

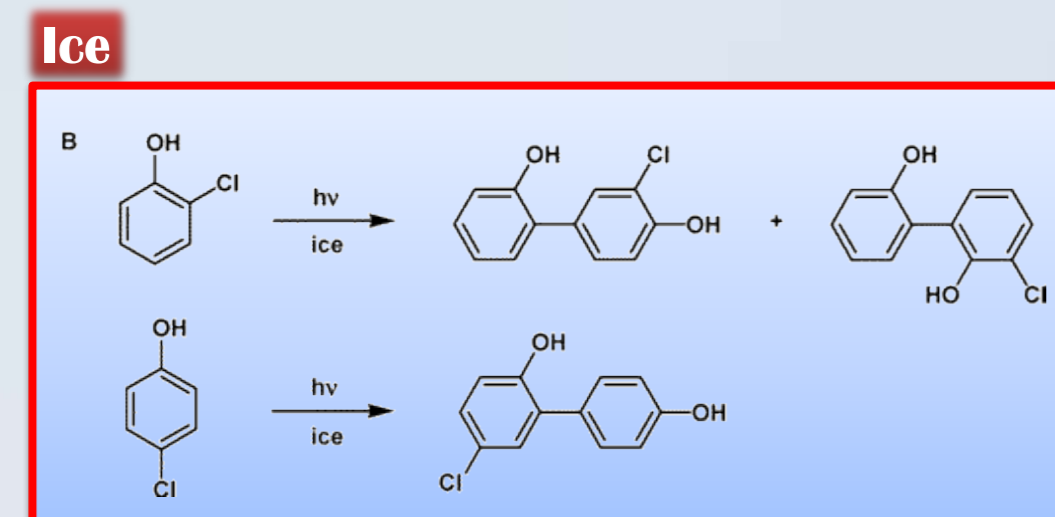
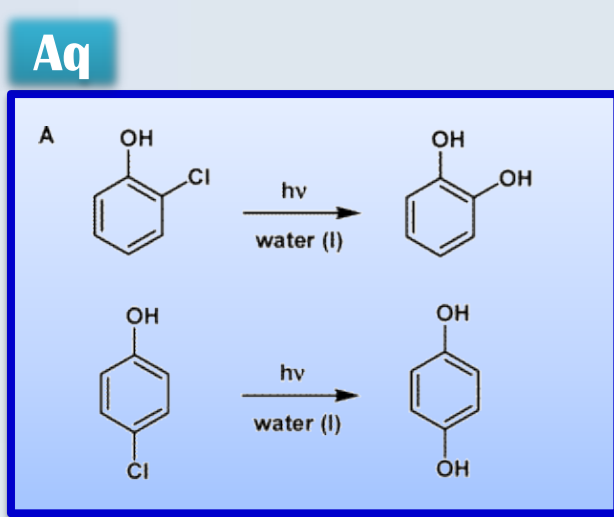
Introduction

Unique reactions in ice phase

[Aqueous] $\text{NO}_2^- \xrightarrow{\text{Dissolved O}_2} \text{NO}_3^-$ (Slow)
Takenaka, N. *Nature*, VOL. 358, 1992
 Takenaka, N. *J. Phys. Chem.*, 100, 13874-13884, 1996

[Ice] $2\text{HNO}_2 + \text{O}_2 \rightarrow 2\text{H}^+ + \text{NO}_3^-$ (Very Fast) [10⁵ Times]

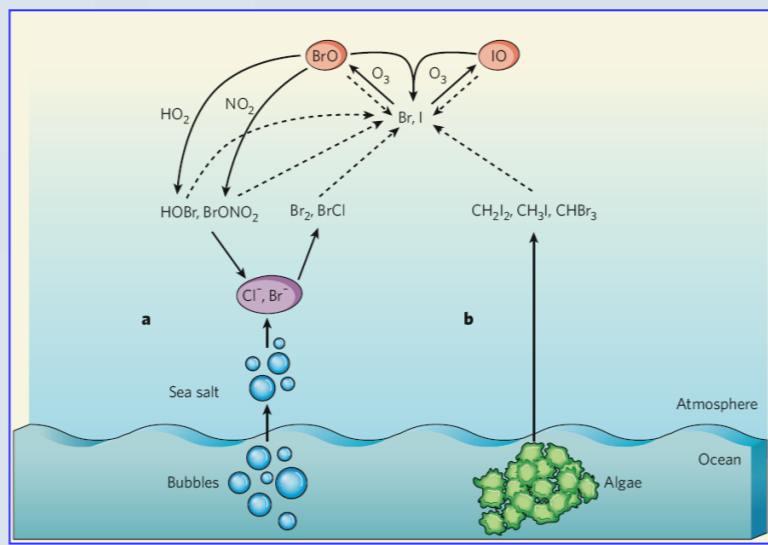
✓ When pH decreases unfrozen solution, NO₂⁻ changes to HNO₂ species. After this stage, the conc. of the reactant(HNO₂) in the unfrozen solution abruptly increase resulting in the acceleration of the rate of formation of NO₃⁻.



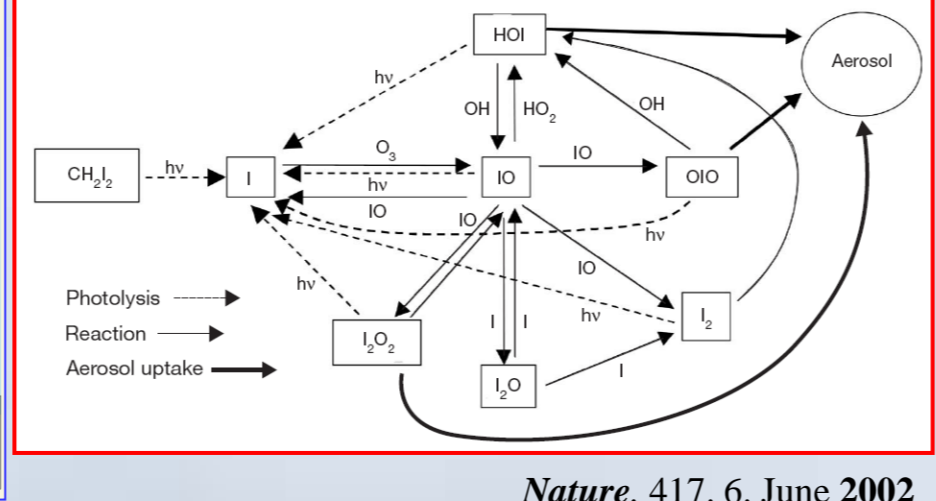
✓ More non-degradable and toxic products can be generated from ice photochemical reaction.

