RN5210

Met vije beste denk
Seoffrey K.

Drugmanite, $Pb_2(Fe_{0.78},Al_{0.22})H(PO_4)_2(OH)_2$:
Its crystal structure and place in the datolite group

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Abstract. — The crystal structure of drugmanite $[Pb_2(Fe_{0.78},Al_{0.22})H(PO_4)_2(OH)_2$, $a = 11.111(5)$, $b = 7.986(5)$, $c = 4.643(3)$ Å, $\beta = 90.41(3)°$, space group $P2_1/a$, $Z = 2]$ has been determined by single-crystal X-ray diffraction methods and refined by full-matrix least-squares techniques to $R = 0.049$ for 723 independent reflexions. $(Fe,Al)O_6$ octahedra are linked by pairs of phosphate tetrahedra to form chains parallel to the c axis. Although hydrogen atoms could not be located directly, consideration of the bond strengths for the oxygen atoms indicates that the chains are linked in the a direction by symmetrical O...H...O bonds with the hydrogen atoms at symmetry centres. The Pb atom is surrounded by ten oxygen atoms at distances varying from 2.27Å to 3.45Å (bond strengths between 0.65 and 0.03).

A systematic description of the datolite group $[A_2BCD_2(XO_4)_2Y_2]$ including datolite, drugmanite, gadolinite, herderite, hingganite (xinganite) and homilite, is given with $a>c$ in space group $P2_1/a$. When the atomic positions are taken into account, the choice of an acute β angle is necessary for datolite and herderite in order to make the structures comparable. The differences in structure (different types of tetrahedra, presence or absence of an octahedrally coordinated cation) are discussed.

Key-words : drugmanite, crystal structure, datolite group, systematic crystal chemistry.

La drugmanite, $Pb_2(Fe_{0.78},Al_{0.22})H(PO_4)_2(OH)_2$: sa structure et sa place dans le groupe de la datolite.

Résumé. — La structure de la drugmanite, $Pb_2(Fe_{0.78},Al_{0.22})H(PO_4)_2(OH)_2$, a été déterminée par diffraction des rayons X ($R = 0.049$ pour 723 réflexions). Les paramètres de la maille sont $a = 11,111(5)$, $b = 7,986(5)$, $c = 4,643(3)$ Å, $\beta = 90,41(3)°$, groupe spatial $P2_1/a$, $Z = 2$. Des chaînes parallèles à l'axe c sont formées par des octaèdres $(Fe,Al)O_6$, liés entre eux par des paires de tétraèdres PO_4. Des ponts hydrogène symétriques entre des tétraèdres lient les chaînes dans la direction [100]. L'atome de plomb est entouré par dix oxygènes à des distances de 2,27 à 3,45Å (force de liaison de 0,65 à 0,03).

Suit une description systématique du groupe de la datolite $[A_2BCD_2(XO_4)_2Y_2]$ comprenant la datolite, la drugmanite, la gadolinite, l'herderite, l'hingganite (xinganite) et l'homilite. Cette description est faite en prenant $a>c$, le groupe spatial étant $P2_1/a$. Les positions atomiques imposent le choix d'une maille avec l'angle β aigu pour la datolite et l'herderite afin de rendre les structures comparables. Les différences entre ces structures (nombre de types tétraèdres, présence éventuelle d'un cation octaèdrique) sont discutées.

Mots-clés : drugmanite, structure cristalline, groupe de la datolite, cristallochimie systématique.

INTRODUCTION

Drugmanite, a new mineral from Richelle, Belgium, was first described by Van Tassel *et al.*, (1979). We have determined its crystal structure by single-crystal X-ray diffraction techniques and have confirmed that it is related to datolite (Ito and Mori, 1951 ; Foit *et al.*, 1973), as well as gadolinite (Ito and Mori, 1951 ; Pavlov and Belov, 1957 ; Miyawaki *et al.*, 1984), herderite (Pavlov and Belov, 1957 ; Lager and Gibbs, 1974) and homilite (Miyawaki *et al.*, 1985), as suggested in the original paper and also to hingganite-(Yb) (Yakubovich *et al.*, 1983) and xinganite (Ximen and Peng, 1986).

