

Lithium-Hydrorhodonite

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Abstract. $M^I M^{II} \text{HSi}_5 \text{O}_{15}$ ($M^I = \text{Li}_{0.85}, \text{Na}_{0.07}, M^{II} = \text{Mn}_{3.61}, \text{Mg}_{0.33}, \text{Ca}_{0.03}, \text{Al}_{0.01}, \text{Fe}_{0.02}^{2+}$), triclinic, $P\bar{1}$, $a = 7.530(3)$, $b = 11.736(5)$, $c = 6.710(3)$ Å, $\alpha = 92^\circ 58(3)'$, $\beta = 95^\circ 14(3)'$, $\gamma = 106^\circ 16(3)'$, $Z = 2$, $D_x = 3.52$ g cm $^{-3}$. Though the structure has been found to be isotopic with the nambulite structure, the M^I atom is essentially coordinated by six O atoms which form a distorted octahedron, the mean $M^I\text{—O}$ bond length being 2.261 Å. Of five independent octahedral positions per cell, Mg is preferentially located at a specific position.

Introduction. Li-hydrorhodonite, a member of the pyroxenoids, was found by Gokhale [see Ito (1972)] in high-grade regional metamorphic rock in India; it has the chemical composition $\text{Li}_{0.85}\text{Na}_{0.07}\text{Mn}_{3.61}\text{Mg}_{0.33}\text{Ca}_{0.03}\text{Al}_{0.01}\text{Fe}_{0.02}^{2+}\text{HSi}_5\text{O}_{15}$ (Ito, 1972). The investigation of the system $\text{Li}_2\text{SiO}_3\text{—Mn}_2\text{SiO}_4\text{—SiO}_2 + \text{H}_2\text{O}$ (Ito, 1972) and the occurrence of nambulite, $(\text{Na}, \text{Li})\text{Mn}_4\text{HSi}_5\text{O}_{15}$ (Yoshii, Aoki & Maeda, 1972), suggest that Na substitutes for Li in Li-hydrorhodonite in the ratio of at least $\text{Li}/\text{Na} = 1$. Narita, Koto & Morimoto (1975) reported the structure of nambulite to be closely related to that of babingtonite, $\text{Ca}_2\text{Fe}^{2+}\text{Fe}^{3+}\text{HSi}_5\text{O}_{15}$ (Araki & Zoltai, 1972), which belongs to one of the two distinct groups of pyroxenoids (Takéuchi, 1976; Takéuchi & Koto, 1977). The present paper reports results of our structural study of Li-hydrorhodonite which was undertaken to observe on the one hand the effects on structure caused by Li—Na substitution and on the other the mode of distribution of Mg over the octahedral positions.

Crystals from the original locality were used for the present study. The cell dimensions (see *Abstract*) were obtained by single-crystal diffractometry ($\lambda = 0.7107$ Å). The space group $P\bar{1}$ was assumed, and later confirmed by the structure refinement. The crystal used for intensity measurements was a trigonal prism, 0.15 mm along the prism parallel to [110]; the dimensions of the cross-section were 0.10 × 0.09 × 0.06 mm. The ω — 2θ

technique was used to measure a total of 4292 reflexions to $\sin \theta = 0.5723$. After correction for Lorentz and polarization factors, the intensities were reduced to structure factors. No corrections were made for absorption ($\mu = 48.3$ cm $^{-1}$ for $\text{Mo K}\alpha$) or extinction.

