Accelerated dissolution of iron oxides in ice media and its environmental effects

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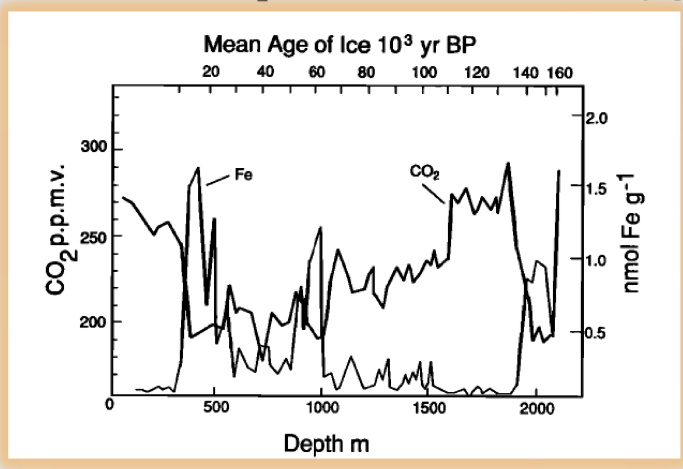
Introduction

Iron Hypothesis

J H Martin *Nature*, VOL 345 10 MAY 1990

Glacial-Interglacial CO_2 Change — J H. Martin *Paleoceanography*, VOL.5, NO.1 PAGES 1-13, 1990



Atmospheric Fe Dust Input → Increase of Primary Productivity → Low CO_2 Concentration → Climate Change

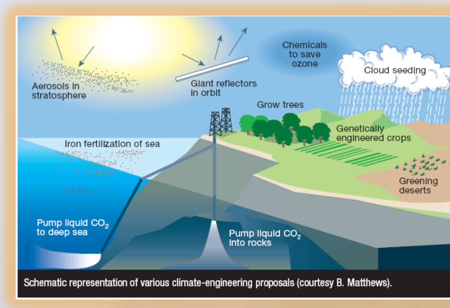
"Iron hypothesis" states that phytoplankton growth and biomass are limited by low concentration of available iron in large regions of the world's oceans where other plant nutrients are abundant.(HNLC)

Geo-Engineering (Iron Fertilization)

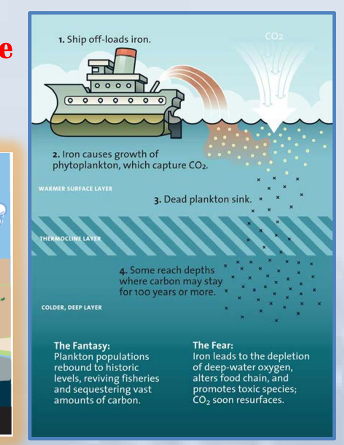
CO_2 Reduction

Climate Change

Geo-Engineering



Iron Fertilization



David W. Keith, *Nature*, VOL 409 , 18 JANUARY 2001

Bio-availibility of Iron

✓ Much of the iron is predicted to be the form of ferric oxides and oxyhydroxides, based on the thermodynamic consideration.
✓ Transformation of iron speciation could be the important process to increase the availability of iron to phytoplankton
✓ Most of the iron oxides have semiconducting properties (Narrow B·G of 2.2eV)

❖ Possible mechanisms of iron dissolution
1. Thermal dissolution
2. *Photoreduction*
3. Complexation with siderophores or similar organic ligands.

Nature, 309, 783-784, 1984
Environ. Sci. Technol., 27, 2056-2062, 1993
Mar. Chem., 46, 319-334, 1994

Photochemical Transformation

Non-bioavailable / Insoluble — Fe_2O_3, Fe_3O_4, FeOOH → Bioavailable / Soluble — Fe^{2+} or Fe^{3+}

