Chapter 3 A biochemical view on the biological sulfur cycle

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Chapter 3

A biochemical view on the biological sulfur cycle

Christiane Dahl

3.1 INTRODUCTION

Sulfur is the tenth most abundant element on Earth (Steudel & Chivers, 2019) and is cycled dynamically between the geosphere and biosphere. Sulfate or sulfide in water and soil and sulfur dioxide in the atmosphere constitute the majority of sulfur in nature (Middelburg, 2000) with the oceans as a major reservoir. Here, sulfur is present in very large quantities as dissolved sulfate and also as sedimentary minerals like gypsum (Sievert *et al*., 2007). Among sulfur-containing minerals, pyrite (FeS_2) is especially ubiquitous (Johnson *et al*., 2012; Muyzer & Stams, 2008).

Sulfur exhibits high reactivity in reduced forms and occurs in several stable oxidation states, ranging from −2 (as in sulfide or reduced organic sulfur) to +6 in sulfate. The most stable form of sulfur in the presence of oxygen is sulfate, while the reduced inorganic forms of sulfur with oxidation states of −2 and zero (as in elemental sulfur) are quite common in anoxic environments. Smaller but significant roles are played by polysulfide, polythionates, thiosulfate, sulfoxides as well as elemental sulfur. Sulfur compounds of mixed valence states like thiosulfate or tetrathionate occur transiently. Organic sulfur compounds like the volatile dimethylsulfide are also important on a global scale. The latter transports sulfur from the oceans to terrestrial regions, and it also affects atmospheric chemistry and the climate system (Charlson *et al*., 1987; Kettle & Andreae, 2000).

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Sulfur is an essential nutrient for life and abundant in all organisms, where it is present in the amino acids methionine and cysteine, in (poly-)peptides, enzyme cofactors, redox-active co-substrates, such as glutathione, as well as in redox-active enzyme cofactors (iron-sulfur clusters), sulfolipids or carbohydrates.

In contrast, the biological roles of inorganic sulfur compounds are comparatively restricted: either they serve as sources for sulfur assimilation and incorporation into the above mentioned organic compounds, or they are employed as donors or acceptors of electrons for dissimilatory energy-conserving electron transport. The latter pathways establish an electrochemical membrane potential which in turn can be used for adenosine triphosphate (ATP) synthesis, nicotinamide adenine dinucleotide (NAD) reduction or other energy-consuming purposes. Dissimilatory sulfur-based energy conservation goes along with mass transformations and is restricted almost exclusively to prokaryotes, while assimilatory sulfur metabolism is not only very common in prokaryotes, but also occurs in plants, algae and fungi. The turnover of assimilatory pathways is comparatively low and the sulfur compounds are incorporated into organic compounds, mainly – but not exclusively – at the sulfide level.

This review summarizes the current knowledge about the various parts of the biological sulfur cycle. I will focus on new developments arising from studies performed during the 20 years that have passed since Thomas Brüser, Piet Lens and Hans G. Trüper published their chapter about the biological sulfur cycle in the first edition of this book (Brüser *et al*., 2000). For further details about particular aspects, the reader is referred to more comprehensive reviews on dissimilatory reduction of sulfur compounds (Grein *et al*., 2013; Muyzer & Stams, 2008; Rabus *et al*., 2015; Venceslau *et al*., 2014) and dissimilatory sulfur oxidation (Dahl, 2015, 2017; Frigaard & Dahl, 2009; Kappler, 2008, 2011; Tanabe *et al*., 2019). More detailed overviews of the biogeochemical sulfur cycle in marine sediments have been published by, e.g. Canfield (2001), Jørgensen and Kasten (2006), Wasmund *et al*. (2017) and Jørgensen *et al*. (2019). Organosulfur compound and assimilatory sulfur metabolism will not be dealt with here and the reader is referred to information provided by others for this part of the sulfur cycle (Cook *et al*., 2008; Kappler & Schäfer, 2014; Kappler *et al*., 2019; Leustek *et al*., 2000; Schäfer *et al*., 2010).

3.2 IMPORTANT INORGANIC SULFUR COMPOUNDS OF THE BIOLOGICAL SULFUR CYCLE

Sulfide, polysulfides, thiosulfate, polythionates, elemental sulfur, bisulfite and sulfate are the most common inorganic sulfur compounds that occur in natural environments. Sulfur compounds of intermediate oxidation states may serve either as electron acceptors or as electron donors in redox processes. In contrast, sulfide and sulfate cannot be further reduced or oxidized, respectively. Sulfide and sulfate are, therefore, the final products of most sulfur compound reduction

or oxidation pathways, respectively. The oxidation states of relevant compounds are listed in Table 3.1.

It is important to recall that free inorganic sulfur compounds are not only produced by biological processes and that abiotic processes and the biological sulfur cycle are interconnected. The abiotic formation of inorganic sulfur substrates can strongly influence the microbial species composition in natural habitats. At this point the various known origins of biologically important inorganic sulfur compounds are briefly summarized.

Hydrogen **sulfide**, the most reduced form of sulfur, is a poisonous, corrosive and foul-smelling gas (Jiang *et al.*, 2016). It is ubiquitous in natural aqueous environments and is often accompanied by **polysulfides.** Hydrogen sulfide occurs naturally in large amounts in underground deposits of "sour" natural gas. In addition, it is found in minerals in soils and rocks or in sulfide-enriched springs and is produced as the end-point of microbial sulfate/sulfur reduction. It is highly soluble in water, where it can dissociate into hydrogen sulfide (HS^-). Except at the highest pH values, the concentration of sulfide (S^{2-}) ions is negligible (Philips & Philips, 2000). Chemical oxidation of hydrogen sulfide ions results in disulfide ions which may be further oxidized to higher inorganic polysulfides and eventually to elemental sulfur (Dahl *et al.*, 2002; Steudel, 1996a). Sulfide is also released by desulfuration of organic compounds that contain reduced sulfur (e.g. proteins). **Sulfide** is formed as the main product of sulfate respiration by bacteria that dominate under anaerobic conditions when organic matter and sulfate are not limiting. Sulfur compounds other than sulfate (e.g. thiosulfate and elemental sulfur) can also serve as electron acceptors for respirations that lead to sulfide (Rabus *et al.*, 2015).

Elemental sulfur naturally occurs in a huge variety of environments, such as volcanic areas including sulfidic springs, deep-sea hydrothermal vents, and hydrocarbon seeps, salt marshes or marine sediments (Cosmidis *et al.*, 2019; Jørgensen & Nelson, 2004; Kamyshny & Ferdelman, 2010; Zopfi *et al.*, 2004). Elemental sulfur can be formed through abiogenic processes when sulfide is

Table 3.1 Inorganic sulfur compounds of biological relevance.

Compound	Chemical Formula	Sulfur Oxidation State
Sulfide	H_2S, HS^-	−2
Polysulfides	$^-S\text{-}S_n\text{-}S^-$	−1 (terminal S)/0 (inner S)
Thiosulfate	$S_2O_3^{2-}$	−1 (sulfane S)/+5 (sulfone S)
Polythionates	$^-{}_3OS\text{-}S_n\text{-}SO_3^-$	0 (inner S)/+5 (sulfone S)
Elemental sulfur	S_n rings or chains	0
Sulfite	HSO_3^-, SO_3^{2-}	+4
Sulfate	SO_4^{2-}	+6

oxidized by molecular oxygen, possibly catalyzed by oxidized metals (Luther *et al*., 2011). At standard conditions, homocyclic, orthorhombic crystalline α-sulfur (α -S_8) (cyclo-octasulfur) is the thermodynamically most stable form (Steudel, 1996a, b). Commercially-available sulfur consists mainly of S_8 rings and polymeric sulfur. Polymeric sulfur consists of very long helically wound chains of almost all sizes (Steudel, 2000). The bright yellow color of elemental sulfur is due to traces of S_7 rings. Besides S_8, biological samples may also contain S_6, S_7 and S_{12} rings, while bigger rings of up to S_{20} are accessible through chemical synthesis (Steudel, 2000). Regardless of the molecular size, all sulfur allotropes are hydrophobic, are not wetted by water and have a very low solubility in water. In the environment, the presence of elemental sulfur is often associated with microbial oxidation of reduced sulfur compounds (Kleinjan *et al*., 2003). Elemental sulfur can be formed by sulfide-oxidizing bacteria (Frigaard & Dahl, 2009; Wasmund *et al*., 2017). In some species, elemental sulfur is the final oxidation product and can be further metabolized by other bacteria. In others, for example in many anoxygenic phototrophic bacteria, intra- or extracellular sulfur globules are formed as transient intermediates during sulfur compound oxidation to sulfate (Dahl, 2017; Frigaard & Dahl, 2009).

Thiosulfate is mainly formed as a product of sulfide oxidation, but can also be formed by the spontaneous non-biological reaction of sulfite with sulfur or polythionates. A further origin of thiosulfate is the biological leaching process where thiosulfate is formed by oxidation of sulfidic minerals like FeS_2, MoS_2 or WS_2 (Vera *et al*., 2013). Release of thiosulfate as a product of taurine fermentation has also been observed (Cook *et al*., 2008). Thiosulfate may furthermore arise as an intermediate or end product of dimethyl sulfide oxidation (de Zwart *et al*., 1997; Koch & Dahl, 2018). Thiosulfate is not only used as an effective electron acceptor in anaerobic respiratory processes (Burns & DiChristina, 2009), but also widely used as an electron donor by sulfur-oxidizing bacteria, because it is chemically stable at neutral to alkaline conditions and non-toxic.

Tetrathionate also can be a natural substrate of sulfur-oxidizing bacteria. It originates from incomplete oxidation processes and can be produced from thiosulfate by a number of bacteria in one oxidation step (Denkmann *et al*., 2012). Tetrathionate can furthermore serve as a terminal electron acceptor, a reaction with special relevance for *Salmonella enterica* serotype Typhimurium in the human gut (Winter *et al*., 2010).

