

THE INTRACRYSTALLINE CATION DISTRIBUTION AND THE
THERMODYNAMICS OF SOLID SOLUTION FORMATION
IN THE SYSTEM $\text{FeSiO}_3\text{-MgSiO}_3$

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ABSTRACT

Using a simple model, the observed distributions of Fe and Mg between *M1* and *M2* sites in orthopyroxenes are shown to be consistent with the measured activity-composition relations in the solid solutions. The substantially non-random cation distribution is shown to make only a small negative contribution to the excess free energy of mixing at temperatures near 1000°C. This negative term may be offset by a small positive enthalpy contribution common to many other binary and ternary oxide solid solutions, but the data do not permit the evaluation of such a term.

INTRODUCTION

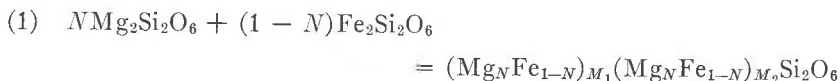
The non-random distribution of iron and magnesium between olivine and pyroxene in the system FeO-MgO-SiO_2 and between the *M1* and *M2* sites of the pyroxene structure has been well established, both in natural mineral assemblages and in experimental equilibrium studies at high temperature. Both the intercrystalline (multiphase) and the intracrystalline (single phase) equilibria have been suggested as geothermometers. A number of thermodynamic models have been proposed to account for the observed distributions (Ramberg and Devore, 1951; Kretz, 1961; Mueller, 1962; Matsui and Banno, 1965; Banno and Matsui, 1966; Grover and Orville, 1969; Virgo and Hafner, 1969; Saxena, 1969). Several of these treatments take into account the existence of two distinct octahedral sublattices in the pyroxene structure, the model of Grover and Orville (1969) being perhaps the most inclusive. Experimentally, the system MgO-FeO-SiO_2 has been studied over a range of temperatures and oxygen partial pressures by, among others, Bowen and Schairer (1935), Muan and Osborn (1965), Nafziger and Muan (1968); Larimer (1968); and Medaris (1969). Nafziger and Muan determined activity-composition relations in the solid solutions and the free energies of formation of the silicate end-members. At 1200–1250°C, the pyroxene solid solution was found to be essentially ideal, whereas the olivine showed a fairly small positive deviation from ideality. Measurements by Larimer (1968) and by Medaris (1969) also indicated that deviations from ideality in both the olivine and pyroxene solid solutions are small or zero at temperatures above 800°C. Calorimetric measurement of the heats of solution of Fe-Mg olivines and pyroxenes in hydrofluoric acid by Sahama and Torgeson (1949) suggest a zero enthalpy of

mixing. Using Mössbauer spectroscopy. Ghose and Hafner (1967) and Virgo and Hafner (1969) have experimentally determined the distribution of Mg and Fe between the $M1$ and $M2$ sites as a function of temperature and composition. They report that between 500 and 1000°C, the variation of cation distribution is adequately represented by a single constant free energy of exchange of about 3.6 kcal/mole $M_2Si_2O_6$. In accord with the magnitude of this energy term, substantial order remains even at 1000°C.

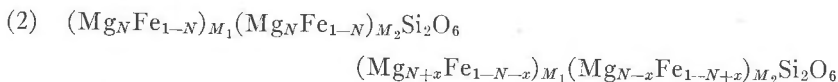
It appears, then, that even though substantial deviation from random mixing over divalent cation sites exists, the deviations from thermodynamic ideality in the pyroxene solid solutions are small or zero. It is the aim of this communication to show that these observations are indeed consistent, *i.e.*, to derive activity-composition relations based on the intracrystalline exchange term of Virgo and Hafner (1969), and to compare these results with experiments. The applicability of a "regular solution" model to these data will also be discussed.

THERMODYNAMICS OF PYROXENE SOLID SOLUTIONS

The formation of a solid solution $(Fe_NMg_{1-N})_2Si_2O_6$ of a partially ordered cation distribution characteristic of the temperature, T , may be visualized as consisting of two steps:



formation of totally disordered solid solution of random cation distribution from the end members, and



ordering of the solid solution, with $x=f(N, T, P)$.