Unique Reactions in Ice Phase

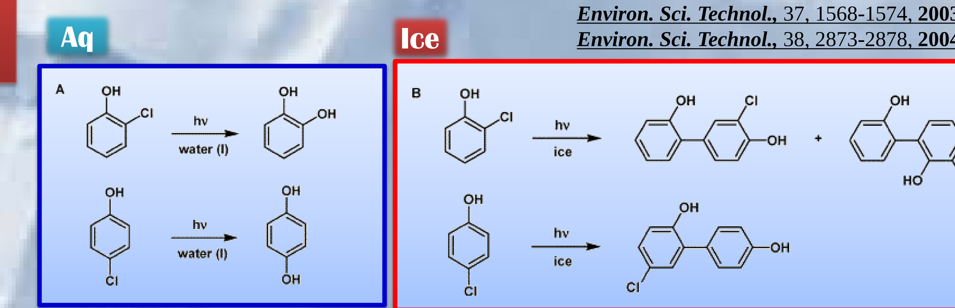
Takenaka, N .*Nature* .VOL 358, 1992
Takenaka, N *J.Phys.Chem*, 100,13874-13884, 1996

[Aqueous] $NO_2^- \xrightarrow[\text{Dissolved } O_2]{OX} NO_3^-$ (Slow)

[Ice] $2HNO_2 + O_2 \rightarrow 2H^+ + NO_3^-$ (Very Fast) [10^5 Times]

✓ When pH decreases unfrozen solution, NO_2^- changes to HNO_2 species. After this stage, the conc. of the reactant(HNO_2) in the unfrozen solution abruptly increase resulting in the acceleration of the rate of formation of NO_3^-.

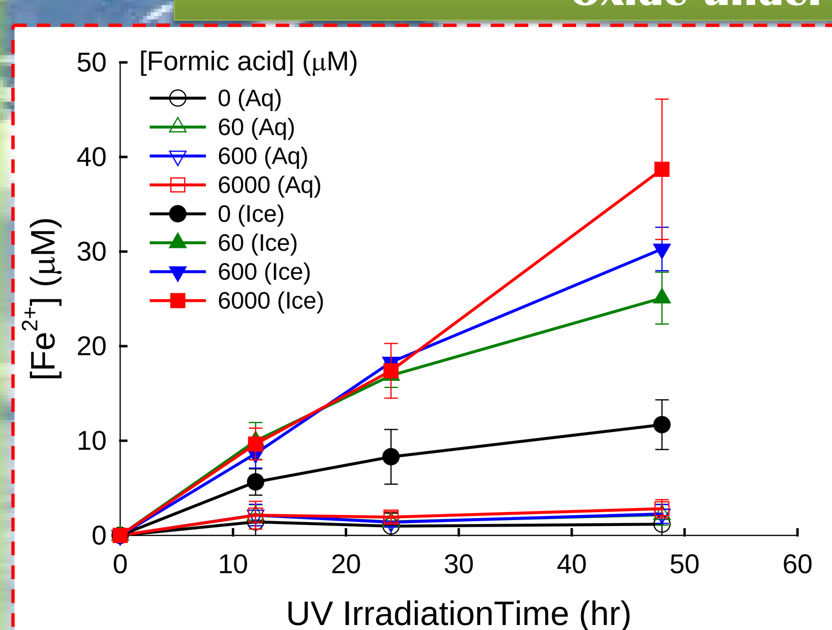
Environ. Sci. Technol., 37, 1568-1574, 2003
Environ. Sci. Technol., 38, 2873-2878, 2004



