Garnet-pyroxene equilibria in the system CaO-MgO-Al2O3SiO2 (CMAS): prospects for simplified (`T-independent') lherzolite barometry and an eclogite-barometer

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Garnet-pyroxene equilibria in the system CaO − MgO − Al₂O₃ − SiO₂ (CMAS): prospects for simplified ('T-independent') lherzolite barometry and an eclogite-barometer

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Abstract. New experimental data on compositions of garnets in two-pyroxene − garnet assemblages in the system CaO − MgO − Al₂O₃ − SiO₂ (CMAS) are presented for conditions between 1,100 and 1,570° C and 30 to 50 kb. Garnets in these assemblages become less calcic with increasing pressure. Garnet-orthopyroxene barometry (Al-solubility-barometry) pertinent to geobarometry for garnet lherzolites has been evaluated with a set of experimental data covering the range 900 to 1,570° C and 15 to 100 kb. Various formulations of this barometer work well to 75 kb. Phase equilibria are not sufficient to positively verify the thermodynamic validity of any of such models. Empirical garnet-orthopyroxene barometry at least in the system CMAS can be formulated to obtain a pressure estimate without previous temperature estimation ($P(\text{kb}) = 34.4 − 19.715 \ln X_{Al}^{M1} + 17.702 \ln X_{Ca}^{M2}$). The potential application of an analogous garnet-clinopyroxene equilibrium is limited because the amount of Ca-Tschermaks in natural clinopyroxenes is usually quite small in garnet lherzolites and many eclogites. The Ca − Mg exchange between garnet and clinopyroxene appears however sufficiently sensitive to pressure to allow calibration of a CMAS barometer. The reaction

$$3\,CaMgSi_2O_6 + Mg_3Al_2Si_3O_{12}$$
$$= 3\,Mg_2Si_2O_6 + Ca_3Al_2Si_3O_{12}$$
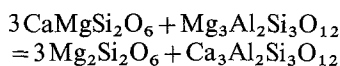
has a $\Delta V°$ of 3.5 cm³. The total pressure dependency of this reaction is however closer to a theoretical $\Delta V°$ of about 5 cm³ when excess volume properties of the phases involved are taken into account. We have calibrated such a barometer (mean error of estimate 2.8 kb) for assemblages with pyrope-rich (py > 80) garnets and orthopyroxenes. This may provide the basis for a geobarometer for eclogites from kimberlites.

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Abbreviations used in the text
CaTs = Ca-tschermak's molecule, CaAl₂SiO₆; cpx = clinopyroxene; di = diopside, CaMgSi₂O₆; en = enstatite, Mg₂Si₂O₆; gr = grossular, Ca₃Al₂Si₃O₁₂; gt = garnet; MgTs = Mg-Tschermak's molecule, MgAl₂SiO₆; opx = orthopyroxene; px = pyroxene; py = pyrope, Mg₃Al₂Si₃O₁₂; a_i^j = activity of component i in phase j; γ = activity coefficient; $\Delta G(I)$ = molar Gibbs free energy difference of reaction (I) at standard state unless specified otherwise; $H(I)$, (ΔH_I) = molar enthalpy (difference) of phase (reaction) (I) at standard state unless specified otherwise; $S(I)$, (ΔS_I) = molar entropy (difference) of phase (reaction) (I) at standard state unless specified otherwise; $V°$, $(\Delta V_I°)$ = molar volume (difference) of phase (reaction) (I) at standard state; X_i^j = mole fraction of component i in phase j

Introduction

Lherzolite and eclogite are the two major types of xenoliths in kimberlites. The investigation of these xenoliths provides important constraints on P, T distributions within the upper mantle and its chemical composition. The most often used and best described barometers for garnet lherzolites are based on the Al-content of orthopyroxene coexisting with garnet. First experimental studies done by Boyd and England (1964), Boyd (1973) and MacGregor (1974) led to pioneering works about P, T distributions in the mantle such as Boyd's (1973) pyroxene geotherm. However in those works data from the simple MgO − Al₂O₃ − SiO₂(MAS) system were extrapolated to complex natural rocks. Based on discrepancies between the Al-contents at one P, T condition in experiments using MAS and natural compositions (Green and Ringwood 1967), methods have been developed to correct for elements such as Ca, Fe (Wood and Banno 1973; Wood 1974; Harley 1984) and Cr (Nickel and Green 1985). These calculations still form the most widely used geobarometers.

The influence of Ca on garnet-orthopyroxene equilibria was recognized by Akella (1976) in a study in the system CMAS and has been confirmed by studies in Fe-bearing systems (Ellis and Green 1979; Wood 1974; Harley and Green 1982). However, Akella's (1976) data have been disputed and are not directly comparable to other laboratories (for a discussion see Howells and O'Hara 1978; Nickel et al. 1985). Other studies in CMAS lack microanalysis to serve as a working foundation for a further improvement of barometry in the CMAS system (Howells and O'Hara 1978; Herzberg 1978). Only recently new reversed CMAS data covering a wide range of P, T conditions were obtained (Perkins and Newton 1980; Yamada and Takahashi 1984; Nickel et al. 1985). In this work we report new data on compositions of garnet coexisting with ortho- and clinopyroxene and combine them with other recent data to evaluate barometry in the CMAS system. It is demonstrated that phase equilibrium data do not provide sufficient constraints to choose from various models used to describe equilibria: the lack of calorimetric data for high-Al orthopyroxenes

hampers a thermodynamically rigorous evaluation of garnet-orthopyroxene equilibrium.

