

# Crystal chemistry of a nonstoichiometric carpholite, $K_x(Mn_{2-x}Li_x)Al_4Si_4O_{12}(OH)_4F_4$ : A chain silicate related to pyroxenes

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## ABSTRACT

The chemical composition of carpholite can be represented as  $M_2Al_4Si_4O_{12}(OH)_8$  ( $M = Mn^{2+}, Fe^{2+}, Mg^{2+}$ ). The nonstoichiometric  $Li^+$ ,  $K^+$ ,  $F^-$ -bearing carpholite that we investigated occurs as white to straw-yellow needles in miarolitic cavities in the Sawtooth batholith, Idaho, and has the composition  $K_x(Mn_{2-x}Li_x)Al_4Si_4(OH)_4F_4$  with  $x \approx 0.65$ . It is orthorhombic, space group *Ccca*, with  $a = 13.715(5)$ ,  $b = 20.302(7)$ ,  $c = 5.138(3)$  Å, and  $Z = 4$ . The atomic positions including H have been refined to an *R* factor of 0.022 on the basis of 852 X-ray reflections. The crystal structure consists of pyroxene-like slabs [T–O–T layers with single silicate chains and Al(1) octahedral bands] parallel to the *c* axis, cross-linked by ( $Li^+$ ,  $Mn^{2+}$ ) and Al(2) octahedral bands. Half the  $(OH)^-$  ions in normal carpholite are replaced by  $F^-$  ions in an ordered fashion.  $Li^+$ , replacing  $Mn^{2+}$  in a distorted octahedral coordination, occupies a site distinct from the  $Mn^{2+}$  position. The  $K^+$  ions partially occupy a large cavity with sixteenfold coordination [ $O_8F_8$ ], which can be described as a truncated octagonal bipyramid. These cages share rectangular faces with adjacent ones to form channels parallel to *c*, which are peculiar to the carpholite structure. There is an additional channel site comparable to the A site in the amphiboles. The carpholite structure type is amenable to a large variety of cationic and anionic substitutions.

## INTRODUCTION

The chemical composition of most naturally occurring carpholites can be represented by  $M_2Al_4Si_4O_{12}(OH)_8$ , where  $M = Mn, Fe, Mg$ . The determination of the crystal structure of ferrocapholite (McGillavry et al., 1956) was followed by determinations of the crystal structures of manganoan carpholite (Naumova et al., 1975; Lindemann et al., 1979) and magnesiocarpholite (Viswanathan, 1981). Occurrences of ferromagnesian carpholites in different parts of the world in different geologic horizons have attracted attention as indicators of high-pressure–low-temperature metamorphic environments (Mottana and Schreyer, 1977). The crystal chemistry of the ferromagnesian carpholites has been described by Viswanathan and Seidel (1979). In this paper, we present the chemical and structural details of a new member of the carpholite family, which is characterized by the coupled substitution  $K^+ + Li^+ \leftrightarrow Mn^{2+}$  and the ordered replacement of half the  $(OH)^-$  ions by  $F^-$ , giving rise to the nonstoichiometric formula  $K_x(Mn_{2-x}Li_x)Al_4Si_4O_{12}(OH)_4F_4$ , with  $x \approx 0.65$ . The coupled-cation substitution is reminiscent of the situation in amphiboles, where the large A site is sometimes partially occupied by  $K^+$  because of the

coupled substitution  $Si^{4+} \leftrightarrow Al^{3+} + K^+$ . Since carpholites share some common structural features with pyroxenes, namely, T–O–T layers with single silicate chains, this similarity with the amphiboles is quite intriguing.

## OCCURRENCE AND CHEMICAL COMPOSITION

The  $K^-$ ,  $Li^-$ , and  $F^-$ -bearing carpholite occurs as white to straw-yellow needles in the miarolytic cavities of the Sawtooth batholith, Idaho. The associated minerals are quartz, microcline, albite, beryl, topaz, bertrandite, helvite, zinnwaldite, fluorite, hematite, and apatite. The nature of the geologic occurrence indicates a relatively low pressure and medium temperature environment for its origin. The average chemical composition (wt% oxides), as determined by the electron microprobe (except Li, which was determined by atomic absorption) is as follows:  $SiO_2$  36.44,  $TiO_2$  0.08,  $Al_2O_3$  30.65,  $MnO$  13.00,  $FeO$  (total) 0.55,  $MgO$  0.08,  $CaO$  0.01,  $BaO$  0.02,  $K_2O$  5.03,  $Na_2O$  0.69,  $Li_2O$  1.19,  $F$  9.21,  $H_2O$  (by difference) 6.93. The chemical formula derived from this analysis on the basis of  $20(O + OH + F)$  gives

