

The structure of ferrarisite, $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 9 \text{H}_2\text{O}$: disorder, hydrogen bonding, and polymorphism with guerinite

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Abstract. — By an automatic diffractometer (MoK α radiation) 2 810 observed reflections were measured on a single crystal of ferrarisite from Sainte-Marie-aux-Mines (Alsace), with the following unit-cell parameters : $a = 8.294(4)$, $b = 6.722(3)$, $c = 11.198(5)$ Å, $\alpha = 106.16(4)$, $\beta = 92.94(4)$, $\gamma = 99.20(4)^\circ$; $Z = 1$, space group $P\bar{1}$. The structure was solved by direct methods and refined by least-squares to $R = 0.033$. One water molecule is disordered over two centrosymmetric positions, and presumably that also implies disorder of hydrogen atoms of other water molecules. Two out of the three independent Ca atoms coordinate, in a very irregular way, seven oxygen atoms. These polyhedra, together with the As tetrahedra, build up (001) layers by sharing edges and vertices. The third Ca atom, which is in special position, has nearly regular octahedral coordination and is sandwiched between the layers, with the formation of very large [010] (and smaller [100]) channels at the border of which the water molecules lie. Possible further occupation of sites in the channels is pointed out. Polymorphism with guerinite, relationships with picroparmacolite and dehydration are discussed.

Key words : ferrarisite, guerinite, crystal structure, disorder, hydrogen bonding.

La structure de la ferrarisite, $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 9 \text{H}_2\text{O}$: désordre, liaison hydrogène et polymorphisme avec la guérinite.

Résumé. — 2 810 réflexions observées ont été mesurées à l'aide d'un diffractomètre automatique (radiation MoK α) sur un monocristal de ferrarisite (Sainte-Marie-aux-Mines, Alsace). Les paramètres de la maille sont : $a = 8.294(4)$, $b = 6.722(3)$, $c = 11.198(5)$ Å, $\alpha = 106.16(4)$, $\beta = 92.94(4)$, $\gamma = 99.20(4)^\circ$; $Z = 1$, groupe spatial $P\bar{1}$. La structure a été résolue par les méthodes directes et affinée par moindres carrés jusqu'à $R = 0,033$. Une des molécules d'eau est désordonnée sur deux positions centrosymétriques, ce qui implique probablement le désordre des hydrogènes d'autres molécules d'eau. Deux parmi les trois atomes de Ca indépendants donnent une coordination très irrégulière avec sept atomes d'oxygène. Ces polyèdres, avec les tétraèdres As, forment des couches (001), leurs arêtes et leurs sommets étant mis en commun. Le troisième atome de Ca, en position spéciale, présente une coordination octaédrique entre deux couches (001); des grands canaux [010] et des plus petits [100] en résultent, avec les molécules d'eau qui occupent leurs bords. La possible occupation d'autres sites dans les canaux est mise en évidence. On discute finalement le polymorphisme avec la guérinite, les relations avec la picroparmacolite et la déshydratation.

Mots clés : ferrarisite, guérinite, structure cristalline, désordre, liaison hydrogène.

INTRODUCTION

Ferrarisite is a new calcium arsenate hydrate fully described by Bari *et al.* (1980), on the basis of samples from Sainte-Marie-aux-Mines (Alsace); it had also been previously reported as a unnamed mineral from Wittichen (Schwarzwald) by Walenta (1972). The mineral occurs with the other arsenates picroparmacolite, pharmacolite, sainfeldite and rauenthalite and has been recognized as a dimorph of guerinite (Pierrot, 1964; Catti and Ferraris, 1974) mainly by comparison of its X-ray powder pattern with that of the artificial product synthesized by Guérin (1978, private communication). A retrospective reading of an old paper by Guérin (1941) shows that the two phases had already been obtained at that time, even if they were not recognized as such but only described as two morphological aspects (noduls and tablets) of the same product.

As a part of a research programme on the hydrogen bonding in the crystalline state and following the structural study of similar phases (Ferraris and Abbona, 1972; Catti and Ferraris, 1974; Catti *et al.*, 1980) the crystal structure of ferrarisite is here described.

CRYSTAL DATA

Colourless crystals selected by H. Bari (B.R.G.M., Orléans) from the type samples of Sainte-Marie-aux-Mines have been used.

