ORDER-DISORDER AND THE ACTIVITY-COMPOSITION RELATION IN A BINARY CRYSTALLINE SOLUTION. I. METAMORPHIC ORTHOPYROXENE

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Abstract

Intra-crystalline cation distribution data on metamorphic orthopyroxenes are used to demonstrate the method of obtaining the activity-composition relation in a binary crystalline solution. The 'strictly regular solution model' of Guggenheim may be used to describe the mixing of cations on individual structural sites. A factor f, analogous to the activity coefficient in the macro-chemical systems, may be calculated as a function of w (as defined by Guggenheim, 1952 or by Thompson, 1967). Plots of $X_A{}^\alpha f_A{}^\alpha$ against $X_A{}^\alpha$, where $X_A{}^\alpha$ is the mole fractions $(A/A+B)$ on the site α of a crystalline solution (A, B) M and $f_A{}^\alpha$ the corresponding activity coefficient, are comparable to the activity-composition diagrams of the macro-chemical system. Activity-composition relation for the crystal (A, B) M with two nonequivalent sites α and β may also be obtained by the relation

$$a_A{}^M = (X_A{}^\alpha f_A{}^\alpha)^{1/2}(X_A{}^\beta f_A{}^\beta)^{1/2}$$

where $a_A{}^M$ is the activity of component A in the macro-crystal.

Introduction

Since the publication of the results on the distribution of Fe^{2+} and Mg in cummingtonite and orthopyroxene by Ghose (1961, 1965) a number of workers have contributed to the theory and data on the intracrystalline distribution of cations in ferromagnesian silicates. Important data on orthopyroxens are published by Virgo and Hafner (1969, 1970). Mueller (1961, 1962) discussed the thermodynamics of such distributions. His discussions show the possibility to use rather simple solution models for the Fe–Mg silicates. In several cases both intercrystalline as well as intra-crystalline distributions seem to be in accord with ideal solid solution models. In certain other cases, it seems that the use of a regular solid solution model (the strictly regular solution of Guggenheim, 1952) is desirable. Such attempts were made by Mueller (1961, 1962, 1964) and more recently by Saxena (1969). If the intra-crystalline distribution of cations is in close agreement with a certain solid solution model, the thermodynamic nature of the solid solution in the mix-crystal can be determined. In this work, we present certain thermodynamic considerations pertinent to the above aspect and demonstrate our approach by taking orthopyroxene as an example.

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THERMODYNAMICS

The equilibrium constant K at a certain temperature and pressure for the ion exchange equilibrium

$$A\alpha + B\beta \rightleftharpoons A\beta + B\alpha \tag{a}$$
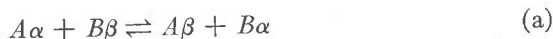
where α and β are binary (A, B) regular solutions (see Mueller, 1964) is given by

$$K_{\mathrm{a}} = \frac{(1 - X_A{}^\alpha)X_A{}^\beta \exp\left\{\left\{(1 - 2X_A{}^\beta)\dfrac{N \cdot w^\beta}{RT}\right\}\right\}}{(1 - X_A{}^\beta)X_A{}^\alpha \exp\left\{\left\{(1 - 2X_A{}^\alpha)\dfrac{N \cdot w^\alpha}{RT}\right\}\right\}} \tag{1}$$

This may also be written as

$$\ln K_{\mathrm{D}} - \ln K = \frac{Nw^\alpha}{RT}(1 - 2X_A{}^\alpha) - \frac{Nw^\beta}{RT}(1 - 2X_A{}^\beta) \tag{2}$$

where K_D is $X_A{}^\beta(1-X_A{}^\alpha)/(1-X_\alpha{}^\beta)X_A{}^\alpha$, R gas constant, T absolute temperature, N Avogadro's number and w a factor used to define the strictly regular solution by Guggenheim (1952). w is sometimes referred to as the interchange energy. For its statistical thermodynamic meaning see Fowler and Guggenheim (1956). Use of this factor has also been made by Thompson (1967, 1969).

Analogous to the above equations describing hetrogeneous equilibrium, we may write equations for the intra-crystalline ion exchange equilibrium. Taking the simplest example of a crystal $(A, B)M$ where we have two nonequivalent sites, we can apply the above equations by considering α and β as two different sites. Note that w^α and w^β are not of the same thermodynamic significance as they are when α and β are end member phases. However, in analogy with the inter-crystalline exchange energy, the intra-crystalline exchange energy continues to be a function of w^α and w^β.