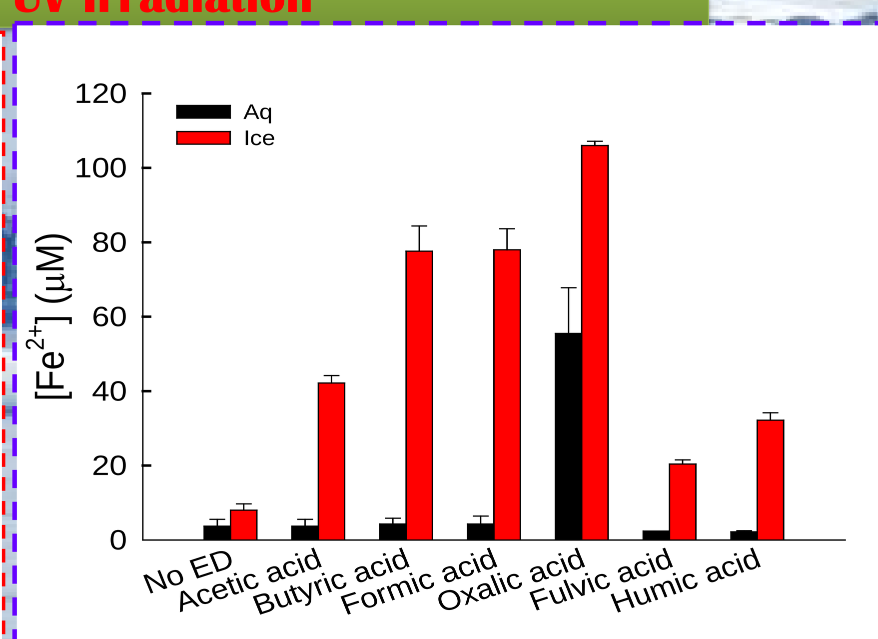
✓ More non-degradable and toxic products can be generated from ice photochemical reaction

Result & Discussion

$Fe(II)_{aq}$ Formation via Photoreductive Dissolution of Iron Oxide under UV Irradiation



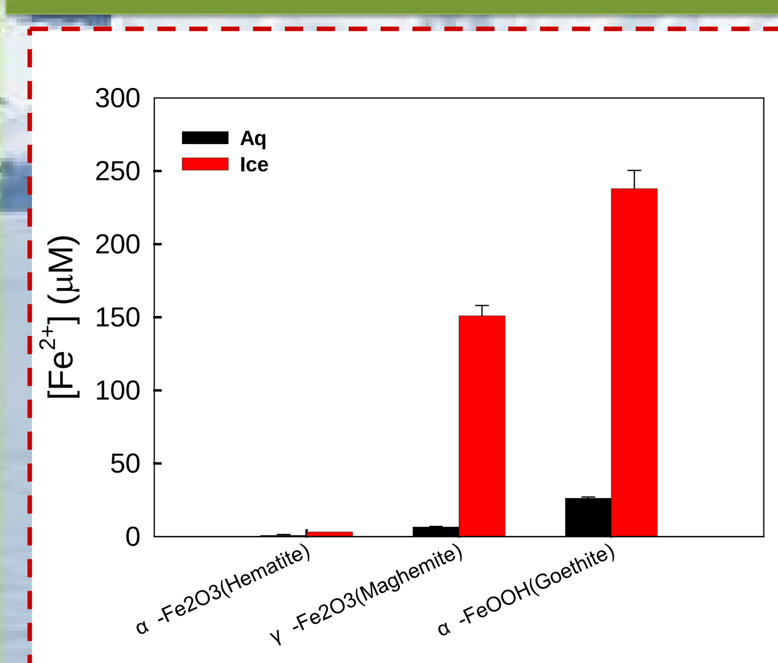
[α-Fe_2O_3(colloid)] = 8 mg/L, pH=3



[α-Fe_2O_3(colloid)] = 16 mg/L, [ED] = 600 μM or 1ppm, pH=3

✓ Photoreductive dissolution of iron oxide is markedly enhanced in ice under UV irradiation(λ>300nm)
✓ The dissolution of hematite in ice was enhanced in the presence of various organic acids

