The Thermodynamics of Pyroxene Geotherms [and Discussion]

R. Powell and E. C. Baughan

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The thermodynamics of pyroxene geotherms

By R. Powell
Department of Earth Sciences, University of Leeds, Leeds LS2 9JT, U.K.

Correctly formulated thermodynamics provides the only reliable means of applying the results of mineral equilibria experiments to the calculation of the temperature and pressure of formation of mineral assemblages. The problems of formulating geothermometers and geobarometers are considered with particular reference to calculating the conditions of formation of garnet lherzolites in kimberlites. Incorrect expressions for the thermodynamics of minerals will provide unreliable methods for calculating conditions of formation. The reactions on which these methods are based must be chosen so that composition parameters which are uncertain in a mineral analysis (for example, the amounts of ferrous iron on each octahedral site in a pyroxene) do not have a central position in a method. For this reason it is suggested that the use of alumina solubility in enstatite in equilibrium with garnet is not suitable as a geobarometer for garnet lherzolites. The orthopyroxene–Ca-rich clinopyroxene miscibility gap geothermometer is shown to be very sensitive to the mineral compositions when more correctly formulated, treating the pyroxenes as non-ideal solutions. Two new methods are presented which are based on Ca–Mg exchange reactions involving orthopyroxene–Ca-rich clinopyroxene and orthopyroxene–garnet. These methods allow the calculation of both temperature and pressure for garnet lherzolites. It is observed that the sheared lherzolites and the granular lherzolites formed at lower pressures than has been suggested previously, implying a steeper geotherm at the time the minerals attained their present compositions.

INTRODUCTION

Kimberlites bring nodules towards the Earth's surface, at least some of which appear to be samples of upper mantle, particularly the garnet lherzolites (see, for example, Nixon, von Knorring & Rooke 1963). The temperatures and pressures of formation of such nodule suites define a temperature–pressure line which can be interpreted in terms of the thermal history of the mantle beneath the kimberlite pipe. Boyd (1973) in his pioneering paper 'A pyroxene geotherm' calculated temperatures and pressures for garnet lherzolites from the Lesotho kimberlites using experimentally determined orthopyroxene–clinopyroxene–garnet equilibria from simple endmember systems. (The term clinopyroxene here refers to diopsidic augites and sub-calcic diopsidic augites.) He interpreted the resulting temperature–pressure line in terms of a fossil geotherm. A remarkable characteristic of this geotherm is that it is kinked, the lower limb being formed mainly by granular garnet lherzolites, while the upper limb is formed mainly by sheared garnet lherzolites. There have been several attempts to account for this kinked geotherm (e.g. Parmentier & Turcotte 1974).

Clearly the results of Boyd's approach are crucially dependent on the applicability of the experimental results in simple systems (CMS ($CaO–MgO–SiO_2$) in the case of the orthopyroxene–clinopyroxene equilibria for the temperature calculation, MAS ($MgO–Al_2O_3–SiO_2$) in the case of the orthopyroxene–garnet equilibria for the pressure calculation) to the garnet lherzolites. The problem is that this extrapolation is fraught with difficulties. The assumption that small compositional differences between natural and simple systems will not affect calculated temperatures (or pressures) can be dangerous. For example, moving from orthopyroxene–clinopyroxene in CMS to orthopyroxene–clinopyroxene–garnet in CMAS (CaO–MgO–Al_2O_3–SiO_2) involves a drastic change in the position of the clinopyroxene limb of the pyroxene miscibility gap, and thus a drastic change (of 200 °C) in the temperature calculated from this limb using Boyd's formula (1973, Table 1) (figure 1).

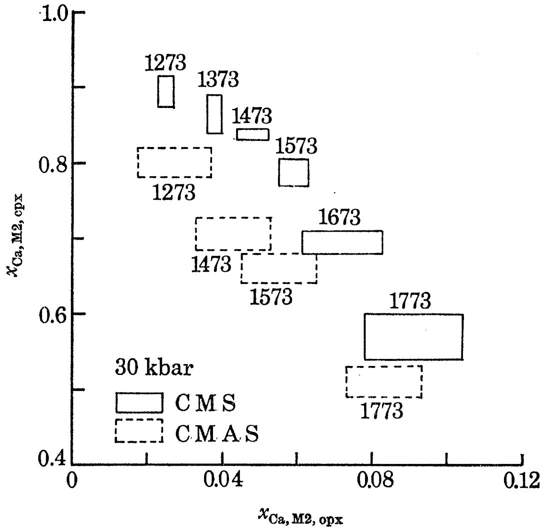

FIGURE 1. A representation of the orthopyroxene–clinopyroxene miscibility gap showing the dramatic effect on the position of the clinopyroxene limb on the addition of garnet to CMS. CMS data from Nehru & Wyllie (1974); CMAS data from Akella (1976).

A thermodynamic analysis of the experimental results provides the best way of calculating the temperatures and pressures of formation of the garnet lherzolites because the methods will be independent of bulk rock composition and of mineraology (e.g. Wood & Banno 1973). Thus a method for calculating temperature which uses the compositions of coexisting orthopyroxene and clinopyroxene, will work whether the orthopyroxene and clinopyroxene are in a garnet lherzolite, in a spinel lherzolite or in a gabbro. However, this assertion depends crucially on the validity of the experimental data and on the correct formulation of the thermodynamics. Equilibration in experiments in these silicate systems is notoriously sluggish, and reversals of equilibria are impossible or equivocal (because of uncertainties in the reaction kinetics). Unequilibrated experimental results obviously provide the wrong starting point for extrapolation to natural systems. The problem with the thermodynamics is that no one knows what the correct formulation is, although it is often possible to say when the formulation is incorrect! The use of oversimplified thermodynamics is no more than empiricism and is unlikely to allow the meaningful extrapolation of the experimental results (see, for example, Mercier & Carter 1975; and unfortunately Powell & Powell 1974).

