

## The crystal structure of picropharmacolite, $\text{Ca}_4\text{Mg}(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 11\text{H}_2\text{O}$

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### Abstract

X-ray diffraction intensities were measured by single-crystal diffractometry ( $\text{MoK}\alpha$  radiation) on picropharmacolite from Sainte-Marie-aux-Mines (Alsace), and the following structure parameters were determined:  $a = 13.547(3)$ ,  $b = 13.500(3)$ ,  $c = 6.710(1)\text{\AA}$ ,  $\alpha = 99.85(1)$ ,  $\beta = 96.41(2)$ ,  $\gamma = 91.60(1)^\circ$ ;  $Z = 2$ , space group  $P\bar{1}$ . The structure was solved by direct methods; the mixed isotropic (oxygen atoms) and anisotropic (heavier atoms) refinement converged to  $R = 0.087$  (1611 reflections). As, Ca, and Mg coordination polyhedra sharing edges and vertices form corrugated (100) layers, which are linked by hydrogen bonding only. Four independent water molecules are sandwiched between adjacent layers, and build up [001] hydrogen-bonded chains. The Mg coordination octahedron and the Ca polyhedra show typical bond distances, so that no significant Ca/Mg substitution should occur in any cation site. The formula of picropharmacolite can then be written as  $\text{Ca}_4\text{Mg}(\text{H}_2\text{O})_7(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ . A close relationship is observed between this structure and those of the two dimorphs guerinite and ferrarisite,  $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 9\text{H}_2\text{O}$ ; in these minerals the layers of polyhedra are also present, but are linked by Ca-O bonds in addition to hydrogen bonds. Cleavage and possible twinning are discussed on structural grounds.

### Introduction

Picropharmacolite is a member of a family of mineral acid arsenates of divalent cations (Pierrot, 1964), and occurs as globular crusts of tiny crystals whose poor quality prevented a crystal structure determination until now. The known phases of the family, whose chemical formula can be written as  $\text{M}_5^{2+}\text{H}_2(\text{AsO}_4)_4 \cdot n\text{H}_2\text{O}$ , can be divided into two groups: species such as sainfeldite,  $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$ , the dimorphs guerinite and ferrarisite,  $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$  (Bari *et al.*, 1980), and chudobaite,  $(\text{Mg,Zn})_5\text{H}_2(\text{AsO}_4)_4 \cdot 10\text{H}_2\text{O}$ , with only one type of  $\text{M}^{2+}$  (except for isomorphous substitution); minerals such as irhtemite,  $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$  (Pierrot and Schubnel, 1972), and picropharmacolite,  $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$  where two different, and presumably ordered, types of  $\text{M}^{2+}$  are present. The Ca and Ca/Mg phases often occur together as accessory minerals which originated by reactions of arsenic ores with surrounding calcareous rocks. The crystal structures of sainfeldite (Ferraris and Abbona, 1972), guerinite (Catti and Ferraris, 1974), ferrarisite (Catti *et al.*, 1980), and chudobaite (Dorner and Weber, 1976) have been determined.

Different crystallochemical formulae have been proposed for picropharmacolite (Abbona and Ferraris, 1976). In most chemical analyses, the  $\text{CaO}/\text{As}_2\text{O}_5$  ratio is slightly higher than 2.0 and the  $\text{MgO}/\text{As}_2\text{O}_5$  ratio fluctuates significantly around 0.5. On the basis of (1) the results obtained by Guérin *et al.* (1967) on synthetic picropharmacolite, (2) the criticism of the available chemical analyses, and (3) a close similarity with the layered structure of guerinite, Abbona and Ferraris favored the hypothesis that there was no solid solution between Ca and Mg in picropharmacolite; a limited substitution involving  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{H}^+$  was, however, not completely excluded. A structural study of picropharmacolite was undertaken to clarify its crystallochemical features and to throw light on its relationships with other members of the family.

