Redox cycling of manganese before the rise of oxygen

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Before the evolution of oxygenic photosynthesis, anoxygenic photosynthetic organisms using different electron donors likely colonized the photic zone. Manganese-oxidizing phototrophs may have been present among these, but are not known today. Herein, we explore the cycling of Mn and mineral formation in anaerobic enrichment cultures of anoxygenic photosynthetic organisms growing in the presence of 1 mM Mn(II) in media that mimic Archean seawater. Manganese oxides containing Mn(II), Mn(III) and Mn(IV) precipitate after one month in the presence of microbes and light. The presence of these minerals was confirmed by X-ray diffraction, X-ray Photoelectron Spectroscopy, Fourier Transform Infrared Spectroscopy, synchrotron-μXRD and X-ray Adsorption Near Edge Structure. Abundant calcite and dolomite also precipitate immediately around microbial cells and biofilms, indicating a high preservation potential of the fine microbial textures and structures. Microbial community composition of enrichment cultures was assessed by 16S rRNA gene amplicon paired-end sequencing on the MiSeq Illumina platform. Strictly anaerobic phototrophs from the phylum Chlorobi were dominant in all cultures, and all cultures also lacked cyanobacteria. These findings demonstrate light-driven, anaerobic, biologically-mediated formation of manganese oxides in the presence of micromolar levels of sulfide. This process should be considered when interpreting the cycling of manganese, sulfur, trace metals and oxygen on the early Earth and in modern anoxic environments.