Mn(II) oxidation by dissolved oxygen at pH 8.5 under various freezing conditions

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Mn(II) oxidation is one of the principal abiotic geochemical process forming diverse Mn (oxyhydr)oxides and thereby controls numerous biogeochemical cycles in the environment. However, its importance has been neglected due to its slow kinetics under the prevailing pH conditions of natural water. Recently, it has been reported that some chemical reactions at subzero temperature can show unusual behavior, such as significant acceleration and/or following unique reaction pathways. To determine characteristic redox behavior of Mn in low-temperature environment and to expand our current understanding of Mn cycle, this study examined homogeneous Mn(II) oxidation under various initial Mn(II) concentration and freezing temperature conditions.

Batch experiment were conducted with varying Mn(II) concentrations (5 – 100 μM or 10 mM) at pH 8.5 with 50 mM CHES buffer under the atmospheric P_{O2} condition. The freezing temperature was controlled to -5, -15, -20 or -30 ℃ with a circulating bath using ethanol as a coolant. The result showed that Mn(II) oxidation was substantially enhanced upon freezing under all experimental conditions. The degree of enhancement was increased with increasing freezing temperature (i.e., -30 ℃ < -20 ℃ < -15 ℃ < -5 ℃). While Mn removal % was similar regardless of $[Mn(II)]_0$ at -20 ℃, it increased with increasing $[Mn(II)]_0$ at -5 ℃, indicating different reaction pathways at each temperature. In addition, the XRD result showed that a mixture of different Mn (oxyhydr)oxides was produced by oxidation and/or precipitation at different temperature. The results of this study suggest that homogeneous oxidation in a low-temperature environment would be far more important than previously understood, and warrant further investigation to better understand the mechanism and potential environmental role of the cryogenic Mn (II) oxidation process.