

Solution properties of almandine-pyropo garnet as determined by phase equilibrium experiments

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ABSTRACT

The thermodynamic mixing properties of almandine-pyropo garnet were derived from phase equilibrium experiments at temperatures of 900 and 1000 °C and pressures from 8 to 14 kbar for the assemblage garnet + rutile + sillimanite + ilmenite + quartz (GRAIL). Almandine (Alm) has essentially ideal behavior in almandine-pyropo garnet over the composition range Alm₈₉–Alm₆₁ at the above experimental conditions. In all experimental products a systematic partitioning of Fe and Mg between garnet and ilmenite was seen with $\ln K_d \approx 1.59$. This partitioning does not appear to be temperature sensitive. The results of this study support the use of garnet mixing models that incorporate ideal or nearly ideal Fe-Mg parameters.

INTRODUCTION

Garnet is an important and abundant mineral in the Earth's crust and mantle and is the essential constituent in many metamorphic reactions that have been calibrated as thermobarometers (see Essene, 1989, for a review). Much information on the metamorphic history of rocks has been obtained through the use of such thermobarometers and through the interpretation of garnet zoning.

For precise estimates of pressure and temperature, the end-member reaction of the geobarometer must be well calibrated, and the solid-solution properties of garnet, predominantly a mixture of almandine, pyropo, grossular, and spessartine, must be well known. This is especially important for *P-T* studies that employ garnet zoning. The almandine-pyropo join ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) is one of the most important limiting garnet solid solutions because most garnets occurring in pelites are composed predominantly of these two components, and several exchange geothermometers are based on the partitioning of Fe and Mg between garnet and some other phase such as biotite or orthopyroxene.

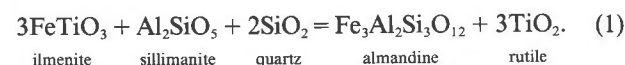
The thermodynamic mixing properties of garnet have been inferred from cationic size considerations, various Fe-Mg exchange experiments, and metamorphic parageneses. Depending on the type of analysis, almandine-pyropo mixing properties have been postulated to be nearly ideal (Aranovich and Podlesskii, 1983, 1989; Berman, 1990; Hackler and Wood, 1989; Hodges and Spear, 1982; Newton and Haselton, 1981) or significantly non-ideal (Ganguly and Saxena, 1984, 1987; Geiger et al., 1987; Moecher et al., 1988; Perkins, 1979). However, to date there have been no direct determinations of activity-

composition relationships for iron magnesium garnet solid solutions. The only other experimental work is the study of Geiger et al. (1987), who measured the excess enthalpy of almandine-pyropo garnets. Examples of Fe-Mg exchange experiments are the studies of O'Neill and Wood (1979) and Hackler and Wood (1989), who determined the Fe-Mg exchange between garnet and olivine. However, those experiments do not permit the garnet and olivine mixing properties to be deduced separately.

This study was undertaken to determine the mixing parameters of almandine-pyropo garnet by means of the phase equilibrium technique (Kozioł and Newton, 1989; Kozioł, 1990; Wood, 1988). This study complements that of Bohlen et al. (1983), in which the end-member reaction for the GRAIL geobarometer, on the basis of the equilibrium between garnet rutile and aluminosilicate ilmenite quartz, was experimentally determined. This study was also designed to complement the work of Kozioł and Newton (1989) and Kozioł (1990), who determined the mixing properties of grossular-rich garnet.

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, as outlined by Cressey et al. (1978) and Schmid et al. (1978). The thermodynamic basis of this technique has been discussed by Wood (1988). The univariant equilibrium of interest is



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In a simple system, when garnet is a solid solution and the other phases have limited or no solid solution, the

activity of almandine in garnet can be determined using the relationship

$$\int_P^{P^0} \Delta V^0 dP = RT \ln K \quad (2)$$

where the standard state is the pure phase at the temperature and pressure of interest, P^0 is the equilibrium pressure of the end-member equilibrium at T , the temperature of the experiment, P is the pressure of the experiment, ΔV^0 is the volume change of Reaction 1, and K is defined as

$$K = \frac{a_{\text{Alm}} \cdot (a_{\text{Ru}})^3}{(a_{\text{Ilm}})^3 \cdot a_{\text{Sil}} \cdot (a_{\text{Qtz}})^2} \quad (3)$$

When the integral on the left side of Equation 2 is evaluated, the activity of almandine in garnet at the temperature and pressure of interest is determined. Equation 2 has been integrated using volume data from Berman (1988). In garnet, the cations mix over three sites per formula unit, giving the following relationship between activity and mole fraction:

$$a_{\text{Alm}}^{\text{Gr}} = (X_{\text{Alm}} \gamma_{\text{Alm}})^3 \quad (4)$$

where X is the mole fraction of $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ in the binary solution and γ is the activity coefficient of $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. Measurement of the garnet composition in equilibrium with rutile, ilmenite, sillimanite, and quartz over a range of P and T permits calculation of γ_{Alm} and the activity-composition relationships. For optimal accuracy in these measurements, compositions must be reversed and all phases well characterized by microprobe analysis. In addition, the end-member curve must be well known. The GRAIL end-member equilibrium, Equation 1, has been tightly reversed by Bohlen et al. (1983), greatly aiding the precision of the determination of γ_{Alm} .

