Ash, sulfate and ice: examining interactions one particle at a time

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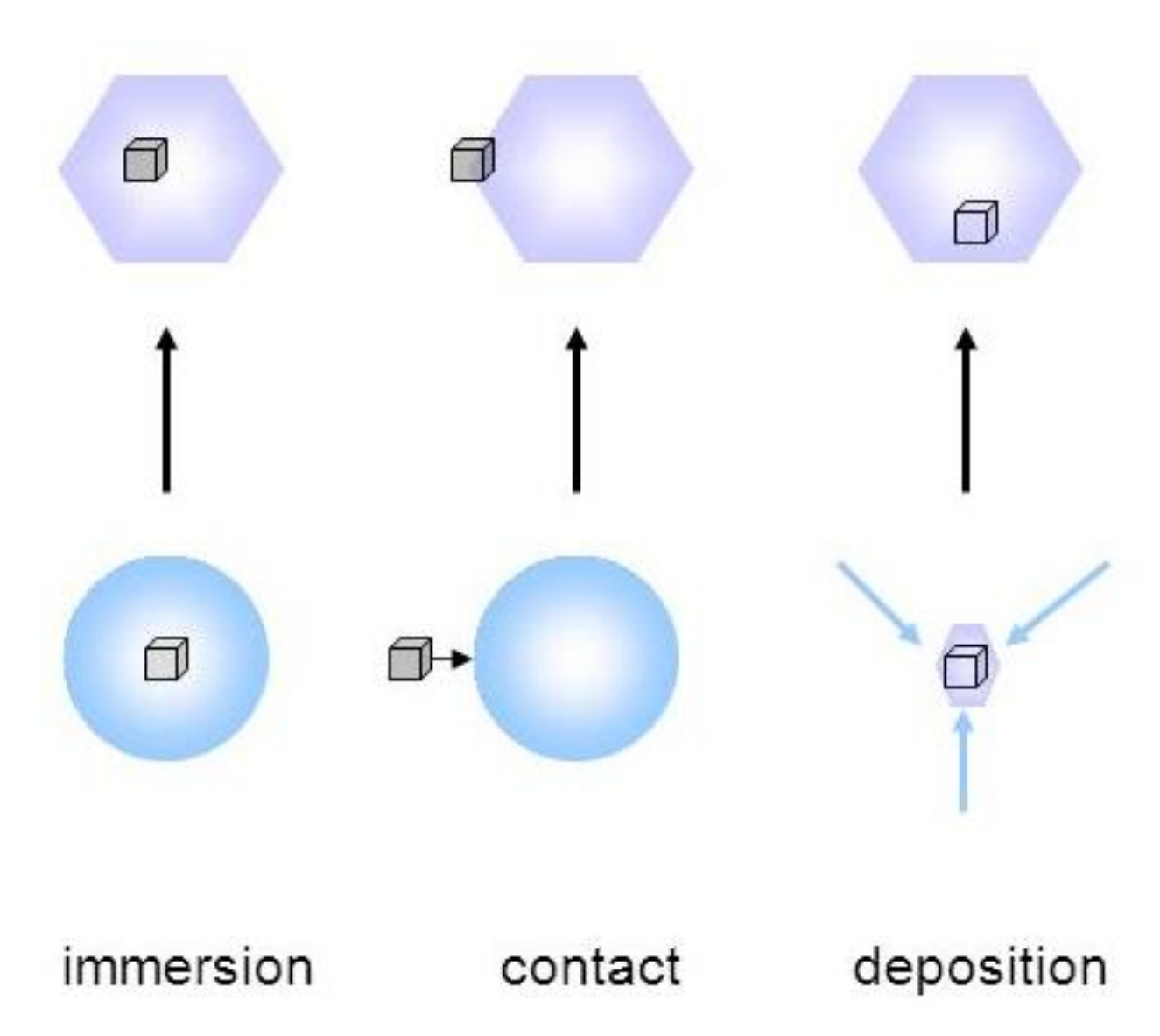
Chapman Conference, 2018

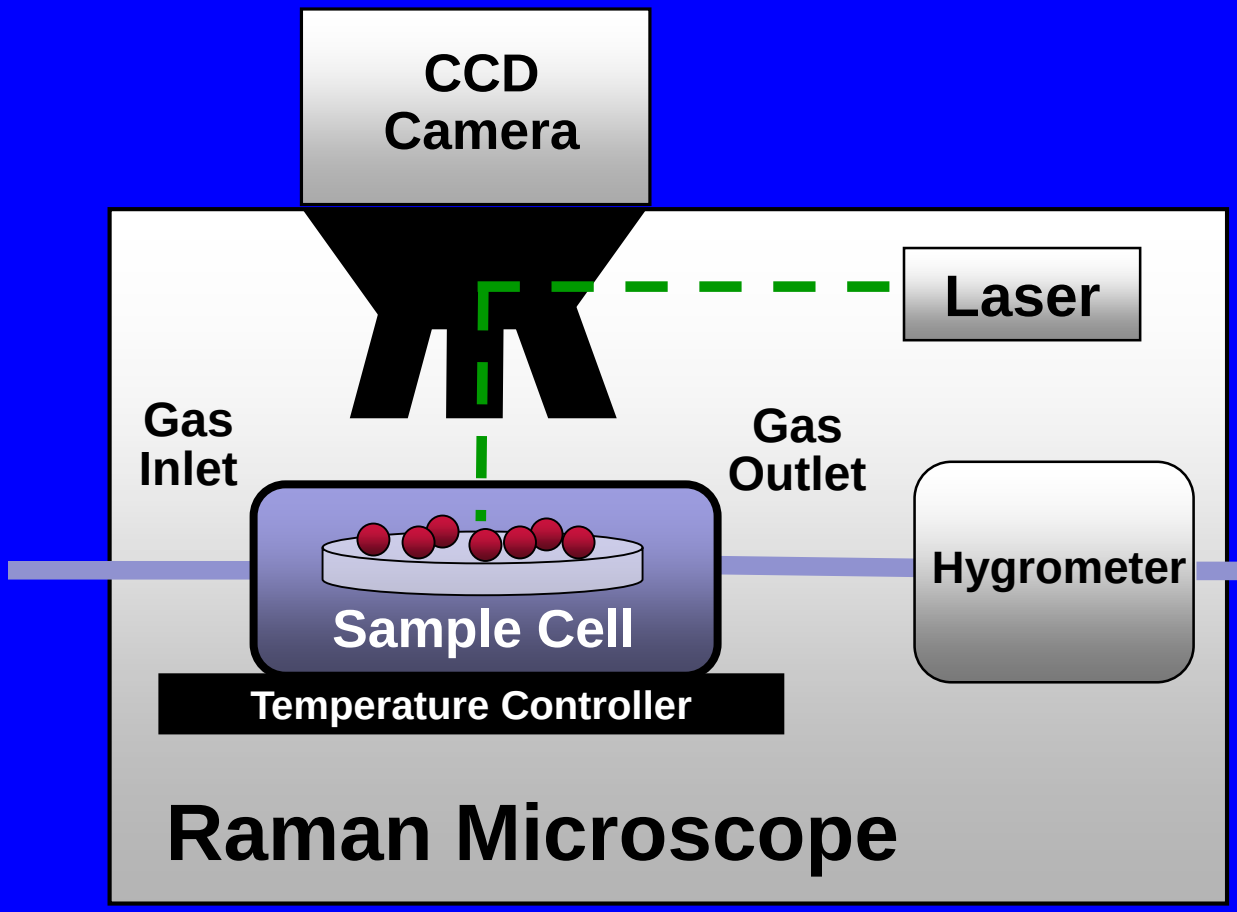
Martin Rietze, Sakurajima plume

Ice Nucleation on Ash



From Thomas Leisner

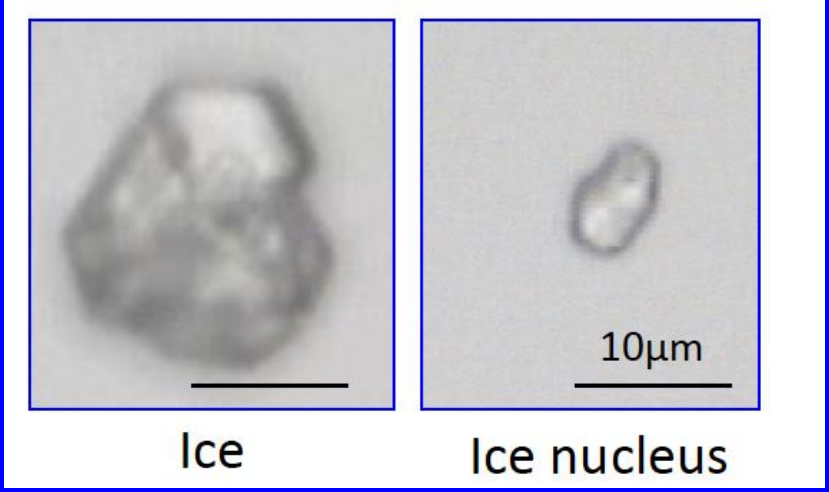
Raman Microscopy: One Particle at a Time

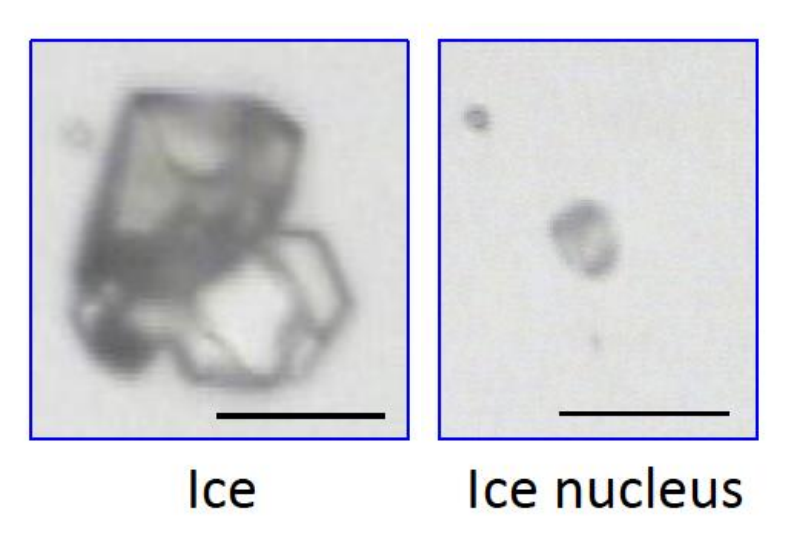


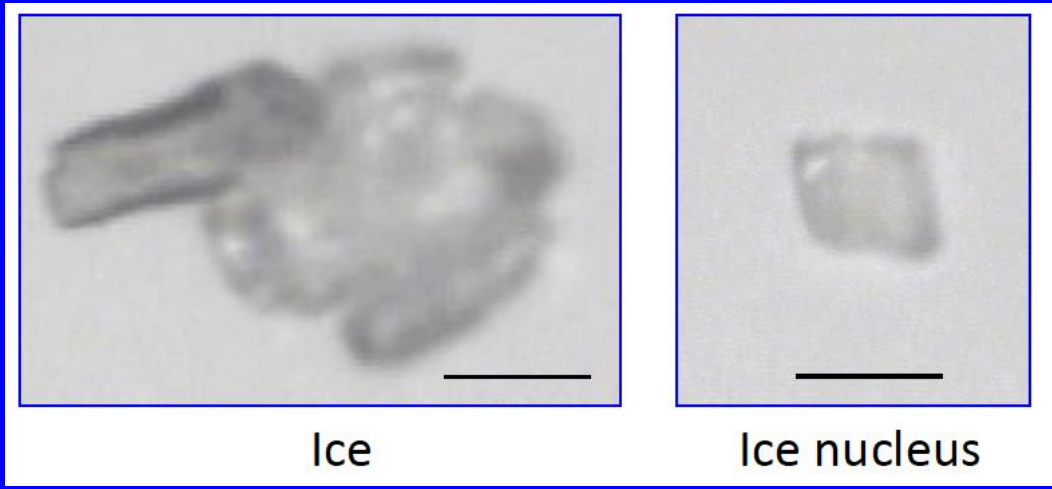
$$S_{ice} = P_{H2O}/VP_{ice}$$

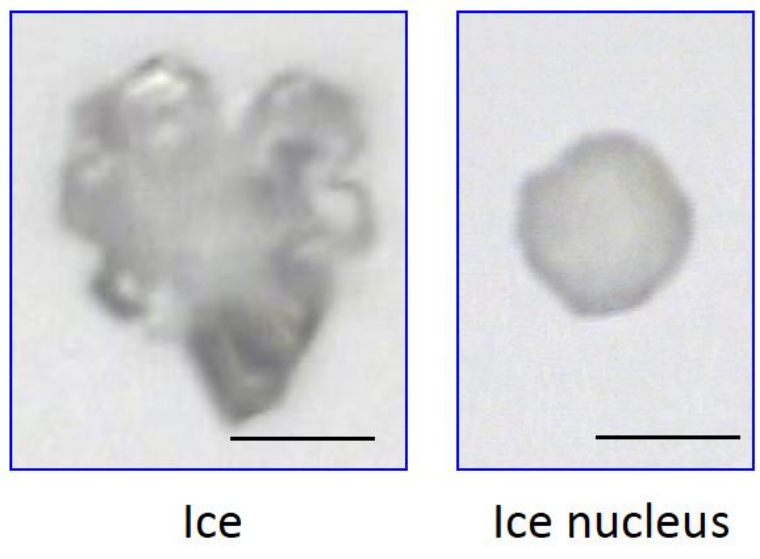
Selective Depositional Ice Nucleation

Examples of Ice and Ash Nucleus

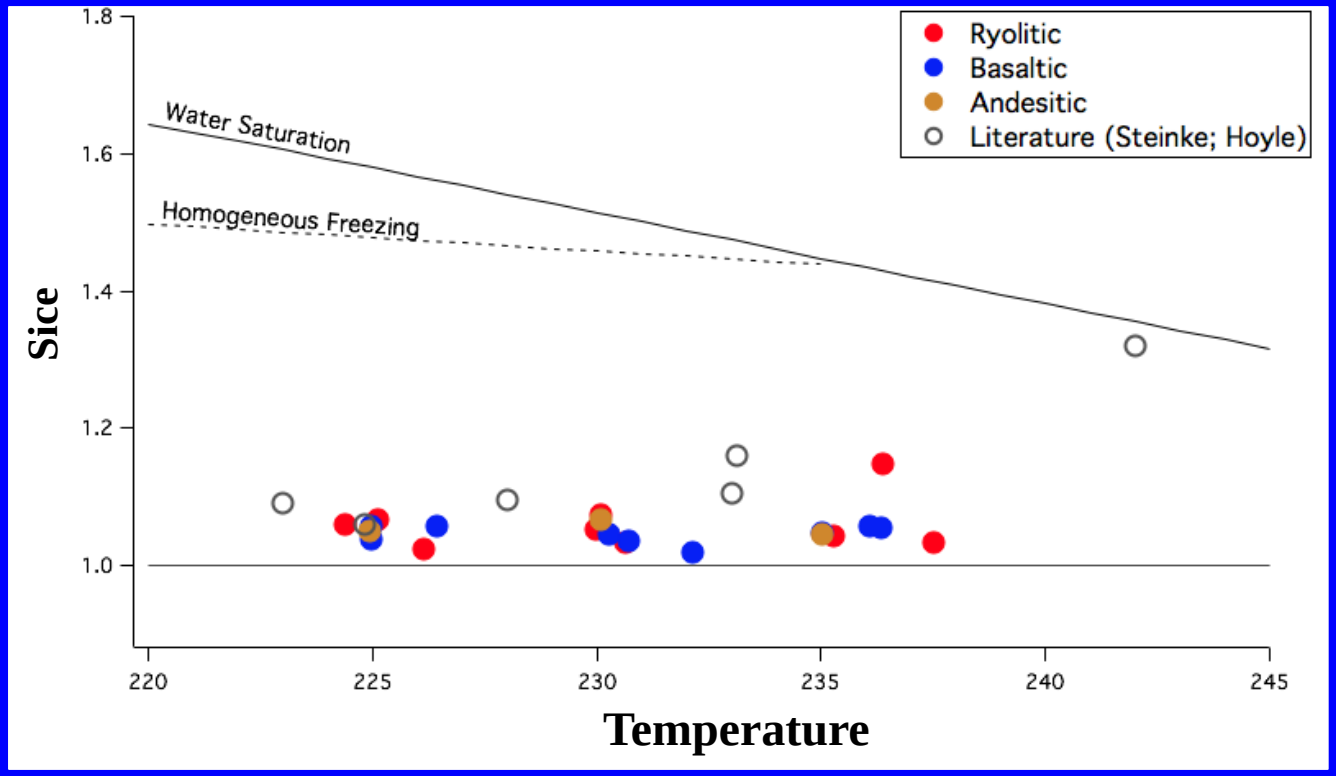








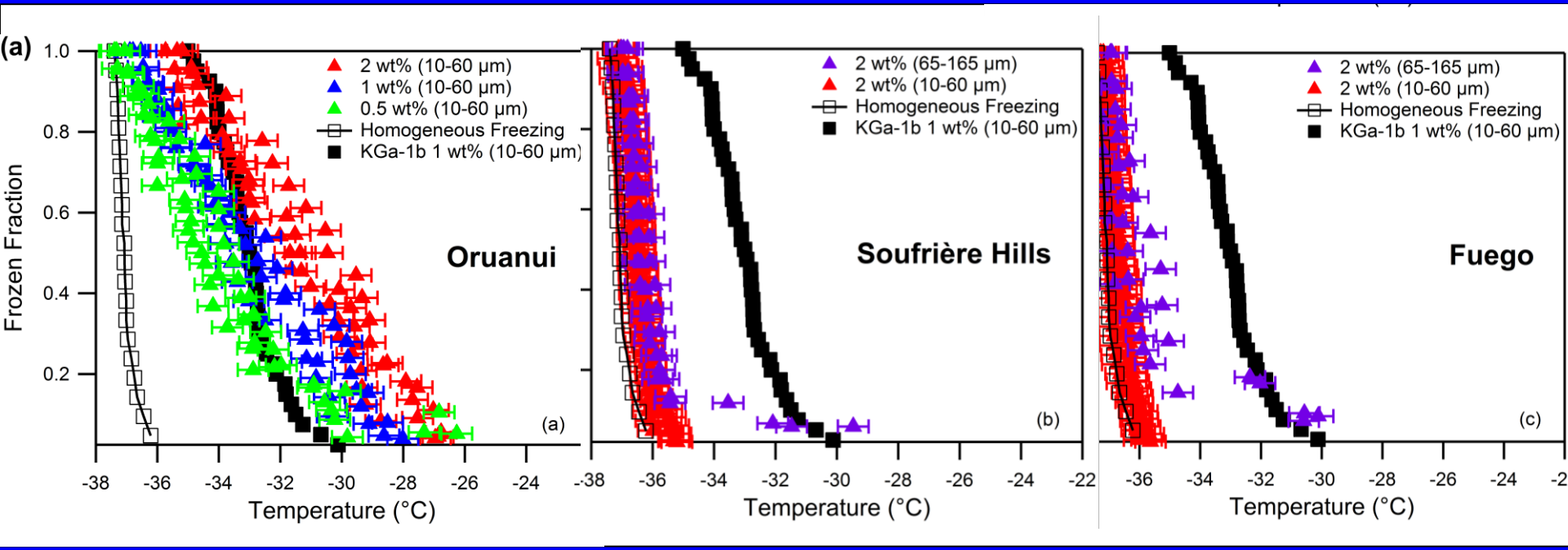
Depositional Nucleation of Ice on Ash



- All ash are effective depositional IN
- No observable difference between rhyolitic, andesitic, basaltic ash
- Similar to mineral dust

