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Review

The origin of the oxygen-evolving complex

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Contents

Abstract

One of the key biochemical developments during the evolution of life was the invention of the oxygen-evolving complex (OEC) of photosystem II, responsible for catalyzing the oxidation of water to molecular oxygen in plants, algae, and cyanobacteria. Though there have been a number of recent, key advances towards understanding how this remarkable chemistry is carried out, it remains a fundamental mystery how this complicated, four electron transfer process originated. Here we review some of these advances and resulting hypotheses on the origin and early evolution of the OEC. In addition, we present evidence suggesting that the four manganese-containing core of the OEC shares structural homology at the atomic level with the active sites of several distinct two manganese-containing enzymes, including manganese catalase, which carries out the oxidation of hydrogen peroxide. We discuss the implications for the plausible origin of oxygenic photosynthesis.
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1. The roots of oxygenic photosynthesis

The invention of oxygenic photosynthesis, the light-driven oxidation of water to molecular oxygen, stands as one of the pivotal evolutionary innovations in the history of life on Earth. The process is carried out only at the oxygen-evolving complex (OEC) of photosystem II (PSII) found in plants and algae, as well as in cyanobacteria from which those eukaryotic lineages acquired the capability. Despite the biological uniqueness of water oxidation to O_2, several of the core proteins of photosystem II have homologs in the so-called type I and type II anoxygenic photosynthetic reaction centers found in six groups of bacteria [1–4]. These homologs have provided a number of important insights into how photosynthesis evolved and have compelled several hypotheses on the origin of oxygenic photosynthesis. Importantly, key differences exist between oxygenic and anoxygenic photosynthetic machinery with no apparent homologs or transitional forms that would provide clues to their development.

Foremost among these differences is the presence and key role of manganese at the site of water oxidation in photosystem II, enabling H_2O to serve as a stepwise electron donor to the photooxidized photosystem. This is distinct from bacterial anoxygenic reaction centers, which rely on redox-active periplasmic proteins as electron donors. Ultimately, these electrons are derived from a variety of (exogenous) reduced compounds such as hydrogen sulfide, ferrous iron, organic car-

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bon, or nitrite. However, no anoxygenic reaction centers have been described that are able to generate a redox potential strong enough to oxidize water, a very weak electron donor. In part, this difference in attainable oxidizing potential is attributable to the presence of chlorophyll in the oxygenic photosystem, whereas all anoxygenic phototrophs contain longer-wavelength absorbing and therefore lower-energy bacteriochlorophyll [5,6]. Though the fact that chlorophyll is a biosynthetic precursor to bacteriochlorophyll spawned the idea that chlorophyll-based photosynthesis evolved earlier (the Granick hypothesis, [7]), phylogenetic evidence supports that bacteriochlorophyll-based photosynthesis is ancestral [8].

The number of structural subunits that make up the functional photosynthetic apparatus is quite different in anoxygenic versus oxygenic phototrophs. The heliobacterial reaction center, for example, is comprised of a single homodimer protein complex with both light harvesting and core photochemical domains [9], and the proteobacterial reaction center is comprised typically of eight or fewer proteins in light-harvesting and reaction center subunits. Alternatively, some oxygenic phototrophs can contain well over 50 structural subunits in photosystems I and II and in light-harvesting complexes such as the phycobilisome. Though differences exist between cyanobacteria, algae, and plants, especially in the light-harvesting complexes, the protein subunits of photosystem I and II are remarkably highly conserved in all three groups, and many of the proteins are highly similar in primary structure.

Evolutionary comparisons of the oxygenic and anoxygenic photosynthetic machinery broadly divide the evolution of the process into three distinct stages. The earliest stage saw the invention of the original reaction center that ultimately gave rise to both types of reaction center (or photosystem) characteristic of all known photosynthetic organisms [10]. Though evidence is sparse, geologists have described laminated, shallow water communities pervasive between 3.5 and 3.0 billion years ago that are consistent with early photosynthesis [11,12]. These predate earliest markers for cyanobacteria or for atmospheric oxygen, so the logical argument is that these would be the progenitors of the modern anoxygenic and oxygenic lineages. A number of plausible electron donors have been proposed for linear electron transport, including molecular hydrogen, hydrogen sulfide or reduced sulfur species, and reduced metals such as ferrous iron [13–16].