This paper is mainly concerned with the thermodynamics of equilibria between orthopyroxene, clinopyroxene and garnet with particular reference to estimating the temperature and pressure of formation of garnet lherzolites in kimberlites. The thermodynamics of crystalline silicates is considered in the first section. This is followed by an examination of previously applied methods and the introduction of some new ones.

THERMODYNAMIC APPROACH

The basis of the application of equilibrium thermodynamics to mineral equilibria is the equilibrium relation for a balanced chemical reaction between the endmembers of the minerals. Thus, for

$$\underset{\text{orthopyroxene}}{Mg_2Si_2O_6} = \underset{\text{clinopyroxene}}{Mg_2Si_2O_6}, \qquad (1)$$

the equilibrium relation is

$$-\Delta G^\circ = RT \ln K. \qquad (2)$$

ΔG° is the standard Gibbs energy of reaction, comprising the sum of the Gibbs energies of the pure endmembers involved in the reaction. This is usually a linear function of temperature T and pressure P. K is the equilibrium constant which takes into account the compositional deviation of natural phases from the endmembers in the reaction. This term is a more or less complicated function of the compositions of the phases and, in general, temperature and pressure. For particular mineral compositions, equation (2) for a reaction defines a PT line, given the temperature and pressure dependence of K and ΔG°. In certain (unusual) cases the PT line so generated may be effectively independent of pressure (a geothermometer), or independent of temperature (a geobarometer) – but more commonly the PT line is intermediate between these two cases. Two such PT lines with a reasonable angle of intersection are required to define both temperature and pressure.

The essence of the thermodynamic approach is the calculation of the unknown parameters in (2) (the PT dependence of ΔG° and K) using the compositions of coexisting minerals at known PT from experiments, to allow the application of (2) to natural mineral assemblages. Although it is safe to assume that ΔG° is a linear function of temperature and pressure, there are no safe assumptions about the dependence of K on composition, temperature and pressure. K for reaction (1) can be written

$$K = \frac{a_{Mg_2Si_2O_6,\,cpx}}{a_{Mg_2Si_2O_6,\,opx}} = \frac{x_{Mg_2Si_2O_6,\,cpx}\,\gamma_{Mg_2Si_2O_6,\,cpx}}{x_{Mg_2Si_2O_6,\,opx}\,\gamma_{Mg_2Si_2O_6,\,opx}}, \qquad (3)$$

where x_i is the mole fraction of i, γ_i is the activity coefficient of i and a_i ($= x_i\gamma_i$) is the activity of i. The problem of formulating K is thus reduced to the problem of formulating x_i and γ_i for each component in each mineral.

Mole fractions

The most satisfactory definition of the mole fraction of i in a complicated phase with many elements and many sites is in terms of the rate of change of the entropy of random mixing with respect to the amount of i in the phase, the other amounts and PT being constant (Powell 1977). The entropy of random mixing is obviously dependent on the crystal structure and the interactions between the atoms or molecules in the phase, so that the mole fractions depend on an adequate characterization of the phase. Considering, for example, a clinopyroxene, the crucial distinction is between atoms mixing randomly on each site, and the mixing of pyroxene molecules in the structure – the latter implying strong short range order effects between atoms in the structure due to local charge balance or size constraints. It can be shown that these short range order effects are only likely to become important when the amounts of the disturbing atoms (for example, Na + Al in clinopyroxene) become substantial (Yarushevskiy 1970). Thus, mixing on sites is likely to be substantially correct for the pyroxenes (and the garnet) in garnet lherzolites, although this may not be true for omphacites in eclogites. For mixing on sites,

$$x_{\mathrm{Mg_2Si_2O_6,\,opx}} = (x_{\mathrm{Mg,\,M1}}x_{\mathrm{Mg,\,M2}}x^2_{\mathrm{Si,\,tet}})_{\mathrm{opx}}. \tag{4}$$

Thus site occupancies are required for calculating mole fractions. Following, for example, Wood & Banno (1973), sodium, calcium and manganese are placed on M2, while aluminium (after filling the tetrahedral site), ferric iron, chromium and titanium are placed on M1, simply on a ionic radius criterion. The distribution of Fe^{2+} and Mg between M1 and M2 provides a problem because this requires knowledge of the thermodynamics of the exchange reaction

$$\mathrm{MgFeSi_2O_6 = FeMgSi_2O_6} \tag{5}$$

for both orthopyroxene and clinopyroxene. The equilibrium relation of (5) for each phase is

$$-\Delta G^\circ = RT \ln\,(a_{\mathrm{FeMgSi_2O_6}}/a_{\mathrm{MgFeSi_2O_6}}). \tag{6}$$

The calculation of site occupancies requires a knowledge of this Gibbs energy of reaction and the activity coefficients in the equilibrium constant. Although this is possible for orthopyroxenes in MS using the data of Virgo & Hafner (1969) and Saxena & Ghose (1971), there are no published data on the effect of other cations, particularly Ca and Al on the site distributions. A few determinations are available for clinopyroxenes notably McCallister, Finger & Ohashi (1976). The assumption that

$$\left(\frac{\mathrm{Mg}}{\mathrm{Fe}}\right)_{\mathrm{M1}} = \left(\frac{\mathrm{Mg}}{\mathrm{Fe}}\right)_{\mathrm{M2}} = \left(\frac{\mathrm{Mg}}{\mathrm{Fe}}\right)_{\mathrm{px}} \quad \text{or} \quad K_{\mathrm{D}}(5) = 1 \tag{7}$$

