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Mechanism of the reaction $Ca_5H_2(AsO_4)_4 \cdot 9\,H_2O$ (ferrarisite) → $Ca_5H_2(AsO_4)_4 \cdot 5\,H_2O$) (dimorph of vladimirite), and structure of the latter phase

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$Ca_5H_2(AsO_4)_4 \cdot 5\,H_2O$, $Ca_5H_2\,(AsO_4)_4 \cdot 9\,H_2O$ / Crystal structure / Dehydration mechanism

Abstract. The new triclinic phase $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 5\,H_2O$, polymorph of monoclinic vladimirite, was obtained by dehydration of $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9\,H_2O$ (ferrarisite) at 60°C. Unit-cell data are: a = 8.286(4), b = 6.673(3), c = 9.743(4) Å, α = 86.58(3), β = 111.10(3), γ = 99.74(3)°; Z = 1, space group $P\bar{1}$. The structure was solved by direct methods and least-squares refined to R = 0.088, using 1200 observed counter reflections (Mo$K\alpha$ radiation). One Ca atom and three water molecules are disordered over centrosymmetrically-related positions. Isostructural (001) layers of Ca and As coordination polyhedra are observed in the structures of both nona- and penta-hydrated phases; however, they differ by a relative shift and sandwich ordered and disordered Ca octahedra, respectively, in the two cases. Dehydration of ferrarisite involves the loss of inter-layer water molecules alternatively from either set of centrosymmetrically-related positions, while layers slide and approach one another. The sandwiched Ca atoms are left attached alternatively to either side of facing layers, and replace their broken coordination bonds by new ones on the side of the shifted layer. This random character of the dehydration reaction is the cause of disorder in the penta-hydrated phase. Crystal-chemical properties of the $M_5(HAsO_4)_2(AsO_4)_2 \cdot n\,H_2O$ phases are analyzed.

Introduction

The group of minerals and inorganic salts of general formula $M_5(HXO_4)_2(XO_4)_2 \cdot n\,H_2O$, where X = As, P and M = Ca, Mg, Mn, Zn, has been the object of several structural and crystal-chemical studies. The crystal structures of the following phases are known: the dimorphs guérinite (Catti

and Ferraris, 1974) and ferrarisite (Catti, Chiari and Ferraris, 1980), $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9\,H_2O$; sainfeldite, $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 4\,H_2O$ (Ferraris and Abbona, 1972) and the isostructural hureaulite, $Mn_5(HPO_4)_2(PO_4)_2 \cdot 4\,H_2O$ (Moore and Araki, 1973; Menchetti and Sabelli, 1973); chudobaite, $(Mg,Zn)_5(HAsO_4)_2(AsO_4)_2 \cdot 10\,H_2O$ (Dorner, 1976; Dorner and Weber, 1976); picropharmacolite, $Ca_4Mg(HAsO_4)_2(AsO_4)_2 \cdot 11\,H_2O$ (Catti, Ferraris and Ivaldi, 1981). Other members of the family not yet studied structurally are vladimirite, $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 5\,H_2O$, irhtemite, $Ca_4Mg(HAsO_4)_2(AsO_4)_2 \cdot 4\,H_2O$, and the compound $Ca_5(HPO_4)_2(PO_4)_2 \cdot 9\,H_2O$.

A peculiar and complicated dehydration behaviour was reported for ferrarisite (Bari, Permingeat, Pierrot and Walenta, 1980; Catti, Chiari and Ferraris, 1980) on the basis of thermogravimetric analyses and high-temperature Guinier powder patterns; moreover, that mineral proves to dehydrate very slowly in dry air at room temperature, and dehydrated crystals were also found in nature at Sainte Marie-aux-Mines (Bari, private commun.) and Wittichen (Walenta, unpublished data). A structural study of synthetic products of dehydration of ferrarisite was then undertaken, to clear their crystal chemical relationships with the known members of that group of minerals which have a lower water content. Another aim of this work was to investigate directly the mechanism of the solid-state dehydration reaction, to test the power and usefulness of the structural approach in solving not only statical but also dynamical problems in crystal science. Some partial results along this line of research have been already obtained: cf. the analysis of the reaction $NaH_2PO_4 \cdot 2\,H_2O \leftrightarrows NaH_2PO_4 \cdot H_2O$ (Catti and Ferraris, 1976), and the study of the topotactic dehydration $Ca_3(AsO_4)_2 \cdot 11\,H_2O$ (new mineral) $\rightarrow Ca_3(AsO_4)_2 \cdot 10\,H_2O$ (rauenthalite), which has been recently completed in our laboratory (Catti and Ivaldi, in preparation).

