

Murakamiite, $\text{LiCa}_2\text{Si}_3\text{O}_8(\text{OH})$, a Li-analogue of pectolite, from the Iwagi Islet, southwest Japan

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Abstract: Murakamiite (IMA2016-066), ideally $\text{LiCa}_2\text{Si}_3\text{O}_8(\text{OH})$, is a new mineral that was recently discovered in an aegirine-augite albitite exposed on the Iwagi Islet, Ehime Prefecture, Japan. It occurs as prismatic crystals and monomineralic aggregates up to 1.7 mm long, is white to colourless with a white streak, and has a vitreous to silky lustre. It has a Mohs hardness of $4\frac{1}{2}$ –5 and is brittle with a splintery fracture and perfect $\{100\}$ and $\{001\}$ cleavage. Measured and calculated densities are $D_{\text{meas}} = 2.86(1)$ and $D_{\text{calc}} = 2.85(1) \text{ g}\cdot\text{cm}^{-3}$, respectively. Murakamiite is optically biaxial (+) and non-pleochroic, with refractive indices (in white light) of $\alpha = 1.602(1)$, $\beta = 1.611(1)$, $\gamma = 1.643(1)$, and with $2V_{\text{meas}} = 56$ – $59(2)^\circ$ and $2V_{\text{calc}} = 57^\circ$. Dispersion is weak, with $r > v$. The optical orientation is $X^\wedge c$ 10 – 11° , $Y^\wedge a$ 10 – 14° , $Z^\wedge b$ 0 – 5° . Murakamiite is triclinic, belonging to space group $P\bar{1}$ with the unit-cell parameters $a = 7.9098(2) \text{ \AA}$, $b = 7.0320(2) \text{ \AA}$, $c = 6.9863(2) \text{ \AA}$, $\alpha = 90.596(2)^\circ$, $\beta = 95.589(2)^\circ$, $\gamma = 102.767(2)^\circ$, $V = 376.98(2) \text{ \AA}^3$ ($Z = 2$). The eight strongest lines in the X-ray powder diffraction pattern are [$d_{\text{obs}}/\text{\AA}(I)(hkl)$]: $2.897(100)(2\bar{2}0)$, $3.055(49)(012, 102, 1\bar{1}\bar{2})$, $3.295(41)(102)$, $3.225(33)(201)$, $3.845(20)(200)$, $2.284(19)(10\bar{3})$, $2.720(15)(12\bar{1}, 2\bar{2}1, 20\bar{2})$, and $6.962(15)(001)$. The chemical composition is (average of sixteen analyses by LA-ICP-MS, H_2O by TG-DTA, wt%): SiO_2 54.94, Al_2O_3 0.01, FeO 0.38, MnO 0.80, MgO 0.04, CaO 34.14, Na_2O 4.37, Li_2O 2.52 and H_2O 2.80. The empirical formula of murakamiite, based on 9 O apfu, is $(\text{Li}_{0.55}\text{Na}_{0.46})_{\Sigma 1.01}(\text{Ca}_{1.98}\text{Mn}_{0.04}\text{Fe}_{0.02})_{\Sigma 2.04}\text{Si}_{2.98}\text{O}_8(\text{OH})_{1.01}$; thus, murakamiite is a H-bearing pyroxenoid with three-periodicity of SiO_4 tetrahedra and the Li-analogue of pectolite. The species is named in honour of the late Professor Emeritus Nobuhide Murakami (1923–1994) of Yamaguchi University, Japan. Type specimens are housed in the National Museum of Nature and Science, Tsukuba, Japan, and the Geological and Mineralogical Museum of Faculty of Science, Yamaguchi University, Japan.

Key-words: murakamiite; new mineral; crystal structure; H-bearing pyroxenoid; pectolite group; *Dreierkette*; lithium; Li-rich albitite; Iwagi Islet; Japan.

1. Introduction

Murakamiite, a Li-analogue of pectolite, was discovered in a metasomatic albitite at Iwagi Islet, Ehime Prefecture, Japan. This locality is also known as the type locality of two other Li-bearing minerals, sugilite (Murakami *et al.*, 1976) and katayamalite (Murakami *et al.*, 1983). Sugilite has the ideal formula $\text{Na}_2\text{K}(\text{Fe}^{3+}, \text{Mn}^{3+}, \text{Al})_2\text{Li}_3\text{Si}_{12}\text{O}_{30}$ (Armbruster & Oberhänsli, 1988) with a milarite-type crystal structure (Kato *et al.*, 1976). Katayamalite, on the other hand, is a Ca–Li–Ti silicate with the ideal formula $\text{KLi}_3\text{Ca}_7\text{Ti}_2(\text{SiO}_3)_{12}(\text{OH})_2$, and according to Kato & Murakami (1985), it has a triclinic structure related to the structure of baratovite (Dusmatov *et al.*, 1976). However, Baur & Kassner (1992) and Andrade *et al.* (2013) concluded that both baratovite [$\text{KLi}_3\text{Ca}_7\text{Ti}_2(\text{SiO}_3)_{12}\text{F}_2$] and katayamalite are monoclinic and struc-

turally identical. Associated pectolite in this murakamiite-bearing albitite was described by Murakami *et al.* (1976, 1983), and several other Li- and H-containing pyroxenoids occur elsewhere as independent species, including tanohaitite and nambulite (e.g. Yoshii *et al.*, 1972; Nagase *et al.*, 2012). Based on these previous studies, we expected the pectolite to be enriched in lithium. During the course of detailed mineralogical study of this albitite, we indeed found “pectolite” with Li_2O content up to 2.78 wt%, which exceeds the $\text{Li}/(\text{Li} + \text{Na})$ molar ratio of 0.5, therefore allowing the definition of a Li-analogue of pectolite.

