Structure of FoxE, the Rhodobacter ferrooxidans SW2 putative iron oxidase

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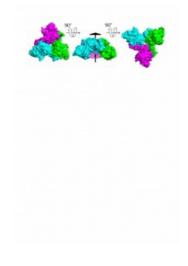
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The ancient metabolism of photoferrotrophy is likely to have played a key role in the biogeochemistry of iron on Early Earth, leading to the deposition of banded iron formations prior to the emergence of oxygenic photosynthesis. Extant organisms still performing this metabolism provide a convenient window to peer into its molecular mechanisms.

The freshwater purple bacterium Rhodobacter ferroxidans SW2 was one of the first photoferrotrophs to be isolated. It is a bacterium containing the operon foxEYZ that was shown to be involved in iron oxidation. The first gene of this operon, foxE, encodes a periplasmatic c-type diheme cytochrome predicted to be the iron oxidoreductase. FoxE was biochemically characterized [1], diffracting crystals were obtained [2] and we present here its crystal structure, determined at 2.5 Ang resolution. The FoxE structure is organized as a trimer with two hemes and a disulfide bridge per monomer. The distance between hemes, their solvent exposure and the surface electrostatics ensure a controlled electron transfer rate. They also guarantee segregation between electron capture from ferrous iron and electron release to downstream acceptors, which do not favour the precipitation of ferric iron. Combined with the functional characterization of this protein, the structure reveals how iron oxidation can be performed in the periplasmic space of this Gram-negative bacterium at circumneutral pH, while minimizing the risk of mineral precipitation and cell encrustation.

[1] Saraiva, I.H. et al. (2012). J. Biol. Chem. 287, 25541-25548.

[2] Pereira, L. et al. (2012). Acta Cryst. F68, 1106-1108.



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