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The activities of components in clinopyroxene and garnet solid solutions and their application to rocks

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Experimental studies of equilibria in chemically simple systems may be quantitatively extrapolated to rocks provided the activities of components in the appropriate complex phases are known. For each solid–solid equilibrium extrapolated in this way a curve of fixed K_i (equilibrium constant) for the rock may be defined in pressure–temperature space. Provided crystallization of the rock takes place under equilibrium conditions, use of two such solid–solid equilibria fixes the pressure and temperature uniquely.

The relations between activities of components and mineral compositions have been determined for $CaAl_2SiO_6$–$CaMgSi_2O_6$–$CaFeSi_2O_6$ clinopyroxene and $Ca_3Al_2Si_3O_{12}$–$Mg_3Al_2Si_3O_{12}$–$Fe_3Al_2Si_3O_{12}$ garnet solid solutions. These activity–composition relations, combined with thermodynamic data on simple equilibria, were then applied to the granulites of South Harris. The equilibria used were:

$$\underset{\text{plagioclase}}{CaAl_2Si_2O_8} \rightleftharpoons \underset{\text{clinopyroxene}}{CaAl_2SiO_6} + \underset{\text{quartz}}{SiO_2},$$

$$\underset{\text{clinopyroxene}}{CaFeSi_2O_6} + \underset{\text{garnet}}{\tfrac{1}{3}Mg_3Al_2Si_3O_{12}} \rightleftharpoons \underset{\text{garnet}}{\tfrac{1}{3}Fe_3Al_2Si_3O_{12}} + \underset{\text{clinopyroxene}}{CaMgSi_2O_6},$$

$$\underset{\text{plagioclase}}{3CaAl_2Si_2O_8} \rightleftharpoons \underset{\text{garnet}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{kyanite}}{2Al_2SiO_5} + \underset{\text{quartz}}{SiO_2}.$$

The intersection of K_i curves for appropriate mineral assemblages of the South Harris granulites yield estimated metamorphic conditions of 825 °C and 13 kbar. The calculated pressure is in excellent agreement with independent estimates (10–13 kbar) based on the presence or absence of garnet in orthogneisses. It is concluded that, for many equilibria, the thermodynamic approach should yield pressure estimates which are accurate to within ± 1–2 kbar. Temperature uncertainties, being dependent on the slopes of K_i curves in pressure–temperature space, are related to these quoted pressure uncertainties.

Introduction

There have been, in recent years, a number of experimental studies of subsolidus equilibria involving mineral phases which are major constituents of crustal and upper mantle assemblages (e.g. Boyd & England (1964), Green & Ringwood (1970), Green & Hibberson (1970)). The compositions of some minerals in these assemblages are potentially sensitive monitors of the values of pressure, temperature and other intensive variables which pertained during crystallization or recrystallization of the rocks concerned. Unfortunately, application of the experimental data, particularly those obtained for chemically simple or 'model' systems to rocks does not necessarily give unequivocal results. This is because there is no exact method of extrapolating experimental data to uninvestigated bulk compositions.

The experiments described in this paper have been performed so as to obtain precise methods for the application of experimental results on simple and complex systems to rocks. The simplest approach, which has been adopted here, is to estimate pressures and temperatures of crystallization of natural mineral assemblages using values of equilibrium constant K_i of appropriate equilibria. This method can, in principle, be used to extrapolate experimental results to all parts of pressure–temperature–composition space, with, in many cases, extremely accurate results.

Equilibrium constants

Consider the equilibrium involving the $CaAl_2Si_2O_8$ component of plagioclase, the $CaAl_2SiO_6$ component of clinopyroxene and the SiO_2 component of quartz:

$$\underset{\text{plagioclase}}{CaAl_2Si_2O_8} \rightleftharpoons \underset{\text{clinopyroxene}}{CaAl_2SiO_6} + \underset{\text{quartz}}{SiO_2}. \tag{1}$$

The equilibrium constant for equilibrium (1), K_1, is defined as follows:

$$K_1 = \frac{a^{\text{cpx}}_{CaAl_2SiO_6}}{a^{\text{plag}}_{CaAl_2Si_2O_8}\, a^{\text{qtz}}_{SiO_2}}. \tag{2}$$

In equation (2), a^j_i refers to the activity of component i ($CaAl_2SiO_6$, $CaAl_2Si_2O_8$, SiO_2) in phase j (clinopyroxene, plagioclase and quartz) at the pressure and temperature of interest. If we take the standard states of each of the three components involved in equilibrium (1) to be the pure phase at the pressure and temperature of interest then K_1 is given by:

$$-RT \ln K_1 = (\Delta H^0_1)_{1\,\text{bar},\,T} - T(\Delta S^0_1)_T + \int_1^P \Delta V^0_1 \,\mathrm{d}P. \tag{3}$$

$(\Delta H^0_1)_{1\,\text{bar},\,T}$, $(\Delta S^0_1)_T$ and ΔV^0_1 refer, respectively to the enthalpy (at 1 bar), entropy and volume changes of reaction (1) at the temperature of interest.