Demarcating the second stage is the radiation of what ultimately would become the first oxygen-evolving phototroph, often equated to a proto-cyanobacterium. Multiple lines of evidence, including widescale geological changes consistent with the appearance of oxygen [17,18] and biomarkers argued as signature for cyanobacteria [19] and for O_2 availability [20], bookend this stage between 2.8 and 2.3 billion years ago. However, there are no clear transitional forms from modern biology that give direct insight into how the remarkable differences that distinguish oxygenic and anoxygenic photosynthesis might have arisen. Even the most primitive known cyanobacteria and algae share nearly the same repertoire of photosystem proteins as highly complex plants [21]. However, some modern organisms have properties that are consistent with what might have been required by a transitional proto-cyanobacterium [22]. These will be discussed below.

The third stage represents the diversification of oxygenic phototrophs, particularly the dawn of eukaryotic photosynthesis and the eventual emergence of land plants. This was marked early on by the primary endosymbiosis that brought photosynthesis into eukaryotes and promulgated the development of algae and plants. The remarkable diversity of modern photoautotrophs required the evolution of a vast range of new capabilities affecting morphology and structure, metabolism, nutrient acquisition, and reproduction. Despite these extensive changes, similarities in the photosynthetic machinery of cyanobacteria and plants suggest the core process has remained fundamentally unchanged.

2. The oxygen-evolving complex: brief overview

The oxygen-evolving complex – and the unique chemistry it carries out – is foremost among the conserved components of the oxygenic photosynthetic machinery. The structure and dynamics of the OEC have been the subject of many biophysical investigations that have been detailed in a number of excellent reviews [23–25] and will be only briefly detailed here. The OEC sits approximately at the membrane–lumen interface, surrounded by four core proteins (D1, D2, CP43, and CP47) of photosystem II and capped by three, so-called OEC proteins (in cyanobacteria, PsbO, PsbV, and PsbT). However, direct ligands to the OEC appear to come almost entirely from D1, with only a single ligand contributed from CP43 [26,27]. The closest residue of subunit D2 is about 10 Å distant, and the closest residues from PsbO and PsbV are almost 15 Å away from the Mn cluster.

The structural components of the OEC include four oxygen-bridged manganese atoms, calcium, and putatively chloride [24]. EPR and X-ray absorption spectroscopy and protein crystallography have been particularly useful in constraining the geometry of the OEC, recently reviewed in [25]. Most recently, polarized extended X-ray absorption fine structure spectroscopy has brought a new level of resolution to bear on the OEC structure, supporting a Mn_4 motif that is quite distinct from what had been advanced based on recent X-ray structural data [28]. Despite these exciting advances, a perfectly legitimate question is whether or how these breakthroughs – which, despite years of careful study and fervent argument, distill down to only a few Angstroms difference between atoms – stand to shed new light on how Nature invented the remarkable capability of water oxidation. Surprisingly enough, and despite the fact that the bridged four manganese cluster was a singular invention, accurately resolving the structure of the OEC may indeed be decidedly important to understanding how it evolved.

2.1. Intermediates en route to oxygenic photosynthesis

The complex electrochemistry carried out at the OEC and the development of a highly oxidizing photosystem II stand as two key events in the development of water oxidation [29–31,22]. It is generally agreed that the development of a strongly oxidizing PSII followed (a) the “switch” from bac-

teriochlorophyll to chlorophyll and (b) mutations in the local environment surrounding primary and secondary electron acceptors (chlorophyll and pheophytin) of PSII. These mutations possibly included structural-spatial changes that "de-dimerized" PSII chlorophylls, as compared to dimeric (special) pair bacteriochlorophylls found in homologous type II reaction centers [30]. Because anoxygenic reaction centers do not generate the highly positive redox potential necessary to oxidize water, the development of a strongly oxidizing RC must have preceded or co-occurred with invention of the water oxidizing complex—and could have resulted from only a few key amino acid replacements [32], as discussed below.

