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Experimental determination of Fe and Mg exchange between garnet and olivine and estimation of Fe-Mg mixing properties in garnet

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ABSTRACT

The partitioning of Fe and Mg between garnet and olivine has been determined as a function of Fe/Mg ratio at 1000 °C and 9.1 kbar. Garnets of composition $X^{gt}_{Fe} = 0.90$, 0.82, 0.60, 0.51, and 0.35 were mixed with olivines of various compositions in a ratio of 10:1 by mass, and the equilibrium olivine composition was determined within narrow limits.

The magnitudes of the garnet interaction parameters are highly correlated with those of the olivine solution. However, assuming $W^{ol}_{FeMg} = W^{ol}_{MgFe} = 9000$ J/mol (two-site basis), we obtain $W^{gt}_{FeMg} = 2080 \pm 1250$ J/mol and $W^{gt}_{MgFe} = 6350 \pm 880$ J/mol (three-site basis) at 1000 °C. The standard-state free-energy change of the exchange reaction

$$\underset{gt}{⅓Mg_3Al_2Si_3O_{12}} + \underset{ol}{½Fe_2SiO_4} = \underset{gt}{⅓Fe_3Al_2Si_3O_{12}} + \underset{ol}{½Mg_2SiO_4}$$

is calculated to be -2000 ± 800 J at 1000 °C and 1 bar, in agreement with recent estimates of the free energy of almandine.

INTRODUCTION

Equilibria involving garnet components have been used widely for geothermometry and geobarometry. In the case of thermometry, the strong preference of Fe^{2+} (relative to Mg^{2+}) for the garnet structure results in large equilibrium constants for Fe-Mg exchange between garnet and most other silicates (garnet-biotite, garnet-clinopyroxene, etc.). These large equilibrium constants translate to significantly temperature-dependent Fe-Mg partition coefficients that in principle, can be used as Fe-Mg exchange geothermometers. Geobarometers involving garnet may be constructed from numerous equilibria that are pressure-dependent because of the high density of garnet.

Calibration of these geothermometers and barometers depends on reversed phase-equilibrium measurements in simple and complex systems, with the application of calorimetric constraints where such data are available (e.g., Perkins and Newton, 1980). Application of the calibrations to rocks also requires knowledge of the mixing properties of garnet solid solutions, which generally contain substantial amounts of at least three of the four components: $Fe_3Al_2Si_3O_{12}$, $Mg_3Al_2Si_3O_{12}$, $Ca_3Al_2Si_3O_{12}$, and $Mn_3Al_2Si_3O_{12}$. These mixing properties are not well constrained. In this paper we consider the properties of binary $(Fe,Mg)_3Al_2Si_3O_{12}$ garnet and give new experimental data that constrains the deviations of this join from ideality.

Calorimetric measurements on binary $(Ca,Mg)_3Al_2Si_3O_{12}$ (Newton et al., 1977), $(Fe,Ca)_3Al_2Si_3O_{12}$, and $(Fe,Mg)_3Al_2Si_3O_{12}$ garnets (Geiger et al., 1987) demonstrate that all three solid solutions are nonideal and that the excess enthalpies are asymmetric functions of composition. However, activity coefficients cannot be derived directly because there are excess entropies of mixing on at least one of the joins (grossular-pyrope, Haselton and Westrum, 1980), and it is possible that such effects occur in the other binaries. In addition, enthalpy measurements are extremely difficult in Fe-bearing systems, and the data are imprecise. Additional data are therefore needed to constrain activities or excess free energies of mixing in the Fe-bearing garnet solutions.

