

## Computer Simulation of the Distribution of Octahedral Cations in Orthopyroxene

JONATHAN W. SNELLENBURG

*Department of Earth and Space Sciences, State University of New York,  
Stony Brook, New York 11790*

### Abstract

A computer method was used to study the effect of minor elements on the ordering of Fe and Mg in the octahedral sites in orthopyroxene. Assuming that Ca and Mn strongly prefer the *M2* sites and that cations order by a scheme of nearest-neighbor site exchanges, the site occupancies observed in natural orthopyroxenes were calculated. The results suggest that much of the increased disorder observed in iron-rich samples may be explained by displacement of Fe by Mn and Ca on the *M2* site. They also indicate that Ca may not hinder ordering in iron-poor samples. Nearest-neighbor exchange is consistent with the lack of complete order usually found in orthopyroxene. The results can be used to explain asymmetry of the distribution coefficient for intracrystalline site exchanges. Increased disorder at elevated temperatures is also modeled.

### Introduction

A complete analysis of order-disorder phenomena must include all aspects of a particular sample's cooling history as well as all constraints imposed by crystal chemistry. This procedure is not practical if complete data are not available. In their absence, an interim approach is to devise an empirical model of the ordering process, as is described here. Computer methods make such models feasible. For example, Krzanowski and Newman (1972) used charge balance as a constraint and calculated the most probable arrangements of octahedral cations in micas. The present technique was developed (Snellenburg, 1972) to treat order-disorder among the octahedral cations in orthopyroxenes. Its aim is to test whether a simple model of the ordering process, in which exchange is limited to nearest cation neighbors, can adequately reproduce the observed distribution of Fe and Mg.

Mössbauer studies of orthopyroxene (Virgo and Hafner, 1969, 1970) indicate that although the distribution of Fe and Mg is temperature dependent, ordering ceases as temperatures fall to approximately 500°C. Complete order is generally not achieved in the process. The distribution also depends on composition. Fe-rich samples exhibit increased disorder relative to an ideal exchange isotherm. Most workers have recognized that Ca and other minor elements should also affect the site occupancies of the major components (see, for example, Blander, 1972). The

extent of their effect is uncertain, but it is possible that  $\text{Ca}^{2+}$ , by displacing  $\text{Fe}^{2+}$  on the *M2* site, can cause the increased disorder just mentioned (Virgo and Hafner, 1970). These features are compared to the results of calculations based on the model presented here.

### Method

The model is an initial approximation to the ordering behavior of orthopyroxene. It is intended to place limits on some of the simplifying assumptions employed in the treatment of ordering phenomena in real crystals. Experimental work must determine the precise mechanism operating in nature. In addition to nearest-neighbor exchange, the model assumes that site preference is governed by ionic radius and that exchange occurs mainly within each octahedral layer. Exchange between layers is, therefore, restricted. A computer program, written in BASIC, performs the calculations. In essence, it places a random array of "cations" on a two-dimensional "lattice" composed of two types of cation sites. An energy difference sufficient to cause ordering between the sites is assumed. The program orders the cations and then determines their site occupancies. The Appendix contains the details of the ordering scheme and subsequent calculations.

To keep the model as simple as possible but still include minor elements, the calculations were restricted

to three species of cations as described below. In view of the limitations of measured site occupancies, the detailed assumptions needed to account for the ordering behavior of every cation did not seem warranted. The Mössbauer technique measures only the distribution of Fe. The site occupancy of the other cations is then calculated from the Fe data. A crystal structure refinement can distinguish between atoms of different scattering power (*e.g.*, Fe and Mg) but cannot resolve similar atoms (*e.g.*, Fe and Mn). Thus, in a refinement, some atoms may be grouped together or fixed on their respective sites while others are varied until the structure converges (see, for example, Takeda, 1972; Burnham *et al.*, 1971, for a description of the techniques).

Site assignments for the model were made on the basis of the size of the ions. Crystal field effects have been cited as the reason for the enrichment of Fe<sup>2+</sup> in the distorted *M2* site (see Burns, 1970, for a discussion). Mn<sup>2+</sup>, whose ionic radius only slightly exceeds that of Fe<sup>2+</sup>, is concentrated more strongly than iron in the *M2* site (Bancroft, Burns, and Howie, 1967). Thus, since Mn<sup>2+</sup> has no additional stabilization energy, the effect of ionic radius must also be important. Fe<sup>2+</sup> is assumed to prefer the *M2* site, but it can occupy either the *M1* or *M2* site. Larger ions, mainly Ca<sup>2+</sup> and Mn<sup>2+</sup>, are assumed to occupy only the larger *M2* site. In the model, ions smaller than Fe<sup>2+</sup> are given no site preference.