(for example, Powell & Powell 1974), will not produce seriously incorrect site occupancies for Mg for garnet lherzolite pyroxenes even if K_{D} (5) is substantially different from 1 because their iron contents are so small. For a binary orthopyroxene, $0.925\mathrm{Mg_2Si_2O_6}$–$0.075\mathrm{Fe_2Si_2O_6}$, ln K_{D} (5) of 0.7 ± 1.0 corresponds to ± 0.029 on each of the site occupancies. This is small compared with $x_{\mathrm{Mg,\,M1}} = 0.902$ and $x_{\mathrm{Mg,\,M2}} = 0.948$, but large compared with $x_{\mathrm{Fe,\,M1}} = 0.098$ and $x_{\mathrm{Fe,\,M2}} = 0.052$.

Activity coefficients

Activity coefficients take account of all the interactions in the structure not covered by the mole fraction. Thus the activity coefficient of i can be defined in terms of the rate of change of the Gibbs energy of mixing minus the entropy of random mixing with respect to the amount of i in the phase, with the other amounts and PT held constant (Powell 1977). The activity coefficients are usually represented as a function of composition with a number of adjustable parameters which are usually a function of temperature and pressure. This function is often referred to as a mixing model. Many mixing models, mostly empirical, have been devised; a comparison of a few of the most commonly used binary models is given by Powell (1974). Almost any model involving more than one adjustable parameter can be used to describe binary phase equilibria data. Thus the choice of mixing model is not constrained by phase equilibria experiments. Further, if the phases in the equilibria experiments (and, in this case, the garnet lherzolites as well) cover a relatively small range of composition, then any asymmetry of the mixing model does not affect the activity coefficients so that a single parameter mixing model can be used.

The most useful models can be derived directly or indirectly by considering near neighbour interactions between atoms in the structure. For a one-site phase, or for next-nearest interactions in a two-site phase, the regular (r) model provides a straightforward starting point for considering non-ideality. Nearest neighbour interactions in a two-site phase can be modelled using a Bragg-Williams (B.W.) formulation, these interactions having been ignored in most geological applications. The form of the activity coefficients for these two models is given in Powell (1977). For example, the activity coefficient of $Mg_2Si_2O_6$ in a binary orthopyroxene can be expressed

$$RT \ln \gamma_{\mathrm{Mg_2Si_2O_6}} = (x^2_{\mathrm{Fe,M1}}\, w_{\mathrm{FeMg,M1}} + x^2_{\mathrm{Fe,M2}}\, w_{\mathrm{FeMg,M2}})_{\mathrm{r}} + (x_{\mathrm{Fe,M1}}\, x_{\mathrm{Fe,M2}}\, w_{\mathrm{MgMgFeFe}})_{\mathrm{B.W.}},$$

where the w's are interaction energies which are usually taken to be linear functions of temperature and pressure. A further example, which is relevant later, is the considerable simplification in the formulation of the activity coefficient ratios which appear in the equilibrium constant for exchange reactions. Consider a pyroxene with Mg, Fe and Al on M1 and Mg, Fe, Ca and Na on M2; then,

$$RT \ln \left(\frac{\gamma_{\mathrm{MgCa}}}{\gamma_{\mathrm{MgMg}}}\right) = [w_{\mathrm{CaMg}}(x_{\mathrm{Mg}} - x_{\mathrm{Ca}})_{\mathrm{M2}} + x_{\mathrm{Fe}}(w_{\mathrm{CaFe}} - w_{\mathrm{FeMg}})_{\mathrm{M2}} + x_{\mathrm{Na}}(w_{\mathrm{CaNa}} - w_{\mathrm{MgNa}})_{\mathrm{M2}}]_{\mathrm{r}} + [w'_{\mathrm{Fe}}\, x_{\mathrm{Fe,M1}} + w'_{\mathrm{Al}}\, x_{\mathrm{Fe,M1}}]_{\mathrm{B.W.}}. \tag{8}$$

Clearly the choice of mole fraction and activity coefficient expressions and the site occupancies will affect the fitting of the experimental data, and thus the calculated conditions of formation of the garnet lherzolites. Further subjectivity arises because there are usually too many unknown parameters to calculate from the very limited available experimental data. A choice has therefore to be made of those parameters which are to be solved for, while the others are assumed to be negligible, for example w_{ij} is set to zero if i and j are geochemically similar, or are given estimated values. Some of these choices can be made less exacting by choosing suitable reactions for consideration. The suitability of a reaction will depend on the simplicity of its equilibrium constant and on the compositions of the phases in the experiments and in the garnet lherzolites. Another aspect of suitability is the ease of application of the method to the natural minerals. The method must not be too sensitive, either to the compositions of the minerals or to the parameters in the calibration (within the context of the model). Therefore it is possible that one method is readily applicable to garnet lherzolites but of no value for gabbros; another may be good for sheared garnet lherzolites but uncertain for granular garnet lherzolites. Some attention is paid to these uncertainties in the next section, making use of the equation for error propagation (see, for example, Anderson 1976). For $y = f(x_1, x_2, \ldots, x_n)$, and uncorrelated errors on x_i, then

$$\sigma_y^2 = \sum_{i=1}^{n} \left(\frac{\partial y}{\partial x_i}\right)^2_{x_{j(i \neq j)}} \sigma^2_{x_i}. \tag{9}$$

Where uncertainty is quoted it refers to one standard deviation (σ), real or estimated.

