

Cite this: *Dalton Trans.*, 2011, **40**, 9076

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PERSPECTIVE

## Oxygen evolving complex in Photosystem II: Better than excellent

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Received 23rd April 2011, Accepted 27th May 2011

DOI: 10.1039/c1dt10746a

The Oxygen Evolving Complex in photosystem II, which is responsible for the oxidation of water to oxygen in plants, algae and cyanobacteria, contains a cluster of one calcium and four manganese atoms. This cluster serves as a model for the splitting of water by energy obtained from sunlight. The recent published data on the mechanism and the structure of photosystem II provide a detailed architecture of the oxygen-evolving complex and the surrounding amino acids. Biomimetically, we expect to learn some strategies from this natural system to synthesize an efficient catalyst for water oxidation, that is necessary for artificial photosynthesis.

### 1. Introduction

The generation of hydrogen from the decomposition of water may be an appealing solution for the future energy concerns associated with diminishing reserves of fossil fuels and global warming scenarios, as discussed by Bockris.<sup>1</sup> A plausible strategy is to employ solar energy to drive *artificial photosynthesis* as a means to capture light energy and generate solar fuels (most commonly H<sub>2</sub>)

*via* electrolytic reactions.<sup>1-3</sup> A detailed analysis of the prospects for generating hydrogen as a renewable fuel from electrolysis of water is available.<sup>1</sup> The anodic reaction is overwhelmingly rate-limiting, resulting in substantial electrode over-voltage (~1 V) when working at current densities required for practical operations; this impacts directly on the conversion efficiencies.

At this high voltage, other chemicals will be formed at the anode and this would be environmentally unacceptable for large-scale H<sub>2</sub> production.<sup>1</sup> Thus, a significant challenge in this endeavor, a prerequisite for a sustainable hydrogen economy, is to design a "super catalyst" for anodic oxidation reaction.<sup>1-3</sup> Water oxidation in Nature is catalyzed by a Mn<sub>4</sub>O<sub>5</sub>Ca complex housed in a protein environment in photosystem II (PSII) that controls reaction coordinates, proton movement and water access.<sup>4-7</sup> (see the latest

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**Mohammad Mahdi Najafpour**

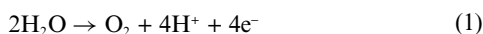
Mohammad Mahdi Najafpour received his PhD in Inorganic Chemistry from Sharif University of Technology, Tehran, Iran, in 2009. He has been a guest scientist in Dr Philipp Kurz's group in the Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel in Germany for six months. Mahdi is a recipient of several awards and fellowships, notably the gold medal of the National Chemistry Olympiad in 2004; he ranked 1st in the Khwarizmi Youth Festival in 2010. Currently, he is a faculty member in Chemistry in the Institute for Advanced Studies in Basic Sciences (IASBS) (Zanjan, Iran). Mahdi and his research group explore manganese compounds as water oxidizing catalysts for artificial photosynthesis.



**Govindjee**

Govindjee was born in Allahabad, India. He received his PhD in 1960 from the University of Illinois, Urbana-Champaign (UIUC), USA, under Prof. Eugene Rabinowitch. He served for 40 years on the faculty in Biophysics, Biochemistry and Plant Biology at the UIUC; currently, he is Prof. Emeritus there. He has studied the primary events of oxygenic photosynthesis, particularly in Photosystem II (PSII), the system that oxidizes water and reduces plastoquinone. He has provided clear understanding of light emission (fluorescence; thermoluminescence) in terms of PSII reactions, and of the unique role of bicarbonate in the electron transport and protonation in PSII. Govindjee is the founding series editor of 'Advances in Photosynthesis and Respiration' (Springer).

1.9 Å resolution structure by Umena *et al.*<sup>7</sup>). PSII is a dimeric, multi-subunit, transmembrane protein complex of ~ 650 kDa molecular weight, found in the thylakoid membranes of plant and algal chloroplasts and in cyanobacteria. The Mn<sub>4</sub>O<sub>5</sub>Ca complex<sup>7</sup> catalyzes water oxidation, and is, thus, responsible for the presence of oxygen in the Earth's atmosphere pool.<sup>8–14</sup> The primary role of PSII in photosynthesis is to use energy obtained from the sunlight to produce charge separation, leading to the reduction of plastoquinone to plastoquinol and the oxidation of water to molecular oxygen.<sup>15–20</sup> This reducing power, augmented by additional photonic energy, absorbed in PSI, produces the reducing power in the form of NADPH. The NADPH and the ATP are used to assimilate carbon dioxide in the “dark reactions” (the Calvin–Benson cycle) of photosynthesis.<sup>21,22</sup> The ultimate source of these low-potential electrons is water, which is oxidized to dioxygen in the oxygen evolving complex (OEC, also called WOC for water oxidizing complex) of PSII according to the four-electron reaction, of course, with energy input coming ultimately from light. The reaction is summarized in eqn (1):



Plants, algae and cyanobacteria use an extensive array of photopigments in PSII, four manganese ions, one calcium ion, and two chloride ions to carry out these reactions. PSII has the unique Mn cluster to oxidize water to molecular oxygen; no other metal has been found to replace manganese in this structure although calcium can be substituted by strontium.<sup>5,23</sup>

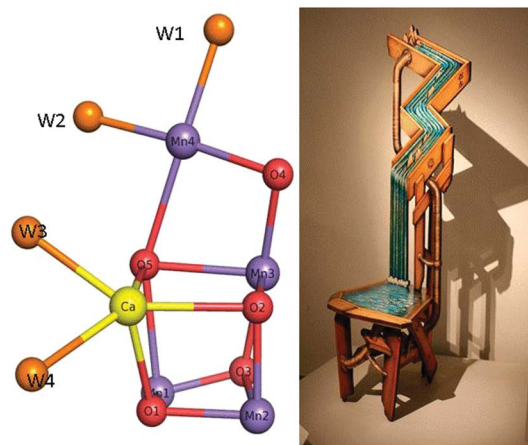
## 2. Structure of manganese–calcium cluster in PSII

