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Fe^{2+},Mg ORDER-DISORDER IN NATURAL ORTHOPYROXENES

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ABSTRACT

The Fe^{2+},Mg distribution over the $M1$ and $M2$ sites in orthopyroxenes from 30 granulites, 2 rocks from the Stillwater complex and 5 volcanic rocks have been measured. The distribution is described using the disordering parameter p, where

$$p = X_1(1 - X_2)/X_2(1 - X_1)$$

and X_1, X_2 are the atomic fractions $Fe^{2+}/(Fe^{2+}+Mg)$ at $M1$ and $M2$, respectively. The data are interpreted in terms of the previously reported heating experiments on natural crystals in the range 500–1000°C. In the region $0 \leq x \leq \sim 0.6$, where $x = Fe^{2+}/(Fe^{2+}+Mg)$ of the crystal, the Fe^{2+},Mg distribution is close to ideal at each site, and p is equal to the equilibrium constant k. In samples from granulites and plutonic rocks, p is approximately 0.028 and this corresponds to an equilibrium distribution temperature of about 480°C. Volcanic orthopyroxenes generally have a more disordered Fe^{2+},Mg distribution with p values equivalent to temperatures of approximately 500–600°C.

In crystals with $x > 0.6$ there is a significant deviation from ideal distribution ($p \neq k$). In this region the relationships between p, k and T are not known. In comparison with the equilibrated Fe^{2+},Mg distribution in crystals at 1000°C it is apparent that the degree of nonideal mixing at the sites *decreases* with temperature.

The effect of foreign cations at $M1$ and $M2$ on p is unknown but it appears that in orthopyroxenes with *small* concentrations of foreign cations, p is primarily determined by the cooling history of the rock, particularly in the range of 600 to 480°C.

INTRODUCTION

Orthopyroxenes commonly occur in plutonic, volcanic, and high grade metamorphic rocks. Significant differences in their properties such as lattice constants, chemical composition, crystal structure, optical properties, etc. are not well known among the rock groups. However, it can be expected that the Fe^{2+} and Mg site occupancy at the crystallographic positions $M1$ and $M2$ may not always follow equilibrium conditions during petrogenesis and subsequent cooling of the rock. In particular, if the mineral is rapidly cooled after crystallization as in some volcanic rocks, the observed Fe^{2+},Mg distribution over the sites may not correspond to annealed conditions. In this paper, the Fe^{2+} occupancies of orthopyroxenes from 32 plutonic and metamorphic rocks, and from 5 volcanic rocks have been investigated using Mössbauer effect spectroscopy. Due to this low number of samples the results presented here are preliminary. Definite conclusions on the general spread of the Fe^{2+} occupancy in terrestrial orthopyroxenes and on significant differences between the groups cannot yet be made but some additional estimates are possible from experimental studies: The Fe^{2+},Mg distribution in orthopyroxenes can be disordered as well as partially ordered in the laboratory at fairly low temperatures, and it appears that the activation energies for the reactions

$$\mathrm{Mg}(M1) + \mathrm{Fe}(M2) \rightleftharpoons \mathrm{Fe}(M1) + \mathrm{Mg}(M2)$$

are rather low (Hafner and Virgo 1969, Virgo and Hafner 1969). Thus, it is unlikely that Fe^{2+},Mg distributions close to the maximum degree of disorder will be found in natural crystals, even from volcanic rocks, unless the rock was subjected to quite an unusual rate of cooling. Also it is of interest to compare the present data of *intra*crystalline distribution over the M positions with the numerous previous studies of the *inter*crystalline partition of iron and magnesium between orthopyroxene and coexisting clinopyroxene, olivine, amphibole, etc.

Bowen and Schairer (1935) demonstrated that almost complete solid solution exists for the orthopyroxene series at atmospheric pressure except for extremely iron-rich compositions. It is an additional task of the present investigation to contribute to a more complete understanding of the "ideal" or "nonideal" behavior of this solid solution. Solid solutions with site preference phenomena become necessarily *nonideal* because of the reduced entropy of mixing. The preference of Fe^{2+} for $M2$ therefore implies a generally nonideal character of the solid solution. Many inferences about the "ideality" or "nonideality" of natural orthopyroxenes have been suggested from relationships between composition and certain physical variables, in particular lattice constants. Strictly speaking, thermodynamics itself tells nothing about these parameters. However, from the work of Vegard and Dale (1928) on binary solid solutions in cubic systems it is generally accepted that there will be a linear relation between the lattice dimensions and chemical composition for a completely random distribution of cations at the sites, provided the molar volume difference between end-members is small (Vegard's Law).

Ramberg and DeVore (1951) concluded from a study of the Fe^{2+},Mg exchange between orthopyroxene and olivine solid solutions that orthopyroxenes of intermediate composition should have a smaller molal free energy than that which corresponds to the same mole fraction in ideal mixtures. They expected that this greater stability would reflect itself in a contraction of the mole volume. They found a negative deviation from Vegard's law for the a and b cell dimensions in natural specimens, thus suggesting an excess volume of mixing and a positive deviation from linearity for the refractive indices. However, Sahama and Torgeson (1949) were not able to detect a significant heat of mixing in three natural orthopyroxenes and therefore suggested *ideal* solution behavior. Subsequent studies of unit cell dimensions from different types of natural systems (Hess 1952, Kuno 1954, Howie 1963) could not verify a deviation from Vegard's Law, in apparent support of the ideality of the system. Nevertheless, some differences in the cell parameters between volcanic, plutonic and metamorphic samples were recognized which were attributed to different elemental concentrations in the octahedral and tetrahedral sites. Howie (1963) suggested that the negative deviations of the cell dimensions taken as evidence of the nonideal nature of the orthopyroxene series by Ramberg and DeVore (1951) could also be interpreted in terms of variations in the Al content. Matsui *et al.* (1968) recently determined the unit cell dimensions of a suite of *synthetic* orthopyroxenes prepared at 1200°C and 45 kbars. They found negative deviations of the a and b parameters consistent with Ramberg and DeVore (1951) and a positive deviation of c. This results in a rather *small* excess volume of mixing in accord with the known Fe^{2+},Mg ordering over the M positions. Smith *et al.* (1969) correlated the cell dimensions of natural orthopyroxenes, mainly from metamorphic rocks with the chemical composition determined from electron probe analyses. Negative deviations of the a and b constants and positive deviations of c are also in agreement with the data of Ramberg and DeVore (1951) and Matsui *et al.* (1968).

It is important to clearly distinguish between the nonideal behavior based on Vegard's Law and the behavior (ideal or nonideal) of the atomic distribution observed at each nonequivalent M position in the crystal structure. The changes in the lattice dimensions of the solid solution are primarily due to the kind of linkage of the tetrahedral (SiO_4) chains and edge dimensions of the $M1$ and $M2$ octahedra. Linkage and edge dimensions are, of course, affected by the actual Fe^{2+} and Mg occupancy numbers at both M positions. The present determination of precise occupancy numbers will be of value for a more complete interpretation of the lattice dimensions.

