Sulfur metabolites in the pelagic ocean

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Abstract | Marine microorganisms play crucial roles in Earth's element cycles through the production and consumption of organic matter. One of the elements whose fate is governed by microbial activities is sulfur, an essential constituent of biomass and a crucial player in climate processes. With sulfur already being well studied in the ocean in its inorganic forms, organic sulfur compounds are emerging as important chemical links between marine phytoplankton and bacteria. The high concentration of inorganic sulfur in seawater, which can readily be reduced by phytoplankton, provides a freely available source of sulfur for biomolecule synthesis. Mechanisms such as exudation and cell lysis release these phytoplankton-derived sulfur metabolites into seawater, from which they are rapidly assimilated by marine bacteria and archaea. Energy-limited bacteria use scavenged sulfur metabolites as substrates or for the synthesis of vitamins, cofactors, signalling compounds and antibiotics. In this Review, we examine the current knowledge of sulfur metabolites released into and taken up from the marine dissolved organic matter pool by microorganisms, and the ecological links facilitated by their diversity in structures, oxidation states and chemistry.

Allelochemicals
Chemicals produced by a living organism that can be beneficial or detrimental to another organism.

Volatile
A molecule that readily vaporizes into air.

Metabolites
Small molecules that are a direct product of metabolism.

Aerosols
Suspensions of solid or liquid particles in gas.

Cloud nucleation
Formation of aerosol particles on which water vapour condenses in the first step of cloud formation.

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https://doi.org/10.1038/s41579-019-0250-1

Inorganic sulfur in the form of sulfate (SO_4^{2-}) has one of the highest concentrations of any dissolved constituent in seawater (~28 mM), indicative of it being a major component of marine salt. From this massive reservoir, sulfur is taken up by marine microorganisms and synthesized into a variety of organic molecules. Eventually, most microbially produced organic sulfur is remineralized and the oxidized sulfur atom returned to the sulfate reservoir. In between, however, it plays central roles in the biology of marine microorganisms and the food webs they sustain, by functioning in metabolism, contributing to membrane structure, supporting osmotic and redox balance, and acting as allelochemicals and signalling molecules. Some marine microorganisms synthesize volatile sulfur metabolites, and a fraction of these escape across the air–sea interface. Despite the small absolute amount, this is the largest natural source of sulfur that is released into the atmosphere. Following oxidation, ocean-derived sulfur influences the acid–base balance of aerosols and rainwater and affects cloud nucleation at a global scale[1–3].

Sulfur metabolite cycling begins when microorganisms acquire and reduce sulfate from seawater, a straightforward process for most. The assimilatory sulfate reduction pathway that converts readily available sulfate to sulfide (H_2S) for incorporation into organic molecules is nearly ubiquitous in marine phytoplankton and bacterioplankton. Once reduced, sulfur is converted into the essential amino acids methionine and cysteine, into cofactors such as biotin and S-adenosylmethionine and into microbial sulfolipid[4] and taurolipid[5] membranes. Sulfur-containing metabolites also function as cell osmolytes[6] and redox buffers[7]. According to the canonical elemental ratio of ocean plankton biomass ($C_{124}N_{16}P_1S_{1.3}$) (REF. [8]), one atom of sulfur needs to be assimilated into marine microbial biomass for every 95 atoms of carbon assimilated.

Although the inorganic sulfur reservoir in seawater greatly exceeds microbial sulfur quotas, the conversion of sulfate (S oxidation state +6) to cysteine (S oxidation state −2) requires an eight-electron reduction. Producing fully reduced sulfur from sulfate has an energy cost to microorganisms of 1,815 kJ mol^{-1}, as compared to 605 kJ mol^{-1} for producing fully reduced carbon from CO_2 (REF. [9]). The expense of sulfate reduction is not usually prohibitive for the photosynthetic phytoplankton in the sunlit ocean. Bacterioplankton, on the other hand, are often energy-limited, and therefore sulfur that has already been reduced and incorporated into organic matter is a valuable commodity. Bacteria can obtain pre-reduced sulfur from the seawater dissolved organic sulfur (DOS) pool, into which labile organic sulfur compounds are released from phytoplankton and other marine microorganisms. Two widespread marine bacterial taxa, the proteobacterial groups SAR11 and SAR86, have actually lost the sulfate assimilation pathway and instead are wholly reliant on scavenging reduced sulfur from seawater[10,11].

The assimilation of sulfur for molecular biosynthesis is one example of the accumulating evidence from both biological and chemical perspectives of a decidedly active role for sulfur metabolite pools in the aerobic ocean. These recent discoveries (and rediscoveries) include the identification of a diverse suite of sulfur-containing molecules synthesized by marine phytoplankton[12–14], characterization of numerous genes mediating DOS metabolism in cultured and uncultured marine microorganisms[14–19], and recognition of the unique biogeochemical roles of DOS in the ocean's microbial network[6,20]. In this Review, we examine sulfur metabolites, defined as sulfur-containing organic molecules that are direct products of metabolism, that are synthesized and catabolized by marine microorganisms in the pelagic ocean, and explore how they function as ecological links between ocean microorganisms.

Organic sulfur cycling in the ocean

An estimated 1,320 Tg of sulfur is fixed by marine phytoplankton into organic material annually[20], of which ~600 Tg is subsequently released into seawater as DOS by various biological processes (FIG. 1). The majority of these phytoplankton-derived metabolites are taken up from the DOS pool by marine bacteria on short timescales (minutes to days)[6,21,22]. The more reduced the sulfur atom is in DOS compared to sulfate, the more readily it can be incorporated into cellular material, and the more energy it yields for bacteria when oxidized back to sulfate. A fraction of the DOS pool (~25 Tg) is volatile and effluxes to the atmosphere (~4% of annual DOS inputs), whereas another ~1 Tg of DOS (0.2%) becomes part of the ocean's non-labile dissolved organic matter pool, with an estimated average lifetime of ~4,000 years[20]. The DOS in this last category includes molecules made more resistant to bacterial processing from biological and chemical transformations[23]. What is unmistakable from this rough budget, and what can change only modestly as more information becomes available, is that the vast majority of phytoplankton-produced organic sulfur released into seawater is rapidly processed and returned to an inorganic form by ocean bacteria[24].

Because the sulfur metabolites travel through the ocean's organic matter reservoirs attached to carbon molecules, microbial processing represents a link between the marine carbon and sulfur cycles. There are suggestions that this linkage may not always have tight stoichiometry, with DOS molecules being cycled more rapidly than the bulk dissolved organic carbon (DOC) pool. Some coastal bacterioplankton communities have been shown to preferentially process organic sulfur from DOC, assimilating organic matter with a 1.6-fold bias towards sulfur-containing molecules[25]. Similarly, bulk elemental measures of surface ocean particulate organic matter compared to depth-integrated values and in situ sulfur assimilation rates indicate selective consumption of newly synthesized organic sulfur in the upper water column[26]. The sulfur-rich compound dimethylsulfoniopropionate (DMSP), with a C:S ratio of 5:1, is the most significant single bacterioplankton substrate so far identified, having high flux rates and very fast turnover times in surface seawater[6,27]. Deeper in the ocean (1,000–5,000 m), the DOC-to-DOS ratios increase

Osmolytes
Organic molecules used by organisms to maintain cellular water balance.

Assimilation
Process by which organisms transform compounds into organic molecules.

Biosynthesis
The process by which organisms assemble the components of molecules.

Biogeochemical
Relating to the cycling of elements through biological, geological and chemical processes.

Tg
Teragram, 10^{12} grams.

Stoichiometry
A quantitative measure of the relationship among elements in a chemical compound.

Turnover times
The times required to completely renew the content of reservoirs.

