

# Complexed Fe(III) in Reducing Sediment Porewater



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Luther et al. (1992) proposed a biogeochemical cycle for iron in salt marsh sediments that includes the solubilization of Fe(III) by organic ligands. Taillefert et al. (2000) demonstrated, using cathodic stripping voltammetry, the existence of organically complexed Fe(III) in a shallow marine sediment. Here we present evidence for complexed Fe(III) in deep marine sediments from the Saguenay Fjord and the Estuary and Gulf of St. Lawrence. The measurements were made with a Au/Hg amalgam micro-electrode with millimetre depth resolution on intact cores. In a typical core, O<sub>2</sub> disappears at 6mm depth, and dissolved Mn(II) appears within 5-10mm depth followed by dissolved Fe(II). The Fe(III) complex first appears as a very prominent peak at about -0.35V (30s deposition at -0.1V followed by a cathodic scan from -0.1V to -1.7V). The peak shifts to more negative potentials (~-0.45V) with depth and is still observed as far down as 10cm in the sediment. Fe(II) always co-occurs with the Fe(III) complex, although dissolved Fe(II) is first seen higher in the sediment profile. The complexed Fe(III) can oxidize sulfide species, providing a pathway to pyrite formation. Pyrite increases with depth in these sediments. Complexed Fe(III) can also act as a terminal electron acceptor in organic matter degradation and thus participate directly in the mineralization of organic matter. The production of Fe(III) complexes appears to be widespread in marine sediments and may play an important role in Fe and S geochemistry.

## REFERENCES

1. Luther, G.W. III, Kosta, J.E., Church, T.M., Sulzberg, B. and Stumm, W.: 1992, *Mar. Chem.*, **40**: 81-103.
2. Taillefert, B., Bono, A.B., and Luther, G.W. III.: 2000, *Environ. Sci. Tech.*, **34**: 2169-2177.