Probing the interactions between iron oxides and sediment organic matter using X-ray absorption spectroscopy

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Sediments and sedimentary rocks make up the largest sink for organic carbon one the planet while approximately 20% of the organic carbon found within marine sediments is bound to reducible iron oxide species [1]. Here we use Scanning Transmition X-ray Microscopy (STXM) as well as X-ray Absorption Near Edge Spectroscopy (XANES) in order to probe the local envrionment of iron oxide-bound organic matter within a variety of marine surface sediments and water column suspended particles. STXM data was collected on beamline 10ID-1 (SM) at the Canadian Light Source, where we analyzed regions with iron co-localized organic carbon, and then obtained spatially relevent NEXAFS images and spectra for these regions at both the carbon K-edge and iron $L_{2\text{-}3}$ edge. From these we are able to determine the speciation of both carbon and iron with a spatial resolution of 40 nm. We see important contributions from aromatic and carboxyl functionalities independent of the presence of iron but see an increase in the relative proporation of aliphatic functionalities in the presence of iron-organic mineral phases.

XANES spectra at the iron K-edge were collected at beamline X26a at the Brookhaven National Synchrotron Light Source and were used to probe the effect bound organic matter has on the X-ray absorption spectra of iron. A shift towards lower energies was seen at the iron edge for synthetic iron oxides precipitated in the presence of organic matter, demonstrating that we can distinguish between iron oxide-bound organic matter and pure iron oxide minerals. XANES spectra were also collected on a variety of surface sediment samples; using linear combination fitting and well-defined end-members, we were able to determine the proportion of sediment iron which is bound to organic matter based on the effect of organic matter on the synthetic iron co-precipitates.

[1] Lalonde, Mucci, Ouellet, Gélinas (2012), *Nature* **483**, 198-200

The role of iron in the diagenesis of organic carbon and nitrogen in sediments: A long-term incubation experiment

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The burial and preservation of organic matter (OM) in marine sediments is tightly coupled to the diagenetic cycles of iron and manganese. These strong iron-OC complexes, formed within the oxic layer of the sediment, are transferred to the deeper anoxic sediment layers through sedimentation, physical reworking and bioturbation; and are metastable over geological timescales [1]. Using a long-term (400-day) incubation, we examined the effect of iron on the early diagenetic transformations of OM in marine sediments. The fate of fresh, algal-derived DOM was monitored by tracking its stable carbon isotopic signature ($\delta^{13}C$). We demonstrate the incorporation of the ^{13}C-depleted tracer into the sediment through sorption (adsorption and co-precipitation with iron oxides). In the presence of iron oxides, we observed increased transfer of the dissolved algal material to the solid phase, revealing the role of iron in shuttling OM from sediment porewaters to sediment particles. Furthermore, we show that the presence of iron has a differential effect on OC and organic nitrogen (ON), with preferential preservation of OC and accelerated degradation of ON in the presence of reactive iron oxide surfaces. Hence, we propose that redox-sensitive metals may play a crucial role in regulating the global redox balance through increased carbon preservation as well as controlling the concentration of reactive nitrogen species in the open ocean.

[1] Hease *et al.* (1997) *Geochim. et Cosmochim. Acta* **61**, 63-72.

DOI:10.1180/minmag.2013.077.5.2
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