Still enigmatic is how the precise geometry and unique mechanism of the OEC came about. Anoxygenic reaction centers are reduced exclusively by single electron transfer reactions, typically mediated by soluble cytochromes acting as electron conduits from exogenous reductants. It is reasonable that the ancestral (pre-OEC) photosystem II was similarly reduced in one-electron steps, for example accepting electrons from a cytochrome *c* or plastocyanin-like protein (donors that, in modern oxygenic phototrophs, shunt electrons to photosystem I). The chemical result of this putative ancestor is appealingly simple: electrons abstracted from various donors are passed directly to the photo-oxidized reaction center, one electron at a time. However, this is quite different from the reaction catalyzed by the modern OEC, where one-electron reductions of PSII must be coupled to a concerted four-electron oxidation of two water molecules.

Understanding this effective leap in complexity has invoked a number of ideas on transitional or energetically intermediate electron donors: more prone to oxidation than water yet still beyond the oxidizing capability of known anoxygenic RCs. Proposed intermediates include hydroxylamine, hydrogen peroxide, hydrazine, nitric oxide or nitrite (the latter of which has recently been observed as an electron donor to type II RCs), and bicarbonate [13,33,34,29,35]. Bicarbonate has been of interest for its long-known accessory role in facilitating oxygen evolution in the OEC. Dismukes et al. [29] have proposed a transitional OEC with bicarbonate (and, subsequently, complexed Mn-bicarbonate) as an integral part of OEC catalysis, owing to the more favorable energetics associated with bicarbonate as a substrate during oxygen production. These favorable energetics get another boost by the likely higher concentration (by 1–3 orders of magnitude) of CO_2 in the Earth's atmosphere at the time that oxygenic photosynthesis evolved.

Though more easily oxidized than water, each of these proposed transitional donors have other associated problems. Except for bicarbonate, all are present only fleetingly in natural environments, due either to limited routes for their synthesis or else instability/rapid breakdown. Except for hydrogen peroxide and bicarbonate oxidation, none of these donors necessitate the multi-electron chemistry characteristic of the modern OEC. As mentioned above, it has been argued that the transition to a highly oxidizing photosystem might have occurred abruptly (i.e. requiring only a few key amino acid substitutions) [30], suggesting that a stepwise progression towards higher potential electron donors en route to water might not have been necessary. If true, the difficult step in OEC evolution becomes the invention of a catalytic "capacitor" able to simultaneously carry multiple charges, as opposed to the ancestral one-electron transfer capability.

One obvious place to look for such catalytic intermediates are other manganese enzymes, of which only a small handful are known with binuclear-manganese active sites, including ribonucleotide reductase, catalase, and arginase [36]. Despite no previously reported sequence or structural homology, several of these enzymes carry out chemical reactions that have some (albeit primitive) parallels to the OEC. McKay and Hartman [33], and later Blankenship and Hartman [34], argued that H_2O_2 could have been a key intermediate en route to oxygenic photosynthesis. Blankenship and Hartman [34] noted the "half-similarity" between the binuclear Mn catalase and the tetranuclear Mn OEC, suggesting that a primitive Mn catalase was the original template upon which the modern OEC was structured. These ideas are often discounted on the basis of requiring a persistent, exogenous source of H_2O_2 and the aforementioned lack of structural similarity between Mn catalase (or other manganese binuclear enzymes) and any of the PSII proteins.

However, several H_2O_2 sources have been identified that might have been important in some niches within Earth's early biosphere. Recently, Liang et al. [37] have advanced models suggesting that Proterozoic snowball Earth events could effectively concentrate photolytic H_2O_2 in local surface environments, analogous to processes presently occurring on Europa where surface H_2O_2 concentrations up to 0.13% have been observed. This plausible peroxide influx, generated and concentrated in photic environments, would constitute a strong selection pressure for H_2O_2 detoxification mechanisms in photosynthetic communities. The biological answer would be dismutation by catalase and possibly peroxide oxidation by photosystem II. Because these routes both produce O_2 as a by-product, this could also mark the advent of biochemical mechanisms for coping with, and ultimately utilizing, molecular oxygen. While these and/or other routes for peroxide formation (for example, catalyzed on the surface of pyrite minerals) [38] could have been operating on the early Earth, almost all occur in aqueous and therefore must address the dilution problem.

