Sulfur Metabolism in Phototrophic Bacteria

Christiane Dahl

Abstract Sulfur is one of the most versatile elements in life due to its reactivity in different oxidation and reduction states. In contrast to the assimilatory provision of sulfur-containing cell constituents that is found in most taxonomic groups, dissimilation is restricted to prokaryotes and serves energy-yielding processes where sulfur compounds are donors or acceptors of electrons. In many anoxygenic phototrophic bacteria, reduced sulfur compounds play a prominent role as electron donors for photosynthetic carbon dioxide fixation. This process is especially characteristic for the green sulfur bacteria (GSB) and the purple sulfur bacteria (PSB). *Allochromatium vinosum* and *Chlorobaculum tepidum*, representatives of the PSB and GSB, respectively, are the workhorses for detailed elucidation of sulfur oxidation pathways. Genes identified in these organisms served as the basis of a genome-based survey of the distribution of genes involved in the oxidation of sulfur compounds in other genome-sequenced anoxygenic phototrophs. These analyses show that dissimilatory sulfur metabolism is very complex and built together from various modules encoding different enzymes in the different organisms. Comparative genomics in combination with biochemical data also provide a clear picture of sulfate assimilation in anoxygenic phototrophs.

Keywords Sulfur metabolism • Purple sulfur bacteria • Sulfur globules • Sulfide • Thiosulfate • Tetrathionate • Sulfate • *Allochromatium vinosum* • Green sulfur bacteria • Sulfur oxidation • Assimilatory sulfate reduction

Introduction

Sulfur exhibits high reactivity in reduced forms and occurs in several stable oxidation states. Sulfate or sulfide in water and soil and sulfur dioxide in the atmosphere constitute the majority of sulfur in nature (Middelburg 2000). Smaller but significant roles are played by polysulfide, polythionates, thiosulfate, sulfoxides, as well

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as elemental sulfur. Sulfur is the element with the highest number of allotropes but only a few occur in biological systems. Sulfur appears in all organisms in many different organic compounds such as amino acids, enzyme cofactors, (poly)peptides, sulfolipids, vitamins, or carbohydrates. The biological roles of inorganic sulfur compounds are comparatively restricted: (1) They can serve as sources for sulfur assimilation and incorporation into the abovementioned organic compounds. (2) They can be employed as donors or acceptors of electrons for energy-generating electron transport. Dissimilatory sulfur-based energy generation goes along with mass transformations and occurs almost exclusively among prokaryotes, while assimilatory sulfur metabolism is not only very common in prokaryotes but also occurs in plants, algae, and fungi.

In oxygenic phototrophic organisms, the redox properties of sulfur-containing metabolites and of sulfur in proteins are very important for the interplay between the reductive assimilative processes of photosynthesis and reactive oxygen species that are formed as side products of photosynthetic electron transport (Dahl et al. 2008b). In anoxygenic phototrophic bacteria, reduced sulfur compounds can play a particularly important role as electron donors for photosynthetic carbon dioxide fixation. In fact, the utilization of sulfur compounds is common to almost all groups of phototrophic prokaryotes: certain species of the cyanobacteria can perform anoxygenic photosynthesis at the expense of sulfide as an electron donor (Arieli et al. 1991, 1994; Shahak and Hauska 2008). A few representatives of the strictly anaerobic Gram-positive heliobacteria as well as members of the filamentous anoxygenic phototrophic (FAP) bacteria of the phylum *Chloroflexi* are able to oxidize reduced sulfur compounds, thiosulfate oxidation is widespread among the photoheterotrophic aerobic anoxygenic phototrophic bacteria, and many of the classical purple non-sulfur bacteria can use thiosulfate and/or sulfide as electron donors. Utilization of reduced sulfur compounds is best known and studied for the purple (families *Chromatiaceae* and *Ectothiorhodospiraceae*) and green sulfur bacteria (phylum *Chlorobi*).

In this chapter the sulfur-oxidizing capabilities of the various groups of phototrophic bacteria will be only briefly described. The reader is referred to a number of previous reviews that still provide valuable sources of information on sulfur compounds used by the various groups as well as on sulfur oxidation patterns (Brune 1989; Brune 1995b; Dahl 2008; Frigaard and Bryant 2008a, b; Frigaard and Dahl 2009; Gregersen et al. 2011; Sander and Dahl 2009). Here, I will focus on new developments arising from studies performed during the past 8–10 years that substantially broadened our knowledge of the biochemical details of the different sulfur oxidation pathways. In addition, a substantial number of additional genome sequences for purple sulfur bacteria became available that allows to draw additional information from comparative analyses of gene arrangements and occurrence. Transcriptomic profiling and comparative proteome analyses for phototrophic model organisms provide further crucial information resources (Eddie and Hanson 2013; Falkenby et al. 2011; Weissgerber et al. 2013, 2014a). A brief overview of assimilatory sulfate reduction metabolism will also be given. Organosulfur compound metabolism will not be dealt with here, and the reader is referred to information provided by others (Baldock et al. 2007; Denger et al. 2004, 2006; Kappler and Schäfer 2014; Visscher and Taylor 1993).

Sulfur Oxidation Capabilities of Phototrophic Bacteria

In the following section, the sulfur oxidation capabilities of the various groups of anoxygenic phototrophic bacteria are very briefly summarized.

Purple Sulfur Bacteria

Purple sulfur bacteria of the families *Chromatiaceae* and *Ectothiorhodospiraceae* preferentially use reduced sulfur compounds as electron donors during photolithoautotrophic growth. The most important difference between the two families is that C*hromatiaceae* produce intracellular sulfur globules when growing on sulfide, thiosulfate, polysulfides, or elemental sulfur, while the *Ectothiorhodospiraceae* accumulate extracellular sulfur. For one member of the *Ectothiorhodospiraceae*, *Thiorhodospira sibirica*, extra- as well as intracellular sulfur deposition has been reported (Bryantseva et al. 1999). All phototrophic members of the *Chromatiaceae* use sulfide and sulfur of the oxidation state zero as photosynthetic electron donors. Several species are limited to these compounds while a range of more versatile species uses several reduced sulfur compounds including thiosulfate and sulfite. Polysulfide oxidation is probably ubiquitous. This does not appear astonishing because polysulfides are formed as intermediates of the oxidation of sulfide en route to sulfur globules (Prange et al. 2004). Polysulfides are especially stable intermediates of sulfide oxidation by members of the *Ectothiorhodospiraceae* because these thrive under alkaline growth conditions which are essential for longer-term stability of polysulfides. Utilization of sulfide, elemental sulfur, and thiosulfate is common to the species of the genus *Ectothiorhodospira*, while species of the genera *Halorhodospira* and *Thiorhodospira* oxidize sulfide to sulfur which is further oxidized to sulfate by some species. Thiosulfate is used only by *Halorhodospira halophila* (Raymond and Sistrom 1969).

Green Sulfur Bacteria

GSB exhibit very little variation in their ability to oxidize sulfur compounds. Almost all members of this group oxidize sulfide and elemental sulfur to sulfate. The only exception is *Chlorobium ferrooxidans* for which only Fe^{2+} and hydrogen are suitable photosynthetic electron donors. In general, GSB have a very high affinity for sulfide, and it is the preferred sulfur substrate even in the presence of other reduced sulfur compounds. Typically, sulfide is first transformed into zero-valent sulfur which is deposited as extracellular sulfur globules. Some strains of the genera *Chlorobaculum* and *Chlorobium* can oxidize thiosulfate (Imhoff 2003), and one strain has been reported to be capable of tetrathionate utilization (Khanna and Nicholas 1982).

Purple Non-sulfur Bacteria

Purple non-sulfur bacteria are to a much lesser extent capable of tolerating and using toxic sulfur compounds such as sulfide than the PSB. The phototrophic *Betaproteobacteria* of the orders *Rhodocyclales* and *Burkholderiales* have not been reported to use reduced sulfur compounds as electron donors. Sulfide inhibits growth at low concentrations (Imhoff et al. 2005). In the genome of *Rubrivivax gelatinosus*, *sox* genes are present indicating the potential for thiosulfate oxidation (Sander and Dahl 2009). Sulfate can be reductively assimilated. Within the alphaproteobacterial purple non-sulfur bacteria, the ability to use reduced sulfur compounds is widespread. Intermediates and final products formed vary considerably between species. Complete oxidation of sulfide to sulfate has been described for several species (Frigaard and Dahl 2009; Imhoff et al. 2005; Sander and Dahl 2009). Thiosulfate is used by many species and either completely oxidized to sulfate or transformed into tetrathionate. Sulfur is also used as a substrate by some species (Sander and Dahl 2009).

Aerobic Bacteriochlorophyll-Containing Bacteria

Aside from cyanobacteria and proteorhodopsin-containing bacteria, aerobic anoxygenic phototrophic (AAP) bacteria are the third most numerous group of phototrophic prokaryotes in the ocean. This functional group represents a diverse assembly of species which taxonomically belong to various subgroups of *Alpha-*, *Beta-*, and *Gammaproteobacteria*. AAP bacteria are facultative photoheterotrophs which use bacteriochlorophyll-containing reaction centers to harvest light energy under fully oxic in situ conditions (Koblizek 2015). Almost 60 strains of AAP are currently fully genome sequenced (tabulated in Koblizek 2015).

In general AAP bacteria cannot grow photolithoautotrophically on reduced sulfur compounds. However, many representatives of this physiological group can oxidize sulfur compounds as additional sources of electrons and grow as sulfur-oxidizing lithoheterotrophs. The ability for thiosulfate oxidation appears to be especially widespread (Sorokin et al. 2000; Yurkov et al. 1994). The genomes of many AAP bacteria contain the genes *soxB*, *soxAX*, *soxYZ*, and *soxCD* encoding a periplasmic thiosulfate-oxidizing multienzyme complex (Friedrich et al. 2005; Sander and Dahl 2009). A recent study furthermore revealed that *sox* genes are present mainly in those members of the widespread and ecologically very important OM60/NOR5 clade that also encode genes enabling aerobic anoxygenic photoheterotrophy, like *Congregibacter litoralis* (*C. litoralis*) DSM 17192^T, *Congregibacter* sp. strain NOR5-3, or *Luminiphilus syltensis* DSM 22749^T (Spring 2014). However, a stringent correlation of genes encoding Sox proteins and subunits of the photosynthetic apparatus was not apparent, because some bacteriochlorophyll *a*-containing strains do not encode Sox proteins.

Acidobacteria

The phylum *Acidobacteria*, a sister clade to the δ-*Proteobacteria* in the domain *Bacteria*, encompasses a large and physiologically diverse group of microorganisms (Ciccarelli et al. 2006). Recently, a phototrophic member of this group was described, *Chloracidobacterium thermophilum* (Bryant et al. 2007; Tank and Bryant 2015a, 2015b), the first aerobic chlorophototroph that has a type I, homodimeric reaction center (RC). Key genes for all known carbon fixation pathways are absent as are genes for assimilatory sulfate reduction. *Cab. thermophilum* is unable to use sulfate as a sulfur source and instead relies on reduced sulfur sources such as thioglycolate, cysteine, methionine, or thiosulfate. Cultures containing sodium sulfide did not show sustained growth, but microscopic analyses revealed that sulfur globules were produced. Similar to green sulfur bacteria, these globules remained associated with the outer surfaces of cells and suggested that sulfide oxidation occurred. The genome lacks any known enzymes for the oxidation of sulfide, so how sulfide oxidation occurs is not clear (Tank and Bryant 2015b).

Phototrophic Gemmatimonadetes

Very recently a BChl *a*-producing, semiaerobic anoxygenic photoheterotroph from the phylum *Gemmatimonadetes*, *Gemmatimonas phototrophica*, has been described (Zeng et al. 2014, 2015). Sulfur oxidation capabilities have not been reported. None of the genome-sequenced members of the *Gemmatimonadetes* contain *sox* genes.

Sulfur Oxidation Pathways

With regard to their sulfur metabolism, phototrophic bacteria are characterized by a great variability of sulfur substrates used and pathways employed. On a molecular genetic and biochemical level, sulfur oxidation is best described in the purple sulfur bacterium *Allochromatium vinosum* and in the green sulfur bacterium *Chlorobaculum tepidum*. An overview of the currently proposed model of sulfur oxidation in *A. vinosum* is shown in Fig. 1. The figure is based on a combination of biochemical evidence, genome sequence information, as well as whole genome transcriptomic profiling and comparative quantitative proteomics (Weissgerber et al. 2011, 2013, 2014a).

Many enzymes involved in sulfur metabolism can readily be identified in genome sequences by sequence homology with known enzymes. The genome sequences of 15 strains of GSB have already been available for several years, and the occurrence of genes related to sulfur oxidation in these organisms has already been extensively tabulated and discussed (Frigaard and Bryant 2008b; Frigaard and Dahl 2009; Gregersen et al. 2011; Venceslau et al. 2014). A greater number of genome sequences

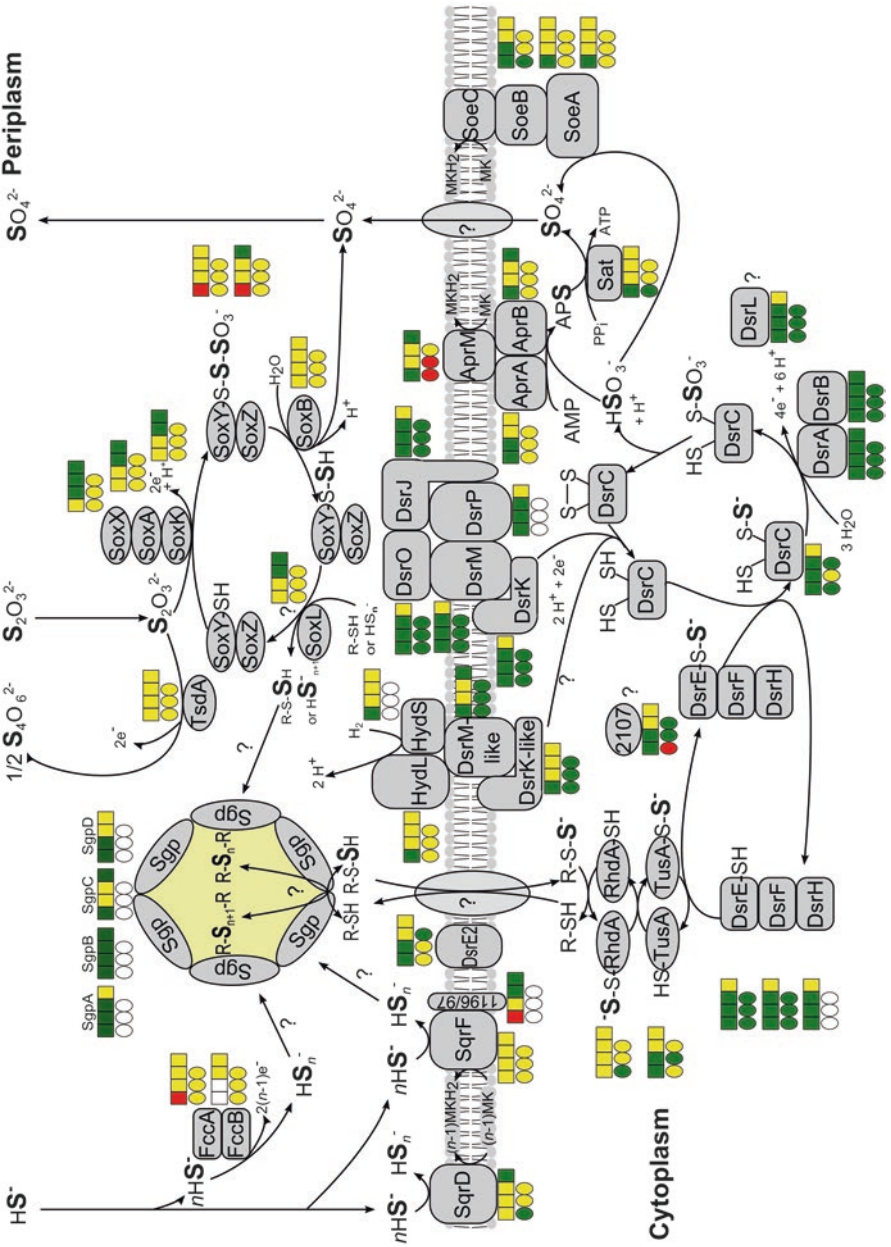

Fig. 1 Current model of sulfur oxidation in *Allochromatium vinosum* (Figure taken from Weissgerber et al. 2014a) (Copyright © American Society for Microbiology, Applied and Environmental Microbiology 80, 2014, 2279–92, doi: 10.1128/AEM.04182–13). The proteomic profiles (*circles*) and transcriptomic profiles (*boxes*) are depicted next to the respective proteins. Relative fold changes in mRNA levels above 2 (*green*) were considered significant enhancement. Relative changes smaller than 0.5 (*red*) were considered to indicate significant decreases in mRNA levels. Relative fold changes between 0.5 and 2 (*yellow*) indicated unchanged mRNA levels.

for purple sulfur bacteria only became available over the last few years (Table 1). This chapter will therefore focus on analyzing this comparatively new set of sequence information.

