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An Experimental Study of Fe – Mg Partitioning Between Garnet and Olivine and Its Calibration as a Geothermometer

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Abstract. The partitioning of Fe and Mg between coexisting garnet and olivine has been studied at 30 kb pressure and temperatures of 900° to 1,400° C. The results of both synthesis and reversal experiments demonstrate that K_D $(=(\text{Fe/Mg})_{\text{gt}}/(\text{Fe/Mg})_{\text{ol}})$ is strongly dependent on Fe/Mg ratio and on the calcium content of the garnet. For example, at 1,000° C/30 kb, K_D varies from about 1.2 in very iron-rich compositions to 1.9 at the magnesium end of the series. Increasing the mole fraction of calcium in the garnet from 0 to 0.3 at 1,000° C increases K_D in magnesian compositions from 1.9 to about 2.5.

The observed temperature and composition dependence of K_D has been formulated into an equation suitable for geothermometry by considering the solid solution properties of the olivine and garnet phases. It was found that, within experimental error, the simplest kind of nonideal solution model (Regular Solution) fits the experimental data adequately. The use of more complex models did not markedly improve the fit to the data, so the model with the least number of variables was adopted.

Multiple linear regression of the experimental data (72 points) yielded, for the exchange reaction:

$$\underset{\text{olivine}}{3\,\text{Fe}_2\text{SiO}_4} + \underset{\text{garnet}}{2\,\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}} \rightleftharpoons \underset{\text{garnet}}{2\,\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}} + \underset{\text{olivine}}{3\,\text{Mg}_2\text{SiO}_4}$$

ΔH^0 (30 kb) of $-10{,}750$ cal and ΔS^0 of -4.26 cal deg^{-1} mol^{-1}. Absolute magnitudes of interaction parameters (W_{ij}) derived from the regression are subject to considerable uncertainty. The partition coefficient is, however, strongly dependent on the following *differences* between solution parameters and these differences are fairly well constrained:

$$W^{\text{ol}}_{\text{FeMg}} - W^{\text{gt}}_{\text{FeMg}} \simeq 800 \text{ cal}$$
$$W^{\text{gt}}_{\text{CaMg}} - W^{\text{gt}}_{\text{CaFe}} \simeq 2{,}670 \text{ cal.}$$

The geothermometer is most sensitive in the temperature and composition regions where K_D is substantially greater than 1. Thus, for example, peridotitic compositions at temperatures less than about 1,300° C should yield calculated temperatures within 60° C of the true value. Iron rich compositions (at any temperature) and magnesian compositions at temperatures well above 1,300° C could not be expected to yield accurate calculated temperatures.

For a fixed K_D the influence of pressure is to raise the calculated temperature by between 3 and 6° C per kbar.

Introduction

There has, in recent years, been considerable interest in the use of solid-solid equilibria to estimate the pressures and temperatures of crystallisation or recrystallisation of rocks. This interest has been stimulated by a number of studies of ultramafic xenoliths from kimberlites and basalts which have indicated that these xenoliths formed over considerable ranges of $P-T$ conditions. For example, Boyd (1973) applied the equilibria:

$$\underset{\text{orthopyroxene}}{\text{Mg}_2\text{Si}_2\text{O}_6} \rightleftharpoons \underset{\text{clinopyroxene}}{\text{Mg}_2\text{Si}_2\text{O}_6} \tag{1}$$

and

$$\underset{\text{orthopyroxene}}{\text{Mg}_2\text{Si}_2\text{O}_6} + \underset{\text{orthopyroxene}}{\text{MgAl}_2\text{SiO}_6} \rightleftharpoons \underset{\text{garnet}}{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}} \tag{2}$$

to a suite of garnet lherzolites from Lesotho kimberlites. He observed that the apparent equilibration conditions defined a fairly simple curve in pressure-

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temperature space and suggested that this curve represents a 'fossil geotherm' sampled by the host kimberlite magma. The ensuing debate has, as far as the experimentalist is concerned, centred around two important questions. Firstly, do the experimental results used by Boyd and others define the true equilibrium relationships for (1) and (2)? Secondly, to what extent may these experimental data be applied to bulk compositions other than those actually studied?

The experimental data of Davis and Boyd (1966) on the system $Mg_2Si_2O_6 - CaMgSi_2O_6$ (Eq. 1) have been largely superseded by a number of recent studies (Nehru and Wyllie, 1974; Mori and Green, 1976; Howells and O'Hara, 1975; Lindsley and Dixon, 1976). Although there now appears to be some consensus on the position of the enstatite-diopside miscibility gap there remain difficulties in its application to rocks. The effect of pressure on the miscibility gap is still relatively poorly defined (Lindsley and Dixon, 1976), and the two-pyroxene geothermometer becomes imprecise at temperatures below about 1,100° C.

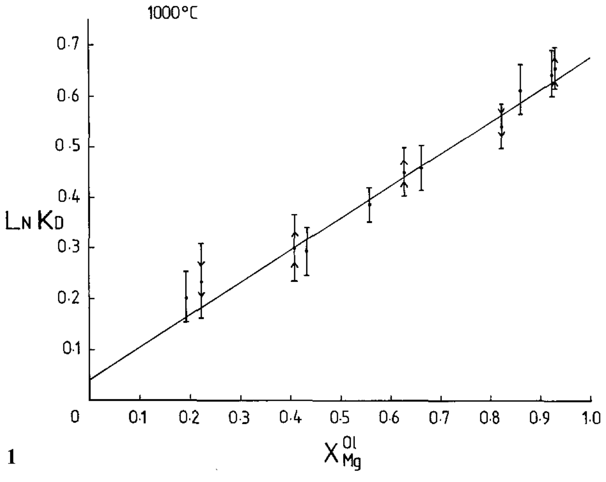
The solubility of alumina in orthopyroxene coexisting with garnet (MacGregor, 1974) has been less subject to further examination than the diopside-enstatite system and most subsequent work has tended to support Macgregor's data (e.g., Wood, 1974; Danckwerth and Newton, 1978). Howells and O'Hara (1978) have, however, suggested that MacGregor's results tend to yield overestimates of the pressures of garnet-lherzolite equilibration.

Extrapolation of Eq. (1) and (2), both investigated in simple Fe- and Ca-free systems, to rocks necessitates some assumptions concerning the nature of mixing in the phases concerned. Wood and Banno (1973) described a simple method of using Eq. (2) as a geobarometer in natural garnet-orthopyroxene assemblages. The extrapolation procedure, based on the assumption of ideal solution in both mineral phases received considerable support from experimental results in Fe- and Ca-bearing systems (Wood, 1974). The ideal solution assumption, although widely used and apparently reasonable for Eq. (2), is not readily applicable to the two-pyroxene geothermometer. Attempts to calibrate the latter for complex systems have required empirical correction factors (Wood and Banno, 1973; Wells, 1977) which have no theoretical basis. Because of their empirical nature, these calibrations hinge on the few available experimental data for complex compositions. When one considers that data for the $Mg_2Si_2O_6 - CaMgSi_2O_6$ system have, after extensive study, only recently reached a satisfactory degree of precision, it becomes apparent that the current status of the two pyroxene geothermometer is, in complex systems, rather unsatisfactory. There is therefore need for a geothermometer which can be used in complex systems with the minimum of extrapolation and which can yield precise results at temperatures below 1,100° C. The calibration of such a geothermometer has been the main object of this study.

