

THE CRYSTAL STRUCTURE OF MANDARINOITE, $\text{Fe}^{3+}_2\text{Se}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$

FRANK C. HAWTHORNE

Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ABSTRACT

The crystal structure of mandarinoite, $\text{Fe}^{3+}_2\text{Se}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$, a 16.810(4), b 7.880(2), c 10.019(2) Å, β 98.26(2)°, V 1313.4 Å³, Z = 4, space group $P2_1/c$, has been solved by direct methods and refined by a full-matrix least-squares procedure to a residual R = 6.4% for 2101 observed (3σ) reflections. The formula unit contains six rather than four water molecules, as reported in previous studies. Three unique SeO_3 trigonal pyramids and two unique FeO_6 octahedra ($\emptyset$ unspecified anion) link by corner-sharing to form a $M_2T_3O_{12}$ framework. Large voids in this framework are occupied by the water molecules, which participate in a hydrogen-bonding scheme that is essential to the anion bond-valence requirements.

Keywords: crystal structure, mandarinoite, selenite.

SOMMAIRE

On a déterminé et affiné la structure cristalline de la mandarinoïte, $\text{Fe}^{3+}_2\text{Se}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$, a 16.810(4), b 7.880(2), c 10.019(2) Å, β 98.26(2)°, V = 1313.4 Å³, Z = 4, groupe spatial $P2_1/c$, par méthodes directes et moindres carrés à matrice entière jusqu'au résidu R = 6.4%, sur 2101 réflexions observées (3σ). La formule contient six molécules d'eau et non quatre, comme on l'avait d'abord proposé. Trois pyramides trigonales SeO_3 uniques et deux octaèdres FeO_6 uniques ($\emptyset$ anion non défini) partagent leurs sommets pour former une charpente $M_2T_3O_{12}$. Les molécules d'eau y occupent de grandes cavités et participent à un système de liaisons hydrogène qui satisfait aux exigences des valences de liaison des anions.

(Traduit par la Rédaction)

Mots-clés: structure cristalline, mandarinoïte, sélénite.

INTRODUCTION

Mandarinoite is a hydrated ferric iron selenite mineral recently described by Dunn *et al.* (1978). It was initially described from the Pacajake mine in Bolivia, where it is associated with penrosite, siderite and various secondary selenite minerals such as chalcomenite, ahlfeldite and cobaltomenite. It is also found in association with leached quartz at the Skouriotissa mine in Cyprus, and in association with poughite at the El Plomo mine in Honduras. A fourth occurrence of mandarinoite was reported by Lasmanis *et al.* (1981) at the De Lamar silver mine,

in Idaho. Here, the mandarinoite occurs in narrow open veinlets associated with drusy quartz and chlorargyrite.

The current study was prompted by the poor compatibility-index (Mandarino 1981) for mandarinoite (Mandarino, pers. comm.), which suggested a discrepancy in the original formula. Despite the temptation to leave mandarinoite with the wrong formula, the present study was eventually undertaken to elucidate this problem.

EXPERIMENTAL

A single crystal of mandarinoite from the De Lamar silver mine, Idaho was kindly supplied for this study by Dr. Joseph A. Mandarino, Royal Ontario Museum (catalogue #M35602). Single-crystal X-ray-precession photographs display monoclinic symmetry with systematic absences $h0\ell$, $\ell = 2n + 1$, $0k0$, $k = 2n + 1$, uniquely determining the space group as $P2_1/c$. Cell dimensions were determined by least-squares refinement of reflections aligned automatically on a Syntex $P2_1$ 4-circle diffractometer; the values (Table 1) agree with those given by Dunn *et al.* (1978). The crystal used to collect the intensity data is irregular in shape, measuring $0.18 \times 0.18 \times 0.12$ mm; the intensity data were collected according to the method of Hawthorne (1979). Two standard reflections were monitored every 50 reflections; no significant change in their intensities was observed during data collection. A total of 4658 reflections was measured over one asymmetric unit to a maximum 2θ of 60° ($\sin\theta/\lambda = 0.704$). The data were corrected for Lorentz, polarization, absorption (ψ scan method: North *et al.* 1968) and background effects, and were reduced to structure factors. A reflection was considered as observed if its magnitude exceeds that of three standard deviations based on counting statistics; of the 4658 unique reflections, 2101 were considered as observed.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms were taken from Cromer & Mann (1968), with coefficients of anomalous dispersion from Cromer & Liberman (1970). R indices are of the form given in Table 1 and are expressed as percentages.

