

Dissolved silica influences the bulk iron redox state and transformation products of photoferrotrophy

ALICE ZHOU AND JENA E. JOHNSON

University of Michigan

Presenting Author: alicez@umich.edu

Chemical sedimentary deposits known as Banded Iron Formations (BIFs) are one of the best surviving records of ancient marine geochemistry. The precursor sediments of many BIFs precipitated from ferruginous, silica-rich waters prior to the Great Oxidation Event at ~ 2.43 Ga [1]. Reconstructing the mineralogy of BIF precursor phases is key to understanding the coevolution of seawater chemistry and early life. Many models of BIF deposition invoke the activity of Fe(II)-oxidizing photoautotrophic bacteria as a mechanism for precipitating Fe(II,III) and/or Fe(III) minerals in the absence of molecular oxygen [2]. The identity of phases produced by ancient photoferrotrophs remains debated, but laboratory experiments provide a means to explore what their mineral byproducts might have been.

Few studies to date have thoroughly characterized precipitates produced by photoferrotrophs in settings fully representative of Archean oceans. Furthermore, there is little data on the extent to which these oxidation products undergo Fe(II)-catalyzed mineral transformation, as might be expected during descent through ferruginous water masses. The concentration of dissolved Si is an important variable in this process, as silicate species may influence the morphology and reactivity of Fe(III)-bearing phases [3, 4]. To address these uncertainties, we cultured *Rhodospseudomonas palustris* TIE-1 as a photoferrotroph in synthetic Archean seawater with an initial $[\text{Fe(II)}_{\text{aq}}]$ of 1 mM and $[\text{Si}_{\text{aq}}]$ spanning 0 mM-1.5 mM. Ferrihydrite was the dominant precipitate across all Si concentrations, even with substantial Fe(II) remaining in solution. Si co-precipitated with ferrihydrite via surface adsorption, although amorphous silica may have formed an additional phase at $[\text{Si}_{\text{aq}}] \geq 1.2$ mM. Lepidocrocite, goethite, and magnetite were only observed at low $[\text{Si}_{\text{aq}}]$ and are interpreted to be products of Fe(II)-catalyzed ferrihydrite transformation. Finally, the fraction of Fe(II) in precipitates increased as a function of $[\text{Si}_{\text{aq}}]$, suggesting that Fe(II) may associate with outer-sphere complexes on siliceous ferrihydrite. These experimental results deepen our understanding of the potential phases initially present in BIF sediments.

References

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