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Geothermobarometry in Four-phase Lherzolites II. New Thermobarometers, and Practical Assessment of Existing Thermobarometers

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ABSTRACT

On the basis of experiments presented in Part I of this series, most of the published thermobarometers relevant to four-phase peridotites are tested here for their ability to reproduce experimental conditions. They were rejected if any systematic discrepancy in either pressure or temperature was discernible. This test cautions against the use of all published versions of thermometers based on the compositions of coexisting ortho- and clinopyroxenes and the use of existing barometers based on the Al content of orthopyroxene coexisting with garnet. Therefore, we formulated new versions of the two-pyroxene thermometer and the Al-in-opx barometer:

$$T_{BKN} = \frac{23\,664 + (24\cdot9 + 126\cdot3\,X^{cpx}_{Fe})P}{13\cdot38 + (\ln K^*_D)^2 + 11\cdot59\,X^{cpx}_{Fe}}$$

with $K^*_D = (1 - Ca^*)^{cpx}/(1 - Ca^*)^{opx}$; $Ca^* = Ca^{M2}/(1 - Na^{M2})$ and $X^{px}_{Fe} = Fe/(Fe + Mg)$; T_{BKN} is in degrees Kelvin and P is in kilobars.

Our new barometer is of the form

$$P_{BKN}(kb) = \frac{-C_2 - \sqrt{(C_2^2 + 4C_3C_1/1000)}}{2C_3}$$

$(C_1 - C_3)$ and site occupancies are given in the text.

Temperatures may also be calculated from the Ca content of opx alone:

$$T_{Ca\text{-}in\text{-}opx}(K) = \frac{6425 + 26\cdot4P}{-\ln Ca^{opx} + 1\cdot843}$$

This thermometer can be applied both to the CMS and the natural system experiments, which may indicate that Fe and Na have counter-balancing effects on the Ca content of opx.

The partitioning of Na between opx and cpx can also serve as a useful thermometer, and was calibrated from natural rock data:

$$T = \frac{35\,000 + 61\cdot5P}{(\ln D_{Na})^2 + 19\cdot8}$$

where T is in degrees Kelvin, P is in kilobars, and $D_{Na} = Na^{opx}/Na^{cpx}$.

The following three published thermobarometers based on further exchange reactions are capable of reproducing experimental conditions:

(a) exchange of Ca between olivine and clinopyroxene as a barometer (P_{KB}),
(b) exchange of Fe and Mg between garnet and clinopyroxene as a thermometer (T_{Krogh}),
(c) exchange of Fe and Mg between garnet and olivine as a thermometer ($T_{O'Neill}$).

Our tests also show that the most accurate pressure and temperature estimates are obtained from the following combinations of thermometers and barometers:

(I) $T_{BKN} + P_{BKN}$,
(II) $T_{BKN} + P_{KB}$,
(III) $T_{Krogh} + P_{BKN}$,
(IV) $T_{O'Neill} + P_{BKN}$.

INTRODUCTION

In Part I we presented the results of new, reversed experiments in a natural peridotitic composition and discussed the changing compositions of minerals as a function of pressure and temperature. Multiple linear regression methods based on very simple mathematical expressions are sufficient to calibrate geothermobarometers based on these changing mineral compositions. The serious disadvantage is that these geothermobarometers can be applied *only* to the particular bulk rock composition which was used in the experiments unless proven otherwise. The accuracy of any necessary extrapolation is unknown. Transfer and exchange reactions *between* minerals are less dependent on compositional effects, i.e., non-ideality effects might cancel each other. Thermobarometers based on such reactions are therefore *a priori* superior to those based on single chemical parameters. General applicability can be shown when a particular formulation of an exchange or transfer reaction can reproduce results of all available experiments both in simple and complex systems. The most promising approach is that of Bertrand & Mercier (1985) and Bertrand *et al.* (1986), who calibrated thermobarometers in the simplest possible system, tested the outcome with available experiments in natural complex systems and, if unsatisfactory, added the next more complex system and tried again. This should yield the best results if reversed experiments are available for the key simple systems and if the natural system experiments are reliable. The latter is difficult to prove and is the most serious drawback of this approach.

All these uncertainties for currently available thermobarometers prompted us to determine reversibly mineral compositions in a natural system with a large enough range of pressures and temperatures to make extrapolations unnecessary. Tests were then undertaken on the applicability of any exchange thermobarometer which can be extracted from the data.

The experimental study was primarily designed to bracket the transfer of the enstatite component between coexisting ortho- and clinopyroxene and the exchange of Al between orthopyroxene and garnet. This approach automatically brackets mineral compositions for further reactions between coexisting minerals which are potentially useful for thermobarometry, e.g., that of Cr between opx and grt and of Al between cpx and grt. The experiments were not designed to reverse strictly the exchange of Fe and Mg between coexisting phases, but the agreement between the results of natural mineral mixes (J4, SC-1) and sintered oxide mixes (SCS) and internal consistency for Mg-richer starting materials (see Part I) indicates a close approach to equilibrium. The present experiments can therefore be used to test and design thermobarometers based on many different transfer and exchange reactions which will yield an internally consistent set of thermobarometers and which should give identical (within error) pressure and temperature estimates for a particular rock sample.

INTRINSIC SUITABILITY OF Fe–Mg EXCHANGE REACTIONS FOR THERMOMETRY

A number of thermometers are based on the exchange of Fe^{2+} and Mg^{2+} between coexisting minerals, e.g., between garnet and olivine, orthopyroxene or clinopyroxene. The

TABLE 1

Fitting parameters of Fe–Mg exchange relations

Pair	$\Delta H/R$	$\Delta S/R$	$\Delta V/R$
ol/opx	$-134(\pm 148)$	$-0.08(\pm 0.11)$	$-2.73(\pm 1)$
ol/cpx	$-1489(\pm 148)$	$-1.07(\pm 0.11)$	$-4.64(\pm 1.1)$
opx/cpx	$-1354(\pm 85)$	$-0.99(\pm 0.06)$	$-2.15(\pm 0.6)$
grt/ol	$-1350(\pm 144)$	$-0.51(\pm 0.11)$	$-7.86(\pm 1.7)$
grt/opx	$-1456(\pm 120)$	$-0.55(\pm 0.09)$	$-9.86(\pm 1.4)$
grt/cpx	$-2862(\pm 143)$	$-1.57(\pm 0.11)$	$-11.67(\pm 1.7)$

exchange appears very nearly ideal except for a dependence on grossular content of garnets (e.g., Ellis & Green, 1979; O'Neill & Wood, 1979; Harley, 1984a). As the grossular content of garnets in our experiments changes only very little it seems justified to fit our data empirically to an equation of the form for ideal systems:

$$-RT \ln K_D = \Delta H - T\Delta S + P\Delta V \tag{1}$$

where $K_D = [(Fe/Mg)^A/(Fe/Mg)^B]$, T is in degrees Kelvin, and P is in kilobars. The fitting parameters ΔH, ΔS, and ΔV divided by R for the various exchange reactions are given in Table 1 and these results recast as thermometers in Fig. 1. This figure shows that the exchange between olivine and orthopyroxene is virtually independent of temperature and depends only very slightly on pressure (ΔV is .the only significant fitting parameter—compare Table 1). The exchange of Fe and Mg is reasonably temperature dependent for all other mineral combinations, which would be a good basis for thermometry. The temperature dependence is largest for the pair grt/cpx, followed by ol/cpx, grt/opx, opx/cpx, and grt/ol as judged from the fit parameter $\Delta H/R$. This sequence is in agreement with data for ΔH listed in thermodynamic tables. It is also to be noted that the fitted ΔV parameters are always similar to ΔV of the exchange reaction calculated from volumetric data. The general agreement of the fit parameter with basic thermodynamic data underlines the quality of the experimental data and also indicates that the garnet behaviour is close to ideal in this compositional range.

EVALUATION OF EXISTING THERMOMETERS

The application of several published Fe–Mg exchange thermometers to the data presented here is shown in Fig. 2a–f. The thermometer developed by Ellis & Green (1979), based on the exchange between garnet and clinopyroxene, yields reasonable temperatures at 1300 and 1400 °C, but increasingly overestimates at low temperatures (although only by ~70 °C at 900 °C; Fig. 2a). The update of the same thermometer by Powell (1985) reproduces the experimental data from 1100 to 1400 °C very well and overestimates slightly at 900 and 1000 °C (Fig. 2b). A further update by Krogh (1988) gives correct estimates even at these temperatures, but with a somewhat increased scatter (Fig. 2c). The better agreement is because of the introduction of a curvilinear (fitted with a quadratic and a linear expression), rather than a linear, correction for X_{Ca}^{Grt} by Krogh, which seems to be a step in the right direction in empirical modelling of complex garnets. The overestimation with the thermometers of both Ellis & Green (1979) and Powell (1985) at low temperatures reflects the non-validity of the linear approach.

The calibration by Harley (1984a) of the exchange of Fe and Mg between garnet and orthopyroxene as a thermometer gives slight overestimates at low, and underestimates at
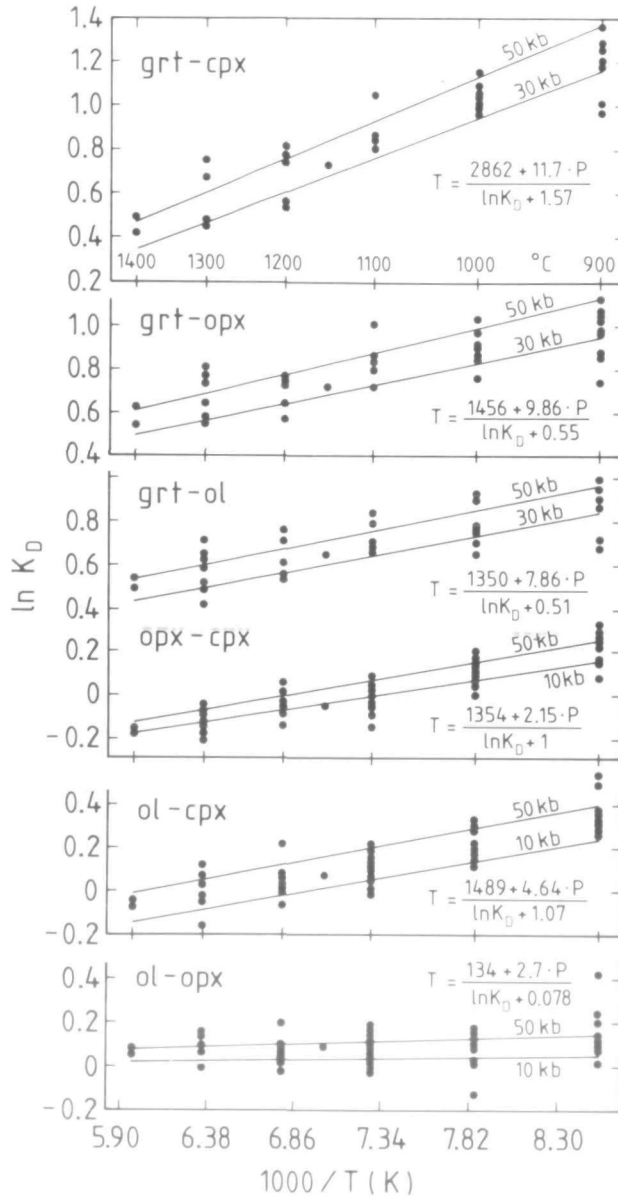
FIG. 1. Ln K_D vs. reciprocal temperature for Fe–Mg exchange equilibria for six different mineral pairs. Dots are ln K_D values calculated from the experimental data given as mg-numbers in table 2 of Part I of this series. These were fitted by a multiple linear regression method to an equation of type (1) (see text). The results are recast in the form of thermometers and given in the figure for each mineral pair. Lines are isobars calculated from these formulae.