2.2. *Probing beyond sequence conservation: active site superposition*

Because of many inherent limitations of structural alignment algorithms (including inability to focus on restricted structural regions or to extend alignments across multiple subunits), we recently developed an approach for determining the optimal superposition of the atoms concentrated around the active sites of two enzymes (details of the method to be published elsewhere). The motivation is based on the fact that the catalytic active site of proteins can be preserved despite extensive changes in protein sequence and structure. Additionally, convergent evolution can result in two unrelated proteins carrying out analogous or even identical reactions, and it would be useful to rigorously assess whether such functional convergence is connected to a fundamental structural motif.

This method is based on a point registration algorithm developed for combining overlapping 2D/3D images [39] based on common subsets of points. While quite useful for detecting similar arrangements of points in space, the method does not have a straightforward statistical interpretation, so we utilized a bootstrapping approach to assess significance, performing structural superpositions on a large subset of structures downloaded from the Protein Databank (PDB). In brief, the method starts with some subset of atoms from two protein structures, for example in a 5 Å sphere around their active sites, and iteratively translates and rotates one set of atoms until a "best fit" with the second set of atoms is found. This "best fit" is specified by the transform/rotate operator that results in the minimum overall distance between closest pairs of atoms from the two models. As with other structure comparison methods, this minimum overall distance is calculated as the root mean squared deviation (RMSD) between each atom/point (a) in the first structure (with n atoms total) and their closest counterpart/point (b) in the second structure (the "nearest neighbor"):

$$\mathrm{RMSD}(a, b) = \sqrt{\frac{1}{n}\sum_{i=1}^{n}|a_i - b_i|^2}$$

Using the Loll et al. [27] photosystem II structure (PDB ID 2axt) amended with the Mn coordinates of model II in Yano et al. [28], structural superpositions were carried out for each Mn atom in the OEC (4 total, one for each Mn) against every Mn atom in all 343 bi-manganese proteins in the PDB (4 OEC Mn atoms × 3888 Mn atoms from all other bi-manganese proteins yielding 15,552 total superpositions). For example, in one run all atoms within 5 Å of Mn_A from the OEC – which includes atoms spanning the D1 and CP43 subunits – were subjected to an iterative "best fit" superposition against all of the atoms within 5 Å of Mn_1 from xylose isomerase. Only rotations and translations are permitted during the alignment, so these are rigid body superpositions.

These >15,000 best fit superpositions were then compared to one another based on their calculated RMSD. These results are plotted as a histogram in Fig. 1. Because such a metric is sensitive to atom density (i.e. two structures with many atoms will register lower RMS distances), and because atom density increases in high resolution models (primarily due to inclusion of H_2O molecules), only atoms assigned to an amino acid and Mn atoms were considered during superpositions.

Remarkably, the best structural matches to the OEC almost all come from known binuclear enzymes, including arginase and agmatinase – distantly related members of the ureohydrolase superfamily [40] – as well as manganese catalase (Fig. 1). This supports an overall conservation of structural geometry at the active sites of these manganese enzymes that is likely closely coupled to mechanism. The reactions carried out by the ureohydrolase superfamily are quite distinct from Mn catalase or PSII, however experiments have shown that arginase does exhibit weak catalase activity [36]. The best fit superposition of the OEC with Mn catalase is shown in Fig. 2, illustrating an overall similarity in the spatial arrangement of atoms, notable proximity between manganese atoms, and several overlapping, similarly