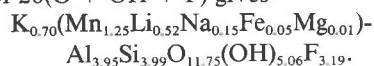
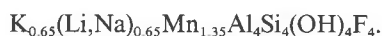


TABLE 1. Nonstoichiometric carpholite: Crystal data

Nonstoichiometric carpholite: straw-yellow needles from Sawtooth batholith, Idaho	
$K_{0.65}(Li_{0.85}Mn_{1.35})Al_4Si_4O_{12}(OH)_4F_4$	
Orthorhombic, <i>mmm</i>	
<i>a</i> (Å): 13.715(5)	$D_{calc}$ (g·cm <sup>-3</sup> ): 3.065
<i>b</i> (Å): 20.302(7)	$\mu$ (MoK $\alpha$ ) (cm <sup>-1</sup> ): 21.93
<i>c</i> (Å): 5.138(3)	Total no. of reflections: 1044
<i>V</i> (Å <sup>3</sup> ): 1430.63	No. of reflections $\geq 2\sigma(I)$ : 852
Space group: <i>Ccca</i>	<i>R</i> : 0.022
<i>Z</i> : 4	$R_w$ : 0.022

The K<sup>+</sup> and (Li<sup>+</sup> + Na<sup>+</sup>) contents range between 0.57 and 0.71, Mn from 1.14 to 1.38, and F from 2.81 to 3.62 per formula unit. For the purposes of crystal-structure determination, we have adopted a simplified formula:



K- and F-bearing carpholites were reported earlier by Chashka et al. (1973) and Marchenko and Goncharova (1981), who proposed the chemical formula (Mn,Zn,Fe<sup>2+</sup>···)<sub>1-x</sub>(K,Li,Na)<sub>2x</sub>Al<sub>2</sub>(Si<sub>2</sub>O<sub>6</sub>)(OH,F)<sub>4</sub>. We will show that the formula we have proposed above is crystal-chemically correct.

### EXPERIMENTAL DETAILS

Preliminary X-ray Weissenberg photographs revealed orthorhombic symmetry. The systematic absences (*hkl*, *h*

+ *k* = odd; *h0l*, *h*, *l* = odd; *0kl*, *k*, *l* = odd; *hk0*, *h*, *k* = odd; *h00*, *h* = odd; *0k0*, *k* = odd; and *00l*, *l* = odd) confirm the space group *Ccca*. Unit-cell dimensions (Table 1) were determined by least-squares refinement from  $2\theta$  values ( $12^\circ \leq 2\theta \leq 24.87^\circ$ ) of 25 reflections measured on an Enraf Nonius CAD 4 diffractometer with MoK $\alpha$  radiation. The crystal dimensions were 0.03 × 0.15 × 0.20 mm. The intensity data were collected on the same diffractometer using the  $\theta$ - $2\theta$  scan mode and MoK $\alpha$  radiation (graphite monochromator). Three standard reflections were measured after every 200 reflections; no significant change in intensities was observed during the data collection. A total of 1045 independent reflections were measured within  $2\theta \leq 60^\circ$ , out of which 852 reflections had intensities greater than  $2\sigma(I)$ , where  $\sigma(I)$  is the standard deviation as determined from counting statistics. The intensities were corrected for Lorentz, polarization, and absorption factors, the latter using psi-scans. The scattering factors including anomalous dispersion for Li, K, Mn, Si, Al, O, F, and H were taken from the *International Tables for X-ray Crystallography*, volume IV (1974). The crystal structure was determined by direct methods, which yielded the positions of all the heavy atoms and oxygens. The Li and H positions were determined from difference-Fourier maps. The partial occupancies of K, Li, and Mn were determined by site occupancy refinement. The least-squares refinement using anisotropic temperature factors for all atoms except H

TABLE 2A. Nonstoichiometric carpholite: Atomic positional and isotropic thermal parameters

