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REVIEWS

# Diversity of Sulfur-Disproportionating Microorganisms

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**Abstract**—Microorganisms disproportionating inorganic sulfur compounds are involved in biogeochemical cycles of elements in the modern biosphere. Sulfur-disproportionating prokaryotes are represented by 30 species of the *Bacteria* domain and belong to the phyla *Proteobacteria, Thermodesulfobacteria*, and *Firmicutes*. Most of the sulfur-disproportionating bacteria belong to four orders of the class *Deltaproteobacteria*. The microorganisms responsible for dismutation of sulfur compounds inhabit freshwater and shallow marine sediments, hypersaline and soda lakes, anthropogenic environments, and various natural thermal ecosystems. Most sulfur-disproportionating organisms are able to use other processes for growth, primarily dissimilatory sulfate reduction. Ability to grow autotrophically was shown for 17 sulfur-disproportionating strains from different phylogenetic groups. The biochemical mechanisms involved in disproportionation of sulfur compounds remain uncertain, which hinders the application of the current omics techniques. Comparative analysis of available complete genomes of the microorganisms capable of elemental sulfur disproportionation is provided. The presence of the complete set of the dissimilatory sulfate reduction genes was found not to be necessary for $S^0$ disproportionation. This process does not require dissimilatory sulfite reductase (Dsr) and adenylyl-sulfate reductase (Apr). Sulfur relay proteins and the elemental sulfur- and/or polysulfides-reducing enzymes are important in sulfur disproportionation, but different microorganisms probably employ different sulfur transferases and polysulfide reductases in these processes.

*Keywords:* disproportionation, sulfur compounds, elemental sulfur, sulfate reduction, autotrophic microorganisms, thermophilic microorganisms, microbial diversity

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## MICROBIAL DISPROPORTIONATION OF SULFUR COMPOUNDS

The biogeochemical cycle of sulfur, one of the most important biogenic elements, is presently caused mainly by prokaryotic activity. Sulfur has eight oxidation states, and can participate in a number of redox reactions. Sulfur-oxidizing and sulfate-reducing microorganisms are the best-studied microbial groups involved in the sulfur cycle (see reviews by Rabus et al., 2015; Wasmund et al., 2017). Another group of microorganisms, bacteria disproportionating inorganic sulfur compounds, such as thiosulfate, sulfite, and elemental sulfur, was discovered much later (Bak and Cypionka 1987). In this review, the terms sulfur-disproportionating microorganisms and sulfur disproportionators will be used for these microorganisms, independent on what specific sulfur compound is disproportionated.

Disproportionation or dismutation is a redox reaction in which a compound with an intermediate oxidation state is simultaneously reduced and oxidized, resulting in formation of two different products. Fermentation is the case of disproportionation of organic compounds. Thus, disproportionation of sulfur compounds may be considered inorganic fermentation:

$$4SO_3^{2-} + H^+ = 3SO_4^{2-} + HS^-,$$

$$\Delta G^{\circ\prime} = -58.9 \text{ kJ mol}^{-1}\, SO_3^{2-};$$

$$S_2O_3^{2-} + H_2O = SO_4^{2-} + HS^- + H^+,$$

$$\Delta G^{\circ\prime} = -22.3 \text{ kJ mol}^{-1}\, S_2O_3^{2-};$$

$$4S^0 + 4H_2O = SO_4^{2-} + 3HS^- + 5H^+,$$

$$\Delta G^{\circ\prime} = +10.3 \text{ kJ mol}^{-1}\, S^0.$$

Under standard conditions, the disproportionation of elemental sulfur is an endergonic reaction, but thermodynamic calculations show that it can be energetically favorable if, at a sulfate concentration of 28 mM (seawater salinity), the $H_2S$ concentration decreases to a level of 1.0–10.0 mM (Finster, 2008). Such sulfide concentration may result from hydrogen sulfide escape to the gas phase or by binding to the chemicals forming poorly soluble sulfides. Manganese (IV) and iron (III) minerals, e.g., ferrihydrite, are the most efficient sulfide scavengers. In the presence of ferrihydrite

disproportionation of elemental sulfur is exergonic even under the standard conditions:

$$3S^0 + 2Fe(OH)_3 = SO_4^{2-} + 2FeS + 2H^+ + 2H_2O,$$
$$\Delta G^{\circ\prime} = -27.5 \text{ kJ mol}^{-1} S^0.$$

Elemental sulfur ($S^0$) may exist in several allotropic modifications, of which cyclic molecules with eight atoms are the most stable ($S_8$). $S^0$ is very poorly soluble in water (~1 μg/L at 25°C) (Kamyshny 2009). In a number of studies soluble polysulfides formed from $S^0$ in the presence of sulfide were shown to act as electron acceptors for microbial cells, rather than elemental sulfur (Blumentals et al., 1990; Schauder and Muller,1993; Poser et al 2013). Disproportionation of some polysulfides provides more energy gain than $S^0$ disproportionation. (Calculated using the data of Thauer et al., 1977; Kamyshny et al., 2004):

$$S_2^{2-} + 4H_2O = SO_4^{2-} + 7HS^- + H^+,$$
$$\Delta G^{\circ\prime} = -15.3 \text{ kJ mol}^{-1} S_2^{2-};$$

$$2S_3^{2-} + 4H_2O = SO_4^{2-} + 5HS^- + 3H^+,$$
$$\Delta G^{\circ\prime} = +0.8 \text{ kJ mol}^{-1} S_3^{2-};$$

$$1.33S_4^{2-} + 4H_2O = SO_4^{2-} + 4.32HS^- + 3.68H^+,$$
$$\Delta G^{\circ\prime} = +12.4 \text{ kJ mol}^{-1} S_4^{2-};$$

$$S_5^{2-} + 4H_2O = SO_4^{2-} + 4HS^- + 4H^+,$$
$$\Delta G^{\circ\prime} = +26.9 \text{ kJ mol}^{-1} S_5^{2-}.$$