Importance of atmospheric iodine

✓ O₃ depletion event



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

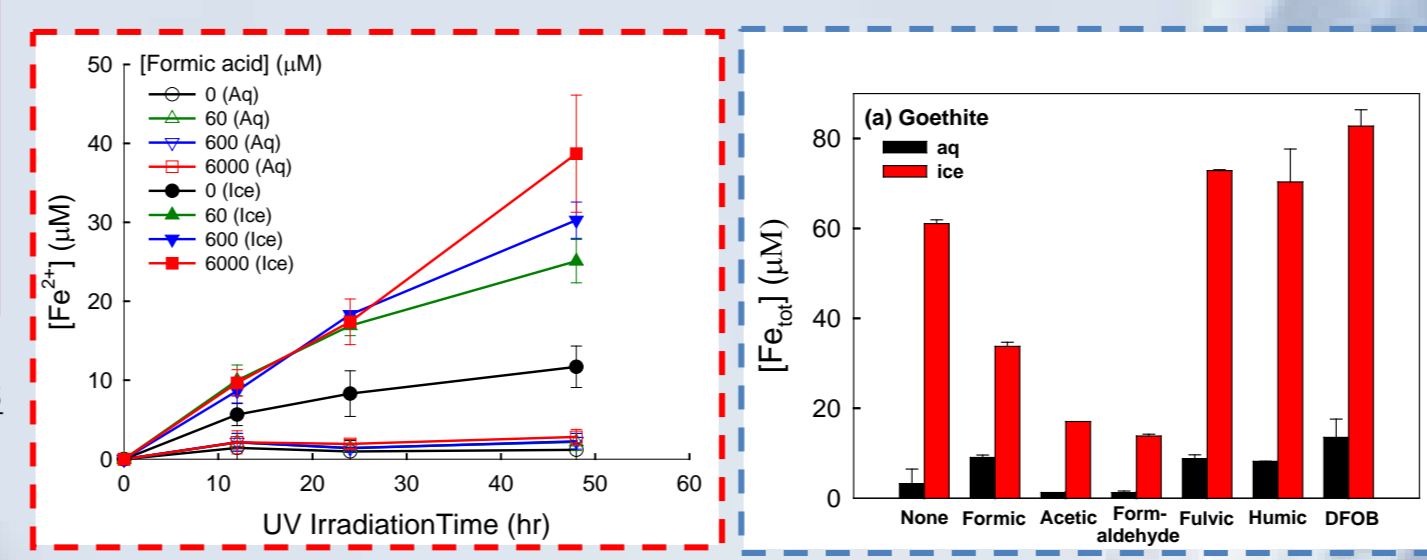


Nature, 453, 26, June 2008
 Science, 291, 19, January 2001

✓ Essential dietary element for mammals
 ✓ Influences the oxidizing capacity of the atmosphere (oxidize or remove org.&inorg.)
 ✓ Enhance depletion of gaseous elemental mercury (Hg⁰) 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

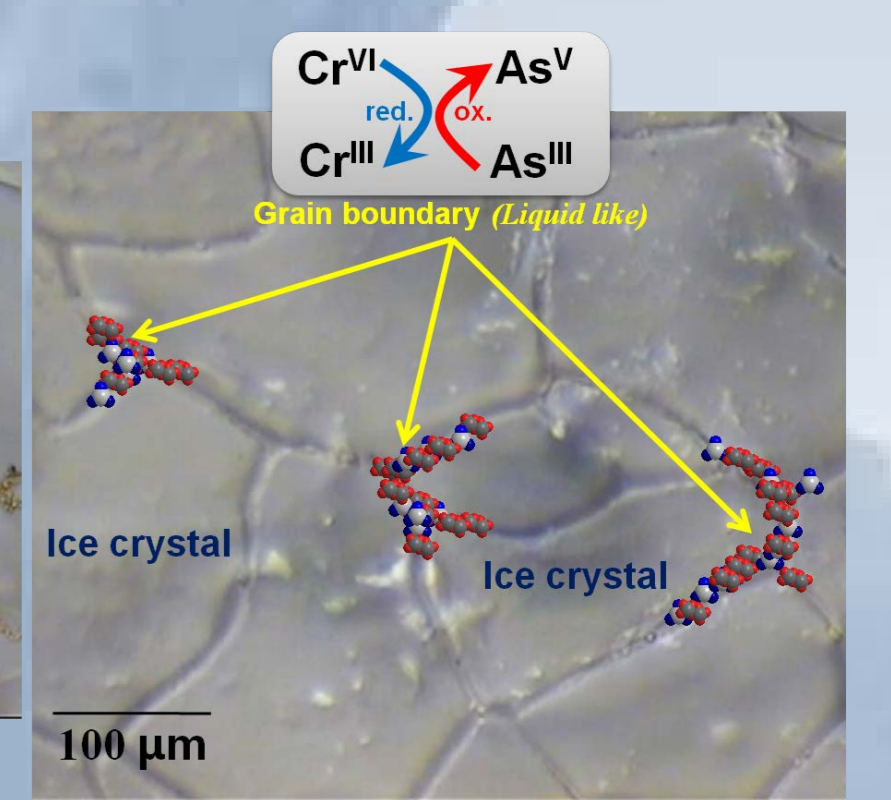
K. Kim and W. Choi, *Environ. Sci. Technol.*, 44, 4142-4148-1574, 2010
 Science, VOL. 328, 1077, 2010, Editor's Choice, "Iron's icy fate"
 Kitae Kim, Daun Jeong, and Wonyong Choi, *Atmos. Chem. Phys.*, 2012, 12, 11125-11133



→ The dissolution of iron oxides which is very slow reaction in aqueous solution was significantly accelerated in ice 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

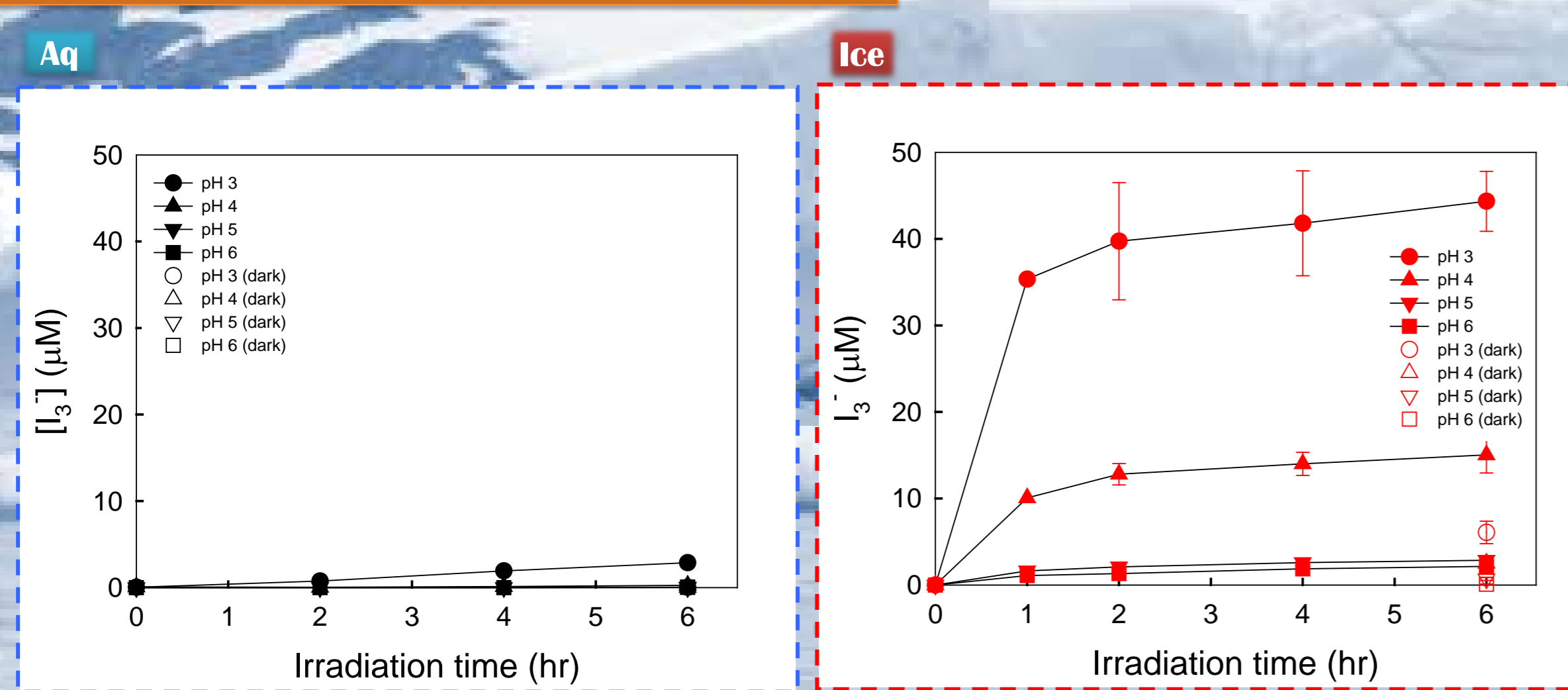
Environ. Sci. Technol., 2011, 45, 2202-2208



