

Thermodynamic modelling of Cr-bearing garnets with implications for diamond inclusions and peridotite xenoliths

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ABSTRACT

A new approach is presented for modelling Cr-rich peridotite compositions and garnet–spinel compositions found in diamonds and xenoliths at conditions relevant to the deep continental Earth. Using recent experimental data, it is now possible to calculate phase relations and mineral compositions relevant to pressures, temperatures, and compositions of the deep lithospheric Earth using free energy minimization techniques. Here we present calculated phase relations in Cr-rich mantle compositions from pressures of 20–60 kbar, and temperatures 800–1400 °C. The model is successful at modelling a wide range of natural mineral compositions which are found as xenoliths in diamond-bearing kimberlites from South Africa, and is illustrated using suites of Cr-rich xenoliths from near Kimberley, South Africa. The model can explain and quantify instances of garnet zonation in naturally occurring mantle rocks as a consequence of pressure–temperature re-equilibration; and shows that not all garnet zonations result from metasomatic processes. This sheds further light on peridotitic diamond inclusions and their abundances, and allows further quantitative constraints to be applied to diamond-indicator mineral chemistry.

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1. Introduction

Natural diamonds are primarily found along with mantle fragments, so-called xenoliths, in kimberlitic eruptive rocks which are mainly found in Archaean cratons (O'Reilly et al., [this issue](#)). The chemical composition of many of the mantle xenoliths from kimberlites is typically depleted in Al and characterized by high Cr/(Cr + Al) when compared to mantle xenoliths from alkali basalts which sample a shallower part of the mantle. The garnets found as inclusions inside diamonds are also often distinctively Cr-rich and Ca-poor e.g., among many others (Smith et al., [this issue](#)). These features imply a correlation between garnet composition and the circumstances and conditions of diamond formation, and as a result Cr-pyrope garnet and Cr-rich spinel are usually the most important two diamond indicator minerals used in the diamond exploration industry (e.g., Fipke et al., 1995; Grütter, [this issue](#)). However, this relation has only been empirically derived. Here we

present a novel approach trying to calculate phase relations based on a set of new thermodynamic data in Cr-rich systems relevant to the deeper Earth's mantle, which will allow quantitative assessment of the *P–T* conditions of diamond formation.

Experimental studies on spinel in the model system CaO–MgO–Al₂O₃–SiO₂ (CMAS) (O'Neill, 1981) show only a limited stability field up to less than 20 kb on a normal continental steady-state geotherm (Fig. 1). However, in simple, Cr-rich systems (e.g., MgO–Cr₂O₃–SiO₂ or MgO–Al₂O₃–Cr₂O₃–SiO₂) the stability field of spinel is extended to pressures of more than 70 kb (Doroshev et al., 1997; Klemme, 2004). In addition to previous studies (Chatterjee et al., 1982; Mattioli and Bishop, 1984; Oka et al., 1984) a number of experiments involving the Mg- and Cr-end members of garnet and spinel (i.e. knorringite and magnesiochromite, respectively) and pyroxenes (Brey et al., 1991; Klemme and O'Neill, 1997; Brey et al., 1999; Klemme and O'Neill, 2000a; Giris et al., 2003; Klemme, 2004; Klemme et al., 2005) have allowed thermodynamic parameters in Cr-bearing systems to be established and thereby allow calculations of *P–T* conditions of formation of spinels and garnets over the whole range of Cr–Al compositions.

Historically, mantle garnet compositions have been divided empirically largely on the basis of their Ca and Cr compositions (Dawson and Stephens, 1975), (Fig. 2a). An important dividing line in

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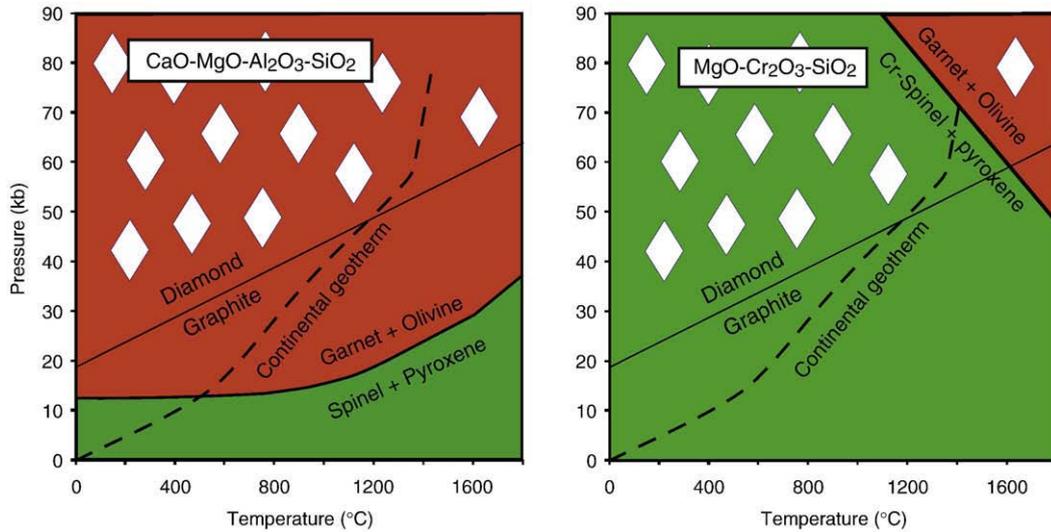