STRUCTURE DETERMINATION

The crystal data for $Pb_2(Fe_{0.78}Al_{0.22})H(PO_4)(OH)_2$ are : monoclinic, space group $P2_1/a$, $a = 11.111(5)$, $b = 7.986(5)$, $c = 4.643(3)$Å, $\beta = 90.41(3)°$, $V = 412(1)Å^3$, D_{calc} $(Z = 2) = 5.55g.cm^{-3}$, $\mu(MoK\alpha) = 428.9cm^{-1}$. Intensity data were collected on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71069$Å) from a single crystal with dimensions $0.09 \times 0.05 \times 0.02$mm, which had previously been used for the cell parameter determination (Van Tassel *et al.*, 1979). A half sphere of reciprocal space up to $2\theta = 50°$ ($0 \leq h \leq 13$, $-9 \leq k \leq 9$, $-5 \leq l \leq 5$) was

measured by the ω-scan technique with a scan width of 1.6°. Backgrounds were measured at 1.6° on either side of the calculated ω value. An absorption correction was performed using the Gaussian approximation of Busing and Levy (1957) as incorporated into the XRAY-76 system (Stewart et al., 1976) used for all computations. The relatively large errors in estimating the crystal dimensions may limit the accuracy of the absorption correction and cause errors in the thermal vibration parameters. The intensities of hkl and h̄k̄l̄ reflexions were averaged thereby reducing the 1450 measured reflexions to a unique set of 723 reflexions, 648 of which were significant at the 3σ level and were considered as observed. The coordinates of the Pb atoms were determined by Patterson methods and the other non-hydrogen atoms were located by Fourier methods. No attempt was made to locate hydrogen atoms. Full-matrix least squares refinement of coordinates and anisotropic temperature factors for all atoms led to $R = 0.049$ for all reflexions and $R = 0.045$ for the 648 observed reflexions only. Atomic scattering factors were calculated for Pb^{2+}, Al^{3+}, P and O^- using the analytical approximation of Cromer and Mann (1968). A weighted scattering factor $(0.78f_{Fe} + 0.22f_{Al})$ was used for the site occupied by Al and Fe. All oxygens were treated as O^-. The scattering factor of Pb^{2+} was corrected for anomalous dispersion using the values given in the International Tables for X-ray Crystallography (1974). Atomic parameters are listed in table I and interatomic distances in table II. The table of observed and calculated structure factor values is available from the authors.

Pb coordination r_0=2.112			O coordination		
Pb to atom	d(Å)	s	O(1) to atom	d(Å)	s
O(3).9	2.27(2)	0.65	P.0	1.56(2)	1.17
O(4).10	2.50(1)	0.35	Pb.5	2.61(2)	0.26
O(5).12	2.53(1)	0.32	Pb.1	3.36(2)	0.03
O(1).5	2.61(2)	0.26	Pb.6	3.45(2)	0.03
O(5).2	2.62(2)	0.25	Total bonding to O(1)		1.49
O(2).0	2.97(2)	0.10			
O(3).6	3.16(2)	0.06	O(2) to atom	d(Å)	s
O(1).2	3.36(2)	0.03	P.0	1.52(2)	1.30
O(3).10	3.41(2)	0.03	Fe.0	2.03(2)	0.45
O(1).6	3.45(2)	0.03	Pb.0	2.97(2)	0.10
Total bonding to Pb		2.08	Total bonding to O(2)		1.85
Fe,Al coordination r_0=1.735			O(3) to atom	d(Å)	s
Fe,Al to atom	d(Å)	s	P.0	1.55(2)	1.20
O(5).2	1.96(1)	0.54	Pb.8	2.27(2)	0.65
O(5).3	1.96(1)	0.54	Pb.6	3.16(2)	0.06
O(4).2	2.00(2)	0.49	Pb.7	3.41(2)	0.03
O(4).3	2.00(2)	0.49	Total bonding to O(3)		1.94
O(2).0	2.03(2)	0.45			
O(2).4	2.03(2)	0.45	O(4) to atom	d(Å)	s
Total bonding to Fe		2.96	P.0	1.56(2)	1.17
			Fe.1	2.00(2)	0.49
			Pb.7	2.50(1)	0.35
P coordination r_0=1.617			Total bonding to O(4)		2.01
P to atom	d(Å)'	s			
O(2).0	1.52(2)	1.30	O(5) to atom	d(Å)	s
O(3).0	1.55(2)	1.20	Fe.1	1.96(1)	0.54
O(1).0	1.56(2)	1.17	Pb.11	2.53(1)	0.32
O(4).0	1.56(2)	1.17	Pb.1	2.62(2)	0.25
Total bonding to P		4.84	Total bonding to O(5)		1.11

TABLE II. — *Drugmanite : bond lengths (d) and strengths (s).*

La drugmanite : longueurs (d) et forces (s) de liaison.

