Metal Oxide Particles as Atmospheric Nuclei: Exploring the Role of Metal Speciation in Heterogeneous Efflorescence and Ice Nucleation

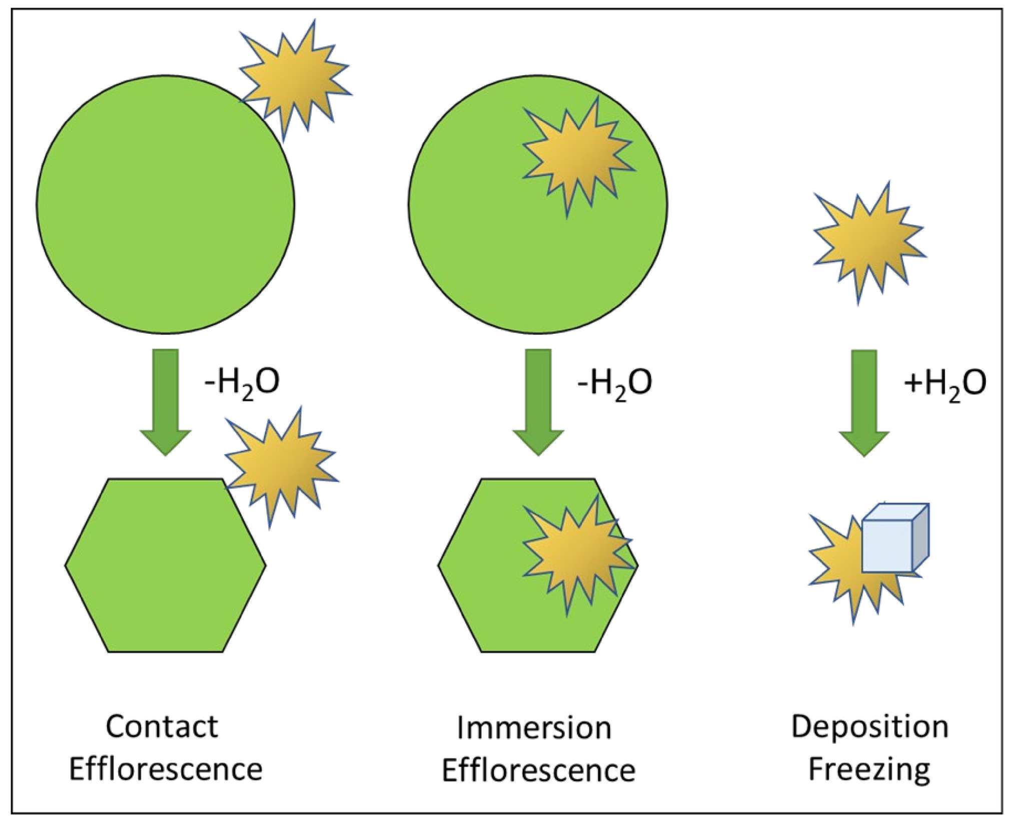
Zachary R. Schiffman[a,b*], Marium S. Fernanders[a,b], Ryan D. Davis[c], and Margaret A. Tolbert[a,b]

[a]Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309, USA, [b]Dept. of Chemistry, University of Colorado, UCB 216, Boulder, CO 80309, USA, [c]Sandia National Laboratories, Albuquerque, New Mexico 87123, USA

