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Mg^{2+}-Fe^{2+} ORDER-DISORDER AND THE THERMODYNAMICS OF THE ORTHOPYROXENE, $(Mg,Fe)_2Si_2O_6$ CRYSTALLINE SOLUTION

PART I. A ^{57}Fe MÖSSBAUER RESONANCE STUDY OF THE Mg^{2+}-Fe^{2+} DISTRIBUTION IN ORTHOPYROXENES AT 500, 600, 700 AND 800°C

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MAY 1970

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GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

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ABSTRACT

The distribution of Mg^{2+} and Fe^{2+} between M1 and M2 sites in orthopyroxene at 500, 600, 700 and 800°C determined by Mössbauer resonance spectroscopy can be expressed by

$$\ln K_D - \ln K_a = \frac{W^{M2}}{RT}(1 - 2X^{M2}_{Fe}) - \frac{W^{M1}}{RT}(1 - 2X^{M1}_{Fe})$$

where K_D is

$$X^{M1}_{Fe}(1 - X^{M2}_{Fe})/X^{M2}_{Fe}(1 - X^{M1}_{Fe}),\ X_{Fe}$$

the mole fraction $Fe^{2+}/(Fe^{2+} + Mg^{2+})$, W an adjustable constant, and K_a the equilibrium constant for the ion-exchange reaction

$$Fe^{2+}(M2)^{2+} + Mg^{2+}(M1) \rightleftharpoons Fe^{2+}(M1)^{2+} + Mg^{2+}(M2) \qquad \text{(a)}$$

The thermodynamic parameters corresponding to the isotherms are:

$T°C$	$\underline{K}_a$	$\underline{W}^{M1}$ (cal/mole)	$\underline{W}^{M2}$ (cal/mole)	$\Delta \underline{G}_a^0$ (cal/mole)
500	0.1882	2791	1099	2565
600	0.2516	2244	1397	2394
700	0.2836	1946	1295	2436
800	0.2780	1524	0921	2729

'Partial' thermodynamic functions of mixing of Mg^{2+}-Fe^{2+} on the individual sites are calculated, using thermodynamic relations established by Guggenheim (1967) for the 'simple mixture' model.

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Mg^{2+}-Fe^{2+} ORDER-DISORDER AND THE THERMODYNAMICS OF THE ORTHOPYROXENE, $(Mg,Fe)_2Si_2O_6$ CRYSTALLINE SOLUTION

PART I. A ^{57}Fe MÖSSBAUER RESONANCE STUDY OF THE Mg^{2+}-Fe^{2+} DISTRIBUTION IN ORTHOPYROXENES AT 500, 600, 700 AND 800°C

INTRODUCTION

Long-range order-disorder phenomenon in alloy phases has been studied extensively. Alloys are characterized, first by a pattern of sites occupied by atoms irrespective of their chemical nature and second by the distribution of the atoms among these sites. This distribution may vary continuously as a function of temperature without a phase transformation. Above a certain critical temperature, the distribution is completely random. With lowering of temperature ordering sets in abruptly, at first increasing rapidly, but becoming complete only as absolute zero is approached.

Long-range order-disorder phenomenon in ferromagnesian silicates, e.g., olivine $(Fe,Mg)_2SiO_4$, orthopyroxene $(Fe,Mg)_2Si_2O_6$, cummingtonite $(Fe,Mg)_7Si_8O_{22}(OH)_2$, etc. differ from that in alloys in several important respects; first, as opposed to alloys, only a certain number of the cations take part in the site exchange while the silicate framework remains more or less undisturbed; second, usually complete solid solution exists between the Mg and Fe end-members and third, there may not be any critical temperature above which complete order is attained. A crystalline solution $(A_x B_{1-x})Z$ may have different cations A and B occupying two different structural sites α and β, and Z the silicate framework which does not change compositionally. Following Dienes (1955) and Mueller (1961, 1962) the order-disorder phenomenon can be treated as an ion-exchange reaction:

$$A(\alpha) + B(\beta) \rightleftharpoons B(\alpha) + A(\beta) .$$

The order-disorder phenomenon as a function of temperature and chemical composition then can be interpreted in terms of the thermodynamics of homogeneous phase equilibria as developed by Gibbs. Orthopyroxene $(FeMg)_2Si_2O_6$, a widely occurring ferromagnesian mineral, provides such a simple case. Here Fe^{2+} and Mg^{2+} can distribute themselves in different amounts between two structural sites M1 and M2, while rest of the silicate framework remains virtually unchanged. The structure of orthopyroxene consists of infinite single silicate chains held together by infinite octahedral strips. Fe^{2+} and Mg^{2+} ions occur within this octahedral strip, made up of M1-0 and M2-0 octahedra. Since the Fe^{2+}-Mg^{2+} exchange between the M1 and M2 sites takes place within a plane (parallel to the bc plane), only octahedral M-0 bonds are broken. As a result, at high temperatures the exchange process is very rapid and the activation energy is comparatively low. Hence above 500°C the equilibrium Fe^{2+}-Mg^{2+} distribution between the M1 and M2 sites can be attained in a matter of weeks. The Mg^{2+}-Fe^{2+} distribution found in orthopyroxenes from metamorphic, plutonic and volcanic rocks, as well as meteorites reflect past thermal history, when temperatures were sufficiently high for Mg^{2+}-Fe^{2+} exchange to take place. To be able to interpret the cooling history of such orthopyroxenes on the basis of the Mg^{2+}-Fe^{2+} distribution data, we must know the equilibrium Mg^{2+}-Fe^{2+} distribution at various temperatures as well as the kinetics of the ordering process.

The first purpose of this paper is to analyze the temperature and compositional dependence of Mg^{2+}-Fe^{2+} order-disorder in orthopyroxene thermodynamically. This is based on experimental data on the site occupancy fraction of Mg^{2+}-Fe^{2+} at the M1 and M2 sites in orthopyroxenes of various composition heated at 500, 600, 700 and 800°C and the use of solution models to explain the mixing of Fe^{2+} and Mg^{2+} on the individual sites. The study of the solution behavior at the sites makes it possible to obtain a thermodynamic model of the orthopyroxene crystalline solution as a whole. Using such a model, thermodynamic functions of mixing of the cations Fe^{2+} and Mg^{2+} in the crystal can be calculated. Since the changes in the silicate framework as a function of temperature and composition are not considered, these functions of mixing, namely, free energy, enthalpy and entropy, are not necessarily the same as those found by calorimetric experiments on the solution of $MgSiO_3$ and $FeSiO_3$, but they would be comparable in magnitude. In part one of this paper, the results of the ^{57}Fe Mössbauer resonance experiments on the determination of the Mg^{2+}-Fe^{2+} site occupancy factors at the M1 and M2 sites are presented. The mixing of Mg^{2+}-Fe^{2+} on the individual sites as a function of composition and temperature is interpreted in terms of Guggenheim's (1967) "simple mixture" model. In part two, the solution theories are explored further and the activity-composition relationships on the sites as well as in the crystal as a whole are established. Finally, these results are used to interpret inter-crystalline cation distribution and other phenomena.

