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Single clinopyroxene thermobarometry for garnet peridotites. Part I. Calibration and testing of a Cr-in-Cpx barometer and an enstatite-in-Cpx thermometer

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Abstract Experimental clinopyroxenes synthesized at 850–1500 °C and 0–60 kbar in the CMS and CMAS-Cr systems and in more complex lherzolitic systems have been used to calibrate a Cr-in-Cpx barometer and an enstatite-in-Cpx thermometer for Cr-diopsides derived from garnet peridotites. The experiments cover a wide range of possible natural peridotitic compositions, from *fertile* pyrolite to *refractory*, high-Cr lherzolite. The barometer is based on the Cr exchange between clinopyroxene and garnet. Pressure is formulated as a function of temperature and clinopyroxene composition:

$$P(\text{kbar}) = -\frac{T(\text{K})}{126.9} \cdot \ln \left[a_{\text{CaCrTs}}^{\text{Cpx}} \right] + 15.483 \cdot \ln \left(\frac{\text{Cr}\#^{\text{Cpx}}}{T(\text{K})} \right) + \frac{T(\text{K})}{71.38} + 107.8,$$

where $a_{\text{CaCrTs}}^{\text{Cpx}} = \text{Cr} - 0.81 \cdot \text{Cr}\# \cdot (\text{Na} + \text{K})$ and $\text{Cr}\# = \left(\frac{\text{Cr}}{\text{Cr} + \text{Al}} \right)$, with elements in atoms per 6 oxygens. This formulation reproduces the experimental pressures to ± 2.3 kbar (1σ) and has a temperature dependence (1.2–2.4 kbar/50 °C, varying with composition) that is weaker than that of the widely used Al-in-Opx barometer (2–3 kbar/50 °C). The enstatite-in-Cpx thermometer includes corrections for the effect of minor components and is formulated as

$$T(\text{K}) = \frac{23166 + 39.28 \cdot P(\text{kbar})}{13.25 + 15.35 \cdot \text{Ti} + 4.50 \cdot \text{Fe} - 1.55 \cdot (\text{Al} + \text{Cr} - \text{Na} - \text{K}) + \left(\ln a_{\text{en}}^{\text{Cpx}} \right)^2},$$

where $a_{\text{en}}^{\text{Cpx}} = (1 - \text{Ca} - \text{Na} - \text{K}) \cdot \left(1 - \frac{1}{2}(\text{Al} + \text{Cr} + \text{Na} + \text{K}) \right)$. The thermometer reproduces the experimental temperatures to ± 30 °C (1σ).

The uncertainties of the present formulations are comparable to, or better than, those of the most widely used thermobarometers for garnet peridotites. P - T estimates obtained for diamond-bearing and graphite-bearing lherzolite xenoliths and peridotitic clinopyroxene inclusions in kimberlitic and lamproitic diamonds confirm the reliability of the thermobarometer. Cr-diopside thermobarometry appears to be a potential tool for obtaining information on the thermal state of the upper mantle and the extent of mantle sampling by deep-seated magmas. We consider the Cr-in-Cpx barometer to be the best alternative to the Al-in-Opx barometer for the evaluation of pressure conditions of equilibration of natural garnet lherzolites. P - T conditions of equilibration can be directly retrieved from the composition of Cr-diopside alone, thus allowing application to partially altered xenoliths, inclusions in diamonds, and loose grains from sediments. We foresee application of the present thermobarometer to evaluation of the diamond potential of kimberlite and lamproite provinces and in diamond exploration where Cr-diopside from deep mantle sources is preserved in the surficial weathering environment.

Introduction

Chromian diopside, defined here as $\text{CaMgSi}_2\text{O}_6$ -rich clinopyroxene with >0.5 wt% Cr_2O_3 , is common in primitive alkaline magmatic rocks as high-pressure phenocrysts, xenocrysts of mantle origin, or as a constituent of peridotite or pyroxenite xenoliths derived from upper mantle wall-rocks. Cr-diopside frequently occurs in heavy mineral concentrates derived from kimberlitic and lamproitic volcanic pipes. In terranes not subject to extensive weathering, it may be dispersed by erosional processes and so serve as an indicator mineral that can be used to locate diamond-bearing pipes (Sobolev 1977; Ramsay 1992; Fipke et al. 1995). However, not all Cr-diopside recovered in diamond exploration programs is likely to be of high-pressure,

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in which diopside and CaCr-Tschermak's (CaCrTs) components in clinopyroxene react to give uvarovite, grossular, pyrope and knorringite components in garnet. The corresponding equilibrium constant is:

$$K = \frac{[a_{\text{gr}_2\text{py}_1}^{\text{Gt}}]^{1/2} \cdot [a_{\text{uv}_2\text{km}_1}^{\text{Gt}}]^{1/2}}{[a_{\text{di}}^{\text{Cpx}}] \cdot [a_{\text{CaCrTs}}^{\text{Cpx}}]} \quad (2)$$

Assuming ideal mixing, in a Na-free clinopyroxene the activity of CaCrTs is equal to the atomic fraction of Cr calculated on a six-oxygen basis. The activity of CaCrTs may be different if a proportion of the Cr atoms are coupled with Na as a kosmochlor component and non-ideal interactions between Cr and Na occur. Partitioning of atomic fractions in clinopyroxene into endmember components is conventionally carried out by first assigning the entire Na or Al_{M1} content (whichever is smaller) to jadeite (e.g., Lindsley 1983) or the entire Na or Cr content (whichever is smaller) to kosmochlor (Morimoto et al. 1988). This approach is too simplistic for natural samples that typically show large and, often, uncorrelated variations in Na, Cr and Al_{M1} . The fraction of Cr atoms that we expect to be controlled by Na should be proportional to the Na content lowered by the fraction of Na that is coupled with Al as jadeite component. A possible, approximate formulation for the activity of CaCrTs is:

$$a_{\text{CaCrTs}}^{\text{Cpx}} = \text{Cr} - x \cdot \left(\frac{\text{Cr}}{\text{Cr} + \text{Al}} \right)_{\text{M1}} \cdot \text{Na} \quad (3)$$

Such an expression requires estimation of the partitioning of Al between M1 and T sites. The fraction of octahedral aluminium can be obtained through one of the following equations:

$$\text{Al}_{\text{M1}} = \text{Al} - (2 - \text{Si}); \quad (4)$$

$$\text{Al}_{\text{M1}} = \text{Al} - \frac{1}{2}(\text{Al} + \text{Cr} + \text{Fe}^{3+} + 2\text{Ti} - \text{Na}), \quad (5)$$

but its estimation is prone to propagation of errors on Si and Fe^{3+} determinations. Even assuming no Fe^{3+} and Ti contributions, Eq. 5 still requires evaluation of three chemical parameters, each sensitive to analytical uncertainties. The Cr# parameter, defined as

$$\text{Cr\#} = \left(\frac{\text{Cr}}{\text{Cr} + \text{Al}} \right), \quad (6)$$

is a useful approximation of the $\left(\frac{\text{Cr}}{\text{Cr} + \text{Al}} \right)_{\text{M1}}$ ratio and reduces the number of chemical variables necessary for the calculation of $a_{\text{CaCrTs}}^{\text{Cpx}}$. The corrected CaCrTs activity becomes

$$a_{\text{CaCrTs}}^{\text{Cpx}} = \text{Cr} - y \cdot \text{Cr\#} \cdot \text{Na}, \quad (7)$$

in which y is an empirical factor with a value between 0 and 1 that can be derived by statistical regression of experimental data. For $\text{Na} = 0$, the activity of CaCrTs as derived from Eq. 7 becomes, as expected, equal to the atomic fraction of Cr in the M1 site. However, if y is not equal to unity, the calculated CaCrTs activity for a

hypothetical Al-free, kosmochlor-rich clinopyroxene would be different from 0, although no CaCrTs component is present. This does not clearly satisfy the desired requirements for CaCrTs activity formulation, but we argue that any bias will only be significant for compositions that are both very high in Cr and very low in Al. These special compositions are uncommon in natural samples, therefore the simplified expression for $a_{\text{CaCrTs}}^{\text{Cpx}}$ is not likely to produce strong errors in normal mantle-clinopyroxene geobarometry.

