

Activity-composition relationships of binary Ca-Fe and Ca-Mn garnets determined by reversed, displaced equilibrium experiments

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ABSTRACT

Activity-composition (a - X) relationships of grossular-spessartine and grossular-almandine garnets have been determined by reversed phase-equilibrium experiments at 900 °C and 1000 °C and 11 to 18 kbar in the assemblage garnet-plagioclase-kyanite-quartz. The addition of 2 to 4 wt% Li_2MoO_4 promoted equilibration. The results indicate that grossular-spessartine garnets mix ideally. Cell-edge measurements indicate no excess volume of mixing. It is therefore reasonable to consider Mn as an ideal diluent of ternary Ca-Fe-Mg garnets. For grossular-almandine, activity-composition relationships are nearly ideal at 900 °C and 1000 °C but can also be described with an asymmetric (subregular) Margules solution model. When the data obtained at 900 °C and 1000 °C are considered together, the calculated free-energy parameters are $W_1 = W_{\text{CaFe}} = -1.09$ kJ/mol of cation and $W_2 = W_{\text{FeCa}} = 2.59$ kJ/mol of cation. These results, together with those of high-temperature oxide melt calorimetry, indicate that excess entropy of Ca-Fe mixing in garnet is effectively zero.

INTRODUCTION

A common approach used to determine the metamorphic and tectonic histories of terranes is to apply geothermometers and geobarometers to unravel the pressure-temperature-time paths of rocks. The geothermometers and geobarometers are based on thermodynamic expressions of equilibrium between coexisting phases. Although knowledge of the thermodynamic properties of the end-member phases has improved markedly through recent analysis of phase equilibrium and calorimetric data (Holland and Powell, 1985; Berman, 1988), progress on the solution properties of minerals has been slower. Garnet is a participating mineral in many useful geothermometers and geobarometers; its solution properties are essential in calculations of the pressures and temperatures recorded by metamorphic rocks. Uncertainty in the activity-composition (a - X) relations of a mineral such as garnet may be one of the largest remaining uncertainties in thermobarometry, as discussed by Essene (1989).

Most garnets within the crust of the Earth are complex multicomponent solutions of the major substituents Ca, Fe^{2+} , Mg^{2+} , and Mn^{2+} on the eight-coordinated X site and Al^{3+} , Fe^{3+} , and Cr^{3+} on the octahedral Y site (Meagher, 1982). To construct a reliable thermodynamic model of mixing, a formidable amount of experimental work is needed to constrain the free energy of mixing of components in this complex solid solution. Initially it is important to define the mixing properties of the principal binary joins, such as grossular-almandine, grossular-pyrope, and grossular-spessartine, which can be used to formulate a comprehensive mixing model (Ganguly and Saxena, 1987, p. 98–102).

There are several ways to constrain mixing behavior of binary garnets. Experiments that determine the displacement of an equilibrium as a function of a given mineral composition are an important source of information, but only if pressure and temperature are well controlled, mineral compositions are well known and reversals are precise. Measurement of the displacement of the reaction $3 \text{ anorthite} = \text{grossular} + 2 \text{ kyanite} + \text{quartz}$ by diluting grossular with other components, first performed by Hensen et al. (1975), provides estimates of activity-composition relationships for a range of garnet compositions. This technique has been used by Cressey et al. (1978) for the Ca-Fe join, by Wood (1988) for the Ca-Mg join, and by Koziol and Newton (1989) for a limited range of Ca-Fe-Mg solid solutions.

Cressey et al. (1978) measured the free energy of grossular-almandine solutions over 850–1100 °C and $0.12 \leq X_{\text{Ca}} \leq 0.79$. Most final garnet compositions were deduced from garnet cell-edge information. They concluded that the activity-composition relationship was nearly ideal with slight negative deviations for Fe-rich compositions and positive deviations for Ca-rich compositions. An apparent temperature dependence of mixing properties was ascribed to excess entropy. Later theoretical studies have questioned whether equilibrium was attained in these experiments (Ganguly and Saxena, 1984; Anovitz and Essene, 1987).

Determination of excess free energy, excess enthalpy, and confirmation of excess entropy are needed for Ca-Fe garnet to formulate an accurate mixing model. Geiger et

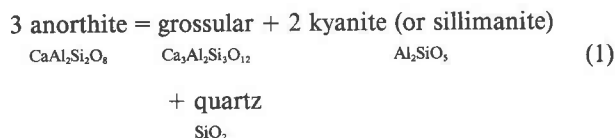
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al. (1987) have measured the excess enthalpy of ten grossular-almandine solutions by alkali borate calorimetry at 760 °C. They found that the enthalpy of mixing of Ca and Fe²⁺ was nearly ideal. Consideration of all the data of Cressey et al. (1978) and Geiger et al. (1987) led to predictions of excess entropy in the models of Ganguly and Saxena (1984) and Anovitz and Essene (1987). However, if only the best-constrained data at 1000 °C of Cressey et al. (1978) are combined with the data of Geiger et al. (1987), then excess entropy is virtually zero (Ganguly and Saxena, 1984, p. 91).