It has often been observed that, relative to other Fe – Mg silicates, garnet has a strong preference for iron over magnesium. This preference, which is temperature dependent may, in principle, be used to establish Fe – Mg exchange geothermometers (Banno, 1970). Råheim and Green (1974) have calibrated such a geothermometer for garnet and clinopyroxene coexisting in basic bulk compositions over a wide temperature range. Although Råheim and Green's geothermometer is potentially applicable to ultramafic compositions problems arise because of the complex nature of solid solution in the garnet and clinopyroxene phases. Råheim and Green found, for example, that the observed pressure dependence of K_D $(=(Fe/Mg)_{gt}/(Fe/Mg)_{cpx})$ was much greater for the bulk compositions studied than would be predicted on the basis of known volumes of the minerals. Wood (1976) suggested that this was due to increasing calcium content of the garnet with increasing pressure, a phenomenon which is much less marked in ultramafic compositions than in the compositions studied by Råheim and Green. The variable oxidation state of iron and the effect of Al substitution on activities of components in the clinopyroxene phase also complicate the use of the garnet-clinopyroxene geothermometer. For ultramafic compositions it seems probable that Fe – Mg exchange between garnet and olivine would present fewer problems of extrapolation than the garnet-clinopyroxene geothermometer. This is because the olivine phases present in ultramafic rocks are essentially binary $Mg_2SiO_4 - Fe_2SiO_4$ solid solutions without substantial Ca, Fe^{3+}, or aluminium contents. The first aim of this study was the determination of Fe – Mg partitioning relationships between garnet and olivine in the system $MgO - FeO - Al_2O_3 - SiO_2$. The influence of calcium on these relationships was then determined by adding variable amounts of $Ca_3Al_2Si_3O_{12}$ component to the garnet phase.

Experimental

Preliminary experiments in the system $MgO - FeO - Al_2O_3 - SiO_2$ were performed on compositions which had been crystallised to the low pressure assemblages olivine-orthopyroxene-spinel or olivine-spinel-mullite. The compositions were prepared by intimately grinding together analytical grade MgO and Al_2O_3 with SiO_2 (ex-tetraethyl orthosilicate) and Fe metal (99.9%) in proportions appropriate to yield 2 olivine:1 garnet. The mixtures were sealed in



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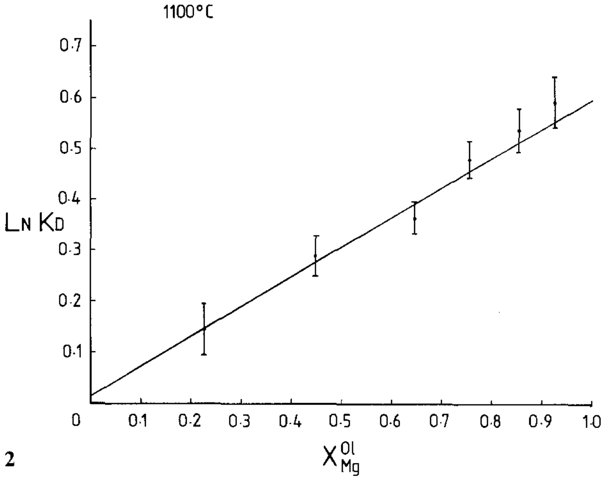

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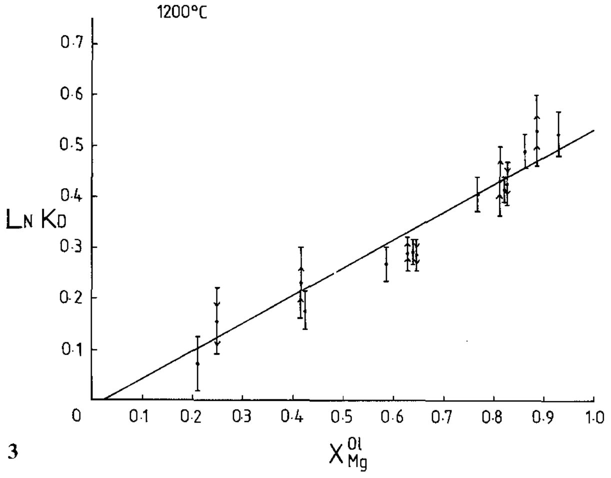

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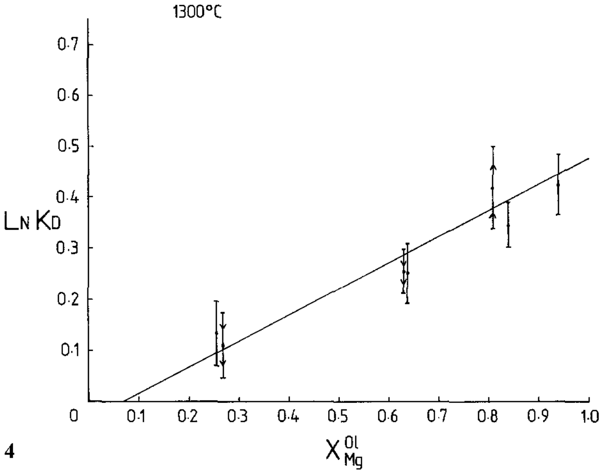

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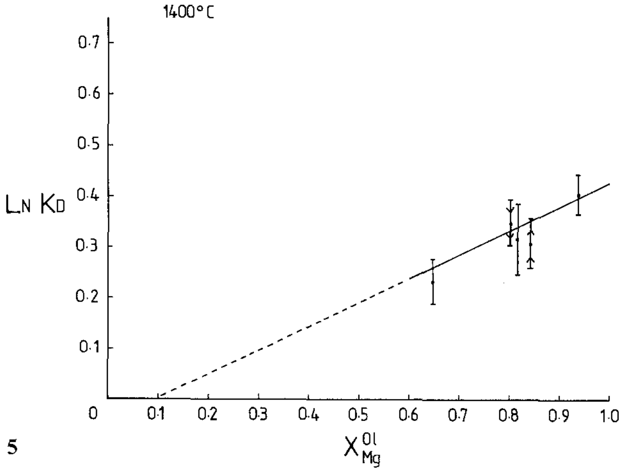

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Figs. 1–5. These figures illustrate the influence of (Mg/Mg+Fe) in olivine ($X_{\mathrm{Mg}}^{\mathrm{ol}}$) on garnet-olivine K_D in the system MgO−FeO−Al_2O_3−SiO_2 at 30kb. Error bars correspond to one standard deviation in K_D obtained from the microprobe analyses. Arrows indicate direction of approach to equilibrium in reversal experiments. Points without arrows correspond to synthesis experiments

gold capsules with slightly more water than necessary to oxidize all of the Fe-metal to Fe^{2+}. The capsules were then run in a cold seal vessel for about 20h at 800° C and 1kb. No metallic iron or magnetite was present in the low pressure crystalline assemblage.

Two methods were used to bracket the approach to equilibrium Fe−Mg partitioning. One involved synthesising olivine and garnet at 30kb and temperatures appropriate to produce high and low values of $K_D(=(\mathrm{Fe/Mg})_{\mathrm{gt}}/(\mathrm{Fe/Mg})_{\mathrm{ol}})$. The products were then re-run at intermediate temperatures and the equilibrium K_D under the latter conditions bracketed. The other method was intimate grinding together of almandine and forsterite ($K_D=\infty$) or of pyrope and fayalite ($K_D=0$). The garnets for the latter starting materials were prepared hydrothermally at 30 kb and 900° C. Both methods produced results consistent with the synthesis experiments (Figs. 1–5).

