

Intermediate in the oxygen-forming transition of the Photosystem II manganese complex discovered by a novel time-resolved X-ray absorption experiment

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In plants and cyanobacteria, driven by light water is oxidized at a tetra-manganese complex bound to the proteins of photosystem II (PSII). For the first time, the redox reactions of the PSII manganese complex were monitored directly by time-resolved X-ray absorption spectroscopy (XAS), at ambient oxygen pressure and temperature using highly active PSII-containing membrane particles prepared from spinach leaves. XAS at the K-edge of manganese probes changes in oxidation state and local structure specifically for the X-ray absorbing Mn ions [1]. Therefore, time-resolved XAS is well suited for monitoring the kinetics of the individual steps in the catalytic cycle of the PSII manganese complex. We have developed an approach which now has facilitated direct monitoring of the S-state transitions by XAS at 10 μ s time resolution. The transitions between five intermediate states of the catalytic S-state cycle were resolved and rate constants determined. Most remarkable, formation of a precursor state prior to the O₂-producing step was detected. This exciting finding leads to an extension of the S-state cycle scheme of photosynthetic water oxidation. The putative mechanistic role of this novel intermediate in photosynthetic water oxidation is discussed in the light of the structural and kinetic information previously obtained for S₁, S₂, S₃ and S₀ [2].

- [1] Dau, H., Liebisch, P. and Haumann, M. (2003) Anal. Bioanal. Chem. 376(5), 562-583. X-ray absorption spectroscopy to analyze nuclear geometry and electronic structure of biological metal centers - Potential and questions examined with special focus on the tetranuclear manganese complex of oxygenic photosynthesis.
- [2] Haumann, M., Müller, C., Liebisch, P., Iuzzolino, L., Dittmer, J., Grabolle, M., Neisius, T., Meyer-Klaucke, W. and Dau, H. (2005) Biochemistry 44, 1894-1908. Structural and oxidation state changes of the photosystem II manganese complex in four transitions of the water oxidation cycle (S₀→S₁, S₁→S₂, S₂→S₃, S_{3,4}⇌S₀) characterized by X-ray absorption spectroscopy at 20 K as well as at room temperature.