Article 133

VALLERIITE AND THE NEW IRON SULFIDE, MACKINAWITE

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Abstract.—Valleriite from Loolekop, South Africa, and Kaveltorp, Sweden, is rhombohedral, space group $R3m$ or $R\bar{3}m$, with $a=3.792$ A, and $c=34.10$ A, and its probable unit-cell content is $6CuFeS_2$. Mackinawite, a new copper-free iron sulfide from the Mackinaw mine, Snohomish County, Wash., is tetragonal, space group $P4/nmm$, with $a=3.679$ A, $c=5.047$ A, and a unit-cell content of $2FeS$. Both minerals evidently have layer structures, in accord with their extreme optical anisotropy. Many occurrences of mackinawite have probably been mistaken for valleriite.

Few minerals have caused mineralogists more justified uncertainty or unsound assurance than the sulfide valleriite. Since its discovery at Nya Kopparberg, Sweden, by Blomstrand (1870) almost a century ago, it has led an uneasy life in the mineralogical literature. Its first description was encumbered with a complex and implausible proposal for composition, which led Petrén (1898) to reject the work of Blomstrand and consign the mineral to the limbo of species discredited as mixtures. It was revived by Ramdohr and Ödman (1932) on the basis of a restudy of the Swedish material already described by Blomstrand and Petrén. Only recently has the existence been suspected of another distinct sulfide phase occurring in mineral assemblages similar to those which contain valleriite (Milton and Milton, 1958; Kouvo and Vuorelainen, 1959). This new phase, which we designate mackinawite, is so similar in physical properties to valleriite that it has evidently been the object of a great deal of confusion. In this article we present new data for valleriite and descriptive data for a previously undefined mineral which we call mackinawite; and we take note of the difficulties that have arisen from confusion of the two minerals.

NEW DATA FOR VALLERIITE

We have not had available Blomstrand's type material from Nya Kopparberg, but our specimen from

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Kaveltorp, described in detail by Ödman (1933), is closely similar. The apparently homogeneous bronzy graphitic mineral gives a characteristic powder pattern, but attempts to obtain single-crystal patterns from tiny flakes yielded such poor information that a unit cell could not be deduced. Fortunately, new material of much better quality from Loolekop in northeast Transvaal, South Africa, recently became available to us through the courtesy of L. R. Page, of the U.S. Geological Survey. The mineral occurrence, in small pea-sized masses in carbonate rock associated with other iron-copper sulfides, is quite like that of the Swedish mineral, but the crystal flakes are generally larger and better formed. The chemical composition is entirely analogous to that found for the Kaveltorp material, and to that given by Blomstrand (see table 133.1), showing again the anomalous presence of about

TABLE 133.1.—*Chemical analyses of valleriite*

Constituent	Sample			
	1	2	3	4
Cu	17.7	17.6	19.8	18.6
Fe	26.3	21.2	20.0	21.1
S	22.5	21.4	21.6	21.3
Al_2O_3	5.1	8.1	8.5	-------
MgO	10.6	16.2	16.0	-------
CaO	0.3	1.7	1.3	-------
K_2O	0.3	------	------	-------
Na_2O	0.6	------	------	-------
H_2O	10.8	12.2	10.8	-------
Insoluble + SiO_2	------	1.8	3.3	-------
Total	94.2	100.2	101.3	-------

1. Nya Kopparberg, Sweden; Blomstrand (1870), from 5 partial analyses.
2. Kaveltorp, Sweden; Blanche Ingram, analyst; MnO, 0.5 percent.
3. Loolekop, South Africa; Blanche Ingram, analyst; MnO, 0.5 percent.
4. Theoretical for $CuFeS_2$, corresponding to 61.0 percent of total.

the same amount of aluminum and magnesium hydroxides together with iron, copper, and sulfur. The characteristic X-ray powder-diffraction pattern, shown in table 133.2, conclusively establishes the identity

