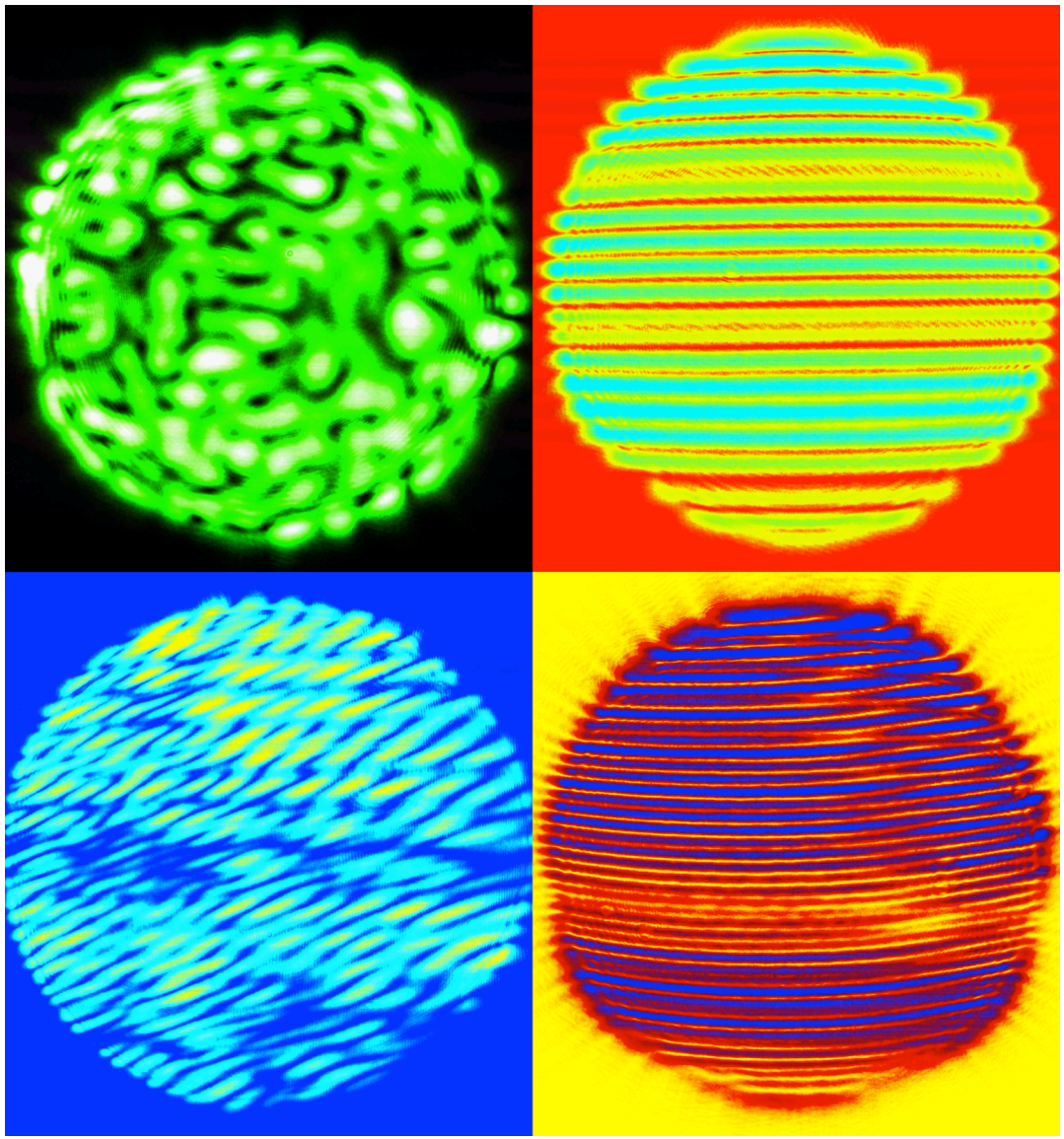
Going Through a Phase:

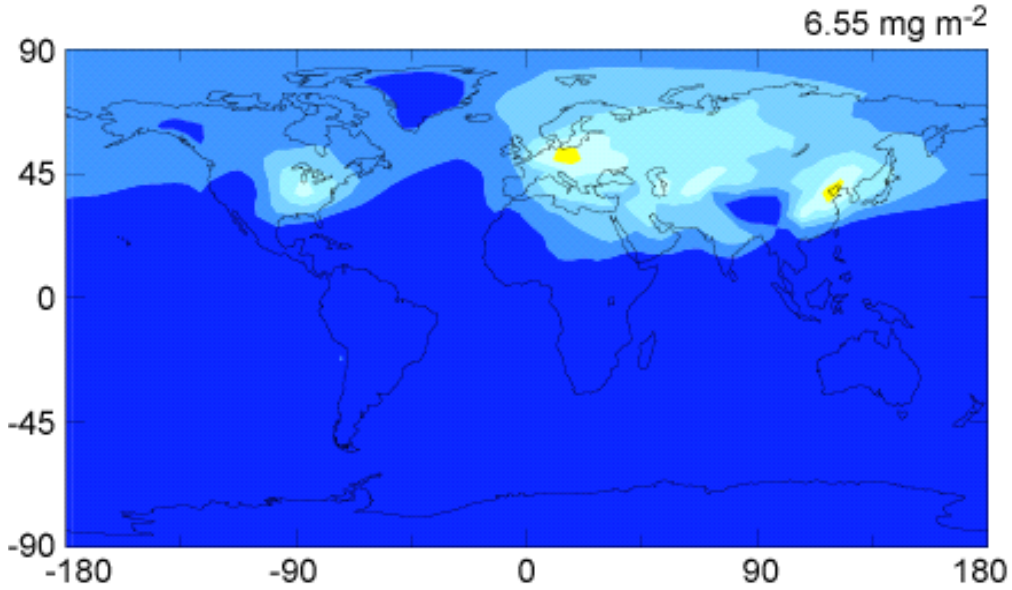
Particulate Water in Atmospheric Aerosol

Margaret Tolbert
University of Colorado

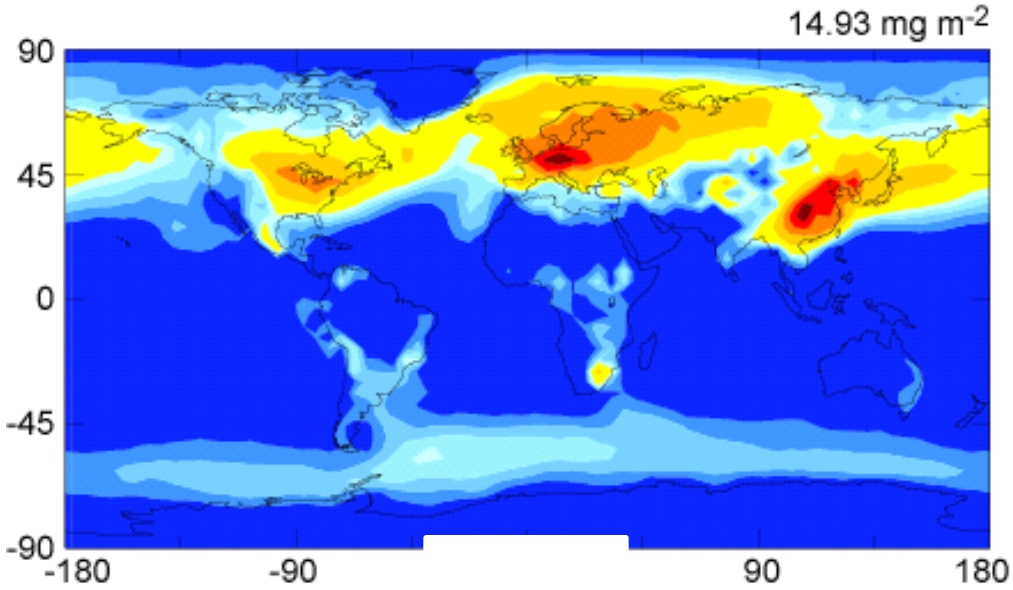


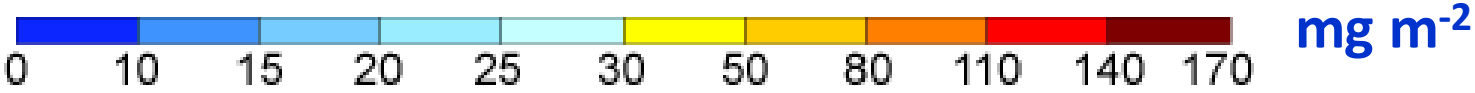
Aerosol water is 2-3 times dry aerosol mass.

Dry sulfate/nitrate/ammonium aerosols



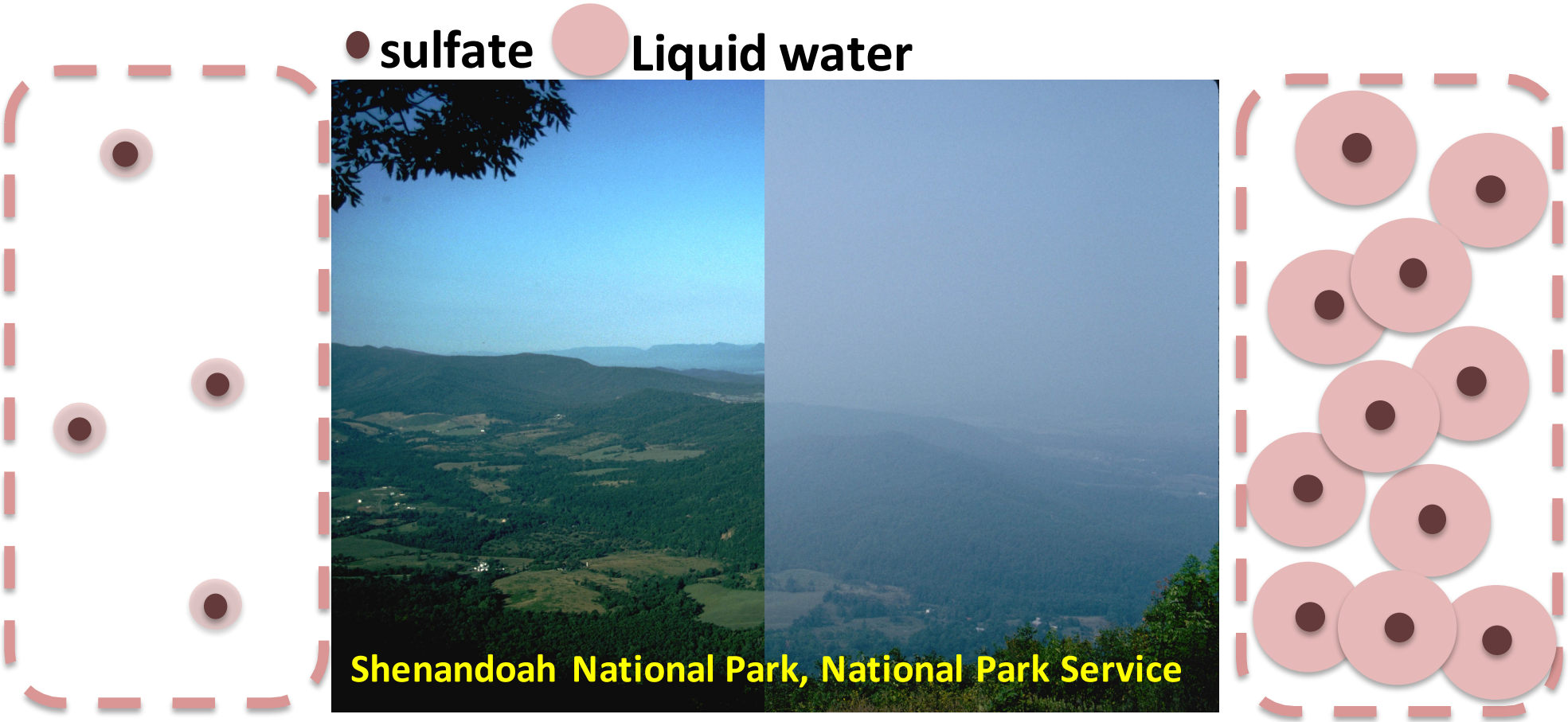
Water associated with sulfate/nitrate/ammonium aerosols





Liao and Seinfeld *JGR* (2005)

Increased particle water impacts visibility, climate, and atmospheric chemistry



- ***Particles must be aqueous before growth***

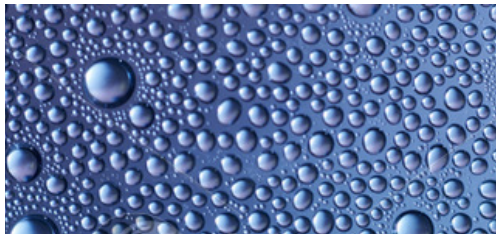
Slide from AM Carlton, 2016

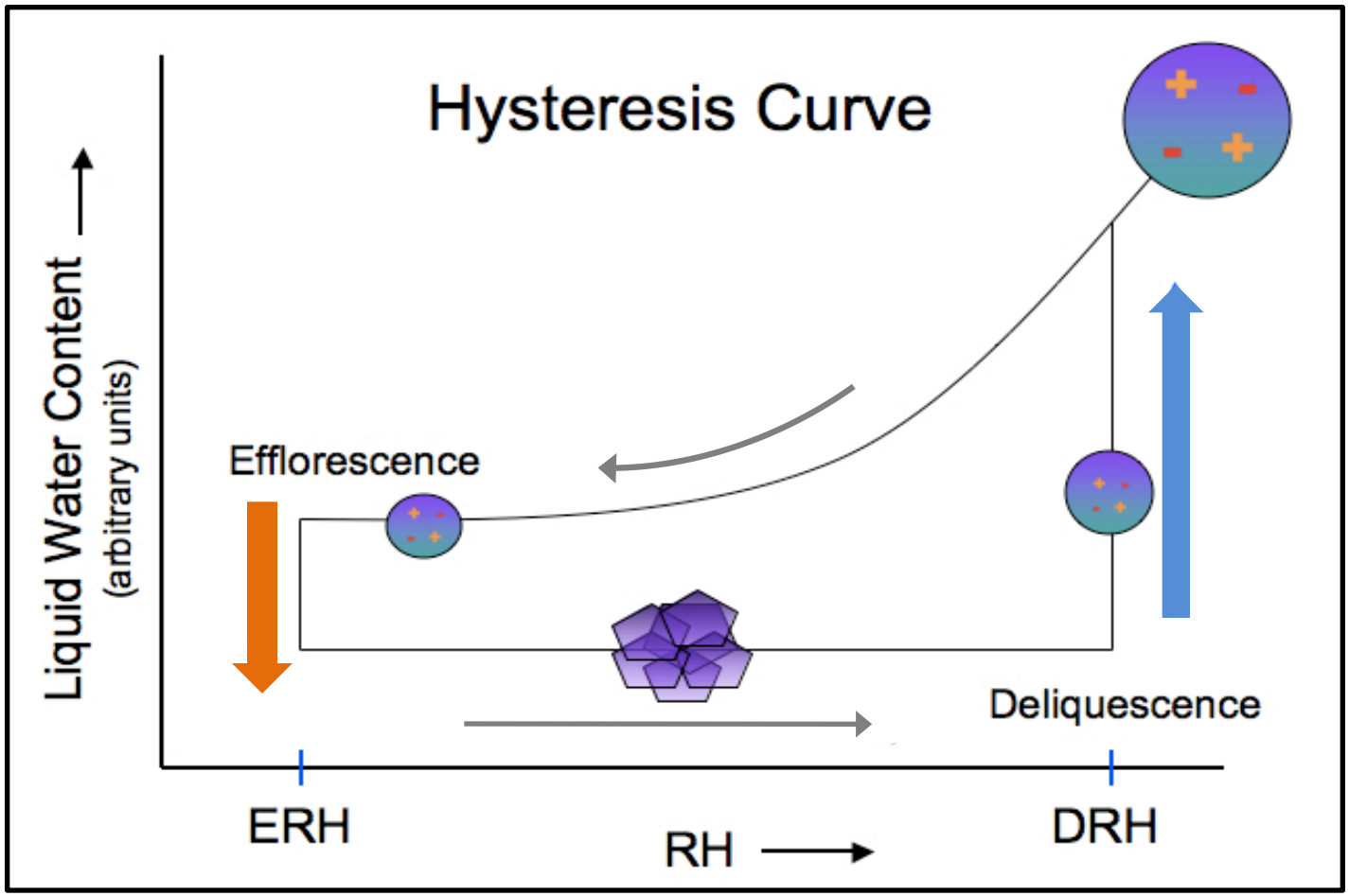
Salt Deliquescence and Efflorescence

$H_2O_{(g)}$ +

deliquescence

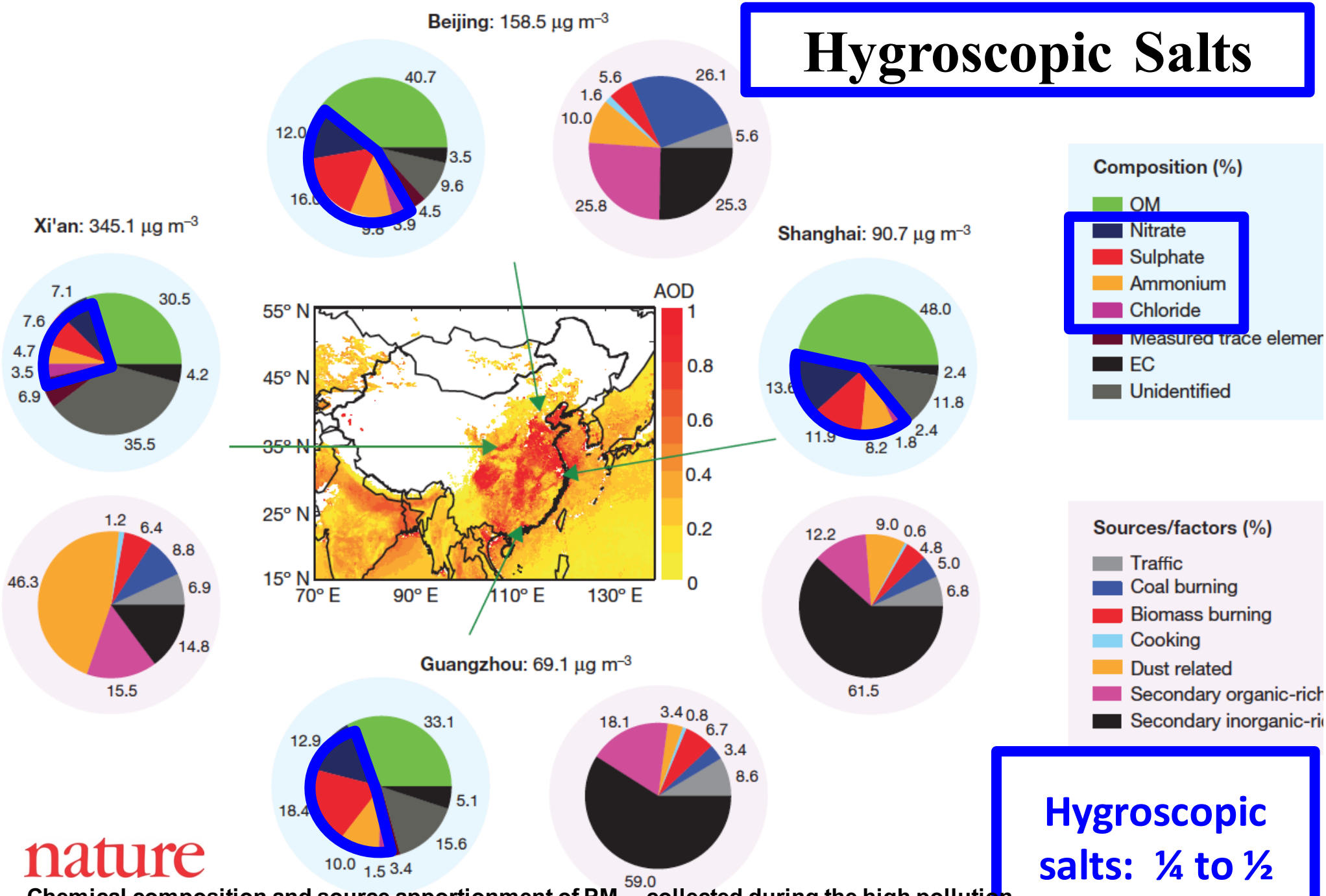
efflorescence





Usually aerosols assumed to remain liquid

Hygroscopic Salts

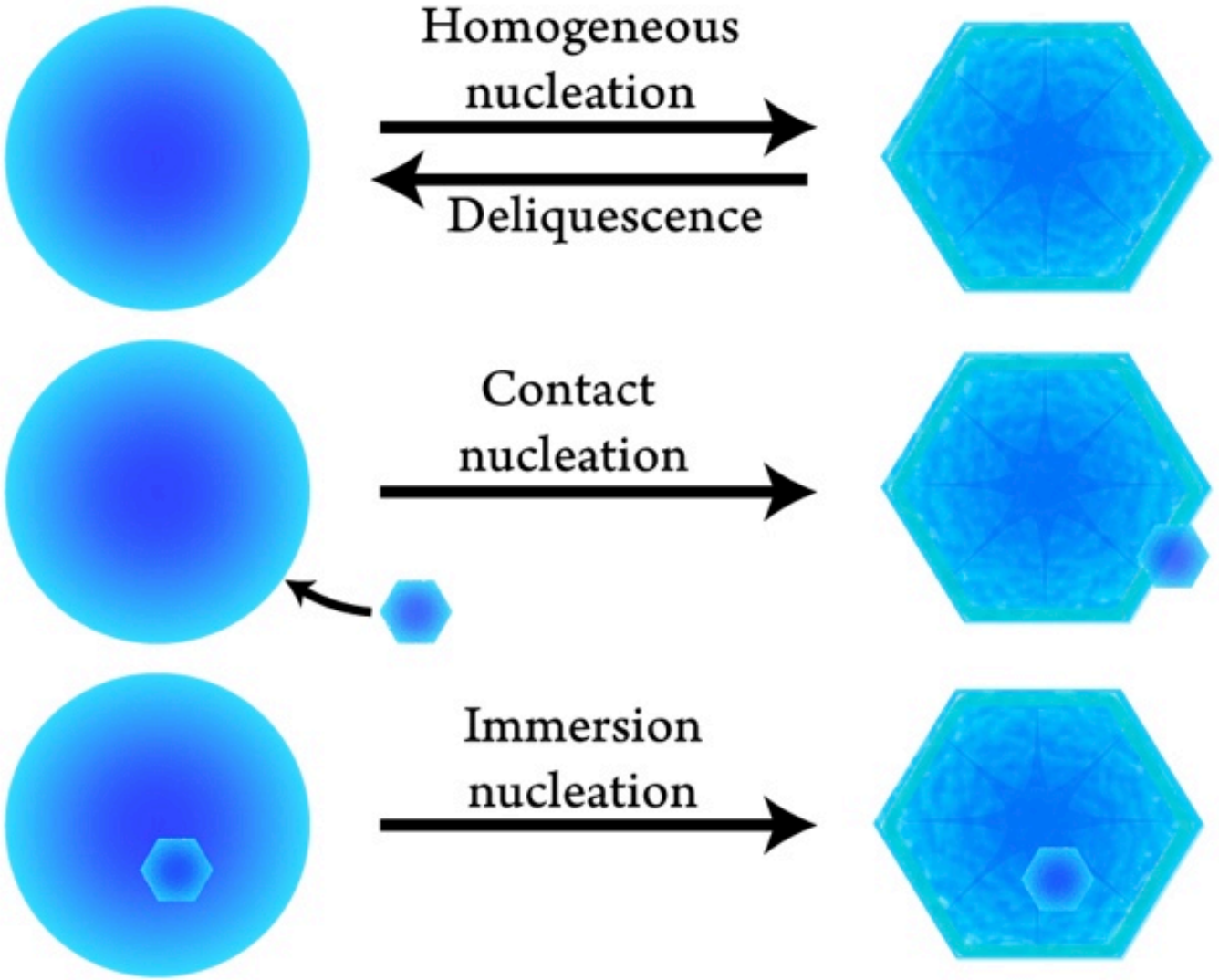


nature

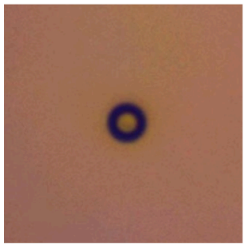
Chemical composition and source apportionment of $PM_{2.5}$ collected during the high pollution events of 5–25 January 2013 at the urban sites of Beijing, Shanghai, Guangzhou and Xi' an.
R-J Huang *et al. Nature* 2014, 1-5 (2014) doi:10.1038/nature13774