### Experimental

A sample of picropharmacolite from Sainte-Marie-aux-Mines (Alsace) was kindly supplied by H. Bari (BRGM, Orléans). After a difficult search (which followed several unsuccessful attempts made previously at our institute on other samples), a tiny needle-like

crystal ( $0.370 \times 0.050 \times 0.016$  mm) elongated along [001] proved to be an acceptable single crystal by Weissenberg photographs, and was selected for all the subsequent measurements on a Philips PW 1100 four-circle diffractometer (MoK $\alpha$  radiation). Through the refinement of 25 measured  $\theta$  values, the following unit-cell constants were determined, in agreement with those of Abbona *et al.* (1969):  $a = 13.547(3)$ ,  $b = 13.500(3)$ ,  $c = 6.710(1)\text{\AA}$ ,  $\alpha = 99.85(1)$ ,  $\beta = 96.41(2)$ ,  $\gamma = 91.60(1)^\circ$ . The space group was assumed to be  $P\bar{1}$  on the basis of diffraction intensity statistics, and later confirmed by the structure solution. Other crystal data are:  $V = 1200.1\text{\AA}^3$ , M.W. = 940.488,  $D(\text{meas}) = 2.62\text{g cm}^{-3}$  (Pierrot, 1961),  $D(\text{calc.}) = 2.60\text{g cm}^{-3}$ ,  $Z = 2$ ,  $F(000) = 928$ ,  $\mu(\text{MoK}\alpha) = 64.8\text{cm}^{-1}$ . The diffraction intensities were measured with the following conditions: graphite monochromator,  $\theta/2\theta$  scan,  $\theta \leq 25^\circ$ ,  $\Delta\theta = 1.5^\circ$ , scanning speed  $0.03^\circ \text{sec}^{-1}$ , background time 10 sec on both sides of each peak, attenuating filter inserted for peak intensities higher than  $40,000 \text{ counts sec}^{-1}$ , three reference reflections. A set of 1710 independent observations was obtained, after removing 2498 reflections having  $I \leq 2\sigma(I)$ ; this unsatisfactory result is clearly to be ascribed to the low diffracting power of the crystal and had to be accepted because better crystals are not known. An experimental absorption correction based on the  $\psi$  scan method (North *et al.*, 1968) was applied, with the coefficient value ranging from 0.84 to 1.26.

### Solution and refinement of the structure

The positions of As and Ca atoms in the unit cell were determined by the MULTAN program based on

direct methods (Germain *et al.*, 1971); the Mg and oxygen atoms were located by subsequent Fourier difference maps. By a least-squares refinement with isotropic thermal parameters,  $R = 0.111$  was obtained. At this stage, 99 weak reflections which showed a large discrepancy between  $F_o$  and  $F_c$  (with  $|F_c| < |F_o|$  always) were assumed to be affected by systematic errors as discussed by Catti *et al.* (1977) and were removed; anisotropic thermal factors were then introduced in the refinement for As, Ca, and Mg atoms only. The final full-matrix cycle with unitary weights led to  $R = 0.087$  for the remaining 1611 reflections ( $R$  was 0.105 including the rejected data). Fractional coordinates and coefficients of the expression

$$\exp\left(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^*\right)$$

are reported in Table 1 for non-oxygen atoms; coordinates and isotropic temperature factors of the other atoms are shown in Table 2. The large values of the  $esd$ 's are due to the poor quality of the experimental data and to the unfavorable ratio (number of observations)/(number of refined parameters). Atomic scattering factors for neutral atoms (*International Tables for X-ray Crystallography*, 1974) and the programs of the SHELX package (Sheldrick, 1976) were used for the calculations.<sup>1</sup>

<sup>1</sup> To receive a copy of the structure factors, order Document Am-81-142 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, NW, Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 1. Fractional coordinates and anisotropic thermal parameters ( $\text{\AA}^2$ ) of heavy atoms

	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
As(1)	0.4780(3) <sup>+</sup>	0.1321(3)	0.2007(5)	2.0(2)	0.6(1)	0.6(1)	-0.5(1)	-0.2(1)	-0.4(1)
As(2)	0.3966(3)	0.4164(3)	0.0624(5)	1.5(2)	0.8(1)	1.0(1)	0.3(1)	-0.3(1)	-0.2(1)
As(3)	0.7177(3)	0.2856(3)	0.5546(5)	1.4(2)	0.7(1)	0.7(1)	-0.2(1)	0.1(1)	-0.5(1)
As(4)	0.8093(3)	0.0155(3)	0.7877(5)	2.3(2)	1.0(2)	0.9(1)	-0.1(1)	-0.2(1)	-0.5(1)
Ca(1)	0.6347(6)	0.3305(5)	0.0702(11)	2.9(4)	0.3(3)	0.9(3)	-0.3(3)	-0.4(3)	-0.4(2)
Ca(2)	0.4987(6)	0.3725(5)	0.5677(10)	2.9(4)	0.4(3)	0.8(3)	-0.4(3)	0.1(3)	-0.2(2)
Ca(3)	0.5733(6)	0.0881(5)	0.7256(11)	1.8(3)	1.0(3)	1.3(3)	-0.5(3)	-0.2(2)	-0.5(2)
Ca(4)	0.6965(6)	0.0195(5)	0.2559(10)	2.4(4)	0.6(3)	1.1(3)	-0.5(2)	0.6(3)	-0.1(2)
Mg	0.8739(9)	0.1952(8)	0.2149(15)	1.8(5)	0.8(4)	0.7(4)	0.3(4)	-0.5(4)	0.1(3)