The three species used in the calculations are designated *F*, *M*, and *C*. Since the mineral formula would be (*F,M*)(*C,F,M*)Si<sub>2</sub>O<sub>6</sub>, the octahedral cations are grouped as follows:

$$F = (\text{Fe}^{2+})$$

These show strong preference for the *M2* site, but may occupy either site initially.

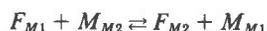
$$M = (\text{Mg}^{2+} + \text{Fe}^{3+} + \text{Ti}^{4+} + \text{Al}^{3+})$$

The *M* cations, with which Mg<sup>2+</sup> is grouped, are small enough to fit in either site.

$$C = (\text{Ca}^{2+} + \text{Mn}^{2+} \text{ and other ions with a radius larger than Fe}^{2+}).$$

The *C* cations are considered to be fixed on the *M2* sites and do not take part in the exchange. Thus, they are intended to measure the effect of blocked sites on the Fe-Mg distribution.

For a given pair of adjacent sites, the exchange reaction is:



for which a simple mass-action expression or distribution coefficient can be written:

$$K_D = \frac{[F_{M2}][M_{M1}]}{[F_{M1}][M_{M2}]} = \frac{[F_{M2}]/[M_{M2}]}{[F_{M1}]/[M_{M1}]}$$

Some measured site occupancies have been determined assuming orthopyroxene is a binary solid solution (*e.g.*, Ghose, 1965; Virgo and Hafner, 1970). Since the present calculations do not always make that assumption, a systematic error results if the binary mole fraction is used in the program. For example, to obtain site populations Mössbauer spectroscopists would multiply their intensity ratio of Fe<sup>2+</sup> between sites by the mole fraction of Fe<sup>2+</sup> defined as:

$$\frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Mg}^{2+}}$$

Because minor elements are present in the octahedral sites of all natural orthopyroxenes, (Fe<sup>2+</sup> + Mg<sup>2+</sup>) does not represent the sum of octahedral cations. Since the model makes provision for these other octahedral cations, the mole fraction of Fe<sup>2+</sup> is more appropriately expressed in this paper as:

$$x_{\text{Fe}^{2+}} = \frac{\text{Fe}^{2+}}{\Sigma \text{ octahedral cations}} = \frac{\text{Fe}^{2+}}{2}$$

for a 6-oxygen formula unit. The difference between the two mole fractions can be seen in Table 1. All comparisons in this paper have been made with the mole fraction based on the sum of octahedral cations.

### Comparison of Calculated and Observed Site Populations

The first set of results to be described assumed the pyroxenes had identical thermal histories and cooled slowly enough to achieve maximum order. Temperature effects will be discussed separately. Table 1 contains data on orthopyroxenes whose site populations have been measured experimentally and for which complete chemical analyses are available. As an initial test of the model, the analyses were recalculated to *F*, *M*, and *C* components, and the site population of each sample was calculated with the model. The observed and calculated site occupancies of these pyroxenes are listed in Table 1. Given the simplicity of the model, the agreement between observation and prediction is very good.

Samples with  $x_{\text{Fe}^{2+}} < 0.5$  generally have less iron in the *M1* site than is predicted. The percent difference between observed and calculated site populations is larger for these pyroxenes than for the Fe-rich samples. These discrepancies are due to the *C* cations and measure the effect of blocked *M2* sites. Figure 1 illustrates this in a better way.

All the observed site populations from Table 1 are plotted in Figure 1. For reference, the dashed line indicates the fraction of Fe<sup>2+</sup> that would be left on the