Various formulations of empirical barometers in the system CMAS are successful in reproducing experimental conditions over a considerable range in P and T (Harley and Green 1982; Nickel and Green 1985; Wood 1974). However, these barometers suffer from a rather large temperature dependence. Thus a barometer applied to natural rocks has not only the problem of correction for various elements, but is also strongly dependent on the accuracy of an applied thermometer. Most reactions used for geothermometry are also pressure dependent. This necessitates an iterative way of estimating P,T conditions of origin and thereby increases error levels. It is shown that at least in CMAS this problem of empirical barometry may be overcome by utilizing the covariance of Ca and Al in orthopyroxene with temperature.

Geobarometry of eclogites from kimberlites however is presently almost impossible. Some models have been proposed to calibrate a geobarometer in the CMAS system based on the solubility of the Ca-Tschermaks component in clinopyroxene coexisting with garnet (Herzberg 1978; Gasparik 1984a). This reaction is potentially useful for the application to eclogitic assemblages, because the molar volume difference is about as large as for the garnet-orthopyroxene reaction. The application to natural systems however is problematic: Apart from the necessity of a careful evaluation of the influence of Na, which is an important constituent in eclogitic clinopyroxenes, it can be shown that natural clinopyroxenes from lherzolites and diamond-bearing eclogites contain only very small quantities of a Tschermak's component or none at all. In this work we demonstrate the possibility of an alternative barometer for eclogites based on the Ca—Mg exchange between garnet and clinopyroxene.

Experimental methods and results

Starting materials for experiments in CMAS were seeded sintered oxides, glasses or crystalline mixes (pure pyrope, enstatite, and diopside). Experimental details are discussed and analyses of pyroxenes presented elsewhere (Nickel et al. 1985).

Garnet growth features vary with pressure, temperature and run duration. Increasing temperature and run duration favour larger crystal growth. The influence of pressure on the garnet growth features is very strong as well. At comparable run conditions (i.e. similar temperatures and run durations, varying between 11 hrs at 1,100° C, 9 h at 1,200° C, 4 h at 1,300° C, 2.5 h at 1,400° C and 2 h at 1,470° C) we obtained garnets with differing character: In experiments at 30 kb garnets are often large (up to 100 microns) and poikilitic with numerous inclusions of all coexisting phases. At 40 kb the glassy starting material yielded numerous tiny garnets (usually <5 microns). Garnets from experiments at 50 kb are also numerous but somewhat larger (to 15–20 microns). They contain only few inclusions and can be analysed quite easily, while the poikilitic character of the low-P garnets or the tiny size of the medium-P garnets often preclude uncontaminated analyses. The various growth features of garnets indicate differing kinetic conditions at different pressures. We assume a sluggish nucleation process of garnet at low pressures (and consequent growth on one
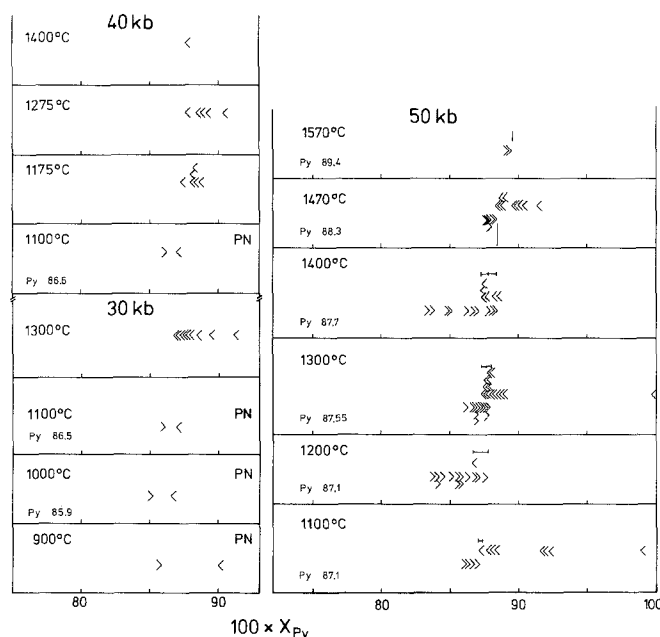

Fig. 1. Molar Ca/Ca + Mg of garnet in experiments at 1,100, 1,200, 1,300, 1,400, 1,470 and 1,570° C at 50 kb, 1,175, 1,275 and 1,400° C and 1,200, 1,300 and 1,400° C at 30 kb respectively. *Arrows pointing to the right* are from glassy starting material, *arrows pointing to the left* from crystalline (pure pyrope) staring material. Overlap region indicated by bar

nucleus), while higher pressure favours fast nucleation in many places of the charge.

