ENHANCED FORMATION OF ATMOSPHERIC IODINE SPECIES IN ICE MEDIA AND ITS IMPACTS ON ANTARCTICA

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Introduction

Unique reactions in ice phase

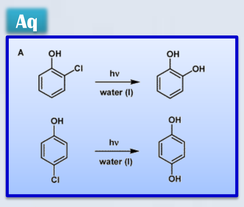
Takenaka, N .***Nature*** .VOL 358, **1992**
Takenaka, N ***J.Phys.Chem***, 100,13874-13884, **1996**

[Aqueous] NO_2^- —(OX, Dissolved O_2)→ NO_3^- **(Slow)**

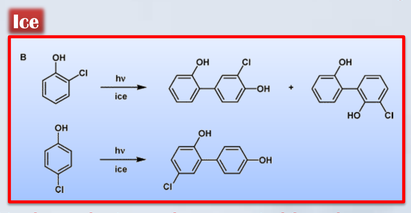
[Ice] $2HNO_2 + O_2 \rightarrow 2H^+ + NO_3^-$ **(Very Fast) [10^5 Times]**

✓ 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^-.

Aq



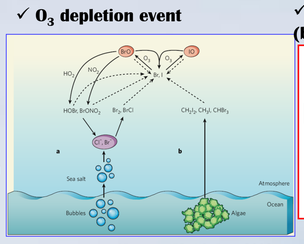
Ice



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

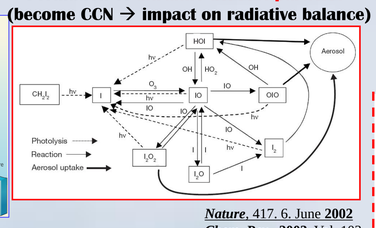
Importance of atmospheric iodine

✓ O_3 depletion event



Nature, 453. 26. June **2008**
Science, 291, 19, January **2001**

✓ Formation of ultrafine aerosol particles (become CCN → impact on radiative balance)



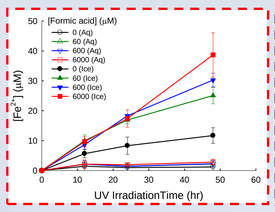
Nature, 417. 6. June **2002**
Chem. Rev., **2003**, Vol. 103

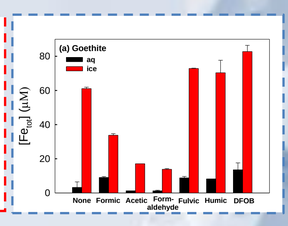
✓ Essential dietary element for mammals
✓ Influences the oxidizing capacity of the atmosphere (oxidize or remove org.&inorg.)
✓ Enhance depletion of gaseous elemental mercury (Hg^0) by oxidation to reactive gaseous mercury (Hg^{II}) (in the polar atmosphere)
✓ Perturbation of OHx/NOx Cycles
→Atmospheric iodine source in Antarctica is still unknown

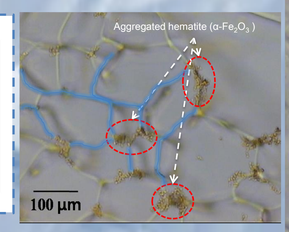
Chem. Rev., 112, 1773-1804, **2012**
Environ. Sci. Technol., **2007**, *41*, 7280–7285
Geophys. Res. Lett., **2003**,Vol 30, 2297
Science, Vol 297 30 August **2002**

Enhanced dissolution of iron oxides in ice

K. Kim and W. Choi, ***Environ. Sci. Technol.***, 44, 4142-4148-1574, **2010**
Science, VOL 328, 1077, **2010**, *Editor's Choice, "Iron's icy fate"*
Kitae Kim , Daun Jeong, and Wonyong Choi. Atmos. Chem. Phys., 2012, 12, 11125-11133



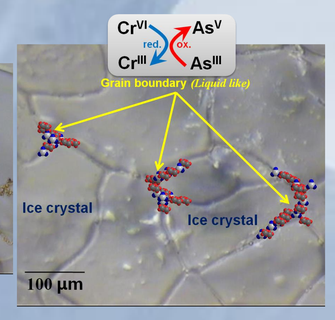




→ The dissolution of iron oxides which is very slow reaction in aqueous solution was significantly accelerated in in phase regardless of presence and absence of irradiation. We suspected that the enhanced dissolution of iron oxides in frozen samples is mostly due to "freeze concentration effect"