Through the LAT routine of the Philips PW 1100 single-crystal diffractometer and with $\lambda = 0.71069$ Å the following parameters of the reduced cell were obtained : $a = 8.294(4)$, $b = 6.722(3)$, $c = 11.198(5)$ Å, $\alpha = 106.16(4)$, $\beta = 92.94(4)$, $\gamma = 99.20(4)^\circ$. The space group $P\bar{1}$ was chosen on the basis of statistical tests of the X-ray diffraction intensities and was confirmed by the successful refinement of the structure. Other data are : $MW = 920.231$, $V = 588.9$ Å³, $D_m = 2.63$ Mg m⁻³ (Bari *et al.*, 1980), $D_c = 2.594$ Mg m⁻³, $Z = 1$, $F(000) = 452$, $\mu(\text{MoK}\alpha) = 9.1$ mm⁻¹.

INTENSITY MEASUREMENTS

The X-ray diffraction intensities were collected with a four circle Philips PW 1100 diffractometer from a

tabular {110} crystal with $0.13 \times 0.32 \times 0.48$ mm dimensions; the largest dimension corresponds to the trace [110] of cleavage {001} on (110). This, as other crystals, turned out to be « multiple », perhaps in connection with the easy {001} cleavage, and the reflections were slightly doubled; the ω scan, however, took the contribution from the full reflection profile. The measurements conditions were: graphite monochromatized MoK α radiation, $\theta \leq 30^\circ$, ω scan width = 3.5° , scanning speed 0.1° s^{-1} , background time = $(\text{scan time}/2)(I_{\text{bkg}}/I_{\text{peak}})^{1/2}$ on each side of the peak, three reference reflections, attenuating filter inserted for $I \geq 60\,000$ counts/s. By rejecting the 616 weakest reflections [$I \leq 2\sigma(I)$], a set of 2 810 independent observations was obtained. Experimental absorption correction according to North *et al.* (1968) was applied.

Scattering factors for neutral atoms were calculated using the parameters for the analytical formula given in International Tables for X-ray Crystallography (1974); the SHELX set of programs was used (Sheldrick, 1976).

SOLUTION AND REFINEMENT OF THE STRUCTURE

Intensity statistics clearly supported centrosymmetry and through combination of direct methods, with the

metric positions with occupation factor 0.5. At the final stage of refinement the hydrogen atoms [except those bonded to W(5) and two bonded to W(1) and W(4) respectively] were located on a difference map. The full-matrix anisotropic refinement (isotropic for the H atoms) converged to $R = 0.033$ with unitary weights. Table I shows the positional parameters and, for the thermal motion, the coefficients U_{ij} of the expression

$$\exp\left(-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} h_i h_j a_i^* a_j^*\right).$$

A list of structure factors is available from authors on request.

DESCRIPTION OF THE STRUCTURE

While Ca (3), which lies on a centre of symmetry, shows quite a regular octahedral coordination, Ca (1) and Ca (2) are very irregularly coordinated by seven oxygen atoms, according to a polyhedron which can be assimilated to an octahedron with a double vertex (Table II).

The structure (Figures 1 and 2) can be described in terms of Ca and As coordination polyhedra that, by