Ramberg and DeVore (1951), Mueller (1961), Binns (1962) and Kretz (1961, 1963) used thermodynamic considerations of the Fe,Mg interphase equilibria between orthopyroxene and coexisting clinopyroxene, amphibole or olivine to predict the ideality or nonideality of the $(Fe,Mg)SiO_3$ solid solution. Deviations from ideal behavior were suggested from the observed compositional dependence of the distribution coefficient for the exchange reaction involving Fe and Mg between the coexisting phases. Mueller (1962, 1969) generally considered the effect of *intra*crystalline distribution over the M sites on the *inter*crystalline coefficients. Similar studies were made by Matsui and Banno (1965) and Banno and Matsui (1966). Grover and Orville (1969) among others attempted an interpretation of the distribution coefficient in orthopyroxene-clinopyroxene and orthopyroxene-olivine systems on the simplified basis of *ideal* distribution behavior at each energetically distinct position.

Finally some experimental studies of activity relationships in orthopyroxenes yielded conflicting results with the above data. Nafziger and Muan (1967) found that the orthopyroxene system is ideal within the experimental error at 1250°C but Kitayama and Katsura (1968) stated that there is a positive deviation from ideality at 1204°C.

Mössbauer spectroscopy of ^{57}Fe offers an especially appropriate method to study the ideality of Fe^{2+},Mg mixing at $M1$ and $M2$, since precise site-occupancy numbers of Fe^{2+} can be determined directly from the ^{57}Fe hyperfine splitting at the sites. Previous site occupancy studies revealed that natural orthopyroxenes equilibrated at 1000°C exhibit a small deviation from ideal distribution at $M1$ and $M2$ for compositions $Fe/(Fe+Mg)=x\geq 0.6$ (Virgo and Hafner 1969). The distribution behavior in unheated terrestrial crystals will be shown below.

EXPERIMENTAL

The ^{57}Fe spectrum of orthopyroxene consists of two superimposed quadrupole split doublets which can be assigned to the two crystallographic positions $M1$ and $M2$. A detailed description of the spectrum was presented previously (Evans *et al.* 1967, Virgo and Hafner 1969). Due to the improved separation of the peaks at low temperature, the absorbers were held at liquid nitrogen temperature while the gamma ray source (^{57}Co in Pd) was at room temperature.

The Mössbauer spectrometer (including a 400 channel analyzer), cryostat, sample preparation, density of natural iron per unit area (1.2–6.1 mg Fe/cm^2), gamma ray source, etc. were the same as for the study of Fe^{2+},Mg order-disorder in heated orthopyroxenes (Virgo and Hafner 1969). For additional information the reader is referred to the description given in that work.

The two mirrored 200 channel spectra ("left side" and "right side") were independently interpreted by fitting four Lorentzian absorption lines to the data on the basis of the least squares technique. The average of "left" and "right" was taken as the final result. In each spectrum the four peaks were sufficiently resolved so that use of line width constraints, etc. was not necessary; the final fits were always 13 variable fits (3 for each Lorentzian and one for the off-resonance count rate). The count rates per channel were of the order of $3\text{–}5\times 10^5$, χ^2 varied between 1.0 and 1.3 per channel. The observed resonance effect was generally about 9 percent for each line of the doublets, *e.g.* for the specimen $XYZ(x=Fe^{2+}/(Fe^{2+}+Mg)=0.877$, 6.1 mg Fe/cm^2 natural iron per unit area).

Several details of the orthopyroxene spectrum are still obscure. For instance it is known that the intensity of the high and low velocity peaks of each doublet are *not* symmetric (*cf.* Table 2), and this has been ascribed to a combination of a difference in the anisotropic Debye-Waller tensors at $M1$ and $M2$ and of paramagnetic relaxation effects. Since such effects may slightly affect our simple approach to determine site occupancy numbers, the spectral data are presented in Table 2 in such way that correction factors may be subsequently applied. In any case the effect of such correction factors will be quite small.

RESULTS AND DISCUSSION

Fe^{2+} Occupancy at $M1$ and $M2$. Description and source of natural samples used in this study are presented in Table 1. Reference is also given to the chemical analyses used to calculate the atomic fractions, $Fe^{2+}/(Fe^{2+}$

TABLE 1. DESCRIPTION AND SOURCE OF SAMPLES

Sample	Literature Reference	Rock Type; Locality	Reference of Chemical Analysis
Samples from Metamorphic Rocks			
K-23	Kuno (1954)	Iron-rich hornfels; Wang-chang-tzu, Je-ho-shen, S.W. Manchuria	1
XYZ	Ramberg and DeVore (1951)	Granulite; W. Greenland	2
X1-132	Choubert (1954)	Granulite; Central Gabon	3
355	Howie (1963)	Granulite; Baffin Island	3
H-8	Kranck (1961)	Silicate rock from iron formation; Mt. Reed area, Quebec	2
V2	Howie and Subramanian (1957)	Granulite; Varberg, Sweden	4
276	Butler (1969)	Silicate rock from iron formation; Gagnon area, Quebec	5
207	Butler (1969)	Silicate rock from iron formation; Gagnon area, Quebec	5
B1-9	Kranck (1961)	Silicate rock from iron formation; Mt. Reed area, Quebec	2
7725	Howie (1963)	Silicate rock from iron formation; Eie Hittero, Norway	4
205	Butler (1969)	Silicate rock from iron formation; Gagnon area, Quebec	5
278	Butler (1969)	Silicate rock from iron formation; Gagnon area, Quebec	5
264	Butler (1969)	Silicate rock from iron formation; Gagnon area, Quebec	5
4642A	Howie (1955, 1963)	Granulite; Pallavaram, Madras	4
68	Gribble (1968)	Cordierite xenolith in basic intrusive; Aberdeenshire, NE Scotland	6
O-1	Binns (1962)	Granulite; Broken Hill, Australia	7
R1742 (12700)	Howie (1955)	Granulite; Pallavaram, Madras	4
3209	Lambert (1968) and Heier	Cape Naturaliste area; Australia	2
68671	Howie and Subramanian (1957)	Granulite; Hatton, Ceylon	4
37218	Ramberg and DeVore (1951)	Granulite; W. Greenland	8
7286	Howie (1958)	Granulite; Sudan	4
CH113	Howie and Subramanian (1957)	Granulite; Pallavaram, Madras	4
O-4	Binns (1962)	Granulite; Broken Hill, Australia	7
277	Butler (1969)	Silicate rock from iron formation; Gagnon area, Quebec	5
R96	Howie (1964)	Granulite; South Harris, Scotland	4
37651	Ghose and Hafner (1967)	Granulite; W. Greenland	9
SP18	Howie (1963)	Granulite; Namaqualand, South Africa	4
115/3	Lambert (1968) and Heier	Granulite; Fraser Ranges, Australia	2
A	Howie (1963)	Granulite; South Savannas, British Guiana	4
274	Butler (1969)	Silicate rock from iron formation; Gagnon area, Quebec	5
Samples from Igneous Rocks			
HK52110301	Kuno (pers. comm.)	Dacite; Nagae near Taguti, Sidara district, Central Japan	10
HK56071001	Kuno (pers. comm.)	Dacite; Near Temple of Horai-zi, Sidara district, Central Japan	10
HK53051501	Kuno (pers. comm.)	Dacite (pumice flow deposit); Sin Kamibasi in Kagasima City, S. Kyusyu	10
HK53051602	Kuno (pers. comm.)	Dacite (welded tuff); Kogasima, N.W. of Kagasima City, S. Kyusyu	10
DOM 1	Hess (1952)	Andesite; W. side of Island of Dominica, West Indies	11
N-5	McCallum (1968)	Norite; Stillwater complex, Montana.	2

References of chemical analysis:

