Hydrogen bonding in the crystalline state.
Structure of talmessite, $Ca_2(Mg, Co)(AsO_4)_2 \cdot 2H_2O$, and crystal chemistry of related minerals

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Abstract. — The crystal structure of a talmessite from Bou-Azzer, $Ca_2(Mg_{0.65}, Co_{0.35})(AsO_4)_2 \cdot 2H_2O$, was solved and refined (R = 0.081) in space group $P\bar{1}$ by 979 reflections measured on an automatic single-crystal diffractometer (MoKα radiation). The unit-cell parameters are: $a = 5.874$ (7), $b = 6.943$ (11), $c = 5.537$ (6) Å, $\alpha = 97.3$ (1), $\beta = 108.7$ (1), $\gamma = 108.1$ (2)°; $Z = 1$. The structure is built up by alternating ($\bar{1}10$) layers of Ca and Mg coordination polyhedra, and is characterized by two unusually short [2.562 (15) and 2.613 (14) Å] hydrogen bonds donated by the H_2O molecule, which account for the high dehydration temperature (460° C) of this mineral. The triclinic minerals $Ca_2Me(XO_4)_2 \cdot 2H_2O$ (X = P or As), regarded as isostructural, are divided in two subgroups (fairfieldite and messelite; collinsite, cassidyite, talmessite and β-roselite) characterized by a closer isostructurality and distinguishable by the cell parameters. Thermal studies were performed on collinsite, fairfieldite and talmessite, showing a dehydration temperature increasing with the strength of hydrogen bonds.

Key words : talmessite, structure, chemical formula, hydrogen bonding, dehydration.

Liaison hydrogène dans l'état cristallin. Structure de la talmessite $Ca_2(Mg, Co)(AsO_4)_2 \cdot 2H_2O$ et cristallo-chimie des minéraux connexes.

Résumé. — La structure cristalline d'une talmessite cobaltifère de Bou-Azzer, $Ca_2(Mg_{0,65}, Co_{0,35})(AsO_4)_2 \cdot 2H_2O$, a été résolue et affinée (R = 0,081) dans le groupe spatial $P\bar{1}$ par 979 réflexions mesurées à l'aide d'un diffractomètre automatique (radiation MoKα). Les paramètres de la maille sont : $a = 5,874$ (7), $b = 6,943$ (11), $c = 5,537$ (6) Å, $\alpha = 97,3$ (1), $\beta = 108,7$ (1), $\gamma = 108,1$ (2)°; Z = 1. La structure est formée de couches ($\bar{1}10$) alternée de polyèdres de coordination de Ca et Mg, et montre deux liaisons hydrogène très courtes [2,562 (15) et 2,613 (14) Å], données par la molécule H_2O, qui expliquent la température de déshydratation élevée (460° C) du minéral. Les minéraux tricliniques $Ca_2Me(XO_4)_2 \cdot 2H_2O$ (X = P ou As), considérés isostructuraux, sont divisés en deux groupes (fairfieldite et messélite; collinsite, cassidyite, talmessite et β-rosélite) qui sont caractérisés par une isostructuralité plus étroite et peuvent se distinguer par les paramètres de la maille. Des études thermiques sur collinsite, fairfieldite et talmessite ont montré que la température de déshydratation de ces minéraux augmente avec la force des liaisons hydrogène.

Mots clés : talmessite, structure, formule chimique, liaison hydrogène, déshydratation.

INTRODUCTION.

The general formula $Ca_2Me(XO_4)_2 \cdot 2H_2O$, where X is P or As and Me^{2+} is a divalent cation, represents a number of minerals with monoclinic or triclinic symmetry. The terms of the latter family, which will be dealt with in this work, are messelite, collinsite, fairfieldite, cassidyite (X = P and Me^{2+} = Fe^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, respectively) and talmessite, β-roselite (X = As and Me^{2+} = Mg^{2+}, Co^{2+}) ; two or more vicariant cations are normally found for Me^{2+}, and the discovery of Ni-rich (Cesbron *et al.*, 1972) and Zn-rich collinsite (Hill *et al.*, 1974) presumes an even larger family.

