

Refinement of the crystal structure of anapaite, $\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$: hydrogen bonding and relationships with the bihydrated phase

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Abstract. — The crystal structure of anapaite from Messel (Hesse), $\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, has been refined ($R = 0.027$) in space group $P\bar{1}$ by 1257 reflections measured on an automatic single-crystal diffractometer ($\text{MoK}\alpha$ radiation); all the hydrogen atoms have been localized and included in the refinement. The unit-cell parameters are: $a = 6.447(1)$, $b = 6.816(1)$, $c = 5.898(1)$ Å, $\alpha = 101.64(3)$, $\beta = 104.24(3)$, $\gamma = 70.76(4)^\circ$; $Z = 1$. Within the framework structure, (100) layers of coordination polyhedra are emphasized in order to describe a plausible crystallochemical path for a phase transition to the bihydrated term (messelite). Bond valence calculations show that Ca is $7 + 1$ coordinated and justify the presence of hydrogen bonds which are unusually short for water molecules (2.597 and 2.600 Å).

Key words: anapaite, structure, hydrogen bonding, dehydration, phase transition.

Affinement de la structure de l'anapaite, $\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$: liaison hydrogène et relations avec la phase bihydratée.

Résumé. — La structure de l'anapaite de Messel (Hesse), $\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, a été affinée ($R = 0.027$) dans le groupe spatial $P\bar{1}$ par 1257 réflexions mesurées à l'aide d'un diffractomètre automatique (radiation $\text{MoK}\alpha$); tous les atomes d'hydrogène ont été localisés et inclus dans l'affinement. Les paramètres de la maille sont: $a = 6.447(1)$, $b = 6.816(1)$, $c = 5.898(1)$ Å, $\alpha = 101.64(3)$, $\beta = 104.24(3)$, $\gamma = 70.76(4)^\circ$; $Z = 1$. Des couches (100) de polyèdres de coordination sont présentes dans la structure, et au moyen d'elles on peut proposer un mécanisme cristalchimique pour la transition à la phase bihydratée (messelite). Des calculs de force de liaison montrent que Ca a une coordination $7 + 1$, et expliquent la présence de liaisons hydrogène très courtes (2,597 et 2,600 Å) données par une molécule H_2O .

Mots clés: anapaite, structure, liaison hydrogène, déshydratation, transition de phase.

INTRODUCTION.

Minerals of the type $\text{A}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ have been classified by Wolfe (1940) and more recently the family has been enlarged by the discovery of switzerite, $(\text{Mn}, \text{Fe})_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Leavens *et al.*, 1967), which forms a monoclinic group together with ludlamite and phosphophyllite; hopeite is orthorhombic, while parahopeite ($\text{A} = \text{Zn}$) and anapaite are triclinic. Previous structural studies (Rumanova *et al.*, 1961; Kumbasar *et al.*, 1968; Chao, 1969) have shown that the latter minerals are not isostructural, because Zn in parahopeite is both four- and six-fold coordinated while Ca and Fe in anapaite are seven- and six-fold coordinated, respectively.

In the frame of our program on hydrogen bonding in the crystalline state, we have refined the crystal structure of anapaite in order to establish its hydrogen bonding scheme, which was not defined in the paper based on bidimensional data by Rumanova *et al.* (1961), and to correlate its topology with that showed by the $\text{Ca}_2\text{Me}(\text{XO}_4)_2 \cdot 2\text{H}_2\text{O}$ triclinic group recently investigated (Catti *et al.*, 1977).

EXPERIMENTAL.

An X-ray diffraction study was performed by a four circle Philips PW 1100 diffractometer on a natural lamellar crystal from Messel (Hesse, Germany),

with dimensions $0.05 \times 0.16 \times 0.20$ mm. The refinement by the routine LAT gave the following unit cell parameters: $a = 6.447(1)$, $b = 6.816(1)$, $c = 5.898(1)$ Å, $\alpha = 101.64(3)$, $\beta = 104.24(3)$, $\gamma = 70.76(4)^\circ$, which closely correspond to values previously reported (Wolfe, 1940; Rumanova *et al.*, 1961). Other data are: space group $P\bar{1}$ (on structural basis), $MW = 398.024$, $V = 235.1$ Å³, $D_m = 2.816$ Mg m⁻³ (Rumanova *et al.*, 1961), $D_c = 2.811$ Mg m⁻³, $Z = 1$, $F(000) = 200e$, μ ($\text{MoK}\alpha$) = 3.0 mm⁻¹.

