

## A crystal-chemical model for *Pbca* orthopyroxene

**M. CHIARA DOMENEGHETTI**

CNR Centro di Studio per la Cristallografia e la Cristallografia, % Dipartimento di Scienze della Terra,  
Università di Pavia, Via Abbiategrosso 209, 27100 Pavia, Italy

**G. MARIO MOLIN**

Dipartimento di Mineralogia e Petrologia, Università di Padova, Corso Garibaldi 37, 35100 Padua, Italy

**VITTORIO TAZZOLI**

Dipartimento di Scienze della Terra, Università di Pavia, Via Abbiategrosso 209, 27100 Pavia, Italy

### ABSTRACT

The study of a crystal-chemical model for *Pbca* orthopyroxene was undertaken using the results of X-ray single-crystal structure refinements and chemical analyses of about 200 samples with different compositions and degrees of order. Multiple linear correlations between compositional and structural variables were searched for using the statistic package SPSS. The coefficients and constant terms of linear equations that allow the prediction of cell parameters and interatomic distances for any orthopyroxene, starting from its crystal-chemical formula, were calculated. From the predicted distances, the geometric refinement program DLS-76 yields the relevant atomic positions, which agree satisfactorily with those measured experimentally. The same results were obtained more quickly using coefficients that directly express the correlation between the atomic fractions at the structural sites and the atomic positions. The calculation of atomic positions makes it possible to study the effects induced on the structure by any variation of chemical composition and cation distribution; in particular it has allowed the prediction of structural properties for fictive end-members. The coefficients for the calculation of cation-O mean bond distances of the regular polyhedra M1 and SiB appear to be nearly correlated to the ionic radii of the cations at these sites, thus justifying the introduction of (M1-O) and (SiB-O) bond distances in the linear equations used for determining or checking M1 and SiB site populations. The prediction of atomic positions can be used for lattice-energy calculations, in order to develop a structure-energy model for orthopyroxene. The coefficients and constant terms of linear equations for the atomic fractions as a function of cell parameters, atomic positions, and mean atomic numbers at M1 and M2 sites were also calculated in order to test the possibility of predicting, for any orthopyroxene, its cation distribution in the absence of chemical analysis.

### INTRODUCTION

Orthopyroxene,  $(\text{Mg,Fe})_2\text{Si}_2\text{O}_6$ , is a rock-forming mineral of great interest for its petrological, crystal-chemical, and thermodynamic significance. It occurs in both igneous and metamorphic rocks and represents one of the most important constituents of the upper mantle. Its structure, which consists of tetrahedral and octahedral chains forming alternating layers, is easily affected even by small variations of composition, temperature, and pressure. The Mg-Fe<sup>2+</sup> exchange reaction between the two nonequivalent crystallographic sites, M1 and M2, and its temperature-dependent kinetics allow the estimation of natural cooling rates for rocks in which this mineral occurs (Ganguly, 1982). This homogeneous reaction has been extensively investigated by Mössbauer spectroscopy (Virgo and Hafner, 1969, 1970; Saxena and Ghose, 1971; Besancon, 1981; Seifert, 1983; Anovitz et al., 1988) and

single-crystal X-ray diffraction (Ganguly and Ghose, 1979; Domeneghetti et al., 1985; Saxena et al., 1987, 1989; Tazzoli and Domeneghetti, 1987; Molin, 1989; Sykes-Nord and Molin, 1993). The results obtained by X-ray diffraction and Mössbauer spectroscopy on the same samples have been compared in both natural (Skogby et al., 1992) and synthetic orthopyroxenes (Domeneghetti and Steffen, 1992). The data obtained by X-ray diffraction on natural and heated samples have revealed trends in structural variations as a function of order-disorder and chemical composition.

The aim of this work is a systematic study of the correlations among all structural and compositional variables from a large number of high-precision structural data of orthopyroxenes, collected with the same experimental procedure, in order to find the coefficients of two series of linear equations. The first series of equations should permit the prediction of the structure (i.e., of the





TABLE 2. Comparison of predicted and observed interatomic distances (Å) in four orthopyroxenes of different composition

	OPX AV77 N.1		OPX S 125 N.9		OPX 10/68/C/N		Ferrosilite P14*	
	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.
SiA-O1A	1.610	1.611(1)	1.613	1.614(1)	1.611	1.610(1)	1.613	1.614(1)
SiA-O2A	1.590	1.589(1)	1.597	1.597(1)	1.599	1.600(1)	1.600	1.602(1)
SiA-O3A	1.645	1.645(1)	1.636	1.636(1)	1.636	1.636(2)	1.634	1.633(2)
SiA-O3AI	1.663	1.664(1)	1.654	1.655(1)	1.654	1.655(2)	1.652	1.651(2)
(SiA-O)	1.627	1.627(1)	1.625	1.625(1)	1.625	1.625(2)	1.625	1.625(1)
O1A-O2A	2.733	2.733(1)	2.751	2.752(1)	2.746	2.742(2)	2.740	2.742(2)
O1A-O3A	2.634	2.634(1)	2.633	2.634(2)	2.635	2.633(2)	2.630	2.631(2)
O1A-O3AI	2.720	2.721(1)	2.688	2.692(2)	2.689	2.688(2)	2.696	2.698(2)
O2A-O3AI	2.488	2.488(1)	2.505	2.504(2)	2.510	2.514(2)	2.508	2.509(2)
O2A-O3A	2.700	2.698(1)	2.684	2.683(2)	2.681	2.680(2)	2.686	2.686(2)
O3A-O3AI	2.633	2.633(1)	2.628	2.628(1)	2.632	2.631(1)	2.634	2.631(1)
SiB-O1B	1.618	1.618(1)	1.647	1.650(1)	1.621	1.621(1)	1.622	1.622(1)
SiB-O2B	1.588	1.590(1)	1.619	1.621(1)	1.600	1.602(1)	1.600	1.600(1)
SiB-O3B	1.675	1.675(1)	1.686	1.685(1)	1.668	1.668(1)	1.667	1.666(1)
SiB-O3BI	1.673	1.675(1)	1.681	1.682(1)	1.663	1.664(1)	1.662	1.663(2)
(SiB-O)	1.639	1.640(1)	1.659	1.660(1)	1.638	1.639(1)	1.637	1.637(1)
O1B-O2B	2.738	2.738(1)	2.789	2.792(2)	2.745	2.746(2)	2.740	2.740(2)
O1B-O3B	2.653	2.654(1)	2.676	2.678(2)	2.645	2.646(2)	2.641	2.642(2)
O1B-O3BI	2.636	2.636(1)	2.668	2.670(2)	2.643	2.644(2)	2.640	2.639(2)
O2B-O3BI	2.671	2.674(1)	2.698	2.700(2)	2.664	2.667(2)	2.665	2.664(2)
O2B-O3B	2.589	2.592(1)	2.624	2.626(2)	2.594	2.595(2)	2.594	2.595(2)
O3B-O3BI	2.761	2.762(1)	2.783	2.783(1)	2.749	2.748(1)	2.758	2.756(1)
M1-O1AII	2.028	2.028(1)	2.019	2.020(1)	2.063	2.062(1)	2.196	2.196(1)
M1-O1AI	2.151	2.151(1)	2.140	2.138(1)	2.170	2.172(1)	2.088	2.086(1)
M1-O1BII	2.172	2.172(1)	2.140	2.139(1)	2.184	2.185(1)	2.123	2.123(1)
M1-O1BI	2.063	2.064(1)	2.038	2.036(1)	2.093	2.092(1)	2.194	2.194(1)
M1-O2AI	2.011	2.012(1)	2.022	2.022(1)	2.068	2.068(1)	2.090	2.086(1)
M1-O2B	2.049	2.049(1)	2.023	2.020(1)	2.097	2.095(1)	2.125	2.124(1)
(M1-O)	2.079	2.079(1)	2.064	2.063(1)	2.112	2.112(1)	2.136	2.135(1)
O1A-O1AIII	3.040	3.039(1)	3.029	3.028(1)	3.063	3.064(1)	3.085	3.084(2)
O1A-O1BIV	2.848	2.849(1)	2.783	2.780(2)	2.878	2.880(2)	2.937	2.933(2)
O1A-O1BV	2.813	2.812(1)	2.827	2.822(2)	2.848	2.848(2)	2.846	2.843(2)
O1A-O1BVI	4.091	4.091(1)	4.054	4.052(2)	4.153	4.151(2)	4.208	4.207(2)
O1A-O2AII	2.983	2.986(1)	2.957	2.957(2)	3.064	3.065(2)	3.122	3.122(2)
O1A-O2AIII	2.987	2.987(2)	3.000	3.002(2)	3.074	3.070(2)	3.104	3.103(2)
O1A-O2BI	4.199	4.198(1)	4.162	4.157(2)	4.265	4.265(2)	4.319	4.318(2)
O1A-O2BII	2.756	2.754(1)	2.750	2.747(2)	2.818	2.816(2)	2.836	2.835(2)
O1B-O1BVII	3.041	3.040(1)	3.007	3.007(1)	3.045	3.046(1)	3.061	3.057(2)
O1B-O2AIV	2.815	2.816(1)	2.817	2.815(2)	2.880	2.880(2)	2.902	2.901(2)
O1B-O2AV	4.174	4.175(1)	4.155	4.154(2)	4.247	4.248(2)	4.277	4.274(2)
O1B-O2BIII	3.071	3.071(1)	3.047	3.044(2)	3.137	3.134(2)	3.197	3.196(2)
O1B-O2BIV	3.148	3.149(1)	3.076	3.075(2)	3.178	3.178(2)	3.242	3.239(2)
O2A-O2BV	2.891	2.890(1)	2.898	2.897(2)	2.942	2.943(2)	2.944	2.942(2)
M2-O1AII	2.109	2.105(1)	2.186	2.185(1)	2.169	2.168(1)	2.157	2.155(1)
M2-O1BIII	2.070	2.068(1)	2.109	2.106(1)	2.132	2.130(1)	2.123	2.123(1)
M2-O2A	2.044	2.038(1)	2.075	2.074(1)	2.044	2.045(1)	2.022	2.021(1)
M2-O2B	1.988	1.990(1)	1.995	1.995(1)	2.003	2.002(1)	1.988	1.989(1)
M2-O3AI	2.294	2.297(1)	2.356	2.354(1)	2.427	2.430(1)	2.456	2.457(1)
M2-O3BII	2.454	2.452(1)	2.356	2.352(1)	2.572	2.573(1)	2.598	2.595(1)
(M2-O)	2.160	2.158(1)	2.179	2.178(1)	2.225	2.225(1)	2.225	2.223(1)
(M2-O) <sub>4</sub>	2.052	2.050(1)	2.091	2.090(1)	2.087	2.086(1)	2.073	2.072(1)
O1-O2AVI	2.909	2.908(1)	2.928	2.927(2)	2.940	2.939(2)	2.928	2.925(2)
O1A-O3AII	3.562	3.563(1)	3.660	3.658(2)	3.769	3.769(2)	3.782	3.784(2)
O1A-O3BIII	4.552	4.545(1)	4.530	4.525(2)	4.724	4.723(2)	4.734	4.732(2)
O1B-O2BVI	2.984	2.982(1)	3.044	3.043(2)	3.028	3.025(2)	3.010	3.008(2)
O1B-O3AIII	4.238	4.240(1)	4.318	4.313(2)	4.412	4.413(2)	4.440	4.442(2)
O1B-O3BIV	3.194	3.190(1)	3.210	3.206(2)	3.369	3.369(2)	3.386	3.391(2)
O2A-O2B	4.025	4.021(2)	4.050	4.050(2)	4.040	4.039(2)	4.006	4.004(2)
O2A-O3BII	3.060	3.057(1)	3.045	3.044(2)	3.093	3.096(2)	3.085	3.083(2)
O2B-O3AI	3.528	3.527(1)	3.635	3.632(2)	3.696	3.696(2)	3.677	3.678(2)
O2B-O3BII	3.453	3.445(2)	3.451	3.449(2)	3.612	3.611(2)	3.597	3.595(2)
O3A-O3BIV	2.904	2.902(1)	2.872	2.869(2)	2.942	2.941(2)	2.954	2.950(2)
SiA-SiAI	3.055	3.054(1)	3.063	3.062(1)	3.077	3.076(1)	3.079	3.078(1)
SiA-SiBI	3.913	3.911(1)	3.898	3.896(1)	3.952	3.952(1)	3.946	3.942(1)
SiA-M1I	3.151	3.150(1)	3.162	3.162(1)	3.200	3.199(1)	3.220	3.219(1)
SiA-M2	2.813	2.812(1)	2.852	2.852(1)	2.875	2.875(1)	2.881	2.880(1)
SiB-SiBII	3.017	3.015(1)	3.017	3.016(1)	3.037	3.037(1)	3.036	3.033(1)
SiB-M1II	3.250	3.250(1)	3.248	3.248(1)	3.275	3.275(1)	3.296	3.296(1)
SiB-M2	3.150	3.156(1)	3.145	3.145(1)	3.132	3.132(1)	3.142	3.143(1)
M1-M2I	2.963	2.959(1)	2.991	2.989(1)	3.004	3.002(1)	2.999	2.996(1)

