Tanohataite, LiMn$_2$Si$_3$O$_8$(OH): a new mineral from the Tanohata mine, Iwate Prefecture, Japan

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Tanohataite, LiMn$_2$Si$_3$O$_8$(OH), the Li analogue of serandite, has been found in a metamorphosed manganese ore deposit of the Tanohata mine, Iwate Prefecture, Japan. The mineral has the triclinic space group $P\overline{1}$ with $a = 7.612(7)$, $b = 7.038(4)$, $c = 6.700(4)$ Å, $\alpha = 90.23(6)^\circ$, $\beta = 94.70(7)^\circ$, $\gamma = 105.26(8)^\circ$, $V = 345.0(3)$ Å$^3$, and $Z = 2$. The seven strongest lines in the X-ray powder diffraction pattern are $d(\AA)$, $(I)$, $(hkl)$: 6.64(35)(001), 3.67(26)(200), 3.13(89)(102), 3.11(69)(211), 2.95(100)(102), 2.81(33)(120), and 2.18(40)(103). Electron microprobe analysis and laser ablation microprobe-inductively coupled plasma-mass spectrometry gave an SiO$_2$ content of 51.97; MnO, 37.99; MgO, 1.06; CaO, 0.41; Na$_2$O, 1.97; Li$_2$O, 3.34; total, 96.74 wt%, corresponding to an empirical formula of (Li$_{0.78}$Na$_{0.22}$)$_{\Sigma1.00}$ (Mn$_{1.86}$Ca$_{0.03}$Mg$_{0.09}$)$_{\Sigma1.98}$ Si$_{3.01}$O$_8$(OH) on the basis of O = 9. Tanohataite is transparent and pinkish white with a vitreous and silky luster. The streak is white. The cleavage is perfect on {001} and {100}. On the Mohs’ scale, the hardness is 5-5½. The calculated density is 3.33 g/cm$^3$. Optically, tanohataite is biaxial positive with $2V_{calc} = 82(2)^\circ$, $\alpha = 1.593(3)$, $\beta = 1.618(3)$, and $\gamma = 1.653(3)$. Tanohataite occurs as an aggregation of fibrous crystals in veinlets composed mainly of quartz, aegirine, Mn-arfvedsonite, nambulite, natrionambulite, and barite.

Keywords: Tanohataite, Tanohata mine, Chemical composition, XRD, TEM

INTRODUCTION

A new wollastonite-group mineral, tanohataite, LiMn$_2$Si$_3$O$_8$(OH), has been found in the Tanohata mine, Tanohata village, Iwate prefecture, Japan, with the mine being known for alkali amphibole-rich manganese deposits (e.g., Nambu et al., 1969a; Matsubara et al., 1985). Tanohataite represents the Li analogue of serandite, NaMn$_2$Si$_3$O$_8$(OH) (e.g., Takéuchi et al., 1976; Takéuchi and Kudo, 1977; Hammer et al., 1998). It has been previously synthesized under hydrothermal conditions at 3 kbar and 300–600 °C by Ito (1972). The mineral data and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (no. 2007–019). The type specimen has been deposited in the National Museum of Nature and Science, Tokyo, Japan, under the registered number NSM-M29298.

OCCURRENCE

The upper-Jurassic sediment-hosted manganese-ore deposits of the Tanohata mine are contact metamorphosed and metasomatized by intrusion of Cretaceous granodiorite (Nambu et al., 1969b). Tanohataite was found at the dump derived from the no. 3 (Matsumaezawa) ore body, which is composed mainly of rhodonite, rhodochrosite, braunite, and tephroite. The no. 3 ore-body includes lens-like veinlets with the occurrence of concentrates of alkali-amphiboles, and various new lithium- and vanadium-
bearing minerals, such as kozulite (Nambu et al., 1969a), suzukiite (Watanabe et al., 1973; Matsubara et al., 1982), natronambulite (Matsubara et al., 1985), potassicaleakeite (Matsubara et al., 2002), and watatsumiite (Matsubara et al., 2003).

Tanohataite occurs as an aggregation of fibrous crystals with quartz (Fig. 1: Color version of Figure 1 is available online from http://joi.jlc.jst.go.jp/JST.JSTAGE/jmps/111130). The size of the aggregation is 0.1–0.5 mm in width and a few mm in length. Individual crystals exhibit an acicular shape with sizes of a few micrometers in width and less than 1 mm in length. The fibrous crystals are elongated along the $b$-axis. The veinlets including tanohataite are composed mainly of quartz and minor amounts of aegirine, Mn-arfvedsonite, nambulite, natronambulite, and barite. Matsubara et al. (2002) indicated that the formation of the no. 3 ore body was strongly affected by hydrothermal fluid from the intruding granodiorite and also concluded that the lens-like veinlets with concentrations of alkali-amphiboles were formed during the later stage of hydrothermal activities.

