

Mixing properties of aluminosilicate garnets: constraints from natural and experimental data, and applications to geothermo-barometry

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Abstract

Thermodynamic and statistical treatment of the compositional dependence of $K_D(\text{Fe-Mg})$ between garnet and various coexisting phases in terms of a multicomponent "simple mixture" model for garnet suggest $\Delta W_{\text{Ca}} (=W_{\text{MgCa}} - W_{\text{FeCa}}) \approx 3000 \pm 500$ and $\Delta W_{\text{Mn}} \approx 3000 \pm 500$ cal/mole of cation at ~ 500 – 1400°C and 500 – 750°C , respectively. The Fe–Ca mixing property derived from the experimental phase equilibrium data of Cressey *et al.* (1978) at 850 – 1100°C , when combined with the Mg–Ca mixing data of Haselton and Newton (1980), yields ΔW_{Ca} that are in sharp disagreement with that suggested by the Fe–Mg partitioning data. We have, therefore, adopted the most reliable set of isothermal data of Cressey *et al.*, namely that at 1000°C , and assumed $\Delta S^{\text{xs}}(\text{Fe-Ca}) \approx \Delta S^{\text{xs}}(\text{Mg-Ca})$ to obtain the W_{H} Margules parameters of Fe–Ca join. Symmetric approximation of these data yield ΔW_{Ca} similar to that suggested by the analysis of the Fe–Mg fractionation data. Statistical and thermodynamic analysis of Cressey *et al.*'s data, however, do not show any necessity for a model of asymmetric ΔS^{xs} , as adopted by Cressey (1981), to treat these data. The thermochemical and natural Fe–Mg partitioning data suggest asymmetric positive deviation from ideality along the Mg–Fe join of garnet with the maximum towards the Fe-end. The implications of these mixing data for the K_D -geothermometers involving garnet, and especially for the garnet–biotite geothermometer, are discussed. The equilibrium pressures of a large number of natural garnet–plagioclase– Al_2SiO_5 assemblages have been calculated on the basis of $\gamma_{\text{Ca}}^{\text{Gt}}$ calculated according to these mixing data and the multicomponent subregular formulation of Wohl (1953). These pressures can be brought into excellent agreement with the Al_2SiO_5 phase diagram of Holdaway (1971) by adjusting the ternary interaction parameter. The magnitude of this adjusted parameter agrees surprisingly well with that approximated according to a method suggested by Wohl.

ABBREVIATIONS AND SYMBOLS

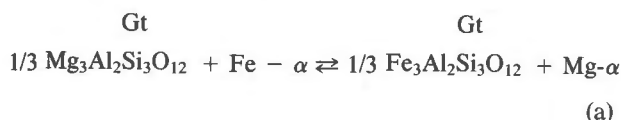
Alm: Almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$)	Gt: Garnet	P_F :	A probability function (see text p. 4)
Ann: Annite ($\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$)	CTs: Ca-Tschermak ($\text{CaAl}_2\text{SiO}_6$)	σ :	Standard deviation
Bt: Biotite	CPx: Clinopyroxene	X_i :	Moles of i/Σ moles of all components in the same site as i
Phl: Phlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$)	OPx: Orthopyroxene	$\Delta G^\circ, \Delta H^\circ, \Delta S^\circ, \Delta V^\circ$:	Gibbs free energy, enthalpy, entropy, and volume change of a reaction, respectively, when all components are in their pure states at 1 bar, T
Plag: Plagioclase	Ol: Olivine	$\Delta G^{\text{xs}}, \Delta V^{\text{xs}}, \Delta S^{\text{xs}}$:	Excess free energy, volume, and entropy of mixing
Fy: Fyropite ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$)	Q: Quartz	\bar{V}_i :	Partial molar volume of a component i
Wo: Wollastonite (CaSiO_3)	Spess: Spessartine ($\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$)	W_{ij} :	'Simple-mixture' interaction parameter between i and j
Gross: Grossularite ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$)	GPAQ: Garnet-plag- Al_2SiO_5 -quartz assemblages	W^{i-j}, W^{j-i} :	Margules parameters for the asymmetric binary join i - j
	CMAS: $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$	ΔW_i :	$W_{\text{Mg}i} - W_{\text{Fe}i}$
K_D :	Fe ²⁺ -Mg distribution coefficient between two co-existing phases.	$a_i^\alpha, \gamma_i^\alpha$:	Activity and activity coefficient of i , respectively, in the phase α
r :	Multiple regression coefficient		

Introduction

Because of its wide range of stability, reactions involving garnet have found extensive applications to the calculation of P - T history of natural rocks. There have, thus, been considerable efforts in recent years by a number of workers to develop activity-composition (a - X) relations in garnets which are essential to such calculations. The main purpose of this work is to critically analyze and refine the binary mixing property data in the $(\text{Fe}, \text{Mg}, \text{Ca})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnets in terms of the constraints imposed by the available data on the Fe-Mg partitioning between garnet and coexisting phases and examine their consequences in certain multicomponent calculations which are of interest in geothermo-barometry.

Analysis of Fe-Mg fractionation data

The Fe^{2+} -Mg fractionation between aluminosilicate garnet, $[\text{M}]_3^{2+}\text{Al}_2\text{Si}_3\text{O}_{12}$, and a coexisting phase α is governed by the exchange equilibrium



for which, at equilibrium,

$$K_a = \left[\frac{(X_{\text{Fe}}/X_{\text{Mg}})^{\text{Gt}}}{(X_{\text{Fe}-\alpha}/X_{\text{Mg}-\alpha})^\alpha} \right] \left[\frac{(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Gt}}}{(\gamma_{\text{Fe}\alpha}/\gamma_{\text{Mg}\alpha})^\alpha} \right] \quad (1)$$

where K_a is the equilibrium constant for (a). For the sake of brevity, the terms within the first and second square brackets will be referred as K_D (distribution coefficient) and K_γ respectively. Assuming that the mixing properties of the two phases can be approximated by a "simple mixture" model (Guggenheim, 1967) within the compositional range of an isothermal-isobaric suite of samples, and neglecting multicomponent interactions, we obtain, following Ganguly and Kennedy (1974),

$$\begin{aligned} RT \ln K_D &= RT \ln K_a(P, T) \\ &+ \left[W_{\text{FeMg}}(X_{\text{Fe}} - X_{\text{Mg}}) + \sum_k (W_{\text{MgK}} - W_{\text{FeK}})(X_{\text{K}}) \right]^{\text{Gt}} \\ &+ \left[W_{\text{FeMg}}(X_{\text{Mg}\alpha} - X_{\text{Fe}\alpha}) + \sum_L (W_{\text{Fe}\alpha} - W_{\text{Mg}\alpha})(X_{\text{L}}) \right]^\alpha \end{aligned} \quad (2)$$

