

Mn(II) oxidation and the formation of Mn (oxyhydr)oxides under various freezing conditions

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Mn (oxyhydr)oxides are among the strongest naturally occurring sorbents and oxidants in the environment. Despite the importance of Mn (oxyhydr)oxides in controlling numerous biogeochemical cycles, the understanding of pathways and controlling factors responsible for their formation is still not clear and yet limited to the environmental conditions outside the cryosphere. Within the cryosphere, the redox behavior of Mn would exhibit different characteristics from those in normal aqueous solutions due to the freezing related phenomenon called ‘freeze-concentration effect’. For expanding the current knowledge of the fate and transport of Mn into those under freezing conditions, this study examined how freezing of aqueous solutions affects Mn(II) oxidation by dissolved oxygen and the concomitant formation of Mn (oxyhydr)oxides under various freezing conditions.

The freezing experiments were conducted with varying Mn(II) concentrations (5 – 100 μ M) at pH 8.5 with 50 mM CHES buffer. The temperature was controlled at a target freezing temperature (-5 – -30 °C) in an ethanol cooling bath. The solid products of 1 mM Mn(II) oxidation at room or a freezing temperature (-5 or -20 °C) were collected and characterized by XRD, XAS, and TEM. The Mn(II) oxidation was substantially enhanced upon freezing under all experimental conditions, and the degree of enhancement increased with increasing freezing temperature. In addition, it appeared that the freezing temperature also affected some of the important physicochemical properties of Mn (oxyhydr)oxides such as particle size and crystallinity. The results of this study substantiated a new pathway of various Mn (oxyhydr)oxides formation, which may prevail in the Earth’s cryosphere and thus significantly impact the biogeochemical cycles tightly associated with Mn in the environment.