

# Geochemical behavior of dissolved Mn(II) in carbonate solution under freezing conditions

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Manganese (Mn) is a ubiquitous and abundant transition metal in the Earth's crust and strongly associated with the fate and transport of numerous (in)organic substances in aquatic environments. Recently, some chemical reactions have been reported to be accelerated in freezing solutions, mainly due to the 'freeze-concentration effect'. This effect may also be applicable to Mn geochemical processes, especially those controlled by dissolved Mn concentration, in natural aqueous systems. It is well known that the rate and extent of abiotic Mn(II) oxidation increase with increasing  $[\text{Mn(II)}]_{\text{aq}}$  and pH. These are also the two principal variables controlling other common reactions of aqueous Mn(II) such as  $\text{MnCO}_3(\text{s})$  precipitation in the presence of dissolved carbonates. This study examines the cryogenic geochemical behavior of dissolved Mn(II) in the presence of dissolved carbonates under the conditions that these two critical processes can occur concurrently.

Batch experiments were conducted with solutions containing 50  $\mu\text{M}$  Mn(II) with 1 mM  $\text{NaHCO}_3$  in 10 mM NaCl as a background electrolyte open to the atmosphere. The solutions were adjusted their initial pH from 6 to 9 and frozen at -5 or -20 °C in a cooling bath up to 3 d. The frozen samples were then thawed at room temperature and monitored the changes in their solution chemistry for additional 30 d. The results showed that dissolved Mn(II) was stable at room temperature but rapidly decreased under freezing conditions. The freezing-induced removal of dissolved Mn(II) resulted in the precipitation of rhodochrosite ( $\text{MnCO}_3$ ), which increased with increasing solution pH and freezing temperature. After thawing the frozen samples, a fraction of rhodochrosite was stable but not redissolved for 30 d in the aqueous solutions. Our results suggest that Mn geochemical processes may not be inert but active and dynamic in the Earth's cryosphere.