However, in the literature, there is no unanimity in writing the chemical formulae of these minerals as bihydrated compounds. In particular, for talmessite Cesbron *et al.* (1972) suggest a formula containing both OH⁻ ions and acidic H atoms on the basis of the high dehydration temperature (about 500° C) and

following previous works (Yakhontova *et al.*, 1956; Bariand *et al.*, 1960 ; Yakhontova *et al.*, 1967) ; if, on the contrary, all the hydrogen is contained in water molecules, as proposed by Pierrot (1964), then these must be very strongly bonded in the crystal so as to account for the high dehydration temperature.

In the frame of our studies on hydrogen bonding (last paper published : Catti *et al.*, 1977), we have accepted with pleasure the suggestion of Professor F. Permingeat to perform a structural investigation on a sample of Co-talmessite which was kindly supplied by himself.

PROBLEMS OF NOMENCLATURE.

The name talmessite was proposed by Bariand *et al.* (1960) for the mineral with ideal formula $Ca_2Mg(AsO_4)_2 \cdot 2H_2O$. Subsequently, Pierrot (1964) proved its identity with the mineral previously named belovite by Nefedov (1953) and arsenate-belovite by Yakhontova *et al.* (1956) [in order to distinguish it from the mineral belovite of the apatite group described

by Borodin *et al.* (1954)] and proposed to name the calcium-magnesium arsenate belovite instead of talmessite on priority grounds. In recent works, the name belovite is left to the mineral of the apatite group, and talmessite is used for the arsenate (Strunz, 1970; Povarennykh, 1972; Cesbron *et al.*, 1972; Féraud *et al.*, 1976), with some exceptions (Fleischer, 1975; Luzgin, 1975).

The I. M. A. Commission on New Minerals and Mineral Names has now accepted talmessite and belovite for the arsenate and the phosphate, respectively.

CRYSTAL DATA.

A sample from Bou-Azzer (Morocco) with a deep pink colour was used and the value 0.35 was assumed for the ratio $Co/(Co + Mg)$, according to a chemical analysis (Bariand *et al.*, 1960) on material of the same locality, studied by Cesbron *et al.* (1972) as well; this value appeared consistent with the structure analysis. By least-squares refinements of 23 θ values measured on a single crystal diffractometer, with $\lambda(MoK\alpha) = 0.71069$ Å, the following parameters of the reduced cell were obtained : $a = 5.874$ (7), $b = 6.943$ (11), $c = 5.537$ (6) Å, $\alpha = 97.3$ (1), $\beta = 108.7$ (1), $\gamma = 108.1$ (2)°; the transformation to the cell previously used in the literature is $\bar{1}00/110/001$. Other data are : space group $P\bar{1}$ (on structural basis), MW $= 404.5$, V $= 196.7$ Å³, $D_m = 3.57$ g cm⁻³ (Bariand *et al.*, 1960), $D_c = 3.42$ g cm⁻³, Z = 1, F(ooo) $= 201$, $\mu(MoK\alpha) = 109$ cm⁻¹.

INTENSITY MEASUREMENTS.

An irregular fragment of single crystal, approximately elongated [$20\bar{1}$] and $0.10 \times 0.13 \times 0.85$ mm large, was used for the data collection with a four circle Philips PW 1100 diffractometer. The measurement conditions were : graphite monochromatized MoKα radiation, $\theta \leqslant 30°$, $\theta/2\theta$ scan, scan width $\Delta\theta = 2.5°$, scanning speed $0.05°$ s⁻¹, background time $= 10$ s on both sides of each scan, three reference reflections (300, 040, 003). By rejecting the 181 weakest reflections [$|F_o| \leqslant 4 \sigma (F_o)$], a set of 979 independent observations was obtained. An absorption correction was unsuccessfully tried because of the strongly irre-

gular, shape of the crystal; as for secondary extinction effects, no reasonable correction was shown by least-squares fitting of the function $I_c/I_o = K (1 + gI_c)$.

SOLUTION AND REFINEMENT OF THE STRUCTURE.

