

Abiotic transformation of iodine species in ice and its environmental implications

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Introduction

Unique Reactions in Ice Phase

[Aqueous] $\text{NO}_2 \xrightarrow{\text{Dissolved } \text{O}_2} \text{NO}_3^-$ (Slow)
 [Ice] $2\text{HNO}_2 + \text{O}_2 \rightarrow 2\text{H}^+ + \text{NO}_2^-$ (Very Fast) [10⁶ 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^- .

Air-snow interaction

High concentration of $\cdot\text{OH}$, HO_2 , nitrous acid, aldehyde, acetone, halogen species near snow pack.
 Photochemistry of NO_2 plays a significant role on perturbation of air composition in snow and ice ($\cdot\text{OH}$ formation).
 $\cdot\text{OH}$ oxidizes NOM to produce carbonyl and halogen species (release to atmosphere).

Freeze concentration effect

Quasi-liquid layer (QLL) : air-ice interface
 Liquid-like layer (LL) : water-ice interface within bulk ice
 Quasi-liquid layer; Liquid-like layer; Grain boundary, micro-pocket, unfrozen solution.

Importance of atmospheric iodine

O_3 depletion event
 Formation of ultrafine aerosol particles (become CCN \rightarrow impact on radiative balance)
 Essential dietary element for mammals
 Influences the oxidizing capacity of the atmosphere (oxidize or remove org. Bromine)
 Enhance depletion of gaseous elemental mercury (Hg^0) by oxidation to reactive gaseous mercury (Hg^2+) (in the polar atmosphere)
 Perturbation of OH/NOx Cycles
 Atmospheric iodine source in Antarctica is still unknown

Result & Discussion

Production of molecular iodine and triiodide in the frozen solution of iodide

Abs. Transmittance vs Wavelength (nm) and $[\text{I}_3^-]$ (μM) vs pH (3-9) under light conditions ($\lambda > 300 \text{ nm}$).
 Bar chart showing $[\text{I}_3^-]$ ($10^7 \text{ molecule/cm}^3$) for different conditions: Ice + air (light), Ice + air (light) + H_2O_2 (dark), Ice + H_2O_2 (dark), Ice + air (light) + H_2O_2 (dark).

Simultaneous and synergic production of bioavailable iron and reactive iodine species in ice

Solar irradiation in an Antarctic region. Bar chart showing $[\text{Fe}^{II}]$ (μM) and $[\text{I}_3^-]$ (μM) vs irradiation time (h) for Magnesium, Antarctic soil dust, Glaciers, and Laboratories. Diagram showing $\text{Fe}^{III}_2\text{O}_3$ on ice grain boundaries being converted to Fe^{II}_{aq} .

Freezing-enhanced oxidation of I⁻ by H₂O₂ peroxide w/ IBP

Microscopic images of ice crystals with IBP. Graph showing $[\text{I}_3^-]$ (μM) vs Time (h) for H₂O₂ solution, BSA, and LeIBP.

Nitrite-Induced Activation of Iodate into Molecular Iodine in Frozen Solution

Graphs showing $[\text{IO}_3^-]$ and $[\text{I}_2]$ vs Reaction time (h) for various conditions. Diagram showing NO_2 and NO_3^- leading to I^- , I_2 , and I_3^- via oxidation and reduction.

Freeze-thaw cycle-enhanced transformation of iodide to organoiodine compounds w/ NOM and Fe(III)

Scatter plot of H/C vs O/C for various organic compounds. Graphs showing $[\text{I}^-]$ and $[\text{OICs}]$ vs Time (h) for 5 cycles of freeze-thaw. Diagram showing the cycle between Fe(III)/Iron oxides and NOM/Aromatics in ice and aqueous phases.

Conclusions

- The production of tri-iodide (I_3^-) via iodide (I^-) oxidation, which is negligible in aqueous solution, is significantly accelerated in frozen solution, both in the presence and the absence of solar irradiation.
- The chemical reaction between iron oxides and iodide (I^-) is markedly accelerated to produce bioavailable iron (Fe^{II}_{aq}) and tri-iodide (I_3^- : evaporable in the form of I_2) in frozen solution (both with and without light irradiation) while it is negligible in aqueous phase.
- The mechanism for I^- activation into I_3^- by H_2O_2 in a frozen solution was developed, and it was found that Arctic extracellular ice-binding glycoprotein (LeIBP) enhanced the I^- activation.
- The chemical reaction between iron oxides and iodide (I^-) in the presence of natural organic matter enhances the formation of organoiodine compounds (OICs) in frozen solution, and freeze-thaw cycling solutions.
- The production of reactive iodine and organoiodine compounds from iodide oxidation can be significantly accelerated in frozen solution containing manganese dioxide and natural organic matter.
- We propose that an accelerated abiotic transformation of I^- in ice media provides a previously unrecognized formation pathway of reactive iodine species and OICs in the polar atmosphere or freeze-thaw cycled circumstances.

Reference
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