We have evaluated garnet equilibrium compositions by plotting the Ca/Ca + Mg ratio of garnets of a given run and differing starting material (Fig. 1). In most high pressure runs we obtain an overlap of Ca/Ca + Mg ratios of garnets from crystalline and glassy material. Glassy starting material is known to form intermediate pyroxenes extremely fast (Mori and Green 1975; Mori 1978), from which garnets with relatively high Ca/Ca + Mg ratios are likely to nucleate. We consider experiments with glassy starting material thus as approaching equilibrium composition from the grossular rich side. The crystalline starting material approaches equilibrium from pure pyrope. Figure 1 shows the compositional spread of the garnets from these two materials, confirming the assumption of reaction directions and demonstrating a compositional zonation in garnet. Processes like "path-looping", which cause overstepping of equilibrium compositions are well known from pyroxenes (e.g. Lane and Ganguly 1980; Perkins et al. 1981; Nickel et al. 1985). In particular in experiments at high pressures, where garnet forming reactions seem to be relatively fast, similar processes for garnet are indicated by the experimental results. Accordingly the overlap range has been taken as a bracket for the garnet composition. Ca/Ca + Mg values of garnets in low-pressure experiments growing from well defined starting points (Perkins and Newton 1980, runs 9–16, using high-Ca and pure pyrope garnets as starting material) do not overlap, but show a compositional gap. This is consistent with the assumption of differing kinetics at differing pressures. The low-P garnets react slower and hence do not reach their equilibrium value, but approach it leaving a compositional gap. We have thus chosen this gap to be the most likely compositional range for equilibri-
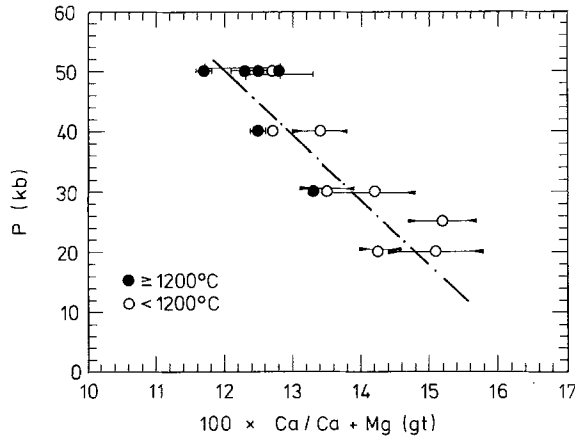
Fig. 2. Molar Ca/Ca+Mg of garnets in CMAS coexisting with two pyroxenes vs. P (kb). Data from Perkins and Newton (1980) and this work. Width of bracket and type of bracket indicated (gap: *inward pointing arrows,* overlap: *line bordered by vertical lines,* halfbracket: *short line ending at most extreme composition found*). For clarity symbols and lines have been displaced slightly to higher and lower pressures, where overlap would occur. *Dash-dot line* shows regression (Eq. (1))

um values. Following the reasoning of Nickel and Brey (1984) for coexisting pyroxenes we used the midpoint of bracket or gap in our mathematical evaluation.
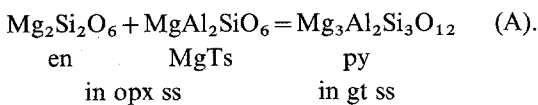
In Fig. 2 the pyrope content of garnets vs. the experimental pressure is plotted. One of the compositional gaps of Perkins and Newton (1980) is extremely large (85.8–90 mole% py at 900° C, 30 kb, run no. 10 of Perkins and Newton 1980), hence equilibrium was not approached closely and this result has been omitted in Fig. 2. The trend of garnets to become less calcic with increasing pressure is apparent. A reggression yielded

$$Ca\# (gt) = 17 - 0.1 * P(kb) \tag{1}$$

where $Ca\# = 100 * Ca/Ca + Mg = 100 * X_{Ca}^{gt}$. Some temperature dependency is indicated, but the quantification is difficult within the error of the data. We have not used the garnet compositions given by Yamada and Takahashi (1984, Figs. 2 and 5) because of internal inconsistencies: the garnet compositions of their high-temperature runs (1,300–1,500° C) at 50 and 75 kb are in good agreement with the data in our Fig. 2, while at 1,200° C they report garnets of much higher grossular contents. At 100 kb there is a substantial solution of pyroxene in garnet, so that the regression from Fig. 2 is not directly applicable.

Orthopyroxene-garnet barometry

The orthopyroxene-garnet barometer is based on the reaction

$$Mg_2Si_2O_6 + MgAl_2SiO_6 = Mg_3Al_2Si_3O_{12} \tag{A}.$$
$$\text{en} \qquad \text{MgTs} \qquad \text{py}$$
$$\text{in opx ss} \qquad \text{in gt ss}$$

The activities of the components of interest in garnet and orthopyroxene are defined as

$$a_{py}^{gt} = (X_{Mg}^{gt})^3 (X_{Al}^{gt})^2 \gamma_{Mg3Al2Si3O12} \tag{2}$$

$$a_{en}^{opx} = X_{Mg}^{M1} X_{Mg}^{M2} \gamma_{Mg2Si2O6} \tag{3}$$

$$a_{MgTs}^{opx} = X_{Al}^{M1} X_{Mg}^{M2} \gamma_{MgAl2SiO6} \tag{4}$$

and accordingly the K_D for reaction (A) is

$$K_D(A) = [(X_{Mg}^{gt})^3 (X_{Al}^{gt})^2]/[(X_{Mg}^{M1}) (X_{Al}^{M1}) (X_{Mg}^{M2})^2] \tag{5}$$

In the MAS system Eq. (5) is equal to

$$K_D(A) = 1/[(X_{Al}^{M1}) (1 - X_{Al}^{M1})], \tag{6}$$

because in the MAS system garnet is always pure pyrope and there is no diopside component in orthopyroxene. In CMAS the K_D for reaction (A) is appreciably influenced by the composition of the garnet because in Eq. (5) the parameter X_{Mg}^{gt} ($= 1 - X_{Ca}^{gt}$) is cubed.