TABLE 133.2.—*X-ray powder-diffraction data for valleriite*

Calculated [1]		Loolekop [2]		Kaveltorp [2]		Kaveltorp [3]	
hkl	d(A)	d(A, obs.)	I	d(A, obs.)	I	d(A, obs.)	I
00.3	11.367	11.39	10	11.48	9	11.5	10
00.6	5.683	5.71	10	5.68	10	5.75	10
00.9	3.789	3.80	5	-----	--	3.83	8
10.1	3.269	3.27	6	3.27	7	3.29	10
10.$\overline{2}$	3.225	3.23	5	-----	--	3.23	8
10.4	3.064	3.07	2	-----	--	3.08	2
10.$\overline{5}$	2.959	2.958	1	2.974	1	-----	--
00.12	2.842	2.846	5	2.842	5	2.87	8
10.7	2.723	-----	--	-----	--	-----	--
10.$\overline{8}$	2.601	2.604	1				
-----	-----			2.531	3	2.48	2
10.10	2.365	2.346	2	2.364	1	2.37	8
00.15	2.273	-----	--	2.275	6	2.29	8
10.$\overline{11}$	2.254	2.259	2	-----	--	-----	--
10.13	2.050	2.041	2	-----	--	2.05	6
10.$\overline{14}$	1.956	-----	--	-----	--	-----	--
11.0	1.896	-----	--	-----	--	1.91	10
00.18	1.894	1.885	5	1.894	6	1.90	10
11.3	1.870	1.860	5	1.870	5	1.87	10
11.6	1.799	-----	--	-----	--	-----	--
10.16	1.788	1.780	1	1.794	1	1.80	8
10.$\overline{17}$	1.712	-----	--	-----	--	-----	--
11.9	1.696	-----	--	-----	--	-----	--
20.$\overline{1}$	1.640	-----	--	-----	--	-----	--
20.2	1.634	-----	--	1.636	1	1.64	4
00.21	1.624	1.629	1	1.620	1	-----	--
20.$\overline{4}$	1.612	-----	--	-----	--	-----	--
20.5	1.596	-----	--	-----	--	1.59	6
11.12	1.577	-----	--	-----	--	-----	--
10.19	1.575	-----	--	-----	--	-----	--
20.$\overline{7}$	1.556	-----	--	-----	--	-----	--
20.8	1.532	1.526	1	1.534	2	1.54	6
10.$\overline{20}$	1.513	-----	--	-----	--	1.52	2
20.$\overline{10}$	1.479	-----	--	1.485	1	1.50	2
11.15	1.456	-----	--	-----	--	1.47	2
20.11	1.451	-----	--	-----	--	-----	--
-----	-----	-----	--	-----	--	1.23	2
-----	-----	-----	--	-----	--	1.22	3
-----	-----	-----	--	-----	--	1.14	4
-----	-----	-----	--	-----	--	1.09	4
-----	-----	-----	--	-----	--	1.06	6
-----	-----	-----	--	-----	--	1.04	10
-----	-----	-----	--	-----	--	1.03	10
-----	-----	-----	--	-----	--	1.01	10

[1] Calculated for unit cell given in table 3.
[2] Patterns made by the authors with FeKα radiation, camera diameter 114.6 mm. Intensities are on a geometric scale.
[3] Data from Hiller (1939).

TABLE 133.3.—*Unit-cell data for valleriite, smythite, and mackinawite*

Property	Mineral species		
	Valleriite [1]	Smythite [2]	Mackinawite [3]
Crystal system.	Rhombohedral	Rhombohedral	Tetragonal
Space group__	$R\overline{3}m$ or $R3m$	$R\overline{3}m$	$P4/nmm$
a (A)_____	3.792±0.005	3.47	3.673±0.001
c (A)_____	34.10±0.05	34.5	5.035±0.002
Cell content	$6CuFeS_2$	$3Fe_3S_4$	$2FeS$
Density (X-ray).	4.26	4.09	4.30
Density (measured).	3.14	4.06	------------

[1] Loolekop, South Africa; unit cell derived from least-squares analysis of first 12 d-spacings of data for Loolekop material, table 133.2; density from Blomstrand (1870).
[2] Bloomington, Ind.; Erd and others (1957).
[3] Synthetic, Berner (1962); parameters derived by least-squares analysis of Berner's diffraction data as shown in table 133.4.

of the South African and Swedish minerals. The powder-diffraction data given by Berry and Thompson (1962) for Kaveltorp valleriite agrees well with that obtained by us.