**zachary.schiffman@colorado.edu*

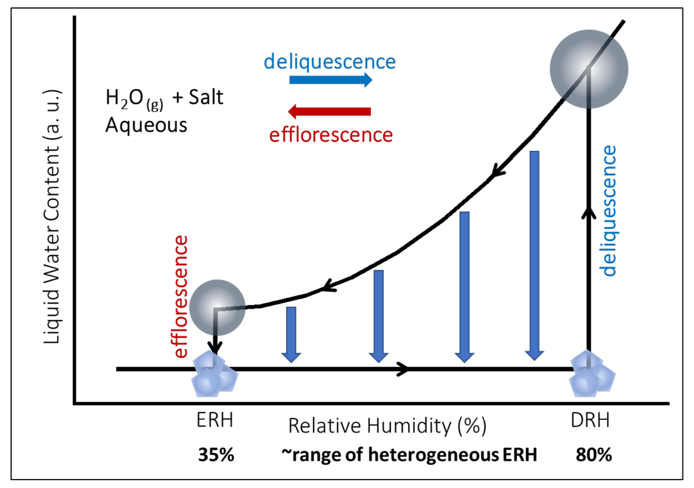
CIRES Rendezvous, May 2023

I. Introduction[1,2]

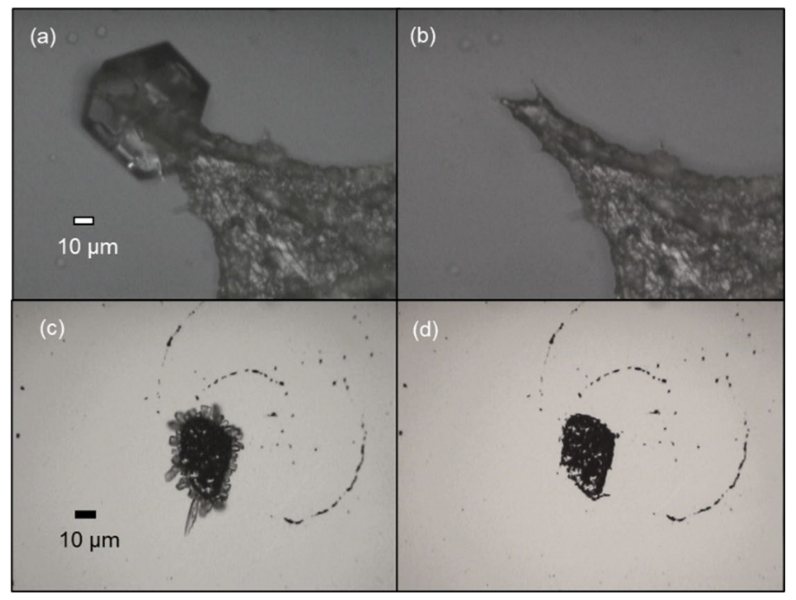


Atmospheric nucleation = Formation of solids

- Mineral dust: 2000 Tg/yr and increasing
- Mineral dust/metallic particles make up >60% ice residuals
- Metals in dust: Oxidized readily in air
- Do metal oxide particles impact atmospheric nucleation?

