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Sulfur Isotope Variability of Oceanic DMSP Generation and Its Contributions to Marine Biogenic Sulfur Emissions

Kathryn L. Van Alstyne Dr.
Western Washington University, kathy.vanalstyne@wwu.edu

Harry Oduro

James Farquhar

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Sulfur isotope variability of oceanic DMSP generation and its contributions to marine biogenic sulfur emissions

Harry Oduro[a,1,2], Kathryn L. Van Alstyne[b], and James Farquhar[a,2]

[a]Department of Geology and Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20742; and [b]Shannon Point Marine Center, Western Washington University, Anacortes, WA 98221

Oceanic dimethylsulfoniopropionate (DMSP) is the precursor to dimethylsulfide (DMS), which plays a role in climate regulation through transformation to methanesulfonic acid (MSA) and non-seasalt sulfate ($NSS\text{-}SO_4^{2-}$) aerosols. Here, we report measurements of the abundance and sulfur isotope compositions of DMSP from one phytoplankton species (*Prorocentrum minimum*) and five intertidal macroalgal species (*Ulva lactuca, Ulva linza, Ulvaria obscura, Ulva prolifera,* and *Polysiphonia hendryi*) in marine waters. We show that the sulfur isotope compositions ($\delta^{34}S$) of DMSP are depleted in ^{34}S relative to the source seawater sulfate by ~1–3‰ and are correlated with the observed intracellular content of methionine, suggesting a link to metabolic pathways of methionine production. We suggest that this variability of $\delta^{34}S$ is transferred to atmospheric geochemical products of DMSP degradation (DMS, MSA, and $NSS\text{-}SO_4^{2-}$), carrying implications for the interpretation of variability in $\delta^{34}S$ of MSA and $NSS\text{-}SO_4^{2-}$ that links them to changes in growth conditions and populations of DMSP producers rather than to the contributions of DMS and non-DMS sources.

cloud condensation nuclei | isotopic fractionation | marine algae | remote atmosphere | sulfate assimilation

Dimethylsulfoniopropionate [DMSP; $(CH_3)_2S^+CH_2CH_2COO^-$] is a secondary metabolite that is produced and stored in large amounts by marine macroalgae (1) and microalgae (2). This β-sulfonium compound is widespread among marine taxa but is particularly abundant within specific groups of phytoplankton, zooplankton, macroalgae, halophytic plants, macroinvertebrates, and fishes (3–5). DMSP plays important ecophysiological functions in marine algae by acting as an antioxidant (6), a cryoprotectant, an osmolyte, and a precursor to an activated defense system (3). It is also an important carbon and sulfur source for marine bacterioplankton (7).

The synthesis of DMSP by algae has been reviewed previously (3, 8). It starts with the assimilation of seawater sulfate into the cytoplasm. The sulfate is subsequently transported into the chloroplasts, where it is reduced to sulfide in the presence of glutathionine and then transformed into cysteine. Cysteine is used to synthesize methionine, which is then transformed into DMSP via one of three pathways that differ among taxonomic groups of plants and algae (9–12). Thus, the biosynthesis of DMSP ultimately depends on the activity of the sulfate assimilation pathway; however, little is known about how DMSP synthesis differs among algae from diverse origins, except that the whole molecule is derived from sulfur amino acids.

DMSP and its cleavage product dimethylsulfide [DMS; $(CH_3)_2S$] have attracted much research interest because of their possible role in climate regulation (13, 14). Since the introduction of the Charlson, Lovelock, Andreae, Warren (CLAW) hypothesis, which argues for feedback between biological DMS production, Earth's solar radiation, and the regulation of global climate (15), there has been an increasing emphasis by environmental scientists on determining the strength of the sea-to-air biogeochemical

sources of DMS. This sea-to-air exchange of DMS is mediated through turbulent diffusive processes in marine environments. Once released into the atmosphere, DMS is oxidized by odd nitrogen (NOx) and odd hydrogen (HOx) species through addition and abstraction reactions (16) to form DMSO, dimethyl sulfone ($DMSO_2$), sulfur dioxide (SO_2), non-seasalt sulfate ($NSS\text{-}SO_4^{2-}$), and methanesulfonic acid (MSA). These products serve as sources for sulfuric acid, which has the potential to create new aerosols that can act as cloud condensation nuclei (CCN) (17). These CCN are thought to regulate cloud formation in the remote atmosphere and may have a significant impact on the Earth's cloud cover and albedo (15–17); however, many details of the connections between the biology, ocean chemistry, and atmospheric chemistry remain to be better understood (18).

