ON ROZENITE AND SIDEROTIL

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ABSTRACT

Melanterite, $FeSO_4.7H_2O$, from Manitoba, Canada, dehydrates to $FeSO_4.4H_2O$ which is monoclinic, $a = 5.945, b = 13.59, c = 7.94$ Å, $\beta = 90° 30'$. Cuprian melanterites, or pisanites, $(Fe,Cu)SO_4.7H_2O$, dehydrate to a pentahydrate series. A naturally occurring pentahydrate from Yerington, Nevada, contains FeO 15.9%, CuO 14.1, CoO 0.35, SO_3 32.99 (by difference), H_2O 36.66. Such pentahydrates are biaxial negative with $2V = 50–65°$, $\alpha \sim 1.513$, $\beta \sim 1.526$, $\gamma \sim 1.536$, whereas $FeSO_4.4H_2O$ is biaxial negative with a very large $2V$ and $\alpha \sim 1.526$, $\beta \sim 1.536$, $\gamma \sim 1.545$. Examination of previously published data shows that "iron-copper chalcanthite" is cuprian $FeSO_4.5H_2O$ and that compilations have attributed optical data determined on $FeSO_4.4H_2O$ as belonging to $FeSO_4.5H_2O$.

Indexed x-ray powder data for $FeSO_4.4H_2O$ and cuprian $FeSO_4.5H_2O$ are given. The strongest lines of the powder pattern of the tetrahydrate are 4.47(10), 5.46(9), 3.97(7), 3.40(6), 6.85(5), and the strongest lines for the pentahydrate are 4.89(10), 3.73(8), 5.57(6), 5.73(5). Synthesis of the ferroan $CuSO_4.5H_2O$ and cuprian $FeSO_4.5H_2O$ series is described and the nomenclature of the pentahydrates and tetrahydrates is discussed. The present writers prefer to retain the mineral names and chemical compositions as originally defined: $FeSO_4.5H_2O$ = siderotil; $FeSO_4.4H_2O$ = rozenite.

INTRODUCTION

Textbooks on optical and descriptive mineralogy state that melanterite, $FeSO_4.7H_2O$, alters by dehydration to form the mineral siderotil having the composition $FeSO_4.5H_2O$. Rosenzweig & Gross (1955) and Kubisz (1960) have found that melanterite dehydrates to form the tetrahydrate, $FeSO_4.4H_2O$, which Kubisz has named rozenite. On reviewing the published new name Fleischer (1961) pointed out that the optical properties of rozenite are identical to those given for siderotil in Dana (Palache, Berman & Frondel, 1951). Noting also that the original chemical analysis of siderotil by Schrauf (1891) was not conclusive, Fleischer suggested that rozenite was an unnecessary name and that siderotil should be used for the tetrahydrate. Midgley (1962) has followed Fleischer's suggestion and referred to the tetrahydrate as siderotil. On the other hand, Baur (1962) prefers to discredit siderotil and retain rozenite for the tetrahydrate.

The present problem of nomenclature originated from an inadequate description by Schrauf (1891) of the mineral which he named siderotil. Confusion began when Larsen & Glenn (1920) assigned optical properties to a supposedly similar mineral and was perpetuated by compilers of data, namely Larsen & Berman (1934), Winchell & Winchell (1956) and Palache *et al.* (1951). These writers combined the name siderotil, having

Schrauf's composition $FeSO_4.5H_2O$, with optical properties which were determined some 30 years later by Larsen & Glenn on unanalyzed materials not from the type locality.

The description of rozenite by Kubisz (1960) contains sufficient data to clearly characterize the tetrahydrate mineral ($FeSO_4.4H_2O$) and thus constitutes a valid description of a mineral that previously had been neither adequately described nor properly named. Unfortunately, Kubisz did not discuss the relationship of his mineral to siderotil (as $FeSO_4.5H_2O$).

Neither Fleischer nor Midgley has recognized that the pentahydrate $FeSO_4.5H_2O$, and particularly the cuprian variety, $(Fe,Cu)SO_4.5H_2O$, may occur in nature and are probably more deserving of the name siderotil than the tetrahydrate. The present writers favour use of the name rozenite for the tetrahydrate (Kubisz, 1960) and propose that siderotil be used for the pentahydrate, thus fulfilling the suggestion that Schrauf (1891) expressed in the following words: "Hieraus würde sich die Formel der Verbindung zu $FeSO_4.5H_2O$ berechnen. Solten fernere Beobachtungen die Existenz eines solchen strahligen wasserarmen Ferrosulphates bestätigen, so würde ich den Namen Siderotil hiefür vorschlagen."

