

## 1998-2004

Schiller, H., Klingelhöfer, S., Hühn, M. and Dau, H. (1998) Photosynth. Res. 55, 95-101. On the long-wavelength spectral forms of chlorophyll-a in Photosystem I: spectroscopic and immunological investigations on a greening mutant of *Scenedesmus obliquus*.

Schiller, H., Dittmer, J., Iuzzolino, L., Dörner, W., Meyer-Klaucke, W., Sole, V.A., Nolting, H.-F. and Dau, H. (1998) Biochemistry 37, 7340-7350. Structure and Orientation of the Oxygen-Evolving Manganese Complex of Green Algae and Higher Plants Investigated by X-ray Absorption Linear Dichroism Spectroscopy on Oriented Photosystem II Membrane Particles.

Dau, H. (1998) Rostock. Meeresbiolog. Beitr. 6, 23-40. Chlorophyll fluorescence measurements for assessment of primary production in aquatic ecosystems - the basics.

Dau, H. (1998) Rostock. Meeresbiolog. Beitr. 6, 47-50. Photoacoustic measurements as a potential tool for assessment of primary production in aquatic ecosystems - the basics.

Beutler, M., Wiltshire, K., Meyer, B., Moldaenke, C. and Dau, H. (1998) In Photosynthesis: Mechanism and Effects (Garab, G., Ed), Vol. V, pp. 4301-4304, Kluwer Academic Publishers, Dordrecht. Rapid depth-profiling of the distribution of 'spectral groups' of microalgae in lakes, rivers and in the sea. The Method and a newly-developed submersible instrument which utilizes excitation of chlorophyll fluorescence in five distinct wavelength ranges.

Dau, H., Iuzzolino, L., Dittmer, J., Dörner, W. and Meyer-Klaucke, W. (1998) In Photosynthesis: Mechanism and Effects (Garab, G., Ed), Vol. II, pp. 1327-1330, Kluwer Academic Publishers, Dordrecht. The Photosystem II manganese complex in its S<sub>3</sub>-state.

Dittmer, J., Iuzzolino, L., Dörner, W., H.-F. Nolting, Meyer-Klaucke, W. and Dau, H. (1998) In Photosynthesis: Mechanism and Effects (Garab, G., Ed), Vol. II, pp. 1339-1342, Kluwer Academic Publishers, Dordrecht. A new method for determination of the edge position of x-ray absorption spectra.

Iuzzolino, L., Dittmer, J., Dörner, W. and Dau, H. (1998) In Photosynthesis: Mechanism and Effects (Garab, G., Ed), Vol. II, pp. 1315-1318, Kluwer Academic Publishers, Dordrecht. A correlation method for quantification of the magnitude of the S<sub>2</sub>-state multiline EPR signal.

\*Dörner, W., Dittmer, J., Iuzzolino, L. and Dau, H. (1998) In Photosynthesis: Mechanism and Effects (Garab, G., Ed), Vol. II, pp. 1343-1346, Kluwer Academic Publishers, Dordrecht. The structure of a partially assembled, di-nuclear PS II manganese complex investigated by EPR and EXAFS spectroscopy on a new core complex preparation.

Dittmer, J. and Dau, H. (1998) J. Phys. Chem. B 102 (42), 8196-8200. Theory of the Linear Dichroism in the Extended X-ray Absorption Fine Structure (EXAFS) of partially vectorially-ordered systems.

