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Orthopyroxene from the Serra de Magé meteorite: A structure-refinement procedure for a *Pbca* phase coexisting with a *C*2/*c* exsolved phase

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ABSTRACT

An X-ray structure-refinement procedure was developed to characterize orthopyroxene from the Serra de Magé meteorite. In the studied sample, the orthorhombic phase coexists with exsolution lamellae of *C*2/*c* augite, parallel to (100), with $a^*_{\text{Opx}} \equiv a^*_{\text{Aug}}$, $[101]^*_{\text{Opx}} \equiv c^*_{\text{Aug}}$, $b^*_{\text{Opx}} \equiv b^*_{\text{Aug}}$. Diffraction maxima of the monoclinic phase overlap those of the orthorhombic phase with $h + l = 2n$, yielding violations of the extinction conditions for space group *Pbca* and simulating the lower symmetry space group $P2_1ca$. Structural parameters of the *Pbca* phase together with the W_{Cpx} parameter, which expresses the fraction of the *C*2/*c* phase present, were refined first. F_c values were calculated using the equation $F_c = \sqrt{(1 - \text{W}_{\text{Cpx}})[F_c]^2_{\text{Opx}} + \text{W}_{\text{Cpx}}[F_c]^2_{\text{Cpx}}}$, with $[F_c]_{\text{Cpx}}$ values taken from the structure refinement of an augite. Observed F_o values were then corrected by subtracting the calculated contribution of the monoclinic phase with use of the equation $F_o^{\text{corr}} = \sqrt{[F_o]^2 - [F_c]^2_{\text{Cpx}}\text{W}_{\text{Cpx}}}$ and used for a further refinement of the orthorhombic phase. The final residual indices, R_{obs}, were 2.11 and 1.78% for two crystals with different augite contents. This refinement procedure confirms *Pbca* as the correct space group and provides more accurate structural parameters for the Serra de Magé orthopyroxene.

INTRODUCTION

In the orthopyroxene from the Serra de Magé meteorite, the presence of reflections $0kl$ with $k = 2n + 1$, in violation of the systematic absence for the *b*-glide plane in the *Pbca* space group, had led to the suggestion of the lower symmetry space group $P2_1ca$ (Harlow et al. 1979), as also proposed for other lunar and terrestrial pyroxenes (Smyth 1974, 1975; Steele 1975; Luo et al. 1992). However, the results of the refinements of two Serra de Magé orthopyroxene crystals according to $P2_1ca$ (Domeneghetti et al. 1995b) did not support the assumption of this lower symmetry space group. Violations of extinction conditions for *Pbca* symmetry, and the monoclinic Laue symmetry 2/*m* (rather than orthorhombic symmetry *mmm*) exhibited by the reflections, were explained by the presence of an exsolved *C*2/*c* augite phase, as already proposed by Sasaki et al. (1984). TEM observations by Domeneghetti et al. (1995b) of microstructures of Serra de Magé orthopyroxene showed augite lamellae, parallel to (100), thicker than 500 Å, and irregularly spaced within the orthopyroxene matrix ($a^*_{\text{Opx}} \equiv a^*_{\text{Aug}}$, $[101]^*_{\text{Opx}} \equiv c^*_{\text{Aug}}$, $b^*_{\text{Opx}} \equiv b^*_{\text{Aug}}$). With this orientation of the monoclinic cell with respect to the orthorhombic cell, all diffraction effects of monoclinic *C*2/*c* augite are superimposed on those of the *Pbca* phase with $h + l = 2n$, thus explaining the monoclinic-like equivalence of the reflections. An estimate of the amount of the monoclinic phase present was obtained from the ratio $100(F_o)^2/(2F_c)^2$, where F_o represents the observed structure factors of the forbidden reflections and F_c represents the calculated structure factors of the corresponding reflections in the *C*2/*c* phase. The latter are from a refinement of an augite sample with about the same composition as the (100) lamellae. The proportion of augite determined for the two crystals was about 4 and 12%, showing a nonhomogeneous distribution of the exsolved phase in different orthopyroxene crystals.