The structure was determined using the weighted tangent-formula method (Main *et al.* 1978). The

TABLE 1. MISCELLANEOUS DATA FOR MANDARINOITE

a	16.810(4) Å	Crystal size	D.18x0.18x0.12 mm
b	7.880(2)	Rad/Mono	Mo/Gr
c	10.019(2)	Total # of $ F_o $	4658
β	98.26(2)°	# of $ F_o > 3 \sigma$	2101
V	1313.4 Å ³	Final $R(\text{obs. data})$	6.4%
Space Group	P2 ₁ /c	Final $R_w(\text{obs. data})$	8.4%
Unit-cell contents 4[Fe ₂ ³⁺ Se ₃ O ₉ ·6H ₂ O]			
Temperature-factor form used: $\exp[-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij}]$			
$R = \Sigma(F_o - F_c) / \Sigma F_o $			
$R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}, w=1$			

phase set with the maximum combined figure of merit resulted in an E-map, the most intense peaks of which could be interpreted in terms of the expected ratio of cations in mandarinoite. Refinement of the atomic positions for three Se and two Fe positions resulted in an R index of 37%. A difference-Fourier map revealed the anion positions, and full-matrix least-squares refinement of all variables for an isotropic thermal model converged to an R index of 10.4%. Temperature factors were converted to the anisotropic form given in Table 1, and least-squares refinement of all variables resulted in convergence at an R index of 6.5%.

It was apparent at this stage that the composition of mandarinoite is Fe₂Se₃O₉·6H₂O rather than Fe₂Se₃O₉·4H₂O as given in the previous study. Three of the six independent H₂O molecules are not bonded to Fe or Se, and presumably are held in the structure solely by a network of hydrogen bonds. The temperature factors for these three water molecules are significantly higher than for the water molecules bonded to Fe³⁺. This is not surprising in view of the weak (hydrogen) bonds holding them in the structure; larger thermal vibrations or slight positional disorder (or both) are to be expected in these circumstances. As a check on the significance of the water molecules in the cavity to the refinement results, the structure was refined omitting each water molecule of the cavity in turn, as well as one of the non-cavity water molecules for comparison. The following results were obtained [atom omitted, R , R_w (observed reflections)]: O(12), 8.3, 10.4%; O(13), 8.0, 10.2%; O(14), 7.7, 9.7%; O(15), 7.9, 10.0%. Comparison with the complete structure ($R = 6.5$, $R_w = 8.5\%$) shows that the presence of each water molecule of the cavity leads to a significant improvement in the residual, and comparison with the results of the refinement omitting O(12) suggests that each of the cavity-water positions is completely occupied.

Examination of a difference-Fourier map calculated at this stage did not give a definite unique set of H positions. Consequently, an attempt was made