Depending on physicochemical conditions, primarily pH and temperature, sulfur disproportionators may probably use either polysulfides or elemental sulfur. Microbial disproportionation of elemental sulfur was reported to occur at low pH, i.e., under conditions when polysulfide production from $S^0$ must be insignificant (Hardisty et al., 2013). Nanocrystals of elemental sulfur are probably acting as intermediates in this process under acidic conditions (Boyd and Druschel,2013). At higher temperatures the solubility of elemental sulfur increases (15 μg/L at 80°C, Kamyshny 2009), and the energy gain from sulfur disproportionation increases. The change in $\Delta G^{\circ\prime}$ of $S^0$disproportionation (at $SO_4^{2-}$ and $H_2S$ concentrations of 28 and 1.0 mM, respectively) at temperature increase from 25 to 70°C is ~10 kJ.

Biogeochemical data indicate that thiosulfate- and sulfur-disproportionating bacteria play an active part in the sulfur cycle in marine ecosystems (Jorgensen, 1990, Canfield and Thumdrup, 1996). Microbial disproportionation of elemental sulfur results in characteristic isotope fractionation, so that the forming sulfide is poor in $^{34}S$ (Canfield and Thumdrup, 1994). Measurement of the isotopic composition of ancient sedimentary rocks and microscopic analysis of minerals and microfossils supported the hypothesis that the microorganisms involved in $S^0$ disproportionation existed and were biogeochemically active in Archean time (Philippot et al., 2007; Wacey et al., 2011).

Disproportionation of sulfur compounds makes it possible for the cells to gain energy for growth using one organic compound as both an electron donor and electron acceptor and thus minimizing their requirements to the chemical composition of the biotope. *Desulfovibrio sulfodismutans*, the first described microorganism able to carry out thiosulfate and sulfite disproportionation, was incapable of autotrophic growth and grew only in the presence of acetate as a carbon source (Bak and Phennig, 1987). Ability to disproportionate thiosulfate and sulfite was subsequently shown for a number of autotrophic microorganisms. Ability of prokaryotes to disproportionate elemental sulfur was discovered later (Thamdrup et al., 1993;Lovley and Phillips, 1994). Until recently, little was known concerning microbial disproportionation of sulfur compounds at elevated temperatures, in spite of the important role the sulfur cycle processes could played in the ancient, probably thermal ecosystems (Jackson and McInerney 2000). Thermophilic chemolithoautotrophic sulfur-disproportionating bacteria were recently isolated from various hydrothermal habitats (Slobodkin et al., 2012, 2013, 2016; Kojima et al., 2016; Frolova et al., 2018).

## SULFUR-DISPROPORTIONATING MICROORGANISMS

Presently, 36 cultured microbial strains are known to disproportionate sulfur compounds. Fourteen of them were isolated under sulfur disproportionation conditions; for the others strains, this ability was shown later (Table 1).

### *Phylogeny*

Sulfur-disproportionating microorganisms are represented by 30 species of the *Bacteria* domain and belong to the phyla *Proteobacteria, Thermodesulfobacteria*, and *Firmicutes* (Table 2). The highest number of sulfur-disproportionating bacteria belongs to four orders of the class *Deltaproteobacteria*: *Desulfobacterales* (4 genera), *Desulfovibrionales* (4 genera), *Desulfurellales* (1 genus), and *Syntrophobacterales* (1 genus). *Dissulfuribacter thermophilus, Dissulfurimicrobium hydrothermale*, and *Dissulfurirhabdus thermomarina* are also *Deltaproteobacteria* with uncertain order and family ranks. Only one sulfur-disproportionating *Pantoea* strain is known among members of the class *Gammaproteobacteria*. Members of the genera *Caldimicrobium, Thermosulfurimonas*, and *Thermosulfuriphilus* belong to the phylum *Thermodesulfobacteria*. Members of the genera *Desulfotomaculum* and *Dethiobacter* belong to the class *Clostridia* within the phylum *Firmicutes*.