Note: standard deviations of the observed interatomic distances are in parentheses.

\* Domeneghetti and Steffen (1992).

cell parameters and atomic positions) of any orthopyroxene from its crystal-chemical formula (i.e., from the cation distribution at the structural sites). The second series of equations should permit, inversely, the prediction of the crystal-chemical formula from the cell parameters and atomic positions.

The prediction of the structure should provide, first of all, the basis for the development of a structure-energy model for *Pbca* orthopyroxenes, such as already proposed by Ottonello et al. (1989) for *Pbnm* olivines and by Ottonello et al. (1992) for *C2/c* pyroxenes. To this purpose, the Gibbs free energy minimization principle will be applied to the results of lattice-energy and entropy calculations to model the degree of order at equilibrium for any orthopyroxene at various *T* and *P* conditions. The prediction of the structure could also have some direct applications, enabling one, for example, to derive all structure parameters of an orthopyroxene only from microprobe analysis and Fe distribution obtained by Mössbauer spectroscopy. This could be particularly useful when an X-ray single-crystal diffractometer is not available or when the poor quality of the crystals prevents the use of this technique. It has to be noted that, in this way, one obtains a sort of mean structure of the sample, which should represent it more closely than a structure determined only from a single crystal picked up from the mass of mineral.

On the other hand, the ability to predict site population from structural data should enable a crystallographer who has collected X-ray single-crystal diffraction data for a sample to obtain a rough evaluation of its site population in the absence of chemical analysis. This could be particularly useful in the study of meteorites, when good crystals of a specific sample are very hard to find. A crystallographer who is reluctant, after X-ray data collection, to destroy for microprobe analysis a very precious and irreplaceable crystal or who even has lost it during the transfer procedures from diffractometer to microprobe could all the same determine the site population through the method presented in this paper.

The precision of these predictions will be continuously improved by adding data for poorly or unrepresented compositions to the orthopyroxene file, as they become available.

## EXPERIMENTAL METHODS

### The orthopyroxene file

A file containing the results of the structure refinement of about 300 natural and synthetic orthopyroxenes with different compositions and degrees of order (some reached by annealing experiments) has been created. X-ray single-crystal data collections and structure refinements of the orthopyroxenes were done at the CNR-CSCC of Pavia over the last ten years following the procedures described in Skogby et al. (1992). It also contains, for 201 samples, the results of the electron microprobe analyses performed on the same crystals as used for the X-ray data collection.

TABLE 3. Cation distribution in three orthopyroxenes selected for testing the model

		OPX AV77 N.1	OPX S 125 N.9	OPX 10/68/C/N
M1	Mg	0.993(2)	0.740(2)	0.439(3)
	Fe <sup>2+</sup>	0.003(2)	0.069(2)	0.542(3)
	Mn	—	0.001	0.018
	Fe <sup>3+</sup>	0.003	0.050	0.001
	Al	—	0.135	—
M2	Ti	—	0.005	—
	Cr	0.001	—	—
	Mg	0.863(2)	0.253(3)	0.010(3)
	Fe <sup>2+</sup>	0.129(2)	0.729(3)	0.922(3)
	Mn	0.005	0.008	0.030
T	Ca	0.003	0.010	0.037
	Si	1.996	1.805	1.999
	<sup>141</sup> Al	0.004	0.195	0.001

Note: standard deviations of the observed atomic fractions are in parentheses.

In order to ensure maximum internal consistency, the results from other laboratories have not yet been included in the file.

The compositional range in atoms per formula unit (apfu) of this data base is the following: Fe<sup>2+</sup>: 0.131–2.000; Mg: 0.0–1.858; <sup>141</sup>Al: 0.0–0.195; Al<sub>tot</sub>: 0.0–0.330; Fe<sup>3+</sup>: 0.0–0.072; Ca: 0.0–0.065; Mn: 0.0–0.089; Ti: 0.0–0.013; Cr: 0.0–0.011. *K<sub>D</sub>* ranges between 0.020 and 0.279. As it concerns the Fe<sup>3+</sup> content, the values have been derived indirectly through charge balance of microprobe data and thus can absorb, to some extent, the errors in the analyses of other elements. However, for the approximately 100 R<sup>3+</sup>-rich samples, the Fe<sup>3+</sup> content agrees with that previously measured on the same samples by Mössbauer spectroscopy (Seifert, 1983; Skogby et al., 1992).

A set of locally written programs is used for file updating through the following procedures: (1) introduction of data referring to new refined samples and revision of already existent data after further refinements or microprobe analyses; (2) calculation of the atomic fractions on the basis of the results of the structure refinement and, if available, of the microprobe analysis, according to the criteria described below; (3) creation, for each sample, of a summarizing table with the more significant parameters: information on data collection and structure refinement, cell parameters, atomic positions, displacement parameters, mean atomic numbers (m.a.n.) at M1 and M2 sites, bond distances, microprobe analysis, crystal-chemical formula, and calculated M1-O mean bond distance.

### Cation distribution

The atomic fractions were calculated on the basis of the results of the structural refinement and microprobe analysis as follows: (1) the amounts of Si, Al<sub>tot</sub>, <sup>141</sup>Al = 2 – Si, <sup>161</sup>Al = Al<sub>tot</sub> – <sup>141</sup>Al, Ti<sup>4+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup> = <sup>141</sup>Al – <sup>161</sup>Al – 2Ti<sup>4+</sup> – Cr<sup>3+</sup>, Mn, and Ca were taken from the chemical analysis; the m.a.n. at the M1 and M2 sites were taken from the structure refinement; (2) <sup>161</sup>Al, Fe<sup>3+</sup>, Ti, and Cr were considered as fully ordered at the M1 site

TABLE 4. Regression coefficients and constant terms for the calculation of atomic positions in *Pbca* orthopyroxenes

