

# ENHANCED PRODUCTION OF ATMOSPHERIC IODINE

## IN ANTARCTICA

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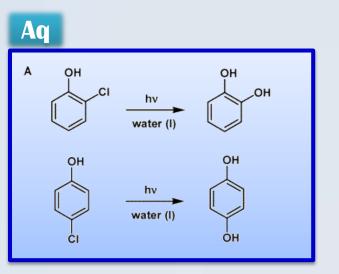
## Introduction

Unique reactions in ice phase <u>Takenaka</u>, N .*Nature* . VOL 358, **1992** Takenaka, N J.Phys.Chem, 100,13874-13884, 1996

[Aqueous]  $NO_2$  NO<sub>3</sub> (Slow)

[Ice]  $2HNO_2 + O_2 \longrightarrow 2H^+ + NO_3^-$  (Very Fast) [10<sup>5</sup> Times]

✓ When pH decreases unfrozen solution, NO<sub>2</sub>- changes to HNO<sub>2</sub> species. After this stage, the conc. of the reactant(HNO<sub>2</sub>) in the unfrozen solution abruptly increase resulting in the acceleration of the rate of formation of NO<sub>3</sub><sup>-</sup>.



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

photo-oxidation to  $I_3$  under UV ( $\lambda > 300$  nm)

## Importance of atmospheric iodine

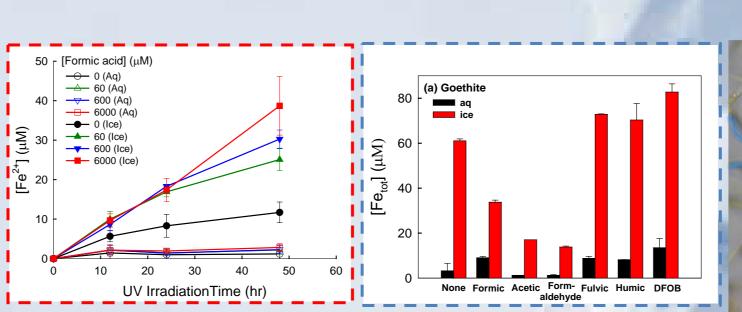
✓ Formation of ultrafine aerosol particles  $\checkmark$   $0_3$  depletion event (become CCN  $\rightarrow$  impact on radiative balance) *Nature*, 417. 6. June **200**2

Nature, 453. 26. June 2008 Science, 291, 19, January 2001 ✓ Essential dietary element for mammals

- ✓ Influences the oxidizing capacity of the atmosphere (oxidize or remove org.&inorg.)
- ✓ Enhance depletion of gaseous elemental mercury (Hg<sup>0</sup>) by oxidation to reactive gaseous mercury (Hg<sup>II</sup>) (in the polar atmosphere)
- ✓ Perturbation of OHx/NOx Cycles Chem. Rev., 112, 1773-1804, 2012 → Atmospheric iodine source in Antarctica Geophys. Res. Lett., 2003, Vol 30, 2297 is still unknown *Science*, Vol 297 30 August **2002**

#### Enhanced dissolution of iron oxides in ice

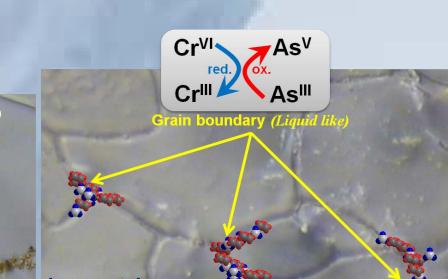
K. Kim and W. Choi, *Environ. Sci. Technol.*, 44, 4142-4148-1574, **2010** Science, VOL 328, 1077, **2010,** Editor's Choice. "Iron's icy fate" Kitae Kim, Daun Jeong, and Wonyong Choi. Atmos. Chem. Phys., 2012, 12, 11125-11133



> 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 Environ. Sci. Technol., 2007, 41, 7280–7285 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

