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Internally consistent solution models for Fe-Mg-Mn-Ti oxides: Fe-Mg-Ti oxides and olivine

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ABSTRACT

An internally consistent model has been developed to describe the partitioning of Fe^{2+}-Mg among olivine, ilmenite, and spinel in the system Fe-Mg-Ti-Si-O that is also consistent with the Fe-Ti exchange and oxidation of ilmenite-magnetite. Additional Fe-Mg exchange experiments between olivine and ilmenite were conducted at high temperatures to reduce the amount of extrapolation among previous calibrations. The ilmenite model is based on an asymmetric multicomponent Margules solution. The solution models for spinels are based on a Taylor series expansion with (1) a modified Akimoto-type cation distribution and (2) a model that incorporates site mixing of the cations. Both adequately describe the activity-composition relations of the spinels given existing data. In addition to providing thermometric information, the Fe^{2+}-Mg partitioning between olivine and oxide can be used to obtain qualitative T-f_{O_2} paths for one oxide + olivine + quartz assemblages.

INTRODUCTION

The application to natural samples of thermometers and barometers based on assemblages of two oxides (ilmenite, spinel) + olivine has been hampered by the uncertainty of the effect of minor elements on calculated temperatures and oxygen fugacities. We have extended the calibration of these thermometers and barometers by refining solution models for ilmenite and spinel that explicitly include Mg and Mn. Although this paper deals with Mg and the effects of Mn are presented elsewhere (Kress et al., in preparation), the models are internally consistent because all the data (see below) were fitted simultaneously. The overall effect of minor elements (i.e., Al, Cr, Mn) on ilmenite-spinel geothermometry and O barometry is discussed elsewhere (Andersen, 1988).

Solution parameters were derived using a combination of nonlinear least-squares and linear programming. The advantages of using a large multiphase data set are that an internally consistent set of parameters can be derived, and the compositional range over which the model is valid is extended. We have not included the effects of nonstoichiometry on the solution properties because most rocks have formed at a pressure where the defect concentration should be low and most petrologists do not analyze for defects. A model that explicitly incorporates defects, while theoretically desirable, will have limited usefulness until the defect concentrations are routinely determined.

In this paper, we present new data on the Fe-Mg partitioning between il_{ss} and ol_{ss} (Table 1) and models for the solution properties of magnesium oxides that are consistent with the olivine solution model of Davidson and Mukhopadhyay (1984). Following Andersen and Lindsley (1988), we have simultaneously derived two spinel models, one in a modified Akimoto type and the other is based on site mixing. Both adequately describe the multiphase equilibrium data. The site model also describes the known site-distribution data, whereas the Akimoto model permits a simpler computation of the macroscopic properties.

The models presented here can also be used to determine T-f_{O_2} relations for ol_{ss} + $oxide_{ss}$ + quartz assemblages. Although the relative temperature insensitivity of the Fe-Mg partitioning between ol_{ss}-$oxide_{ss}$ and il_{ss}-sp_{ss} yields large uncertainties in absolute values of temperature, the assemblage ol_{ss} + $oxide_{ss}$ + qtz can provide qualitative constraints on temperature and f_{O_2}. This is tested using existing experimental data on the assemblage ol_{ss} + il_{ss} + qtz.

As with any solution model based on exchange data, the reader is cautioned against extracting activities of individual components. The uncertainties of the individual activities are much greater than the uncertainties of the differences between the activities.

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TABLE 1. Definitions and abbreviations

${}^{[4]}X$ = site fraction of i on the tetrahedral site, such that $\sum_i {}^{[4]}X_i = 1$
${}^{[6]}X$ = site fraction of j on the octahedral site, such that $\sum_j {}^{[6]}X_j = 1$
α = site multiplicity
γ_i = activity coefficient of i
a_i = activity of component i, $a_i = X_i^{\alpha} \gamma_i^{\alpha}$
arm = armalcolite, $(Mg,Fe^{2+})Ti_2O_5$
fa = fayalite, Fe_2SiO_4
FHQ = fayalite-hematite-quartz equilibrium
FMQ = fayalite-magnetite-quartz buffer
f_{O_2} = oxygen fugacity
fo = forsterite, Mg_2SiO_4
G = molar Gibbs energy
G_i^0 = G of stoichiometric end-member i
G^* = nonconfigurational component of G
$g_i^*, g_{ij}^*, g_{ijk}^*$ = coefficients of Taylor series expansion of G^*
gk = geikielite, $MgTiO_3$
hem = hematite, Fe_2O_3
il = ilmenite, $FeTiO_3$
il_{ss} = $R\bar{3}$ ilmenite in the system $FeTiO_3$-$MgTiO_3$-Fe_2O_3
MH = magnetite-hematite buffer
mgf = magnesium ferrite, $MgFe_2O_4$
mt = magnetite, Fe_3O_4
N_i = number of moles of chemical component i
ol_{ss} = olivine in the system Fe_2SiO_4-Mg_2SiO_4
P = pressure, bars
qan = qandilite, Mg_2TiO_4
QIF = quartz-iron-fayalite buffer
QUIIF = quartz + ulvöspinel = ilmenite + fayalite
qtz = quartz, SiO_2
R = gas constant (8.3143 J/mol·K)
S_{conf} = configurational entropy
sp_{ss} = spinel solid solution in the system Fe_3O_4-Fe_2TiO_4-$MgFe_2O_4$-Mg_2TiO_4
T = temperature (K)
usp = ulvospinel, Fe_2TiO_4
W_{ij} = Margules type terms to describe nonideal mixing
X_i = mole fraction of i
μ_i = chemical potential of component i
μ_i^* = nonconfigurational component of the chemical potential
$\Delta\mu_{ij}^*$ = difference in chemical potentials for exchange or reciprocal reactions

PREVIOUS WORK

The ol_{ss}-il_{ss} thermometer has been calibrated by Bishop (1976) and Andersen and Lindsley (1981). The experiments of Bishop (1976, 1979) were conducted at high pressure and temperature (895–1436 °C, 13 kbar), whereas those of Andersen and Lindsley (1979, 1981) were conducted at relatively low temperatures (700–1000 °C, 1 kbar, 800–900 °C, 13 kbar). In order to resolve differences in extrapolating these two calibrations to regions outside the range of the respective experimental data, additional experiments have been performed at high temperatures and low pressures (1200 °C, 1 atm).

The partitioning of Fe^{2+}-Mg between il_{ss}-sp_{ss} was previously measured by Pinckney and Lindsley (1976), Johnson et al. (1971), and Speidel (1970). The experiments of Pinckney and Lindsley (1976) were conducted at relatively low temperatures (700–1000 °C, 1 kbar) with low Mg contents, and the compositions were reversed, but in the experiments of Speidel (1970), carried out at high temperatures (1160–1300 °C), compositions were not reversed and the spinels may not have been stoichiometric. Johnson et al. (1971) studied the system MgO-FeO-TiO_2 at 1300 °C in the presence of metallic Fe, thus minimizing the Fe^{3+} content, but both the il_{ss} and sp_{ss} are nonstoichiometric.

The partitioning of Fe^{2+}-Mg between ol_{ss} and sp_{ss} can be described in terms of the equations for ol_{ss}-il_{ss} and il_{ss}-sp_{ss} and provides additional constraints on the models for ol_{ss} and sp_{ss}. Experiments on ol_{ss}-sp_{ss} have been conducted in the Ti-free system by Jamieson and Roedder (1984), whereas Rawson and Irvine (1980) and Hill and Sack (1987) have included Ti in the spinels. Both Jamieson and Roedder (1984) and Hill and Sack (1987) reversed the composition of ol_{ss} and sp_{ss}, although the spinels in the experiments of Jamieson and Roedder may not be stoichiometric. The experiments of Rawson and Irvine (1980) were not reversed and the direction of reaction is unknown.

Both Bishop (1979) and Andersen and Lindsley (1981) presented models for il_{ss}. Bishop (1976, 1979) assumed a model for olivine and fitted $FeTiO_3$-$MgTiO_3$ as a strictly regular solution, ignoring the effects of Fe^{3+} in the ilmenite. Andersen and Lindsley (1979, 1981) modeled ol_{ss} as a binary solution and il_{ss} as an asymmetric ternary Margules solution, accounting for the effects of Fe^{3+} by using the data of Pinckney and Lindsley (1976) on Mg-il_{ss}-sp_{ss}.

Previous solution models for the solution properties of iron-magnesium spinel have used either an assumed cation distribution (e.g., Andersen and Lindsley, 1981; Sack, 1982; Engi, 1983) or a model based on the available cation distribution data to account for the effects of cation disorder in the configurational entropy (e.g., O'Neill and Navrotsky, 1983, 1984, Urusov, 1983; Lehmann and Roux, 1984). Andersen and Lindsley (1981) made a simplifying assumption that iron-magnesium-titanium spinels can be described in terms of the ternary, Fe_3O_4-Fe_2TiO_4-Mg_2TiO_4, ignoring reciprocal solution effects. Sack (1982), using available data on spinels and ol_{ss}-sp_{ss}, devised a model for multicomponent spinels in the system Fe-Mg-Al-Cr-Ti-O, but, because of limited data, was forced to make a number of simplifying assumptions. Engi (1983) modeled $(Mg,Fe)(Al,Cr)_2O_4$ spinel with a distribution-of-species approach and a reciprocal salt formulation, the latter requiring terms that are substantially larger in magnitude and more complex in functional form than the speciation model. Although a distribution-of-species approach has many merits, in order to reduce the number of terms in the formulation, it requires a number of assumptions that are difficult to justify for chemically complex spinels.

O'Neill and Navrotsky (1984) presented a model for spinels that is compatible with most cation distribution data. The approach of Urusov (1983) for binary spinels is similar in functional form to that of O'Neill and Navrotsky (1984), although the assumptions used in each model are somewhat different (Navrotsky 1984; Urusov, 1984). However, Trestman-Matts et al. (1983) were not able to fit their cation distribution data for Fe_3O_4-Fe_2TiO_4 spinels to this model without adding an empirical term to the model. Jamieson and Roedder (1984) modeled their data using an asymmetric Margules solution for spinel, assuming that olivine is ideal at the temperature of their experiments. Johnston and Beckett (1986) found that the data of Jamieson and Roedder (1984) are better described using the spinel model of O'Neill and Navrotsky (1983, 1984).

Johnson et al. (1971) calculated qualitative activity-composition relations for $(Fe,Mg)_2TiO_4$ spinel and $(Fe,Mg)TiO_3$ ilmenite using their phase equilibrium data and an activity model for magnesiowüstite and found positive deviations from ideality. However, because of the nonstoichiometry in both the ilmenite and spinel, these data are of limited value in models that do not account for nonstoichiometry.

GIBBS FREE ENERGY

The free energy of a solid solution can be written as

$$G_{\text{total}} = G^* - TS_{\text{conf}}$$

where G*, the nonconfigurational energy, includes both ideal and excess contributions to the free energy,

$$G^* = G_{\text{ideal}} + G_{\text{excess}} \tag{1}$$

which can be written as a Taylor series expansion:

$$\begin{aligned} G^* = g_1^* + \sum_{i=2} X_i g_i^* + \sum_{i=2} \sum_{j=i} X_i X_j g_{ij}^* \\ + \sum_{i=2} \sum_{j=i} \sum_{k=j} X_i X_j X_k g_{ijk}^* \end{aligned} \tag{2}$$

where the summation is over n independent components.

G_{excess} (Eq. 1) is modeled as a multicomponent asymmetric Margules solution (Wohl, 1946, 1953; Andersen and Lindsley, 1981)

$$\begin{aligned} G_{\text{excess}} = \sum_{i} \sum_{j,j\neq i} W_{ij} X_i X_j \left(X_j + \frac{1}{2} \sum_{k,k\neq i,j} X_k \right) \\ + \sum_{i} \sum_{j,j\neq i} \sum_{k,k\neq i,j} W_{ijk} X_i X_j X_k. \end{aligned} \tag{3}$$

Expressions for the activity coefficients for an n component system derived from Equation 3 are then

$$\begin{aligned} &\alpha \mathrm{R} T \ln(\gamma_n) \\ &= \sum_{i} \sum_{j,j\neq i} W_{ij} \\ &\quad \cdot \left\{ X_i X_j (X_j - X_i + 1) - \sum_{m,m\neq n} \right. \\ &\quad \left. \cdot X_m [Q_j (2X_j - X_i + 1) + Q_i (X_j - 2X_i + 1)] \right\} \\ &\quad + \sum_{i} \sum_{j,j\neq i} \sum_{k,k\neq i,j} \\ &\quad \cdot W_{ijk} [X_i X_j X_k - \sum_{m,m\neq n} \\ &\qquad \cdot X_m (Q_i X_j X_k + Q_j X_i X_k + Q_k X_i X_j)] \end{aligned} \tag{4}$$

where Q_i is a term related to $\partial X_i / \partial X_m$ and $Q_i = 1$ ($m = i$), -1 ($n = i$), 0 ($m \neq i$, $n \neq i$).

The configurational entropy, S_{conf}, for molecular mixing can be written as

$$S_{\text{conf}} = -\alpha \mathrm{R} \sum_{i} X_i \ln(X_i)$$

where X_i is the mole fraction of component i, and α is a constant related to the site multiplicity. For a multisite phase with random mixing of cations on each site, the configurational entropy can be written as (Thompson, 1969, 1970)

$$S_{\text{conf}} = -\mathrm{R} \sum_{s} \sum_{i} b_s n_{i,s} \ln(n_{i,s}) \tag{5}$$

where b_s is the number of sites (s) per formula unit and $n_{i,s}$ is the fraction of n_i on site s. For sp_{ss} and il_{ss}, models for the configurational entropy will be developed using Equation 5, with various approximations to the site occupancies.

OLIVINE

We have chosen to use the solution model of Davidson and Mukhopadhyay (1984) to permit extension of our results to Ca-bearing olivine and pyroxene. For the binary, Fe_2SiO_4-Mg_2SiO_4, the model of Davidson and Mukhopadhyay is nearly equivalent to a symmetric Margules model with $W = 7$ kJ and $\alpha = 2$.

