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Analogies Between the Water Oxidation Complex in Photosystem (II) and Sulfite Reductase

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Abstract: In this study analogies between the water oxidation complex in photosystem (II) and Sulfite reductase are reported that are 1) Pool section helps in electron transfer to center section. 2) electron transfer occurs in several steps. 3) a O-X (S or O) is formed broken. 4)Pool sections are Cubic. 5) Center sections are mononuclear complexes. 6) proton transfers are important and 7) hydrogen bonds have important roles. These analogies between two enzymes may be help to know passive structures or mechanisms.

Key words: Analogies, mechanism, photosystem II, sulfite, sulfite reductase, water

Introduction

In 3.5 A° resolution XRD-deduced from Water Oxidation Complex in Photosystem (II) (Fig. 1), the authors (Ferreira *et al*., 2004) describe the electron density attributed to the Mn_4Ca cluster in its resting oxidation state as capped tetrahedral with four metal atoms in the large end and one in a connected small end.

A Ca atom is located in one of the corners of the tetrahedron based upon anomalous diffraction data taken at the Ca absorption edge. The presence of Ca at ~3.4 A° to Mn is supported also by compelling evidence from three types of EXAFS measurements obtained at the Mn, Ca and Sr edges (Ferreira *et al*., 2004). The Mn-Mn intermetal distances within the cube are not adequately resolved in the XRD data and have been set equal for simplicity, yielding a symmetrical trigonal prism of $CaMn_3$. The authors postulate four bridging oxides (not directly observable in their measurements) linking the tetrahedral array of $CaMn_3$ atoms, with one of these oxides (μ_4-oxo) bridging to the fourth Mn atom external to the cube. The resulting $CaMn_4O_4$ cluster can be classified also in terms of the two types of oxide bridges (μ_3-oxo)$_3$(μ_4-oxo) that make up the core.

The O = O bond formation (Najafpour, 2006a, b) is proposed to occur by a nucleophilic attack from a second-substrate water molecule ligated to Ca^{2+} (McEvoy James and Brudvig, 2004).

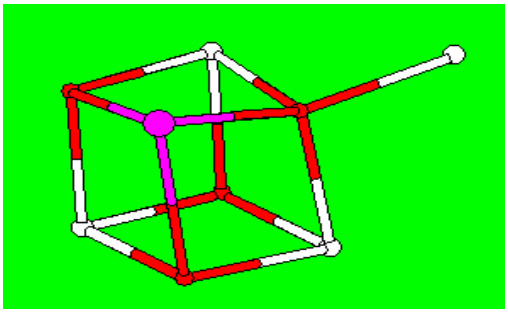

Fig. 1: XRD model of the Water-oxidizing Complex (WOC) oxygen (red), calcium (violet) and Manganese (white)

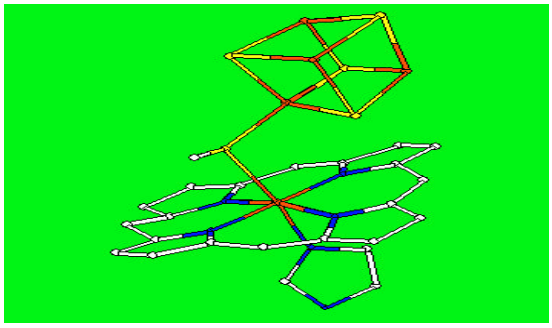

Fig. 2: XRD model of Sulfite reductase. Nitrogen (blue), iron (red), carbon (white) and sulfur (yellow)

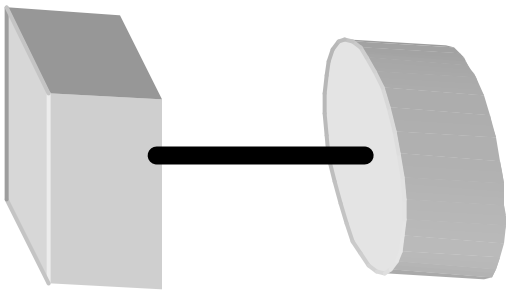

Fig. 3: Both enzymes can be divided to 3 sections. A) pool section, b) center section and c) intermediary section

Sulfite reductases are complex $\alpha_n\beta_m$ oligomers in which the α subunits are flavoproteins while the β subunits contain Fe/S clusters and a siroheme group with high-spin iron. A direct bridging of both types of iron centers (distance about 0.44 nm) via a μ-cysteinate sulfur center was inferred both from spectroscopic and preliminary structural studies (Fig. 2).

