Freeze-induced Mn(II) precipitation in solutions containing dissolved carbonates

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Mn(II) carbonate minerals play a crucial role in manganese geochemistry by controlling Mn(II) mobility and in the carbon cycle by trapping CO_2 through mineralization. Although numerous studies have been conducted on Mn(II) precipitation under a wide range of aqueous conditions, their behaviors in the cryosphere remain poorly understood. It has been proposed that solutes could be concentrated in liquid-like layers during the freezing of water. This process would likely raise the degree of saturation of minerals in the layers, which may induce mineral precipitation. This study examined how freezing affects solid precipitation with solutions containing dissolved Mn(II) and carbonates under freezing conditions.

Batch experiments were performed by freezing solutions containing varying concentrations dissolved Mn(II) (1-50 μM) in the presence of dissolved carbonates at -20 ℃. The carbonate concentrations were adjusted to 1-5 mM with $NaHCO_3$ or the atmospheric CO_2 by purging air into the solution containing a predetermined amount of 2.2-3.3 mM NaOH. The solution pH was controlled at 8.2-8.5 by the concentration of $NaHCO_3$ or the atmospheric CO_2. Our preliminary results showed that the removal of dissolved Mn was enhanced upon freezing under all experimental conditions. The degree of enhancement increased with increasing the initial saturation state of the solution with respect to rhodochrosite ($MnCO_3$). XRD and Mn K-edge XANES results of the solid products indicated that rhodochrosite was the most prominent phase formed through the cryogenic Mn(II) precipitation.