Synthesis experiments for calcium-bearing compositions were performed by intimately grinding grossular garnet (originally prepared at 1.5 kb and 670° C) with the low pressure olivine ± orthopyroxene-spinel ± mullite assemblages discussed above. Reversal experiments were performed by crystallization of these mixtures at high and low temperatures (at 30 kb) and later re-running at intermediate temperatures.

High pressure experiments were performed in a conventional ½-inch piston-cylinder apparatus (Boyd and England, 1960). At temperatures of 1,000° C and above the pressure cell consisted of concentric tubes of talc (outermost) pyrex[1] and graphite (innermost) with inserts of crushable alumina. Talc and graphite were used alone below 1,000° C. Runs at 1,000° C and below were performed in gold capsules sealed with small amounts of water as a flux. At higher temperatures, where water-saturated melting can occur, unsealed graphite capsules were used.

Each experiment was pressed to the required run pressure, brought to temperature, then pressurized to 5 kb over the required pressure before decompressing and maintaining at the required value. Temperature was measured and controlled with a $Pt/Pt_{87}Rh_{13}$ thermocouple. No corrections have been made for possible friction effects on pressure or for pressure effects on the thermocouple emf.

Run products were examined optically and by X-ray difraction. The compositions of the coexisting phases were determined with a Cambridge Geoscan electron microprobe fitted with a Link Systems Model 290-2 KX energy-dispersive system. The accuracy and precision of the system in use at Manchester have been studied in detail by Dunham and Wilkinson (1978). They have shown that for major elements (> 1 wt %) accuracy and precision of the energy dispersive analyses are comparable to those obtained by the 'normal' wavelength dispersive method. In our study at least ten analyses of garnet and of olivine were performed on each run product.

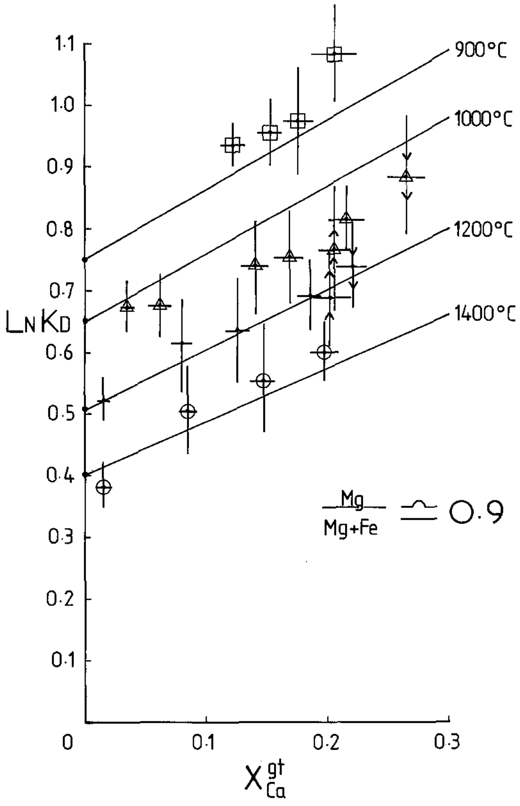

Fig. 6. The influence of calcium content of garnet on K_D at 30 kb and different temperatures. *Points with arrows* are reversal experiments, others are synthesis experiments (see text). □: 900° C; △: 1,000° C; ●: 1,200° C; ○: 1,400° C. The bulk value of (Mg/Mg+Fe) of the starting materials was close to 0.9 for these experiments. Some of the scatter is due to small differences in (Mg/Mg+Fe) for different temperatures

Results

The partitioning of iron and magnesium between coexisting garnet and olivine may be represented by the exchange reaction:

$$\underset{\text{garnet}}{2Mg_3Al_2Si_3O_{12}} + \underset{\text{olivine}}{3Fe_2SiO_4} \rightleftharpoons \underset{\text{garnet}}{2Fe_3Al_2Si_3O_{12}} + \underset{\text{olivine}}{3Mg_2SiO_4} \qquad (3)$$

for which the equilibrium constant is given by:

$$K_a = \frac{a_{Mg_2SiO_4}^{olivine^3} \cdot a_{Fe_3Al_2Si_3O_{12}}^{garnet^2}}{a_{Fe_2SiO_4}^{olivine^3} \cdot a_{Mg_3Al_2Si_3O_{12}}^{garnet^2}}. \qquad (4)$$

In Eq. (4) a_i^j refers to the activity of component i in phase j. The important problem in formulating the geothermometer is, of course, to relate the equilibrium constant, which depends only on pressure and temperature to the measured partition coefficient (K_D) which is generally pressure, temperature *and* composition dependent. In the following discussion K_D is defined as follows:

$$K_D = \frac{X_{Mg}^{olivine} \cdot X_{Fe}^{garnet}}{X_{Fe}^{olivine} \cdot X_{Mg}^{garnet}} \qquad (5)$$

where

$$X_{Mg}^{olivine} = \left(\frac{Mg}{Mg+Fe}\right)_{olivine}$$

$$X_{Fe}^{garnet} = \left(\frac{Fe}{Fe+Mg+Ca}\right)_{garnet} \qquad (6)$$

and so on. It should be noted that the small Ca contents of olivine (< 1 mol %) have been ignored.

Figures 1–5 illustrate the observed temperature and composition dependence of $\ln K_D$ in the system $MgO-FeO-Al_2O_3-SiO_2$ at 30 kb. It can be seen from these figures that $\ln K_D$ is strongly dependent on both temperature and composition. It should also be noted that good agreement has been obtained between our synthesis and bracketing experiments in this system. The temperature and composition regions in which Eq. (3) may, in principle, be used as a

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[1] Brand name of the Corning Glass Company

geothermometer are those in which K_D is substantially greater than 1, $\ln K_D$ substantially greater than 0. Thus, from inspection of Figs. 1–5 it is to be expected that K_D could provide a reasonable geothermometer at temperatures less than 1,300°C and at relatively high values of $X_{\mathrm{Mg}}^{\mathrm{ol}}$ (>0.5). These observations will be discussed in more detail in a later section.

Figure 6 illustrates the dependence of K_D on the calcium content of garnet at 30 kb and for bulk Mg/Mg + Fe of about 0.9. The figure shows that, as predicted by Wood (1976), K_D increases with increasing calcium content of the gartnet. This may be interpreted as due to the different magnitudes of Ca – Fe and Ca – Mg interactions in the ternary Ca – Mg – Fe solid solution.

In summary, it appears that K_D is, at 30 kb, a function of temperature, of the Mg content of olivine and of the Ca content of garnet. Any attempt to calibrate K_D as a geothermometer must, of course, bear in mind the observed compositional dependencies and attempt to treat them in an objective and consistent manner. If mixing in both of the solid solutions were completely ideal then K_D would be independent of composition; the effects of composition on K_D reflect non-ideal mixing in olivine and garnet phases. In order, therefore, to calibrate the geothermometer it is necessary to have some understanding of the nature of mixing and of activity-composition relationships in the two minerals.

Activity-Composition Relationships for Olivine and Garnet

The olivines which occur in ultramafic rocks and which were produced during this study are essentially binary $\mathrm{Mg_2SiO_4}-\mathrm{Fe_2SiO_4}$ solid solutions. For such solid solutions the general relationship between activities of the components and the composition of the phase is (e.g. Wood and Fraser, 1976, p. 102).

$$a_{\mathrm{Mg_2SiO_4}} = (X_{\mathrm{Mg}}^{\mathrm{olivine}} \gamma_{\mathrm{Mg}}^{\mathrm{ol}})^2$$
$$a_{\mathrm{Fe_2SiO_4}} = (X_{\mathrm{Fe}}^{\mathrm{olivine}} \gamma_{\mathrm{Fe}}^{\mathrm{ol}})^2 \tag{7}$$

where $\gamma_{\mathrm{Fe}}^{\mathrm{ol}}$ refers to the activity coefficient of the Fe component of the olivine.