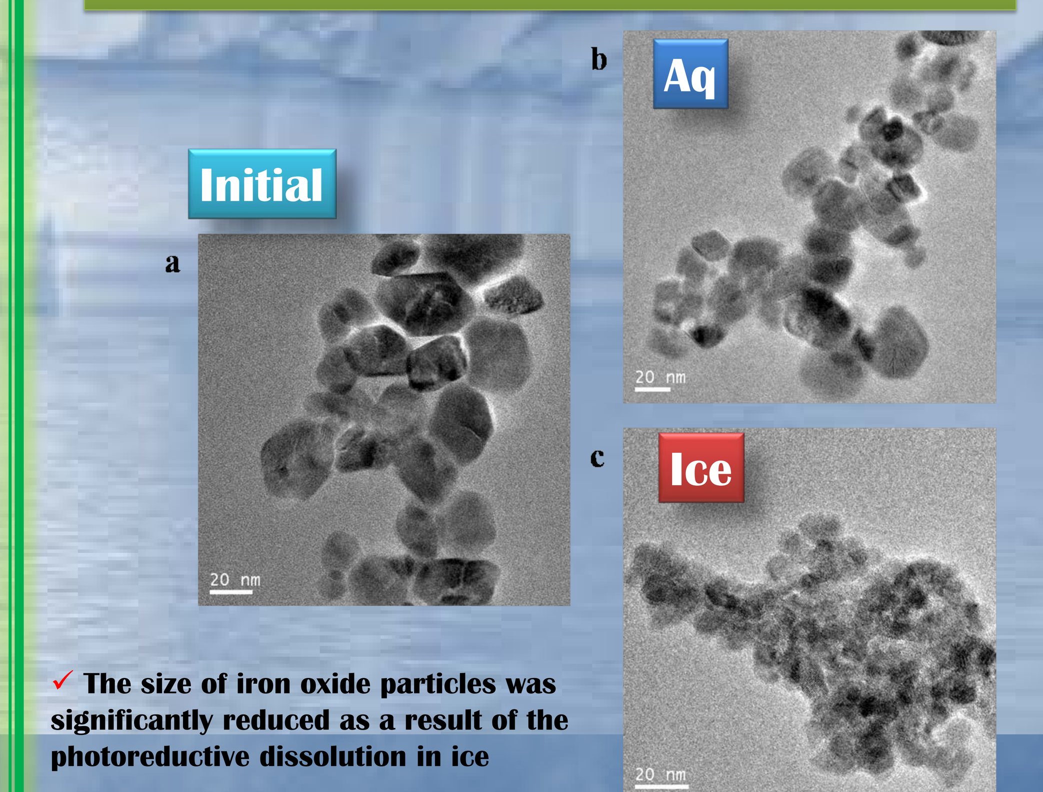
$Fe(II)_{aq}$ Formation via Photoreductive Dissolution of Various Iron oxides



[iron oxide(commercial)] = 0.2 g/L, [ED] = 6000, pH=3.5, 48 h UV

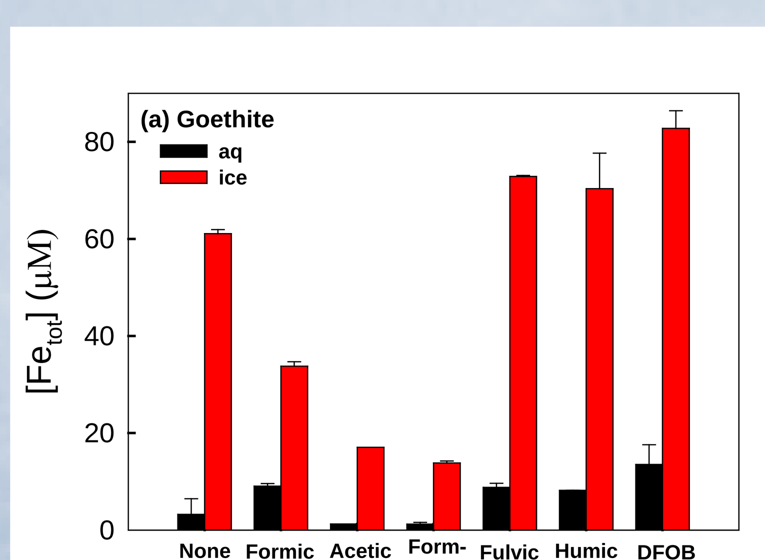
✓ The enhanced photoactivities in ice were also confirmed regardless of the type of iron oxides trapped in ice