Atom	Site occupancy	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^*$
K	0.191(1)	0.0000	0.2500	0.7500	0.0310(5)
Mn	0.299(2)	0.0000	0.37733(11)	0.2500	0.0075(2)
Li	0.206(2)	0.0009(26)	0.3765(11)	0.2580(26)	0.0190**
Al(1)	1.000	0.19536(6)	0.2500	0.2500	0.0065(2)
Al(2)	1.000	0.0000	0.46136(4)	0.7500	0.0073(2)
Si	1.000	0.19323(4)	0.37902(3)	0.9137(1)	0.0060(1)
O(1)	1.000	0.2071(1)	0.29943(7)	0.9312(3)	0.0075(4)
O(2)	1.000	0.0805(1)	0.39809(7)	0.8997(3)	0.0089(4)
O(3)	1.000	0.2456(1)	0.41057(7)	0.1723(3)	0.0085(3)
O(4)(OH)	1.000	0.0689(2)	0.46806(7)	0.4323(3)	0.0085(4)
F	1.000	0.1026(1)	0.30594(7)	0.3667(3)	0.0157(4)
H	1.000	0.1250(20)	0.4620(14)	0.4154(25)	0.0453(26)

Note: Standard deviation in parentheses.

\*  $U_{eq} = (1/3)\sum_i U_{ii}$ .

\*\* *U* (isotropic).

TABLE 2B. Nonstoichiometric carpholite: Anisotropic thermal parameters,  $U_{ij}$ 

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
K	0.0190(7)	0.0546(11)	0.0196(7)	0.0000	0.0000	0.0000
Mn	0.0061(3)	0.0073(3)	0.0058(3)	0.0000	0.0019(3)	0.0000
Al(1)	0.0071(3)	0.0068(3)	0.0058(4)	-0.0002(3)	0.0000	0.0000
Al(2)	0.0068(3)	0.0086(4)	0.0067(4)	0.0000	-0.0008(3)	0.0000
Si	0.0061(2)	0.0064(2)	0.0056(2)	0.0005(2)	0.0000(2)	0.0005(2)
O(1)	0.0093(6)	0.0071(6)	0.0063(6)	0.0006(5)	0.0006(5)	0.0020(5)
O(2)	0.0062(6)	0.0110(6)	0.0095(7)	0.0011(6)	-0.0004(6)	0.0020(5)
O(3)	0.0112(6)	0.0085(6)	0.0061(6)	0.0001(5)	-0.0027(5)	0.0002(6)
O(4)(OH)	0.0060(6)	0.0109(6)	0.0089(7)	0.0009(6)	0.0008(5)	0.0015(5)
F	0.0147(6)	0.0170(6)	0.0156(6)	0.0009(5)	0.0019(5)	0.0053(5)

Note:  $U_{ij} = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ . Standard deviations in parentheses.

TABLE 3. Nonstoichiometric carpholite: Interatomic distances (Å) and angles (°)

