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Microbial sulfate reduction and organic sulfur formation in sinking marine particles

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Climate change is driving an expansion of marine Oxygen Deficient Zones, which may alter the global cycles of carbon, sulfur, nitrogen, and trace metals. Currently, however, we lack a full mechanistic understanding of how oxygen deficiency affects organic carbon cycling and burial. Here, we show that ‘cryptic’ microbial sulfate reduction occurs within sinking particles from the Eastern Tropical North Pacific Oxygen Deficient Zone, and that some microbially-produced sulfide reacts rapidly to form organic S that is resistant to acid hydrolysis. Particle-hosted sulfurization could enhance carbon preservation in sediments underlying O₂-deficient water columns and serve as a stabilizing feedback between expanding anoxic zones and atmospheric CO₂. A similar mechanism may help explain more extreme instances of organic carbon preservation associated with marine anoxia in Earth history.

The oxygen deficient zones (ODZs) of the Eastern Tropical Pacific and Arabian Sea, which currently represent ~0.35% of the total volume of the ocean (1), are expanding rapidly in apparent response to anthropogenic climate change (2–5). Concentrations of dissolved O₂ in ODZs are below ~1 μM and may be effectively zero (<10 nM (6)). Without available O₂, animals are largely excluded and microorganisms must rely on alternative electron acceptors like nitrate, ferric iron, and sulfate to respire organic matter (OM). Microbial sulfate reduction (MSR), which produces sulfide, is canonically expected to occur only when more energetically favorable electron acceptors like nitrate have been locally depleted (7). Intriguingly, however, there is emerging molecular and geochemical evidence that suggests MSR may occur in ODZs despite plentiful dissolved nitrate (8, 9). Active MSR in ODZs could fundamentally alter the biogeochemical cycles of other elements because any sulfide produced could react rapidly with both metals (10) and organics (11) – a process called ‘sulfurization.’ During more severe periods of ocean deoxygenation in Earth history like the Cretaceous Ocean Anoxic Events, reactions with sulfide were globally significant sinks for both dissolved trace metals (12) and potentially atmospheric CO₂ (13). Still, we do not yet know whether MSR is significant in ODZs and how it impacts fluxes of organic carbon to the sediments.

Due to its potential to affect global geochemistry, substantial effort has been devoted in recent years to find evidence of active microbial sulfur cycling within ODZs. Sulfur-cycling transcripts and gene sequences have been detected in both ODZs of the eastern Pacific (8, 9, 14), the Washington margin

(15), and the Arabian Sea (16), while cadmium loss, attributed to CdS formation, was reported in the Northeast Pacific (17). Sulfide was detected in large marine snow from the San Juan Islands (18), and low rates of sulfide production in the ODZ offshore Chile were measured in the water column via radiolabeling experiments (9). Despite this progress, none of this work has yet yielded rates of MSR within the large, sinking particles that are the most probable locations for this metabolism (19), or has explored the impact of sulfide on the composition of sinking organic matter. To predict how expanding ODZs will impact the cycles of carbon and metals in the ocean, we need to know whether MSR and organic matter sulfurization are significant processes in sinking ODZ particles.

We tested the hypothesis that MSR occurs in large particles sinking through the Eastern Tropical North Pacific (ETNP) ODZ by concentrating sinking particles, incubating them with radiolabeled sulfate, and characterizing the products of reactions with any resulting sulfide (20). We deployed a surface-float-tethered particle trap with a 2-m-diameter, 50-μm-mesh net (21) from the R/V Roger Revelle four times in April and May 2018: once at a relatively low particle flux site (‘P2,’ 200 km from the Mexican coast, 17.0°N x 107.0°W, ~3500 m water depth), which included a large-particle-free control, and three times at a relatively high particle flux site (‘P1,’ ~50 km from shore, 20.3°N x 106.1°W, ~1500 m water depth). Particles were trapped at the depth of the secondary nitrite maximum (120–143 m at P1 and 147 m at P2; fig. S1), which represents the depth of most intense nitrate reduction and thus the highest expected rates of anaerobic organic

matter cycling (19). Particles for MSR (sulfide production) rate measurements were transferred from the anoxic particle collector and the net wash to serum bottles and incubated for ~24 hours in the dark with radiolabeled sulfate. After stopping microbial activity in the incubations with excess zinc acetate, we isolated acid-volatile sulfides (AVS, including both dissolved H₂S and metal monosulfides) and measured radioactivity in sulfate, AVS, and hydrolysis-resistant solids. This sampling approach allows us to focus specifically on processes within large, fast-sinking particles, which have been shown to develop internal redox gradients (18, 22, 23) and therefore have the highest probability of supporting MSR. If rates of nitrate utilization within large particles exceed the diffusive resupply of nitrate from the water column, micro-environments within the particle can theoretically support MSR.