TEM Image of Hematite after Reaction

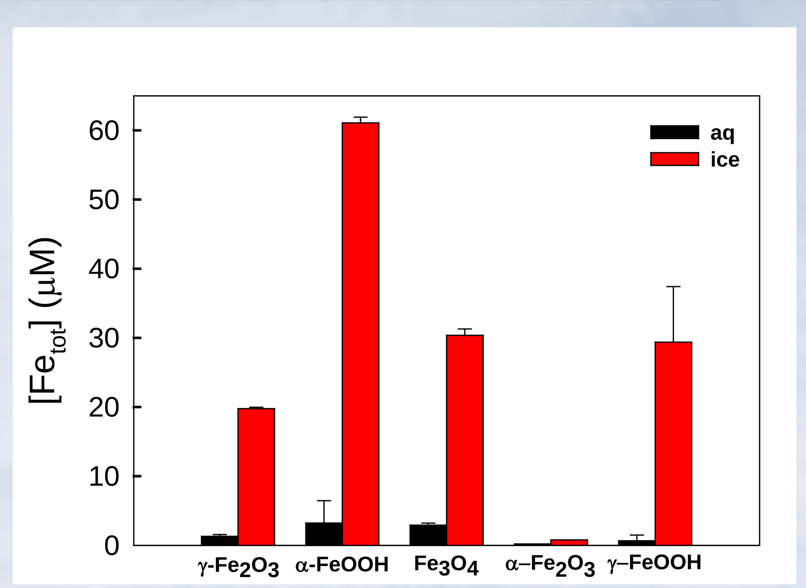


✓ The size of iron oxide particles was significantly reduced as a result of the photoreductive dissolution in ice

