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The Production and Fate of Volatile Organosulfur Compounds in Sulfidic and Ferruginous Sediment

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Key Points:
- Rapid analysis reveals high concentrations of dimethyl sulfide, methanethiol, and dimethylsulfoniopropionate in salt marsh sediment
- Sulfidic sediment contained higher concentrations of methanethiol, and dimethyl sulfide concentrations were higher in ferruginous sediment
- There are different degradation patterns for dimethyl sulfide and methanethiol based on the geochemistry of the environment

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Abstract

Volatile organic sulfur compounds (VOSCs) link the atmospheric, marine, and terrestrial sulfur cycles in marine and marginal marine environments. Despite the important role VOSCs play in global biogeochemical sulfur cycling, less is known about how the local geochemical conditions influence production and consumption of VOSCs. We present a study of dimethyl sulfide (DMS), methanethiol (MeSH), and dimethylsulfoniopropionate (DMSP) in sulfide-rich (sulfidic) and iron-rich (ferruginous) salt marsh sediment from north Norfolk, UK. Initial results illustrate the importance of minimizing time between sampling in remote field locations and laboratory analysis, due to rapid degradation of VOSCs. With rapid analysis of sediment from different depths, we observe high concentrations of DMS, MeSH, and DMSP, with concentrations in surface sediment an order of magnitude higher than those in previous studies of surface water. We measure systematic differences in the concentration and depth distribution of MeSH and DMS between sediment environments; DMS concentrations are higher in ferruginous sediment, and MeSH concentrations are higher in sulfidic sediment. With repeated measurements over a short time period, we show that the degradation patterns for DMS and MeSH are different in the ferruginous versus sulfidic sediment. We discuss potential biogeochemical interactions that could be driving the observed differences in VOSC dynamics in ferruginous and sulfidic sediment.

Plain Language Summary

Oceans and coastal wetlands are dynamic environments where the carbon, sulfur, and iron biogeochemical cycles are tightly coupled. One important process that occurs in these environments is the formation of organic sulfur gases, which are involved in cloud formation and acid rain. Organic sulfur gases can be formed through a number of biological and chemical pathways, but little is known about how environmental conditions influence the chemical and microbial reactions that form these gases. In this study, we investigate how different chemical environments in salt marsh sediment influence the formation and destruction of organic sulfur gases. Different organic sulfur gases are produced in iron-rich environments compared to those produced in sulfide-rich environments. Further, the two geochemical environments also showed different patterns in the breakdown of these gases. These results indicate that the geochemical conditions influence how organic sulfur gases form and how they are released to the atmosphere. These findings have the potential to help explain observed differences in the release of organic sulfur gases among modern-day environments, as well as how the release of organic sulfur gases may have changed throughout Earth history as environmental conditions evolved.

1. Introduction

Organic carbon burial in marine and marginal marine sediment represents the second most important removal path for carbon from Earth's surface environment, after burial of calcium carbonate minerals (Berner, 2003; Des Marais et al., 1992). Within sediment, however, organic carbon can be reoxidized or fermented into methane, through a series of reactions driven largely by populations of archaea and bacteria in anoxic conditions. In marine and marginal marine sediment, sulfate reduction is responsible for oxidizing approximately 50% of organic matter that reaches the seafloor and nearly all the methane that is

produced within sediment (Jørgensen, 1982). While sulfate reduction is not as energetically favorable as oxic respiration, nitrate, iron, or manganese reduction, the high concentration of sulfate in marine and marginal marine environments leads to its dominance over other possible redox couples for the oxidation of organic matter and methane (Jørgensen, 1982). Bacterial iron reduction, which involves the reduction of ferric iron to ferrous iron, also plays an important role in sediment marine biogeochemistry and organic carbon oxidation, responsible for as much as 20% of the global sedimentary oxidation of organic carbon (Weber et al., 2006). The iron cycle is tightly connected to the sulfur cycle since (a) ferrous iron can react with sulfide to form iron monosulfide (FeS) and can eventually form pyrite (FeS_2) and (b) aqueous sulfide, coupled to ferric iron reduction, can be oxidized back to elemental sulfur or even fully oxidized to sulfate (Drobner et al., 1990; Pyzik & Sommer, 1981).

These subsurface interactions among iron, sulfur, and carbon are linked to atmospheric processes through the formation of gases and volatile compounds, including volatile organic sulfur compounds (VOSCs), the two most important of which are dimethyl sulfide (DMS - CH_3-S-CH_3) and methanethiol (MeSH - CH_3SH) (Andreae, 1990; Bentley & Chasteen, 2004; Charlson et al., 1987; Lomans et al., 1997, 2002; Lovelock et al., 1972). DMS and MeSH, and their oxidation products, are involved in environmental phenomena including acid rain and aerosol formation, as well as being important sources of carbon, sulfur, and energy for diverse microbial populations (Eyice et al., 2018; Kappler & Schäfer, 2014; Lomans et al., 2002). DMS and MeSH are key intermediates in the global sulfur cycle, with DMS comprising 75% of the total volatile sulfur flux to the atmosphere, although most of this is understood to be from the open ocean (Chasteen & Bentley, 2004). Although there are anthropogenic activities that produce MeSH and DMS, these sources are minor relative to emissions from natural biological sources, which account for more than 75% and 93% of total emissions of MeSH and DMS, respectively (Lee & Brimblecombe, 2016). In particular, salt marshes are thought to be hot spots for the cycling and production of both DMS and its primary precursor dimethylsulfoniopropionate (DMSP), with previous studies estimating per area emission rates of DMS of more than 1.5 $g{\cdot}S{\cdot}m^{-2}{\cdot}yr^{-1}$, which is an order of magnitude larger than emissions from both the open ocean and other terrestrial sources (approximately 0.1 and 0.001 $g{\cdot}S{\cdot}m^{-2}{\cdot}yr^{-1}$, respectively; Dacey et al., 1987; Steudler & Peterson, 1984).

