

Norrishite, a new manganese mica, $K(\text{Mn}^{3+}\text{Li})\text{Si}_4\text{O}_{12}$, from the Hoskins mine, New South Wales, Australia

RICHARD A. EGGLETON

Department of Geology, Australian National University, Canberra 2601, Australia

PAUL M. ASHLEY

Department of Geology and Geophysics, University of New England, Armidale 2351, Australia

ABSTRACT

Norrishite, a new lithium-manganese (Mn^{3+}) trioctahedral mica, occurs in millimeter-sized crystals as a rock-forming mineral in Mn-rich schists near Grenfell, New South Wales, Australia. It is a monoclinic, $C2/m$, $C2$, or Cm , $1M$ polytype, with $a = 5.293(1)$ Å, $b = 8.936(2)$ Å, $c = 10.077(1)$ Å, and $\beta = 98.0(1)^\circ$. The density, measured by density-gradient column, is $3.264(2)$ g/cm³. The structural formula is $\text{KMn}_2\text{LiSi}_4\text{O}_{12}$ ($Z = 2$), and the empirical cell content is $\text{K}_{1.94}(\text{Mn}_{1.96}\text{Li}_{1.19})[\text{Si}_{3.94}\text{Al}_{0.06}]\text{O}_{11.9}(\text{OH})_{0.3}$. As well as perfect $\{001\}$ cleavage, the mineral has weak $\{100\}$ and $\{010\}$ cleavages and is commonly elongate parallel to a . Mohs hardness = 2.5. Optical properties are $\alpha = 1.636$, $\beta = 1.687$, $\gamma = 1.785$, $2V_z$ (measured at 589 nm) = 74° , $2V$ (calculated) = 75° , $r > v$, Z is parallel to b , $Y \wedge a = 20^\circ$. Norrishite is markedly pleochroic, with X yellow, Y olive-green, and Z orange-brown. It has a major absorption peak at 450 nm (22000 cm⁻¹). The infrared spectrum shows negligible absorption in the region of 3500 cm⁻¹, where H_2O absorbs strongly, and the mineral contains less water than any other analyzed mica. The name is for Dr. Keith Norrish, in recognition of his contributions to layer-silicate mineralogy and analytical methods.

INTRODUCTION

A new Mn-rich member of the mica family, occurring locally in rock-forming amounts, has been found at the abandoned Hoskins mine, a manganese deposit 3 km west of Grenfell in central-western New South Wales (Australian Map Grid Reference 8530-039487). The mica was discovered in the course of petrographic and electron-microprobe examination of manganese silicate-oxide rocks. Norrishite is named after Dr. Keith Norrish of the Commonwealth Scientific and Industrial Research Organization Division of Soils, in recognition of his contribution to layer-silicate research, through both clay mineralogy and the development of analytical methods. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type material has been deposited at the Australian Museum, Sydney. Material for research is available from collections at the Australian National University, Canberra, A.C.T., and the University of New England, Armidale, N.S.W.

OCCURRENCE AND PETROGRAPHY

Norrishite has been found in several manganese silicate-oxide rock samples, occurring as a scatter of small dumped rocks near the main shaft of the Hoskins mine, the largest individual producer of manganese ore in New

South Wales (Bowman, 1977) with a total production of 25700 tons MnO_2 . At this location, a steeply dipping stratiform unit of metamorphosed Mn-rich rocks, up to 8 m thick, is associated with metajasper, metabasalt, and metasiltstone. The Mn-rich rocks are regarded as submarine exhalative precipitates on the basis of lithologic association, bulk chemical composition, and mineral assemblages (Ashley, 1986). The rocks are oxidized to manganese oxide assemblages to a depth of 45 m (Hall, 1959), and therefore, although not found in situ, the unweathered primary norrishite-bearing rocks probably came from below this depth.

Two major mineral associations are evident in the Mn-rich rocks (Ashley, 1986): (1) a "reduced" assemblage containing rhodonite, tephroite, hausmannite, garnet (spessartine-grossular-andradite), calcium-manganese carbonates, quartz, manganoan magnetite, Mn-rich chlorite, and barite and (2) an "oxidized" assemblage containing an Mn-rich alkali amphibole resembling kôzulite (Nambu et al., 1969), Mn-rich alkali clinopyroxene, manganoan pectolite-serandite, braunite, norrishite, calcium and barium carbonates, albite, K-feldspar, quartz, and barite.

"Oxidized" assemblage samples are weakly to moderately foliated and are commonly well laminated, the latter representing primary compositional variations. Individual laminations range from less than 0.5 mm to over 30

mm in thickness and may be rich in one or several of the minerals amphibole, clinopyroxene, braunite, manganian pectolite-serandite, norrishite, carbonate, or feldspar; they are interpreted as primary sedimentary layers.

Although manganese silicate rocks have been long known at the Hoskins mine (Hall, 1959), the first report of the "oxidized" assemblages was by Ryall (1974), who recognized "manganese biotite" (=norrishite), braunite, "Na-Mn-amphibole," and "piedmontite" (misidentification of Mn-rich alkali clinopyroxene). Subsequent petrographic and electron-microprobe studies (Ashley, 1986) confirmed the unique mineral suite of the "oxidized" assemblage, although somewhat similar rocks are known from metamorphosed oxidic manganiferous sediments (Nambu et al. 1969; Brown et al., 1978; Griffin and Mottana, 1982; Reinecke et al., 1985; Reinecke 1986a, 1986b; Mottana, 1986).

