

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

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Fe(II) oxidation has been extensively studied under a wide range of aqueous conditions because not only Fe plays a major role in diverse (bio)geochemical processes but also its redox speciation heavily participates in controlling the fate and transport of other inorganic and organic substances. A recent study showed that the photocatalytic reductive dissolution of iron oxides was substantially accelerated mainly due to the “freeze concentration effect”.[1] 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.[2,3] The solution pH was adjusted with an inorganic acid (HCl, H<sub>2</sub>SO<sub>4</sub>, or HNO<sub>3</sub>) or acetate buffer (0-10 mM). Ten mL of 50 μM Fe(II) solutions were frozen in an ethanol bath at -20 °C for predetermined reaction times (3h-7d) and then rapidly thawed in lukewarm water (ca. 40 °C). Results showed that Fe(II) oxidation did not occur at pH ≤ 4.4 except in the presence of HNO<sub>3</sub> under freezing conditions. The rate and extent of Fe(II) oxidation 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. The Fe(II) oxidation in the presence of HNO<sub>3</sub> may be ascribed to the acid catalytic oxidation by nitrate. When it comes to the presence of acetic acid, water solidification may cause a substantial pH shift upon freezing and thereby enhance the Fe(II) oxidation. Further results of the effects of complexing ligands and pH buffer on Fe(II) oxidation will be presented.

[1] Jeong, D. et al., (2015) *ES&T*. **49**, 12816–12822

[2] Stumm, W. & Lee, G. F. (1961) *Ind. Eng. Chem.* **53**, 143–146

[3] Singer, P. C. & Stumm, W. (1970) *Science*. **167**, 1121–1123