Hygroscopic salts: ¼ to ½ aerosol mass

Phase transitions in this talk



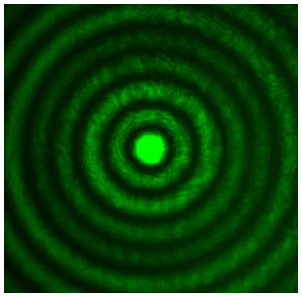
Experimental

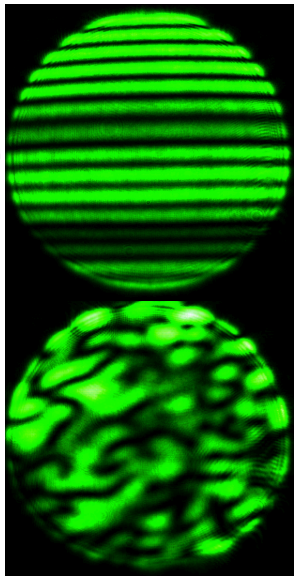


Bright-field

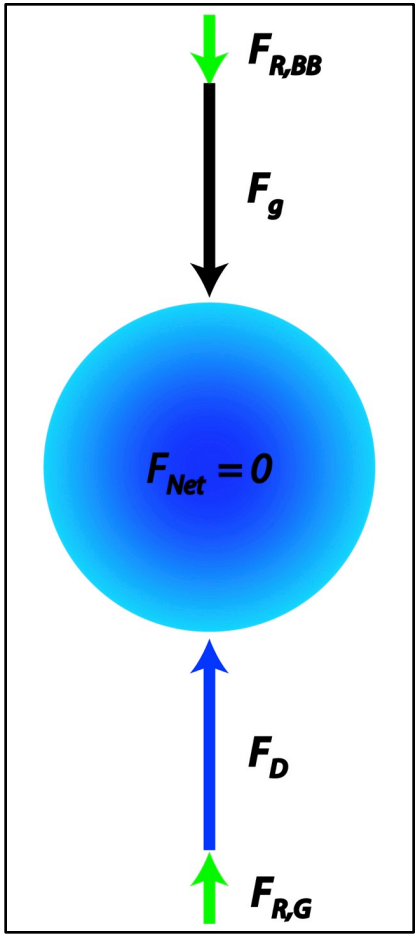
Axicon

Nd:YAG
532 nm

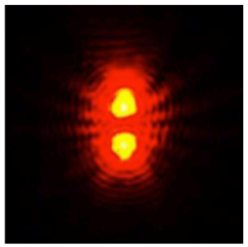




Far field, 532 nm



632.8 nm

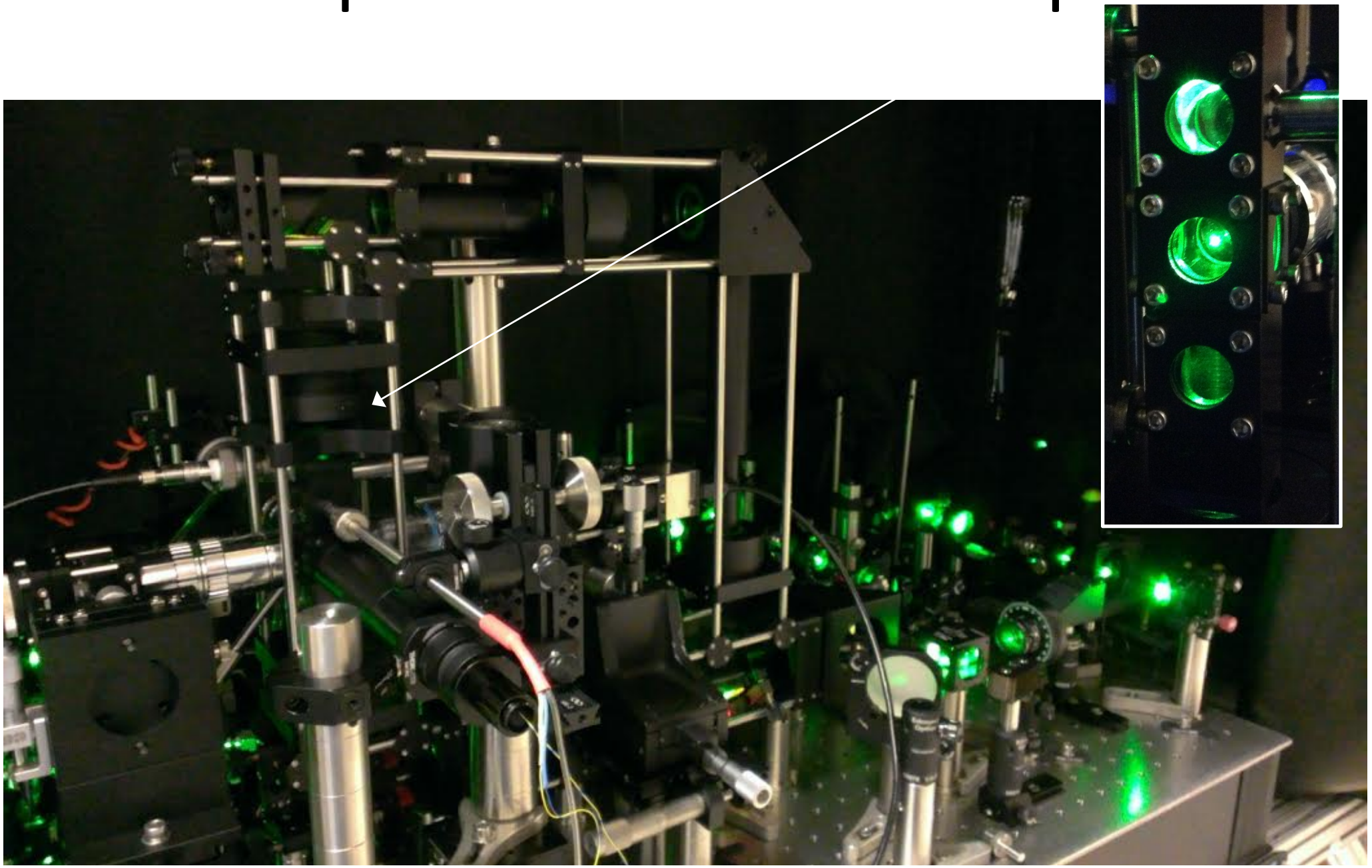


Near-field (or far-field)

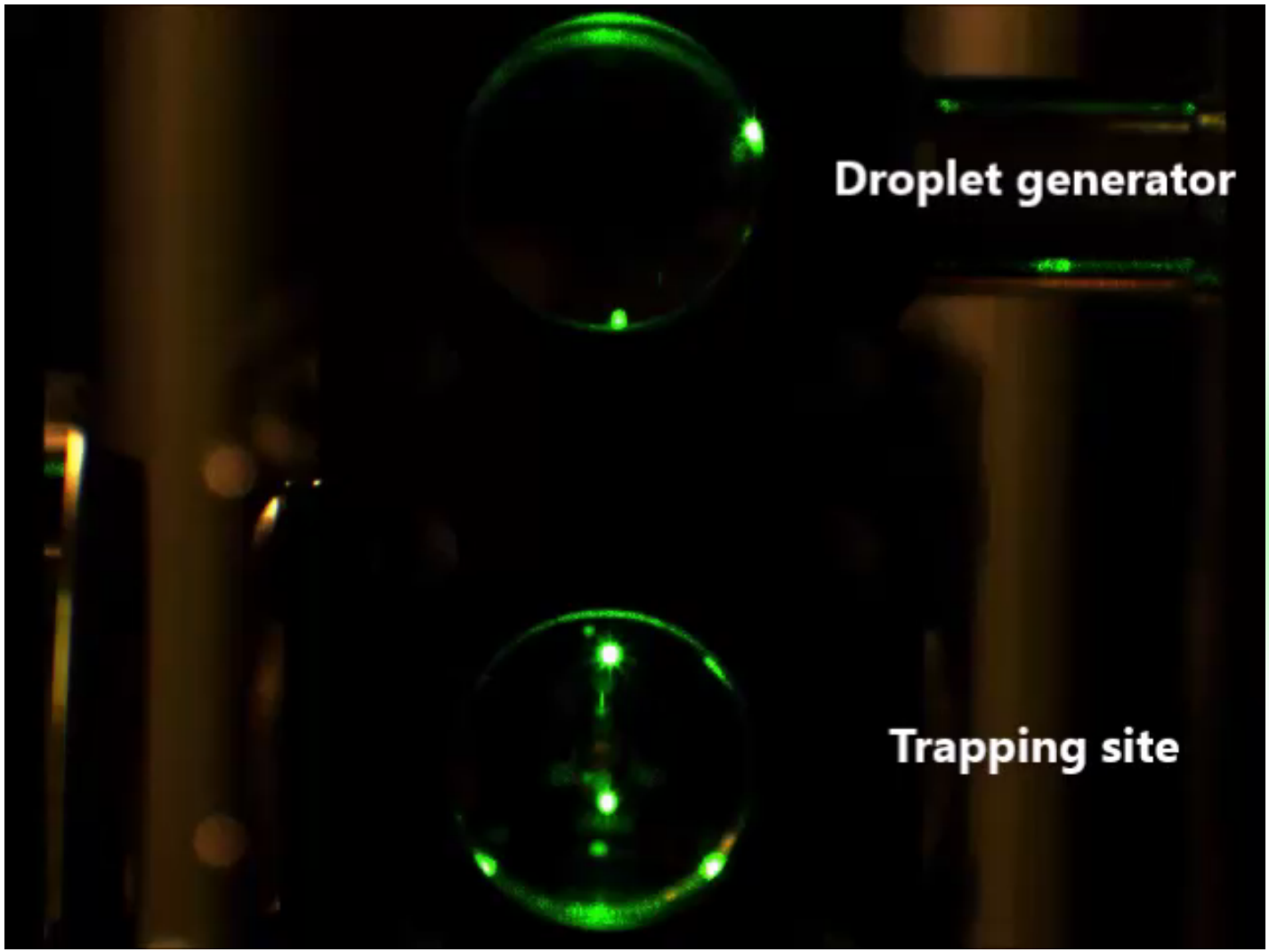
Nd:YAG
532 nm

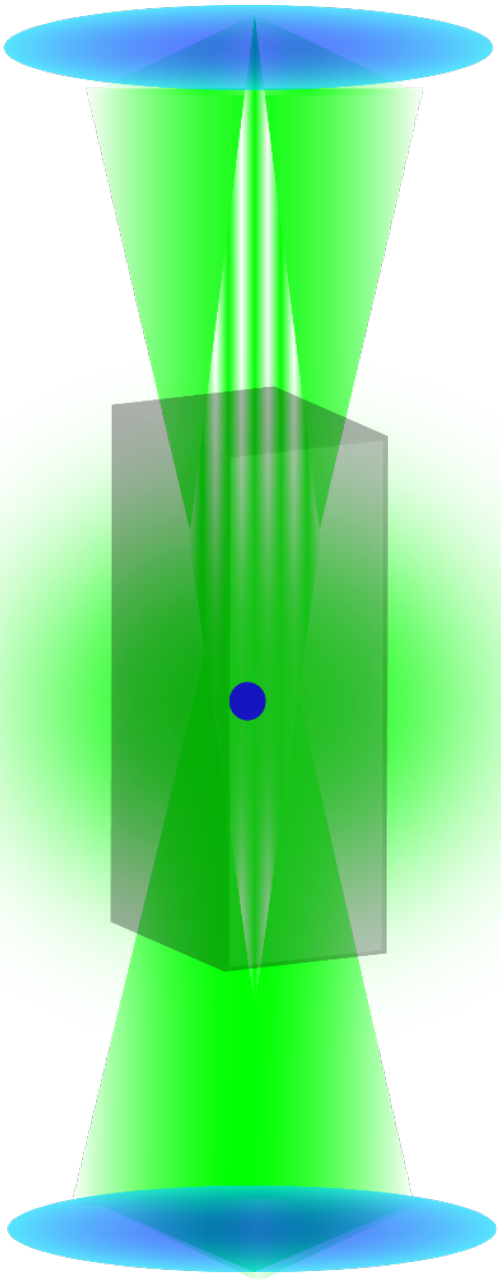
HeNe
632.8 nm

Optical Levitation Setup

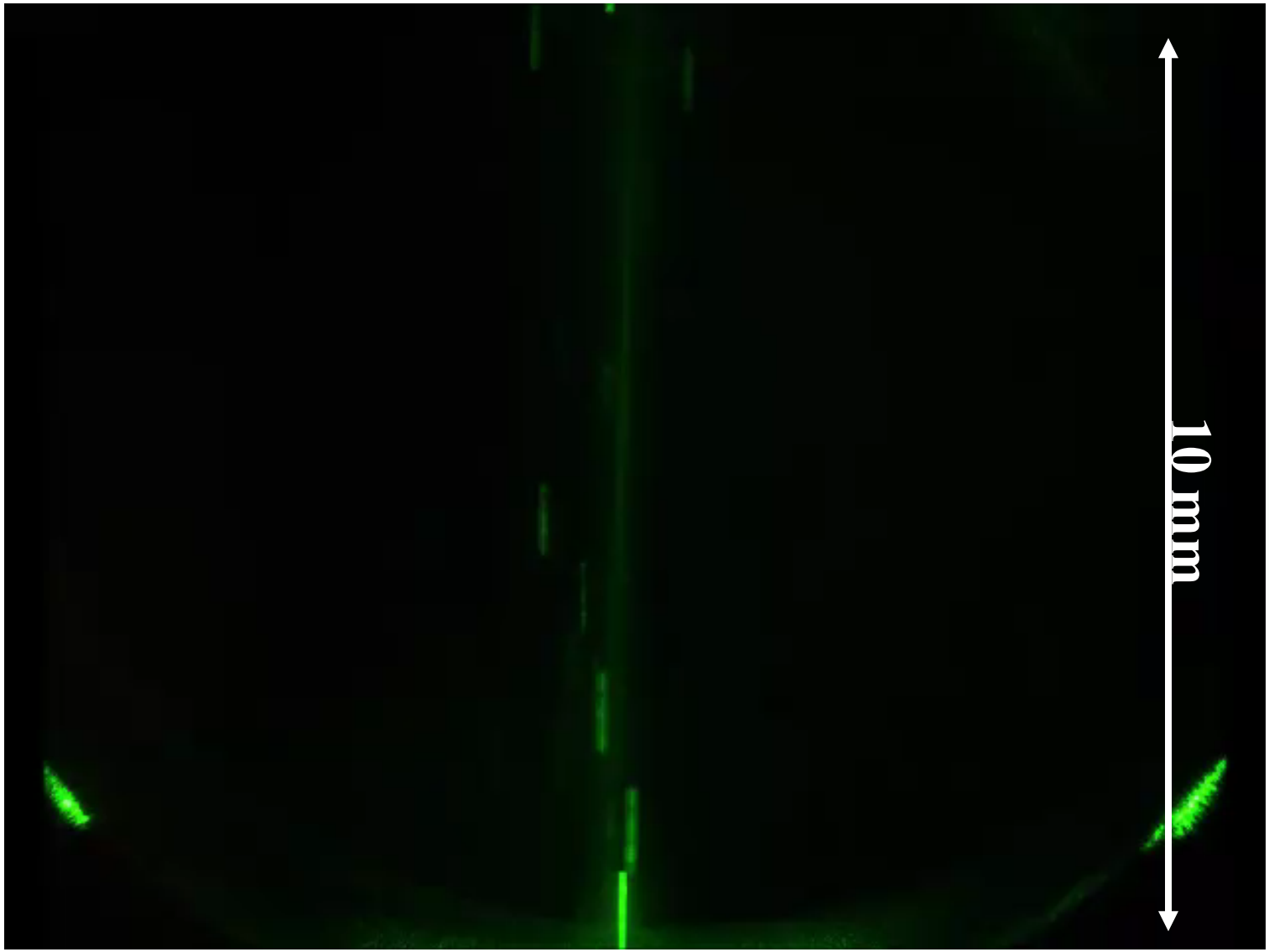


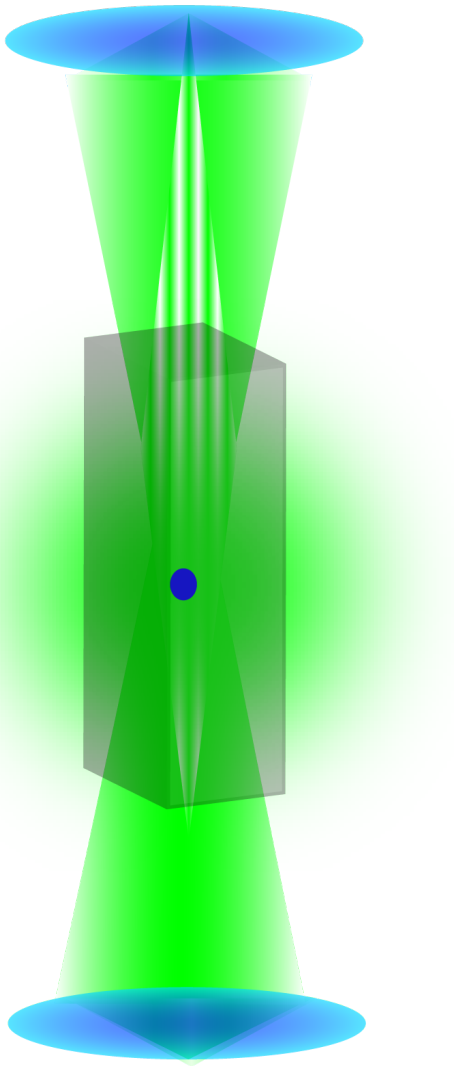
An upward oriented Gaussian beam facilitates initial trapping



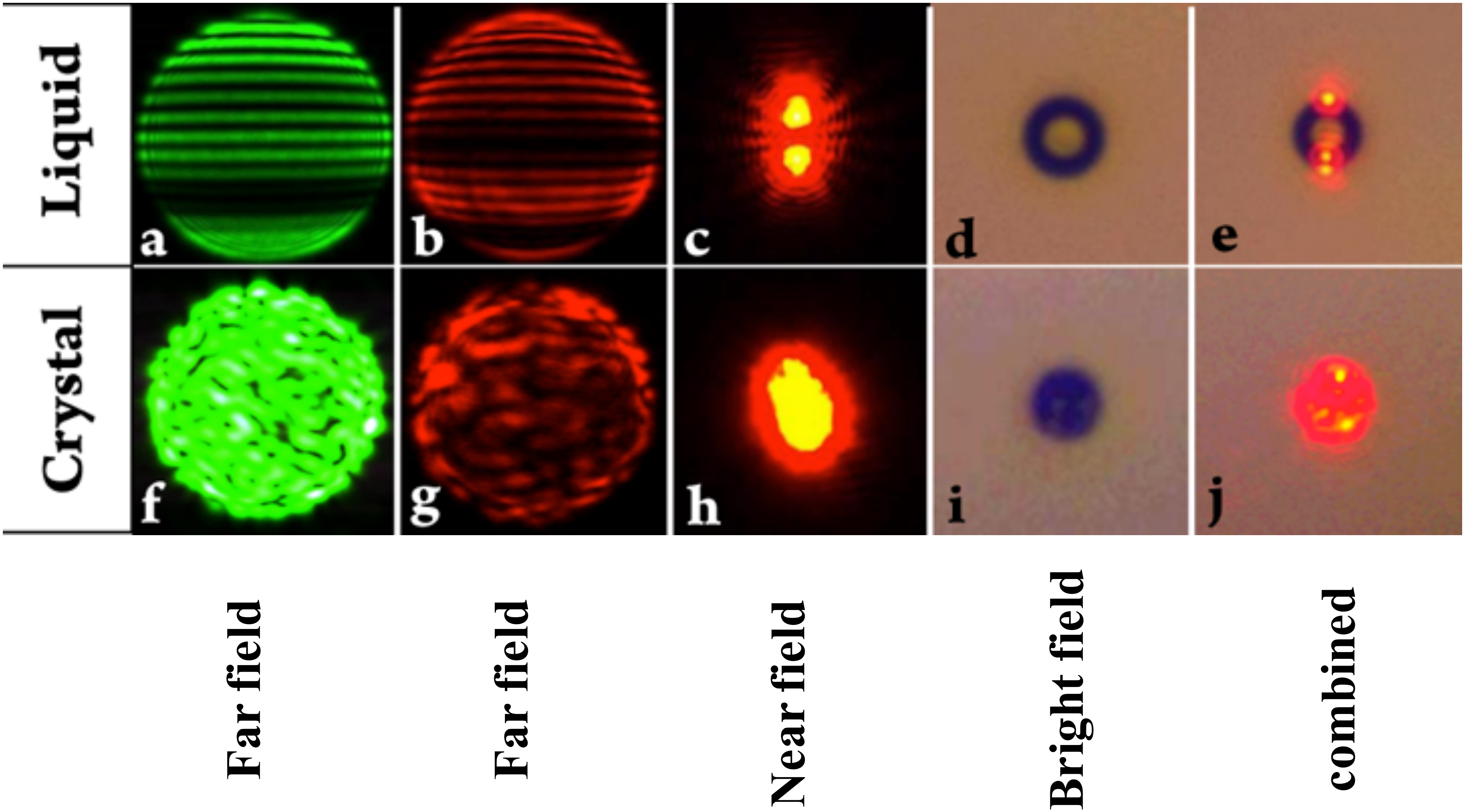


The Bessel beam supplies additional gradient force and can trap 350 nm particles (or less)





