

## MOOIHOEKITE AND HAYCOCKITE, TWO NEW COPPER-IRON SULFIDES, AND THEIR RELATIONSHIP TO CHALCOPYRITE AND TALNAKHITE<sup>1</sup>

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### ABSTRACT

Mooihoekite  $\text{Cu}_3\text{Fe}_9\text{S}_{16}$  occurs with haycockite  $\text{Cu}_4\text{Fe}_8\text{S}_8$  in polished sections from the hortonolite dunite (replacement) pegmatite, Mooihoek Farm, Lydenburg District, Transvaal, South Africa. A second occurrence of mooihoekite and haycockite is in the Duluth Gabbro complex, Minnesota, U.S.A.

Under reflected light mooihoekite has the color of chalcopyrite, but it tarnishes in air and is weakly anisotropic. Indentation micro-hardness  $\text{VHN}_{10} = 261 \text{ kg/mm}^2$ . The mineral is tetragonal:  $a = 10.58(1)$ ,  $c = 5.37(1) \text{ \AA}$  from powder data, with space group  $P4_2m$  and  $D_x = 4.38 \text{ g/cm}^3$ . Synthetic mooihoekite has  $a 10.585(5)$ ,  $c 5.383(5) \text{ \AA}$  from single crystal data,  $D_m = 4.36 \text{ g/cm}^3$ ,  $D_x = 4.37 \text{ g/cm}^3$ . Both powder patterns agree closely with the  $\gamma$ -phase of Hiller and Probsthain (1956).

Haycockite has the color of chalcopyrite under reflected light; it does not tarnish easily. It is weakly to moderately anisotropic. Indentation micro-hardness  $\text{VHN}_{10} = 263 \text{ kg/mm}^2$ . The mineral is orthorhombic, pseudo-tetragonal:  $a \simeq b = 10.71(2)$ ,  $c = 31.56(6) \text{ \AA}$  from single crystal data, with  $D_x = 4.35 \text{ g/cm}^3$ .

The X-ray powder data and some physical properties of mooihoekite and haycockite are compared to those of chalcopyrite and talnakhite.

### INTRODUCTION

The new minerals and their names, mooihoekite and haycockite, have been approved by the Commission for New Minerals and Mineral Names, I.M.A. The name mooihoekite (moi·hük·ait) is for the locality. Haycockite is named for Dr. M. H. Haycock (a former Head of the Mineralogy Section in this laboratory) who wrote a report (unpublished) describing this mineral when he was a graduate student of Professor E. Sampson at Princeton in 1931.

The new minerals were identified in specimens originally collected by Professor Sampson at Mooihoek Farm, No. 147, Lydenburg District, Transvaal, during an International Geological Congress field trip in 1929. Type material containing both minerals is preserved at the National Mineral Collection (10397), Ottawa; at the Royal Ontario Museum (M30992), Toronto; at Princeton University, Princeton, N. J.; at the Smithsonian Institution, Washington, D. C.; and at Heidelberg University (No. 2313a).

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Mineral specimens from a variety of ore deposits have been examined as part of a detailed study of phase relations in the central portion of the Cu-Fe-S system. The existence of certain unusual Cu-Fe sulfide minerals in the chalcopyrite region has been suspected for several years. Their characterization is of considerable importance in ore genesis and in beneficiation studies, as these minerals are expected to have flotation and/or leaching characteristics that differ significantly from those of chalcopyrite.

Reports of poorly characterized minerals approximating chalcopyrite in composition occasionally appear in the literature. The discredited mineral "chalcopyrrhotite" (Geijer, 1924; Yund and Kullerud, 1966; Cabri, 1967) continues to be reported (Ramdohr, 1969; Besson *et al.*<sup>1</sup>, 1971).

The "cubic chalcopyrite" ( $a = 5.28 \text{ \AA}$ ) reported by Bud'ko and Kulagov (1963), now known as the mineral talnakhite, has been shown by Hall and Gabe (1972) to have a cubic structure ( $a = 10.593 \text{ \AA}$ ,  $I\bar{4}3m$ ) consistent with a metal-rich composition and ideal formula of  $\text{Cu}_{18}\text{Fe}_{16}\text{S}_{32}$  (Cabri and Harris, 1971). The mineral, whose composition may be written as  $\text{Cu}_9\text{Fe}_8\text{S}_{16}$ , is equivalent to the  $\beta$ -phase of Hiller and Probsthain (1956).

Hall and Weiblen (1968) reported a chalcopyrite-like mineral  $\text{Cu}_3\text{Fe}_4\text{S}_6$  from the Duluth Gabbro complex, Minnesota, and based the tentative formula on electron probe analyses. This stoichiometry did not appear to have structural implications at the time and was undoubtedly proposed because of the earlier phase equilibrium studies of Merwin and Lombard (1937), and of Schlegel and Schüller (1952). The latter had reported a synthetic high-temperature phase with a composition of  $\text{Cu}_3\text{Fe}_4\text{S}_6$  and referred to it as "intermediate solid solution" (M and L) and "chalcopyrite *b*" (S and S). It would appear that the new mineral of Hall and Weiblen is haycockite, while the synthetic high-temperature phase has a different structure.

Experimental work, briefly reported by Cabri and Harris (1971) and Cabri and Hall (1971), has confirmed the existence of a phase with an X-ray diffraction powder pattern similar to that reported for the  $\gamma$ -phase;  $a = 10.58$ ,  $c = 5.37 \text{ \AA}$  (Hiller and Probsthain, 1956). Although Hiller and Probsthain reported the  $\gamma$ -phase to be a high-temperature phase unstable at room temperature, X-ray powder data indicate that our samples have not changed over a three year period.