THE STRUCTURE

The projections of the structure along the [010] and [001] directions are shown as STRUPLO84 diagrams (Fischer, 1985) in figure 1 ; the main features are chains of alternating $(Fe,Al)O_6$ octahedra and pairs of PO_4 tetrahedra. The Pb^{2+} ions lie between the chains so that each one is surrounded by 10 oxygens at distances ranging from 2.28Å to 3.45Å. No other oxygen is less than 3.77Å from a Pb atom. The Pb coordination polyhedron can be described either as a trigonal prism capped on two prism faces by a single oxygen atom and on the third by two oxygen atoms or, if all atoms more than 3.4Å from the Pb atoms are ignored, as a distorted square antiprism. From the structural formula, it is evident that one hydrogen atom must lie at a special position. In view of the heavy atom content, it was impossible to locate hydrogen atoms directly. It is nevertheless reasonable to place one at the symmetry centre at 1/2, 0, 1/2 between two O(1) atoms which are only 2.40Å apart.

Bond strengths (s) have been calculated from the interatomic distances (r) given in table II

	U_{eq} = 1/3 $\Sigma u_{ij}a^*_i a^*_j \underline{a}_i \cdot \underline{a}_j$			
Atom	10000x	10000y	10000z	1000U_{eq}(Å²)
Pb	3140(1)	964(1)	-83(2)	133(2)
Fe,Al	5000(0)	5000(0)	0(0)	53(10)
P	6044(5)	2567(7)	4839(12)	92(15)
O1	5729(14)	841(20)	6241(34)	167(39)
O2	5049(13)	3009(20)	2706(32)	133(50)
O3	7294(14)	2433(22)	3410(34)	181(49)
O4	6154(13)	3851(20)	7364(35)	154(46)
O5	3526(13)	4066(20)	8327(31)	119(43)