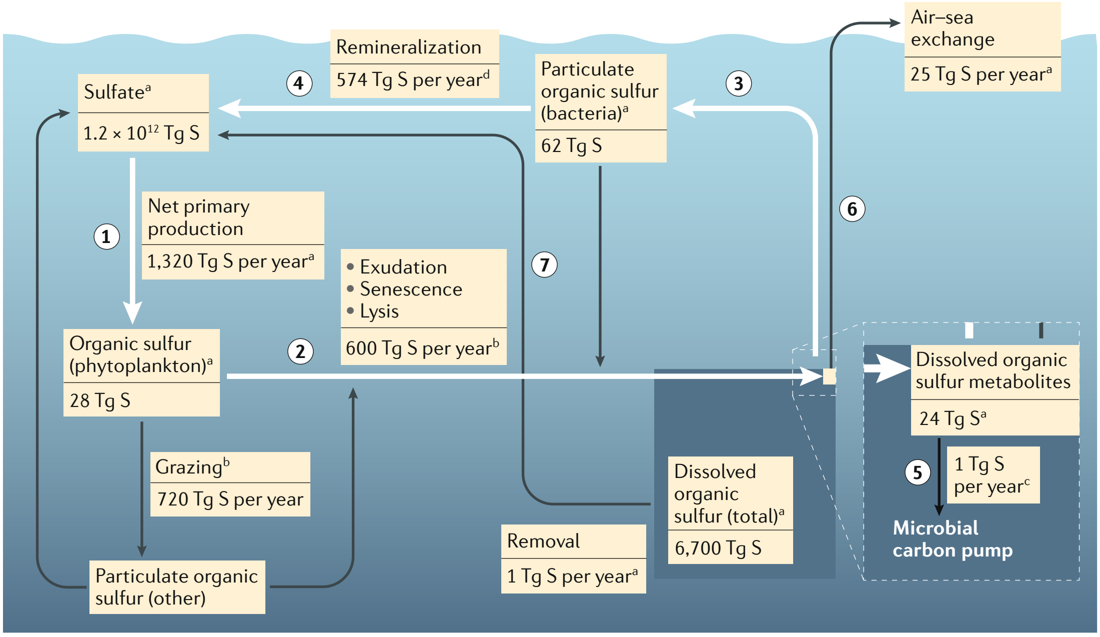


Fig. 1 | **Organic sulfur reservoirs and flux in the pelagic ocean.** In the main cycle (white arrows), sulfate is synthesized into organic sulfur compounds by phytoplankton (flux 1). Sulfur metabolites are subsequently released by phytoplankton into the labile dissolved organic sulfur (DOS) pool, with secondary contributions by grazers and heterotrophic bacteria (flux 2). Bacteria take up sulfur metabolites such as sulfonium compounds, sulfonates, sulfate esters and thiols from the labile component of the DOS pool (flux 3). The sulfur in these organic compounds is subsequently returned to sulfate by bacterial catabolism (flux 4). There are quantitatively minor leaks (black arrows) to the non-labile DOS reservoir via the microbial carbon pump[23] (flux 5), to the atmosphere (flux 6) and from the non-labile DOS back to the sulfate pool (flux 7). [a]Data from REF.[20]. [b]Assumes that 45% of fixed sulfur passes directly or indirectly into the DOS pool, and 55% is entrained into the food web. [c]The refractory DOS formation rate is assumed to equal its removal rate; data from REF.[23]. [d]DOS production minus non-labile DOS formation and air–sea exchange.

relative to the surface (<100 m)[20]. Sulfur-containing components may therefore make up a more rapidly cycled subset of both the labile and non-labile components of the ocean's DOC reservoirs.

Organic sulfur metabolites

Sulfur metabolites fall into a number of chemical classes, defined on the basis of their sulfur oxidation state and covalent bonding patterns. Among the most reduced forms are the sulfonium compounds, which have three organic substituents covalently bonded to a sulfur atom in the −2 oxidation state (SR_3^+) (FIG. 2). The best-studied marine sulfur metabolite is the sulfonium compound DMSP, estimated to account for a remarkable 3–10% of the carbon fixed by marine phytoplankton[17,28,29] and accumulating to intracellular concentrations of up to 300 mM in phytoplankton cells[30,31]. Other sulfonium compounds identified in the marine organic sulfur pool include gonyol, gonylauline, dimethylsulfonioacetate and dimethylsulfoxonium propionate[32–34]. Phosphatidylsulfocholine, the sulfonium analogue of phosphatidylcholine, serves as a membrane lipid in some marine plankton[35].

Two other classes of organic sulfur metabolites that contain fully reduced sulfur (−2) are the sulfides (RSR), which are the sulfur analogues of ethers, and thiols (RSH), the sulfur analogues of alcohols (FIG. 2). Sulfur metabolites in the sulfide group include the essential amino acid methionine, the DMSP degradation product dimethylsulfide (DMS), and the B vitamins thiamine and biotin. Thiols include the essential amino acid cysteine, homocysteine, the cofactor coenzyme A, the antioxidant glutathione and the DMSP degradation product methanethiol. The thiol functional group is important in cellular redox reactions, including oxidation to an organic disulfide (RSSR), in which the sulfur oxidation state becomes −1. The disulfide dimethyldisulfide is produced by marine phytoplankton and contributes to marine aerosols[36].

More oxidized sulfur metabolites with an oxidation state of 0 include the sulfoxides, or compounds with a sulfinyl (SO) functional group attached to two carbon atoms (for example, dimethylsulfoxide (DMSO) and the sulfenic acids (RSOH)). More highly oxidized sulfur metabolites are sulfinic (RSO_2H) and sulfonic (RSO_3H) acids, with oxidation states of +2, and +4, respectively (FIG. 2). The sulfenic and sulfinic forms generally function as intermediates in redox reactions and in the synthesis of sulfonic acids and their associated sulfonate salts (RSO_3^-). The simplest sulfonate, the C1 compound methanesulfonate, is a product of DMS oxidation in the atmosphere, a portion of which is deposited back into the sea[37]. The C2 sulfonates (those having a C2 backbone) in seawater include the compatible solute taurine and its derivatives *N*-acetyltaurine, isethionate, methyltaurine, homotaurine and hypotaurine. The C3 sulfonates are 2,3-dihydroxypropane-1-sulfonate (DHPS), cysteate, sulfolactate and cysteinolic acid (FIG. 2). Membrane sulfolipids can also contain sulfonate moieties. These include sulfoquinovosyldiacylglycerol (SQDG) in the photosynthetic membranes of marine microorganisms and cyanobacterial vesicles[38], and taurolipids in protist membranes[39].

C1 compound
An organic compound that consists of a single carbon atom with attached hydrogen atom(s).

