

Relationship between cation substitution and hydrogen-bond system in hydrous pyroxenoids with three-periodic single-chain of SiO₄ tetrahedra: pectolite, murakamiite, marshallussmanite, serandite and tanohataite

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Abstract: Relationships between cation substitution and hydrogen-bond system in hydrous pyroxenoids with a twisted chain consisting of three SiO₄ tetrahedra are investigated by means of chemical and X-ray single-crystal structural analysis. Minerals with the common crystal-chemical formula $M^3(Me^{1+})^{M1,M2}(Me^{2+})_2[Si_3O_8(OH)]$, $Me^{1+} = Na, Li$ and $Me^{2+} = Ca, Mn, Mg$, comprising pectolite, Li-bearing pectolite, murakamiite, marshallussmanite, serandite, and tanohataite were studied. In pectolite and murakamiite two structurally independent octahedrally coordinated sites (M1 and M2) are occupied by Ca. In marshallussmanite, serandite, and tanohataite, the site occupancies at M1 and M2 are $M^1[Ca_{0.764(7)}Mn_{0.236}]^{M2}[Mn_{0.910(8)}Ca_{0.090}]$, $M^1[Mn_{0.758(4)}Ca_{0.242}]^{M2}[Mn_{1.0}]$, and $M^1[Mn_{0.87(2)}Ca_{0.13}]^{M2}[Mn_{0.943(9)}Mg_{0.057}]$, respectively. The Ca and Mn contents primarily influence <M1–O> and <M2–O> distances and hence the unit-cell parameters. The *a*, *b*, and *c* dimensions increase linearly with Ca content. Moreover, high Li concentration at M3 reduces the cell dimensions. The incorporation of smaller Li⁺ ions for larger Na⁺ ions at M3 modifies the coordination polyhedron due to the shift of the atomic position, and it decreases the coordination number of M3. The oxygen atoms at O3 and O4 host the hydroxyl group, and both oxygen sites may act as donor and acceptor of the hydrogen bond. With increasing Mn content the O3···O4 distance reduces from 2.487(3) Å in murakamiite to 2.447(7) Å in tanohataite. A short O3···O4 distance also facilitates disordered hydrogen bonds. The hydrogen-bond system in pyroxenoids with three-periodic single-chain of SiO₄ tetrahedra depends on (1) the Na and Li position at the M3 site and (2) the O3···O4 distance.

Key-words: Murakamiite; Pectolite; Serandite; Tanohataite; Lithium; pyroxenoid; hydrogen bond; crystal structure.

1. Introduction

Pectolite, NaCa₂Si₃O₈(OH), is a representative hydrous pyroxenoid mineral of the pectolite-pyroxene (*p–p*) series with three-periodic single chains of SiO₄ tetrahedra, *dreiereinfach* chains by Liebau (1985). Serandite NaMn₂Si₃O₈(OH), tanohataite LiMn₂Si₃O₈(OH), and marshallussmanite NaCaMnSi₃O₈(OH) also belong to the same group. They typically occur in cavities and fissures of mafic igneous rocks and as rock-forming minerals in alkaline rocks (e.g. Hammer *et al.*, 1998). We recently found a new species of the Li-analogue of pectolite, murakamiite, with simplified formula LiCa₂Si₃O₈(OH), from Iwagi Islet, Ehime Prefecture, Japan (IMA 2016-066, Imaoka *et al.*, 2017). The crystal structures of the hydrous pyroxenoids with three-periodic chain of SiO₄ tetrahedra are isomorphic (*Z* = 2, space group *P*1̄). The Na ↔ Li and Ca ↔ Mn substitutions are common in this series. The same substitutions also occur in the series with the five-periodic chain of SiO₄ tetrahedra (*fünfeinfach* chain), such as nambulite LiMn₄Si₅O₁₄(OH), natronambulite

NaMn₄Si₅O₁₄(OH), marsturite NaCaMn₃Si₅O₁₄(OH) and lithiomarsturite LiCa₂Mn₂Si₅O₁₄(OH). Coupled heterovalent substitutions such as Na⁺ + 2Ca²⁺ ↔ □ + Y³⁺ + Ca²⁺ are observed in barrydawsonite-(Y), Na_{1.5}CaY_{0.5}Si₃O₈(OH), which is a pectolite-related new mineral (Mitchell *et al.*, 2015). The complete solid-solution series between pectolite and serandite was suggested by Schaller (1955). Marshallussmanite (Origlieri *et al.*, 2013) has an intermediate chemical composition between pectolite and serandite but with ordered Ca–Mn distribution, thus qualifying as mineral species.

The crystal structure of the isomorphic pectolite-group minerals contains an undulating chain built by three SiO₄ tetrahedra per repeat unit, two non-equivalent octahedrally coordinated M1 and M2 sites, and a large M3 polyhedron (Buerger, 1956). The M1 and M2 sites are mainly occupied by Ca and Mn. Na and Li ions locate at M3. A strong hydrogen bond is characteristic in minerals of this group as well as of other hydrous pyroxenoids (e.g. Ohashi & Finger, 1981; Nagashima & Armbruster, 2010). The assignment of oxygen donor and acceptor in the hydrogen bond is often

not straightforward because of very short O3···O4 distance. A disordered distribution of hydrogen bonds in pectolite and serandite has been reported repeatedly (Takéuchi & Kudoh, 1977; Jacobsen *et al.*, 2000; Williams & Weller, 2014). Positional displacement of Na and Li positions within large polyhedra also influences the system of hydrogen bonds in the corresponding series with five-periodic chains (Nagashima *et al.*, 2014).

In order to clarify the relation between chemical composition and structural variations in the hydrous pyroxenoid minerals with three-periodic single chain, we investigated the chemical compositions and crystal structures of pectolite, Li-bearing pectolite, marshallussmanite, serandite and tanohataite, using the following techniques: electron-microprobe analysis (EMPA), laser-ablation inductively coupled-plasma mass spectroscopy (LA-ICP-MS), laser-induced breakdown spectroscopy (LIBS), and single-crystal X-ray diffraction methods. Charge distribution (CD) analysis was also performed. The crystal structure of tanohataite was determined in this study for the first time.

2. Experimental methods

2.1. Samples

Pectolite (No. 1): A specimen from the Jeffrey mine, Quebec, Canada, was studied. The fibrous aggregate of white acicular pectolite crystals (<5 mm long) showed silky luster. The sample was found in pegmatitic albitite, typically associated with albite, apophyllite-(KF), grossular, wollastonite, thomsonite-Ca, and tacharanite (Horváth *et al.*, 2013).

Li-bearing pectolite (No. 2) and murakamiite (No. 3): The specimen is from an aegirine-augite albitite exposed on the eastern part of the Iwagi Islet, Ehime, Japan. Metasomatic rocks of the Iwagi Islet contain peculiar Li-rich silicates, such as murakamiite, Li-bearing pectolite, sugilite, and katayamalite in aegirine-augite albitites. Details of occurrence, physical and optical properties, chemical composition, and result of structural analysis are reported by Imaoka *et al.* (2017). Murakamiite and Li-bearing pectolite occur as prismatic or fibrous transparent colorless crystals (<2 mm long). They commonly form aggregates. Murakamiite and Li-bearing pectolite cannot be distinguished with the naked eye because the chemical composition gradually changes from Li to Na dominance.

Marshallussmanite (No. 4): A specimen from the Wessels mine, Kalahari manganese field, South Africa, was studied. White fibrous crystals of marshallussmanite are associated with sugilite. The length of fibrous aggregates is usually less than 2 mm.

Serandite (No. 5): An aggregate of salmon pink prismatic crystals (*ca.* 2 cm long) associated with aegirine from Mont Saint-Hilaire, Quebec, Canada was used. Serandite occurs in small veins in nepheline syenite. The veins mainly consist of microcline, albite and aegirine (Chao *et al.*, 1967).

Tanohataite (No. 6): A specimen from the Tanohata mine, Iwate, Japan was studied. The Tanohata mine is a

manganese-ore deposit formed by metasomatism of a Cretaceous granodiorite intrusion (Nambu *et al.*, 1969). The manganese ore is mainly composed of rhodonite, rhodochrosite, braunite, and tephroite with lens-like veinlets containing tanohataite (Nagase *et al.*, 2012). The studied tanohataite forms an aggregate of fibrous pale brown crystals. Individual crystals have acicular shape (<1 mm long).