Oxidation of Thiosulfate

Thiosulfate ($S_2O_3^{2-}$) oxidation is conducted by a large number of photo- and chemotrophic sulfur-oxidizing bacteria. In general, two completely different pathways can be differentiated. In the first, two thiosulfate anions are oxidized to tetrathionate. In the second, catalyzed by the periplasmic Sox multienzyme system (Dahl et al. 2008a; Friedrich et al. 2001), multiple steps lead to complete oxidation to sulfate. In some bacteria including *A. vinosum* both pathways coexist (Hensen et al. 2006; Smith and Lascelles 1966). The occurrence of genes related with the two pathways in purple sulfur bacteria is summarized in Table 2.

Oxidation of Thiosulfate to Tetrathionate

The ability to perform the very simple oxidation of two molecules of thiosulfate to tetrathionate according to the equation $2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-}+2e^-$ is widespread among prokaryotes. The reaction is not only well-established intermediate step in the oxidation of reduced sulfur compounds to sulfate in many obligately chemolithoautotrophic bacteria (Lu and Kelly 1988; Müller et al. 2004; Wentzien et al. 1994) but also known for some purple non-sulfur bacteria like *Rhodomicrobium vannieli* and *Rhodopila globiformis* and purple sulfur bacteria including *A. vinosum* (Frigaard and Dahl 2009; Hensen et al. 2006; Then and Trüper 1981).

Despite the well-documented significance of tetrathionate formation in aquatic and terrestrial habitats (Barbosa-Jefferson et al. 1998; Podgorsek and Imhoff 1999; Sorokin 2003), the membrane-bound *doxDA* encoding thiosulfate/quinone oxidoreductase from the thermoacidophilic archaeon *Acidianus ambivalens* was the only tetrathionate-forming enzyme characterized on a molecular level for a long time (Müller et al. 2004). Genes homologous to *doxDA* do not occur in phototrophic prokaryotes. Instead, a gene (*tsdA*) encoding a novel periplasmic 27.2 kDa diheme cytochrome *c* thiosulfate dehydrogenase was identified in *A. vinosum* (Denkmann et al. 2012). The crystal structure of the enzyme revealed two typical class I *c*-type

Fig. 1 (continued) The same color coding is applied to changes on the protein level. Here, values above 1.5 (*green*) and below 0.67 (*red*) were considered significant. Those cases where transcriptomic data were not available or the respective protein was not detected in the proteomic approach are indicated by *white squares or circles*. Changes are depicted that occurred upon a switch from photoorganoheterotrophic growth on malate to photolithoautotrophic growth on, from left to right, sulfide, thiosulfate, elemental sulfur, and sulfite. Changes on sulfite were not determined on the proteome level

Table 1 Genome-sequenced purple sulfur bacteria

Organism	Accession number	S^{2-}	S^0	$S_2O_3^{2-}$	Reference (genome or organism)
Chromatiaceae					
Allochromatium vinosum DSM 180^T	NC_013851, NC_013852, NC_013851	+	+	+	Weissgerber et al. (2011)
Thiorhodovibrio sp. 970	NZ_AFWS02000000	+	+	–	Unpublished
Lamprocystis purpurea DSM 4197	NZ_ARBC00000000	+	+	+	Imhoff (2001)
Thiocapsa marina 5811 DSM 5653^T	NZ_AFWV00000000	+	+	+	Caumette et al. (2004)
Thiocapsa sp. KS1	CVPF01000000	+	+	+	Unpublished
Thiohalocapsa ML1	GCA_001469165	+	+	+	Hamilton et al. (2014)
Thiorhodococcus sp. AK35	NZ_AONC01000000	+	+	+	Unpublished
Thiorhodococcus drewsii AZ1 DSM 15006^T	NZ_AFWT00000000	+	+	+	Zaar et al. (2003)
Thiocystis violascens DSM 198^T	NC_018012	+	+	+	Imhoff et al. (1998)
Marichromatium purpuratum 984 DSM 1591^T	NZ_CP007031	+	+	+	Imhoff et al. (1998)
Thioflaviococcus mobilis DSM 8321^T	NC_019940, NC_019941	+	+	–	Imhoff and Pfennig (2001)
Ectothiorhodospiraceae					
Halorhodospira halophila SL1 DSM 244^T	NC_008789	+	+	+	(Challacombe et al. 2013)
Halorhodospira halochloris str. A DSM 1059^T	CP007268	+	–	+	Singh et al. (2014)
Thiorhodospira sibirica ATCC 700588^T	NZ_AGFD00000000	+	+	–	Bryantseva et al. (1999)
Ectothiorhodospira haloalkaliphila ATCC 51935^T	NZ_AJUE00000000	+	+	+	(Imhoff and Süling 1996)
Ectothiorhodospira sp. PHS-1	AGBG00000000	nd	nd	nd	Kulp et al. (2008)

cytochrome domains wrapped around two hemes. Heme 1 exhibits His/Cys iron coordination and constitutes the active site of the enzyme (Brito et al. 2015). His/Cys heme iron ligation is rare among prokaryotes, usually leads to a low redox potential of the corresponding heme (Bradley et al. 2012; Kappler et al. 2008; Pires et al. 2006; Reijerse et al. 2007), and appears to be of special importance in sulfur-based energy metabolism. In the oxidized state, Heme 2 iron is axially ligated by a histidine and a lysine residue (Fig. 2). Upon reduction, a switch occurs at this heme

Table 2 Genes related to thiosulfate oxidation in genome-sequenced purple sulfur bacteria[a]

Organism	*soxBXAKL*	*soxYZ*	*tsdBA*
Chromatiaceae			
Allochromatium vinosum DSM 180^T	Alvin_2167–2171	Alvin_2111/12	Alvin_0091 (only *tsdA*)
Thiorhodovibrio sp. 970	–	Thi970DRAFT_01660	Thi970DRAFT_02035/36
Lamprocystis purpurea DSM 4197	WP_026199596, WP_020506632–36	WP_020506368/67	–
Thiocapsa marina 5811 DSM 5653^T	ThimaDRAFT_4579–75	ThimaDRAFT_0728/29, 3536–37	–
Thiocapsa sp. KS1	THIOKS1620009–14	THIOKS11770013/12	–
Thiohalocapsa ML1	WP_058554073–79	WP_058556710/09	–
Thiorhodococcus sp. AK35	D779_4156–52	D779_3946–47	D779_1816 (*tsdBA* fusion)
Thiorhodococcus drewsii AZ1 DSM 15006^T	ThidrDRAFT_2415–19	ThidrDRAFT_2534/35	ThidrDRAFT_3922 (*tsdBA* fusion)
Thiocystis violascens DSM 198^T	Thivi_2200, Thivi_3804–01	Thivi_3138/39	Thivi_3993 (*tsdBA* fusion)
Marichromatium purpuratum 984 DSM 1591^T	MARPU_05475–55	MARPU_13720/15	MARPU_02550 (*tsdBA* fusion)
Thioflaviococcus mobilis DSM 8321^T	–	–	Thimo_0460 (*tsdBA* fusion)
Ectothiorhodospiraceae			
Halorhodospira halophila SL1 DSM 244^T	Hhal_1939, Hhal_1948 (*soxXA* fusion), no *soxKL*	Hhal_1941/42	–
Halorhodospira halochloris str. A DSM 1059^T	M911_11275 (*soxB*), no *soxXAKL*	M911_11265/70	–
Thiorhodospira sibirica ATCC 700588^T	–	ThisiDRAFT_0337/36	–
Ectothiorhodospira haloalkaliphila ATCC 51935^T	WP_025282121 (*soxB*), no *soxXAKL*	No *soxY*, WP_025282120 (*soxZ*)	–
Ectothiorhodospira sp. PHS1	ECTPHS_10791, (*soxB*), no *soxXAKL*	ECTPHS_10801/796	–

[a]Genomes were analyzed by BLAST searches using the resources provided by Integrated Microbial Genomes (DOE Joint Genomes Institute, http://img.jgi.doe.gov) and GenBank (http://www.ncbi.nlm.nih.gov). Baits: SoxBXAKL (ADC63088–ADC63092), SoxYZ (SoxY, ADC63033; SoxZ, ADC63034), and TsdA (ADC61061) from *A. vinosum*, TsdB from *Thiomonas intermedia* (D5WYQ6)

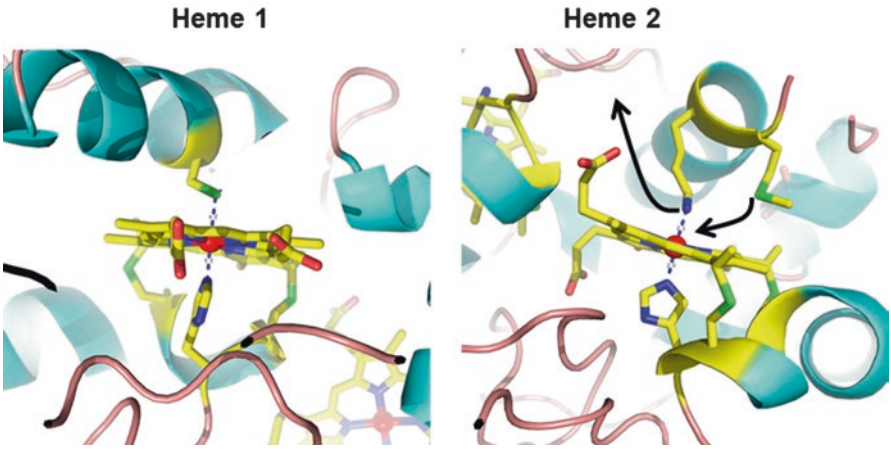

Fig. 2 Heme coordination of *A. vinosum* TsdA (Brito et al. 2015). *Left*: Heme 1 is coordinated by His^{53} and Cys^{96}. *Right*: Heme 2 is coordinated by His^{165} and Lys^{208}. Upon reduction, a ligand switch from Lys^{208} to Met^{209} occurs. Sulfur atoms are shown in *green*

from Lys to Met axial ligation. This change probably affects the redox potential of Heme 2 and may be an important step during the reaction cycle (Brito et al. 2015).

TsdA enzymes of various source organisms exhibit different catalytic bias (Kurth et al. 2015). While the enzyme from the sulfur oxidizer *A. vinosum* is strongly biased toward catalyzing thiosulfate oxidation (Brito et al. 2015), TsdA from *Campylobacter jejuni* acts primarily as a tetrathionate reductase and enables the organism to use tetrathionate as alternative electron acceptor for anaerobic respiration (Liu et al. 2013).

Currently it is largely unclear which redox carriers mediate the flow of electrons arising from thiosulfate oxidation into respiratory or photosynthetic electrons chains. In several organisms including *Thiomonas intermedia*, *Sideroxydans lithotrophicus*, and *Pseudomonas stutzeri*, *tsdA* is immediately preceded by a gene encoding another diheme cytochrome, TsdB (Denkmann et al. 2012). TsdB is not itself reactive with thiosulfate but accepts electrons from TsdA even when TsdA and TsdB do not originate from the same source organism (Denkmann et al. 2012). In the anoxygenic phototrophic purple sulfur bacterium *Marichromatium purpuratum*, TsdA and TsdB form a fusion protein with TsdB constituting the amino-terminal domain. TsdBA fusion proteins are also encoded in other members of the *Chromatiaceae*, e.g., *Thiorhodococcus* sp. AK35, *Thiocystis violascens*, *Thiorhodococcus drewsii*, and *Thioflaviococcus mobilis* (Table 2). However, TsdBA fusions are not a common trait in purple sulfur bacteria. In *A. vinosum*, a *tsdB* gene is not present (Denkmann et al. 2012). In *A. vinosum*, the protein with the closest relationship to *T. intermedia* or *P. stutzeri* TsdB is Alvin_2879. This cytochrome c_4 (previously cytochrome $c\text{-}_{553(550)}$) is membrane bound possibly via the hydrophobic protein Alvin_2880 and has a positive redox potential of +330 mV (Cusanovich and Bartsch 1969).

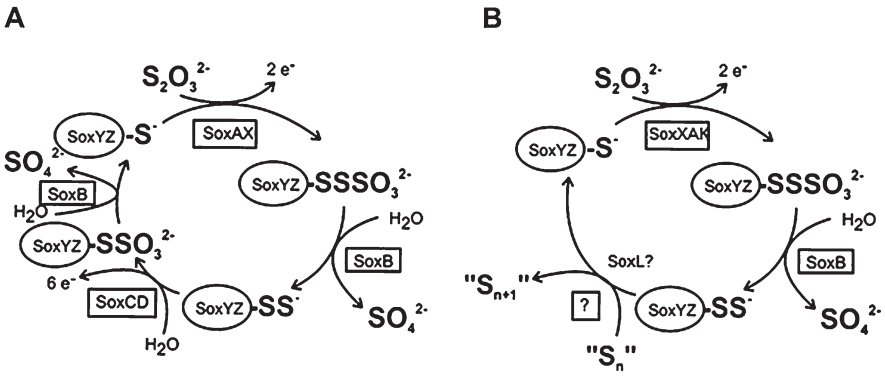

Fig. 3 Model of Sox-mediated thiosulfate oxidation in *Paracoccus pantotrophus* (*left*) and (**a**) *A. vinosum* (*right*). Adapted from (Sander and Dahl 2009). All reactions take place in the periplasm

Another candidate for accepting electrons from TsdA in purple anoxygenic phototrophic bacteria is the high potential iron-sulfur protein (HiPIP). *A. vinosum* and *M. purpuratum* produce HiPIP, and as this protein has a quite positive reduction potential (+350 mV) (Bartsch 1978), it would be well suitable as an electron acceptor for TsdA.

