

Fe(II) oxidation in freezing solutions under varying acidic conditions

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Ice-forming processes can substantially enhance chemical reactions mainly due to the ‘freeze concentration effect’. This phenomenon would potentially prevail over a wide range of surface environments, where natural water freezes. Since it may affect the rate and extent of diverse geochemical processes in the cryosphere, it is necessary to understand the possible effects of freezing on essential (bio)geochemical processes such as the Fe cycle. In particular, the Fe redox cycling in the cryosphere has received increasing attention for its crucial role in controlling the primary productivity in high-nutrient, low-chlorophyll oceans (HNLC) as well as the fate and transport of various elements.

This study investigated Fe(II) oxidation in freezing solutions under dark and acidic conditions, wherein its abiotic reaction is known to be sluggish without any catalyst. The pH of 50 μ M Fe(II) solution was adjusted with varying inorganic acids (HCl, H₂SO₄ or HNO₃) to pH 2.0 – 3.5 or an acetate buffer (0-10 mM) to pH 4.5. Subsequently, the Fe(II) solutions were frozen at -20°C for 3h to 7d and then quickly thawed in lukewarm water (ca. 40 °C). Fe(II) oxidation did not occur at pH \leq 4.4 except in the presence of HNO₃ under freezing conditions and increased with increasing HNO₃ concentration (i.e., pH 2.0 > 2.5 > 3.0 \approx 3.5). The rate and extent of Fe(II) oxidation were significantly increased in the presence of acetate buffer at pH 4.5 compared to those without acetate at -20 °C or with acetate at room temperature. Further study on Fe(II) oxidation under varying subzero conditions should be warranted.