

Two-site multi-cation ordering-disordering in minerals: An alternative kinetic model

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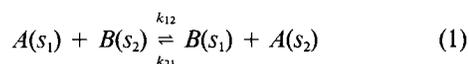
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ABSTRACT

Mueller's model has been widely applied to modeling kinetic experimental data on the ordering-disordering of cations between two nonequivalent sites. This model is valid only for pure or nearly pure binary systems. For ordering-disordering involving three or more cations (multiple cation or multi-cation) between two sites, Mueller's methodology, which is based on a two-cation exchange reaction, yields no explicit general solution. On the basis of a single-cation exchange reaction, we present an alternative kinetic model for multi-cation ordering-disordering in minerals with two nonequivalent sites. This model is not only suitable for binary systems but is also valid for multi-cation ordering-disordering at two nonequivalent sites. In addition, two kinetic coefficients for each individual cation can be easily obtained using nonlinear parameterization. A comparison of reported experimental data with theoretical calculations has shown that our model can fit both binary and multi-cation ordering-disordering very well and can also explain and predict many kinetic features observed in experiments.

INTRODUCTION

Many rock-forming minerals have two intracrystalline sites that show obvious cation ordering-disordering. Well-known examples include the octahedral M1 and M2 sites in olivines, clinopyroxenes, and orthopyroxenes as well as the tetrahedral T1 and T2 sites in monoclinic feldspars and cordierite. Several authors have investigated the theoretical kinetic models of two-site order-disorder processes (e.g., Bragg and Williams 1935; Dienes 1955; Mueller 1967, 1969; Ganguly 1982). Bragg and Williams (1935) discussed the energy change and the dependence of the coefficient of disorder on temperature in the order-disorder transformation of metal-alloy systems. Later, Dienes (1955) extended the theory of Bragg and Williams (1935), which was based on a two-cation exchange reaction in binary alloys. The author presented a second-order chemical-rate differential equation describing the long-range order parameter, but this equation has no explicit general solution. With the aid of numerical calculations, Dienes discussed some theoretical kinetic behavior of AB, AB₃, and nonstoichiometric alloys. Mueller (1967, 1969) modified Dienes's theory and found an explicit solution for binary solid-solution minerals with two nonequivalent sites. The models of Dienes (1955) and Mueller (1967, 1969) were based on a similar two-cation exchange reaction, which can be generally expressed as

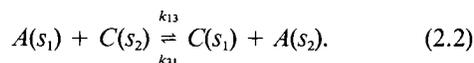
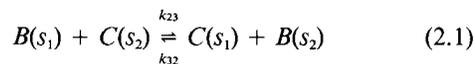


where *A* and *B* are different cations that form solid so-

lutions at sites *s*₁ and *s*₂, and *k*₁₂ and *k*₂₁ are the kinetic coefficients of the forward and backward reactions.

Mueller's model has been widely applied to modeling experimental data on two-cation order-disorder kinetics in minerals with two nonequivalent sites, especially for nearly pure binary solid solutions such as ferromagnesian orthopyroxenes (Virgo and Hafner 1969, 1970; Saxena and Ghose 1971; Besancon 1981; Ganguly 1982; Ghose and Ganguly 1982; Saxena et al. 1987, 1989; Anovitz et al. 1988; Skogby 1992; Sykes-Nord and Molin 1993). However, because Mueller's model is based on the two-cation exchange reaction (Reaction 1) of a binary solid solution, it is valid only for a binary system. For ordering-disordering involving more than two cations in minerals with multicomponent solid solution, Mueller (1967, 1969) could treat such multi-cation ordering-disordering only as a quasi-binary or pseudobinary system, but this methodology fails to give an explicit general solution for the differential equation given by Mueller (1967, 1969). This is clearly demonstrated by the following example.

Suppose that there are three cations, *A*, *B*, and *C*, each of which can undergo ordering-disordering at sites *s*₁ and *s*₂, which occur in equal numbers. The ordering-disordering can be represented by Reaction 1 and the following two quasi-binary exchange reactions according to Mueller's methodology:



According to chemical-rate theory, it follows that

$$\frac{dx_1^A}{dt} = -k_{12}x_1^Ax_2^B + k_{21}x_1^Bx_2^A - k_{13}x_1^Ax_2^C + k_{31}x_1^Cx_2^A \quad (3.1)$$

$$\frac{dx_1^B}{dt} = -k_{23}x_1^Bx_2^C + k_{32}x_1^Cx_2^B + k_{12}x_1^Ax_2^B - k_{21}x_1^Bx_2^A \quad (3.2)$$

where x_q^p is the concentration or site occupancy (mole fraction) of cation p at site q ($p = A, B, C$; $q = s_1, s_2$). Considering the stoichiometry and total composition of the mineral gives the following relations:

$$x_1^A + x_1^B + x_1^C = 1 \quad (4.1)$$

$$x_2^A + x_2^B + x_2^C = 1 \quad (4.2)$$

$$x_1^A + x_2^A = 2x_0^A \quad (4.3)$$

$$x_1^B + x_2^B = 2x_0^B \quad (4.4)$$

$$x_1^C + x_2^C = 2x_0^C = 2(1 - x_0^A - x_0^B) \quad (4.5)$$

where x_0^A , x_0^B , and x_0^C are the total compositions of cations A , B , and C , respectively. For cations A and B at site s_1 , simplifying the above equations gives

$$\frac{dx_1^A}{dt} = a_0 + a_1x_1^A + a_2x_1^B + a_3x_1^Ax_1^B + a_4(x_1^A)^2 \quad (5.1)$$

$$\frac{dx_1^B}{dt} = b_0 + b_1x_1^A + b_2x_1^B + b_3x_1^Ax_1^B + b_4(x_1^B)^2 \quad (5.2)$$

in which the constants are as follows: $a_0 = 2k_{31}x_0^A$, $a_1 = -2k_{12}x_0^B - k_{13} + 2k_{13}(x_0^A + x_0^B) - k_{31}(1 + 2x_0^A)$, $a_2 = 2(k_{21} - k_{31})x_0^A$, $a_3 = k_{12} - k_{21} + k_{31} - k_{13}$, and $a_4 = k_{31} - k_{13}$; $b_0 = 2k_{32}x_0^B$, $b_1 = 2(k_{12} - k_{32})x_0^B$, $b_2 = -2k_{21}x_0^A - k_{23} + 2k_{23}(x_0^A + x_0^B) - k_{32}(1 + 2x_0^B)$, $b_3 = k_{32} - k_{23} + k_{21} - k_{12}$, and $b_4 = k_{32} - k_{23}$.

In principle, the site occupancies of cations A , B , and C at sites s_1 and s_2 can be completely determined by Equations 4.1–5.2 if initial conditions are known. However, there are no explicit general solutions for differential Equations 5.1 and 5.2 because the coefficients of all the quadratic terms are nonzero, except when the system is in equilibrium with $k_{12} = k_{21}$, $k_{23} = k_{32}$, and $k_{13} = k_{31}$, which would not be a kinetic but an equilibrium problem. For the ordering-disordering of more than three cations, the kinetic differential equations deduced from Mueller's model would become more complicated.

The lack of an explicit general solution to Mueller's model for multi-cation ordering-disordering hampers its application to modeling experimental data and estimating the order-disorder kinetic coefficients. In fact, many ferromagnesian minerals have more than two cations that can form solid solution with ordering-disordering at each of the two sites. The most common examples include Fe^{2+} , Mg^{2+} , Ca^{2+} , and Mn^{2+} in orthopyroxene (e.g., Virgo and Hafner 1970; Anovitz et al. 1988; Griffen 1992), Fe^{2+} , Mg^{2+} , and Ca^{2+} in clinopyroxene (McCallister et al. 1976; Molin and Zanazzi 1991), and Fe^{2+} , Mg^{2+} , Mn^{2+} , Ca^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+} in olivine (e.g., Finger 1970; Finger and Virgo 1971; Bish 1981; Annersten et al. 1982,

1984; Nord et al. 1982; Lumpkin et al. 1983; Ericsson and Filippidis 1986; Griffen 1992), as well as Fe^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ca^{2+} in $\text{Me}_3(\text{PO}_4)_2$ orthophosphate with farringtonite-type structure, which is composed of a fivefold-coordinated M1 site and a sixfold-coordinated M2 site (Nord and Ericsson 1985).