high temperatures (Fig. 2d). The T of best agreement, at $\sim 1000\,°C$, is in the temperature region of his CFMAS experiments designed to derive a correction term for non-ideality of Ca–Mg–Fe garnets. Lee & Ganguly (1988) presented a new version based on new experiments in FMAS which, however, overestimates by $\sim 175\,°C$ at $900\,°C$ and $125\,°C$ at $1400\,°C$ (Fig. 2e). Lee & Ganguly's (1988) thermometer gives much better temperature estimates when the correction term for Ca and Mn in garnet is neglected. This term was
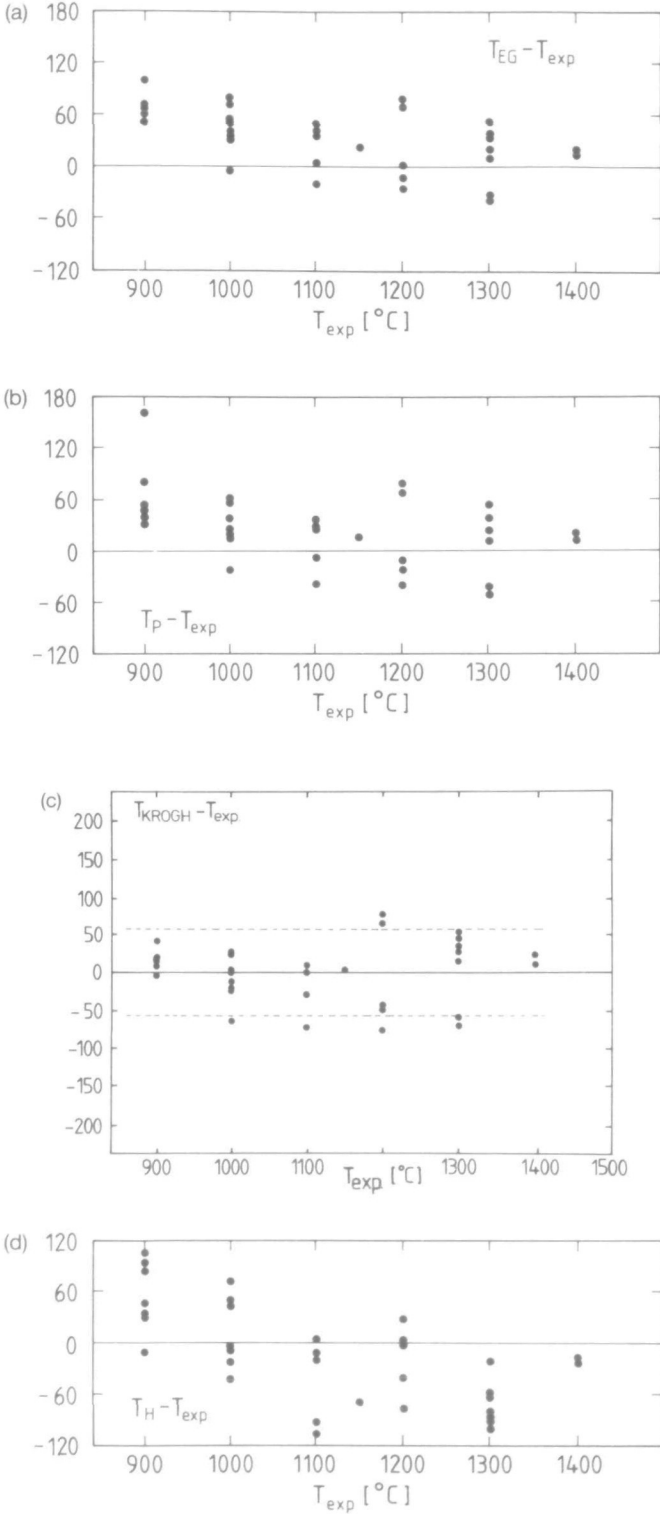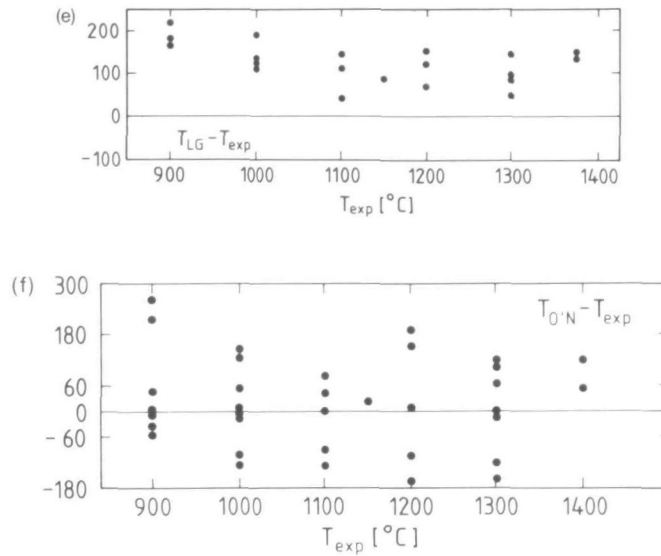
FIG. 2 (a–d)

FIG. 2. Test of various Fe–Mg exchange thermometers for their ability to reproduce experimental temperatures. The results are shown in diagrams of $\Delta T = T_{calc} - T_{exp}$ vs. T_{exp}. Experimental pressures were used to calculate temperatures. (a) Reproduction of experimental temperatures is good at high temperatures with T_{EG} (Ellis & Green, 1979; grt–cpx), but there are increasing overestimates with lower temperatures. (b) T_P (grt–cpx; Powell, 1985) shifts calculated temperatures to somewhat lower values than T_{EG} but is still too high at 900 and 1000 °C. (c) There is a good overall reproduction of experimental temperatures with T_{Krogh} (grt/cpx; Krogh, 1988). It should be possible to calculate realistic temperatures for natural peridotites with this thermometer. (d) Harley's (1984a) grt–opx thermometer (T_H) reproduces experimental temperatures very well at ~1000 °C, a temperature similar to those of his experiments carried out to derive the linear Ca-non-ideality parameter in garnet. There are temperature underestimates above and overestimates below 1000 °C. (e) Lee & Ganguly (1988) carried out new experiments for the partitioning of Fe and Mg between grt and opx in FMAS and included a (Ca + Mn) interaction parameter from Ganguly & Saxena (1984) in their new thermometer (T_{LG}). The application gives serious overestimates of our experimental temperatures. Reproduction is much better when the (Ca + Mn) parameter is neglected, but systematic temperature over- and underestimates are still present. (f) The thermometer of O'Neill & Wood (1979, $T_{O'Neill}$) for the exchange of Fe and Mg between garnet and olivine gives good reproduction at all experimental temperatures, though with a somewhat larger scatter than the thermometers presented in (a)–(e). This thermometer can be applied to natural peridotitic rocks in its present form.

adopted from an independent study of the mixing properties of aluminosilicate garnets by Ganguly & Saxena (1984), and is much higher than the net interaction term $\Delta W^{grt} = (W_{CaMg} - W_{CaFe})^{grt}$ given by Harley (1984a). Carswell & Harley (1989) combined the experimental results of Harley (1984a) and Lee & Ganguly (1988) in FMAS and derived a new thermometric expression with a new, linear interaction term. A single, linear interaction parameter may, however, not be sufficient in view of the systematic deviations in calculated temperatures as seen in Fig. 2d and e.

The experiments by O'Neill & Wood (1979, correction by O'Neill, 1980) on the exchange of Fe and Mg between olivine and garnet cover the range of our garnet compositions and their thermometer reproduces our experimental data very well, even though the scatter is larger than that of the thermometers above (Fig. 2f).

In agreement with Carswell & Gibb (1987a), it is found that other formulations of Fe–Mg exchange thermometers reproduce experiments in natural compositions less satisfactorily than the above versions.

Potentially, the most accurate temperatures (at $T \geqslant 900$ °C) can be calculated with a thermometer based on the transfer of the opx component between coexisting ortho- and

clinopyroxene. The outcome of tests with several commonly used versions of this thermo-meter is shown in Fig. 3. The Wells (1977) formulation reproduces the experiments at 900 °C very well but increasingly underestimates at higher temperatures (Fig. 3a). The formulation by Finnerty & Boyd (1987) yields good results at high temperatures but seriously
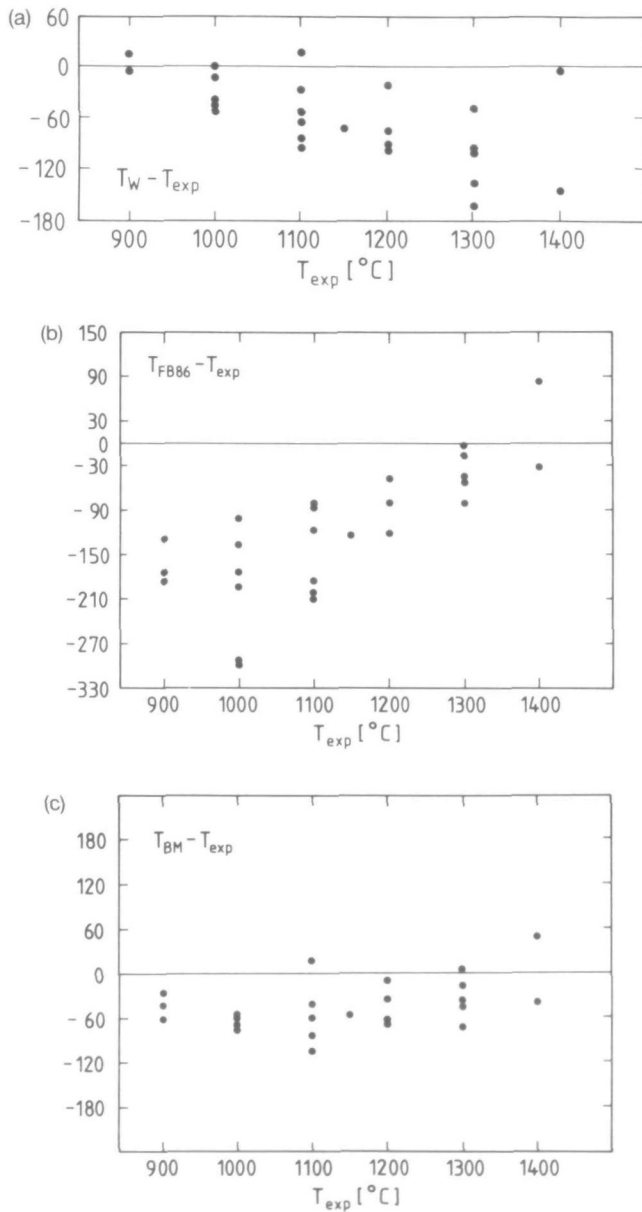