Sulfite is highly reactive. Its nucleophility and strong reducing capacity contribute to its toxicity and antimicrobial action culminating in its widespread use as food preservative and disinfectant (Kappler & Dahl, 2001). In nature it occurs as a consequence of geological and industrial processes and of the anaerobic mineralization of organic matter by dissimilatory sulfate reduction. Various prokaryotes unable to respire sulfate are able to grow at the expense of sulfite reduction by employing a respiratory and presumably also detoxifying process (Simon & Kroneck, 2013). On the other hand, many bacteria also grow

by oxidizing sulfite and some of them seem to be specialized in sulfite oxidation, e.g. *Sulfitobacter* species (Sorokin, 1995). Sulfite is an intermediate in most sulfur compound redox pathways and in some cases is released into the medium to some extent (Neutzling *et al.*, 1985). Such a "leakage" could make sulfite available to other bacteria.

Sulfate is formed under aerobic conditions from most sulfur compounds which are sensitive to oxidation processes. Under oxic as well as under anoxic conditions sulfate is produced by chemotrophic (aerobic and anaerobic) and phototrophic (anaerobic) sulfur compound oxidizing bacteria. Huge amounts of sulfate are dissolved in the oceans (~28 mM) or in minerals like gypsum. Most freshwaters contain about 50 times less sulfate. Soil water concentrations vary depending on climate conditions and mineral composition.

3.3 THE BIOLOGICAL SULFUR CYCLE

Biochemical oxidation and reduction of sulfur compounds constitute the biological sulfur cycle (Figure 3.1) that is not only ongoing today but also had a profound impact on Earth evolution (Colman *et al.*, 2019). Sulfur cycling is tightly interwoven with other important element cycles (carbon, nitrogen, iron and manganese) and has therefore profound implications for ecosystem level processes.

Organisms participate in the sulfur cycle in two fundamentally different ways: the **assimilation** of sulfur compounds serves for the biosynthesis of sulfur-containing cell constituents, while during **dissimilation** sulfur compounds serve as electron donors or acceptors for energy-conserving processes. The vast part of sulfate assimilation is contributed by phototrophic organisms, i.e. plants, algae and cyanobacteria. On a global scale, land vegetation and oceans contribute approximately equal parts to this process (Giordano *et al.*, 2008). Sulfate uptake, reduction and incorporation of sulfide into biomolecules are all highly regulated steps and induced only in the absence of external reduced sulfur compounds.

Under anoxic conditions in the absence of nitrate, sulfate and elemental sulfur are used as electron acceptors of anaerobic respiratory processes. In fact, the dissimilatory reduction of sulfate is the primary driver of biogeochemical sulfur cycling (Rabus *et al.*, 2015; Wasmund *et al.*, 2017). In addition, some sulfur compound respirers can use sulfite, thiosulfate, organic sulfoxides, inorganic polysulfides and/or organic disulfanes as terminal electron acceptors (Hedderich *et al.*, 1999; Simon & Kroneck, 2013). All these processes lead to the release of large amounts of sulfide, which may be chemically oxidized to thiosulfate and polythionates at the oxic/anoxic interface.

In turn, hydrogen sulfide serves as an electron donor for a huge array of chemo- and photolithotrophic bacteria and archaea such as *Acidithiobacillus* or *Acidianus* species (Dahl, 2017; Frigaard & Dahl, 2009; Kletzin *et al.*, 2004; Mangold *et al.*, 2011; Wang *et al.*, 2019). Reduced sulfur compound oxidation can occur aerobically as well as anaerobically, with either oxygen, nitrate or manganese

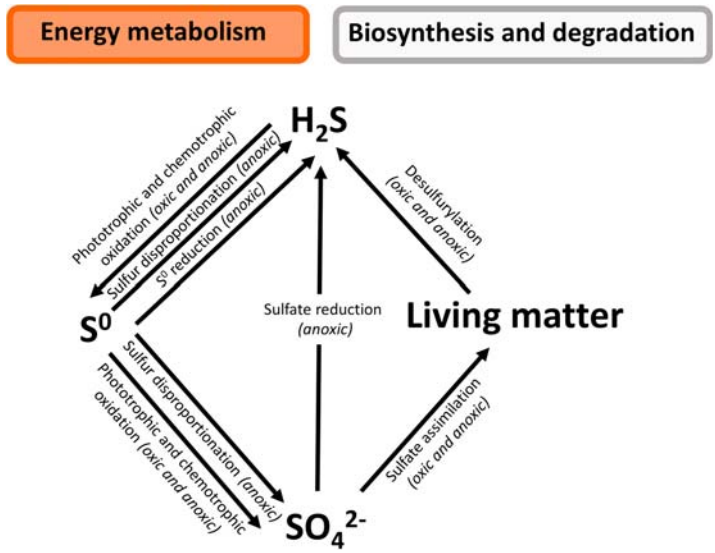

Figure 3.1 Simple view of the biological sulfur cycle. Sulfur, an essential element for life is taken up by sulfate by prokaryotes, eukaryotic microorganisms, plants and in reduced form by animals. Decomposition of dead organic matter releases the sulfur in reduced form, as sulfide. Sulfate-reducing prokaryotes (e.g. *Desulfovibrio* spp.) use sulfate as respiratory electron acceptor and produce large amounts of sulfide which can in turn be oxidized by anaerobic phototrophic sulfur oxidizers (e.g. *Allochromatium* or *Chlorobium* spp.) or by chemolithotrophs (e.g. *Acidithiobacillus* or *Beggiatoa* spp.) under oxic or anoxic conditions. More specialized groups can reduce (e.g. *Desulfuromonas* spp.) or disproportionate (e.g. *Desulfovibrio sulfodismutans*) elemental sulfur.

[Mn(IV)] acting as electron acceptors, or in anoxygenic, anaerobic photosynthesis (Dahl *et al*., 2008; Henkel *et al*., 2019). The microbial oxidation of sulfide establishes a complex network of pathways in the sulfur cycle, leading to intermediate sulfur species, and partly back to sulfate. The intermediates include elemental sulfur, polysulfides, thiosulfate, and sulfite, which are all substrates for further microbial oxidation, reduction or disproportionation. New microbiological discoveries, such as long-distance electron transfer through sulfide oxidizing cable bacteria (Jørgensen *et al*., 2019), add to the complexity.

It should be emphasized here, that the notion that the two major branches of the sulfur cycle, i.e. sulfide oxidation and sulfate reduction, are necessarily performed by distinct sets of organisms has recently been severely shaken, when the Deltaproteobacterium *Desulfurivibrio alkaliphilus* was shown to grow by sulfide oxidation with nitrate (Thorup *et al*., 2017). The organism has the genetic equipment of a sulfate reducer but still it is unable to grow by sulfate reduction.

Rather it oxidizes sulfide to sulfur which is then oxidized by a reversal of the sulfate reduction pathway or disproportionated. Notably, *D. alkaliphilus* is closely related to cable bacteria and may be suited as a blueprint for understanding the physiology of these organisms, for which pure cultures do not yet exist.

The disproportionation of inorganic sulfur compounds is another important process with considerable impact on the biogeochemical sulfur cycle. It is a microbiologically catalyzed chemolithotrophic process in which sulfur compounds of intermediary redox state, like elemental sulfur, thiosulfate, and sulfite, serve as both electron donor and acceptor resulting in the formation of hydrogen sulfide and sulfate as end products (Finster, 2008). Strong evidence has been provided that disproportionating bacteria participate in and enhance the rate of pyrite formation and that they are partly responsible for the isotopic signatures of sulfidic minerals in recent and old sediments. Furthermore, the activity of elemental sulfur disproportionation can be traced back in time as long as 3.5 billion (10^9) years and would thus be one of the oldest biological processes on Earth (Finster, 2008).

One of the most intriguing recent discoveries in sulfur biogeochemistry is the ubiquity of cryptic sulfur cycling (Canfield *et al*., 2010). Cryptic sulfur cycling means rapid recycling of sulfur species, i.e. simultaneous consumption and production of sulfate such that the process does not leave an imprint on the sulfur budget of the ambient environment. Such a cycle can still have massive impact on other intertwined element cycles. In fact, there is growing evidence that sulfur cycling also occurs outside of classical sulfur-compound dominated environments like marine sediments or geologically active zones in environments that were traditionally viewed as largely sulfate-free, fermentative and dominated by methanogenesis (Wasmund *et al*., 2017). For example, cryptic sulfur cycling is inferred to occur in sediments from Aarhus Bay (Baltic Sea) (Holmkvist *et al*., 2011) and Black Sea sediments (Mikucki *et al*., 2009) that were considered to be devoid of active sulfate reduction. Cryptic sulfur cycling has furthermore been described for subglacial lakes where sulfate-sulfur is apparently reduced and re-oxidized back via coupling to reductive iron cycling (Mikucki *et al*., 2009), for sulfide-poor groundwater of the deep terrestrial subsurface (Bell *et al*., 2020) as well as for marine oxygen minimum zones (Canfield *et al*., 2010; Johnston *et al*., 2014) where extensive sulfur cycles are presumably tied to reductive nitrogen cycling.

3.4 DISSIMILATORY REDUCTION OF OXIDIZED SULFUR COMPOUNDS

3.4.1 Dissimilatory reduction of sulfate

Sulfate-reducing prokaryotes are widespread in anoxic habitats where they use sulfate as a terminal electron acceptor mainly for the degradation of organic

compounds. The process results in the production of sulfide. The role of sulfate reduction should not be underestimated as it accounts for more than 50% of organic carbon mineralization in marine sediments (Jørgensen, 1982). Sulfate reducers can grow on a large range of substrates including hydrogen, organic compounds like ethanol, malate, short and long-chain fatty acids, aromatic compounds, sugars, amino acids, alkanes, alkenes and one-carbon compounds such as carbon monoxide or methanethiol (Muyzer & Stams, 2008; Rabus *et al.*, 2015). In addition, the anaerobic oxidation of methane can be coupled to sulfate reduction (Boetius *et al.*, 2000; Nauhaus *et al.*, 2007; Orphan *et al.*, 2001). This process is performed by consortia of sulfate-reducing bacteria that thrive on intermediates produced by methanotrophic archaea performing reverse methanogenesis (Bhattarai *et al.*, 2019; Milucka *et al.*, 2013).

