The effect of temperature on the equilibrium distribution of trace elements between clinopyroxene, orthopyroxene, olivine and spinel in upper mantle peridotite

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Abstract

The abundance of 30 trace elements has been determined in the minerals of 16 well-equilibrated spinel lherzolite xenoliths by laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS). Major elements were analysed by electron microprobe. The xenoliths span a range of equilibration temperatures from 1150 to 1500 K (calculated at an assumed pressure of 1.5 GPa from two-pyroxene geothermometry), allowing the trace-element partitioning relationships among the phases (olivine, orthopyroxene, clinopyroxene, spinel, and in some lower temperature xenoliths, amphibole) to be quantified as a function of temperature. Most elements show smooth partitioning trends among all phases that depend primarily on temperature but with some influences from bulk composition, particularly the amount of Na in clinopyroxene. Although most incompatible trace elements are concentrated into clinopyroxene, the effect of increasing temperature is to redistribute these elements into orthopyroxene and even olivine, such that these latter phases hold non-negligible proportions of many trace elements at the temperature at which peridotite would be in equilibrium with basaltic melts. The inter-crystalline trace-element partition coefficients reported in this study can be used to reconstruct the trace-element abundances in clinopyroxene at melting temperatures, and should also prove useful in elucidating the histories of more complex mantle peridotites with unequilibrated mineral compositions and textures.

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Keywords: Trace-element partitioning; Upper mantle; Peridotite

1. Introduction

Peridotites derived from the upper mantle but available at the Earth’s surface for geochemical and petrological investigation are generally thought to be residues of the partial melting that produces basalt.
The trace-element geochemistry of these peridotites have often been studied to constrain better the melting and melt-extraction processes, but such an approach has several potential pitfalls arising from the complex subsolidus history of the peridotites subsequent to the melt-extraction event. In particular, many peridotites are partially serpentinized or otherwise altered, which has provided an incentive to examine the trace-element patterns of individual phases as an alternative to the probably contaminated whole-rock values; this approach has been made technically possible through the development of SIMS, and latterly laser-ablation ICP-MS microanalytical techniques. However, mantle peridotites have generally recrystallized subsolidus, which must result in the redistribution of trace elements among the phases. In order to carry out modelling of melting relations, it is therefore necessary to reconstruct the compositions of mineral phases at the temperature at which they would be in equilibrium with melt. This requires knowing how the trace elements redistribute during cooling.

The goal of this work is to determine the required intercrystalline trace-element partition coefficients as a function of temperature for a wide variety of trace elements (including most of those used in geochemical modelling) for the spinel-lherzolite facies, by using a set of 16 well-equilibrated spinel-lherzolite xenoliths covering a large range of equilibration temperatures as a set of natural experiments. In addition to this primary aim, a more detailed knowledge of intercrystalline equilibrium trace-element partitioning relations should be useful for checking internal consistency in sets of mineral/melt partition coefficients used in geochemical modelling; for reconstructing original melt compositions of melt inclusions; and for insights into the crystal-chemical controls on trace element substitutions, which are needed for more reliable thermodynamic modelling of partition coefficients. We also envisage that the temperature-dependent partition coefficients established in this work will help in elucidating the petrologic histories of more complex peridotites that preserve textural and geochemical evidence of melt infiltration, metamorphic differentiation and other mantle processes.

Previous work using mineral separates (e.g., Stosch, 1982; Bedini and Bodinier, 1999) and the microanalytical techniques of the electron microprobe (McDonough et al., 1992), SIMS (Hervig et al., 1980), PIXE (e.g., O’Reilly et al., 1991) and laser-ablation ICP-MS (e.g., Norman et al., 1998) has built up a basic understanding of trace-element distributions among peridotite minerals. We draw particular attention to the detailed LA-ICP-MS study of Eggins et al. (1998), which established the approach used in this study.

2. Analytical procedures

Major element analyses were performed on a JEOL JXA8900 electron-microprobe (Institut für Mineralogie und Geochemie der Universität Köln, Germany) under standard conditions (20 kV accelerating voltage, 20 nA beam current, focussed 1 μm beam, 20–100 s counting time depending upon the element). A set of synthetic silicates (for Si, Mg, Ca, Na, K, Mn, Fe) and oxides (for Al, Cr, Ti, Ni) was used for standardization, and data were corrected using the ZAF-algorithm.

Trace elements were measured in situ on polished thin sections by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Research School of Earth Sciences, Australian National University. Ablation was performed in a He atmosphere by an ArF Excimer laser (193 nm) with a pulse energy of 100 mJ and a 5 Hz pulse repetition rate; the ablation time was 60 s. The ablated material was flushed in a continuous argon flow into the torch of an Agilent 7500 Series ICP-MS. Before and after ten unknowns the silicate glass reference material NIST 612 (National Institute of Standards and Technology) and the background count rates were measured for calibration purposes and instrumental drift corrections. To correct for differences in the ablation yield between standard and samples, 43Ca (for clinopyroxene, orthopyroxene and amphibole) and 24Mg (for olivine and spinel) were used as an internal standard, based on the electron-microprobe measurements of CaO and MgO in the minerals. Further information about analytical details including correction procedures, limits of detection, and instrumental errors are described in Eggins et al. (1998). For each mineral, 1–12 analyses with an 84 μm laser spot size were performed within the grain cores.

The quality of the analyses was continually checked throughout the analytical campaign (which
covered two months) on the basalt glass standard USGS BCR-2G. This resulted in 307 replicate analyses, which establish the long-term precision of the method. In Table 1 the average of these analyses is compared with the data published by Norman et al. (1998).

The abundances of Sr, Nd, Sm, and Pb have previously been determined for some separates of clinopyroxene and amphibole by isotope dilution and thermal ionization mass spectrometry (TIMS) using a VG Sector 54 spectrometer (Institut für Mineralogie der Universität Münster, Germany). Pure separates were obtained by hand-picking under a binocular microscope, followed by ultrasonic washing in ultrapure water, and leaching either in cold HF–HNO₃ (5 : 1) for 15 min (Sr, Nd, Sm) or in hot 2N HCl for 2 h (Pb). The separates were spiked with mixed ⁸⁷Rb–⁸⁴Sr and ¹⁴⁹Sm–¹⁴⁶Nd spikes, or a ²⁰⁵Pb spike, respectively, and decomposed with HF–HNO₃ (5 : 1). A description of the cation exchange techniques, the measurement conditions and correction procedures for mass fractionation has been given in Witt-Eickschen and Kramm (1997) and Witt-Eickschen et al. (2003). The comparison with the present results for these elements is given in Fig. 1a.

The results of this LA-ICP-MS study may also be compared with previously published trace element data (Witt-Eickschen and Harte, 1994) for clinopyroxene and amphibole determined by secondary ion mass spectrometry (SIMS). The SIMS analyses were carried out in situ on the same thin sections with a

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Cameca ims-4f ion microprobe (Department of Geology and Geophysics in Edinburgh, U.K.). Detailed information about the analytical conditions, corrections and quantification are given in Witt-Eickschen and Harte (1994).

The REEs in all four phases of one of the xenoliths in our suite, Mo22, have been determined previously by Stosch (1982), using radiochemical neutron activation on hand-picked, HF-washed mineral separates. Agreement of our data with this earlier work is excellent, as shown in Fig. 1b.

3. The xenolith samples

The 16 xenoliths used in this study are typical examples of spinel-lherzolite xenoliths hosted in alkali basalts. Fourteen xenoliths are from Quaternary maar eruptions in the West Eifel, Germany (DW: Dreiser Weiher, MM: Meerfelder Maar), and these were supplemented by one sample each from Cenozoic basalts of the Rother Berg volcano (Westerwald/Germany, RB1189) and the Shavaryn Tsaram volcano (Tariat Depression/Mongolia: Mo22). The petrological, geo-
chemical and Sr–Nd–Pb isotope characteristics for most of the samples have been presented and discussed elsewhere (e.g., Press et al., 1986; Stosch et al., 1986; Witt-Eickschen and Kramm, 1998; Witt-Eickschen et al., 2003). The modal mineralogy and several important geochemical and mineralogical attributes including calculated temperatures of equilibration are listed in Table 2, and the major element mineral compositions are presented in Table 3a–e.

The xenoliths were selected for the major-element homogeneity of all their minerals, as revealed by the previous work. There is no exsolution in the mineral grains detectable either by optical microscope or under the electron microprobe. All grains analysed by LA-ICP-MS were previously checked for zoning by electron microprobe, either by core–rim analyses or full traverses. In addition, trace-element homogeneity was addressed directly by LA-ICP-MS traverses using a 29 μm spot over one selected grain in each of the following samples:

MM1240 (cpx), MM1260 (cpx, opx), MM1213 (cpx, ol), DWv2 (cpx, ol), DW1283 (cpx), DW1342 (cpx, opx), DW599 (cpx, opx), RB1189 (cpx), Mo22 (cpx), MM110 (amph), DW1284 (cpx, opx), DW582 (cpx), MM1278 (cpx, opx), DW210 (cpx, opx, ol), DW211 (cpx, ol).

The xenoliths were also chosen to cover as large a range of equilibration temperatures as possible. Equilibration temperatures were calculated using two formulations of the orthopyroxene–clinopyroxene Ca–Mg exchange equilibrium, from Brey and Köhler (1990). The first utilizes only the composition of the opx:

$$T_{\text{opx}} = \frac{6425 + 26.4P}{-\ln(N_{\text{Ca}}^{\text{opx}})} + 1.843$$ (1)

where $P$ is pressure in kbars, and $N_{\text{Ca}}^{\text{opx}}$ is the number of Ca cations in opx per formula unit of six oxygens.