For the structure determination, the atomic parameters of nambulite (Narita *et al.*, 1975) were used as a starting model; Li was located at the position corresponding to $M(5)$, and the Mn's were distributed over the rest of the octahedral positions. After several cycles of isotropic least-squares calculations with *ORFLS* (Busing, Martin & Levy, 1962), R was 0.041. Throughout the calculations, 1879 reflexions that satisfied the relation $F_o/F_{o\text{max}} \geq 0.05$ were used; non-ionized atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Table 1. Atomic coordinates and isotropic temperature factors for non-hydrogen atoms with their standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å 2)
<i>M</i> (1)	0.5947 (2)	0.6540 (1)	0.0611 (2)	0.62 (2)
<i>M</i> (2)	0.8149 (2)	0.9416 (1)	0.1289 (2)	0.64 (2)
<i>M</i> (3)	0.0384 (2)	0.2349 (1)	0.1801 (2)	0.59 (2)
<i>M</i> (4)	0.2468 (2)	0.5139 (1)	0.2662 (2)	0.77 (2)
<i>M</i> (5)	0.6645 (20)	0.1177 (13)	0.3541 (21)	2.19 (22)
Si(1)	0.2799 (3)	0.0595 (2)	0.3581 (3)	0.60 (3)
Si(2)	0.4739 (3)	0.3269 (2)	0.4281 (3)	0.50 (3)
Si(3)	0.8186 (3)	0.4556 (2)	0.2213 (3)	0.56 (3)
Si(4)	0.0094 (3)	0.7251 (2)	0.3005 (3)	0.56 (3)
Si(5)	0.3510 (3)	0.8533 (2)	0.1143 (3)	0.43 (3)
O(1)	0.1997 (8)	0.0095 (5)	0.5621 (8)	1.00 (8)
O(2)	0.1208 (8)	0.0683 (5)	0.1855 (8)	0.72 (8)
O(3)	0.4471 (7)	0.1829 (5)	0.4170 (8)	0.93 (8)
O(4)	0.3274 (8)	0.3496 (5)	0.2541 (9)	0.92 (9)
O(5)	0.5307 (8)	0.6158 (5)	0.3533 (8)	0.87 (8)
O(6)	0.6936 (8)	0.3838 (5)	0.3890 (8)	0.93 (7)
O(7)	0.9789 (8)	0.3964 (5)	0.1725 (9)	1.15 (9)
O(8)	0.6796 (7)	0.4701 (5)	0.0329 (8)	0.59 (7)
O(9)	0.9324 (8)	0.5853 (5)	0.3370 (8)	1.15 (8)
O(10)	0.8815 (7)	0.7675 (5)	0.1307 (8)	0.71 (8)
O(11)	−0.0225 (8)	0.2030 (5)	0.4827 (9)	1.20 (8)
O(12)	0.2173 (7)	0.7451 (5)	0.2304 (8)	0.80 (7)
O(13)	0.5364 (8)	0.8238 (5)	0.0711 (8)	0.88 (8)
O(14)	0.7656 (8)	0.1204 (5)	0.0850 (8)	0.85 (8)
O(15)	0.3996 (8)	0.9730 (5)	0.2728 (8)	0.88 (8)

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A refinement of site occupancy was then executed based on a slightly idealized chemical composition, $\text{Li}_{0.92}\text{Na}_{0.08}\text{Mn}_{3.66}\text{Mg}_{0.34}\text{HSi}_5\text{O}_{15.0}$, giving the results: 0.96 (1) Mn, 0.04 Mg at $M(1)$; 0.97 (1) Mn, 0.03 Mg at $M(2)$; 0.79 (1) Mn, 0.21 Mg at $M(3)$; and 0.94 Mn, 0.06 Mg at $M(4)$. The isotropic refinement converged to an R of 0.038 ($R_w = 0.045$). The maximum shift of the atomic coordinates as a fraction of the standard deviation in the final cycle was 0.068. Table 1 gives the final atomic parameters.*

Discussion. The structure of Li-hydrorhodonite is best illustrated in the projection on to the $(1\bar{1}1)$ plane (Fig. 1a), which is parallel to the layers of octahedral cations characteristic of pyroxenoids. The corresponding projection of the babingtonite structure is compared in Fig. 1(b). The structure of Li-hydrorhodonite is in general built up on the same principle as that of nambulite, with bands of octahedra formed by O atoms about the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32252 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

