

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  $\alpha$  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  $\alpha$  and  $\beta$  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.

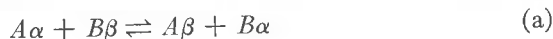
INTRODUCTION

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 orthopyroxenes 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



where  $\alpha$  and  $\beta$  are binary ( $A$ ,  $B$ ) regular solutions (see Mueller, 1964) is given by

$$K_a = \frac{(1 - X_A^\alpha) X_A^\beta \exp \left\{ \left(1 - 2X_A^\beta\right) \frac{N \cdot w^\beta}{RT} \right\}}{(1 - X_A^\beta) X_A^\alpha \exp \left\{ \left(1 - 2X_A^\alpha\right) \frac{N \cdot w^\alpha}{RT} \right\}} \quad (1)$$

This may also be written as

$$\ln K_D - \ln K = \frac{Nw^\alpha}{RT} (1 - 2X_A^\alpha) - \frac{Nw^\beta}{RT} (1 - 2X_A^\beta) \quad (2)$$

where  $K_D$  is  $X_A^\beta(1 - X_A^\alpha)/(1 - X_A^\beta)X_A^\alpha$ ,  $R$  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 heterogeneous 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  $\alpha$  and  $\beta$  as two different sites. Note that  $w^\alpha$  and  $w^\beta$  are not of the same thermodynamic significance as they are when  $\alpha$  and  $\beta$  are end member phases. However, in analogy with the inter-crystalline exchange energy, the intra-crystalline exchange energy continues to be a function of  $w^\alpha$  and  $w^\beta$ .

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

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

When  $\alpha$  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

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

where  $\alpha$  and  $\beta$  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

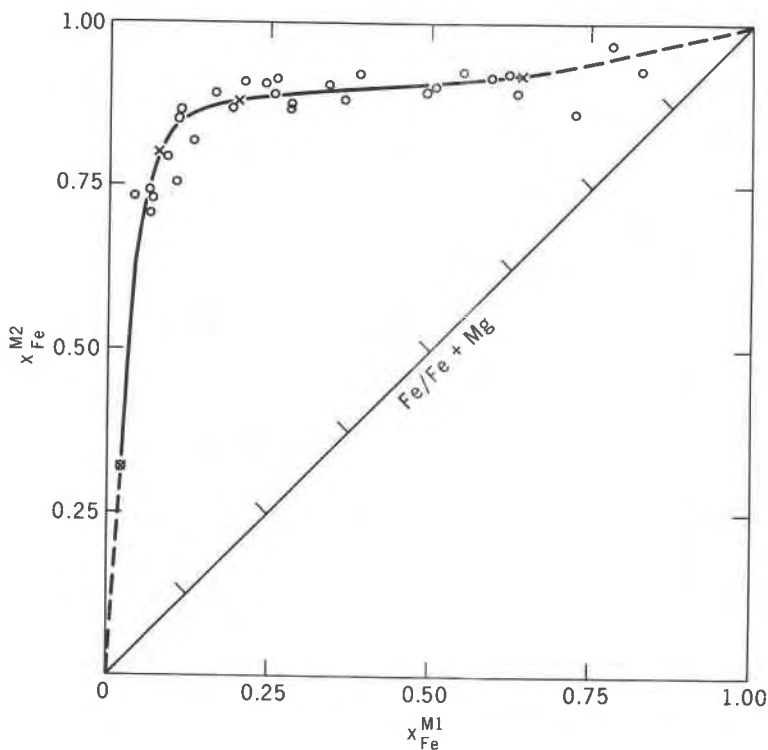


FIG. 1. Distribution of  $Fe^{2+}$  and  $Mg$  between  $M1$  and  $M2$  sites in metamorphic orthopyroxenes. Data from Virgo and Hafner (1970). The curve is drawn through the crosses and represents the relation.

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

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  $\text{Fe}^{2+}$  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  $f_{\text{Fe}}^{M1}$  refers to the 'partial' activity coefficient of  $\text{Fe}^{2+}$  in  $M1$  site.

