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

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ABSTRACT

The Fe\textsuperscript{2+},Mg distribution over the octahedrally coordinated sites M1 and M2 in orthopyroxenes with compositions close to the system Fe\textsubscript{x}Mg\textsubscript{1-x}SiO\textsubscript{3} was investigated at different temperatures and pressures in the orthorhombic phase field. Fe\textsuperscript{2+} distribution and site occupancy numbers were obtained from the electric quadrupole splittings of 57Fe 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 < x < 0.6 the site occupancy is in agreement with the assumption of ideal Fe\textsuperscript{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\textsuperscript{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 AG\textsuperscript{0} for Fe\textsuperscript{2+},Mg exchange between M1 and M2 is apparently constant: 5.6 kcal per mole (formula unit (Fe\textsubscript{x}Mg\textsubscript{1-x})SiO\textsubscript{3}).

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 < 1, the Fe\textsuperscript{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\textsuperscript{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 AlSi 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 57Fe 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\textsubscript{x}Mg\textsubscript{1-x}SiO\textsubscript{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\textsubscript{3}-MgSiO\textsubscript{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\textsuperscript{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 \((x = \text{Fe}/(\text{Fe} + \text{Mg}) = 0.30)\) 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 \(\text{Mg}_2\text{Fe}^{2+}\) 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 \(M_1\) octahedron is nearly regular, but the \(M_2\) octahedron is considerably distorted; it is compressed along its pseudotrigonal axis and elongated along crystallographic \(b\). It is this differential distortion of \(M_1\) and \(M_2\) 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 \(\text{MgSiO}_3-\text{FeSiO}_3\) solid solution series. The average metal-oxygen distances \(M_1\)-\(O\) and \(M_2\)-\(O\) appear to increase towards \(x = 1\). More importantly, the two shortest distances of the \(M_2\) polyhedron are considerably shorter in orthoferrosilite than in hypersthenne \((2.042 \text{ and } 2.013 \text{ Å compared with } 2.066 \text{ and } 2.037 \text{ Å})\). The two largest distances, however, are significantly larger \((2.617 \text{ and } 2.456 \text{ Å compared with } 2.519 \text{ and } 2.405 \text{ Å})\). The trends of the \(M_1\)-oxygen distances are just opposite, although less pronounced. Thus, the \(M_2\) polyhedron becomes more distorted with increasing \(\text{Fe}/(\text{Fe} + \text{Mg})\) ratio while \(M_1\) becomes slightly more regular. This is reflected in an increased separation of the peaks in the \(^{57}\text{Fe}\) hyperfine spectrum due to the increased distinction of the quadrupole splittings at \(M_1\) and \(M_2\) with increasing ratio \(\text{Fe}/(\text{Fe} + \text{Mg})\). 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 \(\text{Fe}^{2+}\) in silicates prefers the more distorted octahedral sites. Morimoto, Appleman, and Evans (1960) found in their structural investigation of a clinopyroxene that \(\text{Fe}^{2+}\) was predominantly at the \(M_2\) sites. The hypersthenne structure \((2x = 0.93)\) determined by Ghose (1965) yielded the following distribution over the sites:

\[
M_1: \quad 0.15 \text{ Fe} + 0.85 \text{ Mg} \\
M_2: \quad 0.10 \text{ Mg} + 0.90 \text{ Fe}
\]

An exception to this rule are the olivines. Birle, Gibbs, Moore, and Smith (1968) did not observe any preference of \(\text{Fe}^{2+}\) for \(M_2\) in spite of the fact that \(M_2\) is more distorted than \(M_1\) in this system.

Ghose (1965) also speculated that the \(M_1\) and \(M_2\) site occupancies in hypersthenne might depend on the temperature. This was subsequently confirmed by the analysis of the \(^{57}\text{Fe}\) hyperfine spectrum of heated hypersthenes (Evans, Ghose, and Hafner 1967, Ghose and Hafner 1967).