The use of sulfur isotopes provides a powerful method for elucidating the mechanisms underlying the transformation of sulfur present in seawater sulfate into biogenic DMSP and the subsequent transfer of this sulfur, via DMS, into the atmosphere. The proportion of $NSS\text{-}SO_4^{2-}$ and MSA derived from DMS and DMSP has previously been explored using sulfur isotopes (19–21). The sulfur isotope compositions of these atmospheric oxidation products have been estimated from measurements of aerosol sulfate (19, 21, 22), measurements of MSA (20), and measurements of the sum of sulfate and MSA in ice cores (23). These constraints have been used, in turn, by other studies to constrain the fraction of $NSS\text{-}SO_4^{2-}$ in atmospheric aerosols.

Direct measurements of the sulfur isotope composition of DMS and DMSP precursors are needed to establish whether these molecules have a singular sulfur isotope composition or, instead, preserve a level of isotopic variability that they may then pass on to their oxidation products, which may complicate interpretations made on the basis of their inferred composition. Recent advances in analyses of methylated sulfur compounds by GC coupled with multicollector inductively coupled plasma MS (24) and Raney nickel hydrodesulfurization (25) provide a unique opportunity to investigate these biochemical processes from the ocean into the atmosphere.

Results and Discussion

DMSP concentrations were measured and shown to differ in five species of intertidal macroalgae and a planktonic dinoflagellate

(Table S1). These differences reflect genetic and environmental factors known to influence the synthesis and degradation of DMSP, and its loss from cells (3, 4). DMSP occurred in relatively high concentrations in all members of the order Ulvales [ranging from 69 ± 13–102 ± 34 μmol/g of fresh mass (FM)], and the concentrations are comparable to previous measurements from ulvoid algae in this region (26). We also observed relatively low DMSP concentrations (21 ± 3 μmol/g of FM) in *Polysiphonia hendryi* (Table S1) even though red algae in this region have also been reported to have high DMSP concentrations (27). These low concentrations may reflect DMSP losses attributable to sample handling and shipping. Degradation of DMSP has been reported during sample handling and has been observed in previous studies with *P. hendryi* (27). We infer that isotope fractionation associated with this type of loss of DMSP is not significant because of the intra- or intermolecular S-bonds that are not entirely disrupted during degradation to induce larger isotopic fractionations. Cellular levels of DMSP were measured for only one phytoplankter, *Prorocentrum minimum*, and were found to have a value of 16 ± 4 μmol/g of FM.

Electrospray ionization (ESI) MS was used to characterize intracellular extracts from both the macroalgae and *Prorocentrum*. We demonstrated the presence of the protonated DMSP molecule (M + H$^+$) at m/z = 135, and its corresponding sodium adduct (M + Na$^+$) at m/z = 157 in all species examined (Fig. S1). Fragmentation product suspected to be glycine a betaine sulfur-bound amino acid derivative gave an N,N-dimethyl sulfur product in the *Prorocentrum* extract with a well-pronounced peak at m/z =107; this fragment was not detectable in the macroalgal extracts. The *Prorocentrum* extract produced other fragments in the spectrum at m/z = 149 (methionine) and at m/z = 163 (a C$_5$-DMSP homolog of DMSP) (Fig. S1A) that were not detected in

the macroalgal extracts. These differences in peaks between the macroalgal and *Prorocentrum* spectra support differences in the operation of the pathways by which DMSP is biosynthesized by macroalgae and *Prorocentrum*. Methionine has been implicated to be an intermediate compound in the synthesis of DMSP through the competitive reaction sequence reviewed by Stefels (3) and Bentley and Chasteen (8) in Fig. 1. The lack of methionine peaks in the ESI-MS spectra of macroalgae (Fig. S1B) and their presence in the *Prorocentrum* spectra imply differences between macroalgae and *Prorocentrum* in the relative strengths of either the methionine source or sink fluxes.