The second formulation uses both opx and cpx compositions:

$$T_{\text{cpx/opx}} = \frac{23664 + (24.9 + 126.3Fe^{\text{cpx}})P}{13.38 + (\ln KD^*)^2 + 11.59Fe^{\text{opx}}}$$ (2)

where

$$KD^* = \frac{(1 - N_{\text{Ca}}^{\text{cpx}}/(1 - N_{\text{Na}}^{\text{cpx}}))}{(1 - N_{\text{Ca}}^{\text{opx}}/(1 - N_{\text{Na}}^{\text{opx}}))}$$

and Fe$^{\text{cpx}}$ and Fe$^{\text{opx}}$ is molar Fe/(Fe+Mg) in cpx and opx, respectively.

There is unfortunately no precise way of calculating pressures in spinel lherzolites; available pressures in spinel lherzolites; available pressures...
Table 3

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b. Major and trace element analyses of orthopyroxenes

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69.0 1.9 66.9 11.3 61.8 6.4 63.9 0.7 63.4 3.7 61.0 3.0 58.0 54.0 6.4

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87 21 215 43 106 11 105 27 77 4 60 8 36 163 15

50 5 84 10 32 3 27 2 23 4 11 4 12 55 3

24 3 33 7 13 0 11 1 11 0 6 1 6 23 3

94 9 116 18 43 2 28 2 37 0 20 1 16 68 5

193 3 161 23 83 4 43 2 63 3 47 2 51 90 6

49 1 39 5 24 0 13 3 17 0 15 1 13 22 1

186 5 138 16 85 5 60 8 71 1 72 3 65 83 10

275 2 199 20 165 1 127 5 134 10 142 7 121 134 11

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sure-sensitive equilibria such as that based on partitioning of Ca between olivine and cpx (Köhler and Brey, 1990) are also temperature dependent, with the result that attempting to calculate temperatures and pressures simultaneously tends to produce results smeared out along a P–T path (which resembles an artificial, and unrealistic, geotherm). For the sake of transparency, we have therefore assumed a pressure of 1.5 GPa for all samples. Fortunately, pyroxene geothermometers are relatively insensitive to pressure,
and changing the assumed pressure by ±0.5 GPa typically changes $T_{\text{opx}}$ and $T_{\text{cpx/opx}}$ by ±25 and 10 K, respectively. Calculated temperatures from both geothermometers are given in Table 2, and compared in Fig. 2a; comparison with a couple of earlier widely used two-pyroxene geothermometers, those of Wells (1977) and Bertrand and Mercier (1985) is made in Fig. 2b and c. Agreement is good, hence the choice of geothermometer does not influence our conclusions, although in detail Eq. (2) gives temperatures at 1.5 GPa that are systematically slightly higher than Eq. (1) (by an average of 54 K with a standard deviation of 28 K). There is no obvious correlation between the differences in calculated temperature and the chemistry of the samples, beyond the obvious effects of the Ca and Mg contents of the pyroxenes that form the basis of all pyroxene geothermometry. In the rest of this paper we shall use Eq. (1) at the assumed pressure of 1.5 GPa (labelled $T_{\text{opx/1.5 GPa}}$ in the figures), which is a somewhat arbitrary decision, influenced by the relative simplicity of its formulation as well as the smoothness of some results.

Based on their calculated equilibration temperatures, we divide the 16 xenoliths into four groups:

I High temperature ($1400 \text{ K} < T_{\text{opx/1.5 GPa}} < 1500 \text{ K}$)
II Intermediate temperature 1 ($1300 \text{ K} < T_{\text{opx/1.5 GPa}} < 1400 \text{ K}$)
III Intermediate temperature 2 ($1200 \text{ K} < T_{\text{opx/1.5 GPa}} < 1300 \text{ K}$)
IV Low temperature ($1100 \text{ K} < T_{\text{opx/1.5 GPa}} < 1200 \text{ K}$)

Groups I and II are anhydrous coarse-grained to recrystallized lherzolite and harzburgite xenoliths. Group I consists of six samples, with cpx REE patterns that in one case are near to that expected for unmetasomatized mantle after melt extraction (MM1260), but otherwise are either convex-upward with maxima at Nd and Sm (MM1240, DW1342, DWv2) or LREE-enriched (DW1283, MM1213) indicating a modest

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**Fig. 2.** Equilibration temperatures calculated from various two-pyroxene geothermometers, all at an assumed pressure of 1.5 GPa, compared against the orthopyroxene-only geothermometer of Brey and Köhler (1990), Eq. (1) in the text, which is referred to as $T_{\text{opx, 1.5 GPa}}$; a) the clinopyroxene–orthopyroxene geothermometer of Brey and Köhler (1990), Eq. (2) in text; b) Wells (1997); c) Bertrand and Mercier (1985).
amount of metasomatism. Group II is similar but more fertile; the xenolith Mo22 is notable as it has near primitive $X_{Mg}^{ol}$ (0.896 vs. 0.890 for the primitive mantle, O’Neill and Palme, 1998), and low Cr<sup>sp</sup> (0.11).

Groups III and IV comprise two and five xenoliths, respectively, with tabular or mosaic equigranular textures originating by extensive shearing and recrystallization. They are considered to be equilibrated immediately below the Moho (Witt-Eickschen et al., 2003), which presently lies at a depth of about 28 km below the Eifel (Mechie et al., 1983; Raikes and Bonjer, 1983). The xenoliths bear Ti-poor pargasitic amphibole (or its breakdown products) in textural and chemical equilibrium with the coexisting minerals (Witt and Seck, 1987; Witt-Eickschen and Harte, 1994). The presence of amphibole, together with the strong enrichment of LREE over HREE, has been attributed to a pre-Quaternary metasomatic episode that affected local parts of the subcontinental lithosphere beneath the Eifel (Witt-Eickschen et al., 2003). The two group III samples (MM110 and MM766) are thought to have undergone a reheating event from about 1150–1250 K, probably caused by a thermal metamorphism from the intrusion of a magma body at the crust–mantle boundary (Witt-Eickschen et al., 1993). The pyroxenes of these reheated xenoliths are chemically zoned with Al and Cr increasing from core to rim, whereas Ca is remarkably constant (Witt-Eickschen et al., 1993).

4. Factors influencing subsolidus partitioning of trace elements in four-phase lherzolites

The trace-element partition coefficient between two phases depends on temperature, pressure, and the major-element compositions of both phases—see O’Neill and Eggins (2002) for a recent discussion. The major-element compositional effects are likely to be particularly important for those trace elements that substitute for a major element with a different ionic charge (heterovalent substitution), since charge balance requires either that the substitution is coupled with another substitution, or that cation or anion vacancies occur. Most of the incompatible trace elements commonly studied by geochemists are of this heterovalent type—e.g., the REEs, HFSEs, U and Th. For example, it is likely that the trivalent REEs substitute into clinopyroxene (in which the major component is diopside, CaMgSi<sub>2</sub>O<sub>6</sub>) by replacing divalent Ca<sup>2+</sup> in the M2 octahedral site, with charge balance maintained by Al<sup>3+</sup> replacing Si<sup>4+</sup> in the tetrahedral site (i.e., as REEMgAlSiO<sub>6</sub>). This means that the chemical potential of the REE<sub>2</sub>O<sub>3</sub> component in cpx depends on the chemical potentials of both Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>.

However, four-phase lherzolites have a low thermodynamic variance (few degrees of freedom), such that the chemical potentials of their major-element components are almost independent of composition, being accordingly specified mainly by temperature and pressure. As pressure is generally highly correlated with temperature in the Earth’s interior, there is, to a first approximation, just one important variable (or degree of freedom) in our suite of xenoliths, namely temperature. This is the first-order approximation; the departures from this approximation will now be discussed.

More than 98% of a typical lherzolite consists of just the five major-element components SiO<sub>2</sub>, MgO, FeO, CaO and Al<sub>2</sub>O<sub>3</sub> (e.g., O’Neill and Palme, 1998); with five components and four phases, the compositions of all phases are completely fixed by specifying temperature, pressure and just one compositional variable, such as (conveniently) $X_{Mg}^{ol}$ (molar Mg/ (Mg+Fe) of olivine). The total variation of $X_{Mg}^{ol}$ in typical spinel-lherzolite xenoliths is from 0.89 (primitive mantle) to ~0.92 (cpx out), which may be significant petrologically but is trivial in thermodynamic terms, and can be ignored. The xenoliths used in this study actually span an even lower range of $X_{Mg}^{ol}$, all but two being within the range 0.913–0.921 (Table 2).

The only temperature-independent variations in the compositions of the phases in a four-phase lherzolite are therefore due to the minor components, which make up less than 2% of the mantle composition. In the present context, the most influential of these components is Cr<sub>2</sub>O<sub>3</sub>, because Cr<sup>3+</sup> substitutes for octahedrally coordinated Al in pyroxenes and spinel (or garnet), lowering the activity of Al<sub>2</sub>SiO<sub>5</sub> in the system (e.g., Liu and O’Neill, 2004). This effect reduces Al<sub>2</sub>O<sub>3</sub> in pyroxenes considerably, and is particularly important in the spinel-lherzolite facies (Klemme and O’Neill, 2000; Liu and O’Neill, 2004). Alumina in pyroxenes is needed to charge-balance many heterovalent substitutions, as pointed out above for the REE. In the spinel-lherzolite assemblage, the chemical po-
tential of Cr$_2$O$_3$ can be characterized by the Cr# of the
spinel (molar Cr/(Al+Cr)). Our xenoliths cover a
useful range, from Cr# = 0.11 to 0.47. However, since
the Cr$_2$O$_3$ substitution affects Al$_2$O$_3$ in cpx and opx in
the same way, its influence should mostly cancel out in
cpx/opx partition coefficients.

