

Mn-Mg distribution in a $C2/m$ manganooan cummingtonite: Crystal-chemical considerations

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ABSTRACT

The crystal structure of a Mn-Mg amphibole from Nsuta, Ghana, with the composition $(Ca_{0.24}Mn_{2.41}Mg_{4.20}Fe_{0.15})Si_8O_{22}(OH)_2$, $C2/m$ symmetry, unit-cell dimensions $a = 9.605(1)$, $b = 18.124(1)$, $c = 5.325(1)$ Å, and $\beta = 102.64(1)^\circ$ has been refined to an R factor of 0.047 on the basis of 1212 nonzero reflections measured on an automated X-ray diffractometer. Site-occupancy refinement indicates that the distorted octahedral M(4) site is nearly filled with Mn^{2+} , whereas small amounts of Mn^{2+} also occur at the smaller octahedral M(1), M(2), and M(3) sites, the sequence of site preference being $M(4) \gg M(1) > M(2) > M(3)$. The site preference of Mn^{2+} for the M(4) site in a Mn-Mg amphibole is nearly twice as strong as that of Fe^{2+} in the Fe-Mg amphibole because of a combination of the larger ionic size of Mn^{2+} and the greater covalency at the M(4) site compared to the M(1), M(2), and M(3) sites; the latter effect is indicated by short M(4)–O(4) bonds and the superhyperfine splitting in Mn^{2+} EPR spectra from trace amounts of Mn^{2+} in tremolite. The compositional limit for the $P2_1/m$ to $C2/m$ phase transition at ambient temperatures is presumably close to $Mn_2Mg_5Si_8O_{22}(OH)_2$, at which the M(4) site is nearly filled with Mn^{2+} .

INTRODUCTION

Since the discovery of very strong Fe-Mg ordering in grunerite and cummingtonite (Ghose and Hellner, 1959; Ghose, 1961), cation distribution in amphiboles has been extensively studied by a variety of techniques including X-ray and neutron diffraction, and infrared, Mössbauer resonance, and electron paramagnetic resonance (EPR) spectroscopies (see Hawthorne, 1983, for a review). Following the prediction of strong site preference of Mn^{2+} for the M(4) site in amphiboles (Ghose, 1965), it has been confirmed in Fe-Mn-Mg amphiboles by Mössbauer resonance spectroscopy (Bancroft et al., 1967), X-ray diffraction (Papike et al., 1969), and a combination of these two techniques (Hawthorne and Grundy, 1977). In a Mn-Mg amphibole with 0.96 Mn per formula unit and $P2_1/m$ symmetry, Papike et al. (1969) found Mn^{2+} to be exclusively located at the M(4) site. This amphibole inverts to $C2/m$ symmetry above 100 °C, and its crystal structure at 270 °C was refined by Sueno et al. (1972). Strong site preference of trace amounts of Mn^{2+} for the M(4) site in tremolite has been detected by the EPR technique (McGavin et al., 1982). In spite of these investigations, several questions remain unanswered: (1) How much Mn^{2+} can enter the smaller octahedral M(1), M(2), and M(3) sites, and how are the site geometries affected? (2) At what compositional limit does the symmetry change from $P2_1/m$ to $C2/m$ in Mn-Mg amphiboles under ambient conditions? In this paper, we attempt to answer these questions according to the results of a crystal-structure refinement of a Mn-Mg amphibole from Nsuta, Ghana, with the composition $(Ca_{0.24}Mn_{2.41}Mg_{4.20}Fe_{0.15})-$

$Si_8O_{22}(OH)_2$ and $C2/m$ symmetry. The Mn:Mg ratio in this amphibole clearly exceeds the composition $Mn_2Mg_5Si_8O_{22}(OH)_2$, considered to be an end-member by Hawthorne (1981). We have also determined the relative difference in the site-preference energies of Mn^{2+} and Fe^{2+} with respect to Mg^{2+} in amphiboles, and we offer a crystal-chemical explanation.

