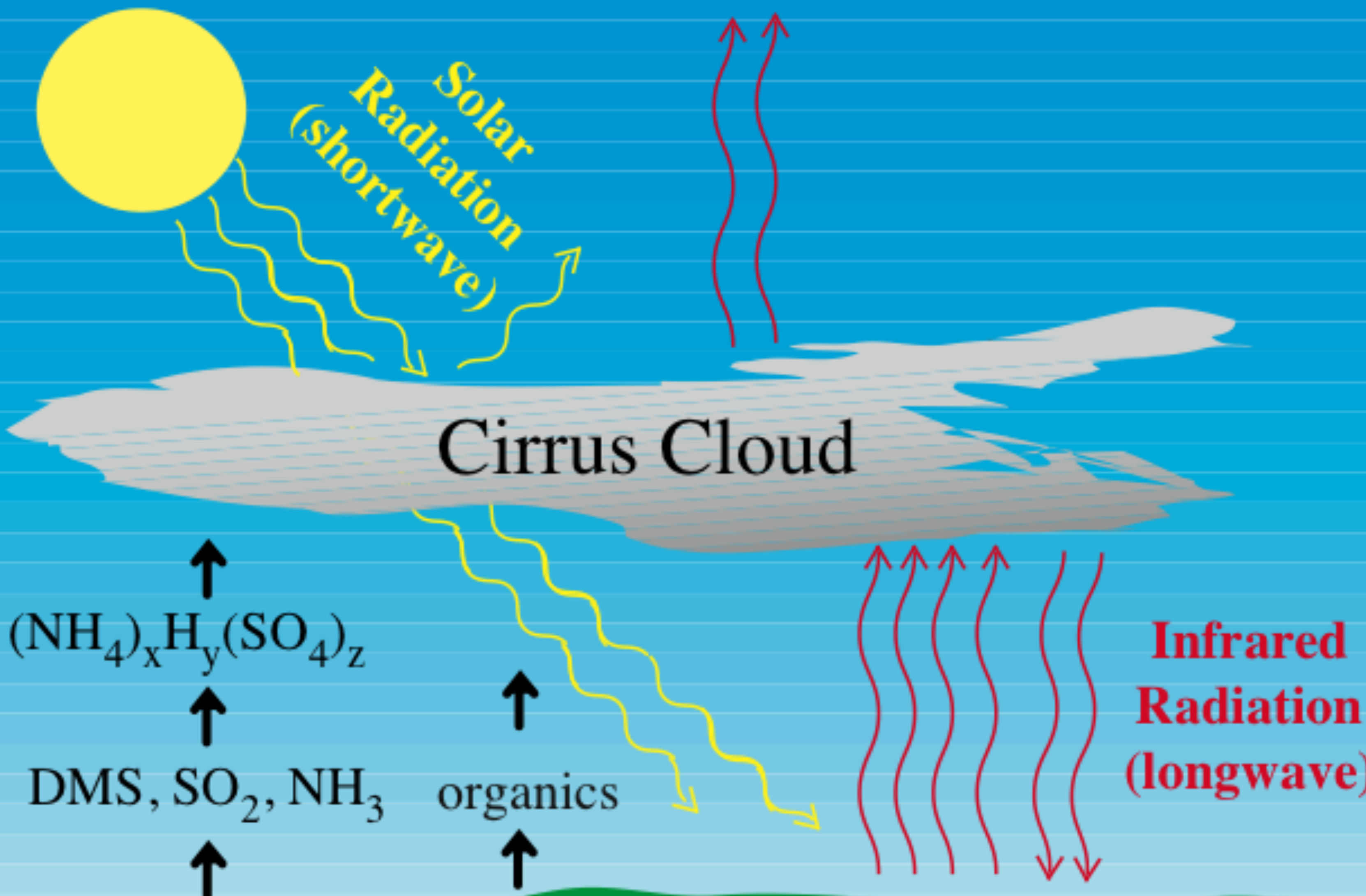
As cold as ice: cirrus cloud formation in the upper troposphere