2.2. Chemical analysis

2.2.1. Electron microprobe analysis

The chemical compositions of murakamiite, pectolite, marshallussmanite, serandite, and tanohataite were determined using a JEOL JXA-8230 electron microprobe analyzer (EMPA) at the Centre for Instrumental Analysis, Yamaguchi University, Japan. Operating conditions were: accelerating voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 1–10 μm . Wavelength-dispersive X-ray spectra were collected with LiF, PET, and TAP monochromator crystals to identify interfering elements and locate the best wavelengths for background measurements. The abundances of Si, Ti, Al, Cr, V, Fe, Mn, Ni, Mg, Ca, Sr, Ba, Na, K, As, P, F, and Cl were measured. Several elements were below the respective detection limits and are thus not shown in Table 1. The following standards were used: wollastonite (Si, Ca), rutile (Ti), corundum (Al), eskolaite (Cr), $\text{Ca}_3(\text{VO}_4)_2$ (V), hematite (Fe), manganosite (Mn), NiO (Ni), periclase (Mg), $\text{SrBaNb}_4\text{O}_{12}$ (Sr, Ba), albite (Na), K-feldspar (K), GaAs (As), KTiOPO_4 (P), fluorite (F), and halite (Cl). The ZAF correction method was used for all elements. The cation ratio was normalized based on O=8.5 applied to pectolites, murakamiite and serandite, or Si=3 to marshallussmanite and tanohataite. The Li concentration of marshallussmanite and tanohataite was calculated based on charge balance.

2.2.2. Laser-ablation inductively coupled-plasma mass spectrometry (LA-ICP-MS)

The Li_2O concentration of Li-bearing pectolite (Sample No. 2) from Iwagi islet was determined by LA-ICP-MS installed at University of Bern, Switzerland. The instrument consists of a pulsed 193 nm ArF Excimer laser (Lambda Physik, Germany) with an energy-homogenized Geolas Pro optical system (Microlas, Germany), coupled with an ELAN DRC-e ICP quadrupole mass spectrometer (Perkin Elmer, USA) operated in standard mode. The instrument was tuned to robust plasma conditions. A spot size of between 32 and 60 μm was used, and the counting time was >50 s for the background and up to 50 s for sample analysis (beam size permitting). The instrument was calibrated against NIST SRM 610 glass. Data reduction employed the program SILLS (Guillong *et al.*, 2008), with internal standardization using EMPA SiO_2 concentration data. More details about instrumental operating conditions and calculation of the limits of detection can be found in Pettke *et al.* (2012).

Table 1. Average chemical composition of hydrous pyroxenoids with three-periodic single-chain of SiO₄ tetrahedra^a.

	1		2 ^b		3 ^c		4 ^d		5		6 ^d	
	Pectolite Jeffrey mine, Quebec, Canada		Li-bearing pectolite Iwagi islet, Ehime, Japan		Murakamiite		Marshallussmanite Wessels mine, South Africa		Serandite Mont Saint-Hilaire, Quebec, Canada		Tanohataite Tanohata mine, Iwate, Japan	
	Av.	Std.	Av.	Std.	Av.	Std.	Av.	Std.	Av.	Std.	Av.	Std.
wt%	n = 19		n = 40		n = 10		n = 17		n = 19		n = 17	
SiO ₂	53.74	0.31	54.57	0.34	54.98	0.50	50.13	0.57	49.53	0.28	51.37	0.32
TiO ₂	0.01	0.01	0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01
Cr ₂ O ₃	0.02	0.03	n.d.		n.d.		0.01	0.03	0.01	0.03	0.01	0.01
V ₂ O ₃	n.d.		n.d.		n.d.		0.01	0.01	0.01	0.01	0.01	0.01
Fe ₂ O ₃	0.07	0.06	0.24	0.07	0.31	0.04	0.11	0.05	0.70	0.22	0.02	0.04
MnO	0.31	0.16	0.59	0.06	0.56	0.08	22.67	1.02	33.29	0.43	37.39	0.33
MgO	0.01	0.01	0.02	0.01	0.04	0.01	0.08	0.02	0.03	0.01	0.78	0.18
CaO	33.13	0.21	33.36	0.45	33.63	0.29	12.91	0.93	3.65	0.58	1.80	0.10
SrO	n.d.		n.d.		n.d.		0.07	0.08	n.d.		n.d.	
BaO	0.03	0.04	n.d.		n.d.		0.04	0.05	0.03	0.04	0.04	0.04
Na ₂ O	9.41	0.17	6.28	0.30	4.21	0.09	7.95	0.27	8.55	0.13	2.65	0.56
K ₂ O	n.d.		0.01	0.01	0.01	0.01	0.02	0.01	n.d.		0.01	0.01
NiO	n.d.		n.d.		n.d.		0.01	0.01	0.02	0.02	0.01	0.01
Li ₂ O	—		1.31	0.05	2.78	0.49	0.35		—		3.00	
F	0.55	0.14	0.02	0.04	n.d.		0.15	0.16	0.09	0.08	0.05	0.07
Cl	n.d.		n.d.		n.d.		0.01	0.01	n.d.		n.d.	
Total	97.28		96.42		96.53		94.53		95.93		97.15	
—O=	0.23		0.01		0.00		0.07		0.04		0.02	
Cation ratio normalized to												
	O = 8.5		O = 8.5		O = 8.5		Si = 3		O = 8.5		Si = 3	
Si	2.96	0.00	3.00	0.01	2.98	0.02	3		2.99	0.00	3	
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00					0.00	0.00	0.00	0.00	0.00	0.00
V ³⁺							0.00	0.00	0.00	0.00	0.00	0.00
Fe ³⁺	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.03	0.01	0.00	0.00
Mn ²⁺	0.01	0.01	0.03	0.00	0.03	0.00	1.15	0.06	1.70	0.02	1.84	0.02
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.07	0.02
Ca	1.96	0.01	1.97	0.02	1.96	0.02	0.83	0.06	0.24	0.04	0.11	0.01
Sr							0.00	0.00				
Ba	0.00	0.00					0.00	0.00	0.00	0.00	0.00	0.00
Na	1.01	0.01	0.67	0.03	0.44	0.01	0.92	0.02	1.00	0.01	0.30	0.06
K					0.00	0.00	0.00	0.00			0.00	0.00
Ni			0.00	0.00			0.00	0.00	0.00	0.00	0.00	0.00
Li			0.29		0.61		0.08 ^d				0.70 ^d	
Total	5.94		5.97		6.03		5.99		5.96		6.02	
F	0.10	0.02	0.00	0.01			0.03	0.01	0.02	0.02	0.01	0.01
Cl							0.00	0.00				

^a Cr as Cr₂O₃, V as V₂O₃, Fe as Fe₂O₃, and Mn as MnO. OH + F + Cl = 1 apfu.^b Li₂O content was analyzed by LA-ICP-MS. Tabulated concentrations represent the average of 10 measurement spots.^c Li₂O content was analyzed by LIBS. Tabulated concentrations represent the average of 11 measurement spots.^d Li ratio was estimated based on charge balance (sum of positive charges = 17).

2.2.3. Laser-induced breakdown spectroscopy (LIBS)

The Li concentration of separated murakamiite grains, mounted with petropoxy resin on a glass slide, was determined using LIBS installed at Gem Research Japan INC, Osaka. The equipment J200-EC (Applied spectra, USA) employed a 266 nm Nd-YAG laser coupled with an optical emission spectrometer. The lithium peak used for calibration was at a wavelength of 670.706 nm. All analyses were carried out using He gas at 1.30 L/min, and a pulse energy of 2 mJ at 10 Hz. The laser beam diameter

was 35 μm, the gate delay and pre-ablation times were 0.3 μs and 0.3 s, respectively, and 25 shots were calculated. The emission spectra were collected in the 185.177–1050.782 nm spectral range covering the main lines of major elements present in the sample (Na, Li, Ca, Fe, Si). Calibrating samples include NIST 610 and 612, a series of synthetic glass standards prepared from a sodium tetraborate flux covering a range of Li₂O concentrations between 86.5 ppm (NIST 612) and 5 wt% (Li-glass).