The $\ln K_D$ values between garnet and various coexisting phases for several suites of natural and synthetic samples, each suite presumably equilibrated at approximately the same P - T condition, have been subjected to least square regressions against the compositional variables within parentheses in the above expression by previous workers and in this work. The values of the interaction parameters, obtained from the regression coefficients, are summarized in Table 1. We have carried out stepwise regres-

sion, which permits evaluation of the effect of inclusion of each variable on the goodness of the statistical fit. Table 1 shows the multiple correlation coefficients (r) and the P_F value, as defined below, associated with the variables at selected stages of regression. The P_F value associated with a variable denotes the probability of observing a F value $((\text{regression coefficient}/\sigma)^2)$ as large as that associated with it from a random set of data. Exclusion of a variable with $P_F > 0.10$ will not have significant influence on the goodness of the fit.

Cressey et al. (1978) and Haselton and Newton (1980) have studied the volumes of mixing in pyrope-grossular and almandine-grossular joins. Both joins show very similar behavior, and have nearly the same ΔV^{xs} of mixing at the same calcium concentration. Consequently ΔW_{Ca} , the pressure dependence of which is given by the relation

$$\left(\frac{\partial \ln \Delta W_{\text{Ca}}}{\partial P} \right)_T = \frac{\Delta V^{\text{xs}}(\text{Mg-Ca}) - \Delta V^{\text{xs}}(\text{Fe-Ca})}{RT} \quad (3)$$

will be insensitive to pressure. Numerical expressions of \bar{V}_{Gr} in both joins are given by Newton and Haselton (1981).

Dahl (1980) has regressed the samples from Kelly Iron Formation along with those from adjacent Carter Creek Area. However, as the inferred equilibration temperatures of the two groups of samples seem to differ by $\sim 70^\circ$ (Dahl, 1979), we have reanalyzed the Kelly samples, which constitute the larger group, separately, assuming that the variations of Ca and Mn contents of the clino- and ortho-pyroxene samples, coexisting with garnet ($X_{\text{Ca}}^{\text{Cpx}} = 0.40 - 0.45$; $X_{\text{Mn}}^{\text{Cpx}} = .00 - .12$; $X_{\text{Mn}}^{\text{Opx}} = .00 - .12$), have no significant effect on K_D . The regression coefficients obtained by us are somewhat different from those of Dahl.

For the data of Ellis and Green (1979) (which are based completely on synthesis experiments), not only the Ca content of garnet, but also that of the coexisting clinopyroxene varied over fairly wide ranges. They fitted the observed variation of $\ln K_D$ at constant P - T against $X_{\text{Ca}}^{\text{Gt}}$, but recognized that the regressed expression of $\ln K_D$ reflects not only the effect of $X_{\text{Ca}}^{\text{Gt}}$, but also that of $X_{\text{Ca}}^{\text{Cpx}}$ and the covariance between these variables. We have, therefore, subjected the data of Ellis and Green to stepwise multiple regression to isolate the effects of $X_{\text{Ca}}^{\text{Gt}}$, $X_{\text{Wo}}^{\text{Cpx}}$ and $X_{\text{CTs}}^{\text{Cpx}}$ on $\ln K_D$. These experimental data, as well as others discussed by Ganguly (1979), suggest that K_D for Gt-Cpx pairs is insensitive to Fe/Mg ratio at least at $T \geq 1100^\circ\text{C}$. The results of stepwise regression of Ellis and Green's data at 1200°C (there are insufficient data at other temperatures) suggest that the variation of $\ln K_D$ is almost completely due to the variation of $X_{\text{Ca}}^{\text{Gt}}$ and $X_{\text{Wo}}^{\text{Cpx}}$. The virtual independence of $\ln K_D$ on X_{CTs} is consistent with the deduction of Wood (1977) that CTs mixes nearly ideally with $\text{CaMgSi}_2\text{O}_6$ and $\text{CaFeSi}_2\text{O}_6$ components in clinopyroxene at $T \geq 1000^\circ\text{C}$.

Table 1. Summary of regression analysis of the compositional dependence of K_D (Fe-Mg) between garnet and a coexisting phase

Garnet Compositions; Range and (average) atomic fractions of		Regressed 'simple mixture' parameters to (P_p) , Ca/mole							Source of Data (Natural/ Experimental)			Assumptions and Constraints	
Fe	Mg	Ca	Mn	W_{FeMg}	ΔW_{Ca}	ΔW_{Mn}	Coexisting phase (a)	α	r^+	T°C	Regression	Assumptions and Constraints	
.34-.65 (.54)	.04-.22 (.09)	.16-.21 (.22)	.01-.32 (.09)	2995±487 (.002)	2148±384 (.002)	3548±287 (.000)	$W_{FeMg}=1705±336$ (.004)	CPx	.997	~745	Dahl (1980); N	This work	$K_D^{f(Mn,Ca)^{CPx}}$ ($X_{Ca}=0.40-0.45, X_{Mn}=0.00-0.12$)
.48-.65 (.64)	.04-.22 (.14)	.16-.19 (.17)	.01-.32 (.13)	1814±1768 (.36)	excluded* ($X_{Ca} \sim \text{const}$)	3638±900 (.016)	$W_{FeMg}=741±772$ (.39)	OPx	.974	"	This work	This work	$K_D^{f(Mn)^{OPx}}$ ($X_{Mn}=0.00-0.12$)
.50-.80 (.70)	.09-.15 (.11)	.03-.24 (.10)	.04-.27 (.09)	1056±1176 (.38)	4912±1297 (.001)	3466±1533 (.032)	excluded* (.000)	Bt	.741	~550	Compiled by Ganguly and Kennedy (1974); N	This work	$W_{FeMg}^{Bt}=0$; T: Gt-Bt geothermometer (this work; see text)
.40-.80 (.60)	.05-.43 (.17)	.05-.29 (.17)	.00-.07 (.02)	2520	3820	excluded* (X_{Mn} negligible)	excluded* (.000)	OPx		~800	Saxena (1979); N	Saxena (1979)	Fe-Mg mixing in OPx according to Saxena (1973)
.22-.56 (.32)	.15-.65 (.43)	.13-.44 (.27)	0	-	5972±816 (.000)	-	$W_{NoEn}-W_{NoPs}=5992±1924$ (.007)	CPx	.927	1200	Ellis and Green (1979), Expt. glass synthesis	This work	$K_D^{f(Fe/Mg)}$, as shown experimentally
Detail data not available (.17)			0	-	2676±201	-	-	Ol	-	900-1400	O'Neill & Wood (1979), Expt. mostly glass synth.	O'Neill & Wood (1979)	Bulk Fe/Mg kept const.
.19-.39 (.27)	.43-.66 (.52)	.12-.45 (.20)	0	-	4556±994	-	-	CPx	-	1100	Compiled by Ganguly (1979), Expt.	Ganguly (1979)	$K_D^{f(Fe/Mg)}$, as shown experimentally
.37-.81 (.55)	.04-.08 (.06)	.03-.26 (.11)	.09-.44 (.28)	2331±929 (.033)	3041±903 (.005)	2807±881 (.009)	-	Bt	.82	~500	Ferry (1980); N, Gt zone samples excluding #5	this work	X_{Al}^{Bt} excluded as $P_F=0.66$ T: Gt-Bt geothermometer (see text)

