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

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ABSTRACT

The Fe^{2+},Mg distribution over the octahedrally coordinated sites $M1$ and $M2$ in orthopyroxenes with compositions close to the system $Fe_xMg_{1-x}SiO_3$ was investigated at different temperatures and pressures in the orthorhombic phase field. Fe^{2+} distribution and site occupancy numbers were obtained from the electric quadrupole splittings of ^{57}Fe at $M1$ and $M2$ determined from nuclear gamma ray resonant absorption spectra taken at liquid nitrogen temperature. The analysis of nine orthopyroxenes equilibrated at 1000°C revealed that in the region $0 \leqslant x < 0.6$ the site occupancy is in agreement with the assumption of ideal Fe^{2+},Mg distribution at each site. The experimental data can therefore be interpreted by simple thermodynamical considerations.

The distribution equilibrium constant was determined for 1000°C, and approximately determined for 800, 700, 600, and 500°C. Fe^{2+},Mg disordering apparently reaches a partially disordered steady state at about 1000°C. No further disorder could be observed in orthopyroxenes by heating at temperatures higher than 1000°C. At about 480°C, ordering is quenched, and no further ordering appears to occur at lower temperatures, even within geological times. Between 500 and 1000°C the standard free energy difference ΔG°_E for Fe^{2+},Mg exchange between $M1$ and $M2$ is apparently constant: 3.6 kcal per mole (formula unit $(Fe,Mg)Si_2O_6$).

From kinetic experiments with an orthopyroxene $x = 0.574$, the rate constants for disordering at 500°C and at 1000°C were estimated. The average activation energy for disordering is about 20 kcal per mole and that for ordering about 15–16 kcal per mole.

In the region $0.7 < x \leqslant 1$, the Fe^{2+},Mg-equilibrium distribution isotherm at 1000°C exhibits a deviation from ideal solution. No effect of pressure on the distribution could be detected.

It is concluded that the Fe^{2+},Mg exchange between the octahedral sites in orthopyroxenes is a rapid process characterized by small energy barriers. In fact, the activation energies for ordering and disordering are considerably lower than those for Al,Si exchange between tetrahedral sites in feldspars. Consequently, orthopyroxenes in metamorphic rocks are generally expected to exhibit equilibrated distributions. Rapidly cooled orthopyroxenes in volcanic rocks, however, may have metastable distributions, the critical range for the cooling rate being between 600 and 500°C.

INTRODUCTION

It has been shown by X-ray diffraction that cations like calcium, iron, magnesium, manganese, and others exhibit various degrees of differential preference among the nonequivalent octahedrally coordinated sites in silicate structures. However, due to the considerable freedom for numerous possible distributions, particularly if more than two cations are present, accurate site occupancies are difficult to obtain for each atom, and the energies involved for atomic exchange among the sites are still largely unknown. In this study we have collected data on the distribution of *ferrous ions* in *orthopyroxenes* from ^{57}Fe hyperfine spectra measured by use of nuclear gamma ray resonance spectroscopy (Mössbauer effect) for several reasons.

Orthopyroxenes are minerals with compositions close to the system $Fe_xMg_{1-x}SiO_3$ with unusually simple silicate structures. The fact that only two nonequivalent octahedral positions are present reduces the problem to the simplest case of atomic distribution. The quadrupole split hyperfine doublets due to ferrous ions at different sites are well separated so that site occupancy numbers can be precisely determined. Moreover, since natural orthopyroxenes often present quasi-binary systems along the $FeSiO_3$-$MgSiO_3$ join, with only small dilution of foreign cations, such data might be used for simple thermodynamical considerations and testing of distribution models as applied to silicates. Numerous previous studies based on measurements of the optical properties and lattice dimensions (Ramberg and DeVore 1951, Hess 1952, Howie 1963, Smith *et al.* 1969), on heats of mixing (Sahama and Torgeson 1949), on measurements of the *intercrystalline* cation distribution between orthopyroxene and coexisting olivine and clinopyroxene phases (Ramberg and DeVore 1951, Mueller 1961, Kretz 1961), and on similar experimental studies (Nafziger and Muan 1967) have already provided valuable, although indirect evidence regarding *intracrystalline* Fe^{2+},Mg distribution in orthopyroxenes.

Evans, Ghose, and Hafner (1967) showed that ferrous iron-magnesium distribution over the octahedral sites in orthopyroxenes is dependent on the temperature. Crystals from volcanic rocks may have a more disordered distribution than from granulite type metamorphic rocks (Ghose and Hafner 1967). Thus, kinetic studies of the disordering and ordering reactions at various temperatures can provide information on the rate of approach to equilibrium states. Such information is mandatory for discussing the thermal history of natural orthopyroxenes. To accomplish this it may be necessary to extrapolate incomplete equilibration data to the true equilibrium states. For example, the predicted slow rate of ordering in orthopyroxenes may prohibit measurements of the equilibrium states at low temperatures. In order to do this the appropriate rate equation will have to be established. Furthermore, from the temperature dependence of the rate constants it is possible to determine the activation energies involved in the diffusion processes leading to ordering and disordering of cations.

These data will lead to a greater understanding of the bonding energies of the cations at the sites.

The most extensive studies of order-disorder relationships have been made in metal alloy systems. However, important differences can be expected for the order-disorder relationship in orthopyroxenes, and some indications of a preferred thermodynamic model to be applied to silicate systems can be suggested. The basic principle involved in the Bragg and Williams (1934, 1935) treatment of order-disorder in metal alloy systems is that the energy necessary for cation exchange between sites depends on the degree of order and *vice versa.* In the ordered phase there is a well-defined exchange energy between the sites and this decreases as disorder increases. At complete disorder the average energy for exchange is zero; the metal sites become statistically identical or equivalent. In terms of the crystal structure, *all* the atoms are involved in the order-disorder relationship and the magnitude of the exchange energy arises from the similarity or dissimilarity of the nearest neighbors. Such systems are referred to as exhibiting cooperative phenomenon. As previously pointed out by Mueller (1962, 1967) the Bragg and Williams' treatment loses much of its meaning when the order-disorder relationships in chain silicates are considered. In this case it seems likely that the energetics of the different sites remain relatively unchanged with large changes of site occupancy. Therefore, an approximately constant exchange energy exists between the different sites over a large temperature range. Under these conditions it seems unlikely that complete disorder could be achieved in silicates such as the orthopyroxenes. As shown by Mueller (1962, 1967), Matsui and Banno (1965), and Grover and Orville (1969) it is convenient to represent the order-disorder relationships by a sliding exchange reaction associated with an approximately constant exchange energy. Consequently, it is simple to set up a rate equation for the time rate of exchange of a cation on a given site and in this way the conditions for equilibrium and for isothermal ordering and disordering can be deduced. The simple treatment used by Mueller (1967) is an extension of a similar approach proposed by Dienes (1955) for alloys. More general theories have been presented (*e.g.* Thompson, 1967) but at present there are insufficient data to warrant models which include many parameters.

Crystal Structure of Orthopyroxenes

The crystal structure of an orthopyroxene (x=Fe/(Fe+Mg)=0.30) was originally determined by Warren and Modell (1930). The structure consists of single silicate chains parallel to the c-axis which are held together by the Mg,Fe^{2+} cations octahedrally bonded to the oxygens of the chains. The octahedra form layers parallel to (100). Recent structural refinements of a natural orthopyroxene with $2x$=0.93 (Ghose 1965) and of a synthetic orthoferrosilite (x=1) (Burnham 1966) yielded accurate interatomic distances and bond angles. The $M1$ octahedron is nearly regular, but the $M2$ octahedron is considerably distorted; it is compressed along its pseudotrigonal axis and elongated along crystallographic b. It is this differential distortion of $M1$ and $M2$ octahedra that causes the distinct quadrupole splittings of the gamma ray resonance spectra.

There are small changes in the size and shape of the octahedra across the $MgSiO_3$-$FeSiO_3$ solid solution series. The average metal-oxygen distances $M1$-O and $M2$-O appear to increase towards $x=1$. More importantly, the two shortest distances of the $M2$ polyhedron are considerably shorter in orthoferrosilite than in hypersthene (2.042 and 2.013 Å compared with 2.066 and 2.037 Å). The two largest distances, however, are significantly larger (2.617 and 2.456 Å compared with 2.519 and 2.405 Å). The trends of the $M1$-oxygen distances are just opposite, although less pronounced. Thus, the $M2$ polyhedron becomes more distorted with increasing Fe/(Fe+Mg) ratio while $M1$ becomes slightly more regular. This is reflected in an increased separation of the peaks in the ^{57}Fe hyperfine spectrum due to the increased distinction of the quadrupole splittings at $M1$ and $M2$ with increasing ratio Fe/(Fe+Mg). It is apparent that these changes in interatomic distances correspond to relatively large energy changes at the sites and are therefore important in interpreting intracrystalline cation distributions on the basis of crystal structure.

It seems to be a general rule that Fe^{2+} in silicates prefers the more distorted octahedral sites. Morimoto, Appleman and Evans (1960) found in their structural investigation of a clinopyroxene that Fe^{2+} was predominantly at the $M2$ sites. The hypersthene structure ($2x$=0.93) determined by Ghose (1965) yielded the following distribution over the sites

$$M1:\ 0.15\ \mathrm{Fe} + 0.85\ \mathrm{Mg}$$
$$M2:\ 0.10\ \mathrm{Mg} + 0.90\ \mathrm{Fe}$$

An exception to this rule are the olivines. Birle, Gibbs, Moore, and Smith (1968) did not observe any preference of Fe^{2+} for $M2$ in spite of the fact that $M2$ is more distorted than $M1$ in this system.

