

Margarita Reza<sup>1,2,3</sup>, Lucia Iezzi<sup>3,4</sup>, Henning Finkenzeller<sup>1,2</sup>, Antoine Roose<sup>3</sup>, Markus Ammann<sup>3</sup> and Rainer Volkamer<sup>1,2,3</sup>

[1] Department of Chemistry & CIRES, [2] University of Colorado Boulder, [3] Paul Scherrer Institute, [4] ETH, Zurich

[Margarita.Reza@Colorado.edu](mailto:Margarita.Reza@Colorado.edu), [Rainer.Volkamer@Colorado.edu](mailto:Rainer.Volkamer@Colorado.edu)

## Introduction

- Most iodine enters the atmosphere from the ocean as gas-phase  $I_2$ .
- Gas-phase  $I_2$  photolyzes and is subsequently oxidized by  $O_3$ , eventually forming iodic acid ( $HIO_3$ ) via  $O_3$  destruction.
- $HIO_3$  efficiently forms particles [1]. Despite this, ~90% of atmospheric iodine resides in the gas phase, even in aged tropospheric air [2].
- This suggests a recycling mechanism whereby particle-phase iodine is reduced and re-enters the gas phase.
- Here, the reduction of particle-phase iodine is investigated via coated wall flow tube (CWFT) experiments using aqueous iodate ( $IO_3^-$ ) films in organic and inorganic matrices.