The two sites in each olivine formula unit are not strictly equivalent and, in principle, Eq. (7) should be modified to take account of cation ordering on these two distinct positions. In practice however, the extent of Fe – Mg order is very small and may be neglected for the purposes of this discussion (Burns, 1970).

Experimental determinations of activity coefficients in olivine at high temperatures (Nafziger and Muan, 1967; Kitayama and Katsura, 1968; Williams, 1971) have lead to the conclusion that this phase exhibits small positive deviations from ideality (γ's >1). Although Williams (1972) used a more complex model Matsui and Nishizawa (1974) have shown that the data on olivine nonideality are adequately represented by the regular solution model (Thompson, 1967). Thus, the activity coefficients for the olivine phase are given by:

$$RT \ln \gamma_{\mathrm{Mg}}^{\mathrm{ol}} = X_{\mathrm{Fe}}^{\mathrm{ol2}} W_{\mathrm{FeMg}}^{\mathrm{ol}}$$
$$RT \ln \gamma_{\mathrm{Fe}}^{\mathrm{ol}} = X_{\mathrm{Mg}}^{\mathrm{ol2}} W_{\mathrm{FeMg}}^{\mathrm{ol}} \tag{8}$$

where $W_{\mathrm{FeMg}}^{\mathrm{ol}}$ probably lies between 0 and 3 kcal at temperatures above 800°C (Obata, 1974; Kawasaki and Matsui 1977).

Kawasaki and Matsui (1977) studied the partitioning of iron and magnesium between $\mathrm{Mg_2SiO_4}-\mathrm{Fe_2SiO_4}$ olivine and $\mathrm{Mg_3Al_2Si_3O_{12}}-\mathrm{Fe_3Al_2Si_3O_{12}}$ garnet at 50 kb and 1,100°C. They found that their data, which show considerable scatter, could be adequately represented by the regular solution model for the Fe – Mg garnet as well as for the olivine solid solution. Thus, with three sites per formula unit on which mixing takes place we have:

$$a_{\mathrm{Mg_3Al_2Si_3O_{12}}}^{\mathrm{gt}} = (X_{\mathrm{Mg}}^{\mathrm{gt}} \cdot \gamma_{\mathrm{Mg}}^{\mathrm{gt}})^3$$
$$a_{\mathrm{Fe_3Al_2Si_3O_{12}}}^{\mathrm{gt}} = (X_{\mathrm{Fe}}^{\mathrm{gt}} \cdot \gamma_{\mathrm{Fe}}^{\mathrm{gt}})^3$$

and, for binary Fe – Mg garnets:

$$RT \ln \gamma_{\mathrm{Mg}}^{\mathrm{gt}} = X_{\mathrm{Fe}}^{\mathrm{gt2}} W_{\mathrm{FeMg}}^{\mathrm{gt}}$$
$$RT \ln \gamma_{\mathrm{Fe}}^{\mathrm{gt}} = X_{\mathrm{Mg}}^{\mathrm{gt2}} W_{\mathrm{FeMg}}^{\mathrm{gt}}. \tag{10}$$

Although this symmetric model appears adequately to represent Fe – Mg garnets, it is demonstrably unsatisfactory for calcium-containing garnets. Newton et al. (1977) have found that the heats of solutions of $\mathrm{Mg_3Al_2Si_3O_{12}}-\mathrm{Ca_3Al_2Si_3O_{12}}$ garnets in lead borate melts indicate asymmetric behaviour in this phase at 970 K. Cressey et al. (1978) have found that $\mathrm{Fe_3Al_2Si_3O_{12}}-\mathrm{Ca_3Al_2Si_3O_{12}}$ garnets also depart strongly from the regular (symmetric) solution model at temperatures of 900°–1,100°C. Since these data indicate the need for a higher-order approximation to Fe – Mg – Ca garnets than that used for Fe – Mg olivines, we initially opted to apply the ternary subregular model (Wohl, 1946) to this phase. The data of Newton et al. (1977) are an excellent fit to such a model and those of Cressey et al. (1978) approximate it reasonably.

The experimental data shown in Figs. 1–6 were used to make a multiple linear regression based on the symmetric model for olivine and the asymmetric model for garnet. We found, however, that the fitted mixing parameters for garnet suggested that a symmetric model would be adequate for $X_{\mathrm{Ca}}^{\mathrm{gt}}$ less than

0.3. In view of the dangers of 'over-fitting' experimental data and the greater simplicity of the symmetric model we decided to return to using this model for ternary garnets. The reader should nevertheless be aware that it only provides a reasonable approximation for the low calcium contents of garnet considered here. The calorimetric and experimental data discussed above demonstrate its inadequancy at high values of $X_{\mathrm{Ca}}^{\mathrm{gt}}$. Assuming a ternary symmetric solution we have for $\gamma_{\mathrm{Fe}}^{\mathrm{gt}}$ and $\gamma_{\mathrm{Mg}}^{\mathrm{gt}}$:

$$\begin{aligned} RT\ln\gamma_{\mathrm{Fe}}^{\mathrm{gt}} &= X_{\mathrm{Mg}}^{\mathrm{gt}^2} W_{\mathrm{FeMg}}^{\mathrm{gt}} + X_{\mathrm{Ca}}^{\mathrm{gt}^2} W_{\mathrm{FeCa}}^{\mathrm{gt}} \\ &\quad + X_{\mathrm{Ca}}^{\mathrm{gt}} X_{\mathrm{Mg}}^{\mathrm{gt}} (W_{\mathrm{FeMg}}^{\mathrm{gt}} + W_{\mathrm{FeCa}}^{\mathrm{gt}} - W_{\mathrm{CaMg}}^{\mathrm{gt}}) \\ RT\ln\gamma_{\mathrm{Mg}}^{\mathrm{gt}} &= X_{\mathrm{Fe}}^{\mathrm{gt}^2} W_{\mathrm{FeMg}}^{\mathrm{gt}} + X_{\mathrm{Ca}}^{\mathrm{gt}^2} W_{\mathrm{CaMg}}^{\mathrm{gt}} \\ &\quad + X_{\mathrm{Fe}}^{\mathrm{gt}} X_{\mathrm{Ca}}^{\mathrm{gt}} (W_{\mathrm{FeMg}}^{\mathrm{gt}} + W_{\mathrm{CaMg}}^{\mathrm{gt}} - W_{\mathrm{FeCa}}^{\mathrm{gt}}). \end{aligned} \tag{11}$$

Although the values of these interaction parameters are not well known, there are sufficient data available for us to place some constraints on their magnitudes. The experiments of Cressey et al. (1978) indicate that $W_{\mathrm{FeCa}}^{\mathrm{gt}}$ is close to zero at 1,000° C; Kawasaki and Matsui showed that $W_{\mathrm{FeMg}}^{\mathrm{gt}}$ is less than $W_{\mathrm{FeMg}}^{\mathrm{ol}}$ at 1,100° C and 50 kb. Applying the symmetric model to the calorimetric data of Newton et al. (1977) indicates that $W_{\mathrm{CaMg}}^{\mathrm{gt}}$ is about 3 kcal. The latter results on $W_{\mathrm{CaMg}}^{\mathrm{gt}}$ are not, however, consistent with the high pressure experiments of Hensen et al. (1975) who found that $W_{\mathrm{CaMg}}^{\mathrm{gt}}$ is temperature dependent with a constant term [W_H see below Eq. (17)] over twice that found by Newton et al., 1977. Despite these inconsistencies we may conclude that the *difference* ($W_{\mathrm{CaMg}}^{\mathrm{gt}} - W_{\mathrm{CaFe}}^{\mathrm{gt}}$) is substantially greater than zero in the temperature range of interest here. As will be shown below it is the difference between these two parameters, rather than their absolute magnitudes which is of importance in Fe–Mg partitioning between garnet and olivine. In support of our conclusion regarding the magnitude of ($W_{\mathrm{CaMg}}^{\mathrm{gt}} - W_{\mathrm{CaFe}}^{\mathrm{gt}}$) Ganguly and Kennedy (1974) suggest, on the basis of coexisting garnet and biotite in metamorphic rocks, that a value 4.6 ±1.2 kcal is appropriate for this difference at 630° C.