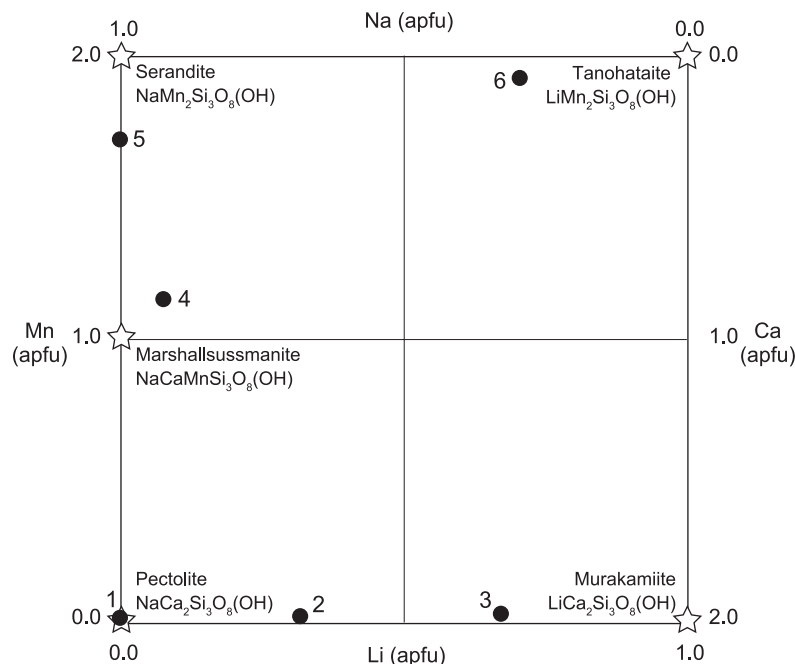


Fig. 1. Compositional variations of pectolite-series minerals. Horizontal and vertical axes show the substitutions of $\text{Mn} \leftrightarrow \text{Ca}$ and $\text{Li} \leftrightarrow \text{Na}$, respectively. Sample numbers locate the analyzed samples and are consistent with those given in Table 1. Star symbols represent the compositions of the pectolite–serandite series minerals derived from their ideal formulae.

2.3. Single-crystal X-ray structure refinement and charge distribution (CD) analysis

X-ray diffraction data for single crystals of all specimens were collected using a Bruker SMART APEX II CCD diffractometer installed at Shimane University, Japan. Crystals were mounted on glass fibers and intensity data were measured at room temperature using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Preliminary lattice parameters and an orientation matrix were obtained from three sets of frames and refined during the integration process of the intensity data. Diffraction data were collected with ω scans at different ϕ settings (ϕ – ω scan) (Bruker, 1999). Data were processed using SAINT (Bruker, 1999). An empirical absorption correction using SADABS (Sheldrick, 1996) was applied. Space group $P1$ was found to be the correct one for all crystals. Crystal structures were refined using SHELXL-97 (Sheldrick, 2008). Scattering factors for neutral atoms were employed throughout.

In case of pectolite and Li-bearing pectolite, the site occupancies of M1 and M2 turned out to be 1.0 Ca within standard deviation. Thus, these occupancies were fixed at 1.0 Ca. In case of marshallsusmanite, the site occupancies at M1 and M2 were both refined with Ca and Mn. Corresponding site occupancies in serandite and tanohataite were refined with Mn. The occupancy of M2 in serandite turned out to be 1.0 Mn within standard deviation and was correspondingly fixed. Occupancies of M1 in both specimens and M2 in tanohataite were below 1.0. Based on the chemical formula the site occupancies at M1 in serandite and tanohataite were subsequently refined with Mn and Ca, and for tanohataite with Mn and Mg at M2. In

all samples, the site occupancy of M3 was refined with Na and Li scattering factors in preliminary refinements. The M3 occupancy in pectolite from Jeffrey mine and serandite from Mont Saint-Hilaire turned out to be 1.0 Na within standard deviation. Thus, the site occupancy at M3 in these minerals was fixed at 1.0 Na. Although closely spaced individual positions of Na and Li were resolved in Li-bearing pectolite from Iwagi islet, their anisotropic displacement parameters were restrained to be equal. The occupancies at Si1–Si3 were fixed at 1.0 Si. Hydrogen positions of the hydroxyl groups were derived from difference-Fourier synthesis and were refined at a fixed value of $U_{\text{iso}} = 0.05 \text{ \AA}^2$ applying a restraint of $\text{O–H} = 0.980(1) \text{ \AA}$ (Franks, 1973). In Li-bearing pectolite, marshallsusmanite, and serandite, two H atom positions were refined. In marshallsusmanite and serandite the hydrogen occupancies at H3 and H4 were fixed to 0.5, whereas in Li-bearing pectolite they were fixed to 0.33 and 0.67, in correspondence with Li and Na occupancies (see discussion section 4.2). The same procedure was applied to the refinement of the murakamiite structure (Imaoka *et al.*, 2017).

In order to validate the refined structures, the charge distribution (CD) analysis was applied following (Nespolo *et al.* 1999, 2001) and Nespolo (2016). The method exploits the experimental bond distances to compute a non-integer coordination number (effective coordination number, ECoN: Hoppe, 1979), and distributes the formal oxidation number, q , of each atom among all its bonds as a function of ECoN. By labeling the computed charges with Q , the q/Q ratio for the cations is the internal criterion for such evaluation (Nespolo *et al.*, 1999, 2001; Nespolo, 2016). $Q(ij)$ and $Q(rs)$ are the charge of PC(ij) and V(rs),

Table 2. Crystallographic data and experimental details of the single-crystal X-ray diffraction analyses.

	1	2	3	4	5	6
	Pectolite	Li-bearing pectolite	Murakamiite ^a	Marshallussmanite	Serandite	Tanohataite
	Jeffrey mine, Quebec, Canada	Iwagi islet, Ehime, Japan	Iwagi islet, Ehime, Japan	Wessels mine, South Africa	Mont Saint-Hilaire, Quebec, Canada	Tanohata mine, Iwate, Japan
Crystal size (mm)	0.015 × 0.05 × 0.20	0.09 × 0.08 × 0.07	0.14 × 0.04 × 0.04	0.02 × 0.055 × 0.135	0.05 × 0.06 × 0.23	0.035 × 0.035 × 0.09
Unit-cell dimensions						
<i>a</i> (Å)	7.9868(2)	7.9429(1)	7.9098(2)	7.7873(3)	7.7260(1)	7.6006(5)
<i>b</i> (Å)	7.0218(2)	7.0275(1)	7.0320(2)	6.9438(2)	6.9058(1)	6.8962(4)
<i>c</i> (Å)	7.0234(2)	7.0014(1)	6.9863(2)	6.8601(2)	6.7764(1)	6.7039(5)
α (°)	90.502(2)	90.567(1)	90.596(2)	90.751(3)	90.514(1)	90.372(6)
β (°)	95.160(2)	95.367(1)	95.589(2)	94.358(2)	94.136(1)	94.488(5)
γ (°)	102.526(2)	102.668(8)	102.767(2)	102.925(2)	102.764(1)	103.054(5)
<i>V</i> (Å ³)	382.79(2)	379.44(1)	376.98(2)	360.33(2)	351.58(1)	341.15(4)
<i>D</i> _{calc} (g/cm ³)	2.88	2.84	2.85	3.20	3.42	3.44
$\theta_{\min}$ (°)	2.6	2.6	2.7	2.7	2.7	2.8
$\theta_{\max}$ (°)	30.5	41.8	30.5	41.3	36.3	30.5
μ (mm ⁻¹)	2.05	2.04	2.05	3.14	3.42	4.29
Collected reflections	2286	15 592	10 439	10 246	12 125	4542
Unique reflections	2286	4906	2297	4413	3368	2045
<i>R</i> _{int} (%)	TWIN (<i>R</i> _{int} of single domain = 2.72%)	1.97	5.39	4.80	1.69	5.53
<i>R</i> _{σ} (%)		2.39	4.22	8.17	1.71	8.86
Miller index limits	0 < <i>h</i> < 11 −10 < <i>k</i> < 9 −10 < <i>l</i> < 9	−13 < <i>h</i> < 14 −12 < <i>k</i> < 13 −13 < <i>l</i> < 13	−11 < <i>h</i> < 11 −10 < <i>k</i> < 10 −9 < <i>l</i> < 9	−14 < <i>h</i> < 14 −12 < <i>k</i> < 12 −12 < <i>l</i> < 11	−12 < <i>h</i> < 11 −10 < <i>k</i> < 11 −11 < <i>l</i> < 11	−10 < <i>h</i> < 10 −9 < <i>k</i> < 9 −9 < <i>l</i> < 9
<i>R</i> ₁ (%)	2.57	2.30	3.28	4.36	1.84	5.40
<i>wR</i> ₂ (%)	12.41	5.54	7.47	10.04	4.83	17.11
No. of parameters	140	146	146	145	143	139
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0853P)^2]$	$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 0.16P]$	$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.32P]$	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2]$	$w = 1/[\sigma^2(F_o^2) + (0.0201P)^2 + 0.17P]$	$w = 1/[\sigma^2(F_o^2) + (0.0948P)^2]$
$\Delta r_{\max}$ (e Å ⁻³)	1.08 (0.03 Å from M2)	0.65 (0.54 Å from O3)	0.56 (0.99 Å from M1)	1.09 (0.74 Å from Si3)	0.56 (0.70 Å from O9)	2.19 (1.44 Å from M3)
$\Delta r_{\min}$ (e Å ⁻³)	−0.69 (1.08 Å from Si1)	−0.65 (0.50 Å from Si2)	−0.56 (0.73 Å from Si2)	−1.02 (0.70 Å from M1)	−0.47 (0.47 Å from M3)	−1.25 (0.81 Å from M1)

