A Thermodynamic model for the subsolidus evolution and melting of peridotite

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ABSTRACT

We present a structural update to the thermodynamic model for calculating peridotite phase relations and melt compositions at 0.01 to 60 kbar and from 600°C to the peridotite liquidus in the system K$_2$O–Na$_2$O–CaO–FeO–MgO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–Fe$_2$O$_3$–Cr$_2$O$_3$ (KNCFMASTOCr), based on the model of Holland et al., 2018 [Melting of Peridotites through to Granites: A Simple Thermodynamic Model in the System KNCFMASHTOCr. Journal of Petrology 59, 881–900]. The new model is better able to predict the phase relations and melting of ultramafic rocks, in particular the abundance of orthopyroxene in the residue and the concentration of silica in the melt. In addition, improvements in modelling Cr-spinels mean that the model is now able to reproduce Cr-content of garnet and spinel above and below the solidus without modification to the knorringite free energy. Model calculations indicate that, for peridotite composition KR4003, the spinel to garnet transition intersects the solidus at 22.1–24.8 kbar and orthopyroxene disappears from the solidus at 29.1 kbar. Below the solidus, the model is able to reproduce the abundances and compositions of phases in experimental studies and natural samples spanning a range of compositions, allowing it to be used for investigating subsolidus equilibration during mantle cooling and pressurisation/decompression. The liquid model provides a good fit to experimental data and is able to replicate the position of the solidus and the composition of both melt and residue at and above the solidus for a range of peridotite compositions. The model may therefore be used to investigate fractional mantle melting and basalt generation in modern geodynamic regimes, and also to explore equilibrium mantle melting in the early Earth. The model can also be used to explore liquid and residue compositions for melting of non-pyrolitic mantle, for which there is a paucity of experimental data. We demonstrate the scope of the model using two case studies investigating the subsolidus evolution and melting of a silica-rich cratonic peridotite from the Kaapvaal craton.

Keywords: Modelling, peridotite, mantle, phase equilibria, basalt

INTRODUCTION

The Earth’s upper mantle is dominated by peridotite, which is composed of variable proportions of olivine, orthopyroxene, clinopyroxene and garnet/spinel. Mineralogical and compositional variability among peridotites is attributed to differences in the depth and degree of partial melting in the mantle, as well as to subsequent metasomatic events. Peridotite variability is particularly evident in xenoliths from Archaean sub-cratonic lithospheric mantle (SCLM), which vary from silica rich harzburgites typical of the Kaapvaal and Siberian cratons, through more normal peridotites from the Slave craton, to silica-poor dunites found in the North Atlantic craton.

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A handful of experimental studies have investigated subsolidus mineral compositions in fertile peridotite with the aim of developing geothermobarometers appropriate to the upper mantle (Brey et al., 1990, 2008; Taylor, 1998). Jennings and Holland (2015) provided the first thermodynamic model for peridotites in the system NCFMASOCr and applied this model to fertile peridotite. However, there remains a need to model complex natural peridotite of variable composition and at subsolidus conditions appropriate to oceanic and cratonic geothermal gradients such that the modal abundances and compositions of minerals can be predicted accurately. This would allow equilibration pressure and temperature to be estimated from the compositions of minerals within peridotites of known bulk composition, an application that would be particularly useful for garnet-free peridotites for which there are no appropriate geobarometers. Such a model could also be used to predict changes in mineralogy and mineral composition that occur during subsolidus re-equilibration following changes in prevailing temperature and/or pressure conditions and would allow modelling of the redistribution of trace elements as a result of this process (e.g. Sun and Liang, 2014).

Above the solidus, numerous experiments have investigated the melting of fertile peridotite with the aim of understanding the origin of basalt (Takahashi and Kushiro, 1983; Baker and Stolper, 1994; Falloon et al., 1999) and komatiite (Takahashi and Scarfe, 1985; Takahashi, 1986; Zhang and Herzberg, 1994; Herzberg and Zhang, 1996, 1997; Walter, 1998). Peridotite melting may also be investigated using thermodynamic models. The generation and differentiation of basaltic melts may be modelled to 30kbar using MELTS and pMELTS (Ghiorso and Sack, 1995; Ghiorso et al., 2002), while phase relationships during peridotite melting may be investigated to 60 kbar using the NCFMASOCr THERMOCALC model of (Jennings and Holland, 2015). The NCFMASOCr model represented a significant advance, but stabilised garnet to higher degrees of melting than observed in experiments and underestimated the Cr-content of garnet, while the KNCFMASHTOCr model (Holland et al., 2018) also overestimated the abundance of orthopyroxene. There thus remained a need to model the melting of peridotite, particularly at high pressures, such that the phase relations and residue and melt compositions are predicted accurately. Such a model would be useful for trace element modelling of the melting process, for predicting the effects of melt rock reaction on melt and residue compositions and for investigating the consequences of melting non-pyrolitic mantle.

In this contribution, we build on the work of Jennings and Holland (2015) and Holland et al. (2018) to develop a new thermodynamic model for peridotite. We then use this model to explore the origin of garnet within cratonic peridotites from Kimberlite (Kaapvaal craton). Finally, we explore the effect of melting silica-rich, non-pyrolitic peridotite mantle.

**MODEL**

The essentials of the model, and the calibration data used, remain much as in the earlier version of Holland et al. (2018) so only the changes and updates will be recorded here. Full details are given in the Appendix. The new model is driven largely by the motivation to agree better with the modal proportion of residual phases in the melting interval of peridotites, as experimentally determined by Walter (1998) and others, as detailed below.

The files necessary for performing the calculations may be found by following links to software at https://www.esc.cam.ac.uk/directory/tim-holland

*Structural changes*

Recognising that the proportion of orthopyroxene in modelled peridotite melt residue was problematic in the earlier models, we address this by several changes to the structure of the
melt model. Firstly, we introduce an intermediate liquid species of enstatite composition to provide greater flexibility in the free energy relations between forsterite and silica. Secondly, we change the size of the silica end-member to Si$_3$O$_6$ in this study, to lie between Si$_2$O$_4$ in Jennings and Holland (2015) and Si$_4$O$_8$ in Holland et al. (2018). Thirdly, we change the sodic melt species from jadeite to nepheline composition and introduce an intermediate albite end-member and a sanidine-composition intermediate-member. These additions should allow better representation of melts undersaturated in silica. Fourthly, we use wollastonite and anorthite end-members (as in Green et al., 2016) in place of the single cats end-member, again for additional flexibility in modelling the Gibbs energy of the melt. The new activity model for melt is given in the Appendix.

Other changes
Apart from the requirement to calibrate the new end-members above, we have taken the opportunity to make the following improvements:
(1) Upgrade was made of the Ti end-members in solids and melt. The heat capacity of rutile used in the Holland & Powell (2011) dataset was from (Robie et al., 1978) whereas we now use the data from Robie and Hemingway (1995). This has led to significant modifications for the Ti-bearing end-members ilm, geik, and pnt.
(2) The spinel model in Holland et al. (2018) assumed Cr-Al mixing that was much too ideal, which then required unreasonable adjustments to the enthalpy of knorringite end-member of garnet in partial compensation. To satisfy simultaneously the MASCr and CMASCr experiments of Klemme and O’Neill (2000) involving garnet, clinopyroxene, orthopyroxene and spinel, and the olivine-spinel Fe-Mg exchange experiments of Engi, (1983), we had to make the interaction energies between picrochromite and the other spinel end-members large and negative. Unlike the near-ideal Cr-Al interactions in clinopyroxene, these large negative energies in spinel may reflect a preference for Cr to order onto one of the two octahedral sites. Whatever the underlying cause, the knorringite free energy is now in agreement with experiments of Turkin et al. (1983) and Klemme, (2004). These adjustments to spinel have been beneficial in slightly raising the pressure of the spinel to garnet lherzolite transition at the solidus for Cr-bearing compositions and much greater changes at lower temperatures as described below. In addition, the spinel model now uses the ulvospinel rather than the qandilite end-member, as this is closer to most natural Ti-rich spinel compositions.
(3) The Landau terms for quartz were modified according to the simple model of Angel et al., (2017). Although the effects on free energy are minimal, the volumes of quartz at high pressures are improved. This has led to minor adjustments in enthalpy for trd, crst, coe and qL end-members.
(4) Plagioclase, and ternary K-Na-Ca feldspars are no longer subdivided into C1 and I1 solutions. The old formalism, as in Holland and Powell (2003) never provided good continuity across the C–I transition. Instead we use an asymmetric solution model with an intermediate end-member of composition an$_{50}$ab$_{50}$. Details will be given elsewhere.