<b>The K polyhedron</b>				
K–O(1)	3.153(4) (×4)			
K–O(2)	3.294(4) (×4)			
K–F	2.674(4) (×4)			
K–F'	3.648(4) (×4)			
<b>The Mn octahedron</b>				
Mn–O(2)	2.154(2) (×2)	O(2)–O(2')	4.223(3)	157.4(1)
Mn–O(4)(OH)	2.272(2) (×2)	O(2)–O(4)	3.089(3) (×2)	88.4(1) (×2)
Mn–F	2.107(2) (×2)	O(2)–O(4')	2.638(3) (×2)	73.1(1) (×2)
		O(2)–F	3.058(3) (×2)	91.7(1) (×2)
		O(4)–O(4')	2.661(3)	71.7(1)
		O(4)–F	3.341(3) (×2)	99.4(1) (×2)
		O(4)–F'	4.327(3) (×2)	162.3(1) (×2)
		F–F'	3.060(3)	93.1(1)
<b>The Al(1) octahedron</b>				
Al(1)–O(1)	1.928(1) (×2)	O(1)–O(1')	2.826(3)	94.7(1) (×2)
Al(1)–O(1')	1.914(1) (×2)	O(1)–O(1'')	3.842(3)	170.4(1)
Al(1)–F	1.808(1) (×2)	O(1)–O(1''')	2.432(3)	78.5(1) (×2)
		O(1)–F	2.661(3)	90.8(1) (×2)
		O(1)–F'	2.776(3)	96.0(1) (×2)
		O(1')–O(1''')	2.738(3)	91.3(1)
		O(1')–F	2.634(3)	90.1 (×2)
		O(1')–F'	3.706(3)	169.3(1)
		F–F'	2.569(3)	90.5(1)
<b>The Al(2) octahedron</b>				
Al(2)–O(2)	1.860(2) (×2)	O(2)–O(2')	2.692(3)	92.7(1)
Al(2)–O(4)(OH)	1.890(2) (×2)	O(2)–O(4)	2.794(3)	96.3(1) (×2)
Al(2)–O(4')(OH)	1.955(2) (×2)	O(2)–O(4')	2.727(3)	91.2(1) (×2)
Mean	1.902	O(2)–O(4'')	3.807(3)	172.2(2) (×2)
		O(2)–O(4''')	2.638(3)	89.4(1) (×2)
		O(4)–O(4')	2.394(3)	77.0(1) (×2)
		O(4)–O(4'')	3.771(3)	171.8(1)
		O(4)–O(4''')	2.878(3)	96.9(1) (×2)
<b>The Si tetrahedron</b>				
Si–O(1)	1.630(2)	O(1)–O(2)	2.656(3)	110.9(1)
Si–O(2)	1.595(2)	O(1)–O(3)	2.628(3)	106.9(1)
Si–O(3)	1.641(2)	O(1)–O(3')	2.698(3)	111.8(1)
Si–O(3')	1.629(2)	O(2)–O(3)	2.675(3)	111.5(1)
Mean	1.624	O(2)–O(3')	2.667(3)	111.7(1)
Si–Si	3.004(1)	O(3)–O(3')	2.572(3)	103.8(1)
Si–O(3)–Si	133.5(1)	Mean	2.649	109.4
Si–Si–Si	117.6(1)			
O(3)–O(3')–O(3'')	174.6(1)			
<b>Hydrogen bonds</b>				
O(4)–H	0.79(3)	O(4)–H...O(3)	3.004(3)	146(1)
H...O(3)	2.321(8)	O(4)–H...O(3')	3.058(3)	136(1)
H...O(3')	2.446(8)			

Note: Standard deviations in parentheses. For the interatomic angle, read O(2)–Mn–O(2'), etc.

and Li yielded a final *R* factor of 0.022 based on 852 unique reflections. Note that we have chosen the origin at  $\bar{1}$  for the orthorhombic space group *Ccca* and have followed the atom nomenclature suggested by Viswanathan (1981). The final atomic positional and thermal parameters and site occupancies are listed in Tables 2a and 2b, and the interatomic distances and angles are listed in Table 3. The standard deviation in Mn–O,F, Al–O,F, and Si–O bond lengths is  $\pm 0.002$  Å and in K–O,F bond lengths is  $\pm 0.004$  Å. The observed and calculated structure factors are in Table 4.<sup>1</sup>

## DISCUSSION

The crystal structure of the nonstoichiometric carpholite consists of pyroxene-like T–O–T slabs consisting of two sets of single silicate chains enclosing an Al(1) octahedral band parallel to the *c* axis, cross-linked by mixed octahedral bands of (Li,Mn) and Al(2) octahedra (Fig. 1). The K<sup>+</sup> ion partially occupies a large cavity with sixteenfold coordination [O<sub>8</sub>F<sub>8</sub>], which is vacant in Mn-, Fe-, and Mg-bearing carpholites. Furthermore, half the (OH)<sup>-</sup> ions in common carpholites are replaced by F<sup>-</sup> ions in an ordered fashion.

### The K coordination

The K coordination polyhedron [K<sup>+</sup>O<sub>8</sub>F<sub>8</sub>] with site symmetry *D*<sub>2</sub>(222) can be described as a doubly truncated octagonal bipyramid (Fig. 2). The K<sup>+</sup> ion occurs within a

<sup>1</sup> A copy of Table 4 may be ordered as Document AM-89-416 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

