# Inner-Sphere Covalent Interactions Control the Ferric Carbon Pump in Marine Sediments

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As the largest sink for organic carbon (OC) on Earth, marine and lacustrine sediments play a major role in maintaining the global redox balance and are of central importance to the global carbon cycle. The majority of the OC preserved within sediments is intimately associated to the sediment mineral matrix, which is composed primarily of silicate minerals and metal oxides. Redox sensitive, nano-scale iron oxides in particular have a strong affinity for OC, forming stable Fe-OC complexes within oxic surface sediments. In fact approximately 20% of the total sediment organic carbon pool is associated to these reducible iron species [1], yet the mechanism by which these organo-mineral compounds sequester OC remains unknown. Here we use a combination of synchrotron X-ray techniques (Hard X-ray Microprobing and Scanning Transmission X-ray Microscopy) to determine, for the first time, the proportion of the sediment iron pool that is associated to OC through direct inner-sphere covalent interactions, as well as the nano-scale distribution/composition of iron-bound OC these environments. Using the Hard X-ray Microprobe we show that between 25.7 and 48.4% of the total reactive iron pool is directly associated to OC through inner sphere organo-mineral interactions in coastal environments, compared to between 0 and 15.4% for pelagic sediments, demonstrating the importance of this ferric OC pump sequestration mechanism in coastal settings. This sedimentary ferric pump protects OC during its critical passage across oxic-to-anoxic redox transitions to the more reducing sediment layers in which OC is better preserved on long time scales.

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