Norrishite, occurring as shiny black flakes up to 1.5 mm across, has been recognized from two contrasting assemblages within the oxidized manganese silicate rocks: (1) It is a major component, up to 25 modal %, of the assemblage amphibole + clinopyroxene + braunite + manganian pectolite + norrishite ± carbonate ± feldspar. Individual laminations containing >40 modal % norrishite attain 6 mm in thickness. (2) It is a minor component (up to 5 modal %) of the rare assemblage quartz + amphibole + clinopyroxene + norrishite ± pectolite ± carbonate. Norrishite apparently coexists stably with the other primary minerals, and no replacement textures are recognized. Inclusions of amphibole, clinopyroxene, and braunite occur sparsely in norrishite, which forms well-crystallized platy grains, commonly displaying a strong preferred orientation coplanar with the rock foliation.

EXPERIMENTAL PROCEDURES

The properties of norrishite have been determined largely on a mineral separate from rock number 820608 (University of New England specimen number). Chemical and thin-section optical data from a second sample (820607) are included in this report.

Optical properties were measured by a combination of flat- and spindle-stage observations. Refractive indices of grains immersed in Cargille index liquids were measured using white light. Optic orientation and $2V$ were determined by the method of Bloss and Riess (1973) using a crystal mounted on goniometer arcs and immersed in oil of refractive index 1.685, following crystallographic orientation by X-ray precession photography. Dispersion of the optic axes was measured directly by spindle stage after the optic axial plane had been set vertical. A polarized optical absorption spectrum was obtained from a single flake of norrishite using a Cary 17 spectrophotometer.

Symmetry and polytype were determined by the precession method. Cell parameters were obtained by least-squares refinement of data from Debye-Scherrer photographs taken with a 114-mm camera with Si and quartz internal standards in separate photographs. The

refinement included the reflections 006, 007, and 008 measured from an oriented aggregate in a Siemens D501 X-ray diffractometer, using an Si standard. In both cases $\text{CuK}\alpha$ radiation was used. Visual estimates of the intensities of Debye-Scherrer lines, and d values of weaker lines, were measured on an uncalibrated 114.6-mm photograph exposed to $\text{CrK}\alpha$ radiation.

Density was determined in a 1-mL pycnometer on 0.3 g of mica, using water as the displacement liquid, and also in a density-gradient column made of a mixture of tetrabromoethane and methylene iodide of density 3.1 g/cm³ layered over methylene iodide, at 0 °C. The column was calibrated by three standard glasses and diopside (measured by Archimedes method to a precision of 0.0005). A gradient from 3.18 to 3.34 g/cm³ was developed over 5 mm and read by cathetometer to 0.01 mm, giving a precision of 0.0003 in reading density. The grains of mineral and standard were approximately 0.1 mm in diameter.

Chemical composition was determined by wavelength-dispersive electron microprobe (Cameca Microbeam, N. Ware, analyst), using as standards microcline, fluorophlogopite, MnO, and San Carlos olivine. The 30-nA beam was rastered over a 12.5- μm square to reduce electron-beam damage. For sample 820607, a second set of analyses was obtained on a Technische Physische Dienst energy-dispersive electron microprobe using a fixed 3-nA beam, and a third set of data was collected on an ETEC energy-dispersive electron microprobe at the School of Earth Sciences, Macquarie University, Sydney, Australia, at 15 kV, 50 nA, and a beam diameter of 3–5 μm , using rhodonite, orthoclase, and cordierite standards. Water (H_2O^-) was measured on 250-mg samples of 820608 by heating overnight to 110 °C, and H_2O^+ was measured by heating the dried sample to 1100 °C in an air stream. A duplicate determination was made by heating to 1100 °C with CuO as an oxidant in N_2 . H_2 was analyzed by gas chromatography using a Carlo Erba 1106 elemental analyzer at the Research School of Chemistry, Australian National University. Total oxidation state was determined by dissolving 0.3 g of sample 820608 in boiling $\text{HF-H}_2\text{SO}_4$, adding excess ammonium ferrous sulfate, then titrating with potassium dichromate. A 40-element analysis of sample 820608 was obtained from the Australian Mineral Development Laboratories; for Li, 100 mg of sample was fused in HF-perchloric acid and analyzed by atomic emission spectroscopy. For the remaining elements, 200 mg of norrishite was dissolved with lithium metaborate, and the acid leach was analyzed by inductively coupled plasma atomic emission spectroscopy. Li was redetermined by atomic absorption spectroscopy using duplicate 100-mg samples of 820608 at a dilution of 1:400 following digestion in perchloric and nitric acid and re-dissolution in 85 mL of dilute HCl.

An infrared spectrum was obtained on a Pye Unicam SP1100 spectrophotometer from 2.5 mg of mica ground to <2 μm with 1.0-g KBr, then pressed to a translucent disc.