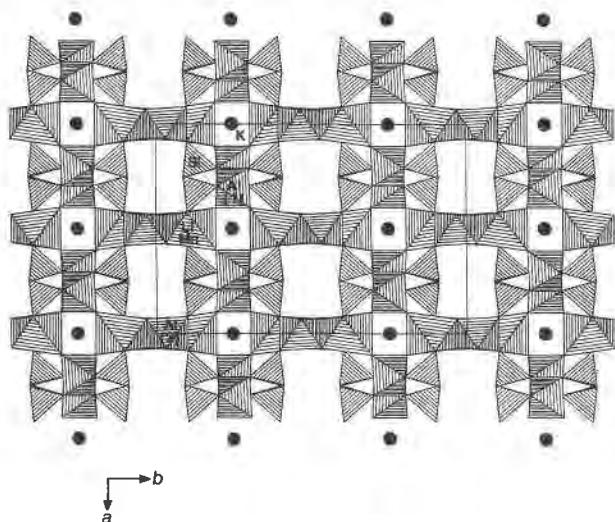


Fig. 1. A polyhedral sketch of the carpholite structure viewed down the  $c$  axis. Note the two different types of channels [A(1) and A(2)] parallel to the  $c$  axis, one of which [A(2)] is partially occupied by  $K^+$  ions (filled circles). Both channels are empty in Mn- and Mg-bearing carpholites.

distorted octagonal ring formed by shared oxygen corners of alternating silicate tetrahedra and aluminum octahedra: Si-Al(1)-Si-Al(2)-Si-Al(1)-Si-Al(2). Two curved rectangular faces consisting of  $F^-$  ions, one occurring above and one below the octagonal ring, truncate the apices of the octagonal bipyramid. These rectangular faces are formed by shared corners of a tetragonal ring of alternating (Li, Mn) and Al(1) octahedra (Fig. 3). The octagonal bipyramids share these rectangular faces with adjacent polyhedra to form channels parallel to the  $c$  axis (Fig. 2b). These channels are unique to carpholite and are reminiscent of similar channels in zeolites. To our knowledge, the sixteenfold coordination sphere of  $K^+$  in carpholite is the largest reported for K so far. The two sets of K-O distances are  $3.153 \text{ \AA} (\times 4)$  and  $3.294 \text{ \AA} (\times 4)$ , where one set of K-F distances is considerably shorter— $2.674 \text{ \AA} (\times 4)$ —and the other set is considerably longer— $3.648 \text{ \AA} (\times 4)$ .

#### The (Li,Mn) octahedron

The substitution of a monovalent ion,  $Li^+$ , for a divalent ion,  $Mn^{2+}$ , in an octahedral site is not very common,

