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# Manganese Oxidation and Oxide Formation in Low Oxygen Marine Systems

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Manganese (Mn) oxides are widespread in ocean systems where they serve as important oxidants and sorbents of nutrients and metals. As Mn oxides are believed to form only in highly oxidizing environments, they have emerged as a promising paleoredox proxy. Yet, the rates and controls on Mn oxidation are still poorly understood due to the complexity and diversity of (a)biotic processes involved in Mn cycling. While Mn oxides have been observed throughout the oxycline within stratified marine waters, the relative role of oxide transport versus in situ oxidation remains unknown. Further, the underlying operative redox reactions involved in Mn oxidation along an oxygen gradient have not been explored. Here, we present findings from an exploration of the cycling of Mn within stratified basins in the Baltic Sea. We quantified Mn(II) oxidation rates as a function of depth using the radioisotope $^{54}$Mn, allowing for low Mn additions and short incubations times. The underlying oxidation pathways were identified at select depths using a parallel set of incubations in the presence of absence of biocides. Using a colorimetric assay, a strong Mn oxide peak was observed at the base of the oxycline at all three basins. X-ray absorption spectroscopy confirmed that the particles are Mn oxides, dominated by Mn(IV). Manganese oxide concentrations declined sharply to zero below this peak, coinciding with the appearance of hydrogen sulfide. Parallel incubations that maintained the in situ oxygen concentrations showed that the waters collected at the base of the oxycline also have the highest Mn uptake and oxidation rates. Addition of the biocide zinc diminished but did not eliminate Mn oxidation, indicating that both biotic and abiotic reactions were operative. These findings point to an underappreciated role for low oxygen reactions in the formation of Mn oxides within stratified marine systems. Thus, subsequent research should aim to identify the organisms and processes involved in microaerophilic Mn oxide formation within stratified waters. Lastly, the decoupling of oxygen and Mn here calls for better constraints on Mn oxide formation pathways to robustly predict their distribution within current and past environments.