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# A statistical model of thermodynamic mixing properties of Ca-Mg-$Fe^{2+}$ garnets

**BISWAJIT MUKHOPADHYAY,[1] M.J. HOLDAWAY,[1] AND ANDREA M. KOZIOL[2]**

[1]Department of Geological Sciences, Southern Methodist University, Dallas, Texas 75275-0395, U.S.A.
[2]Department of Geology, University of Dayton, Dayton, Ohio 45469-2364, U.S.A.

## ABSTRACT

At present the most widely used models of thermodynamic mixing properties of garnet are those that are optimized to fit the experimental phase-equilibrium data along various binary garnet joins using the method of mathematical programming. We conducted a thorough weighted regression analysis of the available volumetric, calorimetric, and phase-equilibrium data. This resulted in a much improved set of *a-X* relationships with the following Margules parameters (in joules, kelvins, bars). $W^G_{FeMg} = -24166 + 22.09T - 0.034P$, $W^G_{MgFe} = 22265 - 12.40T + 0.050P$, $W^G_{FeCa} = 17526 - 14.51T + 0.135P$, $W^G_{CaFe} = -18113 + 15.51T + 0.040P$, $W^G_{MgCa} = 14306 - 2.49T + 0.140P$, $W^G_{CaMg} = 65182 - 20.82T + 0.068P$ (all pfu containing 12 O atoms). The robust regression analyses allowed us to obtain the uncertainties associated with each of the parameters, quantities not available by mathematical programming analysis of phase-equilibrium data. Uncertainty estimates are essential for rigorous quantification of errors associated with mineralogic thermobarometers. From the probabilistic model developed here, we present detailed formulations for ascertaining errors of activity coefficients of the end-member components in any garnet solid solution. This provides an opportunity to evaluate the uncertainties in mineralogic thermobarometers involving garnets of compositions dissimilar to those used in the experiments on which the garnet mixing models are based. The results of this study elicit several significant points. The analysis strongly suggests that there is an excess entropy of mixing along the Fe-Mg join because Fe-Mg mixing in garnet is substantially nonideal. The excess entropy of mixing along the Ca-Mg and Ca-Fe joins is asymmetric and therefore assumption of a large symmetric entropy parameter or no entropy along these joins is an oversimplification. Large uncertainty in the mixing properties exists for Ca-rich garnets. There should be a Ca-Mg-Fe ternary interaction parameter (7110 J/mol).

## INTRODUCTION

Garnet is a key phase in metamorphic and high-pressure igneous rocks and figures prominently in mineralogic thermobarometers, the main tool in unraveling the *P-T* history of crustal and subcrustal segments of the Earth. Consequently, thermodynamic mixing properties of garnet are of immense importance, and construction of a robust mixing model for garnet is imperative for quantitatively rigorous geothermobarometry. Although considerable progress has been made in this field, problems remain. Thermodynamic mixing properties of Ca-Mg-Fe-Mn garnet solid solutions can be approximated by considering constituent binaries, provided that appropriate Margules-type formulations are used (e.g., Ganguly and Saxena 1984). Berman (1990) proposed a comprehensive mixing model on the basis of mathematical programming of the experimentally determined phase-equilibrium data on binary systems available at the time. However, there is a further need to evaluate the model with newer experimental data in binary and ternary systems and to use a completely different technique that can evaluate not only the parameters but also their associated uncertainties.

In this paper we evaluate the available volumetric, calorimetric, and phase-equilibrium data statistically through robust regression techniques (e.g., Mosteller and Tukey 1977) to obtain a subset of data that are all consistent with each other, and from this subset we present an improved set of binary and ternary mixing parameters. Our analyses are based on several phase-equilibrium data that were not used by Berman (1990). For example, our analysis is the first one that resolutely uses the phase-equilibrium data of Koziol and Newton (1989) in conjunction with other data to derive the Ca-Fe and Ca-Mg mixing properties. Similarly, the Fe-Mg–fractionation data of Hackler and Wood (1989) and O'Neill and Wood (1979) that were not used by Berman (1990) play a pivotal role in our analyses of the Fe-Mg join. We do not consider any manganiferous join in this paper because the data on these joins are too exiguous to evoke a statistical appraisal. In several respects, the Ca-Mg-Fe parameters derived here are significantly different from those derived by Berman (1990). We detail our step-by-step derivations so that the interested reader can either verify or modify the model with the emergence of new data and assess

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possible problems of the model. Also presented are quantitative estimations of the uncertainties associated with the thermodynamic mixing properties of garnet. Our analysis should provide an opportunity to assess how well mixing properties of garnet are understood for a mineral with a substantial amount of germane experimental data.

Data for retrieval of free-energy Margules parameters, relevant statistics, and the critical steps in the operational procedure are given in Table 1.[1]

## STATISTICAL REGRESSION VS. MATHEMATICAL PROGRAMMING

There are two common approaches that can be taken to retrieve thermodynamic properties of minerals from experimentally determined phase-equilibrium data. The first involves application of mathematical programming, and the second involves statistical methods such as multiple regression. Although neither of these is superior to the other from the point of view of the thermodynamics of the systems being investigated, multiple regression does in fact that have mathematical strengths. Statistical regression provides the only opportunity to quantify the uncertainties associated with the mixing parameters. It also has the advantage in analyzing certain classes of data, such as the molar volumes and heats of solution, to give additional insights into the mixing behavior of the solid solutions. Mathematical programming cannot be meaningfully applied to cation-partitioning data because in these data the experimental determinations are commonly equilibrium compositions (if equilibrium was achieved) and do not necessarily represent reversals, hence a priori knowledge of experimental brackets for mathematical programming is not available in all cases. Finally, and perhaps most important, except for the Fe-Mg–fractionation data, a severe limitation of all other experimental data is the restricted compositional range over which equilibrium garnet compositions are available (Fig. 1; Table 2). Thus, the retrieved parameters are only as good as the extrapolation schemes that are used. In this respect, robust regression is a superior technique to mathematical programming because (1) in mathematical programming every experimental constraint receives equal weight, so the uncertainties in the application of a mixing model with certain Margules parameters become large in the compositional ranges that have not been covered experimentally; and (2) the regression method is mathematically the only valid method for predicting the value of a dependent variable in its entire domain, within uncertainty (error), from the observed relationships between the dependent and independent variables occurring in a subset of the domain. For quantitative geothermobarometry, it is essential to assess calculated *P* and *T* in the light of permissible ranges of garnet mixing parameters that are retrieved. Because of the optimization technique used by Berman (1990), it was not possible to estimate the range of uncertainties that were permitted by the experimentally limited database used in the model development. In other words, from the technique of retrieving mixing properties by mathematical programming, it is not possible to assess the robustness of the model. The available mixing properties of garnet are from a limited number of studies producing phase-equilibrium, calorimetric, and volumetric data, and hence it is critical to understand the limitations of a model constructed from these data and to confirm the uncertainties in using the model, particularly in those compositional regions in which no experimental data are available for the model calibrations. Further reasons for using robust regression procedure instead of ordinary regression are given below.

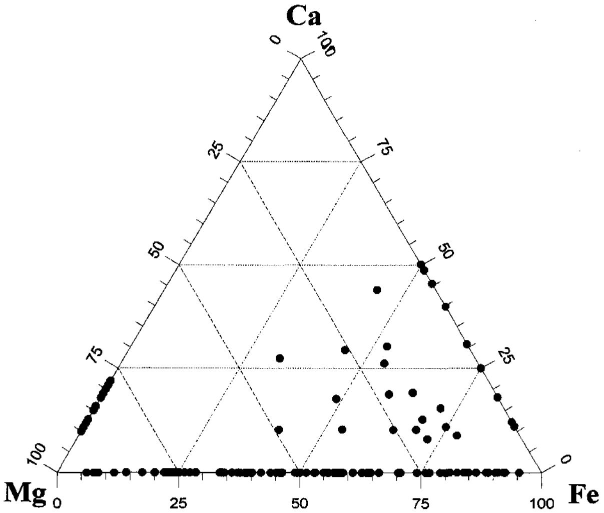

FIGURE 1. Compositions of Ca-Mg-Fe garnet from phase-equilibrium experiments used in the retrieval of thermodynamic properties of garnet.

## METHODOLOGY

Three principal components of the analytical procedure are summarized below.

### End-member thermochemical data

All analyses explicitly depend on the choice of thermochemical properties (enthalpy, entropy, volume, heat capacity, and coefficients of thermal expansion and compressibility) of the end-member phases involved in a reaction that was examined experimentally. We chose the thermodynamic database of Berman (1988, 1990) because it is by far the best data set that is consistent with most of the experimental observations. Second, this database offers an opportunity to compare our garnet model directly with that of Berman (1990). The only disadvantage of using the Berman database is that it does not provide a chance to assess separately the effects of the uncertainties that must be associated with the end-member data on

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[1] A copy of Table 1 can be obtained by ordering Document AM-97-630 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

**TABLE 2.** Experimentally determined phase-equilibrium data sources for determining solution properties of aluminosilicate garnet

| Equilibrium | Garnet join | Composition range | Source |
|---|---|---|---|
| | | **Type 1 reaction*** | |
| 3En + Alm = Py + 3Fs | Fe-Mg | $X_{Fe}$ = 0.220–0.910 | Lee and Ganguly 1988 |
| 3Fo + 2Alm = 2Py + 3Fay | Fe-Mg | $X_{Fe}$ = 0.060–0.954 | Kawasaki and Matsui 1983 |
| | Fe-Mg | $X_{Fe}$ = 0.142–0.905 | O'Neill and Wood 1979 combined with Hackler and Wood 1989 |
| | | **Type 2 reaction**** | |
| 3An = Grs + 2Ky/Sil + Qtz (GASP) | Ca-Fe | $X_{Ca}$ = 0.111–0.502 | Koziol 1990 |
| | Ca-Mg | $X_{Ca}$ = 0.11–0.22 | Hensen et al. 1975 and Wood 1988 |
| | Ca-Mg-Fe | $X_{Ca}$ = 0.081–0.439<br>$X_{Mg}$ = 0.121–0.491<br>$X_{Fe}$ = 0.321–0.781 | Koziol and Newton 1989 |
| 3CaTs = Grs + 2Cor | Ca-Mg | $X_{Ca}$ = 0.203–0.963 | Gasparik 1984 |
| 3Ilm + Sil + 2βQtz = Alm + 3Rut (GRAIL) | Fe-Mg | $X_{Fe}$ = 0.626–0.907 | Koziol and Bohlen 1992 |
| | | **Type 3 reaction**† | |
| 3Fay + 3An = Grs + 2Alm | Ca-Fe | $X_{Ca}$ = 0.33 | Bohlen et al. 1983 |
| 6Ilm + 3An + 3Qtz = Grs + 2Alm + 6Rut | Ca-Fe | $X_{Ca}$ = 0.33 | Bohlen and Liotta 1986 |

* Exchange equilibria involving garnet and a coexisting phase.

** Di- and trivariant equilibria involving garnet solid solution in a univariant reaction in the simple CaO-$Al_2O_3$-$SiO_2$ and FeO-$TiO_2$-$Al_2O_3$-$SiO_2$ systems.

† Equilibria involving a garnet solid solution of fixed composition.

the mixing properties of garnet. Thus, the errors quoted in this paper result from combined experimental errors and uncertainties in the end-member data. The effects cannot be resolved further.

## Thermodynamic mixing properties of other phases

Although Fe-Ca and Ca-Mg mixing parameters derived in this paper are independent of mixing properties of any other phase, the Fe-Mg mixing properties are critically dependent upon the mixing properties of ferromagnesian orthopyroxene (Opx) and olivine (Ol). Mixing properties of certain other phases, such as ilmenite and clinopyroxene, are not well known. For example, clinopyroxene is a complex solid solution in which mixing takes place over three crystallographically independent sites, namely M1, M2, and the TET (tetrahedral) sites. Furthermore, there is Fe-Mg order-disorder over the M1 and M2 sites and Al-Si order-disorder over the M1 and TET sites of clinopyroxene. Unless these complications are resolved, any attempt to use phase-equilibrium data involving garnet + clinopyroxene equilibria for retrieval of garnet mixing properties is fatally flawed. For this reason we do not use garnet-clinopyroxene Fe-Mg–fractionation experiments conducted in a temperature range (700–1000 °C) in which cation ordering may be an important phenomenon. Mixing properties of olivine and orthopyroxene are relatively better understood, and the experimental data are for a temperature range in which significant ordering is less likely.

