The effects of solid-solid phase equilibria on the oxygen fugacity of the upper mantle

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Abstract

Decades of study have documented several orders of magnitude variation in the oxygen fugacity ($f_{O_2}$) of terrestrial magmas and of mantle peridotites. This variability has commonly been attributed either to differences in the redox state of multivalent elements (e.g., Fe$^{3+}$/Fe$^{2+}$) in mantle sources or to processes acting on melts after segregation from their sources (e.g., crystallization or degassing). We show here that the phase equilibria of plagioclase, spinel, and garnet lherzolites of constant bulk composition (including whole-rock Fe$^{3+}$/Fe$^{2+}$) can also lead to systematic variations in $f_{O_2}$ in the shallowest $\sim$100 km of the mantle.

Two different thermodynamic models were used to calculate $f_{O_2}$ vs. pressure and temperature for a representative, slightly depleted peridotite of constant composition (including total oxygen). Under subsolidus conditions, increasing pressure in the plagioclase-lherzolite facies from 1 bar up to the disappearance of plagioclase at the lower pressure limit of the spinel-lherzolite facies leads to an $f_{O_2}$ decrease (normalized to a metastable plagioclase-free peridotite of the same composition at the same pressure and temperature) of $\sim$1.25 orders of magnitude. The spinel-lherzolite facies defines a minimum in $f_{O_2}$, and increasing pressure in this facies has little influence on $f_{O_2}$ (normalized to a metastable spinel-free peridotite of the same composition at the same pressure and temperature) up to the appearance of garnet in the stable assemblage. Increasing pressure across the garnet-lherzolite facies leads to increases in $f_{O_2}$ (normalized to a metastable garnet-free peridotite of the same composition at the same pressure and temperature) of $\sim$1 order of magnitude from the low values of the spinel-lherzolite facies. These changes in
normalized $fO_2$ reflect primarily the indirect effects of reactions involving aluminous phases in the peridotite that either produce or consume pyroxene with increasing pressure: Reactions that produce pyroxene with increasing pressure (e.g., forsterite + anorthite $\rightleftharpoons$ Mg-Tschermak + diopside in plagioclase lherzolite) lead to dilution of Fe$^{3+}$-bearing components in pyroxene and therefore to decreases in normalized $fO_2$, whereas pyroxene-consuming reactions (e.g., in the garnet stability field) lead initially to enrichment of Fe$^{3+}$-bearing components in pyroxene and to increases in normalized $fO_2$ (although this is counteracted to some degree by progressive partitioning of Fe$^{3+}$ from the pyroxene into the garnet with increasing pressure). Thus, the variations in normalized $fO_2$ inferred from thermodynamic modeling of upper mantle peridotite of constant composition are primarily passive consequences of the same phase changes that produce the transitions from plagioclase$\rightleftharpoons$spinel$\rightleftharpoons$garnet lherzolite and the variations in Al content in pyroxenes within each of these facies. Because these variations are largely driven by phase changes among Al-rich phases, they are predicted to diminish with the decrease in bulk Al content that results from melt extraction from peridotite, and this is consistent with our calculations.

Observed variations in FMQ-normalized $fO_2$ of primitive mantle-derived basalts and peridotites within and across different tectonic environments probably mostly reflect variations in the chemical compositions (e.g., Fe$^{3+}$/Fe$^{2+}$ or bulk O$_2$ content) of their sources (e.g., produced by subduction of oxidizing fluids, sediments, and altered oceanic crust or of reducing organic material; by equilibration with graphite- or diamond-saturated fluids; or by the effects of partial melting). However, we conclude that in nature the predicted effects of pressure- and temperature-dependent phase equilibria on the $fO_2$ of peridotites of constant composition are likely to be superimposed on variations in $fO_2$ that reflect differences in the whole-rock Fe$^{3+}$/Fe$^{2+}$ ratios of peridotites and therefore that the effects of phase equilibria should also be considered in efforts to understand observed variations in the oxygen fugacities of magmas and their mantle sources.
Introduction

There has been longstanding interest in the oxygen fugacity ($fO_2$) of mantle-derived magmas and their sources (e.g., Osborn, 1959; Buddington and Lindsley, 1964; Haggerty, 1976; Arculus, 1985; Carmichael, 1991; Frost and Lindsley, 1991; Wood, 1991; Frost and McCammon, 2008). This interest reflects the potential importance of the effects of variations in $fO_2$ on the crystallization sequences and liquid lines of descent of magmas (e.g., Osborn, 1959; Hamilton and Anderson, 1967; Berndt et al., 2004); the variations in $fO_2$ that can be produced by crystallization differentiation of magmas (e.g., Frost and Lindsley, 1991; Kelley and Cottrell, 2012; Birner et al., 2018; Tang et al., 2018); the insights that observed variations in $fO_2$ (or their absence) can give into processes affecting the mantle source regions of magmas through space and time (e.g., Arculus, 1985; Ballhaus et al., 1990; Wood, 1991; Li and Lee, 2004; Lee et al., 2005; Frost and McCammon, 2008; Cottrell and Kelley, 2011; Cottrell and Kelley, 2013; Stagno et al., 2013; Brounce et al., 2014; Brounce et al., 2015; Gaillard et al., 2015; Shorttle et al., 2015; Aulbach and Stagno, 2016; Gaetani, 2016; Bénard et al., 2018b; Birner et al., 2018); and the potential feedbacks between magmatic $fO_2$ and geological processes involving the atmosphere and ocean (e.g., Kasting et al., 1993; Delano, 2001; Kump and Barley, 2007; Frost and McCammon, 2008; Gaillard et al., 2011; Hirschmann, 2012; Gaillard et al., 2015; Brounce et al., 2017; Stolper and Keller, 2018; Stolper and Bucholz, 2019).

As a result of this interest, there have been many studies aimed at quantifying the $fO_2$ levels recorded by igneous rocks. These studies have been based primarily on determinations of the ratios of oxidized to reduced states of multivalent elements in glasses, whole rocks, or coexisting minerals, from which $fO_2$ can then be quantified via experimental calibration and thermodynamic modeling. Several elements have been used to determine (or infer) variations in $fO_2$ (e.g., Cr, Cu, Eu, Fe, S, V), but most such measurements for terrestrial magmas and their sources are based on the oxidation state of Fe (i.e., the $Fe^{3+}/Fe^{2+}$ ratio). These studies have documented variations of up to several orders of magnitude in the $fO_2$ levels of magmas and mantle peridotites relative to standard oxygen buffer assemblages (e.g., Haggerty, 1976; Arculus,
1985; Christie et al., 1986; Mattioli et al., 1989; Ballhaus et al., 1990; Carmichael, 1991; Frost and Lindsley, 1991; Wood, 1991; Frost and McCammon, 2008; Kelley and Cottrell, 2009; Cottrell and Kelley, 2011; Stagno et al., 2013; Brounce et al., 2014; Moussallam et al., 2014; Shorttle et al., 2015; Miller et al., 2016; Moussallam et al., 2016; Brounce et al., 2017; Hartley et al., 2017; Bénard et al., 2018b; Birner et al., 2018; Tang et al., 2018).

Many explanations have been offered for the variations in $fO_2$ observed among magmas and peridotites. Most if not all of these factors probably play a role, including the following: (1) Magmatic $fO_2$ may be inherited from mantle sources that differ in composition (including Fe$^{3+}$/Fe$^{2+}$ ratio). Such source variations could be due to previous melting events (e.g., Wood, 1991; Bénard et al., 2018b; Birner et al., 2018); to addition of recycled components (or metasomatic agents derived from such components) that were oxidized in near-surface environments prior to recycling (e.g., Mattioli et al., 1989; Ballhaus et al., 1990; Carmichael, 1991; Parkinson and Arculus, 1999; Mungall, 2002; Kelley and Cottrell, 2009; Brounce et al., 2014; Brounce et al., 2015; Gaillard et al., 2015; Shorttle et al., 2015; Waters and Lange, 2016; Brounce et al., 2017; Bénard et al., 2018a; Bénard et al., 2018b; Stolper and Keller, 2018; Moussallam et al., 2019; Stolper and Bucholz, 2019); or to equilibration with or addition of graphite- or diamond-saturated C-O-H fluids, carbonates, or carbonate-silicate melts over ranges of pressure ($P$) and temperature ($T$) prior to, synchronous with, or after melting (Eggler, 1983; Blundy et al., 1991; Wood, 1991; Stagno et al., 2013). (2) The action of processes such as crystallization and degassing on mantle-derived melts after segregation from their sources may generate residual liquids that differ in $fO_2$ relative to their parent liquids and sources (e.g., Mathez, 1984; Carmichael, 1991; Frost and Lindsley, 1991; Lee et al., 2005; Burgisser and Scaillet, 2007; Lee et al., 2010; Kelley and Cottrell, 2012; Lee et al., 2014; Grocke et al., 2016; Moussallam et al., 2016; Brounce et al., 2017; Hartley et al., 2017; Birner et al., 2018; Tang et al., 2018; Moussallam et al., 2019). Or (3) variations in $fO_2$ may result from heterogeneous equilibria among phases in subsolidus and partially molten mantle peridotites that shift with varying $P$ and $T$, leading to variations in $fO_2$ even at constant bulk composition. Examples of
this include redistribution of components (including Fe$^{3+}$ and Fe$^{2+}$) between coexisting solid, liquid, and fluid phases with changing $P$ and $T$; addition or subtraction of phases from the assemblage as phase boundaries are crossed; or shifts in the equilibrium constants of redox equilibria with $P$ and $T$ such that $fO_2$ can vary relative to standard redox buffers even when all the phases and their compositions in an assemblage are unchanged (e.g., Wood et al., 1990; Frost, 1991; O'Neill et al., 1993; Ballhaus and Frost, 1994; Ballhaus, 1995; Gudmundsson and Wood, 1995; Woodland and Koch, 2003; Rohrbach et al., 2007; Frost and McCammon, 2008; Stagno and Frost, 2010; Stagno et al., 2013; Jennings and Holland, 2015; Gaetani, 2016; Miller et al., 2016; Birner et al., 2018; Sorbadere et al., 2018).

The focus of this paper is the third of these possibilities: an assessment of variations in $fO_2$ that may result from heterogeneous equilibria among phases in subsolidus mantle peridotites that shift with varying $P$ and $T$. In particular, we evaluate the possibility that significant variations in the $fO_2$ of a subsolidus mantle peridotite can result from changes in the Fe$^{3+}$ concentrations of coexisting phases due to reactions between them, even without any change in whole-rock composition or Fe$^{3+}$/Fe$^{2+}$ ratio. Such an assessment of the potential variability of the $fO_2$ of upper-mantle peridotite as functions of $P$ and $T$ is facilitated by the availability of thermodynamic models that can be used to calculate the abundances and chemical compositions of phases in stable or metastable equilibrium. In this paper we show that the pMELTS (Ghiorso et al., 2002; Antoshechkina and Ghiorso, 2018) and JH-15 (Jennings and Holland, 2015) models predict significant variations in the $fO_2$ of a representative, slightly depleted mantle peridotite composition under dry, melt-free conditions at $P < 40$ kbar. We also show that the subsolidus variations (both stable and metastable) in $fO_2$ of peridotite predicted by these models are driven primarily by the same $P$-sensitive phase equilibria that control the stability of plagioclase ($plag$), aluminous spinel ($sp$), and garnet ($gt$) and the shapes in $P$-$T$ space of alumina isopleths in low-Ca orthopyroxene ($opx$) and higher-Ca clinopyroxene ($cpx$) in mantle peridotites.
Phase equilibria and their effects on the fO₂ of a closed-system, subsolidus peridotite

We use two independent thermodynamically based approaches – pMELTS (Ghiorso et al., 2002; Antoshechkina and Ghiorso, 2018) and the JH-15 model (Jennings and Holland, 2015) implemented in Perple_X (Connolly, 2009) – to calculate by Gibbs free energy minimization the phase assemblages of a slightly depleted mantle composition (“DMM”; Workman and Hart, 2005) over ranges of 1 bar to 40 kbar in $P$ and 1050 to 1600°C in $T$. Each of these two approaches uses Gibbs free energy minimization to determine at a given $P$ and $T$ the equilibrium phase assemblage, including the abundances and compositions of all stable phases and the chemical potential ($\mu$) of each phase and system component. Implementing JH-15 through Perple_X directly provides the chemical potential of O₂, $\mu$ O₂, as O₂ is specified as a system component. In pMELTS, $\mu$ O₂ in the stable assemblage is calculated based on a summation of the chemical potentials of components that represent a balanced reaction with O₂ on one side of the reaction (Asimow and Ghiorso, 1998); in the calculated lowest Gibbs free energy state, all such reactions yield the same $\mu$ O₂. In both models, the $f$O₂ of the equilibrium assemblage is then calculated from the equilibrium $\mu$ O₂, using a $P$-independent but $T$-dependent standard state corresponding to pure O₂ gas at 1 bar. This choice of a standard state for O₂ differs from those chosen for condensed phase components (e.g., Fe₂SiO₄ in ol; Fe₃O₄ in sp, etc.), which are taken to be both $P$ and $T$ dependent, but is the typical choice of standard state for gases (Denbigh, 1971).

The bulk composition of the model peridotite used in these calculations has Fe³⁺/Fe²⁺ = 0.031 and FeO* = 8.17 wt. %; Fe is the only multivalent element considered by either model. Each of the two thermodynamic models has strengths and weaknesses, but by comparing their results we can evaluate which features are potentially robust and which are specific to each model and therefore not currently generalizable.
**P-T contour plots**

Figure 1 superimposes contours (i.e., isopleths) in P-T space of constant $fO_2$ or constant offsets from $fO_2$ reference states for calculated DMM phase equilibria. In this and all subsequent figures, calculations based on pMELTS are shown on the left (i.e., Figs. 1ace) while calculations based on JH-15 are shown on the right (i.e., Figs. 1bdf). All calculated phase assemblages described in this paper are melt-free, so below the calculated solidus (shown as a dashed curve in each panel of Fig. 1), the phase assemblages are stable, composed of $ol$ (olivine) $+ opx + cpx ± plag ± sp ± gt$; but above the stable solidus, the liquid phase is suppressed in the calculations, and metastable, melt-free assemblages are shown. The solidus curves (and the liquidus, which is stable in this P-T range in the pMELTS calculations) are shown only for reference and have no influence on the calculated equilibria: i.e., phase assemblages and $fO_2$ isopleths in stable and metastable solid assemblages are unaffected as they cross the positions of the stable solidus and liquidus. Calculated phase boundaries between $plag$ and $sp$ lherzolite (“$plag$-out”) and between $sp$ and $gt$ lherzolite (“$gt$-in”) are shown as solid green curves (although minor $sp$ is present in the labeled $plag$- and $gt$-lherzolite fields).

The $fO_2$ values in Figures 1a and 1b are not normalized relative to a buffer; they are contours of absolute $\log_{10}fO_2$, where $fO_2$ is in bars. For the DMM composition, both models predict overall isothermal increases in $fO_2$ with $P$ from 1 bar to 40 kbar of ~2-3 orders of magnitude at both 1100°C and 1600°C and isobaric increases with $T$ from 1100°C to 1600°C of ~4–5 orders of magnitude at both 1 bar and 40 kbar. Such isothermal increases in absolute $fO_2$ with increasing $P$ are by definition monotonic with $\muO_2$ and thus represent oxidation of the assemblages on an absolute thermodynamic scale. Broadly similar increases are predicted for

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1 The output of the two models is provided in tabular form and can be downloaded from [http://dx.doi.org/10.22002/D1.1329](http://dx.doi.org/10.22002/D1.1329) or [https://data.caltech.edu/records/1329](https://data.caltech.edu/records/1329). pMELTS results are provided along at 1100 and 1300°C isotherms at intervals of 100 bars from 1 to 4000 bars. JH-15 results are provided at several resolutions, for both completeness and ease of use. The master grid file has full output every 1°C and every 100 bars. The down-sampled grid has results every 100°C and 2000 bars. The 1100 and 1300°C isotherms have results every 100 bars. A README file explains the contents of all supplemental files.
silicate melts of constant composition and for commonly used redox buffers (including the FMQ buffer), reflecting the comparable signs and magnitudes of the standard-state volume and enthalpy changes for redox reactions involving Fe in these systems (e.g., Kress and Carmichael, 1991). Shifts in absolute $fO_2$ controlled either by homogeneous equilibria in a silicate melt or by heterogeneous equilibria among solid redox buffer assemblages are smooth and monotonic in $P$-$T$ space. Figures 1a and 1b, however, show considerable structure, including reversals, high 2nd derivatives, and/or discontinuous changes in the slopes of isopleths at phase boundaries (e.g., at the plag-out and gt-in boundaries) or over narrow $P$ and $T$ intervals in which phase abundances and composition change significantly.

In Figures 1c and 1d, the $\log_{10}fO_2$ values of Figures 1a and 1b have been modified by subtracting the $\log_{10}fO_2$ of the FMQ buffer at each $P$ and $T$; this normalization is referred to as $\Delta$FMQ or FMQ-normalized $fO_2$. This normalization removes much of the variation (i.e., the total variation decreases by $\sim$4.5-5 log units) in absolute $fO_2$ over this $P$ and $T$ range and brings out trends in $P$ that are less clear in Figures 1a and 1b. However, the utility of normalizing $fO_2$ to a particular buffer when studying trends in $P$ and $T$ is limited unless the standard-state volume and enthalpy changes of the buffer reaction closely match those of the redox reactions among the dominant phases in the assemblage (e.g., Kress and Carmichael, 1991). This is a potential issue in natural peridotite compositions for which the phase assemblages do not match the phases of the FMQ buffer (e.g., they lack quartz everywhere and do not always contain $sp$) and for which there are interacting continuous and discontinuous reactions involving the aluminous phases (i.e., plag, sp, and gt) and px (the abbreviation px is used to refer to any pyroxene phase), the effects of which are not fully removed, isolated, or enhanced by this normalization. Nevertheless, normalization to FMQ is standard, so we include it throughout.