The next most influential minor component is
Na$_2$O, which is heavily concentrated into cpx. Unlike
Cr$_2$O$_3$, therefore, this component can be expected
to affect cpx/opx partition coefficients. The
Na$_2$O contents of the cpx in our xenoliths are
quite low, but still vary by a factor of two (Table 2),
which, we shall show, is sufficient to influence many
partition coefficients. Deducing this is only possible
because Na$_2$O is not correlated with temperature in
our samples (Table 2). Although an inverse correla-
tion between Na$_2$O and Cr# might be expected on the
grounds that the former decreases while the latter
increases with melt extraction, no such correlation
is observable in our samples, presumably because
of subsequent metasomatism. For our present pur-
poses this is convenient as it allows us to treat
these two variables as independent in our statistical
examination of the partitioning data. However, TiO$_2$

generally does correlate with Na$_2$O (being, like
Na$_2$O, moderately incompatible), such that crys-
talchemical effects of Ti would not be statistically re-
solvable; in any case, the lower abundance of TiO$_2$
and its more even distribution between cpx and opx
means that it is unlikely to have much influence on
trace-element partitioning in our samples.

Remaining potential minor variables include
redox state and water content. Calculated values of
$\Delta \log fO_2$ relative to QFM (Table 2) show that the
lower temperature xenoliths (Groups III and IV) are
more oxidized relatively, which is consistent with
their more metasomatized nature (cf. McCammon et
al., 2001) and is correlated with the presence of
amphibole (or its breakdown products). While
redox state could be important in controlling the
partitioning of polyvalent elements, the variation in
redox states in our samples is probably too small to
be significant, at least for any trace elements con-
sidered in this study. In any case, since the inferred
variation of redox state correlates empirically with
temperature in our sample suite, it is unlikely that
we would be able to disentangle the effects from
those of temperature.

The primary water content of the minerals in the
xenoliths is unknown; however, the seven lowest
temperature xenoliths contained pargasitic amphibole
as an extra phase (Table 2). The nominally anhydrous
minerals in these samples would therefore have rela-
tively high H$_2$O contents, the level of H$_2$O being
defined by amphibole saturation at the P–T conditions
of equilibration, e.g., according to the reaction:

$$
\begin{align*}
2 \text{CaMgSi}_2\text{O}_6 + 2.5 \text{Mg}_2\text{Si}_2\text{O}_6 + \text{H}_2\text{O} \\
\text{cpx} \quad \text{opx} \\
= \text{Ca}_2\text{Mg}_5\text{Si}_9\text{O}_{22}(\text{OH})_2 + \text{Mg}_2\text{SiO}_4 \\
\text{amphibole} \quad \text{ol}
\end{align*}
$$

The presence of H$_2$O may potentially be an important
control on heterovalent incompatible-element substi-
tutions in some phases, although little is known about
this at present.

In summary: we expect that almost the entire var-
iation of inter-crystalline trace-element partition coeffi-
cients in our 16 samples will depend on just one
independent variable, temperature. This variation will
include not only the direct effect that temperature has
on the thermodynamics of the partitioning reaction,
but also indirect effects that arise through the covari-
ation of temperature with both pressure and mineral
compositions in four-phase spinel lherzolites; this
always needs to be kept in mind when attempting to
make deductions about the controls on partitioning
behaviour from the empirical correlations of partition
coefficients with temperature. In addition, minor con-
tributions from the molar Cr(Cr+Al) ratio in spinel
(Cr#), Na in cpx ($N_{Na}^{cpx}$, the number of Na cations
per formula unit of 6 oxygens), and possible differ-
ences between anhydrous and hydrous samples will
be looked for.

4.1. Data fitting and extrapolation

Since the main reason for undertaking this study is
to extrapolate partition coefficients to the tempera-
tures appropriate for mantle melting, to see how
trace elements are distributed among the solid phases
during melting, the reliability of such extrapolations
needs some comment. The Nernst partition coeffi-
cient $D_M^{\alpha/\beta}$ (defined as the concentration of M in
phase $\alpha$ divided by the concentration of M in
phase $\beta$) is not a rigorous thermodynamic entity.
The reason is that M (or its simple oxide) is in general not a thermodynamically valid component in the context of a partitioning reaction, as it cannot be varied independently (see, for example, a recent discussion in O’Neill and Eggins, 2002). For the thermodynamics of element partitioning to be described rigorously it is necessary to use the equilibrium constant, $K_M$, which is defined for an appropriately balanced partitioning reaction, and includes the activities of those major-element components involved in the substitution of M into both phases (the “stoichiometric controls”). However, as discussed above, the activities of major-element components (SiO$_2$, CaO, MgO and FeO) are more or less buffered in a four-phase lherzolite. The exception is the activity of Al$_2$O$_3$ due to variable Al/Cr ratios. This buffering of the major-element components involved in the “stoichiometric control” allows empirical values of $D_M^{ab} / R$ to be related to a suitable equilibrium constant $K_M$ straightforwardly.

For high-temperature partitioning reactions, the simplified relationship $\ln K_M = -\Delta H^v / RT + \Delta C_p^v / R$ is generally an excellent approximation at constant pressure, as $\Delta C_p^v$ is usually small. Hence the algebraic form of the relationship between $D_M^{ab}$ and temperature should be simply $\ln D_M^{ab} \propto 1/T$. In the context of the present study, this relationship should hold best for cpx/opx partitioning, since the “stoichiometric controls” on trace-element substitution are likely to be the same in both pyroxene phases due to their similar stoichiometry, and, as regards the unbuffered major element component Al$_2$O$_3$, their similar Cr/Al ratios.

In light of these considerations, we have fitted our empirical values of $D_M^{ab}$ (i.e., $D_M^{cpx/opx}$ etc.) to the general equation:

$$\ln D_M^{ab} = a_0 + (a_1 + a_2 \cdot N_{Na}^{cpx} + a_3 \cdot Cr#^{opx}) T_{(cpx, 1.5GPa)}$$

The fitting was carried out by multiple non-linear least-squares regression with uncertainties in $D_M^{ab}$ as calculated from Table 3, or ±5%, one standard deviation, whichever is the larger, and in $T_{(cpx, 1.5GPa)}$ of ±10 K. Obviously $T_{(cpx, 1.5GPa)}$ must be the same for every element in each sample and should not be treated as independently variable in the different regressions, but we have ignored this complication for the sake of computational simplicity. This could be rationalised as allowing for some imperfection in equilibration for trace elements. We ignored the uncertainties in $N_{Na}^{cpx}$ and $Cr#^{opx}$, which have an insignificant effect.

For pairs of elements with similar geochemical properties (i.e., same valence and fairly similar ionic radii, such as the REEs), the two-element distribution coefficient, which is given by the ratio of the partition coefficients $K_{D_M^{ab}} = D_M^{ab} / D_M^{ab}$, should approximate a true equilibrium constant, because the “stoichiometric control” on each element in each phase cancels out across the exchange reaction (e.g., O’Neill and Eggins, 2002). Furthermore, the entropies of such exchange reactions are expected to be small, hence the simple relationship $\ln K_{D_M^{ab}} \approx -\Delta H^v / RT$, with $K_{D_M^{ab}}$ tending to unity as $T$ goes to infinity.

5. Results and discussion

5.1. Rare Earth Elements (REE) and Y

The REE and Y are concentrated into cpx, but with significant amounts also in opx. Only Y and the four heaviest REE analysed in this study, namely Ho, Er, Yb and Lu, are above detection limits in olivine in the majority of the samples. In spinel, only Y, at 5–15 ppb in most samples, is above the limit of detection (~2 ppb); hence, because of its low modal abundance in peridotites, spinel holds a negligible proportion of the REEs.

Fig. 3 shows $\ln D_{RE}^{cpx/opx}$ vs. $1 / T_{(opx, 1.5GPa)}$. The values of $D_{RE}^{cpx/opx}$ decrease systematically with increasing atomic number; there is a large temperature effect for all the REE, but this effect also decreases with increasing atomic number. If we extrapolate these partition coefficients to the dry solidus, values of $D_{RE}^{cpx/opx}$ would only be about 2–3 for the heavy REE. This is in agreement with experimental measurements (e.g., Salters et al., 2002; McDade et al., 2003). Since the modal abundance of opx is initially about twice that of cpx for fertile mantle at its solidus in the spinel-lherzolite facies, and the ratio of opx to cpx increases with melt extraction, it is apparent that the major proportion of the heavy REEs in the residues of anhydrous partial melting.
are actually held in opx. Even for the light REE, the values of $D_{\text{REE}}$ become less than 30 over the melting interval at 1.5 GPa (Fig. 3). For refractory residues with only a few percent residual cpx, such as typical abyssal peridotites, much of the light REE inventory will also reside in opx.