Evaluation of K through Eq. 2 requires knowledge of solid solution behaviour in both clinopyroxene and garnet. A simpler formulation would be highly desirable in order to obtain a viable geobarometric formulation. Figure 1 shows the relation between $a_{\text{CaCrTs}}^{\text{Cpx}}$ (with and without Na correction) and P for a set of experimental clinopyroxenes synthesized at various pressures

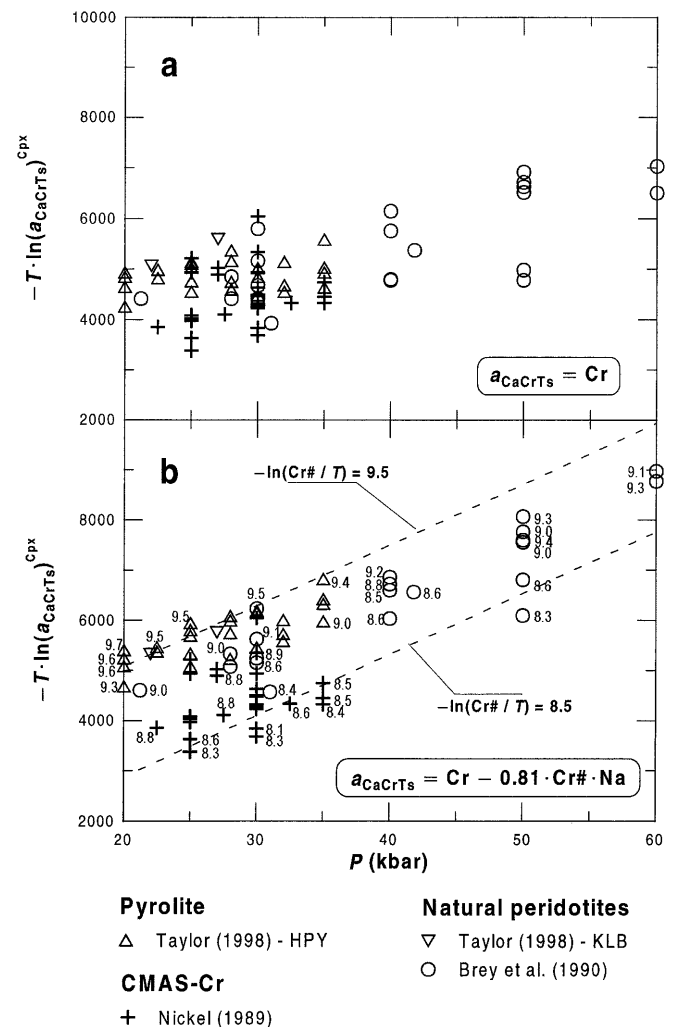


Fig. 1 Variation of $T \ln[a_{\text{CaCrTs}}^{\text{Cpx}}]$, **a** without and **b** with a Na correction (cf., Eq. 10), vs. pressure in experimental peridotites. Labels in **b** are $-\ln(\text{Cr\#}/T)$ values for individual clinopyroxenes. Some labels were omitted for clarity. Peridotite compositions are given in Table 1

Table 1 Starting compositions used in experiments (normalized to 100%) and source of experimental data on lherzolite systems utilized for geobarometer and thermometer calibrations

	HPY-40 ^a	KLB-50 ^a	SC-1 ^b	Mo22 mix ^c	SMACCR ^d
SiO ₂	48.33	48.30	45.27	47.13–47.59	43.7–46.1
TiO ₂	1.16	0.32	0.22	0.17	–
Al ₂ O ₃	6.03	7.18	4.16	4.78	8.5–12.4
Cr ₂ O ₃	0.64	0.62	0.45	0.56	1.5–7.9
FeO	7.84	5.88	7.85	8.26–5.82	–
MnO	–	0.17	–	0.04	–
NiO	–	0.17	–	–	–
MgO	29.82	29.88	38.14	33.08–35.06	29.4–35.4
CaO	5.37	6.88	3.55	5.55	–
Na ₂ O	0.61	0.60	0.36	0.43	–
K ₂ O	0.20	–	–	–	–
P ₂ O ₅	–	–	–	–	–
Cr# ^e	6.6	5.5	6.8	7.3	9.1–31.9
Mg# ^f	87.1	90.0	90.1	87.7–91.5	100.0

^a: Hawaiian pyrolite – 40% olivine and KLB-1 lherzolite – 50% olivine (Taylor 1998)

^b: SC-1 lherzolite (Brey et al. 1990; bulk rock composition after Jagoutz et al. 1979)

^c: Natural mineral mixes used by Brey et al. (1990). Recalculated bulk compositions are given

^d: SiO₂-MgO-Al₂O₃-CaO-Cr₂O₃ lherzolites (Nickel 1989)

^e: 100 Cr/(Cr + Al)

^f: 100 Mg/(Mg + Fe)

(20–60 kbar) and temperatures (900–1400 °C) in different garnet-bearing, lherzolitic systems (Table 1). These comprise: (i) relatively fertile, natural lherzolite compositions (Brey et al. 1990; Taylor 1998); (ii) a fertile pyrolite (Taylor 1998); and (iii) CaO-MgO-Al₂O₃-SiO₂-Cr₂O₃ (CMAS-Cr) lherzolite compositions (Nickel 1989). The data set covers a wide range of possible natural peridotitic compositions, from *fertile* pyrolite to *refractory*, Na-Fe-free, high-Cr, CMAS-Cr lherzolite. From Fig. 1 it appears that the $T \ln[a_{\text{CaCrTs}}^{\text{Cpx}}]$ parameter is sensitive to pressure, particularly if a sodium correction for the CaCrTs activity is adopted (cf., Eq. 7), although the points show significant scatter. The scatter is likely to result mainly from compositional factors that have not yet been taken into account. Analysis of the experimental data indicates that the magnitude of the scatter varies with the Cr# ratio of the clinopyroxene and the temperature of equilibration and that $T \ln[a_{\text{CaCrTs}}^{\text{Cpx}}]$ is well correlated with pressure for a fixed value of $\ln\left(\frac{\text{Cr}\#^{\text{Cpx}}}{T}\right)$, irrespective of the composition of the system. Therefore, the latter parameter can be used to model the effect of compositional changes on the Cr content of clinopyroxene and, thus, isolate the net effect of pressure. We found that the experimental data can be satisfactorily reproduced by an expression of the type

$$P = aT \ln\left[a_{\text{CaCrTs}}^{\text{Cpx}}\right] + b \ln\left(\frac{\text{Cr}\#^{\text{Cpx}}}{T}\right) + cT + d, \quad (8)$$

where $a_{\text{CaCrTs}}^{\text{Cpx}}$ is given by Eq. 7. Equation 8 contains five unknown parameters (including the y factor in Eq. 7), which were fitted by least-squares regression using our experimental data set. Multiple non-linear regression using the program ‘Profit’ yielded the following

geobarometric expression¹ (\pm values are the 1σ uncertainties in the regression fit):

$$P(\text{kbar}) = -\frac{T(\text{K})}{126.9(\pm 7.7)} \cdot \ln\left[a_{\text{CaCrTs}}^{\text{Cpx}}\right] + 15.483(\pm 0.809) \\ \cdot \ln\left(\frac{\text{Cr}\#^{\text{Cpx}}}{T(\text{K})}\right) + \frac{T(\text{K})}{71.38(\pm 12.20)} + 107.8(\pm 6.4) \quad (9)$$

where

$$a_{\text{CaCrTs}}^{\text{Cpx}} = \text{Cr} - 0.81(\pm 0.05) \cdot \text{Cr}\# \cdot \text{Na}. \quad (10)$$