In summary, therefore, we would expect, on applying the symmetric model to our data, the following range and order of values of W_{ij}:

$$3{,}000\ \mathrm{cal} \simeq W_{\mathrm{CaMg}}^{\mathrm{gt}} > W_{\mathrm{FeMg}}^{\mathrm{ol}} > W_{\mathrm{FeMg}}^{\mathrm{gt}} > W_{\mathrm{CaFe}}^{\mathrm{gt}} \simeq 0.$$

Temperature and Composition Dependence of K_D at 30 kb

The relationship between partition coefficient (K_D) and equilibrium constant may readily be determined by applying Eqs. (5) and (7) to Eq. (2):

$$K_a^{1/6} = K_D \left(\frac{\gamma_{\mathrm{Fe}}^{\mathrm{gt}} \cdot \gamma_{\mathrm{Mg}}^{\mathrm{ol}}}{\gamma_{\mathrm{Mg}}^{\mathrm{gt}} \cdot \gamma_{\mathrm{Fe}}^{\mathrm{ol}}} \right). \tag{12}$$

Taking logarithms, multiplying by gas constant R and temperature and rearranging yields:

$$\begin{aligned} RT\ln K_D &= 1/6\,RT\ln K_a + RT(\ln\gamma_{\mathrm{Mg}}^{\mathrm{gt}} - \ln\gamma_{\mathrm{Fe}}^{\mathrm{gt}}) \\ &\quad - RT(\ln\gamma_{\mathrm{Mg}}^{\mathrm{ol}} - \ln\gamma_{\mathrm{Fe}}^{\mathrm{ol}}) \end{aligned} \tag{13}$$

From Eq. (8) we obtain, remembering that the sum of $X_{\mathrm{Fe}}^{\mathrm{ol}}$ and $X_{\mathrm{Mg}}^{\mathrm{ol}}$ is 1.0:

$$RT(\ln\gamma_{\mathrm{Mg}}^{\mathrm{ol}} - \ln\gamma_{\mathrm{Fe}}^{\mathrm{ol}}) = (X_{\mathrm{Fe}}^{\mathrm{ol}} - X_{\mathrm{Mg}}^{\mathrm{ol}})\,W_{\mathrm{FeMg}}^{\mathrm{ol}} \tag{14}$$

Similarly, for the ternary garnets we obtain, from (11):

$$\begin{aligned} RT(\ln\gamma_{\mathrm{Mg}}^{\mathrm{gt}} - \ln\gamma_{\mathrm{Fe}}^{\mathrm{gt}}) &= (X_{\mathrm{Fe}}^{\mathrm{gt}} - X_{\mathrm{Mg}}^{\mathrm{gt}})\,W_{\mathrm{FeMg}}^{\mathrm{gt}} \\ &\quad + X_{\mathrm{Ca}}^{\mathrm{gt}}(W_{\mathrm{CaMg}}^{\mathrm{gt}} - W_{\mathrm{CaFe}}^{\mathrm{gt}}). \end{aligned} \tag{15}$$

In view of the absence of precise data on the magnitudes of the interaction parameters in garnet and olivine, it is necessary after substituting (14) and (15) to estimate their values by fitting Eq. (13) to the experimental observations. From the previous discussion of mixing properties is seems that any gross errors in W_{ij}'s obtained by this method should be apparent and should enable us to improve our solution model for garnet.

The experimental data shown in Fig. 1–6 span a temperature range from 900° to 1,400° C. The equilibrium constant K_a and the interaction parameters may all, in general, be temperature dependent. Thus, we may write the general temperature dependence of the equilibrium constant as follows:

$$1/6\ln K_a = \frac{-\Delta H^0}{6RT} + \frac{\Delta S^0}{6R} \tag{16}$$

where ΔH^0 and ΔS^0 refer to the standard state enthalpy and entropy changes of reaction (3). The standard state for all components in this reaction has been taken to be the pure phase at the pressure and temperature of interest. If we assume that the interaction parameters are also temperature dependent, their form may be represented as follows, after Thompson (1967):

$$W_{ij} = W_{H(ij)} - T W_{S(ij)}. \tag{17}$$

In Eq. (17) W_H and W_S refer to excess enthalpy and entropy contributions to the excess free energy. Substituting Eq. (17) and (16) into (13) we obtain, for K_D:

$$\begin{aligned} \ln K_D &= \frac{-\Delta H^0}{6RT} + \frac{\Delta S^0}{6R} + (X_{\mathrm{Mg}}^{\mathrm{ol}} - X_{\mathrm{Fe}}^{\mathrm{ol}}) \left[\frac{W_H^{\mathrm{ol}}}{RT} - \frac{W_S^{\mathrm{ol}}}{R} \right] \\ &\quad - (X_{\mathrm{Mg}}^{\mathrm{gt}} - X_{\mathrm{Fe}}^{\mathrm{gt}}) \left[\frac{W_{H(\mathrm{FeMg})}^{\mathrm{gt}}}{RT} - \frac{W_{S(\mathrm{FeMg})}^{\mathrm{gt}}}{R} \right] \\ &\quad + X_{\mathrm{Ca}}^{\mathrm{gt}} \left[\frac{W_{H(\mathrm{CaMg})}^{\mathrm{gt}}}{RT} - \frac{W_{S(\mathrm{CaMg})}^{\mathrm{gt}}}{R} - \frac{W_{H(\mathrm{CaFe})}^{\mathrm{gt}}}{RT} + \frac{W_{S(\mathrm{CaFe})}^{\mathrm{gt}}}{R} \right] \end{aligned} \tag{18}$$

Table 1. Regression parameters for Eq. (19)

		Standard error
ΔH^0	-10750 cal	± 810
ΔS^0	-4.26 cal deg^{-1} mol^{-1}	$\pm$ 0.52
W^{ol}_{MgFe}	990 cal mol^{-1}	± 207
W^{gt}_{MgFe}	195 cal mol^{-1}	± 215
$(W^{gt}_{CaMg} - W^{gt}_{CaFe})$	2676 cal mol^{-1}	± 201

These values were derived by fitting Eq. (19), using multiple linear regression, to all 72 experimental points

Instead of fitting Eq. (18) directly to all of our results it was decided to build up a picture of the ranges of values of the various parameters that could be obtained by using different selected parts of the data. Thus, we first fitted (18), using multiple linear regression, to the results in the calcium free system. By fitting isotherms separately and then putting all the data together to obtain the temperature dependence of W_{ij}'s and K_D, the following points emerged: –

1. The observed K_D is insensitive to the absolute magnitudes of W^{ol}_{FeMg} and W^{gt}_{FeMg}, but highly dependent on the *difference* between these two parameters. We obtained, with a variety of regressions, the following approximate relationship:

$$W^{ol}_{FeMg} - W^{gt}_{FeMg} \simeq 800\,\text{cal}. \tag{20}$$

Kawasaki and Matsui (1977) obtained 650±120 cal for this difference at 50 kb and 1,100° C.

