

Ternary excess properties of grossular-pyrope-almandine garnet and their influence in geothermobarometry

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ABSTRACT

The reversed phase equilibrium data of Koziol and Newton (1989) involving grossular (Gr)–pyrope (Py)–almandine (Alm) solid solutions have been analyzed in conjunction with standard state thermodynamic data of Berman (1988) in order to constrain ternary mixing properties for this system. The experimental data are consistent with a single P - T independent ternary interaction parameter, although its magnitude cannot be fixed independently of binary mixing properties. Sensitivity analysis of ternary excess properties to assumed binary interactions offers support for small excess enthalpy and entropy on the Gr-Alm join (Geiger et al., 1987; Koziol, 1990; Berman, 1990), in contrast to calibrations (Ganguly and Saxena, 1984; Anovitz and Essene, 1987) based on the phase equilibrium data of Cressey et al. (1978). The ternary data are consistent with the strongly nonideal Py-Alm parameters of Ganguly and Saxena's (1984) preferred model only when a more positive ternary excess parameter is used than proposed by Ganguly and Saxena (-15 compared to -66.5 kJ/mol on a 12 O atom basis). The experimental data are most compatible, however, with small nonideality on the Py-Alm join. The Py-Alm calibrations of Hackler and Wood (1989), Sack and Ghiorso (1989), and Berman (1990) are consistent with a ternary interaction parameter equal to zero.

The strong influence of the ternary Gr-Py-Alm interaction parameter in thermobarometry calculations is illustrated for several granulites. These calculations indicate that the ideal ternary interaction parameter consistent with available experimental data produces pressures that are lower by as much as 2.4 kbar compared with those computed with the ternary interaction parameter equal to -66.5 kJ/mol. Temperatures differ by as much as 120 °C, with the direction of difference being dependent on specific garnet composition.

INTRODUCTION

Accurate description of garnet activity-composition relations is important in thermobarometric and P - T -time calculations because garnet occurs in a wide range of bulk compositions and over a wide range of metamorphic grades. Most theoretical studies of garnet mixing properties have focused on calibration of binary interactions, assuming that ternary interactions contribute no additional nonideality (e.g., Newton and Haselton, 1981; Hodges and Spear, 1982; Wood, 1987; Berman, 1990). Ganguly and Saxena (1984), however, proposed significant ternary excess parameters from optimization of aluminosilicate polymorph occurrences, with pressures computed with the equilibrium $3 \text{ An} = \text{Gr} + 2 \text{ Ky} + \text{Qz}$, and this feature has been incorporated in some recent calibrations of important barometers (Anovitz and Essene, 1987; Moecher et al., 1988). Several authors (e.g.,

Ganguly and Saxena, 1984; Perkins and Chipera, 1985; Moecher et al., 1988) have noted that, for low-entropy equilibria, many of which are used commonly for the purpose of geobarometry, the difference between ideal and nonideal ternary interactions translates to significant differences in calculated pressures. For this reason, it is imperative to define the nature of ternary garnet interactions.

Koziol and Newton (1989) recently determined important limits on grossular activity in ternary Gr-Py-Alm garnets from reversed experimental data on the displacement of the equilibrium $3 \text{ An} = \text{Gr} + 2 \text{ Ky} + \text{Qz}$ by garnet solid solution. Within the confines of various assumptions about the nature of binary garnet interactions, regression analysis led to the conclusion that their data could not be represented adequately with a single composition-independent ternary interaction parameter, and they presented an empirical model for grossular activity in ternary Gr-Py-Alm garnets. The purpose of the present paper is to evaluate Gr-Py-Alm garnet mixing properties on the basis of Koziol and Newton's (1989) data, using a mathematical technique that allows one to examine both

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TABLE 1. Garnet solution properties (three-site basis) taken from Berman (1990)

Parameter	*	W_H (J/mol)	W_S (J/mol·K)	W_V (J/bar)
Equation 1				
112	21	21560	18.79	0.10
122	12	69200	18.79	0.10
113	31	20320	5.08	0.17
133	13	2620	5.08	0.09
223	32	230		0.01
233	23	3720		0.06
123	0	0	0	

Note: The tabulated ternary constant is to be used with Equation 4; the ternary constant for use with Equations 1 and 2 is given by Equation 3: $W_{123} = 58825$; $W_{S123} = 23.87$; $W_{V123} = 0.265$. Component order: 1 = Gr; 2 = Py; 3 = Alm.

* Parameter notation following Wohl (1946).

the sensitivity of the results to different assumptions about binary garnet mixing properties as well as the constraints the ternary data place on these binary mixing properties. Second, this study will provide garnet solution properties that are internally consistent with the thermodynamic data for end-member minerals given by Berman (1988, 1990). Last, the implications of the inferred garnet ternary mixing properties for thermobarometry are examined.

EQUATIONS FOR MULTICOMPONENT SOLUTIONS

The present study utilizes the form of the general excess equations (Eqs. 9 and 22) derived by Berman and Brown (1984) for multicomponent solutions. For a third-degree polynomial (asymmetric excess model), the activity coefficient of the m th component is calculated from (Berman, 1990):

$$nRT \ln \gamma_m = \sum^p W_{ijk} (Q_m X_i X_j X_k / X_m - 2X_i X_j X_k) \quad (1)$$

where each W refers to $W_G = W_H - TW_S + PW_V$, Q_m is a term that sums how many of the ijk subscripts are equal to m , n is the number of sites on which mixing occurs, and p is equal to the number of excess parameters needed for a given system. This number and the identity of the parameters in a given component system represent all possible permutations of the three subscripts without all three being the same. For the specific case of the ternary garnet solution considered in this paper, Equation 1 expands to

$$RT \ln \gamma_{Gr} = W_{112}(2X_1X_2 - 2X_1^2X_2) + W_{122}(X_2^2 - 2X_1X_2^2) + W_{113}(2X_1X_3 - 2X_1^2X_3) + W_{133}(X_3^2 - 2X_1X_3^2) + W_{223}(-2X_2^2X_3) + W_{233}(-2X_2X_3^2) + W_{123}(X_2X_3 - 2X_1X_2X_3) \quad (2)$$

where the subscripts 1, 2, and 3 refer to the components grossular, pyrope, and almandine. The relationship between this subscript notation and that given by Wohl (1946, 1953) is given in Table 1.