Equations 9 and 10 reproduce the experimental pressures with an uncertainty of ± 2.3 kbar at the 1σ level. No systematic error is apparent from analysis of $P_{\text{cal}} - P_{\text{expt}}$ deviations (Fig. 2a), despite the wide range of compositions utilized for the calibration. Addition of a corrective term for the Mg/(Mg + Fe) ratio of the clinopyroxene did not produce any significant improvement of the fit, suggesting that compositional effects related to the peridotite fertility are adequately accounted for in Eqs. 9 and 10 by the Cr# and Na parameters. This result is encouraging and suggests that the present geobarometer can be applied to a large spectrum of fertile and depleted mantle rocks. The temperature dependence of our geobarometer is reasonably low (1.2–2.4 kbar/50 °C, depending on composition) and only three chemical parameters (Cr, Al and Na) need to be measured to obtain a pressure estimate. It is worth noting that Eq. 9 only requires knowledge of clinopyroxene composition and is independent of the composition of garnet.

Geothermometry of garnet lherzolites

A number of geothermometers can be applied to garnet-lherzolite assemblages. These include formulations which are based on: (i) pyroxenes solvus (e.g., Wells 1977; Kretz 1982; Lindsley 1983; Bertrand and Mercier 1985; Brey and Köhler 1990; Taylor 1998); (ii) Fe-Mg exchange between clinopyroxene and garnet (e.g., Ellis and Green 1979; Krogh 1988), orthopyroxene and garnet (Harley 1984), or olivine and garnet (O’Neill and Wood 1979); (iii) Ni content of garnet in equilibrium with olivine (Griffin et al. 1989; Ryan et al. 1996; Canil 1994, 1999). Few of these methods provide accurate temperature estimates over the entire range of natural peridotite compositions (Taylor 1998). Pyroxene thermometry has proved an especially powerful tool for the estimation of the temperatures of equilibration of natural lherzolites, because it is less sensitive to subsolidus re-equilibration and to uncertainties of Fe²⁺/Fe³⁺ determinations.

¹ An earlier formulation based on Eqs. 7 and 8, with $a = -1/118.7$, $b = 15.153$, $c = 1/114.1$, $d = 109.6$, $y = 0.80$, was calibrated by Taylor and Nimis (1998) using a more extended, but in part less reliable, experimental data set. In applications, Eq. 9 (this work) tends to produce slightly lower pressure estimates, with maximum discrepancies < 2.5 kbar (usually < 1 kbar).

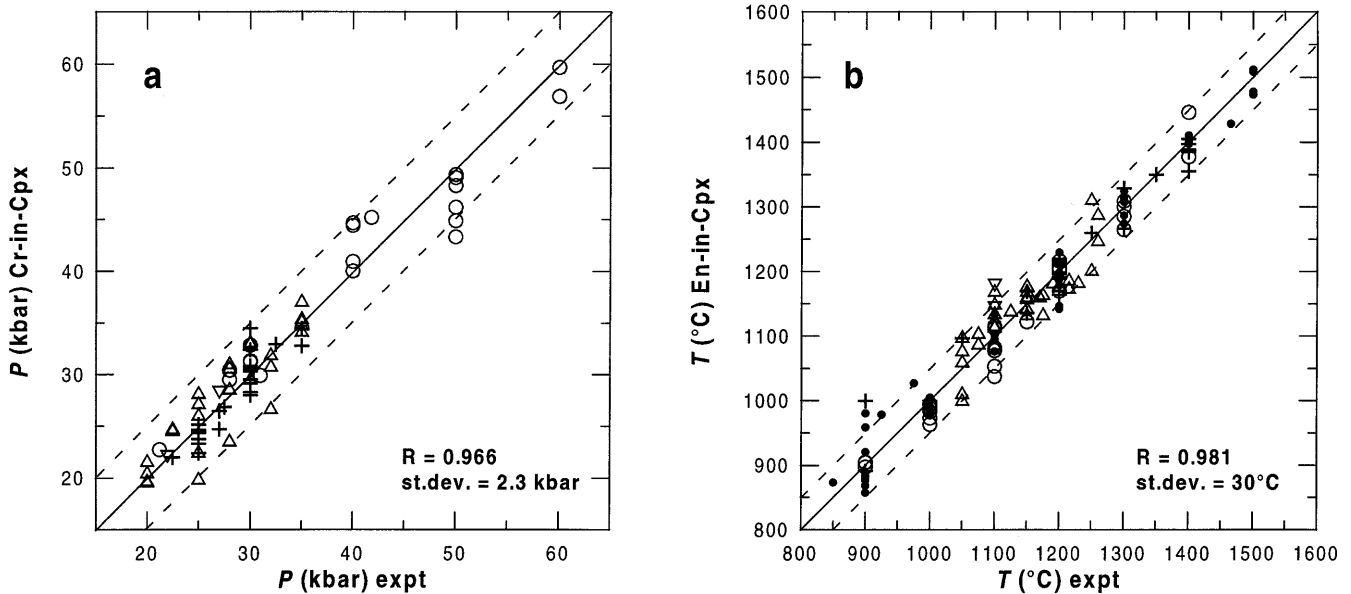


Fig. 2 **a** Calculated vs. experimental pressures for the Cr-in-Cpx barometer. **b** calculated vs. experimental temperatures for the enstatite-in-Cpx thermometer. *Dots* CMS system (Carlson and Lindsley 1988, and refs. therein). Other symbols as in Fig. 1. Reference lines at ± 5 kbar and ± 50 °C are shown

Temperatures have often been estimated by methods that utilize the composition of a single pyroxene, either monoclinic (Mercier 1976, 1980; Kretz 1982; Lindsley 1983; Finnerty and Boyd 1984, 1987) or orthorhombic (Lindsley 1983; Brey and Köhler 1990). These methods are generally based on Ca-Mg equilibria calibrated on simple systems or, at best, on a limited set of data that covers a restricted compositional space approaching that of natural lherzolites. Some of the pyroxene solvus geothermometers give reasonable estimates under favourable conditions (e.g., Finnerty and Boyd 1987), but in many cases yield strongly diverging results (cf., Finnerty and Boyd 1984; Carswell and Gibb 1987a; Taylor 1998), suggesting that compositional factors have not been properly taken into account. For example, Brey and Köhler (1990) showed that the preferred formulation of Finnerty and Boyd (1987) did not reproduce their experimental data on natural fertile lherzolite at $T < 1300$ °C; on the other hand, Taylor (1998) showed on the basis of a more comprehensive experimental set that Brey and Köhler's (1990) two-pyroxene formulation tends to give T overestimates at low temperature and T underestimates at high temperature. For this reason we reconsider the problem of single-pyroxene geothermometry of lherzolites by adopting a larger database and empirical corrections for non-ideal behaviour of clinopyroxene solid solutions. The database is the same as that utilized for our geobarometer calibration, with additional data on the diopside-enstatite join (Carlson and Lindsley 1988, and references therein), and from experiments in the spinel-lherzolite stability field (Brey et al. 1990). Although not within the garnet stability field, the latter experiments still contain clinopyroxene-orthopyroxene pairs and so provide useful constraints for geothermometric calibration under relatively low-pressure conditions.

