Variations in the oxygen fugacity of the upper mantle due to solid-solid phase equilibria and partial melting

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Interest in the redox variability of basalts is increasing due to the growing number of measurements of fO_2–sensitive ratios (e.g., Fe^{3+}/Fe^{2+}) in glasses and minerals. Interpretations of this variability include that it reflects variations in oxygen content (i.e., in Fe^{3+}/Fe^{2+}) of mantle sources, or processes acting on melts after segregation from their sources (e.g., crystallization or degassing). We show here that peridotite phase equilibria can also lead to significant variations in fO_2 and in Fe^{3+}/Fe^{2+} of individual phases, even when the peridotite bulk composition is constant.

Thermodynamic models were used to calculate fO_2 vs. *P* and *T* for a representative peridotite of constant composition (including total oxygen). Under subsolidus conditions, increasing *P* from 1 bar to plagioclase(*plag*)–out leads to an fO_2 decrease of ~1.5 log units relative to FMQ. The spinel (*sp*) lherzolite facies defines a minimum in fO_2, and increasing *P* in this field has little influence on fO_2. With further increases in *P* (to ~30 kbar) after garnet (*gt*) appears, fO_2 increases from the low values of the *sp* lherzolite facies by ~1 log unit. These relatively large changes in fO_2 reflect primarily the indirect effects of reactions involving aluminous phases in the peridotite that either produce or consume pyroxene (*px*) with increasing *P*: Reactions that produce *px* with increasing *P* (e.g., Fo + An = MgTs + Di in *plag* lherzolite) lead to dilution of Fe^{3+}–bearing components in *px* and therefore to fO_2 decreases, while *px*–consuming reactions (e.g., in the *gt* stability field) lead to enrichment of Fe^{3+}–bearing components in *px* and to fO_2 increases.

Although isobaric melting generally leads to decreasing fO_2, isentropic decompression melting can result in ΔFMQ increases of ~1 log unit. This also results from continuous and discontinuous solid–solid phase transitions, with melting itself introducing only relatively small perturbations on melt–absent trends. Shallower melts on a single isentrope are thus expected to have generally higher fO_2 than deeper melts.

We conclude that although observed variations in fO_2 of basalts may reflect mantle metasomatism (e.g, by subduction of oxidizing fluids, sediments, and altered oceanic crust ± the opposing effects of subducted organic material), the effects of peridotite phase equilibria must also be considered.