Crystal Structures and Mineral Chemistry of Hydrated Ferric Sulphates. III. The Crystal Structure of Kornelite

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Abstract

Kornelite, $[Fe_2^{3+}(H_2O)_6(SO_4)_3] \cdot 1.25H_2O$, is monoclinic $P2_1/n$ with $a = 14.30(1)$; $b = 20.12(2)$; $c = 5.425(4)$Å; $\beta = 96.8(1)°$ and $Z = 4$. All atoms, save one water molecule, were located by the symbolic addition method despite the presence of a pronounced $a/2$ pseudo symmetry. Full-matrix least-squares refinement, utilizing 962 reflections, produced a final isotropic R-index of 0.086.

The kornelite structure is composed of corrugated octahedral-tetrahedral layers of composition $[Fe_2^{3+}(H_2O)_6(SO_4)_3]_x^0$ which are parallel to {100}. The layers are joined by hydrogen bonds only. Site-occupancy refinement of the two interlayer water molecules indicates the correct water content of the mineral is 7.25 H_2O. Average cation-oxygen distances are: $Fe(O,Ow) = 1.98$ Å, and S-O = 1.46 Å.

Introduction

This is the third paper in a series dealing with the crystal structures of minerals with the general formula, $Fe_2(SO_4)_3 \cdot nH_2O$. Papers I and II dealt with a pair of polytypic compounds, coquimbite (Fang and Robinson, 1970) and paracoquimbite (Robinson and Fang, 1971). Future papers will deal with the structures of the two remaining species in the system [quenstedtite ($n = 10$) and lausenite ($n = 6$)] and will also attempt to elucidate the structural relations and mechanisms of the dehydration-transformation among members of this interesting mineral group.

This paper describes the structure of an intermediate hydrate, kornelite. The number of water molecules in this mineral, as with so many other hydrates, has been disputed. A statement in Dana's *System of Mineralogy* (Palache *et al*, 1951) reads: "The water content [of kornelite] is somewhat uncertain and may be higher than $7H_2O$." More recently, Cesbron (1964) concluded that the correct value is 7.5 H_2O, based on DTA and chemical analysis. Our structural analysis shows that the water content is actually 7.25 H_2O, a value between the two previously reported.

Collection and Reduction of the X-Ray Data

Because of polysynthetic twinning, considerable time was spent in finding a suitable crystal. The crystal used for intensity measurement (locality: Tintic Standard mine, Dividend, Utah; U. S. National Museum No. 104277) was a platelet of dimensions 0.17 by 0.33 by 0.06 mm. The rotation axis [100] was approximately normal to the platelet. The unit-cell parameters were obtained from precession photographs and measurements with a single-crystal diffractometer. The values thus obtained were $a = 14.30(1)$; $b = 20.12(2)$; $c = 5.425(4)$ Å; $\beta = 96.8(1)°$; and $Z = 4$. The observed systematic absences $h0l$, $h + l$ odd, and $0k0$, k odd, are consistent with the space group $P2_1/n$ reported by Cesbron (1964).

Intensity data were collected with a 0.01°-incrementing Buerger automated diffractometer using $FeK\alpha$ radiation. The diffractometer collects all data in a given Weissenberg layer using a stationary-background, ω-scan, stationary-background counting sequence. The following details are specific to the present analysis. (1) The angular range scanned was chosen as $\omega = [1.5 + (1.0/L)]°$, where L is the Lorentz factor; the scan speed was 1°/min. The integrated count associated with this scan is C. (2) Initial and final backgrounds B_1 and B_2, were each measured for one-fourth the time of the ω-scan. (3) The integrated intensity of a reflection was calculated as $I = C - 2 (B_1 + B_2)$. (4) Within each layer the stability of the entire system was monitored by remeasuring the intensities of pre-selected reflections (no deviations $\geq$ 3 percent from the mean were observed). (5) Intensities which were not significantly different from zero at the 4σ level were considered to be "unobserved" reflections.

All data were corrected for Lp effects and absorption ($\mu = 134.09$ cm^{-1}), and the twelve layers of data (1363 spectra) were merged to a common scale. The resulting 993 independent "non-zero" reflections were used in the subsequent calculations.

