Dissolved and solid-phase Fe and Mn speciation in marine sediments

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Dissolved and solid-phase speciation of iron (Fe) and manganese (Mn) were concurrently measured in the porewaters and sediments recovered from three distinct sites: Cascadia Margin methane seeps, the anoxic Santa Barbara Basin, and in the St. Lawrence Estuary – including a hypoxic site and an oxic fjord site. At all sites and most depths, metal-organic ligand complexes (Mn(III)-L and Fe(III)-L) dominated the porewater speciation, comprising up to 100 % of the total dissolved Mn or Fe. These complexes likely play a previously underestimated role in maintaining oxidized soluble metal species in sediments and in stabilizing organic matter.

In calculating fluxes of Mn and Fe from the sediments to the overlying waters, we found that porewater metals more readily escape to the overlying waters at sites with lower bottom-water O_2 concentrations. In the Santa Barbara Basin and at the Cascadia Margin, porewater speciation was complemented by synchrotron-based X-ray absorption spectroscopy (XAS) to characterize the solid Mn and Fe phases. These data represent the first combination of Mn and Fe sediment porewater analyses with XAS solid-phase characterization of the sediments. We provide evidence for the co-existence of multiple oxidation states of Fe (II and III) and Mn (II, III and IV) in the top 5 cm at all our study sites, indicating highly dynamic sedimentary environments, likely due to microbial activity as well as the interaction of natural and metabolic organic ligands with Mn and Fe. Interestingly, in the Santa Barbara Basin, our sampling coincided with an episode of O_2 intrusion to the anoxic bottom waters of the basin, and our XAS data revealed the presence of a mixed-valence Fe oxyhydroxide phase similar to green rust - a short-lived Fe-oxide that forms at dynamic oxygen-sulfide boundaries. Thus, the relative abundance of mixed-valence Mn and Fe species is the combined result of oxygen-sulfide dynamics, organic matter-metal complexation, and the ecology of the benthic microbiota.