In the crystal as a whole $w_A{}^\alpha$ is related to the activity coefficient as

$$\ln f_A{}^\alpha = \frac{Nw^\alpha}{RT}(1 - X_A{}^\alpha)^2 \tag{3}$$

When α refers to a site in a crystal the above relation no longer carries the same thermodynamic meaning. In order to avoid confusion, we shall denote $f_A{}^\alpha$ as a 'partial' activity coefficient.

If we have the data on the distribution of a cation over two nonequivalent positions and if these data are in close agreement with the regular

solid solution model on each site, we can obtain 'partial' activity coefficients from equations (2) and (3). The activity of a component in the crystal is related to the 'partial' activity coefficients and mole fractions on individual sites as

$$a_A{}^M = (f_A{}^\alpha X_A{}^\alpha)^{1/2}(f_A{}^\beta X_A{}^\beta)^{1/2} \tag{4}$$

where α and β are two nonequivalent sites in a crystal with the composition $(A, B)M$.

DISTRIBUTION OF Fe^{2+} AND Mg IN METAMORPHIC ORTHOPYROXENE

The distribution of Fe^{2+} and Mg in orthopyroxenes from metamorphic rocks has been studied by Virgo and Hafner (1970). These crystals may have cooled from the temperatures of granulite facies. Depending on the
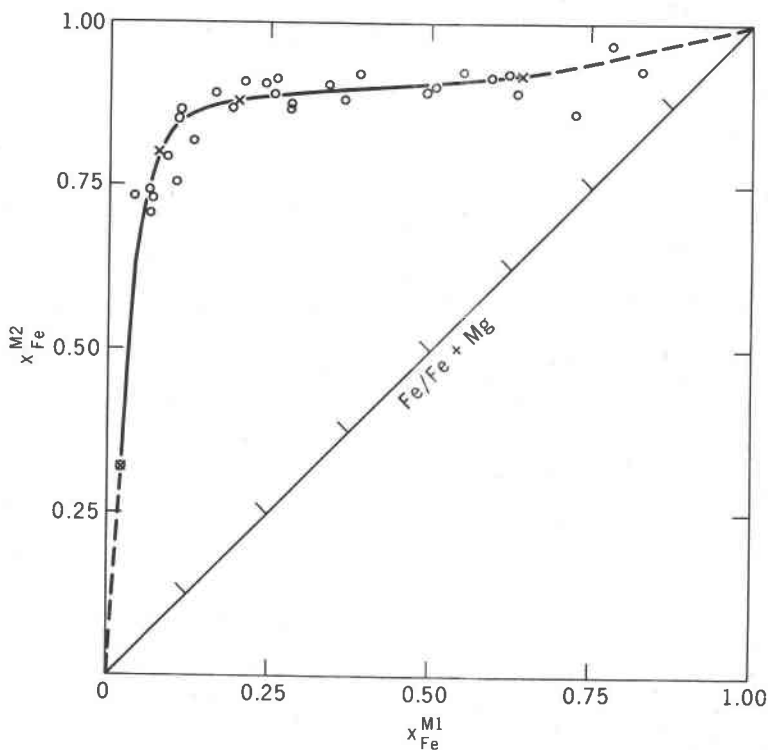

FIG. 1. Distribution of Fe^{2+} and Mg between $M1$ and $M2$ sites in metamorphic orthopyroxenes. Data from Virgo and Hafner (1970). The curve is drawn through the crosses and represents the relation.

$$\ln K_D + 1.5469 = 0.9837(1 - 2X_{Fe}{}^{M2}) - 1.8703(1 - 2X_{Fe}{}^{M1})$$

environment of cooling, these crystals might have equilibrated at different temperatures. The temperature at which ordering ceased may be between 450° and 500°C. Therefore, in this work we cannot be specific about the temperature and the results obtained here would be subject to revision. We are employing a binary solution model. Metamorphic pyroxenes usually have minor amounts of Al, Ti, Mn and Ca besides Fe^{2+} and Mg. The presence of these other ions may also affect the present result somewhat.

In the following text and figures, we shall use superscripts $M1$, $M2$ and Opx to denote that a particular function refers to $M1$ site, $M2$ site and orthopyroxene crystal respectively. The subscript Fe is used to denote the cation we are considering. Thus f_{Fe}^{M1} refers to the 'partial' activity coefficient of Fe^{2+} in $M1$ site.

Figure 1 shows the distribution of Fe^{2+} and Mg between $M1$ and $M2$ sites in orthopyroxene. The data are taken from Virgo and Hafner (1970).