<sup>1</sup> The only polished section containing the "chalcopyrrhotite" reported in this paper was kindly sent by M. Besson for electron probe examination. Fe, Ni, and S were the major elements found and no Cu was detected; this mineral is probably violarite.

Moreover, our DTA and high-temperature X-ray diffraction studies, indicates that the compound is a low-temperature phase and the synthetic equivalent of the mineral mooihoekite.

#### OCCURRENCE AND ASSOCIATED MINERALS

The deposit at Mooihoek, which was mined for platinum in the 1920's and 1930's, is a pipe-shaped hortonolite-dunite pegmatite in the Norite Zone of the Bushveld Igneous Complex. It has been well described by Wagner (1929) and more recently Cameron and Desborough (1964) discuss the origin of these pegmatites.

Mooihoekite and haycockite were found in small massive sulfide samples from the sulfide-poor hortonolite dunite. In polished sections, mooihoekite occurs in areas up to 1 mm<sup>2</sup> and as an intergrowth with haycockite (Figures 1 and 2). Haycockite occurs with dimensions up to about 500 $\mu$ . The larger areas of mooihoekite commonly show fractures filled with veinlets of magnetite ( $\sim 1\mu$  wide), sometimes in a regular octahedral pattern. Other irregular fractures are filled with gangue or with a "valleriite-type" mineral. Troilite always occurs with a copper-rich rim; other minerals are a copper-bearing pentlandite, mackinawite, sphalerite stars, and moncheite (usually occurring as long, well terminated lath-shaped needles, with cross-sections up to 1000  $\times$  5 $\mu$ m). The copper-bearing pentlandite is similar to that reported by Mitenkov *et al.* (1970). Micro-analytical data on copper-bearing pentlandite and copper-bearing troilite will be reported elsewhere.

#### OPTICAL, PHYSICAL, AND CHEMICAL PROPERTIES

Specimens were studied by reflected light after mounting in cold-setting Araldite resin and polishing on lead laps with graded diamond abrasives down to 0-2  $\mu$ m. Final buffing was done for a few seconds with Linde B 0.05  $\mu$ m metallographic polishing compound on a cloth lap.

Under reflected light mooihoekite and haycockite have a color similar to that of chalcopyrite in a freshly polished section. Mooihoekite tarnishes, however, on exposure to air through different hues of pinkish brown to a heavy purplish color but at a rate slower than that reported for talnakhite (Cabri, 1967). Haycockite appears untarnished after several months' exposure to air. Freshly polished sections containing a) mooihoekite with haycockite, b) talnakhite with minor chalcopyrite plus cubanite and pentlandite, and c) chalcopyrite alone, were exposed to the fumes of aqua regia for between one and two minutes. Mooihoekite and talnakhite readily tarnished to light and dark purple, respectively. Haycockite and chalcopyrite were untarn-

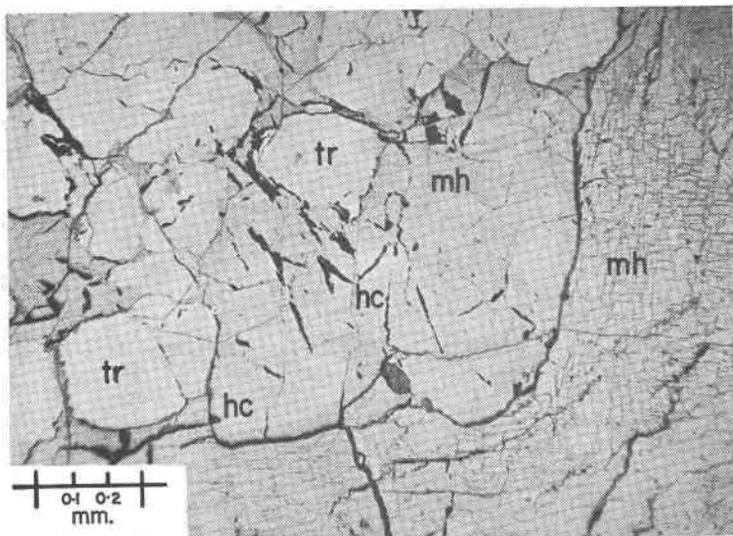


FIG. 1. Photomicrograph showing a large, heavily fractured area of mooihoekite (dark grey, mh) separated by a curving fracture from an area containing an intergrowth of mooihoekite (dark grey, mh) and haycockite (light grey, hc). The rounded light grey areas extending from the top left corner are troilite (tr).

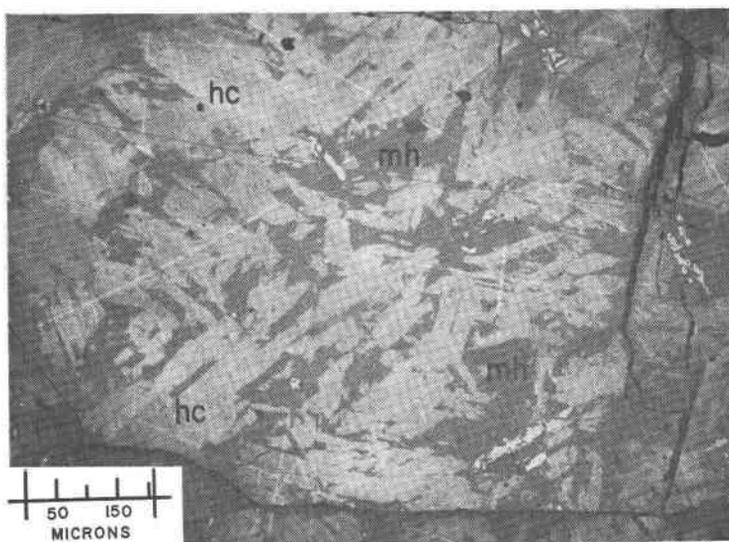


FIG. 2. Photomicrograph showing details of mooihoekite-haycockite intergrowth. Dark grey = tarnished mooihoekite (mh) and light grey = haycockite (hc). The small white lamellar grains are mackinawite.

ished but cubanite and pentlandite became darker with no visible etching. This technique makes the chalcopyrite lamellae more readily visible in the talnakhite matrix.