To test whether some of the scatter in the trends in Fig. 3 may be due to compositional effects we fitted the data for each REE and $Y$ to Eq. (4). For all REE and $Y$, the last term (in $\text{Cr}#$ sp) was found to be insignificant and was dropped, but the terms in $N_{\text{Na}}^{\text{cpx}}$ proved to be significant. Results from the regression analysis for $a_0$, $a_1$, and $a_2$ for each REE and $Y$ are given in Table 4 and are plotted as a function of ionic radius in 8-fold coordination (from Shannon, 1976) in Fig. 4. The parameters $a_0$ and $a_1$ show a linear dependence, that of $a_2$ approximately parabolic. These good systematic relationships prompted us to refit the data globally to a single equation:

$$\ln D_{\text{cpx/opx}}^{\text{REE}} = a_0 + b_0 R_{\text{REE}}^\text{VIII} + \left( a_1 + b_1 R_{\text{REE}}^\text{VIII} \right)/T_{\text{opx}, 1.5\text{GPa}} + \left( a_2 + b_2 R_{\text{REE}}^\text{VIII} + c_2 \left( R_{\text{REE}}^\text{VIII} \right)^2 \right) N_{\text{Na}}^{\text{cpx}}$$

(5)

The resulting best-fit parameters are:

$$a_0 = 18.11, \quad b_0 = -0.192 \text{pm}^{-1}$$

$$a_1 = -50568 \text{K}^{-1}, \quad b_1 = 542 \text{K}^{-1} \text{pm}^{-1}$$

$$a_2 = -560755, \quad b_2 = 10644 \text{pm}^{-1}, \quad c_2 = -49.8 \text{pm}^{-2}$$

The values of $R_{\text{REE}}^\text{VIII}$ from Shannon (1976) are (in pm):

La 116.0; Ce 114.3; Pr 112.6; Nd 110.9; Sm 107.9; Eu 106.6; Gd 105.3; Tb 104.0; Dy 102.7; Ho 101.5; Er 100.4; Tm 99.4; Yb 98.5; Lu 97.7; and $Y$ 101.9. There is no hint of an Eu anomaly in these $D_{\text{cpx/opx}}$ data.

An interesting detail of the thermodynamics of REE incorporation in pyroxenes is revealed by the two-element distribution coefficients $K_{\text{REE/Y}}^{\text{cpx/opx}}$, corresponding to the exchange reactions: $[\text{REE}]_{\text{cpx}} + [Y]_{\text{opx}} = [\text{REE}]_{\text{opx}} + [Y]_{\text{cpx}}$. Note that $K_{\text{REE/Y}}^{\text{cpx/opx}} = D_{\text{cpx/opx}}^{\text{REE}} / D_{\text{cpx/opx}}^{\text{Y}}$, so nothing new is being introduced here; but the two-element distribution coefficient eliminates the stoichiometric control, much of the effect of activity coefficients, and the need to
Table 4
Partitioning of incompatible trace elements between clinopyroxene and orthopyroxene: fits of data in Table 3 by multiple non-linear regression to the semi-empirical equation: ln \( D_{\text{cpx/opx}}^{\text{p}} = a_0 + (a_1 + a_2 N_{\text{Na}}^{\text{cpx}} + a_3 \text{Cr}^{\#}) / T_{\text{opx}, 1.5\text{GPa}} \) where \( N_{\text{Na}}^{\text{cpx}} \) is the number of atoms of Na in cpx per formula unit of six oxygens, and \( \text{Cr}^{\#} \) is molar Cr/(Al+Cr) in coexisting spinel.

<table>
<thead>
<tr>
<th>Element</th>
<th>( a_0 )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>REE and Y</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>−3.94 ± 0.33</td>
<td>11.39 ± 418</td>
<td>13.56 ± 2523</td>
<td>−</td>
<td>3.10</td>
</tr>
<tr>
<td>Ce</td>
<td>−3.28 ± 0.24</td>
<td>10.32 ± 345</td>
<td>8.504 ± 1718</td>
<td>−</td>
<td>3.23</td>
</tr>
<tr>
<td>Nd</td>
<td>−3.32 ± 0.26</td>
<td>9.951 ± 374</td>
<td>4.782 ± 1991</td>
<td>−</td>
<td>1.16</td>
</tr>
<tr>
<td>Sm</td>
<td>−2.85 ± 0.30</td>
<td>8.638 ± 393</td>
<td>3.644 ± 2246</td>
<td>−</td>
<td>0.83</td>
</tr>
<tr>
<td>Eu</td>
<td>−2.27 ± 0.24</td>
<td>7.495 ± 339</td>
<td>3.006 ± 2064</td>
<td>−</td>
<td>0.66</td>
</tr>
<tr>
<td>Gd</td>
<td>−2.34 ± 0.22</td>
<td>7.263 ± 279</td>
<td>3.562 ± 1641</td>
<td>−</td>
<td>0.85</td>
</tr>
<tr>
<td>Dy</td>
<td>−1.66 ± 0.17</td>
<td>5.425 ± 228</td>
<td>4.485 ± 1198</td>
<td>−</td>
<td>0.63</td>
</tr>
<tr>
<td>Ho</td>
<td>−1.56 ± 0.17</td>
<td>4.907 ± 250</td>
<td>5.166 ± 1178</td>
<td>−</td>
<td>0.95</td>
</tr>
<tr>
<td>Er</td>
<td>−1.05 ± 0.17</td>
<td>3.856 ± 224</td>
<td>5.158 ± 1113</td>
<td>−</td>
<td>0.61</td>
</tr>
<tr>
<td>Yb</td>
<td>−0.61 ± 0.15</td>
<td>2.496 ± 200</td>
<td>6.070 ± 980</td>
<td>−</td>
<td>1.14</td>
</tr>
<tr>
<td>Lu</td>
<td>−0.71 ± 0.16</td>
<td>2.254 ± 198</td>
<td>6.578 ± 1066</td>
<td>−</td>
<td>1.63</td>
</tr>
<tr>
<td>Y</td>
<td>−1.26 ± 0.15</td>
<td>4.402 ± 209</td>
<td>5.290 ± 1052</td>
<td>−</td>
<td>0.45</td>
</tr>
<tr>
<td>HFSE</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>−1.09 ± 0.14</td>
<td>2.145 ± 200</td>
<td>8.552 ± 973</td>
<td>−</td>
<td>2.32</td>
</tr>
<tr>
<td>Zr</td>
<td>−4.09 ± 0.20</td>
<td>7.381 ± 279</td>
<td>10.360 ± 1373</td>
<td>1026 ± 285</td>
<td>0.69</td>
</tr>
<tr>
<td>Hf</td>
<td>−3.61 ± 0.37</td>
<td>6.686 ± 458</td>
<td>10.500 ± 2285</td>
<td>870 ± 420</td>
<td>0.46</td>
</tr>
<tr>
<td>Nb</td>
<td>−5.16 ± 0.25</td>
<td>7.822 ± 371</td>
<td>21.414 ± 1838</td>
<td>−</td>
<td>4.23</td>
</tr>
<tr>
<td>Ta</td>
<td>−5.62 ± 0.70</td>
<td>10.176 ± 850</td>
<td>19.131 ± 5266</td>
<td>−</td>
<td>0.48</td>
</tr>
<tr>
<td>Th</td>
<td>−2.21 ± 0.76</td>
<td>6.876 ± 802</td>
<td>18.917 ± 3681</td>
<td>−</td>
<td>4.17</td>
</tr>
<tr>
<td>U</td>
<td>−3.36 ± 0.85</td>
<td>7.465 ± 1075</td>
<td>14.141 ± 4050</td>
<td>−</td>
<td>1.69</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>−2.35 ± 0.15</td>
<td>4.207 ± 198</td>
<td>3.500 ± 418</td>
<td>−</td>
<td>0.67</td>
</tr>
<tr>
<td>Sr</td>
<td>−4.02 ± 0.28</td>
<td>12.405 ± 391</td>
<td>−</td>
<td>−</td>
<td>1.73</td>
</tr>
<tr>
<td>&quot;</td>
<td>−4.23 ± 0.31</td>
<td>11.992 ± 443</td>
<td>4.183 ± 1781</td>
<td>1146 ± 349</td>
<td>0.71</td>
</tr>
<tr>
<td>Ba</td>
<td>−3.39 ± 0.90</td>
<td>7.449 ± 1185</td>
<td>11.800 ± 6521</td>
<td>3478 ± 1304</td>
<td>1.57</td>
</tr>
<tr>
<td>Pb</td>
<td>−7.66 ± 0.73</td>
<td>10.555 ± 923</td>
<td>17.169 ± 6431</td>
<td>−</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Data were weighted assuming uncertainties (1σ) in \( D_{\text{cpx/opx}}^{\text{p}} \) of ±5% or as observed, whichever is larger, and ±10 K in \( T_{\text{opx}, 1.5\text{GPa}} \). Uncertainties in \( N_{\text{Na}}^{\text{cpx}} \) and \( \text{Cr}^{\#} \) were ignored.

* 13 data; b 10 data; c One datum (DW 211) omitted; d One datum (M766) omitted; e Two data (MM1278 and DW1342) omitted; f One datum (DW1284) omitted.

convert from concentrations (ppm) to mole fractions, all of which should make the thermodynamic relationships more transparent. We chose Y as the common element as its higher cosmochemical abundance means that it is relatively accurately determined even in opx, and its properties put it in the middle of the REE spectrum (its geochemical twin is Ho). Fig. 5 shows ln KD_{REE/Y} vs. \( 1/T_{\text{opx}, 1.5\text{GPa}} \). For such an exchange reaction it is usually expected that the entropy of reaction is zero, hence ln KD_{REE/Y} = \( \Delta_{\text{cpx/opx}}^H/RT \), and each line should intersect at ln KD_{REE/Y} = 0 at 1/T = 0 (i.e., KD_{REE/Y} should go to unity as T goes to infinity). Clearly this does not happen, the common intersection being indeed at KD_{REE/Y} = 0, but at \( T_{\text{opx}, 1.5\text{GPa}} = 2720 \) K (in this analysis we neglect the fact that the effect of \( N_{\text{Na}}^{\text{cpx}} \) varies among the REE, which introduces a bit more scatter in the data particularly for La and Ce, but the conclusions are robust). Two end-member explanations (not mutually exclusive) are possible:

1) \( \Delta S^c \) is not zero, but correlates systematically with \( \Delta_{\text{cpx/opx}}^H \)
2) There is an equally systematic pressure dependence of the exchange reaction (i.e., \( \Delta_{\text{cpx/opx}}^V \)), which we are not accounting for, as we are not
using pressure as an independent variable. (As explained above, this is mainly because we expect pressure to correlate with temperature in mantle xenoliths, but also because we do not know the equilibration pressure of our samples accurately).

