Manganese and the evolution of photosynthesis

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Oxygenic photosynthesis is the most important bioenergetic event in the history of our planet—it evolved once within the Cyanobacteria, and remained largely unchanged as it was transferred to algae and plants via endosymbiosis. Manganese plays a fundamental role in this history because it lends the critical redox behavior of the water-oxidizing complex of photosystem II—a cubane cluster of four high-valent redox-active Mn acts as a redox capacitor to adapt the native single electron chemistry of the reaction center to the four-electron oxidation of two water molecules to produce oxygen. The photoassembly of the Mn-bearing water-oxidizing complex largely fuels the hypothesis that Mn(II) once played a key role as an electron donor for anoxygenic photosynthesis prior to the evolution of oxygenic photosynthesis [1-3]. Here we review the growing body of geological and geochemical evidence from the Archean and Paleoproterozoic sedimentary records that demonstrate the oxidative branch of the Mn cycle switched on just prior to the rise of oxygen [4] [5] at *ca*. 2.4 billion years ago. We leverage this data against constraints from the structural biology and biochemistry of photosystem II in Cyanobacteria. These observations highlight that water-splitting in photosystem II evolved independently from a homodimeric ancestral type II reaction center [6] capable of high potential Mn(II)-oxidizing phototrophy. The ancestral homodimer reaction center also evolved a C-terminal extension that sterically precluded the bulky phototrophic electron donors used by other phototrophs like cytochrome c, cupredoxins, or high-potential iron-sulfur proteins, and could only complete direct oxidation of small molecules like Mn^{2+}, and ultimately water [5].

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