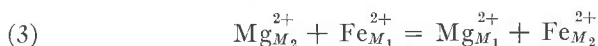
In accordance with the model of Grover and Orville (1969), and with the assumptions of Virgo and Hafner (1969), the following approximations will be made:

- a. Step (1) is characterized by ideal mixing: $\Delta H_1 = 0$,

$$\Delta S_1 = -2R[N \ln N + (1 - N) \ln (1 - N)]^1$$

- b. Step (2) is associated with a constant *molar* enthalpy of exchange, $\Delta H_{\text{exchange}}$, independent of N and T and P , for the reaction:

¹ The thermodynamic parameters used herein need not all refer to, nor be derived from, experimental measurements on samples equilibrated at atmospheric pressure, since the effect of pressure is assumed to be small. Accordingly, these terms are not given the standard state designation: ΔH° , etc.



This enthalpy is approximately equal to the value found by Virgo and Hafner for the standard free energy of exchange,¹ -3.65 kcal/mole, and is exothermic for the reaction as written.

c. The entropy change of step (2) is equal to the change in configurational entropy between the partially ordered and random distributions, assuming random mixing *on each sublattice* in the former.

The extent of ordering occurring at any temperature, *i.e.*, the value of x for a given N , T , may be calculated by looking for a minimum in the free energy change of step (2).

$$(4) \quad \Delta G_2 = \Delta H_2 - T\Delta S_2 = x\Delta H_{\text{exchange}} + RT[(N+x)\ln(N+x) \\ + (1-N-x)\ln(1-N-x) + (N-x)\ln(N-x) \\ + (1-N+x)\ln(1-N+x) - 2N\ln N \\ - 2(1-N)\ln(1-N)]$$

$$(5) \quad \left(\frac{\partial \Delta G_2}{\partial x}\right)_N = 0 = \Delta H_{\text{exchange}} + RT \ln \frac{(N+x)(1-N+x)}{(N-x)(1-N-x)}$$

$$(6) \quad \frac{-\Delta H_{\text{exchange}}}{2.303 RT} = \log_{10} \frac{(N+x)(1-N+x)}{(N-x)(1-N-x)}$$

Calculated values of the degree of order, x , at 500, 1000, and 1250°C are shown in Table 1. These are essentially the same as those given by Virgo and Hafner. One should note that the calculated extent of ordering, x , is symmetric about $N=0.5$, the 50 percent mole fraction.

One can then compute the free energy of step (2) using equation (4) and the values of x found from equation (6), as shown in Table 1. This ΔG value is also equal to the *excess* free energy of formation of the solid solution from its components. Note that this function also symmetric about $N=0.5$.

DISCUSSION

Figure 1 shows the calculated values of ΔH , $T\Delta S^{\text{ex}}$, and ΔG^{ex} for 500°C, where the effects of cation ordering are more pronounced than at

¹ The molar free energy of exchange derived by Virgo and Hafner from the distribution constant consists of an enthalpy term and a *non-configurational* (lattice vibrational) entropy contribution. Since the difference in vibrational entropy between ordered and disordered states is probably quite small, $T\Delta S_{\text{vib}}$ is small compared to ΔH , and $\Delta G_{\text{non-config}} \approx \Delta H_{\text{exchange}}$. On the other hand, the total free energy of the ordering process is the sum of both configurational and non-configurational terms.

TABLE 1. CALCULATED THERMODYNAMICS OF MIXING IN $Mg_2Si_2O_6$ - $Fe_2Si_2O_6$
 SOLID SOLUTIONS [PER MOLE $(Mg_NFe_{1-N})_2Si_2O_6$]