FIG. 3. Reproduction of experimental temperatures with three published versions of thermometers based on the transfer of enstatite component between coexisting ortho- and clinopyroxene [(a) and (c)] or the composition of clinopyroxene only [(b)]. Diagrams are of the same types as for Fig. 2. (a) The thermometer by Wells (1977, T_W) gives good estimates at 900 °C but increasing underestimates at higher temperatures. (b) The thermometer by Finnerty & Boyd (1987, $T_{FB_{86}}$) gives drastic underestimates at low temperatures, but ΔT approaches zero at high temperatures. (c) There is a slight negative deviation of temperatures calculated with the method of Bertrand & Mercier (1985, T_{BM}), which tends to increase with decreasing temperatures.

underestimates at low temperatures (Fig. 3b). The reasons for this discrepancy must lie in the correction for the influence of Fe (hidden in the choice of K_D) and in the neglect of the influence of Na content in clinopyroxene. The thermometer of Bertrand & Mercier (1985) somewhat underestimates temperatures (Fig. 3c) though their treatment of the experimental data is the most comprehensive attempt so far. We attribute this underestimation to the Fe correction of Ca in clinopyroxene, which is based mostly on experiments between 800 and 1000 °C (summarized by Davidson & Lindsley, 1985), a temperature range which is probably too narrow, and with too large a scatter in the experimental results, to yield a universally applicable correction factor. To obtain such a factor, Bertrand & Mercier (1985) fitted $Ca^{M2, cpx}$ as a temperature-dependent linear function of $Fe/(Fe + Mg)$ [for experiments with $Fe/(Fe + Mg) < 0.5$] and obtained $Ca^{M2, CMS} = Ca^{M2, CFMS} + (-0.77 + T/1000)$ [$Fe/(Fe + Mg)$], which means that the influence of Fe on Ca content in cpx should be zero at $T = 497$ °C. Our experiments are reproduced by the Bertrand & Mercier (1985) thermometer if a factor of -0.97 (instead of -0.77) is used, which means, however, that the influence of Fe should be zero at 697 °C. This seems rather unlikely, but comparative tests with natural rock samples show that such a thermometer could be applied for $T > 750$ °C.

A NEW TWO-PYROXENE THERMOMETER

The basis for two-pyroxene thermometry is reversed experiments in the simple CMS system mathematically treated with valid thermodynamic solution models for mixing properties of coexisting pyroxenes. The most recent and comprehensive treatment, from Carlson & Lindsley (1988), can explain all existing pyroxene polymorphs in this system. The reproduction of experimental conditions for coexisting opx and cpx alone is not quite as good as with the simpler solution model of Nickel & Brey (1984, especially at high pressures). Thus the model of Nickel & Brey should be well suited as a starting point for higher-pressure thermometry. However, much simpler, though empirical, models can reproduce experimental temperatures in CMS equally well (e.g., Bertrand & Mercier, 1985; Finnerty & Boyd, 1987). These are preferable as a basis for thermometry as they are less susceptible to analytical errors because of fewer fitted parameters. Use of the empirical power law version of Finnerty & Boyd (1987) is not advisable as errors can propagate rather drastically when applied to conditions outside the experimental range. The fit by Bertrand & Mercier (1985) to an equation of the form (1) needs only one additional non-ideality parameter for clinopyroxene to reproduce experiments in CMS very well.

Ehrenberg (1979) found that $\ln K_D$ of the transfer reaction En(opx) = En(cpx) has a curved relation with reciprocal temperature for CMS experiments, whereas $(\ln K_D)^2$ is linearly dependent. This also holds for the extended data set presented by Nickel & Brey (1984), together with a linear dependence on pressure (Fig. 4a and b). The use of $(\ln K_D)^2$ instead of $\ln K_D$ makes it possible to treat the system CMS as if entirely ideal. We found that such a relationship is valid also for the systems CMAS and CMASCr (SiO_2–MgO–Al_2O_3–CaO–Cr_2O_3—see Fig. 5) and our natural system experiments. We have fitted the midpoints of experimental brackets for CMS [as summarized by Nickel & Brey (1984)], CMAS [summary by Nickel *et al.* (1985), together with the new data of Sen (1985)], CMASCr (Nickel, 1989) and our new natural system data to the following equation:

$$T = (a + bP)/(c + (\ln K_D)^2) \tag{2}$$

where

$$K_D = (1 - Ca^{M2})^{cpx}/(1 - Ca^{M2})^{opx} \tag{3}$$

and P is in kilobars and T in degrees Kelvin, with the following results:

$$\text{CMS: } T = (23\,664 + 24.9P)/(13.38 + (\ln K_D)^2) \quad (2\text{–}60\,\text{kb}) \tag{4}$$
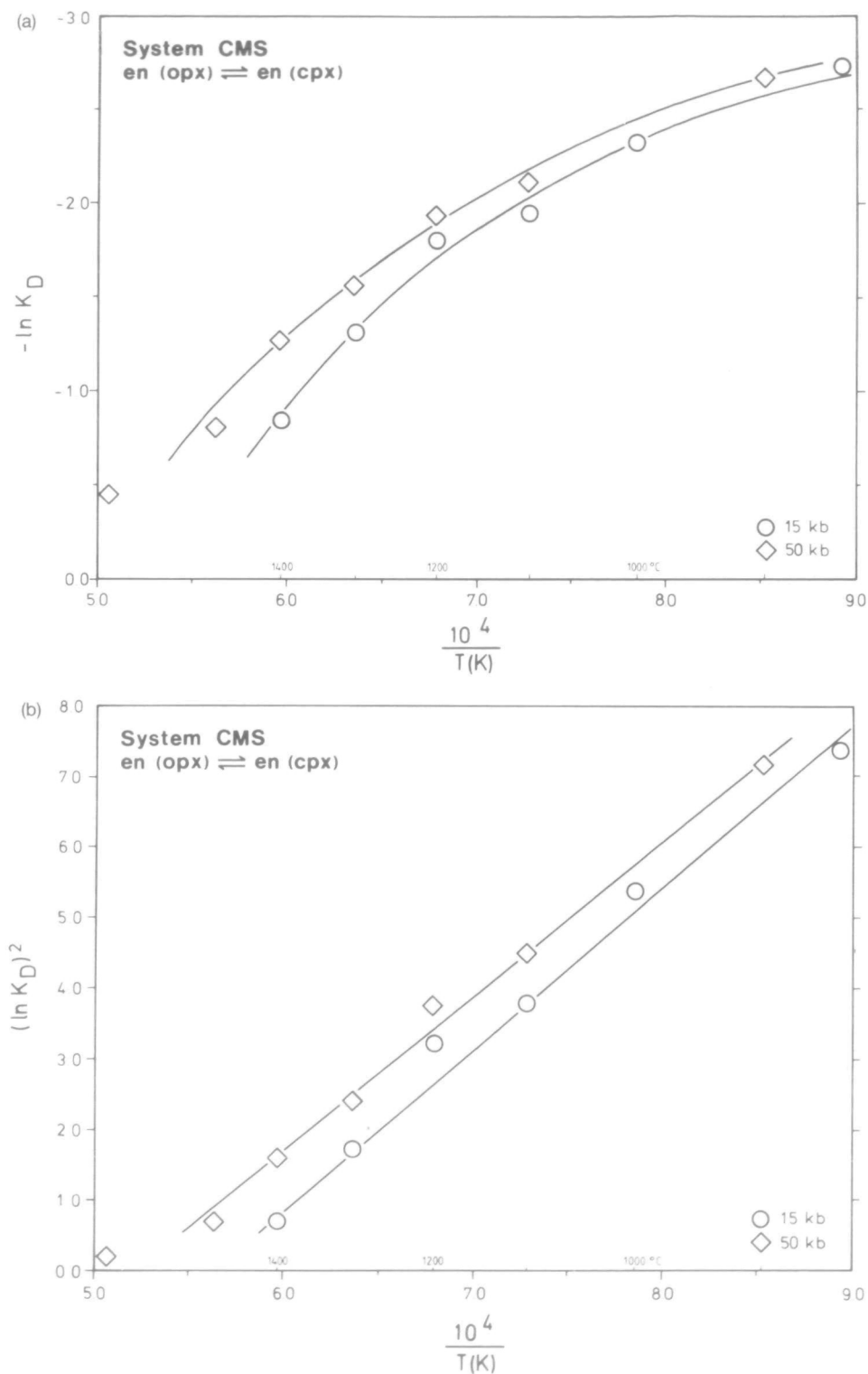
FIG. 4. (a) Diagram of $-\ln K_D$ for the transfer of enstatite component between coexisting orthopyroxene and clinopyroxene in CMS vs. reciprocal temperature. There is a curvilinear relationship as shown here, for example, for 15 kb (Lindsley & Dixon, 1976) and for 50 kb (Brey & Huth, 1984). (b) Following a suggestion by Ehrenberg (1979), we plotted $(\ln K_D)^2$ vs. reciprocal temperature and found a linear correlation. The fit to the data in CMS serves as the basis for our newly developed two-pyroxene thermometer.
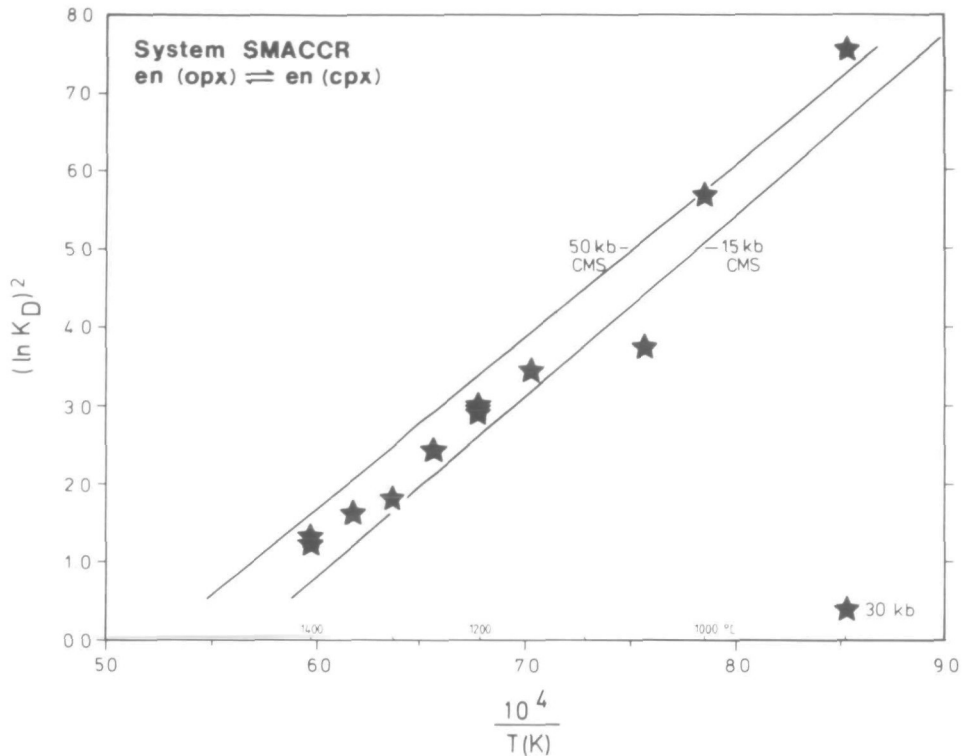
FIG. 5. Results for the transfer of enstatite component between coexisting pyroxenes in the system CMASCr at 30 kb (Nickel, 1989). There is also a linear correlation between $(\ln K_D)^2$ and reciprocal temperature. By comparison with Fig. 4b (lines are taken from that figure) it can be seen that the 30-kb data from CMASCr fall between the 15- and 50-kb data from CMS.

