# Insights into Ancient Manganese Biogeochemistry from Studies of Modern Photosystem II

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The origin of oxygenic photosynthesis was an incredibly important metabolic innovation, irreversibly changing the course of Earth history. Manganese plays a central role in this history. Structural biology and biochemistry of Photosystem II (PSII) in all extant Cyanobacteria lead to the hypothesis that Mn(II) was an electron donor to PSII prior to the evolution of oxygenic photosynthesis, and the geologic record shows that manganese oxidation occurred prior to the rise of atmospheric oxygen. We are studying manganese oxidation in modern Cyanobacteria to provide insights into these biogeochemical processes. *Synechocystis* sp. PCC6803 accumulate high concentrations of manganese (~ 100 mM) greatly exceeding their proteomic requirements. ENDOR spectroscopy of whole cells provides, for the first time, detailed speciation information about this cellular Mn pool and its role in the cell as a potential antioxidant or photosynthetic substrate. Through studies of Cyanobacterial cultures and purified PSII (both wild-type and variant proteins), we are exploring the molecular mechanisms of manganese-oxidizing phototrophy and using our new understanding of these processes to elucidate the evolution of the oxygen-evolving complex.