**Orthopyroxene solution properties.** Berman (1990) assumed ideal Fe-Mg mixing in Opx to retrieve Fe-Mg mixing parameters for garnet exclusively from the Fe-Mg–fractionation data between garnet and orthopyroxene. Orthopyroxene is known to exhibit positive deviation from ideality and to display Fe-Mg ordering (e.g., Sack 1980; Ganguly 1982; Chatillon-Colinet et al. 1983; Yang and Ghose 1994), which may have a substantial effect on Fe-Mg partitioning between garnet and orthopyroxene. However, there is considerable uncertainty regarding the magnitude of the nonideal behavior. Ganguly (1982) analyzed experimentally determined intracrystalline $Fe^{2+}$-Mg distribution in Opx and showed that ordering is pronounced at $T < 1000$ °C. From his analyses, Ganguly further suggested that $W^{M1}_{FeMg} = W^{M1}_{MgFe} = 6376$ J/mol and $W^{M2}_{FeMg} = W^{M2}_{MgFe} = 4519$ J/mol (two-cation basis), which are similar to the values suggested by Sack (1980). Chatillon-Colinet et al. (1983) measured excess enthalpy of mixing of $Mg_2Si_2O_6$-$Fe_2Si_2O_6$ orthopyroxene synthesized at 1120 °C and 20 kbar. On the basis of experiments on heat treatment of a well-ordered natural Opx, they postulated that disordering in Fe-Mg distribution was complete above 1000 °C but that the rate of reordering was sluggish (also suggested by Besancon 1981) in the time interval of calorimetric experiments at 1023 K. Thus, they argued that the measured positive deviation from ideality with $W^{M1}_{FeMg} = W^{M1}_{MgFe} = W^{M2}_{FeMg} = W^{M2}_{MgFe} = 7933 \pm 1674$ J/mol (two cations) represents that of disordered orthopyroxene solutions. Yang and Ghose (1994) suggested $W^{G}_{M2} = 14775 - 7.575T$ (K) (±624) J/mol and $W^{G}_{M1} = 10230 - 2.065T$ (K) (±164) J/mol but noted that their site-occupancy data cannot be extrapolated above 930 °C. Yang and Ghose (1994) also showed that macroscopic excess free energy of mixing of Opx solid solutions, calculated by taking the average of their site-interaction parameters, is consistent with the macroscopic model given by Chatillon-Collinet et al. (1983).

It is impossible to assess the exact state of ordering in the available experimental data. The data that have maximum influence in the actual retrieval process (discussed below) are from the temperature range 1100–1300 °C.

From the discussion above and because of the high experimental temperature used in the calibration process, the assumption of a disordered state for Opx should not introduce any significant error into the mixing paramaters of garnet. Furthermore, as suggested by Ganguly (1982) and Chatillon-Colinet et al. (1983), for a disordered Opx, $W^{M1}_{FeMg} \approx W^{M2}_{MgFe}$. During our analysis, we assumed disordered ferromagnesian Opx and optimized the value of $W^{Opx}_{FeMg} = W^{Opx}_{MgFe}$ to obtain the best fit of the experimental data. We used $W^{Opx}_{FeMg} = W^{Opx}_{MgFe} = 5500$ J/mol (two-cation basis), which is in good agreement with the average of the $W$ values of the two sites proposed by Ganguly (1982). It should also be noted that from an analysis of Fe-Mg–fractionation data between orthopyroxene and olivine, Sack and Ghiorso (1989) proposed $W^{M1}_{FeMg} = W^{M1}_{MgFe} = W^{M2}_{FeMg} = W^{M2}_{MgFe} = 8368 \pm 1046$ J/mol, with negligible free-energy change of the ordering reaction. We cannot reconcile there results because the corresponding olivine solution property derived by Sack and Ghiorso (1989) is inconsistent with that used in this study (discussed below). From the discussion above it should be evident that consideration of disordered orthopyroxene with a positive deviation from ideal mixing behavior represents a much better model than the treatment of Opx as an ideal solution because the $\Delta H$($\sim$11–13 kJ at 1300 K) of disordering in Opx is very large (Besancon, 1981; Chatillon-Colinet et al. 1983; Yang and Ghose 1994).

Finally, the $Al_2O_3$ contents of the orthopyroxene, which constrain the mixing properties of garnet most severely, were low (0.25–1.94 wt%). Some orthopyroxene samples used in the calibration, which were weighted substantially less than the former group, contained $Al_2O_3$ ranging from 1.44 to 4.23 wt%. Thus, mixing of Al in the M1 site could be safely assumed to be ideal, a postulate consistent with the extensive phase-equilibrium data in the MAS system involving magnesian garnet and aluminous orthopyroxene (see Wood and Holloway 1984). To avoid the problem of interference of aluminous orthopyroxene, the data set of Harley (1984) was not used in the present calibration. Berman (1990) noted several other difficulties in using the data set of Harley (1984).

**Olivine solution properties.** For olivine, Hackler and Wood (1989) adopted $W^{Ol}_{FeMg} = W^{Ol}_{MgFe} = 9000$ J/mol (two-cation basis) from consideration of all previous studies relevant to the assessment of this parameter. Substantial controversies exist regarding the magnitude of this nonideal interaction parameter. Sack and Ghiorso (1989) proposed large positive deviation from ideality in olivine with $W^{Ol}_{FeMg} = W^{Ol}_{MgFe} = 16108.4 \pm 502.1$ J/mol. Wiser and Wood (1991) experimentally determined fractionation data between ferromagnesian olivine and ferromagnesian oxides and suggested $W^{Ol}_{FeMg} = W^{Ol}_{MgFe} = 7400 \pm 1600$ J/mol. Subsequently, Seckendorff and O'Neill (1993) experimentally determined Fe-Mg fractionation between olivine and orthopyroxene. These authors, from a statistical analysis of all available fractionation data, noted that it would be inappropriate to use their "best-fit" values; rather they found that great uncertainty lies in a well-defined value of $W^{Ol}_{FeMg} = W^{Ol}_{MgFe}$, which may range from 2000 to 8000 J/mol. In the light of this discussion, it should be apparent that the exact magnitude of nonideality in olivine is uncertain, but a positive deviation from ideality is the most plausible presumption. For this reason, we used the value used by Hackler and Wood (1989) so that our derived parameters for Fe-Mg mixing in garnet could be directly compared with their parameters. However, we tested our model (Table 1B) with the parameters suggested by Wiser and Wood (1991; 7400 J/mol) and found that it is inconsistent with the garnet-orthopyroxene results in comparison with the parameter suggested by Hackler and Wood (1989; 9000 J/mol).

In olivine, Fe-Mg ordering is so slight that it can be neglected (Ottonello et al. 1990; Sack and Ghiorso 1989; Seckendorff and O'Neill 1993; Brown 1982).

### Robust regression technique

Here we summarize the regression procedure and the rationale for it. First, a stepwise regression confirmed that we had sufficient data to extract the coefficients of all the variables that occur in a regression equation (e.g., ten variables in Eq. 1). Then, an ordinary multiple linear regression (OMLR) analysis was implemented. Residual plots did not show any aberration from the basic premises on which regression models are built (see Chatterjee and Price 1991). Only in rare cases are multiple determinations of any measure (e.g., molar volumes, equilibrium compositions, etc.) available for a single composition of garnet. Thus, in fitting a model to such a body of data one should ensure that the fit is not overly determined by one or two observations. In the same vein, even though phase-equilibrium data exist for the whole range of garnet compositions along the join in Fe-Mg systems, data toward the Fe end are more uncertain than those toward the Mg end. This is also true for calorimetric data along the Fe-Mg join. These uncertainties probably resulted from variable oxidation of Fe controlling the $Fe^{2+}$:$Fe^{3+}$ ratio. For this reason the standardized residuals become variable, or, in statistical terms, the data show heteroscedasticity (e.g., see Neter et al. 1990; Rousseeuw and Leroy 1987). Thus, OMLR of these data does not produce unbiased estimates of the parameters. A weighted least-squares estimation becomes necessary. Similarly, in the GASP system (see below), the garnet compositions are either toward the Mg-rich side of the Ca-Mg join, toward the Fe-rich side of the Fe-Ca join, or toward the Fe-rich corner of the Ca-Mg-Fe join (Fig. 1). Thus, a robust regression is particularly important in this situation.

Three types of data can bias the retrieved parameters (Chatterjee and Price 1991): outliers (points with large residuals), leverage points (points outlying in composition space), and influential points (the deletion of which, singly or in combination, causes substantial changes in the estimated coefficients). Points with high leverage that are not influential do not cause problems, but high leverage points that are influential should be investigated because these points are outlying, as far as the regressors are concerned, and also influence the fit (Chatterjee and Price 1991). For example, in the analyses of the volume data, leverage becomes critical only if multiple determinations of an end-member composition are available. The relative leverage and influence of the points are evaluated by comparing two statistics, the "hat diagonal" ($h_{ii}$) and DFFITS. The detailed explanations of these statistics can be found in Chatterjee and Price (1991) and Neter et al. (1990). Because we have no reason to discard the points with high influence, the best strategy would be to dampen their effects with a robust regression (RR) procedure that assigns variable weights to each of the data, depending on how far the data are from the first moment about the origin or in other words depending on the second moment of a datum about the central tendency. There are several procedures available for robust regression (Neter et al. 1990; Mosteller and Tukey 1977; Hoaglin et al. 1983). The most commonly used method is that of least absolute deviation (LAD). To each observation a weight $w_i$ is assigned by minimizing the robustifying function LAD. In other words, the weights are obtained by the method of iteration through minimization of the function LAD. Mathematically, for example, in Equation 5 discussed below, we minimize

$$\sum_{i=1}^{n} |C_i - (\beta_1 X_{i1} + \beta_2 X_{i2})|$$

and the method of iteration continues until no substantial changes in the weights and the estimated β parameters ($W^G$ values) are observed. The final regression is obtained by minimizing

$$\sum_{i=1}^{n} w_i[C_i - (\beta_1 X_{i1} + \beta_2 X_{i2})]^2.$$

The weights ($w_i$), inversely proportional to the error-term variances ($\sigma^2\{\epsilon_i\}$), are scaled to range between 1 and 0 according to the procedure detailed in Mosteller and Tukey (1977). In that way distant outliers (with large LAD residuals) disappear entirely and intermediate cases are gradually downweighted. However, in our analyses no point was weighted zero in a consistent set of data. Furthermore, the LAD is insensitive not only to the outlying data but also to the inadequacies of the model employed (Neter et al. 1990). Two other commonly used robust estimators are Tukey's biweight and Andrews's sine wave functions (Hoaglin et al. 1983). We tested each data set with all three methods. We note that only in the case of volume data is the number of observations large enough to invoke a sophisticated mathematical function, such as the Andrews's sine function, as the robustifying function. For the phase-equilibrium and calorimetric data, observations were not numerous enough to warrant a more sophisticated robust function than LAD.

All phase-equilibrium data and their assignment weights are compiled in Table 1A. Standard errors (σ), root-mean-square errors (RMSE), and coefficients of determination ($r^2$) are given in Table 1B for all sets of data used.