2. ΔS^0 for reaction (3) is close to zero, a value of -4.3 cal deg^{-1} being obtained in the final regression (Table 1). ΔS^0 is generally near zero for exchange reactions because reactant and product phases have the same structures and similar volumes (see Wood and Fraser 1976, p. 39 for a brief discussion of entropy-volume relationships).

3. The ineraction parameters for garnet and olivine may, within the precision of the data be taken to be independent of temperature.

Applying observation (3), which reduces the number of fit parameters from eight to five, Eq. (18) simplifies to the final form:

$$\ln K_D = \frac{-\Delta H^0}{6RT} + \frac{\Delta S^0}{6R} + (X^{ol}_{Mg} - X^{ol}_{Fe})\,W^{ol}_{FeMg} - (X^{gt}_{Mg} - X^{gt}_{Fe})\,W^{gt}_{FeMg} + X^{gt}_{Ca}(W^{gt}_{CaMg} - W^{gt}_{CaFe}). \tag{19}$$

When the complete form of Eq. (19) including Ca terms was fitted to all 72 data points, $(W^{ol}_{FeMg} - W^{gt}_{FeMg})$ remained approximately the same as had been obtained from data on Ca-free runs. Values of ΔH^0 and ΔS^0 of -10750 cal and -4.26 cal deg^{-1} were obtained (Table 1).

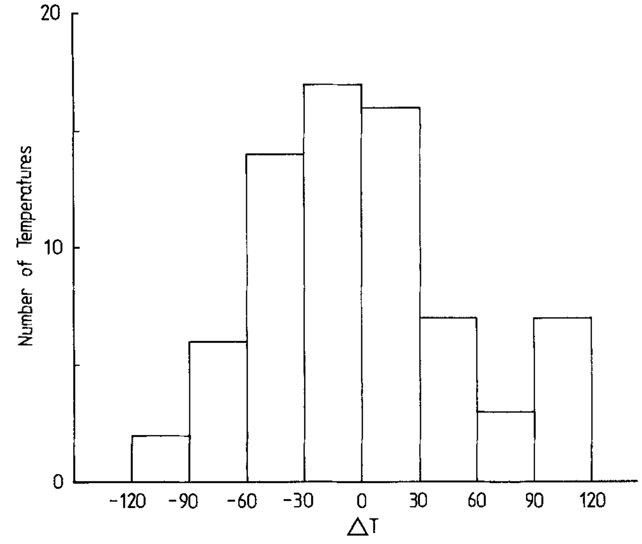

Fig. 7. Histogram showing the differences ΔT between temperatures calculated from our experimental results using Eq. (19) and actual run temperatures. All data points are shown, including the imprecise data at high values of (Fe/Fe+Mg) (see text)

Given the regression parameters of Table 1 it is a straightforward matter to rearrange Eq. (19) to obtain temperature (°K) in terms of phase composition. When this is done [see Eq. (26) below] and apparent temperatures calculated for each of our experiments the regions where a garnet-olivine thermometer would be precise and imprecise become obvious. For example, as can be seen from Figs. 1–6, $\ln K_D$ varies very little between 1,000 and 1,300° C if X^{ol}_{Mg} is small ($\simeq 0.25$ or less). This is the region where $\ln K_D$ is close to 0 (K_D close to 1) and is hence a region of insensitivity to temperature. Similarly, at high temperatures (> 1,300–1,400° C) where K_D approaches 1 over a large part of the composition range, the thermometer must become relatively insensitive. Thus, a garnet-olivine thermometer is best used for very magnesian bulk compositions, such as peridotites, which equilibrated at temperatures less than 1,300–1,400° C.

Apparent temperatures for 75% of our runs calculated using (26), fall within 60° C of the nominal experimental temperatures. These are predominantly the runs at high X^{ol}_{Mg} and low temperatures, 1,200° C and less. However as expected, apparent temperatures, at low X^{ol}_{Mg} and at temperatures of 1,300° C or higher show greater scatter about the experimental temperatures. Figure 7 shows a histogram of results for all our runs, including all of the data shown in Figs. 1–6 together with several points on calcium-bearing compositions with low X^{ol}_{Mg}. As can be seen, a few results deviate by greater than 90° C from the experimental temperatures. These are high temperature and low X^{ol}_{Mg} experiments in which small analytical errors can produce large shifts in apparent temperature. When confined to the appropriate range of composition and temperature, however, K_D, as expressed through Eq. (26) should yield temperatures within 60° C of the true values.

The absolute values of mixing parameters for olivine and garnet derived from the regression are, as discussed earlier subject to considerable uncertainty. Taken at face value, however the constants given in Table 1 indicate small positive deviations from ideality on Fe–Mg garnet and olivine joins with interaction parameters of about 195 and 990 cal respectively. In view of our earlier discussions of mixing parameters these values do not appear unreasonable and should be adequate for limited extrapolation of the data. The difference between W^{gt}_{CaMg} and W^{gt}_{CaFe} (2680 cal) is also within the range expected and should also be reasonable for extrapolation outside the 900°–1,400° C temperature range of our experiments.

Having obtained an equation which is simple, consistent with our experimental data and which yields apparently reasonable mixing parameters at 30 kb, we shall now consider the likely effect of variable pressure on K_D.

Pressure Dependence of K_D

To extrapolate Eq. (19) to pressures other than 30 kb it is necessary to determine the influence of pressure on the equilibrium constant, K_a, and on each of the interaction parameters in the equation.

The effect of pressure on an equilibrium constant at constant temperature is given by:

$$\left(\frac{\partial \ln K_a}{\partial P}\right)_T = \frac{-\Delta V^0}{RT} \tag{20}$$

where ΔV^0 is the standard state volume change of the reaction under the pressure-temperature conditions of interest. The volumes of forsterite and fayalite at 298 K and 1 atm pressure were taken from Fisher and Medaris (1969); those of almandine and pyrope under the same conditions were taken from Kawasaki and Matsui (1977). These data yield a standard state volume change of reaction (3) of -3.69 c.c. (-0.088 cal. bar^{-1}) at 298 K and 1 atm. This volume change is not independent of pressure and temperature however and it is necessary to take account of the compressibility and thermal expansion of olivine and garnet before (20) can be integrated at high P and T.

