CRYSTAL STRUCTURES AND MINERAL CHEMISTRY OF HYDRATED FERRIC SULPHATES: II. THE CRYSTAL STRUCTURE OF PARACOQUIMBITE

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ABSTRACT

The crystal structure of paracoquimbite—$Fe_2(SO_4)_3 \cdot 9H_2O$, space group $R\bar{3}$, $a = 10.93$ Å, $c = 51.30$ Å, $Z = 12$—has been determined by analogy to the structure of coquimbite, and found to differ only in its stacking sequence. Thus the two minerals are polytypic. The main structural features are: (1) clusters of corner sharing polyhedra composed of three iron octahedra and six sulphate tetrahedra, (2) isolated Fe octahedra and (3) water molecules linking the individual structural units via hydrogen bonds. Average cation-oxygen distances are: S(1)-O = 1.47 Å, S(2)-O = 1.48 Å, Fe(1)-O = 1.98 Å, Fe(2)-Ow = 1.98 Å, Fe(3)-O = 1.97 Å, Fe(4)-O,Ow = 1.98 Å and Fe(5)-O,Ow = 1.97 Å. The final isotropic R-index with 549 reflections is 0.078.

INTRODUCTION

Paracoquimbite was first identified by Ungemach (1935) as a rhombohedral modification of coquimbite. Later, Bandy (1938), in his extensive study of the sulphate deposits of Northern Chile, verified Ungemach's conclusion that ferric sulphate enneahydrate indeed exists in two forms. The structure of coquimbite was reported in paper I of this series (Fang and Robinson, 1970). This paper deals with the determination and description of the crystal structure of paracoquimbite. The polytypic relationship between coquimbite and paracoquimbite will be discussed elsewhere.

Crystals of paracoquimbite were obtained from a sample labelled as coquimbite, supplied to us by the U. S. National Museum (Catalog No. 115161, Locality: Chuquicamata, Chile). The two minerals are virtually indistinguishable without the use of X-ray methods.

EXPERIMENTAL

Weissenberg and precession photographs coupled with measurements obtained from a Buerger equi-inclination single-crystal diffractometer gave the following unit-cell information: $a = 10.926 \pm .009$ Å, $c = 51.300 \pm .021$ Å, space group $R\bar{3}$ and $Z = 12$. The refractive indices measured from the crystal used for X-ray data collection, are: ϵ 1.555 ± .002 and ω 1.550 ± .002. A wet chemical analysis yielded no trace of Al_2O_3. [An analysis of the coquimbite sample used for crystal structure determination (Fang and Robinson, 1970) showed considerable Al-for-Fe substitution.]

The crystal used for intensity measurement was a sphere, $r = 0.16$ mm. A total of 1068 reflections were measured, out of which 554 were considered to be "observed." Details of the data reduction procedures are described in paper I. Both Lp and absorption corrections were applied to the raw data.

Determination and Refinement of the Structure

The crystal structure of paracoquimbite was solved by building a trial model from the structure of coquimbite by noting (1) that the c axial length of paracoquimbite is three times as large as that of coquimbite, (2) that this is equivalent to a triply primitive hexagonal unit cell, and (3) that the two minerals are probably polytypic. The atomic coordinates of coquimbite were thus transformed and expanded to obtain the trial paracoquimbite atomic coordinates. An origin shift of $\frac{1}{2}$ the coquimbite c axial length was also incorporated to conform to the origin choice of the International Tables (Henry and Lonsdale, 1965).

The R-index of the trial structure was 0.268. The form factors used were taken from Cromer and Mann (1968) for Fe^{3+}, S, and O. The structure was quickly refined to $R=0.124$ in 3 cycles, by varying only the positional parameters. By varying only the isotropic temperature factors in the next two cycles, R was reduced to 0.107. In the last cycle all parameters were varied resulting in an R-index of 0.087. At this time three strong, low-angle reflections, obviously suffering from extinction, were removed resulting in a decrease of only 0.001 in the R-index. Two additional cycles of refinement, using a weighting scheme previously described (Cannillo, Mazzi, Fang, Robinson, and Ohya, 1971) yielded a final isotropic R-index of 0.078. The positions of H atoms were not determined, however, the distinction between H_2O and O was made from electrostatic considerations.