TABLE 1. Comparison of Calculated and Observed Site Populations

Sample	Method of Analysis	Fe		C	Fraction of Fe <sup>+2</sup> on M1 site		References	
		Fe + Mg	F/2		Observed	Calculated	Analysis	Site Occupancy
HK56051802	W	0.179	0.162	0.077	0.094	0.042	11	11
274-1	P	0.183	0.176	0.064	0.07/.058	0.037	2	1,2
A	P	0.386	0.369	0.032	0.046	0.107	3	1
2	P	0.384	0.375	0.022	0.092	0.113	2	2
SP18	P	0.400	0.382	0.033	0.085	0.114	3	1
HK53051602	W	0.462	0.408	0.115	0.207	0.173	1	1
R96	P	0.430	0.413	0.038	0.123	0.133	3	1
DOM 1	P	0.457	0.431	0.070	0.207	0.163	1	1
CH113	W	0.483	0.440	0.037	0.117	0.155	7	1
277-3	P	0.458	0.441	0.056	.099/0.122*	0.158	2	1,2
HK53051501	W	0.491	0.451	0.066	0.197	0.178	1	1
O4	W	0.475	0.452	0.064	0.135	0.174	6	1
7286	P	0.496	0.477	0.055	0.123	0.185	3	1
4	P	0.503	0.482	0.062	0.15	0.195	2	2
37218	W	0.532	0.500	0.06	0.181	0.203	4	1
HK52110301	W	0.564	0.509	0.077	0.291	0.221	1	1
68671	P	0.531	0.511	0.045	0.154	0.198	3	1
HK56071001	W	0.534	0.516	0.046	0.247	0.207	1	1
68	W	0.577	0.518	0.060	0.247	0.219	5	1
O1	W	0.577	0.544	0.086	0.241	0.249	6	1
R1742	P	0.576	0.545	0.048	0.212	0.229	3	1
4642A	P	0.578	0.545	0.050	0.213	0.233	3	1
264-5	P	0.584	0.554	0.065	0.222/0.226*	0.239	2	1,2
278-6	P	0.623	0.584	0.061	0.273/0.272*	0.261	2	1,2
7725	P	0.652	0.612	0.062	0.290	0.285	3	1
B1-9	P	0.676	0.664	0.032	0.320	0.307	10	10
207-7	P	0.722	0.689	0.069	0.361/0.370*	0.347	2	1,2
V2	P	0.758	0.725	0.086	0.392	0.380	3	1
355	W	0.775	0.727	0.041	0.402	0.353	7	1
XL132	P	0.788	0.756	0.054	0.459	0.386	3	1
XYZ	P	0.877	0.850	0.038	0.447	0.437	9	1
K23	W	0.878	0.855	0.047	0.472	0.445	8	1

References: 1. Virgo and Hafner (1970). 4. Ramberg and DeVore (1951). 8. Kuno (1954).  
2. Saxena and Ghose (1971). 5. Gribble (1968). 9. Virgo and Hafner (1969).  
3. Howie and Smith (1966). 6. Binns (1962). 10. Smyth (1973).  
7. Howie (1963). 11. Takeda (1972).

Definitions: P = electron microprobe; W = wet chemical \* = 500°C data.

M1 site in a completely ordered orthopyroxene with no minor elements present. Since the model is a simplification when applied to individual samples whose cooling histories may be vastly different, two curves, A and B, were calculated for a series of hypothetical compositions to show the general trend of predicted site populations.

Curve A gives the maximum order predicted by the model for a pure Fe-Mg orthopyroxene, that is, it assumes binary solid solution. This curve is the result of several runs of the program, from which the individual configuration yielding the least Fe<sup>2+</sup> on the M1 site was chosen. Very nearly the same minimum site population was obtained in successive sets of five runs. Curve B is drawn through average site populations calculated for a range of iron contents with a C/F ratio of 0.05, since this value is close to those for the majority of the pyroxenes listed in Table 1. The pyroxenes analyzed by Howie and Smith (1966) show a systematic increase of (Ca + Mn) with increasing

Fe<sup>2+</sup> that also corresponds to a C/F ratio of ~0.05. The Fe-Mg distribution indicated by curve B illustrates the effect of blocking the M2 site with large cations. Generally, if  $x_{\text{Fe}^{2+}} < 0.5$ , site populations in the natural orthopyroxenes fall near curve A; if  $x_{\text{Fe}^{2+}} > 0.5$ , curve B is more accurate.

The model indicates that small concentrations of minor elements have not seriously impaired ordering in the iron-poor samples. Sufficient sites are available to the ions that show site preference. If  $x_{\text{Fe}^{2+}} > 0.5$ , and if Ca is present in the M2 sites, increased disorder is expected. Curve B indicates that displacement of Fe<sup>2+</sup> from the M2 sites by large cations can account for much of the disorder seen in samples with small concentrations of minor elements. Samples such as HK53051602, DOM1, and HK53051501 contain significantly larger amounts of Ca and Mn (C/F = 0.141, 0.081, 0.076) and therefore plot above curve B. Their predicted site occupancies, given in Table 1, are above the values indicated by the curve, but less than