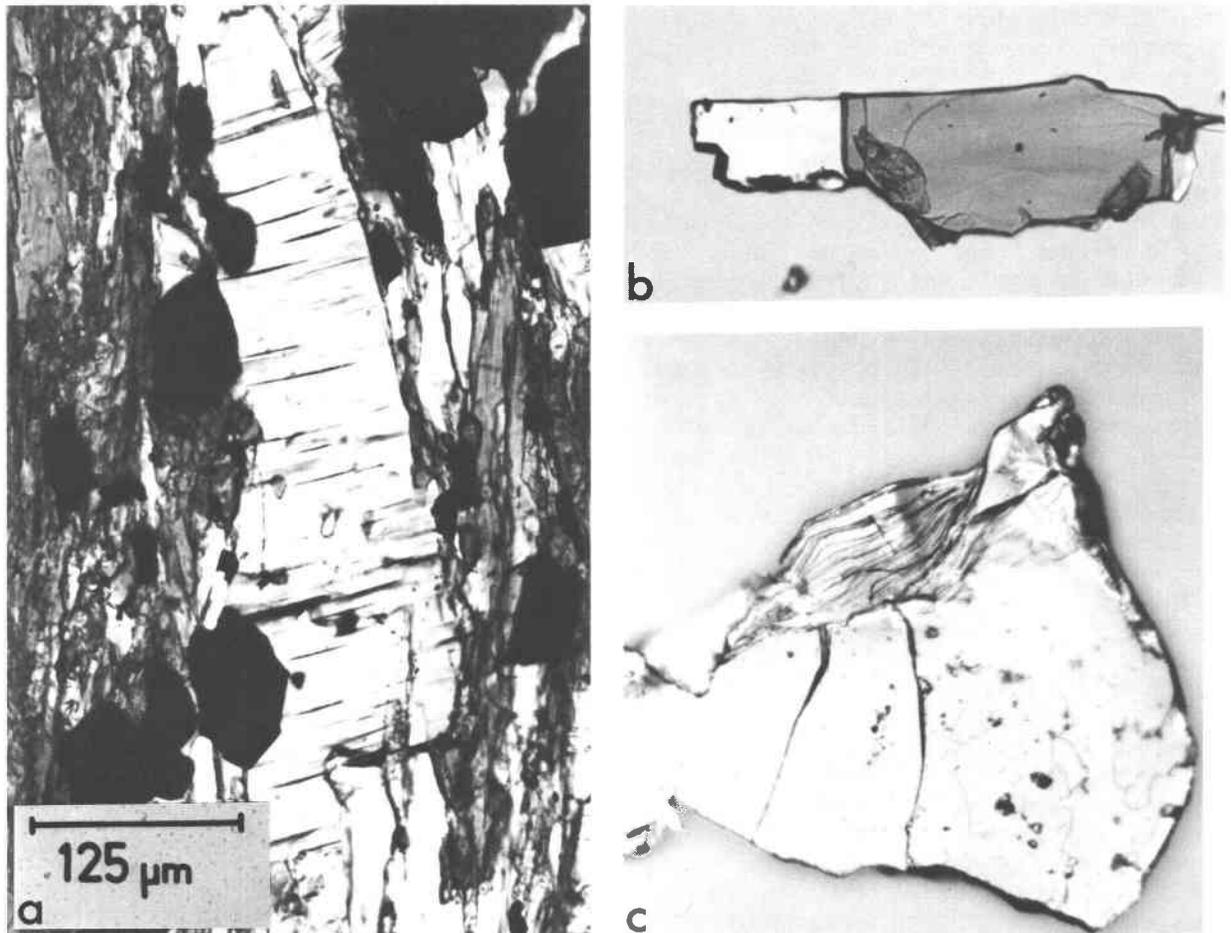


Fig. 1. Optical micrographs of norrishite. (a) Crystal in thin section; (001) is approximately perpendicular to the foliation defined by the amphibole elongation. (b), (c) Crystals of norrishite released from sample 820608 after solution of minor carbonate by dilute HCl. Fig. 1b shows a typical crystal elongate parallel to a with {100}, {010}, and {001} cleavages. Fig. 1c is representative of equally common anhedronal grains showing only {001} cleavage. (Reflected light.) The scale bar on (a) also applies to (b) and (c).

RESULTS

Hand-specimen and thin-section appearance

In hand specimen, norrishite is lustrous, black, with perfect {001} and poor {010} and {100} cleavages. The Mohs hardness is 2.5. In thin section, crystals are commonly oriented at various angles to the plane of foliation, but with some preference for the x -axis to parallel a lineation defined by the long direction of the coexisting amphibole. Some crystals have (001) parallel to the plane of the rock foliation, but it is quite common for (001) to be perpendicular to the foliation and for the crystals to be tabular on (010). Many of the fragments examined after crushing the rock or after releasing the mica by dissolving the carbonate in dilute HCl are elongate parallel to a (Fig. 1). The crystals are strongly pleochroic: brilliant yellow, lime- and olive-green, or honey-brown. Some crystals of the mica are color zoned with a green core and a yellow rim.

