Living on sulfur: 3D architecture and spectroscopy of the iron-sulfur enzymes APS reductase and dissimilatory sulfite reductase

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In nature sulfur is less abundant than oxygen, with elemental sulfur (S^o), sulfate (S^{+6}) and sulfide (S^{-2}) as the most prominent forms. The reduction of sulfate to sulfide, and the reverse reaction, are widespread biological processes. Hereby, microorganisms play a central role. Plants also reduce sulfate for the purpose of biosynthesis, and both animals and plants oxidize reduced sulfur compounds to sulfate.

Sulfate respiration is used for energy conservation by strictly anaerobic bacteria and archaea [1]. The redox equivalents generated by the oxidation of organic compounds are transferred to sulfate as the terminal electron acceptor. There are three key enzymes localized in the cytoplasm or at the cytoplasmic aspect of the inner membrane: ATP-sulfurylase (ATPS), adenosine-5'-phosphosulfate reductase (APSR), and dissimilatory sulfite reductase (SIR). Because of its unfavorable redox potential, sulfate cannot be directly reduced by H_2 or organic acids, and has to be activated to APS catalyzed by ATPS. The enzyme APSR (cofactors FAD, [4Fe-4S]) catalyzes the conversion of APS to sulfite (S^{+4}) and AMP [2], followed by the highly complex enzyme SIR (cofactors siroheme, [4Fe-4S]) which catalyzes the 6e-reduction of sulfite (S^{+4}) to sulfide (S^{-2}).

In this contribution we will focus on the 3D structures of APSR and of catalytically relevant reaction intermediates [2,3]. Furthermore, we will report for the first time on the novel structure of dissimilatory SIR from hyperthermophilic *Archaeoglobus fulgidus* [3]. Finally, spectroscopic (EPR) and mechanistic aspects of both multi-component enzymes will be presented.

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