The derivation of Equations 1 and 2 implies a specific relationship between binary and ternary power series co-

efficients (Anderson and Lindsley, 1981; Helffrich and Wood, 1989). For systems with more than two components, it is therefore more appropriate to use the excess equation suggested by Wohl (1953) and independently derived by Anderson and Lindsley (1981). The Wohl equation can be recast in the more compact form of the excess Equation 1, above, by making the substitution

$$W_{ijk} = (W_{ij} + W_{ij} + W_{ik} + W_{ikk} + W_{jik} + W_{jkk})/2 - C_{ijk} \quad (3)$$

where C_{ijk} is referred to here as the Wohl ternary interaction parameter. Substitution of Equation 3 into Equation 2 yields the following expression for γ_{Gr} written explicitly in terms of the Wohl ternary interaction parameter:

$$RT \ln \gamma_{Gr} = W_{112}[2X_1X_2 - 2X_1^2X_2 + (0.5 - X_1)(X_2X_3)] + W_{122}[X_2^2 - 2X_1X_2^2 + (0.5 - X_1)(X_2X_3)] + W_{113}[2X_1X_3 - 2X_1^2X_3 + (0.5 - X_1)(X_2X_3)] + W_{133}[X_3^2 - 2X_1X_3^2 + (0.5 - X_1)(X_2X_3)] + W_{223}[0.5 - X_1 - 2X_2]X_2X_3 + W_{233}[0.5 - X_1 - 2X_3]X_2X_3 + C_{123}[X_2X_3(2X_1 - 1)]. \quad (4)$$

Note that $X_1 + X_2 + X_3 = 1$; Equation 4 can be rearranged to yield Equation 54a of Wohl (1953) or the ternary equivalent of Equation 6 of Helffrich and Wood (1989), although the ternary constant in the latter equation is of opposite sign. The general Equations 1 and 3 are recommended because they are compact and easy to remember.

METHODOLOGY

The technique of mathematical programming (Berman et al., 1986) has been used to analyze the phase equilibrium data of Koziol and Newton (1989). Each half-bracket on the position of the equilibrium $3An = Gr + 2Ky + Qz$ is cast as an inequality constraint on the Gibbs free energy of reaction, with the directional sense of the inequality constraint reflecting the side from which the equilibrium has been approached:

$$\Delta_r G \leq 0. \quad (5)$$

If garnet is the only phase that exhibits solid solution in the experiment, this can be expanded (for a three-site formula) to

$$\Delta_r G^0 + 3RT \ln \gamma_{Gr} + 3RT \ln X_{Gr} \leq 0. \quad (6)$$

Upon rearrangement, it can be seen that each experiment offers direct linear constraints on the set of Margules parameters used to represent the activity coefficient term if the standard state properties are treated as known and X_{Gr} are obtained from each experiment:

$$W'X' \leq -\Delta_r G^0 - 3RT \ln X_{Gr} \quad (7)$$

where W' represents the set of Margules parameters and X' the sum of all mole fraction coefficients resulting from substitution of Equation 1. If there are no contradictory experimental data, the system of linear inequalities bounds

a feasible region that contains all possible solutions consistent with these data. An objective function maximizing or minimizing some combination of variables is used to obtain a unique solution from within the feasible solution.

Advantages of the mathematical programming approach have been discussed in detail by Berman et al. (1986) and Berman and Brown (1987). With respect to the present analysis, there are two major advantages. First, the exploration of the thermodynamic constraints provided by any experimental data can be achieved because uncertainties in pressure and temperature and in determining compositions of experimental products can be explicitly incorporated. Thus, each constraint relation (Eq. 7) is written not with the nominal experimentally determined values, but with pressure, temperature, and compositions adjusted for estimated uncertainties (± 0.3 kbar, ± 10 °C, and $\pm 0.008 X_{Gr}$). Second, the sensitivity of the results to various assumptions about binary mixing properties can be analyzed conveniently by mapping out the feasible solution space, with appropriate manipulation of the objective function.

The thermodynamic activity of a mineral component can be calculated from the difference between the position of a univariant equilibrium with the end-member mineral and with the solid solution. In this study, preference is given to the position of the end-member equilibrium $3 \text{ An} = \text{Gr} + 2 \text{ Ky} + \text{Qz}$ calculated with the thermodynamic data of Berman (1988, 1990) rather than given by the experimental data of Koziol and Newton (1988) because one of the goals of this study of ternary garnet mixing properties, combined with an analysis of binary mixing properties (Berman, 1990), is to provide internal consistency between garnet solution properties and thermodynamic data for end-member minerals. Such consistency between end-member and solution properties must be established for meaningful applications to natural assemblages.