Based on ionic radii and site sizes Wood and Banno (1973) argued for the restriction of Ca to the M2 and Al to the M1 position in orthopyroxene. These assumptions and the charge balance constraint lead to the following formulations of site occupancies in CMAS:

$$X_{Al}^{M1} = Al_{total}/2 \tag{7}$$

$$X_{Mg}^{M1} = 1 - X_{Al}^{M1} \tag{8}$$

$$X_{Mg}^{M2} = 1 - X_{Ca}^{opx} \tag{9}$$

$$X_{Mg}^{gt} = 1 - X_{Ca}^{gt} \tag{10}$$

where the recalculation of the chemical analyses is based on 6 (pyroxenes) or 12 (garnet) oxygens respectively. These formulations are not necessarily correct. There may be disordering of Al between the M1 and M2 site of pyroxenes (Ganguly and Ghose, 1979). The measured Al disordering may however not be pertinent to the experimental conditions of synthesis because cation distributions between similar sites in orthopyroxene at high temperatures may be unquenchable (e.g. Fe−Mg disorder (Besancon 1981)). Ganguly and Ghose (1979) also noted a restriction of Al to the B tetrahedral site of orthopyroxene and suggested an orthopyroxene endmember of pyrope composition ("opy"). It is however not clear, if the underlying 'Al-avoidance principle' holds since we know of experimentally synthesized orthopyroxenes with more than 25% of a Mg-Tschermaks component (MacGregor 1974; Arima and Onuma 1977; Gasparik and Newton 1984). Recent calculations of short range ordering energies of aluminous pyroxenes (Cohen and Burnham 1985) suggest only a strong preference for the B site. In any case thermodynamic modelling may be done with an arbitrary choice of endmembers and because of the uncertainties we stick to the more traditional choice of endmembers and define the components of the various phases as given in Eqs. (7) to (9).

Various models based on CMAS data give lower values of ΔH of reaction (A) (Wood and Banno 1973; Wood 1974; Harley and Green 1982; Harley 1984; Nickel and Green, 1985) then indicated by calorimetric data (Charlu et al. 1975; Wood and Holloway 1984) or strict thermodynamic models for MAS (Chatterjee and Terhart 1985). Uncertainties lie in the thermochemical data on aluminous orthopyroxenes and the possibility that even such basic thermochemical data as the heat of solution of pure enstatite (Charlu et al. 1975) may be in error (Perkins et al. 1981; Wood and Holloway 1984).

Existing empirical models (Harley and Green 1982; Nickel and Green 1985; Wood 1974) are successful in reproducing experimental conditions in the simple systems MAS and CMAS. We do not present here an update of such
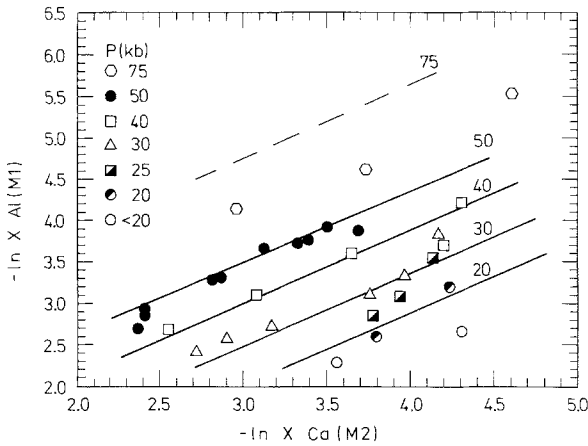
Fig. 3. Experimental data on orthopyroxenes in CMAS from Perkins and Newton (1980), Yamada and Takahashi (1984) and Nickel et al. (1985) in a plot of $-\ln X_{Al}^{M1}$ vs. $-\ln X_{Ca}^{M2}$, covering a temperature range of 900 to 1,570° C. Isobars drawn are calculated according to Eq. (11)

models, because for barometric purposes all models quoted above reproduce the experimental conditions with a standard error of less then 2 kb even for the extended pressure range made available by the more recent data (Yamada and Takahashi 1984; Nickel et al. 1985, this work).

A major problem for the application of barometers is their strong temperature dependence. An error in the temperature estimate by 20° C causes an error of the pressure estimate of about 1 kb. We have therefore attempted to find a mathematical expression for the calculation of pressure without previous temperature estimation. The Ca content of orthopyroxene is strongly temperature dependent. Sachtleben and Seck (1981) have demonstrated that the Ca content of orthopyroxene may be used as a geothermometer even in the natural system. Nickel et al. (1985) have shown that Al and Ca have a strong covariance in ortho- and clinopyroxenes in CMAS. The Ca content of orthopyroxene thus may be used for an empirical correction of the temperature dependence of the Al-solubility in orthopyroxene coexisting with garnet and clinopyroxene: plotting the ex-

perimental data in a diagram of $\ln X_{Ca}^{M2}$ vs. $\ln X_{Al}^{M1}$ (Fig. 3), we can draw linear isobars, which therefore are temperature independent. This allows the calibration of such a barometer and we find that the formulation

$$P(\text{kb}) = 34.4 - 19.715 \ln X_{Al}^{M1} + 17.702 \ln X_{Ca}^{M2} \qquad (11)$$

satisfies most data points in CMAS in the range 15 to 50 kb and 900–1,570° C (mean error of estimate 2.2 kb). Pressures would however be systematically underestimated at 75 (by 10–15 kb) and 100 kb (by 20–35 kb). These conditions are however outside the known rock record (Nickel and Green 1985). The straight extrapolation to natural samples is shown in Fig. 4a and b, where estimates for app. 150 garnet lherzolite nodules via Eq. (11) are compared to the estimates based on a more sophisticated model (Nickel and Green 1985). In the application of Eq. (11) it was only necessary to include all tschermakitic components, thus X_{Al}^{M1} has been replaced by $X_{Al}^{M1} + X_{Cr}^{M1}$, which is calculated as $(Al + Cr - 2Ti + Na)/2$.

