to my proposed name, which is a regrettable situation, but which, in my opinion, is preferable to withholding all the new data.

A polished section containing this new sulfide has been deposited with the Systematic Reference Series, National Mineral Collection, Geological Survey of Canada, and one with the Royal Ontario Museum, Toronto.

POLISHED SECTION EXAMINATION

A vuggy sample reported to contain cubic "chalcopyrite" from Noril'sk was kindly supplied by the Leningrad Mining Institute Museum. Three sections were cut from the original sample, which measured about 4 cm to a

* This was first discovered by Bud'ko and Kulagov (4).

¹ After the galley proofs were issued, I was informed (October 11, 1967) that Bud'ko and Kulagov have now proposed the name Talnakhite to the Min. Soc. U.S.S.R.

side. After mounting in a cold-setting plastic and polishing, microscopic examination of the massive sulfide ore revealed a groundmass consisting of an isotropic chalcopyrite-like colored mineral which tarnished within minutes to various hues of pink and brown. Prolonged tarnishing in air over some months produced various clearly defined iridescent colors for separate grains, which now appeared slightly anisotropic. The principal iridescent shades were dark orange, dull brownish-orange, and dull pinkish-brown, and are shown as two shades of gray in photomicrographs (Fig. 1a). X-ray diffrac-

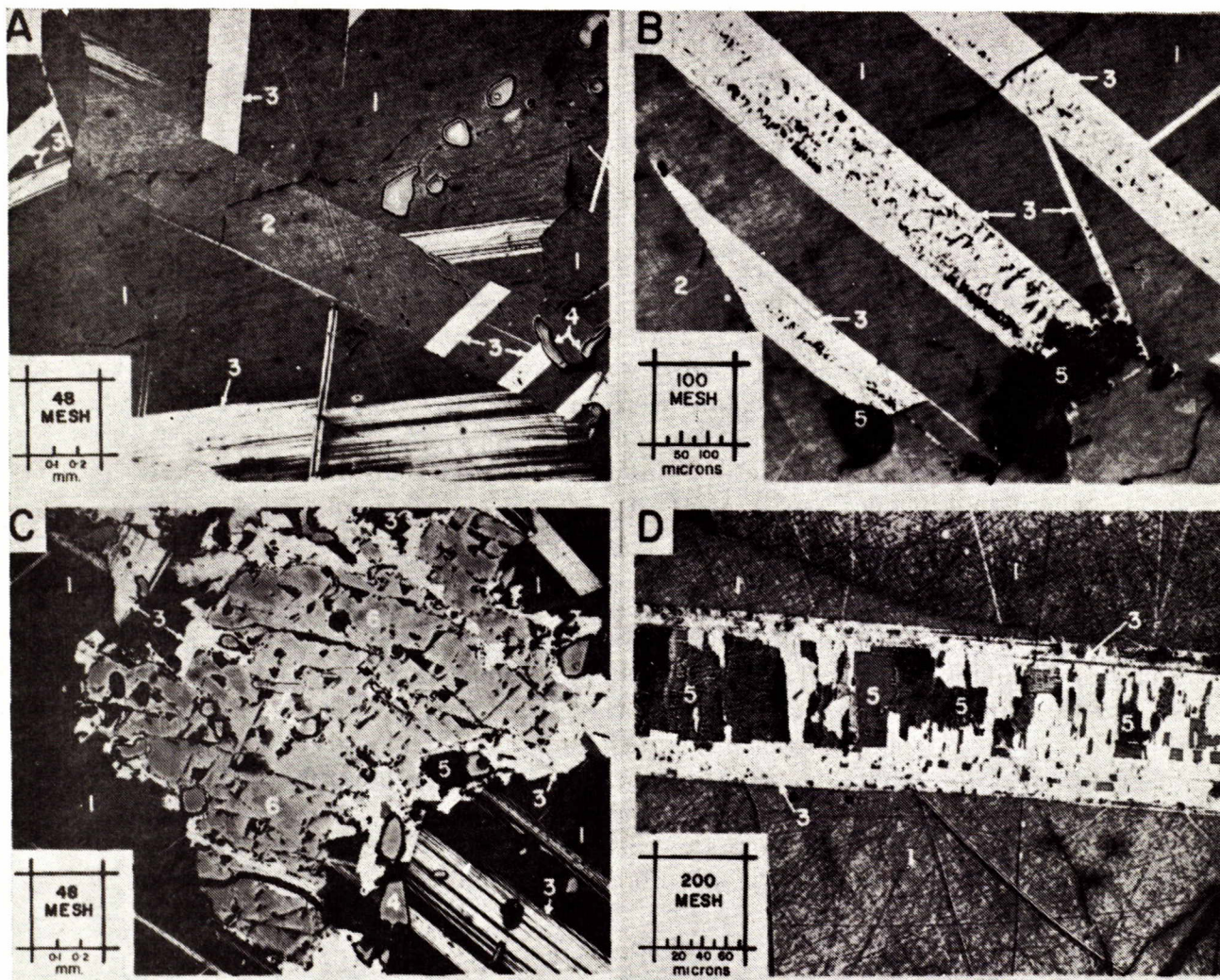


FIG. 1 a. Photomicrograph showing pinkish-brown lath of the new sulfide mineral (2) within large grains of orange new sulfide mineral (1). Typical cubanite lamellae (3) and magnetite inclusions (4) are also shown. All photomicrographs were taken in air with plane polarized light. b. Photomicrograph of cubanite (3) laths exhibiting cracked surface partly replaced by valleriite (5) in a matrix of new sulfide mineral (1, 2). c. Photomicrograph of a pentlandite (6) "eye" surrounded and partly replaced by rim cubanite (3) which contrasts with the more cracked lamellar cubanite. The matrix is again new sulfide mineral (1) and also present are grains of magnetite (4) and valleriite (5). d. Photomicrograph showing the oriented valleriite or mackinawite (5) inclusions in a cubanite (3) lath set in a matrix of new sulfide mineral (1). The surface of the valleriite varies from smooth to rough.

tion proved that these were all the same mineral, which will now be called the new sulfide mineral; the slight anisotropism is assumed to be due to surface phenomena. A few long, thin laths of anisotropic and less tarnished material are interpreted as being tetragonal chalcopyrite.

