

The garnet–orthopyroxene Al barometer: problematic application to natural garnet lherzolite assemblages

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Abstract

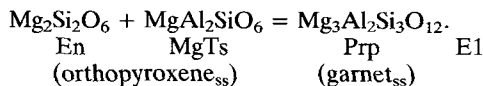
The garnet–orthopyroxene Al barometer specifically considers the Al content of orthopyroxene in equilibrium with garnet resulting from Mg–Tschermarks substitution. It is demonstrated that P – T calibrations of this barometer derived solely from experimental data for the MAS system, such as that favoured by Finnerty and Boyd (1984, 1987) based on the data of MacGregor (1974), cannot be expected to yield meaningful pressure estimates for natural garnet lherzolite assemblages. The presence of additional CaO, FeO and Cr₂O₃ components in natural garnet lherzolites can be expected to influence substantially the Al partitioning between orthopyroxene, garnet and/or spinel at any particular P and T . Thus a more comprehensive barometer formulation is required, such as the one provided by Nickel and Green (1985) that is based on experimental data for the CMAS and SMACCR systems with thermodynamic modelling and addition of an Fe correction term.

It is further emphasised that for orthopyroxenes in natural garnet lherzolites the amount of Al introduced as Mg–Tschermarks substitution cannot be assessed simply as the total Al cation content since such orthopyroxenes frequently contain Al cations linked to Na substitution in $M2$ sites or to Cr, Ti and possibly Fe³⁺ in $M1$ sites. Revised algorithms for the calculation of specific $X_{Al(Ts)}^{M1}$ orthopyroxene contents are presented. Application to analytical data sets for garnet lherzolite xenolith suites in the Thaba Putsoa and Mothae kimberlites generates revised upper mantle P – T arrays which *refute* the widely accepted advocacy by Finnerty and Boyd (1984, 1987) and Finnerty (1989) of an upper-mantle palaeogeotherm beneath northern Lesotho that is markedly inflected to a higher thermal gradient at the depths of derivation of the more chemically fertile, porphyroclastic textured, xenoliths.

KEYWORDS: garnet, orthopyroxene, Al barometer, lherzolite.

Background

In the simple MAS (MgO–Al₂O₃–SiO₂) system, Al₂Mg_{–1}Si_{–1} exchange in orthopyroxene in equilibrium with garnet is represented by the Mg–Tschermarks net transfer reaction:



As ∇V for this reaction is quite large (involving as it does reorganisation of Al–O and Si–O bonds) it is quite strongly pressure dependent. Several other simpler reaction equilibria (notably for Fe²⁺–Mg²⁺ and Ca²⁺–Mg²⁺ exchange between constituent mineral phases) provide useful thermometers with lower dT/dP gradients applicable to garnet lherzolite (Grt + Ol + Opx + Cpx) assemblages. Experience shows that in combi-

nation with any of these thermometers, consideration of the amount of Mg–Tschermarks component in orthopyroxene provides the only really reliable and sensitive barometer currently available for garnet lherzolites. Whilst the Ca–Tschermarks content in the clinopyroxene is also markedly pressure dependent (O'Hara, 1967; Herzberg, 1978; Gasparik, 1984; Wood and Holloway, 1984), problems over the complexity of Al solubility in clinopyroxene (Nickel *et al.*, 1985), possible non-stoichiometry (Wood and Henderson, 1978; Gasparik and Lindsley, 1980) and difficulties over evaluating the quantity and activity of Ca–Tschermarks component in clinopyroxene seriously detract from its use as a sensitive barometer. An alternative Ca-in-olivine barometer (Finnerty and Boyd, 1978; Adams and Bishop, 1986; Finnerty, 1989) is too temperature

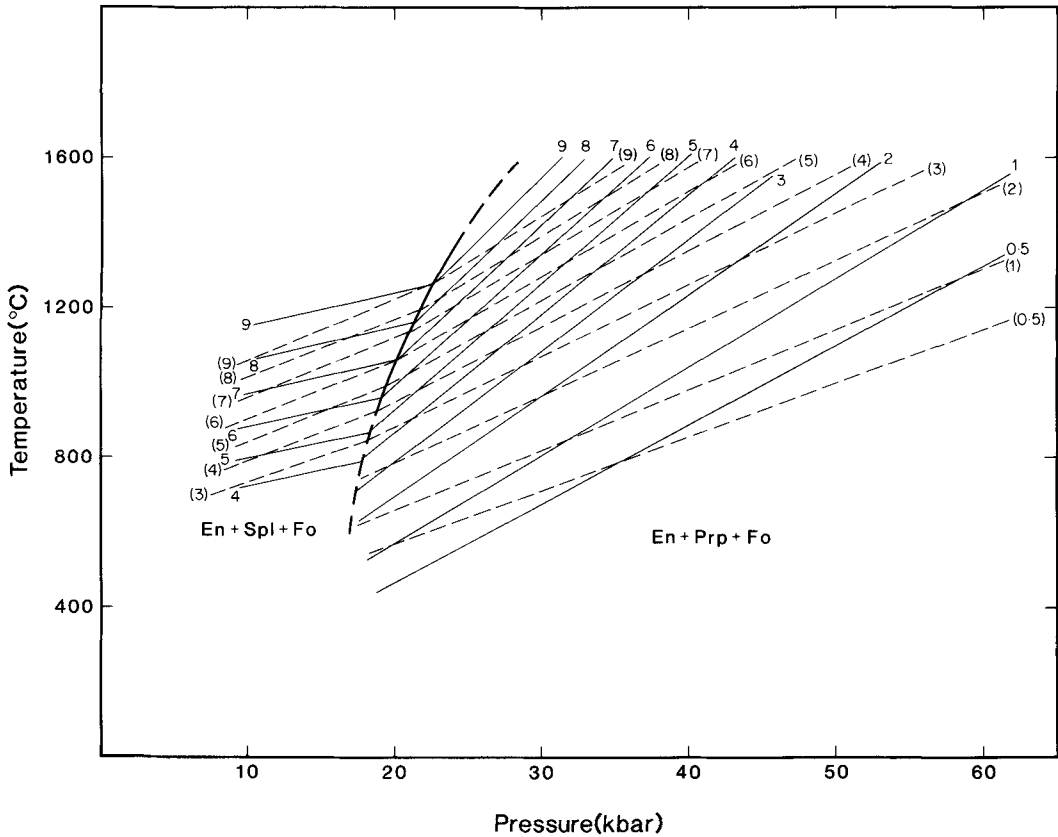


FIG. 1. P - T plot of isopleths for wt. % Al_2O_3 in enstatite, in enstatite + pyrope + forsterite and enstatite + spinel + forsterite assemblages in the MAS system. Isopleths (solid lines) in the garnet peridotite stability field calculated by equation (E2) based on experimental data from Perkins *et al.* (1981). Isopleths (dashed lines) calculated from the linear P - T expression derived from Finnerty and Boyd (1984) from the experimental data of MacGregor (1974). Also shown is the 'best-fit' univariant curve from Perkins *et al.* (1981) for the reaction enstatite + spinel = forsterite + pyrope. Note also the flatter dT/dP gradients of the Perkins *et al.* (1981) isopleths in the spinel peridotite field, compared with the isopleths from MacGregor (1974), indicating that the Al_2O_3 content of enstatite in spinel peridotite is a good thermometer but poor pressure indicator.

dependent to yield sufficiently precise pressure values when paired with available thermometers.