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A single-clinopyroxene geothermometer for lherzolites

Two-pyroxene geothermometry is usually based on the exchange of the enstatite (en) component between clinopyroxene and orthopyroxene (Opx), which can be described by the equilibrium



The temperature dependence of this reaction can be expressed as (Brey and Köhler 1990)

$$T = \frac{a + b \cdot P}{c + \left(\ln \frac{a_{\text{en}}^{\text{Cpx}}}{a_{\text{en}}^{\text{Opx}}} \right)^2} \quad (12)$$

Using a two-site mixing model, the activities of the enstatite component in pyroxenes can be approximately defined as

$$a_{\text{en}} = X_{\text{Mg}}^{\text{M1}} \cdot X_{\text{Mg}}^{\text{M2}}, \quad (13)$$

which, in an Fe-free system, is given by

$$a_{\text{en}} = (1 - \text{Ca} - \text{Na})^{\text{M2}} \cdot (1 - \text{Al} - \text{Cr} - \text{Ti})^{\text{M1}} \quad (14)$$

Expressing Al^{M1} according to Eq. 5, the formulation for a_{en} becomes

$$a_{\text{en}} = (1 - \text{Ca} - \text{Na}) \cdot \left(1 - \frac{1}{2}(\text{Al} + \text{Cr} + \text{Na}) \right). \quad (15)$$

In Fe-bearing systems, Eq. 15 represents the activity of the combined enstatite-ferrosilite component.

In natural peridotitic rocks, $a_{\text{en}}^{\text{Opx}}$ is close to unity and little sensitive to temperature and compositional variations. Equation 12 can therefore be simplified to yield a geothermometric formulation that is based on the composition of the clinopyroxene alone:

$$T = \frac{a + b \cdot P}{c + (\ln a_{\text{en}}^{\text{Cpx}})^2} \quad (16)$$

The large spectrum of compositions used for the calibration allowed us to quantify the influence of minor components on the solubility of enstatite-ferrosilite in clinopyroxene. Corrections for Fe, Ti, Al and Cr were necessary to obtain an acceptable fit by eliminating compositionally dependent systematic deviations among the different data sets. We found that the experimental conditions were best reproduced by the following formulation:

$$T(\text{K}) = \frac{23166(\pm 447) + 39.28(\pm 4.27) \cdot P(\text{kbar})}{13.25(\pm 0.32) + 15.35(\pm 2.90) \cdot \text{Ti} + 4.50(\pm 0.83) \cdot \text{Fe} - 1.55(\pm 0.29) \cdot (\text{Al} + \text{Cr} - \text{Na}) + (\ln a_{\text{en}}^{\text{Cpx}})^2}, \quad (17)$$

where $a_{\text{en}}^{\text{Cpx}}$ is given by Eq. 15.

Equation 17 reproduces experimental temperatures with an uncertainty of ± 30 °C at the 1σ level. As in the case of our Cr-in-Cpx geobarometer, no systematic error is apparent from analysis of $T_{\text{cal}} - T_{\text{expt}}$ deviations (Fig. 2). A squared $\ln a_{\text{en}}^{\text{Cpx}}$ term in Eq. 17 resulted in a significant improvement of the fit and this seems to be in accordance with Brey and Köhler's (1990) observation that reciprocal temperature is linearly dependent on $[\ln(X_{\text{en}}^{\text{Cpx}}/X_{\text{en}}^{\text{Cpx}})]^2$. Different expressions for $a_{\text{en}}^{\text{Cpx}}$, including those adopted by Bertrand and Mercier (1985), Brey and Köhler (1990) and Finnerty and Boyd (1987) produced less satisfactory results and were abandoned.

Equation 17 indicates that the presence of CaAlTs (i.e., $\text{CaAl}_2\text{SiO}_6$) or CaCrTs solid solution components will produce an increase in the calculated temperature, the increase being higher at higher temperatures. This is consistent with experimental evidence for a broadening of the miscibility gap in Al-bearing pyroxenes (Tribaudino and Bruno 1993). However, to obtain a good fit for both low- and high-Ti compositions it was necessary to introduce an independent correction term for Ti. Such correction significantly affected the calculated temperatures for the HPY-40 experiments, which are particularly rich in Ti ($\text{Ti}_{\text{Cpx}} = 0.022\text{--}0.051$ apfu; mean (34) = 0.037 apfu) compared with the rest of the data set ($\text{Ti}_{\text{Cpx}} < 0.015$ apfu). Equation 17 predicts that, whereas enstatite solubility in clinopyroxene is lower at high CaAlTs and CaCrTs levels, the presence of a Ti-component reduces the width of the miscibility gap. This different crystal-chemical behaviour is difficult to explain if Ti substitutes for Mg in the M1 site, since Ti^{4+} has an ionic radius intermediate between those of Al^{3+} and Cr^{3+} (Shannon 1976). The higher charge of Ti^{4+} should, at most, even more strongly favour Ca incorporation due to stabilization of a $\text{CaMg}_{0.5}\text{Ti}_{0.5}\text{AlSiO}_6$ component. However, if Ti^{4+} is able to partition between octahedral and tetrahedral sites, as observed in Ti-rich diopsides from volcanic rocks (Carbonin et al. 1989;

Cundari and Salviulo 1987, 1989; Quartieri et al. 1993), this would increase the charge contribution to the O_3 bridging oxygen atoms ($\text{Al}^{3+} \rightarrow \text{Ti}^{4+}$) and, consequently, inhibit the uptake of Ca via a mechanism similar to that recognized for the $\text{Al}^{3+} \rightarrow \text{Si}^{4+}$ substitution (cf., Dal Negro et al. 1982). Cundari and Salviulo (1989) showed that $^{[4]}\text{Al}^{[6]}\text{Ti} \rightarrow ^{[4]}\text{Ti}^{[6]}\text{Al}$ exchange is favoured by temperature. Quartieri et al. (1993) demonstrated that Ti can even partition *preferentially* into tetrahedral sites in Al-free diopsides. Although we cannot provide any evidence for Ti in four-fold coordination in our experimental pyroxenes, the low standard deviation on

the calculated fitting parameter for Ti (relative error = 20%), the position of the Ti term in Eq. 17 (indicative of a temperature-enhanced effect), and the absence of any clear correlation between Ti content and other compositional factors in our data set suggest that such anomalous behaviour by Ti is a real feature in peridotitic systems. In any case, the Ti content in clinopyroxene from natural garnet peridotite is typically less than 0.020 apfu and, usually, less than 0.010 apfu. A TiO_2 content of 1 wt% (corresponding to ca. 0.025 apfu) would result in a decrease in calculated T of ca. 40 °C. Therefore, the Ti correction will rarely produce significant changes in the calculated temperature values when the geothermometer is applied to natural samples.

Since the corrections adopted for minor components are empirical, it might be argued that they do not reflect real compositional effects and simply make up for other unrecognized factors, due to internal correlations between chemical parameters. If this is the case, application to petrological systems slightly different in composition from those utilized for the calibration could result in strongly biased estimates. This can be checked by applying the geothermometer to experimental data on simple systems in which some of the minor components are absent. If the adopted corrections represent real compositional effects, Eq. 17 should still reproduce the experimental temperatures within reasonable uncertainties. Figure 3 shows the correlations between experimental and calculated temperatures for experiments in $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS) and $\text{Na}_2\text{O-CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (NCMAS) systems. Experimental temperatures are very well reproduced. Some major deviations seem to be unrelated to compositional or physical (P or T) factors and can partly be attributed to uncertainties in the determination of the equilibrium Ca content. The good fit for the CMAS ($\text{Al}_{\text{Cpx}} = 0.02\text{--}0.60$ apfu) and NCMAS ($\text{Na}_{\text{Cpx}} = 0.00\text{--}0.08$ apfu) data demonstrates that the effects of Al and Na are properly accounted for by the adopted enstatite-