In the case of a binary solid solution such as $(Fe,Mg)_3Al_3Si_3O_{12}$, activity data may be obtained by measuring Fe-Mg partitioning between this phase and another whose mixing properties are known. Kawasaki and Matsui (1977) and O'Neill and Wood (1979) performed such experiments on Fe-Mg garnet coexisting with olivine. The relevant Fe-Mg exchange equilibrium is

$$\underset{gt}{⅓\,Mg_3Al_2Si_3O_{12}} + \underset{ol}{½\,Fe_2SiO_4} = \underset{gt}{⅓\,Fe_3Al_2Si_3O_{12}} + \underset{ol}{½\,Mg_2SiO_4}, \quad (1)$$

and the condition of equilibrium may be written as follows, with the standard state referring to the pure phases at the pressure and temperature of interest:

$$\frac{-\Delta G^0}{RT} = \ln \frac{X^{gt}_{Fe} X^{ol}_{Mg}}{X^{gt}_{Mg} X^{ol}_{Fe}} + \ln \frac{\gamma^{gt}_{Fe}\gamma^{ol}_{Mg}}{\gamma^{gt}_{Mg}\gamma^{ol}_{Fe}} = \ln K_D + \ln K_\gamma. \quad (2)$$

In Equation 2, mole fractions of Fe and Mg components (X^{gt}_{Fe}, X^{ol}_{Mg}, etc.) and activity coefficients (γ^j_i) have been

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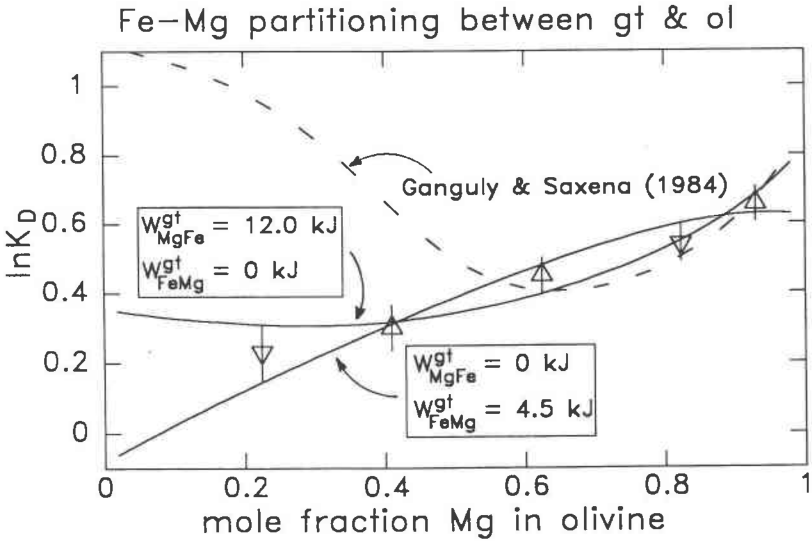

Fig. 1. Fe-Mg partitioning data from O'Neill and Wood (1979) at 1000 °C and 30 kbar [$K_D = (X^{gt}_{Fe}X^{ol}_{Mg})/(X^{gt}_{Mg}X^{ol}_{Fe})$]. Arrows indicate the direction of approach to equilibrium. The solid curves show that there is little constraint placed on the amount of asymmetry in Fe-Mg garnet by these data. This is mainly the result of the absence of data at the extreme Fe-rich end. The dashed curve is the model of Ganguly and Saxena (1984), $W^{gt}_{FeMg} = 2510$ J/mol and $W^{gt}_{MgFe} = 31380$ J/mol. All three curves were calculated assuming that $W^{ol}_{FeMg} = W^{ol}_{MgFe} = 9.0$ kJ/mol as discussed in the text.

substituted for activity as follows, with analogous expressions applying for Mg components:

$$a^{gt}_{Fe_3Al_2Si_3O_{12}} = (X^{gt}_{Fe}\gamma^{gt}_{Fe})^3$$
$$a^{ol}_{Fe_2SiO_4} = (X^{ol}_{Fe}\gamma^{ol}_{Fe})^2. \qquad (3)$$

The available data (Fig. 1) show that ln K_D is a function of olivine composition at constant P and T. This requires that one or both solid solutions are nonideal (ln $K_\gamma \neq 0$), but, as discussed by O'Neill and Wood (1979), partitioning data only enable the difference in nonidealities between the two phases to be determined. Absolute values of the properties of olivine are required for those of garnet to be deduced.