- Iuzzolino, L., Dittmer, J., Dörner, W., Meyer-Klaucke, W. and Dau, H. (1998) Biochemistry 37, 17112-17119 (accelerated publication). X-ray absorption spectroscopy on layered Photosystem II membrane particles suggests manganese-centered oxidation of the oxygen evolving complex for the S<sub>0</sub>-S<sub>1</sub>, S<sub>1</sub>-S<sub>2</sub> and S<sub>2</sub>-S<sub>3</sub> transition of the water oxidation cycle.
- Strasser, B.J., Dau, H., Heinze, I., and Senger, H. (1999) Photosynth. Res. 60, 217-227. Comparison of light-induced and cell cycle-dependent changes in the photosynthetic apparatus - a fluorescence induction study on the green alga *Scenedesmus obliquus*.
- Dau, H., Dittmer, J., Epple, M., Hanss, J., Kiss, E., Rehder, D., Schulzke, C. and Vilter, H. (1999) FEBS Lett. 457, 237-240. Bromine K-edge EXAFS studies of bromide binding to bromoperoxidase from *Ascophyllum nodosum*.
- Schiller, H. and Dau, H. (2000) J. Photochem. Photobiol. B: Biol., 55, 138-144. Preparation protocols for high-activity Photosystem II membrane particles of green algae and higher plants, pH-dependence of oxygen evolution and comparison of the S<sub>2</sub>-state multiline signal by X-band EPR spectroscopy.
- Rehder, D., Schulzke, C., Dau, H., Meinke, C., Hanss, J. and Epple, M. (2000) J. Inorganic Biochem. 80, 115-121. Water and bromide in the active center of vanadate-dependent haloperoxidases.
- Meinke, C., Sole, A.V., Pospisil, P. and Dau, H. (2000) Biochemistry 39, 7033-7040, accelerated publication. Does the structure of the water-oxidizing Photosystem II manganese complex at room temperature differ from its low-temperature structure? A comparative X-ray absorption study.
- Wastl, J., Duin, E. C., Iuzzolino, L., Dörner, W., Link, T., Hoffman, S., Sticht, H., Dau, H., Lingelbach, K. and Maier, U.-G. (2000) J. Biol. Chem. 275 (39), 30058-3063 Eukaryotically encoded and chloroplast located rubredoxin is associated with photosystem II.
- Pospisil, P. and Dau, H. (2000) Photosynth. Res. 65, 41-52. Chlorophyll fluorescence transients of Photosystem II membrane particles as a tool for studying photosynthetic oxygen evolution.
- Dau, H., Iuzzolino, L. and Dittmer, J. (2001) Biochim. Biophys. Acta 1503, 24-39, invited review. The tetra-manganese complex during its redox cycle - X-ray absorption results and mechanistic implications.
- \*Pospisil, P., Haumann, M., Dittmer, J., Sole, A. and Dau, H. (2001) In PS2001 Proceedings, S13-007, pp. 1-4, CSIRO Publishing, Collingwood, Australia [ISBN: 0643 06711 6]. Stepwise transition of the tetra-manganese complex of Photosystem II to a binuclear Mn<sub>2</sub>(μ-O)<sub>2</sub> complex in response to a temperature jump: an X-ray absorption study.
- \*Haumann, M., Grabolle, M., Werthammer, M., Iuzzolino, L., Dittmer, J., Meyer-Klaucke, W., Neisius, T. and Dau, H. (2001)
- Beutler, M., Wiltshire, K. H., Meyer, B., Moldaenke, C. and Dau, H. (2001) HAB2000 Proceedings volume (eds. Hallegraeff, G., Blackburn, S.I., Bolch, C. J., Lewis, R. J.) Intergovernmental Oceanographic Commission of UNESCO, Paris, pp. 202-205. In-situ profiles of phytoplankton: Algal composition and biomass determined fluorometrically.