Geothermometry and geobarometry

Table 1 contains some representative analyses of garnets, orthopyroxenes and clinopyroxenes from garnet lherzolites in kimberlites (from Thaba Putsoa, Nixon 1973). By examining these, and bearing in mind comments from the last section, it is possible to identify those mole fractions that would be unsatisfactory in an equilibrium constant because of the large uncertainties so generated. For example reactions involving iron-bearing endmembers of the pyroxenes will be unsatisfactory.

TABLE 1. THE COMPOSITIONS OF ORTHOPYROXENE, CLINOPYROXENE AND GARNET FROM A REPRESENTATIVE SHEARED GARNET LHERZOLITE (1610) AND A REPRESENTATIVE GRANULAR GARNET LHERZOLITE (1592), BOTH FROM THABA PUTSOA (NIXON 1973)

The garnet is recalculated on 12 oxygens, the pyroxenes on 6 oxygens.

	1610			1592		
	garnet	cpx	opx	garnet	cpx	opx
Si	3.032	1.988	1.970	3.014	1.987	1.974
Ti	0.045	0.008	0.005	0.001	0.001	0.000
Al	1.721	0.105	0.057	1.709	0.101	0.039
Cr	0.122	0.009	0.004	0.269	0.056	0.010
Fe	0.519	0.164	0.206	0.379	0.052	0.120
Mn	0.016	0.004	0.004	0.025	0.002	0.003
Mg	2.202	1.119	1.679	2.164	0.878	1.841
Ca	0.337	0.499	0.059	0.433	0.797	0.012
Na	0.013	0.099	0.021	0.033	0.122	0.005
$x_{\mathrm{Ca,g}}$	0.112	—	—	0.144	—	—
$x_{\mathrm{Mg,g}}$	0.734	—	—	0.721	—	—
$x_{\mathrm{Ca,M2}}$	—	0.499	0.059	—	0.797	0.012
$x_{\mathrm{Mg,M2}}$	—	0.351	0.819	—	0.076	0.923
$x_{\mathrm{Fe,M2}}$	—	—	0.101	—	—	0.060

Some published methods

The main geobarometric method that has been used on garnet lherzolites involves the solubility of alumina in orthopyroxene in equilibrium with garnet, formulated by Wood & Banno (1973) and Wood (1974) as the reaction

$$\underset{\text{garnet}}{\mathrm{Mg_3Al_2Si_3O_{12}}} = \underset{\text{orthopyroxene}}{\mathrm{Mg_2Si_2O_6 + MgAl_2SiO_6}}, \tag{10}$$

for which the equilibrium relation is

$$-\Delta G^\circ = RT \ln \frac{(4x_{\mathrm{Mg,M1}}\, x_{\mathrm{Al,M1}}\, x^2_{\mathrm{Mg,M2}}\, x_{\mathrm{Al,tet}}\, x^3_{\mathrm{Si,tet}})_{\mathrm{opx}}}{(x^3_{\mathrm{Mg}}\, x^2_{\mathrm{Al}})_{\mathrm{g}}} \tag{11}$$

plus any activity coefficient terms. However, particular problems arise with $x_{\mathrm{Al,M1}}$ and $x_{\mathrm{Al,tet}}$ in garnet lherzolite orthopyroxenes because these values are critically dependent on the accuracy of the silica analysis, on small departures from stoichiometry and on the amount of ferric iron in the analysis. This means that this reaction is unsuitable for geobarometry on garnet lherzolites, although it is possible to make some arbitrary simplification (for example, averaging $x_{\mathrm{Al,M1}}$ and $x_{\mathrm{Al,tet}}$, Wood & Banno 1973) and at least obtain the relative pressures in a nodule suite. There is the further problem of the possible overestimation of alumina solubility in pyroxenes in experiments (Howells 1975).

The main geothermometric method that has been used on garnet lherzolites involves the shape of the orthopyroxene–clinopyroxene miscibility gap using the reaction

$$\underset{\text{clinopyroxene}}{\mathrm{Mg_2Si_2O_6}} = \underset{\text{orthopyroxene}}{\mathrm{Mg_2Si_2O_6}}, \tag{12}$$

for which the equilibrium relation is

$$-\Delta G^\circ = RT \ln \frac{(x_{\mathrm{Mg,M1}}\, x_{\mathrm{Mg,M2}}\, x^2_{\mathrm{Si,tet}})_{\mathrm{opx}}}{(x_{\mathrm{Mg,M1}}\, x_{\mathrm{Mg,M2}}\, x^2_{\mathrm{Si,tet}})_{\mathrm{cpx}}} \qquad (13)$$

plus any activity coefficient terms. Wood & Banno (1973) assumed that pyroxenes are ideal solutions and found that ΔG° (30 kbar†) $= 84800 - 44.5T$ (where ΔG° is in joules and T in kelvins) whereas this value is likely to be less than 4000 J (see, for example, Navrotsky & Coons 1976). Calcium–magnesium interactions on M2 are likely to be substantially non-ideal and so the assumption of ideality is unlikely to be correct.