## ANALYSES

### Excess volume of mixing

We begin with the analysis of the volume data from X-ray diffraction studies. Accurate estimations of the parameters of excess volume of mixing are necessary not only for thermobarometric calculations (e.g., Mukhopadhyay 1991) but also for extraction of the enthalpic and entropic contributions to the excess free energy of mixing obtained from an analysis of phase-equilibrium data obtained at high pressure (e.g., 50 kbar). Molar volumes of synthesized garnet along various binary joins were given by Newton et al. (1977), Wood (1988), Ganguly et al. (1993), Geiger et al. (1987), Hackler and Wood (1989), and Koziol (1990). We ignored the data of Cressey et al. (1978) because of the various problems associated with this data set, as noted by Berman (1990). In addition, Koziol and Newton (1989) presented molar volumes of 19 ternary Ca-Mg-Fe garnet samples. We subsumed this data set along with the various binary data (total 85 data points for Ca-Mg-Fe garnet) to fit the molar volume data into the following equation (Mukhopadhyay et al. 1993):

$$\begin{aligned} V = \sum_{i}^{3} X_i V_i^0 &+ X_1X_2(X_2W_{12}^V + X_1W_{21}^V) \\ &+ X_1X_3(X_3W_{13}^V + X_1W_{31}^V) \\ &+ X_3X_2(X_2W_{32}^V + X_3W_{23}^V) \\ &+ X_1X_2X_3C_{123}^V \end{aligned} \quad (1)$$

where

$$\begin{aligned} C_{123}^V = ½(W_{12}^V &+ W_{21}^V + W_{13}^V \\ &+ W_{31}^V + W_{23}^V + W_{32}^V) - W_{123}^V. \end{aligned} \quad (2)$$

Because data on ternary garnet are limited, we tested the model without the ternary data and found that its omission does not cause any significant change in the binary coefficients. We also found that only five observations have relatively higher leverages than the rest of the data points. These are pyrope-rich garnet samples ($X_{Ca}$ = 0.09–0.151) along the Ca-Mg binary join (Wood 1988). Few data points have substantially different influence than the rest of the data. The robust estimation by the method of LAD produced results that are slightly different from those obtained by OMLR. Both produced asymmetric models for each of the three binary joins. The RR using Tukey's biweight and Andrews's sine wave functions, on the other hand, produced similar parameters resulting in lesser asymmetry in the volume of mixing along the three binary joins. The estimated parameters and the associated standard error (1σ) using OMLR and RR (using LAD and Andrews's sine estimator) are compared in Table 3. Because of the lesser influence of individual data points and smaller errors associated with the estimated parameters in the RR procedure (Table 3), we adopted the values obtained in this routine rather than those obtained by OMLR. We used the parameters obtained by the LAD

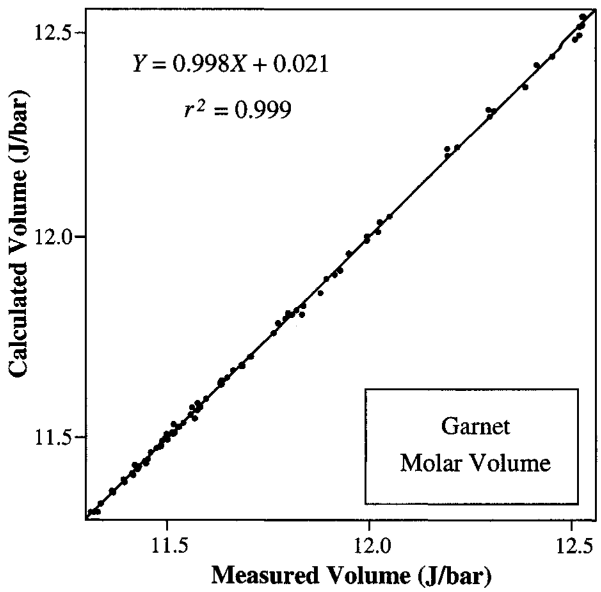

**FIGURE 2.** Measured vs. predicted garnet molar volumes according to RR using the LAD function.

technique because we did so for all other data. Also, several points substantially downweighted by Andrews's sine were weighted more heavily with LAD, suggesting less bias in the weighting procedure in LAD. Figure 2 shows the measured vs. predicted volumes according to the model adopted.

### Excess free energy of mixing

Once the excess volume-of-mixing parameters were fixed, excess free-energy parameters were derived from phase-equilibrium data. For estimation of the excess enthalpy and entropy parameters, calorimetric and phase-equilibrium data were evaluated concurrently.

Three types of experimentally determined phase-equilibrium data are available for estimation of mixing properties of garnet (Table 2). However, the third type listed in Table 2 cannot be used for regression analyses because a garnet of fixed composition was used even though Berman (1990) used these equilibria to propose excess entropy of mixing along the Ca-Fe join. In our final analysis however, we use these equilibria to check that the model does not violate available experimental constraints.

Fe-Mg fractionation between garnet and either olivine or orthopyroxene can be written as

$$\tfrac{1}{3}\mathrm{Mg_3Al_2Si_3O_{12}} + \tfrac{1}{2}\mathrm{Fe_2}\text{-}\alpha = \tfrac{1}{3}\mathrm{Fe_3Al_2Si_3O_{12}} + \tfrac{1}{2}\mathrm{Mg_2}\text{-}\alpha \qquad (3)$$

where α is either olivine or orthopyroxene. For equation 3 we have

$$-(\Delta G^0)^P_T = \mathrm{R}T\ln K_\mathrm{D} + \mathrm{R}T\ln K^\mathrm{Gt}_\gamma + \mathrm{R}T\ln K^\alpha_\gamma. \qquad (4)$$

In principle, all the other terms are known so that R$T$ ln $K^\mathrm{Gt}_\gamma$ is known as a function of the $P$, $T$, and $X$ of each experiment. The regression is performed on

$$C_i = C_{i1}W^\mathrm{Gt}_\mathrm{MgFe} + C_{i2}W^\mathrm{Gt}_\mathrm{FeMg}; \quad i = 1, n, \qquad (5)$$

where, $n$ denotes the number of experiments for which data are available. The constant term $C$ on the left side is calculated from all the known terms in Equation 4, and the constant terms ($C_1$ and $C_2$) on the right side of Equation 5 are the compositional terms in the Margules equation. Thus, for experimental $PTX$ points a set of $C_{i1}$, $C_{i2}$, and $C_i$ may be evaluated. In addition, there must be a point at $C_{11} = C_{12} = C_1 = 0$. The value of robust regression in cases in which the regression curve must pass through the (0, 0) point was emphasized by Rousseeuw and Leroy (1987). For the Fe-Mg exchange equilibria, two additional steps were implemented to derive the thermodynamic mixing properties.

First, experimentally determined fractionation data at a given $P$-$T$ condition were smoothed by fitting a third-degree polynomial to the $X^\mathrm{Gt}_\mathrm{Fe}$ vs. $X^\mathrm{Ol}_\mathrm{Fe}$ or $X^\mathrm{Opx}_\mathrm{Fe}$ plots using the experimental product compositions of the two coexisting phases and including points at (0, 0) and (1, 1). These fits, which reproduced the data very well, passed through the (0, 0) and (1, 1) points. The compositions used for regression analyses were the measured product-garnet compositions and the olivine or orthopyroxene composition computed from the polynomial expression. This smoothing procedure had negligible effect on the actual parameters retrieved but substantially reduced the errors associated with them (Table 1C). This is because some data in the fractionation experiments simply give equilibrium compositions and some may be true brackets. Thus, the smoothing procedure minimized the effect of differential bracketing, particularly in those sets containing only a few data, e.g., those of Lee and Ganguly (1988). To compensate for the error reduction from smoothing, regression errors were multiplied by 2.5 (Table 1C).

Second, the constant terms, $C_i$, on the left side of Equation 5 were calculated for each experimental $P$-$T$ condition. In this process all errors associated with $P$, $T$, end-member thermochemical properties, and thermodynamic mixing properties of the α phase were propagated into the calculated values of $C_i$. Thus, in practice, $C_i$ values were not determined precisely enough. For exchange reactions between ferromagnesian garnet and olivine or orthopyroxene, several experimental data points were determined at a single $P$-$T$ condition. This eliminated systematic errors or correlations in $C_{i1}$ and $C_{i2}$, leaving only random errors. By incrementally changing the value of $C_i$ in 100 J increments, the value of $C_i$ that optimizes the values of $W^\mathrm{Gt}_\mathrm{FeMg}$ and $W^\mathrm{Gt}_\mathrm{MgFe}$ could be found. The optimum value of $C_i$ provides minimum variance of the estimations, RMSE of the estimation process, and maximum $r^2$ of the regression equation. The final amount of adjustment that was necessary to produce the optimum values of $C_i$ ranged from +1.5 kJ for the garnet-olivine fractionation data to −1.5 kJ for the garnet-orthopyroxene fractionation data. The values obtained in these procedures are listed in Table 1B. The magnitude of adjustment

**TABLE 3.** Margules parameters estimated by ordinary multiple regression and robust regression to describe excess volume of mixing in Ca-Fe-Mg garnet

| Parameters estimated (J/bar) | OMLR | RR (Sine function) | RR (LAD function) |
|---|---|---|---|
| $V^0_{Ca}$ | 12.540 ± 0.004 | 12.545 ± 0.003 | 12.538 ± 0.003 |
| $V^0_{Mg}$ | 11.318 ± 0.004 | 11.318 ± 0.002 | 11.318 ± 0.003 |
| $V^0_{Fe}$ | 11.529 ± 0.005 | 11.528 ± 0.002 | 11.529 ± 0.003 |
| $W^V_{CaMg}$ | 0.047 ± 0.039 | 0.092 ± 0.023 | 0.068 ± 0.028 |
| $W^V_{MgCa}$ | 0.153 ± 0.046 | 0.088 ± 0.029 | 0.140 ± 0.034 |
| $W^V_{FeMg}$ | −0.025 ± 0.046 | −0.023 ± 0.024 | −0.034 ± 0.030 |
| $W^V_{MgFe}$ | 0.032 ± 0.046 | 0.046 ± 0.023 | 0.050 ± 0.029 |
| $W^V_{CaFe}$ | 0.056 ± 0.051 | 0.061 ± 0.029 | 0.040 ± 0.035 |
| $W^V_{FeCa}$ | 0.099 ± 0.047 | 0.091 ± 0.028 | 0.135 ± 0.034 |
| $C^V_{CaMgFe}$ | −0.009 ± 0.125 | −0.113 ± 0.072 | −0.076 ± 0.088 |
| $W^V_{CaMgFe}$ | 0.190 ± 0.137 | 0.291 ± 0.079 | 0.276 ± 0.096 |
| **Fit statistics** | | | |
| $r^2$ | 1.00 | 1.00 | 1.00 |
| RMSE | 0.102 | 0.004 | 0.006 |

was nominal considering all sources of uncertainties. Thus, this adjustment reflects these uncertainties and not an overall inconsistency with the actual database of Berman (1988, 1990). The garnet model presented here is consistent with the thermodynamic database of Berman and the solution properties of orthopyroxene and olivine mentioned above within reasonable error, but the later two quantities have uncertainties that are propagated into the uncertainties in the garnet mixing properties. This further justifies building a statistical model of mixing properties rather than a deterministic model that undermines all sources of error. Also, because of the lack of known magnitudes in the uncertainties of the end-member properties in the Berman database, the optimization procedure was needed with OMLR, instead of incorporating the exact uncertainties into the regression procedure.

Another class of experiments, pioneered by Hensen et al. (1975), involves displacement of a univariant equilibrium by solid solution of garnet (Table 3, type 2). For the GRAIL equilibrium, we can write

$$\mathrm{R}T \ln \gamma^{\mathrm{Gt}}_{\mathrm{Fe}} = -(\Delta G^0)^P_T - 3\mathrm{R}T \ln X^{\mathrm{Gt}}_{\mathrm{Fe}} - 3\mathrm{R}T \ln a^{\mathrm{Rut}}_{\mathrm{TiO_2}} + 3\mathrm{R}T \ln a^{\mathrm{Ilm}}_{\mathrm{FeTiO_2}} + \mathrm{R}T \ln a^{\mathrm{Sil}}_{\mathrm{Al_2SiO_5}}. \quad (6)$$

However, use of this equilibrium depends on activities of sillimanite, ilmenite, and rutile. Although Koziol and Bohlen (1992) estimated these latter variables in their experiments, we cannot use them because of lack of proper constraints on their mixing properties. Thus, this equilibrium was not used in the retrieval process; but the calibrated model was applied to the experimental data for model verification.