Optical properties

Norrishite is biaxial positive and pleochroic with X yellow, Y lime-green to olive-green, and Z yellow-brown; the color zoning is only obvious for Y . The optic direction Z is parallel to b ; the optic axial plane is at 70° to (001); hence, sections with (001) vertical have a maximum extinction angle ($Y \wedge a$) of 20° . The refractive indices are $\alpha = 1.636 \pm 0.001$, $\beta = 1.687 \pm 0.001$, and $\gamma = 1.785 \pm 0.005$, and the birefringence = 0.149. The angle $2V_z(\text{Na}) = 74.0^\circ$ measured by direct rotation on a spindle, 73.8° by indicatrix determination using the method of Bloss and Riess (1973), and 75.2° calculated from the refractive indices. Dispersion of the optic axes is strong, $r > v$ ($2V = 71^\circ$ in blue light, 75° in red).

Optical absorption spectra for Y and Z show an intense, broad absorption in the region of 450 nm (22000 cm^{-1}) (Fig. 2 and Table 1). Absorption for Z also shows a shoulder at about 515 nm (19500 cm^{-1}) and a weaker absorption band at 570 nm (17500 cm^{-1}). These bands

TABLE 1. Optical absorption parameters for norrishite

Orientation	Absorption band		ϵ [[g Mn ³⁺ ·L ⁻¹] ⁻¹ ·cm ⁻¹
	position (cm ⁻¹)	width	
Y'	17500	very broad	13
	19600	shoulder	18
	22500	broad	29
Z	18150	sharp	24
	21300	sharp	54
	21750	broad	49

are at similar frequencies to those found for Mn³⁺ in a synthetic phlogopite (22400 and 19500 cm⁻¹, Smith et al., 1983), piemontite (22000 and 18000 cm⁻¹, Burns and Strens, 1967), and kanonaite (22000 and 18000 cm⁻¹, Smith et al., 1982). There are also two small, very sharp absorption lines in the Z spectrum at 551 and 470 nm (18150 and 21300 cm⁻¹); the line at 551 nm is just detectable in the Y spectrum.

Density

The density determined on the 150- to 200-mesh fraction of norrishite by pycnometry after evacuation to remove entrapped air is 3.25 g/cm³ with an estimated error of 0.02. The measurements by gradient show a moderate spread but are higher by 0.03. The density gradient developed after 12 h had a curvature, concave upward, to which a smooth curve was fitted by hand. Five grains of mica (170- to 200-mesh fraction) that showed no evidence of splitting or inclusions when viewed edge-on under a binocular microscope were selected, and these all settled to a single level, at 3.264. Considering the precision of density measurement by gradient (standards to 0.0005, depth measurement to 0.01 mm, and the size of the grains measured being 0.1 mm), the density of norrishite estimated by gradient is 3.264 ± 0.002.

Composition

Analytical results are presented in Table 2. For sample 820607 the ETEC microprobe results (column 2) are slightly lower than those of columns 3 and 4; column 1 shows the total range for all microprobe analyses of this sample. The wavelength-dispersive electron-microprobe data in column 4 have a lower detection limit than the energy-dispersive analyses of columns 2 and 3 and are preferred for the minor elements. Electron-microprobe analysis shows no Fe; hence, the determination of total oxidation state provides a measure of the oxidation state of Mn³⁺. The result of 33.21% Mn₂O₃ is very close to the microprobe-determined value for total Mn expressed as Mn₂O₃ of 33.34. Mn measurements by electron microprobe are therefore expressed as Mn₂O₃, consistent also with the evidence from the optical absorption spectra. Of the 14 analyses averaged in column 3, 12 were from yellow-brown regions and 2 were from green regions; no significant difference was detected between the two groups of analyses. There is a correlation between SiO₂ and Al₂O₃

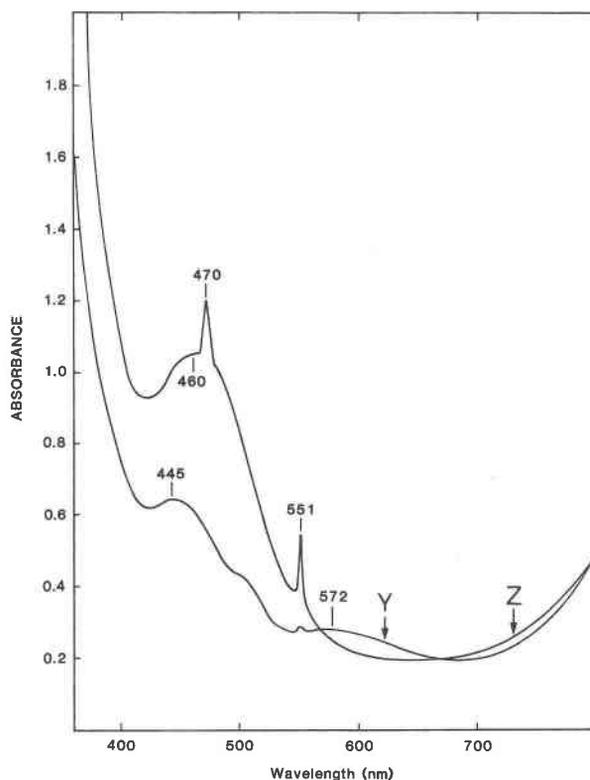


Fig. 2. Polarized optical absorption spectra perpendicular to a 15- μ m flake of norrishite at room temperature. Y' is 20° from Y.

for these 14 analyses in a 2:1 ratio (1:1 atomic), suggesting a small range of Al substitution for Si. Results for H₂O⁻ (0.04, 0.27%) are omitted from the probe totals in the analytical table, because adsorbed water does not remain on the sample surface during microbeam analysis. Gas chromatography detected no H₂; the instrumental detection limit is about 0.1%. The two determinations of H₂O⁺ gave 0.65 and 0.67%, equivalent to 0.07% H. The replicate determinations of Li₂O are appreciably different (2.4% and 3.8%). Both analyses were performed on small quantities of purified mica, the AAS result following significant dilution.

