

The Transition Between Spinel Lherzolite and Garnet Lherzolite, and Its Use as a Geobarometer

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Abstract. The equilibrium between spinel lherzolite and garnet lherzolite has been experimentally determined in the $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system between 800° and 1,100° C. In confirmation of earlier work and predictions from thermodynamic data, it was found that the $P-T$ slope of the reaction was close to zero, the equilibrium ranging from 16.1 kb at 800° C to 18.7 kb at 1,100° C (± 0.3 kb).

The addition of Cr_2O_3 to the system raised the stability field of spinel to higher pressures. It was found that the pressure at which both garnet and spinel could exist with olivine + orthopyroxene + clinopyroxene in the system CMAS – Cr_2O_3 could best be described by the empirical relationship:

$$P = P^0 + \alpha X_{\text{Cr}}^{\text{sp}}$$

where P^0 is the equilibrium pressure for the univariant reaction in the Cr_2O_3 -free system, α is a constant apparently independent of temperature with a value of 27.9 kilobars, and $X_{\text{Cr}}^{\text{sp}}$ is the mole fraction of chromium in spinel.

Use was made of the extensive literature on $\text{Mg}-\text{Fe}^{2+}$ solid solutions to quantitatively derive the effect of Fe^{2+} on the equilibrium. The effect of other components (Fe^{3+} , Na) was also considered.

The equilibrium can be used as a sensitive geobarometer for rocks containing the five phases ol + opx + cpx + gt + sp, and thus provides the only independent check presently available for the more widely applicable geobarometer which uses the alumina content of orthopyroxene in equilibrium with garnet.

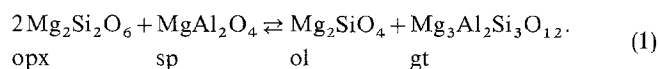
Introduction

It is generally agreed that aluminous lherzolite constitutes a large part of the upper mantle, and is the most acceptable candidate for the source rock of basaltic magmas. Consequently, the transition between the two high pressure forms, spinel lherzolite and garnet lherzolite, is of utmost importance to petrologists. The purpose of this paper is to briefly review the previous published work; to present new experimental data; to calculate the effect of minor components not explicitly studied; and to demonstrate the applicability of the results to some rocks.

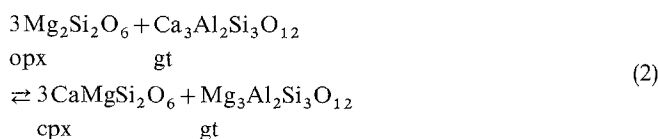
The chemical composition of the upper mantle is not precisely known, and indeed is likely to be heterogeneous. However, examination of those exotic nodules brought up from great depths in kimberlite and alkali basalt eruptions

shows that the five components, CaO, MgO, "FeO", Al_2O_3 and SiO_2 , make up at least 95% by weight of these lherzolites; such an estimate is in excellent accord with geochemical considerations (e.g. the pyrolite model of Ringwood (1962) and many subsequent papers). Of these components, "FeO" is greatly subordinate to MgO, for which it readily substitutes in all the phases under consideration. Thus the simple system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (abbreviated CMAS) provides an excellent point from which to start this investigation.

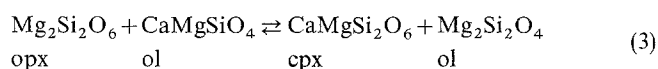
The reaction between spinel lherzolite and garnet lherzolite may in essence be written:



The reaction remains univariant in CMAS if an additional calcium-containing phase is always present to buffer the chemical potential of CaO. Since, by definition, lherzolites contain calcic clinopyroxene, this criterion is obviously met. Of the components in reaction (1), only MgAl_2O_4 spinel may fairly be taken as being a pure phase, with an activity, by the usual definition, of unity. However, the activities of all the other components are controlled by a series of what may be considered as subsidiary reactions. Hence, the calcium content of the garnet is fixed by the reaction:



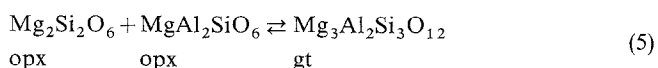
and that of olivine and both pyroxenes by:



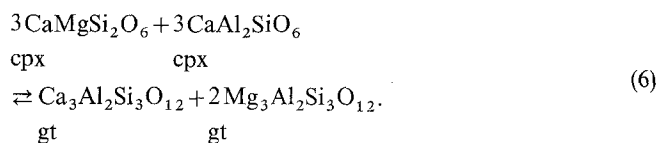
and



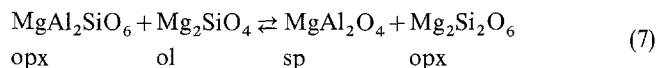
whilst the alumina content of the pyroxenes is controlled by the reactions:



and



There are, of course, other ways in which it is possible to express these compositional interdependencies. For example, reaction (5) may be combined with reaction (1) to give:



which is the reaction that controls the alumina content of enstatite in the spinel lherzolite field.

Reaction (1) in the presence of clinopyroxene was first studied by MacGregor (1965) in the temperature range 1,100°–1,500°C. The results of Kushiro and Yoder (1966), covering the range 1,175°–1,500°C, differ only by the pressure correction which they chose to apply. In contrast to the straight line in P – T space proposed by these investigators for this reaction, O'Hara et al. (1971) found a strong curvature below about 1,300°C such that at the lowest temperature of their experiments (1,100°C) the slope of the reaction had become nearly parallel to the temperature axis. The implication of this was that garnet lherzolite could not be the stable assemblage at normal crustal pressures, however low the temperature. Recently, Jenkins and Newton (1979) were able to extend the range of experimental observation down to 1,000 and 900°C by adding water to the system to increase reaction rates. They also found a very small dP/dT slope, in good agreement with that calculated from high temperature solution calorimetric data. A different approach to the problem has been taken by Obata (1976), who used the experimentally determined isopleths of Al_2O_3 in orthopyroxene in both the spinel lherzolite [reaction (7)] and garnet lherzolite [reaction (5)] fields to deduce the position of reaction (1) from their intersection, at the same time showing that the strong curvature obtained by O'Hara et al. could be explained by the increasing substitution of Al_2O_3 into orthopyroxene along the equilibrium curve with increasing temperature. Herzberg (1978) presented an analogous study using the Al_2O_3 isopleths in clinopyroxene, and came to much the same conclusions, although the calculated position of the reaction differed somewhat from that in Obata's work.

Accordingly, the first step in this study is an experimental re-investigation of reaction (1) in the system CMAS using a slightly different method.

Experimental Strategy

In order to demonstrate that equilibrium has been achieved in any experimental investigation, it is necessary to reverse the reaction (e.g. Fyfe 1960). In the simplest case, where there is no solid solution between any of the phases, the reaction $A+B \rightleftharpoons C+D$ is considered to be reversed if the assemblage $C+D$ can be grown from an initial mixture of $A+B$, and vice versa. The two experiments then bracket the reaction within a range of pressure and/or temperature. Preliminary experiments in this system showed that at 1,000°C garnet was not produced from a starting mixture of ol+opx+cpx+sp below 20.5 kb. Conversely, from ol+opx+cpx+gt, spinel did not appear above 15 kb. Thus, the reaction could only be bracketed within a range of 5.5 kb. The probable cause of this large range is the reluctance of both garnet and spinel to nucleate. Such problems are commonly encountered in experimental petrology, and so the usual procedure is to start with a mixture of all the phases present in the

reaction, and to observe the growth of one assemblage at the expense of the other. This approach has been taken by all the investigators discussed above.