EXAFS (Extended X-ray absorption fine structure) experiments with PSII can be done with a substantially lower X-ray dose than used in XRD (X-ray diffraction) measurements;<sup>6</sup> further, the onset of radiation damage can be precisely determined and controlled by monitoring the Mn K-edge position, thus allowing the collection of data from the intact Mn<sub>4</sub>Ca cluster of PSII.<sup>6</sup> In addition, EXAFS provides metal-to-metal and metal-to-ligand distances with high accuracy (~0.02 Å) and a resolution of ~0.1 Å. Mn EXAFS studies of frozen solutions of PSII preparations have provided accurate distances and numbers of Mn–Mn, Mn–Ca and Mn–Ca ligand vectors in the Mn<sub>4</sub>Ca cluster<sup>6</sup> and have led to the development of several probable structural models for the Mn<sub>4</sub>Ca cluster. Thus, EXAFS provides us with important additional geometric information about the metal site in metalloprotein crystals. Yano *et al.*<sup>6</sup> showed that polarized EXAFS can be used to provide structural models of the Mn<sub>4</sub>Ca active site.

The Mn–Mn inter-metal distances within the cluster are not adequately resolved in the XRD data, and have been set, yielding a symmetrical trigonal prism of CaMn<sub>3</sub>.<sup>6</sup> Yano *et al.*<sup>6</sup> postulated four bridging oxides linking the tetrahedral array of Mn<sub>3</sub>Ca atoms, with one of these oxides (μ<sub>4</sub>-oxo) bridging to the fourth Mn atom external to the cube.<sup>6</sup> However, these investigations do not provide details of the structure of the Mn<sub>4</sub>Ca cluster, the locations of substrate water molecules, or the precise arrangement of the amino-acid side chains and cofactors that may have significant mechanistic consequences in water oxidation.

In 2011, Umena *et al.*<sup>7</sup> reported the crystal structure of manganese–calcium cluster of PSII at an atomic resolution using

a sliding-oscillation method to reduce the X-ray dose illuminated on a unit volume of the crystal.<sup>7</sup> In this structure, one calcium and four manganese ions are bridged by five oxygens (Fig. 1). Four water molecules were also found in this structure; and two of them may serve as the substrate for water oxidation.<sup>7</sup> The whole structure of the Mn<sub>4</sub>CaO<sub>5</sub> cluster resembles a *distorted chair*, with the asymmetric cubane serving as the seat base and the isolated Mn4 and O4 atoms serving as the back of the chair<sup>1</sup> (Fig. 1).<sup>7</sup>



**Fig. 1** Oxygen Evolving Complex (OEC) with the asymmetric cubane serving as the seat base and the isolated Mn4 and one O bridged serving as the back of the chair.<sup>7</sup> The distorted chair on the right is reproduced from: <http://www.flickr.com/photos/32869691@N05/3173474438/>.

The structural models from structure refinement of computational models based on EXAFS simulations by Brudvig's group<sup>24</sup> and Siegbahn's group<sup>25</sup> are also close to the structure found in the 1.9 Å crystal structure of Umena *et al.*<sup>7</sup>

## 3. Evolutionary origin of the Mn<sub>4</sub>Ca cluster in PSII

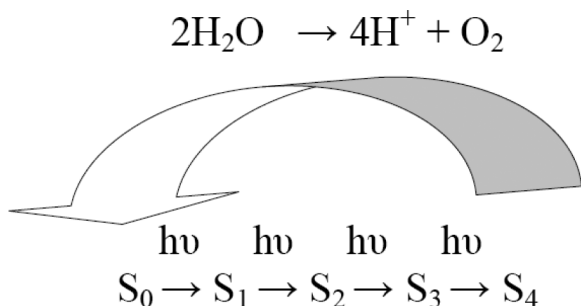
It is known that the Oxygen Evolving Complex (OEC) assembles in a stepwise manner by manganese binding and oxidation reactions.<sup>5</sup> However, the origin of the OEC is an enigma. There are several hypotheses for the origin of the OEC. One involves binuclear-manganese active sites, including ribonucleotide reductase, catalase and arginase.<sup>9,26</sup> It has been argued that H<sub>2</sub>O<sub>2</sub> could have been a key intermediate *en route* to oxygenic photosynthesis.<sup>9,26</sup> Blankenship and Hartman<sup>26</sup> proposed that a primitive Mn catalase was the original template upon which the modern OEC was structured. Raymond and Blankenship<sup>27</sup> developed an approach for determining the optimal superposition of the atoms concentrated around the active sites of PSII and binuclear-manganese proteins. These observations support a common structural core in the OEC and in distinct manganese binuclear enzymes. Mono-nuclear manganese enzymes have also been proposed for the origin of the OEC.<sup>18</sup>

