Marine anoxia initiates giant sulfur-bacteria mat proliferation and associated changes in benthic nitrogen, sulfur, and iron cycling in the Santa Barbara Basin, California Borderland

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Abstract

The Santa Barbara Basin naturally experiences transient deoxygenation due to its unique geological setting in the Southern California Borderland and seasonal changes in ocean currents. Long-term measurements of the basin showed that anoxic events and subsequent nitrate exhaustion in the bottom waters have been occurring more frequently and lasting longer over the past decade. One characteristic of the Santa Barbara Basin is the seasonal development of extensive mats of benthic nitrate-reducing sulfur-oxidizing bacteria, which are found at the sediment-water interface when the basin's bottom waters reach anoxia but still provide some nitrate. To assess the mat's impact on the benthic and pelagic redox environment, we collected biogeochemical sediment and benthic flux data in November 2019, after anoxia developed in the deepest waters of the basin and dissolved nitrate was depleted (down to 9.9 μM). We found that the development of mats was associated with a shift from denitrification to dissimilatory nitrate reduction to ammonium. The zone of sulfate reduction appeared near the sediment-water interface in sediment hosting these ephemeral white mats. We found that an exhaustion of iron oxides in the surface sediment was an additional prerequisite for mat proliferation. Our research further suggests that cycles of deoxygenation and reoxygenation of the benthic environment result in extremely high benthic fluxes of dissolved iron from the basin's sediment. This work expands our understanding of nitrate-reducing sulfur-oxidizing mats and their role in sustaining and potentially expanding marine anoxia.

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Introduction

Naturally occurring low-oxygen waters in the ocean are commonly observed below the ocean's mixed layer where respiration consumes oxygen faster than it is produced or ventilated. When low oxygen conditions occur along the western continental shelf in regions susceptible to upwelling events and/or undergoing eutrophication, organic matter remineralization can frequently drive oxygen concentrations to hypoxic (O_2 < 63 µM) (Middelburg and Levin, 2009) and/or anoxic levels (O_2 < 3 µM) (Fossing et al., 1995b; Canfield et al., 2010). These areas are usually referred to as Oxygen Minimum Zones (OMZs). In the water column of OMZs, nitrogen reduction becomes an important mechanism for organic matter remineralization (Ward et al., 2009). OMZs within coastal basins that experience seasonal changes in upwelling can experience anoxic and nitrate reducing conditions that extend to the benthic environment, especially when high productivity and associated organic matter export coincide with seasonal patterns of physical mixing. This fundamental change in the redox conditions at the sediment-water interface encourages elevated rates of anaerobic microbial processes and can promote organic matter preservation in the sediments (Middelburg and Levin, 2009; Treude, 2011), though a recent study suggests a thin reactive surface layer can provide high rates of organic matter degradation in anoxic environments (Van De Velde et al., 2023). Persistent anoxia in these coastal OMZ can lead to huge releases of sulfide (up to 13.7 mmol m^{-2} d^{-1}) and ammonium (up to 21.2 mmol m^{-2} d^{-1}) into the water column (Sommer et al., 2016).

The Santa Barbara Basin (SBB) is an example of one of these coastal OMZs that experiences seasonal deoxygenation. Drastic changes in water column oxygenation and seafloor redox

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The Santa Barbara Basin (SBB) is a coastal basin in the California Borderland with an approximate maximum depth of 600 m characterized by a seasonally anoxic water column (Sverdrup and Allen, 1939; Sholkovitz and Gieskes, 1971). The transform boundary along the California Borderland heavily affects the geomorphology of basins in this region; these basins become twisted as the plates rub against each other and form a series of "bathtubs" blocked by sills and seamounts off the coast of California. The SBB is bordered by the California coast in the north, the Channel Islands in the south, the Santa Monica basin to the east, and the Arguello Canyon to the west. A sill to the west of the basin at around 475 m depth (Fig. 1) prohibits most water transfer between the Santa Lucia Slope and the deeper waters of the SBB (Sholkovitz and Gieskes, 1971). The highly productive surface waters in the basin provide ample organic matter to the basin's water column, encouraging strong remineralization processes below the euphotic zone, which can induce anoxia below the sill depth, with typically less than 1 µmol O_2 L^{-1} (Sholkovitz, 1973; Emery et al., 1962; Thunell, 1998; Emmer and Thunell, 2000). During upwelling events (usually in Spring), oxygenated waters from the California Current spill over the western sill and ventilate the SBB, increasing oxygen concentrations to approximately 20 µmol O_2 L^{-1} (Goericke et al., 2015). SBB water-column oxygen and nitrogen concentrations have been evaluated through a longitudinal survey by the California Cooperative Oceanic Fisheries Investigations (Calcofi) with data starting in the 1950's . The data collected by this survey shows increasingly ubiquitous anoxia and denitrification in the basin with the SBB becoming completely nitrate-depleted below the sill at least three times between 2012 and 2017 (https://calcof.iorg/data/).¶

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conditions drive complex changes in benthic biogeochemistry and microbiology, evidenced most clearly by the development of thick, expansive mats of giant sulfur-oxidizing bacteria (GSOB) on the SBB seafloor (Bernhard et al., 2003; Prokopenko et al., 2006; Valentine et al., 2016; Kuwabara et al., 1999). A 2016 survey of the basin identified a vast GSOB mat spread over 1.6 contiguous km, confined between 487 and 523 km in the SBB depocenter where conditions were anoxic but not depleted of NO_3^- (Valentine et al., 2016). These GSOB mats have been noted previously in the SBB benthos, appearing at times of anoxia and disappearing when oxygen is present in the bottom water (Reimers et al., 1996b; Kuwabara et al., 1999). Similar GSOB mats have been identified in other transiently deoxygenated OMZs such as the Peruvian/Chilean coast (Sommer et al., 2016; Schulz et al., 1996; Zopfi et al., 2001; Høgslund et al., 2009). The chemoautotrophic bacteria that constitute the bulk of GSOB mats (typically *Thioploca* and/or *Beggiatoa*) utilize sulfide as an electron donor and O_2 or NO_3^- as a terminal electron acceptor (Jørgensen and Nelson, 2004). Some GSOB can hyperaccumulate NO_3^- in cell vacuoles up to 500 mM (Fossing et al., 1995a) and use this NO_3^- reserve to oxidize sulfide that diffuses from the underlying sediment to perform their metabolism. (Huettel et al., 1996; Mußmann et al., 2003; Sayama, 2001).

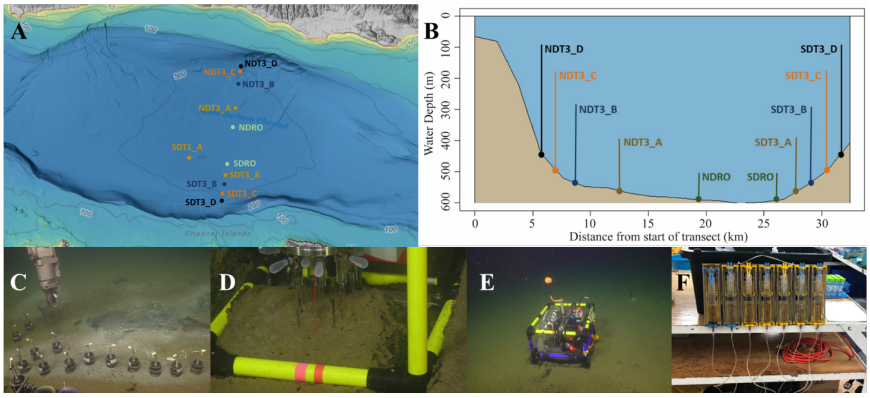

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Figure 1. Maps of sampling locations in the Santa Barbara Basin and photographs of deployed equipment: (A) bathymetric map of the Santa Barbara Basin with locations of all sampled stations; (B) cross-section of the Santa Barbara Basin with locations of all sampled station; (C) sediment push coring with ROV arm; (D) sediment microprofiler; (E) benthic flux chamber; (F) closeup of a syringe system from a benthic flux chamber. The map in (A) was generated using the Bathymetric Data Viewer provided by the National Centers for Environmental Information.

The activity of GSOB mats contribute significantly to element cycling in benthic marine environments with large effects on biogeochemical conditions in the bottom water. Isotopic measurements of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ from NO_3^- in the SBB water column suggest that benthic organisms are responsible for approximately 75% of the total NO_3^- reduction in the SBB (Sigman et al., 2003). Other studies found that GSOB mats inhibit the diffusion of NO_3^- into sediments via hyper-accumulation in vacuoles thereby creating conditions ideal for bacterial heterotrophic sulfate reduction beneath them (Fossing et al., 1995b; Zopfi et al., 2001). These studies suggest that GSOB mats in the SBB may be responsible for the majority of NO_3^- consumption in the basin rather than water-column microbes. Additionally, GSOB mats have been reported to deplete NO_3^- via dissimilatory nitrate reduction to ammonia (DNRA) in the anoxic bottom water of the Peruvian OMZ (Dale et al., 2016) and in the hypoxic transition zone in the Eastern Gotland Basin of the Baltic Sea (Noffke et al., 2016). By contrast, benthic microbial communities in the hypoxic (42 μM) Mauritanian OMZ perform canonical denitrification instead (Dale et al., 2014). The contrast between the Peruvian and Mauritanian OMZ suggests that bottom-water anoxia triggers the appearance of GSOB mats, and that DNRA is more prevalent where GSOB mats are present.

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178 The rapid accumulation and consumption of NO_3^- by GSOB mats has ramifications for the redox
179 conditions in the sediment underneath. The depletion of NO_3^- and shallowing of the nitracline
180 could promote high rates of sulfate reduction in the sediment underneath the GSOB mat. In
181 return, the sulfate reduction zone exists close to the sediment-water interface, providing the
182 GSOB mat with readily accessible sulfide. If a metabolic feedback loop is then established
183 between sulfur-oxidizing bacteria at the sediment-water interface and sulfate-reducing bacteria in
184 the sediment, increased NO_3^- loss from the water column and spreading of sulfidic conditions in
185 SBB sediment is expected. With these mats being potentially crucial to nitrogen and sulfur
186 cycling in sediments underlying OMZs, their biogeochemical transformations and ergo effect
187 upon basin redox conditions are critically important to understanding element cycling in the
188 SBB. Such gained knowledge would have additional benefits for predicting biogeochemical
189 feedbacks to the projected expansion of oceanic oxygen deficiency, in the SBB and in OMZs
190 more general, as a result of global change (Stramma et al., 2008).
191
192 Utilizing in-situ technologies, sediment porewater extraction, solid phase analyses, and
193 radiotracer techniques, this study aims to answer the following overarching questions: (1) Which
194 environmental conditions initiate and sustain the proliferation of GSOB mats? (2) Which
195 biogeochemical transformations occur in the sediment underneath these mats? (3) What role do
196 the mats play in the increasingly prevalent anoxic and nitrate-depleted condition found in the
197 SBB? These investigations represent the first basin-wide geochemical characterization of the
198 Santa Barbara Basin which hosts the largest as-of-yet mapped GSOB mat in the world's oceans.
199 It is the first suite of in-situ flux measurements carried out in the SBB, which is unique to other
200 heavily studied marine settings (e.g., Eastern Gotland Basin, Peruvian upwelling zone) in that it

is an oceanic basin within an upwelling zone. The results presented here also provide geochemical context for a number of other related investigations in the SBB (Robinson et al., 2022; Peng et al., 2023) as well as the first measurements in a multi-year study of biogeochemical changes in response to warming waters and increased stratification on the California coast.

