High-temperature cation distributions in Fe$_3$O$_4$-MgAl$_2$O$_4$-MgFe$_2$O$_4$-FeAl$_2$O$_4$ spinels from thermopower and conductivity measurements

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ABSTRACT

The distribution of cations between octahedral and tetrahedral sites in Fe$_3$O$_4$-FeAl$_2$O$_4$, Fe$_3$O$_4$-MgFe$_2$O$_4$, and Fe$_3$O$_4$-MgAl$_2$O$_4$ solid solutions has been determined in situ at 600 °C to 1400 °C and 1-atm pressure. The method uses a combination of thermopower and electrical conductivity measurements to characterize the partitioning of Fe$^{3+}$ and Fe$^{2+}$ between the two sites. This enables determination of all cation occupancies on the Fe$_3$O$_4$-FeAl$_2$O$_4$ and Fe$_3$O$_4$-MgFe$_2$O$_4$ joins, but requires use of a model to fix one other parameter in Fe$_3$O$_4$-MgAl$_2$O$_4$ solid solutions.

The data have been used to evaluate the applicability of currently used cation-distribution models to spinels. The join Fe$_3$O$_4$-MgFe$_2$O$_4$ fits reasonably well to either the simple constant $K_{2/3}^{3+}$-$e^{+}$ and $K_{2/3}^{3+}$-$e^{+}$ model (Navrotsky and Kleppa, 1967) or to the more complex O'Neill-Nawotsky (1983, 1984) model in which $-RT \ln K_{2/3}$ is predicted to be a linear function of the occupancy of tetrahedral sites by trivalent cations. Cation-distribution data for Fe$_3$O$_4$-FeAl$_2$O$_4$ solid solutions are in quantitative agreement with the O'Neill-Nawotsky model in that $-RT \ln K_{2/3}^{3+}$-$e^{+}$ and $-RT \ln K_{2/3}^{3+}$-$e^{+}$ are linear functions of the degree of inversion. The observed variations of $-RT \ln K_{2/3}^{3+}$-$e^{+}$ do not, however, agree with those in end-member hercynite so that this join only agrees qualitatively with the model. Fe$_3$O$_4$-MgAl$_2$O$_4$ solutions are intermediate in behavior between the other two joins, their cation distributions ($-RT \ln K_{2/3}^{3+}$-$e^{+}$, $-RT \ln K_{2/3}^{3+}$-$e^{+}$, and $-RT \ln K_{2/3}^{3+}$-$e^{+}$) being linear functions of tetrahedral trivalent ions and in broad agreement with the data for pure magnetite, hercynite, and magnesioferrite, respectively.

INTRODUCTION

Spinel is an important constituent of many igneous and metamorphic rocks as well as furnace smelting products. They are also of interest to the ceramic industry mainly because of their magnetic properties. Spinel equilibria have been widely used as petrogenetic indicators (e.g., Sack, 1982; Buddington and Lindsley, 1964; Gasparik and Newton, 1984), but most of these calibrations are limited in application because phase-equilibrium experiments are generally performed only over a narrow temperature range. In spinels, disordering between octahedral and tetrahedral sites greatly influences the partial molar entropies of components and hence the temperature dependencies of activities and interphase partitioning. Therefore, it is necessary to characterize the order-disorder phenomena adequately in order to have confidence in the extrapolation of thermobarometric calibrations outside the experimental temperature ranges. Cation distributions determined on quenched samples are, however, subject to considerable uncertainty because of the tendency for re-ordering during cooling (O'Neill and Navrotsky, 1983). A high-temperature in-situ method is therefore needed to precisely characterize order-disorder phenomena in spinels.

It was shown by Wu et al. (1981) that the thermoelectric coefficient could be used to measure cation distributions in ferrospinels at elevated temperatures when only two cations (e.g., Fe$^{3+}$ and Fe$^{2+}$) are interchanged between octahedral and tetrahedral sites. This method has subsequently been successfully applied to determine cation distributions in Fe$_3$O$_4$ (Wu and Mason, 1981) and the Fe$_3$O$_4$-Fe$_7$TiO$_4$ solid-solution series where it may be assumed that all the Ti is in octahedral coordination (Trestman-Matts et al., 1983). A more complex case was studied by Trestman-Matts et al. (1984), who measured the thermoelectric coefficient in Fe$_3$O$_4$-MgFe$_2$O$_4$ spinels as a function of temperature. In this system, all three cations (Mg, Fe$^{2+}$, and Fe$^{3+}$) are disordered between the two sites, and Trestman-Matts et al. had to use a Mg-Fe$^{3+}$ site-preference energy (obtained from the degree of inversion of pure MgFe$_2$O$_4$), in addition to the measured ratio of Fe$^{3+}$/Fe$^{2+}$ on the octahedral site, to calculate the distributions of all cations in the solid solution. Mason (1985) used a similar strategy to determine cation distributions in Fe$_3$O$_4$-FeAl$_2$O$_4$ spinels at 1700 K.
Mason (1987) showed that the use of conductivity measurements in conjunction with thermopower measurements would, at high temperature, enable complete characterization of cation distributions in ferrospinel solid solutions in which three cations disorder between octahedral and tetrahedral sites. This method obviates the need for a distribution model for one of the cations. In this study we have measured both thermopower and conductivity in Fe$_2$O$_3$-FeAl$_2$O$_4$, Fe$_2$O$_3$-MgFe$_2$O$_4$, and Fe$_3$O$_4$-MgAl$_2$O$_4$ solid solutions over the temperature range 600 to 1400 °C. The technique of Mason (1987) enables the complete calculation of cation distributions in the Fe$_2$O$_3$-MgFe$_2$O$_4$ and Fe$_2$O$_3$-FeAl$_2$O$_4$ systems as a function of temperature. In the Fe$_2$O$_3$-MgAl$_2$O$_4$ solid solution, however, four cations (Fe$^{2+}$, Fe$^{3+}$, Mg, and Al) disorder over the two sites, and a Mg-Al site-preference energy (Wood et al., 1986) must be used in addition to the measured Fe$^{2+}$-Fe$^{3+}$ distribution in order to solve for all intersite cation distributions. The latter join is of considerable petrologic importance because of its calibration as an oxygen barometer for ultramafic rocks (Mattioli and Wood, 1988).