Oxidation of Thiosulfate to Sulfate

The Sox pathway of thiosulfate oxidation is a prime example for the oxidation of protein-bound sulfur atoms in the bacterial periplasm (Friedrich et al. 2001; Zander et al. 2010). Among the many organisms pursuing this pathway, some store sulfur globules as intermediates (e.g., *A. vinosum*), whereas others do not form sulfur deposits (e.g., *Paracoccus pantotrophus*). The Sox pathway in these two physiological groups appears to have one fundamental difference, and this is the involvement of the hemomolybdoprotein SoxCD (Fig. 3).

In non-sulfur-storing organisms, the proposed mechanism for sulfur oxidation requires four different proteins: SoxB, SoxXA, SoxYZ, and SoxCD (Friedrich et al. 2001). The heterodimeric SoxYZ protein acts as the central player and carries pathway intermediates covalently bound to a cysteine residue located near the carboxy-terminus of the SoxY subunit (Appia-Ayme et al. 2001; Quentmeier and Friedrich 2001; Sauvé et al. 2007). The *c*-type cytochrome SoxXA(K) catalyzes the oxidative formation of a disulfide linkage between the sulfane sulfur of thiosulfate and the cysteine of SoxY (Bamford et al. 2002; Ogawa et al. 2008). The sulfone group is then hydrolytically released as sulfate in a reaction catalyzed by SoxB (Sauvé et al. 2009). The next step is oxidation of the SoxY-bound sulfane sulfur to a sulfone by the hemomolybdoprotein SoxCD and again hydrolytic release of sulfate (Zander et al. 2010).

In those organisms forming sulfur as an intermediate, SoxCD is not present and the SoxY-bound sulfane sulfur is transferred to zero-valent sulfur stored in sulfur globules residing in the periplasm by an unknown mechanism, possibly involving the rhodanese-like protein SoxL (Welte et al. 2009). In *A. vinosum, sox* genes are present in two clusters (*soxBXAKL*, Alvin_2167 to 2171, and *soxYZ*, Alvin_2111 and 2112) with *soxBXA* and *soxYZ* being indispensable for thiosulfate oxidation (Hensen et al. 2006). The protein encoded by *soxK* has been identified as a subunit of a SoxXAK complex in the green sulfur bacterium *Chlorobaculum tepidum* (Ogawa et al. 2008) and probably fulfills the same function in purple sulfur bacteria.

Oxidation of Sulfide

Different enzymes are candidates for sulfide oxidation: sulfide/quinone oxidoreductases (SQR) (Schütz et al. 1997) and a flavocytochrome *c* sulfide dehydrogenase (FccAB) (Chen et al. 1994; Meyer and Cusanovich 2003) (Table 3). In *Rhodovulum sulfidophilum*, a member of the *Rhodobacteraceae*, the Sox system is not only essential for thiosulfate oxidation but also indispensable for the oxidation of sulfide in vivo (Appia-Ayme et al. 2001). The same might well be the case for other non-sulfur bacteria containing *sox* genes. In *A. vinosum* mutants deficient in either flavocytochrome *c* (Reinartz et al. 1998), *sox* genes (Hensen et al. 2006), or both (D. Hensen, B. Franz, C. Dahl, unpublished), sulfide oxidation proceeds with wild-type rates indicating that SQR plays the major role.

All characterized SQRs are single-subunit flavoproteins associated with the cytoplasmic membrane (Marcia et al. 2009, 2010b; Shahak and Hauska 2008). Based on the protein structure, six distinct SQR types were identified (Marcia et al. 2010a). Here, the nomenclature suggested by Frigaard and coworkers is followed (Gregersen et al. 2011) to clearly identify the multiple types of *sqr* genes often found in the same organism (Table 3). Members of types SqrA, SqrB, SqrC, SqrE, and SqrF have been biochemically characterized (Arieli et al. 1994; Brito et al. 2009; Cherney et al. 2010; Griesbeck et al. 2002; Marcia et al. 2009; Shuman and Hanson 2016; Zhang and Weiner 2014). The SqrA type exemplified by the functionally well-characterized enzyme from the cyanobacterium *Oscillatoria limnetica* (Bronstein et al. 2000) and the purple non-sulfur bacterium *Rhodobacter capsulatus* (Schütz et al. 1999) does neither occur in green (Gregersen et al. 2011) nor in purple sulfur bacteria (Table 3). The same holds true for SqrE. The SqrD and SqrF types appear to be especially widespread in the family *Chromatiaceae*, while members of the *Ectothiorhodospiraceae* all contain a gene encoding SqrB. The SqrF-type enzyme from *C. tepidum* has recently been shown to have a low affinity for sulfide and a high enzymatic turnover rate consistent with a function as a high sulfide adapted SQR (Chan et al. 2009; Eddie and Hanson 2013). The primary reaction product of the SQR reaction is soluble polysulfide (Griesbeck et al. 2002).

In a variety of sulfide-oxidizing species, flavocytochrome *c* is present as a soluble protein in the periplasm or as a membrane-bound enzyme (Kostanjevecki et al. 2000). The protein consists of a larger flavoprotein (FccB) and a smaller hemoprotein

Table 3 Genes related to sulfide oxidation in genome-sequenced purple sulfur bacteria[a]

Organism	*sqrB*	*sqrC*	*sqrD*	*sqrF*	Alvin_1196/97	*fccBA*
Chromatiaceae						
Allochromatium vinosum DSM 180^T	–	-	Alvin_2145	Alvin_1195	Alvin_1196/97	Alvin_1092/93
Thiorhodovibrio sp. 970	–	–	Thi970DRAFT_02097	Thi970DRAFT_01366	Thi970DRAFT_01366	Thi970DRAFT_02375/76
Lamprocystis purpurea DSM 4197	–	–	WP_020502950	WP_020508508	–	WP_020504674/73
Thiocapsa marina 5811 DSM 5653^T	–	–	ThimaDRAFT_0111	ThimaDRAFT_0710	–	ThimaDRAFT_3288/87 ThimaDRAFT_4140/39
Thiocapsa sp. KS1	–	THIOKS1270020	THIOKS12830013	THIOKS11770025	-	THIOKS11060009/07, THIOKS12860008/09
Thiohalocapsa ML1	-	–	WP_058557406	WP_058558070	–	WP_058554707/06
Thiorhodococcus sp. AK35	–	–	D779_2797	D779_4227	D779_0811/12	D779_2091/90
Thiorhodococcus drewsii AZ1 DSM 15006^T	–	–	ThidrDRAFT_1076	ThidrDRAFT_2526	ThidrDRAFT_3416/17	–
Thiocystis violascens DSM 198^T	–	–	Thivi_0965	Thivi_3129	–	Thivi_4480/81, Thivi_1815/16
Marichromatium purpuratum 984 DSM 1591^T	–	MARPU_16030	MARPU_12080	MARPU_13750	–	MARPU_11175/70
Thioflaviococcus mobilis DSM 8321^T	–	–	Thimo_0569	Thimo_1567	–	Thimo_2236/35

(continued)

Table 3 (continued)

Organism	*sqrB*	*sqrC*	*sqrD*	*sqrF*	Alvin_1196/97	*fccBA*
Ectothiorhodospiraceae						
Halorhodospira halophila SL1 DSM 244^T	Hhal_1665	–	–	–	–	Hhal_1331, Hhal_1163, no *fccA*
Halorhodospira halochloris str. A DSM 1059^T	M911_12365	–	–	–	–	M911_16440, no fccA
Thiorhodospira sibirica ATCC 700588^T	ThisiDRAFT_1596	–	ThisiDRAFT_0159	–	–	ThisiDRAFT_0473, no *fccA*
Ectothiorhodospira haloalkaliphila ATCC 51935^T	WP_025282304	–	–	–	–	WP_025283024, no *fccA*
Ectothiorhodospira sp. PHS1	ECTPHS_10089	–	–	–	–	ECTPHS_01469, no *fccA*

[a]Genomes were analyzed by BLAST searches using the resources provided by Integrated Microbial Genomes (DOE Joint Genomes Institute, http://img.jgi.doe.gov) and GenBank (http://www.ncbi.nlm.nih.gov). Baits: FccAB from *A. vinosum* (AAA23316 and AAB86576), SqrA from *Aquifex aeolicus* (NP_214500), SqrB from *Halorhodospira halophila* (WP_011814451), SqrC from *Chlorobaculum tepidum* (NP_661917), SqrD from *Chlorobaculum tepidum* (NP_661023), SqrE from *Chlorobaculum tepidum* (NP_661769), SqrF from *Aquifex aeolicus* (NP_213539)

(FccA) subunit. The proteins show sulfide/cytochrome *c* activity in vitro (Bosshard et al. 1986). FccAB occurs in many purple and green sulfur bacteria but there are also species that lack it (Frigaard and Dahl 2009; Sander and Dahl 2009). It is possible that FccAB is advantageous under certain growth conditions, and it has been speculated that it might represent a high-affinity system for sulfide oxidation especially suited at very low sulfide concentrations (Brune 1995b).

Oxidation of Polysulfides

Polysulfides occur as the primary reaction product of the oxidation of sulfide in purple (Franz et al. 2009; Prange et al. 2004) and green (Marnocha et al. 2016) sulfur bacteria. It is still unclear how polysulfides are converted into sulfur globules (Fig. 1). Theoretically this could be purely chemical spontaneous process as longer polysulfides are in equilibrium with elemental sulfur (Steudel et al. 1990).

Oxidation of External Sulfur

Many green and purple sulfur bacteria are able to oxidize externally supplied elemental sulfur. Sulfur of oxidation state zero mainly consists of S_8 rings and chain-like polymeric sulfur. Traces of S_7 rings are also present. Elemental sulfur is virtually insoluble in water, and it is still unclear how exactly phototrophs are able to bind, activate, and take up this substrate. *A. vinosum* uses only the polymeric sulfur fraction of commercially available sulfur (Franz et al. 2007). Soluble intermediates like sulfide, polysulfides, or polythionates do not appear to be formed. It therefore seems unlikely that mobilization of elemental sulfur by purple sulfur bacteria involves excretion of soluble sulfur-containing substances that would be able to act on substrate distant from the cells (Franz et al. 2009). Instead, direct cell-sulfur contact appears to be necessary for uptake of elemental sulfur by *A. vinosum* (Franz et al. 2007).

Properties of Sulfur Globules

In anoxygenic phototrophic sulfur bacteria, sulfur formed as an intermediate is never deposited in the cytoplasm. Green sulfur bacteria and members of the *Ectothiorhodospiraceae* form extracellular sulfur globules, and the globules of the members of the family *Chromatiaceae* are located in the periplasmic space (Pattaragulwanit et al. 1998). Independent of the site of deposition, the sulfur appears to be of similar speciation, i.e., long sulfur chains that might be terminated by organic residues in purple sulfur bacteria (Prange et al. 2002). While proteinaceous envelopes have never been reported for extracellular sulfur globules, the

sulfur globules in the *Chromatiaceae* are enclosed by a protein envelope (Brune 1995a). In *A. vinosum* this envelope is a monolayer of 2–5 nm consisting of four different hydrophobic sulfur globule proteins, SgpABCD (Brune 1995a; Pattaragulwanit et al. 1998; Weissgerber et al. 2014a). All of these proteins are synthesized with cleavable N-terminal peptides mediating Sec-dependent transport to the periplasm and share a highly repetitive amino acid sequence rich in regularly spaced proline residues. They are predicted to act purely as structural proteins. A covalent attachment of sulfur chains to the proteins is unlikely as none of the Sgps contains any cysteine residues. The envelope is indispensable for formation and deposition of intracellular sulfur in *A. vinosum*. The 10.5 kDa SgpA and SgpB proteins resemble each other and are in part able to replace each other. SgpC is important for expansion of the globules (Prange et al. 2004). SgpD was only recently detected by investigating the sulfur globule proteome and proved to be the most abundant of the four sulfur globule proteins (Weissgerber et al. 2014a). The relative mRNA levels for the corresponding gene increased drastically with addition of sulfide or thiosulfate to the growth medium (Weissgerber et al. 2013). Genes encoding sulfur globule proteins occur in all genome-sequenced purple sulfur bacteria of the family *Chromatiaceae* but are absent in *Ectothiorhodospiraceae*. The combination of sulfur globule proteins appears to be variable (Table 4).

Oxidation of Stored Sulfur to Sulfite

The oxidative degradation of sulfur deposits in phototrophic sulfur bacteria is still a major subject of research. Besides the comparatively well-characterized Dsr (dissimilatory sulfite reductase) system, a completely new pathway of sulfur oxidation involving a heterodisulfide reductase-like enzyme system is currently emerging (Dahl 2015; Venceslau et al. 2014) and appears to be implemented in several phototrophic members of the family *Ectothiorhodospiraceae* (Table 5).

The Dsr System of Sulfur Oxidation

Currently, the best studied of the sulfur oxidation pathways operating in the cytoplasm is the so-called Dsr pathway (Fig. 4) involving the enzyme reverse dissimilatory sulfite reductase (DsrAB) (Dahl et al. 2005; Pott and Dahl 1998). Low-molecular-weight organic persulfides such as glutathione amide persulfide have been proposed as carrier molecules transferring sulfur from the periplasmic or extracellular sulfur deposits into the cytoplasm (Frigaard and Dahl 2009). It is not yet known how exactly the proposed persulfidic carrier molecules are generated and whether specific enzymes are involved in this process nor have transporters for such molecules be characterized from any sulfur-oxidizing prokaryote. An extensive Cys-SSH-based sulfur relay system exists in *A. vinosum* (Figs. 1 and 4) that traffics sulfur atoms stemming ultimately from sulfur stored in sulfur globules, through a

Table 4 Genes for sulfur globule proteins in genome-sequenced purple sulfur bacteria[a]

Organism	*sgpA*	*sgpB*	*sgpC*	*sgpD*
Chromatiaceae				
Allochromatium vinosum DSM 180^T	Alvin_1905	Alvin_0358	Alvin_1325	Alvin_2515
Thiorhodovibrio sp. 970	Thi970DRAFT_01708	Thi970DRAFT_04390	–	–
Lamprocystis purpurea DSM 4197	WP_020505111	–	–	WP_020502765
Thiocapsa marina 5811 DSM 5653^T	ThimaDRAFT_1252	ThimaDRAFT_2318	ThimaDRAFT_0183	ThimaDRAFT_1208
Thiocapsa sp. KS1	THIOKS11660013	THIOKS12350047, THIOKS11380015, THIOKS11380003	THIOKS12740024	THIOKS11710009
Thiohalocapsa ML1	WP_058555283	WP_058553807	–	WP_058558285
Thiorhodococcus sp. AK35	D779_0250	D779_1210	D779_3526	D779_1498
Thiorhodococcus drewsii AZ1 DSM 15006^T	THIOKS11660013	THIOKS12350047, THIOKS11380015, THIOKS11380003	THIOKS12740024	THIOKS11710009
Thiocystis violascens DSM 198^T	Thivi_3565	Thivi_3773	Thivi_4580	Thivi_3369
Marichromatium purpuratum 984 DSM 1591^T	–	MARPU_02625	MARPU_02425	MARPU_10340

(continued)

Table 4 (continued)