An additional complication arises in cases, such as the one under consideration, if there is solid solution between the phases taking part in the univariant reaction. For example, it is conceivably possible that one or more phases exhibiting solid solution fail to change to the appropriate composition during the experiment. The observed reaction will then be a metastable variation of the true equilibrium state. Jenkins and Newton (1979) paid particular attention to this point by choosing appropriate compositions for their starting materials, such that the Al_2O_3 content for both pyroxenes and the $\text{Mg}_2\text{Si}_2\text{O}_6$ content of clinopyroxene were close to the equilibrium values as estimated from previous experimental and theoretical studies. In order to demonstrate equilibration of garnet, which in this system is a solid solution between $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, these authors duplicated their experiments with starting materials containing a garnet of both high and low Ca content.

Closely related to this problem is the necessity to ensure that the intracrystalline distribution of cations in each phase is appropriate to the conditions of the experiment. In this study this concept is best exemplified by spinel. Numerous authors have shown that many phases with the spinel structure undergo increasing disorder with increasing temperature. For MgAl_2O_4 this effect is particularly pronounced between 800° and 1,100°C (Hafner and Laves 1961; Schmocker et al. 1972), precisely the temperature interval pertinent to this study. The increase in entropy of the spinel with increasing disorder is accompanied by a decrease in enthalpy of formation, as has been demonstrated calorimetrically (Navrotsky and Kleppa 1967). Furthermore, whilst the rate of disordering of a spinel with increasing temperature is relatively rapid, the converse ordering process seems to be sluggish in the extreme (Hafner and Laves 1961).

The experimental strategy that was adopted in this study was designed to take all these factors into account. Two starting materials were prepared to correspond to a high temperature (SM1) and a low temperature assemblage (SM2) in the following manner:

SM1: A gel of appropriate composition prepared by the method of Hamilton and Henderson (1968) was crystallized in a graphite capsule in a conventional piston cylinder apparatus at 25 kb and 1,300°C. Under these conditions the Al_2O_3 content of the pyroxenes are relatively high (Obata 1976; Herzberg 1978), and the mutual clinopyroxene-orthopyroxene solubility relatively extensive. The composition of the garnet was checked by measurement of the unit cell, which when compared with the data of Newton et al. (1977) gave a value of $X_{\text{Fe}}^{\text{gt}} = 0.14$.

SM2: Pure Mg_2SiO_4 , $\text{Mg}_2\text{Si}_2\text{O}_6$ and $\text{CaMgSi}_2\text{O}_6$ were prepared hydrothermally from gels at 800°C and 1 kb. Garnet of composition $\text{Grs}_{20}\text{Py}_{80}$ was prepared in the piston cylinder apparatus in a graphite capsule at 1,100°C and 30 kb. The composition of the garnet was checked by X-ray diffraction. Appropriate amounts of the phases were mixed together and ground under acetone in an agate mortar for 20 min.

Recently a variation on the traditional approach to the determination of a univariant reaction curve has been proposed by Schmid, Wood, and Cressey (1978). An additional component is added to the system, chosen so that it only substitutes into one of the participating phases. The reaction then becomes divariant, and the position of the univariant curve may be calculated using simple thermodynamic methods to extrapolate over a range that is comparable to the inherent precision (i.e. reproducibility) of the experimental apparatus. In this case Cr_2O_3 was chosen as the additional component since it is taken up substantially by spinel to produce a large variation in the unit cell parameter of that phase. This use of the technique is not quite so elegant as that originally employed by Schmid et al., since chromium will also substitute for aluminium in the pyroxenes and garnet, but to so much lesser an extent than in the spinel that model calculations show that the effect produced is negligible. Confirmation of the reliability of the technique can be easily demonstrated by examination of Figs. 2–4 in the section concerning the effect of Cr_2O_3 on the reaction.

Accordingly, a spinel of composition $\text{MgAl}_2\text{O}_4(0.98)\text{MgCr}_2\text{O}_4(0.02)$ was prepared from an oxide mix and crystallized hydrothermally at 800°C and 1 kb. The composition was checked by X-ray diffraction and found that have $X_{\text{Cr}}^{\text{sp}} = 0.018 \pm 0.002$. It was not possible to confirm the structural state of the spinel, however, many studies (e.g. Cooley and Reed 1972; Schmalzried 1961) on other spinels show that the degree of order observed is generally that appropriate to the conditions of synthesis. The spinel was then added to SM1 and SM2, and the mixture ground under acetone.

To deduce the equilibrium univariant curve for reaction (1) from the composition of the spinel the relation

$$P^0 = P + \frac{2RT \ln(1 - x_{\text{Cr}}^{\text{sp}})}{\Delta V_{(1)}} \quad (8)$$

was used, where P^0 is the equilibrium pressure for the univariant reaction, P is the experimental pressure and $\Delta V_{(1)}$ represents the volume change of the reaction. This expression assumes that the activity of the MgAl_2O_4 component is given by simple random mixing of Al and Cr over the octahedral sites of the spinel; and that for the very low Cr contents of interest here the activity coefficient of the MgAl_2O_4 component is the Raoultian ideal of one. Both these assumptions are in retrospect justified by extrapolation from the later experiments in systems of higher Cr content at higher pressures: see Figs. 2–4. The sum of the molar volumes of the pure end member components of reaction (1) gives $\Delta V_{(1)}$ of 0.7929 J/bar at room temperature and pressure; a more appropriate value of 0.7820 has been derived by Jenkins and Newton (1979) by taking into account the stoichiometry and excess volumes of mixing of all phases, and this value has been adopted here. These authors also showed from compressibility and thermal expansion data that the effect of temperature and pressure on $\Delta V_{(1)}$ is negligible.

Experimental Details

The hydrothermal syntheses at low pressure were done in a cold seal vessel using sealed platinum capsules. The high pressure syntheses and all other runs were done in a conventional $\frac{1}{2}$ " internal diameter piston-cylinder apparatus (Boyd and England 1960). The pressure cell consisted of concentric tubes of talc, pyrex glass and graphite, with inserts of crushable alumina. Each experimental run was pressed to the required run pressure, brought to temperature, then pressurized to 5 kb over pressure before decompressing to the required value. The pressure was continuously monitored and adjusted, if necessary (except overnight). Temperatures were measured and controlled with a Pt/Pb₈₇Rh₁₃ thermocouple, separated from the capsule by a thin (~1 mm) ceramic disc. No corrections have been made for possible friction effects on pressure or for pressure effects on the thermocouple e.m.f.

For the high pressure syntheses and the equilibrium runs at 1,100°C a graphite capsule was used. This caused all starting materials to contain a small amount of finely divided graphite, colouring these mixtures a dark grey. For runs at 1,000°C and below, the starting materials were sealed into platinum capsules with some water (~5% by weight). On opening the capsules after each run it was found that the initial graphite had completely disappeared leaving the charge as a bright pink (from the chromium) powder. This was presumed to be due to the reaction of graphite with water, and the subsequent diffusion of hydrogen out of the capsule. Previous authors (e.g. Jenkins and Newton 1979) have found that below about 870°C the lherzolite transition in hydrothermal systems is obscured by the formation of hydrous phases, particularly chlorite. However, the effect of the graphite contamination of the starting materials was to lower considerably the fugacity of water in the charge, enabling the assemblage ol + opx + cpx + gt + sp + chl to be observed at 800°C. It is equivocal whether this method represents a true equilibrium reversal, but in view of the consistency of the results at 800°C with those at higher temperature, they are nevertheless reported.

All run products were examined optically, and by X-ray diffraction. The unit cell edge of the garnet and the spinel were determined by repeated scanning oscillations at $\frac{1}{4}^\circ 2\theta$ per minute using a standard

of ultrapure lead nitrate that itself was carefully calibrated against a standard of X-ray grade silicon. Because of interference from other peaks, only the 420 garnet and 311 spinel reflections were used. At least twelve oscillations were measured with a ruler with a vernier scale that could be read to 0.02 mm.

