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## Thermodynamics of aluminosilicate garnet solid solution: new experimental data, an optimized model, and thermometric applications

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**Abstract** We have experimentally determined the displacement of the equilibrium Grossular + 2 Kyanite + Quartz [ 3 Anorthite (GASP) as a function of garnet composition in the systems Mg-Ca-Mn, Fe-Mg-Ca and Fe-Mg-Ca-Mn at 1000°C. The results were treated along with selected experimental and observational data available in the literature as well as binary parameters from other workers to obtain a set of mutually compatible binary mixing parameters of the quaternary (Fe,Mg,-Ca,Mn)-aluminosilicate garnet solid solution. Attempts to determine equilibrium garnet composition in the GASP equilibrium in the Ca-Mg binary were unsuccessful due to the formation of pyroxene. Calculations of binary and ternary miscibility gaps show that the  $P,T,X$  combination required for unmixing of garnet solid solution is not realized by natural samples. The solution model was applied to account for compositional effects on Fe-Mg exchange between garnet and ortho- or clinopyroxene. Applications of the revised thermometric formulations to selected natural assemblages yield  $P-T$  conditions which are much less sensitive to compositional effects compared to the other available formulations, and are consistent with independent constraints.

### List of symbols

$a_i^a$  and  $g_i^a$ : Activity and activity coefficient of the component  $i$  in the phase  $a$ , respectively, referred to pure component (1 bar,  $T$ ) standard state.

$DG^{XS}$ ,  $DH^{XS}$ ,  $DS^{XS}$ ,  $DV^{XS}$ : Excess Gibbs free energy, excess enthalpy, excess entropy and excess volume of mixing, respectively.

$K_D$ : Equilibrium  $Fe^{2+}$ -Mg distribution coefficient between garnet and a coexisting phase ( $a$ ) defined as  $(Fe^{2+}/Mg)^{Gt}/(Fe^{2+}/Mg)^a$ .

$D\bar{V}$  and  $DV^0$ : Partial molar volume change and end-member molar volume change of a reaction, respectively.

$W_{ij}^G$ ,  $W_{ij}^H$ , and  $W_{ij}^S$ : Subregular free energy, enthalpic and entropic binary interaction parameter, respectively, between the components  $i$  and  $j$ .

$W^{G(i-j)}$ ,  $W^H(i-j)$ , and  $W^S(i-j)$ : Regular solution or simple mixture free energy, enthalpic and entropic interaction parameter, respectively, between the components  $i$  and  $j$ .

$DW_i$ :  $W(Mg-i) - W(Fe-i)$ .

$X_i^a$ : Atomic fraction of the component  $i$  in the phase  $a$  in the site of mixing.

### Introduction

The compositional properties of garnet and coexisting minerals provide important record of the pressure-temperature-time ( $P-T-t$ ) history of the host rocks (e.g. Lasaga 1983; Ganguly and Saxena 1987; Chakraborty and Ganguly 1991, 1992; Spear 1993; Ganguly et al. 1996). These calculations, however, require knowledge of the thermodynamic mixing properties of the multi-component garnet solid solution that are commonly encountered in the natural assemblages. So far, most experimental efforts to constrain a garnet solution model have been confined to the binary and ternary compositions in the Fe-Mg-Ca subsystem. In this work, we report new experimental data involving primarily Mg-Ca-Mn and Fe-Mg-Ca-Mn and to a limited extent Fe-Mg-Ca and Mg-Ca garnet compositions, and develop a comprehensive model for the mixing properties of the (Fe,Mg,-Ca,Mn)-aluminosilicate garnet solid solution, taking into account the constraints imposed by experimental phase equilibrium data from this and other works, along with calorimetric and observational data. Finally we present phase diagrams to illustrate unmixing in the binary and ternary garnet solid solutions, and apply the solution model to develop compositional corrections for the garnet-orthopyroxene and garnet-clinopyroxene Fe-Mg exchange thermometers.

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## Formal aspects of binary and multicomponent solution model

In all studies so far, the properties of garnet solid solution have been analyzed in terms of a regular or a subregular solution model. The excess Gibbs free energy of mixing in a subregular binary join is given by

$$DG^{XS} = (W_{ij}^G X_j + W_{ji}^G X_i) X_i X_j, \quad (1)$$

where  $W^G$  is a free energy interaction parameter. The latter is often decomposed into enthalpic (H), entropic (S) and volumetric (V) contributions according to

$$W_{ij}^G(P, T) = W^G(1, T) + \int_1^P \left( \frac{dW^G}{dT} \right)_P dP \\ = W_{ij}^H(1, T) - TW_{ij}^S(1, T) + (P-1)W_{ij}^V \quad (2)$$

where  $W^G(1, T) = W^H(1, T) - TW^S(1, T)$ , and  $W^V$  is assumed to be independent of pressure. For a regular solution model,  $W_{ij} = W_{ji} = W(i-j)$ . Following common practice, we would assume  $W^H$  and  $W^S$  to be independent of temperature. This assumption, however, cannot be correct (Powell 1974; see Ganguly and Saxena 1987, for a discussion), but the available data, at least in any mineralogical system, do not permit a more sophisticated treatment.

In this work we use the term 'regular solution' in the same sense as 'simple mixture' of Guggenheim (1967), so that  $W(i-j) = f(P, T)$ .  $DG^{XS}$  in a quaternary solution with subregular binaries can be represented as (Cheng and Ganguly 1994)

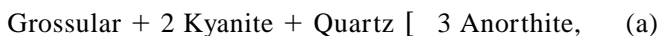
$$DG^{XS} = \sum_{i \neq j} (W_{ij} X_{ji} + W_{ji} X_{ij}) X_i X_j + \sum_{i \neq j \neq k} X_i X_j X_k C_{ijk}, \quad (3)$$

where  $X_{ij} = \frac{1}{2}(1 + X_i - X_j)$  and  $X_{ji} = \frac{1}{2}(1 + X_j - X_i)$  (defining a point in the  $i$ - $j$  binary obtained by normal projection of a quaternary composition), and  $C_{ijk}$  is a ternary interaction parameter, which can be calculated from the corresponding binary parameters when one of the binaries behave nearly ideally.

## Experimental studies

### Phase equilibrium

We investigated the displacement of the equilibrium (acronym: GASP)



as a function of garnet composition at 1000°C, the primary emphasis being in the Mn-bearing compositions. According to the data of Koziol (1990), the reaction rate is too sluggish at 900°C to yield equilibrium garnet compositions in run durations of  $\approx 7$  days. The quenched samples were examined by X-ray diffraction to ensure that all phases (garnet, kyanite and quartz) were present, and also to check for the formation of extraneous phases, and

were analyzed in an electron microprobe to determine the garnet compositions. The experimental data were then modeled to constrain the mixing properties of the garnet solid solution.

### Experimental procedure

All experiments were carried out in a piston-cylinder apparatus. The pressure cell consisted of CsCl outer bushing and a graphite internal resistance furnace. Pressure and temperature were measured and corrected for friction and cold-junction, respectively, according to the procedure of Bose and Ganguly (1995). Following Koziol and Newton (1989), finely ground crystalline starting materials (see next sections below) of garnet, kyanite, and quartz were thoroughly mixed and sealed with  $\text{Li}_2\text{MoO}_4$  flux in gold capsules and held at desired pressures at 1000°C for 102–164 h. Each experiment at a fixed  $P, T$  condition consisted of two capsules ('reversal couple'), one with garnet containing less Ca and the other with garnet containing more Ca than that in the equilibrium composition at the experimental condition (see Lee and Ganguly 1988, for illustration of the cell and capsule geometries).

### Preparation of glasses of garnet compositions

Glasses of both end-member and intermediate garnet compositions in the Fe-Mg-Ca-Mn system were synthesized from appropriate mixtures (with indicated purity levels) of  $\text{Fe}_2\text{O}_3$  (99.99%),  $\text{MgO}$  (99.998%),  $\text{CaO}$  (99.9%) or  $\text{CaCO}_3$  (reagent grade) as source of Ca,  $\text{MnCO}_3$  (99.99%),  $g\text{-Al}_2\text{O}_3$  (>99.9%) and  $\text{SiO}_2$  (99.9%).

A mixture of desired Mg-Ca-Mn garnet composition, prepared from chemicals dried at 120°C, was first decarbonated in a Mo crucible at 800°C under controlled  $f_{\text{O}_2}$  to prevent oxidation of the crucible material. After the decarbonation was complete (which took about 30 minutes for 1.5 gram of mixture), the sample was heated at 1100°C for  $\approx 30$  min, accompanied by readjustment of  $f_{\text{O}_2}$  into the field of Mo, and finally melted between 1350 and 1550°C, depending on the Mg content of the glass. After 30 min, the sample was pulled to the top of the furnace ( $\approx 400^\circ\text{C}$ ), held for  $\approx 30$  s, and quenched in an ice-water bath. The resulting glass was orange-brown in color, and homogeneous to within  $\pm 3\%$  of the average composition, as determined by microprobe spot analyses.

In earlier studies (Geiger et al. 1989; Pattison and Newton 1989; Koziol 1990), Fe bearing glasses of garnet compositions were prepared according to a technique developed by Bohlen et al. (1983), in which a mixture of appropriate composition, with  $\text{Fe}_2\text{O}_3$  as the source of Fe, was melted in a graphite capsule, and the duration of the melting experiment was adjusted so that it was sufficient to reduce all  $\text{Fe}_2\text{O}_3$  to FeO, but was insufficient for the further reduction to metallic Fe. A grass green color of the glass, without any noticeable metallic iron, was considered to be a satisfactory criterion for the formation of glass in which all iron was in a divalent state. However, subsequent analyses of garnet glasses by Mössbauer spectroscopy showed significant amounts of  $\text{Fe}^{3+}$  in several such glasses (Geiger, personal communication).

In this study, we developed a new technique for the preparation of FeO bearing glasses under controlled  $f_{\text{O}_2}$  condition. Since diffusion of oxygen is very slow through melt, the  $\text{Fe}_2\text{O}_3$  in the oxide mixture was reduced prior to melting in a Mo capsule at 1100°C and  $f_{\text{O}_2} \approx 10^{-14}$  bars, which is a condition within the stability fields of both FeO (wüstite) and Mo. It was found that 3 h were adequate to reduce  $\approx 2$  g  $\text{Fe}_2\text{O}_3$  to FeO. The mixture was then rapidly heated to 1480–1580°C, melted and held for  $\approx 45$  min. Immediately after melting,  $f_{\text{O}_2}$  was readjusted to a condition within the wüstite field but below Mo/MoO<sub>2</sub> equilibrium. Although it took  $\approx 20$  min to stabilize  $f_{\text{O}_2}$  in the last step, there can be no significant effect of the transient  $f_{\text{O}_2}$  condition on the oxidation state of iron because of the very slow diffusion rate of oxygen through the melt. The product glass was always grass green in color.