Mooihoekite is weakly anisotropic, whereas haycockite is weakly to moderately anisotropic. Haycockite shows polysynthetic twinning that occasionally appears in polished sections (Figure 3).

Micro-indentation hardness was measured using a Leitz Durimet tester, with both diagonals measured for each indentation (Table 1). The values obtained indicate that mooihoekite, haycockite, and talnakhite are from 27 to 35 percent harder than chalcopyrite; thus presenting a useful diagnostic feature.

The compositions (Table 2) were determined with a Materials Analysis Company electron probe microanalyser, operated at 25 kV for a specimen current of about  $0.035 \mu\text{A}$ . Homogeneous synthetic Cu-Fe-S and Ni-Fe-S standards were used and corrections were applied using Edition VII of a computer program by Rucklidge (1967).

Electron probe microanalyses for chalcopyrite, talnakhite, and the

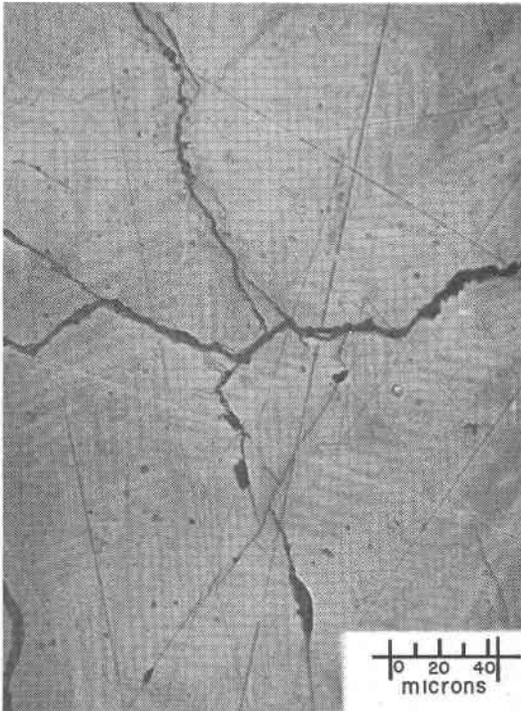


FIG. 3. Photomicrograph showing details of twinning in haycockite.

TABLE 1

Indentation Micro-Hardness VHN(kg/mm<sup>2</sup>), 50 g load

Mineral	Locality	No. of Indentations	Range	Average
Chalcopyrite	Five localities*	25	197-217	206
Talnakhite	Noril' sk, U.S.S.R.	5	271-283	277
Mooihoekite	Mooihoek, Tvl., South Africa	8	250-269	261
Haycockite	Mooihoek, Tvl., South Africa	6	261-266	263

\*5 indentations were measured for each of five chalcopyrites. Their localities, followed by range and average, are: Western Mines Ltd., B.C., Canada: 202-211(208); Echo Bay Mine, N.W.T., Canada: 200-209(205); Siscoe Metals of Ontario, Ont., Canada: 202-217(207); French Creek, Pa., U.S.A.: 197-206(202); Tri-state district, U.S.A.: 208-210(208).

new minerals are shown in Table 2. Each analysis represents the result of 5 or more spot analyses, ordinarily done at different times. These analyses support the composition  $Cu_{1.125}(Fe_{1.115}Ni_{0.01})S_{2.0}$  for mooihoekite,  $Cu_{1.00}(Fe_{1.24}Ni_{0.01})S_{2.0}$  for haycockite,  $Cu_{1.01-1.02}Fe_{1.00-1.02}S_{2.0}$  for chalcopyrite, and  $Cu_{1.125}(Fe_{1.00}Ni_{0.02})S_{2.0}$  for talnakhite.

TABLE 2

Electron-Probe Micro-Analyses in Weight %

Mineral	Range (average)				Totals
	Cu	Fe	Ni	S	
Chalcopyrite Echo Bay Mine	34.84	30.44	0.00	34.35	99.63
Chalcopyrite Western Mines	35.03	31.00	0.00	34.96	100.99
Chalcopyrite Siscoe Metals of Ontario	35.09	31.08	0.00	35.09	101.26
Chalcopyrite Tri-state area	35.15	30.69	0.00	35.19	101.02
Talnakhite Noril' sk area (5 analyses)*	36.86-37.36 (37.15)	28.79-29.47 (29.10)	0.70-0.87 (0.75)	33.06-33.84 (33.31)	99.97-100.69 (100.31)
Mooihoekite (13 analyses)	34.87-36.71 (35.91)	31.38-32.40 (31.88)	0.24-0.30 (0.26)	31.93-33.29 (32.44)	99.51-100.94 (100.49)
Haycockite (15 analyses)	31.83-32.55 (32.16)	34.64-35.46 (35.03)	0.36-0.58 (0.40)	31.94-32.86 (32.41)	98.87-100.94 (100.14)

\*Cabri and Harris (1971).