In order to obtain spinel compositions from the cell edge measurements, pure MgCr_2O_4 was synthesized at 800°C and 1 kb; and MgAl_2O_4 from a mixture of ol + opx + cpx + sp synthesized at 15 kb, 900° and 1,100° C. The MgCr_2O_4 had a cell edge of 8.3334 Å and the two MgAl_2O_4 spinels 8.0840 and 8.0844 respectively, giving an average of 8.0842 Å. For the small concentrations of MgCr_2O_4 of interest here a linear relationship between cell edge and composition was assumed. The garnet composition was determined from the data of Newton et al. (1977) as numerically expressed in Jenkins and Newton (1979).

The continual adjustment of pressure (when necessary) allowed each run to be controlled with ± 0.2 kb of the nominal value. The additional uncertainty arising from the uncertainty in measurement of spinel composition and the appropriate value of ΔV for reaction (1) in the CMAS system comes to about ± 0.1 kb. Hence the precision in reported pressure is ± 0.3 kb. No correction has been made to the nominal pressure for possible friction effects.

The methods described above for CMAS were also used for the investigation of the system CMAS–Cr₂O₃. Three different starting materials were prepared as follows:

SM3: SM1 was mixed with a spinel of composition $\text{MgAl}_2\text{O}_4(0.5) - \text{MgCr}_2\text{O}_4(0.5)$ and a small amount of grossular garnet. The spinel was synthesized hydrothermally at 800°C, 1 kb, and the garnet at 670°C, 1.5 kb. The resulting mixture was ground under acetone for about 20 min.

SM4: In like manner SM1 was mixed with MgCr_2O_4 spinel and grossular garnet, and ground for ~20 min.

SM5: SM4 was pre-reacted in a graphite capsule at 1,000°C, 35 kb, and then lightly reground.

Run products were examined optically and by X-ray diffraction. The unit cell edge of the spinel was determined by measuring the 111 reflection only by repeated scanning oscillations at $\frac{1}{4}^\circ 2\theta$ per minute, using quartz as a standard, as all other peaks were at some conditions obscured by those from other phases. The composition of the spinel was then determined by using a linear interpolation between the cell edges of the two end members (Warshaw and Keith 1954). The low 2θ angle of this reflection, and its poor development in many runs with only a small amount of spinel, meant that the spinel composition could only be determined to about 2 to 5 mole percent.

Results in CMAS

The results of runs in the CMAS system are given in Table 1 and shown graphically in Fig. 1. It is apparent from the consistency in equilibrium pressure calculated from Equation [8] that the reaction has substantially gone to completion, regardless of whether $X_{\text{Cr}}^{\text{sp}}$ has increased or decreased, or which starting mixture was used. This may reflect either the long run times used in this study, or the efficacy of CO₂–H₂O mixtures as a flux, or the contention of Schmidt et al. (1978) that small amounts of additional components do indeed increase reaction rates.

The equilibrium pressure for the univariant reaction at 1,100°C (18.7 ± 0.3 kb) is in excellent agreement with the brackets obtained by O'Hara et al. (1971) of 17.75 and 19.0 kb. However, a small discrepancy exists between the pressures reported here for the reaction at 900° and 1,000°C of 16.7 and 17.3 ± 0.3 kb and those given by Jenkins and Newton (1979) of 15.0 and 16.0 ± 0.5 kb respectively. These latter authors used sodium chloride, as opposed to talc, as the pres-

Table 1. Results of experiments to determine the univariant reaction spinel lherzolite to garnet lherzolite

| $T(^{\circ}\text{C})$ | $P(\text{kb})$ | time (hours) | Starting material | Phase absent | $X_{\text{Cr}}^{\text{sp}}$ | ΔP | Eq. (8) | $X_{\text{Ca}}^{\text{gt}}$ |
|-----------------------|----------------|--------------|-------------------|-----------------|-----------------------------|------------|---------|-----------------------------|
| +800 | 16.8 | 40 | 1 | opx | 0.022 | -0.5 | <16.3 | |
| +800 | 16.2 | 23 | 1 | Gt ^a | 0.012 | -0.3 | >15.9 | |
| +800 | 16.5 | 59 | 1 | — | 0.017 | -0.4 | 16.1 | 0.176 |
| +800 | 16.5 | 65 | 2 | — | 0.016 | -0.4 | 16.1 | |
| 900 | 16.7 | 60 | 1 | Gt | 0.005 | -0.1 | >16.6 | |
| 900 | 17.3 | 44 | 1 | — | 0.022 | -0.6 | 16.7 | |
| 900 | 18.2 | 34 | 2 | — | 0.053 | -1.4 | 16.8 | 0.168 |
| 1,000 | 17.6 | 30 | 1 | — | 0.017 | -0.4 | 17.2 | |
| 1,000 | 18.0 | 42 | 1 | — | 0.027 | -0.8 | 17.2 | 0.164 |
| 1,000 | 18.2 | 47 | 2 | — | 0.030 | -0.8 | 17.4 | |
| 1,100 | 19.8 | 26 | 1 | — | 0.034 | -1.0 | 18.8 | 0.158 |
| 1,100 | 17.8 | 25 | 1 | Gt | 0.010 | -0.3 | >17.5 | |
| 1,100 | 18.4 | 17 | 1 | Gt | 0.009 | -0.3 | >18.1 | |
| 1,100 | 19.5 | 25 | 1 | — | 0.030 | -0.9 | 18.6 | |
| 1,100 | 19.5 | 27 | 2 | — | 0.028 | -0.8 | 18.7 | |

^a Trace Gt; + Chlorite

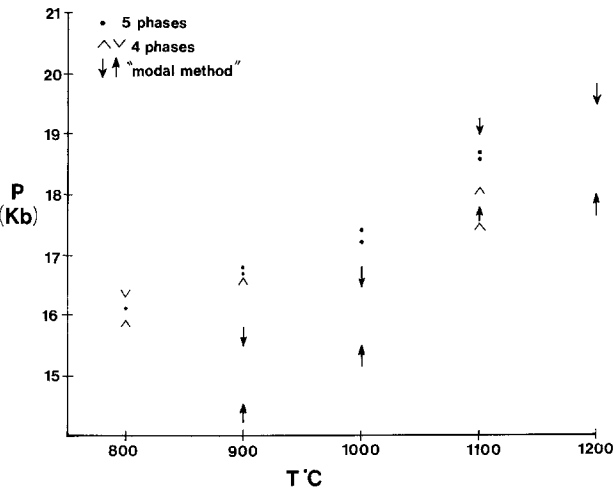


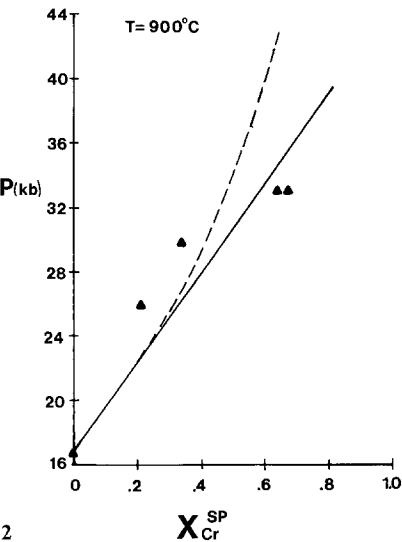
Fig. 1. The univariant equilibrium between spinel lherzolite and garnet lherzolite in the system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. For comparison the brackets obtained by Jenkins and Newton (1979) at 900° and 1,000° C, and those by O'Hara et al. (1971) at 1,100° and 1,200° C, are also shown

sure transmitting medium in their experiments, which may explain this difference. Furthermore, Jenkins and Newton do not explicitly state the method by which they prepared the spinel in their study. It is possible that the discrepancy noted here may reflect the failure of a spinel with a high degree of disorder to re-equilibrate structurally at these low temperatures, thus promoting the metastable growth of gt+ol below the true equilibrium curve.