Enhanced redox conversion in ice

Environ. Sci. Technol., **2011**, *45*, 2202-2208

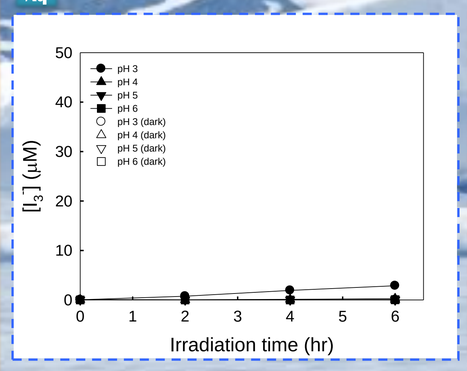


✓ Cr(VI) reduction by organics and As(III) was significantly enhanced in ice phase

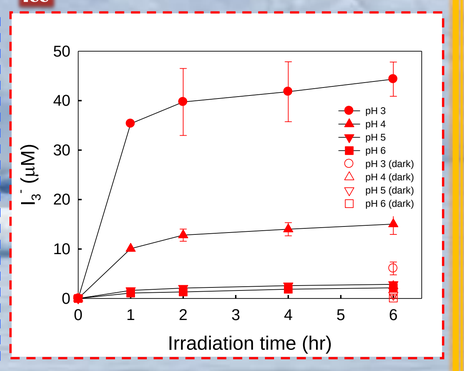
Result & Discussion

I^- photo-oxidation to I_3^- under UV (λ> 300 nm)

Aq



Ice

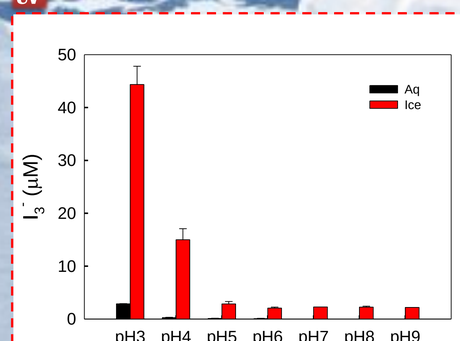


[I^-] = 1mM (KI),6 hr UV irradiation by Medium pressure Hg lamp (UV, λ > 300nm)

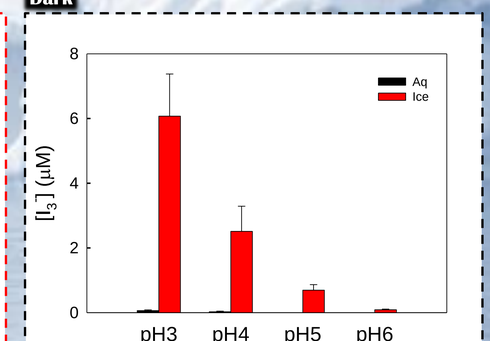
✓ The formation of I_3^- under UV irradiation, which occurs very slowly in aerated aqueous solutions, is significantly accelerated in the polycrystalline ice phase at the pH range of 3 to 6.
✓ At pH 3, I^- photo-oxidation was observed in aqueous solution as well.
✓ I_3^- production was observed in ice even the dark condition.

pH dependence on I^- Oxidation

UV



Dark



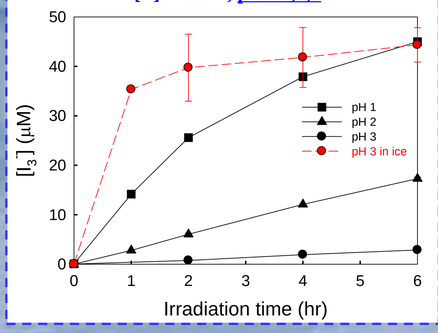
[I^-] = 1mM (KI),6 hr UV irradiation and dark by Medium pressure Hg lamp (UV, λ > 300nm)

$O_2\ (aq) + 4H^+ + 6I^- \rightarrow 2H_2O + 2I_3^-$

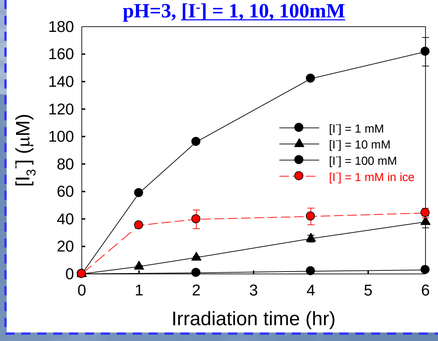
✓ The enhanced photo-oxidation of I^- in ice phase was observed at the pH range of 3 to 9.
✓ Only at pH 3, I^- photo-oxidation was observed in aqueous solution
✓ The oxidation of I^- under dark condition, which occurs very slowly in aerated aqueous solutions, is also accelerated in ice phase at the pH range of 3 to 6