1. H. Kuno (1954, Table 1)
2. D. Virgo and S. S. Hafner (1969), Table 1
3. R. A. Howie (1963), Tables 1, 2, 3
4. R. A. Howie and J. V. Smith (1966), Table 6
5. P. R. Butler (1969) Table 4
6. C. D. Gribble (1968), Table 2
7. R A. Binns (1962), Table 1
8. B. J. Evans, S. Ghose and S. S. Hafner (1967), Table 1
9. S. Ghose and S. S. Hafner (1967), Table 2
10. H. Kuno, pers. comm. Table 4
11. H. H. Hess, pers. comm. Table 4

+Mg). The experimental results are shown in Table 2. Some additional remarks about this table are necessary. Column 2 lists the total atomic fractions $Fe^{2+}/(Fe^{2+}+Mg)$ which were determined directly from the chemical analyses. In all cases, preference was given to recent X-ray emission microanalyses. Where these were not available, analyses obtained by wet chemical techniques were used. The remainder of Table 2 includes the parameters determined from the least squares fits of the Mössbauer resonance spectra for each sample. A discussion of the line widths (columns 3, 4, 5 and 6) and the method used to determine the fraction of Fe^{2+} in $M1$ (column 7) was previously given (Virgo and Hafner 1969) but a restatement of our technique is useful. The fractions $T(M1)$ and $T(M2)$ of Fe^{2+} at $M1$ and $M2$ were determined from the area ratios of the two hyperfine doublets. However, since a statistical analysis showed that the line widths of all four peaks are very nearly the same in orthopyroxene spectra, peak height ratios may be taken as area ratios. Therefore, the fractions were obtained from the simple relations

$$T(M1) = [I(A_1) + I(B_1)]/[I(A_1) + I(B_1) + I(A_2) + I(B_2)] \quad (1)$$

$$T(M2) = [I(A_2) + I(B_2)]/[I(A_1) + I(B_1) + I(A_2) + I(B_2)] \quad (2)$$

Here, I is the peak height of the fitted Lorentzian curve, and A and B are respectively the low and high velocity peaks of each doublet. Equations (1, 2) will only be correct if the absorbers are very thin and the recoilless fraction of ^{57}Fe at $M1$ and $M2$ is the same. It should be noted that using I rather than direct area fits is of great advantage since the determination of I by the least squares method is considerably more precise than that of the area. All spectra were fitted without constraints. Constraining the four widths to be equal does *not* affect I. In order to find the occupancy numbers for Fe^{2+} at both sites the distribution numbers (T) must be related to the chemical analysis of the pyroxene. We prefer to determine the site occupancy numbers from the product of T and the total atomic ratio $2Fe^{2+}/(Fe^{2+}+Mg)$ of the chemical analysis (2 distinct M positions). The site occupancy numbers are then in effect the atomic fractions of $Fe^{2+}/(Fe^{2+}+Mg)$ for each site. In this way the orthopyroxene is approximated by a binary solid solution $(Fe,Mg)_2Si_2O_6$, and consequently the intracrystalline distribution can be considered in thermodynamic terms by a simple binary exchange reaction. Ideally, an exchange reaction involving all cations in the M sites should be considered but for reasons discussed below such an equation cannot be established until intrinsic site occupancies are known for all cations.

It is evident from the chemical analysis that a small concentration of other cations will be present at $M1$ and $M2$. The most likely ions are Al^{3+}, Fe^{3+}, Mn^{2+} and Ca^{2+}. In the Mössbauer spectra of some orthopyroxenes the presence of a very small amount of Fe^{3+} was indeed ob-

TABLE 2. EXPERIMENTAL DATA OF NATURAL ORTHOPYROXENES

Sample	Fe/(Fe+Mg)[a]	Number of spectra	Line width[b] (FWHH) mm/sec				Fraction of Fe^{2+} in $M1$[c]	Fe^{2+} Site occupany number	
			(B_1)	(B_2)	(A_2)	(A_1)		$M1$	$M2$
Samples from metamorphic rocks									
K-23	0.879	2	0.30	0.34	0.31	0.31	0.472	0.828	0.928
XYZ	0.877	7	0.28	0.31	0.30	0.28	0.447	0.784	0.970
X1-132	0.788	1	0.28	0.35	0.33	0.28	0.459	0.723	0.860
355	0.766	1	0.28	0.32	0.30	0.28	0.402	0.623	0.928
H-8	0.761	1	0.26	0.31	0.29	0.27	0.412	0.628	0.895
V-2	0.758	1	0.27	0.30	0.31	0.29	0.392	0.594	0.922
276	0.738	1	0.28	0.29	0.28	0.26	0.372	0.549	0.927
207	0.705	1	0.27	0.29	0.29	0.27	0.361	0.509	0.900
B1-9	0.698	3	0.27	0.29	0.29	0.27	0.356	0.498	0.899
7725	0.652	1	0.31	0.32	0.31	0.31	0.290	0.379	0.926
205	0.625	1	0.26	0.30	0.28	0.29	0.290	0.363	0.886
278	0.623	1	0.26	0.29	0.27	0.26	0.273	0.340	0.905
264	0.591	1	0.26	0.28	0.27	0.26	0.222	0.263	0.920
4642A	0.578	1	0.32	0.35	0.35	0.32	0.213	0.246	0.910
68	0.577	1	0.31	0.39	0.34	0.37	0.247	0.285	0.870
O-1	0.577	1	0.27	0.30	0.29	0.27	0.241	0.278	0.876
R1742	0.576	1	0.33	0.36	0.35	0.33	0.212	0.244	0.908
3209	0.574	3	0.28	0.32	0.31	0.30	0.219	0.251	0.897
68671	0.531	1	0.32	0.32	0.30	0.31	0.154	0.164	0.899
37218	0.531	1	0.27	0.33	0.32	0.26	0.181	0.192	0.869
7286	0.496	1	0.28	0.37	0.35	0.38	0.123	0.112	0.869
CH113	0.483	1	0.33	0.36	0.34	0.36	0.117	0.113	0.853
O-4	0.475	1	0.25	0.32	0.30	0.25	0.135	0.128	0.822
277	0.442	1	0.27	0.30	0.28	0.24	0.099	0.088	0.797
R96[d]	0.430	1	0.38	0.38	0.38	0.38	0.123	0.106	0.754
37651	0.406	1	0.30	0.37	0.38	0.32	0.079	0.064	0.747
SP18	0.400	1	0.28	0.35	0.33	0.31	0.085	0.069	0.732
115/3	0.390	1	0.33	0.32	0.32	0.25	0.083	0.065	0.716
A	0.386	1	0.35	0.34	0.32	0.25	0.046	0.036	0.735
274	0.172	1	0.36	0.31	0.29	0.37	0.070	0.022	0.322
Samples from igneous rocks									
HK52110301	0.564	1	0.27	0.31	0.30	0.27	0.291	0.329	0.800
HK56071001	0.534	1	0.31	0.31	0.30	0.31	0.247	0.264	0.805
HK53051501	0.491	1	0.25	0.30	0.28	0.28	0.197	0.193	0.788
HK53051602	0.462	2	0.28	0.32	0.31	0.32	0.207	0.191	0.734
DOM 1	0.457	2	0.30	0.33	0.32	0.34	0.207	0.189	0.725
N-5	0.272	1	0.30	0.33	0.31	0.25	0.068	0.037	0.506
Synthetic samples									
FS 90	0.900	1	0.27	0.29	0.29	0.27	0.469	0.845	0.955
FS 80	0.800	1	0.28	0.31	0.30	0.27	0.426	0.682	0.918
FS 70	0.700	1	0.29	0.31	0.31	0.28	0.379	0.530	0.870

[a] Atomic fractions (see text).