Intensity statistics suggested the absence of symmetry centre and, indeed, a solution of the structure was found in the space group $P1$ both by direct methods with the program MULTAN (Germain *et al.*, 1971) and by Patterson function. A least-squares isotropic refinement, however, showed that the acentric structural model was crystal-chemically and statistically not different from the centrosymmetric one obtained for collinsite by Brotherton *et al.* (1974). A full-matrix refinement of talmessite was then carried out anisotropically in space group $P\bar{1}$, and convergence was reached (R $= 0.081$) with unitary weights ; a reasonably constant behaviour of $w\Delta^2/vs.$ $|F_o|$ and sin θ was obtained, except for very high $|F_o|$ and very low sin θ values. However, the anisotropic thermal factors of Ca and of O of the water molecule became definitepositive only by rejecting some strong reflections [1] affected by a remarkable F_o/F_c discrepancy. This effect should not be ascribed to a possible substitution of Ca by Co, since the thermal factor obtained for the (Mg, Co) position (Mg hereafter) is regular ; on the other hand a number of electrons different from that (17.25) assumed for the Mg position, would have caused a too large or too small (even negative) thermal factor, already in the isotropic refinement.

TABLE I.

Fractional coordinates and vibrational parameters (Å²) with the significant figures of the e.s.d.'s.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mg	0	0	0	1.09(16)	1.76(18)	1.32(16)	0.72(14)	0.37(13)	-0.22(13)
As	0.3341(2)	0.2460(2)	0.6703(2)	0.21(7)	0.65(8)	0.31(7)	0.13(6)	0.10(6)	-0.19(6)
Ca	0.2949(5)	0.7622(4)	0.6529(5)	0.75(8)	1.27(9)	0.77(8)	0.57(7)	0.43(7)	-0.13(7)
O(1)	0.3420(19)	0.1272(15)	0.9217(18)	1.02(34)	1.42(35)	1.09(31)	0.59(28)	0.56(27)	0.33(27)
O(2)	0.2385(19)	0.0504(16)	0.3986(18)	0.89(31)	1.48(37)	0.73(31)	0.70(28)	-0.10(25)	-0.64(26)
O(3)	0.1550(18)	0.3916(15)	0.6412(19)	1.06(33)	0.90(32)	1.43(33)	0.63(27)	0.49(28)	0.10(26)
O(4)	0.6395(19)	0.3864(16)	0.7149(20)	0.90(34)	1.41(36)	1.52(35)	0.16(29)	0.75(29)	-0.29(29)
W	0.9533(17)	0.2778(14)	0.0745(16)	0.70(34)	1.08(35)	0.40(36)	0.45(30)	0.31(30)	-0.02(30)

Scattering factors for neutral atoms (International Tables for X-ray Crystallography, 1962) and the programs of the X-ray System (Stewart *et al.*, 1970) were used. The final atomic fractional coordinates and the B_{ij} 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 I.

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(1) Such reflections (52) are marked by E in the list of structure factors available from the authors.

Topology of the structure.

The structural features of talmessite are the same as those reported for collinsite (Brotherton et al., 1974) ; some substantial differences from fairfieldite (Fanfani et al., 1970) will be discussed below. However, by considering the structures of this group of minerals from the point of view of connection among Ca coordination polyhedra, their topology can be better emphasized (Fig. 1). Eight oxygen atoms are coordi-
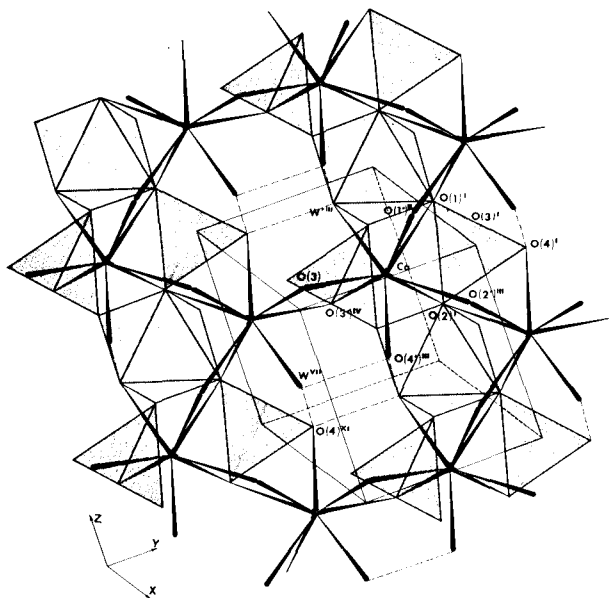

FIG. 1. — Projection of the crystal structure of talmessite onto the (Ī10) plane. Black rods and dashed-dotted lines represent Ca-O coordination bonds and hydrogen bonds, respectively.

nated by Ca and form a very irregular trigonal prism with two pyramided faces (Table II), which shares three of its 17 edges with three different Ca polyhedra ; (Ī10) layers of linked Ca coordination polyhedra are then built up, according to a network with stretched pseudo-hexagonal meshes formed by the Ca – Ca lines. This network can also be described in terms of circumferences determined by eight Ca and containing two other Ca atoms : every circle is in contact with four ones, so that the arrangement is not close packed.