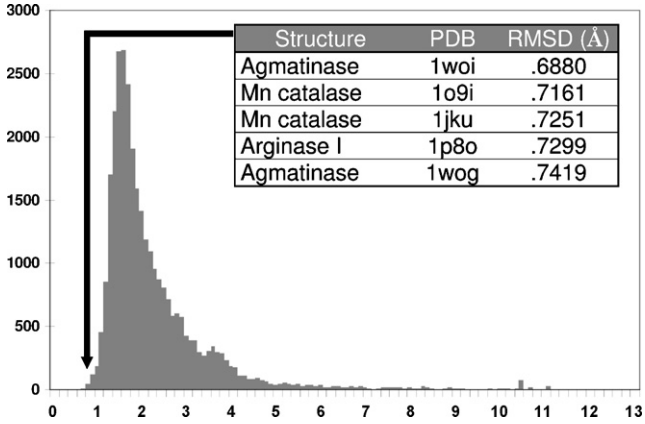

Fig. 1. Histogram of the root mean square deviation (x-axis) of the atomic superposition of the photosystem II OEC (2axt, using Mn coordinates from model II in Yano et al. [28]) vs. 341 bi-manganese proteins from the Protein Databank. The inset shows the top five best fit structures.

charged amino acid ligands. The binuclear cavity of catalase is correspondingly smaller than the OEC cavity and the two structures differ most notably around the two distal/unaligned Manganese atoms of the OEC. Fig. 3 shows the position of Mn cluster-ligating residues within the primary structures of Mn catalase and PSII (D1 and CP43) and underscores the difficulty that standard sequence alignment algorithms would have in detecting this putative homology.

Importantly, the position of the Mn atoms at the heart of the OEC has been intensely investigated and debated, and is still not unambiguously resolved despite recent advances constraining tetramanganese motifs. Recent data has also underscored the potential for X-ray damage to occur to metalloproteins during crystallography that, in the OEC, could influence the positions of the manganese atoms and plausibly their ligands (Ken Sauer, personal communication). Several lines of evidence suggest that these effects do not substantially alter our observations. First, by substituting Mn atoms of the OEC, for instance using the original coordinates of Loll et al. [27] in one run and those from Yano et al. [28] in a second run, we observed minimal changes in RMSD scores, never exceeding 5%. Furthermore, several of the closest structural neighbors to the OEC (listed in Fig. 1) have additional homologs for which crystal structures have been determined. These additional homologs come from different organisms, include active site mutants of wild-type enzymes, and are obtained at varying resolutions and under different experimental conditions. For example, there are eight arginase I homologs – including enzymes from rat, human, and bacteria – that each align with the OEC at an RMSD of 0.8 Å or less. While a more focused approach will ultimately be necessary to determine the net effect of radiation damage to proteins, for example following protein degradation as a function of increasing X-ray energies and exposure times, we believe that our structural superposition results are relatively robust against these effects. While it is feasible that damage to the active site of a metalloprotein may cause us to miss a few structures that are similar to the OEC, it is more difficult to imagine how such damage would result in different, inde-

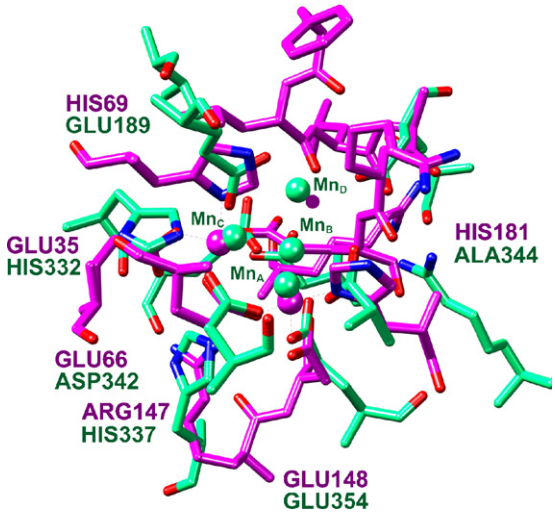

Fig. 2. Optimal superposition of the photosystem II OEC (green backbone) vs. Mn catalase (magenta chain), showing closely aligned residues. The four Mn atoms of the OEC and two Mn atoms of manganese catalase are at the center of the diagram (OEC calcium atom in purple). The PSII structure shown is from Loll et al. [27], with the Mn coordinates updated from Yano et al. [28] (model II).