Thermal expansions for garnet and olivine were taken from Skinner (1966). We calculated volumes at 800° C/1 atm from these data (Table 2) and then used an average thermal expansion for the temperature range 600°–1,000° C in order to extrapolate to higher or lower temperatures. Room temperature compressibilities were obtained from Birch (1966) and from Takahashi and Liu (1970). The expansion and compressibility data, given in Table 2, yield an equation of the following form for the volumes of each of the phases pyrope, almandine, forsterite and fayalite:

Table 2. Volume, thermal expansion and compressibility data

	Forsterite	Fayalite	Almandine	Pyrope
V^0_{298} c.c.	43.59	46.23	115.33	113.22
V_{1073}/V^0_{298}	1.0292	1.0234	1.0191	1.0201
$\alpha \cdot 10^5$ deg^{-1}	4.5	2.3	2.87	2.84
$\beta \cdot 10^4$ kb^{-1}	7.9	9.1	5.26	4.72

$$V^0 = V^0_{1073/1\,\mathrm{bar}}[1+(T-1073)\alpha](1-\beta P). \tag{21}$$

In Eq. (21), α and β refer to thermal expansion and compressibility respectively. Substituting Eq. (21) into (20) we can extrapolate our values of K_a at 30 kb and some temperature T to some other pressure P, by integrating (20) at constant temperature:

$$\begin{aligned}\ln(K_a)_{P,T} = \ln(K_a)_{30,T} &- \frac{2(V_{\mathrm{Alm}})_{30,T}}{RT}\int_{30}^{P}(1-\beta_{\mathrm{Alm}}P)\,dP \\ &- \frac{3(F_{\mathrm{Fo}})_{30,T}}{RT}\int_{30}^{P}(1-\beta_{\mathrm{Fo}}P)\,dP + \frac{2(V_{\mathrm{Pyr}})_{30,T}}{RT}\int_{30}^{P}(1-\beta_{\mathrm{Pyr}}P)\,dP \\ &+ \frac{3(V_{\mathrm{Fa}})_{30,T}}{RT}\int_{30}^{P}(1-\beta_{\mathrm{Fa}}P)\,dP.\end{aligned} \tag{22}$$

Thus, given the data in Table 2, and values of K_a obtained from our experiments, the equilibrium constant may be calculated at any pressure and temperature.

The dependence of an interaction parameter W_{ij} on pressure is given by (Thompson, 1967):

$$\left(\frac{\partial W_{ij}}{\partial P}\right)_T = (W_V)_{ij} \tag{23}$$

where $(W_V)_{ij}$ is defined as follows for the binary ij:

$$V - V_i^0 X_i - V_j^0 X_j = V^{xs} = X_i X_j (W_V)_{ij}. \tag{24}$$

The excess volume term V^{xs} is, of course assumed to be a symmetrical function of composition for the symmetrical solution model adopted here.

Kawasaki and Matsui (1977) have found $(W^{gt}_V)_{\mathrm{FeMg}}$ to be $-(0.3 \pm 4) \cdot 10^{-3}$ cal bar^{-1} at 298 K and 1 atm. In view of the small magnitude of this parameter and its relatively large uncertainty, we assumed that it is zero. In contrast to the pyrope-almandine join, there are appreciable excess volumes of mixing in garnets on the grossular-pyrope and grossular-almandine joins (Newton et al., 1977; Cressey et al., 1978). Cressey et al. (1978) have, however, shown that the influence of Ca on the partial molar volumes of $Fe_3Al_2Si_3O_{12}$ and $Mg_3Al_2Si_3O_{12}$ components is virtually identical. Thus, since the calcium term in Eq. (18) is a *difference* between Ca–Mg and Ca–Fe interactions we may regard this difference as essentially independent of pressure. Hence we have assumed all W_{ij}^{gt} to be pressure-independent. This assumption cannot be extended to olivine, however, since both Fisher and Medaris (1969) and Akimoto and Fujisawa (1968) found appreciable excess volumes on the forsterite-fayalite join. There is some disparity between these authors' results, because $(W_V^{ol})_{FeMg}$ is calculated to be 7.2×10^{-3} cal bar^{-1} from Fisher and Medaris' data but only 3.0×10^{-3} cal bar^{-1} from Akimoto and Fujisawa's data. Fortunately, we are able to discriminate between the two data sets, as far as K_D is concerned, by using the experimental results of Kawasaki and Matsui (1977) at 50 kb and 1,100° C.

Using our value of W_{FeMg}^{gt} of 195 cal (see Table 1) we fitted *most* of Kawasaki and Matsui's data to Eq. (18) to estimate W_{FeMg}^{ol} at 50 kb and 1,100° C. None of Kawasaki and Matsui's data points were reversed and of their 18 results, 4 had a broad spread of garnet and olivine compositions with standard deviations greater than 2.5 mol%. These four points were left out of the regression. The fitting procedure yielded W_{FeMg}^{ol} at 50 kb and 1,100° C of 1,051 cal, compared with our value of 990 cal at 30 kb and 1,100° C. Adding excess volume terms to our 30 kb result gives W_{FeMg}^{ol} of 1,134 cal at 50 kb and 1,100° C if we use the Fisher and Medaris volume data and 1050 cal if we use the Akimoto and Fujisawa volume data. In view of the close agreement between the latter value and that obtained from Kawasaki and Matsui's experiments we adopted the excess volume term calculated from Akimoto and Fujisawa's measurements of olivine cell parameters. Integrating (23) at constant temperature we have with P in kilobars.

$$(W_{FeMg}^{ol})_P = (W_{FeMg}^{ol})_{30} + 3.0(P-30)\,\text{cal} \tag{25}$$

Adding (25) and (22) to (19) we obtain, on rearranging, the following equation for temperature in degrees Kelvin.

$$T = \frac{\begin{array}{c}902 + \text{DV} + (X_{Mg}^{ol} - X_{Fe}^{ol})(498 + 1.51(P-30)) \\ -98(X_{Mg}^{gt} - X_{Fe}^{gt}) + 1347 X_{Ca}^{gt}\end{array}}{\ln K_D + 0.357} \tag{26}$$

In Eq. (26) the DV term is the integrated form of Eq. (22), incorporating thermal expansion and compressibilities for all four phases. Using the thermal expansion and compressibility data of table 2, this term is given by: (P in kilobars)

$$\begin{aligned}\text{DV} = {} & 462.5[1.0191 + (T-1073)]\,(2.87 \times 10^{-5}) \\ & \cdot (P - 2.63 \times 10^{-4} P^2 - 29.76) + 262.4[1.0292 + (T-1073)] \\ & \cdot (4.5 \times 10^{-5})(P - 3.9 \times 10^{-4} P^2 - 29.65) \\ & - 454[1.020 + (T-1073)]\,(2.84 \times 10^{-5}) \\ & (P - 2.36 \times 10^{-4} P^2 - 29.79) - 278.3\,[1.0234 + (T-1073)] \\ & \cdot (2.3 \times 10^{-5})(P - 4.5 \times 10^{-4} P^2 - 29.6)\end{aligned} \tag{27}$$

The four parts of the DV term are volume expressions for almandine, forsterite, pyrope and fayalite respectively. Since the DV term involves temperature, Eq. (26) is best solved, at pressures other than 30 kb, by estimating a value of T(°K) at pressure P (in kilobars) then solving for a new value of T iteratively. The DV term is small so this method converges rapidly. At P equal to 30 kb, (the experimental pressure), the DV term is, of course zero.

As a test of the validity of the pressure terms we calculated apparent temperatures for the experiments of Kawasaki and Matsui at 50 kb and 1,100° C. Their results, excluding the four with very large range of garnet or olivine compositions, yield an average temperature of 1,070° C with a spread of 90° C about the mean. The calculated temperatures for these runs should be raised by about 10° to an average of 1,080° C to take account of the effect of the higher pressure on the uncorrected thermocouple emf (Getting and Kennedy, 1970). Thus agreement between calibrated and observed (nominal) run temperature is, at 50 kb, almost as good as that obtained from our calibration runs at 30 kb. We conclude that the 30 kb results may be extrapolated with confidence over 20–30 kb in pressure using Eq. (26).

