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Manganese speciation in modern Cyanobacteria and its relationship to the evolution of photosynthesis

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Earth's environment was irreversibly changed by the evolution of oxygenic photosynthesis and the rise of atmospheric oxygen. Manganese plays a central role in that event, as the catalytic center of the water-oxidizing complex in photosystem II is a Mn_4CaO_5 cluster. This bioinorganic cluster is an evolutionary singularity: oxygenic photosynthesis evolved only once, and all known oxygenic photosynthetic organisms, from the tiniest microorganisms to the most complex plants, use the same bioinorganic chemistry. The mechanism of this evolution remains poorly understood, but it is clear that manganese was critically important to the process. The controlled oxidation of environmental Mn(II) through stable Mn(III) complexes to a final catalytically-active mixed valence Mn(III,IV) cluster is a remarkable feature of the photoassembly of the water-oxidizing complex. In order to gain insights into the chemistry of these ancient processes, we have been studying manganese speciation in extant Cyanobacteria (*e.g.*, *Synechocystis* sp. PCC6803). We are using a combination of fluorescence, magnetic resonance (EPR/ENDOR), and mass spectrometric techniques to examine manganese concentration, oxidation state, ligand environment, and localization within whole cyanobacterial cells. It has been previously shown that *Synechocystis* sp. PCC6803 accumulates high concentrations of manganese (~ 100 mM), which vastly exceeds its proteomic requirements. EPR and ENDOR spectroscopies show that the speciation of Mn(II) in *Synechocystis* is substantially different from Mn(II) speciation in yeast (*Saccharomyces*) and photosynthetic algae (*Chlamydomonas*), with a smaller contribution from phosphate-based ligands in *Synechocystis* than in the other organisms. From our spectroscopic studies, we are gaining new and detailed speciation information about the cyanobacterial cellular Mn pool, which allows us to understand its role both in the organism as a potential antioxidant or photosynthetic substrate as well as in broader biogeochemical cycling, both today and on the early Earth.