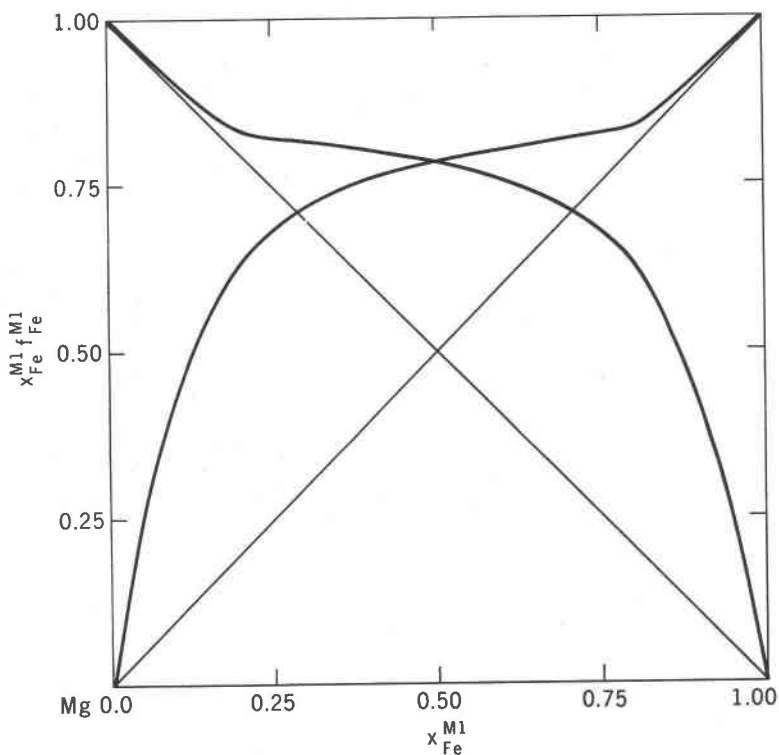FIG. 2. The 'partial' activity of Fe^{2+} at the $M1$ site plotted against the mole fraction X_{Fe}^{M1}.

By using equation (2), a curve is drawn which fits the data best. The equation to the curve in Figure 1 is based on

$$\frac{Nw_{Fe}^{M1}}{RT} = 1.87; \qquad \frac{Nw_{Fe}^{M2}}{RT} = 0.98; \qquad K = 0.21$$

The regular solution model at each site seems to be in close agreement with the distribution data.

By using equation (3) we obtain the partial activity coefficient for different mole fractions. Figures 2 and 3 are plots of $X_{Fe}(= Fe^{2+}/Fe^{2+} + Mg$ in $M1$ or in $M2$) against $f_{Fe}^{M2}X_{Fe}^{M1}$ or $f_{Fe}^{M2}X_{Fe}^{M2}$. The latter two values, if it were a crystal as a whole, would be the activity of Fe end member. We may refer to this as the 'partial' activity.

The mixing at the $M1$ site has a large positive deviation from ideal solution. It may be mentioned here that in the case of a solid solution of two end members, a value of Nw/RT larger than 2.0 leads to a separation
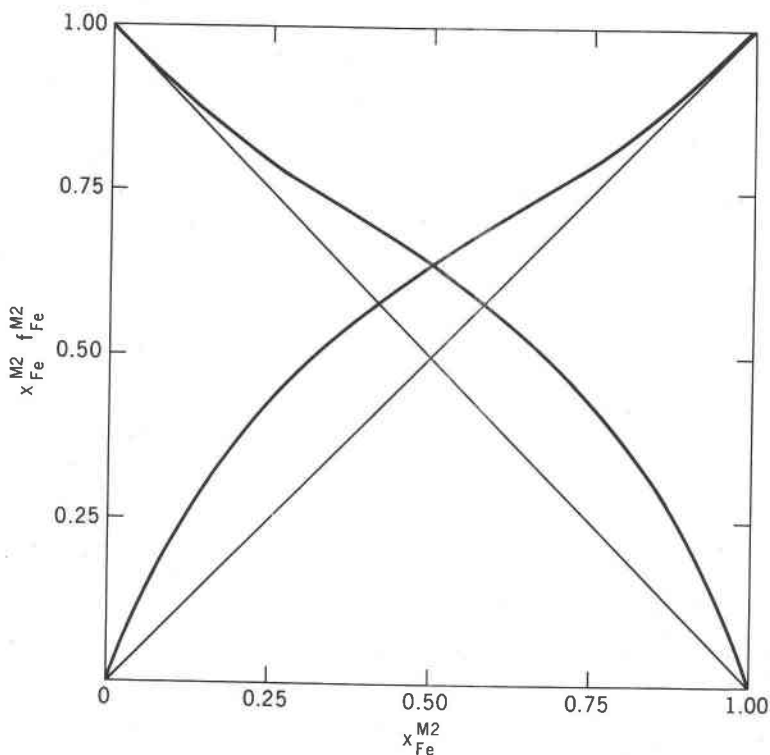