Immersion Ice Nucleation
Frozen Fraction vs Temperature for Ash

Rhyolitic **Andesitic** **Basaltic**



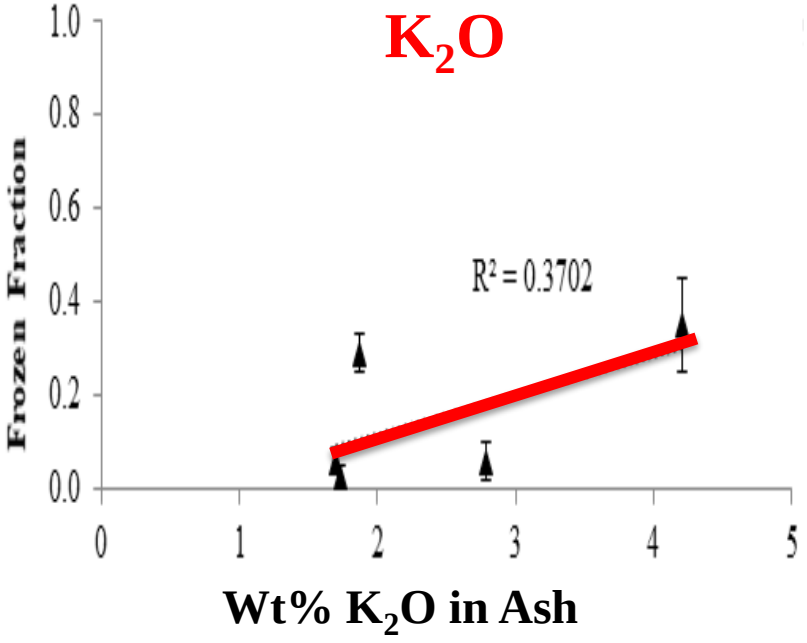
- **Rhyolitic ash showed similar/better IN ability than kaolinite dust**
- **Andesitic and Basaltic similar to homogeneous IN**

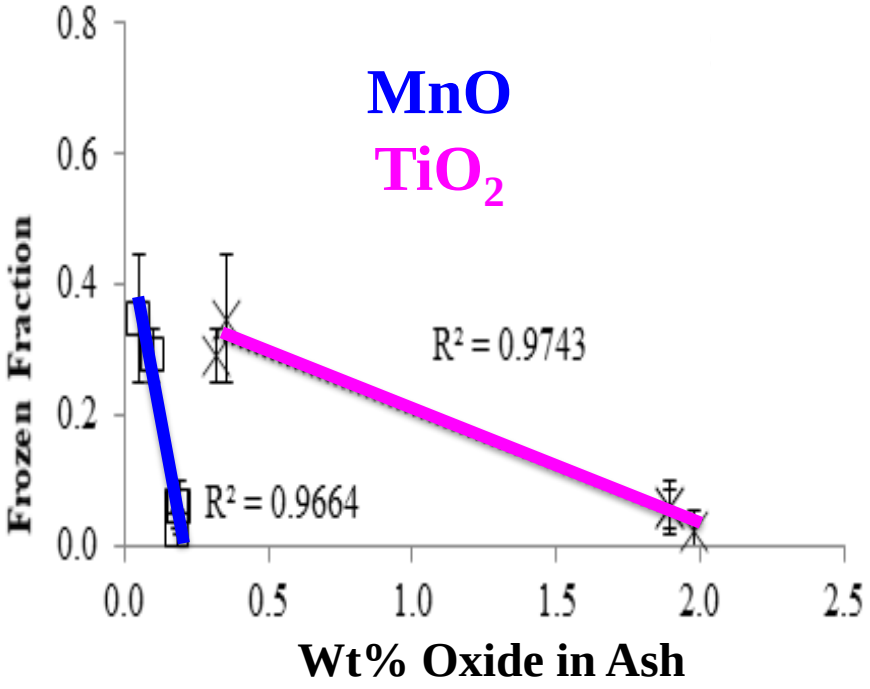
Schill, Genareau and Tolbert, ACP, 2015

X-Ray Fluorescence Analyses of 5 of 8 Ash Samples

Major Elements	OB2	Taupo	NIW	ONW	PINW
	Rhyolite			Basalt	
SiO_2	73.05	73.48	48.43	49.12	49.29
TiO_2	0.36	0.32	1.89	1.90	1.98
Al_2O_3	13.74	13.81	16.22	17.14	17.09
Fe_2O_3	2.23	2.58	11.92	11.36	11.51
MnO	0.05	0.10	0.19	0.18	0.18
MgO	0.70	0.37	7.04	5.73	5.68
CaO	1.64	1.77	8.07	8.46	7.96
Na_2O	3.94	4.72	3.38	3.22	3.40
K_2O	4.21	2.78	1.70	1.73	1.87
P_2O_5	0.08	0.06	1.16	1.16	1.05
Total	100	100	100	100	100

Frozen Fraction at -30°C in Immersion Mode





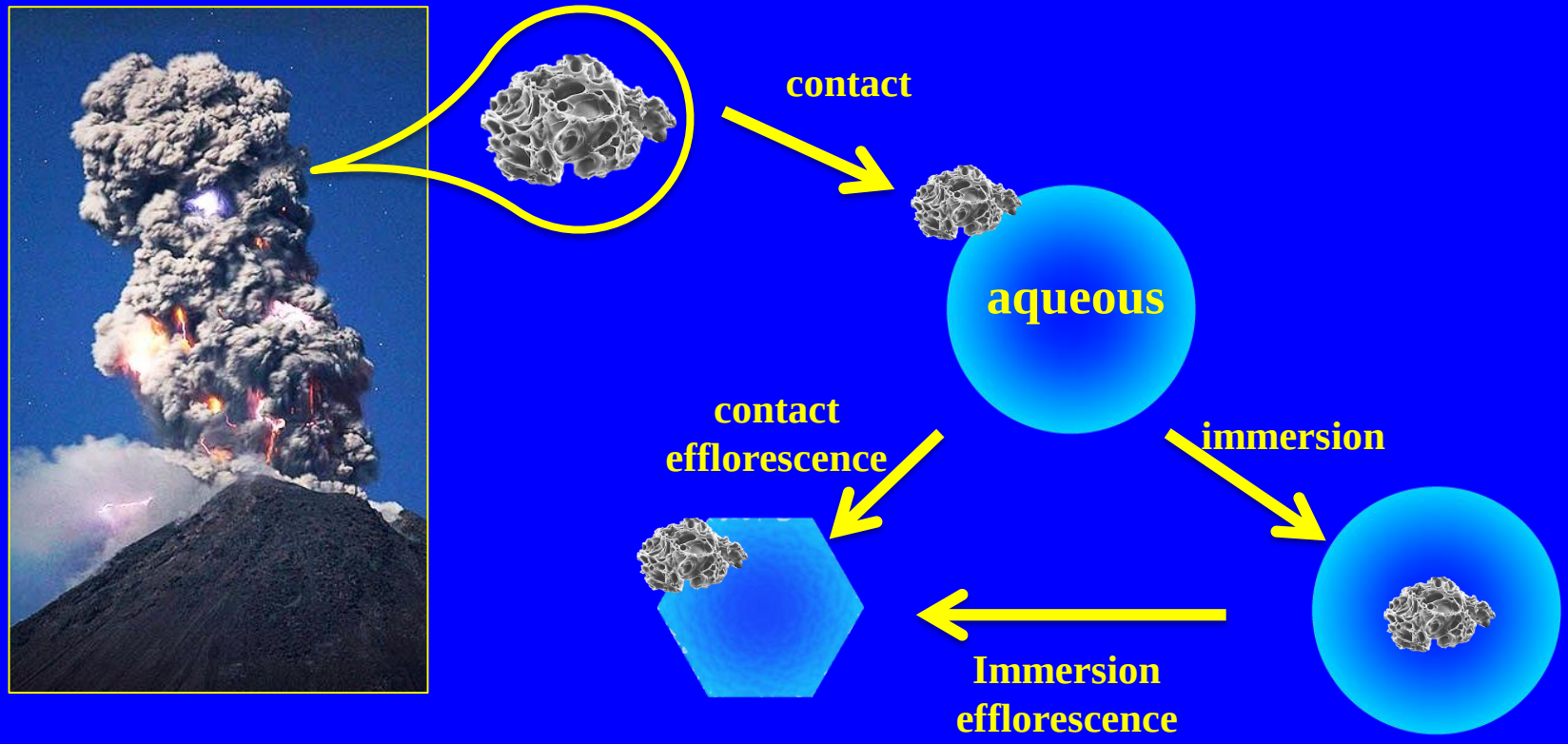
- lower Mn, Ti & higher K (rhyolitic) favors freezing
- role of specific ion interactions (small highly charged ions may not fit into ice lattice well)

Similarities to feldspar: Zolles et al., 2015

Sarychev from International Space Station, June 12, 2009

- Ash excellent IN in deposition mode
- Rhyolitic ash also excellent immersion IN
- Could impact ice near and far from vent
- Could help explain vent lightning

Impacts of Ash on Background Aerosol



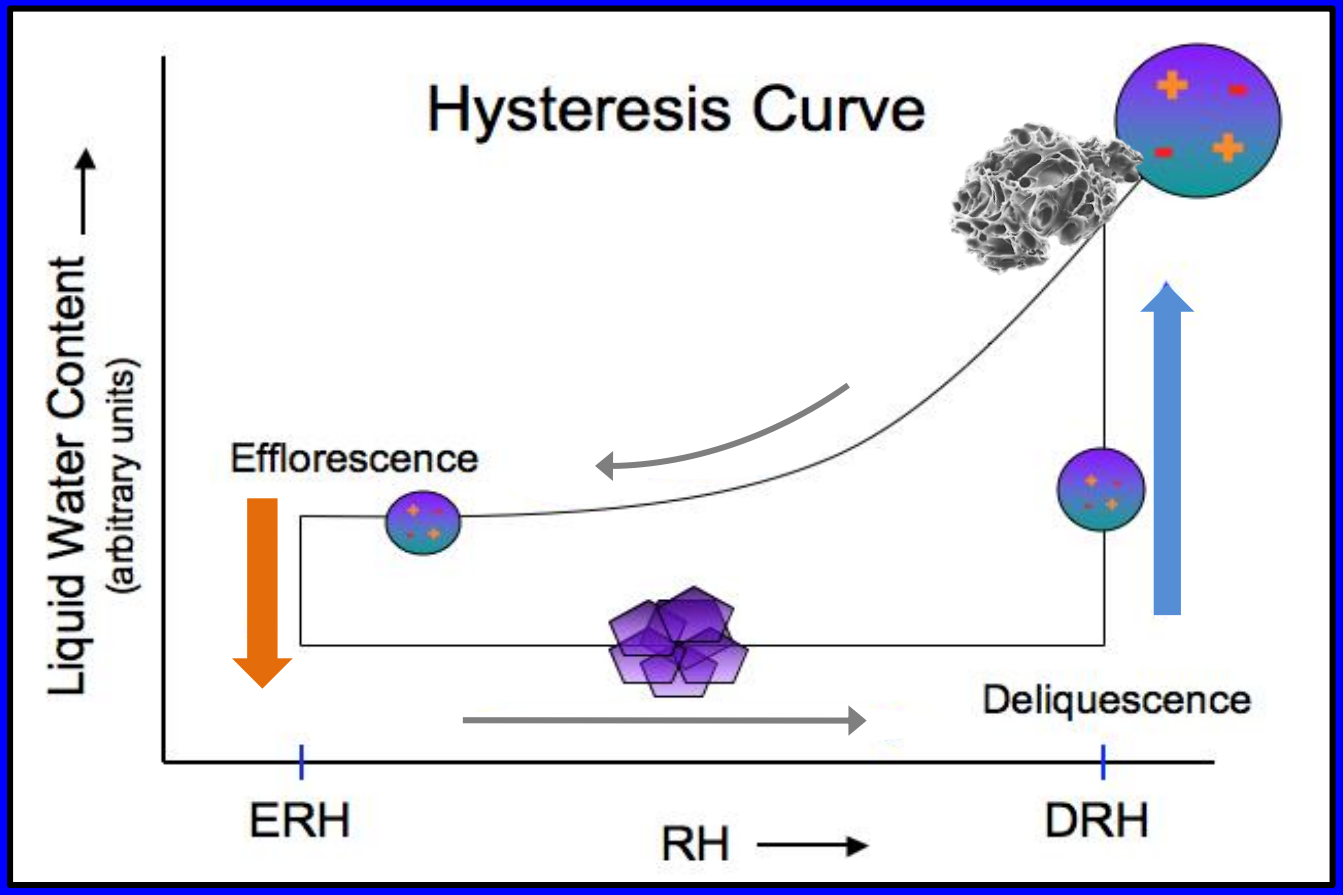
Collisions with ash could induce crystallization