The position of the equilibrium $3 \text{ An} = \text{Gr} + 2 \text{ Ky} + \text{Qz}$, computed with the thermodynamic data of Berman (1988), agrees with the overall distribution of Koziol and Newton's (1988) experimental reversals (adjusted down in pressure by 0.2 kbar to account for their estimation of friction effects in $\frac{3}{4}$ in. NaCl pressure assemblies), although the computed curve is displaced to the low-pressure uncertainty limit (0.3 kbar) of the brackets at 950 and 1050 °C. If these differences indicate experimental difficulties, they may suggest slightly greater friction effects than estimated by Koziol and Newton or an upward displacement of the equilibrium caused by incorporation of small amounts of Li (from the Li_2MoO_4 flux) into the feldspar structure. The former possibility has been ignored in the following analysis because the friction effects should be smaller at the lower pressures of the displaced equilibrium experiments. Koziol and Newton (1989) suggest that feldspars in their experiments incorporate 3–4 mol% $\text{LiAlSi}_3\text{O}_8$. Thermodynamic calculations indicate that this amount of ideal solution would shift the equi-

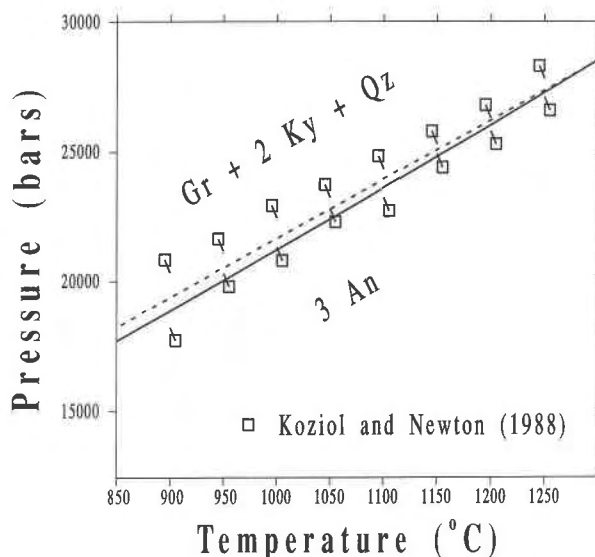


Fig. 1. Comparison of the experimental brackets of Koziol and Newton (1988) for the equilibrium $3 \text{ An} = \text{Gr} + 2 \text{ Ky} + \text{Qz}$ with its position calculated with the thermodynamic data of Berman (1988). Dashed line corresponds to Equation 5a of Koziol and Newton (1988). Symbols represent location of experiments after adjustment of nominal values (end of lines) for P - T uncertainties and the 0.2 kbar friction correction suggested by Koziol and Newton.

librium upward by 0.2 kbar. Therefore, in this analysis of the data of Koziol and Newton (1989), all brackets have been adjusted downward by 0.2 kbar in addition to the 0.2 kbar friction correction recommended by Koziol and Newton.

At 1000 and 900 °C (the temperatures at which the ternary garnet data were gathered), the computed curve lies 0.5–0.6 kbar below the curve best fitted to Koziol and Newton's (1988) data (Fig. 1), but it is still within their brackets. Because of this difference, activity coefficients derived in this study are systematically larger than those derived by Koziol and Newton (1989).

RESULTS

Experiments on the displaced equilibrium $3 \text{ An} = \text{Gr} + 2 \text{ Ky} + \text{Qz}$ give a measure of the activity coefficient of grossular in garnet that can be calculated for a ternary garnet solution with Equation 4. Inspection of Equation 4 shows that any experimental constraints on $RT \ln \gamma_{Gr}$ cannot define the ternary interaction parameter, C_{123} , independent of the binary interactions. In the context of the data of Koziol and Newton (1989), which are concentrated in almandine-rich compositions ($0.12 < X_{Gr} < 0.45$, $0.10 < X_{Py} < 0.5$, $0.45 < X_{Alm} < 0.80$), results are most sensitive to assumed interactions on the Gr-Alm and Py-Alm binaries, and any error in these binary calibrations is transferred to the ternary parameter. Since the mole fraction coefficient for C_{123} , $X_{Py}X_{Alm}(2X_{Gr} - 1)$, is largest when X_{Gr} is smallest, calibration of the ternary parameter is most dependent on the experimental data

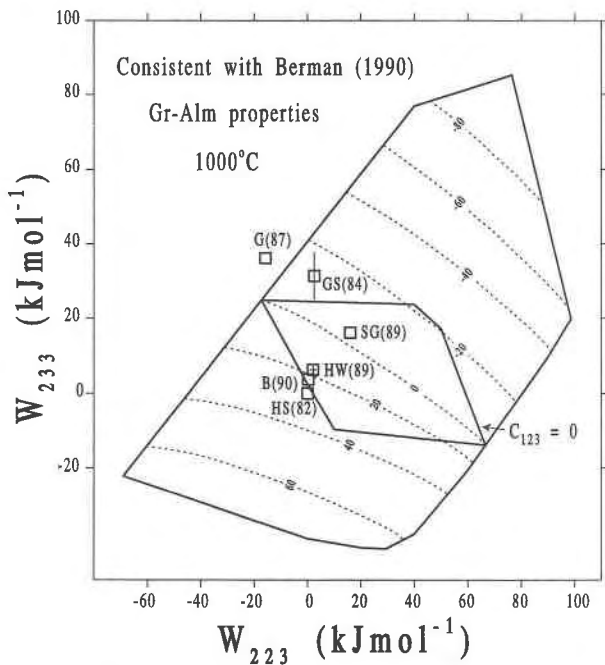


Fig. 2. The range of excess free energy parameters at 1000 °C on the Py-Alm join that are consistent with the ternary phase equilibrium data of Koziol and Newton (1989) assuming the Gr-Py and Gr-Alm model parameters of Berman (1990). Outer polygon is the feasible solution space with the ternary interaction parameter unconstrained. Inner polygon is the feasible solution space with $C_{123} = 0$. Dashed curves are approximate contours of the ternary interaction parameter. Proposed binary mixing parameters: HS(82) = Hodges and Spear (1982); GS(84) = Ganguly and Saxena (1984); G(87) = Geiger et al. (1987); HW(89) = Hackler and Wood (1989); SG(89) = Sack and Ghiorso (1989); B(90) = Berman (1990).

nearest to the Py-Alm binary join, as noted by Ganguly and Saxena (1984, 1987).

