

New insight into the pectolite – serandite series: a single crystal diffraction study of $\text{Na}(\text{Ca}_{1.73}\text{Mn}_{0.27})[\text{HSi}_3\text{O}_9]$ at 293 and 100 K

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Abstract. Using synchrotron radiation, a single crystal investigation has been performed at 293 and 100 K for the structural characterization of the manganoo pectolite, $\text{Na}(\text{Ca}_{1.73}\text{Mn}_{0.27})[\text{Si}_3\text{O}_8(\text{OH})]$ (from the pegmatite at Mt. Koashva, Khibiny alkaline massif, Kola peninsula, Russia). The data obtained are compared with other members of the pectolite – serandite, $\text{Na}(\text{Ca}_{2-x}\text{Mn}_x)[\text{Si}_3\text{O}_8(\text{OH})]$, series. The strong asymmetric hydrogen bond observed in the other members of the series has been confirmed at 293 K ($\text{O3-O4} = 2.473(3) \text{ \AA}$; $\text{H-O3} = 0.97(4) \text{ \AA}$, $\text{H} \dots \text{O4} = 1.50(4) \text{ \AA}$; $\text{O3-H} \dots \text{O4} = 178(4)^\circ$). This bond exhibits strengthening ($\text{O3-O4} = 2.458(2) \text{ \AA}$) and becomes more symmetric at 100 K ($\text{H-O3} = 1.06(4) \text{ \AA}$, $\text{H} \dots \text{O4} = 1.40(4) \text{ \AA}$, $\text{O3-H} \dots \text{O4} = 177(4)^\circ$). The data obtained for 293 K confirm the previously hinted tendency: the higher the content of Mn, the more asymmetric the H-bond. The influence of the asymmetric position of the H-bond on the environment close to the bonded O3 and O4 atoms and the H–Na interaction are discussed. The alternative topological role of the hydrogen bond is considered in comparison to a similar structure $\text{Li}_2\text{Mg}_2[\text{Si}_4\text{O}_{11}]$.

Introduction

The crystal structures (Fig. 1) of minerals occurring along the pectolite – serandite series, $\text{NaCa}_2[\text{Si}_3\text{O}_8(\text{OH})]$ – $\text{NaMn}_2[\text{Si}_3\text{O}_8(\text{OH})]$, have been investigated since the determination of the pectolite crystal structure by Buerger (1956) and a further refinement by Prewitt (1967). The interest in the minerals with the general formula $\text{Na}(\text{Ca}_{2-x}\text{Mn}_x)[\text{Si}_3\text{O}_8(\text{OH})]$ ($0 \leq x \leq 1$) is related to two specific features of their structures. The first one is the uneven distribution of Ca and Mn on the M1 and M2 structural positions. The second feature is the strong asym-

metric hydrogen bond between O3 and O4 atoms (Fig. 1) separated by 2.45–2.48   . Both features are numerically characterized in Table 1 along with the parameters of the triclinic unit cell. The unusual case of a protonated

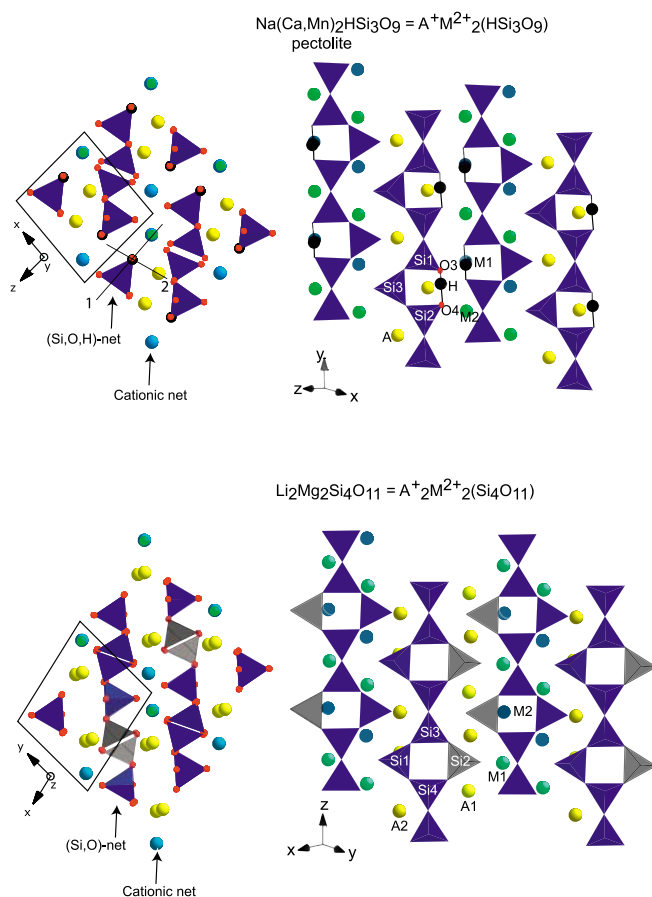


Fig. 1. Crystal structure of the pectolite in comparison to $\text{Li}_2\text{Mg}_2[\text{Si}_4\text{O}_{11}]$. The structure projections are shown on left. The unit cells are indicated. Lines 1 and 2 indicate profile of sections crossing O3, O4, H, Si1, Si2, M1, M2 and O3, O4, H, Na respectively. Both these sections are represented in Fig. 4. A single anionic net with the underlined cationic net is shown on right. The Si_2O_4 -tetrahedron in $\text{Li}_2\text{Mg}_2[\text{Si}_4\text{O}_{11}]$ is indicated by grey in order to only show its topological similarity to the $(\text{O4} \dots \text{H}-\text{O3})$ group in pectolite.

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Table 1. Specific structural characteristics of minerals in the pectolite – serandite, $\text{Na}(\text{Ca}_{2-x}\text{Mn}_x)[\text{HSi}_3\text{O}_9]$, series (space group $P\bar{1}$; $T = 293$ K).