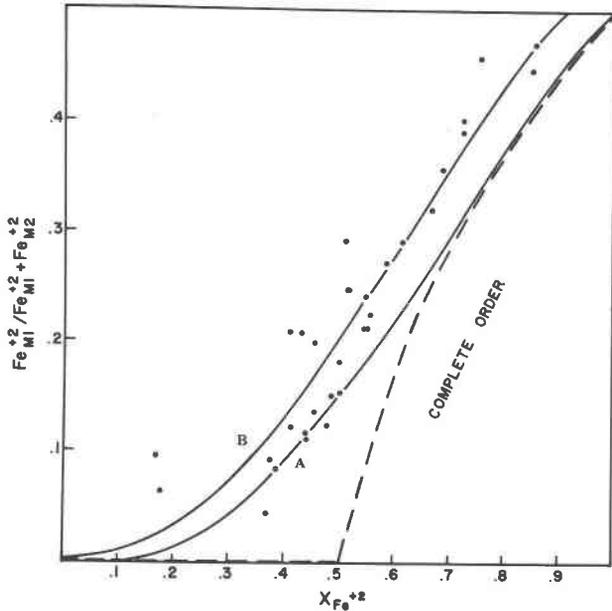


FIG. 1. A comparison of calculated and observed site populations. The points are data from natural orthopyroxenes. The curves are the results of calculations with the model. Curve A:  $C/F = 0$ , curve B:  $C/F = 0.05$ .

the measured values. This indicates, as expected, that at higher concentrations of minor elements (approximately  $C/F > 0.05$ ) simple displacement of  $Fe^{2+}$  does not account for all the observed disorder. Except for one sample mentioned above, samples 274-1 and HK56051802 have the highest concentrations of minor elements ( $C/F = 0.182$  and  $0.194$ , respectively). They also plot above curve B. Unfortunately, because of their composition, they do not provide an adequate test of the calculated curves in this region. Data on pyroxenes with little or no Ca and Mn are needed for this. After temperature effects have been considered, the results of this set of calculations will be discussed further.

### Temperature Effects

Temperature significantly affects site occupancy, but pressure effects are negligible (Virgo and Hafner, 1969). The rapid disordering observed by Virgo and Hafner in heating experiments (1969) is consistent with their data on natural orthopyroxenes (Virgo and Hafner, 1970). In the latter study, only synthetic pyroxenes and some of meteoritic origin show much greater disorder than the samples included in this paper.

Up to this point, it has been assumed in the model that, given the appropriate nearest-neighbor criteria,

the probability of exchanging a pair of cations is unity. The model incorporates the randomizing effect of increasing temperature by successively reducing the probability of exchange. An exchange probability of 1 can be interpreted as a high probability that a cation will reach its preferred site and remain there. Thus, a reduced exchange probability is, in effect, a reduced probability that a cation will remain on the site it prefers.

The data of Saxena and Ghose (1971) on heated orthopyroxenes were compared with the calculated site occupancies. The  $500^{\circ}C$  site occupancies for these samples are included in Table 1. Their data for higher temperatures, excluding sample 274-1, are plotted in Figure 2. The probability of exchange for each of the calculated curves is indicated to the left of each curve. Assuming that the trend of observed site populations in Figure 1 is generally correct, the site occupancies for  $x_{Fe^{2+}}$  between 0 and 0.5 were calculated assuming  $C/F = 0$ . Values for higher iron contents were calculated with  $C/F = 0.05$ . The value for  $x_{Fe^{2+}} = 0.5$  plotted in Figure 2 is an average of the results for the two minor element contents. Although the observed and calculated site occupancies exhibit parallel trends, the data are still too sparse to correlate a temperature with a given probability.

