Photo-oxidation of Fe in Simulated Archean Seawater Requires Short Wavelength UV Light

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Every planet orbiting a star is subject to photochemical reactions that can potentially alter its surface. While most attention has been given to photochemistry in atmospheres, UV radiation can also drive important chemical reactions in aqueous solution. Unfortunately, we do not understand photochemistry in complex aqueous systems well enough to infer its importance on other worlds. We conduct photochemical experiments in simulated Archean seawater. Our starting point mimics the early Earth, when the surface UV flux was high due to the lack of an atmospheric ozone layer. We aim to develop "photogeochemical" models applicable to the Archean and ultimately, exoplanet oceans.

We are investigating the photo-oxidation of dissolved Fe^{2+} to Fe^{3+}. This reaction has been proposed as an explanation for Banded Iron Formations (BIFs) deposited in Archean oceans [1]. The viability of this hypothesis depends on Fe oxidation having a significant quantum yield at wavelengths > 300 nm where light transmission is greater [2], which has been debated [3]. We are revisiting this work with an improved design, including a full-spectrum Xe arc lamp and direct determinations of [Fe^{2+}], [Fe^{3+}], and [Fe_T].

In full-spectrum experiments that include UVC light we observe Fe^{2+} oxidation. Typically, Fe^{2+} is lost at a rate of ~2%/day over 7 to 14 days. Concurrently, [Fe^{3+}] increases, and an insoluble precipitate forms. However, in experiments where light < 320 nm was blocked using a cutoff filter, [Fe^{2+}] and [Fe^{3+}] concentrations remained constant within analytical error, and no precipitate formed, even after 10 days. Upon removal of the filter, [Fe^{2+}] began to decrease at 2%/day, [Fe^{3+}] increased, and a precipitate formed.

These results suggest photo-oxidation at long wavelengths is not a viable source of oxidized Fe for BIFs. Future work will determine the quantum yield vs. wavelength, permitting extrapolation to extrasolar oceans around stars with higher UV flux.

1. Braterman et al., 1983, *Nature* 303: 163. 2. Francois, 1986, *Nature*, 320: 352; 3. Konhauser et al., 2007, *EPSL*, 258: 87.