- Krüer, M., Haumann, M., Meyer-Klaucke W., Thauer, K. R. and Dau, H. (2002) Eur. J. Biochem. **269**, 2117-2123. The role of zinc in the methylation of the coenzyme M thiol group in methanol:coenzyme M methyltransferase from *Methanosarcina barkeri*. New insights from X-ray absorption spectroscopy.
- Haumann, M., Grabolle, M., Neisius, T. and Dau, H. (2002) FEBS lett. **512**, 116-120. X-ray absorption spectroscopy on the tetra-manganese complex of Photosystem II at room temperature: The first EXAFS spectra of higher oxidation states populated by Laser-flash excitation.
- Beutler, M., Wiltshire, K. H., Meyer, B., Moldaenke, C., Lüring, C., Meyerhöfer, M., Hansen, U.-P. and Dau, H. (2002) Photosynth. Res. **72**, 39-53. A fluorometric method for the differentiation of algal populations in-vivo and in-situ.
- Pospisil, P. and Dau, H. (2002) Biochim. Biophys. Acta **1554**, 94-100. Valinomycin sensitivity proves that light-induced thylakoid voltages result in millisecond phase of chlorophyll fluorescence.
- Meinke, C., Solé, A., Neisius, T., Pospisil, P., Haumann, H. and Dau, H. (2002) ESRF 2001 Highlights, pp. 29-30. BioXAS at room temperature.
- Haumann, M., Pospisil, P., Grabolle, M., Müller, C., Liebisch, P., Solé, A., Neisius, T., Dittmer, J., Iuzzolino, L. and Dau, H. (2002) J. Synchrotron Rad. **9**, 304-308. First steps towards time-resolved BioXAS at room temperature: state transitions of the manganese complex of oxygenic photosynthesis.
- Pospisil, P., Haumann, M., Dittmer, J., Solé, A. and Dau, H. (2003) Biophys. J. **84**, 1370-1386. Stepwise transition of the tetra-manganese complex of Photosystem II to a binuclear  $Mn_2(\mu-O)_2$  complex in response to a temperature jump - a time-resolved structural investigation employing X-ray absorption spectroscopy.
- Dau, H. and Haumann, M. (2003) J. Synchrotron Rad. **10**, 76-85. X-ray absorption spectroscopy to watch catalysis by metalloenzymes - Status and perspectives discussed for the water-splitting manganese complex of Photosystem II. (invited review)
- 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. (invited review)
- Haumann, M., Porthun, A., Buhrke, T., Liebisch, P., Meyer-Klaucke, W., Friedrich, B. and Dau, H. (2003) Biochemistry **42**, 11004-11015. Hydrogen-induced structural changes at the nickel site of the regulatory [NiFe] hydrogenase from *Ralstonia eutropha* studied by X-ray absorption spectroscopy.
- Ute Christmann, U., Dau, H., Haumann, M., Kiss, E., Liebisch, P., Rehder, D., Santoni, G. and Schulzke, C. (2004) Dalton Trans. **2004**, 2534-2540. Substrate binding to vanadate-dependent bromoperoxidase from *Ascophyllum nodosum*: A vanadium K-edge XAS approach.
- Dau, H., Liebisch, P. and Haumann, M. (2004) Phys. Chem. Chem. Phys., **2004**, **6**, 4781 - 4792. The manganese complex of Photosystem II in its dark-stable  $S_1$ -state at atomic resolution — EXAFS results in relation to recent crystallographic data.

## 2005

- Müller, C., Liebisch, P., Barra, M., Dau, H. and Haumann M. (2005) Phys. Scripta T115, 847-850. The location of calcium in the manganese complex of oxygenic photosynthesis studied by X-ray absorption spectroscopy.
- Dau, H., Liebisch, P. and Haumann M. (2005) Phys. Scripta T115, 844-846. The manganese complex of oxygenic photosynthesis: Conversion of five-coordinated Mn(III) to six-coordinated Mn(IV) in the S2-S3 transition is implied by XANES simulations.
- Liebisch, P., Haumann M. and Dau, H., (2005) Phys. Scripta T115, 859-861. Simulations of XANES spectra for protein-bound metal centers: Analysis of linear dichroism data.
- Haumann, M., Müller, C., Liebisch, P., Neisius, T. and Dau, H. (2005) J. Synchrotron Rad. 12, 35-44. A novel BioXAS technique with microsecond time resolution to track oxidation state and structural changes at biological metal centers - S-state transitions of the manganese complex of oxygenic photosynthesis.
- \*Dau, H., P. Liebisch and Haumann, M. (2005) Proceedings of the XIIIth International Congress on Photosynthesis, 347-350. Discussion of the structural and oxidation state changes of the Mn<sub>4</sub>Ca complex of Photosystem II on basis of recent X-ray absorption results.
- \*Müller, C., Dau, H. and Haumann, M. (2005) Proceedings of the XIIIth International Congress on Photosynthesis, 257-259. Chelex-treatment to obtain highly active PSII membrane particles with minimal Ca<sup>2+</sup> content for X-ray absorption spectroscopy at the Ca K-edge.
- 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 (S<sub>0</sub>->S<sub>1</sub>, S<sub>1</sub>->S<sub>2</sub>, S<sub>2</sub>->S<sub>3</sub>, S<sub>3,4</sub>->S<sub>0</sub>) characterized by X-ray absorption spectroscopy at 20 K as well as at room temperature.
- Barra, M., Haumann, M. and Dau, H. (2005) Photosynth. Res. 84, 231-237. Specific loss of the extrinsic 18 KDa protein from photosystem II upon heating to 47 °C causes inactivation of oxygen evolution likely due to Ca release from the Mn-complex.
- Burgdorf, T., Löscher S., Liebisch, P., Van der Linden, E., Galander, M., Lendzian, F., Albracht, S. P., Meyer-Klaucke, W., Friedrich, B., Dau, H. and Haumann, M. (2005) J. Am. Chem. Soc. 127, 576-592. Structural and oxidation-state changes at its non-standard Ni-Fe site during activation of the NAD-reducing hydrogenase from Ralstonia eutropha detected by X-ray absorption, EPR, and FTIR spectroscopy.
- Löscher, S., Burgdorf, T., Buhrke, T., Friedrich, B., Dau, H. and Haumann, M. (2005) Biochem. Soc. Trans. 33, 25-27. Unusual structures of the Ni-Fe cofactor in the regulatory and in the NAD-reducing hydrogenase from Ralstonia eutropha.