Salt Deliquescence and Efflorescence

$H_2O_{(g)}$ +

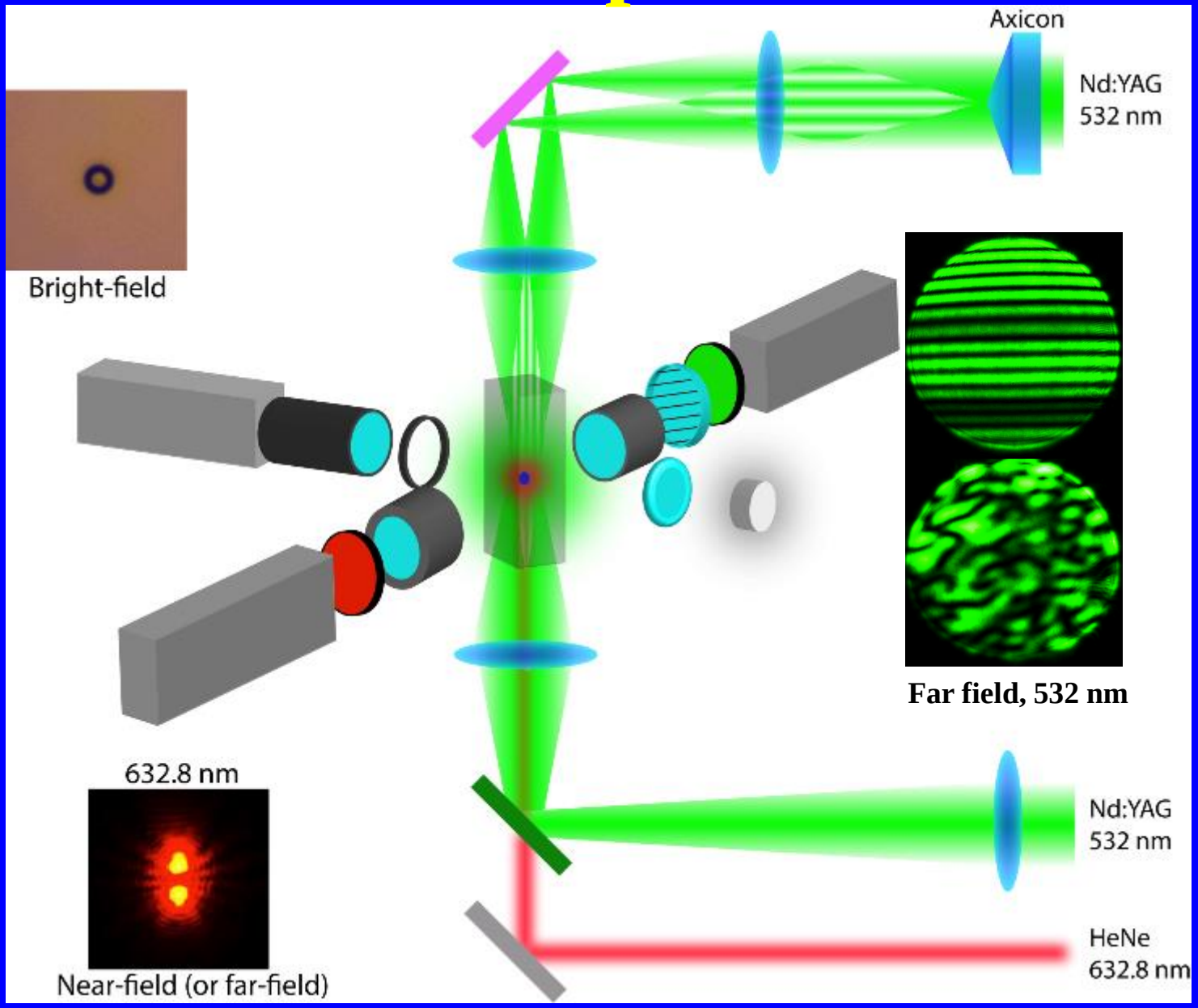
deliquescence

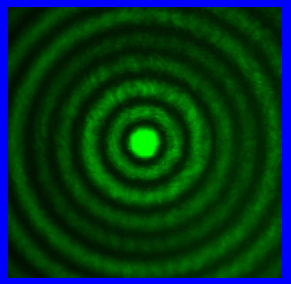
efflorescence

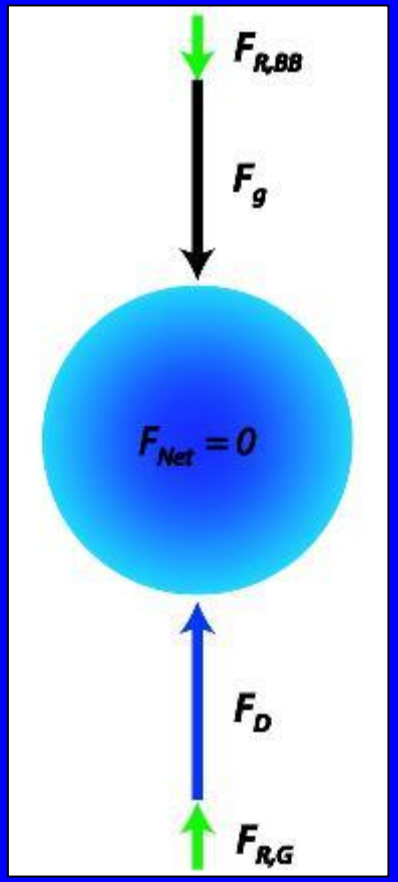


Usually aerosols assumed to remain liquid

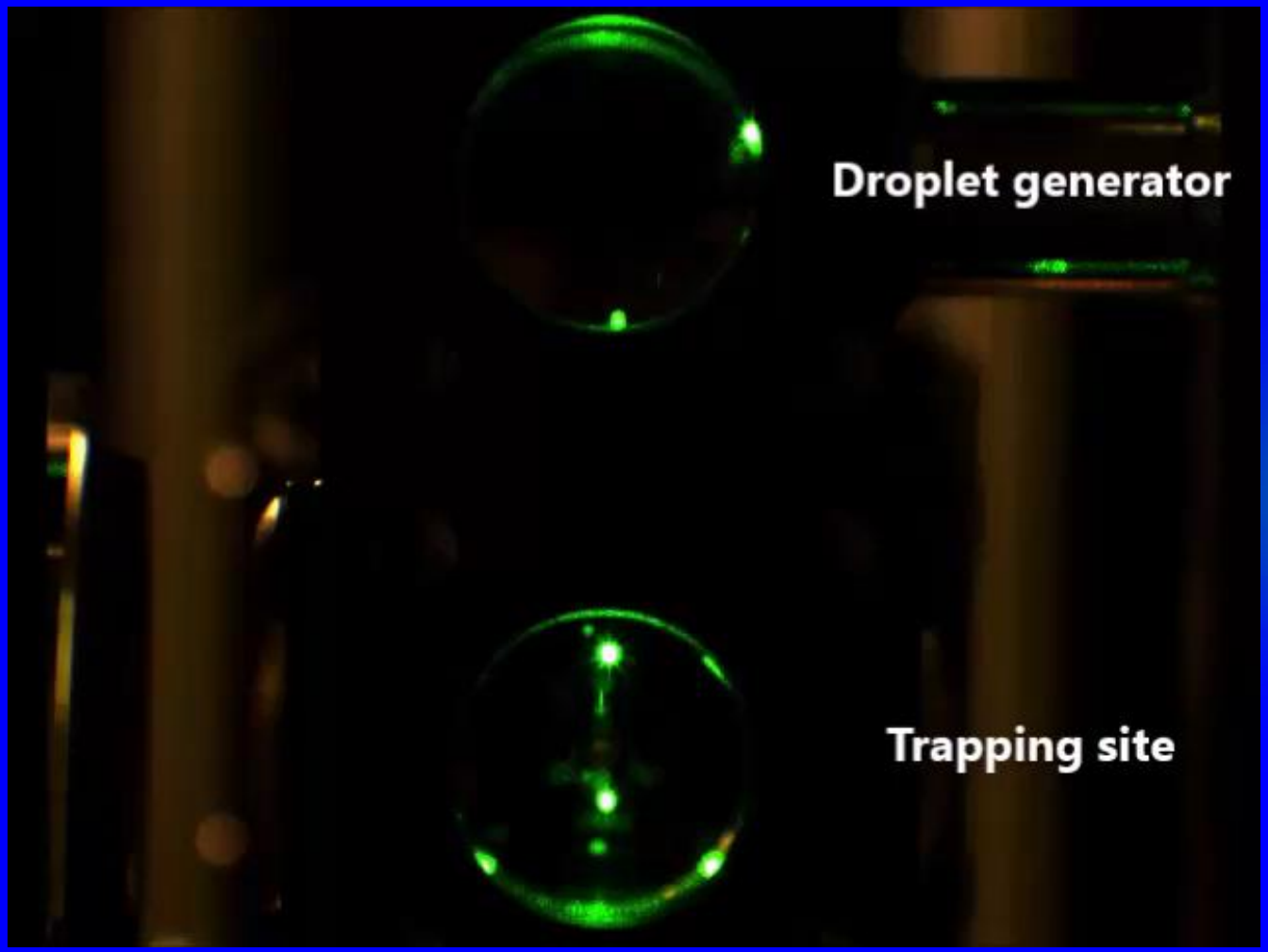
Experimental

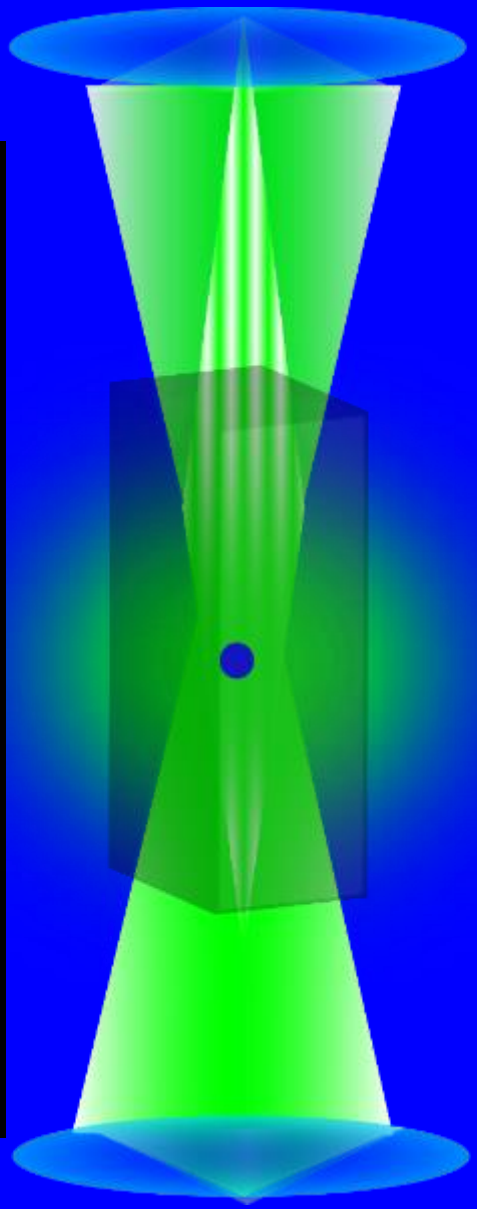






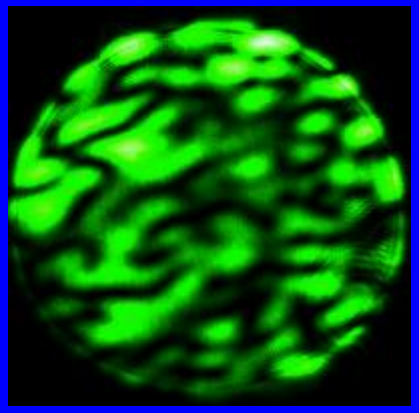
An upward oriented Gaussian beam facilitates initial trapping