Ghose (1965) also speculated that the $M1$ and $M2$ site occupancies in hypersthene might depend on the temperature. This was subsequently confirmed by the analysis of the ^{57}Fe hyperfine spectrum of heated hypersthenes (Evans, Ghose, and Hafner 1967, Ghose and Hafner 1967).

Experimental Techniques

Starting materials. Separation of orthopyroxene from sieved fractions (90–120 mesh) of crushed rock was made using magnetic techniques. The samples were finally handpicked to a purity greater than 99 percent.

Heating experiments. Heating experiments were initially carried out at 1000°C on a series of natural orthopyroxenes with x = 0.88, 0.76, 0.70, 0.63, 0.57, 0.53, 0.41, 0.39, 0.27 and 0.18. Samples with $x = 0.88$, 0.76 and 0.70 were heated under high pressure to prevent either decomposition to $(Mg,Fe)_2SiO_4$ and SiO_2 ($x = 0.88$) or a phase transition to a monoclinic pyroxene ($x = 0.76$ and 0.70), at atmospheric pressure. An initially high temperature was chosen in view of anticipated slow disordering rates at lower temperatures. The phase relationships determined from these heating experiments are in general agreement with the orthorhombic-monoclinic phase transition determined by Bowen and Schairer (1935), although our data show that the position and temperature dependence of the phase boundary is somewhat different. In addition, experiments were carried out in the range 500–1250°C and at atmospheric pressure on two samples with $x = 0.57$ and 0.41. At lower temperatures, no evidence was found for monoclinic pyroxenes suggested from the phase relationships determined by Boyd and England (1965) on $MgSiO_3$ and by Lindsley (1965) on $FeSiO_3$.

Heating of natural samples at atmospheric pressure. In runs where the sample was examined after different periods of heating, approximately 300 mg of granular orthopyroxene were sealed in a quartz tube previously evacuated to a pressure smaller than 5×10^{-4} mm Hg. In some cases smaller amounts of material were used (~100 mg).

The heating experiments were made in two different horizontal furnaces, operated at atmospheric pressure. For runs at temperatures lower than 900°C, a Kanthal wound furnace was used and the temperatures were recorded using chromel-alumel thermocouples. At higher temperatures, a platinum wound furnace and platinum-platinum-rhodium thermocouples were used. In both cases the temperatures were continuously recorded on potentiometers and the temperatures were controlled by proportional-type regulators.

The quartz tube was placed in a well (~2 cm in length) in a fired pyrophyllite cylinder (~3 cm in diameter and ~5 cm in length) and the cylinder was adjusted to the same position in the furnace in all runs by means of an attached stainless steel rod. The measuring thermocouple was placed in a similar well in the pyrophyllite cylinder, approximately 1 cm distant from the center of the quartz tube. The temperature gradient within each well was smaller than 5°C, and the temperatures in both wells were the same. Temperatures listed in Table 2 are considered correct to ±5°C.

At the commencement of a typical run a quartz tube was inserted into the "pyrophyllite" cylinder and this was then retracted from the front of the furnace to a predetermined position in the furnace. Both ends of the furnace were sealed. Subsequently the measuring thermocouple was inserted into its appropriate place in the pyrophyllite cylinder. The furnace had been previously equilibrated at the required temperature of the run. However, since the furnace had been opened to the atmosphere for a short time there was always an initial period of time (about 10 minutes) before the desired operating temperature was again obtained. After a given time, the run was terminated in less than a minute by quenching in water or liquid nitrogen. These different quenching techniques did not result in significantly different cation distributions.

The sample was then removed from the quartz tube and the necessary amount was crushed for optical, X-ray examination and Mössbauer resonance experiments, provided there was no evidence of oxidation. The remainder of the sample was sealed in a second tube and the sample was reheated at the same temperature for an additional period of time. A second portion of the sample was removed and so on. The duration of heating recorded in Table 2 for each sample is the total time of heating at each temperature.

Heating of natural samples under pressure. All runs were conducted in a single stage piston cylinder apparatus (Boyd and England 1960). Talc was used as the pressure transmitting medium in furnace assemblies with a diameter of 0.75 inch. Dry powdered molybdenum sulfide was used as the chamber wall lubricant in all runs.

Approximately 120 mg of orthopyroxene grains were packed into an iron capsule under pressure (to prevent further collapse of the lid of the capsule under pressure of the run and consequently large temperature differences between the capsule and the thermocouple). The arrangement of the furnace assembly was similar to that used by Cohen, Ito and Kennedy (1967, Fig. 1). Previous data had indicated that the degree of oxidation of Fe^{2+} within similar iron capsules was minimal (see also Lindsley 1964). The capsule was insulated from the thermocouple by 0.016 inch disc of fired pyrophyllite and then by a 0.001-inch disc of platinum. The temperature was recorded with a platinum-platinum-rhodium thermocouple on a proportional controller and the temperatures listed in Table 2 are believed to be accurate to ±5°C, neglecting the pressure effect on the output emf of the thermocouple. Data from Hanneman and Strong (1966) indicate that the temperature correction may be +10—20°C in the pressure range of 10 to 20 kbars.

In all experiments, the sample was brought to a pressure close to the desired value and then the temperature increased to 1000°C. The pressure measurement was made after a constant value had been reached. At the termination of each run, quenching was accomplished within less than one minute by switching off the power to the apparatus. The iron capsule was then removed from the talc assembly and furnace and the sample crushed for optical, X-ray diffraction and Mössbauer resonance experiments.

Optical and X-ray diffraction examination of heated samples. An optical and X-ray examination of each heated sample was made to test for the presence of additional phases, *e.g.* proto- or clinopyroxene, olivine, or SiO_2 phases. A monoclinic pyroxene was found in the following runs for times longer than 12 hours: 3209 at 1150°C and 1250°C; B1–9 at 900°C, 1000°C, 1050°C and H–8 at 1000°C. Decomposition products were observed in specimens B1–9 at 1100°C and XYZ at 1000°C. The quenched products for all specimens in Table 1 were pure orthopyroxenes.

On a few occasions, oxidation of the outer surface of the orthopyroxene grains to magnetite was observed. This was usually indicative of a broken vacuum seal during the heating process. In these instances, the runs were repeated. The presence of ferric iron was below the detection level in the Mössbauer resonance spectra before as well as after heating of each sample.

Chemical analyses. X-ray-emission microanalysis was carried out according to the techniques described by Smith (1965) and Howie and Smith (1966). For the samples analyzed by us, XYZ, B1–9, H–8, 3209 and 115/3, orthopyroxene grains were mounted in epoxy cement and polished (see also footnotes to Table 1). The analyses for each element were made by comparison against standard pyroxenes of similar composition. Corrections were then applied according to the factors listed in the above papers. In all cases, a minimum of 12 grains were analyzed and the grains were found to be homogeneous (within experimental error) both within individual grains and between different grains. The chemical analyses for all samples are given in Table 1 and the calculated values of the atomic ratio Fe/(Fe+Mg) are given in table 2 (column 2).

Mössbauer resonance experiments. The Mössbauer resonance experiment (Gruverman, 1965–1968) was performed using a 400-channel analyzer which was operated in time mode in conjunction with a constant acceleration electromechanical velocity generator. The velocity wave form was of symmetrical, triangular shape. The velocity increment per channel used for pyroxene spectra was 0.04 mm sec. Due to the symmetrical velocity shape

TABLE 1. CHEMICAL COMPOSITION OF ORTHOPYROXENES

	Oxides (wt. %)							
Specimen	SiO_2	Al_2O_3	CaO	MgO	FeO	TiO_2	MnO	Fe_2O_3
XYZ[a]	47.38	0.79	0.84	3.83	48.57	—	—	—
H-8	48.74	—	—	7.43	42.26	—	—	—
Bl-9	50.28	—	—	9.44	38.89	—	—	—
O-2	49.27	0.23	0.82	11.98	36.55	0.28		0.09
3209	49.84	0.93	0.93	13.79	33.17	—	—	—
37218	49.63	2.16	1.16	15.22	30.69	0.37	0.30	0.58
37615	51.86	1.03	0.47	20.13	24.48	0.05	0.72	—
115/3	51.13	2.61	0.57	20.70	23.62	—	—	—
N-5[b]	54.49	1.09	1.56	25.13	16.70	0.21	0.33	—
A-50[b]	54.87	1.45	1.59	29.33	11.34	0.10	0.23	—

NUMBER OF IONS ON THE BASIS OF SIX OXYGENS : ATOMIC PROPORTIONS

	Si	Al^{IV}	Al^{VI}	Ca	Mg	Fe^{2+}	Ti	Mn	Fe^{3+}
XYZ[a]	1.9827	0.0173	0.0213	0.0377	0.2388	1.6996	—	—	—
H-8	2.0322	—	—	—	0.4617	1.4737	—	—	—
Bl-9	2.0499	—	—	—	0.5735	1.3262	—	—	—
O-2	1.9766	0.0110[c]	—	0.0351	0.7162	1.2263	0.0084	0.0296	0.0014
3209	1.9854	0.0146	0.0288	0.0397	0.8186	1.1052	—	—	—
37218	1.9319	0.0681	0.0309	0.0484	0.8830	0.9990	0.0107	0.0098	0.0084
37651	1.9792	0.0208	0.0254	0.0192	1.1451	0.7813	0.0013	0.0231	
115/3	1.9404	0.0596	0.0570	0.0232	1.1708	0.7496	—	—	—
N-5	1.9863	0.0137	0.0331	0.0608	1.3653	0.5090	0.0056	0.0102	—
A-50	1.9648	0.0352	0.0258	0.0611	1.5652	0.3395	0.0027	0.0068	—

Specimens XYZ, O-2, 3209, 37218, 37615, and 115/3 are granulites from various areas; H-8 and Bl-9 are silicate rocks from metamorphosed iron formations in Quebec; and N-5 and A-50 are mafic rocks from the Stillwater Complex, Montana.