From equation (3) it may be seen that the equilibrium constant K_1 is a function of temperature and pressure, and that fixing K_1 defines a curve in pressure–temperature space. These curves, for different values of K_1, may be applied to deduce the physical conditions of crystallization of rocks provided the following conditions are met:

(*a*) Standard state thermodynamic data for the equilibrium (ΔH^0_1, ΔS^0_1, ΔV^0_1) are known.

(*b*) The relations between activities of components and mineral compositions are known for the complex phases of interest.

(*c*) The assemblage crystallized in chemical equilibrium.

In the case of reaction (1), standard state entropy and volume data may be obtained from Robie & Waldbaum (1968). The enthalpy of reaction was estimated from the experimental reversal of (1) at 30.8 kbar† and 1400 °C by Hariya & Kennedy (1968). In the system studied by these authors ($CaO–Al_2O_3–SiO_2$) all three phases are pure (all a^j_i equal to 1.0) so that K_1 is equal to 1.0 at 30.8 kbar and 1400 °C. The curve of K_1 equal to 1.0 was extrapolated to lower-temperatures and pressures using the high temperature entropy at 298 K/1 bar volume data of Robie & Waldbaum (1968). The result for K_1 equal to 1.0 was then used to construct curves for different values of K_1 from:

$$\left(\frac{\partial \ln K_1}{\partial P}\right)_T = \frac{\Delta V^0_1}{RT}. \tag{4}$$

(In order to integrate equation (4) the volume change of reaction (1) was assumed constant at the 1 bar, 298 K value).

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† 1 bar = 10^5 Pa.

Lines of constant values of K_1 (uncertainties ± 1 kbar approximately) are shown in the pressure–temperature diagram of figure 1. From the figure it may be seen that this equilibrium is strongly dependent on pressure and virtually independent of temperature. It therefore constitutes a good geobarometer.

For comparison an equilibrium which is a potentially useful geothermometer is illustrated in figure 2:

$$\underset{\text{clinopyroxene}}{\mathrm{CaFeSi_2O_6}} + \tfrac{1}{3}\underset{\text{garnet}}{\mathrm{Mg_3Al_2Si_3O_{12}}} \rightleftharpoons \tfrac{1}{3}\underset{\text{garnet}}{\mathrm{Fe_3Al_2Si_3O_{12}}} + \underset{\text{clinopyroxene}}{\mathrm{CaMgSi_2O_6}}. \tag{5}$$

The equilibrium constant for reaction (5), K_5, is, by analogy with equation (2), defined as follows:

$$K_5 = \frac{a^{\text{cpx}}_{\mathrm{CaMgSi_2O_6}}\, a^{\text{gt}\,\frac{1}{3}}_{\mathrm{Fe_3Al_2Si_3O_{12}}}}{a^{\text{cpx}}_{\mathrm{CaFeSi_2O_6}}\, a^{\text{gt}\frac{1}{3}}_{\mathrm{Mg_3Al_2Si_3O_{12}}}}. \tag{6}$$

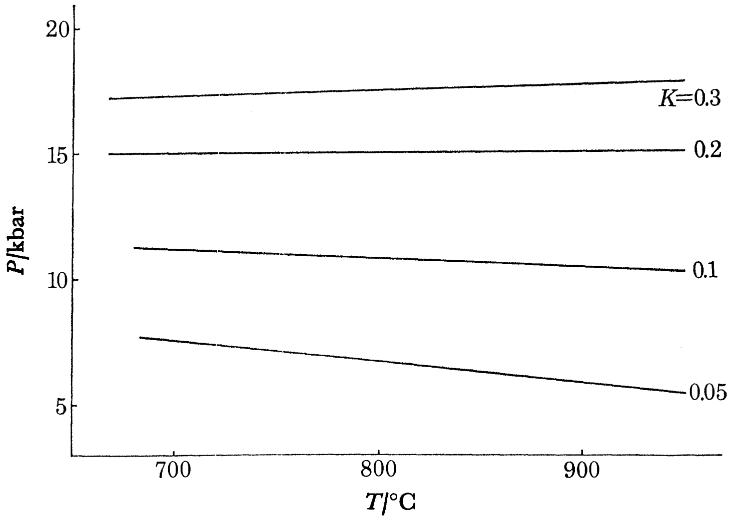

Figure 1. Curves of constant K_1 for the equilibrium:

$$\underset{\text{plagioclase}}{\mathrm{CaAl_2Si_2O_8}} \rightleftharpoons \underset{\text{clinopyroxene}}{\mathrm{CaAl_2SiO_6}} + \underset{\text{quartz}}{\mathrm{SiO_2}}.$$

Standard states are the pure phases at the pressure and temperature of interest.