This new Li-rich species is named murakamiite in honour of the late Professor Emeritus and petrologist Nobuhide Murakami (1923–1994) of the Department of Geology and Mineralogical Sciences, Faculty of Science, Yamaguchi University, Japan. Nobuhide Murakami is known for his outstanding contributions to petrology and

mineralogy, including his studies of the rock-forming minerals in the albitite at Iwagi Islet (Murakami, 1958, 1959, 1967, 1976; Murakami & Maruyama, 1963; Murakami & Matsunaga, 1966), in particular his discovery of sugilite (Murakami *et al.*, 1976) and katayamalite (Murakami *et al.*, 1983). The mineral and name (IMA2016-066) have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC). Type specimens are housed in the National Museum of Nature and Science, Tsukuba, Japan, and the Geological and Mineralogical Museum of Faculty of Science, Yamaguchi University, Japan, under registered numbers NSM M44916 (holotype) and 95235G (cotype), respectively.

2. Occurrence

Murakamiite was discovered in an aegirine-augite albitite exposed in the eastern part of Iwagi Islet, Japan (latitude 34.263°N, longitude 133.161°E). It constitutes *ca.* 2.4% by volume of the albitite, and is associated with albite (79.8 vol%; $\text{Ab}_{99.2}\text{Or}_{0.8}$ – $\text{Ab}_{99.6}\text{Or}_{0.3}\text{An}_{0.1}$), sugilite (8.8%), aegirine-augite (3.0%; $\text{Ae}_{45.5}\text{Jd}_{2.0}\text{Di}_{52.5}$ – $\text{Ae}_{71.1}\text{Jd}_{0.5}\text{Di}_{28.4}$), quartz (2.7%), pectolite (1.0%), alkali feldspar (0.3%; $\text{Or}_{96.6}\text{Ab}_{3.2}\text{An}_{0.2}$ – $\text{Or}_{97.3}\text{Ab}_{2.7}$), and katayamalite (0.1%). Accessory minerals in the albitite include zircon, britholite-(Ce), an unidentified Si–Th–Ca mineral, fluorapatite and titanite. Figure 1 shows a representative example of murakamiite crystal in the aegirine-augite albitite, and Fig. 2 shows the occurrence of murakamiite in thin section.

The contact between the aegirine-augite albitite and adjacent host biotite granitoid is transitional, and lacks a clear intrusive margin, consisting instead of a diffuse zone of quartz albitite and albitized granite. The host biotite granitoid is Late Cretaceous in age with a typical calc-alkaline composition, while the murakamiite-bearing aegirine-augite albitite has extremely high Na_2O and Li contents of 10.44 wt% and 0.05 wt%, respectively (Table S1, freely available online as Supplementary Material linked to this article on the GSW website of the journal, <http://eurjmin.geoscienceworld.org/>). Conspicuous strain-induced textures are exhibited by aegirine-augite, katayamalite and albite.

3. Appearance, physical and optical properties

Murakamiite occurs as finely or coarsely prismatic, mono-mineralic aggregates up to 1.7 mm long. It exhibits purplish-pink fluorescence under long-wave (365 nm) ultraviolet light and is commonly associated with aegirine-augite aggregates. Murakamiite is white to colourless with a white streak and a vitreous to silky lustre. It has a Mohs hardness of 4½–5, is brittle with a splintery fracture, and has a perfect {100} and {001} cleavage (Fig. 2). The density, determined by flotation using heavy liquids, is 2.86(1) g·cm^{−3}, which agrees well with the calculated density of 2.85(1) g·cm^{−3} using the empirical chemical formula.

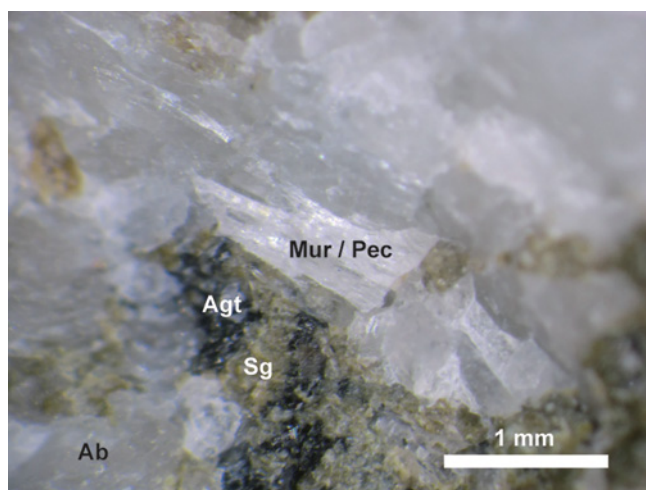


Fig. 1. Photograph showing the representative occurrences of murakamiite or pectolite in aegirine-augite albitite. Murakamiite can be indistinguishable from the pectolite to the naked eyes, because chemical composition gradually changes from Li-dominant murakamiite to Na-dominant pectolite. Mur, murakamiite; Pec, pectolite; Agt, aegirine-augite; Sg, sugilite; Ab, albite.