**THERMOPOWER-CONDUCTIVITY THEORY**

Extensive reviews of cation-distribution theory in ferrspins and the application of thermopower and conductivity measurements to the determination of intersite cation distributions are given by Wu et al. (1981) and Mason (1987). The structural formula for mixtures of Fe$_x$O$_y$, FeAl$_2$O$_4$, MgFe$_2$O$_4$, and MgAl$_2$O$_4$ may be written as

$$\text{Fe}^{2+}_x \text{Fe}^{3+}_y \text{Mg}_{m} \text{Al}_{n} (\text{Fe}^{2+}_p \text{Fe}^{3+}_q \text{Mg}_{r} \text{Al}_{s}) \text{O}_{o}, \quad (1)$$

where the species in parentheses reside on the octahedral sites and the remainder in tetrahedral positions.

Provided small polaron conduction is operative, thermopower measurements can be used to calculate the octahedral valence ratio, $q = \langle \text{Fe}^{3+}/\text{Fe}^{2+} \rangle_{\text{tot}} = e/d$ from the thermoelectric coefficient (Q, in VK$^{-1}$) according to (Wu and Mason, 1981)

$$Q = -\frac{k}{e_0} \left[ \ln \left( \frac{1}{k} \right) - A \right], \quad (2)$$

where $k$ is Boltzmann's constant, $e_0$ is the electronic charge, $b$ is a spin-degeneracy term found to be equal to 2 (Mason and Bowen, 1981), and $A$ is an entropy-of-vibration term that is negligibly small in the case of small polaron conduction (Wu and Mason, 1981). The ratio $(1 - c)/c$ corresponds to the ratio of Fe cations on the conducting sites, where the variable $c$ represents the fraction of conducting sites of lower valence (Fe$^{2+}$) and $(1 - c)$ the fraction of Fe$^{3+}$. In magnetite solid solutions, this ratio is equivalent to the octahedral valence ratio since it has been shown in many studies that small polaron conduction is restricted to the octahedral sites in ferrispinels (e.g., Kuendig and Hargrove, 1969; Mason, 1987). Equation 2 may be rearranged to obtain the octahedral valence ratio

$$q = \frac{e}{d} = \frac{1}{2} \exp (-Q e_0/k). \quad (3)$$

In order to solve explicitly for the intersite distribution of Fe species in Fe$_2$O$_3$-MgFe$_2$O$_4$, Fe$_2$O$_3$-FeAl$_2$O$_4$, and Fe$_3$O$_4$-MgAl$_2$O$_4$ solid solutions, it is also necessary to be able to measure the total concentrations of Fe$^{2+}$ and Fe$^{3+}$ on either the tetrahedral or octahedral sites. This may be achieved by measuring the electrical conductivity since the latter depends on the sum of Fe species participating in conduction.

The electrical conductivity [in (Ω·cm)$^{-1}$] in the case of a small polaron conductor is given by (Tuller and Nowick, 1977; Dieckmann et al., 1983)

$$\sigma = \frac{g N c'(1 - c')e^2 v_0}{kT} \exp \left(-\frac{E_H}{kT}\right), \quad (4)$$

where $g$ is a geometrical factor involving coordination number (constant for a given system), $N$ is the density of conducting sites in cm$^{-3}$, $c'$ is the fraction of conducting sites occupied by charge carriers, $(1 - c')$ is the fraction of available jump sites (Fe$^{2+}$ and Fe$^{3+}$, respectively, in the case of an n-type small polaron conductor), $a$ is the jump distance (cm), $v_0$ is the lattice vibrational frequency responsible for conduction, $E_h$ is the hopping energy, and $T$ is temperature. For an octahedral small polaron process, $c' = d/(d + e) = 1/(1 + q)$ and $(1 - c') = e/(e + d) = q/(1 + q)$, where $q$ is the previously defined octahedral valence ratio. In principle, of course, Equation 4 may only be applied to solve for one parameter ($N$, for example), and the remainder should be known. In order to apply the equation therefore, a simplification is necessary. Mason (1987) suggested that $a$ and $v_0$ should be essentially composition-independent in a given solid solution, in which case we obtain for $N$, the density of conducting sites (in cm$^{-3}$),

$$N = \frac{(\text{constant}/T a)}{c'(1 - c') \exp (-E_H/kT)} \cdot \quad (5)$$

Taking the ratio of $N$ between a solid-solution composition $(x_s)$ and magnetite $(x_m)$ at a fixed temperature then gives

$$\frac{N_{(x_s)}}{N_{(x_m)}} = \frac{\sigma_{(x_s)}[c'(1 - c')]_{(x_s)} \exp \left(-E_{H_{(x_s)}}/kT\right)}{\sigma_{(x_m)}[c'(1 - c')]_{(x_m)} \exp \left(-E_{H_{(x_m)}}/kT\right)}. \quad (6)$$