2. Materials and Methods

2.1 Study Site

The Santa Barbara Basin (SBB) is a coastal basin in the California Borderland with an approximate maximum depth of 600 m characterized by a seasonally anoxic water column (Sverdrup and Allen, 1939; Sholkovitz and Gieskes, 1971). The transform boundary along the California Borderland heavily affects the geomorphology of basins in this region; these basins become twisted as the plates rub against each other and form a series of "bathtubs" blocked by sills and seamounts off the coast of California. The SBB is bordered by the California coast in the north, the Channel Islands in the south, the Santa Monica basin to the east, and the Arguello Canyon to the west. A sill to the west of the basin at around 475 m depth (Fig. 1) prohibits most water transfer between the Santa Lucia Slope and the deeper waters of the SBB (Sholkovitz and Gieskes, 1971). The highly productive surface waters in the basin provide ample organic matter to the basin's water column, encouraging strong remineralization processes below the euphotic zone, which can induce anoxia below the sill depth, with typically less than 1 µmol O_2 L^{-1} (Sholkovitz, 1973; Emery et al., 1962; Thunell, 1998; Emmer and Thunell, 2000). Benthic faunal distribution within the basin is tightly correlated with this sill depth and related oxygen conditions; below the sill, the sea snail *Alia permodesta* is the most commonly found benthic fauna, while sea stars, sea urchins, and other echinoderms increase in density above the sill (Myhre et al., 2018). During upwelling events (usually in Spring), oxygenated waters from the California Current spill over the western sill and ventilate the SBB, reportedly increase bottom water oxygen concentrations to approximately 20 µmol O_2 L^{-1} (Goericke et al., 2015). SBB water-column oxygen and nitrogen concentrations have been evaluated through a longitudinal survey by the California Cooperative Oceanic Fisheries Investigations (Calcofi) with data

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starting in the 1950's . The data collected by this survey shows increasing durations of anoxia and fixed nitrogen loss in the basin with the SBB becoming completely nitrate-depleted below the sill at least three times between 2012 and 2017 (https://calcof.iorg/data/).

2.2 Benthic sediment sampling and instrument deployment

Sediment samples were taken between 30 October and 11 November 2019 during an expedition aboard the research vessel *(R/V) Atlantis* equipped with the remote operated vehicle (ROV) Jason. Samples were taken at stations along a bimodal, north-south transect through the depocenter of the SBB, as well as one station on a separate transect. Details of sampling stations can be seen in Fig. 1A and 1B. Briefly, depocenter stations are labeled as NDRO and SDRO (northern and southern depocenter radial origin, respectively). The remaining stations are named for the cardinal direction (north vs. south) and the transect number (e.g., SDT1-A is on transect 1 while SDT3-A is on transect 3). As station depth decreases, the alpha suffix increases (e.g., NDT3-A is deeper than NDT3-B, etc.).

ROV Jason conducted sediment push coring and deployed automated benthic flux chambers (BFC) and microprofilers at each station. Bottom water oxygen concentration was determined using an Aanderaa 4831 oxygen optode (Aanderaa Instruments, Bergen, Norway) installed on the ROV. Optical modems (Luma 250LP, Hydromea, Renens, Switzerland) installed on the ROV and the BFC and microprofilers were used to transmit deployment settings and start/terminate measurements of the instruments. Multiple push cores (polycarbonate, 30.5 cm length, 6.35 cm inner diameter) per sampling station were retrieved during ROV Jason deployments (Fig. 1C). Replicate cores from each station were transferred to an onboard 6°C cold room upon recovery

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aboard the ship and subsampled for either solid phase analyses, porewater geochemistry, or radiotracer experiments.

2.3 Sediment Core Sub-Sampling

Two replicate ROV push cores that were collected near each other at each station were processed under a constant argon flow to protect redox-sensitive species. Cores were sectioned in 1-cm increments up to 10 cm followed by 2-cm increments. Note, sediments from the NDT3-B station were sliced in 2-cm increments. Sediment subsections were transferred into argon-filled 50-mL conical centrifuge tubes. Sediment samples were centrifuged at 2300 x g for 20 minutes. The centrifugate was subsampled unfiltered as fast as possible (to avoid contaminations with oxygen) for porewater analyses. Solid phase cores were sectioned similar to porewater cores and sub-sampled for sediment density, porosity, and organic matter content. A 10 mL cut-off plastic syringe was used to collect 6 mL of sediment into pre-weighed plastic vials (15 mL snap-cap vials) and stored in the dark at 4°C for sediment porosity and density analysis. Two-mL microcentrifuge tubes were filled with sediment from each depth interval and stored at -30°C for sediment organic matter analyses. One ROV push core per station was sub-sampled with a miniaturized push core (length 20 cm, inner diameter 2.6 cm) and taken immediately to the shipboard radioisotope van for radiotracer experiments (see section 2.5).

2.4 Sediment Porewater Geochemistry

Concentrations of porewater sulfide (Cline, 1969), NH_4^+, PO_4^{3-}, and Fe^{2+} (Grasshoff et al., 1999) were determined shipboard with a Shimadzu UV-Spectrophotometer (UV-1800). Detection limits for sulfide, NH_4^+, PO_4^{3-}, and Fe^{2+} were 1 µM. Subsamples (2 mL) for porewater NO_3^- and

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NO_2^- concentrations were stored in 2-mL plastic vials with an O-ring, frozen shipboard at -30°C and analyzed back at the home laboratory on the same spectrophotometer using the method following (García-Robledo et al., 2014). The detection limit for NO_3^- and NO_2^- was 0.5 µM. Samples for porewater DIC were preserved shipboard with 5 µL saturated HgCl in headspace free glass vials and stored at 4°C for later analysis following (Hall and Aller, 1992). DIC detection limit was 0.1 mM. Total alkalinity was determined shipboard using direct titration of 500 µL of pore water with 0.01M Titrisol® HCl (Pavlova et al., 2008). The analysis was calibrated using IAPSO seawater standard, with a precision and detection limit of 0.05 meq L^{-1}. Subsamples (1 mL) for sulfate and chlorinity were stored in 2-mL plastic vials with an O-ring, frozen shipboard at -30°C and later measured in the lab using a Metrohm 761 ion chromatograph with a methodological detection limit of 30 µM (Dale et al., 2015).

2.5 Solid Phase Analyses

Porosity/Density samples were collected in pre-weighed plastic vials and dried at 50°C for up to 96 hr until the dry weight was stable. Sediment porosity was calculated by taking the difference between wet and dry sediment weight and divided by the volume of the wet sediment. Sediment density was calculated by dividing the wet sediment weight by its volume. Treatment of sediment subsamples for total organic carbon (TOC), total organic nitrogen (TON), and organic carbon isotope composition ($\delta^{13}C$) were modified from (Harris et al., 2001) and sent to the University of California Davis Stable Isotope Facility for analysis using Elemental Analyzer – Isotope Ratio Mass Spectrometry. TOC and TON were calculated based on the sample peak area corrected against a reference material (alfalfa flour). Limit of quantification based on peak area was 100 µg C with an uncertainty of ± 0.2 ‰ for $\delta^{13}C$.

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Deleted: Briefly, samples were dried up to 48 hours at 50°C until the dry weight was stable and then treated with direct addition of 1 mL of 6N HCl to dissolve carbonate minerals. These samples were then washed in triplicate with 1-mL of ultrapure water or until a neutral pH was re-established. Samples were centrifuged at 4255 x g for 20 minutes, the supernatant was decanted, and vials were re-dried at 50°C. A subsample (approximately 10-15 mg of sediment) was then packed into individual 8x5 mm pressed tin capsules

2.6 Sulfate Reduction

To determine ex-situ microbial sulfate reduction rates, whole round sub-cores were injected with 10 µL carrier-free ^{35}S-Sulfate radiotracer (dissolved in water, 200 kBq, specific activity 37 TBq mmol^{-1}) into pre-drilled, silicon-filled holes at 1-cm increments according to (Jørgensen, 1978). These sub-cores were incubated at 6°C in the dark for 6-8 hours. Incubations were stopped by slicing sediment cores in 1-cm increments into 50-mL centrifuge tubes filled with 20-mL zinc acetate (20% w/w) and frozen at -20°C until analysis at the land-based laboratory. Microbial activity in controls was terminated with zinc acetate (20 mL of 20% w/w) before the addition of radiotracer and subsequent freezing. Lab-based analysis of sulfate reduction rates were determined following the cold-chromium distillation procedure (Kallmeyer et al., 2004).

2.7 Benthic In-Situ Investigations

Per station, one to three microprofiler (Fig. 1D) and three BFC (Fig. 1E) deployments were carried out by the ROV Jason at the seafloor. Construction, deployment and operation of automated microprofilers and BFCs followed those described in (Treude et al., 2009). The microprofiler deployed in this study represents a modified, miniaturized version of the instrument described in (Gundersen and Jørgensen, 1990) that was constructed specifically for use by ROV. Microprofilers were outfitted with three O_2-microelectrodes (Glud et al., 2000), two pH-microelectrodes (Revsbech and Jørgensen, 1986), two H_2S-microelectrodes (Jeroschewsky et al., 1996), and one conductivity sensor to determine the position of the sediment-water interface relative to the tips of the microelectrodes. Concentrations of oxygen

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$$SRR = [SO_4] * P_{SED} * \frac{a_{TRIS}}{a_{TOT}} * \frac{1}{t} * 1.06 * 1000$$

(EQ # 1)¶

¶

Where SRR is sulfate reduction rate (nmol cm^{-3} d^{-1}); [SO_4] is porewater sulfate concentration; Ps_{ed} is sediment porosity; a_{TRIS} is radioactivity of the total reducible inorganic sulfur (counts per minute); a_{TOT} is total radioactivity used in incubation (counts per minute); t is incubation time in days; 1.06 is the correction factor for expected isotope fractionation; and 1000 is the factor to convert from mmol L^{-1} to nmol cm^{-3}.

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and sulfide, as well as pH were each calculated from microelectrode readings and averaged for the respective sites where replicates existed.