Slightly distorted Mg coordination octahedra (Table III) lie on (Ī10) planes between adjacent Ca layers. The As tetrahedra (Table IV) share two vertices with the Mg polyhedra, so as to build up a system of parallel [001] chains in (Ī10) planes ; adjacent chains are tied by one of the two independent hydrogen bonds, W– – – – O (4′)^{IX} (^{1}). The linking between Mg and Ca layers is provided by each Ca polyhedron sharing two edges with two Mg octahedra [W^{III} – – – – O (1′)^I and O (1′)^{II} – – – – O (2′)^{III}] and two edges

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($_1$) Symbols with a prime denote atoms subjected to the transformation x̄, ȳ, z̄ ; roman numerals represent the translations : I, +b ; II, +a +b +2c ; III, +a +b +c ; IV, +b +c ; V, —c ; VI, +c ; VII, —a ; VIII, +a ; IX, +2a +b +c ; X, +a —c ; XI, —a —c.

TABLE II.

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

The e.s.d.'s are 0.010 and 0.015 Å for Ca-O and O– – –O distances, respectively ; 0.4° for the angles.

Ca	-	O(1)^I	2. 656 Å
Ca	-	O(2)^I	2. 633
Ca	-	O(3)	2. 431
Ca	-	O(1′)^{II}	2. 446
Ca	-	O(2′)^{III}	2. 769
Ca	-	O(3′)^{IV}	2. 412
Ca	-	O(4′)^{III}	2. 361
Ca	-	(W′)^{III}	2. 398
O(3)	-	O(1′)^{II}	3. 600 Å	95. 2°
O(3)	-	O(3′)^{IV}	2. 917	141. 7
O(3)	-	O(4′)^{III}	2. 978	76. 8
O(3)	-	(W′)^{III}	2. 963	75. 7
O(2′)^{III}	-	O(1)^I	3. 857	90. 6
O(2′)^{III}	-	O(2)^I	3. 243	73. 7
O(2′)^{III}	-	O(1′)^{II}	2. 969	69. 1
O(2′)^{III}	-	O(4′)^{III}	2. 636	61. 2
O(4′)^{III}	-	O(2)^I	3. 356	84. 3
O(4′)^{III}	-	O(1′)^{II}	4. 085	116. 4
O(4′)^{III}	-	O(3′)^{IV}	3. 173	83. 3
O(1)^I	-	O(2)^I	2. 706	61. 5
O(1)^I	-	O(1′)^{II}	2. 953	70. 6
O(1)^I	-	(W′)^{III}	2. 815	67. 5
O(2)^I	-	O(3′)^{IV}	3. 146	77. 0
(W′)^{III}	-	O(1′)^{II}	3. 193	82. 4
(W′)^{III}	-	O(3′)^{IV}	2. 876	73. 5

with two As-tetrahedra [O (1)^I – – – – O (2)^{II} and O (2′)^{III} – – – – – O (4′)^{III}], respectively.

No cleavage plane breaking hydrogen bonds only is possible, so that no one of the cleavages observed for minerals of the group [e. g., {010} and {001} for fairfieldite (Wolfe, 1940)] seems to be preferred on structural grounds.

Hydrogen bonding and chemical formula.

Although the positions of the hydrogen atoms have not been determined, the results of the structural analysis confirm the formula given above for talmessite, Ca_2 (Mg, Co) $(AsO_4)_2 \cdot 2H_2O$, and no evidences seem to support the alternative formula Ca_2 (Mg, Co) $(HAsO_4)_2 (OH)_2$. The only oxygen atom in the anionic group which could carry a hydrogen atom is O (4),

TABLE III.