- Buhrke, T., Löscher, S., Lenz, O., Schlodder, E., Zebger, I., Andersen, L.K., Hildebrandt, P., Meyer-Klaucke, W., Dau, H., Friedrich, B. and Haumann, M. (2005) J. Biol. Chem. 280, 19488–19495. Reduction of Unusual Iron-Sulfur Clusters in the H<sub>2</sub>-sensing Regulatory Ni-Fe Hydrogenase from *Ralstonia eutropha* H16.
- Löscher, S., Zebger, I., Andersen, L. K., Hildebrandt, P., Meyer-Klaucke, W. and Haumann, M. (2005) FEBS Lett 579, 4287-4291. The structure of the Ni-Fe site in the isolated HoxC subunit of the hydrogen-sensing hydrogenase from *Ralstonia eutropha*.
- Dau, H. and Haumann, M. (2005) Photosynth. Res. 84, 325-331. Considerations on the mechanism of photosynthetic water oxidation - dual role of oxo-bridges between Mn ions in (i) redox-potential maintenance and (ii) proton abstraction from substrate water
- Grabolle, M. and Dau, H. (2005) Biochim. Biophys. Acta, 1708, 209-218. The energetics of the primary and secondary electron transfer in Photosystem II membrane particles of spinach revisited on basis of recombination-fluorescence measurements.
- Clausen, J., Junge, W., Dau, H. and Haumann, M. (2005) Biochemistry 44, 12775-12779. Photosynthetic water oxidation at high O<sub>2</sub> backpressure monitored by delayed chlorophyll fluorescence.
- Haumann, M., Liebisch, P., Müller, C., Barra, M., Grabolle, M. and Dau, H. (2005) Science 310, 1019-1021. Photosynthetic O<sub>2</sub>-formation tracked by time-resolved X-ray spectroscopy.

## 2006

- \*Dau, H., Haumann, M., Liebisch, P., Müller, C., Grabolle, M., Barra, M., Loja, P. and Kirilenko, O. (2006) In Metalloproteins and Metalloidproteins (A. Kyriakopoulos et al., eds.) Herbert Utz Verlag, München, pp. 62-66. Photosynthetic O<sub>2</sub>-production at the tetra-manganese complex of photosystem II tracked by novel X-ray absorption experiments.
- \*Krivanek, R., Dau, H. and Haumann, M. (2006) In Metalloproteins and Metalloidproteins (A. Kyriakopoulos et al., eds.) Herbert Utz Verlag, München, pp.18-24. Photothermal spectroscopy to investigate the energetics of photosynthetic water oxidation.
- H. Dau, W. Kuch, R. Püttner, Freie Universität Berlin (Editors) - Research with Synchrotron Radiation 2000-2005, Shaker Verlag, Aachen, 2006.
- Hermes, S., Bremm, O., Garczarek, F., Derrien, V., Liebisch, P., Loja, P., Sebba, P., Gerwert, K. and Haumann, M. (2006) Biochemistry 45, 353-359. A time-resolved iron-specific X-ray absorption experiment yields no evidence for an Fe<sup>2+</sup> --> Fe<sup>3+</sup> transition during QA- --> QB electron transfer in the photosynthetic reaction center.
- Grabolle, M., Haumann, M., Müller, C., Liebisch, P. and Dau, H. (2006) J. Biol. Chem. 281, 4580-4588. Rapid loss of structural motifs in the manganese complex of oxygenic photosynthesis by x-ray irradiation at 10-300 K.

Dau, H. and Haumann, M. (2006) Science 312, 1471-1472 (letter section). Reaction cycle of photosynthetic water oxidation.

Magnuson, A., Liebisch, P., Haumann, M., Höglom, J., Anderlund, M., Lomoth, R., Meyer-Klaucke, W. and Dau, H. (2006) J. Inorg. Biochem., 100, 1234-1243. Bridging-type changes facilitate successive oxidation steps at about 1 V in two binuclear manganese complexes - implications for photosynthetic water-oxidation.