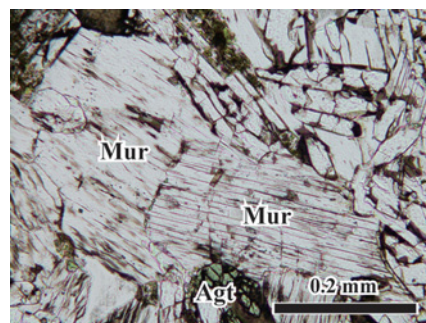


Fig. 2. Murakamiite in aegirine-augite albitite (photomicrograph, plane-polarized light). Mur, murakamiite; Agt, aegirine-augite.

Murakamiite is optically biaxial (+), with $\alpha = 1.602(1)$, $\beta = 1.611(1)$, and $\gamma = 1.643(1)$. Its $2V$ angle measured under white light is 56–59(2)° and its calculated $2V$ is 57°. Dispersion is weak with $r > v$. The mineral is non-pleochroic and the optical orientation is $X^{\wedge}c$ 10–11°, $Y^{\wedge}a$ 10–14°, and $Z^{\wedge}b$ 0–5°.

The Gladstone–Dale compatibility index of murakamiite, $(1 - K_p/K_c)$, calculated with the measured density, is −0.012 and falls into the “superior” category for LA–ICP–MS analyses according to Mandarin (1981); the index value is −0.018 (superior) for EMP and LIBS analyses.

4. Chemical data

Chemical analysis of murakamiite was performed using laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) following the method of Kimura & Chang (2012). The analytical setup consisted of a 200 nm femtosecond LA system (OK Fs2000K, OK Lab, Tokyo, Japan) combined with a quadrupole ICP–MS (iCAP-Qc Thermo Fisher Scientific, Bremen, Germany)

Table 1. Average chemical compositions of murakamiite by LA-ICP-MS, and by EMP and LIBS.

wt%	LA-ICP-MS			EMP and LIBS			
	AVG <i>n</i> = 16	STD	Range	AVG <i>n</i> = 10	STD	Range	Probe standard
SiO ₂	54.94	0.30	54.52–55.67	54.98	0.50	54.47–56.14	CaSiO ₃
TiO ₂	0.00	0.00	0.00	0.01	0.02	0.00–0.04	TiO ₂
Al ₂ O ₃	0.01	0.02	0.00–0.05	0.00	0.00	0.00	Al ₂ O ₃
FeO	0.38	0.03	0.33–0.44	0.28	0.04	0.25–0.37	Fe ₂ O ₃
MnO	0.80	0.03	0.75–0.85	0.56	0.08	0.45–0.68	MnO
MgO	0.04	0.02	0.03–0.08	0.04	0.01	0.01–0.06	MgO
CaO	34.14	0.51	33.11–34.84	33.63	0.29	32.99–34.25	CaSiO ₃
Na ₂ O	4.37	0.34	3.67–5.03	4.21	0.09	4.03–4.33	NaAlSi ₃ O ₈
K ₂ O	0.00	0.00	0.00	0.01	0.01	0.00–0.03	KAlSi ₃ O ₈
Li ₂ O	2.52	0.14	2.32–2.77	2.78*			–
H ₂ O**	2.80			2.80			–
Total	100.00***			99.30			
O = 9							
Si	2.98	0.01	2.96–3.00	2.99	0.02	2.98–3.00	
Ti	0.00	0.00	0.00	0.00	0.00	0.00	
Al	0.00	0.00	0.00	0.00	0.00	0.00	
Fe ²⁺	0.02	0.00	0.01–0.02	0.01	0.00	0.01–0.02	
Mn ²⁺	0.04	0.00	0.03–0.04	0.03	0.00	0.02–0.03	
Mg	0.00	0.00	0.00–0.01	0.00	0.00	0.00	
Ca	1.98	0.03	1.91–2.02	1.96	0.02	1.94–1.99	
Na	0.46	0.04	0.38–0.53	0.44	0.01	0.42–0.46	
K	0.00	0.00	0.00	0.00	0.00	0.00	
Li ⁺	0.55	0.03	0.51–0.60	0.61			
H ⁺	1.01	0.00		1.01			
Total	7.03	0.02		7.05			
Li + Na	1.01	0.03		1.05			
Ca site	2.04	0.03		1.99			

* Li₂O content was analyzed by LIBS.

** Determined by TG-DTA analysis. Data was measured using mixture of murakamiite (*ca.* 71 vol%) and pectolite (*ca.* 29 vol%).

*** Total sum of the LA-ICP-MS data normalized to 97.2 wt% excluding H₂O determined by TG-DTA analysis.

at the Department of Solid Earth Geochemistry, Japan Agency for Marine-Earth Science and Technology (DSEG/JAMSTEC), Yokosuka, Japan. Laser fluence on the sample surface was $\sim 6 \text{ J cm}^{-2}$, and samples were ablated using a rotation raster protocol with a $\sim 20 \mu\text{m}$ diameter laser beam with a 10 Hz laser pulse repetition rate moving at a rate of $11.5 \mu\text{m s}^{-1}$ along the circumference of a circle with a $10 \mu\text{m}$ radius. Ablation craters of $\sim 30 \mu\text{m}$ diameter $\times$ $15 \mu\text{m}$ depth were created after 60 s ablation. The U.S. Geological Survey (USGS) standard reference glass GSE-1G was used as a calibration standard, and the GSD-1G and BHVO-2G standard glasses (USGS), standard reference glasses SRM 610 and SRM 612 from the National Institute of Standard and Technology (NIST), and JR-1 natural obsidian glass from the Geological Survey of Japan (GSJ) were analyzed together with the murakamiite to evaluate the analytical performance, as listed in Table S2 of the Supplementary Material. Analytical results of murakamiite by LA-ICP-MS are listed in Table 1.