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

The e.s.d.'s are 0.010 and 0.015 Å for Mg-O and O---O distances, respectively ; 0.4° for the angles.

Mg	-	$O(1)^V$	2. 135 Å	
Mg	-	$O(1')^{VI}$		
Mg	-	$O(2)$	2. 115	
Mg	-	$O(2')$		
Mg	-	W^{VII}	2. 041	
Mg	-	$(W')^{VIII}$		
W^{VII}	-	$O(1)^V$	3. 086 Å	95. 3°
W^{VII}	-	$O(2)$	2. 994	92. 2
W^{VII}	-	$O(1')^{VII}$	2. 815	84. 7
W^{VII}	-	$O(2')$	2. 882	87. 8
$(W')^{VIII}$	-	$O(1)^V$	2. 815	84. 7
$(W')^{VIII}$	-	$O(2)$	2. 883	87. 8
$(W')^{VIII}$	-	$O(1')^{VII}$	3. 086	95. 3
$(W')^{VIII}$	-	$O(2')$	2. 994	92. 2
$O(1)^V$	-	$O(2)$	2. 969	88. 7
$O(1)^V$	-	$O(2')$	3. 040	91. 4
$O(1')^{VI}$	-	$O(2)$	3. 040	91. 4
$O(1')^{VI}$	-	$O(2')$	2. 969	88. 7

TABLE IV.

Interatomic distances and angles (O-As-O) in the AsO₄ group.

The e.s.d.'s are 0.010 and 0.015 Å for As-O and O---O distances, respectively ; 0.5° for the angles.

As	-	$O(1)$	1. 702 Å	
As	-	$O(2)$	1. 699	
As	-	$O(3)$	1. 659	
As	-	$O(4)$	1. 672	
$O(1)$	-	$O(2)$	2. 706 Å	105. 4°
$O(1)$	-	$O(3)$	2. 807	113. 3
$O(1)$	-	$O(4)$	2. 731	108. 1
$O(2)$	-	$O(3)$	2. 827	114. 7
$O(2)$	-	$O(4)$	2. 636	102. 9
$O(3)$	-	$O(4)$	2. 755	111. 6

TABLE V.

Interatomic distances (Å) and angles (°) in the hydrogen bonds of (a) talmessite (b) collinsite (c) fairfieldite.

For the labelling of the atoms see foot-note (2) p. 234.

(a)	$O(4)^V$---W---$O(4')^{IX}$	2.613(14)	2.562(15)	102.9(5)
(b)	$O(4)^V$---W---$O(4')^{IX}$	2.571(7)	2.613(7)	105.7(3)
(c)	$O(4)^V$---W---$O(3')^{III}$	2.713(9)	2.650(12)	100.3(4)

TABLE VI.

Calculated individual and total (Σ) bond strenghts for each atom in half formula unit in the crystal structure of talmessite (top ; X = As, Me = Mg), collinsite (middle ; X = P, Me = Mg) and fairfieldite (bottom ; X = P, Me = Mn).

	X	Ca		Me	W		Σ
	1. 17	0. 17	0. 26	0. 30			1. 90
O(1)	1. 22	0. 22	0. 21	0. 30			1. 95
	1. 17	0. 24	0. 23	0. 27			1. 91
	1. 18	0. 18	0. 13	0. 32			1. 81
O(2)	1. 19	0. 19	0. 15	0. 33			1. 86
	1. 19	0. 25	0. 15	0. 38			1. 97
	1. 36	0. 27	0. 28				1. 91
O(3)	1. 30	0. 29	0. 25				1. 84
	1. 34	0. 34			0. 26		1. 94
	1. 30	0. 32			0. 28	0. 35	2. 25
O(4)	1. 26	0. 30			0. 28	0. 31	2. 15
	1. 22	0. 26	0. 25		0. 20		1. 93
		0. 29		0. 37	0. 72	0. 65	2. 03
W		0. 30		0. 41	0. 72	0. 69	2. 12
		0. 27		0. 34	0. 80	0. 74	2. 15
	5. 01	1. 90		0. 99	2. 00		9. 90
Σ	4. 97	1. 91		1. 04	2. 00		9. 92
	4. 92	1. 99		0. 99	2. 00		9. 90