Chem. Rev., 2003, Vol. 103

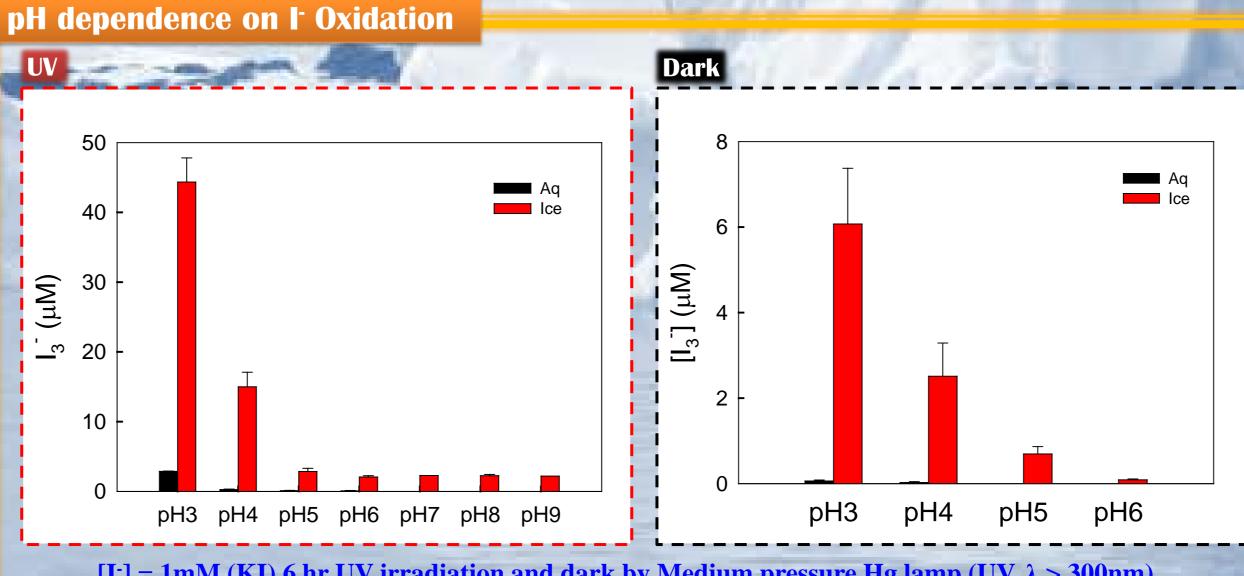
### (M<sub>m</sub>) → pH 5 (dark) ☐ pH 6 (dark) <u>\_</u>ღ 20 pH 6 (dark)

[I<sup>-</sup>] = 1mM (KI),6 hr UV irradiation by Medium pressure Hg lamp (UV,  $\lambda > 300$ nm)

Irradiation time (hr)

- ✓ The formation of I<sub>3</sub> 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<sub>3</sub> production was observed in ice even the dark condition.

Irradiation time (hr)



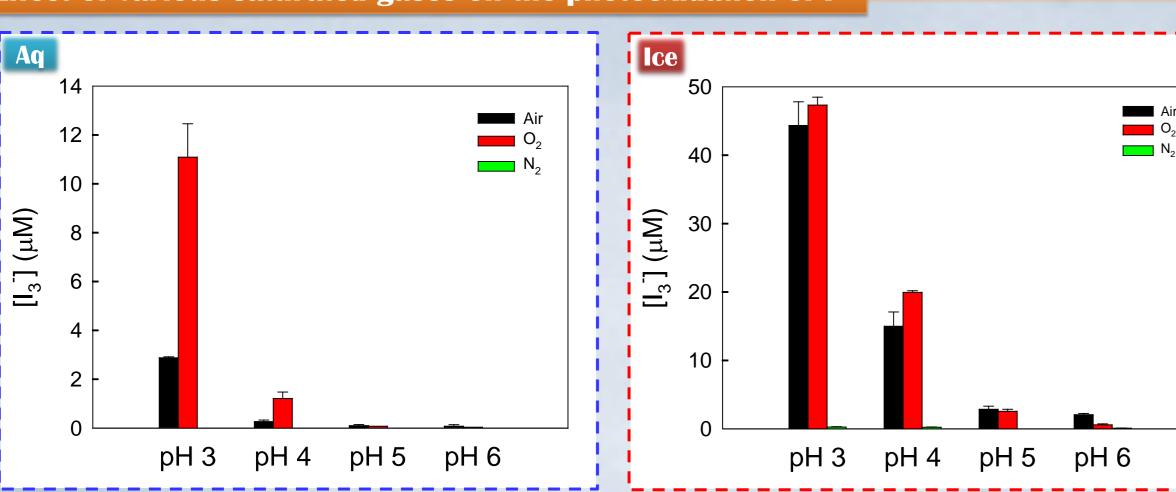
[I<sup>-</sup>] = 1mM (KI),6 hr UV irradiation and dark by Medium pressure Hg lamp (UV,  $\lambda > 300$ nm)  $O_2(aq) + 4H^+ + 6I^- \rightarrow 2H_2O + 2I_3^-$ 