To obtain a more accurate estimate of the exsolved augite and a more accurate structural determination of the orthopyroxene host we designed a procedure for refining the *Pbca* phase in the presence of a *C*2/*c* exsolved phase. We present here the strategy and the results of this refinement procedure applied to the same orthopyroxene samples studied by Domeneghetti et al. (1995b).

EXPERIMENTAL METHODS

Structure-refinement procedures

We used for this study the same set of X-ray single-crystal diffraction data collected by Domeneghetti et al. (1995b) for two Serra de Magé samples, Opx SDM N.13, an untreated crystal, and Opx SDM N.7, disordered by heating at 900 °C for 47 h, 40 min. The intensity data

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were obtained using a Philips PW 1100 four-circle automated diffractometer and graphite-monochromatized Mo*Kα* radiation (λ = 0.71073 Å). Net X-ray diffraction intensities were determined by measuring step-scan profiles and analyzing them by the Lehmann and Larsen (1974) σ_I/I method as modified by Blessing et al. (1974). The reflections hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$ were measured up to $\theta \leq 30°$ in the ω-scan mode. The intensities were corrected for absorption using the semiempirical method of North et al. (1968). The cell dimensions were determined using a locally improved version (Cannillo et al. 1983) of the Philips LAT routine and are reported in Table 1. The values of equivalent pairs in $2/m$ Laue symmetry (hkl and $h\bar{k}l$, $\bar{h}kl$ and $\bar{h}\bar{k}l$) were averaged. We considered as extinct those reflections that are extinct in the *Pbca* space group and are either out of register with nodes of the monoclinic net or in register with nodes absent for the extinction conditions in the *C*2/*c* space group. Considering that all monoclinic reflections overlap orthorhombic reflections with $h + l = 2n$, the indices of the extinct reflections can be found by taking into account the extinction conditions in both *Pbca* and *C*2/*c* space groups, together with the transformation matrix $hkl_{Pbca} \rightarrow hkl_{C2/c}$: ½ 0 −½, 0 1 0, 0 0 1. The resulting extinction conditions are as follows: $h0l$ with $l = 2n + 1$, $hk0$ with $h = 2n + 1$, $0kl$ with $k = 2n + 1$ and $l = 2n + 1$, $0kl$ with $k = 2n + 1$ and $l = 4n$. This agrees with the presence of reflections $0kl$ with $k = 2n + 1$ and $l = 4n + 2$, which are forbidden in the *Pbca* space group and occur in Serra de Magé orthopyroxene. Reflections with $I \geq 3\sigma_I$ were considered as observed and used with unit weights in the structure refinement, which was performed without chemical constraints using a locally modified version of the least-squares program ORFLS (Busing et al. 1962). The program allows the assignment of two scattering curves, f_1 and f_2, to each site and refinement of the occupancy factors $X(f)$ with the constraint $X(f_1) + X(f_2) = 1$. The sum $X(f_1)N_1 + X(f_2)N_2$, where N_1 and N_2 are the atomic numbers referring to f_1 and f_2, provides the mean atomic number at the site. The atomic scattering curves are from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974) and from Tokonami (1965). The ionization states used were 2.0+ for Si, Mg, and Fe and 1.5− for O.

The refinement was performed in two steps. First, starting from the values obtained in the *Pbca* refinement by Domeneghetti et al. (1995b), atomic positions, anisotropic displacement parameters, and occupancy factors at M1 and M2 sites of the orthorhombic phase were refined simultaneously with the fraction W_{Cpx} of the *C*2/*c* exsolved phase. In this procedure, the F_c values were calculated by summing the contribution of both phases with use of the equation $F_c = \sqrt{(1 - W_{Cpx})[F_c]^2_{Opx} + W_{Cpx}[F_c]^2_{Cpx}}$. The $[F_c]_{Cpx}$ values were obtained from the atomic positional and anisotropic displacement parameters of an augite crystal with composition close to that of the (100) lamellae (see Table 3 in Domeneghetti et al. 1995b). These parameters were previously transformed into an appropriate form for the orthorhombic cell of the orthopyroxene by means of the unit-cell transformation matrix 2 0 1, 0 1 0, 0 0 1; the unit-cell origin was also moved by ¼ *a* and ¼ *b* to ensure the coincidence of the *c*-glide plane and the 2_1 screw axes in the *Pbca* and *C*2/*c* unit cells. After a few least-squares cycles, the first step of the refinement reached convergence. For the two crystals, Opx SDM N.13 and Opx SDM N.7, the residual indices R_{obs} were, respectively, 3.20% (for 1725 observed reflections) and 2.25% (for 1918 observed reflections). The calculated fractions of the monoclinic phase were 2.80 and 11.27%, respectively.