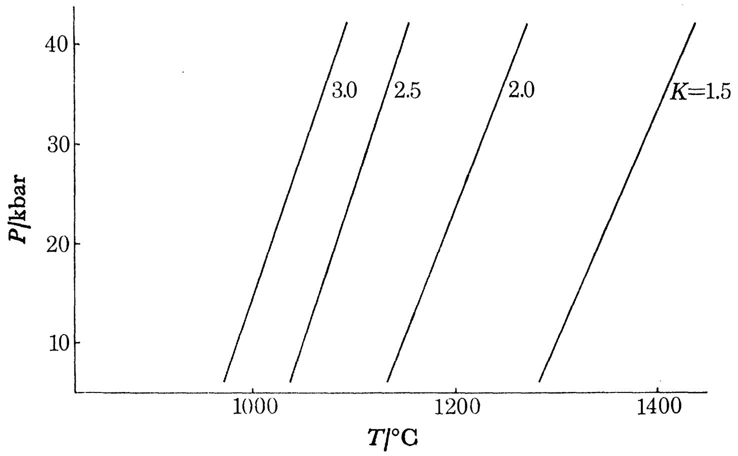

Figure 2. Approximate K_1 curves for the equilibrium:

$$\underset{\text{clinopyroxene}}{\mathrm{CaFeSi_2O_6}} + \tfrac{1}{3}\underset{\text{garnet}}{\mathrm{Mg_3Al_2Si_3O_{12}}} \rightleftharpoons \tfrac{1}{3}\underset{\text{garnet}}{\mathrm{Fe_3Al_2Si_3O_{12}}} + \underset{\text{clinopyroxene}}{\mathrm{CaMgSi_2O_6}}.$$

Although the positions of the K_5 curves illustrated in figure 2 are approximate, the pressure–temperature slopes, based on volume data (equation (4)), are fairly accurate and serve to demonstrate the small pressure dependence of K_5.

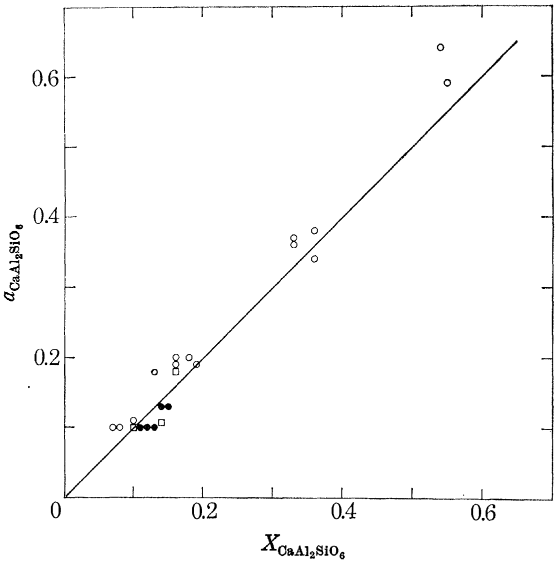

FIGURE 3. Activity ($a_{CaAl_2SiO_6}$) plotted against mole fraction ($X_{CaAl_2SiO_6}$) for the clinopyroxene solid solutions: $CaMgSi_2O_6$–$CaAl_2SiO_6$ (○, Diop–CaTs); $CaFeSi_2O_6$–$CaAl_2SiO_6$ (●, Hed–CaTs); $Ca(Mg_{0.6}Fe_{0.4})Si_2O_6$–$CaAl_2SiO_6$ (□, $Diop_{60}Hed_{40}$–CaTs).

ACTIVITY-COMPOSITION RELATIONS

In order to apply curves of constant K to rocks it is necessary to know how the activities of the simple components of interest vary as functions of the compositions of multicomponent phases.

If we take the standard state of component i to be pure phase j at the pressure and temperature of interest then the general relationship between the activity of component i and the composition of phase j is (see, for example, Wood 1975*b*):

$$a_i^j = (X_i \gamma_i)^n. \tag{7}$$

In equation (7) X_i refers to the mole fraction of component i in phase j and γ_i to the activity coefficient for this component at the composition of interest. The exponent, n, is the number of sites per formula unit on which mixing takes place. In, for example, $Ca(Mg, Fe)Si_2O_6$ clinopyroxene n is equal to 1; in $(Mg, Fe)_3Al_2Si_3O_{12}$ garnet n is three.

It is apparent, therefore that of the three variables determining a_i^j two are readily determined, n from the formula of the mineral and X_i from a chemical analysis of it. In contrast, values of activity coefficients, γ_i, must be determined experimentally in order accurately to calculate activities of components in complex phases. Fortunately, there is evidence (e.g. Wood 1975*b*), that many silicate solid solutions have values of γ_i close to 1.0 (approximately ideal solutions) which, since the composition dependence of γ_i is not large in such cases, greatly facilitates the extrapolation of experimental data to rocks.

Experimental determination of activity coefficients

Let us suppose that the activity–composition relationships of $CaAl_2SiO_6$–$CaMgSi_2O_6$ clinopyroxenes are required. If an experiment is performed in which pure anorthite ($a_{CaAl_2Si_2O_8} = 1$), and pure quartz ($a_{SiO_2} = 1$) coexist, in equilibrium, with a clinopyroxene solid solution at some pressure P and temperature T then we have, from (2):

$$(K_1)_{P,T} = a^{cpx}_{CaAl_2SiO_6}. \tag{8}$$

Provided K_1 is known at the pressure and temperature of the experiment (figure 1) then the activity of $CaAl_2SiO_6$ component in the clinopyroxene under these conditions is also known. If the clinopyroxene is analysed after the experiment ($X_{CaAl_2SiO_6}$ determined) then the relation between $a^{cpx}_{CaAl_2SiO_6}$ and $X^{cpx}_{CaAl_2SiO_6}$ (and hence $\gamma_{CaAl_2SiO_6}$) may be determined.