In the groundmass are irregularly distributed pentlandite "eyes" (containing thin exsolved lamellae of the new sulfide mineral or of tetragonal chalcopyrite), which are generally surrounded by cubanite rims. This cubanite has the same color as the cubanite lamellae in the groundmass but is otherwise quite different. The cubanite laths show peculiar cracks, in contrast to the smooth surface of the rim cubanite (Fig. 1b, c) and some of them contain many oriented vallerite or mackinawite inclusions (Fig. 1 d). The associated minerals consist of magnetite, vallerite, silver-gold alloy, Pd_3Pb , and $\text{Pd}(\text{Bi}, \text{Pb})$ (Cabri and Traill, 1966).

MINERAL SEPARATION AND CHEMICAL ANALYSES

Chips and fragments left over from the polished section preparation were gently crushed in a steel mortar and then sized into $-65 + 100$, $-100 + 200$, $-200 + 270$, and -270 fractions. These sized fractions were run through a Frantz magnetic separator. Polished section examination showed that the new sulfide mineral and the cubanite were preferentially concentrated in the fractions having specific magnetic susceptibilities of $\sim 6.6 \times 10^{-6}$ and $\sim 150 \times 10^{-6}$ e.m.u., respectively. The new sulfide mineral concentration shows up nicely where the chemical analyses for Cu, Ni and Zn are plotted for the various magnetic fractions (Fig. 2). The analyses were obtained using a standard atomic absorption technique and fit quite closely the values obtained by electron probe microanalyses, which is discussed below. The zinc content, though minor, rises to a peak at the more magnetic end. Careful polished-section examination of the fraction containing the most zinc revealed several sphalerite grains under 5 microns. This suggests that the zinc content is due to very small sphalerite grains, which diminish in quantity in the less magnetic fractions, and that the zinc does not occur in the cubic "chalcopyrite" lattice as suggested by Bud'ko and Kulagov (4).

Point counting of grains from two sizes having a specific magnetic susceptibility of about 6.6×10^{-6} gave the following distribution in area percent:

TABLE 1

Mesh size	Number of grains counted	New sulfide mineral	Cubanite	Pentlandite
$- 65 + 100$	638	95.5%	1.5%	3.0%
$- 100 + 200$	760	87.0%	5.5%	7.5%

The new sulfide mineral count also includes some normal tetragonal chalcopyrite, estimated to be between five and ten percent, but no quantitative results are given because of the difficulty of distinguishing the two minerals in the grain mounts.

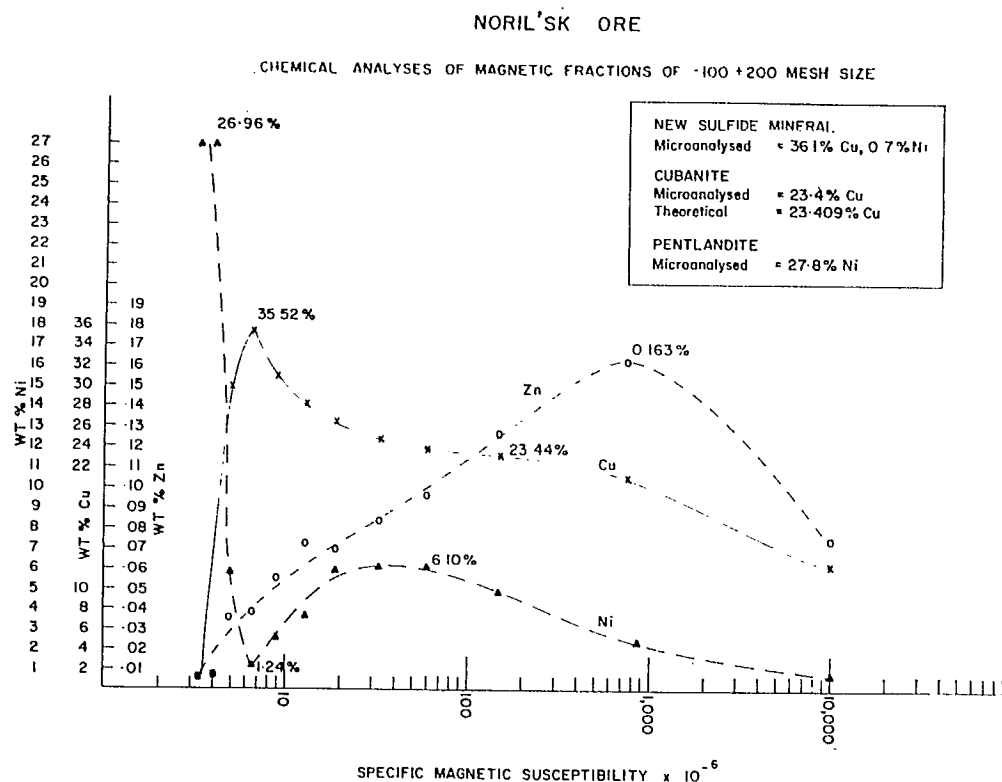


FIG. 2. Chemical analyses of magnetic fractions of -100 +200 mesh size Noril'sk ore.