In Figures 1e and 1f, we show the same pMELTS- and JH-15-calculated results for the DMM composition as in Figures 1a and 1b, but the $\log_{10}fO_2$ values at each $P$ and $T$ have been normalized by subtracting the $\log_{10}fO_2$ of an $ol+opx+cpx\pm sp$ assemblage with the same DMM composition. To obtain this reference assemblage, we minimized Gibbs free energy at each $P$
and $T$ subject to the constraints that plag and gt (and liquid) were suppressed in the pMELTS calculation ($sp$ is required to be present everywhere in the normalizing assemblage for pMELTS because $sp$ is the only host for Cr$^{3+}$ in subsolidus calculations in this model) and that plag, sp, and gt (and liquid) were suppressed in the JH-15 calculation. For the pMELTS model, the normalizing assemblage is the metastable $ol+opx+cpx+sp$ assemblage in the plag- and gt-lherzolite facies; in the $sp$-lherzolite facies, the normalizing assemblage is identical to the stable assemblage and so the normalized $\log_{10} fO_2$ value is exactly zero in this field. For the JH-15 model, the normalizing assemblage under all conditions is a metastable $ol+opx+cpx$ assemblage. The normalizing $ol+opx+cpx\pm sp$ assemblages have no phase appearances or disappearances and limited changes in phase compositions over the $P$-$T$ range of interest (although as described in the caption to Figure 4, in the pMELTS model, the sole $px$ phase at $T \gtrsim 1300^\circ C$ and $P \lesssim 3.7$ kbar is pigeonite rather than $opx$ plus a higher-Ca, diopsidic $cpx$). This normalization removes the general trends of oxidation (i.e., increasing absolute $fO_2$) of the DMM model peridotite seen in Figures 1a and 1b that result from increasing $P$ and $T$ on the dominant $ol+opx+cpx$ assemblage, and it consequently isolates and emphasizes the effects of subsolidus phase changes involving aluminous phases on the structure of the normalized $fO_2$ isopleths. Although we have not shown them, $\Delta FMQ$ values for the $ol+opx+cpx\pm sp$ assemblages (whether stable or metastable) vary smoothly with $P$ and $T$ because there are no phase changes in either the FMQ assemblage or the $ol+opx+cpx\pm sp$ assemblages (except, as mentioned above, for the appearance of pigeonite in the pMELTS calculation at the low $P$ and high $T$, but this has an almost undetectable effect on the normalized $fO_2$ – see $i$ and $ii$ in Figs. 1e, 2a, and 2c). Moreover, the changes in the $\Delta FMQ$ values of these $ol+opx+cpx\pm sp$ reference assemblages are small over the $P$ range of our calculations because the effects of continuous exchanges of components among $ol$, $opx$, $cpx$, $\pm sp$ are modest: e.g., at $1300^\circ C$ over the full 40 kbar range considered, $\Delta FMQ$ varies by $\sim 1.4$ log units for the $ol+opx+cpx+sp$ assemblage based on pMELTS and only $\sim 0.4$ log units for the $ol+opx+cpx$ assemblage based on JH-15.
It is clear from Figures 1e and 1f that most of the remaining structure in the \( fO_2 \) isopleths after normalization to an \( ol+opx+cpx\pm sp \) assemblage of DMM composition (with a total range of \( \sim 1.6 \) log units for the pMELTS model and \( \sim 1.2 \) log units for the JH-15 model) is correlated with \( P \)-dependent phase equilibria involving the aluminous phases in peridotite. Also, most of the \( T \) dependence of the \( fO_2 \) isopleths shown in Figure 1ab and most of the differences between the results of the pMELTS and JH-15 calculations are removed by the normalization to metastable and stable \( ol+opx+cpx\pm sp \) assemblages. The most prominent feature of Figures 1e and 1f is the low-\( fO_2 \) “well” associated with the \( sp \)-lherzolite facies. This and other features are explored in more detail in Figures 2 and 3, which plot various results of the calculated phase equilibria as functions of \( P \) at 1100°C and 1300°C.

Selected isotherms, stable calculations

The low-\( fO_2 \) “well” (or “trough”; Jennings and Holland, 2015) associated with the \( sp \)-lherzolite facies is most evident when normalized to an isocompositional metastable or stable \( ol+opx+cpx\pm sp \) assemblage for DMM (e.g., Figs. 1ef; and Figs. 2ab at 1300°C). For the pMELTS model (Fig. 2a), the \( fO_2 \) of the stable \( plag+ol+opx+cpx+sp \) mineral assemblage decreases smoothly by \( \sim 1.25 \) orders of magnitude relative to the metastable \( ol+opx+cpx+sp \) assemblage as \( P \) increases across the \( plag \)-lherzolite facies, reaching a minimum at the boundary between the \( plag \)- and \( sp \)-lherzolite facies (note again that for the lowest \( P_s \), pMELTS predicts the stabilization of pigeonite, but the effect on calculated \( fO_2 \) is negligible). As mentioned previously, there is no \( fO_2 \) offset between the stable and normalizing assemblages in the \( sp \)-lherzolite facies because the normalizing \( ol+opx+cpx+sp \) assemblage is identical to the stable assemblage for the pMELTS model in this facies. Then, beginning at \( gt \)-in, the \( fO_2 \) of the stable \( gt+ol+opx+cpx+sp \) mineral assemblage increases relative to that of the metastable \( ol+opx+cpx+sp \) assemblage with increasing \( P \) across the \( gt \)-lherzolite facies, steeply at first and with a progressively decreasing slope, resulting in a \( \sim 1.2 \) orders of magnitude increase by 40 kbar (and approximately recovering the 1 bar value).
For the JH-15 model (Fig. 2b), the corresponding changes are a decrease of ~1.3 orders of magnitude in the $fO_2$ of the stable plag-bearing assemblage relative to the metastable $ol+opx+cpx$ assemblage as $P$ increases across the plag-lherzolite facies; a minimum, near-zero, and near-constant $fO_2$ relative to the metastable $ol+opx+cpx$ assemblage across the whole sp-lherzolite facies (the amount of sp is approximately constant and <2 %; see Fig. 3b3 for the comparable results at 1100°C); an abrupt increase in $fO_2$ relative to the metastable $ol+opx+cpx$ assemblage at the appearance of gt; and a more gradual increase (with decreasing slope) after the disappearance of sp from the stable assemblage up to ~30 kbar across the gt-lherzolite facies, peaking at a ~1 order of magnitude increase (i.e., not quite recovering the initial low-$P$ value), then decreasing by ~0.1 orders of magnitude as $P$ increases further to 40 kbar.

The same shifts can be seen in absolute (i.e., unnormalized) $fO_2$ and ΔFMQ at 1100°C for both models (Figs. 3a1 and 3b1), although they are superimposed on the $P$-dependent overall trends associated with increasing $P$ discussed above in connection with Figure 1. Similar trends in ΔFMQ are shown for the KLB-1 fertile peridotite on stable subsolidus isotherms at 800 and 1100°C by Jennings and Holland (2015); this similarity is not surprising given that the same thermodynamic model was used in both cases and because the DMM and KLB-1 bulk compositions, though different, are both relatively fertile.

The modeled 1.0-1.3 orders of magnitude variations in $fO_2$ shown relative to metastable $ol+opx+cpx±sp$ assemblages in Figure 2 are comparable to the individual $fO_2$ ranges of mid-ocean ridge basalts (e.g., Cottrell and Kelley, 2011; Birner et al., 2018), primitive arc magmas (e.g., Kelley and Cottrell, 2009; Brounce et al., 2014), and abyssal peridotites (e.g., Bryndzia and Wood, 1990; Birner et al., 2018). Thus, although as discussed in the Introduction many processes can – and probably do – influence the oxygen fugacities of mantle peridotites and the magmas generated from them by partial melting, according to our modeling, variations in $fO_2$ comparable to those observed in suites of mantle-derived rocks and magmas can also arise from the effects on $fO_2$ of changes in peridotite phase assemblages at constant bulk composition over the $P$ range most relevant to terrestrial magma genesis.
Selected isotherms, metastable calculations

We conducted a series of additional thermodynamic modeling exercises that take advantage of the capability to probe metastable states in both the pMELTS and JH-15 models and thereby to assess the effects of individual phases on the calculated variations in $f_{O_2}$ described above. In Figures 2c and 2d, $f_{O_2}$ values for the DMM bulk composition normalized to $ol+opx+cpx±sp$ assemblages are shown vs. $P$ at 1300°C based on calculations in which the three Al-rich phases ($plag$, $sp$, and $gt$) were selectively suppressed (i.e., prevented from appearing in the assemblage) when calculating the equilibria. As pointed out previously, in the pMELTS calculations (Fig. 2c), we are only able to suppress $gt$ and $plag$ because the presence of $Cr^{3+}$ requires $sp$. In the JH-15 calculations (Fig. 2d), however, we can turn each of the three aluminous phases “on” or “off”. In this way, we explored the role that each of the aluminous phases plays in the modeled variations in $f_{O_2}$ in the stable assemblages.

The key results of these calculations are as follows:

- In pMELTS calculations, when $plag$ and $gt$ are not allowed to form, the assemblage is everywhere $ol+opx+cpx+sp$, which is also the normalizing assemblage, so the normalized $f_{O_2}$ for this assemblage is zero over the whole range in $P$ (corresponding to the horizontal line at 0 in Fig. 2c). Likewise, the metastable state of DMM calculated with JH-15 in which $plag$, $sp$, and $gt$ are all suppressed from the assemblage is $ol+opx+cpx$, which is again the normalizing assemblage, so the normalized $f_{O_2}$ for this assemblage is also zero over the whole range in $P$ (corresponding to the horizontal line at 0 in Fig. 2d).

- The blue curves in Figures 2c and 2d show the model results when we allowed $plag$ – but not $gt$ (or $sp$ in the JH-15 calculations) – to appear in the assemblages. For the JH-15 model (Fig. 2d), $plag$ is stable in the metastable assemblage at $P \lesssim 10$ kbar. This metastable assemblage differs from the stable assemblage (Fig. 2b) only in that $sp$ is not present, and this has only a small effect because the maximum amount of $sp$ in the fully stable calculated assemblage is $<2\%$ in the $plag$-Iherzolite facies (see Fig. 3b3 for the comparable result at 1100°C). The calculated abundance of $plag$ decreases continuously from 1 bar to its disappearance at $P \sim 10$
kbar (i.e., at a slightly higher $P$ than the $\sim 9$ kbar for $\text{plag}$-out calculated for the stable, $sp$-bearing assemblage; Fig. 2b), and this is accompanied by a continuous decrease in the normalized $fO_2$ of the $\text{plag}$-bearing metastable assemblage from 1 bar to the $\text{plag}$-out boundary. The shapes of the normalized $\log_{10} fO_2$ and $\text{plag}$ abundance curves vs. $P$ are similar (i.e., both are concave down: compare the blue curves in Figs. 2d [1300°C] and 3b3 [1100°C]). The decrease in $\text{plag}$ abundance with increasing $P$ in the $\text{plag}$-lherzolite facies is due to discontinuous reactions of $\text{plag} + ol \pm sp$ to produce aluminous $px$ components (e.g., Mg-Tschermak, Ca-Tschermak, and jadeite) $\pm sp$ (e.g., Green and Hibberson, 1970; Borghini et al., 2009); $\text{plag}$ disappears when such reactions have generated sufficiently aluminous $px$ ($\pm sp$) to host all the Al in the bulk composition. That allowing the stabilization of $\text{plag}$ alone, without $sp$, does such a good job at reproducing the trend of decreasing $fO_2$ with increasing $P$ in the fully stable assemblage (compare the $fO_2$ variation in the $\text{plag}$ stability field in Figs. 2b and 2d) – and the complete absence of this behavior when $\text{plag}$ stability is suppressed – demonstrates the essential role of $\text{plag}$ stability and of phase changes involving $\text{plag}$ in the decrease in $fO_2$ with increasing $P$ across the $\text{plag}$-lherzolite facies based on the JH-15 thermodynamic model. The same analysis applies to the pMELTS calculation shown in Figure 2c: Only when $\text{plag}$ is allowed to stabilize in the calculations is the decrease in $fO_2$ associated with the increase in $P$ across the $\text{plag}$-lherzolite facies observed in the output of the model.

- The orange curve in Figure 2d shows the JH-15 model result when $sp$ (but not $\text{plag}$ or $gt$) is allowed to appear in the assemblage (this discussion applies only to the JH-15 modeling, because $sp$ cannot be suppressed in the Cr$^{3+}$-bearing pMELTS calculations). When it is the only Al-rich phase allowed, JH-15 predicts that $sp$ is present in the calculated DMM assemblage over the full $P$ range shown in Figure 2d, whereas it is only present at low-to-intermediate $Ps$ in the stable assemblage (see the orange curve in Fig. 3b3; 1100°C). The persistence of $sp$ to high $P$ when $gt$ is prohibited from being present in the metastable assemblage may reflect in part the energetic favorability of accommodating some of the Cr$^{3+}$

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in sp rather than entirely in the px phases, which in the calculated stable assemblage would partition strongly into the gt. The normalized fO₂ of the sp-bearing assemblages in the absence of plag or gt differs by ≲0.1 log units from the sp-absent equilibria. This might seem surprising because sp can contain significant Fe³⁺ in the form of solid solution toward magnetite (~3 mole %), but in the JH-15 model the abundance of sp is low (≤2 wt. %) even when it is present, and thus its presence or absence has only a minor impact on the concentrations of Fe³⁺-bearing components in the px (see Fig. 4d). This is consistent with an important result of all these calculations: It is the Fe³⁺ contents of the opx and cpx that exert the dominant control on the fO₂ of peridotite over the P-T range we have explored. Note that allowing only sp to form (in the absence of plag or gt) slightly increases the fO₂ relative to the sp-absent ol+opx+cpx assemblage over almost the full P range considered (Fig. 2d). This may reflect that sp takes more Cr³⁺ than Fe³⁺ from the px, resulting in an increase in the activity of ferric-iron-bearing components in the px.

- The purple curves in Figures 2c and 2d show the results when gt is allowed to appear in the calculated assemblages. For the JH-15 model (Fig. 2d), gt appears in the calculated metastable assemblage at ~14.5 kbar, as opposed to at ~18 kbar in the stable calculation (compare Figs. 2b and 2d), reflecting the suppression of sp. As in the stable calculation, the progressive increase in gt abundance with increasing P is accompanied by a correlated increase in the fO₂ relative to the metastable ol+opx+cpx assemblage. This increase in gt abundance with increasing P in the absence of sp as a reactant is due the reaction of aluminous and non-aluminous px components to produce gt (e.g., Green and Ringwood, 1970). That allowing the stabilization of gt alone in the metastable assemblage does such a good job at reproducing the trend in normalized fO₂ of the truly stable assemblage at P >15 kbar (and that no hint of this behavior is present when gt is suppressed; compare the purple curve with the blue and orange curves in Fig. 2d) demonstrates the essential role of gt stability and of phase changes involving gt in the calculated ~1 order of magnitude increase in fO₂ with increasing P across the gt-lherzolite facies in the P range we have investigated.
The almost discontinuous increase in normalized $fO_2$ observed in the stable peridotite calculations at ~18 kbar is due to the narrow coexistence interval of $sp+gt$ in lherzolite and is not present in the metastable calculation where $sp$ is suppressed (e.g., compare the purple curve in Fig. 2d with the black curve in Fig. 2b). The same overall analysis applies to the pMELTS calculation shown in Figure 2c: Only when $gt$ is allowed to form is there an increase in $fO_2$ normalized to the metastable $ol+opx+cpx+sp$ assemblage across the $P$ range of the $gt$-lherzolite facies. Because $sp$ cannot be suppressed in the $Cr^3+$-bearing pMELTS model, the purple curve in Figure 2c and the black curve in Figure 2a are identical (except in the plag stability field).

The results shown in Figure 2 demonstrate that plag and $gt$ are essential for generating the large changes in $fO_2$ observed in the peridotite calculations when they are normalized to the metastable $ol+opx+cpx±sp$ DMM assemblages (Figs. 2a-2d). Without their presence, the normalized $fO_2$ is as low at the $Ps$ of the plag- and $gt$-lherzolite facies as in the $sp$-lherzolite facies. Moreover, the continuous decreases in $fO_2$ of lherzolite assemblages normalized to the metastable $ol+opx+cpx±sp$ assemblages as the $sp$-lherzolite facies is approached, whether with increasing $P$ in the plag-bearing facies or with decreasing $P$ in the $gt$-bearing facies, are highly correlated with the progressive decreases in plag or $gt$ abundance when these phases are permitted in the assemblage (e.g., compare the curves showing plag and $gt$ phase abundances in Figs. 3a3 and 3b3 with the normalized $fO_2$ curves in Figs. 2a and 2b or 2c and 2d).

**Variations in $fO_2$ in the plag-lherzolite facies**

**Coupling between alumina in px and $fO_2$ in the plag-lherzolite facies.** A clue as to the explanation of the correlations between $fO_2$ and $P$-dependent reactions involving the abundances of plag and $gt$ comes from comparing the shapes of the calculated log$_{10}$ $fO_2$ (normalized to the metastable $ol+opx+cpx±sp$ assemblages) vs. $P$ curves with those of curves showing the activity of $Al_2O_3$ in opx vs. $P$. For the pMELTS model, this comparison is between Figure 2a and the
heavier curve showing $\text{Al}_2\text{O}_3$ activity in Figure 2e, and a similar comparison may be made between Figures 2b and 2f for the JH-15 model: As the normalized $\log_{10}f\text{O}_2$ goes down with increasing $P$ across the plag-lherzolite facies, remains constant across the sp-lherzolite facies, and then rises again across the gt-lherzolite facies, the activity of $\text{Al}_2\text{O}_3$ in the opx is anti-correlated with these changes. This is consistent with the correlations discussed above between $f\text{O}_2$ and modal abundance of plag and gt in the model peridotite assemblages (Figs. 3a3 and 3b3 at 1100°C) because the abundances of these phases are connected to transfers of $\text{Al}_2\text{O}_3$ into and out of px.

In the plag-lherzolite facies, the $\text{Al}_2\text{O}_3$ content of px goes up with increasing $P$ at constant $T$ due primarily to the following continuous reactions, which go to the right with increasing $P$:

$$\frac{1}{3} \text{fayalite (ol)} + \frac{2}{3} \text{anorthite (plag)} = \frac{1}{2} \text{Fe-Tschermak (px)} + \frac{1}{2} \text{hedenbergite (cpx)}, \quad (1)$$

and

$$\frac{1}{3} \text{fayalite (ol)} + \frac{2}{3} \text{anorthite (plag)} = \frac{1}{2} \text{Ca-Tschermak (px)} + \frac{1}{2} \text{ferrosilite (opx)}, \quad (2)$$

where Fe-Tschermak and Ca-Tschermak refer, respectively, to the $\text{Fe}^{2+}\text{Al}_2\text{SiO}_6$ and $\text{CaAl}_2\text{SiO}_6$ components in px. These and other numbered reactions are balanced based on end-member component formula units containing a single oxygen (e.g., the formula unit of fayalite is $\text{Fe}_{\frac{2}{3}}\text{Si}_{\frac{1}{3}}\text{O}_3$); given this choice, the total numbers of formula units on both sides of the reactions are equal and the coefficients on both sides of the balanced reactions always sum to one. Although these reactions are more typically written in terms of Mg-bearing end members, we have chosen to focus on the $\text{Fe}^{2+}$-bearing end members for consistency with the graphical analysis presented below. Note that neither reaction (1) nor (2) is a redox reaction. All of the Al atoms in plag are tetrahedrally coordinated by oxygen, but half of the Al in Al-bearing px components is octahedrally coordinated by oxygen; thus, consistent with the generalization that structures with octahedrally coordinated Al have lower volumes than those with tetrahedrally coordinated Al,
the standard-state volume changes of both these reactions is negative, so the right-hand sides of these equilibria are favored with increasing $P$. The generation of Al-bearing $px$ components by Tschermak substitution at the expense of $ol$ and $plag$ results in increasing $Al_2O_3$ content of the $px$ (and hence in the $Al_2O_3$ activity in the $opx$; Figs. 2e and 2f) as $P$ increases across the $plag$-lherzolite facies and the negatively sloped alumina-in-$px$ isopleths in $P$-$T$ space are traversed (e.g., Obata, 1976; Gasparik, 2014). Figures 3a3 and 3b3 show the magnitude of this effect at 1100°C on the amount of $px$ in the peridotite based on the pMELTS and JH-15 models: For both models, the calculated abundances of $cpx$ and $opx$ increase by >100% and 20–25%, respectively, from ~1 bar to $plag$-out. These large increases are not surprising because all the $plag$ in the assemblage at 1 bar (~10 wt. %) plus an equal amount of $ol$ has to be replaced mainly by $px$ when the $plag$-out boundary is reached.