Structure Determination and Refinement of the Structure

The structure was solved by application of the symbolic addition procedure utilizing the SORTE program of Bednowitz (1970). Normalized structure factor statistics strongly indicated centrosymmetry, confirming the previously determined space group. It was noted that the intensity distribution indicated a pseudo-cell with an $a/2$ repeat and thus the sign prediction procedure required great care and frequent manual intervention in order to arrive at the correct solution. After phasing 379 of the 394 strongest E's, the resulting E-map revealed all atoms with the exception of one water molecule.

The refinement was carried out with Finger's (1969) full-matrix least-squares program, starting with the atomic positions derived from the E-map. The scattering factors for Fe^{3+}, S^0 and O^{2-} were taken from Cromer and Mann (1968). The first few cycles of refinement, with only Lp corrected data, indicated rather severe systematic errors due to absorption and, in addition, the isotropic temperature factor (B) of Ow(7) became unreasonably high. Therefore, the data were corrected for absorption employing the program of Prewitt (Wuensch and Prewitt, 1965). The refinement was continued and, after several least-squares cycles varying all positional and thermal parameters, the R-index was lowered to 12.9 percent; however, the B-value of Ow(7) remained high ($B = 9.5$ Å^2). A difference map was made at this stage and the remaining water molecule, Ow(8), was located. The last stage of refinement was carried out by varying the occupancies of the two unbonded water molecules, Ow(7) and Ow(8). Least-squares convergence was obtained at occupancy values of 0.50 for Ow(7) and 0.75 for Ow(8) and we therefore conclude that the correct water content of kornelite is 7.25 H_2O molecules.

During the last least-squares cycle, 31 reflections obviously suffering from extinction were removed, yielding a final isotropic R-index of 8.6 percent. The observed and calculated structure factors are listed in Table 1.[1] The positional and thermal parameters are given in Table 2.

[1] To obtain a copy of Table 1, order NAPS Document No. 02069 from Microfiche Publications, 305 East 46th Street, New York, N. Y. 10017. Please remit in advance $1.50 for microfiche or $5.00 for photocopies. Please check the most recent issue of this journal for the current address and prices.

Description of the Structure

The structure of kornelite is illustrated by two projections (Figs. 1 and 2). The dominant feature of the structure is the corrugated octahedral-tetrahedral layers of composition $[Fe_2^{3+}(H_2O)_6(SO_4)_3]_x^0$ with 6 of the 12 sulphate oxygens participating as vertices of the Fe^{3+} octahedra. The parallel layers (emerging from the plane of the paper in Figure 1) are joined only by hydrogen bonds and not only account for the {100} polysynthetic twinning, but also should give rise to a perfect {100} cleavage. The reported {010} cleavage necessitates breakage through the octahedral-tetrahedral layers, thus rupturing cation-anion bonds. This cleavage, which occurs in the plane of the unbound water molecules (Fig. 2), would be quite difficult to produce.

Interatomic distances and angles are listed in Table 3. The three independent SO_4 tetrahedra have mean S-O values of 1.46, 1.46 and 1.47 Å, in excellent agreement with all other ferric sulphate hydrates. It is interesting to note, however, that within each SO_4 tetrahedron the S-O distances are lengthened when the oxygens involved are also shared by Fe-octahedra. There are two such S-O bonds in each of the three SO_4 groups. This feature has previously been pointed out by the authors in Paper I (Fang and Robinson, 1970).

Both Fe(1) and Fe(2) are coordinated to three

TABLE 2. Atomic Coordinates and Temperature Factors for Kornelite[a]