PREVIOUS WORK

The thermodynamic significance of the distribution of cations among coexisting mineral phases was initially discussed by Ramberg (1944, 1952). Such heterogeneous distributions, now being studied intensively by many petrologists, are related to internal reactions within individual mineral phases. Experimental evidence of homogeneous reactions within ferromagnesian silicates such as cummingtonites and orthopyroxenes were presented by Ghose and Hellner (1959) and Ghose (1961, 1965). These results encouraged thermodynamic treatment of the intra-crystalline distribution of cations on nonequivalent sites and of the heterogeneous equilibria, i.e., the distribution of cations between two or more coexisting phases by Mueller (1961, 1962, 1967, 1969), Matsui and Banno (1965), Banno and Matsui (1966, 1967), Grover and Orville (1969), and Thompson (1969).

Orthopyroxenes have been studied extensively by X-ray diffraction as well as by the Mössbauer resonance technique and the problem of intra-crystalline distribution over M1 and M2 sites is well defined. By X-ray diffraction Ghose (1965) found that Fe^{2+} is preferred strongly at the M2 site and Mg^{2+} at the M1 site. He also predicted the temperature dependence of the site occupancies which was confirmed later by Evans, Ghose and Hafner (1967) and Ghose and Hafner (1967) using the Mössbauer resonance technique. The Mössbauer technique has been used also by Bancroft, Burns and Howie (1967), Marzolf, Dehn and Salmon (1967) and Dundon and Walter (1967) to determine Mg^{2+}-Fe^{2+} distribution in plutonic and volcanic, synthetic and meteoritic orthopyroxenes respectively. Virgo and Hafner (1969) determined the kinetics of Mg^{2+}-Fe^{2+} order-disorder in an intermediate orthopyroxene ($X_{Fe}^{Opx} = 0.575$) and the Mg^{2+}-Fe^{2+} distribution isotherm at 1000°C. Ghose and Hafner (1967) and Virgo and Hafner (1969) presented the order-disorder relations or the intra-crystalline distribution by an ion-exchange equation for Fe^{2+} and Mg^{2+} between M1 and M2 sites.

From these investigations (principally Virgo and Hafner, 1969) it is now generally established that in orthopyroxene (1) the ion-exchange takes place between 480°C to 1000°C and (2) the activation energies required for ordering and disordering are relatively low and (3) the ion-exchange is a rapid process. Ghose and Hafner (1967) and Virgo and Hafner (1969, 1970) assumed that the mixing of Mg^{2+}-Fe^{2+} at the M1 and M2 sites is ideal. This assumption was found to be valid in the case of Mg^{2+}-Fe^{2+} distribution isotherm at 1000°C for $Fe^{2+}/(Fe^{2+} + Mg^{2+})$ in orthopyroxene $X_{Fe}^{Opx} < 0.70$ determined by Virgo and Hafner (1969). They have also determined Mg^{2+}-Fe^{2+} distribution between M1 and M2 sites in one orthopyroxene ($X_{Fe}^{Opx} = 0.575$) at 500, 600, 700, 800 and 1000°C. On the basis of these data on one sample, they extrapolated Mg^{2+}-Fe^{2+} distribution isotherms for 500, 600, 700 and 800°C assuming the ideal solution model for the individual sites to be valid down to 500°C. Virgo and Hafner (1970) also determined Mg^{2+}-Fe^{2+} distribution in a large number of metamorphic and plutonic orthopyroxenes. These distribution data show a small range of scatter, indicating that these orthopyroxenes were presumably quenched around 500°C. However, these data points straddle across the hypothetical distribution isotherms from 500 to 1000°C based on the ideal solution model (Virgo and Hafner, 1970, Figure 1). Obviously the mixing on the M1 and M2 sites is not ideal at lower temperatures. Saxena and Ghose (1970) used the regular solution model to interpret these data and the success of this approach prompted the determination of complete Mg^{2+}-Fe^{2+} distribution isotherms at various temperatures in orthopyroxene.

THERMODYNAMICS

The following abbreviations and symbols are used:

Opx, orthopyroxene

$\underline{X}_{Fe}^{Opx}$, mole fraction $Fe^{2+}/(Fe^{2+} + Mg)$ in the crystal as a whole

$\underline{X}_{Fe}^{M1}$, site occupancy factor or the atomic ratio $Fe^{2+}/(Fe^{2+} + Mg)$ on site M1 and similarly $\underline{X}_{Fe}^{M2}$

$\underline{R}$, gas constant, $\underline{T}$, absolute temperature

$\underline{K}$, equilibrium constant, $\underline{K}_D$, distribution coefficient

$\underline{G}_a$, free energy of the reaction (a)

$\underline{W}^{M1 (or\ M2)}$, an adjustable constant referred to the site M1 (or M2)

$\underline{f}_{Fe}^{M1 (or\ M2)}$, partial activity coefficient for M1 (or M2)

The ion-exchange between the M1 and M2 sites in orthopyroxene, $(Mg,Fe)_2Si_2O_6$ can be written as:

$$Fe^{2+}(M2) + Mg^{2+}(M1) \rightleftarrows Fe^{2+}(M1) + Mg^{2+}(M2) \qquad (a)$$

The equilibrium constant for the above reaction is

$$\underline{K}_a = \frac{\underline{X}_{Fe}^{M1}(1 - \underline{X}_{Fe}^{M2})}{(1 - \underline{X}_{Fe}^{M1})\underline{X}_{Fe}^{M2}} \frac{\underline{f}_{Fe}^{M1}\ \underline{f}_{Mg}^{M2}}{\underline{f}_{Mg}^{M1}\ \underline{f}_{Fe}^{M2}} \qquad (1)$$

and the free energy is $\Delta\underline{G}_a^0 = -RT\ln\underline{K}_a$.

As indicated by Thompson (1969) and Mueller and Ghose (1970), it is not possible to define chemical potential of a cation on different sites in a crystal. Therefore $\underline{f}$ is called the partial activity coefficient here. Equation (1) is written in analogy with the heterogeneous equilibrium distribution of a species between two non-ideal mixtures. M1 and M2 sites are treated as two interpenetrating subsystems; and the thermodynamic relations established for macroscopic systems are used directly. The physical significance of the partial thermodynamic functions of mixing with respect to the sites is not yet clear, but by virtue of the definiteness of the site occupancy factors or the mole fractions at each site, these partial quantities are also definite.

We define a factor $\underline{W}$ such that

$$\ln \underline{f}_{Fe}^{M1} = \frac{\underline{W}^{M1}}{\underline{RT}}(1 - \underline{X}_{Fe}^{M1})^2 \qquad (2)$$

This is analogous to the equation (818.6) derived by Fowler and Guggenheim (1939) in connection with the 'strictly regular' solution model. This crude treatment implies a completely random distribution of the cations within a phase and the change of entropy on mixing is the same as for the ideal solution. The factor W referred to as 'the interchange energy' is independent of temperature in Guggenheim's (1952) original model. In the present paper W is used as an adjustable constant to fit the experimental data, which is not necessarily independent of temperature. This treatment is consistent with Guggenheim's (1967) latest ideas where he calls such solutions 'simple mixtures'.

