S.2.8 Substitution of ILE L177 by His in Rhodobacter sphaeroides reaction center affects interaction of BCHL molecule with the surrounding protein environment

Tatiana Y. Yufina, Lyudmila G. Vasilieva, Ravil A. Khaytopov, Vladimir A. Shivalent
Institute of Basic Biological Problems, Russian Academy of Sciences, Pushchino, Moscow Region, Russia
E-mail: Tat-yufina@yandex.ru

In photosynthetic organisms the conversion of light energy takes place in the membrane-bound pigment–protein complex termed reaction center (RC). It is known that all RC cofactors interact with surrounding protein by relatively weak contacts and so can be easily extracted by organic solvents. In R. sphaeroides RC the isoleucine L177 was substituted by histidine. Our results show that placement of His in the vicinity of P86 and B89 bacteriochlorophyll (BChl) molecules strongly affects the spectral properties of the RC. The RC L (L177)H was found to be active in charge separation with the absorption bands of the monomer BChls being clearly resolved. In contrast, in the spectra of membrane-bound RCs H (L153)M and H (L153)C were essentially the same as those of the WT RCs with the absorption bands of the monomer BChls being clearly resolved. The results of the pigment analysis confirm that the B89 molecule is missing in the H(L153)Y RC. Nevertheless, being associated with photosynthetic membranes, these RCs were able to accomplish the photochemical charge separation showing quantum yield approximately 7% comparing to that of the WT RCs.

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S.2.9 Hydrogencarbonate is not a structural part of the Mn4O2Ca cluster in photosystem II

Dmitriy Shevela, Ji-Hu Su, Vyacheslav Klimov, Johannes Messinger

Since the end of the 1950s hydrogencarbonate (‘bicarbonate’) is discussed as a possible cofactor of photosynthetic water-splitting, and in a recent x-ray crystallography model of photosystem II (PSII) it was displayed as a ligand of the Mn4O2Ca cluster. In this study, we provide strong evidence that hydrogencarbonate (‘bicarbonate’) is not a tightly bound ligand to the water oxidizing complex (WOC) of PSII. This is demonstrated by performing formate and NH2OH additions into PSII samples and simultaneously monitoring the released gaseous products by membrane-inlet mass spectrometry (MIMS). The addition of formate into the PSII samples induces the release of ~0.3 HCO3− per reaction center of PSII. Employing Mn-depleted PSII samples we show that formate does not replace HCO3− from the donor side, but only from the acceptor side of PSII. In contrast, a reductive destruction of the Mn4O2Ca cluster inside the MIMS cell by NH2OH addition does not lead to any CO2/HCO3− release. This indicates the absence of a firmly bound HCO3− to the WOC. We therefore conclude that HCO3− has only ‘indirect’ effects on water-splitting in PSII, possibly by being part of a proton relay network and/or by participating in assembly of the WOC.

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S.2.10 A glimpse into the atomic structure of plant photosystem I ~ 3.5 billion years of perfection

Nathan Nelson
Department of Biochemistry, The George S. Wise Faculty of Life Sciences, The Daniella Rich Institute for Structural Biology, Tel Aviv University, Tel Aviv, Israel
E-mail: nelson@post.tau.ac.il

Photosystem I (PSI) emerged as a homodimeric structure containing several chlorophyll molecules over 3.5 billion years ago, and has perfected its photoelectric properties ever since. The recently determined structure of plant PSI, which is at the top of the evolutionary tree of this kind of complexes, provided the first relatively high-resolution structural model of a super-complex containing a reaction center (RC) and a peripheral antenna (LHCl). The RC is highly homologous to that of the cyanobacterial PSI and maintains the position of most transmembrane helices and chlorophylls during the last 1.5 years of separate evolution. The LHCl is composed of four nuclear gene products (Lhca1–Lhca4) that are unique among the chlorophyll a/b binding proteins in their pronounced long-wavelength absorbance and their assembly into dimers. The current crystal structure provides a picture at near atomic detail of 16 of the 17 protein subunits with an additional subunit (PsaN) being identified for the first time on the luminal side of the supercomplex. The positions of about 3000 amino acids were demonstrated that the attached bacteriochlorophyll is one of the special pair molecules was missing in the acetone – methanol extract of the I

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