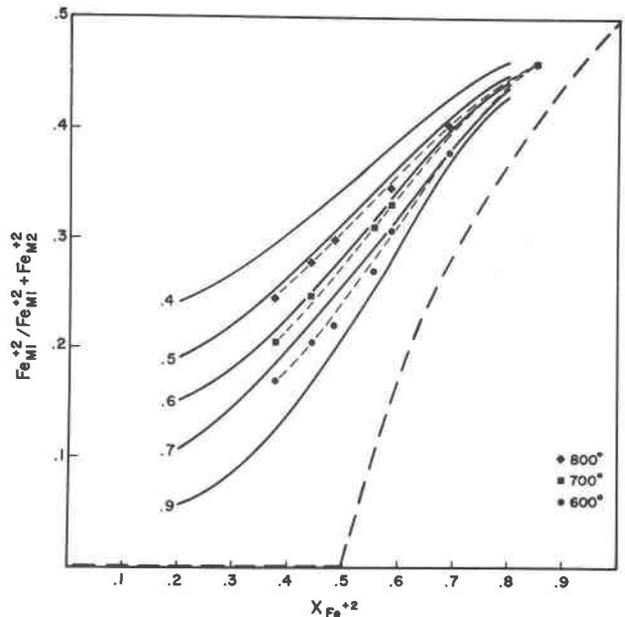


FIG. 2. Plot of site population against  $x_{Fe^{+2}}$  with the probability of exchange reduced. The numbers to the left of the "isotherms" are the probabilities of exchange used in the computer program to simulate elevated temperatures. Dashed line indicates complete order.

### Discussion

To illustrate further the cation distributions expected from nearest-neighbor exchange, the distribution coefficient,  $K_D$ , was calculated using the model site occupancies. Figure 3 is a plot of  $\ln K_D$  against  $x_{Fe^{2+}}$  for  $C/F$  ratios of 0 and 0.05. Average site occupancies were used in both cases. The absolute values of  $\ln K_D$  for intermediate compositions agree with those of Saxena and Ghose (1971); however, the two sets of data diverge at both extremes. In the Mg-rich case, this results from the inclusion of sample 274, which was discussed above. In Fe-rich pyroxenes,  $K_D$  increases because of decreasing Mg on the  $M2$  site. When the model predicts greater order than is observed and the Mg concentration is small, slight changes in site occupancy cause great variation in  $K_D$ . Thus, even a small error in the calculated site occupancy is sufficient to account for the discrepancy between predicted and observed  $K_D$ .

In Figure 3 the model predicts a non-ideal distribution of cations which, in the binary case, would be symmetrical about  $x_{Fe^{2+}} = 0.5$ . Asymmetrical variation of  $\ln K_D$  would result, for example, if natural samples departed from this curve at  $x_{Fe^{2+}} = 0.5$  and began to follow a curve similar to that which includes the minor elements in the calculation.

In summary, the model is consistent with most observations on Fe-Mg ordering in orthopyroxenes. The results suggest that the assumption of only nearest-neighbor exchange is a valid first approximation to intracrystalline cation ordering, but, as stated earlier, it is beyond the scope of the model to pinpoint the specific mechanism which operates in nature. It should be noted, however, that the nearest-neighbor exchange appears to reproduce the incomplete order usually observed in orthopyroxene. Mueller (1969) suggested that an energy barrier exists below 500°C that prevents complete ordering. The calculations are consistent with the suggestion that the barrier may be the activation energy necessary for long-range cation migration. Where the model predicts less order than is observed, it is possible to postulate some degree of long-range cation migration not included in the model. In many cases, the model predicts more order than is observed. This is encouraging because factors which would tend to decrease order were not included in the model. The model assumes implicitly that the cations are distributed randomly over each type of site, *i.e.*, not clustered for size or charge reasons. Also, the degree of site preference may be less than assumed. In this

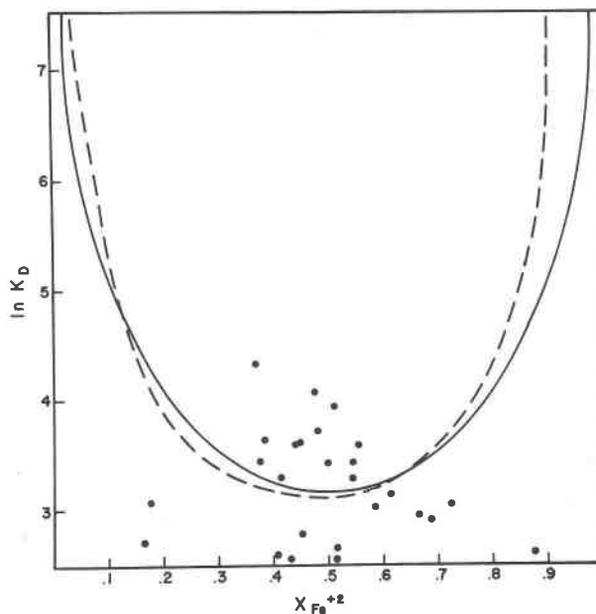


FIG. 3. Plot of  $\ln K_D$  against  $x_{Fe^{2+}}$ . The curves are predicted by the model. Solid:  $C/F = 0$ , dashed:  $C/F = 0.05$ .

case, the initial site assignment or the ordering behavior can be modified with additional data. Finally, events in the cooling history of a specific pyroxene can alter the cation distribution. Consequently, it is possible, by adjusting the probability of  $Fe^{2+}$  exchange and/or the behavior of the minor elements, to duplicate various observed site populations. As more data become available, a model such as this can be used to investigate further the factors which affect the site populations.