In addition to LA-ICP-MS, chemical analyses of major and minor elements were performed using an electron microprobe analyzer (EMP, JXA-8230, JEOL, Tokyo, Japan) at the Centre for Instrumental Analysis, Yamaguchi

University. Results of the EMP analyses of murakamiite and the standards used are listed in Table 1. Analyses were performed using an accelerating voltage of 15 kV, a beam current of 20 nA and a beam diameter of 1–5 μm . Wavelength-dispersion spectra were collected using LiF, PET and TAP monochromator crystals in order 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, P, F, and Cl were measured. Several elements, not listed in Table 1, are below the detection limit. The ZAF correction method was used for all elements. Fragments from the same murakamiite crystal were used for both EMP and X-ray single-crystal analyses.

Lithium concentrations of the murakamiite were determined using laser-induced breakdown spectroscopy (LIBS, J200-EC, Applied Spectra, Fremont, CA, USA) at Gem Research Japan, Osaka, Japan. The LIBS employed a 266 nm Nd:YAG laser coupled with an optical emission spectrometer. The employed Li peak had a wavelength of 670.706 nm. All analyses were carried out under a He gas flow of 1.3 L min^{-1} with a laser pulse energy of 2 mJ at 10 Hz using a laser beam diameter of 35 μm . The gate delay and pre-ablation times were 0.3 μs and 0.3 s,

respectively, and 25 shots were used for calculations. Emission spectra were collected in the 185.177–1050.782 nm spectral range covering the main emission lines of major elements (Na, Li, Ca, Fe, Si). The NIST SRM 610 and 612 glasses, and a synthetic Li-glass were used as calibration standards covering the LiO₂ concentration range between 86.5 ppm (NIST 612) and 5 wt% (Li-glass).

Analytical results of LA-ICP-MS analysis indicate that Li/(Li + Na) molar ratios in murakamiite are >0.5 and occur in a narrow range of Li/(Li + Na) values between 0.52 and 0.60 (Table 1), indicating limited local compositional variations. Murakamiite is also associated with Li-rich pectolite with Li/(Li + Na) values of 0.46–0.50, with which it is coherently intergrown. However, it is unclear whether the chemical intergrowth between murakamiite and Li-rich pectolite is continuous or if there is a solvus gap. Analytical results by EMP and LIBS are consistent with those of LA-ICP-MS (Table 1).

Using the results of the LA-ICP-MS analysis (Table 1), the empirical formula of murakamiite was calculated as (Li_{0.55}Na_{0.46}) Σ 1.01(Ca_{1.98}Mn_{0.04}Fe_{0.02}) Σ 2.04Si_{2.98}O₈(OH)_{1.01} on the basis of 9 O atoms per formula unit (*apfu*). The simplified formula is LiCa₂Si₃O₈(OH), which requires (in wt%) 56.98 SiO₂, 35.45 CaO, 4.72 Li₂O, and 2.85 H₂O for a total of 100 wt%.

5. TG-DTA data

Simultaneous thermogravimetric and differential thermal analysis (TG-DTA) curves were obtained using a differential thermogravimetric analyzer (Rigaku Thermo Plus Evo TG 8120) at the Yamaguchi Prefectural Industrial Technology Institute, Japan. A sample consisting of a mixture of murakamiite (*ca.* 71%) and pectolite (*ca.* 29%) grains was set in a platinum crucible. Alumina was used as a reference material. Thermal treatment was performed using a heating rate of 20 °C min⁻¹ from ambient temperature to 1000 °C. Figure 3 shows the resulting TG-DTA curves, with a sharp endotherm at 737 °C followed by 2.80% loss of weight (Table 1).

6. X-ray crystallography and crystal-structure determination

6.1. X-ray powder diffraction data

X-ray powder diffraction data were collected using an automated X-ray powder diffractometer (SmartLab, RIGAKU, Osaka, Japan) set to transmission mode and installed at Osaka Laboratory, Rigaku Corporation, Japan. The Cu X-ray tube for the CuK α line was operated at 40 kV and 150 mA. A diffraction profile was acquired between 5° and 60° in 2 θ with a step interval of 0.02° in θ . Unit-cell parameters of murakamiite were determined by RIGAKU PDXL software. The calculated pattern was obtained based on the result of single-crystal structural analysis mentioned below, and the observed and calculated powder patterns are

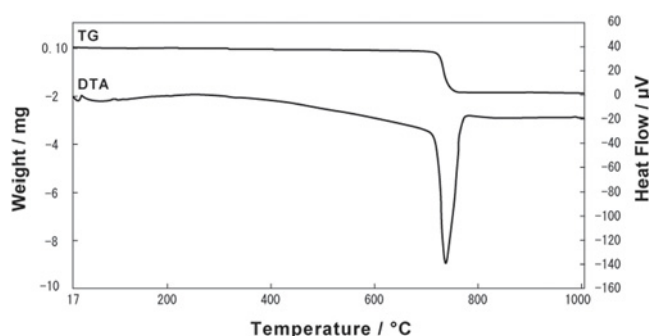


Fig. 3. TG and DTA curves of a murakamiite–pectolite mixture in air.

listed in Table 2. The unit-cell dimensions refined from the powder data are: $a = 7.908(2)$ Å, $b = 7.031(2)$ Å, $c = 6.987(2)$ Å, $\alpha = 90.48(1)^\circ$, $\beta = 95.558(7)^\circ$, $\gamma = 102.62(1)^\circ$ and $V = 377.1(2)$ Å³.