OCCURRENCE OF Mn-Mg AMPHIBOLES

In contrast to the Fe-Mn-Mg cummingtonites, which commonly occur in metamorphosed iron formations (Klein, 1966), nearly pure Mn-Mg amphiboles are relatively rare. They principally occur in nearly iron-free metamorphosed manganese ore deposits. The manganooan cummingtonite we investigated occurs in a metamorphosed manganese carbonate rock from Nsuta, Ghana, intimately associated with a Ca-Mn-Mg carbonate, spessartine, rhodochrosite, talc, and minor amounts of quartz (Jaffe et al., 1961). Similar occurrences have been reported from Balmat, New York (Ross et al., 1969); Buritirama, Brazil (Peters et al., 1977); Tatehira, Japan (Kobayashi, 1977); and the Sausar Group of central India (Dasgupta et al., 1988). At the Indian locality, the Mn-Mg amphibole occurs commonly with pyroxmangite with or without carbonates (rhodochrosite, kutnahorite, calcite). The highest Mn:Mg ratio reported so far in these amphiboles is 2.5:4.5. The manganooan cummingtonite from Ghana is close to this composition. A few small grains of this sample were obtained through the courtesy of Professor H. W. Jaffe, University of Massachusetts at Amherst, Massachusetts. The crystals are pale greenish white in color and long prismatic or acicular in habit.

TABLE 1. Mn-Mg amphibole from Nsuta, Ghana: Crystal data

Mn-Mg amphibole, Nsuta, Ghana			
$\text{Ca}_{0.24}\text{Mn}_{2.41}\text{Mg}_{4.20}\text{Fe}_{0.15}\text{Si}_8\text{O}_{22}(\text{OH})_2$			
<i>a</i> (Å)	9.6045(6)	$\lambda_{\text{MoK}\alpha}$ (Å)	0.71069
<i>b</i> (Å)	18.1244(10)	$\mu_{\text{MoK}\alpha}$ (cm^{-1})	25.57
<i>c</i> (Å)	5.3251(3)	Total no. of reflections	1685
β (°)	102.642(4)	Reflections $\geq 3\sigma(I)$	1212
<i>V</i> (Å ³)	904.52	<i>R</i> factor	0.047
Space group	<i>C2/m</i>	<i>R</i> _w	0.046
<i>Z</i>	2		
<i>D</i> _c (g/cm ³)	3.195		
Crystal size (mm)	0.10 × 0.13 × 0.15		

NOMENCLATURE: MANGANOAN CUMMINGTONITE VS. TIRODITE

The name *tirodite* was first given by Dunn and Roy (1938) to a honey-yellow amphibole occurring as coarse-bladed prisms associated with braunite, spessartine, rhodonite, and quartz in the manganese mines at Tirodi, Maharashtra, India. The chemical analysis of the type material indicates essentially a richteritic composition with significant amounts of Na (1.56 wt% Na₂O) and a minor cummingtonite component. Recalculation of the cation contents at the A and M sites in terms of 24 oxygens yields a total of 7.77, indicating substantial occupancy of the A site. This amphibole is clearly far from a manganoan cummingtonite, in which the A site is vacant. Segeler (1961) mistakenly referred to the manganoan cummingtonites from Talcville, New York as “*tirodite*,” because the yellow amphibole from Tirodi contains substantial amounts of Mn and Mg. Unfortunately, Segeler’s misidentification of manganoan cummingtonite as *tirodite* received the blessings of the IMA Commission on New Mineral Names. Ross et al. (1969) have recommended that the name *tirodite* should not be applied to the Talcville specimens, which they prefer to call manganoan cummingtonite.