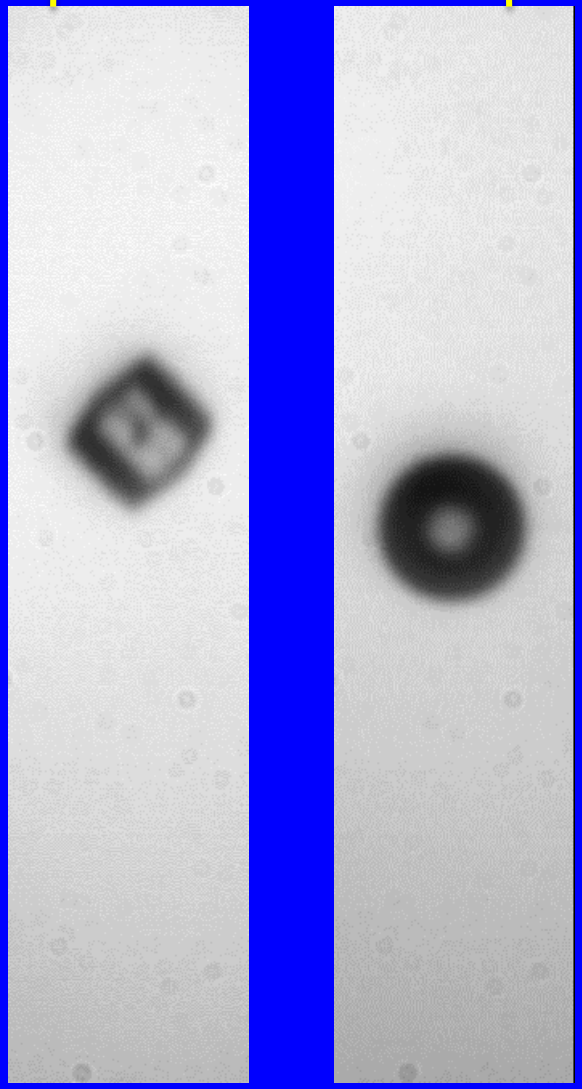


Can trap liquids and solids

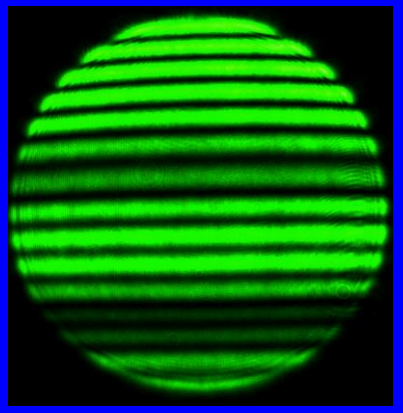
Cubic NaCl crystal

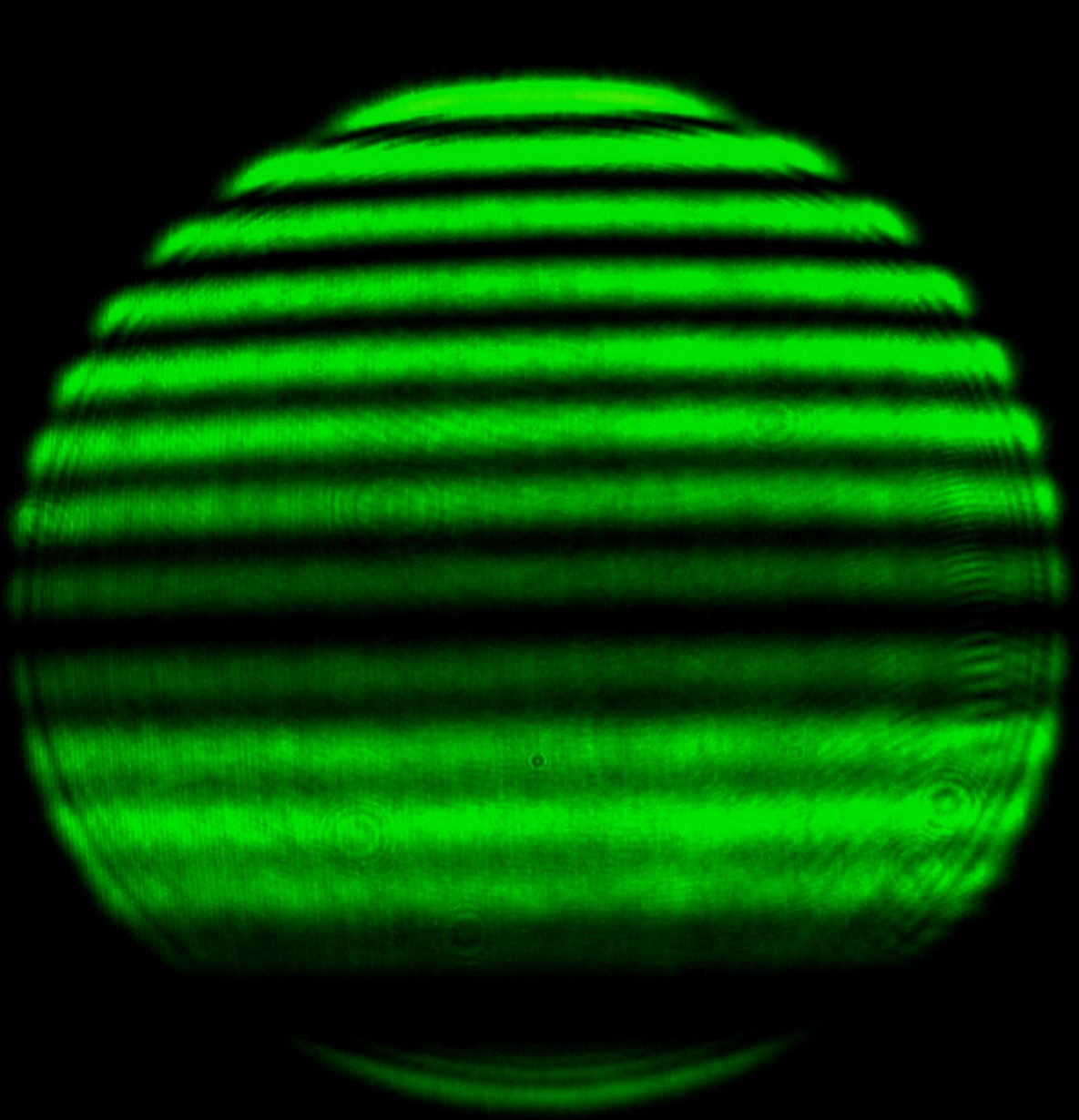


Bright field



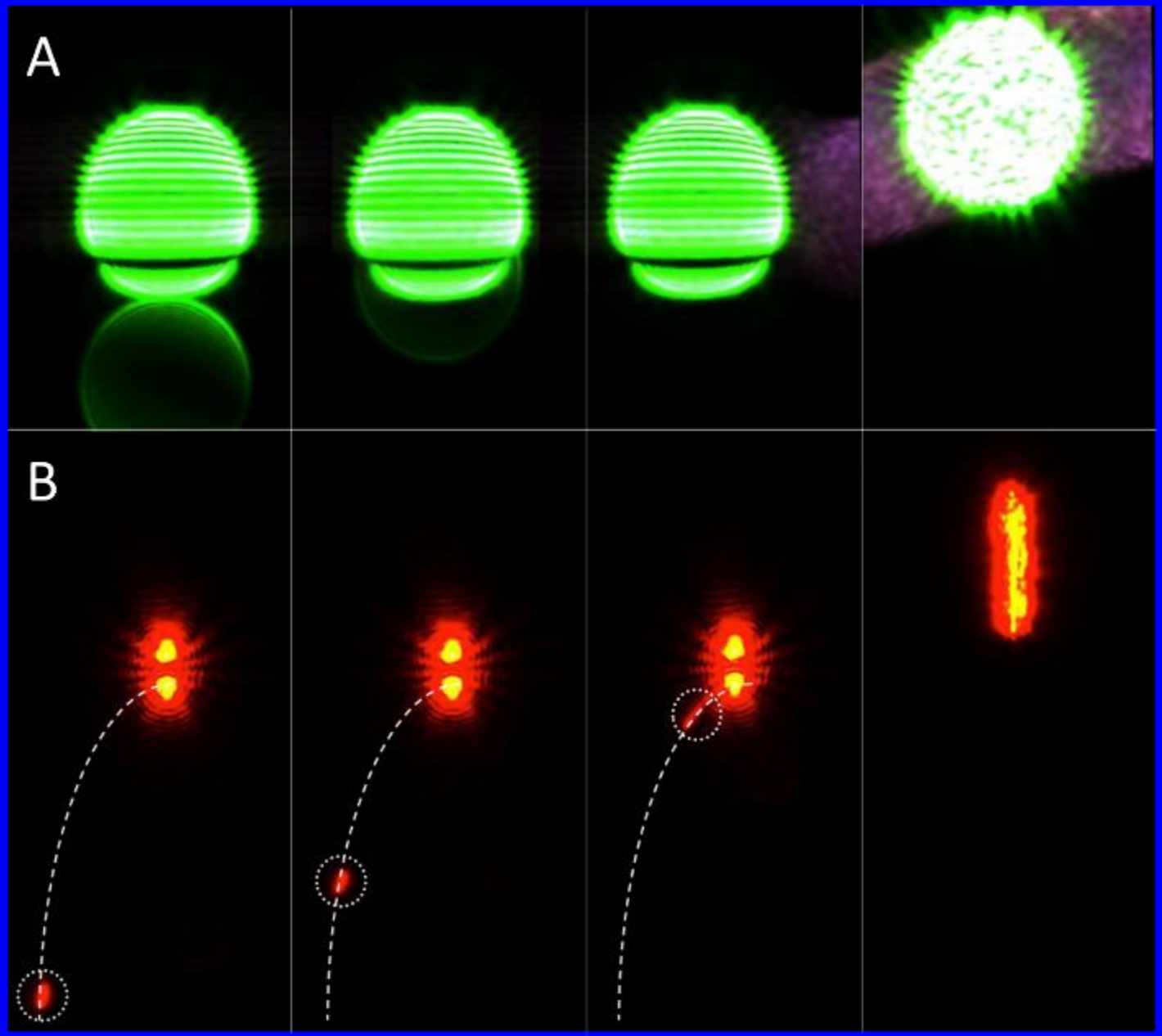
Aqueous NaCl droplet



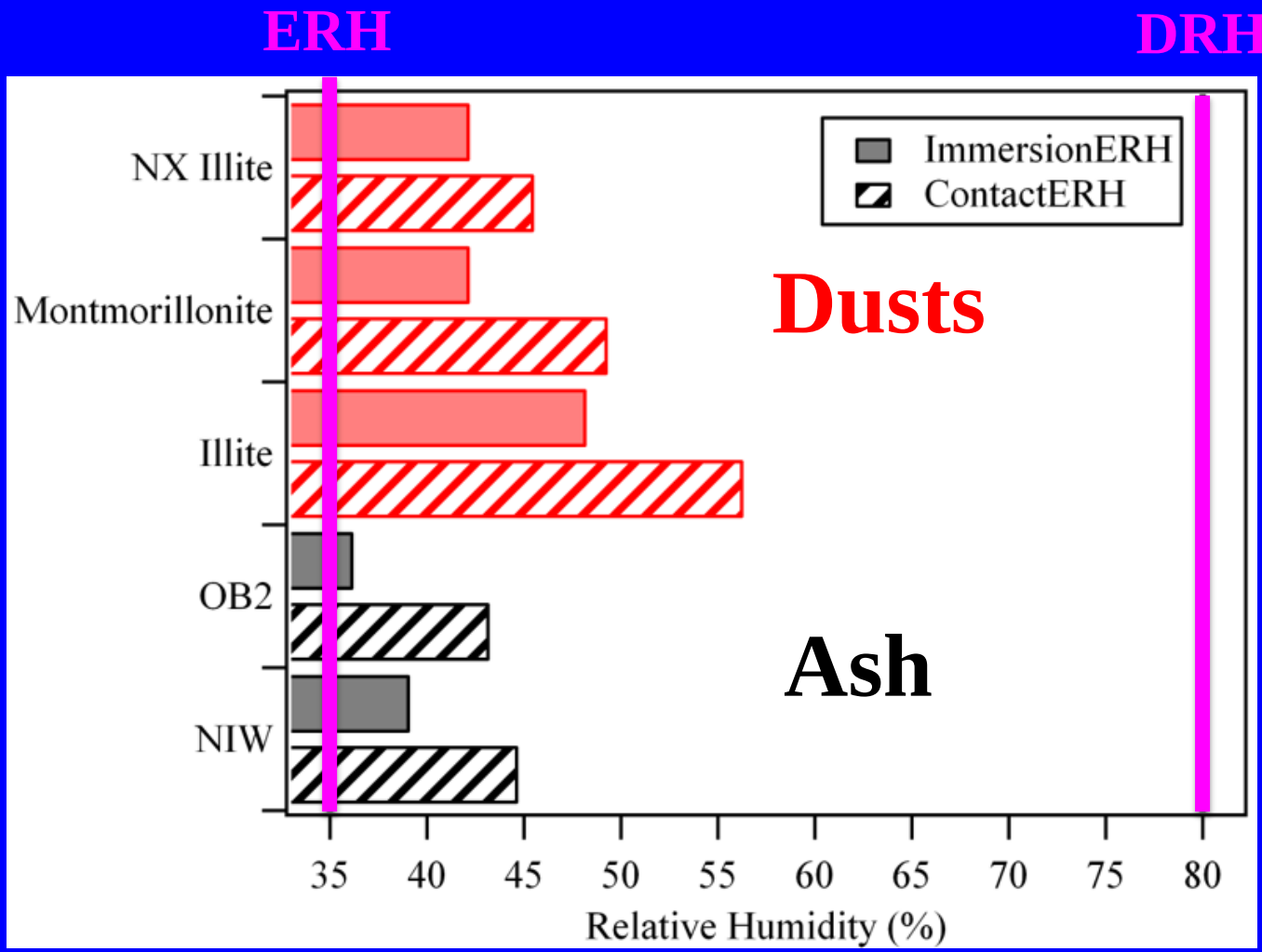


Far-Field Imaging: Homogeneous efflorescence of Na_2SO_4

Contact Efflorescence

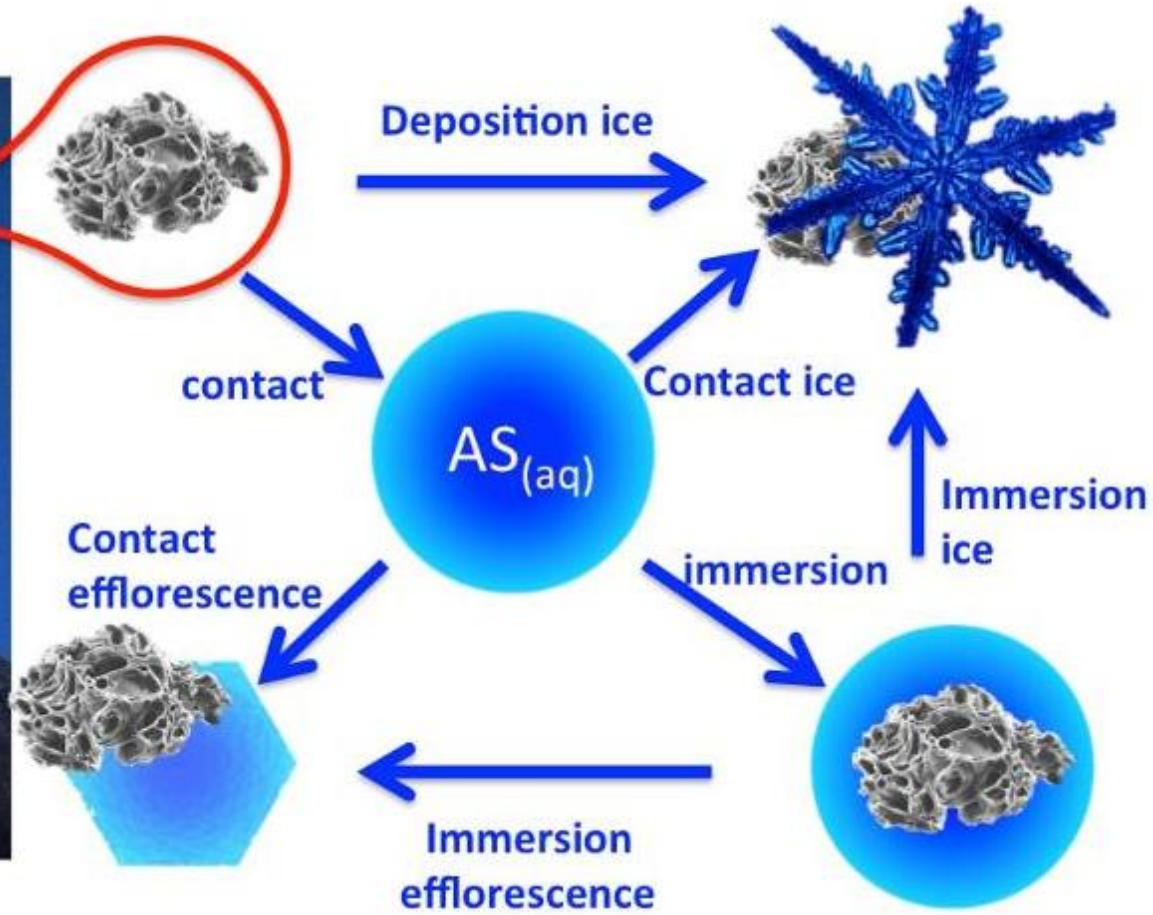


Contact Induces Efflorescence: $(NH_4)_2SO_4$



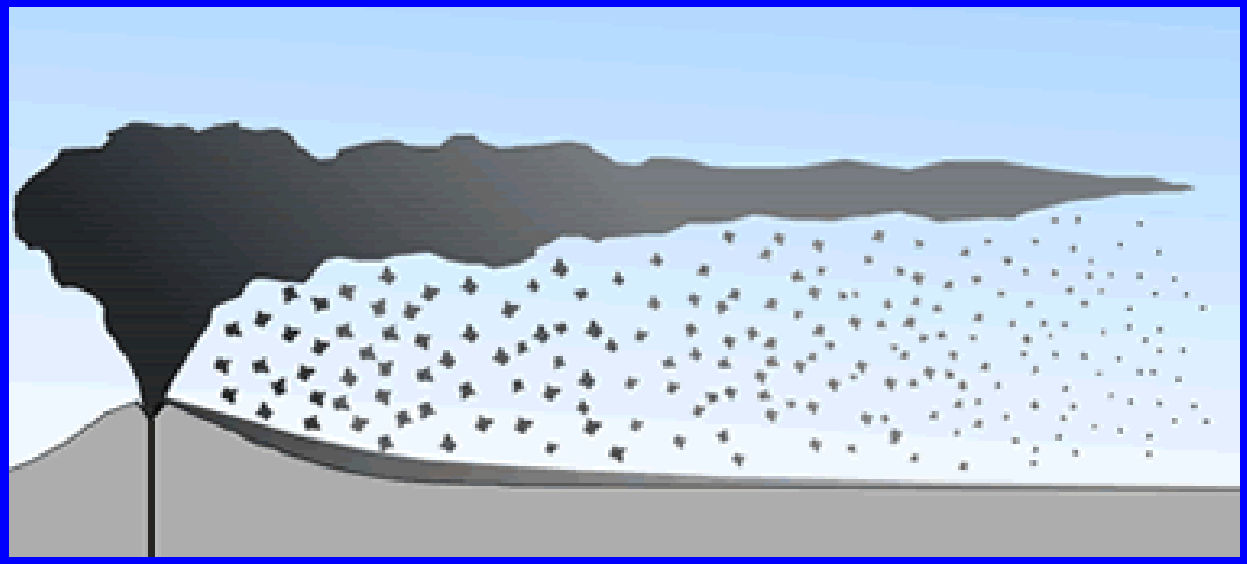
- Contact with ash or dust can lead to solids more of the time
- Solids show less reactivity, less hygroscopic growth

Summary

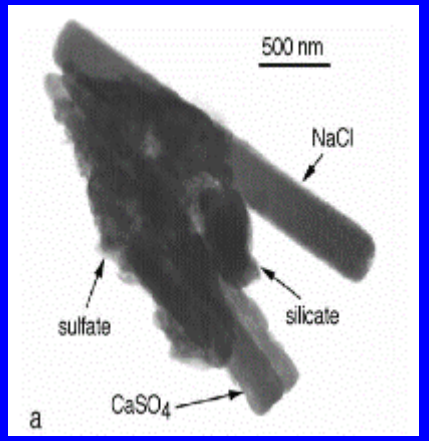


Thanks to NSF, CIRES for funding

Collisions with Ash or Dust could cause Salt Efflorescence



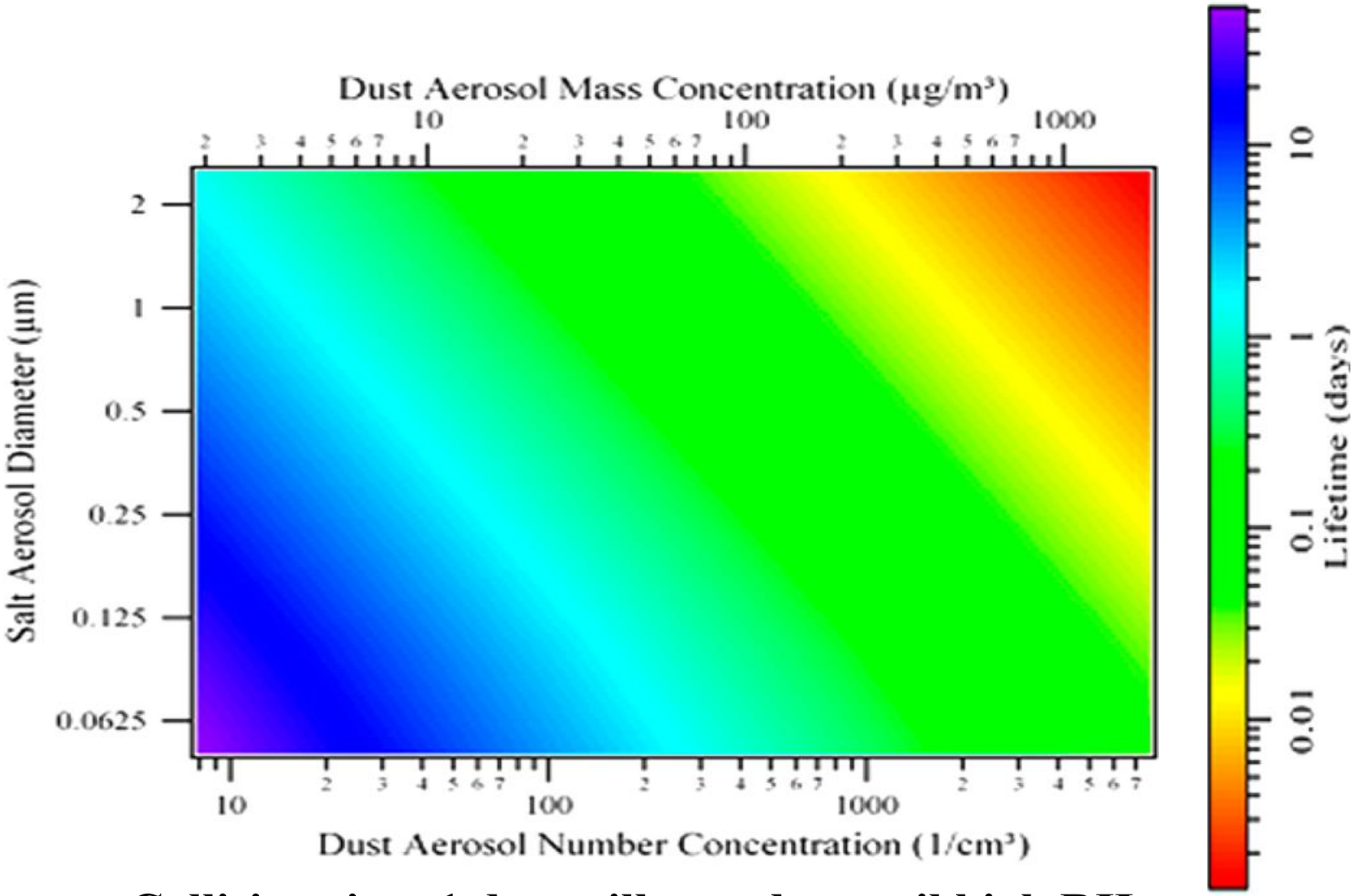
Sulfate-mineral



- **Salts will stay dry until high RH**

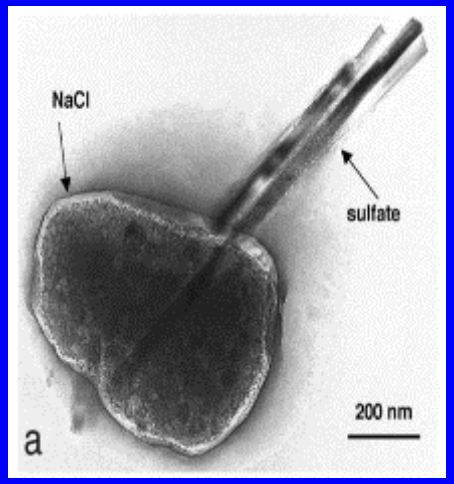
Li et al. (2003) *J. GeoPhys. Res.*, Buseck and Pósfai (1999) *PNAS*