The majority of DMS and MeSH production results from the microbial catabolism of the osmolyte DMSP (Cantoni & Anderson, 1956; Kiene & Capone, 1988). Marine eukaryotes and prokaryotes produce petagrams (10^{15} g) of DMSP in the open ocean (Curson et al., 2017; Ksionzek et al., 2016). Some of these primary DMSP producers can catabolize DMSP themselves, generating DMS and/or MeSH, but the majority of the MeSH and DMS in the surface ocean are generated by marine bacteria catabolizing DMSP that has been released into the environment (Curson et al., 2011). Given that heterotrophic bacteria can both produce and catabolize DMSP, marine sedimentary environments are likely to be regions of high VOSC production due to their high microbial density and concentrations of sulfur-bearing compounds. There remains large uncertainty regarding the amount of DMS and MeSH emitted from coastal wetland environments (salt marshes), whose microbial processes are dominated by microbial iron reduction, sulfate reduction, and sulfide oxidation. For DMS, estimates of emissions from salt marshes range over 2 orders of magnitude from 60 to 5,560 $mg{\cdot}m^{-2}{\cdot}yr^{-1}$ (Hines et al., 1993; Steudler & Peterson, 1984, 1985). For MeSH, the data are sparse and estimates of global fluxes are based largely on extrapolations from data for other gases (Lee & Brimblecombe, 2016). This uncertainty is partially due to the technical challenges involved with measuring these species, which degrade quickly from environmental samples.

DMSP can be catabolized via two main pathways: demethylation and lysis (Figure 1; Curson et al., 2011; Dickschat et al., 2015; Reisch et al., 2011). The bacterial demethylation of DMSP via the DMSP demethylase enzyme "DmdA" liberates methylmercaptopropionate (MMPA) which is further degraded through a Coenzyme-A-dependent pathway to release MeSH (Dickschat et al., 2015). In contrast, many diverse DMSP-lyase enzymes in bacteria and some fungi and algae cleave DMSP to generate DMS directly (Johnston et al., 2016). Recently, it was shown that a wide range of bacteria and algae oxidize DMSP via a third pathway to generate the novel compound dimethylsulfoxonium propionate (DMSOP; Thume et al., 2018). DMSOP can be degraded by some bacteria and algae to generate dimethyl sulfoxide (DMSO - $(CH_3)_2SO$) via unknown DMSOP lyase enzymes.

There are several pathways that produce DMS and MeSH independent of DMSP (Figure 1). For example, many aerobic bacteria found in a variety of environments can generate MeSH from catabolism of the amino acid methionine (MET) and/or can methylate hydrogen sulfide (H_2S), which has been suggested as

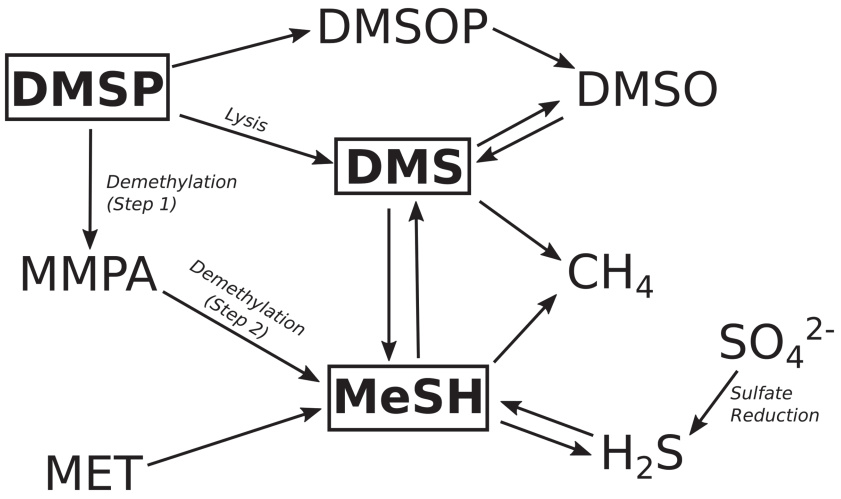

Figure 1. A simplified schematic of pathways involved in the cycling of dimethyl sulfide (DMS) and methanethiol (MeSH). The catabolism of dimethylsulfoniopropionate (DMSP) can produce DMS and MeSH through multiple pathways including lysis, demethylation (via methylmercaptopropionate - MMPA as an intermediate), and another pathway that produces dimethylsulfoxonium propionate (DMSOP) that is further transformed to dimethylsulfoxide (DMSO), which is both a potential precursor of DMS as well as a product of its degradation. MeSH can also be formed from methionine (MET) or sulfide (H_2S) produced from biological sulfate (SO_4^{2-}) reduction. VOSC degradation can further result in the formation of methane (CH_4) and sulfide. The boxes indicate the species that were measured in this study.

a possible sulfide detoxification mechanism (Drotar et al., 1987). DMS can be formed through the further methylation of MeSH by a wide range of aerobic and anaerobic microorganisms, and the genetic potential to generate DMS from MeSH is abundant in many sedimentary environments (Carrión et al., 2015, 2017, 2019; Kiene & Hines, 1995). Furthermore, MeSH can be formed from DMS via microbial demethylation (Kiene & Hines, 1995). DMS can also be either a product of the biological reduction of DMSO or produce DMSO through either photochemical oxidation (Bentley & Chasteen, 2004) or by bacteria containing the DMS hydrogenase gene (*ddhA*; McDevitt et al., 2002) or the trimethylamine monooxygenase gene (*tmm*; Lidbury et al., 2016). Sulfate-reducing bacteria and methanogens are both genetically capable of reducing DMS, with methanogens outcompeting sulfate-reducing bacteria at high concentrations of DMS (Lomans et al., 2002). Ultimately, the cycling of these VOSCs means much of DMS and MeSH produced in sedimentary environments will be consumed by microorganisms as a source of carbon and sulfur (Eyice et al., 2018; Kappler & Schäfer, 2014). All of these transformations are summarized in a simplified depiction of VOSC cycling presented in Figure 1.