^a Imaoka *et al.* (2017)

Note: X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer. Intensity data were measured at room temperature using graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å). Diffraction data were collected with ϕ - ω scan (Bruker, 1999). Data were processed using SAINT (Bruker, 1999). An empirical absorption correction using SADABS (Sheldrick, 1996) was applied. Structural refinement was performed using SHELXL-97 (Sheldrick, 2008). The function of the weighting scheme is $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$, where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$, and the parameters *a* and *b* are chosen to minimize the differences in the variances for reflections in different ranges of intensity and diffraction angle. Space group of all studied specimens is *P*.

Table 3. Number of electrons and cation occupancies.

Site	Observed no. e ⁻	Occupancy
1. Pectolite from the Jeffrey mine		
M1	20 (fix)	Ca _{1.0}
M2	20 (fix)	Ca _{1.0}
M3	11 (fix)	Na _{1.0}
2. Li-bearing pectolite from the Iwagi islet		
M1	20 (fix)	Ca _{1.0}
M2	20 (fix)	Ca _{1.0}
M3	8.39	Na _{0.674(3)} Li _{0.326}
3. Murakamiite pectolite from the Iwagi islet ^a		
M1	20 (fix)	Ca _{1.0}
M2	20 (fix)	Ca _{1.0}
M3	6.31	Li _{0.587(7)} Na _{0.413}
4. Marshallussmanite from the Wessels mine		
M1	21.18	Ca _{0.764(7)} Mn _{0.236}
M2	24.55	Mn _{0.910(8)} Ca _{0.090}
M3	9.98	Na _{0.872(6)} Li _{0.128}
5. Serandite from Mont Saint-Hilaire		
M1	23.81	Mn _{0.758(4)} Ca _{0.242}
M2	25 (fix)	Mn _{1.0}
M3	11 (fix)	Na _{1.0}
6. Tanohataite from the Tanohata mine		
M1	24.37	Mn _{0.87(2)} Ca _{0.13}
M2	24.26	Mn _{0.943(9)} Mg _{0.057}
M3	5.46	Li _{0.69(2)} Na _{0.31}

^a Imaoka *et al.* (2017)

respectively, computed as the result of the distribution of q (ij) and $q(rs)$ based on the CHARDI algorithm, where i and r identify the atomic site, j and s the crystallographic type; PC(ij) represents an atom inside a coordination polyhedron, PC, of the i th chemical species and the j th crystallographic type, V(rs) an atom at the corner (vertex) of a coordination polyhedron, of the r th chemical species and the s th crystallographic type. The σ (%) represents the mean absolute percentage deviation of the computed charges Q with respect to the formal oxidation number q .

3. Results

3.1. Chemical compositions

The average chemical compositions of the studied pectolite (sample No. 1), Li-bearing pectolite (No. 2), murakamiite (No. 3), marshallussmanite (No. 4), serandite (No. 5) and tanohataite (No. 6) are given in Table 1 and Fig. 1. The determined or estimated Li contents in Li-bearing samples are in good agreement with the Li concentration derived from the structural analyses. Pectolite from the Jeffrey mine and serandite from the Mont Saint-Hilaire contain no lithium. The former almost corresponds to the ideal composition of pectolite (Fig. 1). Individual crystals in each studied specimen were relatively homogeneous. The crystals used for structural analysis of samples Nos. 1–5 were picked from the same hand-

specimens on which chemical analyses were collected. Only a polished thin-section of tanohataite (No. 6) was available, thus, the crystal for structural analysis was picked from the thin-section after microprobe analysis.

3.2. Crystal-structure refinements

Crystallographic data and refinement parameters including murakamiite (Imaoka *et al.*, 2017) are summarized in Table 2. Structure refinements in this study converged to R_1 values of 1.84–5.40%. The refined atomic positions and anisotropic displacement parameters are listed in Tables S1 and S2, freely available in the supplementary material linked to the article on the GSW website of the journal: <https://pubs.geoscienceworld.org/eurjmin>. The atomic positions of Na and Li atoms at M3 in Li-bearing pectolite and murakamiite were separately refined. The site-scattering values and determined site-occupancies are listed in Table 3. Selected interatomic distances and distortion parameter for the M1 and M2 octahedra are presented in Table 4. The T–O–T and selected O–M–O angles are listed in Table S3. The crystal structure of murakamiite, which is isomorphic with pectolite, marshallussmanite, serandite, and tanohataite, is shown in Fig. 2.

Tables 5 and S4 show the results of the CD analysis using the CHARDI-2015 program (Nespolo, 2016). The calculated ECoN(ij) for cation sites is listed in Table 5. Excluding tanohataite, the σ value ranges from 1.0 to 2.2% for PC (ij), and from 2.7 to 4.2% for V(rs) (Table S4), which ensured validity of the refined structures. Relative large σ values obtained for tanohataite (6.4% for the center atom and 7.8% for the vertex of coordination polyhedra) are obviously due to the undetermined hydrogen position. The large deviation of $Q(rs)$ from the expected value (–2.00) of O3 (–1.57) and O4 (–1.56) indicates the presence of the H atom between O3 and O4 (Table S4).

4. Discussion

4.1. Cation distributions at the M1 and M2 sites and structural variations

In each structure, the M1O₆ octahedron is slightly larger than M2O₆ (Table 4). Both M1 and M2 sites are fully occupied by Ca ions in pectolite and murakamiite (Table 3). In serandite and tanohataite, Mn²⁺ ions (^{VI}Mn²⁺ = 0.83 Å in Shannon, 1976) predominantly occupy M1 and M2. The Ca ions (^{VI}Ca²⁺ = 1.00 Å) prefer M1 relative to M2 (Table 3). Small amounts of Ca in tanohataite also occupy M1, whereas the smaller Mg ions (^{VI}Mg²⁺ = 0.72 Å) are assumed to occupy M2 (<M1–O> = 2.236 Å and <M2–O> = 2.225 Å in Table 4). In marshallussmanite, the smaller M2 site (<M2–O> = 2.231 Å) is predominantly occupied by Mn²⁺, whereas Ca ions prefer the M1 site (<M1–O> = 2.349 Å). The determined cation distributions at M1 and M2 are consistent with most previous studies (Prewitt, 1967; Takéuchi *et al.*, 1976; Ohashi & Finger, 1978; Jacobsen *et al.*, 2000; Origlieri *et al.*, 2013; Rozhdestvenskaya &

Table 4. Selected interatomic distances (Å) and distortion parameters for the M1 and M2 octahedral sites^a.