6.2. Single-crystal X-ray structural analysis

X-ray diffraction data for single-crystals of murakamiite were collected using a Bruker SMART APEX II CCD diffractometer installed at Shimane University. Crystals were mounted on glass fibres, and intensity data were measured at room temperature using graphite-monochromatized MoK α radiation ($\lambda = 0.71069$ Å). Preliminary lattice parameters and an orientation matrix were obtained from three sets of frames and refined during integration 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. The correct space group was found to be $P\bar{1}$ for all crystals. Crystal structure refinement was performed using SHELXL-97 (Sheldrick, 2008). Scattering factors for neutral atoms were employed throughout. Crystallographic data are summarized in Table 3. Refinements of the structure converged to the R_1 value of 3.28%. The refined atomic positions and thermal displacement parameters are listed in Table 4.

The determined site-occupancies are also listed in Table 4. Although the site occupancies of M1 and M2 were refined with Ca without restraints in the preliminary refinement, those of M1 and M2 turned out to be 1.0 Ca within standard deviation. Thus, the occupancies at these two sites were fixed as 1.0 Ca in the final refinement. The site occupancy of M3 was refined with Na and Li scattering factors in the preliminary refinement. Although closely spaced individual positions of Na and Li were resolved in murakamiite, their anisotropic displacement parameters were restrained to be equal. The occupancies at Si1–Si3 were fixed as 1.0 Si *apfu*. Positions of the hydrogen atoms of the hydroxyl groups were derived from difference Fourier synthesis. Subsequently, hydrogen positions were refined at a fixed value of $U_{iso} = 0.05$ Å² and a bond distance restraint of O–H = 0.980(1) Å (Franks, 1973). In murakamiite, two H atom positions

Table 2. Observed and calculated powder diffraction patterns (CuK α radiation) for murakamiite.

<i>h</i>	<i>k</i>	<i>l</i>	Calculated pattern based on X-ray single-crystal refinement		Observed X-ray powder pattern with transmission mode	
			<i>d</i> _{calc.} (Å)	<i>I</i> _{cal}	<i>d</i> _{meas.} (Å)	<i>I</i> _{meas.}
1	0	0	7.673	7	7.690	6
0	0	1	6.949	17	6.962	15
1	0	1	5.433	9	5.443	7
1	1	1	4.562	5		
1	1	1	4.007	12	4.009	6
2	0	0	3.836	27	3.845	20
0	0	2	3.474	21	3.476	16
1	2	0	3.427	5		
2	1	1	3.396	15	3.398	9
1	0	2	3.294	59	3.295	41
2	0	1	3.222	54	3.225	33
0	1	2	3.141	22	3.149	8
0	2	1	3.114	6		
1	2	1	3.089	6		
0	1	2	3.059	16		
1	0	2	3.050	57	3.055	49
1	1	2	3.047	18		
2	1	1	2.912	8		
1	2	0	2.897	98	2.897	100
2	2	0	2.897	100		
1	2	1	2.739	14		
2	2	1	2.722	12	2.720	15
2	0	2	2.717	18		
3	1	0	2.593	5	2.591	2
3	0	0	2.558	20	2.563	11
1	2	2	2.424	18	2.428	7
0	2	2	2.401	19	2.403	3
0	0	3	2.316	8		
2	2	0	312	10	2.317	13
3	2	0	2.312	10		
1	0	3	2.283	27	2.284	19
3	0	2	2.168	8	2.167	5
3	2	1	2.149	15		
2	2	1	2.141	14	2.148	10
2	2	2	2.004	7		
3	2	2	1.990	7	1.979	2
4	0	1	1.899	5	1.903	2
3	2	2	1.865	5	1.858	3
1	3	2	1.823	7	1.872	2
4	0	1	1.802	5		
4	2	1	1.761	7		
1	4	0	1.758	34		
3	2	1	1.757	6	1.760	13
0	0	4	1.737	11	1.738	6
3	3	2	1.725	6		
2	2	3	1.709	5		
3	2	2	1.707	13	1.708	7
4	2	2	1.698	13	1.698	7
3	2	3	1.697	5		
1	0	4	1.658	5		
2	0	4	1.647	5	1.647	3
3	0	3	1.636	5	1.584	2
4	0	3	1.557	6		
0	4	2	1.557	9	1.558	4
2	4	2	1.545	9	1.542	3

b, broad peak.

Table 3. Experimental detail of the single-crystal X-ray diffraction analysis of murakamiite.