Salt Lifetimes wrt collisions

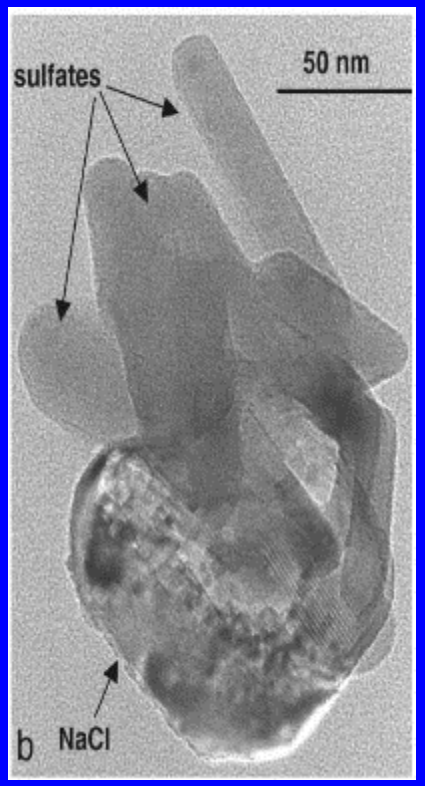


- **Collisions in ~ 1 day, will stay dry until high RH**

Internally Mixed Particles Common

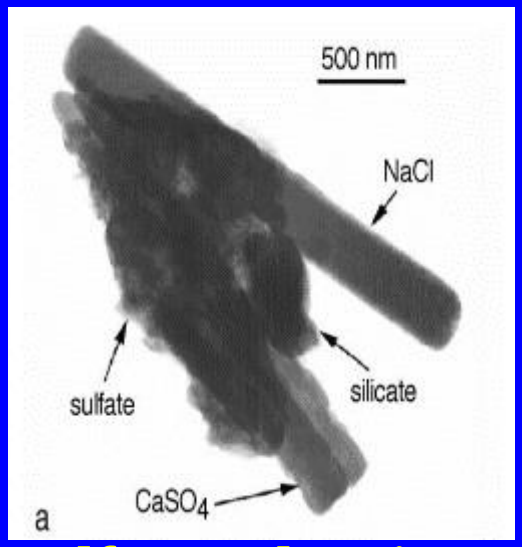


Sulfate-salt

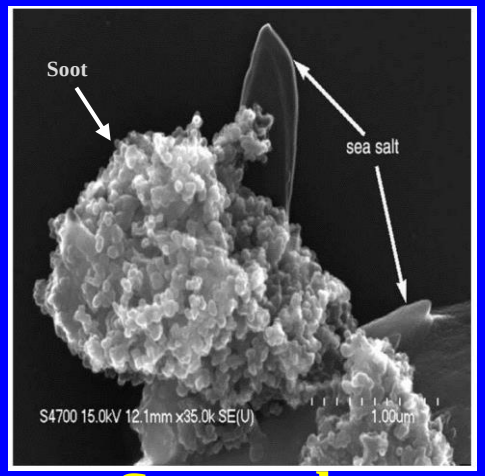


Sulfate-salt

Sulfate-mineral



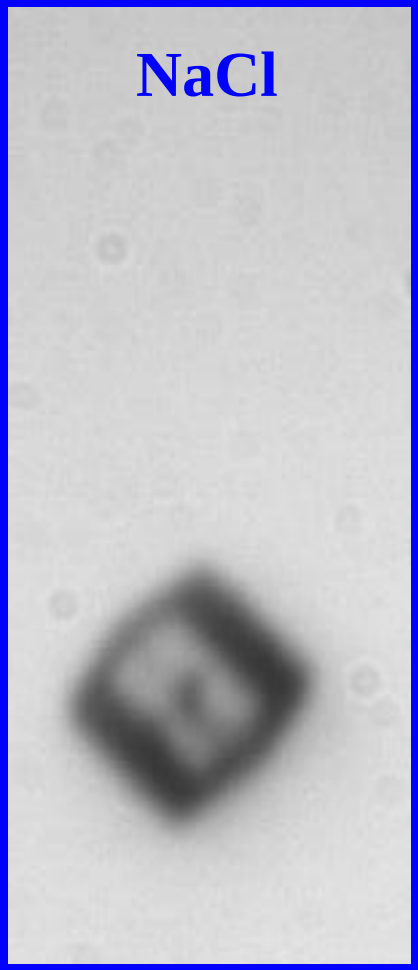
Sulfate-salt-mineral



Soot-salt

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

Contact Efflorescence Not Normally Considered

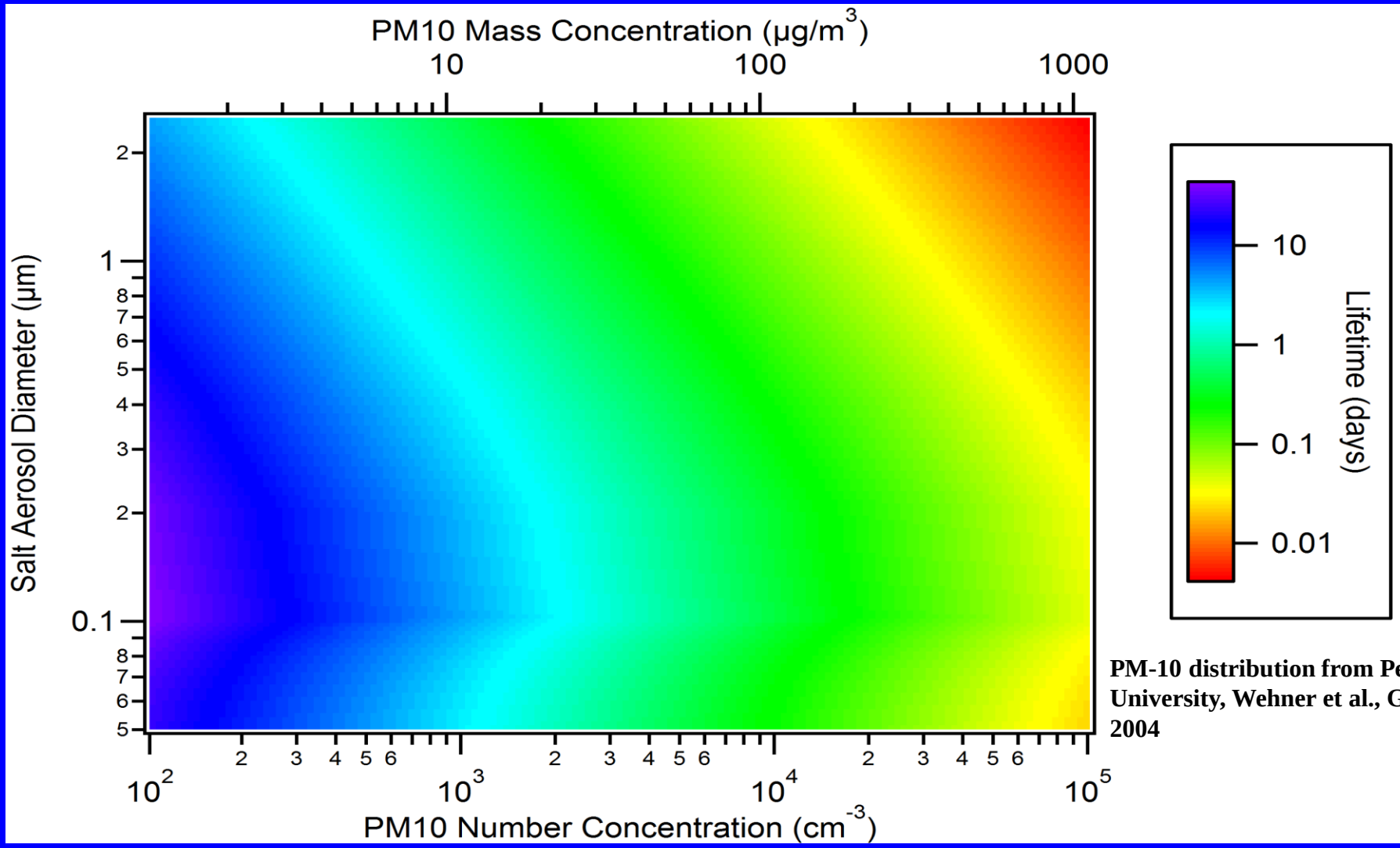


Bright-field imaging of trapped crystals

Thanks to my research group, NSF, NASA and CIRES!

and Prof. Kim Genareau from University of Alabama!

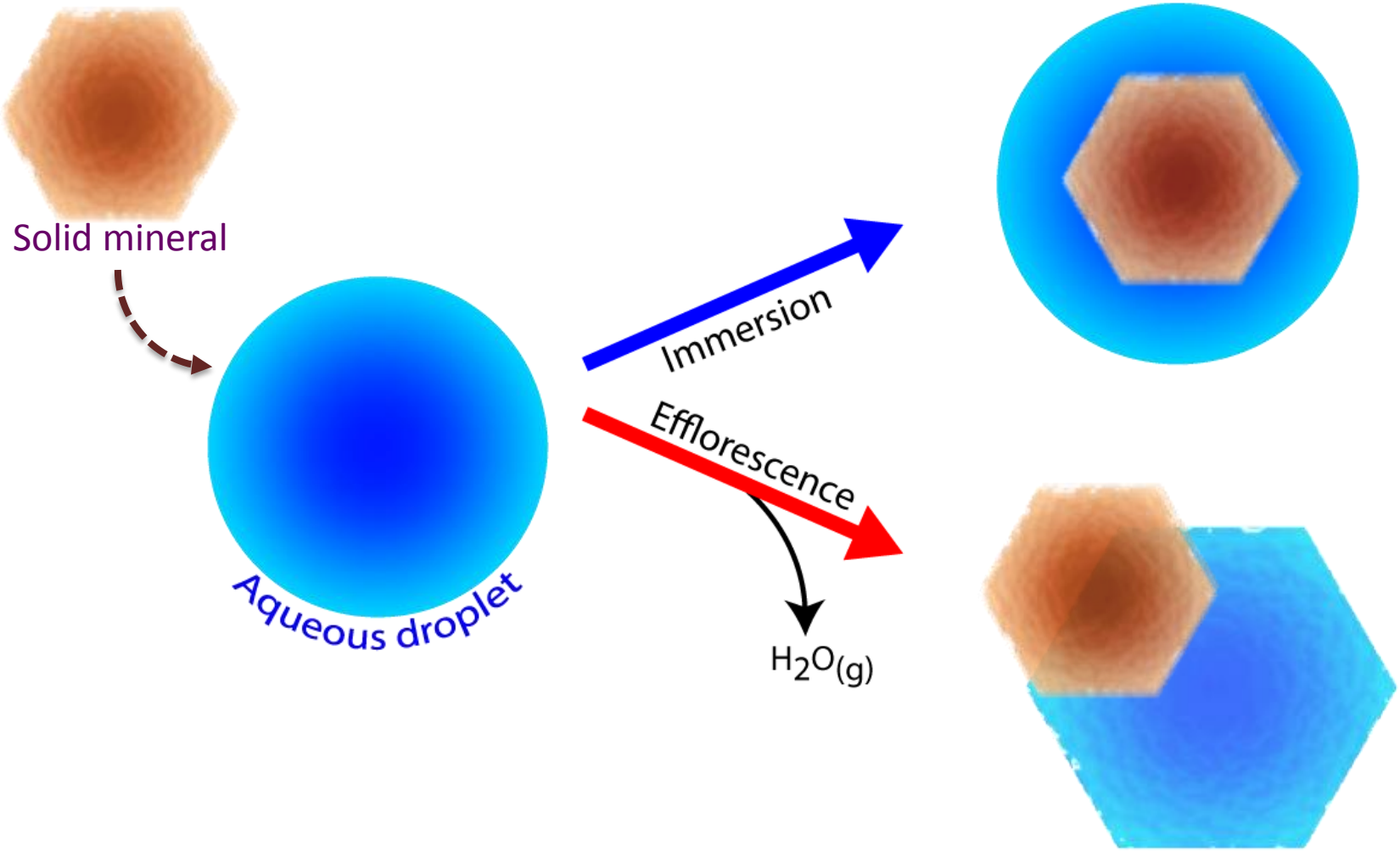
NaCl lifetimes wrt collision in atmosphere



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

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

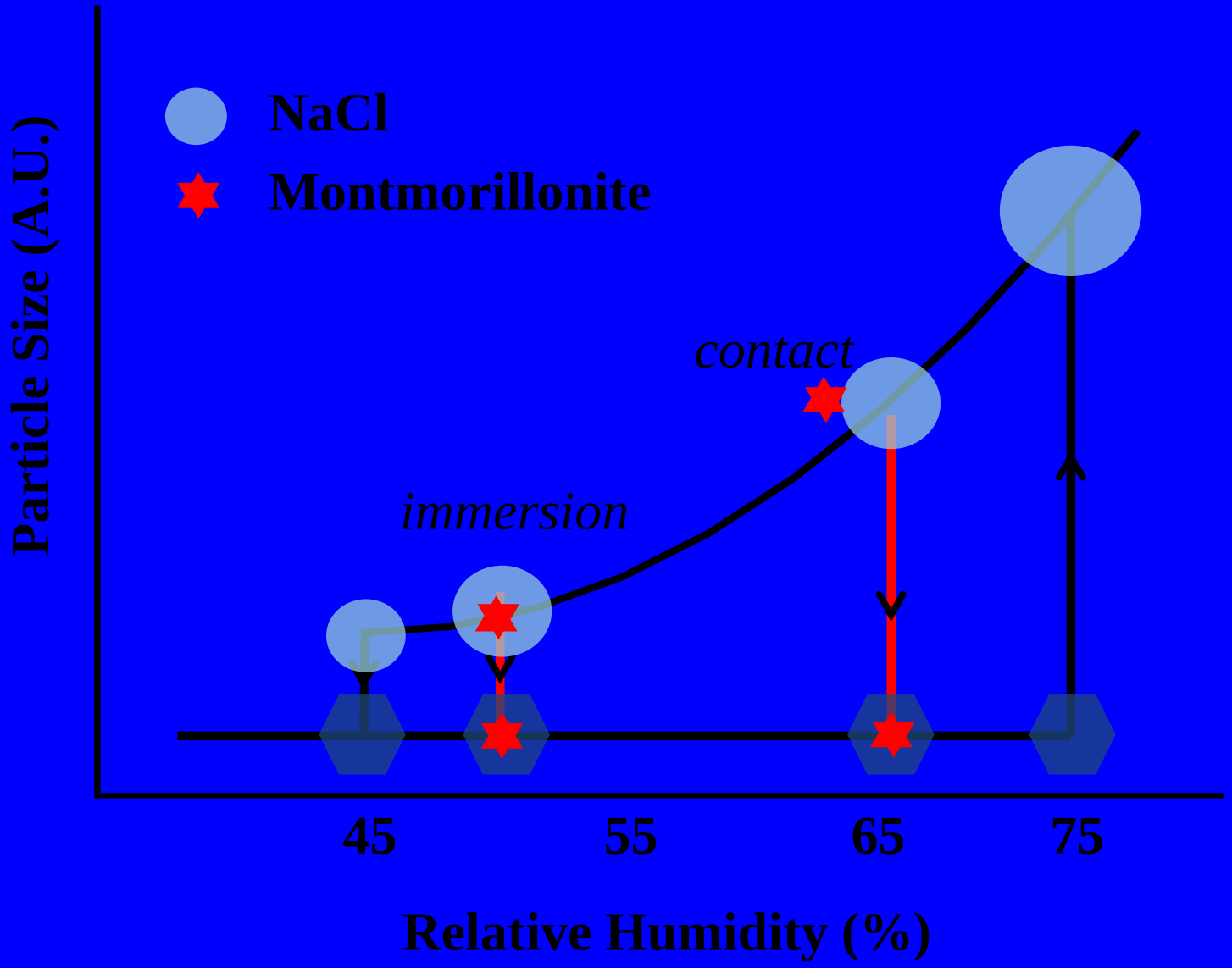
Contact Nucleation w/Mineral Dust or Ash



- ***Compare contact with immersion***

Contact more effective than immersion

Very similar to (-) PSLs



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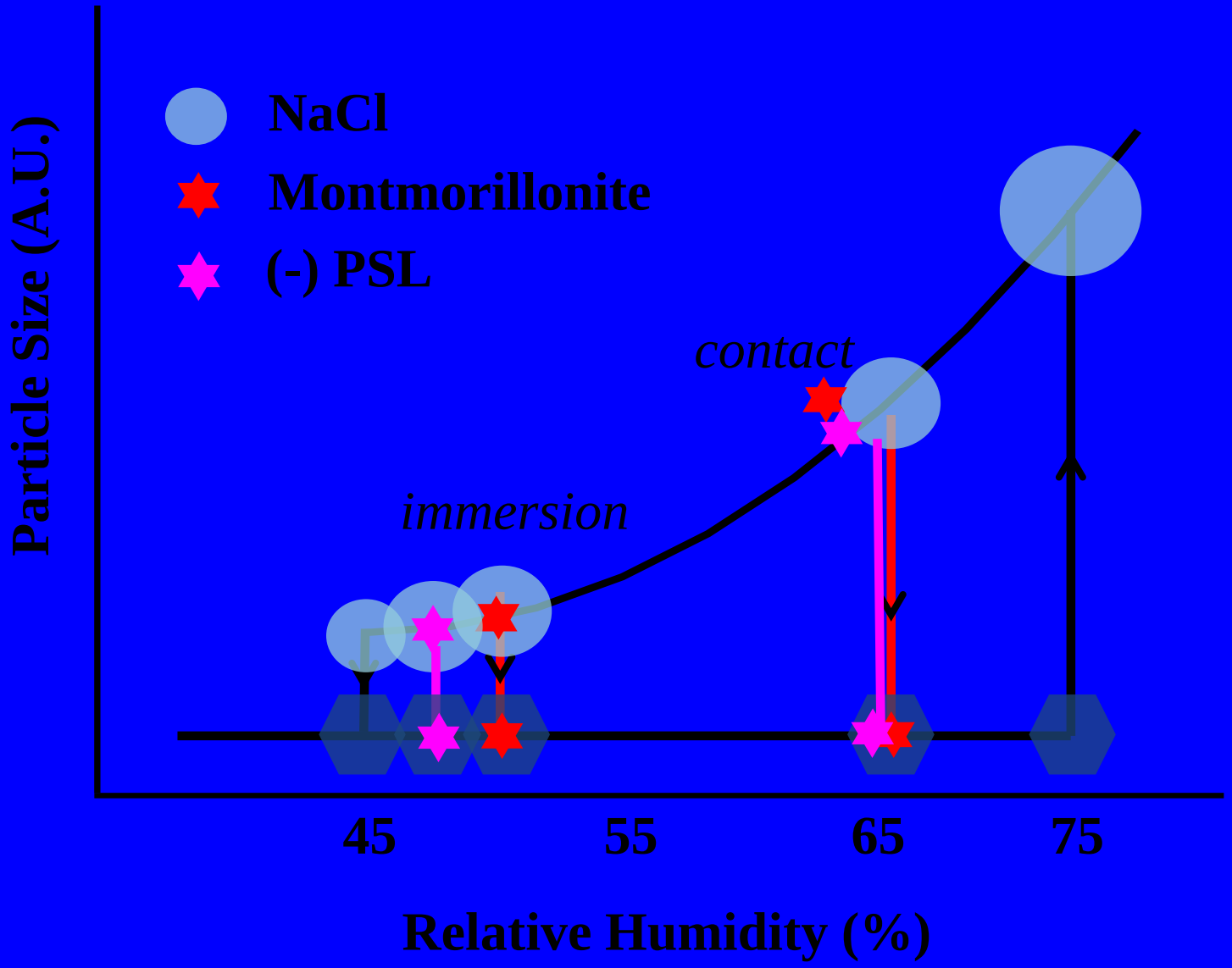
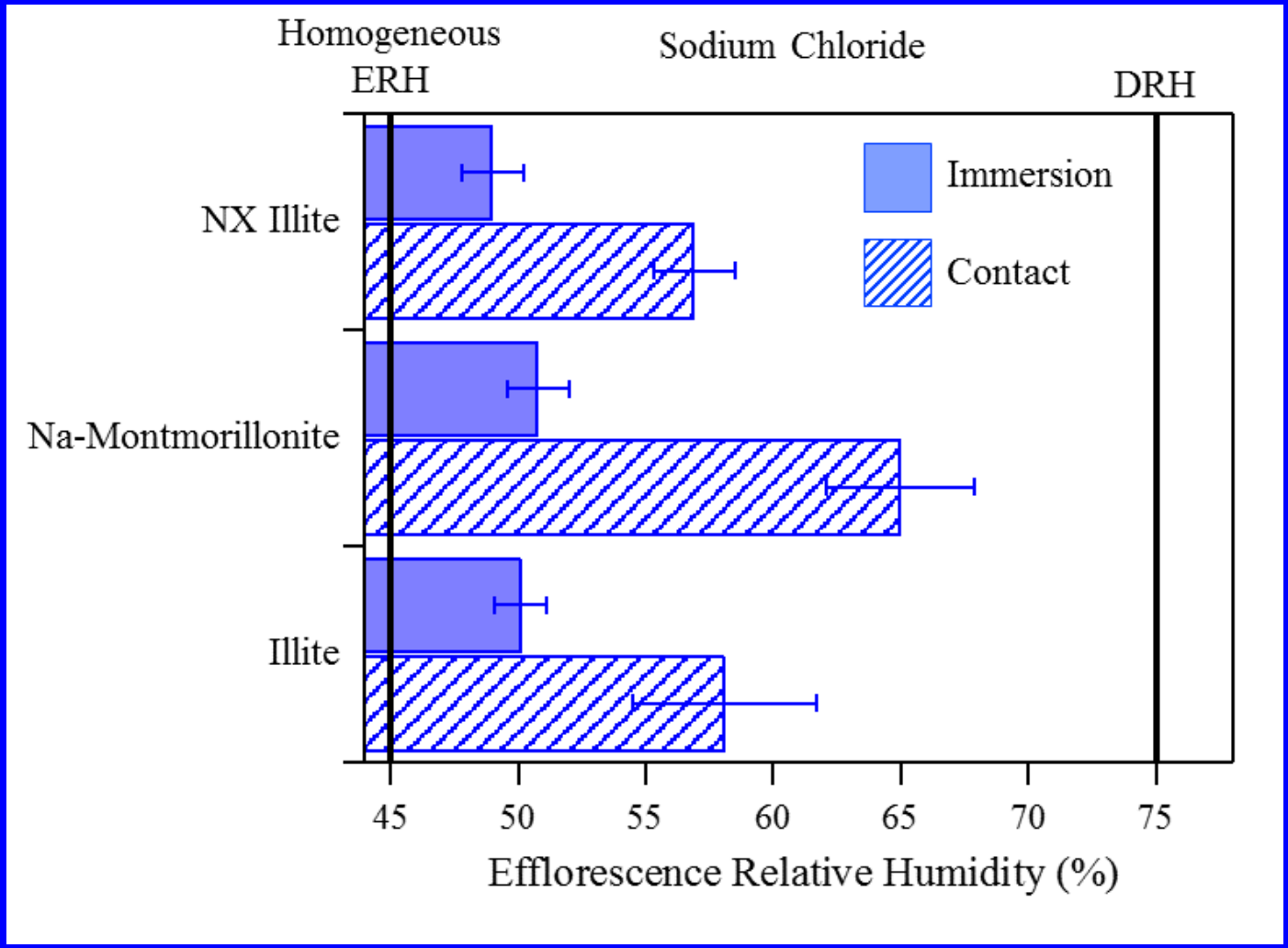
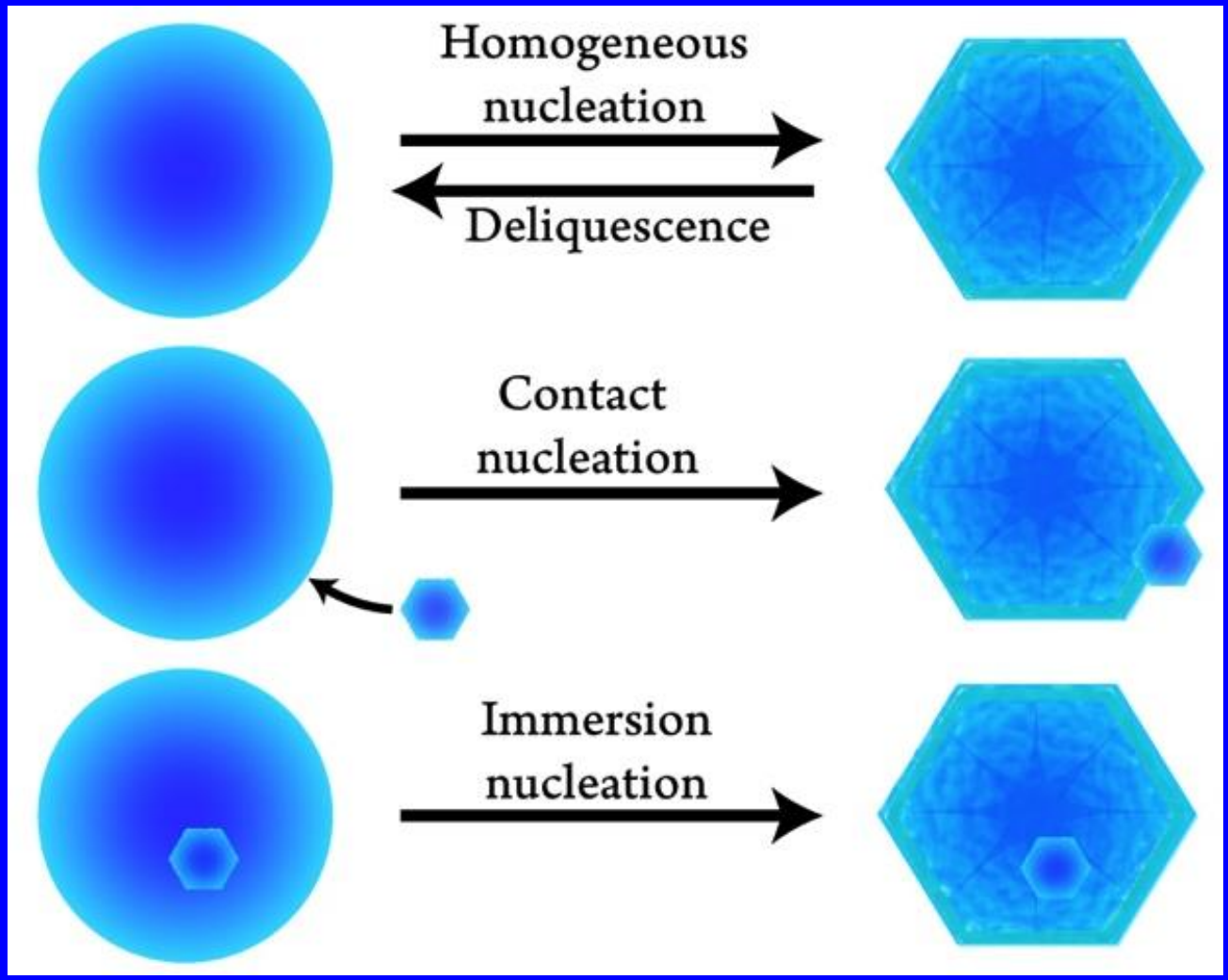