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As(1)	0.52429(5)	0.05829(7)	0.84251(4)	0.99(2)	0.99(2)	1.37(2)	0.47(1)	0.21(1)	0.18(1)
As(2)	0.00723(5)	0.26663(6)	0.83694(4)	1.00(2)	0.95(2)	1.19(2)	0.42(1)	0.32(1)	0.17(1)
Ca(1)	0.68248(10)	0.61888(10)	0.92486(8)	1.09(3)	1.12(4)	1.90(4)	0.52(3)	0.32(3)	0.26(3)
Ca(2)	0.14429(10)	0.80632(10)	0.92317(8)	1.21(4)	1.12(4)	1.50(4)	0.44(3)	0.33(3)	0.17(3)
Ca(3)	0	0	1/2	2.11(6)	2.92(7)	1.30(6)	0.59(5)	0.42(5)	0.49(5)
O(1)	0.4977(4)	0.2986(5)	0.9207(3)	1.38(14)	0.93(13)	2.53(16)	0.55(12)	0.70(12)	0.50(11)
O(2)	0.6562(4)	-0.0360(5)	0.9197(3)	1.52(14)	1.33(14)	2.03(15)	0.85(12)	-0.19(11)	0.48(11)
O(3)	0.3459(4)	-0.1116(5)	0.7934(3)	1.15(13)	1.60(14)	1.82(15)	0.41(12)	0.13(11)	-0.08(11)
O(4)	0.5964(4)	0.0666(6)	0.7006(3)	1.45(15)	3.54(19)	1.69(15)	1.05(14)	0.33(12)	0.10(13)
O(5)	0.1501(4)	0.4493(5)	0.8080(3)	1.98(15)	1.33(14)	2.18(16)	0.61(12)	0.83(12)	-0.02(12)
O(6)	0.0847(4)	0.1522(5)	0.9389(3)	1.27(13)	1.21(13)	1.53(14)	0.64(11)	0.02(11)	0.60(11)
O(7)	-0.1465(4)	0.3721(5)	0.9066(3)	1.43(14)	1.54(14)	2.00(15)	0.63(12)	0.66(12)	0.80(11)
O(8)	-0.0725(4)	0.0764(5)	0.7029(3)	2.12(16)	1.72(15)	1.19(14)	0.23(11)	0.26(12)	0.04(12)
W(1)	0.4747(4)	0.5309(6)	0.7443(4)	2.26(16)	1.90(16)	2.93(19)	0.87(14)	0.14(14)	0.24(13)
W(2)	0.8929(5)	0.7139(5)	0.7724(3)	2.78(18)	1.55(15)	2.37(17)	0.82(13)	0.13(14)	0.44(13)
W(3)	0.1105(7)	0.3627(8)	0.5552(4)	6.4(3)	4.6(3)	3.3(2)	1.4(2)	0.1(2)	-1.7(2)
W(4)	0.2554(7)	-0.0531(12)	0.5718(5)	4.1(3)	13.2(6)	3.2(3)	2.8(3)	0.4(2)	4.3(3)
W(5)	0.6911(12)	0.4288(12)	0.5697(8)	5.7(6)	1.9(4)	3.0(4)	0.6(3)	3.0(4)	0.2(4)
H(04)	0.690(10)	0.081(10)	0.712(10)	3.8					
H(W1)	0.381(10)	0.471(10)	0.777(10)	3.8					
H(W21)	0.901(10)	0.843(10)	0.747(10)	3.8					
H(W22)	0.876(10)	0.596(10)	0.706(10)	3.8					
H(W31)	0.212(10)	0.447(10)	0.514(10)	3.8					
H(W32)	0.133(10)	0.429(10)	0.647(10)	3.8					
H(W4)	0.253(10)	-0.068(10)	0.657(10)	3.8					

TABLE I. — Atomic fractional coordinates and vibrational parameters ($\times 10^2 \text{ \AA}^2$), with estimated standard deviations in parentheses.

program MULTAN (Germain *et al.*, 1971), and of Patterson function the coordinates of the As and Ca atoms were obtained. A subsequent difference Fourier synthesis with the phases as determined by these atoms showed all the oxygen atoms; one water molecule, W(5) (*), is statistically disordered over two centrosym-

metric positions, build up (001) layers held together by the Ca (3) octahedra acting as « columns » along [001]. Large channels along [010] and smaller ones along [100] going through the whole structure are produced; the W(5) disordered water is located in the resulting large cavity and is held in place by hydrogen bonds only. In the (001) layers, which are repeated by the *c* vector only, the shared edges and vertices are:

i) O(1)-O(1')ⁱⁱⁱ and O(6')^v-O(6)ⁱⁱ between pairs of centrosymmetric Ca(1) and Ca(2) polyhedra, respectively;

(*) Atomic symbols with a prime denote atoms subjected to the operation $1 - x, 1 - y, 1 - z$; roman numerals represent the translations: *i*, + *a*; *ii*, + *b*; *iii*, + *c*; *iv*, - *a*; *v*, - *a* + *c*; *vi*, - *a* - *b*; *vii*, - *a* + *b*; *viii*, + *a* + *b*; *ix*, - *b*.