Organism	*sgpA*	*sgpB*	*sgpC*	*sgpD*
Thioflaviococcus mobilis DSM 8321^T	–	Thimo_3285	Thimo_1531	–
Ectothiorhodospiraceae				
Halorhodospira halophila SL1 DSM 244^T	–	–	–	–
Halorhodospira halochloris str. A DSM 1059^T	–	–	–	–
Thiorhodospira sibirica ATCC 700588^T	–	–	–	–
Ectothiorhodospira haloalkaliphila ATCC 51935	–	–	–	–
Ectothiorhodospira sp. PHS1	–	–	–	–

[a]Genomes were analyzed by BLAST searches using the resources provided by Integrated Microbial Genomes (DOE Joint Genomes Institute, http://img.jgi.doe.gov) and GenBank (http://www.ncbi.nlm.nih.gov). Baits: SgpA (Alvin_1905), SgpB (Alvin_0358), SgpC (Alvin_1325), and SgpD (Alvin_2515) from *A. vinosum*

Table 5 Genes related to stored sulfur oxidation in genome-sequenced purple sulfur bacteria[a]

Organism	*rhd-tusA-dsrE2*	*dsr*	*hdr*-like	*lbpA* and biosynthesis
Chromatiaceae				
Allochromatium vinosum DSM 180^T	Alvin_2599–2601	Alvin_1251–1265	–	–
Thiorhodovibrio sp. 970	Thi970DRAFT_01020–22	Thi970DRAFT_01389–75	–	–
Lamprocystis purpurea DSM 4197	WP_040527681 (rhd), WP_02050658081	WP_020504936–22	–	–
Thiocapsa marina 5811 DSM 5653^T	ThimaDRAFT_2004–2002	ThimaDRAFT_2915–2901	–	–
Thiocapsa sp. KS1	THIOKS11130019–17	THIOKS12910007–23	–	–
Thiohalocapsa ML1	WP_058553476–74	WP_058553439–426	–	–
Thiorhodococcus sp. AK35	D779_3058–56	D779_2143–2157	–	–
Thiorhodococcus drewsii AZ1 DSM 15006^T	ThidrDRAFT_0819–817	ThidrDRAFT_2036–2022	–	–
Thiocystis violascens DSM 198^T	Thivi_2161–2159	Thivi_0544--0556, 0030/29 (*dsrRS*)	–	–
Marichromatium purpuratum 984 DSM 1591^T	MARPU_12295–12,285	MARPU_10915–10,850, no *dsrS*	–	–
Thioflaviococcus mobilis DSM 8321^T	Thimo_2639–2637	Thimo_0143–0156, 1749 (*dsrS*)	–	–

(continued)

Table 5 (continued)

Organism	*rhd-tusA-dsrE2*	*dsr*	*hdr*-like	*lbpA* and biosynthesis
Ectothiorhodospiraceae				
Halorhodospira halophila SL1 DSM 244^T	no rhd, Hhal_1937 (tusA) no dsrE2	Hhal_1951–1963, no *dsrRS*		
Halorhodospira halochloris str. A DSM 1059^T	M911_16670 (rhd) M911_11250–11,245	–	M911_11240–11,215	M911_11210—M911_11180
Thiorhodospira sibirica ATCC 700588^T	ThisiDRAFT_1542–1540	–	ThisiDRAFT_1539–1534	ThisiDRAFT_1533 (lbpA1), 2311–12 (dsrE2-lbpA2), 0082 (radSAM1), 0513 (lplA), 1283 (ger), 1859 (radSAM2)
Ectothiorhodospira haloalkaliphila ATCC 51935^T	no rhd, WP_025282116/15	–	WP_025282114–111 (*hdrC1-hyp*), WP_025280421 (*hdrC2*) WP_025282109 (hdrB2)	WP_025282108–105 (lbpA1- rad SAM1), WP_026623531 (lplA), WP_025282103/02 (ger-radSAM2)
Ectothiorhodospira sp. PHS1	ECTPHS_01344 (rhd), 10,821,10,826	–	ECTPHS_10831–10,856	EctPHS_10861–10,891

The following abbreviations designate occurrence of a core set of several genes: *dsr*, *dsrABCEFHMKLJOPNRS*; *hdr*-like, *hdrC1B1AhypC2B2*; *lbpA* and biosynthesis, *lbpA1-dsrE3-lpA2-radSAM1-lplA-ger-radSAM2*

[a]Genomes were analyzed by BLAST searches using the resources provided by Integrated Microbial Genomes (DOE Joint Genomes Institute, http://img.jgi.doe.gov) and GenBank (http://www.ncbi.nlm.nih.gov). Baits: Rhd (Alvin_2599), TusA (Alvin_2600), DsrE2 (Alvin_2601), and Dsr proteins (U84760) from *A. vinosum*. Hdr-like proteins from *Acidithiobacillus caldus* SM-1: HdrC1, Atc_2352; HdrB1, Atc_2351; HdrA, Atc_2350; Hyp, Atc_2349; HdrC2, Atc_2348; HdrB2, Atc_2347; lipoate-binding protein LbpA and its biosynthesis, LbpA1 (Atc_2346), DsrE3 (Atc_2345), and LbpA2 (Atc_2344); radical SAM protein 1 (Atc_2343); single-domain LplA (Atc_2342); geranyl geranyl reductase-like (Atc_2341); and radical SAM protein 2 (Atc_2340) from *Acidithiobacillus caldus* SM-1

cascade of protein persulfide intermediates hosted on a rhodanese, TusA, possibly DsrE2A, DsrE, and DsrC (Stockdreher et al. 2012) to the active site of the enzyme sulfite reductase (Cort et al. 2008; Dahl et al. 2008c; Dahl 2015), the enzyme that catalyzes formation of sulfite.

A *rhd-tusA-dsrE2* or at least a *tusA-dsrE2* arrangement occurs in all currently genome-sequenced sulfur oxidizers harboring the Dsr system (Venceslau et al. 2014) (Table 5). In *A. vinosum* the *tusA* and the *rhd* and the *dsrE2* gene follow the same pattern of transcription as observed for the established cytoplasmic sulfane sulfur-oxidizing proteins (i.e., the Dsr system) (Stockdreher et al. 2014; Weissgerber et al. 2013). A *rhd-tusA-dsrE2*-deficient *A. vinosum* mutant strain, although not viable in liquid culture, was clearly sulfur oxidation negative upon growth on solid media containing sulfide (Stockdreher et al. 2014). TusA is one of the major proteins in *A. vinosum*, and the *rhd* and possibly also the *dsrE2A* encoded protein were identified as entry points for sulfur delivery to this protein (Stockdreher et al. 2014). The rhodanese-like Rhd protein (Alvin_2599) catalyzes sulfur transfer from thiosulfate or glutathione persulfide (GSSH) to cyanide in vitro, and the TusA protein was clearly established as a protein accepting sulfane sulfur from the *A. vinosum* rhodanese (Stockdreher et al. 2014). The DsrE2A protein is less well characterized and its role remains elusive at present (Stockdreher et al. 2014). It is firmly established that *A. vinosum* TusA is an interaction partner of DsrEFH, a hexameric protein arranged in a $\alpha_2\beta_2\gamma_2$ structure (Dahl et al. 2008c). Sulfur transfer between TusA and DsrEFH is reversible in vitro (Stockdreher et al. 2014). From DsrEFH sulfur is transferred to DsrC (Stockdreher et al. 2012).

The eminently important DsrC protein works as the physiological partner of the DsrAB sulfite reductase not only in sulfur-oxidizing but also in sulfate-reducing prokaryotes (Venceslau et al. 2014). DsrC is a member of the DsrC/TusE/RpsA superfamily and contains two strictly conserved redox active cysteines in a flexible carboxy-terminal arm (Cort et al. 2008): Cys_A is the penultimate residue at the C-terminus and Cys_B is located ten residues upstream (Venceslau et al. 2014). When combined in solution in their native, non-persulfurated state, DsrEFH and DsrC form a tight complex (Stockdreher et al. 2012), and each $DsrE_2F_2H_2$ heterohexamer associates with either one or two DsrC molecules. Interaction of DsrEFH with DsrC is strictly dependent on the presence of DsrE-Cys_{78} and DsrC-Cys_A (Cort et al. 2008; Stockdreher et al. 2012).

In Fig. 1 the concept is implemented that persulfurated DsrC serves as the substrate for DsrAB and oxidation of DsrC-Cys_A-S^- by this enzyme is thought to result in persulfonated DsrC (DsrC-Cys_A-SO_3^-) from which sulfite is possibly released by the formation of a disulfide bridge between Cys_A and Cys_B (Stockdreher et al. 2014; Venceslau et al. 2014). However, this proposal is challenged by the very recent finding that a DsrC trisulfide, in which a sulfur atom is bridging the two conserved cysteine residues, is released as the product of the reverse reaction, i.e., sulfite reduction, upon catalysis by DsrAB from a sulfate reducer (Santos et al. 2015). An alternative model is represented in Fig. 4 integrating formation of a DsrC trisulfide possibly by the action of the membrane-bound DsrMKJOP electron-transporting complex that contains the heterodisulfide reductase-like subunit DsrK which could

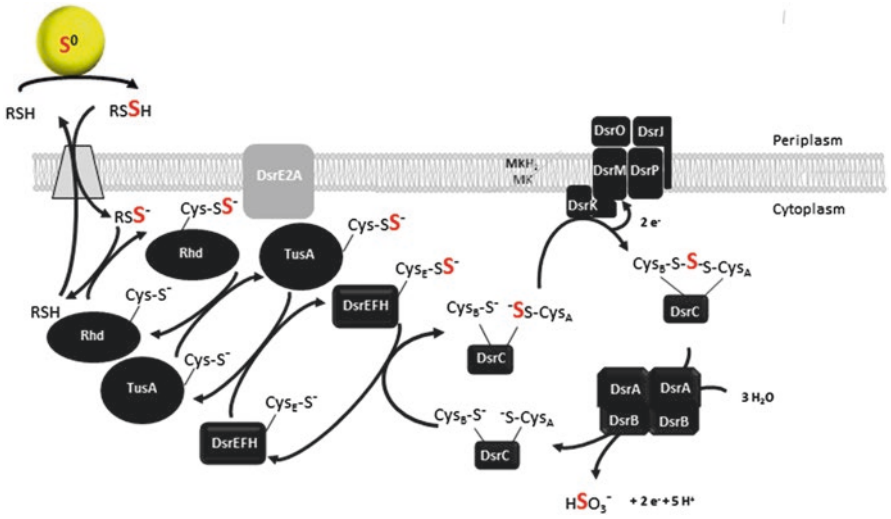

Fig. 4 Model of Dsr-mediated sulfane sulfur oxidation in *A. vinosum* integrating a sulfur-mobilizing function for Rhd, sulfur transfer functions for TusA and DsrEFH, and a substrate-donating function for DsrC. As detailed in the text, the model is based on biochemical as well as on molecular genetic evidence

well characterize the suggested reaction (Grein et al. 2010a, 2010b, 2013; Sander et al. 2006). Electrons released during oxidation of the DsrC trisulfide to DsrC and sulfite may be transferred to the protein DsrL. This iron-sulfur flavoprotein is essential for sulfur oxidation in *A. vinosum* (Dahl et al. 2005; Lübbe et al. 2006). It bears striking sequence similarity to the electron-bifurcating subunit of the NfnAB complex from *Thermotoga maritima* (Demmer et al. 2015) and would have the theoretical capacity for reduction of NAD^+; however, experimental evidence substantiating this idea is currently completely lacking. Understanding the exact mechanistic details of the interaction of DsrC, DsrAB, and the other Dsr proteins is, in fact, one of the most challenging points in research on sulfur-oxidizing prokaryotes.

The Hdr-Like System of Sulfur Oxidation

The *rhd-tusA-dsrE2* arrangement does not only occur in all currently genome-sequenced sulfur oxidizers harboring the Dsr system but also in a wide array of chemo- and also phototrophic sulfur oxidizers that do not contain the Dsr pathway (Venceslau et al. 2014) (Table 5). In these sulfur oxidizers, a gene cluster *hdrC1B1A-hyphdrC2B2* encoding an array of proteins resembling different subunits of archaeal heterodisulfide reductases is inevitably present (Venceslau et al. 2014). As shown in Table 5, genes encoding a putative *hdr*-like complex occur in several phototrophic representatives of the family *Ectothiorhodospiraceae*. The typical arrangement of the *hdr*-like gene cluster is shown in Fig. 5 for a chemotrophic sulfur oxidizer

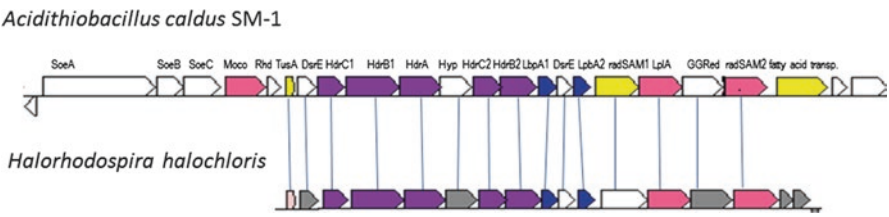

Fig. 5 Comparison of the *hdr*-like gene cluster in *Acidithiobacillus caldus* and *Halorhodospira halophila*. The *soeABC* genes encode a membrane-bound cytoplasmically oriented sulfite-oxidizing enzyme. Rhd, TusA, and DsrE are sulfur-mobilizing and sulfur-transferring proteins, respectively. HdrB1, HdrB2, HdrC1, HdrC2, and HdrA bear similarity to the HdrABC subunits of soluble heterodisulfide reductases from methanogens. Hyp indicates a gene for a hypothetical protein. LbpA1 and LbpA2, lipoate-binding proteins, and LplA, single-domain protein lipoate ligase or more probably octanoylate transferase (Christensen et al. 2011; Christensen and Cronan 2010). radSAM1 and radSAM2 are annotated as radical SAM proteins and could insert sulfur into octanoylated LbpA. Several of the *hdr*-like gene clusters in sulfur oxidizers encode a protein putatively involved in fatty acid transport which could play a role in import of lipoate precursors GGred, similarity to geranyl geranyl reductase, and could be involved in modification of imported fatty acids before they are channeled into the specific lipoylation pathway

(*Acidithiobacillus caldus*) and the phototroph *Halorhodospira halochloris.* In almost all cases, the *hdr*-like gene set is immediately linked with *rhd-tusA-dsrE2* or *rhd-dsrE2* arrangements promoting the notion that an Hdr-like protein complex is involved in the generation of sulfite from disulfide or even more likely protein-bound persulfide intermediates formed during sulfur oxidation. Heterodisulfide reductases (Hdr) are enzymes present in methanogenic archaea and catalyze the reduction of the heterodisulfide, CoM-S-S-CoB, formed in the last step of methanogenesis (Hedderich et al. 2005; Thauer et al. 2008). The general idea of an involvement of a Hdr-like complex and probably also specialized sulfurtransferases (Rhd, DsrE, TusA) in sulfite formation was first put forward by Quatrini and coworkers on the basis of microarray transcriptome profiling and quantitative RT-PCR analyses performed with *A. ferrooxidans* ATCC 23270 (Quatrini et al. 2006, 2009). The suggestion found support in further transcriptional regulation studies not only on several *Acidithiobacillus* species (Chen et al. 2012; Ehrenfeld et al. 2013; Latorre et al. 2016) and the Gram-positive *Sulfobacillus thermosulfidooxidans* (Guo et al. 2014) but also on the thermoacidophilic archaeon *Metallosphaera sedula* (Auernik and Kelly 2010). In addition, proteomic studies showed high levels of Hdr-like proteins in the presence of reduced sulfur compounds (Mangold et al. 2011; Osorio et al. 2013; Ouyang et al. 2013). In several of the cited studies, upregulation in the presence of reduced inorganic sulfur compounds affected the *hdr*-like genes as well as the sulfur transferase genes. Tight functional interaction of the encoded proteins is further indicated by the observation that genes *dsrE* to *hdrB2* constitute a single, distinct transcriptional unit in *A. ferrooxidans* ATCC 16786 (Ehrenfeld et al. 2013). The whole concept is further substantiated by the recent purification of a Hdr-like complex from membranes of *Aquifex aeolicus* (Boughanemi et al. 2016).