	$C_1$ $X_{Fe^{2+}}^{M1}$	$C_2$ $X_{Mn}^{M1}$	$C_3$ $X_{Fe^{3+}}^{M1}$	$C_4$ $X_{Ti}^{M1}$	$C_5$ $X_{Cr}^{M1}$	$C_6$ $X_{Fe^{2+}}^{M2}$	$C_7$ $X_{Mn}^{M2}$	$C_8$ $X_{Ca}^{M2}$	$C_9$ $X_{Al}^{M2}$	$C$	$R^2$
$x_{SIA}$	0.0009	-0.0041	0.0000	0.0000	0.0000	-0.0002	-0.0008	-0.0021	-0.0020	0.2717	0.9540
$\sigma$	0.0000	0.0011	0.0000	0.0000	0.0000	0.0000	0.0002	0.0003	0.0000	0.0000	0.0000
$y_{SIA}$	-0.0014	0.0000	-0.0016	-0.0086	0.0000	-0.0011	-0.0008	0.0000	0.0037	0.3416	0.9793
$\sigma$	0.0000	0.0000	0.0005	0.0031	0.0000	0.0000	0.0003	0.0000	0.0002	0.0000	0.0000
$z_{SIA}$	-0.0045	-0.0297	-0.0050	0.0000	0.0000	0.0031	-0.0040	-0.0132	-0.0325	0.0510	0.9830
$\sigma$	0.0002	0.0071	0.0019	0.0000	0.0000	0.0001	0.0014	0.0022	0.0007	0.0001	0.0003
$x_{SIB}$	-0.0007	0.0000	0.0000	0.0000	0.0000	0.0003	0.0018	0.0043	-0.0038	0.4736	0.9689
$\sigma$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0004	0.0000	0.0000	0.0000
$y_{SIB}$	-0.0019	0.0032	-0.0022	0.0000	0.0000	-0.0013	0.0000	0.0032	-0.0004	0.3374	0.9848
$\sigma$	0.0000	0.0013	0.0004	0.0000	0.0000	0.0000	0.0000	0.0005	0.0001	0.0000	0.0000
$z_{SIB}$	-0.0065	0.0000	-0.0080	-0.0813	-0.0483	-0.0026	-0.0067	0.0000	0.0486	0.7980	0.9944
$\sigma$	0.0002	0.0000	0.0020	0.0127	0.0209	0.0001	0.0013	0.0000	0.0007	0.0001	0.0003
$x_{O1A}$	0.0013	0.0000	0.0019	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0040	0.1835	0.9543
$\sigma$	0.0000	0.0000	0.0006	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000
$y_{O1A}$	0.0029	-0.0155	0.0064	0.0360	0.0000	-0.0032	0.0000	-0.0083	-0.0041	0.3401	0.9142
$\sigma$	0.0001	0.0043	0.0012	0.0114	0.0000	0.0000	0.0000	0.0020	0.0006	0.0000	0.0002
$z_{O1A}$	-0.0088	0.0000	-0.0082	0.0000	0.0000	0.0120	0.0088	0.0163	-0.0244	0.0352	0.9655
$\sigma$	0.0002	0.0000	0.0030	0.0000	0.0000	0.0002	0.0019	0.0031	0.0011	0.0002	0.0005
$x_{O1B}$	-0.0011	-0.0070	-0.0042	-0.0307	-0.0167	-0.0002	0.0013	0.0075	0.0072	0.5624	0.9691
$\sigma$	0.0000	0.0023	0.0006	0.0054	0.0058	0.0000	0.0004	0.0010	0.0003	0.0000	0.0000
$y_{O1B}$	0.0014	0.0000	0.0041	0.0539	0.0000	-0.0048	-0.0024	-0.0129	-0.0124	0.3406	0.9760
$\sigma$	0.0001	0.0000	0.0013	0.0108	0.0000	0.0000	0.0008	0.0017	0.0006	0.0000	0.0002
$z_{O1B}$	-0.0097	0.0000	-0.0112	-0.0983	0.0000	-0.0034	-0.0043	0.0000	0.0543	0.7997	0.9925
$\sigma$	0.0002	0.0000	0.0027	0.0171	0.0000	0.0002	0.0017	0.0000	0.0010	0.0001	0.0004
$x_{O2A}$	0.0007	0.0000	0.0000	0.0119	0.0000	0.0002	-0.0023	-0.0047	-0.0026	0.3111	0.8660
$\sigma$	0.0000	0.0000	0.0000	0.0048	0.0000	0.0000	0.0004	0.0008	0.0002	0.0000	0.0000
$y_{O2A}$	-0.0040	-0.0148	-0.0071	-0.0513	0.0000	-0.0022	0.0000	0.0046	0.0149	0.5022	0.9818
$\sigma$	0.0001	0.0049	0.0013	0.0130	0.0000	0.0001	0.0000	0.0023	0.0007	0.0000	0.0002
$z_{O2A}$	0.0012	0.0000	0.0000	0.0000	0.0000	0.0133	0.0034	0.0113	-0.0376	0.0436	0.9903
$\sigma$	0.0002	0.0000	0.0000	0.0000	0.0000	0.0002	0.0016	0.0026	0.0005	0.0001	0.0004
$x_{O2B}$	-0.0010	0.0000	0.0000	0.0000	0.0000	0.0012	0.0037	0.0079	-0.0031	0.4329	0.9220
$\sigma$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004	0.0007	0.0001	0.0000	0.0000
$y_{O2B}$	-0.0052	0.0000	-0.0091	-0.0631	0.0000	0.0024	0.0043	0.0223	0.0130	0.4830	0.9571
$\sigma$	0.0001	0.0000	0.0015	0.0131	0.0000	0.0001	0.0010	0.0021	0.0007	0.0000	0.0002
$z_{O2B}$	-0.0061	0.0000	-0.0076	0.0000	0.0000	0.0092	0.0182	0.0352	-0.0121	0.6895	0.9518
$\sigma$	0.0002	0.0000	0.0028	0.0000	0.0000	0.0002	0.0017	0.0029	0.0010	0.0001	0.0004
$x_{O3A}$	-0.0003	0.0000	0.0000	0.0000	0.0000	-0.0007	-0.0020	-0.0031	-0.0029	0.3031	0.8959
$\sigma$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004	0.0006	0.0001	0.0000	0.0000
$y_{O3A}$	0.0028	0.0206	0.0000	0.0000	0.0311	0.0107	0.0118	0.0266	0.0000	0.2221	0.9933
$\sigma$	0.0001	0.0051	0.0000	0.0000	0.0142	0.0001	0.0010	0.0014	0.0000	0.0000	0.0002
$z_{O3A}$	-0.0073	-0.0592	-0.0084	0.0000	0.0000	-0.0082	-0.0129	-0.0393	-0.0324	-0.1674	0.9873
$\sigma$	0.0003	0.0098	0.0026	0.0000	0.0000	0.0002	0.0020	0.0030	0.0010	0.0001	0.0004
$x_{O3B}$	0.0005	0.0000	0.0000	0.0232	0.0000	-0.0007	0.0010	-0.0029	-0.0055	0.4477	0.9653
$\sigma$	0.0000	0.0000	0.0000	0.0045	0.0000	0.0000	0.0003	0.0007	0.0002	0.0000	0.0000
$y_{O3B}$	0.0004	0.0000	0.0000	0.0000	0.0000	0.0066	0.0127	0.0349	-0.0316	0.1955	0.9872
$\sigma$	0.0002	0.0000	0.0000	0.0000	0.0000	0.0002	0.0014	0.0023	0.0005	0.0001	0.0003
$z_{O3B}$	-0.0070	0.0000	-0.0136	-0.1090	-0.0950	-0.0102	-0.0183	-0.0339	0.0765	0.6032	0.9907
$\sigma$	0.0004	0.0000	0.0043	0.0369	0.0450	0.0003	0.0030	0.0059	0.0020	0.0002	0.0006
$x_{M1}$	0.0005	0.0000	0.0000	-0.0079	-0.0087	-0.0006	-0.0011	-0.0018	0.0027	0.3759	0.9563
$\sigma$	0.0000	0.0000	0.0000	0.0025	0.0031	0.0000	0.0002	0.0004	0.0000	0.0000	0.0000
$y_{M1}$	-0.0009	-0.0058	-0.0021	0.0000	0.0000	0.0011	0.0000	0.0000	-0.0014	0.6539	0.7833
$\sigma$	0.0000	0.0019	0.0007	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0001
$z_{M1}$	-0.0013	0.0000	0.0000	0.0574	0.0000	0.0097	0.0111	0.0135	-0.0396	0.8663	0.9881
$\sigma$	0.0002	0.0000	0.0000	0.0203	0.0000	0.0002	0.0016	0.0033	0.0007	0.0001	0.0004
$x_{M2}$	-0.0006	0.0059	0.0000	0.0000	-0.0259	0.0010	0.0000	0.0000	0.0117	0.3772	0.9907
$\sigma$	0.0000	0.0017	0.0000	0.0000	0.0060	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000
$y_{M2}$	0.0024	0.0000	0.0000	0.0274	0.0497	-0.0024	-0.0100	-0.0184	-0.0173	0.4856	0.9813
$\sigma$	0.0001	0.0000	0.0000	0.0103	0.0127	0.0000	0.0008	0.0017	0.0004	0.0000	0.0002
$z_{M2}$	-0.0023	0.0000	0.0000	0.0667	0.0000	0.0090	0.0158	0.0168	-0.0435	0.3602	0.9875
$\sigma$	0.0002	0.0000	0.0000	0.0219	0.0000	0.0002	0.0017	0.0036	0.0008	0.0001	0.0004

(Domeneghetti et al., 1985; Tazzoli and Domeneghetti, 1987; Molin, 1989), Ca as fully ordered at the M2 site, Mg, Fe<sup>2+</sup>, and Mn as distributed between the M1 and M2 sites; (3) the M1 site population was calculated, assuming  $X_{Mn}^{M1}$  as included in  $X_{Fe^{2+}}^{M1}$ , by solving the simultaneous equations

$$X_{Mg}^{M1} + X_{Fe^{2+}}^{M1} + X_{Fe^{3+}}^{M1} + X_{Al}^{M1} + X_{Ti}^{M1} + X_{Cr}^{M1} = 1 \quad (1)$$

$$12X_{Mg}^{M1} + 26X_{Fe^{2+}}^{M1} + 26X_{Fe^{3+}}^{M1} + 13X_{Al}^{M1} + 22X_{Ti}^{M1}$$

$$+ 24X_{Cr}^{M1} = m.a.n._{M1} \quad (2)$$

where the unknowns are  $X_{Mg}^{M1}$  and  $X_{Fe^{2+}}^{M1}$ . Equation 1 sets the site at full occupancy. In Equation 2, the m.a.n. given by the structure refinement is expressed as a function of the atomic species occurring at that site; (4) the M2 site population was similarly calculated by solving the simultaneous equations

$$X_{Mg}^{M2} + X_{Fe^{2+}}^{M2} + X_{Ca}^{M2} = 1 \quad (3)$$

$$12X_{\text{Mg}}^{\text{M2}} + 26X_{\text{Fe}^{2+}}^{\text{M2}} + 20X_{\text{Ca}}^{\text{M2}} = \text{m.a.n.}_{\text{M2}} \quad (4)$$

in which the unknowns are  $X_{\text{Mg}}^{\text{M2}}$  and  $X_{\text{Fe}^{2+}}^{\text{M2}}$ , where the latter includes  $X_{\text{Mn}}^{\text{M2}}$ , (5) the atomic fractions of  $\text{Fe}^{2+}$  and Mn at M1 and M2 were recalculated assuming that Mn partitions in the same way as  $\text{Fe}^{2+}$  (Hawthorne and Ito, 1978), i.e.,

$$X_{\text{Mn}}^{\text{M1}}/X_{\text{Mn}}^{\text{OPX}} = X_{\text{Fe}^{2+}}^{\text{M1}}/(X_{\text{Fe}^{2+}}^{\text{M1}} + X_{\text{Fe}^{3+}}^{\text{M1}}).$$

To check the accuracy of the M1 site population, the mean M1-O distance given by the structure refinement is compared with the value calculated by the equation

$$\begin{aligned} \langle \text{M1-O} \rangle_{\text{calc}} = & 2.078X_{\text{Mg}}^{\text{M1}} + 2.135X_{\text{Fe}^{2+}}^{\text{M1}} + 2.030X_{\text{Fe}^{3+}}^{\text{M1}} \\ & + 1.929X_{\text{Al}^{6}}^{\text{M1}} + 1.990X_{\text{Ti}}^{\text{M1}} + 2.010X_{\text{Cr}}^{\text{M1}} \\ & + 2.173X_{\text{Mn}}^{\text{M1}} + 0.006(X_{\text{Fe}^{2+}}^{\text{M2}} - X_{\text{Fe}^{2+}}^{\text{M1}}) \quad (5) \end{aligned}$$

where the coefficients of  $X_{\text{Mg}}^{\text{M1}}$  and  $X_{\text{Fe}^{3+}}^{\text{M1}}$  are the mean bond distances of enstatite and ferrosilite, and the coefficients of the other atomic fractions represent the cation-O mean bond distances for  $\text{Fe}^{3+}$ ,  $^{6}\text{Al}$ , 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. The observed and calculated  $\langle \text{M1-O} \rangle$  distances show very good agreement for all samples: the differences are within the estimated standard deviations given by the structure refinement.

## MODELING THE *Pbca* ORTHOPYROXENE STRUCTURE

### From the cation distribution to the atomic positions

In order to obtain a method for calculating the atomic positions of any orthopyroxene from its crystal-chemical formula, i.e., from the cation distribution at M1, M2, and T sites, multiple linear correlations between structural parameters (as dependent variables) and atomic fractions (as independent variables) were searched for using the statistic package SPSS (version SPSS/PC + 4.0) on the 201 orthopyroxene samples in the file described above. A stepwise selection of independent variables was performed. In this procedure the adopted criteria for accepting or removing a variable were, respectively,  $P_F \leq 0.05$  and  $P_F \geq 0.10$ , where  $P_F$  represents the probability associated with the hypothesis that the coefficient of the variable is zero. Two methods were tried.