Ca(1) - O(1)	2.422(3) Å	Ca(2) - O(3) ⁱⁱ	2.369(3) Å	Ca(3) - O(8)	2.319(3) Å
Ca(1) - O(1') ⁱⁱⁱ	2.351(3)	Ca(2) - O(5)	2.397(3)	Ca(3) - O(8') ^{vi}	2.357(5)
Ca(1) - O(2) ⁱⁱ	2.381(3)	Ca(2) - O(6) ⁱⁱ	2.415(3)	Ca(3) - W(3)	2.343(6)
Ca(1) - O(6') ⁱⁱⁱ	2.422(3)	Ca(2) - O(2') ⁱⁱⁱ	2.365(3)	Ca(3) - W(3') ^{vi}	2.340
Ca(1) - O(7) ⁱ	2.324(3)	Ca(2) - O(6') ^v	2.510(3)	Average	2.439
Ca(1) - W(1)	2.461(4)	Ca(2) - O(7') ^v	2.519(3)		
Ca(1) - W(2)	2.631(4)	Ca(2) - W(2) ^{iv}	2.495(4)		
Average	2.427				
W(2) - O(7) ⁱ	3.062(6) Å	76.1(1)°	O(3) ⁱⁱ - O(5)	3.184(5) Å	83.8(1)°
W(2) - W(1)	3.457(6)	85.4(1)	O(3) ⁱⁱ - O(6) ⁱⁱ	3.237(5)	85.2(1)
W(2) - O(6') ⁱⁱⁱ	3.093(6)	75.3(1)	O(3) ⁱⁱ - W(2) ^{iv}	3.728(5)	100.0(1)
W(2) - O(2) ⁱⁱ	3.041(6)	74.5(1)	O(3) ⁱⁱ - O(2') ⁱⁱⁱ	3.090(5)	81.5(1)
O(1) - O(1') ⁱⁱⁱ	2.788(5)	71.5(1)	O(6') ^v - O(7') ^v	2.669(5)	64.1(1)
O(1) - O(7) ⁱ	2.933(5)	76.3(1)	O(6') ^v - O(6) ⁱⁱ	2.978(5)	74.4(1)
O(1) - W(1)	2.854(6)	71.5(1)	O(6') ^v - W(2) ^{iv}	3.093(5)	76.3(1)
O(1') ⁱⁱⁱ - O(2) ⁱⁱ	3.035(5)	79.8(1)	O(6') ^v - O(2') ⁱⁱⁱ	3.551(5)	93.5(1)
O(1') ⁱⁱⁱ - O(6') ⁱⁱⁱ	3.443(5)	92.3(1)	O(7') ^v - O(2') ⁱⁱⁱ	3.006(5)	75.9(1)
O(1') ⁱⁱⁱ - W(1)	3.588(6)	96.4(1)	O(7') ^v - O(5)	3.089(5)	77.8(1)
O(2) ⁱⁱ - O(6') ⁱⁱⁱ	2.935(5)	75.3(1)	W(2) ^{iv} - O(6) ⁱⁱ	3.135(5)	79.3(1)
O(2) ⁱⁱ - W(1)	3.117(6)	80.1(1)	W(2) ^{iv} - O(5)	3.066(5)	77.6(1)
O(7) ⁱ - O(6') ⁱⁱⁱ	3.129(5)	82.5(1)	O(2') ⁱⁱⁱ - O(6) ⁱⁱ	2.935(5)	75.8(1)
O(7) ⁱ - W(1)	3.984(6)	112.7(1)	O(2') ⁱⁱⁱ - O(5)	4.268(6)	127.3(1)

TABLE II. — Interatomic distances and angles (O — Ca — O) in the Ca coordination polyhedra. The estimated standard deviations are shown in parentheses.