TABLE 1. Crystal and refinement data

	Opx SDM N.13, natural	Opx SDM N.7, heated
a (Å)	18.316(13)	18.320(18)
b (Å)	8.907(7)	8.917(7)
c (Å)	5.218(6)	5.219(6)
V (Å³)	851.2	852.6
Crystal dimensions (μm)	170 × 180 × 200	180 × 310 × 330
Radiation	Mo*Kα*	Mo*Kα*
θ range (°)	2–30	2–30
No. of measured refl.	5438	5625
R_{sym} (*mmm*) (%)	6.3	7.1
No. of ind. refl. (*mmm*)	1247	1252
R_{sym} (2/*m*) (%)	4.4	1.6
No. of ind. refl. (2/*m*)	2743	2808
No. of I_{obs} (in *Pbca*)	851	897
R_{obs} (%)	2.11	1.78
R_{all} (%)	4.24	3.78

Note: R_{sym} (*mmm*) = $\Sigma_{hkl}(I_{hkl} - \bar{I})/\Sigma_{hkl}\bar{I}$, where $\bar{I} = (I_{hkl} + I_{\bar{h}kl} + I_{h\bar{k}l} + I_{\bar{h}\bar{k}l})/4$; R_{sym} (2/*m*) = $\Sigma_{hkl}(I_{hkl} - \bar{I})/\Sigma_{hkl}\bar{I}$, where $\bar{I} = (I_{hkl} + I_{\bar{h}\bar{k}l})/2$; I_{obs} = reflections with $I \geq 3\sigma_I$; and R_{obs} and R_{all} are the final conventional discrepancy indices expressed as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

In the second step of the refinement procedure, the observed F_o values were corrected by subtracting the calculated contribution of the monoclinic phase with use of the equation $F_o^{corr} = \sqrt{[F_o]^2 - [F_c]^2_{Cpx}W_{Cpx}}$. The equivalent pairs in *mmm* Laue symmetry (hkl and $\bar{h}kl$) were then averaged and used for a further refinement of the *Pbca* phase. For the two crystals the refinement converged to residual indices R_{obs} of 2.11% (for 851 observed reflections) and 1.78% (for 897 observed reflections), respectively.

An attempt to refine separately the monoclinic phase was unsatisfactory because its low concentration resulted in weak intensity of the augite reflections. For the same reason, changes in the augite composition (even 10% in Ca and Fe content) do not significantly affect the values of F_o^{corr} or the final result of the refinement of the *Pbca* phase.

Selected interatomic distances and angles, and mean atomic numbers at M1 and M2 sites, are reported in Table 2. The final positional and displacement parameters are reported in Table 3. The observed and calculated structure factors (Tables 4 and 5) have been deposited.[1]

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[1] A copy of Tables 4 and 5 may be ordered as Document AM-96-618 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036. Please remit $5.00 in advance for the microfiche.

TABLE 2. Selected interatomic distances (Å) and angles (°); mean atomic numbers (m.a.n.) at M1 and M2 sites

