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Sulfur in the marine environment

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Abstract

Sulfur is an element commonly occurring in the environment. It is present in the atmosphere, in the hydrosphere, and in live organisms; it is one of the most important physicochemical and geological indicators. Depending on the natural conditions, sulfur compounds in the environment may play the role of electron acceptor or donor in the redox processes. These compounds influence the ion concentration and ion balance in benthic sediments. They also determine the speciation, bioavailability and toxicity of heavy metals. Comprehensive knowledge of the processes mediated by sulfur can be a valuable source of information about the past and present state of the ecosystem.

INTRODUCTION

Sulfur is a mix of four stable isotopes with the following mass numbers: 32 (95.02%), 33, 34 (4.21%) and 36 (Derda 1999). Sulfur is one of the 15 basic elements that build the Earth, and Brown estimated that it constitutes 1.93% (by weight) of our planet (Pempkowiak 1997). Organic forms of sulfur mostly occur in esters (-C-O-S-) and amino acids (Gao et al. 2000), i.e. methionine, cysteine, cystine and homocysteine. This element is also a structural component of coenzymes (coenzyme A, biotin, and thiamine) and hormones (insulin). Sulfur-containing aerosols, various gases of anthropogenic and biogenic origin (DMS) and carbonyl sulfide (COS) are present in the atmosphere. It has been estimated that the mean sulfur content in live organisms, expressed per dry mass unit, ranges from 0.34% in terrestrial plants to about 1.9% in marine fauna; 1.0% is the value commonly used for the majority of organisms (Sievert et al. 2007). A significant amount of sulfur is found in fossil fuels which may contain from 0.1 to 6.0% of this element.

Sulfur is an essential element however; it can also have negative impacts on terrestrial and aquatic ecosystems. The sulfur cycle is closely connected to the cycling of carbon, nitrogen, phosphorus, and iron (Sievert et al. 2007), and it influences all environmental compartments. The main role in the cycling of this microelement has been attributed to gas fluxes (Falkowska, Korzeniewski 1995) and sulfates dissolved in the global ocean. Sulfates undergo numerous redox reactions via chemical and microbiological pathways which makes them an important link in the global sulfur cycle. Microorganism-mediated reduction of sulfates bridging the sulfur and carbon biogeochemical cycles (Berner 1984, Lin et al. 2000) has been considered the most significant decomposition pathway of

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organic matter in marine benthic sediments under anoxic conditions (Jørgensen 1982, Canfield et al. 1993). Pyrite constitutes the largest share of the reduced sulfur present in the environment (Bottrell, Newton 2006). Isotopic composition of sulfur, including pyrite, may also supply valuable insight into the conditions under which sediment deposition occurred (Wilkin et al. 1996; Butler et al. 2004) aiding in paleoenvironmental reconstructions (Schenau et al. 2002; Lyons et al. 2003; McKay, Longstaffe 2003). Based on the data on oxygen and sulfur isotopes in marine sulfates, Bottrell and Newton (2006) reconstructed changes in the global sulfur cycle that have taken place since the mid-Paleozoic. Grasby et al. (2003) have proven the existence of life forms under an Arctic glacier by analyzing the isotopic composition of different sulfur forms.

There are three main reservoirs of sulfur in its global cycle, i.e. sulfates dissolved in marine waters, sulfates bound in evaporates, and sulfides in clastic marine sediments (Bottrell, Newton 2006). The global sulfur cycle is presented in Fig. 1. Sulfur compounds present in the atmosphere, biosphere, and the terrestrial part of the hydrosphere constitute a much smaller portion of the total cycled sulfur, however they play a significant role in the transport

of this microelement in the environment (Table 1). Sulfur is used in many branches of industry (Fig. 2). The human impact on the natural environment results in a positive sulfur budget (Weiner 2003).