✓ 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

is also accelerated in ice phase at the pH range of 3 to 6

✓ The oxidation of I under dark condition, which occurs very slowly in aerated aqueous solutions,

Effect of various saturated gases on the photooxidation of I



 $\checkmark$  I<sub>3</sub> generation was totally retarded in the absence of oxygen even in the ice phase (N<sub>2</sub> condition)

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

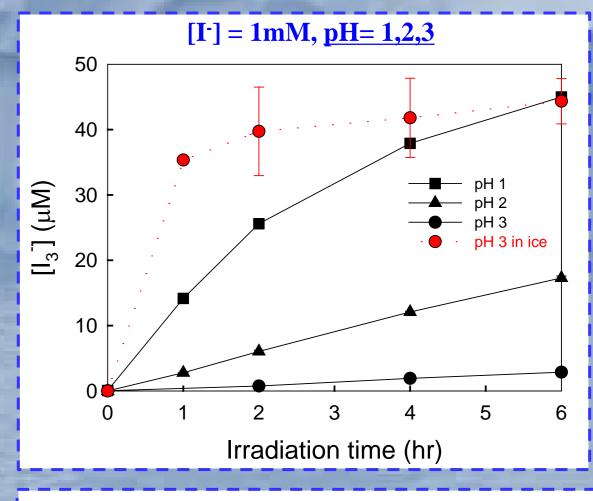
- ✓ Formation of I<sub>3</sub> in aqueous solution was enhanced under O<sub>2</sub>-saturated condition ✓ I<sub>3</sub> formation is more preferable at acidic condition
- ✓ O₂ concentration and proton concentration simultaneously affect I⁻ oxidation
- √ O₂ was already saturated in air-equilibrated ice samples

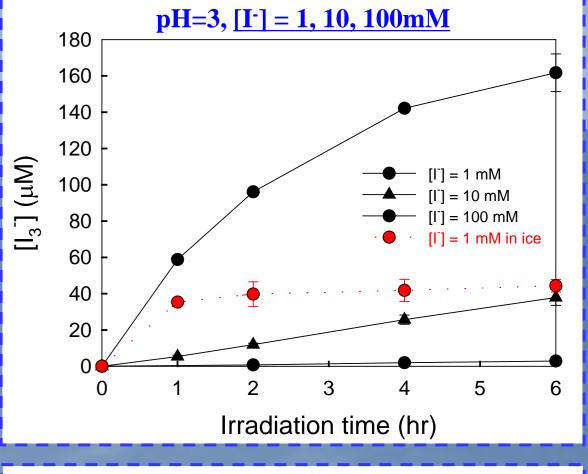
# Temperature effect on the production of $I_3$ under UV Slow freezing Fast freezing -20°C -30°C -10°C $[I^{-}] = 1$ mM (KI), 6 hr UV irradiation, pH = 3