which is involved with W in the only two O...O contacts shorter than 3 Å and is coordinated by a Ca atom only ; the other anionic oxygens are coordinated by two Ca atoms [O (1) and O (2) by Mg as well] and show no O...O short contacts. However, the As-O (4) distance (Table IV) is definitely too short for an As-OH bond. Besides, owing to the close isostructurality of talmessite with collinsite, where the hydrogen atoms were located (Brotherton *et al.*, 1974), it can be concluded that all the hydrogen is carried by the oxygen W which acts as donor of two hydrogen bonds towards O (4) (Table V). One of these is extraordinarily short for a H_2O molecule, and is probably responsible for the peculiar thermal behaviour of talmessite. The only comparable hydrogen bond studied by neutron diffraction [2.546 (5) Å at 4.2 K] was

Some kind of weak interaction could be supported by the slight underbonding of O (3) (Table VI) ; on the other hand, inclusion of multiple O – H – – – O interactions in spite of their configurations improved the bond strengths balance at least in the peculiar case of perchloric acid hydrates (Brown, 1976 *b*).

RELATED MINERALS.

By considering the unit-cell parameters of the triclinic $Ca_2Me (XO_4)_2 \cdot 2H_2O$ minerals (Table VII), two distinct subgroups can be recognized, owing to the α and γ values at least : fairfieldite ([1]) and messelite on one side, and collinsite, talmessite, β-roselite, cassidyite on the other ; this division is confirmed by a closer

TABLE VII.

Lengths (Å) and angles (°) for the reduced unit cell of the triclinic minerals with general formula $Ca_2Me (XO_4)_2 \cdot 2H_2O$.

The refinements are based on partial sets of reflections from the quoted powder spectra.

	a	b	c	α	β	γ
Fairfieldite (1)	5. 79(1)	6. 57(1)	5. 51(1)	102. 3(3)	108. 7(3)	90. 3(3)
Messelite (2)	5. 95(2)	6. 52(2)	5. 45(2)	102. 3(4)	107. 5(4)	90. 8(2)
Collinsite (3)	5. 7344(8)	6. 780(1)	5. 4413(9)	97. 29(1)	108. 56(1)	107. 28(1)
Talmessite (4)	5. 884(4)	6. 995(4)	5. 564(4)	97. 69(9)	109. 69(12)	107. 91(10)
β−roselite (4)	5. 884(6)	6. 963(8)	5. 581(9)	97. 72(8)	109. 24(9)	107. 53(10)
Cassidyite (5)	5. 713(13)	6. 730(15)	5. 430(11)	96. 7(2)	107. 3(3)	104. 7(2)

(1) Fanfani et al. (1970). - (2) Refinement of the powder data given by Frondel (1955); several lines of this spectrum are due to β radiation or to impurities. - (3) Brotherton et al. (1974). - (4) Refinement of the powder data given by Pierrot (1964) for talmessite from Talmessi (Iran) and for β−roselite from Schneeberg (Germany). - (5) Refinement of the powder data given by White et al. (1967).

found in ludlamite, $Fe_3 (PO_4)_2 \cdot 4H_2O$ (Abrahams, 1966) ; as for X-ray studies, similar bonds were found in compounds isostructural with metavariscite, $AlPO_4 \cdot 2H_2O$ (Kniep *et al.*, 1973), where the bond length is 2.598 (2) Å [cf. also Kitahama *et al.* (1975) and papers therein quoted]. A tetrahedral environment [$\angle$ (Ca')^{III} – – – W – – – Mg^{VIII} is 105.5 (4)° ; the angle between the CaWMg and OWO' planes is 80°], typical for most water molecules, is shown by W, which belongs to class 2, type B according to Ferraris *et al.* (1972). The reliability of the proposed hydrogen bonding scheme is confirmed by a calculation of bond strengths according to the universal formula of Brown *et al.* (1976) (Table VI) and to the curves for the hydrogen bond of Brown (1976 *a*) ; it should be remarked that O (4) is overbonded, so that it could not act as donor of a hydrogen bond.

