

THE CRYSTAL STRUCTURE OF ROSELITE

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ABSTRACT

The crystal structure of roselite, $\text{Ca}_2(\text{Mg}_{0.485}\text{Co}_{0.515})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, has been refined in the space group $P2_1/c$ (a 5.801(1), b 12.898(3), c 5.617(1) Å, β 107.42(2)°; $Z=2$), using three-dimensional counter-collected single-crystal X-ray data; the final R index for 1194 observed reflections is 5.8%. Comparison of the cell dimensions obtained in this study with the axial ratios obtained from morphological studies (Peacock 1936) shows that the morphological cell was B -centred. Conversely, the cell derived in earlier X-ray studies (Wolfe 1940) is a half-cell in the B -centred setting. Re-examination of the isostructural mineral brandtite, $\text{Ca}_2\text{Mn}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, showed that the cell derived in previous studies was also a half cell; least-squares refinement of the powder diffraction pattern gave a 5.899(2), b 12.968(4), c 5.684(1) Å, β 108.05(2)°, and single-crystal precession photographs confirmed the space group $P2_1/c$.

Roselite is isostructural with kröhnkite, $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Hawthorne & Ferguson 1975b). The structure is characterized by isolated Mg/Co octahedra that are linked by corner sharing with As tetrahedra to form chains parallel to the c axis. These chains are linked together by the large Ca cations and hydrogen bonding. Two structure types exist in the minerals of the group $\text{Ca}_2\text{M}^{2+}(\text{X}^{5+}\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, the monoclinic roselite structure and the triclinic collinsite, $\text{Ca}_2\text{Mg}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, structure. Identical chains exist in both structures but the attitude of adjacent chains is slightly different, leading to changes in the Ca coordination and hydrogen bonding arrangements.

SOMMAIRE

La structure cristalline de la roséélite, $\text{Ca}_2(\text{Mg}_{0.485}\text{Co}_{0.515})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, a été affinée dans $P2_1/c$ (a 5.801(1), b 12.898(3), c 5.617(1) Å, β 107.42(2)°; $Z=2$) à l'aide des données tridimensionnelles des rayons X, obtenues sur diffractomètre à compteur avec cristal unique. Le résidu final pour les 1194 réflexions est $R=5.8\%$. En comparant les dimensions de la maille ci-dessus aux rapports d'axes morphologiques (Peacock 1936), on remarque que la maille morphologique était à face B centrée. Par contre, la première maille obtenue aux rayons X (Wolfe 1940) n'était qu'une demi-maille B . Et la brandtite, $\text{Ca}_2\text{Mn}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, isotype de la roséélite, avait, elle aussi, été rapportée à une demi-maille; l'affinement du diagramme de poudre par moindres carrés donne la maille: a 5.899(2), b

12.968(4), c 5.684(1) Å, β 108.05(2)°, et les diagrammes de précession confirment le groupe $P2_1/c$.

La roséélite est isotype de la kröhnkite, $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Hawthorne & Ferguson 1975b). La structure est caractérisée par des octaèdres isolés Mg/Co, liés par les sommets aux tétraèdres As pour former des chaînes parallèles à l'axe c . Ces chaînes sont reliées par les gros cations Ca et des ponts hydrogène. On trouve 2 types structuraux parmi les minéraux du groupe $\text{Ca}_2\text{M}^{2+}(\text{X}^{5+}\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, celui de la roséélite, monoclinique, et celui de la collinsite, $\text{Ca}_2\text{Mg}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, triclinique. Les deux types possèdent des chaînes identiques, mais l'orientation relative des chaînes voisines diffère quelque peu, ce qui entraîne des changements dans la coordination du Ca et dans l'agencement des ponts hydrogène.

(Traduit par la Rédaction)

INTRODUCTION

Roselite is a pink hydrated arsenate, $\text{Ca}_2(\text{Co}, \text{Mg})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, that occurs with chalcedony and drusy quartz in cavities in metalliferous quartzose veins. There has been a considerable amount of work on the crystallography of roselite and its isomorph, brandtite ($\text{Ca}_2\text{Mn}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$), and each new study has come to a different conclusion; the present study is no exception. Roselite was initially classed as orthorhombic (Levy 1824) until Schrauf (1873) concluded that it was triclinic, pseudo-orthorhombic. Subsequently, Lindstrom (1918) proposed that brandtite was triclinic and isomorphous with roselite. Aminoff (1919) later proposed that brandtite was monoclinic holohedral with the axial ratios given in Table 1. An extremely detailed study by Peacock (1936) showed roselite to be monoclinic holohedral with axial ratios similar to those earlier established for brandtite (Table 1). Single-crystal X-ray photographs (Wolfe 1940) confirmed the monoclinic symmetry of both species but indicated that the morphological studies had resulted in a double cell. These results were apparently confirmed for brandtite by Dahlman (1951), who solved the structures of brandtite and kröhnkite ($\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$); the cell dimensions obtained by Wolfe (1940) and Dahlman (1951) are given in Table 1. As part of a study on the stereochemistry of the $(\text{As}^{5+}\text{O}_4)^{3-}$ group (Hawthorne 1976a,b), we de-

cided to refine the structure of roselite; however, in view of the results obtained, the study was also extended to include brandtite.