TABLE I. — *Drugmanite : atomic parameters with estimated standard deviations.*
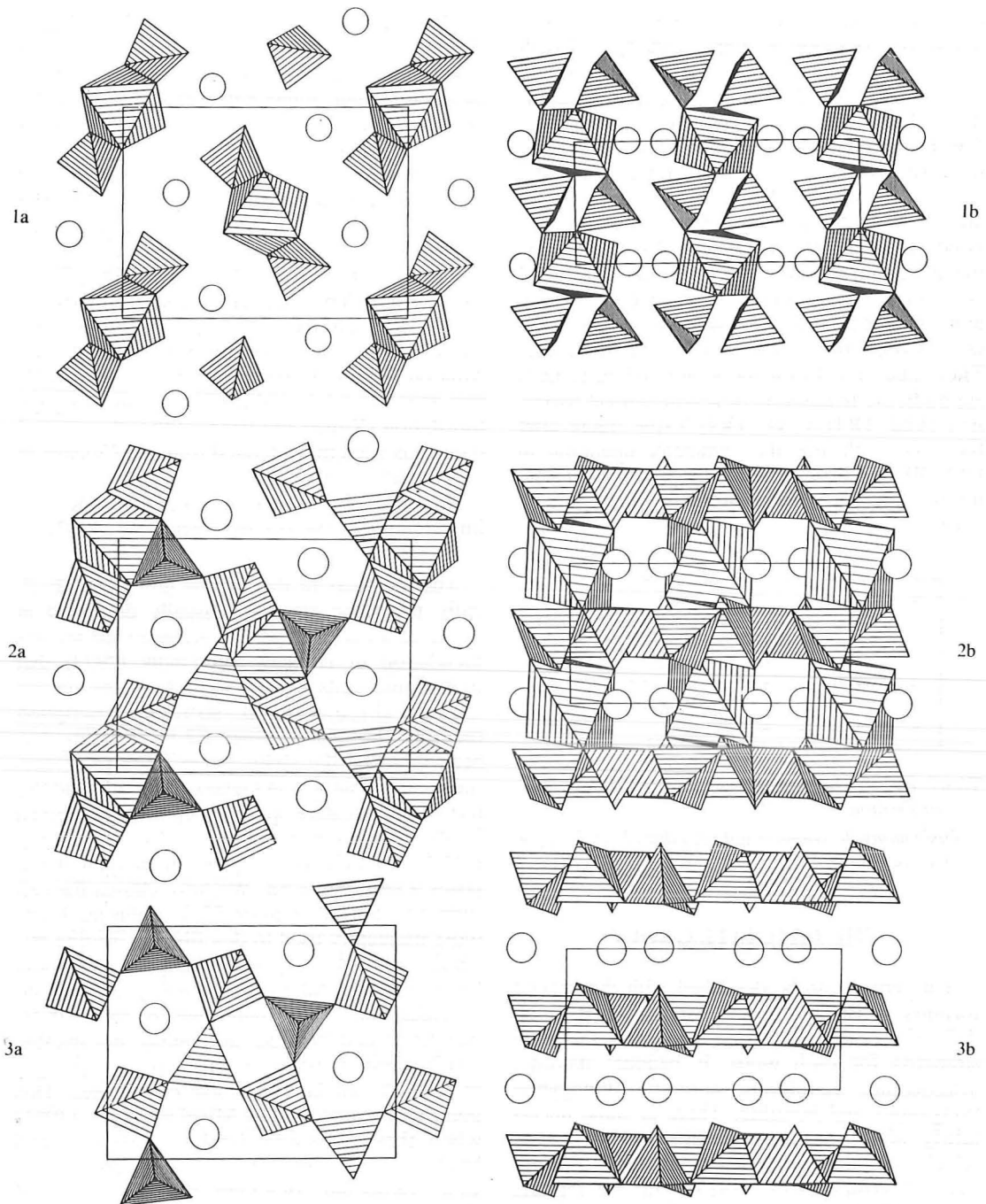
La drugmanite : paramètres atomiques avec écarts-type.

FIG. 1. 2. 3. — *The structure of drugmanite (1), homilite (2) and datolite (3)* projected along the [001] direction with *b* vertical and *a*sinβ horizontal (a) and along the [010] direction with *c* vertical and *a* horizontal (b). Circles denote heavy atoms A.

Les structures de la drugmanite (1), l'homilite (2) et la datolite (3) projetées dans les directions [001] avec *b* vertical et *a* sinβ horizontal (a) et [010] avec *c* vertical et *a* horizontal (b). Les atomes lourds (A) sont représentés par des cercles.

using the expression : $s = \exp((r_0 - r)/B)$, where B is 0.37 and r_0 is the single-bond length for the atoms involved as given by Brown and Altermatt (1985). This expression leads to slightly higher strengths for the shorter bonds and lower strengths for the longer bonds than does the expression $s = (r_0/r)^n$ of Brown and Wu (1976). In table II bonds involving hydrogen atoms are excluded from the calculation of total bond strengths. It can be seen that O(5) needs the remaining hydrogen to bring its total bond strength to approximately 2. The only oxygen atom geometrically well-placed to accept a hydrogen bond from O(5) is O(3).9, 2.91Å away. The value of 1.49 for the total bonding to O(1) supports the hypothesis of a symmetrical hydrogen bond, O(1).0...H...O(1).5 (the figure after the point indicates the symmetry operation in table III which must be applied to the coordinates in table I to give those of the atom concerned).

0	x,	y,	z	7	0.5+x, 0.5-y,	1+z
1	x,	y,	1+z	8	0.5+x, 0.5-y,	z
2	x,	y,	-1+z	9	-0.5+x, 0.5-y,	z
3	1-x,	1-y,	1-z	10	-0.5+x, 0.5-y,	-1+z
4	1-x,	1-y,	-z	11	0.5-x, 0.5+y,	1-z
5	1-x,	-y,	1-z	12	0.5-x, -0.5+y,	1-z
6	1-x,	-y,	-z			

TABLE III. — *Symmetry operations used in describing coordination.*

Opérations de symétrie utilisées dans la description de la coordination.