## Starting materials

Garnets of various compositions were synthesized hydrothermally either from glasses of corresponding compositions, or from mixtures of synthetic end-member garnets (also synthesized from glasses), in sealed gold capsules at 25 kbar, 1000°C, 40–48 h (Table 1). A number of high pressure hydrothermal experiments yielded garnet solid solutions which showed poor resolution of the  $a_1$  and  $a_2$  doublet at  $2\theta > 50^\circ$  in X-ray diffractometer scan using Cu radiation, indicating significant compositional heterogeneity (Ganguly et al. 1993). These samples were ground, remixed and then recycled at 35–40 kbar, 1350–1400°C under dry conditions in a graphite capsule for 24–48 h to achieve homogeneity of compositions.

Attempts to synthesize Fe-Mg-Ca ternary garnets from glasses of appropriate compositions according to the above procedure

were unsuccessful. The products of the high pressure hydrothermal syntheses showed small amount of pyroxenes, which persisted even when the products were recycled to 40 kbar, 1400°C for 20 h. However, single phase Fe-Mg-Ca garnets were successfully synthesized at 25 kbar, 1000°C using mechanical mixtures of synthetic end member garnets, which were sealed with water in gold capsules.

Anorthite was prepared from a stoichiometric mixture of CaO (99.9%), g- $Al_2O_3$  (>99.9%),  $SiO_2$  (99.9%) in a hydrothermal apparatus at 2 kbar, 700°C for 10 days. Kyanite was obtained from Litchfield, Connecticut (FeO content = 0.16 wt%), and quartz was obtained from Lisbon, Maryland (purified by N.L. Bowen and J. Goldsmith).

**Table 1** Experimental conditions for the syntheses of end-member and solid solution garnets, and results ( $Mg\#$   $Mg/(Mg+Fe)$ ,  $Mg'$   $Mg/(Mg+Mn)$ ,  $Gt$  garnet,  $Py$  pyrope,  $Gr$  grossular,  $Alm$  almandine,  $Spess$  spessartine,  $CPx$  clinopyroxene)

Expt. No.	Starting material	$P$ (kbar)	$T$ (°C)	$t$ (h)	Results
<b>Pyrope-grossular</b>					
JW12	Glass	25	1000	20	Py, 500–800 $\mu m$
JW16	Glass	25	1000	24	Gt, 40–50 $\mu m$ , heterogeneous
JW25	Product of JW/16	40	1400	48	Gt( $X_{Ca}=0.073$ ) $\approx 60 \mu m$
JW18	Glass	25	1000	24	Gt + $\approx 5\%$ CPx
JW29	Product of JW/18	40	1400	48	Gt( $X_{Ca}=0.384$ )
JW03	Glass	30	1000	12	Gt( $X_{Ca}=0.797$ ) $\approx 35 \mu m$
<b>Pyrope-grossular-spessartine</b>					
JW58	Glass	25	1000	21	Gt( $X_{Ca}=0.092$ , $Mg'=0.23$ ), $\approx 80 \mu m$
JW64	Glass	25	1000	24	Gt( $X_{Ca}=0.4$ , $Mg'=0.24$ ), $\approx 30 \mu m$
JW61	Glass	25	1000	24	Gt( $X_{Ca}=0.8$ , $Mg'=0.24$ ), $\approx 30 \mu m$
JW66	Glass	25	1000	24	Gt( $X_{Ca}=0.05$ , $Mg'=0.23$ ), $\approx 80 \mu m$
JW57	Glass	25	1000	21	Gt( $X_{Ca}=0.088$ , $Mg\#=0.41$ ), $\approx 50 \mu m$
JW56	Glass	25	1000	20	Gt, $\approx 15 \mu m$ , heterogeneous
JW65	Product of JW/56	37	1400	46	Gt( $X_{Ca}=0.4$ , $Mg'=0.42$ ), homogeneous
JW62	Glass	25	1000	24	Gt( $X_{Ca}=0.8$ , $Mg'=0.44$ ), $\approx 50 \mu m$
JW59	Glass	25	1000	24	Gt( $\approx 20 \mu m$ ), <3% other phases
JW70	Product of JW/59	39	1400	48	Gt( $X_{Ca}=0.1$ , $Mg'=0.68$ ), <30 $\mu m$
JW63	Glass	25	1000	24	Gt( $X_{Ca}=0.4$ , $Mg'=0.7$ ), +15% CPx
JW69	Product of JW/63	40	1400	48	Gt + $\approx 5\%$ CPx
JW68	Mixture of Gr+Py+Spess	25	1000	45	Gt( $X_{Ca}=0.4$ , $Mg'=0.66$ ), + $\approx 3\%$ CPx
JW60	Glass	25	1000	24	Gt( $X_{Ca}=0.8$ , $Mg'=0.7$ ), $\approx 50 \mu m$
JW67	Mixture of Gr+Py+Spess	25	1000	45	Gt( $X_{Ca}=0.2$ , $Mg'=0.68$ ), <2% other phases
<b>Almandine-pyrope-grossular</b>					
JW107	Glass	25	1000	28	Gt( $X_{Ca}=0.1$ , $Mg\#=0.2$ ), + $\approx 5\%$ CPx
JW108	Product of JW108	40	1380	40	Gt + small amount of CPx
JW121	Glass	40	1380	40	Gt + $\approx 3\%$ CPx
JW120	Mixture of Gr+Py+Alm	25	1000	26	Gt( $X_{Ca}=0.1$ , $Mg\#=0.2$ ), $\approx 40 \mu m$
JW124	Mixture of Gr+Py+Alm	25	1000	24	Gt( $X_{Ca}=0.4$ , $Mg\#=0.2$ ), $\approx 20 \mu m$
<b>Almandine-pyrope-grossular-spessartine</b>					
JW91	Glass	25	1000	25	$X_{Ca}=0.8$ , $Mg'=0.5$ , $Mg\#=0.6$ , <3% CPx
JW92	Glass	25	1000	25	$X_{Ca}=0.8$ , $Mg'=0.5$ , $Mg\#=0.1$ , <5% CPx
JW93	Glass	25	1000	24	Gt( $X_{Ca}=0.4$ , $Mg'=0.5$ , $Mg\#=0.6$ ), $\approx 30 \mu m$
JW94	Glass	25	1000	24	Gt( $X_{Ca}=0.4$ , $Mg'=0.5$ , $Mg\#=0.1$ ), $\approx 5\%$ CPx
JW97	Glass	25	1000	24	Gt( $X_{Ca}=0.1$ , $Mg'=0.5$ , $Mg\#=0.6$ ), $\approx 30 \mu m$
JW98	Glass	25	1000	24	Gt( $X_{Ca}=0.1$ , $Mg'=0.5$ , $Mg\#=0.2$ ), + small amount of other phases
JW99	Product of JW91	38	1380	40	Gt + small amount of CPx
JW100	Product of JW92	38	1380	40	Gt + small amount of CPx
JW101	Mixture of Gr+Py+Alm+Spess	25	1020	40	Gt( $X_{Ca}=0.7$ , $Mg'=0.5$ , $Mg\#=0.2$ ), $\approx 30 \mu m$
JW102	Mixture of Gr+Py+Alm+Spess	25	1020	40	Gt( $X_{Ca}=0.1$ , $Mg'=0.5$ , $Mg\#=0.2$ ), $\approx 20 \mu m$
JW103	Mixture of Gr+Py+Alm+Spess	25	1020	40	Gt( $X_{Ca}=0.4$ , $Mg'=0.5$ , $Mg\#=0.2$ ), <2% CPx

**Table 2** Experimental conditions and shifts of garnet compositions in the GASP equilibrium at 1000°C in the ternary subsystems ( $Mg' Mg/(Mg+Mn)$ ,  $Mg\# Mg/(Fe+Mg)$ )

Expt. No	P(kbar)	Time (h)	Starting garnet composition		Final garnet composition		Reaction
			$X_{Ca}$	$Mg'$	$X_{Ca}$	$Mg'$	
Mg-Ca-Mn ternary							
JW89	12.2	143	0.05	0.233	0.130	0.241	Gt growth
JW87	12.2	143	0.42	0.234	0.151	0.225	Gt breakdown
JW73	13.7	102	0.05	0.233	0.159	0.235	Gt growth
JW74	13.7	102	0.42	0.234	0.205	0.229	Gt breakdown
JW80	15.8	161	0.09	0.230	0.279	0.221	Gt growth
JW79	15.8	161	0.42	0.234	0.312	0.243	Gt breakdown
JW76	17.6	119	0.09	0.230	0.405	0.238	Gt growth
JW75	17.6	119	0.79	0.233	0.447	0.250	Gt breakdown
JW95	19.7	106	0.42	0.234	0.641	0.229	Gt growth
JW96	19.7	106	0.79	0.228	0.678	0.229	Gt breakdown
JW71	13.7	102	0.05	0.436	0.150	0.388	Gt growth
JW72	13.7	102	0.43	0.442	0.179	0.397	Gt breakdown
JW82	15.8	161	0.12	0.452	0.253	0.394	Gt growth
JW81	15.8	161	0.43	0.442	0.290	0.379	Gt breakdown
JW78	17.6	119	0.12	0.452	0.397	0.424	Gt growth
JW77	17.6	119	0.81	0.417	0.431	0.413	Gt breakdown; <5% CPx
JW113	17.1	112	0.12	0.452	0.368	0.415	Gt growth
JW114	17.1	112	0.81	0.417	0.392	0.392	Gt breakdown; <5% CPx
JW118	16.9	114	0.12	0.452	0.343	0.387	Gt growth
JW119	16.9	114	0.43	0.442	0.382	0.405	Gt breakdown
JW98	19.7	106	0.12	0.452			Gt+CPx
JW97	19.7	106	0.81	0.417			Almost complete Gt breakdown; CPx growth
JW90	12.2	143	0.05	0.713	0.090	0.678	Gt growth
JW88	12.2	143	0.42	0.686	0.111	0.682	Gt breakdown
JW122	15.8	144	0.10	0.705	0.216	0.711	Gt growth
JW123	15.8	144	0.42	0.686	0.248	0.663	Gt breakdown
JW128	17.0	164	0.10	0.705	0.267	0.699	Gt growth
JW129	17.0	164	0.42	0.686	0.323	0.674	Gt breakdown; <5% CPx
JW84	19.8	114	0.10	0.705	0.528	0.684	Gt growth, <3% other phases
JW83	19.8	114	0.81	0.417			Gt breakdown; CPx growth
Fe-Mg-Ca ternary							
				$Mg\#$		$Mg\#$	
JW125	16.1	142	0.145	0.219	0.283	0.197	Gt growth
JW126	16.1	142	0.410	0.223	0.305	0.231	Gt breakdown
JW130	17.4	144	0.145	0.219	0.378	0.205	Gt growth
JW131	17.4	144	0.410	0.223	0.394	0.212	Gt breakdown