FIG. 3. The 'partial' activity of Fe^{2+} at the $M2$ site plotted against the mole fraction X_{Fe}^{M2}
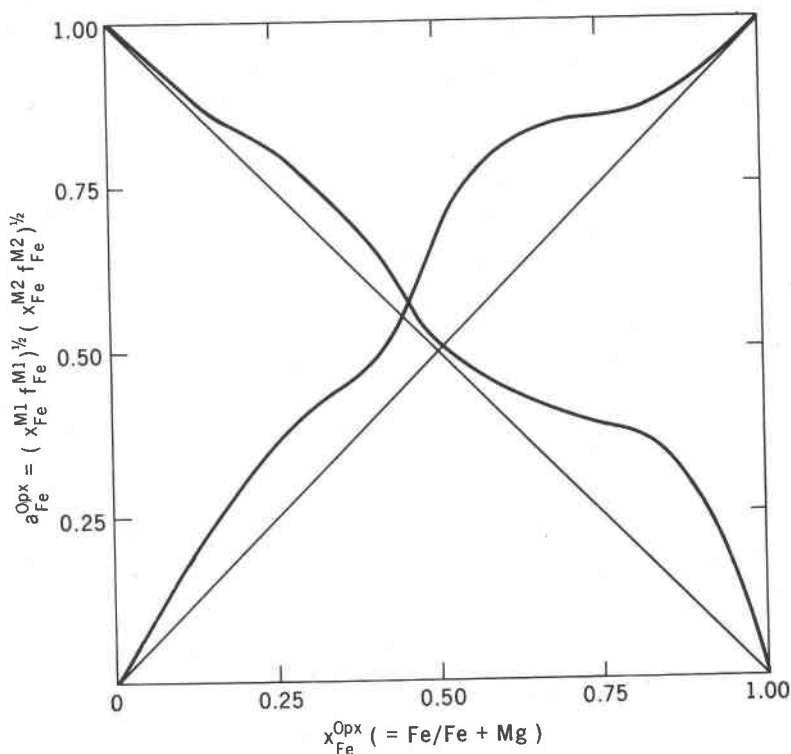
FIG. 4. The tentative activity-composition relation in orthopyroxene at 450–500°C.

of the solution into two separate phases. The $M2$ site is closer to the ideal solution model.

ACTIVITY-COMPOSITION RELATION IN ORTHOPYROXENE

The activity of Fe component end member in orthopyroxene, normalized to the formula (Fe Mg) SiO_3 is given by

$$a_{Fe}{}^{Opx} = (a_{Fe}{}^{M1})^{1/2}(a_{Fe}{}^{M2})^{1/2} \tag{5}$$

Where $a_{Fe}{}^{M1}$ and $a_{Fe}{}^{M2}$ are the activities (referred to as 'partial' activities to avoid confusion with the activity in the crystal as a whole) of the Fe component at $M1$ and $M2$ sites respectively. Substituting

$$a_{Fe}{}^{M1} = f_{Fe}{}^{M1} X_{Fe}{}^{M1}$$

and

$$a_{Fe}{}^{M2} = f_{Fe}{}^{M2} X_{Fe}{}^{M2}$$

in equation (5), we have

$$a_{\mathrm{Fe}}{}^{\mathrm{Opx}} = (f_{\mathrm{Fe}}{}^{M1}X_{\mathrm{Fe}}{}^{M1})^{1/2}(f_{\mathrm{Fe}}{}^{M2}X_{\mathrm{Fe}}{}^{M2})^{1/2} \tag{6}$$

From Figure 1 we can recalculate the mole fractions X_{Fe} in $M1$ and $M2$ sites which correspond to different $X_{\mathrm{Fe}}{}^{\mathrm{Opx}}$ ($= \mathrm{Fe}/\mathrm{Fe}+\mathrm{Mg}$ in the crystal as a whole). By using the Nw/RT values as obtained for $M1$ and $M2$, we can finally plot the mole fraction $X_{\mathrm{Fe}}{}^{\mathrm{Opx}}$ against the product $(X_{\mathrm{Fe}}{}^{M1}f_{\mathrm{Fe}}{}^{M1})^{1/2}(X_{\mathrm{Fe}}{}^{M2}f_{\mathrm{Fe}}{}^{M2})^{1/2}$. This tentative plot is shown in Figure 4, which shows that there is a positive deviation from the ideal solution model. Neither does the shape of the curves conform to a regular solution model. However, it should be remembered that the temperature corresponding to this activity-composition relation is considerably lower than that of the granulite facies of metamorphism (600–650°C). With increasing temperature the solid solution may approach ideality (see Nafziger and Muan, 1967).

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