Production of Total Dissolved Iron from Iron Oxide under Dark Conditions



[α-FeOOH] = 0.2 g/L, [organic ligand] = 6 mM, [fulvic/humic acid] = 1 ppm pH=3

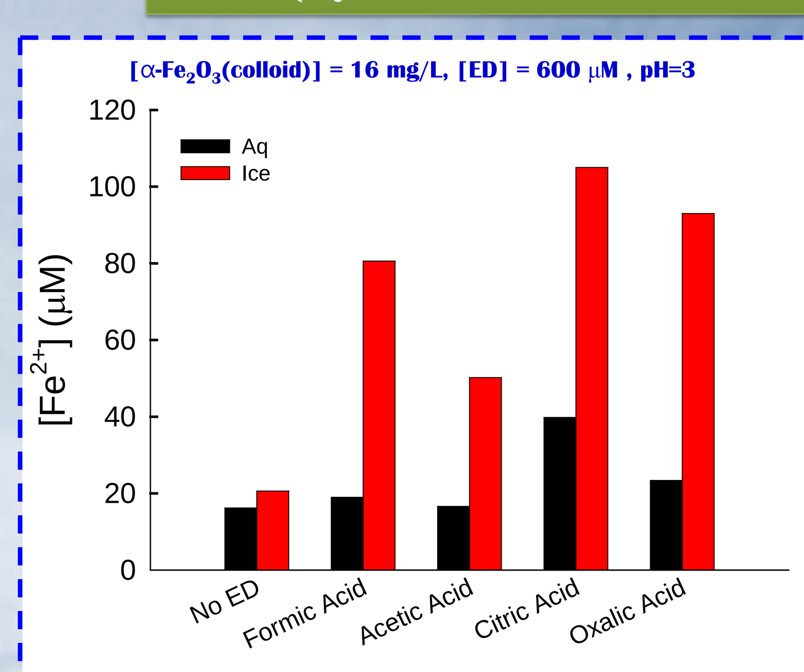


[iron oxide] = 0.2 g L-1 and pH = 3.00 ± 0.05, 72h

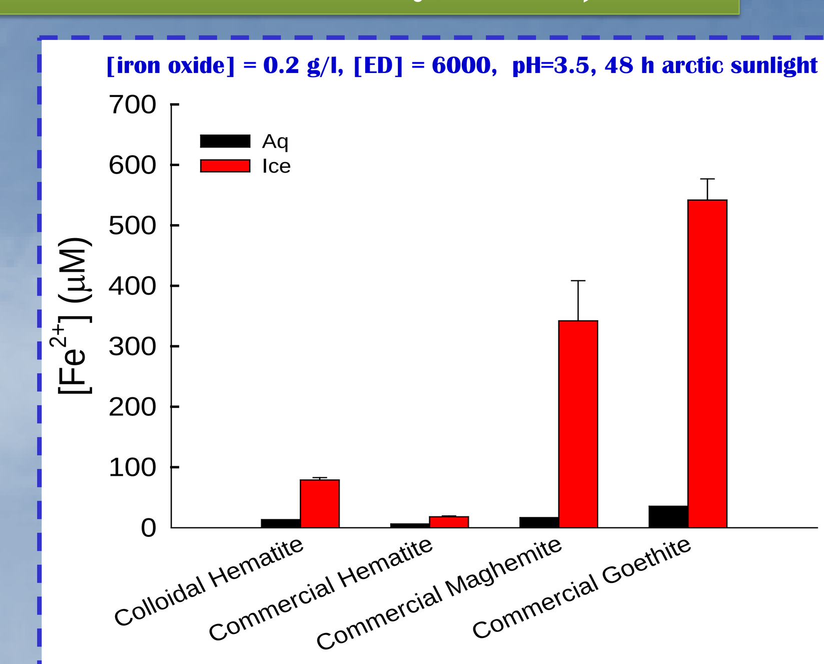
✓ In acidic pH conditions (pH 2, 3, and 4), the dissolution of iron oxides was greatly enhanced in the ice phase compared to that in water. The dissolved iron was mainly in the ferric form, which indicates that the dissolution is not a reductive process

Outdoor Experiment under Solar Radiation (Ny-Ålesund, Svalbard, 78°55´N 14th - 28th May, 2009)

[α-Fe_2O_3(colloid)] = 16 mg/L, [ED] = 600 μM , pH=3

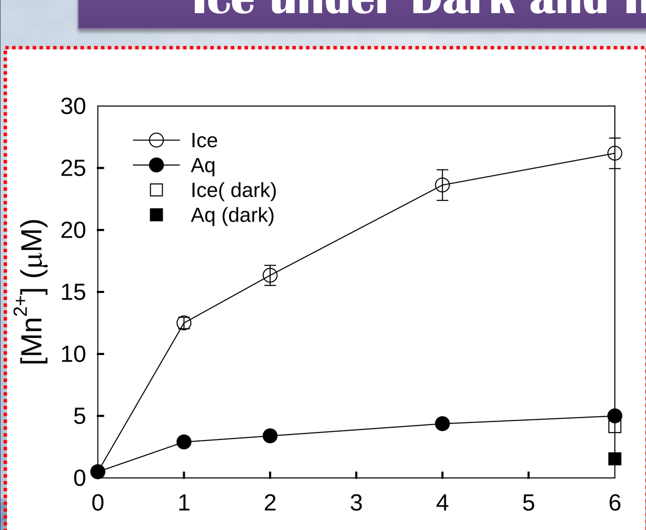


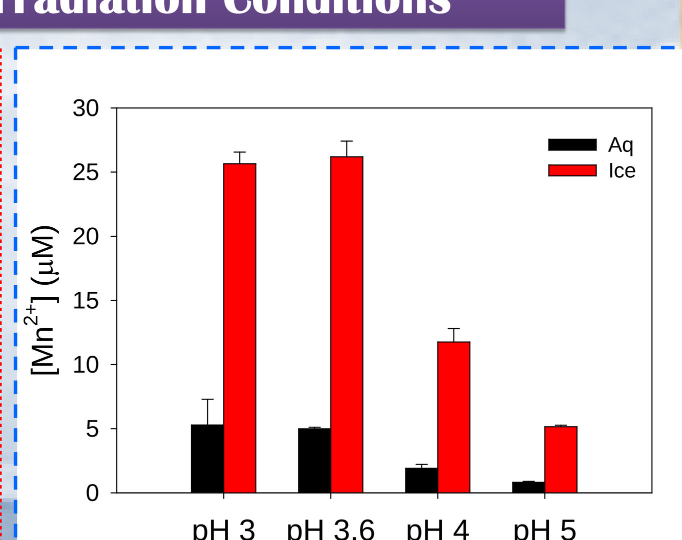
[iron oxide] = 0.2 g/l, [ED] = 6000, pH=3.5, 48 h arctic sunlight