The total Ca from the structural formula (based on 6 oxygen) is taken as X_{Ca}^{M2}. Most estimates agree within ±5 kb but some discrepancies are larger. Some of the discrepancies may be due to analytical uncertainties, because both Al and Ca are often quite low in orthopyroxene. If indeed the analytical uncertainties were the major contributing part of the uncertainty then the error level would have to increase with decreasing temperature, because Ca in orthopyroxene decreases simultaneously and accordingly the error would increase. There is no such indication in Fig. 4a, which clearly demonstrates the possibility of obtaining temperature independent pressure estimates even in natural systems. Fig. 4b shows that Eq. (11) works in the whole range down to less than 20 kb within the quoted uncertainty. However, comparing Fig. 4a and b some systematic differences between different suites or provinces are indicated, which is possibly related to differences in the bulk- and mineral chemistry. A correction may however not be obtained on the basis of estimates from natural rocks, because the thermometer applied (Wells 1977) by Nickel and Green (1985) has a small but systematical error (see discussion there). The correction may only be made on the basis of carefully reversed experiments in complex
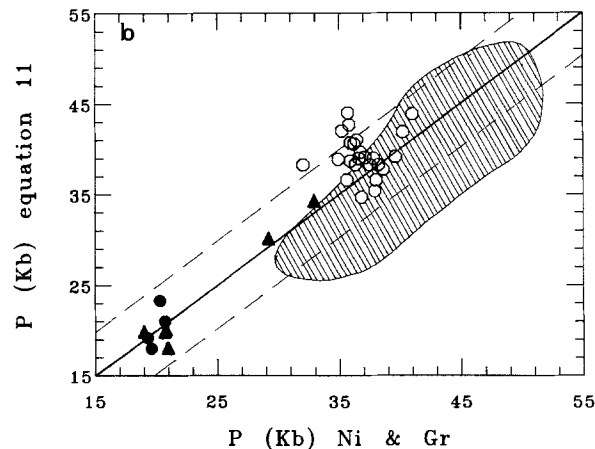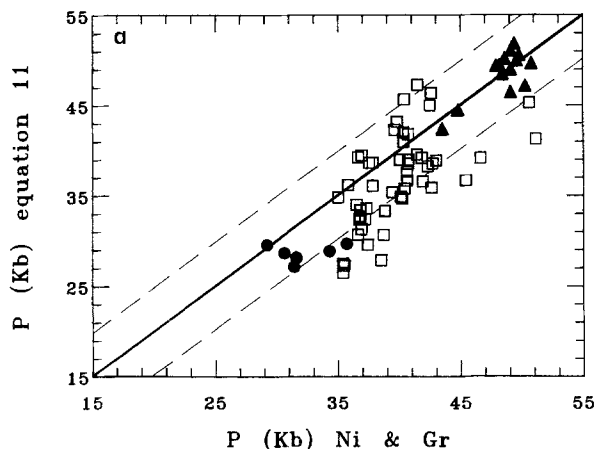
Fig. 4a and b. Comparison of pressure estimates for garnet lherzolite nodules by the method of Nickel and Green (1985; temperature estimates according to Wells 1977) and Eq. (11) (this work). *Solid line* denotes perfect agreement, the *dashed lines* are for ±5 kb discrepancies respectively. Nodules from **a** South Africa with differing equilibration temperatures: *dots* 700–900° C, *squares* 900–1,100° C, *triangles* >1,100° C. **b** Different localities; *hexagons:* Four Corners, USA, *squares:* Australia, *triangles:* Solomon Islands, *shaded area:* South Africa. Data sources see Nickel and Green (1985)

systems (Nickel and Brey, in prep.). Thus at this stage Eq. (11) may be used to give a crude estimate of depth of origin and we prefer to use the method of Nickel and Green (1985) where possible.
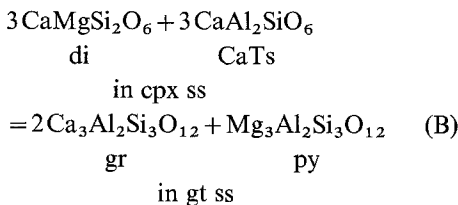
In principle the form of Eq. (11) provides also a pressure-independent thermometer. A weighted regression gave

$$T \, (°C) = 2{,}126 - 68.6 \ln X_{Al}^{M1} + 340.5 \ln X_{Ca}^{M2}. \qquad (12)$$

Its usefulness will also be evaluated with the aid of experiments in natural systems (Nickel and Brey, in prep.). Both the proposed barometer and thermometer will be particularly useful for the evaluation of physical conditions for opx megacrysts.

Garnet-clinopyroxene barometry

Eclogites from kimberlites are essentially bimineralic. Distinctive accessory phases such as kyanite, corundum, graphite or diamond are rare in those samples (Dawson 1980). Geothermometers and -barometers for eclogites from xenoliths in kimberlite thus have to use garnet-clinopyroxene relationships. The availability of mineral data for all coexisting phases in the garnet stability field in CMAS allows the calibration of a barometer based on a reaction between garnet and clinopyroxene analogous to reaction (A):

$$3\,CaMgSi_2O_6 + 3\,CaAl_2SiO_6$$
$$\qquad di \qquad\qquad CaTs$$
$$\qquad\qquad in\ cpx\ ss$$
$$= 2\,Ca_3Al_2Si_3O_{12} + Mg_3Al_2Si_3O_{12} \qquad (B)$$
$$\qquad gr \qquad\qquad py$$
$$\qquad\qquad in\ gt\ ss$$