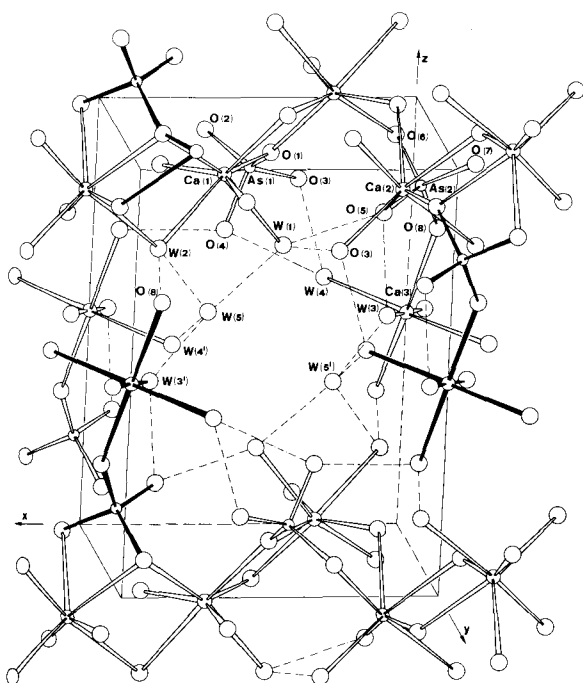


FIG. 1. — Orthographic projection of the crystal structure of ferrarisite along [010]. Dashed-dotted lines shows hydrogen bonds; roman numerals representing translations are not given.

ii) O(2)ⁱⁱ-O(6')ⁱⁱⁱ, W(2)-O(6')ⁱⁱⁱ, O(6')ⁱⁱⁱ and O(7)ⁱ between the Ca(1) polyhedron and four distinct Ca(2) polyhedra;

iii) O(6')^v-O(7')^v between the Ca(2) polyhedron and the As(2) tetrahedron (Table III).

All oxygen atoms of the arsenate group are bonded to

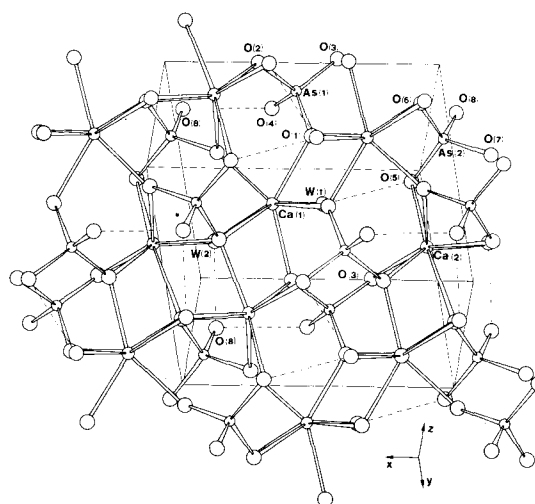


FIG. 2. — Orthographic projection of the crystal structure of ferrarisite onto the (001) plane. Hydrogen bonds and translations as in figure 1.

two Ca atoms with the following exceptions : the acidic-hydrogen carrier O(4) is not Ca coordinated; O(8) is coordinated to Ca(3) only and constitutes the bridge between layers through the sequence As(2)-O(8)-Ca(3)-O(8')^{vi}-As(2')^{vi}; and O(6) is coordinated to three Ca atoms.

As far as the water molecules are concerned, W(1) and W(2) belong to the layer; W(1), coordinated to Ca(1) and Ca(2), supplies a hydrogen bond between the Ca(3) octahedron and the layer. W(3) and W(4) are bonded to Ca(3) only and their hydrogen bonds (Table IV) supply further links between the Ca(3) octahedron, the layer and W(5) which is not Ca coordinated.

DISORDER AND HYDROGEN BONDING

All the water molecules are facing the large cavity described above. W(5), in particular, is statistically disordered between two centrosymmetric positions inside the cavity and is bonded to the structure by hydrogen bonds only. The two highest residues of electron density in the final difference Fourier synthesis are at $p(1)$ ($x = 0.598$, $y = 0.400$, $z = 0.522$; 1.5 electrons) and $p(2)$ ($x = 0.513$, $y = 0.321$, $z = 0.519$; 1.2 electrons) within the cavity; $p(1)$ and $p(2)$ are at 0.88 and 1.54 Å, respectively, from W(5) (to which they must be, therefore, alternative) and at 3.07 and 2.89 Å, respectively,