EXPERIMENTAL METHODS

Starting materials

Natural quartz from Brazil and natural sillimanite (0.95% Fe_2O_3) from Molodezhnaya Station, Antarctica, were used as starting materials. The rutile and ilmenite used were part of synthetic samples from the study of Bohlen et al. (1983). Two ilmenite-geikielite solid solutions ($\text{Ilm}_{97}\text{Geik}_{03}$ and $\text{Ilm}_{92}\text{Geik}_{08}$) were synthesized from finely disseminated mixtures of reagent-grade Fe metal, sintered Fe_2O_3 , TiO_2 , and MgO. These mixtures were reacted in evacuated silica tubes at 900 °C for 3 d. Each preparation yielded ilmenite close to the desired composition and a small amount ($\ll 0.1\%$) of rutile that could be detected optically and in backscattered electron (BSE) imaging but could not be detected by X-ray diffraction analysis.

Garnet used in this study was synthesized from glass of the desired composition. Each glass sample was prepared from a mixture of reagent-grade SiO_2 , Al_2O_3 (corundum), Fe_2O_3 , and MgO and melted in a graphite crucible at 1325 °C for 25 min. These conditions were arrived

at after some experimentation and varied with the size of the graphite crucible and the integrity of the heating elements in the furnace used. The resulting homogeneous glass was dark greenish black with no color changes indicative of an f_{O_2} gradient, nor were there traces of metal precipitation. The glass was finely powdered, loaded into an Au capsule 5 mm in diameter, with 2 wt% graphite, 1 wt% quartz, and 1 mL H_2O , and synthesized at 900 °C, 15 kbar, for 1–2 d. These syntheses yielded homogeneous garnet except for the composition $\text{Alm}_{60}\text{Pyr}_{40}$, which was synthesized at 1070 °C and 19.2 kbar to yield homogeneous garnet. All garnet samples were characterized optically, by X-ray diffraction, and by electron microprobe analysis. All garnet products had a small amount of graphite, and some had a trace ($\ll 0.1\%$) of quartz. Electron microprobe analyses confirmed that the garnets were of the desired composition with little variation, with actual compositions $\text{Alm}_{94.9}\text{Prp}_{5.1}$ (± 0.2 mol%), $\text{Alm}_{70.5}\text{Prp}_{29.5}$ (± 2.9 mol%), $\text{Alm}_{59.4}\text{Prp}_{40.6}$ (± 2.6 mol%).

Apparatus and experimental procedure

Starting mixes of the GRAIL assemblage in stoichiometric proportions appropriate for Equation 1 were prepared using appropriate garnet and ilmenite compositions. The garnets were chosen so as to approach the final composition from the almandine-rich and almandine-poor directions, and the ilmenites were chosen to be close to the composition in exchange equilibrium with the anticipated final garnet composition. For experiments performed at 1000 °C, the finely ground sample was encapsulated without any special precautions to eliminate moisture. About 4 wt% H_2O was added to the capsule for experiments performed at 900 °C. The $\text{Ag}_{80}\text{Pd}_{20}$ sample capsule, sealed by arc welding, was placed into a 3-mm Pt capsule with about 100 mg of Fe metal and 5 mL of H_2O . This outer capsule was also sealed by arc welding.

All experiments were performed in a piston-cylinder apparatus, using an assembly of 2.54 cm in diameter with NaCl pressure medium and Pt-Pt₉₀Rh₁₀ thermocouples. Experiments above 9.8 kbar were made in the low-temperature assembly of Bohlen (1984), and experiments below this pressure were made in a high-temperature assembly where Pyrex sleeves are next to the graphite furnace. Details of this assembly and its calibration are discussed by Bohlen (1984). Experimental conditions and results are listed in Table 1.

Experimental products

The products of all experiments were characterized optically and by X-ray diffraction and electron microprobe analysis. Microprobe analyses were obtained on an ARL-SEMQ electron microprobe with wavelength-dispersive spectrometers. Standards used were synthetic almandine garnet, Kakanui pyrope and synthetic TiO_2 , Fe_2O_3 , and magnesium aluminum spinel. An accelerating potential of 15 kV and sample current of 30 nA were standard operating conditions. Counting times were 20 s, and usually 2–3 counting periods were taken and averaged for

