

## Crystal structure of $P2_1/m$ ferromagnesian amphibole and the role of cation ordering and composition in the $P2_1/m$ - $C2/m$ transition in cummingtonite

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### ABSTRACT

We report structure refinements of three ferromagnesian cummingtonite crystals with  $\text{Mg}/(\text{Mg} + \text{Fe}) \approx 0.63$ . An unheated crystal with  $X_{\text{Mg}}^{\text{M}_4} = 0.051$  has  $C2/m$  symmetry, but crystals heat treated at 600 and 700 °C, with  $X_{\text{Mg}}^{\text{M}_4} = 0.167$  and 0.237, respectively, have  $P2_1/m$  symmetry. In  $P2_1/m$  cummingtonite from this study and from Hirschmann et al. (1994), the A silicate chain is S rotated and the B chain is O rotated. This differs from the structure of  $P2_1/m$  manganian cummingtonite, in which both A and B chains are O rotated (Papike et al., 1969). Documented in nature for the first time, the S-rotated silicate chains in amphibole suggest that, like the  $P2_1/c$  to  $C2/c$  phase transition in clinopyroxene, the change of the A-chain configuration from S to O rotation is intrinsic to the  $P2_1/m$  to  $C2/m$  transformation in ferromagnesian cummingtonite.

Documentation of different space groups for magnesio-cummingtonite crystals that differ only in site occupancies confirms that the M4-site population controls the relative stabilities of the  $C2/m$  and  $P2_1/m$  phases and places limits on the tolerance of the  $C2/m$  structure for Mg on the M4 site. At room temperature, ferromagnesian cummingtonite with  $X_{\text{Mg}}^{\text{M}_4} > 0.15 \pm 0.02$  has  $P2_1/m$  symmetry. In the  $P2_1/m$  structure, the separation between M4-O6A and M4-O6B and between M4-O5A and M4-O5B bond distances increases with increasing Mg content, as does the kinking angle (O5-O6-O5) of the A and B chains. Structural distortions away from  $C2/m$  symmetry, particularly in the configuration of the A chain, are greater for Fe-bearing cummingtonite than for Mn-bearing varieties at similar Mg concentration, indicating that for a given Mg content, ferromagnesian amphibole is more stable in the  $P2_1/m$  structure than manganian amphibole.

### INTRODUCTION

Cummingtonite,  $(\text{Mg,Fe,Mn})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ , occurs in two distinct polymorphs, one with the space group  $C2/m$  and the other  $P2_1/m$ .  $P2_1/m$  cummingtonite was first identified as an exsolved phase from tremolite by Bown (1966) and is restricted to Mg-rich compositions (Robinson and Jaffe, 1969; Ross et al., 1969; Rice et al., 1974; Immege and Klein, 1976; Yakovleva et al., 1978; Ghose, 1982; Hirschmann et al., 1994). Structure refinements of  $P2_1/m$  cummingtonite have been reported in three previous studies. Papike et al. (1969) determined the structure of a  $P2_1/m$  manganian crystal from Gouverneur, New York; Ghose (1982) reported partial structure information on a ferromagnesian cummingtonite; and Hirschmann et al. (1994) refined structures of five heat-treated  $P2_1/m$  ferromagnesian cummingtonite crystals. Using in situ high-temperature X-ray precession photography, Prewitt et al. (1970) found that the  $P2_1/m$  manganian cummingtonite studied by Papike et al. (1969) transforms to the  $C2/m$  structure at  $\sim 45$  °C, and that the transition is reversible and unquenchable. Sueno et al.

(1972) also investigated this sample by high-temperature single-crystal X-ray diffraction and found that the transition takes place at  $\sim 100$  °C.

No data are available relating to the temperature of the  $P2_1/m$ - $C2/m$  phase transition in cummingtonite along the  $(\text{Mg,Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$  join, other than at room temperature. Hirschmann et al. (1994) found that heat-treated cummingtonite crystals with  $X_{\text{Mg}} [= \text{Mg}/(\text{Mg} + \text{Fe} + \text{Mn})] < 0.61$  have the  $C2/m$  structure at room temperature, but those with  $X_{\text{Mg}} > 0.61$  have the  $P2_1/m$  structure. This boundary is consistent with constraints on the Fe substitution in  $P2_1/m$  amphibole from studies of Robinson and Jaffe (1969), Yakovleva et al. (1978), and Ghose (1982) but conflicts with the report by Ross et al. (1969) for  $P2_1/m$  cummingtonite crystals with  $X_{\text{Mg}} = 0.56$  (and with actinolite lamellae) from the Ruby Mountains, Montana. Both  $P2_1/m$  and  $C2/m$  cummingtonite crystals are present in the Ruby Mountains outcrop, but the crystals examined by X-ray diffraction were not the same as those analyzed by microprobe (Ross et al., 1969). The previous data are not sufficient to determine the substitutional limits of Mg in the M4 site in  $P2_1/m$  cummingtonite and to