SULFUR COMPOUNDS IN THE ENVIRONMENT

Lithosphere

Sulfur has been ranked number 16 among the elements in terms of their abundance in the lithosphere, and it constitutes 0.026% of the Earth's crust (Pempkowiak 1997). It can occur in its elemental form and be a component of many minerals that are rather stable in the environment. Elemental sulfur originates from microbial reduction of calcium sulfate in the presence of carbohydrates, or via crystallization on the rocks during volcanic exhalation (Borówka, Cedro 2001). Sulfates and sulfites e.g. gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, anhydrite CaSO_4 , barite BaSO_4 , celestine SrSO_4 and glauberite $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ form during the evaporation of lake and marine waters, and as a result of the chemical reaction between sulfuric acid and calcium carbonate. Sulfides such as galena PbS , pyrite FeS_2 , pyrrhotite FeS , chalcocite Cu_2S , covellite CuS , chalcopyrite CuFeS_2 , cinnabar HgS , and sphalerite ZnS form during the pneumatolytic and hydrothermal phase of magma solidification and due to organic matter decomposition (Borówka, Cedro 2001). Depending on the genesis of a given compound, the isotopic ratio of ^{32}S and ^{34}S varies (Weiner 2003). Sulfate-reducing bacteria preferentially reduce $^{32}\text{SO}_4^{2-}$; therefore sulfides and elemental sulfur of microbial origin have lower of ^{34}S content (Donahue et al. 2008). The analysis of sulfur isotopic composition may yield information on the origin, modes of formation, and range of transformations in many minerals and rocks.

Marine environment

Weathering and leaching of minerals, rocks and the elevated benthic sediments (Sievert et al. 2007), oxidation of sulfides, sulfur partitioning (Bottrell, Newton 2006), and riverine inflow are the most important sources of sulfates in marine waters. Walker (1986) estimated that the annual input of sulfates into the global ocean via the largest rivers in the world equals 10^{14} g of sulfur. A key factor for the sulfur cycle in the natural environment is marine phytoplankton that metabolize this element

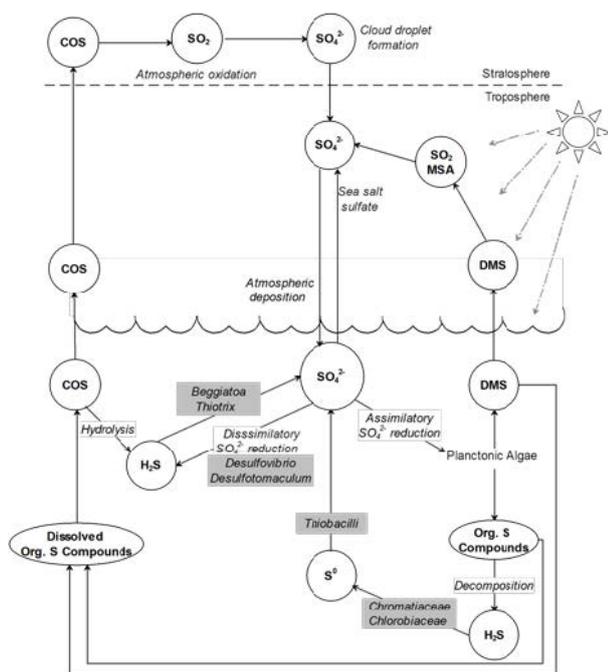


Fig. 1. The sulfur cycle [modified according to Andreae and Jaeschke (1992) and SCOPE (1993)].

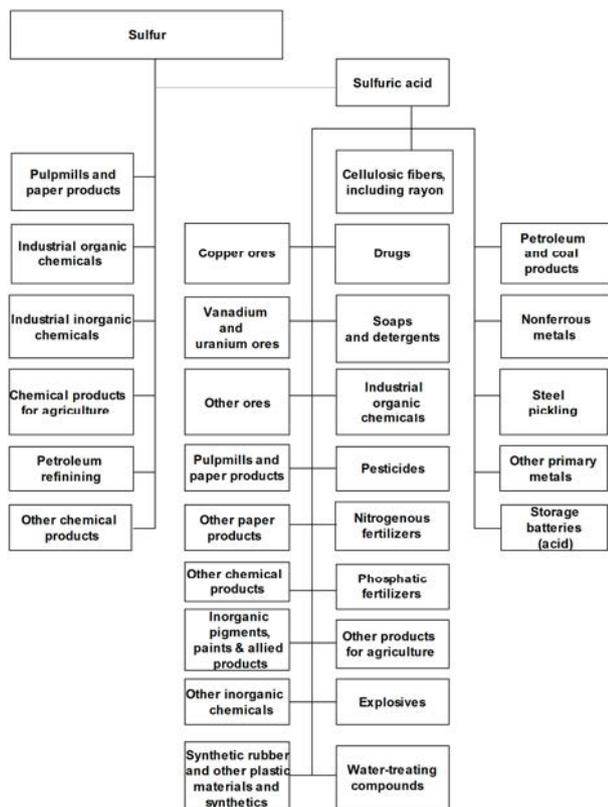


Fig. 2 Different modes of sulfur usage in the world at the beginning of the 21st century [according to Ober (2010)]

Table 1

Sulfur content in specific environmental compartments (Berner, Raiswell 1983; Migdisov et al. 1983; Holser et al. 1988; Weiner 2003).