Freeze concentration effect

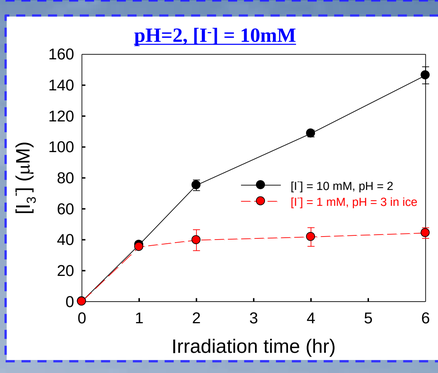
[I^-] = 1mM, pH= 1,2,3



pH=3, [I^-] = 1, 10, 100mM



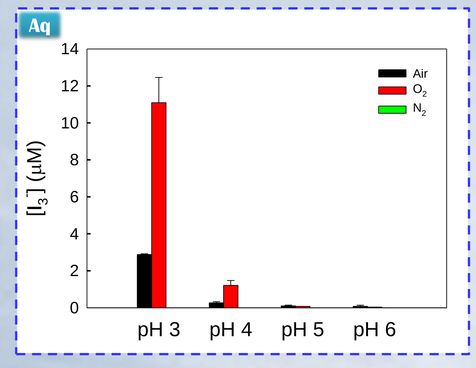
pH=2, [I^-] = 10mM



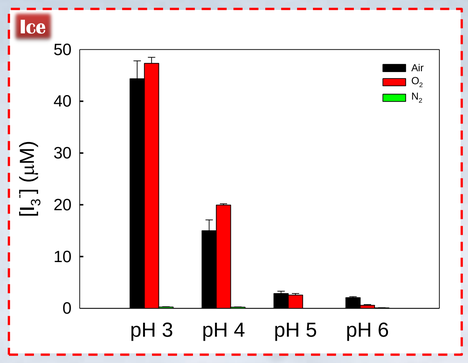
✓In the presence of excess amount of iodide and proton, photooxidative formation of I_3^- was observed even in aqueous sample.
✓Both [I^-] and [H^+] affect I^- oxidation.

Effect of various saturated gases on the photooxidation of I^-

Aq



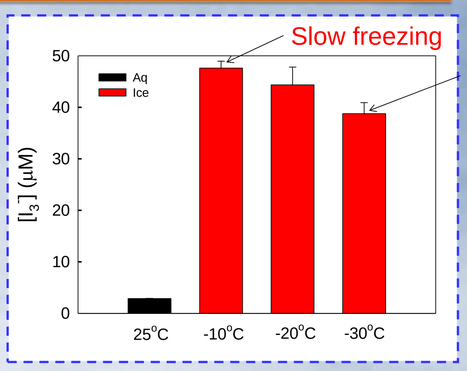
Ice



[I^-] = 1mM (KI), 6 hr UV irradiation, 30 min N_2 or O_2 purging

✓ I_3^- generation was totally retarded in the absence of oxygen even in the ice phase (N_2 condition)
✓ Formation of I_3^- in aqueous solution was enhanced under O_2–saturated condition
✓ I_3^- formation is more preferable at acidic condition
✓ O_2 concentration and proton concentration simultaneously affect I^- oxidation
✓ O_2 was already saturated in air-equilibrated ice samples

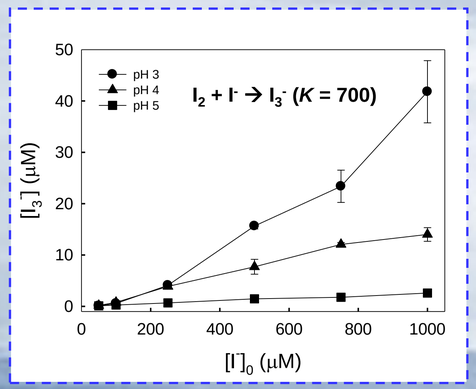
Temperature effect on the production of I_3^- under UV



[I^-] = 1mM (KI), 6 hr UV irradiation, pH =3

✓ I_3^- formation in ice phase was gradually decreased when the ice temperature dropped
✓ The freeze concentration effect was much higher under slow freezing at higher temperature compared to fast freezing at lower temperature