Crystal size (μm)	0.14 × 0.04 × 0.04
Space group	<i>P</i> $\bar{1}$
Cell parameters	
<i>a</i> (Å) = 7.9098(2)	α (°) = 90.596(2)
<i>b</i> (Å) = 7.0320(2)	β (°) = 95.589(2)
<i>c</i> (Å) = 6.9863(2)	γ (°) = 102.767(2)
	<i>V</i> (Å ³) = 376.98(2)
<i>D</i> _{calc} (g/cm ³) = 2.85	
$\theta_{\text{min-max}}$ (°) = 2.7–30.5	μ (mm ^{−1}) = 2.05
Collected reflections = 10 439	Unique reflections = 2297
<i>R</i> _{int} (%) = 5.39	<i>R</i> _{σ} (%) = 4.22
Miller index limits	−11 < <i>h</i> < 11, −10 < <i>k</i> < 10, −9 < <i>l</i> < 9
<i>R</i> ₁ (%) = 3.28	<i>wR</i> ₂ (%) = 7.47
No. of parameters = 146	
Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.32P]$	
Δr_{max} (e Å ^{−3}) = 0.56 (0.99 Å from M1)	Δr_{min} (e Å ^{−3}) = −0.56 (0.73 Å from Si2)

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 ($\lambda = 0.71069$ 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 $P = (\max(F_o^2, 0) + 2 F_c^2)/3$, 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.

were refined. The occupancies of H3 and H4 were fixed as 41% and 59% according to corresponding Li and Na occupancies.

Selected interatomic distances and angles are listed in Table 5. The crystal structure of murakamiite is shown in Fig. 4; it is that of a pyroxenoid with three-periodic chains of SiO₄ tetrahedra, represented as LiCa₂Si₃O₈(OH). Murakamiite is therefore a new member of the group of H-bearing *Dreierketten* pyroxenoids, along with pectolite and serandite, the Mn-analogue of pectolite (Takéuchi *et al.*, 1973, 1976; Ohashi & Finger, 1978; Jacobsen *et al.*, 2000), tanohataite, the Li-analogue of serandite (Nagase *et al.*, 2012), and marshallussmanite, an ordered (CaMn) intermediate member of the pectolite–serandite series (Origlieri *et al.*, 2013) (Table 6).

The bond-valence sums were calculated using the electrostatic strength function of Brown & Altermatt (1985) and the bond-valence parameters of Brese & O'Keeffe (1991). The bond-valence sums of O3 and O4 are 1.57–1.60 and 1.52–1.59 valence units (vu), respectively (Table 7). The bridging oxygen O9 of Si1–O9–Si2 is overbonded (2.20–2.23 vu). Further detailed descriptions of the relationships between cation substitution and the H-bond system in the H-bearing pyroxenoids with three-

Table 4. Refined atomic positions, isotropic and anisotropic mean square displacement parameters ($\text{\AA}^2$) of murakamiite.

Site	neq	$W^{\dagger}$	Site occupancy	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M1	2	i	Ca _{1.0}	0.85911(7)	0.59448(7)	0.14982(7)	0.01053(12)	0.0110(2)	0.0075(2)	0.0133(3)	0.0008(2)	0.0036(2)	0.0014(2)
M2	2	i	Ca _{1.0}	0.84800(7)	0.08540(7)	0.14179(7)	0.00924(11)	0.0100(2)	0.0060(2)	0.0117(2)	−0.0002(2)	0.0026(2)	0.0010(2)
M3 (Li)	2	i	Li _{0.587(7)} Na _{0.413}	0.5501(18)	0.3067(19)	0.304(2)	0.0164(10)	0.011(1)	0.016(2)	0.023(2)	0.010(1)	0.007(1)	0.002(1)
M3 (Na)	2	i		0.5544(5)	0.2552(5)	0.3449(6)	0.00936(15)	0.0118(3)	0.0063(3)	0.0099(3)	0.0003(2)	0.0018(3)	0.0017(2)
Si1	2	i		0.22765(10)	0.40503(10)	0.33818(10)	0.00994(15)	0.0133(3)	0.0062(3)	0.0104(3)	−0.0010(2)	0.0012(3)	0.0024(3)
Si2	2	i		0.22566(10)	0.95957(10)	0.34138(10)	0.00896(15)	0.0077(3)	0.0072(3)	0.0114(3)	0.0000(2)	0.0008(3)	0.0007(2)
Si3	2	i		0.45621(9)	0.73618(10)	0.13855(10)	0.0129(4)	0.0098(9)	0.0116(9)	0.018(1)	−0.0002(7)	0.0029(7)	0.0020(7)
O1	2	i		0.6597(2)	0.7885(3)	0.1198(3)	0.0133(4)	0.0145(9)	0.0122(9)	0.0117(9)	−0.0004(7)	0.0018(7)	0.0018(7)
O2	2	i		0.3340(2)	0.7041(3)	−0.0628(3)	0.0186(4)	0.034(1)	0.0142(9)	0.0116(9)	0.0018(7)	0.0069(8)	0.0106(9)
O3	2	i		0.2001(3)	0.5015(3)	0.5405(3)	0.0184(4)	0.031(1)	0.0112(9)	0.0131(9)	0.0020(7)	0.0054(8)	0.0039(8)
O4	2	i		0.1874(3)	0.8518(3)	0.5399(3)	0.0117(4)	0.0109(9)	0.0103(8)	0.0137(9)	0.0013(7)	0.0021(7)	0.0020(7)
O5	2	i		0.0668(2)	0.3858(3)	0.1760(3)	0.0126(4)	0.0122(9)	0.0115(9)	0.0139(9)	−0.0014(7)	0.0005(7)	0.0024(7)
O6	2	i		0.0648(2)	0.9005(3)	0.1779(3)	0.0141(4)	0.0116(9)	0.0104(9)	0.020(1)	0.0039(7)	0.0014(7)	0.0005(7)
O7	2	i		0.4069(2)	0.5355(3)	0.2643(3)	0.0158(4)	0.0134(9)	0.0123(9)	0.022(1)	−0.0043(7)	0.0025(8)	0.0029(7)
O8	2	i		0.4020(3)	0.9099(3)	0.2669(3)	0.0152(4)	0.024(1)	0.0076(8)	0.0140(9)	−0.0021(7)	−0.0026(8)	0.0048(7)
O9	2	i		0.2790(3)	0.1958(3)	0.3836(3)	0.05(U_{iso})						
H3	2	i		0.195(15)	0.639(5)	0.525(19)	0.05(U_{iso})						
H4	2	i		0.170(11)	0.7094(11)	0.536(13)	0.05(U_{iso})						