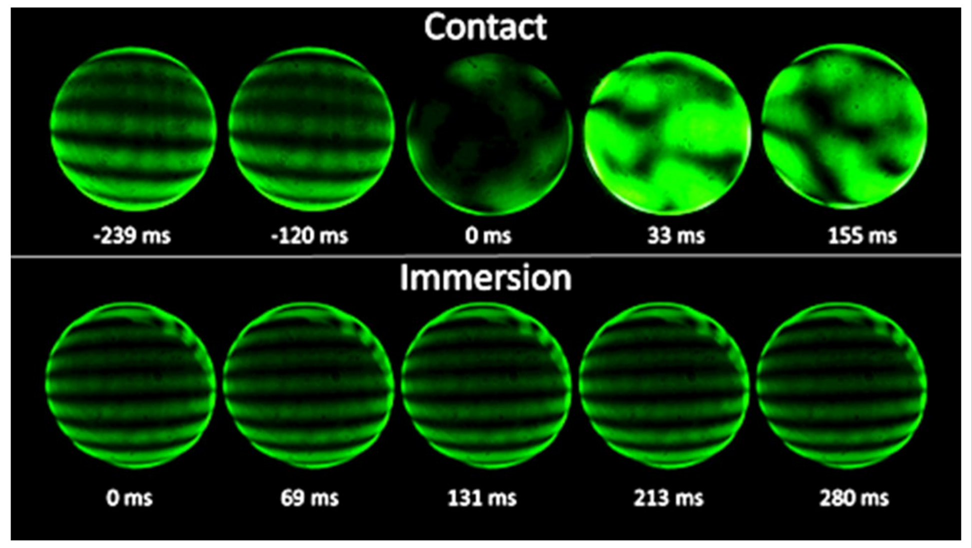


II. Methods[3]



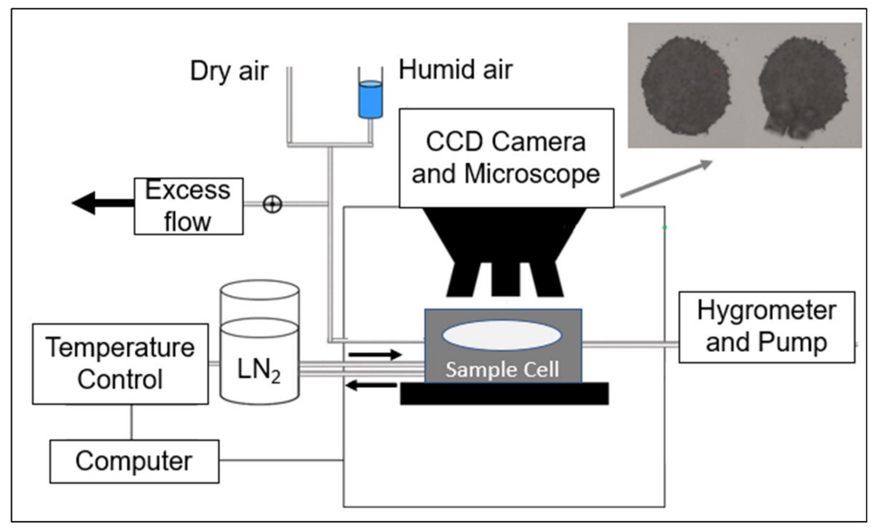
Ice Forming on Metal Oxide Agglomerates

Phase-Change Events of Aqueous Ammonium Sulfate



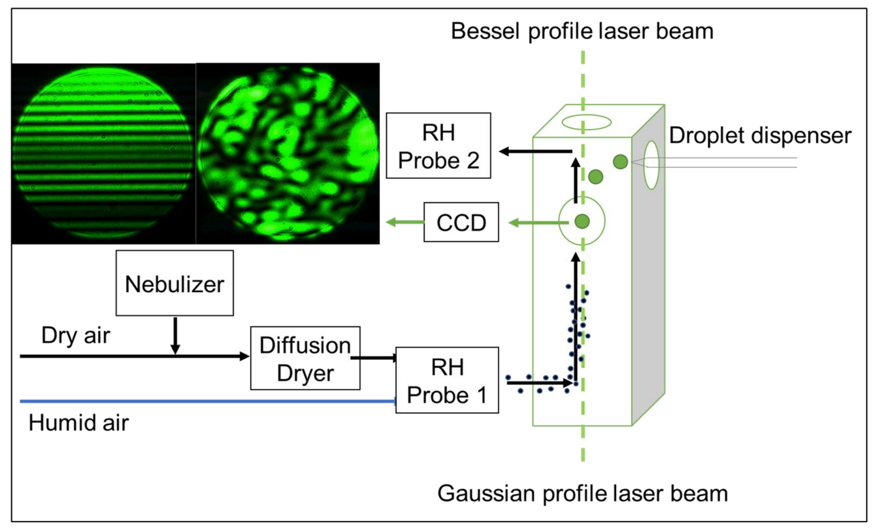
III. Instrumentation[3]

- **Cold Cell Environmental Chamber**



Control of temperature and relative humidity allows for observation of depositional ice nucleation on metal oxide agglomerate particles