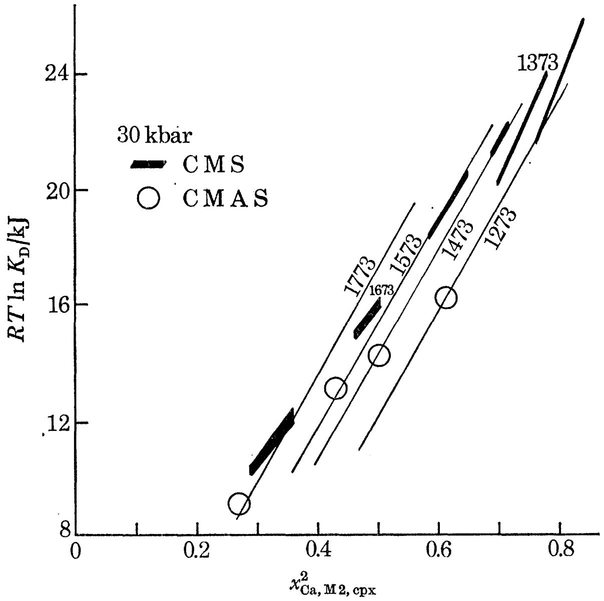

FIGURE 2. $RT \ln K_D$ plotted against $x^2_{\mathrm{Ca,M2,cpx}}$ for the reaction $Mg_2Si_2O_6$ (clinopyroxene) = $Mg_2Si_2O_6$ (orthopyroxene). The slope of the lines gives $w_{\mathrm{CaMg,cpx}}$, while the intercepts give ΔG°. CMS data from Nehru & Wyllie (1974) (error blocks are one standard deviation of the pyroxene compositions); CMAS data from Akella (1976).

The simplest system within which to start calibrating (12) is CMS using the data of Lindsley & Dixon (1976) and Nehru & Wyllie (1974). In CMS (13) becomes

$$-\Delta G^\circ = RT \ln \left(\frac{x_{\mathrm{Mg,M2,opx}}}{x_{\mathrm{Mg,M2,cpx}}}\right) + w_{\mathrm{CaMg,opx}}\, x^2_{\mathrm{Ca,M2,opx}} - w_{\mathrm{CaMg,cpx}}\, x^2_{\mathrm{Ca,M2,cpx}}, \qquad (14a)$$

if the M2 site in the pyroxenes can be treated as a regular solution. The orthopyroxene activity coefficient will be insignificant compared to the other terms and can be ignored, thus:

$$-\Delta G^\circ = RT \ln K_D - w_{\mathrm{CaMg,cpx}}\, x^2_{\mathrm{Ca,M2,cpx}}. \qquad (14b)$$

Thus, a plot of $RT \ln K_D$ against $x^2_{\mathrm{Ca,M2,cpx}}$ allows the calculation of w and ΔG°. Data from CMS are insufficient to calculate these parameters, so data from Akella (1976) in CMAS have to be combined with the CMS data (figure 2). The problem with having to use the CMAS data is that interactions on M1, on the tetrahedral sites, and some between-site terms should appear in (14). Thus the uncertainties on the CMAS points in figure 2 are large.

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† 1 kbar = 10^8 Pa.

Therefore, at 30 kbar,

$$w_{\mathrm{CaMg,\,cpx}} = 33\,500\ \mathrm{J/mol}, \tag{15}$$

$$\Delta G^\circ = 11\,900 - 6.82T,$$

where ΔG° is in joules and T in kelvins. Although it is feasible that there is a small negative temperature dependence to this w, the data are not good enough to differentiate it. The calculated ΔG° fulfils the criterion of being less than 4000 J at least above 900 °C. A 30 kbar temperature in c.m.a.s. can be calculated by substituting (15) into (14) and rearranging:

$$T = (1435 - 4025\, x^2_{\mathrm{Ca,\,M2,\,cpx}})/(0.82 - \ln K_{\mathrm{D}}). \tag{16}$$

Unfortunately the two terms in the numerator are of the same size as the two terms in the denominator, so that small composition differences are dramatically propagated into large temperature differences. Uncertainties in the calculated temperature can be obtained by applying (9) to (16) for the mole fractions, whence

$$\sigma_T \approx \sigma_{x_{\mathrm{Mg,M2,cpx}}} \left| \frac{T}{x_{\mathrm{Mg,\,M2,\,cpx}}(0.82 - \ln K_{\mathrm{D}})} \right|.$$

For 1610 (table 1), $\sigma_T \sim 1.7 \times 10^6\, \sigma_{x_{\mathrm{Mg,M2,cpx}}}$; for 1592 (table 1), $\sigma_T \sim 5400\, \sigma_{x_{\mathrm{Mg,M2,cpx}}}$. The uncertainties are even larger if the uncertainties on the constants are included. Clearly these uncertainties are sufficiently large not to warrant the further development of this reaction.

The conclusions to be reached are that:

(*a*) little is known about the pressure of formation of the garnet lherzolites, except that the sheared lherzolites probably formed at greater depth than the granular garnet lherzolites;

(*b*) temperatures calculated using an ideal mixing model for pyroxenes may be more uncertain than suggested, and that reaction (12) is unsuitable as a geothermometer if the pyroxenes are modelled as regular solutions.

Some new methods

Advantage should be taken of the simplifications in the equilibrium constant for exchange reactions bearing in mind the problems in formulating the thermodynamics of solid solutions in multicomponent systems. Fe–Mg exchange reactions are particularly easy to formulate because of the geochemical similarity of Fe and Mg, but as already argued $x_{\mathrm{Fe,\,M1}}$ and $x_{\mathrm{Fe,\,M2}}$ will be most uncertain for the garnet lherzolite pyroxenes. Further, there is insufficient experimental work in iron-bearing systems to calibrate such reactions.