*'Excluded' means that the variable associated with the mixing parameter at the top of the column has been excluded from regression.
 +The r values are for simultaneous regression against the variables in the corresponding row.

Review and analysis of experimental binary mixing data in garnets

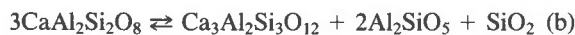
Newton *et al.* (1977) have determined the enthalpy of mixing, ΔH^{mix} , in the pyrope-grossular join by molten $Pb_2B_2O_5$ solution calorimetry at 900 K. The results showed an asymmetric ΔH^{mix} , which can be fitted by a two constant Margules expression. In the Margules treatment, the ΔG^{xs} in a binary join i-j is given by

$$\Delta G^{xs} = (W_G^{i-j}X_j + W_G^{i-i}X_i)X_iX_j \quad (4)$$

in which the fitting constants can be resolved into enthalpy, entropy and volume terms according to

$$W_G(P,T) = W_H(1,T) - TW_S(1,T) + (P-1)W_V \quad (5)$$

For the binary join pyrope-grossular, Haselton and Newton (1980) have derived, from the calorimetric data of Newton *et al.* (1977), $W_H^{Mg-Ca} = 1000 \pm 77$ and $W_H^{Ca-Mg} = 4047 \pm 67$ calories/mole of divalent cation. Cressey (1981) has derived ΔH^{mix} in the pyr-gross join for $X_{Ca} = 0.10-0.20$ from the experimental data of Hensen *et al.* (1975) on the effect of pyrope on the equilibrium



The results are in good agreement with the calorimetric data.

Haselton and Westrum (1980) have measured the heat

capacities of synthetic pyrope, grossular, and $Py_{0.60}Gr_{0.40}$ in the temperature range 10–350K by adiabatic calorimetry. The py-gross solid solution showed an excess heat capacity of mixing which gives a Third law $\Delta S^{xs}(298.15K) \approx 1.078$ cal/deg/mole of cation. Assuming the excess entropy to be symmetrical to composition, and also independent of temperature, Haselton and Newton (1980) suggested $W_s = \Delta S^{xs}/X_{Ca}X_{Mg} = 1.49$ cal/deg/mole of divalent cation at temperatures of geological interest. As shown by Newton and Haselton (1981) and Cressey (1981), the high temperature data of Hensen *et al.* (1975) for the equilibrium (b) lead to values of ΔS^{xs} at 1000–1300°C and $X_{Ca} = 0.10-0.22$ that are in good agreement with above model. From their reversed equilibrium data for spinel- to garnet-periodotite transition in the CMAS system, Jenkins and Newton (1979) have derived $\gamma_{Ca}^{Gt} = 1.78 \pm 0.19$ at 16 kbar, 1000°C, $X_{Ca}^{Gt} = 0.15$. If we now approximate the mixing in the pyrope-grossular join around $X_{Ca} = 0.15$ by a symmetrical form, then combination of the calorimetric ΔH^{xs} at $X_{Ca} = 0.15$ with the above value of γ_{Ca}^{Gt} , reduced to 1 bar according to Newton and Haselton (1981), leads to $\Delta S^{xs} = 0.22 \pm 0.04$, which agrees well with that predicted (0.19) by Haselton-Newton model. Wood and Holloway (1982) have, on the other hand, concluded that a W_s value of zero, rather than 1.5, for $X_{Ca} \leq 0.20$ in the pyrope-grossular join is compatible with the experimentally determined, although largely unreversed,

slope of the spinel- to garnet-periodotite boundary in the CMAS system. We feel, however, that the combined weight of the available calorimetric and phase equilibrium data supports $W_S \approx 1.5$, and the problem with the spinel- to garnet-periodotite transition probably lies in the thermochemical properties of the other phases involved in this transition. We, therefore, express, following Haselton and Newton (1980), the activity coefficient of a component in the pyrope-grossular join, at least for $X_{Ca} \leq 0.20$, according to

$$R \ln \gamma_i = (1 - X_i)^2 [W_H^{i-j} + 2(W_H^{i-i} - W_H^{i-j})X_i - TW_S] + (P - 1)(\bar{V}_i - V_i^0) \quad (6)$$

with the following values of the Margules parameters

$$\begin{aligned} W_H^{Mg-Ca} &\approx 1000 \pm 77 \text{ calories/mole of divalent cation} \\ W_H^{Ca-Mg} &\approx 4047 \pm 77 \text{ calories/mole of divalent cation} \end{aligned} \quad (7)$$

$$W_S^{Mg-Ca} \approx W_S^{Ca-Mg} \approx 1.5 \text{ calories/mole of divalent cation}$$

Cressey *et al.* (1978) have determined the effect of almandine component on the equilibrium (b) on the basis of glass-synthesis and limited reversal experiments, from which they have derived γ_{Gr} and γ_{Alm} at 1 bar, 850–1100°C, for $X_{Ca} = 0.12$ –0.79. Cressey (1981) has derived from these data ΔH^{mix} and ΔS^{xs} at 1 bar, 1000°C in the alm-gross join, and found both quantities to be asymmetric with the maximum towards the Ca-end, which one can fit by using two parameter Margules expressions. However, we prefer to obtain these parameters directly from the original data of Cressey *et al.* (1978), as follows, which reduces propagation of errors, and also permits statistical confidence tests for the derived values.