This study attempts to resolve these discrepancies by constraining the excess free energy of Ca-Fe garnets and by demonstrating the attainment of equilibrium through reversed compositions. The use of NaCl pressure media for more accurate measurements and of a molten oxysalt flux to promote equilibration of the experimental charges have resulted in an improved description of the *a-X* properties of Ca-Fe mixing and a determination of Ca-Mn mixing.

The displaced equilibrium technique

The displaced equilibrium technique involves the determination of a change in pressure (at constant temperature) of a univariant equilibrium as a result of solid solution in one of the phases (Cressey et al., 1978; Schmid et al., 1978). The thermodynamic basis of this technique has been discussed by Wood (1988). The univariant equilibrium of interest is



When only garnet is a solid solution and the other phases are the pure components at unit activities, the activity of grossular in garnet can be determined using the relationship

$$\int_P^{P^0} \Delta V^0 dP = RT \ln a_{\text{grs}}^{\text{grt}} \quad (2)$$

where P^0 is the equilibrium pressure of the end-member equilibrium at T , T is the temperature of the experiment, P is the pressure of the experiment, ΔV^0 is the volume change of Reaction 1, and $a_{\text{grs}}^{\text{grt}}$ is the activity of the grossular component in garnet. When the integral on the left side is evaluated, the activity of grossular in garnet at T and P is determined. Following Koziol and Newton (1989), Equation 2 has been integrated using volume data from Holland and Powell (1985) that incorporate expansivity and compressibility terms. In garnet, the cations mix over three sites per formula unit, giving the following relationship between activity and mole fraction:

$$a_{\text{grs}}^{\text{grt}} = (X_{\text{grs}} \gamma_{\text{grs}})^3 \quad (3)$$

where X_{grs} is the mole fraction of $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ in the bi-

nary solution and γ_{grs} is the activity coefficient of $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. Measurement of the garnet compositions in equilibrium with anorthite, Al_2SiO_5 , and quartz over a range of P and T permits calculation of γ_{grs} and the activity-composition relationships. For optimal precision, the end-member curve must be well known; see Koziol and Newton (1988).

EXPERIMENTAL PROCEDURE

Apparatus

All experiments were performed in a piston-cylinder apparatus, using a 3/4-in. (1.91-cm) diameter assembly with a NaCl pressure medium and a WRe₃-WRe₂₅ thermocouple. Procedures have been described by Koziol and Newton (1989). Temperature uncertainties with these thermocouples are about ±10 °C (Perkins et al., 1981). Experiments performed at 1000 °C and 11.1 kbar were very close to the melting curve of NaCl (Clark, 1959), which was the effective lower pressure limit of the experiments. A correction of -200 bars was applied to the nominal pressure of the piston-out experiments to be in accord with the work of Koziol and Newton (1988). Silver capsules, 1.5-mm diameter and with a 0.153-mm wall thickness, were used. Two capsules, containing mixtures of anorthite, kyanite, and quartz and each with garnet crystals of a different composition, were placed side by side in the salt assembly, with the thermocouple tip between them. Care was taken that the capsules did not touch the graphite sleeve or each other. The thermocouples were protected from contamination by the silver sample capsules by a thin layer of Al₂O₃ cement.

Synthesis and characterization of garnets

Garnets were crystallized from stoichiometric mixtures of glasses of end-member composition as described by Geiger et al. (1987) and Koziol and Newton (1989). Previous workers (Snow, 1943; Yoder and Keith, 1951; Mottana, 1974) made spessartine glass by melting a mixture of oxides in a gas-mixing furnace. An alternative method was devised in the present study for melting large batches of oxide mix. A finely ground mixture of MnO, Al₂O₃, and SiO₂ oxides of the stoichiometry of spessartine was placed in a platinum crucible. This crucible was covered by a pellet 1.91 cm in diameter and 0.5–1 cm thick and made of granular MnO pressed at 15000 lb/in.² (1 kbar). The platinum crucible was pressed tightly around the lid to close air passages, then nested in another crucible filled with loose granular MnO. This setup was placed in a vertical furnace with a strong flow of nitrogen, monitored by observing an outflow stream of bubbles through water. The oxides were melted at 1280–1330 °C for 10–15 min and quenched in water. The resulting quenched glass was clear, orange-brown, and a rosy orange color in small chips, similar to the color described by Mottana (1974). The crucible lid made of MnO remained green except on its outer surface, which became brownish. The MnO buffer was therefore effective. The refractive index of the glass

varied among batches from 1.665 to 1.678 (± 0.002). Oxides melted under flowing nitrogen without the MnO buffer produced a glass of a dark red-brown or burgundy color, indicating substantial oxidation of Mn.

An oxide mix composed of reagent calcite, Al_2O_3 , and SiO_2 equivalent to the composition of grossular was dried at 110 °C, heated to 800 °C overnight to drive off CO_2 , and then melted at 1350 °C in a vertical platinum-wound furnace for 20 min. The resulting glass was finely ground and remelted to a clear glass. Following the procedure of Bohlen et al. (1983b), almandine glass was made from a finely ground mixture of high-purity hematite, Al_2O_3 , and quartz, melted in graphite crucibles at 1375 °C and one bar until the Fe was reduced to Fe^{2+} and there was incipient Fe metal saturation. The glass used in this study was the same as that used in the experimental study of Pattison and Newton (1989). It was clear forest green in color and had no magnetite microcrystals and negligible Fe droplets.