"Al in cpx-isopleths" have accordingly been calculated by Herzberg (1978), Gasparik (1984) and Wood and Holloway (1984). It is also possible to treat the covariance of Ca and Al in clinopyroxene in a similar way as described above for orthopyroxene. Nickel et al. (1985) have shown in their Fig. 6 that T-insensitive isobars may be drawn in a diagram of X_{Al}^{M1-cpx} vs. $(1-Ca)^{cpx}$. These isobars are however not related by linear increments with pressure and thus a barometer or thermometer in the form of Eq. (11) using clinopyroxene is less precise then one using orthopyroxene. Accordingly any combination (e.g. using Al of opx and Ca of cpx) is less precise. There is little hope that reaction (B) may be developed into a useful geobarometer in any way. In garnet lherzolite assemblages clinopyroxenes contain very little if any of a tschermak type molecule (Fig. 5). Most of the Al in clinopyroxene is balanced by Na. This is also true for diamond-bearing eclogites. Kyanite or corundum bearing eclogites show consistently the feature of excess Al^{VI} in clinopyroxene, which is interpreted as kyanite in solid solution in clinopyroxene (Lappin 1978) whereas in SiO_2 oversaturated eclogites the $Ca_{0.5}AlSi_2O_6$ molecule may play an important role (e.g. Wood and Henderson 1978). The determination of the quantity and activity of a Ca-tschermak's type component in clinopyroxene would thus be very difficult, because it would have to rely on extremely precise Al and Si- analyses. Furthermore Al-solubility in clinopyroxene is far more complicated even in the CMAS system than envisaged in the models quoted above, as has been shown by Nickel et al. (1985).

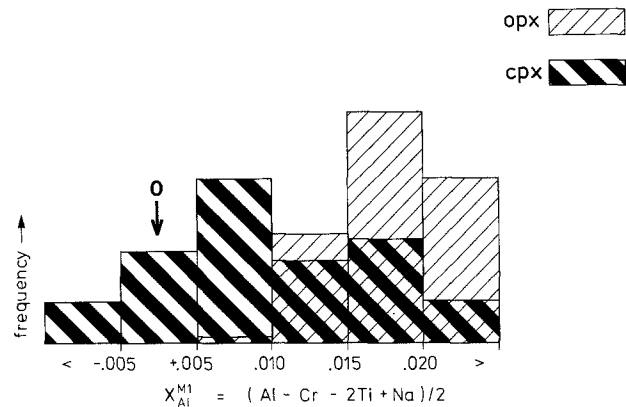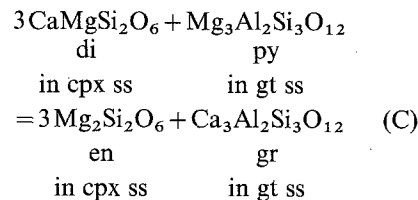We have therefore investigated alternative reactions be-

opx [////]

cpx [\\\\]

Fig. 5. Histogram of concentrations of tetrahedral Al of ortho- and clinopyroxene from natural garnet lherzolite xenoliths. Data sources see Nickel and Green (1985). The Al-content is calculated as $Al_{total} - [(Al - Cr - 2\,Ti + Na)/2]$ of the structural formula. Negative values for Al^{IV} would indicate the presence of significant amounts of Fe^{+++} or a poor analyses

Table 1. Modified parameters for reaction (D) [en(opx) = en(cpx)]

$\Delta H°$	1,673 cal	W^{opx}	5,975 cal
$\Delta S°$	1.037 cal/K	W_H^{cpx}	5,019 cal
$\Delta V°$	0.6272 cm^3	W_S^{cpx}	$- 1.322$ cal/K
		W_V^{cpx}	-12.22 cal/kb

tween garnet and clinopyroxene that may be useful for barometric purposes. We found the reaction

$$3\,CaMgSi_2O_6 + Mg_3Al_2Si_3O_{12}$$
$$\qquad di \qquad\qquad py$$
$$\quad in\ cpx\ ss \qquad in\ gt\ ss$$
$$= 3\,Mg_2Si_2O_6 + Ca_3Al_2Si_3O_{12} \qquad (C)$$
$$\qquad en \qquad\qquad gr$$
$$\quad in\ cpx\ ss \qquad in\ gt\ ss$$

quite promising. The values of ΔH, ΔS and ΔV for reaction (C) were estimated in the following way: volumes of the endmembers pyrope, grossular, diopside and enstatite were taken from Newton et al. (1978, 1979). Refined values for enthalpy and entropy (relative to oxides) at 1000 K for these endmembers have been adopted from Table 2 of Wood and Holloway (1984). The problem of determining ΔH, ΔS and ΔV of reaction (C) lies in the properties of the fictive "en in diopside structure" endmember. Recently Nickel and Brey (1984) have calculated the ΔS, ΔV and non-ideality parameters for Ca − Mg interaction in clinopyroxene based on the exchange reaction

$$Mg_2Si_2O_6 \quad = \quad Mg_2Si_2O_6 \qquad (D)$$
$$\quad en \qquad\qquad en$$
$$in\ opx\ ss \qquad in\ cpx\ ss$$
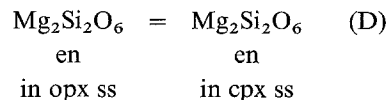
We have updated these values (very minor change) to satisfy the condition $W^{opx} = 5.975$ kcal rather then 8.126 kcal adopted by Nickel and Brey (1984), because the high W^{opx} would predict exsolutions in opx at very high temperatures. The modified values are listed in Table 1. $H(1000K)$ and $S(1000K)$ and $V°$ of the en (cpx) endmember are then calculated by adding the values of ΔH, ΔS and ΔV for reaction (D) to the calorimetrically measured values for

Table 2. Thermodynamic properties of endmembers of reaction (C) in cals, cals/K, and cm^3