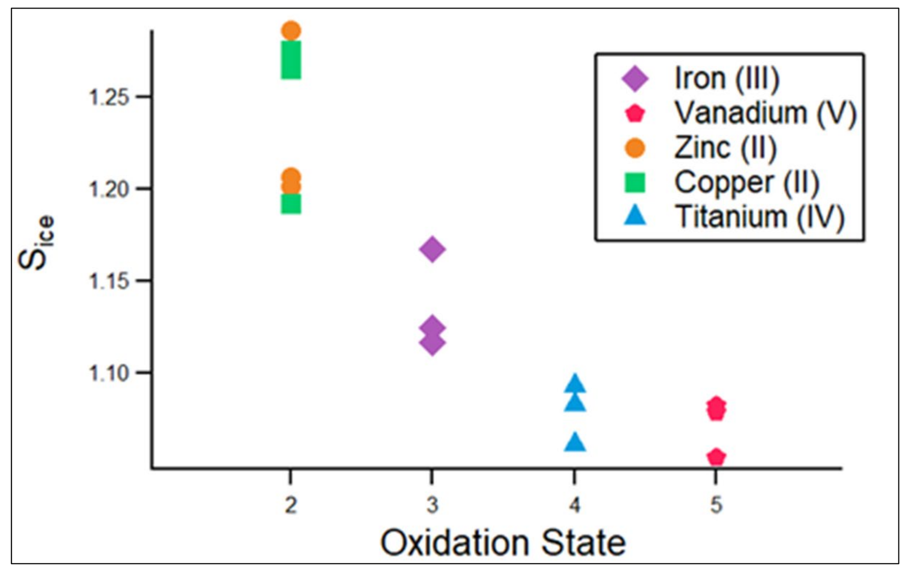
- **Optical Levitator**



Capturing a single droplet and controlling relative humidity allows for observation of collision-based efflorescence events between aqueous salts and metal oxide heterogeneous nuclei