✓ The production of Fe^{2+} from the photodissolution of iron oxides in ice was found to be consistently higher than that in the corresponding aqueous phase, which confirms the laboratory results.

Enhanced Dissolution of Manganese Oxide in Ice under Dark and Irradiation Conditions

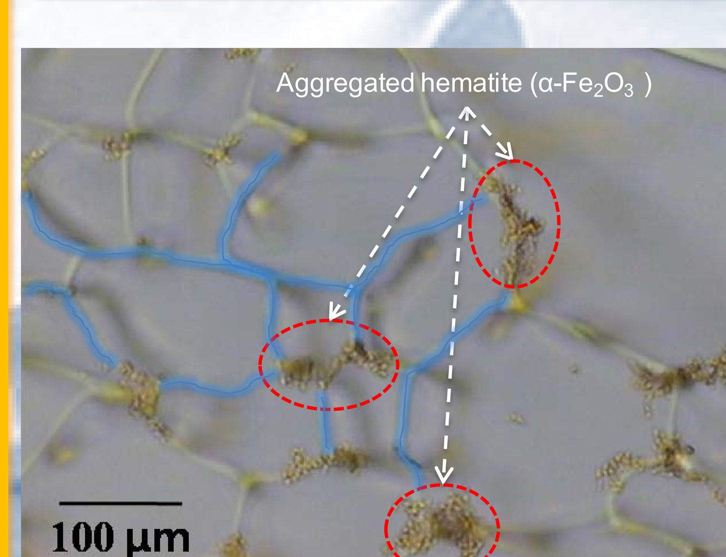




[MnO_2] = 50 μM (2.75 mg/L), [formic acid] = 600 μM, UV irradiation.

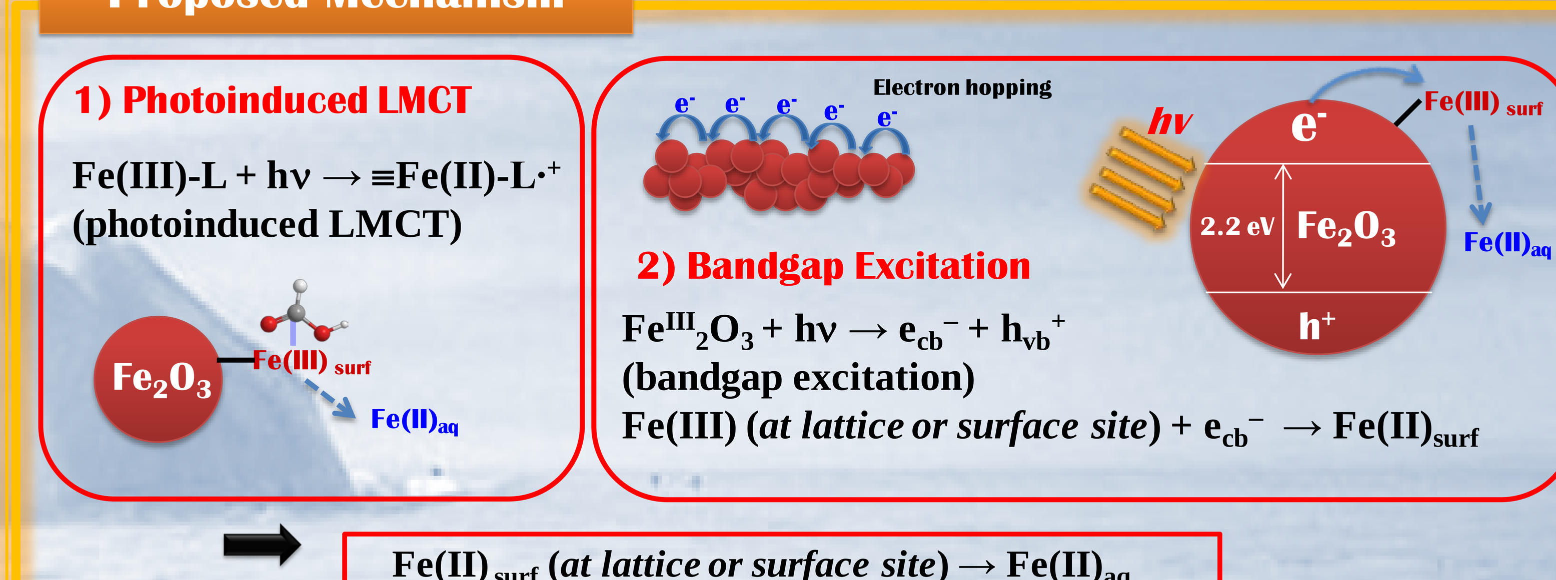
✓ The photoreductive dissolution of MnO2 under UV irradiation which occurs very slowly in aqueous solution, is markedly accelerated in the ice phase even in the absence of light.
✓ The enhanced production of Mn(II)aq via photoreductive dissolution in ice phase was observed at all pH rages tested (pH 3-5).
✓ The dissolution of natural minerals like manganese oxides can be enhanced in icy environments such as polar region, upper atmosphere, and frozen soil.