Atom[b]	Occupancy	x	y	z	B(Å^2)
Fe(1)	1.0	.8303(2)	.1030(2)	.7970(6)	2.9(1)
Fe(2)	1.0	.3330(2)	.1146(2)	.7724(6)	2.8(1)
S(1)	1.0	.6483(2)	.0357(2)	.9931(9)	1.2(1)
S(2)	1.0	.8989(3)	.2432(2)	.0578(9)	1.3(1)
S(3)	1.0	.1544(3)	.0489(2)	.4280(9)	1.3(1)
O(1)	1.0	.5884(7)	.0575(7)	.170(3)	2.3(3)
O(2)	1.0	.7286(7)	.0819(6)	.003(3)	2.3(3)
O(3)	1.0	.3113(8)	.0311(7)	.941(3)	2.7(3)
O(4)	1.0	.6000(7)	.0333(7)	.738(3)	2.4(3)
O(5)	1.0	.4547(7)	.2310(7)	.375(3)	2.5(3)
O(6)	1.0	.3364(7)	.2051(6)	.632(2)	2.2(3)
O(7)	1.0	.9577(7)	.2173(7)	.269(3)	2.8(3)
O(8)	1.0	.8333(7)	.1906(6)	.947(2)	2.1(2)
O(9)	1.0	.0953(8)	.0477(7)	.628(3)	2.9(3)
O(10)	1.0	.1043(7)	.0755(7)	.198(3)	2.4(3)
O(11)	1.0	.8093(7)	.0190(7)	.610(3)	2.6(3)
O(12)	1.0	.2381(7)	.0918(7)	.496(3)	2.5(3)
Ow(1)	1.0	.4423(7)	.1368(7)	.025(3)	2.4(3)
Ow(2)	1.0	.4277(7)	.0754(6)	.565(3)	1.9(2)
Ow(3)	1.0	.2357(8)	.1522(7)	.972(3)	3.2(3)
Ow(4)	1.0	.7429(9)	.1411(8)	.519(3)	4.4(3)
Ow(5)	1.0	.9216(7)	.0599(7)	.060(3)	2.3(3)
Ow(6)	1.0	.9439(7)	.1256(7)	.629(3)	2.4(3)
Ow(7)	0.50	.147(2)	.256(2)	.329(7)	5.2(7)
Ow(8)	0.75	.644(1)	.245(1)	.300(5)	5.4(5)

[a] Standard errors are in parentheses.
[b] All atoms are in general 4-fold positions.

water molecules and three oxygen atoms (one from each of three different sulphate groups). The analogous environments are reflected in the very similar Fe-(O,Ow) distances of the two Fe octahedra. The average cation-anion distance of 1.98 Å (with the Fe-O bonds slightly shorter than the Fe-Ow distances) is in perfect accord with those found in other ferric sulphates.

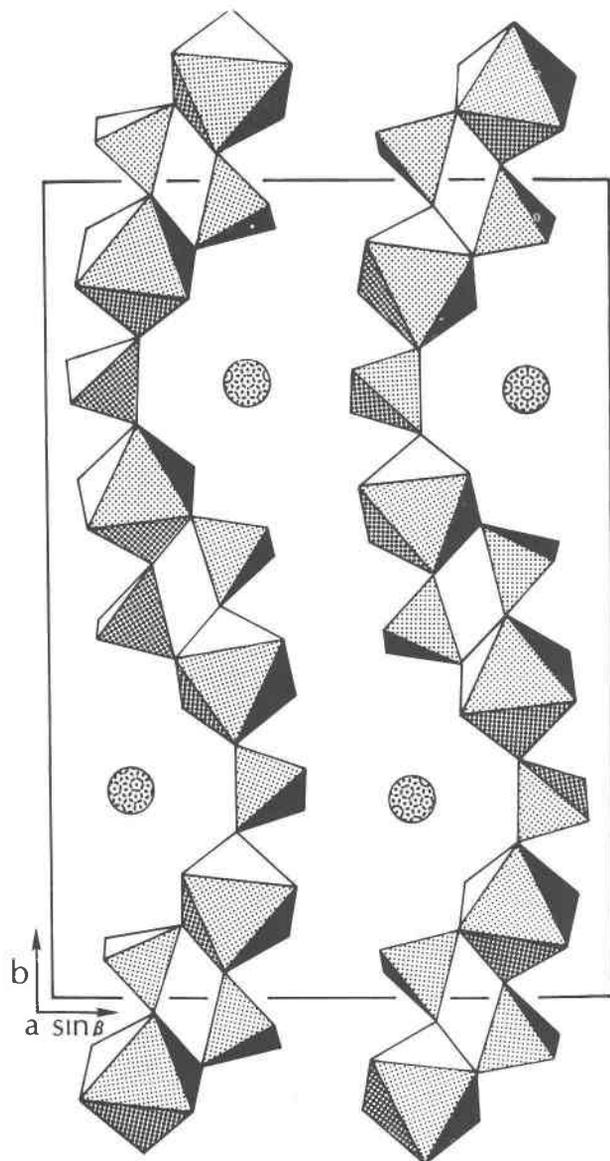A structural classification for ferric sulphates has