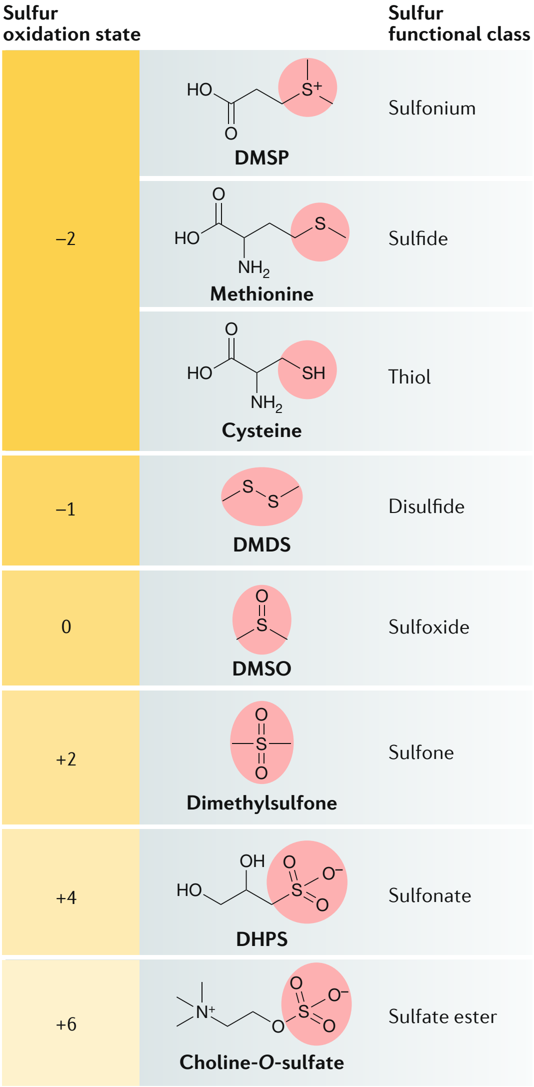
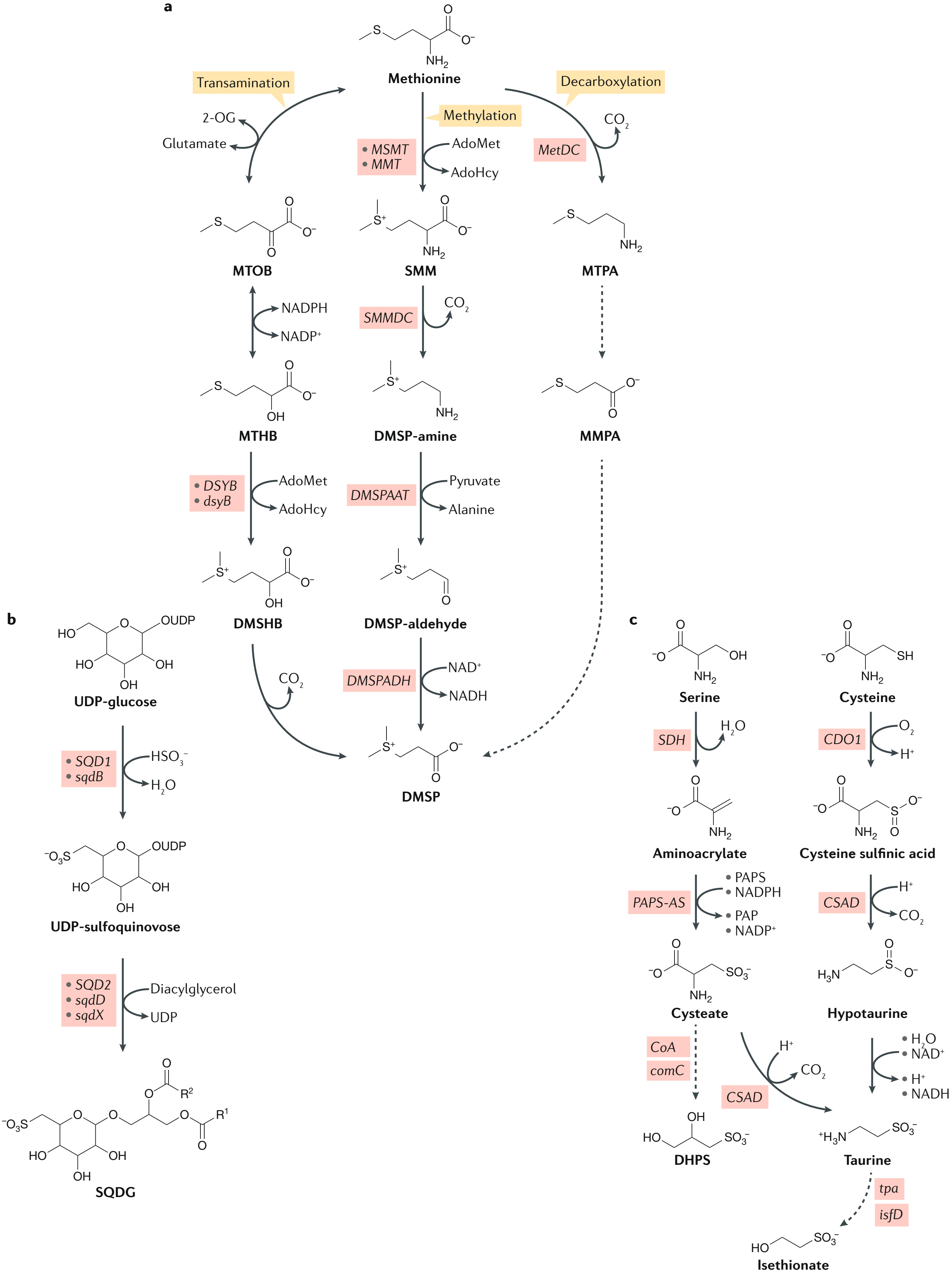


Fig. 2 | **Representative molecular structures and sulfur oxidation states of marine sulfur metabolite classes.** The most reduced forms (top) are sulfoniums, sulfides and thiols, including dimethylsulfoniopropionate (DMSP) and the sulfur-containing amino acids methionine and cysteine. More oxidized forms (middle) include disulfides, sulfoxides and sulfones. The most oxidized (bottom), and therefore least valuable to marine bacteria as a reduced sulfur source, are sulfonates such as 2,3-dihydroxypropane-1-sulfonate (DHPS) and sulfate esters such as choline-*O*-sulfate. DMDS, dimethyldisulfide; DMSO, dimethylsulfoxide.

Sulfate esters ($ROSO_3^-$) contain a fully oxidized sulfur (+6 oxidation state) that is linked to its carbon constituents by oxygen. These include sulfated osmolytes such as choline-*O*-sulfate, as well as the sulfated sugars and saccharides that are common components of marine plankton biomass. Sulfate saccharides represent a diverse chemical class of sulfur-decorated cell wall matrix polysaccharides across many plankton lineages, including glucuronomannan in diatoms and carrageenan in red algae.

From a biogeochemical perspective, the most interesting members of these varied classes of metabolites are those that substantially contribute to the global


a
Methionine
Transamination
2-OG
Glutamate
Methylation
MSMT
MMT
AdoMet
AdoHcy
Decarboxylation
MetDC
CO_2
MTOB
SMM
MTPA
NADPH
$NADP^+$
SMMDC
CO_2
MTHB
DMSP-amine
MMPA
DSYB
dsyB
AdoMet
AdoHcy
DMSPAAT
Pyruvate
Alanine
DMSHB
DMSP-aldehyde
CO_2
DMSPADH
NAD^+
NADH
DMSP
b
UDP-glucose
SQD1
sqdB
HSO_3^-
H_2O
UDP-sulfoquinovose
SQD2
sqdD
sqdX
Diacylglycerol
UDP
SQDG
c
Serine
SDH
H_2O
Aminoacrylate
PAPS-AS
PAPS
NADPH
PAP
$NADP^+$
Cysteate
CoA
comC
CSAD
H^+
CO_2
DHPS
Taurine
tpa
isfD
Isethionate
Cysteine
CDO1
O_2
H^+
Cysteine sulfinic acid
CSAD
H^+
CO_2
Hypotaurine
H_2O
NAD^+
H^+
NADH

◀ Fig. 3 | **Biochemical pathways for marine microbial synthesis of sulfur metabolites.** The pathways outline current knowledge of the major biochemical routes for production of dimethylsulfoniopropionate (DMSP) (part **a**), the sulfolipid sulfoquinovosyldiacylglycerol (SQDG) (part **b**) and C2 and C3 sulfonates (part **c**). Phytoplankton are the dominant sources of these molecules in the surface ocean, although all three types can also be synthesized by some bacteria. Dashed arrows represent hypothetical reactions. AdoHcy, *S*-adenosylhomocysteine; AdoMet, *S*-adenosylmethionine; DHPS, 2,3-dihydroxypropane-1-sulfonate; DMSHB, 4-dimethylsulfonio-2-hydroxybutyrate; MMPA, methylmercaptopropionate; MTHB, 4-methylthio-2-hydroxybutyrate; MTOB, 4-methylthio-2-oxobutanoic acid; MTPA, 3-methylthiopropylamine; PAP, 3-phosphoadenosine 5′-phosphate; PAPS, 3-phosphoadenosine 5′-phosphosulfate; SMM, *S*-methyl-L-methionine; THF, tetrahydrofolate; UDP, uridine diphosphate.

flux of sulfur-linked carbon between phytoplankton and bacteria. However, the roles of most DOS compounds are still unknown, with DMSP being the only well-studied exception[26,40]. Salt interference is a major hurdle for the chemical analysis of organic sulfur compounds in seawater, with salt concentrations 5–6 orders of magnitude higher than those of DOS metabolites (~600 mM, compared to low nanomolar or picomolar levels, respectively)[14]. Solid-phase extraction resins can concentrate organic matter away from salt, but small and polar metabolites do not adhere well[41]. Organic sulfur compounds are also not well represented in metabolite databases; for example, out of 25 sulfur metabolites identified in marine plankton by untargeted mass spectrometry in a recent study, only six were in existing databases[14]. In addition to the DOS metabolites discussed in the following sections, new organic sulfur molecules with roles in the pelagic ocean carbon and sulfur cycles likely remain to be discovered.

Synthesis of organic sulfur metabolites

Marine phytoplankton are considered the principal synthesizers of organic sulfur compounds in the ocean, an expected role, given their responsibility for half of Earth's annual photosynthesis. Heterotrophic marine bacteria acquire phytoplankton-derived DOS from seawater, but they can also synthesize sulfur metabolites de novo, albeit at considerably lower rates.

In phytoplankton, sulfate uptake and assimilation are both highly regulated, in part because of the energetic demands required for sulfate transport and reduction, and also because of the role of sulfur metabolites in photosynthetic activity and cellular redox state. Once transported into a cell, the sulfate ion (sulfur oxidation state +6) is very stable and requires activation by ATP to produce 5′-adenylsulfate (APS) via ATP sulfurylase. From APS, reduction to sulfite (+4) occurs by APS reductase, a primary regulatory point for sulfate assimilation in phytoplankton and plants that is linked to growth rate and photosynthetic activity[14,26,42], or — more commonly for bacteria — by reacting with ATP to form 3-phosphoadenosine 5′-phosphosulfate (PAPS) and then sulfite. The sulfite formed by either route can be used to generate sulfolipids or be further reduced to sulfide (−2) by sulfite reductase. Free sulfide is incorporated into cysteine, the first stable, fully reduced sulfur-containing organic compound in assimilation, through the consecutive action of serine acetyltransferase and *O*-acetylserine (thiol) lyase. Subsequent metabolism of cysteine through a variety of pathways generates other key sulfur compounds (FIG. 3). Finally, PAPS also has a second role in sulfate assimilation because it can act as a direct sulfur donor to organic molecules. Thus, there are three major entry routes of inorganic sulfur into the cellular organic pool: sulfite incorporation into sulfolipids, sulfide incorporation into cysteine and PAPS-mediated sulfonation of organic compounds.