W shows a third contact which is shorter than 3.2 Å and is not an edge of a coordination polyhedron, $W – – – O (3)^x = 3.084 (14)$ Å ; however, owing to the great strength of the recognized hydrogen bonds and to the unfavourable orientation of the $W – – – O (3)^x$ direction, which forms angles of about 70° with the directions of both hydrogen bonds, the possibility of bifurcated hydrogen bonds should be excluded.

similarity of powder spectra within each subgroup of minerals. An analysis of the known structures (fairfieldite in the first subgroup and collinsite and talmessite in the second one) shows that some limited but interesting structural differences correspond to the differences of cell : the atomic positions ([2]) of collinsite and talmessite appear to be very similar, whereas they differentiate clearly from fairfieldite in the x coordinate particularly for O (3), O (4) and W.

Therefore a different hydrogen bonding scheme is observed (Table V) : W donates a hydrogen bond to O (4')^{IX} in the first two structures, but to O (3')^{III} in the third one. Fanfani *et al.* (1970) considered the contact $W – – – O (3)^x = 2.942$ Å instead of $W – – – O (4)^v = 2.713$ Å as hydrogen bond in fairfieldite ; this assumption does not seem to be justified since, contrary to

(1) The quite different unit cell given for this mineral by Hawthorne *et al.* (1977) has been erroneously deduced by comparison with that of cassidyite (Hawthorne, 1977; private communication).

(2) The numbering of atoms in collinsite (Brotherton *et al.*, 1974) and talmessite are the same, while the atoms O (1), O (2), O (3), O (4) of fairfieldite (Fanfani *et al.*, 1970) have been renamed here as O (3), O (4), O (2) and O (1), respectively, in conformity with the former structures.

Fanfani *et al.* (1970) description, W – – – O (4)^v is not an edge of the Ca coordination polyhedron : moreover, O (4) would be clearly underbonded without the hydrogen bond received from W (Table VI).

However, the existence of a bifurcated hydrogen bond cannot be excluded in this case, in view of the reasonable values of the angles [∠O (3)^x – – – W – – – O (3')^{iii} = 102.8° and ∠O (3)^x – – – – W – – – – O (4)^v = 72.8°].

The triclinic minerals with formula Ca_2Me $(XO_4)_2 \cdot$ $2H_2O$ should then be considered to be isostructural to a first approximation only ; more properly, a fairfieldite subgroup and a collinsite subgroup could be defined, showing a much closer internal isostructurality.

Thermal study.

Thermal analyses of talmessite (Bariand *et al.*, 1960 ; Cesbron *et al.*, 1972) showed an unusually high temperature of dehydration, about 500° C, which can be accounted for by the very short hydrogen bonds of
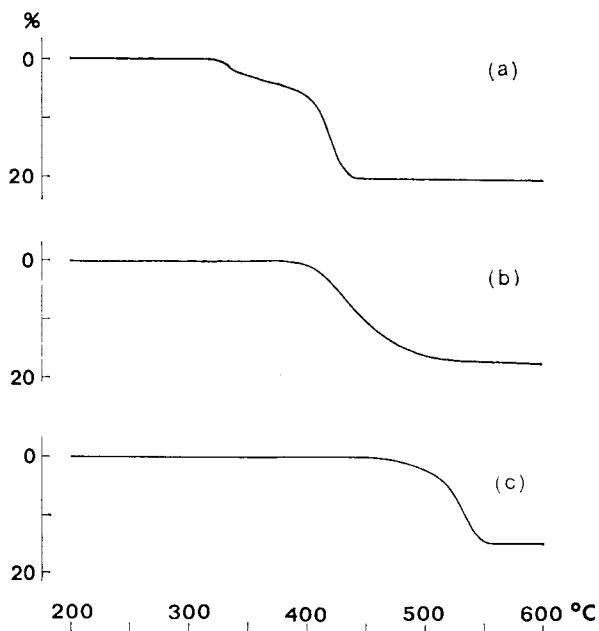
Fig. 2. — TGA curves for (a) fairfieldite, (b) collinsite, (c) talmessite. Percent weight loss is plotted *vs.* temperature ; heating speed 10° C min^{-1} ; samples of about 10 mg.

