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Dissimilatory nitrate reduction to ammonium by benthic microbial mats fuels rapid sulfur oxidation and sediment ferrous iron release in the anoxic Santa Barbara Basin

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Sulfate reduction, a crucial metabolic pathway for organic matter remineralization in marine sediments, produces hydrogen sulfide that can be subsequently utilized by chemoautotrophic organisms. When the water column above marine sediments becomes anoxic, microbial metabolisms at the sediment-water interface shift to take advantage of the electron donors and acceptors available in the new redox conditions. These processes were examined in November 2019 during the AT42-19 expedition aboard RV Atlantis. Samples were collected using ROV Jason at different depths along a transect traversing the Santa Barbara Basin between 440 and 600 m depth. Deeper parts of the basin experience transient deoxygenation that is sometimes associated with a nitrate-depleted zone. Under these conditions, large benthic microbial mats of sulfur-oxidizing bacteria form in the basin. To analyze the effect of these mats on the basin geochemistry, sulfur and nitrogen (SO_4^{2-} , H_2S , NO_3^- , NO_2^- , NH_4^+) consumption and production were examined using sediment push cores and benthic flux chambers. Other redox sensitive compounds (e.g. Fe and PO_4^{3-}) were also measured using these methods. Areal sulfate reduction rates measured in push cores using the ^{35}S -Sulfate radiotracer method were highest in the deepest, anoxic part of the basin ($\sim 4 \text{ mmol m}^{-2} \text{ d}^{-1}$) where microbial mats were most prevalent and the sediment-water interface was anoxic and low in nitrate ($7.3 \mu\text{M}$). Sulfate reduction was noticeably lower at shallow stations ($\sim 2 \text{ mmol m}^{-2} \text{ d}^{-1}$) with oxygenated water, signs of bioturbation, and without mats. Sulfate reduction below the sediment-water interface (0-1 cm sediment depth) was also an order of magnitude higher at deep stations ($\sim 120 \text{ nmol cm}^{-3} \text{ d}^{-1}$) compared to shallow stations ($\sim 18 \text{ nmol cm}^{-3} \text{ d}^{-1}$). Despite high sulfate reduction activity in areas covered by mats, sulfide concentrations were near-zero in the uppermost 2 cm of sediment. Nitrate flux into the sediment and ammonium flux out of the sediment was highest where mats were present ($-2.93 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $11.19 \text{ mmol m}^{-2} \text{ d}^{-1}$ respectively). Additionally, the anoxic depocenter of the basin contains a flux of ferrous iron ($4.10 \text{ mmol m}^{-2} \text{ d}^{-1}$) and phosphate ($3.18 \text{ mmol m}^{-2} \text{ d}^{-1}$) out of the sediment into the water column. Our results provide a direct comparison of redox cycling at the sediment-water interface under vastly different redox conditions within the

same oceanic basin. These results also provide strong evidence that chemoautotrophic sulfur-oxidizing bacteria in sediments of the anoxic Santa Barbara Basin perform dissimilatory nitrate reduction to ammonium and are responsible for rapid sulfur cycling near the sediment-water interface with a concurrent flux of ammonium, iron, and phosphate into the water column.