THE DATOLITE GROUP

This group can be described with the general formula $A_2BCD_2(XO_4)_2Y_2$ where A, B... are defined in table IV which also gives the bond strengths for each atom. It includes datolite, drugmanite, gadolinite, herderite, hingganite (xinganite) and homilite. There is some uncertainly about the composition of hingganite which was originally described as hingganite-(Yb) (Voloshin *et al.*, 1983) with the formula $(Yb_{0.45} Y_{0.20} Er_{0.11} Dy_{0.03} Lu_{0.06} Tm_{0.04} Ca_{0.05})BeSiO_4OH$ from microprobe analysis. These authors, without quoting the source of their information, give for hingganite the following analysis $(Y_{0.51} Yb_{0.20} Er_{0.08} Dy_{0.03} Gd_{0.01} Lu_{0.02} Tm_{0.022} Ca_{0.10})^- (Fe_{0.04}Al_{0.01})BeSiO_4OH$ (we omit elements present as less than 1 atom percent of Si). Yakubovich *et al.*, (1983), in describing the crystal structure of what was apparently the same specimen with identical unit cell dimensions, give the composition $(Yb_{0.23}Y_{0.51}Er_{0.09}Dy_{0.04}Ca_{0.13}) Fe_{0.065}BeSiO_4OH$ (as determined by ''X-ray spectral analysis''). This composition is closer to that of hingganite than hingganite-(Yb). The crystal structure of a hingganite with the composition $(Y_{0.33} Ce_{0.19} Nd_{0.10} La_{0.05} Fe^{3+}_{0.05} Dy_{0.05} Gd_{0.04} Ca_{0.04} K_{0.04} Sm_{0.04} Na_{0.03} Fe^{2+}_{0.03} Pr_{0.02}Er_{0.02} Tb_{0.01} Ho_{0.01} Yb_{0.01})_{1.06} (Be_{0.97} Al_{0.03})_{1.00} (Si_{0.98} Al_{0.05})_{1.03}O_{4.00}[(OH)_{0.77}O_{0.23}]_{1.00}$ as approved by the I.M.A. Commission on New Minerals and Mineral Names (J. Moreau, pers. comm., 1987) has recently been published ; in the English translation (Ximen and Peng, 1986), the mineral name has been transliterated from the Chinese as ''xinganite'' instead of ''hingganite''. This compound should in fact be described as hingganite-(Y) (Nickel and Mandarino, 1987).

The members of the datolite group have basically the same structure, usually described in terms of a cell with $a>c$ (following the recommendation of Donnay and Ondik (1973) that monoclinic cells should have b as the unique axis and also $a>c$ and $\beta>90°$) ; this description requires the space group $P2_1/a$. Datolite has been assigned the space group $P2_1/c$ as recommended by Parthé and Gelato (1984) who advise use of the standard space group setting as given in the International Tables for Crystallography (1983) ; this choice of space group symbol imposes a cell with $c>a$. We have chosen the cell with $a>c$ and space group $P2_1/a$ as this has been most frequently used to describe the datolite minerals. With β nearly 90°, ambiguities can only be resolved by taking the atomic positions into consideration. Those published for drugmanite, gadolinite and homilite are similar but datolite and herderite must be assigned an acute β angle in order to obtain comparable coordinates. This point was overlooked by Miyakawi *et al.* (1984) when they compared datolite, gadolinite and herderite since only bond lengths and angles were considered ; these are scalar quantities and therefore independent of the cell description. The transformations which must be applied to the published cell parameters are (0 0 1 / 0 1 0 / − 1 0 0) for datolite and (1 0 0 / 0 −1 0 / 0 0 −1) with a shift of origin to 1/2 1/2 0 for herderite. Transformed cell parameters are given in

