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PYRITE BURIAL AND SULFUR CYCLING ALONG A HYPOXIC GRADIENT IN THE SAINT-LAWRENCE ESTUARY AND ITS pCO_2 BUFFERING CAPACITY

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The sulfur cycle is interconnected with the iron and carbon cycles and plays a fundamental role in planetary-scale redox processes. At the scale of the St. Lawrence Estuary (SLE), on shorter timescales, pyrite burial limits benthic sulfur cycling and influences the production of alkalinity, which counters increases in atmospheric CO_2 partial pressure. Progressively more hypoxic conditions in the SLE and its impact on biogeochemical cycling, including the sulfur cycle, have been documented by professor Mucci, his colleagues, and others over the past decades. To follow in his footsteps, we investigated further the link between the development of hypoxia, pyrite burial, and the feedback on carbonate chemistry of the water column.

Cores were collected along a hypoxic gradient in the Laurentian Through (west-east transect) as well as from methane seeps, which are abundant in the SLE. Sulfur species including acid volatile sulfur (AVS = H_2S, FeS partly Fe_3S_2) and chromium reducible sulfur (CRS = Pyrite, S^0, Fe_3S_2) showed a minimum AVS-S to CRS-S ratio (from 0.18 to 0.85 west to east) in the most hypoxic conditions, scaling also with sedimentation rate. These results support an enhancement of benthic alkalinity flux with increasing hypoxia. Sulfur isotopic measurements of AVS and CRS fractions suggest an increasing contribution of sulfate reduction with increasing hypoxic conditions both spatially and temporally, which is likely correlated with decreasing benthic macrofaunal activity over time.

At the methane seeps, high methane inputs generate peaks in dissolved inorganic carbon (DIC) and AVS in both cores at approximately 21 and 15 cm depth, corresponding to the sulfate-methane transition. Sulfide produced by anaerobic oxidation of methane also contributes to alkalinity generation when the generated sulfide is subsequently buried as CRS (pyrite). Results show that the AVS concentration >> CRS concentrations, in contrast to other locations in the west-east transect. This pattern has been explained by elevated H_2S and reactive iron concentrations. In seep environments, lower polysulfide formation may be inhibiting pyritization.

Overall, our results support increasing potential for benthic alkalinity generation in hypoxic conditions which can be estimated for the SLE. The role of seep environments will require further development.