While various pathways through which DMS and MeSH can be made and cycled are being elucidated, less emphasis has been given to how changes in the chemical nature of the environment (e.g., the pH, redox state, or concentration of various metals or other geochemical species) will influence the various pathways and the overall generation of DMS and/or MeSH. Microorganisms that produce VOSCs have many metabolic pathways involving the redox cycling of iron, sulfur, and carbon, but it is unclear how sedimentary biogeochemistry influences VOSC production/degradation and vice versa (Antler et al., 2019). Lomans et al. (2002) hypothesized that sulfide-rich (also known as sulfidic) sediment may produce more MeSH and DMS since higher concentrations of sulfide, sulfate, and methyl group-donating compounds can stimulate formation of these VOSCs. Ferrous iron, which is absent in sulfidic environments but abundant in ferruginous (iron-rich) environments, inhibits the formation of VOSCs through precipitation of sulfide minerals, which has led to the suggestion that ferruginous environments are less likely to produce VOSCs (Lomans et al., 2002). In this study, we report the occurrence and degradation of DMS, MeSH, and DMSP in sulfidic and ferruginous salt marsh sediment to elucidate possible links between geochemical conditions and the formation of VOSCs. However, a major challenge in the study of VOSCs is the reactivity of these species, particularly MeSH (Devai & DeLaune, 1994; Kim et al., 2006; Kuster & Goldan, 1987; Perraud et al., 2016; Sulyok et al., 2002; Wardencki, 1998). Because of this, new methods were required for the analysis of these species in sediment samples collected from remote field locations. We thus begin with a series of tests of sample preservation methods before describing results from both rapid analysis and repeat measurements

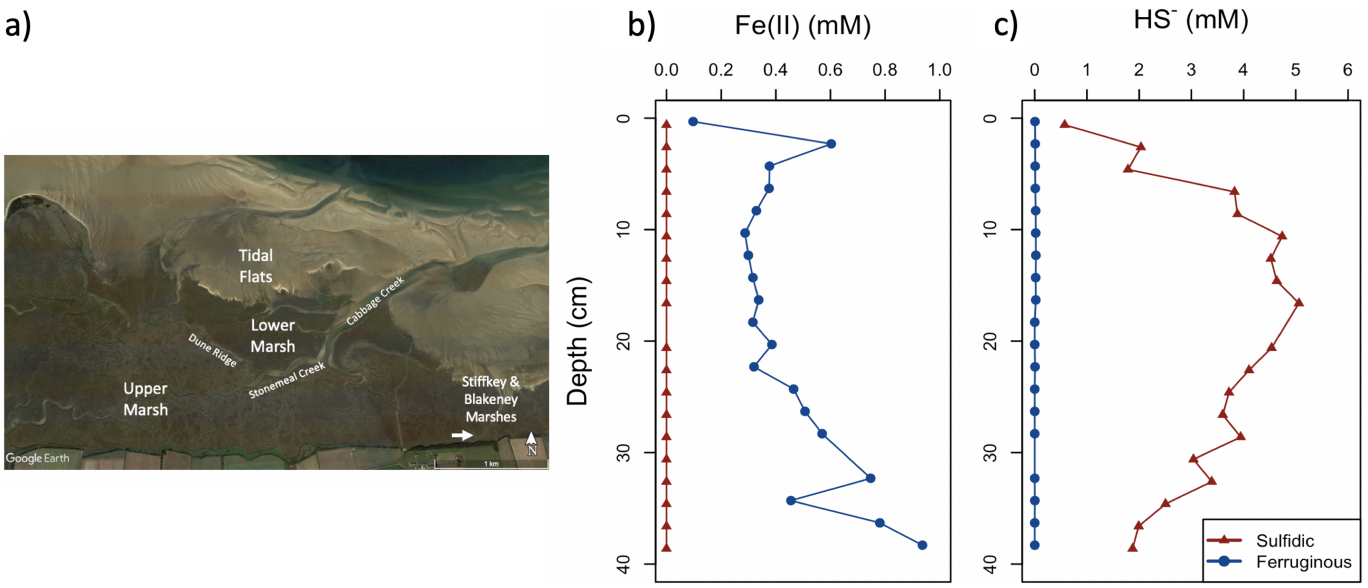

Figure 2. An annotated satellite image of the Warham marsh showing different geomorphological features is shown in (a), Image Credit: Google Earth, Image 2019 DigitalGlobe. Representative pore fluid profiles from the north Norfolk marsh system are shown for ferrous iron (b) and sulfide (c) for ferruginous (blue dot) and sulfidic (red triangle) sediment collected from the north Norfolk marshes. Ferrous iron concentrations in the sulfidic sediment were below detection (<0.1 mM). Ferrous iron and sulfide concentrations in the pore fluids of the ferruginous sediment were collected and measured according to the methods presented in Hutchings et al. (2019), and the presented pore fluid data for the sulfidic sediment is reproduced from Hutchings et al. (2019).

of depth profiles of sediment. We first describe initial tests on homogenized sediment that focused on determining how sediment could be fixed or treated prior to analysis to minimize degradation of the VOSCs. We then describe the methods associated with direct measurement of DMSP, DMS, and MeSH immediately after sampling and during repeat measurements of the same samples a short time later.

2. Materials and Methods

2.1. Study Site

All sampling was conducted in Warham salt marsh, one of several salt marshes situated along the coast of north Norfolk, UK. (52°57′N, 0°53′E). The marsh is vegetated and consists of an older, upper marsh (>2,000 years old) and a younger, lower marsh (post 1950s), which are transected by tidal creeks and numerous shallow pans of water (which are also referred to as ponds; Pye et al., 1990; Figure 2a). All sediment samples were collected from the ponds in the upper marsh, which is only inundated by the highest spring tides (Pye et al., 1990). The sediment in these ponds exhibits distinct geochemical characteristics, with some ponds having sediment that is dark gray to black color with a strong odor of hydrogen sulfide, while other ponds have sediment that appears reddish brown at the surface with no discernible odor (Antler et al., 2019; Hutchings et al., 2019; Mills et al., 2016). Previous research in the north Norfolk salt marshes has shown that the sediment beneath the salt marsh ponds is either ferruginous, with ferrous iron concentrations up to 3 mM and limited aqueous sulfide, or sulfidic, with sulfide concentrations up to 8 mM and limited ferrous iron content (Antler et al., 2019; Hutchings et al., 2019; Mills et al., 2016). Representative pore fluid depth profiles for ferruginous sediment (collected at the Warham marsh in 2017) and sulfidic sediment (collected from the Blakeney marsh in 2014 and reproduced from Hutchings et al., 2019) are presented in Figures 2b and 2c. While these profiles are from two different times and locations within the north Norfolk salt marsh system, prior studies have shown spatial and temporal consistency in the geochemical observations (Antler et al., 2019; Hutchings et al., 2019).