	Opx SDM N.13, natural	Opx SDM N.7, heated
SiA-O1A	1.606(2)	1.606(2)
SiA-O2A	1.597(2)	1.594(2)
SiA-O3A	1.636(2)	1.638(2)
SiA-O3A	1.658(2)	1.657(2)
⟨SiA-O⟩	1.624(2)	1.624(2)
O3A-O3A-O3A	165.51	164.58
SiB-O1B	1.620(2)	1.618(2)
SiB-O2B	1.596(2)	1.595(2)
SiB-O3B	1.666(2)	1.667(2)
SiB-O3B	1.669(2)	1.669(2)
⟨SiB-O⟩	1.638(2)	1.637(2)
O3B-O3B-O3B	143.86	143.13
M1-O1A	2.037(2)	2.046(2)
M1-O1A	2.151(2)	2.161(2)
M1-O1B	2.173(2)	2.178(2)
M1-O1B	2.066(2)	2.076(2)
M1-O2A	2.038(2)	2.041(2)
M1-O2B	2.070(2)	2.073(2)
⟨M1-O⟩	2.089(2)	2.096(2)
M2-O1A	2.159(2)	2.149(2)
M2-O1B	2.117(2)	2.109(2)
M2-O2A	2.051(2)	2.050(2)
M2-O2B	2.004(2)	1.998(2)
M2-O3A	2.371(2)	2.367(2)
M2-O3B	2.528(2)	2.526(2)
⟨M2-O⟩	2.205(2)	2.200(2)
m.a.n.(M1)	13.4(1)	15.4(1)
m.a.n.(M2)	22.5(1)	20.9(1)

Note: Standard deviations are in parentheses.

Electron microprobe analysis

New electron microprobe analyses (EMPA) were collected for orthopyroxene grains of a polished thin section of the Serra de Magé meteorite; this thin section was obtained from the same fragment of the meteorite that provided the two single crystals used in the X-ray analysis. A CAMECA-CAMEBAX electron microprobe, operating with a focused beam (~1 μm) in wavelength-dispersive (WDS) mode at 15 kV and 15 nA sample current, was used. The counting time for peak and background was 20 s. Synthetic end-member mineral standards were used (Domeneghetti et al. 1995b). X-ray counts were converted to oxide weight percentages using the ZAF correction program. Precision of the analyses is ±1% for major elements and 3–5% for minor elements.

Ca concentration profiles along directions perpendicular to exsolved lamellae in the orthopyroxene grains allowed us to select Ca-poor areas suitable for spot analyses. The chemical composition reported in Table 6 represents the average of 15 spot analyses in which the oxide total was 100 ± 1%. The Fe^{3+} content was zero, consistent with the highly reduced state of the meteorite; total cation content was 4.000 ± 0.005 atoms on the basis of six O atoms; the charge balance $3^{[4]}\mathrm{Al} + \mathrm{Na} - 3^{[6]}\mathrm{Al} - 4\mathrm{Ti} - 3\mathrm{Cr}$, where the elements are expressed in terms of atoms per formula unit (apfu), was ≤ 0.005. The mean Ca content measured was 0.036 apfu ($\sigma = 0.005$), with a minimum value of 0.029.

Determination of the site population

Site populations were calculated using the results of both the structure refinements and microprobe analyses. The best value of the atomic fraction X_i^j for each element i at site j was determined with a minimization procedure using the program MINUIT (James and Ross 1975).

The quantity minimized was $M = \Sigma[R_w]^2 = \Sigma[(Q_{calc} - Q_{obs})/\sigma(Q_{obs})]^2$, i.e., the weighted sum of the squares of the residuals (R) between the observed and the calculated values of chemical and structural (Q) parameters, with weights (w) inversely proportional to the relevant standard deviations, σ. The chemical parameters considered