Results and Discussion

Both enzymes can be divided to 3 sections. Pool section, center section and intermediary section (Fig. 3).

Pool section helps in electron transfer to center section and center section is active site. Substrate is attached to center site. In water oxidation complex (Fig. 1):

$CaMn_3O_4$ (cubic) atoms are pool section, active site is Mn (4) (one in a connected. Small end) and intermediary section is μ-O atom. In sulfite reductase Iron/sulfur cluster (Cubic) is pool section, siroheme group with high-spin iron is center section and intermediary section is μ-cysteinate group. Possible mechanisms of Water oxidation and sulfite reduction are shown in Fig. 4. Although two enzymes catalyze the nearly opposite directions of the same chemical reaction, they share mechanistic similarities:

- Pool section helps in electron transfer to center section.
- In both systems electron transfer occurs in several steps.
- In both systems a O-X (S or O) is formed/broken.
- Pool sections are Cubic.

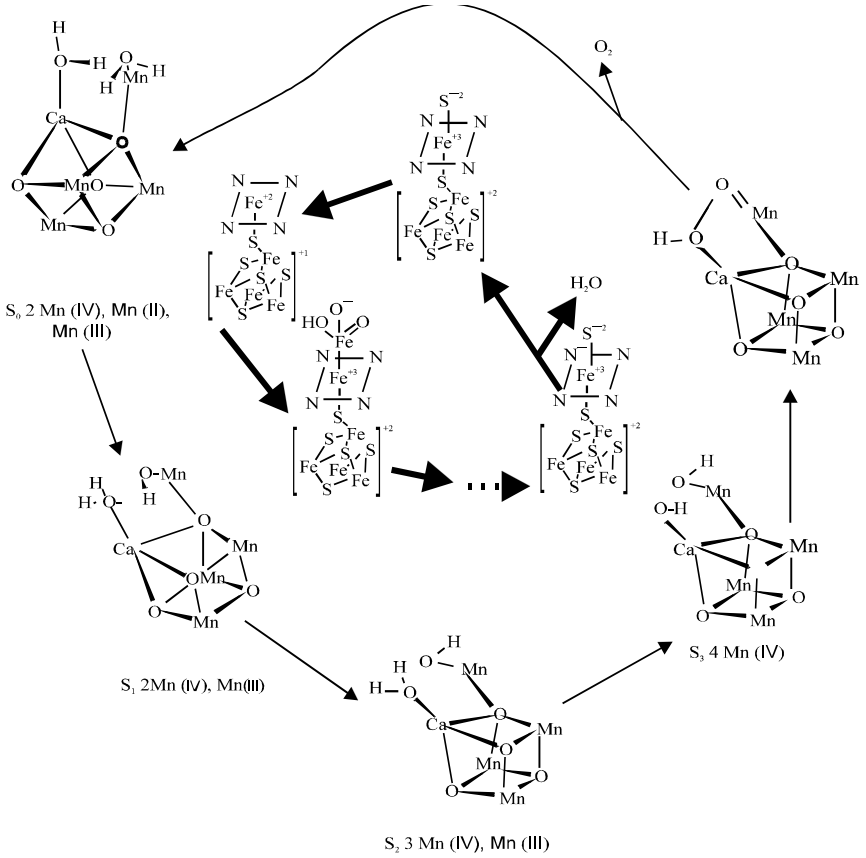

Fig. 4: Mechanisms of water oxidation and sulfite reduction are shown

- Center sections are mononuclear complexes.
- In both systems proton transfer is important.
- In both systems hydrogen bonds have important roles (Najafpour, 2006a, b; Stroupe and Getzoff, 2001)

Analogies between the Water Oxidation Complex in Photosystem (II) and cytochrome oxidase is considered by others (Brudvig Gary and Wikstrom, 2005). These analogies between two enzymes may be help to know passive structures or mechanisms.

Acknowledgments

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