Calibrations for the MAS system

Since Boyd and England (1964) first demonstrated the strong pressure dependence of the Al content of enstatite in equilibrium with pyrope, further MAS system experimental data (and/or thermodynamic analysis) have been provided by MacGregor (1974), Wood and Banno (1973), Danckwerth and Newton (1978), Lane and Ganguly (1980), Perkins *et al.* (1981), Kawasaki and Matsui (1983). A more recent review of the MAS system data by Bertrand *et al.* (1987) supported the validity of the experimental data

provided by Perkins *et al.* (1981). Although Perkins *et al.* (1981) indicated slight curvatures in P - T space of the Al_2O_3 isopleths for enstatite in equilibrium with pyrope, their data are essentially compatible with a linear fit to the isopleths derived by Finnerty and Boyd (1987) which can be expressed in rearranged form as:

$$P = 0.007918 [-T(\ln K - 0.74) - 1976] \quad \text{E2}$$

with $K = (\text{wt. \% } \text{Al}_2\text{O}_3 \text{ in enstatite})/100$

P in kilobars

T in degrees kelvin

The P - T distribution of the Al_2O_3 isopleths (solid lines) for enstatite in equilibrium with pyrope in the MAS system that is calculated from

this expression and based on the Perkins *et al.* (1981) experimental data is shown in Fig. 1. Also indicated for comparison are an additional set of Al_2O_3 isopleths (dashed lines) calculated from an equivalent expression derived from the linear least-squares fit by Finnerty and Boyd (1984) to the MAS system experimental data of MacGregor (1974). Indications are (e.g. Bertrand *et al.*, 1987) that the isopleths based on the Perkins *et al.* (1981) data are to be preferred to those based on the MacGregor (1974) data for the calculation of equilibration conditions for orthopyroxenes within the MAS system.

Calibrations for the CMAS system

It is reasonable to expect that mineral reaction equilibria in natural 4-phase garnet lherzolite assemblages will be somewhat more closely simulated by experimental data on the CMAS ($\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$) system. Akella (1976), Howells and O'Hara (1978), Perkins and Newton (1980), Yamada and Takahashi (1984) and Nickel *et al.* (1985) have all provided direct experimental data on garnet-orthopyroxene equilibria in the SiO_2 undersaturated part of the CMAS system. Uncertainties exist over experimental procedures and satisfactory equilibration with certain of the earlier data. However, the data by Perkins and Newton (1980), Yamada and Takahashi (1984) and Nickel *et al.* (1985) are judged to be more satisfactory and largely compatible as indicated by discussions in Harley (1984), Nickel and Green (1985) and Brey *et al.* (1986).

Fig. 2 shows Al_2O_3 isopleths (solid lines) for orthopyroxenes in equilibrium with garnet + olivine + clinopyroxene in the CMAS system, calculated from the expression:

$$P = 0.001058 [-T(\ln K - 0.94) - 3473] \text{ E3}$$

derived from the linear least-squares fit by Finnerty and Boyd (1987) of the CMAS data from Perkins and Newton (1980). As before $K = (\text{wt.}\% \text{Al}_2\text{O}_3 \text{ in orthopyroxene})/100$, P in kilobars and T in degrees kelvin.

Comparison with Fig. 1 demonstrates that the addition of Ca has a profound effect on garnet-orthopyroxene equilibria and produces significant shifts in the P - T locations of the Al_2O_3 in orthopyroxene isopleths relative to those for the MAS system. Thus P - T calibrations of the garnet-orthopyroxene Al barometer based solely on experimental data for the MAS system cannot be expected to yield meaningful pressure values for garnet lherzolite assemblages.

Calibrations for more chemically complex and natural rock systems

Most natural garnet lherzolites are highly magnesian but even the small amounts of Fe present (typically $\text{Fe}/(\text{Fe} + \text{Mg}) = \text{ca. } 0.1$) may significantly affect garnet-orthopyroxene equilibria. Experimental data on the effect of Fe on the Al content of orthopyroxene in equilibrium with garnet + olivine exists for only a limited range of P - T - X conditions in the FMAS and CFMAS systems (Kawasaki and Matsui, 1983; Wood, 1974). Additional data exist for more Fe- and Si-rich, olivine-free, compositions in these systems (Harley, 1984). These various data clearly demonstrate that the addition of Fe reduces the solubility of Al in orthopyroxene in equilibrium with garnet but that the effect is non-linear and most marked in Fe-rich compositions (see Bertrand *et al.*, 1986).

Several experimental studies (MacGregor, 1970; O'Neill, 1981; Webb and Wood, 1986; Nickel, 1986) have convincingly shown that addition of Cr (invariably present in natural garnet lherzolites) substantially influences the stability of spinel relative to garnet and, hence, the Al partitioning between orthopyroxene and garnet and/or spinel.

The results of these studies of Fe and Cr-bearing systems indicate that, unless the influences of these additional chemical components fortuitously cancel each other out, a garnet-orthopyroxene Al barometer formulation that is based entirely on MAS and/or CMAS system experimental data is unlikely to be satisfactory for natural garnet lherzolites. This is seemingly confirmed by the different P - T locations in Fig. 2 of the Al_2O_3 isopleths (dashed lines) for orthopyroxene in equilibrium with garnet + clinopyroxene + olivine based on the limited experimental data provided by Green and Ringwood (1967) for synthetic multi-component pyrolite compositions, which closely model natural garnet lherzolites.

Thermodynamic modelling of garnet-orthopyroxene equilibria aimed at correcting P - T calibrations based on experimental data for the simple MAS and CMAS systems for the influence of the additional chemical components present in natural rocks was pioneered by Wood and Banno (1973). This led to the publication by Wood (1974) of a garnet-orthopyroxene Al barometer formulation claimed to yield equilibration pressure estimates accurate to within 2-3 kilobars for most natural garnet-orthopyroxene assemblages.

