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The mantle redox profile from metal saturation to melt initiation

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The oxidation state of the Earth's mantle influences the speciation of volatiles and can govern the onset of volatile-induced incipient melting. High-pressure and high-temperature experiments indicate that the pressure dependence of ferric–ferrous equilibria among peridotite minerals systematically drives relative oxygen fugacity downward with increasing pressure. Thermodynamic treatment of these equilibria shows that, for an upper mantle composition with an approximately constant bulk $Fe^{3+}/\Sigma Fe$ ratio, this effect forces progressive reduction with depth until a threshold is reached at which an iron-rich alloy precipitates. Volatile species act to moderate this decrease in oxygen fugacity by themselves becoming increasingly reduced.

Although the precipitation of iron-rich alloy reduces the gradient of oxygen fugacity with depth, experiments at higher pressures and temperatures indicate that reduction continues into the lower mantle. In the lower mantle, the coupled substitution of ferric iron and alumina into the dominant phase, bridgmanite, drives further charge disproportionation of ferrous iron ($3FeO = Fe + Fe_2O_3$), stabilizing metallic Fe. New experiments performed up to 50 GPa can now be used to estimate the redox profile throughout the lower mantle. These results show that pressure has only a minor influence on the intrinsic preference of bridgmanite for ferric iron, whereas the temperature increase through the lower mantle progressively decreases this preference.

As mantle material ascends, these ferric–ferrous equilibria act in the opposite direction. Metallic and ferric iron are consumed and ferrous iron is redistributed into silicates, producing an increase in relative oxygen fugacity with decreasing pressure. This upward shift drives the oxidation of reduced volatile species, modifying C–O–H–S speciation and destabilizing reduced carbon phases. By combining thermodynamic constraints on mineral ferric–ferrous equilibria with models of volatile fluid and melt speciation, we can calculate how this mantle-scale redox gradient controls the conditions under which oxidation during ascent can trigger volatile-assisted melt initiation.