Mineral, x (reference)	Unit cell parameters: a, b, c (Å), α, β, γ (°)	Occupation of M1 and M2 positions (M,%); $\langle \text{M-O} \rangle$ distance (Å)		The O3–H...O4 hydrogen bond characteristics (Å, °)	
		M1	M2	$d(\text{O3-O4})$	$d(\text{H-O}), d(\text{H...O});$ the O–H...O angle
Pectolite, 0 (Prewitt 1967)	7.9882(1) 7.0400(1) 7.0247(1) 90.520 95.181 102.469	Ca, 100; 2.368	Ca, 100; 2.360;	2.482(4)	H–O3 = 0.97, H...O4 = 1.54; O3–H...O4 = 163.2 (unrefined)
Mn-bearing pectolite, 0.057 (Takéuchi and Kudoh 1977)	7.980(1) 7.023(1) 7.018(1) 90.54(1) 95.14(1) 102.55(1)	Ca, 99.8; Mn, 0.2; 2.365	Ca, 94.3; Mn, 5.7; 2.352	2.473(2)	H–O3 = 1.06(5), H...O4 = 1.42(5), O3–H...O4 = 171(1)
Manganoan pectolite, 0.27 (present publication)	7.9572(12) 7.0200(10) 7.0006(11) 90.562(12) 94.962(13) 102.722(13)	Ca, 99.9; Mn, 0.1; 2.371	Ca, 73.0; Mn, 27.0; 2.327	2.473(3)	H–O3 = 0.97(4), H...O4 = 1.50(4); O3–H...O4 = 178(4)
«Schizolite» ^a , 0.77 (Ohashi and Finger 1978)	7.868(4) 6.978(8) 6.920(6) 90.72(6) 94.53(6) 102.92(6)	Ca, 87; Mn, 13; 2.376	Ca, 36; Mn, 64; 2.263	2.473(3)	No data
Ca-rich serandite, 1.67 (Ohashi and Finger 1978)	7.740(9) 6.913(9) 6.789(4) 90.51(6) 94.26(6) 103.05(6)	Ca, 34; Mn, 66; 2.286	Mn, 100; 2.235	2.470(3)	No data
Serandite, 2 (Jacobsen <i>et al.</i> 2000) X-ray study	7.7185(4) 6.9064(5) 6.7624(5) 90.492(5) 94.085(5) 102.775(6)	Mn, 94.4; 2.261	Mn, 98.9; 2.236	2.464(1)	H–O3 = 0.88(3), H...O4 = 1.60(3); O3–H...O4 = 164(3)
Serandite, 2 (Jacobsen <i>et al.</i> 2000) neutron study	7.7163(7) 6.9116(7) 6.7368(5) 90.465(7) 94.037(7) 102.844(7)	Mn, 94.1; 2.262	Mn, 98.3; 2.234	2.467(2)	0.84(5)H1 + 0.16(5)H2: H1–O3 = 1.078(3), H1...O4 = 1.413(3); O3–H1...O4 164.0(3), H2–O4 = 1.074(11), H2...O3 1.407(11); O4–H2...O3 = 168(1)

a: Old name of the pectolite with composition $\text{Na}(\text{Ca}_{1.23}\text{Mn}_{0.77})[\text{Si}_3\text{O}_8(\text{OH})]$

[SiO₄H] tetrahedron (silanol group) is another interesting aspect of pectolite structure.

The ordered Ca and Mn cation distribution in the pectolite – serandite series was precisely described and analyzed by Takéuchi *et al.* (1976) and Ohashi and Finger (1978) in their crystal chemical analyses of pyroxenoids. The [HSi₃O₉] pectolite chain was considered as a pyroxenoid chain by analogy to the [Si₃O₉] wollastonite chain. The experimental basis for their discussion, namely the localization of Ca atoms mainly in M1 position and Mn atoms in M2 position, was obtained from their own high quality crystal structure refinements published in part previously (Takéuchi and Kudoh 1977).

The very strong, but asymmetric, hydrogen bond in pectolite was the object of many structural investigations over a long period from 1956, when Buerger first proposed the presence of an H atom between O3 and O4 atoms, and up to 2000, when Jacobsen *et al.* (2000) using neutron diffraction experiment with serandite revealed two proton positions, H1 and H2, with 0.84 and 0.16 occupations, which were shifted towards O3 and O4 respectively (Table 1). Using X-ray techniques, the same authors found only one electron density maximum, H (0.179(4), 0.621(4), 0.533(4)), shifted towards O3. This electron density position is closed to that published by Prewitt (1967) for pectolite, where the H atom (0.162, 0.625, 0.530) coordinates were extracted from the residual electron density map without refinement. The structure investigation of Mn-bearing pectolite (Takéuchi and Kudoh 1977) also revealed one electron density maximum between O3 and O4 asymmetrically shifted toward O3; the reported coordinates are (0.178(5), 0.645(5), 0.527(6)).

The hydrogen bond was also confirmed for both pectolite and serandite from single-crystal IR spectroscopy by Hammer *et al.* (1998). According to the data obtained from polarized FTIR absorption spectra of pectolite and serandite at 298 and 83 K, there is no essential difference on the hydrogen bond characteristics between the two compositions. The very broad absorption band centred around 1000 cm⁻¹ and parallel to the *b*-axis was associated with the hydrogen bond elongated along the *b*-axis direction. Another and sharper OH bending mode was observed at 1396 cm⁻¹ (pectolite) and 1386 cm⁻¹ (serandite) parallel to the *c*-axis. The absence of the bending motion activity in the *a* direction was linked to the low probability of H moving closer to Na atom along the *a*-axis.