Koziol and Newton (1989) observed that a single composition-independent ternary parameter could not account for their ternary phase equilibrium data when the properties of the Gr-Alm and Py-Alm joins were fixed by the calorimetric calibrations of Geiger et al. (1987). Instead, C_{123} varied with Mg/(Mg + Fe), becoming most negative in Fe-rich compositions. They noted that this dependence of C_{123} on the Mg ratio was reduced but did not disappear by assuming that the Py-Alm join was ideal. These problems led Koziol and Newton to formulate an empirical model for the calculation of γ_{Gr} .

The present mathematical programming analysis of Koziol and Newton's (1989) data supports their observation that a single ternary interaction parameter cannot represent their data with the calorimetric calibrations of the Gr-Alm and Py-Alm binaries (Geiger et al., 1987). An inconsistent solution is also obtained when the binary parameters of Ganguly and Saxena (1984) are used. In contrast to calibrations that have large asymmetric non-ideal mixing on the Py-Alm join, when Py-Alm nonideal-

ity is zero (Hodges and Spear, 1982) or small (Berman and Brown, 1988; Berman, 1990), feasible solutions are obtained. This difference from the modeling results reported by Koziol and Newton stems most importantly from differences in the assumed binary mixing properties but also from the explicit incorporation of compositional uncertainties into the present analysis (see above). The results described above are not sensitive to various calibrations of the Gr-Py join (e.g., Ganguly and Kennedy, 1974; Newton and Haselton, 1981; Wood, 1988; Berman, 1990).

Dependence of ternary interaction parameter to assumed binary mixing properties

In view of the observation that a single ternary interaction parameter can be calibrated successfully with certain models of the component binary systems, it is important to explore this dependence in greater detail with an eye to investigating the extent to which the ternary data can be used to corroborate or constrain models for the binary systems. To test the range of parameter values for each binary system that is consistent with the ternary phase equilibrium data, it is necessary to hold mixing parameters for the other two binaries constant (see Eq. 4). In the calculations that follow, the binary calibrations of Berman (1990) are used, as these are most compatible with what we believe to be the most reliable experimental and thermodynamic data. The effects of assuming alternate binary calibrations are discussed. We will first examine the data in the Py-Alm system, followed by the Gr-Alm system.

Results for the Py-Alm system are summarized in Figure 2. Using the calibration of Berman (1990) for the Gr-Alm and Gr-Py binaries (Table 1), a wide range in excess properties for the Py-Alm system is possible (solid outer line). Only the Py-Alm mixing parameters proposed by Geiger et al. (1987) on the basis of enthalpy of solution data are inconsistent with these broad constraints. The magnitude of the ternary interaction coefficient, C_{123} (contours in Fig. 2), is inversely correlated with the values of the W_{223} and W_{233} binary parameters, with the most negative C_{123} associated with the most positive binary parameters. A much smaller range of binary parameters is consistent with $C_{123} = 0$ (inner polygon in Fig. 2). With the above assumptions regarding the Gr-Alm and Gr-Py binaries, the mixing parameters for the Py-Alm system proposed by Hackler and Wood (1989), Sack and Ghiorso (1989), and Berman (1990) are compatible whereas the calibrations of Hodges and Spear (1982), Ganguly and Saxena (1984), and Geiger et al. (1987) are not.

As might be expected, the results for the Py-Alm excess properties are sensitive to the assumed mixing properties on the other binary joins, particularly the Gr-Alm join. For example, the Hodges and Spear (1982) calibration is entirely consistent with $C_{123} = 0$, but their assumption of ideal mixing on the Gr-Alm join is strongly at odds with calorimetric (Geiger et al., 1987) and phase equilibrium (Cressey et al., 1978; Koziol and Newton, 1989) constraints.

Other calibrations proposed for the Gr-Alm join are plotted in Figure 3, along with the range in Gr-Alm mixing parameters that are consistent with the ternary phase equilibrium data of Koziol and Newton (1989) assuming the mixing parameters for the Py-Alm and Gr-Py joins suggested by Berman (1990). The inner polygon outlines the range of binary mixing parameters consistent with $C_{123} = 0$. The ternary phase equilibrium data clearly discriminate against the large excess free energies of mixing on the Gr-Alm join proposed by Ganguly and Saxena (1984) and more recently by Anovitz and Essene (1987), both of which were based primarily on analysis of the displaced phase equilibrium data of Cressey et al. (1978). On the other hand, the ternary data are compatible with the mixing parameters calculated by Geiger et al. (1987) on the basis of calorimetric data and by Koziol (1990) and Berman (1990) from analysis of the phase equilibrium data of Koziol (1990). These latter three calibrations are also consistent with $C_{123} = 0$.

The calibrations of Ganguly and Saxena (1984) and Anovitz and Essene (1987) invoke large symmetric excess entropy on the Gr-Alm join. The latter authors deduced this model from consideration of the phase equilibrium data of Cressey et al. (1978) together with Geiger et al.'s (1987) enthalpy of solution data. If the Gr-Alm enthalpy data of Geiger et al. are accepted, symmetric excess entropy on this join must be less than about 10 J/mol·K to stay within the feasible region defined by the ternary phase equilibrium data (Fig. 3). This conclusion supports the zero excess entropy suggested by Geiger et al. (1987) and Koziol (1990), as well as the small excess entropy (5.08 J/mol·K) deduced by Berman (1990) from an analysis of the phase equilibrium data of Koziol (1990), Bohlen et al. (1983), and Bohlen and Liotta (1986).

