American Mineralogist, Volume 76, pages 1580–1588, 1991

An experimental study of the effect of Ca upon garnet-ilmenite Fe-Mn exchange equilibria

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ABSTRACT

The influence of $Ca_3Al_2Si_3O_{12}$ (grossular) on Fe-Mn partitioning between coexisting garnet and ilmenite has been investigated at 650–1000 °C, 10 kbar for ternary calcium-manganese-iron garnets of various Fe-Mn ratios. $K^{\text{gar-ilm}}_{\text{DFe-Mn}}$ shows a slight dependence upon $X^{\text{gar}}_{\text{Ca}}$. The experimental results have been combined with the $FeTiO_3$-$MnTiO_3$ activity-composition data of O'Neill et al. (1989) to constrain activity-composition relations in garnet. Mixing in ternary calcium-manganese-iron garnets (up to ≈30 mol% grossular) may be represented by the simple regular solution model with the difference in the binary interaction parameters $(W^{\text{gar}}_{\text{CaFe}} - W^{\text{gar}}_{\text{CaMn}}) = 0.97 \pm 0.20$ kJ/mol of cation. The results are in good agreement with the recent activity data for the individual calcium-iron and calcium-manganese garnet binaries (Koziol, 1990).

For the almandine-spessartine binary solution, the new data reported here give $W^{\text{gar}}_{\text{FeMn}} = 0.62 \pm 0.20$ kJ/mol of cation, in good agreement with previous results from the Ca-free system (Pownceby et al., 1987). Reformulation of the thermometer based on Fe-Mn exchange between garnet and ilmenite to take into account the new data gives

$$T\,(^{\circ}\text{C}) = \left[\frac{14918 - 2200(2X^{\text{ilm}}_{\text{Mn}} - 1) + 620(X^{\text{gar}}_{\text{Mn}} - X^{\text{gar}}_{\text{Fe}}) - 972X^{\text{gar}}_{\text{Ca}}}{\text{R} \ln K_{\text{d}} + 4.38}\right] - 273.15.$$

The thermometer has a resolution of ±30–50 °C.

INTRODUCTION

The partitioning of Fe and Mn between garnet and ilmenite may be represented by the exchange reaction

$$\underset{\text{almandine}}{\tfrac{1}{3}Fe_3Al_2Si_3O_{12}} + \underset{\text{pyrophanite}}{MnTiO_3} = \underset{\text{spessartine}}{\tfrac{1}{3}Mn_3Al_2Si_3O_{12}} + \underset{\text{ilmenite}}{FeTiO_3} \qquad (1)$$

which is highly sensitive to temperature. This, together with the relative compositional and structural simplicity of the two phases, has led to its recently being proposed as a mineralogic thermometer (Ono, 1980; Docka, 1985; Kress et al., 1985; Pownceby et al., 1987). It should prove especially useful for medium-grade metamorphic rocks where the assemblage (garnet + ilmenite) is common and where both garnet and ilmenite may contain substantial Mn^{2+}.

The study of element-partitioning equilibria (such as Reaction 1) also provides a method to constrain the binary mixing properties of garnet crystalline solutions. For example, Pownceby et al. (1987) have presented a reversed experimental determination of Reaction 1 as a function of pressure, temperature, and the ratio Fe^{2+}/Mn^{2+}. They found that the distribution coefficient $K^{\text{gar-ilm}}_{\text{DFe-Mn}}$ depends slightly on the Fe^{2+}/Mn^{2+} ratio, indicating small departures from ideal mixing in one or both phases. Although the observed K_d is sensitive only to the difference in the deviations from ideality of the two solutions, when the partitioning data are combined with the recent activity-composition data for ilmenite-pyrophanite solid solutions (O'Neill et al., 1989), the results indicate mixing in binary almandine-spessartine garnets to be almost ideal.

The same approach can be adopted to constrain mixing properties in more complex garnet solutions. Since natural garnet often closely approaches a ternary solid solution $(Ca,Mn,Fe)_3Al_2Si_3O_{12}$ in many amphibolites, granulites, and peraluminous acid magmas, we decided to

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0003–004X/91/0910–1580$02.00

examine the effects of the grossular component (X^{gar}_{Ca}) on Fe^{2+}-Mn partitioning between coexisting garnet and ilmenite. It is well known that the grossular component exerts a strong influence on Fe^{2+}-Mg partitioning involving garnet (e.g., garnet-olivine, O'Neill and Wood, 1979; garnet-orthopyroxene, Harley, 1984; garnet-clinopyroxene, Ellis and Green, 1979). This effect arises from the large difference in deviations from ideality between Ca-Mg garnets (large positive deviations from ideal mixing) and Ca-Fe^{2+} garnets (close to ideal) and may be modeled using the regular solution formalism, with the difference between the regular solution parameters ($W^{gar}_{CaMg} - W^{gar}_{CaFe}$) constrained to be ≈12 kJ/mol of cation (e.g., O'Neill and Wood, 1979). However, recent experimental work on the garnet Ca-Mn binary (Koziol, 1990) has shown that this join, like the Ca-Fe^{2+} join, shows close to ideal behavior. Hence ($W^{gar}_{CaFe} - W^{gar}_{CaMn}$) ≈ 0, and we expect that a grossular component would not greatly affect Fe^{2+}-Mn partitioning relations. The purpose of this study was to test this hypothesis by direct experimental investigation.

Experiments have been performed over a range of $(Ca,Mn,Fe)_3Al_2Si_3O_{12}$ garnet compositions in the temperature range 650–1000 °C at 10 kbar.

THERMODYNAMIC BACKGROUND

The calculated molar volume change (ΔV^0) for Reaction 1 is −0.025 J/bar (data from Helgeson et al., 1978; Wall et al., 1980; Bohlen et al., 1983). This, together with the negligible excess partial molar volume data for almandine-spessartine (Koziol and Newton, 1987; Koziol, 1990) and ilmenite-pyrophanite solutions (O'Neill et al., 1989), renders Reaction 1 insensitive to pressure; hence, in the following analysis $\Delta G^0_{P,T}$ is assumed to be independent of P. In addition, if the heat capacity difference (ΔC_P) is assumed to be negligible over the temperature range of the experiments then at equilibrium the free energy change of the partitioning reaction $\Delta G^0_{P,T}$ is given by

$$\Delta G^0_{P,T} = RT(\ln \gamma^{gar}_{Fe} - \ln \gamma^{gar}_{Mn}) - RT(\ln \gamma^{ilm}_{Fe} - \ln \gamma^{ilm}_{Mn}) - RT \ln K_d \quad (2)$$

where γ^{gar}_{Fe} is the activity coefficient of Fe^{2+} in the three crystallographically equivalent sites in the garnet structure, γ^{ilm}_{Fe} is the activity coefficient of Fe^{2+} in the ilmenite, etc. K_d, the distribution coefficient, is defined as

$$K_d = \frac{(X^{gar}_{Mn})\cdot(X^{ilm}_{Fe})}{(X^{gar}_{Fe})\cdot(X^{ilm}_{Mn})}. \quad (3)$$

Recently O'Neill et al. (1989) have accurately measured activity-composition relations in $FeTiO_3$-$MnTiO_3$ solutions and found that small positive deviations from ideal mixing can be represented by a regular solution model with $W^{ilm}_{FeMn} = 2.2 \pm 0.3$ kJ/mol (all σ values quoted as 1 s.d.) at temperatures between 750 and 1000 °C. Using this value, the experimental data from the partitioning Reaction 1 can also be described by a simple regular solution model for Fe-Mn garnet as well as for the iron-manganese ilmenite solution (Pownceby et al., 1987; O'Neill et al., 1989).