Substituting the values of f from (2) in (1) for K_a we obtain an expression as used by Mueller (1964) or to facilitate computation in a logarithmic form as used by Saxena (1969)

$$\ln K_D - \ln K_a = \frac{W^{M2}}{RT}(1 - 2X^{M2}_{Fe}) - \frac{W^{M1}}{RT}(1 - 2X^{M1}_{Fe}) \qquad (3)$$

where K_D is the distribution coefficient,

$$\frac{X^{M1}_{Fe}\,(1 - X^{M2}_{Fe})}{X^{M2}_{Fe}\,(1 - X^{M1}_{Fe})}.$$

If the intra-crystalline distribution data are in close agreement with (3), the 'partial' excess thermodynamic functions of mixing on individual sites can be evaluated, which are analogous to those of the macro-system. The 'partial' excess functions of mixing for M1, for example, are

$$\underline{G}^{E} = \underline{X}_{Fe}^{M1} (1 - \underline{X}_{Fe}^{M1}) \underline{W}^{M1} \qquad \underline{W}^{M1} = \underline{W}(T, P) \tag{4}$$

$$- \underline{S}^{E} = \underline{X}_{Fe}^{M1} (1 - \underline{X}_{Fe}^{M1}) \frac{\partial \underline{W}^{M1}}{\partial T} \tag{5}$$

$$\underline{H}^{E} = \underline{X}_{Fe}^{M1} (1 - \underline{X}_{Fe}^{M1}) \underline{W}^{M1} - T \frac{\partial \underline{W}^{M1}}{\partial T} \tag{6}$$

EXPERIMENTAL

Chemical Analysis of the Samples

All pyroxene samples used as starting material were separated from various metamorphic rocks. Separates were hand picked under the microscope to achieve a purity of 98 percent or better. Chemical analyses of these samples, eight of which are new, are listed in Table 1. The microprobe analyses were made by using natural pyroxene standards and the data were processed using the Bence and Albee (1968) correction method. The wet chemical analysis of the sample XYZ is taken from Ramberg and DeVore (1951).

Microscopic examination of the pyroxenes did not show zoning or any significant amount of unmixing. Several grains from each sample were analyzed by the microprobe to check for homogeneity in chemical composition, particularly for iron and magnesium. The grain to grain compositional variation was less than one percent of FeO or MgO. Sample 7, however, was found to be somewhat heterogeneous, where FeO varied within 2 percent.

Heating Experiments

About 50 to 100 mg. of the orthopyroxene sample was loaded in a gold capsule and heated in internally heated cold-seal pressure vessels under an argon pressure of 0.5 to 1.5 Kb. The pressure was measured using bourdon tube gauge. The gold capsules were left open so that argon could pass freely through the capsule during heating. The temperature was measured by using sheathed chromel-alumel thermocouple calibrated at one atmosphere at melting point (800.5°C) of NaCl. It was controlled to within ±3°C and the accuracy in measurement is better than ±10°C. The temperature was monitored continuously on a Honeywell multichannel potentiometer with continuous print-out.

The duration of the heating runs for a close approach to the Mg^{2+}-Fe^{2+} exchange equilibrium was estimated on the basis of the kinetic experiments on orthopyroxenes (Virgo and Hafner, 1969). The orthopyroxene samples were heated at 500° and 600°C for periods of three and two weeks respectively and at 700 and 800°C for a period of one week. In all cases, the heating runs were much longer than that required for equilibration (Virgo and Hafner, 1969, Figure 2). The heated samples were quenched by blowing cold air on the pressure vessel. The temperature dropped down to below 300°C within seconds. The orthopyroxene grains were removed from the gold capsules and examined under the microscope for any possible oxidation.

Mössbauer Resonance Experiments

The Mössbauer resonance spectrometer was of the constant acceleration type. The Doppler shift between the moving source and the stationary absorber was applied by means of an electromechanical drive of the Kankeleit type. 50 mCi ^{57}Co diffused into copper foil was used as the source for the 14.4 keV gamma rays. The absorbers were prepared by mixing 50—100 mg of the finely powdered orthopyroxene with 500 mg of lucite and pressing into a 1" diameter disc. The thickness amounted to about 3—5 mg of Fe per cm^2. All spectra were recorded with the absorbers cooled to liquid nitrogen temperature. For this purpose, a vertical stainless steel cryostat (built by Austin Science Associates) was used so that horizontal transmission geometry could be maintained. The temperature achieved this way must be in the vicinity of 77°K, though an exact measurement of the absorber temperature has not been made. Compared to the room temperature spectra, at liquid nitrogen temperature, the quadrupole splitting of the outer doublet $A_1 - B_1$ due to ^{57}Fe at M1 increases considerably, while the splitting of the inner doublet $A_2 - B_2$ due to ^{57}Fe at M2 remains virtually the same (Shenoy, Kalvius and Hafner, 1969). This results in a considerable improvement in the resolution of the spectra and hence in the calculation of area ratios and site occupancy factors. A 0.004" aluminum foil was placed between the source and the absorber to filter the copper X-rays. The transmitted gamma ray pulses were counted by means of a proportional counter filled with 90% Krypton and 10% methane at 1 atm. The multi-channel analyzer was operated in the time mode.

The pulses were accumulated in 512 channels. In general about 2.5×10^6 counts per channel were recorded for each spectrum. Average counting time was about 20 hours. The spectrometer has been calibrated against a standard Fe-foil of 99.999% purity provided by J. J. Spijkermann of the National Bureau of Standards. Only the inner four lines were used for calibration. The measured line widths of the iron lines are: inner pair 0.26 mm/sec., outer pair 0.28 mm/sec. The calibration spectra were taken every week. No detectable drift in the spectrometer has been found.

A least squares program was used on the IBM 360/75 computer to fit Lorentzian curves to the two overlapping doublets of the orthopyroxene spectra without any constraints. The number of variable parameters was 13, i.e., 3 per absorption peak and 1 for the off-resonant baseline. The chi-square values ranged between 150-300. The calculated standard errors in the line-widths at half-intensity (half-widths) were consistently much higher than those for the line-intensities. However, the calculated area ratios fall on a smooth curve when plotted against the Fe/(Fe + Mg) ratio of the total crystal. This indicates high level of consistency in our results. Absolute limits to the calculated peak areas cannot be ascertained. Incidentally, it was found that for lower counting statistics (1×10^6 counts per channel or less) the calculated errors for half-widths are considerably larger and area ratio vs Fe/(Fe + Mg) ratio of the crystal yields a plot with much greater scatter.