Ehrenfeld et al. 2013 were the first to point out the presence of a *gvcH*-like gene encoding a lipoate-binding protein (Ehrenfeld et al. 2013). On the basis of striking sequence similarity and the presence of a strictly conserved lysine residue known to be required for lipoate attachment (Spalding and Prigge 2010), the name LbpA (lipoate-binding protein A) is suggested for this single lipoyl domain protein. Many sulfur oxidizers carry two copies of the gene indicating a functional dimer. Furthermore, genes encoding another DsrE-like sulfurtransferase and proteins with the potential to act in biosynthesis of protein-bound lipoic acid (two radical SAM proteins, a lipoate-protein ligase, and geranyl geranyl reductase-like protein) are inevitably found in organisms containing *hdr*-like genes but not in sulfur oxidizers pursuing the Dsr pathway (Fig. 5, Table 5). In most cases these genes are immediately linked with the *hdr* genes as shown in Fig. 5, and in some cases they are located at other places in the genome (e.g., in the purple sulfur bacterium *Thiorhodospira sibirica*, Table 5).

Overall, the present circumstantial evidence is quite overwhelming in the argument that a Hdr-like enzyme system including dedicated sulfur transferases (Rhd, DsrE, TusA) and also a dedicated lipoate-binding protein is a central and key element in the bioenergetics of sulfur-oxidizing prokaryotes devoid of the Dsr system (Bobadilla Fazzini et al. 2013; Chen et al. 2012; Dahl 2015; Guo et al. 2014; Mangold et al. 2011; Quatrini et al. 2009; Venceslau et al. 2014). However, genetic experiments that would finally prove this omics-derived concept have so far not been published for any organism, and biochemical studies that would shed light on the underlying reaction mechanism(s) are completely lacking.

Currently, it appears premature to suggest a more detailed model of the Hdr-like mechanism. The LbpA protein is a prime candidate as a sulfur substrate-binding entity that presents the sulfur substrate to different catalytic entities. However, further functions can at present not be assigned.

Oxidation of Sulfite to Sulfate

The last step in the oxidation of reduced sulfur compounds is the oxidation of sulfite yielding sulfate as the final product. Sulfate formation from sulfite is energetically favorable and carried out by a wide range of organisms (Simon and Kroneck 2013). In addition, many purple sulfur bacteria can even use externally available sulfite as photosynthetic electron donor. Two fundamentally different pathways for sulfite oxidation have been well characterized in chemotrophic and phototrophic sulfur-oxidizing bacteria: (1) direct oxidation and (2) indirect, AMP-dependent oxidation via the intermediate adenylylsulfate (adenosine-5′-phosphosulfate).

Oxidation of Sulfite in the Periplasm

Many sulfite-oxidizing enzymes catalyzing direct oxidation of sulfite are located outside the cytoplasmic membrane (in the periplasm in Gram-negative bacteria). The best characterized enzyme belonging to this group, SorAB, stems from the

chemotroph *Starkeya novella* and consists of a molybdopyranopterin (Mo-PPT) cofactor-carrying subunit (SorA) and a monoheme cytochrome *c* (SorB) (Kappler et al. 2000; Kappler and Bailey 2005). SorA-type molybdoproteins without a SorB subunit have been termed SorT (D'Errico et al. 2006; Wilson and Kappler 2009), but recently this discrimination has been questioned (Simon and Kroneck 2013). Neither genes closely related to *sorAB* nor those encoding SorT sulfite dehydrogenases occur in the currently available genomes of anoxygenic phototropic bacteria.

A second option for oxidation of sulfite in the periplasm is the Sox system. It has been shown that sulfite is accepted in vitro as a substrate of the reconstituted Sox system from the chemotroph *Paracoccus denitrificans* (Friedrich et al. 2001; Frigaard and Dahl 2009; Sander and Dahl 2009). Notably, Friedrich and coworkers proved this reaction to be independent on the presence of SoxCD, a molybdohemoprotein catalyzing the six-electron oxidation of SoxY-cysteine-bound persulfide to sulfone sulfur. Purple bacteria that form sulfur globules during thiosulfate oxidation contain the Sox system albeit without the SoxCD proteins (Frigaard and Dahl 2009; Hensen et al. 2006; Meyer et al. 2007). Notably, the presence of SoxB and SoxXA is not essential for sulfite oxidation in *A. vinosum* (Hensen et al. 2006).

However, the periplasmic sulfur substrate-binding protein SoxYZ is needed in parallel to cytoplasmic enzymes for effective sulfite oxidation in *A. vinosum* (Dahl et al. 2013). Genes for this protein are present in purple sulfur bacteria irrespective of the organisms' substrate range with only one exception (*Thioflaviococcus mobilis*), while the presence of SoxXA(K) and SoxB appears to be strictly linked to the ability of the cells to utilize thiosulfate (Table 2).

Oxidation in the Cytoplasm

Indirect Pathway via Adenosine 5′-Phosphosulfate

It is firmly established that a number of purple as well as green anoxygenic phototrophic sulfur bacteria oxidize sulfite in the cytoplasm using an indirect pathway via adenosine-5′-phosphosulfate (APS) catalyzed by APS reductase (AprBA) and ATP sulfurylase (Sat) (Dahl 1996; Frigaard and Dahl 2009; Parey et al. 2013; Rodriguez et al. 2011; Sanchez et al. 2001) (Fig. 1).

In *A. vinosum*, the *sat* gene encoding ATP sulfurylase (Alvin_1118) is located immediately upstream of the *aprMBA* genes encoding membrane-bound APS reductase (Alvin_1119–1121) (Hipp et al. 1997; Weissgerber et al. 2011). AprM is predicted to contain five transmembrane helices with no sequence similarity to any currently known conserved domain or cofactor binding site in the databases. An essential function of AprM as a membrane anchor that allows spatial and functional association of this type of oxidative APS reductase with the membrane has been postulated, and it has been suggested that AprM serves as an entry point into the membrane for the electrons released during formation of APS from sulfite and AMP (Meyer and Kuever 2007). In the currently available complete genome sequences of phototrophic members of the family *Chromatiaceae*, the same gene arrangement

is present in *Thiorhodovibrio* sp. 970 (Table 6). In *Thiocapsa marina* 5811, *Thiorhodococcus drewsii* AZ1, *Thiocystis violascens* DSM 198^T, and *Thioflavicoccus mobilis* DSM 8321^T, *sat* and *aprMBA* are not linked on the chromosome (Table 6). The occurrence of *aprMBA* has also been reported for *Thiococcus pfennigii* 4520 (Gregersen et al. 2011).

The QmoABC complex was first identified in the dissimilatory sulfate-reducing bacterium *Desulfovibrio desulfuricans* (Pires et al. 2003). The complex consists of one membrane (QmoC) and two cytoplasmic subunits (QmoAB). The two QmoC hemes *b* are reduced by quinols, and experimental evidence strongly indicates that the Qmo complex participates in electron flow between the quinone pool and the cytoplasm, i.e., that it acts as the electron-donating unit for APS reductase in sulfate reducers (Frigaard and Dahl 2009; Ramos et al. 2012). The *qmoABC* genes are not only present in sulfate-reducing prokaryotes (Ramos et al. 2012) but occur also in many chemotrophic sulfur-oxidizing bacteria as well as in green sulfur bacteria (Frigaard and Dahl 2009; Rodriguez et al. 2011) and in one further purple sulfur bacterium (*Thiodictyon* sp. Cad16 (Gregersen et al. 2011)). In sulfur oxidizers, QmoABC is thought to act as electron acceptor for the electrons released during formation of APS and would thus have a function analogous to that of AprM. It is thus conceivable to state that the electrons generated by the oxidative formation of APS from sulfite and AMP are fed into the photosynthetic electron transport chain on the level of menaquinone either by AprM or by the much better characterized QmoABC complex (Grein et al. 2013; Meyer and Kuever 2007; Ramos et al. 2012; Rodriguez et al. 2011). It may be especially advantageous to be equipped with the Qmo-related electron-accepting unit for APS reductase. The presence of the HdrA-like QmoA in the Qmo complex opens the possibility that—in reverse to the mechanism suggested for sulfate reducers (Grein et al. 2013; Ramos et al. 2012)—an electron bifurcation occurs that could result in simultaneous reduction of low potential electron acceptors like ferredoxin or NAD^+. Such a process would be of significant energetic advantage especially for chemolithoautotrophic growth because it would result in a lower energy demand for reverse electron flow.

Direct Pathway via SoeABC

Notably the APS reductase pathway is neither generally present in purple sulfur bacteria (Table 6) nor is it essential in *A. vinosum* (Dahl 1996; Sanchez et al. 2001). The *sat* and *aprBA* genes are not present in some members of the *Chromatiaceae* (Meyer and Kuever 2007) and generally absent in *Ectothiorhodospiraceae* (Table 6). Recently the membrane-bound iron-sulfur molybdoprotein SoeABC was identified as a major enzyme catalyzing direct oxidation of sulfite to sulfate in the cytoplasm of *A. vinosum* (Dahl et al. 2013). The function of SoeABC was proven by strongly reduced specific oxidation rates for externally supplied sulfite and by massive excretion of sulfite into the medium during oxidation of sulfide in *A. vinosum* SoeABC-deficient strains. Crude extract of a SoeABC-deficient *A. vinosum* lacked

Table 6 Genes related to sulfite oxidation in genome-sequenced purple sulfur bacteria[a]

Organism	*sat*	*aprBA*	*aprM*	*qmoABC*	*soeABC*
Chromatiaceae					
Allochromatium vinosum DSM 180^T	Alvin_1118	Alvin_1120/21	Alvin_1119	–	Alvin_2491/90/89
Thiorhodovibrio sp. 970	Thi970DRAFT_00961	Thi970DRAFT_00963/64	Thi970DRAFT_00962	–	Thi970DRAFT_00955/56/57
Lamprocystis purpurea DSM 4197	WP_026199081	WP_020504060/59	–	WP_020504182/83/84	WP_020508252/50/49
Thiocapsa marina 5811 DSM 5653^T	ThimaDRAFT_0331	ThimaDRAFT_4551/52	ThimaDRAFT_4550	–	ThimaDRAFT_0331/30/29
Thiocapsa sp. KS1	THIOKS1630011	–	–	THIOKS11840023/24/26	THIOKS12550011/12/13
Thiohalocapsa ML1	WP_058556167	WP_058557029/30	WP_058557048	–	WP_058553485/83/82
Thiorhodococcus sp. AK35	D779_2633	D779_0177/78	D779_0176	–	D779_1687/86/85
Thiorhodococcus drewsii AZ1 DSM 15006^T	ThidrDRAFT_3161	ThidrDRAFT_1495/96	ThidrDRAFT_1494	–	ThidrDRAFT_2883/82/81
Thiocystis violascens DSM 198^T	Thivi_0893	Thivi_3300/299	–	Thivi_3114/13/12	Thivi_4531/32/33
Marichromatium purpuratum 984 DSM 1591^T	–	–	–	–	MARPU_14905/00/14895

(continued)

Table 6 (continued)

Organism	*sat*	*aprBA*	*aprM*	*qmoABC*	*soeABC*
Thioflaviococcus mobilis DSM 8321^T	Thimo_1948	Thimo_1220/19	Thimo_1221	–	Thimo_1580/81/82
Ectothiorhodospiraceae					
Halorhodospira halophila SL1 DSM 244^T	–	–	–	–	Hhal_1934/35/36
Halorhodospira halochloris str. A DSM 1059^T	–	–	–	–	M911_11365/01475/01495
Thiorhodospira sibirica ATCC 700588^T	–	–	–	–	ThisiDRAFT_1377/0834/2148
Ectothiorhodospira haloalkaliphila ATCC 51935^T	–	–	–	–	WP_025282138, WP_025281124, WP_025280412
Ectothiorhodospira sp. PHS1	–	–	–	–	ECTPHS_02816/02811/02806

[a]Genomes were analyzed by BLAST searches using the resources provided by Integrated Microbial Genomes (DOE Joint Genomes Institute, http://img.jgi.doe.gov) and GenBank (http://www.ncbi.nlm.nih.gov). Baits: APS reductase (AprMBA) from *A. vinosum* (U84759), Qmo proteins from *C. tepidum* (QmoA, CT0866; QmoB, CT0867; QmoC, CT0868), SoeABC from *A. vinosum* (SoeA, ADC63403; SoeB, ADC63402; SoeC, ADC63401)

AMP-independent sulfite-oxidizing activity. Further indication for an involvement of SoeABC in dissimilatory sulfur oxidation in *A. vinosum* was gathered during recent genome-wide transcriptional profiling (Weissgerber et al. 2013). Relative transcription of all three *A. vinosum soe* genes was found to be increased about threefold during photolithoautotrophic growth on sulfide or thiosulfate than during photoorganoheterotrophic growth on malate (2.99-, 2.77-, and 2.93-fold increase on sulfide and 1.96-, 1.98-, and 3.00-fold increase on thiosulfate, for *soeA*, *soeB*, and *soeC*, respectively). Changes in the same range were observed for the genes encoding the enzymes of the APS reductase pathway when thiosulfate replaced malate, while relative transcript levels for the *sat-aprMBA* genes were 7.6–9.7-fold higher in the presence of sulfide compared to the presence of malate

In *A. vinosum*, SoeABC is encoded by genes Alvin_2491 (*soeA*), Alvin_2490 (*soeB*), and Alvin_2489 (*soeC*). The protein consists of the 108.95 kDa molybdoprotein SoeA carrying one $[Fe_4S_4]$ cluster at the N-terminus; the 26.995 kDa iron-sulfur protein SoeB, which upon comparison with related structurally characterized proteins (Jormakka et al. 2008) is predicted to bind four $[Fe_4S_4]$ clusters; and a 35.715 kDa NrfD-/PsrC-like membrane protein (Simon and Kern 2008) with eight transmembrane helices. Neither AvSoeA and AvSoeB nor any of the other purple sulfur bacterial SoeA or SoeB proteins listed in Table 6 are synthesized with cleavable TAT signal peptides that are usually present on the active site subunits of the biochemically well-characterized periplasmic sulfur-metabolizing complex iron-sulfur molybdoproteins, i.e., polysulfide and sulfur reductase (PsrABC, SreABC), thiosulfate reductase (PhsABC), or tetrathionate reductase (TtrABC) (Heinzinger et al. 1995; Hensel et al. 1999; Krafft et al. 1992; Laska et al. 2003). SoeA and SoeB are thus located in the cytoplasm and attached to the cytoplasmic membrane by interaction with SoeC. The holoprotein is therefore well suited for oxidation of sulfite generated in the cytoplasm. It should be noted that SoeABC and the periplasmic Sor-type sulfite dehydrogenases belong to completely different families of molybdoenzymes.