Recent studies of the tetrahydrate have shown that many properties previously described for the pentahydrate "siderotil" are really those of the tetrahydrate. In the present paper, the dehydration of the heptahydrate, melanterite, is discussed and properties are given for the tetrahydrate and pentahydrate minerals that may form. Previously published data are re-examined with regard to these properties, and the proposed nomenclature is discussed.

The Dehydration of Melanterite

In 1960, the first author examined a white mineral associated with melanterite on a specimen from Manitoba, Canada, and found that it gave an *x*-ray diffraction pattern in close agreement with that of the artificial compound $FeSO_4.4H_2O$. On exposure to air for several hours at 22° C. and 50 per cent relative humidity, the melanterite dehydrated to form a white powdery coating which, on *x*-ray examination, proved to be the tetrahydrate. It was then shown conclusively by means of a thermogravimetric apparatus that the melanterite from Manitoba dehydrates directly to the tetrahydrate at 21° C. without forming an intervening pentahydrate phase. This evidence is in conflict with the statement of Larsen & Glenn (1920), subsequently repeated in many textbooks, that "Melanterite is commonly coated with a white powder of siderotil and the fine [melanterite] powder will dehydrate after standing for some months to the pentahydrate." It is now known that this white powder was not a pentahydrate, but was a tetrahydrate, and herein the confusion began. Larsen & Glenn gave, for this white tetrahydrate powder, optical properties which have been repeatedly and erroneously attributed, via compilations, as being those of the pentahydrate.

Palache, Berman & Frondel (1951) have pointed out that in the artificial system the tetrahydrate is ordinarily formed by dehydration of the heptahydrate, and Rosenzweig & Gross (1955) have noted that melanterite dehydrates rapidly to $FeSO_4.4H_2O$; the latter authors, however, did not present any evidence to support the statement. The study of the dehydration of melanterite from Manitoba and description of the tetrahydrate mineral were not published when Kubisz (1960) presented details of an almost identical study on melanterite from the "Staszic" mine, Rudki, Poland.

The fact that melanterite forms a tetrahydrate upon dehydration no longer applies when the melanterite contains minor amounts of copper in substitution for iron. Eckel (1933) studied the stability relations of a cuprian melanterite (pisanite) containing 7.2 per cent CuO. Eckel's experimental method was to allow weighed samples to come to equilibrium in artificially-produced atmospheres of known humidity. Abrupt changes in weight were found to occur at three points, the losses in weight corresponding closely to the removal of a definite number of molecules of water of crystallization. These abrupt changes marked the following dehydration stages:

$$(Fe,Cu)SO_4.7H_2O \rightarrow (Fe,Cu)SO_4.5H_2O \rightarrow (Fe,Cu)SO_4.H_2O \rightarrow \text{anhydrous.}$$

No indication of a tetrahydrate phase was found.

A naturally occurring counterpart of Eckel's cuprian iron sulphate pentahydrate has been examined by the writers. The specimen, labelled "Pisanite, Yerington, Nevada" was received from the Royal Ontario Museum in a stoppered glass vial sealed with wax. Chemical analysis of the mineral (Table 5) shows that its formula is $(Fe_{0.55}\,Cu_{0.44}\,Co_{0.01})SO_4.5H_2O$. The mineral consists of sub-fibrous grains that are considerably coarser than the tiny anhedral or fibrous grains, or porous aggregates that are generally characteristic of minerals formed by dehydration. The grain size and texture of the Yerington cuprian iron sulphate pentahydrate suggest that it may not have been formed by dehydration of cuprian melanterite but may have been precipitated from solution.

PROPERTIES OF $FeSO_4.4H_2O$

Physical and Optical Properties

$FeSO_4.4H_2O$ is white to greenish white with a vitreous lustre and white streak. The mineral commonly forms by dehydration of the higher hydrate and its fine-grained nature makes difficult the accurate determination of its physical and optical properties. Contrary to the statement of Midgley (1962, p. 408), the tetrahydrate (and not melanterite) is the stable phase at normal temperatures and humidities. Some oxidation of iron takes place producing a yellowish colouration but the water content remains unchanged.