The influence of the addition of a third cation into a binary solid solution on the ordering-disordering and cation partitioning was studied by Nord and Ericsson (1985) in some ternary orthophosphate systems with farringtonite-type structure, including solid solutions of Zn^{2+} - Fe^{2+} - Ni^{2+} , Zn^{2+} - Fe^{2+} - Mg^{2+} , Zn^{2+} - Fe^{2+} - Co^{2+} , Zn^{2+} - Fe^{2+} - Cd^{2+} , and Zn^{2+} - Fe^{2+} - Ca^{2+} . An increase in Ni mole fraction from 0.05 to 0.25 in the Zn^{2+} - Fe^{2+} - Ni^{2+} system, for example, decreases Fe^{2+} site occupancies from 0.08 to 0.02 at M1 and from 0.58 to 0.12 at M2, respectively, when total $X^{\text{Zn}} = 0.7$. When the total contents of two cations are invariable, the introduction of a third cation changes the Fe^{2+} site occupancies differently. In $(\text{Zn}_{0.50}\text{Fe}_{0.10}\text{Co}_{0.40})_3(\text{PO}_4)_2$ and $(\text{Mg}_{0.50}\text{Fe}_{0.10}\text{Co}_{0.40})_3(\text{PO}_4)_2$, for instance, the substitution of Mg for Zn decreases $x_{\text{Fe}}^{\text{Fe}}$ from 0.1 to 0.04 and increases $x_{\text{Fe}}^{\text{Fe}}$ from 0.11 to 0.22 (Nord and Ericsson 1985).

Ni^{2+} is a common component of ferromagnesian olivine, with its concentration being up to 56.32 wt% (De Waal and Calk 1973). Nord et al. (1982) studied the cation partitioning in synthetic ternary Mg^{2+} - Fe^{2+} - Ni^{2+} olivines. They found that Ni^{2+} in the ternary system shows much stronger preference for the M1 site than Fe^{2+} . This restrains Fe^{2+} , rather than the smaller Mg^{2+} , from residing in M1, forcing Fe^{2+} to become ordered into M2, in contrast to the observation that Fe^{2+} is usually ordered into M1 in Ni-free ferromagnesian olivine (e.g., Finger 1970; Finger and Virgo 1971). In addition, the introduction of Ni^{2+} into Mg-Fe olivine tends to shrink and regulate the M1 polyhedra, affecting the Mg-Fe distribution and consequently the ordering-disordering over a large range of temperatures (Nord et al. 1982).

It is clear from these experiments that the ordering-disordering and partitioning of cations in two-site minerals can be significantly affected by the presence of other cations. Therefore, caution must be applied when using Mueller's model to deal with a multi-cation order-disorder system, which cannot be simplified as a binary solid solution in a general sense.

In this paper, we present an explicit form of the order-disorder kinetic equations for multi-cation ordering-disordering in minerals with two nonequivalent sites. It is shown that our model, in comparison with Mueller's model, is much simpler and more straightforward and can fit reported experimental data well. More importantly, the kinetic coefficients for each individual cation, rather than composite values (as usually given by Mueller's model), can be easily estimated from experimental data.

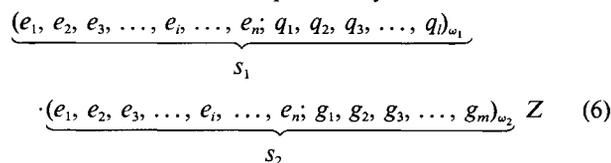
METHODOLOGY

When dealing with the kinetics of a multi-cation order-disorder system, two approaches may be used. The first

is to express the ordering-disordering as a group of two-cation exchange reactions similar to Reactions 1-2.2. This method was adopted by Dienes (1955), Mueller (1967, 1969), and many other investigators. It has been shown to be successful for a pure or nearly pure binary system but fails to give an explicit solution for multi-cation order-disorder processes as discussed earlier. The second methodology, which is adopted in this paper, is to treat the multi-cation ordering-disordering as single-cation exchange reactions between two nonequivalent sites. A fundamental difference between these two approaches is that the order-disorder kinetics is second order according to Mueller's methodology, such as Equations 3.1 and 3.2 or 5.1 and 5.2, but is first order in the second methodology, such as Equations 8.1 and 8.2 in the following section. The present work shows that the advantage of the second method is that explicit solutions for multi-cation ordering-disordering always exist.

KINETIC MODEL

The formula of a two-site, multicomponent solid-solution mineral can be expressed by



where $e_1, e_2, e_3, \dots, e_i, \dots, e_n$ are n exchangeable cations that can undergo ordering-disordering at both sites s_1 and s_2 , whereas $q_1, q_2, q_3, \dots, q_l$ and $g_1, g_2, g_3, \dots, g_m$ are cations that have no ordering-disordering but form solid solutions at the two sites; ω_1 and ω_2 are the number of s_1 and s_2 sites, respectively, per chemical formula unit of the mineral; and the symbol Z represents the rest of the mineral formula irrelevant to the ordering-disordering.

The order-disorder process of any cation e_i can be represented by the following single-cation exchange reaction:



where k_{12} and k_{21} are the kinetic coefficients (s^{-1}) of the forward and reverse exchange reactions of cation e_i between the two sites.

Suppose that the site occupancies or concentrations (mole fraction) of cation e_i at the s_1 and s_2 sites are x_1 and x_2 , respectively; the following kinetic equations apply:

$$\frac{dx_1}{dt} = -k_{12}x_1 + k_{21}x_2 \quad (8.1)$$

$$\frac{dx_2}{dt} = k_{12}x_1 - k_{21}x_2 \quad (8.2)$$

where t is the time (in seconds) of the order-disorder process. Adding Equation 8.1 to 8.2 gives

$$\frac{dx_1}{dt} + \frac{dx_2}{dt} = \frac{d(x_1 + x_2)}{dt} = 0. \quad (9)$$

Therefore, it follows that

$$x_1 + x_2 = x_1^0 + x_2^0 = m_0 \quad (10)$$

where x_1^0 and x_2^0 are the initial site occupancies of the cation at sites s_1 and s_2 , respectively, and m_0 is a constant. Substituting $x_2 = m_0 - x_1$ into Equation 8.1 yields

$$\frac{dx_1}{dt} = -(k_{12} + k_{21})x_1 + k_{21}m_0. \quad (11)$$

Integrating Equation 11 from x_1^0 to x_1 and from t_0 to t gives the result

$$x_1 = \frac{k_{21}m_0}{k_{12} + k_{21}} - \frac{(k_{21}x_2^0 - k_{12}x_1^0)}{k_{12} + k_{21}} \exp[-(k_{12} + k_{21})(t - t_0)]. \quad (12)$$

According to Equation 10, it follows that

$$x_2 = \frac{k_{12}m_0}{k_{12} + k_{21}} + \frac{(k_{21}x_2^0 - k_{12}x_1^0)}{k_{12} + k_{21}} \exp[-(k_{12} + k_{21})(t - t_0)]. \quad (13)$$

When $t_0 = 0$, Equations 12 and 13 are equivalent to

$$x_1 = \frac{k_{21}m_0}{k_{12} + k_{21}} - \frac{(k_{21}x_2^0 - k_{12}x_1^0)}{k_{12} + k_{21}} \exp[-(k_{12} + k_{21})t] \quad (14)$$

$$x_2 = \frac{k_{12}m_0}{k_{12} + k_{21}} + \frac{(k_{21}x_2^0 - k_{12}x_1^0)}{k_{12} + k_{21}} \exp[-(k_{12} + k_{21})t]. \quad (15)$$