TABLE 1. AXIAL RATIOS AND CELL DIMENSIONS (Å) FOR ROSELITE, BRANDTITE AND KROHNKITE

<i>a</i>	<i>b</i>	<i>c</i>	β	Space Group	Reference
<u>Roselite</u>					
0.8780	1.0	0.4398	100.9°	Monoc.	Peacock (1936)
5.60 ¹ Å	12.80 ¹ Å	5.60	100.8°	$P2_1/a$	Wolfe (1940)
5.616(2)	12.893(4)	11.277(3)	101.01(3)°	$B2_1/a$	This study ¹
5.799	12.893	5.616	107.37°	$P2_1/a$	This study ²
5.801(1)	12.898(3)	5.617(1)	107.42(2)°	$P2_1/a$	This study ³
<u>Brandtite</u>					
0.8720	1.0	0.4475	99.5°	Monoc.	Aminoff (1919)
5.65	12.80	5.65	99.5°	$P2_1/a$	Dahlman (1951)
5.664	12.968	11.399	100.24°	$B2_1/a$	This study ⁴
5.899(2)	12.968(4)	5.684(1)	108.05(2)°	$P2_1/a$	This study ³
<u>Krohnkite</u>					
0.4386	1.0	0.4357	108.5°	Monoc.	Palache (1936)
5.807(1)	12.656(2)	5.517(1)	108.32(1)°	$P2_1/a$	Hawthorne & Ferguson (1975b)

¹Single-crystal diffractometer results; ²transformed from *B*-centred to primitive cell; ³from least-squares refinement of powder patterns;

⁴transformed from primitive cell to *B*-centred cell.

TABLE 2. MISCELLANEOUS INFORMATION FOR ROSELITE

Partial Analysis: MgO = 4.42, CoO = 8.71 wt. %			
Unit formula = $\text{Ca}_2(\text{Mg}_{0.485}\text{Co}_{0.515})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$			
	$B2_1/a$	$P2_1/c$	
<i>a</i>	5.616(2)Å	5.799(2)Å	
<i>b</i>	12.893(4)	12.893(4)	
<i>c</i>	11.277(3)	5.616(2)	
β	101.01(3)°	107.37(3)°	
Space Group	$B2_1/a$	$P2_1/c$	
<i>V</i>	800.9Å ³	400.5Å ³	
<i>Z</i>	4	2	

<i>D</i> _{calc}	3.617	No. of $ F_{\text{obs}} $	1521
Crystal Size	0.15 mm	No. of $ F_{\text{obs}} > 4\sigma$	1194
μ_R	0.84	Final <i>R</i> (observed)	5.8%
Rad/Mon	Mo/C	Final <i>R</i> (all data)	6.7%
		Final <i>R</i> _w (observed)	6.7%
		Final <i>R</i> _w (all data)	7.3%

$$R = \frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)}{\sum |F_{\text{obs}}|}$$

$$R_w = \frac{\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum w|F_{\text{obs}}|^2}^{1/2}, w=1$$

$$\text{Temp. factor form used: } \exp \left[- \sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij} \right]$$

EXPERIMENTAL

The crystals used in this investigation are from Schneeberg, Germany. A partial chemical analysis was performed and the results are given in Table 2; unit-cell contents were calculated assuming the formula $\text{Ca}_2(\text{Mg,Co})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ with the Mg,Co ratio derived from the chemical analysis.

