A thermodynamic treatment of chemical reactions in orthopyroxene

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Mixing of Fe and Mg in orthopyroxene crystalline solution can be represented by a multicomponent regular solution model when the molecules ($\text{Mg}^{\text{M1}}\text{Mg}^{\text{M2}}\text{Si}_2\text{O}_6$, $\text{Fe}^{\text{M1}}\text{Fe}^{\text{M2}}\text{Si}_2\text{O}_6$, $\text{Fe}^{\text{M1}}\text{Mg}^{\text{M2}}\text{Si}_2\text{O}_6$ and $\text{Mg}^{\text{M1}}\text{Fe}^{\text{M2}}\text{Si}_2\text{O}_6$) are introduced as its components. In this regular solution model, there are three independent interaction parameters (W^{M1} , W^{M2} and W^{M1M2}) which correspond to the cation interactions between M1 and M1 sites, M2 and M2 sites and M1 and M2 sites, respectively. These parameters can not be determined uniquely by site-occupancy measurements only. Some thermodynamic formulations for orthopyroxene are given by using these parameters.

INTRODUCTION

Interaction of Fe and Mg in orthopyroxene crystalline solution was discussed by SAXENA and GHOSE (1971) on the basis of their site-occupancy measurements. In order to explain the observed compositional dependence of the apparent internal partition constant, they assumed that site-occupancy in both M1 and M2 sites of orthopyroxene can be treated as regular solutions. At the same time, they introduced the concept of chemical potential of ions in M1 and M2 sites. This treatment was followed by SAXENA (1973). Since chemical potential can not be defined for ions in silicates (MUELLER *et al.*, 1970), the physical meaning of the thermodynamic parameters in their discussions, however, is not clear. Also, if there are cation interactions between M1 and M2 sites, their treatment becomes no longer valid. Since M1 and M2 sites form the nearest neighbouring cation pairs, the validity of their treatment is questionable (MATSUI and NISHIZAWA, 1975; BANNO, 1974). A more reasonable solution model is needed in order to understand the nature of chemical reactions in orthopyroxene. In this paper, a treatment based on a multicomponent regular solution model is presented.

THERMODYNAMICS

Let us consider an isolated orthopyroxene whose composition lies in the enstatite-ferrosilite join. As a result of the mixing of Fe and Mg,

the following four kinds of compositional molecules are formed in the crystal (Fig. 1):

Chemical potential for these molecules can be defined as

$$\mu_i = \frac{\partial G}{\partial n_i}$$

where n_i is number of the molecules. Though μ_A and μ_B are hypothetical quantities, they have definite physical meaning in the same way as μ_{En} and μ_{Fs} (BANNO and MATSUI, 1967). Using these four kinds of molecules we can write the equilibrium condition as

$$\begin{aligned} \delta G &= \mu_{\text{En}} \delta n_{\text{En}} + \mu_{\text{Fs}} \delta n_{\text{Fs}} + \mu_A \delta n_A + \mu_B \delta n_B \\ &= 0 \end{aligned}$$

On the other hand, from the condition of isolation, we have:

$$\begin{aligned} 2n_{\text{En}} + n_A + n_B &= \text{const.} \quad 2n_{\text{Fs}} + n_A + n_B \\ &= \text{const.} \end{aligned}$$

Using these equations, we obtain the following equilibrium equations:

$$\mu_A = \mu_B \quad (1)$$

Fig. 1. A schematic representation of the structure of orthopyroxene. Only M1 and M2 sites are represented for simplicity. Since the division of the crystal into molecules is arbitrary, the molecules can be defined in several ways. In this paper, in order to clarify the discussion, the molecules are defined as can be seen. Since the array of M1 and M2 sites forms a two-dimensional strip, there are three directions for the nearest neighbouring M1-M2 pair, i.e. one of which is along *b* axis and the other two are oblique to *b* axis. When the M1-M2 interactions are equivalent in all directions, A-B pair is energetically equivalent to En-Fs pair.

$$2\mu_A = \mu_{En} + \mu_{Fs} \quad (2)$$

Although Eqs. (1) and (2) are derived independently, they correspond to a common internal reaction:

Approximating that cations in each site are distributed at random, we can write the mole-fraction of the molecules as

$$\begin{aligned} X_{En} &= X_{Mg}^{M1} X_{Mg}^{M2}, & X_{Fs} &= X_{Fe}^{M1} X_{Fe}^{M2}, \\ X_A &= X_{Fe}^{M1} X_{Mg}^{M2}, & X_B &= X_{Mg}^{M1} X_{Fe}^{M2} \end{aligned} \quad (3)$$

where X_{Mg}^{M1} etc. are mole-fraction of the cations

in each site. In the present system, we have:

$$X_{Mg}^{M1} + X_{Fe}^{M1} = 1, \quad X_{Mg}^{M2} + X_{Fe}^{M2} = 1 \quad (4)$$

Then we can rewrite Eqs. (1) and (2) as

$$RT \ln K_{(1)} = -\Delta G_{(1)}^{\circ}, \quad K_{(1)} = a_A/a_B,$$

$$K_{(1)} = K' \cdot \gamma_A/\gamma_B \quad (5)$$

$$RT \ln K_{(2)} = -\Delta G_{(2)}^{\circ}, \quad K_{(2)} = a_A^2/a_{En} \cdot a_{Fs},$$

$$K_{(2)} = K' \cdot \gamma_A^2/\gamma_{En} \cdot \gamma_{Fs} \quad (6)$$

$$K' = \frac{X_{Fe}^{M1} X_{Mg}^{M2}}{X_{Mg}^{M1} X_{Fe}^{M2}}$$

where $K_{(1)}$ and $K_{(2)}$ are equilibrium constants, a_i is activity, γ_i is activity coefficient, and K' is apparent internal partition constant. The activity coefficient is given by definition

$$RT \ln \gamma_K = \frac{\partial G_{ex}}{\partial n_K} \quad (7)$$

where G_{ex} is excess free energy in reference to the ideal site-preference model.

Since the molecules are considered to be distributed at random, G_{ex} may be represented by the regular solution model as

$$G_{ex} = n \bar{G}_{ex}, \quad n = n_{En} + n_{Fs} + n_A + n_B \quad (8)$$

$$\bar{G}_{ex} = \alpha_{En \cdot Fs} X_{En} X_{Fs} + \alpha_{En \cdot A} X_{En} X_A$$

$$+ \alpha_{En \cdot B} X_{En} X_B + \alpha_{Fs \cdot A} X_{Fs} X_A$$

$$+ \alpha_{Fs \cdot B} X_{Fs} X_B + \alpha_{A \cdot B} X_A X_B \quad (9)$$

where $\bar{G}_{ex}$ is the molar excess free energy in reference to the ideal site-preference model and $\alpha_{En \cdot Fs}$ etc. are non-ideal parameters. $\alpha_{En \cdot Fs}$ etc. involve several kinds of cation interactions in general. The term $X_{En} X_{Fs}$ etc. correspond to the probability of the molecule pairs formed in the crystal. From Eq. (3), we have:

$$X_{En} X_{Fs} = X_A X_B \quad (10)$$

This is due to the fact that, as shown in Fig. 1,

En-Fs and A-B pairs are identical except for the orientation of the molecules. As a result, statistically the same number of En-Fs and A-B pairs are expected in a unit quantity of the crystal. Using the relations $nX_{En}X_{Fs} = n_{En}n_{Fs}/n$ etc. and Eqs. (7), (8) and (9), we obtain the activity coefficient as given by OKA and MATSUMOTO (1974):

$$RT \ln \gamma_K = \sum_i \alpha_{K \cdot i} X_i - \sum_i \left(\sum_j \alpha_{i \cdot j} X_i X_j \right) \quad (11)$$

In this derivation, it is noted that n in Eq. (8) is not fixed and each n_K in Eq. (7) is independent of each other. Therefore Eq. (10) is not valid in Eq. (7).