Let

$$c_{10} = \frac{k_{21}m_0}{k_{12} + k_{21}} \quad (16)$$

$$c_{11} = -\frac{(k_{21}x_2^0 - k_{12}x_1^0)}{k_{12} + k_{21}} \quad (17)$$

$$c_{20} = \frac{k_{12}m_0}{k_{12} + k_{21}} \quad (18)$$

$$c_{21} = \frac{(k_{21}x_2^0 - k_{12}x_1^0)}{k_{12} + k_{21}} = -c_{11} \quad (19)$$

$$\lambda = -(k_{12} + k_{21}). \quad (20)$$

Equations 14 and 15 can be rewritten as

$$x_1 = c_{10} + c_{11} \exp(\lambda t) \quad (21)$$

$$x_2 = c_{20} + c_{21} \exp(\lambda t). \quad (22)$$

The pairs of Expressions 12 and 13, 14 and 15, and 21 and 22 are the kinetic equations for two-site multi-cation ordering-disordering of a mineral with multicomponent solid solutions. It is worthwhile to note that because our model is based on an exchange reaction of a single cation between the two sites, the kinetic equations are valid for each of the n cations participating in the two-site order-disorder processes.

DISCUSSION

Estimation of coefficients c_{10} , c_{11} , c_{20} , c_{21} , and λ

Different techniques can be used to determine the kinetic site occupancies (concentration-time data) of a cation at each of the two sites at varying temperatures (Ghose and Ganguly 1982; Hawthorne 1983). If a set of the concentration-time data is obtained, nonlinear parameterization methods (nonlinear estimation) can be employed to estimate the coefficients c_{10} , c_{11} , c_{20} , c_{21} , and λ .

Inversion of kinetic coefficients

Given coefficients c_{10} , c_{11} , c_{20} , c_{21} , and λ , we want to find the two kinetic coefficients k_{12} and k_{21} for a given cation. According to Equations 16, 18, and 20, it can be proved that

$$k_{12} = \frac{(c_{10} - m_0)\lambda}{m_0} = -\frac{c_{20}\lambda}{m_0} \quad (23)$$

$$k_{21} = -\frac{c_{10}\lambda}{m_0} = \frac{(c_{20} - m_0)\lambda}{m_0}. \quad (24)$$

Because m_0 is a constant independent of all other variables, it can be easily obtained by the addition of the site occupancies over the two sites at any time, irrespective of whether the data are equilibrium or kinetic values according to Equation 10. The coefficients c_{10} , c_{20} , and λ can be determined by the above-mentioned nonlinear estimations. Thus, the kinetic coefficients k_{12} and k_{21} can be calculated using Equations 23 and 24.

Equilibrium state of cation ordering-disordering

According to Equations 14 and 15, when $t \rightarrow \infty$, we get

$$x_1^E = \lim_{t \rightarrow \infty} x_1 = c_{10} = \frac{k_{21}m_0}{k_{12} + k_{21}} \quad (25)$$

$$x_2^E = \lim_{t \rightarrow \infty} x_2 = c_{20} = \frac{k_{12}m_0}{k_{12} + k_{21}} \quad (26)$$

where x_1^E and x_2^E are the equilibrium site occupancies at sites s_1 and s_2 , respectively. On the other hand, at equilibrium, the following condition must be satisfied: $(dx_1/dt) = (dx_2/dt) = 0$, which is equivalent to $-k_{12}x_1^E + k_{21}x_2^E = 0$. Therefore, the equilibrium distribution coefficient of a given cation between site s_1 and site s_2 on the basis of Reaction 7 is expressed as

$$K_D = \frac{x_2^E}{x_1^E} = \frac{k_{12}}{k_{21}} = \frac{c_{20}}{c_{10}}. \quad (27)$$

Equation 27 has several implications. First, at lower temperatures (e.g., at 773 K for orthopyroxene), the order-disorder rate is very slow, and equilibrium is very difficult to achieve (e.g., Besancon 1981; Ganguly 1982). In this case, the equilibrium distribution coefficient, K_D , cannot be obtained by direct measurements but can be easily calculated from c_{10} and c_{20} , which can be estimated through kinetic experiments using nonlinear parameter-

ization as mentioned above. Second, the ratio of the two kinetic coefficients can be obtained if the equilibrium distribution coefficient is known between the two sites. Thus, in cases in which only equilibrium site-occupancy data are available, the relative magnitude of the two kinetic coefficients of each cation can still be estimated. For example, the equilibrium distribution coefficients of Fe^{2+} ($K_D^{\text{Fe}^{2+}} = k_{12}^{\text{Fe}^{2+}}/k_{21}^{\text{Fe}^{2+}}$) between M1 and M2 sites in orthopyroxenes with differing compositions vary from 1.07 to 20.42 at temperatures ranging from 773 to 1273 K (Virgo and Hafner 1969, 1970; Saxena and Ghose 1971; Besancon 1981; Anovitz et al. 1988; Skogby 1992). This suggests that the forward kinetic coefficient ($k_{12}^{\text{Fe}^{2+}}$) for Fe^{2+} is greater than the reverse kinetic coefficient ($k_{21}^{\text{Fe}^{2+}}$), with $k_{12}^{\text{Fe}^{2+}}/k_{21}^{\text{Fe}^{2+}} \leq 21$ for the orthopyroxenes. On the other hand, the ratios of the two kinetic coefficients for Mg^{2+} are < 1 , with $k_{12}^{\text{Mg}^{2+}}/k_{21}^{\text{Mg}^{2+}}$ varying from 0.29 to 0.94 calculated from the experimental data (Besancon 1981; Anovitz et al. 1988; Skogby 1992). This example shows that different cations usually have different kinetic coefficients and therefore order or disorder at different rates.

Critical temperature of complete disorder

When the concentrations of a given cation at sites s_1 and s_2 are equal and time independent, a completely disordered state is achieved. Considering Equation 10, in this case, it follows that $x_1^E = x_2^E = (x_1^0 + x_2^0)/2 = m_0/2$, which is equivalent to

$$k_{12} = k_{21}. \quad (28)$$

According to Equation 28 and the Arrhenius equation $k = A \exp(-E/RT)$, where A and E are the preexponential factor and activation energy, respectively, the critical temperature, T_c , is given by

$$T_c = \frac{E_{12} - E_{21}}{R \ln \left(\frac{A_{12}}{A_{21}} \right)}. \quad (29)$$

In addition, a reasonable critical temperature has to satisfy another condition: $0 \leq T_c \leq T_s$, where T_s is the temperature beyond which the mineral becomes unstable and transforms into another phase. In other words, if the calculated T_c is negative or so high that it is beyond the stability region of the mineral, reaching the completely disordered state is impossible. The critical temperature for completely disordered ferromagnesian olivine is estimated to be around 1573 K (Finger and Virgo 1971).

Degree of order: A geometric definition

The site occupancies at s_1 and s_2 can be illustrated in Figure 1. Line ODQL represents a completely disordered state ($K_D = 1$) in which the concentrations of a given cation at s_1 and s_2 are equal. OPL is a partially disordered isothermal curve corresponding to $K_D > 1$, whereas OJL corresponds to $K_D < 1$. Point P (x_1, x_2) is any partially ordered state of a given sample. Point A ($0, x_2^0$) and point

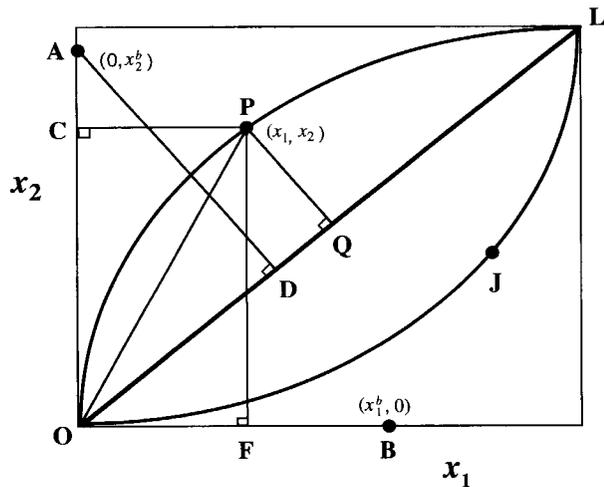


FIGURE 1. Schematic diagram illustrating how the degree of order is geometrically defined. Points B and A represent a completely ordered state of the cation into sites s_1 and s_2 , respectively, whereas point P denotes any partially ordered state. OPL and OJL are the isothermal distribution curves for $K_D > 1$ and $K_D < 1$, respectively. Line ODQL represents the completely disordered state corresponding to $K_D = 1$.