Experimental and structure determination

Crystals of ferrarisite, $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9\,H_2O$, from Sainte-Marie-aux-Mines (Alsace) were heated at 60°C for an hour, and the sample obtained was supplied to us by H. Bari (University of Strasbourg). Using single-crystal rotation and Weissenberg photography (Cu$K\alpha$ radiation) two different phases (characterized by 11.57 and 6.23 Å rotation parameters) were discovered, but could not be separated in sufficient amounts to obtain powder patterns. Only the first phase gave reasonably-diffracting crystals and was selected for a structural study. A needle-like single crystal elongated [$\bar{1}10$], with dimensions $0.02 \times 0.04 \times 0.34$ mm, was mounted on a Philips PW 1100 four-circle automatic diffractometer [λ (Mo$K\alpha$) = 0.71069 Å, graphite monochromator] and used for all the measurements. By angular refinement of 22 centred reflections, the following unit-cell constants were obtained: a = 8.286(4), b = 6.673(3), c = 9.743(4) Å, α = 86.58(3), β =

111.10(3), $\gamma = 99.74(3)°$; $V = 495.4 Å^3$. The measured density was $D_m = 2.81 g cm^{-3}$. On the basis of the chemical formula $Ca_5H_2(AsO_4)_4 \cdot 5H_2O$, which was determined completely after the structure had been solved and refined, the other crystal data are: $M = 848.163$, $Z = 1$, $D_c = 2.84 g cm^{-3}$, $F(000) = 412$, $\mu(MoK\alpha) = 80.3 cm^{-1}$. Statistical tests on the diffraction intensities proved the space group to be $P\bar{1}$.

The intensities of 2900 reflections were collected with the following measurement conditions: $\theta \leq 30°$, ω scan, $\Delta\omega = 4°$, scanning speed 0.05° s^{-1}, background time 10 s on each side of the peak, attenuating filter inserted for intensities higher than 40000 counts s^{-1}, three reference reflections. By removing the reflections with $I \leq 2\sigma(I)$, a final set of 1200 independent observations was obtained.

The structure was solved by the MULTAN program based on direct methods (Germain, Main and Woolfson, 1971). Two As and two Ca atoms in general positions appeared in the solution with the highest combined figure of merit; a subsequent structure-factor calculation followed by a difference map revealed the third Ca atom statistically disordered over centrosymmetrically-related positions, eight oxygen atoms and a water molecule. The full-matrix least-squares refinement with mixed anisotropic (As and Ca atoms) and isotropic (oxygen atoms) thermal factors led to $R = 0.101$. At this stage, three peaks about $4e^-$ high were located on a Fourier difference map and interpreted as further disordered water molecules. These were included in the refinement with occupation factors 0.5 (as for the disordered Ca atom): both by letting their coordinates change and by keeping them constant, convergence was reached with the same R value (0.088). Unitary weights were used, and no corrections for absorption and secondary extinction were applied. The final atomic fractional coordinates and thermal parameters are shown in Table 1; both refined and unrefined coordinates are reported for disordered water molecules: the unrefined values were used for calculations of bond distances and angles. Some unsatisfactory features of the structure determination (large e.s.d.'s of atomic coordinantes, small fraction of observed reflections in the collected data) are related to the poor quality and low diffracting power of the crystal used. Scattering factors for neutral atoms given in the International Tables for X-ray Crystallography (1974) and the SHELX package of programs (Sheldrick, 1976) were used for the calculations. A list of observed and calculated structure factors may be obtained from the authors.

