

Fe(II) oxidation in freezing solutions under acidic conditions

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There is considerable interest in the (bio)geochemical cycling of iron, and its redox speciation heavily participates in controlling the fate and transport of other inorganic and organic substances. Therefore, Fe(II) oxidation has been extensively studied under a wide range of aqueous conditions, but Fe(II) oxidation under freezing conditions has not been studied. The freezing enhanced photocatalytic reductive dissolution of iron oxides has been recently proposed mainly due to the “freeze concentration effect”. It is presumable that Fe(II) oxidation rate under freezing (i.e., sub-zero) conditions may not simply follow the Arrhenius relations obtained under normal (i.e., above zero) aqueous conditions.

This study examined Fe(II) oxidation in freezing solutions under dark and acidic conditions (pH 2.0 – 4.5), where its abiotic reaction without any catalyst is known to be sluggish. The solution pH was adjusted with an inorganic acid (HCl, H₂SO₄, or HNO₃) or acetate buffer (0-10 mM). Ten mL of 50 μ M Fe(II) solutions were frozen in an amber conical tube with thermostatically controlled ethanol bath at -20 °C for predetermined reaction times (3h-7d). The samples rapidly thawed in lukewarm water (ca. 40 °C) for further analysis.

Results showed that Fe(II) oxidation did not occur at pH $\leq$ 4.4 except in the presence of HNO₃ under freezing conditions, and the concentration of HNO₃ also affects the rate of Fe(II) oxidation by oxygen under freezing conditions. The rate and extent of Fe(II) oxidation in frozen solutions were markedly 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. These results possibly make contributions to a better understanding of the iron redox cycling with atmospheric reactions and in cryogenic environments associated with organic matter.

Key words : Fe(II) oxidation, freezing conditions