In order to calculate the exponential term in Equation 6, in $\sigma T$ is plotted versus $1/T$, thereby providing the apparent hopping energy ($E_h$). Mason (1987) showed that the difference in actual hopping energy between a solid-solution composition and pure magnetite is generally given by the difference in apparent hopping energies

$$E_{H_{(x_s)}} - E_{H_{(x_m)}} = E_{H_{(x_m)}} - E_{H_{(x_s)}}. \quad (7)$$

Therefore, with the measurement of $\sigma$ and $q$, the value of $N$ for the solid solution may be calculated provided $N$ is known for pure magnetite. In the latter case, $N$ is equal to the number of octahedral sites per formula unit, 2.
EXPERIMENTAL METHODS

Polycrystalline specimens with the compositions $x = 0.25, 0.5, 0.75$, and $1.0$ in $\text{Fe}^{2+}\text{Fe}^{3+}_x\text{Al}_{2-x}\text{O}_4$, $\text{Fe}^{2+}\text{Mg}_{1-x}\text{Fe}^{3+}_x\text{O}_4$, and $\text{Fe}^{2+}\text{Mg}_x\text{Fe}^{3+}_{2-x}\text{Al}_{2-x}\text{O}_4$ were sintered from powders by repeated cycles of firing and grinding of oxide mixtures in a controlled gas atmosphere. Starting materials were reagent-grade $\text{Fe}_2\text{O}_3$, $\text{Al}^3\text{OH}_3$, and $\text{MgCO}_3$. The $\text{Al}^3\text{OH}_3$ and $\text{MgCO}_3$ were dehydrated and decarbonated, respectively, at $1200 \, ^\circ\text{C}$ for $12$ h. $\text{Fe}_2\text{O}_3$ was dried at $120 \, ^\circ\text{C}$. The resulting oxides were then stored in a desiccator.

Stoichiometric oxide mixtures were pressed into pellets and reacted in a vertical-tube furnace at a temperature of $1300 \, ^\circ\text{C}$. For all samples, the atmosphere in the furnace had a $\text{CO}_2/\text{CO}$ ratio of $333$ ($\log f_{\text{CO}} = -4.7$ at $1300 \, ^\circ\text{C}$), corresponding to conditions of zero deviation from stoichiometry ($\delta = 0$) for the magnetite component in the solid solutions (Dieckmann, 1982). In order to obtain single-phase spinels for every composition, sample pellets were reacted for $8$ h at $1300 \, ^\circ\text{C}$ after which they were ground, pressed into pellets, and again fired at the same temperature. Four such cycles proved sufficient to yield single-phase spinel solid solutions.

Once the desired compositions were prepared, the samples were crushed in a vibratory mill using alumina grinding medium and pressed into pellets at a pressure of $2.75 \times 10^8 \, \text{Pa}$ in a cold isostatic press. The pellets were finally sintered at a temperature of $1300 \, ^\circ\text{C}$ for a period of $20$ h in order to achieve high-density samples. Cell edges and densities (expressed as percentages of the theoretical densities for each composition) were determined after final sintering at $1300 \, ^\circ\text{C}$ (Table 1).

Thermopower and conductivity measurements were made using a four-point measurement technique in which four holes were drilled through rectangular bar specimens measuring approximately $1.5 \times 1.5 \times 15 \, \text{mm}$ with an ultrasonic drill. Each hole was threaded with a $\text{Pt}_6\text{Rh}_{37}$-$\text{Pt}_{30}\text{Rh}_{70}$ thermocouple. The threaded sample bar was then mounted on an eight-bore alumina thermocouple tube. The thermocouple leads were used to pull the fused thermocouple beads snugly against the sample in order to assure electrical contact between the thermocouple beads and the sample (Fig. 1). The sample was positioned off the hot-zone in a vertical, molybdenum disilicide-heated, alumina muffie furnace in such a position as to achieve an approximately $15 \, ^\circ\text{C}$ temperature gradient along the sample.

The thermopower-conductivity measurements were made at $100 \, ^\circ\text{C}$ intervals from $1400 \, ^\circ\text{C}$ down to $600 \, ^\circ\text{C}$ and then back to $1400 \, ^\circ\text{C}$, following a grain-growth stabilization pre-anneal of $8$ h at $1400 \, ^\circ\text{C}$. Readings were recorded after thermal voltages were stable to $\pm 1\%$ over at least $30$ min. At $600 \, ^\circ\text{C}$ and $700 \, ^\circ\text{C}$, specimens were held for at least $12$ h without significant changes in the readings. At all times, a gas mix with $\text{CO}_2/\text{CO}$ ratio of $333$ was passed over the sample at a flow rate of about $1 \, \text{linear cm/s}$.

**Fig. 1.** Schematic illustration of experimental arrangement and typical $\Delta V$ vs. $\Delta T$ plot. $Q_{\text{T}}$ stands for the thermopower of the reference element of the thermocouple.