Calibration of the revised model
The same experimental database as used in Holland et al. (2018) is employed here with the addition of the following:
(1) We have used the bulk composition and solidus temperatures of Walter (1998) at 45, 60 and 70 kbar in place of that of Takahashi et al. (1993)
(2) We have added the garnet-out and the cpx-out boundaries of Walter (1998) at 70 kbar as additional constraints.
(3) The opx-out boundary at 70 kbar of Walter (1998) was used as an added constraint.
The natural data of (Ionov et al., 2010), sample u10, taken at 58 kbar and 1275°C, are used as additional constraints for the Cr partitioning between garnet, clinopyroxene and orthopyroxene.

Model validation

We have calculated the phase diagram for fertile upper mantle peridotite based on the pyrolite-like fertile peridotite composition KR4003 from Walter (1998). The phase diagram for KR4003 is shown in figure 1. We also consider fertile peridotite compositions SC-1, MM-3 and KLB-1 using the respective compositions given by (Jagoutz et al., 1979; Baker and Stolper, 1994; Davis et al., 2009). For comparisons with experimental studies using graphite sample capsules, ferric iron was set to 0.18 wt% Fe$_2$O$_3$ (Fe$^{3+}$/ΣFe=0.02), this value, slightly smaller than that (0.033) used by Jennings and Holland (2015) was selected so that melt produced at the garnet-bearing solidus has $f$O$_2$ closer to that of the experiments. In order to test the accuracy of mineral modes and compositions predicted by the new model using THERMOCALC at conditions above the solidus, we calculated the expected modal abundances, mineral and bulk residue compositions as well as the composition of melt produced during the fertile peridotite partial melting experiments of Baker and Stolper (1994), Falloon et al., (1999) and Walter (1998), which collectively span 10–70 kbar and extend from the solidus to >60% melting. Below the solidus, we calculated the expected compositions of minerals equilibrated in fertile peridotite in the experiments of Brey et al. (1990, 2008), which cover a range of pressure (10–70 kbar) and temperature (900–1400°C) conditions spanning the spinel and garnet stability fields. It should be noted that Brey et al., (1990) added water to the experimental charges to promote reaction with the result that a melt was produced in all low pressure experiments.

In order to test the modelled phase abundances and compositions across a broader range of bulk compositions, we calculated the modal mineralogy and mineral compositions for natural peridotites from Pali Aike, Vitim and Udachnaya using the data provided by Bjerg et al., (2009), Ionov et al., (1993), Ionov (2004) and Ionov et al. (2010). The ferric iron content of the natural peridotites was set to 0.3 wt% Fe$_2$O$_3$ (Fe$^{3+}$/ΣFe=0.03) to reflect the average composition of peridotite xenoliths (Canil et al., 1994). Samples from these locations collectively span a range of equilibration pressures (10–70 kbar) and temperatures (750–1350°C) and a range of compositions (5–35% orthopyroxene and 2–20% clinopyroxene) and extend to silica-rich compositions that cannot be formed by partial melting of fertile peridotite. For consistency, pressures and temperatures were recalculated using the same thermometer-barometer combination: in garnet bearing peridotites $P$ and $T$ were solved iteratively using the two-pyroxene thermometer and the garnet-orthopyroxene barometer of Brey et al. (1990). In garnet-free samples, temperature was calculated using the Ca-in-orthopyroxene thermometer of Brey et al. (1990) modified by Nimis and Grütter (2010) at a pre-set pressure of 15 kbar. We use the mineral modal abundances provided in the source publications. In order to reduce scatter resulting from inaccuracies in the mineral modal abundances, we exclude samples with loss on ignition >2wt.% and/or analytical totals <98wt.% and samples for which the calculated modal mineralogy has a residual SSQ of >1; 10 of 65 samples were removed on this basis. Scatter in plots of observed vs predicted composition is attributed to minor errors in the calculated equilibration conditions, possibly as a result of mineral zoning due to melt infiltration or changes in the prevailing pressure-temperature conditions. In addition, the presence of melt veins in some xenoliths will have affected the composition of the bulk rock, particularly with respect to CaO and Na$_2$O.

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SUBSOLIDUS PHASE RELATIONSHIPS

Position of the spinel to garnet transition
The calculated position of the spinel to garnet transition at the solidus is in the interval 22.1–24.8 kbar in KR4003 (Fig. 1), this is somewhat lower than the 26 kbar estimated for this composition by Walter (1998) and the 31 kbar for the Tunaquillo Lherzolite (Robinson and Wood, 1998). The relatively low $dT/dP$ of garnet-in and spinel-out reactions close to the solidus means that the exact pressure at which they occur are somewhat dependent on the solidus temperature (the transition occurs at 23.9-26.2 kbar 50°C above the solidus).

Disappearance of orthopyroxene
The enstatite content of clinopyroxene increases with pressure and temperature such that pyrolitic compositions are orthopyroxene-free at the solidus at about 30 kbar and higher (Takahashi, 1986; Takahashi et al., 1993; Herzberg and Zhang, 1996; Walter, 1998). The pressure at which orthopyroxene disappears at the solidus is calculated to be 29.1 kbar for KR4003, somewhat lower than the value estimated from the experiments of Walter (1998). The orthopyroxene-out boundary extends down to 1500°C, a maximum of 100°C below the solidus. As noted by Holland et al. (2013), the position of the orthopyroxene out boundary is highly sensitive to composition.

Spinel in the melting assemblage
The change to the spinel model has led to a widening of the spinel field above the solidus and spinel persists in the melt to higher temperatures than in the earlier model of Holland et al., (2018). Spinel is the second last phase to disappear in calculations involving KR4003 (Fig. 1), however in detail the abundance of spinel decreases rapidly in the cpx-field and is only present at very low modal abundances (<0.0015) in the high melt fraction assemblages (liq+ol+opx+spn, liq+ol+spn).

Subsolidus phase abundances
THERMOCALC may be used to model and visualise the modal mineralogy of a given peridotite composition at a range of pressure and temperature conditions and so to assess the changes in mineralogy that occur during cooling and decompression/pressurisation. Mineral isopleths were calculated for the composition KR4003 (Fig. 2). The garnet content of fertile peridotite is greatest at low temperature and at high pressure, reaching a maximum of 0.18. On cooling from the solidus to 1000°C, the garnet content of KR4003 increases by 0.045, the same increase is seen when pressure is increased from 20 to 40 kbar at 1000°C. Within the spinel field, spinel content is almost independent of pressure, increasing by 0.006 for every 100°C of cooling reaching a maximum of 0.045 in KR4003. At low temperatures, modal orthopyroxene decreases with increasing garnet from 0.28 at garnet-in to 0.16 at the highest garnet contents. Modal orthopyroxene also decreases as the modal abundance of clinopyroxene increases in response to the higher solubility of enstatite in clinopyroxene at higher temperature in both the garnet and spinel fields, and is most dramatic in the garnet field where garnet disappears ~80°C below the solidus and the enstatite content of clinopyroxene is 76% in KR4003.

Figure 3 compares the observed and modelled abundances of minerals from Udachnaya, Pali Aike and Vitim. Orthopyroxene, clinopyroxene, garnet, spinel (Fig. 3 a–d) and olivine (not shown) fall on the 1:1 reference line with a standard error of ~1% for garnet and clinopyroxene, 1–2% for orthopyroxene and olivine and 0.4% for spinel. Much of the scatter relates to heterogeneity and analytical error on the natural peridotites, which translate
to error in the phase abundances calculated by least squares mass balance and error on the calculated pressure-temperature conditions. Therefore, THERMOCALC successfully reproduces phase abundances of natural peridotites at subsolidus conditions in the mantle.

The high pressure exsolution experiments of Canil (1991) provide an opportunity to test the accuracy of the THERMOCALC dataset and current model in predicting how modal mineralogy varies in response to changes in temperature and pressure. Canil (1991) used synthetic oxide mixtures based on the average Kaapvaal cratonic (KAP1) and oceanic (AB1) peridotite compositions given in Boyd (1989) to investigate the exsolution of garnet from orthopyroxene with decreasing temperature or increasing pressure. In the experiments of Canil (1991), KAP1 shows systematic variation in orthopyroxene and garnet content with changing PT while olivine remains constant; in AB1 garnet varies systematically, however there is considerable scatter in the reported modal abundances of orthopyroxene and olivine, obscuring the effect of garnet exsolution on the orthopyroxene content of AB1. We used THERMOCALC to predict the modal mineralogy of KAP1 and AB1, firstly from 900°C to the solidus at a constant pressure of 50 kbar (Fig. 3e), and secondly from 40 to 70 kbar at constant temperature of 1450°C (Fig. 3f) to compare with the experimental modes of Canil (1991). The THERMOCALC dataset and model accurately predict the abundance of garnet and orthopyroxene formed in KAP1 and the abundance of garnet formed in AB1 across a range of temperatures and pressures.

