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Bacteria are driving the ocean's organosulfur cycle

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Bacteria are key players in the marine sulfur cycle, from the sunlit ocean surface to the dark abyssal depths. Here, we provide a brief overview of the interlinked metabolic processes of organosulfur compounds, an elusive sulfur cycling process that exists in the dark ocean, and the current challenges that limit our understanding of this key nutrient cycle.

Organically combined sulfur compounds are synthesized by many members of the marine ecosystem, including via the assimilation of inorganic sulfate by phytoplankton (~1.3 billion tons of sulfur each year) [1] (Figure 1). While organosulfur compounds are known mainly as key building blocks of proteins (methionine and cysteine) and photosynthetic membrane lipids – sulfoquinovosyl diacylglycerol (SQDG) – they also have many other cellular functions, such as cell osmolytes, redox balancers, predator deterrents, and hydrostatic pressure protectants, for example, dimethylsulfoniopropionate (DMSP) [2,3]. One of the main reasons behind the increasing interest in the marine sulfur cycle is that it includes the emission of the climatically active gas dimethylsulfide (DMS) to the atmosphere, as well as organosulfur transformations that are tightly linked to carbon cycling in seawater [2]. Here we present recent advances and the current fundamental questions in marine sulfur cycling that would especially benefit from studies on the biogeochemistry of organic sulfur, as well as the various forms of bacteria-mediated metabolism of DMSP and sulfonates.
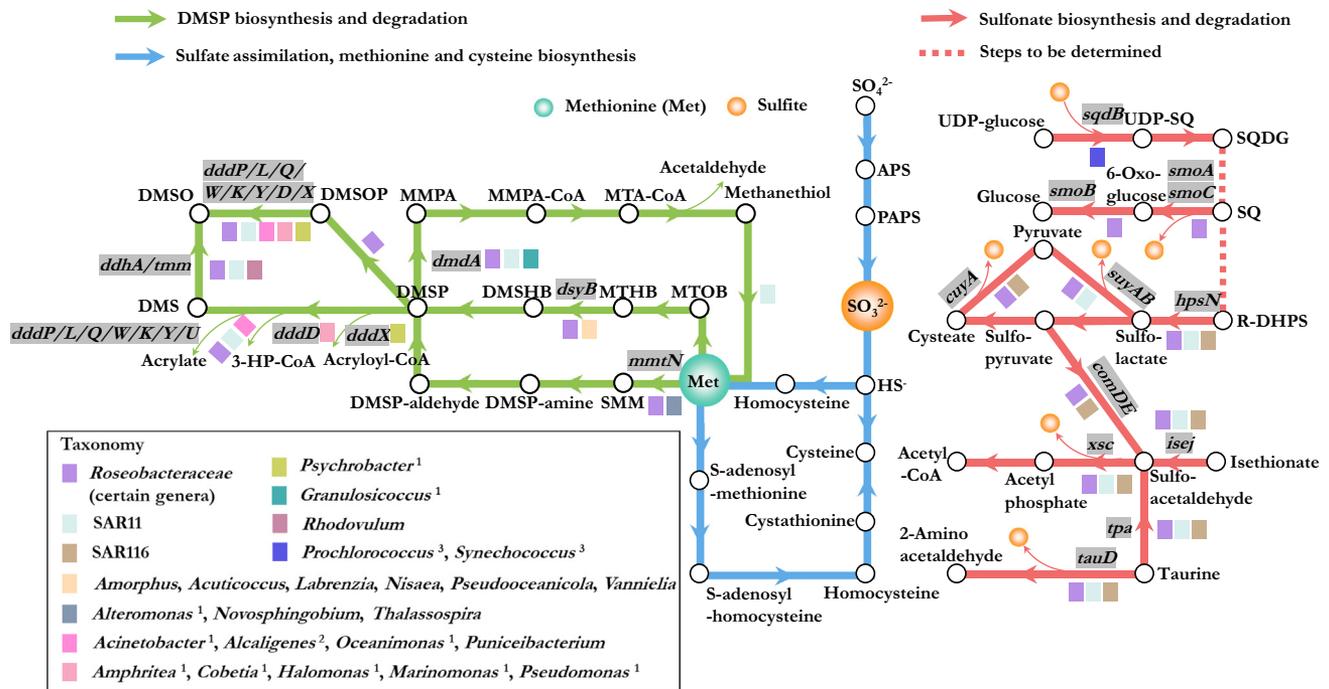
The biogeochemistry of organic sulfur in the ocean