## Experimental results

The experimental results on the change of garnet compositions in the GASP assemblages are summarized in Tables 2 and 3. The garnets were always compositionally zoned, with the core composition usually representing or close to being the original composition. Thus, garnet compositions determined from cell dimensions in the experimental GASP assemblages (Hensen et al. 1975; Cressey et al. 1978; Wood 1988) represent the average composition of the garnets, which are not necessarily their equilibrium composition at the experimental conditions. Figure 1a shows a backscattered electron image of a typical garnet crystal in a quenched experimental product, whereas Fig. 1b illustrates the variation of garnet composition within a 'reversal couple', as determined by microprobe spot analyses of garnet compositions. The most evolved compositions from the low and

high calcium sides were taken to bracket the equilibrium composition of garnet. A discussion of the results for the specific systems follows.

### *Pyrope-grossular garnet*

We made 12 experiments at 14–19.5 kbar, 1000°C with mixtures of binary pyrope-grossular garnet ( $X_{Ca}=0.0, 0.1$  and 0.8) in order to determine the effect of pyrope component on the GASP equilibrium at 1000°C. However, the products of all experiments yielded some amount of pyroxene (with compositions in the system  $CaMgSi_2O_6$ – $CaAl_2SiO_6$ – $Mg_2Si_2O_6$ ) along with garnet, kyanite and quartz. Because of the repeated formation of pyroxene in the experimental products, we did not find it feasible to put unambiguous experimental constraints on the effect of the pyrope component on the GASP equilibrium.

**Table 3** Experimental conditions and shifts of garnet compositions in the GASP equilibrium at 1000° C in the quaternary system (Mg' Mg/(Mg+Mn), Mg# Me/(Fe+Mg))

Expt. No.	P (kbar)	Time (h)	Starting garnet composition			Final garnet composition			Reaction
			X <sub>Ca</sub>	Mg'	Mg#	X <sub>Ca</sub>	Mg'	Mg#	
JW104	14.8	145	0.11	0.53	0.24	0.176	0.478	0.212	Gt growth
JW105	14.8	145	0.41	0.51	0.21	0.252	0.483	0.206	Gt breakdown
JW109	15.9	121	0.11	0.53	0.24	0.275	0.468	0.194	Gt growth
JW110	15.9	121	0.41	0.51	0.21	0.317	0.475	0.197	Gt breakdown
JW115	17.0	122	0.11	0.53	0.24	0.336	0.486	0.181	Gt growth
JW116	17.0	122	0.72	0.51	0.21	0.406	0.481	0.194	Gt breakdown
JW111	15.9	121	0.09	0.49	0.64	0.278	0.505	0.573	Gt growth
JW112	15.9	121	0.39	0.52	0.62	0.317	0.476	0.583	Gt breakdown
JW117	17.0	122	0.09	0.49	0.64	0.362	0.486	0.559	Gt growth
JW127	17.2	122	0.39	0.52	0.62	0.393	0.477	0.572	Gt breakdown

### *Pyrope-grossular-spessartine garnet*

Three sets of garnet compositions with fixed Mg/(Mg+Mn) ratios of 0.23, 0.41 and 0.68 were used to determine the effect of variation of garnet composition in this ternary system on the GASP equilibrium. The results are illustrated in Fig. 2 (a,b,c). The initial garnet compositions are represented by small filled circles, whereas the most evolved garnet compositions are illustrated by tips of arrows pointing in the direction of evolution of garnet composition.

### *Almandine-pyrope-grossular garnet*

We determined the equilibrium compositions of garnet in this ternary system at 16.1 and 17.4 kbar, 1000°C. The initial and the most evolved compositions of garnet are illustrated in Fig. 3 along with the results of Koziol and Newton (1989).

### *Almandine-pyrope-grossular-spessartine garnet*

Two sets of garnet compositions were used to determine the displacement of the GASP equilibrium at 1000°C in this quaternary system. These garnets had Mg/(Mg+Fe) ratio of 0.20 and 0.60, while the Mg/(Mg+Mn) ratio was kept fixed at 0.50. The initial and most evolved garnet compositions at several different pressures are illustrated in Fig. 4 (a,b).

## Modeling of experimental and natural data

The experimental data on the GASP equilibrium determined in this study were modeled along with several sets of experimental data by other workers to develop an optimized thermodynamic model of the (Fe,Mg,Ca,Mn)-garnet solid solution. The additional experimental data used in the modeling were as follows.

(a) The experimental data on the GASP equilibrium by Koziol and Newton (1989) in the Fe-Mg-Ca ternary system, and by Koziol (1996) in the Fe-Mg-Ca-Mn quaternary system.

(b) The results of calorimetric measurements on the enthalpy of mixing at 750°C in the Ca-Mg binary by Newton et al. (1977; Fig. 5).

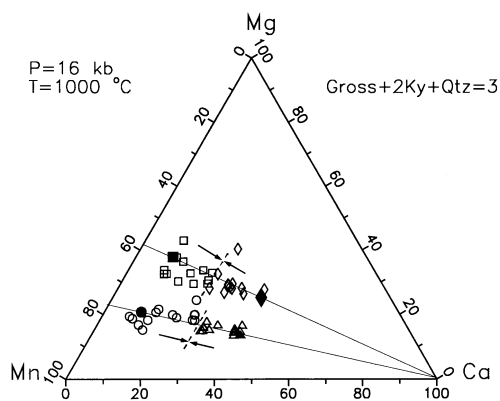
(c) The experimentally determined effect of Ca on the Fe-Mg fractionation between garnet and olivine by O'Neill and Wood (1979; Fig. 6) at 1200 C.

The mixing properties of the Fe-Mg, Fe-Ca, Fe-Mn and Ca-Mn binaries were constrained as discussed in the next section.

## Constraints on binary joins

### *Fe-Mg binary*

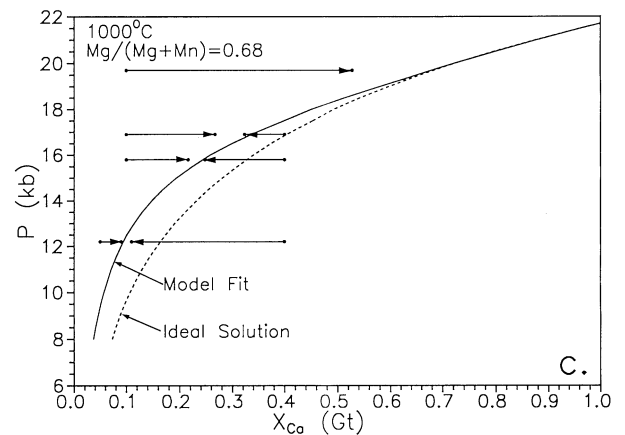
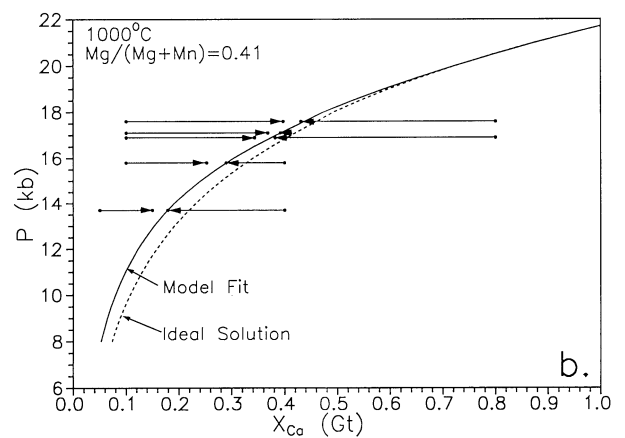
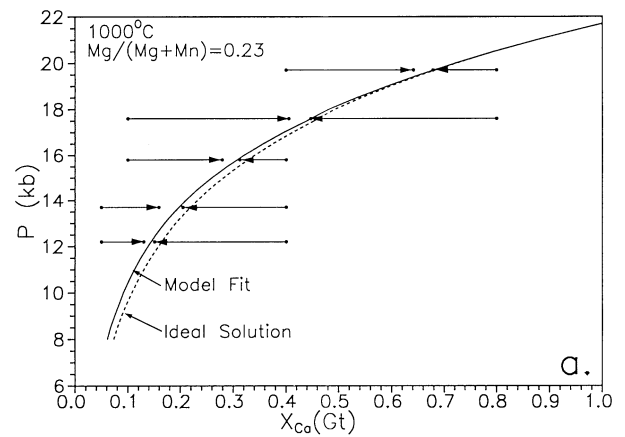
For this binary, we accepted the mixing properties deduced by Hackler and Wood (H-W: 1989), which show a small excess positive Gibbs free energy of mixing, with the maximum towards the Fe-rich end and a nearly ideal behavior towards the Mg rich end. Ganguly and Saxena (1984) deduced a qualitatively similar mixing property, but with a somewhat larger positive deviation from ideality. The H-W model is based on the experimentally determined effect of the Fe/Mg ratio on Fe-Mg fractionation between garnet and olivine at 1000 C (O'Neill and Wood 1979; Hackler and Wood 1989) and satisfied that between garnet and orthopyroxene at 1200°C, 26 kbar (Lee and Ganguly 1988), as well as the phase equilibrium data on the equilibrium garnet + rutile [ ilmenite + sillimanite + quartz (GRAIL) in the Fe-Mg system at 900 and 1000°C (Koziol and Bohlen 1992). Assuming  $DS^{XS} = 0$ , the H-W model yields  $DH^{XS}$  in the binary join, which is compatible with that determined calorimetrically at 750°C by Geiger et al. (1987) except at  $X_{Fe} \geq 0.70$ , where the calorimetric values are much higher than that predicted by the model. This discrepancy may be due to the presence of ferric iron in the Fe-rich synthetic sam-