For sample 820608, column 6 presents Cameca microprobe data obtained on single crystals of the same mineral separate as was used to measure density, cell dimensions, infrared pattern, water content, optical data, the AAS Li analysis, and the atomic spectroscopic analysis of column 7, Table 2.

A structural formula for norrishite from sample 820607 (column 5, Table 2) was calculated on the basis of 24 oxygens from the average of the three results shown in columns 2, 3, and 4 of Table 2, including the Li₂O and H₂O results from columns 6 and 7 and assuming all Mn to be trivalent. For sample 820608, the empirical cell content in column 8 was calculated from the observed cell volume (471.92 Å³) and density (3.264 g/cm³) using

TABLE 2. Chemical analyses of norrishite

	Sample 820607					Sample 820608		
	1	2	3	4	5	6	7	8
SiO ₂	49.11–51.13	49.72	50.14	50.37	7.69	50.98	51.6	7.88
Al ₂ O ₃	0.28–1.64	0.81	0.96	1.31	0.19	0.72	0.93	0.13
TiO ₂	0.09–0.17	0.0	0.06	0.15	0.0	0.05	0.11	0.02
Fe ₂ O ₃	0.10–0.14	0.12	<0.20	<0.02	0.00	<0.05	0.05	0.00
Mn ₂ O ₃	32.76–35.03	33.48	34.23	34.68	3.99	33.34*	31.22	3.92
MgO	0.07–0.49	0.16	0.18	0.32	0.05	0.21	0.23	0.05
Li ₂ O†	n.d.	n.d.	n.d.	n.d.	1.90	3.2	3.2	2.00
CaO	0.0	0.04	<0.02	0.0	0.00	<0.02	0.03	0.00
BaO	—	n.d.	n.d.	0.13	0.02	<0.07	0.04	0.00
Na ₂ O	0.05–0.10	0.07	0.12	0.04	0.00	0.03	0.18	0.01
K ₂ O	9.17–10.50	9.46	10.12	10.39	1.96	9.84	9.35	1.94
F	—	<0.2	n.d.	<0.09	0.0	<0.07	0.0	0.0
Cl	—	n.d.	n.d.	<0.01	0.0	0.0	0.0	0.0
H ₂ O*	—	—	—	—	0.67	n.d.	0.66	0.67
Total (microprobe)		93.81	95.90	97.39		95.17		
Total (microprobe + Li ₂ O + H ₂ O)		97.0	99.07	100.56		98.94	97.90	
Oxygen in structural formula				24				24.22

Note: H₂O* determined on two 0.3-g samples of mineral separate, yielding 0.65% at 1100 °C in air, 0.67% with CuO in N₂. H₂O⁻ determined on the same samples heated to 110 °C, yielding 0.04% and 0.27%. n.d. = not determined. Columns are as follows: (1) Range of all microprobe analyses for sample 820607. (2) ETEC energy-dispersive electron-microprobe analysis; average of 11 analyses. (3) Technische Physische Dienst energy-dispersive microprobe; average of 15 analyses. (4) Cameca Microbeam wavelength-dispersive probe; average of 4 analyses. (5) Structural formula for 820607 normalized to 24 oxygens. (6) Cameca electron-microprobe analysis; average of 8 analyses from 4 mica crystals. (7) Australian Mineral Development Laboratory analysis. Inductively coupled plasma, atomic emission spectroscopy. Total includes Sr 0.01, S 0.11, Ni 0.02, Cu 0.05, Pb 0.01, Zn 0.01, Co 0.05. (8) Empirical structural formula for sample 820608 using column 6 except for Li and H.

* Mn₂O₃ estimated from total oxidation state measurement of 0.3-g sample = 33.21%.

† Li₂O by AES (3.8%) and AAS (2.4%) averaged.

the microprobe analyses of column 6 and average Li₂O and H₂O figures. Omitting minor elements, the formula is KMn₂LiSi₄O₁₂ with Z = 2, which has a calculated density of 3.255.

X-ray crystallography

Precession photographs show a normal 1M mica unit cell, with space group C2/m, Cm, or C2. Cell dimensions from the X-ray powder data are a = 5.293(1), b = 8.936(2),

c = 10.076(1) Å, and β = 98.0(1)°. The indexed powder data are listed in Table 3. Intensities of the basal reflections were measured by diffractometer from a thin, oriented aggregate of norrishite and reduced to structure factors using the Lorentz-polarization factor for a randomly oriented powder. Structure factors were calculated using the following as z coordinates for the atomic planes: Mn, Li = 0.0; Si = 0.275; O, OH = 0.10; basal O = 0.338; and K = 0.5. Temperature factors were taken from the data