It is also encouraging that good results were obtained from only a rough approximation of the structure of orthopyroxene. The array of sites used in the model does not accurately represent their arrangement in the structure. It does, however, maintain the same nearest-neighbor relations. If this approach proves adequate, the more complex site exchange patterns found in other minerals can be treated in a similar fashion.

### Acknowledgments

I wish to thank J. B. Lyons, R. H. Soderberg, and especially W. H. Stockmayer for help and encouragement during the development of the model. C. T. Prewitt and J. J. Papike critically reviewed a preliminary draft of this paper. The quality of the manuscript was greatly improved by discussion with R. T. Dodd and D. H. Lindsley. The model was developed as part of an A. M. Thesis at Dartmouth College. Subsequent work was supported by the Earth Sciences Section, National Science Foundation, NSF Grant AO 21379-001.

## Appendix

### Description of the Model

Recent descriptions of pyroxenes (e.g., Papike *et al.*, 1973) point out that the octahedral sites are essentially sandwiched between successive layers of chains of tetrahedra. It was assumed here that such an arrangement greatly impedes migration of octahedral cations parallel to the *a* axis of the crystal. For this reason, the model employs a two-dimensional lattice, which is topologically equivalent to the arrangement of octahedral sites in the *b-c* plane.

A diagram of the actual arrangement of octahedral sites in orthopyroxene is given in Figure 4-I. The four matrices illustrated are portions of those used in the computer program. The rows of matrix A represent the alternating arrangement of *M* sites. The numerical entries in A are explained in the following description of the model.

In the program, the lattice (matrix A) is set up first. A second matrix, B, consisting of a random array of cations, is then produced by an independent trials process that chooses the cations as if they were being withdrawn one by one from a reservoir containing cations in the same proportion as in the mineral. The reservoir is assumed large enough so that withdrawal of the necessary cations

does not change their relative proportions. The probability of withdrawing a given type of cation is thus equal to its "mole fraction" in the reservoir. The program is designed so that the user determines the composition of the reservoir by specifying values for the mole fractions of  $Fe^{2+}$  and minor elements. The sum of these fractions, if subtracted from 1.0, yields the mole fraction of Mg.

To fill matrix B, a pseudo-random number between 0 and 1 is generated. Then, on the basis of the specified composition, the program assigns either  $Fe^{2+}$ , or a minor element to the entry in B. For example, let  $x_{Fe^{2+}} = 0.5$ . Any pseudo-random number less than or equal to 0.5 designates an  $Fe^{2+}$  ion as the entry in B. A number greater than 0.5 assigns  $Mg^{2+}$  or a minor element depending on their proportions in the reservoir. This operation is repeated until B is filled with cations.

The placing of cations on the lattice is accomplished by adding matrices A and B. The resulting matrix, C, represents the random distribution of cations on the octahedral sites of the disordered crystal. The numerical entries in A and B have been assigned values such that if the cation which favors a site is placed on that site, the corresponding entry in matrix C is zero. A non-zero entry in C indicates an unstable placement. The numbers used in this example were merely convenient for the problem under consideration. In a general case, any integers might be used.

The next step is the ordering of the cations. On the basis of evidence for strong site preference, it seemed reasonable to mimic the ordering process by assuming that an ion will exchange with its nearest neighbor each time appropriate criteria are met. In addition, once on its most favorable site, it remains there during the rest of the calculation.

The assumed pathways for exchange are indicated by the arrows connecting sites in Figure 4-I. This is equivalent to exchanging cations within each row of matrix C. This choice is somewhat arbitrary in that, initially, the most compelling reason for it was ease of calculation. However, it must be realized that the model is designed to be a sample of possible exchanges. This can be seen by comparing Figure 4-I with 4-A. Although nearest-neighbor relations are maintained in matrix A, the actual distance between sites has been ignored. Thus in Figure 4-I to a first approximation, the same sequence of sites is encountered in both *b* and *c* directions. Thus either direction is equivalent in the calculation. In a clinopyroxene, the *M2* coordination polyhedra of adjacent chains share edges, so this assumption of equivalence may not be valid. For the present, the ordering scheme seems adequate because only a small fraction of nearest-neighbors remain unexchanged.

