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Room temperature femtosecond X-ray crystallography of photosystem II

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Light-induced oxidation of water in photosystem II (PS II) by plants, algae and cyanobacteria is responsible for most of the dioxygen in the atmosphere. PS II, a membrane-bound multi-subunit pigment-protein complex, couples the one-electron photochemistry at the reaction center with the four-electron redox chemistry of water oxidation at the Mn4CaO5 cluster in the oxygen-evolving complex (OEC). Under illumination, the OEC cycles through five intermediate S-states (S0 to S4), where S1 is the dark-stable state and S3 is the last semi-stable state before O-O bond formation and O2 evolution. A detailed understanding of the O-O bond formation mechanism remains a challenge, and elucidating the structures of the OEC in the different S-states, as well as the binding of the two-substrate waters to the catalytic sites is a prerequisite for this purpose. The time constants for the various transitions are in the 50 microseconds to 1 ms range. In order to probe the structure of the OEC in multiple illuminated states and evaluate the possible oxygen-evolving mechanisms consistent with these structures, we conducted a simultaneous X-ray emission spectroscopy (XES)/X-ray diffraction (XRD) experiment. Using fs pulses from an X-ray free electron laser, we measured damage free, room temperature (RT) structures of PSII crystals, containing a native-like packing of PSII dimers, of dark-adapted (S1), two-flash illuminated (2F; S3-enriched), and of the ammonia (a water analogue) bound two-flash illuminated (2F-NH3; S3-enriched) PS II. In addition, we investigated a number of different time points in the S3-S0 transition using XES and XRD measurements at various delay times between the final laser pump and the X-ray probe and isomorphous difference maps for the different time points were computed. Various proposed O-O bond formation mechanisms will be discussed in light of these data.

Keywords: photosynthesis, X-ray laser, metal enzymes