ILMENITE CRYSTAL CHEMISTRY

Pure hematite has the disordered $R\bar{3}c$ structure (Pauling and Hendricks, 1925), whereas pure ilmenite and geikielite have the ordered $R\bar{3}$ structure (Barth and Posnjak, 1934; Wechsler and Navrotsky, 1984) with distinct A and B layers; ilmenite appears to retain this structure at least up to 1050 °C (Wechsler, 1978). At higher temperatures there is complete solid solution between ilmenite and hematite, implying that both have the same structure (Ishikawa, 1958). However, only ilmenite close to the $(Fe,Mg)TiO_3$ join is considered here; it should have crystallized in the ordered $R\bar{3}$ form.

The expression for the configurational entropy, S_{conf} (Eq. 5), assuming a random mixing of cations on each site with Fe^{2+} and Mg cations on the A site, Ti restricted to the B site, and Fe^{3+} mixing on both sites (Rumble, 1970, 1977), reduces to

$$\begin{aligned} &S_{\text{conf}} \\ &= -\mathrm{R}\{X_{\text{il}} \ln[X_{\text{il}}(X_{\text{il}} + X_{\text{gk}})] + X_{\text{gk}} \ln[X_{\text{gk}}(X_{\text{il}} + X_{\text{gk}})] \\ &\qquad + 2X_{\text{hem}} \ln(X_{\text{hem}})\}. \end{aligned}$$

For the binaries, this is equivalent to a molecular model with $\alpha = 1$ for $FeTiO_3$-$MgTiO_3$ and $\alpha = 2$ for Fe_2O_3-$FeTiO_3$ and Fe_2O_3-$MgTiO_3$.

Activity expressions for il_{ss} are then

$$\mathrm{R}T\ln(a_{\mathrm{il}}) = \mathrm{R}T\ln[X_{\mathrm{il}}(X_{\mathrm{il}} + X_{\mathrm{gk}})] + \mathrm{R}T\ln(\gamma_{\mathrm{il}})$$
$$\mathrm{R}T\ln(a_{\mathrm{gk}}) = \mathrm{R}T\ln[X_{\mathrm{gk}}(X_{\mathrm{il}} + X_{\mathrm{gk}})] + \mathrm{R}T\ln(\gamma_{\mathrm{gk}})$$
$$\mathrm{R}T\ln(a_{\mathrm{hem}}) = \mathrm{R}T\ln(X^2_{\mathrm{hem}}) + \mathrm{R}T\ln(\gamma_{\mathrm{hem}})$$

where $\mathrm{R}T\ln(\gamma_n)$ is derived from Equation 4.

SPINEL CRYSTAL CHEMISTRY

Sack (1982), in a thermodynamic treatment of spinels in the system Fe-Mg-Al-Cr-Ti-O, expanded G^* (Eq. 1) as a third degree polynomial in terms of composition but because of a limited amount of data was forced to make a number of simplifying assumptions. Because our knowledge of the cation distribution in spinels containing Fe^{2+}, Fe^{3+}, Mg, and Ti is incomplete, especially for compositions within the pseudoquaternary Fe_3O_4-Fe_2TiO_4-$MgFe_2O_4$-Mg_2TiO_4, the same general form as that of Sack (1982) will be followed as a first approximation, except that iron-magnesium spinel will not be considered ideal. As a second approximation, the effects of order-disorder on the configurational entropy will be considered. For both models, the cubic-tetragonal transition for Mg_2TiO_4 at 660 ± 20 °C (which is metastable relative to $MgTiO_3$ + MgO below 947 °C at 1 bar, Akimoto and Syono, 1967) will be ignored.

MODIFIED AKIMOTO MODEL

Only two independent variables are necessary to describe the composition of a stoichiometric spinel in the system Fe^{2+}-Fe^{3+}-Mg-Ti because of the constraints of mass and charge balance. If N_{Ti} and N_{Mg} are taken as the independent variables, then the compositional variables for the expansion of G^* (Eq. 2) are defined as

$$X_2 = N_{\mathrm{Ti}}$$
$$X_3 = N_{\mathrm{Mg}}.$$

The remaining compositional variables in terms of X_2 and X_3 are then

$$N_{\mathrm{Fe^{2+}}} = 1 + N_{\mathrm{Ti}} - N_{\mathrm{Mg}} = 1 - X_3 + X_2$$

and

$$N_{\mathrm{Fe^{3+}}} = 2 - 2N_{\mathrm{Ti}} = 2 - 2X_2$$

where the sum of the cations is given by

$$N_{\mathrm{Fe^{2+}}} + N_{\mathrm{Fe^{3+}}} + N_{\mathrm{Mg}} + N_{\mathrm{Ti}} = 3.$$

As a first approximation to the cation distributions, we will consider that the spinel is perfectly inverse, Ti always replaces Fe^{3+} in the octahedral site (Akimoto, 1954), and Fe^{2+} and Mg are randomly distributed between the octahedral and tetrahedral sites, i.e.,

$${}^{[4]}X_{\mathrm{Fe^{2+}}}{}^{[6]}X_{\mathrm{Mg}}/{}^{[6]}X_{\mathrm{Fe^{2+}}}{}^{[4]}X_{\mathrm{Mg}} = 1.$$

The site occupancies may then be calculated using the total site occupancy

$${}^{[4]}X_{\mathrm{Fe^{2+}}} + {}^{[4]}X_{\mathrm{Fe^{3+}}} + {}^{[4]}X_{\mathrm{Mg}} = 1$$
$${}^{[6]}X_{\mathrm{Fe^{2+}}} + {}^{[6]}X_{\mathrm{Fe^{3+}}} + {}^{[6]}X_{\mathrm{Mg}} + {}^{[6]}X_{\mathrm{Ti}} = 1$$

and mass balance constraints,

$$N_{\mathrm{Fe^{2+}}} = {}^{[4]}X_{\mathrm{Fe^{2+}}} + 2{}^{[6]}X_{\mathrm{Fe^{2+}}}$$
$$N_{\mathrm{Fe^{3+}}} = {}^{[4]}X_{\mathrm{Fe^{3+}}} + 2{}^{[6]}X_{\mathrm{Fe^{3+}}}$$
$$N_{\mathrm{Mg}} = {}^{[4]}X_{\mathrm{Mg}} + 2{}^{[6]}X_{\mathrm{Mg}}$$
$$N_{\mathrm{Ti}} = 2{}^{[6]}X_{\mathrm{Ti}}$$

yielding

$$\begin{aligned}
{}^{[4]}X_{\mathrm{Fe^{2+}}} &= X_2(1 + X_2 - X_3)/(1 + X_2)\\
{}^{[4]}X_{\mathrm{Fe^{3+}}} &= (1 - X_2)\\
{}^{[4]}X_{\mathrm{Mg}} &= (X_2X_3)/(1 + X_2)\\
{}^{[6]}X_{\mathrm{Fe^{2+}}} &= \tfrac{1}{2}(1 + X_2 - X_3)/(1 + X_2)\\
{}^{[6]}X_{\mathrm{Fe^{3+}}} &= \tfrac{1}{2}(1 - X_2)\\
{}^{[6]}X_{\mathrm{Mg}} &= \tfrac{1}{2}X_3/(1 + X_2)\\
{}^{[6]}X_{\mathrm{Ti}} &= \tfrac{1}{2}X_2.
\end{aligned} \qquad (6)$$

The expression for S_{conf} (Eq. 5), combined with the definitions for the site occupancies (Eq. 6), expands to

$$\begin{aligned}
S_{\mathrm{conf}} = -\mathrm{R}\{&X_2(1 + X_2 - X_3)/(1 + X_2)\\
&\cdot\ln[X_2(1 + X_2 - X_3)/(1 + X_2)]\\
&+ (1 - X_2)\ln(1 - X_2)\\
&+ X_2X_3/(1 + X_2)\ln[X_2X_3/(1 + X_2)]\\
&+ (1 + X_2 - X_3)/(1 + X_2)\\
&\cdot\ln[(1 + X_2 - X_3)/(1 + X_2)]\\
&+ (1 - X_2)\ln(1 - X_2) + X_3/(1 + X_2)\\
&\cdot\ln[X_3/(1 + X_2)] + X_2\ln(X_2) - 2\ln(2)\}.
\end{aligned}$$

The nonconfigurational energy, G^*, is expanded as a third-degree power series (Eq. 2) in terms of the independent compositional variables, X_2 and X_3. This expansion for G^* includes the free energy of ideal mixing (including reciprocal solution effects) and the excess free energy. The meanings of the individual g^*_{ijk} can be determined by fixing the compositions to be those of the end-members and binaries and assuming that G_{excess} is similar in form to Equation 3, yielding (definitions of the g^*_{ijk} are listed in Table 2, see also Lindsley et al., 1990).

$$\begin{aligned}
G^* = {}&G^*_{\mathrm{Fe_3O_4}}(1 - X_2 - X_3) + G^*_{\mathrm{Fe_2TiO_4}}X_2 + G^*_{\mathrm{MgFe_2O_4}}X_3\\
&- \Delta\mu^*_{23}X_2X_3 - \tfrac{1}{2}\Delta\mu^*_{2q}X_2X_3(1 + X_2 - X_3)\\
&+ W_{12}X_2(1 - X_2)(X_2 - X_3)\\
&+ W_{21}X_2(1 - X_2)(1 - X_2 + X_3)\\
&+ W_{13}X_3(1 + X_2 - X_3)(X_3 - X_2)\\
&+ W_{31}X_3(1 + X_2 - X_3)(1 - X_3)\\
&+ \Delta W_{q3}X_2X_3(X_2 - 1)
\end{aligned} \qquad (7)$$

where the subscripts for the W terms are defined as 1 = magnetite, 2 = ulvöspinel, 3 = magnesium ferrite, and q = qandilite. This yields three end-member energies ($G^*_{\mathrm{Fe_3O_4}}$, $G^*_{\mathrm{Fe_2TiO_4}}$, and $G^*_{\mathrm{MgFe_2O_4}}$), one reciprocal term, $\Delta\mu^*_{23}$, which is the energy difference for the reciprocal exchange

$$Fe_3O_4 + \tfrac{1}{2}Mg_2TiO_4 = MgFe_2O_4 + \tfrac{1}{2}Fe_2TiO_4$$

TABLE 2. Definition of G^* in terms of end-member and excess energies for the modified Akimoto model

$$\begin{aligned}
g_1^* &= G^*_{Fe_3O_4}\\
g_2^* &= G^*_{Fe_2TiO_4} - G^*_{Fe_3O_4} + W_{21}\\
g_3^* &= G^*_{MgFe_2O_4} - G^*_{Fe_3O_4} + W_{31}\\
g_{22}^* &= W_{12} - 2W_{21}\\
g_{23}^* &= -\Delta\mu^*_{23} - \tfrac{1}{2}\Delta\mu^*_{2q} - \Delta W_{q3} + W_{31} - W_{13} + W_{21} - W_{12}\\
g_{33}^* &= W_{13} - 2W_{31}\\
g_{222}^* &= W_{21} - W_{12}\\
g_{223}^* &= -\tfrac{1}{2}\Delta\mu^*_{2q} + W_{12} - W_{21} - W_{13} + \Delta W_{q3}\\
g_{233}^* &= \tfrac{1}{2}\Delta\mu^*_{2q} + 2W_{13} - W_{31}\\
g_{333}^* &= W_{31} - W_{13}\\
\Delta\mu^*_{23} &= \tfrac{1}{2}(G^*_{Fe_2TiO_4} - G^*_{Mg_2TiO_4}) + G^*_{MgFe_2O_4} - G^*_{Fe_3O_4}\\
\Delta\mu^*_{2q} &= (G^*_{Fe_2TiO_4} + G^*_{Mg_2TiO_4}) - (G^*_{^{[4]}Fe^{2+[6]}Mg^{[6]}TiO_4} + G^*_{^{[4]}Mg^{[6]}Fe^{2+[6]}TiO_4})\\
\Delta W_{q3} &= W_{q3} - W_{3q}
\end{aligned}$$

and a Bragg-Williams type ordering term, $\Delta\mu^*_{2q}$, for the mixing of $(Mg,Fe)_2TiO_4$ spinels,

$$^{[4]}Fe^{2+}\,^{[6]}Fe^{2+}\,^{[6]}TiO_4 + {}^{[4]}Mg\,^{[6]}Mg\,^{[6]}TiO_4$$
$$= {}^{[4]}Fe^{2+}\,^{[6]}Mg\,^{[6]}TiO_4 + {}^{[4]}Mg\,^{[6]}Fe^{2+}\,^{[6]}TiO_4.$$

As noted by Sack (1982), the assumption of random mixing of Fe^{2+}-Mg does not constrain the value of $\Delta\mu^*_{2q}$. The four possible binaries would yield eight asymmetric binary coefficients, of which only five are independent because there are only ten terms in the expansion of G^*. We have chosen to define G^* in terms of the binaries Fe_3O_4-Fe_2TiO_4 (W_{12} and W_{21}), Fe_3O_4-$MgFe_2O_4$ (W_{13} and W_{31}), and a term for the difference of $MgFe_2O_4$-Mg_2TiO_4 (ΔW_{q3}) where

$$\Delta W_{q3} = W_{q3} - W_{3q}.$$

The two asymmetric W terms for $MgFe_2O_4$-Mg_2TiO_4 are not independent of the others or

$$W_{3q} = \Delta\mu^*_{23} - 2\Delta W_{q3} + 2W_{21} - W_{12}$$

and

$$W_{q3} = \Delta\mu^*_{23} - \Delta W_{q3} + 2W_{21} - W_{12}.$$

This is similar to Sack (1982), except for the inclusion of g^*_{33} and g^*_{333} in the expansion of Equation 2, which if zero, would require $W_{13} = W_{31} = 0$.

Activity expressions can then be derived using (Sack, 1982 and Darken and Gurry, 1953)

$$\mu_i = G + \sum_j (N_j - X_j)(\partial G/\partial X_j) \tag{8}$$

where N_j is the number of moles of component j (from the set of linearly independent components, X_2 and X_3). Since

$$\Delta G_i^0 = \mu_i^0 = \mu_i^* - 2RT\ln(2) \tag{9}$$

and

$$\mu_i - \mu_i^0 = RT\ln(a_i) \tag{10}$$

application of Equations 8, 9, and 10 leads to the activity expressions in Table 3.