Single-crystal X-ray precession photographs confirmed the monoclinic symmetry established by earlier studies. However, the unit cell appeared to be twice the volume assigned by Wolfe (1940), with axial ratios in agreement with the morphological work of Peacock (1936). The following systematic extinctions were observed: *hkl*, $h+l = 2n+1$; *h00*, $h = 2n+1$; *0k0*, $k = 2n+1$; *00l*, $l = 2n+1$; this is compatible with the space groups $B2_1/a$ and $B2_1/c$. As indicated by the *B*-centring, an alternative primitive cell of half the volume could have been chosen; however, the *B*-centred cell was retained because of the probable relationship between the structures of roselite and brandtite (Dahlman 1951). Unit-cell parameters were determined from least-squares refinement of fifteen intense reflections aligned automatically on a four-circle diffractometer; the results are given in Table 1. As a check on these values, the powder pattern of roselite was recorded using a Phillips powder diffractometer operating at $1/4^\circ 2\theta/\text{min}$ and using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{Å}$); least-squares refinement subsequently confirmed the single-crystal diffractometer values.

The crystal used in the collection of the intensity data was an irregular equidimensional fragment $\sim 0.15\text{mm}$ in diameter. A total of 1521 intensities was collected over one asymmetric unit out to $2\theta(\text{MoK}\alpha)$ 65° according to the experimental procedure of Hawthorne & Ferguson (1975a). One standard reflection was examined every 50 reflections to check for constancy of crystal alignment; no significant change was noted during the data collection. The data were corrected for absorption, Lorentz, polarization and background effects and converted to structure factors. A reflection was considered as observed if its magnitude exceeded that of four standard deviations based on counting statistics; application of this criterion resulted in 1194 observed reflections.

STRUCTURE SOLUTION AND REFINEMENT

Analytic scattering curves for neutral atoms were taken from Cromer & Mann (1968) with anomalous dispersion coefficients from Cromer & Liberman (1970). Crystal-structure refinement was carried out using the least-squares

TABLE 3. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS IN ROSELITE¹

	x	y	z	$B_{\text{equiv.}} (\text{\AA}^2)$
Mg/Co	0 0	0 0	0 0	0.78(3)
Ca	0.9498(2) 0.5618	0.1216(1) 0.1216	0.7191(1) 0.2307	0.72(2)
As	0.45883(13) 0.21612	0.12035(6) 0.12035	0.89194(7) 0.56689	0.45(2)
0(1)	0.0264(11) 0.9422	0.1739(5) 0.1739	0.5289(5) 0.4974	0.98(8)
0(2)	0.6979(10) 0.2810	0.0531(5) 0.0531	0.8595(5) 0.8384	0.83(8)
0(3)	0.2239(9) 0.2368	0.0352(5) 0.0352	0.8816(5) 0.3423	0.89(8)
0(4)	0.3528(9) 0.4382	0.2060(5) 0.2060	0.7809(5) 0.5719	0.83(8)
0(w)	0.5570(10) 0.8154	0.1386(4) 0.1386	0.5923(5) 0.9647	0.85(8)

¹Upper values are for $B_{21/a}$; lower values are for $P_{2_1/c}$.

program RFINE (Finger 1969); quoted R -indices are of the form given in Table 2 and are expressed as percentages.

Initially, we tried to derive a structure model by assuming that roselite was a modification of the brandtite structure (Dahlgren 1951), but this was unsuccessful. Arsenic and calcium positions were subsequently derived from a three-dimensional Patterson map, and yielded an R -index of 35% in the space group $B_{21/a}$. Difference fourier maps located the positions of the remaining Mg/Co and oxygen atoms, and these were inserted into the refinement, yielding an R -index of 11.6%. Full-matrix least-squares refinement, gradually increasing the number of variables, resulted in convergence at R - and R_w -indices of 7.1 and 7.4% respectively for an isotropic thermal model. At this stage, temperature factors were converted

TABLE 4. ANISOTROPIC TEMPERATURE FACTORS FOR ROSELITE*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg/Co	467(56)	137(11)	167(14)	0	4(22)	0
Ca	414(36)	139(7)	139(9)	-37(14)	0(14)	1(7)
As	184(20)	93(4)	104(5)	-10(5)	31(7)	-1(4)
0(1)	1021(79)	146(31)	138(39)	-33(58)	18(67)	-16(28)
0(2)	541(151)	144(29)	189(40)	103(53)	108(61)	-4(28)
0(3)	583(153)	167(31)	173(39)	-106(56)	52(62)	12(28)
0(4)	355(143)	152(29)	204(40)	-2(52)	-4(61)	47(28)
0(w)	626(151)	137(32)	182(39)	-32(54)	81(64)	-15(27)

* all values $\times 10^5$.