The vast majority of radiolabeled sulfide produced by MSR in our incubations is expected to either reoxidize or react with metals or organics to form solids (24). Because we did not add sulfide to our incubations as a trap (9), the AVS we measured (Fig. 1 and table S1) is likely composed mostly of iron monosulfides rather than dissolved sulfide. Based on our processing methods, radiolabeled S accumulated in the hydrolysis-resistant residual solid phase could potentially include elemental S, organic S, and/or pyrite. Below, we show that this phase is organic S, and so we use that term throughout. P1 experiments (Fig. 1) accumulated as much as 171 ± 10.8 (2 σ) nmol AVS or 1711 ± 100 nmol organic S in 24 hours. P2 experiments contained fewer macroscopic aggregates and did not accumulate any resolvable AVS. The ratio of organic S to AVS produced was variable, which could reflect differences in the reactive iron content of different particle populations. These results also highlight that organic S, which is traditionally not measured as part of radiosulfur incubations, can be a major sink for MSR-derived sulfide.

In order to scale the S cycling rates in our bottles to the water column, we need to assess particle settling rates. Cavan *et al.* found near-shore particle sinking rates in the ETNP that ranged from ~2 to ~120 m/day (25), although the vast majority of particle mass was present in the slow-sinking pool with fluxes closer to 6.5 m/day. An average sinking rate of 6.5 m/day, for a two-meter-diameter net and one-liter collector, would imply a concentration factor of 20,420x; an average sinking rate of 30 m/day would imply a concentration factor of 94,245x. Volume-corrected minimum MSR rates at P1 (average, $n = 8$) are thus approximately 14 pM/hr (for 6.5 m/day,) or 3.0 pM/hr (for 30 m/day). For comparison, measured MSR rates were about 26 times higher (≤ 360 pM/hr) for water samples from the highly productive, O₂-deficient Chilean margin, where surface chlorophyll-a concentrations were correspondingly ~22 times higher (~16 $\mu\text{g chl-a/L}$ off Chile (9) vs. ~0.7 $\mu\text{g chl-a/L}$ at P1). Particle-hosted MSR rates in the

ETNP are therefore roughly comparable to previously reported water-column MSR rates (9) after scaling for local productivity.

By assuming that two organic carbon atoms are oxidized for each sulfate molecule reduced (7), we can also estimate the contribution of MSR to carbon oxidation rates in sinking ETNP particles. An average of at least 0.68 μmol of sulfide per day was produced in bottles from the high-flux site P1 (average, $n = 8$), which is equivalent to ~1.4 $\mu\text{mol/day}$ organic C respiration. The exact mass of carbon in these bottles is not known, so we report calculations for both our best estimate (5 mg C/bottle, see fig. S2) and the flux measured at another near-shore ETNP site (equivalent to ~20 mg C/bottle (25)). We assume an organic carbon turnover rate for fast-sinking particles of 12% per day (25, 26). For 5 mg (20 mg) organic carbon in each bottle, this turnover rate would suggest a total organic carbon respiration of 50 $\mu\text{mol C/day}$ (200 $\mu\text{mol C/day}$), which would mean that MSR accounts for 2.8% (0.7%) of the total expected respiration. Bianchi *et al.* (19) predicted that ~1% of depth-integrated respiration in the ETNP ODZ may be driven by MSR; our estimates for the contribution of MSR to total carbon respiration at our high-particle-flux site (0.7 – 2.8%) are consistent with these theoretical predictions.

We identified the speciation of sulfur in sinking ETNP ODZ particles using sulfur K-edge X-ray absorption spectroscopy (XAS). During incubations, sinking aggregates were macroscopic (>1 mm), composed of dark particles bound in a fluffy near-transparent matrix (fig. S2). This fluffy matrix dissolved during acid hydrolysis, leaving behind both discrete, ~100- μm -long particles as well as more diffuse solids (Fig. 2). Sulfur in the hydrolysable matrix is relatively oxidized, in the form of sulfate esters and some sulfonates (Fig. 3). This material is consistent with the presence of sulfated polysaccharides, which are abundant constituents of exocellular polymers exuded by diatoms and other algae (27) and have been implicated in marine snow formation (28, 29). Polysaccharide exopolymers are likely sinks for sulfide in sinking particles, as sulfide can convert them to more hydrolysis-resistant forms (30).

The speciation of sulfur in the discrete, hydrolysis-resistant particles contrasts the largely oxidized organic sulfur in the hydrolysable matrix. Hydrolysis-resistant S is present primarily as organic sulfides, with smaller amounts of aromatics, disulfides, and more oxidized forms (table S2). We found no evidence of elemental S, pyrite, or a sulfate background within the filters, which demonstrates that the radiolabeled S product from shipboard incubations is predominantly organic sulfur. Discrete particles in Regions 0 and 2 consist mostly of alkyl sulfides ($75.4 \pm 5.9\%$, mean $\pm 1\sigma$ for 'type I', see table S2) with only a few percent each of sulfonates, esters and disulfides. In contrast, diffuse materials in Region 1 and a spot within the large particle from Region 2

(‘type 2’) are more enriched in sulfonates, sulfate esters and disulfides, with only 40.4 ($\pm$ 2.7%) sulfides.