One sulfur metabolite that has been a particular focus of oceanographic research is the sulfonium compound DMSP, due largely to its high production rates by phytoplankton (it can account for half the sulfur in phytoplankton cell biomass[43]) but also because volatile degradation products have links to atmospheric sulfur pools and the formation of cloud condensation nuclei[1]. Three major pathways by which DMSP is synthesized have been identified — transamination, methylation and decarboxylation — that all begin with methionine (FIG. 3). The transamination synthesis route is found across many plankton lineages, including green algae, corals, coccolithophores, diatoms, dinoflagellates and heterotrophic bacteria[44–46], and it may be the most important source of DMSP in the ocean. The methylation synthesis route has two variations, one described in angiosperms and one in bacteria[47–49]. The decarboxylation pathway has been identified in a dinoflagellate[50,51] (FIG. 3). A variety of structurally related sulfoniums can be produced from DMSP. These include gonyol[32,33], dimethylsulfoxonium propionate[34], gonylauline, DMS-acetate[33] and phosphatidylsulfocholine[35]. It was thought that only eukaryotic phytoplankton produce DMSP until the recent molecular characterization of a DMSP biosynthetic gene that encodes the key methyltransferase enzyme in the transamination pathway in both eukaryotes (*DSYB*) and bacteria (*dsyB*)[44,45].

Sulfolipids are an abundant class of sulfur metabolites predominantly found in the thylakoid membranes of photosynthetic organisms, where light-dependent reactions of photosynthesis occur. In eukaryotes and bacteria, the sulfolipid SQDG is synthesized with a unique head group, 6-sulfo-D-quinovose, which is a sulfonated derivative of glucose wherein the 6-hydroxyl group is replaced with a sulfonate group. Although the structure of the sulfoquinovose head group and the SQDG lipid was described by Benson and colleagues 60 years ago[52], the biosynthetic genes for the pathway (*sqdABCD*) were not characterized until the 1990s, using the genetic system of *Rhodobacter sphaeroides*[53–55]. Two key enzymes that have been well characterized are the uridine diphosphate (UDP)-sulfoquinovose synthase (encoded by *sqdB*) and the SQDG synthase (encoded by *sqdD*) (FIG. 3). Identification of these enzymes subsequently led to the characterization of similar biosynthetic pathways in cyanobacteria that involve a homologue of the *sqdB* gene and the alternative SQDG synthase gene *sqdX*[56]. In eukaryotes, SQDG is synthesized in a manner similar to that of cyanobacteria, via the *SQD1* (*sqdB* homologue) and *SQD2* (*sqdX* homologue) genes[57,58] (Supplementary Table 1).

The biosynthesis of C2 and C3 sulfonates is partially characterized. In animals and plants, taurine is typically derived from cysteine through a series of oxidation

Heterotrophic
Describes an organism that must obtain organic compounds for growth and energy.

Redox state
Ratio of the oxidized and reduced forms of molecules.

Angiosperms
A major evolutionary group of plants that has flowers and produces seeds enclosed within a carpel.

Catabolism
Metabolic breakdown of molecules into smaller forms during the production of energy or for use in other reactions.

and decarboxylation steps (FIG. 3). It appears that both marine bacteria[14,59] and eukaryotic algae[60,61] have homologues of genes in this pathway, but algae also possess a serine-derived pathway, an example of PAPS-mediated sulfonation transferring sulfite to generate cysteate[61]. Cysteate can then undergo decarboxylation to taurine, or alternatively it is proposed to go through a series of dehydrogenase and aminotransferase reactions to generate a variety of C3 sulfonates, including DHPS[14].

Box 1 | Marine phytoplankton and bacteria that synthesize sulfur metabolites

Heterotrophic bacteria
Heterotrophic bacteria are key transformers and recyclers of the marine organic sulfur pool. Certain bacteria are capable of degrading dimethylsulfoniopropionate (DMSP) to the climate-active volatile gas dimethylsulfide (DMS)[21,78], a key step in ocean–atmosphere sulfur flux, whereas others synthesize signalling molecules from available sulfur metabolites[81]. Heterotrophic bacteria also enable phytoplankton to synthesize methionine and other essential sulfur compounds by supplying the cofactor vitamin B_{12} (REFS[107,130]). Whereas some heterotrophic marine bacterial taxa are capable of de novo synthesis of sulfur metabolites (for example, Rhodobacteraceae)[44], others must rely exclusively on organic sulfur compounds produced by neighbouring microorganisms to meet their sulfur requirements (for example, SAR11 and SAR86)[10,11].

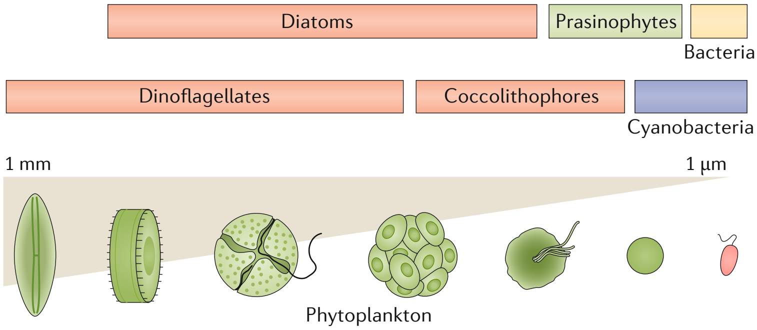
Cyanobacteria
Members include the *Synechococcus* and *Prochlorococcus* lineages, which were first described in the 1970s and 1980s, respectively[131,132]. These small cells dominate open-ocean, nutrient-poor regions of the sea and can substitute sulfolipids (that is sulfoquinovosyldiacylglycerol) for phosphorus-containing lipids in order to deal with the low phosphorus concentrations in their environment[133]. Interestingly, cyanobacteria also produce small sulfolipid-containing vesicles (100 nanometers) that may be a source of dissolved organic sulfur (DOS) in the surface ocean[38].

Prasinophytes
Members of the Chlorophyta (green algae) lineage gave rise to green plants. The prasinophytes include the genera *Ostreococcus* and *Micromonas*, which are among the smallest (~1 µm) free-living eukaryotes[134,135]. These cells can make large quantities of DMSP and taurine derivatives[14].

Coccolithophores
Members include *Emiliania*, a phytoplankton genus that forms massive blooms that can be seen from satellites. Coccolithophores are distinguished by an exoskeleton made of calcium carbonate plates (called coccoliths). These cells synthesize large quantities of DMSP and, notably, also harbour DMSP cleavage genes for the production of DMS[15]. They also synthesize the sulfonate 2,3-dihydroxypropane-1-sulfonate (DHPS)[14].

Dinoflagellates
These cells typically harbour two flagella for motility, and they can be either armoured with cellulose plates (theca) or unarmoured. Dinoflagellates generate large quantities of DMSP[136] and related sulfonium molecules[33], and they are notorious for their toxin-producing bloom events in coastal systems called red tides.

Diatoms
These phytoplankton synthesize an intricate silica cell wall, called a frustule, whose shape defines the two major diatom morphologies: centric (radial symmetry) and pennate (bilateral symmetry). Their cell walls promote faster sinking rates and play an important role in the export of organic matter from the surface ocean[137]. The sulfonates DHPS and cysteinolic acid were first identified in diatoms in the 1960s[12]; these sulfur metabolites are now receiving new attention for their role in diatom–bacteria interactions[22,107].



Although limited, the initial data suggest characteristic patterns of sulfur metabolite synthesis by marine phytoplankton groups (BOX 1). Dinoflagellate cells accumulate DMSP to high millimolar concentrations[62], and taurine to micromolar concentrations[14]. The metabolome of the coccolithophore *Emiliania huxleyi* is also high in DMSP[62], along with DHPS and cysteate, at millimolar and micromolar concentrations, respectively[14]. Diatoms are the most versatile synthesizers of sulfur metabolites, producing DMSP, DHPS, cysteate and sulfolactate, and in some species, isethionate and taurine[14]. Cyanobacteria metabolomes contain millimolar concentrations of cysteate[14]. These sulfur metabolites are released from phytoplankton into the marine DOS pool via a number of mechanisms. Export from living cells (either passive or active[6,22,63]), release into seawater by viral lysis[64] or protist grazing[65], and leakage from cells during bloom senescence[66] are the main processes allowing heterotrophic bacteria access to a pool of labile organic sulfur.