TABLE 5. SELECTED INTERATOMIC DISTANCES AND ANGLES FOR ROSELITE

As-0(1)a	1.668(6) \AA		
As-0(2)	1.696(6)	Ca-0(1)d	2.365(6) \AA
As-0(3)	1.703(6)	Ca-0(2)	2.479(6)
As-0(4)	1.689(6)	Ca-0(2)e	2.502(6)
$\langle \text{As-O} \rangle$	1.689	Ca-0(3)d	2.427(6)
Mg/Co-0(2)b	2.197(6)	Ca-0(4)d	2.487(6)
Mg/Co-0(3)c	2.056(6)	Ca-0(4)f	2.421(6)
Mg/Co-0(w)	2.060(6)	Ca-0(w)	2.399(6)
$\langle \text{Mg/Co-O} \rangle$	2.104	$\langle \text{Ca-O} \rangle$	2.440
<u>As tetrahedron</u>			
0(1)a-0(2)	2.775(8)	0(1)a-As-0(2)	111.2(3) ^o
0(1)a-0(3)	2.785(8)	0(1)a-As-0(3)	111.5(3)
0(1)a-0(4)	2.811(8)	0(1)a-As-0(4)	113.7(3)
0(2)-0(3)	2.730(8)	0(2)-As-0(3)	106.9(3)
0(2)-0(4)	2.787(8)	0(2)-As-0(4)	110.8(3)
0(3)-0(4)	2.640(8)	0(3)-As-0(4)	102.2(3)
$\langle \text{O-O} \rangle$	2.755	$\langle \text{O-As-O} \rangle$	109.4
<u>Mg/Co octahedron</u>			
0(2)g-0(3)h	2.926(8)	0(2)g-Mg/Co-0(3)h	87.0(2) ^o
0(2)g-0(3)i	3.085(8)	0(2)g-Mg/Co-0(3)i	93.0(2)
0(2)g-0(w)j	3.186(8)	0(2)g-Mg/Co-0(w)j	96.8(2)
0(2)g-0(w)k	2.828(8)	0(2)g-Mg/Co-0(w)k	83.2(2)
0(3)h-0(w)j	3.024(8)	0(3)h-Mg/Co-0(w)j	94.7(2)
0(3)h-0(w)k	2.786(8)	0(3)h-Mg/Co-0(w)k	85.3(2)
$\langle \text{O-O} \rangle$	2.973	$\langle \text{O-Mg/Co-O} \rangle$	90.0
<u>Ca polyhedron</u>			
0(1)d-0(2)e	3.511(8)	0(1)d-Ca-0(2)e	92.3(2)
0(1)d-0(4)d	3.102(8)	0(1)d-Ca-0(4)d	79.4(2)
0(1)d-0(4)f	3.533(8)	0(1)d-Ca-0(4)f	95.2(2)
0(1)d-0(w)	2.896(9)	0(1)d-Ca-0(w)	74.9(2)
0(2)-0(2)e	2.978(11)	0(2)-Ca-0(2)e	73.4(2)
0(2)-0(3)	2.926(8)	0(2)-Ca-0(3)	73.2(2)
0(2)-0(4)f	3.387(9)	0(2)-Ca-0(4)f	87.5(2)
0(2)-0(w)	3.164(8)	0(2)-Ca-0(w)	80.9(2)
0(2)e-0(3)	3.442(8)	0(2)e-Ca-0(3)	88.6(2)
0(2)e-0(4)d	4.619(9)	0(2)e-Ca-0(4)d	135.6(2)
0(2)e-0(w)	2.828(8)	0(2)e-Ca-0(w)	70.5(2)
0(3)-0(4)d	2.640(8)	0(3)-Ca-0(4)d	65.0(2)
0(3)-0(4)f	3.981(10)	0(3)-Ca-0(4)f	110.4(2)
0(4)d-0(4)f	3.029(5)	0(4)d-Ca-0(4)f	76.2(2)
0(4)f-0(w)	3.154(8)	0(4)f-Ca-0(w)	81.7(2)
$\langle \text{O-O} \rangle$	3.279	$\langle \text{O-Ca-O} \rangle$	85.7

Equivalent positions: a=1/2+x, y, 1/2+z; b=1-x, -y, 1-z; c=x, y, -z; d=1+x, y, z; e=3/2-x, -y, 3/2-z; f=1/2+x, 1/2-y, z; g=x-1, y, z-1; h=x, y, z-1; i=x, -y, 1-z; j=x-1/2, y, z-1/2; k=1/2-x, -y, 1/2-z.

to anisotropic of the form given in Table 1 and a correction for isotropic extinction (Zachariasen 1968) was introduced into the refinement. Several cycles of least-squares refinement, gradually increasing the number of variables, resulted in convergence at R - and R_w -indices of 5.8 and 6.7% (observed reflections) and 6.7 and 7.3% (all data)¹. Final atomic positions and equivalent isotropic temperature factors are presented in Table 3 and anisotropic temperature factors in Table 4. Interatomic distances and angles were calculated with the program ERRORS (L. W. Finger, pers. comm.) and are presented in Table 5.