<sup>+</sup> Estimated standard deviations are given in parentheses and refer to the last decimal place.

Table 2. Fractional coordinates and isotropic thermal parameters ( $\text{\AA}^2$ ) of oxygen atoms

	x	y	z	B
O(1)	0.427(2) <sup>+</sup>	0.229(2)	0.336(3)	1.3(4)
O(2)	0.394(2)	0.050(2)	0.060(3)	1.7(4)
O(3)	0.559(2)	0.171(2)	0.065(4)	2.1(5)
O(4)	0.540(2)	0.066(2)	0.360(4)	1.8(5)
O(5)	0.310(2)	0.321(2)	0.091(4)	2.3(5)
O(6)	0.334(2)	0.499(2)	-0.033(4)	1.8(5)
O(7)	0.463(2)	0.457(2)	0.285(3)	1.6(4)
O(8)	0.472(2)	0.358(2)	-0.096(3)	1.2(4)
O(9)	0.637(2)	0.253(2)	0.713(3)	0.6(4)
O(10)	0.658(2)	0.367(2)	0.430(4)	2.1(5)
O(11)	0.822(2)	0.338(2)	0.708(4)	1.7(4)
O(12)	0.752(2)	0.192(2)	0.381(3)	0.6(3)
O(13)	0.919(2)	0.045(2)	0.727(4)	2.3(5)
O(14)	0.784(2)	0.087(2)	1.011(4)	1.8(5)
O(15)	0.813(2)	-0.110(2)	0.822(4)	2.4(5)
O(16)	0.713(2)	0.021(2)	0.608(3)	1.3(4)
W(1)	0.818(2)	0.325(2)	0.087(3)	1.4(4)
W(2)	0.319(2)	0.412(2)	0.573(4)	1.7(5)
W(3)	0.400(2)	0.152(2)	0.686(4)	1.5(4)
W(4)	0.814(2)	-0.115(2)	0.239(4)	2.9(6)
W(5)	0.986(2)	0.189(2)	0.033(5)	3.8(6)
W(6)	0.960(2)	0.299(2)	0.437(4)	2.4(5)
W(7)	0.932(2)	0.082(2)	0.348(4)	3.1(6)
W(8)	0.835(2)	0.745(2)	0.493(4)	2.6(5)
W(9)	0.887(2)	0.656(2)	0.019(4)	2.9(6)
W(10)	0.888(2)	0.517(2)	0.678(4)	2.5(5)
W(11)	0.908(2)	0.502(2)	0.267(4)	2.4(5)

<sup>+</sup> Estimated standard deviations are given in parentheses and refer to the last decimal place.

## Discussion

### The role of Ca and Mg

Bond distances within the Ca and Mg coordination polyhedra are reported in Table 3. Magnesium is characterized by a very regular octahedral coordination; Ca(2), Ca(3) and Ca(4) are sevenfold coordinated, and Ca(1) shows C.N. = 6, but with strong angular distortions from octahedral geometry. A second coordination sphere is observed for the Ca atoms, with some Ca-O distances perhaps short enough to reflect a significant interaction: Ca(1)-O(7), Ca(1)-O(12), Ca(2)-W(3), Ca(3)-O(14), Ca(4)-O(3), Ca(4)-W(7), which are 3.25, 3.34, 3.48, 3.26, 3.14, 3.24 Å, respectively. Taking into account the typical values and the wide gap between the bond distances of the