Experiments displacing the reaction 3 anorthite = grossular + 2 kyanite + quartz (abbreviated as GASP) by solid solution of Fe, Mg, or both in grossular garnet provide measurements of the activities and activity coefficients of grossular. Experimental studies (Table 2) have put constraints on the Mg-rich side of the Ca-Mg join, Fe-rich side of the Fe-Ca join, and the Fe-rich corner of the Fe-Ca-Mg plane (Fig. 1; Table 2). For this equilibrium.

$$\mathrm{R}T \ln \gamma^{\mathrm{Gt}}_{\mathrm{Ca}} = -(\Delta G^0)^P_T - 3\mathrm{R}T \ln X^{\mathrm{Gt}}_{\mathrm{Ca}} + 3\mathrm{R}T \ln a^{\mathrm{Plag}}_{\mathrm{An}} \quad (7)$$

where, $\mathrm{R}T\ln\gamma^{\mathrm{Gt}}_{\mathrm{Ca}} = f(W^{\mathrm{G}}_{ij}, X_i)$, $i, j = 1, 3$; $i \neq j$ for a ternary system [see Mukhopadhyay et al. (1993) for the exact formulations]. Thus, the regression can be performed on

$$C_i = C_{i1}W^{\mathrm{Gt}}_{\mathrm{MgCa}} + C_{i2}\mathrm{W}^{\mathrm{Gt}}_{\mathrm{CaMg}} + C_{i3}\mathrm{W}^{\mathrm{Gt}}_{\mathrm{FeCa}} + C_{i4}W^{\mathrm{Gt}}_{\mathrm{CaFe}} + C_{i5}W^{\mathrm{Gt}}_{\mathrm{MgFe}} + C_{i6}W^{\mathrm{Gt}}_{\mathrm{FeMg}} + C_{i7}C^{\mathrm{Gt}}_{\mathrm{CaMgFe}} \quad (8)$$

where, $i = 1, n$; and $n$ is the number of experiments. Only two parameters can be retrieved from the data on the binary Ca-Mg and Fe-Ca systems, but when these two binary systems are combined with the ternary data then theoretically all seven parameters, including that describing the ternary interaction, are retrievable. No Fe-Mg parameters can be meaningfully retrieved from the ternary GASP equilibria because no datum can exist in this system along the Fe-Mg binary. However, if we adopt the Fe-Mg mixing parameters from the analyses presented above, then the terms involving $W_{\mathrm{FeMg}}$ and $W_{\mathrm{MgFe}}$ can be added to the constant term $C_i$ on the left side of Equation 8.

The analyses of GASP equilibria included the following additional steps: (1) The origin was always included in the regression equation. (2) The activity of anorthite was taken from the reported or estimated anorthite composition because of the presence of either lithium molybdate or PbO as flux in the experiments (Table 1A, parts VI–X). (3) Because compositional variation occurs mostly in garnet, the experimental data points must cover a limited range of $P$-$T$ conditions. The $T$ range was ≤200 °C, and the $P$ range was ≤8 kbar. This leads to systematic errors in $C_{ij}$ values, which may well be correlated with $C_i$ values. Thus, no optimization of the constant terms was necessary. Optimization procedures with such data sets often lead to only a small improvement in the estimated parameters. We made slight adjustments to the grossular enthalpy and entropy of the Berman database to calculate the end-member GASP equilibrium precisely as experimentally determined in the same laboratory that did the solid-solution experiments. In this way the values of $C_i$

**TABLE 4.** Mixing parameters (J/mol) corrected from high *P* values (experimental conditions) to 1 atm using $W^V$ values in Table 1

| Data set | *n* | Source | Mean *T* (°C) | $W_{ij}$ | 1σ | $W_{ji}$ | 1σ |
|---|---|---|---|---|---|---|---|
| | | | | $W_{MgFe}$ | | $W_{FeMg}$ | |
| Gt-Opx | 5 | 1 | 979 | 7195 | 481 | 6492 | 1304 |
| Gt-Ol | 15 | 2 | 1000 | 6201 | 269 | 3722 | 1161 |
| Gt-Opx | 24 | 3 | 1100 | 3599 | 1158 | 6632 | 1736 |
| Gt-Opx | 7 | 1 | 1206 | 4669 | 1051 | 11250 | 1114 |
| Gt-Opx | 27 | 3 | 1300 | 1719 | 1589 | 8790 | 1216 |
| | | | | $W_{MgCa}$ | | $W_{CaMg}$ | |
| Binary-GASP | 7 | 4, 5 | 1043 | 30489 | 3707 | 28635 | 1978 |
| | 7 | 4, 5 | 1157 | 28378 | 6204 | 25002 | 2671 |
| | 6 | 4, 5 | 1233 | 22716 | 5316 | 26755 | 2451 |
| Ternary-GASP | 33 | 4–7 | 988 | 11161 | 5351 | 38931 | 2977 |
| | | | | $W_{FeCa}$ | | $W_{CaFe}$ | |
| Binary-GASP | 9 | 6 | 956 | 8082 | 2973 | −1791 | 1972 |
| Ternary-GASP | 33 | 4–7 | 988 | −779 | 3146 | 1447 | 2058 |

*Note:* No correction for *T* was applied; *n* denotes number of experimental data used in the retrieval process; σ indicates standard error of the mean estimates. Sources: 1 = Lee and Ganguly (1988), 2 = Hackler and Wood (1989), 3 = Kawasaki and Matsui (1983), 4 = Hensen et al. (1975), 5 = Wood (1988) 6 = Koziol (1990), 7 = Koziol and Newton (1989).

were calculated within a few hundred joules of the correct values. One additional test was performed to validate this procedure. At the *P* and *T* of the end-member reaction, and when $X_1$ ($X_{Ca}$) was set at 1 and all other *X*s were set at 0, the calculated value of $C_i$ was also 0. Thus, the values of $C_i$ used in the regression analyses are well constrained, and the end-member properties of grossular are consistent with the experimentally determined end-member reaction.

In the CMAS system, Gasparik (1984) gave data on the displacement of the equilibrium

$$\underset{\text{(Ca-Tschermak)}}{CaAlAlSiO_6} = \underset{\text{(grossular)}}{⅓Ca_3Al_2Si_3O_{12}} + \underset{\text{(corundum)}}{⅔Al_2O_3} \quad (9)$$

which is univariant in the Mg-free system but becomes divariant in the CMAS system. This data set is unique in having a wide range of Ca-Mg garnet compositions, but its usage is limited by inadequacies in clinopyroxene solution properties, namely, Mg-Al and Si-Al mixing in the M1 and TET sites, respectively. The Ca-Mg mixing parameters retrieved from the analysis of GASP equilibria were used in testing this equilibrium, and we arrived at a Cpx model that is consistent with calorimetric determinations by Newton et al. (1977). Further details on this aspect are given in subsequent sections.

## MODEL CALIBRATIONS

### Fe-Mg binary join

The Margules parameters describing the excess free energy of mixing of ferromagnesian garnet in various systems were calculated using the method described above. In this analysis, the data sets of Lee and Ganguly (1988) that show <5 experiments at a given temperature were discarded because of their limited statistical significance in comparison with the many data in other sets. Theoretically, Equation 4 differs for different experimental systems, but Equation 5 can be applied to all data. However, we performed the analyses group by group to ensure that the mixing property of the α phase did not unduly affect the results and to detect the effects of *T*, i.e., to determine excess entropy of mixing along this join. Because $W^G_{ij} = W^H_{ij} - TW^S_{ij} + PW^V_{ij}$, the parameters obtained from the analyses of high-pressure (9.1–50 kbar) experimental data were corrected for the pressure of the experiments with the volume-of-mixing parameters (Table 3). The values corrected to 1 atm standard pressure and grouped according to the scheme stated above are presented in Table 4. The uncertainties reported in Table 4 are given by

$$\sigma_W = \left[(\sigma_{W^G})^2\left(\frac{\delta W}{\delta W^G}\right)^2 + (\sigma_P)^2\left(\frac{\delta W}{\delta P}\right)^2 + (\sigma_{W^V})^2\left(\frac{\delta W}{\delta W^V}\right)^2\right]^{1/2}. \quad (10)$$

The $W^G$ and $W^V$ errors were obtained from the regression analyses of the experimental data, whereas the error in *P* was assumed to be 100 bars. These errors were assumed to be uncorrelated in the above formulation because correlations had already been incorporated in the process of estimating $W^G$. The *W* values reported in Table 4 are not superscripted because the effects of temperature were not effaced from these numbers. If we assume that there is no excess entropy of mixing along this join then these are $W^H$ values. From the values presented in Table 4 it is evident that there is an effect of temperature for ferromagnesian garnet, leading to the conclusion that there is excess entropy of mixing along the Fe-Mg join of garnet. To determine the magnitude of entropy, the interaction parameters of Table 4 were plotted against *T*. We employed a regression procedure developed by York (1966). In this procedure each datum was assigned a weight according to the errors in both *X* and *Y* values. In our analyses we assigned an additional weight to the data according to the number of occurrences, i.e., the number of data points. These regressions (*W* vs. *T* in Table 4) give slopes as entropies and intercepts as enthalpies. The values obtained in this procedure are given as model A in Table 5.

**TABLE 5.** Two models for the mixing properties (in J, K, and bar) of ferromagnesian garnet and Ca-Mg garnet

| | Model A | | Model B | |
|---|---|---|---|---|
| | $\mu$ | $1\sigma$ | $\mu$ | $1\sigma$ |
| $W^H_{\mathrm{FeMg}}$ | −26850 | 1556 | −6972 | 9710 |
| $W^H_{\mathrm{MgFe}}$ | 18291 | 1394 | 47732 | 9492 |
| $W^S_{\mathrm{FeMg}}$ | −23.98 | 1.15 | −9.97 | 6.86 |
| $W^S_{\mathrm{MgFe}}$ | 9.56 | 1.02 | 30.59 | 6.77 |
| $W^H_{\mathrm{CaMg}}$ | 65182 | 2786 | 52068 | 3013 |
| $W^H_{\mathrm{MgCa}}$ | 14306 | 3714 | 14367 | 3991 |
| $W^S_{\mathrm{CaMg}}$ | 20.82 | 3.23 | 10.42 | 3.36 |
| $W^S_{\mathrm{MgCa}}$ | 2.49 | 5.16 | 2.54 | 5.29 |

*Note:* See text for differences between models A and B. All parameters are per formula unit.

**TABLE 6.** OMLR and RR analyses of calorimetrically determined heat-of-solution data (J/mol)

| Parameters | OMLR | | RR | |
|---|---|---|---|---|
| | $\mu$ | $1\sigma$ | $\mu$ | $1\sigma$ |
| $W^H_{\mathrm{FeMg}}$ | −11404 | 16560 | −6972 | 9710 |
| $W^H_{\mathrm{MgFe}}$ | 45298 | 15787 | 47732 | 9492 |
| RMSE | 3.04 | | 1.58 | |
| $r^2$ | 0.65 | | 0.86 | |
| **Model A (forCaMg)** | | | | |
| $W^H_{\mathrm{CaMg}}$ | 65188 | 10691 | 65182 | 2786 |
| $W^H_{\mathrm{MgCa}}$ | 14233 | 12982 | 14306 | 3714 |
| RMSE | 1.98 | | 0.44 | |
| $r^2$ | 0.94 | | 1.00 | |
| **Model B (for CaMg)** | | | | |
| $W^H_{\mathrm{CaMg}}$ | 50751 | 8257 | 52068 | 3013 |
| $W^H_{\mathrm{MgCa}}$ | 16484 | 10027 | 14367 | 3991 |
| RMSE | 1.53 | | 0.49 | |
| $r^2$ | 0.95 | | 0.99 | |
| $W^H_{\mathrm{CaFe}}$ | −5867 | 17755 | −18113 | 10064 |
| $W^H_{\mathrm{FeCa}}$ | 3295 | 21434 | 17526 | 11672 |
| RMSE | 4.27 | | 1.93 | |
| $r^2$ | 0.01 | | 0.23 | |

Up to this point there has been no consideration of the calorimetric determination of the heat of solution along various garnet joins (Newton et al. 1977; Geiger et al. 1987). We performed OMLR and RR of the calorimetric data to obtain the enthalpy parameters. The calorimetric determinations have large uncertainties. Thus, OMLR yields large RMSE and small $r^2$. RR, in contrast, significantly improves these statistics. The results of OMLR and RR are compared in Table 6. The enthalpy parameters estimated from calorimetric determinations (Fig. 3) can, in principle, be combined with the average free-energy parameters obtained from phase-equilibrium data to obtain estimates of the entropy parameters. The results are presented as model B in Table 5. The uncertainties in the entropy parameters are calculated according to

$$\sigma_{W^S} = \sqrt{(W^S)^2\left[\frac{(\sigma_{W^J})^2}{(W^J)^2} + \frac{(\sigma_T)^2}{(T)^2}\right]} \qquad (11)$$

where $\sigma_T$ is assumed to be 10 °C; $W^J = W^H - W^G$, and $(\sigma_{W^J})^2 = (\sigma_{W^H})^2 + (\sigma_{W^G})^2$. The enthalpy and entropy parameters in these two models seem different because the maximum divergence between the two straight lines in the $W$ vs. $T$ plot occurs at absolute zero (where $W^H = W^G$). With increasing $T$, the curves in these two models converge toward the experimental $T$ range. Thus, calculations of enthalpy and free energy of mixing along this join at various $P$-$T$ conditions show that these two models yield similar results (note that the enthalpy and entropy parameters in the two models compensate each other to yield similar free energies). Hence, we propose the Fe-Mg mixing model that is a weighted average of these two modes. The weights are proportional to the errors in the estimated parameters, i.e., for example,

$$\begin{aligned} W^H_{\mathrm{MgFe}}\ (\text{final model}) &= W^H_{\mathrm{MgFe}}\ (\text{model A}) \\ &\quad\times \frac{\sigma_{\text{model B}}}{\sigma_{\text{model B}} + \sigma_{\text{model A}}} \\ &\quad+ W^H_{\mathrm{MgFe}}\ (\text{model B}) \\ &\quad\times \frac{\sigma_{\text{model A}}}{\sigma_{\text{model B}} + \sigma_{\text{model A}}}. \end{aligned}$$

The errors are the weighted averages of the errors in the respective models. The final results are presented in Table 7.