Subsolidus phase compositions

Orthopyroxene

There is good agreement between the calculated and observed Al, Cr, Ca (Fig. 4a–c) and FeO (not shown) in orthopyroxene for natural garnet and spinel peridotites. THERMOCALC also successfully predicts the composition of orthopyroxene in garnet-bearing experiments from Brey et al. (1990, 2008). The modelled Al and Cr contents of orthopyroxene from garnet-free experiments are higher and lower, respectively, than observed, and we attribute this discrepancy to the persistence of melt in the low pressure experiments of Brey et al., (1990).

Calcium variation in orthopyroxene is nearly independent of pressure (Fig. 5a). The Al content of orthopyroxene decreases in response to increases in the modal abundance of the Al-bearing phase. The highest Al contents are achieved in the high-temperature region of the spinel field and the lowest in the low temperature high pressure region of the garnet field. Figure 5b shows calculated isopleths for Al in orthopyroxene for the KR4003 composition, illustrating a modest positive slope in the garnet field and are very steep in the spinel field, as observed in experimental studies (e.g. Perkins and Newton, 1981). While figure 5b does not serve as a general Al-in-opx barometer, it can be used to approximate the equilibration pressures of rocks with whole rock compositions that are close to KR4003, and THERMOCALC may be used to model and provide pressure constraints for a range of bulk peridotite compositions.

Clinopyroxene

At first glance, the observed clinopyroxene compositions are not so well reproduced by the new model and deviate from the 1:1 line with increasing concentration (Fig 4). The Ca-content of clinopyroxene is systematically underestimated by the model; however if the phase relations of the natural samples are modelled using a bulk composition calculated by mass balance (using the observed mineral compositions and abundances) rather than XRF, there is a good fit between the modelled and observed Ca content of clinopyroxene in natural peridotites (Fig. 4f). This highlights the potential impact of metasomatism and melt veins on the modelled phase relations of natural peridotites. The measured Ca concentration of

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clinopyroxene in the experiments of Brey et al. (1990) is systematically higher than the modelled Ca-content, and we suggest that this is due to a degree of Na dissolution and loss during the hydrous experiments, with Na loss being compensated by an increase in Ca in clinopyroxene. The model is able to reproduce the Al-content of clinopyroxene at <0.1Al per 6O, however at higher concentrations the Al concentration is systematically underestimated by THERMOCALC. Similarly, the Cr content of clinopyroxene is underestimated by the model. This may suggest that Al-Cr interactions in clinopyroxene are less ideal than assumed in the model.

**Spinel**

The Cr (Fig. 4g) and Al (not shown) contents of spinel are well reproduced for the natural samples, however, the modelled Al and Cr contents deviate below the 1:1 line at high concentrations. In contrast, spinel produced in the geobarometry experiments of Brey et al. (1990) do not sit on the 1:1 line, and we attribute this to the presence of melt in the low pressure runs, which leads to an increase in the Cr content of spinel (Brey et al., 1990).

The miscibility gap between Cr-rich and Cr-poor spinel that is apparent in the earlier peridotite model (Jennings and Holland, 2015) is absent in the updated model. The Cr content of spinel is highly dependent on pressure when plagioclase (or garnet) is present in the assemblage (Fig. 5c), as noted by Jennings and Holland (2015), making it a potentially sensitive barometer in plagioclase-spinel peridotites. In the absence of plagioclase or garnet, the Cr content of spinel is insensitive to pressure and increases with increasing temperature.

**Garnet**

The model is able to predict accurately the concentrations of Cr and Ca in garnet in both natural and experimental samples (Fig. 4h,i), although there is significant scatter about the 1:1 line for the Ca content of garnets from Udachnaya as a result of the effect of melt veins and/or metasomatism on the Ca content of the bulk rock. This represents an important improvement on previous versions of the model which underestimated Cr in garnet (and overestimated Cr in orthopyroxene) and means that THERMOCALC can now be used to better predict the composition of garnet, even at the high Cr-contents of the SCLM.

Pyrope-rich garnet within the SCLM is typically also Cr-rich, typically containing ~5 wt% Cr₂O₃ with values extending up to 21 wt% (e.g. Stachel and Harris, 1997) in xenoliths and inclusions in diamond. These garnets are rich in pyrope-knorringite components, and experiments have shown that the solubility of knorringite in pyrope depends on pressure and is insensitive to temperature under Cr-saturated conditions (e.g. Irifune et al 1982). This has led to the development of Cr-in-garnet geobarometers (e.g. Grutter et al., 2006), the application of which assumes coexistence of Cr-spinel. However, there remains uncertainty in the Al-Cr mixing in garnet and pyroxene. The PT pseudosection in figure 5d shows that, when spinel is present in the assemblage, pressure is the dominant control on the knorringite content of garnet, although temperature becomes important below ~800 °C. However, in the absence of spinel, temperature becomes the dominant control on the knorringite content of garnet such that the highest Cr content is achieved at the solidus in KR4003. Above spinel-out, the Cr-in-garnet isopleths broadly mirror the modal abundance of orthopyroxene, with the Cr content of garnet increasing as enstatite is dissolved into clinopyroxene and as pyrope is exsolved from orthopyroxene. The partition coefficient $D_{\text{g/opx}}$ remains broadly constant from 1100 °C to orthopyroxene out, suggesting that the mechanism by which temperature controls the knorringite content of garnet is via changes in the modal abundance of orthopyroxene.
MELTING OF PERIDOTITE

In the following, we apply THERMOCALC and the new melt model to partial melting of fertile peridotite. Modern-day mantle melting is fractional, therefore it is important that the model can accurately predict the mineralogy, melting reactions and melt compositions at the onset of melting i.e. at the solidus. However, equilibrium processes were also important during magma ocean crystallisation and mantle melting in the Hadean and Archaean, therefore we will also assess the accuracy of the model in predicting mineralogy, melting reactions and melt compositions at higher degrees of melting.

The calculated position of the solidus shows a good fit to experimental data (Fig. 6a), as is expected as the experiments of Walter (1998) were used in calibrating the liquid model. The cusp in the solidus at 9 kbar is caused by an increase in the fusibility of plagioclase before the plagioclase-out boundary, and has been observed in experiments (Borghini et al., 2009) and using the pMELTS and NCFMASOcr THERMOCALC models (Smith and Asimow, 2005; Jennings and Holland, 2015). The calculated temperatures for the liquidus are also agreement with experimental data. Calculated melt fractions indicate very low melt productivity \( \frac{\partial F}{\partial T} \) just above the solidus at 15 kbar, followed by a marked increase in productivity after 3% melting, a feature that was also observed by Hirschmann et al. (1999). However, early melt productivity is not supressed at 45 kbar. Melt productivity decreases after clinopyroxene-out and again after orthopyroxene exhaustion, producing two cusps in the melt productivity curve. At high pressure, melting takes place over a narrower temperature range, resulting in the compressed isopleths seen in the inset in figure 1.

There is excellent agreement between the modelled and experimental melt fractions at 15 kbar, even at high melt fractions (Fig. 6b). At higher pressure (Fig. 6c), the modelled melt fractions at 45 kbar are within 20–30°C of the KR4003 experimental data of Walter (1998) so the fit appears reasonable to \( F=0.4 \) melting. However, the modelled melt fractions at 45 kbar are ca. 100°C lower than the KLB-1 experimental data of Takahashi et al. (1993), this offset may reflect a paucity of experimental data at high pressures, and we suspect that the melt fractions estimated by Takahashi et al. (1993) are too low on the basis that the forsterite contents of the experimental olivines are higher than those produced in MM-3 at 35 kbar (Schutt and Lesher, 2006) and in KR4003 at 40-50 kbar.

Mineral modes and melting reactions on and above the solidus

Constraining the mineral mode and melting reactions is important for quantitative assessment of phase relations and for trace element modelling. Figure 7 shows the modal abundance of minerals in the residue during melting of fertile peridotite KR4003. The sequence of mineral disappearance during melting in the spinel field is clinopyroxene, orthopyroxene, spinel, olivine for KR4003. In the garnet field, the sequence is clinopyroxene, garnet, orthopyroxene, olivine (note above 65 kbar the order of garnet and orthopyroxene is reversed), and trace spinel is present above garnet-out. Clinopyroxene persists in the residue to higher degrees of melting as pressure increases. There is good agreement between the modelled mineral modes and those produced in partial melting experiments at 10 kbar (Baker and Stolper, 1994; Falloon et al., 1999) and 30–60 kbar (Walter, 1998), except at 30 kbar where the discrepancy relates to differences in the calculated position of orthopyroxene-out and the spinel–garnet transitions. Garnet persists to slightly higher degrees of melting than observed in phase equilibria experiments, of Walter (1998) at all pressures.
Reaction coefficients for KR4003 were calculated over a 0–1% melt fraction at the solidus and at 2% melting increments above the solidus (Fig. 7). Olivine is precipitated at the solidus during melting of spinel lherzolite (up to 30 kbar), where it forms at the expense of orthopyroxene, consistent with the experimental observations of Baker and Stolper (1994). Olivine reaches its highest modal abundance at the orthopyroxene-out boundary, before being consumed by partial melting at higher temperatures. Orthopyroxene is precipitated at the solidus above 23 kbar, where it forms at the expense of clinopyroxene and olivine.