* Multiplicity.

periodic single-chains, including pectolite, marshallussmanite, serandite and tanohataite, are given by Nagashima *et al.* (in prep.).

7. Discussion

7.1. Relationships between Li ↔ Na substitution and hydrogen bonding, and the unit-cell volume of murakamiite

The high Li content at M3 modifies the arrangement of O atoms defining the M3 polyhedra in murakamiite. The atomic positions of Li and Na at M3 are separately refined in this study. The ionic radius of Li⁺ (0.92 Å; Shannon, 1976) is smaller than that of Na⁺ (1.18 Å), and it therefore prefers a position in a smaller coordinated polyhedron within the large eight-coordinated polyhedron. Because the increase in Li content shifts the cation at M3 towards the SiO₄-tetrahedron, the ligands O2, O3, and O7 (first to third neighbour O atoms) become closer to the cation at M3, whereas the distances from M3 to O8' and O7' increase considerably (Table 6). As a result, the M3 polyhedra should be represented not as an eightfold coordination, but as a distorted sixfold coordination. A similar phenomenon has been reported in a study of the nambulite group minerals, which belong to the hydrous pyroxenoids with five-periodic chains (Murakami *et al.*, 1977; Nagashima *et al.*, 2014).

Two H positions and the hydrogen-bond system were determined for murakamiite. The donor oxygen atoms are O3 and O4, which is consistent with the bond-valence sum calculations (Table 7). The short distance between O3 and O4, 2.487(3) Å, has already been predicted as involving a very strong hydrogen bond (Table 6), and such bonds are common in hydropyroxenoid-group minerals (e.g. Takéuchi *et al.*, 1973, 1976; Ohashi & Finger, 1981; Nagashima & Armbruster, 2010). The difference in Li and Na positions at M3 in murakamiite is likely to cause the switch of donor and acceptor oxygen atoms. The occupancies of H3 and H4 were therefore fixed as 0.41 and 0.59, respectively, according to corresponding Li and Na occupancies (Table 5).

The unit-cell volume of murakamiite (376.98(2) Å³ in Table 4) is larger than in the isostructural Mn-analogue serandite (347.3–352.8 Å³; Ohashi & Finger, 1978; Jacobsen *et al.*, 2000; Williams & Weller, 2014). The variations in unit-cell parameters are governed mainly by Ca ↔ Mn²⁺ substitutions at the octahedral M1 and M2 sites. The *a*-, *b*-, and *c*-axes also lengthen with increasing Ca content. Furthermore, the unit-cell volume of murakamiite is smaller than that of pectolite (384.0–382.2 Å³; Prewitt, 1967; Takéuchi & Kudoh, 1977). Thus, it is concluded that the Li concentration also affects the unit-cell parameters.

7.2. Genetic aspects of murakamiite formation

An aegirine-augite albitite from Iwagi Islet in southwest Japan, hosted by a Late Cretaceous biotite granitoid, contains rare Li-rich silicate minerals including murakamiite (proposed here), Li-rich pectolite, sugilite and

Table 5. Selected interatomic distances (Å) and bond angles (°).

M1–O1	2.300(2)	M2–O1	2.275(2)
M1–O2	2.343(2)	M2–O2	2.318(2)
M1–O3	2.333(2)	M2–O4	2.318(2)
M1–O5	2.403(2)	M2–O6	2.367(2)
M1–O6	2.387(2)	M2–O6'	2.398(2)
M1–O5'	2.428(2)	M2–O5	2.410(2)
Mean(VI)	2.366	Mean(VI)	2.348
M3–O9	2.24(1)	M3(Li)–Oi	
M3–O2	2.01(1)	M3(Na)–Oi	
M3–O3	2.30(1)		
M3–O4	2.71(1)		
M3–O8	2.78(1)		
M3–O7	2.17(1)		
Mean(VI)	2.37		
M3–O8'			
M3–O7'			
Mean(VIII)			
Si1–O9–Si2	145.8(2)	Si1–O5	1.600(2)
Si2–O8–Si3	138.3(2)	Si1–O3	1.616(2)
Si3–O7–Si1	135.2(1)	Si1–O9	1.637(2)
O3...O4	2.487(3)	Si1–O7	1.643(2)
		Mean(IV)	1.624
		Si2–O4	1.610(2)
		Si2–O6	1.603(2)
		Si2–O9	1.638(2)
		Si2–O8	1.640(2)
		Mean(IV)	1.623
		Si3–O1	1.588(2)
		Si3–O2	1.611(2)
		Si3–O7	1.663(2)
		Si3–O8	1.663(2)
		Mean(IV)	1.631