Pure spessartine garnet was synthesized at 1250 °C and 20 kbar for 21 h. The synthesis produced very pale green-brown crystals with a refractive index greater than 1.780 but less than 1.800, in accord with previous syntheses (Matthes, 1961; Hsu, 1968; Mottana, 1974). Nine grossular-spessartine garnets and four grossular-almandine garnets were synthesized at 1250 °C and 26 kbar in large volume (0.5 to 0.6 g) graphite containers with a soft-glass pressure medium. Synthesis duration was 24–48 h. The resulting material was more than 99% isotropic. The synthetic garnets were homogeneous and very close to their intended compositions, as determined by electron microprobe analysis. Some syntheses had a trace amount of quartz, observable only as a crystal or two in an oil-immersion grain mount. Table 1 gives measured compositions and cell dimensions for grossular-spessartine and grossular-almandine garnets.

Experimental technique

Starting materials consisted of 30 wt% garnet seeds 10–30 μm in size and 70 wt% of a finely ground mixture of synthetic anorthite, natural kyanite, and quartz with 2–4 wt% Li_2MoO_4 added as a flux. The anorthite, kyanite, and quartz were the same as the materials used by Koziol and Newton (1988, 1989). The compositions of the garnet seeds were chosen so as to obtain a reversal by approaching the final composition from both grossular-rich and grossular-poor directions. Experimental durations were generally 3 to 4 d for experiments at 1000 °C and 7 to 8 days for experiments at 900 °C. Thermocouple and furnace integrity were checked during the experiments by monitoring power requirements of the furnace assemblies. Experimental charges were solid dark gray pellets when removed from the capsules. Several small chips of each charge were prepared for analysis by electron microprobe.

Final garnet compositions were determined by energy-dispersive spectroscopy (EDS) on an ARL electron microprobe (Li-drifted Si detector) and on a 1987 Cameca elec-

TABLE 1. Compositions and cell dimensions of synthetic garnets

Actual composition	Standard deviation (mol% grs)	No. of analyses	$a \text{ \AA}^*$	Molar volume* (J/bar)
Grossular-spessartine				
Gr _{85.8} Sp _{14.2}	2.5	31	11.815(2)	12.418(6)
Gr _{70.3} Sp _{29.7}	2.2	19	11.778(1)	12.302(3)
Gr _{50.7} Sp _{49.3}	0.9	31	11.735(2)	12.168(6)
Gr _{39.2} Sp _{60.8}	3.0	19	11.710(2)	12.088(6)
Gr _{29.6} Sp _{70.7}	3.3	31	11.688(3)	12.022(9)
Gr _{20.1} Sp _{79.9}	2.1	30	11.662(2)	11.940(6)
Gr _{10.7} Sp _{89.3}	3.4	40	11.638(2)	11.867(6)
Gr _{0.6} Sp _{99.2}	1.0	24	11.626(2)	11.830(6)
Gr _{02.0} Sp _{98.0}	1.3	29	11.618(1)	11.805(3)
Spessartine	—	—	11.615(2)	11.798(6)
Grossular-almandine				
Gr _{86.1} Alm _{13.9}	0.9	34	11.753(3)	12.220(6)
Gr _{43.7} Alm _{56.3}	1.3	44	11.680(1)	11.995(3)
Gr _{24.6} Alm _{75.4}	3.7	35	11.608(1)	11.775(3)
Gr _{04.6} Alm _{95.4}	0.7	15	11.544(2)	11.580(6)

* Uncertainty (1 σ) in last digit is given in parentheses.

tron microprobe. Operating voltage was 15 kV, with a beam current of 30 nA. Counting time was 1 min.

Equilibration of charges

In most experiments, the garnets changed composition, indicative of an approach to equilibrium. The original garnet compositions persisted in the cores of the garnet grains, and the rims were mostly, but not entirely, of a new composition. The rims varied in thickness from about 2 to 10 μm . Stringent criteria (X_{Si} , X_{Al} , X_{Fe} + X_{Ca} within 0.01 of the stoichiometric value) based upon the microprobe analyses of the starting garnets were used to reject analyses obtained when the electron beam overlapped onto anorthite, quartz, or the quenched flux. The final compositions reported in Tables 2 and 3 are averages of three or four analyses that showed the most change in grossular content.

With the addition of Li_2MoO_4 to the experimental charges, Li or Mo could have been incorporated into garnet or anorthite. Garnets from several experiments were analyzed carefully for Mo. No evidence of Mo solid solution could be found. In the similar study on ternary garnets by Koziol and Newton (1989), anorthites in the experimental products were analyzed by electron microprobe for cation stoichiometry and compared against the analyses of synthetic anorthite used as the starting material and against anorthite grown in experiments on the end-member reaction. The data suggest about 3–4 mol% solution of $\text{LiAlSi}_3\text{O}_8$ component in the feldspars of the experiments using ternary garnets, as seen in the changing amount of Ca measured and the variation of Al/Si ratio. However, there is an equal amount of substitution of Li in anorthite present in experiment 1.58, an experiment on the anorthite breakdown reaction. The calculated grossular activities are the same as if no solid solution were present in the feldspar, and departure from ideal anorthite composition was not incorporated into the cal-

TABLE 2. Experimental results and grossular-spessartine garnet compositions at 1000 and 900 °C

