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Magma ocean cooling controls the mantle oxidation state

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The oxidation state of Earth's mantle influences its chemical differentiation, mantle dynamics, and volatile evolution, yet how it was initially established after core formation and magma ocean crystallization remains poorly constrained. The disproportionation of iron (i.e., $3FeO = Fe + Fe_2O_3$) in a silicate magma-ocean played a crucial role in setting the solid mantle's initial redox state [1, 2]. For example, an initially reducing mantle can become progressively more oxidized if disproportionated Fe metal segregates to the core as the magma ocean solidifies. To calculate the potential for mantle oxidation by disproportionation, it is required to understand how pressure and temperature affect the disproportionation reaction. Here we combine *ab initio* calculations, machine-learning potentials, and thermodynamic integration to quantify iron disproportionation in silicate analogs to a deep magma ocean at 20-140 GPa and 3000-6000 K, conditions relevant to Earth's deep magma ocean stage. The results reveal that at constant oxygen fugacity, there is a moderate increase in ferric iron content with pressure but a substantial increase in ferric iron with decreasing temperature. This strong temperature dependence helps reconcile discrepancies among previous experiments [1, 3, 4], and identifies secular cooling as a potential primary driver of the oxidation of Earth and terrestrial planetary mantles, and by extension, their earliest atmospheres.

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