TABLE 2. ATOMIC POSITIONS FOR MANDARINOITE

Atom	x	y	z	$B_{\text{equiv.}} (\text{\AA}^2)$
Se(1)	0.9814(1)	0.0402(2)	0.3157(1)	0.98(2)
Se(2)	0.2232(1)	0.7278(2)	0.7296(1)	1.00(2)
Se(3)	0.5277(1)	0.4819(2)	0.8133(1)	0.98(2)
Fe(1)	0.3992(1)	0.7447(3)	0.9105(2)	0.91(3)
Fe(2)	0.9056(1)	0.2408(3)	0.0462(2)	0.93(3)
O(1)	0.9804(7)	0.2132(14)	0.4165(9)	1.2(2)
O(2)	0.0778(7)	-0.0288(15)	0.3678(10)	1.3(2)
O(3)	0.9993(8)	0.1372(17)	0.1715(10)	1.6(2)
O(4)	0.3144(7)	-0.1765(16)	0.7662(10)	1.3(2)
O(5)	0.1916(8)	-0.1686(15)	0.5793(9)	1.4(2)
O(6)	0.1688(8)	-0.1602(15)	0.8291(11)	1.5(2)
O(7)	0.5206(8)	0.3855(14)	0.6606(9)	1.3(2)
O(8)	0.4301(7)	0.5483(14)	0.8012(9)	1.0(2)
O(9)	0.4777(8)	0.6841(15)	0.0774(10)	1.4(2)
O(10)	0.3162(8)	-0.4275(17)	0.9668(11)	1.7(2)
O(11)	0.3560(8)	-0.0759(14)	0.0322(10)	1.3(2)
O(12)	0.8857(8)	0.0073(15)	-0.0482(12)	1.6(2)
O(13)	0.6401(8)	0.7601(20)	0.0739(13)	2.3(2)
O(14)	0.2525(15)	0.3129(20)	0.2005(17)	4.2(4)
O(15)	0.1779(9)	0.2416(20)	0.4283(14)	2.5(2)
H(10)A	0.27(1)	0.56(3)	0.93(2)	1.0*
H(10)B	0.35(1)	0.49(3)	0.97(2)	1.0
H(11)A	0.39(1)	0.92(3)	0.12(2)	1.0
H(11)B	0.37(1)	-0.01(3)	0.99(2)	1.0
H(12)A	0.06(1)	-0.05(3)	0.06(2)	1.0
H(12)B	0.11(1)	0.13(3)	0.05(2)	1.0
H(13)A	0.41(1)	0.28(3)	0.41(2)	1.0
H(13)B	-	-	-	-
H(14)A	0.23(1)	0.20(3)	0.57(2)	1.0
H(14)B	0.28(1)	0.39(3)	0.19(2)	1.0
H(15)A	0.15(1)	0.10(3)	0.37(2)	1.0
H(15)B	0.18(1)	0.31(3)	0.35(2)	1.0

* fixed during refinement

TABLE 3. ANISOTROPIC TEMPERATURE-FACTOR COEFFICIENTS*

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Se(1)	12(1)	35(2)	18(1)	-1(1)	3(1)	2(1)
Se(2)	12(1)	37(2)	19(1)	-1(1)	1(1)	4(1)
Se(3)	11(1)	42(2)	17(1)	1(1)	3(1)	1(1)
Fe(1)	11(1)	33(3)	19(1)	1(1)	4(1)	3(2)
Fe(2)	12(1)	39(3)	12(1)	0(1)	2(1)	0(2)
O(1)	10(4)	55(16)	26(8)	-3(6)	4(4)	-28(10)
O(2)	12(4)	58(17)	24(8)	0(7)	-4(4)	10(10)
O(3)	17(5)	95(20)	16(8)	-4(7)	14(5)	1(10)
O(4)	8(4)	79(18)	21(8)	-5(7)	-4(4)	7(10)
O(5)	21(5)	54(16)	13(8)	-7(7)	1(5)	4(9)
O(6)	19(5)	62(17)	30(9)	-3(7)	19(5)	-28(10)
O(7)	20(5)	55(16)	4(7)	4(7)	-2(4)	-3(9)
O(8)	10(4)	49(15)	17(8)	18(6)	4(4)	2(9)
O(9)	20(5)	62(16)	11(8)	7(7)	2(5)	23(9)
O(10)	22(5)	78(19)	24(9)	2(8)	10(5)	13(10)
O(11)	17(4)	46(15)	20(8)	1(6)	-5(5)	20(9)
O(12)	17(5)	48(16)	45(10)	-6(7)	9(5)	-15(11)
O(13)	17(5)	110(24)	54(12)	-6(9)	3(6)	-2(14)
O(14)	76(12)	63(22)	77(17)	-6(14)	31(12)	16(16)
O(15)	26(6)	92(22)	61(12)	-16(9)	9(7)	-7(14)