Single flakes isolated from specimens from Loolekop, South Africa, were studied with the Buerger precession camera in an attempt to obtain single-crystal diffraction patterns. The best photographs were readily interpreted in terms of a rhombohedral unit cell with the properties shown in table 133.3. The similarity in symmetry and dimensions of the valleriite unit cell to that of the recently described iron sulfide, smythite, is striking and significant, although the character of diffraction-intensity distribution on the single-crystal patterns precludes any type of isostructural relationship. The crystallographic studies of Hiller (1939) are not supported by these findings. On the basis of powder

data alone, which correspond well with ours (table 133.2), he deduced an orthorhombic unit cell and even a crystal structure for valleriite. Evidently, his overextended hypotheses need not be further considered.

The crystal structure of valleriite is not yet known, but its crystallography places severe restrictions on its constitution. Just as in smythite, the space-filling sulfur atoms must lie on the threefold symmetry axes, and the hexagonal unit cell is sufficiently large to contain three S_4 units. Accordingly, the c axis length of 34.3 A corresponds to 12 layers of sulfur atoms in closest packing. Further, it is readily deduced that not less than 3 nor more than 4 cations also lie on the threefold axes. This reasoning leads us to the possible formulas: $CuFe_2S_4$, Cu_2FeS_4, and $Cu_2Fe_2S_4$. The chemical analyses, apart from the magnesium and aluminum hydroxides, conform closely with the last. Thus it appears most probable that valleriite is a dimorph of chalcopyrite, $CuFeS_2$.

All single-crystal patterns of valleriite show the presence of a second, much weaker lattice originating from some other phase. This lattice is also rhombohedral, with a hexagonal a axis of about 3.0 A. Its smaller dimension corresponds well to that expected of an oxide compound of some sort. There is little doubt that this lattice is to be associated with the magnesium and aluminum hydroxides which have always appeared in chemical analyses of valleriite. Evidently these hydroxides correspond to a foreign mineral phase, hexagonal or rhombohedral in crystal character, interleaved in syntactical orientation on a submicroscopic scale with the valleriite. The identity of this foreign phase and its genetic relationship to valleriite remain a mystery.

MACKINAWITE

Recently, Milton and Milton (1958) described the occurrence of a sulfide mineral from the Mackinaw

mine in Snohomish County, Wash., which they identified as valleriite, mainly on the basis of its physical properties. The identification was tentative, and the doubt which arose late in their study was explained in a footnote:

Preliminary studies in progress by C. Milton, E. C. T. Chao and H. T. Evans, Jr. indicate that the mineral identified as valleriite is this paper is, in fact, distinct from the type valleriite from Kaveltorp, Sweden. The Mackinaw mineral is probably an undescribed iron sulfide, the Kaveltorp valleriite is perhaps a copper-iron-magnesium sulfide. Probably both these phases, if not others also, are to be found among material from other localities that has been called valleriite.

Both valleriite and mackinawite are extremely anisotropic and strongly reflection pleochroic. This feature is so outstanding that ore microscopists for many years have frequently labelled phases as "valleriite" on the basis of its anisotropism alone. We have observed that the pleochroism differs slightly between the two, valleriite appearing pale yellow to deep creamy brown (Skinner and Milton, 1955), while mackinawite shows a pale pink to pinkish gray color.

The existence of a mineral different from valleriite was first definitely suspected when enough powder was successfully isolated from a chalcopyrite matrix by means of an ultrasonic vibrating needle (Kehl and others, 1957) to obtain a characteristic X-ray diffraction pattern. The pattern showed that a large amount of chalcopyrite and a small amount of cubanite were still present in the sample, but when the characteristic reflections for these minerals were discounted, 14 reflections remained to be associated with the new phase, as shown in table 133.4. These d-spacings bore no relation to those of valleriite.