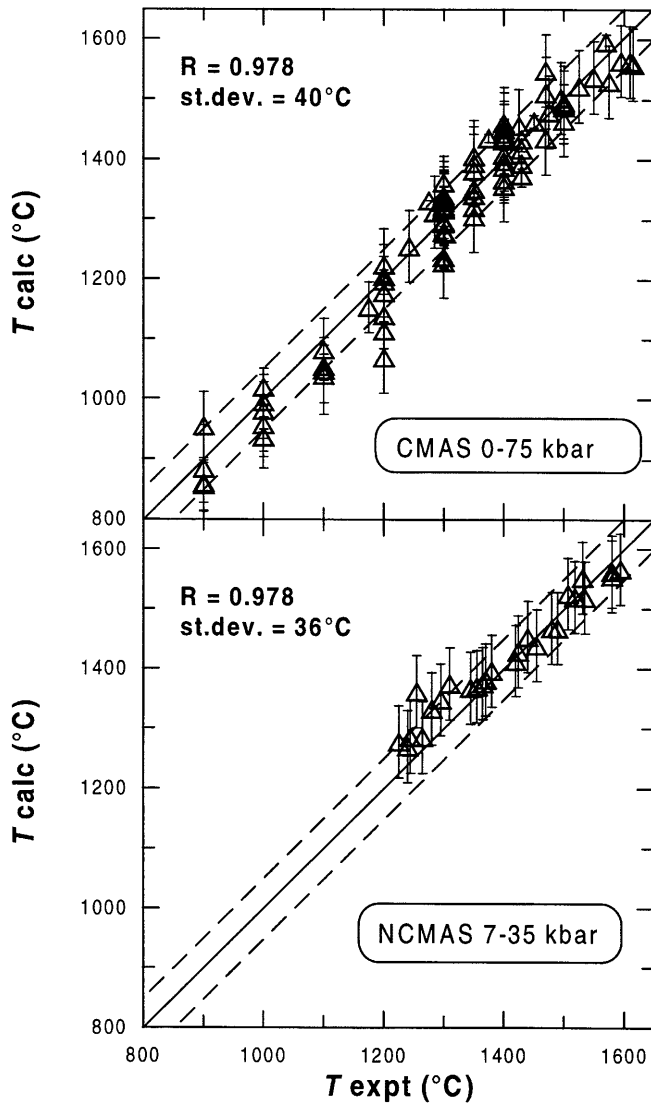


Fig. 3 Test of the enstatite-in-Cpx thermometer against experiments in simple systems. Source of data: *CMAS* Fujii (1977); Gasparik (1984); Gudfinnsson and Presnall (1996); Klemme (1998); Klemme and O'Neill (2000); Nickel et al. (1985); Perkins and Newton (1980); Tribaudino and Bruno (1993); Walter and Presnall (1994); Yamada and Takahashi (1984); *NCMAS* Walter and Presnall (1994). Error bars bracket maximum and minimum temperatures calculated from reversed Cpx compositions. For unreversed experiments a conservative error of $\pm 60^\circ\text{C}$, a value greater than or equal to that of most (90%) reversed experiments, was assumed. Reference lines at $\pm 50^\circ\text{C}$ are shown

diopside mixing model within the compositional space of interest.

Evaluation of Cr-diopside thermobarometry

Calibration statistics

Table 2 summarizes the statistical results obtained for our barometer and thermometer calibrations. Standard deviations of calculated vs. experimental pressures and

Table 2 Overall and partial calibration statistics

	All data	1	2	3	4	5
Thermometer						
N	131	26	34	2	28	41
St. dev. ($^\circ\text{C}$)	30	25	32	91	27	30
Corr. coeff.	0.981	0.989	0.879	–	0.984	0.990
Barometer						
N	76	21	25	2	28	
St. dev. (kbar)	2.3	3.0	2.5	1.2	1.5	
Corr. coeff.	0.966	0.969	0.888	–	0.927	

Source of data 1 Brey et al. (1990); 2 Taylor (1998; HPY-40); 3 Taylor (1998; KLB-50); 4 Nickel (1989; CMAS-Cr); 5 Various refs. (CMS)

temperatures are given for the whole data set and for each experimental suite. We calculated pressures and temperatures by using the experimental temperatures and, respectively, pressures as input values or, alternatively, through an iterative combination of the two formulations. The two types of calculation yielded much the same deviations, indicating that uncertainties in the barometric estimate do not prejudice the results of the thermometry, and vice versa. This is further confirmed by the absence of any correlation between pressure and temperature uncertainties (Fig. 4). Different experimental sets show similar deviations for the thermometer, while pressures for Brey et al.'s (1990) data are on the whole less well reproduced than for the other data sets. The experiments of Brey et al. are the only ones that extend to over 40 kbar. Accordingly, we calculate the 1σ uncertainty of our pressure estimates to be about 2 kbar at $P < 40$ kbar and slightly higher than 3 kbar at $P > 40$ kbar.

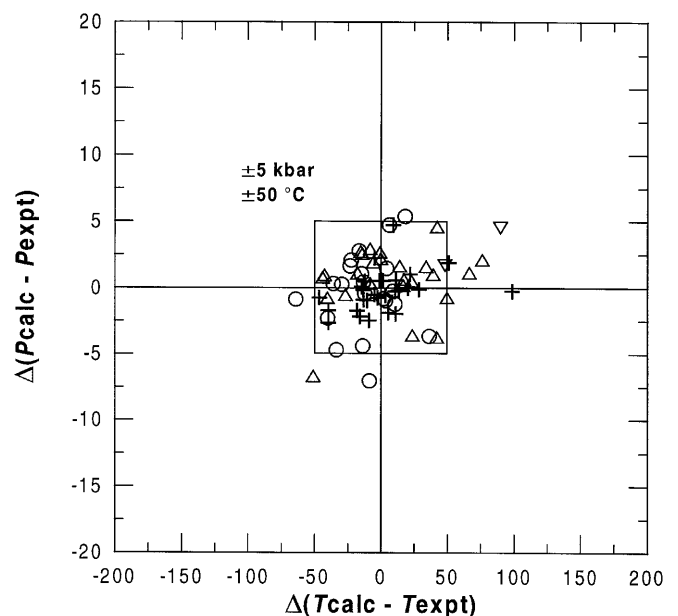


Fig. 4 Test of the Cr-diopside thermobarometer combination. Symbols as in Fig. 1

Constraints from graphite-bearing and diamond-bearing xenoliths and inclusions in diamonds

To test the reliability of our geobarometer and thermometer, we calculated by means of Eqs. 9 and 17 the P - T conditions of equilibration for peridotitic clinopyroxene inclusions in diamonds from kimberlites and lamproites and diamond-bearing and graphite-bearing lherzolite xenoliths from worldwide occurrences. Such samples are suited for evaluating the accuracy of P - T estimates, which should obviously fall within the stability field of diamond or graphite, respectively, as defined experimentally by Kennedy and Kennedy (1976) and theoretically from carbon thermodynamic properties by Chatterjee (1991). The inclusions are generally represented by isolated Cr-diopside crystals or by simple mineral assemblages (Cpx \pm Gt \pm Opx \pm olivine) that rarely allow application of conventional multiphase thermobarometers. Cr-diopsides occurring as isolated inclusions and in Cpx + Gt + Opx \pm olivine-bearing inclusions guarantee the best thermobarometric estimates, because the former maintain their original compositions and the latter can completely reequilibrate with Gt and Opx during a change in P - T conditions after entrapment in the host diamonds. Polymineralic inclusions devoid of orthopyroxene should also yield sound estimates, because the composition of clinopyroxene would be little affected by a thermal change and Cr exchange between clinopyroxene and garnet, which is the base for our barometry, is little sensitive to temperature. Orthopyroxene-free inclusions should therefore yield P - T estimates close to P - T conditions extant at the time of entrapment. Polymineralic inclusions containing both pyroxenes, but free of garnet, would record a thermal event occurring after entrapment, but would yield biased pressure estimates because equilibrium with garnet would not be maintained. Such inclusions were not used for the present test. We utilized Ramsay's (1992) $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ discrimination diagram (Fig. 5) to assign clinopyroxene inclusions to a specific original assemblage and assumed all clinopyroxenes plotting within the garnet-peridotite field of Fig. 5 to have been in equilibrium with both garnet and orthopyroxene at the time of their entrapment in the host diamond.

