Structural Dynamics within the Water and Proton Channels of Photosystem II

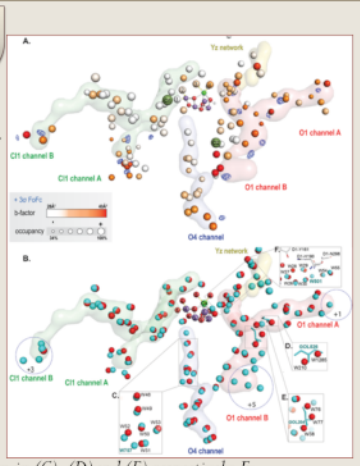
Rana Hussein[1] , Mohamed Ibrahim[1] , Jan Kern[2] , Vittal Yachandra[2], Junko Yuno[2] , Holger Dobbek[1], Athina Zouni[1]

[1]Institut für Biologie, Humboldt-Universität zu Berlin, D-10099 Berlin, Germany; [2]Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley

Abstract

Light-driven oxidation of water to molecular oxygen is catalyzed by the oxygen-evolving complex (OEC) in Photosystem II (PS II). This multi-electron, multi-proton catalysis requires the transport of water substrate to and proton egress from the OEC. Using a high-resolution, all S state averaged 1.89 Å room temperature crystal structure of PS II, as well as refined crystallography data at various time points between the S_2 to S_3 transition, we identified the O1 channel as the water intake pathway. By contrast, proton release occurs via the Cl1 channel and involves a 60° rotation of the D1-E65 sidechain as well as accompanying changes in the water positions. The results show that the chemistry at the catalytic site is well coordinated with the motion of distant residues that play roles in shuttling substrate water and protons essential for the water oxidation reaction.

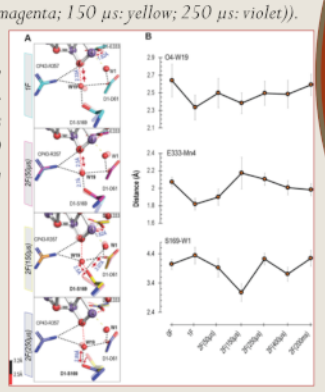
Water channels in the 1.89 Å room temperature resolution structure



A: Fo-Fc electron density omit map contoured at ≥ +3σ in blue for all the proposed water channels. The water molecules are represented in two different scales; color gradient scale, representing the b-factor of each water. The second scale is a size gradient, representing the occupancy. The channels and the network, O1 Channel in red, O4 Channel in blue, Cl1 Channel in green, and Yz network in yellow. B: Comparison between water channels in RT structure and cryo temperature structure. The water molecules detected within 3.5 Å from the water channels in red for the 1.89 Å RT structure and cyan for the 1.95 Å cryo structure PDB ID: 4UB6. Extra water molecules in the 1.95 Å cryo structure (PDB ID: 4UB6) detected within 5 Å away from the bulk are in the yellow circle. Structural differences comparison present in O4 channel, O1 channel A and O1 channel B between 1.89 Å RT structure (colored in red) and the 1.95 Å cryo structure PDB ID: 4UB6 (colored in cyan and labeled in cyan) are shown in (C) ,(D)and (E) respectively. F: Structural differences in waters of Yz network between 1.89 Å RT structure (colored in red and labeled in black) and the cryo structure with PDB ID: 6JLJ (colored and labeled in cyan).

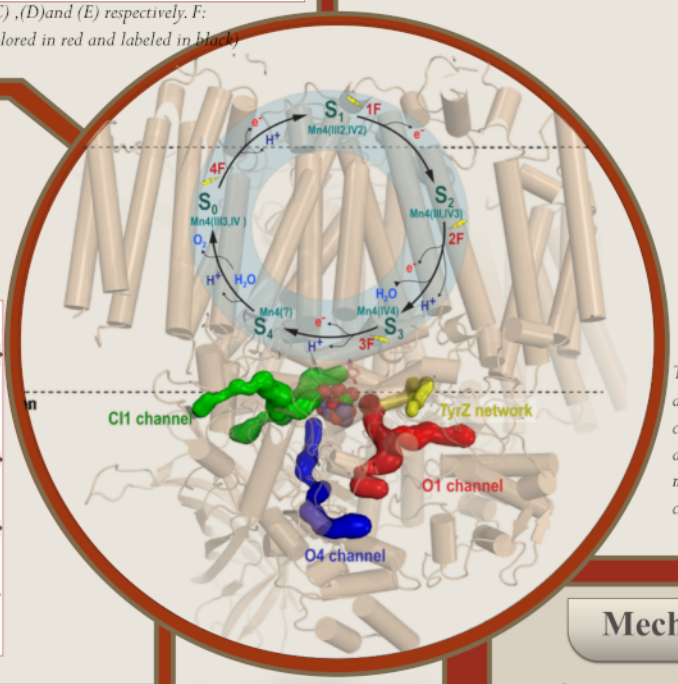
Changes near W1 and O4 environment

A: Structural change in the region of W1 and O4. The structures at different time points indicated in the left margin, each in solid colors overlaid with the earlier time point, which is in a transparent color scheme (0F (white), 1F (teal) and 2F time points (50 µs: magenta; 150 µs: yellow; 250 µs: violet)).