The four thermocouples and their common $\text{Pt}_6\text{Rh}_{37}$ leads provided six $\Delta T$ values and six corresponding $\Delta E$ values. The slope of $\Delta E$ (emf) vs. $\Delta T$ when corrected for the thermopower of $\text{Pt}_6\text{Rh}_{37}$ is then the thermopower ($\text{in } \mu\text{V} \cdot \text{K}^{-1}$) (Fig. 1), i.e.,

$$Q = -\lim_{\Delta T \to 0} (\Delta V/\Delta T).$$

The temperature of the measurement was taken to be the average of the four thermocouples. The experimental uncertainty in each thermopower measurement may be evaluated from the correlation coefficient obtained from a linear regression through the six $\Delta T/\Delta E$ pairs as well as from the $\Delta T$ intercept at $\Delta E = 0$ ($\Delta T$ offset). In general, correlation coefficients were better than $0.995$, whereas values of $\Delta T$ offset were smaller than $\pm 0.3 \, ^\circ\text{C}$.

Limits of the experimental uncertainty in the method used for measuring the thermopower may be evaluated from the maximum error in maximum $\Delta T$, which is estimated at $\pm 1 \, ^\circ\text{C}$ (Wu and Mason, 1981). Assuming a maximum temperature gradient of approximately $15 \, ^\circ\text{C}$, this yields an uncertainty of about $\pm 7\%$.

Following the thermopower measurements, small (milliampere) currents were passed in both directions between the outer thermocouples, and the voltage drop across the inner thermocouples was used to calculate the sample conductivity. This procedure allowed for the thermal voltage drop to be subtracted out of the measured emfs. Con-
ductivity was then corrected for the percentage theoretical density. Experimental uncertainties in the conductivity measurements are difficult to evaluate because of the profound effect that microstructural features may have on the electrical conductivity of polycrystalline samples. The accuracy of the measurements was estimated by comparing the results obtained for magnetite with the results obtained by Dieckmann et al. (1983) on single-crystal magnetite. Measurements were found to be appreciably lower than the Dieckmann et al. results over the experimentally examined thermal range. The difference may be due to grain-boundary effects in the polycrystalline system and to the preparation methods used for the single-crystal specimens.

Following the electrical measurements, the specimen slabs as well as unused slabs of the same composition were mounted and polished for analysis by electron microprobe. In all cases, the used as well as unused material proved to be chemically homogeneous, single-phase spinel. Measured compositions with Feconcentrations calculated from stoichiometry are reported in Table 1. No evidence for Al depletion was found—only the expected and observed—Al contents to be almost identical. The slight decrease in the absolute value of thermopower, as well as the decrease in slope $dQ/d(T)$, indicates that the Al-Fe substitution dominates the Mg-Fe substitution in determining the behavior of the thermoelectric coefficient in this system.

The thermopower data have been fit to a polynomial of the form

$$Q = a + b(T + T) + c(T + T)^3,$$

where $Q$ is in $\mu V/K$. The use of a second-degree term $c$ is only required for three samples for which the statistical $F$-ratio yielded values that were above the 90% confidence level for a quadratic relative to a linear relationship (Be-
TABLE 1.—Continued

<table>
<thead>
<tr>
<th>x</th>
<th>Fe$^{2+}$Mg$_{1-x}$Fe$<em>x$Al$</em>{1-x}$O$_4$</th>
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<td>24.35</td>
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<td>15</td>
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<tr>
<td>0.26</td>
<td>0.52</td>
</tr>
<tr>
<td>0.26</td>
<td>0.48</td>
</tr>
<tr>
<td>8.268(7)</td>
<td>8.2834(7)</td>
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<tr>
<td>91.7</td>
<td>88.6</td>
</tr>
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</table>

The resulting regression lines, therefore, have slopes of $-E/\kappa$ and intercepts of $\ln A_0$.

Values of $E_H$ for the solid-solution compositions are plotted in Figure 4. The activation energy for hopping shows a profound compositional dependence in the Fe$_{2-x}$Fe$_{1-x}$Al$_x$O$_4$ and Fe$_{2-x}$Mg$_{1-x}$Al$_x$O$_4$ systems, increasing from a value of 0.15 eV (magnetite) to about 0.40 eV for the $x = 0.25$ compositions (Fig. 4). The hopping energy in Fe$_{2-x}$Mg$_{1-x}$Fe$_x$O$_4$ solid solutions, on the other hand, changes only slightly, reaching a maximum value of about 0.20 eV for the $x = 0.25$ composition. The calculation of the error bars on the data points will be discussed below.

**CATION DISTRIBUTIONS**

Fe$_2$O$_4$-MgFe$_2$O$_4$ and Fe$_{2-x}$Fe$_{1-x}$Al$_x$O$_4$ solid solutions

For mixtures containing $x$ mole fractions of Fe$_2$O$_4$ and $(1 - x)$ mole fractions of MgFe$_2$O$_4$ and Fe$_{2-x}$Al$_x$O$_4$, respectively, the thermoelectric-conductivity analysis enables calculation of the concentrations of Fe species on octahedral and tetrahedral sites through sets of equations based on compositional as well as mass- and charge-balance restrictions (Table 3).

At fixed mole fractions $(x)$ of Fe$_2$O$_4$, it is necessary to measure two independent variables in Fe$_2$O$_4$-MgFe$_2$O$_4$ and Fe$_{2-x}$Fe$_{1-x}$Al$_x$O$_4$ solid solutions in order to determine the unknowns in the structural formulae (Table 3). In this study, two such variables are given by the thermoelectric and conductivity measurements.