Margaret A Tolbert

Cirrus Clouds and Climate

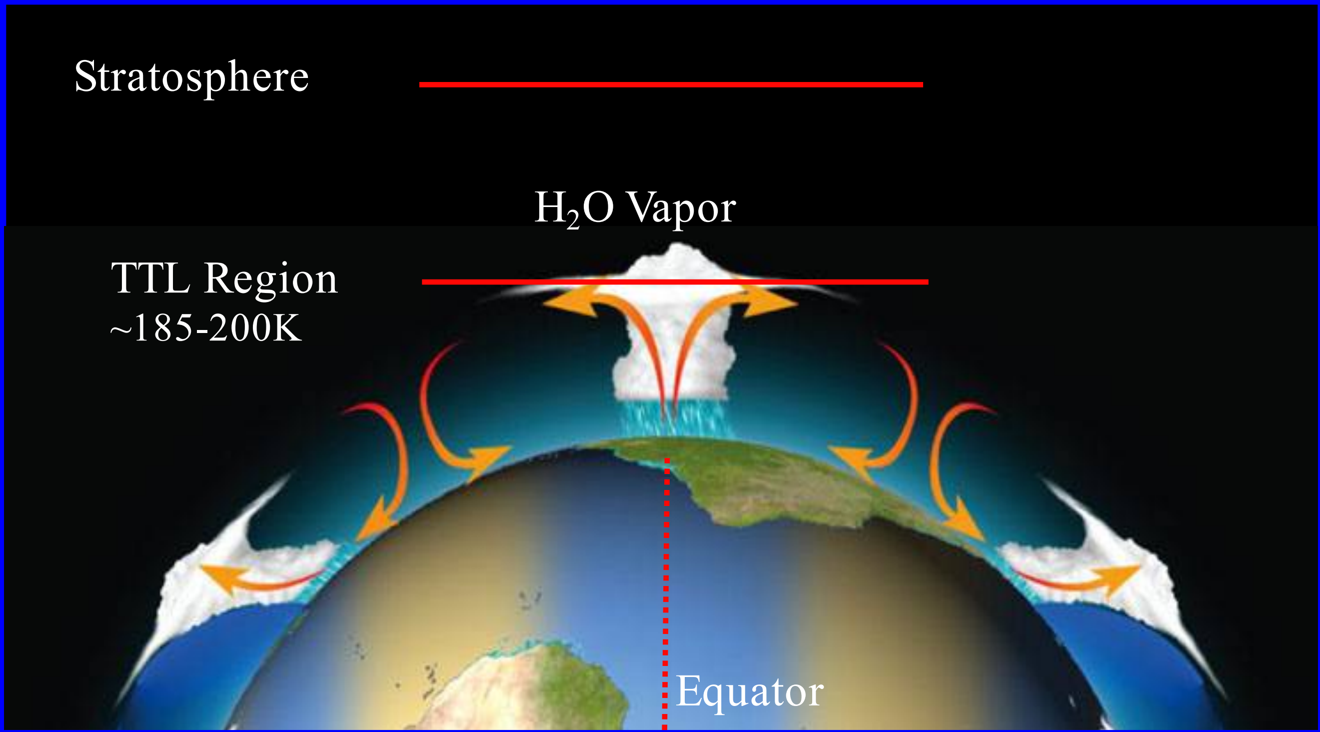


- » Large uncertainties in climate forcing
- » Cloud properties depend on nucleation

Cirrus Clouds

- Mainly ice
- Form in upper troposphere at low temperature
- visible cirrus: cover 30% of earth
- subvisible cirrus: present up to 75% time in tropics
- climate impact: net warming, but details matter
- nucleation mechanism uncertain