TABLE 1. Crystal data and chemical composition for three cummingtonite crystals

	UH1 (unheated)	11a (heat treated at 600 °C)	1c (heat treated at 700 °C)
<i>a</i> (Å)	9.5015(6)	9.5048(4)	9.5057(3)
<i>b</i> (Å)	18.1280(10)	18.1343(8)	18.1187(7)
<i>c</i> (Å)	5.3089(4)	5.3077(2)	5.3059(3)
$\beta$ (°)	102.090(4)	102.009(3)	102.031(3)
Space group	<i>C2/m</i>	<i>P2<sub>1</sub>/m</i>	<i>P2<sub>1</sub>/m</i>
Total refls.	3651	3647	3646
Refls. $>3\sigma$	1412	1858	1755
Refls. $>3\sigma$ , but violate <i>C2/m</i> S.G.	10	418	385
<i>R<sub>w</sub></i> (%)	3.9	4.5	4.7
<i>R</i> (%)	3.1	3.6	4.1
<b>Tetrahedral cations normalized to sum of 8</b>			
Si	7.976	7.971	7.972
<sup>19</sup> Al	0.024	0.029	0.028
<b>Octahedral cations normalized to sum of 7</b>			
<sup>63</sup> Al	0.012	0.015	0.014
Fe	2.487	2.557	2.396
Mg	4.345	4.253	4.423
Mn	0.071	0.066	0.067
Ca	0.085	0.109	0.100
Fe/(Fe + Mg)	0.364	0.376	0.351

characterize the relative roles of the M4 cation occupancies and bulk composition on the location of the phase transition.

#### EXPERIMENTAL PROCEDURES

The sample used in this study, NMNH 118125, is from the collection of the Smithsonian Institution, Washington, DC, and has been investigated by several workers (Burns and Strens, 1966; Bancroft et al., 1967; Ghose and Weidner, 1972; Walter and Salisbury, 1989; Hirschmann et al., 1994). One unheated crystal (UH1) and two heat-treated crystals (11a at 600 and 1c at 700 °C) were studied. The 11a and 1c crystals were dug out of the polished thin sections that were previously studied by Hirschmann et al. (1994). Procedures for collection of X-ray intensity data, structure refinements, and microprobe analyses are similar to those described by Hirschmann et al. (1994). X-ray intensity data were collected for all three crystals on the basis of a primitive lattice and empirically corrected for absorption using  $\psi$  scans. Observed reflections [ $I > 3\sigma_I$ ] were examined by  $\omega$  scans, and no significant diffuse scattering or peak broadening was detected. The structural parameters and site occupancies derived for the 11a and 1c crystals in the present work are not distinguishable from those derived by Hirschmann et al. (1994) at the  $1\sigma$  level. This confirms the assertion of Hirschmann et al. (1994) that empirical absorption corrections do not significantly affect the determined site occupancies for cummingtonite, at least for crystal compositions similar to NMNH 118125.

#### RESULTS

Unit-cell dimensions and other relevant compositional and refinement data are presented in Table 1. The site occupancies, atomic positional coordinates, and isotropic displacement parameters from the final cycles of refine-

ments are listed in Table 2. Selected bond lengths for SiO<sub>4</sub> tetrahedra and MO<sub>6</sub> octahedra are given in Tables 3 and 4, respectively, and bond angles are listed in Table 5. Although the three crystals examined in this study have nearly identical crystal compositions (Table 1), the unheated crystal, UH1, has *C2/m* symmetry, and the heat-treated crystals, 1c and 11a, have *P2<sub>1</sub>/m* symmetry. There are 418 and 385 observed reflections violating the *C2/m* symmetry for crystals 11a and 1c, respectively, but only ten weak reflections for UH1. No reflections violating the *P2<sub>1</sub>/m* symmetry were detected for any of the three crystals. The refined site populations of Mg in the M4 site,  $X_{Mg}^{M4}$ , in crystals UH1, 11a, and 1c are 0.051, 0.167, and 0.237, respectively (Table 2).

#### DISCUSSION

##### *P2<sub>1</sub>/m* crystal structure

A thorough description of amphibole crystal structures is given by Hawthorne (1983). There is only one type of silicate double chain in *C2/m* cummingtonite but two crystallographically distinct double chains, A and B, in *P2<sub>1</sub>/m* cummingtonite. The configurations of the A and B chains in the *P2<sub>1</sub>/m* structure are primarily distinguishable by different degrees of kinking, as defined by the O5-O6-O5 angle; the B chain is always more kinked than the A chain at room temperature. In the *C2/m* crystal, UH1, the O5-O6-O5 angle is 170°, but in the *P2<sub>1</sub>/m* crystals, 1c and 11a, it is ~179° for the A chain and ~163° for the B chain (Table 5).

