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Review article

Dithiol disulphide exchange in redox regulation of chloroplast enzymes in response to evolutionary and structural constraints

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ABSTRACT

Redox regulation of chloroplast enzymes via disulphide reduction is believed to control the rates of CO_2 fixation. The study of the thioredoxin reduction pathways and of various target enzymes lead to the following guidelines:

i) Thioredoxin gene content is greatly higher in photosynthetic eukaryotes compared to prokaryotes;
ii) Thioredoxin-reducing pathways have expanded in photosynthetic eukaryotes with four different thioredoxin reductases and the possibility to reduce some thioredoxins via glutaredoxins;
iii) Some enzymes that were thought to be strictly linked to photosynthesis ferredoxin-thioredoxin reductase, phosphoribulokinase, ribulose-1,5-bisphosphate carboxylase/oxygenase, sedoheptulose-1,7-bisphosphatase are present in non-photosynthetic organisms;
iv) Photosynthetic eukaryotes contain a genetic patchwork of sequences borrowed from prokaryotes including α–proteobacteria and archaea;
v) The introduction of redox regulatory sequences did not occur at the same place for all targets. Some possess critical cysteines in cyanobacteria, for others the transition occurred rather at the green algae level;
vi) Generally the regulatory sites of the target enzymes are distally located from the catalytic sites. The cysteine residues are generally not involved in catalysis. Following reduction, molecular movements open the active sites and make catalysis possible;
vii) The regulatory sequences are located on surface-accessible loops. At least one instance they can be cut out and serve as signal peptides for inducing plant defence.

Contents

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1. Principles of redox regulation of chloroplast enzymes via dithiol-disulphide exchange, what are the actors, what are the targets?

1.1. Diversification of the electron donor systems

Redox regulation by dithiol-disulphide exchange reactions together with the thiol-dependent repair systems (peroxiredoxins (PRX) and methionine sulfoxide reductases (Msr)) is getting ever more attention in all biological systems, but it is clearly in plants and especially in land plants that these processes have become amazingly diversified [1–5]. Ubiquitously present, thioredoxin proteins (TRX) are central to those reactions. They have unmatched ability to reduce (and oxidize) disulphide bonds on target enzymes/proteins that perform reduction reactions. TRX are then reduced at the expense of NADPH via an NADPH-dependent thioredoxin reductase (NTR) in bacteria [6]. The situation is quite similar in animal/mammalian cells with NADPH as the primary electron provider and NTR as a signal transmitter. However, as animal cells evolved multiple compartments, the reducing systems became more diversified with the existence of both cytosolic and mitochondrial systems. In animal cell cytosolic and mitochondrial NTR components are modified by a C-terminal extension possessing a selenocysteine. All animal NTRs have similar properties forming a homodimer with FAD and a redox active selenosulfide together with a disulphide in each subunit. One complication with mammalian thioredoxin reductase genes is their capacity to undergo differential exon splicing leading to the generation of multiple forms of the enzyme in both compartments [7]. Conversely, plants are even more complicated than animal or fungal cells, possessing an extra compartment, the chloroplast which performs oxygenic photosynthesis. Accordingly, currently four different TRX reduction pathways have been described in plant cells [8]. Two of those are similar to those found in animal cells i.e. mitochondrial and cytosolic NTR-based systems. There is though a major difference; NTRs in cytosolic and mitochondrial land plant are of the prokaryotic type, containing the disulphide and FAD but lacking the C-terminal extension and the selenocysteine residue. Selenocysteines are not present in photosynthetic eukaryotes after the green algae lineage [9]. The two other TRX reduction systems are located in the chloroplast; one of these is called NTRC and it is actually a variant of the prokaryotic NTR with a built-in TRX domain in the C-terminus [10–12]. The other is the ferredoxin-thioredoxin system consisting of a redox cascade involving the photosystems, and the following stromal components: ferredoxin (FDX), ferredoxin-thioredoxin reductase (FTR) and chloroplast-located TRXs [13,14]. FTR is a heterodimer with a so called "variable subunit", with a likely protective task [15], and a somewhat larger and more conserved catalytic subunit. The catalytic subunit bears both a [4Fe-4S] centre and the catalytic disulphide. Those four reduction pathways in land plants are schematized in Fig. 1, providing also a list of chloroplast target enzymes for which molecular structural details are available and which will be discussed later in more detail in this review.

1.2. The complex TRX gene family of plants

The diversification of the TRX reductions modes is not the only significant difference between plant cells and other organisms. One additional indicator is the number of TRX genes. Strictly speaking, a TRX should bear a WCGPC redox-active site although WCPPC signature can be quite frequent especially in plants, but other more deviant motifs can also be found [16,17]. Anyway, when considering only the classical (and more numerous) WCGPC containing TRXs, bacterial and animal species contain but only few of those (1–3 sequences on average) [2,18], while land plants have a large content of those genes (nearly 20 on average) with an unequal distribution between compartments with most in chloroplasts (*f*, *m*, *x*, *y*, *z* isoforms) or cytosol (*h* isoforms), whilst mitochondria contain *h* and *o* isoforms [3,5,19]. The expansion of the diversity of TRX genes in plants is not unique to this antioxidant protein. It is even more enhanced for its cousin protein glutaredoxin (GRX) with more than 40 genes of that category in plant genomes, some of them unique to land plants [20]. The reasons for this remarkable enhanced diversity of proteins of the broad redoxin lineage will be discussed in a later section. It is, however, of interest to note that there are connections between the TRX and GRX systems and at least one plant TRX is reduced by a GRX system. It can also be palmitoylated and has the capacity to move from cell to cell [21,22]. Likewise, there are proteins clearly more related phylogenetically to TRXs but with non-canonical active sites which in reality are reduced by glutathione (GSH) and behave as GRXs [17]. The complex interplay between the TRX and GRX systems has been described in a number of recent reviews [3,4,23,24] and recent paper discuss how FTR and NTRC systems can back up one another and, as a consequence, the analysis of mutants of the regulatory cascades needs to be done with circumspection [25–27].

2. Why did redox regulation via dithiol reduction appear?

As noted above, two indicators reflect the expansion of the redox networks in land plants, i.e. the diversification of the reduction routes and the expansion and diversification of the TRX and GRX genes. Actually, a third criterion can be added to that list: the appearance of enzyme target sequences containing critical disulphides needed for ON/OFF regulation in chloroplasts. During the dark phase, plastid enzymes are generally under an oxidized state and turn out inactive whereas in the light phase, enzymes are rather in reduced form and are active. In contrast, plastid glucose