The compositions of mooihoekite and haycockite, along with other minerals reported in the Cu-Fe-S system, are shown in Figure 4.

#### X-RAY DIFFRACTION ANALYSIS

X-ray diffraction powder patterns (Table 3) were obtained by the film method using a 57.3-mm Gandolfi camera and 57.3 and 114.6-mm Debye-Scherrer cameras. In addition, the Guinier multiple-focussing camera was used for resolving the low-angle region of the powder patterns. The resolution on the Debye-Scherrer films was relatively poor, particularly in the case of mooihoekite. In contrast, the Gandolfi camera gave very well-resolved powder patterns of one or more small uncrushed fragments extracted from the polished section. This was especially useful because the same fragments could then be examined on a precession camera to determine whether they were single crystals. In this way single crystals of natural and synthetic mooihoekite were examined to establish the space group and to confirm cell dimensions.

The pattern for talnakhite is essentially the same as that reported previously (Cabri, 1967). The cell dimensions used to calculate the  $d$ -values in this table were obtained from X-ray diffraction powder measurements, corrected for film-shrinkage and calculated using a least-squares XRAY program by R. A. Alden which appeared in a report of the Computer Science Center of the University of Maryland, edited by J. M. Stewart *et al.* The intensities on Table 3 were visually estimated from the films. Accurate cell dimensions for synthetic mooihoekite haycockite, and talnakhite were later measured on a Picker 4-circle automatic diffractometer, using a least-squares fit of the four angles  $2\theta$ ,  $\phi$ ,  $\chi$ ,  $\omega$  (Busing, 1970) and assuming a triclinic cell.

In contrast to X-ray diffraction photographs of single crystals which clearly distinguish these minerals, powder photographs provide an unambiguous identification *only* under suitable conditions. Because most routine identification work is done by the powder method we wish to emphasize that *special* care must be taken with sample preparation and alignment; the choice of radiation, camera type and radius, collimation, exposure times; and the examination of the developed films in order to detect diagnostic features that enable the correct identification of these minerals. The use of a powder diffractometer for the identification of these minerals is to be discouraged because of its insensitivity.

A summary of conditions found most suitable for the X-ray diffraction powder analysis of these minerals follows.  $\text{CoK}\alpha$  radiation with an Fe filter was used with all cameras except the Guinier which did not need a filter. Sample preparation depended on the material avail-

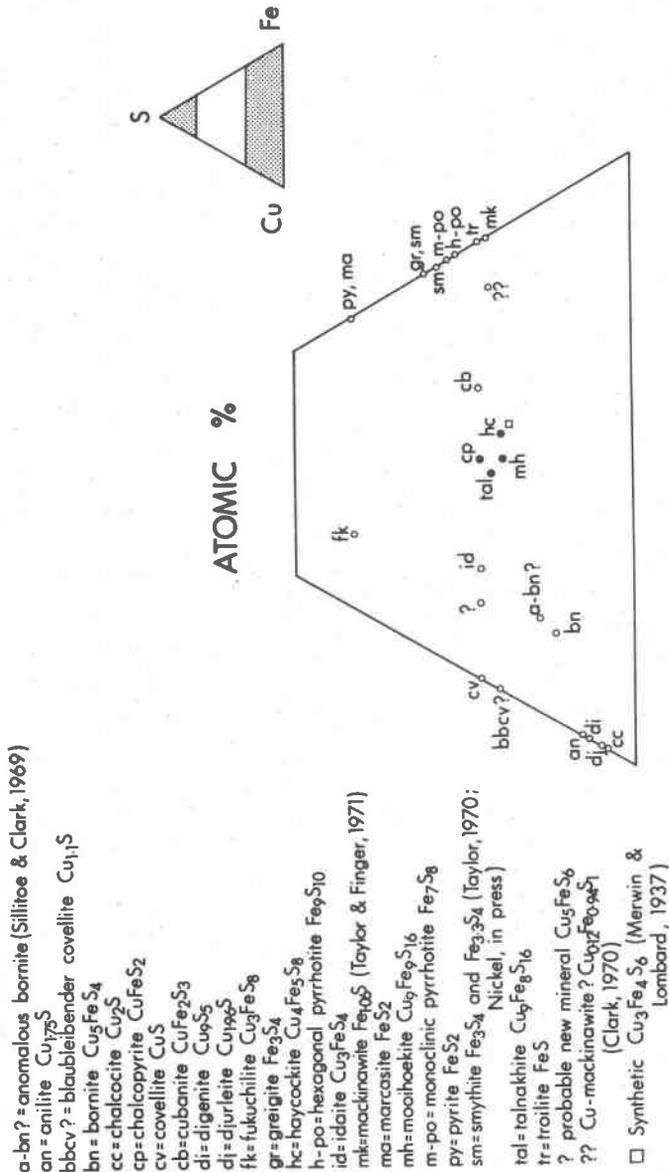


FIG. 4. Part of the Cu—Fe—S system indicating most of the minerals reported in the literature. Some doubtful or incompletely described minerals have been omitted. Mineral compositions are represented by circles, with the filled circles representing the minerals of special interest in this paper. The composition for idaite is that proposed by Levy (1967) and Sillitoe and Clark (1969), whereas the mineral  $\text{Cu}_3\text{FeS}_6$  of Frenzel and Ottemann (1967) is probably a new mineral.

able. If there was sufficient material, the mineral was crushed in a mortar and inserted into a 0.2-mm glass capillary, mounted in a brass rod. Such a sample was exposed for about 60 hours in a 114.6-mm Debye-Scherrer camera with a 0.4-mm collimator. If the mineral occurred as small areas in a polished section, it was located under the microscope and a fragment loosened with a steel needle. The fragment was then removed with a  $\sim 0.1$ -mm glass fibre tipped with collodion. The glass fibre was mounted in a 57.3-mm Gandolfi camera with 0.4-mm collimator and exposed for 18 to 44 hours.

