Photoferrotrophs are inhibited by denitrification in Fe(II)-rich conditions

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Anoxygenic photoautotrophic Fe(II)-oxidizing bacteria, or "photoferrotrophs", were probably a key driver of Fe(III) mineral formation in the Earth's oceans prior to the rise of O_2. As O_2 began to rise and oxygenate the photic zone, these microbes would have seen their habitable space decrease. The transformation from an anoxic to an oxic world would also have facilitated an increase in the concentration of oxidized nitrogen species such as nitrate in the oceans. Nitrate-dependent oxidation of Fe(II) is widespread in modern anoxic environments and could, in theory, have competed with photoferrotrophs for Fe(II) in regions where nitrate, light and low-O_2 conditions co-existed. However, the extent to which nitrate-dependent oxidation of Fe(II) can compete with photoferrotrophy in practice has not been evaluated.

Utilizing various co-culture experiments, we have shown that Fe(II) oxidation by two model freshwater photoferrotrophs (*Rhodobacter ferrooxidans* SW2 and *Chlorobium ferrooxidans* KoFox) is not only out-competed but completely inhibited by the activity of nitrate-dependent Fe(II)-oxidizing bacteria, regardless of whether Fe(II) oxidation is catalyzed enzymatically (as by the autotrophic enrichment culture KS) or by intermediate reactive nitrogen species produced as by-products of heterotrophic denitrification (as by *Acidovorax* sp. BoFeN1). In additional experiments, we also observed inhibition of the freshwater photoferrotrophs as well as two marine photoferrotrophs (*Chlorobium* sp. N1 and *Rhodovulum robiginosum*) during chemodenitrification, where nitrite reacts abiotically with Fe(II).

We primarily attribute this inhibition to the observed accumulation of nitrous oxide (N_2O) during denitrification, which has been previously shown to inhibit key metabolic functions in a diverse range of microbes.

These results suggest that the evolution of the nitrogen cycle over the Great Oxidation Event, particularly the formation of a "laughing gas greenhouse", could represent an as yet unreported control on the extent of Fe(III) mineral formation by photoferrotrophs in the ancient oceans.