The final positional and thermal parameters are listed in Table 1. A table of structure factors calculated in the last least squares cycle has been deposited with the National Auxiliary Publications Service.[1]

Description of the Structure

Figure 1 is a polyhedral representation of the paracoquimbite structure. The main structural features are: (1) polyhedral clusters composed of three Fe octahedra and six S tetrahedra, (2) isolated Fe octahedra, and (3) six water molecules forming very distorted octahedra which contain no cations. The three structural units are interconnected by hydrogen bonds only. The structure can be described as a six-layer stack with a repeat distance of 8.5 Å along the c axis. Each individual layer within the stack contains all three of the main structural features described above.

Interatomic distances and angles in paracoquimbite are given in Table

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[1] Order NAPS Document No. 01517 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, N. Y. 10022: remitting $2.00 for microfiche or $5.00 for photocopies, in advance payable to CCMIC-NAPS.
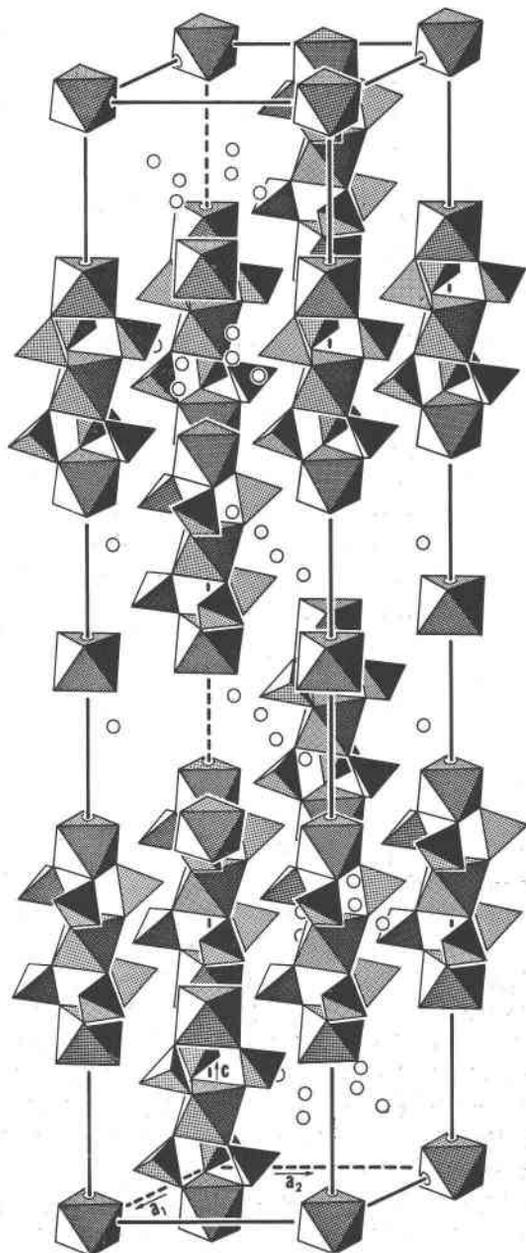
FIG. 1. Polyhedral representation of the paracoquimbite structure. Open circles represent H₂O molecules. The orientation of the coquimbite cell is identical to that of paracoquimbite.

Table 1.   Atomic Coordinates, Temperature Factors and Standard Errors[a]

Atom	Equipoint	x	y	z	B($\AA^2$)
Fe(1)	3a	0	0	0	3.4(3)
Fe(2)	3b	0	0	1/2	3.6(3)
Fe(3)	6c	0	0	.2507(2)	3.2(2)
Fe(4)	6c	0	0	.1677(2)	3.2(2)
Fe(5)	6c	0	0	.6652(2)	3.5(2)
S(1)	18f	.249(9)	.4169(8)	.8756(1)	1.8(1)
S(2)	18f	.584(8)	.7554(8)	.9593(1)	1.8(1)
O(1)	18f	.325(2)	.349(2)	.8650(4)	2.4(4)
O(2)	18f	.655(2)	.682(2)	.9697(4)	2.7(4)
O(3)	18f	.114(2)	.310(2)	.8865(4)	2.5(4)
O(4)	18f	.685(2)	.892(2)	.9486(4)	2.4(4)
O(5)	18f	.223(2)	.493(2)	.8545(4)	2.1(4)
O(6)	18f	.504(2)	.778(2)	.9807(3)	2.1(4)
O(7)	18f	.339(2)	.520(2)	.8960(4)	1.7(4)
O(8)	18f	.481(2)	.662(2)	.9388(4)	2.0(4)
Ow(1)	18f	.171(2)	.073(2)	.8553(4)	2.5(5)
Ow(2)	18f	.929(2)	.826(2)	.9787(4)	2.9(5)
Ow(3)	18f	.446(2)	.114(2)	.9016(4)	2.8(4)
Ow(4)	18f	.886(2)	.550(2)	.9290(4)	2.7(5)
Ow(5)	18f	.596(2)	.434(2)	.8552(4)	2.7(5)
Ow(6)	18f	.575(2)	.410(2)	.9755(4)	2.9(5)