TABLE 1. Experimental conditions and results

Exp.	P (kbar)	Time (h)	Initial X_{Alm}	Final X_{Alm}	a_{ilm}	a_{Rt}	K	Calculated a_{Alm}	Activity coeff.
3.23B	14.0	94	0.80	0.888	0.966	0.979	0.910	0.965	1.06(6)
3.54	12.5	78	0.95	0.808	0.944	0.974	0.844	0.881	1.04(6)
3.13A	12.3	98	0.80	0.825	0.947	0.968	0.851	0.871	1.02(6)
3.8	12.2	117	0.70	0.823	0.949	0.968	0.848	0.866	1.02(6)
3.6A	11.9	48	0.95	0.868	0.959	0.969	0.886	0.850	0.96(5)
3.6B	11.9	48	0.70	0.800	0.948	0.971	0.828	0.850	1.03(6)
3.41	11.4	118	0.95	0.777	0.932	0.986	0.830	0.824	0.99(6)
3.62	11.2	168	0.70	0.740	0.924	0.978	0.791	0.815	1.03(6)
3.38A	10.2	142	0.80	0.708	0.897	0.979	0.781	0.766	0.98(6)
3.38B	10.2	142	0.60	0.691	0.914	0.98*	0.748	0.766	1.02(6)
3.42A	9.9	95	0.80	0.721	0.920	0.983	0.778	0.752	0.97(6)
3.42B	9.9	95	0.60	0.654	0.905	0.981	0.716	0.752	1.05(6)
3.74	8.8	92	0.70	0.614	0.869	0.984	0.702	0.703	1.00(6)
3.70A	8.6	123	0.80	0.675	0.877	0.970	0.754	0.694	0.92(5)
3.68	8.5	116	0.60	0.613	0.885	0.985	0.689	0.690	1.00(6)
3.72	8.0	243	0.60	0.653	0.899	0.972	0.711	0.712	1.00(6)

Note: All experiments performed at 1000 °C except for experiment 3.72, which was conducted at 900 °C. Initial ilmenite composition was Ilm_{100} except for experiments 3.74, 3.70, 3.68, and 3.72, where it was Ilm_{92} .

* Estimated rutile activity.

each analysis. Spectrometer data were reduced using the procedure of Bence and Albee (1968). Single garnet analyses representative of the average composition are given in Table 2. The averaged results for ilmenite and rutile are given in Tables 3 and 4, respectively.

Microprobe analyses of the products revealed a small

amount of Fe and Al in rutile and a small amount of Al and a significant and systematic solution of Mg in ilmenite (see below). In addition, there was a small but significant amount (0.9–2.0 wt%) of TiO_2 in all garnet analyses from experimental products. This level of TiO_2 was not seen in analyses of the almandine standard, nor in anal-

TABLE 2. Selected electron microprobe analyses of garnet

Exp.	3.72	3.23B	3.54	3.13A	3.8	3.6A	3.6B	3.41
Wt%								
SiO ₂	38.5	36.0	36.7	37.1	36.4	36.4	37.5	37.3
Al ₂ O ₃	21.6	20.6	21.0	20.9	20.7	20.8	20.7	21.0
FeO	31.2	40.1	37.3	38.3	38.0	39.4	36.9	36.0
MgO	8.5	1.8	4.1	3.5	3.6	2.4	4.1	4.8
CaO	0.1	0.2	0.1	0.0	0.0	0.1	0.0	0.1
TiO ₂	1.1	1.3	1.3	1.6	1.5	1.0	1.2	1.6
Total	101.0	100.0	100.5	101.4	100.2	100.1	100.4	100.8
Cations								
Si	2.968	2.942	2.941	2.953	2.932	2.956	2.989	2.957
Al	1.958	1.987	1.977	1.957	1.971	1.993	1.949	1.958
Fe	2.011	2.735	2.498	2.548	2.562	2.677	2.459	2.378
Mg	0.98	0.218	0.491	0.42	0.433	0.288	0.49	0.563
Ca	0.007	0.014	0.005	0.003	0.002	0.006	0.004	0.008
Ti	0.065	0.077	0.08	0.093	0.091	0.028	0.072	0.100
Total	7.989	7.973	7.992	7.974	7.991	7.977	7.963	7.964
Exp.	3.62	3.38A	3.38B	3.42A	3.42B	3.74	3.70A	3.68
Wt%								
SiO ₂	38.0	38.1	38.0	37.8	38.2	39.2	38.0	39.0
Al ₂ O ₃	20.9	21.6	21.6	20.9	21.2	21.5	21.3	21.3
FeO	34.6	34.0	32.6	33.8	30.5	29.9	32.1	29.3
MgO	5.7	6.7	7.1	6.2	8.2	9.1	7.6	9.9
CaO	0.3	0.0	0.3	0.1	0.4	0.0	0.0	0.0
TiO ₂	1.5	1.5	1.2	1.9	1.5	1.3	1.4	0.9
Total	101.0	101.9	100.8	100.7	100.0	101.0	100.4	100.4
Cations								
Si	2.979	2.947	2.958	2.966	2.967	2.997	2.964	2.994
Al	1.937	1.974	1.978	1.932	1.94	1.936	1.96	1.929
Fe	2.272	2.20	2.122	2.214	1.981	1.91	2.091	1.878
Mg	0.667	0.773	0.822	0.723	0.949	1.035	0.879	1.133
Ca	0.024	0.001	0.03	0.005	0.032	0.003	0.001	0.003
Ti	0.087	0.086	0.071	0.114	0.087	0.076	0.08	0.051
Total	7.966	7.981	7.981	7.954	7.956	7.957	7.975	7.988

Note: All experiments performed at 1000 °C except for experiment 3.72.