The marine organic sulfur pool, derived from photosynthetic production and microbial processes, is a reservoir of sulfur that consists of dissolved and particulate forms, including nonliving aggregates and living microorganisms. Globally, the amount of dissolved organic sulfur (DOS) (~6.7 billion tons of sulfur) greatly exceeds that of particulate organic sulfur (POS) by more than tenfold, with DOS concentrations generally decreasing with water depth, and the epipelagic zone displaying the greatest decline [1,2,4] (Figure 1B). The metabolic versatility of bacteria allows them to take up DOS from the exudates and viral lysates of phytoplankton, as well as from the decomposed biomass and the organic sulfur sinking from the surface layer into the deep sea. While the majority of the newly assimilated sulfur is converted into sulfate, some of the DOS is utilized for other purposes, such as cellular growth and the synthesis of sulfur-containing secondary metabolites.

The sulfur compounds from phytoplankton and bacteria that are frequently detected in the DOS and POS pools primarily contain the sulfur functional groups thiol, thioether, sulfonium, sulfoxide, and sulfonate (Figure 1C). The sulfur flux of the sulfonium compound DMSP (~240 teragram sulfur per year), generated by surface-dwelling phytoplankton, accounts for approximately 18% of the annual production of organic sulfur in the ocean [1,2]. Nevertheless, bacteria are the key source of organic sulfur in the dark ocean, with a considerable contribution to sulfate assimilation and DMSP production in the deep zone and sediments [5]. Sulfonate is another abundant organic sulfur compound in the ocean, especially given that a petagram of SQDG, which is widespread in phytoplankton, cyanobacteria and photosynthetic bacteria, is produced annually [6]. Moreover, although 2,3-dihydroxypropane-1-sulfonate (DHPS) has been found only in diatoms and coccolithophores, its intracellular content reaches the level of several millimolar, which is comparable to that of DMSP [2]. The structurally unusual dimethylsulfoxonium propionate (DMSOP), found distributed in both seawater and sediments, also has its origin in phytoplankton and bacteria [7,8].

While a majority of organic sulfur is remineralized to sulfate, a minor fraction of organic sulfur (~1 million tons of sulfur) is retained in a refractory state that may remain in the ocean for thousands of years [2] (Figure 1A). Various sulfur-lipids are present throughout the entire water column and make a remarkable contribution to particulate organic carbon (approximately 1–4%), the trend increasing with depth in the Northern Atlantic Ocean, potentially contributing to carbon sequestration [9]. In addition to the biogenic sulfurs, marine sediments contain abundant organic sulfur created from sulfurization reactions that occur when sulfide from microbial sulfate reduction is abiotically incorporated into organic matter via nucleophilic attack on unsaturated double bonds. Recent analysis of sulfur isotopes suggests that the abiotically sulfurized organic matter released from sediment porewater into seawater comprises only a small proportion of the marine DOS pool (on average <8%) [4]. However, it is likely to be highly resistant to mineralization by microorganisms, potentially contributing to the huge reservoir of refractory dissolved organic carbon in the oceans. Similarly, this abiotic sulfurization process also can occur in ocean oxygen-minimum zones or even within the anoxic microenvironments inside sinking particles, and thus enhances the conservation and sequestration of carbon [10]. This sulfurized organic matter is characterized by a high molar ratio of S:C (3–5%), consisting of sulfur-containing aromatics,

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Figure 1. Current understanding of the marine organic sulfur cycle. (A) Conceptual depiction of the organic sulfur cycle. (B) Dissolved organic sulfur (DOS) concentrations and an estimation of DOS stock in the oceanic water column (data from [1,4] respectively). (C) Natural organosulfur compounds and their producers in the ocean. Abbreviations: DHPS, 2,3-dihydroxypropane-1-sulfonate; DMS, dimethylsulfide; DMSO, dimethylsulfoxide; DMSOP, dimethylsulfoxonium propionate; DMSP, dimethylsulfoniopropionate; POS, particulate organic sulfur; SQ, sulfoquinovose; SQDG; sulfoquinovosyldiacylglycerol.

disulfides, alkyl sulfides, sulfoxides, sulfonates, and sulfate esters similar to sulfur compound compositions of black shales [10].