**Experimental Techniques**

**Starting materials.** Separation of orthopyroxene from sieved fractions \((90-120 \text{ mesh})\) 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 \(1000^\circ\text{C}\) on a series of natural orthopyroxenes with \(x = 0.88\),
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 $5 \times 10^{-4}$ mm Hg. In some cases smaller amounts of material were used ($\sim 100$ mg).

The heating experiments were made in two different horizontal furnaces, operated at atmospheric pressure. For runs at temperatures lower than $900^\circ$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 ($\sim 2$ cm in length) in a fired pyrophyllite cylinder ($\sim 3$ cm in diameter and $\sim 5$ 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 $5^\circ$C, and the temperatures in both wells were the same. Temperatures listed in Table 2 are considered correct to $\pm 5^\circ$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.

*order-disorder in orthopyroxenes*

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 $(\text{Mg, Fe})_2\text{SiO}_4$ and $\text{SiO}_2$ ($x = 0.88$) 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 Lindley (1965) on FeSiO$_3$.

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$^{+3}$ within similar iron capsules was minimal (see also Lindley 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 $\pm 5^\circ$C, neglecting the pressure effect on the output emf of the thermocouple. Data from Hunsenman and Strong (1966) indicate that the temperature correction may be $\pm 10-20^\circ$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 $1000^\circ$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$^{3+}$/Fe$^{2+}$+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 waveform was of symmetrical, triangular shape. The velocity increment per channel used for the pyroxene spectra was 0.04 mm sec. Due to the symmetrical velocity shape...
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 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 for each spectrum was ~ 5 X 10^4. Z and 3 are the average values. The number of counts per channel into a copper block which was at room temperature to improve the separation of the Fe\textsuperscript{2+} splittings at efficient routine experiments, the absorber, as well as the entire absorbers within a matter of minutes was a crucial factor for the sites (Virgo and Hafner 1968). Since rapid exchange of (ZOO channels per spectrum). In each case, "left" and "right" be exchanged simply by removing a styrofoam plug. Of course, absorber was at atmospheric pressure, mounted with good ther- automatically refilled, in cycles of about 30 minutes. The effect of temperature and Fe\textsuperscript{2+}-Mg) ratio on these param- ers is planned. The hyperfine parameters, isomer shifts and electric quadrupole interactions are not dis- cussed in this paper. The values obtained are in agreement with our previously published results (Evans, Chose and Hafner 1967, Shenoy, Kalvius and Hafner 1969). An additional report on the effect of temperature and Fe/(Fe+Mg) ratio on these param- eters is planned.

Determination of Fe\textsuperscript{2+} site occupancy factors from hyperfine data. In view of the difficulties involved in obtaining quantita- tive ferrous iron-magnesium distributions and site occupancy factors for M1 and M2 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 prob- lem.

The hyperfine spectrum of orthopyroxenes at room temperature consists of two superimposed quadrupole-split doublets which can be assigned to the two sites M1 and M2. Events,

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

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

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

Insufficient Al to make the Si figure equal to 2.

