A TETRAGONAL IRON SULFIDE

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ABSTRACT

A pleochroic, strongly anisotropic mineral, previously identified as valleriite has been examined by means of x-ray diffraction, chemical analysis, x-ray fluorescence and the electron microprobe. From the data obtained it is inferred that in most cases this mineral, resembling valleriite and found in several Finnish ore bodies, is not valleriite but an iron sulfide. The chemical analyses show Fe 64–54%, S 35%, Ni 0.2–8.3%, Co<0.2–10%. The wet chemical analyses indicate the formula $M_{1.05}S$. The rotation photographs and the tentative indexing of the powder pattern suggest that the mineral is tetragonal (P_4/nmm) with $a=3.676\pm0.002$ Å and $c=5.032\pm0.002$ Å. The d spacings in the x-ray powder pattern are listed.

The unmixing textures (flame-like lamellae and zoning) in some pyrrhotites associated with the tetragonal iron sulfide appeared to be composed of stoichiometric FeS and pyrrhotite, $Fe_{1-x}S$.

INTRODUCTION

In the paper "Valleriit ($=\gg$Unbekanntes Nickelerz$\gg=\gg$frägliches pleochroitisches Mineral$\gg$)" Ramdohr and Ödman (1932) were able to show that the mineral named "Unbekanntes Nickelerz" (Schneiderhöhn, 1929) is the same as valleriite described from Kaveltorp, Sweden. Since that time, routine polished section examinations have shown this strongly pleochroic and anisotropic mineral to be a common constituent of several mineral associations at various localities in all parts of the world. The chemical analyses have yielded a formula $Cu_2Fe_3S_7$ or $Cu_3Fe_4S_7$, but, on the other hand, it has been concluded (Bartholomé, 1958) that valleriite does not belong to the Cu-Fe-S system at all.

An exploratory examination at the Outokumpu laboratories was made of all of the available specimens of minerals resembling valleriite. Early in this work it became apparent that the x-ray powder pattern did not confirm the values given in the literature (*e.g.* ASTM, 3-0018) for valleriite (Kouvo and Vuorelainen, 1959). The prominent lines did not correspond but were quite near to those of kansite, Fe_9S_8 (F. H. Meyer, ASTM, 7–26). In a single case (Vihanti) an x-ray powder pattern identical with that of Kaveltorp valleriite was obtained.

The characteristic x-ray fluorescence spectra obtained for the minute samples picked out from some polished sections showed only iron and some nickel. Traces of cobalt were found.

Other possible suggestions for the existence of an iron sulfide mistaken for valleriite have been put forward. Milton and Milton (1958, p. 432,

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footnote) and Birks *et al.* (1959) have described some minute inclusions of copper-iron sulfide analysed by an electron probe. In spite of the copper content and of the lack of published diffraction data, the optical descriptions together with the *x*-ray fluorescence data suggest that these minerals may be identical.

In a recent paper, Berner (1962) has described a tetragonal iron sulfide prepared by the corrosion of steel in aqueous solutions of hydrogen sulfide. This synthetic product appears to give *x*-ray powder data almost identical with those of the mineral described here and to have a very similar composition, suggesting that, with the exception of the substitutions observed in the natural mineral, (*vide infra*) they are the same compound.[1]

Since the first published data, the work has been continued by separation of mineral fractions for chemical analyses and by using the electron microanalyser for determination of minor elements such as nickel, cobalt and copper in some single mineral grains.

OCCURRENCE

The iron sulfide described in this paper has been identified from several environments. It usually replaces nickel and cobalt pentlandite and
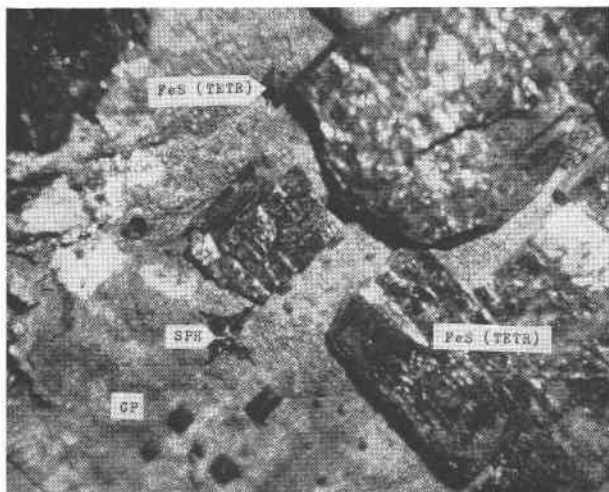

FIG. 1. Crystals of the iron sulfide grown on chalcopyrite in a minute open tension crack in chalcopyrite-pyrrhotite-sphalerite ore; stope U 27, p 1, Outokumpu mine. CP = chalcopyrite, FeS (TETR) = the iron sulfide, SPH = sphalerite. Hand specimen. ×50.