The measurement conditions were: graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$ Å), $\theta \leq 30^\circ$, ω scan, scan width $\Delta\omega = 1.5^\circ$, scanning speed 0.03°s^{-1} , background time = $(\text{scan time}/2)(I_{\text{bck}}/I_{\text{peak}})^{1/2}$, three reference reflections. By rejecting the 118 weakest reflections with $I \leq 2\sigma(I)$ a set of 1257 independent observations was obtained⁽¹⁾. An experimental absorption correction, with coefficient ranging from 1 to 1.234, was applied according to the method of North *et al.* (1968).

REFINEMENT OF THE STRUCTURE.

Starting from the coordinates given by Rumanova *et al.* (1961), four isotropic ($R = 0.039$) and two anisotropic full-matrix least-squares cycles led to

(1) A list of structure factors is available from the authors on request.

TABLE I.

Fractional coordinates and B_{ij} thermal parameters of the expression $\exp \left(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^* \right)$ with the significant figures of the e. s. d.'s in parentheses.

	x	y	z	B_{11} (Å ²)	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0	0	0	0.53(2)	0.77(2)	0.88(2)	0.04(2)	0.25(2)	-0.13(2)
Ca	0.34280(8)	0.20937(8)	0.70749(9)	0.71(2)	0.54(2)	0.71(2)	0.00(2)	0.15(2)	-0.18(2)
P	0.43302(10)	0.71811(9)	0.77170(11)	0.42(2)	0.45(2)	0.60(2)	0.04(2)	0.15(2)	-0.13(2)
O(1)	0.6806(3)	0.6255(3)	0.8844(3)	0.50(6)	0.78(6)	0.86(6)	0.12(5)	0.18(5)	-0.04(5)
O(2)	0.3121(3)	0.5514(3)	0.6789(3)	0.89(6)	0.62(6)	1.02(6)	-0.02(5)	0.21(6)	-0.40(5)
O(3)	0.3274(3)	0.8745(3)	0.9742(3)	0.49(6)	0.89(6)	0.85(6)	-0.28(5)	0.23(5)	-0.14(5)
O(4)	0.4082(3)	0.8467(3)	0.5739(3)	0.83(6)	0.61(6)	0.91(6)	0.24(5)	0.20(5)	-0.22(5)
W(1)	0.0981(3)	0.2196(3)	0.3098(3)	0.65(6)	1.03(6)	1.06(7)	0.09(6)	0.28(6)	-0.27(6)
W(2)	-0.0498(3)	0.2351(3)	-0.2356(4)	0.80(6)	0.96(6)	1.03(7)	0.17(6)	0.11(6)	-0.17(6)
H(1)	-0.022(9)	0.317(8)	0.330(9)	4.1(9)					
H(2)	0.177(10)	0.263(9)	0.239(10)	5.7(9)					
H(3)	-0.137(8)	0.192(8)	-0.355(9)	3.0(9)					
H(4)	-0.140(9)	0.352(9)	-0.187(10)	4.7(9)					

convergence ($R = 0.030$). A subsequent difference Fourier synthesis showed the four independent H atoms, and the final refinement ($R = 0.027$) yielded the parameters reported in table I; unitary weights were used. The main computations were performed with the SHELX system (Sheldrick, 1976), using the analytical form of the scattering factors for neutral atoms reported in the International Tables for X-ray Crystallography (1974).

The coordinates published by Rumanova *et al.* (1961) for the non-hydrogen atoms turned out to be substantially correct even if shifts of several σ were necessary before convergence was attained, particularly for some z coordinates. With respect to the quoted paper a different choice of O(1) (1) and W(2) has been made in order to have a more compact asymmetric unit.

BOND VALENCE AND COORDINATION POLYHEDRA.

Rumanova *et al.* (1961) found that the valence balance calculated according to Pauling's second rule was not quite satisfactory. By applying this rule as generalized by Brown *et al.* (1973), with the values of the parameters given by Brown *et al.* (1976) and the curve of Brown (1976) for the hydrogen bonds, the best results are obtained (table II) when O(3)ⁱⁱ is included in the coordination sphere of Ca (table III).

O(3)ⁱⁱ is the only anionic oxygen coordinated by Fe (table IV) and its coordination to Ca, which was

TABLE II.

Calculated individual and total (Σ) bond strengths for each atom in half formula unit in the crystal structure of anapaite.