Table 1. Chemical Composition of Orthopyroxenes

<table>
<thead>
<tr>
<th>Specimen</th>
<th>SiO\textsubscript{2}</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>CaO</th>
<th>MgO</th>
<th>FeO</th>
<th>TiO\textsubscript{2}</th>
<th>MnO</th>
<th>Fe\textsubscript{2}O\textsubscript{3}</th>
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</thead>
<tbody>
<tr>
<td>XYZ\textsuperscript{a}</td>
<td>47.38</td>
<td>0.79</td>
<td>0.84</td>
<td>3.83</td>
<td>48.57</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>H-8</td>
<td>48.74</td>
<td>—</td>
<td>—</td>
<td>7.43</td>
<td>42.26</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>BI-9</td>
<td>50.28</td>
<td>—</td>
<td>—</td>
<td>9.44</td>
<td>38.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O-2</td>
<td>49.27</td>
<td>0.23</td>
<td>0.82</td>
<td>11.98</td>
<td>36.55</td>
<td>0.28</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>3209</td>
<td>49.84</td>
<td>0.93</td>
<td>0.93</td>
<td>13.79</td>
<td>33.17</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>37218</td>
<td>49.63</td>
<td>2.16</td>
<td>1.16</td>
<td>15.22</td>
<td>30.69</td>
<td>0.47</td>
<td>0.09</td>
<td>0.30</td>
</tr>
<tr>
<td>37615</td>
<td>51.86</td>
<td>1.03</td>
<td>0.47</td>
<td>20.13</td>
<td>24.48</td>
<td>0.15</td>
<td>0.07</td>
<td>0.58</td>
</tr>
<tr>
<td>115/3</td>
<td>51.13</td>
<td>2.61</td>
<td>0.57</td>
<td>20.70</td>
<td>23.62</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>N-5\textsuperscript{b}</td>
<td>54.49</td>
<td>1.09</td>
<td>1.56</td>
<td>29.13</td>
<td>16.70</td>
<td>0.21</td>
<td>0.33</td>
<td>—</td>
</tr>
<tr>
<td>A-50\textsuperscript{b}</td>
<td>54.87</td>
<td>1.45</td>
<td>1.59</td>
<td>29.33</td>
<td>11.34</td>
<td>0.20</td>
<td>0.23</td>
<td>—</td>
</tr>
</tbody>
</table>

Determination of Fe\textsuperscript{2+} site occupancy factors from hyperfine data. In view of the difficulties involved in obtaining quantita- tive ferrous iron-magnesium distributions and site occupancy factors for M1 and M2 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 prob- lem.

The hyperfine spectrum of orthopyroxenes at room temperature consists of two superimposed quadrupole-split doublets which can be assigned to the two sites M1 and M2. Events,
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$^{3+}$ ($M2$). 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-B to M2 site and A-B 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\textsuperscript{2+}-Mg distribution over relative distribution numbers determined from the intensity ratio of the two doublets. The site occupancy numbers for Fe\textsuperscript{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 z 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\textdegree K the hyperfine spectra are complicated by paramagnetic relaxation effects and, for x larger than ~ 0.7, by magnetic ordering. Therefore, simple intensity studies of the two quadrupole-split doublets are best made at temperatures close to 77\textdegree 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. $\chi^2$ 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 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 $\chi$ in the system Fe\textsuperscript{2+}-Mg,SiO\textsubscript{2} 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 $I \cdot T$. Here, $I$ is the peak height of the Lorentzian and $T$ the width at half height. However, the standard error $\Delta I/\Delta T$ of the widths of an individual orthopyroxene fit is about 10–15 times larger than the standard error $\Delta I/\Delta T$ 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 $I \cdot T$ 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 $\chi^2$ by a few units, but did not affect the peak heights of the Lorentzians at all. Least-squares fits can tolerate large variations in $T$ (taken up in the tails) without significantly altering the peak height.

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

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

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

without applying any additional corrections. The precision of this determination is high (Table 5). 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\textsuperscript{2+} + Mg) calculated from Table 1. The experiments on 3209 at 1000\textdegree C and 500\textdegree C, and 115/3 at 1050\textdegree 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\textdegree 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\textdegree 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\textdegree C for 15 hours; then the temperature was reduced to 500\textdegree 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 $\cdot$ T) ratios and are therefore somewhat different (see p. 70). The temperature settings of those runs were approximately the same.

