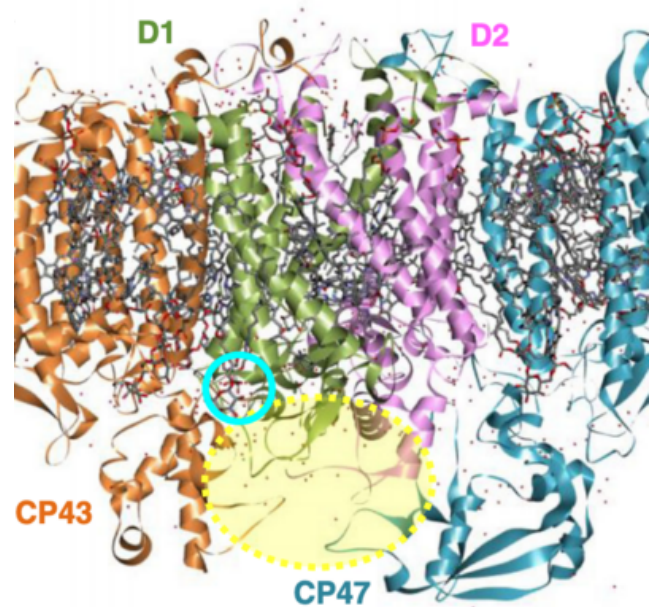


## Spinach brings us a step closer to understanding the evolution of photosynthesis

Start Time: Thursday, December 10, 2020

End Time:



Investigating the process of photosynthetic processes in spinach, a team of scientists around UniSysCat research group leader Prof. Dr. Holger Dau (Freie Universität Berlin) and Einstein Fellow Prof. Dr. Robert Burnap (Oklahoma State University) were able to show how the ancestor of today's photosystem II likely worked and evolved about 3 billion years ago. They published their findings in the prestigious Nature Communications (Open Access: <https://doi.org/10.1038/s41467-020-19852-0>)

The photosynthetic process used by algae, plants and cyanobacteria is a highly complex system. Its current form evolved about 3 billion years ago and caused a major turn in the history of Earth: oxygenic photosynthesis, the conversion of light energy into chemical energy produces oxygen as a waste product. This led to the accumulation of oxygen in Earth's previously anoxic atmosphere to about 21%. Thus, the development of oxygenic photosynthesis enabled the development of life on Earth as we know it.

Water oxidation is a crucial step in the process and is conducted in a protein complex called photosystem II (PSII) that also contains the inorganic oxygen-evolving center  $\text{Mn}_4\text{CaO}_5$ . This manganese (Mn) based center splits water into electrons, protons, and  $\text{O}_2$ . Mn also readily forms oxides, mainly different types of manganese oxide, a mineral that occurs naturally on Earth and has a distinct rusty brown color. However, the natural formation on manganese oxide

requires the presence of  $O_2$  in the atmosphere which in turn means that the formation of the rusty brown mineral should have been nearly impossible in an anoxic atmosphere – unless produced in a previous version of our photosynthetic system (Johnson et al., Proc. Nat. Acad. Sci. USA 110, 11238-11234). This is exactly what Prof. Dr. Holger Dau and Prof. Dr. Robert Burnap demonstrated in their study using spinach: their research showed, how a modified, Mn-free PSII of spinach can produce nanoparticulate manganese oxide from manganese ions in the immediate environment.

Having removed the manganese and slightly modified the remaining PSII complexes, the team observed the production of about 50 to 100 manganese oxide nanoparticles per PSII in a manganese ion rich environment. Using the X-ray facilities at BESSY (Berlin Electron Storage Ring Society for Synchrotron Radiation), the researchers around Prof. Dau and Prof. Burnap could show that the manganese oxide nanoparticles match the Birnessite type, a hydrated manganese oxide structure that also occurs naturally. The slightly modified, Mn-free PSII isolated from spinach was therefore able to form manganese oxide. Based on these findings, the investigators suggest that previous versions of today's PSII – also devoid of a Mn-based oxygen-evolving center - should have been able to produce manganese oxide. More than 3 billion years ago this likely enabled the light-driven formation of manganese oxide in ancient photosystems which suggests a) that early manganese oxide resulted from photosynthesis, b) that the oxygen-evolving  $Mn_4CaO_5$  center may have developed from these manganese oxides and c) that the formation and utilization of manganese oxide nanoparticles was an integral part of a quasi-respiratory activity at the time.

The idea to demonstrate the ability of the modified PSII to form manganese oxide stems from the early studies of scientists at UniSysCat and SFB 1078. Their idea has grown into an independent research project carried out at SFB 1078 and supported by the Einstein Foundation.

**Prof. Dr. Holger Dau**, UniSysCat research group leader and professor for biophysics and photosynthesis at Freie Universität Berlin, investigates processes in biological water oxidation and catalysis. His research aims to develop biotechnological and biomimetic approaches towards light-driven fuel production.

<https://www.unisyscat.de/group-leaders/dau-holger.html>

**Prof. Dr. Robert Burnap** is an internationally acclaimed microbiologist and molecular geneticist at Oklahoma State University and, since 2018, Einstein Visiting Fellow at the Freie Universität Berlin where he works with the Collaborative Research Center "Protonation Dynamics in Protein Function". His studies focus on the release of oxygen in oxygenic photosynthesis by

plants, algae, and cyanobacteria.

<https://www.einsteinfoundation.de/en/media/einstein-questionnaire/robert-burnap/>

Full paper: <https://doi.org/10.1038/s41467-020-19852-0> (Open Access)

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**Light-driven formation of manganese oxide by today's photosystem-II supports evolutionarily ancient manganese-oxidizing photosynthesis.** *Nature Communications* 11, Article number: 6110 (2020).