As(1) - O(1)	1.665(3) Å		As(2) - O(5)	1.677(3) Å	
As(1) - O(2)	1.665(3)		As(2) - O(6)	1.697(3)	
As(1) - O(3)	1.680(3)		As(2) - O(7)	1.679(3)	
As(1) - O(4)	1.739(3)		As(2) - O(8)	1.698(3)	
Average	1.687		Average	1.688	
O(1) - O(2)	2.778(5) Å	113.1(2)°	O(5) - O(6)	2.792(5) Å	111.7(2)°
O(1) - O(3)	2.782(5)	112.6(2)	O(5) - O(7)	2.780(5)	111.9(2)
O(1) - O(4)	2.767(5)	108.8(2)	O(5) - O(8)	2.781(5)	110.9(2)
O(2) - O(3)	2.773(5)	112.0(2)	O(6) - O(7)	2.669(5)	104.5(2)
O(2) - O(4)	2.769(5)	108.8(2)	O(6) - O(8)	2.762(5)	108.9(2)
O(3) - O(4)	2.636(5)	100.9(2)	O(7) - O(8)	2.746(5)	108.8(2)
Average	2.751	109.4	Average	2.755	109.4

TABLE III. — Interatomic distances and O — As — O angles in the As tetrahedra.

The estimated standard deviations are shown in parentheses.

A	B	C	D	AB	BD	BC	CD	CC'	ABA'	CBC'	DBD'	BCD
W(5)	W(1)	H(W1)---O(5)		2.743(10)	2.828(5)	0.95(8)	1.95(8)					
Ca(1)		O(3)		2.461(4)	2.714(5)				94.7(2)		70.1(1)	151(7)
Ca(1)	W(2)	H(W21)---O(8)		2.631(4)	2.735(5)	0.98(7)	1.76(7)					177(8)
Ca(2)		H(W22)---W(5)		2.495(4)	2.791(10)	0.91(9)	2.05(9)	1.57(10)	96.9(1)	112(8)	101.8(2)	138(7)
Ca(3)	W(3)	H(W31)---W(5')		2.357(5)	2.687(10)	1.13(8)	1.59(8)					163(7)
		H(W32)---O(5)			2.718(6)	0.99(12)	1.77(12)	1.68(14)		105(7)	122.5(3)	159(6)
Ca(3)	W(4)	H(W4)---O(3)		2.543(6)	2.706(7)	0.99(11)	1.79(10)					152(7)
W(5')		O(4)		2.699(11)	2.989(7)				108.5(3)		54.9(1)	
W(2)	W(5)	W(4')		2.791(10)	2.699(11)				81.0(3)		131.6(4)	
W(3')		W(1)		2.687(10)	2.743(10)							
		O(4)---H(O4)---O(8)			2.735(5)	0.77(8)	1.98(8)					167(10)

TABLE IV. — Interatomic distances (Å) and angles (°) in the hydrogen bonds; a letter with a prime denotes an atom on the second line of each water molecule. The estimated standard deviations are shown in parentheses.

vely, from W(5'). At first sight, these two sites appear suitable for water molecules, since around them four oxygen atoms are « tetrahedrally » arranged at distances ranging from 2.71 to 3.19 Å [W(1), W(4')^{ix}, W(3') and O(1)] for $p(1)$ and from 2.59 to 3.12 Å [W(1), W(4')^{ix}, O(4')^{ix} and O(4)] for $p(2)$. However, the hypothesis of further disorder of W(5) only seems not to be plausible on the basis of the heights of the electron-density residues; in fact, the height of the peak obtained for W(5) in the electron-density map and the values of its thermal parameters account quite well for the assigned 0.5 occupation factor. Three other hypotheses seem more plausible.

i) The water content of the unit cell is slightly higher than nine (about 1/4 of molecule more);

ii) the high thermal motion of W(3), W(4) and perhaps of W(5) too means that their positions have occupation factors slightly smaller than 1, 1 and 0.5 respectively, and, therefore, part of these molecules can occupy $p(1)$ and $p(2)$;

iii) $p(1)$ and $p(2)$ are occasionally occupied by Ca (not more than 1/10 of Ca all together) or other cations, taking into account that further oxygen atoms, besides those given above, are around $p(1)$ and $p(2)$ within a distance of 3.5 Å and could provide the required coordination; such a situation would be similar to that of guerinite (Catti and Ferraris, 1974).