Component	Sulfur content (g)
Sulphates dissolved in global ocean	1.3×10^{21}
Sulfur in evaporites	$(1.3 \div 8) \times 10^{21}$
Sulfur minerals (pyrite)	6×10^{21}
Atmosphere	10^{12}
Terrestrial part of hydrosphere	10^{15}
Live biomass on land	$(2.5 \div 4.0) \times 10^{15}$
Dead organic matter	$(3.5 \div 6) \times 10^{15}$

in different ways. Sulfates dissolved in the water column are mostly assimilated by plants, and incorporated into amino acids, i.e. cysteine and methionine (Gao et al. 2000, Sievert et al. 2007). However, some are also bound to sulfated polysaccharides in the oxidized form.

In water basins characterized by high

phytoplankton productivity, large amounts of organic matter sink to the bottom, which stimulates microbial activity. That in turns causes the sulfur transport between specific compartments in the aquatic ecosystems. The sulfur cycling in benthic sediments is presented in Fig. 3. Obligatory and facultative aerobic organisms quite quickly exhaust the available supply of oxygen, and later switch to anaerobic processes using the chemical compounds

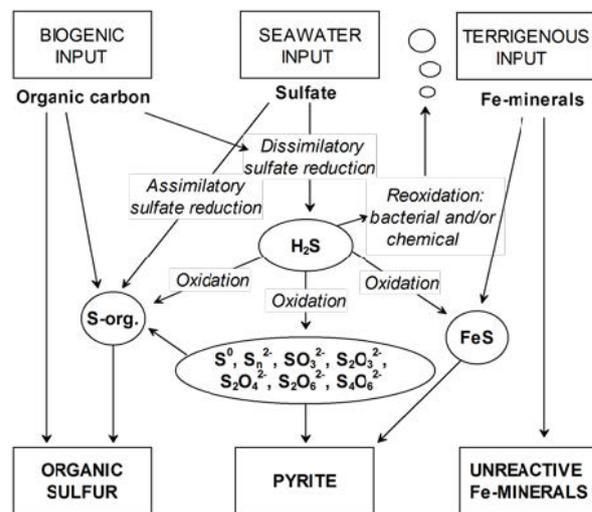
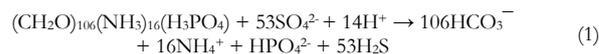


Fig. 3. Schematic representation of the sulfur diagenesis in marine sediments [modified according to Kuene (1975) and Suits&Arthur (2000)].

in the following sequence: manganese (IV) oxides, ferric (III) nitrates and ferric (III) oxides, and sulfates (Keith et al. 1982; Deming, Baross 1993; Sievert et al. 2007). The equation describing organic matter decomposition in the natural environment is as follows (Froelich et al. 1979):



where CH_2O refers to organic matter, which generally has a more complicated formula.

There are two distinguishable pathways of SO_4^{2-} biological reduction: assimilation and dissimilation (Fig. 4). Assimilative sulfate reduction is a source of the reduced sulfur compounds delivered to the plant or bacterial cells which leads to biosynthesis of sulfur-containing amino acids. Depending on the environmental conditions, dissimilative sulfate reduction is mediated by the bacterial genera: *Desulfovibrio*, *Desulfotomaculum*, *Desulfobacterium*, *Desulfococcus*, *Desulfomonas*, *Desulfosarcina*,

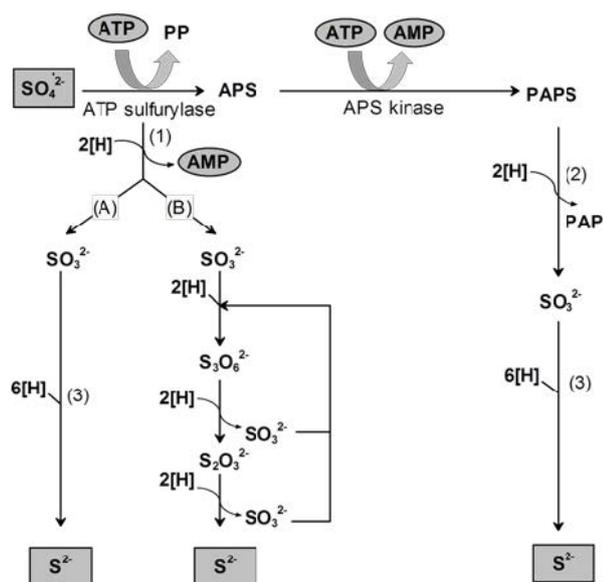
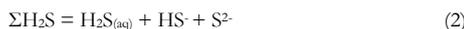


Fig. 4. Pathways of dissimilative sulfate reduction and assimilative sulfate reduction; APS – adenosine 5'-phosphosulfate; PAPS – adenosine 3'-phosphate 5'-phosphosulfate; PAP – adenosine 3'-phosphate 5'-phosphate. Enzymes: (1) APS reductase, (2) PAPS reductase, (3) sulfite reductase (Schlegel 2003).