How does this relate to $fO_2$? At 1 bar, most of the $Fe^{3+}$ in the model peridotite is contained in the $px$ (in JH-15, the fraction of the total $Fe^{3+}$ in DMM contained in $sp$ is only ~1.5 % [Fig. 4b], whereas in pMELTS it is tens of percent [Figs. 4a]), and this remains the case throughout the $plag$-lherzolite facies. Thus, the generation of additional $px$ molecules on the right-hand sides of reactions (1) and (2) as $P$ increases leads to progressive dilution of the $Fe^{3+}$ in $px$, lowering both the concentrations (Figs. 2g and 2h, and 3a2 and 3b2) and activities (Fig. 2e and 2f) of their $Fe^{3+}$-bearing components, which in turn will generally lead to decreasing $fO_2$ relative to the metastable $ol$+$opx$+$cpx$+$sp$ assemblages. Although the pMELTS and JH-15 models differ in their details – particularly in the abundance of $sp$ (compare the orange curves in Figs. 3a3 and 3b3) and the proportion of the $Fe^{3+}$ in the $sp$ (Fig. 4a and 4b) – for both models the dilution of $Fe^{3+}$-bearing components in $px$ is the primary factor in the decrease in $fO_2$ relative to the $plag$-absent metastable assemblages with increasing $P$ in the $plag$-lherzolite facies. It is important to emphasize that $Fe^{3+}$ is basically a passive actor in this process: The absolute quantity of $Fe^{3+}$ in the peridotite is fixed and in both models it is mostly contained in $px$ across the full $P$ range of the $plag$-lherzolite facies; hence its concentration in the $px$ is determined by the $P$-dependent transfer of Al from tetrahedral coordination in the $plag$ to partly octahedral coordination in the
px, which increases the total mass of px, decreases the concentration of Fe\(^{3+}\) (and therefore the activities of Fe\(^{3+}\)-bearing components in the px), and thereby decreases \(fO_2\) by ~1.2-1.3 orders of magnitude normalized to the metastable ol+opx+cpx±sp assemblages; similar effects are seen in the trends of absolute \(fO_2\) and ΔFMQ (Figs. 3a1 and 3b1).

Note that there can be departures from the general rules stated in the previous paragraph that the activity of Fe\(_2\)O\(_3\) (or that of any other Fe\(^{3+}\)-bearing component) in a phase correlates positively with its Fe\(^{3+}\) concentration (e.g., because the activity coefficient is also changing due to variations in the concentrations of other components in the phase) or that \(fO_2\) necessarily correlates simply with this activity with changing \(P\) or \(T\) (e.g., the standard-state free energy changes of reactions by which \(fO_2\) can be calculated vary with \(P\) and \(T\), and such calculations depend on activities of other components, often in other phases, which are also shifting). Despite these potentially confounding factors, this is a widely applied and useful rule of thumb for thinking about how \(fO_2\) will vary with phase compositions (e.g., O'Neill et al., 1993; Ballhaus and Frost, 1994; Ballhaus, 1995; Gudmundsson and Wood, 1995; Woodland and Koch, 2003; Frost et al., 2004; Rohrbach et al., 2007; Frost and McCammon, 2008; Stagno and Frost, 2010) that for the most part successfully rationalizes the results of our thermodynamic modeling. This is especially so when \(fO_2\) is normalized to a metastable DMM ol+opx+cpx±sp assemblage, because the bulk composition is identical for both the stable and normalizing assemblages and the phase compositions and proportions are also similar in both assemblages, with the result that most potentially confounding factors will tend to cancel out.

**Comparison to previous work (plag-bearing assemblages).** Ballhaus and Frost (1994) and Ballhaus (1995) developed a related line of reasoning that also predicted that conversion of plag lherzolite to sp lherzolite would lead to a significant decrease in \(fO_2\). They modeled the stepwise conversion of a fertile sp lherzolite to a plag lherzolite at 12 kbar and 1230°C via the \(sp + cpx + opx = ol + plag\) reaction (see reaction (3), below), and they assumed that the sp contains all the Fe\(^{3+}\) in the system. As the reaction proceeds, sp is consumed, but never exhausted, and as its abundance decreases in the assemblage, the Fe\(^{3+}\) becomes progressively enriched in the
decreasing mass of \textit{sp}, leading to an increase in $fO_2$ of slightly more than 3 orders of magnitude relative to that of the initial, \textit{plag}-free assemblage. Their calculation thus anticipated the results of our modeling that predicts a higher $fO_2$ of \textit{plag} lherzolite relative to a \textit{plag}-absent lherzolite at a given $P$ and $T$, and they attributed it – as we have also done – to a passive increase in the concentration of Fe$^{3+}$ in the dominant Fe$^{3+}$-bearing phases (\textit{sp} in their case; \textit{px} in our case) due to reactions that progressively consume \textit{px}±\textit{sp} and produce \textit{ol}+\textit{plag}.

Although conceptually similar, there are differences between our treatment and that of Ballhaus and Frost (1994) and Ballhaus (1995). The most important is that, according to both of the thermodynamic models we consider here, most of the Fe$^{3+}$ in the system resides in \textit{px}, whether the modeled peridotite is in the \textit{plag}- or \textit{sp}-lherzolite facies, whereas the Ballhaus and Frost (1994) model assumes the \textit{sp} is the sole repository of Fe$^{3+}$. This approximation is inconsistent with our results using the JH-15 model (Fig. 4b) and studies of natural \textit{sp} lherzolites (e.g., Woodland et al., 1992; O'Neill et al., 1993), which together suggest that typically only 10–30 \% of the Fe$^{3+}$ resides in \textit{sp}. As a result of this approximation, the decrease in $fO_2$ upon conversion of \textit{plag} to \textit{sp} lherzolite based on Ballhaus and Frost (1994) and Ballhaus (1995) is 2-3 orders of magnitude larger than what is predicted by our modeling, in which the dilution of Fe$^{3+}$ in the \textit{px} as a result of \textit{px}-producing reactions with increasing $P$ across the \textit{plag}-lherzolite field drives this $fO_2$ change rather than dilution of Fe$^{3+}$ in \textit{sp}. Moreover, as shown in Figure 2d, our results show that this effect is present even when \textit{sp} is not allowed to stabilize in the JH-15 model, demonstrating that for this model \textit{sp} is not the dominant factor in producing a significant decrease in $fO_2$ relative to the metastable \textit{ol}+\textit{opx}+\textit{cpx} assemblage as $P$ increases across the \textit{plag}-lherzolite facies: Indeed, the role of \textit{sp} in this model trend must be almost negligible given that the results are essentially unchanged whether \textit{sp} is or is not allowed to stabilize (compare the \textit{plag}-lherzolite fields in Figs. 2b and 2d). Note, however, that although according to our results the decrease with $P$ in $fO_2$ relative to the metastable \textit{ol}+\textit{opx}+\textit{cpx} assemblage results from the dilution of Fe$^{3+}$ in the \textit{px} by the reaction of \textit{ol}+\textit{plag} to Fe$^{3+}$-free \textit{px} components rather than from dilution of Fe$^{3+}$ in the \textit{sp}, the Fe$^{3+}$ in the \textit{sp} (when it is allowed to stabilize in our models)
nevertheless does go down with increasing extent of consumption of \( ol + plag \) with increasing \( P \) in our modeling; this is mostly due to a passive response to the decreasing \( fO_2 \) driven by the dilution of \( Fe^{3+} \) in the \( px \) phases. Despite these differences, we emphasize that our results agree with the conclusion of Ballhaus and Frost (1994) and Ballhaus (1995) that conversion of \( plag \) lherzolite to \( sp \) lherzolite at a constant \( P \) and \( T \) results in a significant decrease in \( fO_2 \) and that this reflects a dilution of \( Fe^{3+} \) in the dominant phase(s) in which it occurs.

**Graphical analysis of the \( plag \)-lherzolite facies.** The model system on which we focus to illustrate graphically the effects on \( fO_2 \) of heterogeneous equilibria in peridotites is the five-component system \( FeO-Fe_{2/3}O-CaO-Al_{2/3}O-Si_{1/2}O \) (i.e., \( FeO-Fe_2O_3-CaO-Al_2O_3-SiO_2 \), but all components are expressed on a single-oxygen basis). Although it lacks \( MgO \), we show below that this quinary end-member model system captures the essence of the more complex system modeled using pMELTS and JH-15. The phases of interest for \( plag \)-, \( sp \)-, and \( gt \)-lherzolite facies are \( ol \) (the fayalite end member, \( Fe^{2+}SiO_4 \)); \( opx \) (dominantly the ferrosilite end member, \( Fe^{2+}Si_2O_8 \), which is metastable at low \( P \); Lindsley et al., 1964); \( cpx \) (dominantly the hedenbergite end member, \( CaFe^{2+}Si_2O_6 \)); \( plag \) (the anorthite end member, \( CaAl_2Si_2O_8 \)); \( sp \) (the hercynite-magnetite solid solution, \( Fe^{2+}Al_2O_4-Fe^{2+}Fe^{3+}2O_4 \)); and \( gt \) (dominantly the almandine end member, \( Fe^{2+3}Al_2Si_3O_{12} \), at the \( Ps \) of we have modeled, in solid solution with smaller amounts of skiagite, \( Fe^{2+3}Fe^{3+}2Si_3O_{12} \), and grossular, \( Ca_3Al_2Si_3O_{12} \); andradite, \( Ca_3Fe^{3+2}Si_3O_{12} \), can be written as a linear combination of these other \( gt \) end members). Other important components in the \( opx \) are \( Fe \)-Tschermark (\( Fe^{2+}Al_2SiO_6 \)) and \( Fe \)-essenite (\( Fe^{2+}Fe^{3+}AlSiO_6 \)), the assumed dominant \( Fe^{3+} \)-bearing component, although a “ferro-ferri-\( opx \)” species (\( Fe^{2+}Fe^{3+2}SiO_6 \)) could also be used as a component. Likewise, other important components in the \( cpx \) are \( Ca \)-Tschermark (\( CaAl_2SiO_6 \)) and \( Ca \)-essenite (\( CaFe^{3+}AlSiO_6 \)), the assumed dominant \( Fe^{3+} \)-bearing species. Note, however, that all of the components listed for \( opx \) and \( cpx \) can be present in both phases, and several can be written as linear combinations of others: e.g., \( Fe \)-essenite is an equal mix of the \( Fe^{2+}Fe^{3+2}SiO_6 \) and \( Fe \)-Tschermark end members.
Figure 5a shows the positions of each of the components listed in the previous paragraph projected from fayalite and hedenbergite (i.e., from ol+cpx) onto the Si\(_{1/2}\)O-Al\(_{2/3}\)O-Fe\(_{4/3}\)O plane (except for grossular, which in projection plots below the reference triangle on the extension of the Si\(_{1/2}\)O-Al\(_{2/3}\)O join); this projection is related to those used in Woodland and O’Neill (1993; 1995). By restricting our consideration to the end-member system projected from fayalite and hedenbergite, the phase relations of all ol+cpx-bearing assemblages, although schematic, follow the topological rules of a ternary system: In detail, projection from pure hedenbergite preserves the precise projected positions of the end members, whereas projection from the actual Al- and Fe\(^{3+}\)-bearing cpx composition would preserve exact ternary topology; the difference between these choices is expected to be minor for reasonable peridotite compositions so we choose the simple option of projecting from pure hedenbergite but assuming that the projection preserves ternary topology. Note that that we could lump MgO- and FeO-bearing end members of the ferromagnesian phases (i.e., we could replace the FeO component with an (Mg,Fe)O component). Although the rigor of the topologies of the isothermal sections shown in Figure 5 would be lost (in that the variance would be increased by one in all assemblages), the features of this projection would still provide a useful visualization of the phase relations of an MgO-rich peridotite.

Figure 5b shows schematically the projected ol+cpx-saturated phase relations for the entire Si\(_{1/2}\)O-Al\(_{2/3}\)O-Fe\(_{4/3}\)O plane for conditions under which a model mantle peridotite would be in the plag-lherzolite facies. Assemblages containing magnetite-hercynite sp are stable over most of the projected composition space, so in order to illustrate the effects of increasing P on the \(f_{O_2}\) values of naturally occurring low-Fe\(^{3+}\), sp-absent plag-lherzolites in which opx > plag (i.e., near the upper-right edge of the diagram), the relevant low-Fe\(^{3+}\) phase relations from Figure 5b are enlarged in Figure 6a. The composition of a model natural peridotite is shown as a green cross (Fig. 5) or dot (Fig. 6). This composition is schematic in Figures 5 and 6; in particular, the bulk Fe\(^{3+}\) content (X\(_{Fe^{3+}/O}\)) is exaggerated so as to illustrate the effects of interest. The bulk composition lies on an opx+plag tie line in this projection of the four-phase opx+plag+(ol+cpx)
stability field in Figures 5b and 6a. (The appearance of “+(ol+cpx)” at the end of a list of phases indicates that the assemblage contains these two phases and is projected from them in Figures 5 or 6.) The opx+plag tie lines extend from the projected position of anorthite to the projected edge of the opx field (e.g., to the red curves in Figure 6a; these are also positioned arbitrarily so as to illustrate the effects of interest); the important point is that the opx compositions are not pure Fe$^{2+}$Si$_2$O$_6$, but are displaced downwards toward the Al$_{\frac{2}{3}}$O and Fe$_{\frac{2}{3}}$O apices, reflecting the incorporation of Al and Fe$^{3+}$ in the opx.

The important feature of Figure 6a is the change with increasing $P$ in the position of the opx end of the opx+plag tie line that passes through the green dot representing the peridotite bulk composition. As described above, the composition of the opx coexisting with plag becomes progressively richer in Al with increasing $P$, corresponding to progressive downward movement of the edge of the opx field in Figure 6a; i.e., toward the Fe-Tschermak component, which in this projection coincides with pure anorthite. Because the tie lines are radial to anorthite in this projection, the composition of the opx simply moves with increasing $P$ to higher alumina contents along the tie line extending from anorthite, through the peridotite composition, to the opx composition; this is shown by the green arrow moving along this tie line from point $a$ to point $b$ with increasing $P$. The changing projected position of the opx composition relative to the bulk composition illustrates that the opx/plag ratio increases with increasing $P$, in accordance with our expectations based on reactions (1) and (2) and the output of thermodynamic modeling of the natural peridotite composition shown in Figures 3a3 and 3b3. The dotted black lines close to the projected Si$_{\frac{2}{3}}$O-Al$_{\frac{2}{3}}$O edge near the top of Figure 6a represent roughly constant Fe$^{3+}$ concentration (i.e., $X_{\text{Fe}_{\frac{2}{3}}}$O); the Fe$^{3+}$ concentration clearly decreases in the opx coexisting with plag+(ol+cpx), from point $a$ to point $b$ as the alumina content (i.e., $X_{\text{Al}_{\frac{2}{3}}}$O) of the opx increases with increasing $P$. As described above, such decreases in Fe$^{3+}$ concentration will generally lead to a decrease in $fO_2$ relative to a metastable ol+opx+cpx assemblage.

Figure 6a also demonstrates graphically why transformation at constant $P$ and $T$ from a metastable plag-free assemblage to the stable plag-bearing assemblage leads to an increase in
$fO_2$ relative to the metastable assemblage (as shown for the pMELTS and JH-15 models in Figures 2a-2d). The only aluminous phase in the metastable $ol+opx+cpx$ assemblage that appears in the projection shown in Figure 6a is $opx$. Thus, in this projection, the $opx$ in the metastable assemblage coincides with the bulk composition of the peridotite, so both plot at the position of the green dot. When the metastable assemblage transforms to the stable $plag$-bearing assemblage, the green dot representing the bulk composition of the peridotite does not change, and it will lie on a stable $opx+plag+(ol+cpx)$ tie line at the $P$ and $T$ of the transformation. The $opx$ composition at the end of a stable $opx+plag$ tie line passing through the green dot must have a higher Fe$^{3+}$ concentration than the metastable $opx$ plotting at the green dot, and hence given our approximation that $fO_2$ scales with the Fe$^{3+}$ content of the $opx$, the $fO_2$ of the stable assemblage will be higher than that of the metastable assemblage at the same $P$ and $T$.

