H₂S events in the Peruvian oxygen minimum zone facilitate enhanced dissolved Fe concentrations

Christian Schlosser¹, Peter Streu¹, Martin Frank¹, Gaute Lavik², Peter L. Croot¹,³, Marcus Dengler⁴ & Eric P. Achterberg¹

Dissolved iron (DFe) concentrations in oxygen minimum zones (OMZs) of Eastern Boundary Upwelling Systems are enhanced as a result of high supply rates from anoxic sediments. However, pronounced variations in DFe concentrations in anoxic coastal waters of the Peruvian OMZ indicate that there are factors in addition to dissolved oxygen concentrations (O₂) that control Fe cycling. Our study demonstrates that sediment-derived reduced Fe (Fe(II)) forms the main DFe fraction in the anoxic/euxinic water column off Peru, which is responsible for DFe accumulations of up to 200 nmol L⁻¹. Lowest DFe values were observed in anoxic shelf waters in the presence of nitrate and nitrite. This reflects oxidation of sediment-sourced Fe(II) associated with nitrate/nitrite reduction and subsequent removal as particulate Fe(III) oxyhydroxides. Unexpectedly, the highest DFe levels were observed in waters with elevated concentrations of hydrogen sulfide (up to 4 µmol L⁻¹) and correspondingly depleted nitrate/nitrite concentrations (< 0.18 µmol L⁻¹). Under these conditions, Fe removal was reduced through stabilization of Fe(II) as aqueous iron sulfide (FeS₄aqu) which comprises complexes (e.g., FeSH⁺) and clusters (e.g., Fe₂S₃[H₂O₄]). Sulfidic events on the Peruvian shelf consequently enhance Fe availability, and may increase in frequency in future due to projected expansion and intensification of OMZs.
to similar structural homologies found for aqueous zinc and copper sulfide clusters, it has been suggested that the structure of the cluster in solution determines the form of the initial particulate phase. However, mackinawite formation is thermodynamically favored when the ion activity product of H$_2$S and Fe(II) exceeds the thermodynamic stability product of FeSm ($\log K_{sp} = -3.6$). This condition is typically met in euxinic sediments (e.g. Fe(II) > 30 µmol L$^{-1}$; H$_2$S > 10 µmol L$^{-1}$), and represents the initial step of Fe pyrite (FeS$_2$) formation. The formation of FeS$_m$ is also reported to occur in anoxic coastal waters and has been observed in permanently euxinic bottom waters of the Framvaren fjord (Norway), where Fe(II) and H$_2$S levels are in the millimolar range. Because H$_2$S concentrations in these waters are extremely high, Fe sulfide precipitates in the water column as framboidal pyrite. It is, however, unclear whether favorable conditions for Fe sulfide precipitation also occur in the coastal OMZ regions off Peru. The Peruvian OMZ features extremely low O$_2$ concentrations (<50 nmol kg$^{-1}$), with anoxic waters prevailing at depths between 10 to 500 m, which in near shore regions are in direct contact with shelf sediments. The positioning of the OMZ over euxinic shelf sediments facilitates benthic supply of H$_2$S and Fe(II), which accumulates periodically in the overlying waters. H$_2$S and DFe in the Peruvian OMZ waters have been reported to reach concentrations as high as 13 µmol L$^{-1}$ and 300 nmol L$^{-1}$, respectively, during the upwelling season in austral summer and the formation of Fe(II)S minerals resulting in DFe removal has been suggested.

Here we present new data from three locations with different environmental settings on the Peruvian shelf regarding DFe, Fe(II), H$_2$S, nitrate (NO$_3^-$), nitrite (NO$_2^-$), and ammonium (NH$_4^+$) (with the sum of all N species = DIN), O$_2$, and dissolved inorganic phosphorous (DIP) expressed as P$^*$ (P$^*$ = DIP – DIN/16). We examine the mechanisms that control DFe in the Peruvian OMZ, under contrasting conditions of presence and absence of enhanced water column H$_2$S concentrations.