[a] Somewhat different from XYZ-Y1 of Howie and Smith (1966). XYZ-Y1 was used as a reference standard.

[b] N-5 and A-50 were analyzed by I. S. McCallum, using polished thin sections.

[c] Insufficient Al to make the Si figure equal to 2.

two mirror symmetric spectra were obtained simultaneously (200 channels per spectrum). In each case, "left" and "right" spectra were analyzed separately and data presented in Tables 2 and 3 are the average values. The number of counts per channel for each spectrum was $\sim 5 \times 10^5$.

During the experiment, the absorber was held at liquid nitrogen temperature to improve the separation of the Fe^{2+} splittings at the sites (Virgo and Hafner 1968). Since rapid exchange of absorbers within a matter of minutes was a crucial factor for efficient routine experiments, the absorber, as well as the entire cryostat, was thermally isolated by a styrofoam shield. The absorber was at atmospheric pressure, mounted with good thermal contact into a copper block which was at 77°K. It could be exchanged simply by removing a styrofoam plug. Of course, the nitrogen evaporation rate was relatively high (1.5 liters per hour) and consequently the cryostat (capacity 5 liters) was automatically refilled, in cycles of about 30 minutes. The effect on the line widths of metallic iron spectra was found to be tolerable. No significant line broadening could be observed in silicate spectra. The cryostat was in vertical position permitting a horizontal propagation of the gamma rays through the absorber. The self-absorption of the styrofoam shield was about 15 percent. The source (10 mC ^{57}Co diffused into palladium) was kept at room temperature. Source-absorber and absorber-detector distances were $3\frac{1}{2}$ inches. The 14.4 keV gamma rays were detected with a xenon methane filled counter. Two typical orthopyroxene spectra at liquid nitrogen temperature are shown in Figure 1.

Absorbers were made by mixing 60–80 mg of powdered orthopyroxene (< 50–$100 \mu m$) with 0.50 g of lucite. The mixtures were pressed to discs of one-inch diameter at 120°C. The density of natural iron per unit area varied between 3.1 and 4.6 mg Fe/cm^2. The line widths were not observed to change appreciably over twice this range of concentration (Hafner and Virgo, in preparation). The spectra were analyzed with the aid of a computer which performs a least-squares fit of Lorentzian lines to the experimental data. Some details of the fitting procedure are given in the following section of this paper.

The four inner lines of a metallic iron absorber were used for calibration. The full widths at half-peak height measured at room temperature were 0.25 mm/sec (inner lines) and 0.26 mm/sec (outer lines). A line-width study for two orthopyroxene absorbers at 77°K is given in Table 3. The hyperfine parameters, isomer shifts and electric quadrupole interactions are not discussed in this paper. The values obtained are in agreement with our previously published results (Evans, Ghose and Hafner 1967, Shenoy, Kalvius and Hafner 1969). An additional report on the effect of temperature and Fe/(Fe+Mg) ratio on these parameters is planned.

Determination of Fe^{2+} site occupancy factors from hyperfine data. In view of the difficulties involved in obtaining quantitative ferrous iron-magnesium distributions and site occupancy factors for *M*1 and *M*2 and also in view of the different methods used by other groups (e.g. Bancroft, Burns, and Howie 1967) it seems necessary to discuss briefly our approach to this problem.

The hyperfine spectrum of orthopyroxenes at room temperature consists of two superimposed quadrupole-split doublets which can be assigned to the two sites *M*1 and *M*2. Evans,

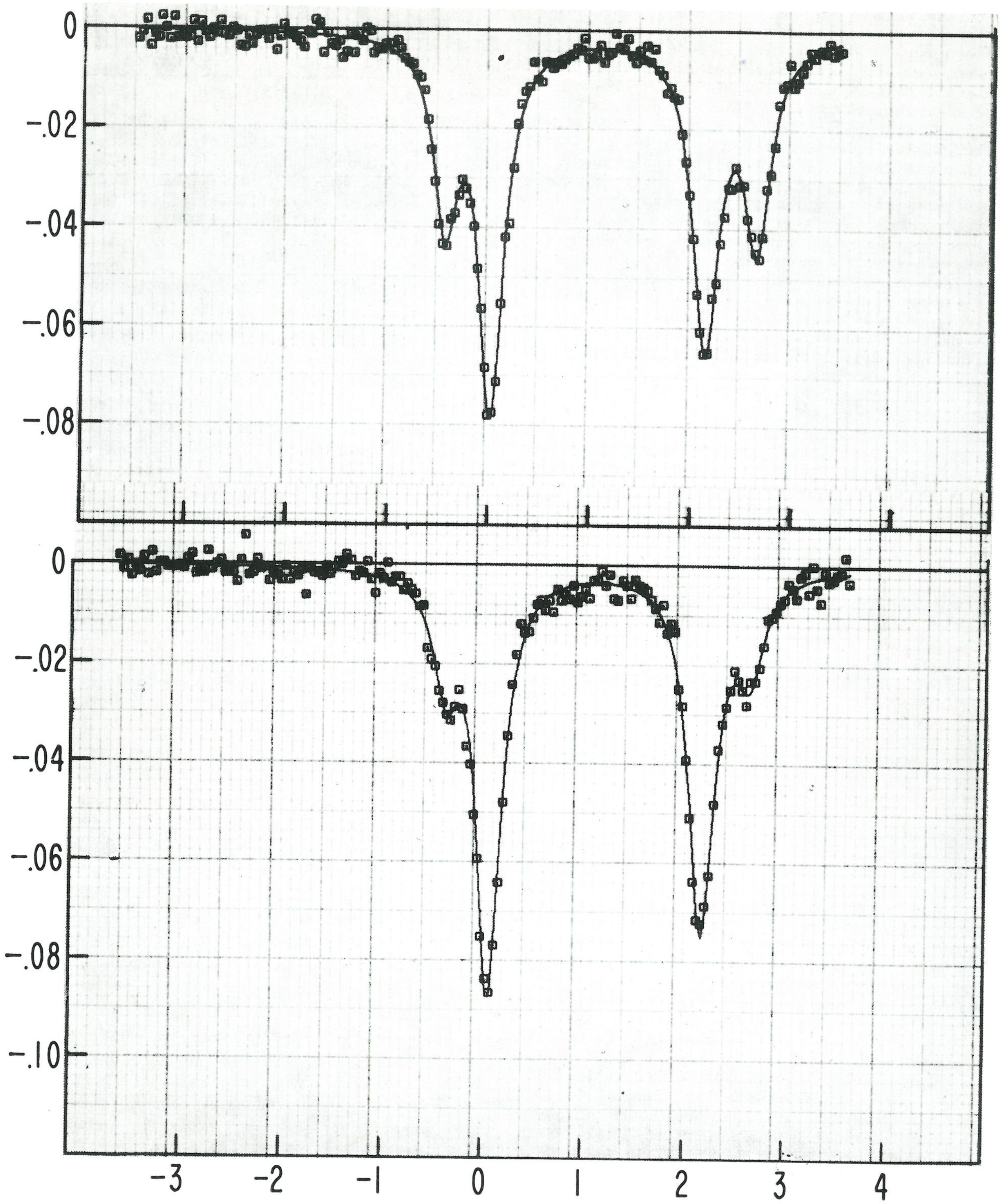

FIG. 1. Mössbauer resonant absorption spectrum of ^{57}Fe in orthopyroxene at 77°K. Outer peaks: doublet due to Fe^{2+}($M1$); inner peaks: doublet due to Fe^{2+}($M2$). Scale of abscissa: mm/sec. Lower spectrum: orthopyroxene 3209 [Fe/(Fe + Mg) = 0.574] unheated. Upper spectrum: Fe^{2+},Mg distribution over $M1$ and $M2$ in 3209 equilibrated at 1000°C.

Ghose, and Hafner (1967) designated the low velocity peak of each doublet by A and the high velocity peak by B. The subscripts 1 and 2 of A and B referred to the stronger and weaker doublet, respectively. Since the assignment of A_1-B_1 to the $M2$ site and A_2-B_2 to $M1$ is now established for orthopyroxenes we shall adjust the subscripts of the peaks to those of the sites. In the present study the Fe^{2+}-Mg distribution over $M1$ and $M2$ was determined from the intensity ratio of the two doublets. The site occupancy numbers for Fe^{2+} were found by multiplication of the relative distribution numbers T referred to one for each sample (equations 1 and 2) with the appropriate factor obtained from chemical analysis (see also p. 75). No attempt was made to determine site occupancy numbers directly from *absolute* intensity measurements of the doublets.