FIG. 1. The kornelite structure as viewed directly down the c axis. Two corrugated M-T layers can be seen emerging from the plane of the paper. The a/2 pseudo-symmetry is apparent. Shaded circles represent interlayer water molecules.
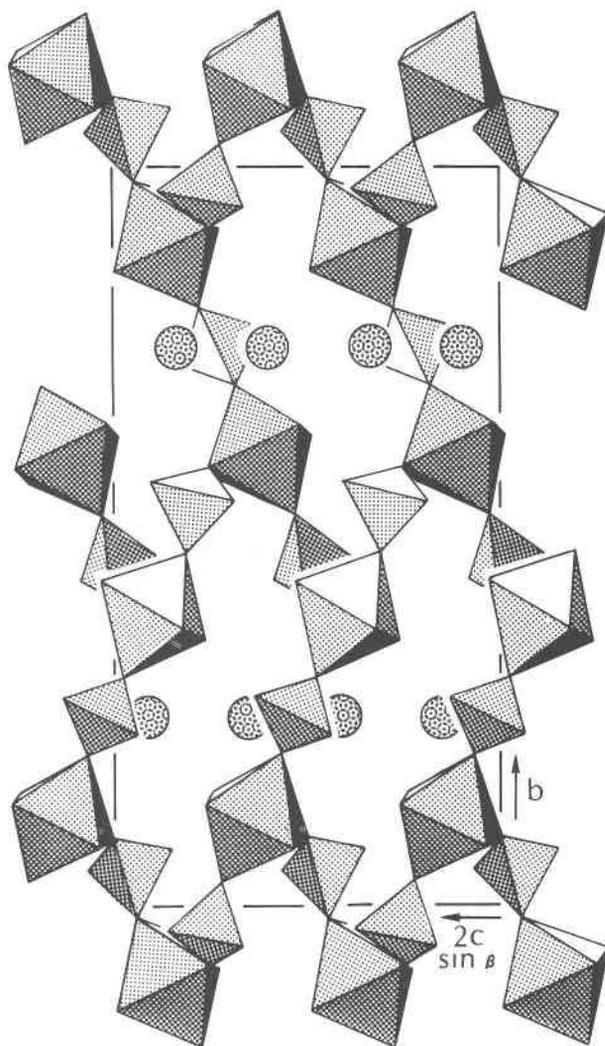

FIG. 2. A view of one of the M-T layers of kornelite as viewed directly down the a axis (a/2 shown). Shaded circles represent the partially occupied interlayer H_2O molecules.

been proposed by Süsse (1971). Süsse treats the unit of one Fe-octahedron (M) and one S-tetrahedron (T) as the basic building block and, in analogy with the criteria used for silicate minerals, classifies the structures into three groups on the basis of their M-T arrangement:

1. Structures with isolated M-T clusters, regardless of the number of polyhedra per cluster or their spatial geometry.

2. Structures composed of one dimensional M-T chains or bands, again disregarding the topology of the M-T polyhedra.

3. Structures made up of two-dimensional M-T sheets, with no consideration given to the arrange-

TABLE 3. Selected Interatomic Distances and Angles for Kornelite[a]