Fig. 1. Pressure–Temperature diagram illustrating the spinel (green) and garnet (red) stability fields in the Cr-free model mantle composition CaO–MgO–Al₂O₃–SiO₂ (O'Neill, 1981; Klemme and O'Neill, 2000a,b) and the simple MgO–Cr₂O₃–SiO₂ system (Klemme, 2004). Also shown are the diamond stability field (white diamonds), the diamond–graphite reaction line (Kennedy and Kennedy, 1976), and a cratonic geotherm (McKenzie et al., 2005). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

such classification is the 'Iherzolite line' (Sobolev et al., 1973) or the 'G10/G9 line' (Gurney, 1984), which classifies garnets from olivine–orthopyroxene–garnet assemblages into either harzburgitic (Ca-poor and essentially without coexisting clinopyroxene) or Iherzolitic (Ca-rich and with coexisting clinopyroxene). Gurney (1984) estimates that 85% of the garnets found as inclusions in diamonds lie in the harzburgitic (G10) field. This empirical observation has been the basis of diamond exploration since the early 1980s. Clearly, it was implied that kimberlitic G10 garnets were stable and of common occurrence in the high pressure diamond stability field.

Fig. 2a illustrates the general CaO–Cr₂O₃ composition fields for garnets in association with mantle rocks; for thermodynamic and mineral formula purposes we present this diagram in terms of atomic proportions rather than the usual weight percentages (Ivanic, 2008). Within the harzburgitic (low Ca) field the peridotitic garnets associated with diamonds have shown a bias to high Cr compositions

(Gurney, 1984); and Grütter et al. (2004) defined an empirical boundary at high Cr for diamond paragenesis garnets using compositions found in Roberts Victor diamond-bearing peridotites. However, up to now the actual pressures and temperatures associated with these special compositions have not been quantitatively constrained with a thermodynamic model.

The aim of this paper is to demonstrate a new thermodynamic model with which we can calculate phase relations, and garnet (and other mineral) compositions in complex and Cr-rich compositions at pressures and temperatures relevant to the deep continental lithosphere. This will allow us to quantify and explain the observed empirical trends in diamond indicator garnets (Grütter, this issue), and thereby refine exploration techniques. The model applies to a wide range of compositions and not just Ca-poor harzburgitic ones. To illustrate the thermodynamic model we present calculated phase relations and mineral compositions for a small subset of well-