* $\beta_{ij} = \beta_{ji} \times 10^4$

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN MANDARINOITE

Se(1)-O(1)	1.699(10)	Fe(1)-O(4)	1.980(11)
Se(1)-O(2)	1.717(11)	Fe(1)-O(7)	1.956(12)
Se(1)-O(3)	1.699(10)	Fe(1)-O(8)	2.007(10)
<Se(1)-O>	1.705	Fe(1)-O(9)	2.032(10)
		Fe(1)-O(10)	2.081(13)
Se(2)-O(4)	1.699(11)	Fe(1)-O(11)	2.066(12)
Se(2)-O(5)	1.728(11)	<Fe(1)-O>	2.021
Se(2)-O(6)	1.694(10)		
<Se(2)-O>	1.707	Fe(2)-O(1)	1.967(10)
		Fe(2)-O(2)	2.011(11)
Se(3)-O(7)	1.698(9)	Fe(2)-O(3)	2.039(13)
Se(3)-O(8)	1.710(10)	Fe(2)-O(5)	2.042(12)
Se(3)-O(9)	1.717(10)	Fe(2)-O(6)	1.994(11)
<Se(3)-O>	1.708	Fe(2)-O(12)	2.074(12)
		<Fe(2)-O>	2.021
O(10)-H(10)A	0.9(2)	H(10)A-O(5)	2.3(2)
O(10)-H(10)B	0.9(2)	H(10)B-O(13)	2.1(2)
O(10)-O(5)	2.629(17)	O(10)-H(10)A-O(5)	104(16)
O(10)-O(13)	2.768(19)	O(10)-H(10)B-O(13)	139(20)
H(10)A-H(10)B	1.5(3)	H(10)A-O(10)-H(10)B	125(21)
O(11)-H(11)A	1.0(2)	H(11)A-O(8)	1.9(2)
O(11)-H(11)B	0.7(2)	H(11)B-O(13)	2.1(2)
O(11)-O(8)	2.810(14)	O(11)-H(11)A-O(8)	162(20)
O(11)-O(13)	2.711(18)	O(11)-H(11)B-O(13)	153(24)
H(11)A-H(11)B	1.4(3)	H(11)A-O(11)-H(11)B	112(22)
		H(12)A-O(1)	2.0(2)
O(12)-H(12)A	0.9(2)	H(12)A-O(3)	2.2(2)
O(12)-H(12)B	1.1(2)	H(12)B-O(15)	2.1(2)
O(12)-O(1)	2.770(16)	O(12)-H(12)A-O(1)	133(19)
O(12)-O(3)	2.886(17)	O(12)-H(12)A-O(3)	109(17)
O(12)-O(15)	2.709(19)	O(12)-H(12)B-O(15)	113(15)
H(12)A-H(12)B	1.6(3)	H(12)A-O(12)-H(12)B	103(18)
O(13)-H(13)A	0.9(2)	H(13)A-O(9)	2.0(2)
O(13)-H(13)B	0.7(2)	H(13)B-O(14)	-
O(13)-O(9)	2.801(19)	O(13)-H(13)A-O(9)	147(21)
O(13)-O(14)	2.715(21)	O(13)-H(13)B-O(14)	-
H(13)A-H(13)B	-	H(13)A-O(13)-H(13)B	-
O(14)-H(14)A	1.3(2)	H(14)A-O(15)	1.6(2)
O(14)-H(14)B	0.8(2)	H(14)B-O(4)	2.4(2)
O(14)-O(15)	2.815(22)	O(14)-H(14)A-O(15)	162(17)
O(14)-O(4)	3.086(20)	O(14)-H(14)B-O(4)	138(20)
H(14)A-H(14)B	1.6(3)	H(14)A-O(14)-H(14)B	92(17)
O(15)-H(15)A	1.3(2)	H(15)A-O(2)	1.6(2)
O(15)-H(15)B	1.0(2)	H(15)B-O(14)	2.1(2)
O(15)-O(2)	2.729(18)	O(15)-H(15)A-O(2)	138(17)
O(15)-O(14)	2.815(21)	O(15)-H(15)B-O(14)	133(19)
H(15)A-H(15)B	1.7(3)	H(15)A-O(15)-H(15)B	97(15)

to derive a hydrogen-bonding scheme from crystal-chemical arguments. As part of this procedure, a bond-valence calculation was carried out (see Table 7) using the curves of Brown (1981). Examination of the bond-valence sums around the O^{2-} anions [O(1) to O(9)] shows that O(2), O(3), O(5), O(8) and O(9) are significantly deficient when compared with their ideal values of 2.0 v.u. (valence units); hence these atoms must be hydrogen-bond acceptors. Baur (1972, 1973) showed that hydrogen bonding does not occur between oxygen atoms of the same co-ordination polyhedron when the central cation has high charge and the co-ordination number is small. Within the bounds of this constraint, the hydrogen-bond acceptors given above each have only one possible hydrogen-bond donor; these are O(15), O(12), O(10), O(11) and O(13), respectively. The atoms O(10), O(11) and O(13) will each act as donor for an additional hydrogen bond; examination of the neighboring oxygen atoms shows that for each of these only one atom is close enough to be an acceptor; these are O(13), O(14) and O(15), respectively.