**Table 1.** Habitats and physiological characteristics of sulfur-disproportionating microorganisms

| Microorganism, strain | *T* optimum, °C | pH optimum | Isolation conditions* | References |
|---|---|---|---|---|
| Freshwater basins | | | | |
| *Desulfobulbus propionicus* 1pr3$^T$ | 39 | 7.1–7.5 | Propionate/$SO_4^{2-}$ | Widdel and Pfennig, 1982; Lovley and Phillips, 1994 |
| *Desulfocapsa thiozymogenes* Bra2$^T$ | 30 | 7.3–7.5 | $S_2O_3^{2-}$ (acetate) | Janssen et al., 1996 |
| *Desulfocapsa* sp. Cad626 | NR | NR | Lactate/$SO_4^{2-}$ | Peduzzi et al., 2003 |
| *Desulfovibrio sulfodismutans* ThAc01$^T$ | 35 | 7.2–7.5 | $S_2O_3^{2-}$ (acetate) | Bak and Pfennig, 1987 |
| *Desulfurella amilsii* TR1$^T$ | 50 | 6.0–6.5 | Acetate/$S^0$ | Florentino et al., 2016 |
| *Desulfovibrio desulfuricans* CSN | NR | NR | Lactate/$SO_4^{2-}$ | Kramer and Cypionka, 1989 |
| Marine coastal sediments | | | | |
| *Desulfocapsa sulfoexigens* SB164P1$^T$ | 30 | 6.7–7.3 | $S^0$ | Finster et al., 1998 |
| *Desulfofustis glycolicus* PerGlyS$^T$ | 28 | 7.3 | Glycolate/$SO_4^{2-}$ | Friedrich et al., 1996 |
| *Pantoea agglomerans* SP1 | 30 | 6.0–7.2 | Acetate/Fe(III) | Francis et al., 2000; Obraztsova et al., 2002 |
| Hypersaline lakes | | | | |
| *Desulfovibrio brasiliensis* LVform1$^T$ | 33 | 7.6 | Formate/$SO_4^{2-}$ | Warthmann et al., 2005 |
| *Desulfovibrio oxyclinae* P1B$^T$ | NR | NR | Ethanol/$SO_4^{2-}$ | Krekeler et al., 1997 |
| Soda lakes | | | | |
| *Desulfonatronospira delicata* AHT 6$^T$ | NR | 10.0 | $S_2O_3^{2-}$ (acetate) | Sorokin et al., 2008a |
| *Desulfonatronospira thiodismutans* ASO3-1$^T$ | NR | 9.5–10.0 | $SO_3^{2-}$ | Sorokin et al., 2008a |
| *Desulfonatronovibrio magnus* AHT22$^T$ | NR | 10.0 | $S_2O_3^{2-}$ (acetate) | Sorokin et al., 2011 |
| *Desulfonatronovibrio thiodismutans* AHT9$^T$ | NR | 9.5–10.0 | $S_2O_3^{2-}$ (acetate) | Sorokin et al., 2011 |
| *Desulfonatronum lacustre* Z-7951$^T$ | 37-40 | 9.5 | $H_2$/$SO_4^{2-}$ | Pikuta et al., 1998 |
| *Desulfonatronum thioautotrophicum* ASO4-1$^T$ | NR | 9.3–10.0 | Formate, acetate /$SO_4^{2-}$ | Sorokin et al., 2011 |
| *Desulfonatronum thiodismunans* MLF1$^T$ | 37 | 10.0 | Formate/$SO_4^{2-}$ | Pikuta et al., 2003 |
| *Desulfonatronum thiosulfatophilum* ASO4-2$^T$ | NR | 9.5 | Pyruvate/$SO_4^{2-}$ | Sorokin et al., 2011 |

**Table 1.** (Contd.)

| Microorganism, strain | *T* optimum, °C | pH optimum | Isolation conditions* | References |
|---|---|---|---|---|
| *Desulfonatronum parangueonense* PAR180$^T$ | 35 | 9.0 | Ethanol/$SO_3^{2-}$ | Perez Bernal et al., 2017 |
| *Desulfurivibrio alkaliphilus* AHT 2$^T$ | NR | 9.5 | $H_2$/$S^0$ | Sorokin et al., 2008b; Poser et al., 2013 |
| *Desulfurivibrio sp.* AMeS2 | NR | NR | $S^0$ | Poser et al., 2013 |
| *Dethiobacter alkaliphilus* AHT 1$^T$ | NR | 9.5 | $H_2$/$S^0$ | Sorokin et al., 2008b; Poser et al., 2013 |
| Antropogenic habitats | | | | |
| *Desulfomonile tiedje* DCB-1$^T$ | 37 | 6.8-7.0 | 3-Chlorobenzoate | DeWeerd et al., 1990; Mohn and Tiedje, 1990 |
| *Desulfotomaculum salinum* 435$^T$ | 60-65 | 7.0 | NR/$SO_4^{2-}$ | Nazina et al., 2005 |
| *Desulfotomaculum salinum* 781 | 60-65 | 7.0 | NR/$SO_4^{2-}$ | Nazina et al., 2005 |
| *Desulfotomaculum thermobenzoicum* TSB$^T$ | 62 | 7.2 | Butyrate/$SO_4^{2-}$ | Tasaki et al., 1991; Jackson and McInerney, 2000 |
| Natural thermal ecosystems | | | | |
| *Caldimicrobium thiodismutans* TF1$^T$ | 75 | 7.5-8.8 | $S_2O_3^{2-}$ | Kojima et al., 2016 |
| *Caldimicrobium rimae* FM8 | 65 | 6.4 | $S^0$ | Merkel et al., 2017 |
| *Caldimicrobium rimae* 76 | 67 | 6.1 | $S^0$ | Merkel et al., 2017 |
| *Dissulfuribacter thermophilus* S69$^T$ | 61 | 6.8 | $S^0$ | Slobodkin et al., 2013 |
| *Dissulfurimicrobium hydrothermale* Sh68$^T$ | 50-52 | 6.0-6.2 | $S^0$ | Slobodkin et al., 2016 |
| *Dissulfurirhabdus thermomarina* SH388$^T$ | 50 | 6.0-6.5 | $H_2$/$SO_3^{2-}$ | Slobodkina et al., 2016 |
| *Thermosulfurimonas dismutans* S95$^T$ | 74 | 7.0 | $S^0$ | Slobodkin et al., 2012 |
| *Thermosulfurimonas marina* S872$^T$ | 74 | 6.7-7.0 | $S^0$ | Frolova et al., 2018 |
| *Thermosulfuriphilus ammonigenes* ST65$^T$ | 65 | 6.5 | $S^0$/$NO_3^-$ | Slobodkina et al., 2017b |

NR stands for not reported.
* Electron donor/acceptor used for isolation. Other compounds acting as carbon sources are indicated in parentheses.