EXPERIMENTAL DETAILS

Chemical analysis

The Mn-Mg amphibole was separated from manganese carbonate rock to 99% purity and analyzed by quantitative emission spectrography by A. L. Hallowell; MnO and MgO + CaO were also determined by wet-chemical methods, which agree with the spectrographic measurements (Jaffe et al., 1961). The chemical analysis, corrected for 5.4% spessartine garnet inclusions in the amphibole and normalized to 7 cations per formula unit, gives $(\text{Ca}_{0.24}\text{Mn}_{2.41}\text{Mg}_{4.20}\text{Fe}_{0.15})\text{Si}_8\text{O}_{22}(\text{OH})_2$.

Measurement of unit-cell dimensions and X-ray diffraction intensities

Single-crystal Weissenberg photographs taken with $\text{CuK}\alpha$ radiation show the crystals to be of relatively poor quality, usually showing streaks associated with strong reflections from parallel growth of several single crystals. After searching through a number of them, one was fi-

nally selected that showed reasonable single-crystal character. This crystal was mounted on a Syntex *PI* diffractometer, automated with a VAX 750 computer. The unit-cell dimensions were refined from 25 reflections with 2θ values between 30° and 45° (Table 1). These values are in fair agreement with those determined by X-ray powder diffraction (Jaffe et al., 1961). Reflections violating the *C2/m* space group were carefully sought, both in Weissenberg photographs and by X-ray diffractometry. Their absence indicates the *C2/m* space group, which has been confirmed by the successful refinement of the crystal structure in this space group. Following the refinement of the orientation matrix, all nonequivalent reflections within a 2θ limit of 65° were measured on the diffractometer with $\text{MoK}\alpha$ radiation and a graphite monochromator. Three standard reflections were measured after every 100 reflections. The scan speed was 3°/min. The total number of reflections measured was 1685, out of which 1212 were greater than $3\sigma(I)$, where $\sigma(I)$ is the standard deviation determined from the counting statistics. The diffraction intensities were corrected for Lorentz, polarization, and absorption factors.

Refinement of the crystal structure

The least-squares refinement was carried out by means of a full-matrix least-squares program on a VAX 750 computer. The scattering factors for neutral atoms Mn, Mg, Ca, Si, O, and H including anomalous dispersion were taken from *International Tables for X-ray Crystallography*, volume IV (1974). Each reflection was assigned a unit weight. All the Ca in the chemical composition was assigned to the M(4) site. As the Fe content was very small (0.15 per formula unit) and the X-ray scattering factors of Fe and Mn are very similar, only Mn and Mg occupancies were refined at the octahedral sites. After several cycles of refinement using isotropic and anisotropic temperature factors, the refinement converged to an *R* factor of 0.047 for 1212 reflections. A final difference-Fourier synthesis showed no significant positive or negative peaks at the octahedral sites or at the O(3) site, the latter indicating the absence of significant amounts of F. An alternate refinement with no Ca at the M(4) site showed no significant change in either atomic parameters or *R* factors. The final atomic positional and thermal parameters are listed in Table 2, and the site occupancies

TABLE 2(A). Mn-Mg amphibole: Atomic positional and isotropic thermal parameters

Atom	x	y	z	$U_{eq} (\times 10^3)^*$
M(1)	0	0.0868(10)	0.5	83(9)
M(2)	0	0.1769(10)	0	63(9)
M(3)	0	0	0	50(12)
M(4)	0	0.2635(1)	0.5	134(6)
Si(1)	0.2951(1)	0.1699(1)	0.7839(2)	84(5)
Si(2)	0.2868(1)	0.0842(1)	0.2776(2)	76(5)
O(1)	0.1143(3)	0.0860(2)	0.2122(6)	89(14)
O(2)	0.1214(3)	0.1721(2)	0.7179(6)	103(14)
O(3)	0.1135(5)	0	0.7122(8)	91(20)
O(4)	0.3745(3)	0.2470(2)	0.7759(6)	124(16)
O(5)	0.3492(3)	0.1298(2)	0.0655(6)	125(15)
O(6)	0.3494(3)	0.1215(2)	0.5575(6)	141(16)
O(7)	0.3444(5)	0	0.2803(9)	135(23)
H	0.195(13)	0	0.787(23)	190

Note: Standard deviations are given in parentheses.