Given the reasonable amount of experimental work in CMAS (Lindsley & Dixon 1976; Akella 1976; Nehru & Wyllie 1974), the obvious reactions to consider are Ca–Mg exchange reactions between orthopyroxene, clinopyroxene and garnet. For the reaction

$$\underset{\text{clinopyroxene}}{\mathrm{CaMgSi_2O_6}} + \underset{\text{orthopyroxene}}{\mathrm{Mg_2Si_2O_6}} = \underset{\text{orthopyroxene}}{\mathrm{CaMgSi_2O_6}} + \underset{\text{clinopyroxene}}{\mathrm{Mg_2Si_2O_6}}, \tag{17}$$

the equilibrium relation in CMAS is

$$-\Delta G^\circ = RT \ln \left\{ \left(\frac{x_{\mathrm{Ca,\,M2}}}{x_{\mathrm{Mg,\,M2}}}\right)_{\mathrm{opx}} \left(\frac{x_{\mathrm{Mg,\,M2}}}{x_{\mathrm{Ca,\,M2}}}\right)_{\mathrm{cpx}} \right\} + w_{\mathrm{CaMg,\,cpx}}(x_{\mathrm{Ca,\,M2}} - x_{\mathrm{Mg,\,M2}})_{\mathrm{cpx}}$$
$$- w_{\mathrm{CaMg,\,opx}}(x_{\mathrm{Ca,\,M2}} - x_{\mathrm{Mg,\,M2}})_{\mathrm{opx}}, \tag{18}$$

assuming that the M2 site in the pyroxenes can be modelled using the regular model. The Bragg-Williams terms in (8) are ignored here because they are likely to be small compared

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with the clinopyroxene activity coefficient term. As $x_{\mathrm{Ca,M2,opx}}$ is small and has a small range both in CMAS and in the garnet lherzolite orthopyroxenes, the orthopyroxene activity coefficient term is approximately constant at a particular pressure and temperature and so can be added to ΔG° to give g; thus,

$$g = RT \ln K_{\mathrm{D}} + w_{\mathrm{CaMg,cpx}}(x_{\mathrm{Ca,M2}} - x_{\mathrm{Mg,M2}})_{\mathrm{cpx}}. \tag{19}$$

A plot of $RT \ln K_{\mathrm{D}}$ against $(x_{\mathrm{Ca,M2}} - x_{\mathrm{Mg,M2}})_{\mathrm{cpx}}$ for the CMS and CMAS data allows the calculation of g and w (figure 3). The 30 kbar data confirm the value of $w_{\mathrm{CaMg,cpx}}$ given in (15). Therefore, with the assumption that w is independent of temperature then g (30 kbar) $= -33900$ J and is also independent of temperature. Combining with the 15 and 28 kbar data of Lindsley & Dixon (1976), then

$$\left.\begin{aligned} g &= -13800 - 670P \quad \text{(where } g \text{ is in joules and } P \text{ in kilobars);} \\ w &= 55450 - 730P \quad \text{(where } w \text{ is in joules/mole and } P \text{ in kilobars).} \end{aligned}\right\} \tag{20}$$

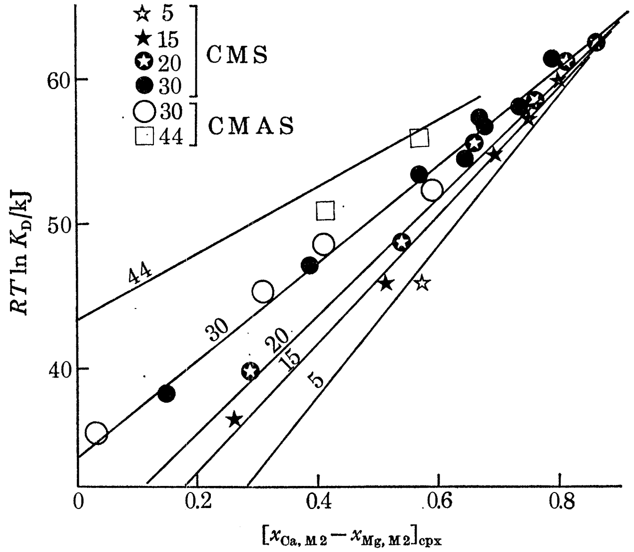

FIGURE 3. RT ln K_{D} plotted against $(x_{\mathrm{Ca,M2}} - x_{\mathrm{Mg,M2}})_{\mathrm{cpx}}$ for the Ca–Mg exchange reaction between orthopyroxene and clinopyroxene. The slope of the lines gives $w_{\mathrm{CaMg,cpx}}$, while the intercept gives $-g$. CMS data at 30 kbar from Nehru & Wyllie (1974), at other pressures from Lindsley & Dixon (1976); CMAS data from Akella (1976). In addition, data from Howells & O'Hara (1975), combined with data from Mori & Green (1976), at higher temperatures plotted on extensions of the appropriate pressure lines.

Substituting (20) into (19) and rearranging gives

$$T = -\{1660 + 80P + (x_{\mathrm{Ca,M2}} - x_{\mathrm{Mg,M2}})_{\mathrm{cpx}}\,(6670 - 88P)\}/\ln K_{\mathrm{D}}. \tag{21}$$

Some idea of the sensitivity of this equation for calculating the temperature at a particular pressure for garnet lherzolites can be obtained by applying (9) to (21), although (21) should be applied only in CMAS. The uncertainty in the temperature with respect to compositional uncertainties is

$$\sigma_T \approx \sigma_{x_{\mathrm{Ca,M2,opx}}} \left| \frac{T}{x_{\mathrm{Ca,M2,opx}} \ln K_{\mathrm{D}}} \right|.$$

For 1610 (table 1), $\sigma_T \sim 9800\,\sigma_{x_{\mathrm{Ca,M2,opx}}}$ (at 40 kbar); for 1592 (table 1), $\sigma_T \sim 13100\,\sigma_{x_{\mathrm{Ca,M2,opx}}}$ (at 20 kbar). Using a 5% relative error on $x_{\mathrm{Ca,M2,opx}}$ (cf. Boyd & Finger 1975), σ_T is 30 and

10 °C respectively. Including uncertainties in the fitted parameters in CMAS, the uncertainties on the temperatures are about 50 °C for the sheared nodules and less than that for the granular nodules.