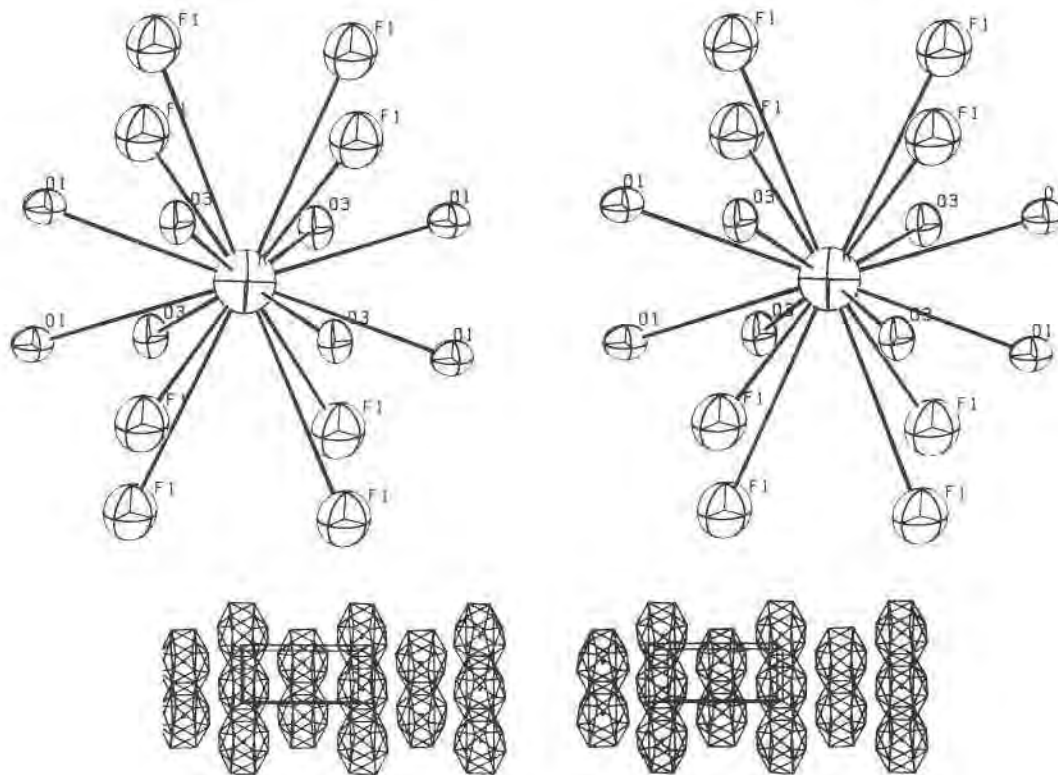


Fig. 2. (a) (upper) A stereoscopic view of the sixteenfold coordination polyhedron around  $K^+$ . (b) (lower) Channels [A(2)] formed by sharing the rectangular faces of the polyhedra containing the  $K^+$  ions.

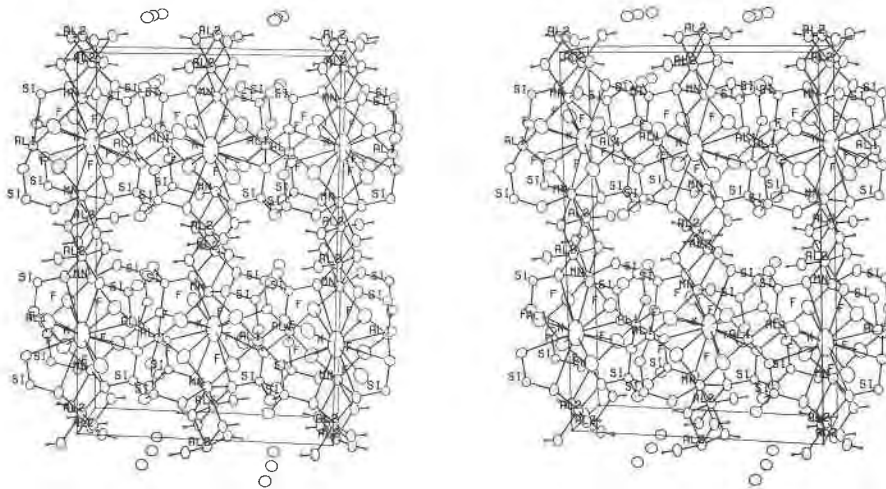


Fig. 3. A stereoview of the carpholite structure showing the details of the pyroxene-type T-O-T slab, the (Li,Mn) and Al octahedral band and the ordered distribution of the (OH)<sup>-</sup> and F<sup>-</sup> ions.

although small amounts of Li<sup>+</sup> substituting for Mg<sup>2+</sup> in the octahedral M(3) site in the Mn-bearing amphiboles juddite and winchite from India have been reported by Ghose et al. (1986). In a difference-Fourier map of the nonstoichiometric carpholite, calculated without the contribution of the Li atom to the structure factors, a small elongated peak appears off the twofold rotation axis ( $\parallel b$ ); this position (Table 2) is different from the Mn position on the  $b$  axis by 0.045 Å. Although the Li position could not be satisfactorily refined because of its low occupancy and weak X-ray scattering factor, it is clear that Li and Mn do not occupy the same position within the distorted octahedral site. The small amount of Na presumably occurs at the Li site. The splitting of the (Li,Mn) site in carpholite is reminiscent of the splitting of the M2 site in pyroxenes along a diad-axis into M2 and M2' due to the simultaneous occurrence of (Ca + Na) (~0.9) and Mg (~0.1) at this site (Rossi et al., 1987).

The [(Li,Mn)O<sub>2</sub>(OH)<sub>2</sub>F<sub>2</sub>] octahedron (point symmetry  $C_2 \parallel b$ ) shares three edges—one (OH)–(OH) edge and two O(2)–(OH) edges—with three adjacent Al(2) octahedra; these shared edges are short, 2.662 and 2.638 Å ( $\times 2$ ), respectively, and the subtended angles at Mn [71.7° and 73.1° ( $\times 2$ )] are much smaller than the ideal 90° octahedral angle. In contrast, the octahedral edge, F–F opposite to the short [(OH)–(OH)] edge is much longer (3.059 Å), and the F–Mn–F angle is 93.1°. This octahedral distortion is common in all carpholites (cf. Viswanathan, 1981). Compared to the corresponding Mn octahedron in Mn-bearing carpholite (Naumova et al., 1975), the (Li,Mn) octahedron is significantly smaller: the (Li,Mn)–O(2) and (Li,Mn)–(OH) distances, (2.153 and 2.273 Å) are shorter by 0.027 and 0.046 Å, respectively. The (Li,Mn)–F distance (2.107 Å), on the other hand, is slightly longer than the corresponding Mn–(OH) distance (2.066 Å) in Mn-bearing carpholite.