Sulfur isotopes (^{32}S, ^{33}S, ^{34}S, and ^{36}S) were measured in macroalgal and *Prorocentrum* extracts, in seawater sulfate, and in gaseous and aqueous DMS that was generated from macroalgal DMSP. The mean DMSP sulfur isotope composition ($\delta^{34}S_{DMSP}$) signatures of the six primary producers ranged narrowly from approximately +18.0 to +19.9‰, with the macroalgal species being the least positive (+18.2 ± 0.6) and the phytoplankton being the most positive (+19.6 ± 0.3‰) (Fig. 2 and Table S2). The δ^{34}S values obtained for phytoplankton DMSP are consistent with reported values of +19.8‰ (28). Pairwise comparisons of seawater sulfate $\delta^{34}S_{SO4}$ (+21 ± 0.3‰) (Table S3) and the δ^{34}S from the algal DMSP yielded values between 1‰ and 3‰ that differed among algal species (Fig. 2). The differences between seawater sulfate and macroalgae were generally larger than the differences between seawater sulfate and *Prorocentrum*.

On the basis of calculated partition function ratios (Table S4), we suggest that methionine-bound sulfur will be ^{34}S-enriched. This enrichment in methionine is interpreted to reflect a more strongly bound sulfur in methionine (C-S-C bonds) relative to that in protein (some C-S-S-C bonds; *SI Materials and Experimental Methods*). Steps downstream of methionine to methylthio-2-
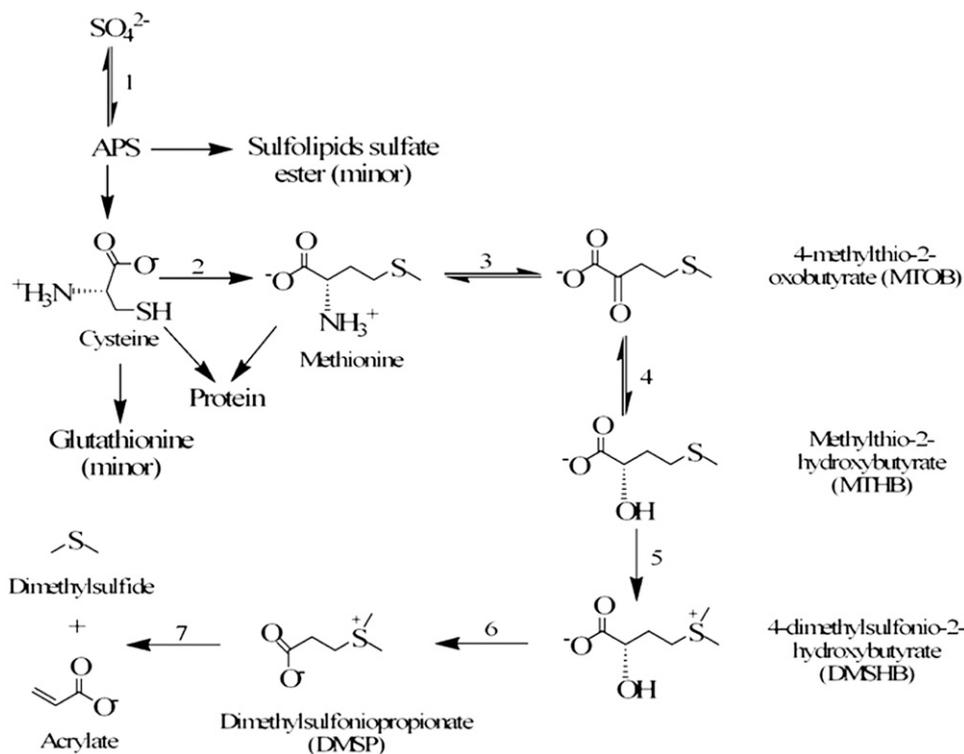