Catabolism of DOS metabolites

Once released into the seawater DOS pool, sulfur compounds become available for uptake. Heterotrophic bacteria are the main consumers of DOS, although phytoplankton have been shown to incorporate exogenous organic sulfur, as well[67–70]. For the metabolites with central roles in cellular function, such as essential amino acids, most major taxonomic groups are represented among the marine bacteria vying for them. For metabolites with nonessential or easily substituted functions, such as those that are one of many substrates available in seawater organic matter, a narrower fraction of marine bacteria tend to have the genetic capability required for catabolism.

The marine bacteria that take up organic sulfur compounds from the DOS pool shunt them to various fates: incorporation into biosynthetic pathways, oxidation for energy, and release from the cell in a reduced form. Which of these outcomes occurs is influenced by the oxidation state of S when it is assimilated, whether the cell has met its biosynthetic sulfur quota, and the toxicity of the sulfur-containing end products. The well-studied metabolite DMSP is the only compound for which all three fates are known to occur following uptake, even simultaneously in the same cell. If bacteria catabolize DMSP via the demethylation pathway, degradation begins with methyl-group removal (mediated by *dmdA*)[17] and ends with methanethiol as the sulfur-containing end product[71] (FIG. 4). Methanethiol is a volatile metabolite with a fully reduced sulfur atom and can be routed into the methionine biosynthesis pathway[11,21]; oxidized as a source of energy[72,73], with the sulfur typically being catabolized through the periplasmic sox system (*soxXYZABCD*); or released into seawater without further catabolism[74]. Marine bacteria may instead degrade DMSP using the alternative cleavage pathway, which is mediated by a variety of non-homologous lyases[45,75,76], with *dddK* and *dddP* being the most frequent

Oligotrophic
An environment containing low levels of nutrients.

Entner–Doudoroff
The name of a bacterial pathway that catabolizes glucose to pyruvate.

Mesopelagic
A region of the pelagic ocean about 200–1,000 m below the surface, where light is present but at levels of <1 % of incident.

in the pelagic ocean[22]. Phytoplankton also play a role in catabolizing DMSP, and an algal DMSP lyase gene (*Alma1*) was recently found in coccolithophores and dinoflagellates that generate large quantities of DMSP[15] (Supplementary Table 1). These various lyases split the DMSP molecule to produce DMS as the sulfur-containing end product. DMS, like methanethiol, is a volatile metabolite with a fully reduced sulfur atom; its two known fates are further oxidation to sulfate or DMSO and direct release through the cell membrane into seawater[21,77] from where it participates in air–sea sulfur exchange (FIG. 1).

Some taxa of marine bacteria harbour genes for both the DMSP demethylation and cleavage pathways (for example, Rhodobacterales and SAR11 members)[71,75,76] and express them simultaneously[78]. Yet, explaining the regulation strategies behind the various combinations of possible catabolism routes remains a challenge, particularly because the release of DMS from bacterial cells[6,21] is difficult to reconcile with the demand for reduced organic matter in oligotrophic marine environments. Non-exclusive hypotheses to explain the regulation of DMSP's fate include response to an oversupply of DOS relative to the cell's sulfur quota[79] and protection against reactive oxygen species, some of which are generated within the DMSP degradation pathways themselves[22,72,80].

Because the sulfur atom in sulfonates is considerably more oxidized (+4) than that in DMSP (−2), the outcome of their utilization by marine bacteria is more constrained. There is only limited evidence that sulfur from sulfonate is assimilated into biosynthetic pathways by marine bacteria[81], and in fact, the +4 oxidation state of the sulfur and the potential toxicity of sulfite (the sulfur-containing end product of sulfonate catabolism[82,83]) suggests relatively little benefit from this strategy. Sulfite can be exported from bacterial cells by several systems. Some bacteria transport sulfite into the periplasm (via TauZ-type and TauE-type transporter systems)[84,85], where it can subsequently be oxidized to sulfate via sulfite-oxidizing enzymes homologous to SorAB[86]. Other bacteria can oxidize sulfite in the cytoplasmic membrane, either to sulfate via SoeABC[87,88] or to APS via AprBA[89]. Marine bacteria can harbour more than one of these pathways in their genome. For example, the Rhodobacterales bacterium *Ruegeria pomeroyi* uses a TauZ-type system to export sulfite generated in C3 sulfonate degradation pathways[84], a SoeABC-type system to export sulfite generated from C2 sulfonates[22] and the SoxXYZABCD system to oxidize thiosulfate generated from DMSP[73].

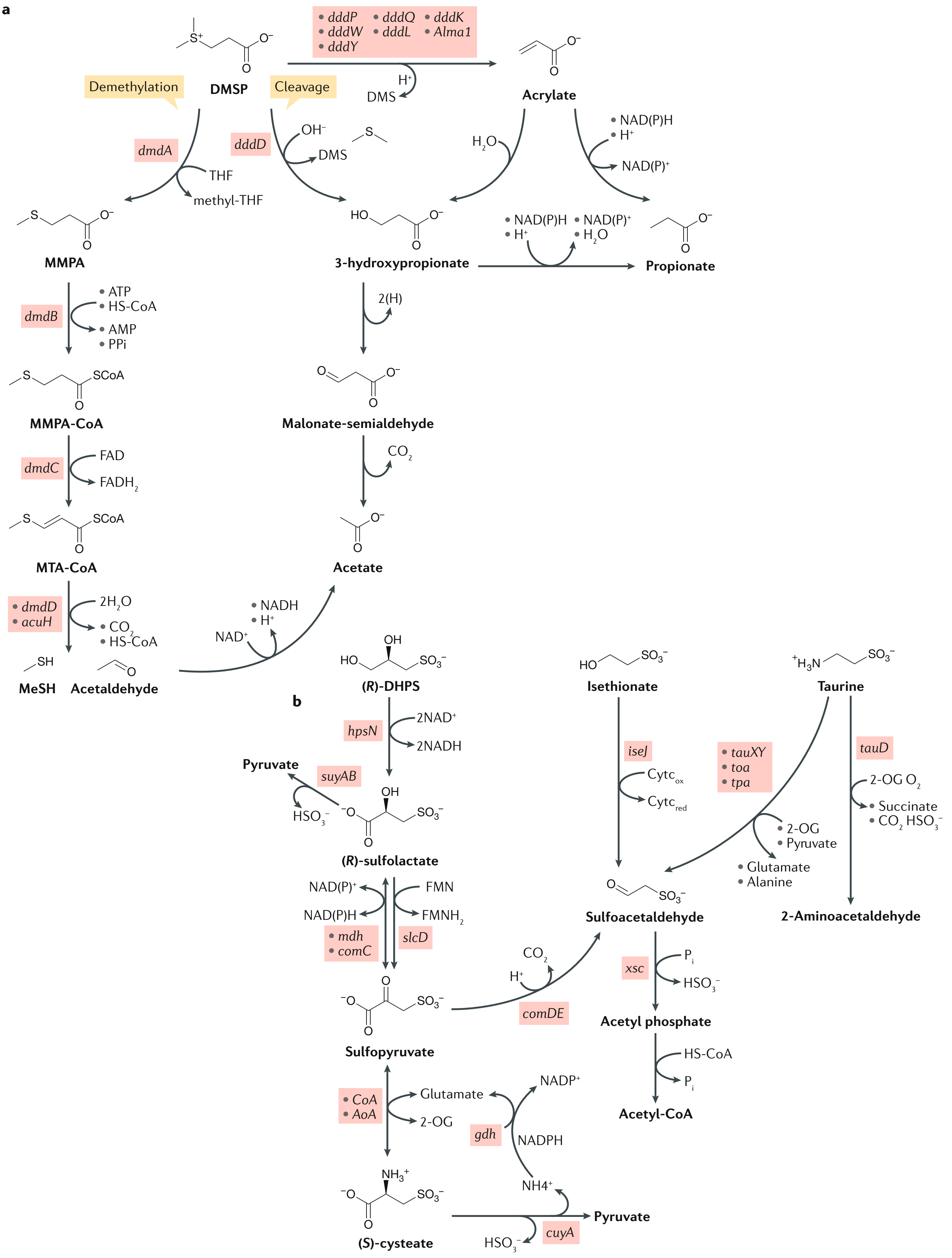
Bacterial catabolism of the C6 sulfonate sulfoquinovose, a molecule that serves as the polar head group for the membrane lipid SQDG, begins with hydrolysis from SQDG by the gene *yihQ*[90]. As sulfoquinovose is the sulfur analogue of glucose-6-phosphate, both known sulfoquinovose catabolic pathways parallel those for glucose catabolism: a glycolysis-like pathway ('sulfoglycolysis')[91] and an Entner–Doudoroff-like pathway[92]. DHPS is the sulfur-containing end product of sulfoglycolysis, whereas sulfolactate is the end product of the Entner–Doudoroff-like pathway, and marine bacteria can further catabolize both via C3 sulfonate degradation pathways (FIG. 4).