ELECTRON PROBE MICROANALYSIS

Dr. R. J. Traill of the Geological Survey of Canada very kindly performed the microanalysis using a modified Elion electron-probe micro-analyzer. Intensities of characteristic X-ray lines for Cu, Fe and S were measured, relative to the intensities of synthetic Cu-Fe sulfides of carefully controlled composition; pure metals were used for the Ni and Co determinations. Corrections for matrix effects were applied following the method suggested by Birks (3) using mass absorption coefficients based on values given by

TABLE 2
ELECTRON-PROBE MICROANALYSES

New sulfide mineral		Cubanite	Pentlandite
Cu	36.1% \pm 0.5	23.4%	*0.2% \pm 0.1
Fe	31.6% \pm 0.5	41.2%	37.3% \pm 0.5
S	31.9% \pm 0.5	34.9%	33.2% \pm 0.5
Ni	0.7% \pm 0.1	Not detected < 0.1%	27.8% \pm 1.0
Co	—	0.1	0.7% \pm 0.1
100.3		99.6	99.2

* Cu variable: 0.2% on three grains, 0.4% and 0.9% on two others.

Smith (15, p. 840) for Ni and Co, for Cu and S in cubanite, and for Cu, Fe and S in pentlandite. The analyses were performed on the $-65 +100$ mesh fraction and at least five grains were analyzed in each case for both the unknowns and the standards, all of which were shown to be homogeneous within the limits of measurement.

SPECIFIC GRAVITY

Careful pycnometric determinations, using toluene as the immersion liquid, were made on the $-65 +100$ and $-100 +200$ mesh fractions of the new sulfide mineral concentrates described in Table 1. The densities obtained for about 600 mg of the former were 4.301, and 4.297, and for about 250 mg of the latter, were 4.30 and 4.28. The mean specific gravity was taken to be 4.29. The specific gravity of this mineral was then calculated by using the point counting results for the poorest concentrate, taking area percent for weight percent, and using the theoretical S.G. for cubanite (4.03) and for pentlandite (5.05). The specific gravity thus calculated, without making allowance for the small amount of normal tetragonal chalcopyrite present (which has a theoretical S.G. of 4.199, using the cell given by Berry and Thompson (1) and assuming stoichiometry), comes to 4.24.

X-RAY DIFFRACTION

Several X-ray diffraction techniques were employed in studying the new sulfide mineral. The powder work was done with 114.6 mm Debye-Scherrer type cameras ($\text{CoK}\alpha$ filtered radiation) using 30–70 hr exposures, and with a Guinier-de Wolff quadruple-focusing camera ($\text{CoK}\alpha_1$ rad.) and 16 hr exposures. The high-temperature powder work was done on evacuated quartz capillaries using a Unicam camera with $\text{CoK}\alpha$ filtered radiation for exposures varying between 100 and 230 hours. These long exposures were necessary in order to bring out weak reflections which are vital to the interpretation of the powder photographs. The X-ray data for the new sulfide mineral is shown in Table 3; that of chalcopyrite, as reported by Berry and Thompson (1) is also given for comparison.

The strongest reflections in both patterns are quite similar. Nevertheless, the new sulfide mineral pattern is characterized by many additional reflections, particularly those at low angles.

Dr. E. J. Gabe of the Mineral Sciences Division, very kindly performed the single-crystal work reported below and suggested the structural inferences. A small irregularly-shaped fragment was selected from the $-65 +100$ mesh fraction ($\sim 6.6 \times 10^{-6}$ specific magnetic susceptibility) for single-crystal work on a precession camera. Unfiltered Cu and Mo radiation was used. These photographs showed that the new sulfide mineral is cubic with systematic absences for $h + k + l \neq 2n$. The Laue group is $m\bar{3}m$ and therefore the space group is either $\text{Im}\bar{3}m$, $\text{I}\bar{4}3$ or $\text{I}\bar{4}3m$. The cell length is 10.64_8 Å. Reflections with all indices even were stronger than the remainder; indeed, the indexing of the strongest reflections agrees precisely with that for tetrahedrite and

TABLE 3

X-Ray Powder Diffraction Data

New Sulfide Mineral (this paper) 114.6 mm camera, CoK α , Fe filter			Chalcopyrite Berry and Thompson (1962)		
I*	d(meas.) Å	hkl	I	d(meas.) Å	hkl
3	7.52	110			
$\frac{1}{4}$	5.33	200			
$\frac{1}{2}$	4.32	211			
4	3.75	220			
2	3.36	310			
10	3.043	222	10	3.03	112
1	2.831	321			
5	2.656	400	$\frac{1}{2}$	2.63	020, 004
2	2.507	411, 330			
$\frac{1}{4}$	2.371	420			
1	2.254	332			
1	2.168	422			
2	2.071	510, 431			
9	1.879	440	4	1.865	220
$\frac{1}{2}$	1.859		8	1.854	024
$\frac{1}{2}$	1.680	620			
7	1.598	622	6	1.591	132
$\frac{1}{4}$	1.580		2	1.573	116, 033
2	1.532	444	$\frac{1}{2}$	1.518	224
$\frac{1}{2}$	1.501	550, 710			
$\frac{1}{4}$	1.443	552			
$\frac{1}{4}$	1.415	642			
$\frac{1}{4}$	1.390	730			
4	1.327	800	1	1.323	040
			$\frac{1}{2}$	1.303	008
5	1.210	662	1	1.214	332
$\frac{1}{2}$	1.202	752	3	1.205	136, 143
2	1.180	840			
6	1.079 a_1	844	6	1.077	244
3	1.079 a_2		3	1.069	228
5	1.0193 a_1	10.2.2, 666	2	1.018	152
2	1.0190 a_2		1	1.014	336
5	0.9360 a_1	880	$\frac{1}{2}$	1.005	1, 1, 10
2	0.9358 a_2				
average $a = 10.61 \text{ Å}$					