The sulfate-reducing prokaryotes are a very heterogeneous group. Many ecologically relevant sulfate reducers belong to the class Deltaproteobacteria (e.g. the genera *Desulfovibrio*, *Desulfobulbus* or *Desulfonema*) with members of the family Desulfobacteraceae often being especially active and abundant. Sulfate reducers are furthermore found among the Gram-positives and the classes *Thermodesulfobacteria* and *Nitrospira* and also include archaea of the genus *Archaeoglobus* (Rabus *et al.*, 2015). In addition, recent molecular ecology surveys based on metagenomics revealed further unexpected diversity of sulfate reducers and localized the trait in as many as 13 newly identified groups including 8 candidate phyla (Anantharaman *et al.*, 2018).

All sulfate reducers described so far use the same pathway for sulfate respiration (Figure 3.2). All involved enzymes reside in the cytoplasm into which sulfate is transported in an active process (Kreke & Cypionka, 1995).

The sulfate anion is very stable and consequently its reduction to bisulfite (HSO_3^-) has a very low redox potential ($E^{0\prime} = -516$ mV (Thauer *et al.*, 1977). Therefore, sulfate is first converted to a mixed anhydride which can be more easily reduced. This activation of sulfate with ATP to form adenosine 5′-phosphosulfate (APS) and pyrophosphate is catalyzed by ATP sulfurylase (Sat, sulfate adenylyltransferase). The reaction is an endergonic process ($\Delta G^{0\prime} = +46$ kJ mol^{-1}) and requires the hydrolysis of the second reaction product pyrophosphate ($\Delta G^{0\prime} = -33$ kJ mol^{-1}) and the subsequent reduction of APS ($\Delta G^{0\prime} = -60$ kJ mol^{-1}) for high efficiency. ATP sulfurylases from sulfate reducers are usually homo-oligomeric enzymes (Gavel *et al.*, 1998; Parey *et al.*, 2013).

The APS/HSO_3^- pair has a redox potential $E^{0\prime}$ of −60 mV and this two-electron reduction is catalyzed by APS reductase, AprBA. AprA is a flavoprotein binding an flavin adenine dinucleotide (FAD) cofactor and AprB binds two [4Fe-4S] clusters. The physiological electron donor for AprBA is the membrane-bound QmoABC complex (Pires *et al.*, 2003), thus coupling the oxidation of menaquinol to the reduction of APS and allowing chemiosmotic energy conservation (Duarte *et al.*, 2016; Ramos *et al.*, 2012).

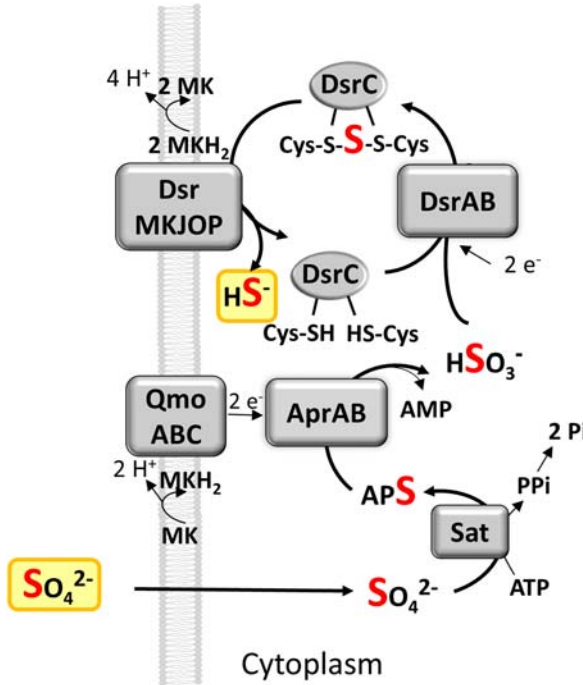

Figure 3.2 Pathway of dissimilatory sulfate reduction. The pathway involves import of sulfate, activation of sulfate to adenosine-5′-phosphosulfate (APS) at the expense of ATP catalyzed by ATP sulfurylase (sulfate adenylyl transferase, Sat), followed by reduction of APS to sulfite and release of AMP. This reaction is catalyzed by APS reductase (AprBA) and electrons are provided from menaquinol (MKH_2) via the QmoABC complex. Sulfite is reduced to a DsrC trisulfide by sulfite reductase (DsrAB). The origin of the electrons for this reduction is unclear for most sulfate reducers. In the last step the DsrC trisulfide is reduced to sulfide and the DsrC protein is regenerated. Here, the electrons most probably also stem from menaquinol and the reaction is catalyzed by the DsrMKJOP complex.

The reduction of sulfite is carried out by dissimilatory sulfite reductase. This enzyme is composed of two related subunits DsrA and DsrB in a $\alpha_2\beta_2$ arrangement. Both subunits carry an iron-tetrahydrophorphyrin (siroheme) that is coupled to a [4Fe-4S] cluster through its cysteine heme axial ligand. The siroheme-[4Fe-4S] sites in the DsrB subunits are catalytically active, while they appear to have a merely structural role in DsrA (Oliveira *et al.*, 2008; Santos *et al.*, 2015; Schiffer *et al.*, 2008). Both DsrA and DsrB also include a ferredoxin domain that binds a second [4Fe-4S] cluster that is most likely responsible for electron transfer between the physiological electron donor and the catalytic site. During sulfite reduction, the protein DsrC works as the physiological partner of

DsrAB. A DsrC trisulfide, in which a sulfur atom is bridging two conserved cysteine residues, is released as the product of the DsrAB-catalyzed reaction (Santos *et al*., 2015). As a consequence, DsrAB catalyzed (bi)sulfite reduction requires only two electrons, with the other two originating from reduced DsrC. The origin of these two electrons is still a major obstacle (Rabus *et al*., 2015; Santos *et al*., 2015). A number, albeit by far not the majority, of sulfate reducers encode the iron-sulfur flavoprotein DsrL, an NAD(P)H-reactive enzyme with the capacity to provide electrons from reduced nicotinamide adenine dinucleotides for DsrAB-catalyzed reduction of sulfite (Löffler *et al*., 2020). In the final step of dissimilatory sulfate reduction, the transmembrane complex DsrMK(JOP) probably serves in electron transfer and reductive release of sulfide from the DsrC protein trisulfide (Grein *et al*., 2013; Santos *et al*., 2015). The electrons needed most likely originate from the menaquinone pool, thus enabling coupling of ΔpH generation across the membrane directly to sulfite reduction and energy conservation.

In addition to the reduction of sulfate, most sulfate reducers can use many other electron acceptors like other sulfur compounds (thiosulfate, sulfite and sulfur), nitrate and nitrite, fumarate or dimethylsulfoxide for growth and can also grow through fermentative reactions (Muyzer & Stams, 2008; Rabus *et al*., 2015).

3.4.2 Dissimilatory reduction of sulfur cycle intermediates

Sulfur compounds of intermediate redox state, such as sulfite, elemental sulfur, polysulfide, or polythionates, serve as respiratory electron acceptors for energy conservation in an ever increasing range of microorganisms (Wasmund *et al*., 2017). On the other hand, the same compounds may be oxidized as electron donors or serve as substrates for disproportionation (see below). We should be aware that sulfur compounds of intermediate redox state usually do not accumulate to high concentrations due to rapid turnover by microorganisms and also by chemical reactions (Jørgensen, 1990b; Wasmund *et al*., 2017; Zopfi *et al*., 2004). Sulfite for example is especially prone to reactions with elemental sulfur yielding thiosulfate.

3.4.2.1 Dissimilatory reduction of sulfite

As evident from section 3.4.1, sulfite is an intermediate in dissimilatory sulfate reduction. It therefore does not appear astonishing that many sulfate reducing prokaryotes can also use externally supplied sulfite. In addition, various organisms unable to respire sulfate can still grow at the expense of sulfite reduction by employing a respiratory process. Espilonproteobacteria like several *Campylobacter* species, *Sulfurospirillum deleyianum* and *Wolinella succinogenes* (Kern *et al*., 2011) belong to this group that also comprises Firmicutes (e.g. *Desulfitobacterium*) and Gammaproteobacteria like species of the genus *Shewanella* (Shirodkar *et al*., 2011; Simon & Kroneck, 2013). These bacteria catalyze sulfite respiration with periplasmic multiheme cytochrome *c* instead of

the cytoplasmically located siroheme-containing DsrAB sulfite reductases (Kern *et al*., 2011; Shirodkar *et al*., 2011).

Sulfite respiration has also been described for *Salmonella typhimurium* and in this case a siroheme-containing cytoplasmic enzyme named AsrABC is used as the catalyst (Huang & Barrett, 1990, 1991). AsrA and AsrC are ferredoxin-like subunits while AsrB may be a flavoprotein. Binding of siroheme to AsrC was also proposed and it is possible that the holoenzyme catalyzes reduction of sulfite with nicotinamide adenine dinucleotide hydride (NADH) in the cytoplasm.

Another type of sulfite reductase (Fsr, coenzyme F_{420}-dependent sulfite reductase) is present in *Methanocaldococcus jannaschii* and other hydrogenotrophic methanogenic archaea. This enzyme again contains siroheme, iron-sulfur clusters and an FAD cofactor that is reduced by coenzyme F_{420}. Sulfite reduction as catalyzed by this enzyme is a detoxification process and additionally allows the use of sulfite as a sulfur source for biosynthetic purposes (Johnson & Mukhopadhyay, 2005).

3.4.2.2 Dissimilatory reduction of thiosulfate

The use of thiosulfate and sulfite as electron acceptors is more widespread than dissimilatory sulfate reduction (Simon & Kroneck, 2013). In fact, most sulfate-reducing prokaryotes cannot only use sulfite but also thiosulfate as an alternative electron acceptor (Rabus *et al*., 2015). In sediments, thiosulfate reduction is primarily carried out by sulfate-reducing bacteria and it has been reported that they prefer thiosulfate over sulfate as an electron donor (Jørgensen, 1990b).