* $U_{eq} = \frac{1}{6}\pi^2 \sum_i U_{ij} a_i^2$.

TABLE 2(B). Mn-Mg amphibole: Anisotropic thermal parameters, $U_{ij} (\times 10^5)$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M(1)	74(8)	87(8)	95(8)	0	35(6)	0
M(2)	67(8)	53(8)	75(8)	0	24(5)	0
M(3)	53(10)	61(10)	42(10)	0	22(8)	0
M(4)	134(5)	137(5)	149(5)	0	71(4)	0
Si(1)	74(4)	65(5)	91(5)	-7(4)	21(3)	-4(4)
Si(2)	81(5)	85(5)	89(5)	-8(4)	24(3)	4(4)
O(1)	51(12)	86(12)	125(13)	-2(10)	11(9)	0(10)
O(2)	86(12)	102(13)	121(12)	-4(10)	22(9)	18(11)
O(3)	84(18)	78(17)	113(18)	0	26(14)	0
O(4)	141(14)	120(14)	109(13)	-43(11)	26(11)	10(10)
O(5)	98(13)	160(14)	122(13)	-17(11)	32(10)	46(11)
O(6)	95(13)	193(15)	136(13)	21(11)	26(10)	-47(12)
O(7)	109(19)	60(17)	233(23)	0	33(17)	0

Note: Form of the anisotropic temperature factor, U_{ij} , is

$$\exp[-2\pi^2(U_{11}h^2a^2 + U_{22}k^2b^2 + U_{33}l^2c^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* \cos \beta^* + 2U_{23}klb^*c^*)].$$

Standard deviations are given in parentheses.

and interatomic bond lengths and angles with their standard deviations are listed in Table 3. The average standard deviation in M-O and Si-O bond lengths is ± 0.003 Å, and in that O-M-O and O-Si-O angles is $\pm 0.01^\circ$. The observed and calculated structure factors are listed in Table 4.¹

RESULTS AND DISCUSSION

Site occupancies and geometries of the octahedral sites

The refined site occupancies indicate the following cation distribution in this amphibole (cf. Mg-Fe cummingtonite, Ghose, 1961): M(1)—Mg 0.850(10), Mn 0.150(10); M(2)—Mg 0.894(9), Mn 0.106(9); M(3)—Mg 0.938(10), Mn 0.062(10); M(4)—Ca 0.120, Mn 0.836 (15), Mg 0.044 (15). An alternate refinement of site occupancy without Ca in the M(4) site yields Mn 0.932(10), Mg 0.068(10). The presence of small but significant amounts of Mn at the smaller octahedral sites is clearly indicated. The site preference of Mn²⁺ for the octahedral sites is M(4) \gg M(1) > M(2) > M(3). This conclusion also holds after taking into account the influence of the small amount of Fe in our sample (see below).

In amphiboles, the M(4) octahedra are the most flexible polyhedra within the octahedral band because they occur at the edges of the T-O-T slabs, which interconnect similar slabs. As Mn²⁺ is intermediate in ionic size (0.83 Å) between Ca²⁺ (1.00 Å) and Fe²⁺ (0.78 Å) (Shannon and Prewitt, 1970), we compare the interatomic distances in the M(4) polyhedra in tremolite, grunerite, and the Mn-Mg amphibole, in which the M(4) sites are occupied essentially by Ca²⁺, Fe²⁺, and Mn²⁺, respectively (Table 5). It can be seen that the polyhedral distortion of M(4) that

results from Mn²⁺ is intermediate between distortions due to Ca²⁺ and Fe²⁺. The differences involve the slightly overbonded oxygens O(5) and O(6) shared between two Si, which are much farther away from Fe²⁺ than they are from Mn²⁺ at the M(4) site. The M(4)—O(4) bonds, involving relatively underbonded oxygen O(4), are the shortest in all three cases. The geometries of the M(4) sites in the Mn-Mg amphibole and the C2/m Mn-Mg-Fe amphibole from Labrador (Papike et al., 1969) are essentially identical within error limits, indicating similar site occupancies.