Experiment	Time (h)	P (kbar)*	Starting composition	Final composition	a ^{1/3} (calculated)	γ _{grs}
1000 °C						
2.21	88	11.0	0.201 0.020	0.143 0.131	0.126 0.126	0.881 0.962
2.22	91	12.7	0.392 0.107	0.195 0.180	0.175 0.175	0.897 0.972
2.8	78	14.1	0.392 0.048	0.233 0.223	0.229 0.229	0.983 1.027
2.20	73	17.0	0.201	0.401	0.398	0.995
2.23	72	18.9	0.703 0.507	0.583 0.573	0.569 0.569	0.976 0.993
900 °C						
2.25	160	8.9	0.201 0.020	0.110 0.090	0.107 0.107	0.973 1.156
2.26	193	11.6	0.392 0.223	0.212 0.209	0.189 0.189	0.900 0.848
2.24	172	13.7	0.392 0.201	0.320 0.308	0.294 0.294	0.919 0.955
2.27	166	16.1	0.703 0.392	0.514 0.500	0.484 0.484	0.942 0.968

* Uncorrected gauge pressure.

TABLE 3. Experimental results and grossular-almandine compositions at 1000 and 900 °C

Experiment	Time (h)	P (kbar)*	Starting composition	Final composition	a ^{1/3} (calculated)	γ _{ca}
1000 °C						
2.30	124	11.1	0.244 0.046	0.119 0.126	0.129 0.129	1.081 1.021
2.28	99	12.6	0.244 0.046	0.182 0.180	0.172 0.172	0.944 0.954
2.31	141	12.5	0.046	0.180	0.169	0.936
2.33	96	16.0	0.437 0.244	0.315 0.301	0.329 0.329	1.045 1.093
2.81	116	18.2	0.661 0.244	0.466 0.434	0.499 0.499	1.071 1.150
2.35	69	19.0	0.661 0.437	0.520 0.484	0.580 0.580	1.116 1.199
900 °C						
2.32	186	9.4	0.244 0.046	0.123 0.100	0.119 0.119	0.966 1.189
2.44	214	12.5	0.437 0.046	0.256 0.244	0.223 0.223	0.873 0.915
2.36	168	14.7	0.437 0.244	0.421 0.376	0.362 0.362	0.859 0.962
2.37	166	16.7	0.661 0.437	0.497 0.479	0.548 0.548	1.102 1.144

* Uncorrected gauge pressure.

culations. Anorthite in these experiments was not analyzed, but it is assumed the same substitution applies.

Al₂SiO₅ polymorphism

A natural kyanite was used as a starting material in the experiments. According to the phase diagram of Holdaway (1971), at a constant temperature of 1000 °C, experiments below about 14 kbar are in the sillimanite stability field. However, X-ray analysis of products of lower-pressure experiments showed that kyanite was present metastably in experiments down to 11 kbar.

Quenched flux and extraneous phases

The Li₂MoO₄ dissolved some kyanite, quartz, and a little garnet to make an intergranular melt. This melt quenched to a Mo-rich aluminosilicate glass, which could be easily avoided during electron microprobe analysis.

Zoisite was identified in quenched charges in the anorthite breakdown study of Koziol and Newton (1988), but was not found in this study. However, X-ray analysis showed the presence of various amounts of an unknown phase represented by a single peak with a *d* value of 3.420 Å. The presence of another phase should not affect the reaction between garnet and the assemblage anorthite, kyanite, and quartz, as long as the latter four phases are present and in equilibrium. The unknown phase may correspond to the presence of brightly reflective beadlets in the interstitial melt areas and may be a molybdate or molybdenum silicate formed during quenching. No other extraneous phases were detected.

RESULTS OF EXPERIMENTS

Volume relations

There is some discrepancy in the published value of the unit-cell constant of spessartine. Ito and Frondel (1968) and Skinner (1956) list 11.621 ± 0.001 Å, but smaller values have been obtained by Hsu (1968), Mot-tana (1974), and Dasgupta et al. (1974). These values are 11.614 ± 0.001 Å, 11.617 ± 0.003 Å, and 11.619 ± 0.001 Å respectively. Spessartine synthesized from stoichiometric glass for this study has a unit-cell constant of 11.615 ± 0.002 Å.

Cell volumes and compositions of the synthetic grossular-spessartine solid solutions are in Table 1. Figure 1 is a plot of composition against volume. A straight line between the volumes of pure spessartine and grossular reproduces all measurements, indicating no excess volume of mixing. In general the volumes of these garnets are smaller than the volumes of four grossular-spessartine garnets measured by Ito and Frondel (1968). Their garnets were synthesized from gels and may have contained small amounts of Mn³⁺ or H₂O. Mn³⁺ has an ionic radius of 0.58 Å (low spin) or 0.65 Å (high spin) as compared to 0.53 Å for Al³⁺ (Shannon and Prewitt, 1969), and its presence in spessartine could account for the larger unit cell.