*Relative intensities visually estimated on a scale of ten.

binnite (16, 17). In view of the similarity of cell lengths, Laue group and intensity patterns it seems probable that the structure of the present material is similar to that of tetrahedrite or binnite. This is in contrast to the proposal of Hiller and Probsthain (11) who postulated a disordered structure

for the β -phase. The structure they proposed does, however, bear a resemblance to the binnite structure and even though there are more atoms, the majority of them are on the same equivalent positions.

Two other fragments from the same concentrate were mounted and examined by single-crystal methods and proved to be identical to the first. Since both the electron-probe microanalysis and single-crystal X-ray diffraction analyses were made from the same concentrate, and both gave consistent results, the probability that the microanalysis corresponds to the grains X-rayed appears excellent. A complete structural study will be undertaken in the near future.

COMPOSITION

The electron microprobe analyses, recast to 100%, were used to obtain a formula of $\text{Cu}_{18.2}\text{Fe}_{18.08}\text{Ni}_{0.32}\text{S}_{32.0}$ giving a calculated specific gravity of 4.41. Assuming an ordered structure, space group symmetry requirements indicate that the nearest fit, using the composition and measured specific gravity, would be a cell containing 36 metal atoms of two species (taking Ni substituting for Fe) and 32 sulfur atoms, which is similar to the formula proposed by Hiller and Probsthain for their β -phase. Taking such a formula and rounding off, namely $\text{Cu}_{18.0}\text{Fe}_{17.7}\text{Ni}_{0.3}\text{S}_{32}$, gives a specific gravity of 4.36. Both the formula and the specific gravity fit reasonably well within the limits of error involved, so that the ideal formula for this new sulfide mineral is $\text{Cu}_{18}(\text{Fe},\text{Ni})_{18}\text{S}_{32}$.

HEATING EXPERIMENTS

Three types of experimental approach were employed in order to determine the thermal stability of this new sulfide mineral. Differential thermal analysis, quench and cooling experiments in sealed evacuated quartz capsules, and high-temperature X-ray diffraction were all used.

The high-temperature X-ray diffraction, although time-consuming and providing incomplete patterns, proved invaluable to this investigation. The high-temperature camera was calibrated by plotting the lattice parameters of sponge Pt in a capillary versus the true and thermocouple temperatures. The temperatures reported below are considered accurate to about $\pm 15^\circ\text{C}$. The results reported in Table 4 are for one sample of the -270 mesh concentrate of the new sulfide mineral heated consecutively at increasing temperatures. Two other samples were X-rayed at 232, 360, 390 and 573°C , and gave essentially similar results but with weaker patterns.

The X-ray data shown in Table 4 indicate that the room temperature body-centered cubic cell of the new sulfide mineral has changed to a pattern which can best be indexed as a tetragonal cell at 190°C . At 360°C two distinct patterns are present, the same tetragonal cell plus a face-centered cubic cell with $a_0 = 5.32\text{ \AA}$, and at 573°C only a f.c.c. cell with $a_0 = 5.36\text{ \AA}$ remains.

D.T.A. was performed on samples in evacuated quartz tubes containing pure ground quartz as internal standard. The difference couple was chromel-alumel and was placed within the sample tube (but sheathed from the sample).

TABLE 4

Fe
High-temperature X-ray Diffraction Data, CoK α Filter

20°C, 96 hours			190°C, 139 hours			360°C, 230 hours			573°C, 105 hours		
I	d	hkl	I	d	hkl	I	d	hkl**	I	d	hkl
1	3.34	310				10	3.075	111 _c	10	3.106	111
10	3.036	222				5-7	3.041	112 _t			
			10	3.043	112	4	2.661	200 _c	4	2.680	200
3	2.676	400	3	2.651	020						
			1	2.615	004						
0-1	2.477	(411)									
		(330)									
0- $\frac{1}{2}$	2.254	332									
8	1.862	440	5	1.869	220	8	1.880	220 _c	9	1.890	220
1	1.841	024*	6-7	1.854	024	5	1.856	024 _t			
						5	1.603	311 _c	7	1.613	311
6	1.589	622	5	1.594	132	3	1.592	132 _t			
			4	1.580	(033)						
					(116)						
1	1.523	444				1	1.331	040 _t	1	1.340	400
3	1.321	800	3	1.336	040	3	1.222	331 _c	2-3a ₁	1.230	331
									$\frac{1}{2}a_2$	1.230	
3	1.214	662	2	1.214	332	1	1.214	332 _t			
1	1.208	752	3	1.204	(136)	2	1.207	136 _t			
					(143)	3a ₁	1.0882	422 _c	4a ₁	1.0962	422
4a ₁	1.0787	844	5a ₁	1.0785	244	1a ₂	1.0880		2a ₂	1.0955	
2a ₂	1.0799		1a ₂	1.0785		2a ₁	1.0801	244 _t			
			1a ₁	1.0712	288	1a ₂	1.0801				
			1a ₂	1.0711							
			2	1.0196	152						
3a ₁	1.0175	(10,2,2)	1	1.0178	336				1a ₁	1.0335	(511)
		(666)							$\frac{1}{2}-1a_2$	1.0333	(333)
1a ₂	1.0171										
2	0.9353	880	1	1.0070	1,1,10	1	0.9432	440 _t			
$a_0 = 10.59 \text{ \AA}$ b.c.c. + minor tetragonal chalcopyrite			$a_0 = 5.29 \text{ \AA}$ $c_0 = 10.42$ tetragonal pattern			$a_0 = 5.32 \text{ \AA}$ f.c.c. + $a_0 = 5.30 \text{ \AA}$ $c_0 = 10.43 \text{ \AA}$ tetra- gonal			$a_0 = 5.36 \text{ \AA}$ f.c.c.		