At room temperature, intensity measurements of the $M1$ and $M2$ doublets are hampered by their strong overlap, especially for compositions with x smaller than 0.7. Due to the differential dependence of the quadrupole splittings on temperature (Shenoy, Kalvius, and Hafner 1969) the peaks are considerably more separated at temperatures lower than room temperature. However, at temperatures well below 77°K the hyperfine spectra are complicated by paramagnetic relaxation effects and, for x larger than $\sim$ 0.7, by magnetic ordering. Therefore, simple intensity studies of the two quadrupole-split doublets are best made at temperatures close to 77°K. At that temperature, the peaks are well separated, but no severe perturbation by relaxation effects could be observed. The spectra could be readily fit by the least squares technique using 13 variables: 3 for each Lorentzian and one for the off-resonance count rate. The off-resonance rate was assumed to be velocity independent. χ^2 varied between 200 and 250.

If the absorber is very thin and if the lines are of Lorentzian shape and do not exhibit width anomalies, the number of ^{57}Fe nuclei populating a crystallographic position will be proportionally related to the total area under the peaks of the doublet, as well as to the recoilless fraction at that position. We have found our absorbers to be reasonably thin, and no thickness corrections were applied. The recoilless fractions $f(M1)$ and $f(M2)$ were assumed to be the same since in orthoferrosilite $f(M1)$ is equal to $f(M2)$ within a few percent (Hafner and Virgo, in preparation) and the dependence of the differential recoilless fraction on x in the system $Fe_{1-x}Mg_xSiO_3$ is still unknown.

Determination of the area ratios of overlapping peaks is a difficult problem. Area ratios are usually obtained from the areas of the least-squares fit Lorentzians which are proportional to the product $I \cdot \Gamma$. Here, I is the peak height of the Lorentzian and Γ the width at half height. However, the standard error $\Delta\Gamma/\Gamma$ of the widths of an individual orthopyroxene fit is about 10–15 times larger than the standard error $\Delta I/I$ of the corresponding peak heights. Statistical analyses of a number of spectra of the same absorbers led to the same result. Two examples are shown in Table 3 (the standard errors in this table are typical for orthopyroxenes). The relatively large errors of the Lorentzian widths and areas are of course due to the strong overlap of the Lorentzian tails even when the peaks are well separated. Therefore, precise area ratios are best obtained from the peak heights I of the Lorentzian fits rather than from products $I \cdot \Gamma$ or direct area fits. A detailed analysis of room temperature spectra of an iron-rich orthopyroxene with quite narrow lines (XYZ) revealed that the widths were the same for all four lines within the experimental error. The widths of the two inner peaks of liquid nitrogen spectra appear to be slightly broader than those of the outer lines, A and B being affected to an equal extent. The magnitude of this effect is about that of the standard error. Taking this into account by a correction factor did not lead to an improvement. Some of the spectra were fitted by constraining all widths to be equal (10 variable fits). This increased χ^2 by a few units, but did not affect the peak heights of the Lorentzians at all. Least-squares fits can tolerate large variations in Γ (taken up in the tails) without significantly altering the peak height.

In the present paper, the fractions $T(M1)$ and $T(M2)$ of Fe^{2+} at $M1$ and $M2$ were determined simply from the relation

$$T(M1) = [I(A1) + I(B1)]/[I(A1) + I(B1) + I(A2) + I(B2)] \quad (1)$$

$$T(M2) = [I(A2) + I(B2)]/[I(A1) + I(B1) + I(A2) + I(B2)] \quad (2)$$

without applying any additional corrections. The precision of this determination is high (Table 3). Possible systematic errors may be due to unknown differences in recoilless fraction and theoretical widths. Since the T values obtained from equations (1,2) are in excellent agreement with simple thermodynamical considerations the systematic errors are believed to be very small.

RESULTS

Some remarks on Table 2. The experimental data on the heated natural samples are given in Table 2. This table requires some additional explanation. The second column gives the atomic proportions Fe/(Fe+Mg) calculated from Table 1. The experiments on 3209 at 1000°C and 500°C, and 115/3 at 1050°C, were not carried out in a continuous manner as previously described. Runs 3209-31, -32, -33, and 3209-25 and -27 are two separate series of experiments at 1000°C. Likewise runs 3209-46, -48, -49 and 3209-54, -55, -56 were made in two different series of experiments, at different times. The site occupancies of the runs -49 and -54 after similar periods of heating give an indication of the reproducibility of the heating experiments. Also runs 115/3-8 and -9 refer to separate runs after similar periods of heating at 1050°C. Run 115/3-8 was the final run of the sequence 115/3-6, -7, and -8, whereas run 115/3-9 was a separate experiment. The experimental conditions for 3209-52 are listed in two rows in Table 2. The sample was first heated at 900°C for 15 hours; then the temperature was reduced to 500°C without removing the sample from the furnace and the sample was held for 168 hours. Runs 37218-E1 and 37651-E2 were made prior to this study using a different experimental technique (Evans, Ghose, and Hafner 1967; Ghose and Hafner 1967). Their spectra were remeasured at liquid nitrogen temperature. The site occupancy numbers for 37218-E1 reported by Virgo and Hafner (1968) were determined from area ($I \cdot \Gamma$) ratios and are therefore somewhat different (see p. 70). The temperature settings of those runs were approximate only.

The number of experiments listed in column 6 refer to the number of Mössbauer resonance experiments on the same absorber. The remainder of Table 2 includes the parameters determined from the least-squares fitting of the Mössbauer resonance spectra for each sample.

The site occupancy numbers in columns 12 and 13 require some further discussion. While the proportions T of Fe^{2+} in $M1$ and $M2$ are unique values for the orthopyroxene phase, chemical analysis of the same phase cannot be precisely determined because of the presence of an exsolved monoclinic pyroxene with lower Mg and Fe, higher Ca and similar Al and Mn contents, in most samples. We have overcome this problem by choosing samples, which on the basis of an optical examination, contain *very small* quantities of a second pyroxene

TABLE 2. HEATING EXPERIMENTS OF NATURAL ORTHOPYROXENES

Sample[a]	Fe/(Fe+Mg)[b]	Experimental conditions			Number of Spectra	Line width[c] (FWHH)				Fraction of Fe^{2+} in M_1[d] (T)	Fe^{2+} Site occupancy number		K_D	ln K_D
		Temperature °C	Duration of heating hours	Pressure kbar		$\Gamma(B_1)$	$\Gamma(B_2)$ mm/sec	$\Gamma(A_2)$	$\Gamma(A_1)$		M_1	M_2		
XYZ-25P	0.877	1000	7.5	18.2	1	0.28	0.31	0.30	0.28	0.474	0.831	0.923	.410	-.891
XYZ-15P	.877	1000	16.0	18.3	2	.28	.32	.31	.28	.481	.843	.911	.525	-.645
H8-20P	.761	1000	17.0	19.2	1	.28	.31	.30	.29	.440	.670	.853	.350	-1.050
B1-9-21P	.698	1000	~12.0	18.2	1	.35	.36	.33	.39	.400	.558	.838	.244	-1.41
0-2-34	.631	1000	~72.0	—[e]	1	.32	.33	.32	.31	.373	.471	.792	.234	-1.45
3209-31	.574	1000	2.1	—[e]	1	.30	.34	.32	.31	.353	.405	.744	234	-1.45
3209-23P	.574	1000	7.6	7.2	1	.32	.35	.33	.33	.371	.427	.722		-1.25
3209-24P	.574	1000	10.5	18.7	2	.32	.36	.36	.34	.360	.413	.736	.252	-1.38
3209-32	.574	1000	10.9	—[e]	1	.31	.34	.32	.31	.365	.419	.730		
3209-33	.574	1000	24.0	—[e]	1	.35	.38	.34	.35	.358	.411	.738	.125	-1.6
3209-25	.574	1000	72.0	—[e]	3	.34	.37	.36	.34	.340	.391	.758		
3209-27	.574	1000	169.0	—[e]	5	.31	.35	.33	.30	.360	.414	.735		
3209-35	.574	800	26.0	—[e]	1	.30	.33	.32	.28	.342	.393	.756		
3209-36	.574	800	57.0	—[e]	1	.29	.32	.30	.29	.347	.398	.751	.219	-1.52
3209-42	.574	700	24.0	—[e]	1	.29	.33	.30	.29	.326	.375	.774	.175	-1.74
3209-44	.574	700	72.5	—[e]	1	.29	.32	.31	.31	.327	.376	.773		
3209-45	.574	700	169.5	—[e]	2	.33	.35	.34	.34	.324	.372	.777	.170	
3209-40	.574	600	24.3	—[e]	1	.30	.33	.31	.31	.310	.356	.793	.144	-1.94
3209-46	.574	500	12.8	—[e]	1	.29	.31	.29	.30	.225	.258	.891		
3209-48	.574	500	29.1	—[e]	1	.31	.32	.30	.32	.230	.264	.885		
3209-49	.574	500	72.5	—[e]	1	.26	.31	.30	.28	.231	.265	.884	.047	-3.05
3209-54	.574	500	71.7	—[e]	1	.37	.34	.33	.26	.239	.274	.875		
3209-55	.574	500	120.2	—[e]	1	.33	.34	.33	.34	.229	.264	.885		
3209-56	.574	500	169.1	—[e]	1	.31	.34	.31	.31	.242	.278	.871		
3209-52	.574	900 500	15.0 168.0	—[e]	1	.32	.36	.34	.31	.324	.372	.777		
37218-E1	.531	1000		—[e]	1	.29	.36	.32	.29	.330	.351	.713	.217	-1.52
37651-E2	.406	1000		—[e]	1	.35	.39	.40	.34	.270	.219	.593	.192	-1.65
115/3-47	.390	1250	15.7	—[e]	1	.29	.39	.36	.30	.293	.229	.552	.241	-1.42
115/3-43	.390	1150	12.5	—[e]	1	.29	.38	.33	.33	.286	.223	.557		
115/3-6	.390	1050	24.0	—[e]	1	.33	.39	.36	.33	.274	.214	.567		
115/3-7	.390	1050	72.0	—[e]	1	.30	.37	.35	.30	.292	.228	.553		
115/3-8	.390	1050	162.5	—[e]	1	.29	.36	.35	.29	.287	.224	.556		
115/3-9	.390	1050	169.1	—[e]	1	.29	.37	.34	.30	.279	.217	.563		
115/3-1	.390	1000	24.0	—[e]	1	.33	.37	.35	.31	.286	.223	.557		
115/3-2	.390	1000	71.0	—[e]	2	.31	.32	.36	.31	.300	.236	.545		
115/3-3	.390	1000	166.0	—[e]	3	.31	.38	.36	.30	.296	.231	.550		
N-5-22	.272	1000	24.0	—[e]	1	.30	.35	.32	.31	.248	.135	.408	.226	-1.48
N-5-23	.272	1000	73.7	—[e]	1	.30	.35	.33	.27	.256	.139	.404		
N-5-24	.272	1000	169.7	—[e]	1	.27	.34	.33	.26	.258	.140	.403		
A-50-30	.178	1000	73.3	—[e]	2	.34	.34	.35	.26	.237	.084	.272	.245	-1.40