Thermosulfobacteria, and *Desulfonema* (Battersby 1988; Korzeniewski 1995; Boon, Vincent 2003; Schlegel 2003). These bacteria grow in anaerobic conditions using many organic compounds as electron donors. Lactate, acetate, propionate, pyruvate, malate, butyrate, formate, succinate, methanol, ethanol, sugars, amino acids, higher fatty acids, indoles and nicotinic acids are the most important source of carbon and energy for sulfur bacteria (Parkes et al. 1989, Schlegel 2003, George et al. 2008). However, the bacterial groups listed above are not all used evenly the substrates listed above. The investigations conducted in the Gulf of Gdańsk (Mudryk et al. 2000) showed that bacteria dwelling in the 0-5 cm sediment layer preferred lactate, bacteria living in the next 5 cm preferred acetate, and bacteria in the 10-15 cm layer preferred propionate. Sulfur-reducing bacteria are usually classified as obligatory anaerobes although it has been proven that some, e.g. certain species from the genus *Desulfovibrio*, may survive up to 24 hours under oxic conditions (Abdollahi, Wimpenny 1990). The extent of sulfate reduction mediated by microbes is controlled by many factors, the most significant being the quality and availability of organic matter, sedimentation rate,

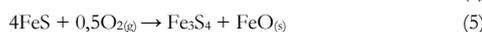
the microbial species diversity, bioturbation, bioirrigation, sediment depth, mode of organic matter oxidation, temperature, salinity, hydrostatic pressure and – as noted by many authors – sulfate concentration (Jørgensen 1982, Gagnon et al. 1996, Lin et al. 2000, Donahue et al. 2008). Hydrogen sulfide is a product of the bacterial reduction of sulfate; it is a transparent toxic gas with a characteristic, irritating odor. The presence of hydrogen sulfide in water basins indicates anaerobic conditions and a high level of degradation of a given ecosystem. H_2S can easily diffuse from deeper sediment layers into the overlying strata and that has a profound impact on the species composition and life processes of the organisms. Some animals that are exposed to the periodic or constant presence of hydrogen sulfide have a certain tolerance level to this gas (Vismann 1996), however the majority of organisms are not resistant to its toxic impact. The species *Macoma baltica* and *Pontoporeia femorata* can exist at H_2S concentrations of up to $1224 \mu\text{mol dm}^{-3}$, while *Saduria entomon* die when the concentration reaches ca. $20 \mu\text{mol dm}^{-3}$ (Janas 1998). Areas constantly contaminated with hydrogen sulfide (called azoic deserts) are completely devoid of macroscopic life forms. H_2S very rarely accumulates in the water column although such a scenario is possible in specific closed bays, fjords, and marginal seas (Brüchert et al. 2003). The Cariaco Basin in the Caribbean Sea and the Black Sea are both examples of basins characterized by a constant oxygen deficit. The Black Sea is the largest anoxic water body in the world. The water column contaminated with hydrogen sulfide reaches a depth of 2100 m (Kholodov 2002). Azoic areas have also been observed in the Baltic Sea, Lake Nitinat (Canada), the Gulf of Cariaco (Venezuela), the Arabian Sea, and the Gulf of Mexico.

Dynamics of H_2S formation are determined by the quantitative input of organic matter, while the presence of this gas creates a significant problem in basins characterized by limited water exchange and pronounced density or thermal stratification. Temperature, salinity, water circulation in the basin, light penetration depth, oxygenation, microbial activity (bioturbation and bioirrigation), pH, the outflows of groundwater and the near-bottom water dynamics have a big influence on the hydrogen sulfide residence time in the aquatic environment. The concentration of hydrogen sulfide dissolved in pore water is usually expressed as the sum of sulfides (Wijsman et al. 2001):



It is pH that has a decisive effect on the share of each species constituting the $\Sigma\text{H}_2\text{S}$ (Vismann 1996, Šukytė et al. 2002). According to Vismann (1996), in pore water with a pH between 6.0 and 6.5 there are no S^{2-} ions, while the dissolved hydrogen sulfide and HS^- ions constitute less than 70% and greater than 30% of the $\Sigma\text{H}_2\text{S}$, respectively. The HS^- ions are a dominant form at $\text{pH} = 8.0\div 10.0$; for pH values greater than 10.0, the S^{2-} ions dominate.