CMAS: $T = (26\,322 + 61 \cdot 1P)/(15 \cdot 88 + (\ln K_D)^2)$ (10–100 kb)   (5)

CMASCr: $T = \text{CMS}$ (25–35 kb)

Natural system: $T = (23\,058 + 38 \cdot 4P)/(14 \cdot 12 + (\ln K_D^*)^2)$ (10–60 kb).   (6)

These equations reproduce experimental data to $\pm 24\,°C$ (1σ) in CMS and CMASCr, to $\pm 31\,°C$ in CMAS, and to $\pm 16\,°C$ in the natural system. The form of K_D is based on the assumption that Ca is restricted to the M2 site of the pyroxenes and that $(Mg^{M1})_{cpx}/(Mg^{M1})_{opx} \approx 1$. Reasons for this assumption were given by Nickel & Brey (1984) and Bertrand & Mercier (1985). For the natural system we use K_D^*, which includes an Na correction of the form given in equations (7) and (8) (see below).

Comparison of equations (4)–(6) shows that the largest differences are between the CMS and CMAS system (see also Nickel et al., 1985). The reason for the difference may be that K_D in the form of (3) is not valid in CMAS. Bertrand & Mercier (1985) had assumed that Al values in both pyroxenes are about equal and $(Mg^{M1})_{cpx}/(Mg^{M1})_{opx}$ should therefore be about unity and K_D(3) valid. In fact, Al values are identical in both pyroxenes at certain P, T conditions only and differ at other conditions (Nickel et al., 1985). In the presence of Al, Ca in opx is always lowered, but is either lowered or increased in cpx depending on pressure and temperature (Nickel et al., 1985). This behaviour therefore requires the consideration of

P, T-dependent Margules parameters for non-ideal interaction of Mg and Al on M1 and *P, T*-dependent cross-site interaction parameters (Ca–Al) for both pyroxenes. The number of parameters to be fitted is too large compared with the number of experiments available; for this reason, Nickel *et al.* (1985) considered these fitted coefficients to be statistically meaningless. We also do not see any possibility to link equations (4) and (5) with simple compositional parameters, and we therefore assume that equation (4) is applicable to CMAS. The experimental data in CMAS are reproduced only to about $\pm 60\,°C$ (1σ) by equation (4), with increasing underestimation of temperature at high pressures.

The close similarity of CMS and CMASCr (we excluded one experiment at 25 kb, 900 °C from the fitting procedure) is surprising as we expect Cr to behave similarly to Al. This probably is the case for its behaviour *on* M1 site, but cross-site Ca–Al and Ca–Cr interactions must counterbalance each other. This influence of Cr must already be rather effective at low concentrations and does not change at higher concentrations, as all three different bulk Cr compositions of Nickel (1989) can be reproduced with equation (4).

The fit parameters [equation (6)] for the Cr-bearing natural system experiments lie much closer to (4) than to (5), as expected from the discussion above. The parameters were derived with a theoretical correction of Ca^{M2} by Na^{M2} as suggested by Bertrand & Mercier (1985), based on statistical mechanics. They defined

$$Ca^* = Ca^{M2}/(1 - Na^{M2}) \tag{7}$$

which changes K_D (3) to

$$K_D^* = (1 - Ca^*)^{cpx}/(1 - Ca^*)^{opx}. \tag{8}$$

The success of this correction for Na with no additional fitting parameter was demonstrated by the above authors with the experiments of Mori & Green (1978) in diagrams of T_{calc} vs. T_{exp}: a very poor reproduction of experimental temperatures before application of the Na correction is in contrast with a rather smooth temperature trend after the application. We find very similar behaviour from our natural system experiments.

Al and Cr in combination do not seem to influence the transfer of enstatite between coexisting opx and cpx, and Na can be accounted for by equation (7), so that it can only be the presence of Fe which causes the difference between equations (4) and (6). In the presence of Fe, Ca strongly decreases in clinopyroxene and somewhat increases in coexisting orthopyroxene as shown by experiments in the CFMS system (Davidson & Lindsley, 1985). Their experiments were mostly between 800 and 1000 °C and at pressures up to 15 kb. Pyroxene compositions are less temperature dependent at these conditions and, in fact, Ca contents of experiments at 900 and 1000 °C partly overlap, as noted by Bertrand & Mercier (1986). We were unable to find simple correction parameters from the data set presented by Davidson & Lindsley (1985) with equation (4) as the basic equation. Also, restriction to Mg-rich compositions with *mg*-numbers > 80 is not possible because only five experiments are available; errors in fit parameters are too large to permit application to our natural system experiments. We therefore base an empirical Fe correction on our experiments in the natural system only and find that the following equation reproduces experimental conditions best:

$$T_{BKN} = \frac{23\,664 + (24\cdot9 + a X_{Fe}^{cpx})P}{13\cdot38 + (\ln K_D^*)^2 + b X_{Fe}^{opx}} \tag{9}$$

with T in degrees kelvin, P in kilobars, K_D^* as in equation (8), $a = 126\cdot3$, $b = 11\cdot59$, and $X_{Fe}^{opx} = Fe/(Fe + Mg)$. This thermometer reproduces our experiments to $\pm 15\,°C$ (1σ) with no systematic dependence on either temperature or pressure (Fig. 6a and b) or compositional parameters. Equation (9) reproduces our natural system experiments somewhat better than
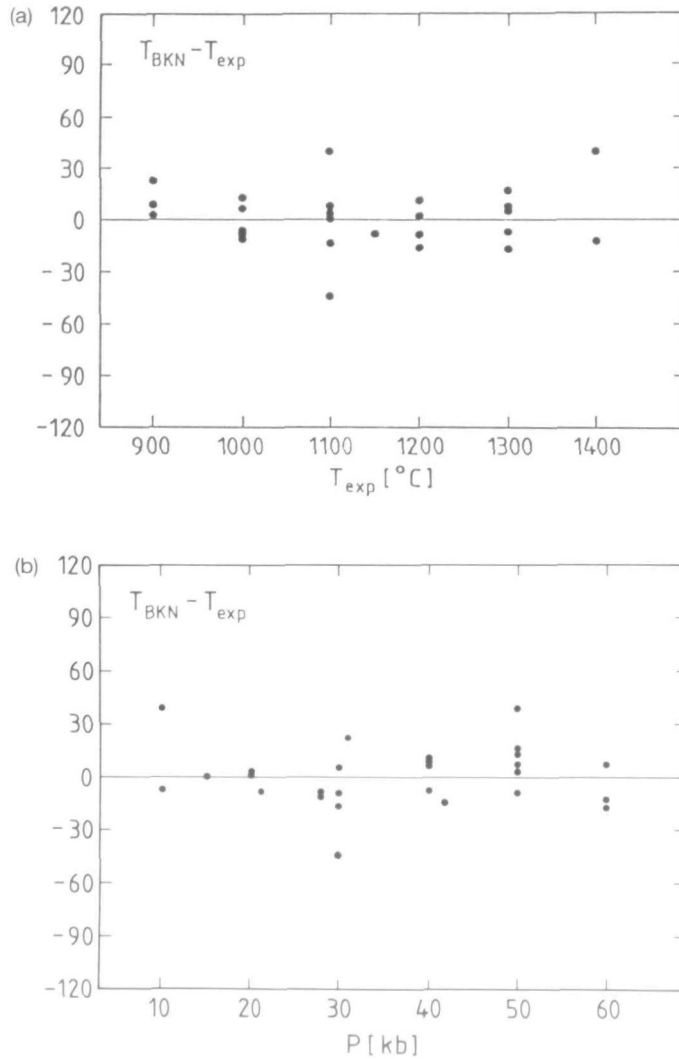
FIG. 6. Reproduction of experimental temperatures with our newly developed thermometer T_{BKN} [equation (9)]. (a) There is no systematic dependence on temperature in a diagram of ΔT vs. T_{exp}. (b) The effect of pressure is also corrected reasonably well as there is no systematic dependence of ΔT on experimental pressure.

equation (6) and can be applied to a wider range of bulk compositions, i.e., with *mg*-numbers ranging from 100 (Fe-free) down to at least 89 (=bulk *mg*-number of the composition used here), and probably down to 80–85, with minimal error.

Ca-IN-OPX THERMOMETRY

Sachtleben & Seck (1981) suggested using Ca in opx as a thermometer and based their calibration on data in CMS at 15 kb by Lindsley & Dixon (1976). Lindsley & Anderson (1983) presented a graphical method for the use of the diopside component in opx as a thermometer from data in CFMS. We have fitted the available reversed experiments in CMS as given by Nickel & Brey (1984) as a function of pressure and reciprocal temperature and
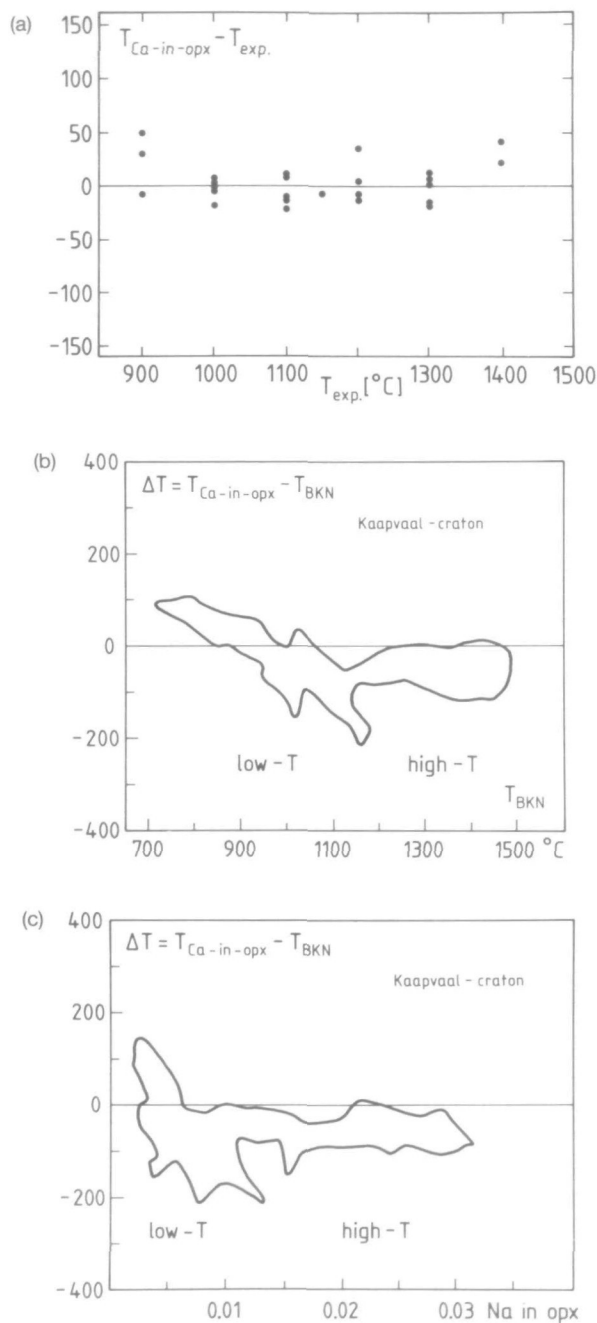
FIG. 7. Reproduction of experimental temperatures with the newly developed thermometer $T_{Ca\text{-}in\text{-}opx}$ [equation (10)] and comparison with the outcome from T_{BKN} in the application to natural rocks. (a) Equation (10) reproduces temperatures of our experiments in the natural system to $\pm 19\,^\circ C$ (1σ), which is almost as good as equation (9). There is no systematic dependence on temperature. (b) Comparison of the application of $T_{Ca\text{-}in\text{-}opx}$ and T_{BKN} to a suite of garnet lherzolites from the Kaapvaal (see text for data source). ΔT for 'low-T' nodules (i.e., those plotting along a conductive continental geotherm) is correlated with T_{BKN}, whereas 'high-T' nodules mostly fall below the zero line. The application of $T_{Ca\text{-}in\text{-}opx}$ to natural rocks does not appear to be satisfactory. (c) ΔT vs. Na content in orthopyroxene (given as number of cations in a structural formula based on six oxygens). The resulting pattern has strong similarities to that seen in Fig. 7b, suggesting an influence of Na^{opx} on Ca^{opx}.