TABLE 3. Atomic positional parameters and displacement parameters

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq} (Å^2)
					Opx SDM N.13, natural					
SiA	0.22851(4)	0.65945(8)	0.5520(1)	0.0066(3)	0.0063(3)	0.0034(3)	−0.0006(3)	−0.0004(2)	0.0003(3)	0.43
SiB	0.47401(4)	0.33650(8)	0.7950(1)	0.0064(3)	0.0058(3)	0.0031(3)	0.0002(3)	−0.0004(2)	−0.0001(3)	0.40
O1A	0.3161(1)	0.8380(2)	0.0440(3)	0.0077(8)	0.0086(8)	0.0043(7)	−0.0002(7)	0.0003(7)	0.0001(7)	0.54
O1B	0.5625(1)	0.3370(2)	0.7957(4)	0.0057(7)	0.0088(8)	0.0045(7)	−0.0001(7)	−0.0018(7)	0.0011(7)	0.50
O2A	0.3111(1)	0.5003(2)	0.0539(4)	0.0098(8)	0.0081(8)	0.0067(8)	−0.0016(7)	−0.0028(7)	0.0004(7)	0.65
O2B	0.4341(1)	0.4852(2)	0.6976(4)	0.0112(8)	0.0087(8)	0.0071(8)	0.0017(7)	0.0004(7)	0.0017(7)	0.71
O3A	0.1976(1)	0.7686(2)	0.3243(4)	0.0096(8)	0.0124(9)	0.0061(8)	0.0016(7)	−0.0003(7)	0.0035(7)	0.74
O3B	0.4473(1)	0.2022(2)	0.5935(4)	0.0105(8)	0.0113(9)	0.0067(9)	−0.0006(7)	−0.0006(8)	−0.0030(7)	0.75
M1	0.37537(4)	0.65467(8)	0.8743(1)	0.0084(4)	0.0071(4)	0.0035(3)	−0.0001(3)	−0.0006(3)	0.0003(3)	0.50
M2	0.37799(3)	0.48326(5)	0.36791(8)	0.0103(2)	0.0096(2)	0.0042(2)	−0.0012(2)	−0.0022(2)	0.0000(2)	0.64
					Opx SDM N.7, heated					
SiA	0.22838(3)	0.65955(7)	0.5514(1)	0.0051(3)	0.0056(3)	0.0041(2)	−0.0007(2)	−0.0008(2)	0.0001(2)	0.39
SiB	0.47386(3)	0.33637(7)	0.7946(1)	0.0050(3)	0.0049(3)	0.0043(3)	0.0006(2)	−0.0001(2)	0.0004(2)	0.37
O1A	0.31602(9)	0.8387(2)	0.0412(3)	0.0064(7)	0.0078(7)	0.0063(7)	0.0001(6)	0.0001(6)	−0.0001(6)	0.54
O1B	0.56216(9)	0.3379(2)	0.7951(3)	0.0047(7)	0.0087(7)	0.0068(7)	−0.0001(6)	−0.0007(6)	0.0003(6)	0.53
O2A	0.31132(9)	0.4996(2)	0.0517(3)	0.0092(8)	0.0076(7)	0.0074(7)	−0.0017(6)	−0.0012(6)	0.0020(7)	0.64
O2B	0.43368(9)	0.4840(2)	0.6951(3)	0.0084(7)	0.0090(8)	0.0077(7)	0.0011(6)	−0.0007(6)	0.0014(6)	0.66
O3A	0.19772(9)	0.7698(2)	0.3246(3)	0.0077(7)	0.0114(8)	0.0074(7)	−0.0004(6)	−0.0012(7)	0.0035(6)	0.70
O3B	0.44762(9)	0.2012(2)	0.5940(3)	0.0084(8)	0.0102(8)	0.0075(8)	−0.0009(6)	−0.0010(7)	−0.0030(6)	0.69
M1	0.37563(3)	0.65440(6)	0.8726(1)	0.0069(3)	0.0061(3)	0.0052(3)	−0.0002(2)	−0.0009(2)	0.0002(2)	0.48
M2	0.37780(3)	0.48378(5)	0.36644(8)	0.0091(2)	0.0096(2)	0.0068(2)	−0.0011(2)	−0.0025(2)	−0.0002(2)	0.67

Note: Standard deviations are in parentheses.