Tetrahedral coordination around S					
S(1)-O(1)	1.43(1)Å	O(1)-O(2)	2.35(1)Å	O(1)-S(1)-O(2)	108.0(8)°
S(1)-O(2)	1.47(1)	O(1)-O(3)	2.41(2)	O(1)-S(1)-O(3)	111.4(8)
S(1)-O(3)	1.49(1)	O(1)-O(4)	2.41(2)	O(1)-S(1)-O(4)	112.8(7)
S(1)-O(4)	1.47(1)	O(2)-O(3)	2.37(2)	O(2)-S(1)-O(3)	106.4(7)
		O(2)-O(4)	2.40(2)	O(2)-S(1)-O(4)	109.3(8)
		O(3)-O(4)	2.41(2)	O(3)-S(1)-O(4)	108.7(8)
MEAN	1.46Å	MEAN	2.39Å	MEAN	109.4°
S(2)-O(5)	1.44(1)Å	O(5)-O(6)	2.37(1)Å	O(5)-S(2)-O(6)	109.9(8)°
S(2)-O(6)	1.46(1)	O(5)-O(7)	2.37(2)	O(5)-S(2)-O(7)	111.1(7)
S(2)-O(7)	1.44(1)	O(5)-O(8)	2.41(2)	O(5)-S(2)-O(8)	110.5(8)
S(2)-O(8)	1.49(1)	O(6)-O(7)	2.39(2)	O(6)-S(2)-O(7)	111.1(8)
		O(6)-O(8)	2.33(2)	O(6)-S(2)-O(8)	103.9(6)
		O(7)-O(8)	2.40(2)	O(7)-S(2)-O(8)	110.2(8)
MEAN	1.46Å	MEAN	2.38Å	MEAN	109.4°
S(3)-O(9)	1.45(1)Å	O(9)-O(10)	2.41(2)Å	O(9)-S(3)-O(10)	111.8(7)°
S(3)-O(10)	1.46(1)	O(9)-O(11)	2.40(2)	O(9)-S(3)-O(11)	109.4(8)
S(3)-O(11)	1.48(1)	O(9)-O(12)	2.41(2)	O(9)-S(3)-O(12)	110.4(8)
S(3)-O(12)	1.49(1)	O(10)-O(11)	2.43(2)	O(10)-S(3)-O(11)	111.2(8)
		O(10)-O(12)	2.37(2)	O(10)-S(3)-O(12)	107.2(8)
		O(11)-O(12)	2.38(2)	O(11)-S(3)-O(12)	106.6(7)
MEAN	1.47Å	MEAN	2.40Å	MEAN	109.4°