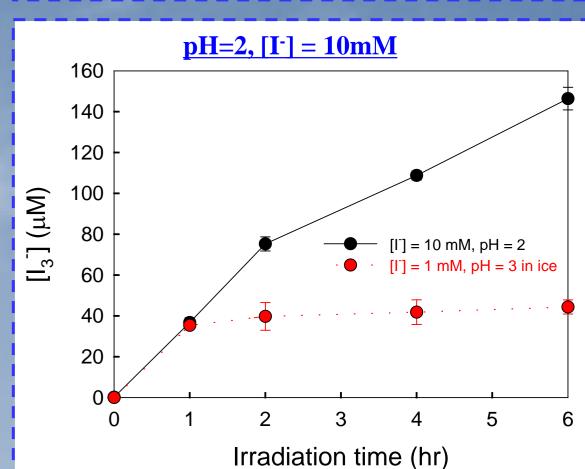
 $\checkmark$   $I_3$  formation in ice phase was gradually decreased when the ice temperature dropped

✓ The freeze concentration effect was much higher under slow freezing at higher temperature compared to fast freezing at lower temperature





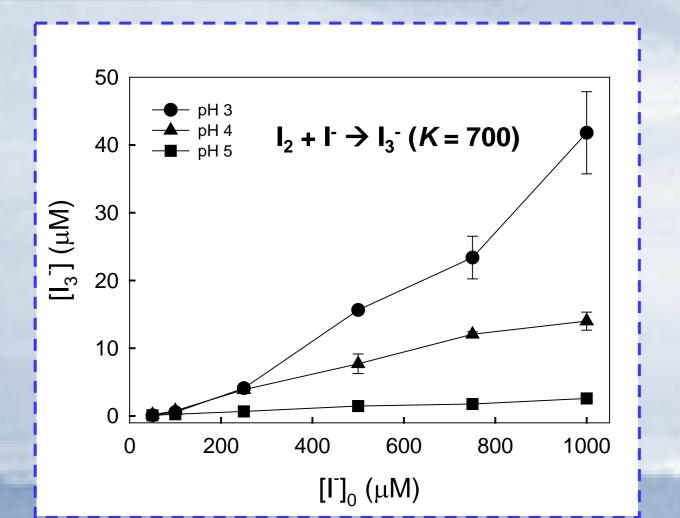




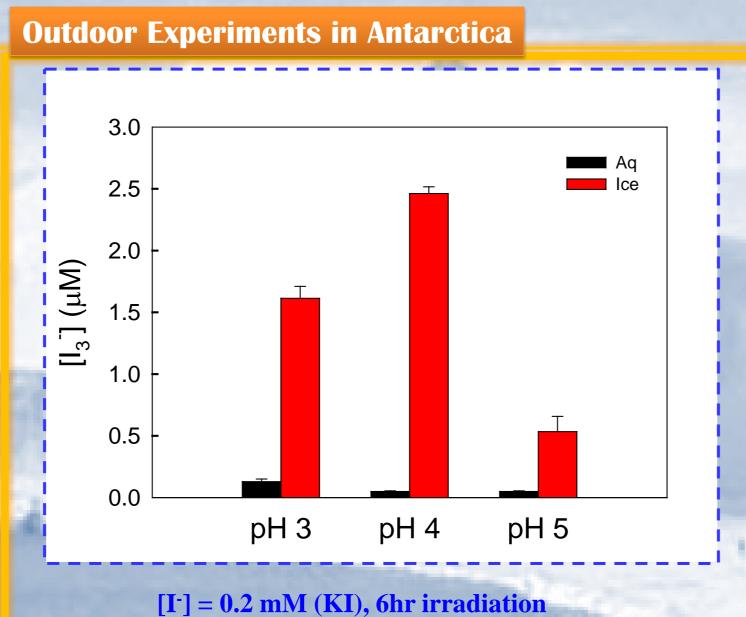
✓In the presence of excess amount of iodide and proton, photooxidative formation of I<sub>3</sub>- was observed even in aqueous sample. ✓ Both [I<sup>-</sup>] and [H<sup>+</sup>] affect I<sup>-</sup> oxidation.