Table 6. Electron microprobe analysis of Serra de Magé orthopyroxene

Chemical composition (avg. of 15 spots)			
Oxide (wt%)		**apfu (based on 6 O atoms)**	
SiO_2	52.42(30)	Si	1.987(7)
Al_2O_3	0.36(6)	Al	0.016(3)
FeO	24.96(22)	Fe^{2+}	0.791(7)
MgO	20.07(21)	Mg	1.134(12)
MnO	0.80(8)	Mn	0.026(3)
TiO_2	0.15(3)	Ti	0.004(1)
Cr_2O_3	0.15(4)	Cr	0.004(1)
CaO	0.88(13)	Ca	0.036(5)
Na_2O	0.01(1)	Na	—
Sum	99.80(40)	Sum	3.998(6)

Note: Standard deviations are in parentheses.

were the atomic fractions of Si, Al, Ti, Cr, Mg, Fe^{2+}, Mn, Ca, and Na. For each element, the residuals (R_1–R_9) are the difference between the sum of its atomic fraction at the structural sites and its total amount, in apfu, determined by the microprobe analysis. The structural parameters are the mean atomic numbers (m.a.n.) at the M1 and M2 sites and the mean bond distances M1-O and SiB-O, the experimental values of which were provided by the structure refinement. The relevant residuals (R_{10}–R_{13}) were then calculated as follows:

$$R_{10} = (12X^{\mathrm{M1}}_{\mathrm{Mg}} + 26X^{\mathrm{M1}}_{\mathrm{Fe}^{2+}} + 26X^{\mathrm{M1}}_{\mathrm{Fe}^{3+}} + 13X^{\mathrm{M1}}_{^{[6]}\mathrm{Al}} + 22X^{\mathrm{M1}}_{\mathrm{Ti}} + 25X^{\mathrm{M1}}_{\mathrm{Mn}} + 24X^{\mathrm{M1}}_{\mathrm{Cr}}) - \mathrm{m.a.n.(M1)} \quad (1)$$

$$R_{11} = [2.078X^{\mathrm{M1}}_{\mathrm{Mg}} + 2.135X^{\mathrm{M1}}_{\mathrm{Fe}^{2+}} + 2.030X^{\mathrm{M1}}_{\mathrm{Fe}^{3+}} + 1.929X^{\mathrm{M1}}_{^{[6]}\mathrm{Al}} + 1.990X^{\mathrm{M1}}_{\mathrm{Ti}} + 2.010X^{\mathrm{M1}}_{\mathrm{Cr}} + 2.173X^{\mathrm{M1}}_{\mathrm{Mn}} + 0.006(X^{\mathrm{M2}}_{\mathrm{Fe}^{2+}} - X^{\mathrm{M1}}_{\mathrm{Fe}^{2+}})] - \langle \mathrm{M1\text{-}O} \rangle_{\mathrm{obs}} \quad (2)$$

$$R_{12} = (12X^{\mathrm{M2}}_{\mathrm{Mg}} + 26X^{\mathrm{M2}}_{\mathrm{Fe}^{2+}} + 20X^{\mathrm{M2}}_{\mathrm{Ca}} + 25X^{\mathrm{M2}}_{\mathrm{Mn}} + 11X^{\mathrm{M2}}_{\mathrm{Na}}) - \mathrm{m.a.n.(M2)} \quad (3)$$

$$R_{13} = [(X^{\mathrm{T}}_{^{[4]}\mathrm{Al}} + 15.4230)/9.4187] - \langle \mathrm{SiB\text{-}O} \rangle_{\mathrm{obs}}. \quad (4)$$

In Equations 1 and 3 the coefficients of the atomic fractions X_i are the atomic numbers of the elements that enter the sites M1 and M2, respectively. In Equation 2 the coefficients of $X^{\mathrm{M1}}_{\mathrm{Mg}}$ and $X^{\mathrm{M1}}_{\mathrm{Fe}^{2+}}$ are the mean bond distances from enstatite and ferrosilite, and the coefficients of the other atomic fractions represent the cation-O mean bond distances for Fe^{3+}, $^{[6]}$Al, Ti, Cr, and Mn, respectively, as currently adopted for the M1 site in pyroxenes. The last term of the equation introduces an empirical correction for the influence of the M2-site population on the size of the M1 polyhedron, as in Equation 5 of Domeneghetti et al. (1995a). In Equation 4 the numerical values come from Equation 18 of Domeneghetti et al. (1995a).