[b] Average of all spectra taken.

[c] The sum of the fractions of Fe^{2+} in $M1$ and $M2$ is equal to one.

[d] This sample was fitted with $\Gamma B_1 = \Gamma B_2 = \Gamma A_2 = \Gamma A_1$.

served, although the amount was always less than one percent of the total Fe^{2+}. Typically a chemical analysis is recalculated on the basis of 6 oxygen atoms and Al is added to Si to give a total of 2.0 for the tetrahedral positions. However, as suggested by Smith *et al.* (1969), if all the substitutions at Si sites were tetravalent and those at octahedral sites were divalent, Al should be equally proportioned between the Si and *M* sites to maintain the charge balance. This assumption is further complicated by the possible preference of trivalent iron for the *M* sites and therefore it is likely that (Al+Fe^{3+}) at the *M* sites equals Al at the Si sites, to achieve charge balance requirements. Manganese is present in low concentrations in most of the samples and in view of its similarity to Fe^{2+}, it will probably partition between the *M* positions. Calcium occurs up to 0.054 cation percent in some volcanic samples (Table 4) although generally less than 0.02 cation percent are present in the remaining samples. By analogy with the Ca-rich monoclinic pyroxenes, Ca is likely to prefer the larger *M*2 position in orthopyroxenes (Warren and Bragg, 1929) and this preference may be maintained at any temperature.

In addition to the uncertainties regarding the partitioning of Al^{3+}, Fe^{3+}, and Mn^{2+}, there is the exsolution problem of a Ca-rich, monoclinic phase. The effect of exsolution on the composition of the orthopyroxene phase will be least for Al since the Al content in both phases will be similar. However, it will result in apparently lower Fe and Mg values and in apparently higher Ca values (actually *higher* Mg values are predicted for extremely iron-rich samples). Of course, this problem is reduced for analyses made with the microprobe since the compositions, at least of coarsely exsolved phases, can be independently determined. Nonetheless, Howie and Smith (1966) found considerable variations in the Ca $K\alpha$ signal even within the orthopyroxene phase and this is probably due to unresolved Ca-rich pyroxene lamellae. Therefore, although the site preference of Ca is perhaps more significant than that of some other elements its absolute concentration in orthopyroxenes is in doubt. This problem can be partially overcome by choosing natural samples with *small* amounts of exsolved phase as determined by optical examination. Cation distribution between sites may be additionally complicated by a tendency for short range ordering between ions of high charge and ions of low charge (Whittaker 1949, Papike and Clark 1968).

In view of the above we believe that the Fe^{2+},Mg site occupancy in orthopyroxenes is best represented on the basis of the simple fraction $Fe^{2+}/(Fe^{2+}+Mg)$ per unit cell until additional information on the site preferences of all elements is available.

Previously published site occupancy data on terrestrial, extra-terrestrial and synthetic pyroxenes are presented in Table 3. In some cases, different methods were used to calculate the Fe^{2+} occupancy numbers (e.g. Bancroft, Burns and Howie 1967, Bancroft and Burns 1967) whereas in other cases (e.g. Dundon and Walter 1967; Marzolf *et al.* 1967) site

Table 3. Previously Published Data on Natural and Synthetic Pyroxenes

Sample	Fe/(Fe+Mg)	Fraction of Fe^{2+} in *M*1[a]	Fe^{2+} site occupancy numbers[b]		Source
			*M*1	*M*2	
Orthopyroxenes from metamorphic rocks					
K-23	0.878	0.51	0.83	0.89	1
355	0.776	0.48	0.66	0.79	1
68671	0.531	0.28	0.25	0.72	1
37218	0.531	0.14	0.15	0.90	2
U.S.N.M. 14147	0.237	0.11	0.05	0.42	3
Pigeonites from igneous rocks					
Hakone	0.446	0.34	0.27	0.47	4
Mull	0.554	0.24	0.27	0.77	5
Orthopyroxenes from meteorites					
A) H-group Chondrites Sharps	0.139	0.29	0.08	0.20	6
B) L-group Chondrites					
Hallingeberg	0.106	0.20	0.04	0.17	6
Barratta	0.167	0.17	0.06	0.28	6
Carraweena	0.199	0.18	0.07	0.33	6
Farmington	0.205	0.48	0.20	0.21	6
C) A-group Chondrites Haraiya	0.611	0.28	0.34	0.88	6
Synthetic orthopyroxenes					
O-Fs_{10}	0.10	0.26[c]	0.05	0.15	3
		0.40[d]	0.08	0.12	
O-Fs_{40}	0.40	0.26[c]	0.21	0.61	3
		0.31[d]	0.25	0.55	
Synthetic clinopyroxenes					
C-Fs_{40}	0.40	0.26[c]	0.21	0.59	3
		0.27[d]	0.22	0.58	
C-Fs_{60}	0.60	0.45[c]	0.54	0.66	3
		0.49[d]	0.59	0.61	

[a,b] See text.

[c] Intensity ratios calculated using areas.

[d] Intensity ratios calculated using peak heights.

Reference List for Sources of Data

1. Bancroft, Burns and Howie (1967)
2. Ghose (1965)
3. Marzolf, Dehn and Salmon (1967)
4. Bancroft and Burns (1967)
5. Morimoto and Guven (1967)
6. Dundon and Walter (1967)

occupancy numbers were not reported. In the latter cases, the occupancy numbers in Table 3 were obtained using the Fe-Mg atomic ratio method.

Orthopyroxenes from metamorphic and plutonic rocks. Site occupancy data for orthopyroxenes from granulite facies rocks from different areas are compared to the data of the previous heating experiments in Figure 1. The overall pattern of the Fe^{2+} occupancy indicates a relatively high degree of order. In the region of $x = Fe^{2+}/(Fe^{2+}+Mg)$ between 0 and ~0.6, the points scatter about a curve of hyperbolic shape in accord with *ideal distribution* assumed at each crystallographic position. An "equilibrium isotherm" with the equilibrium constant,

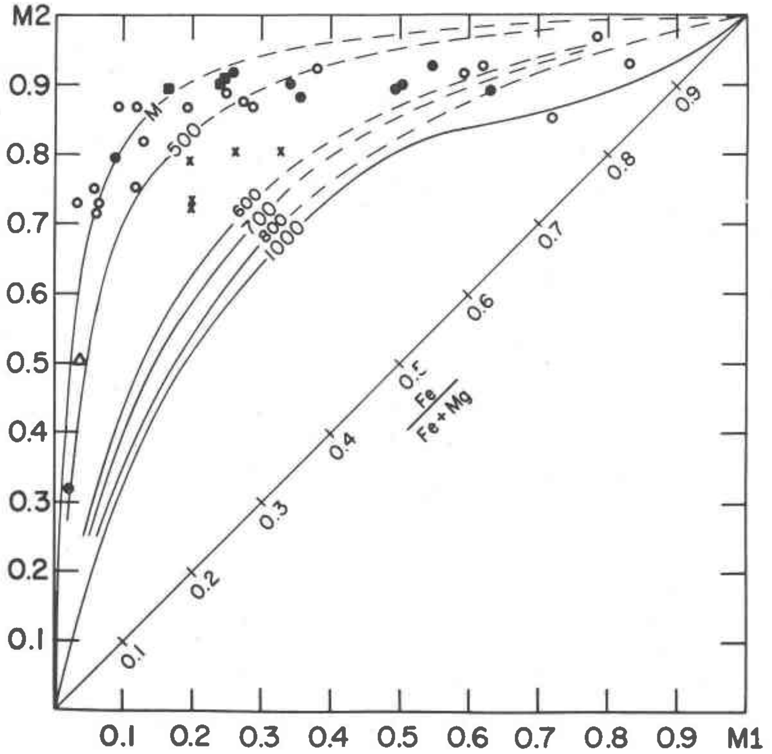

FIG. 1. Plot of Fe^{2+} site occupancy at $M1$ against $M2$ of natural orthopyroxenes. The solid lines refer to experimentally determined equilibrium isotherms at 1000, 800, 700, 600, and 500°C. (cf. Virgo and Hafner 1969, Figures 4 and 5).