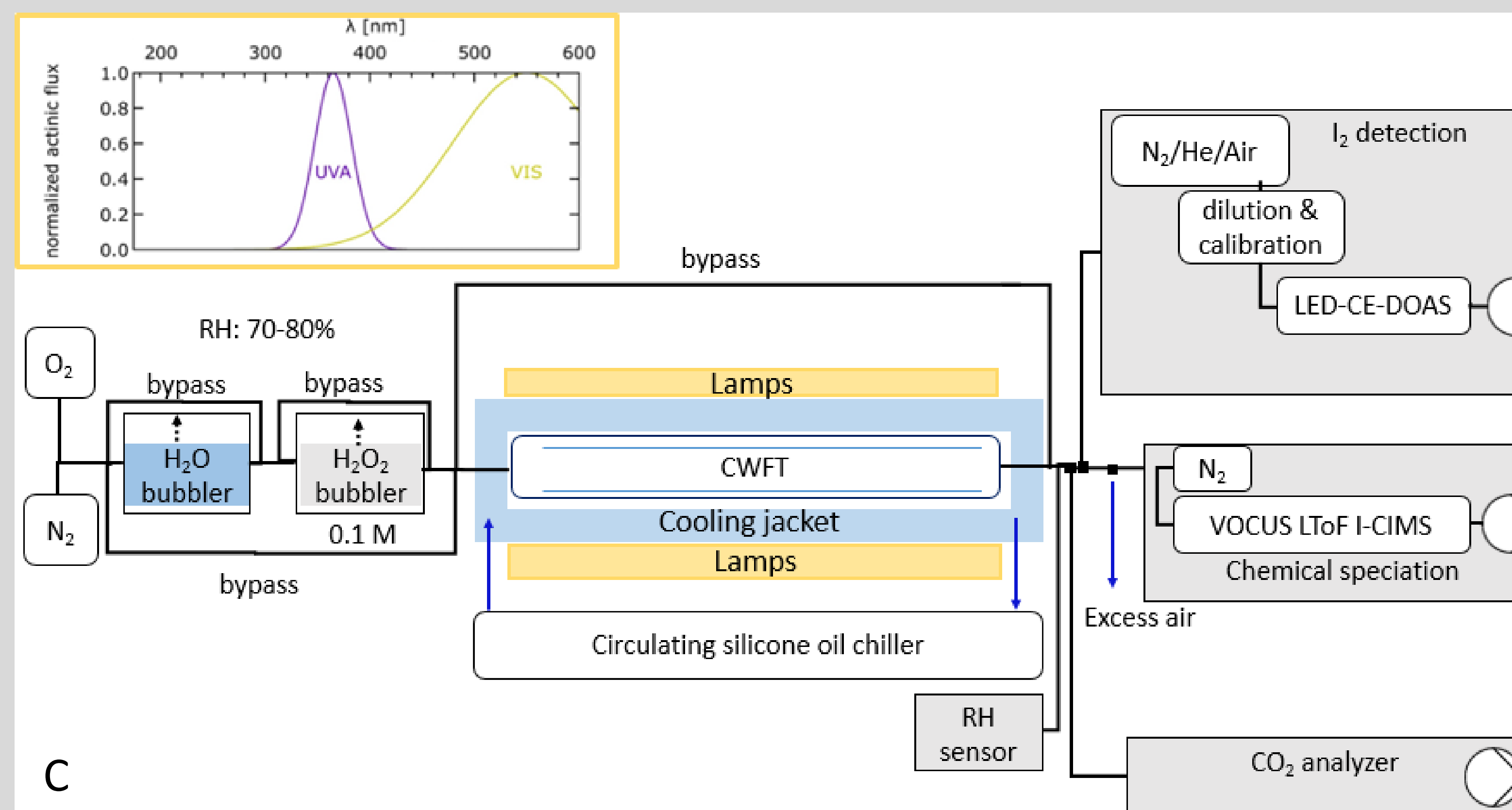
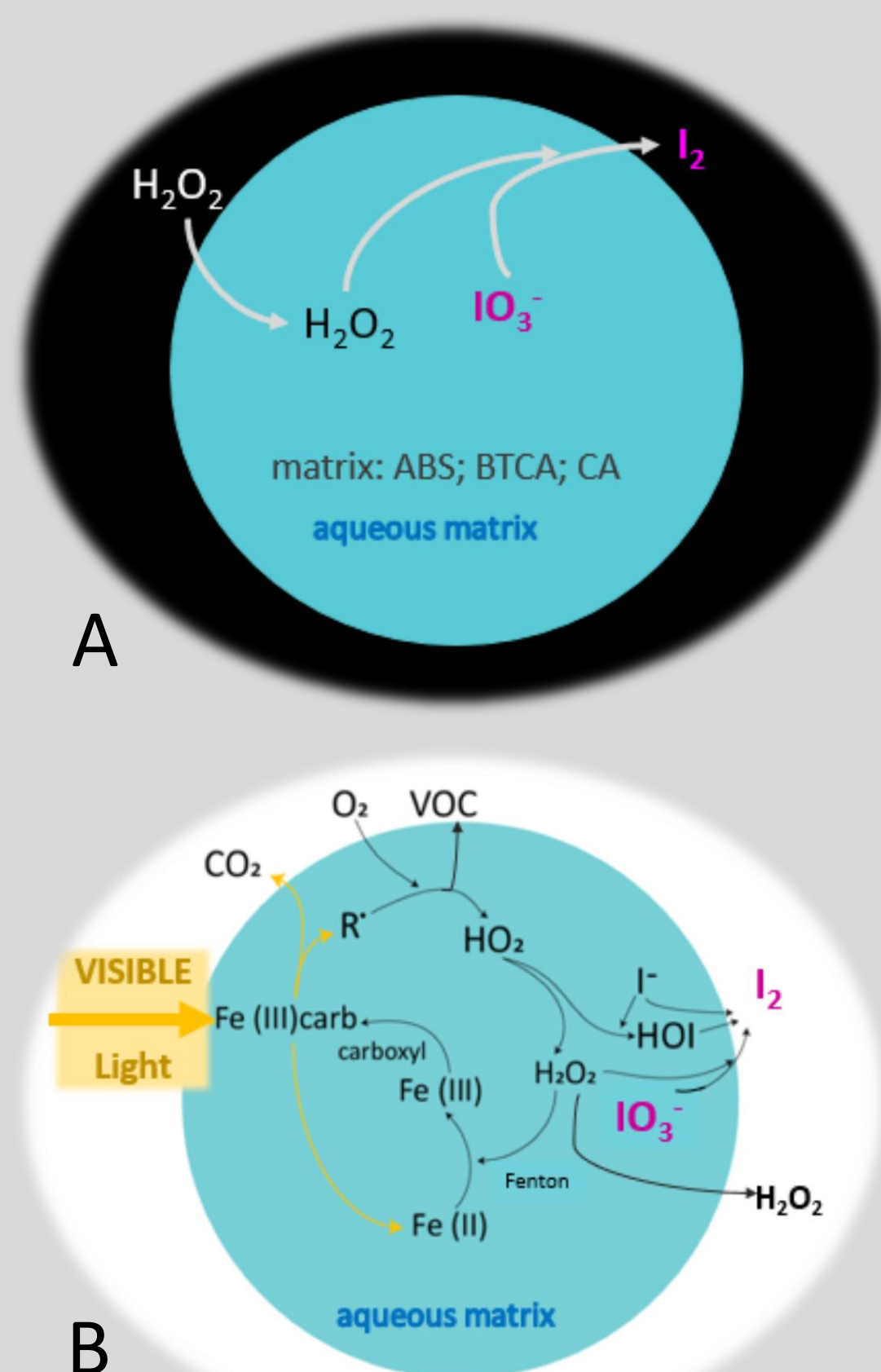


Figure 1: The dark reaction of  $H_2O_2$  with  $IO_3^-$  in aq. organic and inorganic matrices produces gas-phase  $I_2$ . (A) Visible light reduces  $IO_3^-$  to  $I_2$  in the presence of Fe(III) citrate, a known photosensitizer. (B) Sketch of the flow-tube reactor set up. (C)

## Methods

Matrices (iodate : matrix = 1 : 100)

- Ammonium bisulfate (ABS)
- 1,2,3,4-butanetetracarboxylic acid (BTCA)
- Citric acid (CA)
- Fe(III) citrate & citric acid (Fe-Cit / CA)

Experiments:

1. Dark reaction w/  $H_2O_2$
2. Irradiation w/ visible & UVA light, separately
3. Dark reaction w/  $H_2O_2$ , then visible light irradiation
4. Visible light irradiation of dust proxies – Arizona Test Dust (ATD) and Hematite ( $Fe_2O_3$ )

$I_2$  measured via Cavity-Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS).