In the minimization procedure the following constraints were adopted: (1) Fe^{3+} was considered to be equal to zero, as in the microprobe analysis; (2) $^{[6]}$Al, Ti, and Cr were considered to be fully ordered at the M1 site (Domeneghetti et al. 1985; Tazzoli and Domeneghetti 1987), Ca fully ordered at the M2 site, Mg and Fe^{2+} distributed between the M1 and M2 sites, and Mn partitioned in the same way as Fe^{2+} (Hawthorne and Ito 1978); (3) all the structural sites were considered to be fully occupied; (4) the charge balance in isomorphous replacements was constrained by $X_{^{[6]}\mathrm{Al}} + 2X_{\mathrm{Ti}^{4+}} + X_{\mathrm{Cr}} = X_{\mathrm{Na}} + X_{^{[4]}\mathrm{Al(T)}}$.

Table 7. Site population of Serra de Magé orthopyroxenes

Site population		Opx SDM N.13, natural	Opx SDM N.7, heated
T	Si	1.986	1.986
	$^{[4]}$Al	0.014	0.014
M1	Mg	0.897(4)	0.764(4)
	Fe^{2+}	0.091(4)	0.220(4)
	$^{[6]}$Al	0.000	0.000
	Mn	0.003	0.007
	Cr	0.004	0.004
	Fe^{3+}	0.000	0.000
	Ti	0.005	0.005
M2	Mg	0.237(4)	0.364(4)
	Fe^{2+}	0.704(4)	0.581(4)
	Mn	0.023	0.019
	Na	0.000	0.000
	Ca	0.036	0.036
	K_D	0.034	0.180

Note: Standard deviations are in parentheses.

The standard deviations used for weighting the residuals R_1–R_9 came directly from the microprobe analysis, and those for the residuals R_{10}–R_{13} from the structure refinement. The standard deviations of the residuals R_{11} and R_{13} include both the error of the observed values, given by the refinement, and the error of the calculated values, which were estimated to be 0.01 and 0.001 for ⟨SiB-O⟩ and ⟨M1-O⟩, respectively, according to the results of Domeneghetti et al. (1995a).

The calculated site populations for samples SDM N.13 and SDM N.7 are reported in Table 7.

DISCUSSION

The validity of the refinement procedure adopted in this work for the two Serra de Magé orthopyroxene crystals is supported by the final values of the residual indices R_{obs}, which must be compared with those obtained for the same samples by Domeneghetti et al. (1995b) using the traditional refinement in space group *Pbca*. The R_{obs} indices decreased from 2.81 to 2.11% for Opx SDM N.13 and from 5.17 to 1.78% for Opx SDM N.7, which contains a higher fraction of the exsolved phase. The standard deviations of the atomic positional parameters, and consequently those of the interatomic distances, show a comparable improvement. In particular, for Opx SDM N.7 they are reduced to about one-third of the previous values. The displacement parameters also exhibit a general decrease, as is indicated by the new values of B_{eq}.

The results of this work demonstrate that the correct space group for Serra de Magé orthopyroxene is indeed *Pbca* and that the violations of the extinction conditions for *Pbca* space group are due to the exsolved augite lamellae. The adoption of a lower symmetry space group must definitely be rejected for this orthopyroxene and must be questioned also for the other reported $P2_1ca$ orthopyroxenes from lunar and terrestrial occurrences. For these samples, if single crystals are available, the true symmetry could be verified using the method described in this paper.

The refinement procedure adopted here allowed us to determine the fraction of the exsolved $C2/c$ phase, 2.80 and 11.27% for Opx SDM N.13 and Opx SDM N.7, respectively, in good agreement with the approximate values, 4 and 12%, calculated from the intensity of the "forbidden reflections" in *Pbca* space group (Domeneghetti et al. 1995b). Our refinement provided accurate values of the distribution coefficient K_D for both samples with use of a more correct determination of M1 and M2 site populations. The K_D values of 0.034 and 0.180 for Opx SDM N.13 and Opx SDM N.7, respectively, are lower in comparison with those of 0.042 and 0.205 obtained from the site population previously calculated by Domeneghetti et al. (1995b). This indicates that, if the diffraction effects of the exsolved phase are not subtracted from those of the host, the degree of order measured for the orthopyroxene can be lower than the actual value, leading to significant errors in the calculation of the cooling rates.

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