Expressing both ΔH^{mix} and ΔS^{xs} according to the Margules form (Equation 4), we obtain for the Ca-Fe join of garnet

$$\begin{aligned} RT \ln \gamma_{Ca}(1 \text{ atm}, T) / X_{Fe}^2 &= W_H^{Ca-Fe} - TW_S^{Ca-Fe} + \\ 2(W_H^{Fe-Ca} - W_H^{Ca-Fe})X_{Ca} &+ 2(W_S^{Ca-Fe} - W_S^{Fe-Ca})TX_{Ca} \end{aligned} \quad (8)$$

For $W_S^{Fe-Ca} = W_S^{Ca-Fe}$, this expression reduces to Equation (6). The quantity on the left hand side (LHS) of (8) has been obtained from the values in Cressey *et al.* (1978) at $T = 850$ –1100°C, $X_{Ca} = 0.12$ –0.79, and subjected to stepwise regression against T , X_{Ca} and TX_{Ca} . The results suggest essentially no significant influence of the last variable ($P_F = 0.57$, and an increase of r by only 0.003). Consequently, according to the data of Cressey *et al.*, ΔS^{xs} should be treated as a symmetric rather than an asymmetric function in gross-alm join. Thus, comparison of the regressed expression of LHS *vs.* T and X_{Ca} with (8) leads to the following values of the Margules parameters.

$$\begin{aligned} W_H^{Ca-Fe} &\approx 7,031 \pm 424 \text{ per mole of cation} \\ W_H^{Fe-Ca} &\approx 10,281 \pm 372 \\ W_S^{Ca-Fe} &\approx W_S^{Fe-Ca} \approx 6.53 \pm 1.41 \end{aligned} \quad (9)$$

Combination of (7) and (9), however, predicts a negative dependence of $\ln K_D$ on X_{Ca}^{Gt} , which is contrary to

both natural and experimental data (Table 1). Also, the large difference between the above W_S values in the alm-gr and pyr-gr joins implies a strong temperature dependence of $\ln K_D$ *vs.* X_{Ca} , which does not seem to be the case, at least for $X_{Ca} \leq 0.40$, according to the experimental data of O'Neill and Wood (1979) and Ellis and Green (1979). We, therefore, pursue an alternative approach, namely, assume $W_S^{Ca-Fe} \approx W_S^{Ca-Mg}$, so that $\ln K_D$ *vs.* X_{Ca} is insensitive to T , and rederive the W_H parameters from the most reliable set of isothermal data of Cressey *et al.* (1978). Examination of these data shows that the activity-composition relation is well constrained only at 1000°C by sufficient runs with crystalline mixtures. Setting $W_S^{Ca-Fe} \approx W_S^{Fe-Ca} \approx 1.5$ cal/mole, we then obtain, by regressing the 1000°C data according to (8),

$$\begin{aligned} W_H^{Ca-Fe} &\approx -630 \pm 405 \text{ cal/mole of divalent cation} \\ W_H^{Fe-Ca} &\approx 4620 \pm 660 \text{ cal/mole of divalent cation} \end{aligned} \quad (10)$$

If we assume $W_S^{Fe-Ca} = 0$, as suggested by Wood and Holloway (1982) for the pyrope-grossular join, then the same treatment yields

$$\begin{aligned} W_H^{Ca-Fe} &\approx -2539 \pm 405 \text{ cal/mole of cation} \\ W_H^{Fe-Ca} &\approx 1720 \pm 660 \text{ cal/mole of cation} \end{aligned} \quad (11)$$

Synthesis and summary of the mixing data

The ΔH^{mix} in the Ca-Mg and Ca-Fe joins of garnet, calculated according to (7), (10) and (11), are illustrated in Figure 1(a). Symmetric approximations of these data for $X_{Ca} \leq 0.3$ yields $\Delta W_{Ca} \approx 3200$ and ≈ 5000 calories/mole of cation for the $W_S = 1.5$ and $W_S = 0$ models, respectively. These values are within the range of ΔW_{Ca} values derived from the Fe-Mg fractionation data according to the multicomponent 'simple mixture' formulation (Table 1). The binary mixing data in Figure 1, however, suggest that the slope of $\ln K_D$ *vs.* X_{Ca} should decrease with increasing X_{Ca} , and be zero at $X_{Ca} \approx 0.30$ –0.45. The last result is very surprising, and, therefore, we do not recommend use of the binary mixing data for $X_{Ca} > 0.30$. More work should be done at high calcium concentration, especially in the Ca-Fe join, and on the $\ln K_D$ *vs.* X_{Ca} relation. However, we find no significant correlation between $\ln K_D$ and X_{Ca}^{Gt} , between 0.31 and 0.82 (average = 0.62), from the compositional data for coexisting garnet and clinopyroxene in grosspydites from Zagadochnaya kimberlite pipe, USSR (Sobolev *et al.*, 1968). Thus, it seems likely that the dependence of $\ln K_D$ on X_{Ca}^{Gt} decreases with increasing Ca. The ΔW_{Ca} values, derived from Fe-Mg fractionation data (Table 1), average to ≈ 3800 cal/mole of cation, but a value of 3000 ± 500 cal will satisfy all data, except those of Ellis and Green (1979). Since Ellis and Green's data are based completely on glass synthesis, and hence are not constrained by the requirements of equilibrium, we recommend the latter value for $X_{Ca} \leq 0.35$.