Significantly, all *P2<sub>1</sub>/m* ferromagnesian cummingtonite crystals from this study and from Hirschmann et al. (1994) have S-rotated A chains and O-rotated B chains (for illustrations of S and O rotations, see Fig. 1 of Papike and Ross, 1970; for discussion of topology of amphibole structures, see Thompson, 1970; Papike and Ross, 1970; Cameron and Papike, 1979; Law and Whittaker, 1980;

**TABLE 2.** Site occupancies, atomic positional coordinates ( $\times 10^4$ ), and isotropic displacement parameters ( $\text{\AA}^2$ ) for three cummingtonite crystals

		11a (heat treated at 600 °C)			1c (heat treated at 700 °C)	
		UH1 (unheated)	A set	B set	A set	B set
M1	Fe	0.200(3)	0.258(3)		0.250(3)	
	Mg	0.800	0.742		0.750	
	x	0	-2499(1)		-2493(1)	
	y	869(1)	3369(1)		3369(1)	
	z	5000	4929(1)		4923(2)	
	$B_{\text{iso}}$	0.671	0.692		0.673	
M2	Fe	0.091(3)	0.165(3)		0.163(3)	
	Mg	0.903	0.828		0.830	
	Al	0.006	0.007		0.007	
	x	0	-2501(1)		-2501(1)	
	y	1771(1)	4273(1)		4273(1)	
	z	0	9923(1)		9914(2)	
	$B_{\text{iso}}$	0.693	0.653		0.650	
M3	Fe	0.164(6)	0.220(6)		0.211(6)	
	Mg	0.836	0.780		0.789	
	x	0	-2497(2)		-2495(2)	
	y	0	2500		2500	
	z	0	9940(2)		9933(3)	
	$B_{\text{iso}}$	0.521	0.567		0.544	
M4	Fe	0.906	0.778		0.713	
	Mg	0.051	0.167		0.237	
	Ca	0.043	0.055		0.050	
	x	0	-2510(1)		-2517(1)	
	y	2589(1)	5089(1)		5089(1)	
	z	5000	4903(1)		4897(1)	
	$B_{\text{iso}}$	0.931	0.931		0.916	
T1	x	2879(1)	383(1)	5374(1)	386(1)	5368(1)
	y	842(1)	3343(1)	8339(1)	3344(1)	8339(1)
	z	2745(1)	2652(1)	2814(1)	2649(2)	2818(2)
	$B_{\text{iso}}$	0.561	0.514	0.524	0.614	0.499
T2	x	2979(1)	467(1)	5487(1)	461(1)	5491(1)
	y	1688(1)	4194(1)	9182(1)	4194(1)	9183(1)
	z	7812(1)	7718(1)	7876(1)	7710(1)	7880(1)
	$B_{\text{iso}}$	0.572	0.539	0.549	0.575	0.595
O1	x	1142(1)	-1353(3)	3641(3)	-1354(3)	3640(3)
	y	869(1)	3368(1)	8370(1)	3368(1)	8371(1)
	z	2092(2)	2024(4)	2161(4)	2025(5)	2163(5)
	$B_{\text{iso}}$	0.681	0.586	0.688	0.747	0.636
O2	x	1232(1)	-1278(3)	3742(2)	-1275(3)	3740(3)
	y	1721(1)	4223(1)	9229(1)	4228(1)	9229(1)
	z	7193(2)	7086(4)	7262(4)	7075(4)	7267(5)
	$B_{\text{iso}}$	0.722	0.739	0.674	0.655	0.783
O3	x	1133(2)	-1349(4)	3619(5)	-1362(5)	3634(5)
	y	0	2500	7500	2500	7500
	z	7068(4)	7006(5)	7143(6)	7009(7)	7160(7)
	$B_{\text{iso}}$	0.846	0.743	0.854	0.773	0.979
O4	x	3805(1)	1292(3)	6324(3)	1285(3)	6326(3)
	y	2454(1)	4968(1)	9938(1)	4972(1)	9937(1)
	z	7689(2)	7756(4)	7633(4)	7774(5)	7620(5)
	$B_{\text{iso}}$	0.917	0.923	0.927	0.965	0.873
O5	x	3514(1)	1001(3)	6017(3)	1011(3)	6004(3)
	y	1313(1)	3756(1)	8847(1)	3751(1)	8850(1)
	z	646(2)	421(4)	794(4)	403(5)	801(5)
	$B_{\text{iso}}$	1.036	1.052	0.915	1.074	0.920
O6	x	3499(1)	1021(3)	5979(3)	1036(3)	5965(3)
	y	1185(1)	3756(1)	8636(1)	3756(1)	8633(1)
	z	5586(2)	5371(4)	5732(4)	5360(5)	5744(5)
	$B_{\text{iso}}$	1.177	1.213	0.972	1.126	1.093
O7	x	3434(2)	945(4)	5927(4)	951(4)	5918(5)
	y	0	2500	7500	2500	7500
	z	2699(4)	2851(7)	2613(7)	2865(8)	2593(8)
	$B_{\text{iso}}$	1.026	1.153	0.841	0.887	1.167