From this short review on the strong asymmetric hydrogen bond investigation in the pectolite-serandite series, the following conclusions can be drawn: (i) a single electron density maximum associated with the O3–H...O4 hydrogen bond appears at a position, which is identical within 3 standard deviations for all compositions; (ii) this hydrogen bond is extremely strong (O3–O4 = 2.46–2.48 Å) and asymmetric, H–O3 = 0.94–1.06 Å while H–O4 = 1.42–1.54 Å (Table 1); (iii) the angles and distances related to the hydrogen bond, are also independent on the composition, except of a slight difference in the O3–O4 distance between two terminal members of the series (Table 1); (iv) the nonequivalent splitting of H⁺-proton position obtained by neutron diffraction study for serandite is still more symmetrical than the position of the electron density maximum.

As can be seen from the Table 1, the previous structural study of the pectolite – serandite Na(Ca_{2-x}Mn_x)[Si₃O₈(OH)] series has been performed for the minerals with *x* closed to 0 (0 and 0.057) and *x* larger than 0.77 (0.77, 1.67 and 2). The present investigation of the manganoan pectolite (*x* = 0.27) allows us to cover the gap between *x* = 0.057 and *x* = 0.77. Since the strong hydrogen bond appears to be largely independent of the composition, and has been comprehensively investigated at room temperature only, we performed a synchrotron single crystal structure investigation at both 293 and 100 K in order to obtain information about the temperature dependent behaviour of this unusual type of hydrogen bond.

The investigated sample of pectolite was recently found in a pegmatite at Mt. Koashva, Khibiny alkaline massif (Kola peninsula, Russia) in association with natrite, Na₂CO₃, lomonosovite, (Na,Ca)Na₄(Ti,Nb,Fe,Mn)₂O₂[Si₂O₇][PO₄], and aegirine, NaFe[Si₂O₆]. The detailed description of the occurrence has been given by Zubkova *et al.* (2002) in connection with the average structure investigation of natrite. Well formed, colourless and transparent pectolite crystals with maximal size 0.1–0.02 mm were randomly distributed in a bulk sample of coarse-grained natrite.

Experimental

A fragment of the pectolite crystal with a needle-like shape of dimensions 0.12 mm × 0.12 mm × 0.38 mm was selected and mounted on a glass fiber. X-ray diffraction data collection was performed at 293 and 100 K at the Swiss-Norwegian beamline BM01A of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). A Si(111) monochromator was used to select a wavelength of 0.7218 Å. A combination of sagittally focusing monochromator crystal and vertically bent mirror in the beamline provide a focused beam of 0.5 mm diameter. The main experimental characteristics are shown in Table 2. An Oxford Diffraction KM6 diffractometer equipped with a 165 mm diameter CCD area detector was used to record the diffraction images. Temperature control was achieved using a cooled nitrogen gas cryostream supplied by Oxford Cryosystems Ltd. The intensities were integrated and merged with the CrysAlis program (Oxford Diffraction 2002). Lorentz and polarization corrections were applied and absorption effects were corrected using SADABS (*R*_{int} = 0.026 at 293 K and 0.028 at 100 K).

Structure determination and results

A starting structure model was obtained using SHELXL-97 (Sheldrick, 1997). All other calculations have been performed with the JANA2000 system of programs (Petříček *et al.*, 2000). The atomic parameters obtained for Ca1, Ca2, Na and for 9 O atom sites were close to the values reported for pectolite (Prewitt, 1967). Refinement of this model including anisotropic atomic displacement parameters (ADPs) was performed up to *R*[*F* > 3σ(*F*)] = 0.0462 (293 K) and 0.0414 (100 K). *U*_{eq} = 0.015 (293 K) and 0.007 (100 K) appeared essentially higher for the

Table 2. Experimental characteristics for manganooan pectolite, Na(Ca_{1.73}Mn_{0.27})[Si₃O₈(OH)] at 293 and 100 K.

Crystal data		
Cell setting, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
Temperature (K)	293	100
a, b, c (Å)	7.9572(12), 7.0200(10), 7.0006(11)	7.9220(9), 7.0090(9), 6.9770(9)
α, β, γ (°)	90.562(12), 94.962(13), 102.722(13)	90.596(10), 95.037(11), 102.715(12)
V (Å ³)	379.85(10)	376.26(8)
Z	2	2
D_x (Mg mm ⁻³)	2.941	2.971
Radiation type, λ (Å)	synchrotron, 0.7218	synchrotron, 0.7218
μ (mm ⁻¹)	2.51	2.52
Crystal form, color	irregular, colorless	irregular, colorless
Crystal size (mm)	0.12 mm × 0.12 mm × 0.38 mm	0.12 mm × 0.12 mm × 0.38 mm
Data collection		
Diffractometer	Oxford Diffraction KM6	Oxford Diffraction KM6
Data collection method	CCD area detector	CCD area detector
Absorption correction	SADABS	SADABS
No. of measured, independent and observed reflections	3069, 1620, 1344	12897, 1836, 1675
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R_{int}	0.026	0.028
θ_{max} (°)	30.03	30.03
Range of h, k, l	-10 → h → 10; -9 → k → 9; -9 → l → 9	-10 → h → 10; -9 → k → 9; -9 → l → 9
Refinement^a		
Refinement on	F	F
$R[F > 3\sigma(F)]$, $\omega R(F)$, S	0.0355, 0.0451, 2.05	0.0314, 0.0448, 2.21
No. of reflections	1620	1836
No. of parameters	141	141
H-atom treatment	x, y, z have been refined	x, y, z have been refined
Weighting scheme	Based on measured s.u.'s $\omega = 1/(\sigma^2(F) + 0.0001F^2)$	Based on measured s.u.'s $\omega = 1/(\sigma^2(F) + 0.0001F^2)$
(Δ/σ) _{max}	<0.0004	<0.0009
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (eÅ ⁻³)	0.50, -0.59	0.77, -0.66

a: Computer programs: Petříček, V.; Dušek, M.; Palatinus, L. (2000). Jana2000.