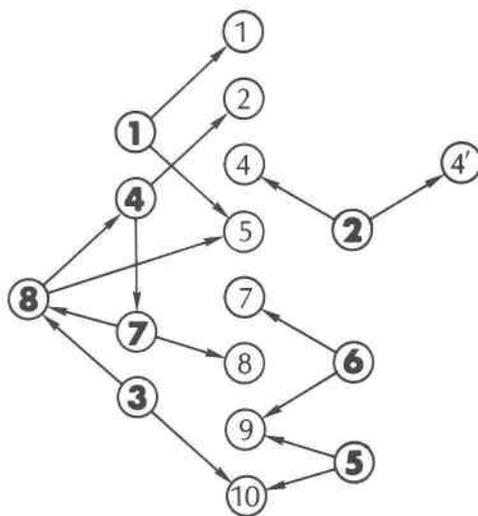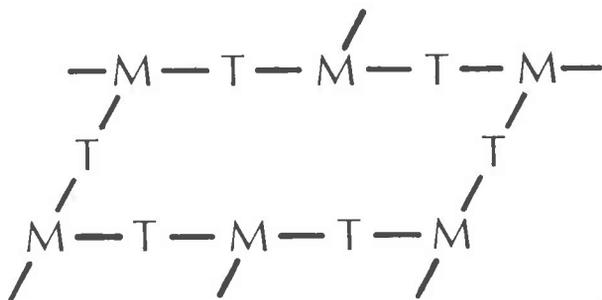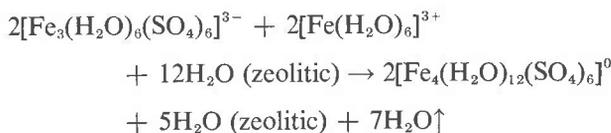| Octahedral coordination around Fe					
Fe(1)-O(2)	1.98(1)Å	O(2)-O(8)	2.69(2)Å	O(2)-Fe(1)-O(8)	86.6(5)°
Fe(1)-O(8)	1.94(1)	O(2)-O(11)	2.84(2)	O(2)-Fe(1)-O(11)	91.6(5)
Fe(1)-O(11)	1.98(1)	O(2)-Ow(4)	2.91(2)	O(2)-Fe(1)-Ow(4)	94.1(5)
Fe(1)-Ow(4)	1.99(2)	O(2)-Ow(5)	2.78(2)	O(2)-Fe(1)-Ow(5)	88.1(5)
Fe(1)-Ow(5)	2.01(1)	O(8)-Ow(4)	2.71(2)	O(8)-Fe(1)-Ow(4)	87.0(6)
Fe(1)-Ow(6)	2.01(1)	O(8)-Ow(5)	2.95(2)	O(8)-Fe(1)-Ow(5)	96.6(5)
		O(8)-Ow(6)	2.80(2)	O(8)-Fe(1)-Ow(6)	90.3(5)
		O(11)-Ow(4)	2.66(2)	O(11)-Fe(1)-Ow(4)	84.0(6)
		O(11)-Ow(5)	2.88(2)	O(11)-Fe(1)-Ow(5)	92.4(6)
		O(11)-Ow(6)	2.88(2)	O(11)-Fe(1)-Ow(6)	92.4(5)
		Ow(4)-Ow(6)	2.88(2)	Ow(4)-Fe(1)-Ow(6)	92.1(6)
		Ow(5)-Ow(6)	2.74(2)	Ow(5)-Fe(1)-Ow(6)	85.9(5)
MEAN	1.98Å	MEAN	2.81Å	MEAN	90.1°
Fe(2)-O(3)	1.96(1)Å	O(3)-O(12)	2.80(2)Å	O(3)-Fe(2)-O(12)	91.4(6)°
Fe(2)-O(6)	1.98(1)	O(3)-Ow(1)	2.84(2)	O(3)-Fe(2)-Ow(1)	91.5(6)
Fe(2)-O(12)	1.96(1)	O(3)-Ow(2)	2.92(2)	O(3)-Fe(2)-Ow(2)	94.6(5)
Fe(2)-Ow(1)	2.00(2)	O(3)-Ow(3)	2.68(2)	O(3)-Fe(2)-Ow(3)	85.0(6)
Fe(2)-Ow(2)	2.02(1)	O(6)-O(12)	2.73(2)	O(6)-Fe(2)-O(12)	88.1(6)
Fe(2)-Ow(3)	2.01(1)	O(6)-Ow(1)	2.82(2)	O(6)-Fe(2)-Ow(1)	90.3(5)
		O(6)-Ow(2)	2.96(2)	O(6)-Fe(2)-Ow(2)	95.4(5)
		O(6)-Ow(3)	2.69(2)	O(6)-Fe(2)-Ow(3)	84.9(6)
		O(12)-Ow(1)	2.71(2)	O(12)-Fe(2)-Ow(1)	86.0(5)
		O(12)-Ow(3)	2.86(2)	O(12)-Fe(2)-Ow(3)	92.3(5)
		Ow(1)-Ow(2)	2.77(2)	Ow(1)-Fe(2)-Ow(2)	87.0(5)
		Ow(1)-Ow(3)	2.95(2)	Ow(1)-Fe(2)-Ow(3)	94.6(5)
MEAN	1.99Å	MEAN	2.81Å	MEAN	90.1°

[a] Standard errors in parentheses.

FIG. 3. Schematic diagram of the donor-acceptor pairs in kornelite. Bold-face numbers depict Ow atoms.

A plausible hydrogen bonding scheme for kornelite can be deduced by assuming that: (1) The oxygen-oxygen (donor-acceptor) distances involved in the hydrogen bonds range from 2.6 to 3.0 Å; (2) "no hydrogen bonds are located in the edge of a coordination polyhedra around a cation, thus bringing the hydrogen atom into coordinating contact with this cation" (Baur, 1972); and (3) all hydrogen atoms participate in hydrogen bonding and no bifurcated hydrogen bonds exist. Figure 3 schematically depicts the hydrogen bonding scheme of kornelite and Table 4 lists the O-O distances and O-Ow-O angles involved.