Using Eq. (11), we can write Eqs. (5) and (6) as

$$\begin{aligned} RT \ln K' = & -\Delta G_{(1)}^\circ + \alpha_{A \cdot B} (X_A - X_B) \\ & + (\alpha_{En \cdot B} - \alpha_{En \cdot A}) X_{En} \\ & + (\alpha_{Fs \cdot B} - \alpha_{Fs \cdot A}) X_{Fs} \end{aligned} \quad (12)$$

$$\begin{aligned} RT \ln K' = & -\Delta G_{(2)}^\circ + (\alpha_{Fs \cdot A} + \alpha_{En \cdot A}) X_A \\ & - (2\alpha_{A \cdot B} - \alpha_{Fs \cdot B} - \alpha_{En \cdot B}) X_B \\ & + (\alpha_{En \cdot Fs} - 2\alpha_{En \cdot A}) X_{En} \\ & + (\alpha_{En \cdot Fs} - 2\alpha_{Fs \cdot A}) X_{Fs} \end{aligned} \quad (13)$$

Since Eqs. (1) and (2) correspond to a common reaction, Eqs. (12) and (13) are identical to each other. Then by comparing the terms in Eqs. (12) and (13), and using (3) and (4), we get the following relations for the thermodynamic parameters.

$$\begin{aligned} \alpha_{Fs \cdot B} = \alpha_{En \cdot A} = W^{M1}, \quad \alpha_{En \cdot B} = \alpha_{Fs \cdot A} = W^{M2}, \\ \alpha_{A \cdot B} = W^{M1} + W^{M2} - W^{M12}, \\ \alpha_{En \cdot Fs} = W^{M1} + W^{M2} + W^{M12} \\ W^{M12} = -\mu_{En}^\circ - \mu_{Fs}^\circ + \mu_A^\circ + \mu_B^\circ \end{aligned} \quad (14)$$

where W^{M1} , W^{M2} and W^{M12} are interaction parameters of Fe and Mg of M1-M1, M2-M2 and M1-M2 pairs, respectively. μ_{En}° etc. are chemical potential of the pure substance*. It is noted that $\alpha_{En \cdot Fs} \neq \alpha_{A \cdot B}$. This indicates that though the pairs A-B and En-Fs are energetically equivalent, the excess free energy is different in the pair formation of $2 A-B \leftrightarrow A-A + B-B$ and $2 En-Fs \leftrightarrow En-En + Fs-Fs$.

Using Eqs. (14), we can write Eqs. (12) and (13) as

$$\begin{aligned} RT \ln K' = & -\Delta G^\circ + W^{M1} (2X_{Fe}^{M1} - 1) \\ & - W^{M2} (2X_{Fe}^{M2} - 1) - W^{M12} (X_{Fe}^{M1} \\ & - X_{Fe}^{M2}) \end{aligned} \quad (15)$$

where $\Delta G^\circ = \Delta G_{(1)}^\circ$.

$\bar{G}_{ex}$ can be represented by using W^{M1} , W^{M2} and W^{M12} as

$$\begin{aligned} \bar{G}_{ex} = & (W^{M1} + W^{M2} + W^{M12}) X_{En} X_{Fs} \\ & + W^{M1} X_{En} X_A + W^{M2} X_{En} X_B \\ & + W^{M1} X_{Fs} X_B + W^{M2} X_{Fs} X_A \\ & + (W^{M1} + W^{M2} - W^{M12}) X_A X_B \end{aligned}$$

Since $X_{En}X_{Fs} = X_A X_B$, W^{M12} does not appear explicitly in $\bar{G}_{ex}$. However, the same care as mentioned before should be given also in the derivation of activity coefficient.

DISCUSSION

Eq. (15) is the complete form of the equation proposed by SAXENA and GHOSE (1971). Unfortunately, the thermodynamic parameters can not be determined uniquely by site-occupancy measurements. This is due to the fact that $\alpha_{En \cdot Fs} \neq \alpha_{A \cdot B}$, while A-B and En-Fs pairs are indistinguishable from the site occupancy data. Eq. (15) can be rewritten as

$$RT \ln K' = -\Delta G^\circ + (W^{M1} - W^{M2}) (2\bar{X}_{Fe} - 1)$$

* μ_A° and μ_B° are hypothetical quantities, but they also have definite physical meanings (BANNO and MATSUI 1967).

Fig. 2 (a)

Fig. 2(a) and (b). Examples of the fit of the experiments by SAXENA and GHOSE (1971) according to Eq. (16).

