

Refinement of the Crystal Structures of $(\text{Mg}_{0.776}\text{Co}_{0.224})\text{SiO}_3$ and $(\text{Mg}_{0.925}\text{Mn}_{0.075})\text{SiO}_3$

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Abstract. Synthetic orthopyroxenes $(\text{Mg}_{0.776}\text{Co}_{0.224})\text{SiO}_3$ [*Pbca*, $Z = 16$, $D_c = 3.437 \text{ g cm}^{-3}$; cell constants at 20°C : $a = 18.233$ (7), $b = 8.836$ (6), $c = 5.188$ (3) Å; $\lambda(\text{Mo } K\alpha) = 0.71069$ Å] and $(\text{Mg}_{0.925}\text{Mn}_{0.075})\text{SiO}_3$ [*Pbca*, $Z = 16$, $D_c = 3.253 \text{ g cm}^{-3}$; cell constants at 20°C : $a = 18.270$ (6), $b = 8.833$ (6), $c = 5.195$ (3) Å; $\lambda(\text{Mo } K\alpha) = 0.71069$ Å] show partial cation ordering over the two non-equivalent octahedral sites in the structure. The $M(2)$ site preference is $\text{Mn} > \text{Co} > \text{Mg}$.

Introduction. Crystals were prepared by the flux method of Ito (1975), with the modification that Li_2SiO_3 was used instead of H_2SiO_3 , thus shortening the equilibration time by a factor of three. Chemical analyses were performed by electron microprobe and atomic absorption:

	(Mg, Co)SiO ₃	(Mg, Mn)SiO ₃
SiO ₂	55.5 wt %	58.0 wt %
MoO ₃	0.02	0.30
V ₂ O ₅	0.28	0.38
Li ₂ O	0.13	0.26
CoO	15.5	—
MnO	—	5.14
MgO	28.9	35.9

Crystals for the X-ray study were taken from the edge of large crystals, as previous studies (Hawthorne & Ito, 1977) showed that the flux-component impurities are concentrated at the core of the crystals. Cell contents were calculated on the basis of two octahedral cations per formula unit, ignoring any Li and V in the analysis. Precession photographs exhibited orthorhombic symmetry with systematic absences $hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$ consistent with the space group *Pbca*. Cell dimensions were determined by least-squares refinement of 30 reflexions automatically aligned on a four-circle diffractometer and confirmed by refinement of ~20 reflexions recorded by the Gandolfi method. Data collection and reduction procedures were as described by Hawthorne & Ito (1977), resulting in 1468 (1469) reflexions for Mg,Co (Mg,Mn) orthopyroxene, of which 898 (960)

were considered as observed (3σ). Scattering factors for neutral atoms were taken from Cromer & Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970). Atomic parameters for orthoenstatite (Hawthorne & Ito, 1977) were used as input to the least-squares program *RFINE* (Finger, 1969a), with the octahedral site-occupancies considered as variable and the total composition of the crystals constrained to be the same as that indicated by the chemical analysis (Finger, 1969b). With anisotropic temperature factors of the form $\exp(-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij})$, convergence occurred at R factors of 3.4 (3.4%) and R_w factors (unit weights) of 3.6 (4.2%) (observed reflexions) for Mg,Co (Mg,Mn) orthopyroxene. Final parameters are given in Table 1. Interatomic distances and angles were

Table 1. Atomic parameters for $(\text{Mg,Co})\text{SiO}_3$ and $(\text{Mg,Mn})\text{SiO}_3$