The ability to respire thiosulfate is conferred by the enzyme thiosulfate reductase which catalyzes the reaction $S_2O_3^{2-} + 2\ e^- + 2\ H^+ \rightarrow HS^- + HSO_3^-$. Thiosulfate reductase activity is not restricted to sulfate-reducing bacteria but can be found in other types of environmentally abundant organisms such as *Shewanella* species (Burns & DiChristina, 2009). Thiosulfate reduction is also prevalent in the human gut, where mitochondria in the colonic mucosa detoxify sulfide produced by intestinal bacteria to thiosulfate (Goubern *et al*., 2007; Libiad *et al*., 2014). The thiosulfate is used as a respiratory substrate by many colonic bacteria such as species of the genera *Salmonella*, *Proteus*, C*itrobacter* and *Edwardsiella* (Barrett & Clark, 1987).

In *Salmonella typhimurium*, thiosulfate respiration is catalyzed by the membrane-bound PhsABC complex. The thiosulfate reduction site is located in the periplasm (Stoffels *et al*., 2012). The *S. typhimurium* enzyme consists of three subunits, PhsABC. The PhsA subunit is a peripheral membrane protein oriented towards the periplasm containing an active site bis(molybdopterin guanine dinucleotide) molybdenum cofactor. PhsC is an integral membrane protein containing two hemes *b*. PhsB is predicted to possess four iron-sulfur centers that transfer electrons between PhsC and PhsA. The naphtoquinone menaquinone is

the sole electron donor to thiosulfate reductase. The reduction of thiosulfate by menaquinol is highly endergonic and consequently, thiosulfate reductase was found to depend on the proton motive force across the cytoplasmic membrane (Stoffels *et al*., 2012).

3.4.2.3 Dissimilatory reduction of tetrathionate

Tetrathionate has long been known to be used by some bacteria as an electron acceptor under anaerobic conditions (Barrett & Clark, 1987). In a single step requiring input of two electrons, tetrathionate is reduced to two molecules of thiosulfate ($E^{0\prime} = +198$ mV) (Kurth *et al*., 2015). Tetrathionate reduction is prevalent in the gut, where tetrathionate is used as a respiratory substrate by a number of species (Oltman *et al*., 1979; Winter *et al*., 2010). The high relevance of tetrathionate as *in vivo* electron acceptor for bacterial pathogenesis is emphasized by the finding that *Salmonella typhimurium* induces host-driven formation of tetrathionate from thiosulfate by reactive oxygen species produced during inflammation. This tetrathionate is then used as a terminal electron acceptor providing the pathogen with a growth advantage over the commensal microbiota lacking this capacity (Winter *et al*., 2010). The food-borne intestinal pathogen *Campylobacter jejuni* may follow a similar strategy (Kurth *et al*., 2016a; Liu *et al*., 2013). Tetrathionate reduction has also been detected in *Wolinella succinogenes*, a close relative of *C. jejuni* (Kurth *et al*., 2017). Tetrathionate respiration has also been reported for environmentally abundant organisms such as *Shewanella* species.

So far, three distinct types of tetrathionate reductases have been described, the iron-sulfur molybdoenzyme TtrABC found in *S. typhimurium* (Hensel *et al*., 1999), the octaheme Otr enzyme from *Shewanella oneidensis* (Mowat *et al*., 2004), and the diheme cytochrome *c* TsdA from *C. jejuni* (Kurth *et al*., 2016a; Liu *et al*., 2013). It should be noted that Otr was later structurally characterized and shown to reduce nitrite and hydroxylamine to ammonia (Atkinson *et al*., 2007).

3.4.2.4 Dissimilatory reduction of sulfur and polysulfides

Microbial reduction of elemental sulfur to hydrogen sulfide has been known for many years and is widespread among bacteria and archaea. Many of these organisms are hyperthermophilic (Hedderich *et al*., 1999). In addition to some sulfate-reducers, numerous bacteria incapable of sulfate reduction can use sulfur as a respiratory electron donor, e.g. species of the genera *Desulfurella, Desulfuromonas*, *Geobacter, Shewanella* or *Thermotoga* (Moser & Nealson, 1996). Due to its low solubility in water, elemental sulfur itself is not well suited as a substrate of bacterial respiration. Elemental sulfur is readily converted to polysulfide in aqueous solutions of sulfide, a product of sulfur respiration, and polysulfides are intermediates of sulfur respiration in most of the known sulfur reducers. In fact, the actual electron acceptor of sulfur respiration in the best

studied model organism, the Epsilonproteobacterium *W. succinogenes*, is polysulfide (Hedderich *et al*., 1999; Klimmek *et al*., 2004). Polysulfide reduction is catalyzed by PsrABC (Krafft *et al*., 1995), a membrane-bound iron-sulfur molybdoprotein resembling PhsABC thiosulfate reductase and TtrABC tetrathionate reductase. In *W. succinogenes,* polysulfide reduction is facilitated by a periplasmic sulfur-binding protein (Sud) (Klimmek *et al*., 1998).

The situation in the hyperthermophilic archaeon *Pyrococcus furiosus* appears to be complex. The originally described cytoplasmic coenzyme A-dependent nicotinamide dinucleotide phosphate hydride (NADPH) sulfur oxidoreductase later turned out not to be essential for sulfur reduction (Bridger *et al*., 2011). Probably, two sulfide dehydrogenase isoenzymes provide a compensatory NADPH-dependent sulfur reduction system (Nsr). Apart from these, a membrane-bound oxidoreductase complex is indispensable for growth on sulfur (Bridger *et al*., 2011), that is proposed to catalyze ferredoxin-dependent reduction of NADP and thereby provide reducing equivalents for sulfur reduction. The substrate for Nsr has been proposed to be colloidal sulfur, i.e. short S^0 chains and S_8.

It should be emphasized that recently the application of metagenomics to marine sediments has revealed potential for sulfur and possibly also thiosulfate reduction in taxa completely undescribed and not previously connected with the sulfur cycle, such as the archaeal phylum Thorarchaeota (Lazar *et al*., 2017; Seitz *et al*., 2016).

3.5 DISSIMILATORY OXIDATION OF REDUCED SULFUR COMPOUNDS

Concerning their physiology, two groups of lithoautotrophic sulfur-oxidizing bacteria can be differentiated: the first are phototrophic prokaryotes that use sulfur compounds as electron donors for CO_2 fixation in the light (Dahl, 2017; Frigaard & Dahl, 2009). The second are chemotrophic sulfur-oxidizing prokaryotes that use the energy derived from the oxidation of sulfur compounds with either oxygen, nitrate or Mn(IV) oxide as respiratory electron acceptors to fix carbon dioxide (Dahl *et al*., 2008; Henkel *et al*., 2019). It should be noted that sulfur compounds are also an important energy source for symbiotic associations of chemoautotrophic sulfur bacteria with marine organisms including unicellular protists, meduzoans, bivalves and nematodes (Abouna *et al*., 2015; Frenkiel *et al*., 1996; Himmel *et al*., 2009; Ott *et al*., 2004). Although first discovered at hydrothermal vents, symbiosis with sulfur oxidizers is by far not limited to these highly specialized environments (Dubilier *et al*., 2008; Petersen *et al*., 2016). In addition, a considerable number of heterotrophs are able to use sulfur compounds as a supplemental electron source during organoheterotrophic growth (Koch & Dahl, 2018).

Sulfur-oxidizing prokaryotes are metabolically and phylogenetically extremely diverse and occur in a wide range of habitats covering the complete pH range from acidic to extremely alkaline environments, as well as a huge temperature

range from hot geothermal aquatic over temperate to low-temperature marine Arctic sediments (Dahl *et al*., 2008). Inorganic sulfur compound-metabolizing archaea, typically of the order *Sulfolobales* within the *Crenarchaeota*, are largely found in volcanic environments due to the abundance of the substrate(s) in these environments. Among the Bacteria, the ability to oxidize reduced sulfur compounds occurs in many different phyla including the Proteobacteria (e.g. the genera *Beggiatoa*, *Thiobacillus*, *Thiomicrospira*, *Thioploca*, *Thiothrix, Thiovulum, Arcobacter, Sulfurovum* or *Sulfurimonas*), Chlorobi, Aquificae, and Chloroflexi (Dahl, 2017; Wasmund *et al*., 2017). Over recent years, metagenome studies have indicated even greater diversity via the detection of genes related to sulfur oxidation not only in Proteobacteria that had before not been associated with sulfur oxidation (Lenk *et al*., 2011, 2012; Pham *et al*., 2008; Thomas *et al*., 2014), but also in new phylogenetic lineages, e.g. the candidate phylum Rokubacteria (Anantharaman *et al*., 2016, 2018). Furthermore, evidence is accumulating that sulfur-oxidizing communities in a given habitat are not necessarily dominated by classical photo- or chemolithoautotrophic sulfur-oxidizing specialists. Rather, sulfur-oxidizing capabilities were assigned to organisms grouped into families known for metabolic versatility, e.g. the alphaproteobacterial Rhodobacteraceae, Rhodocyclaceae or Rhizobicaceae (Bell *et al*., 2020; Lenk *et al*., 2012).

A universal mechanism for the oxidation of reduced sulfur compounds does not exist. Rather, various modules for sulfur compound oxidation can occur alone or in different combinations enabling complete oxidation of the reduced sulfur substrate to sulfate and even providing redundancy of pathways.

Many sulfur-oxidizing prokaryotes thrive in environments that are characterized by steep and opposing gradients of the sulfur compounds they use as electron donors and their respiratory electron acceptor, commonly oxygen. Different strategies have been developed to overcome the spatial separation of oxygen and sulfide including internal storage of nitrate as an alternative electron acceptor and elemental sulfur, an intermediate of sulfide and thiosulfate oxidation. This strategy is for example applied by large sulfur bacteria of the family Beggiatoaceae and in several species, e.g. *Thioploca*, supported by the ability to move towards the limiting substrate by gliding motility.