Orthopyroxene disappears from the solidus at 30 kbar, but at higher pressure orthopyroxene is formed above the solidus, in agreement with the experiments of Walter (1998) and Herzberg and Zhang (1996). Orthopyroxene reaches its highest modal abundance at the clinopyroxene-out boundary, before being consumed by partial melting at higher temperatures. There is good agreement between the reaction coefficients calculated for the modelled and experimental melting trends in both sign and magnitude, except during incongruent melting of clinopyroxene and formation of peritectic orthopyroxene; here the coefficient of the reacting pyroxenes is larger for the modelled than the experimental melting trends, although the sign and relative magnitude remain consistent.

Fe-Mg partitioning

The Mg# is an important parameter to constrain accurately, as it is commonly used as a proxy for the degree of melting when assessing xenolith or lava samples. Fe-Mg exchange between olivine and liquid is expressed by $K_{D}^{Mg} = \frac{\Delta_{Fe} - \Delta_{Mg}}{\Delta_{Fe} - \Delta_{Mg}}$ (Roedder and Emslie, 1970), and this value was calculated for KR4003 at the solidus and at $F=0.1$ where it is compared to published experimental data in figure 8a. The cusp at 10 kbar relates to the plagioclase out boundary where high Na$_2$O and Al$_2$O$_3$ in the melt affects Fe-Mg partitioning, and this cusp has disappeared by $F=0.1$ and so does not appear in experimental data. The modelled trend shows an acceptable fit to the experimental data, and the pressure-dependence, while still perhaps a little large, is an improvement on the earlier NCFMASOCr model of Jennings and Holland, (2015).

The new model reproduces the composition of the melt across the studied pressure range for KR4003, KLB-1 and MM-3 (Fig. 8b). The Mg# of the modelled melts is pressure dependent, with Mg# increasing between 10 and 60kbar for a given degree of melting. The model also reproduces the composition of the KR4003 and KLB-1 residues, in both olivine and bulk Mg# (Fig. 8c,d). By contrast, the calculated olivine and residue Mg-numbers for MM-3 are significantly higher than the experimental value. The origin of the difference between composition of olivine during experimental and modelled melting of MM-3 is unclear. MM-3 has a higher Mg# than KR4003 (90.5 compared to 89.2 (Baker and Stolper, 1994; Walter, 1998)) and so we should expect the residue to have higher Mg# for a given degree of melting as predicted by the model calculations, however the Mg# of the experimental residue is comparable to that of KR4003. We can exclude disequilibrium during diamond aggregate experiments (Wasylenki et al., 2003) as the cause of the offset as the issue is seen in experiments both with (Baker and Stolper, 1994) and without (Falloon et al., 1999) diamond aggregates. It is notable that the value of $K_{D}^{Mg} = \frac{\Delta_{Fe} - \Delta_{Mg}}{\Delta_{Fe} - \Delta_{Mg}}$ calculated from MM-3 experiments is higher than the value calculated from experiments using other starting compositions at the same pressure (Fig. 8a), and olivine is unexpectedly Fe-rich in MM-3 experimental runs. One possible explanation is that temperature gradients existed within the MM-3 experimental capsules, leading to the formation of more Fe-rich olivine in the colder portion of the charge.

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The composition of the first melt produced at the KR4003 solidus is shown in figure 9. The cusp at 9 kbar relates to the plagioclase–spinel transition, above this there is a decrease in the Al$_2$O$_3$, Na$_2$O, K$_2$O, SiO$_2$ and TiO$_2$ content of the melt with increasing pressure. The decrease in the Al$_2$O$_3$ content of the melt is related to the increase in the modal abundance of garnet with increasing pressure, while the decrease in Na$_2$O is driven by the increase in $D^\text{Na}_\text{al}$ with increasing pressure (Blundy et al., 1995; Jennings and Holland, 2015). The high silica content of near-solidus melts at low pressure has been attributed to the high alkali content of these melts, because alkalis cause melt depolymerisation and an increase in the silica activity coefficient. (Hirschmann et al., 1998, 1999). The silica content of the melts declines with increasing pressure partly because the alkali content of the melt decreases, but also because higher pressure melts are already more depolymerised and so the effect of alkalis is diminished (Hirschmann et al., 1998). The TiO$_2$ content of the melt decreases sharply from 1 kbar to the plagioclase spinel transition, and then more gradually to the spinel–garnet transition. Clinopyroxene is the principal host of TiO$_2$ in the model system and the modal abundance of clinopyroxene increases from 6% at 1 kbar to 28% at the 22 kbar; however this accounts for only half of the change in the TiO$_2$ content of the melt. It follows that $D^\text{Ti}_\text{al}$ must decrease with decreasing pressure, indeed the calculated $D^\text{Ti}_\text{al}$ increases 7-fold from 1 to 22kbar. Understanding TiO$_2$ partitioning is vital for investigating mantle melting processes (e.g. Langmuir et al., 1992) and has implications for the partitioning of similar trace elements (Nb$^{5+}$, Ta$^{5+}$, Zr$^{4+}$, Hf$^{4+}$).

The compositions of higher fraction melts of KR4003 are shown figure 10, where they are compared to experimental results over the interval $F=0$ to $F=0.6$. The silica content of the melt decreases sharply in the first 10% melting, this is most marked at low pressure, and the effect is only marginal above 30 kbar. Above $F=0.1$, the silica content of the melt gradually increases with progressive melting, with SiO$_2$ increasing more strongly at low pressure where olivine formed by incongruent melting, and less strongly at high pressure where incongruent melting consumes SiO$_2$. The decrease in the SiO$_2$ content with increasing pressure is well established (e.g. Hirose and Kushiro, 1993). The calculated liquid compositions show the following trends: the MgO content of the melt increases with progressive melting at all pressure, but the MgO starts lower and increases more strongly at lower pressure. The FeO content increases during melting at low pressure, and increases at high pressure. The concentration of Al$_2$O$_3$ in the melt decreases from a high initial value at low pressure, but at higher pressure Al$_2$O$_3$ starts low and remains constant due to the presence of garnet in the residue. The inflection in CaO is related to clinopyroxene exhaustion, which shifts from $F=0.2$ at 10 kbar to $F=32$ at 60 kbar.

There is generally good agreement between the modelled and experimental melt compositions and melting trends (and also the mass balance trends of (Herzberg, 2004) that are based on on the KR4003 experimental data; supplementary info). In detail the modelled concentrations of FeO are slightly high at all pressures relative to the experimental melting trends, while MgO is marginally high and Al$_2$O$_3$ marginally low in the garnet stability field. SiO$_2$, CaO and Na$_2$O are well reproduced. When compared to experimental melts, the model exaggerates the variation in Cr$_2$O$_3$ with pressure at $F>0.25$. The TiO$_2$ content of the melt is underestimated at <10% melting at >20kbar. We do see an increase in TiO$_2$ from solidus to a few percent melting at low pressure as observed experimentally at 10kbar (Baker et al., 1995), but the fit to experimental data is less good and this represents an area for future improvement. Overall, for a given composition and degree of melting, melts produced at low pressure have higher SiO$_2$, Al$_2$O$_3$, CaO and NaO and lower MgO and FeO than those produced at higher pressure.
A similar picture emerges when we consider the compositions of liquids produced from melting of non-pyrolitic peridotite. Figure 11 shows calculated melts of depleted peridotite compositions DMM1 (Wasylenki et al., 2003) and Taniquillo (Robinson et al., 1998; Falloon and Danyushevsky, 2000) and pyroxene-rich peridotite (Kogiso et al., 1998). As with the KR4003 melts, the calculated concentration of FeO is slightly high and Al\textsubscript{2}O\textsubscript{3} slightly low when compared to experimental data for both depleted and enriched peridotite compositions. Otherwise, there is good agreement between the modelled and observed melting trends.

Overall, the accuracy of the predicted liquid compositions both at and above the solidus for a range of peridotite compositions mean that the new THERMOCALC models make a valuable tool for exploring fractional and batch melting of the mantle with application to understanding the origin of basaltic and komatiitic melts.

**Composition of the residue**

The major element composition of residual peridotite depends on both the nature of the parent rock and the conditions of melt extraction. Therefore, accurate modelling of the composition and evolution of melting residues is relevant for understanding the melting history and origin of peridotite xenoliths. Xenoliths from the cratonic lithosphere are re-equilibrated to conditions on the modern geotherm, and observed mineral abundances and compositions do not reflect the conditions of peridotite formation. Therefore, we assess bulk residue rather than individual mineral compositions. Mantle melting is polybaric, whereas this study examines the evolution of KR4003 during isobaric melting, which is important to model accurately, so that the melting model can then be applied to a more realistic polybaric melting scenario.