TABLE 3. Electron microprobe analyses of ilmenite

Exp.	3.72	3.23B	3.54	3.13A	3.8	3.6A	3.6B	3.41	
				Wt%					
FeO	44.1	46.3	46.1	46.4	46.0	46.5	45.9	44.9	
TiO ₂	53.3	52.6	52.3	53.1	53.1	53.0	52.6	53.2	
Al ₂ O ₃	0.4	0.6	0.6	0.6	0.7	0.6	0.6	0.7	
MgO	2.5	0.4	1.1	1.0	0.9	0.6	0.9	1.3	
Total	100.3	99.9	100.1	101.1	100.6	100.7	100.0	100.1	
				Cations					
Fe	0.910	0.965	0.963	0.96	0.951	0.968	0.959	0.931	
Ti	0.987	0.986	0.982	0.988	0.988	0.991	0.988	0.992	
Al	0.011	0.018	0.018	0.018	0.020	0.018	0.014	0.020	
Mg	0.093	0.017	0.039	0.035	0.032	0.023	0.035	0.048	
Total	2.001	1.985	2.001	2.002	1.990	2.00	1.995	1.990	
Points	5	4	5	3	3	3	2	4	
Exp.	3.62	3.38A	3.38B	3.42A	3.42B	3.74	3.70A	3.68	
				Wt%					
FeO	44.5	43.6	44.0	44.2	44.0	42.3	43.6	43.0	
TiO ₂	53.2	53.4	53.4	53.7	53.8	53.9	52.9	53.0	
Al ₂ O ₃	0.7	0.7	0.7	0.6	0.5	1.1	0.7	0.5	
MgO	1.5	2.3	1.8	1.7	2.1	3.0	2.9	2.7	
Total	99.9	100.0	99.9	100.2	100.4	100.3	100.1	99.2	
				Cations					
Fe	0.923	0.898	0.906	0.915	0.905	0.865	0.898	0.975	
Ti	0.993	0.989	0.990	0.997	0.995	0.991	0.979	0.968	
Al	0.019	0.021	0.021	0.019	0.019	0.025	0.019	0.019	
Mg	0.058	0.083	0.064	0.061	0.077	0.109	0.106	0.097	
Total	1.992	1.990	1.980	1.992	1.996	1.989	2.002	1.959	
Points	2	5	3	5	4	5	5	4	

Note: All experiments performed at 1000 °C except for experiment 3.72.

TABLE 4. Electron microprobe analyses of rutile

Exp.	3.72	3.23B	3.54	3.13A	3.8	3.6A	3.6B	3.41	
				Wt%					
FeO	1.3	0.9	1.2	1.5	1.5	1.2	1.2	0.7	
TiO ₂	97.8	98.5	98.0	97.9	97.3	98.2	97.7	99.1	
Al ₂ O ₃	0.9	0.7	0.8	1.0	1.1	1.1	1.0	0.4	
MgO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Total	100.0	100.1	100.0	100.4	99.9	100.5	99.9	100.2	
				Cations					
Fe	0.014	0.010	0.013	0.017	0.016	0.014	0.014	0.007	
Ti	0.980	0.987	0.980	0.980	0.974	0.980	0.980	0.991	
Al	0.013	0.010	0.013	0.016	0.017	0.017	0.016	0.007	
Mg	0.001	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Total	1.008	1.008	1.006	1.012	1.007	1.011	1.009	1.005	
Points	3	2	5	2	2	2	2	2	
Exp.	3.62	3.38A	3.42A	3.42B	3.74	3.70A	3.68		
				Wt%					
FeO	0.9	1.0	0.8	0.9	0.8	1.4	0.7		
TiO ₂	97.8	97.6	99.0	98.7	99.0	97.0	98.4		
Al ₂ O ₃	0.4	0.7	0.5	0.6	0.5	0.9	0.4		
MgO	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
Total	99.1	99.3	100.3	100.2	100.3	99.3	99.5		
				Cations					
Fe	0.075	0.011	0.009	0.010	0.009	0.016	0.007		
Ti	0.968	0.969	0.990	0.988	0.990	0.965	0.979		
Al	0.007	0.010	0.008	0.009	0.008	0.014	0.007		
Mg	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
Total	0.990	0.990	1.007	1.007	1.007	0.994	0.993		
Points	2	2	2	3	3	2	3		

Note: All experiments performed at 1000 °C except for experiment 3.72.

yses of the synthetic garnet used as starting material. Bohlen et al. (1983) postulated that the 1.5 wt% TiO₂ they obtained in their analyses was the result of fine intergrowths of rutile with garnet. We believe the Ti is part of the garnet structure because we did not see any rutile grains in BSE images, even at high power, and the Si cation totals of the garnet were always slightly reduced compared with analyses of standards and synthetic garnet samples.

Spot analyses were taken at different points within the same grain of garnet, rutile, or ilmenite and among several different grains. Garnets were almost always compositionally zoned. The original seed compositions were retained in the core, but the garnet grains developed a rim, varying between 2 and 10 μm in thickness, that had a new composition. This new composition differed from the starting composition by as much as 17 mol%. The three or four analyses with good stoichiometry that were farthest removed from the original composition were considered indicative of the final composition attained. Ilmenite and rutile were unzoned.