Kubisz (1960) reports a measured specific gravity of 2.195 for rozenite. This figure is lower than the range 2.23–2.29 given for $FeSO_4.4H_2O$ in the Handbook of Chemistry and Physics. The calculated specific gravity is 2.29, based on the crystallographic constants of Baur (1960).

Optical properties of the tetrahydrate are given in Table 1. The properties listed in columns I, II and III were determined on minerals that had been positively identified by *x*-ray powder diffraction patterns.

TABLE 1. OPTICAL PROPERTIES OF $FeSO_4.4H_2O$

	I	II	III	IV	V	VI
	α 1.527	1.527*	1.529*	1.526	1.528	1.528
	β 1.536			1.536	1.537	1.537
	γ 1.541*	1.543*	1.543*	1.542	1.545	1.545
sign		(−)	(−)	(−)	(−)	(−)
$2V$		near 90°	near 90°	rather large	rather large	moderate

*Constants determined as α' or γ'

I Manitoba mineral; Tp. 44, R. 28, W. of 1st meridian.
II Rozenite from Staszic (Kubisz, 1960).
III Rozenite from Ornak (Kubisz, 1960).
IV "Siderotil" from dehydration of melanterite (Larsen & Glenn, 1920).
V "Siderotil" from California (Larsen, 1921).
VI "$FeSO_4.5H_2O$," synthetic (Winchell, 1927).

Chemical analyses for I and II are given in Table 2. The properties listed in columns IV, V and VI are also those of the tetrahydrate, but in each case they presumably have been incorrectly reported in the literature as belonging to the pentahydrate.

Chemical Composition

The theoretical composition of the compound $FeSO_4.4H_2O$ is given in Table 2 together with chemical analyses of minerals from Manitoba (analyst: S. Courville), "Staszic" mine, Poland (Kubisz, 1960), and Thames River (Midgley, 1962).

Crystallographic Data

According to Baur (1960, 1961), $FeSO_4.4H_2O$ is monoclinic, space group $P2_1/n - C_{2h}^5$, with $a = 5.97$, $b = 13.64$, $c = 7.98$ Å, $\beta = 90°26'$, and $Z = 4$ .The axial ratio from the *x*-ray measurements, 0.4377:1:0.5850, is in good agreement with the ratio derived from morphological measure-

TABLE 2. CHEMICAL ANALYSES OF $FeSO_4 . 4H_2O$ MINERALS

	Theoretical	Manitoba	Staszic, Poland	Thames River, England
Analytical Data				
FeO	32.09	30.65	31.13	29.9
Fe_2O_3		0.80		
MgO			0.97	
MnO			0.06	
SO_3	35.74	35.91	36.29	34.85
H_2O	32.17	31.90	32.98	30.5
Total	100.00	99.26[a]	100.43 [101.43]	95.25
Combining Ratios				
FeO[b]	1	0.98	1.01	0.98
SO_3	1	1.02	0.99	1.02
H_2O	4	4.02	3.97	3.98

[a] ANALYST: S. Courville. Spectrographic analysis shows 0.01–0.1% Mg, Al, Ni, Cu.
[b] FeO includes Fe_2O_3, MnO, MgO.

ments, 0.4373:1:0.5833, by Marignac (1856). Baur has also determined the crystal structure of $MgSO_4 . 4H_2O$ and shown that it is isostructural with $FeSO_4 . 4H_2O$. On the basis of *x*-ray powder diffraction data, Kubisz (1960) suggested that the minerals rozenite, leonhardtite ($MgSO_4 . 4H_2O$), and ilesite ($MnSO_4 . 4H_2O$), are isomorphous.

X-ray powder diffraction data for natural and synthetic $FeSO_4 . 4H_2O$ have been published by Kubisz (1960), Kossenberg & Cook (1961) and Midgley (1962). None of these writers have indexed their data and considerable variation is reported in the measured spacings. *X*-ray powder diffraction patterns of the Manitoba mineral were taken with a Norelco 114.6 mm. diameter camera using manganese-filtered iron radiation. The pattern was indexed by computer using Baur's unit cell dimensions as a starting point and subsequently modifying these slightly to obtain the best agreement between measured and calculated spacings. The indexed pattern based on $a = 5.945$, $b = 13.59$, $c = 7.94$ Å, $\beta = 90°30'$, is given in Table 3.