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\textsuperscript{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
ORDER-DISORDER IN ORTHOPYROXENES

### Table 2. Heating Experiments of Natural Orthopyroxenes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe/(Fe+Mg)</th>
<th>Experimental conditions</th>
<th>Number of Spectra</th>
<th>Line width (FWHH)</th>
<th>Fraction of Fe&lt;sup&gt;2+&lt;/sup&gt; in M&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Site occupancy number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature °C</td>
<td>Duration of heating hours</td>
<td>Pressure kbar</td>
<td>(B&lt;sub&gt;i&lt;/sub&gt;)</td>
<td>(B&lt;sub&gt;j&lt;/sub&gt;)</td>
</tr>
<tr>
<td>XY2-ZSP</td>
<td>0.877</td>
<td>1000</td>
<td>7.5</td>
<td>18.2</td>
<td>1</td>
<td>0.28</td>
</tr>
<tr>
<td>XY2-15P</td>
<td>0.877</td>
<td>1000</td>
<td>16.0</td>
<td>18.3</td>
<td>2</td>
<td>0.28</td>
</tr>
<tr>
<td>H8-20P</td>
<td>0.761</td>
<td>1000</td>
<td>17.0</td>
<td>19.2</td>
<td>1</td>
<td>0.28</td>
</tr>
<tr>
<td>B1-9-21P</td>
<td>0.698</td>
<td>1000</td>
<td>~12.0</td>
<td>18.2</td>
<td>1</td>
<td>0.35</td>
</tr>
<tr>
<td>0-2-34</td>
<td>0.631</td>
<td>1000</td>
<td>~72.0</td>
<td>1</td>
<td>0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>3200-31</td>
<td>0.574</td>
<td>1000</td>
<td>2.1</td>
<td>1</td>
<td>0.30</td>
<td>0.34</td>
</tr>
<tr>
<td>3200-23P</td>
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<td>1000</td>
<td>7.6</td>
<td>1.7</td>
<td>1</td>
<td>0.32</td>
</tr>
<tr>
<td>3200-24P</td>
<td>0.574</td>
<td>1000</td>
<td>10.5</td>
<td>18.7</td>
<td>2</td>
<td>0.32</td>
</tr>
<tr>
<td>3200-32</td>
<td>0.574</td>
<td>1000</td>
<td>10.9</td>
<td>24.0</td>
<td>1</td>
<td>0.31</td>
</tr>
<tr>
<td>3200-33</td>
<td>0.574</td>
<td>1000</td>
<td>24.0</td>
<td>1</td>
<td>0.35</td>
<td>0.38</td>
</tr>
<tr>
<td>3200-25</td>
<td>0.574</td>
<td>1000</td>
<td>72.0</td>
<td>3</td>
<td>0.34</td>
<td>0.37</td>
</tr>
<tr>
<td>3200-27</td>
<td>0.574</td>
<td>1000</td>
<td>169.0</td>
<td>5</td>
<td>0.31</td>
<td>0.35</td>
</tr>
<tr>
<td>3200-35</td>
<td>0.574</td>
<td>800</td>
<td>26.0</td>
<td>1</td>
<td>0.30</td>
<td>0.33</td>
</tr>
<tr>
<td>3200-36</td>
<td>0.574</td>
<td>800</td>
<td>57.0</td>
<td>1</td>
<td>0.29</td>
<td>0.32</td>
</tr>
<tr>
<td>3200-42</td>
<td>0.574</td>
<td>700</td>
<td>24.0</td>
<td>1</td>
<td>0.29</td>
<td>0.32</td>
</tr>
<tr>
<td>3200-44</td>
<td>0.574</td>
<td>700</td>
<td>72.5</td>
<td>1</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>3200-45</td>
<td>0.574</td>
<td>800</td>
<td>109.5</td>
<td>2</td>
<td>0.30</td>
<td>0.33</td>
</tr>
<tr>
<td>3200-49</td>
<td>0.574</td>
<td>900</td>
<td>24.3</td>
<td>1</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td>3200-46</td>
<td>0.574</td>
<td>900</td>
<td>12.8</td>
<td>1</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td>3200-48</td>
<td>0.574</td>
<td>900</td>
<td>29.1</td>
<td>1</td>
<td>0.31</td>
<td>0.33</td>
</tr>
<tr>
<td>3200-49</td>
<td>0.574</td>
<td>900</td>
<td>72.5</td>
<td>1</td>
<td>0.26</td>
<td>0.31</td>
</tr>
<tr>
<td>3200-54</td>
<td>0.574</td>
<td>900</td>
<td>71.7</td>
<td>1</td>
<td>0.37</td>
<td>0.34</td>
</tr>
<tr>
<td>3200-55</td>
<td>0.574</td>
<td>900</td>
<td>170.2</td>
<td>1</td>
<td>0.33</td>
<td>0.34</td>
</tr>
<tr>
<td>3200-56</td>
<td>0.574</td>
<td>900</td>
<td>169.1</td>
<td>1</td>
<td>0.31</td>
<td>0.34</td>
</tr>
<tr>
<td>3200-32</td>
<td>0.574</td>
<td>900</td>
<td>15.0</td>
<td>1</td>
<td>0.32</td>
<td>0.36</td>
</tr>
</tbody>
</table>