Subsequent alternative formulations of the garnet-orthopyroxene Al barometer, designed to

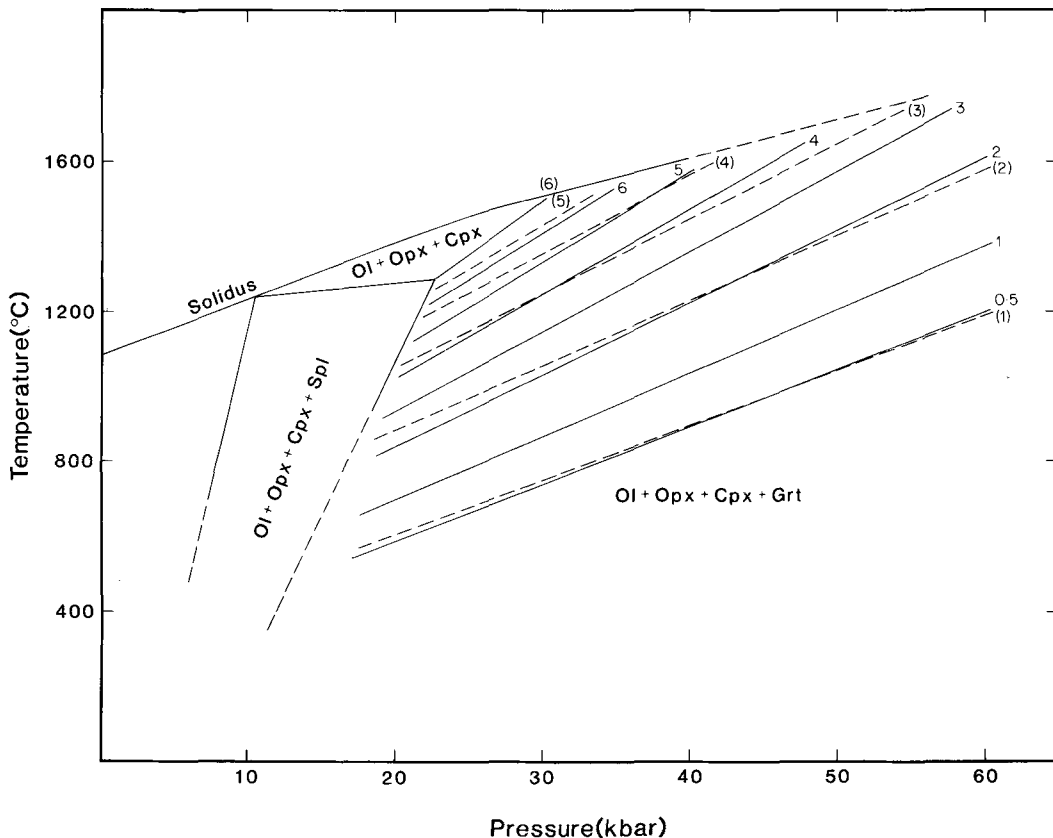


FIG. 2. P - T plot of wt. % Al_2O_3 isopleths (solid lines) for orthopyroxene in equilibrium with garnet + clinopyroxene + olivine calculated by equation (E3) based on the CMAS system experimental data of Perkins and Newton (1980). Also shown for comparison are wt. % Al_2O_3 isopleths (dashed lines) for orthopyroxene in equilibrium with garnet in multi-component pyrolite compositions (Green and Ringwood, 1967) as well as the various pyrolite (\equiv peridotite) assemblage stability fields. This figure reproduced from Carswell and Harley (1990) with permission from Blackie and Son.

be applicable to natural multi-component rock systems have been put forward by Harley and Green (1982), Harley (1984), Nickel and Green (1985) and Bertand *et al.* (1986). Evaluation tests by Carswell and Gibb (1987a) on the ability of these various barometer formulations to reproduce the experimentally recorded equilibration pressures of natural or synthesised multi-component garnet lherzolite assemblages indicated that the formulation provided by Nickel and Green (1985) yields the most accurate pressure values. This result was not surprising since the latter formulation most closely models the compositions of natural garnet lherzolite assemblages being the first to incorporate experimental data on a Cr-bearing system (SMACCR) in addition to CMAS, FMAS and CFMAS system data.

Assessment of $X_{\text{Al}(T_s)}^{M1}$ in orthopyroxenes

Pressure evaluation from garnet-orthopyroxene equilibria, based on the transfer reaction (E1) above, is dependent upon determination of the amount of Mg-Tschermaks component present in the orthopyroxene. This component involves the presence of Al cations in both tetrahedral [$T(B)$] and octahedral [$M1$] structural sites (Table 1). However, in practice most formulations of the garnet-orthopyroxene Al barometer depend on assessment of X_{Al}^{M1} —that is the mole fraction of Al present in the $M1$ sites.

For orthopyroxenes in the simple MAS and CMAS chemical systems all Al present is restricted to Tschermaks substitution and thus equally partitioned between $M1$ and $T(B)$ sites. Hence $X_{\text{Al}(T_s)}^{M1}$ can be accurately assessed from chemical analyses as simply half the total Al

TABLE 1 - PYROXENE SITE OCCUPANCIES

<u>Unit Formula</u>	M2 [8 or 6] 1.0	M1 [6] 1.0	T(B) [4] 1.0	T(A) [4] 1.0	O _{6.0}
<u>Cations</u>	M2	M1	T(B)	T(A)	
Restricted Site Occupancies	Ca ²⁺ Na ⁺ Li ⁺	Cr ³⁺ Fe ³⁺ Ti ⁴⁺	Si ⁴⁺	Si ⁴⁺	
Occupancies Dependent upon P-T Conditions	Mg ²⁺ Fe ²⁺ Mn ²⁺	Mg ²⁺ Fe ²⁺ Mn ²⁺ Al ³⁺ Al ³⁺			

Principal end-members reflecting the most common cation substitutions in orthopyroxenes

M2	M1	T(B)	T(A)
Mg	Mg	Si	Si
Mg	Al	Al	Si
Mg	Cr	Al	Si
Mg	Fe ³⁺	Al	Si
Mg	Ti	Al	Al
Ca	Mg	Si	Si
Na	Al	Si	Si
Na	Cr	Si	Si
Na	Fe ³⁺	Si	Si
Na	Ti	Al	Si
Na	Ti _{0.5} Mg _{0.5}	Si	Si

(plus substitution of Fe²⁺, Mn²⁺, Ni²⁺ for Mg²⁺)

cation content present in the standard unit formula (Table 1) viz.:

$$X_{Al(Ts)}^{M1} = X_{Al}^{M1} = 0.5 X_{Al}^{Total} \quad E4$$

Unfortunately this straightforward relationship does not hold for more chemically complex, natural orthopyroxenes. These may contain minor, although nonetheless significant contents of Cr, Fe³⁺ and Ti in M1 sites and/or Na in M2 sites.

This raises the possibility that some of the Al present in the M1 and T(B) sites may be linked to substitutions other than that corresponding to Mg-Tschermaks (see Table 1). Hence, application of garnet-orthopyroxene Al barometer formulations based on reaction E1 to such natural orthopyroxenes requires rigorous assessment of X_{Al(Ts)}^{M1}—that is the mole fraction of Al cations present in the M1 sites specifically involved in Tschermaks substitution.