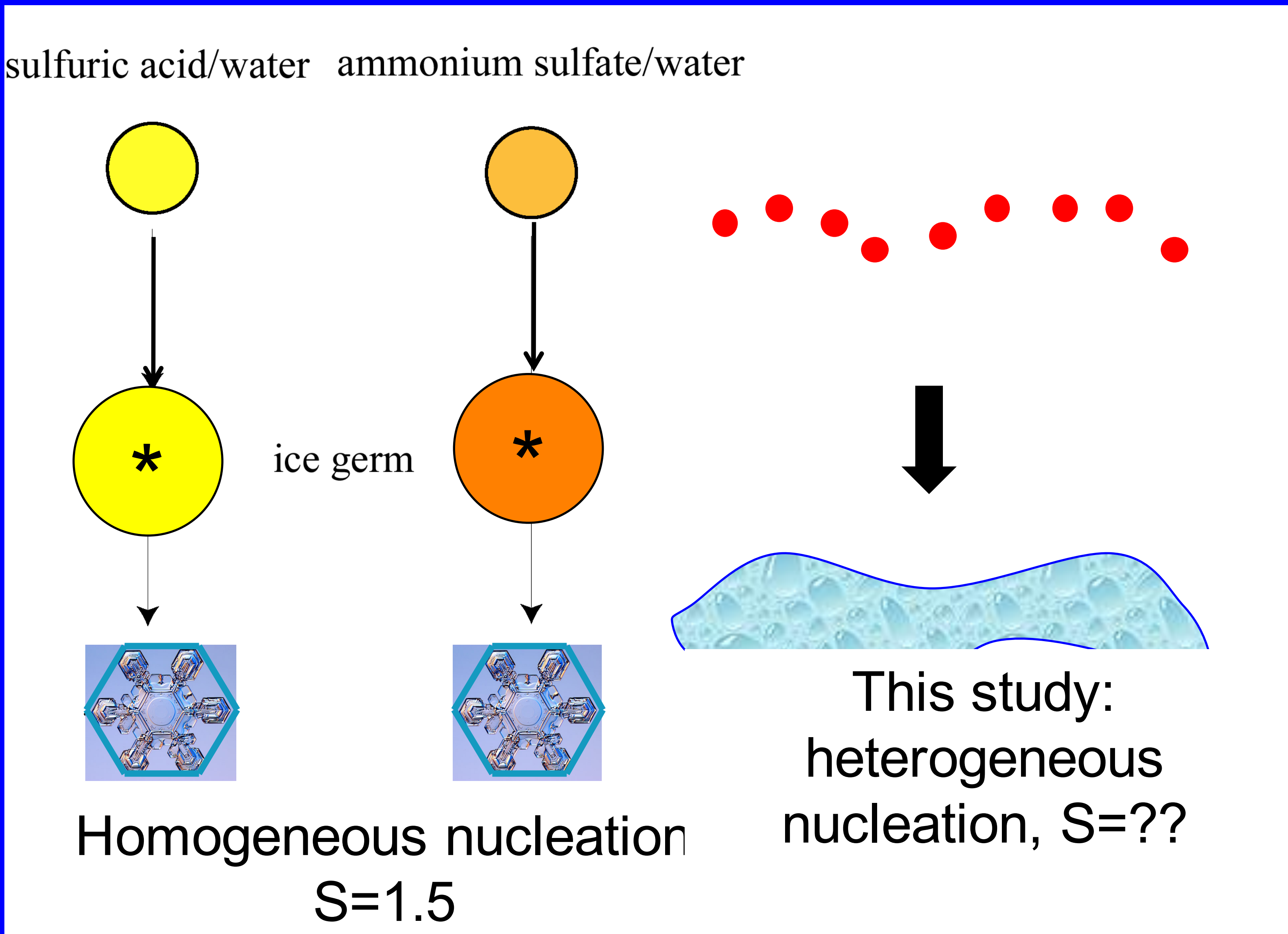
Tropical Tropopause Layer



Freeze-dry air ascending into the stratosphere

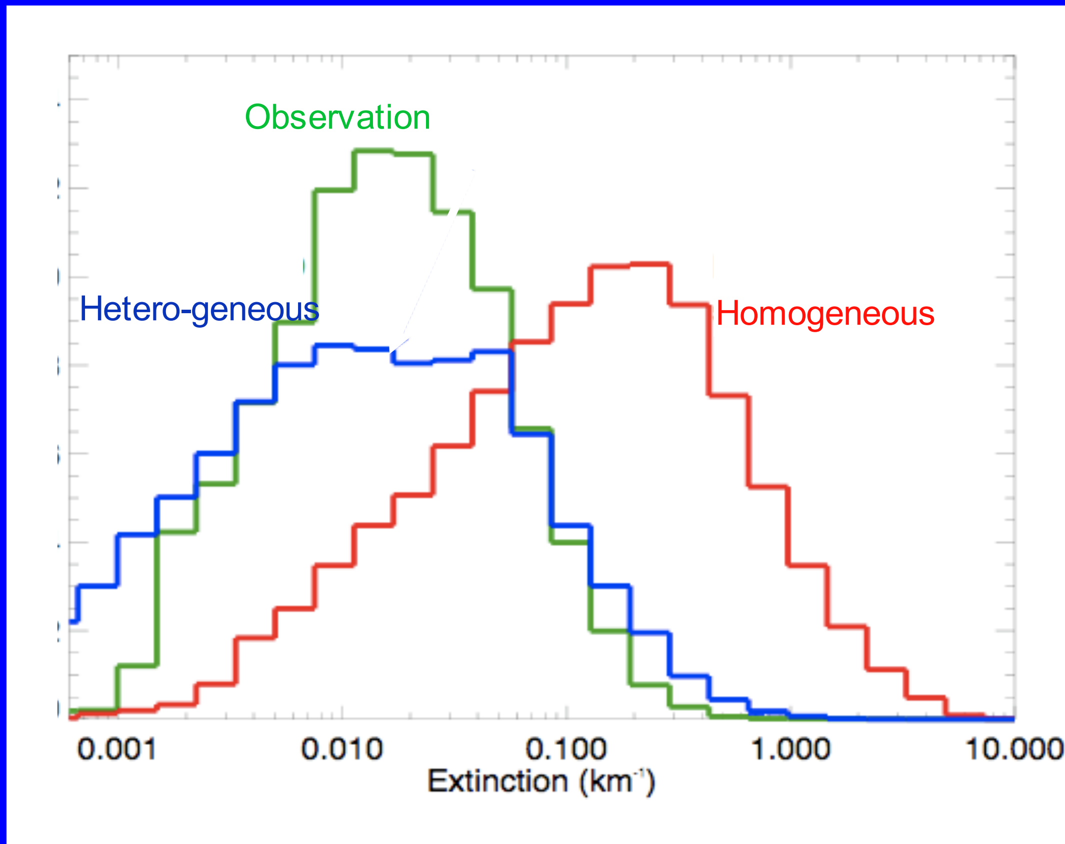
Cirrus nucleation impacts water (ex//increase saturation ratio from 1.0 to 1.2 causes 10-15% increase in stratospheric H_2O).