**Search for the correlations between cation distribution and interatomic distances.** Regression coefficients and constant terms of 70 linear equations that express the interatomic distances as a function of the atomic fractions at the structural sites were calculated. Cation-O and O-O bond distances of SiA, SiB, M1, and M2 polyhedra as well as the shortest cation-cation distances were considered. Table 1 reports the coefficients  $c_i$  and the constant terms  $C_i$  that allow the prediction of the values  $p_i$  of the interatomic distances through the equation

$$p_i = c_{1i}X_{\text{Fe}^{2+}}^{\text{M1}} + c_{2i}X_{\text{Mn}}^{\text{M1}} + c_{3i}X_{\text{Fe}^{3+}}^{\text{M1}} + c_{4i}X_{\text{Ti}}^{\text{M1}} + c_{5i}X_{\text{Cr}}^{\text{M1}}$$

$$+ c_{6i}X_{\text{Fe}^{2+}}^{\text{M2}} + c_{7i}X_{\text{Mn}}^{\text{M2}} + c_{8i}X_{\text{Ca}}^{\text{M2}} + c_{9i}X_{\text{Al}^{6}} + C_i. \quad (6)$$

Full occupancy has been assumed at the M1, M2, and T sites: therefore, to avoid correlations among the independent variables, the following atomic fractions were omitted in Equation 6:

$$X_{\text{Mg}}^{\text{M1}} = 1 - (X_{\text{Fe}^{2+}}^{\text{M1}} + X_{\text{Fe}^{3+}}^{\text{M1}} + X_{\text{Al}^{6}}^{\text{M1}} + X_{\text{Ti}}^{\text{M1}} + X_{\text{Cr}}^{\text{M1}})$$

$$X_{\text{Mg}}^{\text{M2}} = 1 - (X_{\text{Fe}^{2+}}^{\text{M2}} + X_{\text{Mn}}^{\text{M2}} + X_{\text{Ca}}^{\text{M2}})$$

$$X_{\text{Al}^{6}}^{\text{M1}} = 1 - X_{\text{Al}^{6}}$$

$$X_{\text{SiB}} = 1 - X_{\text{Al}^{6}}.$$

Thus in Equation 6 the constant term  $C_i$  expresses the value of the  $i$ th bond distance "predicted" for enstatite.

The regression coefficients and the constant terms of the other three equations that allow the prediction of the cell parameters as a function of the atomic fractions were similarly calculated and are reported in Table 1. Table 2 compares the predicted and experimentally observed interatomic distances of a synthetic ferrosilite and of three orthopyroxenes with different compositions (given in Table 3).

From the predicted interatomic distances  $D_{\text{pred } i}$  and the predicted cell parameters, the relevant atomic positions can be obtained using DLS-76, a program for crystal structure simulation by geometric refinement (Baerlocher et al., 1977). Starting from a set of rough atomic positions, the program refines them together with the cell parameters through a sequence of least-squares cycles, minimizing the function  $\Sigma w_i(D_{\text{pred } i} - D_{\text{ref } i})$ , where  $D_{\text{ref } i}$  are the bond distances corresponding to the refined atomic positions and  $w_i$  are the relevant weights (here assumed to be equal to  $R^2$ , where  $R$  is the multiple correlation coefficient).

For any sample data treated with DLS-76 (in particular for those of Table 2), it was noted that the refined bond distances and cell parameters were nearly identical to the predicted ones, thus suggesting that the geometrical refinement procedure could be skipped.

**Direct search for correlations between cation distribution and atomic positions.** Regression coefficients and constant terms of 30 linear equations that directly express the atomic positions as a function of the atomic fractions were calculated. Table 4 reports the coefficients  $c_i$  and the constant terms  $C_i$  that allow the prediction of the values of the fractional atomic coordinates using Equation 6, where  $p_i$  now represent the values of the atomic positions.

Table 5 compares, for samples of Table 3, the experimentally observed cell parameters and atomic positions with those obtained through the two methods described here. The agreement between predicted and observed values obtained by the direct way is as good as, or even better than, that obtained through the calculation of the interatomic distances. The last approach, which is definitely faster, appears to be the most suitable for predicting cell parameters and atomic positions for any orthopyroxene starting from its cation distribution.

**TABLE 5.** Comparison of observed and predicted cell parameters (Å) and atomic positions (Å) in four orthopyroxenes of different composition

		OPX AV77 N.1			OPX S 125 N.9			OPX 10/68/C/N
		<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>
	obs.	18.240(6)	8.830(2)	5.185(2)	18.258(4)	8.822(2)	5.210(2)	18.384(5)
	calc.1	18.242	8.828	5.187	18.262	8.824	5.211	18.387
	Δ1	0.002	-0.002	0.002	0.004	0.002	0.001	0.003
	calc.2	18.241	8.827	5.187	18.262	8.824	5.211	18.387
	Δ2	0.001	-0.003	0.002	0.004	0.002	0.001	0.003
		<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>
SiA	obs.	0.2716	0.3414	0.0506	0.2712	0.3412	0.0461	0.2718
	calc.1	0.2716	0.3414	0.0511	0.2712	0.3412	0.0461	0.2718
	Δ1	0.0000	0.0000	0.0005	0.0000	0.0000	0.0000	0.0000
	calc.2	0.2717	0.3414	0.0511	0.2712	0.3412	0.0462	0.2718
	Δ2	0.0001	0.0000	0.0005	0.0000	0.0000	0.0001	0.0000
SiB	obs.	0.4736	0.3372	0.7980	0.4731	0.3362	0.8045	0.4737
	calc.1	0.4737	0.3373	0.7978	0.4731	0.3362	0.8043	0.4737
	Δ1	0.0001	0.0001	-0.0002	0.0000	0.0000	-0.0002	0.0000
	calc.2	0.4737	0.3373	0.7978	0.4731	0.3362	0.8043	0.4737
	Δ2	0.0001	0.0001	-0.0002	0.0000	0.0000	-0.0002	0.0000
O1A	obs.	0.1834	0.3398	0.0361	0.1828	0.3375	0.0380	0.1842
	calc.1	0.1835	0.3397	0.0367	0.1829	0.3376	0.0384	0.1842
	Δ1	0.0001	-0.0001	0.0006	0.0001	0.0001	0.0004	0.0000
	calc.2	0.1835	0.3397	0.0367	0.1829	0.3376	0.0384	0.1842
	Δ2	0.0001	-0.0001	0.0006	0.0001	0.0001	0.0004	0.0000
O1B	obs.	0.5624	0.3399	0.7997	0.5635	0.3351	0.8062	0.5619
	calc.1	0.5624	0.3399	0.7994	0.5633	0.3350	0.8061	0.5619
	Δ1	0.0000	0.0000	-0.0003	-0.0002	-0.0001	-0.0001	0.0000
	calc.2	0.5624	0.3399	0.7994	0.5633	0.3350	0.8061	0.5619
	Δ2	0.0000	0.0000	-0.0003	-0.0002	-0.0001	-0.0001	0.0000
O2A	obs.	0.3111	0.5018	0.0447	0.3107	0.5027	0.0462	0.3112
	calc.1	0.3110	0.5020	0.0452	0.3107	0.5027	0.0462	0.3113
	Δ1	-0.0001	0.0002	0.0005	0.0000	0.0000	0.0000	0.0001
	calc.2	0.3110	0.5020	0.0452	0.3107	0.5027	0.0462	0.3113
	Δ2	-0.0001	0.0002	0.0005	0.0000	0.0000	0.0000	-0.0001
O2B	obs.	0.4330	0.4834	0.6902	0.4331	0.4866	0.6937	0.4338
	calc.1	0.4330	0.4834	0.6908	0.4332	0.4864	0.6936	0.4338
	Δ1	0.0000	0.0000	0.0006	0.0001	-0.0002	-0.0001	0.0000
	calc.2	0.4330	0.4834	0.6908	0.4332	0.4865	0.6936	0.4339
	Δ2	0.0000	0.0000	0.0006	0.0001	-0.0001	-0.0001	0.0001
O3A	obs.	0.3030	0.2238	-0.1692	0.3021	0.2302	-0.1809	0.3021
	calc.1	0.3030	0.2236	-0.1688	0.3020	0.2304	-0.1812	0.3022
	Δ1	0.0000	-0.0002	-0.0004	-0.0001	0.0002	-0.0003	0.0001
	calc.2	0.3030	0.2237	-0.1689	0.3020	0.2304	-0.1811	0.3022
	Δ2	0.0000	-0.0001	-0.0003	-0.0001	0.0002	-0.0002	0.0001
O3B	obs.	0.4476	0.1960	0.6026	0.4463	0.1945	0.6089	0.4472
	calc.1	0.4476	0.1964	0.6019	0.4463	0.1947	0.6085	0.4473
	Δ1	0.0000	0.0004	-0.0007	0.0000	0.0002	-0.0004	0.0001
	calc.2	0.4476	0.1964	0.6018	0.4463	0.1947	0.6084	0.4473
	Δ2	0.0000	0.0004	-0.0008	0.0000	0.0002	-0.0005	0.0001
M1	obs.	0.3758	0.6540	0.8671	0.3760	0.6542	0.8661	0.3755
	calc.1	0.3758	0.6540	0.8675	0.3760	0.6543	0.8661	0.3755
	Δ1	0.0000	0.0000	0.0004	0.0000	0.0001	0.0000	0.0000
	calc.2	0.3758	0.6539	0.8675	0.3760	0.6542	0.8661	0.3755
	Δ2	0.0000	-0.0001	0.0004	0.0000	0.0000	0.0000	0.0000
M2	obs.	0.3772	0.4856	0.3605	0.3803	0.4806	0.3586	0.3780
	calc.1	0.3774	0.4852	0.3613	0.3802	0.4806	0.3587	0.3780
	Δ1	0.0002	-0.0004	0.0008	-0.0001	0.0000	0.0001	0.0000
	calc.2	0.3774	0.4851	0.3613	0.3802	0.4806	0.3588	0.3780
	Δ2	0.0002	-0.0005	0.0008	-0.0001	0.0000	0.0002	0.0000

Note: obs. refers to experimental values; the estimated standard deviations of the atomic positions are  $\leq 0.0003$ ; calc.1 refers to values directly predicted by means of regression coefficients given by the SPSS program (see Table 4); calc.2 refers to values obtained, by the DLS program, starting from a set of interatomic distances predicted through the SPSS procedure (see Table 1).

\* Domeneghetti and Steffen (1992).

### From the atomic positions to the cation distribution

The opposite way was also tried to explore the possibility of calculating the cation distribution in orthopyroxenes starting from the X-ray diffraction data, without the support of chemical analysis.