Since there is a general expectation that $\Delta_p V^\circ$ should correlate with $\Delta_p S^\circ$, some combination of both explanations is probable. Non-zero values of $\Delta_p V^\circ$ may originate because there is a difference in coordination geometry of the M2 site between clinopyroxene and orthopyroxene; the site geometries are akin to distorted 8-fold coordination in the former, but distorted 6-fold coordination in the latter. The somewhat unexpected feature is how good the systematic correlation of $\Delta_p S^\circ$ and/or $\Delta_p V^\circ$ with $\Delta_p H^\circ$ is.
Sorting this out highlights a need for some experimental input, since \( T \) and \( P \) can be varied independently in experiments. If the non-zero \( \Delta V^c \) explanation is found to be significant, the partitioning of REE and Y between cpx and opx might make a useful geobarometer.

In Fig. 5 we have also plotted \( K_D^{cpx/opx} \) REE/Y data. This is probably because Sc\(^{3+}\) substitutes into the M1 site of the pyroxene structure, and not, like the REE, into M2.

5.1.1. REE in olivine

Values of \( D_{cpx/ol}^{REE} \) for Ho, Er, Yb, Lu and Y are plotted versus \( 1/T_{(opx, 1.5 \text{ GPa})} \) in Fig. 6, and empirical equations describing the partitioning behaviour are given in Table 5. The amounts of Ho, Er and Lu in ol are not far above detection limits in most samples, hence the scatter in the data. Nevertheless, there is a clear correlation with temperature, extrapolating to values of about 20 for \( D_{cpx/ol}^{La} \) and \( D_{cpx/ol}^{Lu} \) in the melting regime. Thus in highly depleted peridotites with modal ol/cpx ratios greater than 20, the ol will actually hold more of the rock’s heavy REE than the cpx. However, most of the heavy REE inventory, and a significant part of the light REEs too, will be held in opx.

5.1.2. Intercrystalline partitioning of REEs as a function of ionic radius

Values of \( \ln D_{cpx/opx}^{REE} \) and \( \ln D_{cpx/ol}^{REE} \) for Mo22 determined both in this study and by Stosch (1982) are plotted against ionic radius \( R_{\text{VIII}}^{REE} \) in Fig. 7. All sixteen of our samples show similarly monotonically increasing, smooth patterns of \( \ln D_{cpx/opx}^{REE} \) vs. \( R_{\text{VIII}}^{REE} \), whereas several of the other spinel lherzolites analysed by Stosch (1982) show minima in this pattern somewhere between Ce and Sm, e.g., the samples Ib/3, Ib/8, KH-K8 and SC-K2 in his Fig. 5. Unless REE partitioning in these samples is controlled by some unknown crystal-chemical feature not present in our samples, it is likely that such an effect is due to chemical disequilibrium. The rate of diffusion of the REE in cpx decreases systematically with increasing ionic radius (van Orman et al., 2001), i.e., La is more sluggish than Lu; hence on cooling from high temper-
ature, values of $D_{\text{REE}}^{\text{cpx/ol}}$ for the light REE will tend to increase less rapidly than for the heavy REE. This raises the question of whether the even more marked deviations from a monotonic curve of $\ln D_{\text{REE}}^{\text{cpx/ol}}$ vs. IR shown by all eight of the samples analysed by Stosch (1982), including Mo22 (kinked at Nd, see his Fig. 6), is also a disequilibrium feature, or perhaps an analytical artefact caused by the very low levels of light REE in olivine. We are not aware of any crystal-chemical reason why the partitioning of REEs into olivine should not decrease monotonically from Lu to La. This is potentially an important point in determining the significance of REE patterns in very depleted olivine-rich rocks such as melt-channel dunites, or in melt inclusions trapped in olivine. Unfortunately, our results cannot test this, as the light REEs are below the detection limit of LA-ICP-MS in all our xenoliths.

5.2. Scandium

The partitioning of Sc between cpx, opx and ol follows very well defined trends as a function of temperature (Fig. 8), although Sc in opx in one sample (DW 211) seems to be anomalously low. Apart from this, most of the scatter of the data in this diagram is due to the effect of Na in cpx. Regression of the data gives:

$$\ln D_{\text{Sc}}^{\text{cpx/opx}} = -2.354 + (4207 + 3500N_{\text{Na}}^{\text{cpx}})/T$$

($\chi^2_v = 0.67$)

$$\ln D_{\text{Sc}}^{\text{cpx/ol}} = -1.696 + (5481 + 3500N_{\text{Na}}^{\text{cpx}})/T$$

($\chi^2_v = 2.56$)

$$\ln D_{\text{Sc}}^{\text{opx/ol}} = 0.485 + 1511/T$$

($\chi^2_v = 0.89$)

---

![Fig. 6. Partitioning of heavy REEs and Y between cpx and ol. The REEs lighter than Ho are generally below our limit of detection in ol. Extrapolation of the partitioning trends to magmatic temperatures (shaded region) shows that ol will contain a significant proportion of the heaviest REEs in depleted peridotites.](image-url)
For $D_{\text{Sc} \text{cpx/opx}}$ and $D_{\text{Sc} \text{cpx/ol}}$, the coefficients in $N_{\text{Sc} \text{cpx}}$ were constrained to be the same. The partitioning of Sc between cpx and opx in peridotitic and websteritic upper-mantle xenoliths has previously been investigated by Seitz et al. (1999), using SIMS. Their results are compared in Fig. 9a. There is good agreement for the peridotitic samples, but the websterites plot systematically at higher values of $D_{\text{Sc} \text{cpx/opx}}$. In Fig. 9b we show that this is caused by a dependence of $D_{\text{Sc} \text{cpx/opx}}$ on the Mg# of the pyroxenes, by plotting the difference between calculated and measured values of $D_{\text{Sc} \text{cpx/opx}}$ versus the Mg# of the opx. An effect of Fe on Sc partitioning was previously postulated by Glassley and Piper (1978). Since all our samples are all at

Fig. 7. Comparison of values of $D_{\text{REE} \text{cpx/opx}}$ and $D_{\text{REE} \text{cpx/ol}}$ plotted against ionic radius ($R_{\text{REE}}^V$) from this study and from Stosch (1982). The latter was able to determine the light REE in olivine, which are below the limits of detection in this study (c. 1 ppb). However, the values of Ce and La in ol reported by Stosch fall off the extrapolation of the curve of $\ln D_{\text{REE} \text{cpx/ol}}$ vs. $R_{\text{REE}}^V$, which may indicate that these values are compromised by contamination.

Fig. 8. Partitioning of Sc between cpx, opx and ol as a function of $T_{\text{opx, 1.5 GPa}}$. Error bars (one s.d.) are shown where they are larger than the symbol. Much of the scatter is accounted for by the effect of Na in cpx ($N_{\text{Na} \text{cpx}}$).

Mo22
essentially the same Mg# (Table 2) we cannot expect to pick up any effect of Mg# from our data. The example of Sc should therefore provide a warning that our empirical partitioning relationships should not be extrapolated to different compositions with different Mg#, for any element.

Spinel also contains detectable Sc (Table 3d). The partitioning of Sc between cpx and sp can be empirically described by:

$$\ln D_{Sc}^{cpx/sp} = -1.804 + (7901 - 4298Cr^{#sp} \times \frac{3500N_{Na}^{cpx}}{T} + \frac{\chi_2}{1.8}) \quad (6)$$

Despite invoking the extra term in Cr#sp, the fit is markedly less good than for the partitioning among pyroxenes and olivine. The sign of the term in Cr#sp is such that Sc correlates with Cr in spinel, as might be expected from the smaller difference in the ionic radii between Sc and Cr³⁺ than between Sc and Al. This manifests itself in an empirical correlation between the Sc content of the spinel and Cr#sp in our 16 samples.

5.3. High field strength elements (Ti, Zr and Hf, Nb and Ta, plus U and Th)

The correlations of $D_{HF}^{cpx/opx}$ with $D_{Ta}^{cpx/opx}$ and of $D_{Ta}^{cpx/opx}$ with $D_{Nb}^{cpx/opx}$ are shown in Fig. 10a and b. Inter alia, such systematic relationships test the quality of the data, e.g., the good correlation of Nb with Ta implies that the potential isobaric interference of $^{53}Cr+^{40}Ar$ on $^{93}Nb$ is not important in pyroxenes. Fig. 11a shows the relationships of $\ln D_{HFSE}^{cpx/opx}$ versus $1/T_{opx}$ (1.5 GPa). As with the REEs, the HFSEs partition into cpx, but the values of $D_{HFSE}^{cpx/opx}$ are sensitive to temperature, and in particular the amounts of Zr and Hf held in opx become significant at solidus temperatures. The data confirm the experimental observation of Wood et al. (1999) that U is somewhat less incompatible than Th in opx compared to cpx (i.e., $D_{U}^{cpx/opx} < D_{Th}^{cpx/opx}$, as shown in Fig. 11b). This could potentially be of importance in interpreting U decay series data. The fits to Eq. (5) for all HFSEs plus U and Th are included in Table 4.

