Journal of Photochemistry and Photobiology B: Biology 104 (2011) 111–117

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology B: Biology

journal homepage: www.elsevier.com/locate/jphotobiol

Short Review

# Calcium-manganese oxides as structural and functional models for active site in oxygen evolving complex in photosystem II: Lessons from simple models

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ARTICLE INFO

*Article history:*
Available online 21 December 2010

*Keywords:*
Calcium-manganese oxide
Oxygen evolving complex
Structural and functional models
Photosynthesis
Photosystem II

ABSTRACT

The oxygen evolving complex in photosystem II which induces the oxidation of water to dioxygen in plants, algae and certain bacteria contains a cluster of one calcium and four manganese ions. It serves as a model to split water by sunlight. Reports on the mechanism and structure of photosystem II provide a more detailed architecture of the oxygen evolving complex and the surrounding amino acids. One challenge in this field is the development of artificial model compounds to study oxygen evolution reaction outside the complicated environment of the enzyme. Calcium-manganese oxides as structural and functional models for the active site of photosystem II are explained and reviewed in this paper. Because of related structures of these calcium-manganese oxides and the catalytic centers of active site of the oxygen evolving complex of photosystem II, the study may help to understand more about mechanism of oxygen evolution by the oxygen evolving complex of photosystem II.

**Contents**

## 1. Introduction

Manganese is an important transition metal, required for the growth and survival of many living organisms [1,2]. Interest in the chemistry of manganese complexes derives mainly from the fact that such species are involved in important electron transfer reactions in biological systems [1–3].

Photosystem II (PSII) created the aerobic atmosphere on earth and may serve as a model for technical approaches to split water by sunlight, which is a prerequisite for a sustainable hydrogen economy [4]. The enzyme is a dimeric, multi-subunit, transmembrane protein complex, of molecular weight ca. 650 kDa, that is found in the thylakoid membrane of plant chloroplasts and in cyanobacteria. It catalyzes photosynthetic water oxidation, and is, therefore, responsible for the presence of oxygen in the earth's atmosphere [5]. The oxygen evolving complex (OEC) in PSII of green plants contains of a $Mn_4Ca$ cluster (Fig. 1) [3]. There are several properties of manganese that suits it for its role in the OEC in PSII from its elemental abundance to redox properties [6].

In the past few years, a major effort has been devoted to the synthesis of various manganese compounds aimed at simulating the OEC of PSII [7–22]. Only three Mn/Ca heterometallic complexes as structural models to mimic the structure of the active site of $Mn_4Ca$ cluster of PSII have been reported [14].

In spite of the many structural models of the OEC, there are a few functional models for the cluster [8]. Recently, we have studied some calcium-manganese oxides ($CaMnO_3$, $Ca_2Mn_3O_8$, $CaMn_4O_8$

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doi:10.1016/j.jphotobiol.2010.12.009

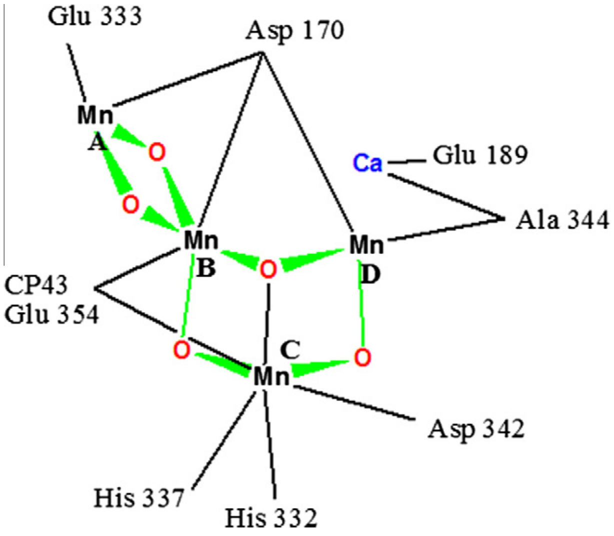

**Fig. 1.** Oxygen evolving complex and the surrounding amino acids [3].

[20], $CaMn_3O_6$ [20], $CaMn_2O_4$ [21,22]) as structural and functional models for the active site in the OEC in PSII. These calcium-manganese oxides as an active site of the OEC may be considered an advantage of synthetic analogues, for, being unencumbered by the amino acids of the protein [23]. These calcium-manganese oxides may also have important implications for the researchers in the field of biological water oxidation chemistry.