¹Structure factors may be obtained, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2.

DISCUSSION

Examination of the roselite structure derived in this study revealed that it is isostructural with brandtite and kröhnkite. In the *B*-centred cell, the corner-linked chains of octahedra and tetrahedra extend along *a*; however, if the cell is transformed to the primitive orientation, these chains extend along *c* as in kröhnkite (Hawthorne & Ferguson 1975b). Table 1 also shows the cell dimensions of roselite in the $P2_1/c$ orientation. Their similarity to those of kröhnkite is very marked, but the significant differences from the cell dimensions of brandtite (Dahlman 1951) prompted us to re-examine this mineral. Single-crystal precession photographs of brandtite from the Harstig mine, Varmland, Sweden (R.O.M. #M11913) exhibited monoclinic symmetry with systematic absences compatible with the space group $P2_1/c$; the cell dimensions were fairly similar to those of roselite in the $P2_1/c$ orientation. The powder pattern was recorded from this crystal using a Gandolfi camera and $\text{CuK}\alpha$ ($\lambda = 1.5418\text{\AA}$) radiation, and a least-squares refinement gave the cell dimensions reported in Table 1. Indexed powder patterns for roselite and brandtite ($P2_1/c$ orientation) are given in Table 6. The cell dimensions of brandtite are compatible with those of roselite and contrast with those reported by Wolfe (1940) and Dahlman (1951). Figure 1 shows the relationships among the cells derived here and those reported by previous workers. The morphological cell of Aminoff (1919) and Peacock (1936) corresponds to the *B*-centred cell initially used here (except for an interchange of the *a* and *c* axes); however, the cell dimensions reported by Wolfe (1940) and Dahlman (1951) do not conform to a proper cell, but seem to be related to the correct cell by the transformation $(-1\ 0\ -\frac{1}{2}/0\ -1\ 0/001)$. This is rather surprising in view of the fact that Dahlman (1951) arrived at the correct structure for brandtite. Examination of the structure factors for brandtite listed by Dahlman indicates that this 'half cell' cannot have been used in the indexing of the reflections, and we are unable to explain his results. Certainly the observed isomorphism between roselite, brandtite and kröhnkite is far more apparent from the correct cell dimensions reported in Table 1.

The structure of roselite is shown in Figure 2, where the hydrogen bonding has been assumed to be the same as that previously observed in kröhnkite (Hawthorne & Ferguson 1975b). Arsenic tetrahedra and Mg/Co octahedra are linked by corner-sharing to form chains that extend along the *c* axis. These chains are linked together