The extension of (21) to apply to multicomponent pyroxenes was made using data from Akella (1976) and the results of calculations on garnet–orthopyroxene equilibria using data from Wood (1974). The form of the extra activity coefficient terms for (18) are given by (8). The significant terms for application to garnet lherzolite pyroxenes are likely to be the one involving $x_{\mathrm{Fe,\,M2,\,opx}}$ and the one involving $x_{\mathrm{Na,\,M2,\,cpx}}$. A reasonable fit of the limited data gives

$$T = -\{1600+80P+(x_{\mathrm{Ca,\,M2}}-x_{\mathrm{Mg,\,M2}})_{\mathrm{cpx}}\,(6670-88P)-1900x_{\mathrm{Fe,\,M2,\,opx}}\}/\ln K_{\mathrm{D}}. \qquad (22)$$

Given that the mixing model chosen for the pyroxenes is more or less correct then the uncertainty on the calculated temperature of a garnet lherzolite at a particular pressure should be less than 75 °C, and probably less than 50 °C for the granular variety.

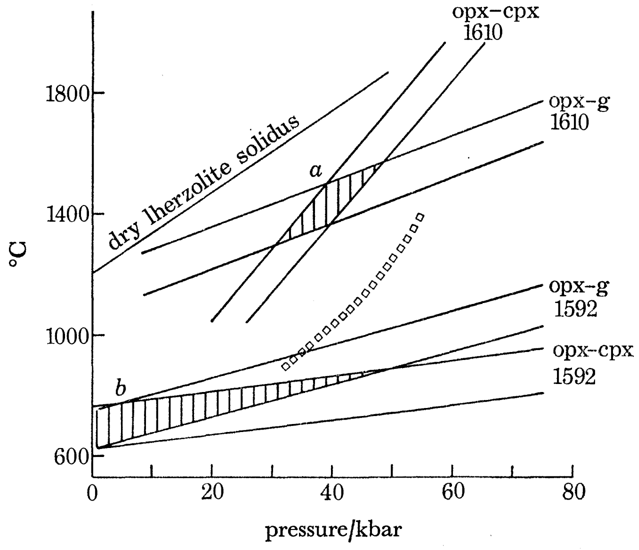

FIGURE 4. Pressure–temperature plot showing the conditions of formation of the garnet lherzolites 1610 and 1592 from Thaba Putsoa, as representatives of sheared (*a*) and granular (*b*) garnet lherzolites respectively. Data from Nixon (1973). The geotherm from Boyd (1973) is also shown (□).

Equation (22) defines a *PT* band for a pyroxene pair. These bands are shown in figure 4 for the representative sheared and granular garnet lherzolites whose analyses are presented in table 1. The other sheared and granular nodules from the Thaba Putsoa group tightly around these examples. The significant feature of these bands is that the conditions of formation of the sheared nodules must either be substantially hotter or substantially shallower than previously suggested. Certainly if the nodules were formed at a higher temperature they would have been approaching the *dry* lherzolite solidus; if they were formed at a lower pressure this would imply that the suggestion of Howells (1975), that alumina solubility in orthopyroxene in equilibrium with garnet has been overestimated, is correct.

Another *PT* band with a reasonable angle of intersection to the one defined by (22) is required to get an estimate of temperature and pressure rather than just a relation between them. The logical choice of reaction to try is

$$\underset{\text{garnet}}{\tfrac{1}{3}\mathrm{Ca_3Al_2Si_3O_{12}}} + \underset{\text{orthopyroxene}}{\mathrm{Mg_2Si_2O_6}} = \underset{\text{garnet}}{\tfrac{1}{3}\mathrm{Mg_3Al_2Si_3O_{12}}} + \underset{\text{orthopyroxene}}{\mathrm{CaMgSi_2O_6}}, \tag{23}$$

for which the equilibrium relation in CMAS is

$$-\Delta G^\circ = RT\ln\left\{\left(\frac{x_{\mathrm{Mg}}}{x_{\mathrm{Ca}}}\right)_{\mathrm{g}}\left(\frac{x_{\mathrm{Ca,\,M2}}}{x_{\mathrm{Mg,\,M2}}}\right)_{\mathrm{opx}}\right\} + w_{\mathrm{CaMg,\,g}}(x_{\mathrm{Ca}}-x_{\mathrm{Mg}})_{\mathrm{g}} - w_{\mathrm{CaMg,\,opx}}(x_{\mathrm{Ca,\,M2}}-x_{\mathrm{Mg,\,M2}})_{\mathrm{opx}}, \tag{24}$$

or, proceeding as for equations (18) and (19),

$$h = RT\ln K_{\mathrm{D}} + w_{\mathrm{CaMg,\,g}}(x_{\mathrm{Ca}}-x_{\mathrm{Mg}})_{\mathrm{g}}. \tag{25}$$