Ca1 = M1 position in comparison to the much lower $U_{\text{eq}} = 0.003$ (293 K) and 0.001 (100 K) characteristic of the Ca2 = M2 position. For both 293 and 100 K experimental temperatures, the maximal value of the different Fourier synthesis of electron density, 1.6 eÅ⁻³, corresponded to the strong and well defined maximum in the Ca2 = M2 position; a weaker maximum, about 1.0 eÅ⁻³ at 293 K and 0.4 eÅ⁻³ at 100 K, was also observed in the Ca1 = M1 (Fig. 2a). Refinement of the Ca1 and Ca2 occupations lead to 1.001(3)Ca and 1.100(3)Ca values in the M1 and M2 positions respectively. These results pointed to the presence of significant amount of Mn in the M2 site. Thus Mn was included in the refinement using the restriction [occupation(Mn) + occupation(Ca) = 1] which improved essentially the different Fourier syntheses calculated for both 293 and 100 K experiments (Fig. 2b). The U_{eq} parameters of M1 and M2 positions converged to 0.011 and 0.0067 for 293 and 110 K respectively. Occupation factors were also refined for Na and Si atoms, however their values did not deviate from 1 by less than 0.5 standard deviations and were further fixed to 1. The corresponding residual electron density (Fig. 2b) indicates maxima of 0.21 eÅ⁻³ (293 K), 0.20 eÅ⁻³ (100 K) in M1, and

0.21 eÅ⁻³ (293 K), 0.12 eÅ⁻³ (100 K) in M2. In the vicinity of Si and Na, we observe values varying from -0.1 to 0.1 eÅ⁻³. The resulting occupations of M1 = 0.999(8)Ca + 0.001(8)Mn and M2 = 0.732(8)Ca + 0.268(8)Mn lead to the Na(Ca_{1.73}Mn_{0.27}) cationic composition of the investigated pectolite crystal. The final positional parameters for all atoms are listed in Table 3. Interatomic cation-oxygen distances are shown in Table 4. Geometrical characteristics of the [SiO₄] tetrahedra are listed in Table 5.

The hydrogen bond between O3 and O4 atoms separated by 2.473(3) Å at 293 K and 2.458(2) Å at 100 K is illustrated in Fig. 3. The residual electron density is analysed in the (xy) section containing the O3 and O4 atoms (Fig. 3). One maximum is clearly observed between O3 and O4 atoms at both temperatures (Fig. 3). This maximum, 0.37 eÅ⁻³ (293 K) and 0.35 eÅ⁻³ (100 K), is closer to O3. The coordinates x, y, z of this maximum were included into refinement as H while the isotropic ADP was fixed as $U_{\text{iso}} = 0.0376$. The residual electron density map presented in Fig. 4, right for both temperatures shows a good approximation of the hydrogen bond by one maximum of electron density. The refined coordinates of H are

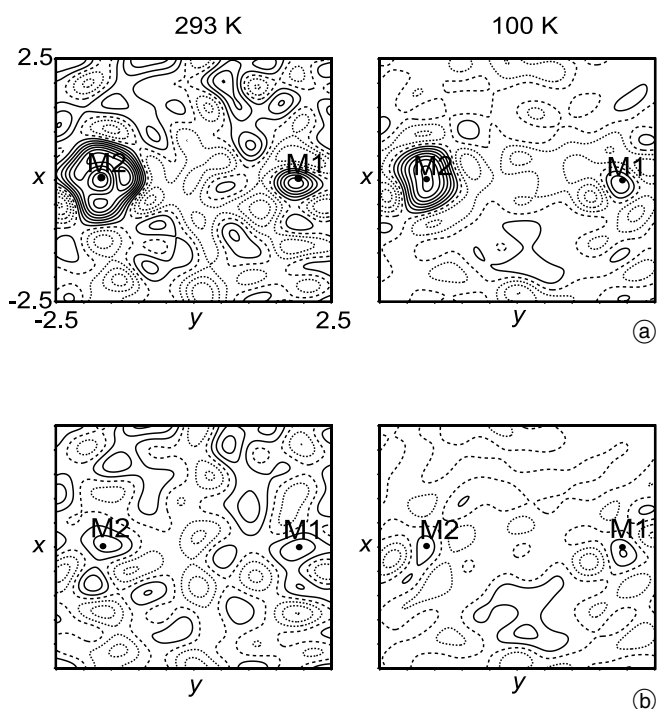


Fig. 2. Difference Fourier xy section (summation along z within 0.1 \AA) crossing the M1 and M2 positions. The section is shown for the 293 K (left) and 100 K (right) measurements. The section has been obtained from (a) the refinement with the M1 = Ca and M2 = Ca and (b) from the refinement yielding M1 = Ca and M2 = $0.268(8)\text{Mn} + 0.732(8)\text{Ca}$. Contours are drawn at intervals of 0.2 e\AA^{-3} ; the zero contours are broken, the negative contours are dashed. Scales are indicated in \AA .

included in Table 3, while the corresponding geometrical characteristics of the hydrogen bond at the two measured temperatures are listed in Table 6.