The BFC consisted of a frame equipped with a cylindrical polycarbonate chamber (inner diameter = 19 cm) with its lower portion sticking out of the frame. The upper side of the chamber was closed by a lid containing a stirrer (Type K/MT 11, K.U.M., Kiel, Germany), oxygen optodes (Type 4330, Aanderaa Data Instruments, Bergen Norway and Hydroflash, Contros/Kongsberg Maritime, Kongsberg, Norway), a conductivity sensor (type 5860, Aanderaa Data Instruments), and a valve. Prior to insertion into the sediments, the chambers were held upside down by the ROV manipulating arms within approximately 10 m of the seafloor and moved back and forth to make sure that water from shallower depth that may have been trapped was replaced by bottom water. Chamber incubations lasted between 240 and 390 minutes. Each BFC was outfitted with a custom-built syringe sampler containing seven syringes that were connected by tubes to sampling ports in the upper wall of the chambers (Fig. 1F): one injection syringe and six sampling syringes that were fired at regular time intervals over the time course of the deployment. The injection syringe contained de-ionized water and the reduction in salinity in the overlaying water after salinity readings stabilized (i.e., full mixing was achieved) 10-30 min after injection was used to determine BFC volumes (Kononets et al., 2021). Samples obtained from the overlaying water of the BFC were examined for the same geochemical constituents as described above (section 2.4). Benthic fluxes of NO_3^-, NH_4^+, PO_4^{3-}, and Fe^{2+} were calculated as follows:

$$J = \frac{\Delta c}{\Delta t} * \frac{V}{A} \qquad \text{(EQ \# 2)}$$

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Where J is the flux in mmol m^{-2} d^{-1}, ΔC is the concentration change in mmol m^{-3}, Δt is the time interval in d, V is the overlying water volume in m^3, and A is the surface area of the sediment covered by the benthic flux chamber in m^2. An average flux within BFC's was calculated for stations of similar depth. One chamber per site contained $^{15}N\text{-}NO_3^-$ in the injection syringe for in-situ nitrogen cycling experiments. Results are reported from two of these chambers (SDRO and NDT3-D) and all $^{15}N\text{-}NO_3^-$ chambers were excluded from benthic flux calculations (see next section).

2.8 In Situ ^{15}N Incubations

Two hundred µmol of ^{15}N-labeled potassium nitrate (99% ^{15}N; Cambridge Isotopes) was injected into the ^{15}N incubation chamber at each site to obtain a final concentration of ~50 – 100 µM ^{15}N-labeled nitrate. Nitrate was amended at this level to prevent its depletion before the last sampling time point (Valentine et al., 2016). Samples for $\delta^{15}N$ analysis were preserved by filling a pre-vacuumed 12-ml exetainer vial with 0.1 ml 7M zinc chloride as a preservative. Another aliquot (~12 ml) of seawater for ammonium isotope analysis (see section 2.7.2) was filtered through 0.2 µm syringe filters and stored frozen. Prior to analyzing the samples in 12-ml exetainer vials, 5 mL of sample was replaced with ultra-high purity helium to create a headspace. The concentration and $\delta^{15}N$ of dissolved N_2 and N_2O was determined using a Sercon CryoPrep gas concentration system interfaced to a Sercon 20-20 isotope-ratio mass spectrometer (IRMS) at the University of California Davis Stable Isotope Facility.

2.9 Ammonium Isotope Analyses

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458 The production of $^{15}NH_4^+$ in seawater samples was measured using a method adapted from
459 (Zhang et al., 2007) and described previously by (Peng et al., 2016). In brief, NH_4^+ was first
460 oxidized to NO_2^- using hypobromite (BrO^-) and then reduced to N_2O using an acetic acid-azide
461 working solution (Zhang et al., 2007). The $\delta^{15}N$ of the produced N_2O was determined using an
462 Elementar Americas PrecisION continuous flow, multicollector, isotope-ratio mass spectrometer
463 coupled to an automated gas extraction system as described in (Charoenpong et al., 2014).
464 Calibration and correction were performed as described in (Bourbonnais et al., 2017). The
465 measurement precision was ±0.2 ‰ for $\delta^{15}N$. Depending on the in-situ ammonium
466 concentration, the detection limit for total NH_4^+ production rates ranged between 0.006 and
467 0.0685 mmol m^{-2} d^{-1}.
468

3. Results

3.1 Bottom water conditions

O_2 and NO_3^- concentrations in the bottom water along the transects can be seen in Table 1. O_2 concentrations below detection as determined by the ROV sensor could in some cases be considered to represent anoxia (0 µM O_2) based on a set of different analytical methods (see discussion section 4.1). Bottom water solute concentrations (as defined by the average T_0 concentration in BFC at each site) can be seen in Suppl. Figs. 1-4. Bottom water NO_3^- concentrations roughly decreased with station depth (e.g., 28 µM at NDT3-D vs. 19 µM at NDRO). Bottom water NO_2^- concentrations were below detection at all stations. Bottom water NH_4^+ concentrations were 9 µM at NDRO and 13 µM at SDRO and below detection in shallower stations. Bottom water PO_4^{3-} concentrations roughly increased with increasing basin depth (e.g., 2 µM at SDT3-D vs. 7 µM at SDRO). Finally, Fe^{2+} was 2 and 5 µM at the NDRO and SDRO stations, respectively and below detection at all shallower stations.

3.2 Sediment characteristics

Photographs of sediment cores with a depth scale are shown below Table 1. Sediment colors were classified according to (Hossain et al., 2014). Cores from the shallowest (D) stations were uniformly reddish in color with small pockets of black. The sediment color changed with station depth, transitioning from a reddish color in the shallowest stations to predominantly black with reddish laminations at the depocenter stations. The band of black sediment appeared at approx. 8 cm sediment depth in the C-station cores and became progressively more ubiquitous with station depth. Notably, NDT3-C sediment (Table 1B) contained black bands from approx. 6-14 cm sediment depth, while SDT3-C sediment (Table 1J) had a much narrower band around 8-10 cm.

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Sediment cores from shallower stations (D and C stations) contained signs of bioturbation (e.g., u-shaped burrows) and, in some cases, contained visible macrofauna, such as polychaetas and mollusks. Deeper in the basin (A and depocenter stations) no signs of bioturbation were detected,

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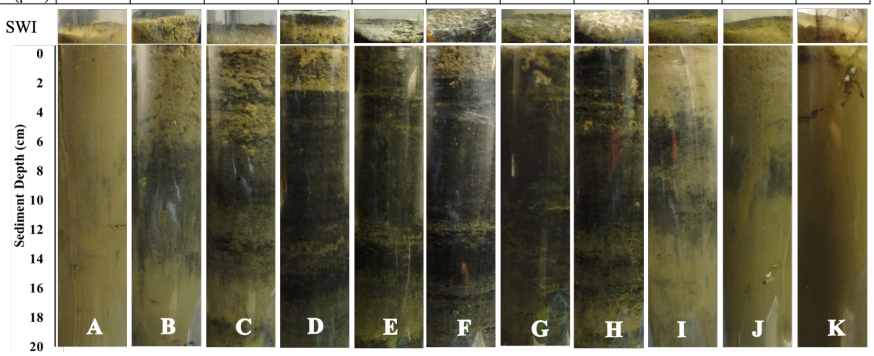
Table 1. Station details and photos of representative ROV push cores taken at each station. Mat presence (Y = yes, N = no) was determined visually. Station water depth and oxygen concentration were determined by sensors attached to ROV Jason (bdl = below detection limit (<3 µM O_2). Anoxia was confirmed by additional methods (see discussion section 4.1). Latitude and longitude were determined by triangulation between the ROV and the ship. Bottom water nitrate concentration was derived from an average of benthic flux chamber nitrate measurements at time 0 for each station (chambers with no calculatable flux and ^{15}N-nitrate addition excluded). Note, benthic flux chambers were not deployed at SDT1-A. Photographs show the sediment-water interface (SWI; top part) and each sediment core in full length (lower part).

Parameter	NDT3-D	NDT3-C	NDT3-B	NDT3-A	NDRO	SDRO	SDT1-A	SDT3-A	SDT3-B	SDT3-C	SDT3-D
Mat Present	N	N	N	Y	Y	Y	Y	Y	N	N	N
Depth (m)	447	498	537	572	580	586	573	571	536	494	447
Latitude (°)	34.363	34.353	34.333	34.292	34.262	34.201	34.212	34.184	34.168	34.152	34.142
Longitude (°)	-120.015	-120.016	-120.019	-120.026	-120.031	-120.044	-120.116	-120.047	-120.053	-120.050	-120.052
Oxygen (µM)	8.7	5.2	12.2	9.2	0.0	0.0	0.0	0.0	1.8	3.1	9.6
Nitrate (µM)	27.3	26.0	11.5	24.4	18.5	9.9		20.4	20.6	16.3	28.0



and the sediment-water interface was colonized by patches of white GSOB mats. Spherical cells (given the moniker 'ghost balls') were found mixed amongst giant sulfur bacteria filaments within the top 0-1 cm of sediment at NDRO (Suppl. Fig. 7). These unknown species had similar morphological characteristics to the species *Thiomargarita namibiensis* (Schulz et al., 1999; Schulz and Schulz, 2005) containing a translucent cell with sulfur granules giving them a ghostly

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white appearance. A small sample of cells (n = 8) were measured, featuring diameters between 48.0 and 99.6 µm, amounting to an average biovolume of 2.5 x 10^5 µm^3, compared to *T. namibiensis* with a cell diameter usually between 100-300 µm (Schulz et al., 1999).

Table 2. Sediment solid phase data: porosity, density, total organic carbon (TOC), total organic nitrogen (TON), C:N ratio, and δ13C. All data were averaged for the top 0-19 cm sediment, except NDT3-C (17 cm), NDT3-A (11 cm) and SDRO (7 cm), where the core length was shorter. Integrated sulfate reduction rates (iSRR) were integrated over 0-14 cm sediment depth. No sulfate reduction rates are available for NDT3-B, SDT3-A, and SDT3-B; rates were not integrated for SDRO due to missing surface samples.

Parameter	NDT3-D	NDT3-C	NDT3-B	NDT3-A	NDRO	SDRO	SDT1-A	SDT3-A	SDT3-B	SDT3-C	SDT3-D
Porosity	0.79 ± 0.03	0.81 ± 0.04	0.86 ± 0.04	0.88 ± 0.03	0.88 ± 0.04	0.87 ± 0.03	0.88 ± 0.03	0.86 ± 0.04	0.85 ± 0.04	0.82 ± 0.04	0.78 ± 0.04
Density	1.21 ± 0.07	1.16 ± 0.08	1.06 ± 0.08	1.05 ± 0.04	1.06 ± 0.03	1.04 ± 0.03	1.11 ± 0.23	1.05 ± 0.05	1.12 ± 0.06	1.22 ± 0.05	1.22 ± 0.03
TOC (%)	2.9 ± 0.5	2.5 ± 0.5	3.6 ± 0.5	3.1 ± 0.4	3.3 ± 0.4	3.5 ± 0.4	4.5 ± 0.5	3.2 ± 0.0	3.6 ± 0.6	3.6 ± 0.8	3.3 ± 0.5
TON (%)	0.3 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.0	0.4 ± 0.1	1.0 ± 0.1	0.4 ± 0.0	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
C:N Ratio	8.9 ± 0.2	8.7 ± 0.5	8.5 ± 0.5	8.2 ± 0.2	8.2 ± 0.4	8.0 ± 0.2	8.6 ± 0.8	8.3 ± 0.6	8.3 ± 0.3	8.7 ± 0.3	8.5 ± 0.2
$\delta^{13}C$ (‰)	-22.4 ± 0.3	-22.4 ± 0.4	-22.2 ± 0.4	-22.1 ± 0.2	-22.1 ± 0.2	-22.0 ± 0.3	-21.3 ± 0.7	-22.1 ± 0.4	-22.0 ± 0.2	-21.9 ± 0.2	-22.0 ± 0.1
Integrated SRR (mmol m^{-2} d^{-2})	2.9	3.8		2.7	4.1		2.9			1.7	1.9

B station cores contained sporadic GSOB filaments slightly deeper in the sediment (approx. 2-4 cm sediment depth). Sediment solid phase parameters (averaged over the entire sediment core depth) can be seen in Table 2. Average sediment porosity increased with basin depth (e.g., from 0.79 at NDT3-D to 0.88 at NDRO). TOC, TON, the C/N ratio, and the $\delta^{13}C$ isotopic signature of organic carbon remained relatively constant (2.5 – 4.5%, 0.1 – 0.4%, 8.0 – 8.7 and 21.3 – 22.4 ‰, respectively) over all stations.