Wood and Kleppa (1981) determined the enthalpy of mixing of Fe-Mg olivine by solution calorimetry at 970 K. Although the data suggest that there is some asymmetry in the mixing properties, it has been shown by Bartholomew (1989) and O'Neill and Wall (1987) that the asymmetry is not statistically significant and that olivine may be regarded, within experimental uncertainty, as a symmetric solution. O'Neill and Wall (1987) gave a W^{ol}_{FeMg} (= W^{ol}_{MgFe}) value of 9130 J/mol with an estimated uncertainty of ±4000 J/mol, and Bartholomew (1989) gave 15000 ± 8000 J/mol (2σ uncertainty) for the mixing parameter derived from Wood and Kleppa's (1981) data. Differences between the two results depend on the assignment of uncertainties and the type of fitting procedure used. Bartholomew (1989) measured the partitioning of Fe and Mg between olivine and aqueous solution at 450–800 °C and 1–4 kbar. His data confirm that olivines are nonideal and that they do not deviate significantly from symmetric solutions, i.e.,

$$2RT \ln \gamma^{ol}_{Fe} = W^{ol}_{FeMg}(X^{ol}_{Mg})^2$$
$$2RT \ln \gamma^{ol}_{Mg} = W^{ol}_{FeMg}(X^{ol}_{Fe})^2. \qquad (4)$$

Although best fits to each of Bartholomew's (1989) isothermal sections give temperature-dependent values of W^{ol}_{FeMg}, the data can all be represented (within 2σ error brackets) by a W^{ol}_{FeMg} of 6000 to 11000 J/mol. Davidson and Mukhopadhyay (1984) derived a W^{ol}_{FeMg} value of 7000 ± 4000 J/mol from the compositions of coexisting olivines in the system (Ca,Mg,Fe)$_2$SiO$_4$. Similarly, fitting of the data of Jamieson and Roeder (1984) on coexisting Fe-Mg olivine and spinel gives a W^{ol}_{FeMg} of 10000 ± 4000 J/mol (O'Neill and Wall, 1987). Finally, measurements of the activity of Fe$_2$SiO$_4$ in olivine at high temperature (Nafziger and Muan, 1967; Kitayama and Katsura, 1968; Speidel and Nafziger, 1968; Williams, 1971) yield W^{ol}_{FeMg} values close to 8000 J/mol.

In summary, the data suggest that olivine is essentially a symmetric solution and that calorimetric and phase-equilibrium data collected between 700 and 1300 °C are consistent with a W^{ol}_{FeMg} value of between 7000 and 11000 J/mol. This enables, in principle, the mixing properties of Fe-Mg garnet to be determined with precision from Fe-Mg partitioning data.

Given that Fe-Mg garnet is an asymmetric solution (Ganguly and Saxena, 1984; Geiger et al., 1987), the activity coefficients for Fe and Mg components may be represented by the subregular model (reviewed by Thompson, 1967):

$$\begin{aligned} 3RT \ln \gamma^{gt}_{Fe} &= [W^{gt}_{FeMg} + 2X^{gt}_{Fe} \\ &\quad \cdot (W^{gt}_{MgFe} - W^{gt}_{FeMg})](X^{gt}_{Mg})^2 \\ 3RT \ln \gamma^{gt}_{Mg} &= [W^{gt}_{MgFe} + 2X^{gt}_{Mg} \\ &\quad \cdot (W^{gt}_{FeMg} - W^{gt}_{MgFe})](X^{gt}_{Fe})^2. \end{aligned} \tag{5}$$

Substituting Equations 4 and 5 into Equation 2 gives

$$\begin{aligned} RT \ln K_D &= -\Delta G^0 + \frac{W^{gt}_{MgFe}}{3}[(X^{gt}_{Fe})^2 - 2X^{gt}_{Mg}X^{gt}_{Fe}] \\ &\quad + \frac{W^{gt}_{FeMg}}{3}[2X^{gt}_{Mg}X^{gt}_{Fe} - (X^{gt}_{Mg})^2] \\ &\quad + \frac{W^{ol}_{FeMg}}{2}(X^{ol}_{Mg} - X^{ol}_{Fe}). \end{aligned} \tag{6}$$