[1] Since the present paper was submitted, Evans *et al.* (1962) have described the occurrence of a mineral, mackinawite, from the Mackinaw Mine, Snohomish County, Washington, whose structure and composition also appear to be very similar to and possibly identical with those of the iron sulfide from Outokumpu.
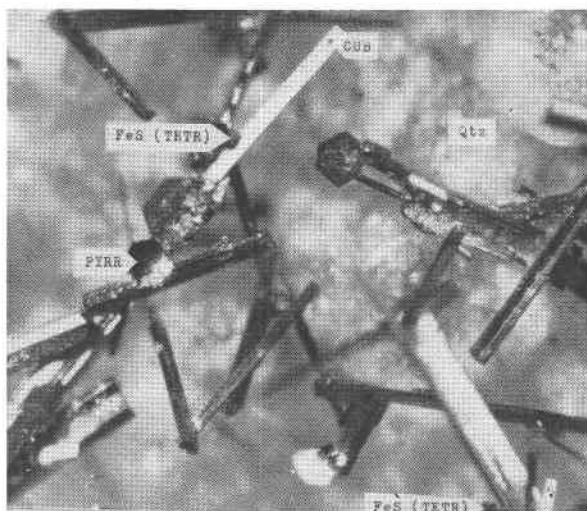
Fig. 2. Needles of cubanite embedded in quartz-serpentine crust of a tension opening in the Outokumpu mine (section 55, z about 290, N 38). CUB = cubanite, FeS (TETR) = the iron sulfide, Qtz = quartz, PYRR = pyrrhotite. Hand specimen. ×50.

chalcopyrite. However, grains which are probably of primary crystallization have also been found. In the Outokumpu mine the mineral has always been found in shear zones, if sulfides are visible. The most common modes of occurrence are described below.

1) Typically the mineral occurs in the Outokumpu serpentinite in which it replaces nickel pentlandite and can be distinguished in grains up to 1 mm in diameter; the mineral paragenesis usually is pyrrhotite—magnetite (in some cases with a core of chromite)—nickel pentlandite; approximately 7% nickel was found in grains studied by means of the microanalyser; samples for mineral separation from this rock were collected from the 320-level (section 71+20, Kp 4 and section 71, V-1) of the Outokumpu mine.

2) As idiomorphic crystals (Fig. 1), discovered in numerous minor open tension cracks (some 0.2×10–15 mm in size) in the Outokumpu chalcopyrite—pyrrhotite—sphalerite ore at about 20 cm from the contact with quartzite. These are closely related to needle-shaped cubanite crystals with some pyrrhotite, quartz, sphalerite (present in some cases as star-like bodies), galena and wurtzite (hexagonal crystals around cubanite needles).

3) Some larger open cracks, coated with a crust composed of secondary quartz and serpentine minerals in the Outokumpu mine (about 1.5 m from the contact of the ore), have also been found to be rich in tiny cubanite crystals with some nickel pentlandite, chalcopyrite, galena, tabular (hexagonal) crystals of pyrrhotite and idiomorphic crystals of the iron sulfide (Figs. 2, 3); microsamples studied by means of x-ray fluorescence did not show any cobalt or copper; nickel content of about 5% was found.

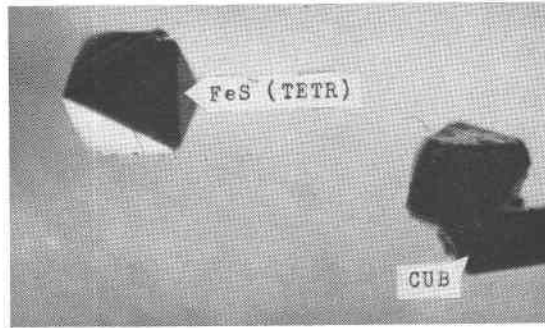4) In chalcopyrite and cubanite in chalcopyrite—cubanite—pyrrhotite assemblage, Outokumpu ore (Fig. 4).