Information on the frequency of DOS catabolic systems in marine bacterial communities offers insights into microbial networks that draw on organic sulfur currencies. The DMSP demethylation gene (*dmdA*) was found in 1 of 5 marine bacteria and archaea surveyed using metagenomics across the world ocean, making it the most abundant DOS utilization gene[22]; the DMSP cleavage genes (sum of *dddP*, *dddK* and *dddD*) were found in 1 in 12 heterotrophic bacterial cells. Among genes for sulfonate processing, those mediating taurine and DHPS utilization were most common (averaging 1 in 12 and 1 in 21 cells, respectively). The distribution of DOS-processing genes in the ocean varies by depth. DMSP genes occur at almost twofold higher frequencies in the genomes of bacteria sampled from surface compared to the mesopelagic waters, whereas sulfonate genes for the uptake of taurine, *N*-acetyltaurine and isethionate are almost twofold more frequent in genomes from the mesopelagic[22]. These disparities likely reflect differences in the biological reactivity of DOS classes as well as dynamic patterns of production sources with depth. Environmental studies that incorporate gene expression patterns provide further insight into the regulation of these genes; for instance, sulfonate degradation genes[14] and DMSP genes[80,93] are actively expressed in surface ocean communities.

Ocean bacterioplankton genomes harbour genetic systems for exporting sulfur-containing end products similar to those described for cultured marine bacteria, including sox genes for oxidizing reduced sulfur in the periplasm, soeABC genes for oxidizing sulfide in the cytoplasmic membrane, tauZ-type genes for exporting sulfite into the periplasm, and the aprBA system for oxidizing sulfite to APS[89]. New genes enabling oxidation and the export of inorganic sulfur derived from sulfur metabolites are being described[94] and may be relevant for marine bacteria.

Ecological networks

The roles of organic sulfur molecules in enabling ecological links between pelagic ocean microorganisms begin with the release of phytoplankton metabolites into seawater (FIG. 1). Marine phytoplankton are estimated to release 10–20% of fixed carbon directly into the DOC pool in coastal systems[66], and up to 40% in oligotrophic systems[95]. One hypothesis to explain this substantial organic matter release from living phytoplankton, referred to as 'dissolved primary production'[96], traces to the six-order-of-magnitude difference in metabolite concentrations inside and outside cells; some release may therefore simply represent passive leakage of small and uncharged molecules through hydrophobic cell membranes[97]. Metabolites can also be released from phytoplankton by active exudation, for benefits related to redox balance, defence and signalling. Finally, phytoplankton export excess organic matter when a stoichiometric imbalance occurs in biomass-building components, a process referred to as 'photosynthetic overflow'. Of these three mechanisms for organic matter release, the first two are known to include organic sulfur


a
dddP
dddQ
dddK
dddW
dddL
Alma1
dddY
DMSP
H^+
DMS
Acrylate
Demethylation
Cleavage
dmdA
THF
methyl-THF
dddD
OH^-
DMS
H_2O
NAD(P)H
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MMPA
3-hydroxypropionate
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H_2O
Propionate
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Malonate-semialdehyde
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Pyruvate
Glutamate
Alanine
tauD
2-OG O_2
Succinate
CO_2 HSO_3^-
Sulfoacetaldehyde
2-Aminoacetaldehyde
xsc
P_i
HSO_3^-
Acetyl phosphate
HS-CoA
P_i
Acetyl-CoA

◀ Fig. 4 | **Biochemical pathways for marine microbial catabolism of sulfur metabolites.** The pathways outline the two major degradation routes for dimethylsulfoniopropionate (DMSP) (part **a**), referred to as demethylation and cleavage on the basis of the function of the first enzyme in each pathway, and for sulfonate compounds (part **b**), for which unique upper-pathway genes lead to a network of shared lower-pathway genes. Cytc, Cytochrome c; DHPS, 2,3-dihydroxypropane-1-sulfonate; DMS, dimethylsulfide; FMN, flavin mononucleotide; $FMNH_2$, reduced flavin mononucleotide; MeSH, methanethiol; MMPA, methylmercaptopropionate; MMPA-CoA, 3-methylmercaptopropionyl-CoA; MTA-CoA, methylthioacryloyl-CoA; THF, tetrahydrofolate.

metabolites[98–101]. By contrast, photosynthetic overflow is thought to consist of organic molecules with high carbon content, such as carbohydrates[102], costing phytoplankton relatively little when inorganic carbon and sunlight are in ample supply[66].

It is difficult to quantify the extents to which the extracellular release of sulfur metabolites contributes to phytoplankton fitness versus represents losses that are too expensive or difficult to contain. In the case of DMSP, possible benefits of release include deterring protist grazing[101] and protecting against reactive oxygen species[103]; these gains potentially explain the observation that DMSP serves as an attractant to phytoplankton taxa unable to synthesize it[99]. Sulfur metabolites could also be enlisted in the photosynthetic overflow mechanism, whereby compounds that are energetically inexpensive to produce from both inorganic carbon and inorganic sulfur act to keep the elemental stoichiometry balanced[104] (FIG. 5). Consistent with this, increased DMSP production has sometimes been observed in phytoplankton when their growth is nitrogen limited[105,106]. Alternatively, the release of sulfur metabolites could be used to balance the reductant pool generated from photosynthesis through the consumption of seven reducing equivalents for each sulfate molecule reduced. Diel patterns in sulfonate accumulation in phytoplankton metabolomes in the oligotrophic North Pacific[14] are consistent with roles in photosynthetic activity and redox balance during daylight hours. Finally, sulfur metabolites could act as low-cost, sulfur-decorated organic molecules that facilitate specific microbial interactions (FIG. 5). With DHPS, for instance, the restricted ability for catabolism among marine bacteria could provide a means for phytoplankton to preferentially cultivate specific bacterial associates[107]. These could include bacteria capable of providing vitamin B_{12}, a cofactor for methionine synthesis and methyl transfer that phytoplankton are unable to synthesize[108]. The feasibility of DOS-enabled mutualism and antagonism between marine microorganisms is more plausible in the context of particles and phycospheres (the microzones surrounding living phytoplankton that are rich in organic matter) that impart microscale structure to exometabolite concentrations in the ocean. Calculations suggest that direct release can generate metabolite pools reaching 200–300 nM organic carbon at phytoplankton cell surfaces. Concentrations decrease with distance from a phytoplankton surface at a rate proportional to the cell diameter; thus, the larger the cell (BOX 1), the more extensive the microzone[109].

Other sources of DOS metabolites in seawater originate from the activities of viruses and protists that prey on plankton[110]. Infection by marine viruses alters the composition of the sulfur-containing exometabolites released by host phytoplankton[111] and bacteria[112], such as methionine, homoserine and thiamine. Protist grazers increase the release rate of phytoplankton-derived DMSP derivatives into seawater as much as sixfold[113], and other sulfur metabolites are likely to track with them. For example, DHPS concentration in the *Thalassiosira pseudonana* metabolome approaches that of DMSP (3 mM and 5–12 mM, respectively)[108], and both would be released during grazing. At the higher trophic levels of marine food webs, the excretion and death of secondary producers are likely also to contribute compounds to the DOS pool, although the 10–20% productivity loss expected at each trophic transfer argues for phytoplankton having the primary role in supplying DOS.