Hydrogen sulfide has a high affinity for binding with metals. In metal-enriched areas, the gas is partially or totally removed from the environment. The formation of metal sulfides is a significant detoxification mechanism for the macrofauna assemblages (Wijnsman et al. 2001) and other bottom-dwelling organisms. Pyrite (FeS_2) and iron sulfides are formed as a result of the reaction between sulfides and iron ions. Iron sulfides are commonly called as AVS (Acid Volatile Sulfide) because they are unstable in the presence of hydrochloric acid. For a long time AVS was considered equivalent to FeS and $\text{FeS}_{(\text{s})}$ however in recent years, a number of publications have proven that AVS compounds are a rather complex and still poorly assessed group. Rickard and Morse (2005) specified the following AVS components: $\Sigma\text{H}_2\text{S}$, $\text{Fe}(\text{SH})^+$, polysulfides, anions of sulfur oxoacids, hydrated iron sulfide $\text{FeS}_{(\text{aq})}$, mackinawite (tetragonal FeS) and greigite (Fe_3S_4). Some interrelations taking place between the AVS components are presented in Fig. 5. Mackinawite and greigite are metastable sulfide minerals. Mackinawite can form in the reaction between $\text{Fe}(\text{II})$ and hydrogen sulfide or hydrosulfide ions, while in the presence of oxygen it is oxidized to greigite and iron (II) oxide (Rickard, Morse 2005):



The products of the reaction between AVS and metals are poorly soluble metal sulfides. Therefore, AVS is considered the main factor that controls the bioavailability of heavy metals such as Cu, Zn, Cd, Ni, Hg, and Pb in sediments (Zago, Giblin 1994; Brouwer, Murphy 1995; Anderson, Wilson 2000). When a molar balance exists between the heavy metals and AVS then both chemicals are immobilized in the sediment (e.g. CdS and NiS) and become unavailable to the organisms. When

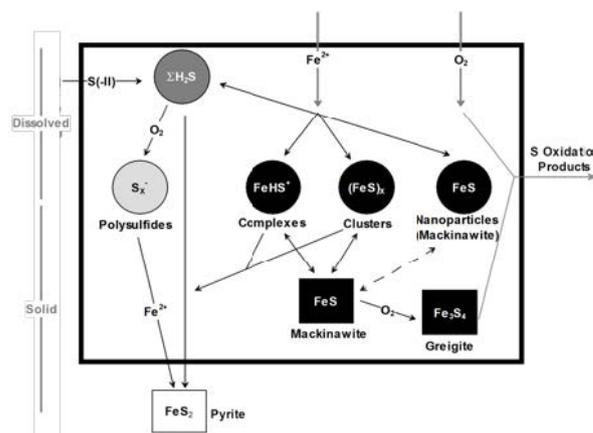
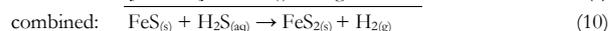
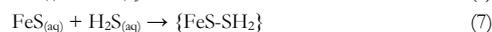
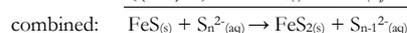
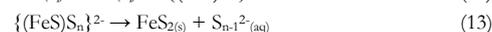
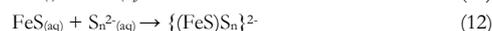


Fig. 5. A complex box model for interactions among AVS components (Rickard, Morse 2005).

the molar ratio of metal to AVS is larger than 1, the sediment is considered toxic (Di Toro et al. 1990). Hydrated iron sulfide is, in other words, a mix of $(\text{FeS})_x$ clusters, where $x: 2 \leq x \leq 150$ (Rickard, Morse 2005). The presence of labile $\text{FeS}_{(\text{aq})}$ secures the transport of $\text{Fe}(\text{II})$ in sulfide-rich ecosystems. Moreover, $\text{FeS}_{(\text{aq})}$ can react with hydrogen sulfide or polysulfides and therefore it plays a key role in pyrite formation (Rickard 1997). Under eutrophic conditions, diagenesis of FeS_2 may already start in the water column (Schenau et al. 2002). Basic reactions in the process of pyrite formation in the aquatic environment are as follows (Butler et al. 2004):