Ice Saturation Ratio: $S = P_{H2O}/VP_{ice}$



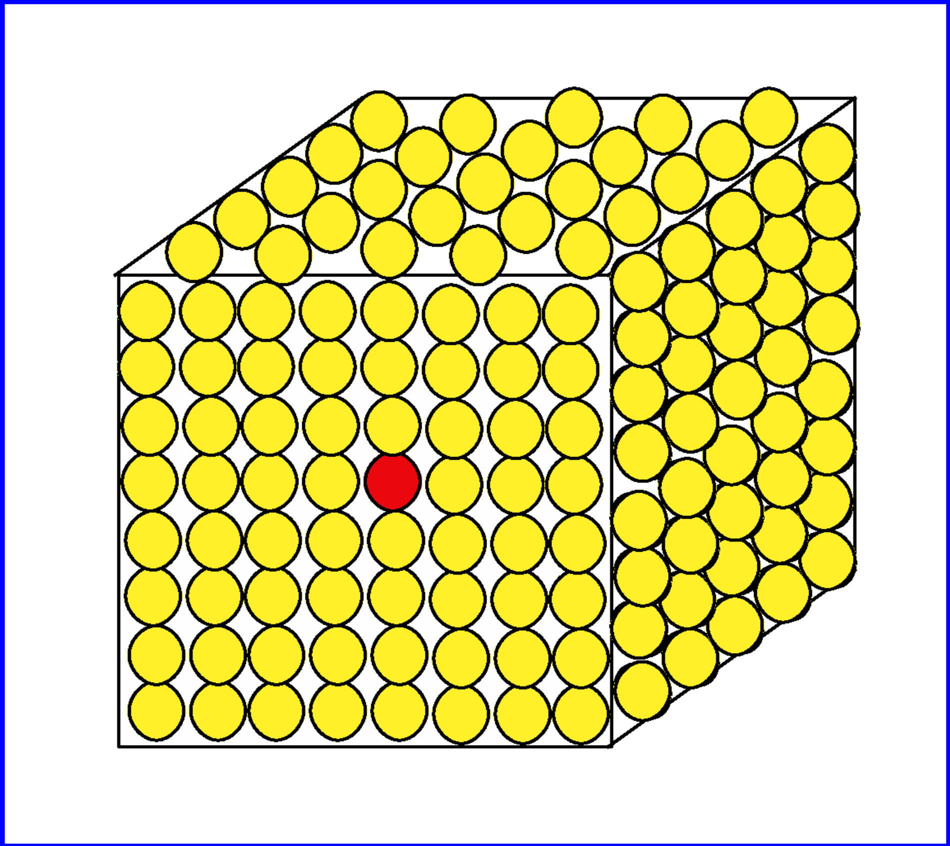
Ice Nucleation in the Upper Troposphere

Adapted from *Jensen et al.*, (2010)



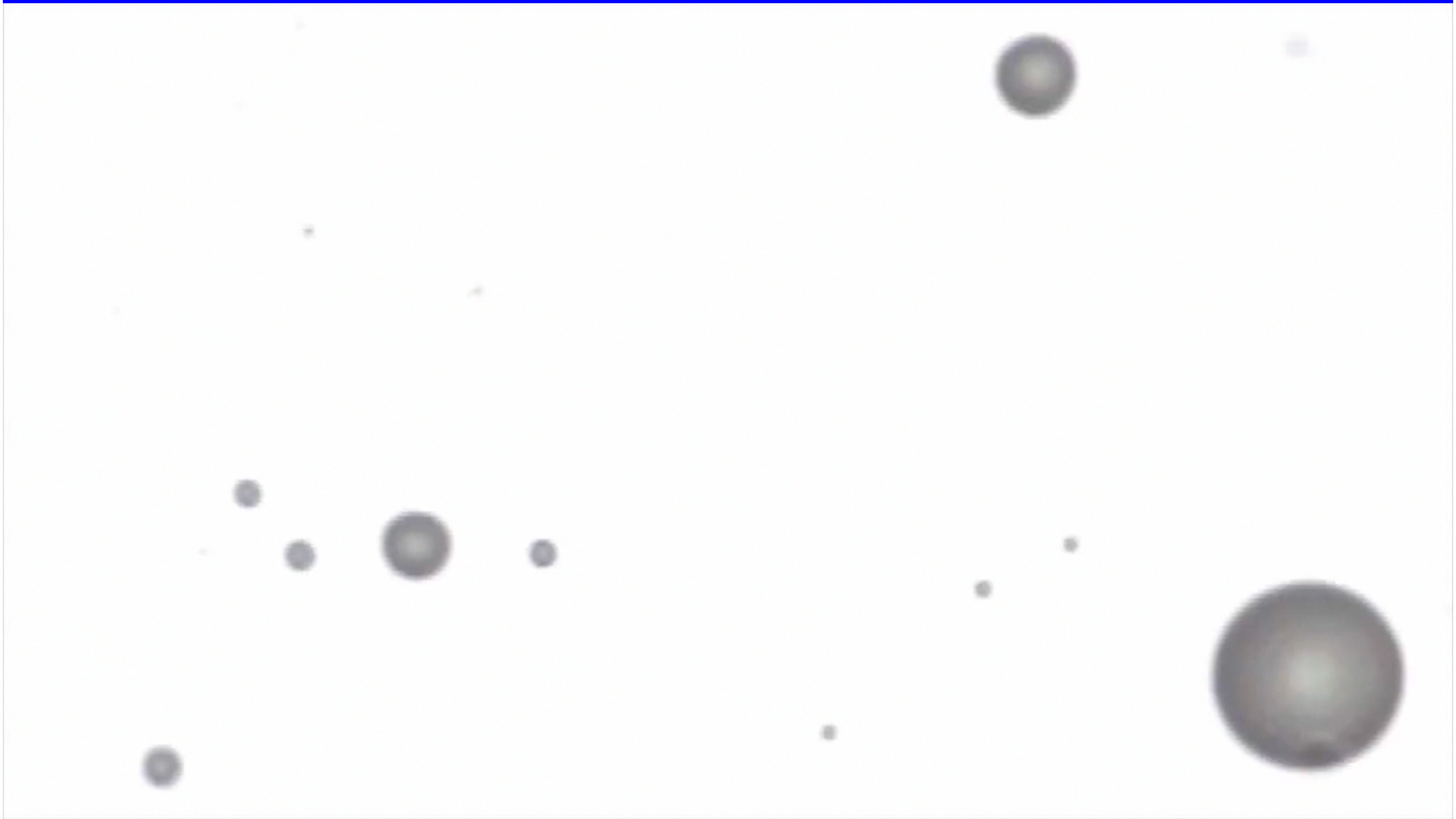
Some observations and modeling studies do not support homogeneous ice nucleation