The graphical analysis based on Figure 6a illustrates the consequences of reactions (1) and (2) and the results of the thermodynamic models, which show increasing Al contents of $px$ as $P$ increases across the $plag$-lherzolite facies. Neglected degrees of freedom in this assemblage that might change the anti-correlation between $X_{Fe^{3+}}O$ and $X_{Al^{3+}}O$ in $opx$ are (1) the presence of $sp$ in the Cr$^{3+}$-bearing calculations and (2) exchange of Fe$^{3+}$ and Al$^{3+}$ components between $opx$ and $cpx$. The first possibility is discussed in the first part of the next section. Regarding the second possibility, such redistribution is occurring to some degree: For example, Figure 3b2 shows for the JH-15 model that the Fe$^{3+}$ partition coefficients between $opx$ and $cpx$ and between $sp$ and both $px$ phases decrease with increasing $P$ across the $plag$-lherzolite facies; the Fe$^{3+}$ content of $cpx$ actually increases slightly over much of this $P$ range while the monotonic decrease of Fe$^{3+}$ in the $opx$ is significant. However, the agreement between the phase relations modeled with pMELTS and JH-15 and those portrayed using the projection from $cpx$ (which neglects its Fe$^{3+}$ and Al$^{3+}$ contents) suggests that the effects of such redistribution do not overwhelm the simple effects of dilution of the Fe$^{3+}$ in the $opx$, which is the major reservoir of Fe$^{3+}$ in the calculated DMM assemblage under these conditions (Fig. 4b).
The effects of spinel

Stabilization of spinel in the plag-lherzolite facies. One aspect of the thermodynamic analysis of natural plag lherzolite that is not fully captured by the simplified graphical analysis of Figure 6a is the effect of Cr\(^{3+}\) on the stabilization of sp. Whereas our analysis of Figure 6a places the model peridotite in the opx+plag+(ol+cpx) stability field, Figure 3 shows that both the pMELTS and JH-15 models yield the assemblage opx+plag+sp+(ol+cpx) throughout the plag-lherzolite facies at 1100°C. The reason for this difference between the thermodynamic calculations of the DMM composition and our graphical treatment of a simplified 5-component model system is that Cr\(^{3+}\)-rich sp is stable everywhere in the plag-lherzolite facies based on both the pMELTS and JH-15 models, but given the low Fe\(^{3+}\) content of the model composition, in the absence of Cr\(^{3+}\), sp would not be present over most of the plag-lherzolite facies, in agreement with the schematic phase relations illustrated in Figure 5 (e.g., the sp-in boundary at 1100°C is calculated to be only ~1.3 kbar lower than the plag-out boundary for this composition based on applying the pMELTS model to a Cr\(^{3+}\)-free DMM composition). Also, as emphasized previously, the two thermodynamic models used here differ from each other in their predicted amounts of sp in the stable assemblages for the DMM composition at 1100°C: The pMELTS calculation yields ~1.4 wt. % sp at 1 bar, increasing progressively to about ~3.9 wt. % when plag disappears from the assemblage at ~7.6 kbar (see the orange curve at Ps less than the plag-out boundary in Fig. 3a3); in contrast, JH-15 has considerably lower sp abundance (~0.4 wt. % at 1 bar), only beginning at ~6 kbar to increase in abundance significantly to ~2.4 % at plag-out at ~8.3 kbar (see the orange curve at Ps less than the plag-out boundary in Fig. 3b3). As indicated previously, the primary reason for these differences in abundance of sp between the two calculations is that, whereas for the pMELTS calculations 100% of the Cr\(^{3+}\) goes into sp — leading to a relatively large amount of Cr\(^{3+}\)-rich sp throughout the plag-lherzolite facies — much of the Cr\(^{3+}\) in JH-15 partitions into the px (e.g., JH-15 predicts that only ~30-60% of the Cr\(^{3+}\) in the system is in sp in the plag-lherzolite field), resulting in a much lower sp abundance until P
approaches that of the plag-out boundary (compare the orange curves at $P_s$ less than the plag-out boundary in Figs. 3a3 and 3b3).

The effects of the stabilization of $sp$ in an Fe$^{3+}$-bearing but Cr$^{3+}$-free plag-lherzolite facies can be understood using the sequence of projected phase equilibria shown in Figures 5b-5e. Given the low abundance of Fe$^{3+}$ in such a peridotite, throughout most of the plag-lherzolite facies a model peridotite composition plots in the four-phase $\text{opx} + \text{plag} + (\text{ol} + \text{cpx})$ field, shown in projection by tie lines between anorthite and Al, Fe$^{3+}$-bearing $\text{opx}$ (Figs. 5b and 6a). However, more Fe$^{3+}$- and/or Al-rich compositions will, at the conditions of Figure 5b, stabilize Fe$^{3+}$-bearing $sp$ and plot in the five-phase $\text{opx} + \text{plag} + \text{sp} + (\text{ol} + \text{cpx})$ field, represented by the $\text{opx} + \text{plag} + \text{sp} + (\text{ol} + \text{cpx})$ triangle in Fig. 5b. As illustrated in the progression from Figures 5b to 5f, the $\text{opx}$ vertex of this triangle sweeps down (reflecting the increasing Al$^{3+}$ content of the $\text{opx}$) and to the right with increasing $P$, and the $sp$ vertex also sweeps to the right. The stoichiometry of the continuous reaction represented by the $\text{opx} + \text{plag} + \text{sp} + (\text{ol} + \text{cpx})$ triangle moving to the right with increasing $P$ is

$$\frac{1}{2} \text{fayalite (ol)} + \frac{1}{2} \text{anorthite (plag)} + \frac{1}{4} \text{hercynite (sp)} + \frac{3}{8} \text{hedenbergite (cpx)} + \frac{3}{8} \text{ferrosilite (opx)}. \quad (3)$$

As a consequence, with increasing $P$ the model Cr$^{3+}$-free peridotite moves from the $\text{opx} + \text{plag} + (\text{ol} + \text{cpx})$ field at low $P$ (Fig. 5b), until a $P$ is reached (that depends on its Fe$^{3+}$ content) at which it plots exactly on the $\text{opx} + \text{plag} + (\text{ol} + \text{cpx})$ edge of the $\text{opx} + \text{plag} + \text{sp} + (\text{ol} + \text{cpx})$ triangle (Fig. 5c). This point represents the $P$ of $sp$-in for the bulk composition shown in Figure 5, but the assemblage is still a plag lherzolite.

With further increases in $P$, the $\text{opx} + \text{plag} + \text{sp} + (\text{ol} + \text{cpx})$ triangle continues to move to the right, passing over the peridotite bulk composition, resulting in a hercynite-magnetite $sp$ solid solution joining the assemblage; the peridotite assemblage is now a $sp + \text{plag}$ lherzolite (Fig. 5d). Continued rightward movement of the triangle with increasing $P$ does not alter the phases in the $sp + \text{plag}$-lherzolite assemblage as long as the green dot remains within the triangle, but the
abundances of plag and ol decrease and those of opx, cpx, and sp increase via reaction (3). Just as previously described for reactions (1) and (2), the production of px components by reaction (3) dilutes Fe\(^{3+}\) in the px; the reaction also produces hercynite that dissolves in the sp, resulting in a concurrent dilution of the magnetite component in the sp. This dilution of Fe\(^{3+}\)-bearing components in the px and sp as the opx+plag+sp+(ol+cpx) triangle sweeps over the model peridotite composition results in a progressive decrease in \(f_{O_2}\) relative to a metastable ol+opx+cpx assemblage (and in absolute \(f_{O_2}\) and ΔFMQ based on the results on DMM shown in Figs. 3a1 and 3b1) that is related to but not identical to the decrease in \(f_{O_2}\) associated with reactions (1) and (2), because these reactions do not involve production of sp. Continued increases in \(P\) eventually result in the triangle moving far enough to the right that its left edge coincides with the projected bulk composition; the abundance of plag in the stable assemblage is zero at this \(P\) (although the assemblage is still plag saturated), corresponding to plag-out for this composition (Fig. 5e). As \(P\) increases beyond this point, the model peridotite plots on opx+sp+(ol+cpx) tie lines and is in the sp-lherzolite facies (Fig. 5f). Note that throughout the movement to the right of the triangle with increasing \(P\), sp-absent reactions (1) and (2) are still proceeding to the right, driving up the alumina content of the px, such that the opx apex of the opx+plag+sp+(ol+cpx) triangle moves continuously down and to the right with increasing \(P\) (i.e., increasing in Al\(_2\)O\(_3\) as the alumina isopleths in \(P-T\) space are crossed, while simultaneously decreasing in Fe\(_2\)O\(_3\)). This is illustrated schematically in Figures 5b-5f. The precise trajectory of the opx apex with increasing \(P\) for a natural peridotite composition requires the simultaneous solution of the equilibria in reactions (1), (2), and (3) (plus any other independent reactions involving opx), which is done implicitly via the energy minimization approaches of the pMELTS and JH-15 calculations.

With still further increases in \(P\), the opx+plag+sp+(ol+cpx) triangle continues to move to the right, getting progressively narrower along with the opx+plag+(ol+cpx) and plag+sp+(ol+cpx) two-phase regions, until anorthite disappears completely from the phase diagrams via the univariant, Fe\(^{3+}\)-free end-member version of reaction (3) (i.e., at the right-edge
of the Si$_{10/3}$O-Al$_{18/3}$O-Fe$_{8/3}$O plane; Fig. 5g). Although plag-out for a Fe$^{3+}$-bearing lherzolite must occur at a lower $P$ than this univariant reaction, the low Fe$^{3+}$ contents of natural peridotites suggest that the $P$ difference between plag-out (Fig. 5e) and the disappearance of plag from the Fe$^{3+}$-free end member system via this univariant reaction (Fig. 5g) is expected to be small. We determined that based on pMELTS, the difference between plag-out in the Cr$^{3+}$-free DMM composition at the full Fe$^{3+}$ content assumed here for DMM and for a Cr$^{3+}$- and Fe$^{3+}$-free DMM equivalent is ~0.3 kbar at 1100°C, consistent with the expectation that this $P$ interval is small.

The $P$ difference between sp-in (Fig. 5c) and plag-out (Fig. 5e) is also expected to be small as it reflects to the passage of the narrow opx+plag+sp+(ol+cpx) triangle over a bulk composition plotting near the Fe$^{3+}$-free edge of the model system shown in Figure 5. Based on pMELTS calculations on a Cr$^{3+}$-free DMM equivalent, the width of this transition is ~1.3 kbar at 1100°C. Similarly, the width of this transition in a Cr$^{3+}$-free KLB-1 equivalent at 1100°C based on the JH-15 model is ~1.2 kbar (see Fig. 3 in Jennings and Holland, 2015). However, these values are likely upper limits to the width of this interval in the model system of Figure 5 because the width of the transition for a Cr$^{3+}$- and Fe$^{3+}$-free DMM equivalent based on pMELTS at 1100°C is still ~0.9 kbar, despite the absence of Cr$^{3+}$ and Fe$^{3+}$; the persistence of this $P$ interval in the Cr$^{3+}$- and Fe$^{3+}$-free composition is probably due to effects such as Fe$^{2+}$-Mg partitioning among the phases (which would not apply to the quinary model system shown in Fig. 5).

Cr$_2$O$_3$ and Fe$_2$O$_3$ have similar effects on the phase equilibria of peridotite systems in that both are concentrated into sp and thus stabilize a sp phase, lowering the $P$ of sp-in and plag-out and raising the $P$ of sp-out (see the section below on the gt-lherzolite facies) relative to systems in which they are absent. Indeed, if Figures 5b-5f were drawn with the lower left apex of the compositional triangle being Cr$_{10/3}$O rather than Fe$_{10/3}$O and Fe$^{3+}$ were replaced with Cr$^{3+}$ in all the mineral formulae, the sequence of isothermal sections would be topologically similar and could be used to analyze the sequence of assemblages of a Cr$^{3+}$-bearing peridotite with increasing $P$. However, the concentration of Cr$_2$O$_3$ in peridotite is usually much higher than that of Fe$_2$O$_3$, so
the bulk composition of the peridotite (i.e., the position of the green dot) would be further to the left and a Cr\(^{3+}\)-rich \textit{sp} would be stabilized at much lower \textit{P} than an Fe\(^{3+}\)-rich \textit{sp} in a Cr\(^{3+}\)-absent system. Given the Cr\(^{3+}\) contents of most peridotites, a Cr\(^{3+}\)-rich \textit{sp} is typically stable at 1 bar (even in the absence of Fe\(^{3+}\)), and their bulk compositions would be in the \textit{opx}+\textit{plag}+sp+(\textit{ol}+\textit{cpx}) triangle throughout the \textit{plag}-stability field (Borghini et al., 2009). This is the case for the pMELTS and JH-15 results for the Fe\(^{3+}\)+Cr\(^{3+}\)-bearing DMM peridotite composition, which predict the presence of Cr\(^{3+}\)-rich \textit{sp} all the way down to 1 bar as shown in Figures 3b3 and 3a3 (this would not be the case for the Cr\(^{3+}\)-absent, Fe\(^{3+}\)-bearing model composition illustrated in Fig. 5). Note that the stabilization of Cr\(^{3+}\)-rich \textit{sp} (which is predicted to contain relatively high Fe\(^{3+}\) concentration; see Figs. 3a2 and 3b2) outside of the nominal \textit{sp}-lherzolite facies is diminished in the JH-15 model relative to the pMELTS model by the partitioning of both Cr\(^{3+}\) and Fe\(^{3+}\) into \textit{px} and/or \textit{gt} (hence the difference between \textit{sp} abundances based on pMELTS [Figs. 3a3] and JH-15 [Fig. 3b3], reflecting that pMELTS does not allow Cr\(^{3+}\) to go into \textit{px} or \textit{gt} or Fe\(^{3+}\) to go into \textit{gt}). Nevertheless, Cr\(^{3+}\) is present in sufficient abundance in most peridotites that chromite-rich \textit{sp} is nearly ubiquitous in peridotites at \textit{Ps} from 1 bar extending to well into the \textit{gt}-lherzolite facies (Pearson et al., 2003; Warren, 2016).

The way in which the stability of Cr\(^{3+}\)-rich \textit{sp} to lower and higher \textit{Ps} relative to Cr\(^{3+}\)-free systems influences the issues we are interested in here is best illustrated by the JH-15 calculations, in which partitioning of Cr\(^{3+}\) into \textit{px} prevents the significant overestimation of \textit{sp} stabilization present in the pMELTS model. Most importantly, the stabilization of Cr\(^{3+}\)-rich \textit{sp} means that the activities of other \textit{sp} components – especially (Mg,Fe)Al\(_2\)O\(_4\) and magnetite – do not have to be high in order for Al\(^{3+}\) and Fe\(^{3+}\) to partition significantly into the \textit{sp} phase. Several features of the results for DMM based on the JH-15 model (Fig. 3) show the onset of significant production of aluminous components in the calculated \textit{sp} in the DMM composition by reactions such as (3) at ~6 kbar: e.g., the simultaneous upswings in \textit{sp}, \textit{opx}, and \textit{cpx} abundances downswings in \textit{plag} and \textit{ol} abundances (Fig. 3b3); the slope-breaks in the progressively decreasing magnetite content (Fig. 3b2) and Cr\# (not shown) and progressively increasing Al\(_2\)O\(_3\)
content (not shown) of the calculated sp; and the changing slope of the calculated concentration of Fe\(^{3+}\) in the opx (Fig. 3b2). Although consumption of plag and ol with increasing \(P\) via reactions (1) and (2) and the concomitant decrease in \(fO_2\) due to Fe\(^{3+}\) dilution in px occur at lower \(P\) than that at which reaction (3) begins to be significant, the effects of Fe\(^{3+}\) dilution on \(fO_2\) (regardless of how – or whether – \(fO_2\) is normalized; see Figs. 2a, 2b, 3a1, and 3b1) are accelerated by the kicking-in of reaction (3) at ~6 kbar, which is in effect analogous to the right edge of the \(opx+plag+sp+(ol+cpx)\) triangle crossing over the bulk composition in Figures 5c-5e.

As described previously, there will be some redistribution of Fe\(^{3+}\) between sp, opx, and cpx with increasing \(P\), but these effects are less important in controlling \(fO_2\) than are the effects of dilution – dominantly in the px and less so in the sp – driven by the volume changes of the continuous solid-solid reactions involving increases in Al-coordination. As explained above, it is this dominant role of px as opposed to sp in this dilution effect that explains why the calculations of Ballhaus and Frost (1994) and Ballhaus (1995) overestimated the decrease in \(fO_2\) upon conversion of plag lherzolite to sp lherzolite relative to our results; i.e., most of the Fe\(^{3+}\) in the system is in the px and this effect occurs whether or not sp is stabilized (see the blue curve in Fig. 2d). We also ran pMELTS simulations on a Cr\(^{3+}\)-free DMM composition, and although the amounts of sp are much lower than in the simulations on the actual Cr\(^{3+}\)-bearing DMM composition, the \(fO_2\) trends are similar in both cases, consistent with the conclusion that sp is not the principal driver of the modeled trends. Nevertheless, the concentration of the magnetite component in sp is still a valuable passive indicator or monitor of \(fO_2\) in peridotites via the reaction \(3 \text{Fe}_2\text{SiO}_4^{ol} + \frac{1}{2} \text{O}_2 \rightleftharpoons 3 \text{FeSiO}_3^{opx} + \text{Fe}_3\text{O}_4^{sp}\) given the ubiquity of \(ol+opx+sp\) assemblages (e.g., Wood, 1991). This is also true for the approach to modeling \(fO_2\) in peridotites using Fe\(^{3+}\)-bearing defects in ol developed by Gaetani (2016): although variations in the small amounts of Fe\(^{3+}\) in ol are unlikely to control variations in peridotite \(fO_2\) with \(P\) and \(T\), they might nevertheless be useful passive tracers of peridotite \(fO_2\).

**The effects of \(P\) on \(fO_2\) in the sp-lherzolite facies.** As described previously, the disappearance of plag from the thermodynamically calculated stable assemblage reflects the
sweeping of the opx+plag+sp+(ol+cpx) triangle to the right in Figure 5 such that, relative to the triangle, the peridotite composition moves from the inside of the triangle (Fig. 5d) to the left of the triangle (i.e., into the opx+sp+(ol+cpx) field; Fig. 5f) with increasing $P$. Although plag disappears from the assemblage at the $P$ of Fig. 5e, as described previously it does not disappear from the isothermal sections until the slightly higher $P$ where the selected isotherm crosses the univariant reaction (3) in the Fe$^{3+}$-absent end-member system (Fig. 5g). The simple topology of Figure 5h then prevails over most of the sp-lherzolite facies, until gt appears near the upper $P$ limit of the sp-lherzolite facies (see Figs. 5i and 5j).

As was the case for the plag-stability field, we can understand changes in $fO_2$ with increasing $P$ in the sp-lherzolite facies by thinking about reactions involving aluminous phases and the $P$-dependent changes in Al-coordination that drive these reactions. A representative reaction in the FeO-Al$_{1/3}$O-Si$_{1/2}$O system is

$$\frac{2}{5} \text{fayalite (ol)} + \frac{3}{5} \text{Fe-Tschermak (px)} = \frac{2}{5} \text{hercynite (sp)} + \frac{3}{5} \text{ferrosilite (opx)}.$$  \hspace{1cm} (4)

The details of the comparable reaction in the MgO-end-member system have been the subject of much investigation, and there is general agreement that, in $P$-$T$ space, alumina isopleths for px in the sp-lherzolite facies are largely insensitive to $P$, reflecting the fact that the standard-state volume change is close to zero for this reaction (e.g., MacGregor, 2015). This is consistent with the calculated peridotite phase equilibria based on either the pMELTS or JH-15 models; i.e., the modeled abundances of ol, sp, and px are essentially constant across the sp-lherzolite facies (Figs. 3a3 and 3b3). As a consequence, the concentrations (Figs. 3a2, 3b2, 2g, and 2h) and activities (Figs. 2e and 2f) of Fe$_2$O$_3$ in px (and sp) in this field also change relatively little, being neither diluted nor concentrated in these phases with changing $P$. For the JH-15 model, this results in an essentially constant $fO_2$ relative to a metastable ol+opx+cpx assemblage (see the orange curve in Fig. 2b) or slightly increasing $\Delta$FMQ (Fig. 3b1), and for the pMELTS model in a slightly decreasing $\Delta$FMQ (Fig. 3a1); this contrasts with the strongly decreasing $fO_2$ with $P$ in
the plag-stability field. The important point is that in both the sp- and plag-stability fields, the effects of heterogeneous phase equilibria on $fO_2$ based on these models can be simply understood by examining changes in the amounts of $px$. In the sp-lherzolite case, the absence of significant $P$ dependence of reaction (4) and the equal amount of $px$ on both sides of the reaction mean that the concentrations (and activities) of $\text{Fe}^{3+}$-bearing components in $px$ (and in sp) are not greatly changed by passive dilution or enrichment as $P$ changes across the sp-lherzolite facies.