Russell and Hall<sup>11</sup> speculated on how such a mineral-derived cluster may have provided the basis for the chemistry of the photosynthetic water oxidation reactions. However, Sauer and Yachandra<sup>28</sup> proposed a possible evolutionary origin for the Mn<sub>4</sub> cluster of the photosynthetic water oxidation complex from

natural  $\text{MnO}_2$  precipitates in the early oceans.<sup>28</sup> They compared the chemical structures of manganese in the minerals with what is known and the OEC to define the parameters of a structural model for the photosynthetic catalytic site by using X-ray spectroscopy.<sup>28</sup> On the other hand, Najafpour<sup>29</sup> proposed a new origin for OEC from manganese-oxidizing bacteria. The manganese-oxidizing bacteria are characterized by their ability to catalyze the oxidation of divalent, soluble  $\text{Mn(II)}$  to insoluble manganese oxides of the general formula  $\text{MnO}_x$ . Further oxidation of  $\text{MnO}_x$  by these bacteria million years ago could produce compounds that were efficient in water oxidation. Thus, those bacteria did not need large amounts of manganese to be oxidized since very few manganese ions are enough for a large amount of water oxidation. Thus, those bacteria could have changed from oxidizing just manganese to oxidizing water.<sup>29</sup> Water oxidation could have been an advantage for water-oxidizing bacteria because the amount of water on the Earth was huge and water-oxidizing bacteria could thus reproduce and survive more than other bacteria. These proposed water-oxidizing bacteria may, thus, have been the origin for cyanobacteria, algae and ultimately plants. It was reported that  $\text{MnO}_x$  could be a catalyst for water oxidation<sup>30</sup> and more interestingly one of us (M.M.N.) showed that incorporation of calcium in mixed-valence manganese oxides, that produced a structure similar to the OEC, greatly improved water oxidation activity of these manganese oxide.<sup>29</sup>

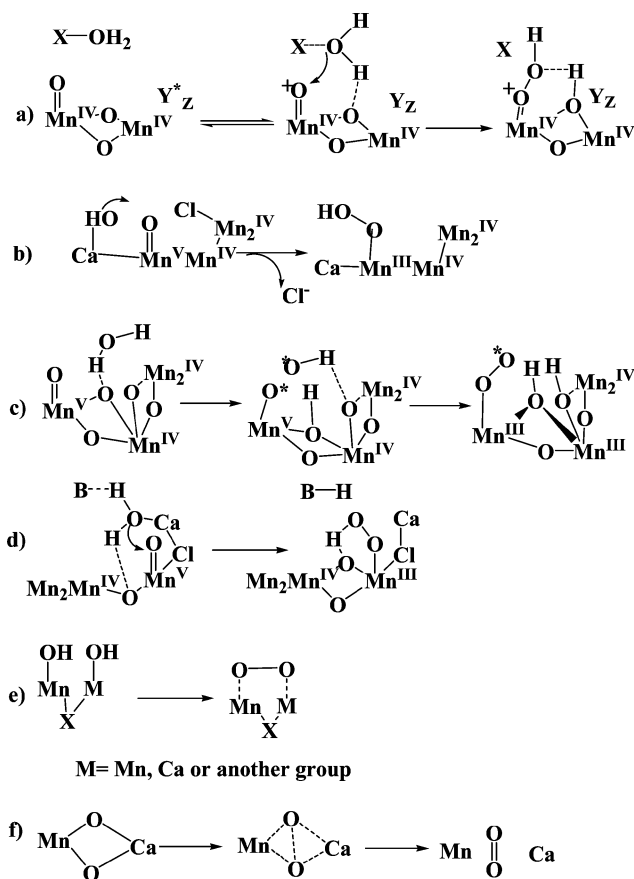
#### 4. Mechanism of oxygen evolution by the $\text{Mn}_4\text{Ca}$ cluster in PSII

One of the great unsolved mysteries in bioinorganic chemistry is the mechanism of water oxidation by the OEC of PSII. Pierre Joliot and Bessel Kok developed the basic principles for the function of the OEC, visualised in the Kok cycle<sup>31–33</sup> (Scheme 1; see Satoh *et al.*<sup>14</sup> for a general description). Oxygen evolution occurs through the “Kok cycle” of five “S-state” intermediates,  $S_0$  through  $S_4$ , where the subscript represents the number of oxidizing equivalents abstracted from the OEC by the photo-oxidized reaction center chlorophyll species (Scheme 1).



**Scheme 1** The Kok cycle (the catalytic cycle of the water oxidation).<sup>31–33</sup> In the  $S_0 \rightarrow S_1$ ,  $S_1 \rightarrow S_2$ ,  $S_2 \rightarrow S_3$ , and  $S_3 \rightarrow S_4$  transitions, light ( $h\nu$ ) is used to oxidize a special chlorophyll molecule, P680, which in turn oxidizes the OEC *via* a redox-active tyrosine, the  $S_4 \rightarrow S_0$  transition is light independent.

There are many proposals for the mechanism of oxygen evolution by the OEC in PSII (Scheme 2). Several models for the mechanism of oxygen evolution in PSII have been based on an asymmetric binding motif for the two-substrate water molecules,



**Scheme 2** Proposed mechanisms for oxygen evolution during the  $S_4 \rightarrow S_0$  transition. They are from **a)** Messinger *et al.*<sup>41</sup>; **b)** Pecoraro *et al.*<sup>36</sup>; **c)** Renger;<sup>42</sup> **d)** Najafpour;<sup>17</sup> **e)** Dau *et al.*<sup>43</sup> and **f)** Limburg *et al.*<sup>37</sup> The models **a–d** are based on nucleophilic attack, by the second water, and **e** and **f** are based on tautomerism on oxygen evolution reactions.<sup>42</sup> Considering the mechanism of manganese containing peroxidase,<sup>40</sup> Renger<sup>42</sup> concluded that a symmetrically bridged peroxide is probably prone to disruption of the O–O bond by reduction to water, whereas terminally ligated peroxide can be oxidized to molecular oxygen.

