

Manganese and the Evolution of Photosynthesis

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Abstract 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. Constraints from the photoassembly of the Mn-bearing water-oxidizing complex fuel the hypothesis that Mn(II) once played a key role as an electron donor for anoxygenic photosynthesis prior to the evolution of oxygenic photosynthesis. Here we review the growing body of geological and geochemical evidence from the Archean and Paleoproterozoic sedimentary records that supports this idea and demonstrates that the oxidative branch of the Mn cycle switched on prior to the rise of oxygen. This Mn-oxidizing phototrophy hypothesis also receives support from the biological record of extant phototrophs, and can be made more explicit by leveraging constraints from 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 capable of high potential photosynthesis and Mn(II) oxidation, which is required by the presence of homologous redox-active tyrosines in the modern heterodimer. The ancestral homodimer reaction center also evolved a C-terminal extension that sterically precluded standard phototrophic electron donors like cytochrome *c*, cupredoxins, or high-potential iron-sulfur proteins, and could only complete direct oxidation of small molecules like Mn²⁺, and ultimately water.

Keywords Great oxidation event · MIF · Detrital pyrite · PSII · WOC · Molecular evolution

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Introduction

After the development of life itself, the evolution of oxygenic photosynthesis is the most fundamental and transformative event in the history of our planet—and manganese plays a special role in this history. The most important biochemical innovation to enable the phototrophic splitting of water and the production of molecular oxygen is the water-oxidizing complex (WOC) of photosystem II (PSII). The WOC is a high-valent cubane cluster of four redox-active Mn centers and a Ca center, bound by oxo-bridges (McEvoy and Brudvig 2006, Umena et al. 2011). And it serves an important function of acting as a type of redox capacitor that adapts the native single electron chemistry of the reaction center for the four-electron oxidation of two water molecules.

How did the WOC originate? In considering the evolutionary history of photosynthesis, Olson (1970) provided the necessary realization that some transitional state came before PSII, and that this ancestral protein would have had some meaningful but different physiology than the water-splitting reactions that characterize PSII. In evolution, the process of exaptation (Gould and Vrba 1982) is a commonly held and useful concept wherein pre-existing structures are recruited and adapted for novel functions. However, compared to other metals like iron, there are only a few protein families that bear Mn cofactors. Blankenship and Hartman (1998) suggested that the WOC might have derived from catalase (which has a binuclear Mn center and performs chemistry with high-valent oxygen species), but sequence and structural data collected since then has not born this out. Indeed one of the truly remarkable features of the WOC is that it is an evolutionary singularity, and shares no meaningful similarity with anything else in the natural protein world.

Photoassembly of the WOC complex provides important insights into WOC evolution. This biosynthetic process demands only Mn^{2+} and light (Tamura and Cheniae 1987); during catalytic turnover and electron transport through the photosystem five electrons are donated from four manganese atoms to produce the basal oxidation state (S_0 ; Mn(III)Mn(IV)_3) of the WOC (McEvoy and Brudvig 2006). It is critical to note that *all water-splitting first begins with manganese oxidation*, and that these electrons derived from manganese are indistinguishable from those later provided by the oxidation of water. This phenomenon highlights a class of ontogeny-recapitulates-phylogeny hypotheses for the WOC, wherein Mn(II) played a role as an electron donor for phototrophy by ancestral anoxygenic phototrophic Cyanobacteria prior to oxygenic photosynthesis (Zubay 1996, Dismukes et al. 2001, Allen and Martin 2007, Johnson et al. 2013a, b). This idea is particularly valuable because it provides clear expectations that can be tested against observations of the geological record. Recently we provided the first strong support for this hypothesis with detailed geological and geochemical data from early Paleoproterozoic strata in South Africa (Johnson et al. 2013a). Below we will briefly review those results, discuss some new ones from other geologic settings, and then develop a more detailed hypothesis for how ancestral PSII might have proceeded from Mn oxidation to water splitting by leveraging observations and constraints from biochemistry and structural biology with evolutionary theory.