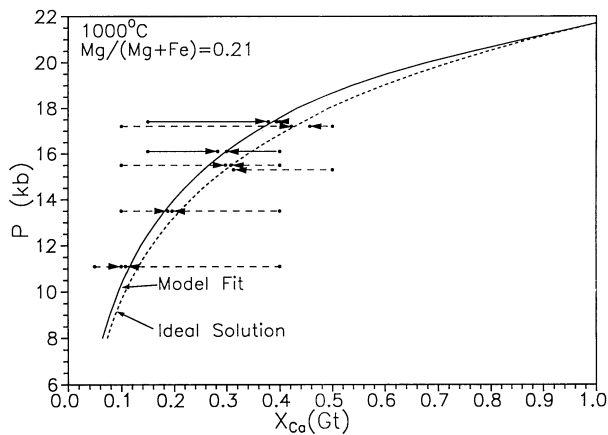
**Fig. 1a** Backscattered electron image showing compositional zoning in a typical garnet crystal in a quenched experimental product consisting of ternary (Mg,Mn,Ca)-garnet, kyanite, anorthite and quartz. **b** Variation of garnet compositions as determined by electron microprobe spot analysis in a 'reversal couple' of the GASP equilibrium in the Mg-Ca-Mn ternary at 16 kbar, 1000°C. The equilibrium garnet compositions, marked by *dashed lines*, are bracketed by the most evolved compositions. The initial garnet compositions are designated by relatively *larger filled symbols*, whereas the direction of change of garnet composition is shown by *arrows*

ples rather than due to an asymmetric  $DS^{XS}$  (which is negligible at  $X_{Fe} < 0.70$  but has a significant positive deviation from ideality at more iron rich compositions).

Bhattacharya et al. (1991) decomposed the mixing property of the Fe-Mg join into enthalpic and entropic contributions by completely accepting the calorimetric data of Geiger et al. (1987) and introducing excess entropy parameters ( $W_{FeMg}^S = -6.385 (+ 0.527)$  and  $W_{MgFe}^S = 5,849 (+ 0.510)$  J/cation-mol) to reconcile the calorimetric data with the experimental phase equilibrium data at 1000–1200°C (Lee and Ganguly 1988). Because of our concern about the presence of ferric iron in synthetic Fe rich garnets, we decided not to incorporate this model in our scheme even though it is self con-



**Fig. 2** Displacement of the equilibrium Grossular + Kyanite + 3 Quartz [ 3 Anorthite as a function of garnet composition at 1000°C in the Mg-Ca-Mn ternary system at Mg/(Mg + Mn) ratios of **a** 0.23, **b** 0.41 and **c** 0.68. The original garnet compositions are represented by *small filled circles*, whereas the most evolved compositions are represented by the *tips of arrows*. The *solid curve* represents the calculated equilibrium boundary according to the optimized 'preferred' mixing parameters summarized in Table 4, whereas the *dashed curves* represent the equilibrium boundaries according to ideal mixing model. The equilibrium boundary calculated according to the alternative model (Table 4) is essentially the same as that calculated from the 'preferred' mixing model in Figs. 2–4



**Fig. 3** Displacement of the equilibrium Grossular + Kyanite + 3 Quartz [ 3 Anorthite as a function of garnet composition at 1000°C in the Fe-Mg-Ca ternary system at Mg/(Mg + Fe) ratio (or Mg#) of 0.21–0.22. The *dashed arrows* represent the results of Koziol and Newton (1989) for Mg# = 0.21 whereas the *solid ones* represent the results of this study for a slightly different Mg# of 0.23. See caption of Fig. 2 for explanation of the *solid* and *dashed curves*. The equilibrium boundary calculated according to the Berman (1990) model is essentially the same as that calculated according to our model if the pressures of both end-member and solid solution equilibria are treated in the same way (see text). See Fig. 1 for the designations of original and most evolved garnet compositions

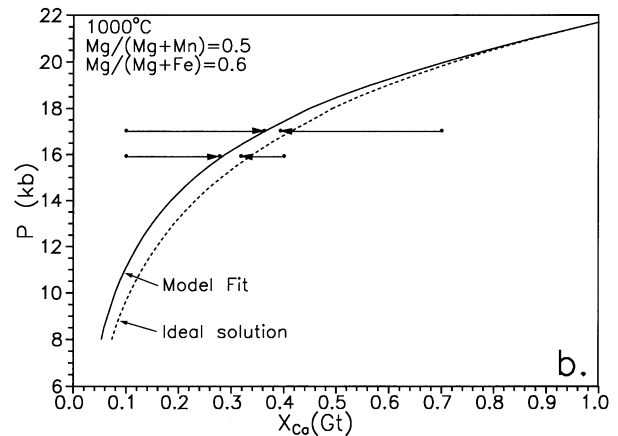
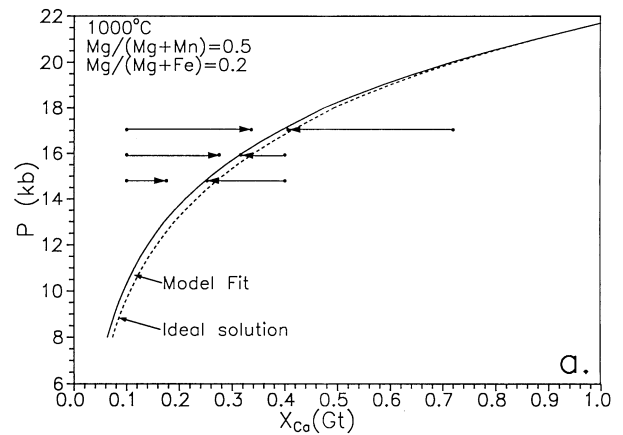
sistent and matches the available phase equilibrium constraints quite well.

#### Ca-Fe binary

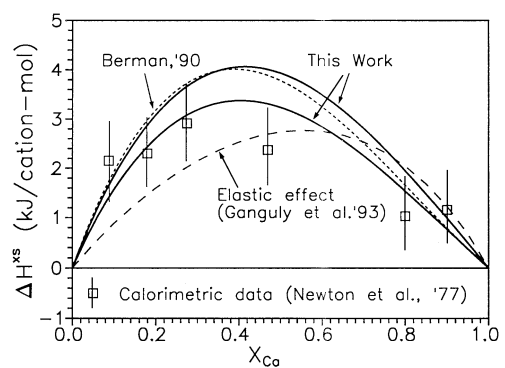
We accepted Berman's (1990) optimized  $W^H$  and  $W^S$  parameters for the Ca-Fe join which were deduced from analysis of the available experimental data on the GASP (Cressey et al. 1978; Koziol and Newton 1989), GRAIL (Bohlen and Liotta 1986) and GAF ( $3 Fa + 3 An = Gr + 2 Alm$ ; Bohlen et al. 1983) equilibria, along with the calorimetric data on the enthalpy of mixing in the binary join (Geiger et al. 1987). The  $W^V$  parameters used in our model are those determined by Geiger et al. (1989) using synthetic crystals in the Ca-Fe join. Although Berman used slightly different  $W^V$  parameters in his optimization analysis, using the results of Geiger et al. does not materially alter the  $W^H$  and  $W^S$  parameters since the  $DV^{XS}$  is very small.

#### Fe-Mn and Ca-Mn binaries

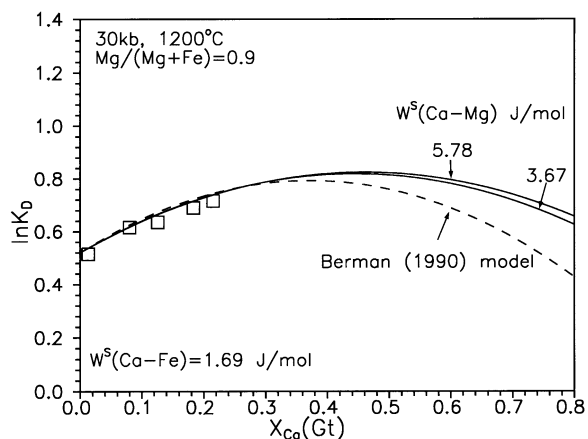
To constrain the mixing properties in these binaries, we used the experimental data on the effect of Ca on Fe-Mn fractionation between garnet and ilmenite, as determined by Pownceby et al. (1991) at 650–1000°C. In these experiments, the equilibrium Fe-Mg fractionations were constrained by approaching from both sides of the equilibrium values. Using  $W^G(Fe-Mn) = 2200$  J/cation-mol for ilmenite (O'Neill et al. 1989), thermodynamic and statistical analysis of their data (O'Neill, personal com-



**Fig. 4** Experimentally determined displacement of the GASP equilibrium as a function of the garnet composition in the quaternary system Fe-Mg-Ca-Mn at Mg/(Mg + Mn) = 0.50 with **a** Mg/(Mg + Fe) = 0.2 and **b** Mg/(Mg + Fe) = 0.6. See caption of Fig. 1 for explanations of original and most evolved garnet compositions and of the *solid* and *dashed curves*. The calculated quaternary equilibrium also agrees with the data of Koziol (1996)



**Fig. 5** Comparison of the excess molar enthalpy of mixing ( $\Delta H^{XS}$ ) in the pyrope-grossular join (1-cation basis), as calculated from the optimized models developed in this work and by Berman (1990) with the calorimetric data of Newton et al. (1977). The latter are shown by *squares* with bars representing  $\pm 1$  s error. Of the two models labelled 'this work', the one with larger  $\Delta H^{XS}$  represents the 'preferred' model (Table 4). The model of Ganguly et al. (1993) represents the elastic contribution to  $\Delta H^{XS}$  arising from mismatch of volume of the end members and  $DV^{XS}$  in the pyrope-grossular binary



**Fig. 6** Comparison of the calculated and experimentally determined effect of Ca concentration in garnet on the Fe-Mg distribution coefficient between garnet and olivine at 30 kbar, 1200°C, and  $Mg\# = 0.9$  (O'Neill and Wood 1979; O'Neill, personal communication). The calculated curves are according to the garnet mixing models developed in this work and by Berman (1990).  $W^S(Fe-Ca)$  was kept fixed at 1.69 J/cation-mol according to Berman (1990).  $W^S(Mg-Ca) = 3.67$  and  $5.78$  J/cation-mol represent the results of two alternative optimizations of garnet mixing property (see text for discussion and Table 4)

munication) show the mixing behavior in the Fe-Ca and Mn-Ca binaries in garnet to be very similar (in that there was no significant effect of Ca on Fe-Mn fractionation), and yield  $W^G(Fe-Mn) = 539 + 109$  J/cation-mol for garnet. We, thus, used these Fe-Mn mixing data along with the constraints that  $W^G_{CaMn} = W^G_{CaFe}$  and  $W^G_{MnCa} = W^G_{FeCa}$ .