The most intriguing strategy of adaptation to gradients of electron donors and acceptors is probably implemented in the so-called cable bacteria. Cable bacteria are filamentous multicellular organisms of the deltaproteobacterial family Desulfobulbaceae (Nielsen *et al*., 2010; Pfeffer *et al*., 2012) found worldwide in marine and freshwater sediments as well as in groundwater (Burdorf *et al*., 2017; Müller *et al*., 2016, 2019; Risgaard-Petersen *et al*., 2015). To date, the Desulfobulbaceae have been known to contain sulfate-reducing or sulfur-disporortionating species but not canonical sulfide oxidizers. Cable bacteria appear in redox gradients and are electrically conductive: they transfer electrons from sulfide oxidation at one end over centimeter distances to oxygen or nitrate reduction at the other end (Bjerg *et al*., 2018; Marzocchi *et al*., 2014).

The mechanism for the necessary long-distance electron transfer that couples oxidative and reductive processes at the far ends of the filaments has also not yet been finally clarified, but it appears to involve periplasmic cytochromes and yet-unidentified conductive periplasmic fibers (Meysman *et al.*, 2019). Recent genome sequencing revealed that cable bacteria likely oxidize sulfide by a reversal of the canonical sulfate reduction pathway (Kjeldsen *et al.*, 2019). In that respect, they resemble their close relative *Desulfurivibrio alkaliphilus* which grows by nitrate-dependent sulfide oxidation and sulfur disproportionation (Thorup *et al.*, 2017). A two-step process is implied where sulfide is initially oxidized to sulfur and then either disproportionated or oxidized to sulfate (Kjeldsen *et al.*, 2019). A recent study on groundwater cable bacteria revealed that cable bacteria not only use sulfide oxidation coupled to oxygen or nitrate reduction for energy conservation but that sulfur disproportionation might constitute the energy metabolism for cells in large parts of the cable bacterial filaments (Müller *et al.*, 2019).

3.5.1 Oxidation of thiosulfate

Thiosulfate oxidation is conducted by a very large number of photo- and chemotrophic bacteria. Two pathways, both of which proceed outside of the cytoplasm (if present, in the periplasm), can be differentiated. In the first, two thiosulfate anions are oxidized to tetrathionate. In the second, multiple steps lead to the end product sulfate. In a number of bacteria both pathways coexist (Hensen *et al.*, 2006; Koch & Dahl, 2018).

3.5.1.1 Oxidation of thiosulfate to tetrathionate

The very simple oxidation of two molecules of thiosulfate to tetrathionate according to the equation $2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ e^-$ is widespread among prokaryotes. It either can occur as an intermediate step in the oxidation of reduced sulfur compounds to sulfate (Dam *et al.*, 2007; Ghosh & Dam, 2009; Lu & Kelly, 1988; Wang *et al.*, 2019; Wentzien *et al.*, 1994) or lead to the formation of tetrathionate as a dead end product, as for example described for phototrophic bacteria (Hensen *et al.*, 2006) or the Alphaproteobacterium *Hyphomicrobium denitrificans* (Koch & Dahl, 2018). Two different enzymes catalyzing the reaction have been described in some detail (Figure 3.3).

The first is the membrane-bound *doxDA*-encoded thiosulfate:quinone oxidoreductase (TQO) which was first characterized from the thermoacidophilic archaeon *Acidianus ambivalens* (Müller *et al.*, 2004). The enzyme transfers electrons into the respiratory chain via quinones. Genes encoding TQO have been identified in several bacterial genera, e.g. *Acidithiobacillus* (Wang *et al.*, 2019). Nothing is known about the catalytic mechanism of the enzyme.

The second enzyme catalyzing tetrathionate formation from thiosulfate is TsdA, a diheme cytochrome *c* first characterized from *A. vinosum* (Brito *et al.*, 2015;

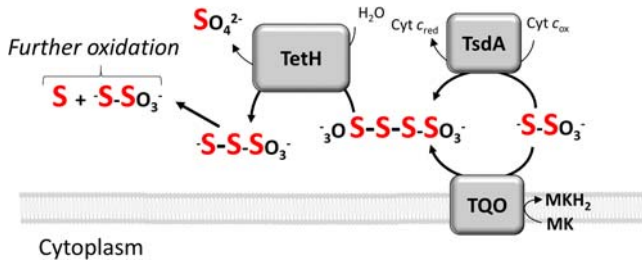

Figure 3.3 Tetrathionate formation and hydrolysis in sulfur oxidizing prokaryotes. TsdA, thiosulfate dehydrogenase; TQO, thiosulfate:quinone oxidoreductase; TetH, tetrathionate hydrolase. Decomposition of disulfanemonosulfonic acid is proposed to occur spontaneously.

Denkmann *et al*., 2012). The crystal structure of the enzyme revealed His/Cys iron coordination for Heme 1, the active site of the enzyme (Brito *et al*., 2015). The reaction mechanism of TsdAs includes a thiosulfate covalently bound to the active site cysteine (Grabarczyk *et al*., 2015b; Kurth *et al*., 2016b). The diheme cytochrome *c* TsdB, which may be fused to TsdA, has been identified as the electron accepting unit (Kurth *et al*., 2016b). Whilst the enzyme from the sulfur oxidizer *A. vinosum* is strongly biased towards 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 an alternative electron acceptor for anaerobic respiration (Liu *et al*., 2013), see section 3.4.2.3.

Further thiosulfate dehydrogenases are much less characterized. A homotetramer of 45 kDa catalyzing tetrathionate formation from thiosulfate was described for *Acidithiobacillus ferrooxidans* (Janiczek *et al*., 2007), but the gene (AFE_0042) identified later encodes a periplasmic 25 kDa protein (Kikumoto *et al*., 2013). The enzyme does not transfer electrons to ubiquinone or horse heart cytochrome *c*. A closely related protein is encoded in the vicinity (AFE_0050) in the same organism. Conspicuously, both genes reside in a cluster of genes together with *doxDA* encoding TQO and genes for rhodanese-like sulfurtransferases (Wang *et al*., 2019). Related genes also occur outside of the Gammaproteobacteria, in sulfur-oxidizing Beta- (e.g. *Sulfuriferula* and *Thiomonas*) and Alphaproteobacteria (e.g. *Acidiphilium*). Clearly more work is necessary to clarify the mechanism and relevance of these enzymes.

The pyrroloquinoline quinone (PQQ)-containing periplasmic enzyme thiol dehydrotransferase from the Betaproteobacterium *Advenella kashmirensis* has also been reported to play a role in thiosulfate-to-tetrathionate conversion (Pyne *et al*., 2018). This enzyme has dual activity catalyzing PQQ-dependent thiosulfate dehydrogenation as well as PQQ-independent thiol transfer (see sections 3.5.1.3 and 3.5.2 and Figure 3.4b).

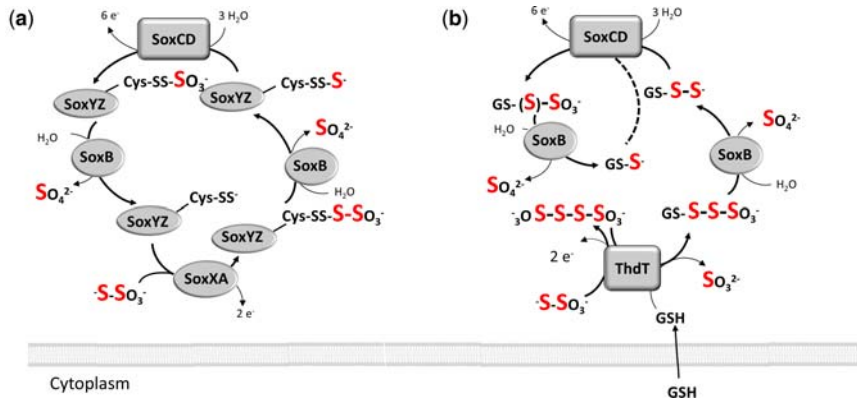

Figure 3.4 The Sox system operating in the periplasm of sulfur-oxidizing bacteria. (a). The Sox system including SoxCD completely oxidizes thiosulfate to sulfate. (b) In *Adevenalla kashimirensis* the enzyme ThdT has a dual function as thiosulfate dehydrogenase forming tetrathionate and as thiol dehydrotransferase mediating reaction of tetrathionate and glutathione and release of sulfite. Subsequent oxidation of the glutathione disulfane adduct is proposed to proceed via iterative action of SoxB and SoxCD (Pyne *et al.*, 2018).

3.5.1.2 Oxidation of thiosulfate to sulfate: the Sox system

The complete oxidation of thiosulfate to sulfate is always initiated, and in many cases also completely performed, in the bacterial periplasm and involves the well-studied thiosulfate-oxidizing Sox multienzyme system. Among the many organisms pursuing this pathway, some form sulfur deposits as intermediates either extracellularly or as intracellular sulfur globules.

In organisms that do not form sulfur deposits, thiosulfate oxidation requires four different proteins: SoxB, SoxXA, SoxYZ and SoxCD (Friedrich *et al.*, 2001) (Figure 3.4a). The heterodimeric SoxYZ protein acts as the central player and serves as a carrier of pathway intermediates (Sauvé *et al.*, 2007). These intermediates are not simply bound to a cysteine residue located near the carboxy-terminus of the SoxY subunit, the true carrier species is a SoxYZ-S-sulfane adduct (Grabarczyk & Berks, 2017). The *c*-type cytochrome SoxXA catalyzes the oxidative formation of a disulfide linkage between the sulfane sulfur of thiosulfate and the persulfurated active site cysteine residue of SoxY. Then, the sulfone group is hydrolytically released as sulfate. This reaction is catalyzed by SoxB (Sauvé *et al.*, 2009; Grabarczyk *et al.*, 2015a) and leaves the original sulfane sulfur of thiosulfate bound to SoxY. The last steps are 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 organisms forming sulfur as an intermediate, SoxCD is usually not present. This truncated system is incapable of oxidizing SoxY-bound sulfane sulfur which

is instead transferred to zero-valent sulfur stored extracellularly or intracellularly in the periplasm. This process occurs via an unresolved mechanism, in some species possibly involving the rhodanese-like protein SoxL (Welte *et al*., 2009). It may be important to note in this regard, that polysulfurated SoxY(S_{3-4})Z species occur as intermediates of thiosulfate oxidation catalyzed by a reconstituted Sox system *in vitro* (Grabarczyk & Berks, 2017). Such polysulfurated species could serve as direct donors for sulfur deposits. For complete oxidation to sulfate, truncated Sox systems must be combined with cytoplasmic sulfur oxidation systems (Tanabe *et al*., 2019), see section 3.5.7 and Figure 3.5.