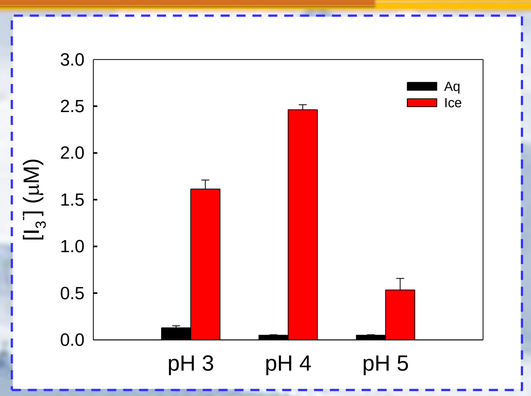
I^- oxidation with various $[I^-]_{initial}$ and pH



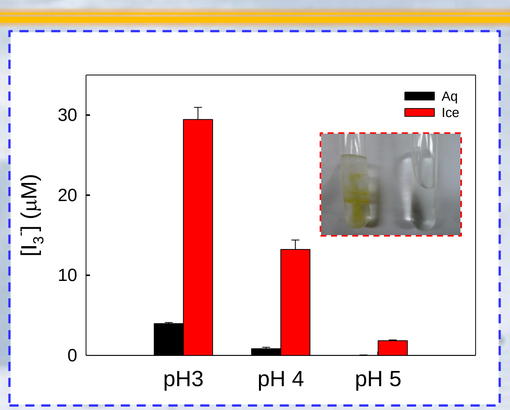
6hr UV irradiation by Medium pressure Hg lamp (UV, λ > 300nm)

✓The formation of I_3^- was efficient in ice when the pH is low and [I^-] is high

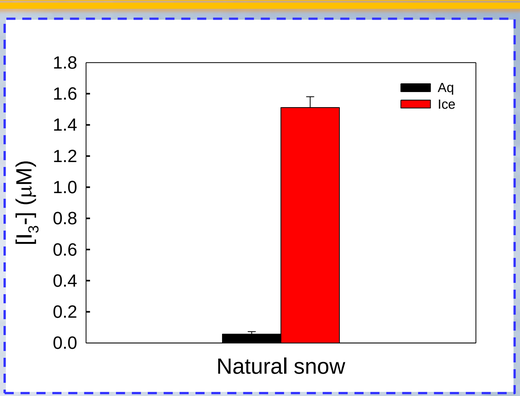
Outdoor Experiments in Antarctica



[I^-] = 0.2 mM (KI), 6hr irradiation



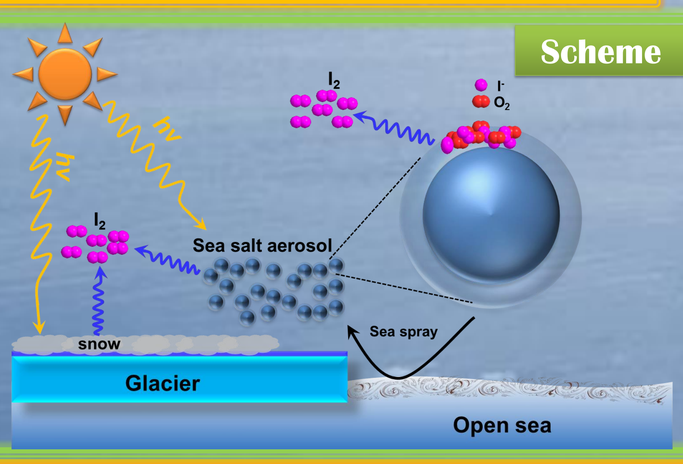
[I^-] = 1 mM (KI), 6hr irradiation



[I^-] = 1 mM , 6hr irradiation, $pH_{initial}$ = 5.35(no pH adjustment)

✓ The production of I_3^- via photooxidative reaction in ice was consistently higher than that in the corresponding aqueous phase, which confirms the laboratory results
✓ Photooxidative generation of I_3^- was markedly enhanced in ice phase(in natural snow)

Scheme



Conclusions

- The photo-oxidation of I^- to I_3^- under UV irradiation, which occurs very slowly in aerated aqueous solutions, is significantly accelerated in the polycrystalline ice phase at the pH range of 3 to 9. (preferable in acidic environment)
- In highly concentrated aqueous solution, red shift of spectrum(>300 nm) and I_3^- formation was observed.
- Photo-oxidative formation of I_3^- was totally retarded in the absence of O_2 even in the ice phase.
- Elevated [I^-], [H^+], and [O_2] (leading to spectrum change) in ice grain boundaries might be related to the enhanced photo-oxidation of I^- in ice phase.
- The outdoor experiments in Antarctic also showed enhanced I_3^- formation via photooxidation in ice.
- Unknown generation pathway for the considerable release of reactive iodine compounds to the atmosphere in polar regions