Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.27786

The Interactive Role of Silica, CO_2 , and pH in Photochemical Oxidation of Iron (II) Under Archean Ocean Conditions

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Oxidized iron minerals in Archean–Paleoproterozoic banded iron formations (BIFs) are often attributed to photosynthetic Fe(II)-oxidizing bacteria or oxygen production by early cyanobacteria. However, in the absence of an ozone layer, intense ultraviolet (UV) radiation may have driven abiotic Fe(II) oxidation. To constrain the conditions that would have enabled photochemical Fe(II) oxidation, we considered the complex Archean ocean chemistry, where elevated CO_2 and dissolved silica (dSi) levels likely interactively shaped pH, light penetration, and iron speciation.

We systematically evaluated Fe(II) photo-oxidation under both shallow shelf and open ocean conditions, assuming substantial UV intensities (>0.1 W m^{-2}) across UV-A, B, and C, reflecting their temporal and depth dependent variability. This revealed a highly dynamic system in which Fe(II) oxidation rates were modulated by pH, silica complexation, and reactive oxygen species. Consistent with [1], Fe(II) mineral formation and complexation with dSi tempered Fe(II) oxidation and Fe(III) mineral formation in some cases. However, Fe(II) mineral precipitation rates only exceeded photo-oxidation rates under a narrow set of conditions, specifically high Fe(II) concentrations, a high CO2 level and pH > 7. At moderate Fe(II) levels (10 – 125 μM), photo-oxidation was the dominant process impacting Fe speciation particularly at pH < 7. Surprisingly, Fe(II) photo-oxidation rates at pH <7 increased with increasing dSi concentration (0.2 – 2 mM), an effect further modulated by the prevailing spectral quality and quantity of UV light. The composition of the resulting ferric phases was strongly influenced by CO2 and dSi levels. Importantly, across most conditions, abiotic oxidation rates with O2 were substantially lower than photochemical oxidation.

Our results suggest that during daylight hours, photo-oxidation could have been a dominant pathway for Fe(II) oxidation in surface waters under moderate Fe concentrations and low pH, even in the presence of 2 mM dSi. This mechanism plausibly operated alongside photoferrotrophic bacteria, influencing the deposition of Fe-bearing minerals. We discuss these findings in the context of ocean stratification, short-term and long-term variability in solar fluxes, and their implications for the formation of BIFs.

Reference

[1] Konhauser, K.O. et al. (2007). Decoupling photooxidation from shallow-water BIF deposition. Earth and Planetary Science Letters, 258:87-100.