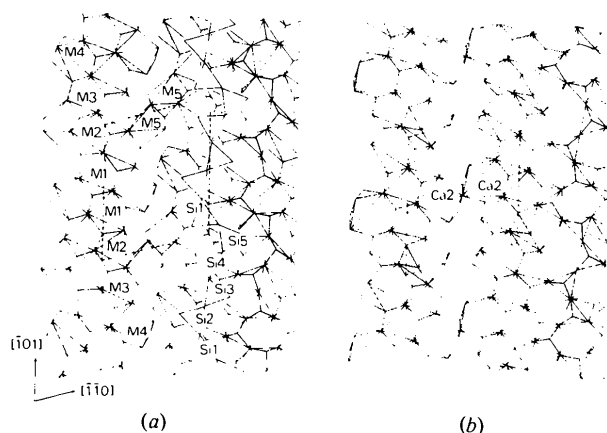


Fig. 1. Comparison of the sheets of polyhedra in the structures of (a) Li-hydrorhodonite and (b) babingtonite, projected on $(1\bar{1}1)$; some of the silicate chains are omitted.

Table 2. $M(5)$ —O distances (Å)

	Li-hydrorhodonite	Nambulite
$M(5)$ —O(1)	2.105 (16)	2.351 (9)
O(3)	2.058 (16)	2.159 (9)
O(11)	2.349 (16)	2.317 (8)
O(14)	2.021 (15)	2.186 (8)
O(15)	2.229 (16)	2.476 (7)
O(15)'	2.801 (15)	2.798 (8)
O(6)	(3.069)	2.705 (9)
O(12)	(3.060)	2.860 (8)
Average	2.261	2.482

(for six bonds)

cations running along $[110]$: each band is attached to a pair of silicate chains which have a periodicity five tetrahedra long. One of the marked features characterizing the difference between these two minerals is ob-

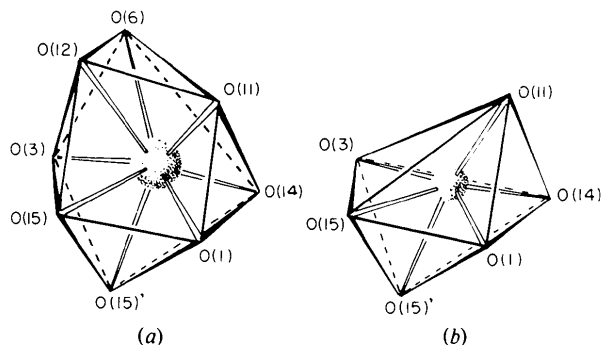


Fig. 2. (a) The polyhedron about $M(5)$ in nambulite and (b) the corresponding polyhedron in Li-hydrorhodonite.

Table 3. Major bond distances (Å) and angles ($^\circ$) with their standard deviations

$M(1)$ octahedron		$M(2)$ octahedron	
$M(1)$ —O(4)	2.248 (6)	$M(2)$ —O(1)	2.144 (5)
O(5)	2.102 (6)	O(2)	2.350 (6)
O(8)	2.420 (6)	O(2)'	2.212 (6)
O(8)'	2.184 (6)	O(10)	2.236 (6)
O(10)	2.190 (6)	O(13)	2.152 (6)
O(13)	2.156 (6)	O(14)	2.261 (6)
Average	2.217	Average	2.226
$M(3)$ octahedron		$M(4)$ octahedron	
$M(3)$ —O(2)	2.212 (6)	$M(4)$ —O(4)	2.177 (6)
O(4)	2.210 (6)	O(5)	2.147 (6)
O(7)	2.067 (6)	O(6)	2.493 (6)
O(10)	2.223 (5)	O(7)	2.118 (6)
O(11)	2.151 (6)	O(8)	2.134 (5)
O(14)	2.135 (6)	O(9)	2.794 (6)
Average	2.167	O(12)	2.804 (6)
		Average	2.381
Si(1) tetrahedron		Longest three	2.697
Si(1)—O(1)	1.618 (6)	Shortest four	2.144
O(2)	1.618 (6)		
O(3)	1.634 (6)	Si(2) tetrahedron	
O(15)	1.649 (6)	Si(2)—O(3)	1.642 (6)
Average	1.630	O(4)	1.617 (6)
		O(5)	1.589 (6)
Si(3) tetrahedron		O(6)	1.652 (6)
Si(3)—O(6)	1.645 (6)	Average	1.625
O(7)	1.603 (6)		
O(8)	1.614 (6)	Si(4) octahedron	
O(9)	1.636 (6)	Si(4)—O(9)	1.620 (6)
Average	1.625	O(10)	1.612 (6)
Si(5) tetrahedron		O(11)	1.625 (6)
Si(5)—O(12)	1.662 (6)	O(12)	1.632 (6)
O(13)	1.577 (6)	Average	1.622
O(14)	1.623 (6)		
O(15)	1.650 (6)	Si(1)—O(3)—Si(2)	138.1 (4)
Average	1.628	Si(2)—O(6)—Si(3)	140.3 (4)
		Si(3)—O(9)—Si(4)	142.2 (4)
		Si(4)—O(12)—Si(5)	131.9 (4)
		Si(5)—O(15)—Si(1)	135.1 (4)