Freeze Concentration Effect



✓*Freeze Concentration Effect* : When solution is solidified, it pushes iron oxide particles and organic acids out of the ordered ice crystal and concentrates them into narrow channels between ice crystals called grain boundary regions.

Proposed Mechanism



✓ Freeze concentration effects increase the concentration of iron oxide particles and organic ligands in the grain boundary region with enhancing the surface complexation and the subsequent LMCT
✓ Within the agglomerates of semiconductor nanoparticles, the charge-pair separation can be facilitated by the electron hopping through the interconnected grain boundaries and the following interfacial electron transfer reactions can be enhanced compared with those occurring on an isolated particle

Conclusions

- The photoreductive dissolution of iron/manganese oxides proceeded slowly in aqueous solution but was significantly accelerated in ice, subsequently releasing more bioavailable iron/manganese upon thawing .
- We hypothesized that the enhanced photoreductive dissolution of iron/manganese oxides in the ice phase is not only due to freeze concentration effect but also to electron hopping through interconnected iron(manganese) oxide particles in grain boundaries facilitating the separation of photoinduced charge pairs.
- Dissolution experiments carried out with model systems under ambient solar radiation of Ny-Ålesund (Svalbard, 78°55´N) also showed that the generation of dissolved Fe(II)/Mn(II) via photoreductive dissolution is enhanced when iron/manganese oxides are trapped in ice.
- The ice(snow)-covered surfaces and ice-cloud particles containing iron(manganese)-rich mineral dusts in the polar and cold environments provide a source of bioavailable iron(manganese) when they thaw.

References

1. Kitae Kim, Wonyong Choi, Michael R. Hoffmann, Ho-Il Yoon and Byong-Kwon Park. "Photoreductive dissolution of iron oxide in ice and Its environmental Implications" *Environ. Sci. Technol.* 2010, 44, 4142–4148
- Editor's Choice, Science, Vol 328, May 28, 2010
- Chemical & Engineering News(C& EN), Latest News, May 17, 2010

2. Daun Jung, Kitae Kim and Wonyong Choi. "Enhanced dissolution of iron oxides in ice " *Atmos. Chem. Phys.*, 2012, 12, 11125-11133. (The first two authors contributed equally)

3. Kitae Kim, Ho-Il Yoon, and Wonyong Choi. "Enhanced Dissolution of Manganese Oxide in Ice Compared to Aqueous Phase under Illuminated and Dark Conditions" *Environ. Sci. Technol.* 2012, 46, 13160-13166.