Regression coefficients  $c_{ij}$  and constant terms  $C_j$  of linear equations of the form

$$X_j = \sum c_{ij}v_i + C_j \quad (7)$$

which express the atomic fractions  $X_j$  at the structural



TABLE 5.—Continued

OPX 10/68/C/N		Ferrosilite P14*		
<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
9.002(2)	5.236(2)	18.423(5)	9.077(2)	5.237(2)
8.999	5.238	18.425	9.077	5.242
-0.002	0.002	0.002	0.000	0.005
8.999	5.238	18.428	9.074	5.242
-0.002	0.002	0.005	-0.003	0.005
<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
0.3397	0.0503	0.2724	0.3391	0.0492
0.3397	0.0502	0.2724	0.3390	0.0496
0.0000	-0.0001	0.0000	-0.0001	0.0004
0.3397	0.0503	0.2723	0.3391	0.0493
0.0000	0.0000	-0.0001	0.0000	0.0001
0.3355	0.7919	0.4732	0.3343	0.7889
0.3354	0.7919	0.4732	0.3343	0.7889
-0.0001	0.0000	0.0000	0.0000	0.0000
0.3354	0.7920	0.4732	0.3344	0.7888
-0.0001	0.0001	0.0000	0.0001	-0.0001
0.3384	0.0424	0.1848	0.3398	0.0382
0.3382	0.0423	0.1848	0.3399	0.0384
-0.0002	-0.0001	0.0000	0.0001	0.0002
0.3382	0.0423	0.1849	0.3398	0.0384
-0.0002	-0.0001	0.0001	0.0000	0.0002
0.3365	0.7913	0.5612	0.3368	0.7865
0.3363	0.7913	0.5612	0.3371	0.7866
-0.0002	0.0000	0.0000	0.0003	0.0001
0.3363	0.7912	0.5612	0.3371	0.7867
-0.0002	-0.0001	0.0000	0.0003	0.0002
0.4982	0.0568	0.3121	0.4961	0.0578
0.4980	0.0569	0.3119	0.4961	0.0580
-0.0002	0.0001	-0.0002	0.0000	0.0002
0.4980	0.0570	0.3120	0.4960	0.0578
-0.0002	0.0002	-0.0001	-0.0001	0.0000
0.4836	0.6965	0.4331	0.4805	0.6923
0.4834	0.6965	0.4331	0.4803	0.6926
-0.0002	0.0000	0.0000	-0.0002	0.0003
0.4834	0.6966	0.4330	0.4804	0.6922
-0.0002	0.0001	-0.0001	-0.0001	-0.0001
0.2353	-0.1816	0.3023	0.2357	-0.1833
0.2352	-0.1819	0.3022	0.2356	-0.1829
-0.0001	-0.0003	-0.0001	-0.0001	-0.0004
0.2352	-0.1818	0.3022	0.2356	-0.1832
-0.0001	-0.0002	-0.0001	-0.0001	0.0001
0.2036	0.5882	0.4475	0.2027	0.5864
0.2035	0.5882	0.4476	0.2024	0.5860
-0.0001	0.0000	0.0001	-0.0003	-0.0004
0.2035	0.5882	0.4476	0.2027	0.5861
-0.0001	0.0000	0.0001	0.0000	-0.0003
0.6543	0.8754	0.3758	0.6540	0.8746
0.6544	0.8754	0.3758	0.6542	0.8747
0.0001	0.0000	0.0000	0.0002	0.0001
0.6543	0.8754	0.3758	0.6543	0.8746
0.0000	0.0000	0.0000	0.0003	0.0000
0.4839	0.3681	0.3777	0.4857	0.3666
0.4837	0.3682	0.3777	0.4856	0.3668
-0.0002	0.0001	0.0000	-0.0001	0.0002
0.4837	0.3683	0.3776	0.4856	0.3667
-0.0002	0.0002	-0.0001	-0.0001	0.0001

sites as a function of cell parameters and atomic positions  $\nu_i$ , were calculated using the SPSS package.

A preliminary search, made to reduce the number of independent variables  $\nu_i$ , showed that (1) the following atomic coordinates appeared to be nearly invariant within the compositional range of the refined samples record-

ed in the file:  $x_{SiA}$ ,  $x_{SiB}$ ,  $x_{O1B}$ ,  $x_{O2A}$ ,  $x_{O2B}$ ,  $x_{O3A}$ ,  $x_{O3B}$ ,  $x_{M1}$ ,  $y_{M1}$ ; (2) the following parameters appeared to be strongly correlated ( $R^2 > 0.95$ ) with other  $\nu_i$  variables:  $z_{M2}$ ,  $z_{O2A}$ ,  $z_{O1B}$ ,  $z_{O3B}$ ,  $z_{SiB}$ ,  $y_{O3B}$ , which are correlated to  $z_{M1}$ ;  $z_{O2B}$  which is correlated to  $z_{O1A}$ ;  $y_{M2}$  which is correlated to  $x_{M2}$ ;  $b$  which is correlated to  $a$ . However, if those variables are left out of the multiple regression calculation, the value of the final correlation coefficient  $R^2$  decreases and the value of the residual sum of squares increases. Therefore, all cell parameters and atomic coordinates were introduced in the computation, allowing the stepwise procedure to select the independent variables to be included in the regression model.

The following atomic fractions were considered as dependent variables  $X_j$ :  $X_{Mg}^{M1}$ ,  $X_{Fe^{2+}}^{M1}$ ,  $X_{Mn}^{M1}$ ,  $X_{Fe^{3+}}^{M1}$ ,  $X_{Al}^{M1}$ ,  $X_{Ti}^{M1}$ ,  $X_{Cr}^{M1}$ ,  $X_{Mg}^{M2}$ ,  $X_{Fe^{2+}}^{M2}$ ,  $X_{Mn}^{M2}$ ,  $X_{Ca}^{M2}$ ,  $X_{Al}^{M2}$ . In determining the atomic fractions at M1 and M2 sites, the relevant m.a.n., given by the refinement, were also added as independent variables because they improved the correlation.

The regression coefficients  $c_{ij}$  and the constant terms  $C_j$ , which allow the prediction of the values of the atomic fractions  $X_j$  through Equation 7, are reported in Tables 6 and 7.

## RESULTS AND DISCUSSION

The regression coefficients referring to cell parameters and cation-O mean bond distances have been analyzed in detail. In this way, we can understand the physical implications of these coefficients and improve our knowledge of the trends already described for these minerals (Domeneghetti et al., 1985; Tazzoli and Domeneghetti, 1987; Molin, 1989). Moreover, the reliability of the predictions of structural parameters and cation distributions has been tested by evaluating the agreement between predicted and observed data in samples both included and not included in the regression analysis.

### Cell parameters

The coefficients of Equations 10, 11, and 12 of Tazzoli and Domeneghetti (1987) have been recalculated, and the following solutions have been obtained

$$a = 18.2158 + 0.0985Fe^{2+} + 0.2367Mn - 0.1784^{[4]}Al \quad (8)$$

$$b = 8.8232 + 0.0872Fe^{2+} + 0.2505Fe^{3+} + 1.4614Ti + 0.1040Mn - 0.5052^{[4]}Al \quad (9)$$

$$c = 5.1833 + 0.0311Fe^{2+} + 0.0437Mn + 0.2082Ca \quad (10)$$

which allow the cell parameters to be calculated from the results only of chemical analysis. However, the data referring to the  $a$ ,  $b$ , and  $c$  parameters in Table 1 show that cell dimensions are not only affected by the bulk chemical composition, but also by the  $Fe^{2+}$  distribution between M1 and M2, i.e., by the degree of ordering in the sample. Thus, a more correct evaluation of the cell parameters is expressed by the following equations:

TABLE 6. Regression coefficients and constant terms for the calculation of atomic fractions at M1 site

		$X_{Mg}^{M1}$	$X_{(Fe^{2+} + Mn)}^{M1}$	$X_{Fe^{3+}}^{M1}$	$X_{Al}^{M1}$	$X_{Ti}^{M1}$	$X_{Cr}^{M2}$
C <sub>1</sub>	a	-0.1798(0.0982)	0.0000(0.0000)	0.0000(0.0000)	0.2703(0.1079)	0.0000(0.0000)	0.0000(0.0000)
C <sub>2</sub>	b	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>3</sub>	c	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>4</sub>	X <sub>SiA</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>5</sub>	Y <sub>SiA</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>6</sub>	Z <sub>SiA</sub>	9.4257(2.7429)	0.0000(0.0000)	10.9244(2.1621)	-9.5702(3.0805)	0.0000(0.0000)	0.0000(0.0000)
C <sub>7</sub>	X <sub>SiB</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>8</sub>	Y <sub>SiB</sub>	0.0000(0.0000)	28.4151(8.4264)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	-0.9163(0.3685)
C <sub>9</sub>	Z <sub>SiB</sub>	-15.8692(3.6266)	0.0000(0.0000)	0.0000(0.0000)	11.7183(4.8890)	0.0000(0.0000)	0.0000(0.0000)
C <sub>10</sub>	X <sub>O1A</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>11</sub>	Y <sub>O1A</sub>	9.7878(3.3831)	-11.3997(3.4031)	0.0000(0.0000)	-9.6612(3.6649)	1.4434(0.4739)	0.0000(0.0000)
C <sub>12</sub>	Z <sub>O1A</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>13</sub>	X <sub>O1B</sub>	-22.6748(7.4730)	23.2695(7.0374)	-22.8255(7.2730)	23.1625(8.0805)	0.0000(0.0000)	0.0000(0.0000)
C <sub>14</sub>	Y <sub>O1B</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>15</sub>	Z <sub>O1B</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>16</sub>	X <sub>O2A</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>17</sub>	Y <sub>O2A</sub>	-11.5486(3.1464)	0.0000(0.0000)	0.0000(0.0000)	10.2353(3.4801)	0.0000(0.0000)	0.0000(0.0000)
C <sub>18</sub>	Z <sub>O2A</sub>	0.0000(0.0000)	-4.4099(1.6037)	6.0477(1.7333)	-4.2093(1.7892)	0.0000(0.0000)	0.0000(0.0000)
C <sub>19</sub>	X <sub>O2B</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	-3.0283(1.0679)	0.0000(0.0000)
C <sub>20</sub>	Y <sub>O2B</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>21</sub>	Z <sub>O2B</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>22</sub>	X <sub>O3A</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>23</sub>	Y <sub>O3A</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>24</sub>	Z <sub>O3A</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>25</sub>	X <sub>O3B</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>26</sub>	Y <sub>O3B</sub>	10.6334(3.1934)	0.0000(0.0000)	0.0000(0.0000)	-10.5122(3.3897)	0.0000(0.0000)	0.0000(0.0000)
C <sub>27</sub>	Z <sub>O3B</sub>	-8.0258(1.8145)	6.7048(1.5399)	-4.8291(1.4681)	7.9314(1.9470)	0.0000(0.0000)	0.0000(0.0000)
C <sub>28</sub>	X <sub>M1</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	-8.2540(2.2500)	0.0000(0.0000)
C <sub>29</sub>	Y <sub>M1</sub>	0.0000(0.0000)	21.9870(5.9430)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	1.9146(0.5434)
C <sub>30</sub>	Z <sub>M1</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
C <sub>31</sub>	X <sub>M2</sub>	0.0000(0.0000)	0.0000(0.0000)	-31.8044(9.3616)	35.6660(13.4551)	0.0000(0.0000)	0.0000(0.0000)
C <sub>32</sub>	Y <sub>M2</sub>	-24.2968(3.9990)	23.7751(2.0088)	-40.7916(4.7464)	35.7889(5.5843)	-2.3275(0.2718)	0.0000(0.0000)
C <sub>33</sub>	Z <sub>M2</sub>	-29.2138(3.9211)	17.3456(2.6745)	-25.1895(3.5186)	32.1721(4.5099)	0.0000(0.0000)	0.0000(0.0000)
C <sub>34</sub>	m.a.n. <sub>M1</sub>	-0.0861(0.0014)	0.0836(0.0018)	0.0000(0.0000)	0.0118(0.0027)	0.0000(0.0000)	0.0000(0.0000)
C <sub>35</sub>	m.a.n. <sub>M2</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	-0.0003(0.0000)
C		57.7979(7.4038)	-55.8202(7.0690)	55.8059(7.2569)	-73.7753(9.3383)	5.0516(1.2939)	-0.9368(0.2850)
R <sup>2</sup>		0.9981(0.0082)	0.9980(0.0085)	0.8647(0.0093)	0.9715(0.0086)	0.5715(0.0017)	0.1422(0.0011)

Note: standard deviations are in parentheses.

