



## **The Rusty Sink: Iron Promotes the Preservation of Organic Matter in Sediments**

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The biogeochemical cycles of iron (Fe) and organic carbon (OC) are strongly linked, each element exerting some degree of control over the other. In the oceans, organic ligands control the concentration of dissolved Fe in the water column. In soils, Fe and OC concentrations are typically correlated, suggesting that they are closely associated. Nevertheless, until now, the role of Fe in the preservation of sedimentary OC has not been clearly established. We determined that 20 to 40% of the total OC in marine and freshwater sediments is closely associated to solid reactive Fe phases (operationally defined as the solid iron phases that are reductively dissolved with sodium dithionite). The highest Fe-bound OC concentrations are found in surface sediments where authigenic Fe oxides accumulate. Even in mature sediments (>500 years), about 20% of the total OC is bound to Fe, suggesting a strong association that results in the protection and preservation of OC from bacterial degradation. Our measurements show that for young and mature sediments collected around the world, solid reactive Fe phases does not provide sufficient surface area for chemisorption of OC onto Fe oxides. Alternatively, we propose that high OC:Fe ratios reflect the existence of largely organic Fe-OC macromolecular structures (through chelation and co-precipitation), attached only minimally to the surface of clay mineral grains. The organic matter in these Fe-OM chelates is 'glued' together by iron ions or nanophases of iron oxide crystals. In most cases, we found isotopic and elemental fractionation between Fe-associated OC and the rest of the sedimentary OC pool, with  $^{13}\text{C}$  and nitrogen-enriched OC preferentially bound to Fe.  $^{13}\text{C}$ -rich OC components such as proteins and carbohydrates have oxygen and nitrogen functionalities that favor the formation of inner-sphere complexes with Fe. The formation of these complexes may explain why these intrinsically labile OC compounds can be preserved on long time-scales in sediments. The sorptive stabilization mechanism, which hypothesizes that particle surfaces have a preservative effect on OC, would not accurately describe the mode of stabilization for all OC in sediments. Since reactive iron phases are metastable in sediments over geological timescales, OC bound to these phases may be preserved from degradation, contributing to the balance of the atmospheric oxygen and carbon dioxide.