## Ca-Mg binary join

For the reasons explained in the section on the processing of Fe-Mg data, the data on binary phase-equilibrium experiments are grouped according to experimental

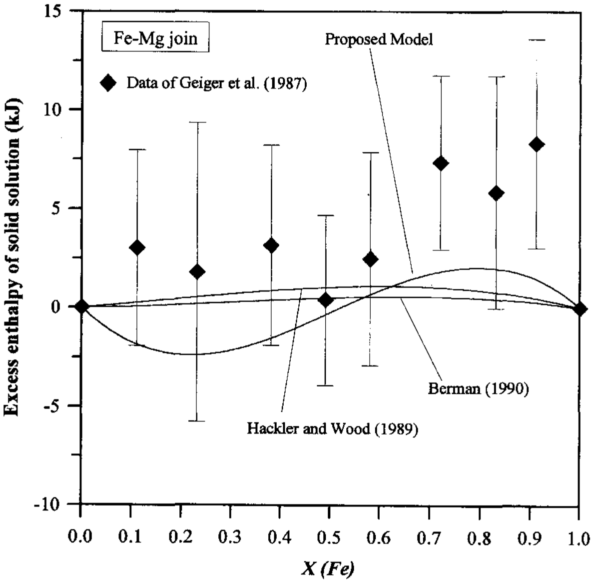

FIGURE 3. Proposed model for the enthalpy of Fe-Mg solid solution of garnet in comparison with the calorimetric measurements of Geiger et al. (1987). Error bars are $2\sigma$ errors calculated from Geiger et al. (1987). Calculated curves for the models of Berman (1990) and Hackler and Wood (1989) are shown for comparison. Note that our proposed model is not based on calorimetric data alone (see Tables 5–7 and text).

**TABLE 7.** Estimated molar mixing properties (in J, K, and J/bar) of Ca-Mg-Fe garnet

| | Berman (1990) | Proposed model with 1σ error |
|---|---|---|
| $W^H_{FeMg}$ | 230.0 | −24166 ± 2657 |
| $W^H_{MgFe}$ | 3720.0 | 22265 ± 2487 |
| $W^S_{FeMg}$ | 0.0 | −22.09 ± 1.92 |
| $W^S_{MgFe}$ | 0.0 | 12.40 ± 1.80 |
| $W^V_{FeMg}$ | 0.01 | −0.034 ± 0.030 |
| $W^V_{MgFe}$ | 0.06 | 0.050 ± 0.029 |
| $W^H_{FeCa}$ | 20320.0 | 17526 ± 11672 |
| $W^H_{CaFe}$ | 2620.0 | −18113 ± 10064 |
| $W^S_{FeCa}$ | 5.08 | 14.51 ± 9.58 |
| $W^S_{CaFe}$ | 5.08 | −15.51 ± 8.14 |
| $W^V_{FeCa}$ | 0.17 | 0.135 ± 0.034 |
| $W^V_{CaFe}$ | 0.09 | 0.040 ± 0.035 |
| $W^H_{CaMg}$ | 69200.0 | 65182 ± 2786 |
| $W^H_{MgCa}$ | 21560.0 | 14306 ± 3714 |
| $W^S_{CaMg}$ | 18.79 | 20.82 ± 3.23 |
| $W^S_{MgCa}$ | 18.79 | 2.49 ± 5.16 |
| $W^V_{CaMg}$ | 0.10 | 0.068 ± 0.028 |
| $W^V_{MgCa}$ | 0.10 | 0.140 ± 0.034 |
| $W^G_{CaMgFe}$ | 0.0 | 7110 ± 8241 |

*Note:* Estimates obtained with the use of mathematical programming in Berman (1990) and regression analysis in this work.

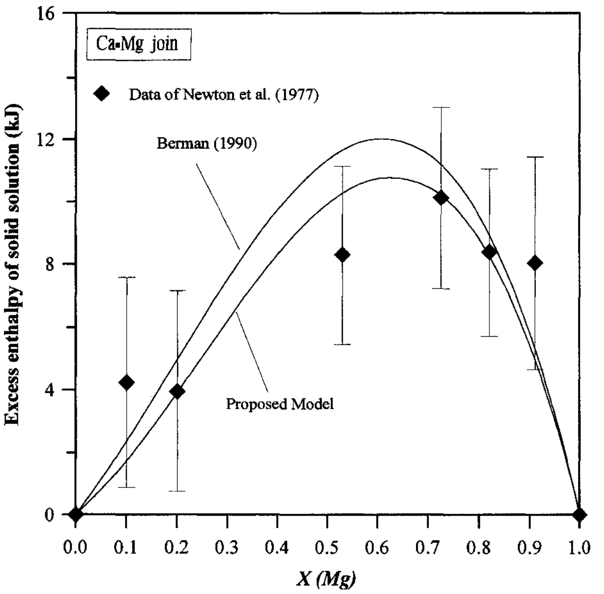

**FIGURE 4.** Proposed model for the enthalpy of Ca-Mg solid solution of garnet in comparison with the calorimetric measurements of Newton et al. (1977). Error bars are 2σ errors calculated from Newton et al. (1977). The model of Berman (1990) is shown for comparison.

temperature: (1) 1000–1100 °C (average $T$ = 1043 °C), (2) 1100–1200 °C (average $T$ = 1157 °C); and (3) 1200–1300 °C (average $T$ = 1233 °C). The data obtained from the analyses of the binary data (Table 2), corrected for $P$ using the $W^V$ parameters (Table 3), are shown in Table 4. In this system an entropic contribution to the energetic interactions can also be derived from the variation of the magnitudes of interactions with temperatures. The ternary GASP data are grouped together, along with the binary data between 900 and 1100 °C (Table 4). Because of the small number of data points at 1200–1300 °C (six) and the limited range of garnet compositions, we used the 33 data points in the binary and ternary systems between 900 and 1100 °C. We performed the York-type regression mentioned above on all the data but had no success in obtaining statistically meaningful slopes and intercepts. Because of the limited $T$ range, the standard errors were large. Because of the limited number of experiments in the binary system alone, these regressions are of limited value. Thus, we combined the RR results of the 33 experiments with the calorimetrically determined enthalpy parameters (Table 6; Fig. 4) to obtain the entropy parameters (Table 5). A significant point must be noted here. Newton et al. (1977) presented three measurements for the heat of solution of end-member pyrope. These are 116.02 kJ/mol (on pyrope synthesized hydrothermally at 1000 °C and 30 kbar), 114.81 kJ/mol (on pyrope synthesized from glass at 1300 °C and 40 kbar), and 113.76 kJ/mol (on pyrope synthesized from glass at 1300 °C and 40 kbar). Berman (1990) used the highest value, whereas Haselton and Newton (1980) used the lowest value. None of these authors explained why these values were chosen. The choice of a particular value for this end-member heat of solution has a vital effect on the excess enthalpy of mixing along the entire Ca-Mg join. We conducted the analyses using the highest and the lowest values of the end-member pyrope heat-of-solution data. We call these model A (using the highest value) and model B (using the lowest value) in Tables 5 and 6.

Haselton and Westrum (1980) measured heat capacity on a single garnet composition of $Mg_{0.6}Ca_{0.4}$ yielding an excess entropy ($S^{excess}$) of 4.51 J. If we apply $W^S_{CaMg}$ = 10.42 J·K and $W^S_{MgCa}$ = 2.54 J·K (model B, Table 5) to

$$S^{excess} = X_{Ca}X^2_{Mg}W^S_{CaMg} + X_{Mg}X^2_{Ca}W^S_{MgCa} \qquad (12)$$

we obtain $S^{excess}$ = 1.74 J/mol for this composition of the garnet. Although Haselton and Westrum (1980) did not quote an error limit for their experimental determinations, we suspect that this value is perhaps within 2σ standard error of the mean determination. If however, we apply $W^S_{CaMg}$ = 20.82 ± 3.23 J·K and $W^S_{MgCa}$ = 2.49 ± 5.16 J·K (model A, Table 5) to Equation 11, we obtain $S^{excess}$ = 3.24 ± 0.85 J/mol for a garnet of $Mg_{0.6}Ca_{0.4}$. This latter value is in good agreement with the calorimetrically determined value of excess entropy, and for this reason we adopted model A. This analysis highlights a significant fact, that excess entropy along this join is highly asymmetric. The analysis also shows that the magnitudes of the symmetric parameters are still consistent with a single calorimetric determination of excess entropy along the Ca-Mg join.

## Fe-Ca binary join

The Fe-Ca interaction parameters were obtained in the same fashion as the Ca-Mg parameters, using all available data collected between 900 and 1100 °C. The calorimetric enthalpy parameters are shown in Figure 5. The results are given in Tables 4, 6, and 7.

### Use of binary interaction parameters and the ternary interaction parameter

Mukhopadhyay et al. (1993) showed that expressing quaternary or higher order thermodynamic excess properties and partial molar quantities in terms of only constituent binary and ternary interaction parameters is theoretically correct. They presented formulations to calculate $G^{\text{excess}}$ in a quaternary system according to

$$G^{\text{XS}} = \sum_{i}^{4} \sum_{<j}^{4} X_i X_j (X_j W_{ij} + X_i W_{ji}) + \sum_{i}^{4} \sum_{<j}^{4} \sum_{<k}^{4} X_i X_j X_k C_{ijk} \tag{13}$$

from which we calculate R$T$ ln $\gamma_i$ according to

$$\mathrm{R}T \ln \gamma_i = 2 \sum_{\substack{j=1 \\ j \neq i}}^{4} X_i X_j W_{ji} + \sum_{\substack{j=1 \\ j \neq i}}^{4} X_j^2 W_{ij} + \sum_{\substack{j \\ j \neq i}}^{4} \sum_{\substack{<k \\ k \neq i}}^{4} X_j X_k C_{ijk} - 2G^{\text{XS}}. \tag{14}$$

In these equations, $C_{ijk}$ is given by

$$C_{ijk} = ½(W_{ij} + W_{ji} + W_{ik} + W_{ki} + W_{jk} + W_{kj}) - W_{ijk}. \tag{15}$$

The analyses of GASP equilibria along with the Fe-Mg interaction parameters derived here resulted in an estimation of a ternary interaction parameter in the Ca-Mg-Fe system (Table 7).

### Calculation of uncertainties in the activity coefficients of end-member components

The greatest significance of the analyses presented above perhaps lies in the value of the probabilistic model in evaluating uncertainties associated with calculations of the activities of end-member components of garnet solid solutions in various geothermobarometric applications. We present below the rigorous formulations for calculations of uncertainties in the activity coefficients of the three major components (grossular, pyrope, and almandine) in a Ca-Mg-Fe garnet. The method can be easily extended to quaternary systems.