resulting in a strong electrophile at the  $S_4$ -state, which is subject to nucleophilic attack by the second substrate.<sup>34</sup> Knerl'man and co-workers<sup>35</sup> have suggested that the Mn-bound species are highly electron deficient (for example  $\text{Mn(v)=O}$ ). Further, Pecoraro and co-workers<sup>36</sup> have proposed that a terminal  $\text{Mn(v)=O}$  undergoes a nucleophilic attack by a  $\text{Ca}^{2+}$  bound hydroxide ligand to form a Mn-bound hydroperoxide. Brudvig and co-workers<sup>37</sup> have also proposed a mechanism in which a  $\text{Ca}^{2+}$  ion plays a role as a weak Lewis acid. In this mechanism, a water molecule bound to calcium reacts with a  $\text{Mn(v)=O}$  species to form the  $\text{O=O}$  bond through a nucleophilic attack.<sup>37</sup> Lee and Brudvig<sup>38</sup> provided direct support for the proposal that  $\text{Ca}^{2+}$  plays a structural role in the early S-state transitions which can be also fulfilled by other cations with similar ionic radius.<sup>38</sup> Further, the functional role of  $\text{Ca}^{2+}$  to activate water in the O–O bond-forming reaction, that occurs in the final step of the S-state cycle, can only be fulfilled by  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ , which have similar Lewis acidities.<sup>39</sup> This idea has been elaborated by Brudvig and co-workers<sup>24</sup> to generate a mechanism that accounts for the detailed oxygen evolution by PSII.<sup>24</sup>

## 5. Structural and functional models for the Mn<sub>4</sub>Ca cluster in PSII

In the past few years, there has been a tremendous surge in research on the synthesis of various manganese compounds aimed at simulating the OEC of PSII<sup>44–69</sup> but very few inorganic complexes have been claimed to be functional models for the OEC.<sup>59,71,72</sup> Recently, one of us (M. M. N.) has studied manganese–calcium oxides as both functional and structural models for the Mn<sub>4</sub>Ca cluster in PSII.<sup>29,46,50,71,72</sup>

## 6. Learning a few strategies used by Nature to oxidize water

In the next sections, we emphasize some of the strategies used by natural systems to oxidize water and hope that they will be incorporated in the artificial systems to synthesize an efficient water oxidizing compound.

### 6.1. Heterogeneity

An important aspect related to the OEC of PSII is its active site that is buried in the protein, and that prevents the interaction of two Mn<sub>4</sub>O<sub>3</sub>Ca clusters. The interaction of two complexes results in decomposition, decoordination or disproportionation.<sup>44,45,57–59</sup> The performance of the sequestered system increases the number of metal cycles manifest in the increased robustness of the catalyst.<sup>56</sup> For example, little oxygen evolution were observed upon mixing aqueous [(terpy)(H<sub>2</sub>O)Mn(O)<sub>2</sub>Mn(H<sub>2</sub>O)(terpy)](NO<sub>3</sub>)<sub>3</sub> with aqueous solutions of Ce(IV),<sup>58</sup> but it catalytically produced O<sub>2</sub> from water when it was adsorbed on clay compounds.<sup>56</sup> The assembly of model complexes into a crystalline, stable and nanoporous array also shows promise for biomimetic catalysis.<sup>70</sup> Thus, it seems better to use a system that has active-site sequestration built in it.

### 6.2. Tetranuclear manganese cluster

The OEC in PSII is a tetranuclear manganese cluster as stated in the previous sections (see Fig. 1). Multinuclear metal clusters used by Nature favor the occurrence of multi-electron and multi-stage complex processes. There are many mono-, di- and trinuclear manganese complexes as structural models for the OEC in PSII;<sup>55,60</sup> these simpler complexes are useful for the isolation of higher-valent complexes. Indeed, we have obtained much information about spectroscopic properties of higher valent manganese compounds.<sup>55,60</sup> However, it is suggested that tetra- and even polynuclear compounds, similar to metal oxides, which favor the occurrence of four-electron water oxidation, could be better functional models for the OEC in PSII.<sup>29,30</sup>

### 6.3. The pH value

The pH plays an important role in affecting and regulating the activity of PSII. The oxidation of water to molecular oxygen involves the transfer of four electrons and four protons. One of the factors which can reduce the potential required for water oxidation considerably is high pH or binding of the released protons by bases with  $pK > 7$ .<sup>55</sup> In addition to this, the effects of pH on the proton and electron transfer, at the redox-active groups, and its role in redox potential of the OEC are important.<sup>55</sup> The biological water

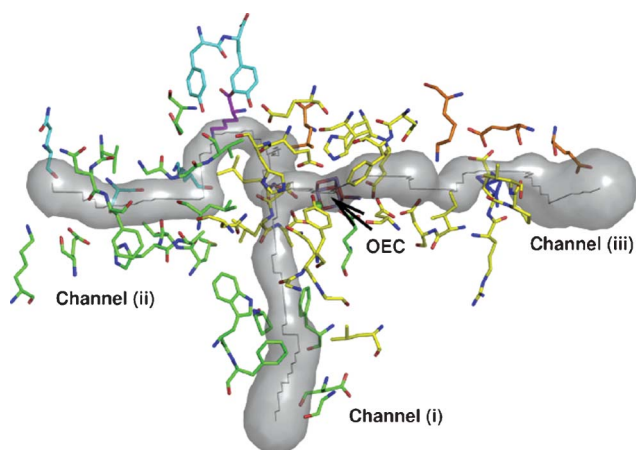
oxidation occurs at the pH of 5 in the lumen of thylakoids.<sup>5</sup> The pH used in many of the artificial water oxidation reaction mixtures may be the most likely cause of the lower yields.<sup>73</sup> High or low pH values result in decomposition, disproportionation, and ligand decoordination.<sup>73</sup> At low pH, the formation of high-valent Mn species is also not favored.<sup>57</sup> Thus, an *optimum* pH value must be sought for in all the artificial systems.