Phase	Pyrope	Grossular	Diopside	en (cpx)
$H(1000K)^a$	$-20,300$	-77510	$-35,320$	$-15,215$ $-15,167^c$
$S(1000K)^a$	185.9	187.2	96.0	94.17 94.55^c
V^{ob}	113.27	125.3	66.08	62.5 63.24^c

^{a} Wood and Holloway (1984)
^{b} Newton et al. (1978, 1979)
^{c} Refined values – this work

en (opx). The resulting estimates are listed in Table 2 and compared to the values derived by Wood and Holloway (1984).
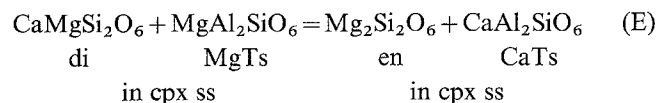
In this way we obtained values for $H(1000K)$, $S(1000K)$ and V° for all endmembers involved in reaction (C). This allows to calculate the values ΔH, ΔS and ΔV for reaction (C), predicting $\Delta H_c = +3249$ cal, $\Delta S_c = -3.065$ e.u. and $\Delta V_c = +3.5$ cm^3. The volume difference argues for a moderate pressure dependency of reaction (C). The total effect of pressure on reaction (C) is however the combined effect of ΔV° and the difference in excess volumes of the endmembers.

The non-idealities of garnet in CMAS result solely from the mixing of Ca and Mg on the dodecahedral site of garnet. At least over a limited compositional range most binary systems can be treated adequately by regular solution models. A symmetric model for garnet yields

$$RT \ln \gamma_{py} = 3 (X^{gt}_{Ca})^2 W^{gt}_{Ca-Mg} \tag{13}$$

$$RT \ln \gamma_{gr} = 3 (X^{gt}_{Mg})^2 W^{gt}_{Ca-Mg}. \tag{14}$$

The W for the the Ca$-$Mg interaction may be P- and/or T-dependent to account for excess entropy and volume. This is discussed later. Non-idealities of clinopyroxenes in CMAS are very complex, in particular the influences of small amounts of Al are difficult to model (Nickel et al. 1985). Nonetheless a thermodynamical treatment of reaction (C) may be attempted because some complicated interactions cancel in the thermodynamic model. The complex behaviour of clinopyroxene makes it necessary to account for non-ideal mixing on both octahedral sites and to consider the influence of cross-site interaction. We evaluate the latter in the context of the model of Wood and Nicholls (1978). Following their procedure we have to look at the cross-site ('reciprocal') reaction within clinopyroxene

$$CaMgSi_2O_6 + MgAl_2SiO_6 = Mg_2Si_2O_6 + CaAl_2SiO_6 \tag{E}$$
$$\quad di \qquad\quad MgTs \qquad\quad en \qquad\quad CaTs$$
$$\qquad in\ cpx\ ss \qquad\qquad\quad in\ cpx\ ss$$

and add the parameter for this exchange to the site terms, which were approximated by symmetrical regular solutions for both of the octahedral sites. This yields

$$RT \ln \gamma^{cpx}_{di} = (X^{M2}_{Mg})^2 W^{cpx}_{Ca-Mg} + (X^{M1}_{Al})^2 W_{Mg-Al} + X^{M2}_{Mg} X^{M1}_{Al} \Delta G(E), \tag{15}$$

$$RT \ln \gamma^{cpx}_{en} = (X^{M2}_{Ca})^2 W^{cpx}_{Ca-Mg} + (X^{M1}_{Al})^2 W_{Mg-Al} + X^{M2}_{Ca} X^{M1}_{Al} \Delta G(E). \tag{16}$$

The two endmembers of clinopyroxene are on opposite sides of the reaction-equation (C) and thus the W's for Mg$-$Al mixing cancel. The W's for Ca$-$Mg interaction will not cancel, because usually X^{M2}_{Ca} is larger or much larger than X^{M2}_{Mg}. The non-ideality parameters for Ca$-$Mg interaction may be taken from the updated version of the Nickel and Brey (1984) model (Table 1). In the calculation of the net influence of the reciprocal interaction (Wood and Nicholls 1978) on reaction (C) the difference X^{M2}_{Ca} and X^{M2}_{Mg} is however multiplied by the usually small value of X^{M1}_{Al}. Thus even if the ΔG of the reciprocal reaction (E) is substantial, there is a tendency for its net influence on reaction (C) to become small. It seems therefore feasible to look at reaction (C) as a first step in terms of non-idealities caused by Ca$-$Mg interactions only and to neglect the reciprocal reaction (E). The expression for reaction (C) becomes then

$$\Delta G^{\circ}(C) = -[RT \ln K_D (C) \\ + 3 (X^{M2}_{Ca})^2 W^{cpx}_{Ca-Mg} + 3 (X^{gt}_{Mg})^2 W^{gt}_{Ca-Mg} \\ - 3 (X^{M2}_{Mg})^2 W^{cpx}_{Ca-Mg} - 3 (X^{gt}_{Ca})^2 W^{gt}_{Ca-Mg}] \tag{17}$$

where

$$K_D(C) = [(X^{M2}_{Mg} X^{gt}_{Ca})/(X^{M2}_{Ca} X^{gt}_{Mg})]^3. \tag{18}$$

Since in CMAS the relationships $X^{M2}_{Mg} = 1 - X^{cpx}_{Ca}$ and $X^{gt}_{Mg} = 1 - X^{gt}_{Ca}$ hold and the $K_D(C)$ has a cubed form, we can simplify Eq. (17) to

$$\Delta G^{\circ}(C) = -3[RT \ln K_D(C) \\ + \{(X^{M2}_{Ca})^2 - (1 - (X^{M2}_{Ca}))^2\} W^{cpx}_{Ca-Mg} \\ + \{(1 - (X^{gt}_{Ca}))^2) - (X^{gt}_{Ca})^2\} W^{gt}_{Ca-Mg}] \tag{19}$$

which is equivalent to

$$\Delta G^{\circ}(C) = -3[RT \ln K'_D(C) + \{2 X^{M2}_{Ca} - 1\} W^{cpx}_{Ca-Mg} \\ + \{(1 - 2(X^{gt}_{Ca}))\} W^{gt}_{Ca-Mg}] \tag{20}$$

with

$$K'_D(C) = [(X^{gt}_{Ca}(1 - X^{M2}_{Ca}))/(X^{M2}_{Ca}(1 - X^{gt}_{Ca}))]. \tag{21}$$