Let us define a vector, **V**, with coordinates $\gamma_i$, $i = 1, 3$. Thus, $\mathbf{V} = (\gamma_1, \gamma_2, \gamma_3)$. Each of these three coordinates is itself a vector, the coordinates of which are given by ten scalars. From Equations 13 and 14 $\gamma_i = f(W_{12}, W_{21}, W_{13}, W_{31}, W_{32}, W_{23}, C_{123}, X_1, X_2, X_3)$. The $3 \times 10$ Jacobian matrix, **J,** can now be defined as $\mathbf{J} = [\nabla_{\gamma i}(f_j)]$; $i = 1, 3$; $j = 1, 10$. The $10 \times 10$ variance-covariance matrix, **U,** can be defined with elements given by $\mathbf{U} = [(\sigma_{ij})]$, where $\sigma_{ij} = \sigma_{ji} = \mathrm{Cov}(f_i, f_j)$, and $\sigma_{ii} = \mathrm{Cov}(f_i, f_i) = \mathrm{Var}(f_i)$. Thus, the variance-covariance matrix of **V**is given by the matrix **v** which is obtained from

$$\mathbf{v} = \begin{pmatrix} \sigma^2_{\gamma_1} & \sigma_{\gamma_1\gamma_2} & \sigma_{\gamma_1\gamma_3} \\ \sigma_{\gamma_1\gamma_2} & \sigma^2_{\gamma_2} & \sigma_{\gamma_2\gamma_3} \\ \sigma_{\gamma_1\gamma_3} & \sigma_{\gamma_2\gamma_3} & \sigma^2_{\gamma_3} \end{pmatrix} = \mathbf{J} \cdot \mathbf{U} \cdot \mathbf{J}^{\mathrm{T}}. \tag{16}$$

Note that while the diagonal elements of **v** give the variance of the end-member components, the off-diagonal elements are the covariances, which are also of importance in exchange thermometers (e.g., the garnet-biotite or garnet-orthopyroxene geothermometers) for which activity coefficients of two end-member components need to be computed. The elements of the Jacobian matrix, **J,** are given by the following partial derivatives, which were obtained from Equations 13 and 14 above.

$$\frac{\partial \gamma_i}{\partial W_{ij}} = \frac{\gamma_i}{\mathrm{R}T}[(1 - 2X_i)X_j^2] \tag{17a}$$

$$\frac{\partial \gamma_i}{\partial W_{ji}} = \frac{\gamma_i}{\mathrm{R}T}[2X_i X_j(1 - X_i)] \tag{17b}$$

$$\frac{\partial \gamma_i}{\partial W_{jk}} = -\frac{\gamma_i}{\mathrm{R}T}[2X_i X_k^2] \tag{17c}$$

$$\frac{\partial \gamma_i}{\partial C_{123}} = \frac{\gamma_i}{\mathrm{R}T}[X_k X_j(1 - 2X_i)] \tag{17d}$$

$$\frac{\partial \gamma_i}{\partial X_i} = \frac{\gamma_j}{\mathrm{R}T}[2(1 - 2X_i)(X_j W_{ji} + X_k W_{ki}) - 2(X_j^2 W_{ij} + X_k^2 W_{ik}) - 2X_j X_k C_{123}] \tag{17e}$$

$$\frac{\partial \gamma_i}{\partial X_j} = \frac{\gamma_i}{\mathrm{R}T}[2X_i(1 - X_i)W_{ji} + 2X_j(1 - 2X_i)W_{ij} - 2X_k(X_k W_{jk} + 2X_j W_{kj}) + X_k(1 - 2X_i)C_{123}] \tag{17f}$$

$$\frac{\partial \gamma_i}{\partial X_k} = \frac{\gamma_i}{\mathrm{R}T}[2X_i(1 - X_i)W_{ki} + 2X_k(1 - 2X_i)W_{ik} - 2X_j(X_j W_{kj} + 2X_k W_{jk}) + X_j(1 - 2X_i)C_{123}] \tag{17g}$$

with $i \neq j \neq k$. The first six diagonal elements of the matrix **U** were calculated from the standard deviations listed in Table 7, using the following relationship:

$$\sigma^2_{W^G_{ij}} = \sigma^2{}_{W^H_{ij}} + T^2\, \sigma^2{}_{W^S_{ij}} + P^2 \sigma^2{}_{W^V_{ij}} + (W^S_{ij})^2 \sigma^2_T + (W^V_{ij})^2 \sigma^2_P + 2\, \rho \sigma_{W^H_{ij}} \sigma_{W^S_{ij}}. \tag{18}$$

The seventh diagonal element was calculated directly from the variance of the ternary interaction parameter. The last three diagonal elements of **U** were obtained from the standard deviations of the analytical data (i.e., errors in $X_i$ values) The off-diagonal elements of **U** that relate to correlation between the composition and the Margules parameters were set at zero because we assumed that $W_{ij}$ values are independent of composition. The covariance between various $W_{ij}$ and $W_{ji}$ pairs was obtained from the calibration of the experimental data described above.

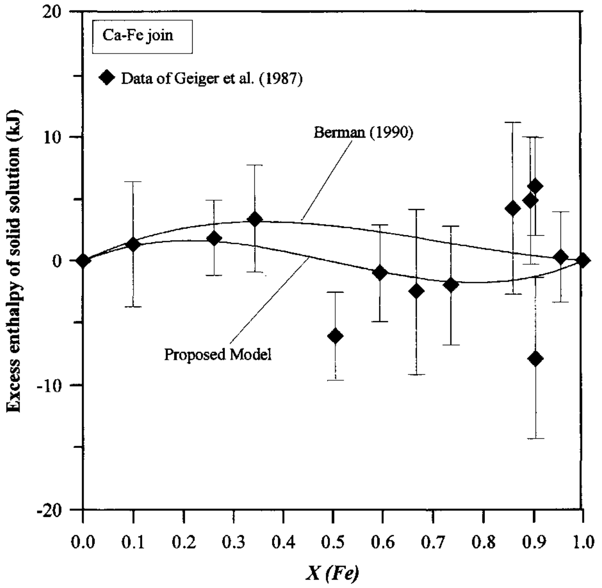

**Figure 5.** Proposed model for the enthalpy of Ca-Fe solid solution of garnet in comparison with the calorimetric measurements of Geiger et al. (1987) and the model of Berman (1990). Error bars are $2\sigma$ errors calculated from Geiger et al. (1987).

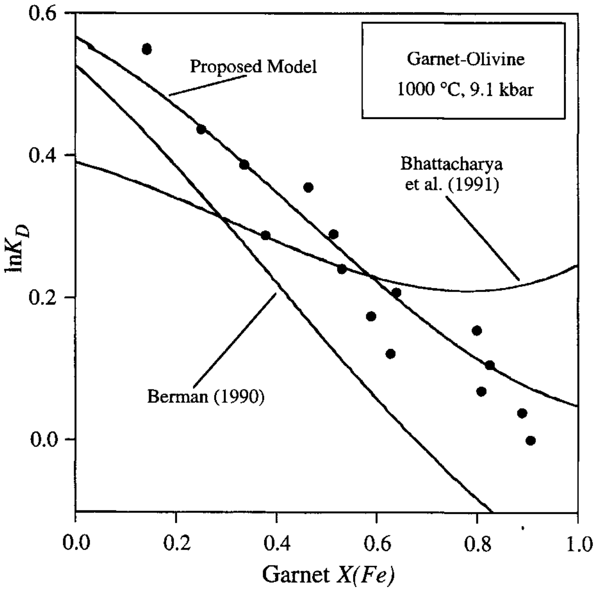

**Figure 6.** Calculated ln $K_D$ between coexisting garnet and olivine at 9.1 kbar and 1000 °C using various garnet models. End-member thermochemical data and olivine solution properties were used as discussed in the text. Experimentally determined fractionation data circles are from Hackler and Wood (1989) and O'Neill and Wood (1979). The $P$-$T$ conditions were the same as those used by Hackler and Wood (1989) to obtain the Fe-Mg–fractionation data.

## MODEL VERIFICATION

The calibrated models were verified through calculations of excess enthalpies along various binary joins, $P$-$T$ conditions of various equilibria (Table 2), and theoretical fractionation of Fe-Mg between garnet and olivine or orthopyroxene.

Figure 3 presents a comparison of the calculated excess enthalpy along the Fe-Mg binary join according to the model proposed here, that of Berman (1990), and that of Hackler and Wood (1989) with the experimental determinations of Geiger et al. (1987). From this plot, the real differences between our model and the others may not be readily understood. Three models were tested against the experimentally determined Fe-Mg–fractionation data. The curves calculated in this process can be directly compared with the experimentally determined $K_D$ values to test the efficacy of the garnet Margules to reproduce the experimental observations. Figure 6 shows the experimental data along with the curves calculated according to the three models. Berman (1990) and Bhattacharya et al. (1991) did not use this experimental data set to derive their models. It is obvious from this plot that their models fail to reproduce garnet-olivine fractionation data. Note that the experimentally determined compositions cannot be treated as experimental brackets because there is no certain way to discern on which side of the equilibrium curve the compositions lie.

Berman (1990) used the garnet-orthopyroxene fractionation data to support his model. The data of Lee and Ganguly (1988) along with those of Kawasaki and Matsui (1983) are plotted in Figure 7. Note that there is no way to support one model over the other with the Lee and Ganguly (1988) data, but our model is more accurate than the others with the Kawasaki and Matsui (1983) data. Eckert and Bohlen (1992) provided brackets (not equilibrium compositions) at two garnet compositions and three temperatures. Our calculated curves fall within these brackets. The data of Eckert and Bohlen (1992) cannot be plotted in diagrams like Figure 7 because of their limited number and bracketed nature. To test further the validity of the derived Margules parameters, we calculated the equilibrium pressure of the experimentally determined, displaced GRAIL Equilibrium 6 in the Fe-Mg system (Koziol and Bohlen 1992). Figure 8 shows the correspondence between the calculated pressure ($P_C$) and the experimental pressure ($P_E$) for the 15 experiments conducted by Koziol and Bohlen (1992) at 1000 °C. In this calculation we used the activities of ilmenite, rutile, and sillimanite as given by these authors. The minor discrepancies can be attributed to the experimental error and the uncertainties in $P_C$ resulting from errors in activity-composition relationships and end-member thermochemical properties. The details of these points are expanded below as applied to the GASP equilibria.

Thirty-three experimental data pertinent to displaced GASP equilibria were used in the retrieval of the Ca-Mg and Ca-Fe Margules parameters. The compositions lie on the Ca-Mg and Ca-Fe binary joins and in the Fe-rich part of Ca-Mg-Fe ternary space. To demonstrate the ability of the model to reproduce the experimental observations, $\Delta P$