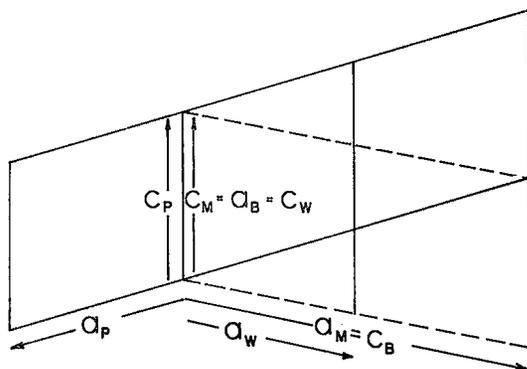


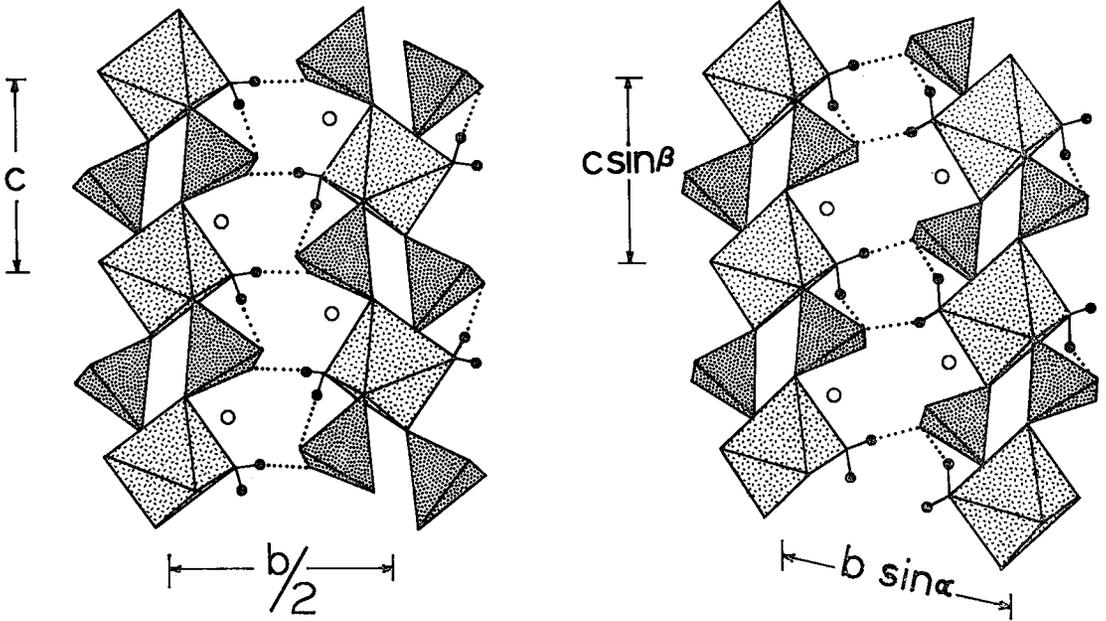
Fig. 1. The relationship between the different cells chosen for roselite. *P* = primitive cell, *B* = *B*-centred cell, *M* = morphological cell, *W* = 'cell' chosen by Wolfe (1940).

by Ca atoms coordinated by seven anions at distances between 2.36\AA and 2.50\AA , in an augmented trigonal prism arrangement (Fig. 3); additional inter-chain linkage is provided by hydrogen bonding which links the octahedron corners to the tetrahedron corners in the *b*-direction (Fig. 2). The weakness of the interchain linkage in the *b*-direction results in the {010} cleavage exhibited by the minerals with this structure.

TABLE 6. INDEXED POWDER PATTERNS FOR ROSELITE AND BRANDTITE.

h	k	ℓ	d _{obs}	d _{calc}	I _{obs}	h	k	ℓ	d _{obs}	d _{calc}	I _{obs}
Roselite ¹											
0	2	0	6.444	6.449	20	1	2	2	2.057	2.057	5
1	1	0	5.089	5.086	20	1	6	0	2.004	2.004	5
0	1	1	4.951	4.949	10	2	5	1	1.908	1.906	5
1	1	1	4.335	4.332	10	2	4	2	1.873	1.872	5
1	2	0	4.197	4.200	10	0	5	2	1.857	1.858	5
1	2	1	3.746	3.745	15	3	1	0	1.827	1.826	5
1	3	0	3.395	3.395	35	1	6	1	1.812	1.814	15
0	3	1	3.354	3.353	60	3	2	2	1.724	1.725	10
1	1	1	3.266	3.268	5	0	2	3	1.721	1.721	15
0	4	0	3.222	3.224	75	2	6	1	1.712	1.711	15
1	2	1	2.993	2.992	100	2	2	3	1.697	1.698	5
2	1	1	2.763	2.763	50	2	6	0	1.697	1.698	10
0	0	2	2.683	2.679	5	0	8	0	1.612	1.612	5
0	1	2	2.625	2.623	5	3	4	0	1.602	1.601	5
2	2	1	2.592	2.590	15	2	5	1	1.568	1.568	5
2	2	0	2.543	2.543	5	1	1	3	1.557	1.557	5
2	3	0	2.326	2.327	10	2	4	2	1.496	1.496	10
1	5	1	2.251	2.250	15	1	1	4	1.394	1.393	5
2	4	0	2.098	2.100	15	4	1	0	1.376	1.376	5
Brandtite ²											
0	2	0	6.482	6.484	25	1	4	1	2.345	2.347	5
1	1	0	5.151	5.148	20	1	5	1	2.271	2.269	15
0	1	1	4.993	4.988	10	2	1	1	2.192	2.192	5
1	1	1	4.403	4.405	10	1	1	2	2.154	2.154	5
1	2	0	4.237	4.242	10	2	4	1	2.154	2.153	5
1	2	1	3.790	3.796	20	1	4	2	2.118	2.118	5
1	3	0	3.424	3.424	30	1	2	2	2.072	2.070	5
0	3	1	3.373	3.376	55	1	3	2	1.949	1.949	5
1	1	1	3.294	3.290	5	2	5	1	1.926	1.927	5
0	4	0	3.241	3.242	70	2	4	2	1.899	1.898	10
1	3	1	3.178	3.176	5	1	1	3	1.874	1.875	5
1	2	1	3.010	3.012	100	3	0	2	1.824	1.824	5
1	0	2	2.799	2.797	5	1	6	1	1.824	1.824	5
1	1	2	2.736	2.734	5	0	2	3	1.735	1.736	10
0	0	2	2.700	2.702	5	3	3	0	1.716	1.716	5
0	1	2	2.642	2.645	5						

¹ powder diffractometer, ² Gandolfi camera



ROSELITE

COLLINSITE

FIG. 2. The structures of roselite (left) and collinsite (right). o = Ca, ● = H. Dotted lines denote hydrogen bonds.