Midgley (1962) has reported unit cell dimensions of $a = 11.82$, $b = 14.08$, $c = 10.96$ Å, $\beta = 101.9°$ for the Thames River mineral, calculated from single-crystal electron diffraction patterns and indexing of the *x*-ray powder pattern. The present writers have attempted, without success, to index Midgley's *x*-ray powder pattern using his proposed unit cell dimensions, and are forced to conclude that the data are incorrect. We also find no basis for the suggestion that the mineral "is isomorphous with the $BaNi(CN)_4 . 4H_2O$ group of substances."

TABLE 3. X-RAY POWDER DATA FOR ROZENITE, MANITOBA: a = 5.945 b = 13.59 c = 7.94 β=90°30′. SPACE GROUP $P2_1/n$
INTENSITIES VISUALLY ESTIMATED. FE RADIATION, MN FILTER

I_{est}	d_{meas}	d_{calc}	*hkl*
5	6.85 Å	6.855, 6.795 Å	011, 020
9	5.46	5.446	110
½	5.17	5.163	021
1	4.73	4.739	101
10	4.47	4.475, 4.474	111, 120
7	3.97	3.970	002
1	3.61	3.603	130
6	3.40	3.398	040
1	3.27	3.275	131
5	3.22	3.220	$\bar{1}12$
4	2.985	2.986	032
5	2.953	2.950	140
½	2.906	2.904	210
1	2.770	2.769	$\bar{1}41$
1	2.722	2.723, 2.720,	220, 211
½	2.673	2.675	$\bar{1}32$
4	2.569	2.571, 2.570	051, 221
½	2.470	2.472, 2.466	150, 023
3	2.430	2.426	$\bar{1}03$
2	2.371	2.377, 2.373, 2.373, 2.369	$\bar{2}31$, $\bar{1}42$, 113, 202
		2.367	231
	2.360	2.363, 2.363, 2.358	142, $\bar{1}51$, 151
½	2.333	2.334	212
½	2.286	2.285, 2.284	033, $\bar{1}23$
3	2.266	2.271, 2.265	123, 060
1	2.236	2.243, 2.237, 2.237	052, 240, 222
½	2.179	2.178	061
½	2.142	2.150, 2.138	241, $\bar{1}33$
½	2.112	2.117, 2.113	160, $\bar{2}32$
½	2.049	2.047, 2.044	$\bar{1}61$, 161
2	1.969	1.974, 1.967, 1.966, 1.964	$\bar{1}43$, 062, 143, $\bar{2}13$
1	1.944	1.948, 1.947, 1.943, 1.942	213, $\bar{2}51$, 242, 251
2	1.890	1.896, 1.890	053, 223
1	1.871	1.870, 1.865	$\bar{1}62$, 162
½	1.819	1.818	$\bar{2}33$
2	1.798	1.803, 1.802, 1.795	153, 260, $\bar{2}52$
1	1.755	1.759, 1.755	$\bar{2}61$, 261
2	1.725	1.721	063

PROPERTIES OF (Fe,Cu)SO_4.5H_2O

Physical and Optical Properties

(Fe,Cu)SO_4.5H_2O is pale green and becomes increasingly bluish with substitution of Cu for Fe. The mineral from Yerington, Nevada, has a vitreous lustre and white streak. Although pure $FeSO_4$.5H_2O is presumably unstable, the cuprian varieties are stable at normal temperatures and humidities and commonly form in nature by dehydration from the higher hydrate, cuprian melanterite.

Optical properties of cuprian iron sulphate pentahydrate are given in

Table 4. The data for the Yerington mineral were measured by Dr. J. Y. H. Rimsaite of the Geological Survey of Canada. Data for the Ducktown and Bingham materials are taken from Larsen (1921).

TABLE 4. OPTICAL PROPERTIES OF $(Fe,Cu)SO_4.5H_2O$

	Yerington, Nev.	Ducktown, Tenn.[1]	Bingham, Utah[1]
α	1.515*	1.513	1.515
β	1.525*	1.526 (computed)	
γ	1.535*	1.534	1.536
sign	(−)	(−)	
$2V$	50°–60°	60°±5°	

*Measured as α', β', γ'. [1] Larsen (1921).