[a] The first part of the sample number refers to the mineral or rock number; the latter part refers to the experiment.
[b] Atomic fractions (see text).
[c] Average of all spectra taken.
[d] The sum of the fractions of Fe^{2+} in $M1$ and $M2$ is equal to one.
[e] Sealed in quartz tubes, previously evacuated to $<5 \times 10^{-4}$ mm Hg.

phase. But single-crystal studies indicate the presence of an exsolved phase even in these cases. Ideally, the proportion of Fe^{2+} in $M1$ and $M2$ should be recast in terms of the total number of sites involved in the exchange reaction. Although it is reasonable to assume that Fe^{2+} and Mg from the chemical analyses will be the major occupants of the $M2$ and $M1$ sites in orthopyroxene, the absolute amounts and relative proportions of other elements in the cation sites are less definitely known (Smith *et al.* 1969). In view of these uncertainties we prefer to proportionate the fraction of Fe^{2+} in $M1$ and $M2$ in terms of $2 \cdot Fe/(Fe + Mg)$ of the mineral according to formula units $(Mg,Fe)_2Si_2O_6$ in the unit cell. The Fe/(Fe+Mg) ratio is determined directly from the chemical analysis. An independent determination of the site occupancy numbers by crystal-structure analysis (Ghose 1965) is in agreement with the values determined from our technique (Virgo and Hafner 1968).

Approach to equilibrium. One of the surprising observations which has resulted from this study is that equilibrium distributions over the octahedral sites $M1$ and $M2$ are accomplished in a short time even at low temperatures. Data on the heating experiments on the natural sample 3209 at atmospheric pressure and at 1000, 800, 700, 600, and 500°C are plotted in Figure 2. A steady value for Fe^{2+} in $M1$ and $M2$ is reached after 11 hours at 1000°C and after 50 hours at 500°C. The initial distribu-

TABLE 3. PRECISION OF HYPERFINE PEAK HEIGHTS AND WIDTHS OF ORTHOPYROXENE 3209

Sample	Spectrum	Line widths (FWHH)				Intensities (referred to sum of I)				Fraction of Fe^{2+}	Fe^{2+}— Site occupancy numbers	
		$\Gamma(B_1)$	$\Gamma(B_2)$ mm/sec	$\Gamma(A_2)$	$\Gamma(A_1)$	$I(B_1)$	$I(B_2)$	$I(A_2)$	$I(A_1)$	in M_1	M_1	M_2
3209–27	V37	0.2970	0.3400	0.3159	0.2900	0.1874	0.2899	0.3516	0.1711	0.3585	0.4118	0.7370
3209–27	V210	.3207	.3620	.3425	.3097	.1900	.2928	.3481	.1690	.3592	.4126	.7362
3209–27	V225	.2778	.3351	.3028	.2828	.1912	.2900	.3471	.1716	.3629	.4169	.7319
3209–27	V226	.2976	.3206	.3022	.2850	.1891	.2897	.3486	.1726	.3617	.4156	.7332
3209–27	V233	.3650	.3919	.3680	.3516	.1896	.2931	.3489	.1683	.3679	.4112	.7376
	Average	.3116	.3499	.3262	.3038					.3600	.4136	.7351
	S.E.	±.0299	±.0248	±.0255	±.0257					±.0021	±.0022	±.0022
3209	V36	.2645	.3097	.3059	.3027	.1131	.3656	.4145	.1069	.2199	.2527	.8961
3209	V100	.2876	.3053	.2969	.2773	.1043	.3621	.4185	.1150	.2193	.2519	.8969
3209	V175	.2987	.3396	.3307	.3106	.1119	.3691	.4134	.1055	.2174	.2494	.8990
	Average	.2836	.3182	.3111	.2968					.2188	.2513	.8973
	S.E.	±.0143	±.0152	±.0143	±.0144					±.0011	±.0014	±.0012

tion in these experiments is plotted on the ordinate axis at zero time. It should be noted that 3209-25 is not plotted in Figure 2 and the results for this sample are not consistent with the remaining runs at 1000°C. However in view of the consistency of the other runs at this temperature and the overall trends it is reasonable to delete this result. Some kinetic data for sample 115/3 (Figure 3) and A-50 (Table 2) also indicate that a similar rapid approach to a steady distribution is obtained. It is not expected that the kinetics of cation exchange in orthopyroxenes at a single temperature will sensitively depend on x (Mueller 1967), but it is not yet definitely known whether the steady values determined in these kinetic experiments represent intrinsic equilibrium values. Kinetic analyses simply define an apparent equilibrium state towards which a measurable rate of approach can be observed.

Experiment 3209-52 was designed to test whether the steady value obtained at 500°C in the disordering reaction represents the true equilibrium value. The results (Table 2) are consistent with the conclusion that intrinsic equilibrium will, in fact, be reached after the appropriate time (see p. 78).

Fe^{2+}-Mg distribution isotherms. The equilibrium values X_1 and X_2 at 1000°C for samples with x=0.178, 0.272, 0.390, 0.406, 0.531, 0.574, 0.631, 0.698, 0.761 and 0.877 are plotted in Figure 4. Most of the points, especially those of the magnesium rich compositions fall close to a hyperbolic curve,

$$k = \frac{X_1(1 - X_2)}{X_2(1 - X_1)} \tag{3}$$

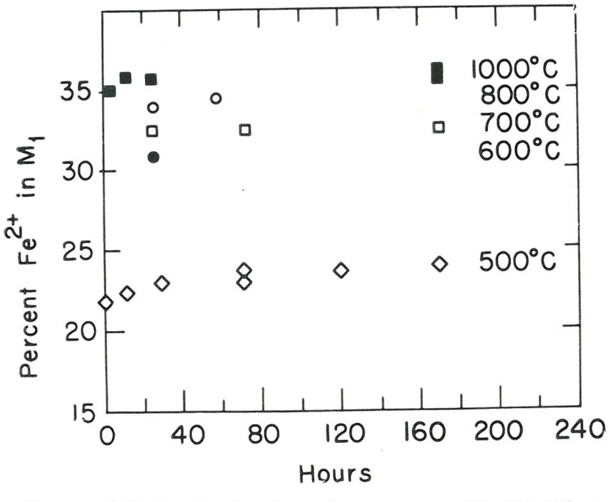

FIG. 2. Fe^{2+} distribution in orthopyroxene 3209 [Fe/(Fe + Mg) = 0.574] as a function of time of heating. The fraction of Fe^{2+} in $M1$ of the unheated sample is 22 percent.

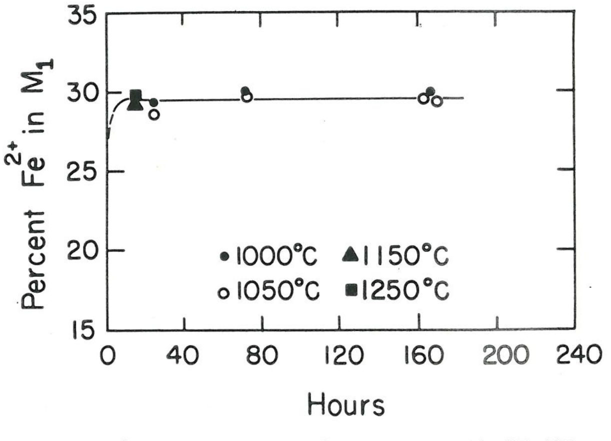

FIG. 3. Fe^{2+} distribution in orthopyroxene 115/3 [Fe/(Fe + Mg) = 0.390] as a function of time of heating. The fraction of Fe^{2+} in $M1$ of the unheated sample is 7 percent.

passing through the points, $X_1 = X_2 = 0$ and $X_1 = X_2 = 1$. This accords with *ideal distribution* ("ideal solution model") for Fe^{2+} and Mg assumed for *each site*, $M1$ and $M2$ (Mueller 1962, Ghose and Hafner 1967). In equation (3), X_1 and X_2 are the site occupancy numbers for Fe^{2+} at $M1$ and $M2$, respectively, and k is the equilibrium constant. k may have any value between zero and unity. In this notation, $k = 1/K$ where K refers to the definition of Mueller (1962) and Ghose and Hafner (1967).