N^a	x^b	ΔH (kcal) ^c	$T\Delta S^{ex}$ (kcal) ^d	ΔG^{ex} (kcal) ^e	$\Delta G^{ex}/N(1-N)$
T=500°C					
0.1	0.080	-0.292	-0.155	-0.137	-1.53
0.2	0.152	-0.555	-0.245	-0.310	-1.94
0.3	0.211	-0.772	-0.351	-0.421	-2.00
0.4	0.252	-0.918	-0.432	-0.486	-2.03
0.5	0.266	-0.972	-0.454	-0.518	-2.07
0.6	0.252	-0.918	-0.432	-0.486	-2.03
0.7	0.211	-0.772	-0.351	-0.421	-2.00
0.8	0.152	-0.555	-0.245	-0.310	-1.94
0.9	0.080	-0.292	-0.155	-0.137	-1.53
T=1000°C					
0.1	0.058	-0.210	-0.100	-0.110	-1.22
0.2	0.107	-0.392	-0.210	-0.182	-1.14
0.3	0.142	-0.518	-0.250	-0.268	-1.28
0.4	0.165	-0.601	-0.292	-0.309	-1.29
0.5	0.172	-0.629	-0.315	-0.314	-1.26
T=1250°C					
0.1	0.050	-0.182	-0.087	-0.095	-1.06
0.2	0.091	-0.331	-0.182	-0.149	-0.93
0.3	0.121	-0.442	-0.217	-0.225	-1.07
0.4	0.140	-0.516	-0.251	-0.265	-1.10
0.5	0.146	-0.534	-0.242	-0.292	-1.17

^a N = mole fraction $Mg_2Si_2O_6$.

^b x = degree of order from eqn. 6, with $\Delta H_{exchange} = -3.65$ kcal.

^c $\Delta H = x\Delta H_{exchange}$.

^d from eqn. 4.

^e $\Delta H^{ex} = \Delta H - T\Delta S^{ex}$.

higher temperatures. It is seen that the negative enthalpy of mixing due to cation ordering is compensated by a negative entropy term, so that the total excess free energy, although still negative, is much smaller in magnitude than the enthalpy term alone. At higher temperatures, the calculated excess free energies are smaller in magnitude, being ~ -0.314 and ~ -0.292 kcal/mole $M_2Si_2O_6$ at $N=0.5$ at 1000 and 1250°C, respectively.

Since the entropy depends in a fairly complex manner on the mole fraction and the temperature, and since this entropy of mixing is not that of a random one-sublattice system, this model is clearly not one of a

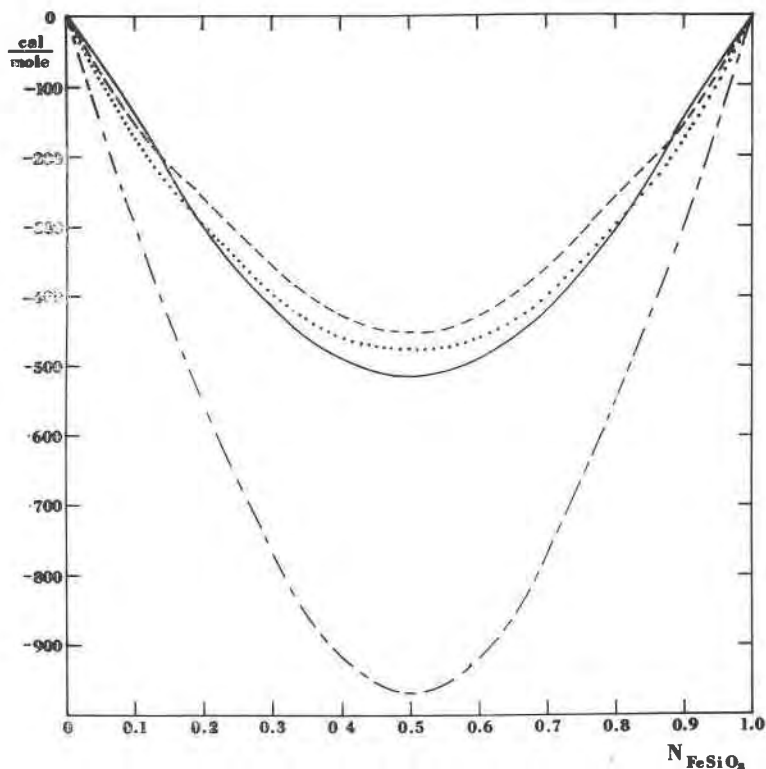


FIG. 1. Excess functions of mixing in magnesium iron pyroxenes at 500°C. All quantities are for the formation of one mole $(Mg_NFe_{1-N})_2Si_2O_6$ from the pure end members. Dashed line: $T\Delta S^{ex}$ (present model); dotted line: ΔG^{ex} ("regular" solution approximation); solid line: ΔG^{ex} (present model); dot dashed-line: ΔH (present model)