[a]In parentheses

2. The two independent SO_4 groups show the usual tetrahedral coordination with mean values of S(1)-O = 1.47 Å and S(2)-O = 1.48 Å, in good agreement with other hydrated-sulphate structures determined in this lab and elsewhere. It has been reported in paper I that there is a lengthening of the S-O distance when the oxygen atom is also bonded to an Fe atom. This is also true in paracoquimbite. Thus there seem to be two groups of S-O distances whose individual lengths vary from 1.46 to 1.47 Å for S-O (non-sharing) and 1.48 to 1.50 for sharing. A difference of about 0.02 Å between the two groups of S-O distances is significant in terms of the π-bonding character of the bond. The average Fe-O distance is 1.96 Å, while the mean Fe-Ow distance is 1.98 Å.

The relatively high temperature factors of the atoms merit some comments. The B's of the two independent Fe atoms in coquimbite (Fang and Robinson, 1970) are $B_{FE(1)} = 1.71$ and $B_{FE(2)} = 2.19$; whereas in paracoquimbite, the five independent Fe atoms have B values ranging

Table 2.   Selected Interatomic Distances and Angles for Paracoquimbite [a]

Tetrahedral coordination around S

S(1)-O(1)	1.46(2) Å	O(1)-O(3)	2.38(3) Å	O(1)-S(1)-O(3)	109(1)
S(1)-O(3)	1.46(2)	O(1)-O(5)	2.40(3)	O(1)-S(1)-O(5)	109(1)
S(1)-O(5)	1.48(2)	O(1)-O(7)	2.39(3)	O(1)-S(1)-O(7)	109(1)
S(1)-O(7)	1.49(2)	O(3)-O(5)	2.40(3)	O(3)-S(1)-O(5)	109(1)
		O(3)-O(7)	2.43(3)	O(3)-S(1)-O(7)	111(1)
		O(5)-O(7)	2.42(3)	O(5)-S(1)-O(7)	109(1)
MEAN	1.47 Å	MEAN	2.40 Å	MEAN	109°
S(2)-O(2)	1.47(2)	O(2)-O(4)	2.41(3) Å	O(2)-S(2)-O(4)	111(1)°
S(2)-O(4)	1.45(2)	O(2)-O(6)	2.42(3)	O(2)-S(2)-O(6)	110(1)°
S(2)-O(6)	1.50(2)	O(2)-O(8)	2.40(3)	O(2)-S(2)-O(8)	108(1)
S(2)-O(8)	1.50(2)	O(4)-O(6)	2.39(3)	O(4)-S(2)-O(6)	108(1)
		O(4)-O(8)	2.44(3)	O(4)-S(2)-O(8)	111(1)
		O(6)-O(8)	2.44(3)	O(6)-S(2)-O(8)	109(1)
MEAN	1.48 Å	MEAN	2.42 Å	MEAN	109°