3.5.1.3 Role of Sox proteins for oxidation of sulfur compounds other than thiosulfate

In 2001, Friedrich and coworkers put forward the idea that Sox proteins could well be involved in the oxidation of sulfur compounds other than thiosulfate and showed that sulfite, sulfur and hydrogen sulfide served as *in vitro* substrates for the reconstituted Sox system of *Paracoccus pantotrophus* (Friedrich *et al*., 2001; Rother *et al*., 2001). At the same time, it was reported for *Rhodovulum sulfidophilum* that the Sox machinery is not only essential for thiosulfate oxidation, but also indispensable for the oxidation of sulfide *in vivo* (Appia-Ayme *et al*., 2001). In the purple sulfur bacterium *Allochromatium vinosum*, the presence of SoxYZ is needed in parallel to the cytoplasmic enzymes for effective oxidation of sulfite (Dahl *et al*., 2013). An important role for SoxYZ independent of other Sox proteins is furthermore strongly indicated by the presence of *soxYZ* genes in a number of phototrophic sulfur bacteria that are unable to metabolize thiosulfate (Dahl *et al*., 2013).

In more recent analyses of *Sulfurimonas* species, members of the class Campylobacteria among the Epsilonproteobacteria, revealed two separate *sox* clusters, $soxXY_1Z_1AB$ and $soxCDY_2Z_2$ (Grote *et al*., 2012; Sievert *et al*., 2008). Sulfur-oxidizing, nitrate-reducing *Sulfurimonas* spp. are widespread in sediments, hydrothermal vent fields, aquifers and subsurface environments such as oil reservoirs and their role in the natural sulfur cycle should not be underestimated. The two different copies of *soxYZ* show a high level of divergence, the gene sets appear to be differentially regulated and the proteins are therefore proposed to be involved in oxidation of different sulfur compounds (Götz *et al*., 2019; Meier *et al*., 2017; Pjevac *et al*., 2018). Remarkably, a *Sulfurimonas* strain incapable of thiosulfate oxidation was described that contains only the $soxCDY_2Z_2H$ cluster and oxidizes elemental sulfur to sulfate and thiosulfate as end products (Lahme *et al*., 2019). In this strain, the lack of SoxB might be overcome by the product of the *soxH* gene, a putative metallohydrolase that may release sulfate from SoxY (Lahme *et al*., 2019).

The $GSSSSO_3^-$ adduct formed during tetrathionate degradation in *Advenella* (see sections 3.5.1.1 and 3.5.2) has been proposed as a further substrate for Sox proteins. The adduct appears as a suitable substrate for SoxB that may

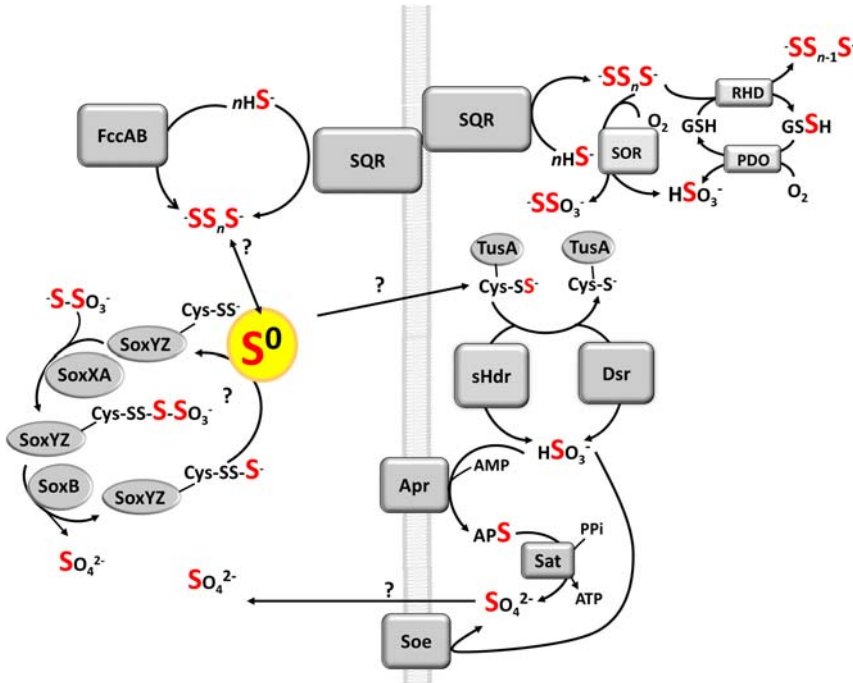

Figure 3.5 Sulfur oxidation pathways in sulfur oxidizers forming zero-valent sulfur as an intermediate and sulfide oxidation/detoxification in the cytoplasm. For clarity reactions are not given with exact stoichiometries. Sulfide oxidation in the periplasm is catalyzed by SQR (sulfide:quinone oxidoreductase) and/or flavocytochrome *c* (FccAB). The sulfur in the resulting polysulfides is accumulated zero-valent sulfur, which is also the product of thiosulfate oxidation mediated by a Sox system lacking SoxCD. Sulfur is transferred into the cytoplasm where it is delivered to the oxidizing system (either Dsr or sHdr) via a sulfur relay system (here summarized as TusA). Sulfide oxidation via SQR can also occur in the cytoplasm as a supplementary or as a detoxification reaction. Rhodanese and sulfur/persulfide dioxygenase (PDO) catalyze subsequent steps. Electrons resulting from the SQR-catalyzed reaction can be fed into the quinone pool. Sulfite is formed by direct reaction with molecular oxygen preventing energy conservation. GSH (GSSH): reduced glutathione (persulfide). Sulfur oxygenase reductase (SOR) also resides in the cytoplasm and catalyzes a dioxygen-dependent disproportionation of elemental sulfur and/or poylsulfides to hydrogen sulfite, thiosulfate, and hydrogen sulfide. Here, SOR is depicted without reductase activity (Rühl *et al.*, 2017).

hydrolytically release the terminal sulfone group as sulfate. SoxCD would then oxidize the first remaining sulfane sulfur, again followed by hydrolytic release of sulfur and one more cycle resulting in oxidation and release of the last remaining sulfane sulfur and regeneration of reduced glutathione (Pyne *et al.*, 2018).

3.5.2 Tetrathionate oxidation

Many sulfur oxidizers can oxidize tetrathionate to sulfate and/or tetrathionate occurs as an intermediate during the oxidation of thiosulfate to sulfate (Dam *et al*., 2007; Ghosh & Dam, 2009; Wang *et al*., 2019). The name "S_4I" (S_4 intermediate) has been coined for the latter pathway which occurs in many beta- and gammaproteobacterial chemolithotrophs, e.g. species of the genus *Acidithiobacillus* (Bugaytsova & Lindström, 2004; Dam *et al*., 2007; Kikumoto *et al*., 2013; Pyne *et al*., 2017, 2018; Rameez *et al*., 2019; Visser *et al*., 1996). Two different enzymes initiating tetrathionate degradation have so far been described.

The first is the enzyme tetrathionate hydrolase, TetH that has been isolated from various acidophilic *Acidithiobacillus* species, *Acidiphilium acidophilum* and the archaeon *Acidianus ambivalens*. Tetrathionate hydrolases are monomeric and/or homodimeric, membrane-associated or soluble enzymes with pH optima in the acidic range acting outside of the cytoplasm (Bugaytsova & Lindström, 2004; de Jong *et al*., 1997; Mangold *et al*., 2011; Protze *et al*., 2011). The enzymes exhibit similarity to proteins of the PQQ dehydrogenase family, however they neither appear to contain PQQ nor do they need it for activity (Kanao *et al*., 2010; Protze *et al*., 2011). The initial products of TetH-catalyzed tetrathionate hydrolysis are sulfate and disulfane monosulfonic acid ($^{-}$S-S-SO_3^{-}) (Figure 3.3). The latter is highly reactive and decomposes spontaneously to sulfur and thiosulfate (Steudel *et al*., 1987). Alternatively, reactions of the disulfane monosulfonic acid with itself were proposed that result in successive chain elongation, finally leading to the production of elemental sulfur and sulfite. Indeed, the comparatively well-studied model organism *A. ferrooxidans* forms sulfur deposits on tetrathionate (Hazeu *et al*., 1988; Steudel *et al*., 1987). Sulfur as well as sulfite could, in principle, serve as substrates for Sox proteins allowing their further oxidation (Friedrich *et al*., 2001), however *sox* genes are not present in all organisms pursuing the S_4 intermediate pathway (Wang *et al*., 2019). Many questions therefore remain to be resolved.

The second enzyme with a described capacity for initiating tetrathionate degradation is the periplasmic enzyme thiol dehydrotransferase from *Advenella kashmirensis* (Pyne *et al*., 2018) (Figure 3.4b). This enzyme cannot only catalyze tetrathionate formation from thiosulfate (see section 3.5.1.1), but also promotes the reaction of tetrathionate with reduced glutathione (GSH) yielding a glutathione sulfodisulfane adduct and sulfite according to the equation $GSH + S_4O_6^{2-} \rightarrow GSSSSO_3^{-} + SO_3^{2-}$. Subsequent oxidation of the glutathione derivative may then proceed via iterative action of SoxB and SoxCD (Pyne *et al*., 2018), see sections 3.5.1.1 and 3.5.1.2 and Figure 3.4b.