Löscher, S., Burgdorf, T., Zebger, I., Hildebrandt, P., Dau, H., Friedrich, B. and Haumann, M. (2006) Biochemistry 45, 11658-11665. Bias from H<sub>2</sub> cleavage to production and coordination changes at the Ni-Fe active site in the NAD<sup>+</sup>-reducing hydrogenase from *Ralstonia eutropha*.

Haumann, M., Barra, M., Loja, P., Löscher, S., Krivanek, R., Grundmeier, A., Andreasson, L. E. and Dau, H. (2006) Biochemistry 45, 13101-13107. Bromide does not bind to the Mn<sub>4</sub>Ca complex in its S<sub>1</sub> state in Cl(-)-depleted and Br(-)-reconstituted oxygen-evolving photosystem II: evidence from X-ray absorption spectroscopy at the Br K-edge.

Barra, M., Haumann, M., Loja, P., Krivanek, R., Grundmeier, A. and Dau, H. (2006) Biochemistry 45, 14523-14532. Intermediates in assembly by photoactivation after thermally accelerated disassembly of the manganese complex of photosynthetic water oxidation.

## 2007

Dau H and Haumann M (2007) Time-resolved X-ray spectroscopy leads to an extension of the classical S-state cycle model of photosynthetic oxygen evolution. Photosynth Res 92: 327-343

Buchta J, Grabolle M and Dau H (2007) Photosynthetic dioxygen formation studied by time-resolved delayed fluorescence measurements--method, rationale, and results on the activation energy of dioxygen formation. Biochim Biophys Acta 1767: 565-574

Krivanek R, Kern J, Zouni A, Dau H and Haumann M (2007) Spare quinones in the QB cavity of crystallized photosystem II from *Thermosynechococcus elongatus*. Biochim Biophys Acta 1767: 520-527

Dau H and Haumann M (2007) Eight steps preceding O-O bond formation in oxygenic photosynthesis--a basic reaction cycle of the Photosystem II manganese complex. Biochim Biophys Acta 1767: 472-483

\*Dau H, Haumann M, Liebisch P, Barra M, Loja P, Löscher S, Kirilenko O, Mertin M, Schafers F, Anderlund M, Ott S and Magnuson A (2007). Towards biomimetic hydrogen production from water - Synthetic models of biological small-atom catalysis investigated by X-ray absorption. In: Kyriakopoulos et al. (eds.) Metallobiomics, pp 7-14, Herbert Utz Verlag, München

Loscher S, Schwartz L, Stein M, Ott S and Haumann M (2007) Facilitated hydride binding in an Fe-Fe hydrogenase active-site biomimic revealed by X-ray absorption spectroscopy and DFT calculations. Inorg Chem 46: 11094-11105

Grabolle M and Dau H (2007) Efficiency and role of loss processes in light-driven water oxidation by PSII. *Physiol Plant* 131: 50-63

## 2008

Haumann, M.; Grundmeier, A.; Zaharieva, I.; Dau, H.

Photosynthetic water oxidation at elevated dioxygen partial pressure monitored by time-resolved X-ray absorption measurements  
in: Proceeding of the National Academy of Sciences USA. - 105 (2008) S. 17384-17389

Dau, H.; Haumann, M.

The manganese complex of photosystem II in its reaction cycle – basic framework and possible realization at the atomic level (invited review)  
in: Coordination Chemistry Review. - 252 (2008) S. 273-295

Dau, H.; Grundmeier, A.; Loja, P.; Haumann, M.

On the structure of the manganese complex of photosystem II – Extended-range EXAFS data and specific atomic-resolution models for four S-states  
in: Philosophical Transaction of the Royal Society London B. - 363 (2008) S. 1237-1244

Krivanek, R.; Dau, H.; Haumann, M.

Enthalpy changes in photosynthetic O<sub>2</sub> formation determined by time-resolved calorimetry using a photothermal beam deflection technique  
in: Biophysical Journal. - 94 (2008) S. 1890-1903

Shutova, T.; Kenneweg, H.; Buchta, J.; Nikitina, J.; Terentyev, V.; Chernyshov, S.; Andersson, B.; Allakhverdiev, S. I.; Klimov, V. V.; Dau, H.; Junge, W.; Samuelsson, G.

The photosystem II-associated Cah3 in Chlamydomonas enhances the O<sub>2</sub> evolution rate by proton removal.  
in: European Molecular Biology Organization (EMBO) Journal. - 27 (2008) 782-791