Chapter 15

Side-Path Electron Donors: Cytochrome $b_{559}$, Chlorophyll Z and β-Carotene

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Summary

β-Carotene (Car), cytochrome (Cyt) b599 and a monomeric chlorophyll (Chl) designated as chlorophyll Z, all undergo oxidation in Photosystem (PS) II under some illumination conditions. These components are not part of the direct electron transfer that leads to water oxidation and plastoquinone reduction and are thus designated ‘side-path electron donors.’ Under the usual conditions of PS II function, the quantum yield for the oxidation of these components is low; however, under certain experimental conditions, particularly low temperatures, the dominant reactions can be those involving the side-path donors. Car is a branch point in the side-path electron donation, being oxidized by P+ (the kinetically competent Chl cation radical), and reduced by Cyt b599, which is itself reduced by electrons from the pool of plastoquinol, possibly through the Q0 site. This all occurs on the D2-side of the reaction center. When the Cyt b599 is pre-oxidized, Car+ is reduced by Chl Z. There are two candidates for Chl Z, the more obvious candidate on the D2 side and the less straightforward candidate on D1 side of the reaction center. The side-pathway is usually rationalized as a photoprotective cycle aimed at removing long-lived P+ and thus limiting oxidative damage. Based on the low quantum yields, we consider this unlikely. Instead we suggest that the side-path constitutes a photoprotective cycle in which the aim is to reduce the Car cation, rather than P+, returning the carotene cation to its unoxidized state, preventing adventitious reactions and allowing it to play its role as a singlet O₂ quencher in the heart of PS II.

I. Introduction

Photosystem II (PS II) is a photochemical enzyme that uses light to drive the reduction of plastoquinone and the oxidation of water. The structure and function of PS II has been extensively reviewed (Goussias et al., 2002; Rappaport and Diner, 2002; Chapters 18–21). Several components have been shown to be oxidized in PS II other than the components directly associated with water oxidation. Cytochrome b599 (Cyt b599), a chlorophyll Z (Chl Z), β-carotene (Car) have all been reported as ‘side-path’ electron donors in PS II. Understanding the side-path donors, their nature, structure, position, how they work and their significance to PS II function are all important for several reasons. First, these species may play roles in the regulation and protection of the reaction center (RC)

Abbreviations: BRC—bacterial reaction center; Car—redox active β-carotene; Carα3 – β-carotene associated with D2; Carα3,41 – β-carotene associated with both D2 and C443; Chl Z – side-path redox-active Chl; Chl – chlorophyll; Chlα3, Chlα4 – monomeric Chls that are bound to D1 and D2, respectively; Cyt b599 – cytochrome b599, D1, D2 – reaction center core proteins; ENDOR – electron nuclear double resonance; EPR – electron paramagnetic resonance; ESEEM – electron spin echo envelope modulation; FTIR – Fourier transform infrared; HYSCORE – hyperfine sub-level correlation spectroscopy; OEC – oxygen evolving complex; P – central cluster of Chls that comprise the primary electron donor; P680, P680 – two monomeric Chls associated with D1 and D2, respectively, that are counterparts to the special pair Chls in the BRC; PS II – Photosystem II; Qa, Qb – primary and secondary plastoquinone electron acceptors; Yc, Yd – redox-active tyrosines bound to D1 and D2, respectively.

II. Location of Accessory Electron Donors

A scheme of the structure of PS II is shown in Fig. 1. This is based on the refined 3.5 Å X-ray diffraction crystal structure (Zouni et al., 2001; Kamiya and Shen, 2003; Ferreira et al., 2004) but is similar in most respects to earlier models that were based on the structure of the purple bacterial reaction center (BRC), comparative spectroscopy, sequence analysis