The author (Wood 1976) has performed such experiments for $CaAl_2SiO_6$–$CaMgSi_2O_6$ solid solutions over the pressure–temperature range 10–25 kbar and 900–1300 °C respectively. The results of activity $a_{CaAl_2SiO_6}$ (taken from K_1, figure 1) plotted against $X_{CaAl_2SiO_6}$ are shown in figure 3 together with a smaller number of data on $CaAl_2SiO_6$–$CaFeSi_2O_6$ and $CaAl_2SiO_6$–$CaMgSi_2O_6$–$CaFeSi_2O_6$ solid solutions. From figure 3 it may be seen that the following approximate relations apply:

(1) In $CaAl_2SiO_6$–$CaMgSi_2O_6$ solutions: $a^{cpx}_{CaAl_2SiO_6} \geqslant X^{cpx}_{CaAl_2SiO_6}$.
(2) In $CaAl_2SiO_6$–$CaMg_{0.6}Fe_{0.4}Si_2O_6$ solutions: $a^{cpx}_{CaAl_2SiO_6} \approx X^{cpx}_{CaAl_2SiO_6}$.
(3) In $CaAl_2SiO_6$–$CaFeSi_2O_6$ solutions: $a^{cpx}_{CaAl_2SiO_6} \leqslant X^{cpx}_{CaAl_2SiO_6}$.

If, as for example, with the $CaAl_2SiO_6$–$CaMgSi_2O_6$ solid solutions shown in figure 3, activity data are available for one component of a binary solution over a wide range of phase compositions then activity coefficients for the other component may be obtained by integrating the Gibbs–Duhem equation:

$$\ln \gamma_1 = -\int_{x_1=1}^{x_1=x_1} \frac{X_2}{X_1}\,\mathrm{d}\ln\gamma_2. \tag{9}$$

Thus the complete mixing properties of a binary solid solution may be obtained from a measurement of the activity–composition relations of one of its components.

A similar procedure to that described above has been used by Hensen *et al.* (1975) to determine the mixing properties of $(Mg, Ca)_3Al_2Si_3O_{12}$ garnet solid solutions. These authors experimented on the assemblage anorthite, quartz, kyanite (or sillimanite) and garnet solid solution to determine activity coefficients for the $Ca_3Al_2Si_3O_{12}$ component in garnet using the equilibrium:

$$\underset{\text{plagioclase}}{3CaAl_2Si_2O_8} \rightleftharpoons \underset{\text{garnet}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{kyanite/sillimanite}}{2Al_2SiO_5} + \underset{\text{quartz}}{SiO_2}. \tag{10}$$

If all phases are pure except garnet then the equilibrium constant, K_{10} of equilibrium (10) is given by:

$$K_{10} = a^{gt}_{Ca_3Al_2Si_3O_{12}}. \tag{11}$$

Curves of constant K_{10}, taken from Schmid & Wood (1976) are shown in figure 4. As with equilibrium (1), the uncertainty on the position of each curve is approximately ± 1kbar. Hensen *et al.* (1975) determined $\gamma^{gt}_{Ca_3Al_2Si_3O_{12}}$ in the composition range $(Ca_{0.1}Mg_{0.9})_3Al_2Si_3O_{12}$ to $(Ca_{0.22}Mg_{0.78})_3\,Al_2Si_3O_{12}$ by experimenting at known pressure and temperature and determining the composition of garnet solid solution at the end of the experiment. In the small composition range studied (limited by the small stability field of the assemblage $\mathrm{gt_{ss}}$-plag–an–ky/(sill)–qz the garnet solid solution exhibits strong deviations from ideality. The activity coefficients for $Ca_3Al_2Si_3O_{12}$ component may be expressed as follows in terms of garnet composition and interaction parameter W:

$$\frac{RT\ln\gamma^{\mathrm{gt}}_{\mathrm{CaAl_2Si_3O_{12}}}}{(1-X^{\mathrm{gt}}_{\mathrm{Ca_3Al_3Si_3O_{12}}})^2}=W. \tag{12}$$