Table 3. Interatomic distances in the Ca and Mg coordination polyhedra

Ca(1) - O(3)	2.35(3) <sup>+</sup> Å	Ca(2) - O(1)	2.38(2) Å
Ca(1) - O(8)	2.42(2)	Ca(2) - O(7)	2.39(2)
Ca(1) - O(9) <sup>v</sup>	2.45(2)	Ca(2) - O(8) <sup>iii</sup>	2.36(2)
Ca(1) - O(10)	2.37(3)	Ca(2) - O(9)	2.71(2)
Ca(1) - O(6') <sup>v</sup>	2.38(3)	Ca(2) - O(10)	2.44(3)
Ca(1) - W(1)	2.48(3)	Ca(2) - O(7')	2.37(2)
Average	2.41	Ca(2) - W(2)	2.51(3)
		Average	2.45
Ca(3) - O(3) <sup>iii</sup>	2.39(3)	Ca(4) - O(4)	2.38(3)
Ca(3) - O(4)	2.41(2)	Ca(4) - O(12)	2.41(2)
Ca(3) - O(9)	2.38(2)	Ca(4) - O(14) <sup>v</sup>	2.41(3)
Ca(3) - O(16)	2.29(3)	Ca(4) - O(16)	2.34(2)
Ca(3) - O(2') <sup>iv</sup>	2.56(2)	Ca(4) - O(2') <sup>i</sup>	2.35(2)
Ca(3) - O(4') <sup>iv</sup>	2.49(3)	Ca(4) - W(4)	2.44(3)
Ca(3) - W(3)	2.52(3)	Ca(4) - W(3') <sup>iv</sup>	2.73(3)
Average	2.43	Average	2.44
	Mg - O(12)	2.10(2) Å	
	Mg - O(14) <sup>v</sup>	2.08(3)	
	Mg - W(1)	2.19(3)	
	Mg - W(5)	2.05(3)	
	Mg - W(6)	2.09(3)	
	Mg - W(7)	2.03(3)	
	Average	2.09	

<sup>+</sup> Estimated standard deviations are given in parentheses and refer to the last decimal place.

Mg octahedron and those of the Ca polyhedra, no Ca/Mg substitution is likely on any of the five cation sites. Picroparmacolite is, therefore, definitely shown to be a species where Ca and Mg are ordered with an atomic ratio 4:1. This should also be true for irhtemite, since this phase can be obtained by dehydration of picroparmacolite (Pierrot and Schubnel, 1972).

### Description of the structure

The Ca, Mg, and As coordination polyhedra are strongly condensed into (100) corrugated layers by sharing edges and vertices with one another (Fig. 1). The following situation is observed: the Ca(2) and Ca(3) polyhedra share their O(9)-O(10) and O(2')<sup>iv</sup>-O(4')<sup>iv</sup> edges<sup>2</sup> with the As(3) and As(1')<sup>iv</sup> tetrahedra,

<sup>2</sup> Symbols with a prime denote atoms subjected to the transformation  $1-x$ ,  $1-y$ ,  $1-z$ ; roman numerals represent the translations: i, +a; ii, +b; iii, +c; iv, -b; v, -c; vi, +a - c; vii, +a - b; viii, -b - c.