	P	Fe	Ca	H(1)	H(2)	H(3)	H(4)	Σ
O(1)	1.25		0.25		0.27		0.20	1.97
O(2)	1.31		0.36	0.27				1.94
O(3)	1.18	0.46	0.26					1.98
			0.08					
O(4)	1.24		0.31			0.17		1.97
			0.25					
W(1)		0.28	0.24	0.73	0.73			1.98
W(2)		0.28	0.20			0.83	0.80	2.11
Σ	4.98	1.02	1.95	1.00	1.00	1.00	1.00	11.95

not taken into account in the previous work, is unusual particularly because the Ca-O(3)ⁱⁱ = 3.061 Å distance exceeds substantially the first seven ones (table III); similar cases are found, e. g., in the structure of β -Ca₃(PO₄)₂ (Mathew *et al.*, 1977). For the sake of simplicity, however, the Ca polyhedron is shown in figure 1 as a distorted pentagonal bipyramid with O(2) and O(4)ⁱⁱ at the apical vertices. O(3)ⁱⁱ faces the largest mesh of this polyhedron, which could be described alternatively as an octahedron with a double vertex, O(1')^{viii}-O(3')^{viii}, shared with the P tetrahedron (table V). The peculiar position of O(3) is reflected by the deviation of its bond lengths from the corresponding average values in the structure.

TOPOLOGY OF THE STRUCTURE.

The structure of anapaite is a three-dimensional framework of Ca, Fe and P coordination polyhedra which share corners and edges with one another.

(1) Symbols with a prime denote atoms subjected to the transformation $\bar{x}, \bar{y}, \bar{z}$; roman numerals represent the translations: I, +b; II, -b; III, +c; IV, +b +c; V, -b -c; VI, -a, -c; VII, +a +b +c; VIII, +a +b +2c; IX, -c; X, +a +2c; XI, -a.

TABLE III.

**Interatomic distances and angles (O-Ca-O)
in the Ca coordination polyhedron.**

The e.s.d.'s are in parentheses.

Ca(1) - O(1') ^{viii}	2.461(2) Å	
Ca(1) - O(2)	2.312(2)	
Ca(1) - O(3') ^{viii}	2.458(2)	
Ca(1) - O(4) ⁱⁱ	2.367(2)	
Ca(1) - O(4') ^{vii}	2.476(2)	
Ca(1) - W(1)	2.484(2)	
Ca(1) - W(2) ⁱⁱⁱ	2.579(2)	
Average	2.448	
Ca(1) - O(3) ⁱⁱ	3.061(2)	
O(2) - O(1') ^{viii}	3.042(3) Å	79.1(1)°
O(2) - O(3') ^{viii}	3.692(3)	101.4(1)
O(2) - O(4') ^{vii}	3.051(5)	59.9(1)
O(2) - W(1)	3.218(3)	84.2(1)
O(2) - W(2) ⁱⁱⁱ	3.832(3)	103.0(1)
O(4) ⁱⁱ - O(1') ^{viii}	4.288(3)	125.3(1)
O(4) ⁱⁱ - O(3') ^{viii}	3.388(3)	89.2(1)
O(4) ⁱⁱ - O(4') ^{vii}	3.067(3)	78.6(1)
O(4) ⁱⁱ - W(1)	3.099(3)	79.4(1)
O(4) ⁱⁱ - W(2) ⁱⁱⁱ	3.503(3)	98.1(1)
W(1) - O(4') ^{vii}	2.985(3)	74.0(1)
W(1) - W(2) ⁱⁱⁱ	3.031(3)	73.5(1)
O(1') ^{viii} - W(2) ⁱⁱⁱ	3.022(3)	73.6(1)
O(1') ^{viii} - O(3') ^{viii}	2.456(3)	59.9(1)
O(3') ^{viii} - O(4') ^{vii}	3.481(3)	89.8(1)

Maximum concentration of heavy atoms is observed in (101) sheets, rather than in the (010) layers emphasized by Rumanova *et al.* (1961). However, in view of the below discussion on the transition to the bihydrated phase, the structure can be usefully

TABLE IV.

**Interatomic distances and angles (O-Fe-O)
in the Fe coordination polyhedron.**

The e.s.d.'s are in parentheses.