TABLE 3. X-ray diffraction data for norrishite

hkl	Intensity	d _{obs}	d _{calc}	hkl	Intensity	d _{obs}	d _{calc}
001	10	10.01	9.98	132*	1	2.24	2.236
002	0.5	4.99	4.99	202	1	2.198	2.197
020	5	4.464	4.468	041	3	2.177	2.180
111	4	4.322	4.318	221*	1	2.15	2.150
021*	2	4.08	4.08	133**	4	2.116	2.115
112	6	3.571	3.571	005**	2	1.996	1.996
003	8	3.329	3.326	223*	2	1.98	1.984
112	7	3.160	3.166	134	1	1.735	1.738
113*	1	2.86	2.848	204	3B	1.695	1.693
023	3	2.671	2.668	006**	2	1.663	1.663
200**	5	2.620	2.620	135	4	1.638	1.636
130**	2	2.586	2.590	243	2B	1.573	1.573
131**	5	2.549	2.550	153, 135	2B	1.535	1.533
004	2	2.495	2.494	331**	4	1.517	1.517
201**	3	2.452	2.452	060**	3	1.490	1.489
132**	6	2.365	2.366	007**	1	1.425	1.425
114	1	2.306	2.304	136, 245	4	1.357	1.357
220, 221*	2	2.26	2.26	008**	1	1.247	1.247

Note: B = broad.

* Line not referred to Si or quartz standard.

** Line used in parameter refinement.

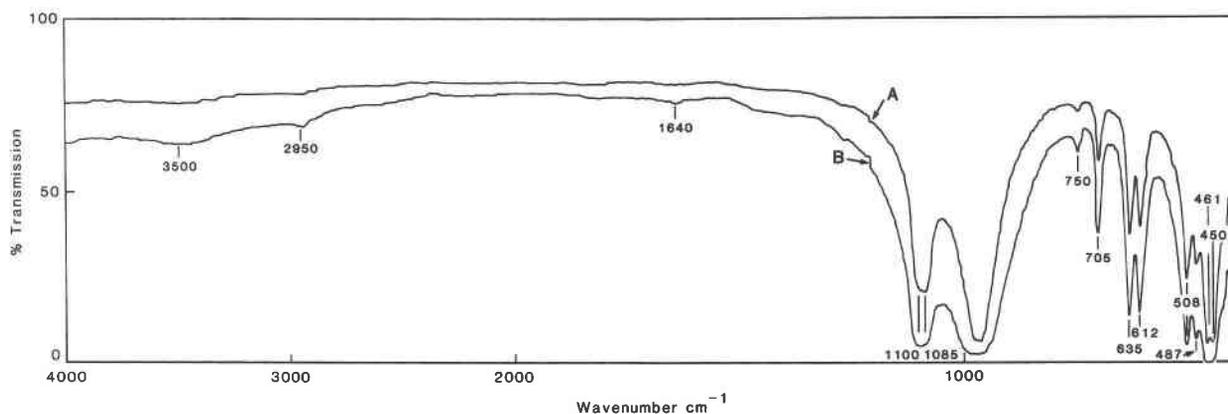


Fig. 3. Infrared absorption spectrum for norrishite, 2.5-mg sample in 1-g KBr. Lower curve using a 0.5-g KBr pressed disc; upper curve using a 0.2-g KBr pressed disc.

of Knurr and Bailey (1986) for Mn-substituted phlogopite. The scattering factors used were those for $(2\text{Mn}^{3+} + \text{Li}^+)/3$, Si^{2+} , 0.96K^+ , and O^- . Slightly better agreement between observed and calculated F values was obtained using an octahedral occupancy of 2.85 rather than 3 (Mn_2Li), but in either case the agreement is close (Table 4). A crystal-structure determination is in progress.

Infrared spectrum

The infrared spectrum (Fig. 3) differs from that of most micas in having almost no absorption in the region around 3500 cm^{-1} , where H_2O is active. This result is in accord with the water analysis, which shows less water than in any other analyzed micas. [See compilations by Foster (1960a, 1960b) and Bailey (1984).] No specific attributions have been attempted for the absorption maxima in the region $400\text{--}800\text{ cm}^{-1}$.

DISCUSSION

The two structural formulae given in Table 2 show an almost ideal number of octahedral cations. For the empirical formula, $[\text{Si} + \text{Al}] = 8.01$, the octahedral cation total is 5.97, and the interlayer cations total 1.94. The number of Mn atoms is close to 4, the ideal amount if Mn and Li are ordered over the octahedral sites, for example with Li in M(1) (the vacant site of a dioctahedral mica) and two Mn atoms in the M(2) sites. A similar ordering pattern was found by Lin and Guggenheim (1983) for an Li-Al, Be-Si brittle mica. The 001 X-ray reflections in micas are sensitive to cation-plane occupancies. Structure-factor calculations using these reflections are entirely consistent with a mica structure for norrishite having an octahedral sheet occupancy close to Mn_2Li .

The oxidation state of Mn in norrishite is 3+, judging from the analysis of total oxidation state. In undistorted octahedral sites, Mn^{3+} is unstable relative to Mn^{2+} and Mn^{4+} , but may be stabilized by octahedral distortion (Burns, 1970). The octahedral sites of all micas are somewhat distorted, being flattened in the z direction (Bailey,

1984), and it is likely that if the M(2) octahedra contain Mn^{3+} , their shared edges will be significantly shortened (as they are in muscovite), reducing the site symmetry enough to stabilize Mn^{3+} .