Results and Discussion

Water column anoxia occurred at all three study sites during the upwelling season in December/January 2008/09 (Fig. 1A–C). The surface mixed layer extended down to ca. 10 m depth at site 1, 20 m at site 2 and 60 m depth at site 3, and was assessed using a fixed density difference criterion ($\Delta \sigma = 0.125$). At all sites, O$_2$ concentrations decreased below the surface mixed layer to levels below the LOD of the CTD mounted O$_2$ sensors. At site 2, O$_2$...
OMZ 9,20,21. In agreement with our results, these studies showed that the reduced Fe(II) form represented the main analyzed just for site 2. Several studies with focus on Fe speciation have been already conducted in the Peruvian 30 m water depth, DFe occurred predominantly in the reduced Fe(II) form (Fig. 1B), an Fe species that has been

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\text{Fe^{II}} = 0.2 \text{ mol L}^{-1}
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**Figure 2.** Distribution of Fe(II) species in percent (dissolved Fe(II) (black), soluble Fe (II) complexes/clusters (FeS_{aq}) (red), and particulate FeS_{pm} (mackinawite) (blue)) at a constant Fe(II) concentration of 0.2\text{ mol L}^{-1} and under increasing hydrogen sulfide (H\textsubscript{2}S) concentrations. The red dashed line represents the average H\textsubscript{2}S concentration in subsurface waters <50 m at site 2 in the Peruvian OMZ.

was 75 \text{ mol L}^{-1} at 2 m depth, and decreased below 20 m to levels undetectable for the STOX sensor. The strong vertical oxygen gradient in the near-surface layers was a consequence of enhanced O\textsubscript{2} consumption by microbial organic matter remineralization. At all three sites the anoxic conditions extended down to the seafloor.

The DFe levels in our study region were considerably higher than those reported for other coastal regions where OMZs prevail, e.g. 1.2–6.3 \text{ mmol L}^{-1} on the north west African shelf 1. The profiles of DFe concentrations at sites 1 and 3 differed pronouncedly from site 2 (Fig. 1A–C). Dissolved Fe concentrations at site 1 increased from 2 \text{ mmol L}^{-1} in the surface layer to 30 \text{ mmol L}^{-1} at 80 m depth. Over a period of 24 h, five separately sampled casts indicated that DFe profiles remained essentially constant (Fig. 1A). Similar to site 1, DFe concentrations at site 3 increased from 2 \text{ mmol L}^{-1} in the surface layer to 60 \text{ mmol L}^{-1} at 90 m depth. Bottom water DFe values at both sites agreed well with reported values for anoxic Peruvian shelf bottom waters of 30 to 60 \text{ mmol L}^{-1} 1,7,17,19–21.

In contrast, DFe at site 2 increased from very high values of 80 \text{ mmol L}^{-1} in the surface waters to ca. 200 \text{ mmol L}^{-1} below 30 m depth, and remained relatively constant at ca. 200 \text{ mmol L}^{-1} down to the seafloor (Fig. 1B). Below 30 m water depth, DFe occurred predominantly in the reduced Fe(II) form (Fig. 1B), an Fe species that has been analyzed just for site 2. Several studies with focus on Fe speciation have been already conducted in the Peruvian OMZ 20,21. In agreement with our results, these studies showed that the reduced Fe(II) form represented the main DFe species in the anoxic part of the water column. However, Fe(II) concentrations in the water column determined during those studies were lower than found during our present study (Fe(II) = 15–73 \text{ mmol L}^{-1} 1,20,12–47 \text{ mmol L}^{-1} 19,0.2–16 \text{ mmol L}^{-1} 21).

The water column at site 2 featured enhanced H\textsubscript{2}S concentrations, coinciding with high DFe levels (Fig. 1B,E). However, an increase in H\textsubscript{2}S concentrations at site 2 was observed with depth including a mid-depth maximum at 50 m (~4 \text{ µmol L}^{-1}; Fig. 1E) and ~3 \text{ µmol L}^{-1} near the seafloor. Elevated DFe concentrations of up to 300 \text{ mmol L}^{-1} during a H\textsubscript{2}S event reaching ~10 \text{ µmol L}^{-1} on the Peruvian shelf in 2012 have also been reported by Scholz, et al. 19, with DFe and H\textsubscript{2}S being released by anoxic sediments.