**Table 2.** Phylogeny of sulfur-disproportionating microorganisms*

| Phylum** | Class | Order | Genus | Species |
|---|---|---|---|---|
| *Firmicutes* | *Clostridia* | *Clostridiales* | *Desulfotomaculum* | *D. salinum, D. thermobenzoicum* |
| | | | *Dethiobacter* | *D. alkaliphilus* |
| *Proteobacteria* | *Gammaproteobacteria* | *Enterobacteriales* | *Pantoea* | *P. agglomerans**** |
| | *Deltaproteobacteria* | *Desulfobacterales* | *Desulfobulbus* | *D. propionicus* |
| | | | *Desulfocapsa* | *D. sulfoexigens, D. thiozymogenes* |
| | | | *Desulfofustis* | *D. glycolicus* |
| | | | *Desulfurivibrio* | *D. alkaliphilus* |
| | | *Desulfovibrionales* | *Desulfonatronospira* | *D. delicata, D. thiodismutans* |
| | | | *Desulfonatronovibrio* | *D. magnus, D. thiodismutans* |
| | | | *Desulfonatronum* | *D. lacustre, D. thioautotrophicum, D. thiodismunans, D. thiosulfatophilum, D. parangueonense* |
| | | | *Desulfovibrio* | *D. brasiliensis, D. desulfuricans***, D. oxyclinae, D. sulfodismutans* |
| | | *Desulfurellales* | *Desulfurella* | *D. amilsii* |
| | | *Syntrophobacterales* | *Desulfomonile* | *D. tiedje* |
| | | Other *Deltaproteobacteria* | *Dissulfuribacter* | *D. thermophilus* |
| | | | *Dissulfurimicrobium* | *D. hydrothermale* |
| | | | *Dissulfurirhabdus* | *D. thermomarina* |
| *Thermodesulfobacteria* | *Thermodesulfobacteria* | *Thermodesulfobacteriales* | *Caldimicrobium* | *C. thiodismutans, C. rimae* |
| | | | *Thermosulfurimonas* | *T. dismutans, T. marina* |
| | | | *Thermosulfuriphilus* | *T. ammonigenes* |

* Based on the 16S rRNA gene sequences.
** All known microoorganisms belong to the *Bacteria* domain.
*** Not the type strain of the species.

### *Habitats*

Sulfur-disproportionating microorganisms occur in various natural and anthropogenic ecosystems (Table 2). *Desulfovibrio sulfodismutans*, the first described sulfur disproportionator, was isolated from anoxic sludge collected from a freshwater ditch near Konstanz, Germany (Bak and Cypionka, 1987; Bak and Phennig, 1987). *Desulfobulbus propionicus, Desulfocapsa thiozymogenes*, and *Desulfocapsa* sp. Cad626 were isolated from the sediments of freshwater lakes and small basins in Europe (Widdel and Pfennig, 1982; Janssen et al, 1996; Peduzzi et al, 2003). *Desulfurella amilsii* was isolated from acidic sediments of the Tinto River, Spain (Florentino et al 2016). Halophilic *Desulfovibrio* were found in hypersaline coastal lakes (Krekeler et al., 1997; Warthmann et al., 2005). However, the highest number of sulfur-disproportionating microbial species was isolated from the sediments of continental soda lakes in Eurasia, Africa, and North America. These alkaliphilic bacteria belong to the genera *Desulfonatronospira, Desulfonatronovibrio, Desul-*

*fonatronum, Desulfurivibrio, Dethiobacter* (Pikuta et al., 1998, 2003; Sorokin et al., 2008a, 2008b, 2011; Poser et al., 2013; Perez Bernal et al., 2017).

*Desulfocapsa sulfoexigens, Desulfofustis glycolicus* and *Pantoea agglomerans* were isolated from coastal marine sediments (Friedrich et al., 1996; Finster et al., 1998; Francis et al., 2000). The presence of sulfur disproportionators in enrichments carrying out anaerobic methane oxidation (AOM) obtained from marine ecosystems is well-documented. Members of the *Desulfosarcina/Desulfococcus* cluster are the main bacterial component of the AOM enrichment from the Isis mud volcano, Mediterranean. While these deltaproteobacteria actively disproportionate disulfide and are capable of autotrophic growth, their role in AOM is not completely clear (Milucka et al., 2012). Mesophilic elemental sulfur-disproportionating bacteria were also found in AOM enrichments from methane seeps of the Elba Island (Mediterranean), hydrotherms of the Guaymas Basin (Gulf of California), and a North Sea oil deposit. However, these microorganisms, related to *Desulfurivibrio, Desulfocapsa*, and uncultured groups of the *Deltaproteobacteria*, are a minor component of the enrichments, and the probability of their involvement in AOM is low (Wegener et al., 2016).

Sulfur disproportionators occur in diverse anthropogenic environments: *Desulfomonile tiedje* was isolated from wastewater sediment, *Desulfotomaculum thermobenzoicum* was retrieved from the sludge of a thermophilic anaerobic digester, while two *Desulfotomaculum salinum* strains were isolated from the mixture of formation and condensation water of a gas condensate deposit (DeWeerd et al., 1990; Tasaki et al., 1991; Nazina et al., 2005).

Sulfur disproportionators were relatively recently found in natural thermal ecosystems. *Thermosulfurimonas dismutans, Dissulfuribacter thermophilus*, and *Thermosulfuriphilus ammonigenes* thrive in deep-sea hydrothermal vents of the Lau spreading center in the Pacific (Slobodkin et al., 2012, 2013; Slobodkina et al., 2017b). *Dissulfurirhabdus thermomarina* and *Thermosulfurimonas marina* occur in shallow marine hydrotherms (Kuril Islands) (Slobodkina et al., 2016; Frolova et al., 2017). *Dissulfurimicrobium hydrothermale, Caldimicrobium thiodismutans*, and two *Caldimicrobium rimae* strains were isolated from terrestrial hot springs in Kamchatka and Japan (Slobodkin et al., 2016; Kojima et al., 2016; Merkel et al., 2017).

Application of molecular techniques to study the distribution of sulfur-disproportionating prokaryotes is limited due to the absence of unequivocal phylogenetic and functional markers. The 16S rRNA genes of *Desulfocapsa* species are constantly detected in the ecosystems with low redox potential, especially in methane seeps (Lloyd et al., 2006; Pjevac et al., 2014; Ruff et al., 2015). The 16S rRNA gene sequences of *Thermosulfurimonas* were detected in deep-sea hydrothermal vents of the Mid-Atlantic Ridge, Guaymas Basin, and Eastern Lau spreading center in the Pacific (Flores et al., 2011; Slobodkin et al., 2012). *Caldimicrobium* species are widespread in Kamchatka hot neutral springs, where their share in the prokaryotic diversity may be from 1 to 52% (Chernyh et al., 2015; Merkel et al., 2017).

