Mn(II) oxidation in aqueous solution under freezing conditions

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Abstract

As the climate change significantly influences icy environment (e.g., artic), there is a rising motivation to understand how freezing and melting of ice would affect the ecosystem within the cryosphere of the Earth. It has been recently reported that some chemical reactions could be significantly accelerated or follow unexpected pathways under freezing conditions. These recent findings suggest that many of ice-related geochemical processes could also be different from what we have previously understood, and thus freezing-thawing cycles may contribute to altering the fate and transport of various inorganic and organic substances. To better assess the impacts of the climate change, it is crucial to understand the controlling factors and the reaction pathways of fundamental geochemical processes under freezing conditions. This study examined abiotic Mn(II) oxidation processes, one of the principal geochemical processes affecting diverse biogeochemical cycles, under various freezing aqueous conditions and investigated the effects of Mn(II) concentration and freezing temperatures on the rate and extent of the reaction.

Batch experiments were conducted with varying Mn(II) concentrations (5 – 100 μM) at pH 8.5 with 50 mM CHES buffer under the atmospheric P_{O2} condition. Ice samples were prepared by placing amber conical tubes in an ethanol coolant at a target freezing temperature (-5, -15, -20 or -30 °C) for a range of reaction time and rapidly thawed in lukewarm water for further analyses. Preliminary results show that Mn(II) oxidation was substantially accelerated upon freezing under all experimental conditions. Both at -5 and -20 °C, the overall rate of cryogenic Mn(II) oxidation apparently followed pseudo-1st order kinetics with respect to Mn(II) concentration.