Figure 12 shows the bulk compositions of residues produced by melting of fertile peridotite KR4003. There is good overall agreement between the calculated and experimental residue trends (and also the mass balance trends of (Herzberg, 2004) that are based on on the KR4003 experimental data; supplementary info), with both the concentration and sense of change being well reproduced. The concentration of SiO\textsubscript{2} in the residue decreases during progressive melting. However, at and above 30 kbar SiO\textsubscript{2} decline is delayed to $F>0.3$ due to the precipitation of orthopyroxene in the melt field at high pressure, consistent with experiments (Takahashi et al., 1993; Walter, 1998). By contrast, SiO\textsubscript{2} decline occurs over a shorter melting interval at low pressure due to the formation of peritectic olivine, consistent with the findings of Baker and Stolper (1994). Concentrations of Al\textsubscript{2}O\textsubscript{3}, CaO, TiO\textsubscript{2} and Na\textsubscript{2}O in the residue decrease sharply during progressive melting due to the exhaustion of clinopyroxene ± garnet. The decline is steepest at low pressure and more gradual at higher pressure because clinopyroxene and garnet persist to higher melt fractions at higher pressure. The calculated SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} residue trends are displaced to slightly higher liquid proportion relative to the experimental data, and in the case of Al\textsubscript{2}O\textsubscript{3} this results from the persistence of garnet to higher degrees of melting in the calculated residues than is observed in experiments. Similarly, the concentration of Cr\textsubscript{2}O\textsubscript{3} in the residue is overestimated at ≥40 kbar and $F>0.25$ because of the calculated over-stability of garnet. For this reason, the widely used ratios Cr\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} and Cr# are well reproduced. A good fit is observed for CaO and Na\textsubscript{2}O, although the model underestimates CaO and overestimates Na\textsubscript{2}O at ≥40 kbar, which relates to the manner in which the model overestimates the jadeite content of clinopyroxene at high pressure, as observed in the subsolidus regime. The overall trend and relative concentration of TiO\textsubscript{2} in the calculated residue is consistent with experimental estimates, even though the model overestimates the absolute TiO\textsubscript{2} content, particularly at high pressure. As

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clinopyroxene is the principal host for titanium in the studied assemblage, this likely reflects a shortcoming in the activity model for clinopyroxene.

Despite minor deviations from experimental observation, the overall fit and accuracy of the predicted residue compositions mean that the THERMOCALC models make a valuable tool for investigating the effects of melt extraction in different geodynamic settings.

APPLICATION TO CRATONIC PERIDOTITES

Garnet exsolution

Peridotite xenoliths from the SCLM are highly refractory, with uniformly high Mg# (>92) and extreme depletion in CaO, Al₂O₃ and Na₂O (Boyd and Mertzman, 1987; Boyd, 1989) consistent with their formation by extensive (30–40%) partial melting of fertile peridotite. Cratonic peridotites typically contain 5–10% Cr-pyrope garnet, which is higher than the garnet contents of experimental pyrolite melting residues of similar Mg# (Walter, 1998; Herzberg, 2004). ‘Excess’ garnet has been attributed to exsolution from orthopyroxene during subsolidus equilibration (Cox et al., 1987; Canil, 1991) or to addition by metasomatizing fluids (Malkovets et al., 2007). Pyroxene megacrysts containing exsolved garnet have been described from several cratons (Aoki et al., 1980; Dawson et al., 1980; Dawson, 2004; Wasch et al., 2009; Gibson, 2017; Tomlinson et al., 2017) and provide a record of previous events in the metamorphic history of cratonic peridotites. Orthopyroxene and garnet within the exsolved megacryst are geochemically indistinguishable from the same phases in the host peridotite at major and trace element level, supporting a common origin for the granular and exsolved portions of such samples (Tomlinson et al., 2017). A close spatial relationship between garnet and orthopyroxene in cratonic peridotites also suggests that garnet within the peridotite formed by exsolution (Cox et al., 1987; Saltzer et al., 2001). However, the extent to which exsolution can explain excess garnet within SCLM peridotites, and the PT path taken by these peridotites to drive exsolution, remain poorly constrained.

Application of the model to unravel subsolidus re-equilibration is illustrated using cratonic peridotite BP002 from the Bultfontein pans, Kaapvaal craton (Tomlinson et al., 2017). Sample BP002 has a non-pyrolitic, silica-rich composition therefore comparison with experimental or model data for fertile peridotite is not appropriate. Silica enrichment manifests as excess orthopyroxene and is important in xenoliths from the Kaapvaal (Boyd and Mertzman, 1987; Boyd, 1989) and Siberian (Ionov et al., 2010) cratons, although orthopyroxene-rich peridotites have also been described from the Slave (MacKenzie and Canil, 1999; Aulbach et al., 2007) and Rae (Schmidberger and Francis, 1999) cratons. The origin of silica enrichment in cratonic peridotites remains unknown and has been attributed to fluid or melt-rock reaction either via serpentinization of oceanic lithosphere in a ridge or arc (Canil and Lee, 2009), reaction with slab-derived hydrous melts in a suprasubduction zone (Kesson and Ringwood, 1989; Kelemen et al., 1998; Parman et al., 2004), or reaction komatiitic melt (Tomlinson and Kamber, 2021) or recycled eclogite in a plume (Aulbach et al., 2011), depending on the preferred melting environment of cratonic lithosphere formation.

Sample BP002 comprises a large orthopyroxene megacryst containing garnet lamellae within coarse granular harzburgite and equilibrated at 44 kbar and 975°C on the modern Kaapvaal geotherm. Table 1 lists mineral compositions and modal proportions for the harzburgite xenolith and orthopyroxene megacryst, the composition of the precursor pyroxene was reconstructed using the modal proportions of garnet and orthopyroxene in the exsolved megacryst. A calculated pseudosection for the bulk composition of harzburgite BP002 is shown in figure 13. We have used the BP002 composition of the harzburgite calculated using the measured mineral compositions and modal abundances, rather than the composition

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measured by XRF because the bulk rock data suffer from elevated Ca and Na due to the presence of ~1% kimberlite melt in vein networks with the xenolith.

Orthopyroxene within the xenolith contains 0.012 Ca and 0.030 Al per 6O, these isopleths converge at 45 kbar and 915°C, in agreement with the equilibration conditions calculated by geothermobarometry (Tomlinson et al., 2017). The calculated garnet content at these conditions is 7.4%, close to the observed value. By contrast, the reconstructed precursor orthopyroxene contains 0.027 Ca and 0.119 Al per 6O, these two isopleths lie close together within the garnet field but diverge within the spinel field precluding a shallow origin and indicating that the precursor orthopyroxene formed in the garnet stability field. The garnet content along this band is ~2.4%, therefore the garnet content of BP002 increased by 5% during exsolution and exsolution may explain a significant portion, but not all of the garnet present in the harzburgite. This is consistent with the higher garnet/orthopyroxene ratio of the harzburgite (0.12) relative the exsolved megacryst (0.18). The calculated garnet content of the precursor harzburgite is consistent with experimental high degree melting residues produced at 50-60 kbar (Walter, 1998; Herzberg, 2004). Therefore, the excess garnet observed in peridotites from the SCLM may be explained by exsolution from pyroxene without the need for metasomatic garnet addition.

The 0.027 Ca and 0.119 Al isopleths within the precursor orthopyroxene intersect the BP002 solidus at 55.5 kbar and 1775°C (Fig. 13), consistent with a high pressure magmatic origin for BP002. Exsolution in this sample was driven by cooling accompanied by moderate ascent, consistent with melting in a plume or with uplift associated with lithospheric thinning.

Melting of silica-enriched mantle

Komatiites are Mg-rich (MgO>18 wt%) lavas that were erupted during the Archaean but only rarely since. They are thought to have been generated by high degrees of mantle melting (>30%) at temperatures that were significantly higher than today (Nisbet and Walker, 1982; Herzberg, 1992). Komatiites are subdivided (Robin-Popieul et al., 2012) into Al-depleted (ADK with Al₂O₃/TiO₂ 5–15), Al-undepleted (AUK with Al₂O₃/TiO₂ 15–25) and Al-enriched (AEK with Al₂O₃/TiO₂ >25). In ADK and AUK, the Al content is thought to reflect the presence or absence of garnet in the source, respectively; however the origin of AEK is less certain. Known occurrences of AEK komatiites are limited to the Kaapvaal craton, where the underlying lithosphere is characterised by silica-rich peridotites such as BP002. The 3.3 Ga Commondale komatiites are exclusively AEK-type and are also enriched in SiO₂ (Wilson et al., 2003), while less extreme Al-enrichment is observed in flows from the upper part of the 3.5–3.2 Ga Barberton komatiite complex (Weltevreden formation). The Commondale komatiites are strongly depleted in incompatible trace elements and have Sm-Nd and Lu-Hf isotope compositions that indicate they were derived from a source that was depleted in the garnet stability field some time before higher degree melting and komatiite generation (Hoffmann and Wilson, 2017; Wilson, 2019; McKenzie, 2020). The origin of this unusual high Al₂O₃/TiO₂ and SiO₂-rich komatiite is uncertain. McKenzie (2020) suggests that the Commondale Komatiites were derived by melting of depleted peridotite that had originally undergone melting in the garnet stability field, while Wilson (2019) suggests that the Commondale komatiites might have been produced by melting of depleted, silica-rich peridotite at 50 kbar.