### *Physiology*

Most sulfur-disproportionating microorganisms may also grow by other energy processes (Table 3). However, no growth-supporting metabolic processes, apart from disproportionation, were found for *Caldimicrobium thiodismutans, Desulfocapsa sulfoexigens*, and *Dissulfurimicrobium hydrothermale* (Finster et al., 1998; Kojima et al., 2016; Slobodkin et al., 2016). A significant number of sulfur disproportionators are capable of dissimilatory sulfate reduction and were originally described as sulfate reducers. Certainly not all sulfate-reducing prokaryotes are capable of disproportionation, and some *Desulfobacter, Desulfobacterium, Desulfotomaculum,* and *Desulfovibrio* do not grow by dismutation (Kramer and Cypionka, 1989). All known sulfur disproportionators are strict anaerobes, except for the facultatively aerobic *Pantoea agglomerans* (Francis et al., 2000). Many sulfur disproportionators, both capable and incapable of sulfate reduction, reduce various electron acceptors, such as sulfite, thiosulfate, elemental sulfur, nitrate, Fe(III), fumarate, etc. (Table 3). Organic compounds or molecular hydrogen are used as electron donors. Many sulfur disproportionators are able to ferment organic compounds, especially pyruvate. A new microbial process of transformation of inorganic compounds, dissimilatory reduction of nitrate to ammonium with elemental sulfur as an electron donor, was recently reported for deep-sea thermophilic sulfur disproportionators *Thermosulfurimonas dismutans, Dissulfuribacter thermophilus,* and *Thermosulfuriphilus ammonigenes* (Slobodkina et al., 2017a; Slobodkina et al., 2017b).

Sulfur disproportionators vary in their capacity for dismutation of various sulfur compounds (Table 3). While thiosulfate is used by most sulfur disproportionators, several microorganisms are unable to disproportionate it. Ability to disproportionate sulfite was tested less often and is known for almost half of the strains. Elemental sulfur is used by all known non-sulfate-reducing sulfur disproportionators, but only two sulfate reducers can use it. The microorganisms for which the ability to disproportionate all three compounds (sulfide, thiosulfate, and elemental sulfur) was shown, include three mesophilic *Desulfocapsa* strains, as well as six thermophilic bacteria: *Caldimicrobium thiodismutans, Dissulfuribacter thermophilus, Dissulfurimicrobium hydrothermale, Thermosulfurimonas dismutans, Thermosulfurimonas marina,* and *Thermosulfuriphilus ammonigenes* (Janssen et al., 1996; Finster et al., 1998; Peduzzi et al., 2003; Kojima et al., 2016; Slobodkin

**Table 3.** Metabolic characteristics of sulfur-disproportionating microorganisms

| Microorganism, strain | Disproportionation of | | | Autotrophic growth | Fermentation | Electron acceptors* |
|---|---|---|---|---|---|---|
| | elemental sulfur | thiosulfate | sulfite | | | |
| Sulfate-reducing microorganisms | | | | | | |
| *Desulfobulbus propionicus* 1pr3$^T$ | + | – | – | + | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$, Fe(III), Mn(IV), $NO_3^-$ |
| *Desulfocapsa thiozymogenes* Bra2$^T$ | + | + | + | + | – | $SO_4^{2-}$ |
| *Desulfocapsa* sp. Cad626 | + | + | + | – | – | $SO_4^{2-}$ |
| *Desulfofustis glycolicus* PerGlyS$^T$ | + | NR | NR | – | – | $SO_4^{2-}$, $SO_3^{2-}$, $S^0$ |
| *Desulfomonile tiedje* DCB-1$^T$ | NR | + | NR | – | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfonatronospira delicata* AHT 6$^T$ | – | + | + | + | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfonatronospira thiodismutans* ASO3-1$^T$ | – | + | + | + | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfonatronovibrio magnus* AHT22$^T$ | – | + | + | - | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfonatronovibrio thiodismutans* AHT9$^T$ | – | + | + | + | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfonatronum lacustre* Z-7951$^T$ | – | + | NR | – | – | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfonatronum thioautotrophicum* ASO4-1$^T$ | – | + | + | + | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfonatronum thiodismunans* MLF1$^T$ | – | + | + | – | – | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfonatronum thiosulfatophilum* ASO4-2$^T$ | – | + | + | – | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfonatronum parangueonense* PAR180$^T$ | – | + | + | – | – | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$ |
| *Desulfotomaculum salinum* 435$^T$ | NR | + | NR | + | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$, $S^0$ |
| *Desulfotomaculum salinum* 781 | NR | + | NR | + | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$, $S^0$ |
| *Desulfotomaculum thermobenzoicum* TSB$^T$ | NR | + | NR | – | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$, $NO_3^-$ |
| *Desulfovibrio brasiliensis* LVform1$^T$ | NR | + | NR | – | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$, $S^0$, Fe(III), DMSO**, fumarate |
| *Desulfovibrio desulfuricans* CSN | NR | – | + | – | NR | $SO_4^{2-}$ |
| *Desulfovibrio oxyclinae* P1B$^T$ | NR | + | + | – | + | $SO_4^{2-}$, $SO_3^{2-}$, $S_2O_3^{2-}$, $S^0$,фумарат |
| *Desulfovibrio sulfodismutans* ThAc01$^T$ | – | + | + | – | NR | $SO_4^{2-}$ |
| Microorganisms incapable of dissimilatory sulfate reduction | | | | | | |
| *Caldimicrobium thiodismutans* TF1$^T$ | + | + | + | + | – | None |
| *Caldimicrobium rimae* FM8 | + | NR | NR | NR | NR | NR |
| *Caldimicrobium rimae* 76 | + | NR | NR | NR | NR | NR |
| *Desulfocapsa sulfoexigens* SB164P1$^T$ | + | + | + | + | – | None |
| *Desulfurella amilsii* TR1$^T$ | + | NR | NR | – | + | $S_2O_3^{2-}$, $S^0$ |
| *Desulfurivibrio alkaliphilus* AHT 2$^T$ | + | NR | NR | – | NR | $S_2O_3^{2-}$, $S^0$, $NO_3^-$ |
| *Desulfurivibrio sp.* AMeS2 | + | NR | NR | – | NR | $S^0$ |
| *Dethiobacter alkaliphilus* AHT 1$^T$ | + | NR | NR | – | NR | $S_2O_3^{2-}$, $S^0$ |
| *Dissulfuribacter thermophilus* S69$^T$ | + | + | + | + | – | Fe(III), $NO_3^-$ |