Examination of individual grains of the mineral in a polished section with an electron-microprobe apparatus by Birks and others (1959) showed that the copper content is very low and that the composition of the mineral is approximately FeS. This finding has been confirmed by new analyses with the electron-probe apparatus in our laboratory. Figure 133.1 (upper left) shows a polished section of ore from the Mackinaw mine containing feathered inclusions of mackinawite, which show as gray regions in the light-gray chalcopyrite matrix. Dark round spots indicate points probed by the electron beam and analyzed by X-ray spectroscopy. Copper was not detected, and on the basis of 16 determinations the following composition was determined by the authors:

	Measured (weight percent)	Theoretical ($Fe_{0.96}Ni_{0.04}S$)
Fe	63±5	60.5
Ni	3.1±0.5	3.0
S	34±4	36.4

The determinations were made by comparison with

TABLE 133.4.—*X-ray powder-diffraction data and unit-cell parameters for mackinawite*

Least-squares parameters:[5]		Synthetic [1]		Mackinaw mine [2]		Outokumpo [3]		"Kansite" [4]	
a		3.673±0.001		3.675±0.002		3.6773±0.003			
c		5.035±0.002		5.030±0.003		5.0217±0.0007			
hkl	d(A,calc.)[6]	d(A,obs.)[6]	I	d(A,obs.)	I	d(A,obs.)	I	d(A,obs.)	I
001	5.035	5.035	100	5.03	100	5.020	VS	5.05	50
101	2.967	2.97	80	2.96	70	2.966	S	2.99	50
110	2.597	2.60	20	-----	---	2.600	VW	----	---
002	2.518	-----	---	-----	---	-----	---	----	---
111	2.308	2.305	80	2.31	90	2.309	S	2.32	100
102	2.077	-----	---	-----	---	-----	---	----	---
200	1.8365	1.835	60	1.838	50	1.838	M	----	---
112	1.8077	1.805	80	1.809	80	1.806	S	1.80	100
201	1.7253	1.723	60	1.729	50	1.726	M	1.73	50
003	1.6784	1.677	20	-----	---	1.674	W	----	---
211	1.5616	1.564	40	1.564	20	1.563	MW	1.54	10
103	1.5265	1.527	20	-----	---	1.523	W	----	---
202	1.4837	-----	---	1.481	20	-----	---	----	---
113	1.4096	1.410	30	1.410	30	1.408	W	1.42	30
212	1.3757	-----	---	-----	---	-----	---	----	---
220	1.2986	1.298	50	-----	---	1.300	MW	1.31	50
004	1.2588	1.258	50	1.257	35	1.259	MW	1.26	50
221	1.2574	-----	---	-----	---	-----	---	----	---
203	1.2389	1.239	30	1.237	30	1.238	W	----	---
104	1.1908	1.190	10	-----	---	1.191	VW	----	---
301	1.1897	-----	---	-----	---	-----	---	----	---
213	1.1739	1.174	20	-----	---	1.173	VW	----	---
310	1.1615	-----	---	-----	---	-----	---	----	---
222	1.1541	-----	---	-----	---	-----	---	----	---
114	1.1327	1.133	50	1.132	35	1.133	MW	----	---
311	1.1318	-----	---	-----	---	-----	---	----	---
302	1.1010	-----	---	-----	---	-----	---	----	---
312	1.0547	1.055	80	1.055	40	1.055	MS	----	---
204	1.0383	-----	---	1.038	20	1.040	B	----	---
223	1.0271	-----	---	-----	---	1.027	B	----	---
005	1.0070	-----	---	-----	---	-----	---	----	---
214	.9991	-----	---	-----	---	.9994	B	----	---
321	.9985	-----	---	-----	---	-----	---	----	---
303	.9891	-----	---	-----	---	-----	---	----	---

[1] Berner (1962).
[2] Measured by E. C. T. Chao on material removed from chalcopyrite matrix with an ultrasonic needle; 13 reflections due to chalcopyrite and 5 due to cubanite are omitted. FeKα radiation, 114.6-mm-diameter camera.
[3] Kouvo and others (1963). V=very strong, S=strong, M=medium, W=weak, B=broad.
[4] Artificial product, measured by Meyer and others (1958); ASTM powder data file No. 7-26.
[5] Unit-cell parameters and standard deviations calculated from the powder-diffraction data by least-squares analysis.
[6] d-spacings calculated for the unit cell found for Berner's synthetic FeS, assuming the space group $P4/nmm$.

analyzed pyrite, pyrrhotite, and pentlandite as primary standards. Accuracy was limited by the small size of the grains, which are only a little larger than the electron beam, and the difficulty of obtaining quite plane surfaces on the relatively soft mackinawite. It is apparent that the determined composition is not significantly different from that corresponding to the formula, $(Fe_{0.96}Ni_{0.04})S$.