Fig. 2 (b)

$$+ (W^{M1} + W^{M2} - W^{M12}) (X_{Fe}^{M1} - X_{Fe}^{M2}) \quad (16)$$

$$\text{where } 2\bar{X}_{Fe} = X_{Fe}^{M1} + X_{Fe}^{M2}$$

In order to examine this solution model, the data of the site-occupancy measurements by SAXENA and GHOSE (1971) are plotted in Fig. 2(a) and (b) according to Eq. (16). The thermodynamic parameters determined by Eq. (16) are listed in Table 1. The linearity expected from Eq. (16) is excellent. The reason for the success of the equation proposed by SAXENA and GHOSE (1971) is obviously due to the fact that Eq. (16) and their equation (Eq. (3) in SAXENA and GHOSE, 1971) have the same mathematical forms, except for the meaning of the thermodynamic parameters. It is interesting to formulate the non-ideal behaviour of orthopyroxene in equilibrium with other minerals.

For an exchange reaction of Fe and Mg between orthopyroxene and other coexisting minerals, it is convenient to treat the quantity $RT \ln (a_{Fs}/a_{En})$. According to the present solution model we have:

$$RT \ln \frac{a_{Fs}}{a_{En}} = RT \ln \frac{X_{Fe}^{M1} X_{Fe}^{M2}}{X_{Mg}^{M1} X_{Mg}^{M2}} + (W^{M1} + W^{M2} + W^{M12}) (1 - 2\bar{X}_{Fe}) - (W^{M1} - W^{M2}) (X_{Fe}^{M1} - X_{Fe}^{M2}) \quad (17)$$

Again, we can not determine the thermodynamic parameters in this equation from the site-occupancy measurements only.

At high temperatures, the third term in Eq. (17)

Table 1. Calculated thermodynamic parameters in Eq. (16). The standard errors are shown in parentheses.

T (°C)	ΔG° (kcal)	$W^{M1} + W^{M2} - W^{M12}$ (kcal)	$W^{M1} - W^{M2}$ (kcal)
800	2.64 (0.31)	2.67 (0.81)	0.42 (0.19)
700	2.53 (0.30)	3.05 (0.68)	0.59 (0.18)
600	1.84 (0.32)	4.58 (0.60)	0.11 (0.22)
500	1.86 (0.20)	4.97 (0.31)	0.91 (0.17)

Fig. 3. Deviation of the term $RT \ln(\bar{X}_{Fe}/\bar{X}_{Mg})$ from $1/2 RT \ln(X_{Fe}^{M1} X_{Fe}^{M2} / X_{Mg}^{M1} X_{Mg}^{M2})$ at 800°C . The source data are given in SAXENA and GHOSE (1971). The deviation can be approximated by Eq. (18) with $\omega = -700 \sim -800$ cal, except for Fe-rich side and extremely Mg-rich side. The theoretical curve is calculated numerically on the basis of Eq. (16) with the parameters in Table 1.

is negligible and $RT \ln(X_{Fe}^{M1} X_{Fe}^{M2} / X_{Mg}^{M1} X_{Mg}^{M2})$ can be approximated as (Fig. 3)

$$RT \ln \frac{X_{Fe}^{M1} X_{Fe}^{M2}}{X_{Mg}^{M1} X_{Mg}^{M2}} \cong RT \ln \frac{\bar{X}_{Fe}}{\bar{X}_{Mg}} + \omega (1 - 2\bar{X}_{Fe}) \quad (18)$$

where $2\bar{X}_{Mg} = X_{Mg}^{M1} + X_{Mg}^{M2}$. $\omega \cong -750$ cal at 800°C .

Then Eq. (17) can be written in a form of the simple solution (THOMPSON, 1967) as

$$\frac{1}{2} RT \ln \frac{a_{Fs}}{a_{En}} = RT \ln \frac{\bar{X}_{Fs}}{\bar{X}_{Mg}} + \alpha (1 - 2\bar{X}_{Fe}) \quad (19)$$

$$\text{where } \bar{\alpha} = \frac{1}{2} (W^{M1} + W^{M2} + W^{M12}) + \omega$$

$\bar{\alpha}$ can be determined from the partition experiments of Fe and Mg between coexisting orthopyroxene and olivine (NAFTZIGER and MUAN, 1967; LARIMER, 1968; MEDARIS, 1969; MATSUI and NISHIZAWA, 1974). Then using Eqs. (16) and (19), W^{M1} , W^{M2} and W^{M12} can be determined simultaneously. However, $\bar{\alpha}$ obtained from these experiments has considerable uncertainty (MATSUI and NISHIZAWA, 1974) and no definite conclusion is given for the magnitude of W^{M1} , W^{M2} and W^{M12} at present.

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