$$\begin{aligned}
 a = & 18.2318 + 0.1333X_{Fe^{2+}}^{M1} + 0.3451X_{Mn}^{M1} \\
 & + 0.1392X_{Fe^{3+}}^{M1} + 0.0599X_{Fe^{2+}}^{M2} + 0.1685X_{Mn}^{M2} \\
 & + 0.4493X_{Ca}^{M2} - 0.1839X_{[4]Al}^T \quad (11)
 \end{aligned}$$

$$\begin{aligned}
 b = & 8.8148 + 0.1614X_{Fe^{2+}}^{M1} + 0.1963X_{Fe^{3+}}^{M1} \\
 & + 1.4189X_{Ti}^{M1} + 0.6306X_{Cr}^{M1} + 0.1010X_{Fe^{2+}}^{M2} \\
 & + 0.1414X_{Mn}^{M2} - 0.4795X_{[4]Al}^T \quad (12)
 \end{aligned}$$

$$\begin{aligned}
 c = & 5.1816 + 0.0252X_{Fe^{2+}}^{M1} + 0.1511X_{Mn}^{M1} \\
 & + 0.0349X_{Fe^{3+}}^{M2} + 0.0414X_{Mn}^{M2} + 0.1936X_{Ca}^{M2} \quad (13)
 \end{aligned}$$

$$\begin{aligned}
 V = & 832.738 + 26.197X_{Fe^{2+}}^{M1} + 24.458X_{Fe^{3+}}^{M1} \\
 & + 17.670X_{Fe^{2+}}^{M2} + 27.756X_{Mn}^{M2} + 74.134X_{Ca}^{M2} \\
 & - 50.522X_{[4]Al}^T \quad (14)
 \end{aligned}$$

(correlation coefficient  $R^2 = 0.991$ ), which shows the influence of the isomorphous replacements on the cell volume of the orthopyroxene. It is not surprising that in Equations 8–14 the coefficients referring to atomic fractions of octahedral cations smaller than Mg, such as  $Fe^{3+}$ , Cr, and Ti, are positive; these coefficients do not increase the values of the cell parameters with respect to that of enstatite but do increase the values with respect to that of a sample with  $X_{[4]Al}^T = X_{[4]Al}^{M1}$ .

These can be used when X-ray diffraction data are lacking, but chemical analysis and  $Fe^{2+}$  distribution between M1 and M2 sites, e.g., from Mössbauer spectroscopy, are available. It can be noted that the  $b$  parameter, which shows the highest correlation coefficient, is not affected by Ca content, whereas the  $c$  parameter is affected by Ca but not by  $[4]Al$  content.

The coefficients in Table 1 also allows the cell volume to be directly calculated by the equation

#### Interatomic distances

From the data referring to the interatomic distances in Table 1, four inferences may be drawn. (1) In the SiA polyhedron, low values of the regression and correlation coefficients confirm that the mean SiA-O bond distance is not affected by the cation distribution, in particular by the presence of  $[4]Al$ , which is restricted exclusively to the SiB site (Ganguly and Ghose, 1979). (2) In the SiB pol-

TABLE 7. Regression coefficients and constant terms for the calculation of atomic fractions at M2 and SiB sites

		$X_{Mg}^{M2}$	$X_{(Fe^{2+} + Mn)}^{M2}$	$X_{Ca}^{M2}$	$X_{Si}^T$	$X_{[Al]}^T$
$C_1$	$a$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_2$	$b$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_3$	$c$	-0.1631(0.0661)	-0.2172(0.0880)	0.3810(0.1542)	0.0000(0.0000)	0.0000(0.0000)
$C_4$	$x_{SiA}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_5$	$y_{SiA}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_6$	$z_{SiA}$	3.3457(0.6108)	4.4805(0.8137)	-7.8208(1.4250)	0.0000(0.0000)	0.0000(0.0000)
$C_7$	$x_{SiB}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_8$	$y_{SiB}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_9$	$z_{SiB}$	-2.8248(0.3759)	-3.7653(0.5008)	6.5882(0.8770)	-3.9867(1.1176)	3.9867(1.1176)
$C_{10}$	$x_{O1A}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{11}$	$y_{O1A}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{12}$	$z_{O1A}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{13}$	$x_{O1B}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{14}$	$y_{O1B}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{15}$	$z_{O1B}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{16}$	$x_{O2A}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{17}$	$y_{O2A}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{18}$	$z_{O2A}$	-1.5808(0.5811)	-2.1117(0.7742)	3.6946(1.3558)	0.0000(0.0000)	0.0000(0.0000)
$C_{19}$	$x_{O2B}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{20}$	$y_{O2B}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{21}$	$z_{O2B}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{22}$	$x_{O3A}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{23}$	$y_{O3A}$	-2.8068(0.9498)	-3.7211(1.2653)	6.5277(2.2160)	0.0000(0.0000)	0.0000(0.0000)
$C_{24}$	$z_{O3A}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	3.9786(0.6023)	-3.9786(0.6023)
$C_{25}$	$x_{O3B}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{26}$	$y_{O3B}$	-4.0878(0.5920)	-5.4615(0.7887)	9.5351(1.3813)	7.2696(0.7259)	-7.2696(0.7259)
$C_{27}$	$z_{O3B}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{28}$	$x_{M1}$	14.3359(3.7399)	19.1128(4.9823)	-33.4997(8.7256)	0.0000(0.0000)	0.0000(0.0000)
$C_{29}$	$y_{M1}$	-8.9766(1.5529)	-11.9919(2.0688)	20.9549(3.6231)	8.9517(3.1773)	-8.9517(3.1773)
$C_{30}$	$z_{M1}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{31}$	$x_{M2}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	-35.9512(4.7881)	35.9512(4.7881)
$C_{32}$	$y_{M2}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{33}$	$z_{M2}$	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{34}$	m.a.n. <sub>M1</sub>	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
$C_{35}$	m.a.n. <sub>M2</sub>	-0.0657(0.0007)	0.0790(0.0010)	-0.0133(0.0017)	0.0000(0.0000)	0.0000(0.0000)
$C$		6.6914(1.9497)	5.5986(2.5974)	-11.2615(4.5489)	12.1302(1.6974)	-10.1302(1.6974)
$R^2$		0.9998(0.0024)	0.9997(0.0032)	0.8254(0.0056)	0.9927(0.0064)	0.9927(0.0064)

Note: standard deviations are in parentheses.

hedron, the SiB-O mean bond distance, expressed as

$$\begin{aligned} \langle \text{SiB-O} \rangle = & 1.6392 + 0.1254X_{[Al]}^T - 0.0330X_{Fe^{3+}}^{M1} \\ & - 0.3776X_{Ti}^{M1} - 0.1996X_{Cr}^{M1} - 0.0027X_{Fe^{2+}}^{M2} \\ & - 0.0166X_{Mn}^{M2} + 0.0474X_{Ca}^{M2} \end{aligned} \quad (15)$$

(correlation coefficients  $R^2 = 0.988$ ), appears to be strongly correlated not only with the  $[Al]$  content but also with the M1 and M2 site populations. However, the influence of octahedral cations is in practice negligible because of the small value of the coefficient of  $X_{Fe^{3+}}^{M2}$ , and the low concentration of the minor cations in the orthopyroxene. If Equation 15 is simplified to

$$\langle \text{SiB-O} \rangle = 1.6392 + 0.1254X_{[Al]}^T \quad (16)$$

and, assuming  $X_{Si}^T + X_{[Al]}^T = 1$ , rewritten as

$$\langle \text{SiB-O} \rangle = 1.6492X_{Si}^T + 1.7646X_{[Al]}^T \quad (17)$$

it can be noted that the coefficients of the atomic fractions of Si and Al correspond essentially to the sum of their effective ionic radii in tetrahedral coordination with that of O (Shannon, 1976), i.e.,  $(0.26 + 1.38) \text{ \AA} = 1.64 \text{ \AA}$  and  $(0.39 + 1.38) \text{ \AA} = 1.77 \text{ \AA}$ , respectively.

In practice, however, if Equation 16 has to be used for deducing the  $[Al]$  content, it is convenient to recalculate its coefficient and constant term, considering the  $\langle \text{SiB-O} \rangle$  bond distance as a linear function of the variable  $X_{[Al]}^T$  alone. This yields the equation

$$X_{[Al]}^T = 9.4187 \langle \text{SiB-O} \rangle - 15.4230 \quad (18)$$

( $R^2 = 0.982$ ), which updates Equation 6 of Tazzoli and Domeneghetti (1987) and allows the derivation, to a good approximation ( $\pm 0.01$ ), of the fraction of  $[Al]$  without data from chemical analysis. (3) In M1 polyhedron, the data of Table 1 confirm a strong correlation between all cation-O bond distances and the cation distribution in the sample. The M1-O mean bond distance may be expressed as

$$\begin{aligned} \langle \text{M1-O} \rangle = & 2.0783 + 0.0516X_{Fe^{2+}}^{M1} + 0.0761X_{Fe^{3+}}^{M1} \\ & - 0.1442X_{[Al]}^T + 0.3265X_{Ti}^{M1} + 0.0062X_{Fe^{2+}}^{M2} \\ & + 0.0154X_{Mn}^{M2} \end{aligned} \quad (19)$$

with  $R^2 = 0.993$ . We therefore conclude that the M1-O mean bond distance is influenced almost completely by the population of the M1 site itself. The coefficients re-

ferring to  $X_{\text{Fe}^{3+}}^{\text{M1}}$  and  $X_{\text{Ti}}^{\text{M1}}$  are positive for the same reason as discussed for Equation 14. At any rate, in order to understand the physical implications of the empirical coefficients of Equation 19, we have recalculated it in the form

$$\begin{aligned} \langle \text{M1-O} \rangle &= 2.0783X_{\text{Mg}}^{\text{M1}} + (2.0783 + 0.0516)X_{\text{Fe}^{2+}}^{\text{M1}} \\ &+ (2.0783 - 0.1442 + 0.0761)X_{\text{Fe}^{3+}}^{\text{M1}} \\ &+ (2.0783 - 0.1442)X_{\text{Al}}^{\text{M1}} \\ &+ [2.0783 - (2 \times 0.1442) + 0.3265]X_{\text{Ti}}^{\text{M1}} \\ &+ 0.0062X_{\text{Fe}^{2+}}^{\text{M2}} + 0.0154X_{\text{Mn}}^{\text{M2}} \\ &= 2.0783X_{\text{Mg}}^{\text{M1}} + 2.1299X_{\text{Fe}^{2+}}^{\text{M1}} + 2.0102X_{\text{Fe}^{3+}}^{\text{M1}} \\ &+ 1.9341X_{\text{Al}}^{\text{M1}} + 2.1164X_{\text{Ti}}^{\text{M1}} + 0.0062X_{\text{Fe}^{2+}}^{\text{M2}} \\ &+ 0.0154X_{\text{Mn}}^{\text{M2}}. \end{aligned} \quad (20)$$

This can be compared with Equation 5, which can be written as

$$\begin{aligned} \langle \text{M1-O} \rangle_{\text{calc}} &= 2.078X_{\text{Mg}}^{\text{M1}} + 2.129X_{\text{Fe}^{2+}}^{\text{M1}} + 2.030X_{\text{Fe}^{3+}}^{\text{M1}} \\ &+ 1.929X_{\text{Al}}^{\text{M1}} + 1.990X_{\text{Ti}}^{\text{M1}} + 2.010X_{\text{Cr}}^{\text{M1}} \\ &+ 2.173X_{\text{Mn}}^{\text{M1}} + 0.006X_{\text{Fe}^{2+}}^{\text{M2}}. \end{aligned} \quad (21)$$