TABLE 3. Activity expressions for spinels using the Akimoto model

$$\begin{aligned}
RT\ln(a_{Fe_3O_4}) = {} & \ln[(1 + X_2 - X_3)(1 - X_2)^2/(1 + X_2)]\\
& + \tfrac{1}{2}\Delta\mu^*_{2q}X_2X_3(1 + 2X_2 - 2X_3)\\
& + \Delta\mu^*_{23}X_2X_3 + W_{12}X_2(X_3 - X_2)(1 - 2X_2)\\
& + W_{21}X_2[2X_2(1 - X_2) + X_3(2X_2 - 1)]\\
& + W_{13}X_3(2X_3 - 2X_2 - 1)(X_3 - X_2)\\
& + W_{31}X_3[2X_3(1 + X_2 - X_3) - X_2] + \Delta W_{q3}X_2X_3(1 - 2X_2)\\
RT\ln(a_{Fe_2TiO_4}) = {} & 2\ln[X_2(1 + X_2 - X_3)/(1 + X_2)]\\
& + \tfrac{1}{2}\Delta\mu^*_{2q}X_3[(X_3 - X_2)(1 - 2X_2) - 1]\\
& + \Delta\mu^*_{23}X_3(X_2 - 1) + W_{12}(1 - X_2)\\
& \cdot[2X_2(1 - X_2 + X_3) - X_3]\\
& + W_{21}(1 - 2X_2)(1 - X_2)(1 - X_2 + X_3)\\
& + W_{13}X_3\{[1 + 2(X_3 - X_2)](X_3 - X_2) - 1\}\\
& + W_{31}X_3[1 + (X_3 - X_2)(1 - 2X_3)]\\
& + \Delta W_{q3}X_3(1 - 2X_2)(X_2 - 1)\\
RT\ln(a_{MgFe_2O_4}) = {} & \ln[X_3(1 - X_2)^2/(1 + X_2)] + \tfrac{1}{2}\Delta\mu^*_{2q}X_2(1 + X_2 - X_3)\\
& \cdot(2X_3 - 1) + \Delta\mu^*_{23}X_2(X_3 - 1)\\
& + W_{12}X_2[(X_2 - X_3)(2X_2 - 1) + X_2 - 1]\\
& + W_{21}X_2[(1 + 2X_2)(1 - X_2) + X_3(2X_2 - 1)]\\
& + W_{13}(1 + X_2 - X_3)[2X_3(1 + X_2 - X_3) - X_2]\\
& + W_{31}(1 + X_2 - X_3)(2X_3 - 1)(X_3 - 1)\\
& + \Delta W_{q3}X_2[X_3(1 - 2X_2) + X_2 - 1]\\
RT\ln(a_{Mg_2TiO_4}) = {} & 2\ln[X_2X_3/(1 + X_2)] + \Delta\mu^*_{2q}(1 + X_2 - X_3)\\
& \cdot[X_2(X_3 - 1) - \tfrac{1}{2}X_3]\\
& + \Delta\mu^*_{23}(X_2 - 1)(X_3 - 2) + W_{12}(X_2 - 1)\\
& \cdot[2X_2(X_2 - X_3) + X_3]\\
& + W_{21}(1 - X_2)[1 + (X_3 - X_2)(1 - 2X_2)]\\
& + W_{13}(1 + X_2 - X_3)[2(1 - X_3)(X_3 - X_2) + X_3]\\
& + W_{31}(1 + X_2 - X_3)(X_3 - 2)(2X_3 - 1)\\
& + \Delta W_{q3}(1 - X_2)[2X_2(X_3 - 1) - X_3]
\end{aligned}$$

SPINEL SITE MIXING

The modified Akimoto model is adequate to explain the macroscopic properties of spinel in equilibrium with ilmenite but is based on an assumed cation distribution for the spinel that is inadequate given the recent work of Wu and Mason (1981) and Trestman-Matts et al. (1983, 1984). In this section, an alternative expression for the mixing properties of spinel is developed using cation distribution data.

With the assumption that Ti is restricted to the octahedral site (de Grave et al., 1975; Wechsler et al., 1984) and that Fe^{2+}, Fe^{3+}, and Mg are disordered between the octahedral and tetrahedral sites but are randomly mixed on each (i.e., no short-range order), then the cation distribution can be described by adding two parameters to the expansion of G^*. The order parameters chosen are

$$X_4 = {}^{[4]}X_{Fe^{3+}}$$

and

$$X_5 = {}^{[4]}X_{Mg}$$

corresponding to the tetrahedral site occupancies of Fe^{3+} and Mg, respectively. The remaining site occupancies can then be written in terms of X_4 and X_5 as

$$\begin{aligned}
^{[4]}X_{Fe^{2+}} &= 1 - X_4 - X_5\\
^{[6]}X_{Fe^{2+}} &= \tfrac{1}{2}(X_2 - X_3 + X_4 + X_5)\\
^{[6]}X_{Fe^{3+}} &= \tfrac{1}{2}(2 - 2X_2 - X_4)\\
^{[6]}X_{Mg} &= \tfrac{1}{2}(X_3 - X_5)\\
^{[6]}X^{Ti} &= \tfrac{1}{2}X_2.
\end{aligned}$$

The configurational entropy (Eq. 5) expands to

TABLE 4. Definition of G* for the model incorporating site mixing in spinels

$g^*_1 = G^*_{{}^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}_2{}^{3+}\mathrm{O}_4}$

$g^*_2 = G^*_{{}^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{TiO}_4} - G^*_{{}^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4} + W_{\mathrm{Fe}} + \tfrac{1}{2}(W_{21} - W_{12})$

$g^*_3 = \Delta\mu^*_{31} - W_{\bar{1}1} + W_{\bar{1}3}$

$g^*_4 = \Delta\mu^*_{1\bar{1}} + W_{\bar{1}1}$

$g^*_5 = \Delta\mu^*_{1\bar{1}} - \Delta\mu^*_{3\bar{3}} + W_{\bar{1}1} + W_{\bar{1}\bar{3}} - W_{\bar{1}3}$

$g^*_{22} = -W_{\mathrm{Fe}} - \tfrac{3}{2}(W_{21} - W_{12})$

$g^*_{23} = W_{\mathrm{Fe}} - W_{\mathrm{Mg}} + W_{13}$

$g^*_{24} = \tfrac{1}{2}(W_{12} + W_{21}) - W_{\mathrm{Fe}} - W_{\bar{1}1}$

$g^*_{25} = \Delta\mu^*_{3\bar{3}} - \Delta\mu^*_{1\bar{1}} + \Delta\mu^*_{\mathrm{Ti}} - W_{\bar{1}1} + W_{\bar{1}3} - W_{13}$

$g^*_{33} = -W_{13}$

$g^*_{34} = W_{\bar{1}1} - W_{\bar{1}3} + W_{13}$

$g^*_{35} = W_{\bar{1}1} - W_{\bar{1}3} - W_{1\bar{3}} + 2W_{13} + W_{33}$

$g^*_{44} = -W_{\bar{1}1}$

$g^*_{45} = -2W_{\bar{1}1} + W_{\bar{1}3} - W_{\bar{1}\bar{3}} + W_{1\bar{3}} - W_{13}$

$g^*_{55} = -W_{\bar{1}1} + W_{\bar{1}3} - W_{\bar{1}\bar{3}} + W_{1\bar{3}} - W_{13} - W_{33}$

$g^*_{222} = W_{21} - W_{12}$

$\Delta\mu^*_{1\bar{1}} = G^*_{{}^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4} - G^*_{{}^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4}$

$\Delta\mu^*_{3\bar{3}} = G^*_{{}^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Mg}{}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4} - G^*_{{}^{[4]}\mathrm{Mg}{}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4}$

$\Delta\mu^*_{31} = G^*_{{}^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Mg}{}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4} - G^*_{{}^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4}$

$\Delta\mu^*_{\mathrm{Ti}} = G^*_{{}^{[4]}\mathrm{Mg}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{TiO}_4} - G^*_{{}^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Mg}{}^{[6]}\mathrm{TiO}_4}$

$W_{\mathrm{Fe}} = \tfrac{1}{2}(W_{12} + W_{21})$

$W_{\mathrm{Mg}} = \tfrac{1}{2}(W_{3q} + W_{q\bar{3}})$

$$\begin{aligned}
S_{\mathrm{conf}} = -\mathrm{R}\{&(1 - X_4 - X_5)\ln(1 - X_4 - X_5) \\
&+ X_4\ln(X_4) + X_5\ln(X_5) \\
&+ (X_2 - X_3 + X_4 + X_5) \\
&\cdot\ln[(X_2 - X_3 + X_4 + X_5)/2] \\
&+ (2 - 2X_2 - X_4)\ln(1 - X_2 - X_4/2) \\
&+ (X_3 - X_5)\ln[(X_3 - X_5)/2] + X_2\ln(X_2/2)\}.
\end{aligned}$$

The nonconfigurational energy, G^*, is derived from a second degree Taylor expansion of Equation 2. [A third degree term, g^*_{222}, has been added to fit the $\mathrm{mt}_{\mathrm{ss}}$-$\mathrm{il}_{\mathrm{ss}}$ data (see Andersen and Lindsley, 1988).] The simplest interpretation of the g^*_{ij} coefficients in this expansion is in terms of mixing between the various end-members, including the inverse and normal cation distributions for the 2-3 spinels. The definitions in Table 4 result from the treatment of $\mathrm{Fe_3O_4}$-$\mathrm{MgFe_2O_4}$ as a symmetric quaternary and $\mathrm{Fe_3O_4}$-$\mathrm{Fe_2TiO_4}$ and $\mathrm{MgFe_2O_4}$-$\mathrm{Mg_2TiO_4}$ as asymmetric ternaries (using G_{excess} as defined by Equation 3). Rewritten in terms of the end-member and nonideal terms,

$$\begin{aligned}
G^* = {}& G^*_{{}^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4}(1 - X_2) + G^*_{{}^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{TiO}_4}X_2 \\
&+ \Delta\mu^*_{1\bar{1}}[X_4 + X_5(1 - X_2)] + \Delta\mu^*_{31}X_3 \\
&+ \Delta\mu^*_{3\bar{3}}X_5(X_2 - 1) + \Delta\mu^*_{\mathrm{Ti}}X_2X_5 \\
&+ W_{\bar{1}1}[(X_4 + X_5)(1 - X_2 + X_3 - X_4 - X_5) - X_3] \\
&+ W_{\bar{1}\bar{3}}X_5(1 - X_4 - X_5) \\
&+ W_{\bar{1}3}[(X_3 - X_5)(1 - X_5 - X_4) + X_5X_2] \\
&+ W_{1\bar{3}}X_5(X_4 + X_5 - X_3) \\
&+ W_{13}(X_3 - X_5)(X_2 - X_3 + X_4 + X_5) \\
&+ W_{\bar{3}3}X_5(X_3 - X_5) \\
&+ \tfrac{1}{2}W_{12}X_2[X_4 - (1 - X_2)(1 - 2X_2)] \\
&+ \tfrac{1}{2}W_{21}X_2[X_4 + (1 - X_2)(1 - 2X_2)] \\
&+ W_{\mathrm{Fe}}X_2(1 - X_2 + X_3 - X_4) - W_{\mathrm{Mg}}X_2X_3.
\end{aligned}$$

As in the previous section, the remaining W terms for $\mathrm{MgFe_2O_4}$-$\mathrm{Mg_2TiO_4}$ can then be written in terms of the others, or

$$\begin{aligned}
W_{3q} &= W_{\mathrm{Mg}} - \tfrac{1}{2}(W_{21} - W_{12}) \\
W_{q\bar{3}} &= W_{\mathrm{Mg}} + \tfrac{1}{2}(W_{21} - W_{12}) \\
W_{3q} &= W_{\mathrm{Mg}} - W_{\mathrm{Fe}} + \Delta\mu^*_{1\bar{1}} - \Delta\mu^*_{3\bar{3}} \\
&\quad - \Delta\mu^*_{\mathrm{Ti}} - W_{\bar{1}3} + W_{1\bar{3}} + W_{12} \\
W_{q3} &= W_{\mathrm{Mg}} - W_{\mathrm{Fe}} + \Delta\mu^*_{1\bar{1}} - \Delta\mu^*_{3\bar{3}} \\
&\quad - \Delta\mu^*_{\mathrm{Ti}} - W_{\bar{1}3} + W_{13} + W_{21}
\end{aligned}$$

and

$$W_{\bar{3}3q} = W_{21} - W_{12}.$$

For internal equilibrium, the free energy of the solution is at a minimum with respect to the order parameters, X_4 and X_5, or

$$\begin{aligned}
&(\partial G/\partial X_4)_{X_2,X_3,X_5} \\
&= 0 \\
&= \mathrm{R}T\ln\{X_4(X_2 + X_4 + X_5 - X_3) \\
&\qquad \div[(1 - X_4 - X_5)(2 - 2X_2 - X_4)]\} \\
&\quad + \Delta\mu^*_{1\bar{1}} + W_{\bar{1}1}(1 - X_2 + X_3 - 2X_4 - 2X_5) \\
&\quad - W_{\bar{1}\bar{3}}X_5 + W_{\bar{1}3}(X_5 - X_3) \\
&\quad + W_{1\bar{3}}X_5 + W_{13}(X_3 - X_5) \\
&\quad + X_2[\tfrac{1}{2}(W_{12} + W_{21}X_2) - W_{\mathrm{Fe}}] \qquad (11)
\end{aligned}$$

and

$$\begin{aligned}
&(\partial G/\partial X_5)_{X_2,X_3,X_4} \\
&= 0 \\
&= \mathrm{R}T\ln\{X_5(X_2 + X_4 + X_5 - X_3) \\
&\qquad \div[(1 - X_4 - X_5)(X_3 - X_5)]\} \\
&\quad + (\Delta\mu^*_{1\bar{1}} - \Delta\mu^*_{3\bar{3}})(1 - X_2) \\
&\quad + \Delta\mu^*_{\mathrm{Ti}}X_2 + W_{\bar{1}\bar{3}}(1 - X_4 + 2X_5) \\
&\quad + W_{\bar{1}1}(1 - X_2 + X_3 - 2X_4 - 2X_5) \\
&\quad + W_{\bar{1}3}(X_2 - X_3 - 1 + X_4 + 2X_5) \\
&\quad + W_{13}(2X_3 - X_2 - 2X_4 - 2X_5) \\
&\quad + W_{1\bar{3}}(X_4 + 2X_5 - X_3) + W_{\bar{3}3}(X_3 - 2X_5). \qquad (12)
\end{aligned}$$

Activity expressions can then be derived using Equation 8, where the standard state is defined as that of the pure component at the temperature and pressure of interest (Eq. 10); these expressions are listed in Table 5.

