



Evidence for iron-sulfate coupling in salt marsh sediments

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Organic carbon burial 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 the ultimate burial of organic carbon and its removal from the surface of the planet. Although the subsurface transformations of organic carbon have been studied extensively, an enigmatic question remains: when organic matter is deposited, what determines whether it will be buried, reoxidized, or undergo methanogenesis?

One hypothesis is that the sulfur cycle, due to the abundance of sulfate in many surface environments, dominates the subsurface oxidation or other fate of organic carbon. However, it has also been suggested that iron may in turn play a key role in determining the behavior of the sulfur cycle. To better understand the controls on these processes, 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. In these sediments there is a high supply of organic carbon, iron, and sulfate (from diurnal tidal cycles). Thus these environments may provide insight into the nature of interactions 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 ($>1\text{mM}$), 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 $\delta^{34}\text{S}$ sulfate remains unchanged with depth. However, $\delta^{18}\text{O}$ sulfate exhibits significant enrichments of up to 5 permil. This decoupling in the sulfur and oxygen isotopes of sulfate is suggestive of a sulfate recycling process in which sulfate is reduced to an intermediate sulfur species and subsequently reoxidized to sulfate. 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.