Using the regular symmetric solution model, Equation 2 may thus be rewritten as

$$RT \ln K_d = W^{gar}_{FeMn}(2X^{gar}_{Mn} - 1) - W^{ilm}_{FeMn}(2X^{ilm}_{Mn} - 1) - \Delta G^0_{P,T} \quad (4)$$

where W^{gar}_{FeMn} and W^{ilm}_{FeMn} are 1.2 ± 0.5 and 2.2 ± 0.3 kJ/mol, respectively.

Equation 4 of course applies only to binary iron-manganese garnet and ilmenite. If Ca is added, the activities of the spessartine and almandine components in garnet will be modified. Assuming a ternary symmetric regular solution model for calcium-manganese-iron garnets in the composition range $0 \leq X^{gar}_{Ca} \leq 0.35$ (cf. O'Neill and Wood, 1979), Equation 4 may be restated as

$$RT \ln K_d = W^{gar}_{FeMn}(X^{gar}_{Mn} - X^{gar}_{Fe}) - W^{ilm}_{FeMn}(2X^{ilm}_{Mn} - 1) + X^{gar}_{Ca}(W^{gar}_{CaFe} - W^{gar}_{CaMn}) - \Delta G^0_{P,T}. \quad (5)$$

At constant pressure and temperature, a plot of [$RT \ln K_d + W^{ilm}_{FeMn}(2X^{ilm}_{Mn} - 1) - W^{gar}_{FeMn}(X^{gar}_{Mn} - X^{gar}_{Fe})$] against X^{gar}_{Ca} will yield a straight line of slope ($W^{gar}_{CaFe} - W^{gar}_{CaMn}$). Note that X^{gar}_{Ca} is correlated with ($W^{gar}_{CaFe} - W^{gar}_{CaMn}$); hence, we only measure the difference in the interaction parameters ΔW_{Ca}.

EXPERIMENTAL APPROACH

Starting materials

Series of oxide mixtures in the systems FeO-MnO-CaO-Al_2O_3-SiO_2 (i.e., garnet) and FeO-MnO-TiO_2 (ilmenite) were prepared using analytical grade TiO_2 (anatase), γ-Al_2O_3, SiO_2 glass, CaO, MnO (prepared by firing $MnCO_3$ at 600 °C in a reducing atmosphere), Fe_2O_3, and Fe metal. All starting materials were analyzed by X-ray powder diffraction to confirm their nature, oven dried at 110 °C, and stored under vacuum until used.

Ilmenite-pyrophanite starting mixtures were prepared by grinding together oxide mixtures of analytical grade MnO, Fe_2O_3, Fe metal, and TiO_2 (anatase). Finely ground (≈5–10 μm) compositions were prepared at 25 mol% intervals along the ilmenite-pyrophanite join ($ilm_{100}pyr_{00}$, $ilm_{75}pyr_{25}$, $ilm_{50}pyr_{50}$, $ilm_{25}pyr_{75}$, $ilm_{00}pyr_{100}$). The ilmenite-pyrophanite solutions were crystallized hydrothermally from the oxide mixtures at 800 °C, 3–5 kbar at the f_{O_2} of the QFM O buffer; see Pownceby et al. (1987) for further experimental details. The crystallized oxide starting compositions used in this study are in fact from the same batch of mixtures prepared for the experiments in Pownceby et al. (1987) and also used in the study by O'Neill et al. (1989). The materials were checked by electron microprobe analysis, which indicated that the solid solutions were both homogeneous and stoichiometric; observed compositions together with unit-cell dimensions from powder XRD characterization are summarized in Table 1 of O'Neill et al. (1989).

Oxide mixtures required to produce garnet compositions with Fe/Mn ratios of 3:1 and 1:3 and X^{gar}_{Ca} values of ≈0.10, 0.20, 0.30, and 0.40 mol% were prepared. Compositions were seeded with finely ground (≈5 μm) iron-manganese garnets synthesized following methods outlined in Pownceby et al. (1987). These seeds were added and reground with the garnet oxide mixtures to make up a total of 5–8 wt% of the final seeded garnet-oxide mix.

Partitioning experiments were prepared by grinding together oxide mixtures of calcium-manganese-iron garnets and crystallized iron-manganese ilmenites. Unequal proportions of garnet-ilmenite oxide mixtures were used in the experiments. An initial mass ratio of ≈20:80 (garnet/ilmenite) was chosen in an attempt to minimize potential problems resulting from Fe-Mn diffusion in garnet, which is expected to be sluggish at $T \leq 1000$ °C (Lasaga, 1983). By using the known rapid Fe-Mn diffusion in ilmenite (Pownceby et al., 1987) and effectively flooding the system with ilmenite, it was anticipated that the initial garnet phase synthesized would be close to the equilibrium composition. Approximately 5 wt% of finely crushed Brazilian quartz (≈10 μm in diameter) was added to the reactants to maintain a high SiO_2 activity, thus inhibiting the substitution of Ti^{4+} for Si^{4+} in the garnet structure and the formation of hydrogarnet. Initial combinations of oxide mixtures of garnet and ilmenite were selected on the basis of Fe-Mn partitioning data reported in Pownceby et al. (1987).

Experimental apparatus

High-pressure experiments were performed in a conventional piston-cylinder apparatus and half-inch furnace assemblies (Boyd and England, 1960). Approximately 10–15 mg of the reactants were sealed in $Ag_{70}Pd_{30}$ capsules measuring 2.0 mm (od) × 0.1 mm (wall thickness) × 8.0 mm, with 5–10 wt% triply distilled-deionized H_2O as a flux. The sample charge was loaded into a pressure cell consisting of concentric tubes of talc (outermost), pyrex, and graphite (innermost). Experiments were conducted at 650–1000 °C (± 5°C), 10 kbar (± 0.5 kbar) for ≈20–130 h.

Each experiment was pressed to the required pressure, brought to temperature, then taken to about 2 kbar over the required pressure before decompressing and maintaining at the required value. Temperature was measured and controlled to within ±5 °C by a $Pt\text{-}Pt_{90}Rh_{10}$ thermocouple. No corrections have been made for possible friction effects on pressure or for pressure effects on the thermocouple emf.

Product identification and analysis

Average grain size of the experimental products ranged from 2 to 50 μm (estimated optically). Ilmenite grains generally occurred as large clusters of small, euhedral platelets up to 50 μm in diameter. When present as isolated, discrete grains, ilmenite was represented by thin, hexagonal crystal forms approximately 20–30 μm in size.

Garnet varied in size from approximately 2 to 40 μm, forming characteristically small patchy distributions interstitial to the larger ilmenite-rich aggregates. In higher temperature experiments ($T \approx 1000$ °C), large subhedral garnet crystals (≈35–45 μm) and smaller (≈20–25 μm) well-developed dodecahedra were occasionally present.