INTRACRYSTALLINE SPINEL EQUILIBRIA

The site occupancy data for Fe_3O_4-Fe_2TiO_4 and $MgFe_2O_4$-Mg_2TiO_4 (see below) can be fitted to Equations 11 and 12 using a conventional least-squares approach. The data for Fe_3O_4-$MgFe_2O_4$, however, are nonlinear because only the valence ratio of $^{[6]}Fe$ is known (see below), requiring the simultaneous solution of Equations 11 and 12. A modified version of the Simplex method (Nedler and Mead, 1965) was used to minimize

$$\sum_i (X_i - x_i)^2$$

where X_i and x_i are the measured and calculated order parameters for data set i. Although this method does not give the uncertainties in the parameters, the overall error of the function can be estimated from the standard deviation of the residuals. Systematic biases in the model can be detected from plots of the original data and model values. The values for the best solution in terms of the minimum number of parameters are listed in Table 6. The terms $(W_{Fe} - W_{Mg} + W_{13})$ and W_{13} are independent of the cation distribution and were derived from the data on sp_{ss}-il_{ss} and sp_{ss}-ol_{ss}.

There have been numerous studies on the cation distribution of $MgFe_2O_4$. Estimates of the tetrahedral site occupancy for $^{[4]}Fe^{3+}$ vs. temperature taken from the literature are shown in Figure 1, along with the calculated curve. These are based on X-ray and magnetic measurements, and although they show some scatter, they are in general agreement. The relatively poor fit ($\sigma_{MgFe_2O_4} = 0.021$) is not surprising given the spread of the data (Fig. 1), which may result from either reequilibration of the cation distribution during the quench or possible nonstoichiometry in the spinels.

Recent measurements of the variation of the Seebeck coefficient with temperature (Wu and Mason, 1981; Trestman-Matts et al., 1983) have shown that the octahedral valence ratio (OVR = $^{[6]}Fe^{2+}/^{[6]}Fe^{3+}$) for Fe_3O_4-Fe_2TiO_4 spinels varies with temperature and composition. The site occupancies can then be calculated from composition and mass balance constraints. Using the same technique, Trestman-Matts et al. (1984) measured the Seebeck coefficient for Fe_3O_4-$MgFe_2O_4$ spinels for four different compositions (Fig. 2). Unfortunately, the site occupancies for this join cannot be explicitly calculated using these data because the Mg distribution is unknown. The low temperature points for Fe_3O_4-$MgFe_2O_4$ (Trestman-Matts et al., 1984) at $X_{Mg} = 0.406$, 0.634, and 0.82, which are shown as solid symbols in Figure 2, appear to be anomalous because the OVR for these spinel compositions exceed the maximum possible value of $1 - X_{Mg}$ and were excluded from the model. The maximum value for the OVR in a spinel of a given Mg content occurs when $^{[6]}X_{Fe^{2+}}$ is at a maximum and $^{[6]}X_{Fe^{3+}}$ is at a minimum. The minimum value for $^{[6]}X_{Fe^{3+}} = ½$ and the maximum value for $^{[6]}X_{Fe^{2+}} = ½(1 - X_{Mg})$, corresponding to a completely inverse distribution. The calculated site distributions shown in Figure 2 are reasonable ($\sigma_{Fe_3O_4\text{-}MgFe_2O_4} = 0.015$) with the worst fit at the higher Mg contents and lower temperatures.

The cation distribution for $MgFe_2O_4$-Mg_2TiO_4 spinels has been measured by Tellier (1967) and de Grave et al. (1975) and is shown in Figure 3. Compared to the Fe_3O_4-Fe_2TiO_4 binary, the data of de Grave et al. (1975) indicate a greater amount of $^{[4]}Fe^{3+}$ at a given temperature and Ti content. The calculated curve is in fair agreement, but the residuals ($\sigma_{MgFe_2O_4\text{-}Mg_2TiO_4} = 0.020$) are not random with respect to X_{Ti} (Fig. 3). It is not clear whether the slight curvature in the data of Tellier (1967) is real or is due to the failure of the magnetic model used to determine the cation distribution as suggested by O'Neill and Navrotsky (1984). In addition, any short-range order present in Mg_2TiO_4 (Wechsler and Navrotsky, 1984) and extending along the join with $MgFe_2O_4$ would introduce a complication in the model that has not been considered.

TABLE 5. Activity expressions for spinels using the site mixing model

$$\begin{aligned}
RT\ln(a_{Fe_3O_4}) = {} & \ln[(1 - X_4 - X_5)(2 - 2X_2 - X_4)^2] + G^*_{^{[4]}Fe^{2+\,[6]}Fe_2^{3+}O_4} \\
& + (\Delta\mu^*_{1\bar{1}} - \Delta\mu^*_{3\bar{3}} - \Delta\mu^*_{Ti})X_2X_5 + W_{\bar{1}1}(X_4 + X_5) \\
& \cdot(X_2 - X_3 + X_4 + X_5) \\
& + W_{\bar{1}3}[(X_4 + X_5)(X_3 - X_5) - X_2X_5] + W_{\bar{1}3}X_5(X_4 + X_5) \\
& + W_{1\bar{3}}X_5(X_3 - X_4 - X_5) \\
& + W_{33}X_5(X_5 - X_3) + W_{13}(X_3 - X_5)(X_3 - X_2 - X_4 - X_5) \\
& + ½W_{12}X_2[X_2(4X_2 - 3) - X_4] \\
& + ½W_{21}X_2[X_2(3 - 4X_2) - X_4] \\
& + W_{Fe}X_2(X_2 - X_3 + X_4) + W_{Mg}X_2X_3 - \mu^0_{Fe_3O_4} \\
RT\ln(a_{Fe_2TiO_4}) = {} & \ln[(1 - X_4 - X_5)(X_2 + X_4 + X_5 - X_3)X_2] + G^*_{^{[4]}Fe^{2+\,[6]}Fe^{2+\,[6]}TiO_4} \\
& + (\Delta\mu^*_{1\bar{1}} - \Delta\mu^*_{3\bar{3}} - \Delta\mu^*_{Ti})X_5(X_2 - 1) - W_{\bar{1}1}(X_4 + X_5) \\
& \cdot(1 - X_2 + X_3 - X_4 - X_5) \\
& + W_{\bar{1}3}[(X_4 + X_5)(X_3 - X_5) + X_5(1 - X_2)] \\
& + W_{\bar{1}3}X_5(X_4 + X_5) \\
& + W_{1\bar{3}}X_5(X_3 - X_4 - X_5) + W_{13}(X_3 - X_5) \\
& \cdot(1 - X_2 + X_3 - X_4 - X_5) + W_{33}X_5(X_5 - X_3) \\
& + ½W_{12}(1 - X_2)[X_4 - (1 - X_2)(1 - 4X_2)] \\
& + ½W_{21}(1 - X_2)[X_4 + (1 - X_2)(1 - 4X_2)] \\
& + W_{Fe}(1 - X_2)(1 - X_2 + X_3 - X_4) \\
& + W_{Mg}X_3(X_2 - 1) - \mu^0_{Fe_2TiO_4} \\
RT\ln(a_{MgFe_2O_4}) = {} & \ln[X_5(2 - 2X_2 - X_4)^2] + G^*_{^{[4]}Fe^{2+\,[6]}Fe_2^{3+}O_4} + \Delta\mu^*_{31} \\
& + (\Delta\mu^*_{1\bar{1}} - \Delta\mu^*_{3\bar{3}})[1 + X_2(X_5 - 1)] + \Delta\mu^*_{Ti}X_2(1 - X_5) \\
& + (1 - X_4 - X_5)[W_{\bar{1}1}(X_3 - X_2 - X_4 - X_5) + W_{\bar{1}3}(1 - X_5)] \\
& + W_{\bar{1}3}[X_2(1 - X_5) - (1 - X_4 - X_5)(X_3 - X_5)] \\
& + (1 - X_5)[W_{13}(X_4 + X_5 - X_3) + W_{33}(X_3 - X_5)] \\
& + W_{13}(X_3 - X_5)(X_3 - X_2 - X_4 - X_5) \\
& + ½W_{12}X_2[X_2(4X_2 - 3) - X_4] + ½W_{21}X_2 \\
& \cdot[X_2(3 - 4X_2) - X_4] \\
& + W_{Fe}X_2(1 + X_2 - X_3 + X_4) + W_{Mg}X_2(X_3 - 1) - \mu^0_{MgFe_2O_4} \\
RT\ln(a_{Mg_2TiO_4}) = {} & \ln[X_2X_5(X_3 - X_5)] + G^*_{^{[4]}Fe^{2+\,[6]}Fe^{2+\,[6]}TiO_4} + 2\Delta\mu^*_{31} \\
& + (\Delta\mu^*_{1\bar{1}} - \Delta\mu^*_{3\bar{3}})(1 - X_5)(1 - X_2) + \Delta\mu^*_{Ti}[X_5 + X_2(1 - X_5)] \\
& + W_{\bar{1}1}[X_3 - X_2 - 1 - (X_4 + X_5)(1 - x_2 + X_3 - X_4 - X_5)] \\
& + W_{\bar{1}3}[1 + X_2 - X_3 - X_4(1 + X_5 - X_3) \\
& + X_5(1 - X_2 + X_3 - X_5)] \\
& + W_{\bar{1}\bar{3}}(1 - X_5)(1 - X_4 - X_5) \\
& + W_{1\bar{3}}[X_4 - X_3 - X_5(X_4 + X_5 - X_3)] \\
& + W_{33}[X_3 - X_5(X_3 - X_5)] \\
& + W_{13}(1 - X_3 + X_5)(X_2 - X_3 + X_4 + X_5) \\
& + ½W_{12}(1 - X_2)[X_4 - (1 - X_2)(1 - 4X_2)] \\
& + ½W_{21}(1 - X_2)[X_4 + (1 - X_2)(1 - 4X_2)] \\
& + W_{Fe}[X_2(X_2 - X_3 + X_4) + 1 + X_3 - X_4] \\
& + W_{Mg}[X_3(X_2 - 1) - 2X_2] - \mu^0_{Mg_2TiO_4}
\end{aligned}$$

TABLE 6. Model parameters (J/mol, J/mol·K)*

	Preferred	Minimum	Maximum
ΔH_{OIII}	−1.4661527E + 04	−1.4723021E + 04	−1.4483356E + 04
ΔS_{OIII}	1.5187286E + 01	1.5147428E + 01	1.5309038E + 01
ΔV_{OIII}**	−9.7300000E − 02		
ΔH_{FeTi}**	2.9435301E + 04		
ΔS_{FeTi}**	4.5123501E + 00		
ΔH_{MgFe}	−2.8368547E + 04	−2.9919742E + 04	−2.7179059E + 04
ΔS_{MgFe}	−1.3222971E + 01	−1.4203763E + 01	−1.2489809E + 01
Ilmenite			
$W_{H,ig}$	8.4055215E + 03	8.3486436E + 03	8.4621592E + 03
$W_{S,ig}$	3.0423203E + 00	2.9888186E + 00	3.0766625E + 00
$W_{V,ig}$	1.0800000E − 02		
$W_{H,gi}$	7.3635693E + 03	7.3621216E + 03	7.6529805E + 03
$W_{S,gi}$	3.4959583E + 00	3.4948959E + 00	3.6954560E + 00
$W_{V,gi}$	1.0800000E − 02		
W_{gh}	2.6651402E + 04	2.6608336E + 04	2.7090381E + 04
W_{hg}	2.6651402E + 04	2.6608336E + 04	2.7090381E + 04
$W_{H,ih}$	4.4204801E + 04		
$W_{S,ih}$†	1.2274390E + 01		
$W_{H,hi}$†	1.2634250E + 05		
$W_{S,hi}$†	1.0060010E + 02		
Spinel (Akimoto distribution)			
$\Delta\mu^*_{H,23}$	2.2323242E + 04	1.6138391E + 04	2.8282242E + 04
$\Delta\mu^*_{S,23}$	1.3994102E + 01	9.7778091E + 00	1.7738436E + 01
$\Delta\mu^*_{2q}$	0.0000000E + 00		
W_{12}†	1.5748030E + 04		
$W_{H,21}$†	4.6175480E + 04		
$W_{S,21}$†	2.3076500E + 01		
W_{13}	0.0000000E + 00		
W_{31}	0.0000000E + 00		
$\Delta W_{H,q3}$	3.9471707E + 04	3.9471707E + 04	4.8350406E + 04
$\Delta W_{S,q3}$	2.3178127E + 01	2.3178127E + 01	3.1921598E + 01
Spinel (Site mixing model)			
$\Delta\mu^*_{H,1\bar{1}}$†	−2.0232200E + 04		
$\Delta\mu^*_{S,1\bar{1}}$†	−1.0946400E + 01		
$\Delta\mu^*_{31}$	−1.6513935E + 04	−1.7326490E + 04	−1.6489066E + 04
$\Delta\mu^*_{H,3\bar{3}}$	−3.8151503E + 04		
$\Delta\mu^*_{S,3\bar{3}}$	−1.1314214E + 01		
$\Delta\mu^*_{H,\mathrm{Ti}}$	−8.8053027E + 02		
$\Delta\mu^*_{S,\mathrm{Ti}}$	3.6781400E − 01		
$W_{\bar{1}1}$†	0.0000000E + 00		
$W_{\bar{1}\bar{3}}$	−1.3107788E + 04	−1.3132656E + 04	−1.2295232E + 04
$W_{\bar{1}3}$	1.6513935E + 04	1.6489066E + 04	1.7326490E + 04
$W_{1\bar{3}}$	−1.3107788E + 04	−1.3132656E + 04	−1.2295232E + 04
W_{13}	−1.3736983E + 04	−1.3761852E + 04	−1.2924428E + 04
$W_{\bar{3}3}$	−2.4827680E + 04		
$W_{H,12}$†	8.622861E + 02		
$W_{S,12}$†	−2.353941E + 01		
$W_{H,21}$†	4.907650E + 04		
$W_{S,21}$†	3.167319E + 01		
$W_{H,\mathrm{Fe}}$†	1.390470E + 04		
$W_{S,\mathrm{Fe}}$†	2.531960E + 01		
$W_{H,\mathrm{Mg}}$	3.8981161E + 04	3.3962559E + 04	4.5510095E + 04
$W_{S,\mathrm{Mg}}$	3.8346156E + 01	3.4599309E + 01	4.3047340E + 01

* $\Delta G = \Delta H - T\Delta S + (P - 1)\Delta V$, $W = W_H - TW_S + (P - 1)W_V$.