Chisholm, 1981; Hawthorne, 1983). Because it would allow a tighter coordination for the small  $\text{Mg}^{2+}$  cation in the M4 site, the hypothetical existence of S-rotated tetrahedral double chains in clinoamphibole was postulated by Thompson (1970), Law and Whittaker (1980), and Hawthorne (1983), but such amphibole structures have

not been previously documented in nature. The structure of primitive ferromagnesian amphibole (Fig. 1) differs from the structure reported by Papike et al. (1969) for  $P2_1/m$  manganian cummingtonite, in which both A and B chains have O rotations. However, the structure refinement of a  $P2_1/m$  manganian cummingtonite crystal

**TABLE 3.** Selected bond distances (Å) within the SiO<sub>4</sub> tetrahedra in three cummingtonite crystals

	UH1 (unheated)	11a (heat treated at 600 °C)		1c (heat treated at 700 °C)	
		A chain	B chain	A chain	B chain
T1-O1	1.614(2)	1.615(3)	1.612(3)	1.619(4)	1.608(4)
-O5	1.618(2)	1.612(3)	1.627(3)	1.615(3)	1.623(3)
-O6	1.624(2)	1.627(3)	1.627(3)	1.624(3)	1.628(3)
-O7	1.617(2)	1.616(2)	1.621(2)	1.617(2)	1.620(2)
Av.	1.618	1.618	1.622	1.619	1.620
Av. A + B		1.620		1.620	
T2-O2	1.624(2)	1.624(2)	1.624(3)	1.615(3)	1.630(4)
-O4	1.602(2)	1.606(3)	1.604(3)	1.609(3)	1.601(3)
-O5	1.633(2)	1.626(3)	1.642(3)	1.628(3)	1.640(3)
-O6	1.648(2)	1.653(3)	1.649(3)	1.664(3)	1.641(3)
Av.	1.628	1.627	1.630	1.629	1.628
Av. A + B		1.629		1.629	

**TABLE 5.** Interatomic angles (°) within the SiO<sub>4</sub> tetrahedra in three cummingtonite crystals

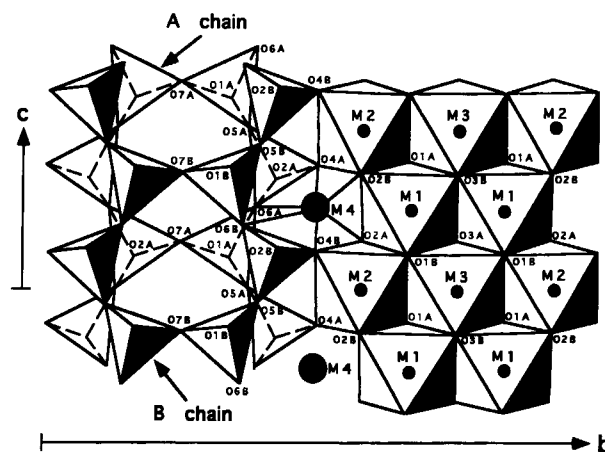
	UH1 (unheated)	11a (heat treated at 600 °C)		1c (heat treated at 700 °C)	
		A chain	B chain	A chain	B chain
O1-T1-O5	110.4(1)	110.4(1)	110.3(1)	110.7(2)	109.9(2)
O1-T1-O6	110.1(1)	110.3(1)	109.7(1)	110.6(2)	109.4(2)
O1-T1-O7	110.3(1)	110.5(2)	110.4(2)	110.5(2)	110.4(2)
O5-T1-O6	108.8(1)	108.2(2)	109.4(2)	108.3(2)	109.8(2)
O5-T1-O7	108.5(1)	108.7(2)	108.5(2)	108.4(2)	108.4(2)
O6-T1-O7	108.7(1)	108.7(2)	108.5(2)	108.2(2)	108.9(2)
O2-T2-O4	116.8(1)	116.7(2)	116.2(2)	116.3(2)	116.3(2)
O2-T2-O5	108.0(1)	108.4(1)	108.0(1)	109.2(2)	107.3(2)
O2-T2-O6	108.8(1)	109.4(1)	108.5(1)	110.1(2)	108.1(2)
O4-T2-O5	109.8(1)	110.7(1)	109.4(1)	110.4(2)	109.9(2)
O4-T2-O6	103.1(1)	101.4(1)	104.0(1)	101.4(2)	104.2(2)
O5-T2-O6	110.3(1)	109.9(1)	110.7(1)	109.1(2)	111.0(2)
O5-O6-O5	170.0(1)	179.2(2)	163.5(2)	178.9(2)	163.1(2)
O5-O7-O6	169.2(1)	177.3(2)	163.1(2)	177.1(2)	162.4(2)
T1-O5-T2	140.0(1)	141.3(2)	138.3(2)	140.6(2)	139.0(2)
T1-O6-T2	140.6(1)	140.4(2)	139.5(2)	139.4(2)	140.0(2)
T1-O7-T1	141.5(1)	142.2(3)	139.7(3)	142.1(3)	139.6(3)