The ΔW_{Mn} values derived from the analysis of the

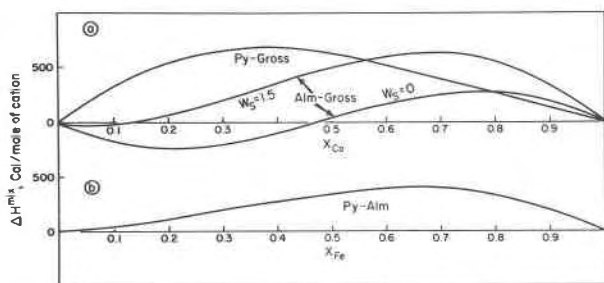


Fig. 1. (a) Heat of mixing in the pyrope-grossular and almandine-grossular joins at 1 bar. Data for the pyrope-grossular join are from Haselton and Newton (1980), whereas those for the almandine-grossular join are derived from the phase equilibrium data of Cressey *et al.* (1978) at 1000°C, assuming $W_S = 0$ and $W_S = 1.5$ cal/mole of cation. (b) A possible model for the heat of mixing in the pyrope-almandine join. The model is believed to define the maximum possible deviation from ideal mixing behavior. ΔS^{SX} is assumed to be negligible.

various sets of natural data are in good agreement, and a value of 3000 ± 500 cal/mole for $X_{Mn} \leq 0.40$ satisfies all data. According to Ganguly and Kennedy (1974), Fe and Mn would mix nearly ideally in garnet solid solution, so that $\Delta W_{Mn} \approx W_{MgMn}$.

The W_{FeMg} values derived from thermodynamic and statistical analyses of the natural data seem to suggest a value of $W_{FeMg} \approx 2500 \pm 500$ cal/mole of cation at $Fe/Mg \approx 3$. Wood and Kleppa (1981) have, on the other hand, suggested a value of $W_{FeMg} \approx 200$ cal/mole of cation for Mg-rich composition (mostly $Fe/Mg < 1$) on the basis of their calorimetric data on the mixing properties of Fe-Mg olivine, and O'Neill and Wood's (1979) data on Fe-Mg fractionation between olivine and garnet. The relatively large nonideality of mixing for the Fe-rich compositions suggested by the natural data could partly be an artifact of the method of statistical treatment of these data in terms of a multicomponent 'simple mixture' model, and neglect of terms correlated with $(X_{Fe} - X_{Mg})$, such as those that will arise owing to the asymmetric behavior of garnet solid solution (*cf.* Wohl, 1953). We have, therefore, carried out further statistical analysis of the data in terms of the expression of $RT \ln(\gamma_{Mg}/\gamma_{Fe})^{Gt}$ with asymmetric Ca-Fe and Ca-Mg joins, and symmetric Fe-Mg binary, but ignoring ternary interaction. The results did not show significant change in the regressed value of W_{FeMg} . Consequently, we suggest that, at least within the temperature range of the natural samples in Table 1, ~ 500 – 750°C , the Fe-Mg join in garnet is asymmetric with $W_{Mg-Fe}^M \approx 2500$ and $W_{Fe-Mg}^M \approx 200$ cal/mole of cation. The ΔS^{SX} in py-gross join is believed to be due to positional disordering of Mg and Ca as a result of the substitution of Mg in an unusually large coordination polyhedron expanded by Ca (Haselton and Westrum, 1980). Similar disordering effect, however, is expected to be minimal in the py-alm solid solution, as Mg^{2+} and Fe^{2+} have similar ionic radii (Shannon and Prewitt, 1969). The nonideal mixing model

for py-alm solid solution, which is illustrated in Figure 1(b), is similar to the mixing property of Fe-Mg olivine (Wood and Kleppa, 1981), and would satisfy both observational and experimental data discussed above. The only problem with this model stems from the data of Ferry and Spear (1978) on the Fe^{2+} -Mg partitioning between binary Fe^{2+} -rich compositions of garnet and biotite. If we assume ideal Fe^{2+} -Mg mixing in biotite, as suggested by both experimental and observational data (Mueller, 1972; Wones, 1972; Schulien, 1975; Ganguly, 1978), then for the exchange equilibrium $1/3 \text{ Py} + 1/3 \text{ Ann} \rightleftharpoons 1/3 \text{ Alm} + 1/3 \text{ Phl}$, Ferry and Spear's data lead to ΔG° (1 bar, 1100 K) = -2442 and -1174 cal for respectively the ideal and the asymmetric Fe-Mg mixing in garnet. The available thermochemical data (Helgeson *et al.*, 1978; Saxena, 1982; Chatillon-Colinet *et al.*, 1983), on the other hand, yield ΔG° (1 bar, 1100 K) = -2509 cal, which agrees almost exactly with the ideal Fe-Mg exchange model. However, the thermochemical data are not well constrained, and there may be some positive nonideality in Fe-Mg biotite to partly compensate the effect of that in garnet.

We have summarized in Table 2 our preferred values for the mixing parameters in (Fe,Mg,Ca,Mn)-garnet solid solution, and illustrate below some applications to the geothermo-barometric calculations involving garnet in multicomponent system.

Fe^{2+} -Mg exchange equilibrium between garnet and coexisting phases

Equation (2) can be combined with the thermodynamic expression of $\ln K$ as a function of P and T to yield the following relation between T and K_D involving garnet and a coexisting phase α for a compositional range over which garnet can be approximated by a symmetrical solution model

Table 2. Summary of mixing data in garnet (cal/mole of cation)

Binary Join	Margules Parameters	Preferred Values (std) at 1 bar	$\Delta W_1^a = W_{Mg-1}^M - W_{Fe-1}^M$
Fe-Mg	W_{Fe-Mg}^M	200	$\Delta W_{Ca} = 3,000 \pm 500$ at $X_{Ca} \leq 0.30$
	W_{Mg-Fe}^M W_S	$2,500 \pm 500$ 0	$\Delta W_{Mn} = 3,000 \pm 500$ at $X_{Mn} \leq 0.30$
Ca-Mg	W_{Ca-Mg}^M W_{Mg-Ca}^M	$4,047 \pm 77$ $1,000 \pm 77$	
	W_S W_{Ca-Fe}^M	1.5 e.u. -630 ± 400	
Ca-Fe	W_{Fe-Ca}^M W_S	$4,620 \pm 660$ 1.5 e.u.	

^a ΔW_1 values have been derived from regression analyses of the compositional dependence of $\ln K_D$, as discussed in the text (and are similar to those in Ganguly (1979)), and are not strongly affected by changes of P and T .

$$T(K) = \frac{A + [W_{\text{FeMg}}(X_{\text{Fe}} - X_{\text{Mg}}) + \Delta W_{\text{Ca}}X_{\text{Ca}} + W_{\text{Mn}}X_{\text{Mn}}]^{Gt}/R}{\ln K_D - \Delta S^{\circ}/R - \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\alpha}} \quad (12)$$

where A stands for the coefficient of $1/T$ in the thermodynamic expression of $\ln K$.