Removal of DFe through the formation of Fe(II) sulfide minerals has been reported for euxinic sediments 27, deep-sea hydrothermal vent systems 33, eutrophic fjord waters 2, and anoxic waters in the bottom boundary layer of the Peruvian OMZ 20. Using Visual MINTEQ, 3.1 44, we calculated the species distribution of dissolved Fe(II), aqueous sulfide (FeS_{aq}; log K = 5.62 24), and Fe(II)S in the crystal structure of mackinawite (log K = −3.62 24), an ubiquitous mineral in low temperature aqueous environments, to determine if Fe(II) formation in the water column at site 2 was feasible (Fig. 2) (concentrations of model parameters used are listed in supplementary material S1). At 13°C and pH 7.65, which is typical for subsurface waters on the Peruvian shelf 65,66, and concentrations of Fe(II) of 200 \text{ mmol L}^{-1} and H\textsubscript{2}S levels of 3 \text{ µmol L}^{-1}, which reflect the bottom water composition at site 2, the ion activity product of the educts (log IAP = −5.466) is below the typical apparent solubility product of mackinawite of log K_{sp} = −3.64 44 (undersaturation with respect to mackinawite: log IAP - log K_{sp} < 0). To validate the robustness of the model a sensitivity test was executed by increasing pH and temperature which would increase log IAP and enhance the likelihood of mackinawite formation. At 40°C and pH 8.5, obviously very unrealistic conditions for the Peruvian OMZ, the log IAP increased slightly to −4.61. This suggests that under the transient conditions typically encountered, the formation of mackinawite is thermodynamically unfavorable in the anoxic bottom waters off Peru.

The mackinawite formation will only commence at Fe(II) and H\textsubscript{2}S concentrations in the higher micromolar range. Our modelling indicates that at pH 7.65, 13°C and 200 mmol Fe(II) L\textsuperscript{-1} more than 2 mmol L\textsuperscript{-1} H\textsubscript{2}S are required to facilitate the formation of mackinawite (Fig. 2). Further, noticeably less H\textsubscript{2}S is required (~10 mmol L\textsuperscript{-1}) at higher Fe(II) levels of >3 \text{ µmol L}^{-1} to attain mackinawite saturation. These required enhanced H\textsubscript{2}S and Fe(II) concentrations for the formation of Fe(II) sulfide minerals in seawater are in agreement with other modelling studies (Fe ≥ 3 \text{ µmol L}^{-1}; H\textsubscript{2}S ≥ 50 \text{ µmol L}^{-1} 44) and earlier observations in anoxic regions such as the Framvaren fjord (Fe ≥ 2 \text{ µmol L}^{-1}; H\textsubscript{2}S ≥ 11 \text{ mmol L}^{-1} 48), Black Sea (Fe ≥ 0.3 \text{ µmol L}^{-1}; H\textsubscript{2}S ≥ 30 \text{ µmol L}^{-1} 49,50), and Baltic Sea (Fe ≥ 2.34 \text{ µmol L}^{-1}; H\textsubscript{2}S ≥ 52 \text{ µmol L}^{-1} 131).

In H\textsubscript{2}S free seawater more than 75% of Fe(II) occurs as a truly dissolved free cation, while the remainder will form complexes with hydroxide (OH\textsuperscript{−}), carbonate (CO\textsubscript{3}\textsuperscript{−}), and chloride (Cl\textsuperscript{−}) ions 52. In the presence of an excess
of H₂S over Fe(II) and above pH 7.5, Feₙₑq becomes the dominant Fe(II) species²⁴ (Fig. 2). Formation of thiolates in sediments⁵³ may result in Fe(II)-thiol complexes, with thiolates also facilitating reduction of Fe(III)⁵⁴. Organic ligands complexing with Fe(III) serve a similar purpose in oxic waters to stabilize Fe⁶⁵. In the sulfide-containing Peruvian waters at site 2, the Fe distribution in the water column was therefore controlled by the total Fe flux from the sediments rather than the equilibrium concentrations of their solid phases. Prolonged sulfidic periods will therefore result in an increase in DFe concentrations in the anoxic water column, as formation of Fe(II)S precipitates like mackinawite is unfavorable at the Fe(II) and H₂S concentrations so far observed in this region.