Remembering that $q = e/d = (Fe^{3+}/Fe^{2+})_{eq}$ and $N = (e + d) = (Fe^{3+} + Fe^{2+})_{eq}$, it may be shown that

$$d = N/(1 + q)$$  \hspace{1cm} (12)

and

$$e = qN/(1 + q).$$  \hspace{1cm} (13)

**Table 2.** Polynomial fit parameters for the thermopower and conductivity data sets

<table>
<thead>
<tr>
<th>Parameter</th>
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<tr>
<td>$B$</td>
<td>-0.517</td>
<td>-0.455</td>
<td>-0.286</td>
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These two measurements fully characterize the Fe$^{2+}$-Fe$^{3+}$ distribution since they directly lead to the calculation of $a$ and $b$ through the relationships given in Table 3.

Uncertainties in the calculated cation distributions were estimated by considering the maximum uncertainties in the thermopower and conductivity measurements as outlined above. Maximum values for $N$ were calculated by combining maximum and minimum values for $[c'(1 - c')]/(c'(1 - c'))_{max}$ and $[c'(1 - c')]/(c'(1 - c'))_{min}$, respectively, with the maximum conductivities for both magnetite and the solid-solution compositions in Equation 6. Minimum $N$ values were calculated from the reverse procedure.

Following the O'Neill-Navrotsky (1983, 1984) model, $\Delta H_D$ values for Fe$_3$O$_4$-MgFe$_2$O$_4$ (mt-mf) and Fe$_3$O$_4$-FeAl$_2$O$_4$ (mt-hc) solid solutions are given by Equations 14 and 15, respectively:

$$\Delta H_D^{\text{mt-mf}} = \text{Mg}_{\text{oct}}[a_{\text{MgFe}^{2+}} + \beta_{\text{MgFe}^{2+}}(\text{Fe}_{\text{oct}}^{3+} + \text{Fe}_{\text{oct}}^{2+})]$$

and

$$\Delta H_D^{\text{mt-hc}} = \text{Fe}_{\text{oct}}^{3+}[a_{\text{Fe}^{2+}} + \beta_{\text{Fe}^{2+}}(\text{Fe}_{\text{oct}}^{3+} + \text{Al}_{\text{oct}})]$$

where $a$ and $\beta$ are energy parameters introduced by O'Neill and Navrotsky (1983). Theoretical cation distributions may be calculated as follows, given the $a$ and $\beta$ values of Table 4. For the Fe$_3$O$_4$-MgFe$_2$O$_4$ join we have

$$-RT \ln \frac{\text{Fe}_{\text{oct}}^{3+} \text{Fe}_{\text{oct}}^{2+}}{\text{Fe}_{\text{oct}}^{3+} \text{Fe}_{\text{oct}}^{2+}} = a_{\text{Fe}^{2+}} + 2\beta_{\text{Fe}^{2+}} \text{Fe}_{\text{oct}}^{2+}$$

and

$$-RT \ln \frac{\text{Mg}_{\text{oct}}\text{Fe}_{\text{oct}}^{3+}}{\text{Mg}_{\text{oct}}\text{Fe}_{\text{oct}}^{2+}} = a_{\text{MgFe}^{3+}} + 2\beta_{\text{MgFe}^{3+}} \text{Mg}_{\text{oct}}$$

and

$$-RT \ln \frac{\text{Mg}_{\text{oct}}\text{Fe}_{\text{oct}}^{3+}}{\text{Mg}_{\text{oct}}\text{Fe}_{\text{oct}}^{2+}} = a_{\text{Fe}^{2+}} + 2\beta_{\text{Fe}^{2+}} \text{Mg}_{\text{oct}}$$

and

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TABLE 3. Mass- and charge-balance constraints and compositional relations in the Fe$_3$O$_4$-FeAl$_2$O$_4$, Fe$_3$O$_4$-MgFe$_2$O$_4$, and Fe$_3$O$_4$-MgAl$_2$O$_4$ solid solutions

<table>
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<tr>
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<th>Structural formula:</th>
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<th>[d + e + p = 2]</th>
<th>[2(a + d) + 3(b + e + n + p) = 8]</th>
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<td>((Fe_3O_4)_{1-x}(MgFe_2O_4)_x)</td>
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<tr>
<td>((Fe_3O_4)_{1-x}(MgAl_2O_4)_x)</td>
<td>(Fe^2+Fe^3+MgAl(Fe^3+Fe^3+MgAl)_2O_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Conductivity data for the respective solid solutions. Solid and open symbols are “down” and “up” temperature measurements, respectively. Results for (A) the Fe$_3$O$_4$-MgFe$_2$O$_4$ system, (B) the Fe$_3$O$_4$-FeAl$_2$O$_4$ system, and (C) the Fe$_3$O$_4$-MgAl$_2$O$_4$ system are plotted as a function of temperature.

Fig. 4. Activation energies of hopping for the Fe$_3$O$_4$-MgFe$_2$O$_4$, Fe$_3$O$_4$-FeAl$_2$O$_4$, and Fe$_3$O$_4$-MgAl$_2$O$_4$ solid solutions as a function of sample composition.
For FeO$_3$-FeAl$_2$O$_4$ solid solutions, the conditions of equilibrium are

$$-RT \ln \frac{Fe^{2+}_{tet}}{Fe^{3+}_{oct}} = \alpha_{Fe^{2+}_{tet}} + 2\beta_{Fe^{2+}_{tet}} Al_{tet}$$

and

$$-RT \ln \frac{Fe^{3+}_{tet}}{Fe^{2+}_{oct}} = \alpha_{Fe^{3+}_{tet}} + 2\beta_{Fe^{3+}_{tet}} Fe^{3+}_{oct}$$