Compared to the low-Mn cummingtonite from Talcville, New York (at 270 °C, C2/m symmetry) (Sueno et al., 1972), in which the smaller octahedral sites M(1), M(2), and M(3) are essentially occupied by Mg, the M(1) and M(2) octahedra in the Mn-Mg amphibole are slightly larger (by about 0.1 Å in average M—O distances) because of higher Mn contents, whereas the M(3) octahedra in both amphiboles are similar in size. The preference of Mn²⁺ for the smaller octahedral sites is strongly influenced by the presence of Fe²⁺. The average sizes of the M(1) and M(3) octahedra in the Mn-Mg amphibole from Ghana (with 0.15 Fe per formula unit) and the Mn-Fe-Mg amphibole from Labrador (with 0.54 Fe per formula unit) (Papike et al., 1969) are identical within error limits, whereas the M(2)—O distances involving O(1) and O(4) are significantly larger in the Mn-Mg amphibole, indicating a higher Mn²⁺ content at the M(2) site. Hence, in the presence of Fe²⁺, Mn²⁺ prefers the M(1) and M(3) sites, whereas Fe²⁺ prefers the M(2) site. A similar conclusion has been reached by Hawthorne and Grundy (1977). Because in the Mn-Mg amphibole most of the Fe is expected to be in the M(4) and M(2) sites, with smaller amounts in the M(1) and M(3) sites, and because the maximum possible Mn²⁺ content at the M(2) site (0.106) is considerably less than that in the M(1) site (0.150), we deduce the Mn²⁺ site preference in the smaller octahedral sites to be M(1) > M(2) > M(3).

¹ A copy of Table 4 may be ordered as Document AM-89-419 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.

TABLE 3. Mn-Mg amphibole: Site occupancies and interatomic distances (Å) and angles (°)