2.2. Homogenized Sediment Tests

Sediment was sampled using 50 cm polyvinyl chloride push core liners, which were sealed in the field and transported to the laboratory for analyses. A layer of overlying pond water was left at the top of the core during transport, and the core was sealed using a rubber stopper at the bottom and the top wrapped in plastic and securely wrapped in tape to ensure there was no loss of material from the core. Two push cores, one each from a single sulfidic and ferruginous pond, were collected in January 2017 from the Warham marsh.

Table 1
Treatments Applied to Homogenized Sediment

Treatment	Addition to sediment	Samples receiving treatment
Live	5 ml Milli-Q water	2 ferruginous, 2 sulfidic
Killed	5 ml Milli-Q water + 0.1 ml 0.1 M NaN_3	2 ferruginous, 2 sulfidic
NaCl	5 ml 4.7 M NaCl solution	2 ferruginous, 2 sulfidic
TBP	5 ml Milli-Q water + 0.01 ml TBP	1 ferruginous, 1 sulfidic
Killed TBP	5 ml Milli-Q water + 0.01 ml TBP + 0.01 ml 0.1 M NaN_3	1 ferruginous, 1 sulfidic

The ponds were selected using the classification protocol described in Hutchings et al. (2019) to identify the sediment as either sulfidic or ferruginous. The cores were then taken to the University of Cambridge (Cambridge, UK) on the same day as sampling, where the sediment between 5 and 20 cm was removed and homogenized in nitrogen-flushed bags. Five ml subsamples of the homogenized sediment were then taken using cut syringes and transferred into 100 ml amber, nitrogen-flushed vials that were crimp sealed with rubber stoppers. Various solutions (Table 1) were added to the vials, creating a slurry, and left undisturbed at room temperature until analysis, which occurred 21–50 hr following field sampling. Sodium azide solution (NaN_3) was added to selected vials to stop biological activity. Tributylphosphine (TBP) was added to two vials (one living, one arrested with NaN_3) 1 hr prior to analysis to cleave adsorbed thiols, including MeSH from the sediment (Mopper & Taylor, 1986; Rüegg & Rudinger, 1977; Vairavamurthy & Mopper, 1989). A sodium chloride (NaCl) solution was used to test the potential for sediment particle ion replacement.

The headspace concentrations of DMS and MeSH in the vials were then analyzed at the University of York (York, UK) in the following 2 days (21–50 hr postfield sampling). The vials were placed on a shaker table (~20 rpm) for 45 min prior to headspace sampling as this was required for the TBP addition and was thus done for all treatments for consistency. A gas-tight syringe was used to withdraw 10–20 ml of gas from the headspace which was condensed onto a liquid nitrogen condensation trap and transferred to a Restek© PoraBond Q column (30 m, 0.32 mm ID, 0.5 μm thickness) within an HP 5972 MSD running in selective ion mode. Helium was used as the carrier gas with a flowrate of 1 ml/min. Samples were standardized using a calibration curve developed using direct injection of low concentration MeSH and DMS standards into the same condensation trap system. Detection limits for this method were <1 pmol for both DMS and MeSH.

From measured headspace concentrations, dissolved concentrations of DMS and MeSH, which have different solubilities, were calculated using partition coefficients from Przyjazny et al. (1983) that were interpolated to correct for salinity (equation (1)). For the concentrated NaCl treatment, the partition coefficients were 5.78 and 4.21 for DMS and MeSH, respectively. For all other treatments, the partition coefficients were 12.59 and 9.17 for DMS and MeSH, respectively. With this, a sum total of the volatile species in the headspace and added liquid phase could then be used to express the amount of volatile species released from the sediment matrix per milliliter of sediment (nmol/ml; equation (2)). All data are presented on this basis, with the headspace concentrations also available in the corresponding data set available for download (https://doi.org/10.17863/CAM.42488).

$$(c_{\text{headspace}}) \times (\text{Partition Coefficient}) = c_{\text{liquid}} \tag{1}$$

$$\frac{(c_{\text{headspace}} V_{\text{headspace}}) + (c_{\text{liquid}} V_{\text{liquid,added}})}{V_{\text{sediment}}} = \text{VOSC released per sediment volume} \tag{2}$$

2.3. Depth Profiles

Two sediment cores, one each from a single sulfidic and ferruginous pond, were collected from the Warham marsh in May 2017 and taken to the University of East Anglia (Norwich, UK) for analysis immediately following sampling. In the lab, the cores were cut in half and sediment was quickly sampled from the inner sediment away from the edges that were in contact with the core liner. Sediment samples were taken from the cores using cut syringes at intervals of 5 cm from the surface to a depth of 20 cm. Two 5 ml sediment samples were taken at each depth in each core—one for headspace VOSC analysis and one for DMSP analysis. The sediment samples were injected and crimp sealed into 120 ml nitrogen-flushed glass vials. Samples of surface water from the top of the cores were also collected for DMSP analysis. For VOSC analyses of the sediment,