Fe - O(3) ^v	2.031(2) Å	
Fe - O(3') ^{iv}		
Fe - W(1)	2.221(2)	
Fe - W(2)	2.223(2)	
Fe - W(2')		
Average	2.158	
O(3) ^v - W(1)	2.984(3) Å	89.1(1)°
O(3) ^v - W(1')	3.034(3)	91.0(1)
O(3) ^v - W(2)	3.049(3)	91.4(1)
O(3) ^v - W(2')	2.973(3)	88.6(1)
W(1) - W(2')	3.150(3)	90.3(1)
W(1) - W(2)	3.135(3)	89.7(1)
Average	3.054(3)	90.0(1)

described in terms of (100) layers built up by water molecules and Fe atoms which sandwich the Ca and P polyhedra between them (fig. 1).

Pairs of centrosymmetrical Ca polyhedra sharing the O(4)ⁱⁱ-O(4')^{vii} edge are confined within a single (100) layer, and they would form [001] chains through the « softly » coordinated O(3)ⁱⁱ atom. The Fe octahedra share their vertices with six distinct Ca polyhedra belonging to two contiguous (100) layers.

HYDROGEN BONDING.

In the framework structure of anapaite hydrogen bonds play a complementary role and contribute to further linkage between (100) layers and [001] chains

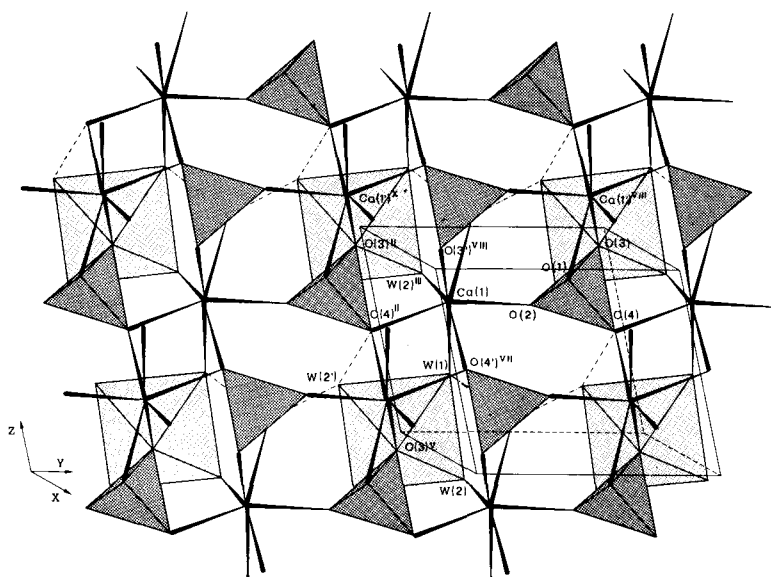


FIG. 1. — Orthogonal projection of the structure of anapaite onto the (100) plane emphasizing a (100) layer. Dashed-dotted lines represent bonds (H atoms are not shown). Not all the atoms mentioned in the text are reported, because either hidden or out of the layer.

TABLE V.
Interatomic distances and angles (O-P-O)
in the PO₄ group

The e.s.d.'s are in parentheses.

P - O(1)	1.540(2) Å	
P - O(2)	1.524(2)	
P - O(3)	1.560(2)	
P - O(4)	1.544(2)	
Average	1.542	
O(1) - O(2)	2.549(3) Å	112.6(1)°
O(1) - O(3)	2.456(3)	104.8(1)
O(1) - O(4)	2.549(3)	111.5(1)
O(2) - O(3)	2.531(3)	110.3(1)
O(2) - O(4)	2.517(3)	110.3(1)
O(3) - O(4)	2.498(3)	107.2(1)
Average	2.517	109.5

The DTA curve of anapaite shows two endothermic peaks at 568 and 588 K and an exothermic peak at 973 K due to the crystallization of the whitlockite-like phase; TGA gives a curve with apparently only one step ending at about 720 K (de Michele *et al.*, 1974), but the corresponding DTG has a double maximum. No thermal analysis are available for Ca₂Fe(PO₄)₂·2H₂O (messelite); however, its behaviour should be comparable with that of the closely isostructural Ca₂Mn(PO₄)₂·2H₂O (fairfieldite), which starts and ends dehydration at 598 and 723 K, respectively (Catti *et al.*, 1977). The double peak in the DTA and DTG of anapaite could therefore be related tentatively to an unstable formation of messelite which, because of low crystallinity, cannot be detected in the high temperature X-ray powder spectrum.

On the other hand, a crystallochemical path for a transition from the four-fold to the two-fold hydrated phase, or vice-versa, can easily be described by comparison of the two crystal structures⁽¹⁾. The bihydrated phase messelite belongs to a triclinic group of «isostructural» minerals with formula Ca₂Me(XO₄)₂·2H₂O which can be divided in two

TABLE VI.