regular solution (Hildebrand and Scott, 1964). On the other hand, the symmetry of the ΔG^{ex} curve with respect to the mole fraction suggests that this curve may be fairly well *approximated* by a regular-like expression

$$(7) \quad \Delta G_T^{ex} = f(T)N(1 - N)$$

where $f(T)$ is constant at a given temperature. Values of $\Delta G^{ex}/N(1-N)$ shown in the last column of Table 1, show this indeed to be the case, with $f(T)$ becoming more negative with decreasing temperature. Figure 1 compares the ΔG^{ex} curve calculated from the model above for 500°C with that calculated using equation (7) with

$$f(T) = \left(\frac{\Delta G^{ex}}{N(1-N)} \right)_{av} = 1920 \text{ cal.}^1$$

The two curves are quite similar, and very good experimental activity data, particularly near both ends of the composition range, would be required to distinguish between them. At higher temperatures, the two curves would be even more nearly coincident.

Furthermore, activities in solid solutions in ternary systems such as FeO-MgO-SiO₂ are often calculated from the experimentally determined conjugation lines (Muan, 1967; Nafziger and Muan, 1968) using the regular solution approximation:

$$(8) \quad \log \gamma = \alpha(1 - N)^2.$$

This approximation is especially useful when the deviation from ideality is small and the relative uncertainty in $\log \gamma$ is large. Accordingly, it is of interest to compute the activity-composition curves in the system FeSiO₃-MgSiO₃ using equation (8), and

$$(9) \quad \alpha = \left(\frac{\Delta G^{ex}}{N(1-N)} \right)_{average} \times \frac{1}{2 \times 2.303 RT}$$

where the factor of two converts to kcal/mole *M*SiO₃. The calculated activity-composition curves for 500°C, 1000°C, and 1250°C are shown in Figure 2. Particularly for the higher temperatures, at which experimental activity data have been or can be obtained, the deviations from ideality are small. At 1250°C, the temperature of Nafziger and Muan's measurements, $a_{\text{FeSiO}_3} = 0.48$ at $N_{\text{FeSiO}_3} = 0.50$. That value probably is within the limits of error of their statement that the pyroxene solid solution is practically ideal. The data of Medaris (1969) and of Larimer (1968) also point to the conclusion that any deviations from ideality in the pyroxene are small. Medaris, using the model of Grover and Orville (1969) to interpret his data, reports a molar exchange free energy for reaction (3), the *intra*-crystalline exchange of -2.94 kcal/mole, in satisfactory agreement with the value of -3.65 kcal/mole obtained by Virgo and Hafner (1969), which was used in the present calculations.

Thus, it is seen that very nearly ideal activity-composition relations at 1000–1300°C are consistent with the degree of cation order found by Mössbauer spectroscopy and with the above model of the energetics of

¹ Calculated values of $f(T)$ for different compositions at a given temperature deviate from the average value by about $\pm 10\%$. Some of this variation may be due to scatter in the original data, but a part of it to the differences between a regular solution model and the present model.