#### Modeling procedure

The modeling was carried out by the well known optimization program MINUIT (James and Ross 1975). Starting with guessed input values of the binary interaction parameters, the program calculated

(a) the position of the GASP equilibrium in the above ternary and quaternary systems according to the equilibrium condition (kyanite and quartz being assumed to be stoichiometric)

$$-3RT \ln(X_{Ca} g_{Ca})^{Gt} + \sum_1^p (D\bar{V}_a)_{T,X}^{-p} \& (DV_a^p)_{T,dP} = 0, \quad (4)$$

(b)  $DH^{XS}$  in Mg-Ca join according to the subregular model

$$DH^{XS} = (W_{CaMg} X_{Mg} + W_{MgCa} X_{Ca}) X_{Mg} X_{Ca}, \quad (5)$$

and

(c) the effect of Ca on  $K_D(Fe-Mg)$  between garnet and olivine for a fixed  $Fe/(Fe+Mg)$  ratio according to

$$RT \ln K_D = RT \ln K_D(X_{Ca}=0) - RT \ln(g_{Fe}/g_{Mg})^{Gt}. \quad (6)$$

The expressions for the activity coefficients ( $g_i$ ) were developed according to the multicomponent subregular model of Cheng and Ganguly (1994). For the calculation

of the integrals in Eq. 4, the thermal expansion coefficient,  $\alpha$ , and compressibility,  $\beta$ , were taken from the optimized database of Berman (1988), it being assumed that  $\bar{V}_i$  and  $V_i^o$  have the same  $P$ - $T$  dependencies. In Eq. 6, olivine was treated as a binary solution of the Fe and Mg end-members (since  $X_{Ca}^{Ol} \leq 0.01$ ); further, since the bulk  $Fe/(Fe+Mg)$  ratio was kept fixed (0.90) in the experimental studies (O'Neill and Wood 1979), it was assumed that the observed variation of  $K_D$  was essentially due to that in the Ca concentration in garnet.

The GASP equilibria,  $DH^{XS}$  in the Ca-Mg join, and  $RT \ln K_D$  vs  $X_{Ca}^{Gt}$ , as calculated from Eqs. 4, 5 and 6 from a set of values of the interaction parameters, were compared with the experimental data, the interaction parameters were changed automatically in the next step, and the process was repeated to yield a set of optimized values of the interaction parameters until the squares of the deviations between the calculated and experimental values were minimized. In these calculations, the experimentally determined equilibrium value of  $X_{Ca}^{Gt}$  in the GASP reaction at 1000°C was allowed to be any point within a reversal bracket (Figs. 2, 3, 4), and of the calorimetric  $DH^{XS}$  in the Ca-Mg join was allowed to be any point within the  $\pm 1s$  of the mean calorimetric value at a given composition (Fig. 5). The calculations were repeated with different initial values of the interaction parameters, and in each case the same set of optimized values of the interaction parameters was obtained.

Haselton and Westrum (1980) determined the  $DS^{XS}$  of a garnet solid solution of  $Pyr_{60}Gr_{40}$  composition from calorimetric measurements of the  $DCp^{XS}$  at 10–350 K. Assuming that the  $DS^{XS}$  is symmetric to composition, their results yield  $W^S(Mg-Ca) = 6.26 + 0.42$  J/cation-mol K. This result was not included in the optimization process through MINUIT, but was used as an external test of the result. The optimization of all experimental phase equilibrium data at 1000 and 1200°C and of calorimetric enthalpy of mixing data at 750°C in Mg-Ca join discussed above yields  $W^S(Mg-Ca) = 3.67$  J/cation-mol, which does not agree with the value derived from the heat capacity data of Haselton and Westrum (1980). However, it was found that neglecting only one datum from the calorimetric  $DH^{XS}$  in the Mg-Ca join at  $X_{Ca} = 0.47$  (Fig. 5) yields  $W^S(Mg-Ca) = 5.78$  J/cation-mol, which agrees well with its calorimetric value.

The results of optimization analysis both including and excluding the calorimetric  $DH^{XS}$  datum at  $X_{Ca} = 0.47$  are summarized in Table 4. We prefer the results obtained by excluding this calorimetric  $DH^{XS}$  datum since the derived  $W^S(Mg-Ca)$  value agrees with that calculated from the calorimetric heat capacity data in the Mg-Ca join. The GASP equilibrium in the Mg-Mn-Ca, Fe-Mg-Ca and Fe-Mg-Ca-Mn systems,  $DH^{XS}$  in the Mg-Ca binary, and  $\ln K_D(Fe-Mg)$  between garnet and olivine vs  $X_{Ca}^{Gt}$ , as calculated according to the models summarized in Table 4, are illustrated in Figs. 2, 3, 4, 5 and 6, respectively. We also show in Figs. 5 and 6 the calculated  $DH^{XS}$  and  $\ln K_D$  curves, respectively, according to the Berman (1990) model.



**Table 4** Summary of the internally consistent binary subregular interaction parameters in aluminosilicate garnets.  $W_{ij}^H$ ,  $W_{ij}^S$  and  $W_{ij}^V$  are respectively the enthalpic (J/mol), entropic (J/mole-K) and volumetric (J/bar) contributions to the subregular free energy parameter ( $W_{ij}^G$ ) on one-cation basis. For the Ca-Mg binary, there are two alternative solutions. The one associated with  $W^S=5.78$  J/cation-mol is the *preferred model*

Parameter (ij)	$W_{ij}^H$	$W_{ij}^S$	$W_{ij}^V$
CaMg	21627	5.78	0.012 <sup>a</sup>
MgCa	18522	3.67	
	9834	5.78	0.058 <sup>a</sup>
	7388	3.67	
CaFe	873 <sup>b</sup>	1.69 <sup>b</sup>	0 <sup>c</sup>
FeCa	6773 <sup>b</sup>	1.69 <sup>b</sup>	0.03 <sup>c</sup>
MgFe	2117 <sup>d</sup>	0	0.07 <sup>e</sup>
FeMg	695 <sup>d</sup>	0	0 <sup>e</sup>
MgMn	12083	7.67	0.04 <sup>e</sup>
MnMg	12083	7.67	0.03 <sup>e</sup>
FeMn	539 <sup>f</sup>	0	0.04 <sup>e</sup>
Mn-Fe	539 <sup>f</sup>	0	0.01 <sup>e</sup>

<sup>a</sup> Ganguly et al. (1993); <sup>b</sup> Berman (1990); <sup>c</sup> Geiger et al. (1989); <sup>d</sup> Hackler and Wood (1989); <sup>e</sup> Geiger et al. (1994); <sup>f</sup> Powenby et al. (1991), modified (O'Neill, personal communication)

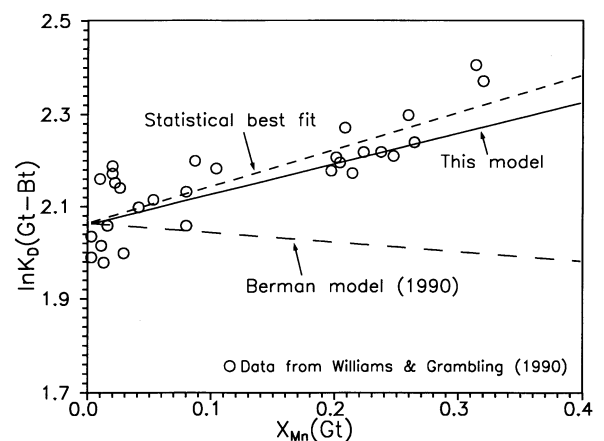
The garnet solution model developed by Berman (1990) seemed to have fitted the ternary data of Koziol and Newton (1989) quite satisfactorily. However, Berman adjusted the pressure of the end-member GASP reaction by Koziol and Newton (1988) downwards by 300 bars from the nominal pressure of 21.70 kbar, but did not adjust the pressures of the experiments in the ternary system. We argue that since both the end-member and the solid solution equilibria were determined by the same workers following the same procedure and using the same flux (which is also the flux used in our work), it is not justified to make pressure adjustments of selected data. All data should have similar errors in pressure, so that their relative pressures should be essentially unaffected. The equilibrium boundary in the Fe-Mg-Ca system calculated according to Berman's model (1990) is almost indistinguishable from that calculated according to the solution model developed in this work (Fig. 3) if no friction correction is applied selectively to the nominal pressure (21.7 kbar) of the end-member reaction.

The experimental data used to retrieve the mixing property of the Mg-Mn binary are restricted to 1000 C, and consequently the ideal mixing of this join inferred from the optimization analysis should not be extrapolated to lower temperature. Further, we recall that the Fe-Mg mixing model of Hackler and Wood (1989), which is adopted in this work, are based on Fe-Mg partitioning data at 1000°C. Their analysis of the calorimetric  $DH^{XS}$  data in the Fe-Mg join (Geiger et al. 1987) and Berman's (1990) analysis of the Fe-Mg mixing properties at lower temperature are suggestive, but not conclusive, of little or no  $DS^{XS}$  mixing in this binary join. Careful calorimetric measurement of  $DH^{XS}$  of well characterized samples are needed in both Fe-Mg and Mg-Mn joins to sort out their mixing behavior at lower temperatures.

## Modeling of natural data

In this section we try to constrain the Mg-Mn mixing property in garnet at lower temperature from the observed compositional dependence of  $K_D(\text{Fe-Mg})$  between garnet and biotite in a suite of nearly isothermal-isobaric assemblages from Pecos Baldy, New Mexico (Fig. 7), as reported by Williams and Grambling (1990). The variation of  $K_D(\text{Fe-Mg})$  must be due to the variation of components in garnet and biotite with significant non-ideal mixing behavior. However, since Ti, Al and  $\text{Fe}^{3+}$  contents of these biotites have very restricted ranges (0.06–0.10, 1.59–1.90, and 0.19–0.22 cations, respectively, per 11 oxygen), and biotite and garnet are unlikely to have significantly different nonideal Fe-Mg interactions according to the analysis of the Fe-Mg mixing in biotite by Mueller (1972) and Ganguly and Saxena (1987), and of that in garnet by Hackler and Wood (1989) and Berman (1990), the large variation of  $K_D$  in the Pecos Baldy assemblages should be primarily due to the variation of Mn ( $\approx 0$ –30 mol%) and Ca ( $\approx 3$ –8 mol%) contents of garnet. The observed compositional dependence of  $K_D$ , however, implies a much larger positive deviation from ideality of the Mg-Mn join than that deduced above from the experimental data at 1000°C, which suggest a significant entropy effect on the mixing property in the Mg-Mn join of garnet so that the  $W^G(\text{Mg-Mn})$  increases with decreasing temperature.