FIG. 3. Enlargement of cubanite and the iron sulfide of FIG. 2. CUB=cubanite, FeS (TETR) = the iron sulfide. Immersed in alcohol under microscope. ×100.

5) Replacing cobalt pentlandite in pyrrhotite—cobalt pentlandite—chalcopyrite—cubanite assemblage (Fig. 5) in sample from a shear zone in the Outokumpu mine (285-level, Mpl 3, section 68+4). The cobalt content of this pentlandite is not known. However, a fraction of cobalt pentlandite from the same area showed 42.73 wt. % cobalt (Kouvo *et al.*, 1959).

6) Independent grains in hisingerite; mineral association: magnetite—hisingerite—pyrrhotite—cubanite; a shear zone in Outokumpu mine (D8 area, section 38+20, z about 295).
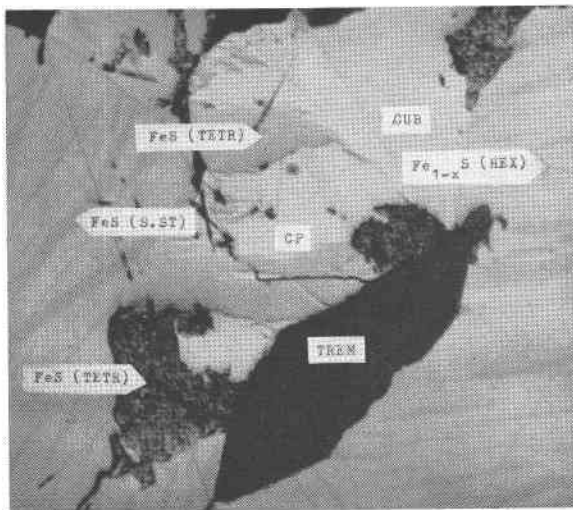

FIG. 4. Tetragonal iron sulfide, FeS (TETR), in chalcopyrite (CP) and cubanite (CUB). 285n9, Outokumpu. Lamellar phase in pyrrhotite, $Fe_{1-x}S$ (HEX), is composed of stoichiometric FeS (hexagonal superstructure). TREM = tremolite. Polished section. Color of the FeS-flames changed darker than pyrrhotite through oxidation. Appearance of FeS (TETR) varies in photomicrograph due to strong pleochroism. Nicols ‖. ×150.
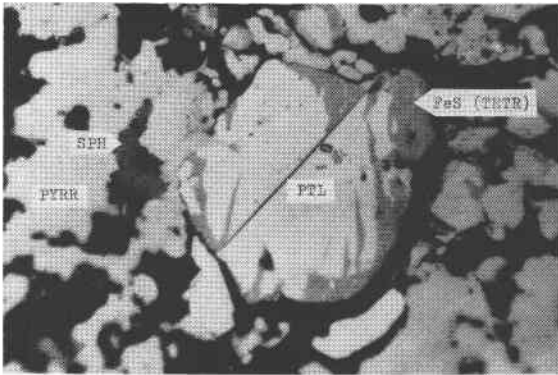
FIG. 5. Cobalt pentlandite replaced by the iron sulfide. PTL=cobalt pentlandite, PYRR=pyrrhotite, SPH=sphalerite. Sample from a shear zone in the Outokumpu mine (285-level, Mpl 3, section 68+4). Polished section. Nicols ||. ×400.

7) In chalcopyrite in chalcopyrite—cubanite—pyrrhotite—cobalt pentlandite assemblage, Varislahti ore.

8) Independent grains in magnetite with pyrrhotite, and in massive chalcopyrite with magnetite, pyrrhotite and native silver, Ylöjärvi ore.

9) Some sulfide droplets found in boulders of hornblende gabbro from Möhkö, Ilomantsi, are composed of chalcopyrite, pyrrhotite and nickel pentlandite; the iron sulfide also normally appears here in chalcopyrite or between chalcopyrite and pyrrhotite.