Genes encoding proteins related to SoeABC are present in purple as well as green sulfur bacteria and have in the past years repeatedly been speculated to be involved in the oxidation of sulfite generated by the Dsr system in the cytoplasm (Frigaard and Bryant 2008b; Frigaard and Dahl 2009) (Table 6). Notably, *soeABC*-like genes co-localize with *dsr* genes in several green sulfur bacteria and in *Halorhodospira halophila* (Dahl 2008; Frigaard and Dahl 2009).

The possession of the APS reductase pathway in addition to or instead of SoeABC may be advantageous because additional energy is gained by substrate phosphorylation in the ATP sulfurylase catalyzed step by transferring the AMP moiety of APS onto pyrophosphate (Parey et al. 2013).

Sulfate Assimilation

Sulfate assimilation by in anoxygenic phototrophic bacteria has been extensively covered in previous reviews (Frigaard and Dahl 2009; Sander and Dahl 2009). Some anoxygenic phototrophic bacteria are very much specialized for living in

habitats with reduced sulfur compounds and such bacteria usually completely lack a sulfate reduction pathway. On the other hand, very many versatile purple sulfur and non-sulfur bacteria and even a few green bacteria are able to assimilate and reduced sulfate in the absence of a reduced source of sulfur. Among the filamentous anoxygenic bacteria, the ability to assimilate sulfate may or may not be present.

Here, the assimilatory sulfate reduction pathway in *A. vinosum* is presented as an example (Fig. 6). The pathway commences with the uptake of sulfate via the membrane-bound components of a periplasmic substrate-binding transport system similar to the situation in *E. coli* (Kredich 1996). Once inside the cell, sulfate is activated to adenosine-5′-phosphosulfate by the enzyme ATP sulfurylase (Leustek and Saito 1999). Assimilatory ATP sulfurylases occur in two different forms: a heterodimeric CysDN type as in *E. coli* (Leyh 1993) and a homo-oligomeric Sat-related type as found in other bacteria, plants, and fungi (Foster et al. 1994; MacRae et al. 2001). Both types occur in anoxygenic phototrophic bacteria (Frigaard and Dahl 2009; Sander and Dahl 2009). The sulfate reduction pathway in *A. vinosum* does not involve formation of phosphoadenosine- 5′-phosphosulfate (Neumann et al. 2000). Instead, a CysH-type iron-sulfur cluster binding APS reductase catalyzes reductive cleavage of APS yielding sulfite and AMP. Sulfite is finally reduced to sulfide by an assimilatory sulfite reductase. In the case of *A. vinosum*, this enzyme is a ferredoxin-dependent CysI-type siroheme-[4Fe-4S] cluster-containing protein as it also occurs in cyanobacteria, algae, and higher plants (Dhillon et al. 2005). This enzyme type is common in anoxygenic phototrophic bacteria (Frigaard and Dahl 2009). Biosynthesis of cysteine requires the formation of *O*-acetyl-L-serine, which is then further transformed to cysteine catalyzed by cysteine synthase B (CysM) in a reaction that is dependent on the availability of sulfide (Fig. 6) (Hensel and Trüper 1976). It is well established that the CysTWA ABC-type transporter in conjunction with the periplasmic binding protein CysP transports not only sulfate but also thiosulfate into the cytoplasm (Sirko et al. 1995). In *Salmonella typhimurium* and *E. coli*, cysteine synthase B (CysM) also accepts thiosulfate as a substrate and hooks it up to *O*-acetylserine resulting in the formation of *S*-sulfocysteine (Kredich 1992). *S*-sulfocysteine is then reduced to cysteine resulting in the release of sulfite (Nakatani et al. 2012; Sekowska et al. 2000). Glutathione, thioredoxins, or glutaredoxins have been discussed as possible reductants in this reaction (Funane et al. 1987; Nakatani et al. 2012; Woodin and Segel 1968). A similar reaction sequence is also probable for the assimilation of thiosulfate in *A. vinosum* (Fig. 6). In fact, thiosulfate was previously detected intracellularly in *A. vinosum* (Franz et al. 2009).

During photoorganoheterotrophic growth of *A. vinosum* on organic acids like malate, sulfide for biosynthesis of sulfur-containing cell constituents is provided by the assimilatory sulfate reduction pathway in an energy-consuming process (Fig. 6) (Neumann et al. 2000), while sulfide is readily available without any input of energy under sulfur-oxidizing conditions. Accordingly, the presence of reduced sulfur compounds results in elevated relative mRNA and protein levels for genes/proteins of central enzymes of oxidative sulfur metabolism, while transcript and protein levels for genes/proteins involved in assimilatory sulfate reduction are negatively affected (Weissgerber et al. 2013, 2014a). These responses are positively correlated to the

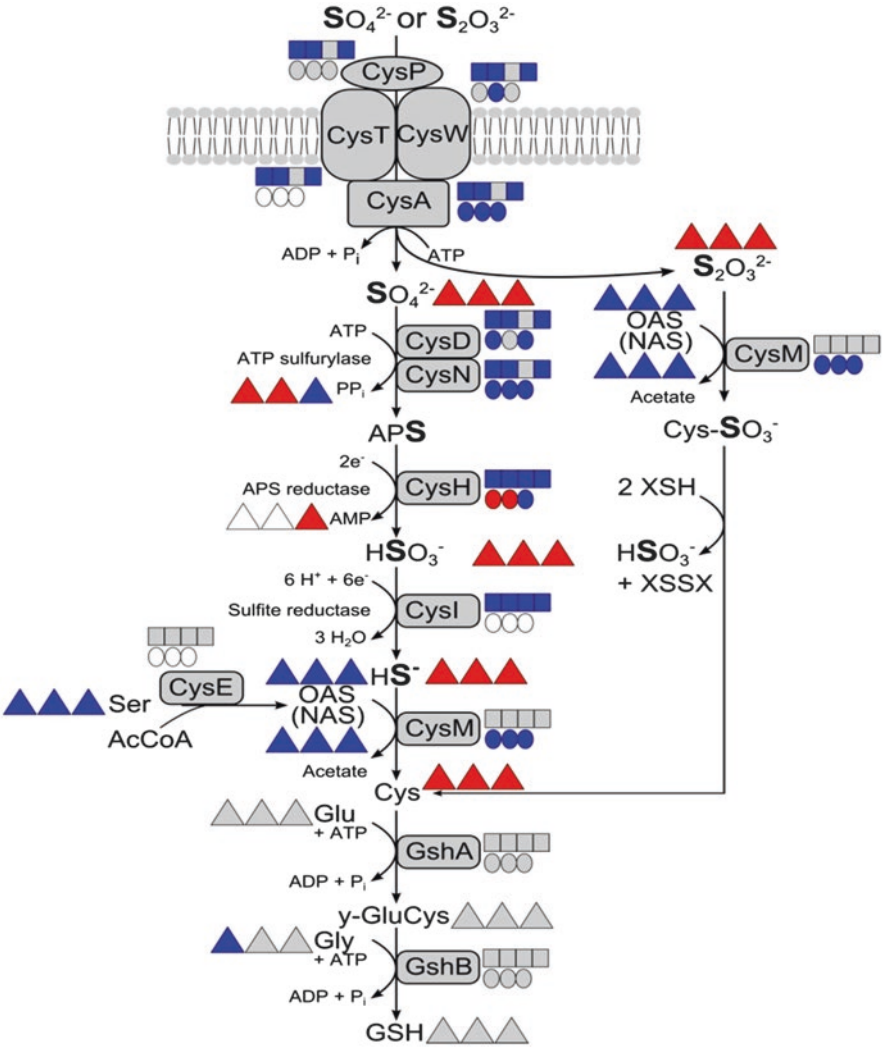

Fig. 6 Current model of assimilatory sulfate reduction in *A. vinosum*. *CysE* serine *O*-acetyltransferase (Alvin_0683), *CysM* cysteine synthase B (Alvin_2228), *GshA* glutamate/cysteine ligase (Alvin_0863), *CysM* cysteine synthase B (Alvin_2228); *GshA* glutamate/cysteine ligase (Alvin_800), *GshB* glutathione synthetase (Alvin_0197), *γ-GluCys* γ-glutamylcysteine, *GSH* glutathione, *XSH* glutathione, reduced thioredoxin or glutaredoxin, *XSSX* oxidized glutathione, thioredoxin or glutaredoxin (see text for further explanation). The transcriptomic (*boxes*) (Weissgerber et al. 2013), proteomic (*circles*) (Weissgerber et al. 2014a), and metabolomic profiles (*triangles*) (all relative to growth on malate) are depicted next to the respective protein/metabolite. Relative fold changes in mRNA levels above 2 (*red*) were considered significantly enhanced. Relative changes smaller than 0.5 (*blue*) were considered as indicating significant decreases in mRNA levels. Relative fold changes between 0.5 and 2 (*gray*) indicated unchanged mRNA levels. The same color coding is applied to changes on the protein and metabolome levels. Here, values above 1.5 (*red*) and below 0.67 (*blue*) were considered significant. Those cases, where transcriptomic data was not available or the respective protein or metabolite was not detected in the proteomic or metabolomic approach, respectively, are indicated by *white squares, circles, or triangles*. Sulfur compounds added, from left to right, sulfide, thiosulfate, elemental sulfur, and sulfite. Changes on sulfite were not determined on the proteome and metabolome levels. Figure reproduced from (Weissgerber et al. 2014b)

concentration changes of the metabolites of the affected metabolic pathways (Weissgerber et al. 2014b) (Fig. 6). It is conceivable to assume that the interplay between the processes of dissimilatory sulfur oxidation and assimilatory sulfate reduction is regulated in a similar manner in other anoxygenic phototrophic bacteria capable of pursuing both pathways.

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References

Appia-Ayme C, Little PJ, Matsumoto Y et al (2001) Cytochrome complex essential for photosynthetic oxidation of both thiosulfate and sulfide in *Rhodovulum sulfidophilum*. J Bacteriol 183:6107–6118

Arieli B, Padan E, Shahak Y (1991) Sulfide-induced sulfide—quinone reductase acitivity in thylakoids of *Oscillatoria limnetica*. J Biol Chem 266:104–111

Arieli B, Shahak Y, Taglicht D et al (1994) Purification and characterization of sulfide-quinone reductase, a novel enzyme driving anoxygenic photosynthesis in *Oscillatoria limnetica*. J Biol Chem 269:5705–5711

Auernik KS, Kelly RM (2010) Physiological versatility of the extremely thermoacidophilic archaeon *Metallosphaera sedula* supported by transcriptomic analysis of heterotrophic, autotrophic, and mixotrophic growth. Appl Environ Microbiol 76:931–935

Baldock MI, Denger K, Smits THM et al (2007) *Roseovarius* sp. strain 217: aerobic taurine dissimilation via acetate kinase and acetate-CoA ligase. FEMS Microbiol Lett 271:202–206

Bamford VA, Bruno S, Rasmussen T et al (2002) Structural basis for the oxidation of thiosulfate by a sulfur cycle enzyme. EMBO J 21:5599–5610

Barbosa-Jefferson VL, Zhao FJ, Mcgrath SP et al (1998) Thiosulphate and tetrathionate oxidation in arable soils. Soil Biol Biochem 30:553–559

Bartsch RG (1978) Cytochromes. In: Clayton RK, Sistrom WR (eds) The photosynthetic bacteria. Plenum Press, New York, pp 249–279

Bobadilla Fazzini RA, Cortes MP, Padilla L et al (2013) Stoichiometric modeling of oxidation of reduced inorganic sulfur compounds (Riscs) in *Acidithiobacillus thiooxidans*. Biotechnol Bioeng 110:2242–2251

Bosshard HR, Davidson MW, Knaff DB et al (1986) Complex formation and electron transfer between mitochondrial cytochrome c and flavocytochrome c552 from *Chromatium vinosum*. J Biol Chem 261:190–193

Boughanemi S, Lyonnet J, Infossi P et al (2016) Microbial oxidative sulfur metabolism: biochemical evidence of the membrane-bound heterodisulfide reductase-like complex of the bacterium *Aquifex aeolicus*. FEMS Microbiol Lett 363

Bradley JM, Marritt SJ, Kihlken MA et al (2012) Redox and chemical activities of the hemes in the sulfur oxidation pathway enzyme SoxAX. J Biol Chem 287:40350–40359

Brito JA, Denkmann K, Pereira IAC et al (2015) Thiosulfate dehydrogenase (TsdA) from *Allochromatium vinosum*: Structural and functional insights into thiosulfate oxidation. J Biol Chem 290:9222–9238

Brito JA, Sousa FL, Stelter M et al (2009) Structural and functional insights into sulfide:quinone oxidoreductase. Biochemistry 48:5613–5622

Bronstein M, Schütz M, Hauska G et al (2000) Cyanobacterial sulfide-quinone reductase: cloning and heterologous expression. J Bacteriol 182:3336–3344

Brune DC (1989) Sulfur oxidation by phototrophic bacteria. Biochim Biophys Acta 975:189–221

Brune DC (1995a) Isolation and characterization of sulfur globule proteins from *Chromatium vinosum* and *Thiocapsa roseopersicina*. Arch Microbiol 163:391–399

Brune DC (1995b) Sulfur compounds as photosynthetic electron donors. In: Blankenship RE, Madigan MT, Bauer CE (eds) Anoxygenic photosynthetic bacteria. Kluwer Academic Publishers, Dordrecht, pp 847–870

Bryant DA, Costas AMG, Maresca JA et al (2007) *Candidatus* Chloracidobacterium thermophilum: an aerobic phototrophic Acidobacterium. Science 317:523–526

Bryantseva IA, Gorlenko VM, Kompantseva EI et al (1999) *Thiorhodospira sibirica* gen. nov., sp. nov., a new alkaliphilic purple sulfur bacterium from a Siberian Soda lake. Int J Syst Bacteriol 49:697–703

Caumette P, Guyoneaud R, Imhoff JF et al (2004) *Thiocapsa marina* sp. nov., a novel, okenone-containing, purple sulfur bacterium isolated from brackish coastal and marine environments. Int J Syst Evol Microbiol 54:1031–1036

Challacombe JF, Majid S, Deole R et al (2013) Complete genome sequence of Halorhodospira halophila SL1. Stand Genomic Sci 8:206–214

Chan L-K, Morgan-Kiss R, Hanson TE (2009) Functional analysis of three sulfide:quinone oxidoreductase homologs in *Chlorobaculum tepidum*. J Bacteriol 191:1026–1034

Chen ZW, Koh M, van Driessche G et al (1994) The structure of flavocytochrome c sulfide dehydrogenase from a purple phototrophic bacterium. Science 266:430–432

Chen L, Ren Y, Lin J et al (2012) *Acidithiobacillus caldus* sulfur oxidation model based on transcriptome analysis between the wild type and sulfur oxygenase reductase defective mutant. PLoS One 7:e39470

Cherney MM, Zhang Y, Solomonson M et al (2010) Crystal structure of sulfide:quinone oxidoreductase from Acidithiobacillus ferrooxidans: insights into sulfidotrophic respiration and detoxification. J Mol Biol 398:292–305

Christensen QH, Cronan JE (2010) Lipoic acid synthesis: a new family of octanoyltransferases generally annotated as lipoate protein ligases. Biochemistry 49:10024–10036

Christensen QH, Martin N, Mansilla MC et al (2011) A novel amidotransferase required for lipoic acid cofactor assembly in *Bacillus subtilis*. Mol Microbiol 80:350–363