Mineral	A	B	C	D	X	O1	O2	O3	O4	Y
Drugmanite	Pb	Fe,Al	H	-	P					OH
	2.08	2.98	(1)	-	4.83	1.48	1.85	1.94	2.00	1.12
Datolite	Ca	-	-	B	Si					OH
	2.13	-	-	2.98	3.93	2.02	1.96	2.00	1.98	1.09
Gadolinite	Y	Fe	-	Be	Si					O
	2.68	1.87	-	2.02	3.91	1.89	1.80	1.91	1.81	1.20
Herderite	Ca	-	-	Be	P					OH,F
	2.06	-	-	2.08	4.93	2.00	2.01	1.97	2.01	1.08
Hingganite -(Y)	Y,Ce	-	-	Be	Si					OH
	2.73	-	-	2.08	3.94	1.82	1.90	2.07	1.87	1.10
Hingganite -(Yb)	Y,REE	(Fe)	-	Be	Si					OH
	2.89	1.74	-	2.50	3.88	1.98	2.16	1.94	2.12	1.55
Homilite	Ca	Fe	-	B	Si					O
	2.15	2.00	-	2.81	3.91	1.99	2.06	1.97	2.16	1.69

TABLE IV. — *The datolite group.*
Le groupe de la datolite.

table V which differs from table 7 of Miyawaki *et al.* in the β values for datolite and herderite. The atomic coordinates, recalculated on the basis of the new cell, are reported in table VI.

The datolite group can be divided into three subgroups :

— drugmanite, in which there are chains of octahedra and tetrahedra parallel to the c-axis (Figure 1) and linked by symmetrical O...H...O bonds across the symmetry centre at 1/2 0 1/2. In the other structures, the orientation of the XO_4 tetrahedra is such that the closest oxygen-oxygen inter-chain contact (across the symmetry centre at 1/2 0 1/2) ranges from 2.69 to 2.94Å compared with 2.40Å in drugmanite.

— gadolinite and homilite, in which the chains are linked by BeO_4 or BO_4 tetrahedra to form a three-dimensional network (Figure 2) and

— datolite, herderite and hingganite, of which the first two have no octahedral atoms at a symmetry centre and the last, which has a negligible occupation of this site. Here, the two types of tetrahedra form sheets perpendicular to the c-axis which are linked only by the large eight-coordinated cation (Figure 3). In figure 1a, 2a and 3a the XO_4 tetrahedra are those with two faces visible while the DO_4 tetrahedra in figures 2a and 3a have either a single face or three faces visible. Drugmanite differs from the other minerals of the datolite group that it has only one

		a(Å)	b(Å)	c(Å)	β(°)	V(Å³)
Drugmanite	Pb_2 (Fe,Al)H □ $(PO_4)_2(OH)_2$	11.111(5)	7.896(5)	4.463(3)	90.41(3)	391.5
Datolite	Ca_2 □ □$B_2(SiO_4)_2(OH)_2$	9.636(8)	7.608(4)	4.832(4)	89.60(7)	354.2
Gadolinite	REE_2 Fe □$Be_2(SiO_4)_2O_2$	10.000(2)	7.565(2)	4.768(1)	90.31(2)	360.7
Herderite	Ca_2 □ □$Be_2(PO_4)_2(OH)_2$	9.879(2)	7.661(1)	4.804(1)	89.98(2)	363.6
Hingganite-(Y)	Y_2 □ □$Be_2(SiO_4)_2(OH)_2$	9.930(6)	7.766(7)	4.768(3)	90.17(1)	367.9
Hingganite-(Yb)	Y_2 (Fe) □$Be_2(SiO_4)_2(OH)_2$	9.888(5)	7.607(3)	4.740(2)	90.45(4)	356.5
Homilite	Ca_2 Fe □$B_2(SiO_4)_2O_2$	9.786(2)	7.621(2)	4.776(1)	90.61(2)	356.1

TABLE V. — *Cell parameters of datolite group minerals referred to space group $P2_1/a$.*
Paramètres de la maille des minéraux du groupe de la datolite rapportés au groupe spatial $P2_1/a$.