The feasible region of Figure 3 shifts to more positive excess parameters when the Py-Alm parameters ($W_{223} = 36.17$; $W_{233} = -15.76$ kJ/mol) of Geiger et al. (1987) are used (upper polygon in Fig. 3) instead of those of Berman (1990), reflecting the positive correlation between the Gr-Alm and Py-Alm parameters in Equation 4. In contrast to the previously discussed results, none of the proposed Gr-Alm calibrations is compatible with Koziol and Newton's ternary data and these parameters for the Py-Alm join. When the Py-Alm properties of Ganguly and Saxena (1984) are used, the feasible region is shifted to a lesser extent so that it encompasses the Gr-Alm mixing properties of Koziol (1990) and Berman (1990) but narrowly excludes those of Geiger et al. (1987). These results indicate that the ternary phase equilibrium data are most compatible with small deviations from ideality on the Py-Alm join given, for example, by the calibrations of Hodges and Spear (1982), Hackler and Wood (1989), and Berman (1990).

DISCUSSION

The mathematical programming analysis discussed above demonstrates that displaced phase equilibrium data of Koziol and Newton (1989) are consistent with a single ternary interaction parameter only for specific ranges in

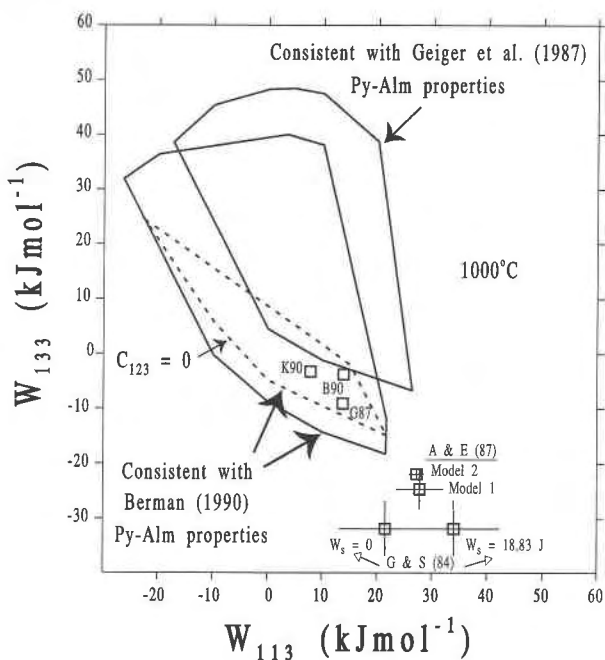


Fig. 3. The range of excess free energy parameters at 1000 °C on the Gr-Alm join that are consistent with the ternary phase equilibrium data of Koziol and Newton (1989), assuming the Gr-Py and Py-Alm model parameters of Berman (1990). Upper polygon shows the effect of using the Py-Alm model of Geiger et al. (1987). Outer polygons are feasible solution spaces with the ternary interaction parameter unconstrained. Dashed inner polygon is the feasible solution space with $C_{123} = 0$. Note that only the Gr-Alm calibrations of Geiger et al. (1987, G87), Koziol (1990, K90), and Berman (1990, B90) are consistent with the ternary data. Other Gr-Alm mixing properties are: A & E (87) = Anovitz and Essene (1987); G & S (84) = Ganguly and Saxena (1984). If available, uncertainties are shown.

the mixing properties of the Py-Alm and Gr-Alm binary systems. Although the exact magnitude of this interaction parameter cannot be fixed without fixing all binary mixing properties, the added constraints provided by the ternary data clearly support calibrations of the Gr-Alm join with small excess free energies of mixing (Geiger et al., 1987; Koziol, 1990; Berman, 1990) but cannot discriminate between them. For the Py-Alm join, the ternary data are consistent with a range of mixing properties, although they are most compatible with small nonideality (e.g., Hodges and Spear, 1982; Hackler and Wood, 1989; Berman, 1990). The last set of parameters, reproduced in Table 1, is consistent with a range in C_{123} values between -0.8 and 30.1 kJ/mol. Until more data become available to allow further refinement, $C_{123} = 0$ is assumed. This value is considerably more positive than proposed by Ganguly and Saxena (1984) for both their preferred binary parameters (-66.5 kJ/mol) and their calculations assuming ideal Py-Alm mixing (-31.4 kJ/mol), and it is also more positive than that which is consistent with their preferred Py-Alm properties and the ternary phase equilibrium data (Fig. 2).

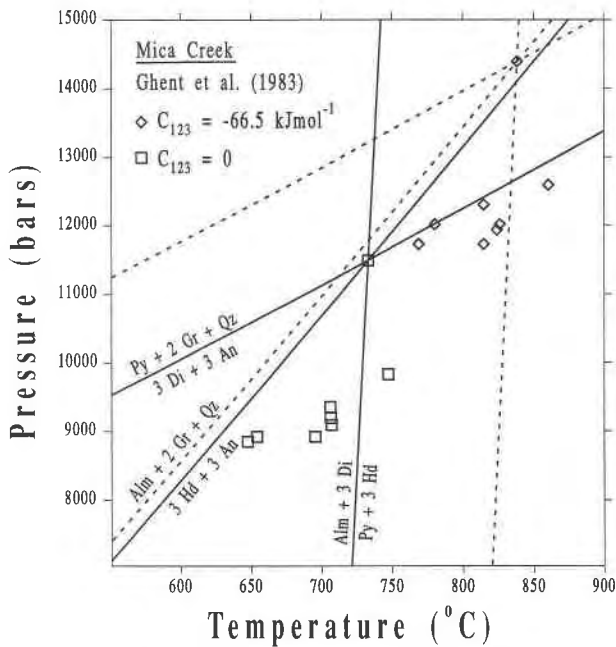


Fig. 4. Comparison of pressures and temperatures computed from the intersection of the Di, Hd, and garnet-clinopyroxene equilibria for metabasites from Mica Creek, British Columbia (Ghent et al., 1983). Solid curves and squares show intersections with Table 1 garnet properties ($C_{123} = 0$). Dashed curves and diamonds were computed with Table 1 parameters except for $C_{123} = -66.5$ kJ/mol. See text for discussion.