Ciccarelli FD, Doerks T, von Mering C et al (2006) Toward automatic reconstruction of a highly resolved tree of life. Science 311:1283–1287

Cort JR, Selan UM, Schulte A et al (2008) *Allochromatium vinosum* DsrC: solution-state NMR structure, redox properties and interaction with DsrEFH, a protein essential for purple sulfur bacterial sulfur oxidation. J Mol Biol 382:692–707

Cusanovich MA, Bartsch RG (1969) A high potential cytochrome *c* from *Chromatium vinosum* chromatophores. Biochim Biophys Acta 189:245–255

D'Errico G, Di Salle A, La Cara F et al (2006) Identification and characterization of a novel bacterial sulfite oxidase with no heme binding domain from *Deinococcus radiodurans*. J Bacteriol 188:694–701

Dahl C (1996) Insertional gene inactivation in a phototrophic sulphur bacterium: APS-reductase-deficient mutants of *Chromatium vinosum*. Microbiology 142:3363–3372

Dahl C (2008) Inorganic sulfur compounds as electron donors in purple sulfur bacteria. In: Hell R, Dahl C, Knaff DB, Leustek T (eds) Sulfur in phototrophic organisms. Springer, Dordrecht, pp 289–317

Dahl C (2015) Cytoplasmic sulfur trafficking in sulfur-oxidizing prokaryotes. Iubmb Life 67:268–274

Dahl C, Friedrich CG, Kletzin A (2008a) Sulfur oxidation in prokaryotes. In: Encyclopedia of Life Sciences (ELS), John Wiley & Sons, Ltd., Chichester, p http://www.els.net/ [DOI: 10.1002/9780470015902.a0021155]

Dahl C, Hell R, Leustek T, Knaff DB (2008b) Introduction to sulfur metabolism in phototrophic organisms. In: Hell R, Dahl C, Knaff DB, Leustek T (eds) Sulfur metabolism in phototrophic organisms. Springer, Dordrecht, pp 1–14

Dahl C, Schulte A, Stockdreher Y et al (2008c) Structural and molecular genetic insight into a wide-spread bacterial sulfur oxidation pathway. J Mol Biol 384:1287–1300

Dahl C, Engels S, Pott-Sperling AS et al (2005) Novel genes of the *dsr* gene cluster and evidence for close interaction of Dsr proteins during sulfur oxidation in the phototrophic sulfur bacterium *Allochromatium vinosum*. J Bacteriol 187:1392–1404

Dahl C, Franz B, Hensen D et al (2013) Sulfite oxidation in the purple sulfur bacterium *Allochromatium vinosum*: identification of SoeABC as a major player and relevance of SoxYZ in the process. Microbiology 159:2626–2638

Demmer JK, Huang H, Wang S et al (2015) Insights into flavin-based electron bifurcation via the NADH-dependent reduced ferredoxin:NADP oxidoreductase structure. J Biol Chem 290:21985–21995

Denger K, Smits THM, Cook AM (2006) Genome-enabled analysis of the utilization of taurine as sole source of carbon or of nitrogen by *Rhodobacter sphaeroides* 2.4.1. Microbiology 152: 3197–3206

Denger K, Weinitschke S, Hollemeyer K et al (2004) Sulfoacetate generated by *Rhodopseudomonas palustris* from taurine. Arch Microbiol 182:154–158

Denkmann K, Grein F, Zigann R et al (2012) Thiosulfate dehydrogenase: a wide-spread unusual acidophilic *c*-type cytochrome. Environ Microbiol 14:2673–2688

Dhillon A, Goswami S, Riley M et al (2005) Domain evolution and functional diversification of sulfite reductases. Astrobiology 5:18–29

Eddie BJ, Hanson TE (2013) *Chlorobaculum tepidum* TLS displays a complex transcriptional response to sulfide addition. J Bacteriol 195:399–408

Ehrenfeld N, Levicán G, Parada P (2013) Heterodisulfide reductase from *Acidithiobacilli* is a key component involved in metabolism of reduced inorganic sulfur compounds. Adv Mater Res 825:194–197

Falkenby LG, Szymanska M, Holkenbrink C et al (2011) Quantitative proteomics of *Chlorobaculum tepidum*: insights into the sulfur metabolism of a phototrophic green sulfur bacterium. FEMS Microbiol Lett 323:142–150

Foster BA, Thomas SM, Mahr JA et al (1994) Cloning and sequencing of ATP sulfurylase from *Penicillium chrysogenum*: identification of a likely allosteric domain. J Biol Chem 269: 19777–19786

Franz B, Gehrke T, Lichtenberg H et al (2009) Unexpected extracellular and intracellular sulfur species during growth of *Allochromatium vinosum* with reduced sulfur compounds. Microbiology 155:2766–2774

Franz B, Lichtenberg H, Hormes J et al (2007) Utilization of solid "elemental" sulfur by the phototrophic purple sulfur bacterium *Allochromatium vinosum*: a sulfur K-edge XANES spectroscopy study. Microbiology 153:1268–1274

Friedrich CG, Bardischewsky F, Rother D et al (2005) Prokaryotic sulfur oxidation. Curr Opin Microbiol 8:253–259

Friedrich CG, Rother D, Bardischewsky F et al (2001) Oxidation of reduced inorganic sulfur compounds by bacteria: emergence of a common mechanism? Appl Environ Microbiol 67: 2873–2882

Frigaard N-U, Bryant DA (2008a) Genomic and evolutionary perspectives on sulfur metabolism in green sulfur bacteria. In: Dahl C, Friedrich CG (eds) Microbial sulfur metabolism. Springer, Heidelberg, Heidelberg, pp 60–76

Frigaard N-U, Bryant DA (2008b) Genomic insights into the sulfur metabolism of phototrophic green sulfur bacteria. In: Hell R, Dahl C, Knaff DB, Leustek T (eds) Sulfur metabolism in phototrophic organisms. Springer, Dordrecht, pp 337–355

Frigaard N-U, Dahl C (2009) Sulfur metabolism in phototrophic sulfur bacteria. Adv Microb Physiol 54:103–200

Funane K, Iwahashi H, Nakamura T (1987) Metabolism of *S*-sulfocysteine in *Salmonella typhimurium*. Role of thioredoxin in the reduction of *S*-sulfocysteine. Agric Biol Chem 51: 1247–1256

Gregersen LH, Bryant DA, Frigaard N-U (2011) Mechanisms and evolution of oxidative sulfur metabolism in green sulfur bacteria. Front Microbiol 2:116. doi:10.3389/fmicb.2011.00116

Grein F, Pereira IAC, Dahl C (2010a) The *Allochromatium vinsosum* DsrMKJOP transmembrane complex: biochemical characterization of individual components aids understanding of complex function in vivo. J Bacteriol 192:6369–6377

Grein F, Ramos AR, Venceslau SS et al (2013) Unifying concepts in anaerobic respiration: Insights from dissimilatory sulfur metabolism. Biochim Biophys Acta 1827:145–160

Grein F, Venceslau SS, Schneider L et al (2010b) DsrJ, an essential part of the DsrMKJOP complex in the purple sulfur bacterium *Allochromatium vinosum*, is an unusual triheme cytochrome *c*. Biochemistry 49:8290–8299

Griesbeck C, Schütz M, Schödl T et al (2002) Mechanism of sulfide-quinone oxidoreductase investigated using site-directed mutagenesis and sulfur analysis. Biochemistry 41:11552–11565

Guo X, Yin H, Liang Y et al (2014) Comparative genome analysis reveals metabolic versatility and environmental adaptations of *Sulfobacillus thermosulfidooxidans* strain ST. PLoS One 9:e99417

Hamilton TL, Bovee RJ, Thiel V et al (2014) Coupled reductive and oxidative sulfur cycling in the phototrophic plate of a meromictic lake. Geobiology 12:451–468

Hedderich R, Hamann N, Bennati M (2005) Heterodisulfide reductase from methanogenic archaea: a new catalytic role for an iron-sulfur cluster. Biol Chem 386:961–970

Heinzinger NK, Fujimoto SY, Clark MA et al (1995) Sequence analysis of the *phs* operon in *Salmonella typhimurium* and the contribution of thiosulfate reduction to anaerobic energy metabolism. J Bacteriol 177:2813–2820

Hensel G, Trüper HG (1976) Cysteine and S-sulfocysteine biosynthesis in phototrophic bacteria. Arch Microbiol 109:101–103

Hensel M, Hinsley AP, Nikolaus T et al (1999) The genetic basis of tetrathionate respiration in *Salmonella typhimurium*. Mol Microbiol 32:275–287

Hensen D, Sperling D, Trüper HG et al (2006) Thiosulphate oxidation in the phototrophic sulphur bacterium *Allochromatium vinosum*. Mol Microbiol 62:794–810

Hipp WM, Pott AS, Thum-Schmitz N et al (1997) Towards the phylogeny of APS reductases and sirohaem sulfite reductases in sulfate-reducing and sulfur-oxidizing prokaryotes. Microbiology 143:2891–2902

Imhoff JF (2001) Transfer of *Pfennigia purpurea* Tindall 1999 (*Amoebobacter purpureus* Eichler and Pfennig 1988) to the genus *Lamprocystis* as *Lamprocystis purpurea* comb. nov. Int J Syst Evol Microbiol 51:1699–1701

Imhoff JF (2003) Phylogenetic taxonomy of the family *Chlorobiaceae* on the basis of 16S rRNA and *fmo* (Fenna-Matthews-Olson protein) gene sequences. Int J Syst Evol Microbiol 53:941–951

Imhoff JF, Pfennig N (2001) *Thioflavicoccus mobilis* gen. nov., sp nov., a novel purple sulfur bacterium with bacteriochlorophyll *b*. Int J Syst Evol Microbiol 51:105–110

Imhoff JF, Süling J (1996) The phylogenetic relationship among Ectothiorhodospiraceae: a reevalution of their taxonomy on the basis of 16S rDNA analyses. Arch Microbiol 165:106–113

Imhoff JF, Hiraishi A, Süling J (2005) Anoxygenic phototrophic purple bacteria. In: Brenner DJ, Krieg NR, Staley JT, Garrity GM (eds) Bergey's manual of systematic bacteriology. Springer, New York, pp 119–132

Imhoff JF, Süling J, Petri R (1998) Phylogenetic relationships among the *Chromatiaceae*, their taxonomic reclassification and description of the new genera *Allochromatium*, *Halochromatium*, *Isochromatium*, *Marichromatium*, *Thiococcus*, *Thiohalocapsa*, and *Thermochromatium*. Int J Syst Bacteriol 48:1129–1143

Jormakka M, Yokoyama K, Yano T et al (2008) Molecular mechanism of energy conservation in polysulfide respiration. Nat Struct Mol Biol 15:730–737

Kappler U, Bailey S (2005) Molecular basis of intramolecular electron transfer in sulfite-oxidizing enzymes is revealed by high resolution structure of a heterodimeric complex of the catalytic molybdopterin subunit and a *c*-type cytochrome subunit. J Biol Chem 280:24999–25007

Kappler U, Schäfer H (2014) Transformations of dimethylsulfide. Met Ions Life Sci 14: 279–313

Kappler U, Bennett B, Rethmeier J et al (2000) Sulfite: cytochrome *c* oxidoreductase from *Thiobacillus novellus*—Purification, characterization, and molecular biology of a heterodimeric member of the sulfite oxidase family. J Biol Chem 275:13202–13212

Kappler U, Bernhardt PV, Kilmartin J et al (2008) SoxAX cytochromes, a new type of heme copper protein involved in bacterial energy generation from sulfur compounds. J Biol Chem 283:22206–22214

Khanna S, Nicholas DJD (1982) Utilization of tetrathionate and ^{35}S-labelled thiosulphate by washed cells of *Chlorobium vibrioforme* f. sp. *thiosulfatophilum*. J Gen Microbiol 128: 1027–1034

Koblizek M (2015) Ecology of aerobic anoxygenic phototrophs in aquatic environments. FEMS Microbiol Rev 39:854–870

Kostanjevecki V, Brige A, Meyer TE et al (2000) A membrane-bound flavocytochrome c-sulfide dehydrogenase from the purple phototrophic sulfur bacterium *Ectothiorhodospira vacuolata*. J Bacteriol 182:3097–3103

Krafft T, Bokranz M, Klimmek O et al (1992) Cloning and nucleotide sequence of the *psrA* gene of *Wolinella succinogenes* polysulphide reductase. Eur J Biochem 206:503–510

Kredich NM (1992) The molecular basis for positive regulation of *cys* promoters in *Salmonella typhimurium* and *Escherichia coli*. Mol Microbiol 6:2747–2753

Kredich NM (1996) Biosynthesis of cysteine. In: Neidhardt FC (ed) *Escherichia coli* and *Salmonella typhimurium*. Cellular and molecular biology. American Society for Microbiology, Washington, pp 514–527

Kulp TR, Hoeft SE, Asao M et al (2008) Arsenic(III) fuels anoxygenic photosynthesis in hot spring biofilms from mono lake, California. Science 321:967–970

Kurth J, Dahl C, Butt JN (2015) Catalytic protein film electrochemistry provides a direct measure of the tetrathionate/thiosulfate reduction potential. J Am Chem Soc 137:13232–13235

Laska S, Lottspeich F, Kletzin A (2003) Membrane-bound hydrogenase and sulfur reductase of the hyperthermophilic and acidophilic archaeon *Acidianus ambivalens*. Microbiology 149: 2357–2371

Latorre M, Ehrenfeld N, Cortes MP et al (2016) Global transcriptional responses of *Acidithiobacillus ferrooxidans* Wenelen under different sulfide minerals. Bioresour Technol 200:29–34

Leustek T, Saito K (1999) Sulfate transport and assimilation in plants. Plant Physiol 120: 637–643

Leyh TS (1993) The physical biochemistry and molecular genetics of sulfate activation. Crit Rev Biochem Mol Biol 28:515–542

Liu Y-W, Denkmann K, Kosciow K et al (2013) Tetrathionate stimulated growth of *Campylobacter jejuni* identifies TsdA as a new type of bi-functional tetrathionate reductase that is widely distributed in bacteria. Mol Microbiol 88:188

Lu W-P, Kelly DP (1988) Respiration-driven proton translocation in *Thiobacillus versutus* and the role of the periplasmic thiosulphate-oxidizing enzyme system. Arch Microbiol 149:297–302

Lübbe YJ, Youn H-S, Timkovich R et al (2006) Siro(haem)amide in *Allochromatium vinosum* and relevance of DsrL and DsrN, a homolog of cobyrinic acid *a,c* diamide synthase for sulphur oxidation. FEMS Microbiol Lett 261:194–202

MacRae IJ, Segel IH, Fisher AJ (2001) Crystal structure of ATP sulfurylase from *Penicillium chrysogenum*: insights into the allosteric regulation of sulfate assimilation. Biochemistry 40: 6795–6804

Mangold S, Valdés J, Holmes DS et al (2011) Sulfur metabolism in the extreme acidophile *Acidithiobacillus caldus*. Front Microbiol. doi:10.3389/fmcib.2011.00017

Marcia M, Ermler U, Peng GH et al (2010a) A new structure-based classification of sulfide:quinone oxidoreductases. Proteins: Struct, Funct, Bioinf 78:1073–1083

