

Structure of intermediates of the water oxidation reaction in photosystem II

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Photosystem II (PSII) catalyzes the light driven oxidation of water into dioxygen, protons and electrons. This reaction takes place at the oxygen evolving complex (OEC) a Mn_4CaO_5 cluster, through five intermediate S-states (S_0 to S_4), S_1 being the dark-stable state and S_3 the highest oxidized semi-stable state before O-O bond formation and O_2 evolution. We have been using fs X-ray pulses from an X-ray free electron laser (XFEL) to study the geometric and electronic structure of the OEC over the reaction cycle and recently reported high-resolution (around 2 Å) structures of PSII at room temperature for the four stable states in the S-state cycle as well as for two time points in the S_2 - S_3 transition.

Our results reveal important structural changes including the binding of one additional ‘water’, O_x , during the $S_2 \rightarrow S_3$ state transition. The binding of the additional oxygen O_x in the S_3 state between Ca and Mn1 suggests O-O bond formation mechanisms involving O5 as one substrate, where O_x is either the other substrate oxygen or is perfectly positioned to refill the O5 position during O_2 release [1].

We also explored the extended network of H-bonds between amino acid residues and waters connecting the OEC to the bulk solvent. We observed several significant changes in this network during the S-state cycle. Based on these data we will discuss the dynamics of the catalytic site and its environment over the reaction cycle.

Reference

1. Kern J, et al. (2018) *Nature* **563**, 421