As shown above, the iron sulfide tends to occur with special relation to the pentlandites and to chalcopyrite and cubanite. It has also been identified in several other associations.

PROPERTIES

Macroscopically the crystal faces of this iron sulfide are tinged with bronze, but the fresh fracture surfaces are white-gray. Powdered material is black. The mineral is soft, being readily scratched by a needle. Crystals are usually tetragonal basal plates or simple pyramidal combinations with perfect basal cleavage (Figs. 1, 3). Typically grains are irregular in shape as shown in Fig. 4.

The optical properties are virtually identical with those given for valleriite in several descriptions. Under the microscope the mineral is easily recognized by strong pleochroism and anisotropy. On polished surfaces the properties have been found as follows:

Color: reddish gray (in air); internal reflections not found.

Pleochroism and anisotropy: very strong in gray to reddish (in air); undulatory extinction common.

Hardness: greater than that of pyrrhotite but lower than that of cobalt pentlandite rich in cobalt; Nomarski interference contrast equipment or simply diagonal illumination was used for observation.

Tests with chemical reagents (may be dependent on the chemical composition): HNO_3, HCl, $FeCl_3$, KCN, $HgCl_2$ negative, CrO_3+HCl slow reaction.

The mineral is weakly magnetic, and the associated pyrrhotite causes difficulty in obtaining a clean separation.

CHEMICAL COMPOSITION

Two samples of serpentinite from the 320-level (Kp 4, section $71+20$ and $V-1$, section 71) of the Outokumpu mine were collected for mineral separation.

To obtain sufficient material for quantitative analyses, the heavy fraction from a Denver shaking-table was floated using a laboratory scale flotation cell. Pentlandite was first removed from the other sulfides. In the next step the iron sulfide was floated with pyrrhotite. Magnetite was left among the silicates. The results were controlled by x-ray examination of the separated fractions. It was found that the iron sulfide was still collected after almost all pyrrhotite had been removed.

As mentioned earlier, the similarity in magnetic properties with pyrrhotite caused difficulty when a Frantz type isodynamic separator was used. The mineral was therefore concentrated after this stage by means of a home-made A.C. transformer-table and finally by hand picking. The remaining impurities were composed mainly of serpentine intimately crystallized with the iron sulfide, of inclusions of nickel pentlandite, and of some separate grains of chalcopyrite.

About 1.5 grams of the iron sulfide were obtained in this way from both of the samples collected for chemical analyses.

The chemical analyses yielded the results shown in Table 1. Unfortunately, the mineral fractions were not sufficiently pure to allow the normal analytical precision. The deficiencies in the totals are most probably due to the partial solubility of the impurities and to the water content of serpentine minerals crystallized with the mineral.

However, from these numbers one can conclude that the mineral in question is an iron sulfide. The polished sections prepared of the mineral powder showed that the copper originated from chalcopyrite and was not a considerable constituent of this mineral. On the other hand, micro-analyser work on the same material gave a nickel content of 7% thus confirming that the small inclusions of pentlandite were not important.

ELECTRON-PROBE ANALYSES

The two varieties of the iron sulfide which were analysed chemically were fairly similar and both rich in nickel. Since contamination of this material with other minerals could invalidate analyses for minor elements, electron-probe analyses were made on single grains in polished

TABLE 1. CHEMICAL ANALYSES OF THE IRON SULFIDE FROM
SERPENTINITE, OUTOKUMPU MINE

Analyst, Lasse Kosomaa, M.A.

		Wt.%		Atomic ratios	Wt.% —Cu	Atomic ratios and formula on basis of S=1.0000
		Orig.	Recalc.			
I.	Fe	50.40	55.94	1.0016	56.00	0.9112
	Ni	7.44	8.26	0.1407	8.28	0.1282 $M_{1.046}S$
	Co	0.38	0.42	0.0071	0.42	0.0065
	Cu	0.08	0.09	0.0014	—	
	S.	31.80	35.29	1.1005	35.29	$Fe_{0.91}Ni_{0.13}Co_{0.007}S$
	Insol.	4.60				
	Total	94.70	100.00		100.00	
II.	Fe	52.40	56.35	1.0090	56.37	0.9226
	Ni	7.60	8.17	0.1392	8.18	0.1274 $M_{1.056}S$
	Co	0.34	0.37	0.0062	0.37	0.0057
	Cu	0.05	0.05	0.0008	—	
	S.	32.60	35.06	1.0934	35.08	$Fe_{0.92}Ni_{0.13}Co_{0.006}S$
	Insol.	3.20				
	Total	96.19	100.00		100.00	