M(1) octahedron; site occupancy: Mn 0.150(10), Mg 0.850(10)			
M(1)-O(1)	2.072(3) (×2)	O(1)-O(2)	3.101(4) (×2)
M(1)-O(2)	2.122(3) (×2)	O(1)-O(2)'	2.840(4) (×2)
M(1)-O(3)	2.098(3) (×2)	O(1)-O(3)	3.087(5) (×2)
Mean	2.097	O(1)-O(3)'	2.787(4) (×2)
		O(2)-O(2)	2.908(5)
		O(2)-O(3)	3.120(3) (×2)
		O(3)-O(3)	2.776(9)
			95.3(1) (×2)
			85.2(1) (×2)
			95.5(1) (×2)
			83.9(1) (×2)
			86.5(1)
			95.4(1) (×2)
			82.9(2)
M(2) octahedron; site occupancy: Mn 0.106(9), Mg 0.894(9)			
M(2)-O(1)	2.157(3) (×2)	O(1)-O(1)'	2.785(5)
M(2)-O(2)	2.095(3) (×2)	O(1)-O(2)	3.073(4) (×2)
M(2)-O(4)	2.037(3) (×2)	O(1)-O(2)'	2.840(4) (×2)
Mean	2.096	O(1)-O(4)'	3.029(4) (×2)
		O(2)-O(4)	2.861(4) (×2)
		O(2)-O(4)	3.061(4) (×2)
		O(4)-O(4)'	2.998(6)
			80.4(2)
			92.5(1) (×2)
			83.8(1) (×2)
			92.4(1) (×2)
			87.6(1) (×2)
			95.6(1) (×2)
			94.8(2)
M(3) octahedron; site occupancy: Mn 0.062(10), Mg 0.938(10)			
M(3)-O(1)	2.090(3) (×4)	O(1)-O(1)'	3.117(6) (×2)
M(3)-O(3)	2.066(4) (×2)	O(1)-O(1)''	2.785(6) (×2)
Mean	2.082	O(1)-O(3)	3.084(5) (×4)
		O(1)-O(3)'	2.787(4) (×4)
			96.5(1) (×2)
			83.5(1) (×2)
			95.8(1) (×4)
			84.2(1) (×4)
M(4) octahedron; site occupancy: Ca 0.120, Mn 0.836(15), Mg 0.044(15)			
M(4)-O(2)	2.204(3) (×2)	O(2)-O(2)'	2.908(6)
M(4)-O(4)	2.103(3) (×2)	O(2)-O(4)	2.861(4) (×2)
M(4)-O(5)	3.118(3) (×2)	O(2)-O(4)'	3.018(4) (×2)
M(4)-O(6)	2.593(3) (×2)	O(2)-O(6)	4.535(5) (×2)
Mean of 6	2.300	O(2)-O(6)'	4.050(5) (×2)
Mean of 8	2.505	O(4)-O(6)	2.542(5) (×2)
		O(6)-O(6)'	3.085(6)
			82.5(1)
			83.2(1) (×2)
			89.0(1) (×2)
			141.8(1) (×2)
			114.9(1) (×2)
			64.6(1) (×2)
			73.0(1)
Si(1) tetrahedron			
Si(1)-O(1)	1.617(3)	O(1)-O(5)	2.665(4)
Si(1)-O(5)	1.617(3)	O(1)-O(6)	2.660(4)
Si(1)-O(6)	1.627(3)	O(1)-O(7)	2.664(4)
Si(1)-O(7)	1.623(2)	O(5)-O(6)	2.624(4)
Mean	1.621	O(5)-O(7)	2.621(4)
		O(6)-O(7)	2.646(4)
		Mean	2.647
			111.0(2)
			110.2(2)
			110.6(2)
			108.0(2)
			108.0(2)
			109.0(2)
			109.47
Si(2) tetrahedron			
Si(2)-O(2)	1.628(3)	O(2)-O(4)	2.743(4)
Si(2)-O(4)	1.597(3)	O(2)-O(5)	2.651(4)
Si(2)-O(5)	1.645(3)	O(2)-O(6)	2.681(4)
Si(2)-O(6)	1.665(3)	O(4)-O(5)	2.667(4)
Mean	1.634	O(4)-O(6)	2.542(5)
		O(5)-O(6)	2.709(4)
		Mean	2.666
			116.5(2)
			108.2(2)
			109.0(2)
			110.7(2)
			102.4(2)
			109.9(2)
			109.45
Si(1)-Si(1)'	3.054(2)	Si(1)-O(7)-Si(1)'	140.4(3)
Si(1)-Si(2)	3.070(2)	Si(1)-O(5)-Si(2)	140.5(2)
Si(1)-Si(2)	3.097(2)	Si(1)-O(6)-Si(2)	140.4(2)
O-H bond			
O(3)-H	0.80(12)		

Note: Standard deviations are given in parentheses.

Relative site preference of Mn²⁺ and Fe²⁺ in clin amphiboles

The preference of Mn²⁺ for the M(4) site is known to be much stronger than that of Fe²⁺ with respect to Mg²⁺ (Bancroft et al., 1967; Papike et al., 1969; Hawthorne and Grundy, 1977). The present Mn-Mg distribution data can be compared with the Fe-Mg distribution data in cummingtonites (Hafner and Ghose, 1971) to obtain a more quantitative estimate of the difference in site preference energies of Mn²⁺ and Fe²⁺. Consider the ion-exchange reactions



and



For the distribution coefficients, we can write

$$K_D = \frac{X_{\text{Mn}}^{\text{M1,2,3}}(1 - X_{\text{Mn}}^{\text{M4}})}{(1 - X_{\text{Mn}}^{\text{M1,2,3}})X_{\text{Mn}}^{\text{M4}}} \quad (3)$$

and

TABLE 5. M–O distances (Å) at the M(4) sites in tremolite, Mn-Mg amphibole, and grunerite