Discussion

The low values of the R -factors and the low residual electron density (Table 2) justify the composition $\text{Na}(\text{Ca}_{1.73}\text{Mn}_{0.27})[\text{Si}_3\text{O}_8(\text{OH})]$ (Table 1). The refined occupations along with identical ADP parameters of the M1 and M2 positions (Table 3), and the average M1–O and M2–O distances (Table 1 and 4; Fig. 5) justifies the Ca

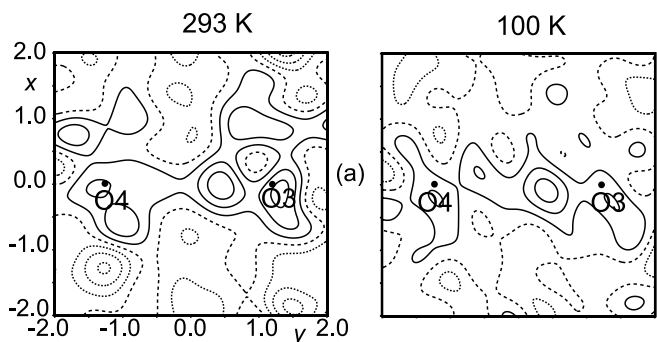


Fig. 3. Illustration of the H position determination in the O4...H...O3 strong hydrogen bond at 293 K (left) and 100 K (right). The difference Fourier xy section (summation along z within 0.5 \AA) crosses the O4 and O3 atoms. Contours and scale drawing is similar to Fig. 2, however, contours are drawn at intervals of 0.1 e\AA^{-3} . The section has been obtained from refinements without H atom.

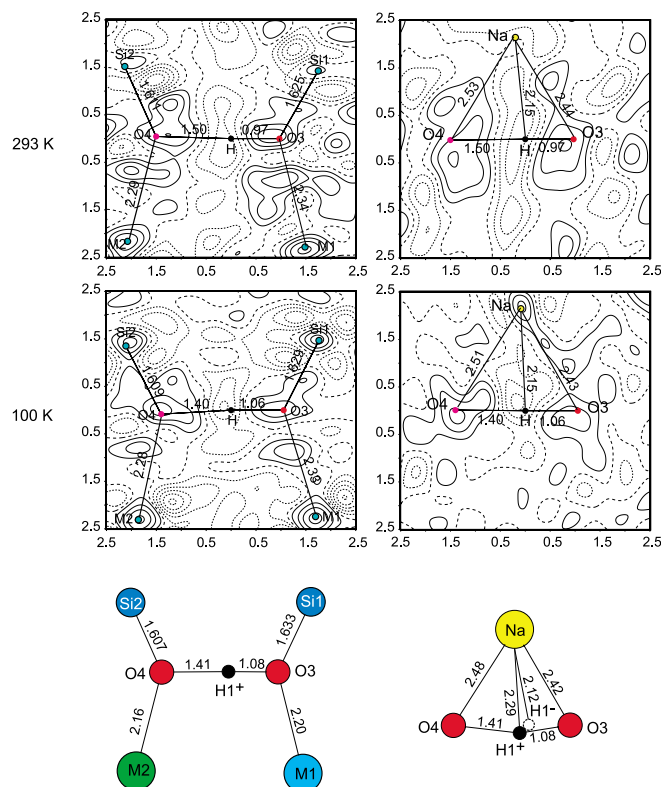


Fig. 4. Illustration of the influence of the asymmetric position of H-bond on the environment around the bonded O3 and O4 atoms. The difference Fourier sections cross O3, Si1 and H1 (left) and O3, Na and H1 (right). Summation normal to the sections within 0.5 \AA covers others shown atoms deviating with less than 0.1 \AA from the selected sections. Contours are drawn at intervals of 0.1 e\AA^{-3} . Scale and distances are indicated in \AA . In the bottom, the corresponding atomic planes are drawn on the basis of structural data obtained for serandite (M1 = M2 = Mn) from neutron diffraction experiment by Jacobsen *et al.* (2000). The dashed contoured circle labeled as H1⁻ indicates position of the electron density maximum. Only H1 position with 84% occupancy is shown, while H2 position (16% occupancy) is missing.

and Mn distribution on M1 and M2 positions. The preference of Mn atoms in the M2 position is in agreement with the crystal chemical analysis published by Takéuchi *et al.* (1976) and Ohashi and Finger (1978). The unit cell parameters measured at 293 K are also in accord with the refined composition since they are in a proper agreement with data obtained previously for the series pectolite – serandite (Fig. 5).

The comparison of the non-hydrogen atom characteristics obtained at two different temperatures (Table 3–5) can be summarized in the following way. The coordinates of all corresponding atomic positions are identical within 1–3 standard deviations (Table 3). In comparison to 293 K, the average Si–O distances in $[\text{SiO}_4]$ tetrahedra are slightly reduced at 100 K by about 0.1% (Table 5) confirming the typical rigid behaviour of the $[\text{SiO}_4]$ group; the decrease of the average M–O distances in the M1, M2 and Na octahedra (Table 4) are slightly higher (about 0.4%). These distances represent the changes responsible for the unit cell volume decrease in the lower temperature structure (Table 2).

The most interesting observation in the lower temperature structure concerns the atoms participating in the strong O3–H...O4 hydrogen bond (Table 6). The

Table 3. Positional parameters for manganooan pectolite, Na(Ca_{1.73}Mn_{0.27})[Si₃O₈(OH)], at 293 K (upper lines) and 100 K (lower lines).