The nonlinear simultaneous equations were solved using the Newton-Raphson method (e.g., Gerald and Wheatley, 1984, p. 133–159) and the results for the FeO$_3$-MgFe$_2$O$_4$ and FeO$_3$-FeAl$_2$O$_4$ solid solutions, calculated at 1000 °C are presented as the solid curves in Figures 5 and 6, respectively. The solid lines are curves based on Equations 16 to 19 with the best-fit values of $\alpha$ and $\beta$ given in Table 4. It may be seen from Figure 5 that the model works well for FeO$_3$-MgFe$_2$O$_4$ spinels, but is less satisfactory for FeO$_3$-FeAl$_2$O$_4$ solid solutions (Fig. 6). This may be ascribed to the different degrees of disorder of the end-members magnetite, hercynite, and magnesioferrite and of the solid solutions between them.

The O'Neill-Navrotsky model requires that each of the cation-distribution equilibria (Eqs. 16 to 19) be a linear function of the degree of inversion ($Al_{tet} + Fe^{3+}_{tet}$) and that $\alpha$ and $\beta$ for each equilibrium be constant. It works well for FeO$_3$-MgFe$_2$O$_4$ because both end-members in the solid solution have similar degrees of disorder at any particular temperature. Thus the partition coefficients

$$K_{Fe^{2+}_{tet}}^{Fe^{3+}_{tet}} = \frac{(Mg_{tet} Fe^{3+}_{tet})}{(Fe_{tet} Fe^{2+}_{tet})}$$

and

$$K_{Fe^{2+}_{tet}}^{Fe^{3+}_{tet}} = \frac{(Fe_{tet} Fe^{2+}_{tet})}{(Fe_{tet} Fe^{3+}_{tet})}$$

are virtually independent of composition and the degree of inversion. The $\beta$ term, therefore, does not change across the solid-solution series. In fact, dependence on the degree of inversion is so small that both $-RT \ln K_{Fe^{2+}_{tet}}^{Fe^{3+}_{tet}}$ and

### Table 4. Internally consistent parameter set used for the calculation of intersite cation distributions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{Fe^{2+}_{tet}}$</td>
<td>33.75</td>
</tr>
<tr>
<td>$\beta_{Fe^{2+}_{tet}}$</td>
<td>-26.36</td>
</tr>
<tr>
<td>$\alpha_{Fe^{3+}_{tet}}$</td>
<td>50.98</td>
</tr>
<tr>
<td>$\beta_{Fe^{3+}_{tet}}$</td>
<td>-32.85</td>
</tr>
<tr>
<td>$\alpha_{Mg^{2+}_{tet}}$</td>
<td>20.96</td>
</tr>
<tr>
<td>$\beta_{Mg^{2+}_{tet}}$</td>
<td>-19.13</td>
</tr>
<tr>
<td>$\alpha_{Mg^{3+}_{tet}}$</td>
<td>38.19</td>
</tr>
<tr>
<td>$\beta_{Mg^{3+}_{tet}}$</td>
<td>-25.62</td>
</tr>
<tr>
<td>$\alpha_{Fe^{2+}_{oct}}$</td>
<td>-12.79</td>
</tr>
<tr>
<td>$\beta_{Fe^{2+}_{oct}}$</td>
<td>7.23</td>
</tr>
</tbody>
</table>
$-RT \ln K_{3p-Fe^{3+}}$ could be modeled as constant as originally proposed by Navrotsky and Kleppa (1967). In the Fe$_2$O$_3$-FeAl$_2$O$_4$ system, on the other hand, Fe$_2$O$_3$ is always substantially more inverse than FeAl$_2$O$_4$, and for this solid solution, both $\alpha$ and $\beta$ terms are very important. Our observed partitioning behavior suggests that $-RT \ln K_{3p-Fe^{3+}}$ is, as predicted, a function of the degree of inversion in the system (Fig. 7) and that the $\alpha$ and $\beta$ parameters for this exchange equilibrium agree well with those for pure magnetite. Similarly, the partitioning behavior of $-RT \ln K_{3p-Al}$ is also a linear function of the degree of inversion over the examined compositional range (Fig. 8), but the $\alpha$ and $\beta$ parameters in this case do not agree with those for pure hercynite. Moreover, $\alpha_{Fe^{2+}-Al}$ and $\beta_{Fe^{2+}-Al}$ need to be composition dependent to describe the partitioning behavior.

**Fe$_2$O$_3$-MgAl$_2$O$_4$ solid solutions**

In this system, measurements of three of the four cation-distribution equilibria (Eqs. 16 to 19) are required to fully characterize the distributions of cations between octahedral and tetrahedral sites. Given measurements of the Fe$^{3+}$-Fe$^{2+}$ distribution, it is necessary to fix the distribution of one other cation in order to derive all site occupancies. If we assume that the O'Neill-Navrotsky model works for the Fe$_2$O$_3$-MgAl$_2$O$_4$ join, then the concentration of tetrahedral Al is given by (extended form of Eq. 19)

$$\alpha_{Fe^{2+}-Fe^{3+}} + Al_{tet}(\beta_{Fe^{2+}-Fe^{3+}} + \beta_{Fe^{2+}-Al}) + 2Fe_{tet}^+\beta_{Fe^{2+}-Fe^{3+}}$$

$$+ (\beta_{Fe^{2+}-Fe^{3+}} + \beta_{Fe^{2+}-Mg})Mg_{oct} = -RT \ln \frac{Fe_{tet}^+Fe_{oct}^{3+}}{Fe_{tet}^{2+}Fe_{oct}^{3+}}.$$