B $(x_1^b, 0)$ represent the completely ordered state of the cation into sites s_2 and s_1 , respectively. For binary solid solutions, the coordinates of points A and B are $(0, 1)$ and $(1, 0)$, respectively. For multicomponent solid solutions, point A is located between $(0, 0)$ and $(0, 1)$, and point B is located between $(0, 0)$ and $(1, 0)$, because the concentrations x_1^a and x_2^a of the cation at sites s_1 and s_2 in the completely ordered state are not equal to 1 but are located somewhere between 0 and 1.

The degree of order of a given cation at point P can be described by the distance PQ of point P to the completely disordered line ODQL. The distance from a completely ordered state A to the completely disordered line ODQL is AD . The degree of order is defined by normalizing PQ relative to AD : $\delta = (PQ/AD)$. Let $K_D = x_2/x_1$, it can be proved that the degree of order is given by

$$\delta = \frac{\sqrt{2[(x_1)^2 + (x_2)^2] \sin \left[\frac{\pi}{4} - \arctan(K_D) \right]}}{x_1 + x_2} = \frac{\sqrt{2[1 + (K_D)^2] \sin \left[\frac{\pi}{4} - \arctan(K_D) \right]}}{1 + K_D} \quad (30)$$

In a completely disordered state, $K_D = 1$, according to Equation 30, $\delta = 0$. When the cation is completely ordered into site s_1 , $K_D = 0$, then from Equation 30, $\delta = 1$. In contrast, if the cation is completely ordered into site s_2 , then $K_D = +\infty$, and the limiting value is

$$\lim_{K_D \rightarrow +\infty} \delta = 1. \quad (31)$$

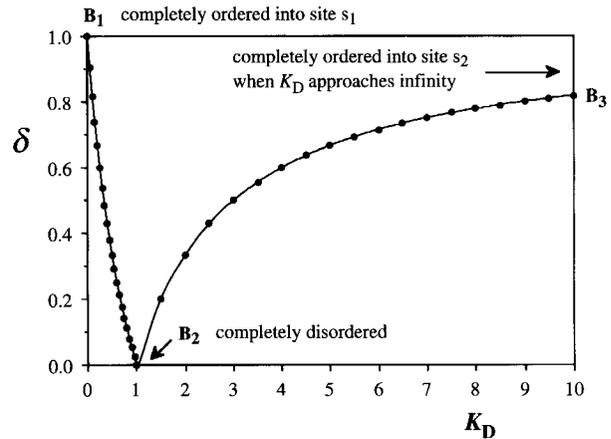


FIGURE 2. Theoretical curve of the degree of order plotted as a function of the distribution coefficient, K_D . Points B_1 and B_3 represent the completely ordered state of a cation into sites s_1 and s_2 , respectively. Point B_2 is the completely disordered state. Curves B_1B_2 and B_2B_3 correspond to $K_D < 1$ and $K_D > 1$, respectively.

For a partially ordered state, δ varies between 0 and 1. Figure 2 shows the theoretical δ - K_D curve of Equation 30. If we know the distribution coefficient, K_D , we can get the degree of order from the diagram. Curve B_1B_2 represents the order degree for $K_D < 1$, and curve B_2B_3 represents that for $K_D > 1$. Because of this, δ makes it easier to compare the degree of order for a given mineral at different temperatures, pressures, and compositions when K_D is known.

Some characteristics of kinetic curves

The derivative of kinetic Equations 21 and 22 can be generally expressed as

$$\frac{dx_i}{dt} = c_{i1} \lambda \exp(\lambda t). \quad (32)$$

Because $\lambda < 0$, if $c_{i1} < 0$, the site occupancy is a monotonically increasing function according to Equation 32; if $c_{i1} > 0$, then the site occupancy is a monotonically decreasing function. No local maximum or minimum can occur in a two-site order-disorder process. Considering Equations 17 and 19, if

$$\frac{x_2^0}{x_1^0} > \frac{k_{12}}{k_{21}} = K_D \quad (33)$$

the site occupancies x_1 and x_2 correspond to increasing and decreasing functions, respectively; if

$$\frac{x_2^0}{x_1^0} < \frac{k_{12}}{k_{21}} = K_D \quad (34)$$

the result is just the opposite. Inequalities 33 and 34 indicate that the initial site occupancies and kinetic coefficients play a decisive role in determining the variation trends of cation order-disorder processes.

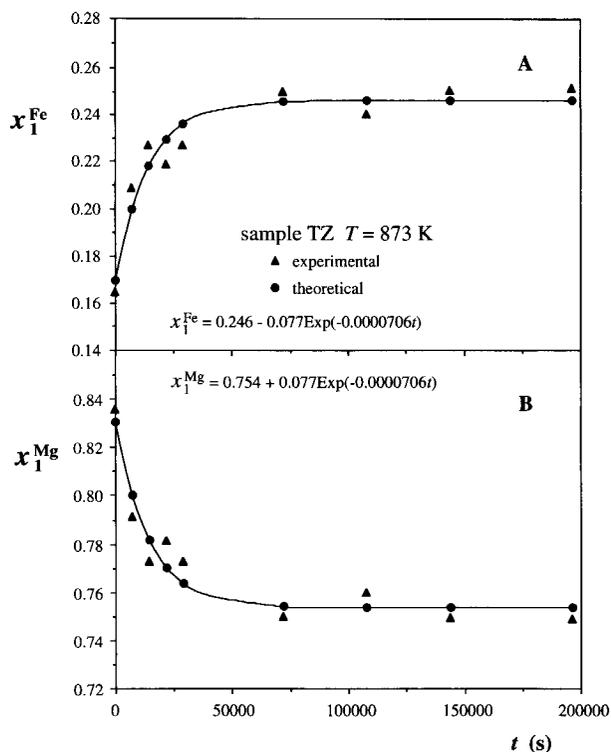


FIGURE 3. Theoretical curves showing that two-site order-disorder processes are either a monotonously increasing function (A) or a monotonously decreasing function (B), as illustrated by the disordering of Fe^{2+} and Mg^{2+} at the M1 site in an orthopyroxene. The parameters are estimated from the experimental data (solid triangles) for sample TZ of Besancon (1981).

COMPARISON WITH EXPERIMENTAL DATA

Experimental test

Numerous experiments on the ordering-disordering of different cations in various minerals with two nonequivalent sites have been reported in the literature, but most of these experimental data are equilibrium site occupancies. Orthopyroxenes, however, are an exception. Several researchers have investigated the kinetic site occupancies of Fe^{2+} and Mg^{2+} at the M1 and M2 sites in orthopyroxenes using Mössbauer spectrometry (Virgo and Hafner 1969; Besancon 1981; Anovitz et al. 1988; Skogby 1992) and single-crystal X-ray structure refinements (Saxena et al. 1987, 1989; Sykes-Nord and Molin 1993). To test our model, it may be useful to consider the following three cases for orthopyroxene.