Fig. 1. Biosynthetic pathway of DMSP/DMS by marine algae through assimilatory sulfate reduction via methionine enzymatic biotransformation. The reaction processes involved in seawater sulfate assimilation by marine algae species are as follows: (1) carrier-bound sulfate reduction, (2) transsulfuration to methionine biosynthesis, (3) transamination, (4) reduction, (5) methylation, (6) oxidative decarboxylation, and (7) cleavage/degradation [scheme modified from Stefels (3) and Kiene et al. (7)]. Calculated fractionation factors for S-bonding ($\alpha^{34}S_{compound-methionine}$) in metabolic intermediates are provided in *SI Materials and Experimental Methods* and Table S4.
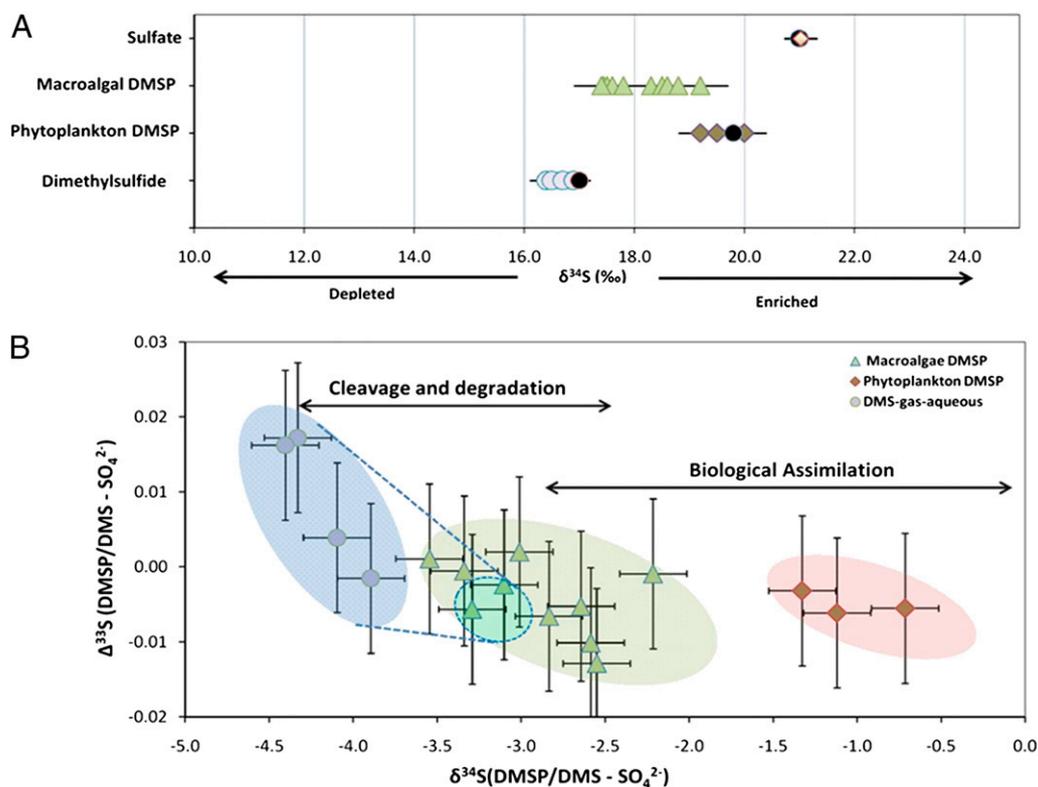
Fig. 2. (*A*) Summary plot of $\delta^{34}S$ enrichment and depletion of sulfate, macroalgal DMSP, planktonic DMSP, and aqueous/gas phase experimental data for DMS. (*B*) S-isotope plot of $\Delta^{33}S$ vs. $\delta^{34}S$ for biological assimilatory process of seawater sulfate assimilation by macroalgal/phytoplankton to form cellular DMSP; subsequent degradation experiments of ulvoid DMSP yielded aqueous and gas phase DMS. All the data are normalized to starting seawater sulfate compositions.