Using the measured Fe$^{3+}$-Fe$^{2+}$ distributions, Equation 20 is readily solved for Al$_{tet}$. Then, with the site and mass-balance constraints of Table 3, all cation occupancies are fixed. The results are shown in Figure 9 together with calculated curves obtained from the O'Neill-Navrotsky treatment. The latter were derived by solving Equation 20 together with the analogous expansions of Equation 18 and a Mg-Fe$^{2+}$ exchange equilibrium obtained from Equations 16 and 17,

$$\alpha_{Fe^{2+}-Al} + Fe_{tet}^{3+}(\beta_{Fe^{2+}-Fe^{3+}} + \beta_{Fe^{2+}-Al}) + 2Al_{tet}\beta_{Fe^{2+}-Al}$$

$$+ (\beta_{Fe^{2+}-Al} + \beta_{Fe^{2+}-Mg})Mg_{oct} = -RT \ln \frac{Al_{oct}Fe_{tet}^{2+}}{Al_{tet}Fe_{oct}^{3+}}.$$

$$\alpha_{Fe^{2+}-Mg} + Fe_{tet}^{3+}(\beta_{Fe^{2+}-Fe^{3+}} + \beta_{Fe^{2+}-Mg})$$

$$+ Al_{tet}(\beta_{Fe^{2+}-Al} + \beta_{Fe^{2+}-Mg})$$

$$+ 2Mg_{oct}\beta_{Fe^{2+}-Mg} = -RT \frac{Mg_{oct}Fe_{tet}^{3+}}{Mg_{tet}Fe_{oct}^{3+}}.$$

**Fig. 6.** Calculated intersite cation distributions compared to the measured values at 1000 °C in Fe$_2$O$_3$-FeAl$_2$O$_4$ solid solutions.
Fig. 7. Intersite distributions of Fe$^{2+}$ and Fe$^{3+}$ as a function of tetrahedral trivalent ions at 1000 °C for the FeO$_2$-MgFeO$_2$, FeO$_2$-FeAl$_2$O$_4$, and FeO$_2$-MgAl$_2$O$_4$ solid solutions. Solid line calculated from the $\alpha$ and $\beta$ values for pure magnetite agrees well with the observed partitioning data. The $x = 0.50$ data point for the FeO$_2$-MgAl$_2$O$_4$ system is not shown for clarity. It plots between the magnetite and 25% magnetite-75% spinel data points.

As can be seen from Figure 9, the observed distributions, which have the assumption that the Fe$^{2+}$-Fe$^{3+}$ distribution obeys the O’Neill-Navrotsky model, are in good agreement with the model values in which all four cations are forced to obey the model. Although the argument has an element of circularity to it, it is clear that the Fe$^{2+}$-Fe$^{3+}$ cation-partitioning data are broadly consistent with the simple model.

**DISCUSSION**

In the simplest type of model (Navrotsky and Kleppa, 1967), the logarithm of any particular intersite distribution coefficient ($-RT \ln K_{cd}$) is a constant independent of the degree of inversion. The O’Neill-Navrotsky model (Eqs. 16–19), on the other hand, predicts a linear dependence of $-RT \ln K_{cd}$ on the tetrahedral occupancy of trivalent ions. Figure 7 shows the 1000 °C data that we have collected for the joins FeO$_2$-MgFeO$_2$, FeO$_2$-FeAl$_2$O$_4$, and FeO$_2$-MgAl$_2$O$_4$ and for pure magnetite plotted so as to illustrate the dependence of $-RT \ln K_{cd}$ on the degree of inversion. It may be seen that
the data for FeO-MgFeO, FeO-FeAlO, and FeO-MgAlO fit quite well to the O'Neill-Navrotsky model using the \( \alpha \) and \( \beta \) values derived from pure magnetite. The fit obtained for FeO-MgFeO does not provide a stringent test of the model, however, since the data also fit reasonably well to the constant \(-RT \ln K_{cd}\) (Navrotsky-Kleppa) model. In FeO-FeAlO (Fig. 8), \(-RT \ln K_{cd}^{Fe^{2+}-Al}\) is approximately linearly dependent on total trivalent ion occupancy, exhibiting qualitative agreement with the O'Neill-Navrotsky model. The FeAl distribution data for this join are not, however, reproduced by the \( \alpha^{Fe^{2+}-Al} \) and \( \beta^{Fe^{2+}-Al} \) values for pure hercynite. Therefore the O'Neill-Navrotsky model does not fit unless provision is made for compositional dependence of the \( \alpha^{Fe^{2+}-Al} \) and \( \beta^{Fe^{2+}-Al} \) parameters. A detailed discussion of the implications of these observations for predicting the macroscopic thermodynamic properties of spinels will be presented in a future paper.