	x	y	z	B_{eq} (Å ²)
(Mg,Co)SiO ₃				
<i>M</i> (1)	0.37586 (6)	0.6543 (1)	0.8677 (2)	0.52 (2)
<i>M</i> (2)	0.37703 (5)	0.4869 (1)	0.3604 (2)	0.61 (2)
Si(<i>A</i>)	0.27180 (5)	0.3414 (1)	0.0514 (2)	0.38 (2)
Si(<i>B</i>)	0.47337 (5)	0.3368 (1)	0.7969 (2)	0.35 (2)
O(1 <i>A</i>)	0.1833 (1)	0.3397 (3)	0.0365 (5)	0.50 (4)
O(2 <i>A</i>)	0.3107 (1)	0.5028 (3)	0.0462 (5)	0.61 (4)
O(3 <i>A</i>)	0.3032 (1)	0.2242 (3)	-0.1688 (5)	0.65 (4)
O(1 <i>B</i>)	0.5622 (1)	0.3396 (3)	0.7983 (5)	0.50 (4)
O(2 <i>B</i>)	0.4325 (1)	0.4831 (3)	0.6890 (5)	0.51 (4)
O(3 <i>B</i>)	0.4475 (1)	0.1960 (3)	0.6015 (5)	0.54 (4)
(Mg,Mn)SiO ₃				
<i>M</i> (1)	0.37558 (6)	0.6539 (1)	0.8685 (2)	0.42 (3)
<i>M</i> (2)	0.37702 (5)	0.4847 (1)	0.3622 (2)	0.59 (2)
Si(<i>A</i>)	0.27165 (4)	0.3414 (1)	0.0506 (2)	0.28 (2)
Si(<i>B</i>)	0.47384 (4)	0.3375 (1)	0.7977 (2)	0.29 (2)
O(1 <i>A</i>)	0.1832 (1)	0.3392 (3)	0.0374 (4)	0.45 (3)
O(2 <i>A</i>)	0.3105 (1)	0.5025 (3)	0.0447 (4)	0.56 (4)
O(3 <i>A</i>)	0.3030 (1)	0.2248 (3)	-0.1714 (5)	0.58 (4)
O(1 <i>B</i>)	0.5628 (1)	0.3398 (3)	0.7991 (4)	0.45 (3)
O(2 <i>B</i>)	0.4335 (1)	0.4845 (3)	0.6921 (5)	0.62 (4)
O(3 <i>B</i>)	0.4473 (1)	0.1975 (3)	0.6015 (4)	0.51 (4)