** Robie et al. (1978).

† Andersen and Lindsley (1988).

For the binary Fe_2TiO_4-Mg_2TiO_4, the model predicts a very small preference of Mg vs. Fe^{2+} for the tetrahedral site that decreases with increasing temperature.

INTERCRYSTALLINE EQUILIBRIA

Ilmenite-spinel

Chemical equilibrium between sp_{ss}-il_{ss} is described by the Fe-Ti exchange reaction

$$FeTiO_3 + Fe_3O_4 = Fe_2TiO_4 + Fe_2O_3$$

where

$$\Delta G^0_{\mathrm{FeTi}} = -RT \ln(a_{\mathrm{usp}}a_{\mathrm{hem}})/(a_{\mathrm{mt}}a_{\mathrm{il}}) \quad (13)$$

the oxidation reaction

$$4Fe_3O_4 + O_2 = 6Fe_2O_3$$

where

$$\Delta G^0_{\mathrm{Oxid}} = -RT \ln[a^6_{\mathrm{hem}}/(a^4_{\mathrm{mt}}f_{O_2})] \quad (14)$$

and the Fe^{2+}-Mg exchange reaction,

$$FeTiO_3 + MgFe_2O_4 = Fe_3O_4 + MgTiO_3$$

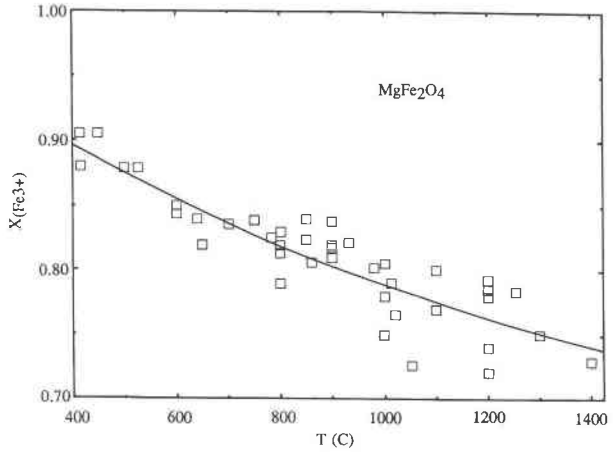

Fig. 1. Measured values for ${}^{[4]}X_{\mathrm{Fe^{3+}}}$ vs. T for $MgFe_2O_4$ spinels. The curve is calculated from the site mixing model. Data from Faller and Birchenall (1970), Kriessman and Harrison (1956), Brabers and Klerk (1977), and Pucher (1971).

where

$$\Delta G^0_{\mathrm{FeMg}} = -RT\ln[a_{\mathrm{mt}}a_{\mathrm{gk}}/(a_{\mathrm{mgf}}a_{\mathrm{il}})] \tag{15}$$

or alternatively

$$2FeTiO_3 + Mg_2TiO_4 = Fe_2TiO_4 + 2MgTiO_3$$

and

$$\Delta G^0_{\mathrm{FeMg'}} = -RT\ln[a_{\mathrm{usp}}a^2_{\mathrm{gk}}/(a_{\mathrm{qan}}a^2_{\mathrm{il}})]$$
$$= \Delta G^0_{\mathrm{FeMg}} - 2\Delta\mu^0_{23}$$

where

$$\Delta\mu^0_{23} = \tfrac{1}{2}(\mu^0_{\mathrm{usp}} - \mu^0_{\mathrm{qan}}) + \mu^0_{\mathrm{mgf}} - \mu^0_{\mathrm{mt}}. \tag{16}$$

Experiments at relatively low Mg contents of $\mathrm{sp_{ss}}$ and $\mathrm{il_{ss}}$ have been conducted by Pinckney and Lindsley (1976), Johnson et al. (1971), and Speidel (1970). The experiments of Johnson et al. (1971) and Speidel (1970) were conducted at high temperatures. They have not been reversed, and the spinel may not be stoichiometric. The results have therefore been excluded from the modeling. Values for $\Delta G^0_{\mathrm{Oxid}}$ are from Haas (personal communication) as are values for the buffer curves for the experiments of Pinckney and Lindsley (1976).

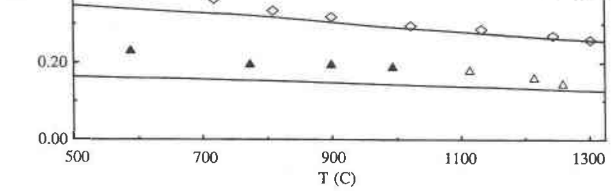

Fig. 2. Measured values for ${}^{[6]}X_{\mathrm{Fe^{2+}}}/{}^{[6]}X_{\mathrm{Fe^{3+}}}$ vs. T for Fe_3O_4-$MgFe_2O_4$ spinels. The curve is calculated from the site mixing model. As discussed in the text the low temperature points (solid symbols) at $X_{\mathrm{Mg}} = 0.406$, 0.634, and 0.82 were not used in the model. Data from Trestman-Matts et al. (1984).

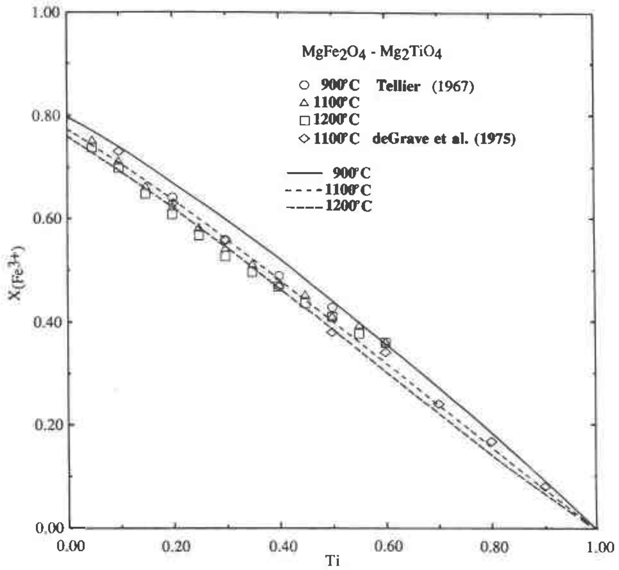

Fig. 3. Measured values for ${}^{[4]}X_{\mathrm{Fe^{3+}}}$ vs. Ti for $MgFe_2O_4$-Mg_2TiO_4 spinels at 900 °C, 1100 °C, and 1200 °C. The curves are calculated from the site mixing model. Data from Tellier (1967) (900 °C = circles, 1100 °C = triangles, 1200 °C = squares) and de Grave et al. (1975) (1100 °C = diamonds).

One complication in using linear programming is that the oxidation reaction (Eq. 14) is not independent of the exchange reactions (Eqs. 13 and 15). Each reversal describes a volume of feasible solutions bounded by surfaces in K_{Oxid}, K_{FeTi}, and K_{FeMg} space; the apexes of that volume are the extreme compositional values. Under the assumption that these surfaces are planar, additional equations can be written to describe this volume as a series of intersecting planes. This approach ensures that the values of f_{O_2} are compatible with the other parameters determined using linear programming.

Olivine-ilmenite

Equilibrium between $\mathrm{ol_{ss}}$ and $\mathrm{il_{ss}}$ can be described by the exchange reaction

$$2MgTiO_3 + Fe_2SiO_4 = 2FeTiO_3 + Mg_2SiO_4 \tag{17}$$

where

$$\Delta G^0_{\mathrm{OlIl}} = -RT\ln[a^2_{\mathrm{il}}a_{\mathrm{fo}}/(a^2_{\mathrm{gk}}a_{\mathrm{fa}})].$$

Given the starting composition, each $\mathrm{ol_{ss}}$-$\mathrm{il_{ss}}$ experiment (Andersen and Lindsley, 1979, 1981; Andersen, 1983; Bishop, 1976, 1979; Fig. 4, Tables 7 and 8) provides a single constraint on the activity ratio, whereas a

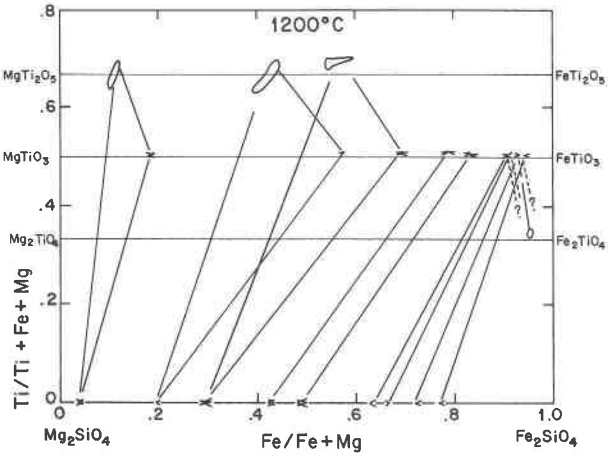

Fig. 4. Diagram of experimental products listed in Table 7. Arrows indicate direction of reaction. Sp_{ss} and arm_{ss} have not been reversed.

reversal provides upper and lower bounds on the ratio. Since linear programming provides an exact solution to a system of inequalities, the uncertainties in the compositions of the olivine and ilmenite have been included, combined with the experimental uncertainties in temperature of ±5–10 °C.

Olivine-spinel

The Fe^{2+}-Mg distribution between ol_{ss} and sp_{ss} can be described using

$$2MgFe_2O_4 + Fe_2SiO_4 = 2Fe_3O_4 + Mg_2SiO_4$$

or given values for the Fe^{2+}-Mg exchange between ol_{ss}-il_{ss} (Eq. 17) and between il_{ss}-sp_{ss} (Eq. 15),

$$\Delta G_{\mathrm{OlSp}} = -RT\ln[a_{\mathrm{fo}}a^{2}_{\mathrm{mt}}/(a_{\mathrm{fa}}a^{2}_{\mathrm{mgf}})]$$
$$= \Delta G^{0}_{\mathrm{OlIl}} + 2\Delta G^{0}_{\mathrm{MgFe}}. \qquad (18)$$

Table 7. New experimental data for il_{ss} and ol_{ss} in equilibrium with Fe at 1200 °C in evacuated silica tubes

Experiment no.	Initial comp	Duration (h)	Products*	
67	$Il_{90}Fa_{90}$	240.0	$Il_{92.5}Fa_{72.5}$	spinel
68	$Il_{100}Fa_{80}$	240.0	$Il_{94.5}Fa_{78.0}$	spinel
69	$Il_{80}Fa_{80}$	240.0	$Il_{90.5}Fa_{63.5}$	spinel ?
70	$Il_{100}Fa_{50}$	240.0	$Il_{91.0}Fa_{66.4}$	spinel ?
71	$Il_{80}Fa_{50}$	243.7	$Il_{83.0}Fa_{48.0}$	
72	$Il_{100}Fa_{30}$	243.7	$Il_{83.0}Fa_{49.0}$	
73	$Il_{70}Fa_{50}$	237.5	$Il_{78.5}Fa_{42.0}$	
74	$Il_{90}Fa_{30}$	237.5	$Il_{79.0}Fa_{42.5}$	
75	$Il_{60}Fa_{30}$	237.5	$Il_{69.5}Fa_{29.0}$	armalcolite
76	$Il_{80}Fa_{10}$	237.5	$Il_{69.0}Fa_{31.0}$	armalcolite
77	$Il_{0}Fa_{10}$	237.5	$Il_{18.5}Fa_{4.0}$	armalcolite
78	$Il_{20}Fa_{0}$	237.5	$Il_{18.5}Fa_{4.0}$	armalcolite
79	$Il_{40}Fa_{20}$	232.0	$Il_{57.5}Fa_{19.5}$	armalcolite
80	$Il_{60}Fa_{10}$	232.0	$Il\_\_Fa_{22.2}$	armalcolite

* $Il = 100X_{Fe}/(X_{Fe} + X_{Mg})$.

Table 8. Experimental data for il_{ss} and ol_{ss} from Bishop (1976, 1979) at 13 kbar

Experiment no.	Temperature (°C)	Duration (h)	X^{Il}_{Fe}**	Hem (mol%)	X_{fa}
86H	1431	2.3	0.477	0	0.163
55H	1412	2.5	0.539	3	0.192
85H	1381	3.2	0.534	0	0.197
82H	1305	5.3	0.555	1	0.206
50H	1309	5.4	0.541	0	0.190
83H	1205	10.7	0.576	2	0.199
53H	1216	15.8	0.548	6	0.189
51H	1109	31.3	0.554	11	0.175
74H	1108	35.3	0.567	4	0.179
84H	1004	118.0	0.592	7	0.161
54H	998	112.5	0.618	11	0.184
65H	900	5.0	0.583	11	0.138
90R	1305	5.3	0.718	2	0.335
59R	1309	4.8	0.718	2	0.315
89R	1205	12.4	0.658	2	0.252
88R	1205	11.7	0.739	2	0.331
63R	1207	12.9	0.719	2	0.307
87R	1104	27.9	0.734	4	0.308
60R	1107	24.2	0.743	2	0.286
78R	1004	76.7	0.679	0	0.266
58R	1008	53.3	0.759	1	0.298
77R	943	260.8	0.685	2	0.232
66R	900	58.7	0.724	1	0.228
61R	910	285.5	0.760	1	0.266

* The experiment numbers ending in H started with il + fo, those ending in R started with gk + fa.
** $X^{Il}_{Fe} = X_{Fe^{2+}}/(X_{Fe^{2+}} + X_{Mg})_{Il}$.