hydroxybutyrate (MTHB) are reversible, which also allows expression of potentially large isotope effects associated with methylation of MTHB to 4-dimethylsulfonio-2-hydroxybutyrate, attributable to changes in the bonding for S in this bio-transformation (S bound to 2 or 3 C atoms; Fig. 1). The relationship between sulfur-bearing amino acids, particularly methionine, and DMSP $\delta^{34}S$ values does not, however, support this as an explanation for these changes because of higher flow of sulfur from methionine to protein, which might be implied by lower methionine content as indicated by spectral peaks in Fig. S1*A*. That would yield ^{34}S enrichments in the products rather than the observed depletions. The critical step is interpreted to be competition between methionine and protein production from cysteine in the reaction network. The correspondence between smaller sulfur isotope fractionations and cellular methionine occurrence in marine microalgae reflects a higher demand for protein synthesis from cysteine and methionine by algae compared with phytoplankton. The difference between $\Delta^{33}S_{SO4}$ and $\Delta^{33}S_{DMSP}$ was within analytical uncertainties, consistent with the assimilation of sulfate being a mass-dependent process without significant variability being introduced by the mixing of the highly fractionated metabolite sulfur pools (29). The differences in transfer of sulfur through the pathways for the production of DMSP (mixing between metabolite pools) are inferred on the basis of the differences among the $\delta^{34}S_{DMSP}$ values for macro-algae and *Prorocentrum*.

Sulfur isotope compositions were determined for DMS generated by the cleavage of DMSP obtained from *Ulva lactuca* and *Ulva linza* (Table S5). The $\delta^{34}S_{DMS}$ values were lower relative to $\delta^{34}S_{DMSP}$ values by 1.2‰ for both green algae (*U. lactuca* and *U. linza*) (Fig. 2). The measured $\Delta^{33}S_{DMS}$ values were enriched by 0.013‰ (Fig. 2), which is at the level of estimates for 2σ

analytical uncertainty. In all cases, the proportion of the aqueous DMS to the initial DMSP was less than 1%; thus, the measured fractionations are assumed to be representative of the fractionations associated with the process of producing aqueous DMS. It is not known whether the sulfur isotope fractionation rates associated with the cleavage of DMSP to form DMS will differ among taxonomic groups of organisms. The branching bio-geochemical pathways associated with the loss of DMS to the atmosphere and the recycling of DMS back to the biota via as-similation could also result in additional variability in the sulfur isotope composition of dissolved oceanic and out-gassed DMS.