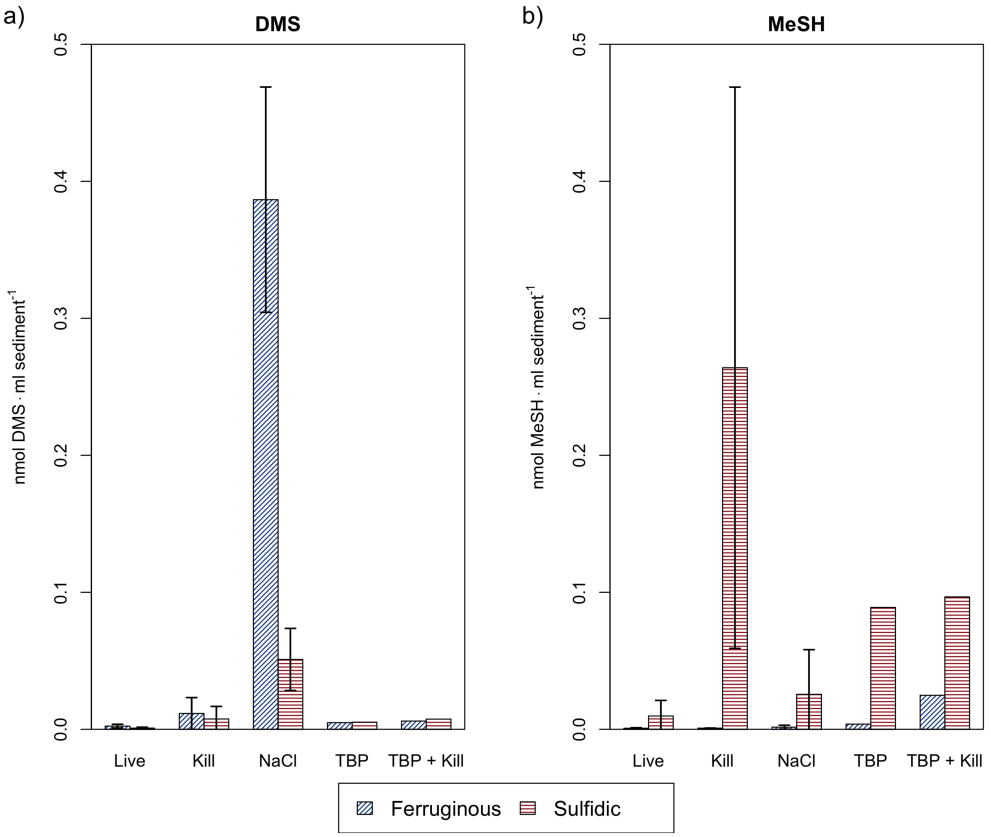

Figure 3. Results from the homogenized sediment tests with error bars showing variance for treatments with replicates. The concentration of DMS (a) is similar in the ferruginous and sulfidic sediment except when concentrated NaCl solution was added. Under this condition, the DMS concentration was far higher in the ferruginous samples. The concentration of MeSH (b) is much higher in the sulfidic sediment than in the ferruginous, and the concentration was greatly enhanced by treating the sediment in various ways. Overall, there was considerable variability across the different treatments, with no treatment demonstrating clear preservation of both compounds.

5 ml of Milli-Q water was added to the vials and they were gently mixed by hand to ensure a homogeneous slurry and that there were no sediment particles adhered to the sides of the vials. The concentration of DMS and MeSH in the headspace of vials (100 µl assayed) was measured using a gas chromatograph with a flame photometric detector (Agilent 7980A) and a HP-INNOWax 30 m × 0.320 mm capillary column (Agilent Technologies J&W Scientific). The detection limits for this method are 0.09 µMol and 2 µMol for DMS and MeSH, respectively. Headspace concentrations were then used to calculate the released DMS and MeSH per ml of sediment using equations (1) and (2) as described previously. Initial measurements of each sediment type and depth were made between 5 and 6.5 hr after marsh sampling. The vials were then left without agitation or any further amendments at room temperature for a brief incubation period of 1.5 hr. Analysis was then repeated on the same samples (now 6.5–8 hr after marsh sampling) to assess degradation of volatile species.

For DMSP analysis in the sediment samples from discrete depths, the sediment samples were injected into 120 ml nitrogen-flushed glass vials and crimp sealed. Five ml of 10 M sodium hydroxide (NaOH) was added to the sediment samples and the vials were left undisturbed overnight. The following day, the headspace was sampled and analyzed using the same procedure as above and the DMSP was measured as DMS in the headspace, which forms when any DMSP present in the sample is hydrolyzed by the NaOH (Dacey et al., 1987; Simó et al., 1996; Vogt et al., 1998). To measure DMSP content in the overlying surface water from the ponds, samples were first preserved by mixing 25 ml of surface water with 250 µl 50% H_2SO_4 immediately after being taken from the tops of the cores, which stabilizes DMSP in ocean water (Curran et al., 1998; Kiene & Slezak, 2006). Then, 5 ml of preserved samples was mixed with 1 ml of 10 M NaOH in sealed glass vials and incubated in the dark for 16 hr at 22 °C. The released DMS was measured using the purge and trap

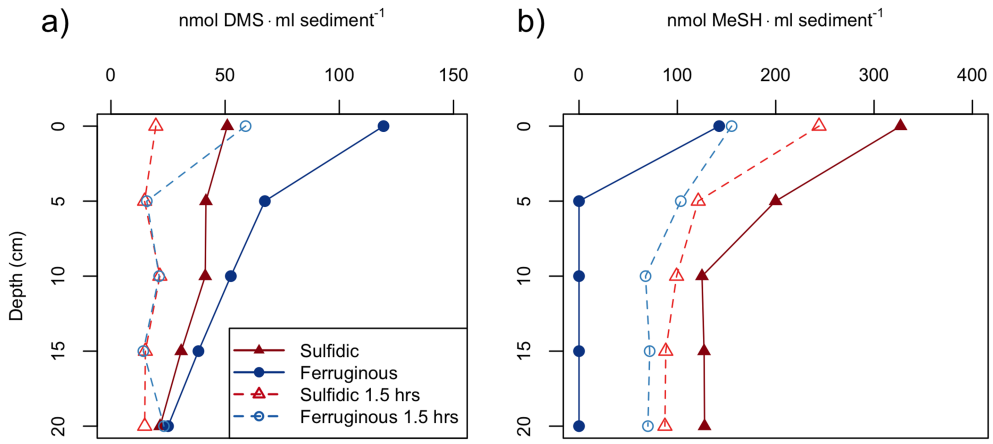

Figure 4. Depth profiles of DMS (a) and MeSH (b) in sulfidic (red triangles) and ferruginous (blue circles) sediment. Solid lines denote initial measurements, and dashed lines denote measurements following the 1.5 hr incubation period.

method in which sulfur gases were sparged from the sample with nitrogen and trapped in a loop of tubing immersed in liquid nitrogen. The trapped gases were desorbed with hot water (>90 °C) and analyzed by gas chromatography.