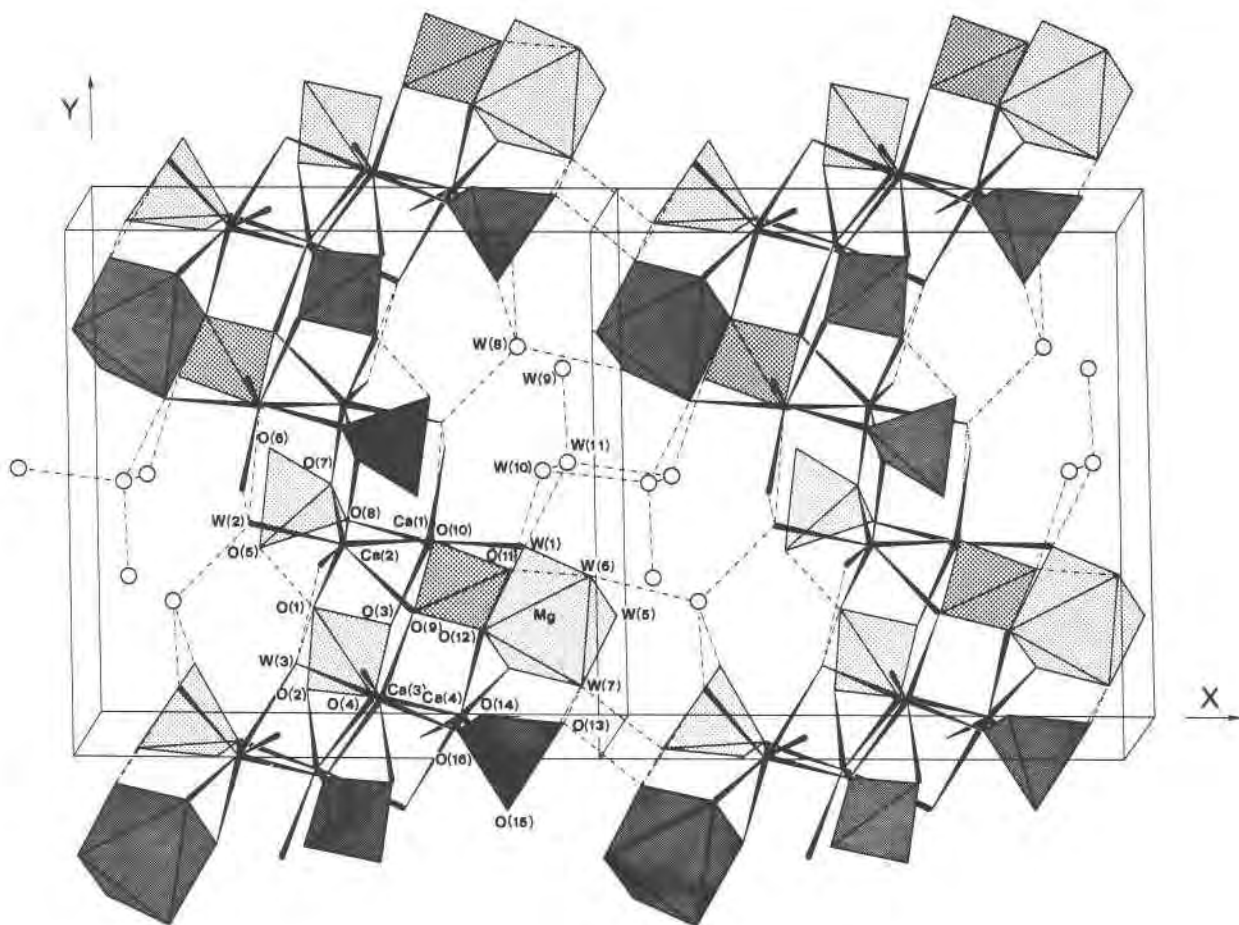


Fig. 1. Projection onto the (001) plane of the structure of picropharmacolite. As and Mg coordination polyhedra, Ca-O bonds (black rods), and lattice water molecules (circles) are emphasized. Hydrogen bonds are represented as dashed-dotted lines.

respectively; the Mg octahedron is linked to Ca(4) by sharing the O(12)–O(14)<sup>v</sup> edge. Ca(1) is linked to the Ca(2)<sup>v</sup> and Ca(3)<sup>v</sup> polyhedra by the O(8)–O(9)<sup>v</sup> and O(3)–O(9)<sup>v</sup> edges; Ca(2) shares its O(8)<sup>iii</sup>–O(9) and O(7)–O(7') edges with Ca(1)<sup>iii</sup> and Ca(2')<sup>v</sup>, respectively; Ca(3) shares O(3)<sup>iii</sup>–O(9), O(4)–O(16), and O(4')<sup>iv</sup>–W(3) with Ca(1)<sup>iii</sup>, Ca(4), and Ca(4')<sup>iv</sup>; Ca(4) is linked to Ca(3) and Ca(3')<sup>iv</sup> by sharing the O(4)–O(16) and O(4)–W(3')<sup>iv</sup> edges. Vertex-sharing is omitted, for simplicity. A two-dimensional network of coordination polyhedra is thus defined in (100) layers related by a (Fig. 2). These layers take on a corrugated shape in the (001) plane, because the Mg octahedra project away from the plane of the layer, and are linked by hydrogen bonds donated by water molecules, among which W(8), W(9), W(10), and W(11) are not coordinated by cations and are sandwiched between the layers. In particular, W(9), W(10), and W(11) are hydrogen-bonded to their cen-

trosymmetrical related molecules and to those related to them by *c*, so as to form [001] chains.