● Orthopyroxenes from the metamorphic iron formations in Quebec (Kranck 1961; Butler 1969).

■ Orthopyroxenes from granulites in the Madras and Ceylon areas.

○ Orthopyroxenes from granulites.

× Orthopyroxenes from volcanic rocks.

$$k = X_1(1 - X_2)/X_2(1 - X_1) = 0.028 \qquad (3)$$

has been drawn through the scatter of the points in this region on the basis of the least squares principle (curve "*M*" in Figures 1, 2, and 3). In terms of the results of Virgo and Hafner (1969) this corresponds to an equilibrium Fe^{2+} distribution at approximately 480°C. This temperature is significantly lower than the crystallization temperatures generally assumed for orthopyroxenes in rocks of the granulite facies.

An orthopyroxene from the norite zone of the Stillwater Complex is also plotted in Figure 1. It shows a high degree of order which is within the scatter of the metamorphic samples. A second sample (A-50) from this zone was also analyzed. However, it was quite magnesium rich ($x=0.178$) and no iron at $M1$ could be detected.

It may be surprising that none of the investigated metamorphic orthopyroxenes were found to be more completely ordered than indicated in Figure 1. For example, complete order for specimen 3209 ($x=0.574$) implies a further increase of the Fe^{2+} occupancy at $M2$ from 0.90 to 1.00. Since orthopyroxenes can be *partially* ordered by dry annealing in the laboratory at quite low temperatures (500°C), cation exchange certainly can take place relatively rapidly (Virgo and Hafner 1969). In view of this it is astonishing that cation migration within the crystal is apparently not possible at temperatures less than approximately 480°C. We believe that there is an "energy barrier" close to 480°C which determines a rather sharp beginning of the cationic exchange processes between the *M* sites.

The points of the metamorphic orthopyroxenes in Figure 1 exhibit considerable scattering which is undoubtedly very much larger than the reproducibility of the Mössbauer spectrum (cf. Table 1 in Hafner and Virgo 1969 and Table 3 in Virgo and Hafner 1969). There are several reasons for this. First, the Fe^{2+},Mg exchange between the sites will be affected by the presence of other cations at the *M* positions. The samples used in this study generally contain small concentrations of other *M* cations and this may obviate a much larger scatter than that observed in Figure 1. Second, analytical errors in the atomic fraction $Fe^{2+}/(Fe^{2+}+Mg)$ may exist. This is probably a major error source in our site occupancy determination. A reasonable estimate of the error in $Fe^{2+}/(Fe^{2+}+Mg)$ ratio determined from electron microprobe analyses is 2 percent, which gives a total relative error in the site occupancy numbers of similar magnitude. Third, samples with $0 \leq x \leq 0.6$ previously heated at 1000°C (Virgo and Hafner 1969, Fig. 3) indicate a close approach to equation (3). Moreover, samples from the same geological area, *e.g.* those from the metamorphic iron formations in Quebec, exhibit a rather small scattering (Fig. 1). These data suggest that there may be differences between groups of samples from different areas and this may be related to *different cooling histories* for such areas, especially at temperatures close to the "energy barrier" at 480°C. Additional experimental studies of the "energy barrier" and related studies of orthopyroxenes from different areas would probably lead to further clarification. In this connection, the higher degree of disorder in sample X1-132 seems to be inconsistent with the remaining iron-rich samples and this may be associated with a rather high calcium concentration or an anomalous cooling history.

It is evident from Figure 1 that the Fe^{2+} site occupancy in samples with $x > \sim 0.60$ deviates significantly from the ideal isotherm established for the Mg-rich part of the system. These samples occur in a narrow area which crosses the hyperbolic curves corresponding to temperatures between 500 and 1000°C. Of particular importance are the group of samples from the metamorphic iron formations in Quebec (Kranck 1961, Butler 1969, Figure 2) which were taken from an area of uniform metamorphic grade and include samples from adjacent field locations. In addition the *inter*crystalline exchange of Fe^{2+},Mg between coexisting orthopyroxene and clinopyroxene suggests a close approach to chemical equilibrium (Butler, 1969). This strongly supports a uniform temperature of metamorphism for these samples. These results imply that there is a *deviation* from ideal distribution in Fe-rich orthopyroxenes with x greater than approximately 0.5.

The conclusion of nonideal behavior is in agreement with the data obtained for iron-rich orthopyroxenes heated at 1000°C (Virgo and Hafner, 1969). It was found that in crystals with $x = 0.761$ and 0.877, the equilibrium values for X_1 and X_2 at 1000°C deviate from the ideal distribution curve towards a more disordered distribution, which implies an excess preference of Fe^{2+} for the $M1$ site compared to the more magnesium-rich part of the solid solution. The nature of this deviation is not yet fully explored. In particular, it is uncertain whether it is simply due to small concentrations of calcium at $M2$. From the comparison of the equilibrium distribution curve at 1000°C with the scatter of the unheated metamorphic samples it is concluded that the deviation from ideal distribution must *decrease* with increasing temperature.

Orthopyroxenes from extrusive igneous rocks. The site occupancy numbers for 5 orthopyroxenes from volcanic rocks are also plotted in Figure 1. These samples indicate variable but generally lower degrees of order than the metamorphic orthopyroxenes. However, the inferred temperature corresponding to the degree of disorder is less than 600°C and therefore significantly less than the probable initial crystallization temperatures for orthopyroxenes in these rocks. Geological evidence per-

TABLE 4. CHEMICAL COMPOSITION OF VOLCANIC ORTHOPYROXENES
Oxides (wt. %)

Specimen	SiO_2	Al_2O_3	CaO	MgO	FeO	Fe_2O_3	TiO_2	MnO	Na_2O	K_2O
HK53051602[a]	51.07	1.30	1.31	16.65	24.52	3.28	—	1.48	0.16	0.03
HK53051501[a]	51.00	1.47	0.67	16.29	27.96	1.23	0.10	1.16	—	—
HK52110301[a]	48.95	0.24	0.85	13.28	30.66	3.93	0.75	0.93	0.11	0.03
HK56071001[a]	49.24	0.49	0.17	15.24	31.16	2.03	—	0.90	0.12	—
Dom. 1[b]	51.15	0.72	1.12	17.71	26.55	—	0.45	0.72	—	—

Number of Ions on the Basis of Six Oxygens: Atomic Proportions

	Si	Al^{IV}	Al^{VI}	Ca	Mg	Fe^{2+}	Fe^{3+}	Ti	Mn	Na	K
HK53051602	1.9500	0.0586	0.0086	0.0536	0.9473	0.8149	0.0940	—	0.0479	0.0118	0.0012
HK53051501	1.9677	0.0323	0.0343	0.0275	0.9367	0.9021	0.0356	0.0030	0.0380	—	—
HK52110301	1.9430	0.0114[c]	—	0.0362	0.7854	1.0178	0.1172	0.0224	0.0312	0.0084	0.0014
HK56071001	1.9503	0.0288[c]	—	0.0071	0.8997	1.0327	0.0604	—	0.0299	0.0090	—
Dom. 1	1.9844	0.0156	0.0010	0.0466	1.0239	0.8614	—	0.0131	0.0235	—	—

[a] Standard gravimetric analysis by H. Haramura.
[b] Electron microprobe analysis by C. R. Knowles.
[c] Insufficient Al to make the Si figure equal to 2.

taining to most of these samples is sparse but the crystallization temperature of orthopyroxene from such rocks is probably in excess of 1000°C.