Unit-cell constants of the four synthetic grossular-almandine solid solutions and the garnets of Geiger (1986) are in Figure 2. As in Geiger's study, the garnets of this study were synthesized in graphite crucibles at high pres-

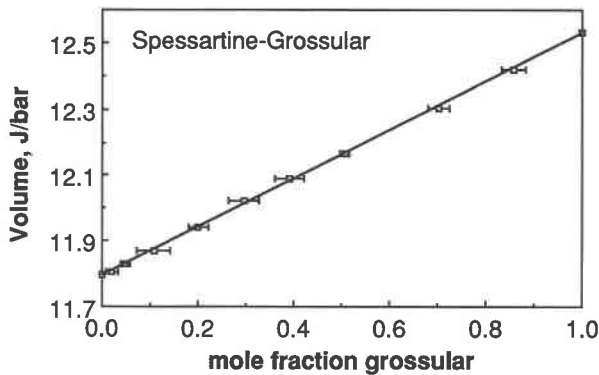


Fig. 1. Volumes of spessartine-grossular garnets. Data are from Table 1. Ideal mixing is shown by the straight line drawn between spessartine (11.798 J/bar) from this study and grossular (12.531 J/bar) from Skinner (1956). Horizontal bars show 2σ compositional uncertainty as determined from energy-dispersive electron-microprobe analysis. Uncertainties in measured volume are about the size of the symbols.

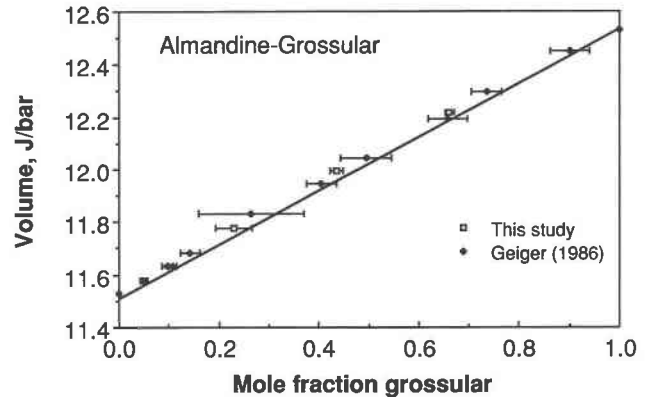


Fig. 2. Volumes of grossular-almandine garnets. Open squares: data from this study (see Table 1). Filled diamonds: data from Geiger (1986). Ideal mixing is shown by the straight line drawn between almandine (11.511 J/bar) from Bohlen et al. (1983a) and grossular (12.531 J/bar) from Skinner (1956). Uncertainties in compositions and volumes as in Fig. 1.

tures, where the oxygen fugacity should be quite low. Mössbauer resonance analyses of Geiger's pure almandine indicated that less than one percent of the total Fe present was Fe^{3+} (Geiger et al., 1987). No Mössbauer analyses were performed on the garnets in this study. However, since the unit-cell constants and volumes of these garnets agree with those of Geiger (1986), the Fe^{3+} contents are probably very small and should not affect the phase-equilibrium results.

In their work on the grossular-almandine join, Cressey et al. (1978) derived a volume-composition curve that showed a slight negative deviation from ideality for one datum at $\text{Grs}_{20}\text{Alm}_{80}$ and positive deviation at the more grossular-rich end. This implies strong variation of the partial molar volume of grossular, \bar{V}_{grs} over the join. The volume-composition relationship has been reexamined using the data of this study and that of Geiger (1986). A plot of composition versus volume (Fig. 2) indicates some positive deviation from ideal behavior at high grossular content, but the deviation is not large. Depending on the values chosen for the molar volumes of almandine and grossular, the derived Margules parameters describing excess volume of mixing change significantly. In addition, although small, yet variable, amounts of Fe^{3+} do not greatly affect the phase-equilibrium data, they do affect the measured volumes of the garnets. Because of the small excess volumes of mixing measured and these uncertainties, the correction to the activity of grossular in garnet for \bar{V}_{grs} [Eq. 6 of Cressey et al. (1978)] was ignored.

Activity of grossular in binary garnets

Experimental reversals of compositions of grossular-spessartine garnets were obtained at 1000 and 900 °C. Experimental conditions and compositions of garnets are in Table 2. The activities of grossular listed were calculated from Equation 2. There is no excess volume correction for grossular activity in these garnets because of

the volume ideality of the join. Uncertainties in the data are discussed below. To illustrate activity-composition relationships, mole fraction versus $(a_{\text{grs}}^{\text{grs}})^{1/3}$ is plotted in Figures 3a and 3b for grossular-spessartine. Any deviation from ideality is smaller than experimental uncertainties.

Reversals of grossular-almandine compositions were obtained at 1000 and 900 °C over the range 11 to 18 kbar. The results are in Table 3. It was difficult to locate equilibrated garnet rims in the experiments at 900 °C, and the reversal brackets are broad. The kinetics of the reaction are very slow at 900 °C, and this discouraged experiments at lower temperatures.

The data are plotted in activity-composition diagrams (Fig. 4a, 4b) to illustrate possible non-ideal behavior. As a first approximation, the grossular-almandine join is essentially ideal at both temperatures and does not require a complicated expression to relate composition and activity.