	Tremolite (Papike et al., 1969)	Mn-Mg amphibole (This paper)	Grunerite (Finger, 1969)
Site occupancy			
	Ca 0.95	Ca 0.120	Fe 0.985(8)
	Na 0.05	Mn 0.836(15) Mg 0.044(15)	Mg 0.015
M(4)–O(2) (×2)	2.397(2)	2.204(3)	2.135(5)
–O(4) (×2)	2.321(2)	2.103(3)	1.988(4)
–O(5) (×2)	2.767(2)	3.118(3)	3.298(5)
–O(6) (×2)	2.539(2)	2.593(3)	2.757(5)
Mean of 6	2.419	2.300	2.293
Mean of 8	2.506	2.505	2.545

$$K_D = \frac{X_{\text{Fe}}^{\text{M}1,2,3}(1 - X_{\text{Fe}}^{\text{M}4})}{(1 - X_{\text{Fe}}^{\text{M}1,2,3})X_{\text{Fe}}^{\text{M}4}}, \quad (4)$$

respectively, where $X_{\text{Fe-Mn}}^{\text{M}4}$ and $X_{\text{Fe-Mn}}^{\text{M}1,2,3}$ are mole fractions at the M(4) and the M(1), M(2), and M(3) sets of sites, respectively. Assuming ideal mixing of Mn-Mg and Fe-Mg at the M(4) and the M(1), M(2), and M(3) set of sites, the distribution coefficient, K_D , can be taken to have the same value as the equilibrium constant, K . In that case, if we assume a cation-equilibrium temperature for both amphiboles to be 600 °C (873 K), the values of the Gibbs free-energy change, ΔG^0 , for the exchange reactions can be calculated as

$$\Delta G^0 = -RT \ln K. \quad (5)$$

We have taken ΔG^0 as the site-preference energy, because it is a quantitative measure of the site preference for a transition-metal ion with respect to Mg for a particular octahedral site in pyroxenes and olivines (cf. Ghose and Wan, 1974). Table 6 lists the K_D and ΔG^0 values for the Mn-Mg and Fe-Mg cummingtonites with comparable Mn: Mg and Fe-Mg contents. Note that the site-preference energy for Mn^{2+} (18.33 kJ/mol) is nearly twice as large as that for Fe^{2+} (8.95 kJ/mol). Provided that no strong interaction between Fe^{2+} and Mn^{2+} is present, these site-preference energies should enable us to estimate the relative cation distribution in Fe-Mn-Mg amphiboles.

The strong site preference of Fe^{2+} for the M(4) site with respect to Mg in cummingtonites is primarily due to the stronger covalent bonding of Fe^{2+} at this site as shown by the short M(4)–O(4) bonds (1.988 Å in grunerite), which are considerably shorter than the sum of the respective ionic radii (Ghose, 1961, 1982). The stronger covalent bonding is further confirmed by the smaller isomer shift of Fe^{2+} at this site compared to the values at M(1), M(2), and M(3) as determined from ^{57}Fe Mössbauer spectra (Hafner and Ghose, 1971). In the case of Mn^{2+} , the much larger size of Mn^{2+} (0.83 Å) compared to Mg^{2+} (0.66 Å) is the most important driving force for the very strong site preference of Mn^{2+} for the M(4) site. However, a higher degree of covalency of Mn^{2+} at this site also plays an important role, as in the case of Fe^{2+} . In the Mn-Mg

TABLE 6. Mn-Mg and Fe-Mg distributions in cummingtonites: K_D and ΔG^0 values ($T = 873$ K)