* The first part of the sample number refers to the mineral or rock number; the latter part refers to the experiment.

### Notes
- Atomic fractions (see text).
- Average of all spectra taken.
- d The sum of the fractions of Fe<sup>2+</sup> in M<sup>1</sup> and M<sup>2</sup> is equal to one.
- e Sealed in quartz tubes, previously evacuated to <3x10^-4 mm Hg.

Phase. But single-crystal studies indicate the presence of an exsolved phase in these cases. Ideally, the proportion of Fe<sup>2+</sup> in M<sup>1</sup> and M<sup>2</sup> should be recast in terms of the total number of sites involved in the exchange reaction. Although it is reasonable to assume that Fe<sup>3+</sup> and Mg from the chemical analyses will be the major occupants of the M<sup>2</sup> and M<sup>1</sup> 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<sup>2+</sup> in M<sup>1</sup> and M<sup>2</sup> in terms of 2·Fe/(Fe+Mg) of the mineral according to formula units (Mg,Fe)<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> 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 M<sup>1</sup> and M<sup>2</sup> are accomplished in a short time even at low temperatures. Data on the heating experiments on the natural sample 2009 at atmospheric pressure and at 1000, 800, 700, 600, and 500°C are plotted in Figure 2. A steady value for Fe<sup>2+</sup> in M<sup>1</sup> and M<sup>2</sup> 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectrum</th>
<th>Line Widths (FWHH)</th>
<th>Intensities (referred to sum of I)</th>
<th>Fraction of Fe$^{2+}$</th>
<th>Site occupancy numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Gamma(B_1)$</td>
<td>$\Gamma(B_2)$</td>
<td>$\Gamma(A_2)$</td>
<td>$\Gamma(A_4)$</td>
</tr>
<tr>
<td>3209-27</td>
<td>V37</td>
<td>0.2970</td>
<td>0.3400</td>
<td>0.3159</td>
<td>0.2900</td>
</tr>
<tr>
<td>3209-27</td>
<td>V210</td>
<td>0.3207</td>
<td>0.3620</td>
<td>0.3425</td>
<td>0.3097</td>
</tr>
<tr>
<td>3209-27</td>
<td>V225</td>
<td>0.2778</td>
<td>0.3351</td>
<td>0.3028</td>
<td>0.2828</td>
</tr>
<tr>
<td>3209-27</td>
<td>V226</td>
<td>0.2976</td>
<td>0.3206</td>
<td>0.3022</td>
<td>0.2850</td>
</tr>
<tr>
<td>3209-27</td>
<td>V233</td>
<td>0.3650</td>
<td>0.3919</td>
<td>0.3680</td>
<td>0.3516</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.3116</td>
<td>0.3499</td>
<td>0.3262</td>
<td>0.3038</td>
</tr>
<tr>
<td>S.E.</td>
<td></td>
<td>±0.0299</td>
<td>±0.0248</td>
<td>±0.0255</td>
<td>±0.0257</td>
</tr>
<tr>
<td>3209</td>
<td>V36</td>
<td>0.2645</td>
<td>0.3097</td>
<td>0.3059</td>
<td>0.3027</td>
</tr>
<tr>
<td>3209</td>
<td>V100</td>
<td>0.2876</td>
<td>0.3053</td>
<td>0.2969</td>
<td>0.2773</td>
</tr>
<tr>
<td>3209</td>
<td>V175</td>
<td>0.2987</td>
<td>0.3396</td>
<td>0.3307</td>
<td>0.3106</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.2836</td>
<td>0.3182</td>
<td>0.3111</td>
<td>0.2968</td>
</tr>
<tr>
<td>S.E.</td>
<td></td>
<td>±0.0143</td>
<td>±0.0152</td>
<td>±0.0143</td>
<td>±0.0144</td>
</tr>
</tbody>
</table>