3.3 Sediment porewater geochemistry

Total alkalinity (Figs. 2 A-E & 3 A-F) increased steadily with sediment depth at all stations starting with, on average, 2.4 mM in the core supernatant reaching a maximum at the respective deepest sediment sample (20 cm). Porewater alkalinity and DIC also increased with basin depth,

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(Figs. 2 A-E & 3 A-F) indicating that total alkalinity was dominated by the carbonate system. Porewater DIC was, on average, 2.2 mM in the core supernatant and reached maximum concentrations at the deepest sediment depth (20 cm) at most stations.

Porewater PO_4^{3-} profiles (Figs. 2 A-E & 3 A-F) were markedly different between the depocenter and shallower C and D stations. Porewater PO_4^{3-} concentrations in the depocenter and A stations generally increased with sediment depth but several profiles (NDT3-C, NDT3-A, SDRO, SDT1-A) remained unchanged or decreased deeper in the sediment (starting at approx. 10 cm). The profiles in C and D stations showed a peak in PO_4^{3-} concentrations near the sediment-water interface, particularly in the northern basin. Below 2 cm, PO_4^{3-} decreased with sediment depth, but sometimes showed a second small peak deeper in the sediment (12-14 cm at NDT3-D and 10-12 cm at SDT3-D).

Porewater NH_4^+ concentrations (Figs 2 & 3 A-E) showed trends often similar to alkalinity and DIC; NH_4^+ concentrations increased downcore and were higher at depocenter than at D stations (e.g., 370 and 91 µM at 20 cm for SDRO and SDT3-D, respectively). Porewater NO_2^- (Suppl. Table 1) and NO_3^- (Figs. 2 F-J & F G-L) concentrations were at or near zero below 2 cm at every station, except at SDRO and NDT3-A where large peaks in NO_3^- (376 and 81 µM, respectively) and NO_2^- (37 and 5 µM, respectively) occurred in the top 1 cm.

Porewater Fe^{2+} concentrations (Figs. 2 F-J & 3 G-L) were several orders of magnitude higher at shallower D stations (max. 722 and 395 µM at NDT3-D and SDT3-D, respectively) compared to depocenter stations (max. 13 and 51 µM at NDRO and SDRO, respectively). NDT3-C porewater

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Fe^{2+} concentration (Fig. 2G) peaked in the top 1 cm of sediment (similar to deeper stations) while SDT3-C porewater Fe^{2+} concentration (Fig. 3H) peaked around 5-cm sediment depth. Fe^{2+} concentrations reached a max. at 0-2 cm and declined sharply with depth in depocenter and A-station sediment. Northern basin sediment was similar, but the decline in Fe^{2+} below 0-2 cm was less pronounced.

Maximum porewater sulfide concentrations (Figs. 2 F-J & 3 G-L) were several orders of magnitude lower at the shallower D-stations (5 and 4 µM at NDT3-D and SDT3-D, respectively) compared to A stations (350 and 148 µM at NDT3-A and SDT1-A, respectively). Unlike Fe^{2+}, peaks in sulfide concentration occurred deeper in the sediment (e.g., below 5 cm depth at A stations). Porewater sulfate concentrations (Figs. 2 K-O & 3 M-R) decreased slightly with depth, but never reached values below 20 mM at any station.

3.4 In-situ microprofiling

Microprofiler O_2 and sulfide measurements are shown in Fig. 4. Oxygen was rapidly consumed within the first 0-1 cm of sediment at every station where O_2 was detected in the bottom water (i.e., at all stations except NDRO, which showed no positive signal of oxygen in the water compared to the sediment; note that no oxygen profile is available for SDRO). Sulfide concentrations from microsensors showed similar trends to spectrophotometric measurements, albeit with different absolute values (below detection in shallower B-, C- and D-stations that lacked mats and >1,000 µM at A- and depocenter stations). Microprofiler pH (Fig. 4) was near 7.5 in the bottom water at all stations, and slowly decreased to near 7.0 in the lower parts (3-5

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cm) sediment at most stations except NDT3-C and SDT3-B, pH at 2.5 cm at SDT3-B reached 6.77, which was the lowest observed during this expedition.

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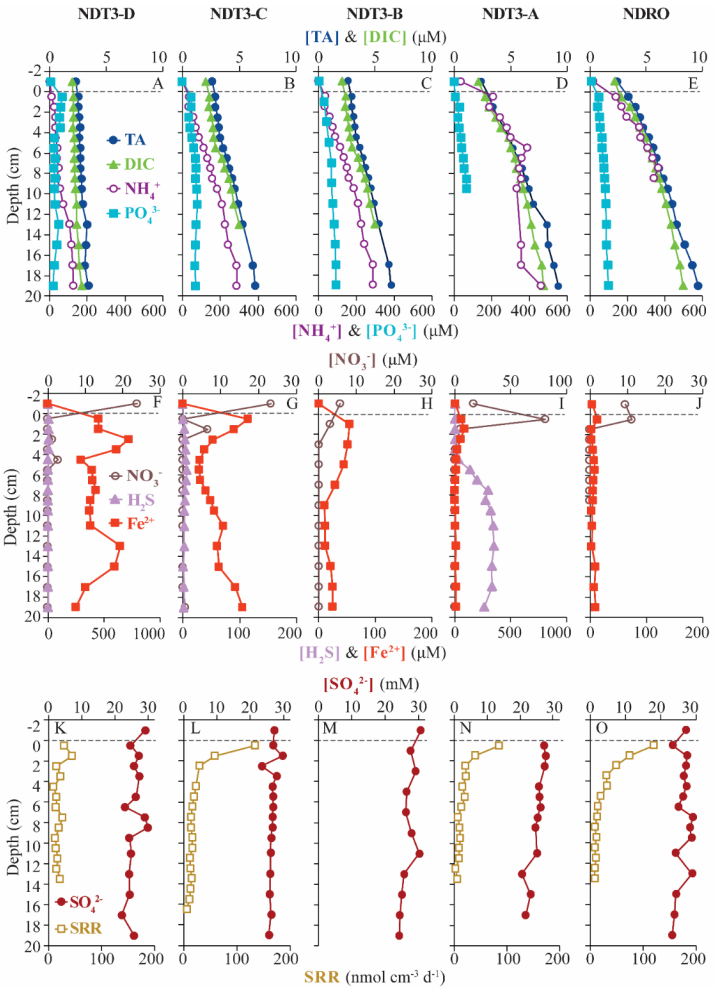

Figure 2. Biogeochemical data from ROV sediment push cores collected at stations on the northern transect (NDT3) and in the northern depocenter (NDRO): total alkalinity (TA), dissolved inorganic carbon (DIC), ammonium (NH_4^+), phosphate (PO_4^{3-}) in the first row; nitrate (NO_3^-), total sulfide (sulfide), and iron (II) (Fe^{2+}) in the second row; sulfate (SO_4^{2-}) and bacterial sulfate reduction rate (SRR) in the third row. Data analyzed from sediment core supernatant are plotted at -1 cm sediment depth; the dotted line connotes the sediment-water

interface. Note the change in scale on the primary x-axis in panel I and the change in scale of the secondary x-axis in panels F and I. No spectrophotometric sulfide data is available for NDRO and NDT3-B and no SRR data is available for NDT3-B. For station details see Fig. 1 and Table 1.

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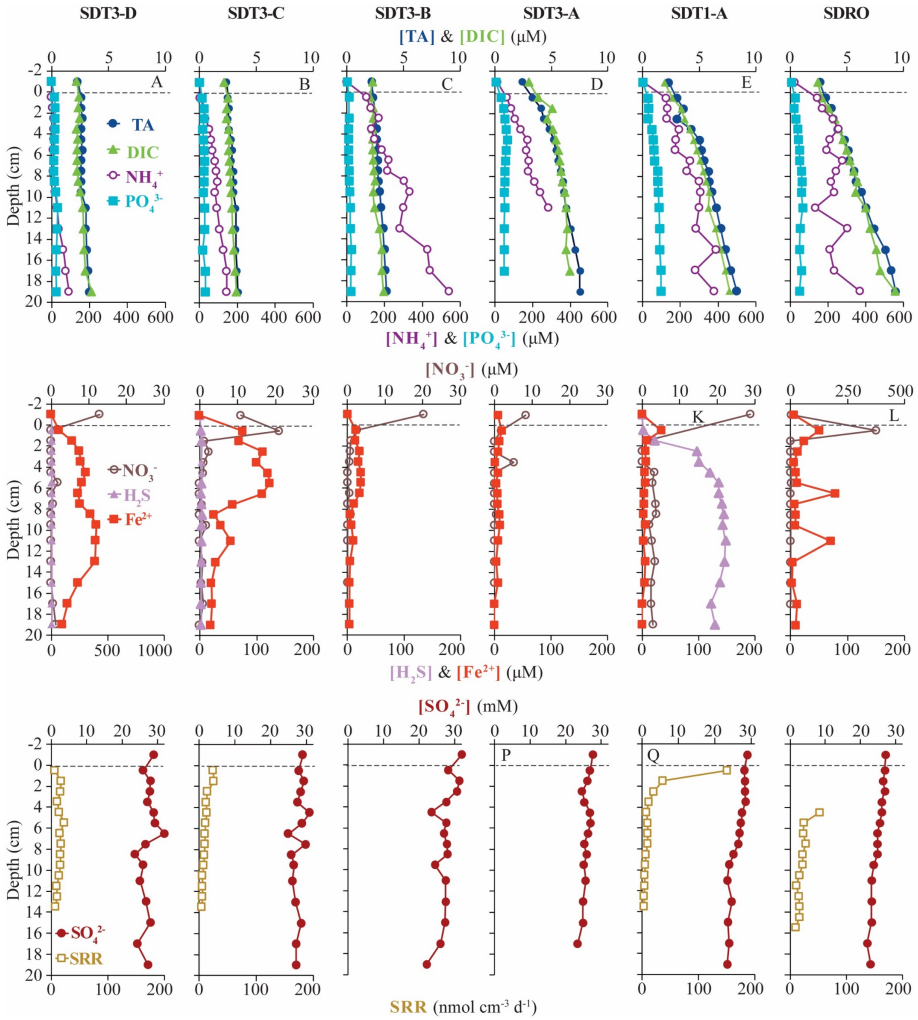

Figure 3. Biogeochemical data from ROV sediment push cores collected at stations on the two southern transects (SDT1 and SDT3) and the southern depocenter (SDRO): total alkalinity (TA), dissolved inorganic carbon (DIC), ammonium (NH_4^+), phosphate (PO_4^{3-}) in the first row; nitrate (NO_3^-), total sulfide (sulfide), and iron (II) (Fe^{2+}) in the second row; sulfate (SO_4^{2-}) and bacterial sulfate reduction rate (SRR) in the third row. Data analyzed from sediment core supernatant are plotted at -1 cm sediment depth; the dotted line connotes the

sediment-water interface. Note the change in scale on the primary x-axis in panel L and the change in scale of the secondary x-axis in panel G. No sulfide nor SRR data are available for SDT3-B and -A; spectrophotometric sulfide data and the top 0-4 cm of SRR data are not available for SDRO. For station details see Fig. 1 and Table 1.