Each garnet analysis was cast into mole fractions separately and recalculated on a site by site basis, where $X_{\text{Alm}} = X_{\text{Fe}} \cdot (X_{\text{Al}})^{2/3} \cdot X_{\text{Si}}$. The microprobe data of Bohlen et al. (1983) were used to calculate the activity of sillimanite by the relationship $a_{\text{Sil}} = X_{\text{Sil}} = X_{\text{Si}} \cdot X_{\text{Al}}$, and a_{Sil} was found to be 0.97 at 1000 °C. The activity of rutile, always within 0.03 of unity, was taken to be equal to the mole fraction of rutile, calculated as $X_{\text{Ru}} = X_{\text{Ti}}/X_{\text{tot}}$, where X_{tot} was the total number of cations in the analysis. The ilmenite mole fraction was calculated as $X_{\text{Fe}} \cdot X_{\text{Ti}}$ (on a cation basis).

DISCUSSION

Results of experiments

The results of experiments conducted at 1000 and 900 °C are given in Table 1. For an experiment at a given pressure and temperature, the activity of almandine in garnet may be calculated by Equation 2, and this value for each set of experimental conditions is noted in Table 1 as calculated a_{Alm} . X_{Alm} , as measured by electron microprobe analysis, cannot be compared directly to this value because the other phases involved in the experiments are not at unit activity, as noted above, and their activity values must be substituted into Equations 2 and 3. The extent of nonideal mixing in ilmenite geikielite as predicted by the model of Anderson and Lindsley (1981) is negligible at these compositions at 1000 °C; therefore this correction to the ideal activity of ilmenite was ignored. Starting with the definition of K , the equilibrium constant (Eq. 3), we define K' as the cube root of the apparent equilibrium constant of Reaction 1:

$$K' = \frac{a_{\text{Alm}}^{\text{ideal}} \cdot a_{\text{Ru}}}{a_{\text{Ilm}} \cdot (a_{\text{Sil}})^{1/3}} \quad (5)$$

where $a_{\text{Alm}}^{\text{ideal}}$ corresponds to X_{Alm} measured by the experiments. In effect, K' is the mole fraction of almandine obtained after accounting for solid solution in the other

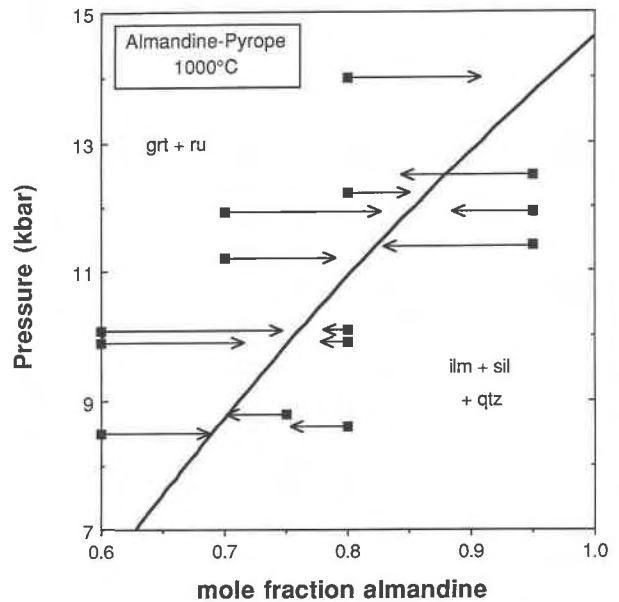


Fig. 1. P - X_{Alm} diagram at constant temperature of 1000 °C. Solid line: displacement in pressure of the GRAIL equilibrium (Eq. 1) by solid solution in almandine garnet, calculated by Equation 2, assuming ideal mixing in garnet. Experimental data obtained in this study are also plotted. Filled boxes: starting composition of almandine-pyropite garnet. Arrow tips: K' or final composition of garnet adjusted for the reduced activities of ilmenite, rutile, and sillimanite. See text for details.

phases. The value of K' is compared against a_{Alm} calculated from Equation 2, as described above. Equation 4 may be rewritten as

$$a_{\text{Alm}}^{\text{Grt}} = K' \cdot \gamma_{\text{Alm}} \quad (6)$$

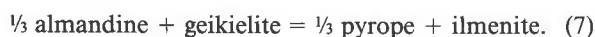
where $a_{\text{Alm}}^{\text{Grt}}$ is the calculated value and γ_{Alm} is the activity coefficient. A graphical presentation of the data at 1000 °C is given as Figure 1. In this and all further figures, values for K' , the adjusted mole fraction of almandine, are plotted. In this isothermal section, the calculated displacement of the univariant reaction (Eq. 1) if Mg-Fe mixing in the garnet were ideal is shown by the solid line. The change in the garnet compositions from initial (filled boxes) to final (arrow heads) is also shown. The final compositions are very close to the curve for ideal mixing, and therefore there is little to no excess free energy of mixing for iron magnesium garnet solutions at 1000 °C. Very limited data were obtained at 900 °C, but one half reversal indicates that iron magnesium garnets behave similarly at this temperature.