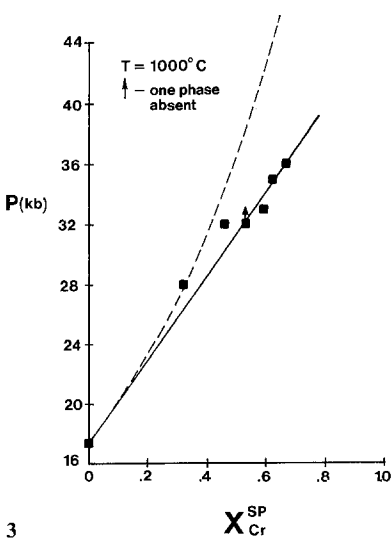
The Addition of Cr_2O_3 to CMAS

The results of experiments in the system $\text{CMAS}-\text{Cr}_2\text{O}_3$ are presented in Table 2 and Figs. 2-4. Cr_2O_3 is heavily partitioned into one of the phases in reaction (1), spinel, thus creating a divariant assemblage of ol+gt+opx+cpx+sp which can exist over a fairly wide pressure interval. Were spinel to be the only chromium containing phase, the equilibrium could be expressed by:

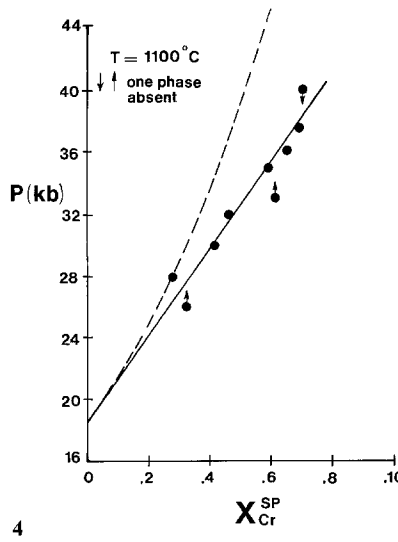
$$\frac{(P-P^0)\Delta V(1)}{RT} = -\ln a_{\text{MgAl}_2\text{O}_4} \quad (9)$$



2



3



4

Figs. 2-4. The effect of Cr_2O_3 on the transition between spinel and garnet lherzolite in the system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Cr}_2\text{O}_3$ at 900° C, 1,000° C and 1,100° C

and the curve for this expression has been plotted in each figure by assuming a two-site ideal solution model for the spinel ($a_{\text{MgAl}_2\text{O}_4} = X_{\text{Al}}^{\text{sp}^2}$). It can be seen that the experimental data approach this ideal situation closely at low values of $X_{\text{Cr}}^{\text{sp}}$ and low pressures, but diverge quite markedly at higher pressures. There are two reasonable "end-member" explanations for this:

1. MgAl_2O_4 – MgCr_2O_4 spinels mix with a positive deviation from ideality.

2. Cr (and hence Ca) increasingly substitute into garnet with increasing pressure, as observed in natural ilherzolite.

The truth probably lies somewhere in between these two extremes. Unfortunately, it was impossible to determine the composition of the garnet by electron microprobe methods as in every run the garnet crystals, although fairly large (~50–100 μm) and euhedral, were packed with myriads of small inclusions, even though the garnets grown in pure CMAS were almost completely inclusion free.

It appears that, for no good theoretical reason, the relationship between equilibrium pressure and $X_{\text{Cr}}^{\text{sp}}$ may be adequately expressed by a simple linear equation. Regression of the data in Table 2 according to the expression

$$P = P^0 + \alpha X_{\text{Cr}}^{\text{sp}} (kb) \quad (10)$$

yields values of α of 27.5, 28.5 and 27.6 at 1,100°, 1,000° and 900° C respectively. A mean value of α , weighted according to the number of datum points at each temperature, is 27.9. A purely empirical expression of this type cannot be extrapolated with confidence to any higher pressure and $X_{\text{Cr}}^{\text{sp}}$ than the range covered in the experiments.

The Systems CMAS–"FeO" and CMAS– Cr_2O_3 –"FeO"

Quantitatively, "FeO" is a much more important component of natural ilherzolite compositions than Cr_2O_3 ; however, since it substitutes in a fairly even way for MgO in each of the phases in reaction (1) (and also in clinopyroxene) its net effect on the position of the equilibrium is likely to be less dramatic. What this effect may be is neither so readily amenable

to experimental investigation, because of iron loss to noble metal capsules and the problems of precisely controlling the oxidation state: as will be shown later, quite minor amounts of Fe^{3+} may be supposed to counteract the addition of more substantial amounts of Fe^{2+} . Fortunately, there is now a considerable amount of information available in the literature on the thermodynamic properties of iron-magnesium solid solutions, and on the partitioning of iron and magnesium between the various phases of garnet-spinel ilherzolites, and it therefore seems timely to attempt to solve the problem by calculation.

The equilibrium of reaction (1) may be written:

$$\Delta G(1)^0 + P^0 \Delta V(1) = -RT [\ln a_{\text{Mg}_2\text{SiO}_4}^0 + \ln a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^0 - 2 \ln a_{\text{Mg}_2\text{Si}_2\text{O}_6}^0 - \ln a_{\text{MgAl}_2\text{O}_4}^0] \quad (11)$$

where the superscript 0 refers to the iron-free system at a pressure of 1 bar and the temperature of interest. On addition of iron, the equilibrium shifts to another pressure such that:

$$\Delta G(1)^0 + P \Delta V(1) = -RT [\ln a_{\text{Mg}_2\text{SiO}_4} + \ln a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}} - 2 \ln a_{\text{Mg}_2\text{Si}_2\text{O}_6} - \ln a_{\text{MgAl}_2\text{O}_4}]. \quad (12)$$

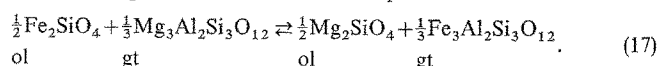
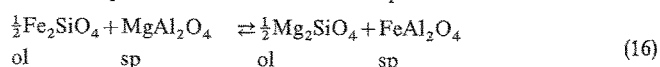
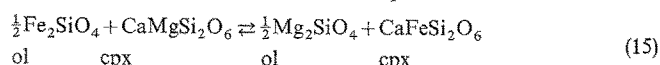
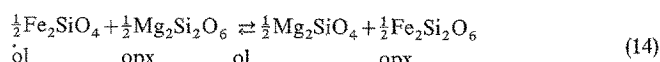
Subtracting (11) from (12) and assuming that $\Delta V(1)$ remains constant over the small change of pressure, one obtains:

$$\frac{(P - P^0) \Delta V(1)}{RT} = \ln \left(\frac{a_{\text{Mg}_2\text{SiO}_4}^0}{a_{\text{Mg}_2\text{SiO}_4}} \right) + \ln \left(\frac{a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^0}{a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}} \right) - 2 \ln \left(\frac{a_{\text{Mg}_2\text{Si}_2\text{O}_6}^0}{a_{\text{Mg}_2\text{Si}_2\text{O}_6}} \right) - \ln \left(\frac{a_{\text{MgAl}_2\text{O}_4}^0}{a_{\text{MgAl}_2\text{O}_4}} \right). \quad (13)$$

The role of Fe^{2+} on the activities in the relationship expressed in (13) above may be thought of as being due to three points, which, in likely order of importance are:

1. The dilution of Mg with Fe^{2+} , which depends on how much iron is partitioned into each phase;
2. The effect of Fe^{2+} on the subsidiary reactions (2) to (6);
3. The change in activity coefficients due to Fe^{2+} –Mg and other non-ideal interactions.