Figure 1 shows the reversed Fe-Mg partitioning data at 1000 °C and 30 kbar of O'Neill and Wood (1979) plotted with curves calculated from Equation 6 and best-fit values of ΔG^0. As can be seen, the highly asymmetric garnet model (dashed curve) of Ganguly and Saxena (1984) cannot be reconciled with the partitioning data given a W^{ol}_{FeMg} value of 9.0 kJ/mol. In addition, the fit with their garnet model does not markedly improve if W^{ol}_{FeMg} is varied between 0 and 20 kJ/mol. In a recent discussion, Lee and Ganguly (1988) noted that the asymmetric models of Ganguly and Saxena (1984) and Geiger et al. (1987) (assuming $W_S = 0$) do not fit experimental data on Fe-Mg partitioning at 1200 °C between garnet and orthopyroxene, if orthopyroxene is assumed to be ideal. Thus, the model of Ganguly and Saxena (1984) is incompatible with the available partitioning data at $T \geq 1000$ °C. The model proposed by Geiger et al. (1987) is also incompatible with the partitioning data at $T \geq 1000$ °C if $W_S \cong 0$. The olivine-garnet partitioning data do not, however, place very good constraints on the extent of asymmetry in Fe-Mg garnet solution because of the lack of reversals at low mole fractions of Mg_2SiO_4 component in olivine. The available data would allow, with W^{ol}_{FeMg} of 9.0 kJ/mol, values of W^{gt}_{FeMg} of 0 to 4.5 kJ/mol and W^{gt}_{MgFe} of 12.0 to 0 kJ/mol (see Fig. 1). If data at low mole fractions of Mg component were available, however, the extent of asymmetry in garnet mixing properties would be well constrained. The purpose of this study was, therefore, to obtain reversed values of K_D over a wide range of Mg/Fe ratios with particular attention to compositions close to the Fe end of the series. The experiments were performed at a nominal pressure of 12 kbar and at a temperature of 1000 °C, the latter enabling comparison with the 1000 °C reversals of O'Neill and Wood (1979).

EXPERIMENTAL METHODS

Garnet synthesis

Stoichiometric oxide mixes were prepared by grinding together dried (at 1100 °C), analytical-grade Al_2O_3, MgO (from decarbonated $MgCO_3$), and Fe_2O_3 (dried at 120 °C) with crushed silica glass in an agate mortar. The mixes were placed in Mo crucibles and melted at 1-atm pressure at temperatures between 1400 and 1575 °C in a low f_{O_2} atmosphere. Mixtures of CO and CO_2 were used to control f_{O_2} at between 0.1 and 0.6 log units below the iron-wüstite (IW) buffer. After between 6 and 18 h, the crucibles were pulled from the furnace and quenched in water to produce green glasses with homogeneity, as determined by microprobe analysis, of better than ±0.5 mol%.

Garnets were synthesized at 15 kbar and 1100 °C in a piston-cylinder apparatus (Table 1). Durations of the syntheses were between 4 and 10 h. The cell edges of the synthetic garnets were determined by making 12 measurements of the positions of the (640) and (642) peaks relative to the (311) peak of Si metal ($d_{311} = 1.63747$ Å) using Cu$K\alpha_1$ radiation ($\lambda = 1.5405981$ Å). The garnets were analyzed with the JEOL 733 microprobe at Northwestern University using an accelerating voltage of 15 kV and a Faraday cup current of 30 nA. Between 30 and 50 analyses of each product were made, and the data were reduced with Bence-Albee correction procedures and a range of natural garnet and olivine standards. The synthetic garnets were found to be slightly less homogeneous than the glasses, standard deviations ranging between 1.0 and 2.5 mol% of the Fe and Mg end-members. Mössbauer spectra of all five garnets were obtained at room temperature using a 50-mCi source of ^{57}Co in Pd. The spectra were collected until there were approximately 5 × 10^5 counts per channel. Fitting of the spectra with Fe^{2+} and Fe^{3+} doublets of Lorentzian shape indicated that Fe^{3+} was not detectable, which indicates that less than 2% of the Fe is ferric in the synthetic garnets. Small particles (<1 vol%) of Mo metal were present as inclusions in the synthetic garnets, and these contained a few percent Fe in solution. Mo could not be detected in the garnets except in these inclusions.