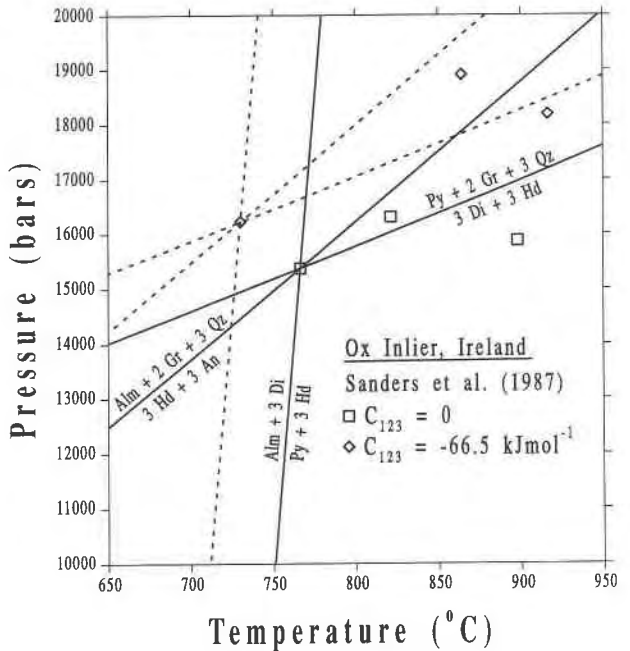


Fig. 5. Comparison of pressures and temperatures computed from the intersection of the Di, Hd, and garnet-clinopyroxene equilibria for gneisses from northeast Ox Inlier, Ireland (Sanders et al., 1987). Solid curves and squares show intersections with Table 1 garnet properties ($C_{123} = 0$). Dashed curves and diamonds were computed with Table 1 properties except for $C_{123} = -66.5$ kJ/mol. See text for discussion.

Jordan et al. (1950) reported a technique for estimation of ternary interaction parameters. With this technique C_{123} is computed by $C_{123} = [(W_{112} - W_{122}) + (W_{133} - W_{113}) + (W_{223} - W_{233})]/2$ and can change sign depending on the choice of components 2 and 3. Ganguly and Saxena's (1984) optimization of GASP barometry with aluminosilicate polymorph occurrences produced $C_{123} = -66.5$ kJ/mol, in good agreement with this estimation scheme using their preferred binary parameters. More recently, Ganguly and Saxena (1987) have urged extreme caution in applying this estimation scheme, a point supported by Helffrich and Wood (1989). The present analysis displays the inadequacy of the above estimation scheme, with the value of C_{123} (± 34.4 kJ/mol) predicted using the properties for garnet in Table 1 being outside the range that is consistent with Koziol and Newton's ternary phase equilibrium data. In contrast, the Wohl equation (Eq. 4) with $C_{123} = 0$ is consistent with these phase equilibrium data. These results demonstrate the success of Wohl's (1953) equation, which was derived to permit "a better founded prediction of the behavior of ternary systems from that of the three binary pairs" (Wohl, 1953, p. 218).

APPLICATIONS

Although the experimental data of Koziol and Newton (1989) constrain only the grossular activity coefficient,

the use of the Margules equation in this calibration of the Gr-Py-Alm garnet mixing parameter also allows the effect of the ternary interaction coefficient on the pyrope and almandine activity coefficients to be computed. This has important consequences for petrological calculations because each of these garnet end-members is involved in a wide range of commonly used geothermometers and barometers.

Ganguly and Saxena (1984) utilized the influence of the Gr-Py-Alm garnet interaction parameter in their empirical calibration of the garnet-aluminosilicate-quartz-plagioclase (GASP) barometer. Optimum agreement of GASP pressures with aluminosilicate polymorph occurrences was found with $C_{123} = -66.5$ kJ/mol, using their preferred Mg-Fe garnet mixing properties. In their calibration of garnet-orthopyroxene-plagioclase-quartz barometers, Perkins and Chipera (1985) noted, however, that use of ternary interaction parameters with Ganguly and Saxena's (1984) binary garnet mixing parameters produced significantly worse results. Our analysis of Koziol and Newton's phase equilibrium data indicates that the Gr-Py-Alm interaction parameter is indeed small, supporting Perkins and Chipera's (1985) calculations.

Because $RT \ln \gamma_i$ is dependent on $C_{123}(2X_i - 1)$ through combination of Equations 1 and 3, the calibration of $C_{123} = 0$ compared with -66.5 kJ/mol (Ganguly and Saxena, 1984) leads to activity coefficients that are smaller when

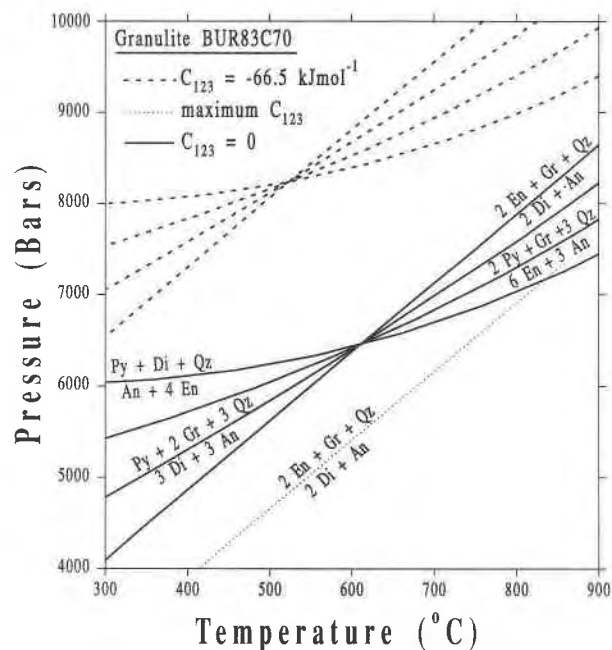


Fig. 6. Comparison of four geobarometers computed for granulite BUR83C70 (Anovitz and Essene, 1990) with the binary mixing parameters in Table 1 and $C_{123} = 0$ (solid curves) vs. $C_{123} = -66.5$ kJ/mol (dashed curves). The light dotted curve shows the position of one equilibrium computed with $C_{123} = 34.4$ kJ/mol (the upper limit compatible with the ternary phase equilibrium data of Koziol and Newton, 1989) and the binary garnet mixing parameters of Berman (1990).