#### DENSITY MEASUREMENTS

Density information on these minerals is essential because the electron probe and X-ray diffraction analyses do not distinguish between a metal-rich and a sulfur-deficient compound. The measured density of talnakhite, reported as  $4.24 \text{ g/cm}^3$  by Cabri (1967), is lower than the calculated value of  $4.29 \text{ g/cm}^3$ , probably due to over-correction for an impurity of pentlandite. The grains of natural mooihoekite and haycockite were too small for density determination. Density measurements could be made on synthetic mooihoekite using Clerici solution (BDH laboratory reagent), however. Fragments were immersed in this solution and degassed in a vacuum desiccator. The density of the solution was adjusted by slowly mixing with dilute Clerici solution until the fragments neither rose nor fell. The density of the liquid was then measured by weighing it in a 10-ml pycnometer after removing the fragments. This procedure gave a value of  $4.36 \text{ g/cm}^3$  and this is close to the calculated value of  $4.37 \text{ g/cm}^3$  assuming a metal-rich composition shown on Table 4. The density of a crystal of chalcopyrite from Western Mines Ltd., Vancouver Island, B. C., Canada, was measured as  $4.23 \text{ g/cm}^3$  by this method to provide a standard. The value compares favorably with the calculated value of  $4.20 \text{ g/cm}^3$ .

#### DISCUSSION

The compositional and structural similarity of mooihoekite, haycockite, chalcopyrite, and talnakhite, as well as their relationship to the high-temperature polymorph of chalcopyrite, is apparent from the data presented. This similarity has made the separate identification of minerals within the chalcopyrite family particularly difficult. In this discussion it is, therefore, helpful to briefly outline what is currently known about these minerals.

The high-temperature polymorph of chalcopyrite was reported by Donnay and Kullerud (1958) to have a sphalerite-like cell with  $a = 5.26 \text{ \AA}$  and disordered metals after quenching at room temperature.



MOOIHOEKITE AND HAYCOCKITE

TABLE 3 (cont.)

Chalcopyrite Western Mines, B. C., Canada 114.6mm Debye-Scherrer a=5.28(1), c=10.40(1)Å			Talnakhite Noril'sk, U. S. S. R., 57.3mm Gandolfi a=10.59(1)Å			Mooihoekite Mooihoek, Transvaal, S. A., 57.3mm Gandolfi a=10.58(1), c=5.37(1)Å			Synthetic Mooihoekite 57.3mm Gandolfi a=10.58(1), c=5.37(1)Å			Mooihoekite Mooihoek, Transvaal, S. A., 57.3mm Gandolfi a=10.58(1), c=5.37(1)Å			Haycockite Mooihoek, Transvaal, S. A., 57.3mm Gandolfi a=10.58(1), c=5.37(1)Å				
I	d(meas.)	d(calc.)	hkℓ	I	d(meas.)	d(calc.)	hkℓ	I	d(meas.)	d(calc.)	hkℓ	I	d(meas.)	d(calc.)	hkℓ	I	d(meas.)	d(calc.)	hkℓ
6	1.590	1.591	312	7	1.599	1.597	620	4	1.612	1.615	223	3	1.615	1.612	6	1.612	1.612	626	
3	1.572	1.573	116	6	1.531	1.529	444	3	1.593	1.597	621	6	1.597	1.586	4	1.586	1.588	22.18, 362	
1	1.517	1.517	224	3	1.443*	1.441	721, 623	2	1.528	1.535	442	2	1.533	1.536	1	1.535	1.536	4.4, 12	
				1	1.415*	1.415	642												
				1	1.390*	1.391	730												
3	1.321	1.321	400	4	1.323	1.324	800	1	1.341	1.343	004	2	1.346	1.339	4	1.333	1.339	800	
1	1.302	1.301	008	4	1.321	1.321	800	4	1.323	1.323	800	4	1.323	1.327	2	1.325	1.327	656	
2	1.210	1.211	332	5	1.213	1.215	662	5	1.219	1.222	623	5	1.223	1.312	2	1.313	1.312	0.0, 24	
3	1.203	1.203	316	1	1.199	1.199	752	2	1.213	1.215	661	2	1.214	1.227	3	1.227	1.227	666	
				2	1.184	1.181	840	1	1.197	1.197	404	1	1.196	1.217	5	1.214	1.217	6.2, 18	
5	1.075	1.076	424	4	1.079	1.081	844	4	1.089	1.091	444	3	1.091	1.089	6	1.089	1.089	8.4, 12	
2	1.067	1.067	228	6	1.079	1.081	844	6	1.081	1.083	842	6	1.083	1.079	4	1.077	1.079	4.4, 24	
				5	1.019	1.019	666	2	1.022	1.032	225	1	1.033	1.030	3	1.031	1.030	10.2, 6	
2B	1.017	1.016	512	5	1.019	1.019	666	3	1.018	1.023	663	2	1.025	1.024	2	1.022	1.024	6.6, 18	
1B	1.012	1.011	336	3	1.019	1.019	666	3	1.018	1.019	10.2, 1	4	1.018	1.012	2	1.011	1.012	2.2, 30	
1B	1.003	1.002	1.1, 10	2	0.942	0.942	880	4	0.942	0.942	804	3	0.943	0.947	3	0.946	0.947	880	
1	0.935	0.934	440	2	0.936	0.936	880	2	0.935	0.935	880	3	0.935	0.937	6	0.937	0.937	8.0, 24	
3	0.928	0.928	408, 515	5	0.936	0.936	880	2	0.935	0.935	880	3	0.935	0.937	6	0.937	0.937	8.0, 24	

+ Cell dimensions shown were calculated from d-values obtained from powder films. \*Measured from 114.6 Debye-Scherrer films.