Chemical Composition

A chemical analysis of the mineral from Yerington, Nevada, is given in Table 5. Iron, copper and cobalt were determined by *x*-ray spectrography by G. R. Lachance; water determination by S. Courville; sulphur trioxide by difference. The formula calculated from the analysis is $(Fe_{.55}Cu_{.44}Co_{.01})SO_4.5H_2O$.

TABLE 5. CHEMICAL ANALYSIS OF $(Fe,Cu)SO_4.5H_2O$, YERINGTON, NEVADA

		Molecular Ratios	
FeO	15.9	0.221	1
CuO	14.1	0.177	
CoO	0.35	0.005	
SO_3	32.99*	0.412	1.02
H_2O	36.66	2.034	5.05
	100.00		

*SO_3 by difference.
ANALYSTS: G. R. Lachance, S. Courville.

Crystallographic Data

$FeSO_4.5H_2O$ was reportedly synthesized and morphologically described by Marignac (1856) as being triclinic, pinacoidal, with $a{:}b{:}c$ = 0.596:1:0.577, $\alpha = 98°39'$, $\beta = 110°28'$, $\gamma = 74°27'$. These values are very close to those of chalcanthite, but this is not unexpected as the Cu-Fe cations have very similar ionic radii. On the other hand, Palache *et al.* (1951) report that the existence of $FeSO_4.5H_2O$ as an artificial compound is doubtful. Synthetic $(Fe,Cu)SO_4.5H_2O$ was prepared in the present study both by crystallization from solutions and by dehydration of synthetic heptahydrates. Crystals used in the present *x*-ray work were formed by dissolving chemical grade sulphates of iron and copper in water acidified with a few drops of concentrated H_2SO_4. The solution was evaporated in an oven at 55° C. and the precipitated crystals removed while a small amount of the liquid still remained. Crystals so formed remain stable under laboratory conditions for several months provided that they are dried with a tissue in order to remove any liquid carried over from the crystallizing solution.

Synthetic $(Fe,Cu)SO_4.5H_2O$ has a habit similar to that of chalcanthite. The 0.5 × 0.5 mm. crystal used in the *x*-ray work shows, by analogy to chalcanthite morphology, the following prominent forms: {111}, {110}, {100}, {110}, {010}. The crystal is pale greenish blue in colour and biaxial negative with measured $(-)2V = 63°$ (universal stage). *X*-ray spectrographic analysis shows the Fe:Cu ratio to be 100:70. Using copper radiation, rotation and 0-level Weissenberg photographs about *a*, *b*, and *c*, and precession photographs taken with b^* as the dial axis show that $(Fe,Cu)SO_4.5H_2O$ is triclinic and crystallographically similar to chalcanthite. Data obtained for the *x*-ray cell are summarized in Table 6.

TABLE 6. *X*-RAY CELL OF $(Fe,Cu)SO_4.5H_2O$ AND $CuSO_4.5H_2O$

Rotation	Reciprocal dimensions from Weissenberg and precession films	Calculated cell from reciprocal values	Chalcanthite–$CuSO_4.5H_2O$[1]
$a = 6.22$ Å ±0.1	$a^* = 0.1745$	$a = 6.26$ Å	$a = 6.12$ Å
$b = 10.59$	$b^* = 0.0966$	$b = 10.63$	$b = 10.69$
$c = 6.00$	$c^* = 0.1761$	$c = 6.06$	$c = 5.96$
	$\alpha^* = 87°30'$	$\alpha = 92°08'$	$\alpha = 97°35'$
	$\beta^* = 69°48'$	$\beta = 110°10'$	$\beta = 107°10'$
	$\gamma^* = 103°00'$	$\gamma = 77°05'$	$\gamma = 77°33'$
	$\beta = 109°47'$	$V = 368$ Å^3	
		$a{:}b{:}c = 0.589{:}1{:}0.570$	$a{:}b{:}c = 0.572{:}1{:}0.557$

[1] Reported in Palache *et al.* (1951). Converted from kX.