Observations from the Geologic Record

Manganese is the third most abundant transition metal in Earth's crust, where it is present only as Mn(II) and substitutes for ferrous iron in a wide variety of primary igneous minerals

(Turekian and Wedepohl 1961). Rock weathering, therefore, provides a substantial flux of Mn^{2+} to Earth surface waters. Mn^{2+} is also soluble unless oxidized to Mn(III) or Mn(IV) which subsequently undergoes hydrolysis and forms insoluble oxide phases that rapidly sediment (Stumm and Morgan 1996). Compared to iron or sulfur, however, manganese requires high potential oxidants (like O_2 or species derived from O_2) to undergo redox cycling. In addition, the oxidation of Mn(II) is comparatively sluggish even in environments with abundant O_2 , particularly in the absence of biological catalysts (Morgan 2005). This forms the logic for a geologic test of the Mn-phototrophy hypothesis for the origin of the WOC derived above: if correct, Mn-oxidation should have occurred prior to the evolution of oxygenic photosynthesis and in the (effective) absence of molecular oxygen or other oxidants thereby derived.

Throughout Archean time (>2.5 Ga), seawater (both surface and deep) contained elevated levels of Mn^{2+} (Fischer and Knoll 2009). This inference is supported by a substantial body of observations of the chemistry of Archean carbonates (Veizer et al. 1989a, Veizer et al. 1989b, Veizer 1985, Ronov and Migdisov 1971, Beukes 1987, Sumner 1997, Sumner and Grotzinger 1996, Sumner and Grotzinger 2004), and shows no Mn oxidation with the only sink for Mn(II) derived from rock weathering as a trace constituent of $CaCO_3$ minerals precipitated on carbonate platforms. The same was not true for iron and sulfur, which had already developed complex redox cycles by that time (e.g., - Fischer and Knoll 2009, Fischer et al. 2014). Furthermore, iron—the largest pool of available donors and acceptors before water-splitting—was effectively removed from surface seawater by phototrophs suggesting that autotrophs living in surface seawater during Archean time were electron-limited (Beukes 1987, Fischer and Knoll 2009, Kappler et al. 2005, Kharecha et al. 2005). These observations are important because they provide an additional answer for the question “Why did nature choose manganese” for water-splitting (Armstrong 2008). The presence of Mn^{2+} in surface seawater would have provided an evolutionary opportunity for those anoxygenic phototrophs, however in order to oxidize Mn(II) they would need to develop high potential photosynthesis to exploit the resource—an evolutionary path that would end in water oxidation (Johnson et al. 2013a).

Confirming a historical prediction of the Mn-phototrophy hypothesis, the earliest authigenic Mn deposits (reflecting Mn oxidation and sedimentary concentration of oxides) occur shortly before the rise of O_2 , in the ~2.415 Ga Koegas Subgroup preserved in the Griqualand West structural sub-basin of the Kaapvaal Craton of South Africa (Schröder et al. 2011, Johnson et al. 2013a). These strata are comprised of near-shore marine deltaic deposits on the western margin of the Kaapvaal craton that accumulated horizons of Mn-rich iron formation tied to lobe-switching on the delta. Independent observations of mass anomalous fractionation of multiple sulfur isotope ratios in authigenic pyrite coupled with the widespread occurrence of detrital pyrite demonstrated that O_2 levels remained far too low to explain the observed Mn-rich sediments (Farquhar et al. 2000, Pavlov and Kasting 2002). With subsequent work we also observed detrital uraninite (a redox-sensitive U-bearing phase) in this sequence and developed a kinetic sediment transport model that combines chemical and physical weathering to quantitatively estimate environmental O_2 levels in Earth surface environments at that time (Johnson et al. 2014). The redox sensitive detrital grains in the Koegas Subgroup show no oxidation on their path from bedrock to soils and hillslopes, channels, bars, and floodplains, ultimately to their depocenter in the basin. This provides an unambiguous and well-understood redox proxy that constrains O_2 at that time to extremely low levels—concentrations many orders of magnitude too small to explain the Mn-enrichments (Johnson et al. 2013a, 2013b). Altogether this ecosystem-scale paleoenvironmental evidence strongly suggests that Mn^{2+} was