I. 320-level, section 71+20, Kp 4, Outokumpu mine.
II. 320-level, section 71, V-1, Outokumpu mine.

mounts of four specimens. These determinations, the results of which are shown in Table 2, were carried out using pure metals as standards; the electron beam accelerating voltage was 20kV. and the incident beam was normal to the surface of the specimen. X-rays were collected in a direction at 40° to the surface. The results quoted are corrected for absorption of the x-rays, but no correction has been applied for the effect of differences in atomic number between specimen and standard since the magnitude of such a factor appears at present to be uncertain. It is possible, but unlikely, that this omission could introduce an error of a few per cent in the overall metal content.

The close similarity of the observed concentrations of metal to those in the chemical analyses strengthens confidence in the latter and confirms that both cobalt and nickel can substitute in appreciable amounts, but that the content of copper is very low. The apparently low total metal content observed in the second and third analyses is not immediately explicable; it seems just possible that it is due to oxidation of the surface of the iron sulfide, which would have the effect of reducing the proportion of metal in the volume irradiated by the electron beam.

The comparatively large error quoted for the measurement of cobalt in the close intergrowth of the sulfide with cobalt pentlandite is the result of fluctuations introduced by finely disseminated pentlandite in the apparently uniform sulfide region. These small inclusions of the cobalt rich material can be seen in the scanning pictures (Fig. 6).

CRYSTALLOGRAPHY

Crystals of the iron sulfide found during this work range from some tens of microns to 1 mm in diameter. Most are subhedral and irregularly formed. However, some simple idiomorphic crystals have been found among the cubanite needles (Figs. 1–3). These crystals appear to be a combination of two tetragonal pyramids. The prism faces were not found.

The x-ray diffraction pattern obtained for the mineral with both nickel-filtered copper and manganese-filtered iron radiation are given in Table 3. By this means it was possible to elucidate the structural relationship to valleriite, pyrrhotites and smythite (Erd et al., 1957) in an early stage of this work. In the first paper (1959) it was pointed out that the powder pattern is close to that given for kansite (Meyer et al., 1957). Kansite, however, is cubic (F.C.).

To test the lattice, some single crystal photographs were taken using a crystal from the material shown in Figs. 2 and 3. This work was kindly done by Mr. A. Häkli, Lic, Phil., at the Geochemical Laboratory of the University of Helsinki using a Weissenberg camera and Ni-filtered

TABLE 2. ELECTRON-PROBE MEASUREMENTS ON IRON SULFIDE.
METAL CONTENTS IN WEIGHT PER CENT

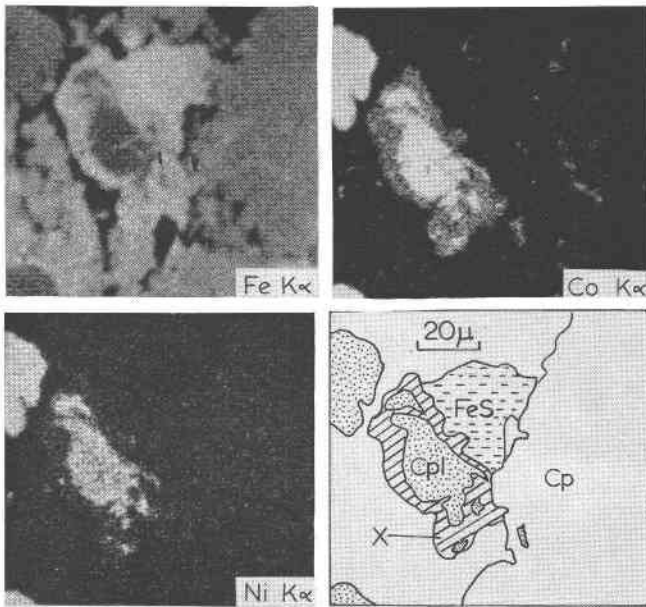| Specimen	Fe	Ni	Co	Cu	Total Metal (mean)
In chalcopyrite	63.2±2	0.2	0.2	<0.1	
Ylöjärvi deposit	64.7±2	0.2	0.2	<0.1	64.2
Idiomorphic crystals with magnetite and cubanite	58.9±2	0.5±0.2	0.2	<0.1	
Outokumpu ore	60.0±2	—	—	—	60.2
In chalcopyrite and cubanite (Fig. 4)	55.1±2	5.0±0.3	<0.2	<0.5	
Outokumpu ore	53.1±2	5.4±0.3	<0.2	<0.5	59.5
Replacing Co-pentlandite (Fig. 5 and 6) Outokumpu ore	—	1.9±0.2	10.7±1	—	—