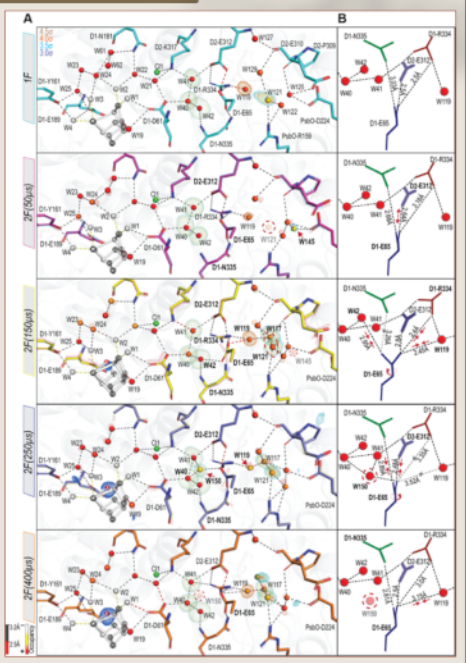
The H-bond length is color-coded, as described at the bottom left. 2F(150 µs) structural data shows rotation in the D1-S169 sidechain effecting the H-bonding network.

B: Distance changes for selected bond lengths within the W1 and O4 environment during the $S_1 \rightarrow S_3$ transition. Error bars represent the SD calculated by generating 100 randomly perturbed datasets and re-refining

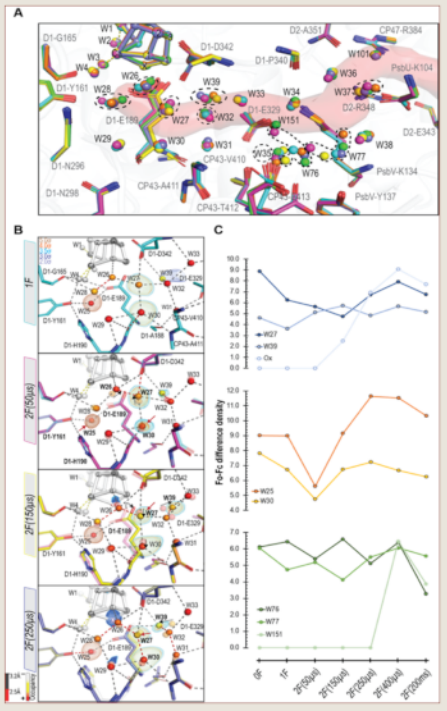


Structure changes in Cl1 Channel

A: structural changes in the protein and water molecules during the transition at different time points: (1F (teal) and 2F time points (50 µs: magenta; 150 µs: yellow; 250 µs: violet; 400 µs: orange)). Each model overlaid with the model of the earlier time point, shown in a transparent color. The waters are colored based on their occupancies, represented by a color gradient from white to red as shown at the bottom left. The positions for certain waters are confirmed by Fo-Fc omit-maps contoured at different σ levels (3.5σ, 4σ) with the exception for W25, W119 and Ox omit maps contoured at (5σ, 4.4σ and 3σ respectively). The H-bond length is color-coded, as described at the bottom left. Appearance and disappearance of W121, W117, W121, W145 and W150 at different time points are marked with red dashed circle. B: Model of the structure changes within the second bottleneck of the Cl1 water channel. The rotation of the D1-E65 at 2F (150 µs) are marked by red circle arrow. Appearance and disappearance of W150 at 2F (250 µs) and at 2F (400 µs) respectively are marked with red dashed circle.



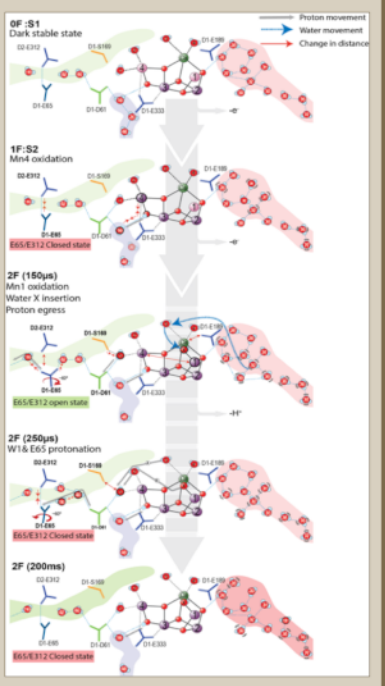
Structure changes in Cl1 Channel



A: The structure changes in O1 Channel are shown for all time points between the $S_2 \rightarrow S_3$ (1F (teal) and 2F time points (50 µs: magenta; 150 µs: yellow; 250 µs: violet; 400 µs: orange; 200 ms: green)). O1 channel is in red. Waters that show significant movement during the $S_2 \rightarrow S_3$ transition are marked with black dashed circle. B: structural changes in the beginning of O1 channel during the transition at different time points: (1F (teal) and 2F time points (50 µs: magenta; 150 µs: yellow; 250 µs: violet)). Each model overlaid with the model of the earlier time point, shown in a transparent color. The waters are colored based on their occupancies, represented by a color gradient from white to red as shown at the bottom left.

The positions for certain waters are confirmed by Fo-Fc omit-maps contoured at different σ levels (3.5σ, 4σ) with the exception of W30 at 1F and Ox omit maps contoured at (2σ and 3σ respectively). The H-bond length is color-coded, as described at the bottom left. Movement of W26, W27, W39 and D1-E189 are marked with black dashed arrow. C: Fo-Fc for certain omitted waters in O1 channel and Cl1 channel.

Mechanism



1-S1 →S2 transition:
-Mn4 oxidation
distance between W19 and O4 is decreased
2- S2 →S3 transition:
-2F150µs:

- *Mn1 oxidation*
- *E189 move away from the cluster Ox electron density detection*
- *S169 moves significantly results in decreasing the distance to W1*
- *E65 side chain turning 60 degree*

-2F250µs:

- *S169 moves back to its original position*
- *E65 turning back*
- *detection of extra electron density (W150) very close to W40 and in hydrogen bond distance from E65*

-2F400µs:

- *disappearance of W150*
- *detection of extra electron density (W151) in O1 channel*

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Mohamed Ibrahim
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