3.5.3 Oxidation of sulfide and polysulfides

Initial oxidation of sulfide is typically catalyzed by sulfide quinone oxidoreductases (SQRs) and flavocytochrome *c* sulfide dehydrogenases (Frigaard & Dahl, 2009)

(Figure 3.5). Both enzymes belong to the disulfide reductase protein family, both depend on FAD as a cofactor for activity and both produce polysulfide as the initial product. Accumulation of polysulfides leads to sulfur precipitation outside the cell or the sulfur is stored internally as sulfur globules (Brito *et al*., 2009; Cherney *et al*., 2010; Frigaard & Dahl, 2009; Griesbeck *et al*., 2000, 2002; Marcia *et al*., 2009; Schütz *et al*., 1999).

Virtually nothing is known about the oxidation of polysulfides and their transformation into sulfur deposits. Theoretically, this could be a purely chemical process as longer polysulfides are in equilibrium with elemental sulfur (Steudel *et al*., 1990).

3.5.3.1 *Sulfide:quinone oxidoreductase*

SQRs do not only occur in prokaryotes but also in mitochondria of lower and higher eukaryotes. In the latter as well as in many heterotrophic prokaryotes, SQRs do not primarily serve in energy conservation by feeding electrons into electron transport chains on the level of quinones, but instead their main purpose is sulfide detoxification. Along this line, mitochondrial SQR interacts with a rhodanese that is proposed to transfer the zero-valent sulfane sulfur formed during the reaction to glutathione (GSH) to produce glutathione persulfide (GSSH) (Libiad *et al*., 2014). Persulfide dioxygenase (PDO) then oxidizes the sulfane sulfur in GSSH to sulfite (Kabil & Banerjee, 2012). In heterotrophic bacteria, genes for related SQRs are usually genetically linked with PDO genes (Guimaraes *et al*., 2011; Liu *et al*., 2014a; Shen *et al*., 2015; Xia *et al*., 2017). PDO is a cytoplasmic soluble enzyme and accordingly SQR interacting with it has been localized on the cytoplasmic side of the membrane (Gao *et al*., 2017) (Figure 3.5).

In dissimilatory sulfur-oxidizing prokaryotes, SQR has been proposed to be located at the outer surface of the cytoplasmic membrane (Christel *et al*., 2016; Mangold *et al*., 2011; Quatrini *et al*., 2009), the same localization as has been experimentally verified for the enzyme from *Rhodobacter capsulatus* (Schütz *et al*., 1999). In accordance, polysulfides, the primary products of sulfide oxidation in purple and green sulfur bacteria instantly accumulate outside of the cells, in the medium (Marnocha *et al*., 2016; Prange *et al*., 2004).

3.5.3.2 *Flavocytochrome* c *and multitude of sulfide-oxidizing systems*

In a variety of sulfide oxidizing species, flavocytochrome *c* is present as a soluble protein in the periplasm or as a membrane-bound enzyme (Frigaard & Dahl, 2009). It consists of a flavoprotein (FccB) and a hemoprotein (FccA) and has sulfide:cytochrome *c* oxidoreductase activity *in vitro*.

Many prokaryotes have a variety of sulfur-oxidizing modules, for example *Marichromatium purpuratum* encodes three different SQRs as well as FccBA (Dahl, 2017). *A. vinosum* mutants deficient in either flavocytochrome *c* (Reinartz *et al*., 1998), *sox* genes (Hensen *et al*., 2006) or both (unpublished) still exhibit

sulfide oxidation rates comparable to the wildtype, indicating that SQR plays the major role. It is possible that FccAB is advantageous under certain growth conditions and that each of the multiple sulfide-oxidizing modules conveys adaptation to different environmental sulfide concentrations.

3.5.4 Oxidation of external sulfur

Elemental sulfur is virtually insoluble in water and how exactly it is made available as a substrate still requires more research. Most information is available for *Acidithiobacilli* that attach to sulfur by glycocalx-like extracellular polymeric substances, specifically lipopolysaccharides (Bryant *et al*., 1984; Espejo & Romero, 1987; Gehrke *et al*., 1998). Biofilms formed on the surface of elemental sulfur by cells of the thermoacidophilic archaeal species *Acidianus* also comprise an extracellular matrix that contains carbohydrates, proteins and lipids. The lipids are suggested to mediate initial attachment of the cells to sulfur while sugars like glucose and mannose are thought to be important for further colonization of sulfur and a mature biofilm architecture (Zhang *et al*., 2019). For the purple sulfur bacterium *A. vinosum*, intimate physical cell-sulfur contact was also established as a prerequisite for sulfur uptake (Franz *et al*., 2007). After attachment of the cells, sulfur needs to be mobilized. In *A. ferrooxidans* and *Acidiphilum* spp. this step involves thiols of specific outer-membrane proteins and transport into the cytoplasm as persulfide sulfane sulfur (Rohwerder & Sand, 2003). Glutathione plays a catalytic role in this step.

3.5.5 Biogenic sulfur globules

A large portion of sulfur oxidizers form sulfur deposits as intermediates, both extracellularly and intracellularly (Dahl, 2020; Marnocha *et al*., 2016, 2019). Formation of extracellular sulfur globules is typical for green sulfur bacteria and even name-giving for sulfur oxidizers of the gammaproteobacterial family Ectothiorhodospiraceae while intracellular sulfur globules typically occur in magnetotactic sulfur oxidizers, in purple sulfur bacteria of the family Chromatiaceae and in sulfur oxidizing bacterial endosymbionts (Dahl, 2020). Extracellular biogenic sulfur globules have properties clearly distinguishing them from abiotic elemental sulfur, such that the green sulfur bacterium *C. tepidum* can grow on self-produced sulfur globules but other forms of elemental sulfur do not support growth. In this case, the biogenic sulfur globules are enveloped by a layer of proteins and polysaccharides that enables cell-sulfur interactions and probably keeps the sulfur in a bioavailable form (Marnocha *et al*., 2019).

Usually the diameter of sulfur globules is in the range of 1–3 µm. The sulfur can comprise 20 to 34% of the cell dry mass (Dahl, 2020; Nelson & Castenholz, 1981). The general target compartment for sulfur storage is the bacterial periplasm. Intracellular sulfur globules are encased by a protein envelope consisting of one or more structural proteins resembling cytoskeletal keratins or plant cell wall

proteins. The chemical nature of the sulfur in the globules has been the subject of intensive controversy (Dahl, 2020; Dahl & Prange, 2006; George *et al*., 2002, 2008). In most cases, the sulfur appears to be present as S_8 rings in a nano-crystalline form possibly mixed with linear polysulfides (Dahl, 2020).

3.5.6 Sox-independent, cytoplasmic oxidation of sulfane sulfur to sulfite

Except for sulfide detoxification, all pathways described so far take place outside of the cytoplasm. As outlined above in section 3.5.1.2, the periplasmic enzyme SoxCD catalyzes the oxidation of carrier-bound sulfane sulfur to the level of a sulfone group and feeds electrons into respiratory or light-driven electron transport at the level of *c*-type cytochromes. If SoxCD is not present, the oxidation of zero-valent sulfane sulfur to sulfite is achieved in the cytoplasm by multienzyme systems allowing more efficient energy conservation.

How the sulfur is transferred into the cytoplasm for further oxidation is currently still an enigma. For organisms forming periplasmic sulfur deposits, low molecular weight organic persulfides such as glutathione amide persulfide have been proposed as carrier molecules (Dahl, 2017; Frigaard & Dahl, 2009). It is not known how these proposed carrier molecules may be generated nor have any transporters for such molecules been characterized. In *Hyphomicrobium denitrificans*, a gene encoding a predicted sulfur compound transporter resides in the same cluster as *soxYZ* and other *sox* genes and in the immediate vicinity of the genes for the cytoplasmic sulfane sulfur-oxidizing system. This predicted transporter has been suggested to pick up sulfur from periplasmic SoxYZ and to shuttle it over the cytoplasmic membrane onto cytoplasmic sulfur-binding proteins (Koch & Dahl, 2018). Experimental evidence supporting this proposal has not been provided so far.

Once transported into the cytoplasm, rhodanese-, DsrE- and TusA-like sulfurtransferases constitute a persulfide shuttling system that delivers sulfur very specifically to the target enzymes catalyzing its oxidation to sulfite (Dahl, 2015; Liu *et al*., 2014b; Tanabe *et al*., 2019; Venceslau *et al*., 2014). Two fundamentally different pathways have been described to achieve this purpose (Figure 3.5). Both pathways have in common the possibility that at least some of the electrons released can be shuttled onto NAD^+. This would considerably reduce the need for energy-demanding reverse electron flow in lithoautotrophic sulfur oxidizers.

3.5.6.1 rDsr pathway

The rDsr pathway with reverse acting dissimilatory sulfite reductase rDsrAB as its key enzyme has been characterized in quite some detail. A typical *dsr* gene cluster can consist of up to 15 different genes and may be linked with the genes for the sulfurtransferases providing DsrAB with oxidizable sulfur. In the model organism *A. vinosum*, a rhodanese-like protein and a DsrE-like protein were identified as

entry points for sulfur delivery to the TusA protein. TusA moves the sulfur onto DsrEFH from where it is transferred to the final sulfur-accepting protein DsrC. It is assumed but not yet experimentally proven that the membrane-bound DsrMKJOP electron-transporting complex oxidizes persulfurated DsrC, thus generating DsrC trisulfide which then serves as the substrate for reverse acting dissimilatory sulfite reductase. The electrons released by the oxidation of the sulfur bridged in the DsrC trisulfide to sulfite are probably transferred onto NAD^+. This reaction is catalyzed by the iron-sulfur flavoprotein DsrL (Löffler *et al*., 2020).

3.5.6.2 sHdr pathway

Many sulfur-oxidizing prokaryotes such as species of the bacterial genera *Acidithiobacillus* and *Aquifex* or archaeal sulfur oxidizers like *Sulfolobus* or *Acidianus* do not have the genetic capacity for rDsr-driven generation of sulfite. Instead, these organisms run a new pathway named the sulfur-oxidizing heterodisulfide reductase-like (sHdr) pathway due to the involvement of polypeptides resembling the HdrA, B and C subunits of heterodisulfide reductase from methanogenic archaea (Cao *et al*., 2018; Koch & Dahl, 2018). The rDsr and sHdr pathways occur virtually exclusively. Very few organisms bear the genetic potential for both oxidation routes (Berben *et al*., 2019; Koch & Dahl, 2018).