The formation of Feₙₑq stabilizes DFe via an increased soluble pool (as opposed to oxygenated waters in which DFe is dominated by Fe(III)-ligands and colloids⁶⁶), and hence facilitates vertical diffusive DFe fluxes in the Peruvian OMZ. Vertical diffusive DFe fluxes were determined for site 2 by combining eddy diffusivities determined from microstructure measurements sampled in the same region during January 2012 (FS Meteor cruise M92)⁶⁸ and DFe concentration from this study. Altogether, 102 microstructure profiles were collected at shelf stations with bottom depth between 80 m and 100 m. The microstructure shear and temperature measurements were performed using a MSS90-D profiler (S/N 32, Sea & Sun Technology). Standard processing procedures were used to determine the rate of kinetic energy dissipation of turbulence in the water column (please see Schafstall et al.⁶⁹ for a detailed description). Subsequently, eddy diffusivities were determined from Kₓ = ΓeN⁻² where N is stratification and Γ is mixing efficiency for which a value of 0.2 was used (Fig. S1).⁷⁰ Between mid-deep waters (40 m) and the surface (10 m), an average eddy diffusivity of Kₓ = 3.1 × 10⁻⁴ m² s⁻¹ was obtained (Fig. S1). We employed the method of de Jong et al.⁷¹ and obtained a vertical diffusive DFe flux PDFe = KₓDFe/ε (with z being depth) from mid-depth waters at 40–60 m into the surface mixed layer of 101 μmol m⁻² d⁻¹. Upper and lower 95% confidence limits were determined to be 164 μmol m⁻² d⁻¹ and 69 μmol m⁻² d⁻¹ based on a Gaussian error propagation⁷². This vertical diffusive flux is in a range similar to reported benthic DFe fluxes (10–866 μmol m⁻² d⁻¹) from shallow Peruvian shelf sediments⁶. It indicates an important role of Feₙₑq in the anoxic waters of the Peruvian OMZ, which through stabilization facilitates Fe supply to surface ocean phytoplankton communities on the shelf and possibly further afield by filaments and mesoscale eddies that move off shore, away from the coast⁶⁶.

In the absence of H₂S in the anoxic water column at sites 1 and 3, DFe concentrations were 72 to 94% lower in bottom waters than at site 2. Vertical diffusive water column fluxes calculated using a Kₓ = 3.1 × 10⁻⁴ m² s⁻¹ at sites 1 and 3 were concurrently reduced by 88 to 97% (7.60 ± 4.13 μmol m⁻² d⁻¹), which indicates that supply and removal processes in anoxic water columns may differ and may depend on controls other than O₂.

Organic matter remineralization processes in anoxic environments are mainly controlled by anaerobic microbial processes involving nitrogen, sulfur and Fe for electron-transfer reactions⁶¹. Of relevance for the Peruvian OMZ is the reduction of nitrate, coupled with the oxidation of H₂S by filamentous bacteria of the family Desulfobulbaceae⁶²,⁶³. A similar coupling of anaerobic microbial denitrification with Fe(II) oxidation has been documented for chemolithothrophic organisms in freshwater sediments⁶⁴,⁶⁵, suboxic aquifers⁶⁶, marine coastal sediments⁶⁷, and for the anoxic water column off the coast of Peru, where Fe(II) oxidizers such as Marinobacter aquaeolei are active⁶⁸.

Transient accumulations of H₂S have been reported for anoxic Peruvian, Namibian and Indian shelf waters that were depleted in nitrate/nitrite⁶⁶–⁷². These euxinic waters form the extreme end point of ocean conditions, with fully oxygenated waters being the opposite end point⁷³. We suggest that the coupled process of anaerobic microbial denitrification and H₂S oxidation depletes nitrate and allows DFe to accumulate in anoxic bottom waters in the Peruvian OMZ. The extent of anaerobic microbial denitrification in the Peruvian anoxic environments is mainly controlled by H₂S levels and less by Fe(II) given that H₂S concentrations are an order of magnitude higher than those of Fe(II).

Depending on H₂S and nitrate concentrations, two distinct and one advanced scenarios can be envisaged (Fig. 3). Scenario 1: Under conditions of an anoxic water column (no measurable H₂S) above the sediments and in the presence of nitrate and nitrite (i.e. denitrification and anammox has not fully removed nitrate and nitrite) bacteria at the sediment-water interface will reduce these nitrogen species and thereby utilize both H₂S and Fe(II). During that process all the sulfide and a significant fraction of the Fe(II) will be oxidized. Insoluble Fe(III)oxyhydroxide particles are consequently formed near the sediment-bottom water interface, leading to an accumulation of reactive solid Fe phases near the sediment surface. Any Fe(II) that diffuses across the sediment-bottom water interface into the water column is then oxidized by O₂/H₂O₂ or, in the absence of O₂, via nitrate-dependent Fe(II) oxidizing microbes with the Fe remaining either as organically complexed Fe(III) (Feₐq), or is lost by scavenging processes and insoluble particle formation, as was documented by Heller et al.⁷⁸. This situation was observed at sites 1 and 3 (Fig. 1A–C and F) and is illustrated in Fig. 3 (left schematic).