Heterogeneous ERH of NaCl by Single Particles



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

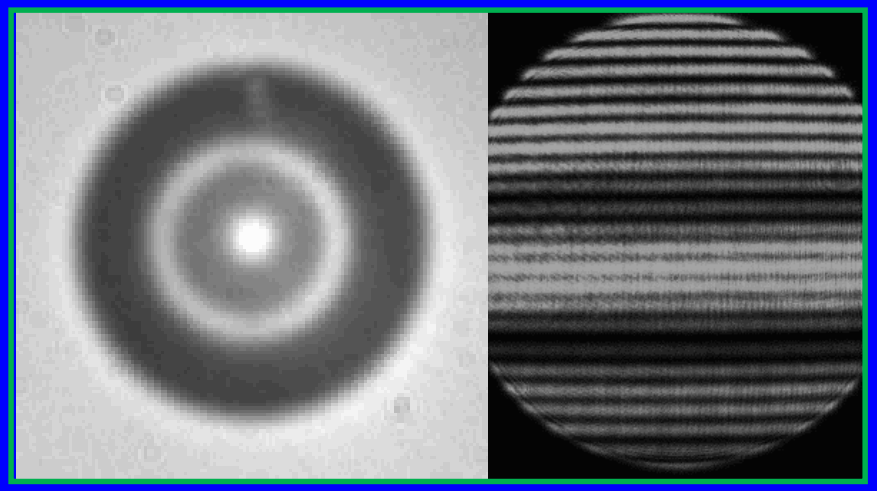
Phase transitions in this talk

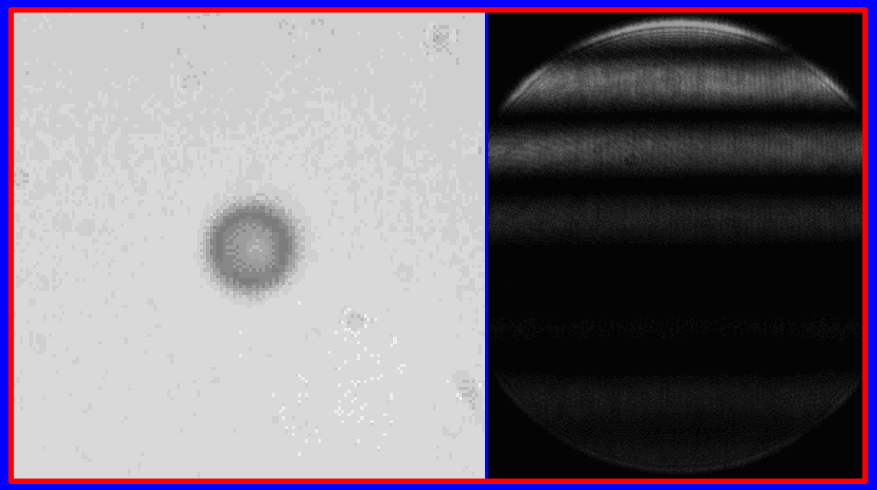


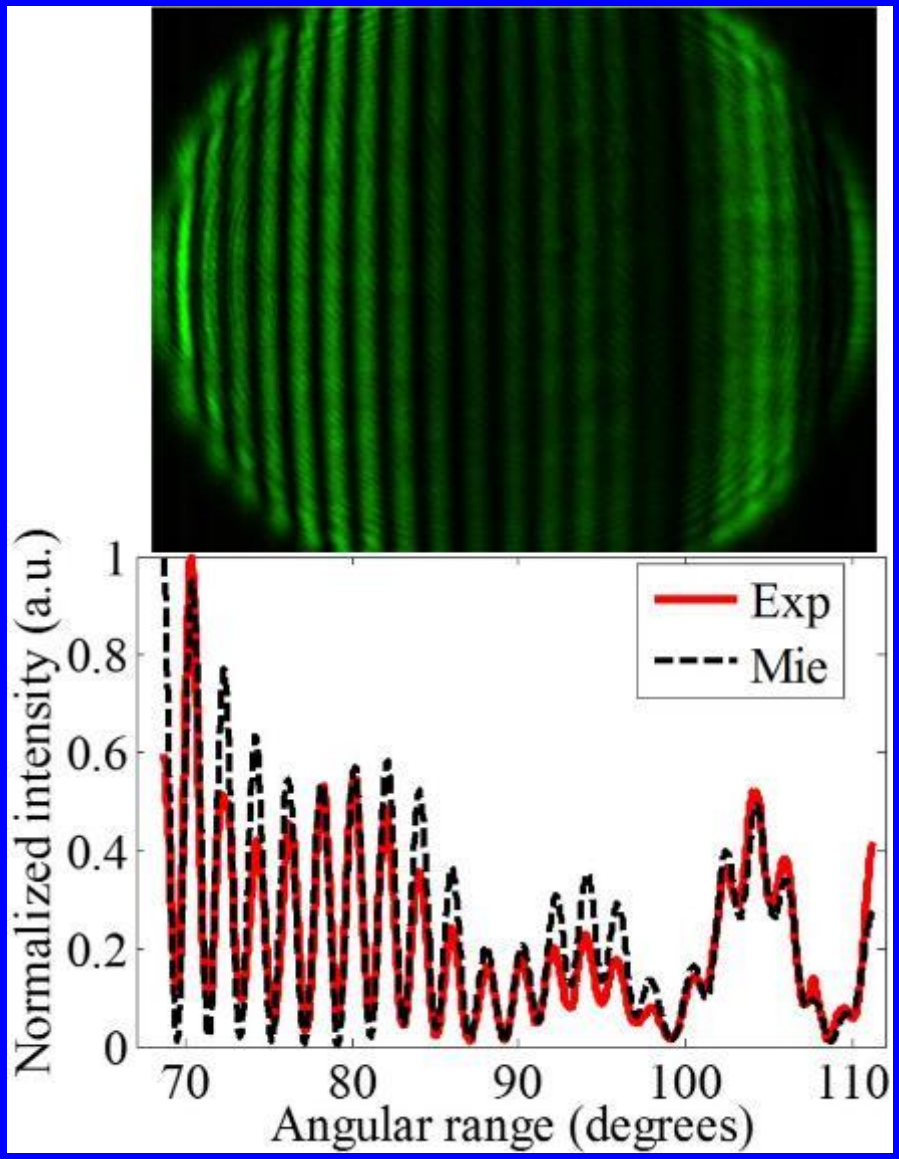
Sizing:Evaporation of a Glycerol Droplet

Droplet Sizing

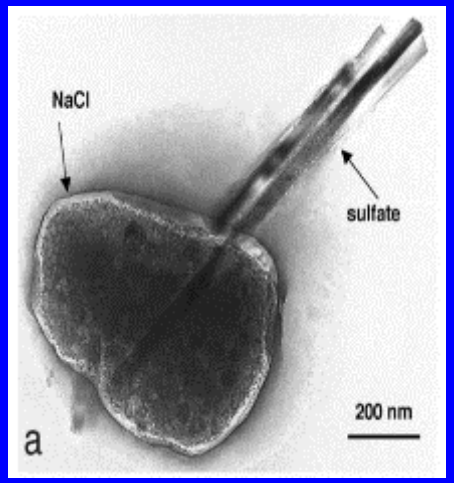
$D_p = 17.589 \pm 0.006\ \mu m$

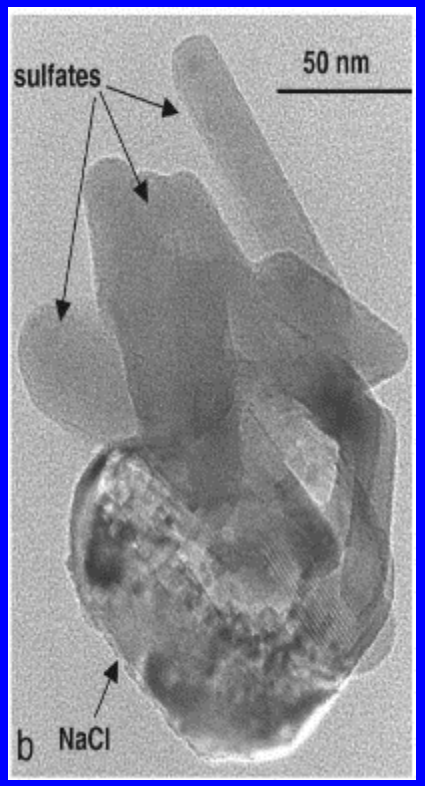


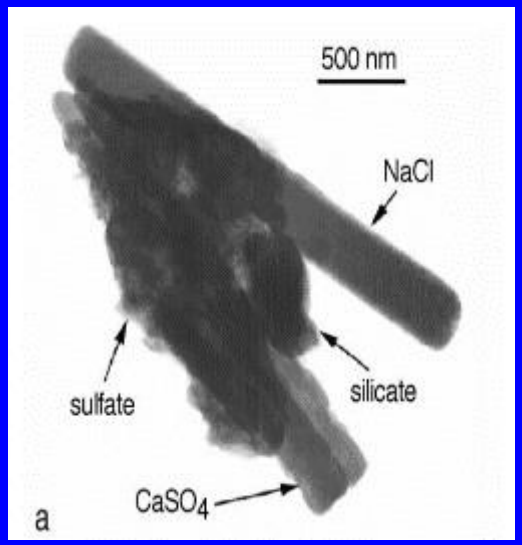


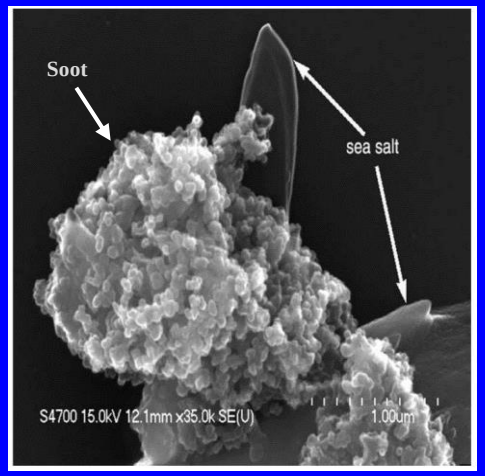


Internally Mixed Particles Common in Atmosphere



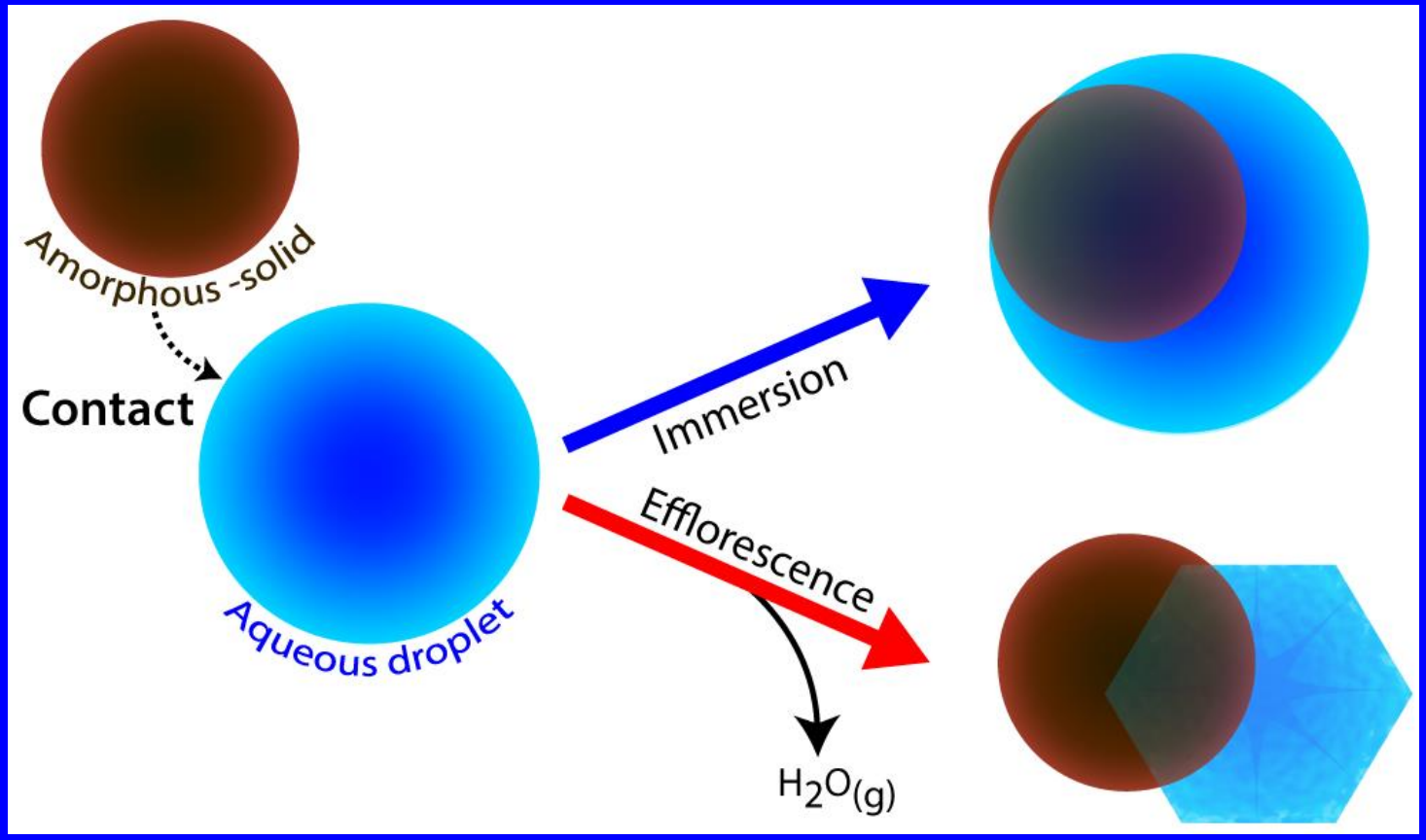






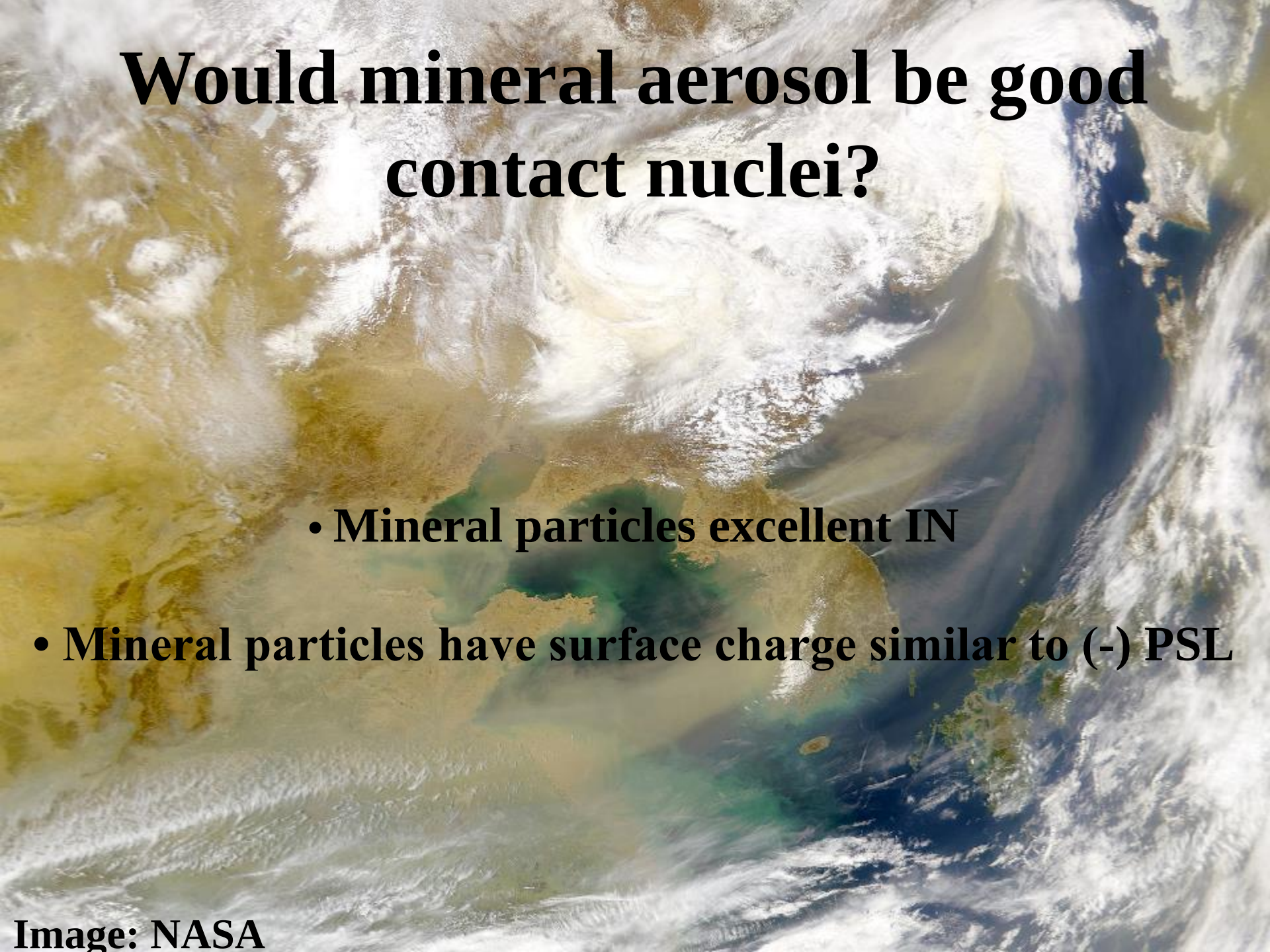
Li et al. (2003) *J. GeoPhys. Res.*, Buseck and Pósfai (1999) *PNAS*

Contact nucleation using functionalized amorphous organic particles



polystyrene latex spheres as CN: examine surface charge

Would mineral aerosol be good contact nuclei?



