Cyanobacterial Mn(II) as defense against oxidative stress

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Life on Earth today uses manganese both to generate dioxygen through oxygenic photosynthesis and to protect itself from deleterious oxidation reactions. Mn(II) plays a critical role in modern biology in protecting cells from oxidative stress, both as a cofactor in antioxidant proteins such as superoxide dismutase and catalase and in the form of small-molecule inorganic complexes. Prior to the evolution of oxygenic photosynthesis and the subsequent rise of oxygen, ~ 2.35 billion years ago, cells would have had no evolutionary pressure to develop antioxidant proteins, so early life must have depended entirely on inorganic chemistry for protection from oxidation. Cellular Mn(II) concentrations in modern *Synechocystis* are vastly higher than its proteomic requirements, suggesting a continuing role for Mn(II) in antioxidant biology. Mn(II) speciation studies by electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) spectroscopies support this hypothesis. We have now examined Mn(II) concentrations and speciation across a range of extant Cyanobacteria using mass spectrometry, EPR, and ENDOR. We are exploring variations in the Cyanobacterial cellular Mn pool that provide insights into Mn biogeochemical cycling today and on the early Earth.