#### Hydrogen bonding

Since hydrogen atoms have not been located, a scheme of hydrogen bonding can only be inferred on the basis of distances and angles involving the oxygen atoms. The two H atoms which, according to the chemical composition, belong to the tetrahedral anions should be carried by the oxygen atoms O(5) and O(15), showing the longest As–O bond distances in the As(2) and As(4) tetrahedra, respectively (Table 4). O(5) is involved in a short distance (2.64 Å) to O(2), and O(5) . . . O(2) corresponds then to a hydrogen bond donated by an anionic OH (Table 5); O(15) has two long distances to O(2')<sup>iv</sup> (3.08 Å) and W(5')<sup>vii</sup> (3.07 Å), and two others to W(4) and W(8)<sup>iv</sup> (2.81 and 2.74 Å): the shortest one is a good candidate to represent the hydrogen bond donated by the second an-

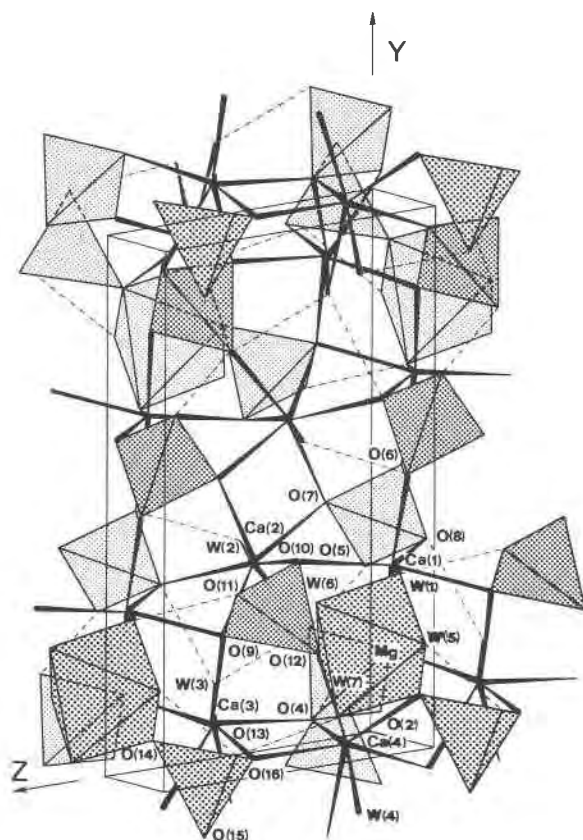


Fig. 2. Projection onto the (100) plane of one layer of the structure of picropharmacolite.

ionic OH in the structure. If this assumption is accepted, the hydrogen bonding scheme can be unambiguously determined for all water molecules but three, W(9), W(10), and W(11), which are hydrogen bonded to one another with no unequivocal indication of the donor–acceptor functions. The ambiguity has not been solved by a bond valence balance calculation (Brown and Wu, 1976), since the results obtained for the different possible schemes are not significantly different, owing to the large *esd*'s of bond distances which propagate onto the bond valence errors. However, the assignment reported in Table 5 is characterized by slightly more plausible values of the C...B...C' angles, particularly as far as W(9) is concerned.

On the basis of the proposed hydrogen bonding scheme, and of the observed roles of Ca, Mg and H<sub>2</sub>O, the formula of picropharmacolite can be written as Ca<sub>4</sub>Mg(H<sub>2</sub>O)<sub>7</sub>(AsO<sub>3</sub>OH)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub> · 4H<sub>2</sub>O.

The only 'direct' (*i.e.* not *via* interlayer water molecules) hydrogen bond which links adjacent layers is W(7)...O(13')<sup>vii</sup>. The interlayer water molecule

W(8) bridges layers by means of the W(8)...W(2') and W(6)...W(8')<sup>viii</sup> bonds; the [001] chain of the other water molecules which are not coordinated by cations [W(9), W(10), W(11) and their symmetry-related ones] is linked to the layers of polyhedra by the W(9)...O(5')<sup>v</sup>, W(5)...W(9')<sup>vi</sup>, W(10)...W(11), and W(1)...W(11) hydrogen bonds. Each of W(8), W(9), and W(10) is hydrogen bonded with three H<sub>2</sub>O molecules and an oxygen atom, while W(11) forms all four hydrogen bonds with water molecules, and then behaves as H<sub>2</sub>O in ice. This water molecule is characterized by a very regular tetrahedral environment, with W...W distances and W...W...W angles ranging from 2.68 to 2.88 Å and from 94° to 128°, respectively; only a little distortion is observed with respect to the bonding configuration of water in ice phases stable at room pressure, where the hydrogen bonds range from 2.75 to 2.80 Å (Franks, 1972, p. 118–123). This situation should be compared to the much more distorted configurations shown by water molecules of the same type in crystal hydrates, *e.g.* in Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 22H<sub>2</sub>O (Catti *et al.*, 1981).