Position	Occupation	x	y	z	U _{eq}
M1	1 Ca	0.85251(9)	0.59369(8)	0.14474(9)	0.0112(2)
		0.85336(6)	0.59378(5)	0.14446(6)	0.00672(16)
M2	0.732(8) Ca + 0.268(8) Mn	0.84816(8)	0.08421(7)	0.13873(8)	0.0109(2)
		0.84894(6)	0.08458(5)	0.13864(5)	0.00666(15)
Si1	1	0.21830(13)	0.40373(11)	0.33730(12)	0.0101(3)
		0.21919(9)	0.40374(8)	0.33767(8)	0.0063(2)
Si2	1	0.21198(13)	0.95569(11)	0.34603(12)	0.0104(3)
		0.21262(9)	0.95553(8)	0.34697(8)	0.0068(2)
Si3	1	0.45050(12)	0.73888(11)	0.14434(12)	0.0109(3)
		0.45141(9)	0.73893(8)	0.14468(8)	0.0070(2)
H	1	0.181(5)	0.637(6)	0.544(6)	0.0376 ^a
		0.181(5)	0.650(5)	0.537(5)	0.0376 ^a
Na	1	0.55319(18)	0.25546(19)	0.3454(2)	0.0217(5)
		0.55351(13)	0.25457(12)	0.34426(13)	0.0112(3)
O1	1	0.6538(3)	0.7937(3)	0.1252(3)	0.0144(8)
		0.6547(2)	0.7933(2)	0.1246(2)	0.0100(5)
O2	1	0.6712(3)	0.2897(3)	0.0553(3)	0.0145(8)
		0.6713(2)	0.2897(2)	0.0546(2)	0.0104(5)
O3	1	0.1880(3)	0.5004(3)	0.5399(3)	0.0142(8)
		0.1876(2)	0.5011(2)	0.5407(2)	0.0086(5)
O4	1	0.1704(3)	0.8477(3)	0.5441(3)	0.0151(8)
		0.1704(2)	0.8470(2)	0.5449(2)	0.0097(5)
O5	1	0.0627(3)	0.3866(3)	0.1733(3)	0.0117(8)
		0.0630(2)	0.3869(2)	0.1733(2)	0.0083(5)
O6	1	0.0595(3)	−0.1019(3)	0.1762(3)	0.0132(8)
		0.0596(2)	−0.1016(2)	0.1762(2)	0.0093(5)
O7	1	0.4008(3)	0.5341(3)	0.2676(3)	0.0142(8)
		0.4016(2)	0.5340(2)	0.2685(2)	0.0094(5)
O8	1	0.3942(3)	−0.0920(3)	0.2800(3)	0.0142(8)
		0.3954(2)	−0.0916(2)	0.2813(2)	0.0102(5)
O9	1	0.2641(3)	0.1929(3)	0.3879(3)	0.0128(8)
		0.2647(2)	0.19314(19)	0.3892(2)	0.0076(5)

a: Unrefined parameters

Table 4. The M–O and Na–O distances (Å) in manganooan pectolite, Na(Ca_{1.73}Mn_{0.27})[Si₃O₈(OH)] at 293 and 100 K.

M1 = Ca	293 K		100 K		
	293 K	100 K	M2 = (Ca _{0.73} Mn _{0.27})	100 K	
–O1	2.331(3)	2.321(2)	–O1	2.268(2)	2.265(1)
–O2	2.343(2)	2.340(1)	–O2	2.275(3)	2.270(2)
–O3	2.339(2)	2.331(1)	–O4	2.291(2)	2.280(1)
–O5	2.443(3)	2.431(2)	–O5	2.408(2)	2.400(1)
–O5	2.379(2)	2.366(2)	–O6	2.345(3)	2.333(2)
–O6	2.389(2)	2.381(1)	–O6	2.379(2)	2.369(2)
Average	⟨2.371⟩	⟨2.362⟩	Average	⟨2.327⟩	⟨2.320⟩
Na–O2	2.303(3)	2.293(2)			
–O3	2.441(2)	2.433(2)			
–O4	2.526(3)	2.508(2)			
–O7	2.558(3)	2.552(2)			
–O8	2.505(3)	2.488(2)			
–O9	2.291(3)	2.283(2)			
Average	⟨2.437⟩	⟨2.426⟩			

O3–O4 distance is shorter by 0.6% (from 2.473 to 2.458 Å), while the average decrease of the O–O distances (including O3–O4) is about 0.2%. A similar observation has been mentioned by Jacobsen *et al.* (2005). The electron density maximum associated with H is slightly shifted from O3 toward O4 (Table 3, Figs. 3 and 4): the O3–H distance increase from 0.97(4) to 1.06(4) Å, while the H...O4 distance decrease from 1.50(4) to 1.40(4) Å. These results indicate that the hydrogen bond becomes stronger and more symmetric at 100 K. The reason of a more symmetric H-bond at lower temperature might be linked to the shift of the H-bond electron density towards the proton position, which has been found at room temperature (Fig. 4). In the present study the ratio $d(\text{O3–H}) : d(\text{H...O4})$ is equal to 0.97 : 1.50 = 0.647 at 293 K and 1.06 : 1.40 = 0.757 at 100 K (Fig. 5d); the last value being very close to 1.078 : 1.413 = 0.762 characteristic of the H1 (main) proton position as reported by Jacobsen *et al.*, (2000).

Table 5. Distances (Å) and angles (°) in [SiO₄] tetrahedra in manganian pectolite, Na(Ca_{1.73}Mn_{0.27})[Si₃O₈(OH)] at 273 and 100 K.

[SiO ₄]	293 K	100 K	[Si ₂ O ₄]	293 K	100 K
Si1–O3	1.625(3)	1.629(2)	Si2–O4	1.611(2)	1.609(2)
Si1–O5	1.597(2)	1.595(2)	Si2–O6	1.605(2)	1.604(2)
Si1–O7	1.653(2)	1.645(2)	Si2–O8	1.660(3)	1.655(2)
Si1–O9	1.635(2)	1.631(2)	Si2–O9	1.642(2)	1.642(1)
Average	⟨1.628⟩	⟨1.625⟩	Average	⟨1.629⟩	⟨1.628⟩
Elongation ^a	1.004211	1.000128	Elongation ^a	1.000805	0.999561
O3–Si1–O5	114.94(14)	114.52(10)	O4–Si2–O6	114.31(12)	114.24(9)
O3–Si1–O7	107.05(11)	107.12(8)	O4–Si2–O8	108.21(13)	108.29(9)
O3–Si1–O9	106.20(12)	106.22(8)	O4–Si2–O9	109.07(11)	109.22(8)
O5–Si1–O7	111.30(12)	111.30(8)	O6–Si2–O8	110.69(13)	110.76(9)
O5–Si1–O9	112.89(11)	113.04(8)	O6–Si2–O9	110.10(12)	110.92(9)
O7–Si1–O9	103.65(13)	103.89(9)	O8–Si2–O9	102.82(12)	102.76(9)
Angle variance ^a	19.077	17.763	Angle variance ^a	14.256	14.600
[Si ₃ O ₄]	293 K	100 K			
Si3–O1	1.596(3)	1.590(2)			
Si3–O2	1.614(2)	1.609(2)			
Si3–O7	1.674(2)	1.674(2)			
Si3–O8	1.673(3)	1.673(2)			
Average	⟨1.639⟩	⟨1.636⟩			
Elongation ^a	1.000757	1.001140			
O1–Si3–O2	115.61(13)	115.59(9)			
O1–Si3–O7	109.52(13)	109.63(9)			
O1–Si3–O8	110.16(12)	110.26(8)			
O2–Si3–O7	108.39(11)	108.34(8)			
O2–Si3–O8	108.46(13)	108.44(9)			
O7–Si3–O8	104.06(12)	103.93(8)			
Angle variance ^a	13.927	15.003			