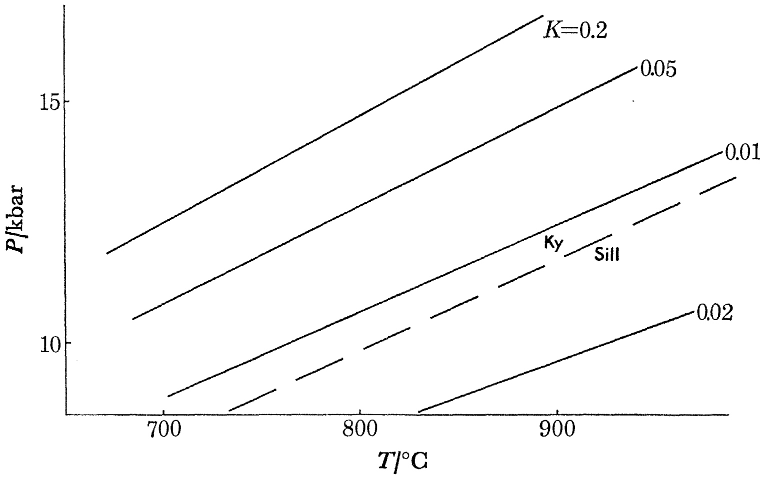

FIGURE 4. K_i curves for the equilibrium:

$$\underset{\text{plagioclase}}{3\mathrm{CaAl_2Si_2O_8}} \rightleftharpoons \underset{\text{garnet}}{\mathrm{Ca_3Al_2Si_3O_{12}}} + \underset{\substack{\text{kyanite}\\\text{or sillimanite}}}{2\mathrm{Al_2SiO_5}} + \underset{\text{quartz}}{\mathrm{SiO_2}}.$$

The non-ideal interaction parameter, W, appears to be strongly dependent on temperature in the temperature range 1000–1300 °C. The following equation for W was obtained with T in kelvins:

$$W = 31200-18.0T \quad (\mathrm{J\,mol^{-1}}). \tag{13}$$

Since $(Ca, Mg)_3Al_2Si_3O_{12}$ garnet solid solutions have n equal to three (equation (7)) the activity coefficients were calculated from:

$$a^{\mathrm{gt}}_{\mathrm{CaAl_2Si_3O_{12}}} = (X^{\mathrm{gt}}_{\mathrm{Ca_3Al_2Si_3O_{12}}}\,\gamma^{\mathrm{gt}}_{\mathrm{Ca_3Al_2Si_3O_{12}}})^3. \tag{14}$$

Cressey & Schmid (in preparation) have performed similar determinations of $\gamma^{\mathrm{gt}}_{\mathrm{Ca_3Al_2Si_3O_{12}}}$ in $(Ca, Fe)_3Al_2Si_3O_{12}$ and $(Ca, Mg, Fe)_3\,Al_2Si_3O_{12}$ garnet solid solutions. These authors have found that, in the composition range up to 30 mol percent $Ca_3Al_2Si_3O_{12}$ component $(Ca, Fe)_3Al_2Si_3O_{12}$ garnets are approximately ideal ($\gamma_{\mathrm{Ca,\,Al_2Si_3O_{12}}}$ equal to 1). The activity coefficient for the $Ca_3Al_2Si_3O_{12}$ component in $(Ca, Mg, Fe)_3Al_2Si_3O_{12}$ garnet solutions is dependent on the Mg/Fe ratio of the garnet and varies approximately linearly between the values for binary $(Ca, Mg)_3Al_2Si_3O_{12}$ and $(Ca, Fe)_3Al_2Si_3O_{12}$ solid solutions.

Distribution of iron and magnesium between garnet and clinopyroxene

The iron–magnesium exchange equilibrium (5) is, as has been shown, a potentially useful geothermometer. The equilibrium constant for this reaction (equation (6)) may, taking garnet and clinopyroxene to have n equal to three and one respectively, be written as follows:

$$K_5 = \frac{(X^{\mathrm{gt}}_{\mathrm{Fe_3Al_2Si_3O_{12}}}\,\gamma^{\mathrm{gt}}_{\mathrm{Fe_3Al_2Si_3O_{12}}})\,(X^{\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}}\,\gamma^{\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}})}{(X^{\mathrm{gt}}_{\mathrm{Mg_3Al_2Si_3O_{12}}}\,\gamma^{\mathrm{gt}}_{\mathrm{Mg_3Al_2Si_3O_{12}}})\,(X^{\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}}\,\gamma^{\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}})}. \tag{15}$$

In equation (15) X^j_i refers to the mole fraction of component in i phase j.

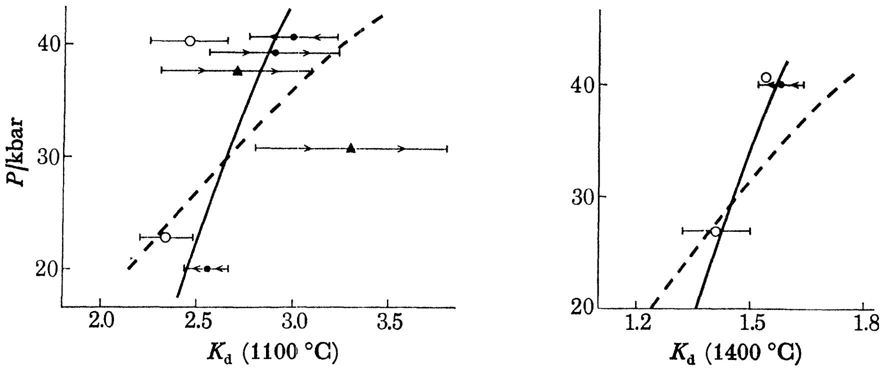

Figure 5. Observed and calculated (——) pressure dependence of iron–magnesium distribution between garnet and clinopyroxene (K_d). - - - -, Råheim & Green (1974) – basaltic compositions; ○, Hensen (1973) – ultramafic compositions; ▲, Akella & Blyd (1974) – ultramafic compositions; ●, Wood (unpublished) – ultramafic compositions. Arrows indicate the direction of approach to equilibrium, where known.