Fig. 6. Scanning pictures obtained from electron-probe analyser showing distribution of iron, cobalt and nickel in intergrowth of cobalt pentlandite (Cpl) and the new sulfide (X) (Cp=chalcopyrite, FeS=pyrrhotite). The sulfide mineral X contains about 11% Co and about 2% Ni.

copper radiation and established the lattice as tetragonal, with the following cell constants:

$$a = 3.676 \pm 0.002 \text{ Å}$$
$$c = 5.032 \pm 0.002 \text{ Å}$$

Unit cell: primitive tetragonal (probably P_4/nmm)

Values for the lattice parameters (a and c) are valid in this case for a material having about 5% nickel.

HEAT TREATMENTS

Preliminary heat treatments of portions of the same material used for analysis I (Table 1) were carried out in an open crucible in a muffle furnace. Examination of the x-ray powder patterns and some polished sections showed the following results:

1. 40 min. at 200° C., no changes found in the iron sulfide.
2. 40 min. at 210° C., new phase appeared yielding a hexagonal pyrrhotite x-ray pattern; traces of strongest lines of the iron sulfide still visible.
3. 40 min. at 230° C., lines of the iron sulfide not found; only pyrrhotite visible.
4. 40 min. at 250° C., specimen still homogeneous pyrrhotite.
5. 40 min. at 300° C., specimen still homogeneous pyrrhotite.

6. 40 min. at 350° C., this product after similar heat treatment at 350° C. showed an additional faint line at 2.50 Å (probably due to some magnetite among pyrrhotite).

In connection with differential thermal analyses of various sulfides at the Bureau of Mineral Research, Rutgers University, some thermograms were also obtained from this iron sulfide. The work was kindly undertaken by Mr. William Lodding of Rutgers University.

Results from the DTA of this iron sulfide are as follows:

| | In nitrogen | | | In vacuum | |
peak	°C.	cal./g.	peak	°C.	cal./g.
exo	130	vw	exo	160	0.02
endo	245	1.50	endo	245	1.50
endo	630	vw	endo	620	0.30
			endo	830	vw
endo	990	w	endo	980	w

Laboratory numbers of Rutgers for these runs are 1583 and 1588 respectively. Materials were not x-rayed before or after the run.

TABLE 3. X-RAY POWDER DATA FOR THE IRON SULFIDE FROM T 35 AREA, OUTOKUMPU MINE

hkl	d_{obs}(Å)	d_{calc}(Å)	I
001	5.03	5.03	vs
101	2.97	2.97	s
110	2.60	2.60	vw
111	2.31	2.31	s
200	1.838	1.838	m
112	1.808	1.808	s
201	1.725	1.727	m
003	1.674	1.676	w
211	1.562	1.563	mw
103	1.524	1.526	w
113	1.409	1.409	w
220	1.300	1.300	mw
004	1.258	1.258	mw
203	1.240	1.239	w
301	1.190	1.190	vw
213	1.174	1.174	vw
311	1.133	1.133	mw
312	1.055	1.055	ms
204	1.037	1.038	B
223	1.027	1.027	B
214	1.000	0.999	B
303	0.989	0.989	B