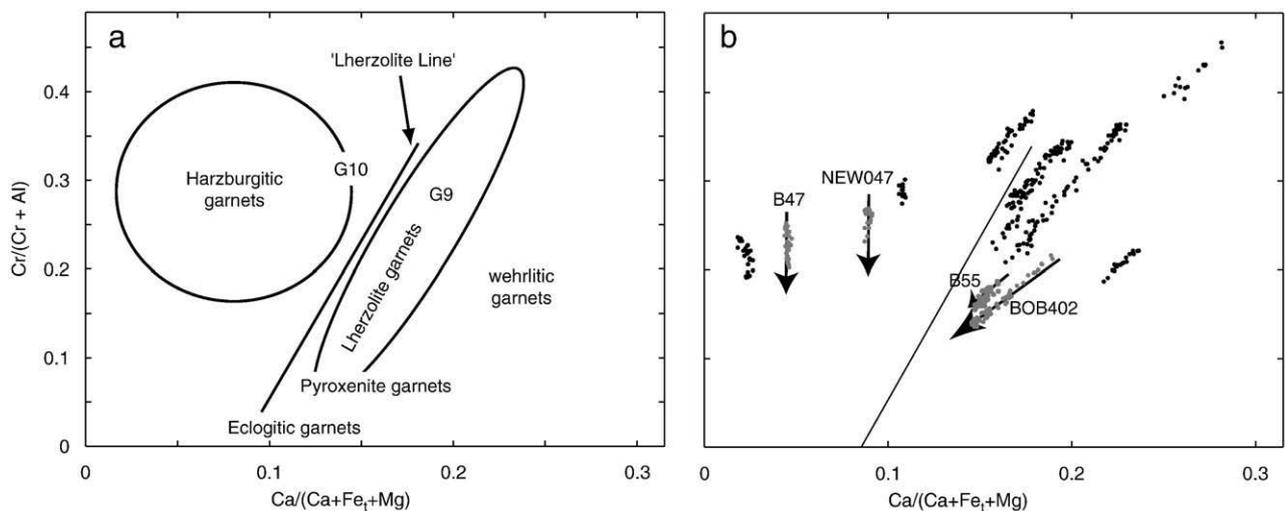


Fig. 2. (a) Garnet Ca/(Ca + Fe_t + Mg) vs. Cr/(Cr + Al) diagram illustrating the location of the Iherzolite line (Sobolev et al., 1973; Gurney, 1984) which separates G10 harzburgitic garnets at low-Ca from G9 Iherzolitic garnets at higher Ca. The approximate fields for garnets from wehrlitic, pyroxenitic and eclogitic xenoliths are also shown. (b) as for (a) except showing the garnet zonation trends in peridotitic samples from Newlands (NEW047) and Bobbejaan (B47, B55, BOB402) kimberlites (Ivanic, 2008). The natural garnets from Iherzolitic samples B55 and BOB402 are strongly zoned in Ca/(Ca + Fe_t + Mg) and Cr/(Cr + Al) which is evident from steep positive slopes in such a Ca/Cr diagram (arrows). The natural garnets (arrows) from the harzburgitic samples B47 and NEW047 exhibit much steeper, almost vertical slopes at much lower Ca/(Ca + Fe_t + Mg) and similar Cr/(Cr + Al). Garnets from these samples always have high Ca and Cr cores and zonation trends from core to rim are indicated by arrows. Refer to text for further information. Fe_t = total Fe as measured by electron microprobe.

Table 1
Bulk compositions.

	B47	NEW047	B55	BOB402
SiO ₂	42.8	42.8	38.8	41.6
Al ₂ O ₃	12.2	12.2	14.8	11.5
Cr ₂ O ₃	5.9	5.9	10.1	9.6
FeO	5.8	5.8	9.1	7.7
MgO	32.2	30.8	18.9	20.2
CaO	1.2	2.6	8.0	8.9
Na ₂ O	0	0	0.4	0.5

Bulk compositions of four peridotite xenoliths used for thermodynamic modelling. Details are given by Ivanic (2008). Bulk rock compositions were estimated from electron microprobe analysis of minerals and modal abundances.

characterized natural xenoliths which cover a wide range of rock types ranging from low-Ca garnet-rich harzburgite, to higher Ca garnet-rich lherzolite and wehrlite (Ivanic, 2008).

The samples comprise garnet-rich xenoliths less than 2 cm in diameter, derived from coarse kimberlite concentrate from the Newlands and Bobbejaan kimberlites, South Africa. In these xenoliths garnet is often >50% modal abundance and often exhibits a granuloblastic texture with approximately 120° grain boundary triple junctions. The matrix may be of harzburgitic (clinopyroxene free) or lherzolitic (clinopyroxene present) affinity. Orthopyroxene and olivine are usually completely altered to serpentine by secondary alteration. In some cases the edges of the samples, which were in contact with kimberlite magma, have been altered to kelyphite. Garnet in these xenoliths may be considerably higher modally than other minerals due to removal of serpentine through mine crushing processes. However, since garnet appears to have reacted with adjacent minerals in the samples forming zonation, thermodynamic treatment of the samples as a whole is considered acceptable.

Care was taken to exclude samples with garnets showing evidence for metasomatic overprinting of the types described by Burgess and Harte (2004). The samples referred to in this paper are without any normal evidence of metasomatism in the form of garnet core-to-rim Ti and/or REE zonation. For details refer to Ivanic (2008).

