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Fe Disproportionation and Earth's Early Oxidation: Magma ocean or Bridgmanite Crystallization?

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The comparatively oxidized character of Earth's mantle originated in the Hadean, most likely by disproportionation of Fe^{2+} to Fe^{3+} and Fe^{0}, with the latter ultimately removed to the core. Disproportionation could have been driven by bridgmanite crystallization in the lower mantle or by stabilization of Fe^{3+} in silicate liquid in a deep magma ocean. Experimental studies show that both are feasible, and they may not be mutually exclusive. Establishing their relative contributions influences understanding of the early Earth, including consequences for the redox state of the surface and atmosphere on ultimate crystallization of the magma ocean and the possible role of the lower mantle in any subsequent mantle redox evolution.

Stabilization of Fe^{3+} in high pressure silicate melts occurs because of the comparatively small partial molar volume of Fe_2O_3. Multiple experimental and first principles studies demonstrate that a deep terrestrial magma ocean in equilibrium with core-destined alloy has non-negligible Fe^{3+}, though they differ markedly in their quantification. Less-widely appreciated is that Fe^{3+} is also stabilized by high temperatures (Wang et al., this session). Zhang et al. (2024) presented laser heated diamond anvil (LH-DAC) experiments, analyzed by synchrotron Mössbauer spectroscopy (SMS), which suggest that the Fe^{3+} in a deep magma ocean at 28-53 GPa can match the Fe^{3+}/Fe^{T} needed for the redox budget of the modern mantle. New LH-DAC experiments and SMS analyses at 31-73 GPa document bridgmanite/melt partitioning of Fe^{3+} and Fe^{2+}. Fe^{3+} is moderately compatible in Brg relative to Fe^{2+}, but, in combination with incorporation of Fe^{2+} in co-crystallizing ferropericlase, leads to magma ocean solidification that is undersaturated in Fe alloy. This is partly because the f_{O2} required to saturate alloy from a crystallizing mantle is marginally lower than during core formation (alloy in the latter has greater Ni, Si, O), and because the conditions of metal saturation from melt require lower Fe^{3+}/Fe^{T} as temperature and pressure decrease along the solidus. Consequently, disproportionation during near-solidus crystallization of bridgmanite is not favored, making the formation of a deep oxidized layer unlikely and promoting oxidation of the surface and atmosphere in the earliest solidified Earth.