Intensities by visual estimate. Calibrating substance: silicon. Camera and goniometer technique. Faint line at 2.50 Å possible.
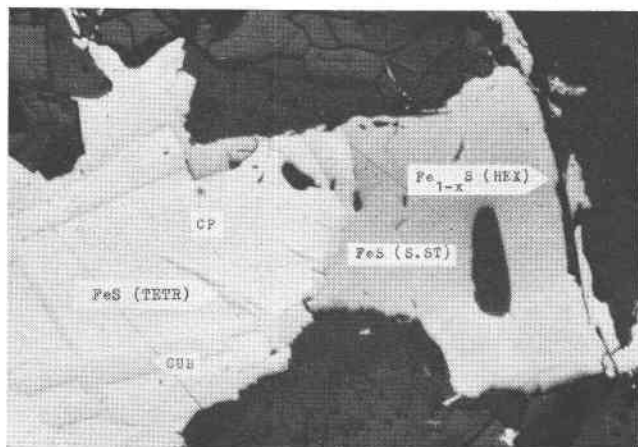
FIG. 7. Stoichiometric FeS (hexagonal superstructure) rimmed by pyrrhotite, $Fe_{1-x}S$ (HEX). Stope D8, Outokumpu. Polished section. CP=chalcopyrite; CUB=cubanite; FeS (S.ST)=stoichiometric FeS; FeS (TETR)=the tetragonal iron sulfide. Color of the stoichiometric FeS changed darker than that of pyrrhotite through oxidation. Nicols ∥. ×150.

As indicated above, serpentine minerals were the most plentiful impurities found in the material used for chemical as well as for the DTA measurements. Hence, the endotherms at 620, 630° C. and at 980, 990° C. are probably due to silicates.

According to the preliminary heat treatments mentioned above, the endotherm at 245° C. is most probably due to the phase transformation in the iron sulfide. The exotherms at 130 and 160° C. are just above the limit of detection.

UNMIXING TEXTURES IN HEXAGONAL FeS

In several occurrences, the associated pyrrhotite exhibits an unmixing texture, flame-like lamellae (Fig. 4) or zoning (Fig. 7). This texture, common in nature, has been studied in some detail in another connection (Kouvo and Vuorelainen, 1962). The results will be repeated briefly here.

The lamellar phase in pyrrhotite, $Fe_{1-x}S$, was found to be composed most commonly of FeS of stoichiometric composition. However, the reverse association, lamellae of iron deficient pyrrhotite, $Fe_{1-x}S$, in a matrix of stoichiometric FeS, was not uncommon. In addition to these modes of occurrence, grains of FeS of stoichiometric composition were noted to be rimmed by pyrrhotite, $Fe_{1-x}S$ (frequently barely ∥(0001)). In addition, grains composed only of FeS at stoichiometric composition were found in the Outokumpu ore.

In polished section the stoichiometric FeS is lighter in color and softer

than pyrrhotite, $Fe_{1-x}S$, but turns darker in an oxidized surface (Figs. 4, 7).

As a result of powder diffraction studies and chemical analyses, a hexagonal superstructure was found for materials containing iron as follows: $Fe_{1.009}S$ (single phase), $Fe_{1.001}S$ (single phase) and $Fe_{1.000}S$ rimmed by $Fe_{1-x}S$).

Heating of tetragonal FeS yielded FeS of normal hexagonal structure.

The cell dimensions of FeS and $Fe_{1-x}S$ of various compositions were examined in detail. The d(102) values for pyrrhotites deficient in iron correspond well to those given by Arnold and Reichen (1962). The values of the cell dimensions for FeS at or near the stoichiometric composition are somewhat larger than 2.091_5 Å given for true FeS: $Fe_{1.009}S$ gave 2.094_6, 2.094_0 and 2.094_2 Å (using various standards); $Fe_{1.000}S$, 2.098_7 and 2.097_9 Å; $Fe_{1.001}S$, 2.094_7 and 2.094_6 Å. A value of 2.098_6 Å was obtained for FeS from the Porvoo meteorite (normal hexagonal structure B-8). The measurements were made with a Norelco diffractometer using the technique described by Holland *et al.* (1955) (except settling). A camera technique was also used. The reflections were measured relative to silicon and industrial diamond dust, the standards being checked against CaF_2. The final values are the average of five measurements.

CONCLUSIONS

1. Crystal structure data, lattice studies, chemical data and some heat treatments have all led to the conclusion that the iron sulfide as described above is a distinct mineral.

2. Single crystal films yielded the lattice dimensions $a = 3.676 \pm 0.002$ Å and $c = 5.032 \pm 0.002$ Å and space group probably P_4/nmm. The differences between the valleriite structure and that of this iron sulfide on the basis of x-ray investigation led to separation of these two minerals, which show a close optical relationship. On the other hand, the analogy of the kansite structure with that of this iron sulfide has been pointed out.