The products were mounted in epoxy resin, then polished flat for microprobe analysis. A statistically adequate population (≈10–15) of garnet and ilmenite grains from each experimental charge was analyzed using an automated ARL-SEMQ2 electron microprobe equipped with wavelength dispersive TAP, LIF, and PET crystal spectrometers. Synthetic ilmenite and pyrophanite plus natural grossular and diopside were used as standards. An accelerating potential of 15 kV, a sample current of 20 nA, and a beam diameter of 3–5 μm were standard operating conditions. Counting times were sufficient to collect ≥200 000 counts for all major elements in standards and unknowns. Spectrometer data were reduced using the correction procedures of Colby (1968).

Ilmenite experimental products were homogeneous on the scale of the electron microbeam analysis (3–5 μm) and did not exhibit discernible changes in grain size during the experiments. This suggests that Fe-Mn exchange took place by diffusion rather than solution-reprecipitation of ilmenite. Garnet occasionally displayed slight compositional inhomogeneity in $X^{\text{gar}}_{\text{Ca}}$, particularly in experiments conducted at low temperatures ($T \approx 650$–800 °C). Consequently, the composition of the garnet was determined from microprobe analyses made as close to contacts with ilmenite grains as possible without introducing edge effects (Elphick et al., 1985; Lee and Ganguly, 1988). SEM and backscattered electron images of the experimental products allowed accurate location and analysis of grain margins.

Analyses totaled 100 ± 2%. Structural formulae based on three O atoms totaled 2.00 ± 0.02 cations for ilmenites, whereas for garnets, structural formulae based on 12 O atoms yielded cation totals of 8.00 ± 0.03. Thus we were unable to detect any Fe^{3+} on the basis of stoichiometry (admittedly an inaccurate method, cf. Wood and Virgo, 1989) in either ilmenite or garnet. At the f_{O_2} and temperature of synthesis that we employed, the $FeTiO_3$ composition is expected to yield an ilmenite-hematite solid solution with $X_{Fe_2O_3} \approx 0.02$–0.03 and a correspondingly small amount of excess TiO_2 (e.g., Brothers et al., 1987). Addition of Mn to the system will lower $X_{Fe_2O_3}$, but small amounts are still expected for the $X_{FeTiO_3} \approx 0.75$ and 0.50 compositions. Although the f_{O_2} was not monitored during the actual experiments, it is believed to be significantly lower than QFM, hence the negligible Fe^{3+}. In spite of this, the results are in perfect agreement with the data in Pownceby et al. (1987), which were buffered at QFM (see discussion below).

For each analysis, the mole fraction of each component was calculated, and the mean and standard deviation of this ratio was obtained for both phases in each experiment, using at least ten successful analyses. Mole fractions of $X^{\text{ilm}}_{\text{Fe}}$ in the ilmenite were calculated using the method for binary solid solutions outlined in Seifert and O'Neill (1987). For the garnet analyses, the molar ratio N_{Mn}/N_{Fe} was calculated and the mean and standard de-

TABLE 1. Summary of experimental parameters and results of experiments on garnet-ilmenite partitioning

Garnet comp.	Ilmenite comp.	Experiment no.	T (°C)	ln K_d	X^{ilm}_{Mn}*	X^{gar}_{Mn}	X^{gar}_{Ca}	Time (h)
Alm$_{22.5}$Sp$_{67.5}$Gr$_{10}$	Ilm$_{25}$Pyr$_{75}$	8803-1	800	1.097	0.728(3)	0.832(2)	0.064(6)	47.5
	Ilm$_{50}$Pyr$_{50}$	8803-2	800	1.183	0.496(2)	0.710(4)	0.070(6)	47.5
	Ilm$_{25}$Pyr$_{75}$	8715-1	900	0.961	0.735(1)	0.830(2)	0.056(5)	46
	Ilm$_{50}$Pyr$_{50}$	8715-2	900	1.014	0.519(2)	0.697(3)	0.068(6)	46
Alm$_{20}$Sp$_{60}$Gr$_{20}$	Ilm$_{25}$Pyr$_{75}$	8811-1	700	1.247	0.726(2)	0.796(4)	0.117(4)	115.66
	Ilm$_{50}$Pyr$_{50}$	8811-2	700	1.361	0.485(1)	0.688(5)	0.125(7)	115.66
	Ilm$_{25}$Pyr$_{75}$	8722-1	800	1.105	0.732(4)	0.753(3)	0.156(6)	70.25
	Ilm$_{50}$Pyr$_{50}$	8722-2	800	1.187	0.495(3)	0.660(3)	0.135(3)	70.25
	Ilm$_{25}$Pyr$_{75}$	8716-1	900	0.954	0.736(4)	0.754(2)	0.142(4)	46
	Ilm$_{50}$Pyr$_{50}$	8716-2	900	1.037	0.511(3)	0.635(5)	0.149(6)	46
	Ilm$_{25}$Pyr$_{75}$	8813-1	1000	0.813	0.746(2)	0.733(3)	0.156(4)	29.5
	Ilm$_{50}$Pyr$_{50}$	8813-2	1000	0.886	0.501(3)	0.603(2)	0.149(7)	29.5
Alm$_{17.5}$Sp$_{52.5}$Gr$_{30}$	Ilm$_{25}$Pyr$_{75}$	8812-1	700	1.243	0.723(2)	0.708(2)	0.213(3)	129.5
	Ilm$_{50}$Pyr$_{50}$	8812-2	700	1.365	0.487(1)	0.645(3)	0.181(5)	129.5
	Ilm$_{25}$Pyr$_{75}$	8721-1	800	1.088	0.736(3)	0.670(1)	0.219(6)	70
	Ilm$_{50}$Pyr$_{50}$	8721-2	800	1.175	0.497(3)	0.599(2)	0.214(3)	70
	Ilm$_{25}$Pyr$_{75}$	8717-1	900	0.940	0.742(3)	0.715(5)	0.187(3)	35
	Ilm$_{50}$Pyr$_{50}$	8717-2	900	1.033	0.497(2)	0.599(3)	0.185(5)	35
Alm$_{15}$Sp$_{45}$Gr$_{40}$	Ilm$_{25}$Pyr$_{75}$	8806-1	700	1.226	0.715(2)	0.572(3)	0.361(3)	88.5
	Ilm$_{50}$Pyr$_{50}$	8806-2	700	1.356	0.492(3)	0.493(2)	0.376(5)	88.5
	Ilm$_{25}$Pyr$_{75}$	8720-1	800	1.085	0.720(2)	0.609(2)	0.311(6)	48
	Ilm$_{50}$Pyr$_{50}$	8720-2	800	1.173	0.500(3)	0.531(1)	0.305(5)	48
	Ilm$_{50}$Pyr$_{50}$	8818-1	800	1.206	0.441(1)	0.499(2)	0.312(6)	73.75
	Ilm$_{75}$Pyr$_{25}$	8818-2	800	1.247	0.347(3)	0.443(4)	0.319(2)	73.75
	Ilm$_{25}$Pyr$_{75}$	8718-1	900	0.957	0.724(2)	0.616(5)	0.293(9)	34
	Ilm$_{50}$Pyr$_{50}$	8718-2	900	1.021	0.505(2)	0.505(2)	0.316(3)	34
	Ilm$_{25}$Pyr$_{75}$	8719-1	900	0.927	0.788(2)	0.573(2)	0.366(4)	37.5
	Ilm$_{50}$Pyr$_{50}$	8719-2	900	1.025	0.507(3)	0.486(3)	0.344(9)	37.5
	Ilm$_{25}$Pyr$_{75}$	8801-1	950	0.883	0.737(4)	0.549(2)	0.370(3)	30
	Ilm$_{50}$Pyr$_{50}$	8801-2	950	0.950	0.512(2)	0.466(1)	0.362(5)	30
	Ilm$_{25}$Pyr$_{75}$	8814-1	1000	0.807	0.736(1)	0.544(4)	0.369(5)	16
	Ilm$_{50}$Pyr$_{50}$	8814-2	1000	0.904	0.508(1)	0.461(3)	0.358(3)	16
	Ilm$_{75}$Pyr$_{25}$	8816-2	1000	0.935	0.355(2)	0.384(2)	0.343(6)	11.75

Note: Data for experiments using garnet Fe/Mn ≈ 0.33. $P = 10$ kbar.