a: Angle variance (°²) $s^2_q = \bar{2} (q_i - 109.47^\circ)^2/5$ (Robinson *et al.* 1971); quadratic elongation $\langle l \rangle = \bar{2} (l_i/l_{avr})^2/4$

The $d(\text{O3–H}) : d(\text{H} \dots \text{O4})$ ratio characteristic of the manganian pectolite, Na(Ca_{1.73}Mn_{0.27})[Si₃O₈(OH)], at 293 K adds a third dot in the compositional dependence of the H-bond asymmetry in the pectolite – serandite series (Fig. 5d). Two other values of this ratio calculated on the basis of the refined H position are associated with almost pure pectolite, NaCa_{1.943}Mn_{0.057}[Si₃O₈(OH)], and pure serandite, NaMn₂[Si₃O₈(OH)] (Table 1). The manganian pectolite reinforces the tendency of the dependence hinted on the basis of these two values: the higher the content of Mn, the more asymmetric the H-bond.

The influence of the asymmetric position of the H-bond on the environment close to the bonded O3 and O4 atoms can be analysed in the following way. Each of these O atoms is bonded with one Si atom, one M atom, and one Na atom (Figs. 1 and 4). The H-bond constricts the O3 and O4 atoms, the O3 atom being more hitched than O4 because of the H-bond asymmetry. The result of the O3–O4 constriction is an elongation of the O3(4)–Si and O3(4)–M distances (Fig. 4, left) and a decrease of the O3(4)–Na distances (Fig. 4, right). The elongation of O3–Si1 and O4–Si2 can be estimated in relation to O5–Si1 and O6–Si2 respectively, where O5 and O6 are non-bridged O atoms (similar to O3 and O4). The estimation shows that the distance O3–Si1 is essentially (about

1.75%) more elongated than O4–Si2 with 0.25% elongation. Longer O3–Si1 (O3–M1) in comparison to O4–Si2 (O4–M2) (Fig. 4, left) and shorter O3–Na in comparison to O4–Na (Fig. 4, right) are the results of the H-bond asymmetry. The shift of the H-bond electron density maximum towards the O4 affects essentially the O4–Na distance, which decreases from 2.526(3) to 2.508(2) Å (about 0.7%), while the average ⟨Na–O⟩ distance decreases by 0.45%.

The short distance between Na and the maximum of H-bond electron density (Fig. 4, top-right and middle-right) is another interesting detail of the manganian pectolite. This specific feature is also characteristic of the serandite structure (Fig. 4, bottom-right). A comparison between the electron density and the proton positions of H atom (Fig. 4, bottom-right) reported by Jacobsen *et al.* (2000) for serandite hints to a small dipole splitting of H atom, which has a component toward Na⁺ ion. The proton position is about 0.17 Å further away from Na (H1⁺–Na = 2.29 Å) than the maximum of H-electron density (H1–Na = 2.12 Å) (Fig. 4, bottom-right). The Na–H line is close to the *a*-axis direction, hence the absence of the H-bond vibration parallel to *a* (polarized FTIR absorption spectra reported by Hammer *et al.* (1998)) might be due to the H–Na interaction.

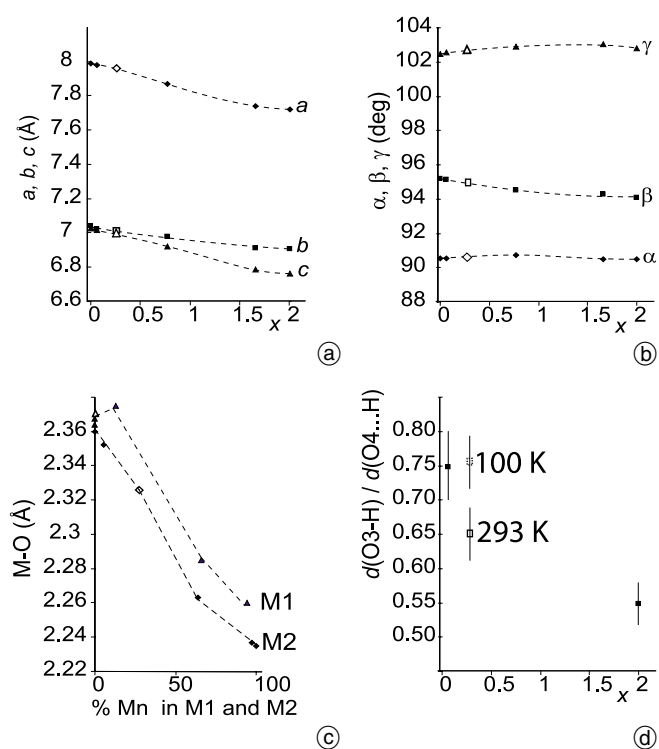


Fig. 5. Some compositionally dependent structural characteristics of the pectolite – serandite series, $\text{Na}(\text{Ca}_{2-x}\text{Mn}_x)[\text{Si}_3\text{O}_8(\text{OH})]$: (a) and (b) unit cell parameters versus x ; (c) $\langle \text{M}-\text{O} \rangle$ interatomic distances in M1 and M2 octahedra versus the composition of the corresponding M position; (d) the ratio of the O3–H and H...O4 distances in the hydrogen bond versus x (refined data obtained with only X-ray experiments). The open signs refer to data obtained in the present work: in (a), (b) and (c), at 293 K; in (d) at 293 and 100 K. The dark signs correspond to previously published data listed in Table 1. The experimental points are connected for a better visualization only.