Fig. 9. a) Partitioning of Sc between cpx and opx: the results of Seitz et al. (1999) using SIMS compared with the equation derived from the present work, using $T_{opx}$ (1.5 GPa). Samples include both garnet and spinel lherzolites and garnet websterites. Values of $D_{Sc}^{cpx/opx}$ were calculated using $T_{opx}$ (method of Brey and Köhler, 1990) at an assumed single pressure of 1.5 GPa from the major-element opx and cpx analyses of Seitz et al.; these are shown as solid symbols with error bars (1 s.d., of the SIMS Sc analyses, as reported by Seitz et al., 1999). For the spinel lherzolites and garnet websterites, our assumed pressure of 1.5 GPa is mostly quite close to the pressures of equilibration estimated by Seitz et al., see their Table 1. For the four garnet lherzolites, which equilibrated at substantially higher pressures than the assumed 1.5 GPa, we have additionally plotted values of $D_{Sc}^{cpx/opx}$ calculated using $T_{opx}$ as estimated by Seitz et al., as open symbols. This displaces these data off the 1:1 line, indicating that the pressure-dependence of $D_{Sc}^{cpx/opx}$ is close to that of $T_{opx}$. Agreement is good for most samples, with the difference between observed and calculated values being mostly due to the lower Mg# of some of the websteritic samples in the Seitz et al. (1999) study, which is demonstrated in Fig. 9b by plotting the difference between calculated and observed values of $D_{Sc}^{cpx/opx}$ versus the Mg# of the opx.
The partitioning of Ti, Zr and Nb between cpx and ol is plotted as a function of inverse temperature in Fig. 12 (Hf, Ta, Th and U are generally below detection limits in ol). Unlike for the REEs, the values of $D_{HFSE}^{cpx/ol}$ do not define a clear linear trend with $1/T$ (opx, 1.5GPa). This is not due to analytical errors, as the amounts of Ti in olivine are orders of magnitude above detection limits and should be accurately determined. There is experimental evidence (Hermann et al., 2005) that the mode of Ti substitution in olivine changes as a function of temperature and $H_2O$ fugacity; at high temperatures in an anhydrous environment, Ti substitutes for Si on the tetrahedral site, whereas at low temperature in the presence of $H_2O$ the substitution of Ti is into the octahedral site (i.e., similar to the titanoclinohumite structural unit). The parallel behaviour of Zr and Nb (Fig. 12) indicate that these trace elements may behave similarly.

5.4. Sr, Ba and Pb

These elements form large-radius divalent cations that are expected to substitute for $Ca^{2+}$ in minerals. Their ionic radii in 8-fold coordination (from Shan-
non, 1976) increase in the order Ca (112 pm) < Sr (118 pm) < Pb (129 pm) < Ba (149 pm). The partitioning of Sr between cpx and opx shows a regular trend with temperature (Fig. 13); the array lies parallel to and in between those of the lightest REEs, La and Ce, although Sr is usually thought to have an incompatibility (i.e., bulk mineral/melt partition coefficient) that is in between Pr and Nd (Sun and McDonough, 1989). The greater preference of Sr for cpx over opx compared to Ca fits with simple crystal-chemical expectations that the larger cation would be preferentially incorporated into the mineral with the larger crystallographic site, namely the M2 site in cpx. It is therefore surprising to find that Pb is much more evenly partitioned between cpx and opx than Ca or Sr, and extrapolation of the present data suggests that Pb may even prefer opx at magmatic temperatures (Fig. 13). However, considering the propensity of Pb to contaminate surfaces and the low levels of Pb in opx, this behaviour is in need of further confirmation. Nevertheless, if real, this behaviour may be due to the compressibility of the Pb$^{2+}$ cation; the high atomic

Fig. 11. Temperature dependence of the partitioning between cpx and opx of a) Ti, Zr and Ta; and b) U and Th. The data for Hf and Nb are not shown for clarity since they define trends very similar to that for Zr. The important point is that at magmatic temperatures (shaded region), a substantial part of the HFSE inventory will be held in opx. Note also that $D_{\text{Th}}^{\text{cpx/opx}} > D_{\text{U}}^{\text{cpx/opx}}$ at a given temperature.
number of Pb means that the outer electrons are shielded from the nucleus by more shells of inner electrons than in Ca or Sr. This should lead to Pb anomalies on Onuma diagrams, as previously noted by Blundy and Wood (1994). In keeping with this explanation, the values of $D_{\text{Ba}}^{\text{cpx/opx}}$ are intermediate between $D_{\text{Sr}}^{\text{cpx/opx}}$ and $D_{\text{Pb}}^{\text{cpx/opx}}$ (Fig. 13), although the data are rather scattered due to the low levels of Ba in opx.

5.5. Phosphorus

Phosphorus is another unusual element among the more incompatible trace elements, in that the
phase with the highest P abundance is ol rather than cpx in anyhydrous spinel lherzolites; the sequence of P contents is generally amph > ol ≥ cpx > opx >> sp (Table 3; see also Brunet and Chazot, 2001), although incerature-dependent trends for the partition coefficients are not obvious (Fig. 14). The data for $P_{\text{cpx/opx}}$ and $D_{\text{P/cpx/ol}}$ appear to show a kink versus temperature between the anydrous and the amphibole-bearing samples (i.e., between Groups I + II and III+IV, Table 2) that might indicate that the substitution mechanism in cpx in the hydrous samples is different from that in the anhydrous samples. The partitioning between ol and opx is somewhat more regular (Fig. 14), with $D_{\text{opx/ol}}$ increasing with temperature to ~1 at the dry solidus. An approximate relationship is:

$$D_{\text{P/ol}} = 0.84 - 2204/T$$

The value of $\chi^2$ for the regression is 6.5 even after omitting one aberrant datum, DW1342 (Fig. 14); hence this cannot be considered a good fit. The implication is that the details of the partitioning of P may depend on coupled substitutions involving minor components (for example H$_2$O) not accounted for in Eq. (1), which are needed to provide the charge-balance for the substitution of P$^{5+}$ for Si$^{4+}$ in silicates.

5.6. Nickel and cobalt

Ni and Co substitute for the major-elements Mg and Fe$^{2+}$ in all four phases of a spinel lherzolite, forming simple solid solutions with nearly ideal thermodynamic mixing properties (e.g., Seifert and O’Neill, 1987). The partitioning of both Ni and Co between olivine and orthopyroxene has been experimentally investigated by von Seckendorff and O’Neill (1994) in the systems MgO–FeO–SiO$_2$F$_{\text{NiO}}$F$_{\text{CoO}}$ at 900–1600°C and 2.0 GPa. These experiments consisted of quasi-reversals (i.e., paired experiments starting with both high Ni or Co and low Ni or Co), and used a BaO–B$_2$O$_3$ flux (see von Seckendorff and O’Neill, 1993). Most runs were near $X_{\text{Mg}}$=0.9 composition, but the effect of Mg/Fe$^{2+}$ ratio was also investigated. The results can be summarized as:

$$\ln K_{\text{Ni/Mg}}^{\text{ol/opx}} = 1419/T - 0.241$$

$$\ln K_{\text{Co/Mg}}^{\text{ol/opx}} = (771 + 400X_{\text{Fe}}^{\text{ol}})/T - 0.094$$

These equations are based on 37 and 34 experiments, respectively. The Ni series included one
multi-anvil run at 9.0 GPa confirming that the effect of pressure is negligible. That a term in $X_{Fe}^{ol}$ is required to fit the Co data, but not the Ni data, is consistent with the observation that mixing of Mg and Ni in olivines is ideal but mixing of Mg and Co is similar to that of Mg and Fe in showing small positive deviations from ideality (Seifert and O’Neill, 1987).

The observed distribution coefficients from the xenoliths (Table 3) are compared to the experiments in Fig. 15a,b. For the Mg–Ni exchange reaction there is complete agreement, for the Mg–Co reaction the empirical data plot about 10% lower in $K_{D_{Co/Mg}}^{ol/opx}$ than predicted from the experiments. The reason for this is unknown. A possibility is that Al$_2$O$_3$ ($\pm$ Cr$_2$O$_3$) in opx, which was not included in

![Graph a](image1.png)

![Graph b](image2.png)

Fig. 15. a) Distribution of Ni and Mg and Co and Mg between olivine and orthopyroxene as a function of temperature. Solid lines summarize the experimental study of von Seckendorff and O’Neill (1994); dashed lines are empirical fits to the present data. b) Distribution of Ni and Mg and Co and Mg between olivine and clinopyroxene as a function of temperature. Dashed lines are empirical fits to the data.
the experimental study, may affect matters, but there is no obvious correlation between the magnitude of the discrepancy and Al in opx in the present xenolith data. Regression of the present data (Table 3) gives:

\[
\ln KD_{Ni/Mg}^{ol/opx} = 1703/T(BKN\, opx) - 0.419
\]

\[
\ln KD_{Co/Mg}^{ol/opx} = 940/T(BKN\, opx) - 0.286
\]

These empirical fits are also given in Fig. 15a,b for comparison.

For \( KD_{Ni/Mg}^{ol/opx} \), both the experimental results of von Seckendorf and O’Neill (1994) and the present data are in excellent agreement with the pioneering empirical SIMS study of Hervig et al. (1980) on trace-element partitioning in mantle xenoliths. These latter authors obtained \( \ln KD_{Ni/Mg}^{ol/opx} = 1630/T(\text{Wells}) - 0.333 \), based on the Wells (1977) two-pyroxene geothermometer.