Since the environment of W(11) is so similar to that typical of H<sub>2</sub>O molecules in ice, disorder of hydrogen atoms might occur and would account for the ambiguous donor–acceptor functions between the hydrogen-bonded W(11), W(10), and W(9) lattice water molecules.

As far as intra-layer hydrogen bonds are concerned, two facts can be pointed out: the W(1)...O(11)<sup>v</sup> bond (2.58 Å) is unusually short, as the donor is a water molecule, and the O(6)<sup>iii</sup>...W(2)...O(10') bond angle (75°) is very narrow with respect to values normally observed in crystal hydrates (Ferraris and Franchini-Angela, 1972). Two similar cases, respectively, were discussed by Catti *et al.* (1977) and by Catti (1979).

#### *Crystallochemical relations with guerinite and ferrarisite*

From the chemical point of view, picropharmacolite can be considered as derived from either of the Ca end-member dimorphs, guerinite and ferrarisite, by substitution of one out of five Ca atoms with magnesium and addition of two more water molecules. By examining the crystal structures of the two latter minerals (Catti and Ferraris, 1974; Catti *et al.*, 1980), many similarities are observed with that of picropharmacolite: layers of condensed polyhedra [with (101) orientation in guerinite and (001) in ferrarisite] are present in all cases, and the cell constants of the two dimorphs ( $a = 17.63$ ,  $b = 6.734$ ,  $c = 23.47$  Å,  $\beta =$

Table 4. Interatomic distances and O-As-O angles in the AsO<sub>4</sub> groups

As(1) - O(1)	1.67(2) <sup>+</sup> Å	As(2) - O(5)	1.77(3)Å		
As(1) - O(2)	1.66(2)	As(2) - O(6)	1.60(3)		
As(1) - O(3)	1.64(3)	As(2) - O(7)	1.65(2)		
As(1) - O(4)	1.68(2)	As(2) - O(8)	1.67(2)		
Average	1.66	Average	1.67		
As(3) - O(9)	1.71(2)	As(4) - O(13)	1.63(3)		
As(3) - O(10)	1.67(3)	As(4) - O(14)	1.71(3)		
As(3) - O(11)	1.71(2)	As(4) - O(15)	1.75(3)		
As(3) - O(12)	1.68(2)	As(4) - O(16)	1.69(3)		
Average	1.69	Average	1.70		
O(1) - O(2)	2.78(3)Å	113(1)°	O(9) - O(10)	2.67(3)Å	105(1)°
O(1) - O(3)	2.73(3)	111(1)	O(9) - O(11)	2.74(3)	106(1)
O(1) - O(4)	2.73(3)	109(1)	O(9) - O(12)	2.88(3)	117(1)
O(2) - O(3)	2.73(4)	112(1)	O(10) - O(11)	2.82(4)	113(1)
O(2) - O(4)	2.64(3)	104(1)	O(10) - O(12)	2.70(3)	108(1)
O(3) - O(4)	2.66(4)	107(1)	O(11) - O(12)	2.75(3)	108(1)
Average	2.71		Average	2.76	
O(5) - O(6)	2.71(4)	107(1)	O(13) - O(14)	2.78(4)	112(1)
O(5) - O(7)	2.77(3)	108(1)	O(13) - O(15)	2.71(4)	106(1)
O(5) - O(8)	2.72(4)	105(1)	O(13) - O(16)	2.80(4)	115(1)
O(6) - O(7)	2.75(3)	116(1)	O(14) - O(15)	2.80(4)	108(1)
O(6) - O(8)	2.72(3)	113(1)	O(14) - O(16)	2.76(3)	108(1)
O(7) - O(8)	2.69(3)	108(1)	O(15) - O(16)	2.75(4)	106(1)
Average	2.73		Average	2.77	

<sup>+</sup> Estimated standard deviations are given in parentheses and refer to the last decimal place.