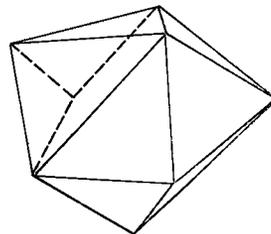
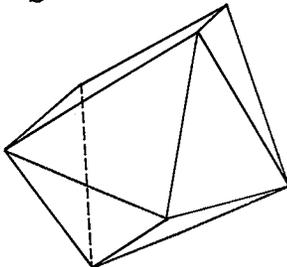
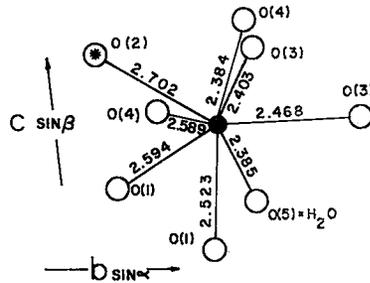
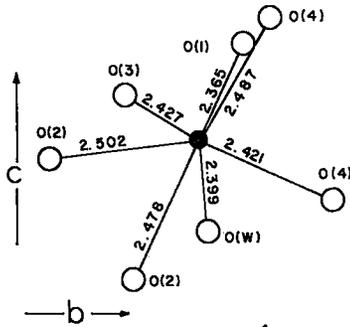


FIG. 3. The coordination of Ca in roselite (left) and collinsite (right). * indicates the additional anion that moves into the coordination sphere of Ca in collinsite.

Table 7 summarizes the compositional and crystallographic data of the minerals with the general formula $\text{Ca}_2\text{M}^{2+}(\text{X}^{5+}\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$. With the exception of collinsite, the cell dimensions presented here were derived from least-squares refinement of previously published powder patterns, as a variety of settings have been used for this group and it was thought desirable to standardize the setting to that used for collinsite by Brotherton *et al.* (1974). The similarity of the powder patterns indicates that only two structure types are present in this series, the monoclinic roselite-type structure and the triclinic collinsite-type structure. Figure 2 shows that the two structures are very similar. Both are characterized by isolated M^{2+} octahedra that are linked by corner sharing with $(\text{X}^{5+}\text{O}_4)^3-$ tetrahedra to form chains of the general stoichiometry $(\text{M}^{2+}\text{X}_2^{5+}\text{O}_8 \cdot 2\text{H}_2\text{O})^+$ extending parallel to the *c* axis. However, the different attitude of adjacent chains in the two structures leads to differences in the inter-chain linkage. In the collinsite structure (Fig. 2), the right-hand chain is rotated 180° with respect to the corresponding chain in the roselite structure; because the octahedra are tilted with respect to the chain axis, this produces a relative displacement of the water molecules in adjacent chains, leading to a slightly different arrangement of hydrogen bonds. In collinsite, the two distinct hydrogens both hydrogen bond to the same anion; in order to compensate for the decrease in bond strength around the remaining anions due to this arrangement of the hydrogen bonding, the coordination around the Ca cation changes slightly and an additional anion moves into the coordination sphere. The Ca coordination in both structures is shown in Figure 3; the anion arrangements in both structures are topologically very similar, the addi-

tional coordinating anion in the collinsite structure leading to a biaugmented trigonal prism arrangement.

Bond strength tables for roselite and collinsite are shown in Table 8, where the differences in the anion coordinations are immediately apparent. Whereas in the roselite structure, the O(1) and O(4) atoms are hydrogen bond acceptors, only the O(4) anion is an acceptor in the collinsite structure. In order to maintain the ideal bond strength sum around the 'deserted' anion [O(3) in the collinsite structure], an additional bond is formed with a neighboring Ca cation. However, this does not involve a change in cation coordination; although the anion arrangements around the Ca cation are topologically very similar in both structures, the difference in space group symmetry involves a re-labelling of the equivalent atoms in the coordination polyhedron, and it is this that effects the coordination changes around O(3) and O(4) in collinsite. The actual increase in Ca coordination in collinsite is caused by the occurrence of an additional bond to the O(2) anion [\equiv O(3) in roselite]. The Mg-O(3) bond is weaker than the corresponding Co/Mg-O(2) bond in roselite, due to the much stronger bonding with the water molecule in collinsite and hence the O(3) anion shifts to become part of the coordination sphere of another neighboring Ca cation.