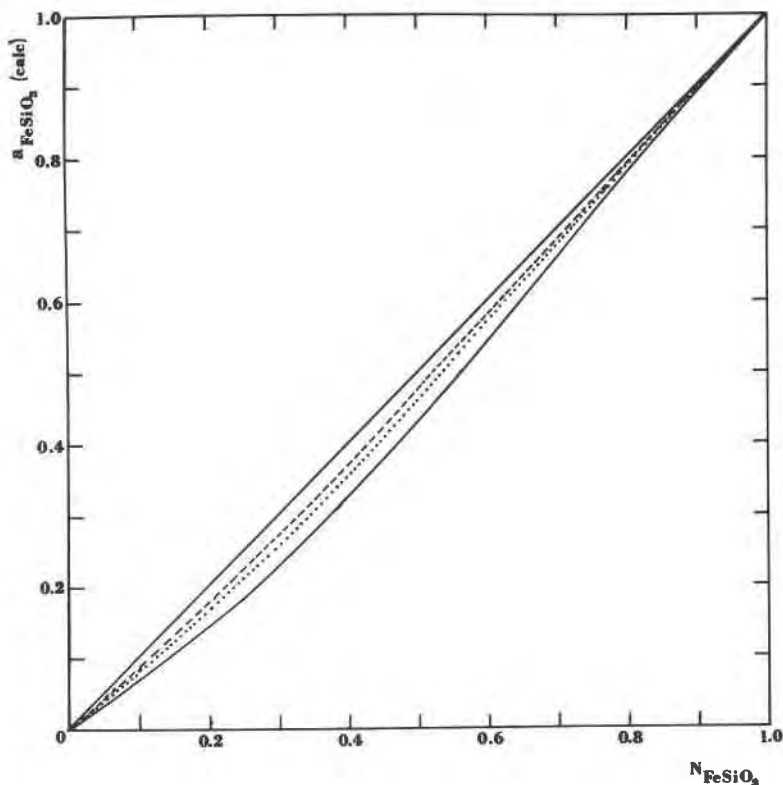


FIG. 2. Calculated activity-composition relations in system $\text{FeSiO}_3\text{-MgSiO}_3$. Light solid line: Raoult's law behavior; dashed curve: calculated, 1250°C ; dotted curve: calculated, 1000°C ; solid curve: calculated, 500°C .

the ordering process. It is worth stressing that quite substantial deviations from random mixing on the two sublattices lead to almost no deviations from ideal activity-composition relations.

So far as we have assumed that the only contribution to the enthalpy of mixing is negative, and arises from the ordering of cations in $M1$ and $M2$ sites. In a number of oxides crystallizing in the rocksalt structure, and in some olivine solid solutions, in which no redistribution of cations among nonequivalent sites occurs, positive deviations from ideality have been found (Driessens, 1968). Although the exact nature of the interactions leading to these deviations has not been completely elucidated, changes in coulombic and repulsion energies, and "strain" resulting from the mixing, in a solid, of cations of unequal sizes, are probably responsible. The system FeO-MgO , in particular, shows large positive deviations

from ideality (Hahn and Muan, 1962), possibly associated with changes in the deviation from stoichiometry (Driessens, 1968). According to Nafziger and Muan (1968), the series $\text{Fe}_2\text{SiO}_4\text{-Mg}_2\text{SiO}_4$ also shows positive deviations, though these were not detected by Medaris (1969). It seems not unlikely, then, that some small positive "lattice" contribution to the enthalpy of mixing is present in the pyroxenes also. Were this the case, and were this contribution essential independent of the degree of cation ordering, it would not affect the thermodynamics of reaction (2), while changing step (1) from an ideal to an approximately regular mixing process. Within this approximation, the entropy of mixing and degree of order would remain the same as before, but the enthalpy of mixing would become less negative. The overall deviations from ideality would also become less negative, and might indeed become positive. The superposition of positive lattice contributions on negative cation-ordering contributions to the free energy of mixing has recently been inferred for the spinel systems, $\text{Co}_2\text{TiO}_4\text{-Zn}_2\text{TiO}_4$ and $\text{Ni}_2\text{TiO}_4\text{-Zn}_2\text{TiO}_4$ (Navrotsky and Muan, 1970), and has been suggested as a possibility for olivines and pyroxenes by Matsui *et al.* (1968). However, the activity data in the pyroxenes do not warrant an attempt to quantitatively separate the two free energy terms. According to Nafziger and Muan, the deviation from ideality in the pyroxene may indeed be slightly positive, $\alpha = +0.07 \pm 0.12$, but this effect is smaller in magnitude than the experimental uncertainty of their measurements.

Calorimetric measurements of the heats of solution of olivine and pyroxene solid solutions in the system FeO-MgO-SiO_2 , by Sahama and Torgeson (1949), indicate both silicate solid solutions to have essentially zero enthalpies of mixing. The model presented here predicts negative heats of mixing, dependent on the degree of order and therefore on the thermal history of the samples. For pyroxenes representative of a high temperature cation distribution, at $T \sim 1000^\circ\text{C}$, a heat of mixing of -0.3 kcal/mole $M\text{SiO}_3$ at $N = 0.5$ is predicted. Particularly since the pure iron end-member, ferrosilite, does not exist, and its enthalpy of solution must be extrapolated from the calorimetric data, it is quite likely that such a relatively small deviation from ideality would not have been detected. On the other hand, a zero enthalpy of mixing might result from the addition of a small positive "lattice" term to the negative ordering enthalpy term, as discussed above. Since the actual cation distributions of Sahama and Torgeson's samples are not known, and the experimental uncertainties are fairly large, these data do not provide conclusive evidence for or against the existence of the positive lattice term.