Recent advances in our understanding of organosulfur metabolism in marine bacteria

Marine bacteria synthesize DMSP via transamination (mediated by *dsyB*) and methylation (mediated by *mmtN*) pathways (Figure 2) that are analogous to the pathways in many phytoplankton [2]. Although a limited number of phytoplankton, such as coccolithophores and dinoflagellates, can degrade DMSP to DMS (mediated by DMSP lyase Alma1), bacteria are the dominant degraders of DMSP in the ocean through the demethylation (mediated by DMSP demethylase DmdA) and cleavage (mediated by 'Ddd' DMSP lyases) pathways [2]. Recently, it was found that Alma1 from phytoplankton, as well as bacterial DMSP lyases, can also cleave DMSOP to liberate dimethylsulfoxonium propionate (DMSO) [8]. DHPS can be produced by *Escherichia coli* K-12 decomposing sulfoquinovose (SQ) via reactions analogous to the Embden–Meyerhof–Parnas pathway [6], but this pathway is not found in phytoplankton and marine bacteria.

DHPS can be catabolized by marine *Roseobacteraceae* via a pathway homologous to the one found in the soil bacterium *Cupriavidus pinatubonensis* JMP134 [11]. Over the past four decades SQ-degrading microorganisms have been discovered in terrestrial, freshwater, and intestinal environments, and the associated routes for SQ catabolism have been determined [6]. Until recently, marine bacterial utilization of SQ had been demonstrated only with *Roseobacteraceae* isolates (*Dinoroseobacter shibae* DFL 12 and *Roseobacter denitrificans* OCh 114) [12]. Approximately half of the *Roseobacteraceae* genomes have been

Figure 2. Known metabolic routes for the synthesis and consumption of major organic sulfur compounds in marine bacteria. Those bacteria that contain experimentally validated metabolic pathways are indicated by colored boxes around the corresponding genes. In the 'Taxonomy' box, genera with no superscript belong in the Alphaproteobacteria; those with superscript '1' belong in the Gammaproteobacteria; those with superscript '2' belong in the Betaproteobacteria; those with superscript '3' belong in the Cyanobacteria. Abbreviations: 3-HP-CoA, 3-hydroxypropionate-CoA; APS, adenosine 5'-phosphosulfate; DMS, dimethylsulfide; DMSHB, 4-dimethylsulfonio-2-hydroxybutyrate; DMSO, dimethylsulfoxide; DMSOP, dimethylsulfoxonium propionate; DMSP, dimethylsulfoniopropionate; MMPA, 3-methylthiopropylamine; MMPA-CoA, 3-methylmercaptopropionyl-CoA; MTA-CoA, methylthioacryloyl-CoA; MTHB, 4-methylthio-2-hydroxybutyrate; MTOB, 4-methylthio-2-oxobutanoic acid; PAPS, 3'-phosphoadenylyl-sulfate; R-DHPS, R-2,3-dihydroxypropane-1-sulfonate; SMM, S-methylmethionine; SQ, sulfoquinovose; SQDG, sulfoquinovosyldiacylglycerol; UDP, uridine diphosphate. The enzyme names for corresponding genes are as follows: *comDE*, sulfopyruvate decarboxylase; *cuyA*, cysteate sulfolyase; *dddP/L/Q/W/K/Y/D/X/U*, DMSP cleavage enzymes; *ddhA*, dimethylsulfide dehydrogenase; *dmdA*, dimethylsulfoniopropionate demethylase; *dsyB*, 4-methylthio-2-hydroxybutyrate S-methyltransferase; *hpsN*, DHPS dehydrogenase; *isej*, isethionate dehydrogenase; *mmtN*, methionine S-methyltransferase; *smoA*, flavin reductase; *smoB*, oxidoreductase; *smoC*, SQ monooxygenase; *sqdB*, UDP-SQ synthase; *suyAB*, sulfolactate sulfolyase; *tauD*, taurine dioxygenase; *tmm*, trimethylamine monooxygenase; *tpa*, taurine aminotransferase; *xsc*, sulfoacetaldehyde acetyltransferase.

found to contain homologs for all of the enzymes (SmoABCD) in the oxidative desulfurization pathway of the soil bacterium *Agrobacterium tumefaciens* C58 [6]. Microbial enzymes capable of catalyzing the degradation of SQDG to SQ have been found in terrestrial and intestinal environments [6], but the enzymes and mechanisms of SQDG degradation in marine systems are still unknown.