*Reflection due to tetragonal chalcopyrite.

**Subscript c signifies major contribution from a cubic cell and t signifies the same from a tetragonal cell.

as well as within a similar tube filled with alumina. The temperature couple consisted of Pt-PtRh 13%. The signal from the difference couple was amplified by going through a D.C. microvolt amplifier and then to the chart recorder. Heating rates were varied, but were generally either 6° or 12° C per minute.

Certain features of the D.T.A. results made interpretation difficult, and

this is thought to be due to different sample conditions. Some of these difficulties were of the nature of exothermic or endothermic migrations on heating. There were, however, certain thermal phenomena which were consistent and reproducible. All five separate samples examined gave some sort of reproducible endothermic peak on heating, mostly around 80°C , but as high as 165°C in one case. This peak generally shrank on continued heating, but represents the breakdown of the new sulfide mineral to a tetragonal cell as shown above. On further heating, an excellent and reproducible peak was always produced around 250°C and a weaker, but also reproducible peak, around 490°C . The former represents the formation of a f.c.c. and the latter the entire breakdown of the tetragonal cell to one f.c.c. cell. A peak at 390°C appeared only on second, and subsequent runs. On heating to a higher temperature another endothermic phenomenon appeared around 615°C , which is attributed to the break-down of pentlandite. The exothermic phenomena on cooling were more diffuse since cooling rates could not be controlled. Typical D.T.A. curves are shown in Figure 3 for the same sample

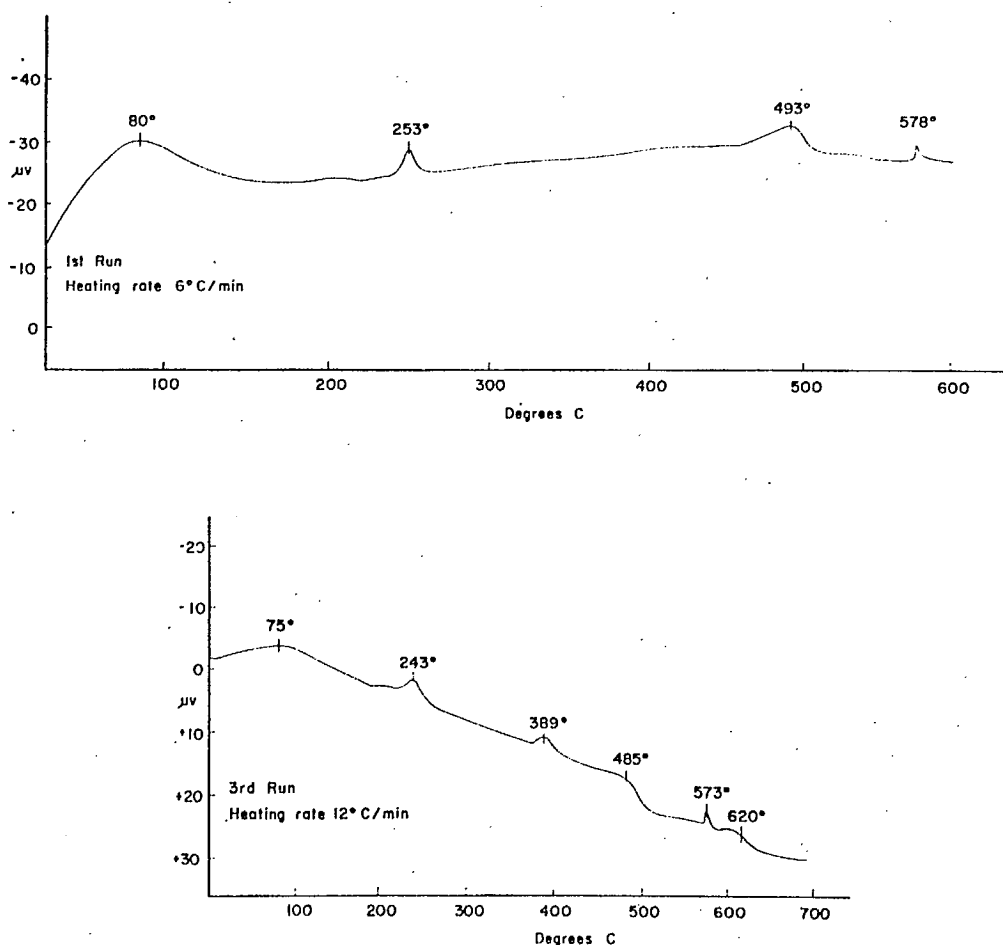


FIG. 3. Differential thermal analysis curves of a $-200 +270$ mesh concentrate of the new sulfide mineral on first heating and on a third heating.

for the first and the third heating experiments. The temperatures of endothermic phenomena on heating the same sample are shown in Table 5.