An evaluation of the quality of clinopyroxene analyses based on crystal chemical criteria is necessary to obtain a meaningful test. We deem that cations sums on both T and M1 + M2 sites >1.990 on a six-oxygen basis may be considered as sufficiently accurate for geothermobarometric purposes. All other analyses were judged to be unreliable and were therefore excluded. We also restricted the compositional range of the clinopyroxene to Cr_2O_3 contents lower than 5 wt%. This limitation only excluded a few uncommon, very kosmochlor-rich samples (e.g., Sobolev 1977), for which our simplified Cr-activity model is probably inaccurate. A small number of clinopyroxenes were characterized by very low values of the pressure-dependent parameter

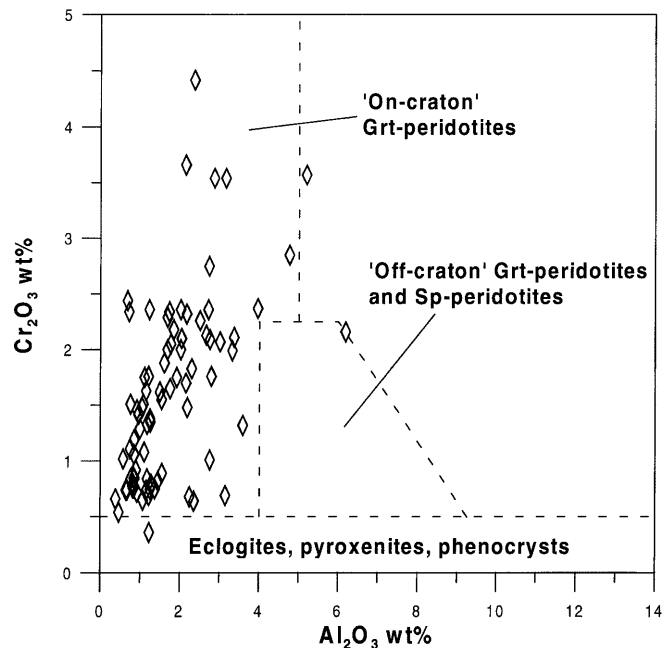


Fig. 5 Cr-diopside inclusions in diamonds from worldwide occurrences in Ramsay's (1992) classification diagram. Source of data: Daniels and Gurney (1989); Gurney et al. (1984, 1986); Harris et al. (1994); Hervig et al. (1980); Hutchinson (1997); Jaques et al. (1989, 1994); Meyer et al. (1994); Moore and Gurney (1989); Otter and Gurney (1989); Richardson et al. (1993, unpubl. data set); Rickard et al. (1989); Sobolev (1977); Sobolev et al. (1976, 1989, 1997a, b); Stachel and Harris (1997a, b); Stachel et al. (1998, and unpubl.); Tsai et al. (1979); Wilding et al. (1994). Polymineralic inclusions containing both clinopyroxene and orthopyroxene but devoid of garnet were not considered (see text)

$a_{\text{CaCrTs}}^{\text{Cpx}}$ (cf., Eq. 10), due to their very low Cr contents. Propagation of analytical errors is crucial for such analyses and, therefore, calculated pressures may be highly uncertain. We considered a lower limit of 0.003 for $a_{\text{CaCrTs}}^{\text{Cpx}}$ as safe for our geobarometric calculations and discarded analyses showing lower values for this parameter. Most analyses showed non-negligible K_2O contents. Where reported, any K was added to Na before P - T calculation.

Our geobarometer is temperature-dependent and our geothermometer is pressure-dependent, therefore P - T estimates were obtained through an iterative combination of the two formulations. The results of our calculations for the diamond-bearing and graphite-bearing samples are shown in Fig. 6. All graphite-bearing samples plot within the graphite stability field. Most of the diamond-bearing samples yield P - T pairs consistent with the diamond stability field and the others plot close (within 4 kbar) to the graphite-diamond univariant line. Use of other thermobarometers on the same and on other diamond inclusions, when permitted by the coexisting mineral assemblages, similarly produced P - T pairs within the diamond stability field or straddling the graphite-diamond boundary (Jaques et al. 1990, 1994; Wilding et al. 1994). Therefore, our thermobarometer does not show any particular systematic bias compared

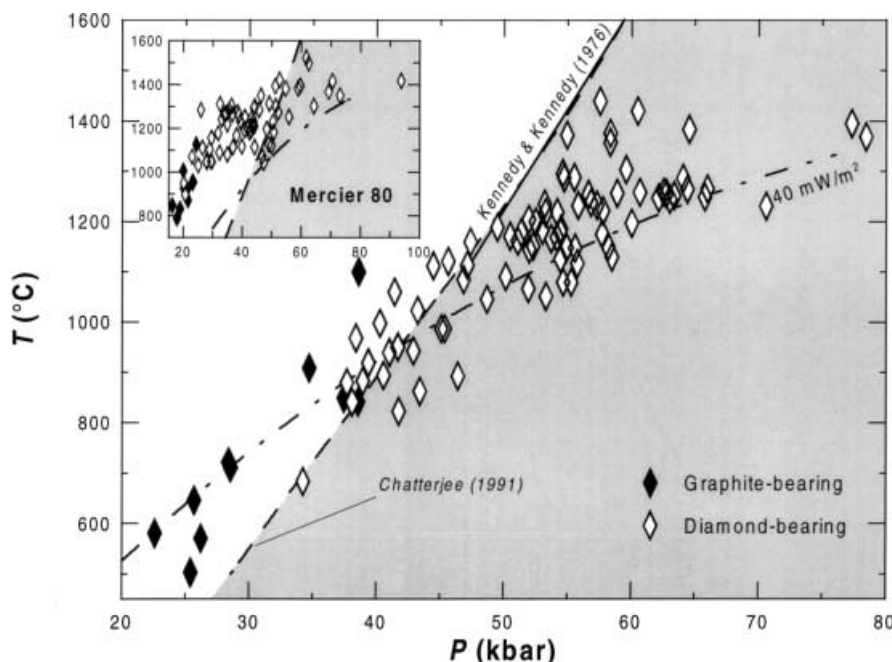


Fig. 6 P - T conditions for Cr-diopsides coexisting with diamond or graphite from worldwide occurrences estimated by using Eqs. 9 and 17, and (inset) Mercier's (1980) single-pyroxene thermobarometer. Open symbols diamond-bearing, garnet-peridotite xenoliths and inclusions in diamonds; solid symbols graphite-bearing, garnet-peridotite xenoliths. Source of data for diamond inclusions as in Fig. 5. Additional data for diamond-bearing xenoliths: Boyd and Finnerty (1980); Dawson and Smith (1975); Jaques et al. (1990); McCallum and Egler (1976); Pokhilenko et al. (1977); Shee et al. (1982). Source of data for graphite-bearing xenoliths: Boyd and Finger (1976); Pearson et al. (1994). Graphite-diamond boundary based on experiments (solid line; Kennedy and Kennedy 1976) and thermodynamic properties of carbon (dashed line; Chatterjee 1991). Conductive 40-mW/m² geotherm after Pollack and Chapman (1977)

with other, widely used methods. Several sources of errors may account for some points falling on the wrong side of the diamond-graphite boundary: (i) uncertainty of the geobarometer calibration (all of them are within 2σ of the boundary); (ii) uncertainty in the location of the graphite-diamond reaction; (iii) inaccuracy of chemical analyses; (iv) reequilibration to lower pressure without transformation of diamond; (v) lack of complete equilibration in diamond inclusions and in xenoliths. It is worth noting that errors in temperature estimates are not a feasible explanation. Because of the temperature-dependence of the geobarometer (ca. 1.5 kbar/50 °C), any change of nominal temperature will force the P - T points to move parallel to the graphite-diamond boundary. The effect of analytical uncertainties on thermobarometry can be evaluated by performing several electron microprobe analyses on a single clinopyroxene grain and calculating P - T for each analysis. Twenty point analyses (WDS) on a clinopyroxene from a garnet-lherzolite xenolith (FRB348) from Bultfontein, South Africa, gave the following average oxide composition and standard deviations: $\text{SiO}_2 = 55.06 \pm 0.65$, $\text{TiO}_2 = 0.02 \pm 0.02$, $\text{Al}_2\text{O}_3 = 1.60 \pm 0.03$, $\text{Cr}_2\text{O}_3 =$

