

AN EVOLUTIONARY AND COMPARATIVE VIEW OF THE PHOTOSYSTEMS

A. William Rutherford

iBITEC-S, URA CNRS 2096, CEA Saclay, Gif-sur-Yvette F-91191, France alfred.rutherford@cea.fr

The understanding of the photosynthetic reaction centres has benefited greatly from the comparative approach. The diverse bacterial reaction centres provided many useful insights for dealing with the complexities of the plant (algal and cyanobacterial) reaction centres, “the photosystems”. This kind of thinking was extended to an evolutionary view and this proved useful as a constant additional constraint for understanding features of the photosystems. Specific predictions were made that were proved correct by subsequent physical measurements (spectroscopy and crystallography) [1-4]. The main features of the cofactors (their chemical natures, positions, geometries and environments), some of the amino acids around the cofactors and the basic protein structures were established years before crystallographic models became available.

In the current era of crystallographic models, many aspects of the function of the photosynthetic reaction centres remain to be understood. Here again comparative and evolutionary approaches provide insights. In this talk I will review the features of the reaction centres with a focus on the evolutionary view. I will try to explain the features of the different reaction centres in an evolutionary context. For this I will focus on Photosystem II, the water oxidising enzyme, the most complicated reaction centre and arguably the most important reaction centre in terms of its impact on the biosphere and atmosphere.

Photosystem II (PSII) seems to have evolved from an ancestor that was homodimeric in terms of its protein core and contained a special pair of chlorophylls as the photo-oxidisable cofactor. We proposed that one key event in the evolution of PSII was a mutation that resulted in the separation of the two pigments that made up the special chlorophyll pair, making them into two chlorophylls that were neither special nor paired. These two chlorophylls, along with the two adjacent monomeric chlorophylls, were very oxidising, a property proposed to be intrinsic to monomeric chlorophylls in the environment provided by reaction centre proteins. Other (electrostatic) changes in the environments of the pigments also contributed to further increasing their redox potentials allowing water oxidation and oxygen evolution. The highly oxidising homodimeric reaction centre would probably have been not only inefficient in terms of photochemistry and charge storage but also wasteful in terms of protein and/or pigments undergoing damage due to the oxidative chemistry. These problems would have constituted selective pressures in favour of the lop-sided, heterodimeric system that exists as PSII today, in which the highly oxidised species are limited to only one side of the heterodimer: the sacrificial, rapidly turned-over D1 protein [4].

[1]Nitschke, W. and Rutherford A. W. (1991) *Trends in Biochem. Sci.* 16, 241-245. Photosynthetic reaction centres variations on a common structural theme?

[2]Rutherford A. W. and Nitschke W. (1996) in *"Origin and Evolution of Biological Energy Conversion"* (Baltcheffsky H. ed) VCH New York pp 143- 173 Photosystem II and the quinone -iron -containing reaction centers: comparisons and evolutionary perspectives.

[3]Nitschke W., Mattioli T. and Rutherford A. W. (1996) in *Origin and Evolution of Biological Energy Conversion* (Baltcheffsky H.) VCH New York. pp.177-203 The FeS-Type Photosystems and the Evolution of Photosynthetic reaction center

[4]Rutherford, A. W. and Faller P. (2003) *Philosophical Trans* 358, 245-253 Photosystem II: evolutionary perspectives