### 6.4. Proton and electron transfer

Oxidation–reduction reactions are involved in many biological reactions. In water oxidation, the OEC is oxidized *via* a redox-active tyrosine.<sup>14</sup> However, oxidation of the OEC without any proton loss leads to an increase in positive charge of the OEC; a high positive charge on the OEC can lead to a significant increase in redox potentials and unwanted reactions from a highly oxidized cluster. To avoid the production of high-energy intermediates, Nature has used proton-coupled electron transfer (PCET) mechanisms.<sup>74</sup> In PCET, either an electron transfer is followed by a proton transfer or a proton transfer is followed by an electron transfer. Both the electron and proton content between reactants and products is changed in PCET reactions.<sup>75</sup> PCET provides a molecular-level basis for energy transduction between proton transfer and electron transfer.<sup>75</sup> Wang *et al.*<sup>76</sup> have modeled proton coupled electron transfer in a mixed-valence oxomanganese complex [(bpy)<sub>2</sub>Mn<sup>III</sup>(μ-O)<sub>2</sub>Mn<sup>IV</sup>(bpy)<sub>2</sub>]<sup>3+</sup> (bpy = 2,2′-bipyridyl).<sup>76</sup> They found that the  $pK_a$ 's of the oxo ligands depend strongly on the oxidation states of the complex **1**, changing by approximately 10 pH units upon the reduction of Mn<sub>2</sub><sup>III,IV</sup> to Mn<sub>2</sub><sup>III,III</sup> in complex **1**. These computational results suggest that the reduction of Mn<sub>2</sub><sup>III,IV</sup> to Mn<sub>2</sub><sup>III,III</sup> in complex **1** is coupled to protonation of a di-μ-oxo bridge. The details of how electrons and protons are transferred in oxidation–reduction reactions are very important in selecting good strategies to synthesize a good catalyst that could oxidize water with low energy input in artificial photosynthesis.

### 6.5. Channels

There are three channels that lead from the OEC to the luminal side of PSII for oxygen, water and protons (Fig. 2).<sup>77,78</sup> There are, as yet, no synthetic model complexes with groups that control proton, water and oxygen movements. Styring and co-workers<sup>79</sup> have discussed the importance and the possible existence of a gating mechanism for controlling substrate water access to the Mn<sub>4</sub>Ca cluster. All the proposed functional assignments of these channels have been based on electrostatic, structural and orientational grounds. Styring and co-workers<sup>79,80</sup> have proposed that O<sub>2</sub> should be removed quickly to avoid <sup>1</sup>O<sub>2</sub> formation through reactions with excited chlorophylls; this can be accomplished by having a large channel system with four exit pathways, and this would be more suited for O<sub>2</sub> removal. It appears that an effective mechanism coupled to structural changes in the Mn<sub>4</sub>Ca cluster, with the optimum positions of associated ligands, during the Kok's S-state cycle, for water to reach the Mn may operate in PSII.<sup>79,80</sup> Vassiliev and co-workers<sup>81</sup> have considered molecular dynamics simulations for the analysis and visualization of water flow in PSII.<sup>81</sup> Their investigation of water movement in PSII has introduced a novel perspective to the study of the supply of

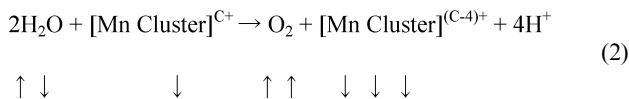


**Fig. 2** The figure shows channels for hydrophobic oxygen (i), water (ii) and protons (iii), all leading to the catalytic  $Mn_4Ca$  cluster of PSII. OEC stands for Oxygen Evolving Complex (reproduced from ref. 34).

water to the OEC, and has showed that the functional PSII is characterized by a branched water supply structure with multiple control points. Their investigations show that the loss of the OEC from PSII causes a transition to a simpler, straighter and wider channel with two permanent openings, that is well suited for the transport of ions required to rebuild the  $Mn_4Ca$  cluster.<sup>81</sup> Thus, it is necessary to do research on this aspect of the problem before the efficient artificial system can be built.

### 6.6. Spin balance

Many chemical reactions involve a change in spin state and are formally forbidden.<sup>24,82–84</sup> The spin-balance theory shows that spin-flipping processes, during chemical reactions, often have a high activation energy.<sup>82–84</sup> The OEC has an odd-electron state and using the strategy in the OEC, biological water oxidation involves no change in spin-state (the arrows show the spins of the electrons):



It has been reported that the overvoltage of the oxygen evolution reaction has been the largest source of energy loss in water electrolysis, and the major source of this overvoltage is the spin inversion required to produce triplet oxygen.<sup>82,84,85</sup> This theory must also be considered in synthesizing model complexes.

### 6.7. Outer bonds

We know that the primary coordination sphere impacts on many properties of metalloproteins, including electronic structure, Lewis acidity, stabilization of metal complexes, and coordination geometry.<sup>86</sup> The secondary coordination sphere around the metal ion in proteins is also important and is strongly correlated with function.<sup>86–90</sup> The outer hydrogen bonds are very important in water oxidation in PSII and they could decrease the activation energy for water oxidation (for example, leading to a weakening of the  $M-OH$  bond<sup>17</sup>). One factor that can considerably reduce the potential required for water oxidation is binding of the released protons by hydrogen bonds.<sup>17,89,90</sup> Hydrogen bonds are the most common type of secondary coordination sphere used

by biomolecules. Urea-based ligands have been developed that create rigid organic frameworks to form a secondary coordination sphere in model complexes.<sup>86,87</sup> Zong and Thummel<sup>88</sup> have synthesized a very interesting family of ruthenium complexes that are robust catalysts as compared to others previously reported. In these complexes, the water molecule could be H-bonded to an uncomplexed naphthyridine-nitrogen ligand.<sup>88</sup>