As mentioned in the introduction, the pectolite structure was studied in the frame of the crystal chemical analysis of pyroxenoids (Ohashi and Finger, 1978). However, the presence of the hydrogen bond in the $[\text{HSi}_3\text{O}_9]$ pectolite chain was ignored in this discussion. Considering the topological role of the H-bond in pectolite, an alternative crystal chemical analysis can be proposed. The topological role of the H-bond in pectolite ($\text{Na}(\text{Ca},\text{Mg})_2[\text{HSi}_3\text{O}_9] = \text{A}^+\text{M}^{2+}_2[\text{HSi}_3\text{O}_9]$) can be interpreted in comparison to the very similar structure of $\text{Li}_2\text{Mg}_2[\text{Si}_4\text{O}_{11}] = \text{A}^+_2\text{M}^{2+}_2[\text{Si}_4\text{O}_{11}]$ (Czank and Bissert, 1993), which is also triclinic with unit cell parameters $a = 8.645$, $b = 7.401$, $c = 6.884$ Å, $\alpha = 104.71$, $\beta = 101.08$, $\gamma = 99.41^\circ$. As shown in Fig. 1, both these structures can be presented as alternating anionic (Si,O) and cationic nets. In $\text{A}_2\text{M}_2[\text{Si}_4\text{O}_{11}]$, the anionic (Si,O)-net consists of $[\text{Si}_4\text{O}_{11}]$ ribbons, which are formed by connected 4-fold rings of $[\text{SiO}_4]$ tetrahedra. In $\text{AM}_2[\text{HSi}_3\text{O}_9]$, the anionic (Si,O,H)-net consists of $[\text{HSi}_3\text{O}_9]$ ribbons, each of them being topo-

logical analogues of $[\text{Si}_4\text{O}_{11}]$ differing by replacement of one $[\text{SiO}_4]$ tetrahedron by (O4...H–O3) group per 4-fold ring (Fig. 1). The two connected O atoms are distant by 2.538 Å in $\text{A}_2\text{M}_2[\text{Si}_4\text{O}_{11}]$ and by about 2.47 Å in $\text{AM}_2[\text{HSi}_3\text{O}_9]$ (pectolite). The similar translation vectors along the ribbon elongation, $c = 6.88$ Å in $\text{Li}_2\text{Mg}_2[\text{Si}_4\text{O}_{11}]$ and $b = 7.01$ Å in pectolite, reinforce this analogy. Hence, the (O4...H–O3) group plays the same topological role as an $[\text{Si}_2\text{O}_4]$ tetrahedron in the 4-fold ring of the (Si,O)-ribbon (Fig. 1). The replacement of $[\text{SiO}_4]^{4-}$ by $(\text{O4}\dots\text{H}-\text{O3})^{3-}$ is consequently followed by the loss of one A^+ atomic position resulting in a rearrangement of the rest A^+ ion in the cationic net, while the arrangement of the M^{2+} ions is identical in both structure (Fig. 1). This topological analysis shows that pectolite cannot be considered as a pyroxenoid and that the $[\text{SiO}_4\text{H}]$ (silanol) entity should not be considered in pectolite.

Summary

The crystal structure of the manganian pectolite with a high content of Mn, $\text{Na}(\text{Ca}_{1.73}\text{Mn}_{0.27})[\text{Si}_3\text{O}_8(\text{OH})]$, has been characterised at 293 and 100 K. It is shown that the O3–H...O4 strong hydrogen bond becomes stronger and more symmetric at 100 K. The shift of the H-bond electron density towards the proton position might be a possible reason of a more symmetric H-bond at lower temperature. The influence of the hydrogen bond on the environment close to the bonded O3 and O4 atoms has been considered: the constriction of O3 and O4 by the asymmetric H-bond gives rise to an asymmetric elongation of the corresponding O–Si distances and a shortening of the Na–O distances. At room temperature, the manganian pectolite justifies the dependence between composition and degree of asymmetry previously hinted: the higher the content of Mn, the more asymmetric H-bond. The proposed Na–H interaction can explain the absence of the H-bond vibration parallel to a observed by Hammer *et al.* (1998). An alternative topological role of the H-bond has been considered: the (O4...H–O3) group in pectolite-serandite structures plays the same topological role as an $[\text{Si}_2\text{O}_4]$ tetrahedron in the 4-fold ring of the (Si,O)-ribbon in $\text{Li}_2\text{Mg}_2[\text{Si}_4\text{O}_{11}]$; hence, pectolite cannot be considered as a pyroxenoid.

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Table 6. The strong hydrogen bond characteristics in manganian pectolite, $\text{Na}(\text{Ca}_{1.73}\text{Mn}_{0.27})[\text{Si}_3\text{O}_8(\text{OH})]$ at 293 and 120 K.

T (K)	$d(\text{O3}-\text{O4})$ (Å)	$d(\text{H}-\text{O3}), d(\text{H}\dots\text{O4})$ (Å); the O3–H...O4 angle ($^\circ$)
293	2.473(3)	0.97(4), 1.50(4); 178(4)
100	2.458(2)	1.06(4), 1.40(4); 177(4)

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