Presumably the distribution of W(5) between two centrosymmetric positions involves disorder for some H atoms which are hydrogen-bonded to it. In particular, two hydrogen atoms bonded to W(1) and W(4) may have not been located because disordered. O(5)-O(3)ⁱⁱ and O(3)-O(4) are edges of Ca(2) and As(1) coordination polyhedra, respectively, and the values of the angles O(5) ... W(1) ... O(3)ⁱⁱ = 70.1° and O(3) ... W(4) ... O(4) = 54.9° are largely below the range known for the acceptor-oxygen-acceptor angle in hydrogen bonds donated by water molecules (Ferraris and Franchini-Angela, 1972). By comparing then these very narrow O ... W ... O angles with the expected value of about 108° for the H — W — H angles, at least one of the hydrogen bonds donated by W(1) and W(4) should be very far from linearity and therefore energetically less favoured (Brown, 1976). It seems therefore plausible to hypothesize that, without affecting the positions of H(2) and H(7), each one of W(1) and W(4) can have its second hydrogen atom in two alternative positions; then a tetrahedral or a triangular coordination with Ca along the H — W — H bisector may be attained, according to whether the W(5) position is occupied or vacant. This kind of disorder can also explain the very high thermal parameters and anisotropy of W(4), which is coordinated by Ca(3) only, while W(1) belonging to the layer is held in place more firmly.

DIMORPHISM WITH GUERINITE

By comparing the values of guerinite cell parameters [$a = 17.63$ (1), $b = 6.734$ (3), $c = 23.47$ (2) Å, $\beta = 90.6(1)^\circ$] with those of ferrarisite, a very strict connection between the two crystal structures could be foreseen; in fact, besides the identity between the two b parameters, a and c of ferrarisite are approximately submultiples of the corresponding parameters in guerinite. Actually just the main features of the two structures are similar, i.e. the (001) layers of coordination polyhedra in ferrarisite and the ($\bar{1}01$) layers in guerinite, with respect to which only b has the same orientation and corresponds to the thickness of two « chains » of Ca polyhedra in the layer.

In the unit cell of guerinite two ($\bar{1}01$) layers are present, which are built up by the Ca polyhedra; these are linked to each other and to the As tetrahedra by sharing not only vertices and edges, as in ferrarisite, but also faces. Most water molecules (five of which out of 45 in the cell are disordered) are sandwiched between the layers and one Ca out of 25 in the cell is disordered over two pairs of centrosymmetric positions in a large cavity bridging the layers. The partially occupied cavity corresponds to the Ca (3) site in ferrarisite and could be the keystone to understand the dimorphism of $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 9 \text{H}_2\text{O}$, with its two phases present in the same natural environment. Both phases have been obtained in the laboratory at room temperature (Guérin, 1941): ferrarisite by hydrolysis of $\text{CaHAsO}_4 \cdot 2 \text{H}_2\text{O}$ or, perhaps sometimes, of a mixture of several hydrates with formula $\text{CaHAsO}_4 \cdot n \text{H}_2\text{O}$ (Catti and Ferraris, 1973) and guerinite by direct synthesis (Guérin, 1941, 1978 (Private communication); Pierrot, 1964). Order/disorder phenomena and kinetics should probably play an important role in the formation of both dimorphs, so as to account for their genesis in the same pressure-temperature conditions.

STRUCTURE AND PHYSICAL PROPERTIES

A phase probably derived from ferrarisite by dehydration has been noted in samples of the mineral kept at room temperature in laboratory (Bari *et al.*, 1980); this phase could correspond to the first product which is obtained by heating of ferrarisite in a high-temperature Guinier powder camera. On the other side, the first two products of dehydration of

ferrarisite obtained with this camera, which are unidentified, do not coincide with those (unidentified as well) obtained from guerinite; further dehydration of both the minerals, and of sainfeldite too (Catti and Ferraris, 1974), leads to a common unidentified phase and then eventually to $5 \text{CaO} \cdot 2 \text{As}_2\text{O}_5$.

A spontaneous dehydration of ferrarisite would be easily explained by the removal of its loosely bonded water molecule W(5) from the described cavity. Presumably a product of dehydration obtained through the loss of W(5) only would be a member of the family $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot n \text{H}_2\text{O}$ with $n = 8$, to be added to those already known with $n = 9$ (ferrarisite and guerinite), $n = 5$ (vladimirite) and $n = 4$ (sainfeldite) (Pierrot, 1954).

The easy {001} cleavage corresponds to breaking the structure along the loosely linked (001) layers.