The precision of hyperfine peak heights and widths of orthopyroxene 3209 is plotted in Figure 2 for a function of time of heating. The fraction of Fe$^{2+}$ in $M_1$ of the unheated sample is 22 percent.

![Figure 2](image2.png)

![Figure 3](image3.png)

...
passing through the points, \( X_1 = X_2 = 0 \) and \( X_1 = X_2 = 1 \). This accords with ideal distribution ("ideal solution model") for \( \text{Fe}^{2+} \) and \( \text{Mg} \) 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 \( \text{Fe}^{2+} \) 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 \((x < 0.63)\) 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 \((x = 0.761 \text{ and } x = 0.877)\) 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 \( \text{Fe}^{2+} \),\( \text{Mg} \) distribution is still unknown. However, it is known that orthopyroxenes with compositions within this region \((-0.7 < x < 1.0)\) 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 \( \text{Fe}(1)-O(2)-\text{Fe}(2) \) or \( \text{Fe}(1)-O(5)-\text{Fe}(2) \). The excess stabilization energy of

\[
[\text{Fe}^{2+}] (\text{Fe}^{2+} + \text{Mg}) = 0.574.
\]

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

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.

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 \( 0 \leq x \leq 0.574 \) 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 \( \text{Fe} \)-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 \( 0 \leq x \leq 0.5 \), the system behaves very nearly ideal.

Also plotted in Figure 5 is the curve representing the distribution of \( \text{Fe}^{2+} \) and \( \text{Mg} \) 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.
Free energy of the exchange reaction. The standard Gibbs free energy change, $\Delta G^o_r$, for the disordering reaction,

$$\text{Mg}(1) + \text{Fe}^{2+}(2) \rightarrow \text{Fe}^{2+}(1) + \text{Mg}(2) \quad (4)$$

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

$$\Delta G^o_r = -RT \ln k \quad (5)$$

Values of $\Delta G^o_r$ 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, $\Delta G^o_r$ 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 $\Delta G^o_r$ are presumably not consistent with ideal distribution but to date there are insufficient data to verify a significant deviation. The average value of $\Delta G^o_r$ 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, $\text{MgSiO}_3=835 \times 10^{-24} \text{cm}^3$ and $\text{FeSiO}_3=876 \times 10^{-24} \text{cm}^3$ (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-1SP ($x=0.877$) 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

$$\text{FIG. 6. Fe}^{2+},\text{Mg order-disorder as a function of temperature for the sample 3209 \ (Fe^{2+}/(Fe^{2+}+Mg) = 0.574). Vertical dashed line refers to the site occupancy number (X2) for the natural sample 3209.}$$
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 $x=\text{Fe}/(\text{Fe}+\text{Mg})$ 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 $X_2$ 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 $\text{Fe}^{2+}$-$\text{Mg}$ disorder in either ortho- or clinopyroxenes. Consequently the strong preference of $\text{Fe}^{2+}$ 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 $\text{Fe}^{2+}$ 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 $\Delta G_k^o$ over the experimental temperature range is assumed. The time rate of change of $\text{Fe}^{2+}$ at $M2$ at constant temperature is