The peak nomenclature is as follows: lower velocity peaks, A1 and A2; higher velocity peaks B2 and B1. The inner pair, A2 - B2 from ^{57}Fe at the M2 site is always more intense than the outer pair, A1 - B1 from ^{57}Fe at the M1 site. This site assignment is unambiguous and is based on the known preference of Fe for the M2 site (Ghose, 1965). The site occupancy factors were calculated assuming the recoilless fraction at the M1 and M2 sites to be equal. The site occupancy factor for M1, for example, is given by

$$\left[I_{A1}\times\Gamma_{A1}+I_{B1}\times\Gamma_{B1}\right]\Big/\left[I_{A1}\times\Gamma_{A1}+I_{A2}\times\Gamma_{A2}+I_{B1}\times\Gamma_{B1}+I_{B2}\times\Gamma_{B2}\right]\times 2\,Fe^{2+}/(Fe^{2+}+Mg^{2+}) \ ,$$

where I is the intensity Γ, half width of a Mössbauer resonance peak. Calculated this way, the site occupancy factors for M1 and M2 are the mole fraction $Fe^{2+}/(Fe^{2+} + Mg^{2+})$ at each site.

RESULTS

Table 2 lists the results of the Mössbauer experiments on the heated orthopyroxenes. Figure 1 shows the distribution of Fe^{2+} and Mg^{2+} between M1 and M2 sites at 500, 600, 700 and 800°C. The curves represent least squares fit of the data to equation (3). The data for $\underline{K}_a$, $\underline{W}^{M1}$, $\underline{W}^{M2}$ and $\Delta\underline{G}^0_a$ for the four Mg-Fe distribution isotherms are listed in Table 3 and are plotted against 1/T in Figure 2.

DISCUSSION

Site Occupancy Factors

For calculating the site occupancy factors $\underline{X}_{Fe}^{M1}$ and $\underline{X}_{Fe}^{M2}$, cations such as Al^{3+}, Ti^{4+}, Mn^{2+} and Ca^{2+} present in low concentration were not considered, since there is no unambiguous way of assigning these cations to either M1 or to M2 sites. Ca^{2+} could be restricted to the M2 site but the usual occurrence of microscopic or submicroscopic exsolution lamallae of calcium rich pyroxene makes this procedure dubious. Distribution of Mn^{2+} between M2 and M1 (with a preference for M2) is not known. Likewise, Al^{3+} could be present not only in the octahedral M1 and M2 sites, but also in the T1 and T2 tetrahedral sites.

In six of the nine samples used, the total of the ions Al^{3+}, Ti^{4+}, Mn^{2+} and Ca^{2+} was less than 4 percent of the total of Fe^{2+} and Mg^{2+}. Further as these ions are distributed between M1 and M2, and in the case of Al^{3+} and Ti^{4+} among M1, M2, T1 and T2, they are not likely to affect the use of a binary solution model significantly. The influence of these additional components can only be evaluated when the present results are compared with those on pure synthetic Fe^{2+}-Mg^{2+} pyroxenes.

Distribution of Fe^{2+} and Mg^{2+}

The deviation of the solution behavior at each site from the ideal solution model is shown in Figure 3, where ln $\underline{K}_D$ is plotted against $\underline{X}_{Fe}^{Opx}$. If the mixing is ideal on both sites, the curves drawn in this figure would be straight lines parallel to the abscissa. Virgo and Hafner (1970) noted the non-ideal behavior at the sites also and discussed the isotherms as being ideal in the Mg-rich part and non-ideal in the Fe-rich part. From the present results it is obvious that a non-ideal model is needed, which is compatible with the entire set of isotherms.

The isotherm at 500°C in Figure 1 is very similar to the curve for the Mg^{2+}-Fe^{2+} distribution data from metamorphic orthopyroxenes (Saxena and Ghose, 1970). The free energies of ion exchange reaction (a) do not change significantly with change in temperature (Table 3). These values are less than those determined by Virgo and Hafner (1969), since the non-ideality effect on the sites has been taken into account. Note that the $\Delta \underline{G}_a^0$ at 500°C does not differ appreciably from the values at other temperatures as it did in Virgo and Hafner's (1969) work.

All the isotherms shown in Figure 1 cross at about $\underline{X}_{Fe}^{Opx} = 0.86$ (sample 9). The Mg-Fe^{2+} distribution data for sample 9 at different temperatures are very similar. This means that there is little change in the site occupancy factors $\underline{X}_{Fe}^{M1}$ and $\underline{X}_{Fe}^{M2}$ in the temperature range of 500 to 800°C for this sample. Although small changes in $\underline{X}_{Fe}^{M1}$ and $\underline{X}_{Fe}^{M2}$ with temperature in this compositional range cannot be determined reliably with the present experimental technique, the fact that the isotherms for 500°C crosses the isotherm for 800°C may be meaningful on the basis of the consistency of the entire distribution model. Such crossover of distribution isotherms is not unusual when one or both of the coexisting phases are non-ideal solutions (Saxena, 1969). However, the discussion of this aspect should be postponed until more experimental data in this composition range are available.

Mixing on the M1 Site

The energy parameter $\underline{W}^{M1}$ decreases with increasing temperature, as shown in Figure 2. The linear relation can be approximated by:

$$\ln \underline{W}^{M1} = 20.0377 - 1.818 \ln \underline{T} \qquad (7)$$

where $\underline{W}^{M1}$ is measured in cal/mole. The decrease in $\underline{W}^{M1}$ with increasing temperature indicates that the mixing of Mg and Fe^{2+} on the M1 site approaches ideality with increase in temperature. Using equations (4, 5, 6) the partial excess free energy of mixing, partial excess entropy of mixing and partial excess heat of mixing have been computed. Variation of these partial functions with $\underline{X}^{M1}_{Fe}$, which indicates that the partial excess functions decrease with increasing temperature, is shown in Figure 4.

Mixing on the M2 Site

$\underline{W}^{M2}$ does not change systematically with change in temperature (Figure 2). For example, $\underline{W}^{M2}$ at 500°C is not significantly different from $\underline{W}^{M2}$ at 600°C and 700°C. It is reasonable to assume that $\underline{W}^{M2}$ does not change much with change in temperature between 500 to 700°C. In such a case,

$$\underline{G}^{E} = \underline{H}^{E} \text{ and } \underline{S}^{E} = 0.$$

The partial $\underline{G}^{E}$ at 800°C may be somewhat different from partial $\underline{H}^{E}$ and there may be slight partial excess entropy. In the case of M2 site, the solution model is closer to Guggenheim's (1952) original 'strictly regular' solution model.

CONCLUSIONS

The experimental data on the distribution of Mg^{2+} - Fe^{2+} between M1 and M2 sites in orthopyroxenes heated at various temperatures as determined by the Mössbauer resonance technique were found to yield smooth distribution isotherms, which are in better agreement with distribution curves based on Guggenheim's "simple mixture" model, rather than the ideal solution model for the sites. The deviation from the ideal solution model increases with decrease in temperature. Mixing of Mg^{2+} and Fe^{2+} on the M1 site was found to be more non-ideal than that on the M2 site. The success of such a model explains the apparent inconsistencies in the interpretation of the Mg-Fe distribution data by Virgo and Hafner (1969, 1970) who tried to fit the ideal solution model at the sites. However, the non-ideal distribution in part of the 1000°C isotherm (Virgo and Hafner, 1969) does not agree with the present model. The expected $\underline{W}^{M1}$ and $\underline{W}^{M2}$ values for 1000°C (see Figure 2) are quite small and the distribution curve approaches closely to that of the ideal model. The close to ideal behavior would be true for the entire composition range and not for only a part of it. In view of this discrepancy, a redetermination of the 1000°C isotherm is highly desirable.