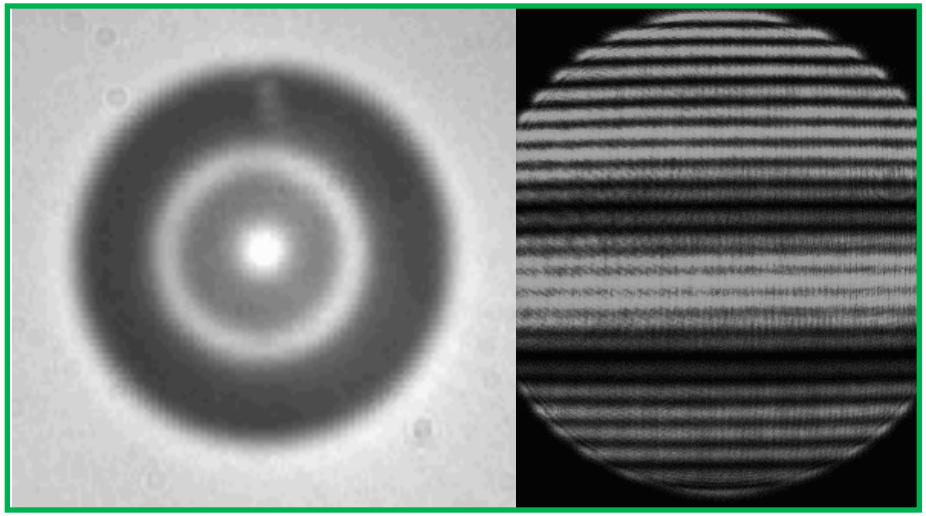
Liquid vs Solid

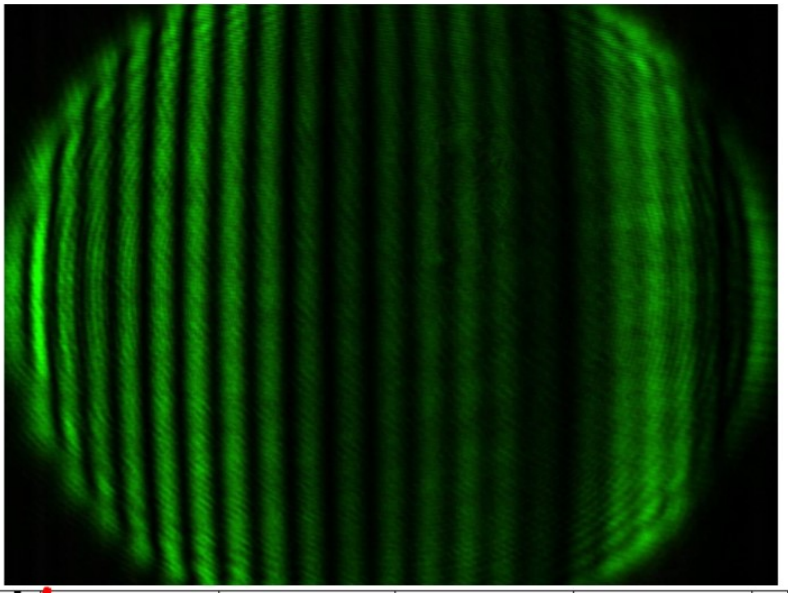


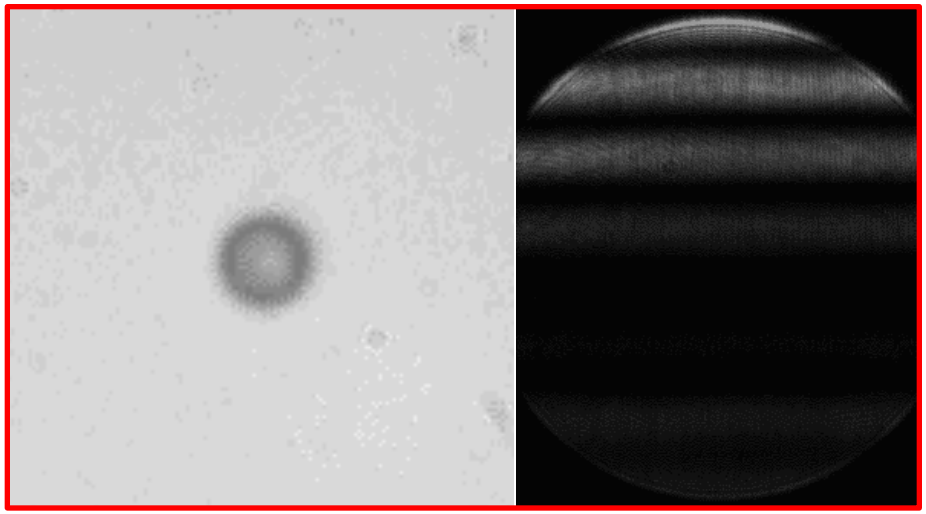
Sizing:Evaporation of a Glycerol Droplet

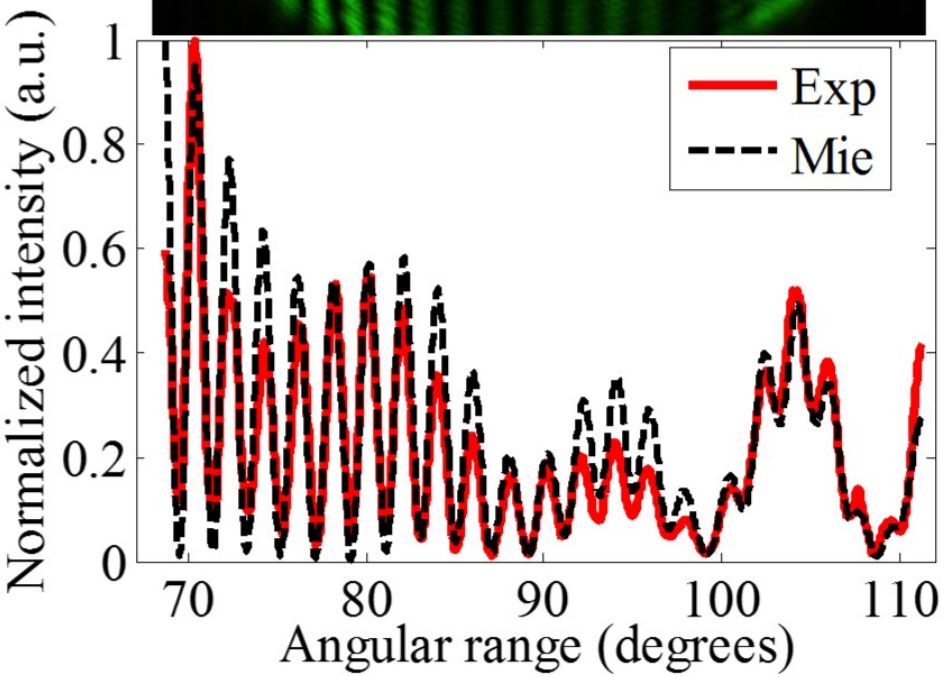
Droplet Sizing

$D_p = 17.589 \pm 0.006\ \mu m$

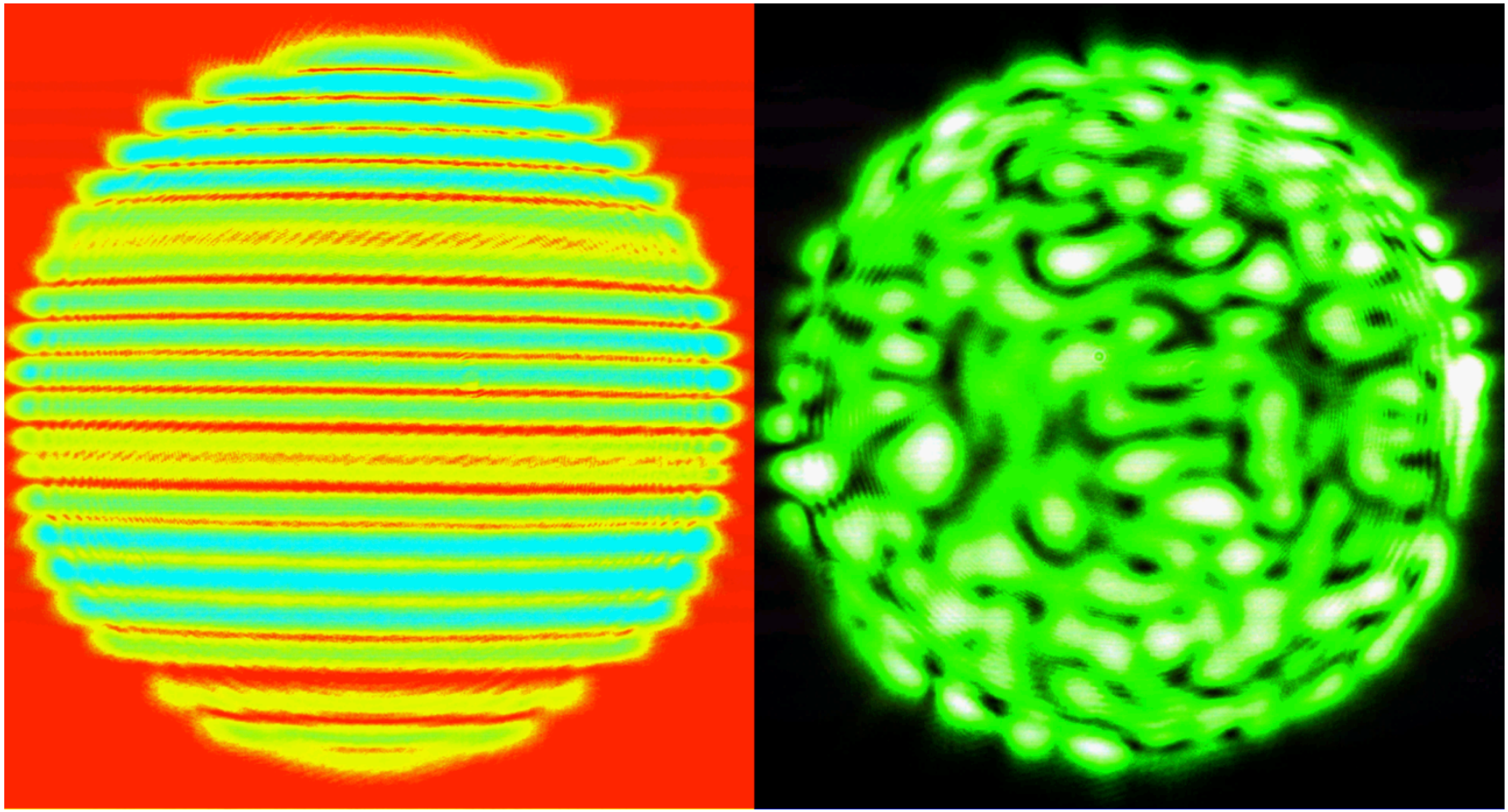




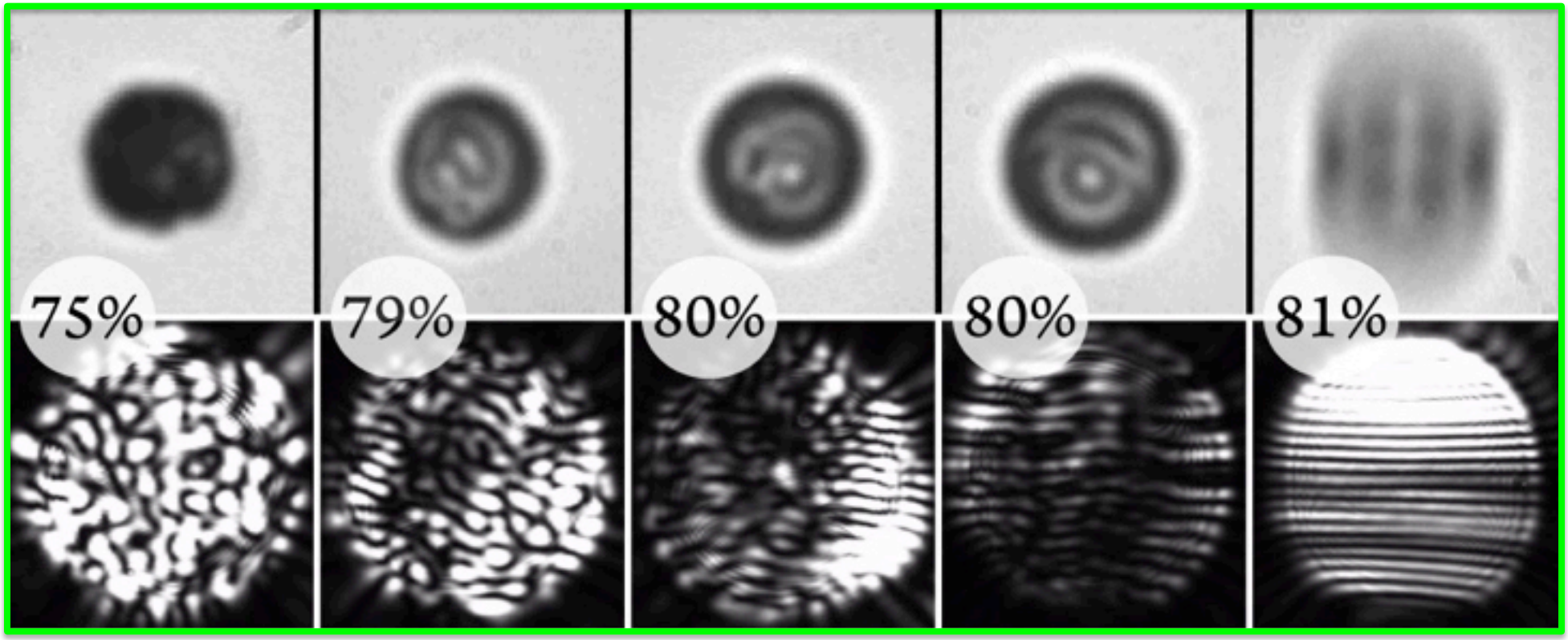




Homogeneous Phase Transitions of Hygroscopic Salts

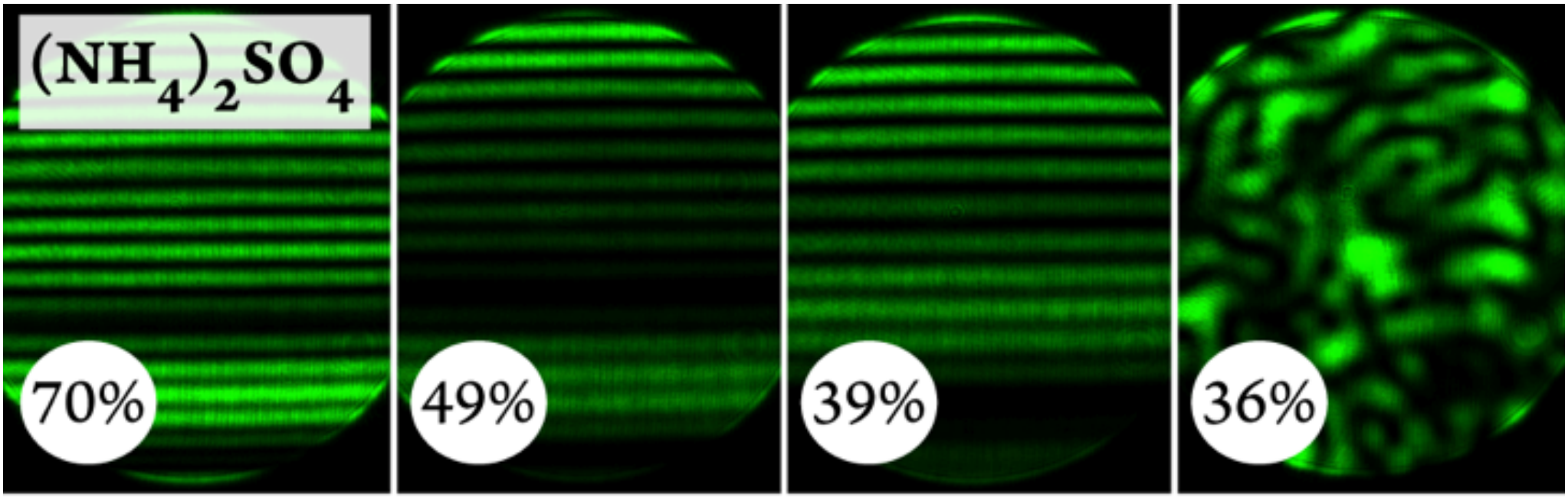


Ammonium Sulfate Deliquescence

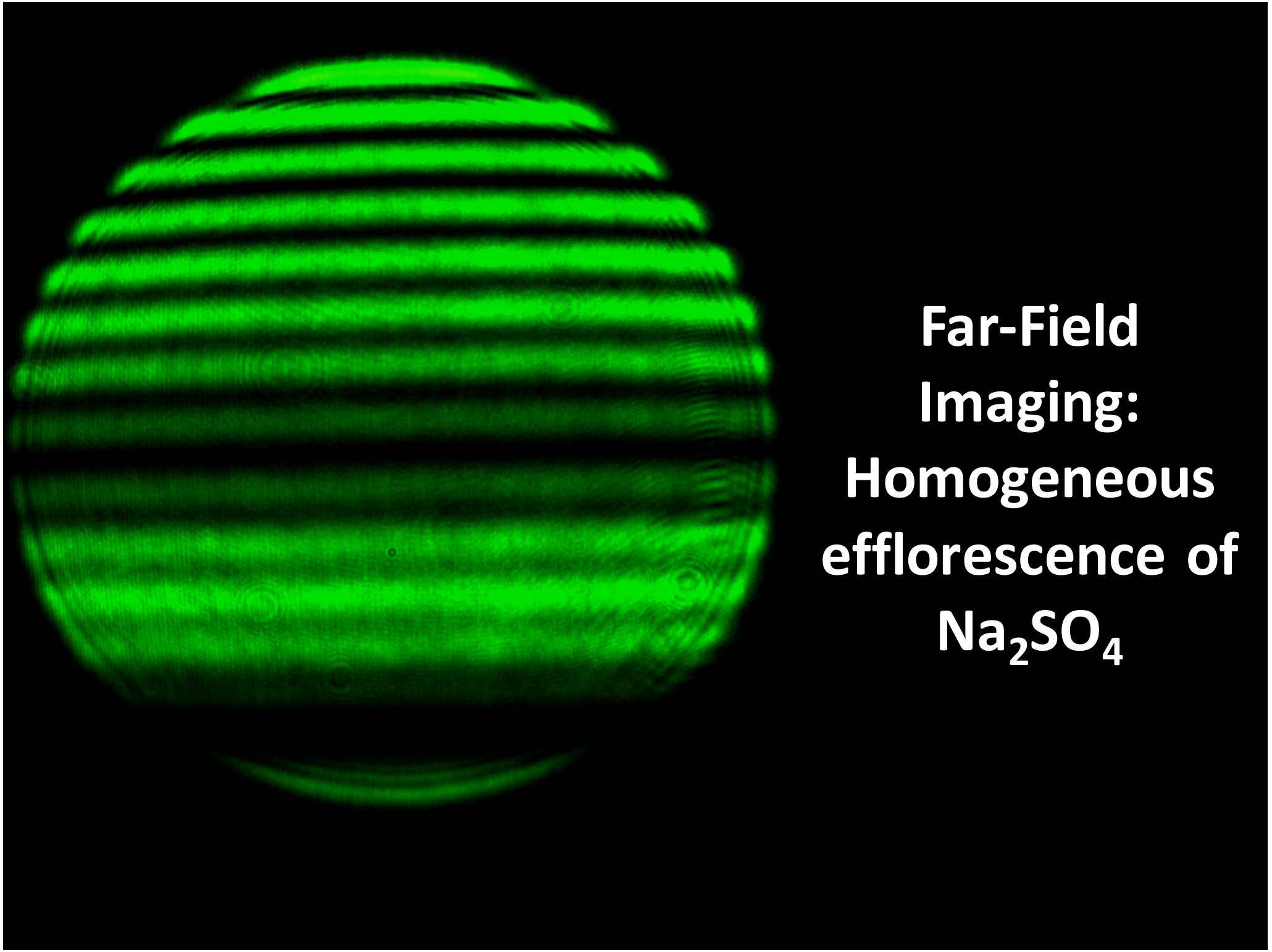


- water uptake by 79% RH
- fully deliquesced by 81% RH

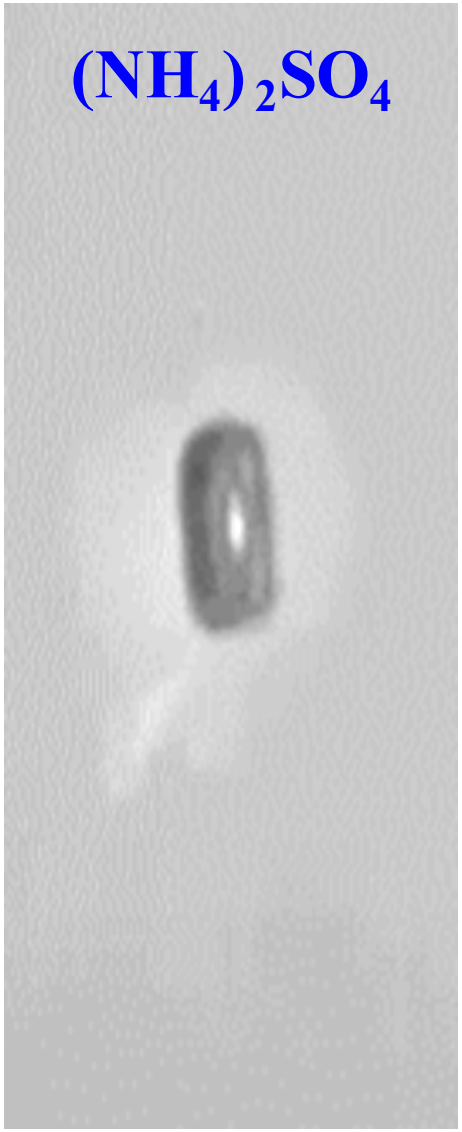
AS Homogeneous Efflorescence

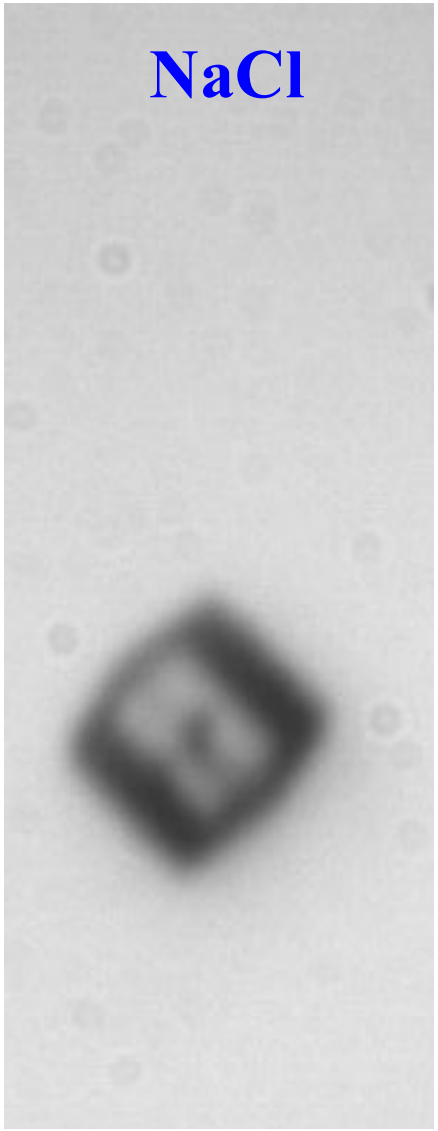


Lower RH


Far-Field Imaging: Homogeneous efflorescence of Na_2SO_4

Bright-field imaging of trapped crystals

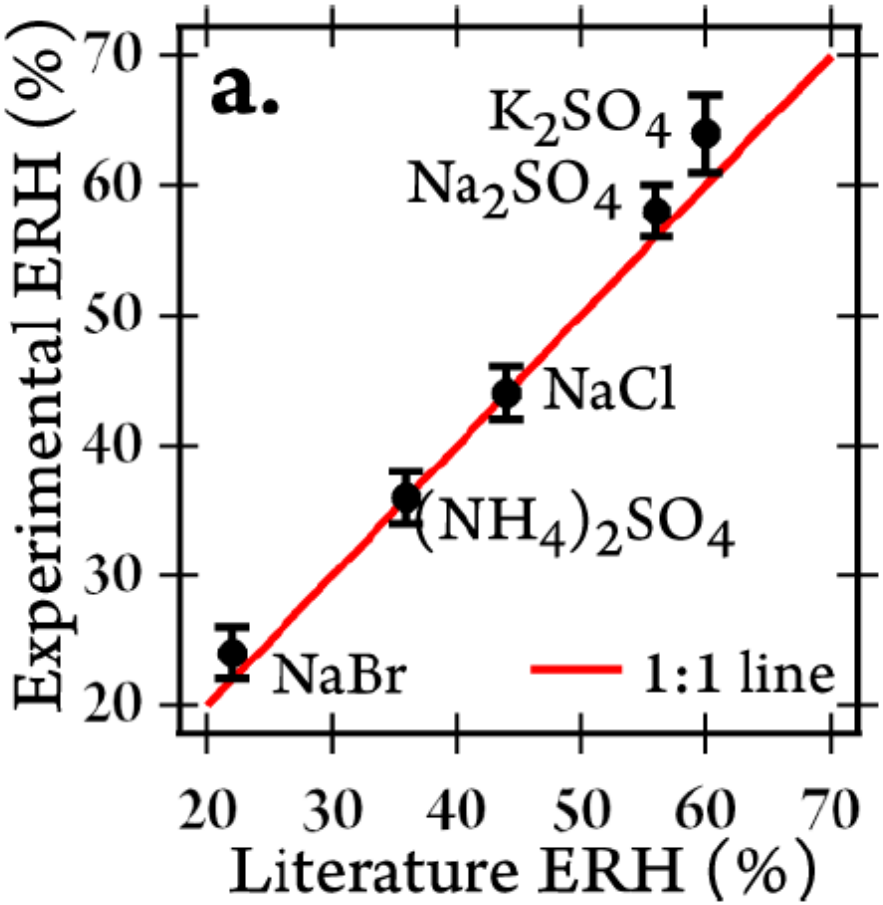




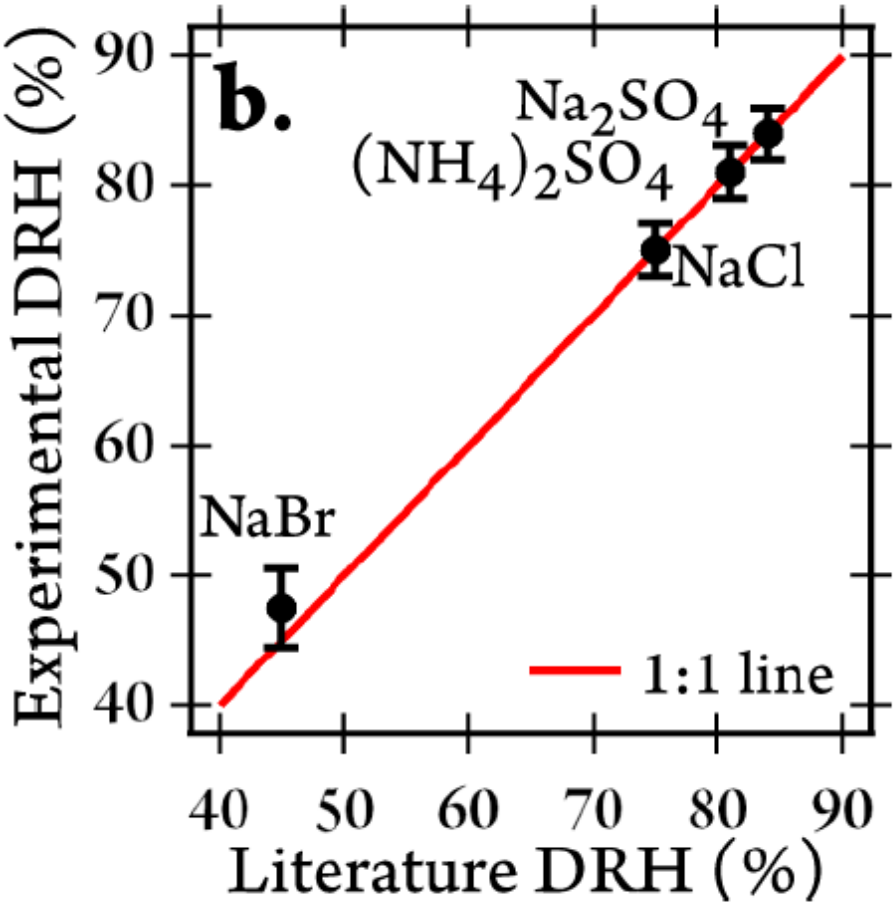
The rigidity of the crystalline surface make it difficult to trap