Table 5. Interatomic distances and angles involving the hydrogen bonds and water molecule environments

A	B	C	BC	ABA'	CBC'
Ca(1) <sup>+</sup>		O(11) <sup>v</sup>	2.58		
Mg	W(1)			112	100
Ca(2)		O(6) <sup>iii</sup>	2.69		
W(8')	W(2)	O(10')	3.00	122	75
Ca(3)		O(1)	2.78		
Ca(4')	W(3)		96	84	
		O(8) <sup>iii</sup>	3.00		
Ca(4)		O(15) <sup>v</sup>	2.81		
W(8) <sup>iv</sup>	W(4)			126	91
		W(7)	3.00		
Mg	W(5)	O(13) <sup>v</sup>	2.63		
		W(9') <sup>vi</sup>	2.77	-	122
		O(11)	2.75		
Mg	W(6)	W(8') <sup>i</sup>	2.87	-	118
		O(13)	2.70		
Mg	W(7)	O(13') <sup>vii</sup>	2.73	-	95
O(15) <sup>ii</sup>		W(4) <sup>ii</sup>	2.76		
W(6')	W(8)			102	116
		W(2')	2.86		
W(10) <sup>v</sup>		O(5') <sup>v</sup>	2.73		
W(5') <sup>vi</sup>	W(9)			105	110
		W(11)	2.88		
W(11)		O(11)	2.60		
W(11') <sup>i</sup>	W(10)	W(9) <sup>iii</sup>	2.70	86	114
W(1)		W(10)	2.77		
W(9)	W(11)	W(10') <sup>i</sup>	2.77	113	94
		O(5)	2.64		
		O(15)	W(8) <sup>iv</sup>	2.74	

<sup>+</sup> The estimated standard deviations are 0.04Å and 1° for distances and angles, respectively. A' and C' atoms belong to the line below the corresponding B.

90.6° and  $a = 8.294$ ,  $b = 6.722$ ,  $c = 11.198$ Å,  $\alpha = 106.16$ ,  $\beta = 92.94$ ,  $\gamma = 99.20^\circ$ , respectively) show  $b$  and  $\beta$  values closely resembling  $c$  and  $\gamma$  of picroparmacolite. However, the linking between layers is quite different in the three structures; in ferrarisite and guerinite, it is provided by highly hydrated Ca coordination polyhedra bridging adjacent layers (in the latter case these Ca atoms are disordered, so that the bonding is weaker), whereas in picroparmacolite the layers are linked by hydrogen bonds only. This decreasing strength of the interlayer bonding is partly reflected by the trend of the corresponding interplanar distances, which are  $d_{001} = 10.701$ ,  $d_{101} = 14.120$  and  $d_{100} = 13.447$ Å in ferrarisite, guerinite, and picroparmacolite, respectively; values of distances for guerinite and picroparmacolite are affected by the corrugation of layers.

The crystallization mechanisms of the two dimorphs of  $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 9\text{H}_2\text{O}$  and of  $\text{Ca}_4\text{Mg}(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 11\text{H}_2\text{O}$  from solutions of suitable chemical compositions can now be postulated. The highly hydrated  $\text{Mg}^{2+}$  ions probably have a tendency to enter the same positions bridging adjacent layers which are occupied by  $\text{Ca}^{2+}$  ions in the Ca end members, owing to the great stability of such Mg coordination polyhedra. But, on the other hand, Mg octahedra are smaller and much less liable to deformation than the calcium polyhedra, so that they are

less suitable for linking different layers; the linkage is thus attained through hydrogen bonding of additional water molecules; each Mg octahedron remains attached to the surface of only one layer.

### Structure and physical properties

On the basis of the structural features, the {100} cleavage is very likely to occur, since breaking only of weak interlayer hydrogen bonds would be involved; {110} and {110} cleavages as well are likely on crystallochemical grounds, as just a few coordination bonds would be broken.

Because of the similarity between *a* and *b* values the lattice is dimensionally pseudo-tetragonal, favoring multiple {*hk*0} twinning. In particular, (110) and (110) planes show similar structural features which make {110} and {110} twinning even more probable. Actually some easy parting along [001] is observed in fibrous needle-like crystals of picropharmacolite, and that could be either a {*hk*0} cleavage or an effect of the fibrousness. On the other hand the [001] texture could be related to multiple {*hk*0} twinning.

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