The distribution coefficients for Mg–Ni and Mg–Co partitioning between ol and cpx are similarly sensitive to temperature, and can be described by the equations:

\[
\ln KD_{Ni/Mg}^{ol/cpx} = 1773/T - 0.422
\]

\[
\ln KD_{Co/Mg}^{ol/cpx} = 1857/T - 0.758
\]

The interesting feature of the partitioning of Mg and Ni between ol and sp is that the distribution coefficient varies strongly with the Cr content of the spinel, as well as temperature. The empirical fit gives:

\[
\ln KD_{Ni/Mg}^{ol/sp} = (1722Cr^{##})/T - 1.118
\]

The sensitivity to \( Cr^{##} \) is not unexpected, because spinel is a reciprocal solid solution (Wood and Nicholls, 1978), with a large positive free energy for the reciprocal reaction:

\[
\text{NiAl}_2\text{O}_4 + \text{MgCr}_2\text{O}_4 = \text{NiCr}_2\text{O}_4 + \text{MgAl}_2\text{O}_4
\]

(7)

The positive free energy is caused by the relative instability of NiCr2O4, due to the very large octahedral site preference of Cr^{3+} forcing Ni^{2+}, itself with a well-known preference for octahedral coordination, onto the tetrahedral site of the spinel. The partitioning of Mg and Co between ol and sp also depends on Cr^{##}, but in the opposite way—i.e., increasing Cr^{##} increases Co in spinel, which must be due to the relatively high stability of CoCr2O4 (similar to FeCr2O4). The partitioning is well described by the equation:

\[
\ln KD_{Co/Mg}^{ol/sp} = (-1536 - 1179Cr^{##})/T
\]

5.7. Chromium, vanadium and gallium

These three elements occur mainly as the 3+ cations in systems pertinent to the Earth’s mantle, although other oxidation states are possible in anomalously reducing or oxidizing environments for Cr and V, but not Ga (i.e., Cr^{2+} and V^{2+}, V^{4+} and perhaps V^{5+}); the occurrence of these other oxidation states can be expected to have important consequences for the geochemical behaviour of these elements, e.g., as shown by Seifert and Ringwood (1988) for the lunar geochemistry of Cr and V. Chromium needs to be treated as a major element in peridotitic systems, since the activity of Cr2O3 has a large effect on the solubility of Al2O3 in pyroxenes. Klemme and O’Neill (2000) studied the partitioning of Cr and Al between orthopyroxene and spinel in the system MgO–Al2O3–SiO2–Cr2O3 experimentally, but found that the kinetics of the system were so sluggish that decent results could not be obtained below 1300 °C. The present data, therefore, are potentially valuable in that such well equilibrated, compositionally homogeneous xenoliths constitute natural experiments that can guide extrapolation of the laboratory experimental results to lower temperatures, and into more chemically complex systems.

Klemme and O’Neill (2000) found that the partitioning of Cr between orthopyroxene and spinel can be represented by the exchange reaction:

\[
\text{MgAl}_2\text{O}_4 + \text{MgCr}_2\text{SiO}_6 = \text{MgCr}_2\text{O}_4 + \text{MgAl}_2\text{SiO}_6
\]

(8)

This defines \( KD_{Cr/sp}^{ol/px} \) as \( ([Al_2O_3]^{px}/[Al_2O_3]^{sp}) ([Cr]^{sp}/([Cr]^{px})) \). The important point is that using MgCrAlSiO6 as a pyroxene component does not fit the data well, despite its reasonableness as deduced
from crystallographic principles. From the data in Table 3 we obtain:

\[
\ln KD_{\text{Al/Cr}}^{\text{opx/sp}} = \left( 1215 + 3137Cr^{\#p} \right) / T - 0.391
\]

\[ (\lambda^2 = 0.74) \]

The small value of \( \lambda^2 \) shows that the data are well fitted by this simple model. Furthermore, the magnitude of the term in \( Cr^{\#p} \) is similar to that expected from a more rigorous thermodynamic treatment of reaction (8), as this term is equivalent to the Margulies interaction parameter for mixing in the join MgAl\(_2\)O\(_4\)–MgCr\(_2\)O\(_4\) \((W_{\text{Al-Cr}}/R = 2377 \text{ K from Klemme and O’Neill, 2000})\). Further comparison of these results with the simple-system experiments is beyond the scope of this paper, as the addition of FeO to the system is expected to have a large effect by stabilizing Cr in spinel relative to pyroxene, as well as decreasing the total amount of Al\(_2\)O\(_3\) plus Cr\(_2\)O\(_3\) dissolved in pyroxene.

The partitioning of Cr and Al between opx and cpx is shown in the plot of ln KD\(_{\text{Al/Cr}}^{\text{cpx/opx}} \) vs. 1/T in Fig. 16. There are now a large number of melting experiments of natural spinel lherzolite compositions that include studies with significant Cr in pyroxenes (Falloon et al., 1999, Pickering-Witter and Johnston, 2000; Schwab and Johnston, 2001) and also in the system CMAS-Cr\(_2\)O\(_3\) (Liu and O’Neill, 2004); these show that KD\(_{\text{Al/Cr}}^{\text{cpx/opx}} \) is ~1 at solidus temperatures in the range 10–2.0 GPa, which is consistent with the trend displayed in Fig. 16. However, the present data show that Cr distributes preferentially into cpx with cooling below the solidus. Fitting all the data in the above-mentioned experimental studies (76 data) gives:

\[
\ln KD_{\text{Al/Cr}}^{\text{cpx/opx}} = \left( -1141 - 2302N_{\text{Na}}^{\text{cpx}} \right) / T + 0.905
\]

The influence of \( N_{\text{Na}}^{\text{cpx}} \) implies a non-zero free energy for the reciprocal reaction \( \text{CaCr}_2\text{Si}_2\text{O}_6 + 2 \text{NaAl-Si}_2\text{O}_6 = \text{CaAl}_2\text{Si}_2\text{O}_6 + 2 \text{NaCrSi}_2\text{O}_6 \) in cpx, although this parameter is not constrained well from the presently available data, which are all at low or zero \( N_{\text{Na}}^{\text{cpx}} \).

The amount of Cr in olivine (\([\text{Cr}]^{\text{ol}}\), here given in ppm) is very sensitive to temperature (Fig. 17), as previously emphasised by Stosch (1981) and Hervig and Smith (1982); the curiosity here is the relative insensitivity of \([\text{Cr}]^{\text{ol}}\) to \( Cr^{\#p} \), which compositional parameter reflects the activity of Cr\(_2\)O\(_3\) in each xenolith. A working hypothesis is that the thermodynamics of the substitution of Cr in olivine, unlike that in pyroxenes, is indeed controlled directly by charge-coupling with Al, according to a reaction of the type:

\[
\text{MgCr}_2\text{O}_4 + 1/2 \text{MgAl}_2\text{O}_4 = \text{MgCrAlO}_4 \quad (9)
\]

In this case \([\text{Cr}]^{\text{ol}}\) would be proportional to the product \( \text{Cr}^{\#p}(1 - \text{Cr}^{\#p}) \) rather than just simply proportional to \( \text{Cr}^{\#p} \), and a semi-empirical model
incorporating this functional form was found to give a better fit to the data. Assuming the form of reaction Eq. (9), we obtain:

\[
\ln [\text{Cr}]_{\text{ol}} = \ln K_{\text{Cr}^2+/\text{Cr}^{3+}} (1 - \text{Cr}^{2+}) - 10070/T + 14.47
\]

although \(\chi^2_v\) is 5.3, with the uncertainty in [Cr]_{ol} taken as 5% or as observed, whichever is larger. Unfortunately we did not determine the Al contents of olivines, so are not able to test this hypothesis further.

Although there can be extensive substitution of Cr\(^{2+}\) in olivine at very high temperatures or very low oxygen fugacity (Li et al., 1995), circumstantial evidence argues against significant Cr\(^{2+}\) in the olivine of these xenoliths. Firstly, there is no perceptible dependence of [Cr]\(^{3+}\) on Δlog fO\(_2\), although this may be because the range of covered by the xenoliths is not large. More convincingly, there is a remarkable coherence in the partitioning of Cr and V between all four phases, as illustrated, for example, by the parallel behaviour of \(D_{\text{Cr}^{2+}}^{\text{ox}}\) and \(D_{\text{Cr}^{3+}}^{\text{ox}}\) (Fig. 18); this suggests that Cr and V share the same oxidation state in every phase.

It is known from the previous work of Hervig and Smith (1982) that the trend for \(D_{\text{Cr}^{3+}}^{\text{ox}}\) vs. 1/T may look reasonably coherent in a suite of spinel lherzolites (Fig. 18a), but is different in garnet lherzolites, presumably due to the role of Al\(_2\)O\(_3\) in providing the thermodynamic “stoichiometric control” on Cr solubilities, as discussed above. The stoichiometric control for V is likely to be similar, suggesting that the partitioning of V can be treated accurately using two-element distribution coefficients with Cr. Regressions of our Cr and V data are entirely consistent with this, the results being:

\[
\begin{align*}
\ln K_{\text{Cr}^{2+}/\text{V}}^{\text{opx}} &= 864/T - 0.394 \quad (\chi^2_v = 1.1) \\
\ln K_{\text{Cr}^{3+}/\text{V}}^{\text{ol}} &= 532/T - 0.329 \quad (\chi^2_v = 1.3) \\
\ln K_{\text{Cr}^{3+}/\text{V}}^{\text{sp}} &= (3571 - 1163\text{Cr}^{3+})/T - 0.554 \quad (\chi^2_v = 1.8)
\end{align*}
\]

where the uncertainties in \(K_{\text{Cr}^{2+}/\text{V}}^{\text{opx}}, K_{\text{Cr}^{3+}/\text{V}}^{\text{ol}}\), and \(K_{\text{Cr}^{3+}/\text{V}}^{\text{sp}}\) were calculated from the data in Table 2.