	1	2	3	4	5	6
	Pectolite	Li-bearing pectolite	Murakamiite ^b	Marshallussmanite	Serandite	Tanohataite
M1-O1	2.317(3)	2.3083(7)	2.300(2)	2.312(2)	2.2369(9)	2.182(4)
M1-O2	2.331(3)	2.3374(7)	2.343(2)	2.355(2)	2.2772(9)	2.267(4)
M1-O3	2.340(2)	2.3346(8)	2.333(2)	2.310(2)	2.2259(9)	2.175(5)
M1-O5	2.381(2)	2.3912(7)	2.403(2)	2.322(2)	2.2187(8)	2.191(5)
M1-O6	2.386(4)	2.3823(7)	2.387(2)	2.376(2)	2.3004(8)	2.276(4)
M1-O5'	2.429(4)	2.4302(7)	2.428(2)	2.418(2)	2.3697(9)	2.327(4)
Mean(VI)	2.364	2.3640	2.366	2.349	2.2715	2.236
DI (oct)	0.015	0.016	0.017	0.015	0.019	0.024
σ_{θ} (oct) ²	69.30	73.19	76.64	120.86	97.20	93.01
M2-O1	2.308(3)	2.2863(7)	2.275(2)	2.161(2)	2.1760(8)	2.151(4)
M2-O2	2.312(3)	2.3121(7)	2.318(2)	2.168(2)	2.1921(9)	2.223(4)
M2-O4	2.321(2)	2.3157(8)	2.318(2)	2.201(2)	2.1648(8)	2.144(5)
M2-O6	2.368(4)	2.3655(7)	2.367(2)	2.242(2)	2.2488(8)	2.226(5)
M2-O6'	2.410(2)	2.4024(7)	2.398(2)	2.271(2)	2.2590(8)	2.269(4)
M2-O5	2.431(4)	2.4152(7)	2.410(2)	2.338(2)	2.3663(8)	2.337(4)
Mean (VI)	2.358	2.3495	2.348	2.231	2.2345	2.225
DI (oct)	0.019	0.019	0.019	0.024	0.025	0.024
σ_{θ} (oct) ²	70.50	67.90	65.47	56.44	80.12	84.19
		Na–Oi	Li–Oi	Li–Oi	Na–Oi	
M3-O9	2.296(2)	2.235(1)	2.310(9)	2.24(1)	2.170(4)	2.250(2)
M3-O2	2.307(2)	2.266(1)	2.071(9)	2.01(1)	2.233(4)	2.261(2)
M3-O3	2.467(2)	2.411(1)	2.336(8)	2.30(1)	2.354	2.353(2)
M3-O7	2.537(3)	2.528(1)	2.197(8)	2.17(1)	2.545(4)	2.591(2)
M3-O4	2.496(3)	2.462(1)			2.399(4)	2.532(2)
M3-O8	2.526(3)	2.511(1)			2.489(4)	2.434(2)
M3-O8'						2.721(2)
Mean	2.438(VI)	2.402(VI)	2.229(IV)	2.18(IV)	2.365(VI)	2.449(VII)
Si1-O5	1.600(2)	1.6001(7)		1.600(2)		1.598(2)
Si1-O3	1.625(2)	1.6208(8)		1.616(2)		1.616(2)
Si1-O9	1.632(3)	1.6324(7)		1.637(2)		1.624(2)
Si1-O7	1.645(2)	1.6447(7)		1.643(2)		1.647(2)
Mean (IV)	1.625	1.6245		1.624		1.621
Si2-O4	1.603(2)	1.6085(8)		1.610(2)		1.611(2)
Si2-O6	1.605(2)	1.6044(7)		1.603(2)		1.610(2)
Si2-O9	1.642(2)	1.6377(7)		1.638(2)		1.623(2)
Si2-O8	1.656(2)	1.6477(8)		1.640(2)		1.648(2)
Mean (IV)	1.626	1.6245		1.623		1.623
Si3-O1	1.595(2)	1.5922(7)		1.588(2)		1.595(2)
Si3-O2	1.609(2)	1.6081(7)		1.611(2)		1.608(2)
Si3-O7	1.667(2)	1.6673(7)		1.663(2)		1.668(2)
Si3-O8	1.672(2)	1.6678(7)		1.663(2)		1.665(2)
Mean(IV)	1.636	1.6338		1.631		1.634
O3...O4	2.472(3)	2.479(1)		2.487(3)		2.462(3)

^a $DI(\text{oct}) = 1/6 \sum |R_i - R_{\text{av.}}|/R_{\text{av.}}$ (R_i : M–O bond length, $R_{\text{av.}}$: average M–O distance for an octahedron) (Baur, 1974) and $\sigma_{\theta}(\text{oct})^2 = \sum_{i=1}^{12} (\theta_i - 90^\circ)^2 / 11$ (θ_i : O–M–O angle) (Robinson *et al.*, 1971).

^b Imaoka *et al.* (2017).

Table 5. Calculated effective coordination number, ECoN(*ij*) for cations sites.

		M1	M2	M3 (Li)	M3 (Na)	Si1	Si2	Si3	H3	H4
1	Pectolite	5.94	5.91	—	6.00	3.99	3.97	3.94	1.83	—
2	Li-bearing pectolite	5.94	5.91	3.99	5.72	3.99	3.98	3.94	1.81	1.82
3	Murakamiite ^a	5.92	5.91	3.79	5.39	3.99	3.99	3.94	1.81	1.80
4	Marshallussmanite	5.94	5.84	—	6.02	3.98	3.99	3.94	1.81	1.78
5	Serandite	5.89	5.81	—	6.44	3.98	3.98	3.96	1.83	1.81
6	Tanohataite	5.86	5.81	5.25	—	3.99	3.99	3.97	—	—

^a Imaoka *et al.* (2017).

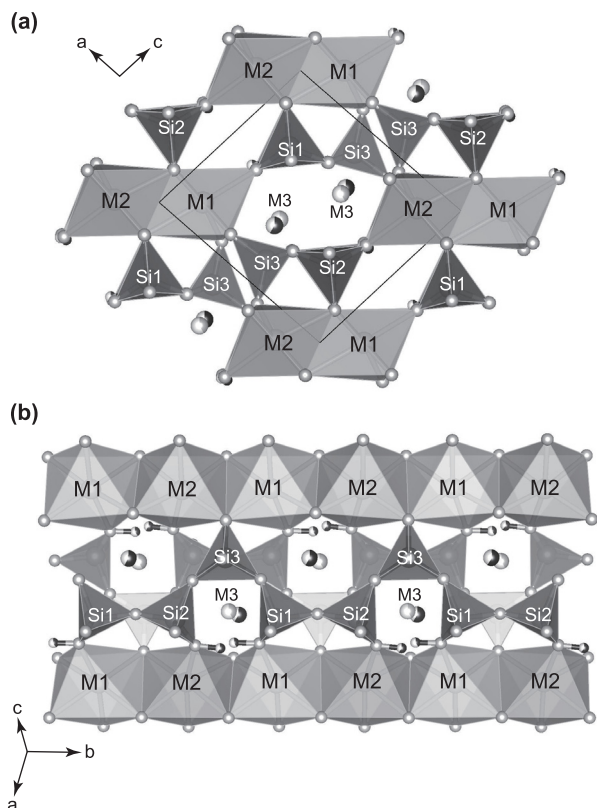


Fig. 2. Crystal structure of murakamiite, isomorphic with pectolite, serandite, marshallussmanite, and tanohataite, projected parallel to **b** (a), and the arrangement of octahedra with three-periodic silicate chains, projected on (101) (b). Images drawn with the program VESTA 3 (Momma & Izumi, 2011).

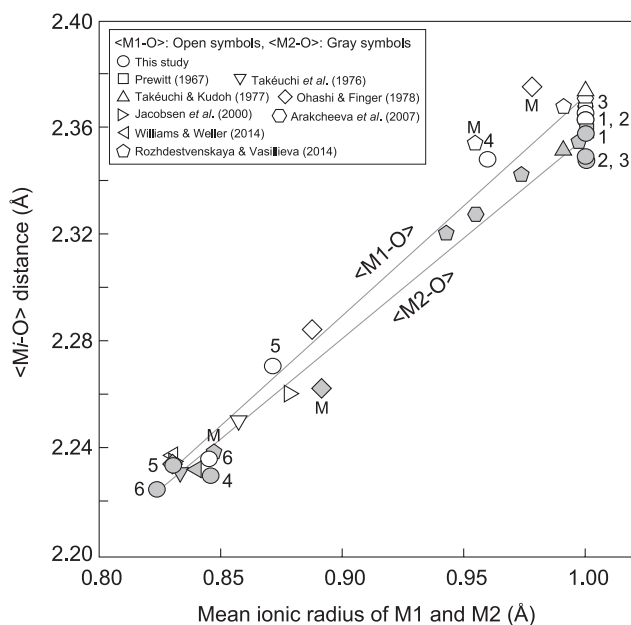


Fig. 3. Relationship between $\langle \text{M1-O} \rangle$ distance and the mean ionic radius (Shannon, 1976) of M1 and M2 (Å). Open and gray symbols represent the $\langle \text{M1-O} \rangle$ and $\langle \text{M2-O} \rangle$ distances, respectively. Sample numbers refer to those given in Table 1. The functions of regression lines are $\langle \text{M1-O} \rangle = 0.819x + 1.553$ ($R^2 = 0.97$) and $\langle \text{M2-O} \rangle = 0.752x + 1.605$ ($R^2 = 0.99$). The symbols labelled “M” represent the data obtained from marshallussmanite by Ohashi & Finger (1978) and Rozhdestvenskaya & Vasilieva (2014).