Octahedral coordination around Fe

Fe(1)-Ow(2)	1.98(2)Å [x6]	Ow(2)-Ow(2)	2.86(4)Å [x6]	Ow(2)-Fe(1)-Ow(2)	92.6(8)°[x6]
		Ow(2)-Ow(2)	2.74(3) [x6]	Ow(2)-Fe(1)-Ow(2)	87.4(8)°[x6]
MEAN	1.98 Å	MEAN	2.80 Å	MEAN	90.0°
Fe(2)-Ow(5)	1.98(2)Å [x6]	Ow(5)-Ow(5)	2.82(4)Å [x6]	Ow(5)-Fe(2)-Ow(5)	91.0(8)°[x6]
		Ow(5)-Ow(5)	2.77(3) [x6]	Ow(5)-Fe(2)-Ow(5)	89.0(8) [x6]
MEAN	1.98 Å	MEAN	2.80 Å	MEAN	90.0°
Fe(3)-O(7)	1.97(2)Å [x3]	O(7)-O(7)	2.83(4)Å [x3]	O(7)-Fe(3)-O(7)	91.9(8)°[x3]
Fe(3)-O(8)	1.97(2) [x3]	O(7)-O(8)	2.69(3) [x3]	O(7)-Fe(3)-O(8)	86.0(8) [x3]
		O(8)-O(7)	2.79(2) [x3]	O(8)-Fe(3)-O(7)	90.1(8) [x3]
		O(8)-O(8)	2.84(4) [x3]	O(8)-Fe(3)-O(8)	92.1(8) [x3]
MEAN	1.97 Å	MEAN	2.79 Å	MEAN	90.0°
Fe(4)-O(5)	1.96(2)Å [x3]	O(5)-O(5)	2.88(3)Å [x3]	O(5)-Fe(4)-O(5)	94.7(8)°[x3]
Fe(4)-Ow(1)	2.00(2) [x3]	O(5)-Ow(1)	2.69(3) [x3]	O(5)-Fe(4)-Ow(1)	85.7(9) [x3]
		Ow(1)-O(5)	2.81(3) [x3]	Ow(1)-Fe(4)-O(5)	90.6(8) [x3]
		Ow(1)-Ow(1)	2.81(4) [x3]	Ow(1)-Fe(4)-Ow(1)	89.1(9) [x3]
MEAN	1.98 Å	MEAN	2.80 Å	MEAN	90.0°
Fe(5)-O(6)	1.95(2)Å [x3]	O(6)-O(6)	2.84(4)Å [x3]	O(6)-Fe(5)-O(6)	93.2(8)°[x3]
Fe(5)-Ow(6)	1.99(2) [x3]	O(6)-Ow(6)	2.87(3) [x3]	O(6)-Fe(5)-Ow(6)	93.5(8) [x3]
		Ow(6)-O(6)	2.67(3) [x3]	Ow(6)-Fe(5)-O(6)	85.2(9) [x3]
		Ow(6)-Ow(6)	2.77(4) [x3]	Ow(6)-Fe(5)-Ow(6)	88.3(9) [x3]
MEAN	1.97 Å	MEAN	2.79 Å	MEAN	90.0°

[a] Standard errors in parentheses.

from 3.2 to 3.5. It is also noted that the temperature factor ratio of Fe:O is larger than normal in both structures. At the suggestion of Dr. Paul Moore, of the University of Chicago, we reran the least-squares calculations to explore the possibility that the high B's might be due to a scaling-factor effect. First, the B's of all atoms were manually lowered to values which were more typical of each atomic species and "locked" while all other parameters were varied through two cycles of least-squares. In the third cycle the B's were also varied and they immediately returned to their previous high values. Thus, the relatively high degree of thermal motion would seem to represent physical reality. However, the B's of Fe, which are relatively higher than the B's of other atoms, can be largely

accounted for by the fact that no anomolous dispersion correction was applied, as was pointed out by the referee, although the data were collected with CuKα radiation.

REFERENCES

BANDY, M. C. (1938) Mineralogy of three sulphate deposits of northern Chile. *Amer. Mineral.* **23**, 669–760.

CANNILLO, E., F. MAZZI, J. H. FANG, PAUL D. ROBINSON, AND Y. OHYA (1971) The crystal structure of aenigmatite. *Amer. Mineral.* **56**, 427–446.

CROMER, D. T., AND J. B. MANN (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A24**, 321–324.

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.

HENRY, N. F. M., AND K. LONSDALE (1965) *International Tables for X-ray Crystallography. Vol.* 1. The Kynoch Press, Birmingham, England.

PANT, A. K., AND D. W. J. CRUICKSHANK (1968) The crystal structure of α-Na$_2$Si$_2$O$_5$. *Acta Crystallogr.* **B24**, 13–19.

UNGEMACH, P. (1935) Sur certains minéraux sulfatés du Chili. *Bull. Soc. Franc. Mineral.* **58**, 97–221.