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

Image: NASA

Conclusion

Particles collide in the atmosphere

Lattice match one factor in contact efflorescence

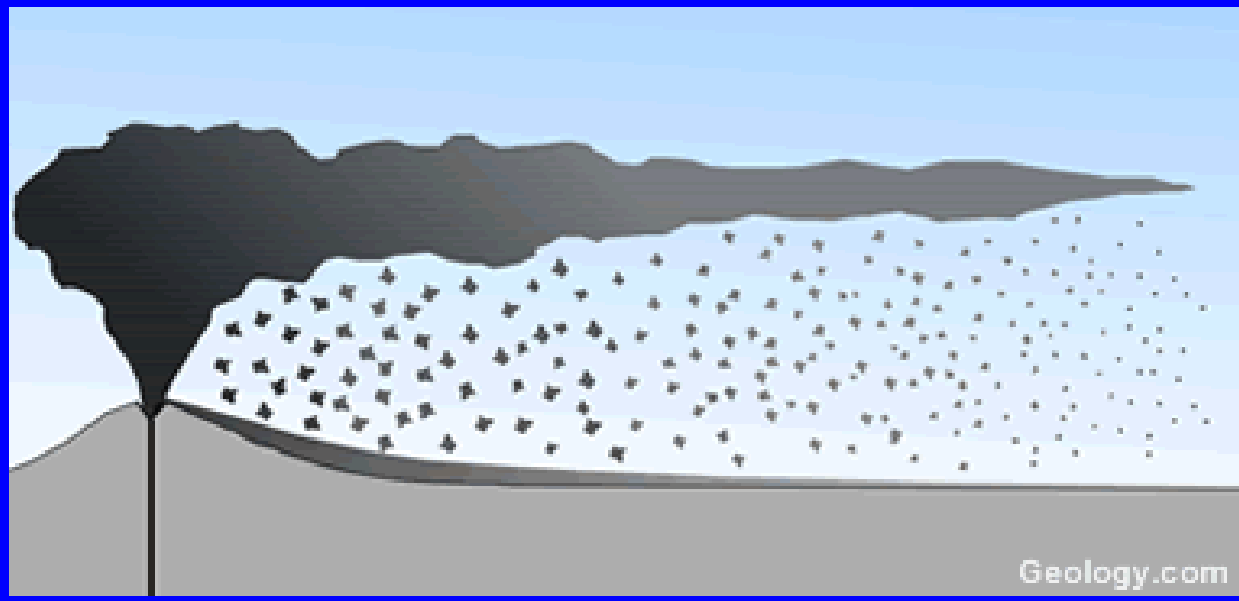
Contact more effective than immersion

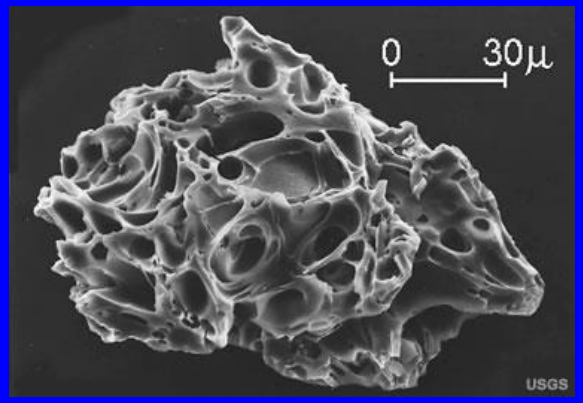
Ion specific effects for contact efflorescence

Atmospheric contact: more solid particles

Volcanic Ash

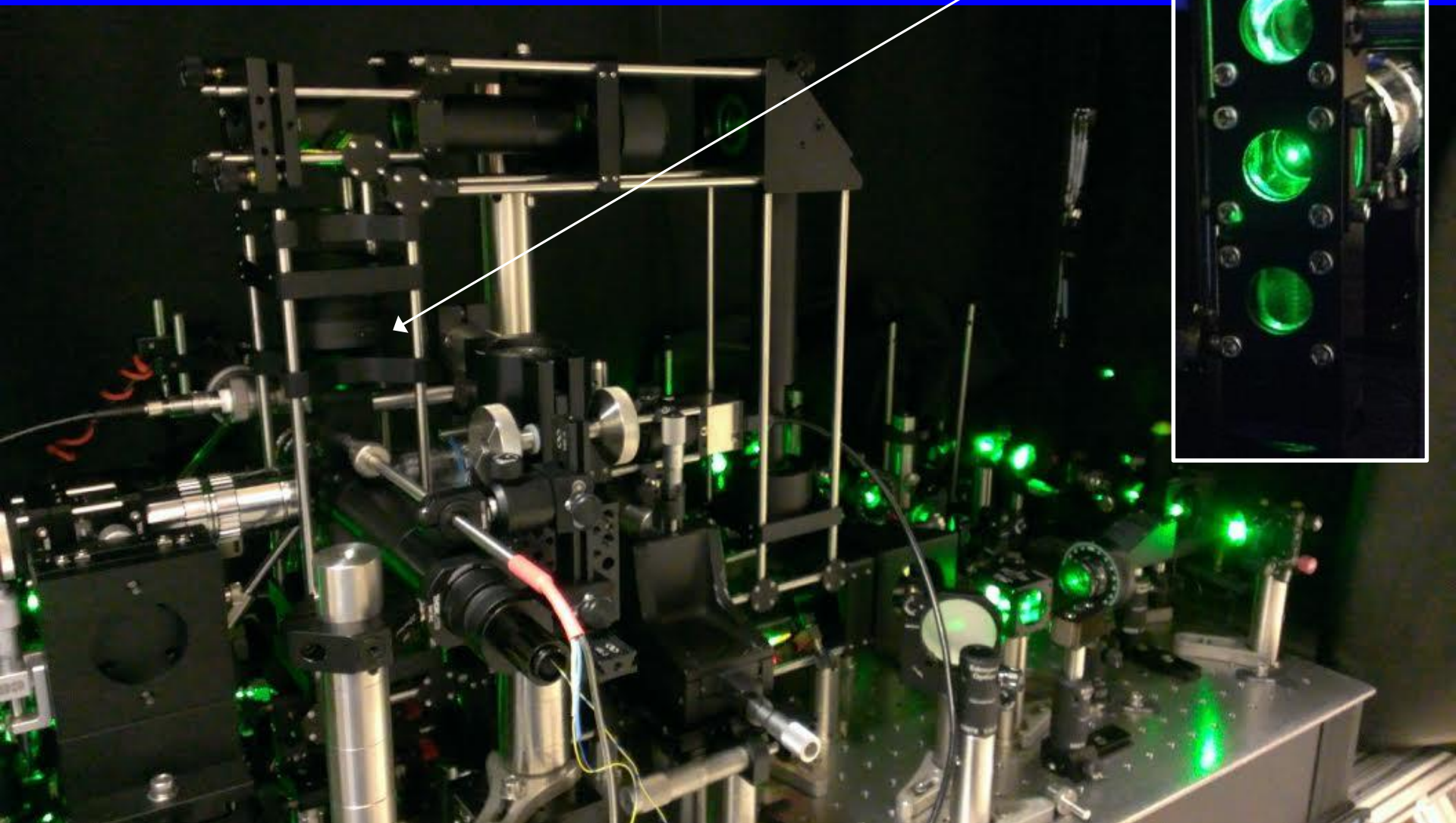
Mt. St. Helens, 1980





- Hard, irregular
- Some low density, small
- Can travel 1000s km
- Near and far impacts on atm

Optical Levitation Setup

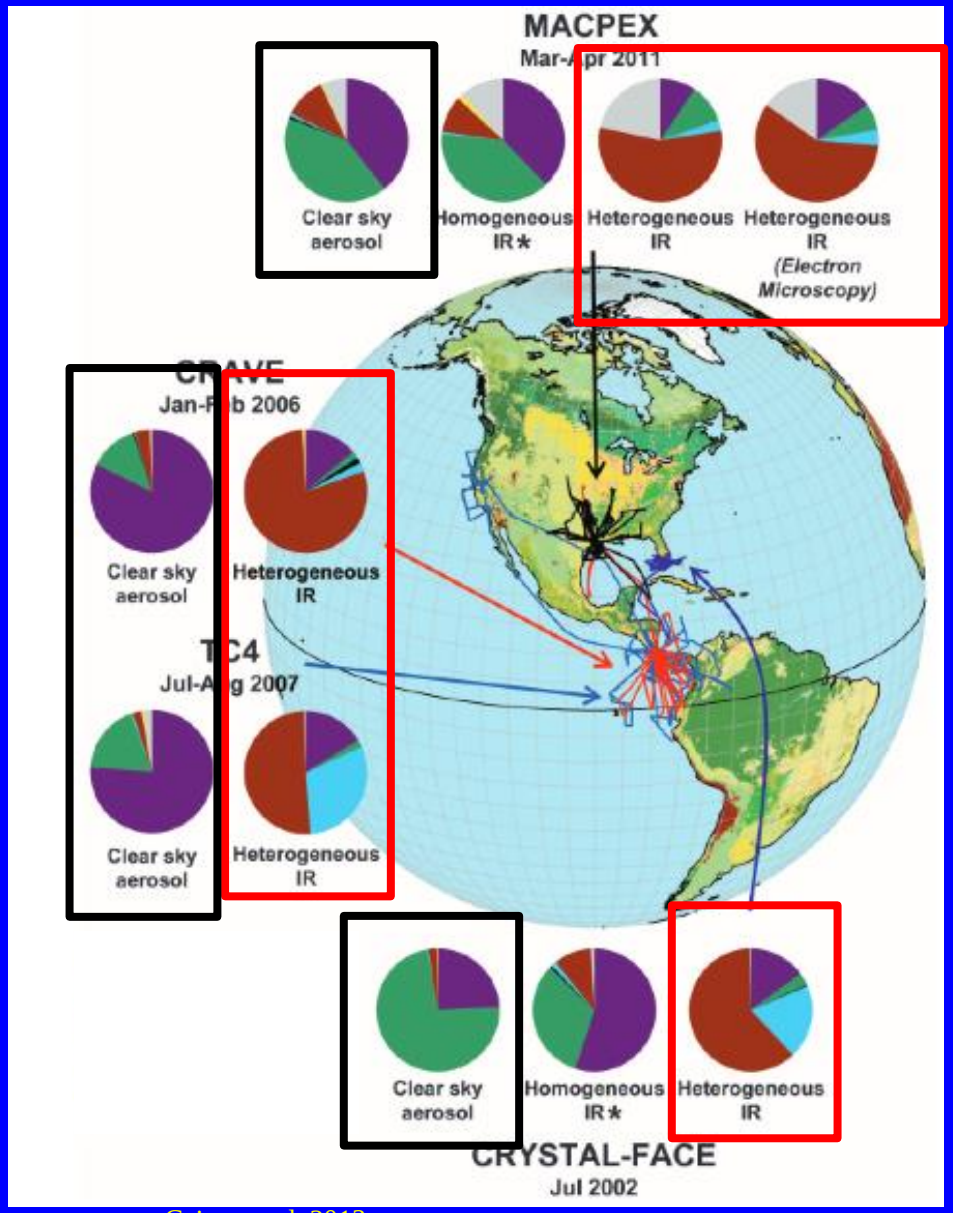


Volcanic Lightning

- Charge separation from ash or ash-ice
- Ash may act as IN
- Leads to tribocharging from ice-ice or ice-ash collisions
- Vent lightning or impact ice formation downwind

Martin Rietze, Sakurajima plume

Mineral Dust Excellent IN



- 1000-3000 Tg/yr mineral aerosol emitted in the atmosphere
- vs 200 Tg/yr volcanic ash

Sulfate/Org/Nitrate
Biomass burning
Elemental carbon
Sea salt
Mineral dust/Metallic
Oil combustion
Other