The key distinguishing characteristic of this mineral, namely, its X-ray powder-diffraction pattern, was soon found to resemble that of an artificial iron sulfide labelled "kansite" by Meyer and others (1958). This substance was identified by its X-ray pattern in the corrosion product caused by the action of hydrogen sulfide on pipeline steel. It could not be isolated for ordinary chemical and physical tests, but it did yield a rather diffuse X-ray pattern of 10 measurable lines (see table 133.4). These matched approximately the recorded pattern for pentlandite, and Meyer and others derived from it a cubic unit cell with $a=10.1$ A. Following this lead, they suggested a composition of Fe_9S_8 for this phase, by analogy with pentlandite. Our X-ray data (table 133.4) showed a close relationship
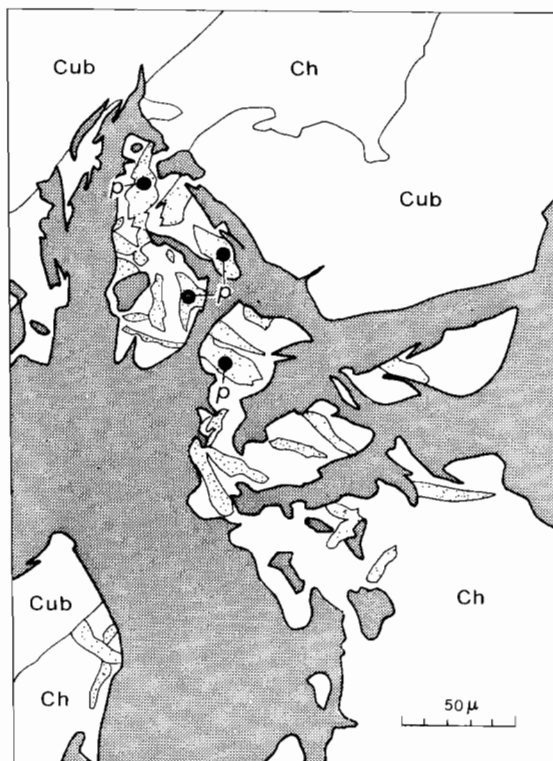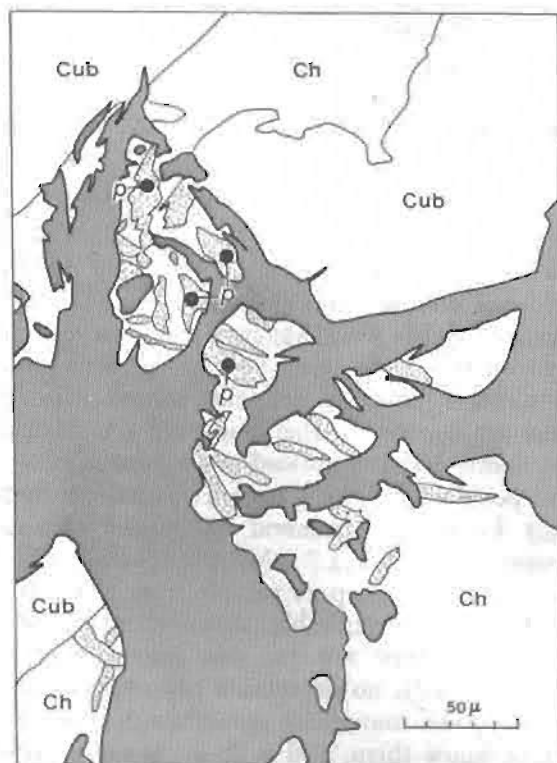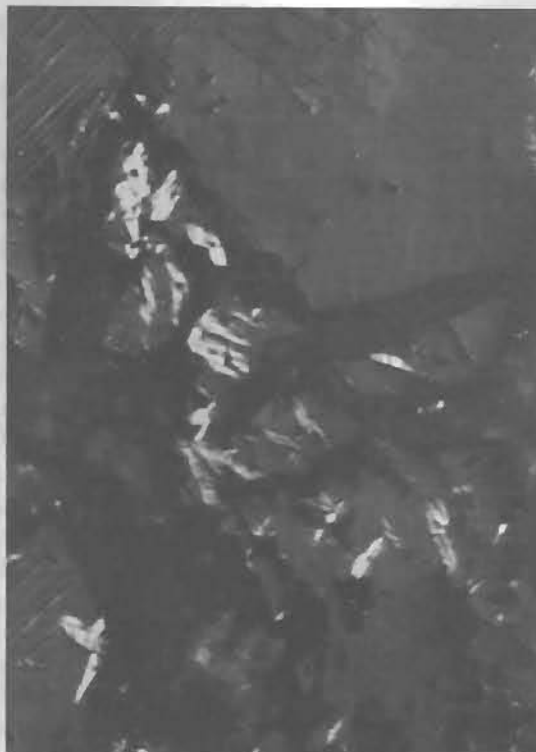
FIGURE 133.1.—Polished section showing mack-inawite from the Mackinaw mine, Snohomish County, Wash. The upper left view (plain light) shows cubanite (Cub in lower left drawing) as medium gray, chalcopyrite (Ch) as light gray, and the silicate gangue as black. The mackinawite in the chalcopyrite appears as dark-gray streaks that are brightly illuminated between crossed nicols, as shown in the upper right view. Four mackinawite areas probed by the electron beam are shown by p in the lower left drawing and as black-stained spots in the upper left view.