An approximate temperature of the Pecos Baldy assemblage can be deduced from the garnet-biotite Fe-Mg exchange thermometer determined experimentally by Ferry and Spear (1978) in the binary Fe-Mg system, and  $K_D(\text{Fe-Mg})$  between garnet and biotite in the natural samples with minimal concentration of the other components. Two such samples are No. 77–85B and 77–420, which have a combined concentration of Ca and Mn in garnet of  $\approx 3\%$  (Williams and Grambling 1990). These samples yield a temperature of  $\approx 485^\circ\text{C}$  if we neglect the



**Fig. 7** Variation of the Fe-Mg distribution coefficient between garnet and biotite as a function of Mn content of garnet in a suite of rocks from Pecos Baldy, New Mexico. Data (circles) are from Williams and Grambling (1990). The  $\ln K_D$  vs  $X_{\text{Ca}}^{\text{Gt}}$  relationships calculated from the preferred model (Table 4) and Berman (1990) model are shown by solid and dashed lines respectively

possible nonideal effect of Al, Ti and Fe<sup>3+</sup> in biotite (Patiño Douce et al. 1993) and the small effect of the Ca and Mn in garnet. The thermodynamic relation governing the compositional dependence of  $K_D(\text{Fe-Mg})$  between garnet and biotite in a multicomponent system can be derived by expanding the relation (e.g. Ganguly and Kennedy 1974)

$$RT\ln K_D = RT\ln K - RT\ln \left( \frac{g_{Fe}}{g_{Mg}} \right)^{Gt} + RT\ln \left( \frac{g_{Fe}}{g_{Mg}} \right)^{Bt} \quad (7)$$

Assuming that the Mg-Mn and Fe-Mn binary joins in garnet behave as a regular solution whereas the other joins behave as subregular solution, and that biotite behaves as a regular solution with ideal Fe<sup>2+</sup>-Mg binary, the expansion of Eq. 7 yields

$$\begin{aligned} RT\ln K_D = & RT\ln K - [W_{CaMg}(-2X_{Ca}X_{Mg}+A) + W_{MgCa}(-X_{Ca}^2+A) \\ & + W_{CaFe}(2X_{Ca}X_{Fe}+B) - W_{FeCa}(X_{Ca}^2+B) \\ & + W_{MgFe}(2X_{Mg}X_{Fe}-X_{Fe}^2+C) \\ & + W_{FeMg}(X_{Mg}^2-2X_{Mg}X_{Fe}+C) - DW_{Mn}X_{Mn}]^{Gt} \\ & - [DW_{Ti}X_{Ti} + DW_{Al}X_{Al} + DW_{Fe^{3+}}X_{Fe^{3+}}]^{Bt} \end{aligned} \quad (8)$$

where

$$A = \frac{1}{2} X_{Ca}(X_{Mg} - X_{Fe} - X_{Mn})$$

$$B = \frac{1}{2} X_{Ca}(X_{Mg} - X_{Fe} + X_{Mn})$$

$$C = \frac{1}{2} (X_{Ca} + X_{Mn})(X_{Mg} - X_{Fe})$$

We regressed the  $\ln K_D(\text{Fe-Mg})$  data for the Pecos Baldy samples (Williams and Grambling 1990) against  $X_{Mn}(\text{Gt})$  according to Eq. 8 by constraining the mixing properties in all the binary joins of garnet excepting Mg-Mn, according to the data summarized in Table 4, and treating the mixing properties of biotite in three different ways, viz (a) models **a** and **b** of Patiño-Douce et al. (1993) for the mixing of Al and Ti, (b) ideal mixing of Al and Ti, and (c) unconstrained values of  $DW_{Ti}$  and  $DW_{Al}$ .

All iron in garnet was treated as Fe<sup>2+</sup>, as in the work of Williams and Grambling (1990). The regression with unconstrained biotite properties yielded  $DW_{Ti} = -59 + 22 \text{ kJ/cation-mol}$  (+ 1 s) and  $DW_{Al} \odot 0$ . These values may be compared with the mixing models derived by Patiño-Douce et al. (model **a**:  $DW_{Ti} = -10 + 15$  and  $DW_{Al} \odot 2.7 + 10 \text{ kJ/cation-mol}$ , and model **b**:  $DW_{Ti} = -12.3 + 15$  and  $DW_{Al} \odot 22.2 + 10 \text{ kJ/cation-mol}$ ). From this comparison, we prefer the model **a** of Patiño Douce et al. (1993) to their model **b** since the DW parameters therein are much closer to those derived in the unconstrained regression. In all these regression analyses,  $DW_{Fe^{3+}}$  (Bt) turned out to be an insignificant variable (P factor = 0.35), which is most likely due to its restricted compositional range rather than the equality of interaction of Fe<sup>3+</sup> with Fe<sup>2+</sup> and Mg. Further, we carried out the regression with *unconstrained Fe-Mg mixing in garnet*, but with  $W_{FeMg} = W_{MgFe}$ , in addition to unconstrained binary mixing properties in biotite in the Fe-Mg-Al system. The  $W^G(\text{Mg-Mn})$  values in garnet derived

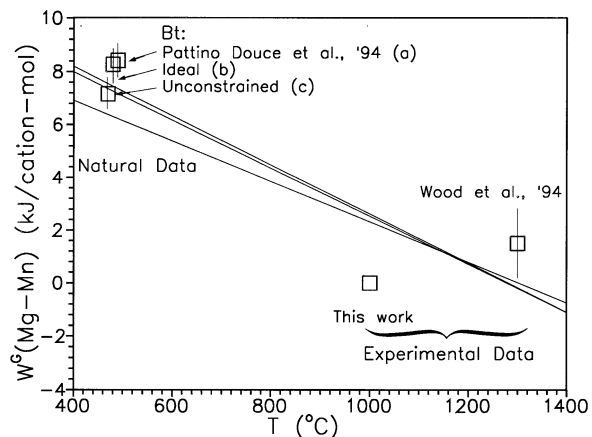
from the above analyses fall within a restricted range of  $7162 + 639 \text{ J/cation-mol}$ . These results suggest the Mg-Mn mixing in garnet to be have significantly larger positive deviation from ideality at  $\approx 500^\circ\text{C}$  than deduced above at  $1000^\circ\text{C}$  from the experimental phase equilibrium data.

Our results for Mg-Mn mixing in garnet derived from the experimental phase equilibrium data at  $1000^\circ\text{C}$  and natural data at  $\approx 485^\circ\text{C}$  are illustrated in Fig. 8 along with that of Wood et al. (1994) at  $1300^\circ\text{C}$ , which was derived from experimental data on Fe-Mg partitioning between garnet and olivine as a function of  $X_{Mn}(\text{Gt})$ . If it is assumed that  $W^G$  is a linear function of temperature according to  $W^G = W^H - TW^S$ , then these data suggest a minimum value of  $W^S(\text{Mg-Mn})$  of  $7.67 \text{ J/cation-mol K}$ . The resulting expression is

$$W^G(\text{Mg-Mn}) = 12083 - 7.67T \quad (9)$$

In addition, when the Fe-Mg mixing property in garnet was unconstrained, we obtained  $W^G_{MgFe} = W^G_{FeMg} = 3271 + 1905 \text{ J/cation-mol}$ , which is compatible with their high temperature ( $\approx 1000^\circ\text{C}$ ) nearly ideal values, but does not preclude a significant positive  $DS^{XS}$ .

From analyses of the compositional dependence of  $K_D$  between garnet and clinopyroxene in granulite facies rocks from several localities ( $T = 650\text{--}850^\circ\text{C}$ ) encompassing a large range of Mn concentration in garnet ( $X_{Mn} = 0\text{--}0.97$ ), Sengupta et al. (1989) deduced  $W^G(\text{Mg-Mn}) = 6.7 + 2.1 \text{ kJ/cation-mol}$  at the average temperature these rocks. Their results are compatible with Eq. 9. However, they constrained the mixing parameters in the



**Fig. 8** Regular solution (or simple mixture) interaction parameter per cation-mole in Mg-Mn join vs temperature. The  $W^G$  parameters at  $485^\circ\text{C}$  are based on the analyses of compositional dependence of  $K_D$  between garnet and biotite in a suite of samples from Pecos Baldy, New Mexico (Williams and Grambling 1990), treating biotite and garnet mixing properties in several different ways (see text). **a** Al and Ti mix according to the model **a** of Patiño Douce et al. (1993), **b** Al and Ti mix ideally, **c** Al and Ti mixing were unconstrained. In all these, the binary joins in garnet (except Mg-Mn) were constrained according to the preferred model in Table 4. Modeling with unconstrained Fe-Mg mixing in garnet and unconstrained Al and Ti mixing in biotite yields essentially the same result as **a**

other binary joins of garnet according to Ganguly and Saxena (1984).

The compositional dependence of  $K_D$  calculated for the Pecos Baldy samples according to the garnet solution models derived in this work and by Berman (1990) are illustrated in Fig. 7 by solid and dashed lines, respectively. These lines represent least squares fits to the calculated  $\ln K_D$  vs  $X_{Mn}(Gt)$ , assuming that there is no effect on  $K_D$  from the possible nonideality of the biotite solid solution.