the water molecules, as discussed above. Since no such studies were found in the literature for other minerals of the group, we decided to fill the gap, so as to investigate the relations between hydrogen bonding and dehydration behaviour more thoroughly in this peculiar class of minerals. TGA (Fig. 2) and DSC (Fig. 3) analyses, and powder spectra with a high temperature Guinier camera (from 20° to 800° C, CuKα radiation) were performed on the available material : talmessite from Bou-Azzer (Morocco), collinsite from Lake François (Canada) and fairfieldite from Foote Mine (King's M. t, N. Carolina).
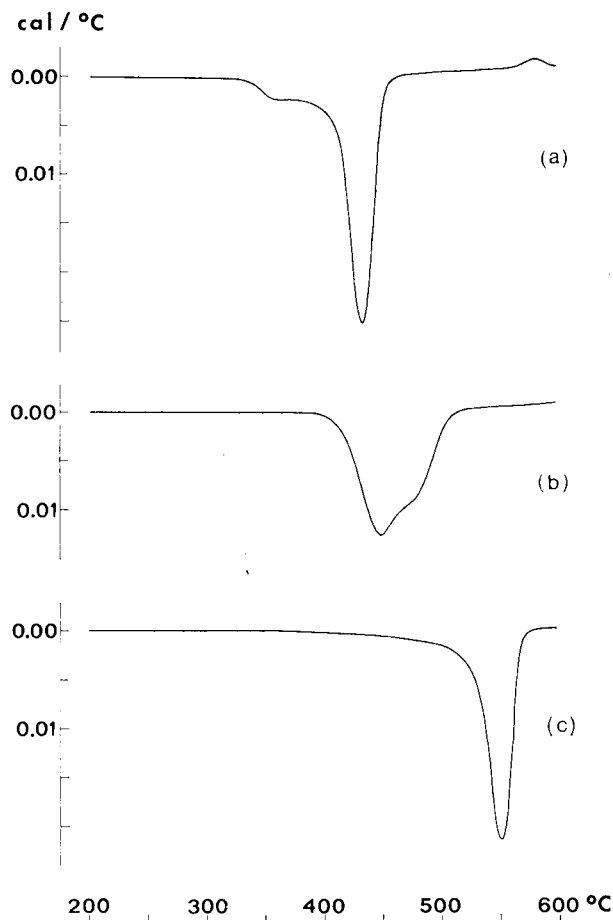
Fig. 3. — DSC (differential scanning calorimetry) curves for (a) fairfieldite (0.102 mg), (b) collinsite (0.092 mg), (c) talmessite (0.104 mg).

With a good accord of the three thermal techniques, the dehydration process is shown to start at temperatures of 325, 390 and 460° C for fairfieldite, collinsite and talmessite, respectively ; the trend is then clear : the stronger (shorter) the hydrogen bonds are, the higher is the dehydration temperature. By comparison of the powder spectra results with data reported for whitlockite-type compounds (ASTM 9-169; Calvo *et al.*, 1975), the products of dehydration should correspond to $(Ca, Me^{2+})_3 (XO_4)_2$. The previous thermal studies of talmessite are substantially confirmed, except for the early weight loss observed by those authors in TGA experiments, which should be due to absorbed water as already suggested by Cesbron *et al.* (1972).

Two different stages in the dehydration process can be observed more (fairfieldite, DSC and TGA curves) or less (collinsite, DSC) clearly ; for talmessite only a slight asymmetry in the DSC endothermic peak occurs. The interpretation of these phenomena is not very simple, because the two water molecules in the chemical formula should be expected to get out of the crystal lattice simultaneously, owing to their crystallographic equivalence. However, two hypotheses at least can be put forward : 1) during the dehydration process, a slight structural rearrange-

ment occurs, which involves the hydrogen bonding mainly and can then hardly be detected by X-ray spectra (e. g., a transition between collinsite- and fairfieldite-type structures) ; the activation energy of the dehydration reaction would therefore change, accounting for the two-stages process ; 2) the solid-state dehydration is coupled with a boiling effect of a « solution » formed by the freed water.

The small exothermic DSC peak (570°C) of fairfieldite corresponds to that found for talmessite by Cesbron et al. (1972) at 690° C ; it should be present for collinsite as well, at a temperature higher than 600° C. Such effect ought to be related to a process of crystallization of the whitlockite-type phase, since in the Guinier powder spectra of all the three minerals a large region of low crystallinity is present, extending

from the temperature of starting dehydration up to the temperature where the exothermic phenomenon appears.

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