The selected Newlands and Bobbejaan garnets characteristically show extensive compositional zonation in Cr/(Cr + Al) and sometimes Ca/(Ca + Mg + Fe). Specific samples discussed in this paper are: B55 (lherzolitic), BOB402 (wehrlitic), B47 (low Ca harzburgitic), NEW047 (high Ca harzburgitic); which all contain more than 4 wt.% Cr₂O₃ but with a wide range of CaO extending from low-Ca harzburgitic compositions to high-Ca lherzolitic ones (Fig. 2b). The extensive Cr/(Cr + Al) garnet zonation is interpreted to be caused by re-equilibration due to changes in pressure and temperature (Ivanic, 2008). Bulk rock compositions for the xenoliths were calculated from mineral analyses and modal proportions (Table 1).

2. Description of model and method

We use the 'Perplex' programs to calculate phase relations for our selected rock compositions (Connolly, 1990; Connolly and Petriani, 2002). The Perplex uses free-energy minimization to compute mineral

compositions and mineral modes for specified bulk compositions, temperature and pressure. For further details on numerical methods and previous applications refer to Connolly (1990) and Connolly and Petriani (2002) and some applications of the model in Cr-free mantle compositions have been reported (Kelly et al., 2003). The current database (<http://www.perplex.ethz.ch/>) includes internally consistent thermodynamic data (Holland and Powell, 1998) with additional data for Cr-spinels, Cr-garnets, and Cr-pyroxenes based on a series of recent experimental and thermodynamic studies (Brey et al., 1991; Klemme and O'Neill, 1997; Brey et al., 1999; Girmis and Brey, 1999; Klemme et al., 2000; Klemme and O'Neill, 2000a,b; Girmis et al., 2003; Klemme, 2004). This allows Cr-rich peridotitic bulk rock compositions like those of the Newlands and Bobbejaan samples in this study to be modeled thermodynamically in complex systems.

Thermodynamic data for Cr-bearing endmembers relevant here are listed in Table 2. The model contains thermodynamic endmember data and mixing properties for Cr-bearing spinels (Oka et al., 1984), eskolaite-corundum solid solution (Chatterjee et al., 1982), garnets (Mattioli and Bishop, 1984), and pyroxenes. For Cr-bearing pyroxenes, we adopted a simplified mixing model which is based on the Klemme and O'Neill (2000a) experiments. As there is only little data for Cr-bearing clinopyroxene we adopted a simple model also based on the Cr-Al mixing described by Klemme and O'Neill (2000a). Note that the thermodynamic model for pyroxenes is not quite complete, yet, as it does not, e.g. allow for Ca in orthopyroxene. This causes slight problems when one calculates orthopyroxene compositions. See below for some discussion. Thermodynamic data for knorringite (Mg₃Cr₂Si₃O₁₂) are based on the Klemme (2004) experiments, and ideal mixing for Cr-Al bearing garnets was assumed based on the measurements by Mattioli and Bishop (1984). The model itself and the database used are available for download on the world-wide-web at <http://www.perplex.ethz.ch/>.

3. Results and discussion

Phase diagram sections were generated for each bulk rock composition (Table 1) at temperatures between 800 and 1400 °C and pressures between 20 and 60 kb (Fig. 3a–d). To illustrate the response of mineral compositions to changes in pressure and temperature for our selected bulk compositions, we have plotted garnet and spinel compositions in Fig. 3e–h. Furthermore, we have plotted modal abundances of minerals (vol.%) along a typical steady state continental geotherm (McKenzie et al., 2005) in Fig. 3i–l.

The selected bulk compositions range from the harzburgitic samples (B47 and NEW047) through to lherzolitic samples (B55 and BOB402) with higher CaO and Cr₂O₃ (Table 1). Our calculations show that these changes in bulk composition from harzburgite to lherzolite affect phase relations rather drastically. Comparing Fig. 3a and b to Fig. 3c or d one can see that the spinel stability field extends to much higher pressure and temperatures in lherzolitic compositions, and this corresponds with the expected increase in clinopyroxene stability at higher CaO bulk compositions.