Råheim & Green (1974) have performed high-pressure experiments on bulk compositions approximating natural basalts and have determined values of the empirical distribution coefficient, K_d, as a function of temperature and pressure. K_d is defined as follows:

$$K_d = \frac{X^{\mathrm{gt}}_{\mathrm{Fe}}}{X^{\mathrm{gt}}_{\mathrm{Mg}}}\cdot\frac{X^{\mathrm{cpx}}_{\mathrm{Mg}}}{X^{\mathrm{cpx}}_{\mathrm{Fe}}}, \tag{16}$$

where $X^{\mathrm{gt}}_{\mathrm{Fe}}$, $X^{\mathrm{cpx}}_{\mathrm{Mg}}$, etc. refer to the mole fractions of iron component in garnet, magnesium component in clinopyroxene and so on. It may readily be seen that the empirical distribution coefficient K_d corresponds to K_5 *if* all activity coefficients for the two mineral phases are 1. Since, however, it has been shown that $\mathrm{Ca_3Al_2Si_3O_{12}}$-bearing garnet solid solutions are non-ideal it is apparent that K_d cannot equal K_5 if the garnet in question contains calcium. It may also be seen that, from a consideration of the form of K_5 (equation (15)), increasing $\mathrm{Ca_3Al_2Si_3O_{12}}$ content of the garnet will tend to increase K_d. This is due to the marked non-ideality of $\mathrm{(Ca, Mg)_3Al_2Si_3O_{12}}$ solid solutions and results in an increase of $\gamma^{\mathrm{gt}}_{\mathrm{Mg_3Al_2Si_3O_{12}}}$ with increasing calcium content of garnet; $\gamma^{\mathrm{gt}}_{\mathrm{Fe_3Al_2Si_3O_{12}}}$ is little affected by such a compositional change. An increase in $\gamma^{\mathrm{gt}}_{\mathrm{Mg_3Al_2Si_3O_{12}}}$ must, in order to keep K_5 constant at any pressure and temperature, result in a decrease in $X^{\mathrm{gt}}_{\mathrm{Mg_3Al_2Si_3O_{12}}}$. Hence K_d increases.

Råheim & Green (1974) found that, for basaltic compositions, increasing pressure at any temperature results in a more rapid increase in K_d than would be predicted from the volume change of reaction (5) (equation (4)). However, garnets crystallized from the bulk compositions studied by these authors have increasing $Ca_3Al_2Si_3O_{12}$ contents with increasing pressure. It thus seems possible that some of the pressure effect observed by these authors is, in fact, a compositional effect controlled by the calcium content of garnet.

In order to test this hypothesis experiments have been performed by the author at pressures between 20 and 45 kbar on garnet and clinopyroxene crystallized from ultramafic bulk compositions. For such compositions the $Ca_3Al_2Si_3O_{12}$ content of garnet does not change as pressure is increased. Hence the pressure dependence of K_d may be obtained independent of any compositional dependence. Results, shown in figure 5, indicate that the pressure dependence of K_d for ultramafic compositions is indeed much less than that found for basaltic compositions by Råheim & Green. It seems likely that at least some of the difference between the two sets of data is due to the influence of $Ca_3Al_2Si_3O_{12}$ content of garnet on K_d. The results obtained by the author and others on ultramafic compositions (figure 5) are, however, in good agreement with Råheim & Green's data at 30 kbar. It is suggested therefore that for garnets with relatively low $Ca_3Al_2SiO_{12}$ contents ($X_{Ca_3Al_2Si_3O_{12}} < 0.25$) Råheim & Green's (1974) data at 30 kbar be extrapolated to other pressures using equation (4) with the observed $\Delta V°$ of -1.0 cm³.

APPLICATION TO MINERAL ASSEMBLAGES OF SOUTH HARRIS GRANULITES

As a test of the thermodynamic data presented here a small area of high-grade metamorphic rocks (South Harris, Scotland) has been chosen for study. In an area approximately 5 km square the following assemblages (among others) are found exposed (Dearnley 1963; Wood 1975*a*):

(*a*) Garnet–kyanite–plagioclase–quartz (in paragneisses).
(*b*) Garnet–clinopyroxene–plagioclase (orthogneisses).
(*c*) Clinopyroxene–orthopyroxene–plagioclase–quartz (orthogneisses).