Comparison with Literature Values

Efflorescence



Deliquescence



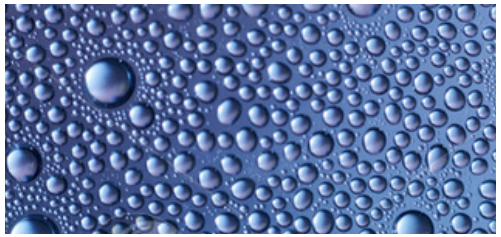
Deliquescence RH > Efflorescence RH

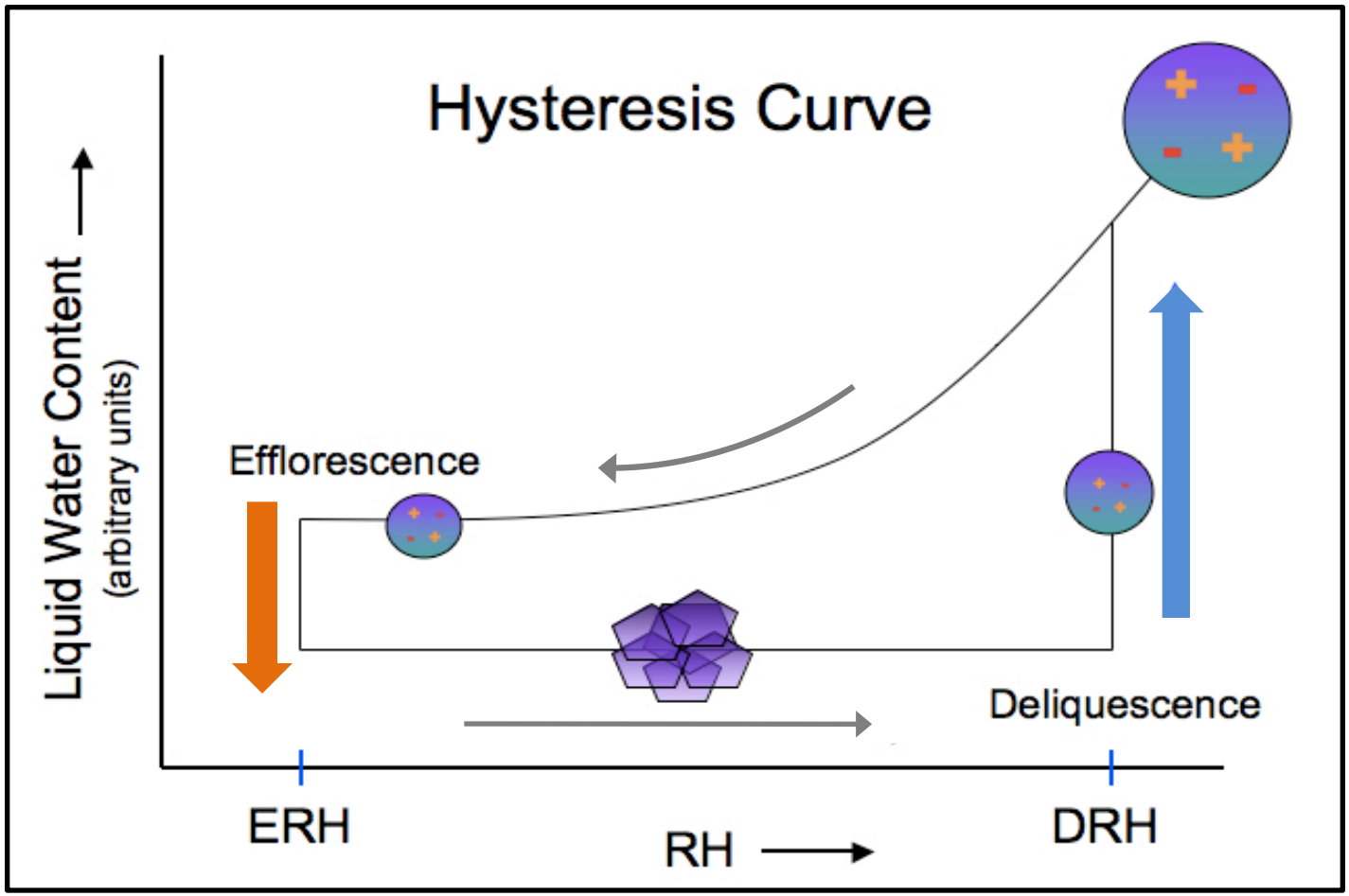
Salt Deliquescence and Efflorescence

$H_2O_{(g)}$ +

deliquescence

efflorescence

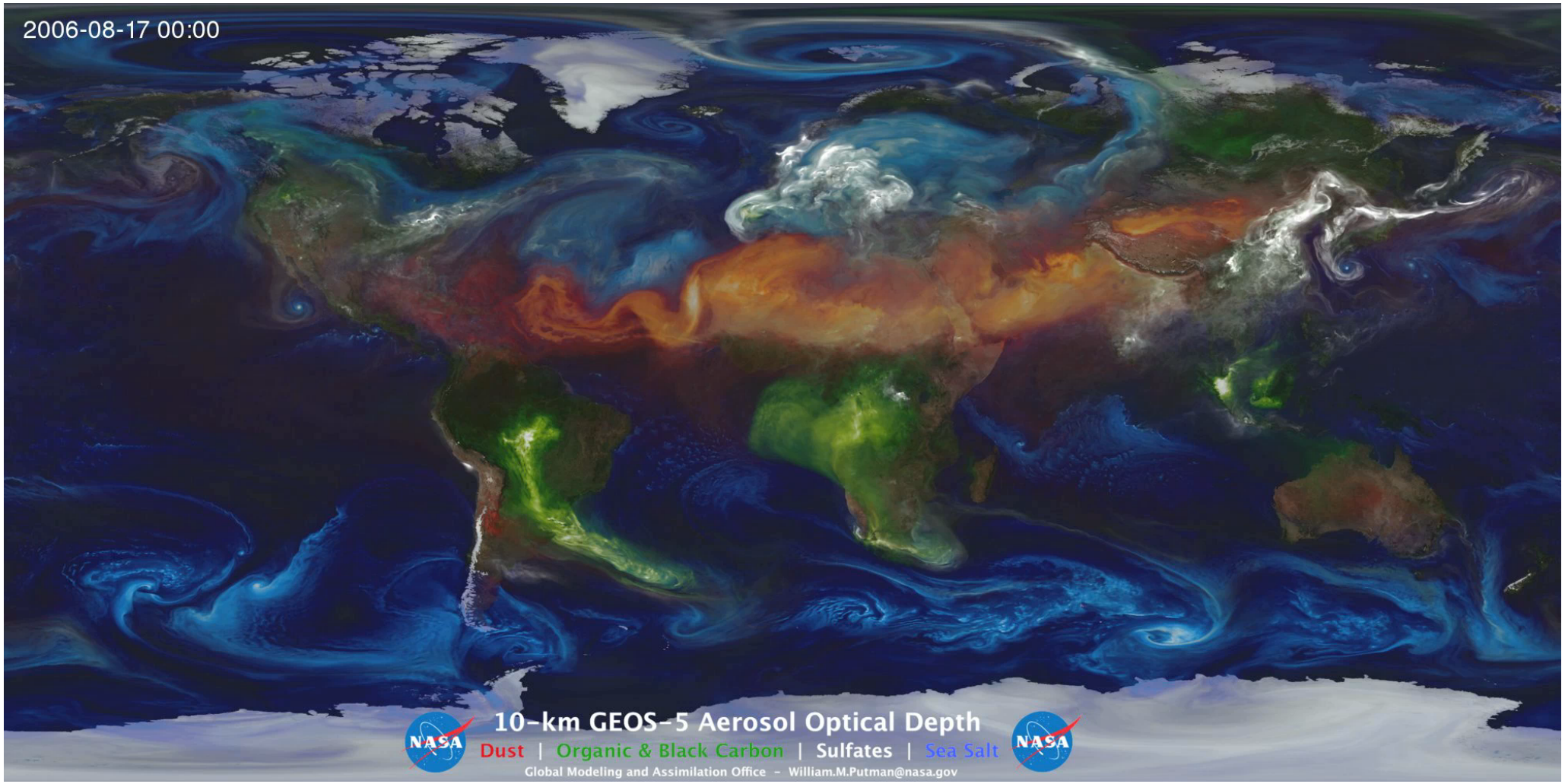




Usually aerosols assumed to remain liquid

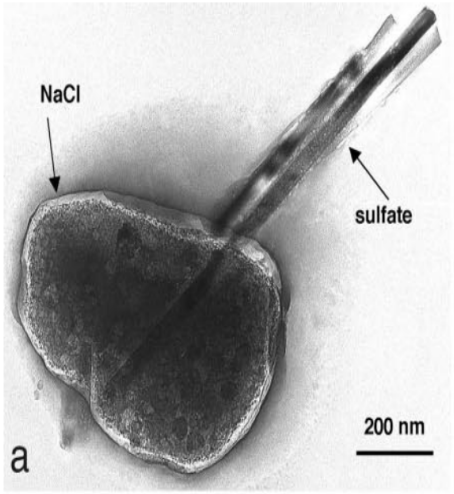
Contact

Global Hi-Res Aerosol Simulation

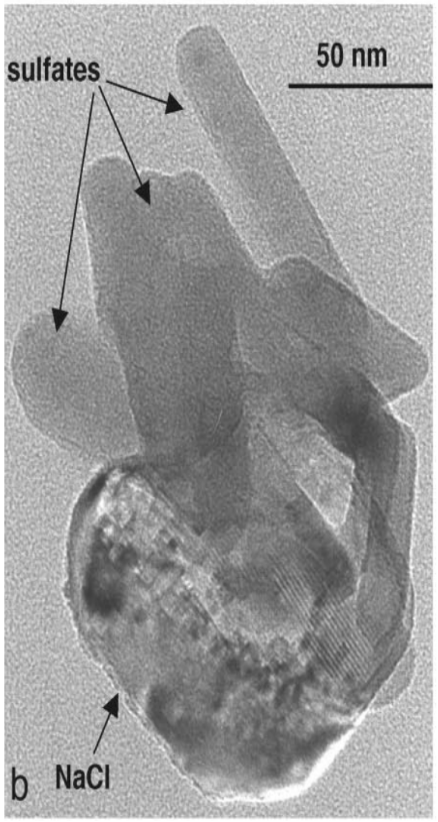


http://gmao.gsfc.nasa.gov/research/aerosol/modeling/nr1_movie/

Internally Mixed Particles Common in Atmosphere

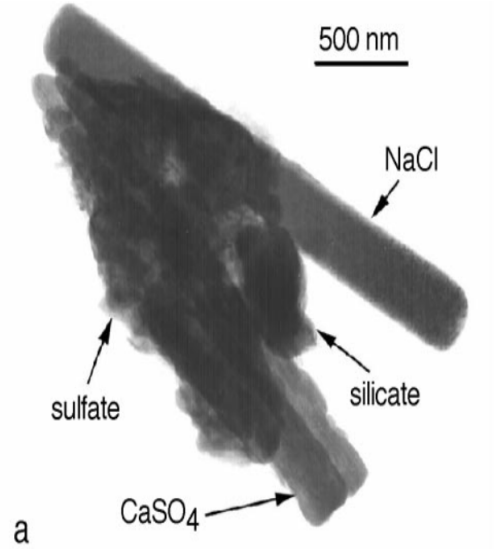


Sulfate-salt

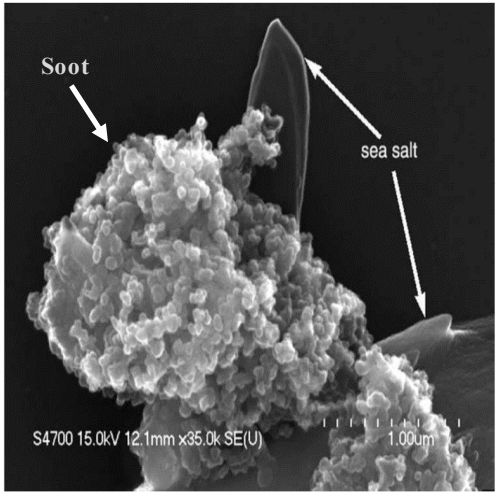


Sulfate-salt

Sulfate-mineral



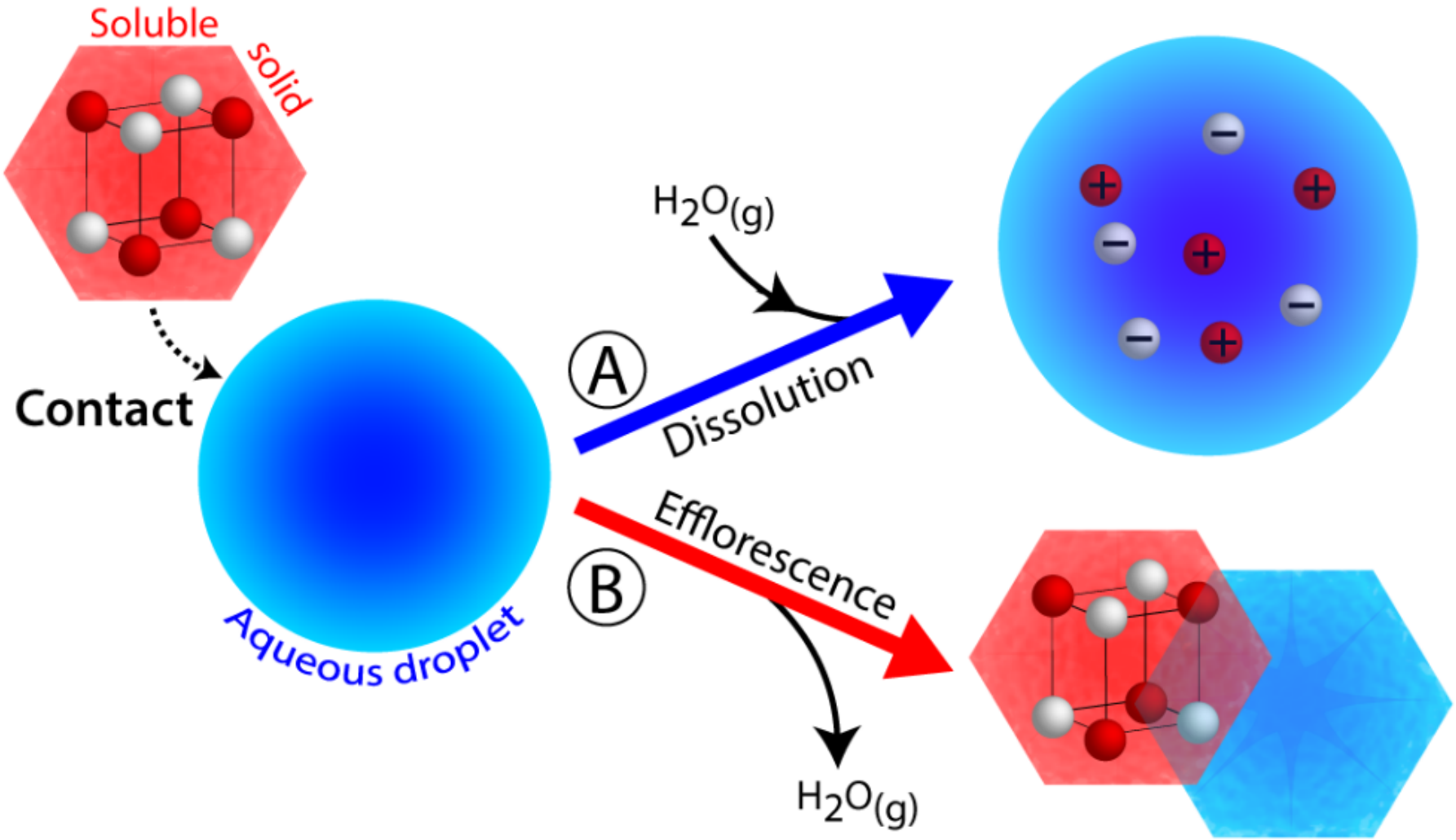
Sulfate-salt-mineral



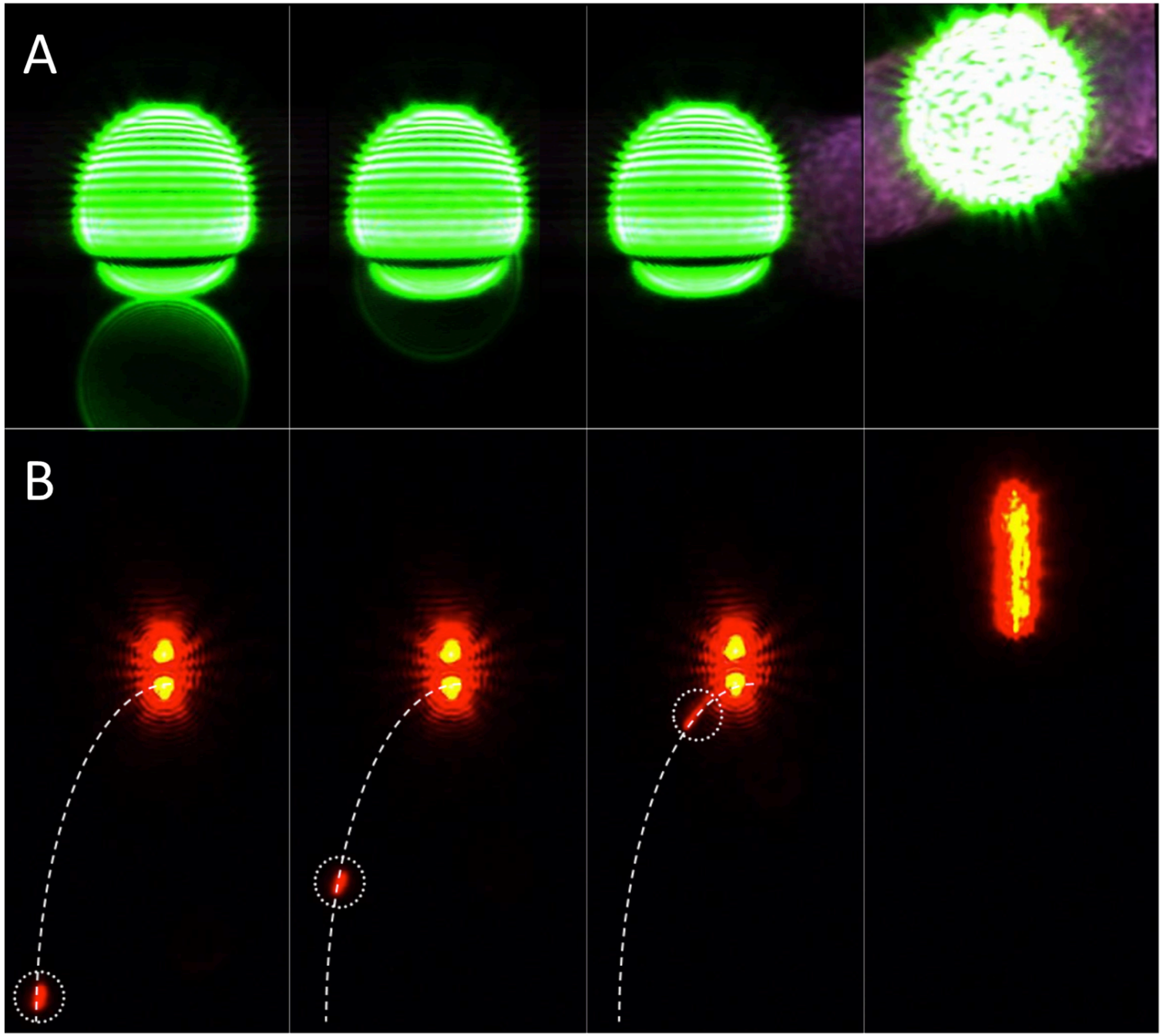
Soot-salt

Li et al. (2003) *J. GeoPhys. Res.*, Buseck and Pósfai (1999) *PNAS*

What happens to the water upon contact?