It is difficult to place actual numerical values or the uncertainties introduced by the simple nature of this model. The energy and vibrational

entropy changes associated with interchanging iron and magnesium on nonequivalent sites are certainly sensitive to the exact geometry of that site, which does not remain identically unchanged with variations of temperature, pressure, and composition. The data of Virgo and Hafner suggest that the interchange energy is constant to about ± 10 percent at temperatures above 500°C . If one were to attempt to represent the thermodynamics of interchange by a model with two energy parameters, the resulting correction terms to any calculated interchange energy at one P, T, N_{FeSiO_3} would presumably be of that magnitude. Since a prior lattice energy calculation of the necessary precision is not practicable for these systems, all models must contain empirical energy parameters derived from experimental data. It is the author's opinion that much more extensive experimental cation distribution data than those presently available would be needed before one could rationally distinguish among various plausible more complex models.

However, whatever model one chooses, the conclusion that the state of equilibrium cation distribution is of only *slightly* more negative free energy than the random state will apply. Accordingly, deviations from ideal activity-composition relations due to cation ordering will be small, as noted in this paper. The actual form and magnitude of the enthalpy and excess entropy of mixing will depend on the model chosen and on the presence of non-ideal "lattice" contributions, as noted.

CONCLUSIONS

Nearly ideal thermodynamic behavior of pyroxene solid solutions in the system $\text{FeSiO}_3\text{-MgSiO}_3$ at temperatures near 1000°C is consistent with the observed cation distributions over $M1$ and $M2$ sites and the exchange energy for this process calculated by Virgo and Hafner (1969). The non-random distribution of cations leads to *small negative* excess free energies of mixing, which may be partially or totally compensated by a small positive lattice term not closely tied to the degree of order. Thus, the existence of a non-random cation distribution among two non-equivalent sites need not noticeably affect the activity-composition relations in the solid solutions, although the effect on enthalpy and entropy separately may be significant.

The *intercrystalline* exchange of iron and magnesium between olivine and pyroxene is largely governed by the difference in free energies of formation $\Delta(\Delta G^{\circ})$ of the iron and magnesium end-members (Nafziger and Muan, 1968) if the solid solutions are nearly ideal. Since Medaris (1969) and Larimer (1968) have shown that the distribution constant is nearly independent of temperature in the range $900\text{-}1200^{\circ}\text{C}$, one may conclude that the term $\Delta(\Delta G^{\circ})/RT$ remains fairly constant in this range. This con-

clusion cannot be checked against standard free energy data because of the instability of ferrosilite (Nafziger and Muan, 1968; Akimoto, 1964) and the consequent lack of detailed thermodynamic data for it. Since neither the *intercrystalline* distribution constant nor the deviation from ideality of the solid solution seem to be very temperature sensitive, these parameters are not suitable for use as geothermometers. The *intracrystalline* cation distribution among *M1* and *M2* sites of pyroxene is significantly temperature dependent, and may serve as an indication of the lowest temperature at which equilibrium was attained (Virgo and Hafner, 1969). If the cation distribution coefficient, x , is known to ± 0.02 , and in view of the uncertainties associated with the model, it is probably possible to estimate this temperature to about $\pm 40^\circ$, depending somewhat on the purity and composition of the sample, and on the actual value of T .

The effect of impurities, particularly of calcium, on the *intercrystalline* and *intracrystalline* distributions of iron and magnesium and on the thermodynamics of solid solution formation has not been considered and may be a significant complication in geologic systems, although Larimer's data suggest that 1 percent CaO by weight does not influence the *intercrystalline* distribution coefficient. Similarly, the effect of pressure, primarily to stabilize ferrosilite (Akimoto, 1964) and extend the range of the pyroxene solid solution, must be considered when dealing with samples originating from a high pressure environment.

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