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

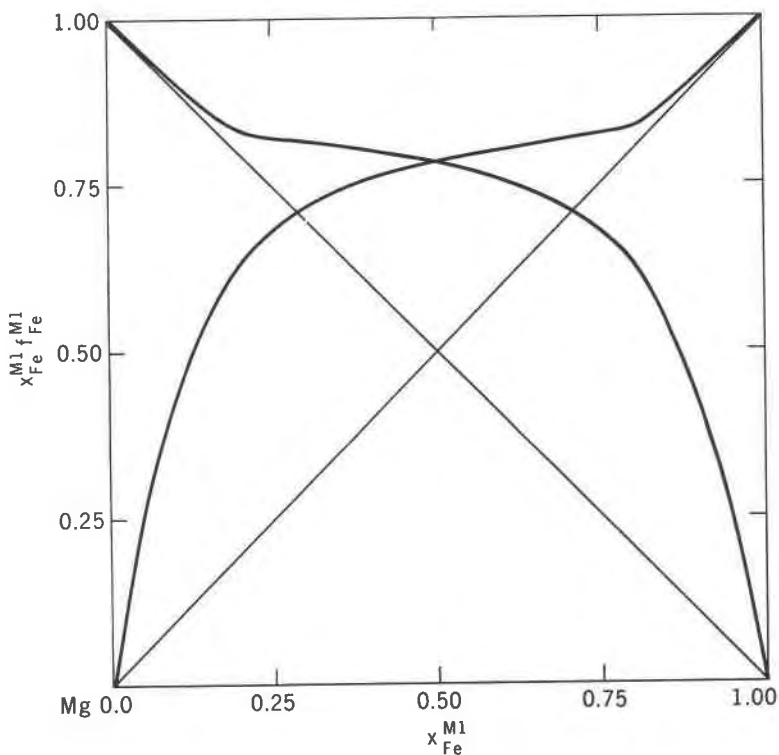


FIG. 2. The 'partial' activity of  $\text{Fe}^{2+}$  at the  $M1$  site plotted against the mole fraction  $X_{\text{Fe}}^{M1}$ .

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

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

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  $X_{\text{Fe}}$  (=  $\text{Fe}^{2+}/\text{Fe}^{2+} + \text{Mg}$  in  $M1$  or in  $M2$ ) against  $f_{\text{Fe}}^{M2} X_{\text{Fe}}^{M1}$  or  $f_{\text{Fe}}^{M2} X_{\text{Fe}}^{M2}$ . 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

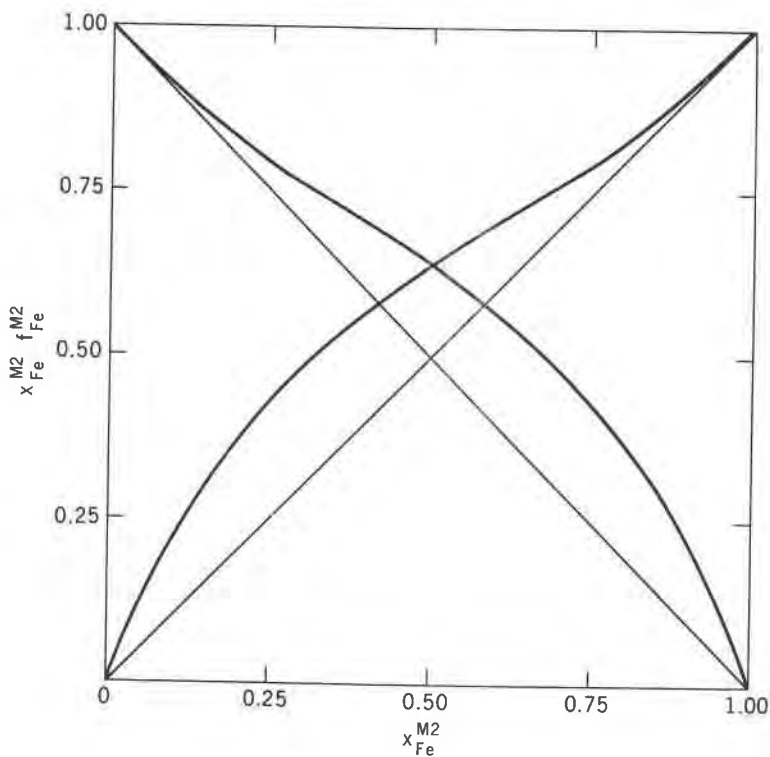


FIG. 3. The 'partial' activity of  $\text{Fe}^{2+}$  at the  $M2$  site plotted against the mole fraction  $X_{\text{Fe}}^{M2}$