The comparison tells us four things. (1) The values of the coefficients of Equation 20 are generally close to those of Equation 21 and therefore to the end-members' mean bond distances. (2) The agreement is very high for the coefficients of the atomic fractions of the major components  $\text{Fe}^{2+}$ , Mg, and Al, although there is some discrepancy for minor elements. However, this discrepancy is on the same order of magnitude as the precision of the microprobe analysis of these elements for such concentrations. (3) A slight influence of the M2 site population on the M1-O mean bond distance is confirmed by Equation 20, which exhibits the same coefficient for  $X_{\text{Fe}^{2+}}^{\text{M2}}$  and also provides a correction for  $X_{\text{Mn}}^{\text{M2}}$ . (4) In the M2 polyhedron, the M2-O mean bond distance exhibits a strong correlation with its own site population but is affected by the Fe content of the M1 site (regression coefficient = 0.016) more than the M1-O mean bond distance is affected by the Fe content of M2. This is a consequence of the behavior of the M2-O3A and M2-O3B bond distances, the longest of the polyhedron, which are the most affected by the population of the M1 site (regression coefficients for  $X_{\text{Fe}^{2+}}^{\text{M1}} = 0.073$  and  $0.069$ , respectively). The M2-O mean bond distance is also influenced by the  $\text{Si} = \text{Al}$  substitution in the SiB tetrahedron (regression coefficient =  $-0.092$ ). The shortening of this mean bond distance is due almost entirely to the shortening of the M2-O3B bond distance (regression coefficient =  $-0.844$ ), arising from the substitution of Al in SiB. This corroborates the results of Domeneghetti et al. (1985), Tazzoli and Domeneghetti (1987), and Molin (1989), that the shortening of the mean

M2-O bond distance is primarily due to substitution of Al in the SiB site rather than substitution of smaller trivalent cations in the M2 site.

#### Prediction of the structural parameters and cation distribution

To test the precision of our crystal-chemical model, the predicted values of structural parameters and cation distribution were first compared with the observed values in orthopyroxenes of different composition included in the regression.

In Table 2, the predicted interatomic distances obtained through Equation 8, using the regression coefficients and the constant terms given in Table 1, are compared with the observed values in three samples with different  $\text{Fe}^{2+}$  and  $\text{R}^{3+}$  content (see Table 3) and with the observed values in a synthetic ferrosilite sample. It can be noted that the agreement is very good: in samples S125, 10/68/C, and ferrosilite, the largest discrepancies are within three times the estimated standard deviations given by the structure refinement; few discrepancies larger than three times the estimated standard deviations occur and these only in the Fe-poor sample, AV77. In Table 5, the predicted cell parameters and atomic positions obtained for the same samples through Equation 8, using the regression coefficients and the constant terms given in Tables 1 and 4, are compared with the observed values. The values of the cell parameters agree within the experimental error for all samples. The atomic positions are also reproduced quite accurately for samples S125, 10/68/C, and ferrosilite; for sample AV77 some discrepancies higher than the estimated standard deviations occur, particularly in the atomic coordinate  $z$ .

In general, the comparison between predicted and observed values shows that our structure modeling gives more accurate results for  $\text{Fe}^{2+}$ -rich samples than for  $\text{Fe}^{2+}$ -free and  $\text{Fe}^{2+}$ -poor samples. This can be explained by considering that in the orthopyroxene file used for this study, the  $\text{Fe}^{2+}$ -poor samples are numerically less represented than the  $\text{Fe}^{2+}$ -rich samples. In particular the file does not contain, at present, experimental data for enstatite.

Since the constant terms given in Tables 1 and 4 express directly the predicted values of the cell parameters, interatomic distances, and atomic positions for enstatite, a comparison with the experimental values of a synthetic enstatite sample (Ganguly and Ghose, 1979) was made to test the accuracy of the model. The predicted  $b$  and  $c$  cell parameters, as well as SiA-O, SiB-O, and M1-O bond distances, agree with the experimental data within 0.004 Å. The  $a$  parameter and M2-O bond distances agree within 0.011 Å. Nearly all the predicted atomic positions agree with the experimental values to the third decimal place; the coordinate  $z$  appears to be the most poorly reproduced, with a maximum discrepancy of 0.0014 for  $z$  of the M2 cation.

The accuracy of the model was also tested on two samples not studied in our laboratory and not used in the

**TABLE 8.** Comparison of observed and predicted cell parameters (Å) and atomic positions (Å) in two orthopyroxenes not used in the regression

		OPX Bondoc N.1*			OPX Estherville N.1*		
		<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
	obs.	18.279(2)	8.857(1)	5.199(1)	18.265(2)	8.850(2)	5.201(1)
	calc.1	18.257	8.851	5.197	18.259	8.850	5.198
	Δ	-0.022	-0.006	-0.002	-0.006	0.000	-0.003
		<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
SiA	obs.	0.2716	0.3411	0.0506	0.2716	0.3411	0.0504
	calc.1	0.2715	0.3413	0.0511	0.2715	0.3413	0.0508
	Δ	-0.0001	0.0002	0.0005	-0.0001	0.0002	0.0004
SiB	obs.	0.4738	0.3371	0.7974	0.4739	0.3371	0.7974
	calc.1	0.4737	0.3371	0.7972	0.4738	0.3371	0.7973
	Δ	-0.0001	0.0000	-0.0002	-0.0001	0.0000	-0.0001
O1A	obs.	0.1834	0.3391	0.0388	0.1834	0.3391	0.0388
	calc.1	0.1834	0.3389	0.0390	0.1834	0.3388	0.0389
	Δ	0.0000	-0.0002	0.0002	0.0000	-0.0003	0.0001
O1B	obs.	0.5625	0.3386	0.7990	0.5626	0.3387	0.7994
	calc.1	0.5623	0.3385	0.7995	0.5624	0.3385	0.7996
	Δ	-0.0002	-0.0001	0.0005	-0.0002	-0.0002	0.0002
O2A	obs.	0.3109	0.5016	0.0473	0.3108	0.5016	0.0470
	calc.1	0.3110	0.5018	0.0475	0.3109	0.5019	0.0473
	Δ	0.0001	0.0002	0.0002	0.0001	0.0003	0.0003
O2B	obs.	0.4336	0.4841	0.6932	0.4337	0.4843	0.6932
	calc.1	0.4334	0.4844	0.6930	0.4334	0.4845	0.6931
	Δ	-0.0002	0.0003	-0.0002	-0.0003	0.0002	-0.0001
O3A	obs.	0.3027	0.2265	-0.1718	0.3027	0.2263	-0.1717
	calc.1	0.3028	0.2266	-0.1715	0.3027	0.2267	-0.1718
	Δ	0.0001	0.0001	0.0003	0.0000	0.0004	-0.0001
O3B	obs.	0.4474	0.1986	0.5998	0.4475	0.1984	0.5997
	calc.1	0.4474	0.1978	0.5990	0.4474	0.1979	0.5990
	Δ	0.0000	-0.0008	-0.0008	-0.0001	-0.0005	-0.0007
M1	obs.	0.3756	0.6544	0.8693	0.3754	0.6544	0.8689
	calc.1	0.3756	0.6542	0.8691	0.3756	0.6542	0.8690
	Δ	0.0000	-0.0002	-0.0002	0.0002	-0.0002	0.0001
M2	obs.	0.3778	0.4838	0.3634	0.3778	0.4838	0.3634
	calc.1	0.3774	0.4850	0.3627	0.3774	0.4848	0.3626
	Δ	-0.0004	0.0012	-0.0007	-0.0004	0.0010	-0.0008

Note: obs. refers to experimental values; the estimated standard deviations of the atomic positions are  $\leq 0.00025$ ; calc.1 refers to values directly predicted by means of regression coefficients given by the SPSS program (see Table 4).

\* Ganguly et al. (1994).

regression. These samples, selected because of the very high precision of their structural determinations and chemical analyses, come from Bondoc and Estherville mesosiderites (Ganguly et al., 1994). In Table 8, the predicted cell parameters and atomic positions for these samples are compared with the observed values. The agreement is generally good. Among the cell parameters, the maximum discrepancy ( $\Delta = 0.022$ ) was observed for *a* of sample Bondoc N.1, whereas among the atomic positions the coordinate *y* of the M2 cation appears to be the most poorly reproduced ( $\Delta = 0.0010$  and  $0.0012$ ).

In Table 9 the observed site populations of orthopyroxenes of different composition are compared with those predicted by Equation 7, using the regression coefficients and constant terms given in Tables 6 and 7. As already specified, Bondoc N.1 and Estherville N.1 OPX samples were not used in the regression. Because of the difficulty of distinguishing between  $\text{Fe}^{2+}$  and Mn, we have considered the sum of the atomic fractions of these two cations as a single dependent variable. It is evident from the comparison that, in all the samples included in the regression, the atomic fractions of Mg and  $\text{Fe}^{2+} + \text{Mn}$  at both M1 and M2 sites are predicted within three times the esti-

mated standard deviations given by the structure refinement. In samples not included in the regression, the atomic fractions of Mg in M1 and M2 are predicted very accurately, whereas the predicted atomic fractions of  $\text{Fe}^{2+} + \text{Mn}$  and of  $\text{Fe}^{3+}$  in M1 appear to be slightly overestimated. The atomic fraction of  $^{141}\text{Al}$  at the SiB site is also approximated well in all samples. Minor cations, such as  $^{61}\text{Al}$ ,  $\text{Fe}^{3+}$ , Ti, Cr, and Ca, are generally predicted less accurately, since up to now they remain poorly represented in the orthopyroxene file.

The results obtained by multiple linear regression demonstrate the reliability of this approach and its usefulness in deriving structural parameters from cation distribution and vice versa. In particular, it is now possible to provide expected structural parameters for such fictive orthopyroxene end-members as "orthopyrope," OPY (Ganguly and Ghose, 1979; Lane and Ganguly, 1980)  $\frac{1}{2}(\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12})$ , as well as the corresponding Fe component labeled here as "orthoalmandine," OAL. According to Löwenstein's rule for Si =  $^{141}\text{Al}$  substitution, these components represent limiting aluminous components of orthopyroxene (Ganguly and Ghose, 1979). Table 10 reports the values of some significant structural parameters

TABLE 9. Comparison of observed and predicted site populations in orthopyroxenes of different composition

		OPX AV77 N.1		OPX S 125 N.9		OPX 10/68/C/N		Ferrosilite P14*		OPX Bondoc N.1**		OPX Estherville N.1**	
		Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.
M1	Mg	0.993(2)	0.987	0.740(2)	0.739	0.439(3)	0.442	—	0.003	0.9791(17)	0.980	0.9730(19)	0.971
	Fe <sup>2+</sup> + Mn	0.003(2)	0.006	0.070(2)	0.065	0.560(3)	0.558	1.000	1.002	0.0019	0.010	0.0060	0.019
	Fe <sup>3+</sup>	0.003	-0.001	0.050	0.053	0.001	—	—	-0.006	—	0.005	—	—
	<sup>16</sup> Al	—	0.004	0.135	0.136	—	-0.002	—	—	0.002	0.007	0.003	0.009
	Ti	—	—	0.005	0.005	—	—	—	-0.001	0.001	0.001	0.002	0.002
	Cr	0.001	0.002	—	—	—	—	—	—	0.016	0.001	0.016	0.001
M2	Mg	0.863(2)	0.863	0.253(3)	0.254	0.010(3)	0.012	—	—	0.6495	0.647	0.6491	0.648
	Fe <sup>2+</sup> + Mn	0.134(2)	0.135	0.737(3)	0.739	0.952(3)	0.954	1.000	0.998	0.3295	0.324	0.3249	0.324
	Ca	0.003	0.002	0.010	0.007	0.037	0.034	—	0.003	0.020	0.029	0.026	0.029
	Na	—	—	—	—	—	—	—	—	0.001	—	—	—
T	Si	1.996	1.995	1.805	1.802	1.999	2.000	2.000	2.007	1.9842	1.987	1.9784	1.988
	<sup>14</sup> Al	0.004	0.005	0.195	0.198	0.001	—	—	-0.006	0.0158	0.013	0.0216	0.012

Note: standard deviations of the observed atomic fractions are in parentheses.