Using the calculated cell volume of 368 Å^3, and assuming two molecules per unit cell, the calculated S.G. of $(Fe,Cu)SO_4.5H_2O$ with Fe:Cu = 55:45 is 2.212. The specific gravity of the Yerington mineral was determined to be 2.1–2.2, by suspension in heavy liquids. Larsen (1921) reports a specific gravity of 2.2 for "iron-copper chalcanthite."

ADDITIONAL OCCURRENCES OF CUPRIAN $FeSO_4.5H_2O$ AND RELATED MINERALS

Besides the aforementioned occurrences of cuprian $FeSO_4.5H_2O$ at Ducktown, Tenn., Bingham, Utah, and Yerington, Nevada, a mineral labelled chalcanthite from Grandola, Lisbon, Portugal was found to give the $FeSO_4.5H_2O$ type of pattern, though with some differences in reflec-

TABLE 7. *X*-RAY POWDER DATA FOR CUPRIAN $FeSO_4.5H_2O$, YERINGTON, NEVADA. (ROM 12086) Pattern indexed on cell with *a* 6.26, *b* 10.59, *c* 6.05 Å, α 92°08′, β 110°10′, γ 77°05′

I_{est}	d_{meas}	d_{calc}	*hkl*	I_{est}	d_{meas}	d_{calc}	*hkl*
½	10.3 Å	10.31	010	4	2.92	2.93	210
5	5.73	5.73	100			2.92	$11\bar{2}$
6	5.57	5.57	110	2	2.86	2.86	200
2	5.07	5.07	011	2	2.76	2.77	012
10	4.89	4.88	$01\bar{1}$	3	2.72	2.74	$\bar{2}11$
1	4.57	4.59	$1\bar{1}0$			2.71	$01\bar{2}$
1	4.35	4.35	120	4	2.68	2.69	$1\bar{3}0$, $1\bar{2}1$
3	3.90	3.90	021, $12\bar{1}$			2.67	131
8	3.73	3.74	$02\bar{1}$	½	2.61	2.61	$2\bar{1}0$
2	3.44	3.44	030	1	2.573	2.578	040
1	3.29	3.29	130			2.577	140
4	3.21			½	2.528	2.531	022
2	3.07	3.07	$21\bar{1}$	½	2.499	2.492	230
		3.06	$13\bar{1}$	3	2.444	2.439	$02\bar{2}$

Manganese filtered iron radiation; camera diam. 11.46 cm. Line at 3.21 Å appears in all patterns but cannot be indexed satisfactorily with the selected cell.

tions at lower *d*-spacings. *X*-ray spectrographic analysis by fusion in sodium bisulphate gave Cu:Fe:Zn = 100:94:53. Zincian pisanite (Fe:Cu:Zn = 100:80:3) described by Keating & Berry (1953) has now dehydrated to the ferroan pentahydrate. A pentahydrate mineral associated with $CoSO_4.4H_2O$ and $CoSO_4.6H_2O$ from Walton, Nova Scotia contains, Cu, Fe, Ni, Co and Zn in the respective ratio of 100:69:53:37:2. Pale blue "boothite" from the Pyrite mine, Alameda County, California (U.S.N.M. R-6140) also gives an *x*-ray powder pattern similar to that obtained from $(Fe,Cu)SO_4.5H_2O$. Optically, the mineral is very fine-grained and probably a dehydration product of the heptahydrate. The refractive indices $n_{min.}$ 1.503, $n_{max.}$ 1.517 are close to those of the mineral pentahydrite, $MgSO_4.5H_2O$, described by Milton & Johnston (1938). Qualitative spectrographic analysis of the Alameda mineral showed that magnesium is the major constituent. The Cu:Fe:Zn ratio was determined by *x*-ray fluorescence analysis to be 100:34:9. Placed in an artificial humid atmosphere, the Alameda mineral forms a monoclinic heptahydrate which gives an *x*-ray pattern characteristic of the melanterite group. Under identical conditions, hydration of several additional magnesium sulphate minerals led to the formation of the orthorhombic polymorph, epsomite ($MgSO_4.7H_2O$). If formed under natural conditions, the monoclinic heptahydrate of the Alameda mineral would be a cuprian kirovite.