3. Results

3.1. Homogenized Sediment Tests

There was considerable variability in the measured concentrations of both DMS and MeSH across the different treatments in the homogenized sediment experiments (Figure 3). For DMS, the measured concentrations for the various treatments were consistent with one another, with the exception of the concentrated saline solution, which yielded significantly higher concentrations for both sediment types. Ferruginous samples showed approximately eightfold higher DMS concentrations than those for sulfidic samples under these high salt conditions, which could just be a result of ion replacement, although it is unclear why it would yield concentrations so significantly different from the other treatments. While the mechanism that caused high DMS release from enhanced sodium chloride solutions is unclear, we further hypothesize that the addition of concentrated NaCl led to disruption of the osmotic balance in cells and cell lysis, allowing the subsequent enzymatic lysis of the now available DMSP (Yoch et al., 1997). There were no significant differences observed for the other treatments or in the amount of DMS observed between ferruginous and sulfidic sediment. The addition of TBP, a compound targeted toward cleaving disulfide bonds, did not yield higher DMS concentrations, which is expected since DMS is not thought to form disulfide bonds with sediment.

The MeSH concentration in samples was generally higher than those of DMS in both sediment types (Figure 3b) and the impact of the treatments also differed. TBP addition yielded higher concentrations of MeSH, indicating the presence of thiols adsorbed to the sediment, although we cannot differentiate between thiols that were adsorbed in situ, and adsorption that occurred when sediment was disturbed as part of the sampling process. The concentrated NaCl solution did not lead to significantly higher concentrations of MeSH as it did for DMS, but the addition of sodium azide solution did yield higher levels of MeSH in the samples from sulfidic sediment, potentially indicating inhibition of biological degradation upon addition of the sodium azide. Indeed, Carrión et al. (2019) found appreciable MeSH consumption rates in surface salt marsh sediment. Across all treatments, sulfidic sediment exhibited higher concentrations of MeSH than ferruginous sediment.

3.2. Depth Profiles of VOSCs

The highest DMS and MeSH concentrations in both sediment types occurred near the surface, and the concentrations decreased with depth (Figure 4—solid lines). While depth profile samples were analyzed rapidly after sampling, they were treated in an identical manner to the "live" homogenized sediment samples and demonstrated similar behaviors; there was more MeSH in the sulfidic sediment at all depths than there was DMS. There were detectable DMS concentrations (above detection limit equivalent of 3.1 nmol DMS ml

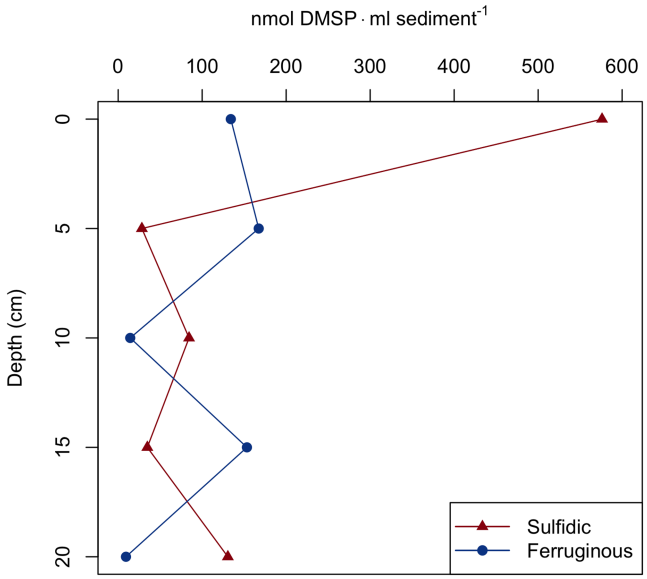

Figure 5. DMSP concentrations in ferruginous (blue circles) and sulfidic (red triangles) sediment. Concentrations in the overlying surface water were 1.15 and 1.10 μM (equivalent to nmol DMSP ml water^{-1}) in the ferruginous and sulfidic sediment, respectively.

sediment^{-1}) at all depths in both sediment types, although the DMS concentrations in the ferruginous sediment were consistently higher (Figure 4a). In the ferruginous sediment, MeSH concentrations decreased to below detection limit (equivalent to 62 nmol MeSH ml sediment^{-1}) below the surface but remained detectable in all the sulfidic sediment samples at depth (Figure 4b).

After a further 1.5 hr, DMS and MeSH measurements were repeated (Figure 4—dashed lines). At all depths, the concentrations of DMS decreased for both sediment types (Figure 4a). We note that the DMS concentration in the ferruginous sediment decreased to a greater degree, such that at some depths there was no longer an observable difference in concentration between the sediment types, as there was in the initial measurements. The MeSH concentrations (Figure 4b) in the sulfidic sediment decreased at all depths. In contrast, MeSH concentrations increased at all depths in the ferruginous sediment, even in samples where there had been no measurable MeSH 1.5 hr prior. This is perhaps due to biological degradation of DMS generating MeSH, considering the substantial decrease in DMS concentrations observed over the same time period. Despite increased MeSH concentrations in ferruginous sediment and decreased concentrations in sulfidic sediment, MeSH concentrations in sulfidic sediment remained higher than those in ferruginous sediment at all depths. DMSP concentrations in the overlying surface water were 1.10 and 1.15 μM (equivalent to nmol DMSP ml water^{-1}) for the sulfidic and ferruginous sediment, respectively. These concentrations are relatively minimal compared to within the sediment where DMSP sharply increased in near-surface sediment, particularly in the sulfidic sediment which had a notably high concentration of DMSP (Figure 5). DMSP concentrations fluctuated at lower sediment depths, ranging between 0 and 200 nmol DMSP ml sediment^{-1}.

4. Discussion

4.1. Fixation of Remote Field Samples

There did not appear to be a definite, uniformly applicable method that allowed us to chemically treat samples in the field for long-term transport and storage, prior to laboratory analysis. Our results (Figure 3) were ambiguous in this regard but clearly demonstrated substantial loss of material over the time between sampling and analysis when compared to more immediate analysis after sampling (which yielded 2–3 orders of magnitude higher concentrations—Figure 4). Furthermore, there was no one chemical treatment that yielded consistently higher concentrations for both volatile species to suggest the treatment was properly preserving, or releasing, the volatile species from the sampled sediment. Within the various treatments, the observed variability between replicates suggests that either or both biological and physical degradation of volatiles cannot be entirely prevented across the time required for collection and analysis of these samples or even between analysis of replicates of the same sample (~60 min at York). Thus, it appears that the best way to ensure more accurate measurement of volatile organosulfur species is to minimize sample disruption and the amount of time between sampling and analysis. Additionally, these tests suggest that DMS and MeSH in sediment may be sufficiently concentrated such that detection is possible without the need for preconcentration techniques, allowing analysis of samples in the field or at a laboratory close to the field site.