Equation (13) may be solved if we let the composition of the olivine be fixed at some iron to magnesium ratio. Then the amount of iron in each of the other phases is controlled by a series of exchange reactions between olivine and respectively, orthopyroxene, clinopyroxene, garnet and spinel, which may be written:



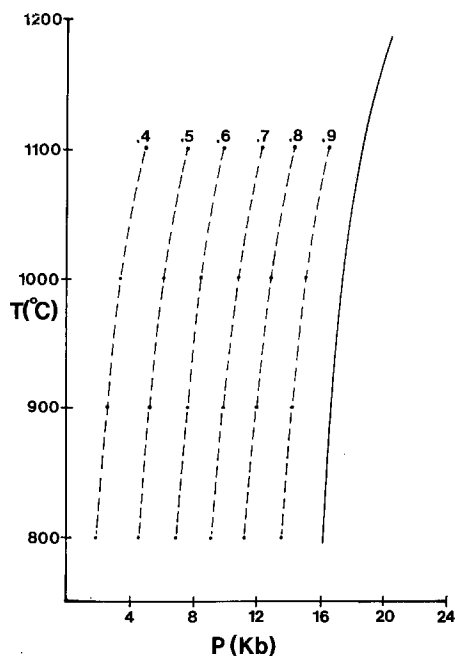
The literature contains varying amounts of experimental data on all these partitioning reactions, and therefore allows the computation of point 1 mentioned above. At the same time activity coefficients for the Fe^{2+} –Mg interactions are also obtained: their total effect on Eq. [13] is likely to be small (for the twin reasons that they represent only small amounts of free energy relative to $\Delta G(1)$ and that they will tend to cancel each other out) but since they are available

Table 2. Experimental results in the system CMAS– Cr_2O_3

| $T(^{\circ}\text{C})$ | $P(kb)$ | Starting material | Cell edge of spinel (\AA) | of $X_{\text{Cr}}^{\text{sp}}$ | Time (hours) | Phases missing |
|-----------------------|---------|-------------------|--------------------------------------|--------------------------------|--------------|----------------|
| 900 | 26 | 3 | 8.137 | 0.21 | 47 | |
| 900 | 31 | 3 | 8.169 | 0.34 | 45 | |
| 900 | 33 | 4 | 8.243 | 0.64 | 54 | |
| 900 | 33 | 5 | 8.252 | 0.67 | 66 | |
| 1,000 | 28 | 3 | 8.163 | 0.32 | 68 | |
| 1,000 | 32 | 3 | 8.198 | 0.46 | 48 | |
| 1,000 | 32 | 5 | 8.216 | 0.53 | 50 | gt |
| 1,000 | 33 | 4 | 8.230 | 0.59 | 24 | |
| 1,000 | 35 | 5 | 8.238 | 0.62 | 24 | |
| 1,000 | 36 | 4 | 8.251 | 0.67 | 22 | |
| 1,100 | 26 | 3 | 8.164 | 0.32 | 22 | gt |
| 1,100 | 28 | 3 | 8.153 | 0.28 | 16 | |
| 1,100 | 30 | 3 | 8.187 | 0.41 | 44 | |
| 1,100 | 32 | 3 | 8.198 | 0.46 | 24 | |
| 1,100 | 33 | 5 | 8.236 | 0.61 | 21½ | gt |
| 1,100 | 35 | 5 | 8.232 | 0.59 | 21½ | |
| 1,100 | 36 | 4 | 8.246 | 0.65 | 66 | |
| 1,100 | 37½ | 4 | 8.256 | 0.69 | 7 | |
| 1,100 | 40 | 4 | 8.262 | 0.71 | 23 | cpx |

Table 3. Thermodynamic constants for reactions (13) to (16)

| Reaction | ΔH (J) | ΔS (J/°K) | ΔV (J/kb) | W_{MgFe} (J) | Other interaction parameters (J) |
|---------------|----------------------|----------------------|----------------------|---|---|
| (14) (opx-ol) | 1,870 | -0.93 | 32 | ol = 3,760 + 13 P opx = 1,580 - 31 P | |
| (15) (cpx-ol) | 9,620 (P = 30 kb) | 10.64 | 36 | ol = 3,760 + 13 P cpx = 0 | |
| (16) (sp-ol) | -5,940 (P = 1 kb) | -4.18 | -28 | ol = 3,760 + 13 P sp = 0 | |
| (17) (gt-ol) | -7,490 | -2.97 | -62 + corrections | ol = 3,760 + 13 P gt = 800 | $W_{\text{MgCa}}^{\text{gt}} = 11,200$ $W_{\text{FeCa}}^{\text{gt}} = 0$ |

**Fig. 5.** The calculated effect of "FeO" on the transition between spinel and garnet lherzolite. Contours are shown in $X_{\text{Mg}}^{\text{ol}}$

they might as well be used. Point 2, the effect of Fe^{2+} on reactions (2) to (6), can, in principle, be evaluated using a similar subtraction method to that embodied in Equation [13] for the main reaction, but, for simplicity, only reaction (2) has in fact been considered (see Appendix 1). Nevertheless, even after such simplifications we are left with a large system of inter-related equations, none of which are linear. For this reason the details of the assumptions, activity - composition models and methods of calculation have been relegated to Appendix 1, and the thermodynamic parameters used are summarized in Table 3. The results of the calculation for the Cr_2O_3 -free system are shown graphically in Fig. 5. The accuracy of the calculation will decrease with increasing iron, but most natural lherzolites are sufficiently iron-poor for the error to remain small.

In many natural lherzolites olivine predominates over all the other phases in modal proportion. This, coupled with the fact that the distribution of iron and magnesium between olivine and the next most abundant phase, orthopyroxene, is relatively insensitive to changes in temperature and pressure, means that olivine and orthopyroxene act as a reservoir for

ferrous iron: thus the incoming of a new phase in small amounts should cause negligible change in the composition of the olivine. Consequently, Fig. 5 may be used directly to predict the pressure at which the transition between spinel lherzolite and garnet lherzolite will occur along any geotherm.

Other Components

Na_2O

Sodium is partitioned almost entirely into clinopyroxene. The effect of this may be deduced from perusal of reaction (2). The addition of sodium to the clinopyroxene will reduce the activity of the $\text{CaMgSi}_2\text{O}_6$ component, thus shifting reaction (2) to the right, so forming a garnet with lower calcium content and moving the equilibrium for reaction (1) to a higher pressure. For the typical clinopyroxenes in natural lherzolites this effect is probably negligible, but cannot reliably be quantified through lack of data on the mixing properties of sodic pyroxenes.

Fe_2O_3

The exact chemical behaviour of ferric iron in lherzolites is not known, not least because analyses mostly do not differentiate between ferric and ferrous iron. However, crystal chemical considerations lead one to believe that Fe_2O_3 behaves similarly to Cr_2O_3 ; support for this conclusion comes from the experimental investigation that MacGregor (1970) undertook on reaction (1) in complex systems with variable ratios of Al_2O_3 : Cr_2O_3 : Fe_2O_3 . Unfortunately it is not possible to draw any conclusions about the relative magnitudes of the effects of Cr_2O_3 and Fe_2O_3 from this study, as these two components are very highly positively correlated in MacGregor's starting mixtures. Therefore, as a first approximation it has been assumed that the value of α from Equation [10] may be multiplied by $X_{\text{Fe}^{3+}}^{\text{sp}}$ to derive the change in pressure of the equilibrium with increasing Fe^{3+} content of the spinel.