Discussion and Conclusions

Equation (26) is based on esxperiments performed in the temperature range 900°–1,400° C at 30 kb. The extrapolation to pressures other than 30 kb has been tested using the 50 kb experiments of Kawasaki and Matsui and found to yield temperatures in good agreement with their nominal run temperature. Thus, we consider that Eq. (26) provides a good geothermometer for magnesium-rich garnet-olivine assemblages equilibrated close to, or within, the temperature range 900°–1,400° C and at pressures up to about 60 kb.

Although comparison with other geothermometers cannot prove the general validity of Eq. (26) it can demonstrate any obvious inconsistencies with earlier results. It is particularly instructive to compare garnet-olivine temperatures with those obtained

Table 3.

Rock No.	*T* °K; Wells, 1977	*T*; assuming $P = 30$ kb	*T* °K	*P*Kb
Ref. (a)				
1595	1154	1155	1135	26.2
1567	1187	1172	1169	29.2
1592	1192	1162	1153	28.3
1570	1202	1185	1188	30.5
1573	1212	1113	1072	22.2
1569	1225	1201	1201	30.0
1568	1206	1141	1110	24.3
1572	1212	1197	1204	31.3
1917	1251	1268	1334	43.1
1559B	1215	1230	1265	36.8
1582	1327	1265	1312	38.8
2001	1468	1528	1653	57.9
1591	1517	1506	1616	54.6
E3	1540	1498	1595	50.5
1924	1535	1537	1647	53.7
1925	1557	1529	1632	51.9
1611	1588	1497	1589	49.1
1610	1610	1543	1642	51.3
1566	1630	1543	1643	51.4
1596	1643	1674	1794	59.4
1597	1648	1672	1797	60.8
Ref. (b)				
160-4-8	1083	1016	988	25.3
9-5-2c	1078	1089	1073	27.1
264.3	1112	1093	1050	26.3
Ref. (c)				
GO-103	974	955	878	16.3

(a) Nixon and Boyd (1973)
(b) Evans and Trommsdorf (1978)
(c) Mori and Banno (1973)
(d) Wells (1977)
(e) *T* and *P* obtained from the garnet-olivine thermometer and the orthopyroxene-garnet barometer of Wood (1974)

from calibrations of equilibrium (1), the two-pyroxene geothermometer. This is because the garnet-olivine thermometer is complementary to the two-pyroxene thermometer, the former being most sensitive at low temperatures, where K_D is large, and the latter most sensitive at high temperatures where the pyroxene miscibility gap is small. Available methods for calculating temperatures from coexisting pyroxenes vary from completely ignoring the effects of components other than $CaMgSi_2O_6$ and $Mg_2Si_2O_6$ in the two phases to making various empirical corrections for the influence of iron and/or aluminium. We chose to compare our results with the most recent empirical approach, that of Wells (1977). Wells takes account of the influence of Fe^{2+} on the two-pyroxene miscibility gap but ignores any possible pressure effect. Thus, using garnet lherzolites from Lesotho, Japan and Switzerland as examples we calculated temperatures from Wells' Eq. (5) and from Eq. (26) of this work. To estimate pressures for our Eq. (26) we used the Al_2O_3 contents of orthopyroxenes coexisting with garnets in the lherzolite nodules. The pressure calculations were based on the calibration of Wood (1974) and used Eq. (12) of his paper.

A comparison of results of the two-pyroxene and garnet-olivine thermometers is given in Table 3. It may be seen that garnet-olivine temperatures are generally lower than two-pyroxene temperatures in the region where the former are more precise than the latter ($\leq$1,100° C) and higher where they are less precise ($T \geq$ 1,250°–1,300° C). In general, however there is good agreement between the two sets of results, differences on the order of 100° C only appearing at temperatures less than 900° C or pressures approaching 60 kb. Since the results on which Wells based his calibration were almost all produced at 30 kb or lower we believe that some of the differences at high pressure are due to the influence of pressure on the two pyroxene miscibility gap. Wells ignored pressure effects because of their uncertain magnitude, but it does appear that there is a tendency for the miscibility gap to widen with increasing pressure (Mori and Green, 1976). This effect would produce temperature discrepancies of the correct sign. The differences at low temperature are almost certainly due to the imprecise nature of the 2-pyroxene thermometer at temperatures less than 1,000° C.

In order to illustrate further the effect of pressure on calculated temperatures we repeated the calculations for the lherzolites at a fixed pressure of 30 kb (Table 3). These results indicate that increasing pressure raises the calculated temperature for a particular K_D by between 3 and 6° C per kbar in the $P-T$ range of garnet-lherzolite stability. For any particular rock the pressure dependence of calculated temperature is not constant, but decreases with increasing pressure. Using the compositions of coexisting garnet and olivine in a Lesotho lherzolite xenolith we calculated the apparent equilibration temperature over a wide range of assumed equilibration pressure. The results, shown in Fig. 8, indicate that the rate of change of temperature with pressure decreases from about 6°/kb at 10 kb to 3°/kb at 70 kb. This effect is due to the decreasing volume change of the exchange reaction with increasing pressure.

In conclusion it appears that coexisting garnet and olivine provide a precise geothermometer for magnesium rich bulk compositions such as garnet-lherzolites. Although the observed partition coefficient K_D is a function of pressure, temperature and bulk composition, the relative chemical simplicity of the phases has enabled separation of the effects of these different parameters. Since we have been able to separate the influences of the intensive variables, the garnet-olivine geothermometer is more reliable than

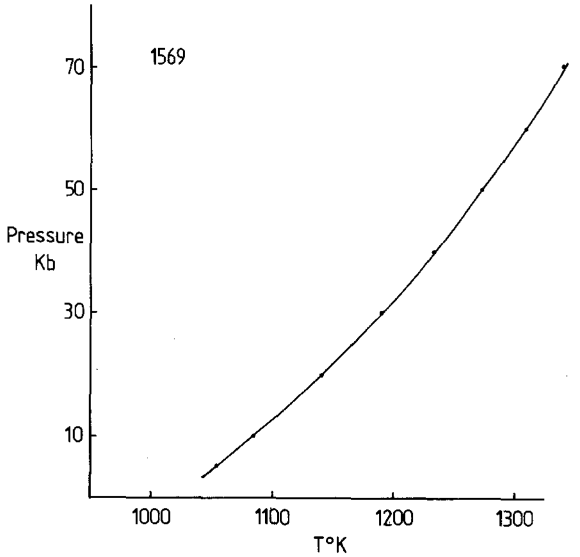

Fig. 8. $P-T$ curve for nodule 1569 (Nixon and Boyd, 1973) calculated from garnet-olivine partitioning using Eq. (26). Note the decrease in dT/dP with increasing pressure

the current calibration of the garnet-clinopyroxene geothermometer (Råheim and Green, 1974). In the latter case there are unresolved problems concerned with the influences of:

(a) The calcium content of garnet
(b) The aluminium content of clinopyroxene
(c) The oxidation state of iron in the clinopyroxene
(d) The distribution of Fe and Mg between $M1$ and $M2$ sites in the clinopyroxene

In the current work we have elucidated (a); (b), (c), and (d) do not apply because of the chemical and structural simplicity of olivine. The effect of calcium that we hae found should also be of similar magnitude for other Fe – Mg exchange thermometers involving garnet, e.g., garnet-cordierite; garnet-biotite and garnet-clinopyroxene. The garnet olivine geothermometer is more precise than the two pyroxene geothermometer at temperatures less than 1,200° C and is probably more reliable than the latter at higher temperature if the pressure is substantially greater than 30 kb.

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