Assuming a reasonable geometry of the H_2O molecule for the remaining hydrogen atoms allowed a sensible hydrogen-bond network to be postulated, assuming straight ($O-H \dots O = 180^\circ$) hydrogen bonds with $H-O$ (donor) distances of 1 Å. These positions were input into the structure model, and the positional parameters were refined. All H positions converged to reasonable values except H(13)B: this was omitted from the final cycles of refinement. However, other criteria indicate a hydrogen bond $O(13)-H(13)B \dots O(14)$. Full-matrix least-squares refinement of all variables except for the H atom isotropic temperature-factors (which were fixed at 1.0 Å^2) converged to R indices of 6.4 (observed reflections) and 16.4 (all data) and R_w indices of 8.4 (observed reflections) and 30.3% (all data); this is not a significant improvement over the refinement with no hydrogen atoms included. Final parameters are given in Tables 2, 3 and 4. Observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Interatomic distances and angles, and the magnitudes and orientations of the principal axes of the thermal ellipsoids, calculated with the program ERRORS (L. W. Finger, pers. comm.), are given in Tables 5 and 6.

TABLE 5. POLYHEDRON DIMENSIONS IN MANDARINOITE

O(1)-O(2)	2.605(16)Å	O(1)-Se(1)-O(2)	99.4(5)°
O(1)-O(3)	2.591(14)	O(1)-Se(1)-O(3)	99.4(6)
O(2)-O(3)	2.564(16)	O(2)-Se(1)-O(3)	97.3(6)
<O-Se(1)>	2.587	<O-Se(1)-O>	98.7
O(4)-O(5)	2.580(15)	O(4)-Se(2)-O(5)	97.7(5)
O(4)-O(6)	2.616(17)	O(4)-Se(2)-O(6)	100.9(6)
O(5)-O(6)	2.586(14)	O(5)-Se(2)-O(6)	98.2(6)
<O-Se(2)>	2.594	<O-Se(2)-O>	98.9
O(7)-O(8)	2.562(14)	O(7)-Se(3)-O(8)	97.5(5)
O(7)-O(9)	2.678(13)	O(7)-Se(3)-O(9)	103.3(5)
O(8)-O(9)	2.588(15)	O(8)-Se(3)-O(9)	98.1(6)
<O-Se(3)>	2.609	<O-Se(3)-O>	99.6
O(4)-O(7)	2.808(17)	O(4)-Fe(1)-O(7)	91.0(5)
O(4)-O(8)	2.901(16)	O(4)-Fe(1)-O(8)	93.4(5)
O(4)-O(10)	2.817(16)	O(4)-Fe(1)-O(10)	87.8(5)
O(4)-O(11)	2.772(15)	O(4)-Fe(1)-O(11)	86.5(5)
O(7)-O(8)	2.793(16)	O(7)-Fe(1)-O(8)	89.6(5)
O(7)-O(9)	2.868(14)	O(7)-Fe(1)-O(9)	91.9(5)
O(7)-O(11)	3.045(17)	O(7)-Fe(1)-O(11)	98.4(5)
O(8)-O(9)	2.968(15)	O(8)-Fe(1)-O(9)	94.6(5)
O(8)-O(10)	2.714(16)	O(8)-Fe(1)-O(10)	83.2(5)
O(9)-O(10)	2.916(19)	O(9)-Fe(1)-O(10)	90.3(5)
O(9)-O(11)	2.775(17)	O(9)-Fe(1)-O(11)	85.2(4)
O(10)-O(11)	2.903(17)	O(10)-Fe(1)-O(11)	88.9(5)
<O-Fe(1)>	2.856	<O-Fe(1)-O>	90.0
O(1)-O(2)	2.888(15)	O(1)-Fe(2)-O(2)	93.1(5)
O(1)-O(3)	2.790(15)	O(1)-Fe(2)-O(3)	88.3(4)
O(1)-O(5)	2.918(17)	O(1)-Fe(2)-O(5)	93.4(5)
O(1)-O(12)	2.770(16)	O(1)-Fe(2)-O(12)	86.5(5)
O(2)-O(3)	2.935(18)	O(2)-Fe(2)-O(3)	92.9(5)
O(2)-O(5)	2.863(16)	O(2)-Fe(2)-O(5)	89.9(5)
O(2)-O(6)	2.944(17)	O(2)-Fe(2)-O(6)	94.6(5)
O(3)-O(6)	2.831(18)	O(3)-Fe(2)-O(6)	89.2(5)
O(3)-O(12)	2.886(17)	O(3)-Fe(2)-O(12)	89.2(5)
O(5)-O(6)	2.824(16)	O(5)-Fe(2)-O(6)	88.8(5)
O(5)-O(12)	2.861(17)	O(5)-Fe(2)-O(12)	88.1(5)
O(6)-O(12)	2.772(15)	O(6)-Fe(2)-O(12)	85.9(5)
<O-Fe(2)>	2.856	<O-Fe(2)-O>	90.0