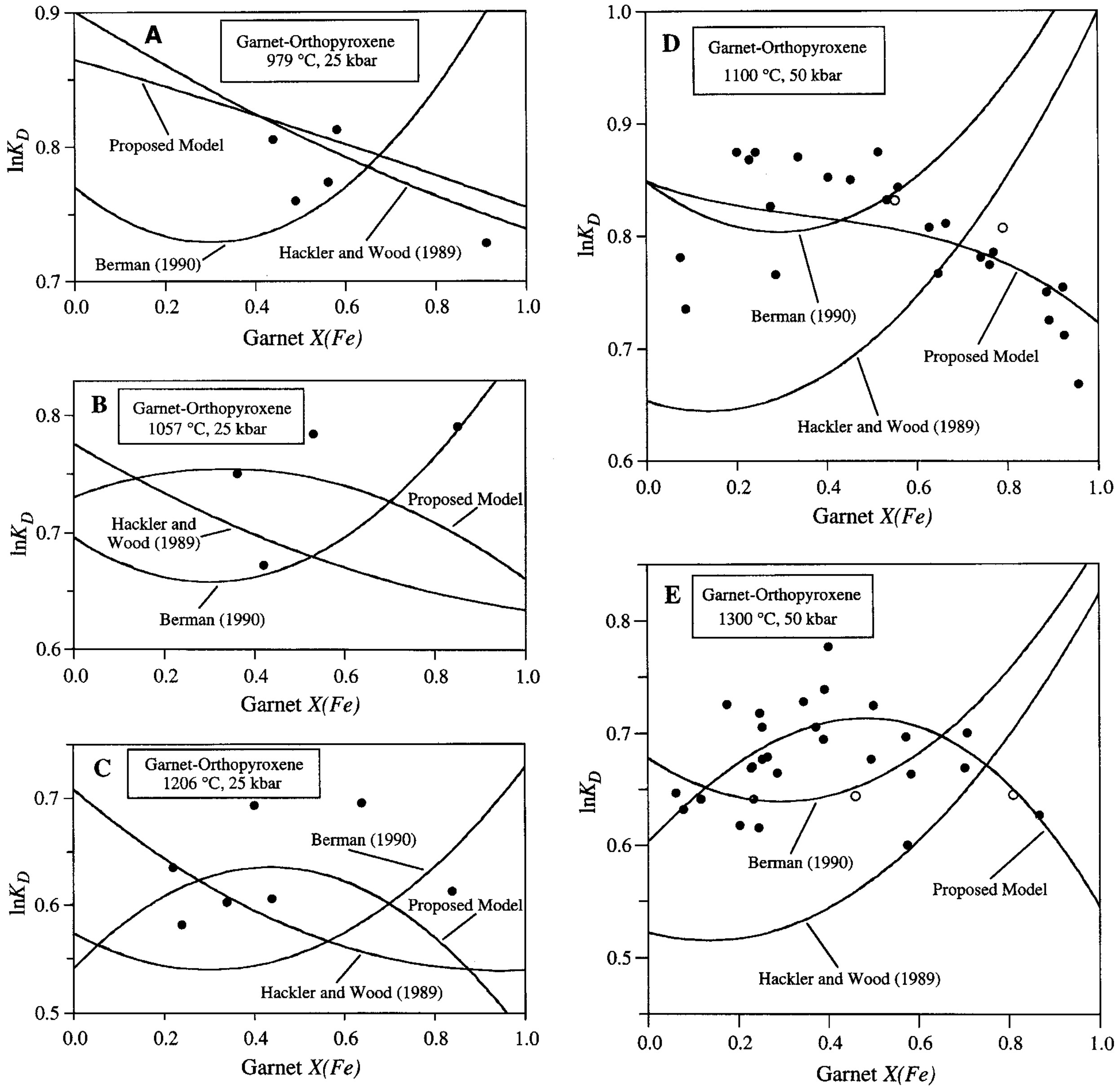

**Figure 7.** Calculated ln $K_D$ between coexisting garnet and orthopyroxene using various garnet models. End-member thermochemical data and orthopyroxene solution properties were used as discussed in the text. Experimentally determined fractionation data are from Lee and Ganguly (1988) (**A**, **B**, and **C**) and Kawasaki and Matsui (1983) (**D** and **E**). Experimental data of Lee and Ganguly in **A**, **B**, and **C** were corrected to a constant pressure of 25 kbar. In **D** and **E**, open circles represent Lee and Ganguly data at the given *T*, corrected to 50 kbar.

$= P_C - P_E$ was computed for the 33 experiments. We emphasize here that the proposed model can by no means provide a deterministic approach. In other words, it is imperative that an evaluation of uncertainties in the $P_C$ values be ascertained before they are compared with the $P_E$ values. The procedure illustrated with the GASP equilibria can be extended to all geobarometric applications to natural systems. Kohn and Spear (1991) used the end-member GASP equilibria, experimentally determined by Koziol and Newton (1989), and York regression (discussed above) to obtain a straight line in a *P*-*T* space in the following slope-intercept form:

$$P = b + mT \qquad (19)$$

where the mean estimates and 1σ uncertainties of these estimates are given as $b = -7222.0 \pm 889.0$ and $m = 22.68 \pm 0.65$. This end-member equation was used to reproduce the experimental data (Table 2). For a displaced equilibrium, $P$ was calculated from

$$P = b + mT - \frac{\mathrm{R}T}{\Delta V^0} \ln K_X - \frac{3\mathrm{R}T}{\Delta V^0} \ln \gamma^{\mathrm{Gt}}_{\mathrm{Ca}} \tag{20}$$

where

$$K_X = (X^{\mathrm{Gt}}_{\mathrm{Ca}})^3/(a^{\mathrm{An}}_{\mathrm{Ca}})^3.$$

The uncertainties in the calculated $P$ were obtained from

$$\sigma^2{}_{P_C} = \mathbf{H}\cdot\mathbf{W}\cdot\mathbf{H}^{\mathrm{T}} \tag{21}$$

where

$$\mathbf{H} = \left(\frac{\partial P}{\partial b}\ \frac{\partial P}{\partial m}\ \frac{\partial P}{\partial T}\ \frac{\partial P}{\partial \Delta V^0}\ \frac{\partial P}{\partial K_X}\ \frac{\partial P}{\partial \gamma^{\mathrm{Gt}}_{\mathrm{Ca}}}\right)$$

$$= \left(1\ T\ m - \frac{\mathrm{R}\ln(K_X\cdot\gamma^{\mathrm{Gt}}_{\mathrm{Ca}})}{\Delta V^0}\ \frac{\mathrm{R}T\ln(K_X\cdot\gamma^{\mathrm{Gt}}_{\mathrm{Ca}})}{(\Delta V^0)^2}\ \frac{\mathrm{R}T}{\Delta V^0 K_X}\ \frac{\mathrm{R}T}{\Delta V^0 \gamma^{\mathrm{Gt}}_{\mathrm{Ca}}}\right)$$

$$\mathbf{W} = \begin{pmatrix} 889^2 & -576.5 & 0 & 0 & 0 & 0 \\ -576.5 & 0.65^2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 5^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.00783^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sigma^2_{K_X} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sigma^2_{\gamma^{\mathrm{Gt}}_{\mathrm{Ca}}} \end{pmatrix}.$$

The nonzero off-diagonal elements are the covariance between $m$ and $b$, which was obtained from ρ, the correlation between $m$ and $b$, using the relationship Cov($mb$) = $\rho S_m S_b$. Kohn and Spear (1991) gave the value of ρ as −0.9977. The uncertainty in $K_X$ was calculated according to

$$\sigma^2_{K_X} = \left(\frac{\partial K_X}{\partial X^{\mathrm{Gt}}_{\mathrm{Ca}}}\right)^2 \cdot \sigma^2_{X^{\mathrm{Gt}}_{\mathrm{Ca}}} + \left(\frac{\partial K_X}{\partial a^{\mathrm{Pl}}_{\mathrm{Ca}}}\right)^2 \cdot \sigma^2_{a^{\mathrm{Pl}}_{\mathrm{Ca}}}$$

$$= [3(X^{\mathrm{Gt}}_{\mathrm{Ca}})^2(a^{\mathrm{Pl}}_{\mathrm{Ca}})^{-3}]^2\sigma^2_{X^{\mathrm{Gt}}_{\mathrm{Ca}}} + [-3(X^{\mathrm{Gt}}_{\mathrm{Ca}})^3(a^{\mathrm{Pl}}_{\mathrm{Ca}})^{-4}]\sigma^2_{a^{\mathrm{Pl}}_{\mathrm{Ca}}}$$

and $\sigma^2_{\gamma^{Gt}_{Ca}}$ is calculated from Equation 15. In these calculations the uncertainties used in the compositional parameters are as follows. Activity of anorthite was used according to the experimentalist's estimation (e.g., 0.98 ± 0.02 for the experiments of Koziol 1990; Koziol and Newton 1989; 0.96 ± 0.4 for the experiments of Wood 1988; and 0.999 ± 0.001 for the experiments of Hensen et al. 1975). Uncertainties in the garnet compositions were assumed to be 1.5 mol% for the experiments of Koziol (1990) and Koziol and Newton (1989), 2 mol% for the experiments of Wood (1988), and 3 mol% for the experiments of Hensen et al. (1975). Uncertainty in the experimental temperature was considered to be 5 °C and that in the pressure (for use in Eq. 17), 250 bars. The results of the calculations are presented in Table 8. It is apparent from these results that the proposed model is in good agreement with all experimental observations. The ΔP values are all within about $2\sigma_{P_C}$ (except for Experiments 12 and 22, which is $3\sigma_{P_C}$), which means the model has ~95% probability of reproducing all experimental observations, including those on the binary joins. Finally, we computed ΔP for the type 3 equilibria (Table 2). For the experimental data of Bohlen et al. (1983) ΔP ranges between −200 and −800 bars, whereas for those of Bohlen and Liotta (1986) ΔP varies between −800 and −1300 bars. The values of ΔP are larger using Berman's garnet model, ranging between 1000 and 2000 bars. We suspect that there are some systematic errors associated with these equilibria.

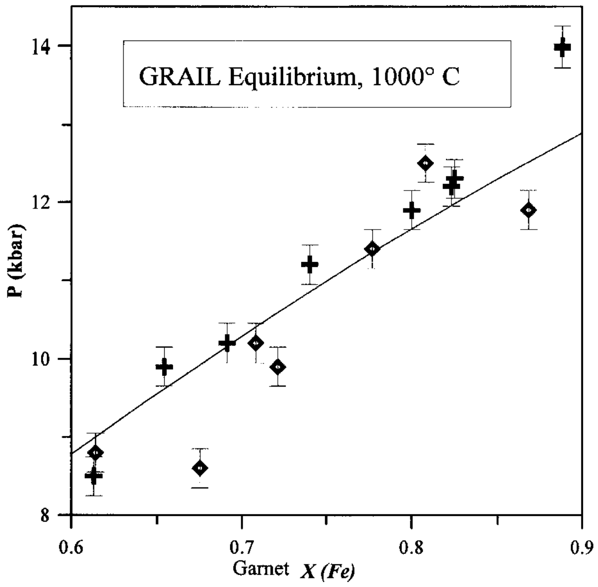

**FIGURE 8.** Experimentally determined and calculated $P$ as a function of mole fraction of almandine for the GRAIL equilibrium in the Fe-Mg system. Diamonds are experimental determinations (with error bars) from Fe-rich starting garnet, plus signs are experimental determinations (with error bars) from Mg-rich starting garnet, and the curve is the best fit of the calculated values.

Finally, one of the limitations of the model lies in the Ca-Mg join because of the limited number of GASP data along this join. However, we applied our Ca-Mg garnet model to the experimental data of Gasparik (1984), who used Ca-Mg garnet spanning the entire join (Table 3). The discrepancy Gasparik (1984) and Wood and Holloway (1984) noted between the phase-equilibrium data and the calorimetric heat-of-solution data on $CaMgSiO_6$-$CaAlAlSiO_6$ clinopyroxene determined by Newton et al. (1977) is removed if a completely disordered model of clinopyroxene is adopted, an assumption in accord with crystallographic data on aluminous clinopyroxene (e.g., Okamura et al. 1974). Wood (1979) also found such convergence between his phase-equilibrium data, which involved no garnet but aluminous clinopyroxene (Ca-Mg-Fe-A1 system), anorthite, and quartz, with the calorimetric data of Newton et al. (1977). In other words, our garnet model, when applied to the experimental data of Gasparik (1984), produces a clinopyroxene solution model that is consistent with calorimetric determinations and other phase-equilibrium data.