$X_i < 0.5$ and larger when $X_i > 0.5$, differences that are greatest when X_i is furthest from 0.5. For many geobarometers (see below) that have garnet components with $X_i < 0.5$ on the high-pressure side of equilibria, the smaller activity coefficients computed with $C_{123} = 0$ produce significantly lower pressures, particularly for low-entropy reactions that are extremely sensitive to perturbations of the parameters of the model. For Fe-Mg exchange thermometers, the influence of the ternary interaction parameter is most profound in extremely ferroan ($X_{Alm} \gg 0.5$, $X_{Py} \ll 0.5$) or extremely magnesian ($X_{Py} \gg 0.5$, $X_{Alm} \ll 0.5$) bulk compositions because the changes of γ_{Alm} and γ_{Py} in opposite directions reinforce each other. To illustrate these systematics, the examples summarized below compare calculations using the binary garnet mixing parameters of Berman (1990) with either $C_{123} = 0$ or $C_{123} = -66.5$ kJ/mol. It should be noted, however, that Ganguly and Saxena (1984) calibrated the latter value using highly asymmetric Mg-Fe mixing parameters recommended for successful application to garnets with $X_{Alm} > 0.75$; they reported that a value of $C_{123} = -31.38$ kJ/mol was more appropriate for calculations assuming ideal Mg-Fe mixing. The effect of the smaller ternary interaction parameter can be estimated visually on Figures 4–7 by points approximately halfway between those calculated with $C_{123} = 0$ and $C_{123} = -66.5$ kJ/mol. The general effect of as-

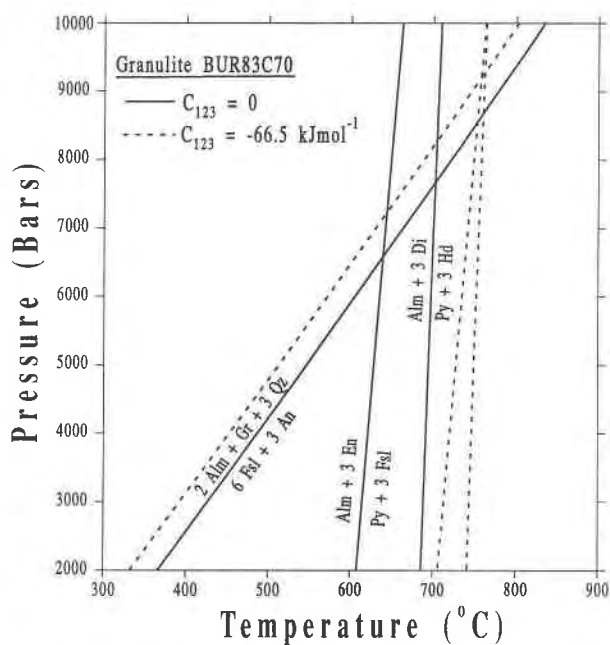


Fig. 7. Comparison of equilibria computed for granulite BUR83C70 (Anovitz and Essene, 1990) with Table 1 binary mixing parameters and $C_{123} = 0$ (solid curves) vs. $C_{123} = -66.5$ kJ/mol (dashed curves).

suming the asymmetric Py-Alm mixing properties of Ganguly and Saxena (1984) in the following comparisons is to moderate the pressure differences but to amplify temperature differences.

Mica Creek, British Columbia

The initial thermodynamic calibration by Newton and Perkins (1982) of the equilibrium diopside + anorthite = grossular + pyrope + quartz predicted pressures that required an empirical correction of +2.2 kbar to give results similar to other geobarometers. Recently Moecher et al. (1988) have undertaken a recalibration of this barometer (Di) as well as the Fe equivalent of the equilibrium (Hd) hedenbergite + anorthite = grossular + almandine + quartz using the Ganguly and Saxena (1984) quaternary garnet solution parameters with the Gr-Alm parameters of Anovitz and Essene (1987). In general, these calibrations lead to quite reasonable agreement in pressures computed with the Di and Hd equilibria compared with the equilibrium (Fs) ferrosilite + anorthite = grossular + almandine + quartz and compared to constraints imposed by the kyanite + sillimanite equilibrium. A notable exception involves sillimanite zone metabasites from Mica Creek, British Columbia (Ghent et al., 1983), for which Moecher et al. (1988) computed average pressures of 10.5 ± 0.6 and 9.8 ± 0.9 kbar with the Di and Hd equilibria, respectively. They note, however, that the proximity of the kyanite-sillimanite and garnet-clinopyroxene isograds places a maximum pressure constraint of 7.8 ± 1 kbar at an upper temperature limit of 700 °C