Interatomic distances (Å) and angles (°) for the water molecules and the hydrogen bonds.

A primed letter is for an atom on the second line of each water molecule; significant figures of the e.s.d.'s in parentheses.

A	B	C	D	AB	BC	CD	CC'	BD	ABA'	CBC'	DBD'	BCD
Fe	W(1)	H(1)---	O(2') ^{iv}	2.221(2)	0.86(6)	1.78(6)		2.600(3)				160(5)
Ca		H(2)---	O(1') ^{vii}	2.484(2)	0.88(6)	1.72(6)	1.42(9)		139.4(1)	110(7)	114.6(1)	174(6)
Fe	W(2)	H(3)---	O(4') ⁱ	2.223(2)	0.85(5)	1.96(5)		2.786(3)				162(5)
Ca ^{ix}		H(4)---	O(1') ^{vi}	2.579(2)	0.86(6)	1.87(6)	1.31(8)		106.5(1)	100(7)	89.2(1)	170(6)

via the bonds donated by W(1) and W(2), respectively (table VI). Both water molecules belong to class 2, type B according to Ferraris *et al.* (1972) and, in order to compensate the high bond valence received through the coordination to two bivalent ions, they donate hydrogen bonds which are shorter than the average value of 2.810 Å indicated in the same paper. In particular, W(1) is one of the strongest hydrogen bonded water molecules ever found in crystal structures, as recently discussed for talmessite (Catti *et al.*, 1977).

RELATIONSHIPS WITH THE BIHYDRATED PHASE.

According to an X-ray powder spectrum obtained with a high temperature Guinier camera from 293 to 973 K, anapaite disappears at about 540 K and, after a long interval of low crystallinity, a whitlockite-like phase appears clearly at about 920 K; that should correspond to the formation of the anhydrous phase Ca₂Fe(PO₄)₂, which is probably isomorphous with α-Ca₃(PO₄)₂ (whitlockite).

subgroups (fairfieldite and messelite; collinsite, casidyite, talmessite and β-roselite); these are distinguishable by their cell parameters and are characterized by a closer isostructurality (Catti *et al.*, 1977). The proposed path for the transition can be illustrated with reference to the layers of Ca coordination polyhedra shown in fig. 1 of the paper on talmessite (Catti *et al.*, 1977) and in fig. 1 of this paper, respectively; O(1), O(2), O(3) and O(4) in the latter correspond to O(2), O(4), O(1) and O(3) in the former, respectively⁽²⁾.

The main steps of the dehydration reaction would be: (i) W(2)ⁱⁱⁱ is expelled from the coordination spheres of Ca and Feⁱⁱⁱ; (ii) O(3) comes nearer to Ca

(1) Cech *et al.* (1958) have found that messelite and anapaite were simultaneously present in the same crystal, with the former in the core. This association is probably very usual, since a water content of 2-3H₂O is normally reported in messelite (Taborszky, 1977).

(2) For the sake completeness, however, it must be kept in mind that the role of O(3) and O(4) are interchanged in talmessite and fairfieldite as discussed by Catti *et al.* (1977).

and is tightly coordinated by it, so that the $\text{Ca}(\text{I})$ and $\text{Ca}(\text{I}')^*$ polyhedra are now linked by sharing the $\text{O}(3)^{\text{II}}\text{-O}(3')^{\text{VIII}}$ edge; (iii) $\text{O}(\text{I})$ enters the coordination sphere of Ca bringing its coordination number from 7 to 8, and causes the $\text{Ca}(\text{I})$ and $\text{Ca}(\text{I}')^{\text{VIII}}$ polyhedra to share the $\text{O}(\text{I})\text{-O}(\text{I}')^{\text{VIII}}$ edge. The empty corner of the Fe^{III} coordination octahedron is, finally, occupied by $\text{O}(\text{I})^{\text{XI}}$, which belongs to the lower (100) layer not shown in fig. 1. Then, the bidimensional network of Ca polyhedra observed in the less hydrated structure

is attained, and every Fe octahedron shares corners with two pairs of centrosymmetrical P tetrahedra.

We would like to thank warmly V. de Michele (Museo Civico di Storia Naturale, Milano) for supplying the sample of anapaite. The X-ray intensities were measured at the Centro di Studio del C. N. R. per la Cristallografia Strutturale, Pavia. Research supported by the Consiglio Nazionale delle Ricerche, Roma.

Reçu le 8 février 1979.

Accepté le 9 mars 1979.

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