**Table 3.** (Contd.)

| Microorganism, strain | Disproportionation of | | | Autotrophic growth | Fermentation | Electron acceptors* |
|---|---|---|---|---|---|---|
| | elemental sulfur | thiosulfate | sulfite | | | |
| *Dissulfurimicrobium hydrothermale* Sh68$^T$ | + | + | + | + | – | None |
| *Dissulfurirhabdus thermomarina* SH388$^T$ | + | – | + | + | – | $SO_3^{2-}$ |
| *Pantoea agglomerans* SP1 | + | NR | NR | + | NR | $S^0$, Fe(III), $NO_3^-$, фумарат, АХДС***, Cr(VI) |
| *Thermosulfurimonas dismutans* S95$^T$ | + | + | + | + | – | $NO_3^-$ |
| *Thermosulfurimonas marina* S872$^T$ | + | + | + | + | – | $NO_3^-$ |
| *Thermosulfuriphilus ammonigenes*ST65$^T$ | + | + | + | + | – | $NO_3^-$ |

NR stands for not reported.
* Electon acceptors used in the processes other than sulfite, thiosulfate, and elemental sulfur disproportionation.
** DMSO, dimethyl sulfoxide.
*** AQDS, 9,10-antraquinone-2,6-disulfonate.

et al., 2012, 2013, 2016; Slobodkina et al., 2017b; Frolova et al., 2018).

Sulfides in the form of $H_2S$, $HS^-$, or $S^{2-}$, which are formed in the course of sulfur compounds disproportionation, may have a toxic effect on microbial growth. In laboratory cultures, addition of ferrihydrite (poorly crystalline Fe(III) oxide) significantly decrease sulfide concentration in the medium. Depending on strain sensitivity to sulfide, some microorganisms probably grow only in the presence of ferrihydrite, while others can grow without it (Slobodkin et al., 2012, 2013; Poser et al., 2013). The pH of the medium is probably less important, since disproportionation of $S^0$ in the absence of ferrihydrite was demonstrated not only in alkaline, but also in neutral conditions, when the concentration of $H_2S$, the most toxic sulfide form, should be higher (Poser et al., 2013; Florentino et al., 2019).

Many organisms can grow autotrophically while disproportionating sulfur compounds, with $CO_2$ or its anions being the sole carbon source. Capacity for autotrophic growth was shown for 17 sulfur-disproportionating strains from several phylogenetic groups (Table 3). Other microorganisms require a carbon source, i.e., acetate.

Sulfur-disproportionating microorganisms are represented by both mesophilic and thermophilic species (Table 1). Among 13 thermophilic (with optimal growth temperature above 50°C) sulfur disproportionators, *Thermosulfurimonas dismutans*, growing at 92°C, is the most extreme (Slobodkin et al., 2012). Sulfur-disproportionating prokaryotes isolated from soda lakes are obligate halophiles with pH optimum for growth at 9.5–10.0 (Table 1). Acid-tolerant *Desulfurella amilsii*, which reduces sulfur at pH 3.0, was shown to disproportionate elemental sulfur at pH 6.5 (Florentino et al., 2019). $S^0$ disproportionation is probably involved in anaerobic metabolism of *Acidithiobacillus ferrooxidans* growing at pH 1.8 in the presence of Fe(III) (Osorio et al., 2013).

## BIOCHEMICAL MECHANISMS OF DISPROPORTIONATION OF SULFUR COMPOUNDS

Little is known concerning the biochemical mechanisms of disproportionation of sulfur compounds and the enzymes involved in this process. Early research, which included measurement of the enzymatic activity, inhibitor analysis, and radoitracer experiments, did not result in unequivocal description of the disproportionation pathways. These data indicate that sulfate and sulfite disproportionation by *Desulfovibrio*-strains probably involves action of adenosine phosphosulfate (APS) reductase and includes reverse electron flow, with sulfite and elemental sulfur as the possible intermediates of thiosulfate disproportionation (Kramer and Cypionka, 1989; Cypionka et al., 1998). Thiosulfate disproportionation by *Desulfocapsa sulfoexigens* involves participation of sulfite oxidoreductase, thiosulfate reductase, dissimilatory sulfite reductase, ATP sulfurilase, and APS reductase; however, the enzymes responsible for $S^0$ oxidation by this organism have not been identified (Frederikson and Finster, 2003; Finster, 2008).