Chemical analyses of the 5 volcanic orthopyroxenes are shown in Table 4. Comparing the chemical compositions with those reported in the literature for the metamorphic samples does not reveal any significant distinction. As mentioned before, the Fe^{2+},Mg distribution is expected to be perturbed by some Ca ions present at *M*2. There appears to be an inverse correlation in that volcanic crystals with smaller amounts of Ca show a slightly higher degree of Fe^{2+},Mg order. However, the number of volcanic samples investigated is too low for a proof of such a correlation and no such relationship could be detected in the metamorphic samples. There is no doubt that the varying degree of order in the volcanic samples must be primarily due to the different cooling rates of the rocks. Such samples may have been cooled in a matter of days, particularly in the case of certain pyroclastic deposits, and consequently, the duration of time at successively lower temperature will be short.

The five orthopyroxenes of volcanic origin were somewhat accidentally collected and they may turn out to be atypical. It is not unlikely that volcanic orthopyroxenes cover a wider range of disorder in Figures 1 and 4, and some may possibly possess Fe^{2+} occupancies corresponding to higher equilibrium temperatures than 600°C. A detailed study of the site occupancy of volcanic orthopyroxenes from geologically well-known areas would certainly be of interest.

Review of Previously Published Site Occupancy Numbers. Virgo and Hafner (1968) published site occupancies measured at 77°K for sample 37218 ($x=0.532$). The present results (Table 2) indicate a slightly more disordered distribution of Fe^{2+},Mg than those previously reported. In the earlier work the fractions of Fe^{2+} at $M1$ and $M2$ were obtained from the ratios of the fitted areas whereas in Table 2 the area ratios were assumed to be equal to the ratios of the peak heights I. The difference between the present and the earlier data reflects the relatively large statistical errors of the widths Γ of the fitted Lorentzian curves. The results in Table 2 are still in good agreement with the site occupancy determined by Ghose (1965) using X-ray diffraction (Table 3, Fig. 2).

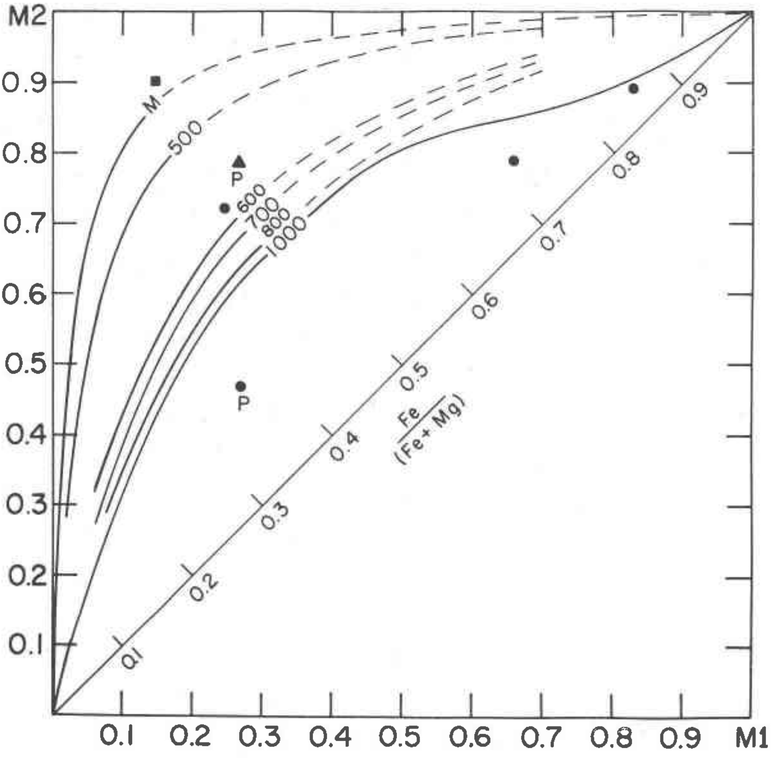

FIG. 2. Plot of previously published Fe^{2+} site occupancy at $M1$ against $M2$ of orthopyroxenes from granulites and pigeonites.

● Orthopyroxenes from granulites (Bancroft, Burns and Howie, 1967)
■ Orthopyroxene 37218 (Ghose, 1965)
▲
P Pigeonite (Morimoto and Güven, 1967)
●
P Pigeonite (Bancroft and Burns, 1967)

Other data in the literature (Table 3, Fig. 2, 3) generally reveal large discrepancies in the site occupancy numbers compared with the present results. Bancroft, Burns and Howie (1967) presented data for 5 orthopyroxenes (in addition, data for a Mn-rich orthopyroxene was given). The spectra were taken at room temperature and resolution of the two doublets corresponding to Fe^{2+} in $M1$ and $M2$ was not possible for the Mg-rich compositions $x=0.29$ and $x=0.46$. Samples 68671, 355 and K23 were also included in the present study so that a direct comparison is possible. The scattering of the data of Bancroft *et al.* is large and the points in Figure 2 are not consistent with the trends of orthopyroxenes from metamorphic rocks observed in this study. However, there is fair agreement for sample K23. This is of course explained by the fact that for very iron-rich pyroxenes some resolution of the two doublets is obtained even when the absorber is held at room temperature.

Marzolf *et al.* (1967) reported the spectrum of a metamorphic orthopyroxene with $x=0.277$ (Table 3, Fig. 3). Their data reinterpreted in terms of site occupancy numbers, indicate slightly higher amounts of Fe^{2+} in $M1$ compared to the metamorphic orthopyroxenes plotted in Figure 1. Since this sample was measured at room temperature, the error of the site occupancy is probably large.

Dundon and Walter (1967) investigated the proportions T of Fe^{2+} at $M1$ and $M2$ in 3 orthopyroxenes from slowly cooled igneous rocks (two samples are from the Stillwater complex, one sample from the Bushveld intrusive), and in the orthopyroxene DOM 1 from an andesite flow. They found that all these samples have completely ordered ferrous ion at least within their limits of detection. Their results (room temperature spectra) for the samples from slowly cooled rocks are in approximate agreement with the samples analyzed by us from the Stillwater complex, but we find a significantly higher degree of disorder in the more quickly cooled sample from the volcanic rock. Dundon and Walter also reported distribution numbers $T\ (M1)$ and $T\ (M2)$ for 25 orthopyroxenes from various meteorites which will be discussed in a later section of this paper.