(1) Two-cation ordering-disordering in pure binary solid solutions. Only Fe^{2+} and Mg^{2+} are assumed to take over the M1 and M2 sites, and other trace or minor cations are neglected. As a first approximation, the system is treated as a two-cation order-disorder process in a pure binary solid solution of Fe and Mg at each of the two sites. Reported experimental data include those of Besancon (1981), Anovitz et al. (1988), and Skogby (1992).

(2) Two-cation ordering-disordering in multicompo-

nent solid solutions. Both Fe^{2+} and Mg^{2+} as well as other cations such as Ca^{2+} , Mn^{2+} , Fe^{3+} , $^{60}\text{Al}^{3+}$, and Ti^{4+} are considered to occupy the M1 and M2 sites, but the site occupancies of these cations, except for Fe^{2+} and Mg^{2+} , are assumed to be constant. Therefore, only Fe^{2+} and Mg^{2+} participate in the order-disorder processes. Experiments of this sort include those of Saxena et al. (1987) and Sykes-Nord and Molin (1993).

(3) Multi-cation ordering-disordering in multicomponent solid solutions. More than two cations, such as Fe^{2+} , Mg^{2+} , and Mn^{2+} , are considered to be involved in the ordering-disordering, but the site occupancies of other cations as mentioned above are still assumed to be constant. The only available kinetic data of this kind were published by Saxena et al. (1989).

Figure 3 shows the experimental results of Besancon (1981) for the orthopyroxene sample TZ at 873 K. The site occupancy of Fe^{2+} at M1 increases with time because $c_{10}^{\text{Fe}} = -0.077 \pm 0.009 < 0$ and finally approaches its asymptote, $c_{10}^{\text{Fe}} = 0.246 \pm 0.004$; in contrast, the concentration of Mg^{2+} at M1, which is estimated from the site occupancies of Fe^{2+} at M1 by assuming that $x_1^{\text{Fe}} + x_1^{\text{Mg}} = 1$ (pure binary solution), decreases with time because $c_{10}^{\text{Mg}} = 0.0770 > 0$ and gradually approaches another asymptote, $c_{10}^{\text{Mg}} = 0.754 \pm 0.004$. The two asymptotes are the equilibrium concentrations of Fe^{2+} and Mg^{2+} , respectively, at M1. These features are consistent with the characteristics that have been predicted from theoretical Equation 32. Figure 4 demonstrates the experimental data of Skogby (1992) on the ordering-disordering in an orthopyroxene (sample AV77) at 923 K, which was treated as a binary solid solution.

Saxena et al. (1987) and Sykes-Nord and Molin (1993) studied the order-disorder kinetics in orthopyroxenes by considering the site occupancies of not only Fe^{2+} and Mg^{2+} but of other cations as well. They assigned Ca^{2+} and Mn^{2+} to the M2 site and ^{60}Al , Fe^{3+} , Cr^{3+} , and Ti^{4+} to the M1 site, and the concentrations of these cations were assumed to be constant at both sites. The experimental results for samples OPXS95-13 at 1023 K (Saxena et al. 1987) and OPX4 at 898 K (Sykes-Nord and Molin 1993) are illustrated in Figure 5. Similar results for the ferromagnesian ordering-disordering in orthopyroxenes have been given by other investigators (Virgo and Hafner 1969; Anovitz et al. 1988), but for brevity are not replotted here.

Saxena et al. (1989) experimentally investigated the order-disorder kinetics of the cations Mn^{2+} , Fe^{2+} , and Mg^{2+} in orthopyroxenes. Their results for sample OPX10 at 873 K are shown in Figure 6. Nonlinear estimations give the following kinetic coefficients: $k_{12}^{\text{Mn}} = (1.47 \pm 0.27) \times 10^{-4} \text{ s}^{-1}$, $k_{21}^{\text{Mn}} = (4.14 \pm 1.32) \times 10^{-5} \text{ s}^{-1}$; $k_{12}^{\text{Mg}} = (4.59 \pm 0.79) \times 10^{-5} \text{ s}^{-1}$, $k_{21}^{\text{Mg}} = (1.77 \pm 0.25) \times 10^{-4} \text{ s}^{-1}$; $k_{12}^{\text{Fe}} = (1.81 \pm 0.27) \times 10^{-4} \text{ s}^{-1}$, $k_{21}^{\text{Fe}} = (4.43 \pm 0.75) \times 10^{-5} \text{ s}^{-1}$.

From these diagrams, the following conclusions can be made. First, the experimental results can be fitted well with model Equations 21 and 22 in cases of ferromag-

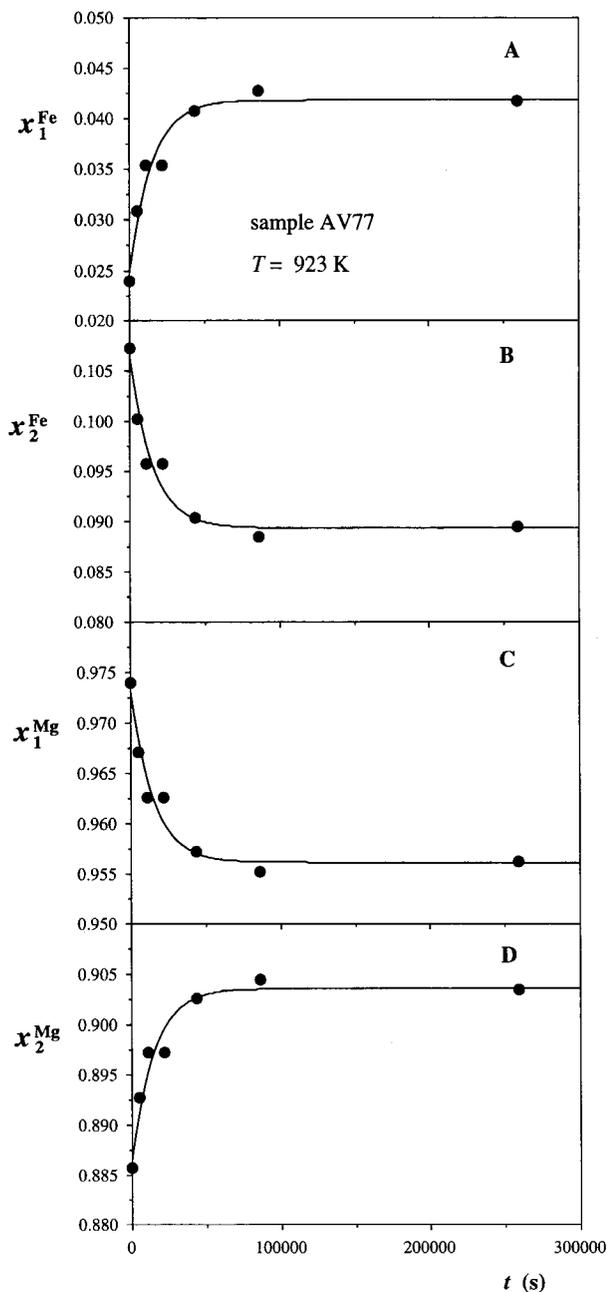


FIGURE 4. Two-cation ordering-disordering in a pure binary solid solution. Calculated values (curves) are compared with the experimental site occupancies (solid circles) of Fe^{2+} and Mg^{2+} at the M1 and M2 sites in orthopyroxene sample AV77 at 923 K measured by Skogby (1992). The site occupancies are (A) Fe^{2+} at M1, (B) Fe^{2+} at M2, (C) Mg^{2+} at M1, and (D) Mg^{2+} at M2.

nesian ordering-disordering in pure binary (Figs. 3 and 4) and multicomponent (Fig. 5) solid solutions, as well as multi-cation (Mn^{2+} , Fe^{2+} , and Mg^{2+}) ordering-disordering in multicomponent systems (Fig. 6).