FIGURE 133.1.—Polished section showing mack-inawite from the Mackinaw mine, Snohomish County, Wash. The upper left view (plain light) shows cubanite (Cub in lower left drawing) as medium gray, chalcopyrite (Ch) as light gray, and the silicate gangue as black. The mackinawite in the chalcopyrite appears as dark-gray streaks that are brightly illuminated between crossed nicols, as shown in the upper right view. Four mackinawite areas probed by the electron beam are shown by p in the lower left drawing and as black-stained spots in the upper left view.

with "kansite," but on the other hand it was certain that the Mackinaw mine iron sulfide could not be cubic because of its high anisotropy in polished section (fig. 133.1, upper right).

Meanwhile, Kouvo and Vuorelainen (1959) published a short paper describing a new iron sulfide mineral resembling vallerite but distinct from it. They list the X-ray diffraction data obtained from this mineral, consisting of 23 lines (table 133.4). These contain the lines found by us for the Mackinaw mineral and also, as they noted, for "kansite," as well as many other lines. They found the mineral in chalcopyrite assemblages, showing strong pleochroism and very strong optical anisotropy, quite analogous to the Mackinaw mineral. Evidently, Kouvo and Vuorelainen were able to prepare pure samples from which they could obtain sharper and stronger X-ray patterns than we have been able to get.

Subsequently, evidence for the formation of an iron sulfide phase in the sediments of the Mystic River, Boston, Mass. was found by Berner (1962). He noted that this phase, as identified by its X-ray diffraction pattern, is the same as one which he prepared synthetically by the action at room temperature of an aqueous solution of H_2S on reagent-grade iron wire in the absence of air. The pattern corresponds well with those of the Mackinaw mine and Outokumpo minerals, and "kansite." Berner discovered that all these patterns can be quite satisfactorily indexed on the basis of a primitive tetragonal unit cell with parameters which he gave as $a=3.679\pm0.002$ A and $c=5.0471\pm0.002$ A. It was found that this crystallography closely resembled that described by Hägg and Kindström (1933) for FeSe, for which they determined the crystal structure. Berner further showed that a similar structure for tetragonal FeS yielded calculated diffraction intensities which agreed well with those observed for the natural and artificial iron sulfide phase. Thus, the key to the constitution of these phases is provided.

Kouvo and others (1963) have now described their study of the new iron sulfide in detail, based on beautifully crystallized material associated with cubanite, pyrrhotite, and chalcopyrite from Outokumpo and other Finnish localities. Single crystals up to 1 mm in size allowed these authors to determine the unit-cell dimensions and symmetry by the Weissenberg method. They found a tetragonal unit cell in the probable space group $P4/nmm$, with parameters which they reported as $a=3.676\pm0.002$ A and $c=5.032$ A.