served in the coordination polyhedra about Li(Na) atoms at the $M(5)$ position. This position in nambulite has eight near O atoms, whereas in Li-hydrorhodonite the position is shifted to one side so that it has six near O atoms; the coordination polyhedra are essentially octahedral (Fig. 2). The $M(5)$ —O distances in the two minerals are compared in Table 2.

Other bond lengths for Li-hydrorhodonite are listed in Table 3.

The close structural relationship between these two minerals and babingtonite appears somewhat puzzling since the number of cations in the latter is different from the numbers in the former two. Fig. 1(a) and (b) shows that the babingtonite structure is, in principle, derivable from the nambulite (or Li-hydrorhodonite) structure by removing the $M(5)$ atoms; the babingtonite structure can thus be regarded as a cation-deficient structure of the nambulite type. It is to be noted that the Ca(2) position in the babingtonite structure, which corresponds to $M(4)$ in Li-hydrorhodonite, is occupied by the larger Ca, increasing the size of the polyhedron; the polyhedron shares an edge with the adjacent polyhedron which is related to the former by inversion (Fig. 1b).

Silicate chains of Li-hydrorhodonite are attached to octahedral bands in a way that is typical of pyroxenoids of the p - p (pectolite-pyroxene) series (Takéuchi, 1976; Takéuchi & Koto, 1977); the triplet of tetrahedra Si(1), Si(5), Si(4) is not attached to the same octahedron as in wollastonite, which belongs to the other series of pyroxenoids. For pyroxenoids of the p - p series, Takéuchi, Kudoh & Yamanaka (1976) pointed out that octahedra like $M(2)$, whose location relative to the silicate chain corresponds to that of $M(1)$ in pectolite, is better able to accommodate relatively larger cations. This means, in turn, that the Mg atoms which

are smaller than the major cations, Mn, in the present structure are expected to be located in octahedral positions other than $M(2)$. Our result, that Mg is located at $M(3)$, is fully in accord with the view given by Takéuchi *et al.* (1976).

The short distance of 2.464 (8) Å between O(1) and O(11) strongly suggests the existence of a hydrogen-bonded system. An account is given in a paper published elsewhere (Takéuchi & Koto, 1977) of the hydrogen-bonded systems of pyroxenoids in the pectolite-pyroxene series in general.

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Polymeric Copper(II) Chloride–1,4-Dioxan (3:2)

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Abstract. $C_8H_{16}Cl_6Cu_3O_4$, monoclinic, $C2/m$, $a = 7.880$ (6), $b = 12.045$ (14), $c = 9.208$ (13) Å, $\beta = 106.45$ (2)°, $Z = 2$, $D_x = 2.30$, $D_m = 2.29$ (1) g cm⁻³; $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 128$ cm⁻¹. Zigzag $(\text{CuCl}_2)_\infty$ chains lie along c . Each Cu atom is also bonded to two O atoms of dioxan molecules, which cross-link the chains in the ac plane.

Introduction. Slow recrystallization from acetonitrile usually gave clumps of fine needles, but larger prisms were occasionally formed. The latter were mostly split, but a data set adequate for resolving the structure was obtained from two crystals sealed in capillaries. Equi-inclination Weissenberg photographs of the levels 0–5 kl and $h0$ –5 l were scanned by a microdensitometer