The site occupancy numbers for the five magnesium-rich samples ($x \leqslant 0.63$) were used for a least squares fit to equation (3) with k as variable. The fitted curve ($k = 0.235 \pm 0.005$) is plotted in Figure 4. The agreement between the experimental points and the theoretical equation is excellent.

Two heated iron-rich samples ($x = 0.761$ and $x = 0.877$) exhibit a marked, well-defined deviation from the ideal curve. It is concluded that in this region there is a deviation from ideal mixing at $M1$ and $M2$. We have no explanation for this in terms of crystal structure. The effect of small concentrations of calcium at $M2$ on the Fe^{2+},Mg distribution is still unknown. However, it is known that orthopyroxenes with compositions within this region ($\sim 0.7 < x \leqslant 1.0$) are magnetically ordered at very low temperatures (Shenoy, Kalvius and Hafner 1968). Inspection of the two refined crystal structures at room temperature (Ghose 1965, Burnham 1966) shows that the cations at $M1$ and $M2$ touch two common oxygens, O_2 and O_5. Thus it appears likely that the superexchange interaction which produces magnetic ordering is of the form Fe(1)-O(2)-Fe(2) or Fe(1)-O(5)-Fe(2). The excess stabilization energy of this superexchange interaction could lead to some short-range iron-iron clustering at adjacent $M1$ and $M2$ sites in the phase field of the paramagnetic solid solution above the Néel temperature.

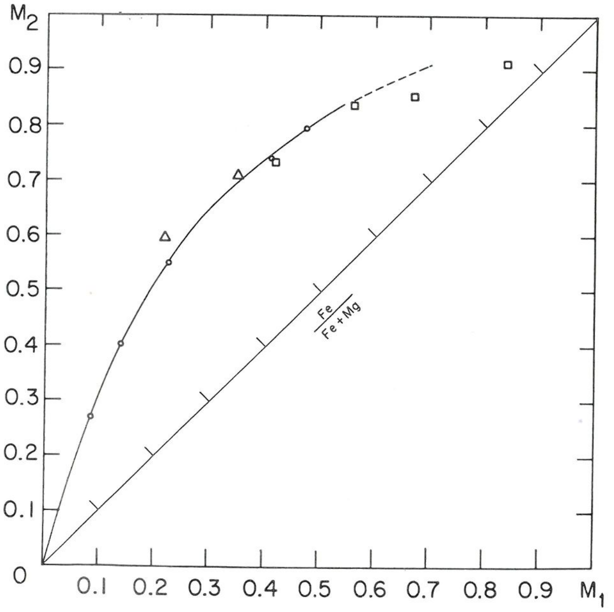

FIG. 4. Equilibrium isotherm of Fe^{2+} over $M1$ and $M2$ in orthopyroxenes at 1000°C.
Circles: samples heated at atmospheric pressure.
Squares: samples heated under high pressure.
Triangles: previously published data (approximate temperature).

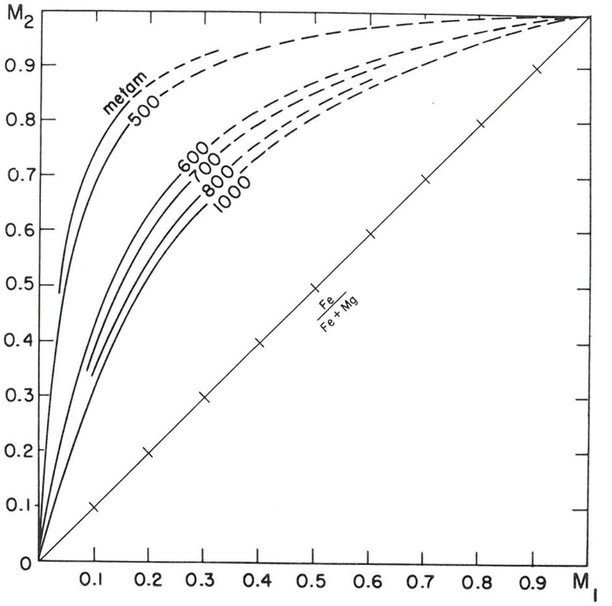

FIG. 5. Ideal equilibrium distribution isotherms for Fe^{2+}. The curve "metam" refers to the unheated sample, 3209 [$Fe^{2+}/(Fe^{2+} + Mg) = 0.574$].

The equilibrium constant ($k = 0.235$) of the 1000°C isotherm (Fig. 4) is somewhat higher than that previously estimated by Ghose and Hafner (1967) on the basis of the two heated samples, 37218 and 37651 ($k = 0.15$). This difference is primarily due to the increased resolution of the two doublets in spectra measured at 77°K.

Equilibrium values have been determined for sample 3209 at 800, 700, 600 and 500°C. Since the hyperbolic shape of the distribution isotherm is well established at 1000°C, the equilibrium constants for the region $0 \leqslant x \leqslant 0.574$ at lower temperatures may be determined from the heating experiments on this sample. The equilibrium constants are shown in Table 4 and the distribution curves are plotted in Figure 5. There is considerable evidence that the deviation from the ideal behavior at the Fe-rich end of the series is in fact enhanced at lower temperatures (Virgo and Hafner, in preparation). Nevertheless it may be suggested that in the region $0 \leqslant x \leqslant 0.5$, the system behaves very nearly ideal.

Also plotted in Figure 5 is the curve representing the distribution of Fe^{2+} and Mg in some metamorphic orthopyroxenes (Virgo and Hafner, in preparation). This curve corresponds to a temperature slightly less than 500°C. Certainly this temperature is significantly lower than the crystallization temperature of orthopyroxenes in the granulite facies of metamorphism. It is interpreted as the critical temperature below which additional cation ordering between $M1$ and $M2$ appears not possible even within geological times.

TABLE 4. EQUILIBRIUM CONSTANTS AND STANDARD GIBBS FREE ENERGY

Temperature °C	Equilibrium constant k	Standard Gibbs free energy $\Delta G_E°$, kcal/mole
500	0.051	4.57
600	.148	3.31
700	.173	3.39
800	.211	3.32
1000	.235	3.66
		3.65(avg)

Free energy of the exchange reaction. The standard Gibbs free energy change, $\Delta G_E°$, for the disordering reaction,

$$Mg(1) + Fe^{2+}(2) \rightleftharpoons Fe^{2+}(1) + Mg(2) \qquad (4)$$

is related to k, the equilibrium constant as defined previously, by

$$\Delta G_E° = - RT \ln k \qquad (5)$$

Values of $\Delta G_E°$ determined from the values of X_2 and X_1 (Table 2) and equation (3) at 500, 600, 700, 800 and 1000°C are given in Table 4. Between 600 and 1000°C, $\Delta G_E°$ is approximately constant. This is not surprising since the change of entropy over this range is expected to be small. The value at 500°C is significantly higher than the other values and this may represent an inconsistency in the thermodynamic model. Large variations of $\Delta G_E°$ are presumably not consistent with ideal distribution but to date there are insufficient data to verify a significant deviation. The average value of $\Delta G_E°$ including the value at 500°C is 3.65 kcal.

Effect of pressure on site occupancy numbers. The similarity of unit-cell volumes of the end-member compositions, $MgSiO_3 = 835 \times 10^{-24}cm^3$ and $FeSiO_3 = 876 \times 10^{-24}cm^3$ (Robie, Bethke, Toulmin and Edwards, 1966) suggests that hydrostatic pressure on orthopyroxenes should have little effect on any differential distribution of Mg and Fe^{2+} throughout the solid solution. This follows, since the *differential* properties of the sites depend only on volume changes as a second-order effect. This is confirmed from the experimental data. Sample 3209 (x=0.574) was heated at 1000°C and at pressures close to atmospheric pressure, 7.2 kbar, and 18.7 kbar. The results are given in Table 2 and also plotted in Figure 3. The high pressure runs straddle the equilibrium values of this sample with the run at 7.2 kbar indicating a slightly higher proportion of Fe^{2+} in $M1$. The very slight difference in X_2 and X_1 between runs XYZ-25P and XYZ-15P (x=0.877) is not interpreted to be due to a pressure effect. It is reasonable to expect larger experimental errors in the case of these high pressure runs in view of the experimental technique (*e.g.* larger temperature gradients across the sample and larger inherent errors in the temperature). It is probably true that the samples heated under pressure do not represent temperatures as close to 1000°C as the runs at atmospheric pressure (see p. 67). However, this effect will be small in view of the comparatively smaller variation in site occupancy with temperature for high temperature values. In summary, it is concluded that there is no proof for a significant pressure dependence of the Fe^{2+}-Mg distribution isotherms in the orthopyroxene system.

Maximum disorder, maximum order and nature of the transition. Equilibrium values for X_2 for sample 3209 are plotted against temperature in Figure 6 and a smooth curve has been drawn through the points assuming a continuous transformation. The nature of the order-disorder relationship in orthopyroxene requires some additional comments. The hyperfine parameters (nuclear quadrupole splitting, isomer shift and line width) determined from the gamma-ray resonance spectrum depend on the local environment of the sites within a radius of a few lattice constants. No significant dependence of these parameters on the degree of order-disorder was found. The hyperfine spectrum of orthopyroxene measures therefore, the intrinsic average occupancy at the $M1$ and $M2$ lattice complexes. Consequently terms like long-range order or short-range order have no real meaning in this study.