We used THERMOCALC to investigate the composition of the liquid produced by isobaric batch melting of silica-rich, depleted harzburgite BP002 at 30-60 kbar. In figure 14, we compare the modelled melt trends to the parental Commondale komatiite composition calculated by Wilson (2019) and to Barberton parental magma compositions from Robin-Popieul et al. (2012). The ratios CaO/Al₂O₃ and Al₂O₃/TiO₂ are commonly used to estimate
the degree and depth of mantle melting for komatiite genesis (Nisbet and Walker, 1982). Relative to partial melts of fertile peridotite, CaO/Al₂O₃ is displaced to lower values and Al₂O₃/TiO₂ to higher values when melting the depleted, silica-rich peridotite (Fig. 14). MgO is also higher in the BP002 melting residues. The composition of the Commondale parental magma is comparable to the melt produced after 20–25% melting of BP002 at ~60 kbar and 1870°C. The BP002 starting material had already undergone 40% melting (based on bulk Mg#), therefore the cumulative degree of melting envisaged is 60–65%, which is similar to the 68% melting at 50 kbar calculated by Wilson (2019) for the Commondale komatiite by trace element modelling. The calculated melt trends indicate that melting of silica-rich depleted peridotite is a viable mechanism for generating the Commondale AEK, as suggested by Wilson (2019). The parental magma of the Barberton AEK may be produced either by extremely high degree melting (>>60%) of fertile peridotite, or by lesser degrees of melting of depleted, silica- and alumina-enriched peridotite. Thus, variability in AEK composition may reflect variation in the degree of orthopyroxene enrichment in the Kaapvaal lithosphere, in addition to differences in the depth and degree of melting.

Generation of the Commondale AEK by high pressure melting of silica enriched peridotite requires that this material was already present at a depth of 180 km by 3.3 Ga. One way of achieving this is if silica enrichment is the product of high pressure reaction between peridotite with earlier komatiitic (Tomlinson and Kamber, 2021) or eclogite-derived (Aulbach et al., 2009) melts in an upwelling plume. Alternatively, if silica enrichment is the result of melt-rock reaction at low pressure (Helmstaedt and Schulze, 1989; Kelemen et al., 1998; Parmann et al., 2004), tectonic thickening of the cratonic root must have already occurred by 3.3 Ga.

SUMMARY AND CONCLUSIONS

We provide a structural update to the KNCFMASTOCr model for peridotite compositions. The revised model performs well at 0-60 kbar and at 600°C to liquidus temperatures, such that the phase relations and mineral and melt compositions are predicted accurately both above and below the solidus. In particular, the updated model is able to accurately reproduce orthopyroxene and SiO₂ contents in the melting residue and replicates the Cr contents of garnet and orthopyroxene, both of which were problematic in the previous version.

The model has been tested for a wide range of compositions and PT conditions using a number of peridotite xenoliths and is able to predict the observed phase abundances as well as the compositions of mineral phases. This allows exploration of subsolidus evolution of mantle rocks, something that is not easy to investigate experimentally due to the difficulty of achieving equilibration at subsolidus conditions. Where the bulk composition is known, the model may also be used to estimate PT conditions for garnet-free xenoliths based on subtle variations in phase composition. The model can be used to explore the origin of basaltic and komatiitic melts. For example, the effect of pressure on the major element composition of komatiitic melts, and the effect of producing melt from heterogeneous mantle. The addition of Ti to the NCFMASCrO model of Jennings et al. (2015) allows comparison with natural komatiites, for which Al₂O₃/TiO₂ is a key parameter used to estimate depth of melting.

There is scope to further improve the model, such as to refine the Al-Cr interactions in clinopyroxene. In particular, minor deficiencies in the melt model are indicated by the presence of tiny amounts of spinel at high melt fractions. There is also scope for further development to the model to incorporate volatiles such as H₂O and CO₂, both of which have an important effect on phase equilibria and melt compositions (e.g. Green, 1973; Gaetani and Grove, 1998; Dasgupta and Hirschmann, 2010) and are relevant to the melting of carbonated mantle (e.g. Dalton and Presnall, 1998; Brey et al., 2008). It would also be interesting to
extend the model to higher pressure to allow investigation of magma ocean crystallisation and the evolution of the early Earth, as some komatiites may have been produced by melting at pressures of 90 kbar (Sossi et al., 2016) or greater (McKenzie, 2020).

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**APPENDIX**

**melt model**

Table A1: Melt end-members and model site assignment used in this study

|   | M       | F       |
|---|---------|---------|
| slL | Al      | AlSi    |
| woL | Ca      | Si      |
| fo2L | Mg$_4$ | Si$_2$  |
| fa2L | Fe$_4$ | Si$_2$  |
| q3L | –       | Si$_3$  |
| ekL | –       | Cr      |
| tiL | –       | Ti      |
| hmL | –       | Fe$^{4+}$ |
| neL | –       | NaAlSi  |
| kjL | –       | KAlSi$_2$ |
| anL | –       | CaAl$_2$Si$_2$ |
| abL | –       | NaAlSi$_3$ |
| kfL | –       | KAlSi$_3$ |
| enL | –       | Mg$_2$Si$_2$ |

The melt model, as discussed in the text, is described in terms of 9 compositional variables ($wo$, $ne$, $kj$, $sl$, $fo$, $fa$, $hm$, $ek$, $ti$) representing the 10 external end-members ($q3L$, $woL$, $neL$, $kjL$, $slL$, $fo2L$, $fa2L$, $hmL$, $ekL$, $tiL$), where the amount of $q3L$ is found by difference. The thermodynamic description is complemented by addition of four additional internal (associate) species $CaAl_2Si_2O_8$ ($anL$), $NaAlSi_3O_8$ ($abL$), $KAlSi_3O_8$ ($kfL$) and $Mg_2Si_2O_6$ ($enL$). The 14 end-member proportions (with $\sum p_i = 1$) are

\[
\begin{align*}
    p_{q3L} &= 1 + y_{an} - 1/2 y_{en} - s (1 + y_{an} + 2/3 y_{ab} + 1/6 y_{en} + 1/3 y_{kf}) \\
    p_{woL} &= wo (1 + y_{an} + 2/3 y_{ab} + 1/6 y_{en} + 1/3 y_{kf}) - y_{an} \\
    p_{neL} &= ne (1 + y_{an} + 2/3 y_{ab} + 1/6 y_{en} + 1/3 y_{kf}) - y_{ab} \\
    p_{kjL} &= kj (1 + y_{an} + 2/3 y_{ab} + 1/6 y_{en} + 1/3 y_{kf}) - y_{kf} \\
\end{align*}
\]
\( p_{st} = s(1 + y_{an} + 2/3 \, y_{ab} -1/6 \, y_{en} +1/3 \, y_{kf}) - y_{an} \)
\( p_{fo2L} = fo (1 + y_{an} + 2/3 \, y_{ab} -1/6 \, y_{en} +1/3 \, y_{kf}) -1/2 \, y_{en} \)
\( p_{fa2L} = fa (1 + y_{an} + 2/3 \, y_{ab} -1/6 \, y_{en} +1/3 \, y_{kf}) \)
\( p_{hml} = hm (1 + y_{an} + 2/3 \, y_{ab} -1/6 \, y_{en} +1/3 \, y_{kf}) \)
\( p_{pkf} = kf (1 + y_{an} + 2/3 \, y_{ab} -1/6 \, y_{en} +1/3 \, y_{kf}) \)
\( p_{en} = en \)
\( p_{fa} = fa \)
\( p_{fo} = fo \)
\( p_{sl} = sl \)
\( p_{wo} = wo \)
\( p_{an} = an \)
\( p_{ab} = ab \)
\( p_{en} = en \)
\( p_{kf} = kf \)

where \( s = ek + fa + fo + hm + ne + kj + sl + wo + ti \).

The proportions of the internal end-members (anL, abL, kfL, enL) are determined from the internal equilibrium relations along with all the other mineral–melt equilibria in the system.