\* Domeneghetti and Steffen (1992).

\*\* Samples not used in the regression, Ganguly et al. (1994).

predicted for OPY and OAL compared with the observed values for enstatite and ferrosilite. It can be noted that in OPY the *c* parameter maintains the same value as in enstatite, thus showing that the presence of Al does not cause even the small contraction of *c* assumed by Tazzoli and Domeneghetti (1987); it causes only an appreciable contraction of the *b* parameter and a small change of *a*, as already noted by the same author. The mismatch between tetrahedral layers, enlarged by the presence of <sup>14</sup>Al in SiB, and octahedral layers, contracted by the presence

of <sup>16</sup>Al in M1, can be observed in OPY by the significant increase in the kink of the B chains (decrease in the O3B-O3B-O3B angle), which causes two SiB cations to approach each other within a distance of <3 Å, and by the increase of M1 octahedral distortion (OQE). The values predicted for OAL show that this mismatch, due to the simultaneous presence of Al in the SiB and M1 sites, is only partly relieved by the substitution of Fe<sup>2+</sup> for Mg in the structure. These crystal-chemical considerations are qualitative. Only an energy model, involving lattice-energy and entropy calculations, will give a quantitative description of the way in which isomorphous replacement influences the stability of the orthopyroxene structure. The present results are a basis for such work, which is currently in progress.

TABLE 10. Observed and predicted structural parameters for real and fictive end-members

	Enstatite* Mg <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> obs.	OPY ½(Mg <sub>3</sub> Al <sub>2</sub> - Si <sub>3</sub> O <sub>12</sub> ) pred.	OAL ½(Fe <sub>3</sub> Al <sub>2</sub> - Si <sub>3</sub> O <sub>12</sub> ) pred.	Ferrosilite P14** Fe <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> obs.
<i>a</i> (Å)	18.223(4)	18.140	18.266	18.423(5)
<i>b</i> (Å)	8.819(2)	8.575	8.757	9.077(2)
<i>c</i> (Å)	5.181(1)	5.182	5.229	5.237(2)
(SiA-O)	1.628(1)	1.628	1.625	1.625(1)
TQE (SiA)	1.0098	1.0091	1.0074	1.0074
TAV (SiA) (°)	39.41	37.29	30.36	30.26
O3A-O3A-O3A	158.97	159.05	167.91	168.67
(SiB-O)	1.640(1)	1.704	1.700	1.637(1)
TQE (SiB)	1.0052	1.0061	1.0056	1.0045
TAV (SiB) (°)	19.53	23.50	21.80	17.22
O3B-O3B-O3B	139.06	130.11	133.97	143.70
(M1-O)	2.078(1)	2.006	2.037	2.135(1)
OQE (M1)	1.0089	1.0116	1.0105	1.0090
OAV (M1) (°)	26.84	35.40	33.23	29.21
M2-O3B	2.448(1)	2.027	2.135	2.595(1)
(M2-O)	2.151(1)	2.107	2.170	2.223(1)
OQE (M2)	1.0491	1.0488	1.0633	1.0704
SiB-SiB	3.014	2.991	3.009	3.033

Note: standard deviations are given in parentheses. TQE = tetrahedral quadratic elongation; OQE = octahedral quadratic elongation; TAV = tetrahedral angle variance; OAV = octahedral angle variance. TQE =  $\sum_{i,j} (l_{ij}/l_0)^2/4$  where  $l_0$  is the center to vertex distance for a regular tetrahedron whose volume is equal to that of a real tetrahedron with bond lengths  $l_i$ . TAV =  $\sum_{i,j} (A_{ij} - 109.47)^2/5$  where  $A_{ij}$  are the tetrahedral angles O-T-O. OQE =  $\sum_{i,j} (l_{ij}/l_0)^2/6$  where  $l_0$  is the center to vertex distance for a regular octahedron whose volume is equal to that of a real octahedron with bond lengths  $l_i$ . OAV =  $\sum_{i,j} (A_{ij} - 90)^2/11$  where  $A_{ij}$  are the angles O-M-O (Robinson et al., 1971).

\* Ganguly and Ghose (1979).

\*\* Domeneghetti and Steffen (1992).

## ACKNOWLEDGMENTS

We are grateful to E. Cannillo for his help in the organization and management of the orthopyroxene file. This manuscript has benefited by the informal review of Michael Carpenter and the formal review of Jiba Ganguly. Financial support was provided by the CNR (Centro di Studio per la Cristallografia e la Cristallografia, Pavia; Centro di Studio sui Problemi dell'Orogeno delle Alpi Orientali, Padua).

## REFERENCES CITED

- Anovitz, L.M., Essene, E.J., and Dunham, W.R. (1988) Order-disorder experiments on orthopyroxenes: Implications for the orthopyroxene geospeedometer. *American Mineralogist*, 73, 1060-1073.
- Baerlocher, Ch., Hepp, A., and Meier, W.M. (1977) DLS-76: A program for the simulation of crystal structures by geometric refinement. Institute of Crystallography and Petrography, Eidgenossische Technische Hochschule, Zurich, Switzerland.
- Besancon, J.R. (1981) Rate of cation disordering in orthopyroxenes. *American Mineralogist*, 66, 965-973.
- Domeneghetti, M.C., and Steffen, G. (1992) M1, M2 site populations and distortion parameters in synthetic Mg-Fe orthopyroxenes from Mössbauer spectra and X-ray structure refinements. *Physics and Chemistry of Minerals*, 19, 298-306.
- Domeneghetti, M.C., Molin, G.M., and Tazzoli, V. (1985) Crystal-chemical implications of the Mg<sup>2+</sup>-Fe<sup>2+</sup> distribution in orthopyroxenes. *American Mineralogist*, 69, 987-995.
- Ganguly, J. (1982) Mg-Fe order-disorder in ferromagnesian silicate: II. Thermodynamics, kinetics and geological implications. In *Advances in physical geochemistry*, vol. 2, p. 58-99. Springer-Verlag, New York.

- Ganguly, J., and Ghose, S. (1979) Aluminous orthopyroxene: Order-disorder, thermodynamic properties and petrologic implications. *Contributions to Mineralogy and Petrology*, 69, 375–385.
- Ganguly, J., Yang, H., and Ghose, S. (1994) Thermal history of mesosiderites: Quantitative constraints from compositional zoning and Fe-Mg ordering in orthopyroxenes. *Geochimica et Cosmochimica Acta*, 58, 2711–2723.
- Hawthorne, F.C., and Ito, J. (1978) Refinement of the crystal structures of  $(\text{Mg}_{0.776}\text{Co}_{0.224})\text{SiO}_3$  and  $(\text{Mg}_{0.925}\text{Mn}_{0.075})\text{SiO}_3$ . *Acta Crystallographica*, B34, 891–893.
- Lane, D.L., and Ganguly, J. (1980)  $\text{Al}_2\text{O}_3$  solubility in orthopyroxenes and in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ : A reevaluation and mantle geotherm. *Journal of Geophysical Research*, 85(B12), 6963–6972.
- Molin, G.M. (1989) Crystal-chemical study of cation disordering in Al-rich and Al-poor orthopyroxenes from spinel lherzolite xenoliths. *American Mineralogist*, 74, 593–598.
- Ottonello, G., Della Giusta, A., and Molin, G.M. (1989) Cation ordering in Ni-Mg olivines. *American Mineralogist*, 74, 411–421.
- Ottonello, G., Della Giusta, A., Dal Negro, A., and Baccarin, F. (1992) A structure energy model for  $C2/c$  pyroxenes in the system Na-Mg-Ca-Mn-Fe-Al-Cr-Ti-Si-O: Thermodynamic data, systematic and estimation. In *Advances in physical geochemistry*, vol. 10, p. 194–238. Springer-Verlag, New York.
- Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation, a quantitative measure of distortion in coordination polyhedra. *Science*, 172, 567–570.
- Saxena, S.K., and Ghose, S. (1971)  $\text{Mg}^{2+}$ - $\text{Fe}^{2+}$  order-disorder and the thermodynamics of the orthopyroxene crystalline solution. *American Mineralogist*, 56, 532–559.
- Saxena, S.K., Tazzoli, V., and Domeneghetti, M.C. (1987) Kinetics of  $\text{Fe}^{2+}$ -Mg distribution in aluminous orthopyroxenes. *Physics and Chemistry of Minerals*, 15, 140–147.
- Saxena, S.K., Domeneghetti, M.C., Molin, G.M., and Tazzoli, V. (1989) X-ray diffraction study of  $\text{Fe}^{2+}$ -Mg order-disorder in orthopyroxene: Some kinetic results. *Physics and Chemistry of Minerals*, 16, 421–427.
- Seifert, F. (1983) Mössbauer line broadening in aluminous orthopyroxenes: Evidence for next nearest neighbors interactions and short-range order. *Neues Jahrbuch für Mineralogie Abhandlungen*, 148, 141–162.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Skogby, H., Annersten, H., Domeneghetti, M.C., Molin, G.M., and Tazzoli, V. (1992) Iron distribution in orthopyroxene: A comparison of Mössbauer spectroscopy and X-ray refinement results. *European Journal of Mineralogy*, 4, 441–452.
- Sykes-Nord, J.A., and Molin, G.M. (1993) Mg-Fe order-disorder reaction in Fe-rich orthopyroxene: Structural variations and kinetics. *American Mineralogist*, 78, 921–931.
- Tazzoli, V., and Domeneghetti, M.C. (1987) Crystal-chemistry of natural and heated aluminous orthopyroxenes. *Physics and Chemistry of Minerals*, 15, 131–139.
- Virgo, D., and Hafner, S.S. (1969)  $\text{Fe}^{2+}$ -Mg order-disorder in heated orthopyroxenes. *Mineral Society Special Paper*, 2, 67–81.
- (1970)  $\text{Fe}^{2+}$ -Mg order-disorder in natural orthopyroxenes. *American Mineralogist*, 55, 201–223.

MANUSCRIPT RECEIVED MAY 13, 1994

MANUSCRIPT ACCEPTED NOVEMBER 8, 1994