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

Result & Discussion

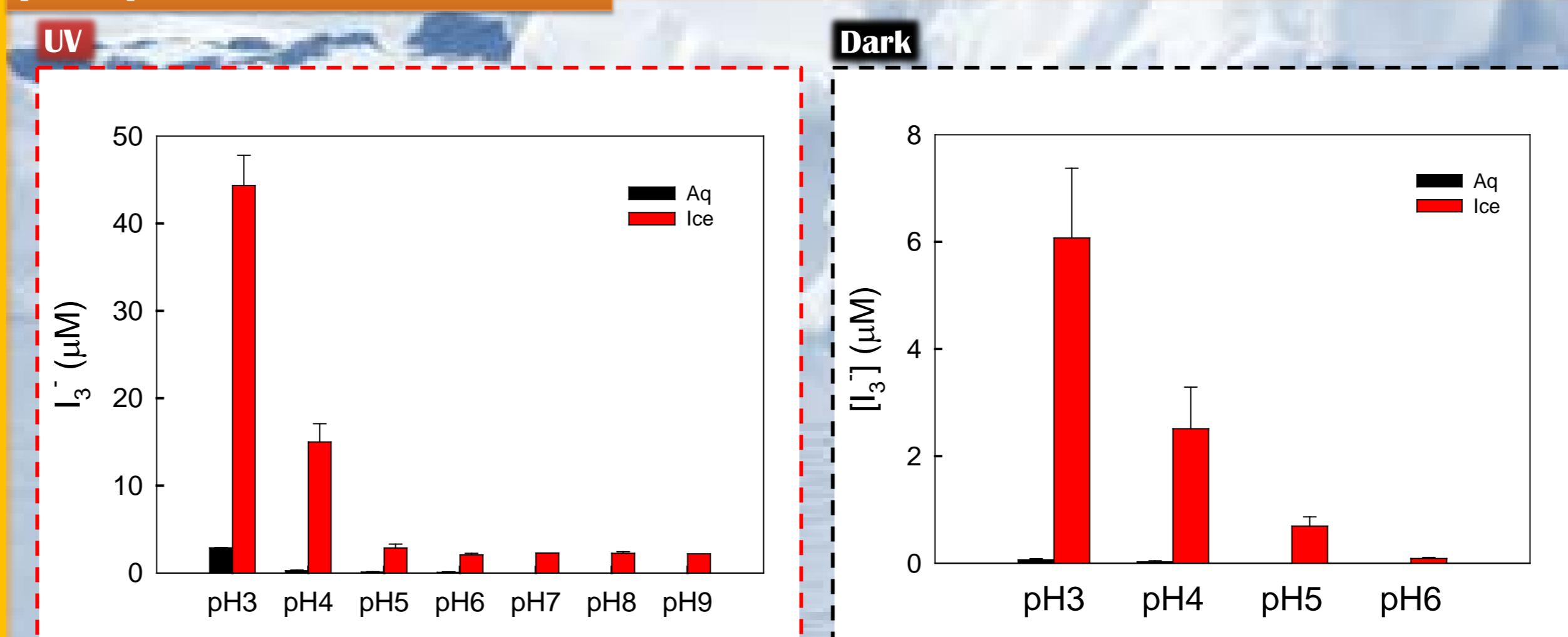
I⁻ photo-oxidation to I₃⁻ under UV (λ > 300 nm)



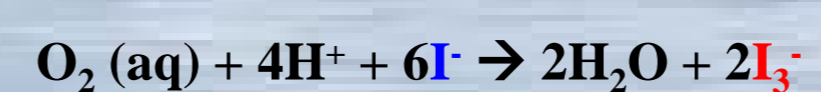
[I⁻] = 1mM (KI), 6 hr UV irradiation by Medium pressure Hg lamp (UV, λ > 300nm)

✓ The formation of I₃⁻ 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.
 ✓ I₃⁻ production was observed in ice even the dark condition.