Cirrus Cloud Nucleation Selective



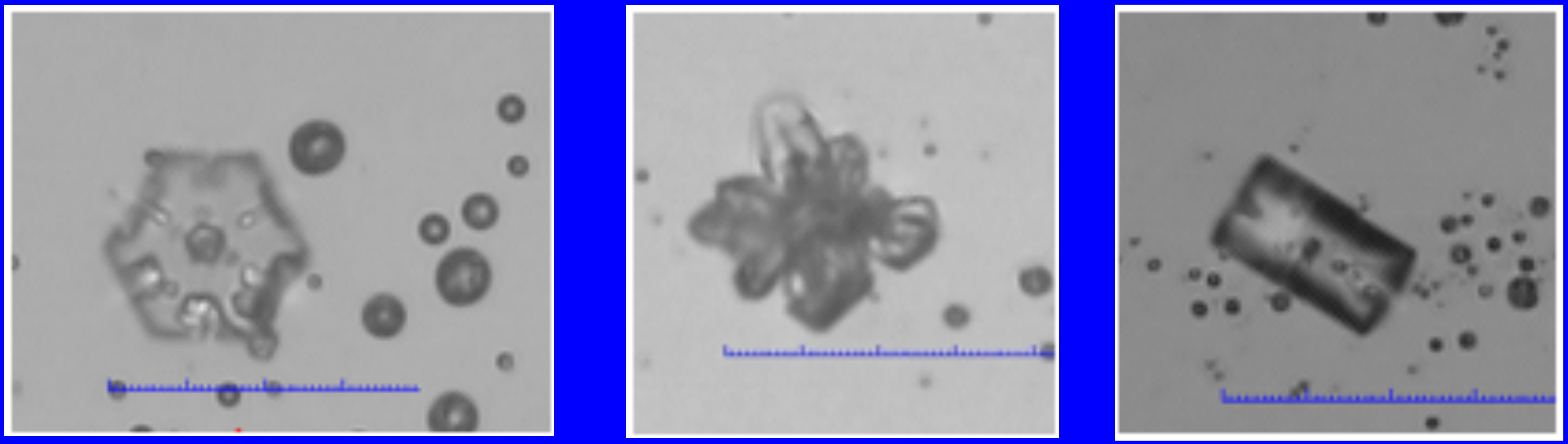
Only 1 in 10^4 aerosol particles nucleate ice!

Selective Ice Nucleation

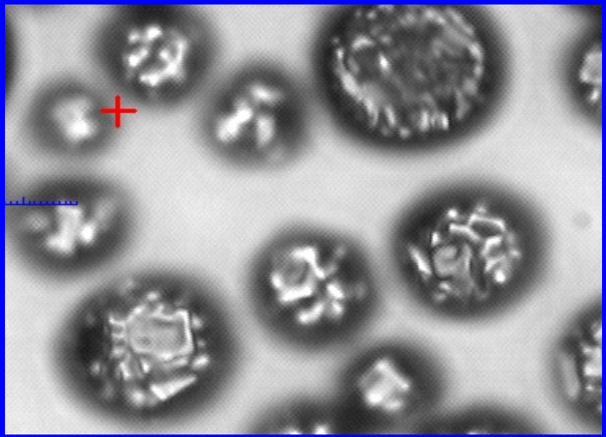


Heterogeneous Ice Nucleation Selective

Heterogeneous nucleation:



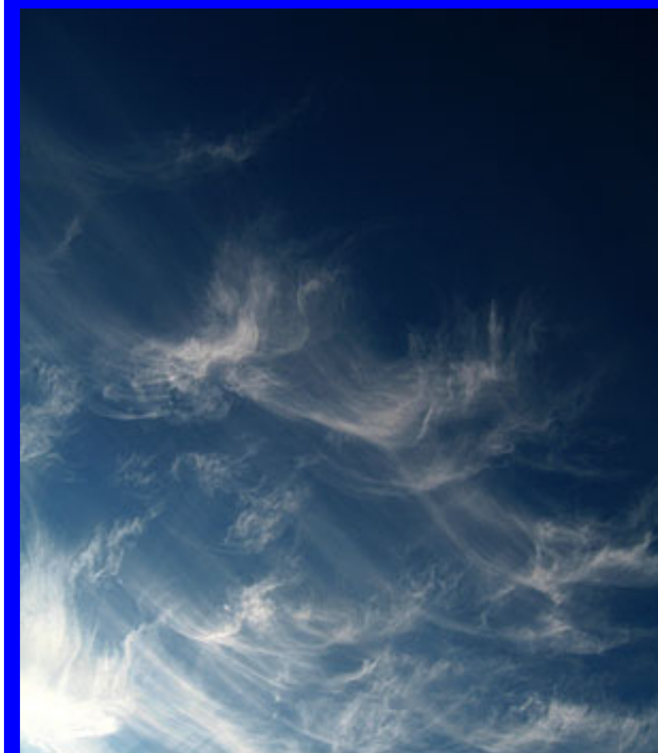
Homogeneous nucleation:



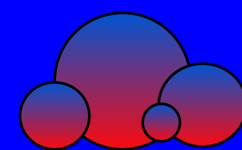
Factors important for Ice Nucleation

Cirrus: Optically thin due to low ice concentration

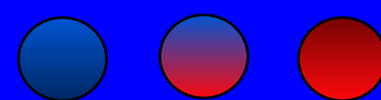
Only 1 in ~10000 particles act as IN



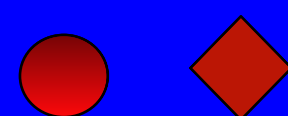
1. Particle size



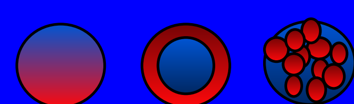
2. Composition



3. Phase



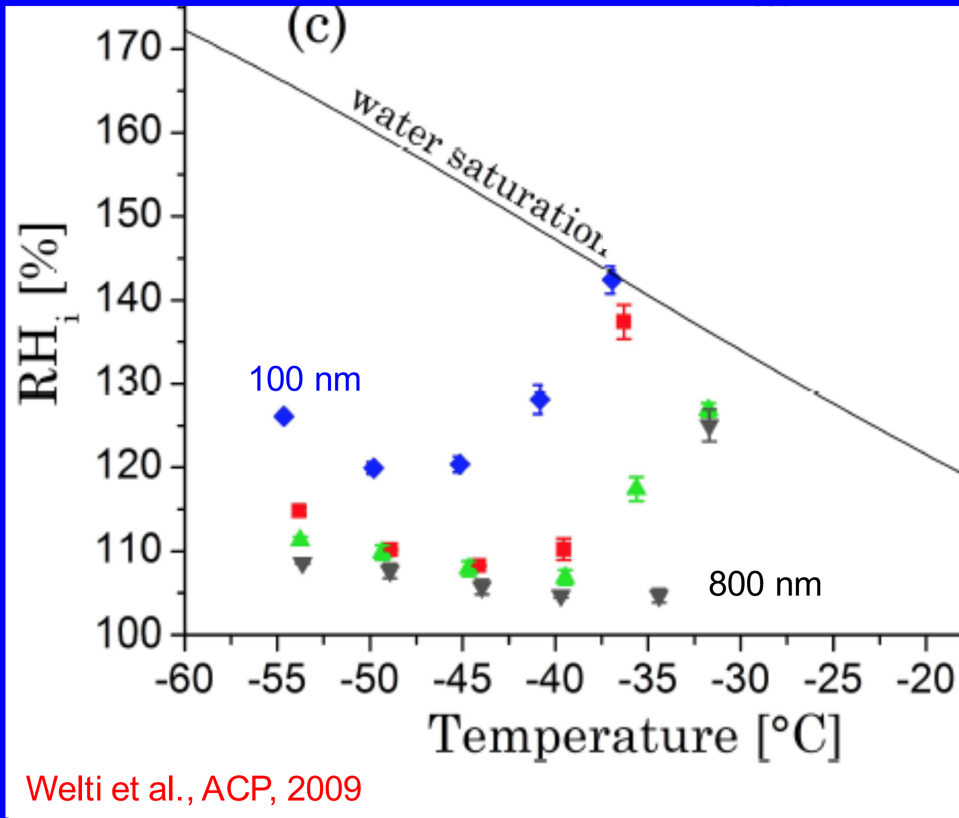
4. Chemical Distribution



Increasingly difficult to measure

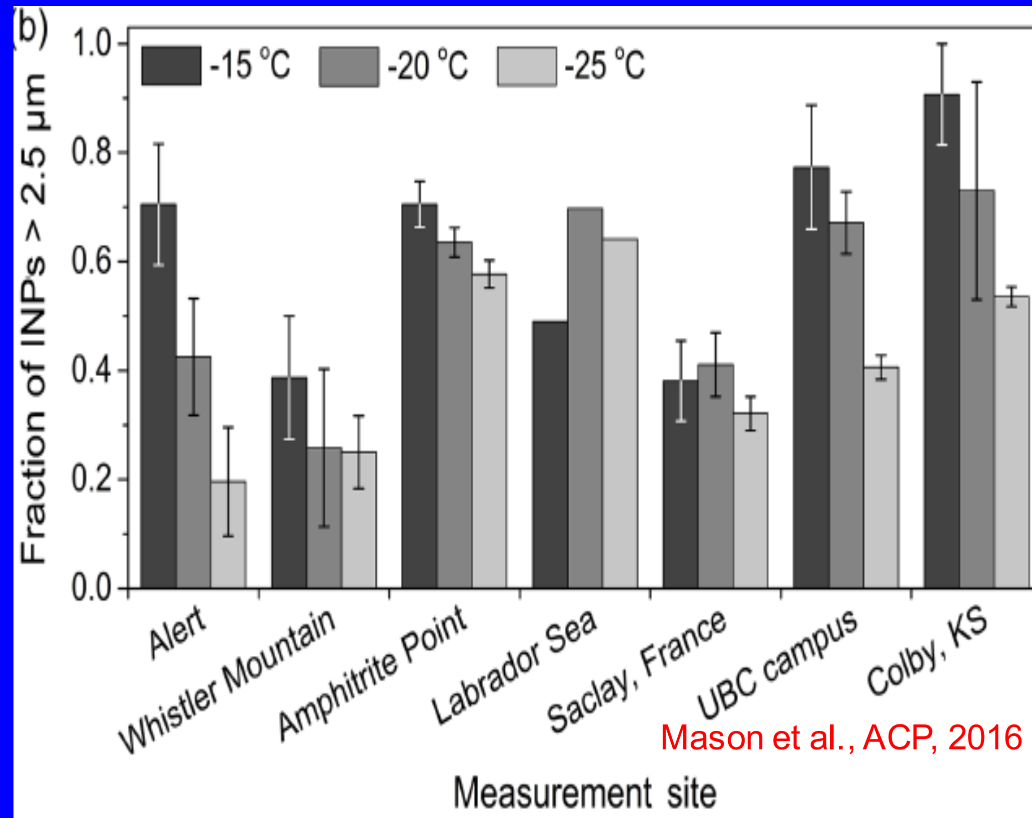
Large particles better ice nuclei

Lab (S_{ice} on illite)



Small particles require higher S_{ice}

Field (size of residual)