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Table 1

Chemical Analyses of Orthopyrozenes.

Ref. No.	1	2	3	4	5	6	7	8	9
SiO_2	56.51	51.23	52.98	51.75	51.40	51.05	49.64	48.39	47.5
Al_2O_3	0.00	1.59	0.03	0.72	0.08	0.04	0.06	0.33	1.20
TiO_2	0.02	0.06	0.12	0.21	0.18	0.15	0.22	0.30	0.28
*FeO	11.76	23.46	27.80	30.11	33.80	35.13	40.73	41.80	46.00
MnO	1.77	0.09	0.98	0.84	0.80	0.78	0.84	1.00	0.05
MgO	29.49	21.13	18.46	16.71	13.51	11.95	8.79	7.28	3.99
CaO	0.28	0.48	0.49	0.64	0.62	0.52	0.74	0.86	0.92
Na_2O	0.02	0.00	0.05	0.08	0.11	0.15	0.08	0.18	n.d
K_2O	0.00	0.00	0.01	0.05	0.02	0.02	0.02	0.03	n.d
Total	99.85	98.04	100.92	101.11	100.52	99.79	101.12	100.17	99.95
Fe/(Fe+Mg)	0.181	0.381	0.455	0.500	0.580	0.620	0.720	0.760	0.86

*FeO is total iron calculated as FeO. n. d. = not determined.

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1. Sample No. 274, Butler, Jr. (1969).
2. Sample No. T3/66, Saxena (1968).
3. Sample No. 277, Butler, Jr. (1969).
4. Sample No. 10, Arendalite, collected by Saxena from the type locality in Norway.
5. Sample No. 264, Butler, Jr. (1969).
6. Sample No. 278, Butler, Jr. (1969).
7. Sample No. 207, Butler, Jr. (1969).
8. Sample No. 10/68, charnockite from Varberg, collected by Saxena.
9. Sample No. XYZ, Ramberg and DeVore (1951).

Table 2

Line Widths and Intensities of the Mossbauer Spectra and the Calculated Site Occupancy Factors at the M1 and M2 Sites of Orthopyroxenes. $(Fe, Mg)_2Si_2O_6$.

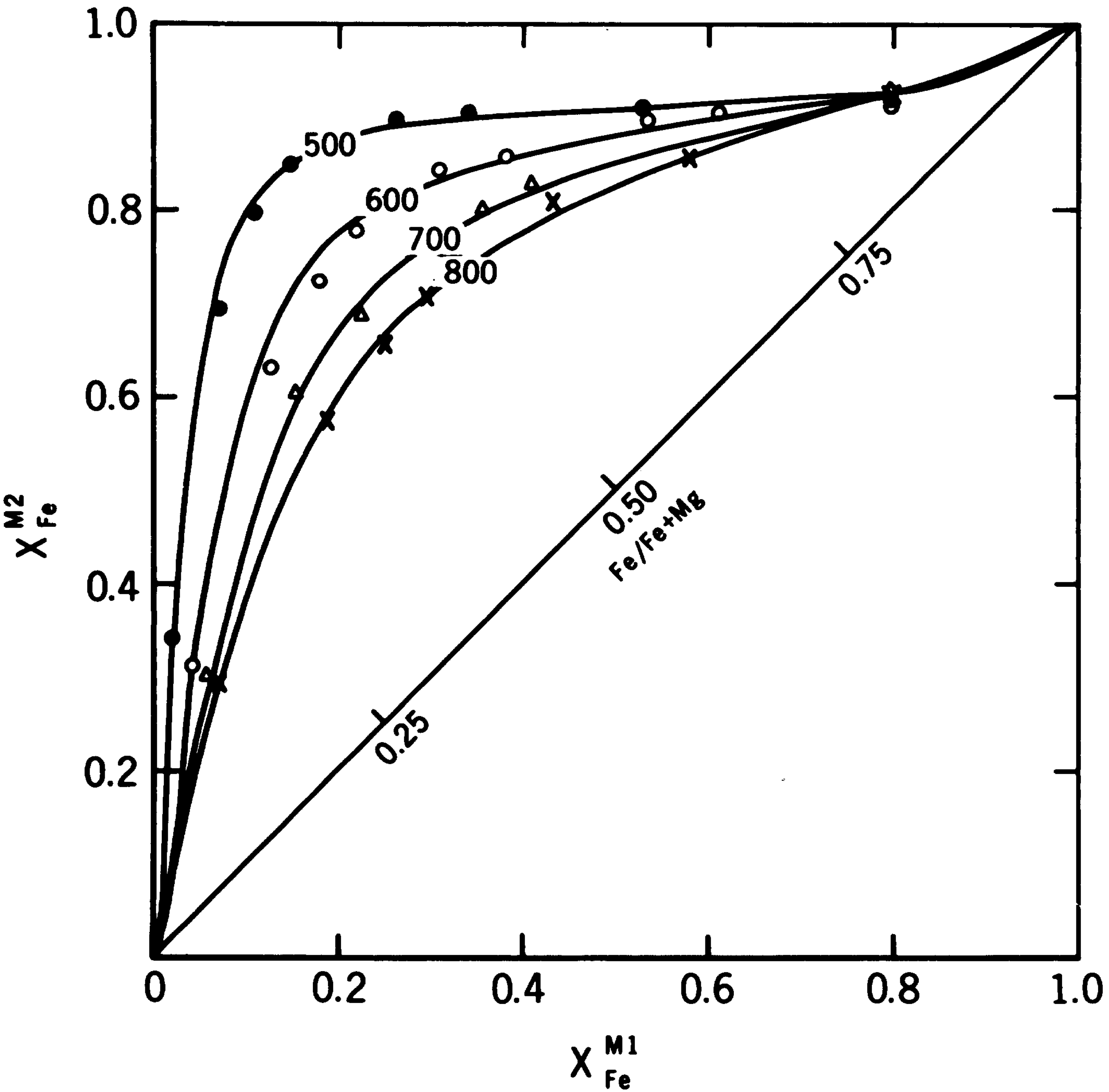
		Line widths (full width at half height) mm/sec				Intensities referred to $I(A_1 + A_2 + B_1 + B_2) = 1.0$				Fe^{2+} site occupancy factors	
Ref. No.	X^{Opx}_{-Fe}	A1	A2	B2	B1	A1	A2	B2	B1	X^{M1}_{Fe}	X^{M2}_{Fe}
						500°C					
1.	0.181	.2583	.3514	.2588	.2725	.0243	.5305	.4036	.0415	0.021	0.341
2.	0.381	.2612	.3441	.3054	.3167	.0606	.5207	.3750	.0435	0.070	0.692
3.	0.455	.2915	.3059	.2650	.3457	.0523	.4951	.3939	.0585	0.111	0.799
4.	0.500	.3244	.3366	.3294	.3380	.0803	.4551	.3942	.0703	0.150	0.850
5.	0.580	.2454	.3013	.2825	.3014	.1143	.4268	.3355	.1232	0.262	0.897
6.	0.620	.2754	.3390	.2917	.3413	.1273	.4057	.3175	.1495	0.337	0.920
7.	0.720	.2798	.2982	.2867	.3065	.1767	.3411	.2903	.1918	0.533	0.907
						600°C					
1.	0.181	.2131	.3462	.2693	.3461	.0684	.5128	.3469	.0718	0.046	0.316
2.	0.381	.3972	.3911	.3818	.4025	.0785	.4822	.3545	.0848	0.129	0.632
3.	0.455	.2895	.3462	.3106	.3166	.1031	.4368	.3450	.1151	0.186	0.726
4.	0.500	.2677	.3582	.3169	.3128	.1169	.4284	.3248	.1298	0.219	0.781
5.	0.580	.2686	.3408	.3079	.3356	.1327	.4061	.3120	.1491	0.310	0.849
6.	0.620	.2920	.3121	.2832	.2866	.1460	.3839	.3001	.1698	0.382	0.857
7.	0.720	.2879	.3093	.2905	.3000	.1771	.3584	.2576	.2069	0.545	0.895
8.	0.760	.3308	.3255	.3116	.3001	.1999	.3346	.2586	.2069	0.613	0.905
9.	0.860	.2915	.3075	.3154	.3169	.2234	.2910	.2403	.2453	0.797	0.922
						700°C					
1.	0.181	.3621	.3695	.3543	.2842	.0943	.4549	.3677	.0830	0.059	0.303
2.	0.381	.3580	.4020	.3418	.4112	.0946	.4602	.3387	.1065	0.156	0.605
3.	0.455	.3478	.2913	.3076	.2992	.1243	.4132	.3552	.1072	0.255	0.685
5.	0.580	.2958	.2809	.2929	.2990	.1416	.3853	.3127	.1604	0.360	0.800
6.	0.620	.3411	.3343	.3400	.3173	.1583	.3604	.3029	.1783	0.910	0.829
9.	0.860	.2838	.3133	.2990	.2951	.2182	.2893	.2370	.2554	0.710	0.929
						800°C					
1.	0.181	.2853	.2815	.2904	.2443	.1031	.4402	.3576	.0989	0.069	0.293
2.	0.381	.3446	.3602	.3323	.3645	.1228	.4421	.3148	.1202	0.187	0.575
3.	0.455	.3268	.3347	.3387	.3727	.1296	.3987	.3317	.1398	0.252	0.657
4.	0.500	.3546	.3509	.3270	.3546	.1382	.3888	.3212	.1517	0.298	0.701
6.	0.620	.2780	.3084	.2984	.2981	.1642	.3504	.2920	.1933	0.429	0.811
7.	0.720	.3026	.2862	.3009	.3019	.1884	.3334	.2716	.2066	0.579	0.860
9.	0.860	.2891	.3128	.3060	.2992	.2206	.2903	.2351	.2539	0.794	0.926