Structural disorder in $Ca_5H_2(AsO_4)_4 \cdot 5H_2O$

Bond distances within the calcium coordination polyhedra are reported in Table 2. The disordered Ca(3) atom shows a slightly distorted coordination octahedron, in which the three disordered water molecules W(1′), W(3), W(4) are contained as well, then following Ca(3) in their statistical distribution over centrosymmetrically-related positions. The Ca(2) polyhedron has seven

Table 1. Atomic fractional coordinates and thermal parameters ($\times 10^2$ Å^2) of $Ca_5H_2(AsO_4)_4 \cdot 5\,H_2O$, with e.s.d.'s in parentheses. For disordered water molecules, unrefined coordinates are reported as well. The U_{ij} values are coefficients of the expression $\exp\left(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}\, h_i\, h_j\, a_i^*\, a_j^*\right)$

	x	y	z	o.f.	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	0.4621(3)	0.1278(3)	0.8103(3)		2.2(1)	0.7(1)	4.0(2)	0.5(1)	2.3(1)	0.8(1)
As(2)	−0.0476(3)	0.3509(3)	0.8099(3)		1.8(1)	0.5(1)	2.4(2)	−0.3(1)	1.5(1)	−0.2(1)
Ca(1)	0.6525(7)	0.6519(6)	0.9093(7)		1.6(2)	0.5(2)	4.8(4)	−0.1(2)	1.7(3)	−0.3(2)
Ca(2)	0.1172(7)	0.8458(7)	0.9150(6)		2.1(3)	0.8(2)	3.3(3)	−0.2(2)	2.0(2)	−0.2(2)
Ca(3)	−0.148(2)	0.304(2)	0.422(1)	0.5	5.9(8)	4.0(6)	1.1(6)	−3.7(6)	1.4(6)	−0.4(4)
O(1)	0.466(2)	0.332(2)	0.901(2)		2.2(3)					
O(2)	0.624(2)	−0.002(2)	0.900(2)		1.8(3)					
O(3)	0.266(2)	−0.021(2)	0.756(2)		2.0(3)					
O(4)	0.488(2)	0.207(3)	0.647(2)		2.9(4)					
O(5)	0.095(2)	0.549(2)	0.783(2)		1.7(3)					
O(6)	0.065(2)	0.182(2)	0.930(2)		1.4(3)					
O(7)	−0.177(2)	0.419(2)	0.894(2)		2.3(3)					
O(8)	−0.178(2)	0.232(2)	0.649(2)		1.6(3)					
W(1)	0.434(5)	0.641(6)	0.653(5)	0.5	3.5(9)					
	0.439	0.637	0.650							
W(2)	0.817(3)	0.832(3)	0.720(2)		2.9(4)					
W(3)	−0.072(7)	0.640(8)	0.524(6)	0.5	5.8(1.4)					
	−0.077	0.640	0.517							
W(4)	0.137(6)	0.287(6)	0.540(5)	0.5	3.6(9)					
	0.135	0.286	0.538							

Table 2. Interatomic distances in the calcium coordination polyhedra. The e.s.d.'s are 0.02 Å

Ca(1) – O(1)	2.40 Å	Ca(2) – O(3)^{II}	2.35 Å
Ca(1) – O(1′)^{III}	2.40	Ca(2) – O(5)	2.37
Ca(1) – O(2)^{II}	2.35	Ca(2) – O(6)^{II}	2.38
Ca(1) – O(6′)^{III}	2.42	Ca(2) – O(2′)^{III}	2.37
Ca(1) – O(7)^{I}	2.31	Ca(2) – O(6′)^{V}	2.47
Ca(1) – W(1)	2.50	Ca(2) – O(7′)^{V}	2.46
Ca(1) – W(2)	2.78	Ca(2) – W(2)^{IV}	2.52
Average	2.45	Average	2.42
Ca(3) – O(8)	2.33 Å		
Ca(3) – W(3)	2.38		
Ca(3) – W(4)	2.23		
Ca(3) – O(3′)^{VI}	2.47		
Ca(3) – O(5′)^{IV}	2.32		
Ca(3) – W(1′)^{IV}	2.35		
Average	2.35		

An unprimed figure in parentheses denotes an atom of the asymmetric unit; primed figures mean atoms subjected to the transformation $1-x$, $1-y$, $1-z$; roman numerals represent the translations: I, $+\mathbf{a}$; II, $+\mathbf{b}$; III, $+\mathbf{c}$; IV, $-\mathbf{a}$; V, $-\mathbf{a}+\mathbf{c}$; VI, $-\mathbf{a}-\mathbf{b}$; VII, $+\mathbf{a}+\mathbf{b}$

vertices and is completely ordered. Ca(1) is bonded to six ordered atoms and to the disordered W(1) molecule, so that its local coordination number is alternatively seven or six according to which of the two centrosymmetrically-related sites is occupied by W(1): on the average, C.N. = 6.5. The very short Ca(3) – W(4) bond distance (2.23 Å) is to be remarked, and could be due to low accuracy of atomic positions and to disorder of both atoms involved; however, the average Ca – O length in the Ca(3) octahedron is quite regular, so that such a short bond might be really required to balance other longer ones.