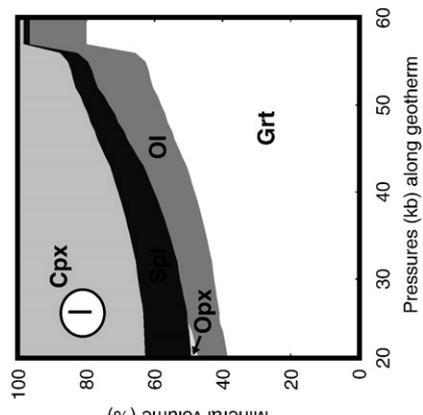
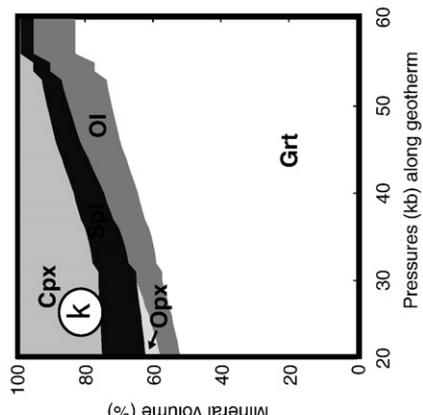
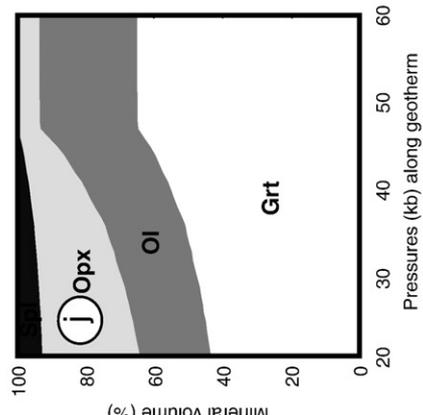
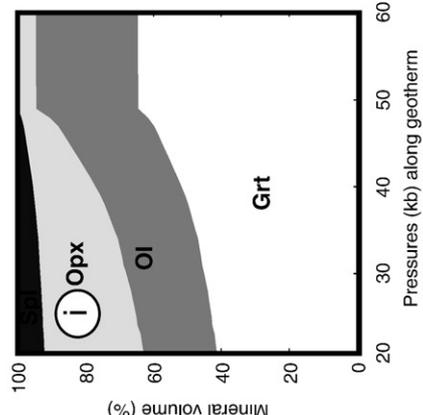
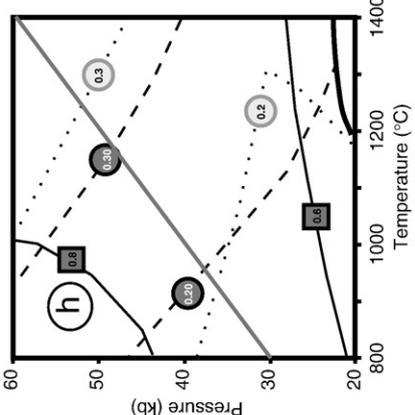
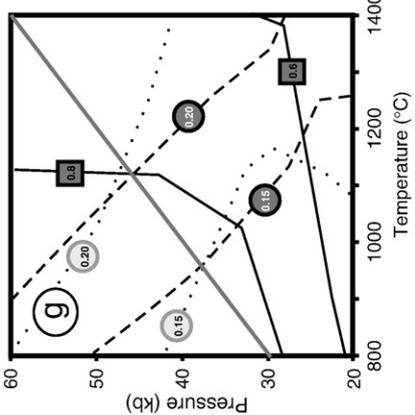
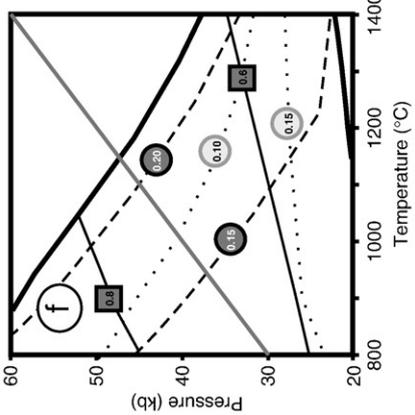
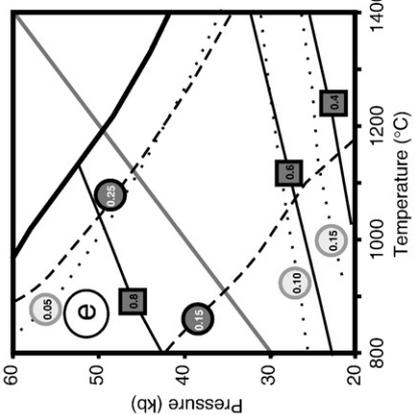
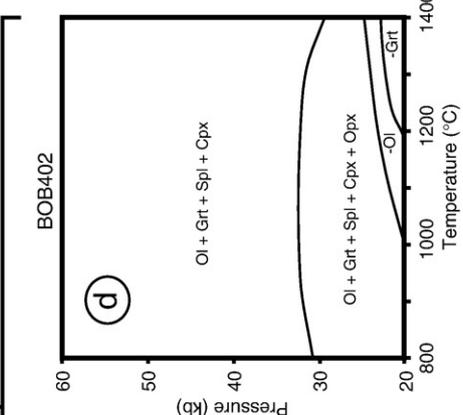
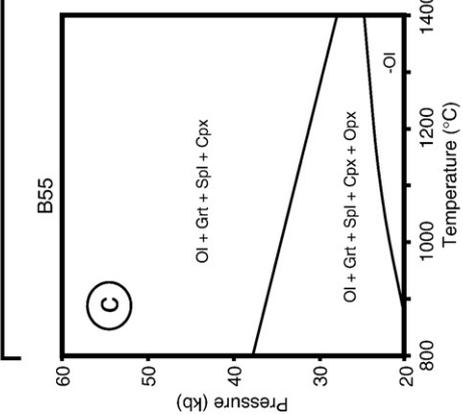
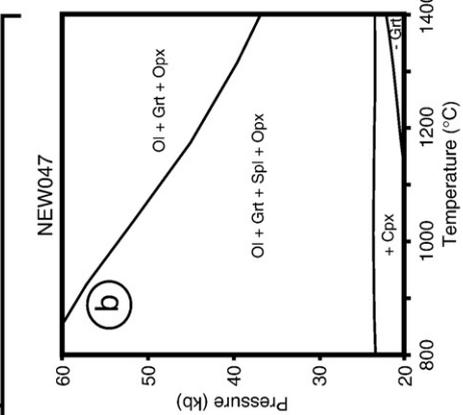
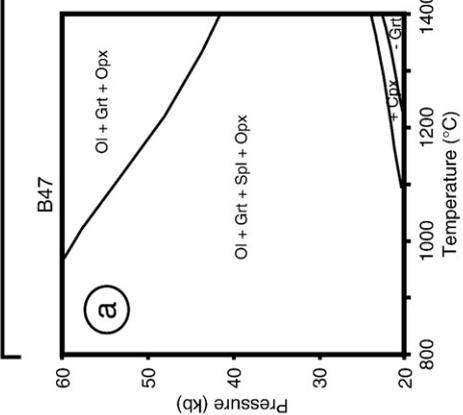
Table 2
Thermodynamic data.