Table 3

Thermodynamic Parameters of Fe^{2+}-Mg^{2+} Ion-Exchange Between M1 and M2 Sites in Orthopyroxene, $(Fe,Mg)_2Si_2O_6$ According to Equation (3)

		cal/mole		
T°C	$\underline{K}_a$	$\underline{W}^{M1}$	$\underline{W}^{M2}$	$\Delta \underline{G}_a^0$
500	0.1882	2791	1099	2565
600	0.2516	2244	1397	2394
700	0.2836	1946	1295	2436
800	0.2780	1524	921	2729

LIST OF FIGURES


1.0
0.8
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0.4
0.2
X_{Fe}^{M2}
0
0.2
0.4
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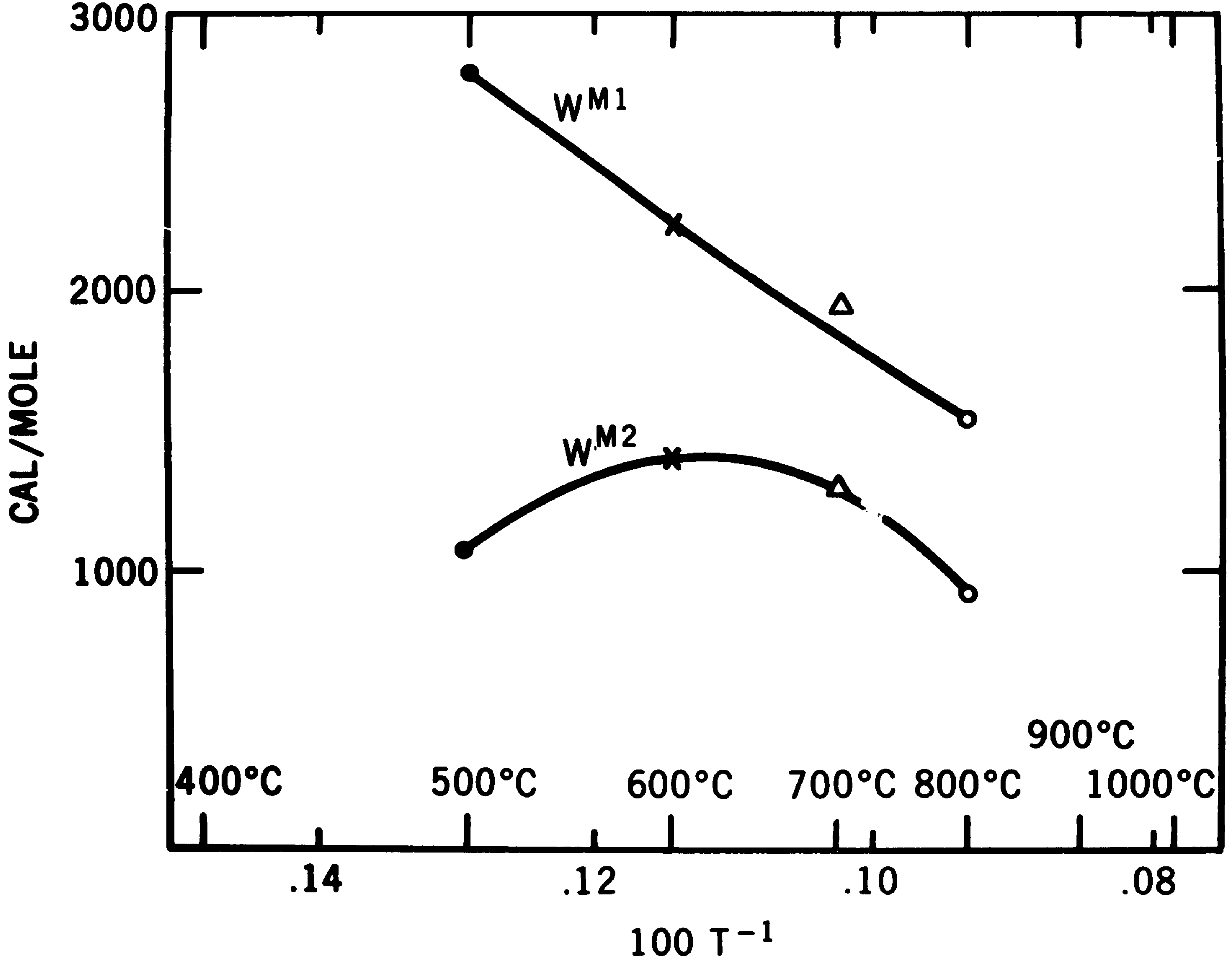
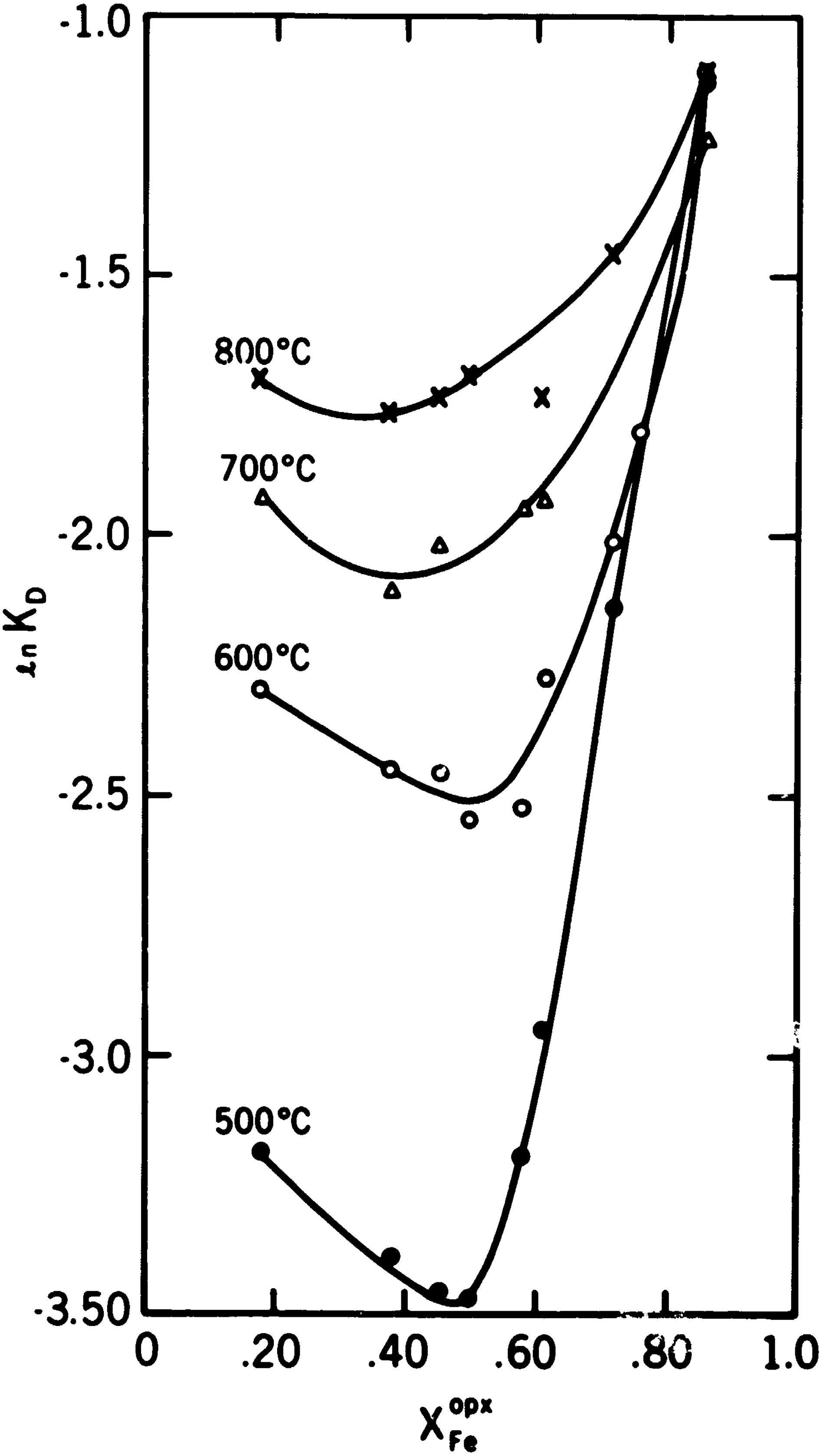
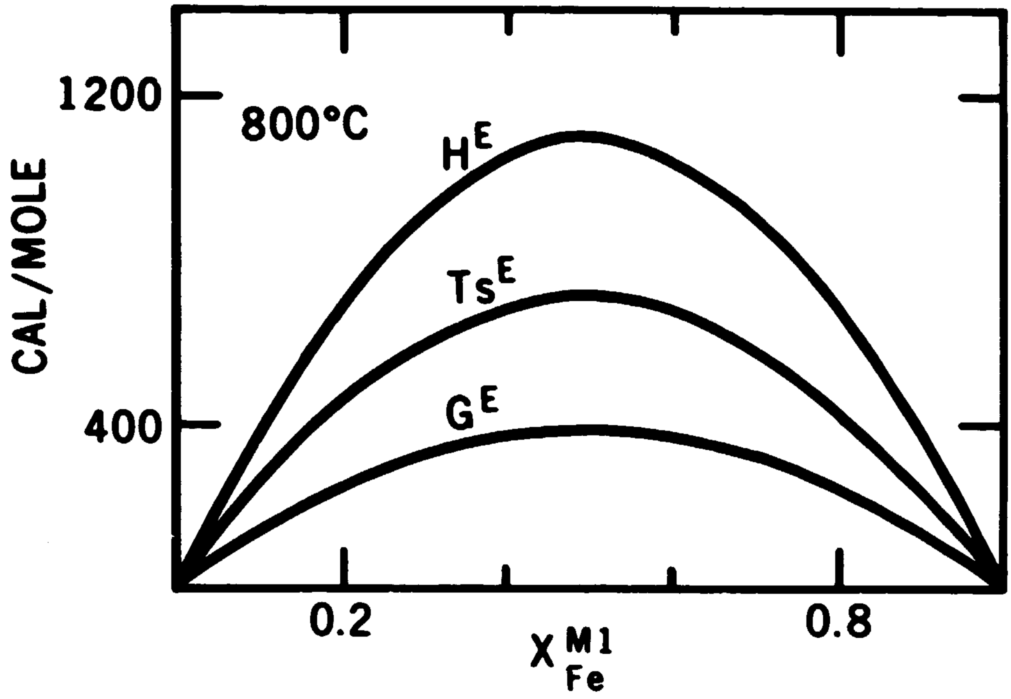
X_{Fe}^{M1}
500
600
700
800
0.25
0.50
0.75
Fe/Fe+Mg