In the context of the schematic phase relations illustrated in Figure 5, the previous paragraph means that the lower boundary of the opx field (i.e., the upper termination of the opx+sp+(ol+cpx) tie lines at the edge of the red opx field) does not move significantly (either up or down) with increasing $P$, and the orientations of the tie lines (i.e., the $\text{Fe}^{3+}$/Al partitioning between opx and sp) do not change significantly, and thus the $\text{Fe}^{3+}$ content of the opx in the assemblage is largely unchanged. Note, however, that even if the edge of the opx field coexisting with sp were moving toward or away from the Si$_{1/2}$O vertex, the topology of the diagram predicts smaller effects on $fO_2$ compared to the analysis of the plag-lherzolite assemblage (Fig. 6a) because the opx-sp tie lines are considerably longer than the opx-plag tie lines (and are not anchored to the $\text{Fe}^{3+}$-free projected anorthite point) and the opx/sp ratio is significantly higher than the opx/plag ratio. Thus, the same movement of the edge of the opx field toward or away from more aluminous px compositions would have less influence on the mole fraction of $\text{Fe}^{3+}$ in the opx and hence on $fO_2$ in the sp-lherzolite facies than in the plag-lherzolite facies.

**Variations in $fO_2$ in the gt-lherzolite facies**

**Graphical analysis of the gt-lherzolite facies.** The transition from sp lherzolite to gt lherzolite can also be visualized using the projection shown in Figure 5. Starting from the sp-lherzolite facies represented graphically by Figure 5h, we assume gt first appears via the univariant reaction $\frac{3}{4}$ ferrosilite + $\frac{1}{4}$ hercynite = $\frac{1}{4}$ fayalite + $\frac{3}{4}$ almandine in the FeO-Al$_{1/3}$O-Si$_{1/2}$O ternary system; this univariant reaction projects onto the Si$_{1/2}$O-Al$_{1/3}$O edge of the bounding triangle (Fig. 5i). In reality, it is more likely that gt first appears in this MgO-free model
lherzolite system by a univariant reaction among hedenbergite, ferrosilite, hercynite, fayalite, and a binary grossular-almandine \( gt \) in the CaO-FeO-Al\(_2\)O\(_3\)-SiO\(_2\) quaternary sub-system (MacGregor, 1967). This univariant reaction would still project along the Si\(_{1/2}\)O-Al\(_{2/3}\)O edge of the bounding triangle of Figure 5i, but the position of the binary \( gt \) would be displaced from almandine toward grossular, which in this projection plots farther down towards hercynite (or even beyond it if the \( gt \) were sufficiently rich in grossular). Although we cannot rule out the first appearance of \( gt \) as a quinary, Fe\(^{3+}\)-bearing \( gt \), our assumption that it first stabilizes as an Fe\(^{3+}\)-free (or perhaps Fe\(^{3+}\)-poor) \( gt \) in the model system of Figure 5 is consistent with the results of Woodland and O’Neill (1993) and the JH-15 model (Jennings and Holland, 2015). For simplicity, we choose to show the first appearance of \( gt \) as pure almandine in Figure 5 because including Ca- and/or Fe\(^{3+}\)-bearing \( gt \) end members (such as grossular, andradite, and/or skiagite) would add complexity but no additional graphical insights unless the first-appearing \( gt \) were significantly more Fe\(^{3+}\)-rich than predicted by the JH-15 model.

Increasing \( P \) beyond the univariant appearance of almandine in the Fe\(^{3+}\)-free model system produces a configuration such as that shown in Figure 5j, with a three-phase \( opx+sp+gt+(ol+cpx) \) triangle sweeping across the diagram to the left, opening up (1) a two-phase \( gt \)-lherzolite facies with the assemblage \( opx+gt+(ol+cpx) \) for more \( opx \)-rich compositions plotting above almandine and to the right of the \( opx+gt+(ol+cpx) \) edge of the triangle, and (2) a second two-phase region, \( gt+sp+(ol+cpx) \), below almandine and to the right of \( gt+sp+(ol+cpx) \) edge of the triangle. The triangle is initially narrow and close to the projected Si\(_{1/2}\)O-Al\(_{2/3}\)O join, so at the \( P \) of Figure 5j, the peridotite composition (shown by the green symbol) is still in the \( sp \)-lherzolite facies (i.e., it is in the two-phase \( opx+sp+(ol+cpx) \) field covering most of the diagram). As described above, we assume that \( gt \) first appears as a stable phase at pure almandine. However, with increasing \( P \), \( gt \) is assumed to be a binary solid solution extending from almandine towards skiagite. This solid solution is shown in each panel after Fig. 5i as a red horizontal line, the Fe\(^{3+}\)-rich end of which extends progressively further toward skiagite with increasing \( P \), reflecting the increasing stability
of Fe$^{3+}$-bearing gt at higher $P$ (e.g., O'Neill et al., 1993; Woodland and O'Neill, 1993; Rohrbach et al., 2007; Stagno and Frost, 2010; Jennings and Holland, 2015).

With increasing $P$, the $opx+sp+gt+(ol+cpx)$ triangle continues moving to the left (i.e., the field of gt stability expands), and at the $P$ shown in Figure 5k, the left (i.e., the $opx+sp+(ol+cpx)$) edge of the triangle has reached the green symbol, corresponding to gt-in. Beyond this point, gt joins the assemblage, as with further increase in $P$, the left edge of the triangle passes over the bulk composition, after which the green symbol plots within the triangle (Fig. 5l) and the phase assemblage is $opx+sp+gt+(ol+cpx)$, corresponding to a sp+gt lherzolite. Note that the $P$ of the gt-in reaction depends on the Fe$^{3+}$ content of the bulk composition; it is always at higher $P$ than the univariant reaction in the end-member Fe$^{3+}$-free system (Fig. 5i), and the difference increases for lherzolites with higher Fe$^{3+}$ contents, as demonstrated by MacGregor (1970).

However, just as was shown above that in the absence of Cr$^{3+}$ there is only a small $P$ difference between the $Ps$ of sp-in, plag-out, and the plag$\rightarrow$sp univariant reaction in the Fe$^{3+}$-free subsystem in a low-Fe$^{3+}$ composition such as DMM, the $P$ difference between the appearance of gt in the Fe$^{3+}$-free end-member system and in a low-Fe$^{3+}$ lherzolite is expected to be small. Based on pMELTS calculations at 1100$^\circ$C, the $P$ difference between the univariant gt-in reaction in a Cr$^{3+}$- and Fe$^{3+}$-free DMM equivalent and gt-in in a Cr$^{3+}$-free composition that has the full complement of Fe$^{3+}$ of our model DMM composition is 0.8 kbar, consistent with this expectation.

With still further increases in $P$, the $opx+sp+gt+(ol+cpx)$ triangle moves far enough to the left that the upper right edge of the triangle (i.e., the $opx+gt+(ol+cpx)$ edge) reaches the bulk composition (Fig. 5m), and the amount of sp in the assemblage is zero at this point, corresponding to sp-out. At higher $P$, the bulk composition is in the $opx+gt+(ol+cpx)$ two-phase region (Fig. 5n), and the peridotite is a gt lherzolite. The $P$ where sp-out occurs clearly depends both on the bulk composition of the peridotite (i.e., it would be higher for higher Fe$^{3+}$ contents because the triangle would have to move further to the left for higher Fe$^{3+}$ contents in order for the composition no longer to fall within the triangle) and on the Fe$^{3+}$ content of the gt apex of the
triangle (i.e., if the *gt* were assumed to be Fe$^{3+}$-free, the upper-right edge of the triangle would cross over the peridotite bulk composition at higher *P* than if, as depicted in Figure 5m, the *gt* contains Fe$^{3+}$). Moreover, as described previously for the *plag*→*sp*-lherzolite transition, addition of Cr$^{3+}$ to the system has effects similar to (and, due its higher concentration, larger than) those of Fe$^{3+}$ in broadening the *P* interval over which the *sp*→*gt*-lherzolite transition occurs (O'Neill, 1981; Nickel, 1986). Cr$^{3+}$, like Fe$^{3+}$, increases the *P* of both *gt*-in and *sp*-out, with a larger effect on *sp*-out (Jennings and Holland, 2015). As mentioned previously in connection with the *plag*→*sp*-lherzolite transition, this could be understood qualitatively with diagrams comparable to those of Figure 5 but in which Fe$_{\frac{2}{3}}$O is replaced by Cr$_{\frac{2}{3}}$O. Note again, however, that *sp* only disappears from the assemblage if and when the Cr$^{3+}$ content is fully accommodated in *px*+*gt*; this never occurs in pMELTS because the only subsolidus host for Cr$^{3+}$ in this model is *sp*.

The sequence of phase assemblages with increasing *P* illustrated by the model isothermal sections shown in Figures 5h-5n corresponds well to the thermodynamically calculated sequence of phase assemblages shown in Figures 3a3 and 3b3 and to experimental results (e.g., O'Neill, 1981; Nickel, 1986; Robinson and Wood, 1998). Focusing on the JH-15 calculations, as *P* increases from the *sp*-lherzolite facies (Fig. 5h), *gt* appears as the left edge of the *opx*+*sp*+*gt*+(*ol* +*cpx*) triangle moves from right to left over the bulk composition (Figs. 5j→5k). As *P* increases and the triangle continues to move to the left, both the abundance and Fe$^{3+}$ content of *gt* increase while the abundance of *sp* decreases and its Fe$^{3+}$ content increases over a narrow *P* range until *sp* is exhausted when the right edge of the triangle coincides with the bulk composition (Fig. 5m; Figs. 3b3 and 3b2). The narrow *P* range of *sp*+*gt* lherzolite stability in DMM based on JH-15 (0.5-0.6 kbar; Fig. 3b3) reflects the narrowness of the *opx*+*sp*+*gt*+(*ol* +*cpx*) triangle in Figure 5k-5m, due its nearness to the Fe$^{3+}$-free edge of the diagram (because of the low Fe$^{3+}$ and Cr$^{3+}$ contents in the DMM composition); to the fact that this model bulk composition (like most natural peridotites) plots near the *opx* apex of the three-phase triangle (where the triangle is narrowest) because *opx* is significantly more abundant than *gt* in the relevant *P* range; and to the capacity of *gt* to dissolve significant Cr$^{3+}$. Note that the calculated width of this transition based
on JH-15 is similar (0.3-0.4 kbar) to that of the fertile KLB-1 composition (Jennings and Holland, 2015). The overall sequence of phase assemblages is similar for the pMELTS calculation, although again sp never disappears from the Cr³⁺-bearing assemblage in this case (i.e., the bulk composition never exits the opx+sp+gt+(ol+cpx) triangle).

The sequence of phase assemblages in a representative peridotite composition with increasing $P$ described in the previous paragraphs is associated with a progressive increase in $fO_2$ relative to FMQ or to a metastable ol+opx+cpx±sp assemblage of as much as 1-1.5 orders of magnitude from gt-in up to ~30 kbar (Figs. 3a1, 3b1, 2a, 2b). That this increase in normalized $fO_2$ is related primarily to stabilization of $gt$ was demonstrated previously using the results of the metastable calculations shown in Figure 2. In particular, using either pMELTS (Fig. 2c) or JH-15 (Fig. 2d), the discontinuous increase in the slope of the $fO_2$ vs. $P$ trend at gt-in and the downward curvature of the $fO_2$ vs. $P$ curve in the $gt$ stability field are only present when $gt$ is allowed to appear in the assemblage. Although they differ in detail, that the pMELTS (Figs. 2a vs. 2c) and JH-15 (Figs. 2b vs. 2d) models both produce similar results for the effects of $gt$ on $fO_2$ normalized to a metastable ol+opx+cpx±sp assemblage demonstrates that the connection between increasing $fO_2$ and the production of $gt$ over the $P$ range we have modeled does not depend strongly on the treatment of Fe³⁺ and Cr³⁺ in $gt$ or px or on other differences between the two thermodynamic models.

**Coupling between alumina in px and $fO_2$ in the $gt$-lherzolite facies.** The increase in $fO_2$ relative to metastable ol+opx+cpx±sp assemblages that results from $gt$ stabilization with increasing $P$ is the reverse of the effect of plag destabilization described previously. Figures 2c and 2d show that $fO_2$ increases in going from a metastable $gt$-absent assemblage in the pMELTS calculation or a metastable $gt$+sp-absent assemblage for the JH-15 calculation to a more stable $gt$-bearing assemblage (e.g., from the horizontal lines at zero to the elevated purple curves above ~20 kbar in Fig. 2c and ~14.5 kbar in Fig. 2d). In the pMELTS model, $gt$ forms from the metastable, $gt$-free assemblage by reactions between sp and px such as
¼ hercynite (sp) + ¼ ferrosilite (opx) = ¼ almandine (gt) + ¼ fayalite (ol), \( \text{(5)} \)

and by reactions between \( px \) components alone (i.e., without \( sp \)) such as

\[
\frac{1}{2} \text{Mg-Tschermak} (px) + \frac{1}{2} \text{enstatite} (px) = \text{pyrope} (gt), \tag{6a}
\]

or the equivalent for the model Fe\(^{2+}\)-end-member system shown in Figure 5,

\[
\frac{1}{2} \text{Fe-Tschermak} (px) + \frac{1}{2} \text{ferrosilite} (px) = \text{almandine} (gt). \tag{6b}
\]

For the JH-15 model, only reactions (6a) and (6b) apply because \( sp \) is not present in the metastable reference assemblage or in the stable assemblage in Figure 2d. Similar \( px \)-consuming reactions that generate grossular-bearing \( gt \) can be written with Ca-Tschermak, hedenbergite, or diopside \( px \) components. Reactions (5) and (6) show that formation of one mole of \( gt \) consumes one mole of \( px \) (on a single oxygen basis). Based on either model, for an isobaric, isothermal transformation from the metastable \( gt \)-absent to the \( gt \)-bearing assemblages, the decrease in the amount of \( px \) (and \( sp \) in the pMELTS calculations) results in increases in the concentrations (and activities) of their Fe\(^{3+}\)-bearing components and therefore in the \( fO_2 \). As described and emphasized above for the case of \( plag \) consumption via reaction with \( ol \) (such as reactions [1] and [2]), this effect is primarily a passive one, driven by redistribution of Al towards the more stable (and lower molar volume components) on the right-hand sides of reactions (5) and (6) rather than to reactions involving Fe\(^{3+}\) \textit{per se}. However, the concave down trend in \( fO_2 \) with \( P \) relative to the metastable \( ol+opx+cpx\pm sp \) assemblage reaches a maximum for the JH-15 model at \(~30 \text{ kbar} \), and as described below, we attribute this primarily to the effects of redistribution of Fe\(^{3+}\) between \( px \) and \( gt \) due to the progressively increasing amount of Fe\(^{3+}\) in \( gt \) relative to \( px \) with increasing \( P \) in the \( gt \)-lherzolite field: i.e., the fraction of Fe\(^{3+}\) in the stable system that is in \( gt \) as opposed to \( px \) increases from \(~6\% \) at \( sp \)-out to almost 50\% at 40 kbar. Note that the concave down shape of \( \log_{10} fO_2 \) (normalized to a metastable \( gt \)-free assemblage) vs. \( P \) is present in the pMELTS calculations (including for a Cr\(^{3+}\)-free composition, which avoids artifacts due to the overstabilization of \( sp \)), which do not include any Fe\(^{3+}\) in the \( gt \). Thus, although likely
amplified in the JH-15 model due to progressive partitioning of Fe$^{3+}$ into gt with increasing $P$, this feature probably also reflects the progressively diminishing effectiveness of reactions (6a) and (6b) at increasing the modal abundance of gt at the expense of px with increasing $P$, which in turn diminishes the effect of concentration of Fe$^{3+}$ with progressive gt formation; this is consistent with the concave down trend of gt abundance and concave up trends in opx and cpx abundances shown in Figs. 3a3 and 3b3. Note also that for the JH-15 calculation, allowing sp to be stable in the initial metastable assemblage has only a minor effect on its $fO_2$ (i.e., compare the orange curve with the horizontal line in Fig. 2d), so these same statements apply to conversion of a metastable sp lherzolite to the more stable assemblage in which gt is the only stable high-Al phase.

The analysis of the previous paragraph focuses on the role of gt formation without considering the interaction between sp and gt in their overlapping stability fields. The transition from sp lherzolite to gt lherzolite over a small $P$ range was anticipated in our discussion of Figures 5j-5n earlier in this section, reflecting the narrow interval of increasing $P$ required for passage of the $opx+gt+sp+(ol+cpx)$ triangle over the peridotite composition. The importance of this 0.5-0.6 kbar $P$ interval between gt-in and sp-out in the JH-15 model (Fig. 3b3) is manifested in Figures 2b and 3b1 by the steep ~0.5 log unit increase in both absolute and normalized (either $\Delta$FMQ or relative to a metastable ol+opx+cpx assemblage) $fO_2$ over this $P$ interval. Significantly, this increase in $fO_2$ is accompanied by a large increase in gt abundance from 0 to ~10 wt. % while opx abundance decreases by ~30% (from ~27 to 19%) and cpx abundance decreases by ~15% (from ~15 to 13%).

The leftward movement of the $opx+gt+sp+(ol+cpx)$ triangle across the model peridotite composition with increasing $P$ (Figs. 5k-5m) can be understood via the stoichiometry of reaction (5) or by a comparable reaction involving consumption of Ca-bearing pyroxene components. Thus, as with the sp-absent reactions (6a) and (6b), for every mole of gt generated, one mole of px is consumed. Again, because most of the Fe$^{3+}$ in the system is in px both before and after the sp$\rightarrow$gt-lherzolite transition (especially for the JH-15 calculations; Figs. 4b and 4d), the
consumption of Fe$^{3+}$-free px components by reaction (5) leads to increases in the concentrations and activities of Fe$_2$O$_3$ in the residual opx and cpx and a concomitant increase in $f$O$_2$ over the narrow $P$ interval in which sp and gt coexist in the JH-15 model (Figs. 3b1-3b3). This effect is also qualitatively understandable graphically by comparing Figure 5j (just below gt-in) and Figure 5n (just above sp-out): The tie-line between opx and sp is much longer in Figure 5j than the tie-line between opx and gt in Figure 5n, and thus for the same bulk composition (the green symbol), the abundance of opx in the assemblage is lower in the gt-lherzolite facies than in the sp-lherzolite facies, leading to concentration of Fe$^{3+}$ in the opx and therefore to higher $f$O$_2$ in the gt-lherzolite assemblage relative to the sp-lherzolite assemblage; note that such quantitative features can be misleading in projections such as that used in Figure 5, but the substantial decreases in opx abundance inferred with decreasing $P$ graphically accompanying the sp$\rightarrow$gt-lherzolite transition is confirmed by the JH-15 calculations (both for opx and cpx; Fig. 3b3).