	S ₂₉₈ [°] J mol ⁻¹ K ⁻¹	ΔH J mol ⁻¹	V J bar ⁻¹	a J mol ⁻¹ K ⁻¹	b J mol ⁻¹ K ⁻²	c J K mol ⁻¹	d J mol ⁻¹ K ^{-0.5}
FeCr ₂ O ₄	152.2	-1332863	4.441	139.75	0.294 × 10 ⁻¹	-3359576	474.8
MgCr ₂ O ₄	119.6	-1650534	4.356	221.24	-0.10203 × 10 ⁻²	-1757210	-1247.9
Cr ₂ O ₃	83.1	-1046177	2.9054	227.25	-0.2132 × 10 ⁻¹	3543029	-2567.3
MgCr ₂ SiO ₆	169.3	-2494378	6.2	220.0	0.47 × 10 ⁻²	-3780000	-1016.0
c-MgCr ₂ SiO ₆	176.3	-2611446	6.656	196.2	0.18 × 10 ⁻²	-5163200	-226.4
Mg ₃ Cr ₂ Si ₃ O ₁₂	357.9	-5275960	11.318	633.5	0	-5196.1	-4375

S₂₉₈[°] is the standard entropy, ΔH the enthalpy of formation, V the volume at 1 bar, a, b, c, d are the coefficients in the heat capacity polynomial Cp = a + bT + cT⁻² + dT^{-0.5}. The Cr-Tschermaks molecule was used instead of more traditional pyroxene endmembers to ensure that Cr-rich pyroxenes were modelled correctly in Cr-rich systems. See Klemme and O'Neill (2000a) for further discussion on pyroxene endmembers.

HARZBURGITES

LHERZOLITES



(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

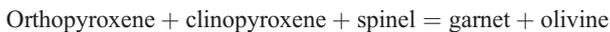
(j)

(k)

(l)