being used by anoxygenic phototrophs as an electron donor prior to the evolution of oxygenic photosynthesis and rise of oxygen at ~ 2.3 Ga.

A global test of this hypothesis is still hindered by the general scarcity of well-preserved and sufficiently studied sedimentary basins of early Paleoproterozoic age, however several broadly coeval deposits exist that support this idea. Turee Creek strata from Western Australia of broad similar age to the Koegas deposits contain a thin horizon enriched in Mn, though the paleoenvironments and processes of Mn-mineralization aren't as well constrained at present (Williford et al. 2011). Another thin horizon in the middle of the Huronian Supergroup (Sekine et al. 2011) also contains Mn-enrichments possibly deposited prior to the rise of O₂ (Kopp et al. 2005). Earlier deposits in the ~ 2.9 Ga Witswatersrand and Mozaan basins of South Africa contain horizons in the stratigraphy, including shales and iron formations, that contain levels of manganese (Smith 2007, Planavsky et al. 2014) elevated relative to those seen throughout other Archean successions (Klein 2005). These basins also contain abundant detrital pyrite and uraninite (e.g., Frimmel 2005) and sulfur isotope mass anomalies (Ono et al. 2006, Guy et al. 2012) that show extremely low free environmental oxygen at that time. But while it's tempting to draw support for Mn-phototrophy deeper into Archean time, more detailed work is required to untangle the complex petrogenesis and multiple phases of mineralization present in these metamorphic rocks before any robust conclusions can be drawn about paleoenvironmental redox processes operating in the Witswatersrand and Mozaan basins (Smith 2007).

So a growing set of observations from the geological record support the notion of a Mn-oxidizing transitional state during the evolution of oxygenic photosynthesis. However these observations only offer a broad brush ecosystem-scale paleoenvironmental view on this process. To arrive at a deeper understanding of how ancestral photosynthesis evolved from single electron oxidation reactions to the four electron splitting of water, we need to draw on observations and constraints by structural biology, biochemistry, and genomics.

Additional Constraints from Biochemistry and Structural Biology

From electron transfer mechanics, highly conserved structural features, and phylogenetic analyses it is clear that PSII is most closely related to RCII, and that PSII and RCII evolved to become a heterodimeric reaction centers independently (Sadekar et al. 2006). So one can infer that the ancestor of RCII and PSII was an anoxygenic type II reaction center (e.g., cytochrome *c* - quinone oxidoreductase) homodimer that received electrons from single electron carrier small soluble proteins (like cytochrome *c*, cupredoxins, and high potential iron-sulfur proteins). It produced low potential oxidants (< -400 mV) as evidenced by the wide diversity of extant anoxygenic phototrophs with distal electron donors of ferrous iron, reduced S compounds, organic compounds, or molecular hydrogen in addition to cyclic electron transport (Hohmann-Marriott and Blankenship 2011). We also infer that it reduced menaquinones (Schoepp-Cothenet et al. 2009) from evolutionary analysis of the distribution of "high-potential" quinones currently in nature. From the Granick hypothesis (and observations of pigments in RCI) it is also reasonable to infer that it contained chlorophyll a (Granick 1957, Bryant and Liu 2013).