In terms of the M and F sites of Table A1 the numbers and sum of species units on each site are:

- **M sites:** Mg = 4fo; Fe = 4fa; Ca = wo; Al = sl; \( \sum M = 4fo + 4fa + wo + sl \).
- **F sites:** AlSi = p_{sil}; Si = p_{ wol}; Si_2 = p_{iol} + p_{fal}; Si_3 = p_{qil}; Cr = p_{ekil}; Ti = p_{tii}; Fe^{3+} = p_{hmli}; NaAlSi = p_{nei}; KAlSi_2 = p_{kji}; CaAlSi_2 = y_{an}; NaAlSi_3 = y_{kq}; KAlSi_3 = y_{ki}; Mg_2Si_2 = y_{en}; \( \sum F = 1 \).

The ideal activities are then given by mixing on sites as:

- \( a_{q3L} = p_{q3L} \)
- \( a_{sil} = AlM (\sum M)^{1/4} \, p_{sil} \)
- \( a_{wol} = CaM (\sum M)^{1/4} \, p_{wol} \)
- \( a_{fo2L} = (Mg_M)^{4/3} (\sum M)^{1/4} (p_{iol} + p_{fal}) \)
- \( a_{fa2L} = (Fe_M)^{4/3} (\sum M)^{1/4} (p_{iol} + p_{fal}) \)
- \( a_{ne} = p_{ne} \)
- \( a_{hml} = p_{hml} \)
- \( a_{ek} = p_{ek} \)
- \( a_{ti} = p_{ti} \)
- \( a_{kj} = p_{kj} \)
- \( a_{an} = p_{an} \)
- \( a_{ab} = p_{ab} \)
- \( a_{en} = p_{en} \)
- \( a_{kf} = p_{kf} \)

Non-ideal interactions are expressed in terms of regular solution energies \( W(i,j) = a + bT + cP \) in kJ for end-members \( i \) and \( j \), as follows:

\[
\begin{align*}
W(q3L, sil) &= 10.7 - 0.1 \, P \\
W(q3L, wL) &= 14.7 \\
W(q3L, foL) &= 45.6 - 0.54 \, P \\
W(q3L, faL) &= 4.9 - 0.56 \, P
\end{align*}
\]
W(q3L,ekL) = -4 - 0.02 P
W(q3L,tiL) = 31.6
W(q3L,kjL) = 2.3 + 0.07 P
W(q3L,anL) = -14.1 + 0.02 P
W(q3L,enL) = 2.3 + 0.07 P
W(q3L,abL) = -0.1
W(q3L,kfL) = 33.3 - 0.41 P
W(q3L,efL) = -24.1 + 0.84 P
W(q3L,fo2L) = 6.2 - 0.15 P
W(q3L,fa2L) = 2.7
W(q3L,neL) = 16.8
W(q3L,hmL) = -5
W(q3L,ekL) = -3
W(q3L,tiL) = 14.2 - 0.03 P
W(q3L,kjL) = 6.9 + 0.02 P
W(q3L,anL) = 4.6
W(q3L,abL) = 0
W(q3L,enL) = 2.5 + 0.01 P
W(q3L,kfL) = 4
W(fo2L,fa2L) = 33 + 0.04 P
W(fo2L,neL) = 26
W(fo2L,efL) = -21 - 0.02 P
W(fo2L,fo2L) = 0
W(fo2L,fa2L) = 10
W(fo2L,tiL) = 7.8 + 0.03 P
W(fo2L,kjL) = -1.1 + 0.03 P
W(fo2L,anL) = 9.8
W(fo2L,abL) = 4.1
W(fo2L,enL) = 13.3 + 0.09 P
W(fo2L,kfL) = 9.8
W(fo2L,neL) = 17.7 - 0.21 P
W(fo2L,efL) = 1.2 + 0.02 P
W(fo2L,efL) = 0
W(fo2L,ekL) = -3
W(fo2L,tiL) = 2.2 - 0.16 P
W(fo2L,kjL) = 2.3
W(fo2L,anL) = -5.2 - 0.02 P
W(fo2L,abL) = 1.9
W(fo2L,efL) = 1.4 + 0.36 P
W(fo2L,kfL) = 5.6
W(fo2L,neL) = 7.7 - 0.05 P
W(fo2L,efL) = -30
W(fo2L,ekL) = 0
W(fo2L,tiL) = -9.5 + 0.02 P
W(fo2L,kjL) = 8.9
W(fo2L,anL) = -6.5
W(fo2L,abL) = 0.6
W(fo2L,efL) = 2.9
W(fo2L,kfL) = -6.5
W(fo2L,efL) = 10
W(fo2L,ekL) = 0
W(fo2L,tiL) = 10.4 + 0.14 P
W(fo2L,kjL) = -5.2

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The enthalpies of end-members are those in the updated Holland & Powell (2011) dataset, with increments expressed as a difference ($H_{\text{mod}} = H_i - H_{i,\text{ref}}$). Where an end-member is made from a linear combination of others $H_{\text{mod}}$ is relative to that combination (Table 2). As before the increment is expressed as $H_{\text{mod}} = a_i + b_i T + c_i P$ in kJ, and the van Laar parameter $\alpha$ is a ratio relative to 1.0. Approximate uncertainties from Monte Carlo runs are $a_i (0.2)$, $b_i (0.0002)$, $c_i (0.002)$, $\alpha_i (0.05)$.

Table 2: $H_{\text{mod}}$ increments (in kJ) to Gibbs energies of end-members in the dataset (tc-ds634) revised from Holland & Powell (2011) and van Laar parameters ($\alpha$)

| $H_{i,\text{mod}}$ | $a$  | $b$  | $c$  | $\alpha$ | ref        |
|---------------------|------|------|------|----------|------------|
| q3L                 | 0.47 | 0    | -0.078 | 1.0      | 3 qL       |
| sIL                 | 7.86 | 0    | -0.337 | 1.45     | sIIIL      |
| woL                 | -0.09| 0    | -0.102 | 1.45     | woL        |
| fo2L                | 9.73 | 0    | -0.176 | 2.0      | 2 foL      |
| fa2L                | 16.52| 0    | -0.034 | 1.0      | 2 faL      |
| neL                 | 33.11| 0    | 0.306  | 1.0      | abL-2qL    |
| hmL                 | 3.76 | 0    | -0.037 | 1.0      | 0.5 hemL   |
| ekL                 | 24.98| 0    | 0.170  | 1.0      | 0.5 eskL   |
| tiL                 | 0.42 | 0    | -0.257 | 1.0      | ruL        |
| kjL                 | 22.93| 0    | 0.292  | 1.0      | kspL-qL    |
| anL                 | -102.80| 0.055 | 0.031 | 1.0      | woL+siIL   |
| abL                 | 5.02 | 0    | -0.082 | 1.0      | abL        |
| kfL                 | 5.22 | 0    | -0.086 | 1.0      | kspL       |
| enL                 | 19.89| 0    | -0.371 | 1.0      | foL+qL     |

**Spinel model**

Spinel is the same model as in Holland et al. (2018) but with the following revised interaction energies (in kJ pfu):

\[
W(\text{nsp,isp}) = -6.7 \\
W(\text{nsp,nhc}) = 3.6 \\
W(\text{nsp,ilhc}) = -9.8 \\
W(\text{nsp,nmt}) = 43.2 \\
W(\text{nsp,int}) = 49.5 \\
W(\text{nsp,pcr}) = -38.4 -0.08 P \\
W(\text{nsp,usp}) = 40.0 \\
W(\text{isp,nhc}) = 2.7 \\
W(\text{isp,ilhc}) = -3.5
\]
W(isp,nmt) = 36.8
W(isp,imt) = 20.7
W(isp,pcr) = -21.6 -0.08 P
W(isp,usp) = 38.2
W(nhc,ihc) = -6.0
W(nhc,nmt) = 17.5
W(nhc,imt) = 51.6
W(nhc,pcr) = -53.8
W(nhc,usp) = 25.7
W(ihc,nmt) = -4.1
W(ihc,imt) = 10.0
W(ihc,pcr) = -38.8
W(ihc,usp) = 21.0
W(nmt,imt) = 18.1
W(nmt,pcr) = 12.1
W(nmt,usp) = 5.2
W(imt,pcr) = -8.7
W(imt,usp) = 21.5
W(pcr,usp) = 15.0
W(nsp,pcr) = 10

In addition, the asymmetry parameter for usp is set at $\alpha = 0.9$.