This equilibrium may also be written as

$$Mg_2TiO_4 + Fe_2SiO_4 = Fe_2TiO_4 + Mg_2SiO_4$$

with

$$\Delta G_{\mathrm{OlSp'}} = -RT\ln[a_{\mathrm{fo}}a_{\mathrm{usp}}/(a_{\mathrm{fa}}a_{\mathrm{qan}})]$$
$$= \Delta G^{0}_{\mathrm{OlIl}} + 2\Delta G^{0}_{\mathrm{MgFe}} - 2\Delta\mu^{0}_{23} \qquad (19)$$

where $\Delta\mu^{0}_{23}$ is defined in Equation 16.

Experiments for ol_{ss}-sp_{ss} equilibria have been conducted by Jamieson and Roedder (1984), Hill and Sack (1987), and Rawson and Irvine (1980). The data of Rawson and Irvine (1980) have not been reversed and have been excluded from the modeling. Those experiments of Jamieson and Roedder (1984) and Hill and Sack (1987) for which the tie lines have rotated relative to the starting materials have been included. However it was necessary to ignore any nonstoichiometry in the spinels, as a defect model for the spinels is outside the scope of this paper. As with the ol_{ss}-il_{ss} equilibria, Equation 18 (or Eq. 19) can be rewritten in terms of inequalities by considering the change in the composition relative to the starting composition of the starting materials and an assumed ±5–10 °C uncertainty in temperature.

DISCUSSION

Model parameters were derived using linear programming by a simultaneous linear programming solution to the il_{ss}-sp_{ss} data, the ol_{ss}-il_{ss} data, and the ol_{ss}-sp_{ss} data. In addition, the Mn-il_{ss}-$garnet_{ss}$ data of Kress (1986) and Mn-il_{ss}-sp_{ss} data of Mazzullo et al. (1975) were also fit to

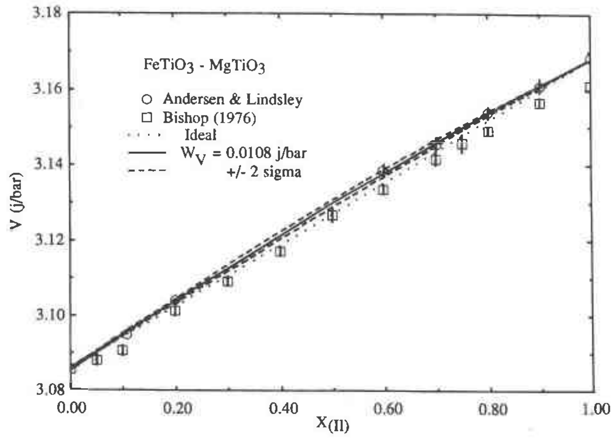

Fig. 5. Volume data for il-gk from Andersen and Lindsley (1979), Robie et al. (1978), and this study. The solid line (dashed = $\pm 2\sigma$) is calculated using $W_{V,ig} = 0.0108 \pm 0.0019(1\sigma)$, and the dotted line is for ideal mixing.

assure internal consistency. Values for the O buffers for the il_{ss}-sp_{ss} experiments and ΔG_{Oxid} are from Haas (personal communication) and have an uncertainty in f_{O_2} of ± 0.05–0.19 log units. The value for ΔV_{OIII} is calculated using Robie et al. (1978). We have rerefined the $W_{V,ig}$ term (Fig. 5) using least squares, obtaining a symmetric $W_{V,ig} = 0.0108(19)$. The small volumes determined by Bishop (1976) might be caused by the presence of a hematite component in those samples. One experiment labeled B61 (Bishop, 1976) was found to be inconsistent with the others and was excluded from the modeling. The model values from the linear programming are based on a set of inequalities derived from the bracketed experimental compositions. The inequalities only define an area of feasible solutions, the preferred values listed in Table 6 are only one such feasible solution and were derived from an objective function that minimizes the size of the W_S terms. The minimum and maximum values listed in Table 6 are based on objective functions that minimize or maximize the value of each parameter. These values are not independent of each other, but are simply listed to show the ranges of model values that are compatible with the data. It should be emphasized that random combinations of maximum and minimum values from Table 6 may well lie outside the volume of feasible solutions.

The join il-gk is required to be asymmetric, although the pressure-dependent term is symmetric and derived from a least-squares solution of the volume data. The W terms for this join could be forced to be symmetric at the price of an asymmetric olivine model.

For the spinel model with the Akimoto distribution, the Fe_3O_4-$MgFe_2O_4$ and Fe_2TiO_4-Mg_2TiO_4 binaries can be considered ideal, whereas the site mixing model requires nonideal parameters for both (Figs. 6 and 7). However, the activities for the site mixing model on the binary Fe_3O_4-$MgFe_2O_4$ approach the Akimoto model at high temperatures because the data of Jamieson and Roedder (1984) require both spinel models to have similar activities at high temperatures. Calculated activities for this binary are compatible with those calculated by Nafziger (1973) based the site-defect data for spinel-hematite and spinel-magnesiowüstite.

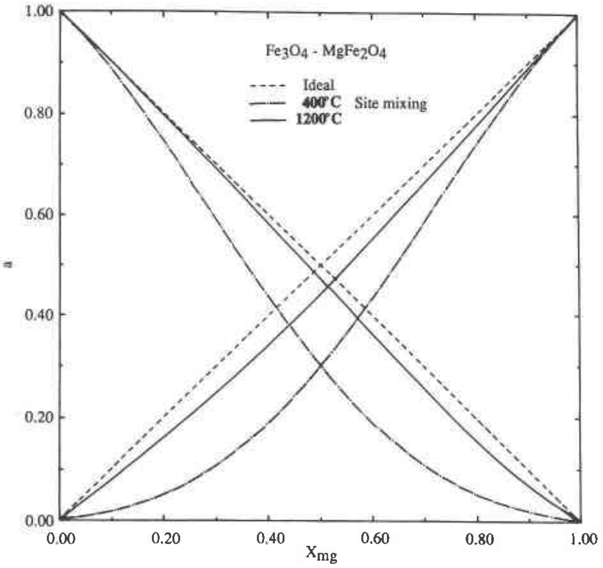

Fig. 6. Calculated values for the activities on the binary Fe_3O_4-$MgFe_2O_4$ at 400 (dot-dash lines) and 1200 °C (solid lines) using the site-mixing model. The Akimoto model is ideal (dashed lines).

Since there are no phase equilibria data on or near the $MgFe_2O_4$-Mg_2TiO_4 binary, it is not surprising that the two spinel models show the largest difference for the activities on this join (Fig. 8). The Akimoto model is essentially

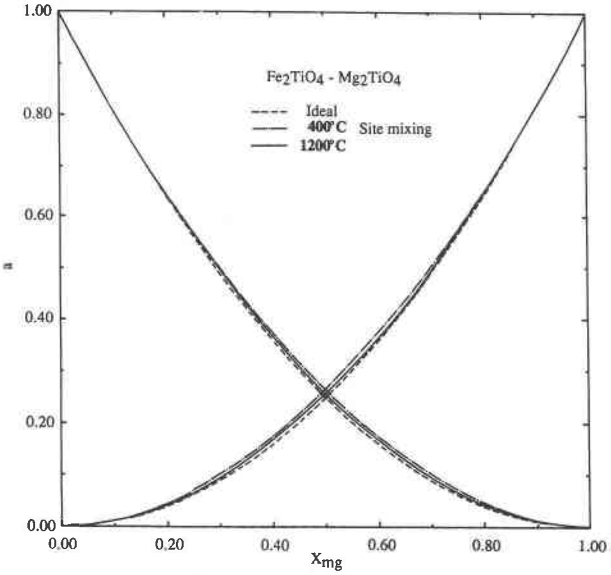

Fig. 7. Calculated values for the activities on the binary Fe_2TiO_4-Mg_2TiO_4 using then site-mixing model at 400 (dot-dash lines) and 1200 °C (solid lines). The Akimoto model can be considered to be ideal (dashed lines).

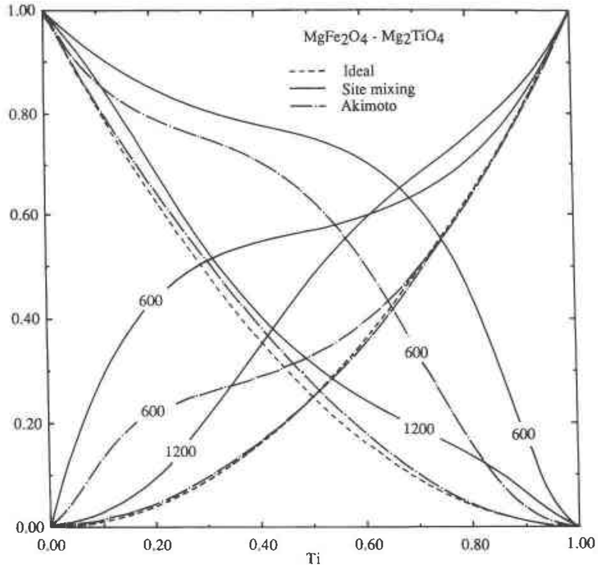

Fig. 8. Calculated values for the activities on the binary $MgFe_2O_4$-Mg_2TiO_4 at 600 and 1200 °C using the Akimoto model (dot-dash lines) and the site-mixing model (solid lines). The Akimoto model is essentially ideal (dashed line) at 1200 °C.

ideal, at high temperature, with a consolute point at 530 °C, $X_2 = 0.3$, whereas the site-mixing model shows positive deviations from ideality and the corresponding consolute point is at 556 °C, $X_2 = 0.42$. However, this difference is not surprising given the large extrapolation in composition from the data used in the calibration.

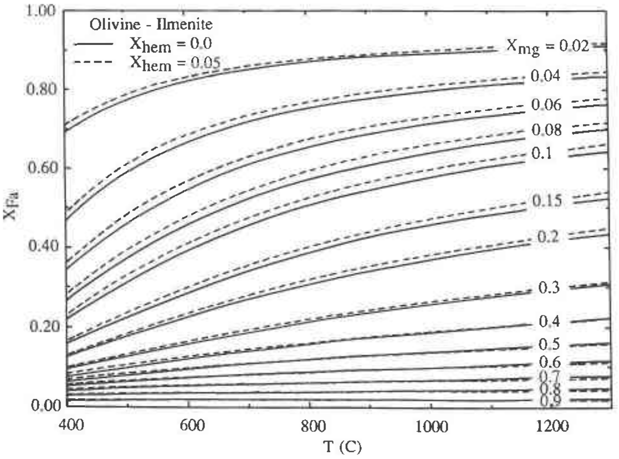

Fig. 9. Calculated isopleths of $X^{il}_{Mg} = X_{gk}/(X_{il} + X_{gk})$ for coexisting ol_{ss} and il_{ss} as a function of temperature, $X_{hem} = 0$ (solid lines) and $X_{hem} = 0.05$ (dashed lines), 1 bar.

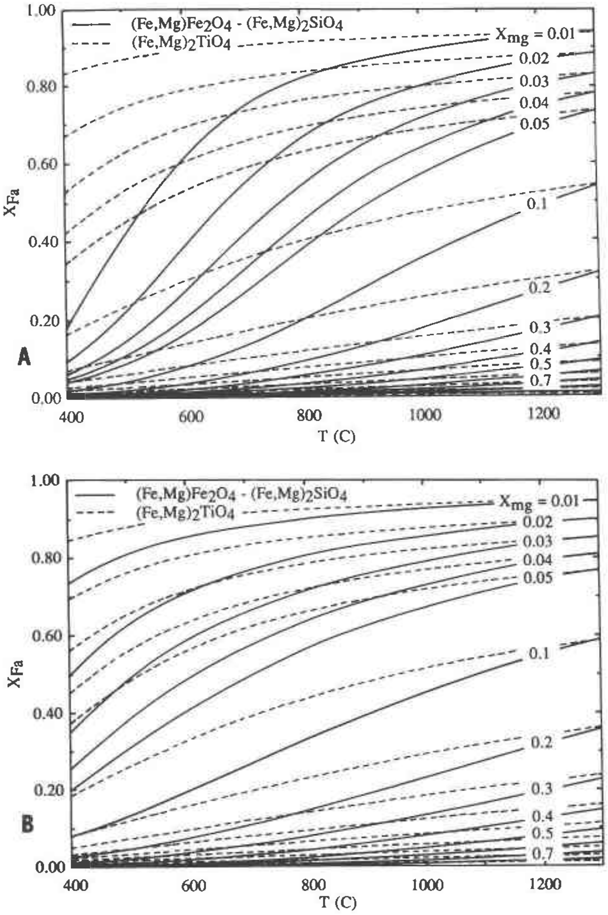

Fig. 10. **(A)** Calculated isopleths of X^{sp}_{Mg} for coexisting ol_{ss}-sp_{ss} with $X^{sp}_{Ti} = 0$ (solid lines) and $X^{sp}_{Ti} = 1$ (dashed lines) using the modified Akimoto model for the spinels. **(B)** Calculated isopleths of X^{sp}_{Mg} for coexisting ol_{ss}-sp_{ss} with $X^{sp}_{Ti} = 0$ (solid lines) and $X^{sp}_{Ti} = 1$ (dashed lines) using the site-mixing model for the spinels.