As a specific application of expression (12) (also see Ganguly, 1979), let us consider the experimental data of Ferry and Spear (1978) on Fe–Mg fractionation between coexisting garnet and biotite. These data have been widely used for the estimation of temperature of equilibration between natural garnet–biotite pairs, but mostly without proper regard for the compositional effects. In their experimental work, Ferry and Spear kept the garnet composition essentially fixed at that of the starting composition, $\text{Alm}_{90}\text{Py}_{10}$, by using a very large garnet/biotite ratio. Thus, combining their expression for $\ln K_D$ vs. $1/T$ with Equation (2), we obtain

$$\ln K(P, T) \approx \frac{2089 - 0.8W_{\text{FeMg}}^{Gt}/R + 9.45P(\text{kbar})}{T} - 0.782 \quad (13)$$

The expressions of A (coefficient of $1/T$) and $\Delta S^{\circ}/R$ (= -0.782) in (13) may now be substituted into Equation (12) to obtain an explicit relation between T and K_D for coexisting garnet and biotite. For a given garnet composition, W_{FeMg}^{Gt} may be obtained through symmetric approximation of the Fe–Mg mixing illustrated in Figure 1(b), according to

$$W_{\text{FeMg}}^{Gt} \approx W^{\text{Fe-Mg}}[\text{Mg}/(\text{Mg} + \text{Fe}^{2+})]^{Gt} + W^{\text{Mg-Fe}}[\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})]^{Gt} \quad (14)$$

The “garnet-zone” samples of Ferry (1980), which have average garnet composition as shown in Table 1, and an average of $\ln K_D = 2.22$, represent an interesting suite of samples to illustrate and test the application of the above formulation of the Gt–Bt geothermometer. Symmetric approximation at the average garnet composition according to (14) yields $W_{\text{FeMg}} \approx 2270$ cal. Using ΔW_{Ca} and ΔW_{Mn} from Table 2 along with this W_{FeMg} , we obtain $T = 510^{\circ}\text{C}$ at the inferred pressure (Ferry, 1980) of ~ 3.5 kbar (an uncertainty of ± 500 cal in the W values leads to an uncertainty in T of $\pm 75^{\circ}\text{C}$). The model of ideal Fe–Mg mixing, on the other hand, leads to $T = 628^{\circ}\text{C}$. We could gain some idea about which of these temperature estimates is more appropriate by considering samples with $(X_{\text{Fe}} - X_{\text{Mg}})^{Gt}$ value very close to 0.80, since in these cases the effect of uncertainty of W_{FeMg} value will be minimal. This is due to the fact that in the expression of T according to (12) and (13), W_{FeMg} is multiplied by the factor $[(X_{\text{Fe}} - X_{\text{Mg}})^{Gt} - 0.8]/R$. Two such samples are Nos. 932 and 913 with $(X_{\text{Fe}} - X_{\text{Mg}}) = .73, .75$, $X_{\text{Ca}} = .039, .033$ and $X_{\text{Mn}} = .091, .086$, respectively. These samples yield $T = 490\text{--}530^{\circ}\text{C}$ for the extreme values of W_{FeMg} of 0 and 2300 cal, the latter being due to (14), which is in good

agreement with the average estimate of T with nonideal W_{FeMg} . This encouraging agreement notwithstanding, the application of the proposed asymmetric Fe–Mg mixing model in garnet to compositions with $\text{Fe}/\text{Mg} < 3$ should be made with caution. The statistical analyses of Goldman and Albee (1977) on the compositional dependence of K_D , and comparison of the biotite compositions produced in Ferry and Spear’s experiments with those in the garnet zone samples of Ferry (1980), suggest that the correction for the effects of Al(VI) and Ti in biotite should lead to an upward revision of the calculated temperature.

Plagioclase–garnet– Al_2SiO_5 equilibrium

Kretz (1959) first recognized the pressure sensitivity of the ratio of calcium content in coexisting garnet and plagioclase, as defined by equilibrium (b) (also see Ghent, 1976). Recently, Newton and Haselton (1981) have derived the following expression for the plag–garnet– Al_2SiO_5 equilibrium

$$P \approx [P^{\circ}\Delta V_{(b)}^{\circ} - 3RT \ln a_{\text{Ca}}^{Gt}/a_{\text{An}}^{\text{Plag}}/\Delta \bar{V}_{(b)}] \quad (15)$$

where the activities are at 1 bar, T , and P° is the equilibrium pressure of (b) at T when all the components are in their respective pure states. They have solved expression (15) for a large number of natural samples, with very little Mn in garnets, by assuming the symmetric “simple mixture” model, with $W_{\text{FeMg}} \approx W_{\text{FeCa}} \approx 0$, to be adequate for the ternary (Fe, Mg, Ca)-garnet solid solution for the compositional range encountered in the natural assemblages. We have, instead, expressed γ_{Ca}^{Gt} according to the modified ternary subregular formulation of Wohl (1953), as given in the Appendix (Equation A.1), and the binary mixing parameters in Table 2, and recalculated the equilibrium pressures for these GPAQ assemblages neglecting, as a first approximation, the ternary constant C_{123} . The T , P° , ΔV° , and $\Delta \bar{V}$ data are taken from Newton and Haselton¹, while a_{An} is from either these workers or calculated according to Saxena and Ribbe (1972). The a_{An} model of Newton and Haselton is based on their calorimetric ΔH^{mix} measurement at 700°C of high structural state plagioclase, and a random ΔS^{mix} value constrained by the “aluminum avoidance” principle. Their reason for adopting the Al-avoidance ΔS^{mix} model is that it leads, in combination with the calorimetric ΔH^{mix} , to ΔG^{mix} value which is in good agreement with that deduced by Orville (1972) from his cation exchange experiments at 700°C between aqueous chloride solution and high structural state plagioclase. Saxena and Ribbe (1972) have, on the other hand, derived a_{An} directly from thermodynamic and statistical analysis of Orville’s data.