IV. Results[3]

Effect of Oxidation State on Nucleation

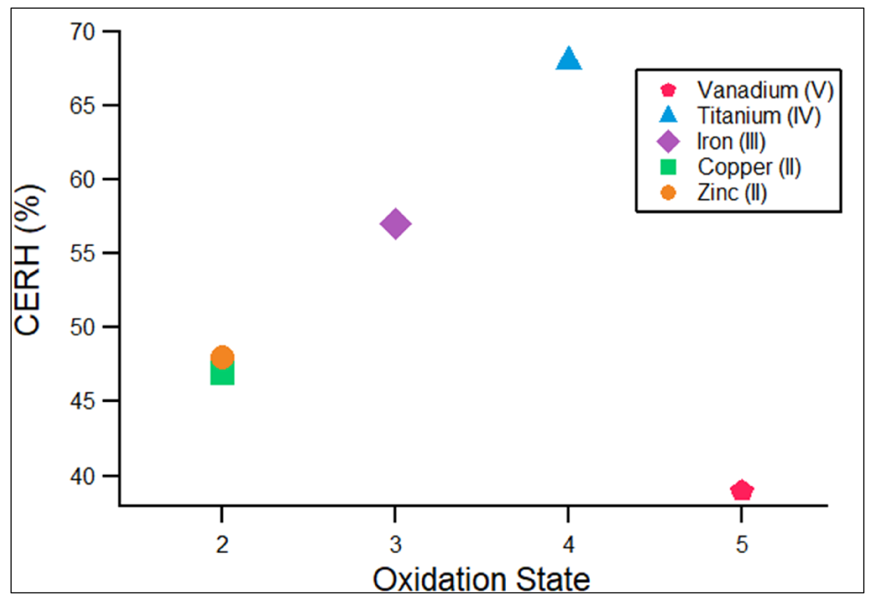


$$S_{ice}(T) = \frac{P_{H_2O}(T)}{VaporP_{ice}(T)}$$

$$CERH = RH \text{ when } P_{eff} = 0.5$$

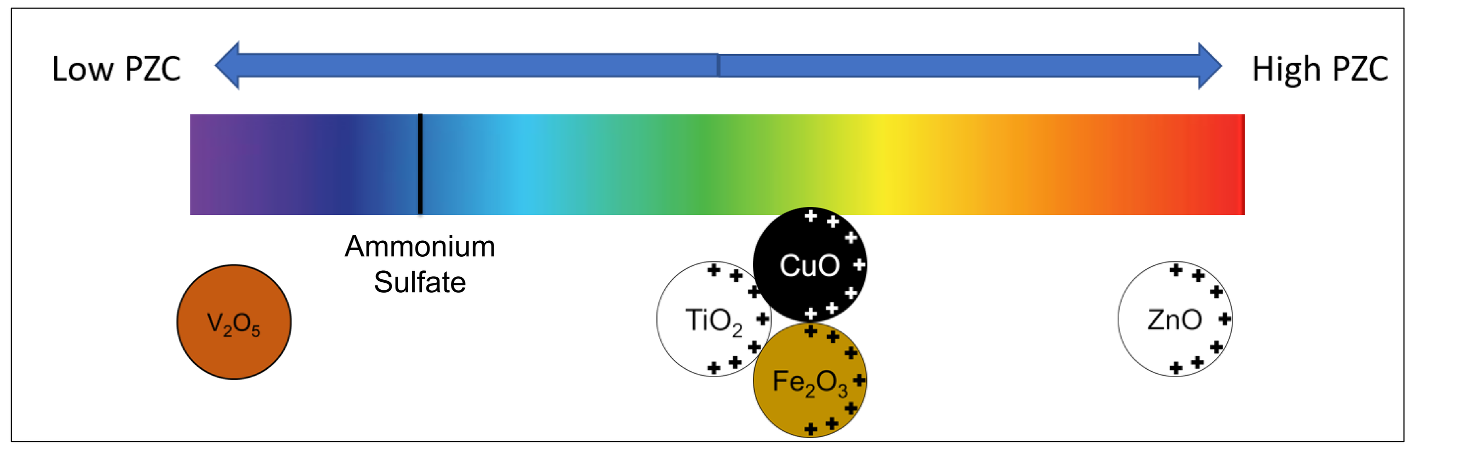
Apparent trend: the higher the oxidation state of the metal cation, the higher the nucleation ability (in both freezing and contact efflorescence modes)