**PHYSICAL AND OPTICAL PROPERTIES**

The mineral is transparent and pinkish white in color with a vitreous and silky luster. The color changes to black on oxidation. The streak is white. The fracture is fibrous because of the aggregation texture. The cleavage is perfect on {001} and {100}. On the Mohs’ scale, the hardness is 5–5.5. Using the empirical formula and the unit cell parameters, the density is calculated to be 3.33(1) g/cm$^3$. The refractive indices, $\alpha = 1.593(3)$, $\beta = 1.618(3)$, and $\gamma = 1.653(3)$, were measured using a liquid immersion method at room temperature. The refractive indices of the immersion liquids were determined using an Abbe refractometer. Optically, the mineral is biaxial positive with $2V = 82(2)\degree$, which was calculated using the refractive indices. Pleochroism was not observed.

The form and color of tanohataite are similar to those of serandite and rhodonite. Characteristics for distinguishing tanohataite from these two minerals are brittleness and luster. Serandite and rhodonite are more brittle than tanohataite and are easily ground to a powder. In contrast, tanohataite exhibits a strong flexibility like asbestos.

**CHEMISTRY**

The lithium content of the mineral was analyzed by laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS) in the Zenhokyo (the former Gemological Association of All Japan) laboratory using standard procedures with a quadrupole ICP-MS (Agilent 7500 series) and Q-switched Nd:YAG laser ablation system (New Wave UP-213) at a wavelength of 213 nm. The analysis of the tanohataite crystal used a spot size of 60 µm at a pulse rate of 5 Hz and with a beam energy of 3.6 J/cm$^2$. Quantitative results for trace elements were obtained through calibration of relative element sensitivities using the NIST (National Institute of Standards and Tech-
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The infrared absorption spectrum of tanohataite, presented in Figure 2, was measured by Fourier-transform infrared spectroscopy (FT-IR; JEOL Diamond-20 spectrometer) with a mercury-cadmium-telluride detector cooled by liquid nitrogen. The FT-IR measurements were carried out using the crystalline sample, and the small polycrystalline fragments of specimen were set on a KBr plate. The sample aperture was 100 µm × 100 µm and the resolution was 2 cm$^{-1}$. The incident infrared beam was nearly normal to the $b$-axis (fiber axis). Figure 2 also shows the spectra of serandite from the Tanohata mine and from Mont St. Hilaire, Quebec, Canada, without the polarizing plate. For comparison, these three spectra were measured under the same conditions. The measured serandite crystals were oriented according to the perfect cleavages of (001) and (100), and the incident beam was normal to the $b$-axis. All spectra were measured in the range 700–5000 cm$^{-1}$.

The stretching mode of the SiO$_4$ tetrahedra was observed around 1200–800 cm$^{-1}$, and the bending modes and lattice modes of the remaining structural constituents occur at lower energies (Farmer, 1974). Relatively sharp peaks at 1394 cm$^{-1}$ and 1640 cm$^{-1}$ and broad peaks between 2500 cm$^{-1}$ and 3700 cm$^{-1}$ were observed. The peak at 1394 cm$^{-1}$ is assigned to an OH stretching mode, which corresponds to the same modes in pectolite and serandite at 1396 cm$^{-1}$ and 1386 cm$^{-1}$, respectively (Hammer et al., 1998). It can be derived from the extremely strong Si-OH***O bond, which is typically observed in the central tetrahedron of the C-shaped triplet part of the SiO$_4$ chain in hydrous pyroxenoid (e.g., Nagashima et al., 2010). Thus, the peak located at 1394 cm$^{-1}$ indicates that tanohataite has a structural OH very similar to those of the other hydrous pyroxenoids.

Generally, the peak near 1640 cm$^{-1}$ can be assigned to the OH-stretching mode of molecular H$_2$O. However, according to Nakamoto et al. (1955) and Libowitzky (1999), the OH stretching mode is observed around this wavenumber when strong hydrogen bonding is present in the crystal structure. In tanohataite, the intensity of the 1640 cm$^{-1}$ peak changed depending on the angle between the $b$-axis and the direction of the polarized light. This polarizing property suggests that the 1640 cm$^{-1}$ peak could be related to strong hydrogen bonding. However, further crystallographic analysis is needed to assign the peaks exactly.