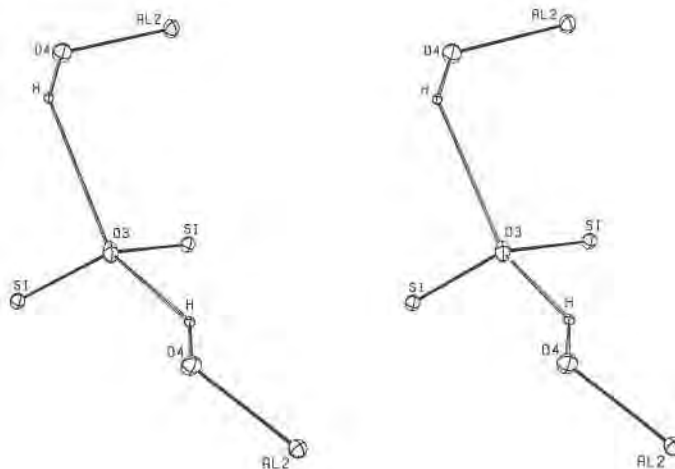


Fig. 4. Hydrogen-bonding scheme in the nonstoichiometric carpholite.

TABLE 5. Nonstoichiometric carpholite: Some possible cation and anion substitutions

	8A(1)	4A(2)	8M	8Al(1)	8Al(2)	16Si	16(OH)(1)	16(OH)(2)
Mn <sub>2</sub> Al <sub>4</sub> Si <sub>4</sub> O <sub>12</sub> (OH) <sub>8</sub>	□	□	Mn	Al	Al	Si	OH	OH
Fe <sub>2</sub> Al <sub>4</sub> Si <sub>4</sub> O <sub>12</sub> (OH) <sub>8</sub>	□	□	Fe	Al	Al	Si	OH	OH
Mg <sub>2</sub> Al <sub>4</sub> Si <sub>4</sub> O <sub>12</sub> (OH) <sub>8</sub>	□	□	Mg	Al	Al	Si	OH	OH
KLi <sub>2</sub> Al <sub>4</sub> Si <sub>4</sub> O <sub>12</sub> F <sub>4</sub> (OH) <sub>4</sub>	□	K	Li	Al	Al	Si	F	OH
KLi <sub>2</sub> Al <sub>4</sub> Si <sub>4</sub> O <sub>12</sub> F <sub>8</sub>	□	K	Li	Al	Al	Si	F	F
NaKLi <sub>2</sub> Al <sub>4</sub> (Si <sub>4</sub> Al) <sub>2</sub> O <sub>12</sub> F <sub>8</sub>	½Na	K	Li	Al	Al	½Si + ½Al	F	F

Note: □ = vacancy.

### The Al octahedra

There are two different types of Al octahedra in carpholite. The [Al(1)O<sub>4</sub>F<sub>2</sub>] octahedron (point symmetry  $C_2 \parallel a$ ) forms the pyroxene-like T–O–T slab with the silicate chains, whereas the [Al(2)O<sub>2</sub>(OH)<sub>4</sub>] octahedron (point symmetry  $C_2 \parallel b$ ) is part of the mixed (Li,Mn) and Al octahedral band, which is perpendicular to the plane of the T–O–T slab (Fig. 1). Both octahedra are tetragonally distorted; the Al(1) octahedron is shortened, whereas the Al(2) octahedron is elongated along the apical direction. Within the Al(1) octahedron, the two Al(1)–F distances (1.808 Å) are considerably shorter than the four Al(1)–O distances (avg.  $1.921 \pm 0.007$  Å). In contrast, within the Al(2) octahedron, the four Al(2)–(OH) distances (avg.  $1.923 \pm 0.033$  Å) are considerably longer than the two Al(2)–O distances (1.860 Å).