Concentrates of the new sulfide mineral of various mesh sizes were placed in evacuated sealed quartz tubes and heated in horizontal electric furnaces (controlled using chromel-alumel or platinel thermocouples as sensors) for periods varying from eight months at 70° C to 24 hours at 700° C. The temperatures are considered accurate to $\pm 5^\circ$ C and the thermocouples were checked at temperature against a calibrated Pt-PtRh 10% thermocouple. Most furnaces were controlled to better than $\pm 5^\circ$ C but this was dependent on the actual temperature. Most of these experiments were rapidly quenched in ice water and then X-rayed immediately. The X-ray patterns produced could be interpreted, but with difficulty. This difficulty is attributed to the similarity of the patterns as well as to kinetic factors and

TABLE 5

D. T. A. Endothermic Results for a -200 + 270 mesh Concentrate of the New Sulfide Mineral

*1st run heated at 6°/min to 600° C	*2nd run heated at 6°/min to 600° C	3rd run heated at 12°/min to 700° C	4th run heated at 12°/min to 750° C
79° C	89° C	75° C	145° C
251° C	246° C	243° C	245° C
	379° C	389° C	389° C
489° C	475° C	485° C	475° C
573° C qtz	573° C qtz	573° C qtz	573° C qtz.
		620° C	610° C

*Minor corrections applied using the 573° C quartz peak as internal standard.

TABLE 6

	Pattern 1	Pattern 2	Pattern 3	Pattern 4	Pattern 5
Temp. °C	20, 70	150, 210 232	240, 280 362, 430	490, 582	700
Phases present	(b. c. c.) + cp + pn + cb	(b. c. c.) + cp + pn and very minor bn	? + cp + pn and very minor bn	? + cp	f. c. c. cell + minor cp

Abbreviations: (b. c. c.) = new sulfide mineral, cp = chalcopyrite, pn = pentlandite, cb = cubanite, bn = bornite.

metastable phases. Table 6 shows the patterns grouped according to the temperatures from which they were quenched.

The very weak, and often blurred, reflections attributed to bornite in patterns 2 and 3 occurred at about 3.25, 3.12, 2.73 and 1.92 Å and correspond to the strongest reflections of bornite. The question mark in pattern 3 could be indexed as f.c.c. with $a_0 \sim 5.34$ Å, except for a diffuse band at 7.4 Å. Since the other reflections characteristic of the large cubic cell (b.c.c.), namely at 4.3, 3.34, 2.82, 2.25 and 2.07 Å, are missing, it is considered probable that the f.c.c. cell exists, but that it partly orders to the body-centered cubic cell of the new sulfide mineral on quenching. The question mark in pattern 4 could also be indexed as f.c.c. with $a_0 \sim 5.3$ Å and a diffuse band at 7.4 Å. However, in contrast to pattern 3, only three reflections characteristic of the larger cubic cell are missing—4.3, 2.25, and 2.07 Å. Pattern 5 is undoubtedly f.c.c. with $a_0 \sim 5.3$ Å, and shows reflections with the following hkl values: 110, 111, 200, 211, 220, 310, 311, 222, 400, 331, 422, and 511. Weak reflections corresponding to the 024 and 116 reflections of tetragonal chalcopyrite are also present.

Cooling from 700° C and 582° C to room temperature in about 24 and 19 hours, respectively, produced the new sulfide mineral, tetragonal chalcopyrite and pentlandite.

DISCUSSION

There is no doubt from the data presented above that we are dealing with a discrete mineral whose thermal behavior bears a close relation to other phases in the Cu-Fe-S system. It is suggested that the relationship of this new mineral to other phases in the system, assuming that Ni is replaced by Fe, is as shown in Figures 4 and 5.* In these figures it is assumed that the complicated phase relations in the quaternary system can be represented by projecting onto the ternary Cu-Fe-S plane. The X-ray diffraction and D.T.A. results can then be interpreted as follows: Somewhere above the range 70–90° C the new sulfide mineral breaks down to form two tetragonal phases of different compositions. Of these, the predominant phase is similar to the tetragonal form of cubanite reported by Yund and Kullerud (1966). The other, very minor phase, represents bornite. Very likely the small amount of orthorhombic cubanite present in the concentrate inverts to the tetragonal form above about 213° C but this does not register a well-defined endothermic peak on the D.T.A. On further heating, above the range 236–248° C, both forms of the tetragonal cubanite variety invert to a f.c.c. cell of about 5.32 Å. This confirms the data reported by Yund and Kullerud and one can interpret the X-ray pattern taken at 360° C as consisting of such a f.c.c. cell plus the tetragonal chalcopyrite, which remains unchanged. Heating above the range 470–500° C then apparently transforms the tetragonal chalcopyrite to a f.c.c. cell with $a_0 \sim 5.36$ Å, which is isostructural with the f.c.c. cubanite. This corroborates the data of Yund and Kullerud. It is also possible that, because of changes in tie-line positions due to quaternary

* The assumption is made that this mineral can exist without the presence of Ni since Hiller and Probsthain (1956) synthesized such a compound from Cu + Fe + S.