Unfortunately there are far fewer data from which to calculate h and $w_{\mathrm{CaMg,\,g}}$, specifically Akella (1976) and Wood (1974). However, Hensen, Schmid & Wood (1975) presented experimental data from which they calculated $w_{\mathrm{CaMg,\,g}} = 31200-18T$ (where w is in joules and T in kelvins) with no pressure dependence. The experimental data do not, however, preclude a small pressure dependence, because they span a small pressure range. The experimental data of Raheim & Green (1974) can be reconciled with the relatively well known volume change of the Fe–Mg garnet–clinopyroxene exchange reaction (-0.091 J/bar, Robie, Bethke & Beardsley 1967) if $w_{\mathrm{CaMg,\,g}} = 23800-18T+420P$ (where w is in joules, T in kelvins and P in kilobars). Certainly the smaller enthalpy contribution to this w is more consistent with the enthalpy of solution measurements of Newton, Charlu & Kleppa (1977). Application of (25) to the experimental results of Akella (1976) gives $h = -62500+38T-525P$ (where h is in joules, T in kelvins and P in kilobars). The addition of iron to the system requires an addition of terms from (8). Of these the most significant should be an $x_{\mathrm{Fe,\,M2,\,opx}}$ term (cf. equation (22)). Application of (25) to the data of Wood (1974) gives $(w_{\mathrm{FeCa}}-w_{\mathrm{FeMg}}) = 15900$ J, with the expected result that w_{FeCa} is greater than w_{FeMg} in orthopyroxene. The above can be rearranged to give

$$T = \frac{7500+63P-(2870+50P)\,(x_{\mathrm{Mg}}-x_{\mathrm{Ca}})_{\mathrm{g}}-1900x_{\mathrm{Fe,\,M2,\,opx}}}{4.58-\ln K_{\mathrm{D}}-2.16(x_{\mathrm{Mg}}-x_{\mathrm{Ca}})_{\mathrm{g}}}. \tag{26}$$

The uncertainty in the calculated temperature at a particular pressure due to compositional uncertainties is

$$\sigma_T \approx \sigma_{x_{\mathrm{Ca,\,M2,\,opx}}}\left|\frac{T}{x_{\mathrm{Ca,\,M2,\,opx}}\{4.58-\ln K_{\mathrm{D}}-2.16(x_{\mathrm{Mg}}-x_{\mathrm{Ca}})_{\mathrm{g}}\}}\right|.$$

For 1610 (table 1), $\sigma_T \sim 7200\,\sigma_{x_{\mathrm{Ca,\,M2,\,opx}}}$ (at 40 kbar); For 1592 (table 1), $\sigma_T \sim 14500\,\sigma_{x_{\mathrm{Ca,\,M2,\,opx}}}$ (at 20 kbar). Using a conservative 5 % relative error on $x_{\mathrm{Ca,\,M2,\,opx}}$, σ_T is 20 and 10 °C respectively. Although (26) is formulated on less data than (22), it would be surprising if the uncertainty on the calculated temperature (at a particular pressure) is greater than 75 °C. PT bands for 1610 and 1592 are plotted in figure 4. The intersections with the orthopyroxene–clinopyroxene bands support the earlier conclusion that the published pressure estimates for the sheared garnet lherzolites are too high. Further, this may also be true for the granular garnet lherzolites.

Discussion

The above calculations imply that equilibrium was not reached in most experimental studies on alumina solubility in orthopyroxene coexisting with garnet. One way that this serious accusation could be correct is if pyroxenes on first crystallizing accept too much alumina (for equilibrium) and are then incapable of rejecting enough to reach equilibrium in the duration of the experiments. If this is correct then it is possible that this could also occur in nature when pyroxenes crystallize from a silicate liquid at high temperatures and pressures. A further implication is that Akella's experimentally generated pyroxenes contain too much alumina. This will not affect the above calculations as long as exchange equilibrium was achieved between the M2 sites. This should be correct if the between-site interactions are not important, a reasonable assumption given the form of the expressions.

If the calculations are indeed correct, then one explanation of the steeper 'geotherm' for these garnet lherzolites is that these assemblages were formed long before kimberlite eruption during a time when the geothermal gradient was much higher (during the last period of major volcanism?). This would involve the mantle behaving like a metamorphic belt, with the mineral equilibria in the assemblages being frozen-in sometime during the long, slow cooling to the geothermal gradient at the time of eruption. This explanation depends on the assumption that the shearing process and any accompanying frictional heating has not affected the mineral compositions. Certainly, any interpretation of calculated temperatures and pressures depends on when and how this shearing took place.

Clearly if geothermometric/geobarometric calculations are to be performed with confidence they should be based on a much larger experimental data set, with more attention being paid to the form of the mole fraction and activity coefficient expressions.

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Discussion

E. C. Baughan (*Shrivenham, Oxfordshire, U.K.*). Dr Powell's first figure shows different authors disagreeing about the variation of a given standard Gibbs free energy change as a function of pressure and temperature. Of these variations the first depends on the volume change and the second on the entropy change; these can be *independently* measured from density and specific heat respectively.

Have such checks been made, and have they proved useful?

R. Powell. Although the temperature and pressure dependence of a Gibbs energy of reaction are measurable, there are some general problems in dealing with silicates and a specific problem concerning the reactions considered in this paper. The general problems relate to the difficulty of performing calorimetry on many silicates – due, for example, to the possiblity of non-equilibrium order–disorder in the phases during the calorimetric experiments. Small discrepancies due to this and other factors are crucial in calculating enthalpies and entropies of reaction because these values are usually small, at least for the solid–solid reactions considered here. The specific problem relates to the use of the $CaMgSi_2O_6$ component in orthopyroxene as it is not possible to synthesize pure $CaMgSi_2O_6$ with an orthorhombic structure.