There are basically two alternative approaches to the calculation of this key compositional parameter in such orthopyroxenes:

(A) Al^[T] = 2.0000 - Si⁴⁺
(in 6 oxygen unit formula)

thus: Al^[M1] = Al^[Total] - Al^[T]

hence specifically X_{Al(Ts)}^{M1} =
Al^[M1] - (Na^[M2] - Cr - Fe³⁺) E5

Note that the last term in this equation corrects for the possible amount of Al in M1 sites linked to Na in M2 sites after first taking into account Na linked to Cr in ureyite (NaCrSi₂O₆) and/or Fe³⁺ in acmite (NaFe³⁺Si₂O₆). If Na < (Cr + Fe³⁺) then of course this last term must be taken as zero.

In practice this approach generally has to be rejected since analytical Si values are not determined with sufficient precision to enable reliable evaluation of the Al content of the tetrahedral sites. Consequently serious errors may arise in the assessment of X_{Al(Ts)}^{M1}—see column III in Table 2.

(B) X_{Al(Ts)}^{M1} = 0.5 [Al^{Total} - (Cr + Fe³⁺ + 2Ti - Na)] E6

This algorithm, unlike E4, calculates X_{Al(Ts)}^{M1} as half the Al cations present only after subtraction of the amount of Al involved in Cr₁Al₁^[T]Mg₋₁Si₋₁, Fe₁³⁺Al₁^[T]Mg₋₁Si₋₁ and Ti₁Al₂^[T]Mg₋₁Si₋₂ substitutions, after first taking accounts of any Cr and Fe³⁺ present which can be coupled with Na in ureyite and acmite molecules, respectively. This approach follows (but extends through also considering the Fe³⁺ content) the calculation procedure proposed by Nickel and Green (1985) for application of their barometer formulation. The advantage over approach (A) is that it is insensitive to any errors in the determined Si content, although it obviously requires accurate analysis of the minor contents of Na, Cr, Ti and Fe³⁺ present.

Carswell and Gibb (1987b) demonstrated that high P-T orthopyroxenes in certain garnet lherzolite xenoliths show a positive correlation between Al and (Na-Cr), signifying the presence in solid solution of some jadeite component. In such orthopyroxenes there are excess Na cations present over the number which can be coupled with Cr, Fe³⁺ and Ti. In these cases the calculation algorithm proposed by Nickel and Green (1985) and its extended version E6 given here, become invalid since they would add any excess Na to the total Al content in the calculation of X_{Al(Ts)}^{M1}.

For such sodic orthopyroxenes, Carswell and Gibb (1987b) proposed that the equivalent algorithm with changed signs should be used, viz:

$$X_{Al(Ts)}^{M1} = 0.5 [Al^{Total} - (Na - Cr - Fe^{3+} - 2Ti)] \quad E7$$

However, this algorithm is in fact incorrect if all Ti present is assigned to the MgTiAl₂^[T]O₆ molecule ('Ti-Tschermaks'), as advocated by Nickel and Green (1985) in following established

procedure (e.g. Kushiro and Aoki, 1968; Mysen and Griffin, 1973). With an assumption that $\text{Ti}_1\text{Al}_2^{[7]}\text{Mg}_{-1}\text{Si}_{-2}$ is the valid Ti substitution in orthopyroxenes with $\text{Na} > (\text{Cr} + \text{Fe}^{3+} + \text{Ti})$ then the correct algorithm is:

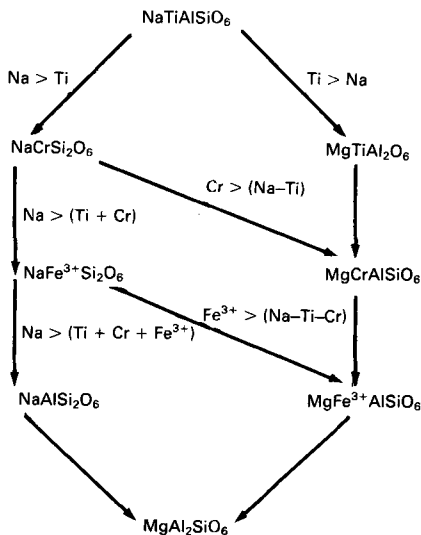
$$X_{\text{Al(Ts)}}^{M1} = 0.5[\text{Al}^{\text{Total}} - (\text{Na}-\text{Cr}-\text{Fe}^{3+}) - 2\text{Ti}] \quad \text{E8}$$

The observed positive correlation between Na and Ti contents in the jadeite-bearing, high-pressure, orthopyroxenes from Thaba Putsoa and Mothae garnet lherzolite xenoliths suggests that Ti substitution may be linked to Na. Moreover, crystal-chemical considerations in high-pressure orthopyroxenes are unlikely to favour Ti substitution linked to *two* tetrahedrally co-ordinated Al cations, as required in the 'Ti-Tschermaks' molecule (Table 1).

A feasible linked Na-Ti substitution is $\text{Na}_1\text{Ti}_{0.5}\text{Mg}_{-1}^{M2}\text{Mg}_{-0.5}^{M1}$ as represented by the $\text{NaTi}_{0.5}\text{Mg}_{0.5}\text{Si}_2\text{O}_6$ end-member molecule ('Ti-Jadeite')—see Table 1. Algorithm E7 is valid for calculation of $X_{\text{Al(Ts)}}^{M1}$ in sodic orthopyroxenes in this case.

An alternative and perhaps acceptable compromise is to consider Ti to be present in a hybrid pyroxene component, $\text{NaTiAl}^{[7]}\text{SiO}_6$ (Table 1), corresponding to a combination of $\text{Na}_1\text{Ti}_{0.5}\text{Mg}_{-1}^{M2}\text{Mg}_{-0.5}^{M1}$ and $\text{Ti}_1\text{Al}_2^{[7]}\text{Mg}_{-1}\text{Si}_{-2}$ substitutions.

Giving preference to NaTiAlSiO_6 over $\text{MgTiAl}_2\text{O}_6$, an appropriate flow chart for the calculation of the Mg-Tschermaks component in orthopyroxene is then as follows:



From this end-member calculation sequence for cation allocation it can be deduced that for orthopyroxenes with $\text{Na} > (\text{Cr} + \text{Fe}^{3+} + \text{Ti})$ then:

$$\begin{aligned} X_{\text{Al(Ts)}}^{M1} &= 0.5 [\text{Al}^{\text{Total}} - (\text{Na}-\text{Cr}-\text{Fe}^{3+}-\text{Ti}) - \text{Ti}] \\ &= 0.5 [\text{Al}^{\text{Total}} - (\text{Na}-\text{Cr}-\text{Fe}^{3+})] \quad \text{E9} \end{aligned}$$

Note that in this case there is in fact no Ti correction term present in the algorithm, since a tetrahedrally co-ordinated Al is allocated for every Ti linked to Na.