Calculated isopleths of coexisting ol_{ss}-il_{ss} are shown in Figure 9 for $X_{hem} = 0$ and $X_{hem} = 0.05$ (dashed lines) at 1 bar pressure. Temperatures estimated for coexisting ol_{ss} and il_{ss} will be too high if the effect of X_{hem} is ignored. For ol_{ss}-sp_{ss}, calculated isopleths are shown in Figure 10A for the Akimoto model and in Figure 10B for the site mixing model at $X^{sp}_{Ti} = 0$ and $X^{sp}_{Ti} = 1$. Both spinel models show the preference of Mg for the silicate that is somewhat diminished with increasing Ti content of the spinel. Because the mixing properties of both spinel models are very similar for $(Fe,Mg)_2TiO_4$ (see Fig. 7), the isopleths at $X^{sp}_{Ti} = 1$ are similar but diverge significantly at $X^{sp}_{Ti} = 0$. The Akimoto model predicts a much greater preference of Mg for olivine than the site-mixing model. For il_{ss}-sp_{ss} with $X^{sp}_{Ti} = 1$ and $X^{ilm}_{hem} = 0$, isopleths calculated using the Akimoto model are shown as dashed lines and those for the site model as solid lines in Figure 11. Both models predict a slight preference of Mg for ilmenite.

The partitioning of Fe^{2+}-Mg among il_{ss}, sp_{ss}, and ol_{ss} is relatively temperature insensitive as shown in Figures 9–11. Except at low temperatures, the isopleths are nearly flat, which would yield large uncertainties in any temperatures estimated from these exchange reactions. In ad-

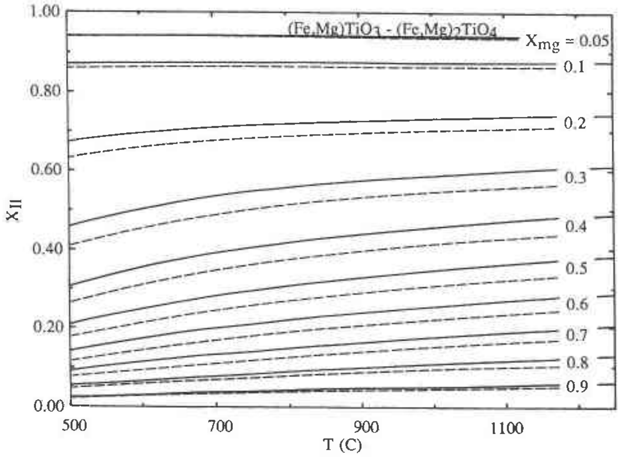

Fig. 11. Calculated isopleths of X^{sp}_{Mg} for coexisting il$_{ss}$-sp$_{ss}$ with $X^{sp}_{Ti} = 1$ and $X^{il}_{hem} = 0$ using the modified Akimoto model (dashed lines) and site model (solid lines) for the spinels.

dition, for most rocks where the modal abundance of olivine is much greater than that of the oxides, the effect of the reequilibration of compositions upon cooling would be a negligible or very slight increase in the Mg content of the olivine.

For the purposes of il$_{ss}$-sp$_{ss}$ geothermometry and O barometry, the effect of Mg on the thermometric information obtained is dependent on the amount of Mg in the oxides. In addition to providing more accurate values for T and f_{O_2}, temperatures calculated from the exchange of Fe^{2+}-Mg allow a useful indication of the degree of equilibrium between the two oxides. If only one oxide is present, precluding the use of the il$_{ss}$-sp$_{ss}$ geothermometer and O barometer, and assemblage ol$_{ss}$ + oxide (il$_{ss}$ or sp$_{ss}$) + quartz can be used to derive qualitative estimates for T and f_{O_2} based on the displacement of the equilibria FMQ

$$2Fe_3O_4 + 3SiO_2 = 3Fe_2SiO_4 + O_2$$

or FHQ (Frost et al. 1988)

$$2Fe_2O_3 + 2SiO_2 = 2Fe_2SiO_4 + O_2.$$

The relative insensitivity of the partitioning of Fe^{2+}-Mg between Fe-rich olivine and oxides (Figs. 9 and 10), combined with the low Mg content of the oxides and compositional uncertainties, result in large uncertainties in absolute values for calculated temperatures and f_{O_2}. Qualitative results for T-f_{O_2} paths can be obtained and are shown in Figure 12. For clarity, only one set of spinel isopleths for a Ti content of 0.8 with X_{Mg} [= Mg/(Mg + Fe^{2+})] = 0, 0.01, 0.03, and 0.05 is shown (long-dash short-dash lines) with the corresponding olivine isopleths (short-dash lines). These radiate to higher values of f_{O_2} from the four-phase QUIlF (quartz + 2 ulvöspinel = 2 ilmenite + fayalite) assemblage (Frost et al. 1988, Fig. 12 solid lines). For olivine + ilmenite + quartz, one set of ilmenite isopleths with $X_{hem} = 0.01$ and X_{Mg} [= $X_{gk}/(X_{gk} + X_{il})$] = 0, 0.01, and 0.05, is shown along with the corresponding olivine isopleths. The shallow intersection of the ol$_{ss}$ and il$_{ss}$ or sp$_{ss}$ isopleths results in large uncertainties in estimated temperatures but does allow the phases to be used for qualitative estimates of temperature and f_{O_2}.

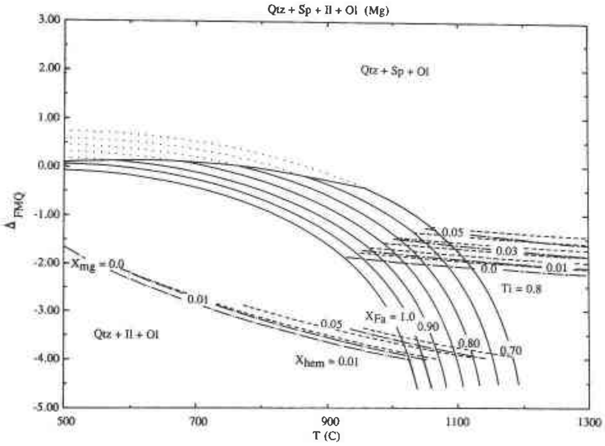

Fig. 12. Temperature vs. ΔFMQ (= $\log_{10} f_{O_2} - \log_{10} f_{O_2}$FMQ) for olivine + oxide + quartz assemblages at 1 bar. For clarity only, one ilmenite and spinel composition is plotted and the effects of pressure and melting have been ignored. The solid lines are the univariant curves for olivine + ilmenite + spinel + quartz, the heavy solid line is the approximate location of the reaction, olivine = pyroxene + quartz (Smith, 1971), the dashed lines are olivine isopleths, the dash-dot lines are for an ilmenite with $X_{hem} = 0.01$ and X_{Mg} = 0.0, 0.01, and 0.05, and the long dash–short dash lines are for a spinel with $X_{Ti} = 0.8$ and X_{Mg} = 0.0, 0.01, 0.03, and 0.05. The shallow intersection of olivine-oxide isopleths makes this a poor geothermometer and O barometer, but it can be used to provide qualitative estimates of T and f_{O_2}.

A maximum temperature for the assemblage ol$_{ss}$ + il$_{ss}$ + qtz can be obtained from the displacement of FHQ and its intersection with QUIlF. The assemblage ol$_{ss}$ + il$_{ss}$ + qtz is constrained to temperatures and f_{O_2} below that of QUIlF. Likewise, a minimum temperature for the assemblage ol$_{ss}$ + sp$_{ss}$ + qtz is obtained from the intersection of FMQ with QUIlF (a maximum temperature is obtained from the melting of ol$_{ss}$). The assemblage ol$_{ss}$ + sp$_{ss}$ + qtz is constrained to temperatures and values of f_{O_2} above that of QUIlF. Since the stability of ol$_{ss}$ + qtz is pressure dependent (Smith, 1971), the region of T-f_{O_2} in which the assemblage ol + oxide + qtz is stable decreases with increasing pressure.

Although we have not experimentally calibrated either of these reactions, there are some experimental data available to test the oxidation reaction involving olivine, ilmenite, and quartz. Andersen and Lindsley (1979) reported the appearance of quartz in exchange experiments involving Fe-rich olivine and ilmenite, conducted at an f_{O_2} defined by the Co-CoO buffer. Temperatures and values of f_{O_2} calculated from the extreme compositional values of these experiments are shown in Figure 13. Although the hematite contents of these experiments have

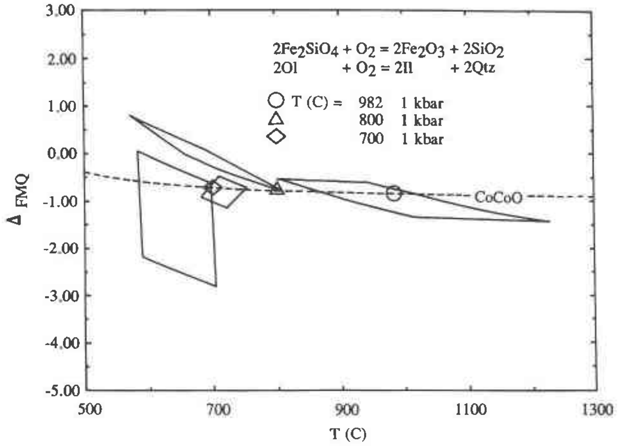

Fig. 13. Temperature vs. ΔFMQ (= $\log_{10} f_{O_2} - \log_{10} f_{O_2}$FMQ) for selected ol_{ss}-il_{ss} data of Andersen and Lindsley (1979) in which quartz was also present at 982 °C (circle), 800 °C (triangle), and 700 °C (diamonds), 1 kbar pressure and f_{O_2} defined by the Co-CoO buffer. These experiments were used only to constrain the partitioning of Fe^{2+}-Mg between ol_{ss}-il_{ss} and not the oxidation reaction involving ol_{ss}, il_{ss}, and quartz. These experiments are used to demonstrate the internal consistency of the thermodynamic data and solution models. The polygons represent calculated temperatures and f_{O_2} from the exchange and oxidation reactions based on extreme compositions from the experiments. Note that the brackets at 800 °C are only consistent with the temperature of the experiment at one extreme of the bracket that is also at the Co-CoO buffer.

not been reversed, there is a composition within the bracket that is also consistent with the f_{O_2} of the experiment. For the 800 °C experiment, the only composition that is consistent with the temperature of the experiment is at the extreme compositional limit of the bracket; it is also the only composition that yields a consistent f_{O_2}. Even though this may be fortuitous, it does provide a check on the internal consistency of the models.

CONCLUSIONS

A solution model has been developed for coexisting ol_{ss}-il_{ss}, sp_{ss}-il_{ss}, and ol_{ss}-sp_{ss} using linear programming. The ilmenite solution model is based on asymmetric ternary Margules solution and is internally consistent with a spinel model based on a modified Akimoto cation distribution and a spinel model that includes the effects of site mixing. The Akimoto model is simpler in functional form and is adequate to describe the macroscopic properties of iron-magnesium-titanium spinels. The Fe-Mg partitioning between ol_{ss}-il_{ss}-sp_{ss} is relatively temperature insensitive, which limits the usefulness of that partitioning in geothermometry. These models, however, will allow more precise estimates of T and f_{O_2} for il_{ss} and sp_{ss} and, in addition, qualitative estimates of T and f_{O_2} for ol_{ss} + oxide(il_{ss} or sp_{ss}) + qtz assemblages.

Programs to calculate temperatures and f_{O_2} for coexisting oxides and olivine are available from the authors.

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APPENDIX 1

Experimental conditions

Starting materials were the same as those of Andersen and Lindsley (1979) and consisted of mechanical mixtures of ol$_{ss}$ and il$_{ss}$ of known composition. In order to reverse the Fe^{2+}-Mg distribution, each mechanical mixture was paired with another having the same bulk composition, but with different olivine and ilmenite compositions. These were placed in Fe capsules in order to minimize the Fe^{3+} content. These capsules were then sealed within evacuated silica tubes and reacted for 9–10 d at 1200 °C. Pt-Pt 10% Rh thermocouples were used to monitor the temperature; precision of the temperature is estimated to be ± 5 °C. Starting compositions, experimental conditions, and products are listed in Table 7. Products were identified optically, from X-ray powder patterns and from microprobe analyses. All compositions were determined with an ARL-EMX-SM automated electron microprobe using the reduction techniques of Bence and Albee (1968) and Albee and Ray (1970). Compositions of the products are shown in Figure 4. The microprobe analyses for the ilmenite show a small but consistent excess of Ti (<1%) relative to stoichiometry and may indicate the presence of Ti^{3+}.

Spinel mixing models

For a phase with n independent compositional variables the nonconfigurational energy, G^*, can be written as

$$G^* = G_{\mathrm{ideal}} + G_{\mathrm{excess}} \tag{A1}$$

which can be expanded as a Taylor series

$$G^* = g_1^* + \sum_{i=2} X_i g_i^* + \sum_{i=2} \sum_{j=i} X_i X_j g_{ij}^* + \sum_{i=2} \sum_{j=i} \sum_{k=j} X_i X_j X_k g_{ijk}^* \tag{A2}$$

where the summation is over n variables, which includes both ideal and excess contributions to the free energy.

The excess function is assumed to be the sum of the individual ternaries and binaries (Andersen and Lindsley, 1981),

$$G_{\mathrm{excess}} = \sum_{i} \sum_{j,j \neq i} W_{ij} X_i X_j \left(X_j + \frac{1}{2} \sum_{k,k \neq i,j} X_k \right) + \sum_{i} \sum_{j,j \neq i} \sum_{k,k \neq i,j} W_{ijk} X_i X_j X_k \tag{A3}$$

where for a ternary,

$$W_{ij} = -g_{jj}^* - 2g_{jjj}^*$$

$$W_{ji} = -g_{jj}^* - g_{jjj}^*$$

$$W_{ik} = -g_{kk}^* - 2g_{kkk}^*$$

$$W_{ki} = -g_{kk}^* - g_{kkk}^*$$

$$W_{jk} = -g_{jj}^* + g_{jk}^* - g_{kk}^* - g_{jjj}^* + g_{jkk}^* - 2g_{kkk}^*$$

$$W_{kj} = -g_{jj}^* + g_{jk}^* - g_{kk}^* - 2g_{jjj}^* + g_{jjk}^* - g_{kkk}^*$$

$$W_{ijk} = g_{jjj}^* + g_{kkk}^* - ½(g_{jkk}^* + g_{jjk}^*) \tag{A4}$$

and

$$g_{jj}^* = W_{ij} - 2W_{ji}$$

$$g_{jk}^* = ½(W_{ij} - 3W_{ji} + W_{ik} - 3W_{ki} + W_{jk} + W_{kj}) + W_{ijk}$$

$$g_{kk}^* = W_{ik} - 2W_{ki}$$

$$g_{jjj}^* = W_{ji} - W_{ij}$$

$$g_{jjk}^* = ½(3W_{ji} - 3W_{ij} + W_{ki} - W_{ik} - W_{jk} + W_{kj}) - W_{ijk}$$

$$g_{jkk}^* = ½(W_{ji} - W_{ij} + 3W_{ki} - 3W_{ik} + W_{jk} - W_{kj}) - W_{ijk}$$

$$g_{kkk}^* = W_{ki} - W_{ik}. \tag{A5}$$

By setting the composition to the limiting end-members, binaries, and ternaries, the g_{ijk}^* can be defined in terms of end-member energies and Margules-type coefficients for excess energies of mixing.