The dehydration of coquimbite to kornelite may be written in their structural formulas (unit cell content) as follows:

$$2[Fe_3(H_2O)_6(SO_4)_6]^{3-} + 2[Fe(H_2O)_6]^{3+}$$
$$+ 12H_2O \text{ (zeolitic)} \rightarrow 2[Fe_4(H_2O)_{12}(SO_4)_6]^0$$
$$+ 5H_2O \text{ (zeolitic)} + 7H_2O\uparrow$$

Thus it is seen that transformation involves increased polymerization (*i.e.*, sharing more corners) of the isolated *M-T* clusters of coquimbite to form the layer arrangement of kornelite. The five H_2O molecules represent the zeolitic water present in the unit cell of the kornelite sample under investigation. However, since the zeolitic H_2O molecules Ow(7) and Ow(8) are so loosely held in the structure, it is quite probable that their occupancies can vary from 0.5 to 1.0. In this event the generalized formula for korne-

ment of *M-T* linkages within the sheet. Although not an ultimate classification, it provides some basis for a detailed classification of sulphate structures. Based on this scheme, kornelite is classified as a two-dimensional sheet structure. The *M-T* linkage forms a parallelogram with six *M-T* units as shown schematically below.

TABLE 4. Deduced Hydrogen Bonds in Kornelite

O(A)···Ow···O(B)	O(A)-Ow	Ow-O(B)	O(A)-Ow-O(B)
O(1)···Ow(1)···O(5)	2.673 Å	2.675 Å	103.4°
O(4)···Ow(2)···O(4')	2.670	2.739	91.1
O(10)··Ow(3)···O(8)	2.822	2.567	105.1
O(2)···Ow(4)···O(7)	3.027	3.087	141.5
O(9)···Ow(5)···O(10)	2.780	2.650	94.2
O(7)···Ow(6)···O(9)	2.710	2.674	105.6
O(8)···Ow(7)···Ow(8)	2.869	2.864	97.6
O(5)···Ow(8)···Ow(4)	2.795	2.720	108.8

lite should be written as $[Fe_2^{3+}(H_2O)_6(SO_4)_3] \cdot 1\text{-}2$ H_2O, thus explaining the past confusion concerning H_2O content. The mineral lausenite ($n = 6$) may be the case of zero occupancy in both sites. The confirmation of this postulate must await the structure analysis of lausenite.

Acknowledgments

References

BAUR, W. H. (1965) On hydrogen bonds in crystalline hydrates. *Acta Crystallogr.* **19**, 909–916.

—— (1972) Prediction of hydrogen bonds and hydro-gen atom positions in crystalline solids. *Acta Crystallogr.* **B28**, 1456–1465.

BEDNOWITZ, A. L. (1970) SORTE-A program to aid in the implementation of the symbolic addition method for the direct determination of centrosymmetric crystal structures. *In,* F. R. Ahmed, Ed., *Crystallographic Computing.* Munksgaard, Copenhagen, Denmark, pp. 58–62.

CESBRON, F. (1964) Contribution à la Minéralogie des sulfates de fer hydratés. *Bull. Soc. franc. Minéral. Cristallogr.* **87**, 125–143.

CROMER, D. T., AND J. B. MANN (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A 24**, 321–323.

FANG, J. H., AND P. D. ROBINSON (1970) Crystal structures and mineral chemistry of hydrated ferric sulphates. I. The crystal structure of coquimbite. *Amer. Mineral.* **55**, 1534–1540.

FINGER, L. W. (1969) The crystal structure and cation distribution of a grunerite. *Mineral. Soc. Amer. Spec. Pap.* **2**, 95–100.

PALACHE, C., H. BERMAN, AND C. FRONDEL (1951) *The System of Mineralogy . . . of Dana,* 7th ed., Vol. 2. John Wiley and Sons, Inc., New York.

ROBINSON, P. D., AND J. H. FANG (1971) Crystal structures and mineral chemistry of hydrated ferric sulphates. II. The crystal structure of paracoquimbite. *Amer. Mineral.* **56**, 1567–1572.

SÜSSE, P. (1971) Kristallchemie und Klassifikation der natürlichen Ferrisulphate. *Fortsch. Mineral.* **49**, 119–121.

WUENSCH, B. J., AND C. T. PREWITT (1965) Corrections for X-ray absorption by a crystal of arbitrary shape. *Z. Kristallogr.* **122**, 24–59.