### Expression of activity coefficients in the quaternary garnet solid solution

Following the general expression of  $RT\ln g_i$  in a multi-component subregular solution developed by Cheng and Ganguly (1994), the activity coefficient of Fe in the quaternary subregular garnet solid solution can be expressed as

$$\begin{aligned}
 RT\ln g_{Fe} = & (1-2X_{Fe})(W_{FeMg}X_{Mg}^2 + W_{FeCa}X_{Ca}^2 + W_{FeMn}X_{Mn}^2) \\
 & + 2(1-X_{Fe})(W_{MgFe}X_{Mg}X_{Fe} + W_{CaFe}X_{Ca}X_{Fe} \\
 & + W_{MnFe}X_{Mn}X_{Fe}) \\
 & - 2(W_{MgCa}X_{Mg}X_{Ca} + W_{CaMg}X_{Ca}X_{Mg} + W_{MgMn}X_{Mg}X_{Mn} \\
 & + W_{MnMg}X_{Mn}X_{Mg} + W_{MnCa}X_{Mn}X_{Ca} + W_{CaMn}X_{Ca}X_{Mn}) \\
 & + \frac{1}{2}(1-2X_{Fe})[X_{Mg}X_{Ca}(W_{FeMg} + W_{MgFe} + W_{FeCa} \\
 & + W_{CaFe} + W_{MgCa} + W_{CaMg}) \\
 & + X_{Mg}X_{Mn}(W_{FeMg} + W_{MgFe} + W_{FeMn} + W_{MnFe} \\
 & + W_{MgMn} + W_{MnMg}) \\
 & + X_{Ca}X_{Mn}(W_{FeCa} + W_{CaFe} + W_{FeMn} + W_{MnFe} \\
 & + W_{CaMn} + W_{MnCa})] \\
 & - X_{Mg}X_{Ca}X_{Mn}(W_{MgCa} + W_{CaMg} + W_{MgMn} + W_{MnMg} \\
 & + W_{CaMn} + W_{MnCa}). \quad (10)
 \end{aligned}$$

The activity coefficient of any other component J (i.e. Mg, Ca or Mn) follows from the above expression by the following substitutions  $W_{FeK} [ W_{JK}$  and  $W_{FeJ} [ W_{JFe}$ .

### Unmixing of garnet solid solutions

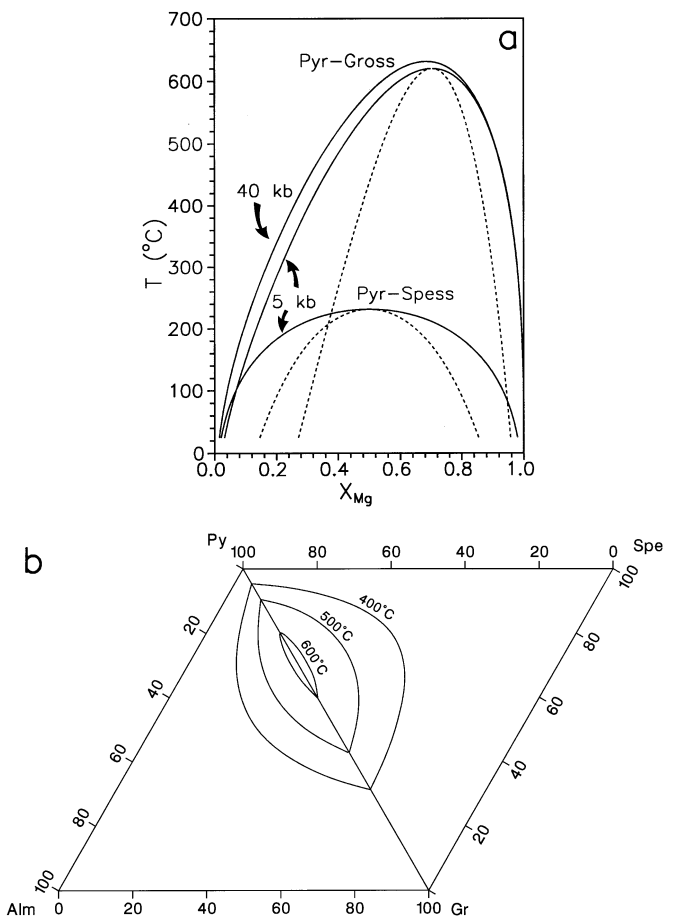
Using the preferred data for the mixing properties in the binary joins, as summarized in Table 4 and Eq. 9, we calculated the binary and ternary solvi and binary spinodals of the garnet solid solution. The binary solvi were calculated according to the equilibrium condition  $RT\ln X_1^a + RT\ln g_1^a = RT\ln X_1^b + RT\ln g_1^b$   $RT\ln X_2^a + RT\ln g_2^a = RT\ln X_2^b + RT\ln g_2^b$ . (11)

The ternary solvus must satisfy an additional analogous relation for the third component. This system of equations was solved numerically as a function of pressure and temperature. The results for the Mg-Ca and Mg-Mn binaries are illustrated in Fig. 9a, and those for the Fe-Mg-Ca and Mn-Mg-Ca ternaries are illustrated in Fig. 9b. Also shown in Fig. 9a are the spinodals for the Ca-Mg and Mg-Mn joins at 5 kbar, which were calculated

according to the spinodal condition  $d^2G/dX^2 = 0$  (e.g. Ganguly and Saxena 1987).

The pressure dependence of the solvus in the Ca-Mg join, as calculated in this work, is very different from that calculated by Haselton and Newton (1980). This difference is due to different volumetric properties of the Ca-Mg join used in the two sets of calculations. Whereas Haselton and Newton used the volumetric properties by Newton et al. (1977), we used those determined by Ganguly et al. (1993) from Rietveld refinement of synthetic and compositionally homogeneous samples in the Ca-Mg join (Table 4). The latter results have been substantiated by single crystal X-ray determination of a few samples (L. Ungaretti, personal communication) selected from those used by Ganguly et al. (1993).

Our results (Fig. 9) suggest that the combination of temperature and composition required for unmixing gar-



**Fig. 9** **a** Chemical solvi or binodals (solid lines) and spinodals (dashed lines) in the grossular-pyrope and spessartine-pyrope binaries, as calculated from the 'preferred' garnet mixing model (Table 4). Also shown is the pressure dependence of the solvus in the grossular-pyrope binary calculated according to the volumetric data of Ganguly et al. (1993). **b** Calculated miscibility gaps at 5 kbar in the almandine-pyrope-grossular and pyrope-grossular-spessartine ternaries as a function of temperature. The pressure dependence of the ternary solvi is insignificant within the range of pressure of geological interest

net fall outside those realized by the natural samples. For example, at  $\approx 500^\circ\text{C}$ , which is a temperature near the garnet isograd, the garnet compositions are too far off the pyrope-grossular binary to be candidates for exsolution, whereas for the garnets whose compositions lie near the pyrope-grossular binary, such as those in grosspydites (Sobolev et al. 1968), the crystallization temperature is much above the calculated critical temperature  $\approx 620^\circ\text{C}$ . Schmetzer and Bank (1981) reported almost binary pyrope-spessartine garnets with compositions ranging from near the spessartine end to  $\approx 60\%$  pyrope from Tanzania and Sri Lanka. Their data also incorporate those of similar garnets by Jobbins et al. (1978) and Schmetzer and Ottemann (1979). These data are not incompatible with the miscibility gap shown in Fig. 9a, as the crystallization temperatures of these garnets certainly lie above the calculated critical temperature of  $\approx 230^\circ\text{C}$  in the pyrope-spessartine binary, which further decreases with the incorporation of additional components.

### Refinement of garnet-orthopyroxene and garnet-clinopyroxene geothermometers

The equilibrium condition for Fe-Mg exchange between garnet and a coexisting mineral *a* (Mg-Gt + Fe-*a* [ Fe-Gt + Mg-*a*, written on single cation basis) yields

$$\ln K_D = [\ln K(1, T) + \frac{1}{RT} \Delta \bar{V} dP] - \ln \left( \frac{g_{Fe}}{g_{Mg}} \right)^{Gt} + \ln \left( \frac{g_{Fe}}{g_{Mg}} \right)^a \quad (12)$$

where the activity coefficients ( $g_i$ ) are at 1 atm (0.101 MPa),  $T$ , and

$$K_D = \frac{(X_{Alm}/X_{Pyr})^{Gt}}{(X_{Fe-a}/X_{Mg-a})^a} \quad (13)$$

The explicit expression of the term  $RT \ln (g_{Fe}/g_{Mg})^{Gt}$  is obvious from Eqs. 7 and 8.

It is a common practice to write  $K_D$  as

$$K_D = \frac{(Fe^{2+}/Mg)^a}{(Fe^{2+}/Mg)^b} \quad (13')$$

Equations 13 and 13' are equivalent in the case of Fe-Mg fractionation between garnet and orthopyroxene, but not equivalent for that between garnet and clinopyroxene due to the partial occupancy of the M2 site by Fe and Mg (Ganguly 1979). In the systems considered above,  $\Delta \bar{V} \ll \Delta \bar{V}^o$  (e.g. Ganguly et al. 1993).

Experimental data (Lee and Ganguly 1988) show that the Fe-Mg exchange between *garnet and orthopyroxene* is essentially independent of the Fe/Mg ratio so that the  $\ln K_D$  determined in the Fe-Mg binary should approximately equal the terms within the square brackets of Eq. 12, which we denote as  $\ln K'$ . Using the data of Lee and Ganguly (1987), we then obtain.

$$\ln K' (Gt-OPx) \ll \frac{1981 (+ 166) + 11.9 P(\text{kbar})}{T} - 0.97 \quad (14)$$

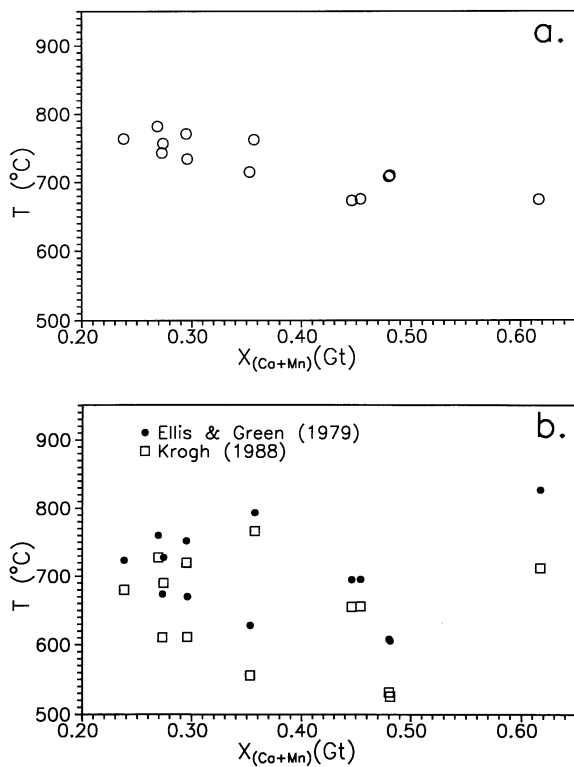
For the Fe-Mg exchange between *garnet and clinopyroxene*, substitution of the expression of  $K_D$  given by Eq. 13' in Eq. 12 causes an inherent error which leads to a dependence of  $K_D$  on the Ca content of clinopyroxene (Blander 1972; Ganguly 1979). In the absence of adequate data to address this problem, we develop below a restricted formulation of the garnet-clinopyroxene geothermometer for assemblages with  $X_{Ca}(\text{CPx}) = 0.40-0.45$ , for which, according to Ganguly (1979), as modified by Ganguly and Saxena (1987),

$$\ln K' (Gt-CPx) \ll \frac{4100 + 11.07 P(\text{kbar})}{T} - 2.40 \quad (15)$$

The above expression represents an *effective* equilibrium constant in that it has implicitly incorporated a nearly constant error term, arising from the substitution of Eq. 13' for  $K_D$  in Eq. 12.