### 6.8. Oxidant

The OEC is linked to the reaction center II chlorophyll ( $P_{680}$ ) via a redox-active tyrosine residue on the D1 subunit, labeled as  $Y_Z$ .<sup>91</sup> The  $Y_Z$  subunit is close enough to the OEC to be intimately involved in the chemical catalysis of water oxidation, rather than simply acting as the immediate oxidant of the OEC.<sup>16</sup> The  $Y_Z/Y_Z$  potential is around 1.0 V.<sup>10,16</sup> However, many of the oxidants used in water oxidation reactions (for example: ceric ammonium nitrate (1.4 V vs. NHE) or Oxone<sup>TM</sup> (1.7 V vs. NHE (normal hydrogen electrode) are more powerful than PSII.<sup>16</sup> The oxidants result in decomposition of catalysts in many reactions. Najafpour *et al.*<sup>52</sup> have found that  $Ce(IV)$  may act not only as a simple oxidant, but may simultaneously be coordinated.<sup>52</sup> This issue should be considered in water oxidation experiments that use  $Ce(IV)$  as an oxidant.<sup>52</sup>

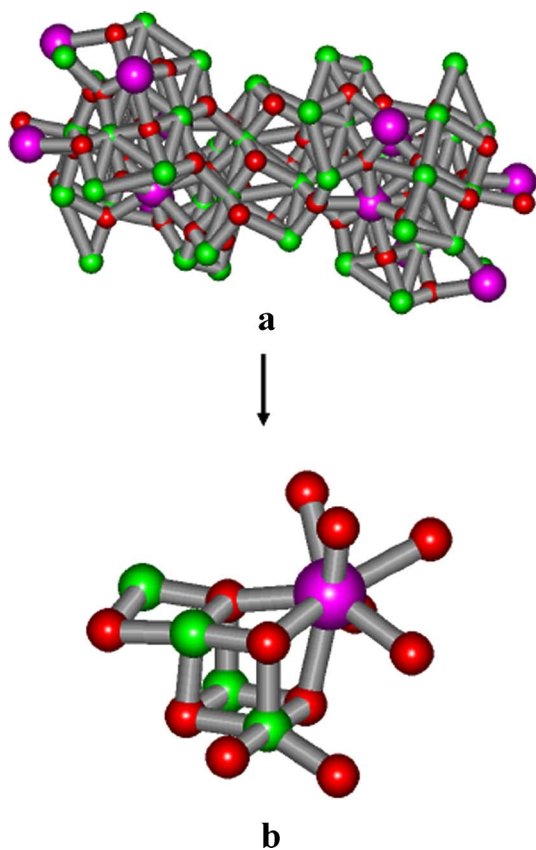
### 6.9. Role of calcium and chloride

There have been many proposals for the mechanism of oxygen evolution by the OEC in PSII.<sup>17,91–93</sup> Available data support two proposals for the function of  $Ca^{2+}$  in the mechanism of oxygen evolution by the OEC.<sup>94,95</sup> A number of experiments demonstrate a requirement for  $Ca^{2+}$  for the functional assembly and stability of the OEC. Another proposed role for  $Ca^{2+}$  is a structural one. Limburg *et al.*<sup>36</sup> and Pecoraro *et al.*<sup>37</sup> have postulated a specific role for calcium in ligating one of the substrate waters. Brudvig's group<sup>96</sup> has reported the first experimental evidence for a direct role of calcium in the mechanism as a Lewis acid. This ligated water or hydroxide forms the  $O-O$  bond of  $O_2$  by attacking the oxygen of a terminal  $Mn(V)=O$  species in the  $S_4$  state. Understanding the role of calcium is important in synthesizing a catalyst for water oxidation. Najafpour and co-workers<sup>29,46,49,50,71,72</sup> have discovered that – in analogy to the OEC – incorporation of calcium in the manganese oxide system greatly improves water oxidation activity of the manganese oxides. The rate of oxygen evolution of these oxides depends on calcium in these manganese oxides (manganese calcium oxide > manganese oxide) and oxidation number of manganese ions in manganese oxides. The rate of oxygen evolution by  $Mn(III)$  oxides is higher than the rate of oxygen evolution by  $Mn(IV)$  oxides. Najafpour<sup>50</sup> has studied two mixed-valence manganese calcium oxides (manganese (III, IV) calcium oxides) with the aim of investigating the oxide systems that are very closely related to the elemental composition and oxidation number of manganese ions in the  $Mn_4O_5Ca$  core of the OEC in PSII.<sup>50</sup>

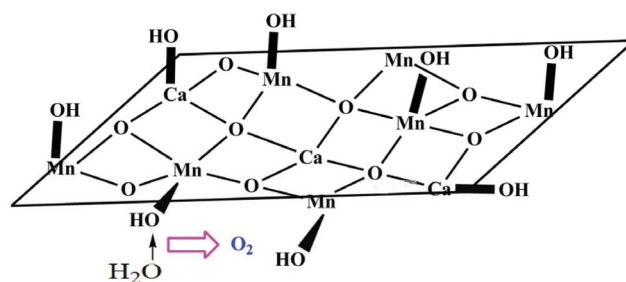
The most active calcium–manganese oxides in oxygen evolution reactions are amorphous powders<sup>29,46,49,50,72</sup> and a structure could therefore not be identified by XRD method. However, the structure of these amorphous powders have now<sup>72</sup> been evaluated, using extended-range X-ray absorption spectroscopy (XAS),