The hmL (Fe$_2$O$_3$) component was calibrated as discussed in Jennings & Holland (2015) and Holland et al. (2018). The clinopyroxene free energy increment (DQF) for the kjd end-member is adjusted to -4.0 + 1.35 P.
|                | bulk (mass balance) | bulk (XRF) | xenolith | Orthopyroxene* | Garnet* | Garnet* | Orthopyroxene* | Precursor* |
|----------------|---------------------|------------|----------|----------------|---------|---------|----------------|------------|
| SiO₂           | 48.18               | 46.06      | 41.59    | 58.15          | 42.41   | 41.73   | 58.38          | 56.65      |
| TiO₂           | 0.01                | 0.02       | 0.01     | 0.02           | 0.02    | 0.01    | 0.01           | 0.01       |
| Al₂O₃          | 1.96                | 1.70       | 0.75     | 21.26          | 21.91   | 0.74    | 2.94           |            |
| Cr₂O₃          | 0.38                | 0.39       | 0.27     | 3.52           | 3.53    | 0.27    | 0.61           |            |
| FeO            | 5.51                | 5.63       | 6.52     | 3.99           | 6.37    | 6.27    | 4.00           | 4.24       |
| MnO            | 0.08                | 0.10       | 0.07     | 0.08           | 0.25    | 0.26    | 0.07           | 0.09       |
| MgO            | 43.41               | 41.31      | 51.83    | 36.45          | 21.70   | 21.88   | 36.20          | 34.71      |
| CaO            | 0.48                | 0.63       | 0.32     | 4.48           | 4.39    | 0.33    | 0.75           |            |
| Na₂O           | 0.03                | 0.05       | 0.07     | 0.04           | 0.04    | 0.04    | 0.07           | 0.07       |
| K₂O            | 0.01                | 0.05       | 0.01     | 0.02           | 0.02    | 0.02    | 0.01           | 0.01       |
| LOI            |                     |            |          | 2.48           |         |         |                |            |

Table 1: Mineral compositions and modal abundances of BP002 xenolith and exsolved megacryst (*from Tomlinson et al. 2017) and calculated mineral modal abundances and compositions of the precursor xenolith. XRF analysis was conducted by Actalabs and the data used to calculate modal mineral abundances by least squares mass balance.
Figure 1: PT pseudosection for KR4003 in the system KNCFMASOCR. Phases: g, garnet; sp, spinel; pl, plagioclase; ol, olivine; cpx, clinopyroxene; opx, orthopyroxene; liq, liquid. Inset shows isopleths for liquid. Progressively darker fields indicate increasing variance, and thus decreasing number of phases. Inset shows isopleths for modal proportion of liquid.
Figure 2: Isopleths of constant modal phase abundance in PT space calculated for KR4003 at subsolidus conditions. Phase fields correspond to those in figure 1.
Figure 3: Observed and calculated mineral modal abundances for (a–d) natural peridotites from Pali Aike (Bjerg et al., 2009), Vitim (Ionov et al., 1993; Ionov, 2004) and Udachnaya (Ionov et al., 2010), Calculations are based on XRF bulk compositions for the natural samples; (e–f) experimental peridotites from Canil (1991), solid lines KAP1, dashed lines AB1 and natural data for these samples are from Boyd (1989).
Figure 4: Observed and calculated mineral compositions for natural peridotites from Pali Aike (Bjerg et al., 2009), Vitim (Ionov et al., 1993; Ionov, 2004) and Udachnaya (Ionov et al., 2010) and experimental peridotites (Brey et al., 1990, 2008). Calculations are based on XRF bulk compositions for the natural samples. The inset in (f) shows the calculated Ca concentration of cpx in natural peridotites calculated using the bulk composition determined by mass balance, scale is the same as the main plot.
Figure 5: Isopleths for phase compositions in PT space calculated for KR4003 at subsolidus conditions. Phase fields correspond to those in figure 1.

390x383mm (300 x 300 DPI)
Figure 6: (a) Calculated solidus (solid lines) and liquidus (dashed lines) for KR4003 compared to experimental data and other parameterisations for KLB-1 and KR4003 (Takahashi et al., 1993; Walter, 1998; Herzberg et al., 2000; Hirschmann, 2000; Katz et al., 2003). (b) Variation in melt fraction (F) with temperature calculated for KR4003 at 15 kbar compared to experimental data (Hirose and Kushiro, 1993; Takahashi et al., 1993); (c) Variation in melt fraction (F) with temperature calculated for KR4003 at 45 kbar compared to experimental data (Takahashi et al., 1993; Ghiorso et al., 2002).
Figure 7: Modal mineral abundances for melting (left) and reaction coefficients (right) calculated for composition KR4003 at various pressures. Calculated trends are compared to the experimental data for MM-3 at 10 kbar (Baker and Stolper, 1994; Falloon et al., 1999) and for KR4003 at higher pressures (Walter, 1998), note for 40 kbar we have plotted the experimental data for 40 and 45 kbar.
Figure 8: Plots showing the effect of mineral-melt Fe-Mg partitioning. (a) $K_{D_{\text{Fe-Mg}}}^{(\text{ol-liq})}$ as a function of pressure calculated for KR4003 at the solidus (solid line) and at $F=0.12$ (dashed line), compared to experimental data for peridotites KR4003 (Walter, 1998), KLB-1 (Canil et al., 1992; Hirose and Kushiro, 1993; Takahashi et al., 1993; Herzberg and Zhang, 1996) and MM-3 (Baker and Stolper, 1994; Falloon et al., 1999) and other starting compositions (Roedder and Emslie, 1970; Kinzler, 1997; Tuff et al., 2005; Davis et al., 2011; Matzen et al., 2011). Calculated Mg# in (b) liquid; (c) olivine; and (d) bulk residue produced by melting KR4003 (solid lines) and MM-3 (dashed lines) at 10–60 kbar (maximum and minimum pressure labelled). Melt, olivine and residue compositions are compared to experimental data for KR4004 (Walter, 1998), MM-3 (Baker and Stolper, 1994; Falloon et al., 1999; Lesher et al., 2003) and KLB-1 (Canil et al., 1992; Hirose and Kushiro, 1993; Takahashi et al., 1993; Herzberg and Zhang, 1996).
Figure 9: Calculated composition of melts produced at the solidus (F=0.01) of KR4003 at various pressures compared to near-solidus experimental data for MM-3 at 10 and 15 kbar (Baker et al., 1995; Falloon et al., 2008) and for KLB-1 at 30 kbar (Davis et al., 2011), 40 kbar (Walter, 1998) and 50kbar (Herzberg and Zhang, 1996).
Figure 10: Calculated composition of liquids produced during melting of KR4003 (black lines) and MM-3 (grey lines) in 10 kbar increments from 10 to 60 kbar (minimum and maximum pressures are labelled). Calculated trends are compared to experimentally derived melts of MM-3 at 10 and 15 kbar (open symbols; Baker and Stolper, 1994; Baker et al., 1995; Falloon et al., 1999) and KR4003 at 30–70 kbar (closed symbols; Walter, 1998). Experimental data for KLB-1 are shown for comparison (asterisks; Herzberg & Zhang, 1996; Hirose & Kushiro, 1993; Takahashi et al., 1993).

420x261mm (300 x 300 DPI)
Figure 11: Calculated composition of melt produced from depleted peridotite compositions DMM1 (Wasylenki et al., 2003) and Tinaquillo (Robinson et al., 1998; Falloon and Danyushevsky, 2000) and pyroxene-rich peridotites (Kogiso et al., 1998). Tinaquillo T.I. shown as solid lines and symbols, TQ-40 as dashed lines and open symbols; pyroxene-rich peridotites KH1 shown as solid lines and symbols, KH2 as dashed lines and open symbols.
Figure 12: Calculated composition of residue produced after melting of KR4003 (black lines) and MM-3 (grey lines) in 10 kbar increments from 10 to 60 kbar (minimum and maximum pressures are labelled). Calculated trends are compared to experimental residues after melting of MM-3 at 10 and 15 kbar (open symbols; Baker and Stolper, 1994; Baker et al., 1995; Falloon et al., 1999) and KR4003 at 30–70 kbar (closed symbols; Walter, 1998).

420x261mm (300 x 300 DPI)
Figure 13: (a) PT Pseudosection of BP002 in the system KNCFMASTOCR. Phases: g, garnet; sp, spinel; pl, plagioclase; ol, olivine; cpx, clinopyroxene; opx, orthopyroxene; liq, liquid. Progressively darker fields indicate increasing variance, and thus decreasing number of phases. Phase relations were calculated using the bulk composition determined by mass balance using the observed phase compositions and abundances. (b) Isopleths for orthopyroxene calculated for xenolith BP002, bold lines indicate the composition of orthopyroxene prior to garnet exsolution.

373x189mm (300 x 300 DPI)
Figure 14: Calculated composition of liquid produced by isobaric melting of silica-enriched peridotite BP002 at 30–60 kbar and F=0–0.6, compared with the composition of liquids produced by melting fertile peridotite KR4003 (Walter, 1998); dashed lines show melting increments of 0.1. Also plotted are the calculated compositions of parental magmas of komatiites from Commondale (Wilson, 2019) and Barberton (Robin-Popieul et al., 2012); AEKs are shown as solid symbols.