

Freezing-induced Fe(II) oxidation at pH 4.5 - 7.0

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Recent studies have reported that freezing of solutions can enhance some chemical reactions mainly due to the ‘freeze concentration effect’. This abnormal phenomenon would be primarily important in the Earth’s cryosphere including polar, high- and mid-latitude, and alpine regions where perennial or seasonal freezing occurs because it could affect the rate and extent of diverse geochemical processes in the cryosphere. Particularly, it is crucial to understand the potential effects of freezing of natural waters on the primary processes governing the elemental cycles. Considering the notable role of iron (Fe) redox in various (bio)geochemical processes that controls not only the bioavailability of Fe but also the fate and transport of other substances in the environment, it is necessary to examine Fe redox under cryogenic conditions. However, Fe redox behaviors under freezing conditions under naturally prevalent pH conditions have been rarely investigated.

This study examined the oxidation of dissolved Fe(II) in freezing solutions at a naturally common pH range. Solutions containing 100 μM dissolved Fe(II) were adjusted to an initial pH at 4.5, 5.5, 6.5, or 7.0 without a buffer. Subsequently, Fe(II) oxidation was examined by freezing the solutions at -5 or -20°C or at $+2^\circ\text{C}$ as a control in a thermostatic bath under dark and oxic conditions. After predetermined reaction times, frozen samples were thawed by immersing the sample containers in cooled water at $+5^\circ\text{C}$ to prevent additional oxidation. Then, the thawed solutions were filtered using syringe filters ($0.2\ \mu\text{m}$) and acidified to measure the concentration of dissolved Fe(II) and total dissolved Fe (TDFe).

Results showed that Fe(II) removal was greatly enhanced upon freezing ($T = -20^\circ\text{C}$) at $\text{pH}_0 \geq 5.5$ compared to those at $+2^\circ\text{C}$. Upon freezing the solutions, dissolved Fe(II) was rapidly removed for the first 30 min, which was accompanied with the decrease in pH. This rapid drop of pH is attributable to the solution acidification by Fe(II) oxidation. The solid product formed by the cryogenic Fe(II) oxidation was identified as 2-line ferrihydrite based on TEM analysis. The rates of cryogenic Fe(II) oxidation in the initial stage of freezing were comparable with those at $+25^\circ\text{C}$ based on the Fe(II) oxidation kinetics reported elsewhere, showing that this reaction did not simply follow the Arrhenius relations under sub-zero aqueous conditions. These results present a new pathway of Fe(II) oxidation that may potentially be active in the cryosphere.

Key words : Fe(II) oxidation, freezing conditions, ice geochemistry, Fe redox cycle, cryosphere