pH dependence on I⁻ Oxidation

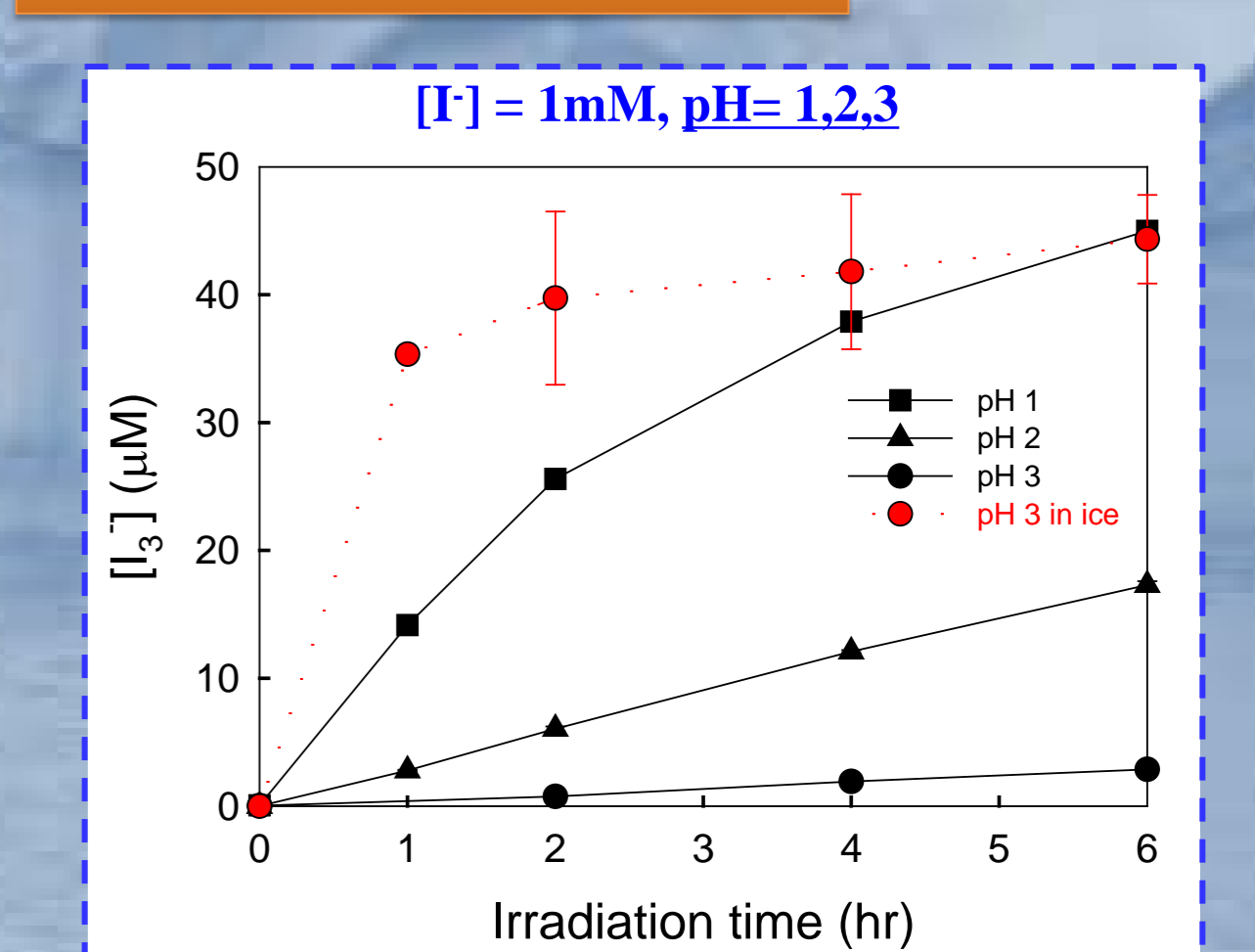


[I⁻] = 1mM (KI), 6 hr UV irradiation and dark by Medium pressure Hg lamp (UV, λ > 300nm)

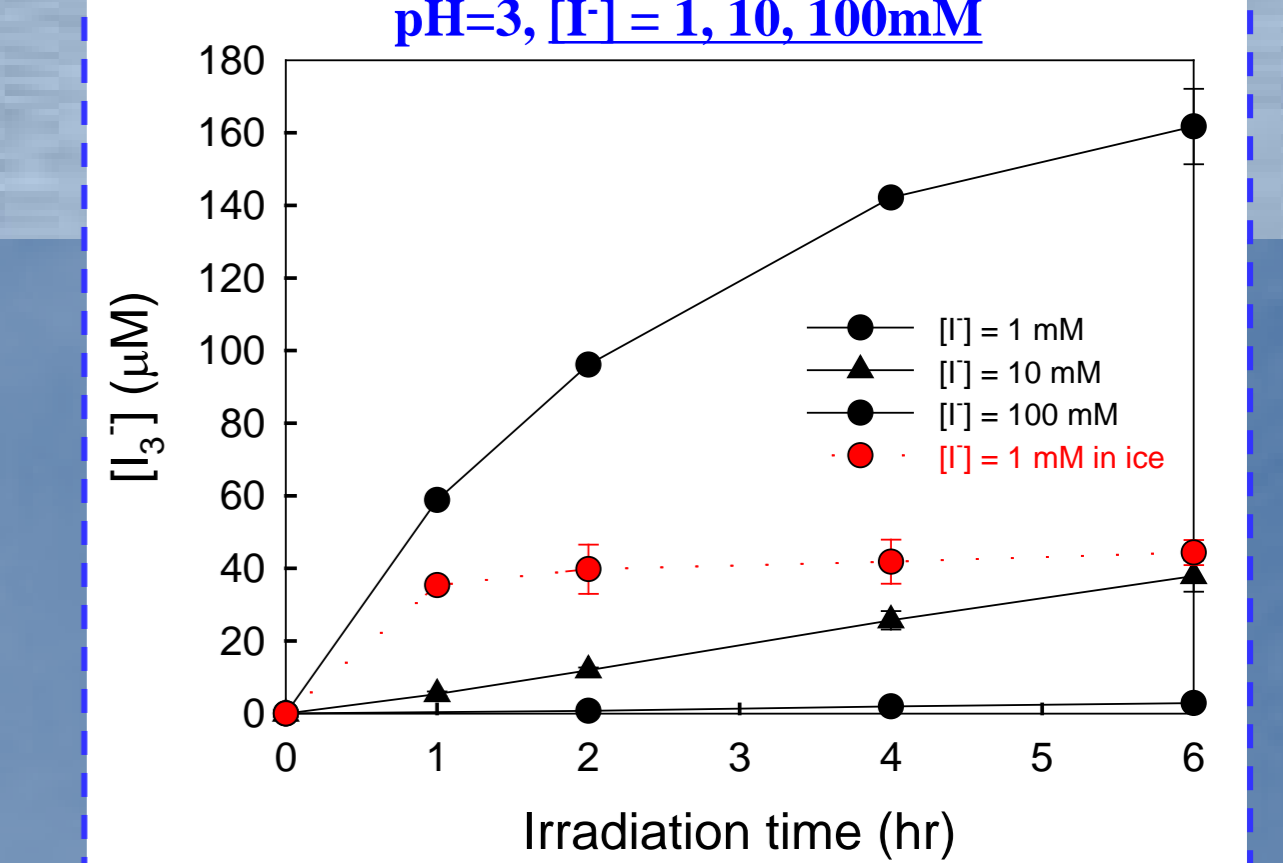


✓ The enhanced photo-oxidation of I⁻ in ice phase was observed at the pH range of 3 to 9.
 ✓ Only at pH 3, I⁻ photo-oxidation was observed in aqueous solution
 ✓ The oxidation of I⁻ under dark condition, which occurs very slowly in aerated aqueous solutions, is also accelerated in ice phase at the pH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