Most ice residuals supermicron

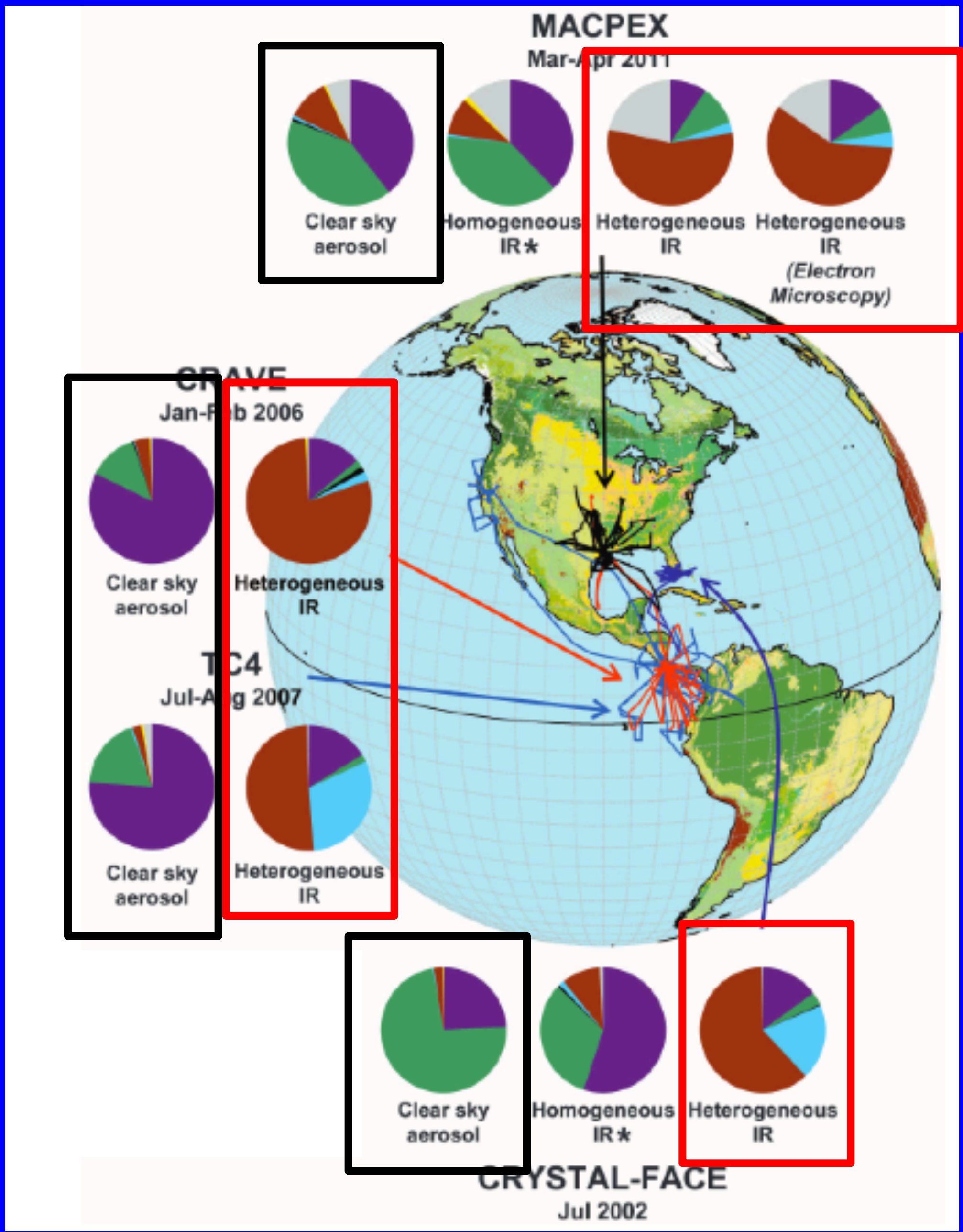
Factors important for Ice Nucleation

Cirrus: Optically thin due to low ice concentration

Only 1 in ~10000 particles act as IN

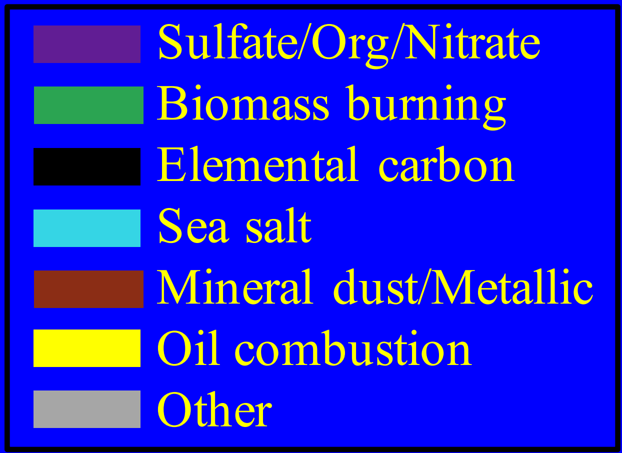
1. Particle size — Larger better
2. Composition
3. Phase
4. Chemical Distribution