B = Broad

This sphalerite-like cell can be considered as the basic building block (although the metals need not be disordered) for the crystal structures of chalcopyrite, talnakhite, mooihoekite, and haycockite. Yund and Kullerud (1966) and Mukaiyama and Izawa (1970) reported a large compositional range for high-temperature chalcopyrite which extended out to cubanite. This range includes the compositions of mooihoekite, haycockite, and talnakhite. Vaasjoki (1971), however, has recently proposed that high-temperature cubanite is not isostructural with high-temperature chalcopyrite.

Chalcopyrite has the space group  $I\bar{4}2d$  (Pauling and Brockway, 1932) and an ordered antiferromagnetic arrangement of the  $\text{Fe}^{3+}$  atoms (Donnay *et al.*, 1958). The chalcopyrite cell dimensions determined in this study (Table 3) compare favorably with most values in the literature. The small deviations in unit cell values occasionally reported are conceivably due to errors in the X-ray diffraction powder method. The rarely reported weak super-lattice reflections listed for chalcopyrite by Mukaiyama *et al.* (1968) were observed in this study (Table 3). There was no evidence that chalcopyrite deviates significantly from either its accepted stoichiometric composition of  $\text{CuFeS}_2$  or its  $I\bar{4}2d$  cell with  $a = 5.28$  and  $c = 10.40 \text{ \AA}$ .

Talnakhite has a metal-rich stoichiometric composition of  $\text{Cu}_9\text{Fe}_8\text{S}_{16}$  (Cabri and Harris, 1971) and a crystal structure ( $I\bar{4}3m$   $a = 10.593 \text{ \AA}$ ) with the metal positions partly ordered (Hall and Gabe, 1972). Mössbauer and magnetic susceptibility measurements (Cabri and Goodman, 1970; Townsend *et al.*, 1971) indicate that talnakhite has an antiferromagnetic structure similar to that of chalcopyrite. Earlier work by Cabri (1967) showed that talnakhite decomposes on heating to several intermediate high-temperature phases before disordering completely to the high-temperature polymorph of chalcopyrite. These intermediate phases appear to support the contention that talnakhite is a stable phase at low temperature, and the disordered high-temperature cell is the stable phase above  $\sim 500^\circ\text{C}$ .

The metal:sulfur ( $M:S$ ) ratio for mooihoekite and haycockite is 1.125 as calculated from the electron probe results listed on Table 2. The value for chalcopyrite is 1.000. Four possible structural configurations give rise to a  $M:S$  ratio of 1.125: metal addition, sulfur deficiency, metal substitution, or combinations of these. The cell dimension and density measurements strongly support the first of these alternatives. The cell volumes, reduced to  $V/Z$  for purposes of comparison (Table 4), increase linearly with  $M:S$  ratio. Considering the ionic radii for the Cu, Fe, and S atoms it is most improbable that a sulfur deficiency or metal substitution would give rise to such a volume

TABLE 4  
Physical Data for the Chalcopyrite Family

	Composition	Space Group	Cell dimension (Å)			Cell Vol. $V(\text{Å}^3)$	Z	V/ $Z\text{Å}^3$	$D_x$ ( $\text{g/cm}^3$ )	M/S	Structural Composition
			a	b	c						
Chalcopyrite Western Mines Ltd., B. C., Canada	$\text{Cu}_{1.0}^{\text{Fe}}\text{Fe}_{1.0}^{\text{S}}\text{S}_2$ , 0	$\bar{4}2d$	5.28(1)	10.40(1)		289.94	4	72.5	4.20	1.000	$\text{Cu}_4\text{Fe}_4\text{S}_8$
Talnakhite, Noril'sk, U.S.S.R.	$\text{Cu}_{1.12}(\text{Fe}_{1.00}\text{Ni}_{0.02})\text{S}_2$ , 0	$\bar{4}3m$	10.593(5) <sup>b</sup>			1188.66	16	74.3	4.29	1.063	$\text{Cu}_{18}(\text{Fe}, \text{Ni})_{16}\text{S}_{32}$
Mooihoekite, Tvl., South Africa	$\text{Cu}_{1.125}(\text{Fe}_{1.115}\text{Ni}_{0.01})\text{S}_2$ , 0	$\bar{F}42m$	10.58(1)	5.37(1)		601.10	8	75.1	4.38	1.125	$\text{Cu}_9(\text{Fe}, \text{Ni})_9\text{S}_{16}$
synthetic	$\text{Cu}_{1.125}\text{Fe}_{1.125}\text{S}_2$ , 0		10.585(5) <sup>c</sup>	5.383(5) <sup>c</sup>		603.12		75.4	4.37		$\text{Cu}_9\text{Fe}_9\text{S}_{16}$
Haycockite, Tvl., South Africa	$\text{Cu}_{1.00}(\text{Fe}_{1.24}\text{Ni}_{0.01})\text{S}_2$ , 0	$\bar{F}m\bar{3}m$	10.71(2) <sup>d</sup>	31.56(6) <sup>d</sup>		3620.06	48	75.4	4.35	1.125	$\text{Cu}_{48}(\text{Fe}, \text{Ni})_{60}\text{S}_{96}$
High-temperature chalcopyrite	$\sim\text{Cu}_2\text{Fe}_2\text{S}_4$	$\bar{F}m\bar{3}m$	5.36(1) <sup>f</sup>			153.99	2	77.0	3.96	range	$\sim\text{Cu}_2\text{Fe}_2\text{S}_4$

a. Cabri and Harris (1971).

b. Single crystal value, Hall and Gabe (1972).

c. Single crystal values.

d. Single crystal values; true cell is orthorhombic, pseudo-tetragonal.

e. Single crystal data, Donnay and Kullerud (1958).

f. Powder data, X-rayed at 573°C, Cabri (1967).

increase. The same argument has been applied by Donnay and Shewman (1971) in deciding the structural formula of pentlandite.