TABLE 6. VIBRATION ELLIPSOIDS FOR MANDARINOITE

	R.M.S. Displacement	Angle to X-axis	Angle to Y-axis	Angle to Z-axis
Se(1)	0.092(3) ^A 0.107(3) 0.132(3)	101(3) ^O 90(5) 11(3)	108(9) ^O 162(8) 94(5)	18(9) ^O 108(9) 88(3)
Se(2)	0.094(3) 0.110(3) 0.130(3)	88(3) 100(6) 10(6)	117(7) 152(7) 98(6)	28(7) 114(7) 104(4)
Se(3)	0.092(3) 0.114(3) 0.126(3)	99(4) 76(10) 17(9)	93(6) 166(10) 76(10)	4(5) 93(6) 88(3)
Fe(1)	0.090(4) 0.104(4) 0.125(4)	107(7) 70(9) 26(7)	116(13) 151(13) 79(8)	28(12) 113(13) 74(6)
Fe(2)	0.078(4) 0.111(4) 0.130(4)	94(3) 87(10) 5(6)	91(6) 177(9) 87(10)	4(4) 92(6) 94(3)
O(1)	0.06(3) 0.12(2) 0.16(2)	94(19) 174(18) 95(18)	51(9) 96(18) 40(9)	39(9) 81(20) 128(9)
O(2)	0.09(2) 0.13(2) 0.15(2)	68(19) 127(43) 134(42)	110(20) 143(41) 60(44)	37(15) 87(35) 53(15)
O(3)	0.05(4) 0.16(2) 0.18(2)	119(9) 141(37) 114(49)	93(8) 116(57) 27(57)	21(9) 109(12) 96(20)
O(4)	0.08(3) 0.12(2) 0.16(2)	50(26) 46(26) 108(17)	89(15) 66(19) 24(19)	49(27) 134(28) 73(15)
O(5)	0.08(2) 0.12(2) 0.18(2)	92(11) 109(16) 19(16)	99(21) 158(18) 109(16)	11(15) 97(22) 99(9)
O(6)	0.02(9) 0.14(2) 0.19(2)	118(9) 126(15) 49(15)	64(10) 143(14) 114(16)	34(7) 80(14) 58(7)
O(7)	0.04(4) 0.13(2) 0.17(2)	86(8) 77(20) 13(19)	86(13) 167(19) 78(20)	13(8) 87(13) 103(7)
O(8)	0.05(4) 0.09(2) 0.16(2)	136(10) 92(23) 47(9)	48(11) 81(22) 44(10)	76(29) 166(29) 90(11)
O(9)	0.03(6) 0.15(2) 0.17(2)	89(8) 61(36) 29(36)	116(9) 141(27) 63(32)	28(9) 118(9) 86(18)
O(10)	0.09(2) 0.16(2) 0.18(2)	107(11) 68(39) 28(33)	107(13) 156(31) 73(40)	19(12) 103(17) 76(14)
O(11)	0.05(3) 0.14(2) 0.17(2)	79(10) 116(25) 29(24)	124(12) 142(15) 106(21)	39(10) 112(18) 121(13)
O(12)	0.11(2) 0.14(2) 0.17(2)	86(28) 37(27) 54(27)	28(19) 77(31) 114(15)	64(25) 132(29) 53(23)
O(13)	0.15(2) 0.17(2) 0.19(2)	30(46) 68(55) 110(28)	71(24) 84(40) 20(27)	75(57) 165(56) 89(37)
O(14)	0.13(3) 0.19(2) 0.33(3)	81(7) 76(8) 16(7)	25(17) 115(17) 92(6)	115(17) 154(16) 82(7)
O(15)	0.15(2) 0.17(2) 0.21(2)	55(19) 75(34) 141(17)	35(17) 96(35) 56(15)	91(40) 171(22) 99(22)