The transition from anoxygenic to oxygenic phototrophy was a complex process that required the acquisition of three unique biochemical attributes: 1) a photosystem capable of oxidizing high-potential ($> +820$ mV) electron donors, 2) a bioinorganic complex that could catalyze the oxidation H₂O to O₂ (the WOC), 3) and the coupling of two photosystems in

series to generate low potential electron donors (ferredoxin and NADPH) capable of readily fixing CO₂ into biomass. It is possible to ordinate the evolution of these features since the origin of the WOC required the presence of a pre-existing high-potential photosystem to provide the oxidizing potential to split water. Furthermore the CP43 subunit of PSII, which evolved from a duplication of the N-terminus of PSI (Mix et al. 2005), provides ligands for the WOC. This strongly suggests some type of high-potential anoxygenic phototrophy that utilized two photosystems was a direct precursor to oxygenic phototrophy.

A number of powerful evolutionary insights can be gained from structural observations of the PSII heterodimer composed of the D1 and D2 proteins. Features shared by both sides of the protein can be confidently assigned to the ancestral state, and would have contributed to its catalytic characteristics. Redox-active tyrosines are present at homologous positions in the heterodimer. These residues demonstrate that the homodimeric ancestor received electrons from both sides of the protein and must have been capable of generating high potential oxidants—far higher than required for typical anoxygenic photosynthesis but in line with the requirements for manganese and water oxidation (Rutherford and Faller 2002). Furthermore a homologous C-terminal extension consisting of a loop (likely caused by a read-through) exists on the periplasmic side of both D1 and D2 that makes it biologically impossible to feed electrons from standard phototrophic electron donors like cytochrome *c*, cupredoxins, or high-potential iron-sulfur proteins to P680⁺, because the distances would be too large for effective electron transfer (>25 Å). This requires that the ancestral homodimer could only oxidize small molecules like Mn²⁺, and ultimately water via the WOC, directly. We hypothesize that prior to heterodimerism, the ancestral PSII only oxidized manganese and did not yet form a fully functional WOC because 1) the WOC is only present on one side of the extant reaction center, and 2) two functional WOCs—which would be required by a homodimeric ancestral PSII capable of water oxidation—would have to coordinate the transfer of eight electrons to oxidize water on both sides of the protein complex (Fig. 1). This is evolutionarily unpalatable as coordinating four electron transfers is already sufficiently taxing. However Mn-oxidation by both sides of the protein complex is viable and might have some advantages in being able to rapidly provide electrons to the photosystem. For this reason, we view the evolution of heterodimerism in PSII as effectively synchronous with the origin of the water oxidizing complex, as it is unclear how to break this symmetry at present.

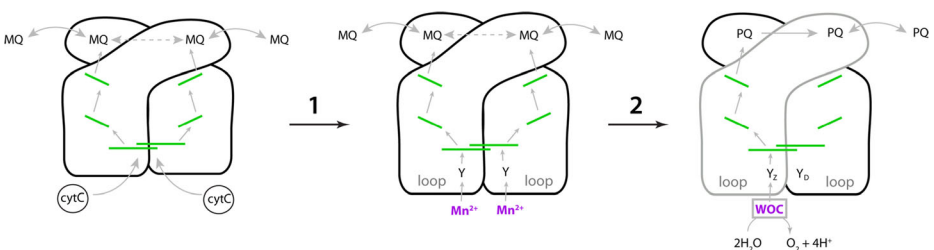


Fig. 1 Schematic showing steps in the evolution of water-splitting by photosystem II according to constraints from structural biology of PS(II). Reaction centers are shown as a dimer. Pathways of electron flow are marked with *gray arrows*. Thick *green lines* show chlorophyll pigments. *MQ* menaquinol, *PQ* plastoquinol, *cytC* cytochrome *c* or similar small protein single electron carrier. Relative time moves *left to right*. The center panel describes the electron transfer path most consistent with observations of Mn-phototrophy from the geologic record (Johnson et al. 2013a, b) and molecular evolution (e.g., Sadekar et al. 2006). Rightmost panel describes the electron transfer path in the extant PSII heterodimer found in oxygenic Cyanobacteria

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