* Numbers in parentheses represent the standard deviation cited for the value to their immediate left.

viation of this ratio determined. Since $X_{Fe} + X_{Mn} + X_{Ca} = 1$, X^{gar}_{Fe} may be calculated from

$$X^{gar}_{Fe} = (1 - X^{gar}_{Ca})/(1 + R) \tag{6}$$

where R is defined as the ratio N_{Mn}/N_{Fe}. The expected standard deviation of X^{gar}_{Fe} can be obtained from Equation 7 assuming the equation for the propagation of small errors (e.g., Bevington, 1969):

$$(\sigma_{X^{gar}_{Fe}})^2 = (\sigma_{X^{gar}_{Ca}})^2(\delta_{X^{gar}_{Fe}}\delta_{X^{gar}_{Ca}})^2 + (\sigma_R)^2(\delta_{X^{gar}_{Fe}}/\delta_R)^2. \tag{7}$$

Results of this anlaysis and experimental conditions are summarized in Tables 1 and 2 for initial garnet Fe/Mn ratios of 1:3 and 3:1, respectively.

Attainment of equilibrium

Results from the partitioning experiments (Tables 1 and 2) indicate a remarkable degree of internal consistency. The difference between individual calculated ln K_d values for each temperature and X^{ilm}_{Mn} studied varies only between ±0.02 log units, suggesting a close approach to equilibrium partitioning. This result is not unexpected because the data in Pownceby et al. (1987) indicate equilibrium is established fairly rapidly in the garnet-ilmenite system. The Δ ln K_d measured between experiments using different ilmenite-pyrophanite starting compositions also suggests that equilibrium was quickly established.

It should be noted that the experimental strategy adopted in this study is different from the one we used earlier in Pownceby et al. (1987). There, we reversed the Fe-Mn distribution reaction between ilmenite and garnet using the method pioneered by Ferry and Spear (1978), which is applicable for cation partitioning between two phases when the interdiffusion of the partitioning species in one of the phases is rapid on the experimental time scale (e.g., ilmenite in our experiments). The method works by using a large excess of the kinetically sluggish phase (garnet) so that the composition of this phase needs to change only very slightly. Equilibrium is thereby reached through larger changes in the composition of the rapidly diffusing phase. By doing two experiments, starting with ilmenite compositions on either side of the estimated equilibrium composition, equilibrium was demonstrated by the convergence of the ilmenite compositions toward a final value. However, the convergence was not complete, resulting in distribution coefficient "brackets" (superficially analogous to the P,T brackets obtained in reversals of univariant phase equilibria) within which the equilibrium K_d lies. This indeterminacy means there is some loss of precision in this type of experiment. Our aim in this study was to increase precision; accordingly, we wanted to grow the kinetically sluggish phase (garnet) in an environment buffered in Fe-Mn chemical potential by a large excess of the rapidly diffusing phase (ilmenite), which had been crystallized previously. We also provide abundant garnet nuclei, which helps to keep the grain size of the garnet small and similar to that of the ilmenite.

TABLE 2. Summary of experimental parameters and results of experiments on garnet-ilmenite partitioning

Garnet comp.	Ilmenite comp.	Experiment no.	T (°C)	ln K_d	X_{Mn}^{ilm}*	X_{Mn}^{gar}	X_{Ca}^{gar}	Time (h)
$Alm_{67.5}Sp_{22.5}Gr_{10}$	$FeTiO_3$	8802-1	800	1.374	0.039(2)	0.128(2)	0.066(2)	57.1
	$Ilm_{75}Pyr_{25}$	8802-2	800	1.281	0.210(2)	0.459(2)	0.061(4)	57.1
	$FeTiO_3$	8714-1	900	1.190	0.044(1)	0.122(3)	0.068(3)	47.1
	$Ilm_{75}Pyr_{25}$	8714-2	900	1.132	0.220(2)	0.428(2)	0.083(7)	47.1
$Alm_{60}Sp_{20}Gr_{20}$	$FeTiO_3$	8708-1	700	1.568	0.027(1)	0.097(1)	0.175(4)	48.5
	$Ilm_{75}Pyr_{25}$	8708-2	700	1.476	0.230(2)	0.480(2)	0.153(5)	48.5
	$FeTiO_3$	8808-1	700	1.573	0.029(1)	0.102(2)	0.182(6)	95.5
	$Ilm_{75}Pyr_{25}$	8808-2	700	1.472	0.180(1)	0.415(5)	0.149(4)	95.5
	$FeTiO_3$	8704-1	800	1.352	0.022(3)	0.067(2)	0.169(3)	50
	$FeTiO_3$	8704-2	800	1.322	0.029(2)	0.083(2)	0.172(3)	50
	$FeTiO_3$	8705-1	800	1.334	0.027(2)	0.082(1)	0.145(4)	36
	$Ilm_{75}Pyr_{25}$	8705-2	800	1.273	0.193(5)	0.393(6)	0.147(2)	36
	$Ilm_{50}Pyr_{50}$	8817-1	800	1.161	0.433(2)	0.598(3)	0.157(3)	93.2
	$FeTiO_3$	8707-1	900	1.205	0.030(2)	0.080(2)	0.155(3)	47
	$Ilm_{75}Pyr_{25}$	8707-2	900	1.125	0.209(4)	0.367(2)	0.160(9)	47
	$FeTiO_3$	8810-1	1000	1.037	0.045(1)	0.101(2)	0.139(7)	34
	$Ilm_{75}Pyr_{25}$	8810-2	1000	0.999	0.233(3)	0.394(3)	0.128(5)	34
	$Ilm_{50}Pyr_{50}$	8815-2	1000	0.903	0.436(2)	0.580(3)	0.116(6)	16
$Alm_{52.5}Sp_{17.5}Gr_{30}$	$FeTiO_3$	8712-1	650	1.676	0.046(2)	0.154(3)	0.248(5)	93.8
	$Ilm_{75}Pyr_{25}$	8712-2	650	1.601	0.137(3)	0.336(4)	0.237(4)	93.8
	$FeTiO_3$	8709-1	700	1.533	0.029(1)	0.087(2)	0.229(4)	73
	$Ilm_{75}Pyr_{25}$	8709-2	700	1.459	0.202(3)	0.409(4)	0.217(5)	73
	$FeTiO_3$	8809-1	700	1.523	0.016(1)	0.054(1)	0.224(3)	100
	$Ilm_{75}Pyr_{25}$	8809-2	700	1.441	0.199(2)	0.403(2)	0.212(6)	100
	$FeTiO_3$	8710-1	800	1.317	0.029(1)	0.075(1)	0.248(7)	45.75
	$Ilm_{75}Pyr_{25}$	8710-2	800	1.241	0.227(3)	0.378(2)	0.253(5)	45.75
	$Ilm_{50}Pyr_{50}$	8817-2	800	1.132	0.466(2)	0.535(4)	0.267(4)	93.2
	$FeTiO_3$	8711-1	900	1.197	0.035(1)	0.082(2)	0.237(4)	47
	$Ilm_{75}Pyr_{25}$	8711-2	900	1.105	0.243(2)	0.379(2)	0.229(5)	47
	$FeTiO_3$	8807-1	900	1.184	0.022(1)	0.051(1)	0.257(7)	24.5
	$Ilm_{75}Pyr_{25}$	8807-2	900	1.116	0.239(2)	0.370(2)	0.243(9)	24.5
	$Ilm_{50}Pyr_{50}$	8816-1	1000	0.890	0.458(2)	0.439(3)	0.348(5)	11.75
$Alm_{45}Sp_{15}Gr_{40}$	$FeTiO_3$	8805-1	800	1.296	0.037(2)	0.079(2)	0.354(7)	95.5
	$Ilm_{75}Pyr_{25}$	8805-2	800	1.229	0.212(3)	0.306(4)	0.362(5)	95.5
	$FeTiO_3$	8706-1	900	1.186	0.027(2)	0.054(3)	0.361(6)	48
	$Ilm_{75}Pyr_{25}$	8706-2	900	1.121	0.179(4)	0.261(3)	0.351(5)	48
	$FeTiO_3$	8713-1	1000	1.049	0.036(1)	0.062(5)	0.349(9)	44.3
	$Ilm_{75}Pyr_{25}$	8713-2	1000	0.985	0.239(2)	0.293(3)	0.359(4)	44.3
	$FeTiO_3$	8804-1	1000	1.024	0.041(1)	0.070(2)	0.346(5)	27
	$Ilm_{75}Pyr_{25}$	8804-2	1000	0.991	0.247(2)	0.310(3)	0.330(7)	27
	$Ilm_{50}Pyr_{50}$	8815-1	1000	0.901	0.478(3)	0.457(4)	0.340(7)	16