The method used to effect an exchange is illustrated in the following example. Consider two types of ions, *X* and *Y*, and two types of sites, *x* and *y*. The site favored by *X* is *x*, and that favored by *Y* is *y*. There are four possible placements:

*X* on *x* (*Xx*)

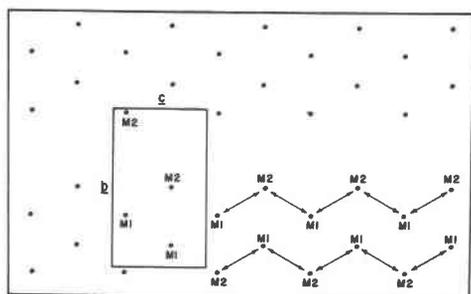
*Y* on *y* (*Yy*)

*X* on *y* (*Xy*)

*Y* on *x* (*Yx*)

The first two are stable and the corresponding entries in matrix C are zero. The last two are unstable and a non-zero entry appears in C. If the *x* and *y* sites alternate in the lattice (as in Fig. 4A) and exchanges are made only within rows, each unstable ion has two possible nearest neighbors. These are:

$Xy - Yx$  or  $Yx - Xy$



I

0	0	1	0	0	1	0	0	1	0	1
0	1	0	0	1	0	0	1	0	0	1
0	0	1	0	0	1	0	0	1	0	1
0	1	0	0	1	0	0	1	0	0	1
0	0	1	0	0	1	0	0	1	0	1
0	1	0	0	1	0	0	1	0	0	1
0	0	1	0	0	1	0	0	1	0	1
0	1	0	0	1	0	0	1	0	0	1

A

-1	0	0	-1	-1	0	0	0	-1	0	-1
-1	0	0	0	-1	-1	0	0	0	0	0
-1	0	0	-1	0	0	0	-1	0	-1	0
-1	0	0	0	-1	0	0	0	-1	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
-1	0	0	-1	-1	0	0	0	-1	0	-1

B

-1	0	0	-1	1	0	1	-1	1	-1	0
-1	0	-1	0	0	1	0	0	0	0	0
-1	1	-1	0	0	-1	1	-1	1	1	1
-1	0	0	0	0	0	0	-1	0	0	1
-1	0	0	0	0	0	0	0	0	0	0
-1	1	1	0	0	-1	0	0	1	0	0
0	0	0	0	0	0	0	0	0	0	0
-1	1	-1	0	0	1	-1	0	0	0	1
-1	1	-1	0	0	1	-1	0	0	0	1

C

-1	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	-1	0	0	0	0	0	0	0	1
-1	0	0	0	0	0	0	0	-1	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	-1	0	0	0	0	0	0	0	1
0	0	0	0	0	0	0	0	0	0	0

C'

FIG. 4. A comparison of orthopyroxene "M" sites with the matrices used to represent them in the computer program. *Explanation:* I: the arrangement of *M* cations in the *b-c* plane; atom positions from Ghose (1965). Arrows indicate assumed exchange pathways. **A:** Matrix A, the "lattice"; 0 = *M2* site, 1 = *M1* site. **B:** Matrix B, a random array of "cations"; 0 =  $Fe^{2+}$ , -1 =  $Mg^{2+}$ . **C:** Matrix C = A + B, cations as initially "placed" on lattice. **C':** Matrix C after ordering.

and

$$Xy - Xx \text{ or } Yx - Yy$$

In order to reach a stable location, an ion must displace another ion. This can happen only when these adjacent ions are of different types. This is the case in the first situation. An exchange will occur, resulting in two zero entries in matrix C. In the second arrangement, a stable ion is placed adjacent to an unstable one. Since the former is fixed and cannot be dislodged, there is no change. Matrix C' results when all possible nearest neighbor exchanges are completed. The program then calculates the total degree of disorder by summing the remaining non-zero entries in matrix C'. The fraction of "Fe<sup>2+</sup>" on "M1 sites" is given by the sum of the non-zero entries in "M1 sites" divided by the total "Fe<sup>2+</sup>" placed in matrix B,

$$\frac{n\text{Fe}^{2+}_{M1}}{n\text{Fe}^{2+}_{M1} + n\text{Fe}^{2+}_{M2}}$$

This fraction may be compared directly to site occupancies determined from Mössbauer spectra, for example.