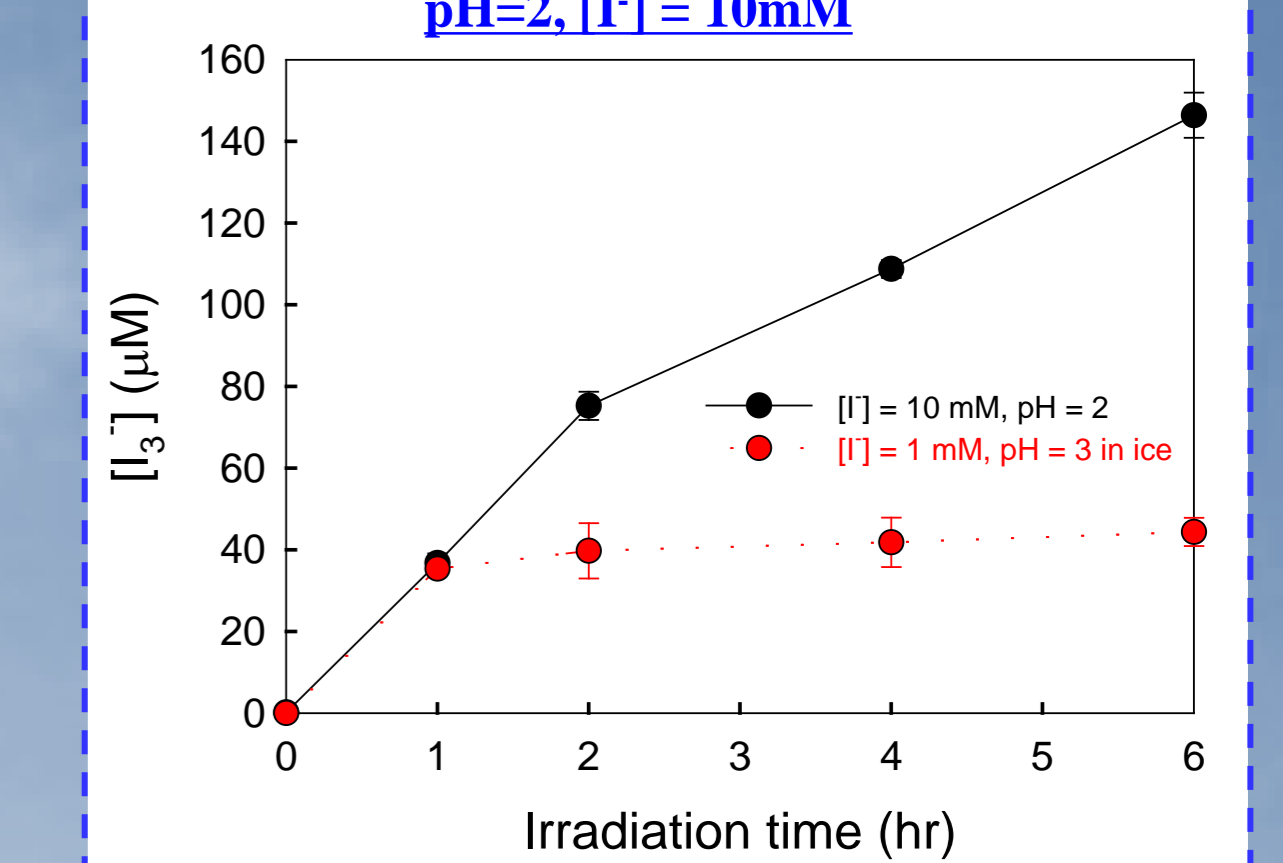
Freeze concentration effect



[I⁻] = 1mM, pH = 1, 2, 3



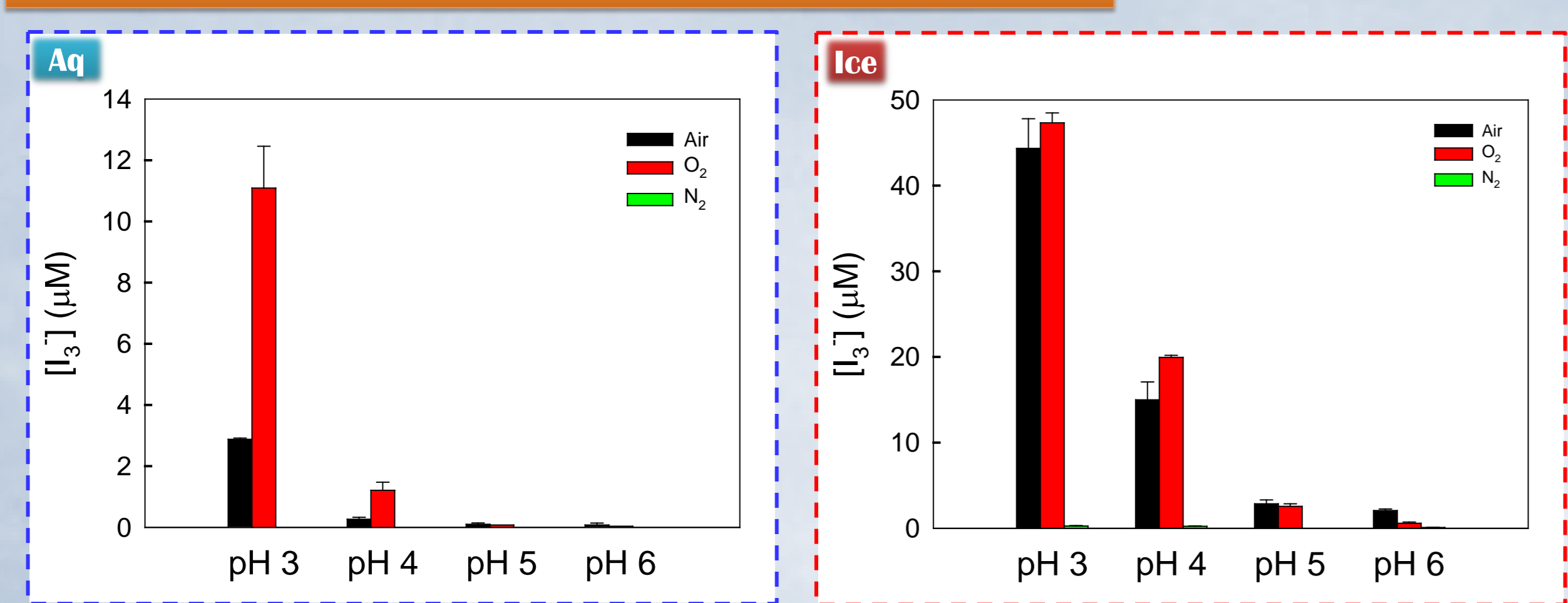
pH=3, [I⁻] = 1, 10, 100mM



pH=2, [I⁻] = 10mM

✓ In the presence of excess amount of iodide and proton, photooxidative formation of I₃⁻ was observed even in aqueous sample.
 ✓ Both [I⁻] and [H⁺] affect I⁻ oxidation.

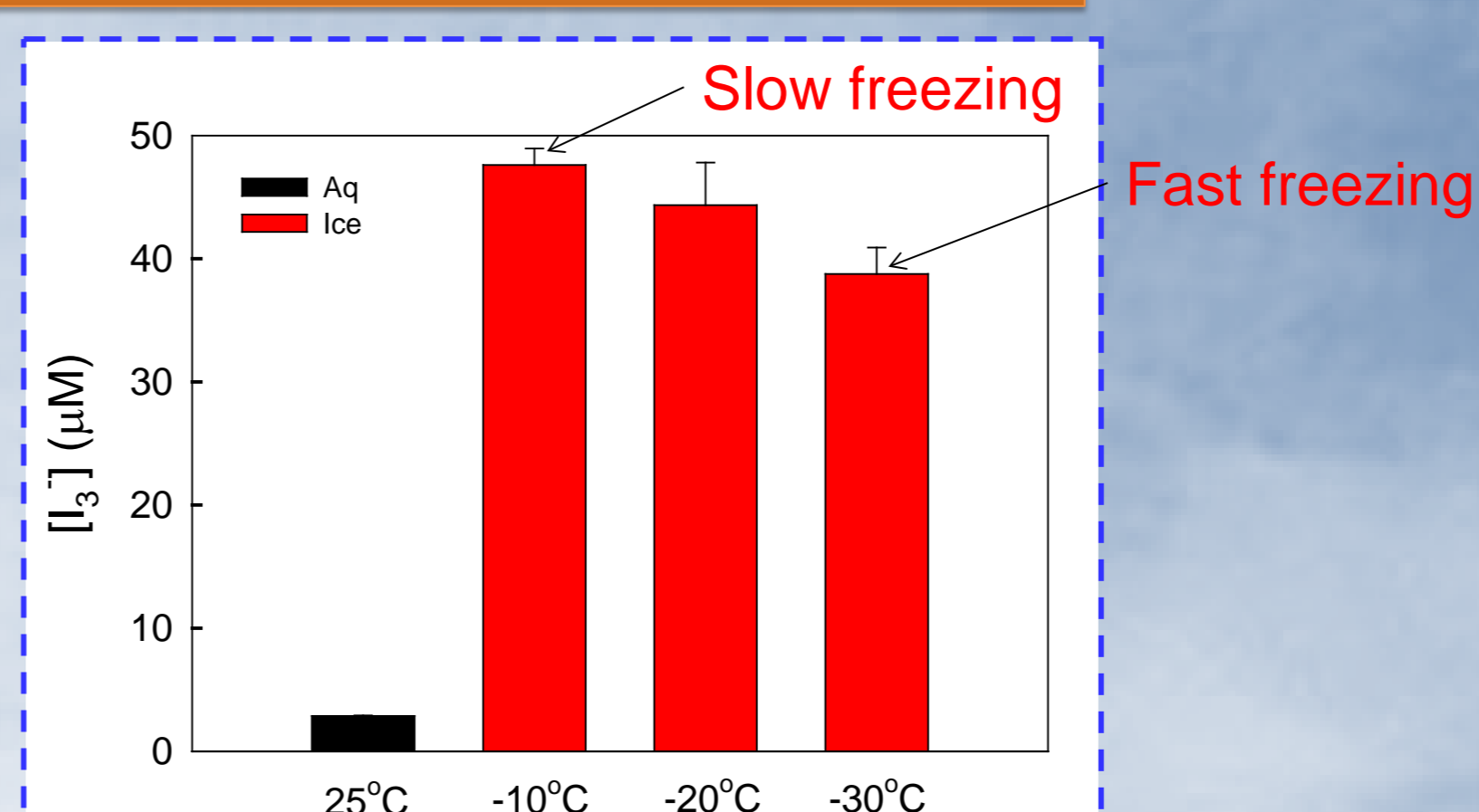
Effect of various saturated gases on the photooxidation of I⁻