Note: Data for experiments using garnet Fe/Mn ≈ 3.0. $P = 10$ kbar.

* Numbers in parentheses represent the standard deviation cited for the value to their immediate left.

That this method does produce extremely precise results may be seen from the data in Tables 1 and 2 and Figure 1. We argue for attainment of equilibrium in these experiments since (1) our results show a remarkable degree of internal consistency and (2) we observe no zoning in the ilmenite for the time-temperature conditions at which we (Pownceby et al., 1987) previously established that the ilmenite compositions would change by substantial amounts if they were not in equilibrium with the garnet.

An isothermal distribution between coexisting garnet and ilmenite pairs is shown in Figure 1 for the experiments at 800 °C. The circles represent the compositions of the initial garnet-ilmenite oxide mixes; the squares represent the analyzed distribution of Mn and Fe at the completion of the experiment. Corresponding starting and product compositions are connected by lines with arrows that indicate the direction of approach to equilibrium. For the sake of clarity, only selected data are shown. Additionally, the results from Pownceby et al. (1987), derived from tightly reversed experiments at 800 °C in the binary Fe-Mn garnet-ilmenite system, are provided for comparison. Although the experimental method used in this study was different from that in Pownceby et al. (1987), it may be seen that the compositions of the coexisting garnet and ilmenite extrapolate to the Ca-free values.

RESULTS

Partitoning data are represented graphically in Figure 2 where ln K_d is plotted against X_{Ca}^{gar}. In each graph, the slope of the equilibrium K_d vs. X_{Ca}^{gar} is constrained by the intercept with the measured K_d at $X_{Ca}^{gar} = 0.0$. According to the previous experimental results in Ono (1980) and Pownceby et al. (1987), an increase in the pyrophanite component of the ilmenite solid solution will displace K_d to lower values. Because partitioning data were obtained for more than one ilmenite-pyrophanite composition (Tables 1 and 2), two or more lines of best fit are provided on each graph at each temperature and pressure surveyed.

The experimental partitioning data were subjected to a nonlinear least-squares regression analysis (e.g., Kawasaki and Matsui, 1978, 1983; Seifert and O'Neill, 1987),

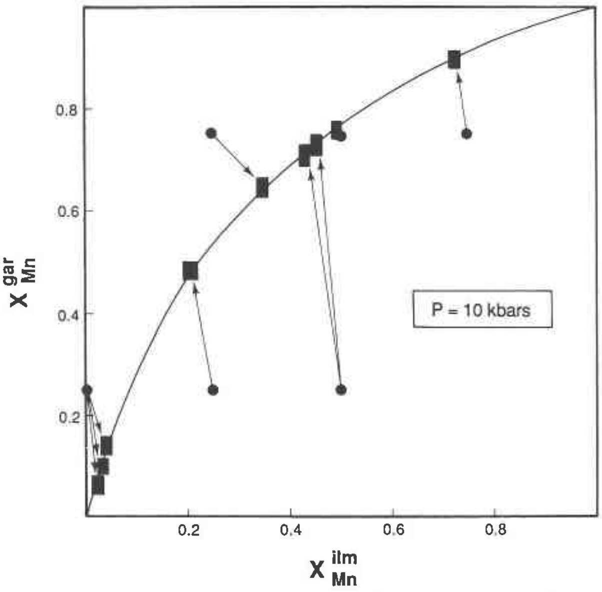

Fig. 1. Experimental data for the distribution of Mn^{2+} between coexisting garnet and ilmenite at 10 kbar. Circles represent the compositions of the initial garnet-ilmenite oxide mixtures; the boxes represent the analyzed distribution of Mn and Fe^{2+} at the conclusion of the experiments (shown only for 800 °C data). The solid line distribution isotherm is from the 800 °C, 5 kbar reversal data in the binary Fe-Mn garnet-ilmenite system determined by Pownceby et al. (1987). The size of the boxes gives the mean analytical error.

with data weighted according to the standard deviation from the microprobe analyses. We used the value of $W^{ilm}_{FeMn} = 2.2 \pm 0.3$ kJ/mol from O'Neill et al. (1989). The results are presented in Table 3. The last column of Table 3 also shows the reduced χ^2 [i.e., $\chi^2/(N - n - 1)$] where N = number of data points (74 in total), and n = number of parameters determined in the regression. The reduced χ^2 is expected to be approximately unity (e.g., Bevington, 1969, p. 187–189) if the model is an adequate fit to the experimental data.

The results show that the regular symmetric solution model provides a good description of the experimental data, with the difference in the interaction parameters $(W^{gar}_{CaFe} - W^{gar}_{CaMn}) = 972 \pm 205$ J/mol of cation. Furthermore, the results from the regression analysis provide estimates of $\Delta H^0_{1,T}$ and ΔS^0_T that are in good agreement with results derived in Pownceby et al. (1987) from experiments in the binary Fe-Mn garnet-ilmenite system. Estimates for $\Delta H^0_{1,T}$ and ΔS^0_T are -14.92 ± 0.99 kJ/mol (-17.11 ± 4.22) and -4.38 ± 0.18 J/mol·K (-6.03 ± 4.10), respectively; data from Pownceby et al. (1987) are given in parentheses for comparison. The regression also gives $W^{gar}_{FeMn} = 620 \pm 47$ J/mol; since this value is closely correlated with that assumed for W^{ilm}_{FeMn}, we include the uncertainty in the latter to suggest that the final uncertainty in W^{gar}_{FeMn} is ± 200 J/mol.