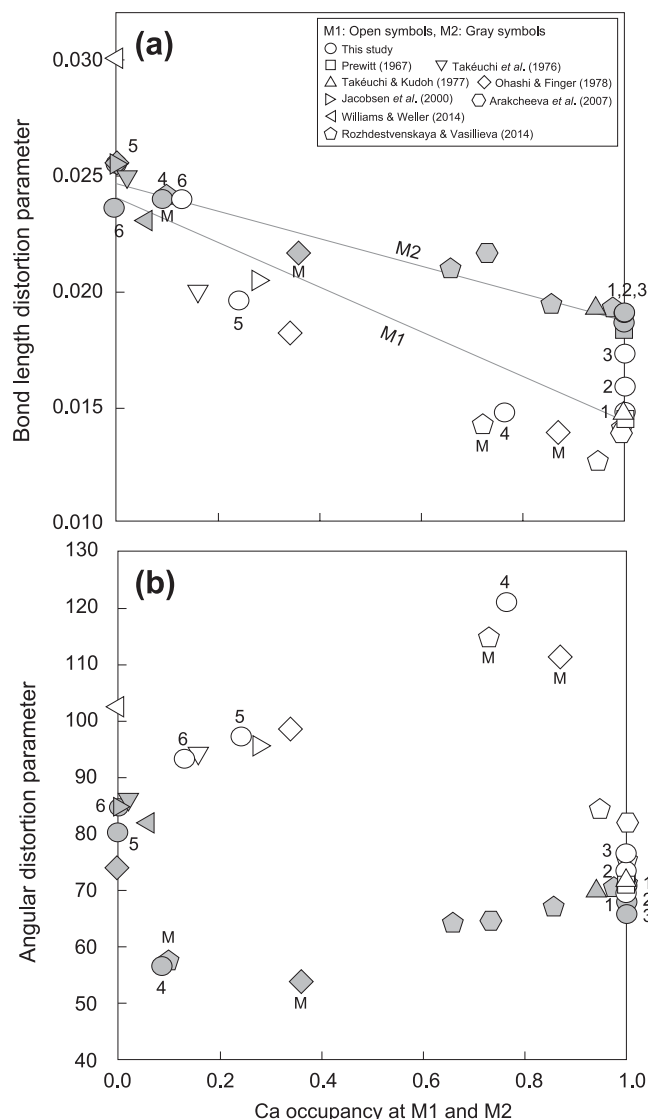


Fig. 4. Bond-length distortion (a) and angular distortion (b) parameters as a function of Ca occupancy at M1 and M2. Definitions are given in Table 4. Open and gray symbols represent M1 and M2, respectively. The functions of regression lines of the M1 and M2 octahedra in Fig. 4a are $y = -0.010x + 0.024$ ($R^2 = 0.75$), and $y = -0.006x + 0.025$ ($R^2 = 0.94$), respectively.

Vasilieva, 2014). The only exception is serandite reported by Williams & Weller (2014), in which the M2 site was predominantly occupied by Ca.

The $\langle \text{M1-O} \rangle$ and $\langle \text{M2-O} \rangle$ distances increase with increasing mean ionic radius at each site (Fig. 3). The M2O_6 octahedron shows isotropic expansion. In the M1O_6 octahedron, the M1-O_5 distance is strongly variable from 2.19 Å in tanohataite to 2.40 Å in murakamiite (Table 4). The other M1-O_i distances increase regularly with ionic radius. Rozhdestvenskaya & Vasilieva (2014) pointed out that $\langle \text{M1-O} \rangle$ is almost constant between 1.0–2.0 Ca apfu (corresponding to 0.0–1.0 ($\text{Mn}^{2+} + \text{Fe}^{2+}$) apfu) in the pectolite-serandite series and it linearly decreases with Ca < 1.0 apfu, and $\langle \text{M2-O} \rangle$ varies *vice versa*. As a result of this study, it is concluded that $\langle \text{M1-O} \rangle$ and $\langle \text{M2-O} \rangle$

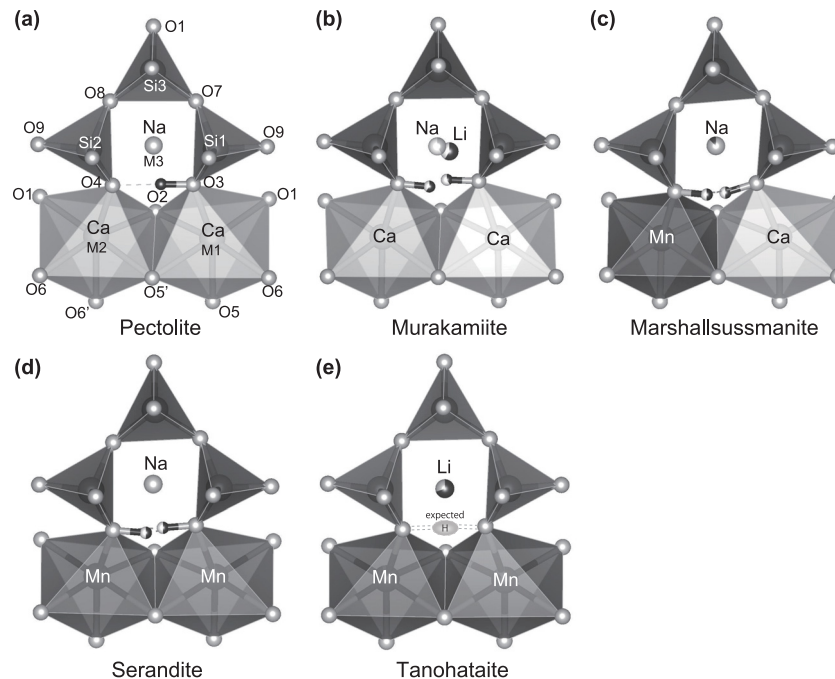


Fig. 5. Topological cation environment around M3 in pectolite (a), murakamiite (b), marshallsussmanite (c), serandite (d), and tanohataite (e). The expected H position was drawn in Fig. 5c though it could not be determined.

are directly influenced by the cation occupation at each site. As shown in Fig. 4a, an increase in Ca content reduces the bond-length distortion (Baur, 1974) of M1 and M2. On the other hand, the angular distortion (Robinson *et al.*, 1971) has no systematic variation with Ca and Mn contents (Fig. 4b). Figure 5 shows the topological environment of the M1 and M2 octahedra. The combination of extension of M1–O1 and M1–O2 and shortening of M2–O1 and M2–O2 distances increases the O1–M1–O2 angle (105.85°) and decreases that for O1–M2–O2 (98.39°) (Tables 4 and S3, Fig. 5c). The smaller size of M_2O_6 octahedra due to Mn^{2+} substitution reduces the lengths of the O1–O6 and O2–O5' shared edges with M_1O_6 (Fig. 5c). It also causes the change of the O1–M2–O6 and O2–M2–O5' angles. If both M1 and M2 are predominantly occupied by the same cation, Ca(M1)–Ca(M2) or Mn(M1)–Mn(M2), the angular distortion may be inhibited when compared to an occupancy by different cations, Ca(M1)–Mn(M2) (Table 4).

The unit-cell volumes of the studied specimens increase with increasing Ca content (Fig. 6a), which is also supported by previous studies (Prewitt, 1967; Takéuchi *et al.*, 1976; Ohashi & Finger 1978; Jacobsen *et al.*, 2000; Origlieri *et al.*, 2013; Williams & Weller, 2014). The *a*, *b* and *c* dimensions also lengthen with increasing Ca content, but the increase rates of the *a* and *c* dimensions are steeper than that of the *b* dimension (Fig. 6b). As shown in Fig. 2b, the variation of the *b* dimension is identical to that of the Si_3O_9 -chain length. In agreement with results by Takéuchi & Kudoh (1977), the length of the three-periodic single chain increases with Ca content at the octahedral sites. The chain length is 7.02–7.03 Å in the Ca-dominant series, >6.944 Å in marshallsussmanite, and > ca. 6.90 Å

in the Mn-dominant series (Fig. 6b). The crystal structure of pyroxenoids is mainly built by a stack of two different layers parallel to [101], one consists of SiO_4 tetrahedra and the other of MO_6 octahedra (Fig. 2a). The substitution of Ca for Mn^{2+} makes the MO_6 -layer thicker, which leads to lengthening of the *a* and *c* dimensions rather than of the *b* dimension. In addition, the unit-cell volume decreases with increasing substitution of Na by Li ($^{\text{VI}}\text{Li}^+ = 0.76 \text{ \AA}$, $^{\text{VI}}\text{Na}^+ = 1.02 \text{ \AA}$) in sets of both Ca- and Mn-dominant samples [in Fig. 6a, pectolite (No. 1) vs. murakamiite (No. 3), and serandite (No. 5) vs. tanohataite (No. 6)].