On the other hand, for orthopyroxenes with $\text{Na} < (\text{Cr} + \text{Fe}^{3+} + \text{Ti})$ the correct algorithm for the calculation of $X_{\text{Al(Ts)}}^{M1}$ remains in all cases as given in E6 above, regardless of whether available Ti is allocated in preference to $\text{MgTiAl}_2\text{O}_6$, NaTiAlSiO_6 or $\text{NaTi}_{0.5}\text{Mg}_{0.5}\text{Si}_2\text{O}_6$ end-members.

Application to garnet lherzolite xenoliths from the Thaba Putsoa and Mothae kimberlites, northern Lesotho

Application of the garnet-orthopyroxene Al barometer to this particular suite of garnet lherzolite samples illustrates the contrasting P - T results and divergent geological interpretations which can arise through the employment of different barometer calibrations and data handling approaches.

The documentation by Nixon and Boyd (1973) of chemically and texturally contrasting types of garnet lherzolite xenoliths in the kimberlite diatremes of northern Lesotho (notably at the Thaba Putsoa and Mothae localities) has generated considerable ongoing interest in view of implications for interpretation of the thermal state and geodynamics of the upper mantle (e.g. Green and Guegen, 1974; Mercier, 1979; MacKenzie, 1989). Thermobarometric studies of constituent mineral assemblages (Boyd, 1973; Boyd and Nixon, 1973, 1975) convincingly demonstrated that the more chemically fertile, porphyroclastic textured, xenoliths had equilibrated under higher P - T conditions and had thus originated at deeper mantle levels than associated coarse, granoblastic textured, xenoliths. Continuing emphasis has been placed (Finnerty and Boyd, 1984, 1987; Finnerty, 1989) on deductions, based on thermobarometric assessment, that the higher P - T equilibration conditions for the deformed garnet lherzolite xenoliths define an upper-mantle palaeogeotherm which is markedly inflected to higher temperatures at depths below about 150 kilometres.

Vigorous advocacy of the reality of such a high- T inflection by Finnerty and Boyd (1984, 1987) and Finnerty (1989) stems from acceptance of P - T estimates for these xenoliths (Fig. 3a) derived from application of their preferred formulation of the garnet-orthopyroxene Al barometer, based on the MAS system experimental

TABLE 2 - ORTHOPYROXENE COMPOSITIONS IN GARNET IHERZOLITE XENOLITHS FROM THABA PUTSOA AND MOTHAE

Xenolith Samples	I	II	III	IV	V	VI	VII	VIII	IX
	wt. % Al ₂ O ₃	Total X _{Al} ^{M1}	X _{Al} ^{M1} (Ts)	X _{Al} ^{M1} (Ts)	X _{Al} ^{M1} (Ts)	X _{Al} ^{M1} (Ts)	X _{Al} ^{M1} (Ts)	X _{Al} ^{M1} (Ts)	wt. % Na ₂ O
	100	2							(Cr+Ti-Na)
	FB 86	E4	E5	E6 (NG85)	E6/E7	E6/E8	E6/E9		
THABA PUTSOA: COARSE - GRANOBLASTIC TEXTURED XENOLITHS									
PHN 1595	0.0093	0.0186	0.0000	0.0154	0.0154	0.0154	0.0154	0.04	0.0065
PHN 1569 ^g	0.0095	0.0192	0.0013	0.0154	0.0154	0.0154	0.0154	0.04	0.0076
PHN 1567	0.0093	0.0189	0.0000	0.0168	0.0168	0.0168	0.0168	0.07	0.0040
PHN 1592	0.0096	0.0194	0.0125	0.0169	0.0169	0.0169	0.0169	0.08	0.0050
PHN 1570	0.0091	0.0185	0.0000	0.0154	0.0154	0.0154	0.0154	0.05	0.0062
PHN 1573	0.0090	0.0180	0.0147	0.0154	0.0154	0.0154	0.0154	0.05	0.0053
PHN 1568	0.0101	0.0203	0.0210	0.0178	0.0178	0.0178	0.0178	0.07	0.0051
PHN 1572	0.0096	0.0192	0.0073	0.0168	0.0168	0.0168	0.0168	0.08	0.0049
THABA PUTSOA: PORPHYROCLASTIC TEXTURED XENOLITHS									
PHN 1582	0.0088	0.0183	0.0000	0.0164	0.0164	0.0085	0.0143	0.19	-0.0022
PHN 1591	0.0100	0.0203	0.0072	0.0190	0.0190	0.0190	0.0190	0.13	0.0028
E3	0.0121	0.0249	0.0026	0.0246	0.0246	0.0194	0.0223	0.21	-0.0022
PHN 1610	0.0138	0.0283	0.0101	0.0314	0.0253	0.0143	0.0198	0.31	-0.0115
PHN 1566	0.0137	0.0279	0.0024	0.0314	0.0245	0.0146	0.0195	0.36	-0.0118
PHN 1611	0.0136	0.0280	0.0000	0.0300	0.0260	0.0145	0.0202	0.31	-0.0097
PHN 1596	0.0146	0.0294	0.0073	0.0347	0.0240	0.0168	0.0204	0.41	-0.0143
PHN 1597	0.0135	0.0275	0.0148	0.0332	0.0217	0.0140	0.0178	0.43	-0.0154
MOTHAE: COARSE - GRANOBLASTIC TEXTURED XENOLITHS									
PHN 1559B	0.0079	0.0160	0.0050	0.0148	0.0148	0.0148	0.0148	0.13	0.0022
BD 2125 ^d	0.0079	0.0159	0.0068	0.0145	0.0145	0.0145	0.0145	0.10	0.0026
PHN 1917	0.0071	0.0142	0.0000	0.0121	0.0121	0.0121	0.0121	0.09	0.0041
MOTHAE: PORPHYROCLASTIC TEXTURED XENOLITHS									
PHN 2001	0.0097	0.0198	0.0077	0.0198	0.0198	0.0104	0.0151	0.25	-0.0047
PHN 1924	0.0127	0.0258	0.0000	0.0322	0.0195	0.0133	0.0164	0.40	-0.0158
PHN 1925	0.0139	0.0281	0.0049	0.0364	0.0199	0.0127	0.0163	0.47	-0.0201

g - primary graphite bearing
d - primary diamond bearing

data of MacGregor (1974), in combination with a two-pyroxene solvus thermometer formulation (FB86). However, as discussed in previous sections with reference to Figs. 1 and 2, not only has the MacGregor (1974) MAS system experimental data on garnet-orthopyroxene Al equilibria now been superseded by more reliable data (cf. Bertrand *et al.*, 1987) by Perkins *et al.* (1981), but no barometer calibration based on the simple MAS (or for that matter even the CMAS system) can be expected to yield geologically meaningful results for Fe and Cr-bearing natural garnet lherzolite assemblages. Moreover, in their application of the garnet-orthopyroxene Al barometer calibration based on MacGregor (1974), Finnerty and Boyd (1984, 1987) only crudely assessed the amount of Mg-Tschemaks component present as the total weight fraction of Al₂O₃ determined in the orthopyroxene. From previous discussion it should be obvious that, whilst such data treatment ought to be satisfactory for orthopyroxenes crystallising within the simple MAS or CMAS systems, it is quite inappropriate for the more chemically complex orthopyroxenes encountered in the garnet lherzolite xenoliths in question.