[I⁻] = 1mM (KI), 6 hr UV irradiation, 30 min N₂ or O₂ purging

✓ I₃⁻ generation was totally retarded in the absence of oxygen even in the ice phase (N₂ condition)
 ✓ Formation of I₃⁻ in aqueous solution was enhanced under O₂-saturated condition
 ✓ I₃⁻ 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

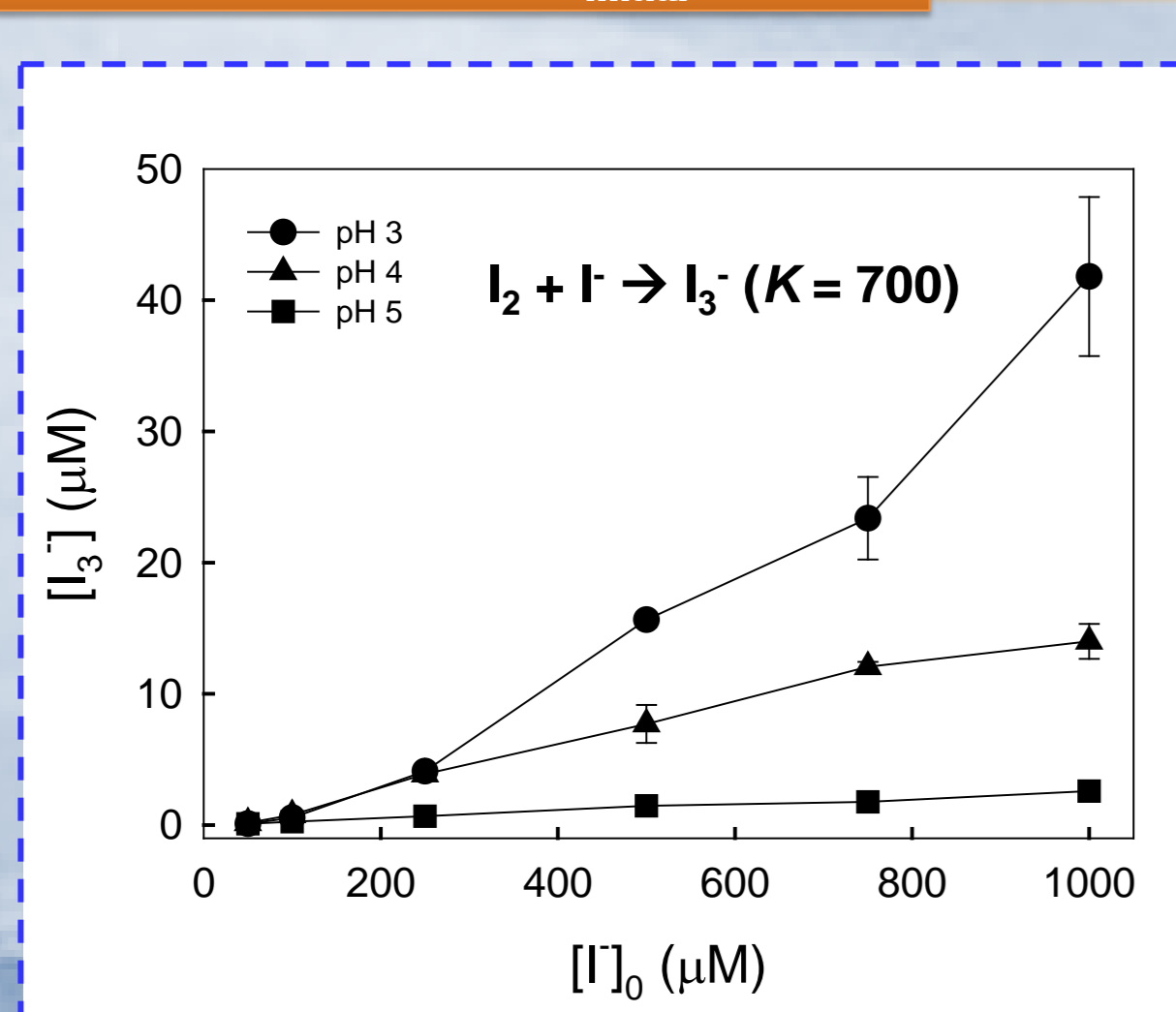
Temperature effect on the production of I₃⁻ under UV