In considering the uncertainties of these results, one must include uncertainties in electron microprobe analysis. Uncertainties in the compositions of garnet, rutile, ilmenite, and sillimanite cause an estimated uncertainty of approximately ± 0.017 in the value for K' , the adjusted mole fraction of almandine. The main factors contributing to the uncertainty in the calculated a_{Alm} from Equation 2 are the uncertainty in P^0 , the pressure of the end-

member equilibrium (Eq. 1), and the uncertainty in P , the pressure of the experiment. The end-member curve was precisely bracketed by Bohlen et al. (1983) to within 200 bars, and the piston-cylinder apparatus employed in the Menlo Park laboratory is precise to ± 100 bars (laboratory unpublished data). The 2σ uncertainty of ± 600 bars in the difference between P^0 and P leads to an uncertainty of ± 0.026 (for large differences) to ± 0.034 (for small differences) in the calculated value of a_{Alm} . The combination of uncertainties stemming from composition and pressure determination leads to a 2σ uncertainty of ± 0.06 in the value of γ_{Alm} as listed in Table 1.

Fe-Mg exchange between garnet and ilmenite

A systematic partitioning of Fe and Mg between garnet and ilmenite was noted and followed as the experiments progressed. This exchange can be described by the reaction



The distribution coefficient, K_d , is defined as

$$K_d = \frac{X_{\text{Mg}}^{\text{Grt}} \cdot X_{\text{Fe}}^{\text{Ilm}}}{X_{\text{Fe}}^{\text{Grt}} \cdot X_{\text{Mg}}^{\text{Ilm}}} \quad (8)$$

Other studies have experimentally determined the partitioning of Fe and Mg (or Mn) between ilmenite and an iron magnesium silicate (Bishop, 1980; Pownceby et al., 1987), but there is little information on Fe-Mg partitioning between garnet and ilmenite (but see Green and Sobolev, 1975). Although these experiments were not designed to measure the K_d of this exchange, we did note a systematic partitioning of Fe and Mg with an average or best fit K_d of 4.9, or $\ln K_d$ of 1.59 (Fig. 2A). These experiments were performed over a range of pressures, but their results can be compared because the volume change of this reaction is extremely small (± 0.019 J/bar). The data in Figure 2A are reversed in terms of garnet mole fraction but all final ilmenite-geikielite compositions were approached from ilmenite-rich compositions (pure ilmenite except for the most magnesian compositions; see Table 1). Still, the very regular results at 1000 °C are another indication that equilibrium between garnet and ilmenite was approached.

Green and Sobolev (1975) performed synthesis experiments on a pyrolite and an olivine-basanite composition and obtained microprobe analyses of coexisting garnet and ilmenite. They found regular partitioning of Fe and Mg between these two phases with a K_d of approximately 4.0 ± 0.5 . This value did not appear to be sensitive to temperature, pressure, or composition. The compositions they investigated were more magnesian [$\text{Mg}(\text{Mg} + \text{Fe})$ of garnet = 0.41–0.73; of ilmenite = 0.15–0.47] than those of this study (see Fig. 2B). Although it was suggested previously (Kozioł and Bohlen, 1990) that this exchange might be a geothermometer, Green and Sobolev (1975) have shown that the K_d for garnet ilmenite is insensitive to temperature over the range 900–1100 °C.

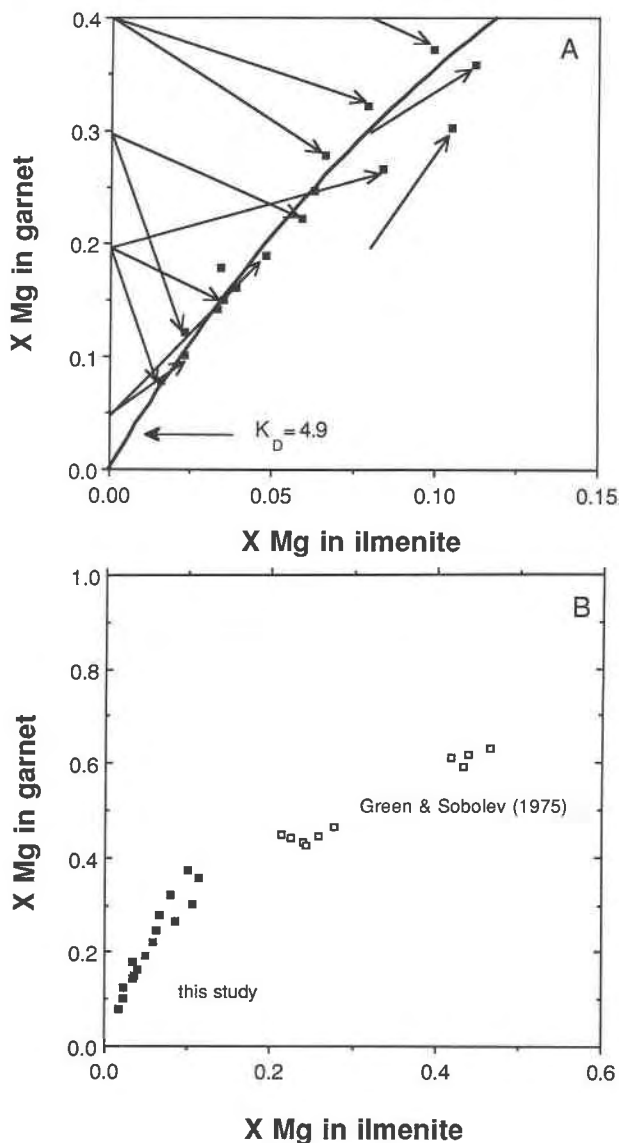


Fig. 2. Experimental data for the distribution of Mg^{2+} between coexisting garnet and ilmenite. X_{Mg} : mole fraction of the Mg end-member of garnet or ilmenite. (A) Final compositions obtained in this study at 1000 °C (filled squares). Arrows indicate extent of change of selected initial garnet-ilmenite pairs to final compositions as listed in Table 1. A K_d value of 4.9 best fits all the data. (B) Comparison of data from this study (filled squares) to the data of Green and Sobolev (1975) (open squares) obtained at 950–1050 °C.