Table 2. *Interatomic distances (Å) and angles (°)*

	(Mg,Co)SiO ₃	(Mg,Mn)SiO ₃		(Mg,Co)SiO ₃	(Mg,Mn)SiO ₃
Si(A)—O(1A)	1.616 (3)	1.617 (2)	Si(B)—O(1B)	1.620 (3)	1.625 (2)
Si(A)—O(2A)	1.593 (3)	1.592 (3)	Si(B)—O(2B)	1.593 (3)	1.592 (2)
Si(A)—O(3A)	1.644 (3)	1.650 (3)	Si(B)—O(3B)	1.673 (3)	1.675 (2)
Si(A)—O(3A)	1.664 (3)	1.661 (3)	Si(B)—O(3B)	1.674 (3)	1.680 (2)
⟨Si(A)—O⟩	1.629	1.630	⟨Si(B)—O⟩	1.640	1.643
M(1)—O(1A)	2.029 (3)	2.029 (3)	M(2)—O(1A)	2.096 (3)	2.113 (2)
M(1)—O(1A)	2.148 (3)	2.147 (3)	M(2)—O(2A)	2.035 (3)	2.056 (3)
M(1)—O(2A)	2.015 (3)	2.011 (3)	M(2)—O(3A)	2.307 (3)	2.299 (3)
M(1)—O(1B)	2.069 (3)	2.063 (3)	M(2)—O(1B)	2.063 (3)	2.079 (2)
M(1)—O(1B)	2.168 (3)	2.173 (3)	M(2)—O(2B)	1.983 (3)	2.000 (3)
M(1)—O(2B)	2.053 (3)	2.050 (3)	M(2)—O(3B)	2.464 (3)	2.466 (3)
⟨M(1)—O⟩	2.080	2.079	⟨M(2)—O⟩	2.158	2.169
O(1A)—O(2A)	2.734 (3)	2.737 (3)	O(1A)—Si(A)—O(2A)	116.9 (2)	117.1 (1)
O(1A)—O(3A)	2.636 (4)	2.644 (3)	O(1A)—Si(A)—O(3A)	107.9 (1)	108.1 (1)
O(1A)—O(3A)	2.726 (4)	2.721 (3)	O(1A)—Si(A)—O(3A)	112.4 (1)	112.2 (1)
O(2A)—O(3A)	2.706 (4)	2.703 (3)	O(2A)—Si(A)—O(3A)	113.4 (1)	113.0 (1)
O(2A)—O(3A)*	2.496 (4)	2.497 (3)	O(2A)—Si(A)—O(3A) ^s	100.1 (1)	100.3 (1)
O(3A)—O(3A)	2.634 (1)	2.636 (1)	O(3A)—Si(A)—O(3A)	105.5 (1)	105.6 (1)
⟨O—O⟩	2.655	2.656	⟨O—Si(A)—O⟩	109.4	109.4
O(1B)—O(2B)	2.742 (3)	2.744 (3)	O(1B)—Si(B)—O(2B)	117.2 (1)	117.1 (2)
O(1B)—O(3B)	2.651 (4)	2.662 (3)	O(1B)—Si(B)—O(3B)	107.2 (1)	107.5 (1)
O(1B)—O(3B)	2.635 (4)	2.651 (3)	O(1B)—Si(B)—O(3B)	106.3 (1)	106.7 (1)
O(2B)—O(3B)	2.591 (4)	2.593 (3)	O(2B)—Si(B)—O(3B)	105.0 (1)	105.0 (1)
O(2B)—O(3B)	2.675 (4)	2.679 (3)	O(2B)—Si(B)—O(3B)	109.9 (1)	109.9 (1)
O(3B)—O(3B)	2.764 (2)	2.759 (2)	O(3B)—Si(B)—O(3B)	111.3 (1)	110.6 (1)
⟨O—O⟩	2.676	2.681	⟨O—Si(B)—O⟩	109.5	109.5
O(1A)—O(1A)	3.040 (3)	3.039 (2)	O(1A)—M(1)—O(1A)	93.4 (1)	93.4 (1)
O(1A)—O(2A)	2.990 (4)	2.986 (3)	O(1A)—M(1)—O(2A)	95.3 (1)	95.3 (1)
O(1A)—O(1B) ^s	2.849 (3)	2.840 (3)	O(1A)—M(1)—O(1B) ^s	85.4 (1)	85.0 (1)
O(1A)—O(2B) ^s	2.746 (4)	2.760 (3)	O(1A)—M(1)—O(2B) ^s	84.5 (1)	85.2 (1)
O(1B)—O(1A) ^s	2.849 (3)	2.840 (3)	O(1B)—M(1)—O(1A) ^s	85.0 (1)	84.9 (1)
O(1B)—O(2A)	2.822 (4)	2.822 (3)	O(1B)—M(1)—O(2A)	87.4 (1)	87.7 (1)
O(1B)—O(1B)	3.039 (3)	3.045 (2)	O(1B)—M(1)—O(1B)	91.7 (1)	91.8 (1)
O(1B)—O(2B)	3.088 (4)	3.067 (4)	O(1B)—M(1)—O(2B)	97.0 (1)	96.5 (1)
O(1A)—O(2A)	2.979 (4)	2.979 (3)	O(1A)—M(1)—O(2A)	91.3 (1)	91.5 (1)
O(2A)—O(2B)	2.899 (4)	2.904 (3)	O(2A)—M(1)—O(2B)	90.9 (1)	91.3 (1)
O(2B)—O(1B)	3.153 (4)	3.142 (3)	O(2B)—M(1)—O(1B)	96.6 (1)	96.1 (1)
O(1B)—O(1A) ^s	2.809 (3)	2.811 (3)	O(1B)—M(1)—O(1A) ^s	81.2 (1)	81.2 (1)
⟨O—O⟩	2.939	2.936	⟨O—M(1)—O⟩	90.0	90.0
O(1A)—O(1B) ^s	2.809 (3)	2.811 (3)	O(1A)—M(2)—O(1B) ^s	85.0 (1)	84.2 (1)
O(1A)—O(2B) ^s	2.746 (4)	2.760 (3)	O(1A)—M(2)—O(2B) ^s	84.6 (1)	84.3 (1)
O(1A)—O(2A)	2.902 (4)	2.920 (3)	O(1A)—M(2)—O(2A)	89.2 (1)	88.9 (1)
O(1A)—O(3A)	3.570 (4)	3.586 (3)	O(1A)—M(2)—O(3A)	108.3 (1)	108.7 (1)
O(1B)—O(2B)	2.976 (4)	2.989 (3)	O(1B)—M(2)—O(2B)	94.7 (1)	94.2 (1)
O(1B)—O(2A)	2.822 (4)	2.822 (3)	O(1B)—M(2)—O(2A)	87.0 (1)	86.1 (1)
O(1B)—O(3B)	3.197 (4)	3.210 (3)	O(1B)—M(2)—O(3B)	89.4 (1)	89.5 (1)
O(2B)—O(3A)	3.517 (4)	3.560 (3)	O(2B)—M(2)—O(3A)	109.9 (1)	111.6 (1)
O(2B)—O(3B)	3.445 (4)	3.475 (3)	O(2B)—M(2)—O(3B)	101.0 (1)	101.6 (1)
O(2A)—O(3A) ^s	2.496 (4)	2.497 (3)	O(2A)—M(2)—O(3A) ^s	69.9 (1)	69.7 (1)
O(2A)—O(3B)	3.065 (4)	3.077 (3)	O(2A)—M(2)—O(3B)	85.3 (1)	85.3 (1)
O(3A)—O(3B)	2.900 (4)	2.898 (3)	O(3A)—M(2)—O(3B)	74.8 (1)	74.8 (1)
⟨O—O⟩	3.037	3.050	⟨O—M(2)—O⟩	89.9	89.9
M(1)—M(1)	3.097 (1)	3.104 (1)	Si(A)—O(3A)—Si(A)	135.0 (1)	135.1 (1)
M(1)—M(2)	3.019 (1)	3.026 (2)	Si(B)—O(3B)—Si(B)	128.4 (1)	128.7 (1)
M(1)—M(2)	2.953 (1)	2.970 (2)	O(3A)—O(3A)—O(3A)	160.1 (1)	160.6 (2)
M(1)—M(2)	3.170 (1)	3.195 (1)	O(3B)—O(3B)—O(3B)	139.6 (1)	140.7 (2)
Si(A)—Si(A)	3.056 (1)	3.060 (1)			
Si(B)—Si(B)	3.014 (1)	3.024 (1)			