¹ R. C. Newton (private comm.) has pointed out that the expression of P° (Sill) given in Newton and Haselton (1981) is erroneous. The correct expression, derived by Edgar Froese, is $P^{\circ}(\text{Sill}) = -1.17 + 0.0238 T(^{\circ}\text{C})$, which yields $P^{\circ}(\text{Sill})$ in kbar. We have taken this correction into account.

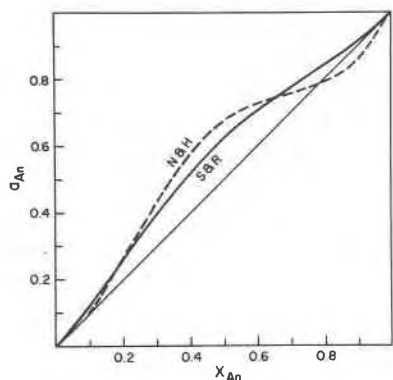


Fig. 2. Comparison of the activity-composition relation of anorthite in binary plagioclase solid solution at 700°C according to Saxena and Ribbe (1972) and Newton and Haselton (1981). The recent reformulation of Orville's data by Blencoe *et al.* (1982) produces essentially the same a - X relation as that according to Saxena and Ribbe.

The two a_{An} models are compared in Figure 2. The agreement of calculated pressures with the experimental Al_2SiO_5 phase diagram of Holdaway (1971) is unsatisfactory, but is somewhat better with the Saxena and Ribbe (1972) a_{An} model, which also reduces the dispersion of pressures calculated for different assemblages from the same locality relative to those obtained from Newton and Haselton model. We, therefore, accept $a_{An}(S\&R)$ as more appropriate, at least for the purpose of calculating equilibrium pressures of GPAQ assemblages.

Finally, we seek to improve the agreement of these calculated pressures with the Al_2SiO_5 phase diagram by

introducing a C_{123} term. From the definition of this term, and its relationship with the binary interaction parameters (Wohl, 1946, 1953), it seems highly unlikely that it could be insignificant for a ternary solution with the asymmetric and nonideal binaries proposed here for garnet. However, it can only be determined from appropriate experimental data when all the binaries are known. In the present work, a perfect and critically balanced agreement of the calculated GPAQ pressures (for the $a_{An}(S\&R)$ model) with the Al_2SiO_5 phase diagram is found with $C_{123} = -5300$ calories. The results are illustrated in Figure 3. The uncertainties ($\pm \sigma$) of the W_H values translate into an uncertainty of $\sim \pm 600$ bars in the calculated pressures. A much larger magnitude of the constant is permissible, in terms of compatibility with the Al_2SiO_5 phase diagram, if one datum from Otter Lake, Quebec, is neglected. Wohl (cited in Jordan *et al.*, 1950) has suggested a method of approximating C_{123} , from a knowledge of the binary interactions, as follows:

$$C_{123} \approx 1/2[(W^{2-1} - W^{1-2}) + (W^{1-3} - W^{3-1}) + (W^{3-2} - W^{2-3})] \quad (16)$$

This expression allows the sign of C_{123} to be either positive or negative depending on the arbitrary choice of the components 2 and 3. Note that the rest of the expression of $RT \ln \gamma_i$ is unaffected by the choice of components 2 and 3. We obtain almost exactly the same magnitude of C_{123} as above by substituting the binary parameters from Table 2 in Equation (16). A negative value requires $Mg \equiv 2$ and $Fe \equiv 3$. This agreement is probably fortuitous, but it at least suggests that the magnitude of the ternary constant should be significant.

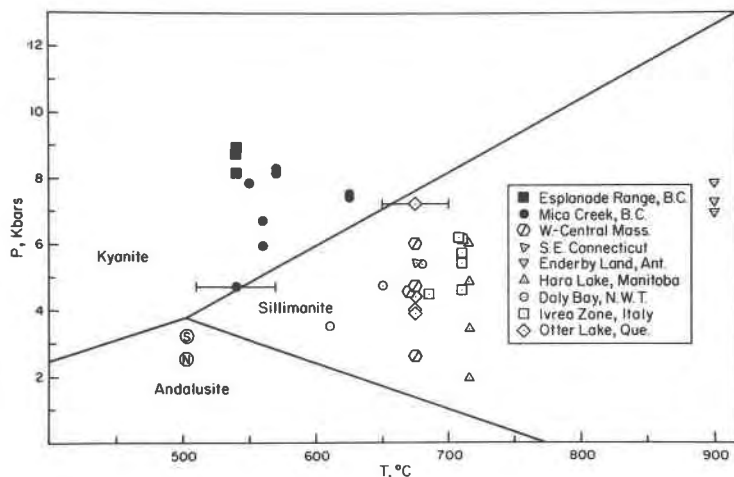


Fig. 3. Calculated pressures for the natural garnet-plagioclase- Al_2SiO_5 -quartz assemblages. Filled symbols: kyanite bearing assemblages; open symbols: sillimanite bearing assemblages. The data for the assemblages within the box have been summarized by Newton and Haselton (1981), and the sources are referenced therein. Horizontal bars indicate the range of temperature estimated in the original works. (N) and (S): Average P - T condition of the assemblages from Mt. Moosilauke area described by Hodges and Spear (1982), according to a_{An} after Newton and Haselton and Saxena and Ribbe (1972), respectively.

As evident from the ternary expression of Wohl (Appendix, A.1), the contribution of the constant C_{123} to $RT\ln\gamma_1$ is relatively large if X_1 is a dilute component, such as Ca in the GPAQ assemblages.

Use of ideal Fe–Mg mixing model for garnet raises the calculated pressures for GPAQ assemblages by ~ 600 bars, and, thus, requires a much smaller magnitude of the ternary interaction term, $C_{123} \approx -2500$, to produce comparable agreement with the Al_2SiO_5 phase diagram as in the case of the asymmetric Fe–Mg mixing model.

Hodges and Spear (1982) have recently presented the mineral–chemical data and P – T calculations for a suite of garnet–biotite–plag–sillimanite (\pm andalusite)–quartz assemblages from Mt. Moosilauke, New Hampshire. On the basis of the distribution of the three aluminum–silicate polymorphs in the metapelites near Mt. Moosilauke, they concluded that the P – T condition of the above assemblages should be close to that of Al_2SiO_5 triple point. These assemblages, thus, provide an opportunity for testing the thermo–barometric formulations presented above.