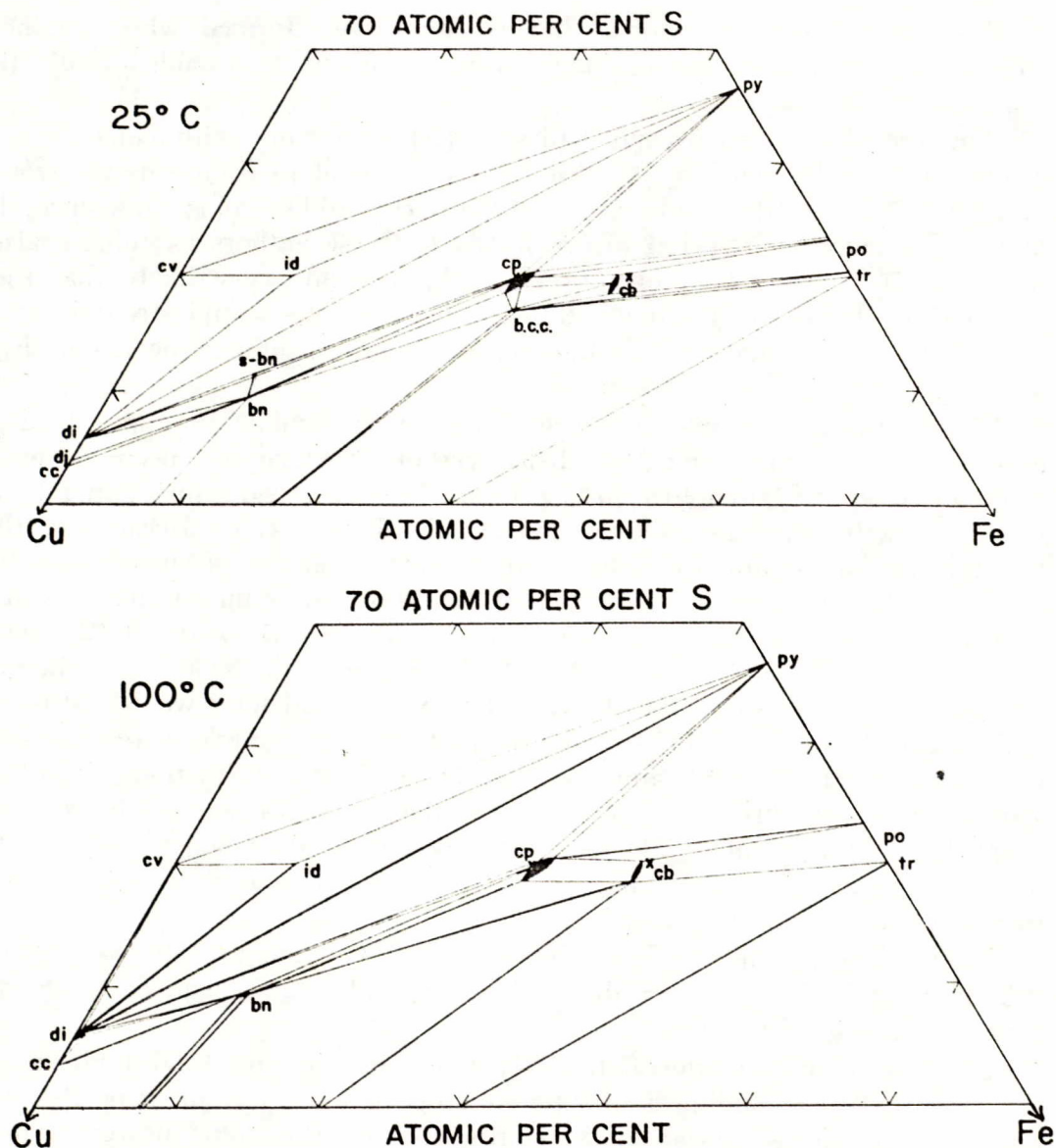


FIG. 4 (Top). Hypothetical phase relations in a portion of the Cu-Fe-S system at 25° C coexisting with vapor. Many of the tie-lines are taken from a chapter on "Sulfide mineral stabilities" by P. B. Barton, Jr., and B. J. Skinner in "Geochemistry of Hydrothermal Ore Deposits" (in press), edited by H. L. Barnes; Holt, Reinhart, and Winston, New York. py = pyrite, po = pyrrhotite, cb = cubanite, cp = chalcopyrite, bn = bornite, s-bn = sulfur-rich bornite, cc = chalcocite, di = digenite, cv = covellite, id = idaite, tr = troilite, b.c.c = new sulfide mineral. Because of uncertainties, the py-cc tie-line, "blaubleibender" covellite and Fe_3S_4 have been omitted. Compositions of binary and ternary phase regions are schematic, and have been taken from the 200° C isotherm of Yund and Kullerud (1966). The cross represents stoichiometric cb.

FIG. 5. (Bottom). Hypothetical phase relations in a portion of the Cu-Fe-S system at 100° C coexisting with vapor. Reference and abbreviations are the same as in Figure 4. Compositions of binary and ternary phase regions are schematic, especially the cb area which contains "tetragonal" cb formed from the breakdown of new sulfide mineral as well as orthorhombic cb.

solid solutions, some tetragonal chalcopyrite is also formed when the new sulfide mineral breaks down, but this was difficult to establish with the impure materials available.

The report by Bud'ko and Kulagov (5) of troilite with cubanite and chalcopyrite in the vein ores of Noril'sk, is pertinent to Figure 4. It would be very difficult, indeed, to have a chalcopyrite-troilite join; and since the new sulfide mineral, referred to previously by these authors as cubic chalcopyrite, occurs in the vein ores of Noril'sk, it seems very likely that they are indeed referring to this new sulfide mineral. This would strengthen the probability of the suggested tie-lines b.c.c.-cubanite-troilite indicated in Figure 4.

The new sulfide mineral appears to be very similar in appearance to descriptions of a mineral called chalcopyrrhotite, which has been variously discredited or attributed to other species. The history of this mineral has been succinctly summarized by Yund and Kullerud (18). Because of this apparent similarity, attempts were made to obtain samples of chalcopyrrhotite from the type locality for re-examination. Two museum samples labelled chalcopyrrhotite from the type locality, as reported by Blomstrand (2), were obtained. The first, U.S.N.M. No. R718, came from Nya Kopparberget, Sweden; and the second, from Kaveltorp, Sweden, had the Swedish Museum of Natural History No. G6389. Six chips from each sample were examined in polished section and all minerals checked by X-ray diffraction. The two samples were essentially similar, except that they varied in the relative proportions of minerals. Their mineralogy consisted principally of chalcopyrite, cubanite (in laths and anhedral masses), sphalerite (in stars and irregular grains), and hexagonal pyrrhotite.