	Mn-Mg amphibole Nsuta, Ghana	Fe-Mg amphibole* Quebec, Canada
Total $X^{\text{Mn}}/X^{\text{Fe}}$	0.350	0.378
$X_{\text{Mn}}^{\text{M}4}/X_{\text{Fe}}^{\text{M}4}$	0.950	0.728
$X_{\text{Mn}}^{\text{M}1,2,3}/X_{\text{Fe}}^{\text{M}1,2,3}$	0.127	0.199
K_D	0.0077	0.093
ΔG^0 (kJ/mol)	18.33	8.95

* Ghose (1961); Hafner and Ghose (1971).

amphibole, the M(4)–O(4) bonds are shorter by about 0.1 Å than the sum of ionic radii of Mn^{2+} and O^{2-} . Further supporting evidence for increased covalent bonding comes from the EPR spectra of trace amounts of Mn^{2+} in tremolite, in which Mn^{2+} shows a very strong site preference for the M(4) site (McGavin et al., 1982). The superhyperfine splitting parameter, \bar{A} for Mn^{2+} at the M(4) site is smaller by about 10 MHz than that at the M(1), M(2), and M(3) sites, indicating a much stronger covalency of the Mn^{2+} –O bonds at the M(4) site. Hence, in the Mn-Mg amphiboles, a combination of both ionic size and relative covalency effects are responsible for the much stronger site preference of Mn^{2+} for the M(4) site.

Compositional dependence of the $P2_1/m$ to $C2/m$ transition in Mn-Mg amphiboles

In the Mn-Mg amphibole with $P2_1/m$ symmetry, the M(4) site is occupied by 0.48 Mn^{2+} (Papike et al., 1969), whereas in the $C2/m$ phase, the Mn^{2+} occupancy is 0.84–0.93. Although the exact compositional limit at which the phase transition takes place cannot be determined at this time, we suggest that the compositional limit is close to $\text{Mn}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, at which the M(4) site is nearly filled with Mn^{2+} . A determination of the phase diagram with respect to both chemical composition and temperature would be of interest.

Configuration of the double silicate chains

The configuration of the double silicate chains is similar to that in other clinoamphiboles. The average Si–O distances in T(1) and T(2) tetrahedra are 1.621 and 1.634 Å, respectively. The T(1) tetrahedron is very regular with very little angular distortion, and the Si–O_{br} bond Si(1)–O(7) is not significantly different from the Si–O_{nbr} bonds. The T(2) tetrahedron, in contrast, is much more distorted with Si(2)–O(4) (1.597 Å) as the shortest and Si(2)–O(6) (1.665 Å) as the longest bonds. The oxygens O(4) and O(6) are also involved in the largest (116.5°) and the smallest (102.4°) O–Si–O angles. The Si–O_{br} bonds Si(2)–O(5) and Si(2)–O(6) are longer than the Si–O_{nbr} bonds. These two Si–O_{br} bonds are also significantly longer than the corresponding ones in grunerite (Finger, 1969), indicating close steric interaction with the M(4) site, when it is occupied by a larger cation such as Mn^{2+} as opposed to Fe^{2+} . The three Si–O–Si angles are very close to each other with an average value of $140.4^\circ \pm 0.1^\circ$. The chain

kinking angle, O(5)–O(6)–O(5) is 173.5° compared to the value of 173.0° in Mn-Mg amphibole at 270 °C with *C2/m* symmetry (Sueno et al., 1972).

SUMMARY AND CONCLUSIONS

The site preference of Mn²⁺ for the M(4) site is nearly twice as strong as that for Fe²⁺ in amphiboles. Small amounts of Mn²⁺ can occur in the smaller octahedral sites, M(1), M(2), and M(3). The symmetry change *P2₁/m* to *C2/m* most likely occurs at the Mn:Mg ratio 2:5.

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