The core genes *shdrC1B1AhyphdrC2B2* that probably encode a hexameric $HdrA_2C_1C_2B_1B_2$ complex (Ernst *et al*., 2020), are usually accompanied by genes for rhodanese, DsrE- and TusA-like proteins as well as by a gene for a lipoate-binding protein (LbpA). Just like the sHdr proteins themselves, the latter has been proven to be indispensable for sulfur oxidation in the model organism *H. denitrificans* (Cao *et al*., 2018). The exact function of lipoate within the catalytic cycle of the Hdr-LbpA-based sulfur oxidation system is currently unclear, but it may either serve as a substrate binding entity during sulfur oxidation or exclusively function as a redox switch. In the second case, the sulfur substrate would be oxidized on one of the sulfur-binding proteins encoded in *shdr* gene clusters. In any event, all suggestions of the sHdr mechanism that have so far been put forward (Cao *et al*., 2018; Ernst *et al*., 2020; Tanabe *et al*., 2019) include the reduction of lipoate to dihydrolipoate at the end of the reaction cycle. Its reoxidation and concomitant reduction of NAD^+ would be catalyzed by dihydroliponamide dehydrogenase.

3.5.6.3 Formation of sulfite via reactions involving molecular oxygen

Two different enzymes have been described in sulfur-oxidizing prokaryotes that catalyze reactions of reduced sulfane sulfur with molecular oxygen. Such reactions clearly prevent energy conservation because they can neither be coupled with electron transfer nor with substrate-level phosphorylation. Still, evidence has been collected that these enzymes may be important at least in acidophiles (Wang *et al*., 2019).

3.5.6.3.1 Sulfur dioxygenase

The role of sulfur dioxygenases (SDOs) in chemolithotrophic sulfur oxidizers has been best studied for *Acidithiobacillus* species. The actual substrate for the SDO-catalyzed reaction is sulfane sulfur bound to glutathione, i.e. glutathione persulfide (GSSH, and also GSS_nH with $n > 1$) (Rohwerder & Sand, 2003). *Acidithiobacillus* species contain one or two copies of *sdo* genes. The encoded proteins appear to reside in the cytoplasm (Wu *et al*., 2017). The *in vivo* role of the various SDO proteins was studied in mutant strains of *A. ferrooxidans* and *A. caldus* yielding somewhat inconclusive results (Wang *et al*., 2014; Wu *et al*., 2017), but showing that the absence of SDOs neither impaired elemental sulfur oxidation activities nor prevented growth on externally provided elemental sulfur (Wu *et al*., 2017). It has been put forward that SDOs in *Acidithiobacillus* spp. are mainly involved in sulfane sulfur oxidation in the cytoplasm. Nothing is known about how the sulfur is distributed between the energy-conserving sHdr system and the SDOs that clearly prevent energy conservation.

Enzymes with sulfide dioxygenase or persulfide dioxygenase (PDO) activity also occur in mitochondria of animals and plants as well as in a number or heterotrophic bacteria (Kabil & Banerjee, 2012; Sattler *et al*., 2015; Xia *et al*., 2017). These proteins work together with cytoplasmically oriented sulfide: quinone oxidoreductases and play an important role in the detoxification of intracellular sulfide (Guimaraes *et al*., 2011; Liu *et al*., 2014a).

3.5.6.3.2 Sulfur oxygenase reductase

Sulfur oxygenase reductase (SOR) is another enzyme catalyzing the reaction of elemental sulfur with molecular oxygen (Figure 3.5). This enzyme, first reported in several acidophilic and thermophilic archaea, catalyzes the disproportionation of cytoplasmic elemental sulfur and/or polysulfides to thiosulfate, sulfite, and sulfide (Kletzin, 1989; Kletzin *et al*., 2004). The enzyme from *Thioalkalivibrio paradoxus* does not have reductase activity (Rühl *et al*., 2017). The *sor* gene is also present in some, though not in all *Acidithiobacillus* species and it has been put forward that that the enzyme is supplementary, but not necessary, for cytoplasmic elemental sulfur oxidation (Chen *et al*., 2012; Christel *et al*., 2016; You *et al*., 2011).

3.5.7 Oxidation of sulfite

Sulfite-oxidizing enzymes (SOEs) are molybdenum-containing enzymes that exist in almost all forms of life where they carry out important functions in protecting cells and organisms against sulfite-induced damage (Kappler, 2008, 2011). In lithotrophic sulfur oxidizers they are furthermore important for transfer of the two electrons released during oxidation of sulfite to sulfate into respiratory or photosynthetic electron transport.

3.5.7.1 Oxidation of sulfite outside of the cytoplasm

Most bacterial SOEs reside in the bacterial periplasm and react with *c*-type cytochrome electron acceptors (Kappler & Enemark, 2014). This allows feeding respiratory electron transport at the level of cytochrome *c* oxidase. As already pointed out by others (Kappler & Enemark, 2014), the energy yields from this reaction are low, and usually sulfite oxidation alone will not support cell growth.

SorAB sulfite dehydrogenase from *Starkeya novella* was the first SOE characterized from a bacterial host (Kappler *et al*., 2000). It consists of the catalytic molybdoprotein SorA and a small c-type cytochrome, SorB. Over the past two decades, at least six other bacterial SOEs have been purified and only one of these might contain a heme redox center as an integral part of the enzyme. Thus, most of the bacterial SOEs contain only molybdenum redox centers (Kappler & Enemark, 2014).

Even sulfur-oxidizers containing sulfite-generating enzyme systems in the cytoplasm (rDsr or sHdr) may have to rely on further oxidation of sulfite outside of the cytoplasm because they lack cytoplasmic sulfite-oxidizing enzyme systems. In these cases, a gene encoding a TauE-like potential sulfite exporter may be encoded in the vicinity of the *shdr* genes (Koch & Dahl, 2018).

3.5.7.2 Oxidation of sulfite in the cytoplasm

Direct, one step oxidation of sulfite to sulfate can also occur in the bacterial cytoplasm (Figure 3.5) as has first been shown for the purple sulfur bacterium *A. vinosum*. In this organism, the membrane-bound, polysulfide reductase-like iron-sulfur molybdoprotein SoeABC appears to be the major sulfite-oxidizing agent (Dahl *et al*., 2013). Genes encoding proteins related to SoeABC not only occur in purple and green phototrophic sulfur bacteria but also in a large number of chemotrophs, indicating general importance for this enzyme (Dahl *et al*., 2013; Wang *et al*., 2019).

It is firmly established that an array of anoxygenic phototrophic as well as of chemotrophic sulfur bacteria oxidize sulfite in the cytoplasm using an indirect pathway via adenosine-5′-phosphosulfate catalyzed by APS reductase (AprBA) and ATP sulfurylase (Sat) (Figure 3.5). This pathway constitutes the reversal of sulfate activation to APS and APS reduction to sulfite occurring in dissimilatory sulfate-reducers. The electrons released during the formation of APS from sulfite and adenosine monophosphate (AMP) can be fed into electron transfer chains via two different modules, depending on the organism. The first is the transmembrane protein AprM (Dahl *et al*., 2013; Meyer & Kuever, 2007) and the second is the QmoABC complex that serves the reverse function, i.e. electron transport from quinol to APS in sulfate reducers (Grein *et al*., 2013; Ramos *et al*., 2012).

3.6 SULFUR DISPROPORTIONATION

The disproportionation of sulfur compounds in energy metabolism was discovered in sulfate-reducing bacteria, when *Desulfovibrio desulfodismutans* was found to metabolize thiosulfate and sulfite according to SO_3^{2-} or $S_2O_3^{2-}$ to HS^- plus SO_4^{2-} (Bak & Pfennig, 1987). In fact, thiosulfate and sulfite disproportionation is common among sulfate reducers, albeit not always coupled to growth (Krämer & Cypionka, 1989). While thiosulfate and sulfite disproportionation are exergonic reactions, the disproportionation of elemental sulfur is endergonic under standard conditions. Nevertheless, sulfur disproportionation according to:

$$4\,S^0 + 4\,H_2O \rightarrow {SO_4}^{2-} + 3\,HS^- + 5\,H^+ \;\Delta G^{0\prime} = 10.2\,\mathrm{kJ\,mol^{-1}}$$

can support growth in the environment when the produced hydrogen sulfide is scavenged by iron and manganese oxides (Finster, 2008; Thamdrup *et al*., 1993). Growth coupled to elemental sulfur disproportionation is found predominantly in the family Desulfobulbaceae and often goes along with autotrophy (Finster *et al*., 2013). Both thiosulfate and elemental sulfur disproportionation are very relevant processes in marine and freshwater sediments and may belong to the earliest metabolic processes on earth (Jørgensen, 1990a, b; Fike *et al*., 2008; Thamdrup *et al*., 1993)

Studies of the biochemistry of sulfite and thiosulfate disproportionation of a few isolates indicate reversal of the sulfate reduction pathway during disproportionation. It has been proposed for two *Desulfovibrio* strains that ATP is formed by substrate level phosphorylation via ATP sulfurylase (Krämer & Cypionka, 1989). In addition, a reversed electron transport step is probably necessary for the reduction of thiosulfate to sulfide and sulfite fueled by electrons stemming from the oxidation of sulfite to APS (Finster, 2008; Krämer & Cypionka, 1989). In a second study, somewhat contradictory results were obtained that do not support an initial reductive cleavage of thiosulfate (Cypionka *et al*., 1998). Once produced, sulfite is further oxidized along the APS reductase pathway and possibly also via direct sulfite:oxidoreductase catalyzed oxidation (Frederiksen & Finster, 2004). Clearly, more work is necessary to fully understand the biochemistry underlying the microbial disproportionation of sulfur compounds.

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