Some results on the cation distribution in *pigeonites* from volcanic rocks are worthy of mention. Bancroft and Burns (1967) reported the site occupancy numbers for a pigeonite $(FeMgCa)SiO_3$ from an andesite of the Hakone volcano. Their results (Table 3, Fig. 2) suggest a very *high* degree of disorder corresponding to an equilibrium temperature higher than 1000°C but this is inconsistent with the structural refinement of the Mull pigeonite $(FeMgCa)SiO_3$ by Morimoto and Güven (1967, Table 3; Fig. 3). More experimental work will be needed in the systems $FeSiO_3$-$MgSiO_3$ as well as $FeSiO_3$-$MgSiO_3$-$CaSiO_3$ to permit definite conclusions on the Fe^{2+},Mg distribution in pigeonites.

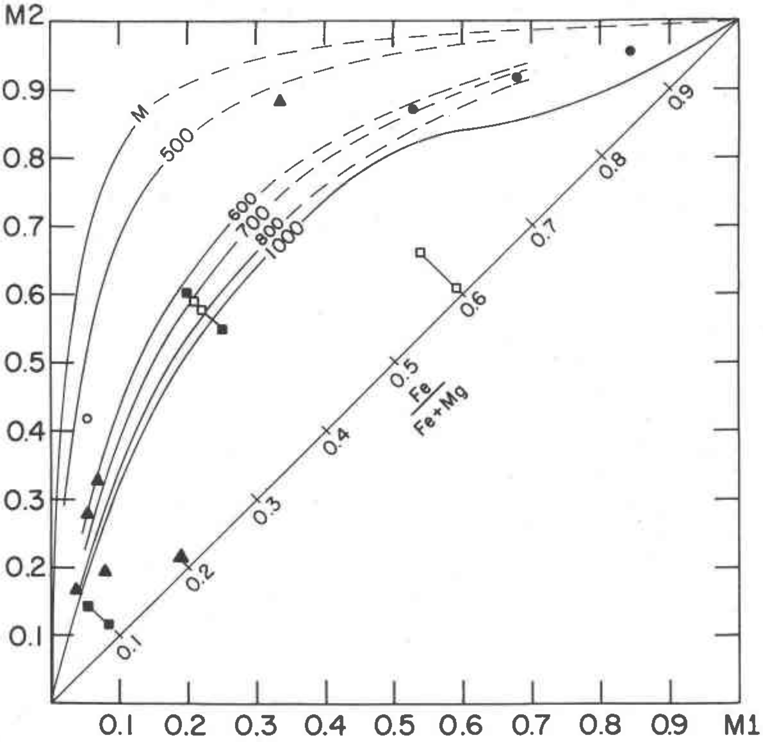

FIG. 3. Plot of previously published Fe^{2+} site occupancy at *M*1 against *M*2 of orthopyroxenes from meteorite samples and natural and synthetic ortho- and clinopyroxenes.

- ▲ Orthopyroxenes from meteorites (Dundon and Walter, 1967; samples which are ordered and those with higher degrees of olivine contamination have been omitted).
- ● Orthopyroxenes synthesized at 1200°C, 45 kbar, 45 minutes (Akimoto, pers. comm.)
- ■ Synthetic orthopyroxenes (Marzolf, *et al.* 1967). Each sample is represented by two symbols designating the use of "areas" and "peak heights" for the site occupancy determination (see text).
- □ Synthetic calcium free clinopyroxenes (Marzolf *et al.* 1967). Each sample is represented by two symbols designating the use of "areas" and "peak heights" for the site occupancy determination (see text).
- ○ Orthopyroxene from a granulite (Marzolf *et al.* 1967).

Synthetic Ortho- and Clinopyroxenes. The site occupancy numbers of three orthopyroxenes with $x=0.7$, 0.8 and 0.9, synthesized at 1200°C, 45 k bars for 45 minutes (Akimoto, pers. comm.), were determined (Table 2, Fig. 3). Also plotted in Figure 3 are two orthopyroxenes with $x=0.1$ and 0.4 which were investigated by Marzolf *et al.* (1967). In the latter case, site occupancies were calculated using both the method of "areas" and "peak heights." Both sets of data are generally inconsistent with the data on heated crystals and in particular Akimoto's samples are characteristic of either disequilibrium or a high degree of ordering of Fe^{2+} and Mg. Marzolf *et al.* also measured the fractions of Fe^{2+} in the M sites for a synthetic orthoferrosilite. They found less than half of Fe^{2+} in $M2$ and suggested that this may be caused by an "oversimplified computer fitting procedure." Their site occupancy values for two synthetic, Ca-free clinopyroxenes with $x=0.4$ and $x=0.6$ are not in agreement with each other and the more iron-rich sample has a significantly higher degree of disorder.

The disordering parameter p in pyroxenes. The parameter

$$p = X_1(1 - X_2)/X_2(1 - X_1) \qquad (4)$$

can be used as a measure of the degree of Fe^{2+} disorder in a pyroxene $M\mathrm{SiO}_3$, and it would be interesting to know more about its general variance in different natural or synthesized systems. X_1 and X_2 in (4) are the respective site occupancy numbers of Fe^{2+} at the positions $M1$ and $M2$ as previously noted. Of course, p can be equivalently defined for any cation M that partitions between $M1$ and $M2$ (e.g. Mg, Mn, Al), but here we are primarily concerned with Fe^{2+}. The p (Fe^{2+}) values for some natural orthopyroxenes ($x<\sim 0.60$) from metamorphic and volcanic rocks are plotted in Figure 4. Also plotted is an ordering experiment carried out as follows: an orthopyroxene ($x=0.574$, $p=0.038$) was disordered at 900°C ($p=0.223$) and then held at 500°C for seven days. The observed degree of disorder after this time was $p=0.170$.

In the binary orthopyroxene system $Fe_xMg_{1-x}SiO_3$ in the range $0\leq x<0.6$, p is nearly identical to the *equilibrium constant k*, since for ideal distribution at $M1$ and $M2$, $p=k$. Therefore, an equilibrium temperature T(°K) can be assigned in this range to each p according to the relation

$$T = - \Delta G_E^{\circ}/R \ln p$$

Here, ΔG_E° is approximately invariant in the range between 500 and 1000°C ($\sim$3.6 kcal per unit cell), and R is the gas constant. In the range $0.6<x\leq 1$ the situation is more complex, and more experiments are needed to establish the relationship between the equilibrium temperature and p. In clinopyroxene systems, the dependence of p on temperature is unknown. Virgo and Hafner (1969) showed that the effect of pressure on p is negligibly small.