derived the following thermometric expression:

$$T_{\text{Ca-in-opx}}(K) = \frac{6425 + 26\cdot4\,P}{-\ln \text{Ca}^{\text{opx}} + 1\cdot843}.$$

(10)

This thermometer reproduces the experiments in CMS to $\pm 26\,^\circ C$ (1σ) and the natural system experiments to $\pm 19\,^\circ C$ (1σ) (Fig. 7a), which is not quite as good as equation (9). The good reproduction was expected from the agreement of isotherms calculated with equation (10) and the Ca content of opx from our experiments (see fig. 8b in Part I). The agreement is somewhat surprising because Ca in opx increases in the presence of Fe compared with the Fe-free system (see Lindsley & Anderson, 1983). However, Ca contents in opx are lowered in the presence of Al (Nickel *et al.*, 1985) and may also be lowered on M2 through the presence of Na in the natural system to counterbalance the effect of Fe. We cannot substantiate this suggestion as Na is low in our experiments and (in opx) below the detection limit of the EDS system attached to the electron microprobe (only few experiments were measured with WDS).

Application of equation (10) to natural garnet peridotites from the Kaapvaal craton yields different results to equation (9) (Fig. 7b): 'low-temperature' peridotites (those plotting along a conductive geothermal gradient; see part III) form an array oblique to the zero-line,
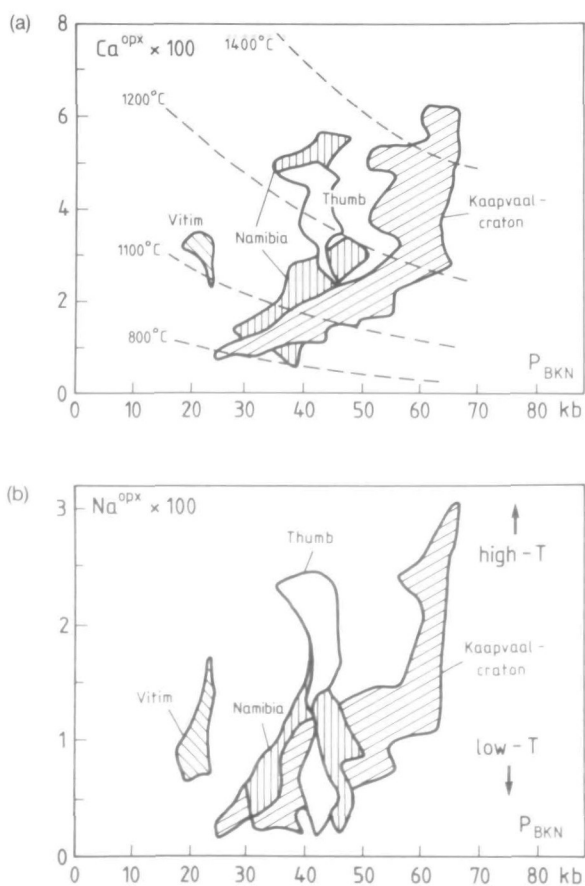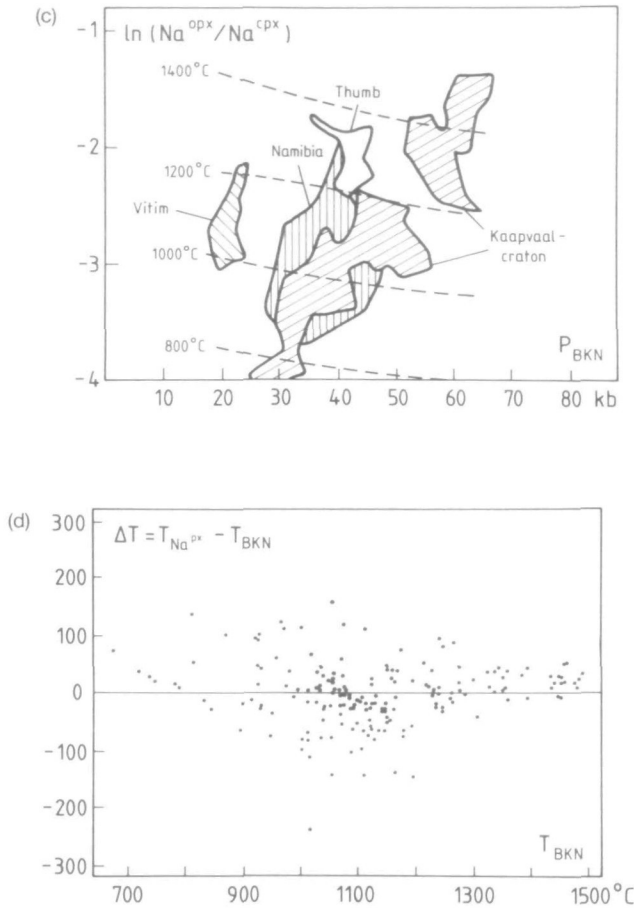

FIG. 8(a, b)

FIG. 8. Thermometry based on the partitioning of Na between opx and cpx. The thermometer is developed by using published mineral data from garnet lherzolites (see text for data source) and pressures and temperatures calculated with P_{BKN} and T_{BKN}. (a) Distribution of a mostly temperature-dependent chemical parameter Ca^{opx} in a composition–pressure diagram for the mineral data set used. Isotherms are calculated from equation (10) of this study. (b) The distribution of Na^{opx} is very similar to Ca^{opx} in a composition–pressure diagram, suggesting a strong dependence on temperature of Na^{opx}. However, it also depends on bulk composition; therefore the partitioning of Na between opx and cpx needs to be explored. (c) Partitioning of Na between opx and cpx. The fields for Namibia, The Thumb and the 'low-T'-suite of garnet lherzolites from Kaapvaal craton overlap more extensively than in (a), suggesting an almost P-independent effect of temperature. This is verified by the fitting procedure (data from Namibia were not used because of the large scatter in this diagram) and can be seen from the slope of the isotherms calculated from equation (11). The spacing of the isotherms is wider at low temperatures than for Ca^{opx} [compare (a)]. A thermometer based on the partitioning of Na between opx and cpx should be especially useful at these conditions. (d) Comparison of temperatures calculated for garnet lherzolites from The Thumb, Vitim and the Kaapvaal craton with equation (11) and T_{BKN} [equation (9)]. Pressures used for calculating temperatures with equation (11) are those derived from the combination of T_{BKN} [equation (9)] and P_{BKN} (Table 3). Temperatures agree within $\pm 56\,°C$ (1σ).

whereas 'high-temperature' peridotites (those plotting at temperatures above a geothermal gradient) plot below zero. A very similar pattern can be seen in a diagram of ΔT vs. Na^{opx} (Fig. 7c), which demonstrates the influence of Na on Ca content of opx. We were not able to devise a reasonable correction scheme from natural mineral compositions. Use of this rather promising thermometer must be viewed with caution at present.

PARTITIONING OF Na BETWEEN OPX AND CPX

The similar patterns in Fig. 7b and c must be the result of a covariation of Ca and Na in opx, which is apparent from a comparison of Fig. 8a and b. In these diagrams we have used data for garnet lherzolites from Vitim (east of Lake Baikal, courtesy D. Ionov), The Thumb (Ehrenberg, 1979, 1982, 1984), Namibia (Mitchell, 1984) and the Kaapvaal craton (Cox *et al.*, 1973; Nixon & Boyd, 1973; Dawson & Smith, 1975; Boyd & Nixon, 1978; Hervig *et al.*, 1986; Cox *et al.*, 1987). *P*, *T* conditions of equilibration can be estimated by relating their positions to the isotherms shown in Fig. 8a [isotherms are calculated from equation (10)]. Figure 8b, showing Na^{opx} vs. pressure, is very similar in appearance to Fig. 8a, and a strong temperature dependence of Na^{opx} is suggested. However, Na content in opx is not buffered by an Na-saturated phase and also depends on bulk composition. This excludes the use of Na^{opx} as a thermometer in an analogous fashion to Ca^{opx}, which is buffered by coexisting cpx. Great potential for thermometry should lie in the distribution of Na between opx and cpx (Fig. 8c), as already pointed out by Hervig *et al.* (1986). This is explored in the following.

Conditions of origin for nodules from the localities given above span a wide grid of pressures and temperatures (see Fig. 8a). This offers the possibility for designing a derivative thermometer based on mineral compositions from natural rocks and *P*, *T* conditions calculated with reliable thermometers and barometers. We have used T_{BKN} [equation (9)] as a thermometer and P_{BKN} (Table 3) as a barometer and fitted $(\ln D_{Na})^2$ to an equation of type (1) with the following result:

$$T = \frac{35\,000 + 61 \cdot 5P}{(\ln D_{Na})^2 + 19 \cdot 8} \qquad (11)$$

where *T* is in degrees Kelvin, *P* is in kilobars, and $D_{Na} = Na^{opx}/Na^{cpx}$. The data set from Namibia was not used for the fitting procedure because Na^{opx} appears somewhat erroneous, probably because of the strong serpentinization of these nodules. Temperatures calculated with equation (11) agree with those calculated with T_{BKN} [equation (9)] to $\pm 56\,°C$, with no systematic dependence on either pressure or temperature (Fig. 8d). The great potential of this new thermometer seems to lie in the application at low temperatures because of its higher resolution relative to equations (9) and (10). This becomes obvious from a comparison of the spacing of the calculated isotherms given in Fig. 8a and c.

EVALUATION OF EXISTING BAROMETERS

Carswell & Gibb (1987a, 1987b) tested 13 barometer versions based on the Tschermak's molecule content of opx coexisting with grt, and found that only the calibration by Nickel & Green (1985) yielded satisfactory results. We reach very similar conclusions from tests of these barometers with the experimental data set presented in Part I. Examples are given in Fig. 9a and b for the barometric fomulations of Nickel & Green (1985) and Finnerty & Boyd (1987). Our experiments from 28 to 60 kb are reproduced most closely with the formulation of Nickel & Green, but only in the pressure range of the experiments, on which their calibration was based. Extrapolation to higher pressures fails (Fig. 9a). Nickel & Green (1985) neglected MAS and based their barometer mostly on experiments in the systems CMAS, FMAS, CFMAS, and CMASCr with pressures from 10 to 35 kb.

