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Perspectives on Mantle Redox - *F.W. Clarke Medal Lecture*

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Mantle redox, which has far-reaching consequences for our planet and its evolution, may be approached from the perspective of oxidation state (e.g., $Fe^{3+}/\Sigma Fe$ ratios) or the perspective of thermodynamic equilibrium (i.e., oxygen fugacity). Over the past 15 years, improvements in analytical techniques for measuring oxidation state, as well as improvements in thermodynamic/empirical models for calculating oxygen fugacity (fO_2), have highlighted the complex interplay between these two approaches.

These nuances are apparent when assessing crustal production at mid-ocean ridges, where relatively simple melting dynamics and tectonic divergence provide insight into the convecting upper mantle. Erupted volcanics at ridges (basalts) represent melts that were produced in thermodynamic equilibrium with residual mantle (peridotite) during melting. Yet, despite fO_2 equilibrium, peridotite bulk $Fe^{3+}/\Sigma Fe$ ratios are significantly lower than those of basalt, due to peridotite's large modal abundance of olivine, which does not host appreciable Fe^{3+}. This 'redox paradox' (McCammon, 2005) has important implications for mantle melting. While the bulk $Fe^{3+}/\Sigma Fe$ of the upper mantle decreases during melting, its fO_2 remains relatively constant, as the mode of ferric-bearing minerals decreases relative to the mode of olivine. This conclusion is supported by both natural samples and empirical/thermodynamic modeling (Birner et al., 2018/2021/2024), which indicate that sub-ridge mantle that undergoes spinel-field melting records fO_2 values near QFM, regardless of whether the mantle experienced 0-5% melting at a slow-spreading ridge or 15-20% melting at a fast-spreading ridge.

The relationship between oxidation state and fO_2 also controls the redox-depth profile of the upper mantle, as Fe^{3+} redistributes between mineral phases as a function of pressure and temperature. A combination of natural samples, modeling, and experiments suggest that during decompression, a garnet-bearing peridotite at constant $Fe^{3+}/\Sigma Fe$ will first increase in fO_2, reach an apex around 4 GPa, and then decrease in fO_2 as it transitions into the spinel stability field. This fO_2 turnover has important implications for deep melting, such as in the early Earth or at modern hotspots, as melting that initiates at pressures near this turnover may produce melts and residues with highly variable fO_2 from an initial mantle of constant bulk oxidation state (Birner et al., 2024).