from the same sample (NMNH 115046) studied by Papike et al. (1969) shows that the A chain is S rotated with a kinking angle of 179.0(2)° and the B chain O rotated with a kinking angle of 164.9(2)° (Yang and Smyth, unpublished data).

There are many similarities between clinopyroxene and clinoamphibole crystal structures (e.g., Ghose, 1982; Hawthorne, 1983) and phase transition mechanisms (Prewitt et al., 1970; Sueno et al., 1972). The discovery of S-rotated A chains in *P2<sub>1</sub>/m* ferromagnesian cummingtonite makes clinoamphiboles topologically more similar to clinopyroxenes than previously known, since the A and B silicate chains in *P2<sub>1</sub>/c* clinopyroxene are also S and O rotated, respectively (e.g., Cameron and Papike, 1981). This suggests that, like the *P2<sub>1</sub>/c* to *C2/c* phase transition in clinopyroxene (Brown et al., 1972; Smyth, 1974), the *P2<sub>1</sub>/m* to *C2/m* transformation in ferromagnesian cummingtonite may also require changing the A-chain configuration from S to O rotation because all silicate chains in *C2/m* cummingtonite are O rotated.

**TABLE 4.** Selected bond distances (Å) within the MO<sub>6</sub> octahedra in three cummingtonite crystals

	UH1 (unheated)	11a (heat treated at 600 °C)		1c (heat treated at 700 °C)	
		A set	B set	A set	B set
M1-O1	2.064(1)	2.064(3)	2.064(3)	2.057(3)	2.070(3)
-O2	2.131(1)	2.122(3)	2.147(3)	2.125(3)	2.147(3)
-O3	2.085(1)	2.095(3)	2.082(3)	2.089(3)	2.092(3)
Av. of 6	2.093	2.096		2.096	
M2-O1	2.140(1)	2.149(3)	2.140(3)	2.150(3)	2.135(3)
-O2	2.081(1)	2.087(3)	2.089(3)	2.089(3)	2.090(3)
-O4	2.046(2)	2.036(3)	2.051(3)	2.030(3)	2.051(3)
Av. of 6	2.089	2.092		2.091	
M3-O1	2.094(1)	2.094(3)	2.100(3)	2.093(3)	2.100(3)
-O3	2.070(2)	2.079(4)	2.055(4)	2.065(5)	2.061(5)
Av. of 6	2.086	2.087		2.086	
M4-O2	2.153(1)	2.148(3)	2.136(3)	2.143(3)	2.131(3)
-O4	2.003(2)	2.006(3)	2.000(3)	2.020(3)	1.991(3)
-O6	2.693(2)	2.549(3)	2.806(3)	2.541(3)	2.814(3)
-O5	3.151(2)	3.336(3)	3.028(3)	3.347(3)	3.021(3)
Av. of 6	2.283	2.274		2.274	
Av. of 8	2.500	2.501		2.501	



**Fig. 1.** The *P2<sub>1</sub>/m* ferromagnesian cummingtonite structure viewed along *a*\*. To better show the kinking of silicate chains, the structural data of sample KL14a, heat treated at 600 °C (Hirschmann et al., 1994), were used for the figure. Note that the apex of the O5A-O6A-O5A angle points toward the M4 cation, and the trigonal aspects of the six-membered rings of both A and B chains point in the same direction (+c); however, the apex of the O5A-O6A-O5A angle in *P2<sub>1</sub>/m* manganocummingtonite points away from the M4 cation, and the trigonal aspect of the six-membered rings of the A chain points to -c and that of the B chain to +c (Papike et al., 1969).

ture, the O6A and O5B atoms in the  $P2_1/m$  structure move closer to the M4 cation, but the O6B and O5A atoms move farther away because of the S rotation of the A chain and the O rotation of the B chain. The average M4-O6 distance in the  $P2_1/m$  structures (2.68 Å) is slightly shorter than that in the  $C2/m$  structure (2.69 Å), but the average M4-O5 distance is longer (3.18 vs. 3.15 Å).