* s = edge shared between polyhedra.

calculated with the program *ERRORS* (L. W. Finger, personal communication) and are given in Table 2.*

Discussion. The results of the site-population refinement for (Mg,Co)SiO₃ [$M(1) = 0.129(3)\text{Co} + 0.871\text{Mg}$, $M(2) = 0.319\text{Co} + 0.681\text{Mg}$] and (Mg,Mn)SiO₃ [$M(1) = 0.023(4)\text{Mn} + 0.977\text{Mg}$, $M(2) = 0.127\text{Mn} + 0.873\text{Mg}$] indicate the $M(2)$ site-preference $\text{Mn} > \text{Co} > \text{Mg}$. This is qualitatively in accord with the results of Hawthorne & Ito (1977) for (Mg,Co,Mn)SiO₃ and Ghose, Okamura, Wan & Ohashi (1974) for (Mg,Co)SiO₃. In addition, the $M(2)$ preference $\text{Mn} > \text{Mg}$ is also exhibited by the $P2_1/c$ phase of (Mg,Mn)SiO₃ (Ghose *et al.*, 1974). Ghose, Wan & Okamura (1975) have suggested the $M(2)$ site-preference $\text{Mn}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Mg} > \text{Ni}^{2+}$ for the (Mg, M^{2+}) orthopyroxenes. In terms of the exchange reaction $M_{M(1)}^{2+} + \text{Mg}_{M(2)} = M_{M(2)}^{2+} + \text{Mg}_{M(1)}$, the degree of ordering may be characterized by the parameter $K^d = X_{M(1)}^{M^{2+}}[1 - X_{M(2)}^{M^{2+}}]/X_{M(2)}^{M^{2+}}[1 - X_{M(1)}^{M^{2+}}]$; results for the synthetic orthopyroxenes so far examined are:

(Ni,Mg)SiO ₃	1.315	Ghose <i>et al.</i> (1975)
(Co,Mg)SiO ₃	0.398	Ghose <i>et al.</i> (1975)
(Co,Mg)SiO ₃	0.316	This study
(Fe,Mg)SiO ₃	0.154	Ghose <i>et al.</i> (1975)
(Zn,Mg)SiO ₃	0.116	Ghose <i>et al.</i> (1975)
(Zn,Mg)SiO ₃	0.316	Morimoto, Nakajima, Syono, Akimoto & Matsui (1975)
(Cu,Mg)SiO ₃	~0	Ghose & Wan (1976)
(Mn,Mg)SiO ₃	0.162	This study.

These results broadly correspond to the site-preferences suggested by Ghose *et al.* (1975). However, the results of Morimoto *et al.* (1975) and this study differ significantly both from this scheme and from the corresponding results of Ghose *et al.* (1975). Virgo & Hafner (1969) have shown that the degree of cation ordering in natural (Mg,Fe) orthopyroxenes is a function of thermal history, with K^d values varying from ~0.05 for equilibration at 500°C to ~0.25 for

equilibration at 1000°C. Thus the disparities in the results listed above could result from differences in equilibration temperatures stemming from different synthesis conditions. The crystals for the present study were synthesized by slow cooling to 600°C and subsequent quenching, and probably represent an approach to maximum order. Unfortunately, the synthesis conditions for the other orthopyroxenes are not known, but the more cation-disordered distribution obtained for (Co,Mg)SiO₃ by Ghose *et al.* (1975) suggests a higher equilibration temperature provided there is no deviation from ideal mixing at the $M(1)$ and $M(2)$ sites over the compositional range spanned by both crystals.

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* Lists of structure factors, anisotropic temperature factor coefficients and the magnitudes and orientations of the principal axes of the thermal ellipsoids have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33141 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.