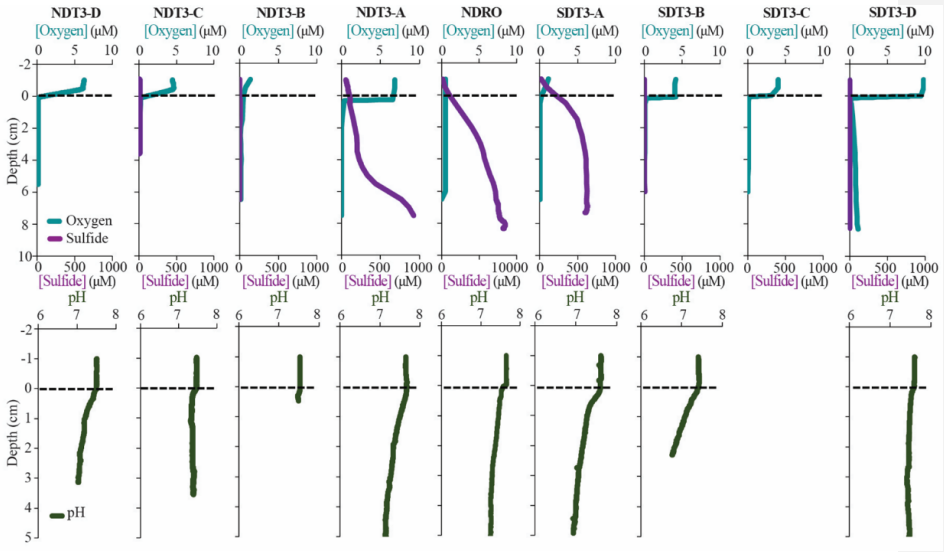

Figure 4. In-situ sediment microprofiler results for all stations (except SDT1-A and SDRO): oxygen (O_2) and total sulfide (sulfide) concentration in the first row; pH profiles in the second row. Note the change in scale on the secondary x-axis for NDRO sulfide. Values determined in the overlying water are plotted at negative sediment depths; the dotted line connotes the sediment-water interface.

3.5 In-situ fluxes of benthic solutes

NO_3^-, NH_4^+, PO_4^{3-}, and Fe^{2+} flux measured in the BFC revealed different patterns of uptake and release from the sediment throughout the basin (Fig. 5 and Suppl. Figs. 1-4). BFC O_2 concentrations were compromised by O_2 release from the chamber's polycarbonate walls, which prevented an accurate calculation of O_2 fluxes from BFC sensor data. NO_3^- was consumed at all stations as indicated by a negative flux (i.e., a flux into the sediment). On the contrary, benthic release (i.e., a flux out of the sediment) was observed for all other analyzed solutes (NH_4^+, PO_4^{3-},

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and Fe^{2+}), with the lowest fluxes in the shallow D and C-stations and highest fluxes in the depocenter. Ammonium fluxes were the highest of all the determined solutes and showed the largest difference between deep and shallow stations, with a flux of 1.6 mmol m^{-2} d^{-1} at NDT3-C (there were no measurable NH_4^+ fluxes in D-station chambers) and reaching 11.1 ± 3.1 mmol m^{-2} d^{-1} (n = 3) at the two depocenter stations. The depocenter ammonium flux far-outpaced the concomitant flux of nitrate into depocenter sediments (-3.2 ± 0.7 mmol m^{-2} d^{-1}, n = 3). Iron and phosphate fluxes were similar at depocenter stations (4.1 ± 0.7, n = 3, and 3.2 ± 0.7, n = 3, mmol m^{-2} d^{-1}, respectively). Alkalinity and DIC concentrations from flux chambers (Suppl. Figs. 5 and 6) remained constant at all stations and thus no DIC flux was calculated. Results from BFCs injected with $^{15}N\text{-}NO_3^-$ at the SDRO and NDT3-D station are shown in Fig. 6. The rates of denitrification, anammox, and N_2O production were higher at SDRO compared to NDT3-D. $^{15}NH_4^+$ production (DNRA) was one order of magnitude higher at the SDRO station (2.67 mmol m^{-2} d^{-1}) compared to the NDT3-D station (0.14 mmol m^{-2} d^{-1}). DNRA accounted for a much higher percentage of NO_3^- reduction at SDRO (54.1%) than NDT3-D (13.3%).

3.6 Sulfate reduction rates

Vertical profiles of bacterial sulfate reduction as determined by the radioisotope technique differed throughout the basin (Figs. 2 & 3). Peaks in sulfate reduction were seen in the top 0-1 cm of sediment at stations with a visible GSOB mat on the surface (120.2, 151.0, and 85.3 nmol cm^{-3} d^{-1} at NDRO, SDT1-A, and NDT3-A, respectively). Sediments at most shallower basin depths exhibited peaks slightly deeper in the sediment and of lower magnitude (25.5, 44.5, 22.5 nmol cm^{-3} d^{-1} at SDT3-C, NDT3-D, and SDT3-D respectively). NDT3-C had no visible GSOB mats but exhibited a peak (133.7 nmol cm^{-3} d^{-1}) in sulfate reduction at 0-1 cm depth, similar to

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deeper stations (e.g., NDRO in Fig. 2O), which differed from other shallow stations (e.g., SDT3-C in Fig. 3N). The integrated sulfate reduction rate (0-14 cm depth) at NDRO (4.1 mmol m^{-2} d^{-1}) was noticeably higher than most other stations with the exception of NDT3-C (3.8 mmol m^{-2} d^{-1}) (Table 2). NDT3-D and NDT3-C exhibited higher integrated rates (2.9 and 3.8 mmol m^{-2} d^{-1}) than their southern station counterparts SDT3-D and SDT3-C (1.9 and 1.7 mmol m^{-2} d^{-1}).

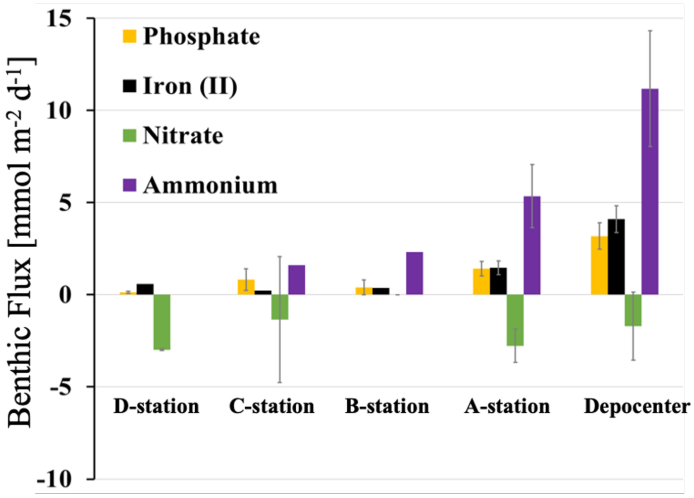

Figure 5. Benthic fluxes of solutes (positive flux = release from the seafloor; negative flux = uptake by the seafloor) determined with in-situ benthic flux chambers. Rates were averaged for stations of same depth from the northern and southern transect and the depocenter (NDRO and SDRO). Note, giant sulfur-oxidizing bacterial mats were found at depocenter and A-stations. Error bars represent standard errors.

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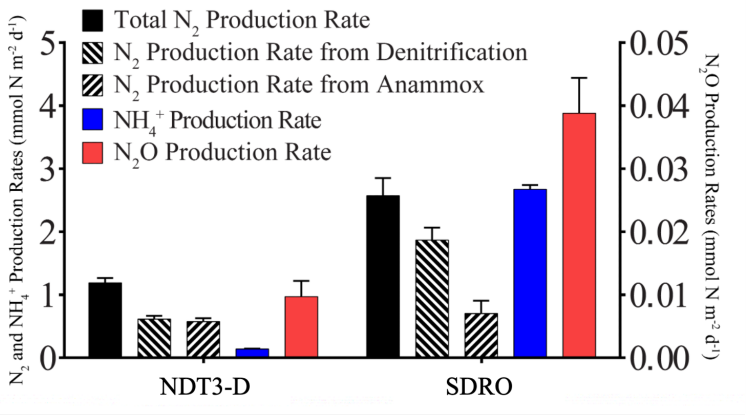

Figure 6. Areal rates of total N_2 production, denitrification, anammox, NH_4^+ production (DNRA), and N_2O production

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4. Discussion

4.1 Giant sulfur-oxidizing bacterial mats proliferated in response to deoxygenation in the Santa Barbara Basin

The SBB is an ideal environment to study the effect of transient deoxygenation on benthic biogeochemistry. In Fall 2019, when this expedition took place, the SBB was undergoing a transition from oxygenated to virtually anoxic conditions (Qin et al., 2022). When the AT42-19 cruise occurred, most of the bottom water in the basin was hypoxic (A-, B-, C-, and D-stations), except for the depositional center. Separate O_2 measurements from the ROV sensor (O_2 below detection limit, Table 1), microprofilers (no signal change between water column and sediment, Fig. 4), and Winkler titration from CTD/rosette casts (uniform non-zero value below 500 m (Qin et al., 2022)) indicated full anoxia in the bottom water at the deeper stations (NDRO and SDRO). Notably, bottom water conditions revealed a slight asymmetry between the basin transects (Fig. 1); bottom water along the northern transect generally had more O_2 and NO_3^- than the southern transect (e.g., 9 µM O_2 at NDT3-A and 0 µM O_2 at SDT3-A). This asymmetry indicated differences in the circulation and/or microbial communities between the northern and southern portions of the basin. Whether this asymmetry is a permanent feature of the basin or symptomatic of the specific conditions in November 2019 is unclear; previous studies in the SBB have been restricted to the depocenter or one side of the basin (Sholkovitz, 1973; Reimers et al., 1996a; Kuwabara et al., 1999). Regardless of bottom water oxidant concentration, the energetically most favorable terminal electron acceptors (O_2 and NO_3^-) disappeared in a very narrow zone below the sediment-water interface (Fig. 4 and Figs. 2 and 3, respectively), consistent with their expected rapid consumption by the benthic microbial community.