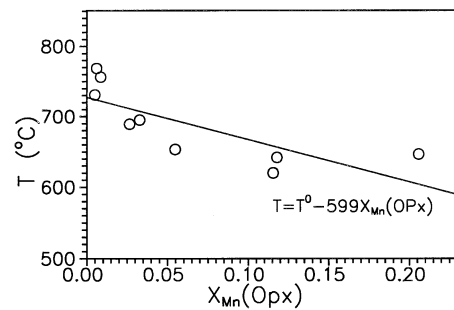
Syntheses experiments by Råheim and Green (1974) suggest  $K_D(\text{Fe-Mg})$  between garnet and clinopyroxene, as defined by Eq. 13', to be essentially independent of Fe/Mg ratio, whereas 'reversal' experiments by Pattison and Newton (1989) show a rather complex dependence of this  $K_D$  on the Fe/Mg ratio. The results of Råheim and Green (1989) are not definitive as they did not demonstrate attainment of equilibrium, whereas those of Pattison and Newton (1974) have been a subject of considerable debate (see, for example, Perkins and Vielzeuf 1992). Thus, in the absence of definitive experimental data, we assume, by analogy with the results in the garnet-orthopyroxene pairs (Lee and Ganguly 1988), that  $K_D'$  between garnet and clinopyroxene is also insensitive to Fe/Mg ratio as long as the M2 site in clinopyroxene has a nearly constant Ca content. We have, thus, neglected the Fe-Mg interaction terms in the expressions of  $\ln(g_{Fe}/g_{Mg})$  for garnet, orthopyroxene and clinopyroxene (Eq. 12) in order that the Fe-Mg fractionations in the garnet-orthopyroxene and garnet-clinopyroxene pairs are independent of Fe/Mg ratio. It should also be noted that the carefully reversed experiments of Perkins and Vielzeuf (1992) show the  $K_D'$  between olivine and clinopyroxene to be essentially independent of Fe/Mg ratio for  $X_{Fe}(\text{CPx}) \geq 0.30$ .

Dahl (1980) described a suite of granulite samples from the Ruby Range, Montana with widely variable Ca and Mn concentration in the garnets ( $X_{Ca} = 0.15-0.54$ ,  $X_{Mn} = 0.02-0.44$ ). We estimated the temperatures of these assemblages on the basis of the compositions of coexisting garnet-clinopyroxene and garnet-orthopyroxene pairs, using Eqs. 12, 14 and 15 and the preferred garnet solution model in Table 4. The nonideality of the pyroxenes has been neglected as a first approximation, but treated later in an empirical form. The estimated temperatures of the Ruby Mountain assemblages are illustrated in Figs. 10a and 11 for the garnet-clinopyroxene and garnet-orthopyroxene assemblages, respectively. Fig. 10b shows the temperatures estimated from the garnet-clinopyroxene geothermometers of by Ellis and Green (1979) and Krogh (1988), which have been used widely in the literature.



**Fig. 10** Temperatures of garnet-clinopyroxene pairs at 6 kbar from Ruby Mountain, Montana, described by Dahl (1980), as estimated from **a** the thermometric formulation developed in this work and **b** those developed by Ellis and Green (1979) and Krogh (1988)

The garnet-clinopyroxene geothermometric temperatures obtained from the present formulation show much less scatter than those from the formulations of Ellis and Green (1979) and Krogh (1988), which, in principle, are not valid for systems with significant concentration of Mn. However, there seems to be a systematic dependence of the estimated temperatures on  $X_{Ca} + X_{Mn}$  in garnet in our formulation. This dependency could be the result, at least partly, of the correlated compositional variations of clinopyroxene. However, since Mn is very dilute in the clinopyroxene ( $X_{Mn}=0.00-0.06$ ), the observed variation of temperature should be due to the variation of Ca content of clinopyroxene ( $X_{Ca}=0.40-0.51$ ). It has been shown by Blander (1972) that increasing Ca content of clinopyroxene tends to increase the  $K_D$ , which would lead to an underestimation of temperature. However, we still do not have a reliable method of correcting for this effect. Also the statistical correlation of the estimated temperature with the Ca content of clinopyroxene in the samples from the Ruby Mountain is too poor ( $r^2=0.51$ ) to be meaningful. Nonetheless, we note that the three lowest temperature samples have the highest Ca contents in clinopyroxene ( $X_{Ca}=0.47-0.51$ ), which are beyond the range ( $X_{Ca}=0.40-0.45$ ) for which our garnet-clinopyroxene thermometer has been formulated. Neglecting these three samples, we obtain  $744 \pm 25^\circ\text{C}$  for the garnet-clinopyroxene assemblages from the Ruby Mountain range, Montana, where the uncertainty indicates  $\pm 1\text{s}$



**Fig. 11** Estimated temperatures of garnet-orthopyroxene pairs at 6 kbar from Ruby Mountain, Montana, described by Dahl (1980) as function of Mn concentration in orthopyroxene. The least squared fit to the data suggest a positive correction of  $DT \approx 599 (X_{Mn})^{OPx}$  to the temperature estimated from our thermometric formulation (see text)

value. If these three samples are included, then the temperature estimate changes to  $729 \pm 37^\circ\text{C}$ .

For the garnet-orthopyroxene assemblages, we find a fairly systematic dependence of the estimated temperatures on the  $X_{Mn}(OPx)$ , which varied between 0.00 and 0.21. On the basis of these data, we suggest an empirical correction of temperature by adding a  $DT$  value to the estimated temperatures as

$$DT = 599 (X_{Mn})^{OPx} \quad (16)$$

Incorporating this correction, we get  $728 \pm 31^\circ\text{C}$  as the temperature of the Ruby Mountain garnet-orthopyroxene assemblages, which are in excellent agreement with those derived for the garnet-clinopyroxene assemblages, and also with the 'consensus' temperature of  $750 \pm 50^\circ\text{C}$  derived by Dahl (1979) from comparison of the temperatures estimated from several thermometers.

Using core compositions of the coexisting garnet and clinopyroxene, and Ellis and Green (1979) formulation, Tuccillo et al. (1992) obtained metamorphic temperatures between 620 and  $650^\circ\text{C}$  for the Britt domain of the Ontario Grenville orogen, Canada, as compared to a temperature of  $700 \pm 50^\circ\text{C}$  that they anticipated from the mineral assemblages and the pattern of regional distribution of temperature inferred from other thermometers. Application of the garnet-clinopyroxene thermometric formulation developed above yields  $702 \pm 14^\circ\text{C}$  ( $\pm 1\text{s}$ ), which is in very good agreement with the anticipated temperature. However, note that for these samples  $X_{Ca}(CPx) \approx 0.47-0.48$ , which is slightly higher than the Ca concentration in clinopyroxene for which our thermometric formulation is valid, so that the metamorphic temperature could be somewhat higher.

## Discussion

The mixing parameters summarized in Table 4 should be viewed more as *effective* binary parameters which, when used together, are consistent with the available phase equilibrium constraints, both experimental and natural,

and the limited amount of calorimetric data on the enthalpy and entropy of mixing.

We recall that a large positive deviation from ideality in the Mg-Mn join was derived from modeling the compositional dependence of  $K_D(\text{Fe-Mg})$  between garnet and biotite, and that this deviation persisted even when the constraints on all the binaries excepting the Fe-Ca and Mg-Ca joins in garnet were relaxed (Fig. 8). Thus, if the inferred low temperature Mg-Mn mixing property in garnet is an artifact of the errors in the constrained properties, then it should be traced to those in the Fe-Ca and Mg-Ca binaries in garnet. In this work, we accepted the Fe-Ca mixing model of Berman (1990) and our result for the mixing property in the Mg-Ca binary is similar to his.

It should also be noted that the optimized  $DH^{XS}$  in the Mg-Ca binary has a sense of asymmetry which is opposite to that of the heat of mixing due to elastic strain,  $DH^{XS}(\text{elastic})$ , as calculated by Ganguly et al. (1993; Fig. 5). The calculated asymmetry of  $DH^{XS}$  vs  $X_{Ca}$  in this work results from that in the calorimetric data of Newton et al. (1977). The reason for these opposing senses of asymmetry in the net and elastic  $DH^{XS}$  is not clear. The maximum in the calculated value of  $\ln K_D(\text{Fe-Mg})$  between garnet and olivine vs  $X_{Ca}^{Gt}$  (Fig. 6) is a consequence of different senses of asymmetry in the Fe-Ca and Mg-Ca joins.

Cheng and Ganguly (1994) have developed a method of calculating the ternary interaction parameter from the binary mixing properties when at least one of the binaries is nearly ideal. Since each ternary subsystem in the quaternary garnet solid solution has one nearly ideal binary, the ternary interaction parameters can be calculated according to their method (Cheng and Ganguly 1994, Eq. 13). However, as these turn out to be small, neglecting the ternary parameters causes relatively minor error in the phase equilibrium calculations.

Our garnet-clinopyroxene geothermometer (and also those of Ellis and Green 1979; Krogh 1988; Pattison and Newton 1989) should not be applied to eclogites unless these are mantle derived ( $T > 1000^\circ\text{C}$ ). At lower temperatures (metamorphic eclogites), Na has a significant effect on the  $K_D$  (Koons 1984; see Ganguly and Saxena 1987, for thermodynamic analysis), which we are still not in a position to correct for, owing to the lack of the necessary thermodynamic and experimental data. We further emphasize that our garnet-clinopyroxene formulation is valid for assemblages in which  $X_{Ca}(\text{CPx})=0.40-0.45$ . Temperatures would be underestimated for assemblages with higher  $X_{Ca}(\text{CPx})$  and vice versa.

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**Note added in proof** A computer program in BASIC to calculate garnet-orthopyroxene and garnet-clinopyroxene thermometric temperatures is available from the authors on request.