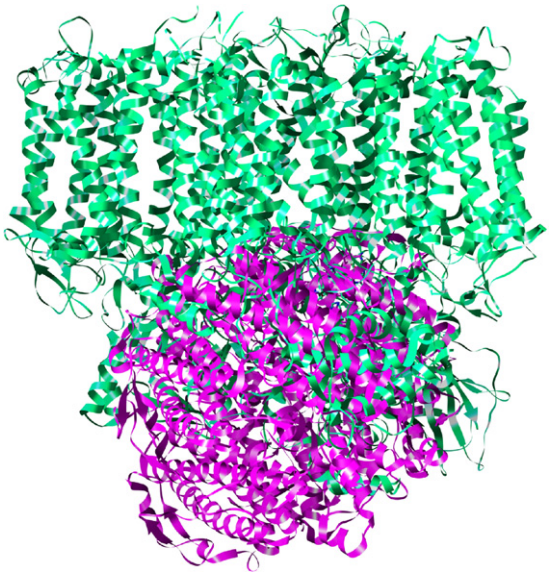

Fig. 4. Structural alignment resulting from applying the optimal superposition rotation/translation operators to the entire protein complexes of photosystem II (green, using the Loll et al. [27] structure) and Mn manganese catalase (magenta). Mn catalase sits in the same periplasmic position as the three PSII OEC stabilizing subunits.