$$
\frac{-dX_2}{dt} = -K_{12}X_1(1 - X_3) + K_{21}X_2(1 - X_1)
$$

where $X_1$ and $X_2$ are the site occupancy numbers of $\text{Fe}^{2+}$ 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 $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$ ratio of the orthopyroxene and relating the rate constants $K_{12}$ and $K_{21}$ to the equilibrium constant

$$k = \frac{K_{21}}{K_{12}} = \frac{X_1(1 - X_3)}{X_2(1 - X_1)}$$

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

$$(1 - k)X_2^o + X_2(k(2X - 1) - 2X - 1) + 2x \geq 0$$

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

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

where

$$a = \left[ k \cdot t (x - \frac{1}{2})^3 + k \right] / k_{-1}$$

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

and

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

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

In equation (9), $\Delta t$ is the time interval and $X_2'$ and $X_2'_{o}$ are the values of $X_2$ at the upper and lower limits of the integration. $X_2'_{o}$ is the initial site occupancy number of $\text{Fe}^{2+}$ 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
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 ($K_{21} \Delta t$) is taken as a variable. The following values were approximately determined in this way,

$$K_{21}(500^\circ C) \approx 6 \times 10^{-6} \text{ (min}^{-1});$$

$$K_{21}(1000^\circ C) \approx 1 \times 10^{-4} \text{ (min}^{-1}).$$

These data can be used to determine the activation energy ($E_{aD}$) 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:

$$K_{21} = A \exp \left(-\frac{E_{aD}}{RT}\right)$$

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

$$E_{aD} \approx 20 \text{ kcal} \text{ per mole (formula unit } (\text{Fe,Mg})_2\text{Si}_2\text{O}_6).$$

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 $K_{31}$ 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 $E_{ao}$, for ordering

$$E_{ao} = 14.8 \text{ kcal}$$

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

$$\frac{d \ln k}{dT} = \frac{\Delta G^o_k}{RT^2},$$

and from equation (10) that

$$\frac{d \ln k}{dT} = \frac{E_{ao} - E_{aD}}{RT^2}.$$ 

Thus we find

$$E_{ao} = E_{aD} - \Delta G^o_k$$

In this way, the estimated activation energy of ordering is

$$E_{ao} = 16.5 \text{ kcal}.$$

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.

![Figure 8](image-url)
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

$$K_{12}(500°C) = 6 \times 10^{-4} \text{ (min)}^{-1}.$$  

Consequently, the time to reach 50 percent of the equilibrium value would be $\sim 15$ days. The time for 95 percent would be $\sim 145$ 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-S2 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 $\Delta G^o_x$ for the Fe$^{2+}$, Mg exchange in orthopyroxenes with exchange energies of ferrous and magnesium ions in other systems. The standard interaction enthalpy for Mg and Al exchange between octahedral and tetrahedral sites in spinel (MgAl$_2$O$_4$), 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$_2$O$_4$, MgGa$_2$O$_4$) however, have considerably lower standard interaction enthalpies which are of about the same magnitude as $\Delta G^o_x$ 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 $\sim 3.1$ kcal for a hypothetical Fe$^{2+}$,Mg exchange in spinels, Fe$^{2+}$ preferring the (distorted) octahedral sites.

It is difficult to compare $\Delta G^o_x$ with that of the Al,Si interexchange 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 $M1$ and $M2$ 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

$$\text{Al(I)} + \text{Si(II)} \rightarrow \text{Al}_a \text{Si}_b \text{Si}_a \text{Si}_b (I) + \text{Al}_b \text{Si}_a \text{Si}_b (I).$$ \hspace{1cm} (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 $M1$ and $M2$ 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)$_4$O$_8$ framework and related shifts of Na and K ions to satisfy charge balance requirements. The exchange of Fe$^{2+}$ and Mg between $M1$ and $M2$ 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 $\sim 90$ 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 crystallisation 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 tempera-
tures attained (Ghose and Hafner 1967). A more detailed analysis of rapidly cooled natural orthopyroxenes with metastable, partially ordered Fe<sup>2+</sup>-Mg distribution would be of considerable interest.

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