The Ca(1) and Ca(2) polyhedra and the two AsO_4 tetrahedra build up (001) layers (Fig. 1) by sharing the following edges and vertices: O(6′)^{V} – O(7′)^{V} between the Ca(2) polyhedron and the As(2′)^{V} tetrahedron; O(1) – O(1′)^{III} and O(6)^{II} – O(6′)^{V} between pairs of centrosymmetrically-related Ca(1) and Ca(2) polyhedra, respectively; O(2)^{II} – O(6′)^{III}, O(6′)^{III} – W(2), O(7)^{I} and O(6′)^{III} between the Ca(1) and four distinct Ca(2) polyhedra. The Ca and As polyhedra lie in the middle and on the surfaces of each layer, respectively, as is shown by the z coordinates of Ca and As atoms. Adjacent layers are related by the **c** vector and sandwich the disordered Ca(3) octahedra (Fig. 2), forming large channels along [010]; on crystal-chemical grounds, they should be called "pseudo-layers" more appropriately, since linking between them is provided not only by hydrogen bonds but also by Ca – O coordination bonds.

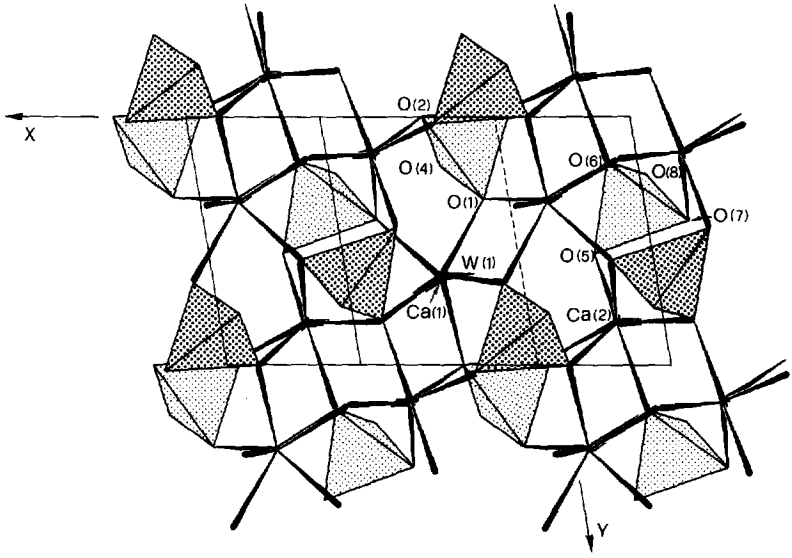

Fig. 1. Orthogonal projection of a single (001) layer of the structure of $Ca_5H_2(AsO_4)_4 \cdot 5\,H_2O$. AsO_4 tetrahedra and Ca–O coordination bonds (black rods) are emphasized

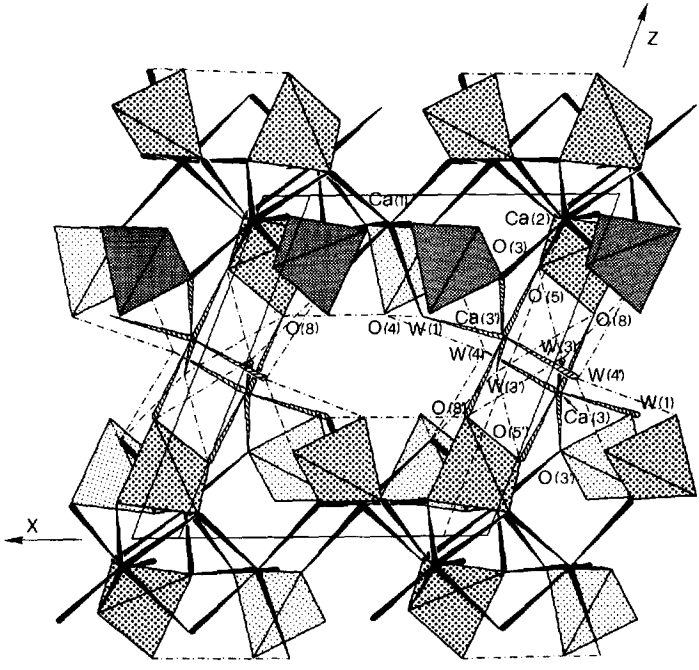

Fig. 2. Projection of the crystal structure of $Ca_5H_2(AsO_4)_4 \cdot 5\,H_2O$ on to the (010) plane. Coordination bonds of the disordered calcium atom are symbolized as dashed rods. Dashed-dotted lines show hydrogen bonds. Roman numerals representing translations are not given