#### oxidation with various [l-] initial and pH

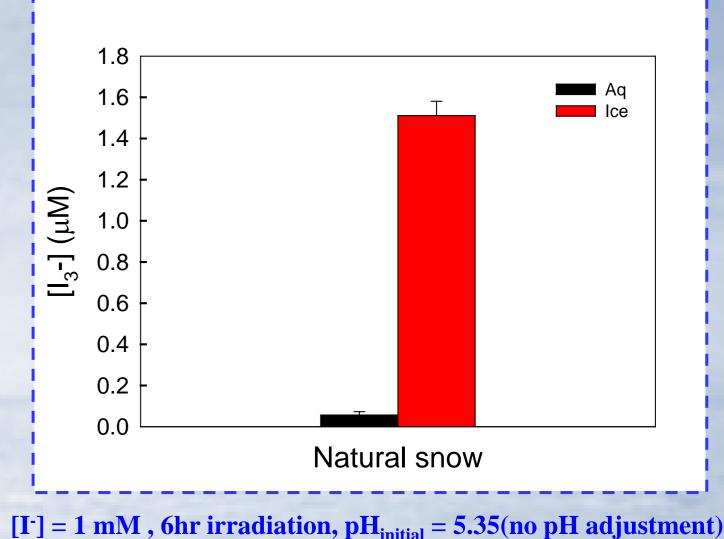
and [l-] is high



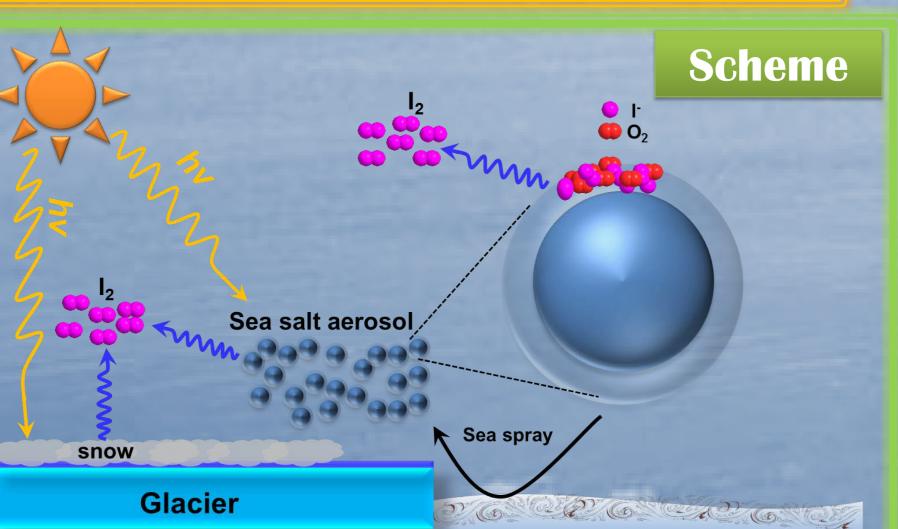
6hr UV irradiation by Medium pressure Hg lamp (UV,  $\lambda > 300$ nm) √The formation of I<sub>3</sub><sup>-</sup> was efficient in ice when the pH is low



30 20  $[I^{-}] = 1 \text{ mM (KI)}, 6 \text{hr irradiation}$ 



✓ The production of I<sub>3</sub> via photooxidative reaction in ice was consistently higher than that in the corresponding aqueous phase, which confirms the laboratory results



Open sea

## Conclusions

- **♣** The photo-oxidation of I to I<sub>3</sub> 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<sub>3</sub> formation was observed.
- $\blacksquare$  Photo-oxidative formation of  $I_3^-$  was totally retarded in the absence of  $O_2$  even in the ice phase.

✓ Photooxidative generation of I<sub>3</sub> was markedly enhanced in ice phase(in natural snow)

- Elevated [I<sup>-</sup>], [H<sup>+</sup>], and [O<sub>2</sub>] (leading to spectrum change) in ice grain boundaries might be related to the enhanced photo-oxidation of I<sup>-</sup> in ice phase.
- **↓** The outdoor experiments in Antarctic also showed enhanced I<sub>3</sub> formation via photooxidation in ice.
  - Korea Polar Research Institute (www.kopri.re.kr)

**↓** Unknown generation pathway for the considerable release of reactive iodine compounds to the atmosphere in polar regions