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In the present study, benthic GSOB mats were primarily limited to the anoxic depocenter of the SBB. Similarly, such mats were replete in the core of the anoxic Peruvian OMZ (Levin et al., 2002; Sommer et al., 2016; Mosch et al., 2012), but absent from the seafloor below the hypoxic, i.e., slightly oxygenated, Mauritanian OMZ (Schroller-Lomnitz et al., 2019). GSOB mats in November 2019 were observed deeper in the basin than in October 2013 (Valentine et al., 2016) but in a similar location to June 1988 (Reimers et al., 1996a) and April 1997 (Kuwabara et al., 1999). During the 2013 sampling, dense GSOB mats were confined to depths between approx. 500-570 m (equivalent to the B-stations from this expedition), corresponding with anoxic conditions in the bottom water. This habitat was sandwiched between an anoxic, anitric (i.e., nitrate-free) deep and a hypoxic, nitrigenated (i.e., nitrate-rich) shallower water layer (Valentine et al., 2016). The difference in depth distribution of GSOB mats between the 2013 and 2019 expedition provides evidence that GSOB mats in the SBB are ephemeral and proliferate where the bottom water is anoxic but not anitric.

As our study represents only a snapshot of an oxygen- and nitrate-driven mat dynamic, we can only speculate how areas of the basin that did not contain GSOB mats in November 2019 fit into this dynamic. For example, mat-forming sulfur bacteria found slightly deeper in the sediment at B-stations (see section 3.2) could be progenitors to surface sediment colonization of thick GSOB mats, as has been recorded in other transiently deoxygenated environments (Jørgensen, 1977). Alternatively, these subsurface colonies could also be remnants of a former surface GSOB mat that retreated under changing redox conditions. Oxygenated conditions in the water preceding the 2019 expedition would, in this context, suggest the mats migrated following a previous anoxic event (Qin et al., 2022). If deoxygenation persisted in the SBB after the AT42-19 cruise,

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then anitria (i.e., anitric conditions - similar to anoxia) would likely follow in the deepest basin water. These conditions would be similar to those seen in 2013 (Valentine et al., 2016), where GSOB mats formed a contiguous "donut ring" at shallower basin depths. Interestingly, GSOB mats in the Eastern Gotland Basin of the Baltic Sea were confined to a hypoxic transition zone, where O_2 was < 30 µM but did not reach anoxia, while no mats were observed at deeper anoxic locations (Noffke et al., 2016). This difference in distribution compared to the SBB suggests that GSOB mats proliferate under different conditions (anoxic or hypoxic), potentially depending on the species of mat-forming bacteria present and whether they specialize in aerobic or anaerobic chemosynthesis.

4.2 Shift from benthic denitrification to dissimilatory nitrate reduction to ammonium in response to complete deoxygenation in the Santa Barbara Basin

Benthic uptake and release of nitrogen species by SBB sediment appeared to be affected by the presence of GSOB mats. While total benthic nitrate uptake was similar between D- and depocenter stations based on in-situ NO_3^- flux measurements (Fig. 4), NH_4^+ release from the sediment into the water column increased where GSOB mats were present (Fig. 5). This trend is supported by the porewater profiles of NH_4^+, which showed a steeper increase over sediment depth at deeper stations (Figs. 2 & 3). Incubations with $^{15}N\text{-}NO_3^-$ revealed that N_2 production (denitrification and anammox) accounted for 86% of NO_3^-/NO_2^- reduction in the shallow basin, while NH_4^+ production (DNRA) accounted for 13% and N_2O production accounted for 1% (NDT3-D, Fig. 6; Peng et al., 2023)). In contrast, most (54%) of NO_3^- reduction at the depositional center occurred via DNRA; N_2 production accounted for 45% and N_2O production

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accounted for 1% of NO_3^- reduction at the SDRO (Fig. 6; Peng et al. 2023). It is important to note that these results only describe patterns of NO_3^- reduction in the basin, while other mechanisms of nitrate uptake by sediment (e.g., hyper-accumulation of nitrate into vacuoles) are more difficult to calculate accurately. It is also important to note that diatoms hyper-accumulate nitrate (Kamp et al., 2011) and meiofauna (e.g., nematodes) can positively impact rates of denitrification (Bonaglia et al., 2014). Both diatoms and meiofauna were seen in SBB depocenter and A-station sediments in November 2019 (data not shown), so their impact on SBB benthic nitrogen cycling is likely important and remains to be disentangled from the mats themselves.

This data suggests a transition from denitrification-dominated sediment in the oxygenated basin to an increasing influence of DNRA on N cycling in the deeper, anoxic basin. Placed in the context of other OMZs, Mauritanian shelf sediment was dominated by denitrification (Dale et al., 2014), similar to SBB shallow sediment (below hypoxic water) while core Peruvian OMZ sediment was dominated by DNRA, similar to sediment of the deeper SBB (below anoxic water) (Sommer et al., 2016). Nitrate reduction in sediment below the seasonally hypoxic Eckernförde Bay (Dale et al., 2011) and below the hypoxic transition zone of the Eastern Gotland Basin (Noffke et al., 2016) also showed increased DNRA where GSOB mats were present, though with an order of magnitude lower NH_4^+ flux (avg. 1.74 mmol m^{-2} d^{-1} and max. 1.10 mmol m^{-2} d^{-1}, respectively) than the SBB depocenter.

While our study suggests a shift from denitrification to DNRA during deoxygenation of SBB bottom water, other studies examined changes in benthic nitrogen cycling under reverse conditions, i.e., the reoxidation of the environment following anoxia (Hylén et al., 2022; De

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Brabandere et al., 2015). After a decadal oxygenation event in the Eastern Gotland Basin (Baltic Sea) in 2015-2016, sediment exhibited a slight increase in denitrification, but remained dominated by DNRA and N_2O production (Hylén et al., 2022). The lack of N_2 production via denitrification following this oxygenation event was attributed to the reoxygenation event being too weak to substantially oxidize sediments, which would favor denitrification (Hylén et al., 2022). In an engineered reoxygenation event of the By Fjord on Sweden's western coast, where dissolved O_2 and NO_3^- content of anoxic and anitric bottom water was artificially increased to approx. 130 µM O_2 and 20 µM NO_3^- over a period of roughly 2 years, denitrification rates were increased by an order of magnitude and DNRA rates were also stimulated (De Brabandere et al., 2015). Comparing our results to these two studies suggests that DNRA bacteria are more resilient to weak reoxygenation events and thrive in transiently deoxygenated systems that remain hypoxic (O_2 < 63 µM). The frequency and magnitude of reoxygenation and deoxygenation of SBB bottom waters, and the effect of these processes on the benthic microbial community, could be a major factor supporting some of the highest recorded total nitrate reduction rates in a natural benthic marine setting (Peng et al., 2023).

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Table 3. Example reactions of nitrate reduction pathways with associated energy yield in respect to the electron donor (H_2 or HS^-) and electron acceptor (NO_3^-) and electron accepting capacity. Modified from Table 2 in (Tiedje et al., 1983).

Reaction	$\Delta G^{o'}$ (kcal mol^{-1})		Electrons per NO_3^-
	H_2 / HS^-	NO_3^-	
Chemoheterotrophic Denitrification			
$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6H_2O$	-53.6	-133.9	5
Chemoautotrophic Denitrification			
$8NO_3^- + 5HS^- + 3H^+ \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O$	-177.9	-111.2	5
Chemoheterotrophic DNRA			
$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O$	-35.8	-143.3	8
Chemoautotrophic DNRA			
$NO_3^- + HS^- + H^+ + H_2O \rightarrow NH_4^+ + SO_4^{2-}$	-107.0	-107.0	8

A high ratio of electron donor to electron acceptor favors DNRA over denitrification (Marchant et al., 2014; Hardison et al., 2015; Tiedje et al., 1983) and this ratio appears to be critical in determining the dominant nitrate reduction pathway in SBB sediments, similar to the Eastern Gotland Basin (Hylén et al., 2022) and the By Fjord (De Brabandere et al., 2015). Example energy yields for denitrification and DNRA are shown in Table 3. As discussed in (Tiedje et al., 1983), heterotrophic denitrification yields more energy per mol of electron donor than DNRA. However, the reverse is true when considering energy yield per mol of electron acceptor (NO_3^-). DNRA also yields 3 more electrons per molecule of NO_3^- than denitrification. Tiedje et al. argued that in environments that are starved of powerful terminal electron acceptors, such as anoxic, organic-rich sediment, the energy yield per electron acceptor and additional electrons available for transfer could push nitrate reduction towards DNRA. Multiple laboratory and model studies have converged on an electron donor to acceptor ratio of approximately 3 to encourage DNRA over denitrification (Hardison et al., 2015; Algar and Vallino, 2014) though other studies have found higher values (Porubsky et al., 2009; Kraft et al., 2014). Sulfide concentrations near the sediment-water interface at the SBB depocenter (approx. 200 µM at 0.5 cm depth; Fig. 3, NDRO) would favor chemoautotrophic DNRA over denitrification at ambient marine nitrate concentrations (approx. 28 µM). Additionally, DNRA appears to be the preferred nitrate reduction pathway for chemoautotrophs that utilize iron or sulfide as an electron donor (Caffrey et al., 2019; Kessler et al., 2019; An and Gardner, 2002). As GSOB mats hyper-accumulate nitrate from the bottom water into their intracellular vacuoles, the resulting decline in electron acceptors at the sediment-water interface coupled with an elevation of the sulfate reduction zone would create an electron donor to acceptor ratio that favors DNRA. Since GSOB mats in the SBB seem to prefer DNRA, starving the bottom water of electron acceptors coupled

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with the high sulfate reduction rates could give them a competitive advantage and allow them to proliferate into the largest-yet mapped GSOB mat in Earth's oceans, as seen in other expeditions (Valentine et al., 2016; Reimers et al., 1996a; Kuwabara et al., 1999).