Table 2 lists the different values which can be calculated by the various different approaches

and algorithms outlined previously, for the key orthopyroxene composition $X_{Al(Ts)}^{M1}$ involved in the pressure evaluation. The mineral analysis data base is from Nixon and Boyd (1973), Boyd and Finger (1975), Dawson and Smith (1975)—as also employed by Finnerty and Boyd (1984, 1987). Note that, for all calculations of $X_{Al(Ts)}^{M1}$ values, zero Fe³⁺ contents are assumed in orthopyroxenes in the absence of Mössbauer studies, despite the fact that such studies of garnet lherzolite xenolith garnets indicate the presence of significant Fe³⁺ (Luth *et al.*, 1988). Unfortunately stoichiometrically-calculated Fe³⁺ contents in these electron microprobe orthopyroxene analyses are highly variable (0.00–2.72 wt.% Fe₂O₃) and considered unreliable since they are critically dependent on accurate and precise analysis of other elemental contents. The strong positive correlation between the contents of Al and (Na–Cr) in sodic orthopyroxenes in the high-*P*–*T* garnet lherzolite xenoliths (Carswell and Gibb, 1987b, Fig. 3) indicates that amounts of any Fe³⁺ present as acmite substitution must be small. Moreover, in the cation allocation treatment followed for orthopyroxenes with Na > (Cr + Fe³⁺ + Ti) in algorithms E7–E9, underestimation of $X_{Al(Ts)}^{M1}$ due to neglect of any small

TABLE 3 - CALCULATED PRESSURE-TEMPERATURE VALUES FOR GARNET LHERZOLITE XENOLITHS FROM THABA PUTSOA AND MOTHAE

Xenolith Samples	I		II		IV		V		VI		VII	
	P	T	P	T	P	T	P	T	P	T	P	T
THABA PUTSOA: COARSE - GRANOBLASTIC TEXTURED XENOLITHS												
PHN 1595	34.2	877	32.6	875	35.1	877	35.1	877	35.1	877	35.1	877
PHN 1569 ^d	36.5	918	33.3	914	36.3	917	36.3	917	36.3	917	36.3	917
PHN 1567	37.4	927	33.8	923	35.3	924	35.3	924	35.3	924	35.3	924
PHN 1592	38.1	944	34.3	940	36.2	942	36.2	942	36.2	942	36.2	942
PHN 1570	39.0	948	35.0	944	37.6	947	37.6	947	37.6	947	37.6	947
PHN 1573	40.2	964	36.9	961	39.1	963	39.1	963	39.1	963	39.1	963
PHN 1568	38.7	965	34.7	960	36.6	962	36.6	962	36.6	962	36.6	962
PHN 1572	41.0	991	36.9	987	38.9	989	38.9	989	38.9	989	38.9	989
THABA PUTSOA: PORPHYROCLASTIC TEXTURED XENOLITHS												
PHN 1582	51.5	1137	45.8	1131	47.6	1133	47.6	1133	58.5	1145	49.8	1135
PHN 1591	62.1	1336	51.1	1320	52.4	1322	52.4	1322	52.4	1322	52.4	1322
E3	61.2	1374	52.7	1361	53.0	1361	53.0	1361	57.6	1368	54.8	1364
PHN 1610	63.0	1443	55.3	1430	53.2	1427	57.6	1434	69.5	1453	62.7	1442
PHN 1566	64.2	1460	55.5	1445	53.1	1441	58.2	1450	69.0	1468	62.9	1458
PHN 1611	62.8	1434	55.4	1422	54.0	1420	56.8	1425	68.9	1444	62.0	1433
PHN 1596	64.0	1477	56.9	1465	53.4	1459	61.2	1472	68.8	1485	64.6	1478
PHN 1597	66.0	1486	58.5	1473	54.5	1466	63.4	1481	72.9	1498	67.6	1488
MOTHAE: COARSE - GRANOBLASTIC TEXTURED XENOLITHS												
PHN 1559B	40.6	946	37.2	943	38.3	944	38.3	944	38.3	944	38.3	944
ED 2125 ^d	46.4	1035	41.4	1029	42.8	1031	42.8	1031	42.8	1031	42.8	1031
PHN 1917	47.6	1031	42.6	1026	45.0	1028	45.0	1028	45.0	1028	45.0	1028
MOTHAE: PORPHYROCLASTIC TEXTURED XENOLITHS												
PHN 2001	61.0	1312	54.0	1302	54.0	1302	54.0	1302	66.2	1319	59.2	1309
PHN 1924	61.7	1396	54.8	1385	50.5	1379	60.4	1394	68.2	1407	63.9	1400
PHN 1925	60.9	1408	54.3	1398	49.2	1390	61.3	1409	70.5	1424	65.4	1416

Labelled columns I-VII correspond to those in Table 2 for the different evaluations of the amount of Mg-Tschermaks component in the orthopyroxenes.

Pressures (in kilobars) all calculated from the calibration of Nickel and Green (1985), except those in column I based on the MacGregor (1974) calibration favoured by Finnerty and Boyd (1984, 1987).

Temperatures (in degrees centigrade) all calculated from the two pyroxene solvus thermometer calibration of Bertrand and Mercier (1985).