Yurk *et al.* (1960) have described, from the Kerch and Tasman iron ore beds of the Ukraine, a mineral reputed to be natural $FeSO_4.5H_2O$. They report the following analysis, corresponding to their formula $(FeO)_{0.95}(SO_3)_{1.00}(H_2O)_{4.94}$:

Fe_2O_3	0.58%
FeO	28.64
SO_3	34.12
H_2O	37.92
Total	100.26 (101.26)

This pentahydrate is stated to be a secondary mineral occurring as crusts on melanterite, and is also stated to have formed by partial dehydration of the heptahydrate. The present writers must question this data by Yurk *et al.*, particularly since no *x*-ray data were reported. Moreover, their refractive indices, $\alpha = 1.527–1.528$; $\beta = 1.533–1.534$—are those of the tetrahydrate.

SYNTHESIS

Experiments were made to determine the composition ranges (Cu/Fe ratios) through which compounds of the types $CuSO_4.5H_2O$, $(Fe,Cu)SO_4.5H_2O$, and $FeSO_4.4H_2O$ may exist as stable phases. $(Fe,Cu)SO_4.5H_2O$ forms by dehydration of heptahydrates, or it can be directly precipitated from heated solutions. The dehydration technique, which is the simpler method, was used for the study outlined below.

A series of aqueous solutions containing various proportions of chemical grade $CuSO_4.5H_2O$ and $FeSO_4.7H_2O$ were acidified with a few drops of concentrated sulphuric acid and allowed to crystallize at room temperature. A tendency was noted for the composition of the crystallizing salts to change as the mother liquor was evaporated. Homogeneous fractions were obtained by selecting small crops of the first crystals that precipitated from the solutions. These crystals were dried with tissues and allowed to stand for 24 hours at room temperature to reach stability. The compounds thus formed were identified by *x*-ray diffraction patterns, and analyzed by *x*-ray spectrography to determine their Cu/Fe ratios.

In summation, the experiments showed that, in the artificial system, pentahydrates giving a chalcanthite-type pattern crystallize from copper-iron sulphate solutions throughout the composition range $Cu/Fe = \propto$ to $Cu/Fe = 1.4$ and that heptahydrates having a melanterite-type structure form in the composition range $Cu/Fe = 1.0$ to $Cu/Fe = 0$. When removed from solution the pentahydrates remain stable at room temperature, whereas the heptahydrates dehydrate within 24 hours at 45 per cent relative humidity to form: (1) compounds giving the $(Fe,Cu)SO_4.5H_2O$ type pattern throughout the composition range $Cu/Fe = 1.0$ to $Cu/Fe = 0.05$; or (2) the compound $FeSO_4.4H_2O$ when Cu is absent or only a very minor amount is present ($Fe/Cu \simeq 18.0$).

Interpreting these results in terms of probable natural occurrences leads to the following conclusions.

(1) The tetrahydrate mineral is the stable hydrate formed by dehydration of pure or nearly pure melanterite under normal atmospheric conditions. In the presence of copper the composition of the tetrahydrate is restricted to the range $FeSO_4 . 4H_2O$ to $(Fe_{.95}Cu_{.05})SO_4 . 4H_2O$. As little as 1.2 weight per cent copper present in melanterite may cause the pentahydrate to form on dehydration.

(2) the unnamed iron-copper pentahydrate mineral described in this paper is a member of an isomorphous series which, in the artificial dehydration system, is stable throughout the composition range $(Fe_{.95}Cu_{.05})SO_4 . 5H_2O$ to about $(Cu_{.5}Fe_{.5})SO_4 . 5H_2O$. The copper-rich end point has not been established precisely but is known to lie between $(Cu_{.58}Fe_{.42})$ and $(Cu_{.50}Fe_{.50})$ in synthetic material. These pentahydrates, which are stable under normal conditions of temperature and humidity, form by dehydration of their corresponding heptahydrates, that is, melanterite and pisanite.

(3) Chalcanthite crystallizes readily from copper-rich sulphate solutions and remains stable under normal atmospheric conditions throughout the composition range $CuSO_4 . 5H_2O$ to $(Cu_{.6}Fe_4)SO_4 . 5H_2O$. In our experiments, boothite, the heptahydrate of equivalent composition, did not crystallize from the solutions.