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

✓ I₃⁻ 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

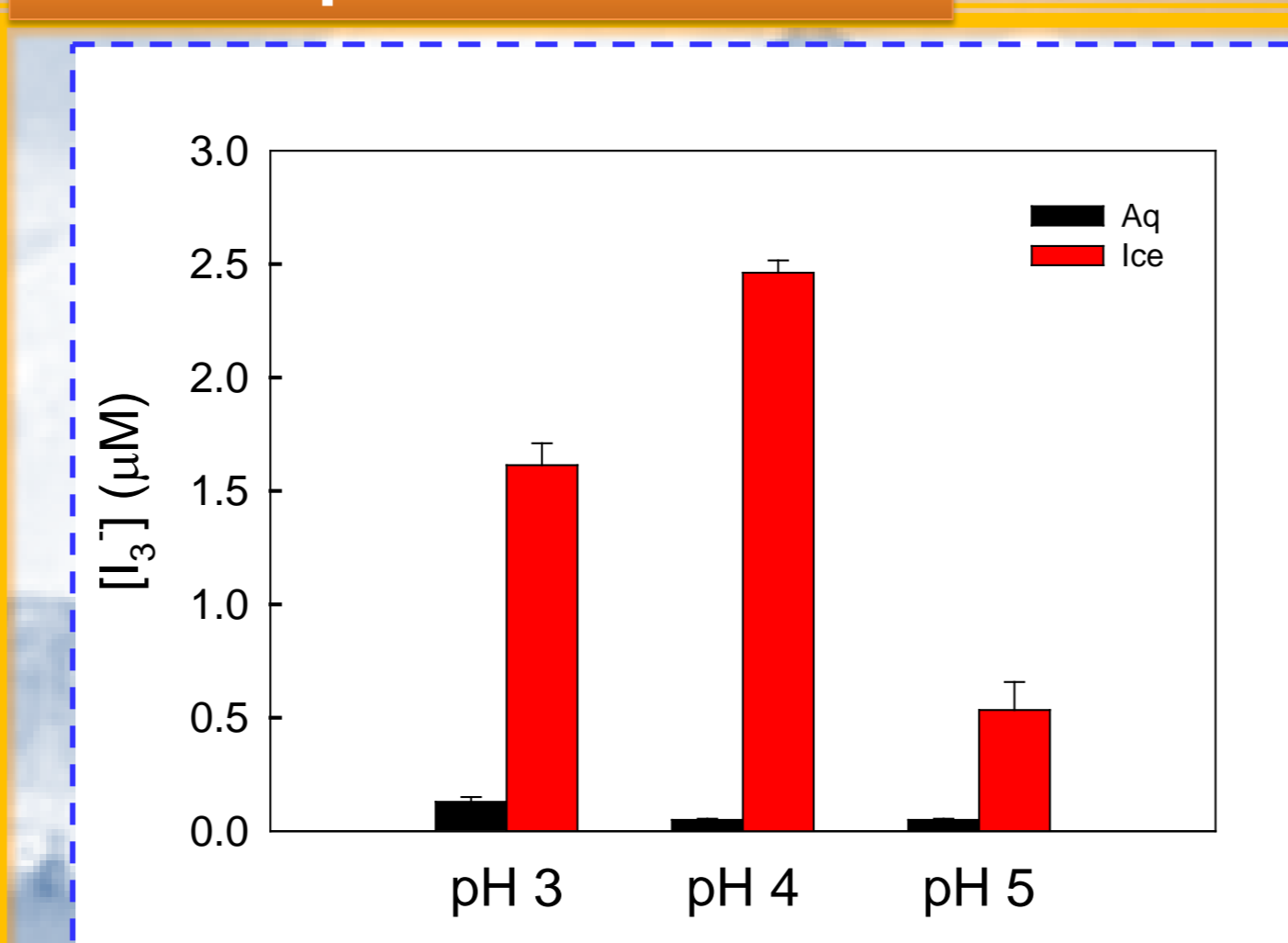
I⁻ oxidation with various [I⁻]_{initial} and pH



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

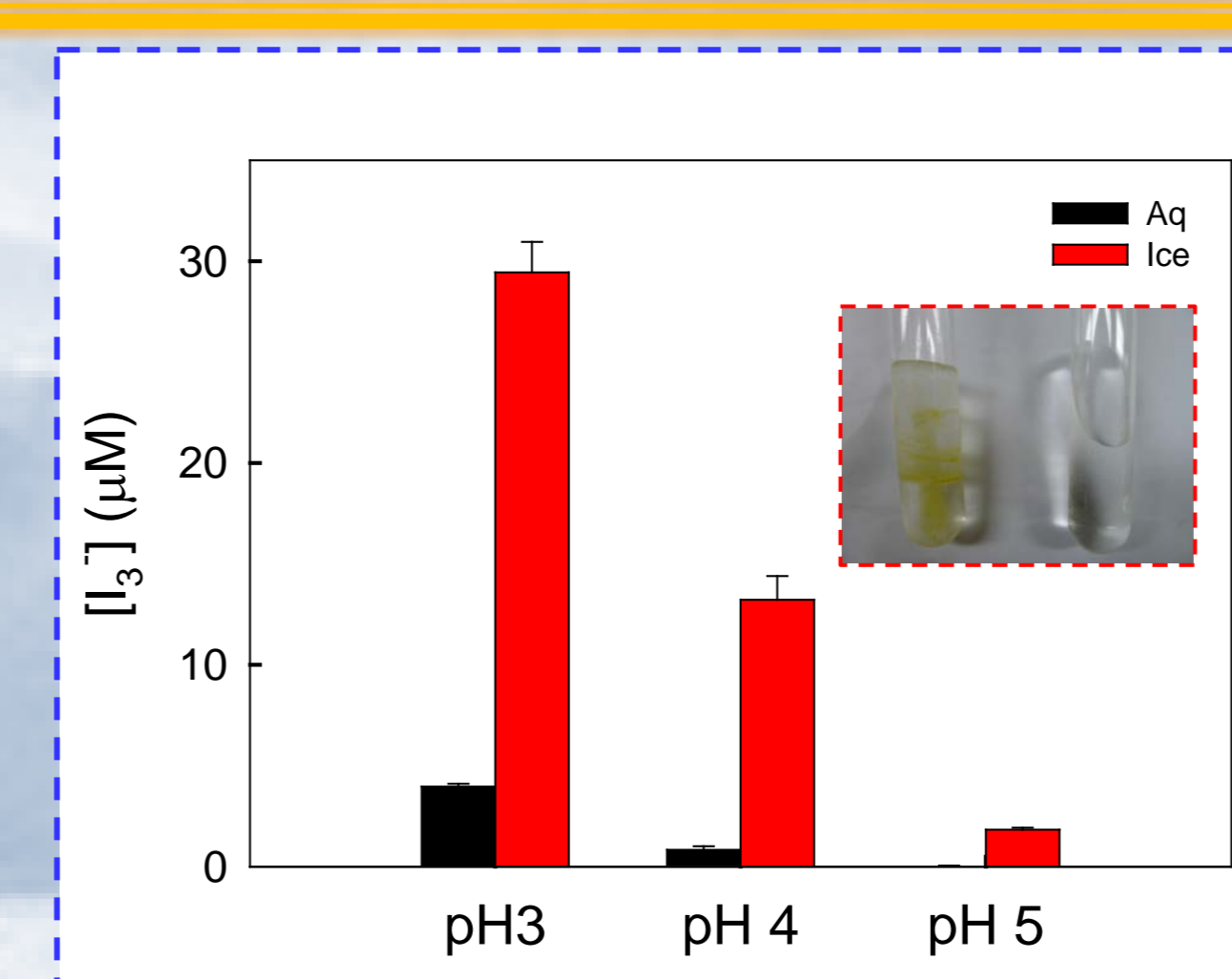
✓ The formation of I₃⁻ was efficient in ice when the pH is low and [I⁻] is high