and



FeS_2 formation is also limited in environments with high pH (Böttcher et al. 2001) and low organic carbon content (Lin et al. 2000, 2002). The amount of formed pyrite depends, among other things, on the input of dissolved sulfide, the level of transformation of the dissolved AVS into minerals, the availability of the reactive organic matter and reactive iron, and the availability of an

oxidizing agent which limits the formation of FeS_2 (Neumann et al. 2005). As a result of the life functions of organisms, iron sulfides can be transferred out of the environment of their origin and later oxidized. In marine waters FeS_2 is oxidized when it comes in contact with O_2 and MnO_2 ; first, thiosulfates and polysulfides are formed, and next, sulfates. In the case of FeS , the biological pathway of oxidation is possible via polysulfides into elemental sulfur by an electron detachment from nitrate ions (Schippers, Jørgensen 2002).

Under special conditions, the formation of organosulfur compounds (S_{org}) in sediments may become the competing pathway (Lojen et al. 2004). Organosulfur compounds can form as a result of the reaction between H_2S and dead organic matter. However, in this case, polysulfides are more important because they react faster with lipids as compared to disulfides and H_2S (De Graaf et al. 1992). Brüchert (1998) claims that reoxidation of inorganic sulfides and hydrogen sulfide is a key process in the S_{org} formation. Organic sulfide formation is supported by the high sulfur content in humic and fulvic acids (Brüchert, Pratt 1996; Brüchert 1998) which are the products of degradation of lignin, carbohydrates and proteins (Nyström et al. 1996). Sulfur bound to fulvic and humic acids is called FA-S and HA-S, respectively (Pempkowiak 1997). Fulvic acids dissolve in water irrespective of the pH that results in the formation of iron-sulfur complexes; humic acids precipitate in acidic environments (Derda 1999). Organic sulfides build large 3-D arrays of biomolecules connected via sulfur bridges, which possibly prevent microbiological degradation and therefore secure the retention of S_{org} in sediments (Kohnen et al. 1991).

Diffusion of H_2S is possible only when the entire sediment layer is anoxic and the amount of reactive iron is not sufficient for iron sulfide formation. According to Jørgensen (1982), ca. 75-90% of sulfides in the marine environment undergo reoxidation. Therefore, the bulk of H_2S is not retained in the sediment as sulfides, but rather gets oxidized due to reactions with O_2 , NO_3^- , iron (III) oxide and manganese (IV) oxide, and microbial processes (Jørgensen 1977; Thamdrup et al. 1994; Schenau 2002; Bottrell, Newton 2006). The basic products of sulfide oxidation are elemental sulfur S^0 , polysulfides S_n^{2-} , thiosulfate $\text{S}_2\text{O}_3^{2-}$ and sulfate SO_4^{2-} , while for environmental pH values less than 7 the possible products are hyposulfite $\text{S}_2\text{O}_4^{2-}$, hyposulfate $\text{S}_2\text{O}_6^{2-}$ and tetrathionate $\text{S}_4\text{O}_6^{2-}$ (Šukytė et al. 2002).

Sulfide-oxidizing microbes are mainly colorless sulfur bacteria in the form of strands (*Beggiatoa*, *Thiothrix* and *Thioploca*), short rods (*Thiobacillus*, *Thiovulum* and *Macromonas*) and large unicellular structures (*Achromatium*). They also occur as obligatory anaerobes, such as green sulfur bacteria (*Chlorobium*) and purple sulfur bacteria (*Chromatium*) (Schlegel 2003). The genera *Beggiatoa*, *Thiothrix*, *Thioploca* and *Achromatium* are chemotrophic and use sulfur as an energy source. They are able to accumulate sulfur in the form of intercellular globules, which are used for obtaining energy via oxidation into SO_4^{2-} during H_2S deficiency (Korzeniewski 1995; Schlegel 2003). The genus *Beggiatoa* occurs massively in places with unstable oxygen conditions and low benthic dynamics, forming dense and spreading mats. Despite the fact that the filaments produced by *Beggiatoa* are colorless, the colonies of these bacteria are white because of the accumulated intercellular sulfur (Fig. 6). Some prokaryotic organisms, e.g. *Beggiatoa*, *Thioploca* and *Thiomargarita* oxidize sulfide by reducing nitrate ions that are stored in vacuoles; this way nitrate ions