Error analysis

In formulating activity-composition relationships, one must take account of uncertainties in both the calculated activities and the measured compositions. The uncertainty in composition is determined by the width or separation of the reversal bracket and also by the uncertainty of electron microprobe analysis, which is about ± 0.008 in X_{grs} (A. Koziol, unpublished data). For example, in experiment 2.30 (Table 3) the midpoint of the reversal bracket is $X_{\text{grs}} = 0.122$, but the bracketing compositions are $X_{\text{grs}} = 0.119$ and $X_{\text{grs}} = 0.126$. The uncertainty on the final garnet composition is judged to be the square root of the sum of squares of (a) one-half the reversal bracket width and (b) ± 0.008 in X_{grs} in both bracketing compositions, for an estimated error of ± 0.012 for X_{grs} in this case.

Uncertainties in the activity of grossular calculated from Equation 2 are sensitive to uncertainties in P^0 , the pres-

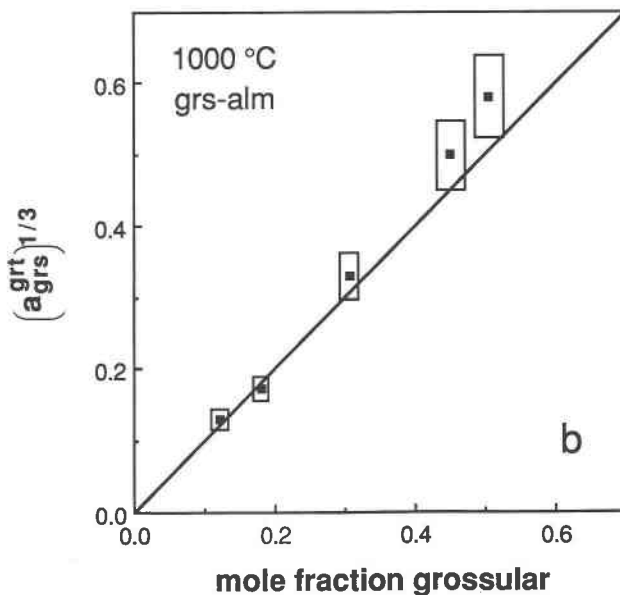
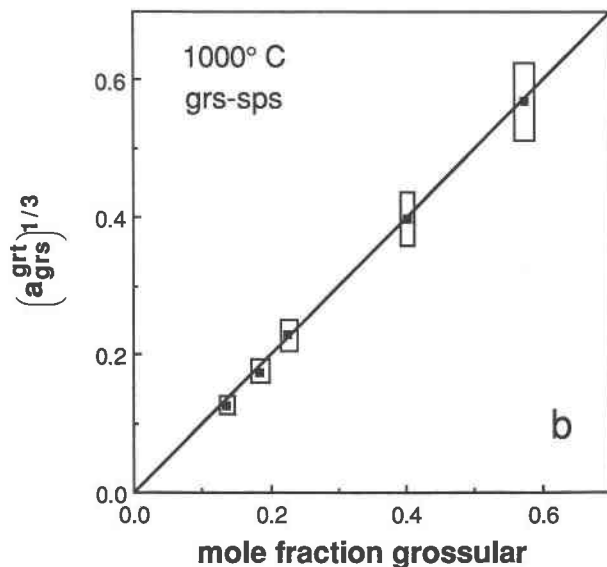
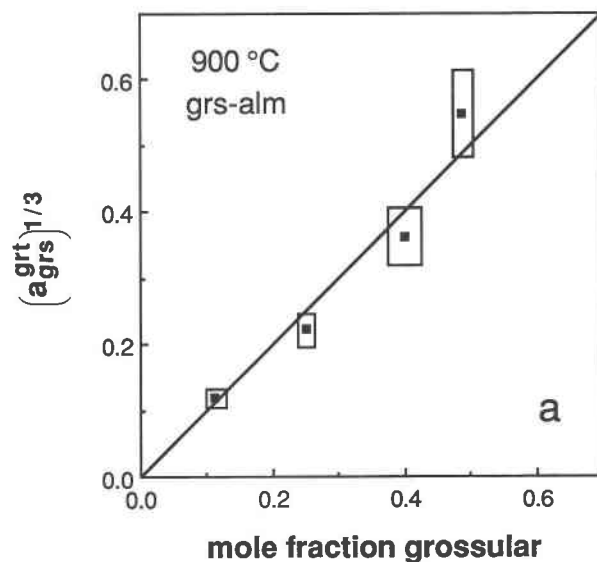
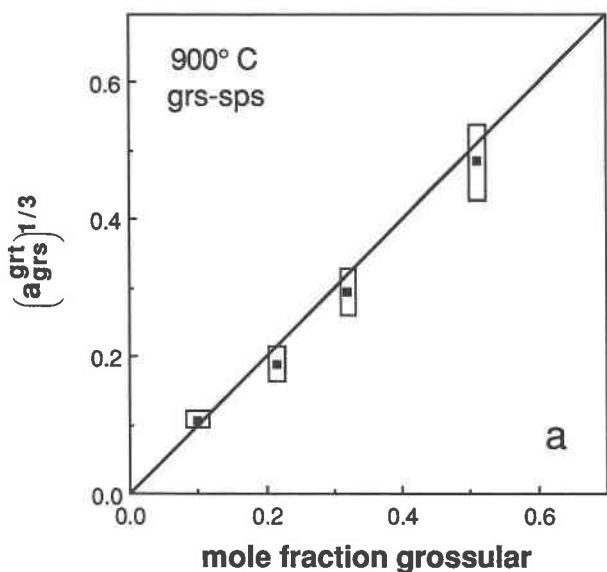


Fig. 3. Activity-composition relationship for the grossular component in grossular-spessartine garnets shown by a plot of measured X_{grs} against the cube root of calculated activity of grossular. Data (filled squares) are from Table 2. Ideal mixing behavior is shown by the straight line. Uncertainties in X_{grs} and activity (unfilled boxes) are discussed in the text. (a) Data obtained at 900 °C. (b) Data obtained at 1000 °C.