The behaviour of Ga is found to be very similar to that of Cr and V, with its concentration decreasing in the order sp \(\gg\) cpx–opx \(\gg\) ol. Unfortunately we chose to measure the \(^{69}\)Ga isotope, which is affected slightly by an interference from \(^{29}\)Si\(^{40}\)Ar. A better choice would have been \(^{71}\)Ga. Based on subsequent work on other xenoliths, the interference inflates the pyroxene abundances by \(-0.2\) ppm, which is a barely significant proportion of the amounts observed and has been ignored. However, the interference dominates the levels in ol (which is probably \(-0.1\) ppm); Ga abundances in ol are therefore not
reported. Two-element distribution coefficients for Ga and Cr are:

\[
\ln KD_{\text{cpx/opx}}^{\text{Cr/Ga}} = -1783/T + 0.790 \quad (\chi_v^2 = 0.76)
\]

\[
\ln KD_{\text{cpx/sp}}^{\text{Cr/Ga}} = (-345 + 2635Cr^{3+})/T - 0.137 \quad (\chi_v^2 = 1.9)
\]

Although the partitioning relations of V and Ga among the solid phases in spinel lherzolite are similar to those of Cr, the partitioning of V and Ga between these phases and silicate melt is quite different from that of Cr, with V and Ga being moderately incompatible whereas Cr is compatible. This suggests that consideration of Cr–V–Ga systematics may have the potential to be a useful tool in understanding basalt petrogenesis.

5.8. Amphibole

Amphibole is preserved in four of our xenoliths, two each in groups III and IV, which groups have equilibrated 100 K apart (Table 2). The amphibole is a chrome pargasite, in which Na\(_2\)O (±K\(_2\)O) is an essential structural component, with Na + K more-or-less filling the A site. In cpx, by contrast, Na\(_2\)O behaves thermodynamically much like a trace-element component, being a relatively minor substitutant into the M2 site. Consequently the partitioning of Na between amphibole and cpx provides a good example of a partitioning relationship that is controlled by crystal chemistry rather than intensive thermodynamic variables such as temperature or pressure. The fact that \(N_{\text{cpx}}^{\text{Na}}\) changes by over a factor of two in the amphibole-bearing samples indicates that it is some component other than Na\(_2\)O that controls the amounts of amphibole, plausibly H\(_2\)O (see reaction Eq. (3) above).

That amphibole is in chemical equilibrium with the other peridotite minerals is attested to well by the smooth amph/cpx REE partitioning patterns, shown in Fig. 19. Three samples have flat patterns of \(D_{\text{REE}}^{\text{amph/cpx}}\) vs. ionic radius (\(R_{\text{VIII}}\)), the fourth (MM110) defines a very smooth linear trend in which \(D_{\text{REE}}^{\text{amph/cpx}}\) decreases with decreasing \(R_{\text{VIII}}\). There is nothing obvious in the chemistry of the amphibole in MM110 to explain why it should behave differently. Apart from the heavy REEs in MM110, there is a remarkably good correlation of \(D_{\text{REE}}^{\text{amph/cpx}}\) with \(N_{\text{Na}}^{\text{cpx}}\), which is nearly quantitatively that expected from the
influence of \( N_{\text{Na}}^{\text{cpx}} \) on cpx/opx and cpx/ol partitioning relations as given in Tables 4 and 5, except that the quadratic dependence of \( D_{\text{REE}}^{\text{cpx/opx}} \) on \( N_{\text{Na}}^{\text{cpx}} \) is not evident (this should cause curved, not flat patterns). This might be rationalised by assuming that the curvature caused by the effect of Na in cpx is counterbalanced by a structural control in amphibole. In fact, the three samples with flat \( D_{\text{REE}}^{\text{amph/cpx}} \) vs. IR can be fitted within analytical uncertainty to the expression:

\[
\ln D_{\text{amph/cpx}}^{\text{REE}} = a_0 + b_0 R_{\text{REE}}^{\text{VIII}} + c_0 \left( R_{\text{REE}}^{\text{VIII}} \right)^2 - \left( a_2 + b_2 R_{\text{REE}}^{\text{VIII}} + c_2 \left( R_{\text{REE}}^{\text{VIII}} \right)^2 \right) N_{\text{Na}}^{\text{cpx}}
\]

(cf. Eq. (5)), with the values of \( a_2, b_2 \) and \( c_2 \) constrained to the values from the global fit of the \( D_{\text{cpx/opx}}^{\text{REE}} \) vs. IR data. These fits are shown in Fig. 19. The light REE in MM110 agree well with this fit, it is the decrease of heavy REE in the amphibole of this sample that is anomalous. Obviously, though, invoking the terms \( b_0 \) and \( c_0 \) to counterbalance the \( b_1 \) and \( c_1 \) terms is special pleading given the few data and further work is required.

The most distinctive features of amphibole trace-element chemistry are the enormous enrichments relative to cpx of the “large-ion lithophile elements” (LILs) K, Rb and Ba. Among the HFSEs, Nb and Ta are also greatly enriched but Zr and Hf are not, and neither are Th and U. The values of \( D_{\text{Ba}}^{\text{amph/cpx}} \) are \( \sim 10^3 \) (Rb is below detection limits in cpx, while K was not determined in this study, hence quantification of these partition coefficients is not possible), while values of \( D_{\text{Nb}}^{\text{amph/cpx}} \) are \( \sim 10^{-2} \). The latter are considerably higher than values of \( D_{\text{Ta}}^{\text{amph/cpx}} \), by about a factor of 4. All these peculiarities are well known, and almost exactly similar partitioning patterns have been observed previously in other mantle xenoliths containing coexisting amphibole and cpx (e.g., Lee et al., 1996; Glaser et al., 1999, their Fig. 6), and in comparisons of experimental determinations of amphibole/melt and cpx/melt partition coefficients (Brennan et al., 1995; Green, 1995). They mean that the role of amphibole in any mantle melting process should be obvious from anomalously low Ba/Th or Nb/Zr ratios. In particular, Ba would appear to become a compatible element if pargasitic amphibole is in the source.

6. Conclusions

Equations summarizing the intercrystalline partition coefficients for incompatible trace elements as a function of temperature are listed for \( D_{\text{M}}^{\text{cpx/opx}} \) in Table 4, and for \( D_{\text{M}}^{\text{cpx/ol}} \) in Table 5. These equations allow the amounts of these incompatible trace elements present in the minerals at magmatic temperatures to be calculated, if the modal amounts of cpx, opx and ol
Green et al. (2000) run 1080°C, 2 GPa

MPY-90 1255°C, 1.5 GPa

McDade et al. (2003) Tinaquillo lherzolite 1315°C, 1.5 GPa
at this temperature are reconstructed from the major-element phase relations.

The equations in Table 4 may be evaluated for internal consistency with experimental work in which cpx/melt and opx/melt partition coefficients were measured in the same run, since \( D^{\text{M}}_{\text{cpx/melt}} = D^{\text{M}}_{\text{cpx/opx}} / D^{\text{M}}_{\text{opx/melt}} \) at the temperature of the experiment. For example, in Fig. 20 a,b and c, we compare some experimental values of \( D^{\text{M}}_{\text{cpx/opx}} \) for large suites of trace elements obtained in this way with our own results. Agreement is generally good, although there are some inconsistencies, the cause of which should become clearer as the experimental database on trace-element partitioning in multiply saturated phase assemblages increases.

A most important conclusion from this study is that opx can be a significant carrier of many incompatible trace elements at magmatic temperatures. In the case of the HFSEs (Ti and Zr), the role of opx as the host phase been pointed out previously by Rampone et al. (1991) and McDonough et al. (1992), from analyses of subsolidus re-equilibrated opx/cpx pairs as found in actual peridotites; but here we emphasise that opx will also host a substantial fraction of the whole-rock budget of other incompatible trace elements, when values of \( D^{\text{M}}_{\text{cpx/opx}} \) are extrapolated back to magmatic temperatures.

In fact, it is a common assumption in the literature on the geochemistry of peridotites that cpx carries most of the whole-rock’s incompatible trace elements. This may indeed be the case after subsolidus re-equilibration (with the exception of HFSEs, noted above), which permits using cpx analyses, obtained with SIMS or LA-ICP-MS, as a proxy for whole-rock values. But it is not then valid to use these measured subsolidus cpx concentrations with values for cpx/melt partition coefficients (\( D^{\text{M}}_{\text{cpx/melt}} \)) to calculate the melt trace-element abundances that were in equilibrium with the peridotite. The data presented here show that the temperature-dependence of cpx/opx and even cpx/ol partition coefficients results in significant fractions of incompatible trace elements being held in opx (± ol) at magmatic temperatures, which will repartition during subsolidus cooling into cpx. For example, the partition data plotted in Fig. 7 suggests that steeply sloping REE patterns in cpx, thought to be characteristic of “ultra-depleted” melts, could instead be generated by subsolidus re-equilibration of residual peridotite, in which the cpx is produced from the CaO that was held in opx and ol at the temperature of the melting regime.

The interpretation of cpx trace-element patterns (indeed, any kind of mineral trace-element pattern) in terms of equilibrium with a melt (or fluid) therefore requires not only the reconstruction of mineral compositions as a function of temperature, but also an estimate of the temperature at which the rock would have been in equilibrium with the melt or fluid. This requires that the major-element and volatile content of the melt or fluid and its stability relations be known. Disembodied trace-element data, divorced from their major-element contexts and considered in isolation from phase-equilibrium constraints, are likely to lead to erroneous conclusions.

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