Mixing properties of iron magnesium garnets

The data in this study were collected over a range of pressures and compositions, and the activity coefficients cannot be compared directly unless there is no excess volume of mixing in almandine-pyrope garnets. The comprehensive unit-cell measurements of Geiger et al. (1987) show a very slight asymmetry in the volumes of mixing that may be neglected for the purposes of this paper. As noted above and in Figure 1, our experiments

indicate that the excess free energy of mixing of iron magnesium garnet solutions is close to zero, at least at 1000 and 900 °C. Because our data cover only a limited range of compositions and temperature, the results from other studies are considered here in order to constrain further the mixing properties of this solid solution.

The enthalpy of mixing of almandine-pyrope garnet has been determined by Geiger et al. (1987) using calorimetric methods. They found that almandine-pyrope solid solutions have apparently large excess enthalpies of mixing, most pronounced near the almandine-rich end of the series. Large uncertainties are associated with these calorimetric measurements. Modeling the data asymmetrically, they obtained $W_{\text{H}}^{\text{H}} = 12.06$ kJ, $W_{\text{H}}^{\text{Alm}} = -5.25$ kJ for one cation of mixing. Such significant excess enthalpies of mixing, if combined with our results, may indicate a sizable excess entropy of mixing, by the relationship $\Delta G^{\text{ex}} = \Delta H^{\text{ex}} - T\Delta S^{\text{ex}}$. However, the limitations of these two sets of data make such a conclusion highly uncertain.

Fe-Mg partitioning studies constrain a linear combination of the mixing properties of the two phases, such as biotite garnet (Ferry and Spear, 1978), olivine garnet (O'Neill and Wood, 1979; Hackler and Wood, 1989), and cordierite garnet (Aranovich and Podlesskii, 1983). If the solution properties of the other phase are well known, then the almandine-pyrope mixing properties can be calculated. In this way Ferry and Spear (1978) concluded that almandine-pyrope garnets were nearly ideal at Fe-rich compositions, based on their garnet-biotite exchange experiments. Similarly, O'Neill and Wood (1979) and Hackler and Wood (1989) suggested almandine pyrope is nearly ideal from garnet-olivine partitioning data, as did Aranovich and Podlesskii (1983) from garnet-cordierite exchange experiments. Berman (1990) has employed a number of garnet-orthopyroxene Fe-Mg exchange studies to extract iron magnesium garnet properties by mathematical programming analysis. He obtained $W_{\text{FeMg}} = 0.08$ kJ/mol, $W_{\text{MgFe}} = 1.24$ kJ/mol for one cation of mixing.

A number of researchers have used compositional data of coexisting Fe-Mg phases from natural occurrences, well characterized petrologically in terms of temperature and pressure, to constrain garnet properties (Dahl, 1980; Hodges and Spear, 1982; Hoinkes, 1986). Others have combined petrologic data with experimental data (Chatterjee, 1987; Ganguly and Saxena, 1984, 1987). A recent analysis by Williams and Grambling (1990) examined coexisting garnet and biotite pairs from rocks in northern New Mexico where metamorphic conditions are well known. Fe and Mg content of the garnets and $\ln K_d$ of garnet-biotite partitioning were clearly linked to the spessartine content of garnet. Because of this, parameters for Mg-Fe and Mg-Mn mixing in garnet cannot be independently determined, but a range of paired values is permitted. Ideal mixing of Mg-Fe in garnet is allowed, but Williams and Grambling prefer slightly nonideal mixing and adopt the values of Hackler and Wood (1989) of $W_{\text{FeMg}} = 0.7$ kJ/mol of cation, $W_{\text{MgFe}} = 2.12$ kJ/mol of cation.

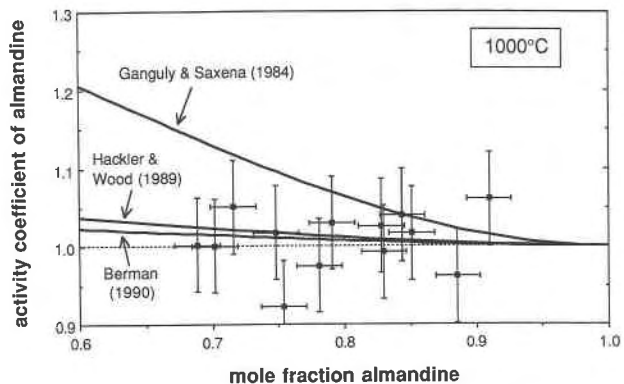


Fig. 3. Activity coefficient of almandine (γ_{Alm}) vs. mole fraction almandine for a portion of the almandine-pyrope join, as determined from representative mixing models and the experimental data of this study. Filled squares: data collected at 1000 °C, plotted at the adjusted garnet composition (see Table 1) with uncertainties (described in text) shown by brackets. Solid curves: predictions of various mixing models, as noted. Dotted line: ideal mixing behavior.