In an earlier study (Wood 1975*a*) the pressure and temperature of granulite metamorphism were estimated, respectively, to be 10–13 kbar and 800–860 °C. These estimates were based on the presence or absence of garnet in orthogneisses (pressure), the extent of solid solution between orthopyroxene and clinopyroxene (temperature), and some data on iron–magnesium distribution between garnet and clinopyroxene (temperature). Additional estimates of the physical conditions of metamorphism can now be made. Assemblage (*a*) can be placed on a line of constant K_{10}, assemblage (*b*) on a line of K_5 and assemblage (*c*) on a line of constant K_1. The values of K for each of these three equilibria as functions of pressure and temperature were taken from figures 1, 2 and 4 and activity coefficients for components of each of the phases from Orville (1972) (for plagioclase) and the work described above. The compositions of minerals in the natural assemblage were derived from Wood (1975*a*) and, in the case of assemblage (*a*), from unpublished data by the author.

The results of the calculation of pressure–temperature curves for each of the natural assemblages (*a*), (*b*) and (*c*) from South Harris are shown in figure 6. The shaded area shown in this figure is the region of apparent 'bracketing' of the pressure and temperature of metamorphism described previously (Wood 1975*a*). The shaded area has an estimated uncertainty of at least ± 1 kbar and possibly greater than ± 2 kbar. From figure 6 it can be seen that the new pressure–temperature estimates based on application of equilibria 1, 5 and 10 to these rocks are in excellent agreement with the earlier results. The intersections of the three sets of lines, for equilibria 1, 5 and 10 is at about 13 kbar and 825 °C; the estimated pressure is between 0.5 and 1 kbar above the shaded area derived from previous calculations.

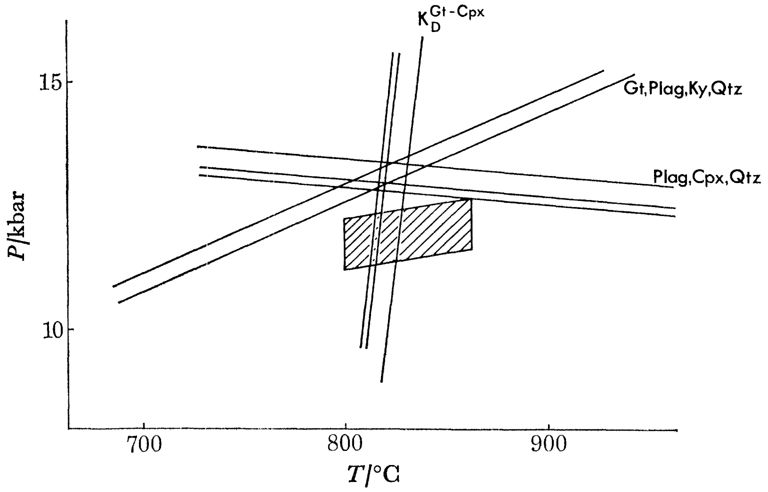

FIGURE 6. K curves for natural assemblages from South Harris. Assemblage plag, cpx, qz denotes equilibrium (1); assemblage gt, plag, ky, qz denotes equilibrium (10); assemblage gt, cpx denotes equilibrium (5). Shaded area is the apparent region of 'bracketing' of metamorphic pressure and temperature derived from other equilibria (Wood 1975*a*).

CONCLUSIONS

Experimental studies of the thermodynamic properties of clinopyroxene and garnet solid solutions have revealed the following:

(1) The activity of $CaAl_2SiO_6$ component in clinopyroxene solid solution is given by:

$$a^{cpx}_{CaAl_2SiO_6} = X^{cpx}_{CaAl_2SiO_6}\,\gamma^{cpx}_{CaAl_2SiO_6}.$$

In $CaAl_2SiO_6$–$CaMgSi_2O_6$ solid solutions $\gamma^{cpx}_{CaAl_2SiO_6}$ is slightly greater than 1.0; in $CaAl_2SiO_6$–$CaFeSi_2O_6$ solutions it is slightly less than 1.0. A bulk composition having Mg/(Mg + Fe) equal to 0.6 yielded $\gamma_{CaAl_2SiO_6}$ of approximately 1.0.

(2) The activity coefficient of the $Ca_3Al_2Si_3O_{12}$ component of $(Ca, Mg)_3Al_2Si_3O_{12}$ garnet solid solutions is, in the composition range $(Ca_{0.1}Mg_{0.9})$ to $(Ca_{0.22}Mg_{0.78})$, given by:

$$\frac{RT\ln\gamma^{gt}_{Ca_3Al_2Si_3O_{12}}}{(1-X^{gt}_{Ca_3Al_2Si_3O_{12}})^2} = 31200-18.0T \quad (\mathrm{J\ mol^{-1}}).$$

$(Ca, Fe)_3Al_2Si_3O_{12}$ solid solutions are, in contrast, virtually ideal in the composition range ($X_{Ca_3Al_2Si_3O_{12}}$ up to 0.3) most commonly observed in nature.

The activity-coefficients of garnet and clinopyroxene when combined with thermodynamic data (K_i) on simple equilibria enable calculation of P–T curves for many subsolidus mineral assemblages. In the examples chosen, (*a*) garnet–plagioclase–kyanite–quartz, (*b*) garnet–clinopyroxene, and (*c*) clinopyroxene–plagioclase–quartz, pressure–temperature estimates for a group of rocks metamorphosed under similar conditions are in excellent agreement.