## 2. A possible evolutionary origin for the $Mn_4$ cluster in photosystem II

Photosynthesis changed the Earth's biosphere from at least 3500 million years ago [24,25]. However, it is an enigma that when oxygen producing photosynthetic cyanobacteria evolved from their anoxygenic photosynthetic bacterial precursors [24,25]. The OEC in PSII found in cyanobacteria and in the thylakoid membrane of plant chloroplasts share a conserved functional core and are believed to have evolved from a single common ancestor [24–28]. There are several hypothesises for the origin of the OEC. One hypothesis suggests that the OEC originated in the Mn catalase and it was argued that $H_2O_2$ could have been a key intermediate enroute to oxygenic photosynthesis [29,30]. Mono-nuclear manganese enzymes have also been proposed for the origin of the OEC [31]. It is also proposed that an iron binding site which had evolved earlier took on Mn ions in place of the Fe ions and formed the precursor to the OEC [28]. Another suggestion is that the protoenzyme was derived from a component of a natural early marine manganese precipitate that contained a $CaMn_4O_x$ cluster [32–35]. It is noted that the bond types and lengths of the manganese ions in the tunnel mineral hollandite ($Ba_{0.2}Ca_{0.15}K_{0.3}Mn_{6.9}Al_{0.2}Si_{0.3}O_{16}$) are directly comparable to those in the OEC and can be considered as a structural [32–35] and functional [22] model for the OEC and it is proposed that these minerals may be assimilated by early cyanobacteria during the Archaean period, approximately 3200–2800 million years ago to form the OEC [32,34,35]. In a new assessment of the OEC of PSII the Archaean ocean may have sufficient Mn and Ca ions that with alkaline conditions may have enabled proto-cyanobacteria to assemble oxide mineral as functional compliments of early active site of PSII [22]. The structure of these calcium-manganese oxides could be changed and modified by amino acids to form the OEC in PSII [32]. Interestingly, it is reported that peptides may have contributing to the formation of controlled nanoparticle assemblies [33]. Amino acids in PSII may also have similar effect in assembly of very small particles of calcium-manganese oxides resulted in the $CaMn_4$ cluster in PSII.

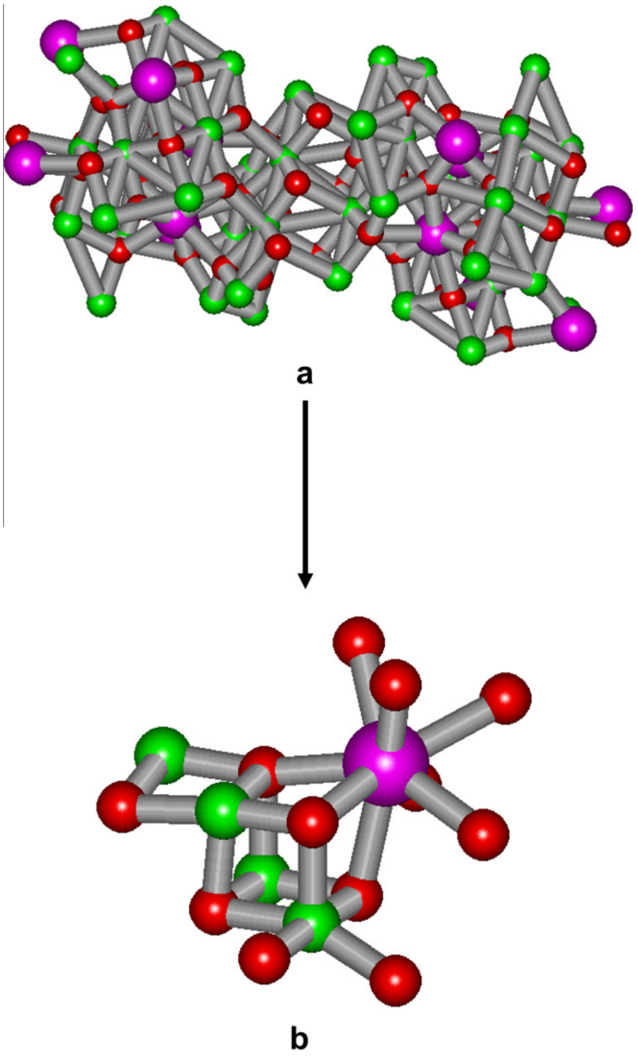

**Fig. 2.** The structure of $CaMn_3O_6$ (a) and the structure contains [$Mn_4CaO_x$] subunits similar to that found in the oxygen evolving complex in PSII (b).

The active site of the OEC could be also synthesized by hydrothermal reactions [36]. Hydrothermal reactions include the various techniques of synthesizing substances from high-temperature solutions at high vapour pressures and usually in chemistry and geological sciences used to synthesize materials from heterogeneous reactions in aqueous media above 100 °C and 1 bar [36]. Hydrothermal techniques have been widely used in the synthesis of metal oxides [21,36]. These techniques have also been studied for the mimicking of geothermal processes [32]. Manganese, calcium, short wavelength UV radiation (as oxidant) from a younger Sun, alkaline conditions and high-temperature under hydrothermal condition could produce such calcium-manganese precipitates in the early Earth [32]. Hydrothermal procedures could be used to synthesize calcium-manganese oxides with sub structures similar to structure of active site of the OEC (Fig. 2) [21,22].

## 3. Structural models for the $CaMn_4$ cluster in photosystem II

The determination of the structure of the $Mn_4Ca$ cluster is an important issue to understand the mechanism of water oxidation by the OEC in PSII. Both Mn EXAFS [3] and X-ray diffraction