In the Bertrand *et al.* (1986) version of the Al-in-opx barometer, the influence of Cr was neglected, and calculated pressures were influenced most strongly by a Ca-in-garnet correction term which depends on pressure only as derived from experimental results in CMAS (Bertrand *et al.*, 1986; Brey *et al.*, 1986). In the natural system it depends mostly on
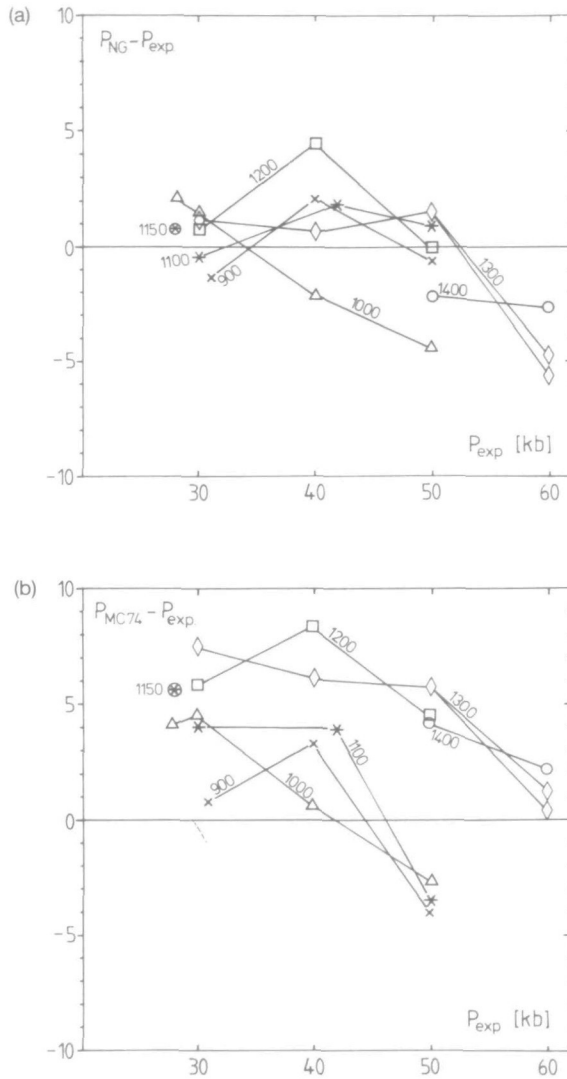
FIG. 9. Reproducibility test for two published barometers (Al-in-opx) with our experimental results in diagrams of $\Delta P = P_{calc} - P_{exp}$ vs. P_{exp}. (a) The barometer of Nickel & Green (1985) reproduces experimental pressures reasonably well at low pressures but underestimates at high pressures. There is no dependence on temperature. (b) ΔP from a comparison of the preferred barometer version of Finnerty & Boyd (1987, MC 74) with P_{exp} shows two temperature groupings at 900–1100 °C and 1200–1400 °C, and both positive and negative deviations with a negative correlation of ΔP with pressure.

temperature (fig. 10d in Part I) and this leads to erroneous pressure calculations with the barometer of Bertrand *et al.* (1986).

Finnerty & Boyd (1984, 1987) used a simple fit to Al concentrations in opx determined by MacGregor (1974) in MAS as a barometer. Application to natural system experiments is, however, not satisfactory (Fig. 9b).

The evaluation of existing barometers shows the need for a new calibration which is capable of reproducing experimental conditions for all available systems and over the whole pressure range.

A NEW BAROMETER

We have chosen the thermodynamic evaluation for the MAS system by Gasparik & Newton (1984) as the basis for our new barometer because of the simple ideal solution model for opx ($W_{MgAl} = 0$). The thermodynamic treatment of the same MAS data by Chatterjee & Terhart (1985) reproduced the experimental data equally well, but opx was treated there as non-ideal. This would only cause more complexities without gaining accuracy when the thermodynamic evaluation is extended to other systems. The parameters obtained by Gasparik & Newton (1984) are reproduced in Table 2, which also gives an overview of the strategy and assumptions used for modelling the more complex systems. The results of the applied multiple linear regression method are also shown.

The best reproduction of experimental data in CMAS was obtained by treating garnet as a binary regular solution with only pressure-dependent on-site interactions ($W_G^{CaMg} = W_H$).

TABLE 2

Thermodynamic modelling of Al solubility in orthopyroxene coexisting with garnet

We have taken the equation from Gasparik & Newton (1984) for the system MAS as the cornerstone on which to build our models for the more complex systems. Gasparik & Newton assumed $W_{MgAl} = 0$ and found

$$RT \ln \frac{1}{X_{Mg}^{M1} X_{Al}^{M1}} + 5510 - 88{\cdot}91T + 19T^{1{\cdot}2} + [-0{\cdot}832 - 8{\cdot}78 \times 10^{-5}(T - 298) + 16{\cdot}6 \times 10^{-7}P]P = 0$$

We define

$$A \equiv 5510 - 88{\cdot}91T + 19T^{1\ 2} + [-0{\cdot}832 - 8{\cdot}78 \times 10^{-5}(T - 298) + 16{\cdot}6 \times 10^{-7}P]P$$

and abbreviate: Dat = Data source, Ass = Assumptions, Mod = solution model, FIP = Fit Parameters, Rep = Reproduction of experimental pressures

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System CMAS

Dat: Nickel *et al.* (1985); Brey *et al.* (1986)
Ass: neglect Ca interactions in opx

Mod: $RT \ln \dfrac{(1 - X_{Ca}^{grt})^3}{X_{Mg}^{M1} X_{Al}^{M1}} + A + 3(X_{Ca}^{grt})^2 (W_H + PW_V)_{CaMg} = 0$

FIP: $W_H = -82\,458$ J/mol $\pm 17\,100$; $W_V = 3{\cdot}3$ J/b mol $\pm 0{\cdot}5$

Rep: $\pm 1{\cdot}6$ kb (1σ)

System FMAS

Dat: Kawasaki & Matsui (1983); Harley (1984*b*); Lee & Ganguly (1988)
Ass: $W_{FeMg} = 0$, $W_{FeMg}^{opx} = 0$, opx = ternary reg. sol. in M1

Mod: $RT \ln \dfrac{1}{X_{Al}^{M1}(1 - X_{Al}^{M1})} + A - [(X_{Fe}^{M1})^2 + X_{Mg}^{M1} X_{Fe}^{M1} - X_{Fe}^{M1} X_{Al}^{M1}](W_H - TW_S)_{FeAl} = 0$

FIP: $W_H = 80\,942$ J/mol ± 7100; $W_S = 46{\cdot}7$ J/K mol $\pm 5{\cdot}2$

Rep: $\pm 2{\cdot}2$ kb (1σ)

System CFMAS

Dat: Harley (1984*b*)
Ass: garnet = ternary regular solution

Mod: $RT \ln \dfrac{(1 - X_{Ca}^{grt})^3}{(1 - X_{Al}^{M1})(1 - X_{Ca}^{M2})^2 X_{Al}^{M1}} + A + 3(X_{Ca}^{grt})^2 (W_H + PW_V)_{CaMg}$ (CMAS)

$+ 3X_{Fe}^{grt} X_{Ca}^{grt}(W_{CaMg} - W_{CaFe})^{grt} - [(X_{Fe}^{M1})^2 + X_{Mg}^{M1} X_{Fe}^{M1} - X_{Fe}^{M1} X_{Al}^{M1}](W_H - TW_S)_{FeAl} = 0$ (FMAS)

FIP: $(W_{CaMg} - W_{CaFe})^{grt} = 17\,793$ J/mol ± 1700

Rep: $\pm 0{\cdot}9$ kb (1σ)

System CMASCr

Dat: Nickel (1989)
Ass: $W_{MgCr}^{opx} = W_{CrAl}^{opx} = 0$; $W_{AlCr}^{grt} = 0$

Mod: $RT \ln \dfrac{(1 - X_{Ca}^{grt})^3 (X_{Al}^{grt})^2}{X_{Mg}^{M1}(X_{Mg}^{M2})^2 X_{Al}^{M1}} + A + 3(X_{Ca}^{grt})^2 (W_H + P W_V)_{CaMg}$ (CMAS)

    $+ X_{Ca}^{grt} X_{Cr}^{grt} (\Delta H_{rec} - T\Delta S_{rec} + P\Delta V_{rec})_{CaCr} = 0$

FIP: $\Delta H_{rec} = 1\,163\,900$ J/mol $\pm 113\,000$; $\Delta S_{rec} = 420$ J/K mol ± 66;

    $\Delta V_{rec} = -13.5$ J/b mol ± 2.4

Rep: ± 1.2 kb (1σ)

Natural system

Dat: this study, Part I;   *Ass*: $(X_{Fe}^{M1})^2 - X_{Fe}^{M1} X_{Al}^{M1} \approx 0$

Mod: $RT \ln \dfrac{(1 - X_{Ca}^{grt})^3 (X_{Al}^{grt})^2}{X_{MF}^{M1}(X_{MF}^{M2})^2 X_{Al, T3}^{M1}} + A + 3(X_{Ca}^{grt})^2 (W_H + P W_V)_{CaMg}^{grt}$ (CMAS)

    $+ 3X_{Fe}^{grt} X_{Ca}^{grt} (W_{CaMg} - W_{CaFe})^{grt}$ (CFMAS)

    $+ X_{Ca}^{grt} X_{Cr}^{grt} (\Delta H_{rec} - T\Delta S_{rec} + P\Delta V_{rec})_{CaCr}^{grt}$ (CMASCr)

    $+ X_{Fe}^{grt} X_{Cr}^{grt} (\Delta H_{rec} - T\Delta S_{rec} + P\Delta V_{rec})_{FeCr}^{grt}$

    $- X_{Mg}^{M1} X_{Fe}^{M1} (W_H - W_S T)_{FeAl}^{opx} = 0$ (FMAS)

FIP: $\Delta H_{rec} = -1\,250\,000$ J/mol $\pm 302\,000$; $\Delta S_{rec} = -565$ J/mol ± 236; $\Delta V_{rec} = 10.5$ J/bar mol ± 3.5
Rep: 2.2 kb (1σ)

$+ P W_V$). The reversed experiments by Perkins & Newton (1980), Nickel *et al.* (1985), and Brey *et al.* (1986) were used for fitting the non-ideality parameters. We did not use the data by Yamada & Takahashi (1984), nor their updated values as given by Bertrand *et al.* (1986), because the garnet compositions have systematically higher pyrope contents compared with other studies in CMAS.

Experimental data in the system FMAS are available from Kawasaki & Matsui (1983), Harley (1984*a*), and Lee & Ganguly (1988). All three studies show a certain degree of internal inconsistency so that it is not possible to make a choice for a seemingly better-quality data set. We have used only experiments with $[Mg/(Mg + Fe)]^{opx} \geqslant 0.5$ for the fitting procedure and weighted the experiments by Kawasaki & Matsui (1983) by 1/3 (because all data are only from two temperatures at '50 kb'). Following the suggestion by Gasparik & Newton (1984), we have also assumed a pressure of 46 kb rather than 50 kb for these experiments. Like Harley (1984*b*, and references cited therein) we have treated opx as a two-site solid solution, but with ideal mixing on M2, statistical distribution of Fe and Mg between M1 and M2, no cross-site interactions, and with M1 as a ternary regular solution. This reduces the non-ideality terms for opx as given by Harley [1984*b*, his equations (6) and (7)] to the form given in Table 2. However, we found it necessary to express $W_G^{FeAl} = W_H - T W_s$. Mixing of Fe and Mg in garnet was taken as ideal. The experimental data are reproduced to ± 2.2 kb (1σ).