Scenario 2: Reductive removal of the nitrate and nitrite pool in the sediment, in association with H₂S oxidation, allows enhanced sediment-water H₂S and Fe(II) fluxes resulting in an accumulation of these species in the water column. The oxycline in the upper water serves as a removal filter, with e.g. oxidation of Fe(II) to Fe(III) in the presence of oxygen and hydrogen peroxide⁶⁴. This scenario is proposed for site 2 (Fig. 1B and E) and resulted in the sulfidic event with H₂S concentrations of up to 4 μM and Fe(II) concentrations of up to 200 nM (Fig. 3, middle schematic). We assume that such a scenario is temporarily confined. Advanced scenario 2: Long lasting release of sedimentary H₂S and Fe(II) raises concentrations of both compounds in the water column, with highest concentrations expected at the sediment-bottom water interface. We hypothesize that under such conditions, log IAP > log Kₛ sp, resulting in the formation of mackinawite at the sediment-bottom water interface (Fig. 3, right schematic). Due to a lack of observational data, we do not know if such an advanced scenario can occur in the more turbulent Peruvian OMZ, or if it just arises in water bodies as stagnant as the Black Sea⁷⁹ and the Framvaren fjord⁸⁰.
The coupling of Fe(II) and nitrite in OMZs is under debate in the scientific community. Hong and Kester found a linear relationship between nitrite and Fe(II) for samples from the OMZ along the Peruvian shelf and suggested this represented a common sediment source. More recently, several trace metal studies conducted in open ocean OMZs observed a deep Fe(II) maximum that coincided with elevated nitrite and DFe (Fe(II) + Fe(III)) levels at the same depths. In the Peruvian OMZ a filament with elevated Fe(II) and nitrite concentrations in the center of the otherwise DFe rich OMZ has been located in the anoxic core zone between 300 m and 400 m water depth. The filament extended from the coast to ca. 1,000 km off-shore and was related to off-shore Fe transport. A similar pattern has also been described for the OMZ in the Arabian Sea and both were interpreted as a coupling between nitrate reduction and Fe(II) accumulation, with Fe(III) being microbially reduced. In contrast, Rickard and Luther III, Scholz, et al., and Heller, et al., suggested a role for nitrite in the oxidation of Fe(II) and an accumulation of particulate Fe oxyhydroxides in the anoxic water column off Peru.

Periodic sulfidic events occur in the Peruvian OMZ. Our observations indicate that the present conditions are not favorable for the formation of mackinawite in the anoxic Peruvian waters given that Fe(II) and H2S concentrations remain consistently too low to exceed the solubility product of Fe(II) sulfide minerals. At micromolar H2S concentrations, aqueous Fe sulfide complexes and clusters become the dominant Fe(II) species and buffer DFe through prevention of scavenging, thereby enhancing Fe solubility in the euxinic water column.

Oxygen minimum zones are projected to expand and intensify as a consequence of reduced oxygen solubility related to ocean warming, increased stratification of the water column, changes in oxygen consumption via biotic respiration, and changes in the large-scale overturning circulation. This will likely result in more frequent H2S events and associated enhanced Fe(II) concentrations in coastal OMZs. For the eastern tropical South Pacific off Peru it has been shown that eddies frequently forming at the coast can transport coastal waters far offshore within days and weeks. This scenario may enhance the supply of DFe to local surface waters and potentially to the Fe depleted South Pacific gyre system, with positive feedbacks for primary productivity and nitrogen fixation.

Figure 3. The left part of the sketch illustrates Scenario 1: H2S and the majority of Fe(II) are removed at the sediment-bottom water interface by oxidizing both compounds with NO3− and NO2− to sulfate (SO42−) and iron oxyhydroxides (Fe(III)OOH). In the water column, Fe(II) is oxidized by NO3− and O2 with subsequent formation of particulate Fe(III)OOH and organically complexed Fe (Fe(III)L). A small fraction of Fe(II) is kept in solution by photochemical reduction processes in the surface. The middle part of the sketch illustrates Scenario 2: After H2S reduced most of the NO3−/NO2− present in the sediments, H2S and Fe(II) can diffuse without restriction across the sediment-water interface and upwards in the water column until they are oxidized at the oxycline, with subsequent formation of particulate Fe(III)OOH, organically complexed Fe (Fe(III)L) and sulfate (SO42−). Similar to Scenario 1, a small fraction of Fe(II) is kept in solution by photochemical reduction processes in surface waters. The right part of the sketch illustrates Advanced scenario 2: Similar to scenario 2, but due to long lasting sedimentary release, H2S and Fe(II) concentrations increase in the water column. We hypothesize that elevated concentrations of H2S and Fe(II) in the millimolar range facilitate the precipitation of mackinawite (FeSm) at the sediment-bottom water interface.
Materials and Methods