We have also tested a model in which the Ca-Fe join

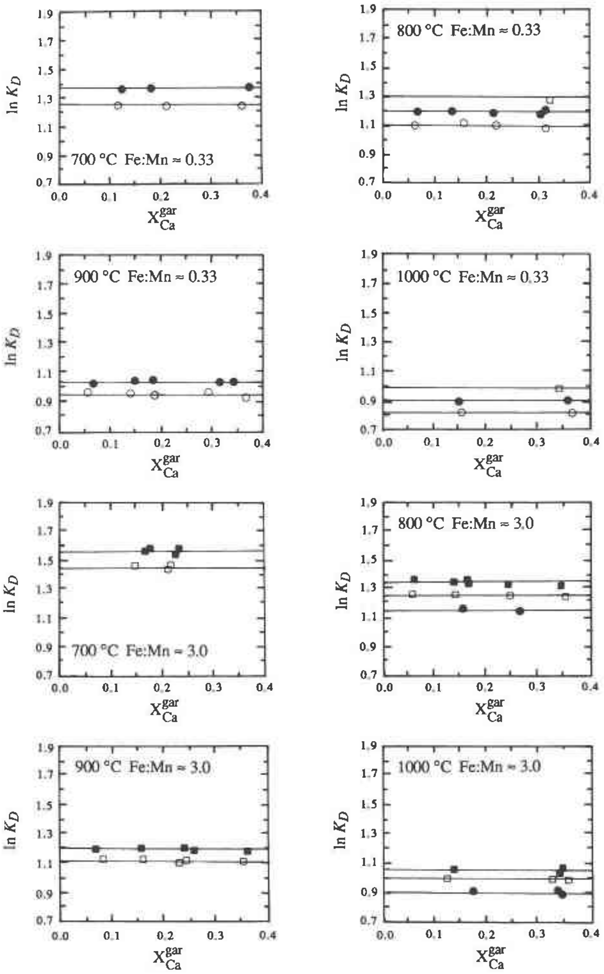

Fig. 2. Experimentally determined variation in ln K_d with X^{gar}_{Ca} at 700–1000 °C, 10 kbar. Error bars correspond to one standard deviation in K_d, obtained from the microprobe analyses. Isochemical ilmenite data are connected by solid lines. Symbols defined as follows: filled squares are $X^{ilm}_{Mn} = 0.00$; open squares are $X^{ilm}_{Mn} = 0.25$; filled circles are $X^{ilm}_{Mn} = 0.50$; and open circles are $X^{ilm}_{Mn} = 0.75$.

is a subregular solution, but the Ca-Mn join is regular. This gives the expression (from Andersen and Lindsley, 1981)

$$\begin{aligned} RT \ln K_d = {} & W^{gar}_{FeMn}(X^{gar}_{Mn} - X^{gar}_{Fe}) + W^{gar}_{MnCa} \cdot X^{gar}_{Ca} \\ & - W^{gar}_{FeCa}(X^2_{Ca} + \tfrac{1}{2}X_{Mn}X_{Ca} - \tfrac{1}{2}X_{Fe}X_{Ca})^{gar} \\ & - W^{gar}_{CaFe}(\tfrac{3}{2}X_{Fe}X_{Ca} + \tfrac{1}{2}X_{Mn}X_{Ca})^{gar} \\ & - W^{ilm}_{FeMn}(2X^{ilm}_{Mn} - 1) - \Delta G^0_{P,T}. \end{aligned} \tag{8}$$

We found that compositional range covered by our experiments (basically just two Fe-Mn ratios) was not sufficient for a regression based on this equation. Accordingly, we made the further approximation that $W^{gar}_{CaMn} = 0$ (Koziol, 1990). The parameters from this regression are also given in Table 3; we find negligible improvement in the fit to the data and $W^{gar}_{CaFe} \approx W^{gar}_{CaMn}$ within the limits

TABLE 3. Summary of regression parameters

W^{gar}_{FeMn} *	$(W^{gar}_{CaFe} - W^{gar}_{CaMn})$	W^{gar}_{FeCa}	W^{gar}_{CaFe}	χ^2	Model
620 ± 200	972 ± 205	—	—	1.19	Regular
539 ± 218	—	2468 ± 821	1696 ± 534	1.18	Subregular
169 ± 47	—	2590**	−1090**	1.41	Subregular

* All data derived assuming a value for W^{ilm}_{FeMn} of 2200 kJ/mol (from O'Neill et al., 1989).
** Data from Koziol (1990).

of uncertainty. Note that our data do not support a subregular model with negative departures from ideal mixing at low X^{gar}_{Ca}; see discussion below.

DISCUSSION

The experimental data presented above constrain the effect of Ca in garnet on Fe-Mn ln K_d values in the Ca-Mn-Fe garnet-ilmenite system. Results indicate that at temperatures between 650 and 1000 °C, the influence of X^{gar}_{Ca} upon Fe-Mn partitioning is small and may be described accurately, using the regular solution model, as the difference in the interaction parameters ($W^{gar}_{CaFe} - W^{gar}_{CaMn}$).

Our study can determine only the simultaneous difference in the effect of X^{gar}_{Ca} on γFe and γMn; thus it is different from that reported recently by Koziol (1990) on the effects of Fe and Mn on γCa in the individual calcium-iron and calcium-manganese garnet binaries (using displacement of the grossular-anorthite-Al_2SiO_5-quartz univariant equilibrium). When taken together, however, the studies should provide tighter constraints on the mixing models for calcium-iron-manganese than could either considered in isolation: our model should be consistent with the data of Koziol and vice versa.

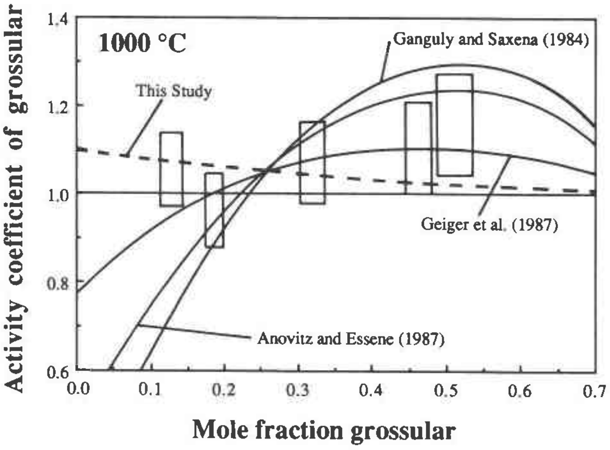

Fig. 3. A plot of the activity coefficient of grossular (γCa) determined in this study at 1000 °C against composition for a portion of the grossular-almandine binary join, with comparison to previous studies. The solid curves are the asymmetric Margules models proposed by each study as noted. Boxes represent the data from Koziol (1990). The results of this study (dashed line) are represented by a symmetric Margules model parameter for grossular-almandine equal to 972 ± 205 kJ/mol. Assuming an error in γCa of 0.02–0.05 (1σ), all of the data from Koziol (1990) can be fitted by the symmetric one-parameter model.