Outdoor Experiments in Antarctica

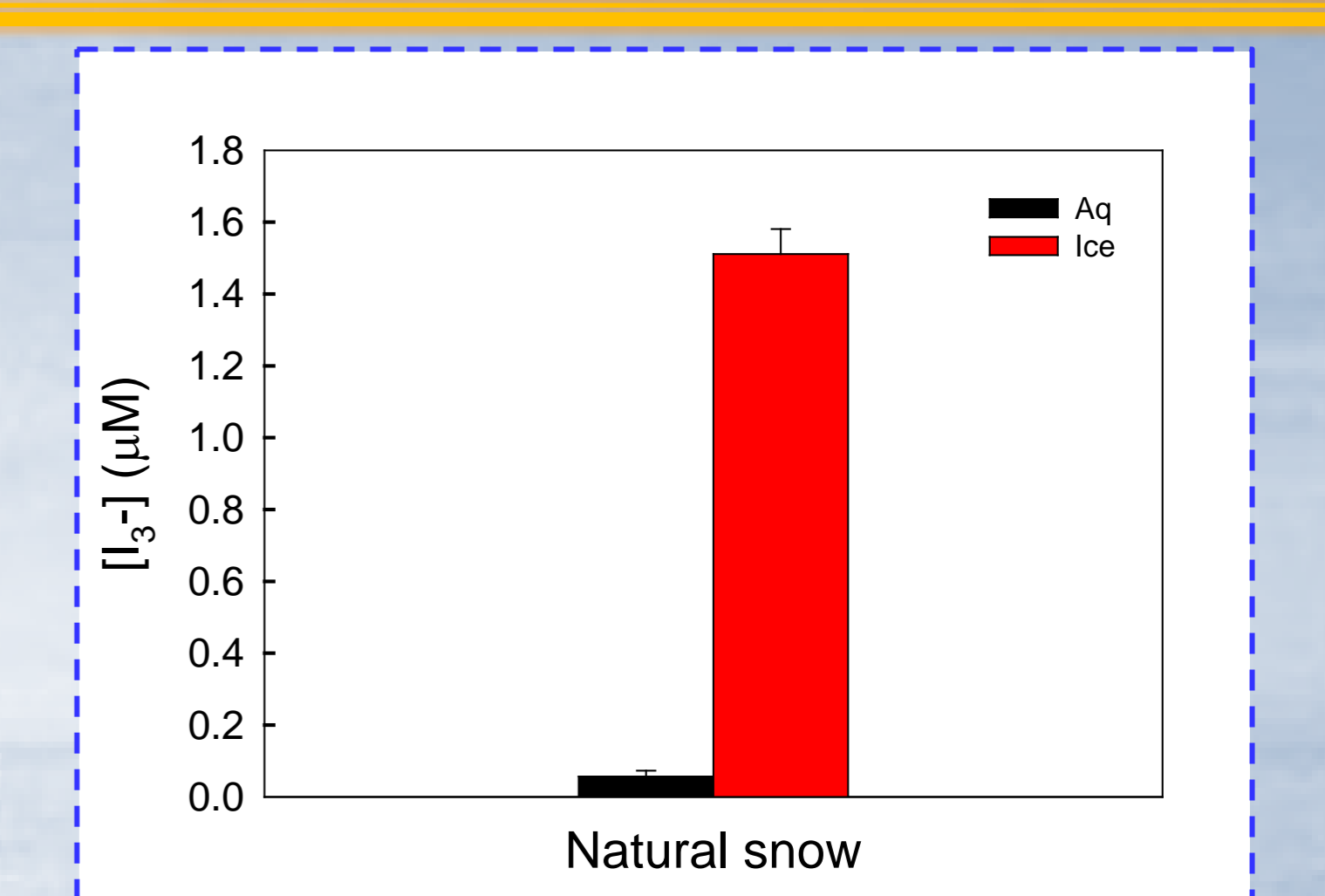


[I⁻] = 0.2 mM (KI), 6hr irradiation

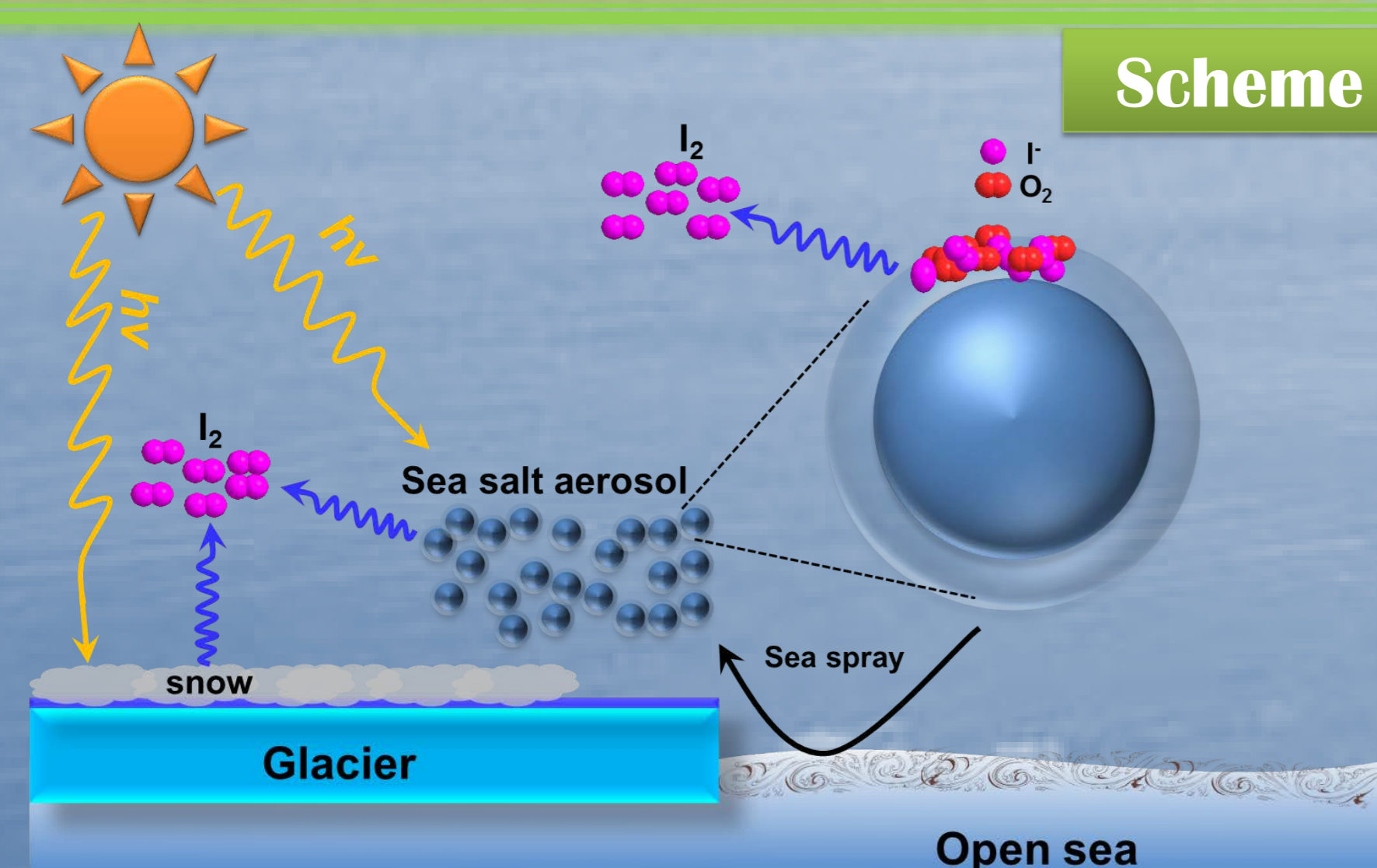
✓ The production of I₃⁻ via photooxidative reaction in ice was consistently higher than that in the corresponding aqueous phase, which confirms the laboratory results
 ✓ Photooxidative generation of I₃⁻ was markedly enhanced in ice phase (in natural snow)



[I⁻] = 1 mM (KI), 6hr irradiation



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



Conclusions

- ✚ The photo-oxidation of I⁻ to I₃⁻ 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 I₃⁻ formation was observed.
- ✚ Photo-oxidative formation of I₃⁻ was totally retarded in the absence of O₂ even in the ice phase.
- ✚ Elevated [I⁻], [H⁺], and [O₂] (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 I₃⁻ formation via photooxidation in ice.
- ✚ Unknown generation pathway for the considerable release of reactive iodine compounds to the atmosphere in polar regions