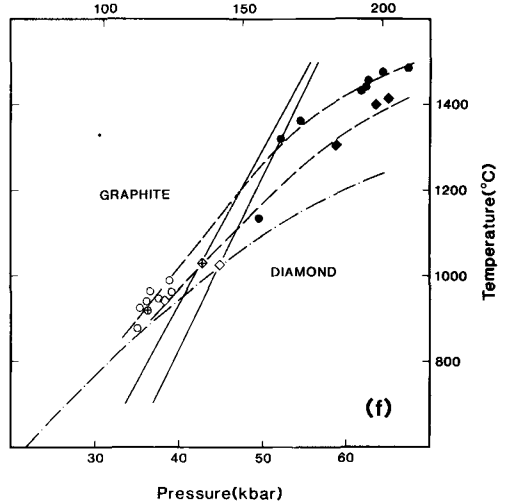
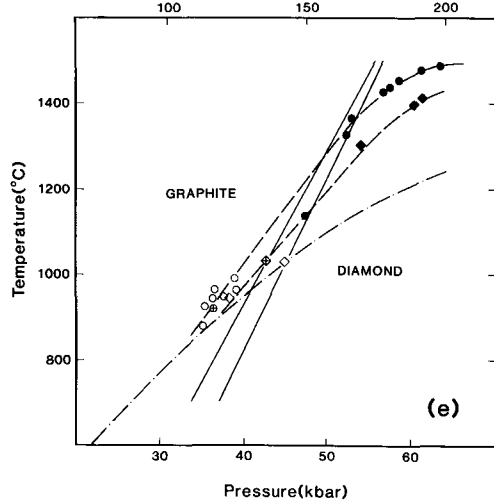
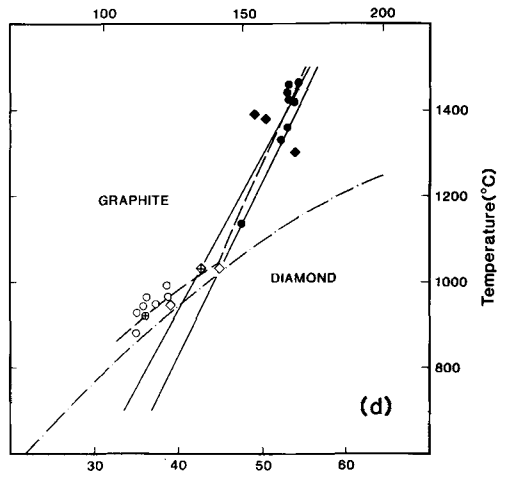
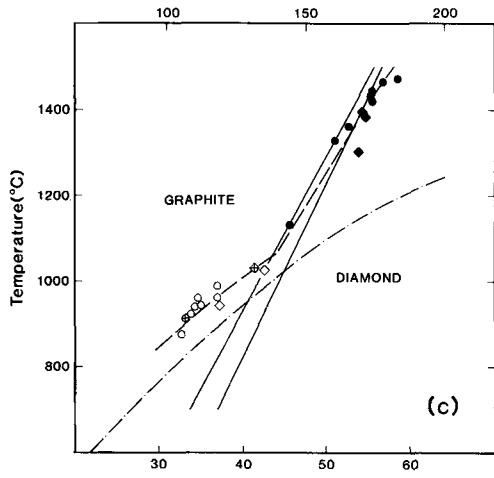
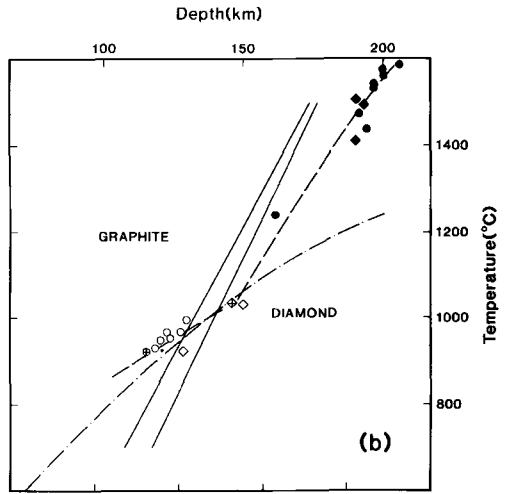
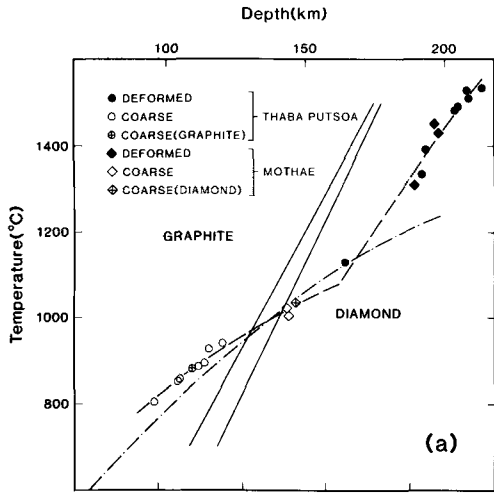
amounts of Fe^{3+} present as $Na_1Fe_1^{3+}Mg_{-1}Mg_{-1}$ substitution is counterbalanced in effect by the assumption that all Cr is present as $Na_1Cr_1Mg_{-1}Mg_{-1}$ substitution rather than $Cr_1Al_1^{IV}Mg_{-1}Si_{-1}$.

The Al_2O_3 weight fraction values in column I of Table 2, as employed by Finnerty and Boyd (1984, 1987) for pressure evaluation, assume that

all analytically determined Al is present as Mg-Tschermaks component; as likewise with the values in column II which will yield similar relative equilibration pressures throughout the analysed xenolith sample set.

The highly variable and in many cases quite unrealistic values in column III, with zero $X_{Al(Ts)}^{M1}$ in almost a third of the xenolith samples, demon-

FIG. 3. P - T plots of comparative P - T equilibration estimates, from Table 3 and Finnerty and Boyd (1984, 1987) for garnet lherzolite xenoliths from the Thaba Putsoa and Mothae kimberlites of northern Lesotho. Note the contrasting forms of the P - T arrays and implied upper mantle geotherms (heavy dashed lines) in the various individual plots based on the following barometer/thermometer pairings and assessments of Al contents in orthopyroxene involved in Mg-Tschermaks substitution. (a) MacGregor (1974)/Finnerty and Boyd (1986) pairing as favoured by Finnerty and Boyd (1984, 1987), with all Al taken as relating to Mg-Tschermaks substitution. (b) MacGregor (1974)/Bertrand and Mercier (1985) pairing again with all Al taken as relating to Mg-Tschermaks substitution. (c) Nickel and Green (1985)/Bertrand and Mercier (1985) pairing with $X_{Al(Ts)}^{M1}$ taken as $0.5 X_{Al}^{Total}$ according to equation E4. (d) Nickel and Green (1985)/Bertrand and Mercier (1985) pairing with $X_{Al(Ts)}^{M1}$ values calculated in all cases by algorithm E6 as proposed by Nickel and Green (1985). (e) Nickel and Green (1985)/Bertrand and Mercier (1985) pairing with $X_{Al(Ts)}^{M1}$ calculated by a combination of algorithms E6 and E7 as proposed by Carswell and Gibb (1987b), which allocates Ti preferentially to $NaTi_{0.5}Mg_{0.5}Si_2O_6$. (f) Nickel and Green (1985)/Bertrand and Mercier (1985) pairing with $X_{Al(Ts)}^{M1}$ calculated by a combination of algorithms E6 and E9, which allocates Ti preferentially to $NaTiAlSiO_6$. Also shown for reference purposes are a predicted shield geotherm (---) from Pollock and Chapman (1977) corresponding to 40 mWm^{-2} surface heat flow and the alternative lower and higher pressure experimental determinations of the graphite-diamond transition from Bundy *et al.* (1961)/Bundy (1980) and Kennedy and Kennedy (1976), respectively.



strate the futility of approach (A) using equation E5 as outlined earlier due to inadequate precision in the determination of Si values.

The $X_{\text{Al(Ts)}}^{\text{M1}}$ values listed in columns IV–VII in Table 2 are identical for orthopyroxenes in the more chemically depleted, granoblastic textured, xenoliths for which $\text{Na} < (\text{Cr} + \text{Ti})$ and algorithm E6 is valid. Note, however, that all values for these particular xenoliths are lower than those in column II due to the recognition that some Al present is linked to Cr and/or Ti in M1 sites and is not involved in Mg-Tschermaks substitution.