Second, the kinetic characteristics of experimental data are in good agreement with the theoretical features that

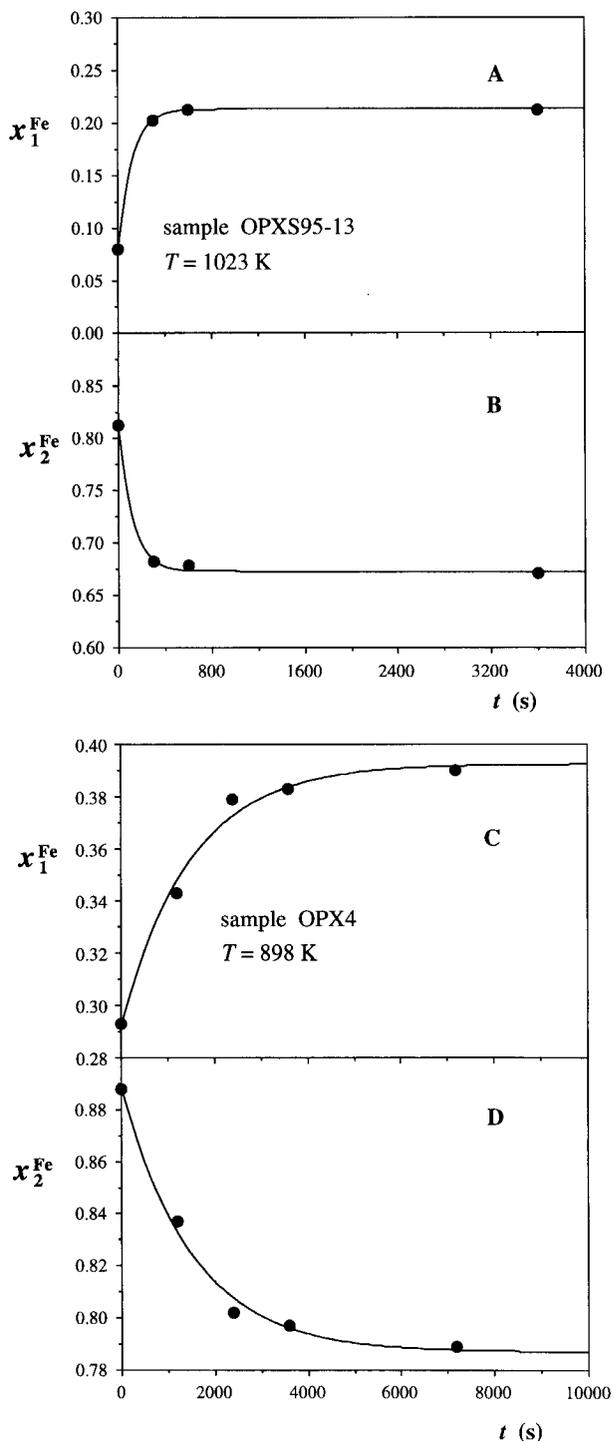


FIGURE 5. Two-cation ordering-disordering in a multicomponent solid solution. Calculated results (curves) based on the model are compared with the experimental site occupancies (solid circles) of Fe^{2+} at the M1 and M2 sites in the orthopyroxenes. (A) Fe^{2+} at M1 and (B) Fe^{2+} at M2 in sample OPXS95-13; (C) Fe^{2+} at M1 and (D) Fe^{2+} at M2 in sample OPX4. Experimental data are from Saxena et al. (1987) and Sykes-Nord and Molin (1993).

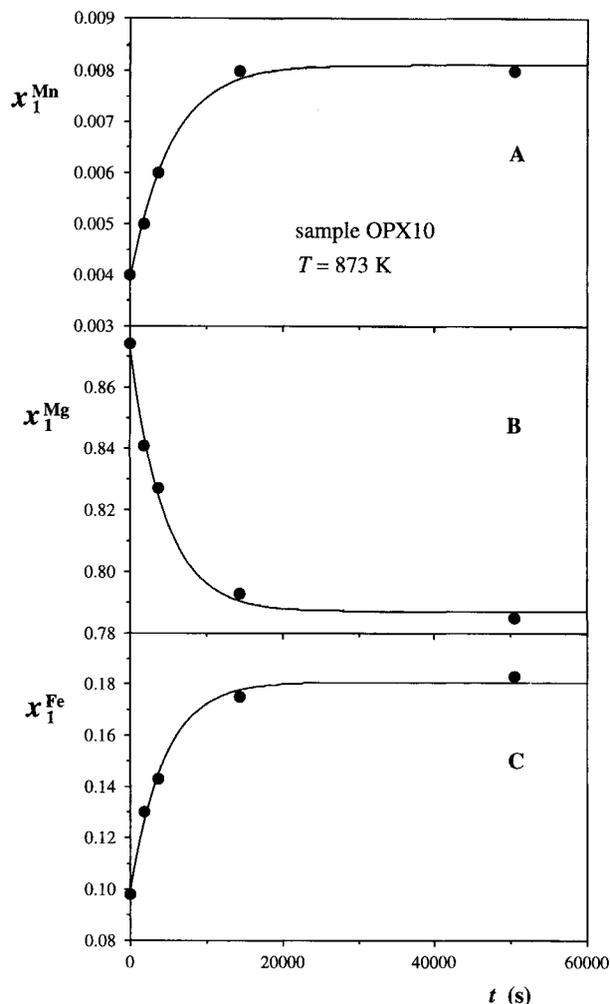


FIGURE 6. Multi-cation ordering-disordering in a multicomponent solid solution, as illustrated by Mn^{2+} , Mg^{2+} , and Fe^{2+} disordering in orthopyroxene sample OPX10. (A) Mn^{2+} at M1, (B) Mg^{2+} at M1, and (C) Fe^{2+} at M1. The experimental data (solid circles) (Saxena et al. 1989) are in agreement with the theoretical calculations (curves).

are predictable from our model. These features include the following.

(1) Variation trends of the site occupancies of a cation with time (kinetic curves). Given sample AV77 as an example (Fig. 4), the initial values of x_2^0/x_1^0 for Fe^{2+} and Mg^{2+} in the unheated natural sample are 4.47 and 0.909, respectively (Skogby 1992). The kinetic coefficients, which are estimated from the experimental data, are given as follows: $k_{12}^{\text{Fe}} = (4.59 \pm 1.29) \times 10^{-5} \text{ s}^{-1}$, $k_{21}^{\text{Fe}} = (2.15 \pm 0.65) \times 10^{-5} \text{ s}^{-1}$; and $k_{12}^{\text{Mg}} = (3.28 \pm 0.86) \times 10^{-5} \text{ s}^{-1}$, $k_{21}^{\text{Mg}} = (3.47 \pm 0.91) \times 10^{-5} \text{ s}^{-1}$. Because $K_{12}^{\text{Fe}} = k_{12}^{\text{Fe}}/k_{21}^{\text{Fe}} = 2.14 < (x_2^0/x_1^0)_{\text{Fe}} = 4.47$, we can expect that the site occupancies of Fe^{2+} increase at M1 but decrease at M2 with increasing time according to Inequality 33. Similarly, because $K_{12}^{\text{Mg}} = k_{12}^{\text{Mg}}/k_{21}^{\text{Mg}} = 0.945 > (x_2^0/x_1^0)_{\text{Mg}} = 0.909$, the concentrations of Mg^{2+} are expected to decrease at M1

and increase at M2 according to Inequality 34. These theoretical predictions are consistent with the experimental results shown in Figure 4.