Some comments on the beginning and ending of order can be made. At high temperatures there appears to be a gradual approach to higher degrees of disorder. Experiments were made on sample 3209 (x=0.574) at 1055, 1150 and 1250°C but in each case the quenched pyroxene was a monoclinic type. However, site occupancies were determined on quenched orthorhombic samples of 115/3 (x=0.390) at 1055, 1150 and 1250°C. In these runs the degree of disorder was *unchanged* from the results for 1000°C (Fig. 3). It is possible that in these samples and also for other high temperature runs the cation distribution changed to a more ordered configuration during the quench. The temperature dependence of the rate constants for the ordering reaction is not known. However, data on the rate

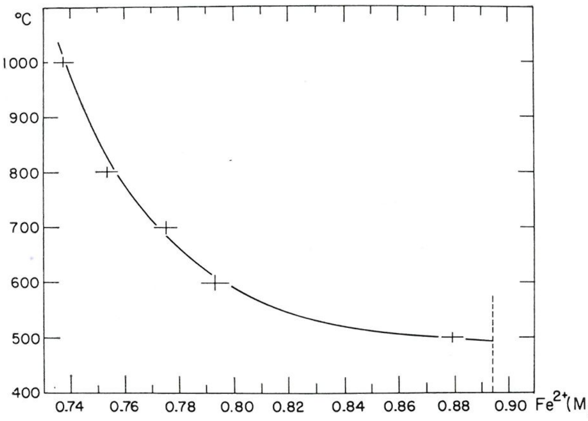

FIG. 6. Fe^{2+},Mg order-disorder as a function of temperature for the sample 3209 [$Fe^{2+}/(Fe^{2+} + Mg) = 0.574$]. Vertical dashed line refers to the site occupancy number (X_2) for the natural sample 3209.

constant at 500°C are similar to that for the disordering rate. Therefore since the quench was carried out in a matter of seconds it seems likely that the ordering of cations during the quenching procedure was small. It is on this basis that we propose a "limiting temperature" for disordering which will be close to 1000°C. The 1000°C isotherm in Figure 4 therefore corresponds to the maximum degree of disorder possible in the orthorhombic phase field for compositions with $x=\mathrm{Fe}/(\mathrm{Fe}+\mathrm{Mg})$ smaller than 0.70. It is apparent from Figure 3 that the site occupancy values are considerably different from those corresponding to complete disorder. For sample 3209, this would imply a further change in X_1 of approximately 38 percent. This is unlikely to occur because the energetic difference between the $M2$ and $M1$ sites is approximately maintained over the complete temperature range. Even in higher temperature monoclinic pyroxenes, this difference between the sites still exists. There is no evidence that the degree of differential distortion of $M1$ and $M2$ would significantly depend on Fe^{2+}-Mg disorder in either ortho- or clinopyroxenes. Consequently the strong preference of Fe^{2+} for the $M2$ site found in orthopyroxenes at lower temperatures will be maintained with increasing temperature and will provide a limit to the maximum degree of disorder in the orthorhombic phase field.

As the temperature is reduced below 500°C, there are no further changes in X_1 and X_2. Heating experiments have not been made below 500°C but comparatively rapid kinetics for the ordering reaction (see later section) does not preclude the existence of more highly ordered states. The inferred low temperatures corresponding to the cation distribution in the unheated sample 3209 suggests a cooling history consistent with a high degree of order. Because of the likely slow cooling and subsequent adjustment to equilibrium conditions at successively lower temperatures, this sample probably represents one of the best examples for expected *maximum order*. It is surprising then to find that the sample is not closer to complete order. This would imply a further decrease in $M1$ by approximately 28 percent. We believe that there is a sharp beginning to disorder in orthopyroxenes (dotted line in Fig. 6) and this is associated with an "energy barrier" close to 480°C.

Kinetics of the disordering reaction. The present data are too sparse to analyze the kinetics of the exchange reaction (eq. 4) in detail. However, since the distribution of Fe^{2+} and Mg in the orthopyroxene system over a large range of composition can be well represented by the ideal distribution model, estimates of the rate constants for ordering and disordering at different temperatures as well as activation energies for the diffusion processes can be obtained from a simple kinetic analysis of the experimental data. In the following, we adopt a model developed by Mueller (1967).

The process of ordering or disordering is considered as an ideal interchange reaction (eq. 4) involving the partitioning of ferrous and magnesium ions between $M1$ and $M2$. A constant or slightly varying exchange energy $\Delta G_E{}^\circ$ over the experimental temperature range is assumed. The time rate of change of Fe^{2+} at $M2$ at constant temperature is

$$\frac{-dX_2}{dt} = -K_{12}X_1(1 - X_2) + K_{21}X_2(1 - X_1) \qquad (6)$$

where X_1 and X_2 are the site occupancy numbers of Fe^{2+} at $M1$ and $M2$ respectively. K_{12} and K_{21} are the specific rate constants for the opposing reactions in equation (4) referred to two sites per volume unit and are solely functions of temperature.

Using the substitution

$$X_1 = 2x - X_2$$

where x is the $\mathrm{Fe}^{2+}/(\mathrm{Fe}^{2+}+\mathrm{Mg})$ ratio of the orthopyroxene and relating the rate constants K_{12} and K_{21} to the equilibrium constant

$$k = \frac{K_{21}}{K_{12}} = \frac{X_1(1 - X_2)}{X_2(1 - X_1)} \qquad (7)$$

Equation (6) can be integrated for a fixed value of x, depending on whether the term

$$(1 - k)X_2{}^2 + X_2(k(2x - 1) - 2x - 1) + 2x \gtrless 0 \qquad (8)$$

i.e. whether (8) is greater than zero (isothermal ordering) or less than zero (isothermal disordering). The integrated expression becomes

$$\mp K_{21}\Delta t = (k/2a) \ln \left[\frac{\mp a - b}{a + b}\right] \Bigg|_{X_2{}'}^{X_2{}'} \qquad (9)$$

where

$$a = [k_{-1}{}^2(x - \tfrac{1}{2})^2 + k]^{\frac{1}{2}}$$

$$b = k_{-1}(X_2 - x) + \frac{k_{+1}}{2}$$

and

$$k_{-1} = 1 - k$$
$$k_{+1} = 1 + k$$

In equation (9), Δt is the time interval and $X_2{}''$ and $X_2{}'$ are the values of X_2 at the upper and lower limits of the integration. $X_2{}'$ is the initial site occupancy number of Fe^{2+} at $M2$. The upper signs in equation (9) refer to the case for ordering *i.e.* an increase of X_2 with time whereas the lower signs represent disordering.

Thus a logarithmic dependence of the site occupancy numbers with time can be expected at a fixed temperature. The experimental data are consistent with this prediction although they are too sparse to test the validity of the rate equation (6). It would be of interest to perform a number of short-time heating experiments for verification of equation (6).

The time dependence of X_2 was calculated for orthopyroxene 3209 ($x=0.574$) at 500, 600, 700, 800 and 1000°C (Fig. 7). The saturation value at each temperature corresponds, of course, to the equilibrium values in Figure 2. It

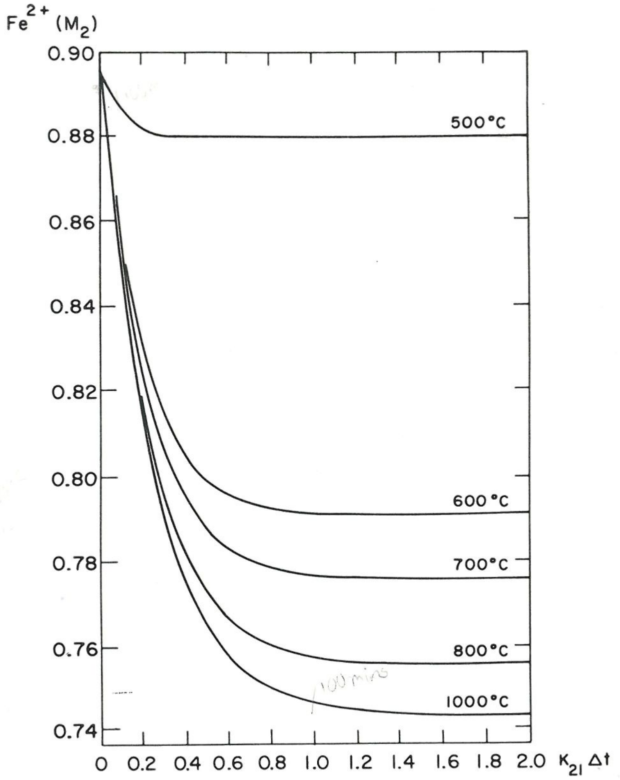

FIG. 7. Computed site occupancy number X_2 [Fe/(Fe + Mg) = 0.574] as function of time Δt on the basis of the ideal distribution model: Disordering.