Olivine synthesis

Synthetic Fa_{20}, Fa_{40}, Fa_{60}, Fa_{80}, and Fa_{100} were the same olivines as those used by Wood and Kleppa (1981). Fa_{50} and Fa_{70} were made from mixtures of Fe_2O_3, MgO, and SiO_2 that were pelletized and reacted in a 1-atm furnace at a temperature about 100 °C below the solidus and an f_{O_2} 0.05 log units below IW. The mixtures were reacted for between 3 and 8 h, then ground, repressed, and reacted again. Four cycles of grinding and reacting were used, and the resulting olivines were found, by electron microprobe, to be homogeneous to within ±0.5 mol% Fe_2SiO_4.

Partitioning experiments

Crystalline garnet and olivine were ground together under water in a ratio of 10:1 by mass. This was done so that the relatively refractory garnet was not required to change composition substantially during re-equilibration (Ferry and Spear, 1978). The mixtures were packed into holes drilled in a thin disc of graphite and covered with graphite caps. Up to four 2-mm-deep holes were drilled

TABLE 1. Measured compositions and cell edges of the synthesized garnets

Intended composition	Measured composition	a_0 (Å)	σ
$Alm_{90}Py_{10}$	$Alm_{89.8}Py_{10.2}$	11.521	0.001
$Alm_{80}Py_{20}$	$Alm_{82.0}Py_{18.0}$	11.517	0.001
$Alm_{60}Py_{40}$	$Alm_{59.5}Py_{40.5}$	11.500	0.001
$Alm_{50}Py_{50}$	$Alm_{51.4}Py_{48.6}$	11.493	0.001
$Alm_{35}Py_{65}$	$Alm_{34.7}Py_{65.3}$	11.482	0.001

in each disc so that up to four experiments could be conducted simultaneously. In addition, a dimple was placed in the middle of the disc so that the chromel-alumel thermocouple would be in the same vertical position as the samples. The thermocouple positioning was verified upon dismantling the cell after the experiment. Experiments were performed in a non–end-loaded piston-cylinder apparatus using ¾-inch-diameter (1.905 cm) pressure-cell assemblies with talc–Pyrex glass as insulating sleeves. Temperature monitoring and control were via a Chromel-Alumel thermocouple positioned as described above. Pressure was applied via the piston-in technique in that the final pressure adjustment at the desired temperature was from low pressure to high pressure. Nominal P and T conditions for all experiments were 12 kbar and 1000 °C with an estimated precision of ±0.5 kbar and ±3 °C, respectively. Although no correction was made for the effect of pressure on the emf, the experiments of Getting and Kennedy (1970) suggest that approximately 3 °C should be subtracted from the nominal temperature. In agreement with the observations of Perkins (1983), who used a similar capsule arrangement, we found no evidence of significant drift of thermocouple emf under these conditions. Mattioli and Bishop (1984) calibrated pressure loss for the talc–Pyrex cell that we used. Using their temperature-dependent correction gives an actual pressure of 9.1 kbar for the nominal conditions employed in this study. Although we used 9.1 kbar as the corrected pressure in our analysis, the effect of pressure on K_D is extremely small, and the difference between 12 kbar and 9.1 kbar changes ln K_D by only 0.015. Such a difference is well within the uncertainty of our experiments.