TABLE 7. EMPIRICAL BOND-VALENCE TABLE FOR MANDARINOITE

	Fe(1)	Fe(2)	Se(1)	Se(2)	Se(3)	Σ
O(1)		0.581	1.364			1.945
O(2)		0.510	1.283			1.793
O(3)		0.480	1.373			1.853
O(4)	0.557			1.373		1.930
O(5)		0.470		1.255		1.725
O(6)		0.539		1.395		1.934
O(7)	0.600				1.373	1.973
O(8)	0.518				1.316	1.834
O(9)	0.486				1.279	1.765
O(10)	0.422					0.422
O(11)	0.443					0.443
O(12)		0.435				0.435
O(13)						-
O(14)						-
O(15)						-
Σ	3.026	3.015	4.020	4.023	3.968	-

tions: Fe(1) is co-ordinated by four oxygen atoms and two water molecules in a pseudo-octahedral arrangement, and Fe(2) is co-ordinated by five oxygen atoms and one water molecule in a pseudo-octahedral arrangement. Variations in Se-O and Fe-O bond-lengths can be rationalized in terms of the anion bond-valence requirements, as is apparent from the bond-valence table (Table 7) calculated using the parameters given by Brown (1981).

There are three unique water molecules in the structure that are not bonded to any cation. However, their positions are well-defined, and they participate in a complex scheme of hydrogen-bonding that is essential to the anion bond-valence requirements of the structure.

Each (SeO₃) group corner-links to three FeO₆ octahedra (O unspecified anion) to form a framework structure of general stoichiometry $^{vi}M_2^{iii}T_3O_{12}$. Figure 1 shows slices through the structure at $x \sim 0.0$ and ~ 0.5 ; these consist of graphically identical sheets of composition $^{vi}M_2^{iii}T_2O_{15}$. These two sheets are cross-linked into a framework by the third (SeO₃) group, as shown in Figure 2. This leaves large cavities in the structure that are occupied by the hydrogen-bonded water molecules. Figure 2 also shows the proposed hydrogen-bonding scheme.

Chemical formula

In the original description of mandarinioite, the H₂O content was not analyzed directly owing to the paucity of the material; H₂O was assumed to be the difference between the sum Fe₂O₃ + SeO₂ and 100%. A comparison of the composition derived by electron-microprobe analysis with the ideal formula Fe³⁺₂Se₃O₉·6H₂O derived from the structure is shown in Table 8. Both the Fe₂O₃ and SeO₂ values from the microprobe analysis are $\sim 6\%$ too high (6.3

DISCUSSION

Description of the structure

There are three unique Se positions in mandarinioite, each of which is co-ordinated to three oxygen atoms to form characteristic SeO₃ trigonal pyramidal groups. There are two unique Fe³⁺ posi-