3. The isomorphous substitution accompanying the introduction of nickel, cobalt and possibly copper, is confirmed by examination by the x-ray microanalyser. The formula, arrived at by wet chemical analyses represents a variety of $Fe_{0.91}Ni_{0.13}Co_{0.007}S$ showing a metal/sulfur ratio of about 1.05. Sulfur content 35.1–35.3% was found.

4. The mineral has been found to replace nickel- and cobalt pentlandites, chalcopyrite and cubanite. The single crystals on the walls of open cracks suggest the possibility of an alternative mode of occurrence as a primary mineral. The idiomorphic crystals from tension openings and from minute tension cracks have been found with needle shaped cubanite,

hexagonal pyrrhotite, chalcopyrite, quartz, galena and wurtzite. Some starlike sphalerites were found in the same association.

5. Results of x-ray and microscopic examination and chemical analyses of some associated pyrrhotites indicated that the flame-like unmixing texture is composed of stoichiometric FeS lamellae in pyrrhotite, $Fe_{1-x}S$, or vice versa, of $Fe_{1-x}S$ lamellae in a matrix composed of true FeS. Crystals of stoichiometric FeS were found in the Outokumpu ore and some of these appeared to be rimmed by iron-deficient $Fe_{1-x}S$.

ACKNOWLEDGMENTS

REFERENCES

ARNOLD, R. G. AND LAURA E. REICHEN (1962) Measurement of the metal content of naturally occurring, metal-deficient, hexagonal pyrrhotite by an x-ray spacing method. *Am. Mineral.* **47,** 105.

BARTHOLOMÉ, PAUL (1958) On the paragenesis of copper ores. *Studia Univ. "Lovanum",* *Fac. Sci.* 4. Editions de L'Universite, Leopoldville.

BERNER, R. A. (1962) Tetragonal FeS, a new iron sulfide. *Science,* **137,** 669.

BIRKS, L. S., E. J. BROOKS, I. ADLER, AND CHARLES MILTON (1959) Electron probe analysis of minute inclusions of a copper-iron mineral. *Am. Mineral.* **44,** 974–978.

ERD, RICHARD C., HOWARD T. EVANS, JR. AND DONALD H. RICHTER (1957) Smythite, a new iron sulfide, and associated pyrrhotite from Indiana. *Am. Mineral.* **42,** 309–333.

EVANS, HOWARD T., ROBERT A. BERNER AND CHARLES MILTON (1962) Valleriite and mackinawite (abs.) 1962 *Ann. Meet. Geol. Soc. Am.,* Houston, Texas.

HOLLAND, H. D., W. B. HEAD, III, G. G. WITTER, JR. AND G. B. HESS (1955) A new method for mounting samples for powder x-ray spectrometry. *Am. Mineral.* **40,** 761.

KOUVO, OLAVI AND YRJÖ VUORELAINEN (1959) Valleriitista. *Geologi* **11,** 32–33; *Mineral. Abs.* **14,** 162.

———— MAIJA HUHMA AND YRJÖ VUORELAINEN (1959) A natural cobalt analogue of pentlandite. *Am. Mineral.* **44**, 897–900.

———— AND YRJÖ VUORELAINEN (1962) Magneettikiisun kokoomuksesta ja rakenteesta. *Geologi* **14**, 79.

MEYER, F. H., R. L. RIGGS, McGLASSON AND J. D. SUDBURY (1957) Corrosion products of mild steel in hydrogen sulfide environments. *Corrosion* **14**, 109t–115t.

MILTON, CHARLES AND DANIEL J. MILTON (1958) Nickel-gold ore of the Mackinaw mine, Snohomish county, Washington. *Econ. Geol.* **53**, 426–447.

RAMDOHR, P. AND O. ÖDMAN (1932) Valleriit. *Geol. Fören Förhandl.* **54**, 89–97.

SCHNEIDERHÖHN, H. (1929) Erzmikroskopische und spektrographische Untersuchung von Platinführenden Nickel-Magnetkiesgesteinen des Bushveld Igneous Complex, Transvaal. *Chemie Erde* **4**, 252–286.