4.2. Configuration of M3 polyhedra and hydrogen bond system

According to the refinements, the site occupancy of M3 is $\text{Na}_{0.674(3)}\text{Li}_{0.326}$ in Li-bearing pectolite, $\text{Li}_{0.587(7)}\text{Na}_{0.413}$ in murakamiite, $\text{Na}_{0.872(6)}\text{Li}_{0.128}$ in marshallsussmanite, and $\text{Li}_{0.69(2)}\text{Na}_{0.31}$ in tanohataite (Table 3). The M3 polyhedron of Li-free pectolite has six-fold coordination with the apices O9, O2, O3, O4, O8, and O7 (Table 4), supported by CD calculation (Table 5). The substitution of Na^+ ions by Li^+ ions at M3 modifies the arrangement of O atoms defining the M3 polyhedra. Due to the small ionic radius of Li^+ , the atomic position at M3 shifts towards the SiO_4 tetrahedron, and the ligands O2, O3, O7 get closer to the cation at M3 (Fig. 5b). As a result, the Li-centered M3 polyhedron is no longer six-fold coordinated, but it adopts a four-fold coordination. The decrease of coordination number of M3 is also supported by the calculated ECoN (3.79) for M3 of murakamiite (Table 5). On the other hand, in the Mn-analogue series, the M3 site is seven- and six-fold coordinated in serandite and tanohataite, respectively

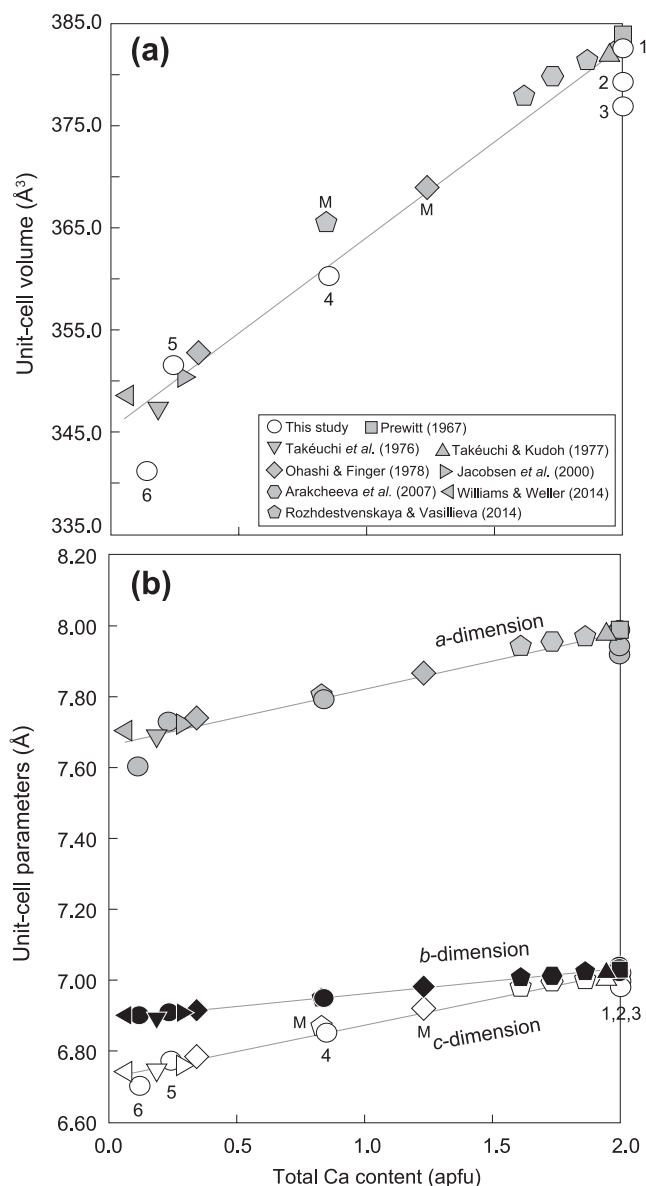


Fig. 6. Variation of unit-cell volume (Å³) (a) and parameters (Å) (b) as a function of total Ca content (apfu). In Fig. 6b, the unit-cell parameter *a*, *b*, and *c* are represented as gray, closed, and open symbols. The plots labelled “M” represent the data obtained from marshallussmanite by Ohashi & Finger (1978) and Rozhdestvenskaya & Vasilieva (2014). The functions of regression lines are unit-cell volume (Å³) = 18.66*x* + 345.40 (*R*² = 0.97) and *a* (Å) = 0.156*x* + 7.665 (*R*² = 0.94), *b* (Å) = 0.072*x* + 6.888 (*R*² = 0.99), and *c* (Å) = 0.148*x* + 6.728 (*R*² = 0.98).

(Table 4). The calculated ECoN varies from 6.44 for serandite to 5.25 for tanohataite (Table 5). The decrease of oxygen coordination due to the substitution of Li for Na has also been reported for nambulite-group minerals belonging to the hydrous pyroxenoids with five-periodic chain (Murakami *et al.*, 1977; Nagashima *et al.*, 2014). The increased Li content reduces the eight-coordinated Na-dominant site to a distorted six-fold coordination (Murakami *et al.*, 1977) or five-fold coordination (Nagashima *et al.*, 2014), because the smaller ionic radius of Li⁺ compared to that of Na⁺ prefers a position in a

smaller “pocket” within the large polyhedron and the Li⁺ ions are displaced from the gravity center of the polyhedron. The off-center shift of the cation at M3 is listed in Table 6. The center of gravity was calculated assuming eight-fold coordination for all specimens. The cation shift from the center of gravity with increasing Li content is confirmed for each of the Ca- and Mn-dominant series (Fig. 7) but the effect is more pronounced for the Ca-dominant series. In tanohataite, no significant modification of atomic position can be detected despite the high Li content (Fig. 7). The size of the M3 polyhedron of the Mn-dominant series is inherently smaller than that of the Ca-dominant series if the distances between the cation and the first six neighbor oxygen atoms are compared (<M3–O> = 2.438 Å in pectolite and 2.398 Å in serandite, Table 4).

The H positions and the hydrogen bonding system were determined for pectolites, murakamiite, marshallussmanite, and serandite. One H position (H3) was determined in the pectolite structure. Split H positions (H3 and H4) were determined in Li-bearing pectolite, murakamiite, marshallussmanite and serandite. Thus, the hydrogen bonding systems are O3–H3···O4 and O4–H4···O3. The result of CD calculations for tanohataite also suggests that the H atom is placed between the O3 and O4 site (Table S4); however, the role of donor/acceptor oxygen cannot be determined.

The Li(M3)–O3 distance in murakamiite [2.30(1) Å] is shorter than Na(M3)–O3 in pectolite [2.467(2) Å] and the relation for the M3–O4 distances is reversed. The M3–O4 distance of murakamiite [2.71 Å (not shown in the list)] is longer than that in pectolite [2.496(3) Å] (Table 4). The variation of M3–O3 and M3–O4 distances implies that the donor and acceptor oxygen atoms are switched in Na- and Li-analogue series. In each Li-bearing pectolite and murakamiite, the Li(M3)–O3 distance is shorter than the Na(M3)–O3 distance, and the Li(M3)–O4 distance is longer than the Na(M3)–O4 distance. Decreasing M3–O3 and increasing M3–O4 distances observed in Li-analogue murakamiite causes a higher positive charge for O3 and a smaller one for O4. Thus, O4 is more privileged to bind to H⁺ and behaves as a donor whereas O3 acts as acceptor.

In Li-free pectolite from the Jeffrey mine (sample No. 1), only O3 seems to play a role as donor based on the determined hydrogen position. However, *Q*(*rs*) for O3 (−2.18) is lower than the theoretical value of −2, and that for O4 is higher, −1.91 (Table S4). This implies that H partially also bonds to O4, and a distribution ratio of 80% for O3 and 20% for O4 may be estimated. The O3···O4 distances for the Ca-dominant series are 2.47–2.49 Å, which is similar to pectolite (Takéuchi & Kudoh, 1977). These authors also assumed O3 as donor for the OH group but they could not exclude the random (= disorder) model that eventually both O3 and O4 may act as H donors and acceptors. The short O···O distance of 2.38 Å in scheuchzerite, containing the [Si₉O₂₅(OH)] loop-branched chain (Brugger *et al.*, 2006), is assumed to show a disordered hydrogen bond between the two closely spaced oxygen atoms. The disordered hydrogen bond (O3···O4 =

Table 6. The off-center shift of the cation at M3.