Fig. 4. Activity-composition relationship for the grossular component in grossular-almandine garnets shown by a plot of measured X_{grs} against the cube root of calculated activity of grossular. Data (filled squares) are from Table 3. Ideal mixing behavior is shown by the straight line. Uncertainties in X_{grs} and activity (unfilled boxes) are discussed in the text. (a) Data obtained at 900 °C. (b) Data obtained at 1000 °C.

sure of the end-member reaction, and in P , the pressure of the experiment. Koziol and Newton (1988) judged the position of the anorthite breakdown curve to be determined within ± 450 bars at 1000 °C and ± 510 bars at 900 °C. The uncertainty in the pressure of the experiments of this study is ± 300 bars. The square root of the sum of squares of these values results in estimated uncertainties of ± 540 bars at 1000 °C and ± 590 bars at 900 °C for the pressure term in Equation 2. Therefore grossular

activities calculated from Equation 2 have uncertainties of about 10%. Uncertainties in ΔV° have little effect and have been neglected.

DISCUSSION

Grossular-spessartine

The data indicate that grossular and spessartine mix ideally or nearly so, and activities of both components in

this binary solution can be assumed to be ideal for the purposes of thermodynamic calculations.

Mn-substitution in natural garnet can be considerable in low-grade parageneses, and possible perturbation of geothermometers by Mn, especially the garnet-biotite geothermometer, has been discussed by several authors (Hodges and Spear, 1982; Perchuk, 1982; Williams and Grambling, 1985). To define the perturbation, the Mn-Ca, Mn-Fe, and Mn-Mg interactions must be well understood. Lacking previous experimental data, an upper limit of 5.67 kJ/mol has been proposed for a symmetrically nonideal Ca-Mn join, based on differences in ionic radii (Ganguly and Kennedy, 1974). Mn-Fe mixing has been approximated by an ideal model (Ganguly and Saxena, 1984) but Mg-Mn mixing in garnet has been considered strongly nonideal, with $W_{\text{MgMn}} = 13.4 \pm 2.5$ kJ/mol for a symmetric model (Ganguly and Kennedy, 1974). Hodges and Spear (1982) concluded that Mn mixes ideally in garnet with respect to the other cations, based on paragenetic analysis of a near-triple point occurrence of Al_2SiO_5 polymorphs. Hoinkes (1986) noted that regression analysis of his garnet-biotite $\ln K_D$ data implied ideal mixing of spessartine with Fe-Mg garnet at amphibolite facies conditions.

Experimental work by Pownceby et al. (1987) places further constraints on Fe-Mn mixing in garnet. Their analysis of the partitioning of Fe and Mn between garnet and ilmenite, treated as symmetrical solutions, indicates that $W_{\text{FeMn}}^{\text{ilm}} - W_{\text{FeMn}}^{\text{gar}} = 1.26$ kJ/mol. This result, together with experimental data on Fe-Mn ilmenite solutions (H. O'Neill, unpublished data; cited in Pownceby et al., 1987), indicates that Fe-Mn mixing in garnet is nearly ideal, with minor positive deviations.

Grossular-almandine

To a first approximation this join also is ideal, but a better description of the join may be obtained by fitting an asymmetric Margules model to the activity data:

$$RT \ln \gamma_1 = (1 - X_1)^2 [W_1 + 2X_1(W_2 - W_1)], \quad (4)$$

where W_1 , W_2 are the two Margules parameters. Since the results for both 900 °C and 1000 °C are very similar, the data at both temperatures were combined. Least squares analysis gives $W_{\text{Ca}} = -1.09$ kJ/mol of cation, $W_{\text{Fe}} = 2.59$ kJ/mol of cation.

Previous estimates of excess free energy for the Ca-Fe garnet join are based on theoretical as well as experimental data. An upper limit of 5.7 kJ/mol for the excess free energy of this join was based on the difference in ionic radii between the two cations (Ganguly and Kennedy, 1974). More recently, Bohlen et al. (1983a) obtained experimental data on the reaction fayalite + anorthite = garnet ($\text{grs}_{33.3}\text{alm}_{66.7}$) over the temperature range 750–1050 °C. Their data imply that the mixing properties of this one composition is nearly ideal.

Ganguly and Saxena (1984) used paragenetic, experimental, and calorimetric data to constrain the mixing properties of $(\text{Fe,Ca,Mg,Mn})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnets. The pri-

mary input to the model was experimental and paragenetic data on Fe-Mg partitioning between garnet and another phase, such as clinopyroxene or biotite. Their analysis of the data of Cressey et al. (1978) indicated that excess entropy in Fe-Ca garnets could be modeled with a single (symmetric) parameter, unlike the asymmetric model suggested by Cressey et al. (1978). Retaining only the 1000 °C experiments of Cressey et al. (1978) that were performed with crystalline starting materials, Ganguly and Saxena obtained, by a second regression, enthalpy parameters of $W_{\text{CaFe}} \approx -2.6 \pm 1.7$ kJ/mol and $W_{\text{FeCa}} \approx 19.3 \pm 2.8$ kJ/mol for one cation mixing.