The garnets in the Mt. Moosilauke assemblages have $X_{\text{Mn}} = 0.09$ – 0.17 (average 0.13), so that $\gamma_{\text{Ca}}^{\text{Gt}}$ has to be expressed in terms of a quarternary solution model. Following Jordan *et al.* (1950), we have extended Wohl's (1953) ternary expression into the quarternary system (eqn. A.2, Appendix), and obtained an expression of $RT\ln\gamma_{\text{Ca}}^{\text{Gt}}$ in the quarternary garnet solid solution (Equation A.3). Approximate calculations, according to (16), of the additional ternary interaction terms suggest that these terms will have negligible effect on $RT\ln\gamma_{\text{Ca}}^{\text{Gt}}$ for garnet compositions in the Mt. Moosilauke assemblages.

We have recalculated the P – T condition of the Mt. Moosilauke assemblages according to the above formulations of the Gt–Bt geothermometer and GPAQ equilibrium, and a_{An} according to both Newton and Haselton (1981) and Saxena and Ribbe (1972). \bar{V}_{Gr} was calculated from the ternary model of Newton and Haselton (1981) after normalizing the garnet compositions to Py–Alm–Gross ternary solution. This method is unlikely to introduce an error in excess of $\pm 1 \text{ cm}^3$ in $\Delta\bar{V}_{(\text{b})}$, and hence an error in excess of $\sim \pm 50$ bars in the calculated pressures. The averages of the estimated P – T conditions for each set of calculations are illustrated in Figure 3. The estimated temperatures, and the estimated pressure according to a_{An} (S&R) are in good agreement with the "field expectations", in that these are close to the Al_2SiO_5 triple point (Holdaway, 1971), but below the field of kyanite. The pressures calculated according to a_{An} (N&H) are on the average ~ 1.2 kbar lower than the Al_2SiO_5 triple point.

We, therefore, conclude that combination of $\gamma_{\text{Ca}}^{\text{Gt}}$ model developed in this paper after Wohl's formulation with the $\gamma_{\text{An}}^{\text{Plag}}$ derived by Saxena and Ribbe from Orville's (1972) experimental data leads to satisfactory estimate of pressure on the basis of the garnet–plag– Al_2SiO_5 –Q equilibrium. Hodges and Spear (1982) have suggested empirical adjustments in the garnet and plagioclase solid solution

properties, namely $W_{\text{MgMn}}^{\text{Gt}} \approx W_{\text{FeMn}}^{\text{Gt}} \approx 0$, and $\gamma_{\text{An}}^{\text{Plag}} \approx 2.0$, so that their adopted formulations for garnet–biotite and garnet–plag– Al_2SiO_5 equilibria yield P – T estimates close to the Al_2SiO_5 triple point for Mt. Moosilauke assemblages. The formulations presented above obviates these empirical adjustments.

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Appendix

Expression of γ_1 in a multicomponent solution

In a ternary solution, γ_1 can be expressed, according to the modified formulation of Wohl (1953), as follows

$$\begin{aligned}
 RT \ln \gamma_1 = & \sum_{j=2,3} X_j^2 [(W^{1-j} + 2X_1(W^{j-1} - W^{1-j})) \\
 & + X_2 X_3 \left\{ \frac{1}{2} \left[\sum_j (W^{j-1} + W^{1-j}) - W^{2-3} - W^{3-2} \right] \right. \\
 & + X_1 \sum_j (W^{j-1} - W^{1-j}) + (X_2 - X_3)(W^{2-3} - W^{3-2}) \\
 & \left. - (1 - 2X_1)C_{123} \right\} \quad (A.1)
 \end{aligned}$$

where C_{123} is a ternary constant which accounts for the interactions within the possible ternary complexes ijk and ijj , *etc.*

Following Jordan *et al.* (1950), this expression can be extended into the quaternary system by adding the following terms to the right hand side of (A.1)

$$\begin{aligned}
 \Delta RT \ln \gamma_1 = & X_4^2 [W^{1-4} + 2X_1(W^{4-1} - W^{1-4})] \\
 & + \sum_{k=2,3} X_4 X_k [1/2(W^{4-1} + W^{1-4} + W^{k-1} + W^{1-k} \\
 & - W^{4-k} - W^{k-4}) + X_1(W^{4-1} - W^{1-4} + W^{k-1} \\
 & - W^{1-k}) + (X_k - X_4)(W^{k-4} - W^{4-k}) \\
 & - (1 - 2X_1)C_{14k}] + 2X_2 X_3 X_4 (W^{4-2} \\
 & - W^{2-4} + C_{234}) \quad (A.2)
 \end{aligned}$$

Using the binary parameters summarized in the Table 2, and assuming, according to Ganguly and Kennedy (1974), that the binary joins involving Mn are symmetric, with $W_{\text{FeMn}} \approx W_{\text{CaMn}} \approx 0$, and hence $W_{\text{MgMn}} \approx \Delta W_{\text{Mn}} \approx 3000 \pm 500$ cal, we obtain from the above expressions and Equation (16)

$$RT \ln \gamma_{\text{Ca}}^{\text{Gt}} \approx A_1 X_{\text{Mg}}^2 + A_2 X_{\text{Fe}}^2 + X_{\text{Mg}} X_{\text{Fe}} [3168 - 3.0T \\ + 2203 X_{\text{Ca}} + 2300(X_{\text{Mg}} - X_{\text{Fe}}) - C_{123}(1 - 2X_{\text{Ca}})] \\ + X_{\text{Mg}} X_{\text{Mn}} [-476 - 1.5T - 3047 X_{\text{Ca}} - C_{124}(1 - 2X_{\text{Ca}})]$$

$$+ X_{\text{Fe}} X_{\text{Mn}} [1995 - 1.5T + 5250 X_{\text{Ca}} - C_{134}(1 - 2X_{\text{Ca}})] \\ + 2C_{234} X_{\text{Fe}} X_{\text{Mg}} X_{\text{Mn}} \quad (\text{A.3})$$

where

$$A_1 = 4047 - 1.5T - 6094 X_{\text{Ca}}$$

$$A_2 = -630 - 1.5T + 10,500 X_{\text{Ca}}$$

$$C_{123} \approx -5300, C_{124} \approx -1523, C_{134} \approx 2625$$

$$C_{234} \approx -1150, \text{ with } 1 = \text{Ca}, 2 = \text{Mg}, 3 = \text{Fe}, 4 = \text{Mn}.$$