The Use of the Equilibrium Between Spinel Lherzolite and Garnet Lherzolite as a Geobarometer

The pioneering study of Boyd (1973), on the use of chemical equilibria on lherzolite samples brought up from great depths by kimberlite eruptions to determine the temperature and pressure of equilibration of these unique examples of the

Table 4. The geothermometry and geobarometry of some garnet-spinel-lherzolite nodules

| Nodule | $T(^{\circ}\text{K})$ gt-ol ⁴ | $T(^{\circ}\text{K})$ opx-cpx ⁵ | $T(^{\circ}\text{K})$ ol-sp ^{6,4} | $T(^{\circ}\text{K})$ gt-cpx ⁷ | $P(\text{kb})$ | $X_{\text{Al}}^{\text{opx}}$ |
|----------------------|---|---|---|--|----------------|------------------------------|
| Lesotho ¹ | | | | | | |
| 1,595 | 1,155 | 1,154 | 1,206 | 1,183 | 31.4 | 0.037 |
| 1,567 | 1,172 | 1,187 | 1,217 | 1,220 | 32.6 | 0.038 |
| 1,592 | 1,162 | 1,192 | 1,160 | 1,173 | 33.4 | 0.039 |
| 1,570 | 1,185 | 1,202 | 1,174 | 1,181 | 32.6 | 0.037 |
| 1,573 | 1,113 | 1,212 | 1,143 | 1,236 | 31.8 | 0.036 |
| 1,572 | 1,197 | 1,212 | 1,139 | 1,333 | 32.7 | 0.038 |
| Malaita ² | | | | | | |
| 3,567 | 1,295 | 1,181 | 1,081 | 1,210 | 23.5 | 0.113 |
| N.S.W. ³ | | | | | | |
| 75210052/39 | 1,608 | 1,331 | 1,161 | 1,436 | 25.1 | 0.184 |

¹ Nixon and Boyd (1973)² Nixon and Boyd (1979)³ Ferguson and Sheraton⁴ This work⁵ Wells (1977)⁶ Engi (1978)⁷ Ellis and Green (1979)

upper mantle, has stimulated great interest in the precise geothermometry and geobarometry of these rocks. In addition to the original geothermometer using the orthopyroxene-clinopyroxene equilibrium, there are now a number of other experimentally determined geothermometers available to confirm Boyd's broad conclusions. However, geobarometry of these rocks still depends on the alumina content of orthopyroxene co-existing with garnet. Since a few nodules contain the five phase assemblage ol + opx + cpx + gt + sp, the equilibrium between spinel lherzolite and garnet lherzolite, which, as can be seen from the preceding sections, is very insensitive to temperature in the range 900°–1,100° C, can profitably be used to evaluate the effectiveness of the aluminous orthopyroxene geobarometer.

The procedure for using this geobarometer is outlined in the following verbal algorithm:

1. Estimate T hence P^0 (for the reaction in CMAS).
2. Calculate $P = P^0 + 27.9(X_{\text{Cr}}^{\text{sp}} + X_{\text{Fe}^{3+}}^{\text{sp}})$.
3. Calculate the pressure correction for Fe^{2+} using the method and data of Appendix 1.

It is a simple matter to estimate qualitatively the likely errors in this procedure. Firstly, we have systematic errors in the pressure and temperature calibration of the experimental apparatus. However, since the purpose of this exercise is to compare the pressures of equilibration of different rocks, these systematic errors (which are also present in experimental calibrations of other geobarometers) will not be further considered. Non-systematic errors may be due to:

1. The error in the estimate for T . The $P-T$ gradient for reaction (1) is 100° C/kb at 1,000° C: hence an uncertainty in T of $\pm 50^{\circ}\text{C}$ corresponds to an uncertainty in P^0 of only $\pm \frac{1}{2}\text{kb}$. This may be compared with the aluminous orthopyroxene geobarometer, in which the $P-T$ gradient of an isopleth of Al_2O_3 is $\sim 15^{\circ}\text{C}/\text{kb}$ (Wood 1974) and so in which $\pm 50^{\circ}\text{C}$ corresponds to $\pm 3.3\text{kb}$.
2. The error in the estimate of P^0 from the experiments ($\pm 0.3\text{kb}$).
3. Any errors involved in constraining the experimental data to fit the empirical expression of Eq. [10]. Most of these errors will produce a systematic error in the calculated equilibrium pressure; but there may also be a non-systematic component in comparing systems at different T and $X_{\text{Cr}}^{\text{sp}}$.
4. Errors in the correction procedure for Fe^{2+} .
5. Errors in the analytical data of the minerals in the rocks. Of these, overwhelmingly the most important will be the errors in the analysis of the spinel, the Fe^{3+} content of which must be obtained by assuming perfect stoichiometry in

a microprobe analysis. An uncertainty of ± 0.05 in $X_{\text{Cr}}^{\text{sp}} + X_{\text{Fe}^{3+}}^{\text{sp}}$ will cause an uncertainty of $\pm 1.5\text{kb}$. This is similar to the expected uncertainty in changing $X_{\text{Al}}^{\text{Mg}}$ from 0.020 to 0.018 in the aluminous orthopyroxene geobarometer (Wood 1974; Equation [12]).

The geobarometer has been applied to six nodules from the Thaba Putsoa kimberlite, Lesotho (Nixon and Boyd 1973). The results are tabulated in Table 4. Also shown for comparison are the results on two nodules containing more aluminous spinel from Malaita, Solomon Islands (Nixon and Boyd 1979) and New South Wales (Ferguson and Sheraton 1979). Temperatures were calculated using:

- a) The olivine-garnet geothermometer of O'Neill and Wood (1979), assuming $P = 30\text{kb}$;
- b) The two pyroxene geothermometer of Wells (1977);
- c) An olivine-spinel geothermometer formulated from reaction (16) and corrected for Cr and Fe^{3+} by using the thermodynamic data for reactions (A9) and (A10);
- d) The clinopyroxene-garnet thermometer of Ellis and Green (1979).

Pressure was calculated assuming the temperature of (a). Also shown is $X_{\text{Al}}^{\text{opx}}$, the main ingredient of the aluminous orthopyroxene geobarometer.

It is particularly interesting to note that all the Lesotho nodules fall within a very narrow range of calculated equilibration pressures. These nodules also have almost identical alumina content in orthopyroxene, and show no systematic trends for the temperatures calculated using all three methods. This strongly suggests to the author that all the nodules equilibrated at essentially the same temperature and pressure, and that the apparent "geotherm" that they would record if only the aluminous orthopyroxene method was used as a geobarometer is, in fact, merely due to the temperature dependence of that geobarometer coupled with the uncertainties in the accompanying geothermometer. It therefore appears to be of utmost importance that both the precision and the accuracy of the various geothermometers be fully evaluated for the mineral assemblages to which they are applied before the results they purport to record can be described as part of a "geotherm". This has been done for four nodules from Lesotho by Boyd and Finger (1975); however, they only calculate the uncertainty in temperature to be expected from the variation in Ca/Ca+Mg in diopside when applied to the simple pyroxene miscibility gap in the system CMAS.

In conclusion, it has been shown that the equilibrium between garnet and spinel lherzolites is particularly sensitive to the Cr^{3+} , and also the Fe^{3+} , content of the rock, since

both these species are heavily partitioned into the spinel. The alumina content of the spinel can be used as an alternative geobarometer for those rare rocks that contain the five phases garnet, spinel, olivine and two pyroxenes in equilibrium. The application of this geobarometer to some upper mantle nodules from Lesotho casts doubt on the precision of the currently available geothermometers.

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Appendix

The following is a summary of the activity-composition models and the experimental partitioning data between olivine and the other phases of reactions (1) and (2) which it is necessary to use in order to correct the equilibrium of reaction (1) for compositions containing Fe^{2+} .

Olivine

Olivine is taken to be a simple symmetric regular solution (Thompson 1967) in the binary Mg_2SiO_4 – Fe_2SiO_4 . The two crystallographic sites are assumed to be thermodynamically equivalent, so that we may write:

$$\ln a_{\text{Mg}_2\text{SiO}_4} = 2 \ln X_{\text{Mg}}^{\text{ol}} + 2 \frac{W_{\text{MgFe}}}{RT} (1 - X_{\text{Mg}}^{\text{ol}})^2. \quad (\text{A1})$$

In the iron-free system the olivine of interest is nearly pure MgSiO_4 , so that $a_{\text{Mg}_2\text{SiO}_4}^0 = 1$.