Anovitz and Essene (1987) analyzed experimental data in the $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ system to determine Ca-Fe mixing properties of garnet. The experimental determinations of the reactions almandine + 3 rutile = 3 ilmenite + sillimanite + quartz (GRAIL) (Bohlen et al., 1983b) and 3 anorthite = grossular + 2 Al_2SiO_5 + quartz (GASP) (Kozioł and Newton, 1986) were used to calculate the P - T position of 2 garnet + 6 rutile = 6 ilmenite + 3 anorthite + 3 quartz (GRIPS) with its garnet of $\text{grs}_{33.3}\text{alm}_{66.7}$. This reaction is also tightly determined experimentally (Bohlen and Liotta, 1986). Self-consistent formulation of all of these data places constraints on the a - X relations of the grs-alm join. To be consistent with the studies cited above and with the calorimetry data of Geiger et al. (1985), Anovitz and Essene (1987) set their excess entropy parameter to a symmetric $W^S = 6.3$ J/(mol·K) and derived the excess enthalpy parameters $W_{\text{CaFe}} = 0.628 \pm 0.321$ kJ/mol and $W_{\text{FeCa}} = 17.081 \pm 0.440$ kJ/mol for one cation mixing.

The mixing of almandine with grossular and almandine with pyrope has been studied by Geiger et al. (1987) using high-temperature oxide-melt solution calorimetry. They found that the grossular-almandine solid solution has small excess enthalpy and that almandine-pyrope solid solutions have significant excess enthalpies of mixing, especially near the almandine-rich end of the join. The results for grossular-almandine were expressed by an asymmetric Margules model, with enthalpy parameters (W^H) of $W_{\text{CaFe}} = -3.03$ kJ and $W_{\text{FeCa}} = 4.56$ kJ for 1 mol of cation. Geiger et al. (1987) suggested that excess entropy is close to zero in this join.

Low-temperature heat-capacity measurements, needed to obtain directly the excess entropy of solid solutions, require very large quantities of sample, and to date only one garnet solid solution ($\text{prp}_{60}\text{grs}_{40}$) has been measured (Haselton and Westrum, 1980). This study showed a considerable excess entropy of mixing in the pyrope-grossular join, but the one solid solution measured is insufficient to define the behavior of the whole join. Given the lack of adiabatic calorimetric data for grossular-almandine, displaced-equilibrium measurements in conjunction with the solution calorimetry may be used to obtain an estimate of excess entropy.

A comparison of the present data obtained at 1000 °C to the models of Ganguly and Saxena (1984), Anovitz and Essene (1987), and Geiger et al. (1987) is made in

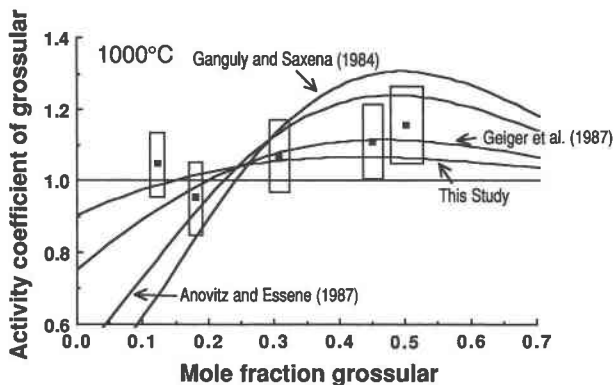


Fig. 5. A plot of the activity coefficient of grossular (γ_{grs}) determined in this study at 1000 °C against composition for a portion of the grossular-almandine join, and comparison to previous studies. Data are from Table 3. The value of γ_{grs} at the midpoint of each reversal is plotted as a small square. Width of the error box is determined by uncertainty in composition (X_{grs}). Uncertainty in γ_{grs} due to uncertainty in the calculated activity is shown as vertical extent of the boxes. The solid curves are the asymmetric Margules models for each study, as noted. The results of this study (see text) have the parameters (in kJ/mol of cation) $W_{\text{Ca}} = -1.09$ and $W_{\text{Fe}} = 2.59$.

Figure 5, which plots composition versus activity coefficient. The data from this study agree with the trend predicted by the calorimetric measurements of Geiger et al. (1987) with the assumption of negligible excess entropy. The temperature baseline of the present experiments is too short and the reversals at 900 °C too broad to clarify or verify this assumption with any confidence.

In conclusion, the present displaced-equilibrium measurements of the excess free energy of grossular-almandine join show that this garnet join is nearly ideal. These new data can be used with ternary (Ca,Fe,Mg) activity data to construct a comprehensive formulation of ternary behavior. The ideal mixing of Ca and Mn determined in this study, when combined with the ideal behavior of Fe-Mn garnets (Pownceby et al., 1987), makes it reasonable to consider Mn as an ideal diluent of Ca-Fe-Mg garnets. The energetics of Mn-Mg interactions in garnet are unknown, but the combined content of these components in crustal garnets is usually small, so that the effect of this interaction may be negligible.

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