The b cell dimension (8.936 \AA) is very short compared to most other trioctahedral micas (e.g., 9.221 \AA in manganian phlogopite and $9.00\text{--}9.03\text{ \AA}$ in lepidolites), but longer than the value of 8.76 \AA that Lin and Guggenheim (1983) found for a brittle mica with an $\text{Al}_2\text{Li}_{0.5}$ octahedral sheet. The ionic radius of Mn^{3+} (0.785 \AA) is less than that of Mg^{2+} (0.86 \AA) or Fe^{2+} (0.92 \AA), producing a smaller octahedral sheet than in phlogopite or biotite. The tetrahedral sheet of norrishite is nearly pure Si and can reduce b to 8.936 \AA by a tetrahedral rotation of about 12° , just outside the range of observed rotations for trioctahedral micas of $1^\circ\text{--}11^\circ$, but considerably less than the rotations of $21.8^\circ\text{--}22.6^\circ$ in ephesite (Slade et al., 1987).

Norrishite is comparable to oxybiotite in its low (OH + F) content. This raises the possibility that the mineral originally formed with Mn^{2+} and the normal OH content of other micas and that it subsequently became oxidized and dehydrated. Two arguments suggest that this is not the case. First, norrishite appears to be in complete equilibrium with braunite ($\text{Mn}^{2+}\text{Mn}_3^{2+}\text{SiO}_{12}$) and the other manganese silicates of the oxidized assemblage, it is not found in the reduced assemblage at the Hoskins mine,

TABLE 4. Observed and calculated structure factors for norrishite 001 reflections

hkl	F_{obs}	F_{calc}
001	32.0	33.6
002	7.2	9.1
003	71.9	70.9
004	31.8	32.1
005	37.4	-37.3
006	26.4	25.2
007	27.1	26.3
008	36.7	36.2
009	12.2	12.0
$\Sigma F_o - F_c / \Sigma F_o = 0.028$		

and the analyzed samples are quite unweathered. Thus Mn^{3+} accords with the overall oxidized nature of the host rock and its association with other Mn^{3+} -bearing minerals (Abraham and Schreyer, 1976; Brown et al., 1978; Keskinen, 1981; Ashley, 1984; Mottana, 1986). Second, as Guggenheim and Eggleton (1987) showed, a true mica structure is not found for layer silicates having an all-Si tetrahedral sheet and a mean octahedral cation radius of more than 0.73 Å (ionic radii from Shannon, 1976). The average cation radius for $(2Mn^{2+} + Li)$ is 0.81 Å, whereas for $(2Mn^{3+} + Li)$, the radius is 0.68 Å, the same as for polyolithionite and celadonite. On crystal-chemical grounds, therefore, it is unlikely that norrishite could have crystallized with Mn^{2+} .

Norrishite has similarities to montdorite (Robert and Maury, 1979), which has octahedral Mn, and to taenolite, which contains Li; both also have a low tetrahedral Al content. Other Mn-bearing micas are manganian phlogopite and biotite (Guggenheim and Kato, 1984), masutomilite, a 1M trioctahedral mica with octahedral Mn, Li, and Al (Nagashima et al., 1975), and hendricksite, an (Mn,Zn) mica. These contain much less Mn than norrishite and are relatively unoxidized. Alurgite contains a small amount of Mn, but is dioctahedral (Heinrich and Levinson, 1955).

Norrishite differs from all other micas in having an octahedral sheet that contains four Mn^{3+} and two Li ions per eight silicons, giving an octahedral sheet charge of 14. Substitution of other cations for Mn in the octahedral sheet is negligible; there is no detectable Fe (Table 2, column 1), and MgO and TiO_2 are well under 1%. The interlayer contains essentially K ions with trace amounts of Na and Ba. The water content (H_2O^+) is remarkably low for a mica containing no F, but is quite consistent with the Mn^{3+} and the consequent high octahedral sheet charge.

Norrishite differs optically from other micas in its pleochroic scheme, in having inclined extinction, and in having a positive optic sign. The presence of noticeable {100} and {010} cleavages in addition to the usual perfect basal cleavage is another distinctive property of norrishite.

ACKNOWLEDGMENTS

We thank C. Foudoulis for technical assistance in mineral separation, X-ray diffraction, and infrared spectroscopy, J. Wasik for the oxidation state and water analyses, and L. Krausz for obtaining the optical absorption spectrum. This work was supported by a Faculty Research Grant of the Australian National University.