Matsui and Nishizawa (1974) have shown that in applying the simple regular solution model to Fe^{2+}/Mg partitioning data between two co-existing phases it is only possible to derive the *difference* between the magnitude of the W parameters for each of the phases with any certainty (e.g. $W_{\text{MgFe}}^{\text{ol}} - W_{\text{MgFe}}^{\text{opx}}$). Therefore, in order to preserve internal consistency, the value for $W_{\text{MgFe}}^{\text{ol}}$ derived from the experimental study of O'Neill and Wood (1979) on olivine-garnet equilibria has been used throughout in the analyses of the data on the other exchange reactions. Little chauvinism is intended.

Orthopyroxene

Orthopyroxene solid solutions present a considerably more complex problem than olivines, since the mixing of a number of components over four crystallographically distinct sites is involved. In order to reduce the problem to a manageable level we must adopt some simplifying assumptions. The data on the Fe^{2+} – Mg exchange reaction between olivine and orthopyroxene in the subsystem MgO –“ FeO ”– SiO_2 suggest that these binary Fe^{2+} – Mg orthopyroxenes may, too, be treated as a simple regular solution. If we extend this regular solution model to the multicomponent system, then we obtain, treating each site individually:

$$RT \ln \gamma_{\text{Mg}_2\text{Si}_2\text{O}_6}(\text{M1 site}) = W_{\text{FeMg}}^{\text{M1}} (X_{\text{Fe}}^{\text{M1}})^2 + W_{\text{MgAl}}^{\text{M1}} (X_{\text{Al}}^{\text{M1}})^2 + (W_{\text{MgFe}}^{\text{M1}} + W_{\text{MgAl}}^{\text{M1}} - W_{\text{FeAl}}^{\text{M1}}) (X_{\text{Fe}}^{\text{M1}}) (X_{\text{Al}}^{\text{M1}}) \quad (\text{A2})$$

and so on for the other sites. But in the iron-free system,

$$RT \ln \gamma_{\text{Mg}_2\text{SiO}_6}(\text{M1 site}) = W_{\text{MgAl}}^{\text{M1}} (X_{\text{Al}}^{\text{M1}})^2. \quad (\text{A3})$$

Now, suppose that, since Fe^{2+} is so much more similar to Mg in

its crystallochemical properties than to Ca or Al, $W_{\text{MgAl}}^{\text{M1}} = W_{\text{FeAl}}^{\text{M1}}$, etc., and that the introduction of small amounts of Fe^{2+} has no effect on the Ca or Al content of the orthopyroxene (i.e. has no effect on the subsidiary reactions (4) and (5)). Then, subtracting (A3) from (A2) we obtain:

$$RT \ln \left(\frac{\gamma_{\text{Mg}_2\text{Si}_2\text{O}_6}}{\gamma_{\text{Mg}_2\text{SiO}_6}^0} \right) = W_{\text{MgFe}}^{\text{M1}} (X_{\text{Fe}}^{\text{M1}} (1 - X_{\text{Mg}}^{\text{M1}})) \quad (\text{A4})$$

and so on for the other sites. By a similar argument we can ignore any reciprocal terms between the sites by assuming that they, too, cancel. Furthermore, as in the original extraction of the thermodynamic parameters from the olivine-orthopyroxene Fe^{2+}/Mg partitioning experiments, we treat the Fe^{2+}/Mg ratio as being the same in both sites, and therefore the same as that in the phase as a whole, so that $W_{\text{FeMg}}^{\text{M1}} = W_{\text{FeMg}}^{\text{M2}}$. This gives the expression:

$$RT \ln \left(\frac{a_{\text{Mg}_2\text{Si}_2\text{O}_6}}{a_{\text{Mg}_2\text{SiO}_6}^0} \right) = RT \ln \left(1 - \frac{X_{\text{Fe}}^{\text{M1}}}{X_{\text{Mg}}^{\text{M1}}} \right) \cdot \left(1 - \frac{X_{\text{Fe}}^{\text{M2}}}{X_{\text{Mg}}^{\text{M2}}} \right) + W_{\text{MgFe}}^{\text{opx}} [X_{\text{Fe}}^{\text{M1}} (X_{\text{Fe}}^{\text{M1}} + X_{\text{Al}}^{\text{M1}}) + X_{\text{Fe}}^{\text{M2}} (X_{\text{Fe}}^{\text{M2}} + X_{\text{Ca}}^{\text{M2}})].$$

The Al and Ca contents of the sites may be estimated, if required, from other experimental work in the literature. However, for temperatures $< 1,000^\circ\text{C}$ and the pressure range of interest in this study the amount of both these species in the orthopyroxene is very low, and so, for the small values of X_{Fe} (~ 1) appropriate to natural compositions, errors in the activity ratio of only about 2% (corresponding to an error in $P - P^0$ of about 0.05 kb) will result from completely ignoring them. Thus, similar to the expression for olivine, we may use:

$$RT \ln \left(\frac{a_{\text{Mg}_2\text{Si}_2\text{O}_6}}{a_{\text{Mg}_2\text{SiO}_6}^0} \right) = 2RT \ln (1 - X_{\text{Fe}}^{\text{opx}}) + 2W_{\text{MgFe}}^{\text{opx}} (X_{\text{Fe}}^{\text{opx}})^2. \quad (\text{A6})$$

A number of authors have experimentally determined the partitioning of iron between olivine and orthopyroxene [reaction (14)] in the simple system MgO –“ FeO ”– SiO_2 . The pertinent data are summarized in Matsui and Nishizawa (1974).

For the purposes of this study this data have been reduced in the following manner:

1. Using the olivine interaction parameter of O'Neill and Wood (1979) the data of Matsui and Nishizawa themselves at $1,000^\circ\text{C}$ and 30 kb (which cover the largest range in composition) were linearly regressed to yield $\Delta G(14)$ and the interaction parameter for orthopyroxene ($W_{\text{MgFe}}^{\text{opx}}$).
2. The pressure dependence ($\Delta V(14)$) of the reaction, and that of $W_{\text{MgFe}}^{\text{opx}}$ were determined from the molar volume versus composition data of Matsui et al. (1968).
3. These parameters were applied to the data of Larimer (1968) at 1,100, 1,200° and 1,300° C, 1 atm. (which are entirely at the high magnesium end of the composition range) and to the synthesis data only of Medaris (1969) at 800° and 900° C to determine the temperature dependence of the reaction ($\Delta H(14)$ and $\Delta S(14)$).

Clinopyroxene

Clinopyroxene solid solutions are treated in an analogous manner to orthopyroxene, so that:

$$RT \ln \left(\frac{a_{\text{CaMgSi}_2\text{O}_6}}{a_{\text{CaMgSiO}_6}^0} \right) = RT \ln \left(1 - \frac{X_{\text{Fe}}^{\text{cpx}}}{X_{\text{Mg}}^{\text{cpx}}} \right) + W_{\text{MgFe}}^{\text{cpx}} (X_{\text{Fe}}^{\text{cpx}} (1 - X_{\text{Mg}}^{\text{M2 cpx}})). \quad (\text{A7})$$

No such body of data as given for reaction (14) exists for olivine-clinopyroxene partitioning [reaction (15)]. However, Mori and Green (1978, p. 92) have presented an algorithm for this equilibrium based on their experimental results on synthetic compositions resembling natural systems. This algorithm has here been modified to take into account both the nonideality of the olivine and the pressure dependence of the reaction by assuming $X_{\text{Mg}}^{\text{ol}} = 0.9$ and $P = 30$ kb. $\Delta V(15)$ was calculated from the molar volume data of Turnock et al.

(1973) on clinopyroxenes, Fisher and Medaris (1969) on olivines. $W_{\text{MgFe}}^{\text{cpx}}$, for lack of any evidence to the contrary, was assumed to be zero.