Conclusions and Implications for Marine Atmosphere
In the remote atmosphere, MSA, and NSS-SO$_4^{2-}$ aerosols are the principal oxidation products ($\sim$80%) of DMS (MSA/NSS-SO$_4^{2-}$ is between $\sim$0.1 and 0.4) (30). These products are produced through reaction chains involving few branches and predominantly unidi-rectional radical abstraction and addition reactions (16). Given the high proportion of the ultimate sulfate product (NSS-SO$_4^{2-}$) and the general similarity in the molecular structure of the re-action intermediates, it is inferred that the sulfur isotope com-position of NSS-SO$_4^{2-}$ will approximate that of oceanic DMS emissions. Direct measurements of MSA collected over the Pa-cific Northwest Ocean yielded $\delta^{34}S$ values of 17.7 $\pm$ 0.7‰ (20), which is within the range of $\delta^{34}S_{DMSP}$ reported here (Fig. 3), taking into account fractionations associated with degradation of DMSP to DMS. Marine biogenic sulfate $\delta^{34}S_{NSS-SO4}$ values have been estimated to range from +14 to +22‰ (19), with meas-urements of Pacific aerosols being +15.6 $\pm$ 3.1‰ (21), North Atlantic coastal aerosols being +22‰ (22), and Greenland ice cores being +18.6 $\pm$ 0.9‰ (23). These are similar to the DMS
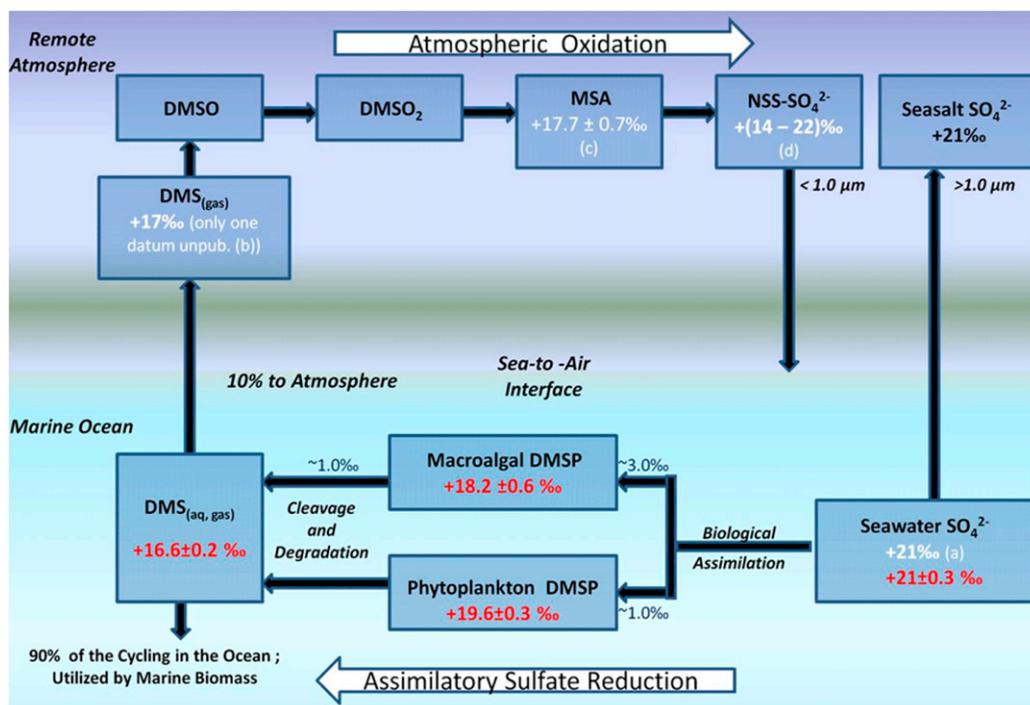
Fig. 3. Sulfur isotope compositions of the major biogenic sulfur products' formation and transformations in the ocean by marine algae and emissions of DMS to the atmosphere produce the two major oxidation products, MSA and NSS-SO$_4^{2-}$. The δ^{34}S compositions in red are from this study, whereas δ^{34}S values in white are compiled data [a and b (28), c (20), and d (19)] from different independent measurements in different geographical regions. aq, aqueous; unpub., unpublished.

sulfur isotope compositions predicted on the basis of DMSP measurements.

Although we do not rule out additional factors unrelated to specific sulfur sources that may exert a secondary influence on the sulfur isotope compositions of reaction chain products, our measurements support the hypothesis that variations in the sulfur isotope composition of NSS-SO$_4^{2-}$ can be tied to variations in the sulfur isotope composition of regional oceanic or coastal DMS emissions. These regional DMS sulfur isotope compositions are, in turn, ultimately derived from the sulfur isotope compositions of the DMSP that is produced by different types of organisms that may be growing under different environmental conditions or at different life cycle or bloom stages. Studies seeking to use sulfur isotopes to constrain the fractional contribution of sulfate resulting from the oxidation of biogenic DMS/DMSP to NSS-SO$_4^{2-}$ aerosols will need to take into account the resulting levels of heterogeneity of ~1–10‰ that are introduced by variations in δ^{34}S$_{DMSP}$. However, this heterogeneity also provides an opportunity to track changes in source DMS/DMSP that reflect changes in ecological or environmental conditions in different geographical regions.

