Poster Presentation

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Crystallographic studies on Mn atoms in Photosystem II using K-edge wavelength

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Molecular oxygen on Earth is generated from photosynthesis by cyanobacteria, algae and plants, where water molecules are split by Photosystem II (PSII). PSII catalyzes light-induced water oxidation leading to the production of protons, electrons and molecular oxygen. The catalytic center of oxygen evolving complex (OEC) in PSII is composed of four Mn atoms and one Ca atom organized in a Mn4CaO5-cluster, which cycles through several different redox states to accomplish the catalytic process. Cyanobacterial PSII is a multi-subunits membrane protein complex composed of 17 membrane-spanning subunits, 3 membrane-extrinsic subunits and about 80 co-factor molecules with a total molecular weight of 350 kDa as a monomer. We reported the PSII structure at 1.9 Å resolution prepared from Thermosynechococcus vulcanus (PDB code: 3ARC)[1]. We determined unambiguously the positions of the atoms in OEC using the electron density map corresponding to each of five metal atoms and five oxygen atoms, for the first time. However, the valences of each of the four Mn atoms and their participation in the redox reactions in OEC are not fully understood. In order to uncover the catalytic mechanism of light-induced water oxidation by OEC, it is important to determine the valence of each Mn atom as well as to solve the detailed structure. In this study, we analyze the electronic state of each Mn atom in OEC by X-ray crystallographic analysis using Mn K-absorption edge wavelength. The Mn K-absorption edge depends on the oxidation number, and the anomalous scattering factor changes greatly for the Mn atoms in different oxidation states. We collected the anomalous difference data from PSII crystals using the wavelength (~1.8921 Å) on the Mn K-absorption edge at beamline BL38B1 and BL41XU of SPring-8 in Japan. The calculated anomalous difference Fourier map indicated different intensities among the four Mn atoms in OEC. This may suggest the different electronic state among the four Mn atoms in OEC. However, there is a possibility that these Mn atoms are reduced by X-ray exposures to some extent, and so the valences of these Mn atoms were not determined completely. We will discuss the relationship between peak heights of the anomalous difference Fourier map and the valence among the four Mn atoms in OEC.

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