Cooling Rates of Orthopyroxenes. Dry heating experiments on natural orthopyroxenes (Virgo and Hafner 1969) revealed that the equilibrium

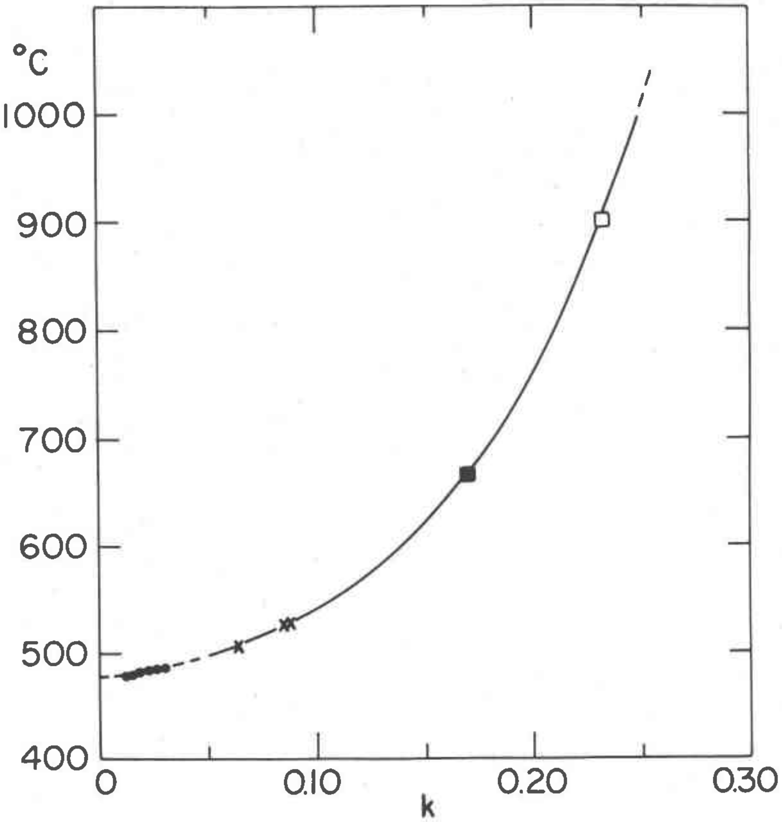

FIG. 4. Plot of temperature (°C) against the distribution coefficient (k) for Mg-rich natural and heated orthopyroxenes. Since only orthopyroxenes with $Fe^{2+}/(Fe^{2+}+Mg)$ $<\sim 0.6$ are plotted, k is equal to the disordering parameter p.

● Orthopyroxenes from granulites.

× Orthopyroxenes from volcanic rocks.

☐ Orthopyroxene 3209 ($Fe/(Fe+Mg)=0.574$) heated at 900°C, 15 hours and then heated at 500°C, 168 hours (■).

distribution of Fe^{2+} and Mg at temperatures close to the crystallization temperature of pyroxene in a magma or in a metamorphic rock is rapidly attained. In disordering experiments, equilibrium at 1000°C was reached after 11 hours and at 500°C after 50 hours. Some preliminary ordering experiments indicated that ordering of Fe^{2+},Mg can occur rapidly at low temperatures. Consequently, it is not expected that disordered distributions are metastably preserved during the cooling history of the rock until fairly low temperatures. This is consistent with the fact that in the region where the distribution isotherms are known ($x \leq 0.6$), no

Fe^{2+},Mg distribution corresponding to a temperature higher than approximately 600°C could be observed in crystals from terrestrial rocks (cf. Fig. 1). Below 600°C a drastic discrepancy between the rates of disordering and ordering appears to occur. While disordering can still be achieved in the laboratory at 500 or 550°C, certain orthopyroxenes from volcanic rocks with Fe^{2+},Mg distributions corresponding to 550–600°C do not exhibit any further Fe^{2+} ordering within geological times. The critical temperature of ~600°C seems to be an upper limit for the usefulness of Fe^{2+},Mg order-disorder as a cooling history indicator. It must be due to the *relatively rapid cooling* at *low temperatures* that some orthopyroxenes from volcanic rocks possess significantly higher quench temperatures than those from intrusive igneous and metamorphic rocks.

Since the rate constant for the Fe^{2+},Mg ordering in orthopyroxene can be experimentally determined, quantitative estimates of the cooling rates of volcanic orthopyroxenes from the observed $M1$, $M2$ site occupancy appear possible, at least in principle, by integration of the rate equation with respect to temperature and time. At present, the empirical rate equation for the ordering process is not sufficiently known, and additional kinetic experiments are necessary. Such a study would certainly be applicable to volcanic pyroxenes rapidly cooled at temperatures below the critical limits of about 600°C and to some "unequilibrated" extraterrestrial pyroxenes. In fact, orthopyroxenes in meteorites with disordered Fe^{2+},Mg distributions were first described by Dundon and Walter (1967).

Dundon and Walter reported distributions $T(M1)$ and $T(M2)$ for 25 orthopyroxenes from "equilibrated" and "unequilibrated" meteorite samples. Orthopyroxenes from "equilibrated" chondrites were found to be generally ordered whereas "unequilibrated" chondrites exhibited a variable degree of disorder. Some site occupancy numbers calculated from their data are given in Table 3 and plotted in Figure 4. The scarcity of data and the uncertainties associated with the evaluation of ^{57}Fe hyperfine splittings measured at room temperature prevent a more detailed discussion of the observed Fe^{2+},Mg distribution in terms of the various models proposed for the origin of chondrites. Dodd (1969) interpreted the higher degree of Fe^{2+},Mg disorder in most of the "unequilibrated" chondrites in support of the hypothesis of initial rapid quenching from a melt and subsequent low-temperature metamorphism. According to the kinetic experiments of Virgo and Hafner (1969) this metamorphism cannot have reached temperatures higher than approximately 480°C. The highly ordered orthopyroxenes from "equilibrated" chondrites, however, suggest slow cooling following metamorphism in the range 600–820°C (Dodd 1969, p. 192). This interpretation is certainly consistent with the recent kinetic studies, although the Fe^{2+},Mg order could be equally well interpreted as a simple product of crystal-liquid equilibrium that was cooled slowly.

It should be noted that generally the analyses of the ^{57}Fe hyperfine spectra of meteoritic pyroxenes is complicated due to the possible contamination of small amounts of olivine or clinopyroxene. The quadrupole split doublet observed in olivine accidentally overlaps with that of $M1$ in orthopyroxene. Moreover, orthopyroxenes of "unequilibrated" chondrites often exhibit variable Fe/Mg ratios. Therefore, "broad line widths" and line shape anomalies may be expected. Dundon and Walter (1967) reported systematically larger line widths compared to the widths of terrestrial pyroxenes (Table 2).

In conclusion the extent of Fe^{2+},Mg migration within plutonic pyroxene structures at different temperatures can be discussed. Estimates of the crystallization temperatures of Ca-poor pyroxenes in rocks from basic intrusives such as the Bushveld, Stillwater and Skaergaard are in the range 1050–1200°C. There are consistencies between the temperatures determined from heating studies of natural rocks, *e.g.* Tilley *et al.* (1963), Brown (1967) and empirical results based on the Fe and Mg exchange between coexisting ortho- and clinopyroxenes (*e.g.* McCallum 1968). Experimental data (Brown 1967) indicated that the coarse exsolution phenomenon involving cation migration over distances of about 50 microns occurs within Ca-poor pyroxenes from these rock types between 1000 and 1050°C. At slightly lower temperatures the monoclinic pyroxene inverts to the orthorhombic structure. Pressure is known to have only a slight effect on these temperatures. However, electron microprobe analyses of host and exsolved phases of orthorhombic and monoclinic pyroxenes (Boyd and Brown 1967, 1968; McCallum 1968) indicated that there is further equilibration of Fe^{2+},Mg between the coarser lamellae and host crystal (migrations over approximately 2 μ distances) as the rock is cooled. McCallum (1968) estimated that the observed annealed state between exsolved and host phases in Stillwater pyroxenes corresponds to temperatures in the range 600–800°C. Finally, results from this study showed that diffusion paths of the order of a few lattice constants are possible down to temperatures of 480°C.

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