This work has demonstrated that the S-isotopic composition of assimilated seawater sulfate to DMS/DMSP varies from species to species, and that the metabolic pathways may have a direct impact on the isotopic composition of biogenic MSA and NSS-SO$_4^{2-}$ aerosols. Further work is warranted to extend this isotopic approach and to constrain the δ^{34}S of oceanic and atmospheric DMSP, DMS, and other methylated sulfides associated with the organic S-cycle better and to refine the global fluxes of DMS in remote environments.

Materials and Experimental Methods

Algal Sampling. Five macroalgal species (*U. lactuca, U. linza, Ulvaria obscura, Ulva prolifera,* and *P. hendryi*) were collected by hand from intertidal or shallow subtidal habitats at Ship Harbor, Anacortes, WA (48° 30′ N, 122° 40′

W) and Penn Cove, Coupeville, WA (48° 14′ N, 122° 44′ W). The algae were brought back to the Shannon Point Marine Center in Anacortes, WA, where the green algae were identified by examining microscopic sections. All algae were cleaned of visible epiphytes and then shipped on ice on the day of collection to the Stable Isotope Laboratory at the University of Maryland, College Park, for intracellular DMSP analysis.

DMSP from marine phytoplankton was sampled in April 2009 from an extensive bloom of *P. minimum* in the York River, a tidal estuary that is a tributary of the Chesapeake Bay in Virginia. To select sites for further sampling of DMSP, 1.0-L subsurface seawater samples were analyzed for chlorophyll a (an indicator of high phytoplankton productivity). On the same day, at the selected sites, samples of 50 L of seawater containing plankton and particulate DMSP were taken from different transects; within 5 h of collection, the samples were filtered through a Whatman GF/F filter under vacuum (<5 mmHg) in a dark room. Residues from filtrates were lysed in liquid nitrogen before DMSP analysis. At each of the sampling sites, seawater sulfate samples were also collected. They were processed for sulfate by first acidifying with 0.5 mol·L^{-1} HCl and then precipitating the sulfate as BaSO$_4$ with 1.0-mol·L^{-1} BaCl$_2$ solution.

Analysis of DMS-Isotope Composition. The production of DMS from macroalgae was investigated to elucidate the sulfur isotope composition of the aqueous and gas phase DMS in ocean–atmosphere interactions. In these experiments, two macroalgal species (*U. lactuca* and *U. linza*) from Washington State were tested for DMSP production and conversion into DMS. Fresh algal samples were placed in clean, 1.0-L silanized Erlenmeyer flasks containing 1.0 L of deoxygenated filtered seawater. The flasks were immediately sealed with gas-tight seals, leaving no head space, and incubated at 2 °C for 48 h in a dark room. The DMS generated by the breakdown of the algal DMSP was sampled with an aqueous phase extraction to recover the DMS dissolved in the seawater and by purge and trap followed by the precipitation of DMS to recover gaseous DMS. In the aqueous phase extraction, DMS was extracted with carbon tetrachloride at −10 °C and then reextracted with 30 mL of 5% (vol/vol) HgCl$_2$ to precipitate the DMS into a white crystalline mercury complex (e.g., 3DMS-2Hg) (25, 31). The precipitated DMS complexes were stored at 4 °C in dark-brown Niskin bottles for later S-isotope analysis. The gaseous DMS produced by the cleavage of DMSP was stripped out with ultra-high-purity nitrogen, and dried through a connected Naffion and a glass tubing containing K$_2$CO$_3$. The gaseous DMS was finally trapped with 5% (vol/vol) HgCl$_2$ to precipitate DMS as mercury complexes.

Purified algal DMSP samples and 3DMS-2Hg were reduced to Ag_2S with a modified Raney nickel hydrodesulfurization method described by Oduro et al. (25). Precipitated $BaSO_4$ was reduced to H_2S by boiling in 25 mL of 5-N HCl and Thode solution [a mixture 320 mL of hydroiodic acid (HI), 524 mL of (hydrochloric acid [HCl], and 156 mL of hypophosphoric acid [H_2PO_3])]. In all distillation-reduction reactions, the evolved H_2S was captured with an $AgNO_3/HNO_3$ buffer solution as Ag_2S for S-isotope analyses as an SF_6 gas.

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