	Li content at M3	Off-center shift (Å)	Calculated position of center of gravity			References
			<i>x</i>	<i>y</i>	<i>z</i>	
1) Pectolite	—	0.542	0.4289	0.7320	0.5801	This study
2) Li-bearing pectolite	0.326	ave. 0.689	0.4294	0.7324	0.5796	
Off-center shift of Na and Li is 0.542 and 0.835 Å, respectively.						
3) Murakamiite ^a	0.587	ave. 0.704	0.4303	0.7327	0.5793	
Off-center shift of Na and Li is 0.533 and 0.874 Å, respectively.						
4) Marshallsussmanite	0.128	0.4987	0.4259	0.7360	0.5802	
5) Serandite	—	0.4612	0.4253	0.7330	0.5822	Prewitt (1967)
6) Tanohataite	0.69	0.525	0.4267	0.7325	0.5821	
Pectolite	—	0.530	0.3711	0.7167	0.5314	
Pectolite	—	0.539	0.3706	0.7168	0.5313	Takéuchi & Kudoh (1977)
Pectolite	—	0.531	0.4279	0.7332	0.5801	Arakcheeva <i>et al.</i> (2007)
Pectolite (Sample No. 2)	—	0.540	0.4287	0.7321	0.5802	Rozhdestvenskaya & Vasilieva (2014)
Pectolite (Sample No. 4)	—	0.536	0.4284	0.7327	0.5802	
Pectolite (Sample No. 6)	—	0.527	0.4278	0.7335	0.5802	
Marshallsussmanite (Sample No. 8)	—	0.491	0.4257	0.7357	0.5805	Ohashi & Finger (1978)
Marshallsussmanite (SCH)	—	0.742	0.4015	0.7742	0.5573	
Serandite (SRN)	—	0.698	0.4024	0.7365	0.6185	
Serandite	—	0.683	0.4015	0.7703	0.5621	Takéuchi <i>et al.</i> (1976)
Serandite	—	0.687	0.4013	0.7706	0.5618	Jacobsen <i>et al.</i> (2000)
Serandite	—	0.633	0.3999	0.7701	0.5640	Williams & Weller (2014)

^a Imaoka *et al.* (2017).

Note: Center of gravity was calculated using the eight O atoms surrounding the cation at M3, such as O9, O2, O3, O4, O8, O7, O8' and O7'.

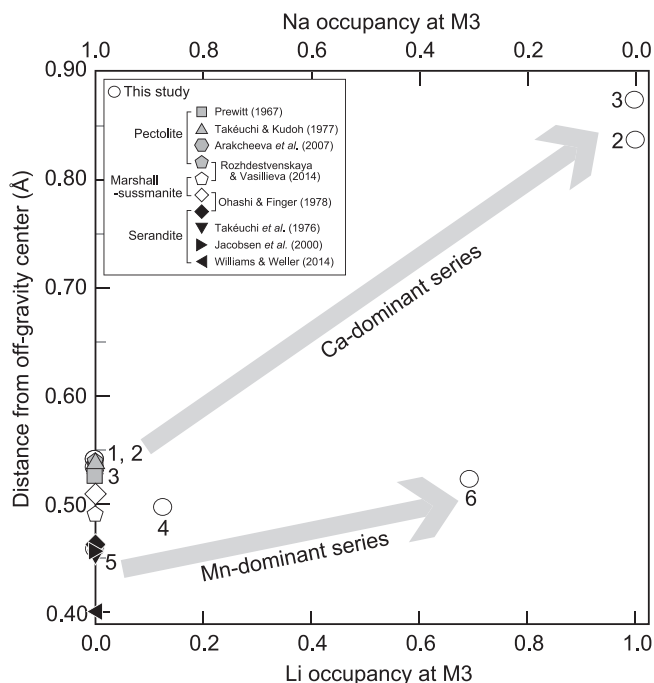


Fig. 7. The cation shift (Å) from the center of gravity vs. Li and Na content at M3 (apfu) based on the data listed in Table 6. The Na and Li positions at M3 in murakamiite and Li-bearing pectolite were separately determined. Thus, the off-center distance was estimated from individual atomic positions. The shifts derived from Li and Na positions are plotted at 1.0 Li and at 1.0 Na, respectively. Sample numbers represent those given in Table 1.

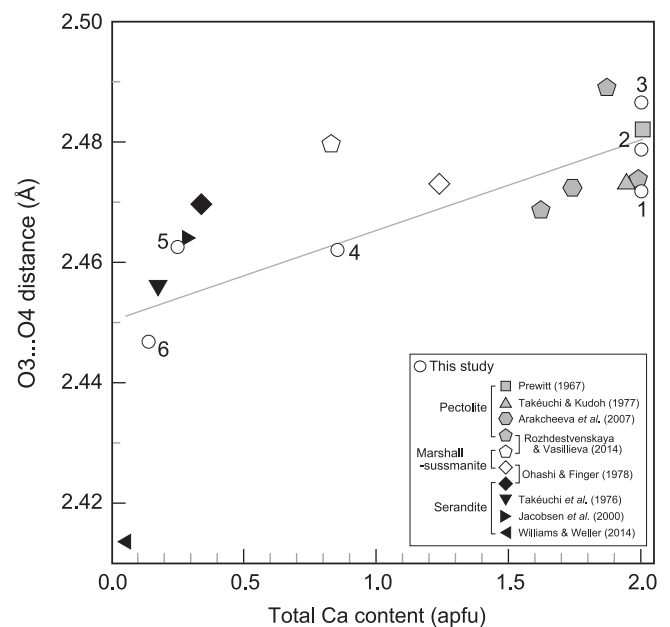


Fig. 8. Relationship between the distance of O3...O4 distance (Å) and the total Ca content (apfu). The function of the regression line is $y = 0.015x + 2.450$ ($R^2 = 0.50$).

2.46 Å, O3—H...O4 ~ 84% and O4—H...O3 ~ 16%) in end-member serandite has been reported by Jacobsen *et al.* (2000). Furthermore, a TOF neutron-diffraction study of serandite (Williams & Weller, 2014) indicated a clear

preference (~60–80%) for the hydrogen atom to bind to O3 at and below room temperature, while the distribution between the O3 and O4 sites approached statistical 50:50% at high temperature. In their study, the O3···O4 distance varies from *ca.* 2.41 Å (4 K–298 K) to 2.50 Å (800 K). The O3···O4 distance in our serandite was 2.46 Å. On the other hand, the study of pectolite by Arakcheeva *et al.* (2007) reported a more symmetric H-bond at lower temperature (100 K) relative to room temperature (293 K). In their study, O3–H and H···O4 distances are 0.97 and 1.50 Å at 293 K and change to 1.06 and 1.40 Å at 100 K, respectively. The two H positions H3 and H4 were also confirmed in this study, despite the fact that only Na ions occupy the M3 site. In the Mn-dominant series, a O3···O4 distance is considered to dominate the hydrogen bonding system. As mentioned above, an increase in Mn content decreases the length of the chain period (*b*-dimension in Fig. 6b). In fact, the O3···O4 distance and the chain length are positively correlated (Fig. 8). Thus, Mn and Ca distributions at M1 and M2 affect the hydrogen-bonding system in an indirect manner because the Ca content and the chain length are also positively correlated. The main factors influencing the hydrogen-bond system in pyroxenoids with three-periodic chain therefore are (1) the true positions of Na and Li at M3 related to the configuration and size of the M3 polyhedra (Figs. 5 and 7), and (2) the O3···O4 distance related to the Ca and Mn content at M1 and M2 (Fig. 8). The system of hydrogen bonds in hydrous pyroxenoids with a five-periodic chain was only governed by factor 1 (Nagashima *et al.*, 2014). In the latter series, there was no correlation between cation distribution at octahedral sites and chain length. In nambulite and marsturite, members of this series, Mn and Ca are distributed at the octahedral M1–M3 and seven-coordinated M4 sites. These four polyhedra may counterbalance each other and cancel the effect of Ca ↔ Mn substitution on chain length.

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