Data for the system CFMAS were also given by Harley (1984*b*). They can be reproduced to ± 0.9 kb (1σ) by combining CMAS and FMAS and treating garnet as a ternary regular solution (Thompson, 1967), explicitly given for garnets by Harley (1984*b*). With the assumption of $W_{FeMg}^{grt} = 0$, this ternary solution model reduces to the form given in Table 2. It was then crudely assumed for the fitting procedure that $(W_{CaMg} - W_{CaFe}) = $ constant.

Only the experimental data of Nickel (1989) exist for the system CMASCr (900–1400 °C, 22–35 kb). Two experiments at 1000 and 1050 °C and 30 kb were not used here for the fitting procedure because their P, T conditions could not be reproduced reasonably well by any model applied. Based on the parameters from CMAS we found it best to have $W_{MgCr}^{opx} = W_{CrAl}^{opx} = W_{AlCr}^{grt} = 0$ and to attribute the difference in Al solubility in opx between CMASCr and CMAS to pressure- and temperature-dependent reciprocal interaction of Ca and Cr in garnet (Wood & Nicholls, 1978; Nickel & Green, 1985). This reproduces the experiments to ± 1.2 kb (1σ).

The combination of parameters from CFMAS and CMASCr should reproduce the natural system experiments if no further on-site or cross-site interactions occur from the combined presence of Fe and Cr. This is not the case, and we had to introduce pressure- and temperature-dependent reciprocal parameters for cross-site interaction of Fe and Cr in garnet (Table 2) which largely counterbalance the reciprocal parameters for Ca–Cr. The

TABLE 3

Formulation of barometer (P in kilobars; T in degrees Kelvin) and site occupancies

$$P = \frac{-C_2 - \sqrt{(C_2^2 + 4C_3 C_1/1000)}}{2C_3}$$

$C_1 = -RT \ln K_D - 5510 + 88.91 T - 19T^{1\cdot2} + 3(X_{Ca}^{grt})^2 \times 82\,458$
$\quad + X_{Mg}^{M1} X_{Fe}^{M1}(80\,942 - 46.7T) - 3X_{Fe}^{grt} X_{Ca}^{grt} 17\,793$
$\quad - X_{Ca}^{grt} X_{Cr}^{grt}(1.164 \times 10^6 - 420.4T) - X_{Fe}^{grt} X_{Cr}^{grt}(-1.25 \times 10^6 + 565T)$

$C_2 = -0.832 - 8.78 \times 10^{-5}(T - 298) + 3(X_{Ca}^{grt})^2 \times 3.305$
$\quad - X_{Ca}^{grt} X_{Cr}^{grt} 13.45 + X_{Fe}^{grt} X_{Cr}^{grt} 10.5$

$C_3 = 16.6 \times 10^{-4}$

$K_D = \dfrac{(1 - X_{Ca}^{grt})^3 (X_{Al}^{grt})^2}{X_{MF}^{M1}(X_{MF}^{M2})^2 X_{Al,\,TS}^{M1}}; \qquad R = 8.3143 \text{ J/K mol}$

Site occupancies:
(1) pyroxenes [after Nickel & Green (1985) and Carswell & Gibb (1987a)]
    (a) $X_{Al}^{M1} = (Al + Na - Cr - Fe^{3+} - 2Ti)/2$
    (b) $X_{Al,\,TS}^{M1} = Al^{M1}$ due to Tschermak's component
        jadeite $= Na - Cr - Fe^{3+} - 2Ti$
        (b$_1$) if jadeite < 0, then $X_{Al,\,TS}^{M1} = (Al + jadeite)/2$
        (b$_2$) if jadeite > 0, then $X_{Al,\,TS}^{M1} = (Al - jadeite)/2$
          no Ti correction term is necessary here according to Carswell (1989), if NaTi is preferred over MgTi
    (c) Mg and Fe on M1 and M2

$X_{Mg}^{M1} = X_{MF}^{M1} \times X_{MF}$

$X_{Mg}^{M2} = X_{MF}^{M2} \times X_{MF}$

$X_{Fe}^{M1} = X_{MF}^{M1} \times (1 - X_{MF})$

$X_{MF}^{M1} = (1 - X_{Al}^{M1} - Cr - Fe^{3+} - Ti)$

$X_{MF}^{M2} = (1 - Ca - Na - Mn)$

$X_{MF} = Mg/(Mg + Fe)$

(2) garnets

$X_{Al}^{grt} = Al/(Al + Cr)$ $X_{Ca}^{grt} = Ca/(Ca + Mg + Fe + Mn)$

$X_{Cr}^{grt} = Cr/(Cr + Al)$ $X_{Fe}^{grt} = Fe/(Ca + Mg + Fe + Mn)$

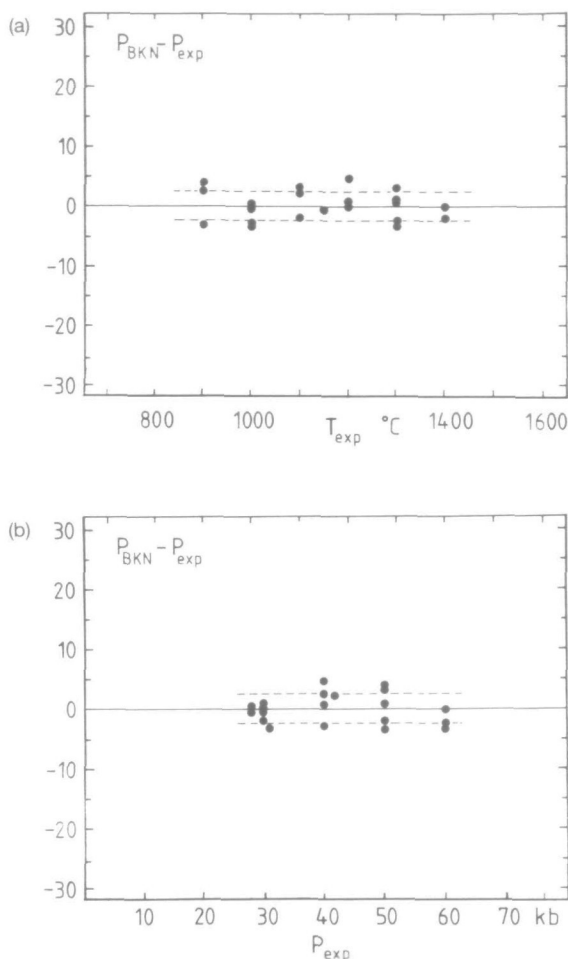$\qquad\qquad\qquad\qquad\qquad X_{Mg}^{grt} = Mg/(Ca + Mg + Fe + Mn)$

FIG. 10. Reproduction of experimental pressures with our newly developed barometer P_{BKN} (Table 3). There is no systematic dependence on either temperature (a) or pressure (b). Lines indicate 1σ error of 2·2 kb.

Fe–Cr interaction parameters were fitted from the experimental data set presented in Part I. The equation for the natural system has a simple quadratic form; the solution is given in Table 3, where the form to be used for calculating pressures and site distribution of cations is also given. Our natural system experiments are reproduced to $\pm 2\cdot2$ kb (1σ) (Fig. 10).

APPLICATION

In the above tests of available geothermobarometers, either experimental temperature or pressure was taken to test for the other parameter. For the application to natural rocks, pressures and temperatures have to be calculated simultaneously from mineral data. All thermometers and barometers contain a pressure or temperature correction term respectively such that any systematic error in either calculated pressure or temperature fortifies the error in the other parameter. We have therefore tested many combinations of thermometers and barometers by simultaneously calculating pressures and temperatures from mineral compositions from our experiments and plotting $\Delta P \,(= P_{calc} - P_{exp})$ vs. $\Delta T \,(= T_{calc} - T_{exp})$.

Only the combinations shown in Fig. 11a–d fulfil the requirement that deviations in calculated pressure and temperature should centre around zero. In Fig. 11e and f this requirement is not fulfilled.

The combination of our newly calibrated two-pyroxene thermometer [T_{BKN}, equation (9)] and Al barometer (P_{BKN}, Table 3) reproduces experimental conditions to $\pm 20\,°C$ and ± 3 kb (1σ) with an arithmetic mean at $+4\,°C$ and $+0.3$ kb (Fig. 11a). Errors in either calculated pressure or temperature would shift the other parameter along the dashed line in Fig. 11a which is oblique to dP/dT slopes corresponding to typical conductive continental geotherms. Thus statistically distributed analytical errors of minerals would increase scatter along a geotherm, whereas systematic errors would cause deviation from a conductive geotherm.

The combination of the Ca–ol/cpx barometer (P_{KB}, exchange of Ca between olivine and clinopyroxene; Köhler, 1989; Köhler & Brey, in press) with T_{BKN} is accurate to $\pm 23\,°C$ and ± 4.4 kb (1σ), with a mean at $+1\,°C$ and -0.4 kb (Fig. 11b). The pronounced covariation of ΔP with ΔT (dashed line) with a very oblique angle to conductive continental geotherms reflects the strong temperature dependence of the Ca–ol/cpx barometer. This combination is therefore very sensitive to any error in calculated temperature, which would always cause deviation from a geotherm. This apparent drawback, however, represents a very powerful tool to check for disequilibrium effects considering the fast diffusion rates of Ca in olivine (Jurewicz & Watson, 1988). Any heating or cooling event would almost immediately be reflected in the Ca contents of the olivines, and pressure under- and overestimates respectively would result. This aspect was discussed in more detail by Köhler (1989) and Köhler & Brey (in press).

The covariation of calculated ΔP and ΔT in Fig. 11c is caused by the stronger pressure dependence of the thermometer by Krogh (1988) as compared with T_{BKN}. Krogh's thermometer (Fe–Mg exchange between garnet and clinopyroxene) together with the Al–in–opx barometer (P_{BKN}, Table 3) reproduces experimental conditions to $\pm 62\,°C$ and ± 5.2 kb (arithmetic mean $-10.6\,°C$ and $+0.8$ kb). The slope of the covariation line is in the range of slopes for continental geotherms.