Fig. 8. Intersite distributions of Fe\(^{2+}\) and Al as a function of total tetrahedral trivalent ion occupancy in FeO-FeAlO solid solutions. Best-fit \( \alpha \) and \( \beta \) parameters to the solid-solution data are significantly different from those calculated for pure hercynite.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (kJ/mol)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha^{Fe^{2+}-Fe^{3+}} )</td>
<td>-33.75 ± 1.92</td>
<td>This study</td>
</tr>
<tr>
<td>( \beta^{Fe^{2+}-Fe^{3+}} )</td>
<td>-26.36 ± 1.34</td>
<td>(see below)*</td>
</tr>
<tr>
<td>( \alpha^{Fe^{2+}-Al} )</td>
<td>-30.72 ± 2.01</td>
<td>(see below)*</td>
</tr>
<tr>
<td>( \beta^{Fe^{2+}-Al} )</td>
<td>-17.00 ± 1.84</td>
<td>(see below)*</td>
</tr>
<tr>
<td>( \alpha^{Fe^{3+}-Al} )</td>
<td>17.88 ± 3.07</td>
<td>Wood et al. (1986)</td>
</tr>
<tr>
<td>( \beta^{Fe^{3+}-Al} )</td>
<td>38.19 ± 0.31</td>
<td>Wood et al. (1986)</td>
</tr>
<tr>
<td>( \beta^{Mg-Al} )</td>
<td>-25.62 ± 0.54</td>
<td>Wood et al. (1986)</td>
</tr>
</tbody>
</table>

* Bohlen et al. (1986); Hill (1984); Chassagneux and Rousset (1976); Yagnik and Mathur (1968).
† Pauthenet and Bochirol (1951); Kriessman and Harrison (1956); Epstein and Frackiewicz (1958); Mozi and Paladino (1963); Blasse (1964); Tellier (1967).
As noted earlier, irreversible thermopower results were obtained in some experiments at high mole fractions of MgAl₂O₄. A possible explanation for this behavior is that it is due to disequilibrium order-disorder phenomena. In their NMR study of order-disorder relations in MgAl₂O₄, Wood et al. (1986) found that the macroscopically determined entropy of Mg-Al disorder is much lower than would be predicted from the octahedral-tetrahedral cation distribution. They then concluded that there was substantial short-range order in the spinel structure that acts to lower the configurational entropy. Similar short-range ordering has also been proposed for MgFe₂O₄ spinel by Kroger (1964 and references therein). In this study it was found that the differences between reversible and irreversible thermopower measurements increased with increasing MgAl₂O₄ content of the spinel. It is therefore possible that the irreversible thermopower measurements are due to the same type of short-range ordering phenomenon that has already been discussed with respect to MgAl₂O₄ (Wood et al., 1986).

Samples sintered at 1300 °C and then quenched should be relatively disordered. We suggest that if such samples are returned to the furnace at 1400 °C they remain relatively disordered with higher Fe³⁺/Fe²⁺ ratios on the octahedral site than the reversible material. As they are cooled, the free-energy difference between disordered and ordered states progressively increases until at about 900 °C the samples undergo rapid short-range ordering. Thereafter, repeated heating and cooling cycles produced reversible thermopower results corresponding to the equilibrium extent of short-range order. The only unusual feature of our observations is that disequilibrium is apparently maintained for long periods (up to approximately 48 h) at very high temperatures. This must be due either to an extremely small free-energy difference between ordered and disordered states at high temperatures or to a kinetic barrier to ordering. During the cooling cycle from 1400 °C down to 900 °C, the sample undergoes appreciable long-range ordering of Mg and Al as well as Fe²⁺ and Fe³⁺, and it is possible that the highly (long-range) disordered Mg-Al distribution at high temperature initially inhibits clustering of Fe³⁺ and Fe²⁺. If this is the case, the Fe²⁺ and Fe³⁺ will reorder rapidly once a critical value of the inversion parameter for MgAl₂O₄ is reached.

It is unclear at this stage how the cation-distribution analysis might be affected by short-range ordering. The lack of a quantitative model precludes the explicit treatment of short-range order in the calculation of cation distributions.

**CONCLUSIONS**

The thermopower-conductivity technique has been successfully employed to examine intersite cation distributions in FeO₄-MgFeO₄, FeO₄-FeAl₂O₄, and FeO₄-
MgAl₂O₄ solid solutions. The measurements indicate that Fe²⁺-Fe³⁺ distributions become increasingly inverse in Fe₂O₃-MgFe₂O₄ solid solutions with magnetite dilution, whereas they become more normal in the Fe₂O₃-FeAl₂O₄ system as magnetite content decreases. In Fe₂O₃-MgAl₂O₄ solid solutions, the Fe⁺⁺-Fe³⁺ distribution is similar to that of magnetite. In addition there are strong enrichments of both Fe²⁺ and Fe³⁺ on the tetrahedral site in the dilute magnetite part of the solid-solution series. In situ measurements of cation distributions provide a necessary bridge between macroscopic thermodynamic measurements of free energy, entropy, etc. and the hypothetical ordering schemes generally used for spinel end-members. The latter may only be used to extrapolate thermodynamic properties if they can be confirmed by direct measurement at high temperature. In this study, we have found that the O'Neill-Navrotsky (1983, 1984) model of cation distribution provides a good approximation of the properties of Fe₂O₃-MgFe²⁺O₄ spinels, but it is less successful in predicting cation distributions in Fe₂O₃-FeAl₂O₄ solid solutions. In Fe₂O₃-MgAl₂O₄ spinels, the Fe⁺⁺-Fe³⁺ partitioning data are broadly consistent with calculated values assuming that all four cations in the solid solution behave according to the O'Neill-Navrotsky model. From this study, it is evident that a more accurate representation of cation distributions in complex spinel solid solutions may be achieved by also considering the compositional dependencies of the various distribution coefficients. Such a model, using a second-degree Taylor expansion of the vibrational part of the Gibbs free energy of a solid solution in terms of both compositional and order parameters will be presented in a forthcoming paper.

ACKNOWLEDGMENTS

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