Sampling locations and sampling. Seawater samples for trace metal analysis were collected at three sites on the Peruvian shelf during the upwelling season in December and January 2008/2009 (RV Meteor cruise M77-3). Sites were located at 10.00°S, 78.38°W (1), 12.33°S, 77.00°W (2) and 16.00°S, 74.24°W (3) (Fig. 1). The water depth was 112 m at site 1, 98 m at site 2 and 255 m at site 3. Samples for trace metal analysis were collected using trace metal clean Go-Flo bottles (General Oceanics) attached to a Kevlar wire. Go-Flo bottles were deployed once at sites 2 and 3, while at site 1 the Go-Flo bottles were deployed five times within 24 h. After recovery, bottles were transferred into a clean lab container. The seawater samples were filtered using cartridge filters (0.2 µm, Sartorbran 300, Sartorius) and dispensed into acid cleaned 1 L low density polyethylene (LDPE, Nalgene) bottles. The samples were then acidified with quartz distilled hydrochloric acid to pH 1.8 (17.8 µmol H+ L−1). Unfiltered seawater samples for on-board Fe(II) analysis were dispensed into opaque acid cleaned 60 mL LDPE bottles under normal filtered air. The Fe(II) analysis was carried out immediately after sample collection. All sample handling was performed in a laminar flow hood.

Sample analysis. Dissolved Fe concentrations were determined half a year later using graphite furnace atomic absorption spectrometry (Perkin Elmer, 4100 ZL) following Grasshoff et al.84. The blank and limit of detection (LOD) (three times the standard deviation of the blank measurement) for Fe concentrations were 0.104 nmol L−1 and 0.079 nmol L−1, respectively. The accuracy of the analytical procedure was evaluated by the analysis of certified seawater standard NASS-5 (National Research Council of Canada) and SAFe. Our Fe values agree well with the certified values for NASS 5 and the SAFe data (NASS 5: 26.3 ± 1.1 nmol kg−1 (certified: 25.7 ± 2.0 nmol kg−1); SAFe S: 0.112 ± 0.013 nmol kg−1 (census: 0.093 ± 0.008 nmol kg−1); SAFe D2: 0.83 ± 0.13 nM Fe (census: 0.93 ± 0.023 nmol kg−1)). The precision of the method is 3–5%.

Fe(II) concentrations were measured on samples collected at site 2 immediately upon collection by a chemiluminescence flow injection analysis following the method of Croot and Laan85, which has a LOD of 0.1 nmol L−1 Fe(II).

Nutrient and O2 samples were obtained using Niskin bottles (General Oceanics) on a stainless steel CTD rosette deployed at the same locations. Nutrient samples were analyzed for NO3− and DIP using an autoanalyser (TRAACSS800, Bran&Lubbe) following Grasshoff et al.86. NO3− was determined spectrophotometrically86 and NH4 was analyzed fluorometrically87 on board. Oxygen concentrations in the water column were measured by a Seabird O2 sensor that was calibrated with oxygen concentrations determined from CTD water samples (Winkler method88). The latter caused a LOD of 2 µmol kg−1. Additionally, at site 2 a switchable trace O2 sensor (STOX) with a LOD of 50 nmol kg−1 was used86,87. For H2S measurements seawater samples were collected with a pump-CTD88 and were analyzed spectrophotometrically88. At the pH of seawater H2S represents the dominant hydrogen sulfide species, which is why the term H2S for our study refers to the sum of H2S, HS−, and S2−.

Data availability. The dataset generated during this study is available in the GEOMAR-OSIS repository (https://portal.geomar.de/de/osis/).

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Author Contributions

C.S. and P.L.C. designed the research; C.S., P.L.C. and M.D. collected the samples/data; C.S., G.L. and P.S. analyzed the samples; C.S., P.L.C., G.L., M.F. and E.A. wrote the manuscript.

Additional Information

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