4.3 Microbial mat proliferation and benthic phosphate remineralization dependent on high rates of organic matter degradation in the Santa Barbara Basin

Organic carbon content of the benthic environment appears to be a key control on sulfate reduction rates near the sediment-water interface as well as microbial mat proliferation. Sulfate reduction rates in the SBB depocenter are most similar in magnitude and profile (i.e., highest rates found at the sediment-water interface and decline drastically thereafter) to those found in sediments below the transiently deoxygenated portion of the Peruvian shelf (e.g., 4.1 mmol m^{-2} d^{-1} at the SBB NDRO station vs. 2.5-3.8 mmol m^{-2} d^{-1} at 128-144 m water depth on the Peruvian margin (Gier et al., 2016; Treude et al., 2021)). The TOC content of surface sediments in these two regions are both high and within the same order of magnitude (maximum recorded TOC of 5.2% at the 0-1 cm margin at the SDT1-A station compared with 7.6% in the Peruvian margin 145 m depth (Noffke et al., 2012)). In comparison, sulfate reduction rates in the SBB were at least one order of magnitude lower than found in sediment below the OMZ on the Namibian Shelf, which has much higher TOC contents of >10% (Brüchert et al., 2003; Bremner, 1981). Sulfate reduction rates in the shelf sediments below the Eastern Arabian OMZ were much lower (0.18 – 1.27 mmol m^{-2} d^{-1}) than rates in the SBB depocenter (Naik et al., 2017) despite similar hypoxic to anoxic bottom water conditions. These lower sulfate reduction rates were attributed to the relatively low amount of pelagic primary productivity and ergo benthic organic matter

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Declining nitrate concentrations may be as important as anoxia itself to GSOB mat proliferation. Anoxia could trigger the uptake of NO_3^- into bacterial vacuoles, creating declining NO_3^- concentrations that are more favorable to DNRA in the bottom water. In these conditions, GSOB in the SBB benthic environment could utilize their ability to perform DNRA to out-compete similar denitrifying taxa, and proliferate into thick, contiguous mats.High ratios of electron donor (organic matter or sulfide) to electron acceptor (nitrate) encourage DNRA over denitrification (Marchant et al., 2014; Hardison et al., 2015; Caffrey et al., 2019; Kessler et al., 2019; An and Gardner, 2002). In these nitrate-deficient areas in the ocean, DNRA linked to anaerobic ammonium oxidation (anammox) can be more thermodynamically favorable and thus organisms that participate in this consortium could have a competitive advantage over other denitrifying organisms (Jensen et al., 2011). NO_2^- was at or near-zero concentrations in the sediment porewater of all stations, except in the 0-1 cm depth interval of two stations (SDRO and NDT3-A) featuring GSOB mats (Suppl. Table 1). These spikes in NO_2^- (an… [1]

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delivery in the Eastern Arabian OMZ compared to other upwelling systems (Naik et al., 2017). The organic matter content of the sediment appears to be important in the proliferation of GSOB mats; too much TOC could result in toxic levels of sulfide at the sediment-water interface (*Beggiatoa* exhibit an aversion to sulfidic sediments but toxicity has not been quantified) (Preisler et al., 2007), whereas too little sulfide would not provide enough electron donor for the GSOB's chemoautotrophic metabolism.

The profiles of several indicators for benthic anaerobic organic matter remineralization (total alkalinity, DIC, PO_4^{3-}, NH_4^+) increased in steepness with increasing water depth (Figs. 2 A-E & 3A-F). One divergence from this trend can be seen in PO_4^{3-} profiles from the shallow C- and D-stations, which also featured low rates of sulfate reduction. PO_4^{3-} profiles in these sediments track closely to Fe^{2+} profiles; both solutes dip in concentration in areas with visible iron sulfide formation (e.g., 5-11 cm in NDT3-D as seen in Fig. 2A). Additionally, several stations that exhibited high sulfate reduction rates in surface sediment (e.g., SDT1-A) showed almost no change in PO_4^{3-} at depths below 5 cm (e.g., Fig. 2 K-O compared to Fig. 2 A-E). This phenomenon has been previously documented in SBB sediment and is attributed to the precipitation of carbonate fluorapatite (Reimers et al., 1996a). The confinement of these flat PO_4^{3-} profiles to stations with >100 nmol cm^{-3} d^{-1} sulfate reduction in surface sediment suggests that this mineralogical sink of PO_4^{3-} in SBB sediment may be dependent on high sulfate reduction rates, owing to the bicarbonate produced by sulfate reduction (Reimers et al., 1996a), and is not found throughout the basin. Flat PO_4^{3-} profiles were also reported from the transiently deoxygenated portion of the Peruvian OMZ, where phosphate mineral precipitation has been documented (Noffke et al., 2012). Similar to the shallow margins of the SBB, PO_4^{3-} in

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Mauritanian OMZ porewater tracks closely with changes in porewater Fe^{2+} (Schroller-Lomnitz et al., 2019), indicating that iron mineralization/dissolution mechanisms hold a greater influence on PO_4^{3-} concentrations under hypoxic bottom waters.

4.4 Iron oxide exhaustion is critical for raising the sulfate reduction zone close to the sediment-water interface in Santa Barbara Basin sediment.

The hyper-accumulation of NO_3^- by GSOB mats potentially facilitates sulfate reduction close to the sediment-water interface in the SBB (e.g., NDRO and NDT3-A as seen in fig. 2N and 2O) by starving the sediment of this more powerful electron acceptor. The rise of the sulfate reduction zone at NDT3-C (fig. 2L) further suggests that the exhaustion of iron oxides and the formation of iron sulfide below the sediment-water interface may play a crucial role in controlling the distribution of sulfate reduction as well. SBB sediments showed a wide vertical and horizontal heterogeneity of redox states based on visual appearance (Fig. 1A-K). Sediment beneath the hypoxic bottom water at the shallowest D-stations was reddish, consistent with a high content of iron oxides. Interestingly, porewater Fe^{2+} concentrations in shallower parts of the basin (e.g., NDT3-D, max. ~700 µM Fe^{2+}) were an order of magnitude larger than those found in both the Peruvian (max ~60 and ~30 µM Fe^{2+}, respectively; (Noffke et al., 2012; Plass et al., 2020) and Mauritanian (max. ~50 µM Fe^{2+}; Schroller-Lomnitz et al 2019) OMZ. It should be noted that porewater samples for geochemical analyses were unfiltered and hence reported iron concentrations include aqueous, colloidal, and nanoparticulate species. Regardless, all these components represent bioavailable sources of iron. Further, since filtering through 0.45 or 0.2 µm filters only removes a fraction of colloidal particles and no nanoparticles (Raiswell and

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Canfield, 2012), potential surplus porewater iron in SBB samples in comparison to studies that applied filtering was likely minimal.

Deeper in the basin, bands of black sediment that appear mid-core at NDT3-C (6-14 cm) and SDT3-C (6-10 cm) indicate the formation of iron sulfides as a result of sulfide produced by sulfate reduction (Canfield, 1989). Both D-stations had similar bottom water conditions (Table 1), sulfate reduction rates (Fig. 3W-AG), porewater concentrations of solutes (Figs. 2 and 3), and visual sediment characteristics (Section 3.1). On the contrary, there are some noticeable differences in the porewater geochemistry between the two C-stations. At the C-stations, peaks in sulfate reduction were in the surface sediment, above the iron sulfide layers, and declined below approximately 4 cm, indicating a discrepancy between observed peak sulfate reduction activity and the mineralogical clues left behind by the process. Comparing NDT3-C and SDT3-C, iron sulfide formation (Table 1B compared to 1J), porewater Fe^{2+} profiles (Fig. 2G compared to Fig. 3H), and sulfate reduction rates (Fig. 2L compared to Fig. 3N) show that NDT3-C sediment appears to be in transition towards a more sulfidic state, while SDT3-C sediments still mimic the shallow D-station ferruginous state. While sulfate reduction rates for B-stations are not available due to technical issues during sample processing, porewater Fe^{2+} profiles show a similar difference between the north and south basin (Fig. 2H compared to Fig. 3I) as did visual sediment characteristics (Table 1C compared to 1I). This difference in biogeochemical profiles and apparent minerology between the north and south C- and B-stations could be a result of hydrographic and/or bathymetric differences in the basin (Sholkovitz and Gieskes, 1971; Bograd et al., 2002), but a discernable link between the differences in sediment biogeochemistry and the differences in bottom water oxygen (Table 1) need to be further explored.

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Moved up [2]: NDT3-C porewater Fe^{2+} concentration (Fig. 2G) peaked in the top 1 cm of sediment (similar to deeper stations) while SDT3-C porewater Fe^{2+} concentration (Fig. 3H) peaked around 5-cm sediment depth.

Moved up [3]: NDT3-C sediment (Table 1B) exhibited iron sulfide formation from approx. 6-14 cm sediment depth, while SDT3-C sediment (Table 1J) had a much narrower band around 8-10 cm (the same depth at which Fe^{2+} concentrations decrease in the porewater).

Moved up [4]: the sulfate reduction rate at NDT3-C (Fig. 2L) mirrored deeper station profiles (e.g., NDRO in Fig. 2O) rather than other shallow station profiles (e.g., SDT3-C in Fig. 3N). While sulfate reduction rates for B-

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Deeper in the basin (depocenter and A-stations), porewater Fe^{2+} concentrations in sediment beneath anoxic bottom water (max. 84 µM Fe^{2+}) were similar to concentrations found below the Peruvian OMZ in 2008 under anoxic bottom water conditions (78 m water depth, max. 80 µM Fe^{2+}) (Noffke et al., 2012). These deep basin porewater Fe^{2+} concentrations were, however, an order of magnitude larger than those found at a similar site on the Peruvian shelf (75 m water depth, max. 1 µM Fe^{2+}) in 2017 during a kelvin-wave-associated "Coastal El Niño" event that created oxygenated bottom waters during the sampling and the disappearance of previously observed dense GSOB mats (Plass et al., 2020). As the SBB water column was undergoing rapid deoxygenation in the weeks preceding this study (Qin et al., 2022), the sediments below the sill appeared to be actively shifting from a ferruginous state to a sulfidic state, with this change starting around the C-stations and being complete in the depocenter. Comparing apparent iron sulfide formation with dips in porewater Fe^{2+} concentrations in C-station profiles (Fig. 1B compared to Fig. 2G and Fig. 1J compared to Fig. 3H) signals a shift away from a ferruginous state occurring just below the SBB sill.

C-station porewater Fe^{2+} concentrations and sulfate reduction rates indicate that migration of the sulfate reduction zone towards the sediment-water interface is associated with iron sulfide formation deeper in the sediment. The activity (or lack thereof) of cable bacteria, which are able to bridge the gap between the oxidized sediment-water interface and reduced sediment below using a biofilament (Pfeffer et al., 2012), could explain the interplay between sulfate reduction and iron cycling in SBB sediments. Cable bacteria, such as *Ca.* Electronema sp., contain genes involved in DNRA (Kjeldsen et al., 2019) and can perform nitrate reduction in incubation

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experiments (Marzocchi et al., 2014), but their direct transformation of NO_3^- in the environment appears limited (Kessler et al., 2019) and they appear to be inactive in anoxic aquatic environments (Seitaj et al., 2015; Marzocchi et al., 2018; Hermans et al., 2019). Cable bacteria primarily conduct aerobic sulfide oxidation (Pfeffer et al., 2012), though they can also utilize Fe^{2+} as an electron donor (Seitaj et al., 2015). The maximum recorded filament length of cable bacteria is 7 cm (Van De Velde et al., 2016), though typically they are not stretched completely vertically through the sediment. The appearance of black sediment in the SBB C-station sediments, starting at approx. 5 cm depth, could be an indication that cable bacteria are oxidizing iron sulfides at that sediment depth and prevent their formation at shallower depths. Further, cable bacteria have been found to directly compete with GSOB in transiently deoxygenated systems, with cable bacteria active under oxygenated conditions and GSOB active in anoxic conditions (Seitaj et al., 2015). Cable bacteria can also prevent the benthic release of sulfide, which is toxic to many pelagic animals, via the creation of an iron-oxide buffer (formed through Fe^{2+} oxidation) in near-surface sediments (Seitaj et al., 2015). Therefore, if cable bacteria activity in the SBB decreased with declining oxygen concentrations below the sill, the iron oxide buffer they create could have been reduced, encouraging the sulfate reduction zone to migrate towards the sediment surface (as seen at NDT3-C). Cable bacteria can sometimes be detected in sediments via a slight pH increase (typically pH > 8) (Schauer et al., 2014), which was not reflected in our pH results, but this phenomenon is more typically seen in the laboratory and not the field (Hermans et al., 2019).