Density measurements provide strong additional evidence for metal addition in mooihokite. The measured density of synthetic mooihokite was  $4.36 \text{ g/cm}^3$ , and the theoretical values, assuming metal addition, sulfur deficiency, and metal substitution, are 4.37, 3.88, and  $4.12 \text{ g/cm}^3$  respectively. Because of the very small amount of material and the size of the fragments available, it was not possible to measure reliably the densities of mooihokite and haycockite. However, the  $V/Z$  values clearly show that the compositional form of these minerals will be similar to that of synthetic mooihokite and that metal addition is the dominant structural mechanism.

The electron probe, X-ray diffraction, and density measurements for mooihokite are consistent with the metal-rich stoichiometric composition  $\text{Cu}_9(\text{Fe}, \text{Ni})_9\text{S}_{16}$ . Synthesis of mooihokite shows that Ni is not essential to this structure and that the composition can be expressed simply as  $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ . The cell dimensions for mooihokite obtained from X-ray diffraction powder data (Table 3) are close to the values determined for synthetic single crystals using a 4-circle diffractometer (Table 4). Crystals of natural and synthetic mooihokite exhibit a strong tendency for micro-twinning parallel to  $\{201\}$ . Mooihokite has the space group  $P4_2m$ . Mössbauer and magnetic susceptibility measurements (Townsend *et al.*, 1971) indicate that mooihokite has an antiferromagnetic structure significantly different from those of chalcopyrite and talnakhite. The thermal characteristics of synthetic mooihokite are similar to those of talnakhite. Mooihokite forms an intermediate high-temperature phase before transforming to the completely disordered form of high-temperature chalcopyrite.

The X-ray diffraction powder pattern of haycockite (Table 3) can be completely indexed on a tetragonal cell with  $a = 10.71$  and  $c = 15.75 \text{ \AA}$ . Single crystal films and diffractometer measurements, however, clearly show a diffraction pattern that is inconsistent with this cell. First, the intensities of the  $0kl$  and  $h0l$  reflections are not equivalent and this reduces the symmetry of the cell; second a number of weak superlattice reflections require a doubling of the  $15 \text{ \AA}$   $c$ -axis; and third, the diffractometer measurement of the cell dimensions shows a small but detectable difference between the  $a$  and  $b$  values. These measurements indicate that the cell is primitive orthorhombic with  $a \simeq b = 10.71(2)$  and  $c = 31.56(6) \text{ \AA}$ . The metal-rich composition  $\text{Cu}_{1.0}(\text{Fe}, \text{Ni})_{1.25}\text{S}_{2.0}$  implied by the cell volume changes and density information discussed above support a cell content of  $\text{Cu}_{48}(\text{Fe}, \text{Ni})_{60}\text{S}_{96}$ . The composition may be written as  $\text{Cu}_4(\text{Fe}, \text{Ni})_5\text{S}_8$ .

Haycockite could not be synthesized by the procedures developed for talnakhite and mooihoekite. At high temperatures, material with the bulk composition of haycockite appears to have a crystal structure equivalent to high-temperature chalcopyrite. No heating experiments were possible on the mineral because sufficient material of acceptable purity could not be obtained.

Although attempts to synthesize haycockite have not been exhaustive, we suggest that this mineral was formed by exsolution from a high-temperature solid solution in a way similar to that proposed by Buerger (1971) for the exsolution of cubanite from a high-temperature chalcopyrite solid solution.

#### *Distinctive Features Under Reflected Light*

During routine examinations of polished sections, mooihoekite and haycockite may be mistaken for talnakhite and chalcopyrite, respectively. In fact, if the section is examined immediately after polishing, the new minerals may be mistaken for chalcopyrite. Minerals which look like chalcopyrite in a freshly polished section and tarnish after prolonged exposure to air or after short exposure to the fumes of aqua regia require careful quantitative analysis by electron probe or by powder X-ray diffraction to distinguish mooihoekite from talnakhite. If a chalcopyrite-like mineral does not tarnish, initial identification as chalcopyrite or haycockite is possible from microhardness tests. Later quantitative analysis by electron probe or by powder X-ray diffraction may be necessary to confirm this identification.

#### *Distinctive Features on X-ray Diffraction Powder Patterns*

The X-ray diffraction powder patterns of mooihoekite and haycockite cannot be distinguished from one another or from those of chalcopyrite and talnakhite, except under suitable conditions. Mooihoekite, haycockite, and talnakhite are distinguished from chalcopyrite by weak, or very weak, low-angle reflections which occur in the region of the pattern most subject to darkening and extraneous lines.