Site mixing model

In order to explicitly include the effects of cation disorder on the mixing properties for spinels containing Fe^{2+}, Fe^{3+}, Mg^{2+}, and Ti^{4+}, two order parameters have to be included in the expansion of G^* (Eq. A3). The compositional variables for a stoichiometric spinel are defined as

$$X_2 = N_{\mathrm{Ti}}$$

$$X_3 = N_{\mathrm{Mg}}$$

where N_i is the number of cations per 4 O atoms. Restricting Ti^{4+} to the octahedral site, the order parameters are defined as

$$X_4 = {}^{[4]}\mathrm{X}_{\mathrm{Fe}^{3+}}$$

$$X_5 = {}^{[4]}\mathrm{X}_{\mathrm{Mg}^{2+}}$$

where $0 \leq X_4 + X_5 \leq 1$. However, these parameters are not independent of the composition, i.e., $X_5 < X_3$ and $X_4 < 2 - 2X_2$. The remaining site occupancies are then

$${}^{[4]}X_{\mathrm{Fe}^{2+}} = 1 - X_4 - X_5$$

$${}^{[6]}X_{\mathrm{Fe}^{2+}} = ½(X_2 - X_3 + X_4 + X_5)$$

$${}^{[6]}X_{\mathrm{Fe}^{3+}} = ½(2 - 2X_2 - X_4)$$

$${}^{[6]}X_{\mathrm{Mg}^{2+}} = ½(X_3 - X_5)$$

$${}^{[6]}X_{\mathrm{Ti}^{4+}} = ½X_2.$$

The nonconfigurational energy, G^*, is defined using a second degree Taylor expansion in terms of the independent compositional (X_2 and X_3) and order variables (X_4 and X_5). The third degree term g_{222}^* has been added to fit the mt-il data of Buddington and Lindsley (1964) and Spencer and Lindsley (1981). The significance of the g_{ijk}^* terms can then be determined by setting the compositions to the end-members and binaries.

Binaries

The binary $\mathrm{Fe_3O_4}$-$\mathrm{MgFe_2O_4}$ is modeled as a quaternary with two normal and two inverse end-members in which the mole fractions can be written as

$$X_{{}^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4} = 1 - X_4 - X_5$$

$$X_{{}^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4} = X_4 - X_3 + X_5$$

$$X_{{}^{[4]}\mathrm{Mg}{}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4} = X_5$$

$$X_{{}^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Mg}{}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4} = X_3 - X_5.$$

The meaning of the g_{ij}^* terms can be equated to a symmetric Margules type model ($W_{ij} = W_{ji}$, $g_{ijk}^* = 0$) for the excess terms using Equations A1 and A3, and

$$G_{\mathrm{ideal}} = \sum_{i} X_i G_i^*$$

or substituting in the mole fractions of the end members as defined above:

$$G^* = G^*_{{}^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4}(1 - X_4 - X_5) + G^*_{{}^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4}(X_4 - X_3 + X_5)$$

$$
\begin{aligned}
&+ G^*_{^{[4]}\mathrm{Mg}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4} X_5 \\
&+ G^*_{^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Mg}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4}(X_3 - X_5) \\
&+ W_{\bar{1}1}(1 - X_4 - X_5)(X_4 - X_3 + X_5) \\
&+ W_{\bar{1}\bar{3}}X_5(1 - X_4 - X_5) \\
&+ W_{\bar{1}3}(1 - X_4 - X_5)(X_3 - X_5) \\
&+ W_{1\bar{3}}X_5(X_4 - X_3 + X_5) \\
&+ W_{13}(X_3 - X_5)(X_4 - X_3 + X_5) \\
&+ W_{\bar{3}3}X_5(X_3 - X_5). \qquad \text{(A6)}
\end{aligned}
$$

Before simplifying and relating Equation A6 to the expansion of Equation A2, it will be convenient to define the differences in the inverse and normal end-member energies as

$$\Delta\mu^*_{1\bar{1}} = G^*_{^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4} - G^*_{^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4}$$

$$\Delta\mu^*_{3\bar{3}} = G^*_{^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Mg}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4} - G^*_{^{[4]}\mathrm{Mg}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4}$$

and

$$\Delta\mu^*_{31} = G^*_{^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Mg}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4} - G^*_{^{[4]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{3+}\mathrm{O}_4}.$$

Then for Equation A6

$$
\begin{aligned}
G^* = {} & G^*_{^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4} + X_3(\Delta\mu^*_{31} - W_{\bar{1}1} + W_{\bar{1}3}) \\
&+ X_4(\Delta\mu^*_{1\bar{1}} + W_{\bar{1}1}) \\
&+ X_5(\Delta\mu^*_{1\bar{1}} - \Delta\mu^*_{3\bar{3}} + W_{\bar{1}1} + W_{\bar{1}\bar{3}} - W_{\bar{1}3}) \\
&- X_3^2 W_{13} + X_3X_4(W_{\bar{1}1} - W_{\bar{1}3} + W_{13}) \\
&+ X_3X_5(W_{\bar{1}1} - W_{\bar{1}3} - W_{1\bar{3}} + W_{\bar{3}3} + 2W_{13}) \\
&- X_4^2 W_{\bar{1}1} + X_4X_5(-2W_{\bar{1}1} - W_{\bar{1}\bar{3}} + W_{\bar{1}3} \\
&\qquad + W_{1\bar{3}} - W_{13}) \\
&+ X_5^2(-W_{\bar{1}1} - W_{\bar{3}3} - W_{\bar{1}\bar{3}} + W_{\bar{1}3} + W_{1\bar{3}} - W_{13}) \qquad \text{(A7)}
\end{aligned}
$$

and equating terms in Equation A7 and the expansion of Equation A2 yields the definitions in Table 4 which can then be solved for $\Delta\mu^*_{ij}$ and W_{ij}.

The terms $\Delta\mu^*_{1\bar{1}}$ and $\Delta\mu^*_{3\bar{3}}$ are the differences between the inverse and normal cation distribution for pure magnetite and magnesium ferrite, and $\Delta\mu^*_{31}$ is the difference between an inverse magnesium ferrite and inverse magnetite. The W_{ij} are excess energies of mixing with $W_{\bar{1}1}$ and $W_{\bar{3}3}$ for pure magnetite and for pure magnesium ferrite [or mixing of Fe^{2+} (or Mg) with Fe^{3+} between the tetrahedral and octahedral sites], and $W_{\bar{1}3}$ and $W_{1\bar{3}}$ are for Fe^{2+} and Mg on the tetrahedral and octahedral sites for a completely normal and inverse spinel. The inclusion of the cross terms $W_{\bar{1}\bar{3}}$ and W_{13} allows for nonideal mixing of charge-coupled substitutions of $^{[4]}Fe^{2+}\,^{[6]}Fe^{3+}$ – $^{[4]}Fe^{3+}\,^{[6]}Mg$ and $^{[4]}Fe^{3+}\,^{[6]}Fe^{2+}$ – $^{[4]}Mg\,^{[6]}Fe^{3+}$.

The pseudobinary, Fe_3O_4-Fe_2TiO_4, is modeled as a ternary solution using Equations A2 and A4. Using the definitions in Equation A4 and because $g^*_{444} = g^*_{224} = g^*_{244} = 0$,

$$W_{\bar{1}1} = W_{1\bar{1}}$$

$$W_{2\bar{1}} - W_{\bar{1}2} = W_{21} - W_{12} = W_{\bar{1}12}$$

then simplifying the definitions for W_{21}, W_{12} and $W_{\bar{1}12}$,

$$W_{21} = -g^*_{22} + g^*_{24} - g^*_{44} - g^*_{222}$$

$$W_{12} = -g^*_{22} + g^*_{24} - g^*_{44} - 2g^*_{222}$$

$$W_{\bar{1}12} = g^*_{222}.$$

In this subsystem there are three end-member energies, six binary W's, and one ternary W, but there are only seven g^*_{ijk} (Eq. A4), so not all of the W's are independent because the third degree terms, g^*_{224} and g^*_{244}, have been set to zero. This leads to relations such as $W_{\bar{1}12} = W_{2\bar{1}} - W_{\bar{1}2} = W_{21} - W_{12}$.

For Fe_2TiO_4-Mg_2TiO_4, $X_2 = 1$, $X_4 = 0$, and Equation A2 reduces to

$$
\begin{aligned}
G^* = {} & g^*_1 + g^*_2 + g^*_{22} + X_3(g^*_3 + g^*_{23}) + X_5(g^*_5 + g^*_{25}) \\
&+ X_3^2 g^*_{33} + X_3X_5 g^*_{35} + X_5^2 g^*_{55} + g^*_{222} \qquad \text{(A8)}
\end{aligned}
$$

or using the previous definitions of g^*_{ijk} and defining

$$
\begin{aligned}
\Delta\mu^*_{2q} &= G^*_{^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{TiO}_4} + G^*_{^{[4]}\mathrm{Mg}^{[6]}\mathrm{Mg}^{[6]}\mathrm{TiO}_4} \\
&\quad - (G^*_{^{[4]}\mathrm{Mg}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{TiO}_4} + G^*_{^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Mg}^{[6]}\mathrm{TiO}_4}) \\
&= 2g^*_{33} + g^*_{35} \\
&= W_{\bar{1}1} + W_{\bar{3}3} - W_{\bar{1}3} - W_{1\bar{3}}
\end{aligned}
$$

and

$$
\begin{aligned}
\Delta\mu^*_{\mathrm{Ti}} &= G^*_{^{[4]}\mathrm{Mg}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{TiO}_4} - G^*_{^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Mg}^{[6]}\mathrm{TiO}_4} \\
&= g^*_5 + g^*_{25} + g^*_{35} + g^*_{55}
\end{aligned}
$$

then g^*_{25} can be defined as

$$g^*_{25} = \Delta\mu^*_{3\bar{3}} - \Delta\mu^*_{1\bar{1}} + \Delta\mu^*_{\mathrm{Ti}} - W_{\bar{1}1} + W_{\bar{1}3} - W_{13}.$$

Equation A8 can then be rewritten as

$$
\begin{aligned}
G^* = {} & G^*_{^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{TiO}_4} \\
&+ \tfrac{1}{2}X_3(G^*_{^{[4]}\mathrm{Mg}^{[6]}\mathrm{Mg}^{[6]}\mathrm{TiO}_4} - G^*_{^{[4]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{Fe}^{2+}{}^{[6]}\mathrm{TiO}_4}) \\
&+ \Delta\mu^*_{\mathrm{Ti}}(X_5 - \tfrac{1}{2}X_3) - \Delta\mu^*_{2q}(\tfrac{1}{2}X_3 - X_3X_5 + X_5^2) \\
&+ W_{13}(X_3 - X_5)(1 - X_3 + X_5) \\
&+ W_{\bar{1}3}X_5)(1 - X_5).
\end{aligned}
$$

The pseudobinary $MgFe_2O_4$-Mg_2TiO_4 is then treated in the same way as that for Fe_3O_4-Fe_2TiO_4. Because the third degree terms other than g^*_{222} have been set to zero,

$$W_{\bar{3}3} = W_{3\bar{3}}$$

and

$$W_{q\bar{3}} - W_{\bar{3}q} = W_{q3} - W_{3q} = W_{\bar{3}3q}.$$

Because only one third degree term has been included (g^*_{222}), the ternary coefficient (W_{33q}) is the same for both magnetite-ulvospinel and magnesium ferrite-qandilite.

Summary

Using the above definitions, the nonconfigurational energy, G^*, can be rewritten as

$$
\begin{aligned}
G^* = {} & G^*_{^{[4]}\mathrm{Fe}^{2+[6]}\mathrm{Fe}_2^{3+}\mathrm{O}_4}(1 - X_2) + G^*_{^{[4]}\mathrm{Fe}^{2+[6]}\mathrm{Fe}^{2+[6]}\mathrm{TiO}_4}X_2 \\
& + \Delta\mu^*_{1\bar{1}}[X_4 + X_5(1 - X_2)] + \Delta\mu^*_{31}X_3 \\
& + \Delta\mu^*_{33}X_5(X_2 - 1) + \Delta\mu^*_{\mathrm{Ti}}X_2X_5 \\
& + W_{\bar{1}1}[(X_4 + X_5)(1 - X_2 + X_3 - X_4 - X_5) - X_3] \\
& + W_{\bar{1}3}X_5(1 - X_4 - X_5) \\
& + W_{\bar{1}3}[(X_3 - X_5)(1 - X_5 - X_4) + X_2X_5] \\
& + W_{1\bar{3}}X_5(X_4 + X_5 - X_3) \\
& + W_{13}(X_3 - X_5)(X_2 - X_3 + X_4 + X_5) \\
& + W_{33}X_5(X_3 - X_5) \\
& + \tfrac{1}{2}W_{12}X_2[X_4 - (1 - X_2)(1 - 2X_2)] \\
& + \tfrac{1}{2}W_{21}X_2[X_4 + (1 - X_2)(1 - 2X_2)] \\
& + W_{\mathrm{Fe}}X_2(1 - X_2 + X_3 - X_4) - W_{\mathrm{Mg}}X_2X_3.
\end{aligned}
$$