Table 3. Interatomic distances and O – As – O angles in the AsO_4 groups. The e.s.d.'s are 0.02 Å and 0.8° for distances and angles, respectively

As(1) – O(1)	1.66 Å		As(2) – O(5)	1.69 Å	
As(1) – O(2)	1.67		As(2) – O(6)	1.71	
As(1) – O(3)	1.67		As(2) – O(7)	1.70	
As(1) – O(4)	1.73		As(2) – O(8)	1.70	
Average	1.68		Average	1.70	
O(1) ... O(2)	2.78 Å	113.1°	O(5) ... O(6)	2.79 Å	110.0°
O(1) ... O(3)	2.77	112.5	O(5) ... O(7)	2.83	113.1
O(1) ... O(4)	2.74	108.0	O(5) ... O(8)	2.81	111.6
O(2) ... O(3)	2.78	112.3	O(6) ... O(7)	2.67	103.5
O(2) ... O(4)	2.73	107.0	O(6) ... O(8)	2.79	109.9
O(3) ... O(4)	2.67	103.4	O(7) ... O(8)	2.76	108.5
Average	2.75	109.4	Average	2.78	109.4

Table 4. Interatomic distances and angles in the hydrogen bonds. The e.s.d.'s are 0.03 Å and 1° for distances and angles, respectively

W(1) ... O(4)	2.97 Å		
W(2) ... $O(8)^{VII}$	2.71		
W(2) ... $W(3)^{I}$	2.87	$O(8)^{VII}$ ... W(2) ... $W(3)^{IV}$	108°
W(2) ... W(4′)	2.86	$O(8)^{VII}$ ... W(2) ... W(4′)	96
W(3) ... $O(8')^{IV}$	3.09		
W(3) ... O(5)	2.55	$O(8')^{IV}$ ... W(3) ... O(5)	110
W(4) ... O(3)	2.91		
W(4) ... O(4)	2.86	O(3) ... W(4) ... O(4)	55
O(4) ... $O(8)^{I}$	2.73	As(1) – O(4) ... $O(8)^{I}$	115

Bond lengths and angles of AsO_4 groups are shown in Table 3. The As(1) – O(4) distance is by far the longest one within the As(1) tetrahedron, whereas As – O distances in the other AsO_4 group are equal within the e.s.d.'s; then O(4) is shown to carry the acidic hydrogen atom. The O(4) ... $O(8)^{I}$ contact corresponds to the acidic hydrogen bond donated by O(4). Geometrical features of hydrogen bonds are reported in Table 4; the hydrogen bonding scheme was determined unambiguously, assuming that the edges of coordination polyhedra can not be hydrogen bridges. W(2) donates an ordered hydrogen bond to $O(8)^{VII}$, and another one which is statistically distributed between the disordered water molecules $W(3)^{I}$ and W(4′). W(1) is characterized by one hydrogen bond only, but appears to receive a sufficient bond strength by being coordinated both to Ca(1) and to Ca(3). An unusually short hydrogen bond (2.55 Å) is donated by the disordered water W(3) to O(5); W(4) shows a very small O ... W ... O′ angle

(55°), which yet is accounted for by the two acceptors O(3) and O(4) belonging to the same AsO_4 tetrahedron.