Simultaneous with reaction (5) being driven to the right with increasing $P$, the right-hand sides of reactions (6a) and (6b) are also favored with increasing $P$. Thus, if we only looked at reaction (5), one might conclude that with its consumption of the ferrosilite component of the opx, it would lead to a passive increase in the concentration in the opx of Al$_2$O$_3$ (i.e., in the concentration of the Fe-Tschermak component) as well as of Fe$_2$O$_3$ (which leads to the large increase in $f$O$_2$ across the narrow sp$\rightarrow$gt-lherzolite transition). However, this is counteracted by the consumption of the Fe-Tschermak component via reaction (6b) as the transition from sp$\rightarrow$gt lherzolite is crossed with increasing $P$, such that the Al$_2$O$_3$ concentration of the opx is little changed over this small $P$ interval (Fig. 2h). Graphically, this means that the opx apex of the opx+gt+sp+(ol+cpx) triangle moves little over the small $P$ interval between Figure 5k and 5m. As described above for the comparable discussion for the plag$\rightarrow$sp-lherzolite transition, the details of the trajectory of the opx apex across the sp$\rightarrow$gt-lherzolite transition requires simultaneous solution of the equilibria in reactions (5) and (6) and other independent reactions among the phases and components in the system, and therefore cannot be fully evaluated by focusing on one reaction alone.
Although the same increases in absolute and normalized $fO_2$ with $P$ just above $gt$-in seen in the JH-15 calculation are present in the pMELTS calculation (Figs. 2a and 3a1), they are more gradual because the treatment of $Cr^{3+}$ in pMELTS widens the $P$ interval over which most of the hercynite transfers into $gt$. Note that because at least some $sp$ is always present in the pMELTS calculations (albeit at low abundances beyond the transitional region above $gt$-in; Fig. 3a3), the increases in $fO_2$ with $P$ resulting from reactions (5) and (6) are accompanied by a substantial progressive increase in the concentration (Fig. 3a2) and activity of the magnetite component in the residual $sp$. This is shown in Figures 5k-5n by the progressive leftward movement of the $sp$ corner of the $opx+sp+gt+(ol+cpx)$ triangle with increasing $P$. Although as described previously for the region of $sp+plag$ coexistence, $opx$ and $cpx$ still contain more than 50% of the $Fe^{3+}$ in the system in the pMELTS calculations (Fig. 4a), $sp$ contains the remainder of the $Fe^{3+}$ in the system and is a major reservoir for $Fe^{3+}$. Nevertheless, the overall similar shapes and magnitudes of $fO_2$ variations in the pMELTS and JH-15 models as the $gt$ field is traversed with increasing $P$ suggests that this artifact of the pMELTS model does not exert significant control over the $fO_2$ variations correlated with the phase changes involving aluminous phases on which we have focused. Note that we also ran the pMELTS calculations on a $Cr^{3+}$-free DMM composition; in this case, just as it does for the $Cr^{3+}$-bearing JH-15 model, $sp$ disappears from the phase assemblage at a $P$ just above $gt$-in, and $fO_2$ relative to a metastable $ol+opx+cpx±sp$ assemblage increases steeply in this zone reflecting the passage of the narrow $opx+sp+gt+(ol+cpx)$ triangle over the $Cr^{3+}$-free composition; i.e., when the artifact of the pMELTS modeling always stabilizing $sp$ is removed, this difference between the pMELTS and JH-15 models in the low-$P$ region of the $gt$-lherzolite facies is no longer present.

**The effect of $Fe^{3+}$ in $gt$.** To this point, we have emphasized the importance of passive dilution or enrichment of $Fe^{3+}$ in the dominant $Fe^{3+}$-bearing phases ($opx + cpx$) that accompanies their production or consumption as a result of heterogeneous equilibria to explain the changes in $fO_2$ relative to metastable $ol+opx+cpx±sp$ assemblages that are observed in our models. As described previously, however, redistribution of $Fe^{3+}$ between phases does occur, and can also
play a role. The most important example of this in our modeling is the progressive transfer of Fe\(^{3+}\) from \(px\) to \(gt\) from \(gt\)-in up to 40 kbar based on the JH-15 calculations; the results of Jennings and Holland (2015) suggests this trend continues to at least 60 kbar. The concentration of \(gt\) in Fe\(^{3+}\) relative to \(px\) with increasing \(P\) is well known and related to equilibria such as 2 fayalite + ferrosilite + \(\frac{1}{2}\) \(O_2\) = skiagite, where the right-hand side is strongly favored by increasing \(P\) (e.g., Wood et al., 1990; Woodland and O'Neill, 1993; Ballhaus, 1995; Gudmundsson and Wood, 1995; Rohrbach et al., 2007; Frost and McCammon, 2008; Stagno and Frost, 2010). In the output of the JH-15 model, this is manifested by the continuously increasing Fe\(^{3+}\) content of the \(gt\) with increasing \(P\) at 1100°C starting from its appearance at \(gt\)-in (see the purple curve in Fig. 3b2) and the decreasing Fe\(^{3+}\) concentration in the \(opx\) above \(\sim 18\) kbar and in the \(cpx\) above \(\sim 23\) kbar (Fig. 3b2): Starting from \(gt\)-in at \(\sim 15\) kbar, with increasing \(P\) up to 40 kbar, \(D(Fe^{3+})_{gt/opx}\) (i.e., \(Fe^{3+}\)\(_{gt}/Fe^{3+}\)\(_{opx}\)) increases from 0.18 to 1.8, and \(D(Fe^{3+})_{gt/cpx}\) increases from 0.48 to 2.6. Thus, with increasing \(P\) in the \(gt\)-lherzolite facies, there is a competition between the tendency to concentrate Fe\(^{3+}\) in the \(px\) via reactions (5) and (6) — although as mentioned previously this effect diminishes continuously above \(sp\)-out for the JH-15 model (Fig. 3b3) and above \(gt\)-in for the pMELTS model (Fig. 3a3) — and the transfer of Fe\(^{3+}\) from \(px\) to \(gt\) due to the progressive increases in \(D(Fe^{3+})_{gt/opx}\) and \(D(Fe^{3+})_{gt/cpx}\). The passive concentration of Fe\(^{3+}\) in \(px\) dominates close to \(gt\)-in, but the partitioning of Fe\(^{3+}\) into \(gt\) becomes progressively more important with increasing \(P\), and we speculate that this results in the broad maximum in \(fO_2\) at \(\sim 30\) kbar when normalized to a metastable \(ol+opx+cpx\) assemblage (Fig. 2b); this maximum is also present for \(\Delta FMQ\) but not in absolute \(fO_2\) (Fig. 3b1). This explanation for the decrease in \(fO_2\) relative to a metastable \(gt+sp\)-absent assemblage at \(P \geq 30\) kbar is closely related to that proposed by Ballhaus and Frost (1994) and Ballhaus (1995), although for reasons explained below, their expectation that \(fO_2\) would decrease immediately above \(gt\)-in is inconsistent with our modeling.

We have not extended our modeling above 40 kbar, but the isothermal decrease in \(\Delta FMQ\) predicted here above \(\sim 30\) kbar (Fig. 3b1) is also predicted by the JH-15 model to extend on
isotherms to 60 kbar for the fertile KLB-1 peridotite (Jennings and Holland, 2015) and on a
geotherm up to 70 kbar for the moderately depleted Y-17 peridotite (Miller et al., 2016). The
continuation of this trend in ΔFMQ to these high Ps may be due in part to continued transfer of
Fe$^{3+}$ into gt (especially in the lower P part of the 40-70 kbar interval), but the difference in the
standard-state volume changes of the FMQ and skiagite-formation reactions also contribute to
this effect when the $fO_2$ is reported as ΔFMQ (Frost and McCammon, 2008).

The pMELTS calculation does not have a maximum in $fO_2$ relative to a metastable gt-absent
assemblage in the gt-lherzolite field (Fig. 2a). Because pMELTS does not partition any Fe$^{3+}$ into
gt, the absence of this feature in the pMELTS results is consistent with our explanation that this
maximum in the JH-15 results relates to the transfer of Fe$^{3+}$ from px to gt with increasing P.

Note, however, that the pMELTS calculations do generate a maximum in ΔFMQ in the gt field at
about 20 kbar (Fig. 3a1) — consequently, the progressive divergence with increasing P above 20
kbar between the FMQ buffer curve (dashed, black) and the absolute $fO_2$ curve for DMM (solid,
black) based on the pMELTS calculations (Fig. 3a1) that results in this maximum in ΔFMQ (the
red, solid curve) must reflect other factors.

The decrease in $fO_2$ relative to a metastable gt+sp-free assemblage above ~30 kbar for the
DMM peridotite composition based on JH-15 is small, and the details depend on many factors
embedded in the JH-15 thermodynamic model, including the variations in activity coefficients of
the various components for each phase with increasing P due changing phase compositions and
the balance among products and reactants involving many independent heterogeneous equilibria,
each shifting with P (and T) based on its changing standard-state free energy change. All of these
factors are dealt with implicitly in both the pMELTS and JH-15 models, but interpreting the
output in terms of which factors dominate is not always straightforward when the factors are
pulling in different directions. Nevertheless, we think this is probably a robust result. Supporting
this is the observation that the broad maximum in $fO_2$ relative to a metastable gt+sp-free
assemblage at about 30 kbar is straddled by the Ps at which Fe$^{3+}$ becomes compatible in gt
relative to opx and cpx (i.e., $D[Fe^{3+}]_{gt/opx}$ and $D[Fe^{3+}]_{gt/cpx}$ first exceed 1.0 at 33 and 26 kbar,
respectively), because this is a rough indicator of where the consequences of Fe\(^{3+}\) in \(gt\) will begin to dominate.

We can put the effects of progressive partitioning of Fe\(^{3+}\) into \(gt\) relative to \(px\) into a graphical context using the projections shown in Figures 5 and 6. With increasing \(P\) in the \(gt\)-lherzolite facies (i.e., above \(sp\)-out, represented by Fig. 5n), the concentration of Fe\(^{3+}\) in \(opx\) for the DMM composition based on JH-15 initially increases. Under these conditions this change in Fe\(^{3+}\) in \(opx\) can be illustrated using Figure 6b, an enlargement of the region around the \(gt\)-lherzolite facies (i.e., the \(gt+opx+(ol+cpx)\) field in Fig. 5n). Based on the JH-15 model, at \(sp\)-out, \(D(Fe^{3+})_{gt/opx}\) and \(D(Fe^{3+})_{gt/cpx}\) are ~0.2 and 0.5, and \(D(Fe^{3+)/Al}_{gt/opx}\) is ~0.06. Based on this partitioning of Fe\(^{3+}\) into \(px\) relative to \(gt\) (and the strong Fe\(^{3+}/Al\) partitioning, which affects tie-line slopes in Figs. 5 and 6), we show in Figure 6b a graphical treatment that approximates the \(gt\) as Fe\(^{3+}\)-free near the low-\(P\) limit of \(gt\) stability. This assumption that the \(gt\) is Fe\(^{3+}\)-free maximizes the effects of reactions (6a) and (6b), and it applies exactly to a Cr\(^{3+}\)-free pMELTS calculations (which neither overstabilize \(sp\) due to the treatment of Cr\(^{3+}\), nor places any Fe\(^{3+}\) in the \(gt\)). At low \(P\) (i.e., just above \(sp\)-out) the \(opx\) coexisting with \(gt+(ol+cpx)\) plots at point \(c\) at the upper end of the tie line from \(gt\) to \(opx\) that passes through the bulk composition (shown as a green dot). As \(P\) increases, the \(opx\) coexisting with \(gt+(ol+cpx)\) becomes less abundant and poorer in Al due to reactions (6a) and (6b) proceeding to the right. This is represented in Figure 6b by point \(d\), which is on the edge of the \(opx\) phase field where it intersects with the extension to higher ratios of ferrosilite to the Fe-Tschermak-component of the tie line between almandine and point \(c\) that passes through the peridotite composition (shown as the green dot); this follows from the fact that neither the peridotite composition nor the composition of the Fe\(^{3+}\)-free \(gt\) (neglecting grossular) have changed, so the \(opx\) must lie on the same tie line at low and high \(P\) given the approximation in this construction that the \(gt\) is Fe\(^{3+}\)-free. The movement of the \(opx\) to lower Al contents with increasing \(P\) at constant \(T\) reflects the well-known configuration in \(P-T\) space of alumina isopleths in \(opx\) in the \(gt\)-lherzolite facies that results from reactions (6a) and (6b). The main result of this simple graphical construction is that the higher \(P\) \(opx\) (point \(d\)) has
higher a higher Fe\textsuperscript{3+} content than the lower $P$ $opx$ (point $c$) based on the $c \rightarrow d$ trajectory across the dotted black lines of roughly constant Fe\textsuperscript{3+} content. The effect of $gt$ formation on the concentration of Fe\textsuperscript{3+} in $opx$ as $P$ increases illustrated in Figure 6b is the reverse of the effect of $plag$ consumption with increasing $P$ shown in Figure 6a, and in both cases, the increase in the concentrations of Fe\textsuperscript{3+} components in the $px$ – whether going down $P$ in the $plag$-lherzolite facies or up $P$ in the $gt$-lherzolite facies – will generally result in a concomitant increase in $fO_2$ relative to a metastable $ol+opx+cpx$\pm$sp$ assemblage (Fig. 2a and 2b). The progressive increase in $gt$ abundance at the expense of the $px$ with increasing $P$ in the $gt$-lherzolite facies present in both the JH-15 and pMELTS models (Figs. 3a3 and 3b3) is also illustrated graphically in Figure 6b by the position of the bulk composition relative to the lengthening $gt+opx+(ol+cpx)$ tie line.

As described above for $plag$ lherzolites, Figure 6b also demonstrates graphically why transformation at constant $P$ and $T$ from a metastable $gt$-free assemblage to the stable $gt$-bearing assemblage leads to an increase in $fO_2$ relative to the metastable assemblage (Figs. 2a-2d). The only aluminous phase in the metastable $ol+opx+cpx$ assemblage that appears in the projection shown in Figure 6b is $opx$. The $opx$ in the metastable assemblage must therefore in projection coincide with the bulk composition of the peridotite; i.e., both plot at the position of the green dot. When the metastable assemblage transforms to the stable, $gt$-bearing assemblage, the green dot representing the bulk composition of the peridotite must lie on a stable $opx+gt+(ol+cpx)$ tie line at the $P$ and $T$ of the transformation. Provided that the $gt$ is Fe\textsuperscript{3+}-poor, the $opx$ composition at the end of a stable $opx+gt$ tie line passing through the green dot must have higher Fe\textsuperscript{3+} concentrations than the metastable $opx$ plotting at the green dot, and hence the $fO_2$ of the stable assemblage will generally be higher than that of the metastable assemblage (although as described in the next paragraph, this result could change if the $gt$ were sufficiently Fe\textsuperscript{3+}-rich).

Figure 6c illustrates a more realistic situation for the high-$P$ end of the range we have considered and in which the transfer of Fe\textsuperscript{3+} from $px$ into $gt$ is inferred to have an effect on $fO_2$, e.g., by 40 kbar, D(Fe\textsuperscript{3+})\textsubscript{$gt$/$opx$} and D(Fe\textsuperscript{3+})\textsubscript{$gt$/$cpx$} have increased to ~1.8 and 2.6, and D(Fe\textsuperscript{3+}/Al)\textsubscript{$gt$/$opx$} has increased to ~0.13. As in Figure 5, the $gt$ now includes significant solid solution from
almandine toward the skiagite end member shown as a red horizontal line (labeled “gt ss” in Fig. 6c). The red edges of the opx field are shown schematically for three Ps. The three black dotted lines are lines of roughly constant projected Fe$^{3+}$/O content, comparable to those shown in Figures 6a and 6b. Three schematic tie lines are shown, extending from gt compositions 1, 2, and 3 to opx compositions e, f, and g, respectively, with P increasing in this tie-line sequence from the low P limit of the gt stability field up to a P above the fO$_2$ maximum shown in Figures 2b and 2d. The key feature of this exaggerated construction is that the Fe$^{3+}$ content of the gt increases from essentially zero for the 1-e tie line to a significant amount for the higher-P 3-g tie line. When coupled with the upward movement of the edge of the opx field upward with increasing P in Figure 6c and with the requirement that each tie line must pass through the bulk peridotite composition (i.e., the green dot in Fig. 6c), this leads to a progressive clockwise rotation of the tie lines (corresponding to an increase with increasing P in D[Fe$^{3+}$]$_{gt/opx}$ from <1 for the 1-e and 2-f tie lines to >1 for the 3-g tie line). This rotation of the tie lines generates the e→f→g sequence of opx compositions. Although the details will depend on the interplay between the rotation of the tie lines and the movement of the edge of the opx field with P, for the schematic example given in Figure 6b, this leads initially to an increase in the concentration of Fe$^{3+}$ in the opx with increasing P (from e to f) followed by a decrease with a further increase in P (from f to g): To the degree that the Fe$^{3+}$ content of the pyroxene correlates positively with the activity of Fe$_2$O$_3$, which in turn correlates positively with fO$_2$ relative to the metastable gt+sp-free assemblage, the schematic sequence shown graphically in Figure 6c predicts that with increasing P, fO$_2$ relative to the metastable gt+sp-free assemblage will initially increase, reach a maximum, and then decrease. Although oversimplified, this graphical treatment can rationalize our preferred explanation of the fO$_2$ maximum in the gt-lherzolite field observed in the output of the JH-15 model when fO$_2$ is given relative to a metastable ol+opx+cpx assemblage (Figs. 2b and 2d) as due to the balance between the retreat of the edge of the opx field and the increase in the Fe$^{3+}$ content of the gt with increasing P.
In summary, we infer that the small (~10%) decrease in log$_{10}$ƒO$_2$ relative to a metastable ol+opx+cpx assemblage that JH-15 predicts from ~30 to 40 kbar is real and not an artifact, and the discussion in this section demonstrates that it can be rationalized by considering the increasing Fe$^{3+}$ contents of the gt in the model at this range of $P_s$. Nevertheless, this effect is small relative to the overall effects of gt formation on ƒO$_2$: The main result based on the JH-15 model, as illustrated in Figures 2b and 2d, is that the progressive formation of gt primarily via reaction (5) in the narrow $P$ interval between gt-in and sp-out and then via reactions (6a) and (6b) up to ~30 kbar is accompanied by an increase in ƒO$_2$ of ~1 order of magnitude relative to a metastable gt±sp-free assemblage; most of the progressive increase in ƒO$_2$ from gt-in to ~30 kbar develops nearest the gt-in boundary, where the Fe$^{3+}$ content of the gt is small relative to that of the opx + cpx. Moreover, the pMELTS model, which does not include any Fe$^{3+}$ in the gt shows essentially the same behavior with a similar magnitude increase in ƒO$_2$ as the JH-15 model (compare the panels on the left side of Figure 2 to those on the right), and the correspondence with the JH-15 model is even better if the pMELTS calculation is done on a Cr$^{3+}$-free equivalent of the peridotite bulk composition (i.e., it has the same narrow transition interval with sp+gt-bearing assemblages with a steep increase in ƒO$_2$ with $P$). That the two models are so similar even though the pMELTS model excludes Fe$^{3+}$ from gt is a strong indication that the 1st-order effects are not overwhelmed by the incorporation of Fe$^{3+}$ into gt in this $P$ range, even though this effect appears to result in a noticeable perturbation in the results of the JH-15 model at the high-$P$ end of the calculations we have done.