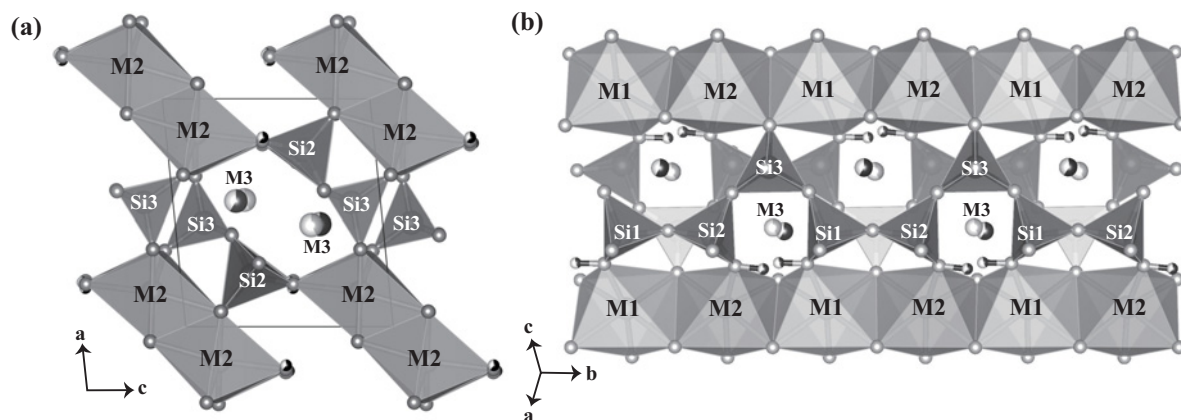


Fig. 4. Crystal structure of murakamiite projected onto (010) (a), and the arrangement of octahedra with three-periodic silicate chains (b) drawn with the program VESTA 3 (Momma & Izumi, 2011).

katayamalite. The transitional nature of the contact between the aegirine-augite albitite and the host granitoid suggests a metasomatic origin of the albitite by hydrothermal alteration of the granitoid. The murakamiite-bearing aegirine-augite albitite is characterized by high Na₂O (10.44 wt%) and Li (0.05 wt%), and low SiO₂ (67.7 wt%) and K₂O (0.35 wt%) compared with the typical calc-alkaline host biotite granitoid (SiO₂ = 76–78 wt %, Na₂O = 3.0–3.5 wt %, K₂O = 4.4–4.7 wt %, Li = 66–76 ppm) (Table S1), indicating Na–Li gain and Si–K loss during metasomatism. Whole-rock chemical data and mineralogy suggest a process of impregnation of the Na- and Li-rich minerals (murakamiite, Li-rich pectolite, sugilite and katayamalite) into the aegirine-augite albitite.

The results suggest that the mineral assemblage of the aegirine-augite albitite was formed by alkali-fluid metasomatism (albitization) of the biotite granitoid. Moreover, conspicuous strain-induced textures exhibited by the aegirine-augite albitite suggest that murakamiite, Li-rich pectolite, sugilite and katayamalite are the products of dynamic metasomatic recrystallization in a shear zone. In this environment, deformation-induced fracturing probably facilitated the circulation of a Na- and Li-rich metasomatic fluid. The origin of the unusually Na- and Li-rich fluid is unknown and is beyond the scope of this paper, but it will be an important topic of future research.

Table 6. Minerals that are structurally and compositionally related to murakamiite, H-bearing pyroxenoids with three-periodic chains of SiO₄-tetrahedra.

Mineral name	Ideal formula	Reference
Pectolite	NaCa ₂ Si ₃ O ₈ (OH)	Prewitt (1967), Ohashi & Finger (1978)
Murakamiite	LiCa ₂ Si ₃ O ₈ (OH)	This work
Marshallussmanite	NaCaMnSi ₃ O ₈ (OH)	Origlieri <i>et al.</i> (2013)
Serandite	NaMn ₂ Si ₃ O ₈ (OH)	Takéuchi <i>et al.</i> (1973, 1976), Ohashi & Finger (1978), Jacobsen <i>et al.</i> (2000)
Tanohataiite	LiMn ₂ Si ₃ O ₈ (OH)	Nagase <i>et al.</i> (2012)

Table 7. Bond-valence sum calculations of murakamiite.

M1	2.06	2.06
M2	2.16	2.16
Na at M3 CN=8	0.86	
Li at M3 CN=6		1.00
Si1	4.18	4.18
Si2	4.20	4.20
Si3	4.11	4.11
O1	1.99	1.99
O2	2.01	2.17
O3	1.57	1.60
O4	1.59	1.52
O5	2.01	2.01
O6	2.08	2.08
O7	2.03	2.15
O8	2.06	1.98
O9	2.23	2.20

Note: Because the positions of Li and Na at M3 were refined separately in murakamiite, bond-valence sums were calculated based on Li–O_i and Na–O_i distances at M3. The positions of the O atoms coordinated by the cation at M3 are considered to be influenced by the split M3 positions.
CN, coordination number.

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