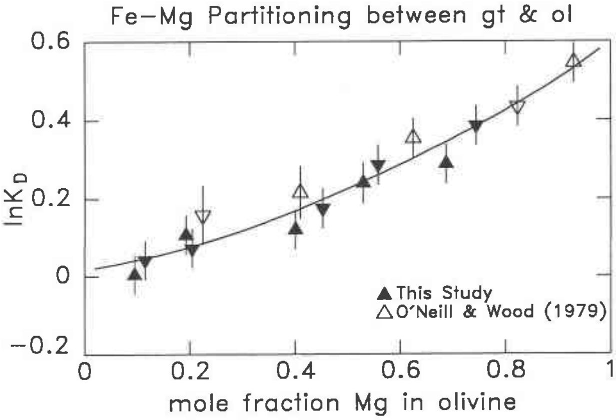

Fig. 2. Experimental results of the partitioning experiments at 1000 °C and 9.1 kbar. Arrows indicate direction of approach to equilibrium, and vertical bars show the uncertainty in ln K_D. The data of O'Neill and Wood (1979) have been corrected to 9.1 kbar using the equation of O'Neill (1980). The curve is a fit to all data and assumes that olivine is a symmetric solution with the olivine interaction parameter being 9.0 kJ/mol. The values derived for garnet are W^{gt}_{FeMg} = 2080 ± 1250 J/mol and W^{gt}_{MgFe} = 6350 ± 880 J/mol. The uncertainties for the garnet interaction parameters (1σ) are based on the precision of the experimental data. The interaction parameter for olivine is based on two sites, and the interaction parameters for garnet are calculated on a three-site basis.

Partition coefficients were calculated from electron-microprobe analyses of the synthetic garnets and olivines using the operating conditions and correction procedures described above. Between 10 and 50 olivine grains were analyzed from each product in order to find the one showing greatest reaction, i.e., the greatest change in Fe/Mg ratio. After finding the most reacted olivine, several analyses were made of the surrounding garnet from as close to the garnet-olivine interface as possible. These were averaged to calculate K_D. In any particular partitioning experiment, each olivine grain, ranging from 5 to 30 μm in diameter was, within experimental uncertainty, homogeneous. Garnets were found to be slightly inhomogeneous, the edges adjacent to olivine crystals exhibiting the expected small change in Fe or Mg required to compensate for the change in olivine composition (Table 2). Error bars in Figure 2 were calculated from a combination of uncertainties in microprobe counting statistics and the observed heterogeneities of garnet adjacent to olivine.

RESULTS

We were able to obtain precise reversals of Fe-Mg partitioning between garnet and olivine at low mole fractions of the Mg component in the two phases (Fig. 2, Table 2). It can also be seen that the data overlap completely the results of O'Neill and Wood (1979) when the latter are corrected to 9.1-kbar pressure. The results place tight constraints on the difference between nonidealities in olivine and garnet phases, but not their absolute values. We tested this assertion by fitting the data to Equation 6

TABLE 2. Selected experimental results for Fe-Mg partitioning between garnet and olivine

Experiment	Temperature (°C)	Pressure (kbar)	Duration (h)	Initial composition	Final composition
gtol 3B	1000	9.1	91.5	$Alm_{82.0}$ + Fa_{100}	$Alm_{82.6}$ + $Fa_{81.0}$
gtol 3C	1000	9.1	91.5	$Alm_{82.0}$ + Fa_{60}	$Alm_{80.7}$ + $Fa_{79.6}$
gtol 8A	1000	9.1	98.5	$Alm_{51.4}$ + Fa_{50}	$Alm_{53.0}$ + $Fa_{47.0}$
gtol 8B	1000	9.1	98.5	$Alm_{51.4}$ + Fa_{40}	$Alm_{51.4}$ + $Fa_{44.2}$
gtol 9A	1000	9.1	97	$Alm_{59.5}$ + Fa_{50}	$Alm_{59.0}$ + $Fa_{54.7}$
gtol 9B	1000	9.1	97	$Alm_{59.5}$ + Fa_{70}	$Alm_{62.8}$ + $Fa_{59.9}$
gtol 9D	1000	9.1	97	$Alm_{89.8}$ + Fa_{100}	$Alm_{90.5}$ + $Fa_{90.5}$
gtol 10B	1000	9.1	95	$Alm_{89.8}$ + Fa_{80}	$Alm_{88.9}$ + $Fa_{86.5}$
gtol 10C	1000	9.1	95	$Alm_{34.7}$ + Fa_{40}	$Alm_{37.7}$ + $Fa_{31.2}$
gtol 10D	1000	9.1	95	$Alm_{34.7}$ + Fa_{20}	$Alm_{33.5}$ + $Fa_{25.5}$