Fig. 3e–h illustrate the change of garnet and spinel composition with pressure and temperature for the four different bulk compositions. With increasing CaO in bulk composition from harzburgite (Fig. 3a–b) to lherzolite (Fig. 3c–d), we observe that garnet compositions are a complex function of pressure and temperature, e.g. we observe only slight effects of P and T on the Ca-isopleths for garnet in harzburgitic compositions (Fig. 3e–f) but much stronger effects of P and T on garnet compositions in lherzolitic bulk compositions (Fig. 3g–h). Spinel isopleths for $\text{Cr}/(\text{Cr} + \text{Al})$ are nearly always positively sloped in P – T space, whereas the garnet $\text{Cr}/(\text{Cr} + \text{Al})$ isopleths are negatively sloped in P – T . This is in good agreement with recent experimental observations (Girnis et al., 2003). The higher Cr and Ca concentration in the lherzolitic samples tend to stabilize spinel and clinopyroxene, respectively. Furthermore, looking along a geotherm (light grey line in Fig. 3e–h) one can see that garnet $\text{Cr}/(\text{Cr} + \text{Al})$ and $\text{Ca}/(\text{Ca} + \text{Fe}_t + \text{Mg})$ in lherzolite decrease rapidly with decreasing P and T , whereas in harzburgite only the $\text{Cr}/(\text{Cr} + \text{Al})$ decreases rapidly with P – T at more or less constant $\text{Ca}/(\text{Ca} + \text{Fe}_t + \text{Mg})$. We also observe that spinel compositions also decrease in $\text{Cr}/(\text{Cr} + \text{Al})$ with decreasing P – T along a cratonic geotherm.

Fig. 3i–l illustrates the modal proportions for our four bulk compositions along a continental cratonic steady state geotherm (grey line in Fig. 3e–h) (McKenzie et al., 2005). We observe, in all cases, that garnet and olivine abundances decrease with decreasing P and T , whereas spinel and pyroxene modes increase. Furthermore, the calculations illustrate nicely how modal proportions in the mantle obey the reaction between spinel peridotite to garnet peridotite (O'Neill, 1981; Robinson and Wood, 1998; Klemme and O'Neill, 2000b) which is as follows



At lower pressures and temperatures (Fig. 3i–l) we find more normal peridotitic mineral compositions and modal proportions. However, an increase in pressure leads, in all cases, to very garnet and olivine-rich rocks, which are virtually olivine garnetites.

3.1. Calculated vs. natural garnet compositions

In order to test whether the model conforms well to P – T – X trajectories in natural samples we show in Fig. 4 calculated garnet compositions (lines) over a range of pressures and temperatures (1400–800 °C, 60–30 kbar) along a continental steady state geotherm (McKenzie et al., 2005) for our four different bulk rock compositions. The garnets from the natural samples are strongly zoned in major elements. The garnet cores are always higher in $\text{Cr}/(\text{Cr} + \text{Al})$ in both harzburgites and lherzolites; in addition CaO is invariably higher in the cores of the lherzolite samples (Fig. 2b). The observed zonation trends have been interpreted to be caused by re-equilibration due to changes in pressure and temperature (Ivanic, 2008). Now we can test this hypothesis using our thermodynamic model generating some quantitative constraints.

We find that the calculated garnet compositions agree well with the observed zonation trends in the natural samples, both in location and in slope for the major elements (Fig. 4). Minor discrepancies may be readily explained because the thermodynamic model used does not contain Mn, Ti and K, and it does not account, yet, for Na in garnet or Ca in orthopyroxene.

Overall, however, the slopes of the zonation trends are well reproduced in our model and in lherzolitic samples these mark the

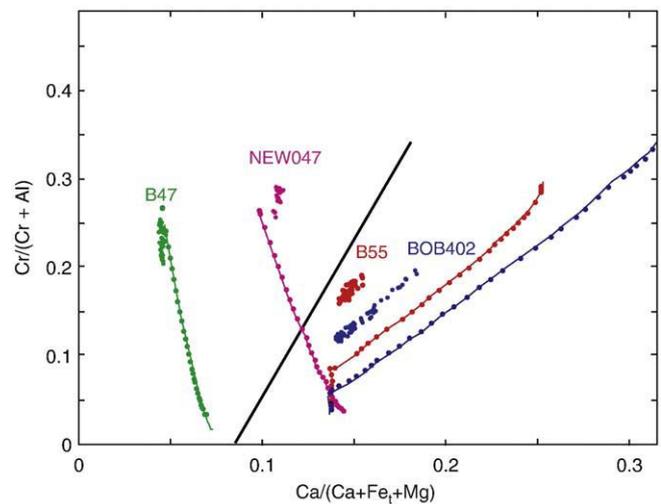


Fig. 4. Garnet $\text{Ca}/(\text{Ca} + \text{Fe}_t + \text{Mg})$ is plotted against $\text{Cr}/(\text{Cr} + \text{Al})$ cation compositions for garnets from our natural samples (B47, NEW047, B55, BOB402; c.f. Fig. 2b) compared to calculated garnet compositions (dots connected by coloured lines) along a continental geotherm (from 1400 °C, 60 kbar to 800 °C, 30 kbar, see also Fig. 3.) for identical bulk rock compositions. Note that calculated garnet compositions reproduce observed garnet zonation trends in all four samples. Hence the observed natural zonation trends can be explained by decompression on a continental geotherm, see text for more discussion. The calculations also indicate that garnet cores from harzburgitic samples (B47, NEW047) originate from much higher pressures than the lherzolitic garnets. Fe_t = total Fe as measured by electron microprobe. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