Brotherton *et al.* (1974) remarked on the unusual nature of the Mg coordination in collinsite. Whereas in roselite and kröhnkite, the octahedron is strongly elongated along the O(2)-O(2) axis, it is extremely compressed along the O(5)-O(5) axis in collinsite. The reason for this is certainly not apparent from the bond strength table (Table 8); the bond strength sum around O(5) shows a large excess (0.281 v.u.) over the

TABLE 7. MINERALS OF THE $\text{Ca}_2\text{M}^{2+}(\text{X}^{5+}\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ GROUP

Name	Formula	a(Å)	b(Å)	c(Å)	α°	β°	γ°	Sp.Gr.	Ref.
Roselite	$\text{Ca}_2(\text{Co,Mg})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$	5.801(1)	12.898(3)	5.617(1)	90	107.42(2)	90	$\text{P2}_1/\text{c}$	1
Brandtite	$\text{Ca}_2\text{Mn}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$	5.899(2)	12.968(4)	5.684(1)	90	108.05(2)	90	$\text{P2}_1/\text{c}$	1
β -Roselite	$\text{Ca}_2(\text{Co,Mg})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$	5.918(9)	7.025(8)	5.600(6)	97.5(1)	108.9(1)	108.4(1)	$\text{P}\bar{1}$	2
Talmessite	$\text{Ca}_2\text{Mg}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$	5.868(3)	6.985(4)	5.578(3)	97.72(5)	109.15(3)	107.52(7)	$\text{P}\bar{1}$	3
Collinsite	$\text{Ca}_2\text{Mg}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	5.734(1)	6.780(1)	5.441(1)	97.29(1)	108.56(1)	107.28(1)	$\text{P}\bar{1}$	4
Cassidyite	$\text{Ca}_2\text{Ni}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	5.71	6.73	5.41	96.8	107.4	104.6	$\text{P}\bar{1}$	5
Fairfieldite	$\text{Ca}_2(\text{Mn,Fe})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	5.76(1)	6.96(1)	5.51(1)	95.6(2)	108.7(3)	109.3(2)	$\text{P}\bar{1}$	2

¹This study; ²refined from unindexed powder patterns given by Frondel (1955); ³refined from data given by Pierrot (1964); ⁴Brotherton *et al.* (1974); ⁵White *et al.* (1967).

TABLE 8. BOND STRENGTH TABLES¹ FOR ROSELITE AND COLLINSITE

Roselite						
	Ca	Mg/Co	As	H(1) ²	H(2) ²	Σ^2
0(1)	0.323		1.290	(0.387)		1.613(2.000)
0(2)	0.243 0.230	0.271 ^{x2}	1.205			1.949
0(3)	0.276	0.378 ^{x2}	1.185			1.839
0(4)	0.239 0.281		1.226		(0.254)	1.746(2.000)
0(5)	0.296	0.374 ^{x2}		(0.613)	(0.746)	0.670(2.026)
Collinsite						
	Ca	Mg	P	H(51) ²	H(52) ²	Σ^2
0(1)	0.185 0.219	0.299 ^{x2}	1.212			1.915
0(2)	0.145 0.188	0.326 ^{x2}	1.187			1.846
0(3)	0.250 0.293		1.268			1.811
0(4)	0.308		1.240	(0.226)	(0.226)	1.548(2.000)
0(5)	0.307	0.426 ^{x2}		0.774	0.774	0.543(2.281)

¹calculated from the curves of Brown & Shannon (1973); ²hydrogen bond strengths were calculated by assigning sufficient bond strength to the acceptor anion to achieve an ideal bond strength sum of 2.0. Bond strengths are in valence units (v.u.).

ideal value of 2.0, and the disposition of hydrogen bonds to both donor and acceptor anions together with the bond strengths calculated around the Ca and P cations suggest that the octahedron should be strongly *elongated* along the O(5)-O(5) axis. Much more satisfactory bond strength sums are attained if it is assumed that H(51) forms one very strong hydrogen bond with O(4) and H(52) forms a weak hydrogen bond with O(3), thus accounting for the very compressed nature of the Mg octahedron in collinsite, which may be seen as a result of the strong H(51)-O(4) bond. Although this is rather speculative, the bond strength model for the hydrogen bonding arrangement proposed by Brotherton *et al.* (1974) does depart much further from ideality than is generally encountered in inorganic structures. An infrared study of these species might resolve this point.

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