SUMMARY AND PROPOSED NOMENCLATURE

Of the compounds examined in the present study, attention has been focused on three specific minerals, *viz.*, $FeSO_4 . 4H_2O$, $CuSO_4 . 5H_2O$, and $(Fe,Cu)SO_4 . 5H_2O$. It has been shown that $CuSO_4 . 5H_2O$ and $(Fe,Cu) SO_4 . 5H_2O$ form an isomorphous series and several mineral counterparts of the ferroan compound have been noted. Chalcanthite is the accepted mineral name for $CuSO_4 . 5H_2O$. The mineral may occur as almost pure $CuSO_4 . 5H_2O$ or Cu may be replaced by Fe or other elements, including, Mg, Zn, Co, Ni, and Mn. It is therefore convenient to arbitrarily divide these isomorphous sulphate minerals on the basis of the dominant cation present in a member. Thus, in the Cu–Fe series, the single name chalcanthite may be applied to those pentahydrates with $Cu > Fe$, and the adjectival modifier, ferroan, used only in a literary sense. Likewise, a single mineral name may be conveniently used to designate that part of the series in which $Fe > Cu$, including the end-member compound $FeSO_4 . 5H_2O$. Whether or not the pure end-member exists is of academic interest only.

When formed as a dehydration product, the third compound examined in the present study, $FeSO_4 . 4H_2O$ tolerates little substitution of Cu for Fe in its structure but may form limited or complete isomorphous series by substitution of other elements, notably Mg, Mn, and Zn.

Optical properties of both $FeSO_4.4H_2O$ and cuprian $FeSO_4.5H_2O$ were first reported by Larsen & Glenn (1920). They erroneously assumed that the tetrahydrate they examined was a pentahydrate (and hence listed the mineral with the chalcanthite group and called it "siderotil"; Larsen & Glenn, 1920, p. 228). They also recognized that this "siderotil" had different properties from that of cuprian $FeSO_4.5H_2O$ and they named the latter compound "iron-copper chalcanthite." Had Larsen & Glenn recognized that their "siderotil" was a tetrahydrate, they would likely have given this compound a new name, and would have referred to cuprian $FeSO_4.5H_2O$ as cuprian siderotil.

In reviewing the proposed new name, rozenite, Fleischer (1961) pointed out that the optical properties given by Kubisz are identical to those ascribed by Larsen & Glenn (1920), and Larsen (1921) as belonging to "siderotil" ($FeSO_4.4H_2O$). Fleischer therefore concluded that rozenite is an unnecessary name.

The original description of siderotil by Schrauf (1891) is clearly inadequate as it is not accompanied by optical data of any significance and the analysis is not definitive for either the tetra or pentahydrate. Our experimental work has shown that both these compounds are easily synthesized and remain stable under natural conditions of temperature and humidity. The description of rozenite by Kubisz (1960) clearly characterized the tetrahydrate mineral ($FeSO_4.4H_2O$) and thus constitutes the first valid description of either of these compounds. Schrauf clearly interpreted his analysis as being that of the pentahydrate for which he proposed the name siderotil. It is therefore incorrect, in our opinion, to accept siderotil as the tetrahydrate and to discredit rozenite in its favour. Baur (1962) also suggests that the name rozenite ($FeSO_4.4H_2O$) be retained. The present writers prefer to accept *rozenite* for the tetrahydrate and retain *siderotil* for the pentahydrate series ($FeSO_4.5H_2O$–$(Fe,X)SO_4.5H_2O$), where X is any other cation or group of cations individually less abundant than Fe.

The Chalcanthite Group

The mineral names proposed for the pentahydrate sulphates in the present paper follow those adopted in the *System of Mineralogy* by Palache *et al.* (1951). The isostructural pentahydrate salts of Cu, Fe, and Mg are thus named, respectively, chalcanthite, siderotil, and pentahydrite. It is suggested that the naming of these sulphates be done on the basis of the dominant cation present in the mineral. Thus $(Cu, Fe, Mg)SO_4.5H_2O$ would be named chalcanthite even though $Fe + Mg > Cu$.

THE MELANTERITE GROUP

Examination of the nomenclature system in use for the various members of the melanterite series[1] points out the obvious advantage of using the simplified system proposed above. It is suggested that consideration should be given for adopting the simplified terminology to the heptahydrates of this group.

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[1] Palache *et al.* (1951, pp. 500–501).