### The single silicate chain

The configuration of the single silicate chain is similar to such chains in other carpholites and Al-bearing pyroxenes such as jadeite, NaAlSi<sub>2</sub>O<sub>6</sub>, and spodumene, LiAlSi<sub>2</sub>O<sub>6</sub> (Clark et al., 1969), with one distinction: one of the bridging bonds [Si–O(3'), 1.629 Å] is slightly shorter than a nonbridging bond [Si–O(1), 1.630 Å]. The reason for this anomalous situation is not clear. The other bridging bond [Si–O(3), 1.641 Å] is considerably longer, and the nonbridging Si–O(2) bond (1.596 Å) is the shortest. The absorption peaks in the infrared spectrum at 875, 980, and 1090 cm<sup>-1</sup> (Marchenko and Goncharova, 1981) can be correlated with the Si–O stretching vibrations of the Si–O(3), [Si–O(1) + Si–O(3')], and Si–O(2) bonds. The significant difference in the lengths of the two nonbridging bonds can be explained on the basis of their bonding geometry. Oxygen O(1) is bonded to 2Al(1) + Si + K and is slightly overbonded (2.063 e.v.u.). If we neglect the weak K–O interaction (K–O distance = 3.153 Å), the bonding configuration is nearly trigonal planar. The oxygen atoms O(2), on the other hand, are significantly underbonded (1.863 e.v.u.) to (Li,Mn) + Al(2) + Si + K. The Si–O–Si angle is 133.5°, and the chain-kinking angle, O(3)–O(3')–O(3''), is 174.6°.

### The (OH)–F substitution and the hydrogen bonding

The position occupied by F in the nonstoichiometric carpholite corresponds to the (OH)(1) position in Mn, Fe,

Mg-bearing carpholites. The ordered (OH)–F substitution can be clearly seen in Figure 3. However, the variable (OH)–F ratio in the chemical composition indicates replacement of up to one F out of four by (OH) at the F site. The O(4)–H distance is 0.79 Å. The oxygen atom, O(3), bonded to two Si, is the recipient of two weak hydrogen bonds from two different (OH) groups (Fig. 4); the H···O(3) distances are 2.321 and 2.446 Å, and the corresponding O(4)–H···O(3) angles and O(4)–O(3) distances are 146° and 136° and 3.004 and 3.058 Å, respectively. This weak hydrogen bonding is confirmed by an infrared absorption peak at 3595 cm<sup>-1</sup> (Chaska et al., 1973), the nonbonded OH frequency being 3735.2 cm<sup>-1</sup> (Nakamoto, 1978).

### THE CARPHOLITE STRUCTURE TYPE AND POSSIBLE IONIC SUBSTITUTIONS

The coupled Li<sup>+</sup> + K<sup>+</sup> ↔ Mn<sup>2+</sup> and (OH)<sup>-</sup> ↔ F<sup>-</sup> substitutions in the nonstoichiometric carpholite show the possibility of further ionic substitutions in this structure type, which is more versatile than the amphibole structure in this respect. In addition to the channel site [A(2)] occupied by K<sup>+</sup>, there is another set of open channels parallel to the *c* axis located at ¼, 0 and ¼, ½ along *a* and *b* (Figs. 1, 3). The environment around this channel site [A(1)] (8*h*: ¼,0,*z*) is similar to the A site in the amphiboles in that it is enclosed by silicate chain layers along *a* and octahedral bands along *b*. However, because of symmetry and multiplicity of this site, two cations cannot simultaneously occur adjacent to each other because of the impossibly short (~2.6 Å) cation-cation separation. Hence, substitution at this site, coupled with the substitution in neighboring tetrahedral and octahedral sites, is limited to ≤0.5. We enumerate (in Table 5) some of the possible ionic substitutions in the various cationic and anionic sites and the resulting chemical compositions; remembering that Mg<sup>2+</sup> and Al<sup>3+</sup> can be replaced by other divalent and trivalent ions (including transition-metal ions) of comparable ionic sizes, the possibilities, in fact, are quite large.

### ACKNOWLEDGMENTS

This research is supported in part by NSF grant EAR-8719638 (S.G.) and computing funds from Tennessee Earthquake Research Center (P.K.S.G.). We thank M. W. Phillips, University of Toledo, for a review.

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MANUSCRIPT RECEIVED DECEMBER 8, 1988

MANUSCRIPT ACCEPTED MAY 2, 1989