

The Mn₄Ca cluster in Photosynthesis - Where are the electrons?

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The oxygen-evolving complex (OEC) located in the PSII membrane-bound protein in plant, algae, and cyanobacteria catalyses the water-oxidation reaction. The OEC, with four Mn and one Ca, couples the 4-electron chemistry of water oxidation with the one-electron photochemistry of the reaction center by sequentially storing oxidizing equivalents through five intermediate S-states (S_i, i = 0 to 4), before one molecule of dioxygen is evolved. The Mn₄CaO₅ cluster provides a high degree of redox and chemical flexibility so that several oxidizing equivalents can be stored during the S-state cycle. To understand the mechanism of water oxidation in detail, it is crucial to know how the electronic and geometric structure of Mn₄CaO₅ changes during the catalysis and how the nature of the Mn-oxo bridges is affected by that. The S-states can be isolated by rapid freeze-quench after illumination but ideally the experiments are performed in a time-resolved manner at room temperature with in-situ illumination.

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