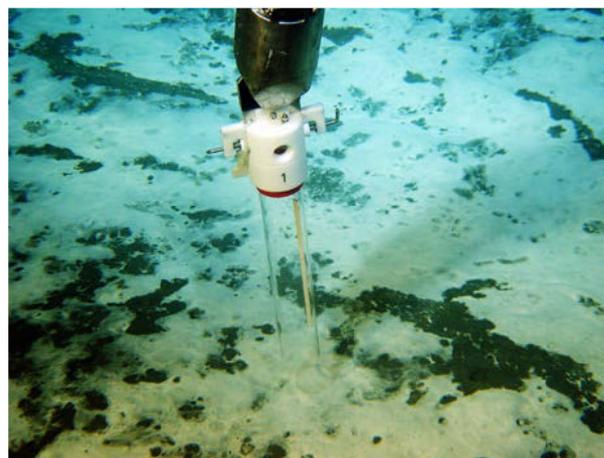


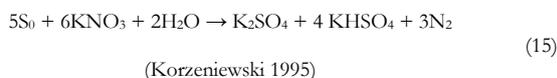
Fig. 6. *Beggiatoa* mats in the Arctic Sea.

(http://www.mpi-bremen.de/en/Research_at_the_Haakon_Mosby_Mud_Volcano.html)

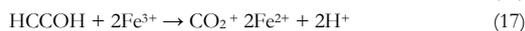
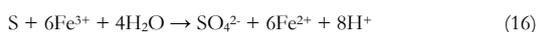
are transported into deeper layers of sediment (Fossing et al. 1995, Brüchert et al. 2003, Sievert et al. 2007). In order to store the biggest possible amount of nitrate, these organisms reach a large size and can sometimes be observed macroscopically. Anaerobic bacteria, e.g. *Chromatium* oxidize sulfide during photosynthesis (Schlegel 2003), which is possible thanks to phototrophic pigments, i.e. bacteriochlorophyll and carotenoids that absorb infrared light, as follows:



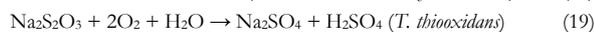
Sulfur bacteria are widely used in biohydrometallurgy. Particular attention should be paid to chemolithotrophic, acidophilic bacteria from the genus *Thiobacillus* which are highly tolerant of the presence of the majority of heavy metals although they do not tolerate high concentrations of silver and mercury. They mostly use thiosulfates and elemental sulfur as electron donors as well as sulfides (*T. thiooxidans*), thiocyanates (*T. thioparus*) and Fe^{2+} ions (*T. ferrooxidans*) (Schlegel 2003). Despite being classified as aerobes, some species from the genus *Thiobacillus* can also exist under anaerobic conditions. In such a case, the species *T. denitrificans* is able to perform denitrification, as follows:



while *T. ferrooxidans* reduces iron (III) (Pronk et al. 1991):



The examples of sulfur compound oxidation under oxic conditions are presented below (Bitton 2005):



Atmosphere

Dimethyl sulfide (DMS) is one of the most important biogenic sulfur compounds present in the atmosphere. Volcanic eruptions, vegetation and, to the greatest extent, marine phytoplankton, which use the exogenic amino acid methionine to synthesize dimethylsulfoniopropionate (DMSP), are considered the main emission sources of DMS (Gao et al. 2000). DMSP is a precursor of DMS, and its amount depends on the photoautotrophic species that synthesizes the compound. The biggest DMSP share is attributed to haplophytes, dinoflagellates and chrysophytes, while a decidedly smaller share is attributed to diatoms (Iverson et al. 1989). The annual synthesis of DMSP has been estimated at ca. 1.6×10^{15} g of sulfur. Between 1 and 2% of it is released into the atmosphere as dimethyl sulfide (Sievert et al. 2007) which readily diffuses from water

due to poor solubility. DMS is one of the gases that transport sulfur from the ocean to land areas. Gao et al. (2000) estimated that it constitutes 50% of the global input of organosulfur species into the atmosphere. The annual DMS emission within the European continental shelf is higher than in the open ocean; it equals 10^{15} g, which is equivalent to 5.2×10^{14} g S year⁻¹ (Kettle et al. 1999). DMS in the atmosphere undergoes dimethylation followed by oxidation into acidic aerosol molecules (MSA) which influence the properties of the forming clouds and therefore the amount of solar irradiance reflected back into space (Andrews et al. 2000, Malin 2006). Based on the described phenomenon, a hypothesis about the influence of DMS production on the Earth's climate was formulated in the late 1980s (Bates et al. 1987, Pham et al. 1996, Norris 2003).