**Comparison to previous work (gt-bearing assemblages).** In addition to their analysis described above of the change in ƒO$_2$ that would accompany the conversion of plag lherzolite to sp lherzolite, Ballhaus and Frost (1994) and Ballhaus (1995) developed a related analysis to predict changes in ƒO$_2$ that result from the conversion of sp lherzolite to gt lherzolite. They modeled the step-wise conversion of a fertile sp lherzolite to a gt lherzolite at 25 kbar and 1280°C via $sp + px = ol + gt$ reactions (e.g., reaction [5]), and they assumed that when both gt and sp are present, Fe$^{3+}$ is, at most, weakly partitioned into the sp (i.e., D[Fe$^{3+}$]$_{gt/sp}$ = Fe$^{3+}_{gt}$/Fe$^{3+}_{sp}$
As the reaction proceeds, three moles of gt are produced for every mole of sp consumed (see reaction [5]). Thus, if the reaction reaches completion (i.e., sp is exhausted) the same number of moles of Fe$^{3+}$ that were initially in the sp are dissolved in the larger number of moles of gt, leading to a lower concentration of Fe$^{3+}$ in the gt, and all other things being equal, this would correspond to a lower $fO_2$. If, as Ballhaus and Frost (1994) assumed, the reaction never goes to completion (i.e., there is always residual Cr$^{3+}$-rich sp), the extent of the decrease in $fO_2$ due to this reaction would depend on the value of $D(Fe^{3+})_{gt/sp}$, such that at a given extent of reaction more of the Fe$^{3+}$ would be retained in the sp at lower D values and the predicted decrease in $fO_2$ due to this reaction would be smaller than if the D were larger (see Fig. 3 in Ballhaus and Frost, 1994): at 90% reaction, $fO_2$ is predicted to decrease by ~0.3-0.4 log units for $D(Fe^{3+})_{gt/sp} = 0.5$ and by ~1.5 log units for $D(Fe^{3+})_{gt/sp} = 1.0$. Note that in contrast to the effects of decreasing Fe$^{3+}$ in sp due to its increasing modal in abundance on conversion of plag lherzolite to sp lherzolite, which was the basis of their prediction of a large decrease in $fO_2$ due to such a transformation, in the case of the sp-to-gt-lherzolite transformation, Ballhaus and Frost (1994) attributed the $fO_2$ shift to a transfer of Fe$^{3+}$ from one phase (sp) to another (gt) as the reaction proceeds.

The prediction of Ballhaus and Frost (1994) and Ballhaus (1995) that the $fO_2$ decreases by ~0.4-1.5 orders of magnitude when sp lherzolite converts to gt lherzolite is opposite in sign to our results, which predict an increase in $fO_2$ of the DMM peridotite composition we have modeled of ~0.5 orders of magnitude over the narrow $P$ interval of the sp→gt-lherzolite transition followed by an additional ~0.5 order of magnitude increase within the gt-lherzolite facies up to ~30 kbar for the JH-15 model relative to a metastable gt+sp-free assemblage (Fig. 2b); Jennings and Holland (2015) obtained similar result for ΔFMQ also using the JH-15 model for a fertile peridotite (see their Fig. 13). Modeling using pMELTS predicts a continuous increase of ~1 order of magnitude relative to a metastable gt-free assemblage from the gt-in boundary at ~20 kbar up to 40 kbar (Fig. 2a).
The difference between our results and those of Ballhaus and Frost (1994) and Ballhaus (1995) reflects two factors:

- Ballhaus and Frost (1994) assumed that the effects of px could be neglected because their modal abundances of opx and cpx do not change significantly at this (or the plag→sp-lherzolite) phase transition. However, according to both of the models applied here, the px abundances decrease considerably as the gt-in boundary is crossed going up P, and as a consequence Fe$^{3+}$ is passively enriched in the px, resulting in the modeled increases in $fO_2$. It is also important that both models we have used yield the result that most of the Fe$^{3+}$ in the system is in the px at gt-in (>50% for pMELTS and >90% for JH-15; see Figs. 4a and 4b); and at sp-out, where sp has been exhausted and the amount of garnet has reached ~10 wt. %, the JH-15 model still has >90% of the Fe$^{3+}$ in the px. Thus, although by 40 kbar in the JH-15 model, ~50% of the Fe$^{3+}$ in the system has transferred from px into gt, the assumption by Ballhaus and Frost (1994) and Ballhaus (1995) that px is not a major reservoir for Fe$^{3+}$ is the primary source of the difference between our results and theirs. Although ongoing improvements to the pMELTS and JH-15 thermodynamic models can be expected to lead to changes in the details, unless these models are significantly miscalibrated in their treatment of Fe$^{3+}$ in px, the predicted increase in $fO_2$ near the low-P end of the gt-lherzolite facies is probably robust.

- Based on the JH-15 model, $D(\text{Fe}^{3+})_{\text{gt} \leftrightarrow \text{sp}}$ is ~0.13-0.15 in the narrow interval over which gt and sp coexist at 1100°C. This is significantly lower than the values of 0.5-1.0 assumed by Ballhaus and Frost (1994) and Ballhaus (1995) and would diminish significantly and perhaps reverse their calculated decrease in $fO_2$ on incomplete reaction of sp lherzolite to gt lherzolite. We note, however, that as described above, stronger partitioning of Fe$^{3+}$ into gt relative to px with increasing P is predicted by the JH-15 model (Fig. 3b2) to result eventually in a decrease in $fO_2$ relative to the maximum at $P \sim 30$ kbar (Fig. 2b) for reasons related to those given by Ballhaus and Frost (1994) and Ballhaus (1995) for their expectation of a decrease in $fO_2$ in the gt-lherzolite field relative to a sp-bearing, gt-free assemblage. It is conceivable that at high...
enough $P$ (beyond the 40 kbar upper $P$ limit of our calculations) enough of the Fe$^{3+}$ will have transferred to $gt$ from $px$ such that a situation similar to the end-state of their calculation will have been achieved and the $fO_2$ will have decreased relative to that a metastable $gt$-free lherzolite, as they predict. However, based on our analysis, this is not relevant to the lower $P$ range of the $gt$-lherzolite facies modeled here, where the $gt$ is predicted to be relatively Fe$^{3+}$-poor and reactions involving consumption of $px$ (reactions [5] and [6]) lead to increases in the activity of Fe$^{3+}$-bearing components and thereby result in a significant increase in $fO_2$ relative to a metastable $gt$-absent assemblage (Fig. 2d).

Although we did not apply the pMELTS and JH-15 models to $P > 40$ kbar, it is nevertheless possible to connect our results to those obtained by others for the deeper upper mantle and transition zone. As mentioned above, Jennings and Holland (2015) applied the JH-15 model to the KLB-1 fertile peridotite on isotherms at 800, 1100, and 1400°C and along the solidus from 1 bar to 60 kbar, and Miller et al. (2016) applied it to the composition of a moderately depleted peridotite from the Siberian craton (Y-17) on a model geotherm from 30 to 70 kbar. $\Delta FMQ$ from their calculations under subsolidus conditions decreases continuously with increasing $P$ above ~30 kbar, plausibly reflecting both the effects on $fO_2$ of continued transfer of Fe$^{3+}$ from $px$ to $gt$ discussed previously and the large, negative standard-state volume change for the skiagite-forming reaction (2 fayalite + ferrosilite + $\frac{1}{2}$ $O_2$ = skiagite) relative to that of the FMQ buffer, which leads, even for a phase assemblage with essentially unchanging phase abundances and compositions, to a large decrease in $\Delta FMQ$ (e.g., Gudmundsson and Wood, 1995; Frost and McCammon, 2008; Miller et al., 2016). Despite the differences in the modeled peridotite compositions, the calculated trends of $\Delta FMQ$ vs. $P$ from Jennings and Holland (2015) are nearly identical to ours where they overlap (1100°C, <40 kbar); likewise, the slope in $\Delta FMQ$ vs. $P$ from Miller et al. (2016) at 30-40 kbar is similar to ours, although somewhat steeper, perhaps reflecting at least in part the difference between an isothermal path and the geotherm they modeled.
As $P$ increases beyond the point at which most of Fe$^{3+}$ in the peridotite has transferred from $px$ to $gt$, we anticipate that, relative to a metastable $ol+px$ assemblage, the $fO_2$ will not initially change significantly, because of the probable absence of major changes in phase abundances or redistribution of Fe$^{3+}$, although $\Delta$FMQ will continue to decrease (e.g., Wood et al., 1990; Gudmundsson and Wood, 1995; Frost and McCammon, 2008; Jennings and Holland, 2015; Miller et al., 2016). However, Fe$^{3+}$-poor $px$ progressively transforms into majorite components in the $gt$ with further increases in $P$, and this is expected to lead to dilution of Fe$^{3+}$ in the $gt$, and thus to decreasing $fO_2$ relative to metastable assemblages in which this $px \rightarrow gt$ transformation has not occurred (O’Neill et al., 1993; Ballhaus, 1995; Rohrbach et al., 2007; Frost and McCammon, 2008), analogous to what we and Ballhaus and Frost (1994) and Ballhaus (1995) propose to account for the large decrease in $fO_2$ with increasing $P$ across the $plag$-lherzolite field. With further increases in $P$ into the transition zone, the Fe$^{3+}$ in the $gt$ is expected to partition in significant amounts into ringwoodite and wadsleyite, further diminishing the Fe$^{3+}$ content of the $gt$ and thus leading to an even greater decrease in $fO_2$ relative to metastable assemblages without these phases (O’Neill et al., 1993; Frost and McCammon, 2008); this predicted change in $fO_2$ due to redistribution of Fe$^{3+}$ is analogous to the explanation we have for the decrease in $fO_2$ relative to a $gt\pm sp$-free metastable assemblage at $P \geq 30$ kbar, reflecting the progressive transfer of Fe$^{3+}$ from $px$ to $gt$. These anticipated changes in $fO_2$ at $P$s beyond those we have considered are expected to be manifested whether $fO_2$ is expressed relative to an appropriate metastable reference assemblage or as $\Delta$FMQ.

**Effects of $T$ and bulk composition**

We have emphasized the effects of $P$ on changes in $fO_2$ driven by heterogeneous equilibria in peridotites because the effects of $T$ are minor in comparison. This is illustrated in Figures 1c-1f, where the trends in $fO_2$ for a melt-free DMM peridotite relative to FMQ or relative to a metastable $ol+opx+cpx\pm sp$ assemblage are shown to be essentially unchanged with increasing $T$ other than a widening of the $sp$-lherzolite facies (mostly due a positive $P-T$ slope of the $gt$-in
curve) and overall decreases in ΔFMQ and in fO₂ normalized to a metastable ol+opx+cpx±sp assemblage at constant P with increasing T. This latter effect is only present outside the sp-lherzolite facies for fO₂ values normalized to the metastable assemblages because they are constant at zero for the pMELTS model and nearly so for the JH-15 model. Jennings and Holland (2015) show similarly small trends for ΔFMQ for KLB-1 as functions of T. Given the minor effects of T compared to those of P, trends along isentropes would be similar to the isothermal trends shown in Figures 2 and 3 and by Jennings and Holland (2015).

Although our discussion has focused on the DMM composition, our conclusion that heterogeneous equilibria among Al-rich phases in peridotites are the principal drivers of changes in fO₂ with increasing P predicts that the fO₂ changes (whether in absolute fO₂, ΔFMQ, or relative to metastable ol+opx+cpx±sp assemblages) displayed by our modeling across the plag- and gt-lherzolite facies will diminish with progressive depletion due to melt extraction, reflecting the decrease in the Al contents of peridotites as a function of depletion. In order to determine the predicted magnitude of the effects of depletion, we ran pMELTS calculations on a Cr³⁺-free equivalent of the moderately depleted Y-17 gt lherzolite (~1.4 wt. % Al₂O₃, compared to ~4.0 wt. % in DMM) modeled by Miller et al. (2016), assuming an Fe₂O₃ content of 0.25 wt. %, similar to that used in our modeling of DMM. Normalized to a metastable ol+opx+cpx±sp assemblage, fO₂ for Y-17 decreases by ~1.6 log units from 1 bar to plag-out (vs. a ~2.2 log units decrease for the Cr³⁺-free DMM composition) and increases by ~1.1 log units from gt-in to 40 kbar (vs. a ~2.2 log unit increase for the Cr³⁺-free DMM composition). Although more extensive and systematic modeling to explore the effects of progressive depletion on the phase-equilibrium-driven changes in the fO₂ of peridotite should be conducted – including the decrease in Fe³⁺ content of the peridotite with progressive melt extraction (Pearson et al., 2003; Cottrell and Kelley, 2011; Sorbadere et al., 2018) – this preliminary set of results for a less fertile, Al-poor peridotite is consistent with our conclusion that the P-dependent changes in fO₂ for the DMM peridotite composition are driven by reactions involving the major Al-bearing phases.
Implications

(1) Both the pMELTS and JH-15 models predict significant variations in \( fO_2 \) for a peridotite of constant bulk composition (including its oxygen content) under stable and metastable subsolidus conditions with increasing \( P \). For example, based on the JH-15 model, at 1100°C, the \( fO_2 \) relative to a metastable \( ol+opx+cpx \) assemblage decreases by \( \sim 1.25 \) log units as the normative abundance of \( plag \) decreases from its 1 bar value to zero at the upper \( P \) limit of the \( plag \)-lherzolite facies. The modeled \( fO_2 \) varies little across the \( sp \)-lherzolite facies and then increases by \( \sim 1 \) log unit up to a maximum at \( \sim 30 \) kbar with the progressive formation of \( gt \), above which it decreases by \( \sim 0.1 \) log units. Similar variations are also predicted by the pMELTS model. These relatively large predicted variations in \( fO_2 \) do not primarily reflect heterogeneous equilibria that redistribute \( Fe^{3+} \) between phases. Instead, according to both models, most of the \( Fe^{3+} \) in the peridotite remains in \( px \) across this \( P \) range, and the changes in \( fO_2 \) are primarily driven by changes in the non-\( Fe^{3+} \)-bearing components of the \( px \) associated with reactions that generate or consume the major aluminous phases (e.g., \( plag \), \( sp \), \( gt \)). Reactions that generate non-\( Fe^{3+} \)-bearing \( px \) components with increasing \( P \) (e.g., reactions [1], [2], and [3] in the \( plag \)-lherzolite facies) lead to dilution of \( Fe^{3+} \) in \( px \) and decreases in its activity and thus to a decrease in \( fO_2 \). Reactions that consume non-\( Fe^{3+} \)-bearing \( px \) components with increasing \( P \) (e.g., reactions [5] and [6] in the \( gt \)-lherzolite facies) lead to enrichment of \( Fe^{3+} \) in residual \( px \) and increases in its activity, and thus to an increase in \( fO_2 \). Such reactions – which are responsible for the well-known sequence of \( plag \to sp \to gt \) lherzolite with increasing \( P \) and the topology in \( P-T \) space of alumina isopleths in \( px \) – do not directly produce, consume, or transfer significant \( Fe^{3+} \)-bearing components, yet they indirectly (or passively) drive the systematic changes in \( fO_2 \) with \( P \). Most importantly, these \( fO_2 \) changes are predicted to be simply and strongly correlated with the well-known dominant changes in phase equilibria and mineral chemistry of peridotites in the upper \( \sim 100 \) km of the upper mantle, and they are of comparable magnitude to the variations in \( fO_2 \) observed within suites of natural basalts and peridotites. The small decrease in
modeled $fO_2$ relative to a metastable $ol+opx+cpx$ assemblage using JH-15 from 30 kbar to 40 kbar probably reflects the competition between the effects of $px$ consumption to produce $gt$ and the progressive transfer of $Fe^{3+}$ from $px$ to $gt$ with increasing $P$.

(2) In analyzing the changes in $fO_2$ predicted by the pMELTS and JH-15 models, we relied heavily on the ability of these thermodynamic models to probe metastable states: First we were able to demonstrate the importance of specific phases in producing the observed changes by selectively excluding them from the equilibrium assemblages; for example, if an effect on $fO_2$ appeared when a particular phase was allowed to appear in the stable or metastable assemblage but disappeared when the phase was excluded from the assemblage, we inferred that this phase played a role in producing the observed effect. Second, rather than normalizing the modeled $fO_2$ to standard buffers such as FMQ, we emphasized normalizations to metastable assemblages (e.g., $ol+opx+cpx$) that lacked the dominant aluminous phases. This allowed isolation of the quantitative effects of the reactions that produce variations in $fO_2$ by comparing the $fO_2$ of the same composition at the same $P$ and $T$ of assemblages with and without these Al-rich phases.

(3) It is widely accepted that the $\Delta FMQ$ values of peridotites decrease continuously with increasing $P$ in the mantle, but our results on the DMM peridotite composition and those of Jennings and Holland (2015) on the fertile KLB-1 peridotite composition demonstrate a more complex trend in the upper ~100 km of the upper mantle: At constant $T$, $\Delta FMQ$ decreases with increasing $P$ across the $plag$-lherzolite field; followed by roughly constant $\Delta FMQ$ across the $sp$-lherzolite field; this is followed first by a steep increase from just above $gt$-in up to $sp$-out (or to where the residual $sp$ is $Cr^{3+}$-rich) and then by a slower, concave down increase in $\Delta FMQ$ across the $gt$-lherzolite field to a maximum at ~20-30 kbar (at 1100°C), above which $\Delta FMQ$ decreases. From this point on, the widely accepted trend of decreasing $\Delta FMQ$ probably prevails (although for $P$ up to 70 kbar, the decrease is smaller than has been generally supposed; Miller et al., 2016), reflecting first the continuing effects of transfer of $Fe^{3+}$ from $px$ to $gt$, then dilution of $Fe^{3+}$ in the $gt$ due to transfer of the dominant silicate
components of the px into gt as majoritic components, and finally to transfer of Fe$^{3+}$ from majoritic gt to ringwoodite and wadsleyite (Frost and McCammon, 2008).