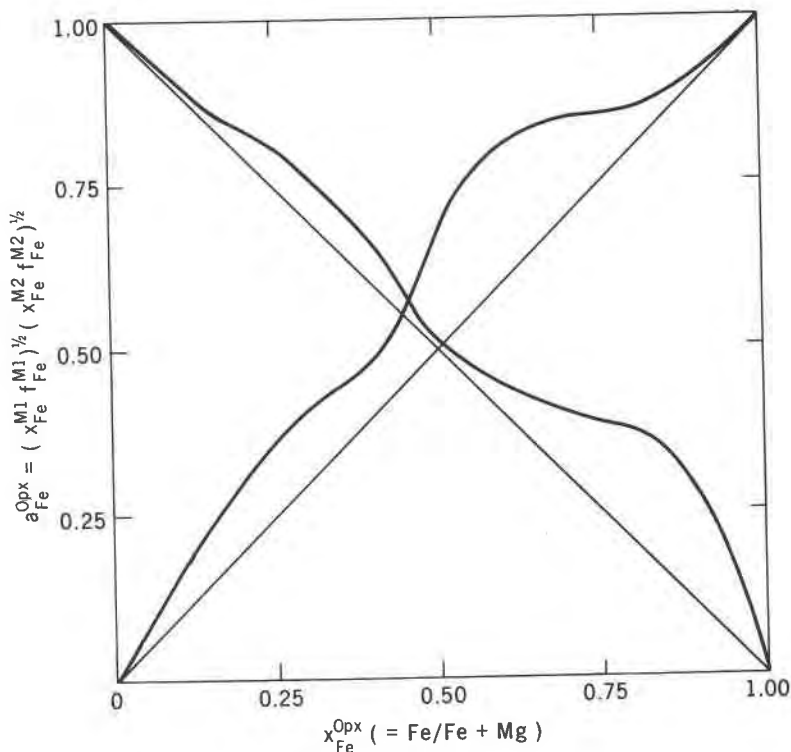


FIG. 4. The tentative activity-composition relation in orthopyroxene at 450–500°C.

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<sub>3</sub> is given by

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

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

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

From Figure 1 we can recalculate the mole fractions  $X_{\text{Fe}}$  in  $M1$  and  $M2$  sites which correspond to different  $X_{\text{Fe}^{\text{Opx}}}$  ( $= \text{Fe}/\text{Fe} + \text{Mg}$  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  $X_{\text{Fe}^{\text{Opx}}}$  against the product  $(X_{\text{Fe}^{\text{M1}}} f_{\text{Fe}^{\text{M1}}})^{1/2} (X_{\text{Fe}^{\text{M2}}} f_{\text{Fe}^{\text{M2}}})^{1/2}$ . 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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#### REFERENCES

- FOWLER, R., AND E. A. GUGGENHEIM (1956) *Statistical Thermodynamics*. Cambridge.
- GHOSE, S. (1961) The crystal structure of cummingtonite. *Acta Crystallogr.* **14**, 622–627.
- (1965)  $\text{Mg}^{2+}$ - $\text{Fe}^{2+}$  order in orthopyroxene  $\text{Mg}_{0.93}\text{Fe}_{0.07}\text{Si}_2\text{O}_6$ . *Z. Kristallogr.* **122**, 81–99.
- GUGGENHEIM, E. A. (1952) *Mixtures*. Oxford University Press, London.
- MUELLER, R. F. (1961) Analysis of relations among Mg, Fe and Mn in certain metamorphic minerals. *Geochim. Cosmochim. Acta*, **25**, 267–296.
- (1962) Energetics of certain silicate solid solutions. *Geochim. Cosmochim. Acta*, **26**, 581–598.
- (1964) Theory of immiscibility in mineral systems. *Mineral. Mag.* **33**, 1015–1023.
- NAFZIGER, R. H. AND A. MUAN (1967) Equilibrium phase compositions and thermodynamic properties of olivines and pyroxenes in the system  $\text{MgO}$ - ${}^{44}\text{FeO}$ - $\text{SiO}_2$ . *Amer. Mineral.* **52**, 1364–1385.
- SAXENA, S. K. (1969) Silicate solid solution and geothermometry. 1. Use of the regular solution model. *Contrib. Mineral. Petrology*, **21**, 338–345.
- THOMPSON, J. B. JR. (1967) Thermodynamic properties of simple solutions. In P. H. Abelson, ed., *Researches in geochemistry, II*, John Wiley and Sons, New York, 340–361.
- (1969) Chemical reactions in crystals. *Amer. Mineral.* **54**, 341–375.
- VIRGO, D., AND S. S. HAFNER (1969)  $\text{Fe}^{2+}$ , Mg order-disorder in heated orthopyroxenes. *Mineral. Soc. Amer. Spec. Pap.* **2**, 67–81.
- (1970)  $\text{Fe}^{2+}$ , Mg order-disorder in natural orthopyroxenes. *Amer. Mineral.* **55**, 201–223.

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