1.46 ± 0.05 , $\text{FeO} = 2.12 \pm 0.09$, $\text{MnO} = 0.04 \pm 0.03$, $\text{MgO} = 17.01 \pm 0.15$, $\text{CaO} = 21.15 \pm 0.19$, $\text{Na}_2\text{O} = 1.31 \pm 0.05$, $\text{K}_2\text{O} = 0.01 \pm 0.01$. Calculated P - T conditions were $P = 42.8 \pm 1.3$ kbar and $T = 971 \pm 40$ °C. Errors related to analytical precision appear to be fairly small and comparable to those derived from calibration statistics ($\sigma_P = 2.3$ kbar; $\sigma_T = 30$ °C).

The assumption that all Fe is present as Fe^{2+} may constitute an additional source of error. A significant Fe^{3+} content will increase the fraction of tschermakitic components and, therefore, produce a broadening of the pyroxene miscibility gap. Hence, neglecting Fe^{3+} will cause an underestimation of T . For natural peridotites this effect will be negligible because of the low Fe^{3+} contents in clinopyroxene (Canil and O'Neill 1996). The effect of Fe^{3+} on pressure estimates is not directly obvious. Fe^{3+} is likely to behave similarly to Cr^{3+} , which has the same charge and only slightly smaller size (Shannon 1976). Since tschermakitic components in clinopyroxene in equilibrium with garnet decrease with increasing pressure (e.g., Brey et al. 1990), we expect P to be overestimated for Fe^{3+} -rich samples. Pressures calculated for peridotitic clinopyroxenes by assuming that Fe^{3+} behaves exactly as Cr (i.e., $\text{Cr} = \text{Cr} + \text{Fe}^{3+}$) and using ferric iron contents measured by Mössbauer spectroscopy (Canil and O'Neill 1996) are lower than and within 6 kbar (mean of 13 samples = 2.6 kbar) of those calculated by ignoring Fe^{3+} . Such a correction would increase, rather than diminish, the number of diamond inclusions plotting within the graphite stability field. The effect of Fe^{3+} on pressure estimates is probably small and, at present, any correction for Fe^{3+} seems unwarranted.

Cr-diopside thermobarometry independently confirms the tendency of some diamond-bearing samples to straddle the graphite-diamond boundary and seems to

exclude uncertainty in Fe^{3+} determination as the cause of this behaviour. Inaccuracy of chemical analyses is a possible, but perhaps not a unique explanation. In any case, the accuracy of Cr-diopside thermobarometry appears to be comparable with that claimed for the most widely used thermobarometers. It is worth noting that the P - T points in Fig. 6 tend, as expected for a craton-type lithosphere, to be aligned (mostly within $\pm 80^\circ\text{C}$) along geotherms close to the 40-mW/m^2 conductive geotherm of Pollack and Chapman (1977), further demonstrating the internal consistency of Cr-diopside thermobarometry. By contrast, Mercier's (1980) single-Cpx methods may yield grossly erroneous results (see inset in Fig. 6).

Cr-in-Cpx versus Al-in-Opx

We have calculated pressures and temperatures for a suite of mantle xenoliths from the classic Lesotho kimberlites (Nixon and Boyd 1973; Boyd and Finger 1976) by using the enstatite-in-Cpx geothermometer in combination with three different geobarometers, including our Cr-in-Cpx barometer and the two most recent versions of the Al-in-Opx barometer (Brey and Köhler 1990; Taylor 1998). The results (Fig. 7) show that the Cr-in-Cpx barometer compares favourably with the Al-in-Opx barometers for the coarse-textured xenoliths. The agreement with the Taylor estimates is particularly good, with a maximum difference of 3 kbar and a mean difference of 1 kbar, while the Brey and Köhler estimates are systematically lower by 4 kbar, on average. The accord is conversely very poor for the sheared xenoliths, for which the three barometers may give markedly diverging results. The scatter is likely to derive from incomplete equilibration among minerals during

thermal and metasomatic events that accompanied the development of the shearing (cf., Smith et al. 1993). The Cr-in-Cpx barometer yields a much narrower pressure span for these xenoliths, suggesting a greater robustness of this barometer to short-lived thermal/chemical perturbations.

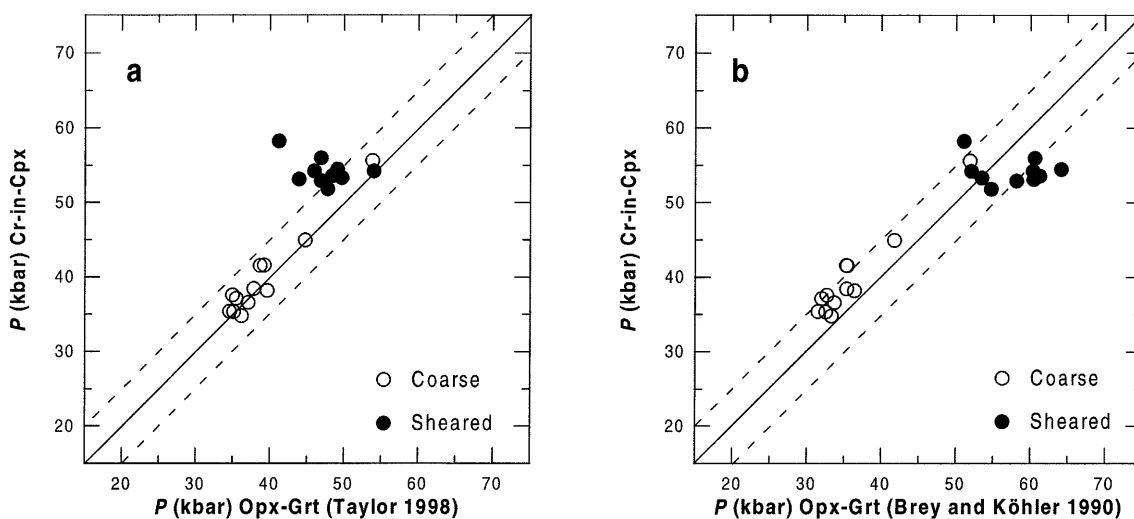
Cr-diopsides from Kimberley, South Africa

Figure 8 shows P - T arrays calculated for Cr-diopside from heavy-mineral concentrates from the "Big Hole", Kimberley, South Africa, using mineral analyses obtained by both EDS and WDS electron microprobe methods. The P - T array in both cases is similar indicating both analytical methods can yield reliable data if correctly calibrated. The P - T data indicate thermal conditions equivalent to a ca. 38 mW/m^2 conductive geotherm, similar to that obtained in previous investigations (e.g., Griffin et al. 1995). There is sampling of the diamond stability field at pressures >40 kbar, consistent with the diamondiferous nature of the host kimberlite. Further examples and applications are discussed in Part 2.

