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

EDWARD M. STOLPER<sup>1,\*,\dagger</sup>, OLIVER SHORTTLE<sup>1,2</sup>, PAULA M. ANTOSHECHKINA<sup>1</sup>, AND PAUL D. ASIMOW<sup>1</sup>

<sup>1</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena 91125, California, U.S.A.

<sup>2</sup>Department of Earth Sciences and Institute of Astronomy, University of Cambridge, Cambridge CB3 0HA, U.K.

ABSTRACT

Decades of study have documented several orders of magnitude variation in the oxygen fugacity ( $f_{\text{O}_2}$ ) 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.,  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) 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  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) can also lead to systematic variations in  $f_{\text{O}_2}$  in the shallowest  $\sim 100$  km of the mantle.

Two different thermodynamic models were used to calculate  $f_{\text{O}_2}$  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  $f_{\text{O}_2}$  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  $f_{\text{O}_2}$  and increasing pressure in this facies has little influence on  $f_{\text{O}_2}$  (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  $f_{\text{O}_2}$  (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  $f_{\text{O}_2}$  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  $\text{Fe}^{3+}$ -bearing components in pyroxene and therefore to decreases in normalized  $f_{\text{O}_2}$ , whereas pyroxene-consuming reactions (e.g., in the garnet stability field) lead initially to enrichment of  $\text{Fe}^{3+}$ -bearing components in pyroxene and to increases in normalized  $f_{\text{O}_2}$  (although this is counteracted to some degree by progressive partitioning of  $\text{Fe}^{3+}$  from the pyroxene into the garnet with increasing pressure). Thus, the variations in normalized  $f_{\text{O}_2}$  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  $\rightarrow$  spinel  $\rightarrow$  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  $f_{\text{O}_2}$  of primitive mantle-derived basalts and peridotites within and across different tectonic environments probably mostly reflect variations in the chemical compositions (e.g.,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  or bulk  $\text{O}_2$  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  $f_{\text{O}_2}$  of peridotites of constant composition are likely to be superimposed on variations in  $f_{\text{O}_2}$  that reflect differences in the whole-rock  $\text{Fe}^{3+}/\text{Fe}^{2+}$  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.

**Keywords:** Oxygen fugacity, thermodynamics, mantle, basalt, phase equilibrium, peridotite