The oxidative branch of sulfur disproportionation is presently the least understood. None of the studied genomes contains the genes encoding the enzymes of known pathways for thiosulfate and elemental sulfur oxidation, such as the Sox enzyme system sulfur oxy-

genase-reductase (Sor), or sulfide: quinone oxidoreductase (Sqr). The presence of dissimilatory sulfite reductase (Dsr) genes in the genomes of most sulfur disproportionators supports the suggestion that, similar to sulfur-oxidizing bacteria, sulfane oxidation to sulfite is catalyzed by this enzyme operating in reverse direction. At the same time, in sulfur disproportionators possessing the Dsr system, the DsrAB subunits belong to the reductive type (Thorup et al., 2017). Moreover, no genes encoding dissimilatory sulfite reductase were found in the genome of *Dethiobacter alkaliphilus* (Melton et al., 2017). Completeness of sequencing of this genome (95.8%) is, however, insufficient for unequivocal conclusion of the absence of the DsrAB genes. Another hypothesis suggests that elemental sulfur oxidation is carried out by the QmoABC electron transport complex and heterodisulfide reductase (Quatrini et al., 2009; Finster et al., 2013; Mardanov et al., 2016). Further sulfite oxidation to sulfate probably also occurs via the reversible sulfate reduction pathway involving APS reductase. The genes encoding this enzyme were found in all known genomes of sulfur disproportionators, except for *Desulfurella amilsii,* which probably uses another, presently unknown pathway of sulfite oxidation (Florentino et al., 2017). In addition to the genes of dissimilatory sulfate reduction, the genomes of most microorganisms also contain the genes of membrane-bound molybdopterin oxidoreductases, which may be involved in sulfur metabolism as subunits of thiosulfate, polysulfide, or tetrathionate reductases.

Differential proteomic research on sulfur disproportionation was carried out on *Desulfurella amilsii* (Florentino et al., 2019). Sixteen proteins were identified only in the cultures grown under conditions of sulfur disproportionation, while 112 proteins exhibited significant differences in activity for the cultures grown under conditions of sulfur reduction and sulfur disproportionation. The elemental sulfur-disproportionating cultures exhibited the highest relative content of rhodanese-like sulfur transferase (DESAMIL20_2007), while most proteins of the Dsr complex were not detected.

## COMPARATIVE ANALYSIS OF THE GENOMES OF ELEMENTAL SULFUR-DISPROPORTIONATING MICROORGANISMS

Uncertainty concerning the molecular mechanisms underlying sulfur disproportionation hinders the application of genomic data for investigation of this process. Although analysis of complete genomes in order to determine the biochemical pathways of sulfur metabolism has been carried out at different level of detail for six organisms, genomic determinants of sulfur disproportionation were not revealed (Finster et al., 2013; Mardanov et al., 2016; Slobodkina et al., 2017a; Thorup et al., 2017).

As of March 2019, 18 complete genomes of the microorganisms capable of thiosulfate, sulfite, and elemental sulfur disproportionation have been in public domain. In the present work, comparative analysis of all available complete genomes of the microorganisms capable of $S^0$ disproportionation (10 genomes) was carried out. The analyzed genes and gene clusters included the genes for dissimilatory sulfate reduction, the genes associated with sulfur activation and transfer into the cell, and the genes of membrane-bound molybdopterin oxidoreductases involved in sulfur metabolism (Table 4). The work was carried out using the bioinformatic approaches provided by the RAST (http://rast.nmpdr.org) and IMG/M (https://img.jgi.doe.gov) servers.

None of the studied genomes contained all the genes chosen for analysis. Most genomes contained the key genes for dissimilatory sulfate reduction (Pereira et al., 2011), including *sat* (sulfate-adenylyl transferase), *aprAB* (A and B subunits of adenylyl-sulfate reductase), the *dsrABD* cluster (dissimilatory sulfite reductase), *dsrC* (protein component of the dissimilatory sulfite reductase), *dsrMK* (electron-transporting complex associated with adenosyl phosphosulfate reductase). As was stated above, *Dethiobacter alkaliphilus*, with the genome lacking both *dsrABD* and *dsrC, dsrMK*, and *qmoABC*, as well as *Desulfurella amilsii,* possessing the Dsr system genes, but not *aprAB, qmoABC,* and *sat*, were exceptions.

None of the genomes contained the *sox*, *sor*, or *sqr* genes encoding the proteins responsible for sulfur and thiosulfate oxidation and homologous to those occurring in sulfur-oxidizing microorganisms. The *dsrL* homologue encoding the Fe-S- and flavin-containing NAD(P)-dependent oxidoreductase involved in sulfur oxidation in *Allochromatium vinosum* (Lübbe et al., 2006) was found only in the genome of *Desulfurella amilsii*. Most microorganisms share the genes associated with activation of insoluble sulfur compounds and their transfer into the cells. These include *tusA*, encoding a small sulfur-transporting protein of the sulfotransferase family, *dsrE2*,encoding a small transmemebrane protein, and *dsrE*, encoding the protein acting as a sulfur donor for DsrC in sulfur-oxidizing bacteria (Stockdreher et al., 2012; Venceslau et al., 2014). However, none of these three genes occurs in the genome of *Desulfurella amilsii*, while *Dethiobacter alkaliphilus* has no *dsrE*. Homologues of the DESAMIL20_2007 gene encoding the rhodanese-like sulfur transferase in *Desulfurella amilsii*, a specific protein predominant under sulfur disproportionation conditions (Florentino et al., 2019), is present in the genomes of *Dissulfuribacter thermophilus* and *Thermosulfurimonas dismutans*. The genes of other sulfur transferases with two rhodanese domains (SseA) were detected in the genomes of six analyzed sulfur disproportionators. The genes of molybdopterin-containing thiosulfate and polysulfide reductases (*phsA/psrA*) were found in all analyzed microorganisms, except for