	element	drugman. Pb	datol. Ca	gadolin. REE	herder. Ca	hing.-Y Y	hing.-Yb Y	homil. Ca
A	x	.31395(3)	.33611(4)	.32854(3)	.3309(3)	.3312(2)	.33301(9)	.33389(3)
	y	.09643(3)	.10618(5)	.10828(3)	.1116(3)	.1108(3)	.1089(1)	.10224(5)
	z	−.00835(3)	.00824(8)	.00013(3)	.0026(3)	.0010(4)	−.0013(2)	.00685(7)
	element	Fe,Al	-	Fe	-	-	Fe	Fe
B	x	.50000	-	.50000	-	-	(.50000)	.50000
	y	.50000	-	.50000	-	-	(.50000)	.50000
	z	.00000	-	.00000	-	-	(.00000)	.00000
	element	H	-	-	-	-	-	-
C	x	.50000	-	-	-	-	-	-
	y	.00000	-	-	-	-	-	-
	z	.50000	-	-	-	-	-	-
	element	-	B	Be	Be	Be	Be	B
D	x	-	.3415(2)	.3355(3)	.3398(4)	.335(4)	.335(1)	.3382(2)
	y	-	.4107(3)	.4143(4)	.4141(5)	.447(7)	.413(2)	.4081(2)
	z	-	.4317(4)	.4642(6)	.4630(9)	.415(5)	.448(3)	.4596(4)
	element	P	Si	Si	P	Si	Si	Si
X	x	.6044(5)	.58440(5)	.58722(6)	.5815(1)	.5806(12)	.5791(3)	.58380(5)
	y	.2567(7)	.23374(7)	.22150(9)	.2290(1)	.2258(12)	.2237(4)	.23243(6)
	z	.4838(12)	.5312(1)	.5192(1)	.5292(1)	.5152(21)	.5190(7)	.5305(1)
O1	x	.573(2)	.5376(2)	.5303(2)	.5396(2)	.536(3)	.5332(8)	.5359(1)
	y	.085(2)	.0992(2)	.0869(2)	.1012(3)	.088(4)	.088(1)	.1009(2)
	z	.624(4)	.7599(3)	.7607(4)	.7534(5)	.759(5)	.764(2)	.7625(3)
O2	x	.505(1)	.4575(1)	.4518(2)	.4585(2)	.452(3)	.4499(8)	.4553(1)
	y	.301(2)	.3010(2)	.2871(2)	.2835(3)	.288(4)	.284(1)	.2991(2)
	z	.271(3)	.3306(3)	.3248(4)	.3479(5)	.327(5)	.326(2)	.3283(2)
O3	x	.729(1)	.7104(1)	.6954(2)	.6935(2)	.694(3)	.6950(8)	.7090(1)
	y	.243(2)	.1654(2)	.1524(3)	.1555(3)	.150(3)	.153(1)	.1648(2)
	z	.341(4)	.3245(3)	.3089(4)	.3331(5)	.308(5)	.300(2)	.3304(3)
O4	x	.615(1)	.6460(1)	.6419(2)	.6428(2)	.148(2)	.6485(8)	.6439(1)
	y	.385(2)	.4124(2)	.3935(2)	.3941(4)	.492(4)	.391(1)	.4137(2)
	z	.737(4)	.6848(3)	.6847(4)	.6695(5)	.684(5)	.687(2)	.6828(3)
O5	x	.353(2)	.3363(2)	.3329(2)	.3332(2)	.330(3)	.3305(8)	.3411(1)
	y	.407(2)	.4137(2)	.4126(3)	.4123(3)	.413(3)	.412(1)	.4130(2)
	z	.833(4)	.7412(3)	.7979(4)	.7961(5)	.708(5)	.786(2)	.7583(3)
H(O5)	x	?	.405(5)	-	?	.43(5)	?	-
	y	?	.444(7)	-	?	.48(7)	?	-
	z	?	.80(1)	-	?	.80(12)	?	-

TABLE VI. — *Comparison of atomic coordinates in the datolite group.*
Comparaison des coordonnées atomiques dans le groupe de la datolite.

type of tetrahedral atom and its cell is 10 % larger. A correlation between these two features can be seen from a study of the tetrahedron formed by O(2).0, O(3).9, O(4).3 and O(5).0 around the second tetrahedral atom. The average O-O distances are 2.42Å and 2.45Å for datolite and homilite (BO_4), 2.66Å, 2.65Å and 2.69Å for gadolinite, herderite and hingganite (BeO_4) and 3.10Å for drugmanite, where there is no central atom to pull the oxygens closer together.

ACKNOWLEDGEMENTS

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