Orthopyroxenes in the more fertile, porphyroclastic textured, xenoliths are distinctly more sodic (Table 2, column VIII). In the majority of cases such orthopyroxenes have $\text{Na} > (\text{Cr} + \text{Ti})$ in which case algorithm E6 (Nickel and Green, 1985) becomes invalid with a double negative effect resulting in spuriously high $X_{\text{Al(Ts)}}^{\text{M1}}$ values—see Table 2, column IV (even higher than those in column II which assume that all Al is present as Mg-Tschermaks substitution). For such sodic orthopyroxenes the $X_{\text{Al(Ts)}}^{\text{M1}}$ values in columns V–VII are all significantly lower and more realistic. Differences between the values in columns V–VII are entirely due to variations in the way in the Ti contents have been allocated (viz. use of algorithms E7–E9 respectively). As previously discussed, consideration of the crystal chemistry of these high-pressure orthopyroxenes suggests that preference should be given to the values in columns V or VII, corresponding to Ti allocation to $\text{NaTi}_{0.5}\text{Mg}_{0.5}\text{Si}_2\text{O}_6$ or NaTiAlSiO_6 , respectively.

The effects of these different assessments of the amounts of Al in the orthopyroxenes involved in Mg-Tschermaks substitution are shown by the P – T values listed in Table 3, calculated in a reiterative manner from selected barometer/thermometer pairings by an updated version of the Carswell and Gibb (1980, 1987a) Fortran program (NODMINS 4). For comparative purposes all temperatures have been calculated from the two-pyroxene solvus thermometer of Bertrand and Mercier (1985) that was judged in evaluation tests by Carswell and Gibb (1987b) to be somewhat superior to the equivalent calibration favoured by Finnerty and Boyd (1987)—labelled by them FB86. However, there is general agreement between Carswell and Gibb (1987b) and Finnerty and Boyd (1984, 1987) that the choice of any particular thermometer calibration makes little significant difference to the resultant contrasting P – T arrays for the Thaba Putsoa and Mothae garnet lherzolite xenolith suites that are illustrated in Fig. 3(a–f). Thus, the MacGregor (1974)/Bertrand and Mercier (1985) barometer/

thermometer pairing generates a P – T array (Fig. 3b) with an apparent marked inflection to a higher thermal gradient at greater depths, in the same manner as the MC 74/FB 86 pairing (Fig. 3a) favoured by Finnerty and Boyd (1987).

The existence of a ‘high T ’ inflection is also seemingly endorsed (Fig. 3d) when the Nickel and Green (1985) barometer calibration is employed with $X_{\text{Al(Ts)}}^{\text{M1}}$ calculated from algorithm E6, as proposed by Nickel and Green (1985). However, it must be re-emphasised that for the majority of the higher temperature, porphyroclastic textured, xenoliths, algorithm E6 yields invalid high $X_{\text{Al(Ts)}}^{\text{M1}}$ values (Table 2, column IV) which in turn lead to spuriously low pressure estimates (Table 3, column IV and Fig. 3d) at assessed temperatures.

In marked contrast the Nickel and Green (1985)/Bertrand and Mercier (1985) barometer/thermometer pairing yields P – T arrays (Fig. 3e and f) which if anything are inflected to a lower rather than a higher thermal gradient for the xenoliths of deepest derivation, when $X_{\text{Al(Ts)}}^{\text{M1}}$ in orthopyroxene is assessed as in columns V and VII in Table 2. Such an inflection to a lower thermal gradient at deeper mantle levels is consistent with a ‘normal’ transition from rigid, thermally conducting, lithosphere down into thermally convecting, asthenosphere (Mercier and Carter, 1975; Harte, 1978). Interestingly in Fig. 3e and f the P – T arrays for xenoliths from Thaba Putsoa and Mothae (with one notable exception, PHN 1582) appear to define slightly separate upper-mantle geotherms which may relate to lateral variations in the thermal state of the upper mantle beneath northern Lesotho at the time of kimberlite eruption.

Unfortunately there is no unequivocal solution as far as selective allocation of the contents of certain minor elements (such as Ti) in orthopyroxenes is concerned. Preferential allocation of Ti to $\text{NaTi}_{0.5}\text{Mg}_{0.5}\text{Si}_2\text{O}_6$, as in the E6/E7 algorithm combination utilised for the P – T array in Fig. 3e, in effect maximises $X_{\text{Al(Ts)}}^{\text{M1}}$ values and hence minimises the pressure estimates. At the other extreme, allocation to $\text{MgTiAl}_2\text{O}_6$ minimises $X_{\text{Al(Ts)}}^{\text{M1}}$ values and maximises the pressure estimates (see columns VI in Tables 2 and 3). The resultant P – T array for the Thaba Putsoa and Mothae xenolith suites is not illustrated in Fig. 3 but is in effect even more markedly inflected to a lower thermal gradient, than those in Fig. 3e and f, for the deeper level xenoliths. However, consideration of the crystal chemistry of the high P – T orthopyroxenes, combined with evidence of increased scatter of the resultant P – T estimates—including values which in the case of the relatively

Ti-enriched xenolith sample PHN 1582 plot below the predicted shield geotherm, caution against acceptance of values based on Ti allocation to $\text{MgTiAl}_2\text{O}_6$.

The intermediate $X_{\text{Al(Ts)}}^{\text{M1}}$ values and pressure estimates, based on preferential allocation of Ti to the hybrid end-member NaTiAlSiO_6 constitute a somewhat subjective but possibly justifiable compromise, in view of other decisions made in cation allocation. It must be re-emphasised, however, that regardless of which Ti allocation procedure is selected (algorithms E7, E8 or E9) the calculated P - T arrays are inflected in all cases to lower thermal gradients at the depths of derivation of the higher temperature, deformed, garnet lherzolite xenoliths.

From the foregoing thermobarometric analysis of the Thaba Putsoa and Mothae garnet lherzolite xenolith suites it is concluded that the 'high T ' inflected mantle geotherms vehemently advanced by Finnerty and Boyd (1984, 1987) and Finnerty (1989) are entirely spurious. Moreover, they are not so much artifacts of the particular calibration of the garnet-orthopyroxene Al barometer employed (although that is important for rigorous assessment of depths of xenolith derivation), but rather of the manner in which the key composition parameter that is used in pressure evaluation (the amount of Al in orthopyroxene specifically involved in Mg-Tschermaks substitution) has been assessed. In particular it is essential to take account of the fact that orthopyroxenes may contain Al linked to Na substitution in $M2$ sites or to Cr, Ti and Fe^{3+} in $M1$ sites, when applying the garnet-orthopyroxene Al barometer to natural garnet lherzolite assemblages. An important corollary is that accurate pressure evaluation requires careful analytical measurement of the minor element contents in the orthopyroxene.

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