COMPARISON WITH PICROPHARMACOLITE

The crystal structure of picropharmacolite is not known, but Abbona and Ferraris (1976) have suggested the formula $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 11 \text{H}_2\text{O}$ supported by analogies with the crystal data of guerinite (Catti and Ferraris, 1974). Following Abbona and Ferraris (1976), one can note that also the strongest reflection (001) in the powder pattern of ferrarisite (Bari *et al.*, 1980) corresponds to the structural layer of coordination polyhedra as in guerinite; besides, ferrarisite and guerinite share with picropharmacolite the value of a cell edge which is parallel to the layers in the first two minerals. The hypothesis of Abbona and Ferraris (1976) of a layered structure for picropharmacolite related to that of guerinite is, therefore, strengthened by comparison with ferrarisite. Besides, since the d_{hkl} corresponding to the strongest reflection (100 or 010), and therefore to the presumed layers, has in picropharmacolite a value (13.6 Å) nearer to that of guerinite (14.4 Å) than to that of ferrarisite (10.9 Å) it seems plausible to think of weakly linked layers as in first mineral rather than to more strongly connected layers as in the latter.

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REFERENCES

- ABBONA, F. and FERRARIS, G. (1976). — On the crystal chemistry of picropharmacolite. *Amer. Mineral.*, 61, 326-328.
- BARI, H., PERMINGEAT, F., PIERROT, R. and WALENTA, K. (1980). — Ferrarisite $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9 \text{H}_2\text{O}$, une nouvelle espèce minérale dimorphe de la guerinite. *Bull. Minéral.*, 103, 533-540.
- BROWN, I. D. (1976). — On the Geometry of O-H...O Hydrogen Bonds. *Acta Cryst.*, A32, 24-31.
- CATTI, M., CHIARI, G. and FERRARIS, G. (1980). — Fluckite $\text{CaMn}(\text{HAsO}_4)_2 \cdot 2 \text{H}_2\text{O}$, a structure related by pseudopolytypism to krautite $\text{MnHAsO}_4 \cdot \text{H}_2\text{O}$. *Bull. Minéral.*, 103, 129-134.
- CATTI, M. and FERRARIS, G. (1973). — Hydrogen Bonding in the Crystalline State. Crystal Structure of $\text{CaHAsO}_4 \cdot 3 \text{H}_2\text{O}$. *Acta Cryst.*, B29, 90-96.
- CATTI, M. and FERRARIS, G. (1974). — Crystal Structure of $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 9 \text{H}_2\text{O}$ (Guerinite). *Acta Cryst.*, B30, 1789-1794.
- FERRARIS, G. and ABBONA, F. (1972). — The Crystal Structure of $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 4 \text{H}_2\text{O}$ (Sainfeldite). *Bull. Soc. fr. Minéral. Cristallogr.*, 95, 34-41.

- FERRARIS, G. and FRANCHINI-ANGELA, M. (1972). — Survey of the Geometry and Environment of Water Molecules in Crystalline Hydrates Studied by Neutron Diffraction. *Acta Cryst.*, B28, 3572-3583.
- GERMAIN, G., MAIN, P. and WOOLSON, M. M. (1971). — The Application of Phase Relationships to Complex Structures. III. The Optimum Use of Phase Relationships. *Acta Cryst.*, A27, 368-376.
- GUERIN, H. (1941). — Sur les arsénates alcalino-terreux. Étude du système $\text{As}_2\text{O}_5\text{-OCa-OH}_2$. *Ann. de Chim.*, 16, 101-153.
- International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham, Kynoch Press.
- NORTH, A. C. T., PHILLIPS, D. C. and MATHEWS, F. S. (1968). — A Semi-Empirical Method of Absorption Correction. *Acta Cryst.*, A24, 351-359.
- PIERROT, R. (1964). — Contribution à la minéralogie des arsénates calciques et calcomagnésien naturels. *Bull. Soc. fr. Minéral. Cristallogr.*, 87, 169-211.
- SHELDRICK, G. M. (1976). — SHELX 76. Program for crystal structure determination. Univ. of Cambridge, England.
- WALENTA, K. (1972). — Die Sekundärminerale der Co-Ni-Ag-Bi-U-Erzgänge im Gebiet von Witthichen im mittleren Schwarzwald. *Aufschluss*, 23, 279-332.
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