**TABLE 8.** Comparison of $P_E$ (kbar) and $P_C$ (kbar) for the GASP equilibria in the Ca-Mg-Fe system at 900–1100 °C

| Expt. | $X_{Ca}$ | $X_{Mg}$ | $X_{Fe}$ | $a^{Gt}_{Ca}$ | $\sigma a^{Gt}_{Ca}$ | $P_E$ | $P_C$ | $\sigma_{P_C}$ | $\Delta P$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.1110 | 0.1420 | 0.7470 | 0.1260 | 0.0170 | 11.10 | 11.55 | 0.71 | 0.45 |
| 2 | 0.1555 | 0.1310 | 0.7135 | 0.1728 | 0.0167 | 12.70 | 13.10 | 0.52 | 0.40 |
| 3 | 0.1040 | 0.2075 | 0.6885 | 0.1240 | 0.0179 | 11.10 | 11.48 | 0.75 | 0.38 |
| 4 | 0.1920 | 0.1710 | 0.6370 | 0.2157 | 0.0169 | 13.50 | 14.18 | 0.43 | 0.68 |
| 5 | 0.3030 | 0.1685 | 0.5285 | 0.3282 | 0.0164 | 15.50 | 16.24 | 0.30 | 0.74 |
| 6 | 0.4395 | 0.1210 | 0.4395 | 0.4552 | 0.0158 | 17.30 | 17.84 | 0.24 | 0.54 |
| 7 | 0.1035 | 0.2550 | 0.6415 | 0.1281 | 0.0186 | 11.10 | 11.63 | 0.75 | 0.53 |
| 8 | 0.1880 | 0.2215 | 0.5905 | 0.2180 | 0.0175 | 13.50 | 14.24 | 0.44 | 0.74 |
| 9 | 0.2620 | 0.1950 | 0.5430 | 0.2911 | 0.0168 | 15.30 | 15.65 | 0.33 | 0.35 |
| 10 | 0.1045 | 0.3590 | 0.5365 | 0.1410 | 0.0203 | 11.10 | 12.10 | 0.75 | 1.00 |
| 11 | 0.1775 | 0.3350 | 0.4875 | 0.2235 | 0.0190 | 13.60 | 14.36 | 0.46 | 0.76 |
| 12 | 0.2940 | 0.2590 | 0.4470 | 0.3325 | 0.0173 | 15.40 | 16.30 | 0.31 | 0.90 |
| 13 | 0.1035 | 0.4910 | 0.4055 | 0.1581 | 0.0230 | 11.10 | 12.66 | 0.75 | 1.56 |
| 14 | 0.2740 | 0.4045 | 0.3215 | 0.3392 | 0.0192 | 15.90 | 16.40 | 0.32 | 0.50 |
| 15 | 0.0895 | 0.1295 | 0.7810 | 0.1000 | 0.0168 | 8.30 | 9.04 | 0.81 | 0.74 |
| 16 | 0.0815 | 0.1958 | 0.7227 | 0.0968 | 0.0179 | 8.30 | 8.89 | 0.88 | 0.59 |
| 17 | 0.1290 | 0.1825 | 0.6885 | 0.1494 | 0.0175 | 10.60 | 10.85 | 0.58 | 0.25 |
| 18 | 0.1225 | 0.0000 | 0.8775 | 0.1277 | 0.0158 | 11.10 | 11.62 | 0.64 | 0.52 |
| 19 | 0.1810 | 0.0000 | 0.8190 | 0.1874 | 0.0159 | 12.60 | 13.50 | 0.45 | 0.90 |
| 20 | 0.3080 | 0.0000 | 0.6920 | 0.3156 | 0.0165 | 16.00 | 16.05 | 0.30 | 0.05 |
| 21 | 0.4550 | 0.0000 | 0.5450 | 0.4618 | 0.0176 | 18.20 | 17.91 | 0.24 | −0.29 |
| 22 | 0.5020 | 0.0000 | 0.4980 | 0.5084 | 0.0181 | 19.00 | 18.38 | 0.23 | −0.62 |
| 23 | 0.1115 | 0.0000 | 0.8885 | 0.1138 | 0.0155 | 9.40 | 9.62 | 0.66 | 0.22 |
| 24 | 0.2500 | 0.0000 | 0.7500 | 0.2568 | 0.0162 | 12.50 | 13.29 | 0.34 | 0.79 |
| 25 | 0.3985 | 0.0000 | 0.6015 | 0.4091 | 0.0200 | 14.70 | 15.39 | 0.26 | 0.69 |
| 26 | 0.4880 | 0.0000 | 0.5120 | 0.5000 | 0.0182 | 16.70 | 16.29 | 0.24 | −0.41 |
| 27 | 0.2000 | 0.8000 | 0.0000 | 0.3610 | 0.0543 | 17.00 | 16.67 | 0.75 | −0.33 |
| 28 | 0.2200 | 0.7800 | 0.0000 | 0.3780 | 0.0517 | 17.00 | 16.90 | 0.68 | −0.10 |
| 29 | 0.1280 | 0.8720 | 0.0000 | 0.2816 | 0.0441 | 15.00 | 15.49 | 0.81 | 0.49 |
| 30 | 0.1500 | 0.8500 | 0.0000 | 0.3096 | 0.0414 | 16.00 | 15.95 | 0.70 | −0.05 |
| 31 | 0.1100 | 0.8900 | 0.0000 | 0.2316 | 0.0632 | 15.00 | 16.21 | 1.45 | 1.21 |
| 32 | 0.1600 | 0.8400 | 0.0000 | 0.2965 | 0.0557 | 17.30 | 17.51 | 1.00 | 0.21 |
| 33 | 0.2100 | 0.7900 | 0.0000 | 0.3473 | 0.0498 | 18.50 | 18.34 | 0.76 | −0.16 |

*Note:* The $\sigma a^{Gt}_{Ca}$ is uncertainty in the activity of grossular component in garnet resulting from errors in the Margules parameters (Tables 6 and 7) and compositional variables (see text for details). Uncertainty in $P_E$ is 0.25 kbar, and uncertainty in $P_C$ is $\sigma_{P_C}$. $\Delta P = P_C - P_E$. Experiment numbers are assigned in this paper for sake of reference only. The compositional data noted for experiments 1–17 were not given previously.

## COMPARISON WITH PREVIOUS MODELS

The real differences among the various models are briefly highlighted by calculation of the excess free energy of mixing along the binary joins at geologically relevant $P$-$T$ conditions.

Ganguly and Saxena (1984) derived their model on the Fe-Mg join from natural Fe-Mg–fractionation data between garnet and another ferromagnesian phase such as olivine, orthopyroxene, or clinopyroxene by assuming a symmetric solution for quaternary garnet. They suggested $W_{MgFe} \approx 31.38 \pm 6.28$ kJ/mol and $W_{FeMg} \approx 2.51$ kJ/mol as two asymmetric interaction parameters. There are several problems with this analysis involving natural data and various other solid solutions. Berman (1990) used experimentally determined Fe-Mg–fractionation data between coexisting garnet and orthopyroxene to constrain the mixing parameters of ferromagnesian garnet. Using the Fe-Mg partitioning data between garnet and olivine, Hackler and Wood (1989) give $W_{MgFe} = 6.35 \pm 0.88$ kJ/mol and $W_{FeMg} = 2.08 \pm 1.25$ kJ/mol. Bhattacharya et al. (1991), on the other hand, presented a mixing model of ferromagnesian garnet with $W^H_{MgFe} = 36.17$ kJ/mol, $W^S_{MgFe} = 17.55 \pm 1.5$ J/mol, $W^H_{FeMg} = -15.77$ kJ/mol, and $W^S_{FeMg} = 19.16 \pm 1.58$ J/mol on the basis of the garnet-orthopyroxene Fe-Mg–fractionation data of Kawasaki and Matsui (1983) and the calorimetric measurements of Geiger et al. (1987).

Figure 9 shows the excess free energy of mixing of ferromagnesian garnet at a petrologically common $P$-$T$ condition according to the proposed model and three other models based on experimental data. The uncertainties associated with the proposed model (calculated from the standard errors quoted in Table 7) are also shown. Note that on the Mg-rich side of the join the model of Berman (1990) falls approximately within the uncertainty limit permitted by the proposed model, but toward Fe-rich compositions the model presented here shows marked deviation from the other three models. According to our model there is substantial nonideality in garnet with $X_{Fe} > 0.5$, whereas according to the model of Berman (1990) nonideality in the whole compositional range of ferromagnesian garnet is negligible. In the model of Bhattacharya et al. (1991), however, nonideality in ferromagnesian garnet is much more pronounced than what is proposed here.

For the Ca-Mg binary join, our model is in good agreement with that of Berman (1990) toward the Mg-rich end. However, our analyses have been able to detect the asymmetric entropy parameters that have significant effects on excess free energy of mixing in various compositional ranges and at different temperatures. Figure 10 shows the excess free energy of mixing of Ca-Mg garnet according to these two models at a geologically significant $P$-$T$ con-

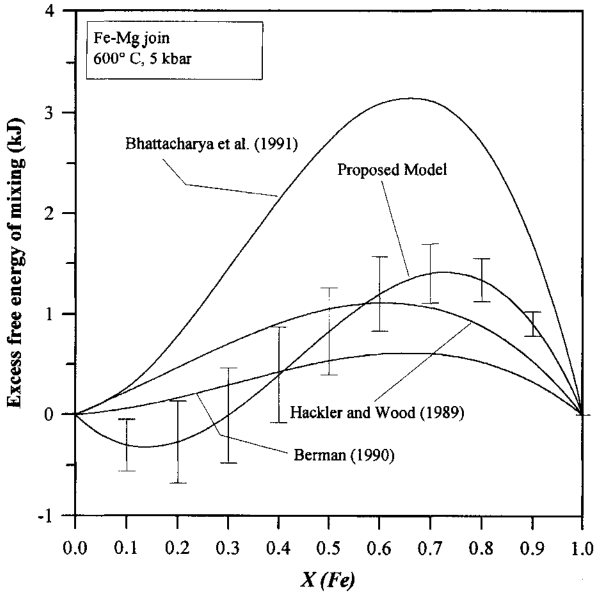

**FIGURE 9.** Excess free energy of mixing in the Fe-Mg solid solution of garnet at 600 °C and 5 kbar. The uncertainties associated with the proposed model were calculated from 2$\sigma$ errors (Table 7).

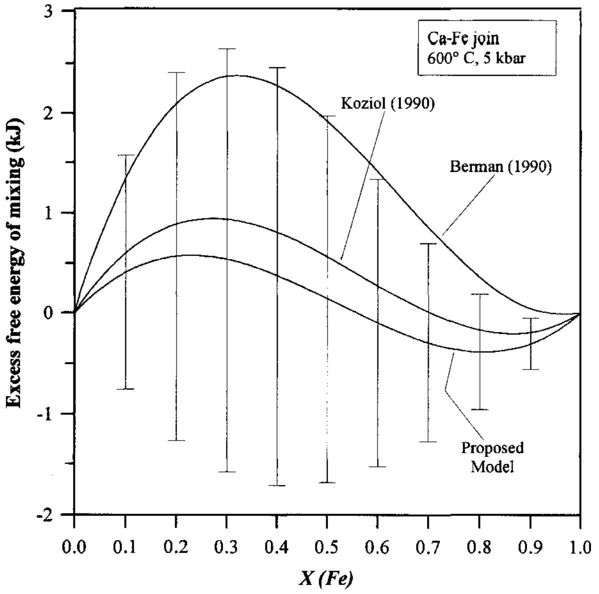

**FIGURE 11.** Excess free energy of mixing in the Ca-Fe solid solution of garnet at 600 °C and 5 kbar. The uncertainties associated with the proposed model were calculated from 2$\sigma$ errors (Table 7). Note the large uncertainties in this join.

dition. Consideration of only binary phase-equilibrium data along this join resulted in a somewhat symmetric regular-solution model because of the very restricted range of garnet compositions used in these experiments. Although usage of the ternary data considerably improved the overall model, uncertainty toward the Ca-rich end of this join may still be a problem with thermodynamics of mixing in a garnet solid solution. However, encouraging results were obtained with the phase-equilibrium data of Gasparik (1984), which involved Ca-rich garnet (discussed above).

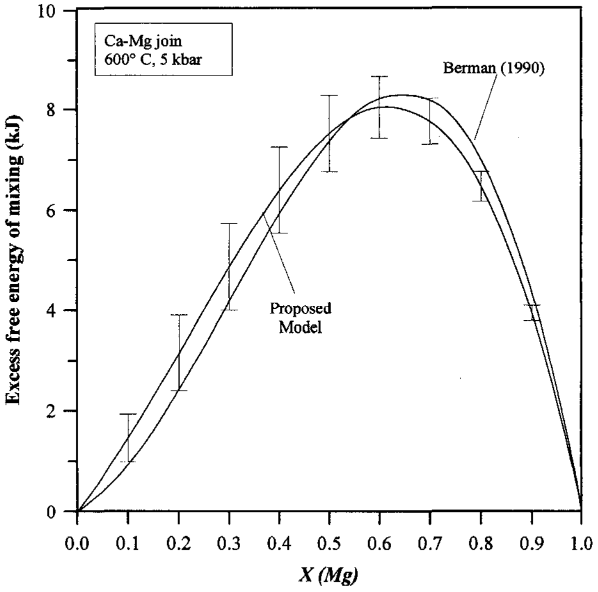

**FIGURE 10.** Excess free energy of mixing in the Ca-Mg solid solution of garnet at 600 °C and 5 kbar. The uncertainties associated with the proposed model were calculated from 2$\sigma$ errors (Table 7).

Koziol (1990) suggested nearly ideal mixing behavior of garnet along the Fe-Ca join ($W_{CaFe} = -3.27$ kJ/mol and $W_{FeCa} = 7.77$ kJ/mol). Taking ternary data into consideration makes a significant difference toward the Ca-rich side of the join (Fig. 11). On the basis of the experimental data of Bohlen and Liotta (1986), Berman (1990) proposed a small excess entropy of mixing along this join. We previously noted the overall discrepancy of this set of experiments with all the models. GASP data are far superior to those of Bohlen and Liotta (1986) in terms of compositional variability of garnet. Thus, our analyses have better determined the excess entropy of mixing along this join.

## ACKNOWLEDGMENTS

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