

## Iron-mediated cryptic sulfur cycling in salt marsh sediments

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The burial of organic carbon in shallow marine sediments represents an important net sink in the global carbon cycle. Microbially mediated oxidation of organic matter in oxic, suboxic, and anoxic sediments however, prevents its removal from the short-term carbon cycle. In modern settings, sulfate reduction dominates the subsurface oxidation of organic carbon due to the abundance of sulfate in many surface environments. It has also been suggested, however, that the iron and sulfur cycles are intimately linked in the anoxic subsurface.

To better understand how the dynamics of iron and sulfur cycling impact subsurface carbon cycling, we are using stable isotope and geochemical techniques to explore the microbially mediated oxidation of organic carbon in salt marsh sediments in North Norfolk, UK. These sediments exhibit high levels of organic carbon, dissolved iron, and sulfate, making them ideal laboratories to study the nature of coupling between the carbon, iron, and sulfur cycles. A series of sampling missions was undertaken in the autumn and winter of 2013-2014.

In subsurface fluid samples we observe very high ferrous iron concentrations (>1mM), indicative of extended regions of iron reduction (to over 30cm depth). Within these zones of iron reduction we would predict no sulfate reduction, and as expected  $\delta^{34}\text{S}_{\text{sulfate}}$  remains unchanged with depth. However,  $\delta^{18}\text{O}_{\text{sulfate}}$  exhibits significant enrichments of up to 5‰. The observed decoupling of the sulfur and oxygen isotopes of sulfate is suggestive of a sulfate recycling process in which sulfate is reduced to an intermediated sulfur species and subsequently reoxidized to sulfate; this cycle must be quasi-quantitative to produce the suite of geochemical observations. Taken together, these data suggest that microbial assemblages in these salt marsh sediments facilitate a cryptic cycling of sulfur, potentially mediated by iron species in the zone of iron reduction. Constraints on the mechanism of iron-sulfate coupling will be discussed in the context of microbial ecology data and geochemical models.