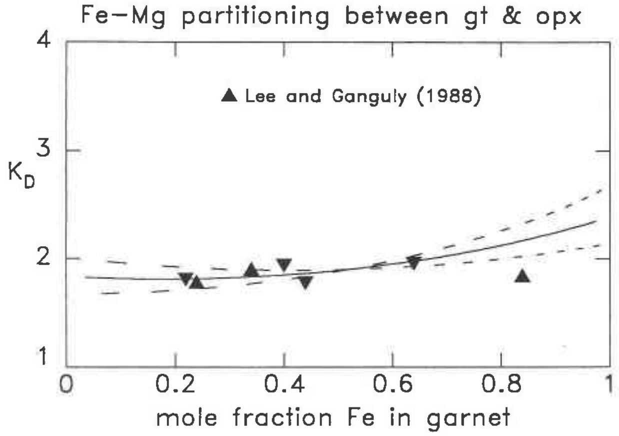

Fig. 3. Triangles are garnet-orthopyroxene Fe-Mg partitioning data, $K_D = (X^{gt}_{Fe}X^{opx}_{Mg})/(X^{gt}_{Mg}X^{opx}_{Fe})$, from Lee and Ganguly (1988), and indicate the direction of approach to equilibrium. The curves were calculated using the garnet mixing model obtained in this study. The solid curve was calculated from the best-fit garnet values $W^{gt}_{FeMg} = 2080$ J/mol and $W^{gt}_{MgFe} = 6350$ J/mol, assuming that orthopyroxene is an ideal solution. The dashed curves were calculated using the maximum and minimum values of garnet nonideality consistent with the properties of olivine (i.e., dashed line with steepest slope for garnet properties consistent with $W^{ol}_{FeMg} = 11000$ J/mol).

by multiple linear least-squares regression with the assumption that $W^{gt}_{MgFe} = W^{gt}_{FeMg}$. This approach resulted in values for W^{ol}_{G} and W^{gt}_{G} of 4120 J/mol and −3220 J/mol, respectively, with a correlation coefficient of 0.9978. With a correlation coefficient of virtually 1.0, it is clear that the properties of one phase must be known independently if the cation-exchange data are to be used to extract solution properties.

The experimental data were fitted to Equation 6 by fixing the value of W^{ol}_{FeMg} at the value of 9000 J/mol (two-site basis). This yields W^{gt}_{MgFe} of 6350 ± 880 and W^{gt}_{FeMg} of 2080 ± 1250 J/mol (three-site basis) where the uncertainty represents one standard deviation. The best-fit values are asymmetric in the same sense as the parameters of Ganguly and Saxena (1984) and the enthalpy results of Geiger et al. (1987). Although the asymmetric fit of garnet to the partitioning data is justified statistically by the F_x test (at the 97% confidence level), the extent of asymmetry is small and, within experimental error, the Fe-Mg garnet solid solution can fit a symmetric model with $W^{gt}_{FeMg} = W^{gt}_{MgFe} = 4780 \pm 720$ J/mol. Uncertainty in the value of W^{ol}_{FeMg} propagates directly into uncertainties in W^{gt}_{FeMg} and W^{gt}_{MgFe} because, as was stated above, the olivine and garnet mixing parameters derived from the regression are highly correlated. Thus, if W^{ol}_{FeMg} is 11000 J/mol, the best-fit values of W^{gt}_{FeMg} and W^{gt}_{MgFe} are 5060 ± 1210 and 9820 ± 850 J/mol (1σ), respectively, whereas for a W^{ol}_{FeMg} of 7000 J/mol, W^{gt}_{FeMg} is −880 ± 1290 J/mol and W^{gt}_{MgFe} is 2890 ± 910 J/mol.