Spatial differences in the speciation of organic sulfur likely reflect heterogeneities in the sources and types of organic matter that combine to form large marine particles. Sources of organic sulfides include both S-bearing amino acids in proteins that survived strong acid hydrolysis, as well as OM sulfurization reactions (31). Similarly, sulfonates and esters can represent primary biogenic sulfur from organisms in the surface ocean (32, 33), like the hydrolyzable exopolymers, or they can also be produced during OM sulfurization reactions alongside organic sulfides, disulfides, and aromatics (34). XAS results integrate organic S formed both before and during field incubations, so any combination of these organic S forms could be the products of de novo sulfurization during shipboard incubations. Still, it is clear that that hydrolysis-resistant OM can be a significant sink for the sulfide produced during particle-hosted MSR.

The organic S production we observe in sinking particles is sufficient to drive a significant change in the properties of the OM sinking to, and potentially preserved in, underlying marine sediments. Sulfurization involves cross-linking and rearrangement of organic molecules, which is thought to enhance the preservation potential of OM by reducing its compatibility with exoenzymes (35, 36). The extent of sulfurization is reflected in the molar S:C ratio of OM, which ranges from typically $\leq 1\%$ for fresh algal biomass to 3–5% in many black shales (13, 37, 38). If we assume that roughly 80% of the original 5 mg (20 mg) C in each bottle from the 143-m high-flux trap ($n = 4$) dissolved during hydrolysis (32), then an average of 0.83 μmol organic S accumulated in a pool of $\sim 80\text{--}340 \mu\text{mol}$ C over the course of the 24-hours incubation. By this calculation, the molar S:C ratio of non-hydrolyzable organic matter increased by roughly 0.3–1.1% per day, which is the right order of magnitude to generate “strongly sulfurized” OM (S:C ≥ 3 mol%) within a few days of sinking through the water column. Particles therefore appear to be a feasible source of sulfurized OM to marine sediments, at least under sufficiently reducing and high-particle-flux conditions. The majority of hydrolysable, unsulfurized biomass is then remineralized by microbial processes before deeper burial (39), leaving behind the sulfurized component. Particle-hosted sulfurization could thus provide an explanation for observations of high OM burial in sediments underlying ODZs that do not intersect the sediment-water interface (40).

The organic S speciation in modern ODZ particles is also very similar to that reported from ancient kerogens in black shales from Ocean Anoxic Event 2 (13) (Fig. 3), which have sequestered vast amounts of OM for the last 94 million years (41). During this event, much of the southern proto-North Atlantic was sulfidic and preserved particularly S-rich OM, which could be the result of rapid sulfurization in sinking

particles (13). The hydrolysis-resistant organic S in these shales, like that in ODZ particles, consists mostly of organic sulfides, with $\sim 10\%$ contributions each from disulfides, aromatics, and sulfonates. The intriguing resemblance between actively sulfurizing particulate OM and ancient OM in shales allows for the interpretation that the same reactions that sulfurize OM in modern ODZ particles also facilitated elevated OM burial during periods of much more intense O_2 depletion in Earth history. Particle-hosted OM sulfurization is thus a potentially powerful mechanism to enhance OM preservation in sediments under anoxic conditions.

In modern ODZs, rates of particle-hosted MSR and OM sulfurization appear to be highly variable in both time and space, making any attempt to estimate the global scale of their effects on organic carbon burial premature. Mechanistically, however, we might expect expanding ODZs to likewise expand the scale of marine particle-hosted OM sulfurization in the ocean. This would represent a negative feedback with climate and atmospheric CO_2 : elevated CO_2 leads to ODZ expansion that then drives enhanced CO_2 sequestration in the form of sedimentary OM. Future research using this sampling approach will allow us to quantify the significance and environmental sensitivities of particle-hosted MSR and OM sulfurization on a global scale.

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SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S3

Tables S1 and S2

References (42–44)

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Fig. 1. Accumulation of radiolabeled S as acid-volatile and organic sulfur in particle incubations. Samples are arranged arbitrarily along the x-axis; note the y-axis is log scale. 'Sample type' describes whether particles were obtained from the strictly anoxic collector (AC) or recovered from the net wash (NW). Shading groups samples from individual deployments (table S1). Error bars that reach the x-axis indicate results that are not significantly different from zero. See fig. S1 for hydrographic context.

Fig. 2. Sinking particles on glass microfiber filters after high-temperature acid treatment. Selected map regions (R0, R1, and R2) show the spatial distribution of reduced S (2473.0 eV) on filters, with color indicating relative absorbance from low (blue) to high (red). Numbered white circles show locations at which full spectra were collected; see fig. S3 and table S2 for full maps and data. All scale bars are 100 μm , and pixels represent $\sim 5 \mu\text{m}^2$.

Fig. 3. Speciation of sulfur in ETNP particles and 94-million-year-old black shales. Bars represent the relative abundances of different sulfur moieties by linear deconvolution fitting in SIXPACK. Only high quality spot fits ($x^2 < 2$) are shown; see table S2 for uncertainties and fit parameters. Bars for black shales (13) and pre-acidification particles represent averages of all available data. Figure 2 includes a key to spot locations for acidified ETNP particles from regions R0, R1, and R2.