### Method of Calculation

To obtain the site occupancies given in Table 1, matrices A and B were given the dimension 50 × 50. This size was a compromise between a reasonable computing time and adequate sample size. Larger dimensions greatly increase the time for calculation but do not significantly increase precision. One run of the program performs the ordering 10 successive times and then averages the results. The results for each of the 10 configurations differ slightly. The difference is largest when one of the major components is present in low concentration (e.g.,  $x_{\text{Fe}^{2+}} = 0.1$ ). However, the average site occupancies obtained for all compositions are essentially constant. Any modification to this general procedure is noted in the main part of the paper.

### References

- BANCROFT, G. M., R. G. BURNS, AND R. A. HOWIE (1967) Determination of the cation distribution in the orthopyroxene series by the Mössbauer effect. *Nature*, **213**, 1221-1223.
- BINNS, R. A. (1962) Metamorphic pyroxenes from the Broken Hill district, New South Wales. *Mineral. Mag.* **33**, 320-338.
- BLANDER, M. (1972) Thermodynamic properties of orthopyroxenes and clinopyroxenes based on the ideal two-site model. *Geochim. Cosmochim. Acta*, **36**, 787-799.
- BURNHAM, C. W., Y. OHASHI, S. S. HAFNER, AND D. VIRGO (1971) Cation distribution and atomic thermal vibrations in an iron-rich orthopyroxene. *Am. Mineral.* **56**, 850-876.
- BURNS, R. (1970) *Mineralogical Applications of Crystal Field Theory*. Cambridge University Press, Cambridge.
- GHOSE, S. (1965) Mg<sup>2+</sup>-Fe<sup>2+</sup> order in an orthopyroxene Mg<sub>0.98</sub>Fe<sub>1.07</sub>Si<sub>2</sub>O<sub>6</sub>. *Z. Kristallogr.* **122**, 81-99.
- GRIBBLE, C. D. (1968) The cordierite-bearing rocks of the Haddo House and Arnage Districts, Aberdeenshire. *Contrib. Mineral. Petrol.* **17**, 315-330.
- HOWIE, R. A. (1963) Cell parameters of orthopyroxenes. *Mineral. Soc. Am. Spec. Pap.* **1**, 213-222.
- , AND J. V. SMITH (1966) X-ray emission microanalysis of rock-forming minerals. V. Orthopyroxene. *J. Geol.* **74**, 443-462.
- KRZANOWSKI, W. J., AND A. C. D. NEWMAN (1972) Computer simulation of cation distribution in the octahedral layers of micas. *Mineral. Mag.* **38**, 926-935.
- KUNO, H. (1954) Study of orthopyroxenes from volcanic rocks. *Am. Mineral.* **39**, 30-46.
- MUELLER, R. F. (1969) Kinetics and thermodynamics of intracrystalline cation distributions. *Mineral Soc. Am. Spec. Pap.* **2**, 83-93.
- PAPIKE, J. J., C. T. PREWITT, S. SUENO, AND M. CAMERON (1973) Pyroxenes: comparison of real and ideal structural topologies. *Z. Kristallogr.* **138**, 254-273.
- RAMBERG, H., AND G. DEVORE (1951) The distribution of Fe<sup>2+</sup> and Mg<sup>2+</sup> in coexisting olivines and pyroxenes. *J. Geol.* **59**, 193-210.
- SAXENA, S. K., AND S. GHOSE (1971) Mg<sup>2+</sup>, Fe<sup>2+</sup> order-disorder and the thermodynamics of the orthopyroxene crystalline solution. *Am. Mineral.* **56**, 532-559.
- SMYTH, J. R. (1973) An orthopyroxene structure up to 850°C. *Am. Mineral.* **58**, 636-648.
- SNELLENBURG, J. W. (1972) *A Computer Model of the Cation Distribution in Orthopyroxene*. M. A. Thesis, Dartmouth College, 56p.
- TAKEDA, H. (1972) Crystallographic studies of coexisting aluminian orthopyroxene and augite of high-pressure origin. *J. Geophys. Res.* **77**, 5798-5811.
- VIRGO, D., AND S. S. HAFNER (1969) Fe<sup>2+</sup>-Mg order-disorder in heated orthopyroxenes. *Mineral. Soc. Am. Spec. Pap.* **2**, 67-81.
- , AND ——— (1970) Fe<sup>2+</sup>-Mg order-disorder in natural orthopyroxenes. *Am. Mineral.* **55**, 201-233.

Manuscript received, March 18, 1974; accepted for publication, January 8, 1975.