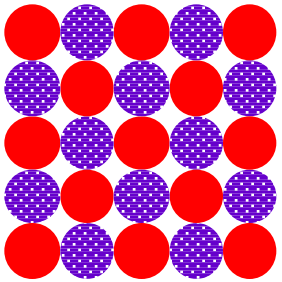


Contact Efflorescence: PSL on AS

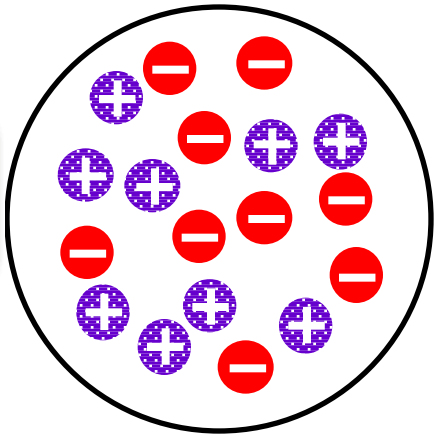


NH_4NO_3 assumed always aqueous

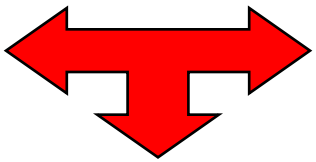
$NH_4NO_{3(s)}$



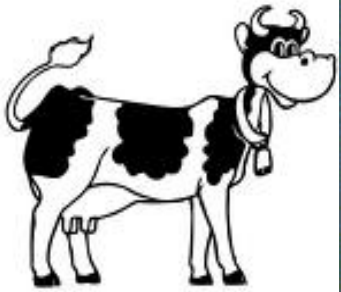
$NH_4NO_{3(aq)}$



HNO_3

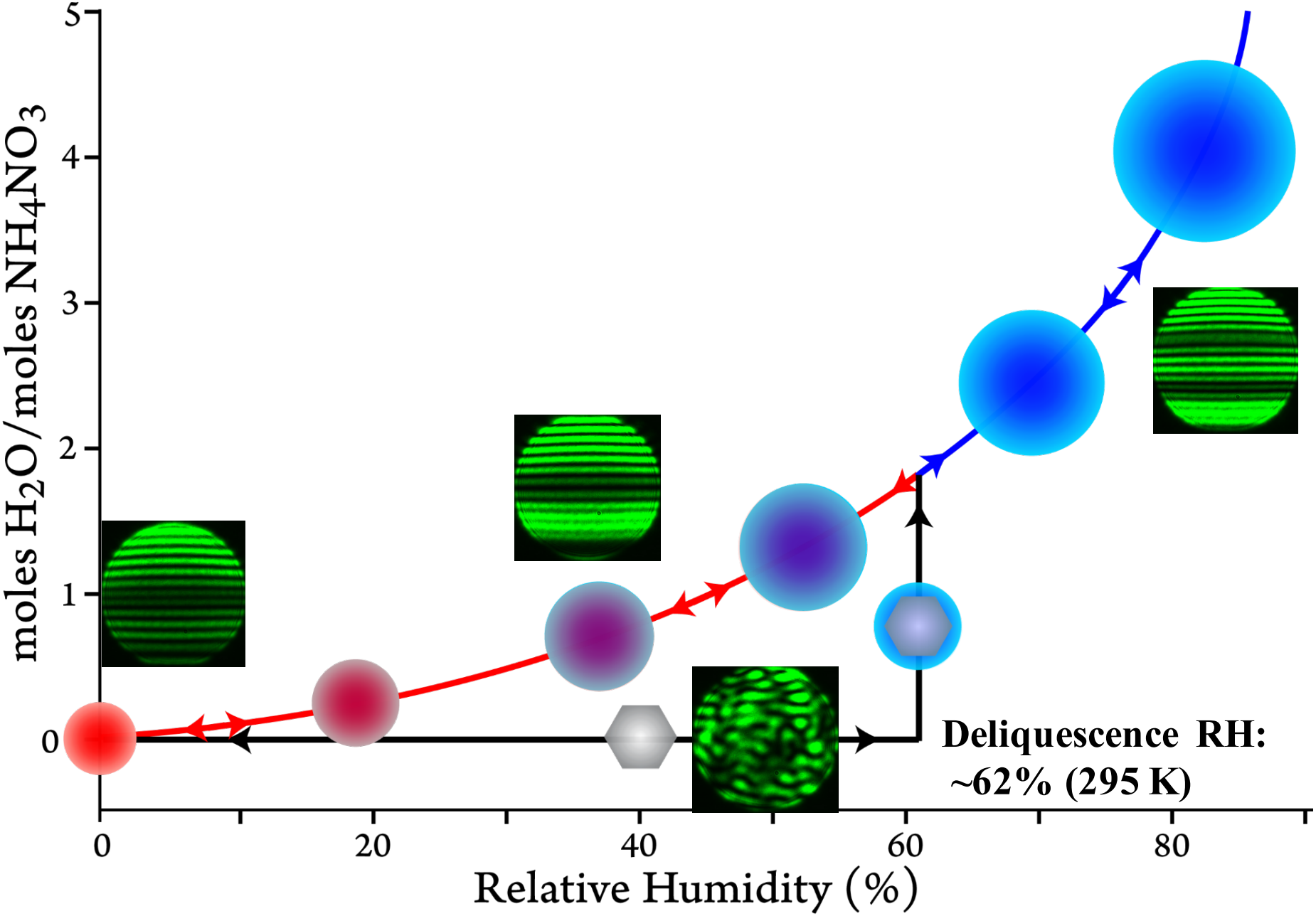


NH_4NO_3

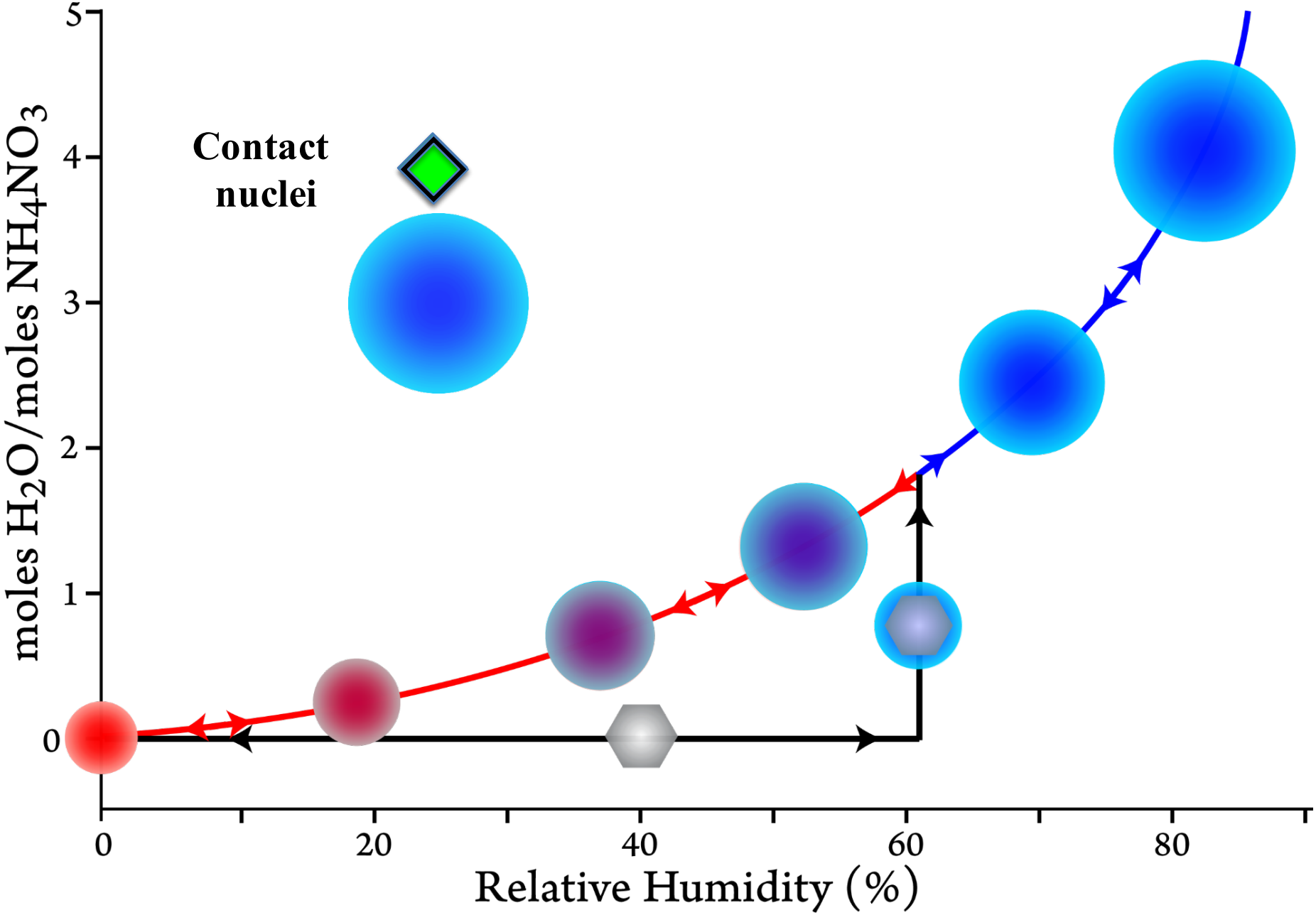


NH_3

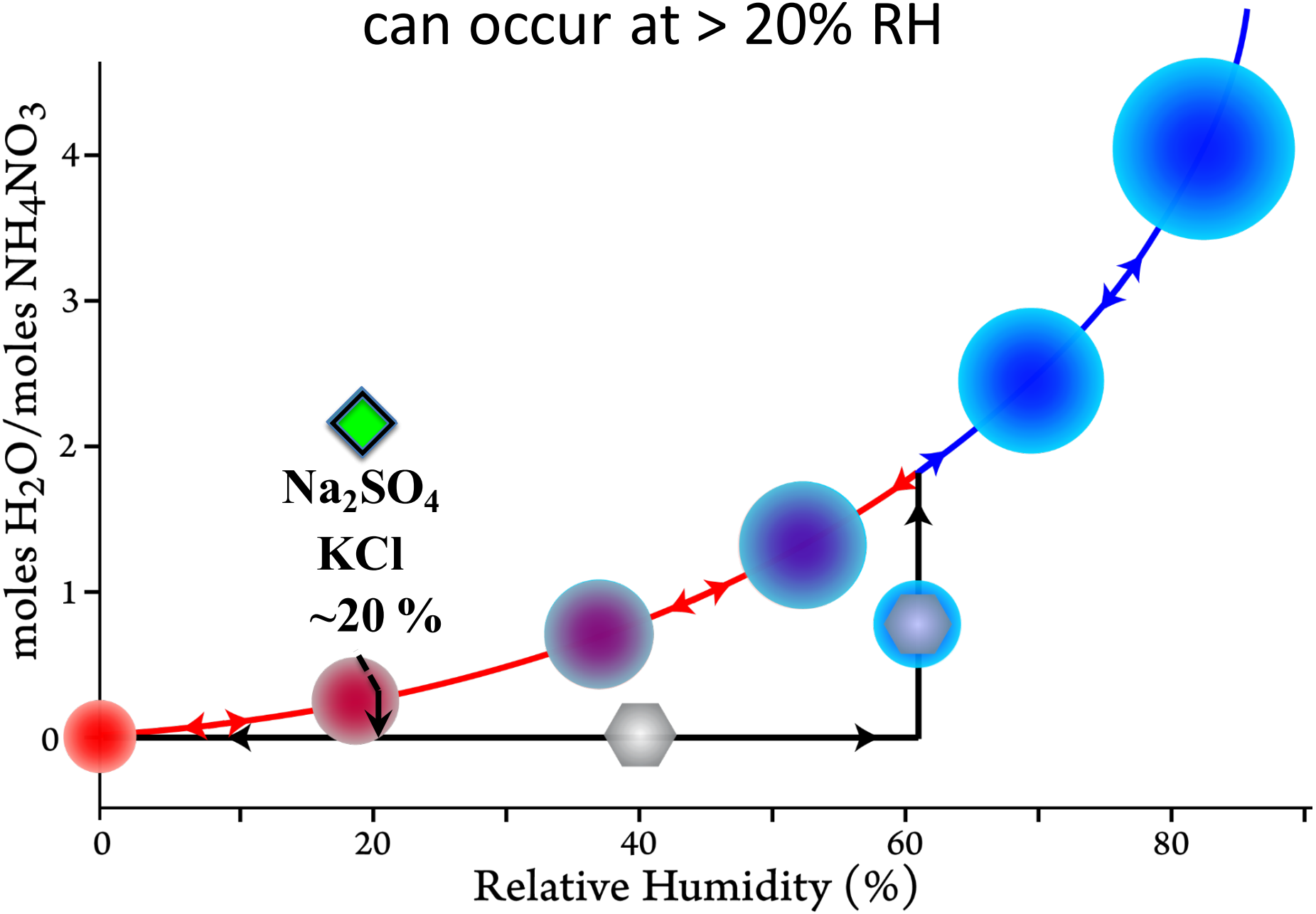
$NH_4NO_{3(aq)}$ does not homogeneously effloresce

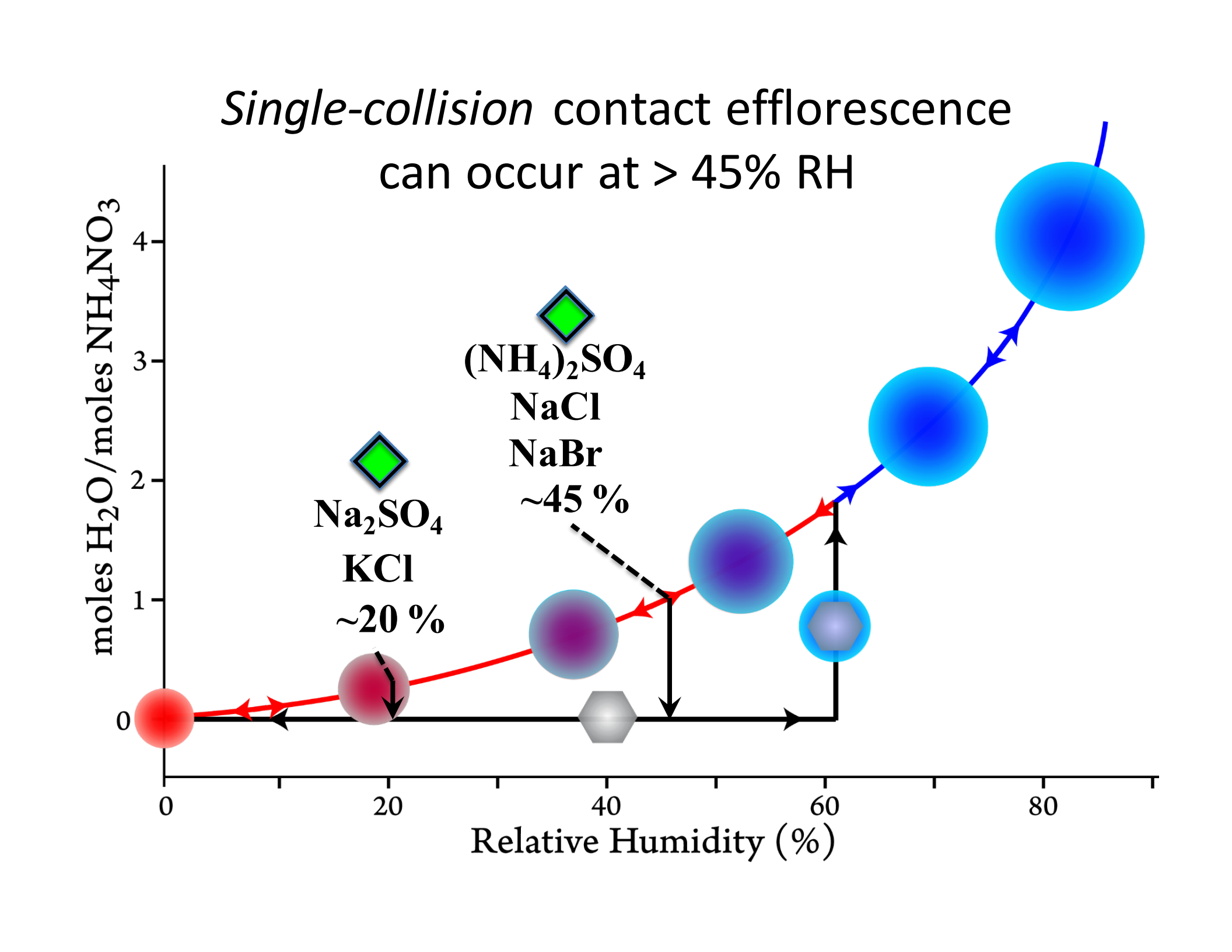


Contact efflorescence of $NH_4NO_{3(aq)}$ droplets

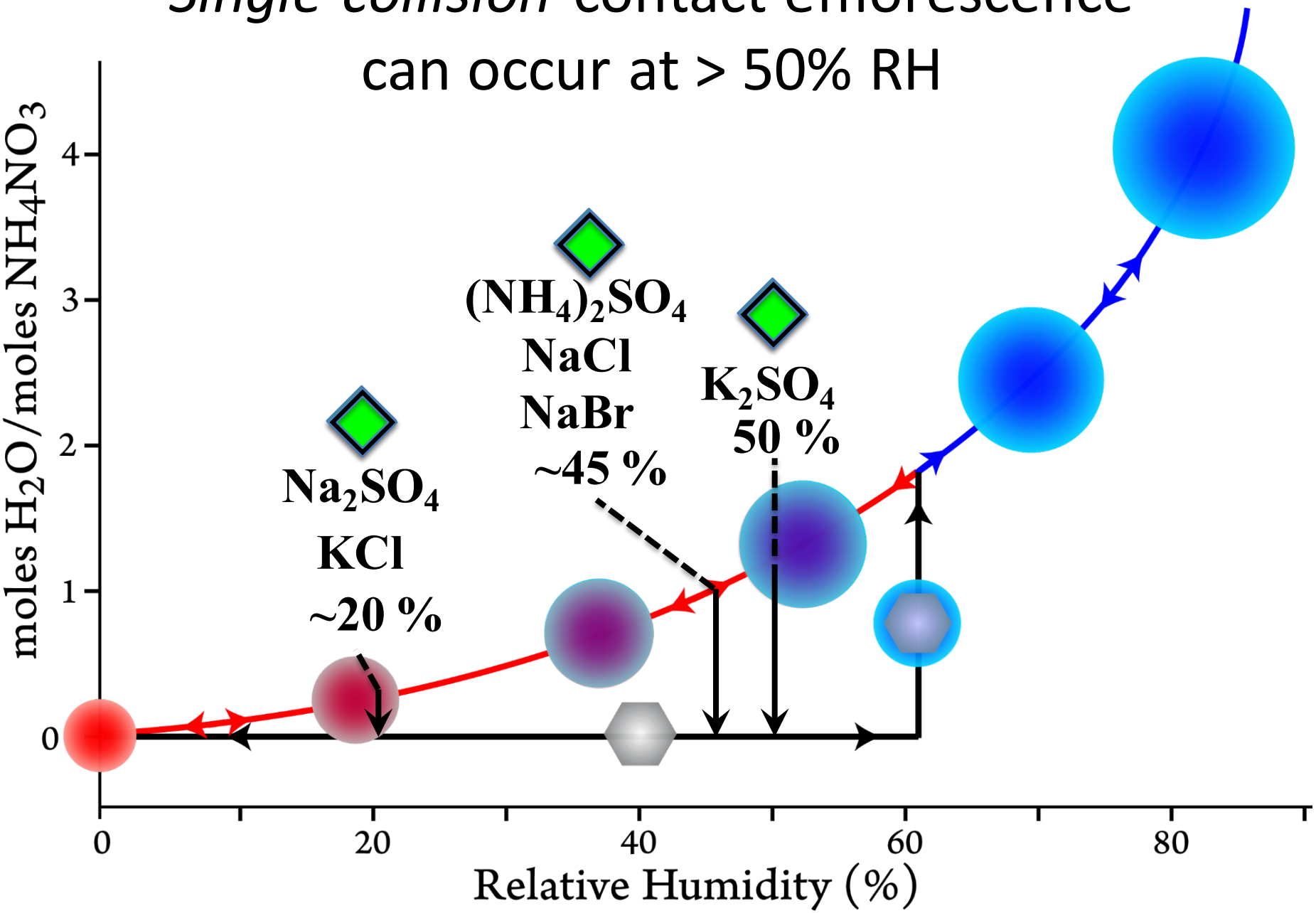


Single-collision contact efflorescence can occur at > 20% RH

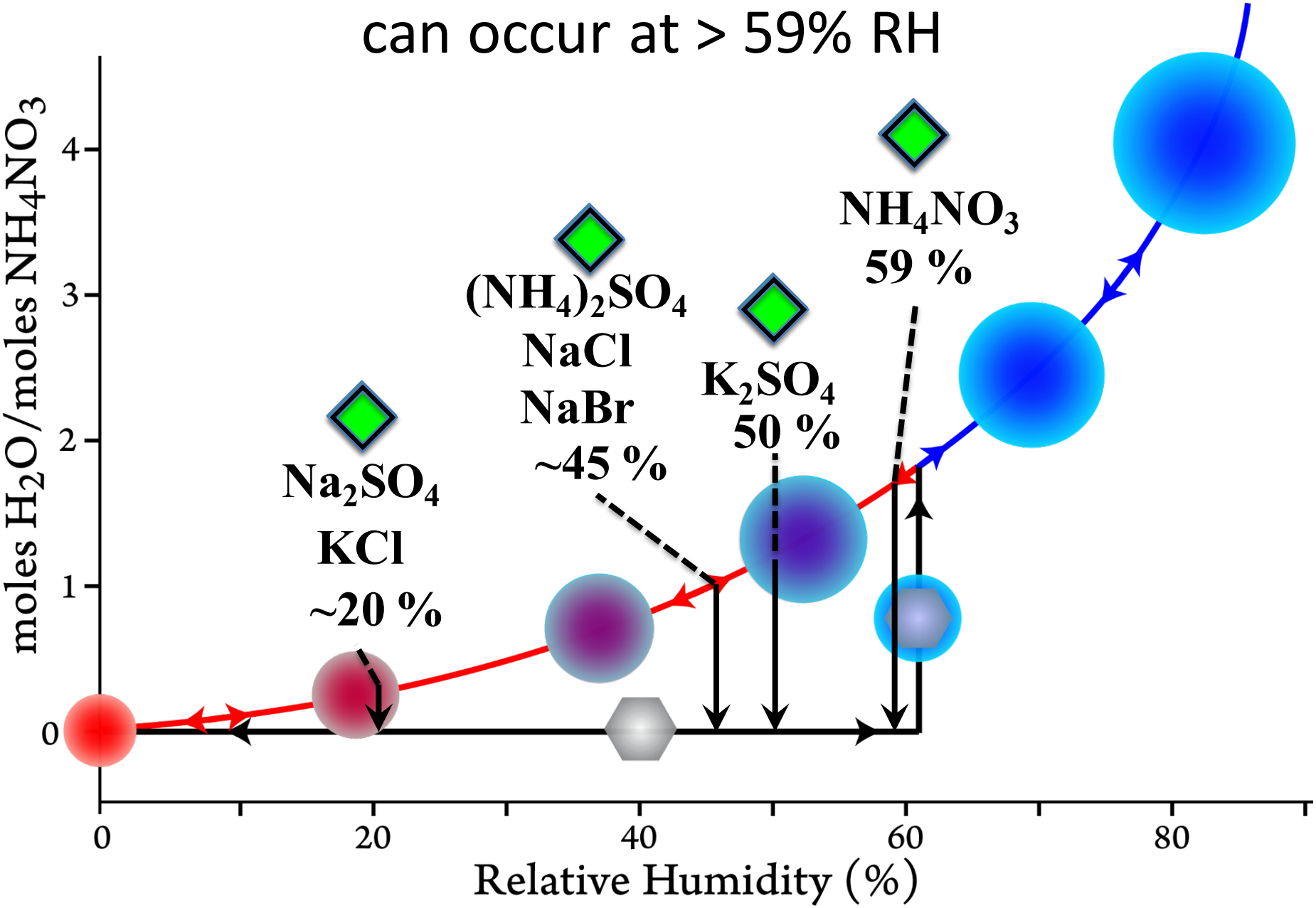



Single-collision contact efflorescence
can occur at > 45% RH
moles H_2O/moles NH_4NO_3
0
1
2
3
4
$(NH_4)_2SO_4$
NaCl
NaBr
~45 %
Na_2SO_4
KCl
~20 %
0
20
40
60
80
Relative Humidity (%)