The importance of the time to analysis for organosulfur species is shown in Figure 6. Here we plot the total VOSC concentration measured versus the time elapsed since sediment was put into the vials for all sediment samples that we studied; in this compilation we have included additional data from a further campaign of samples collected from the same sites and analyzed at the University of York (York Pilot Sets 1 and 2). The absolute concentrations of both DMS and MeSH at 3 hr postsampling were close to 1,000 times higher than when they were analyzed 7–30 hr after sampling in the pilot study at the University of York. The rapid degradation of VOSCs illustrates the need for prompt analysis after sample retrieval to reduce degradation, whether biotic or abiotic, which has previously been reported to be rapid and significant (Kiene, 1988; Lyimo et al., 2009). A more comprehensive suite of time-based measurements would allow determination of whether the curve shown in Figure 6 can be used to back-calculate the initial concentration

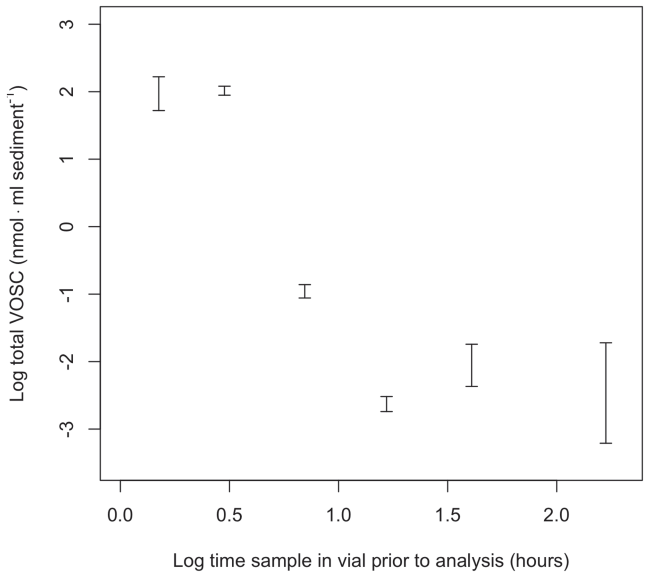

Figure 6. The range in log change in total VOSC concentration versus the log time passed between initiating vial incubations and analysis of the incubation headspace samples. Data are presented for two sets of the "Live" homogenized sediment samples analyzed at University of York, the depth samples analyzed at the University of East Anglia (UEA), and other pilot data collected from the same sites and analyzed at the University of York in two sets of replicates. In order to be comparable to the homogenized sediment, sediment samples from 10 cm are presented for studies where sediment was sampled at discrete depths (UEA and York Pilot) since the depth profiles indicated concentrations at 10 cm were of intermediate values relative to the range of concentrations observed across the sediment depths used in the homogenized sediment analysis (5–20 cm). The different sediment types are grouped according to sampling campaign, and from left to right the campaigns are UEA initial measurements, UEA secondary measurements, York Pilot Set 1, York Homogenized Set 1, York Homogenized Set 2, and York Pilot Set 2. Note that the York Pilot Sets 1 and 2 (nonhomogenized) are not presented elsewhere in this paper.

in the field, which is likely to be significantly higher than even a few hours later in the laboratory. However, relatively rapid analysis likely would still be required to measure concentrations before samples become too degraded.

There are other potential factors responsible for the differences in concentrations observed across the different sampling campaigns. Although our previous research in this and other regional field locations has not shown a strong seasonal dependency in DMS production and/or the rate of microbial metabolism in subsurface sediment (Antler et al., 2019; Hutchings et al., 2019; Mills et al., 2016; Redeker et al., 2018), the depth profile analysis was done in the spring, while the homogenized sediment tests were performed in the winter, so in situ seasonal differences may have played a role in the observed differences in concentration. Likewise, while the field sampling protocol was consistent across all sampling campaigns, it is possible that differences in instrumentation and sample preparation contributed to some of the differences we observed. Homogenization of the samples may have resulted in loss of volatile species, although the observed concentrations were still similar to the nonhomogenized samples analyzed at similar time points (Figure 6). Similarly, while there was the potential for some loss of volatile species during transport between the field and the lab, trials where sediment cores were processed and samples sealed into vials in the field (Figure 6—York Pilot Sets 1 and 2) did not yield significantly different concentrations to suggest substantial loss from the cores during transport. It is worth noting, however, that while sampling, instrumentation, and treatments may have varied, there were consistent patterns observed between VOSC concentrations in ferruginous and sulfidic sediment. As such, while the presented values should not be interpreted as definitive in situ concentrations of volatile species, they should be perceived as indicative of how differences in aqueous geochemical environments impact VOSC dynamics.

4.2. Depth Profiles of VOSCs and Cycling of Organusulfur Molecules in Anoxic Sediment

Extensive prior studies in the north Norfolk salt marshes have characterized the dichotomous nature of the sediment geochemical environments as described earlier (Antler et al., 2019; Hutchings et al., 2019; Mills et al., 2016). Taking the observed differences in concentrations of VOSCs within the context of these differing geochemical environments, we note potential avenues by which aqueous geochemical dynamics can influence the production and fate of VOSCs. Typically, either iron reduction or microbial sulfate reduction dominates in an anoxic sedimentary environment, and there are accompanying differences in the abundance of microbial communities and concentrations of aqueous chemical species. The presence/absence of different aqueous species can impact other biogeochemical processes both by providing potential reactants, as well as by changing the thermodynamic favorability of further chemical reactions. Higher DMS concentrations in ferruginous than sulfidic sediment and conversely higher concentrations of MeSH in sulfidic than ferruginous sediment were observed in both the homogenized sediment tests and the subsequent depth profiles. This suggests that there are fundamental differences in the production and destruction of the VOSCs in these different geochemical conditions. These measurements also revealed higher concentrations of both VOSCs in surface sediment, closer to the sediment-water interface, and concentrations that decreased with sediment depth. Both sediment types also exhibited concentrations of DMSP that were far higher than in the overlying surface water. Since our observations represent single time point VOSC concentration measurements, we cannot resolve which combination of biotic and abiotic reactions was responsible for the reduced VOSC concentrations with depth in the sediment. For example, it could be that VOSCs are being produced at all sediment depths with greater rates of consumption deeper below the sediment-water interface or it could be that VOSCs are primarily produced in the upper part of the sediment and diffuse downward through sedimentary pore waters to consumption deeper below the surface.

