A unique Mn redox cycle in the Ross Sea

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The speciation of Mn in seawater has been revised in the last decade to include soluble Mn(III)-L complexes, in addition to soluble Mn(II) and insoluble Mn(III/IV) oxides. These Mn(III)-L complexes can make up to 100 % of the dissolved Mn (dMn) pool and are important redox species as they can donate or accept electrons. We measured the speciation of soluble Mn spectrophotometrically in the water column of 12 sites in the Ross Sea and Terra Nova Bay polynyas of the Southern Ocean, during the 2018 austral summer. We additionally collected particulate samples to examine the oxidation state and bonding environment of Mn within particles throughout the water column. We found that Mn(III)-L complexes made up to 100 % of the total dMn and ranged in concentration from 1 to >10 nM, with highest Mn(III)-L concentrations measured in surface waters near the ice edge, and above the sediment-water interface, indicating that dMn inputs likely include ice melt and sediment resuspension. These data present the first measurements of Mn(III)-L in the Southern Ocean, and their abundance suggests that they are formed through diverse pathways and/or have long lifetimes. Interestingly, X-ray Absorption Near Edge Structure (XANES) spectroscopy revealed that particulate Mn (pMn; >0.2 µm) was largely reduced (average oxidation state 2.1 – 2.8), suggesting that pMn is likely dominated by intracellular Mn. This finding is highly unusual for oceanic pMn, which is typically dominated by Mn oxides (average oxidation state 3.7 – 4.0). Additionally, we were unable to isolate Mn(II) or Mn(III)-oxidizing bacteria, even after 2 months of growth, and shipboard colorimetric assays indicated that Mn oxide concentrations were non-detectable (> 0.01 nM). This is puzzling as, to our knowledge, this is the first oceanic site where Mn-oxidizing bacteria have not been found. Thus, we posit that Mn oxides are not being formed in the Ross Sea, which may be due to the absence of Mn-oxidizers, lack of Mn oxide templates, and/or that Mn binding ligands are preventing complete oxidation and precipitation of oxide minerals. These findings may shed light on previously unexplained nutrient-type profiles for dissolved cobalt in this region, which is typically a scavenged element. As Mn contributes to the cycles of many other elements (N, C, O, Fe, Cu, Cr, Co, Zn, Ni, etc.), its atypical redox chemistry in the Ross Sea merits further attention.