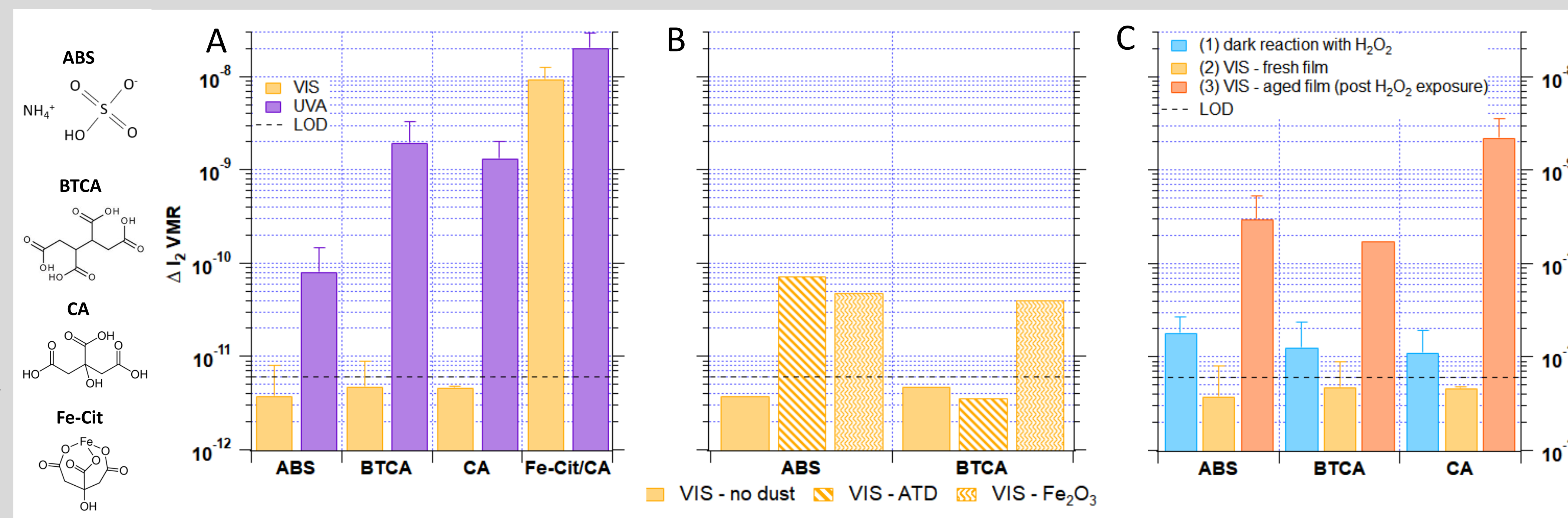


Figure 2: Delta  $\Delta I_2$  volume mixing ratio, VMR released from  $IO_3^-$  is calculated by subtracting the background  $I_2$  from the maximum signal during irradiation. Adding a known chromophore, Fe-Cit, results in the largest release of  $I_2$  under visible light. (A) Dust proxies in aq.  $IO_3^-$  films can enhance  $I_2$  released from visible light irradiation. (B)  $I_2$  produced from irradiated films aged with  $H_2O_2$  (red) is greatly enhanced compared to dark (blue) and photochemical (orange) control experiments using fresh films. (C)

## Results

- Visible light triggers  $IO_3^-$  reduction in the presence of a chromophore.
- $I_2$  is observed in the absence of a chromophore under UVA light due to unknown processes.
- During the photochemical Fe-Cit / CA experiment with visible light, the fraction of  $IO_3^-$  consumed to form  $I_2$  ranges from 30 to 70%.
- The  $I_2$  released from aged films irradiated with visible light was substantially greater than from irradiated fresh films, or fresh films exposed to  $H_2O_2$  in the dark.
- A chromophore is produced from the reaction of  $IO_3^-$  with  $H_2O_2$  in both inorganic and organic aq. films.
- ATD enhances  $I_2$  released from  $IO_3^-$  under visible light in inorganic aq. films.
- $Fe_2O_3$  enhances  $I_2$  release in both inorganic and organic aq. films.

## Conclusions

- A photochemical pathway was discovered in which visible light is sufficient for reducing  $IO_3^-$  to  $I_2$ .
- This effect is more pronounced after the exposure of  $IO_3^-$  to  $H_2O_2$ .
- Dust proxies enhance the release of  $I_2$  under visible light, supporting field measurements of  $I_2$  release from dust in the free troposphere [3].

## References

- [1] He et al., Science, (2021) doi:10.1126/science.abe0298
- [2] Koenig et al., PNAS, (2020) doi:10.1073/pnas.1916828117
- [3] Koenig et al., Sci. Adv., (2021) doi:10.1126/sciadv.abj6544

## Acknowledgments

Funding provided by the Swiss National Science Foundation (project grant 188662, scientific exchange grant 199407) and the U.S. National Science Foundation award AGS 2027252.