response of garnet composition to the presence of clinopyroxene in peridotite. Over our pressure–temperature range clinopyroxene is calculated to be stable in BOB402 and B55, but not in the harzburgitic samples B47 and NEW047. This agrees well with natural assemblages observed. The small kink at the low end of the lherzolitic garnets in Fig. 4 represents the response of the garnet compositions to the incoming of orthopyroxene (Fig. 3k and l).

In terms of the slopes of the garnet trajectories in Fig. 4, our model explains that in the harzburgitic garnets, Ca partitions only into garnet, and garnet compositions are simply controlled by bulk compositions and modal properties in a spinel-bearing system. Hence the Ca composition of garnet does not change much with P – T as garnet modes (at rather low Ca bulk rock compositions) do not vary much along the geotherm (see Fig. 3i and j). However, the lherzolitic samples have clinopyroxene present and garnet CaO content seems to be controlled primarily by the changing modal abundance of clinopyroxene (see Fig. 3k and l). We have adopted the P – T path of decompression as following a model geotherm because we assume the overall changes in P and T conditions over time will largely correspond to those of such a geotherm. Small-scale P – T departures from a model geotherm may have occurred but we have no knowledge of the tectonic setting for decompression. Calculated isobaric cooling and isothermal decompression paths, although not shown here, yield trajectories which match less well than the geothermal path used.

The observed zonations in natural garnet samples (Fig. 2) can be simply explained by decompression along a model geotherm. Whilst other changes in garnet compositions, as projected into Cr_2O_3 –CaO diagrams, have been explained by a variety of metasomatic processes (Griffin et al., 1999; Burgess and Harte, 2004) these are not required to explain the chemical compositions of the natural samples studied here. Note that the zonation trends of our natural garnet samples

Fig. 3. (a–d) Phase diagrams for bulk rock compositions for samples B47, NEW047, B55 and BOB402 arranged in order of increasing $\text{Ca}/(\text{Ca} + \text{Fe}_t + \text{Mg})$ composition. Assemblages are shown using mineral abbreviations from Kretz (1983). (e–h) garnet and spinel compositional isopleths for the four samples in sequence. Garnet $\text{Cr}/(\text{Cr} + \text{Al})$ shown in dark grey circles and dashed line, garnet $\text{Ca}/(\text{Ca} + \text{Fe}_t + \text{Mg})$ shown in light grey circles and dotted line, and spinel $\text{Cr}/(\text{Cr} + \text{Al})$ shown in dark grey squares and solid black lines. A steady-state continental geotherm is shown as a light grey line ranging from 60 kbar 1400 °C down to 30 kbar and 800 °C (McKenzie et al., 2005). (i–l) Modal proportions (% volume) of minerals present in each bulk rock composition are shown for pressures and temperature along the geotherm shown in e–h.

coincide with garnet compositions from mineral separates commonly used in diamond exploration.

4. Conclusions

1. We have shown that we can successfully model Cr-bearing peridotitic mineral assemblages using our thermodynamic model for pressures and temperatures relevant to the subcontinental lithospheric mantle. The model is able to closely reproduce natural mineral compositions for a given bulk composition, and it can be used to predict changes in mineral composition and modal abundance with changing pressure and temperature.
2. Specific zonation trends in natural mantle garnets from diamondiferous kimberlites may now be explained by geothermal decompression P - T paths at constant bulk composition, without needing to invoke processes of metasomatism. Features of the observed chemical variation of natural diamond indicator minerals (garnet, clinopyroxenes and Cr-spinel) may be explained by variation in pressures and temperatures of formation and re-equilibration.
3. Using our model we calculate increasing Cr/(Cr + Al) for harzburgitic garnets with increasing pressure and temperature along a geotherm. Thus we can explain why Cr-rich garnets in harzburgite are likely to be present in diamond-bearing rock, and hence are so-called diamond indicator minerals. However, in terms of pressure and temperature, there is no a priori reason to exclude high-Ca high-Cr lherzolitic garnets as potential diamond indicator minerals.

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