#### Effect of $X_{Mg}^{M4}$ on $P2_1/m$ vs. $C2/m$ structure stability

At room temperature, the  $C2/m$  structure appears to tolerate only a small proportion of  $Mg^{2+}$  cations in the M4 site, as indicated by the observation that crystal 11a with  $X_{Mg}^{M4} = 0.167$  has the  $P2_1/m$  structure. Our results suggest that the  $P2_1/m$ - $C2/m$  transition composition at room temperature is a function of the Fe-Mg distribution in the structure. Combining the present results with those of Hirschmann et al. (1994) shows that cummingtonite crystals with  $X_{Mg}^{M4} \leq 0.126$  have the  $C2/m$  structure, and those with  $X_{Mg}^{M4} \geq 0.167$  have the  $P2_1/m$  structure. The sole exception to this is crystal 21a with  $X_{Mg}^{M4} = 0.196$ , which Hirschmann et al. (1994) reported as having  $C2/m$  symmetry. This crystal has a bulk composition ( $X_{Mg} = 0.621$ ) just slightly less Mg rich than NMNH 118125. New X-ray intensity data collected for crystal 21a (Yang, unpublished data) reveal that it probably has the  $P2_1/m$  structure because there are approximately 100 observable reflections violating  $C2/m$  symmetry. Unfortunately, structure refinement of these data based on  $P2_1/m$  symmetry did not converge after 15 cycles of refinement and failed to produce reasonable and precise atomic positional coordinates. The maximum  $X_{Mg}^{M4}$  tolerated in the  $C2/m$  structure at room temperature is less than that (0.23) postulated by Hawthorne (1983).

The relative stabilities of  $P2_1/m$  vs.  $C2/m$  phases have been previously considered in terms of bulk composition (e.g., Yakovleva et al., 1978; Ghose, 1982; Hirschmann et al., 1994). On the other hand, several workers have emphasized the importance of the M4 cation occupancies to the phase transition (Ross et al., 1968, 1969; Papike et al., 1969; Prewitt et al., 1970; Sueno et al., 1972; Ghose, 1982; Hawthorne, 1983). The substitution of sufficient proportions of small  $Mg^{2+}$  cations for relatively large cations (e.g.,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Ca^{2+}$ , etc.) in the M4 site of  $C2/m$  amphibole reduces the size and thus the effective coordination number of the M4 site. This eventually causes collapse of the M4 site. The structural response to such a change is differential and independent distortion of the A and B tetrahedral chains, which principally involves the relative rearrangement of the O5 and O6 anions in adjacent chains. Coupled with the independent adjustment of the A and B chains is the splitting of the M4-O bond lengths, especially the M4-O5 and M4-O6 distances, giving rise to  $P2_1/m$  symmetry. In the case of NMNH 118125, heat-treated crystals (11a and 1c) should have had  $C2/m$  symmetry while they were held at high temperatures because the difference in size between  $Mg^{2+}$  and  $Fe^{2+}$  cations would be compensated by large amplitudes of thermal vibration. Accordingly, the structural differ-

ences between unheated  $C2/m$  and heat-treated  $P2_1/m$  crystals are likely to arise during quenching from high temperature. In this process, the high Mg concentrations in the M4 site induced by disorder at high temperatures were preserved, but the thermal vibration amplitude of the M4 cation was greatly reduced, resulting in collapse of the M4 site and the  $C2/m$  to  $P2_1/m$  phase transition. Owing to differing thermal expansion of the  $MO_6$  octahedra and  $SiO_4$  tetrahedra in cummingtonite (Sueno et al., 1972), the effect of increasing temperature on the structure is similar to that of substitution of larger cations into the M4 site.

#### Effect of composition and $X_{Mg}^{M4}$ on $P2_1/m$ amphibole structure

To characterize the dependence of cummingtonite structures on bulk composition ( $X_{Mg}$ ) and Mg occupancy in the M4 site ( $X_{Mg}^{M4}$ ) at room temperature, we may consider variations in the M4-O5 and M4-O6 distances (Fig. 2) and O5-O6-O5 angles (Fig. 3) because they are the most sensitive to the  $P2_1/m$ - $C2/m$  structural transformation. In Figure 3, the O5-O6-O5 angles of the S-rotated A chain are plotted above  $180^\circ$  ( $360^\circ - \angle O5-O6-O5$ ) and those of the O-rotated B chain below  $180^\circ$ , which is the same convention as that generally applied to the O3-O3-O3 angle in pyroxenes (Smyth, 1974; Sueno et al., 1976).