DMSP can be catabolized by a broad spectrum of bacterial groups for growth, while the ability to degrade sulfonates is restricted to a limited number of phylogenetically diverse bacterial taxa (Figure 2) [11–13]. Bacteria can easily utilize DMSP

as a sole carbon source for growth, while bacteria can rapidly consume DHPS and SQ in the presence of other bio-labile organic carbon [11,12,14], which could potentially be explained by a priming effect whereby bacteria utilize labile substrates to generate energy and thus enhance the ability to catabolize those sulfonates [14]. In addition, the sulfite derived from desulfonation of sulfonates may inhibit bacterial growth, possibly owing to its cellular toxicity [11,12]. In contrast, there is no release of inorganic reduced sulfur from bacterial DMSP pathways (Figure 2). Thus, marine DMSP is more bioavailable than DHPS and SQ.

Future research directions on the ocean organic sulfur cycle

While DMSP has undergone extensive laboratory and field studies, there are still unsolved questions for DMSP metabolism. For example, the steps involved in DMSP synthesis in one dinoflagellate, via a decarboxylation pathway, have not been determined, and the pathways in which phytoplankton and bacteria transform DMSP to DMSOP need to be addressed in future research. Compared to DMSP, our knowledge about the microorganisms capable of sulfonate decomposition and production, and the distributions and amounts of sulfonates in the ocean, is still limited. Furthermore, with respect

to the microbial metabolism of sulfonates, advances in the ocean lag behind those of other ecosystems. Therefore, an integrated approach is needed when seeking to identify novel marine sulfonate-degrading strains and metabolic enzymes by combining microbial ecology, enzymology, crystallography, and metabolomics. A similar strategic approach previously enhanced our understanding of DMSP cycling.

Another major challenge is to address the poorly understood mineralization of organic sulfur derived from primary producers and its conversion into refractory compounds in marine systems. The marine DOS pool encompasses a diverse and largely unexplored molecular space. The long-term stability of deep-sea DOS is a result of not only abiotic sulfurs but also microbial-derived sulfur metabolites. We need to acquire fundamental information on the properties and reactivities of DOS, which would provide tracers for both their origin and involvement in biogeochemical cycles. However, an accurate assessment of the spatial variations in DOS concentration and composition remains a challenge due to biases associated with solid-phase extraction of organic matter from seawater [15]. Organic sulfur concentrations based on direct measurement have been established, showing that there is no correlation of organic sulfur and organic carbon or organic nitrogen concentrations in the sea water column [15]. Even though microbes play a key role in the degradation of sinking particulate organic carbon degradation, the microbial breakdown of the organic sulfur in particles is still poorly understood. Studies that reveal additional details about the microbial processes of organic sulfurs in particulate organic carbon remineralization will be crucial in addressing the deep-sea sulfur cycle.

Like carbon, the cycling of sulfur may be affected by future ocean warming, with acidification and hypoxia arising from anthropogenic climate change. Despite the existing evidence for oceanic DMS emission undergoing an increase due to warming, it remains unknown whether the flow of sulfur-containing carbon from phytoplankton to bacteria will vary greatly over space and time. A recent study combing time series observations and modeling data suggested that marine phytoplankton may be resilient to climate-driven changes in nutrient availability [16]. Nutrient uptake plasticity as a potential mechanism for phytoplankton to maintain high primary productivity [16] can allow cyanobacteria and algae to overcome decreased phosphate availability in the future ocean through a sulfolipid–phospholipid substitution strategy, and a shift in phytoplankton community composition. Marine sulfur cycling is thus linked to the cycling of carbon and phosphorus, resulting in a critical question of the extent to which the consequences of bacteria-mediated sulfur cycling may impact other cycles, or how they are intertwined both at present and under future environmental change. To assess the microbial contribution to sulfur cycling in the context of climate change, there is a need to collect systematic data on biogenic sulfur dynamics and to conduct more multifactor experimental studies in the field, using the established tools of microbial ecology such as high-resolution mass spectrometry, metaomics, bioinformatics, sulfur isotopes, and ecological models.

Declaration of interests

No interests are declared.

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