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). These results reveal similarities between the amorphous powders and the OEC in PSII. Two different Ca-containing motifs were identified in these amorphous manganese–calcium oxides. One of them results in the formation of  $\text{Mn}_3\text{CaO}_4$  cubes, as also proposed for the OEC in PSII.<sup>71</sup> Other calcium ions likely interconnect oxide-layer fragments. It was concluded that these readily synthesized manganese–calcium oxides are the closest structural and functional analogs to the native PSII catalyst found so far.<sup>71</sup>

The mechanism of oxygen evolution by  $\text{CaMn}_2\text{O}_4$ , using  $^{18}\text{O}$ -enriched water, has also been studied.<sup>72</sup> These results show that oxygen evolution in the presence of single-electron oxidants such as cerium(IV) is “real” water oxidation.<sup>72</sup> Further, these experiments do not show any clear indication for the involvement of surface oxido species in the oxygen evolution reaction from water.<sup>72</sup> Similar studies may help in the further understanding of the mechanism of oxygen evolution by the OEC in PSII because of related structure of these manganese–calcium oxides and the OEC in PSII.<sup>71,72</sup> A possible mechanism for water oxidation by these manganese calcium oxides is presented in Fig. 4. In these biomimetic water oxidizing catalysts, calcium ions most probably activate manganese oxide, perhaps, by changing structures of  $\text{MnO}_2$  and  $\text{Mn}_2\text{O}_3$  to another more active structures (tunnel or layer structures).



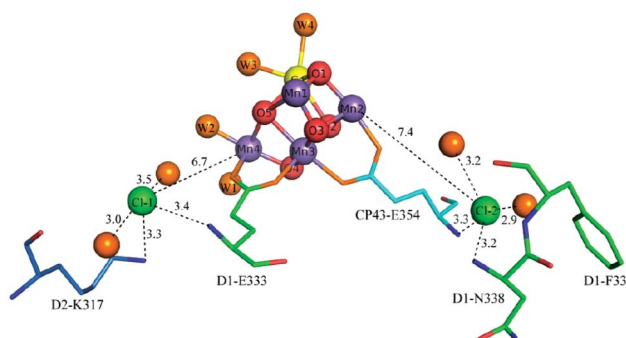
**Fig. 3** (Top; a) The structure of  $\text{CaMn}_3\text{O}_6$  as a biomimetic water oxidizing catalyst. (Bottom; b) The structure of  $\text{CaMn}_3\text{O}_6$  contains  $[\text{Mn}_4\text{CaO}_5]$  sub-units similar to that found in the OEC in PSII<sup>50</sup> (oxygen: red; manganese: green; calcium: violet) (reproduced from ref. 29).



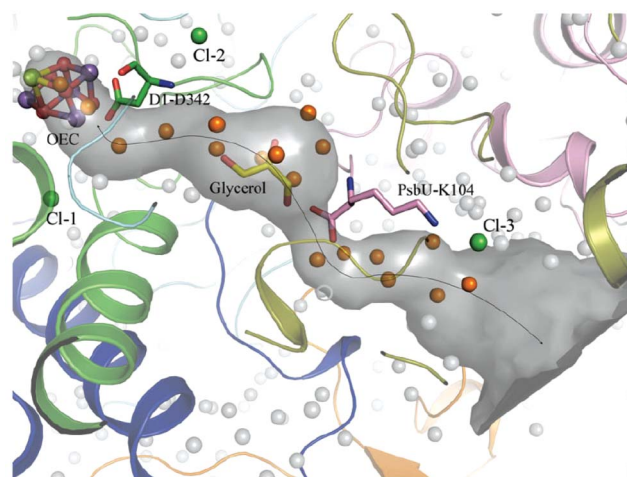
**Fig. 4** A proposed mechanism for water oxidation by calcium–manganese oxides. Before water oxidation, manganese ions in the oxide should be oxidized by the oxidants.

Another ion that should be considered to form a good water oxidizing catalyst is chloride. It has been known that  $\text{Cl}^-$  is an essential ion for maximal oxygen evolving activity in PSII.<sup>95</sup> A variety of proposals have been advanced to explain the  $\text{Cl}^-$  requirement for OEC: redox activity as a bridging ligand between Mn atoms, to regulate the redox properties of the Mn cluster, electron or proton transfer, a bridging ligand between  $\text{Ca}^{2+}$  and one of the Mn ions involved in  $\text{H}_2\text{O}$  oxidation or as a ion ligated solely to  $\text{Ca}^{2+}$ .<sup>95</sup> In the crystal structure of the manganese–calcium cluster of PSII at atomic resolution, two  $\text{Cl}^-$  binding sites are clearly visible in the electron density map.<sup>7</sup> These results show that there are no  $\text{Cl}^-$  ions in the first coordination sphere of the  $\text{Mn}_4\text{CaO}_5$  cluster.<sup>7</sup> There are four groups surrounding each of the two  $\text{Cl}^-$  binding sites, two water molecules and two amino acid residues.<sup>7</sup> In the published atomic structure, two amino acids not only have an interaction with  $\text{Cl}^-$  ions (with their backbone nitrogen) but are also coordinated to the  $\text{Mn}_4\text{CaO}_5$ . Kawakami *et al.* have proposed that release of these  $\text{Cl}^-$  ions may affect the stable coordination of these two residues to the  $\text{Mn}_4\text{CaO}_5$ -cluster, resulting in an inactivation of oxygen evolution.<sup>7</sup> Kawakami *et al.* have further suggested that the two  $\text{Cl}^-$  ions may also function in maintaining the proton exit pathways as these are located at the entrance of two possible proton exit paths.<sup>7</sup>

There is also an additional  $\text{Cl}^-$  ion found in the high-resolution structure that is at a distance of around 25 Å to the  $\text{Mn}_4\text{CaO}_5$  cluster.<sup>7</sup> This  $\text{Cl}^-$  ion is located at the exit of a hydrogen-bond network from the  $\text{Mn}_4\text{CaO}_5$ -cluster to the luminal surface (Fig. 6) and may serve as one of the anion supply pathways, or water inlet/proton exit pathways.<sup>7</sup>



**Fig. 5** Structure of the two  $\text{Cl}^-$  binding sites in the vicinity of the  $\text{Mn}_4\text{CaO}_5$  cluster (reproduced from ref. 7).