Mechanism of the dehydration reaction

By comparing the unit-cell constants of $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 5\,H_2O$ with those of ferrarisite, $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9\,H_2O$ (Table 5), the a, b and γ values prove to be very similar, whereas c, α and β differ substantially in the two cases. The two triclinic lattices show approximately the same periodic patterns on (001) planes, but are related by a sliding of these planes which causes α, β and c to change; besides, the interplanar distance d_{001} is shorter in the lower hydrate (9.096 Å) than in the other one (10.701 Å). The atomic fractional coordinates of the two structures are roughly alike; however, they would show a much closer similarity if referred to (**a**, **b**, **c***) frames, so as to cancel the effect of different obliquities of the **c** vectors with respect to (001) planes. Then both phases are built up by (001) pseudolayers of Ca(1), Ca(2) and As coordination polyhedra which are substantially isostructural, but show different relative orientations and spacings in the two structures. The inter-layer Ca(3) atoms lie on symmetry centres in the higher hydrate, while they are disordered over centrosymmetrically-related positions in the lower one; the different crystal-chemical behaviour of the Ca(3) coordination octahedra in each case is the key to understanding the mechanism of the dehydration process.

In Figures 3 and 4 the unit-cell contents of the nona- and penta-hydrated phases, respectively, are shown in projection on to the (001) planes. Since the asymmetric units have been chosen in the upper layers for both structures, the upper faces of the two unit-cells coincide, whereas the two lower faces are related by the inter-layer shift vector $\boldsymbol{s} = 0.3514\,\mathbf{a} - 0.4935\,\mathbf{b}$. The dehydration reaction of ferrarisite can be thought to start by the loss of three inter-layer loosely-bonded water molecules in the unit-cell: that which is not Ca-coordinated and is statistically distributed over the W(5) and W(5′) sites, and alternatively either W(3) and W(4) or W(3′) and W(4′), which are coordinated to Ca(3). Then facing layers must slide (by the distance $s = 4.752$ Å) and approach (by 1.605 Å) to each other, so as to replace the two empty corners of Ca(3) coordination octahedra by new atoms. During the sliding process, Ca(3) is left attached either to the upper layer by O(8) or to the lower one by O(8′), according to whether W(3′) and W(4′) or W(3) and W(4) are lost, respectively. In the former case, the three Ca(3) coordination bonds pointing downwards are broken, and O(8′), W(3′), W(4′) are substituted by O(5′), O(3′) and W(1′), respectively; W(1) gets away from the structure, having lost the hydrogen bond with W(5) without replacing it in any way. In the latter case, the three upward bonds of Ca(3) break and O(8), W(3) and W(4) are replaced by O(5), O(3) and W(1), while W(1′) is lost.

Table 5. Crystal data of $M_5(HAsO_4)_2(AsO_4)_2 \cdot nH_2O$ phases. For references, see text

	a	b	c	α	β	γ	S.G.	Z
$Mg_5(HAsO_4)_2(AsO_4)_2 \cdot 10H_2O$ chudobaite	7.797	6.616	10.484 Å	80.55	97.88	95.77°	$P\bar{1}$	1
$Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9H_2O$ ferrarisite	8.294	6.722	11.198	106.16	92.94	99.20	$P\bar{1}$	1
$Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9H_2O$ guérinite	17.63	6.734	23.47		90.6		$P2_1/n$	5
$Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 5H_2O$ new phase	8.286	6.673	9.743	86.58	111.10	99.74	$P\bar{1}$	1
$Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 5H_2O$ vladimirite	5.81	10.19	22.7		82.7		$P2_1/c$	3

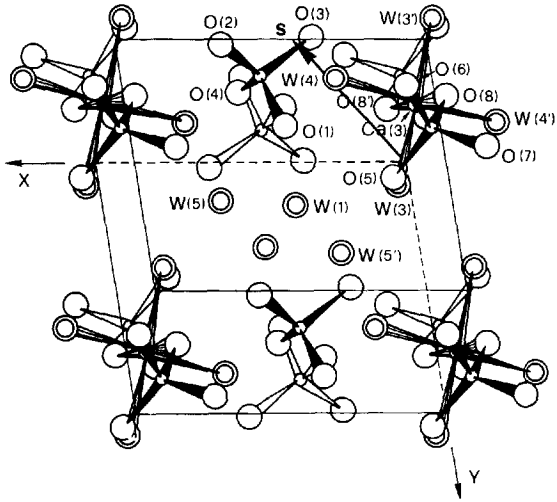

Fig. 3. Part of the unit-cell content of $Ca_5H_2(AsO_4)_4 \cdot 9\,H_2O$ (ferrarisite) projected on to the (001) plane. The **s** vector shows the shift of the lower layer occurring in the dehydration reaction