The combination of P_{BKN} and the O'Neill (1980) Fe–Mg exchange thermometer between garnet and olivine reproduces our experiments to $\pm 113\,°C$ and ± 7.1 kb, with a mean at $-17\,°C$ and -1.4 kb.
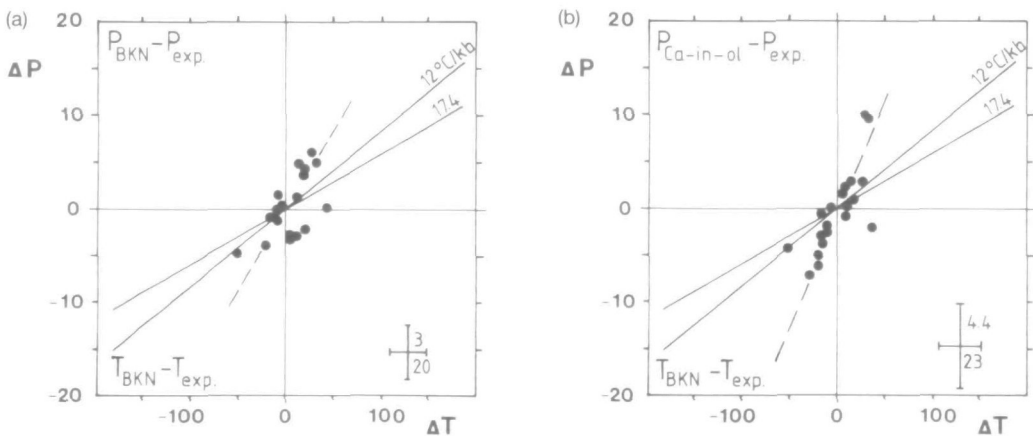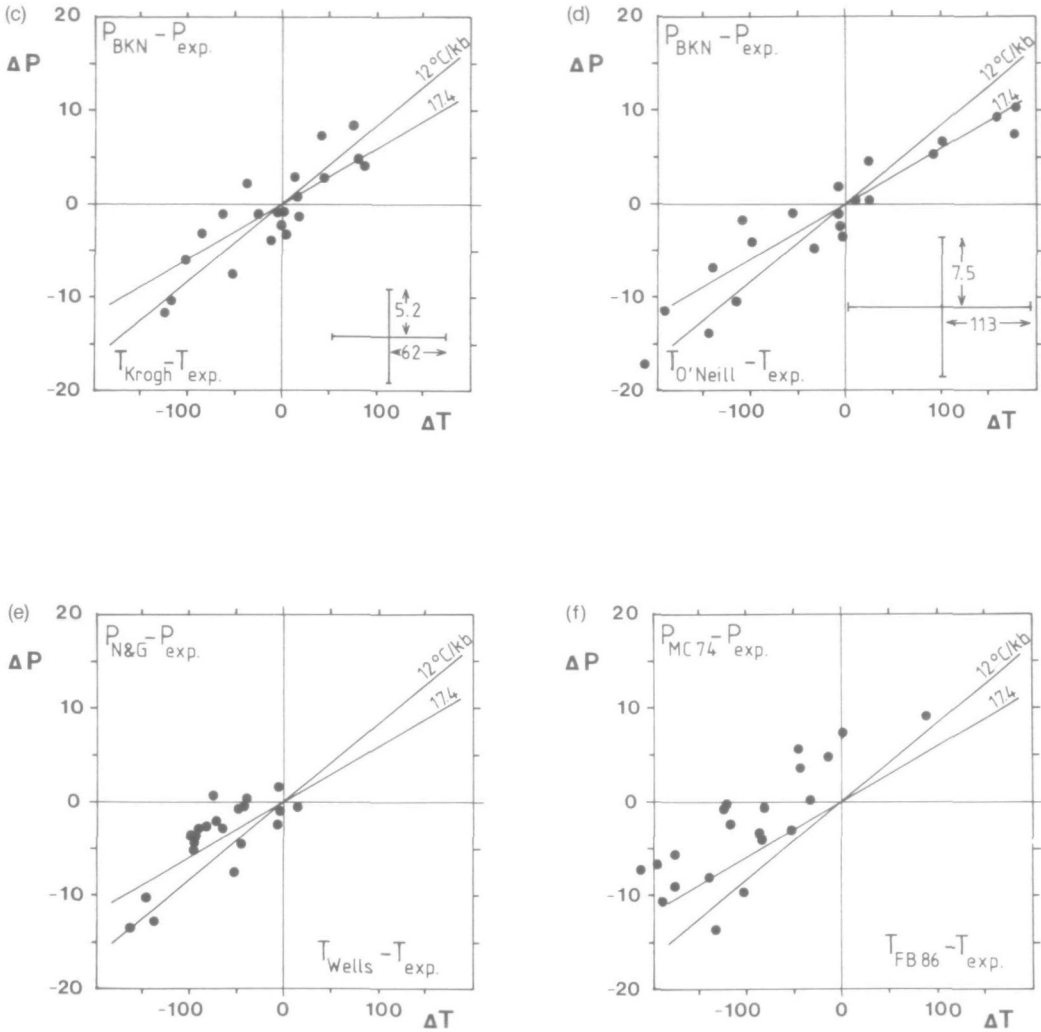

FIG. 11(a,b)

FIG. 11. Test of combination of various thermometers and barometers for reproduction of experimental results in the natural systems. The outcome is shown in diagrams of $\Delta P = P_{calc} - P_{exp}$ vs. $\Delta T = T_{calc} - T_{exp}$. Shown in the figures are also slopes of conductive continental geotherms. (a) T_{BKN} combined with P_{BKN} reproduces experimental conditions to ± 3 kb and $\pm 20\,°C$ (1σ). The correlation of ΔP and ΔT has a slope (— — —) steeper than continental geotherms (solid lines) which will shift calculated P, T conditions off a geotherm in case of error in either of the parameters. This combination is the most accurate in calculation of pressures and temperatures for natural peridotitic samples. (b) The combination of T_{BKN} with $P_{Ca-ol/cpx}$ (Köhler, 1989; Köhler & Brey, in prep.) reproduces experimental conditions to $\pm 5\cdot4$ kb and $23\,°C$ (1σ). The correlation line of ΔP with ΔT has a steeper slope than in (a) because of the higher temperature dependence of this barometer. This combination is not as accurate as the combination T_{BKN} and P_{BKN} but will be most useful to check for equilibrium in the rocks. (c) T_{Krogh} combined with P_{BKN} gives larger errors with $\pm 62\,°C$ and $\pm 5\cdot2$ kb (1σ) but the (correlated) deviations are centered at close to zero. The slope of the correlation is such that any error in either calculated pressure or temperature will move calculated P, T conditions along a geotherm. Again, it will be most useful to apply this combination simultaneously with all other combinations to test for internal equilibrium of the rocks and obtain qualitative information on the oxidation state by comparison with the two-pyroxene thermometer (see text). (d) $T_{O'Neill}$ combined with P_{BKN} shows the largest error ($\pm 113\,°C$, $\pm 7\cdot5$ kb) of those combinations for which deviations center at around zero. The correlation of errors has a slope parallel to continental geotherms. Application of this combination will give direct hints on the oxidation state of natural rocks because Fe^{3+} resides in garnet and calculated temperatures will be underestimated if Fe^{3+} is not corrected for. (e) This is a combination of T_{Wells} (Wells, 1977) with P_{NG} (Nickel & Green, 1985), which tends to shift calculated P, T conditions to lower pressures and temperatures. (f) The combination of T_{FB86} with P_{MC74} (Finnerty & Boyd, 1987) strongly deviates from zero for most P, T conditions.

It is most important to note that calculated pressure and temperature residuals with both Fe–Mg exchange thermometers in combination with the Al-in-opx barometer are correlated such that they fall along conductive continental geotherms. Any analytical or systematic error therefore expands or contracts the range of calculated pressures and temperatures along a geotherm.

Calculated temperatures will also be strongly affected by the presence of Fe^{3+} in either cpx or grt. There is usually no correction for Fe^{3+} in microprobe analyses because the methods are rather imprecise. By assuming all Fe as Fe^{2+}, temperatures calculated with T_{Krogh} will be overestimated if, in reality, there is more Fe^{3+} in cpx relative to grt and underestimated in the opposite case. They may also be correct if Fe^{3+} in both garnet and clinopyroxene are approximately equivalent. The presence of Fe^{3+} in garnet will always lead to underestimation of temperatures with $T_{O'Neill}$. The net effect of the presence of Fe^{3+} will almost always be a shift of calculated pressures and temperatures along an apparent geotherm. Deviations in temperatures calculated with Fe–Mg thermometers from the two-pyroxene thermometer can, however, be used to judge relative oxidation states of rock samples. A more extensive discussion on the influence of oxidation state is included in Part III of this series (to be submitted, and Brey, 1989).

The mean values of ΔT and ΔP for any combination of other thermometers and barometers all significantly deviate from zero and cannot be used to calculate P, T conditions of natural rock samples. Examples are shown for combinations of the Wells (1977) two-pyroxene thermometer with the Nickel & Green (1985) barometer (the deviation is mostly caused by the thermometer, Fig. 11e) and the preferred combination of Finnerty & Boyd (1987), i.e., the cpx thermometer FB_{86} with the Al-in-opx barometer MC_{74} (Fig. 11f).

ACKNOWLEDGEMENTS

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APPENDIX

Worked example

	Olivine		Orthopyroxene		Clinopyroxene		Garnet		Spinel	
	Wt.%	AFU	Wt.%	AFU	Wt.%	AFU	Wt.%	AFU	Wt.%	AFU
SiO$_2$	40·78247	0·998536	56·99903	1·970900	55·56289	1·990443	42·25450	2·998126	0·00000	0·000000
TiO$_2$	0·00000	0·000000	0·00000	0·000000	0·00000	0·000000	0·28088	0·014991	0·00000	0·000000
Al$_2$O$_3$	0·04856	0·001401	1·25146	0·051000	1·89475	0·079997	22·22844	1·858838	0·00000	0·000000
Cr$_2$O$_3$	0·03351	0·000649	0·26337	0·007200	0·52958	0·014999	2·22683	0·124922	0·00000	0·000000
FeO	10·24079	0·209691	6·42004	0·185648	4·43318	0·132812	7·40843	0·439601	0·00000	0·000000
MnO	0·00000	0·000000	0·00000	0·000000	0·00000	0·000000	0·28269	0·016989	0·00000	0·000000
MgO	48·97674	1·787674	33·52752	1·728252	20·33242	1·085832	20·73014	2 192743	0·00000	0·000000
CaO	0·09487	0·002489	1·53858	0·057000	16·15299	0·619977	4·58810	0·348793	0·00000	0·000000
Na$_2$O	0·00000	0·000000	0·00000	0·000000	1·09417	0·075997	0·00000	0·000000	0·00000	0·000000
Total	100·17695	3·000439	100·00001	4·000000	99·99998	4·000057	100·00002	7·995003	0·00000	0·000000
mg-value	0·895016		0·903000		0·891017		0·833000		0·000000	
fe-value	0·104984		0·097000		0·108983		0·167000		0·000000	
X_{Al}^{M1}			0·021900		0·070497					
$X_{AL,T3}^{M1}$	0·000000		0·021900		0·009500					
$X_{Mg,Fe}^{M1}$	0·000000		0·970900		0·914503					
$X_{Mg,Fe}^{M2}$	0·000000		0·943000		0·304026					
X_{Mg}^{M1}	0·895016		0·876723		0·814838					
X_{Mg}^{M2}	0·892789		0·851529		0·270892					
X_{Fe}^{M1}	0·000000		0·094177		0·099666					
X_{Fe}^{M2}	0·000000		0·091471		0·033134					
X_{Al}							0·937028		0·000000	
X_{Cr}							0·062972		0·000000	
X_{Ca}							0·116337			
X_{Fe}							0·146625			

T_{BKN} $+ P_{BKN}$ = 1389/59·1 T_{BKN} $+ P_{Ca-in-ol}$ = 1379/55·1

T_{BKN} $+ P_{exp}$ = 1391 T_{exp} $+ P_{BKN}$ = 59·9

$T_{Ca-in-opx}$ $+ P_{exp}$ = 1421 T_{Krogh} $+ P_{exp}$ = 1411.

$T_{O'Neill}$ $+ P_{exp}$ = 1453