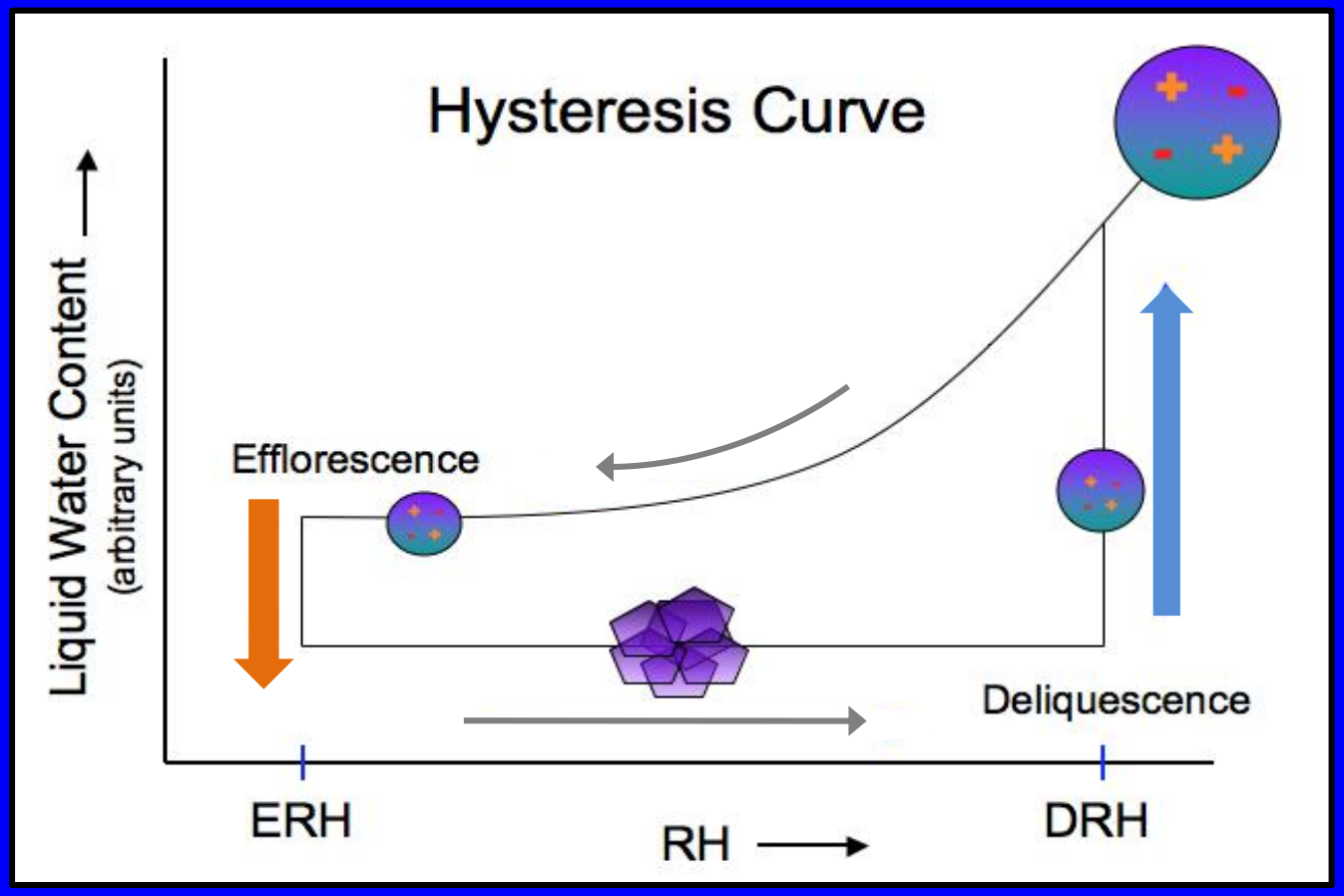
Czizco et al. 2013

Salt Deliquescence and Efflorescence

$H_2O_{(g)}$ +

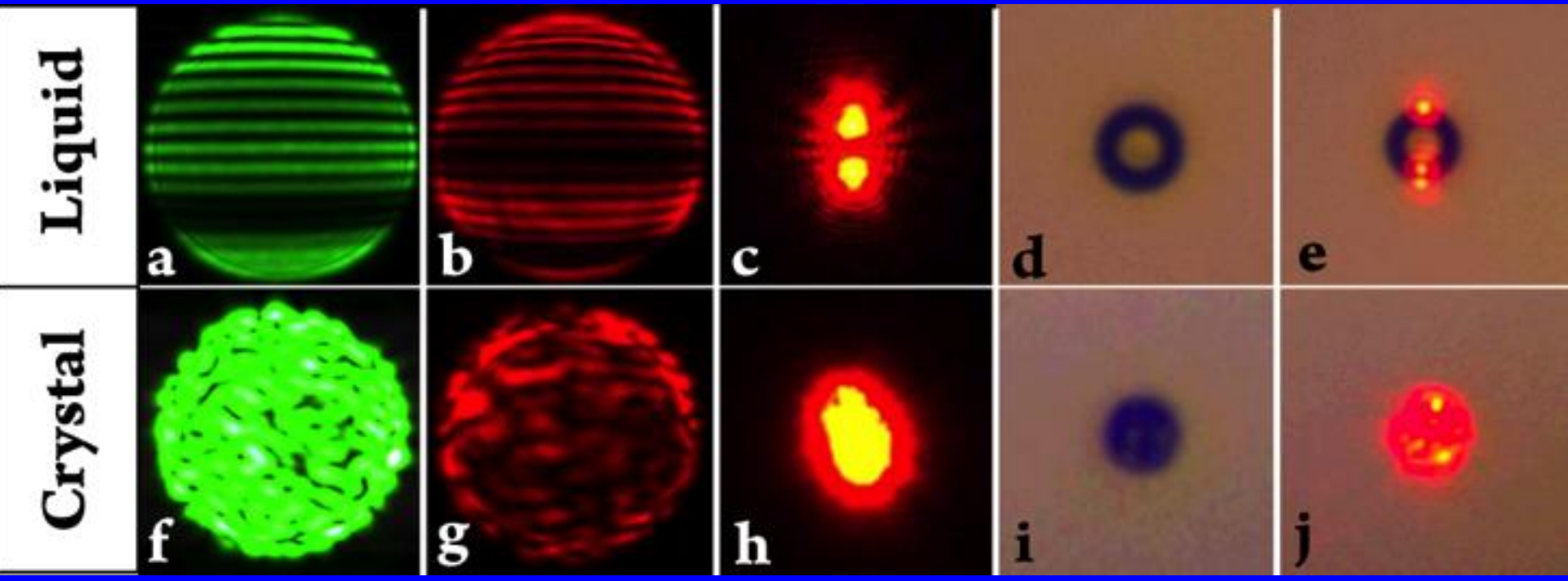
deliquescence

efflorescence



Usually aerosols assumed to remain liquid

Liquid vs Solid



Far field

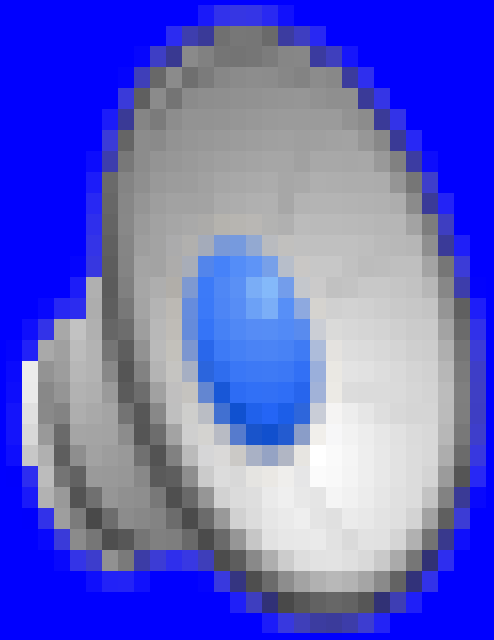
Far field

Near field

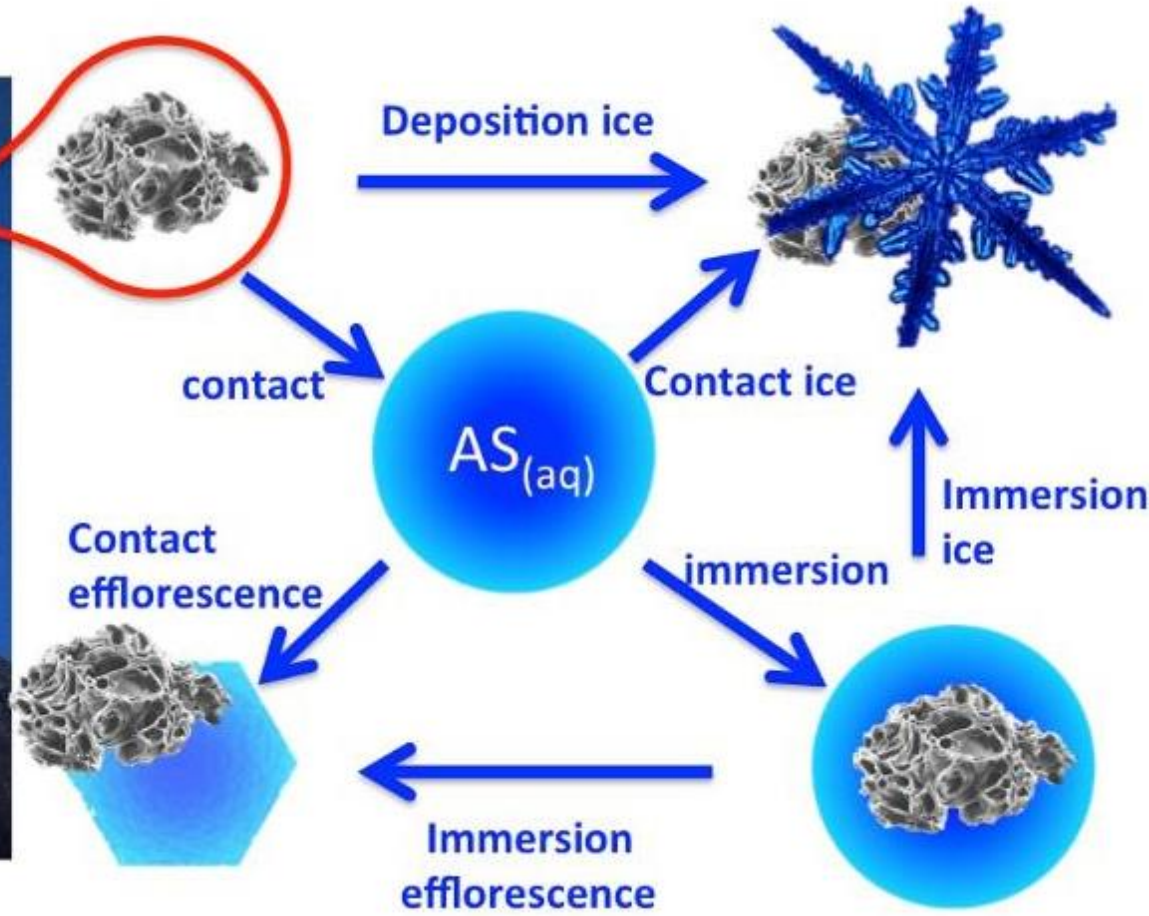
Bright field

combined

Contact Efflorescence



Impacts of Ash on Background Sulfate



- Can influence phase state of background aerosol
- Can serve as ice nucleus in atmosphere

Ash Properties

Magma Type	Basalt	Andesite	Rhyolite
SiO_2	50%	60%	70%
Viscosity	Low	Intermediate	High
Gas content	Low	Intermediate	High
Explosiveness	Nonexistent	Intermediate	Explosive

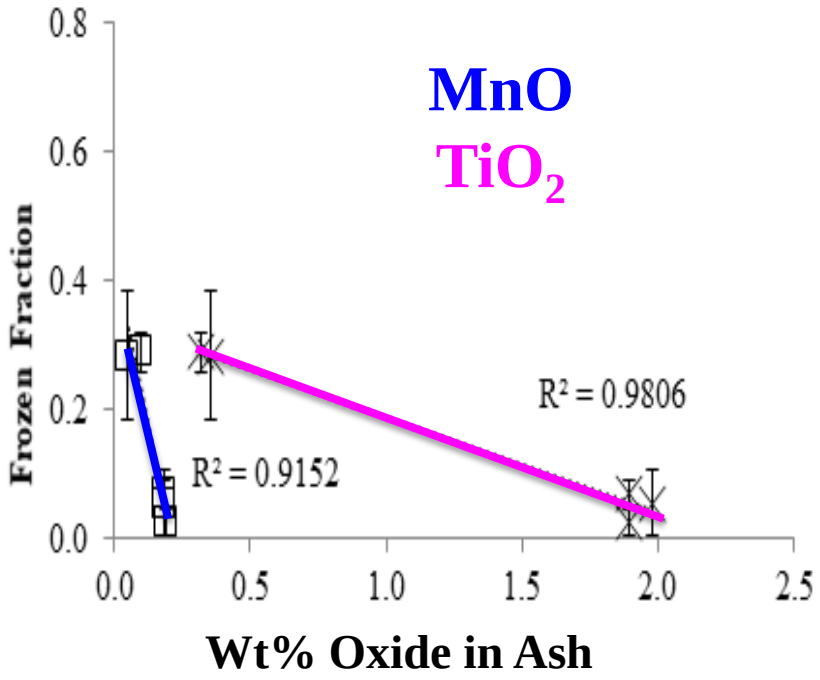
Our studies: **4 samples** **1 sample** **3 samples**

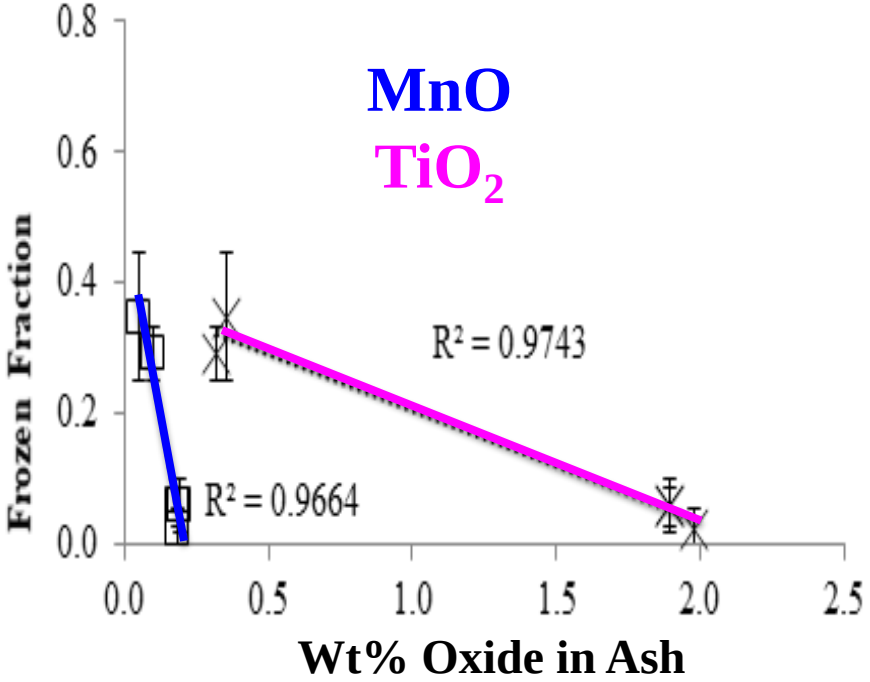
Immersion Ice Nucleation on Ash

- each droplet contains ash
- measure the frozen fraction vs temperature

Frozen Fraction at -30°C in Immersion Mode

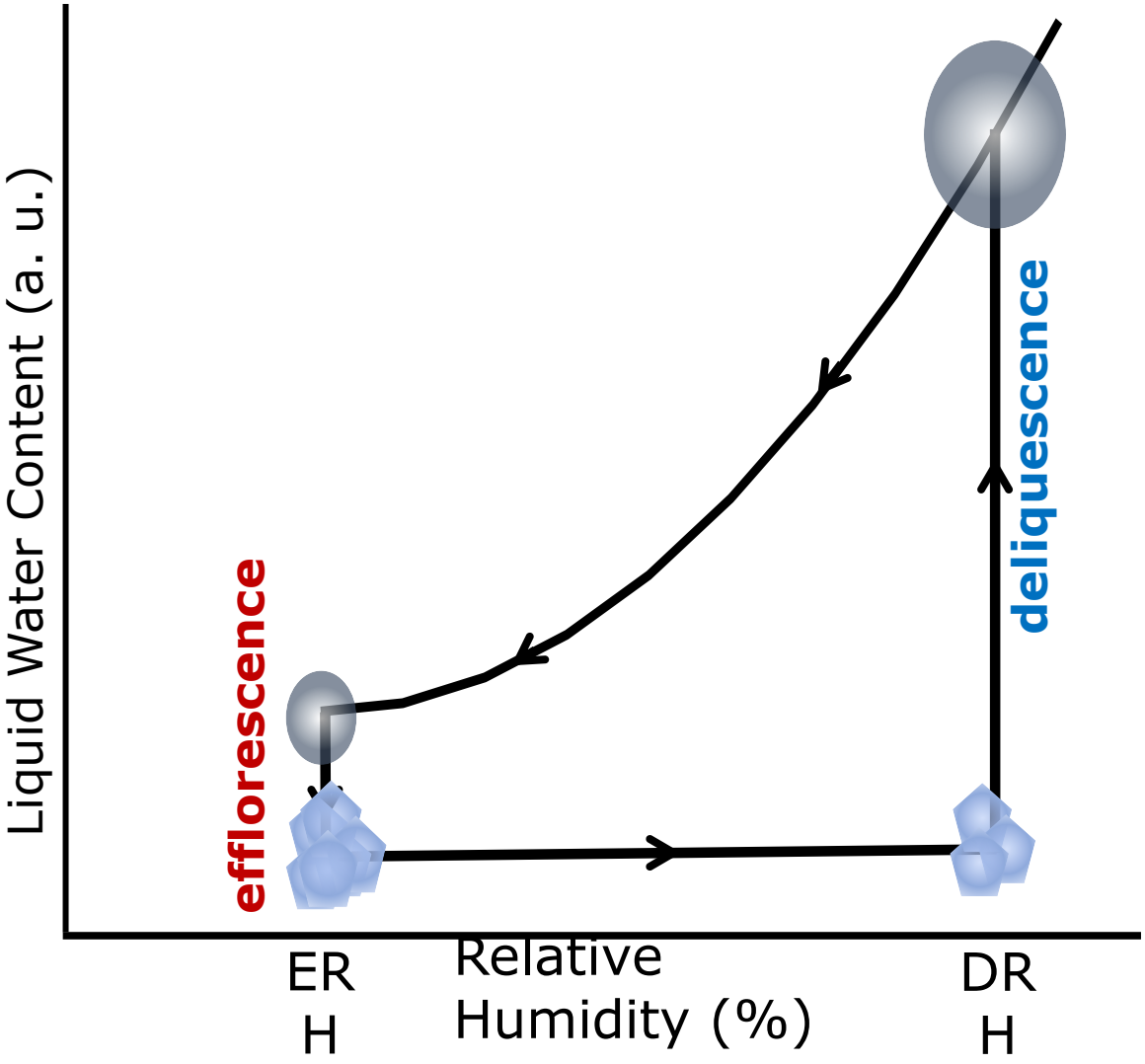
1 wt% ash **2 wt% ash**



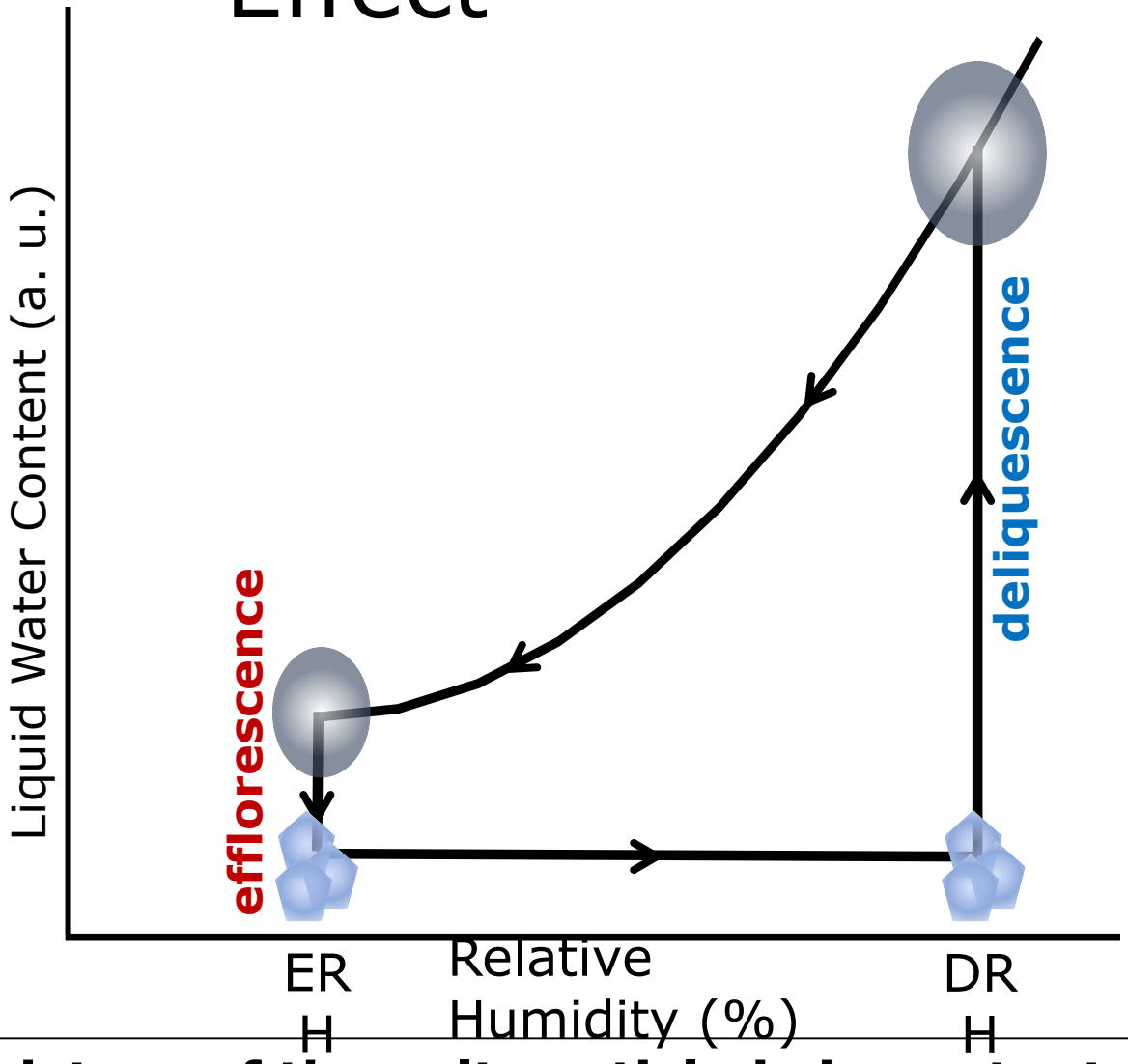


- more ash favors higher frozen fraction
- lower Mn, Ti (rhyolitic) favors higher frozen fraction
- role of specific ion interactions (small highly charged ions may not fit into ice lattice well)

Hysteresis Effect



Hysteresis Effect



The RH history of the salt particle is important and explains