Koziol's experiments and those of Wood (1988) using the same equilibrium show that the Ca-Mn binary is ideal ($W^{gar}_{CaMn} = 0$) within tight constraints; we will accept this ideality as axiomatic. We then obtain $W^{gar}_{CaFe} = 972$ J/mol. This result also describes the Ca-Fe data of Koziol adequately, as shown in Figure 3. However, Koziol has given best fit values for her experiments in the form of a subregular model with $W^{gar}_{CaFe} = -1.09$ and $W^{gar}_{FeCa} = 2.59$ kJ/mol. We have used these values in a regression of our data, again using $W^{ilm}_{FeMn} = 2200$ and $W^{gar}_{CaMn} = 0$. The results are given in Table 3; we find that the reduced χ^2 increases to 1.41, whereas the calculated W^{gar}_{FeMn} decreases to 169 ± 47 J/mol, which is outside the limits established from garnet-ilmenite equilibria in the Ca-free system. Thus our data argue for the simpler almandine-grossular model, although the difference is slight. Of course, this conclusion would not be valid if, for example, the Ca-Mn join is not quite ideal but shows subtle S-shaped deviations from ideality that mirror the form of those proposed for Ca-Fe.

Finally, our data (like those of Koziol, 1990), exclude the models of Ganguly and Saxena (1984) and of Anovitz and Essene (1987). Both our model and Koziol's are consistent with the calorimetrically determined enthalpy of mixing measured by Geiger et al. (1987).

Implications for garnet-ilmenite exchange geothermometry

Since small to moderate amounts of a grossular component ($X^{gar}_{Ca} \leq 0.35$) will have only a small effect on the calculated Fe-Mn partition coefficient between coexisting garnet and ilmenite, the original thermometric expression of Pownceby et al. (1987) remains useful. However, the additional results presented here permit a slightly improved reformulation of the garnet-ilmenite geothermometer:

$$T\,(^\circ\mathrm{C}) = \left[\frac{14918 - 2200(2X^{ilm}_{Mn} - 1) + 620(X^{gar}_{Mn} - X^{gar}_{Fe}) - 972X^{gar}_{Ca}}{R\ln K_d + 4.38}\right] - 273.15. \qquad (9)$$

Temperatures calculated using Equation 9 for the Ca-bearing experimental data are compared with the temperatures of the experiments in Figure 4. The agreement between calculated temperatures and those of the experiments is very good, with most calculated temperatures plotting within ±40 °C of the experimental temperature.

Equation 9 also provides a precise geothermometer for natural Fe^{3+}, Mg-poor systems in which the garnet-ilmenite assemblage is inferred to have coexisted in equilibrium. For natural garnet-ilmenite pairs from several well-documented regional metamorphic terranes (see Pownceby et al., 1987 for the complete dataset), a comparison of temperatures predicted using the above expression and those calculated using the equivalent expression from Pownceby et al. (1987) show minor (± 10–20 °C) temperature differences. These terranes range from upper-greenschist to upper-amphibolite facies and are particularly suitable for application of garnet-ilmenite thermometry since the garnet and ilmenite are frequently rich in both Fe and Mn components, and vary little from their respective binary solid solutions. Although Equation 9 works well for these Mn-rich systems, in higher temperature terranes (e.g., granulite, ultramafic) or in samples with low $X_{\mathrm{Mn}}^{\mathrm{bulk}}$, it becomes important to take special care in obtaining accurate values for the ratio Mn/(Mn + Fe) in ilmenite. The problem of obtaining adequate analytical precision for trace element geothermometers or geobarometers has been discussed before (e.g., Mn-Mg exchange between garnet and clinopyroxene, Carswell, 1974 and Delaney et al., 1979; Ca exchange between olivine and clinopyroxene, Köhler and Brey, 1990), and a number of EMP techniques such as long counting times or alternative analytical methods such as the ion microprobe have been recommended. Low Mn contents should not prohibit use of the garnet-ilmenite geothermometer, provided that reasonably accurate trace element analyses of Mn can be obtained.

A more serious problem in using garnet-ilmenite geothermometry is rapid rates for Fe-Mn diffusion in ilmenites. We note that in our experiments (both those reported here and especially in Pownceby et al., 1987), large changes in ilmenite composition are readily observable at 600 °C in a matter of days. It is thus probable that in slowly cooled metamorphic rocks, matrix ilmenite will reequilibrate with other modally more abundant Mn-containing ferromagnesian phases such as biotite, which also allow rapid cation diffusion. This may lead to a substantial compositional change in the ilmenite while leaving the refractory garnet unaffected, and calculated temperatures will be meaningless. (In general, they will be too high, as $K_{\mathrm{DFe\text{-}Mn}}^{\mathrm{ilm\text{-}biot}}$ may be expected to increase with decreasing T, causing enrichment of Mn in the ilmenite.) Our experience is that, in many such cases, ilmenite included in garnet is effectively shielded from reequilibration by the comparatively slow Fe-Mn diffusion in garnet (Lasaga, 1983) and records temperatures either at the time of garnet growth or near the peak of prograde metamorphism. This situation contrasts with that usually obtained for garnet-biotite Fe-Mg exchange geothermometry. The large modal abundance of biotite in most metapelites means that Fe/(Mg + Fe) in biotite is close to Fe/(Mg + Fe) in the bulk rock, and consequently the composition of the biotite will not change much during closed-system cooling. Thus peak metamorphic temperatures are preserved by matrix biotite. Garnet-ilmenite geothermometry thus yields information of a type different from that obtained using garnet-biotite exchange equilibria.

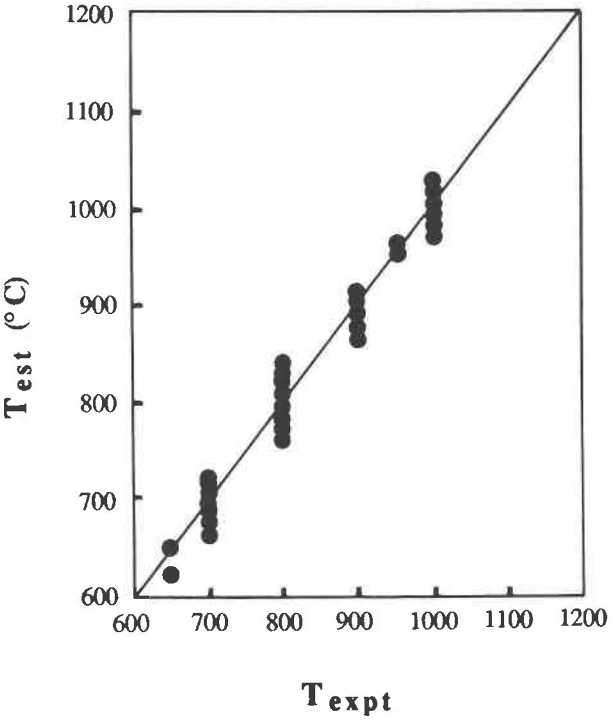

Fig. 4. Temperatures calculated using Equation 9 (T_{est}), plotted against nominal experimental temperatures (T_{expt}). Diagonal line represents perfect agreement.

