

G035 STRUCTURAL CHARACTERIZATION OF REDUCED AND CHEMICALLY SUBSTITUTED DERIVATIVES OF THE MN CLUSTER IN THE PHOTOSYNTHETIC OXYGEN EVOLVING COMPLEX

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Water oxidation in Photosystem II of higher plants is catalyzed by the oxygen evolving complex (OEC) which contains 4 essential Mn ions, Ca^{2+} , and Cl^- as cofactors. Despite its importance in the photosynthetic process, the geometry and oxidation state of the cluster during its catalytic cycle have yet to be unambiguously determined. We have used X-ray Absorption Spectroscopy (XAS) in an effort to elucidate the structure of the native state. It has been proposed that hydroxylamine acts as a 2 electron reductant in the dark to form a state formulated S_{-1} . [1] The absorption edge shift we observe in the dark of samples treated with hydroxylamine (100 μM , 3 min.) is consistent with this interpretation. Hydroquinone (200 μM , 30 min.) induces an edge shift in the dark that indicates the presence of 1-2 Mn(II) not present in the control (S_1) state. Both of these dark reductions can be completely reversed with steady state illumination for 3 minutes, consistent with the observed minimal activity loss.

Past EXAFS analysis of the control S_1 state indicated the presence of a shell of low Z ligands @ 1.9 \AA , 2-3 Mn-Mn vectors at 2.7 \AA , and 1 Mn-Mn/Ca vector at 3.3 \AA . [3] The hydroquinone reduced sample has a new shell of ligands at circa 2.1 \AA , half the number of Mn-Mn vectors at 2.7 \AA and no interaction at 3.3 \AA . These changes are completely reversed with illumination. Changes in the EXAFS of the hydroxylamine treated sample will also be discussed.

The identity of the 3.3 \AA scatterer has yet to be resolved. The disappearance of this feature with reduction and its reappearance upon the photooxidation of the Mn may argue for a Mn-Mn interaction. In addition, we have recently finished a study in which Sr^{2+} , Dy^{3+} and La^{3+} replace Ca. None of these substitutions cause a significant change in the 3.3 \AA peak.

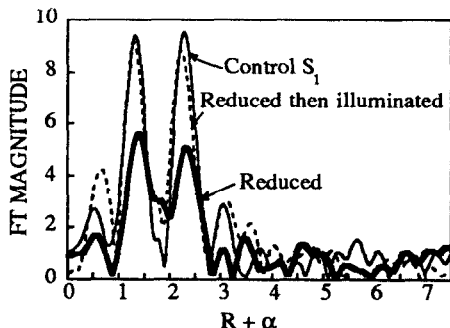


FIGURE 1: EXAFS spectra of control, hydroquinone reduced and reduced then illuminated.

- 1) H. Kretschmann, et al. *Biochim. Biophys. Acta*, 1059, 208-214 (1991).
- 2) P. Riggs, et al. *J. Am. Chem. Soc.*, 114, 10650-20651 (1992).
- 3) J. Penner-Hahn et al. *J. Am. Chem. Soc.* 112, 2549-2557 (1990).