Several taxa of marine bacterioplankton are emerging as DOS specialists, having the genetic capability to make use of multiple organic sulfur metabolites. In the surface ocean, SAR11 members can catabolize DMSP, DHPS and taurine. In fact, the SAR11 isolate *Pelagibacter* strain NP1 grows at its highest rate on the combination of just these three compounds, with DMSP providing reduced sulfur, DHPS providing carbon and energy and taurine providing carbon and a glycine precursor, for which SAR11 is auxotrophic[14]. Rhodobacteraceae members can catabolize DMSP, DHPS, cysteate, taurine, isethionate, *N*-acetyltaurine and choline-*O*-sulfate. On the basis of their genomic and ecological characteristics, it is likely that SAR11 cells and the members of the Rhodobacteraceae with streamlined genomes[114] scavenge DOS from bulk seawater as free-living cells. Rhodobacteraceae members with large and well-regulated genomes, which are proposed to have expanded their genomes coincident with the diversification of eukaryotic phytoplankton[114], are instead presumed to process DOS in particle and phycosphere microzones where concentrations are high and dynamic. Less is known about the ecology of bacterial DOS connoisseurs deeper in the water column. In the deep ocean, the *Thioglobus* species or SUP05 group members carry genes for DMSP cleavage and taurine uptake[22,115]; SAR324 cells carry genes for DMSP demethylation, DHPS catabolism and isethionate uptake; and marine Actinomycetes species carry genes for DMSP cleavage and *N*-acetyltaurine transport[22,116].

Once taken up by heterotrophic marine bacteria, sulfur metabolites fulfil a number of functions. In addition to serving as a source of energy and reduced sulfur for biosynthesis[78], DMSP can also be concentrated internally to serve as an osmolyte, reaching 70 mM in some marine bacteria[117]. Heterotrophic bacteria play a role in the release of organic sulfur compounds into the DOS pool, although likely in considerably lower amounts than are released by phytoplankton. Bacterial-derived organic sulfur exometabolites include thiamine and biotin[118], the antimicrobial tropodithietic acid[119] and the volatile organic sulfur compounds methanethiol and DMS[6].

To explore the ecological links between sulfur metabolites and marine microorganisms in the aerobic ocean, we enumerated organic sulfur catabolism genes in metagenomes from two oceanographic time series, the Bermuda Atlantic Time-Series (BATS)[120] and the Hawaii Ocean Time-Series (HOT)[121], in monthly samples over a

Antimicrobial
A chemical that kills or inhibits the growth of microorganisms.

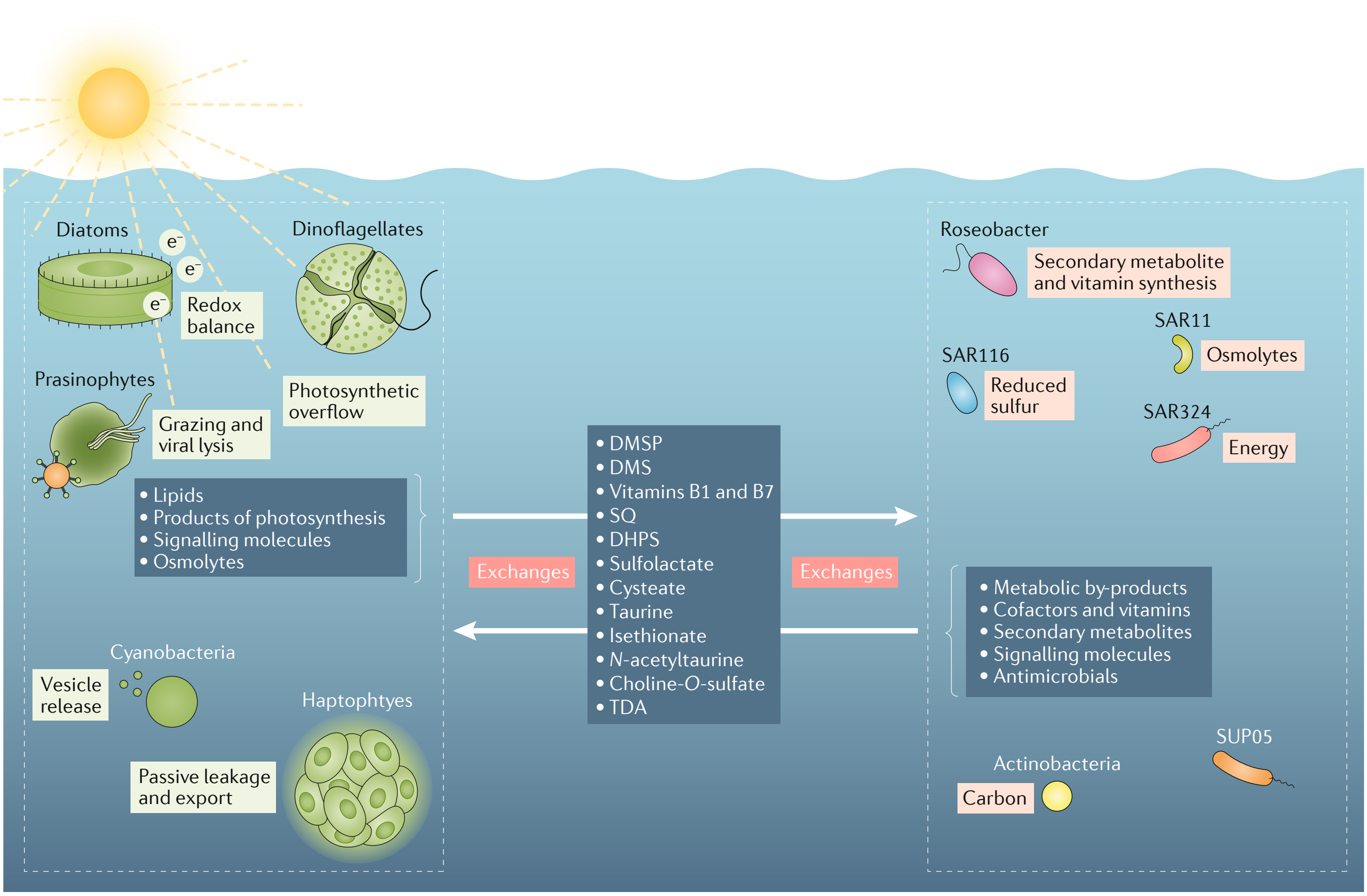

Fig. 5 | **The ecological network of marine microbial synthesizers and consumers of organic sulfur metabolites.** Organic sulfur compounds (left blue box) are produced primarily by phytoplankton and released into the dissolved organic sulfur (DOS) pool by a variety of mechanisms, including passive leakage, active transport for redox balance or photosynthetic overflow, protist predation and viral lysis, and lipid vesicle release (light green boxes). These molecules are taken up from the DOS pool primarily by heterotrophic microorganisms for use as substrates or to be reworked into cofactors, vitamins and signalling molecules (light pink boxes), some of which are released back into seawater (right blue box). In some cases, DOS forms the basis of mutualistic exchanges between specific phytoplankton and bacteria. The suite of known sulfur metabolites synthesized and consumed by marine microorganisms (centre blue box) continues to expand. DHPS, 2,3-dihydroxypropane-1-sulfonate; DMS, dimethylsulfide; DMSP, dimethylsulfoniopropionate; SQ, sulfoquinovose; TDA, tropodithietic acid.

two-year period (2003–2004) (FIG. 6). The abundance of catabolic genes from heterotrophic bacteria (*dmdA* representing DMSP catabolism[17], *hpsN* representing DHPS catabolism[18] and *xsc* representing C2 and C3 sulfonate catabolism[122]) was analysed in relation to biological and chemical inventories and biogeochemical rate measurements at each site[120,121] (Supplementary Table 2), as well as eukaryotic synthesis gene abundance (*DYSB* representing DMSP synthesis, *SQD1* representing sulfolipid synthesis and *CDO1* representing sulfonate synthesis)[44,57,61]. The relative abundance of bacterial DOS gene abundance was highly seasonal, particularly in surface waters (FIG. 6). The catabolic genes *dmdA* and *hpsN* were positively correlated with primary production rates at both oligotrophic ocean locations, and *xsc* was correlated with primary production rates at HOT (Supplementary Fig. 1). Other measures of standing stocks and flux did not have significant relationships to bacterial gene abundance (Supplementary Table 2). In a study in the North Pacific Subtropical Gyre, the expression of eukaryotic organic sulfur synthesis genes and intracellular concentrations of sulfur metabolites were found to follow a diel cycle, also co-varying with phytoplankton activity[14]. These field data highlight an active cycle of labile DOS that is closely coupled to phytoplankton productivity across time and depth in the ocean.