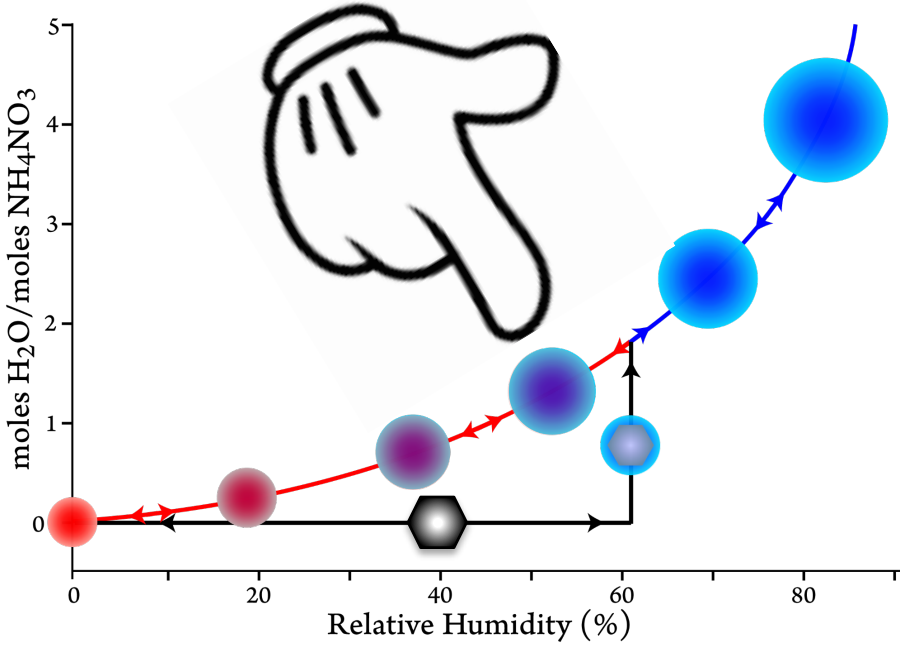
Single-collision contact efflorescence can occur at > 50% RH



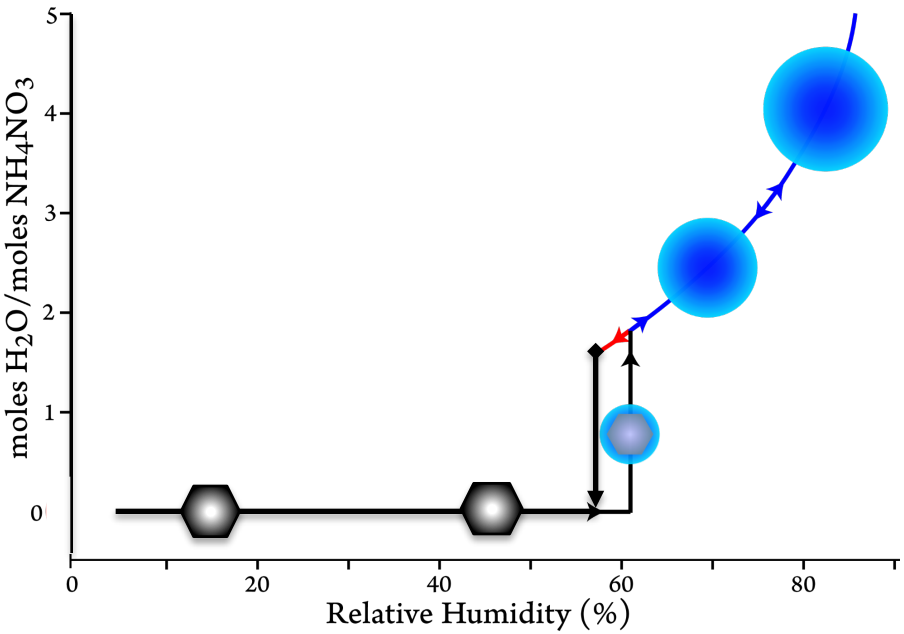
Single-collision contact efflorescence can occur at > 59% RH



Contact impacts phase

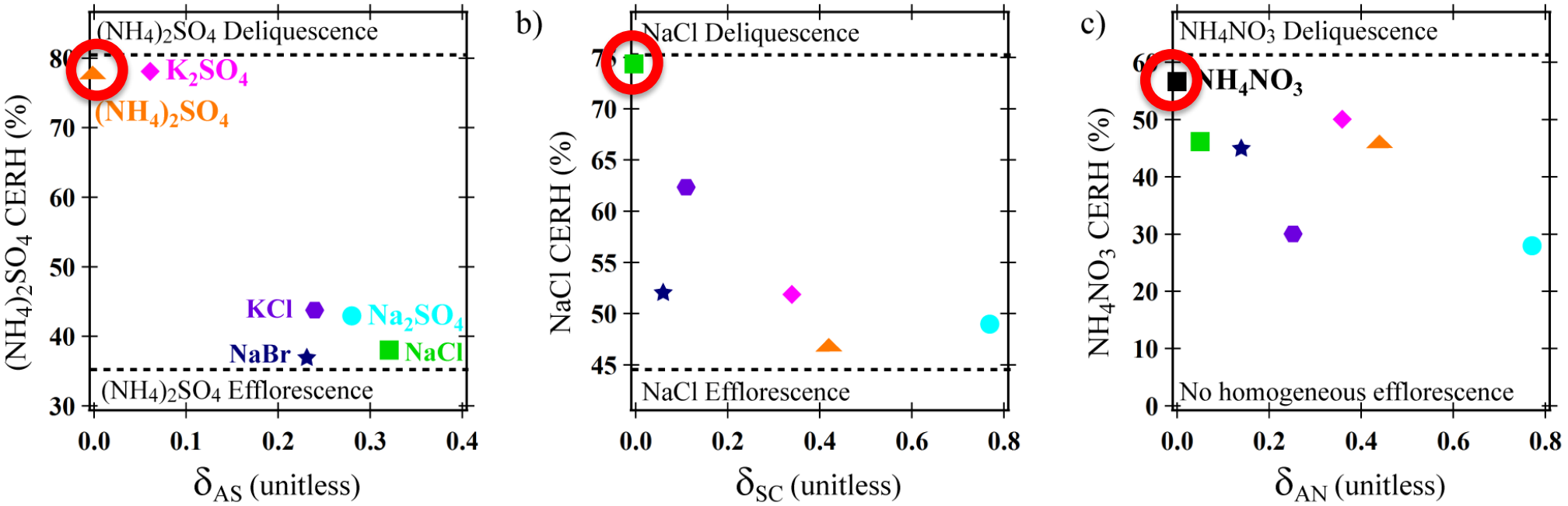


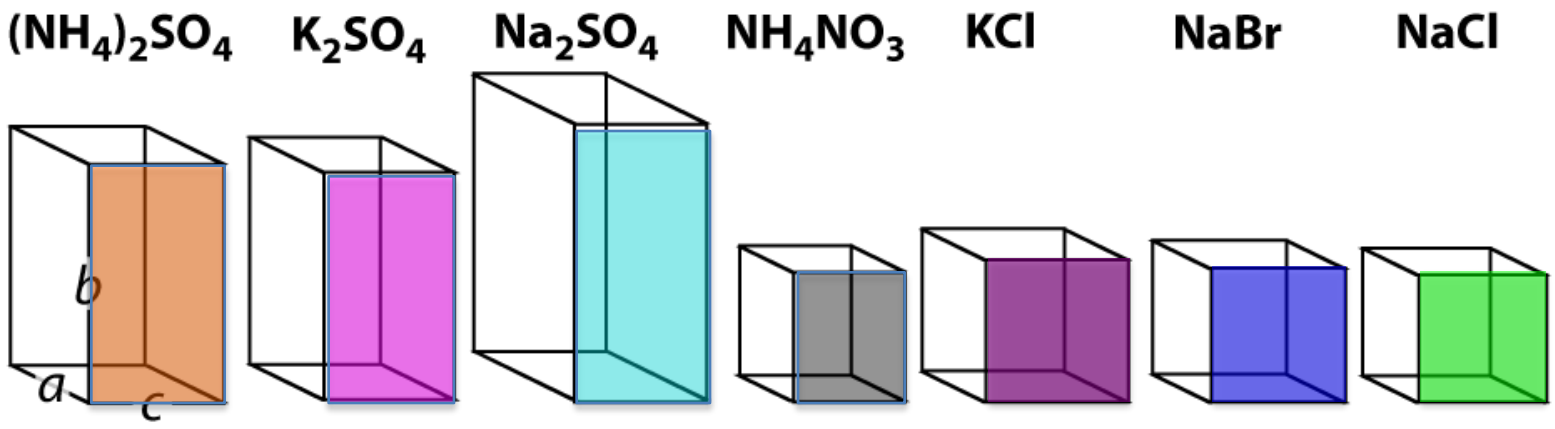
Always liquid NH_4NO_3



Mostly solid NH_4NO_3

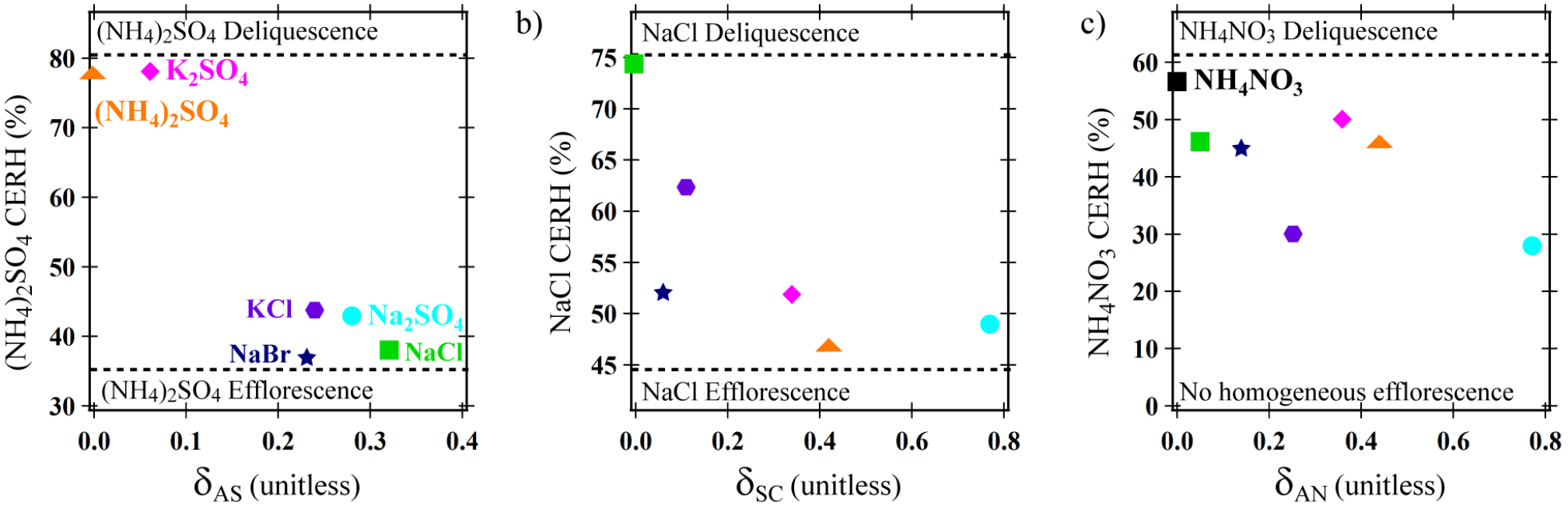
Contact Efflorescence RH vs lattice match

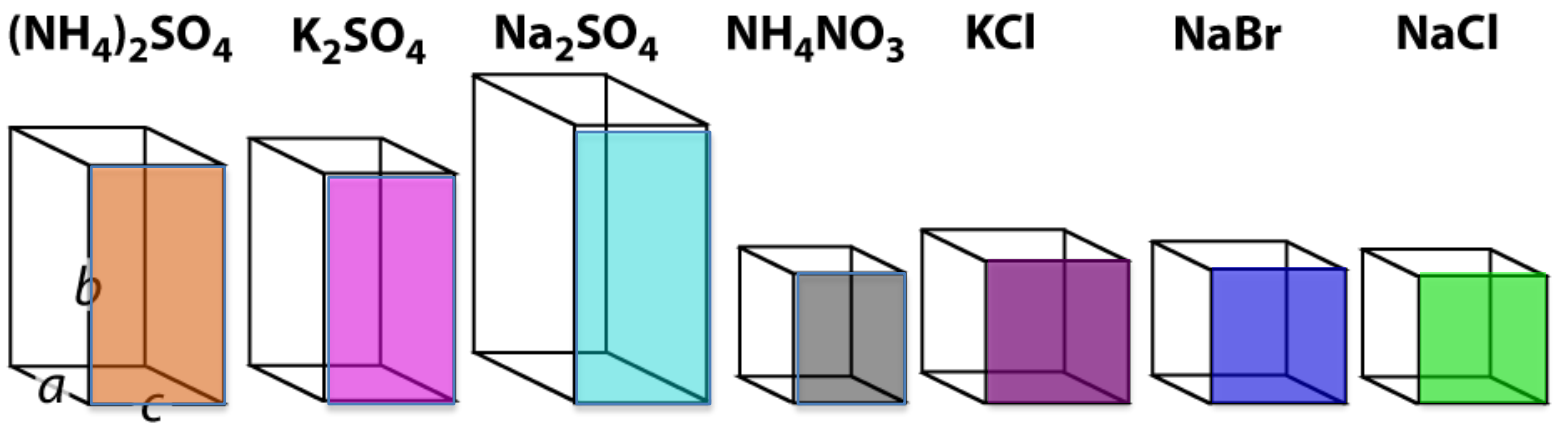




- *"Perfect" match: shuts down supersaturation*

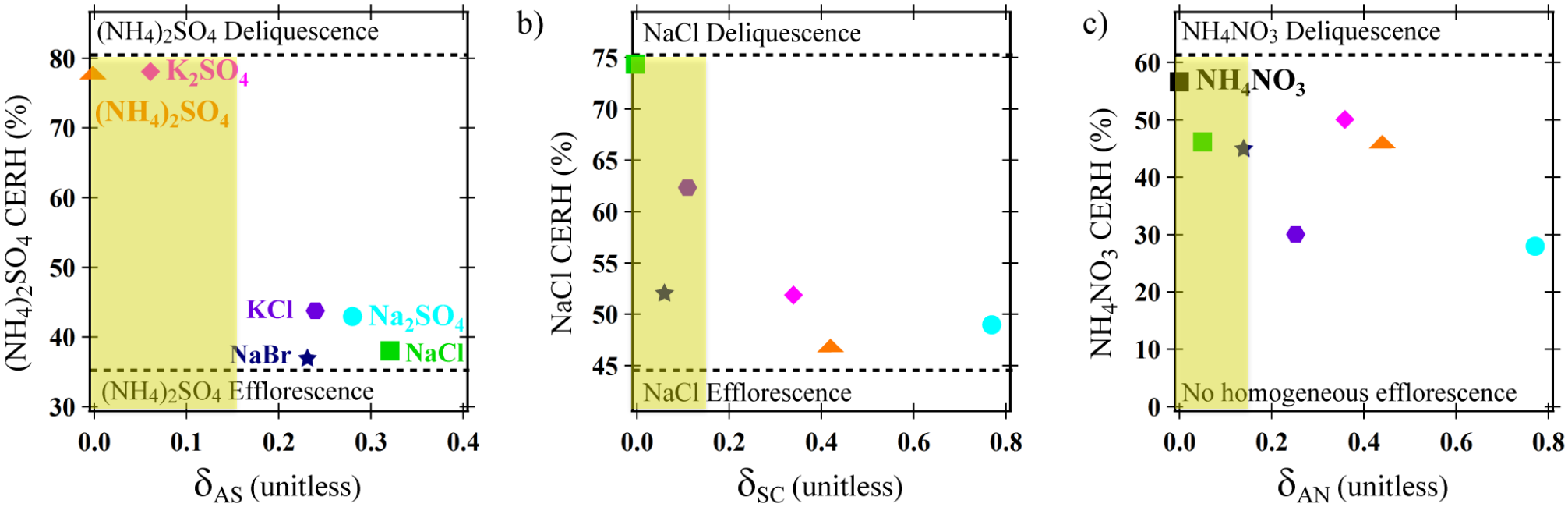
Contact Efflorescence RH vs lattice match

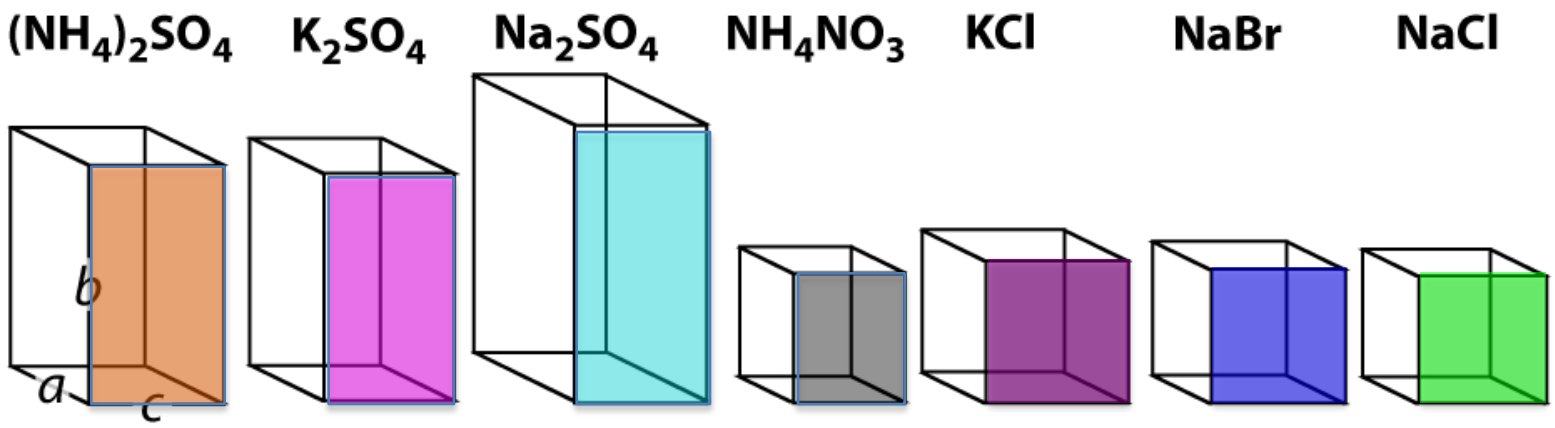




- *"Perfect" match: shuts down supersaturation*
- *Efflorescence RH generally decreases with poor lattice match*

Contact Efflorescence RH vs lattice match





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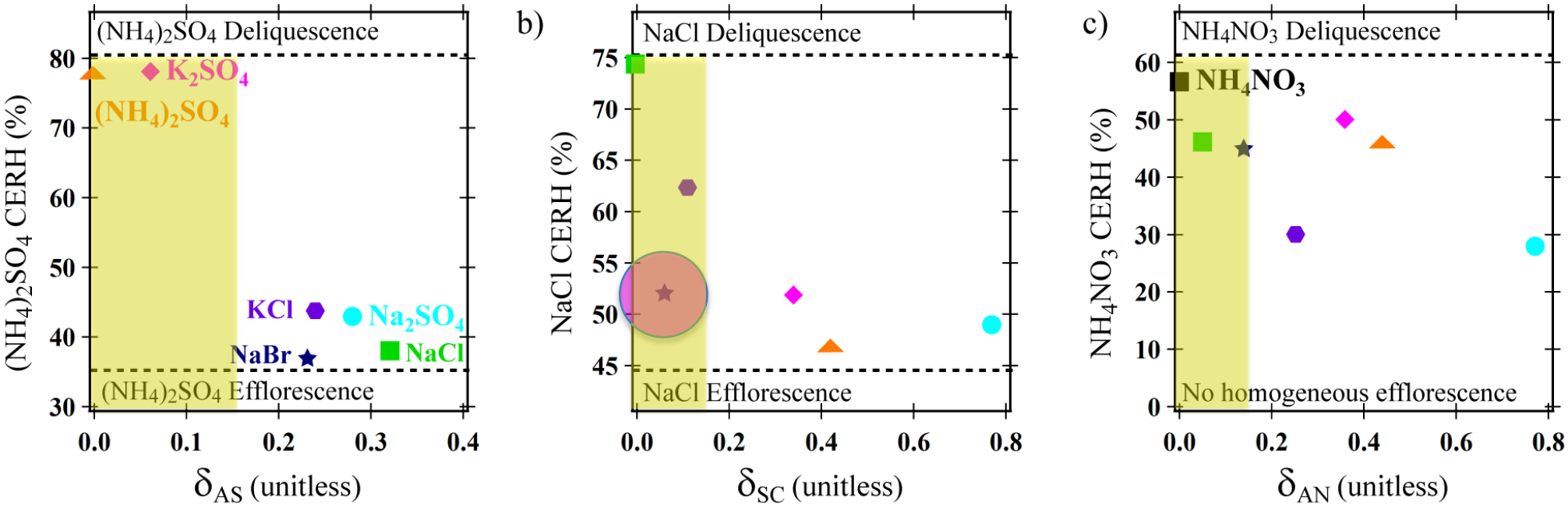
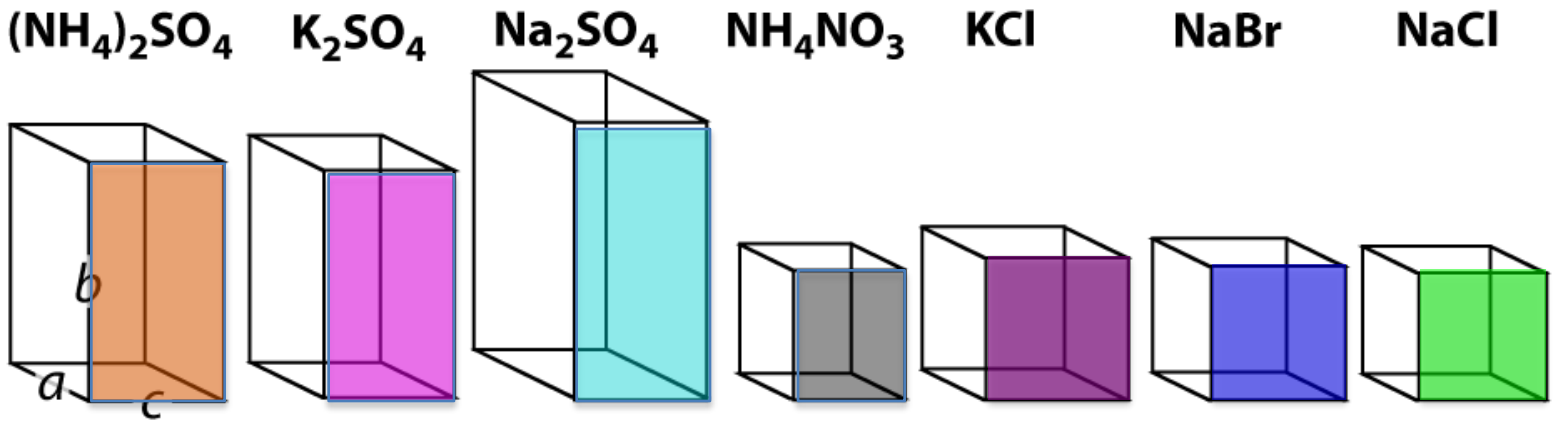
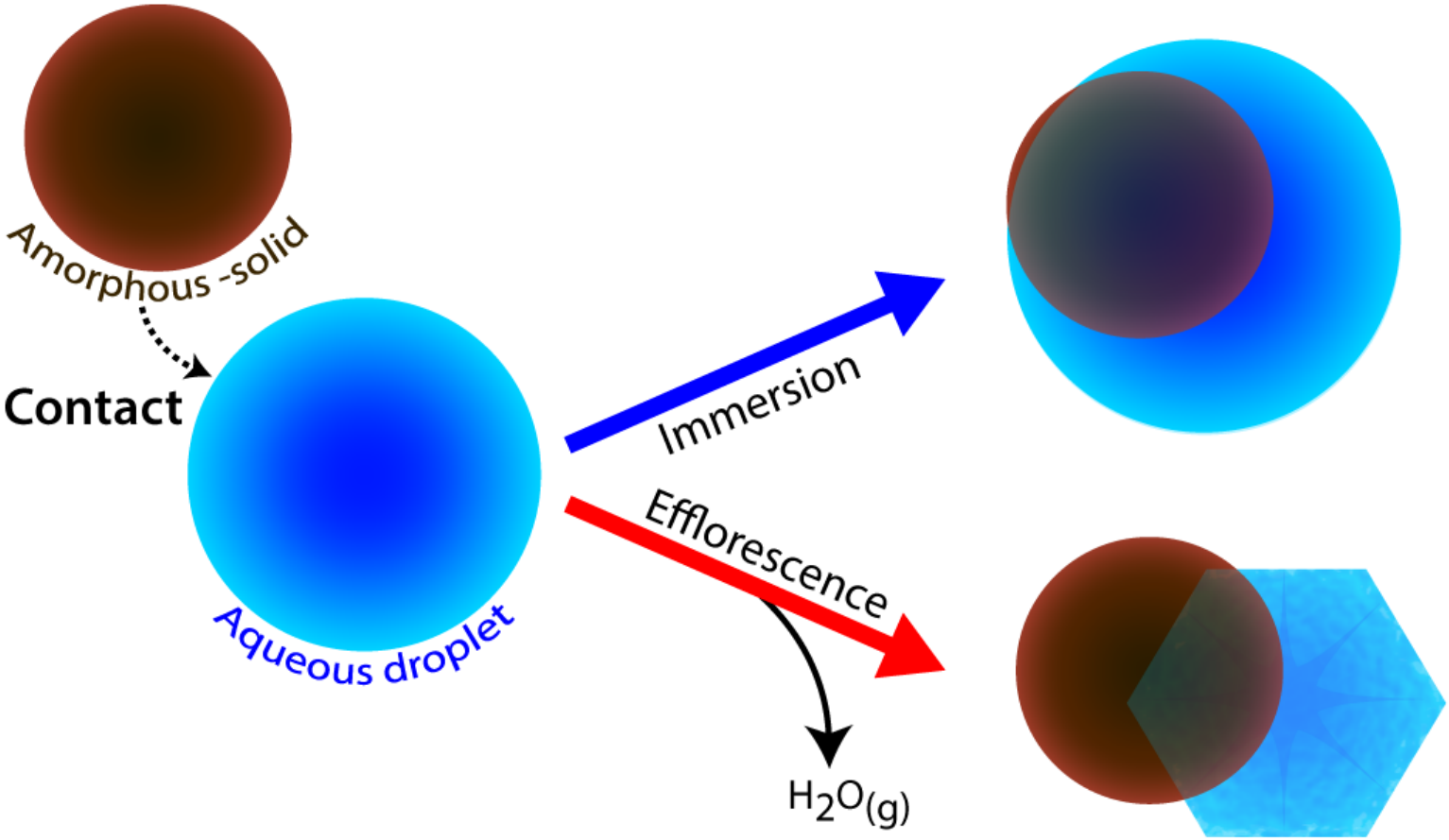
Contact Efflorescence RH vs lattice match





Aqueous NaBr can induce efflorescence!