4.5 Iron and phosphate flux into SBB bottom water is a feature of transient deoxygenation.

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Release of dissolved iron and phosphate from sediment below anoxic waters is a well-documented phenomenon (e.g., (Mortimer, 1941; Van Cappellen and Ingall, 1994; Van De Velde et al., 2020; Noffke et al., 2012)) and this phenomenon is seen in the SBB as well. As postulated previously (Kuwabara et al., 1999), basin flushing oxidizes iron sulfides at the sediment-water interface, providing ample substrate for microbial iron reduction once anoxia returns. This iron reduction initiates high rates of Fe^{2+} release from SBB depocenter sediment (Fig. 5). Iron reduction further releases iron-bound PO_4^{3-} (Mortimer, 1941) as seen by high benthic fluxes of PO_4^{3-} at the depocenter (Fig. 5), although notably some of this PO_4^{3-} release is likely attributed to organic matter degradation (Van Cappellen and Ingall, 1994). High benthic Fe^{2+} and PO_4^{3-} fluxes were also seen on the Peruvian shelf during transient anoxia (Noffke et al., 2012). The release of these solutes was interpreted to be sourced from a layer of reactive iron hydroxides existing near the sediment surface, likely established during a recent oxygenation event. Similar conditions, i.e., visibly oxidized (reddish) sediment laminae and a thin zone of iron reduction apparent from a peak in Fe^{2+} at the sediment-water interface, were found in sediment from the SBB depocenter. Deeper in the persistently anoxic core of the Peruvian OMZ, sediment appears to have little to no flux of Fe^{2+} and PO_4^{3-} into the bottom water (Noffke et al., 2012). Here, iron at the sediment-water interface is hypothesized to be locked up in iron sulfides, which are rarely re-oxidized due to persistent anoxia.

In a different study from the Eastern Gotland Basin in the Baltic Sea, enhanced elemental fluxes were observed during a decadal oxygen flushing event (Van De Velde et al., 2020), which was attributed to enhanced elemental recycling, or cycles of mineral precipitation in the water column followed by mineral dissolution once those minerals sink to the sediment. Notably, the iron flux

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observed in the Eastern Gotland Basin (max. 0.08 mmol m^{-2} d^{-1}) (Van De Velde et al., 2020) was two orders of magnitude lower than the flux observed in the anoxic depocenter of the Santa Barbara Basin (max. 4.9 mmol m^{-2} d^{-1}). It is further notable that benthic fluxes of PO_4^{3-} in the SBB depocenter were also an order of magnitude higher than fluxes in the Eastern Gotland Basin's hypoxic transition zone (3.6 vs. 0.23 mmol PO_4^{3-} m^{-2} d^{-1}) - both of which contained GSOB mats, but while the SBB was anoxic and the Eastern Gotland Basin was hypoxic (Noffke et al., 2016). These differences in Fe^{2+} and PO_4^{3-} flux between the SBB and the Eastern Gotland Basin suggest that reoxidation of the sediment-water interface during basin flushing, as opposed to water-column-associated reoxidation, appears to encourage higher benthic iron fluxes.

Fe^{2+} and PO_4^{3-} flux from the SBB depocenter were also approximately five times higher (Fig. 5) compared to the anoxic Peruvian shelf (4.9 vs. 0.9 mmol Fe^{2+} m^{-2} d^{-1} and 3.6 vs. 0.8 mmol PO_4^{3-} m^{-2} d^{-1}, respectively) (Noffke et al., 2012). Based on Fe^{2+} profiles, the zone of iron reduction in Peruvian shelf sediments extended down to approx. 10 cm, while the zone appeared to be much shallower and narrower (less than the top 5 cm) in the SBB depocenter. These differences in magnitude of Fe^{2+} concentration and Fe^{2+} and PO_4^{3-} flux between the SBB depocenter and the Peruvian shelf could be attributed to differences in the recency and magnitude of reoxygenation events. The release of Fe^{2+} from sediment into the bottom water could create a buffer against reoxygenation in transiently deoxygenated systems, giving a competitive advantage to anaerobic benthic metabolisms (Dale et al., 2013; Wallmann et al., 2022). Additionally, both Fe^{2+} and PO_4^{3-} release from the SBB sediment could allow for higher rates of primary productivity if those constituents diffused into the photic zone (Robinson et al., 2022). The fate of Fe^{2+} and

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PO_4^{3-} diffusing into SBB waters from the sediment-water interface is a focus of ongoing work within the basin.

5 Conclusions

This research expands upon the wealth of science already conducted in the SBB and other transiently deoxygenated environments by examining changes in benthic biogeochemistry promoted by the onset of anoxia. Our main interpretations are summarized in Fig. 7. We found that GSOB mats proliferate in the SBB where the bottom water is anoxic and nitrate concentrations are declining (Fig. 7, A- and depocenter stations). Nitrate uptake by SBB sediment is similar regardless of GSOB mat presence, but these mats appear to initiate a shift from denitrification to DNRA as the primary nitrate reduction pathway (Fig. 7, beginning at B-stations). The zone of sulfate reduction rises to the sediment-water interface where GSOB mats are present (Fig. 7, A-stations), possibly because the hyper-accumulation of nitrate into their intracellular vacuoles starves the environment of this more powerful electron acceptor. However, following the natural order of electron acceptor utilization (Boudreau and Jorgensen, 2001), iron oxides near the sediment-water interface must be exhausted before sulfate reduction can dominate surface sediments and GSOB mats can proliferate in the SBB (Fig. 7, depocenter stations). If anoxic events become longer and more frequent in the SBB because of global warming (see, e.g., (Qin et al., 2022; Stramma et al., 2008)), the iron oxide buffer built up in shallower basin depths could be exhausted, allowing for surface sulfate reduction and the proliferation of GSOB mats in shallower margins of the basin than currently seen. Further, the same transient deoxygenation that allows for these mats to re-stablish themselves also allows for a high Fe^{2+} and PO_4^{3-} flux into the SBB water column. In order to fully understand the complex

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Deleted: initiating a shift from primarily denitrification to an increase in DNRA. We conclude that GSOB mat proliferation in the SBB is confined to areas of the benthic environment with anoxic (though not completely anitric) bottom water. The sulfate reduction zone is elevated to the surface sediments underneath theses mats, but mat presence alone seems insufficient to change the depth of sulfate reduction

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changes in the benthic environment in response to deoxygenation, genomic and molecular work of the upper sediment community needs to be characterized. Overall, the insights gleaned from this research will aid in the understanding of fundamental biogeochemical changes that occur when marine environments become anoxic.

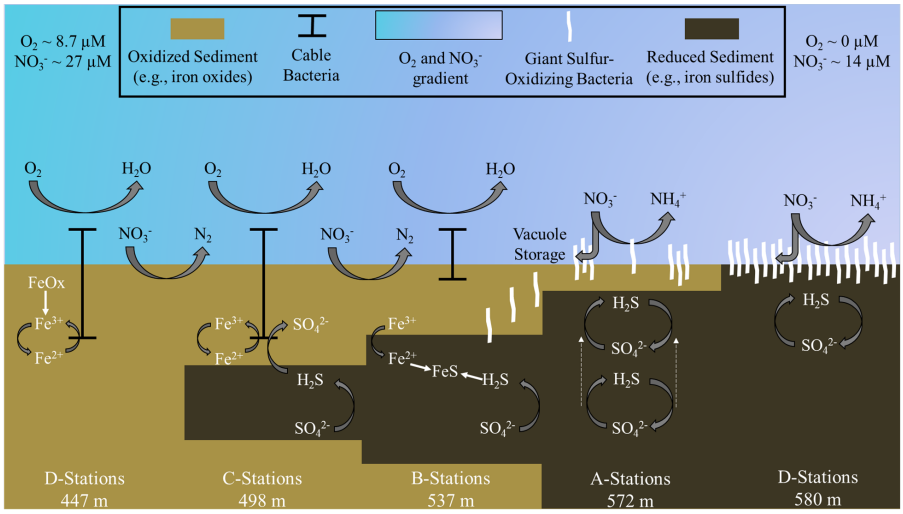

Figure 7: Schematic of biogeochemical processes in the Santa Barbara Basin along the depth gradients studied in October/November 2019. Teal to Lavender gradient represents a decline in O_2 and NO_3^- concentrations with basin depth. In the shallower, hypoxic basin (D-stations), denitrification and iron reduction are dominant and reduced iron is rapidly re-oxidized in near-surface sediment by cable bacteria. Deeper in the basin (A-stations and depocenter), nitrogen cycling shifts towards dissimilatory nitrate reduction to ammonia (DNRA). Reduced iron combines with sulfide, produced by sulfate reduction, diffusing from deeper sediment layers to form iron sulfides. As oxygen concentration approaches zero between the A-stations and the basin's depocenter, giant sulfur-oxidizing bacteria hyper-accumulate nitrate in their intracellular vacuoles. Nitrate removal combined with the exhaustion of available iron oxides in the near-surface sediments allows the zone of sulfate reduction to migrate towards the surface (see dashed arrows at A-stations), providing the giant sulfur-oxidizing bacteria with sufficient reduced sulfur to proliferate into thick, contiguous mats. Note: Figure is not to scale, and processes are simplified to illustrate main concepts.

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Data availability.

Biogeochemical data presented in this manuscript are accessible through the Biological & Chemical Oceanography Data Management Office (BCO-DMO) at the following landing pages: https://www.bco-dmo.org/dataset/867007; https://www.bco-dmo.org/dataset/867113; https://www.bco-dmo.org/dataset/867221; https://www.bco-dmo.org/dataset/896706

Author contributions.

TT, DV, FK, NL, and JT designed the project. DJY, SK, JT, DR, and TT processed sediment cores at sea. DJY conducted geochemical analyses of sediment porewater and benthic flux chamber water. DJY prepared TOC and TON samples. DR and SK analyzed sediment porosity and density. TT and SK performed shipboard sulfate reduction incubations. DJY and DR conducted sulfate reduction analyses. DJY, NL, and JT transformed and interpreted ROV Jason data. FJ and FW operated BFC and microprofilers and analyzed associated data. XP conducted ^{15}N experiments and analyses. All authors reviewed and edited the manuscript.

Competing interests.

At least one of the (co-)authors is a member of the editorial board of Biogeosciences.

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