ACKNOWLEDGMENTS

This work was part of the Ph.D. thesis research of Mark I. Pownceby (Monash University, September 1989). The experiments were performed in the laboratory of I.A. Nicholls with financial assistance provided by a Commonwealth Postgraduate Scholarship (M.I.P.) and a Monash University Special Research Grant (V.J.W.). Charles Geiger is thanked for a constructive review, and Jeff Taylor (as always) reviewed an earlier version of this manuscript. Critical reviews by Victor Kress and Jeffrey Grambling are appreciated; we hope the paper is much improved as a consequence of their help.

REFERENCES CITED

Andersen, D.J., and Lindsley, D.H. (1981) A valid Margules formulation for an asymmetric ternary solution: Revision of the olivine-ilmenite thermometer, with applications. Geochimica et Cosmochimica Acta, 45, 847–853.

Anovitz, L.M., and Essene, E.J. (1987) Compatibility of geobarometers in the system $CaO\text{-}FeO\text{-}Al_2O_3\text{-}SiO_2\text{-}TiO_2$ (CFAST): Implications for garnet mixing models. Journal of Geology, 95, 633–645.

Bevington, P.R.C. (1969) Data reduction and error analysis for the physical sciences. McGraw Hill, New York.

Bohlen, S.R., Wall, V.J., and Boettcher, A.L. (1983) Experimental investigations and geological applications of equilibria in the system $FeO\text{-}TiO_2\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$. American Mineralogist, 68, 1049–1058.

Boyd, F.R., and England, J.L. (1960) Apparatus for phase-equilibria measurements at pressure up to 50 kb and temperatures up to 1750 °C. Journal of Geophysical Research, 65, 741–748.

Brothers, S.C., Lindsley, D.H., and Hadjigeorgiou, C. (1987) The hematite-ilmenite ± rutile oxybarometer: Experimental calibration. Eos, 68, 461.

Carswell, D.A. (1974) Comparative equilibration temperatures and pressures of garnet lherzolites in Norwegian gneisses and in kimberlite. Lithos, 7, 113–121.

Colby, J.W. (1968) Quantitative microprobe analysis of thin insulating films. Advanced X-ray Analysis, 11, 287–305.

Delaney, J.S., Smith, J.V., Dawson, J.B., and Nixon, P.H. (1979) Manganese thermometer for mantle peridotites. Contributions to Mineralogy and Petrology, 71, 157–169.

Docka, J.A. (1985) Ilmenite-garnet Mn Fe exchange: Calibration from naturally occurring pairs. Geological Society of America Abstracts with Programs, 16, 491.

Ellis, D.J., and Green, D.H. (1979) An experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg exchange equilibria. Contributions to Mineralogy and Petrology, 71, 13–22.

Elphick, S.C., Ganguly, J., and Loomis, T.P. (1985) Experimental determination of cation diffusivities in aluminosilicate garnets: I. Experimental methods and interdiffusion data. Contributions to Mineralogy and Petrology, 90, 36–44.

Ferry, J.M., and Spear, F.S. (1978) Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. Contributions to Mineralogy and Petrology, 66, 113–117.

Ganguly, J., and Saxena, S. (1984) Mixing properties of aluminosilicate garnets: Constraints from natural and experimental data, and applications to geothermo-barometry. American Mineralogist, 69, 88–97.

Geiger, C.A., Newton, R.C., and Kleppa, O.J. (1987) Enthalpy of mixing of synthetic almandine-grossular and almandine-pyrope garnets from high-temperature solution calorimetry. Geochimica et Cosmochimica Acta, 51, 1755–1763.

Harley, S.L. (1984) An experimental study of the partitioning of Fe and Mg between garnet and orthopyroxene. Contributions to Mineralogy and Petrology, 86, 359–373.

Helgeson, H.C., Delaney, J.M., Nesbitt, H.W., and Bird, H.W. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A, 1–228.

Kawasaki, T., and Matsui, Y. (1978) Non-linear least squares techniques in element partition equilibria. Geochemical Journal, 12, 173–181.

——— (1983) Thermodynamic analysis of equilibria involving olivine, orthopyroxene and garnet. Geochimica et Cosmochimica Acta, 47, 1661–1679.

Köhler, T.P., and Brey, G.P. (1990) Calcium exchange between olivine and clinopyroxene calibrated as a geothermometer for natural peridotites from 2 to 60 kb with applications. Geochimica et Cosmochimica Acta, 54, 2375–2388.

Koziol, A.M. (1990) Activity-composition relationships of binary Ca-Fe and Ca-Mn garnets determined by reversed, displaced equilibrium experiments. American Mineralogist, 75, 319–327.

Koziol, A.M., and Newton, R.C. (1987) Experimental determination of spessartine-grossular solid solution relations. Eos, 68, 460.

Kress, V.C., Bohlen, S.R., and Lindsley, D.H. (1985) Experimental calibration of Fe-Mn exchange between coexisting garnet and ilmenite. Eos, 66, 388.

Lasaga, A.C. (1983) Geospeedometry: An extension of geothermometry. In S.K. Saxena, Ed., Kinetics and equilibrium in mineral reactions, p. 81–115. Springer, New York.

Lee, H.Y., and Ganguly, J. (1988) Equilibrium compositions of coexisting garnet and orthopyroxene: Experimental determinations in the system $FeO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$, and applications. Journal of Petrology, 29, 93–113.

O'Neill, H.St.C., and Wood, B.J. (1979) An experimental study of Fe-Mg partitioning between garnet and olivine and its calibration as a geothermometer. Contributions to Mineralogy and Petrology, 70, 59–70.

O'Neill, H.St.C., Pownceby, M.I., and Wall, V.J. (1989) Activity-composition relations in $FeTiO_3\text{-}MnTiO_3$ ilmenite solid solutions from EMF measurements at 1050–1300 K. Contributions to Mineralogy and Petrology, 103, 216–222.

Ono, A. (1980) Partitioning of Fe and Mn between garnet and ilmenite: An experimental study. Journal of the Japanese Association for Mineralogy, Petrology, and Economic Geology, 75, 160–163.

Pownceby, M.I., Wall, V.J., and O'Neill, H.St.C. (1987) Fe-Mn partitioning between garnet and ilmenite: Experimental calilbration and applications. Contributions to Mineralogy and Petrology, 97, 116–126.

Seifert, S., and O'Neill, H.St.C. (1987) Experimental determination of activity-composition relations in $Ni_2SiO_4\text{-}Mg_2SiO_4$ and $Co_2SiO_4\text{-}Mg_2SiO_4$ olivine solid solutions at 1200 K and 0.1 MPa and 1573 K and 0.5 GPa. Geochimica et Cosmochimica Acta, 51, 97–104.

Wall, V.J., Clemens, J.D., Essene, E.J., Treiman, A.F., and Westrum, E.F., Jr. (1980) Thermodynamic properties and phase equilibria for ilmenite. Eos, 46, 1146–1147.

Wood, B.J. (1988) Activity measurements and excess entropy-volume relationships for pyrope-grossular garnets. Journal of Geology, 96, 721–729.

Wood, B.J., and Virgo, D. (1989) Upper mantle oxidation state: Ferric iron contents of lherzolite spinels by ^{57}Fe Mössbauer spectroscopy and resultant oxygen fugacities. Geochimica et Cosmochimica Acta, 53, 1277–1291.

MANUSCRIPT RECEIVED JULY 30, 1990
MANUSCRIPT ACCEPTED MAY 14, 1991