Conclusions and future directions

Sulfur is a required macronutrient for marine microorganisms that is distinguished from other nutrients in seawater by the fact that it is available in considerable excess over cellular demands. For the price of the energy required for reduction and assimilation, sulfur is readily available for microbial growth. Because phytoplankton cells are typically energy replete, they are free to use sulfur in a variety of ways beyond its role as a nutrient. For instance, phytoplankton vary their production and release of sulfur metabolites in relation to light availability, cellular redox state and salinity, suggesting roles beyond cell growth and maintenance. Once taken up by heterotrophic bacteria, organic sulfur compounds play important roles as substrates for nutrient acquisition

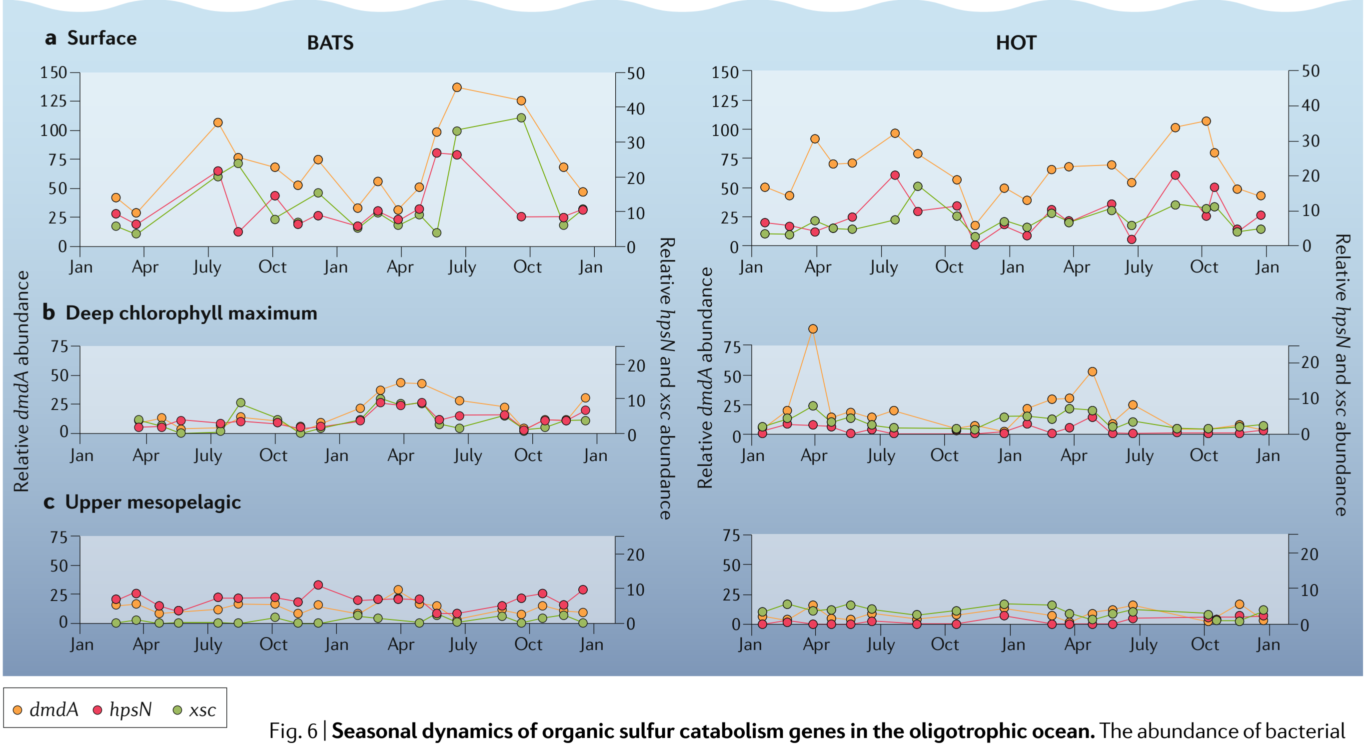

Fig. 6 | **Seasonal dynamics of organic sulfur catabolism genes in the oligotrophic ocean.** The abundance of bacterial genes mediating the catabolism of labile organic sulfur compounds is shown for the Bermuda Atlantic Time-Series Study (BATS) station in the Sargasso Sea, Atlantic Ocean[120] (left), and the Hawaii Ocean Time-Series (HOT) Station ALOHA in the North Pacific Subtropical Gyre[121] (right). Monthly metagenomic data collected over two years (2003–2004)[138] in the surface (part **a**), deep chlorophyll maximum (part **b**) and upper mesopelagic (part **c**) layers were searched for genes mediating dimethylsulfoniopropionate (DMSP) demethylation (*dmdA*) and sulfonate oxidation (*hpsN* and *xsc*). Relative gene abundance peaked in the spring and autumn in both sample years in surface waters. These seasonal patterns diminish with depth in the water column, as does the relative number of bacteria capable of organic sulfur metabolism. Significant correlations between relative gene abundance and rates of primary production (Supplementary Fig. 1, Supplementary Table 2) suggest close temporal coupling of DOS production and consumption. Gene abundances were determined by hidden Markov models built with experimentally verified genes and are plotted as percentages of *recA* counts (a single-copy bacterial and archaeal gene) following normalization to gene length (Supplementary Methods).

and energy metabolism. In fact, bacteria in the SAR11 clade, arguably some of the most abundant organisms on Earth[123], exhibit their fastest growth on a strict diet of DOS[14]. The correlation between primary production and bacterial catabolic genes observed in ocean gyres (FIG. 6; Supplementary Table 2) is consistent with the temporal coupling of phytoplankton synthesis of sulfur metabolites and bacterial uptake of DOS. Bacteria also rework organic sulfur into specialized molecules such as cofactors (vitamins and coenzymes), signalling compounds and antibiotics, some of which are released back into the DOS pool (FIG. 5). Evidence is accumulating from biological and chemical analyses that sulfur-containing molecules make up a more rapidly cycled subset of the ocean's DOC reservoir.

The labile organic sulfur metabolites that function as carbon and energy currencies in marine microbial networks have been challenging to measure, in part because of the diversity of chemicals found in the DOS pool and the analytical hurdles to measuring small, polar molecules in seawater. Of the several hundred sulfur-containing compounds detected in seawater, only a handful can be identified through publicly available databases[14,20]. However, new analytical and computational methods for mining metabolomic datasets are improving identification in cells and seawater[14,81,124,125]. These approaches include better internal standard normalization for mass spectral data[14,126], computational techniques for the identification of sulfur-containing metabolites[14,81,125], leveraging bacterial loss-of-function mutants[63] and the development of methods for improved extraction of polar molecules from seawater. Discovery of novel sulfur metabolites through model systems and field studies is broadening our understanding of the organisms and genes that mediate organic sulfur cycling, as well as elucidating the biogeochemical consequences of microbial release and consumption[60,99,127].

The diversity of structures, oxidation states and reactivities found among sulfur metabolites represents potential opportunities for niche differentiation in marine microorganisms. Phytoplankton production[14] and release[22] show characteristic sulfur metabolite signatures by taxonomic group, whereas bacterial genomes show characteristic patterns of DOS utilization. Accordingly, this abundant and chemically versatile atom may provide opportunities for mutualistic microbial interactions mediated through sulfur-embellished molecules[20,25], an area ripe for future study.

Earth's changing climate is predicted to decrease photosynthesis rates in the ocean and to favour smaller

Deep chlorophyll maximum
A region below the ocean surface where maximum concentrations of chlorophyll are found.

Niche
The set of interactions of a species with the other members of its community and with the abiotic factors of its environment.

Mutualistic
A symbiotic relationship between two organisms that is beneficial to both.

phytoplankton cells that are better able to compete for nutrients[128,129]. In turn, shifts in phytoplankton activity and community composition have implications for the flux of sulfur metabolites through the marine organic matter pool. Some sulfur metabolites, such as DMSP and DHPS, are synthesized primarily by larger phytoplankton expected to be at a disadvantage in a warming ocean, whereas other metabolites, such as cysteate, sulfolactate and taurine, are more characteristic of smaller eukaryotic phytoplankton and cyanobacteria, predicted to increase in dominance in the coming decades[14,43,62] (BOX 1). Oceanographic measures of organic carbon, nitrogen and phosphorus flux and fate have yielded fundamental insights into the regulation of plankton stoichiometry, pathways of nutrient cycling, and microbial interactions in the ocean. Similar measures of the chemical attributes and biological functions of sulfur molecules will better resolve the roles of this element in ocean biogeochemistry and provide insights into how the network of marine microorganisms that produce and consume organic sulfur might be reshaped over the coming decades.

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Acknowledgements

This work was supported by grants from the Simons Foundation (542391, M.A.M.) and the National Science Foundation (IOS-1656311 and OCE-PRF-1521564). The authors thank S. Sharma, for bioinformatic support, and F. Ferrer-González, B. Nowinski, J. Schreier, W. Schroer, C. Smith and M. Uchimiya, for helpful comments.

Author contributions

The authors contributed equally to all aspects of the article.

Competing interests

The authors declare no competing interests.

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Supplementary information is available for this paper at https://doi.org/10.1038/s41579-019-0250-1.

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