(2) According to Equation 19, theoretically, the coefficients c_{11} and c_{21} for a given cation in site-occupancy Functions 21 and 22 should have equal absolute values but opposite signs at the two sites; and both sites should have the same λ value. Therefore, assuming there are no experimental errors, the above parameters estimated from the experimental site occupancies of a given cation at the two sites should satisfy these requirements. Given sample AV77 (Skogby 1992) as an example of a binary system, nonlinear estimations from the site occupancies of Fe^{2+} at M1 give the coefficients $c_{11}^{\text{Fe}} = (-1.69 \pm 0.18) \times 10^{-2}$, $\lambda_1 = (-6.74 \pm 1.76) \times 10^{-5}$. The site occupancies of Fe^{2+} at M2 give $c_{21}^{\text{Fe}} = (1.69 \pm 0.18) \times 10^{-2}$, $\lambda_2 = (-6.74 \pm 1.76) \times 10^{-5}$. Therefore, $c_{11}^{\text{Fe}} = -c_{21}^{\text{Fe}}$ and $\lambda_1 = \lambda_2 = \lambda$. Similarly, Mn^{2+} in the multi-cation ordering-disordering in the orthopyroxene sample OPX10 of Saxena et al. (1989) is another example. At the M1 site, $c_{11}^{\text{Mn}} = (-4.19 \pm 0.21) \times 10^{-3}$, $\lambda_1 = (-1.89 \pm 0.26) \times 10^{-4}$; and at the M2 site, $c_{21}^{\text{Mn}} = (4.19 \pm 0.21) \times 10^{-3}$, $\lambda_2 = (-1.89 \pm 0.26) \times 10^{-4}$. Within experimental uncertainties, the value of c_{11} in each example is considered to be identical to that of c_{21} for a given cation, and this is consistent with the theoretical requirements.

Disordering vs. ordering experiments

Before any kinetic experiment, a natural or synthetic starting material must be partially or completely pre-equilibrated at a certain temperature, T_0 , here called the initial temperature. At this temperature, a cation gains its initial site occupancies (either equilibrium or kinetic) by either geological processes or laboratory heating before a kinetic experiment is conducted at a different temperature T . If $T > T_0$, this experiment is usually called a disordering experiment; if $T < T_0$, it is referred to as an ordering experiment because most cations usually become more disordered with increasing temperature.

Initial equilibrium site occupancies for a fixed total composition of a mineral affect the kinetic behavior of the cation, leading to kinetic curves of the ordering experiments that are different from those of the disordering experiments at the same temperature and pressure. To illustrate this, consider the example of an orthopyroxene with total composition $x^{\text{Fe}} = 0.515$, which is the same as sample TZ of Besancon (1981). On the basis of experimental data (Besancon 1981) and nonlinear parameterization, we get the following Arrhenius relations for kinetic coefficients with temperature:

$$\ln k_{12}^{\text{Fe}} = (17.15 \pm 1.23) + (-23630 \pm 1180)/T \quad (35)$$

$$\ln k_{21}^{\text{Fe}} = (17.94 \pm 0.88) + (-25257 \pm 846)/T. \quad (36)$$

Now suppose that a series of kinetic experiments were conducted on this sample at the same temperature, 873 K, and that all conditions for the kinetic experiments are exactly the same except for the initial pre-equilibration

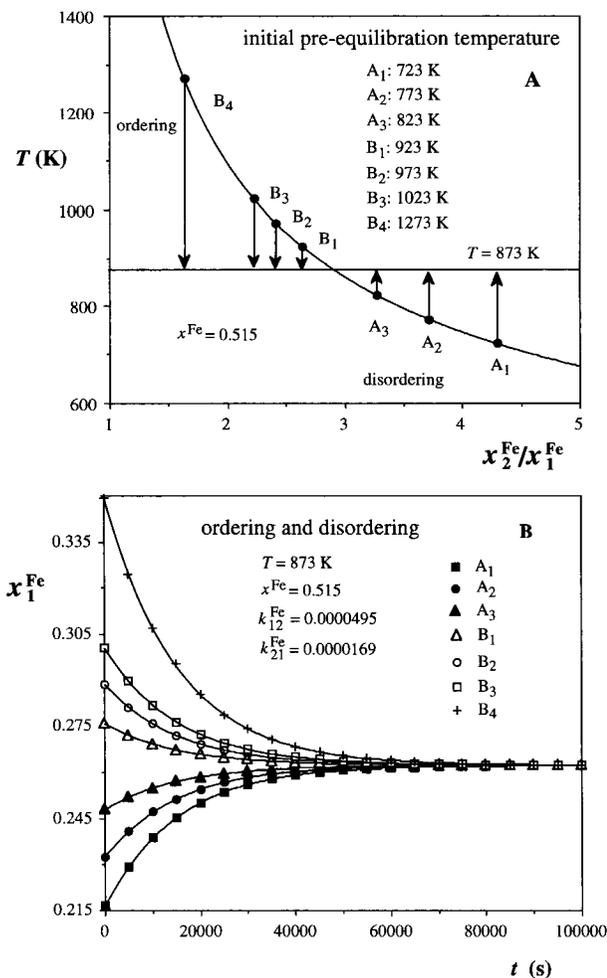


FIGURE 7. Effect of initial equilibrium site occupancies on ordering and disordering experiments. (A) Starting samples for the ordering (B₁–B₄) and disordering (A₁–A₃) experiments are assumed to have gained equilibrium site occupancies at different temperatures before the kinetic experiments were conducted at 873 K. Values of $T-x_2^{\text{Fe}}/x_1^{\text{Fe}}$ were calculated from experimental results for the orthopyroxene sample TZ of Besancon (1981). (B) Kinetic site occupancies strongly depend on the initial site occupancies of the samples, showing an increase for disordering experiments A₁–A₃, in contrast to a decrease for ordering experiments B₁–B₄.

temperatures. In Figure 7A, samples A₁, A₂, and A₃ are assumed to have been pre-equilibrated at 723, 773, and 823 K, respectively, and they represent disordering kinetic experiments because the kinetic experimental temperature (873 K) is higher than the initial pre-equilibration temperatures. Similarly, samples B₁, B₂, B₃, and B₄ are assumed to have been pre-equilibrated at 923, 973, 1023, and 1273 K, respectively, and they correspond to ordering kinetic experiments. Combining Equations 10 and 25 with Equations 35 and 36, we get the initial equilibrium site-occupancy data; for example, $x_1^{\text{Fe}} = 0.218$ and $x_2^{\text{Fe}} = 0.811$ at 773 K, and $x_1^{\text{Fe}} = 0.302$ and $x_2^{\text{Fe}} =$

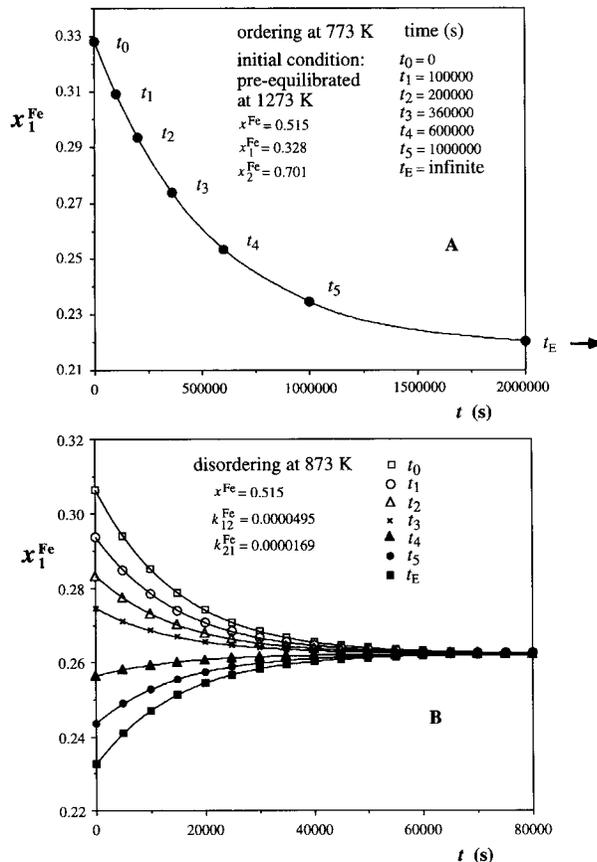


FIGURE 8. Influence of initial kinetic site occupancies on ordering and disordering experiments. (A) Starting samples (e.g., orthopyroxene) first gain equilibrium site occupancies at $t_0 = 0$ and $T = 1273 \text{ K}$, then obtain kinetic site occupancies at different times corresponding to t_1 – t_5 at 773 K, and finally reach equilibrium at $t = t_E = \text{infinite}$ and $T = 773 \text{ K}$. The initial conditions and kinetic coefficients were calculated from the results for orthopyroxene sample TZ of Besancon (1981). (B) Different initial kinetic site occupancies strongly affect the kinetic behavior of a cation as illustrated by the disordering of Fe^{2+} at M1 at 873 K in the orthopyroxene, giving different kinetic curves.