Contact nucleation using functionalized amorphous organic particles



polystyrene latex spheres as CN: examine surface charge

PSLs are not expected to be effective heterogeneous nuclei

Amidine PSLs:

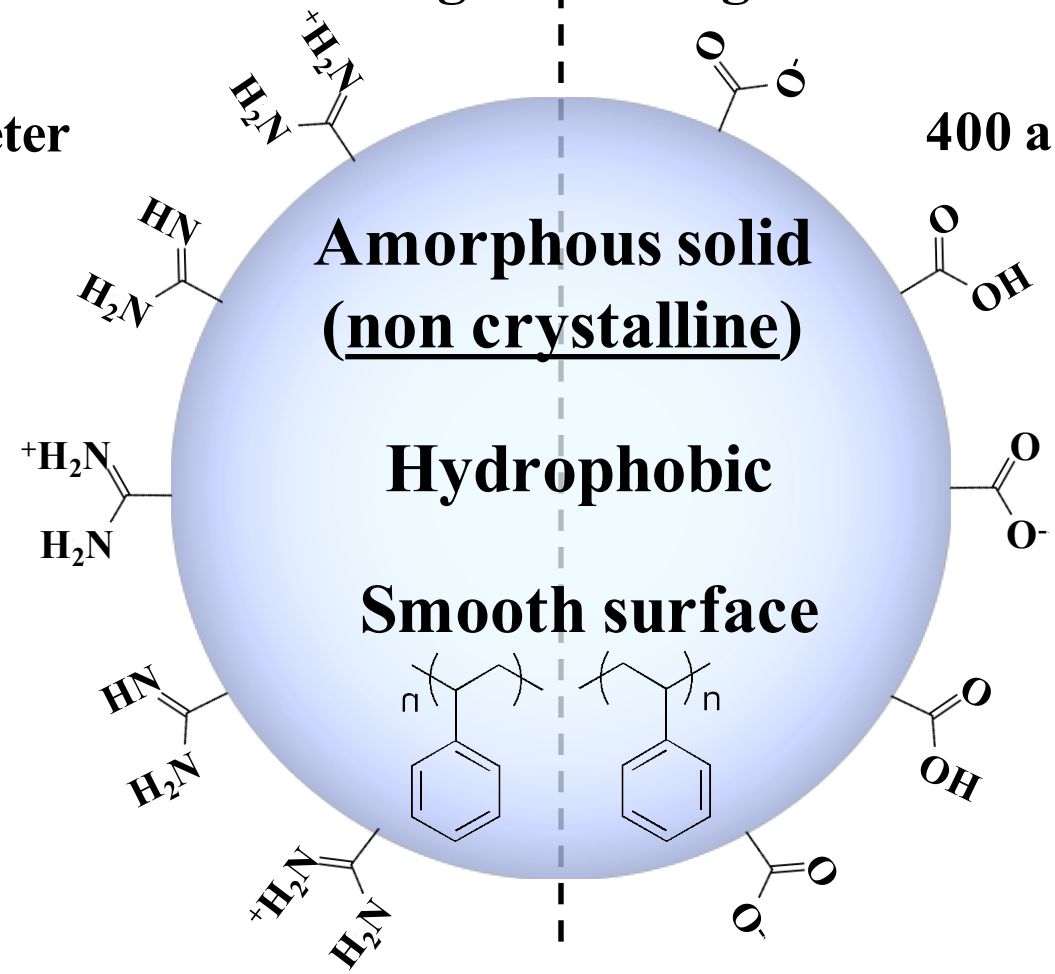
- **$NH_2NH/NH_2NH_2^+$ surface groups**
- **Positive net surface charge**

400 nm diameter

Carboxyl PSLs:

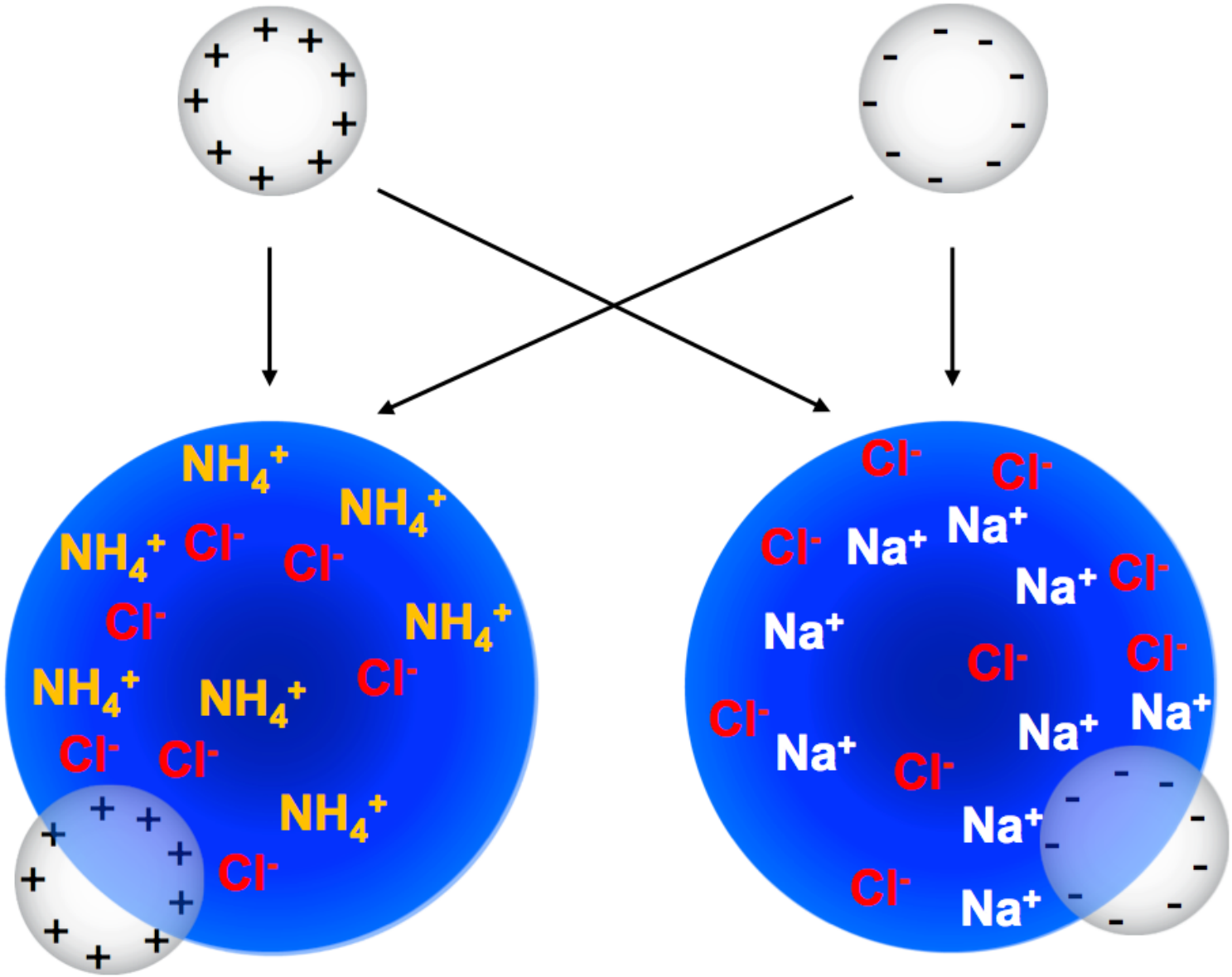
- **$COOH/COO^-$ surface groups**
- **Negative net surface charge**

400 and 800 nm diameter

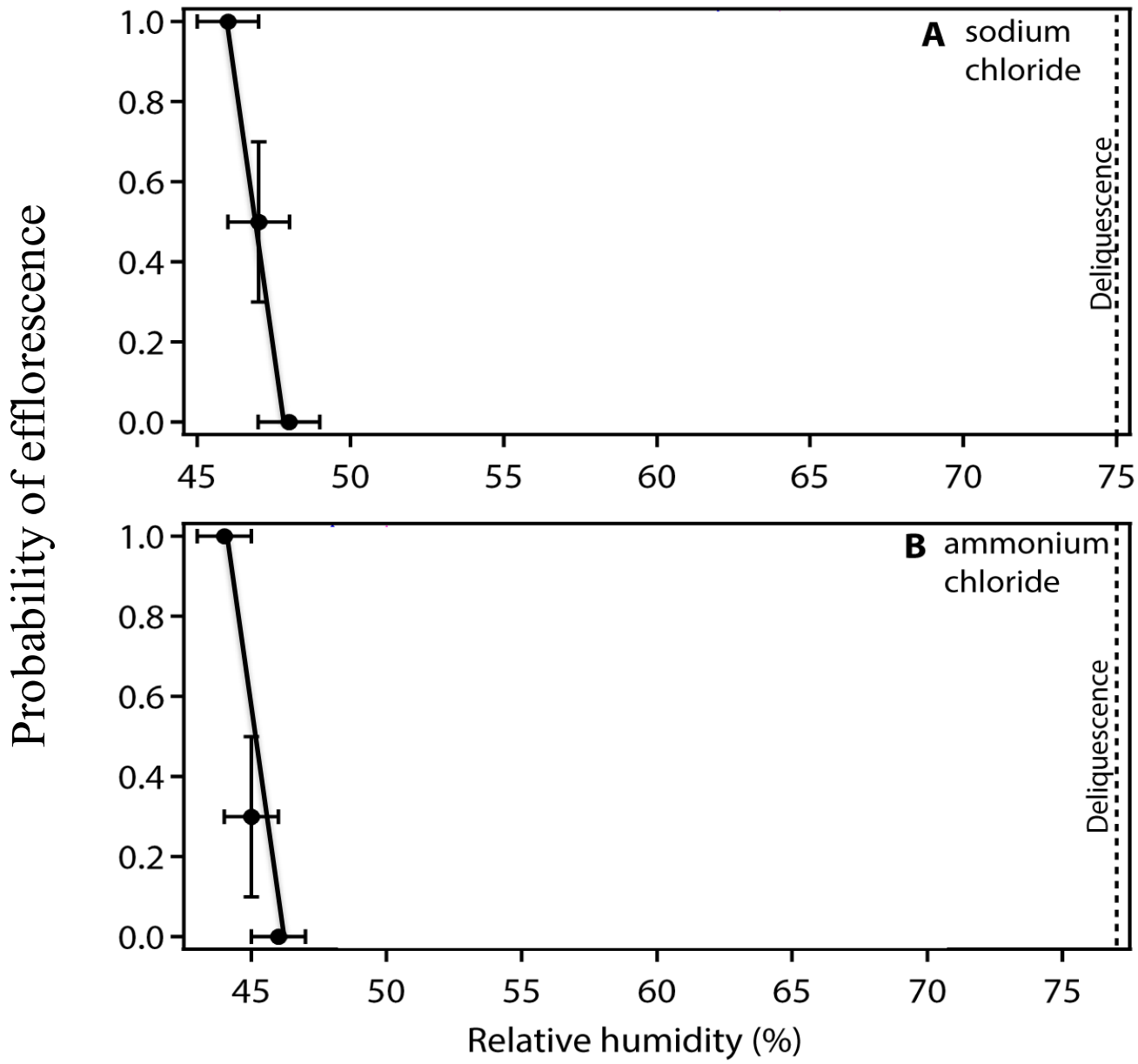


Polystyrene latex spheres (PSLs)

functionalized with carboxyl (-) or amidine (+)

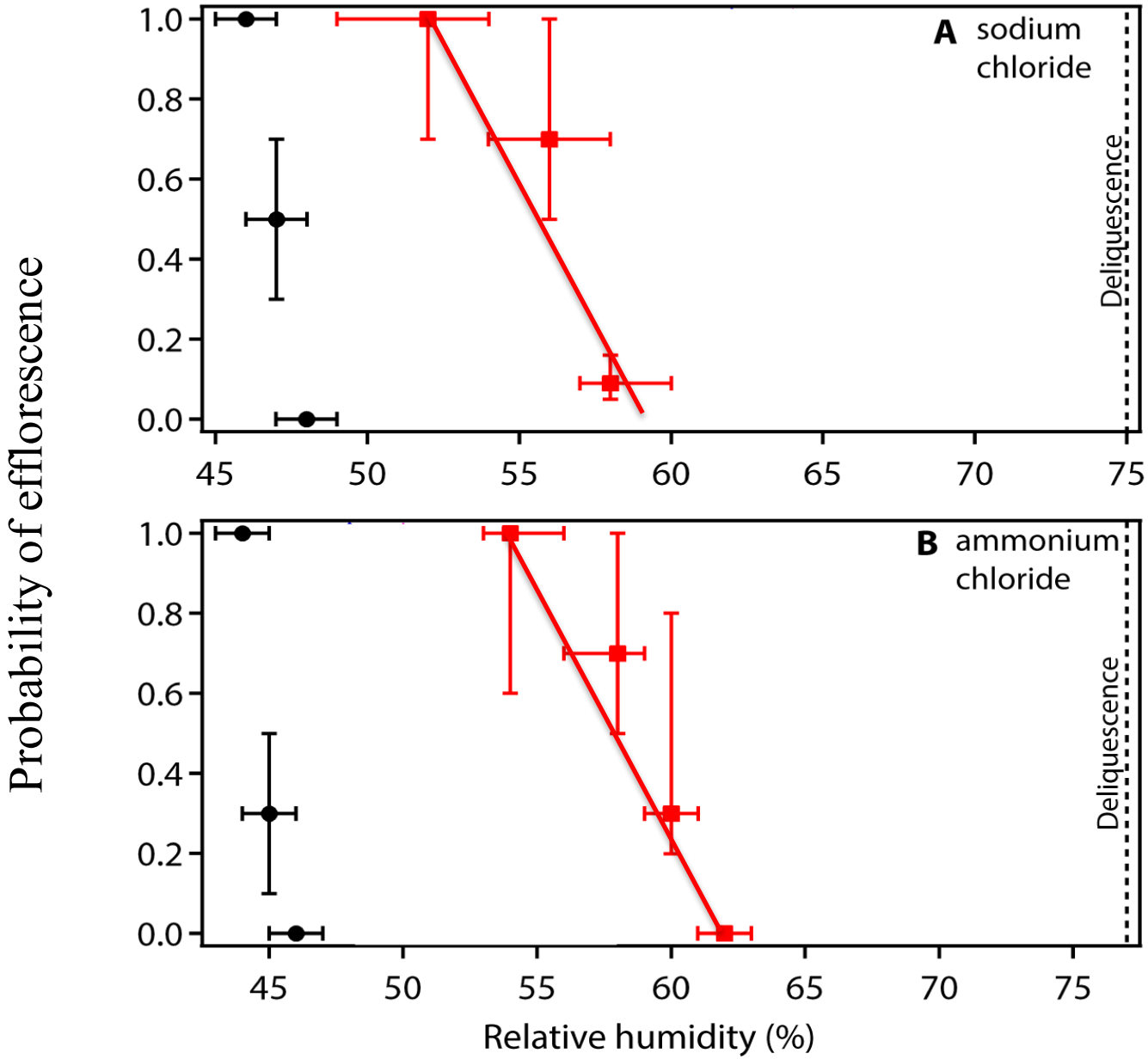


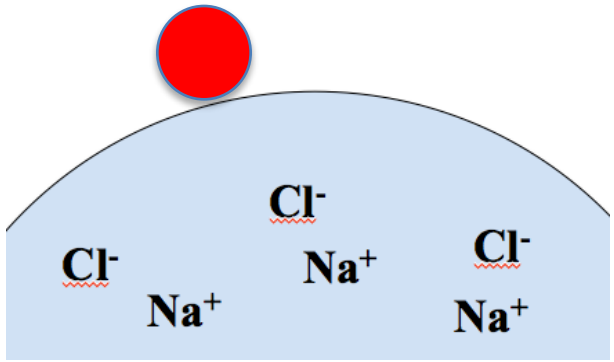
Homogeneous Efflorescence / PSL Immersion