Carbonyl sulfide is another organosulfur compound that forms mainly during photochemical reactions between sulfur and carbon (Ferek, Andreae 1984), the biodegradation of dissolved organic matter (Uher, Andreae 1997) and volcanic eruptions (Levine 1989). COS formation in the dark is also possible; it results from the reaction between polysulfide and carbon monoxide (Kamyshny et al. 2003). Carbonyl sulfide, like DMS, diffuses very readily from water into the air. Natural sources of COS constitute ca. 65% of its overall emission into the atmosphere. The most significant anthropogenic sources of COS are carbon disulfide CS_2 , vehicle exhaust fumes, coal burning industrial plants, the fish processing industry, and the petroleum and rubber industries. COS emissions from the European continental shelf have been estimated at 1.14×10^{13} g year⁻¹, while those from river estuaries have been estimated at 4.2×10^{12} g year⁻¹ (Uher 2006). A study conducted in 1994 in the USA by the EPA showed the highest COS concentrations over salt marshes (EPA 1994). The retention time for COS in the troposphere ranged from 2 to 6 years (Ulshöfer, Andreae 1997). Carbonyl sulfide is transported into the stratosphere where it undergoes photooxidation, becoming a very important source of aerosols, which are removed from the atmosphere via precipitation or dry deposition (Pham et al. 1996). Every year 4×10^{12} g of sulfur reach the land in the form of sulfate aerosols (Weiner 2003).

Oxidation of dimethyl sulfide and carbonyl sulfide in the atmosphere leads not only to aerosol creation, but also to sulfur dioxide formation. According to the Convention on Long-Range Transboundary Air Pollution, overseen by the United

Nations Economic Commission for Europe, sulfur dioxide is the most dangerous air pollutant. High SO₂ concentrations in the air may cause respiratory ailments and have a negative impact on human circulatory systems. Oil refineries, other industrial plants that burn fossil fuels and households (e.g. heated by burning coal) are the most important anthropogenic sources of SO₂ (Andrews et al. 2000). Natural sources such as volcanic eruptions and hydrogen sulfide oxidation presently contribute a much lower share of global SO₂ emissions due to increased global development in the 20th century. Nevertheless, the regional impact of natural sources may still be significant. Azad et al. (2005) demonstrated that sulfur dioxide is the main gas emitted during the day from the intertidal zone of the East China Sea. Its concentration is high enough to have a polluting effect on the air quality in the adjacent cities. Most sulfur dioxide in the atmosphere is oxidized to sulfur trioxide. It forms sulfurous acid when it reacts with water. The products of both reactions end up as sulfuric acid or sulfate salts that get deposited on the Earth's surface as so-called acid rain. This specific type of precipitation causes, among other things, acidification of soil and surface waters, deterioration of buildings (Andrews et al. 2000), diseases and dying out of forests, decreased quality of agricultural production, increased metal mobility in soil and the deterioration of freshwater ecosystems (Falkowska, Korzeniewski 1995).

Carbon disulfide, methanethiol and hydrogen sulfide are other gaseous sulfur compounds present in the atmosphere. Gas fluxes have great importance in the global sulfur cycle. The direct input of sulfur compounds from the atmosphere into the seas and oceans is of secondary significance however in the case of the terrestrial part of hydrosphere, it is very important. In addition, large amounts of sulfur enter the rivers via runoff from agricultural land, decomposition of organic matter on land, and chemical and mechanical weathering of rocks. Next, sulfur is discharged into the seas mainly in the form of dissolved sulfates of sodium, potassium, magnesium and calcium.

CONCLUSION

This review article describes the current state of knowledge of the global sulfur cycle, focusing on the marine environment. Sulfur is one of the most important components of the environment, as along with carbon, nitrogen, and phosphorus,

and it influences all environmental compartments. Human impact on the atmospheric and marine sulfur balance is significant. Although oceanological studies on sulfur have become an interesting theme for researchers over the past several decades, further investigation is needed.

Bacterial sulfate reduction has been considered the most significant pathway of organic matter decomposition in marine anoxic sediments. Further research on the role of sulfur reducing bacteria in the marine environment, and therefore on the addition of sulfur during the early diagenesis of organic matter will contribute to a better understanding of the organic matter cycle and diagenetic processes in ocean water and bottom sediments. Moreover, studies on pore water hydrogen sulfide removal via iron sulfidization as a final stage of diagenetic processes in bottom sediments are required. There is a strong relationship between acid volatile sulfides and heavy metals such as Cu, Zn, Cd, Ni, Hg, and Pb in sediments. Detailed investigation in this field may give valuable information about controlling the bioavailability of heavy metals in aquatic systems and their toxic effects on particular links of the overall food chain. The continuation of research on DMS cloud formation and its influence on the intensity of acid deposition could be the next step towards a solution to such important problems as global warming and acidification of aquatic ecosystems.

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