As  $C2/m$  and  $P2_1/m$  cummingtonite crystals and the M4 site become more magnesian, both M4-O5 and M4-O6 distances (the average ones for the  $P2_1/m$  structure) decrease. In the  $P2_1/m$  structure, the differences between the M4-O5A and M4-O5B distances and the M4-O6A and M4-O6B distances increase with increasing Mg concentration (Fig. 2). Interestingly, although both A and B chains become more kinked with increasing Mg content in the  $P2_1/m$  structure, the average values of the two chain-kinking angles in the same crystals are essentially the same ( $\sim 171^\circ$ ) as those determined for  $C2/m$  cummingtonite (Fig. 3). There is excellent agreement between the limited structural data reported by Ghose (1982) for a  $P2_1/m$  magnesian cummingtonite and the trends defined by the present work and that of Hirschmann et al. (1994) (Figs. 2 and 3). Although the trends in Figures 2 and 3 do not provide any evidence for the nature of the  $P2_1/m$ - $C2/m$  phase transition, they clearly indicate that the structural distortion from  $C2/m$  symmetry increases with increasing  $X_{Mg}$  and  $X_{Mg}^{M4}$  values.

#### The $P2_1/m$ - $C2/m$ transition in ferromagnesian vs. manganoan cummingtonite

Compared with manganoan cummingtonite (Papike et al., 1969),  $P2_1/m$  ferromagnesian cummingtonite with similar Mg concentration shows markedly larger structural distortions away from  $C2/m$  symmetry (Figs. 2 and 3). For example, the differences between the M4-O6A and M4-O6B distances and between the kinking angles of the A and B chains for manganoan cummingtonite are less than half of what they would be for ferromagnesian

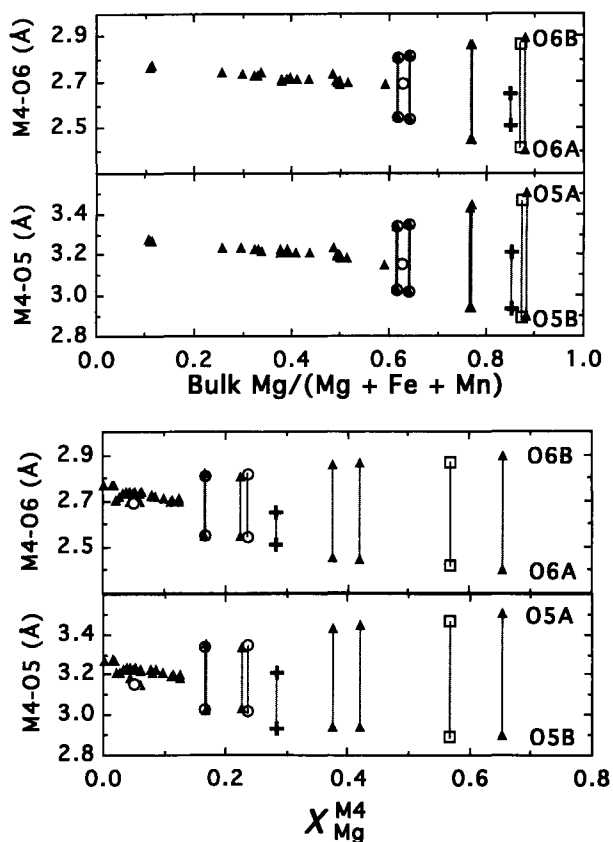


Fig. 2. M4-O6 and M4-O5 distances (in angstroms) in  $C2/m$  and  $P2_1/m$  cummingtonite. Top panels show distances against the molar  $Mg/(Mg + Fe + Mn)$  of the macroscopic crystal. Bottom panels show distances against the mole fraction of Mg in the M4 site. The split M4-O5 and M4-O6 distances in  $P2_1/m$  cummingtonite are joined with lines. Symbols not joined by lines are from  $C2/m$  cummingtonite. Circles = this study; triangles = Hirschmann et al. (1994); squares = Ghose (1982); crosses = manganian cummingtonite (Papike et al., 1969).