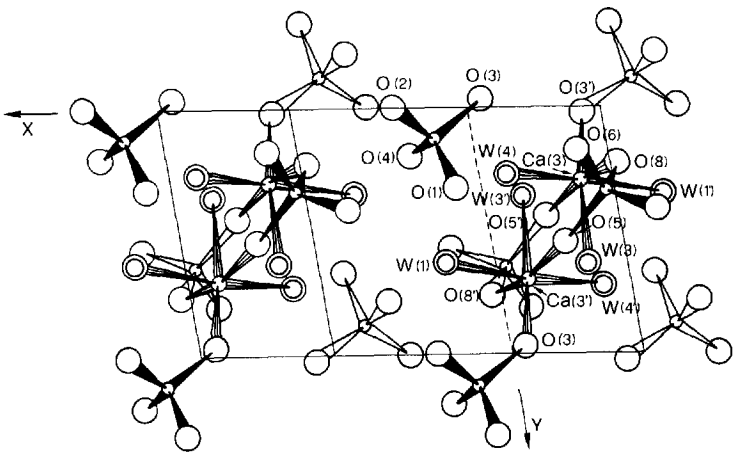

Fig. 4. Part of the unit-cell content of $Ca_5H_2(AsO_4)_4 \cdot 5\,H_2O$ projected on to the (001) plane. The Ca atoms and W molecules shown are disordered over centrosymmetrically-related positions, as a consequence of the dehydration reaction

On the whole, four water molecules in the unit cell have been set free during the dehydration process, in agreement with the stoichiometry of the reaction. The W(2) molecule has not been involved, as it is twofold Ca-coordinated and plays an essential role for the internal layer stability. The observed dehydration mechanism has a clear random character, since

sometimes W(3), W(4), W(1′) and sometimes their centrosymmetrically-related molecules are lost from the structure of $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9\,H_2O$; but this is necessary to remove the loosely-bonded water molecules without changing the internal structure of layers, so that just a comparatively small energy change is involved in the process. On the other hand, the random nature of the dehydration reaction is the direct cause of disorder in the structure of $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 5\,H_2O$.

Crystal-chemistry of the $M_5(HAsO_4)_2(AsO_4)_2 \cdot n\,H_2O$ phases

Crystallographic data of the members of this family of crystal hydrates with $n \geq 5$ are reported in Table 5; the unit cell of chudobaite has been transformed according to $\bar{1}00/00\bar{1}/0\bar{1}\bar{1}$, for better comparison with other phases. The dehydration product of ferrarisite, $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 5\,H_2O$, is proved to be a polymorph of vladimirite, whose monoclinic cell constants were reported by Pierrot (1964). If the *a* parameter of vladimirite is increased three-fold then a strong similarity appears between its *a* and *c* values and those of guérinite, analogous to what is observed for the *a* and *b* parameters of the dimorph of vladimirite and those of ferrarisite. Therefore, on the basis of symmetry and unit-cell geometry, it can be inferred that there are two dimorphic series formed by the $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9\,H_2O$ and $Ca_5(AsO_4)_2(AsO_4)_2 \cdot 5\,H_2O$ terms: one triclinic (ferrarisite and the phase studied in this work), and another one monoclinic (guérinite and vladimirite). Dehydration of the nona-hydrated terms should lead preferentially to penta-hydrated terms belonging to the same series, if the reaction is carried out slowly enough.

All phases reported in Table 5 (with the possible exception of vladimirite, whose structure is still unknown) show some common structural features: (i) they contain pseudo-layers of coordination polyhedra sandwiching a few cations octahedrally coordinated and, in the higher hydrates, lattice water molecules as well; (ii) they have an odd number of formula-units in the cell; (iii) the inter-layer cations are either in special positions or statistically disordered, so as to account for even multiplicities of space groups and odd numbers of cations in the unit-cell. Chudobaite belongs to the same structural type of ferrarisite and of the dimorph of vladimirite, sharing with them the triclinic symmetry, the (001) orientation of layers and similar unit-cell constants; besides, its inter-layer cations lie on symmetry centres as in ferrarisite, whereas they are disordered in guérinite. However, the topology of coordination polyhedra inside the pseudo-layers generally changes in the different structures, except for the case of ferrarisite/dimorph of vladimirite; for instance, the layers of chudobaite contain chains of Mg octahedra and are practically isostructural with the layers observed in the structure of krautite, $MnHAsO_4 \cdot H_2O$ (Catti and Franchini-Angela, 1979).

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