V_2O_5 as outlier in contact efflorescence

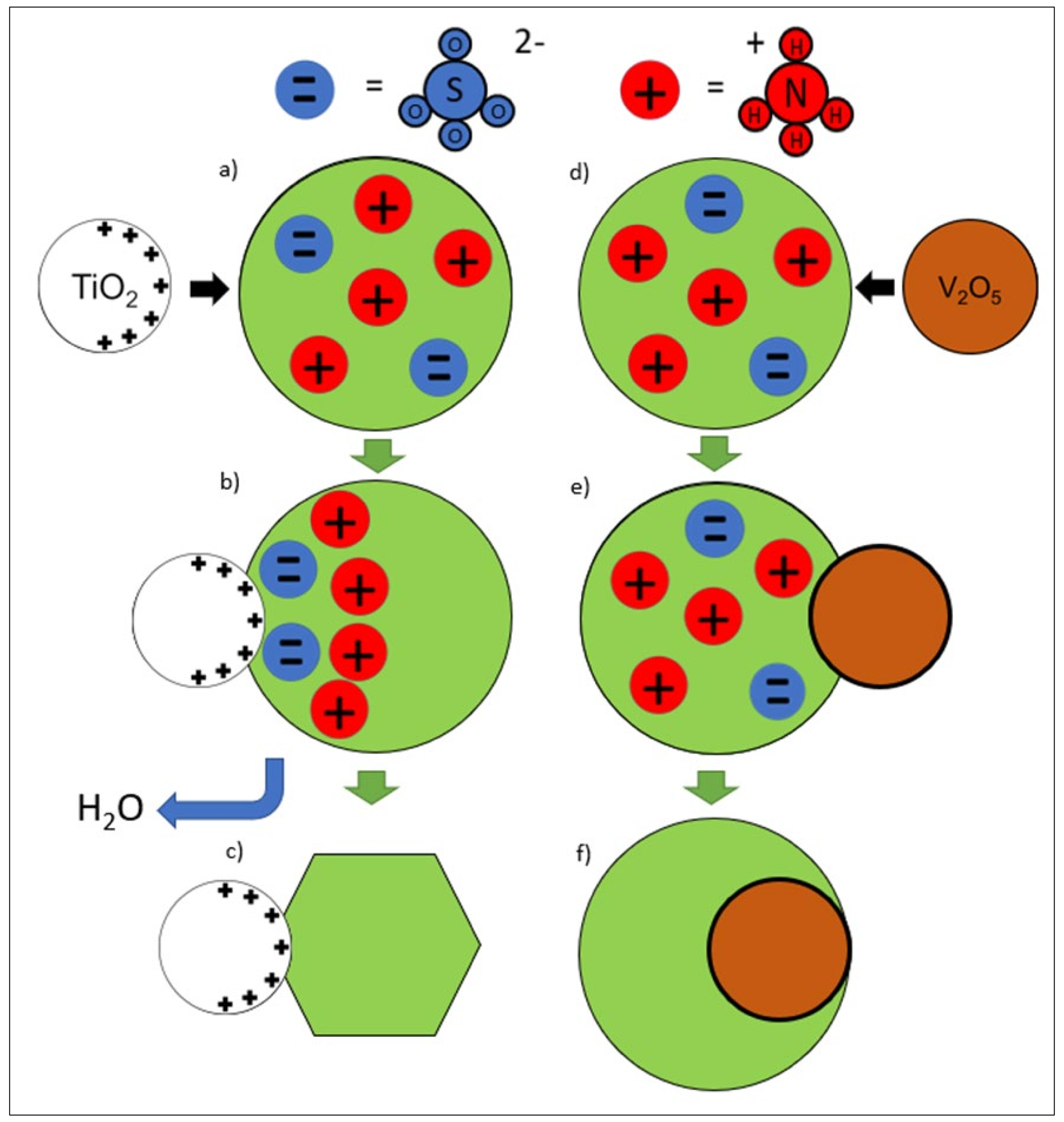


V. Discussion[3,4]

Transient Ion Effects



- Point of Zero Charge (PZC) greater than pH of ammonium sulfate (~4) → positive surface potential
  - Therefore, stronger interactions with sulfate anions in aerosol solution
  - Explains the outlier of V_2O_5 (weakly negative to neutral surface potential)
- Disruption of aqueous phase may lead to instability and subsequent efflorescence phase-change



V. Conclusions

- **Oxidation state appears to provide an apparent trend in nucleation**
- **Nucleation likely depends on several factors including transient ion interactions**
- **Atmospheric salts may exist in solid phase more often than previously thought**

Acknowledgements

Z.R.S. was supported in part by the CIRES Graduate Student Research Award and the NOAA Cooperative Agreement with CIRES, NA17OAR4320101. This work was also supported in part by NSF grant AGS 1925191. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

References

[1] Tang, M.; Cziczo, D. J.; Grassian, V. H. *Chem. Rev.* 2016, *116, 4205−4259.*
[2] Cziczo, D. J.; Froyd, K. D.; Hoose, C.; Jensen, E. J.; Diao, M.; Zondlo, M. A.; Smith, J. B.; Twohy, C. H.; Murphy, D. M. *Science*, 2013, *340(6138), 1320-1324*.
[3] Schiffman, Z.R.; Fernanders, M. S.; Davis, R.D.; Tolbert, M.A. *ACS Earth Space Chem.*, 2023.
[4] Davis, R. D.; Tolbert, M. A. *Sci. Adv.* 2017, *3, 7, 1-8.*