In general, the X-ray diffraction powder pattern of mooihoekite most closely resembles that of talnakhite; but doublets in the mooihoekite pattern (002,400; 402,440; 223,621; 004,800; 444,840) are single reflections for the talnakhite pattern (400; 440; 622; 800; 840). The mooihoekite powder patterns can be distinguished from those of chalcopyrite and haycockite patterns because the relative *intensities* of the strongest doublets in the chalcopyrite pattern (200,004; 220,204; 312,116; 400,008; 332,316; 424,228) appear reversed in the mooihoekite pattern (002,400; 402,440; 223,621; 004,800; 623,661; 444,842). This

apparent reversal of intensities led Kullerud and Donnay (1970) to propose that the synthetic compound  $\text{Cu}_{1.11}\text{Fe}_{1.11}\text{S}_2$  had an expanded chalcopyrite cell with  $c/2a$  greater than one. This interpretation has subsequently been revised on density grounds (Donnay and Kullerud, 1971).

The haycockite pattern most closely resembles that of chalcopyrite, except for weak low-angle reflections at 4.42 (204), 4.10 (214), 3.74 (206), and 2.42 Å (2.2.10). In an early interpretation prior to single crystal studies, the haycockite cell was considered to be based on an expanded chalcopyrite cell (Cabri and Hall, 1971). The X-ray patterns are very similar in corresponding reflections, even to the relative intensities of their doublets.

A mixture of mooihoekite and talnakhite is difficult to recognize and interpret from X-ray diffraction powder patterns. The same difficulty arises with a mixture of haycockite and chalcopyrite but this is unlikely to occur, since the presence of mooihoekite with troilite suggests a mooihoekite-troilite tie-line and this prohibits the haycockite-chalcopyrite assemblage. Table 5 summarizes the *key* reflections for distinguishing these four minerals.

#### A SECOND OCCURRENCE OF MOOIHOKITE AND HAYCOCKITE

Polished sections of troctolite from the basal Duluth Gabbro complex have been analyzed by optical, electron probe, and X-ray powder diffraction methods. Initial studies showed the sulfide minerals were very small grains intergrown, and further work was thought unfeasible. Following the characterization of mooihoekite and haycockite from South Africa, however, these minerals occurring in the basal Duluth complex could be identified. The analyses of these minerals presented on Table 6 are less reliable than those on Table 2 because the grains

TABLE 5

Key Reflections for Identification from X-Ray Diffraction Powder Patterns

Chalcopyrite			Talnakhite			Mooihoekite			Haycockite		
I	d(meas.)	hkl	I	d(meas.)	hkl	I	d(meas.)	hkl	I	d(meas.)	hkl
2	4.71	101	3	7.48	110	2	7.48	110			
			4	3.75	220	2	3.76	201	2	4.42	204
						1	2.68	002	1	3.74	206
3	2.64	200	5	2.65	400	2	2.64	400	4	2.67	400, 1.1.11
1	2.60	004							3	2.62	0, 0, 12
			2	2.08	431	1	2.09	312			

are much smaller and inclusions of mackinawite undoubtedly influenced some of the analyses. Other opaque minerals associated with mooihoekite and haycockite in the samples from the Duluth Gabbro are native copper, troilite, pentlandite, cubanite, and magnetite.

Considering the relative inaccuracy of the electron probe analyses, the composition of mooihoekite ( $\text{Cu}_{1.05}\text{Fe}_{1.14}\text{Ni}_{0.01}\text{S}_{2.0}$ ) and of haycockite ( $\text{Cu}_{0.96}\text{Fe}_{1.26}\text{Ni}_{0.01}\text{S}_{2.0}$ ) are sufficiently close to the values for type material reported on Table 2. One grain in this study which appeared tarnished in polished section, similar to mooihoekite or talnakhite, gave electron probe values close to that of haycockite. We are uncertain whether this is due to a poor analysis or whether this represents yet another distinct mineral.

Debye-Scherrer patterns were obtained for mooihoekite and haycockite from the Duluth Gabbro complex, but these were of poor quality. This was especially the case for mooihoekite because the reflections were too broad to justify a reliable unit cell determination. Approximate cell dimensions found for the haycockite from the Duluth Gabbro were  $a \simeq b = 10.68(5)$ ,  $c = 31.56(12)$  Å.

Chalcopyrite was not found in these sections but our examinations were not exhaustive. Four *untarnished* grains, which had the appearance of chalcopyrite, were found to be haycockite by electron probe analysis. These grains are probably the mineral reported as the "yellow phase with the approximate formula of  $\text{Cu}_3\text{Fe}_4\text{S}_6$ " by Hall and Weiblen (1968). The *tarnished* grains that were analyzed (other than the one discussed above) gave electron probe analyses close to the composition of mooihoekite. These grains probably correspond to the mineral reported as "talnakhite" by Hardyman (1970). This identification had been based on the tarnishing properties of the mineral and on an earlier composition for talnakhite ( $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ , Cabri, 1967). This is inconsistent with the more recent composition of  $\text{Cu}_9\text{Fe}_8\text{S}_{16}$  (Cabri and Harris, 1971) and it now seems that this mineral from the Duluth Gabbro is not talnakhite but mooihoekite.

TABLE 6

Electron-Probe Microanalyses in Weight % from Duluth Gabbro

Mineral	Range (Average)				Totals
	Cu	Fe	Ni	S	
Mooihoekite (4 analyses)	33.61-34.90 (34.08)	31.83-32.74 (32.47)	0.23-0.25 (0.24)	32.72-32.98 (32.84)	99.24-100.25 (99.65)
Haycockite (4 analyses)	30.44-32.50 (31.26)	34.63-36.42 (36.12)	0.09-0.30 (0.23)	32.40-33.11 (32.86)	99.82-101.47 (100.46)

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