0.728 at 973 K. Figure 7B clearly demonstrates that the site occupancies of Fe^{2+} at M1 for the ordering kinetic experiments are very different from those of the disordering experiments. In this example, the disordering experiments correspond to monotonically increasing functions, but the ordering experiments correspond to monotonically decreasing functions. Fe^{2+} at M2 and Mg^{2+} at both sites show similar behavior.

On the other hand, the kinetic history of the samples also has a strong influence on the site occupancies of the cation in any kinetic experiment. Assume, for example, that an orthopyroxene sample (e.g., sample TZ) had been equilibrated at 1273 K and then becomes partially ordered at different times at 773 K. In Figure 8A, points t_1 – t_5 represent a series of partly equilibrated or ordered samples at 773 K, whereas points t_0 and t_E represent sam-

ples that completely equilibrated at 1273 and 773 K, respectively. Using these samples as starting materials, we calculated different kinetic curves corresponding to these points at 873 K (Fig. 8B). Clearly, samples with varying degrees of order yield different kinetic curves. From these two examples, it can be observed that the initial equilibrium concentrations of a cation and the kinetic history of the samples significantly affect the kinetic site occupancies of the cation in any experiment. In other words, it is impossible to replicate a kinetic experiment or reproduce the experimental data at a given temperature and pressure for a sample with exactly the same composition, without knowing the initial kinetic or equilibrium site-occupancy data. The above examples also demonstrate that the equilibrium site occupancies and kinetic coefficients of a cation are independent of initial site occupancies (equilibrium or kinetic). All curves in Figures 7B and 8B give the same kinetic coefficients and yield the same equilibrium site occupancies for the cation. This is easily proved from Equations 23 and 24. Therefore, the best way to repeat or duplicate an experiment (especially an experiment that involves natural samples) might be to test whether the kinetic coefficients and equilibrium site occupancies are the same, rather than the kinetic site occupancies.

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REFERENCES CITED

- Annersten, H., Ericsson, T., and Filippidis, A. (1982) Cation ordering in Ni-Fe olivines. *American Mineralogist*, 67, 1212–1217.
- Annersten, H., Adetunji, J., and Filippidis, A. (1984) Cation ordering in Fe-Mn silicate olivines. *American Mineralogist*, 69, 1110–1115.
- Anovitz, L.M., Essene, E.J., and Dunham, W.R. (1988) Order-disorder experiments on orthopyroxenes: Implications for the orthopyroxene geospeedometer. *American Mineralogist*, 73, 1060–1073.
- Besancon, J.R. (1981) Rate of cation disordering in orthopyroxenes. *American Mineralogist*, 66, 965–973.
- Bish, D.L. (1981) Cation ordering in synthetic and natural Ni-Mg olivine. *American Mineralogist*, 66, 770–776.
- Bragg, W.L., and Williams, E.J. (1935) The effect of thermal agitation on atomic arrangement in alloys. *Proceedings of Royal Society of London*, 151A, 540–566.
- De Waal, S.A., and Calk, L.C. (1973) Nickel minerals from Barberton, South Africa: VI. Liebenbergite, a nickel olivine. *American Mineralogist*, 58, 733–735.
- Dienes, G.L. (1955) Kinetics of order-disorder transformation. *Acta Metallurgica*, 3, 549–557.
- Ericsson, T., and Filippidis, A. (1986) Cation ordering in the limited solid solution $\text{Fe}_2\text{SiO}_4\text{-Zn}_2\text{SiO}_4$. *American Mineralogist*, 71, 1502–1509.
- Finger, L.W. (1970) Fe/Mg ordering in olivines. *Carnegie Institution of Washington Year Book*, 69, 302–305.
- Finger, L.W., and Virgo, D. (1971) Confirmation of Fe/Mg ordering in olivines. *Carnegie Institution of Washington Year Book*, 70, 221–225.
- Ganguly, J. (1982) Mg-Fe order-disorder in ferromagnesian silicates: II. Thermodynamics, kinetics, and geological applications. In *Advances in Physical Geochemistry*, 2, 58–99.
- Ghose, S., and Ganguly, J. (1982) Mg-Fe order-disorder in ferromagnesian silicates. In *Advances in Physical Geochemistry*, 2, 3–57.
- Griffen, D.T. (1992) *Silicate crystal chemistry*, 442 p. Oxford University Press, Oxford, U.K.
- Hawthorne, F.C. (1983) Quantitative characterization of site-occupancies in minerals. *American Mineralogist*, 68, 287–306.
- Lumpkin, G.R., Ribbe, P.H., and Lumpkin, M.E. (1983) Composition, order-disorder and lattice parameters of olivines: Determinative methods for Mg-Mn and Mg-Ca silicate olivines. *American Mineralogist*, 68, 1174–1182.
- McCallister, R.H., Finger, L.W., and Ohashi, Y. (1976) Intracrystalline Fe^{2+} -Mg equilibria in three natural Ca-rich clinopyroxenes. *American Mineralogist*, 61, 671–676.
- Molin, G., and Zanazzi, P.F. (1991) Intracrystalline Fe^{2+} -Mg ordering in augite: Experimental study and geothermometric applications. *European Journal of Mineralogy*, 3, 863–875.
- Mueller, R.F. (1967) Model for order-disorder kinetics in certain quasi-binary crystals of continuously variable composition. *Journal of Physics and Chemistry of Solids*, 28, 2239–2243.
- (1969) Kinetics and thermodynamics of intracrystalline distributions. *Mineralogical Society of America Special Papers*, 2, 83–93.
- Nord, A.G., Annersten, H., and Filippidis, A. (1982) The cation distribution in synthetic Mg-Fe-Ni olivines. *American Mineralogist*, 67, 1206–1211.
- Nord, A.G., and Ericsson, T. (1985) Cation distribution studies of some ternary orthophosphates having the farringtonite structure. *American Mineralogist*, 70, 624–629.
- Saxena, S.K., and Ghose, S. (1971) Mg^{2+} - Fe^{2+} order-disorder and the thermodynamics of the orthopyroxene crystalline solution. *American Mineralogist*, 56, 532–559.
- Saxena, S.K., Tazzoli, V., and Domeneghetti, M.C. (1987) Kinetics of Fe^{2+} -Mg distribution in aluminous orthopyroxenes. *Physics and Chemistry of Minerals*, 15, 140–147.
- Saxena, S.K., Domeneghetti, M.C., Molin, G.M., and Tazzoli, V. (1989) X-ray diffraction study of Fe^{2+} -Mg order-disorder in orthopyroxene: Some kinetic results. *Physics and Chemistry of Minerals*, 16, 421–427.
- Skogby, H. (1992) Order-disorder kinetics in orthopyroxenes of ophiolite origin. *Contributions to Mineralogy and Petrology*, 109, 471–478.
- Sykes-Nord, J.A., and Molin, G.M. (1993) Mg-Fe order-disorder reaction in Fe-rich orthopyroxene: Structural variations and kinetics. *American Mineralogist*, 78, 921–931.
- Virgo, D., and Hafner, S.S. (1969) Fe^{2+} -Mg disorder in heated orthopyroxenes. *Mineralogical Society of America Special Paper*, 2, 67–81.
- (1970) Fe^{2+} , Mg order-disorder in natural orthopyroxenes. *American Mineralogist*, 55, 201–223.

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