Using the values from Table 1 for Ca$-$Mg non-idealities in clinopyroxene and the estimates for ΔH, ΔS and ΔV for reaction (C) we can look at the non-idealities in garnet. This is very problematic: A number of studies have convincingly argued for excess entropy of pyrope-grossular garnets (e.g. Hensen et al. 1975; Haselton and Newton 1980; Haselton and Westrum 1980; Newton and Perkins 1982; Ganguly and Saxena 1984). Calorimetrically measured garnet data for $py_{60}gr_{40}$ (Haselton and Westrum 1980) do show excess entropy, but highly magnesian garnets ($py > 80$) may not. Gasparik (1984b) has argued for a discontinuity in the properties of py$-$gr garnets occuring at about py_{80} and Wood and Holloway (1984) presented arguments for highly assymetric excess functions, so that garnets with compositions around py_{85} show no excess entropy. We have fitted the data set of this study, which deals exclusively with highly magnesian garnets ($py > 80$) and found that the phase equilibria do not necessitate an excess entropy term. The simple regular solution model term W_{Ca-Mg} from Eqs. (13) and (14) was sufficient to satisfy most data points when split into excess enthalpy and excess volume term. A multiple linear regression yielded $W_H = 2,402$ cal and $W_v = 24.369$ cal/kb. It should be stressed that the formulation is an empirical one and is not meant to apply to the full compositional spectrum of garnets. For this purpose more compli-
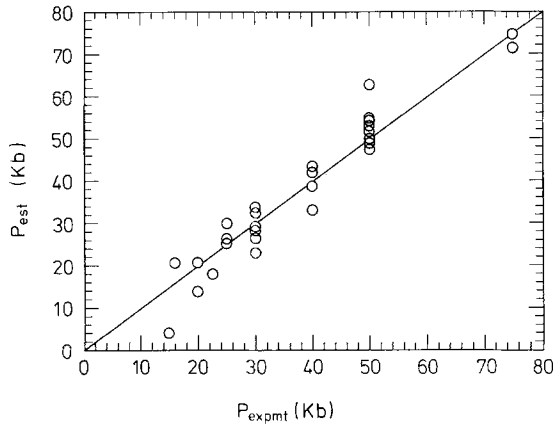
454

Fig. 6. P of the experiments in CMAS vs. the P estimated via Eq. (22)

cated models (or perhaps very simple empirical equations working with the aid of canceling effects) have to be developed once more reversed phase equilibrium studies involving high-Ca garnets become available. But we want to emphasize the fact that the pressure dependence of reaction (C) is large enough to allow the calibration of a barometer, which has in the context of the simple model presented the form

$$P = \{1/[V^\circ + 3(2X_{Ca}^{M2} - 1)\ W_v^{cpx} + 3(1 - 2X_{Ca}^{gt})\ W_v^{gt}]\}*$$
$$\{-3[RT\ln K_D'(C) + 3(W_H^{cpx} - TW_s^{cpx})(2X_{Ca}^{M2} - 1)$$
$$+ 3\,W_H^{gt}(1 - 2*X_{Ca}^{gt})]\}. \tag{22}$$

The combination of ΔV° and excess volume properties of the phases involved yields the net effect of pressure on reaction (C). It is expressed by the factor $[\Delta V^\circ + 3(2X_{Ca}^{M2} - 1)\ W_v^{cpx} + 3(1 - 2X_{Ca}^{gt})\ W_v^{gt}]$. Inserting the values derived we get $83.65 - 36.66*(2X_{Ca}^{M2 - cpx} - 1) + 73.11*(1 - 2X_{Ca}^{gt})$, which is at least for assemblages with highly magnesian garnets in the order of 115 cals/kb, equivalent to a ΔV° of nearly 5 cm^3 in an ideal reaction and is thus lower, but comparable to the ΔV° of the opx-gt reaction (A) (8 to 9 cm^3).

The precision and accuracy of the barometer in the form of Eq. (22) is not as good as the gt-opx barometer. Fig. 6 shows the reproduction of the experimental conditions, the mean error of estimate is 2.8 kb and two conditions (900° C, 15 kb of Perkins and Newton (1980) and 1200° C, 50 kb of Yamada and Takahashi (1984) show large discrepancies. This is attributed to the smaller pressure dependency of reaction (C), the simplified treatment of Ca − Mg interaction in garnet and the complete neglect of reciprocal interaction in clinopyroxene. A better understanding of garnet mixing properties will improve the calibration of the Ca/Mg-barometer. In particular experiments involving the reversal of garnet compositions in simple and complex systems with lower py content in a eclogitic assemblage are of great importance (in prep.). But it is promising that two experiments of Gasparik (1984b) in a cpx − gt-corundum assemblage with py-contents around py 80 (runs 584 and 596) are reproduced by Eq. (22) within 2 kb.

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