**Table 4.** The genes of sulfur metabolism proteins in elemental sulfur-disproportionating microorganisms

| Gene or gene cluster | Microorganism | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cat | Dbp | Des | Det | Dva | Dam | Dfg | Dta | Dit | Tsd |
| *sat* | + | + | + | + | + | None | + | + | + | + |
| *aprAB* | + | + | + | + | + | None | + | + | + | + |
| *qmoABC* | + | + | + | + | + | None | + | None | + | + |
| *dsrABD* | + | + | + | AB | + | AB | + | None | + | + |
| *dsrC* | + | + | + | + | + | + | + | None | + | + |
| *dsrMK* | + | + | + | M | + | + | + | None | + | + |
| *dsrL* | None | None | None | None | None | + | None | None | None | None |
| *tusA* | + | + | + | + | + | None | + | + | + | + |
| *dsrE* | + | + | + | + | + | None | + | None | + | + |
| *dsrE2* | + | + | + | + | + | None | + | + | + | + |
| DESAMIL20_2007 | None | None | None | None | None | + | None | None | + | + |
| *sseA* | None | None | + | None | + | + | + | None | + | + |
| *phsA/psrA* | + | + | + | + | + | + | + | None | + | + |
| *sudhAB* | None | None | None | None | None | + | + | + | None | None |

Designations: *sat,* sulfate adenylyl transferase;*aprAB,* adenylyl-sulfate reductase subunits alpha and beta; *dsrABD,* sulfite reductase, dissimilatory-type subunits alpha, beta and clustered protein DsrD; *dsrC,* dissimilatory sulfite reductase, small protein DsrC; *dsrMK,* sulfite reduction-associated electron transfer complex, proteins DsrM and DsrK; *qmoABC,* APS reductase-associated electron transfer complex QmoABC; *dsrE,*DsrE sulfur-transporting protein; *tusA,* sulfur relay protein TusA; *dsrE2,* transmembrane sulfur-transporting protein; *dsrL*, ron-sulfur flavoprotein with proposed NAD(P)H: acceptor oxidoreductase; *phsA/psrA*, polysulfide reductase / thiosulfate reductase chain A; *sudhAB*, sulfide dehydrogenase subunit A and B; DESAMIL20_2007, thiosulfate sulfurtransferase, rhodanese from *Desulfurella amilsii* TR1$^T$; *sseA*, 3-mercaptopyruvate sulfurtransferase SseA, contains two rhodanese domains.
Cat, *Caldimicrobium thiodismutans* TF1$^T$; Dbp, *Desulfobulbus propionicus* 1pr3$^T$; Des, *Desulfocapsa sulfoexigens* SB164P1$^T$; Det, *Desulfocapsa thiozymogenes* Bra2$^T$; Dva, *Desulfurivibrio alkaliphilus* AHT 2$^T$; Dam, *Desulfurella amilsii* TR1$^T$; Dfg, *Desulfofustis glycolicus* PerGlyS$^T$; Dta, *Dethiobacter alkaliphilus* AHT 1$^T$; Dit, *Dissulfuribacter thermophilus* S69$^T$; Tsd, *Thermosulfurimonas dismutans* S95$^T$.

*Dethiobacter alkaliphilus*. Homologues of the genes encoding the cytoplasmic NAD(P)-dependent hydrogenase, which also catalyzed polysulfide reduction to sulfide (Ma et al., 2000) (sulfide dehydrogenase, SUDH), were found in the genomes of *Desulfurella amilsii, Desulfofustis glycolicus*, and *Dethiobacter alkaliphilus*.

Thus, a complete set of dissimilatory sulfate reduction genes is not required for ability to disproportionate elemental sulfur. The presence of the Dsr (dissimilatory sulfite reductase) and Apr (adenylyl-sulfate reductase) enzyme complexes is probably also not required for this process. While the proteins transferring the sulfur-containing groups and the enzymes reducing elemental sulfur and/or polysulfides are the components important for sulfur disproportionation, sulfur transferases and polysulfide reductase of different structure may be responsible for these processes in different microorganisms.

## CONCLUSION

Disproportionation of sulfur compounds makes it possible to microorganisms to obtain energy using a single inorganic compound as both an electron donor and electron acceptor. About 50% of the cultured sulfur disproportionators are capable of autotrophic growth. Chemolithoautotrophic microorganisms are an important component of the biogeochemical cycles of carbon and other biogenic elements. Ability of chemolithoautotrophs to carry out primary production of organic matter enables existence of autonomous microbial communities, which probably played an important part in formation of the early Earth biosphere. While the role of microbial disproportionation of sulfur compounds in the present-day biogeochemical cycle of sulfur has been insufficiently studied, wide occurrence of thiosulfate, sulfite, and $S^0$ disproportionation among prokaryotes inhabiting diverse marine and terrestrial biotopes indicate an important biological role of these microorganisms. The presently known sulfur-disproportionating prokaryotes belong to 30 bacterial species, most of which are members of the class *Deltaproteobacteria*. While ability to disproportionate sulfur compounds is common among sulfate-reducing bacteria, it is not a universal feature of this physiological group. Interestingly, the genomes of some sulfur-disproportionating bacteria unable to reduce sulfate contain a complete set of the genes required for dissimilatory sulfate reduction, so that the reason why these microorganisms are incapable of $SO_4^{2-}$ reduction in laboratory cultures remains unclear.

Although a number of microorganisms were described, for which dismutation of sulfur compounds is the only type of energy metabolism, it is premature to state the existence of obligate sulfur disproportionators. Thus, *Thermosulfurimonas dismutans* was recently shown to oxidize elemental sulfur with nitrate as an electron acceptor. New physiological properties may possibly be discovered in other "obligate" sulfur disproportionators. Only hypothetical descriptions of the biochemical mechanisms of sulfur compounds disproportionation exist presently, and the key enzymes of this process have not been determined, which hinders the application of modern omics methods for investigation of this process. Comparative analysis of complete genomes of the elemental sulfur-disproportionating bacteria did not reveal the set of proteins required for $S^0$ dismutation, which was common to all microorganisms. Existence of several different pathways for disproportionation of sulfur compounds is therefore quite probable.

## COMPLIANCE WITH ETHICAL STANDARDS

The authors declare that they have no conflict of interest. This article does not contain any studies involving animals or human participants performed by any of the authors.

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