If $K_{21}\Delta t$ [illegible]

is possible to determine the rate constants for the disordering reaction by fitting values of X_2 from Figure 2 to the curves in Figure 7. In this procedure the unit of the abscissa (K_{21} Δt) is taken as a variable. The following values were approximately determined in this way, lnK/yr.

$$K_{21}(500°C) \approx 6 \times 10^{-5}\ (\mathrm{min}^{-1}) \quad 3.45$$
$$K_{21}(1000°C) \approx 1 \times 10^{-2}(\mathrm{min}^{-1}). \quad 8.57$$

These data can be used to determine the activation energy (Ea_D) for the rate controlling step in the disordering diffusion process, assuming a linear relationship between $\ln K_{21}$ and T^{-1} in accord with the Arrhenius equation:

$$K_{21} = A \exp\left(-Ea_D/RT\right) \tag{10}$$

In this equation A is a constant that includes the entropy of activation and will be independent of temperature provided there is no change in the mechanism of diffusion over the temperature 500–1000°C. Data for the disordering reaction in orthopyroxenes give a value of

Q = 20.0 [illegible] Kcal
K* = 1.44 (+17)

$$Ea_D \approx 20 \text{ kcal}$$

per mole (formula unit $(Fe,Mg)_2Si_2O_6$). This activation energy corresponds to the energy barrier which must be surmounted for diffusion to occur. Implicit in this derivation is that the activation is independent of temperature and it will hold provided the exchange process can be regarded as ideal. Certainly this is not so at 1000°C for orthopyroxenes with $x > 0.70$. The deviation from ideal behavior at low temperatures is not completely known, and it is possible that the non-ideal behavior extends over a larger composition range as the temperature is reduced.

The rate constants K_{12} for the ordering reaction can, of course, be derived from the rate constants of disordering via equations (6) and (7). Using the Arrhenius relationship equation (10) an activation energy Ea_O, for ordering

$$Ea_O \approx 14.8 \text{ kcal}$$

is obtained. A somewhat different approach follows from equation (5). Since it was observed that $\Delta G_E°$ is approximately invariant with respect to temperature, it follows that

$$\frac{d \ln k}{dT} \approx \frac{\Delta G_E°}{RT^2},$$

and from equation (10) that

$$\frac{d \ln k}{dT} = \frac{+Ea_D\text{-}Ea_O}{RT^2}.$$

Thus we find

$$Ea_O \approx Ea_D - \Delta G_E^0$$

In this way, the estimated activation energy of ordering is

$$Ea_O \approx 16.5 \text{ kcal}.$$

This value is in fair agreement with the 14.8 kcal determined from the rate constants.

Kinetics of the ordering reaction. Experiments on ordering are of considerable value since they yield independent tests of rate equation, rate constants, and activation energies. A single ordering experiment was performed with pyroxene 3209 at 500°C (Table 2, run 52). In Figure 8 the rate curve is plotted using equation (9). The initial value X_2' at 1000°C (determined from Fig. 2) was used instead of 900°C (Table 2), since X_2' at 900°C was not measured.

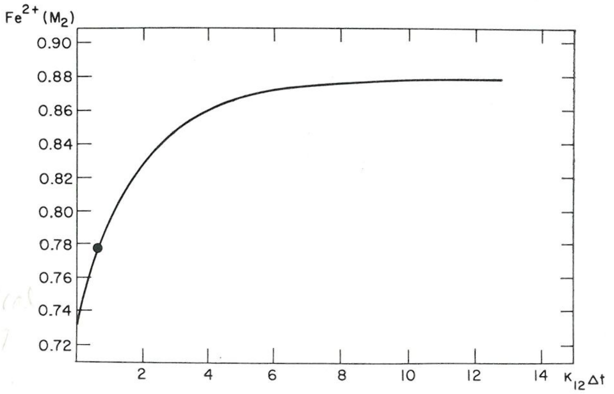

FIG. 8. Computed site occupancy number X_2 [Fe/(Fe + Mg) = 0.574] as function of time Δt on the basis of the ideal distribution model: Ordering. The point represents the partially ordered orthopyroxene 3209–52 (cf. Table 1).

The very slight difference between X_2 at 900 and 1000°C (Fig. 6) does not significantly alter the absolute position of the rate curve in Figure 8. The rate constant for ordering as estimated from this experiment is

$$K_{12}(500°\mathrm{C}) = 6 \times 10^{-5}\ (\mathrm{min}^{-1}).$$

Consequently, the time to reach 50 percent of the equilibrium value would be ~ 15 days. The time for 95 percent would be ~ 145 days.

While the rate constant for ordering is generally expected to be higher than that for disordering at a given temperature according to rate equation (6), it is of interest to note that K_{12} as determined from experiment 3209-52 is about 20 times smaller than derived from the disordering kinetics. In fact at 500°C, ordering and disordering rates appear to be very nearly the same. Considering the heat treatment of the crystals at high temperature prior to the ordering at 500°C, this result is not surprising, and it seems quite probable that the rate equation (6) is inadequate for the complexity of ordering processes. More experiments will be needed to explore the ordering kinetics in orthopyroxenes.

Discussion

It is of interest to compare the *standard Gibbs free energy difference* $\Delta G_E°$ for the Fe^{2+}, Mg exchange in orthopyroxenes with exchange energies of ferrous and magnesium ions in other systems. The standard interchange enthalpy for Mg and Al exchange between octahedral and tetrahedral sites in spinel ($MgAl_2O_4$), for instance, is considerably higher; 9-11 kcal (Navrotsky and Kleppa 1967). In fact, while some Mg,Al disordering is known to occur, substantial disorder has not been observed. Several oxides of the *inverse* spinel type ($MgFe_2O_4$, $MgGa_2O_4$) however, have considerably lower standard interchange enthalpies which are of about the same magnitude as $\Delta G_E°$ in orthopyroxenes. Unfortunately no data on Fe^{2+},Mg interchange in spinels have been reported to date. Estimates of octahedral and tetrahedral site preference energies for Fe^{2+} and Mg in spinels by Navrotsky and Kleppa (1967) would indicate a difference of ~3.1 kcal for a hypothetical Fe^{+2},Mg exchange in spinels, Fe^{2+} preferring the (distorted) octahedral sites.

It is difficult to compare $\Delta G_E°$ with that of the Al,Si interchange among the nonequivalent tetrahedral sites in triclinic alkali feldspars. One might assume, on the basis of the small differences in interatomic distances and bond angles compared to the high differential distortion of *M*1 and *M*2 in orthopyroxenes, that the exchange energy would be smaller. Holm and Kleppa (1968) found some indication that disordering in albite occurs energetically in a "two-step" process. The first step could be interpreted by the reaction

$$\mathrm{Al}(I) + \mathrm{Si}(II) \rightarrow \mathrm{Al}_{0.5}\mathrm{Si}_{0.5}(I) + \mathrm{Al}_{0.5}\mathrm{Si}_{0.5}(II). \quad (11)$$

This corresponds to a standard enthalpy change of 2.4 kcal mole^{-1} at 700°C. It is most likely, however, that the above reaction is only partially complete. Certainly, the intrinsic disordering reaction is more complex than equation (11). In either case, the exchange energy for the complete exchange would be somewhat higher than in orthopyroxenes, but this is a very approximative estimate.

An analysis of the time dependence of X_1 and X_2 at constant temperature on the basis of the ideal solution model has enabled the *activation energies* for Fe^{2+},Mg disordering and ordering in orthopyroxenes to be estimated. The energies of 15-20 kcal involved for the exchange between *M*1 and *M*2 are *low*. This is in contrast with some well-known order-disorder phenomena in silicates, especially Al-Si exchange between tetrahedral sites.

Data from McKie and McConnell (1963) indicated an activation energy of 74 kcal mole^{-1} for the dry heating of Amelia albite at temperatures about 900°C. McConnell and McKie (1960) also determined a value of 60 kcal mole^{-1} for the hydrothermal ordering of synthetic albites. A large number of heating experiments on alkali feldspars are indicative of considerably high activation energies although the experimental data have not, as yet, been interpreted in terms of a rate equation. Brown's (1965) estimate of 20 kcal mole^{-1} for potassium feldspar is probably rather low. The difference in the activation energies for orthopyroxenes compared with feldspars can be qualitatively explained in terms of the different crystal structures. The ordering of Si and Al in the feldspars is not merely a matter of arranging different atoms on a fixed set of lattice positions but each movement of Si and Al involves additional distortion of the $(Al,Si)O_4$ framework and related shifts of Na and K ions to satisfy charge balance requirements. The exchange of Fe^{2+} and Mg between *M*1 and *M*2 in orthopyroxenes does not significantly affect the SiO_4-chain linkage and the octahedral bonds are probably of lower strength than the tetrahedral bonds in feldspars. Pauling (1960) estimated the strength of Si-O bonds to be ~90 kcal mole^{-1} which is in approximate agreement with the removal of Si from the SiO_4 tetrahedra in feldspars.

The low activation energies in the orthopyroxenes account for the rapid kinetics of the disordering and ordering reactions and consequently the relatively small temperature effect on the rates. The low value for the ordering reaction suggests that cation distributions corresponding to *crystallization* temperatures may not be preserved in rocks which are slowly cooled through geological time. The low temperatures corresponding to the measured values of X_2 and X_1 in the metamorphic sample 3209, suggests that there has been considerable ordering of the cations during the cooling history of the metamorphic rock. Our experimental data do not preclude however the usefulness of this order-disorder relationship, as an indicator of the thermal history of orthopyroxenes and their geological environments. In the case of rocks which are quickly cooled, *e.g.* volcanic rocks, it seems likely that the cation distribution may reflect temperatures closer to the maximum temperatures attained (Ghose and Hafner 1967). A more detailed analysis of rapidly cooled natural orthopyroxenes with metastable, partially ordered Fe^{2+},Mg distribution would be of considerable interest.

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