Apparent P - T estimates for non-garnet-peridotite Cr-diopsides

Cr-diopsides in strongly depleted or metasomatized spinel peridotites may show very low contents of Al_2O_3 , comparable to those of typical clinopyroxenes from garnet lherzolite. Nimis (1998) showed that $\text{Al}_2\text{O}_3/\text{MgO}$ relations can be useful to distinguish anomalous clinopyroxenes of metasomatic origin. Yet some low-Al, low- P Cr-diopsides may still be misidentified as derived from garnet peridotites based on Ramsay's (1992) and Nimis' (1998) classification diagrams. This may be of great importance when single-clinopyroxene thermobarometry is applied to isolated mineral grains of uncertain origin, as those occurring in heavy-mineral concentrates.

Fig. 7a,b Cr-in-Cpx vs. Al-in-Opx barometry for peridotite xenoliths from Lesotho based on mineral analyses in Nixon and Boyd (1973) and Boyd and Finger (1976)



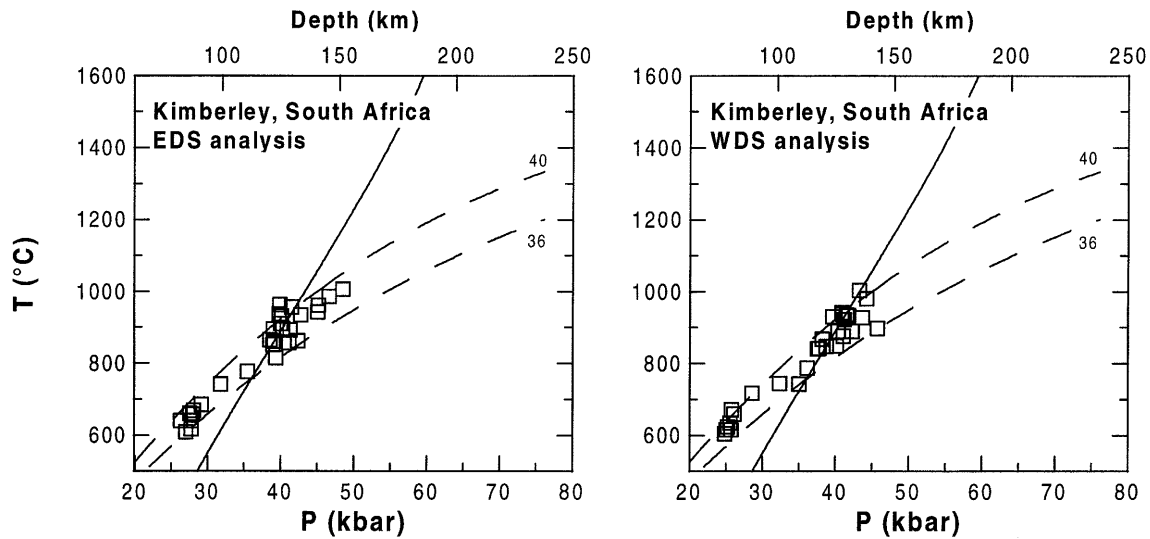


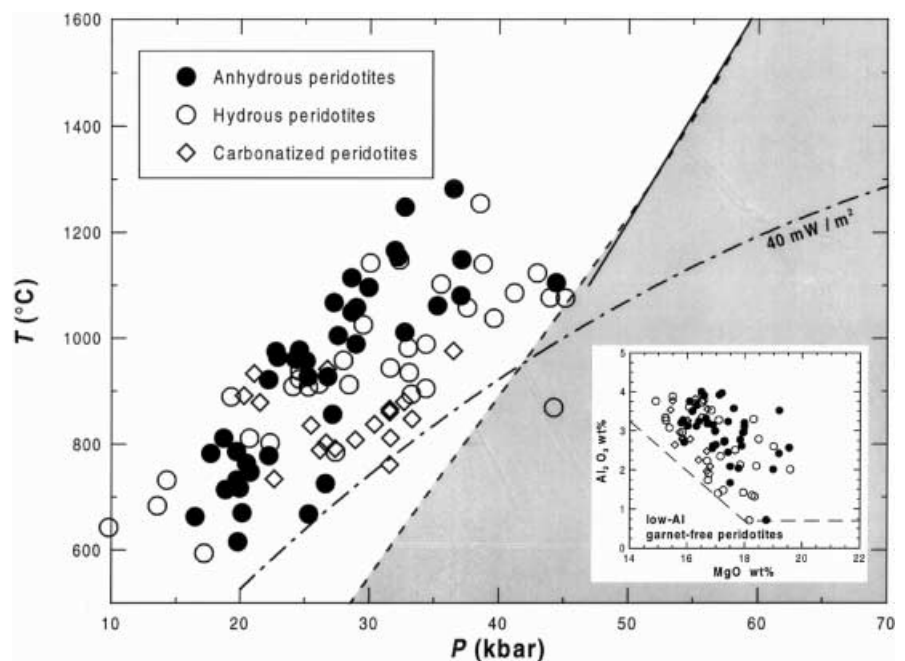
Fig. 8 Thermobarometry of Cr-diopsides from heavy-mineral concentrates from the “Big Hole”, Kimberley, South Africa, using mineral analyses obtained by both EDS and WDS electron microprobe methods. Conductive 40- and 36-mW/m² geotherms after Pollack and Chapman (1977)

We have calculated *apparent* P - T values for ninety-three Cr-diopsides from the literature that are derived from garnet-free peridotites and yet plotted within the ‘on-craton’ garnet-peridotite field in Ramsay’s (1992) diagram (Fig. 5) and in the high- Al_2O_3 , high-MgO field proposed by Nimis (1998) to discriminate clinopyroxenes from ‘normal’ peridotites from those in low- P , metasomatic peridotites (Fig. 9). They comprise clinopyroxenes from both anhydrous and hydrous spinel peridotites, including carbonatized lithotypes. The calculated P - T values are obviously meaningless, because

clinopyroxene was not in equilibrium with orthopyroxene *and* garnet in these rocks. Such fictive estimates may however be useful to evaluate the possible bias produced on assessment of diamond potential by an improper application of Cr-diopside thermobarometry.

Figure 9 shows that the bulk of the calculated P - T values plot within the graphite stability field and, mostly, at temperatures higher than for a normal continental conductive geotherm. This exercise shows that once samples plotting in the low- Al_2O_3 , low-MgO field of Nimis (1998) are discarded, no major effect on evaluation of diamond potential is likely to occur. Any bias can eventually be limited if a large number of grains are utilized and only P - T points aligned close to a continental conductive geotherm are considered. Trace-element analysis may also be helpful to distinguish between metasomatized and unmetasomatized samples.

Fig. 9 ‘Apparent’ P - T conditions for Cr-diopsides in garnet-free peridotites from worldwide occurrences unduly plotting within the ‘on-craton’ garnet-peridotite field of Ramsay (1992). **Inset** Same Cr-diopsides in the Al_2O_3 vs. MgO classification diagram of Nimis (1998). Samples plotting within the low- Al_2O_3 field (*garnet-free peridotites*) were not considered and are not shown in either diagram



Conclusions

Cr-diopside thermobarometry is a powerful tool for obtaining information on the thermal state of the upper mantle and the extent of mantle sampling by deep-seated magmas. The uncertainties of the methods proposed here are comparable to, or better than, those of the most widely used thermobarometers for garnet peridotites. The present methods are applicable over a wide compositional range, from extremely refractory to very fertile peridotite compositions. In particular, the present Cr-in-Cpx barometer represents the best alternative to the Al-in-Opx barometer for the evaluation of pressure conditions of equilibration of natural garnet lherzolites. *P-T* conditions of equilibration can be simultaneously retrieved from the composition of the Cr-diopside alone, thus allowing application to partially altered xenoliths, inclusions in diamonds, and loose grains from diamond exploration mineral concentrates.

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