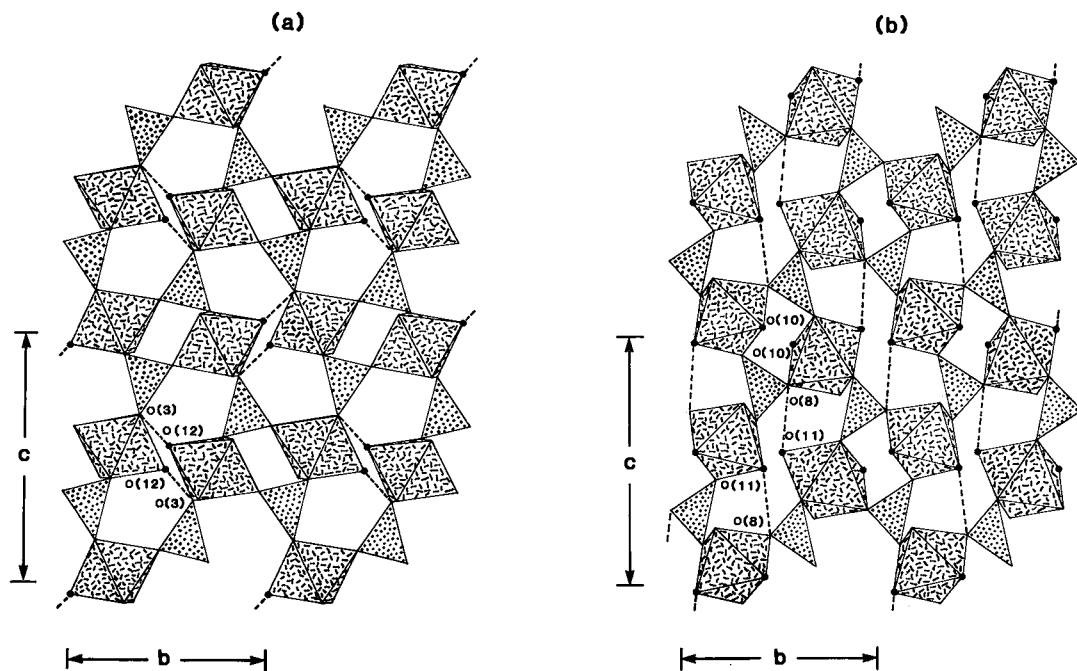


FIG. 1. The crystal structure of mandarinoite viewed down X : (a) $M_2T_2O_{15}$ sheet at $x \sim 0$; (b) $M_2T_2O_{15}$ sheet at $x \sim 0.5$.

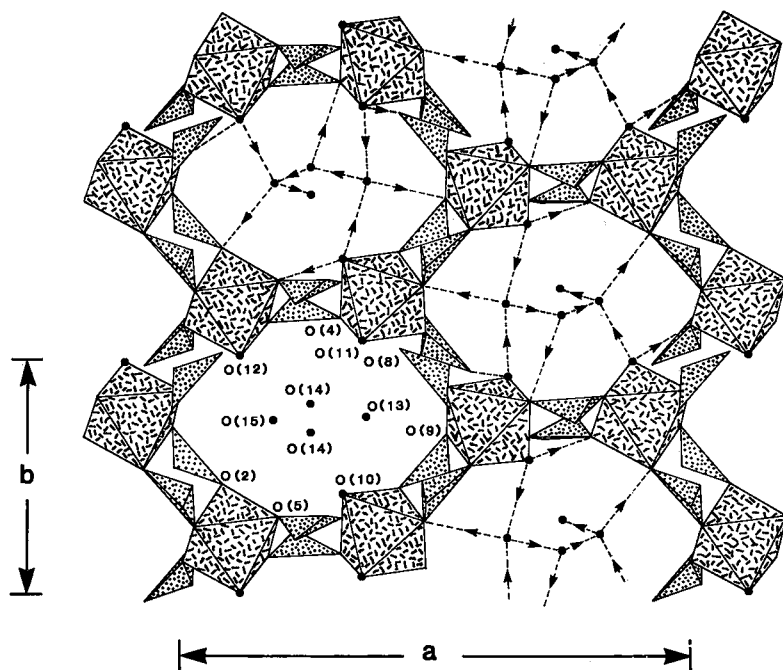


FIG. 2. The crystal structure of mandarinoite viewed down Z ; the arrows indicate the direction (donor to acceptor) of the hydrogen bonds. Symmetrically equivalent O(13) and O(15) atoms are included in this view.

TABLE 8. CHEMICAL COMPOSITION OF MANDARINOITE

	Microprobe*	Structure
Fe ₂ O ₃	28.68 wt. %	26.86 wt. %
SeO ₂	59.53	55.98
H ₂ O	(11.79)	17.16
Σ	<u>100.00</u>	<u>100.00</u>

*Dunn et al. (1978)

and 6.0%, respectively); the fact that the discrepancies are equal suggests that mandarinoite may have lost H₂O under the electron beam during microprobe analysis. The compatibility index (Mandarino 1981) for the original data is in the poor category, whereas for the revised composition it is in the excellent category.

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