Kouvo and others (1963) also were able to obtain good chemical and electron-probe analyses leading to a formulation $(Fe_{0.91}Ni_{0.13}Co_{0.007})S$, with no Cu present. The slight departure from stoichiometry is also reminiscent of the behavior of other iron sulfide phases. The close correspondence between the chemical and physical data given by Kouvo and others for their "tetragonal iron sulfide" and those found by us for the Mackinaw material leaves no doubt that the two are the same mineral. We have named the mineral "mackinawite" in allusion to the locality name. Dr. Olavi Kouvo, who gave the first clear description of this new mineral (Kouvo and others, 1963), has generously agreed to this choice of name.

The X-ray powder-diffraction data given by Berner for synthetic iron sulfide and by Kouvo and others for the Mackinaw mine material are given in table 133.4. We have subjected all these data to least-squares analysis in order to find the best unit-cell parameters for each set. For this purpose we have used a new self-indexing computer program written for our Burroughs B220 digital computer, which extracts the standard deviations of the parameters from the inverse matrix of the normal equations based on the residuals of the measured 2θ angles. These unit-cell parameters and standard deviations are shown at the beginning of table 133.4. The result for Berner's data is given in table 133.3 to represent the pure FeS phase. The differences between the cell parameters as we found them and the published values are hardly significant. The variation in the three sets of cell parameters doubtless reflects the influence of the substitution of varying amounts of Ni for Fe, but the data available now are not sufficient to define this variation quantitatively.

CONFUSION OF VALLERIITE AND MACKINAWITE

To the ore microscopist, the outstanding characteristic of both valleriite and mackinawite is their extreme anisotropism. Ramdohr and Ödman (1932) in their restudy of Blomstrand's material evidently considered the evidence of this striking anisotropism to be more significant than the available chemical information and assumed on this basis that the material was identical with a mineral found by Schneiderhöhn (1929) in the platinum-ore deposits of the Transvaal. In his careful studies, Schneiderhöhn noticed in sections of chalcopyrite and pentlandite, lamellar or irregular inclusions of a highly birefringent mineral, which he termed an "unbekanntes Nickelerz." Most important, he was able to isolate enough pure sample from a pentlandite matrix for a spectrographic analysis, which showed that the anisotropic mineral was primarily an iron-nickel sulfide, with no detectable copper. All aspects of his description match the properties of mackinawite as we now know them, and it seems entirely probable that mackinawite is actually the mineral he describes in "Lehrbuch der Erzmikroskopie" (Schneiderhöhn and Ramdohr, 1931), without mentioning the Swedish mineral, and without giving it a name. Ramdohr, in subse-

quent editions of his "Die Erzmineralien" (Ramdohr, 1960), combined the information about the South African and Swedish occurrences into one description under the name "Valleriit." Consequently, most subsequent descriptions of a soft sulfide mineral having extreme anistropism and occurring as fine inclusions in chalcopyrite or pentlandite have given it the name "valleriite," even though no other evidence was available to establish the identification. Thus, the numerous literature references to valleriite are ambiguous and could equally well apply to mackinawite.

In conclusion, we believe that the occurrence in other sulfide crystals of tiny inclusions giving the appearance of an exsolution phase is quite characteristic of mackinawite and not valleriite, and that as this feature is usually mentioned in most literature references to "valleriite," probably what these references describe is actually mackinawite. Authentic valleriite, on the other hand, has been established from only two localities, Loolekop in South Africa, and southern Sweden. A probable third locality has been reported by Skinner and Milton (1955) at the Elizabeth mine, South Stratford, Vt. X-ray powder patterns of a soft highly birefringent sulfide mineral from this mine show reflections for chalcopyrite, pyrrhotite, and a third phase. The d-spacings for this phase match those determined for Kaveltorp valleriite, and the data given by Hiller (1939). Kouvo and Vuorelainen (1959) also mention an occurrence of valleriite at Vihauti, Finland, verified by its diffraction pattern. The validity of any given occurrence of valleriite or mackinawite may evidently be established only by X-ray diffraction or electron-microprobe techniques. From what we know now, it appears that mackinawite is a common and widespread mineral, while valleriite is quite rare.

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