The results imply that pressure–temperature estimates based on a combination of thermodynamic data for simple equilibria and activity–composition relationships for solid solutions should, in many cases, be accurate to within 1–2 kbar.

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Note added in proof, 27 *April* 1977. A new study of reaction (1) (Wood, unpublished) necessitates a small downward revision of the values of $a_{\mathrm{CaAl_2SiO_6}}$ shown in figure 3. It does not, however, affect the pressure–temperature estimates shown in figure 6.

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Discussion

M. J. O'HARA (*Department of Geology, Edinburgh University*). Ultrabasic rocks from the Leverburgh paragneiss belt, South Harris, contain sparse garnet, in addition to abundant spinel (Livingstone 1967) implying pressures of *ca.* 15 kbar (O'Hara *et al.* 1971). Cordierite is reported in adjacent pelitic paragneisses (Davidson 1943), implying pressures of less than *ca.* 11 kbar (Hensen & Green 1971). Fresh pelitic gneisses containing large prisms of kyanite and large garnets display abundant orientated needles of sillimanite enclosed within the outer zones of those garnets. Clearly, even where they are not manifestly polymetamorphic, in the sense of having undergone two or more separate orogenic or metasomatic events, the mineralogy is recording several stages in the pressure–temperature history of these rocks. This is not surprising because the uplift and erosion leading to recovery of such rocks to low pressure and temperature is a process requiring hundreds of millions of years. A geothermometer based upon distribution of Ca, Mg + Fe between two pyroxenes, one based on Mg, Fe distribution between clinopyroxene and garnet, and geobarometers based on the distribution of aluminous components between orthopyroxene and garnet, or clinopyroxene and plagioclase would each be expected to 'close' at different pressures and temperatures, the problem being analogous to that encountered in radiometric dating (e.g. Dodson 1976). Studies on fresh granulite facies Scourian metamorphic rocks suggest for example that two feldspar parageneses may have 'closed' at *ca.* 1200 °C on a 1 cm scale, *ca.* 950 °C on a 1 mm scale, and *ca.* 500 °C on a 50 μm scale, while pyroxene and pyroxene–garnet parageneses apparently closed at temperatures below 850 °C (despite rare textural evidence of the higher temperature events (O'Hara 1961, Fig. 7)). Ilmenite–magnetite lamellar intergrowths closed below 500 °C although the original magnetite–ulvospinel solid solutions (see O'Hara 1961, Fig. 6) require temperatures greater than 850 °C for their formation.

Under these circumstances the close consistency which you report between 5 different methods of estimating the pressure and temperature of the S. Harris gneisses might be a source of embarrassment more than a cause for satisfaction, although it is conceivable that all five closed at the same time. Can you comment on this, and give us more information on the textural relations of the minerals used to establish temperatures and pressures in these gneisses?

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B. J. Wood. The close agreement of the five different methods of estimating pressure and temperature of metamorphism (figure 6) cannot be the result of coincidence or of some interdependency of the different methods. The results are based on independent sets of experiments performed in four different laboratories with several different types of starting material. It is considered, therefore, that the pressure-temperature region of intersection shown in figure 6 does indeed represent conditions close to the peak of granulite metamorphism. The author would not dispute, however, that particular phases within a rock should 'close' with respect to diffusion at different times in its cooling history. It is necessary, therefore, to consider the reasons why the different phases used in this study all ceased equilibrating at approximately the same time.

The rocks all come from an area which has undergone at least one later retrograde metamorphism (Dearnley 1963). The extent of retrogression is not uniform, however, and it is possible to find specimens in which little hydration of pyroxene to amphibole or of garnet to biotite has taken place. The specimens used to obtain the results shown in figure 6 were all selected for their lack of retrograde minerals. Thus, the mineralogical changes which took place during cooling involved diffusion and re-equilibration between the granulite facies minerals rather than the nucleation and growth of new phases. In such cases the apparent closure temperatures for the different assemblages will depend on the slowest diffusion steps in the re-equilibration processes.

Re-equilibration in the cases discussed would involve either (*a*) diffusion of Ca, Mg and Fe in garnet or (*b*) diffusion of Al in clinopyroxene. Each of these diffusion processes is expected to have an extremely high activation energy, probably of the order of 400 kJ mol^{-1} (Yardley 1977; Lacy 1965). The exponential variation of diffusion coefficient with reciprocal temperature results in large temperature dependencies of equilibration or diffusion distances in minerals. Consider, for example, an assemblage of minerals with appropriate size and diffusion coefficients such that they may equilibrate in 2 Ma at 850 °C. If the activation energy for diffusion is 400 kJ mol^{-1} then equilibrium at 750 °C would be attained only after 150 Ma. Thus, if the peak of metamorphism in such a case was 850 °C the equilibrium element distributions would be 'quenched-in' at a temperature very close to the metamorphic peak given that orogenic times are of the order of tens of millions of years. It seems probable that such a situation obtained for the particular mineral assemblages discussed here. It resulted in close correspondence between apparent 'closure' temperatures for the several different assemblages considered.

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