cummingtonite with similar bulk composition or  $X_{Mg}^{M4}$ . These structural differences imply that the energy difference between the  $P2_1/m$  and  $C2/m$  structures is greater for ferromagnesian cummingtonite than for manganian cummingtonite. In addition to the relatively small size of the  $Fe^{2+}$  cation, the larger structural distortion for the Fe-bearing phase is attributable to the ligand field stabilization energy (LFSE) gained by  $Fe^{2+}$  in the highly asymmetric M4 site of the  $P2_1/m$  structure. Because the  $Mn^{2+}$  ion is electronically symmetric and has no LFSE, it does not achieve any energetic stabilization by increased distortion of the M4 site from the site symmetry  $C_2$  in the  $C2/m$  structure to  $C_1$  in the  $P2_1/m$  structure (e.g., Goldman and Rossman, 1977). It therefore follows that substitution of the small  $Fe^{2+}$  cation into the highly distorted ( $C_1$ ) M4 site of the  $P2_1/m$  structure does not destabilize this structure as much as substitution of the larger  $Mn^{2+}$  cation, and, that for similar Mg concentrations and site occupancies, the  $P2_1/m$  structure is more stable for fer-

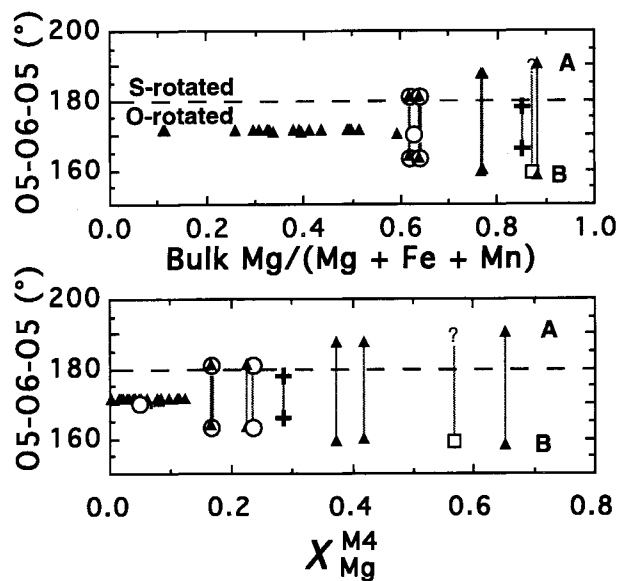


Fig. 3. Kinking angles (O5-O6-O5) in  $C2/m$  and  $P2_1/m$  cummingtonite. Symbols, citations, and description of axes are the same as in Fig. 2. Angles of the A and B chains of the same  $P2_1/m$  crystal are joined with lines. Symbols not joined by lines are from  $C2/m$  cummingtonite. Because Ghose (1982) reported only the O5B-O6B-O5B angle, this datum is joined with a question mark. To maintain the analogy with pyroxenes, the S-rotated A-chain kinking angles are plotted above  $180^\circ$  ( $360^\circ - \angle O5-O6-O5$ ) and the O-rotated B-chain kinking angles below  $180^\circ$ .

romagnesian cummingtonite than for manganian cummingtonite. This reasoning is consistent with the observation that the structure of crystal 21a with 1.44 wt% MnO (Hirschmann et al., 1994) is close to the phase transition at room temperature, even though it has more Mg in the M4 site than other Mn-poor crystals (e.g., 1c and 11a, 0.55% MnO; Hirschmann et al., 1994), which have well-developed  $P2_1/m$  structure. With increasing Mg content, departure from  $C2/m$  symmetry increases for  $P2_1/m$  ferromagnesian cummingtonite, indicating that relative stability of the  $P2_1/m$  structure also increases.

The greater stability of the  $P2_1/m$  structure inferred for ferromagnesian cummingtonite relative to manganian cummingtonite can be used to anticipate the stability of Mg-rich ferromagnesian cummingtonite at high temperature. Manganian cummingtonite with  $X_{Mg}^{M4} = 0.28$  from Gouverneur, New York, inverts to the  $C2/m$  structure at  $\sim 100^\circ C$  (Sueno et al., 1972). Presumably, the analogous ferromagnesian cummingtonite with  $X_{Mg}^{M4} = 0.28$  would be more stable in the  $P2_1/m$  structure and would therefore invert to the  $C2/m$  structure at a temperature greater than  $100^\circ C$ . Because the phase transition in ferromagnesian cummingtonite at room temperature occurs near  $X_{Mg}^{M4} = 0.15$ , we speculate that very Mg-rich cummingtonite, such as heat-treated KL14a ( $X_{Mg}^{M4} = 0.65$ ; Hirschmann et al., 1994) could have transition temperatures much higher than  $100^\circ C$ . This calls into question the common

assumption that  $P2_1/m$  cummingtonite is stable only at very low temperatures (e.g., Robinson et al., 1982).

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