computed with the garnet + clinopyroxene equilibrium diopside + almandine = hedenbergite + pyrope. To illustrate the influence of the ternary garnet interaction parameter in thermobarometric results, P - T results for the Mica Creek samples have been computed with standard-state thermodynamic data from Berman (1988, 1990, and unpublished data for hedenbergite) combined with the activity models of Fuhrman and Lindsley (1988) for plagioclase, Newton (1983) for ortho- and clinopyroxene, and Berman (1990) with $C_{123} = 0$ for garnet (solid curves and squares in Fig. 4). Garnet-clinopyroxene temperatures range between 650 and 750 °C. Average pressures at 650 °C, the temperature used by Ghent et al. (1983), are 9.0 and 8.4 kbar for the Di and Hd equilibria. When $C_{123} = -66.5$ kJ/mol is used with the same binary garnet parameters, the results are shifted systematically to higher pressures and temperatures (dotted curves and diamonds in Fig. 4): average pressures are shifted to 10.9 and 8.7 kbar for the Di and Hd equilibria, and temperatures are shifted to 770–870 °C. Although the discrepancy with the upper pressure constraint (6.9 kbar at 650 °C, calculated with the data of Berman, 1988) imposed by the occurrence of sillimanite in these samples still remains, the above comparisons clearly show the large effect of the present calibration of $C_{123} = 0$ in producing temperatures that are 100–120 °C lower and pressures that average 1.9 and 0.3 kbar lower with the Di and Hd barometers. The larger effect on the Di barometer reflects the Mica Creek garnet compositions with $X_{\text{Py}} \ll 0.5$ and X_{Alm} close to 0.5, so that the decrease in γ_{Gr} caused by $C_{123} = 0$ relative to $C_{123} = -66.5$ kJ/mol is reinforced by a large decrease in γ_{Py} and a small change in γ_{Alm} .

Ox Inlier, Ireland

Figure 5 illustrates results for gneisses from the northeast Ox Inlier, Ireland (discussed recently by Sanders et al., 1987) that are more magnesian in bulk composition ($0.35 < X_{\text{Py}} < 0.46$; $0.26 < X_{\text{Alm}} < 0.41$). In these samples with both X_{Py} and $X_{\text{Alm}} < 0.5$, the calculated temperature differences with $C_{123} = 0$ and $C_{123} = -66.5$ kJ/mol are much smaller since both γ_{Py} and γ_{Alm} increase and partly cancel in the garnet-clinopyroxene exchange equilibrium. In contrast to the Mica Creek samples, γ_{Alm} increases more than γ_{Py} because $X_{\text{Alm}} < X_{\text{Py}}$, producing higher temperatures with $C_{123} = 0$. Average pressures computed with $C_{123} = 0$ are about 1.3 and 1.8 kbar lower for the Di and Hd equilibria, respectively.

Algonquin Park, Ontario

As a last example, Figure 6 summarizes the effects of the Gr-Py-Alm interaction parameter on pressures computed for a granulite (no. BUR83C70) from Algonquin Park, Ontario, reported by Anovitz and Essene (1990). Four equilibria can be used as geobarometers for the reported garnet + plagioclase + orthopyroxene + clinopyroxene + quartz assemblage in the system MgO-CaO-Al₂O₃-SiO₂. Only two of the equilibria are independent, intersecting at 6.5 kbar and 615 °C when $C_{123} = 0$ is used

(solid curves). When $C_{123} = -66.5$ kJ/mol is assumed along with the same set of binary mixing parameters, the curves (dashed in Fig. 6) move upward by 2 to 2.4 kbar, intersecting at 8.2 kbar and 525 °C. For the BUR83C70 garnet composition of Gr₁₈Py₁₉Alm₆₀Sp₀₃, γ_{Gr} and γ_{Py} equal 1.32 and 1.29 with the Table 1 properties, compared with 1.64 and 1.57 with the same model incorporating $C_{123} = -66.5$ kJ/mol. The difference of 30% in pressure that is directly attributable to the influence of the ternary interaction coefficient (Fig. 6) clearly has important implications when the barometric data are used as constraints in thermal and crustal evolution models and underscores the significance of the experimental data of Koziol and Newton (1989) in allowing this difference to be resolved.

Anovitz and Essene (1990) used the Fs equilibrium to compute a preferred pressure of 9.6 kbar at 725 °C. For this sample with $X_{\text{Alm}} = 0.6$, this equilibrium is much less sensitive to the effects of the ternary interaction parameter, the difference between $C_{123} = 0$ and $C_{123} = -66.5$ kJ/mol translating to a difference of 0.5 kbar in pressure (Fig. 7). The higher pressure computed by Anovitz and Essene (1990) compared to Figure 6 stems mostly from the significant slope of Fs equilibrium combined with a higher temperature computed with the garnet + clinopyroxene equilibrium.

Figure 7 illustrates the effect of the ternary interaction parameter on temperatures calculated with the garnet + clinopyroxene thermometer as well as the garnet + orthopyroxene equilibrium almandine + enstatite = pyrope + ferrosilite. Solid curves are computed with the garnet properties in Table 1 ($C_{123} = 0$), and dashed curves show their positions when $C_{123} = -66.7$ kJ/mol is used. For the BUR83C70 sample, the latter curves are shifted to higher temperatures by approximately 100 °C and 55 °C for the garnet-orthopyroxene and garnet-clinopyroxene thermometers, respectively. The lower temperatures are a direct consequence of our analysis of Koziol and Newton's (1989) experimental data, but they clearly are too low to represent peak metamorphic conditions. Although garnet-clinopyroxene temperatures below 700 °C are not exclusively produced with the thermodynamic data used in this paper (see Figs. 4 and 5), the results for BUR83C70 emphasize the general influence of ideal ternary interactions in lowering temperatures for samples with $X_{\text{Alm}} > 0.5$ to the extent that their significance as peak metamorphic conditions may be questioned, a point that has been the focus of several recent studies (Pattison and Newton, 1989; Frost and Chacko, 1989). It should be noted however that the pressures and temperatures computed above incorporate nonnegligible uncertainties in mixing data for plagioclase and pyroxenes as well as standard state thermodynamic data. Only after these uncertainties are reduced will it be possible to assess the degree to which resetting has occurred and is dependent on different uplift histories. For this reason, we do not wish to dwell on this much larger scale question other than to stress the need to compute (or recompute) pressures and temperatures with the small ternary garnet in-

teraction parameter calibrated on the basis of Koziol and Newton's (1989) experimental data.

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