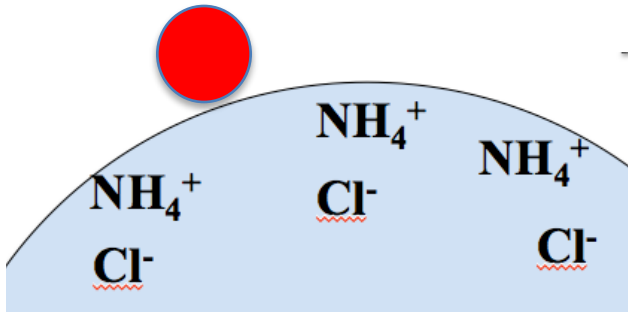


- ***similar DRH and ERH***
- ***immersion not effective***

Contact with 400 nm amidine (+) PSL

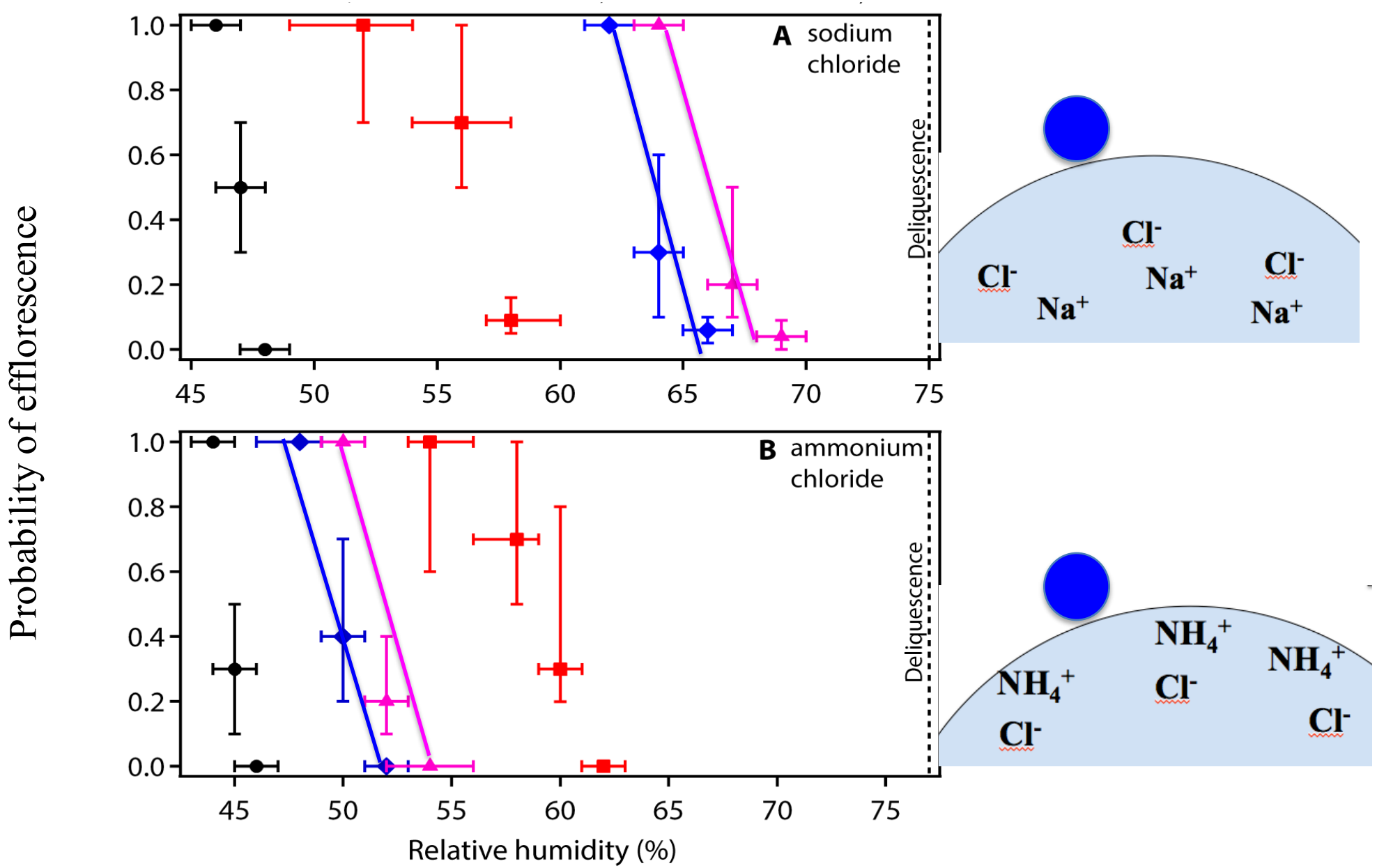






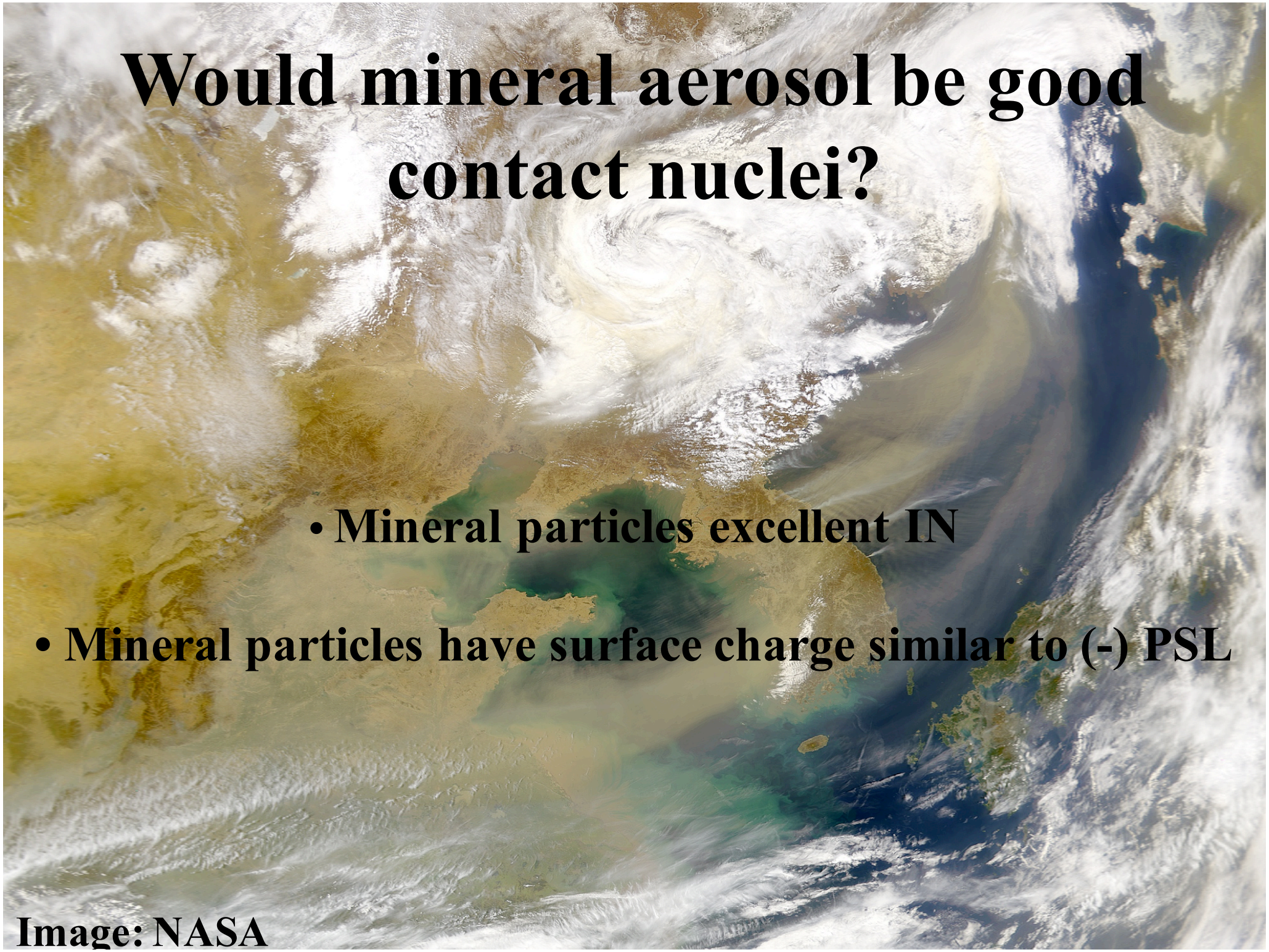
- ***contact with amorphous spheres raises ERH***
- ***similar contact induced ERH for both salts (with Cl^- counter ion)***

Contact with 400 and 800 nm carboxyl (-) PSL



- *(-) PSLs induce efflorescence at higher RH for NaCl*
- *Related to Na^+ low surface propensity? Ion-specific effects?*

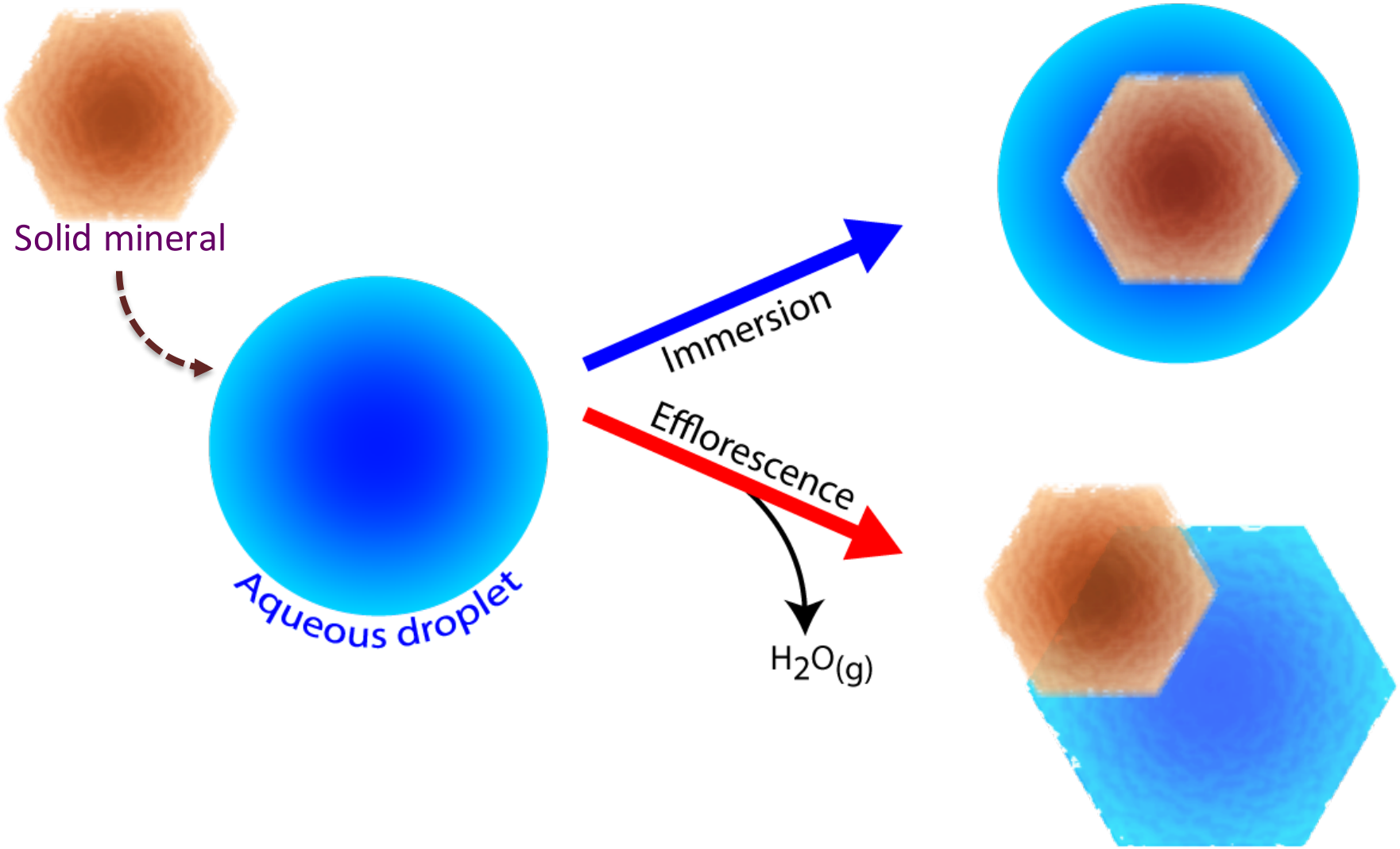
Would mineral aerosol be good contact nuclei?



- Mineral particles excellent IN
- Mineral particles have surface charge similar to (-) PSL

Image: NASA

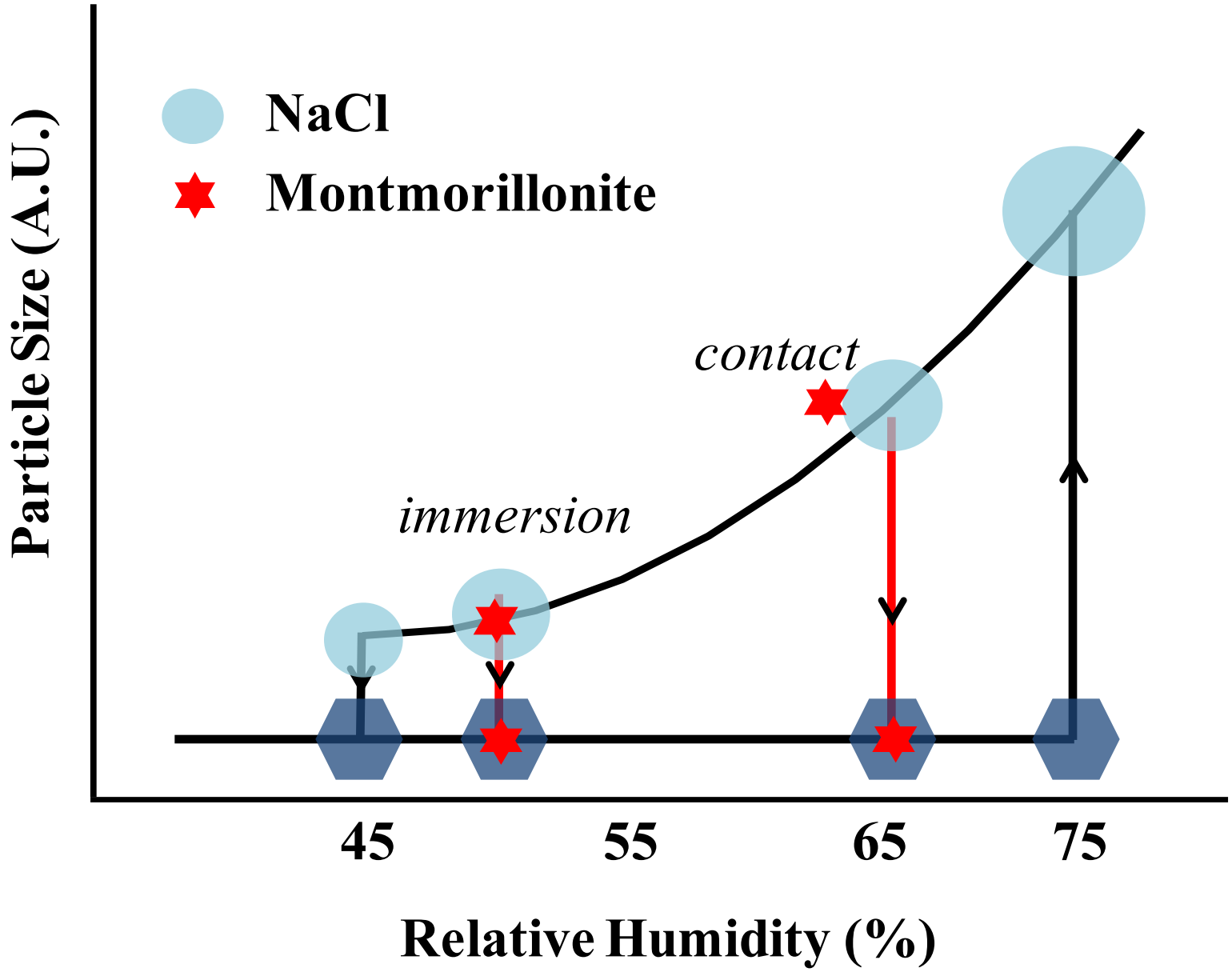
Contact Nucleation with Mineral Dust



- ***Compare contact with immersion***

Contact more effective than immersion

Very similar to (-) PSLs



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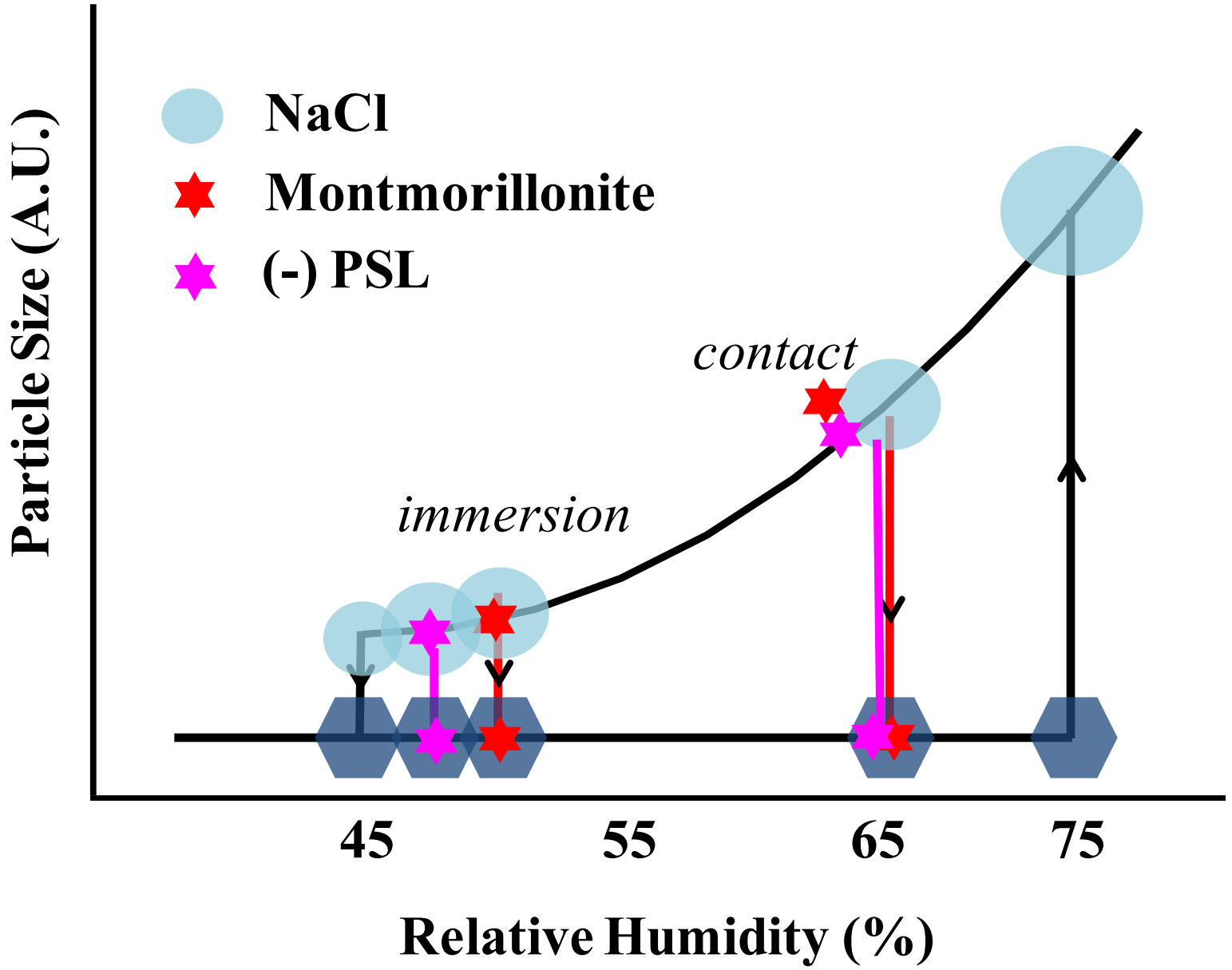
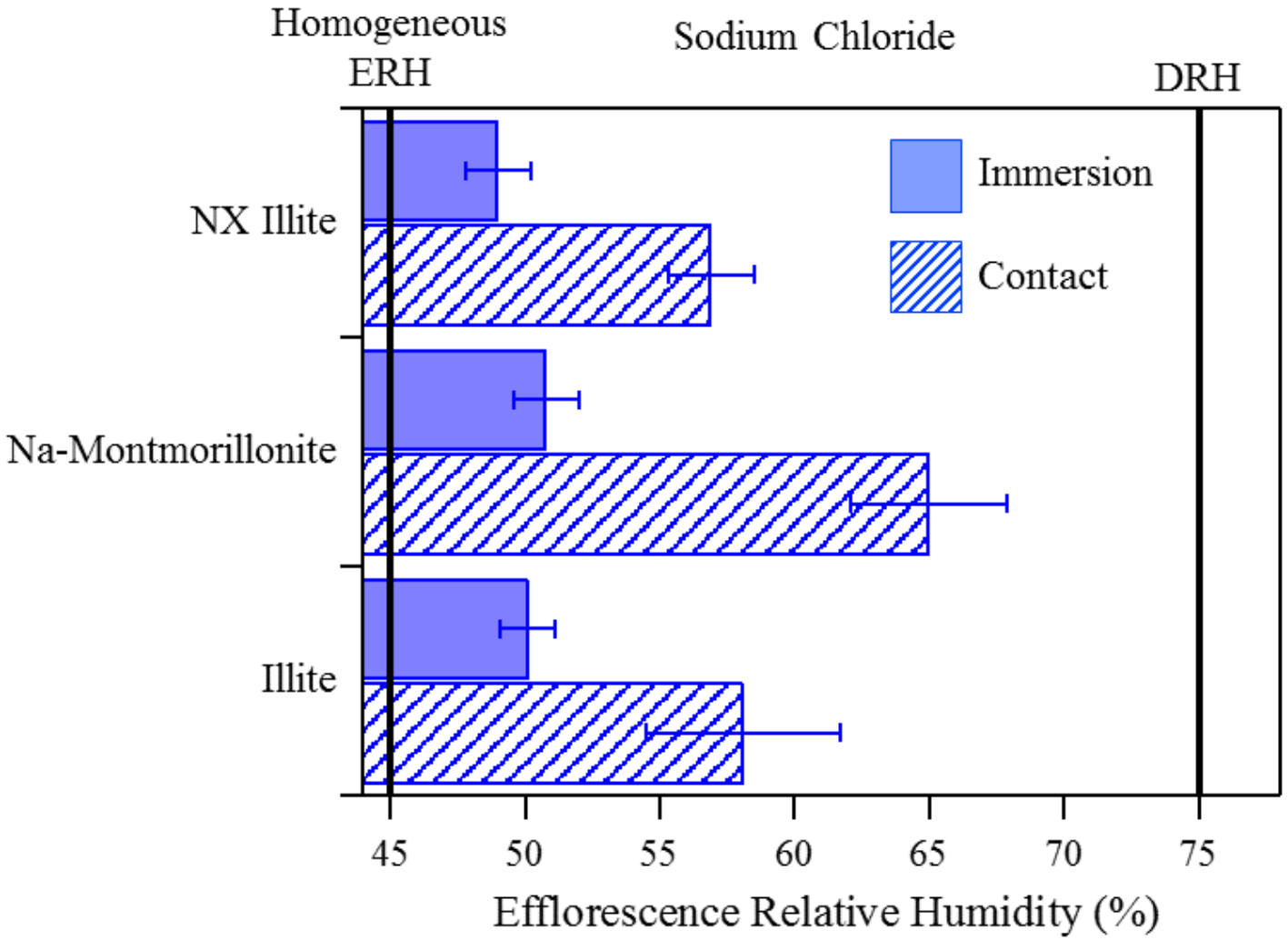
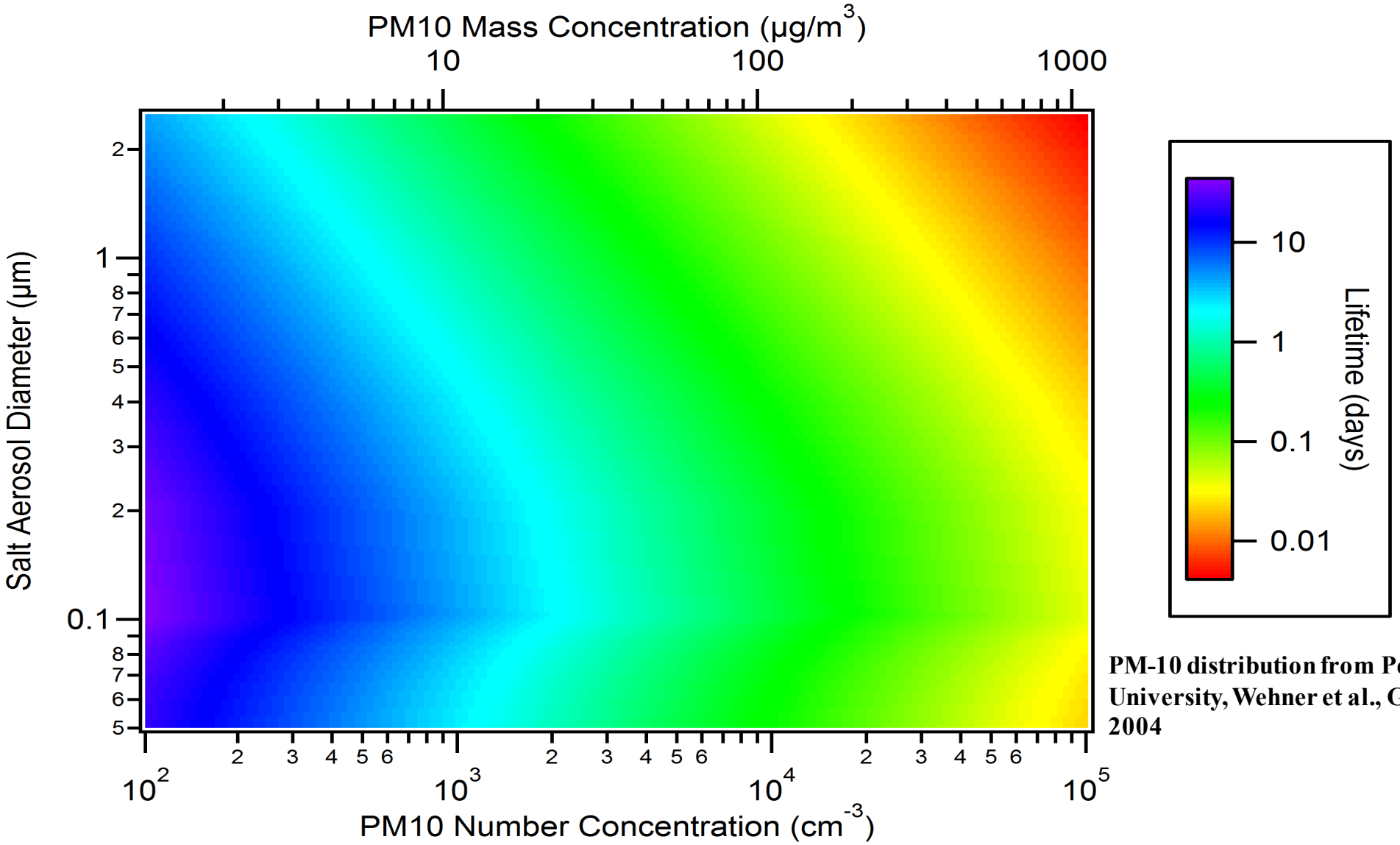


Heterogeneous ERH of NaCl by Single Particles



- ***Contact and immersion ERH higher than homogeneous ERH***
- ***Single collision contact ERH higher than immersion ERH***
- ***Similar behavior for illite, montmorillonite, (-) PSL***

NaCl lifetimes wrt collision in atmosphere



PM-10 distribution from Peking University, Wehner et al., GRL, 2004

- NaCl collides in ~ 1 day
- Effloresced NaCl will stay dry until high RH

Conclusion

Particles collide in the atmosphere

Lattice match one factor in contact efflorescence

Contact more effective than immersion

Ion specific effects for contact efflorescence

Atmospheric contact: more solid particles

Acknowledgments

- Tolbert group
- Sara Lance
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