Hyperoxide detoxication

Various families of enzymes participate in the detoxification of reactive oxygen species (ROS) and in particular hydroperoxides.

Superoxide dismutases (SOD) catalyze the transformation of the superoxide anion $O_2^{\cdot -}$ into hydroperoxide H_2O_2 characterized by the metal present in their active site. They have been identified in chloroplasts (CuZn-SOD thylakoidal, Fe-SOD stromatic), in mitochondria (Mn-SOD), in peroxisomes (CuZn-SOD) and in the cytosol (CuZn-SOD).

Catalases (CAT), especially in peroxisomes and glyoxysomes, can also dismutate H_2O_2 into H_2O and O2.

Other enzymes that detoxify H_2O_2 hydroperoxide participate in cycles involving ascorbate and glutathione such as the **ascorbate-glutathione cycle** (AGC) or **redoxin-like** enzymes.

1. Ascorbate-glutathione cycle (AGC)

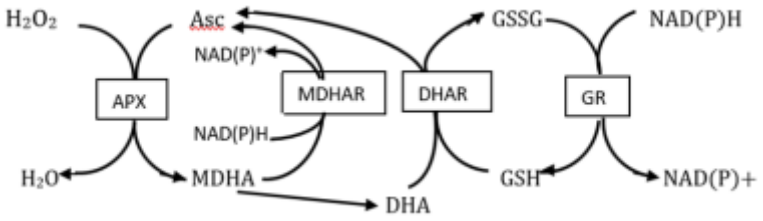

Figure 1: Ascorbate-Glutathione or Halliwell-Asada-Focus cycle. APX: Ascorbate peroxidase; Asc: Ascorbate; DHA: Dehydroascorbate; DHAR: Dehydroascorbate reductase; GR: Glutathione reductase; GSH: Reduced Glutathione; GSSG: Oxidized Glutathione; MDHA: Monodehydroascorbate; MDHAR: Monodehydroascorbate reductase. [Source: author's diagram]

The essential role of ascorbate and glutathione results from their participation in the ascorbate-glutathione cycle (AGC), also known as the Halliwell-Asada-Foyer cycle, after the scientists who identified it (Figure 1).

This mechanism, which includes the enzymes ascorbate peroxidase (APX), monodehydroascorbate reductase (MDHAR), dehydroascorbate reductase (DHAR), and glutathione reductase (GR), is present in chloroplasts, cytosol, and mitochondria. The functioning of the cycle, which detoxifies the hydroperoxide H_2O_2, depends on the reducing molecule NAD(P)H.

2. Detoxification by redoxin enzymes

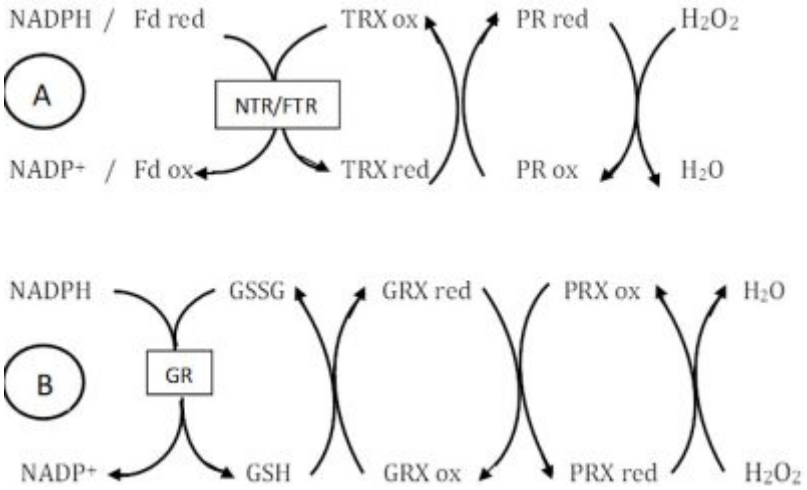

Figure 2. H_2O_2 hydroperoxide detoxification systems. A. Chloroplastic system involving peroxiredoxin and thioredoxin and operating either with membrane ferredoxin or stromatic NADPH. B. Cytosolic system working with peroxiredoxin and the glutaredoxin/glutathione couple. Fd: Ferredoxin; FTR: Ferredoxin thioredoxin reductase; GR: Glutathione reductase; GRX: Glutaredoxin; GSH: Reduced glutathione; GSSG: Oxidized glutathione; NTR: NADPH thioredoxin reductase; PRX: Peroxiredoxin; TRX: Thioredoxin. [Source: author's diagram]

Redoxins, thioredoxins (TRX), glutaredoxins (GRX) and peroxiredoxins (PRX), found in chloroplasts, mitochondria and cytosol, play an important role in detoxification processes. Figure 2 shows two examples of their function, one in the chloroplast with the TRX/PRX association (Figure 2A), the other in the cytosol with the GRX/Glutathione association (Figure 2B). In the chloroplast, two systems, thioredoxin (TRX) and peroxyredoxin (PRX), coexist, one membrane-based and involving PSI ferredoxin, the other stromatic and involving NADPH delivered during photochemical reactions.