REFERENCES CITED

- Abraham, K., and Schreyer, W. (1976) A talc-phengite assemblage in piemontite schist from Brezovica, Serbia, Yugoslavia. *Journal of Petrology*, 17, 421–439.
- Ashley, P.M. (1984) Piemontite-bearing rocks from the Olary district, South Australia. *Australian Journal of Earth Sciences*, 31, 203–216.
- (1986) An unusual manganese silicate occurrence at the Hoskins mine, Grenfell district, New South Wales. *Australian Journal of Earth Sciences*, 33, 443–456.
- Bailey, S.W. (1984) Crystal chemistry of the true micas. In S.W. Bailey, Ed., *Micas*. Mineralogical Society of America Reviews in Mineralogy, 13, 13–57.
- Bloss, F.D., and Riess, D. (1973) Computer determination of $2V$ and indicatrix orientation from extinction data. *American Mineralogist*, 58, 1052–1061.
- Bowman, H.N. (1977) Forbes 1:250,000 metallogenic map. Mine data sheets and metallogenic study. Geological Survey of New South Wales.
- Brown, P., Essene, E.J., and Peacor, D.R. (1978) The mineralogy and petrology of manganese-rich rocks from St. Marcel, Piedmont, Italy. *Contributions to Mineralogy and Petrology*, 67, 227–233.
- Burns, R.G. (1970) Mineralogical aspects of crystal field theory. University Press, Cambridge, England.
- Burns, R.G., and Strens, R.G.J. (1967) Structural interpretation of polarized absorption spectra of the Al-Mn-Fe-Cr epidotes. *Mineralogical Magazine*, 36, 204–226.
- Foster, M.D. (1960a) Interpretation of the composition of trioctahedral micas. U.S. Geological Survey Professional Paper 354-B, 11–48.
- (1960b) Interpretation of the composition of lithium micas. U.S. Geological Survey Professional Paper 354-E, 115–147.
- Griffin, W.L., and Mottana, A. (1982) Crystal chemistry of clinopyroxenes from the St. Marcel manganese deposit, Val d'Aosta, Italy. *American Mineralogist*, 67, 568–586.
- Guggenheim, S., and Eggleton, R.A. (1987) Modulated 2:1 layer silicates: Review, systematics, and predictions. *American Mineralogist*, 72, 724–738.
- Guggenheim, S., and Kato, T. (1984) Kinoshitalite and Mn phlogopites: Trial refinements in subgroup symmetry and further refinement in ideal symmetry. *Mineralogical Journal (Japan)*, 12, 1–5.
- Hall, L.R. (1959) Manganese. Mineral Industry Geological Survey of New South Wales, 25.
- Heinrich, E.W., and Levinson, A.A. (1955) Studies in the mica group; Mangan-muscovite from Matkär, Finland. *American Mineralogist*, 40, 1132–1135.
- Keskinen, M. (1981) Petrochemical investigation of the Shadow Lake piemontite zone, eastern Sierra Nevada, California. *American Journal of Science*, 281, 896–921.
- Knurr, R.A., and Bailey, S.W. (1986) Refinement of Mn-substituted muscovite and phlogopite. *Clays and Clay Minerals*, 34, 7–16.
- Lin, J.-C., and Guggenheim, S. (1983) The crystal structure of a Li,Be-rich brittle mica: A dioctahedral-trioctahedral intermediate. *American Mineralogist*, 68, 130–142.
- Mottana, A. (1986) Blueschist-facies metamorphism of manganiferous cherts: A review of the alpine occurrences. *Geological Society of America Memoir* 164, 267–299.
- Nagashima, K., Harada, K., and Honda, M. (1975) Masutomilite, a new mineral from Tanakamiyama, Shiga Prefecture, Japan. *Japanese Geoscience Magazine*, 26, 319–324 (not seen; extracted from *Mineralogical Abstracts*, 29, 78–3478).
- Nambu, M., Tanida, K., and Kitamura, T. (1969) Kôzulite, a new alkali amphibole from Tanohata mine, Iwate Prefecture, Japan. *Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists*, 62, 311–328.
- Reinecke, T. (1986a) Crystal chemistry and reaction relations of piemontites and thulites from highly oxidized low-grade metamorphic rocks at Vitali, Andros Islands, Greece. *Contributions to Mineralogy and Petrology*, 93, 56–76.
- (1986b) Phase relations of surssasite and other highly oxidized low-grade, high-pressure metamorphic rocks from Evvia and Andros Islands, Greece. *Contributions to Mineralogy and Petrology*, 94, 110–126.
- Reinecke, T., Okrusch, M., and Richter, P. (1985) Geochemistry of ferromanganian metasediments from the islands of Andros, Cycladic blueschist belt, Greece. *Chemical Geology*, 53, 249–278.
- Robert, J.L., and Maury, R.C. (1979) Natural occurrence of a (Fe,Mn,Mg) tetrasilicic potassium mica. *Contributions to Mineralogy and Petrology*, 68, 117–123.
- Ryall, A.R. (1974) Geology of the Grenfell area, New South Wales. B.A. Honours thesis, Macquarie University, Sydney, Australia.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.

- Slade, P.G., Schultz, P.K., and Dean C. (1987) Refinement of the ephesite structure in $C1$ symmetry. *Neues Jahrbuch für Mineralogie Monatshefte*, 15, 257–287.
- Smith, G., Hälenius, U., and Langer, K. (1982) Low temperature spectral studies of Mn^{3+} bearing andalusite and epidote type minerals in the range 3000–5000 cm^{-1} . *Physics and Chemistry of Minerals*, 8, 136–142.
- Smith, G., Hälenius, U., Annersten, H., and Ackerman, L. (1983) Optical and Mössbauer spectra of manganese-bearing phlogopites: $Fe^{3+}(IV)$ - $Mn^{2+}(VI)$ pair absorption as the origin of reverse pleochroism. *American Mineralogist*, 68, 759–768.

MANUSCRIPT RECEIVED AUGUST 10, 1987

MANUSCRIPT ACCEPTED JULY 10, 1989