Marcia M, Langer JD, Parcej D et al (2010b) Characterizing a monotopic membrane enzyme. Biochemical, enzymatic and crystallization studies on Aquifex aeolicus sulfide:quinone oxidoreductase. Biochim Biophys Acta, Biomembr 1798:2114–2123

Marcia M, Ermler U, Peng GH et al (2009) The structure of *Aquifex aeolicus* sulfide:quinone oxidoreductase, a basis to understand sulfide detoxification and respiration. Proc Natl Acad Sci U S A 106:9625–9630

Marnocha CL, Levy AT, Powell DH et al (2016) Mechanisms of extracellular S(0) globule production and degradation in Chlorobaculum tepidum via dynamic cell-globule interactions. Microbiology 162(7):1125–1134

Meyer TE, Cusanovich MA (2003) Discovery and characterization of electron transfer proteins in the photosynthetic bacteria. Photosynth Res 76:111–126

Meyer B, Kuever J (2007) Molecular analysis of the distribution and phylogeny of dissimilatory adenosine-5′-phosphosulfate reductase-encoding genes (aprBA) among sulfur-oxidizing prokaryotes. Microbiology 153:3478–3498

Meyer B, Imhoff JF, Kuever J (2007) Molecular analysis of the distribution and phylogeny of the *soxB* gene among sulfur-oxidizing bacteria—evolution of the Sox sulfur oxidation enzyme system. Environ Microbiol 9:2957–2977

Middelburg J (2000) The geochemical sulfur cycle. In: Lens P, Hulshoff Pol W (eds) Environmental technologies to treat sulfur pollution. IWA Publishing, London, pp 33–46

Müller FH, Bandeiras TM, Urich T et al (2004) Coupling of the pathway of sulphur oxidation to dioxygen reduction: characterization of a novel membrane-bound thiosulphate:quinone oxidoreductase. Mol Microbiol 53:1147–1160

Nakatani T, Ohtsu I, Nonaka G et al (2012) Enhancement of thioredoxin/glutaredoxin-mediated L-cysteine synthesis from S-sulfocysteine increases L-cysteine production in *Escherichia coli*. Microb Cell Fact 11:62

Neumann S, Wynen A, Trüper HG et al (2000) Characterization of the *cys* gene locus from *Allochromatium vinosum* indicates an unusual sulfate assimilation pathway. Mol Biol Rep 27:27–33

Ogawa T, Furusawa T, Nomura R et al (2008) SoxAX binding protein, a novel component of the thiosulfate-oxidizing multienzyme system in the green sulfur bacterium *Chlorobium tepidum*. J Bacteriol 190:6097–6110

Osorio H, Mangold S, Denis Y et al (2013) Anaerobic sulfur metabolism coupled to dissimilatory iron reduction in the extremophile *Acidithiobacillus ferrooxidans*. Appl Environ Microbiol 79:2172–2181

Ouyang J, Liu Q, Li B et al (2013) Proteomic analysis of differential protein expression in *Acidithiobacillus ferrooxidans* grown on ferrous iron or elemental sulfur. Indian J Microbiol 53:56–62

Parey K, Demmer U, Warkentin E et al (2013) Structural, biochemical and genetic characterization of ATP sulfurylase from *Allochromatium vinosum*. PLoS One 8:e74707

Pattaragulwanit K, Brune DC, Trüper HG et al (1998) Molecular genetic evidence for extracytoplasmic localization of sulfur globules in *Chromatium vinosum*. Arch Microbiol 169:434–444

Pires RH, Lourenco AI, Morais F et al (2003) A novel membrane-bound respiratory complex from *Desulfovibrio desulfuricans* ATCC 27774. Biochim Biophys Acta 1605:67–82

Pires RH, Venceslau SS, Morais F et al (2006) Characterization of the *Desulfovibrio desulfuricans* ATCC 27774 DsrMKJOP complex—a membrane-bound redox complex involved in the sulfate respiratory pathway. Biochemistry 45:249–262

Podgorsek L, Imhoff JF (1999) Tetrathionate production by sulfur oxidizing bacteria and the role of tetrathionate in the sulfur cycle of Baltic Sea sediments. Aquat Microb Ecol 17:255–265

Pott AS, Dahl C (1998) Sirohaem-sulfite reductase and other proteins encoded in the *dsr* locus of *Chromatium vinosum* are involved in the oxidation of intracellular sulfur. Microbiology 144: 1881–1894

Prange A, Chauvistré R, Modrow H et al (2002) Quantitative speciation of sulfur in bacterial sulfur globules: X-ray absorption spectroscopy reveals at least three different speciations of sulfur. Microbiology 148:267–276

Prange A, Engelhardt H, Trüper HG et al (2004) The role of the sulfur globule proteins of *Allochromatium vinosum*: mutagenesis of the sulfur globule protein genes and expression studies by real-time RT PCR. Arch Microbiol 182:165–174

Quatrini R, Appia-Ayme C, Denis Y et al (2006) Insights into the iron and sulfur energetic metabolism of *Acidithiobacillus ferrooxidans* by microarray transcriptome profiling. Hydrometallurgy 83:263–272

Quatrini R, Appia-Ayme C, Denis Y et al (2009) Extending the models for iron and sulfur oxidation in the extreme acidophile *Acidithiobacillus ferrooxidans*. BMC Genomics 10:394

Quentmeier A, Friedrich CG (2001) The cysteine residue of the SoxY protein as the active site of protein-bound sulfur oxidation of *Paracoccus pantotrophus* GB17. FEBS Lett 503:168–172

Ramos AR, Keller KL, Wall JD et al (2012) The membrane QmoABC complex interacts directly with the dissimilatory adenosine 5′-phosphosulfate reductase in sulfate reducing bacteria. Front Microbiol 3:137

Raymond JC, Sistrom WR (1969) *Ectothiorhodospira halophila*—a new species of the genus *Ectothiorhodospira*. Arch Mikrobiol 69:121–126

Reijerse EJ, Sommerhalter M, Hellwig P et al (2007) The unusal redox centers of SoxXA, a novel *c*-type heme-enzyme essential for chemotrophic sulfur-oxidation of *Paracoccus pantotrophus*. Biochemistry 46:7804–7810

Reinartz M, Tschäpe J, Brüser T et al (1998) Sulfide oxidation in the phototrophic sulfur bacterium *Chromatium vinosum*. Arch Microbiol 170:59–68

Rodriguez J, Hiras J, Hanson TE (2011) Sulfite oxidation in *Chlorobaculum tepidum*. Front Microbiol 2:112. doi:10.3389/fmcib.2011.00112

Sanchez O, Ferrera I, Dahl C et al (2001) In vivo role of APS reductase in the purple sulfur bacterium *Allochromatium vinosum*. Arch Microbiol 176:301–305

Sander J, Dahl C (2009) Metabolism of inorganic sulfur compounds in purple bacteria. In: Hunter CN, Daldal F, Thurnauer MC, Beatty JT (eds) Purple bacteria. Springer, Dordrecht, pp 595–622

Sander J, Engels-Schwarzlose S, Dahl C (2006) Importance of the DsrMKJOP complex for sulfur oxidation in *Allochromatium vinosum* and phylogenetic analysis of related complexes in other prokaryotes. Arch Microbiol 186:357–366

Santos AA, Venceslau SS, Grein F et al (2015) A protein trisulfide couples dissimilatory sulfate reduction to energy conservation. Science 350:1541–1545

Sauvé V, Bruno S, Berks BC et al (2007) The SoxYZ complex carries sulfur cycle intermediates on a peptide swinging arm. J Biol Chem 282:23194–23204

Sauvé V, Roversi P, Leath KJ et al (2009) Mechanism for the hydrolysis of a sulfur-sulfur bond based on the crystal structure of the thiosulfohydrolase SoxB. J Biol Chem 284:21707–21718

Schütz M, Maldener I, Griesbeck C et al (1999) Sulfide-quinone reductase from *Rhodobacter capsulatus*: requirement for growth, periplasmic localization, and extension of gene sequence analysis. J Bacteriol 181:6516–6523

Schütz M, Shahak Y, Padan E et al (1997) Sulfide-quinone reductase from *Rhodobacter capsulatus*. J Biol Chem 272:9890–9894

Sekowska A, Kung HF, Danchin A (2000) Sulfur metabolism in *Escherichia coli* and related bacteria: facts and fiction. J Mol Microbiol Biotechnol 2:145–177

Shahak Y, Hauska G (2008) Sulfide oxidation from cyanobacteria to humans: sulfide-quinone oxidoreductase (SQR). In: Hell R, Dahl C, Knaff DB, Leustek T (eds) Sulfur metabolism in phototrophic organisms. Springer, Dordrecht, pp 319–335

Shuman KE, Hanson TE (2016) A sulfide:quinone oxidoreductase from *Chlorobaculum tepidum* displays unusual kinetic properties. FEMS Microbiol Lett 363

Simon J, Kern M (2008) Quinone-reactive proteins devoid of haem b form widespread membrane-bound electron transport modules in bacterial respiration. Biochem Soc Trans 36:1011–1016

Simon J, Kroneck PM (2013) Microbial sulfite respiration. Adv Microb Physiol 62:45–117

Singh KS, Kirksey J, Hoff WD et al (2014) Draft genome sequence of the extremely halophilic phototrophic purple sulfur bacterium *Halorhodospira halochloris*. J Genet 2:118–120

Sirko A, Zatyka M, Sadowy E et al (1995) Sulfate and thiosulfate transport in *Escherichia coli* K-12: evidence for a functional overlapping of sulfate- and thiosulfate-binding proteins. J Bacteriol 177:4134–4136

Smith AJ, Lascelles J (1966) Thiosulphate metabolism and rhodanese in *Chromatium* sp. strain D. J Gen Microbiol 42:357–370

Sorokin DY (2003) Oxidation of inorganic sulfur compounds by obligately organotrophic bacteria. Microbiology 72:641–653

Sorokin DY, Tourova TP, Kuznetsov BB et al (2000) *Roseinatronobacter thiooxidans* gen. nov., sp. nov., a new alkaliphilic aerobic bacteriochlorophyll a—containing bacterium isolated from a soda lake. Microbiology 69:75–82

Spalding MD, Prigge ST (2010) Lipoic acid metabolism in microbial pathogens. Microbiol Mol Biol Rev 74:200–228

Spring S (2014) Function and evolution of the Sox multienzyme complex in the marine Gammaproteobacterium *Congregibacter litoralis*. ISRN Microbiol 2014:597418

Steudel R, Holdt G, Visscher PT et al (1990) Search for polythionates in cultures of *Chromatium vinosum* after sulfide incubation. Arch Microbiol 155:432–437

Stockdreher Y, Sturm M, Josten M et al (2014) New proteins involved in sulfur trafficking in the cytoplasm of *Allochromatium vinosum*. J Biol Chem 289:12390–12403

Stockdreher Y, Venceslau SS, Josten M et al (2012) Cytoplasmic sulfurtransferases in the purple sulfur bacterium *Allochromatium vinosum*: evidence for sulfur transfer from DsrEFH to DsrC. PLoS One 7:e40785

Tank M, Bryant DA (2015a) *Chloracidobacterium thermophilum* gen. nov., sp. nov.: an anoxygenic microaerophilic chlorophotoheterotrophic acidobacterium. Int J Syst Evol Microbiol 65:1426–1430

Tank M, Bryant DA (2015b) Nutrient requirements and growth physiology of the photoheterotrophic Acidobacterium, *Chloracidobacterium thermophilum*. Front Microbiol 6:226

Thauer RK, Kaster AK, Seedorf H et al (2008) Methanogenic archaea: ecologically relevant differences in energy conservation. Nat Rev Microbiol 6:579–591

Then J, Trüper HG (1981) The role of thiosulfate in sulfur metabolism of *Rhodopseudomonas globiformis*. Arch Microbiol 130:143–146

Venceslau SS, Stockdreher Y, Dahl C et al (2014) The "bacterial heterodisulfide" DsrC is a key protein in dissimilatory sulfur metabolism. Biochim Biophys Acta 1837:1148–1164

Visscher PT, Taylor BF (1993) Organic thiols as organolithotrophic substrates for growth of phototrophic bacteria. Appl Environ Microbiol 59:93–96

Weissgerber T, Sylvester M, Kröninger L et al (2014a) A comparative quantitative proteome study identifies new proteins relevant for sulfur oxidation in the purple sulfur bacterium *Allochromatium vinosum*. Appl Environ Microbiol 80:2279–2292

Weissgerber T, Watanabe M, Hoefgen R et al (2014b) Metabolomic profiling of the purple sulfur bacterium *Allochromatium vinosum* during growth on different reduced sulfur compounds and malate. Metabolomics 10:1094–1112

Weissgerber T, Dobler N, Polen T et al (2013) Genome-wide transcriptional profiling of the purple sulfur bacterium *Allochromatium vinosum* DSM 180^T during growth on different reduced sulfur compounds. J Bacteriol 195:4231–4245

Weissgerber T, Zigann R, Bruce D et al (2011) Complete genome sequence of *Allochromatium vinosum* DSM 180^T. Stand Genomic Sci 5:311–330. doi:10.4056/sigs.2335270

Welte C, Hafner S, Krätzer C et al (2009) Interaction between Sox proteins of two physiologically distinct bacteria and a new protein involved in thiosulfate oxidation. FEBS Lett 583:1281–1286

Wentzien S, Sand W, Albertsen A et al (1994) Thiosulfate and tetrathionate degradation as well as biofilm generation by *Thiobacillus intermedius* and *Thiobacillus versutus* studied by microcalorimetry, HPLC, and ion-pair chromatography. Arch Microbiol 161:116–125

Wilson JJ, Kappler U (2009) Sulfite oxidation in *Sinorhizobium meliloti*. Biochim Biophys Acta 1787:1516–1525

Woodin TS, Segel IH (1968) Glutathione reductase-dependent metabolism of cysteine-S-sulfate by *Penicillium chrysogenum*. Biochim Biophys Acta 167:78–88

Yurkov VV, Krasil'nikova EN, Gorlenko VM (1994) Thiosulfate metabolism in the aerobic bacteriochlorophyll-a-containing bacteria *Erythromicrobium hydrolyticum* and *Roseococcus thiosulfatophilus*. Microbiology 63:91–94

Zaar A, Fuchs G, Golecki JR et al (2003) A new purple sulfur bacterium isolated from a littoral microbial mat, *Thiorhodococcus drewsii* sp. nov. Arch Microbiol 179:174–183

Zander U, Faust A, Klink BU et al (2010) Structural basis for the oxidation of protein-bound sulfur by the sulfur cycle molybdohemo-enzyme sulfane dehydrogenase SoxCD. J Biol Chem 286:8349–8360

Zeng Y, Feng F, Medova H et al (2014) Functional type 2 photosynthetic reaction centers found in the rare bacterial phylum Gemmatimonadetes. Proc Natl Acad Sci U S A 111:7795–7800

Zeng Y, Selyanin V, Lukes M et al (2015) Characterization of the microaerophilic, bacteriochlorophyll a-containing bacterium *Gemmatimonas phototrophica* sp. nov., and emended descriptions of the genus *Gemmatimonas* and *Gemmatimonas aurantiaca*. Int J Syst Evol Microbiol 65:2410–2419

Zhang Y, Weiner JH (2014) Characterization of the kinetics and electron paramagnetic resonance spectroscopic properties of *Acidithiobacillus ferrooxidans* sulfide:quinone oxidoreductase (SQR). Arch Biochem Biophys 564:110–119