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Biological Mechanisms

Illuminating Water Oxidation

Elusive state in photosynthetic oxygen production is observed spectroscopically

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One of the elusive secrets of photosynthesis, the biological process that makes life on Earth possible, has been uncovered. Researchers have observed an oxidation state involved in generating oxygen. The work could lead to better ways to convert sunlight into other forms of energy.

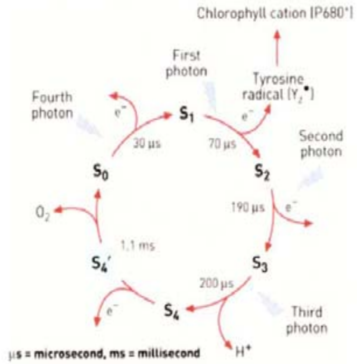
In photosynthesis, water is oxidized to molecular oxygen, the source of the O_2 we breathe and the atmospheric ozone that protects us from ultraviolet radiation. The electrons liberated are then used to synthesize carbohydrates, the source of food we eat. The process is carried out with nearly 100% efficiency and no toxic by-products in photosystem II, a multisubunit protein complex found in photosynthetic organisms. The catalytic center of photosystem II is a tetramanganese cluster coupled to a redox-active tyrosine residue called Y_Z.

In the water oxidation process, four successive photons of light induce photosystem II to traverse five oxidation states, S_0 through S_4. S_0 to S_3 had been observed spectroscopically, but not S_4. It wasn't known if S_4 is just a fleeting transition state or a more long-lived intermediate. Also, because O_2 formation starts at the S_4 state, the actual mechanism of O_2 generation was not known.

Now, Michael Haumann, Holger Dau, and coworkers in the department of physics at the Free University of Berlin have observed S_4 by using high-intensity, time-resolved X-ray absorption spectroscopy (*Science* **2005,** *310,* 1019). It's an intermediate.

The measurements "would have been impossible without the high-brightness, third-generation synchrotron sources that provide higher X-ray flux" than was previously available for such experiments, note enzyme specialists James E. Penner-Hahn and Charles F. Yocum of the University of Michigan in an associated commentary. "With this demonstration of feasibility, a wide range of other applications of microsecond time-resolved X-ray absorption spectroscopy to chemically and biologically important reactions can now be imagined."

It had been proposed earlier that S_4 might be created by electron transfer from photosystem II's Mn_4 complex to a Y_Z radical ($Y_Z^{\bullet}$). The new study indicates that S_4 forms instead by deprotonation. This suggests that the photosynthetic cycle includes a sixth oxidation state. "The deprotonation must be followed by electron transfer to $Y_Z^{\bullet}$, thus implying an S_4' state," the researchers note. S_4' may also be either a transition state or an intermediate. With mysteries like that still to be solved, efforts to fathom the intricacies of photosynthesis will continue.



ADDED STATE In photosynthetic oxygen generation, photons move photo-system II through five successive oxidation states, S_0 through S_4. Haumann, Dau, and coworkers observed the elusive S_4 state spectroscopically, but their study revealed that another state (S_4') must be present as well.

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