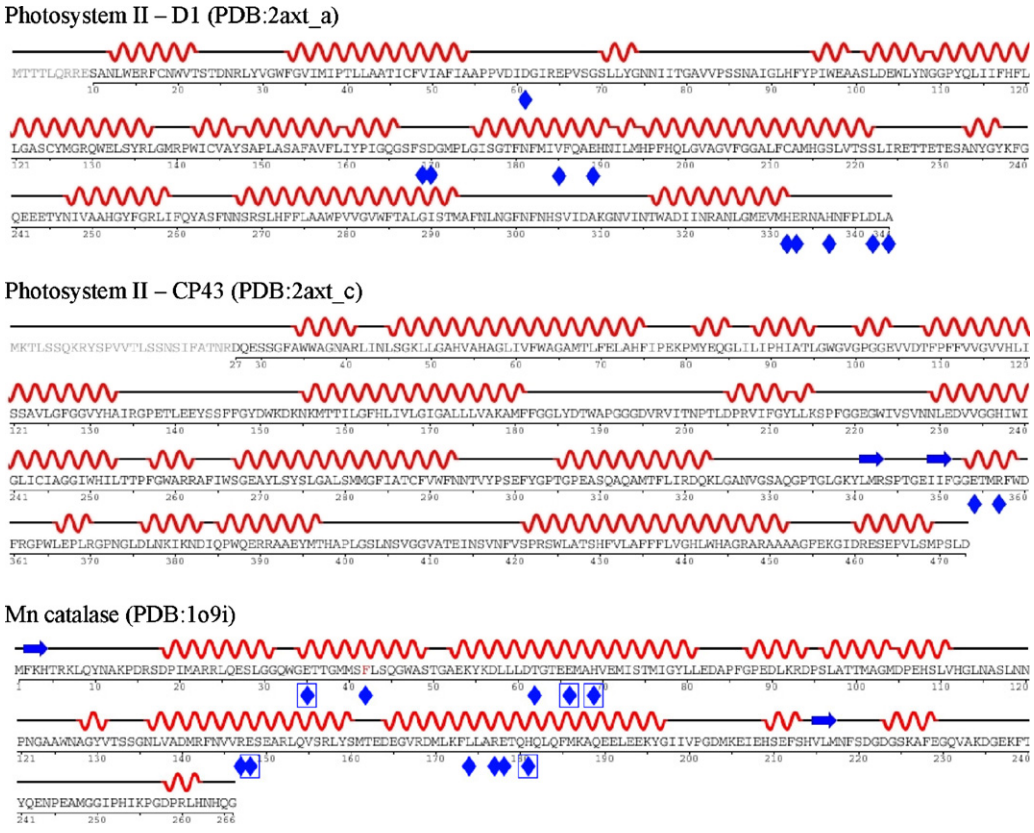

Fig. 3. Primary and secondary structures of the protein subunits surrounding the manganese catalytic core of photosystem II and Mn catalase. Only subunits with residues within 5 Å of the Mn cluster are shown, with the amino acids included in the structural superposition denoted by blue diamonds. Direct ligands to the Mn cluster of Mn catalase, as determined from high resolution crystal structures, are indicated by boxes around diamonds. The Mn ligands in the OEC have yet to be resolved to make such assignments unambiguously.

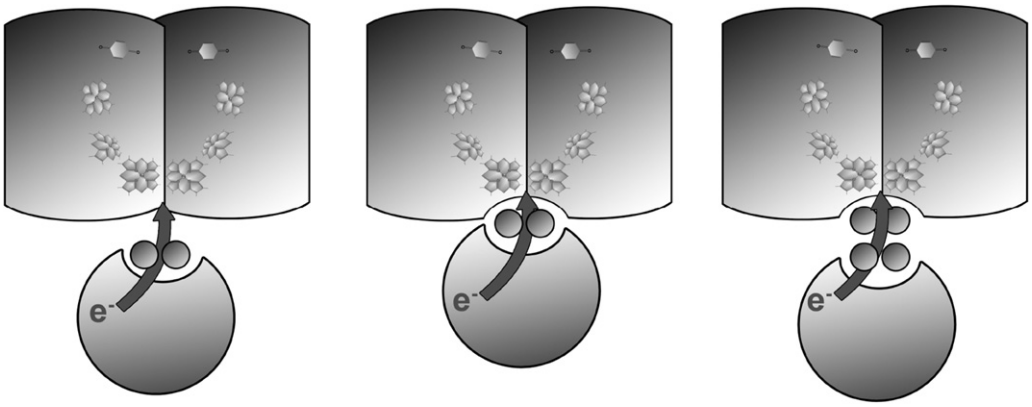

Fig. 5. Schematic showing how a primitive Mn binuclear enzyme, such as Mn catalase, might have served as a template for the development of the OEC tetramanganese cluster. At left, the Mn binuclear enzyme donates electrons to the primitive OEC. Because electron transfer efficiency is strongly influenced by distance, amino acid residues facilitating the tight interaction of the OEC and the soluble Mn binuclear enzyme would have been selected for, as depicted in the center panel. Ultimately, this would have resulted in a separate Mn binuclear site on the OEC (right panel) with its geometry inverted relative to the e-donor protein, as observed in the Mn catalase:OEC superposition. Continued interaction with the Mn binuclear enzyme would then juxtapose four manganese atoms—the earliest appearance of the tetramanganese OEC.

pendently determined protein structures looking more similar to the OEC.

These observations support a common structural core in the OEC and in distinct manganese binuclear enzymes. This might possibly have arisen independently through convergent evolution to an optimal catalytic geometry, as has been suggested for bacterial versus eukaryotic serine protease enzymes [41]. For example, the coordination chemistry of high-valence manganese may strongly constrain the charge and spacing of surrounding ligands. Further studies of how Mn valency constrains or determines local geometry in available manganoenzyme structures will ultimately be necessary to resolve this. However, we suggest here that the structural similarities observed are more logically the result of an intertwined evolutionary history of the OEC and Mn binuclear enzymes.

Best fit superposition places the Mn catalase edge-to-edge with the OEC (Fig. 4), overlapping the position of the extrinsic photosystem proteins that form a stabilizing "cap" over the tetramanganese complex. Notably, this means that the Mn site in catalase is inverted (relative to the protein center of mass) as compared to PSII, consistent with the idea of a periplasmic protein that could donate electrons to a primitive photosystem (see Fig. 5). In an ancestral complex, such an edge-to-edge interaction would have facilitated rapid electron transfer to the photo-oxidized photosystem, supporting the idea that a manganese binuclear enzyme, possibly oxidizing hydrogen peroxide, may have served as an electron donor to photosystem II.