**Fig. 6** Detailed structure of the Cl binding sites showing a hydrogen-bond network connecting the Mn<sub>4</sub>CaO<sub>5</sub>-cluster and Cl-3 (reproduced from ref. 7).

### 6.10. Four-electron water oxidation

A four-electron water oxidation is certainly easier than four sequential one-electron oxidation or two sequential two-electron oxidation because in those cases the first steps (H<sub>2</sub>O to hydrogen peroxide and hydroxyl radical) are more endergonic than the four-electron water oxidation, and results in low over-voltage for practical operations.<sup>16</sup>

### 6.11. Regulating oxidizing power

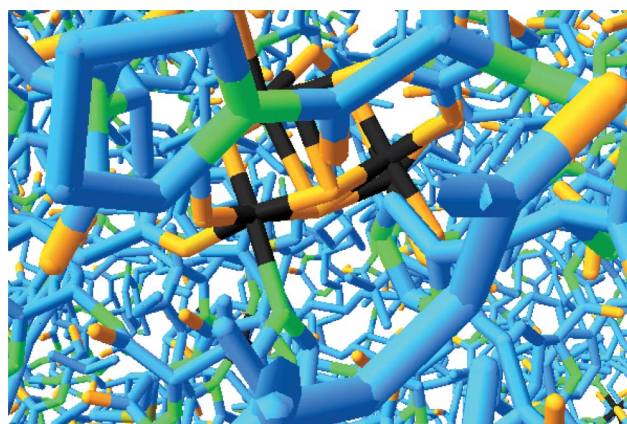
If the S<sub>2</sub> → S<sub>0</sub> (Scheme 1) two-electron couple (~0.8 V) has a higher potential than the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O couple (~1.5 V), there could be a risk of oxidizing water too soon in the S-state cycle, producing H<sub>2</sub>O<sub>2</sub>.<sup>16</sup> Regulating oxidizing power is important in oxidizing water with high yields; this point must be considered in constructing synthetic models.

### 6.12. Manganese

During the past few years, there has been a tremendous surge in research on the synthesis of various Mn complexes aimed at simulating the OEC.<sup>44,45,55–62</sup> Fe, Co, Ni, Ru and Ir-based catalysts also show promise for water oxidation.<sup>97–104</sup> Compared to manganese, they are rare, expensive and (or) relatively toxic. An important point is that the first-row transition metals have smaller d-orbitals compared to other metals and therefore have smaller crystal field activation energies for transitions between oxidation states during oxygen evolution reaction.<sup>85,105</sup>

### 6.13. Amino acids

Although PSII consists of hundreds of amino acids, there are only a small fraction of the residues that come in direct contact with the manganese–calcium cluster, and an even smaller fraction—three to four residues on the average—that are directly involved in catalysis (Fig. 7).<sup>7</sup> Many amino acids in PSII are involved in proton, water and oxygen transfer. Roles for the residues that come in contact directly with the manganese–calcium cluster include regulation of charges and electrochemistry of the Mn–Ca cluster, and help in coordinating water molecules at appropriate metal sites



**Fig. 7** Hundreds of amino acids are in PSII but few of them are directly coordinated to the manganese–calcium cluster (calcium and manganese ions are shown in black).

and maintaining the stability of the cluster. The PSII manganese stabilizing protein is a highly conserved extrinsic component of the OEC. Its deletion from the photosystem may cause a dramatic lowering of the rate of oxygen evolution.<sup>106</sup> The photosystem II manganese stabilizing protein has also been suggested to be important in linking the active site of OEC with the lumen and to be involved in a proton-transfer network.<sup>106</sup> A simple inorganic manganese–calcium core without coordinated amino acids shows much lower activity than the OEC in PSII.<sup>29,46,49,50,71,72</sup>

## 7. Concluding remarks

Finally, we would like to mention a different approach taken in the laboratory of Thomas Wydrzynski:<sup>53</sup> they introduced a reverse engineering approach to build a simple, light-driven photo-catalyst based on the organization and function of the donor side of the PSII reaction centre and a bacterioferretin molecule has been ‘coaxed’ using genetic engineering to include the chromophores for light absorption and Mn complexes for water oxidation; Wydrzynski’s research group has succeeded in observing oxidation of manganese in this engineered system.<sup>53</sup> Recently Nam *et al.*<sup>107</sup> have introduced a biologically based nanostructure for visible-light driven water oxidation that uses a genetically engineered virus scaffold to mediate the co-assembly of zinc porphyrins (photosensitizer) and iridium oxide clusters (water oxidizing catalyst). Their results suggest that the biotemplated nanoscale assembly of functional components is a promising route to improved photocatalytic water-splitting systems.<sup>107</sup>

## Acknowledgements

We are thankful to Professor Gary Brudvig of Yale University for his valuable suggestions for the improvement of this paper. M.M.N. is grateful to the Institute for Advanced Studies in Basic Sciences for support. We are thankful to Professor J. R. Shen for sharing the proofs of ref. 7a and b before they were printed. This paper was written through interactions, discussions and exchange of information between the two authors (M.M.N. and Gov) *via* e-mail only. Govindjee is thankful to Jeff Haas and his staff of the University of Illinois for help with internet facilities.

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