A comparison of representative nearly ideal and non-ideal mixing models with our experimental results is made in Figure 3. This graph of the adjusted mole fraction of almandine against the activity coefficient of almandine (γ_{Alm}) is a plot of the values of γ_{Alm} at 1000 °C, predicted by the mixing models of Berman (1990), Hackler and Wood (1989), and Ganguly and Saxena (1984). It also includes the experimental data, plotted as squares, as well as an indication of the uncertainties in the data (brackets). Although only a small portion of the join could be investigated, it is clear that the experimental data are consistent with the models of Hackler and Wood (1989) and Berman (1990).

Implications for geobarometry

In general, these results provide confirmation of nearly ideal mixing behavior of almandine-rich garnets and therefore improve our confidence in estimates of temperature and pressure calculated from garnet geothermometers and geobarometers. These results support Berman's (1990) garnet model and other models (Hodges and Spear, 1982; Newton and Haselton, 1981) that incorporate nearly ideal Fe-Mg mixing.

A barometer that is rather sensitive to values of the activity of almandine is the garnet-rutile-sillimanite-ilmenite-quartz geobarometer or GRAIL (Bohlen et al., 1983). The GRAIL barometer has a small volume change compared with many others and a rather flat slope. Bohlen et al. (1983) formulated this geobarometer with experimental reversals of the end-member reaction and a nonideal model for garnet solid solution from Perkins (1979), which provides for a temperature-dependent symmetric model for Fe-Mg mixing in garnet: $W_{\text{FeMg}} = 14.57 - 5.02T$ (°C, kJ/mol, one cation of mixing). In their analysis of the GRAIL barometer, Bohlen et al. (1983)

stated that a nonideal garnet model was necessary for estimating the correct pressures for kyanite- and sillimanite-bearing assemblages. Otherwise, pressures in the sillimanite field would be calculated for kyanite-bearing rocks, or pressures in the andalusite field would be calculated for sillimanite-bearing rocks. The effect of using an ideal model is to reduce pressure estimates.

We conducted a reexamination of GRAIL assemblages as reported in the literature to check that ideal Fe-Mg mixing was consistent with field evidence. Well-characterized assemblages from the studies of Aggarwal and Nesbitt (1987), Baker (1985), Fletcher and Greenwood (1979), Hattori (1967), Labotka (1980), and Stäubli (1989) that preserved two Al_2SiO_5 polymorphs or that were estimated to have equilibrated near an Al_2SiO_5 phase boundary were chosen. Temperatures estimated by the garnet-biotite geothermometer of Ferry and Spear (1978) were recalculated using Berman's (1990) garnet model, or in some cases the author's estimates were used. Pressures were calculated with the calibration of Bohlen et al. (1983) using Perkins's garnet model (given above) and using an ideal garnet solution model, where all cation interactions are assumed to be zero. Such a model ignores the demonstrable nonideality of Fe-Ca and Mg-Ca (see Berman, 1990) and represents the end-member case. Results were compared against the aluminosilicate diagram of Holdaway (1971) with modifications to the kyanite-sillimanite boundary by Bohlen et al. (1991). We find that temperatures calculated using different solution models for garnet in the garnet-biotite geothermometer are virtually the same. Estimated pressures are slightly lower than those estimated by the previous calibration, but are always close (within 1 kbar) to the kyanite-sillimanite phase boundary. Ideal mixing in almandine-pyropite garnet is compatible with the reported GRAIL parageneses in the papers cited.

Another thermobarometer that is affected by assumed iron magnesium garnet mixing properties is spinel-quartz-garnet-sillimanite (Bohlen et al., 1986), which can be used to estimate either temperature or pressure. This thermobarometer is based on experimental reversals of the equilibrium $3 \text{hercynite} + 5 \text{quartz} = \text{almandine} + \text{sillimanite}$, and the formulation is independent of any garnet or spinel solution model, as explained by Bohlen et al. (1986). However, the activity of almandine in garnet must be determined, and the use of the nonideal garnet model of Ganguly and Saxena (1984) was suggested by Bohlen et al. (1986). The use of a nearly ideal garnet model has the effect of increasing the estimated temperature and lowering the estimated pressure calculated from the thermobarometer.

CONCLUSION

The determination of solid-solution properties of minerals greatly improves the calibration of many geothermometers and geobarometers. This new determination of almandine-pyropite mixing especially aids the many formulations of thermobarometers that involve garnet. Ac-

ording to recent work by Kohn and Spear (1991), uncertainties in the mixing properties of garnet account for a significant amount of the uncertainty in the final pressure estimate, especially for the garnet- Al_2SiO_5 -quartz-plagioclase and garnet-plagioclase-clinopyroxene-quartz geobarometers. This uncertainty is not eliminated by the work presented here and in similar studies; however, it is greatly reduced, and investigation of the P - T history of metamorphic terranes may proceed with more assurance.

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