3. Templating a binuclear active site

If a manganese binuclear enzyme was indeed the predecessor to the OEC, how did the unique four-manganese structure and water oxidation chemistry develop? One possibility – illustrated in Fig. 5 – is that the manganese binuclear cluster progressively became more closely associated with photosystem II, by mutations that facilitated binding and eventually direct ligation to the Mn atoms – in effect, the active site of one enzyme served as a template for the evolution of a second, closely interacting enzyme. This Mn specificity, carried on the D1 subunit, ultimately resulted in a de facto, "copycat" binuclear Mn binding site on PSII. Though this would have freed PSII from dependence on a soluble Mn enzyme, continued interaction between the two complexes would result in the juxtaposition of four Mn atoms – the first functional Mn_4 complex. Not only does this provide the structural underpinnings for the modern OEC, but also minimally doubles the charge-carrying capacity of the cluster, depending on the oxidation state of the Mn atoms.

What sort of chemistry was taking place as this early photocatalyst developed? Assuming that the evolution of the highly oxidizing PSII occurred fairly quickly (i.e. few evolutionary steps), the issue of energetic intermediates en route to H_2O subsides, and recenters on (a) how this newfound (but potentially dangerous) oxidizing potential could be safely used or dissipated and (b) what feasible/available chemical reactions could take advantage of this energy. The binuclear-manganese site suggests concerted two-electron reactions were feasible, making H_2O_2 a plausible electron donor in environments where it was not limiting.

This envisioned peroxidase/peroxide oxidation reaction would generate two electrons and two protons from a single peroxide substrate. This is distinct from the reaction catalyzed by the modern Mn catalase, which catalyzes the disproportionation of two H_2O_2 molecules into water and oxygen, without generating free electrons or protons. So, whereas the modern catalase functions as a H_2O_2:H_2O_2 oxidoreductase – one molecule of peroxide oxidizing the second – in the primitive unimolecular version, the oxidized photosystem takes the place of the second molecule of H_2O_2. This ancient enzyme would have thereby functioned as a H_2O_2:photosystem oxidoreductase, using photon energy to drive a transmembrane charge separation, defusal of a potentially damaging compound, and generation of energetic electrons for synthesizing biomass.

Could water have been used as an electron donor during a more primitive stage of OEC development? This is something of the inverse of the peroxide hypothesis discussed above, which might be called "oxygen first" as the ancestral OEC would have been generating oxygen before evolving the capability to oxidize water. An ancestral OEC that oxidized water only part-way – presumably to hydrogen peroxide – is attractive from a mechanistic perspective. The net reaction requires two H_2O molecules, exactly analogous to the modern OEC, and would be a two-electron transfer reaction, a viable transitional step en route to the four-electron transfer capacity. However, such a reaction would require a photooxidant of at least 1.35 V (the standard potential for H_2O oxidation to H_2O_2 at pH 7), greater than the ~1.1 V that the modern OEC can generate and presumably well beyond what the proto-OEC was capable of. The major energetic barriers to water oxidation come in the initial step(s) of electron abstraction, so working "backwards" from the molecular oxygen product (which is not difficult to produce) and hydrogen peroxide substrate, ultimately to water as a substrate, follows a path of least energetic resistance.

4. Summary

The past three decades have brought exciting and occasionally stunning advances in our understanding of the function, diversity, and evolution of photosynthesis in Nature. Research is closing in on solving the structure of the oxygen-evolving complex of photosystem II, undoubtedly one of the most remarkable inventions in all of biology. Though the origin of this complex, and its ultimate green capability to oxidize water, remains enigmatic, a number of intriguing hypotheses have been advanced and new methods developed, many of which have stimulated ideas in other fields. Here we have discussed possible origins of the OEC and developed a new method revealing evidence for an ancient superfamily of manganese proteins from which the OEC was born. Our hope is that, by understanding its natural history, we can gain a toehold on how this unique chemical capability came about and possibly can be advanced as a clean and ubiquitous source of energy.

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