(4) The overall trend in absolute $fO_2$ (and thus in $\mu O_2$) with increasing $P$ up to 40 kbar based on our results is to higher values (Figs. 3a1 and 3b1). The only deviation from this is in the plag-lherzolite field, where the decrease in absolute $fO_2$ due to reaction of ol + plag to form px components is large enough to reverse the overall trend toward increasing absolute $fO_2$ with increasing $P$. The results of Jennings and Holland (2015) extend this trend to increasing absolute $fO_2$ with increasing $P$ to 60 kbar (based on converting the $\Delta$FMQ values in their Figure 13 to absolute $fO_2$). The trend in absolute $fO_2$ with $P$ is concave downward outside the plag-lherzolite field, and it is possible that absolute $fO_2$ decreases beyond some higher $P$ outside of the range of current calculations. The well-known trend to more negative values of $\Delta$FMQ with increasing $P$ above ~30 kbar occurs because even though the calculated absolute $fO_2$ of the DMM peridotite and that of the FMQ buffer both increase with $P$, the absolute $fO_2$ of the FMQ buffer increases more steeply (see Figs. 3a and 3b).

Thus, based on the models presented here, $\mu O_2$ is to predicted to increase with $P$ along an isotherm from ~10 kbar to at least 60 kbar in an isocompositional mantle corresponding to DMM. This increase in $\mu O_2$ means that oxygen would flow from peridotite at higher $P$ to peridotite at the same $T$ but lower $P$ in contact across a rigid barrier that is capable of maintaining the difference in $P$ but is semi-permeable with respect to oxygen; this would continue until $\mu O_2$ is equalized in the high and low $P$ peridotites. This flow of oxygen due to the higher absolute $fO_2$ of the higher $P$ peridotite would occur despite the fact that the higher $P$ peridotite has a lower $\Delta$FMQ, which might be misinterpreted as suggesting that it is more reduced in an absolute sense and that oxygen would flow in the opposite direction. Although the conditions of this thought experiment are unlikely to be approximated in nature, the point is that it is important to take care in drawing conclusions from use of reference frames that depend on the thermodynamic properties of buffer assemblages.
(5) The interpretation of the $fO_2$ variations we have modeled as being driven by phase changes among the dominant Al-rich phases in the upper ~100 km of the mantle suggests that these variations will be progressively muted in peridotites increasingly depleted by extraction of melt because the Al contents of peridotites decrease significantly with progressive depletion. We have validated this suggestion with limited calculations using pMELTS, but more extensive applications of these models are necessary to document and understand fully the effects on the trends we have discussed with major element composition. Note that the effects of $T$ are minor compared to those of $P$, and as a consequence the results would be similar along isotherms and isentropes.

(6) Returning to the issues raised in the Introduction, numerous studies have documented several orders of magnitude variation in $\Delta$FMQ of terrestrial basaltic magmas and mantle peridotites. The range of $fO_2$ among unaltered peridotites provides direct evidence of variability in the mantle, and although processes such as crystallization, assimilation, and degassing can affect the $fO_2$ of a magma, it is probable that at least some – perhaps most – of the range of $fO_2$ observed in relatively primitive magmas reflects variations inherited from their mantle sources. These variations in the $fO_2$ of basalts and their mantle sources have mostly been attributed to variations in the chemical compositions of their sources (including their oxygen contents) due, for example, to subduction of oxidizing agents such as fluids, sediments, and altered oceanic crust or to the opposing effects of subducted organic material; to control by equilibration with fluids (especially graphite- or diamond-saturated fluids); or to the effects of partial melting (e.g., depletion of Fe$^{3+}$ in the residue and the resulting reduction).

However, our thermodynamic modeling and its interpretation suggest that the effects of $P$- and $T$-dependent phase equilibria on $\Delta$FMQ of a relatively fertile subsolidus peridotite of constant composition can be >1 order of magnitude between 1 bar and 40 kbar, which is comparable to most of the variability among peridotites and within suites of each of the most abundant basaltic magma types on Earth. The results of recent experiments (Davis and Cottrell, 2018; Sorbadere et al., 2018) suggest that the $fO_2$ values of partial melts may
remain similar to those of their unmelted peridotite sources up to a few tens of percent partial melting. This suggests in turn that the effects of heterogeneous phase equilibria on the $fO_2$ values of subsolidus DMM peridotite presented here may be manifested in the $fO_2$ values of melts produced by low degrees of partial melting of relatively fertile peridotites.

Overall, the systematic and significant effects of phase equilibria in subsolidus peridotite on $fO_2$ that we have modeled here are expected to be superimposed in the mantle on the more commonly invoked sources of $fO_2$ variability in magmas and peridotites that result in variations in bulk composition (especially $\text{Fe}^{3+}/\text{Fe}^{2+}$ of the mantle). Consequently, such effects should also be considered in efforts to understand observed variations in the oxygen fugacities of magmas and their mantle sources of up to $\sim$1-2 orders of magnitude.

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Figure captions

Figure 1. P-T sections for the slightly depleted DMM mantle composition (Workman and Hart, 2005), for which 3% of the Fe is present as Fe$^{3+}$ and Fe is assumed to be the only heterovalent cation. Contours in each panel reflect log$_{10}$$f$O$_2$ in absolute terms or relative to buffers or other assemblages. Panels (a), (c), and (e) on the left were calculated with the pMELTS model (Ghiorso et al., 2002). Panels (b), (d), and (f) on the right were calculated with the JH-15 model (Jennings and Holland, 2015). The “jitters” in some of the contours reflect imperfect convergence of the energy minimizations. The larger “zigzags” in the pMELTS model (most noticeably those labeled i and ii in panel [e]; these are explained in the text and in detail in the caption to Fig. 4) are due to the stabilization of pigeonite at the expense of opx + diopsidic cpx, which occurs at slightly higher $P$ for a given $T$ in the metastable ol+opx+cpx+sp assemblage than in the stable DMM assemblage. All calculated values of $f$O$_2$ in this and subsequent figures are for melt-free assemblages: Below the dashed black solidus curves, the melt-free assemblages are stable; above the solidus, the melt-free assemblages are metastable relative to partially or fully molten assemblages. The plag-out and gt-in boundaries are shown in green; the fields between these boundaries are labeled by the dominant Al-rich phase (i.e., plag lherzolite, sp lherzolite, or gt lherzolite). Contours in panels (a) and (b) show absolute values (i.e., unnormalized) of log$_{10}$$f$O$_2$, where $f$O$_2$ is in bars. Contours in panels (c) and (d) show the difference in log$_{10}$$f$O$_2$
between that of the calculated stable assemblage of that of the FMQ buffer ("ΔFMQ"). Contours in panel (e) show the difference in log₁₀\(fO_2\) between that of the calculated stable assemblage and that of the stable (in the sp-lherzolite facies) or metastable (in the plag- and gt-lherzolite facies) \(ol+opx+cpx+sp\) assemblage for the DMM composition calculated using pMELTS. Because the stable and normalizing assemblages are identical in the sp-lherzolite facies, the normalized \(fO_2\) is precisely zero in this field. Contours in panel (f) show a similar normalization of log₁₀\(fO_2\) relative to a metastable \(ol+opx+cpx\) assemblage for the DMM composition in all facies calculated using the JH-15 model. As discussed in the text, (e) and (f) isolate the effects of Al-rich phases on the \(fO_2\) of lherzolite by comparing the \(fO_2\) of the same composition at the same \(P\) and \(T\) of assemblages with and without these Al-rich phases. As also discussed in the text, the most prominent feature of this figure, particular panels (e) and (f), is the pronounced low-\(fO_2\) “well” associated with the sp-lherzolite facies in both models. The gray dotted lines in (a)-(d) are the 1100°C isotherms for the calculations shown in Fig. 2; the grey dashed lines in (e) and (f) are the 1300°C isotherms for the calculations shown in Figs. 3 and 4.

**Figure 2.** Calculated subsolidus variations for the DMM bulk composition with \(P\) at 1300°C of normalized log₁₀\(fO_2\), mole fractions of Al³⁺ and Fe³⁺ in opx, and activities of Al₂O₃ and Fe₂O₃ in opx. The panels on the left are based on pMELTS; the panels on the right are based on JH-15. (a) Isothermal section showing the difference between log₁₀\(fO_2\) of the most stable melt-free assemblage for the DMM composition (which is metastable at low \(P\) relative to a partially molten assemblage) and the log₁₀\(fO_2\) of an \(ol+opx+cpx+sp\) assemblage corresponding to the DMM composition (which is metastable relative to plag- and gt-bearing assemblages at \(\leq 9\) kbar and \(\geq 19\) kbar, respectively) based on pMELTS. (b) Isothermal section showing the difference between log₁₀\(fO_2\) of the most stable melt-free assemblage for the DMM composition (which is metastable at low \(P\) relative to a partially molten assemblage) and the log₁₀\(fO_2\) of the DMM composition in a metastable \(ol+opx+cpx\) assemblage based on JH-15. (c) Further metastable results from pMELTS at 1300°C, normalized to an \(ol+opx+cpx+sp\) assemblage; along the blue
curve, plag and sp are the only aluminous phases other than opx and cpx allowed to form, whereas along the purple curve only gt and sp are allowed. (d) Further metastable results from JH-15 at 1300°C, normalized to an ol+opx+cpx assemblage; along the blue curve, plag is the only aluminous phase other than opx and cpx; along the orange curve, sp is the only such phase; and along the purple curve, gt is the only such phase. (e, f) Activities of Al₂O₃ and Fe₂O₃ in opx vs. P at 1300°C for the pMELTS and JH-15 results shown in panels (a) and (b) of this figure. For pMELTS the standard states for Al₂O₃ and Fe₂O₃ are chosen to be internally consistent with the Berman (1988) thermodynamic dataset and the opx solid solution model (Sack and Ghiorso, 1994); in JH-15 this approach is not possible, so corundum (cor) and hematite (hem) are used as standard states. Calculations in pMELTS (not shown) using cor and hem as the standard states result in activities of Al₂O₃ and Fe₂O₃ that are the same in all assemblage phases, by definition, and more closely resemble the JH-15 results (e.g., activity of Al₂O₃ is increased, and activity of Fe₂O₃ is decreased, relative to the results shown in panel [e]). (g, h) Mole fractions of Al³⁺ and Fe³⁺ on a cation basis (equivalent to mole fractions of Al₂O₃ and Fe₂O₃ for opx stoichiometry) vs. P at 1300°C for the pMELTS and JH-15 results shown in panels (a) and (b) of this figure. The labels i and ii in the pMELTS panels indicate discontinuities associated with the stabilization of pigeonite discussed in the text and in the caption to Fig. 4.

Figure 3. Calculated stable subsolidus variations for the DMM bulk composition vs. P at 1100°C. The panels on the left (a1-a3) are based on pMELTS calculations; the panels on the right (b1-b3) are based on the JH–15 model. (a1, b1) Absolute (i.e., unnormalized) log₁₀fO₂ is shown in black and ΔFMQ is shown in red. The absolute log₁₀fO₂ of the FMQ buffer is shown as a dashed black curve for reference. (a2, b2) Mole fractions of Fe³⁺, on a cation basis, for the phases in the calculated stable assemblages. (a3, b3) Fractions (by weight) of the phases in the calculated stable assemblages. Phases in the bottom three rows are ol (green), opx (black), cpx (gray), plag (blue), sp (orange), and gt (purple). Phase boundaries (labeled plag-out, gt-in, sp-
out; these labels are referenced to changes in the stable assemblage with increasing $P$) are shown as colored vertical dashed lines.

**Figure 4.** Calculated distributions of Fe$^{3+}$ between coexisting phases (excluding $ol$ and $plag$, which are assumed to contain no Fe$^{3+}$) in peridotitic assemblages for the DMM bulk compositions based on pMELTS (panels [a] and [c]) and JH-15 (panels [b] and [d]) as functions of $P$ at 1300°C. The y axes in (a) and (c) (and for each of the subpanels in [c] and [d]) show for each phase (distinguished by the color coding) the total quantity of Fe$^{3+}$ contained in that phase divided by the total quantity of Fe$^{3+}$ contained in the DMM bulk composition. Panels (a) and (b) show the results for the most stable melt-free assemblage for the DMM composition (which is metastable at low $P$ relative to a partially molten assemblage; i.e., these panels show the Fe$^{3+}$ distributions associated with Figs. 2a and 2b). Panels (c) and (d) show the results for the various metastable assemblages described in the text and shown in Figs. 2c and 2d. Note that the bottom panels in (c) and (d) represent the reference assemblages for $fO_2$ used in Fig. 2. The nearly discontinuous decreases in the fraction of Fe$^{3+}$ in $cpx$ with increasing $P$ at low $P$ in (a) and (c) (labeled $i$ and $ii$, and associated with corresponding changes in the fractions of Fe$^{3+}$ in $opx$ and $sp$) reflect the stabilization of pigeonite relative to $opx + diopsidic cpx$ (i.e., effectively the passage of a diopsidic $cpx + pigeonite cpx + opx$ three-phase triangle over the DMM bulk composition) in the pMELTS calculations at the lowest $Ps$. This feature appears at lower $P$ in the presence of $plag$ (0.75 kbar; labeled $i$ in [a] and the top panel of [c]) than it does when $plag$ is suppressed (3.7 kbar; labeled $ii$ in the lower two panels of [c]). This change in the nature of the $cpx$ has only a small effect on the trend in $fO_2$ with $P$, although it is visible in Figs. 2a and 2c (where the occurrence of the transition in DMM is labeled $i$ and the occurrence of the transition in the reference $ol+opx+cpx+sp$ assemblage is labeled $ii$). Note that this feature is not present in Fig. 3 because pigeonite is only stabilized above ~1300°C in DMM; also, this feature is not present in the stable subsolidus DMM assemblage, only in the low $P$ region in which we show the metastable subsolidus assemblage by suppressing the stabilization of liquid.
Figure 5. Schematic subsolidus phase equilibria in the five-component system FeO-Fe\textsubscript{5/3}O-CaO-Al\textsubscript{3/2}O-Si\textsubscript{3/2}O (i.e., FeO-Fe\textsubscript{2}O\textsubscript{3}-CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} with components and phase compositions all defined on a single-oxygen basis), projected from ol (i.e., fayalite, Fe\textsubscript{5/3}Si\textsubscript{1/3}O) and cpx (i.e., hedenbergite, Ca\textsubscript{3}Fe\textsubscript{9}Si\textsubscript{1/3}O) onto the Si\textsubscript{3/2}O-Al\textsubscript{3/2}O-Fe\textsubscript{5/3}O plane. As described in the text, although schematic, this model system provides a graphical framework for understanding the sequence of phases and their compositions with increasing $P$ as calculated by the pMELTS and JH-15 models for the DMM peridotite compositions. (a) Projected positions of the major end members of $\text{px}$, $\text{gt}$, and $\text{sp}$. (b)-(n) Sequence of isothermal sections going up in $P$. A model bulk peridotite composition is shown as a green cross at the same location in all panels. Stable phases are shown in red; the $\text{sp}$ solid solution between magnetite and hercynite is shown as a red line at the base of each triangle, and the $\text{gt}$ solid solution between skiagite and almandine is shown as a red line in the panels in which it is stable ([j]-(n)); the projected $\text{opx}$ solid solution is shown as a red region extending downward from pure ferrosilite (at the Si\textsubscript{3/2}O apex) to Fe\textsuperscript{3+}- and Al-bearing compositions. Tie lines are gray, and three-phase triangles (in projection) are blue with a purple interior. All $\text{opx} + \text{sp}$ tie lines are drawn assuming $(\text{Fe}^{3+}/\text{Al})_{\text{sp}}/(\text{Fe}^{3+}/\text{Al})_{\text{opx}} = 1$; the JH-15 model predicts lower values, the pMELTS model predicts lower to higher values, and partitioning in natural peridotites is ~0.7 (Canil and O'Neill, 1996); variations in this ratio would affect the orientation of the tie lines but not the sequence of assemblages or overall topologies. Although the trends with increasing $P$ are unaffected, the model peridotite position and the compositions of coexisting solid solutions have all been exaggerated to unrealistically high Fe\textsuperscript{3+} contents for better visibility. The relation of these diagrams to the output of the pMELTS and JH-15 models is described in detail in the text.

Figure 6. Enlargement of the upper right regions of the schematic phase diagrams from (a) Fig. 5b for the plag-lherzolite facies; (b) Fig. 5n for the gt-lherzolite facies if the gt is assumed to be Ca- and Fe\textsuperscript{3+}-free (i.e., pure almandine); and (c) Fig. 5n for the gt-lherzolite facies if the gt is
assumed to have a non-negligible quantity of Fe$^{3+}$, which increases with increasing $P$ on the skiagite-almandine join ("gt ss"). These diagrams are described in detail in the text to illustrate graphically the opposite effects on the Fe$^{3+}$ content of opx (and hence on $fO_2$) of the production of quadrilateral and aluminous px components as $P$ increases across the plag-lherzolite facies and the consumption of these px components as $P$ increases across the gt-lherzolite facies. As in Fig. 5, the Fe$^{3+}$ contents of the bulk peridotite (green dot) and of the opx coexisting with plag in (a) and with gt in (b) have been exaggerated for the purposes of this illustration. The Fe$^{3+}$ contents of the bulk peridotite, px, and gt have been even further exaggerated in (c). The black dotted lines in each panel approximate constant Fe$^{3+}$ contents, with the lines to the left having higher Fe$^{3+}$. 
Figure 1
**Figure 3**

**pMELTS: CNFMASO+Ti+Cr**

(a1) **log($f_{O_2}$)** vs **Pressure (GPa)** at 1100°C

(a2) X($FeO_{1.5}$) vs **Phase fraction**

(a3) **Phase fraction** vs **Pressure (GPa)**

**Perple_X: CNFMASO+Cr**

(b1) **log($f_{O_2}$)** vs **Pressure (GPa)** at 1100°C

(b2) X($FeO_{1.5}$) vs **Phase fraction**

(b3) **Phase fraction** vs **Pressure (GPa)**
Figure 4

**Ferric iron budget by phase**

- **pMELTS**
  - a. plg-out
  - b. gt-out

- **Perple_X (JH15)**
  - c. plg-out
  - d. gt-out

Pressure (GPa) @ 1300°C
Figure 5
a. plag-lherzolite facies

b. gt-lherzolite facies (gt is pure almandine)

c. gt-lherzolite facies (gt is an almandine-skiagite ss)

Projected from Fa & Hd

Figure 6