CAL/MOLE
3000
2000
1000
W^{M1}
W^{M2}
900°C
400°C
500°C
600°C
700°C
800°C
1000°C
.14
.12
.10
.08
100 T^{-1}


-1.0
-1.5
-2.0
-2.5
-3.0
-3.50
0
.20
.40
.60
.80
1.0
$\ln K_D$
X_{Fe}^{opx}
800°C
700°C
600°C
500°C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Ts^E
G^E
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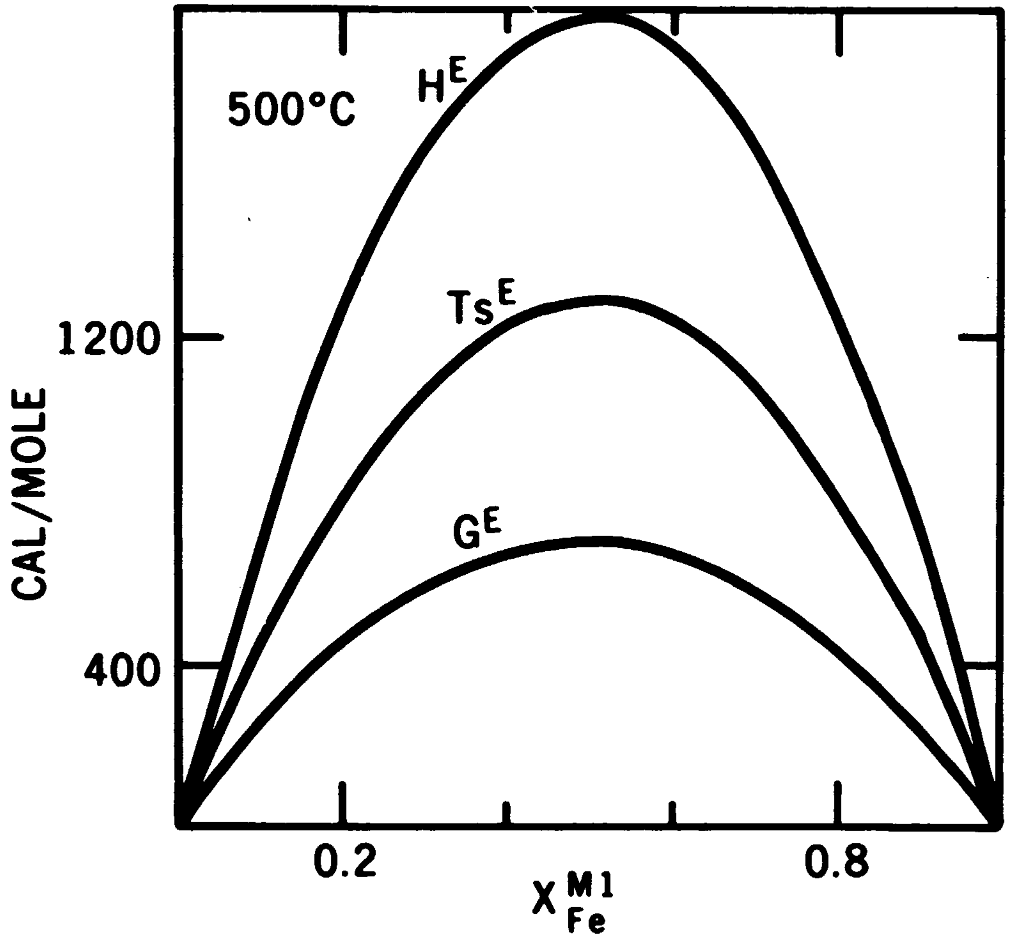
400
CAL/MOLE
0.2
0.8
X_{Fe}^{M1}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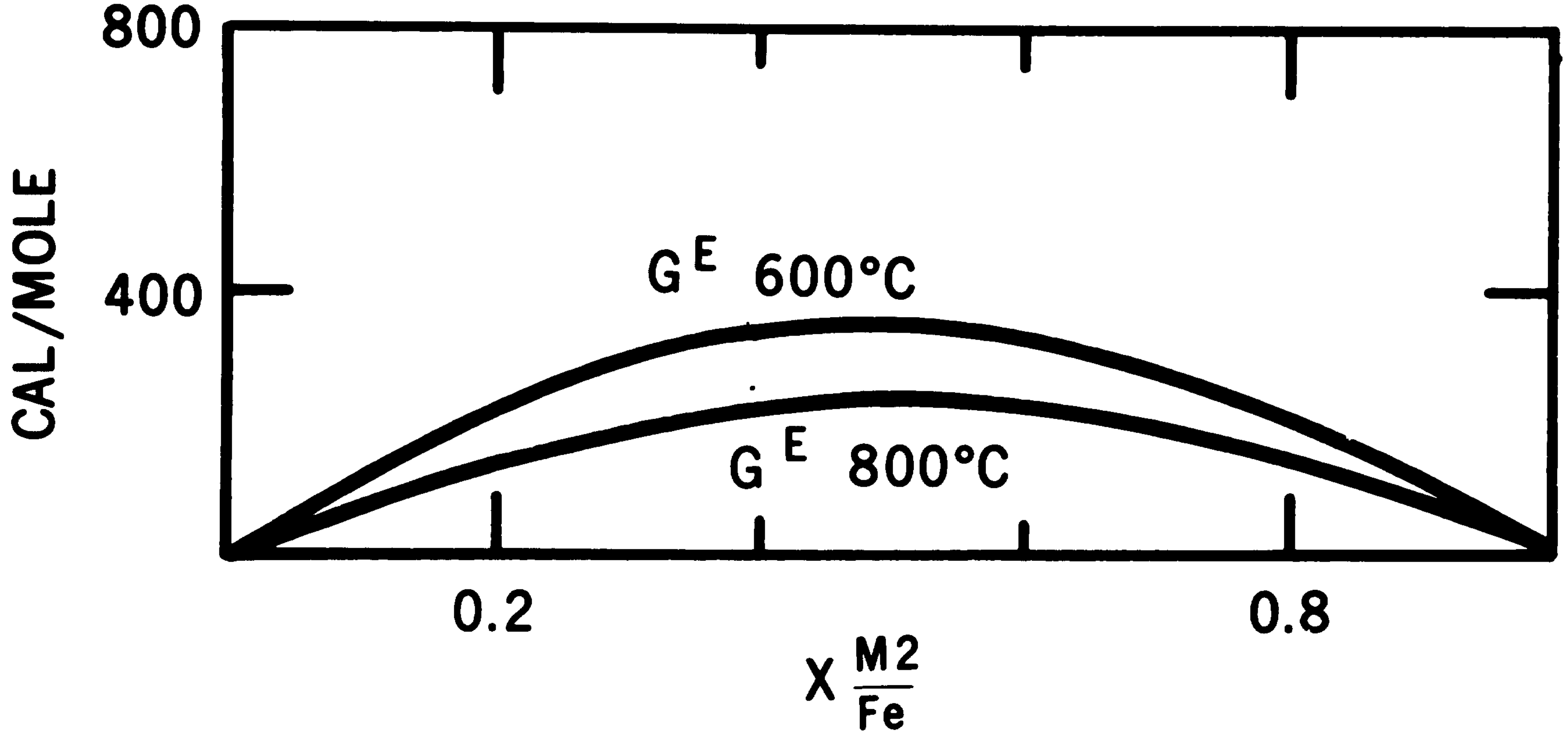
0.8
X_{Fe}^{M1}


800
400
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G^E 600°C
G^E 800°C
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0.8
X^{M2}_{Fe}