

A rusty carbon sink in estuarine sediments? Evaluation of an iron oxide burial experiment.

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Iron oxides are known to play a key role in preserving organic carbon (OC) from mineralization, contributing to its burial, and consequently regulating CO₂ and O₂ atmospheric concentrations. Approximately 20% of OC in sediments is associated with iron minerals, the so-called “Rusty carbon sink”. Yet, the formation and stability of this organo-mineral association remain unclear, particularly in the natural environment.

In this study, quartz grains, ferrihydrite-2-lines (FH2L) and 6-lines (FH6L) coated quartz grains were buried within 4 modified passive autosamplers (peepers) in a mudflat in the Scheldt (Appels, Belgium). Each peeper (~30 cm in length) comprises 3 columns of 12 traversing holes, each row filled with one of the minerals, separated from the sediments by a 63 μm pore size mesh. The peepers were collected after 3, 10, 18, and 23 months of exposure to the sediments. To date, this is the first *in situ* experiment aimed at following the dynamics of OC-Fe association in sediments over depth.

A combination of different techniques, electron microscopic and spectroscopic (FIB, SEM, TEM, TEM-EELS, XPS), thermogravimetric (TGA-DTA coupled with mass spectrometry) and classical solid phase analyses were used to characterize the neo-formed organo-mineral associations. Over time, dissimilatory iron oxide reduction decreased the iron content of both 2L and 6L ferrihydrite, while OC accumulated over the residual iron. The OC pool consisted of thermo-labile (200-400°C), recalcitrant (400-550°C) and refractory carbon (550-650°C), identified via XPS as aromatic, alkene, and aliphatic compounds. FIB sections cut through the iron-coated grains showed the OC localized within the Fe-OC associations. This study sheds new insights onto the least-known processes regulating carbon burial in benthic environments, providing a broader perspective of the Fe-OC association that underlie the so-called 'rusty carbon sink'.