

The Possible Photochemical Origins of Banded Iron Formations. P. R. Castleberry¹, S. J. Romaniello², and A. D. Anbar^{1,2}, ¹School of Molecular Sciences, Arizona State University, Tempe AZ (email: pcastleb@asu.edu), ²School of Earth and Space Exploration, Arizona State University, Tempe AZ

Introduction: Banded iron formations (BIFs) are among the earliest possible indicators for oxidation of the Archean biosphere. However, the origin of BIFs remains debated. Proposed formation mechanisms include oxidation of Fe(II) by O₂^[1], photoferrography (a type of direct microbial Fe oxidation)^[2], and abiotic UV photooxidation of Fe(II)^[3]. Resolving this debate could help determine whether BIFs are really indicators of O₂, biological activity, or neither.

Prior experimental work on Fe(II) photooxidation disagrees regarding both the wavelengths required for the reaction and the reaction rates, and has thus arrived at dissimilar conclusions about the potential importance of photooxidation for BIF deposition^[4,5]. Braterman et al. (1983)^[4] found light >400 nm caused photooxidation and concluded photochemistry could precipitate Fe rapidly enough to create BIFs. Braterman inferred photooxidation by pH change and did not directly measure Fe precipitation. In contrast, later work by Konhauser et al. (2007)^[5], who measured Fe precipitation directly, reported that light >~350 nm had no effect. This results in much slower photooxidation kinetics, leading these authors to conclude that photooxidation may have been negligible compared to rates of photoferrography. Both experiments used light sources that poorly match the solar spectrum; either a Hg lamp or Hg lamp and UV-A lamp.

We seek to improve on these studies by by directly measuring the rate of aqueous Fe loss. We also conducted an experiment using a continuum light source that simulates natural sunlight.

Methods: We conducted two experiments using different light sources. The first experiment used a Hg lamp with wavelength cut-off filters ($\lambda > 400$ nm, > 345 nm, and > 295 nm) to determine the wavelength sensitivity of the photooxidation reaction. The second used a Xe arc lamp, approximating the solar spectrum. A third experiment, using the Xe arc lamp plus cutoff filters is currently in progress. We created an anoxic environment inside of a quartz vessel by continuously flowing 98% N₂/2% CO₂ gas through the reactor over the course of the experiment. The solution contained FeCl₂ (0.18 mM), NaCl (56 mM), and NaHCO₃ (10 mM), at pH ~7.3. We took filtered (0.2 μ m) samples of the liquid by syringe every 12 hours and used quadrupole ICP-MS to measure [Fe] and [Na].

We also constructed a simple photochemical model based on François 1986^[6] to calculate BIF deposition rates for an Archean ocean.

Results and Discussion: Using a Hg lamp and a series of cut-off filters, we determined that UV light > 345 nm does not cause Fe precipitation. This finding disagrees with Braterman et al. 1983 but is consistent with Konhauser et al. 2007. One possible explanation for the difference is that the two studies measured Fe oxidation rates differently. Braterman et al. inferred Fe photooxidation from pH change. In contrast we directly measured Fe photooxidation by decreases in [Fe].

We based our ocean photochemical model on François 1986^[6] but recalculated the reaction rates assuming that only light < 345 nm causes photooxidation, which decreases predicted rates by 5 – 6 fold. The reaction rate is sensitive to [Fe] and given upper limit estimates for the [Fe] of Archean seawater^[7], the calculated Fe deposition rate is 9 mg Fe cm⁻² yr⁻¹. This is at the lower end of estimated BIF formation natural rates of 9-43 mg cm⁻² yr⁻¹^[8] for the Hamersley Basin BIF. In comparison to photoferrography, which can generate Fe oxides at a rate of 500 mg Fe cm⁻² yr⁻¹ for similar [Fe]^[9], photochemistry may be less competitive.

Experiments using the Xe lamp showed measurable effects in hours, demonstrating the potential for Fe to photooxidize significantly in a natural environment. Photooxidation could have been an important background process pervasive in shallow-water environments such as lakes, rivers, or the open ocean, not subject to biological limits such as nutrient availability or protection from surface UV. Quantifying the importance of this background oxidation is a work in progress.

Conclusions: Wavelength cutoff filter experiments showed Fe(II) photooxidation and precipitation does not occur with light > 345 nm. This leads to modeled Fe photooxidation rates at the low end of published BIF deposition rates. These results suggest that photooxidation could contribute to, but is unlikely to be completely responsible for, large rapidly deposited BIFs such those in the Hamersley Basin.

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