**THERMAL ANALYSIS**

The thermogravimetry (TG) and differential thermal anal-
analysis (DTA) of tanohataite with the associated quartz were carried out using a thermal analyzer (Rigaku TG-8120) up to 900 °C at a rate of 10 °C/min in open air conditions (Fig. 3). For comparison, TG and DTA curves of serandite from Mont St. Hilaire are presented. The DTA curve of tanohataite shows a broad exothermic peak around 500-700 °C and a sharp exothermic peak at 730 °C. Weight gain was observed at 730 °C during the TG. Serandite exhibits double exothermic peaks around 640-720 °C. According to previous DTA and TG studies on pectolite and serandite (Yogi et al., 1968; Semenov et al., 1976), endothermic peaks were observed for pectolite at 730-740 °C and for serandite at 640-725 °C. The peak corresponds to

Table 2. Powder X-ray diffraction data of tanohataite and synthetic LiMn$_2$Si$_3$O$_8$(OH)£

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Figure 3. Differential thermal analysis (DTA) and thermogravimetry (TG) curves for tanohataite, and serandite.
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Tanohataite also has an endothermic peak at 713 °C before the exothermic peak at 730 °C. Tanohataite oxidized sluggishly from 500 °C, and the oxidation reaction was complete by 730 °C in the wake of dehydration. After heating to 900 °C, tanohataite decomposed to black and opaque amorphous materials.

**X-RAY DIFFRACTION**

The powder X-ray diffraction (XRD) pattern for tanohataite was obtained using an X-ray powder diffractometer (Phillips, Expert Powder) with Ni-filtered CuKα radiation generated at 40 kV and 55 mA. The X-ray diffraction data for tanohataite are given in Table 2 along with reference data from LiMn$_2$Si$_3$O$_8$(OH) synthesized by Ito (1972). The indexing of the XRD pattern was based on the serandite structure with the space group $P\overline{1}$ (Takéuchi et al., 1976). The unit cell parameters, refined by least squares using the software of Holland and Redfern (1997), are $a = 7.612(7)$ Å, $b = 7.038(4)$ Å, $c = 6.700(4)$ Å, $\alpha = 90.23(6)^\circ$, $\beta = 94.70(7)^\circ$, $\gamma = 105.26(8)^\circ$, $V = 345.0(3)$ Å$^3$, and $Z = 2$. The lengths and angles are consistent with the data for serandite (Takéuchi et al., 1976).

**TEM OBSERVATION**

Transmission electron microscopy (TEM) observations for tanohataite were carried out using a JEOL JEM-2010 type TEM. Specimens for TEM observation were prepared by the conventional crush method. The sample was ground in an agate mortar to obtain fine fractured particles. The particles were dispersed in ethyl alcohol, and a drop of the resultant suspension was placed on a microgrid coated with a carbon film.

Diffuse streaks parallel to $a^*$ of the $k = 2n + 1$ reflections are a common characteristic structural feature of the pectolite-group (Müller, 1976) and wollastonite-group minerals (e.g., Müller and Wenk, 1975; Jefferson and Thomas, 1975; Hutchison and McLaren, 1976). Jeffery (1953) suggested that this streaking was caused by stacking faults parallel to (100) with a displacement vector of $1/2b$. Wenk (1969) suggested that the polytypism of wollastonite could be explained by periodic (100) stacking faults with a $1/2b$ displacement vector.

Typical $hk0$ electron diffraction patterns of selected areas in tanohataite are shown in Figure 4. Diffuse streaks develop along $a^*$ in the layers $k = 2n + 1$. Figure 4a shows slightly diffuse diffraction maxima in the layers $k = 2n + 1$ connected by streaks along $a^*$; these indicate stacking disorder with faults parallel to (100). Weak diffuse streaks are also seen in the layers $k = 2n$, and they are due to dynamic diffraction effects. Figure 4b shows the diffraction pattern of sub-microscopically (100) twinned crystals. Because of the geometry of the twinned unit cells, the diffraction spots of the individuals are only observed in the layers $k = 2n + 1$ and coincide with the matrix reflections in the layers $k = 2n$.

In spite of careful observation, we could not find a crystal that gave a diffraction pattern analogous to parawollastonite and parapestolite. In the diffraction patterns of parawollastonite and parapestolite, the diffraction max-

![Figure 4](image-url)
ima of triclinic pectolite in the layers \( k = 2n + 1 \) disappear, and additional reflections appear at \( 1/2a^* \) in these layers (Müller and Wenk, 1975; Müller, 1976).

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SUPPLEMENTARY MATERIAL

Color version of Figure 1 is available online from http://joi.jlc.jst.go.jp/JST/JSTAGE/jmps/111130.

REFERENCES