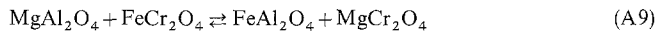
Spinel

Since the original study of Irvine (1967, 1969) the iron-magnesium exchange reaction between olivine and spinel [reaction (16)] has received considerable attention for use as a potential geothermometer. Nevertheless, there is as yet poor agreement as to an accurate evaluation of the thermodynamic data (Roeder et al., 1979). Engi (1978) has presented some experimental data in the temperature range 650°–800°C that are well reversed, and these have been used. However, the range in Fe/Mg ratio in this study is not adequate to determine the mixing properties of the spinel solid solution, and so this has been assumed to be ideal; moreover the narrow temperature interval of the experiments does not permit the calculation of the temperature dependence of the reaction with any great confidence.

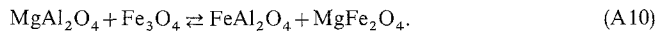
It is quite apparent from all of these studies that the Cr (and Fe^{3+}) content of the spinel exerts a lot of influence on the Fe^{2+}/Mg partitioning reaction, due to the reciprocal solid solution effect (e.g. Wood and Nicholls 1978). Hence, for these complex systems we must first take into account the effect of these components on reaction (16) by expressing this equilibrium as:

$$RT \ln K_D(16) = -\Delta G(16) + (1 - 2X_{\text{Mg}}^{\text{ol}}) W_{\text{MgFe}}^{\text{ol}} + X_{\text{Cr}}^{\text{sp}} \Delta G(A9) + X_{\text{Fe}^{3+}}^{\text{sp}} \Delta G(A10) \quad (A8)$$

where $\Delta G(A9)$ refers to the free energy of the reaction:



and $\Delta G(A10)$ to the reaction:



$\Delta G(A9)$ has been taken from the data of Engi (1978) as 20,460 – 2.09T (Joules) and $\Delta G(A10)$ from that in Robie et al. (1978) as 10,150 – 1.74T.

Reaction (16) may be easily formulated as a geothermometer: the consistent results obtained with it (see Table 4) give great confidence in the thermodynamic values used above.

Thus, using the same approach we may write:

$$RT \ln \left(\frac{a_{\text{MgAl}_2\text{O}_4}^{\text{ol}}}{a_{\text{FeAl}_2\text{O}_4}^{\text{ol}}} \right) = RT \ln (1 - X_{\text{sp}}^{\text{Fe}^{2+}}) + X_{\text{sp}}^{\text{Fe}^{2+}} X_{\text{sp}}^{\text{Cr}} \Delta G(A9) + X_{\text{sp}}^{\text{Fe}^{2+}} X_{\text{sp}}^{\text{Fe}^{3+}} \Delta G(A10). \quad (A11)$$

Garnet

Whilst the work of Newton et al. (1977) on $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ – $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and Cressey et al. (1978) on $\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{12}$ – $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnet solid solutions have shown that the symmetric regular solution model is not applicable over the entire composition range, O'Neill and Wood (1979) found that this model adequately described the mixing properties of garnets with low Ca contents. Hence, in the Cr_2O_3 -free system:

$$RT \ln a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}} = eRT \ln X_{\text{Mg}}^{\text{gt}} + 3W_{\text{MgCa}}^{\text{gt}} (X_{\text{Ca}}^{\text{gt}})^2 + 3W_{\text{MgFe}}^{\text{gt}} (X_{\text{Fe}}^{\text{gt}})^2 + 3(W_{\text{MgFe}}^{\text{gt}} - W_{\text{FeCa}}^{\text{gt}} - W_{\text{FeCa}}^{\text{gt}} + W_{\text{MgCa}}^{\text{gt}}) (X_{\text{Fe}}^{\text{gt}} \cdot X_{\text{Ca}}^{\text{gt}}) \quad (A12)$$

and

$$RT \ln a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^0 = 3RT \ln X_{\text{Mg}}^{\text{gt}^0} + 3W_{\text{MgCa}}^{\text{gt}} (X_{\text{Ca}}^{\text{gt}^0})^2 \quad (A13)$$

where the value of $X_{\text{Ca}}^{\text{gt}^0}$ has been determined in this study along the equilibrium curve (Table 1).

The partitioning data for garnet and olivine are taken from O'Neill and Wood (1979), which also yields values for $W_{\text{MgFe}}^{\text{ol}}$, $W_{\text{MgFe}}^{\text{gt}}$ and the difference ($W_{\text{MgCa}}^{\text{gt}} - W_{\text{FeCa}}^{\text{gt}}$). The work of Cressey et al. (1978) on almandine-grossular solid solutions suggests that $W_{\text{FeCa}}^{\text{gt}} \approx 0$ in the

temperature, pressure and composition range of interest here; hence $W_{\text{MgCa}}^{\text{gt}} \approx 11,200$ joules/mole, which is in fair agreement with the calorimetric data of Newton et al. (1977).

To determine the efficacy of this correction procedure for the change in calcium content of the garnet (and orthopyroxene) the experimental results in this study may be compared with those on the subsystem $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ obtained by Wood (1978) with the same experimental apparatus. The calculated equilibrium pressure at 1,000° and 1,100°C, using $X_{\text{Ca}}^{\text{M1opx}}$ of 0.025 and 0.04 (taken from Nehru 1976), in the calcium free system is 22.6 and 23.8 kb respectively, which is in perfect agreement with the experimental brackets of 22–23.3 and 23.5–24 kb.

The large difference in magnitude between the interaction parameters $W_{\text{MgCa}}^{\text{gt}}$ and $W_{\text{FeCa}}^{\text{gt}}$ causes the calcium content of the garnet to change with the addition of Fe^{2+} to the system. This change may be calculated from equilibrium (2) by using an argument similar to that used to derived Equation [13] for the effect of Fe^{2+} on reaction (1). This produces the expression:

$$(P - P^0) \Delta V(2) = \ln \left(\frac{X_{\text{Ca}}^{\text{gt}}}{X_{\text{Mg}}^{\text{gt}}} \right) - \ln \left(\frac{X_{\text{Ca}}^{\text{gt}^0}}{X_{\text{Mg}}^{\text{gt}^0}} \right) - \frac{W_{\text{MgCa}}^{\text{gt}}}{RT} (2X_{\text{Mg}}^{\text{gt}^0} + 2X_{\text{Ca}}^{\text{gt}} + X_{\text{Fe}}^{\text{gt}} - 2) + \left(\frac{W_{\text{FeCa}}^{\text{gt}} - W_{\text{MgFe}}^{\text{gt}}}{RT} \right) X_{\text{Fe}}^{\text{gt}} + \ln \left(\frac{a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{cpx}}}{a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{gt}}} \right) - \ln \left(\frac{a_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}}}{a_{\text{MgSi}_2\text{O}_6}^{\text{gt}}} \right). \quad (A14)$$

Where again the superscript 0 refers to the iron-free system at 1 bar pressure. $\Delta V(2)$ calculated from the molar volume of the end-members is 0.26 J/bar, in fortuitously good agreement with the value of 0.25 J/bar calculated for the pressure dependence of reaction (2) from the experimental work of Kushiro et al. (1967). It thus appears that the calcium content of garnet in equilibrium with two pyroxenes decreases with increasing pressure and iron content of the system.

Equation [A14] may be combined with the solutions to reactions (14) to (17) to give a series of non-linear equations that must be solved by reiteration to yield the equilibrium pressure for reaction (1) for any composition of olivine. However, considerable time and effort may be saved if we replace (A14) with the simple empirical expression (when $P - P^0$ is small):

$$X_{\text{Ca}}^{\text{gt}} = X_{\text{Ca}}^{\text{gt}^0} - 0.1 X_{\text{Fe}}^{\text{gt}} \quad (A15)$$

which has been obtained by comparing the results of calculations on (A14) over a range of temperatures and garnet compositions. This approximation must perforce be used in correcting the equilibrium for Fe^{2+} in Cr-containing and natural systems, where X_{Ca}^0 is not known.

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