Despite molecular advances in our understanding of DMSP catabolism (Johnston et al., 2016), molecular insights into DMSP biosynthesis, certainly in sediment, are few and far between (Williams et al., 2019). Depth profile measurements of DMSP from the north Norfolk surface sediment showed that there were comparable concentrations of DMSP in both ferruginous and sulfidic sediment, which suggests that the observed differences in VOSC concentrations are not simply due to differences in the availability of DMSP. It is possible that microbes in the different sediment environments have different preferences for DMSP catabolism, favoring either demethylation (MeSH generating) in sulfidic versus lysis (DMS generating) in ferruginous sediment. It is thought that the demethylation pathway dominates in marine environments (Kiene & Linn, 2000; Kiene et al., 2000), although the role of physical and chemical environmental parameters on DMSP degradation pathways remains unclear, especially in sediment environments. Although DMSP is typically thought to be the primary precursor for DMS and MeSH in marine environments (Cantoni & Anderson, 1956; Kiene & Capone, 1988), our results suggest there are other potentially important factors in determining how much of each VOSC is produced. Indeed, recent metagenomics work on the Norfolk salt marsh system discovered widespread occurrence of bacteria with genes for DMSP-independent cycling of MeSH and DMS (Carrión et al., 2019). However, the study by Carrión et al. (2019) focused on aerobic sediment in the upper 3 cm and did not distinguish between ferruginous and sulfidic sediment, which our results suggest are a further layer of complexity impacting VOSC cycling in these systems.

Further differences between the sediment types were also observed over the course of a short incubation period during which significant changes were found in concentrations of both MeSH and DMS within the same sediment samples. In sulfidic sediment, there was loss of both DMS and MeSH over the course of the short incubation period. In contrast, in ferruginous sediment we observed a loss of DMS over the course of the short incubation period but an increase in MeSH. It is possible that these changes could be the result of biotic and/or abiotic chemical reactions, particularly for the more chemically reactive MeSH. However, the chemical (i.e., abiotic) half-life for methyl iodide in sea water, as a proxy for MeSH, is in the order of 20 days (Pubchem database. methyl iodide, cid=6328, n.d., n.d.), suggesting that biological consumption is responsible for the more rapid observed changes. Similarly, the decrease in DMS concentrations in both sediment types suggests that biological degradation of DMS also occurred.

With the differences in microbial communities and activity, the resulting differences in the dominant aqueous chemical species may also play a role in observed differences in VOSC concentrations between sediment types. In sulfidic sediment, there is a high concentration of aqueous sulfide and this sediment has also been observed to be methanic (Antler et al., 2019; Hutchings et al., 2019; Mills et al., 2016). Methylation of sulfide to produce MeSH becomes an available pathway that is not possible in environments where there is no aqueous sulfide or methane. Ferruginous sediment does not have any aqueous sulfide, since any that is produced will be rapidly captured by abundant ferrous iron to form FeS (Antler et al., 2019). It has been hypothesized that the reaction of methane and sulfide to form MeSH in anaerobic, estuarine sediment is a thermodynamically favorable process (Sørensen, 1988). It is therefore possible that methylation of sulfide could be driving the high concentrations of MeSH observed in sulfidic sediment. Further, MeSH degradation pathways have lower free energy yields in sulfidic and methanogenic conditions, relative to the pathways for DMS degradation (Scholten et al., 2003). This means that MeSH degradation could be relatively thermodynamically inhibited in the presence of sulfide and methane; this could explain why there are higher concentrations of MeSH in the sulfidic sediment.

Determining precise mechanisms of VOSC cycling in these sediment types is beyond the scope of this study, and the involvement of other potential precursors and degradation products, including methionine and DMSO, cannot be ruled out. Nonetheless, this study does support the growing evidence of the complex, interconnected nature of carbon, sulfur, and iron cycling in salt marsh environments. While the Carrión et al. (2019) study was able to identify previously unobserved molecular mechanisms for VOSC cycling in the Norfolk salt marsh system, that study also recognized the presence of other unidentified genes active in VOSC cycling, including DMSP-independent pathways, that were likely involved in the biological/chemical interactions observed in this study. Regardless of the exact molecular mechanisms, it is important to consider the implications of the interplay between aqueous geochemistry and the production and destruction of VOSCs. Through the connection between aqueous geochemistry and VOSCs, physical and biological changes to marine and marginal marine systems have the potential to extend beyond sediment and

surface waters to biosphere-atmosphere dynamics by affecting the production and fate of VOSCs via changes in geochemical processes.

5. Conclusion

We present evidence of both the abundance of organosulfur species as well as the varying dynamics of these species in different geochemical sedimentary environments. Initial tests have demonstrated the importance of rapid analysis, as well as differences in the prevalence of VOSCs in ferruginous and sulfidic environments, notably the prominence of MeSH in sulfidic sediment. Depth profiles of DMSP, MeSH, and DMS exhibited high concentrations of VOSCs and further revealed differences between sediment types. While DMSP was abundant in both types of sediment, ferruginous sediment contained more DMS and less MeSH compared to sulfidic sediments. Further, sulfidic sediment exhibited simultaneous degradation of both species, whereas there was an increase in MeSH concurrent with degradation of DMS in ferruginous sediment. With differences in microbial community composition and concentrations of aqueous species, there are a number of possible ways in which aqueous biogeochemistry interacts with VOSC cycling. Further work is necessary to elucidate the exact mechanism(s) driving the interactions between VOSC production and sedimentary geochemistry. While much work has been done on VOSCs in open ocean environments, these results suggest the importance of sedimentary environments as hot spots of VOSC production, with the geochemical environment of the sediment potentially being an important determining factor in the production and fate of VOSCs.

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