Preliminary attempts to find other examples of chalcopyrrhotite or the new sulfide mineral in ores from Sudbury, Insizwa, and Iglukunguaq (Greenland), have so far proved fruitless.

Dr. Ramdohr, who devoted nearly five pages in his 1960 textbook to chalcopyrrhotite, including four photomicrographs from four deposits, was unable to provide material for comparison. Dr. Ramdohr, however, in a personal communication of December 22nd, 1965, to Dr. E. H. Nickel of our Division, suggested it was a high-temperature mixed crystal identical to the isotropic cubanite of Kullerud. However, in his textbook, he points to the similarity in polished section of chalcopyrrhotite and cubanite II. Since the isotropic form of cubanite (cubanite II) has recently been shown to exist in nature by Genkin et al. (10), there still remains this mineral called chalcopyrrhotite, which looks like isotropic cubanite but has not yet been quantitatively characterized or equated with cubic cubanite. A subsequent personal communication from Dr. Gabrielson (3 August 1967) stated that sample #G6389, described above, was taken from the original material analyzed by Blomstrand. This is additional evidence to discredit the name chalcopyrrhotite. (See also Yund and Kullerud, 18, p. 482.)

The new sulfide mineral is very likely formed in certain Cu-Fe-Ni-S ores where low temperatures and low sulfur vapor pressures prevailed.

It could also form under conditions of mild metamorphism of a sulfide ore which permitted a loss of sulfur. The β -phase described by Hiller and Probsthain (11) is very probably identical to this mineral. The author is not entirely in agreement with some of their data, and a full understanding of the Cu-Fe-S system is still lacking. It is hoped to pursue the investigation of certain aspects of this system at some future date.

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MINERAL SCIENCES DIVISION, MINES BRANCH,
DEPARTMENT OF ENERGY, MINES AND RESOURCES,
OTTAWA, CANADA,
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REFERENCES

1. Berry, L. G., and Thompson, R. M., 1962, X-ray powder data for ore minerals: The Peacock Atlas, Geol. Soc. America Mem. 85.
2. Blomstrand, C. W., 1870, On some new Swedish minerals and the composition of pyrrhotite: Öfvers. K. Vetensk. Akad. Förh., Stockh., v. 27, p. 19-27.
3. Birks, L. S., 1963, Electron-probe Microanalysis: Interscience Publishers, New York, 253 p.
4. Bud'ko, I. A., and Kulagov, E. A., 1963, Natural cubic chalcopryrite: Doklady Akad. Nauk. SSSR, v. 152, p. 408-410.
5. Bud'ko, I. A., and Kulagov, E. A., 1966, Troilite in vein ores of Noril'sk and Talnakh: Doklady Akad. Nauk. SSSR, v. 169, p. 428-429.
6. Buerger, N. W., and Buerger, M. J., 1934, Crystallographic relations between cubanite segregation plates, chalcopryrite matrix, and secondary chalcopryrite twins: Amer. Min., v. 19, p. 289-303.
7. Cabri, L. J., and Traill, R. J., 1966, New palladium minerals from Noril'sk, western Siberia: Can. Mineralogist, v. 8, p. 541-550.
8. Donnay, G., and Kullerud, G., 1958, High-temperature chalcopryrite: Carnegie Inst. Wash. Yearbook, v. 57, p. 246.
9. Frueh, A. J., 1958, Some applications of X-ray crystallography to geologic thermometry: Jour. Geol., v. 66, p. 218-223.
10. Genkin, A. D., Filimonova, A. A., Shadlun, T. N., Soboleva, S. V., and Troneva, N. V., 1966, On cubic cubanite and cubic chalcopryrite: Geol. Rudnykh Mestorozhdenii, v. 8, p. 41-54.

11. Hiller, J. E., and Probsthain, K., 1956, Thermische und röntgenographische Untersuchungen am Kupferkies: *Zeit. Krist.* v. 108, p. 108-129.
12. Merwin, H. E., and Lombard, R. H., 1937, The system, Cu-Fe-S: *ECON. GEOL.*, v. 32, p. 203-284.
13. Ramdohr, P., 1960, Die Erzminerale und ihre Verwachsungen: Akademie-Verlag, Berlin.
14. Schlegel, H., and Schüller, A., 1952, Die Schmelz- und kristallisationsgleichgewichte im System Kupfer: Eisen-Schwefel und ihre Bedeutung für die Kupfergewinnung: *Freib. Forsch.*, RB.H2.
15. Smith, J. V., 1965, X-ray emission microanalysis of rock-forming minerals. I. Experimental Techniques: *Jour. Geol.*, v. 73, p. 830-864.
16. Wuensch, B. J., 1964, The crystal structure of tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$: *Z. Krist.*, v. 119, p. 437-453.
17. Wuensch, B. J., Takéuchi, Y., and Nowacki, W., 1965, Refinement of the crystal structure of binnite, $\text{Cu}_{12}\text{As}_4\text{S}_{13}$: *Z. Krist.*, v. 123, p. 1-20.
18. Yund, R. A. and Kullerud, G., 1966, Thermal stability of assemblages in the Cu-Fe-S system: *Jour. Petr.*, v. 7, p. 454-488.