The extent of olivine nonideality at 1000 °C is well constrained by the experimental studies cited earlier. Our data give the magnitudes of Fe-Mg nonideality in garnet and demonstrate that the extent of asymmetry in excess free energy on this join is extremely small.

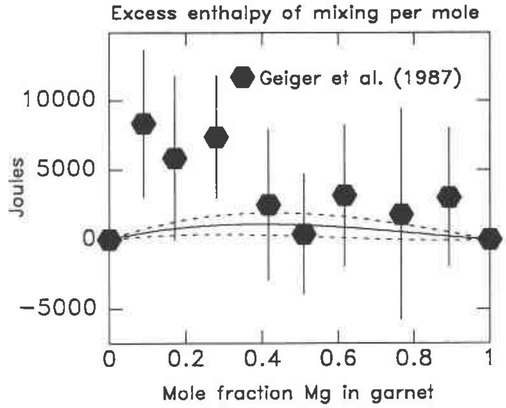

Fig. 4. Enthalpy of mixing data from Geiger et al. (1987). The solid curve was calculated from the best-fit free-energy parameters derived in this study, and the two dashed curves are the maximum and minimum deviations from ideality consistent with the properties of olivine (i.e., maximum values correspond to $W^{ol}_{FeMg} = 11000$ J/mol). Note that the sense of asymmetry is the same for the free energy and the enthalpy measurements but that the enthalpy data show a much greater deviation from ideality.

Lee and Ganguly (1988) have determined the partitioning of Fe and Mg between garnet and orthopyroxene at 26 kbar and 1200 °C. In Figure 3 we compare their results with K_D values calculated from our garnet mixing data and their assumption of ideal *a*-*X* relations for orthopyroxene solution ($a^{opx}_{FeSiO_3} = X^{opx}_{FeSiO_3}$). Our result for garnet agrees with the observed weak dependence of K_D on Fe/Mg ratio. This confirms that Fe-Mg garnets show small nonideality and that the nonidealities are not strongly asymmetric.

Figure 4 shows a comparison of our values of excess free energy for the pyrope-almandine join with the measured excess enthalpies of Geiger et al. (1987). The data agree over most of the join, and the sense of asymmetry in enthalpy measurements is the same as that in excess free energy. The two disagree in magnitude, however, for compositions close to almandine. This disagreement may be the result of the presence of small asymmetric excess entropies in the solid solution. Alternatively, it is possible that there are small errors in the heat-of-solution measurements at the Fe end of the series. There are several experimental problems that arise in enthalpy measurements on Fe-rich materials (control of oxidation state for example), and, as has been discussed by Newton (1987), the available data on pure almandine are inconsistent with enthalpy (Chatillon-Colinet et al., 1983) and phase-equilibrium (Bohlen et al., 1983) measurements on this phase. The latter were regarded by Newton (1987) as being more reliable. Regardless of the origin of these small discrepancies, our measurements pertain to activity coefficients in Fe-Mg garnet whereas the measurements of

Geiger et al. (1987) give the enthalpy contributions to activity coefficients. It is necessary therefore to weigh our results heavily when considering the effects of Fe-Mg solid solution on geothermometers and barometers involving garnet.

Our experimental data, as discussed earlier, agree with those of O'Neill and Wood (1979). We can therefore add little to their calibration of the garnet-olivine geothermometer except to remind the reader that the equation given by O'Neill and Wood (1979) for the weak pressure dependence of K_D is incorrect. O'Neill (1980) has given the correct form of the pressure term. Within the uncertainties, our value for the free-energy change of Reaction 1, -2000 ± 800 J, agrees with that derived by Kawasaki and Matsui (1983). Our value for the free-energy change is also in good agreement with other phase-equilibrium studies involving almandine and recent free-energy estimates for almandine (Woodland and Wood, 1989).

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