Mineral Dust Excellent IN



Czizco et al. 2013

- 1000-3000 Tg/yr mineral aerosol emitted in the atmosphere

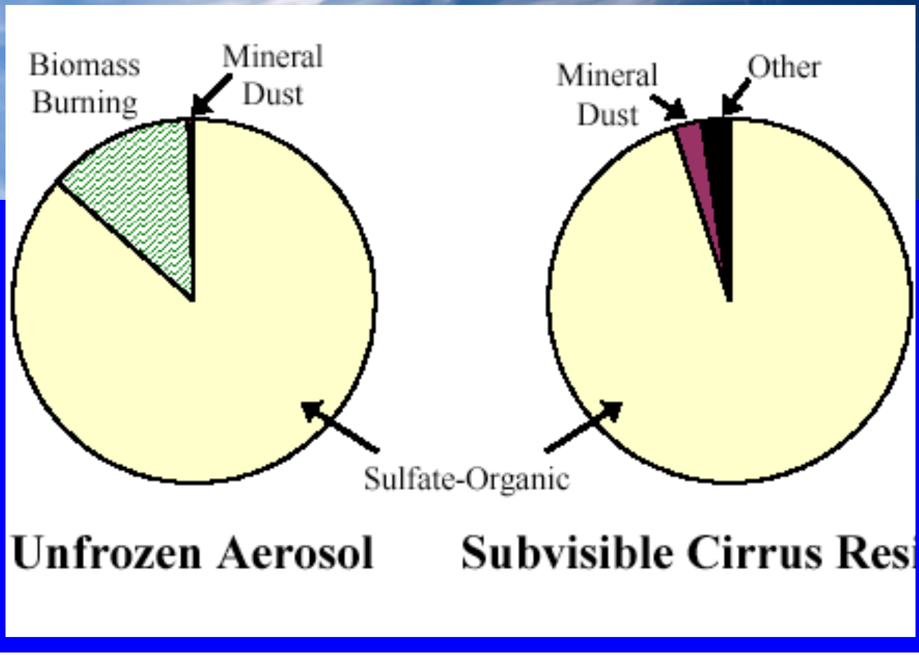


Cirrus IN in the Tropical Tropopause Layer (TTL)

Species considered good heterogeneous IN are not present in TTL

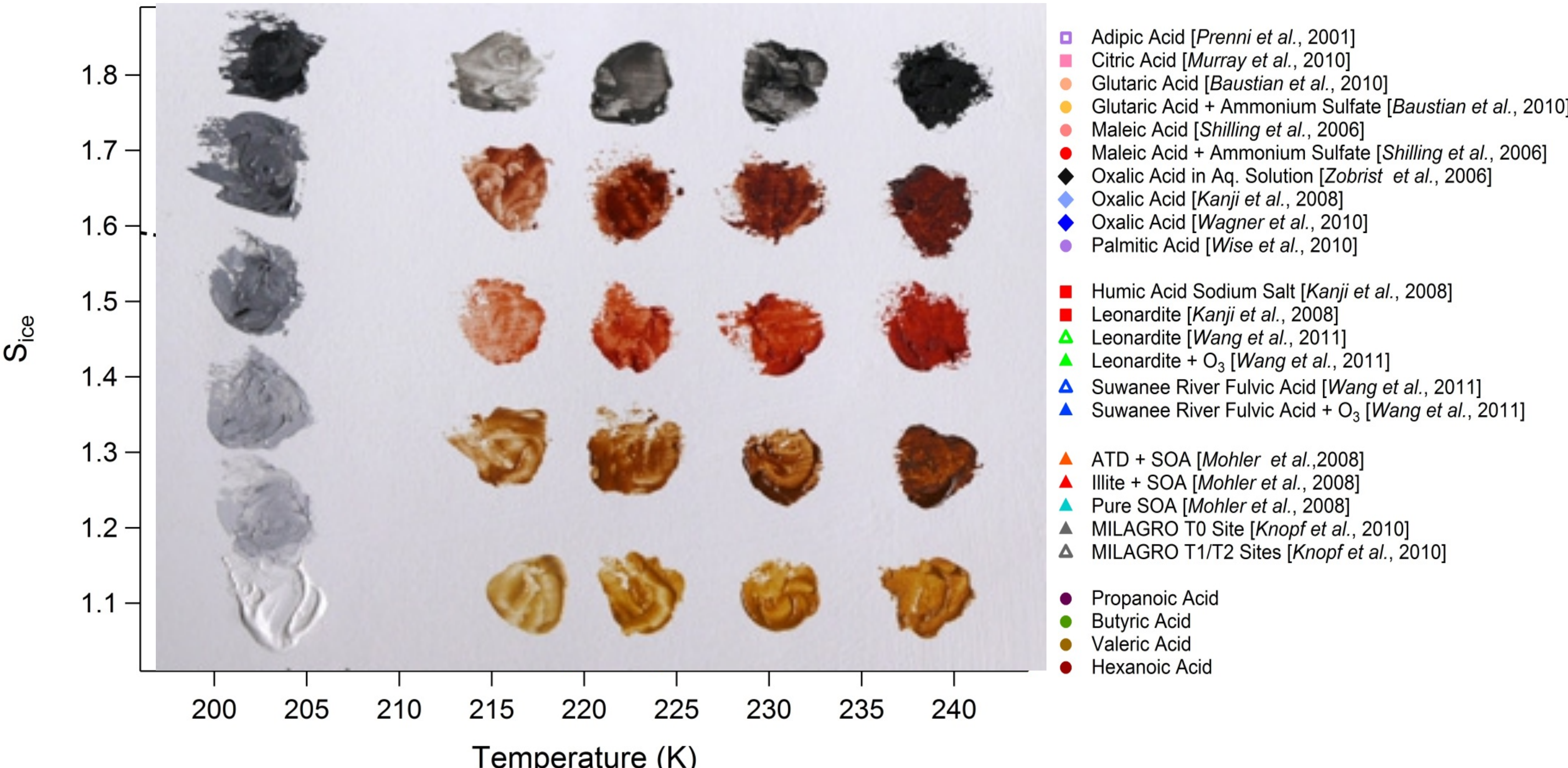
- sulfate/organic main IN in TTL

Froyd et al., 2009



Heterogeneous Ice Nucleation on Organics

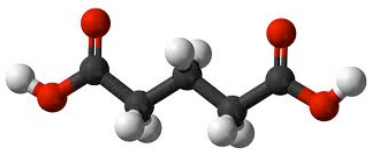
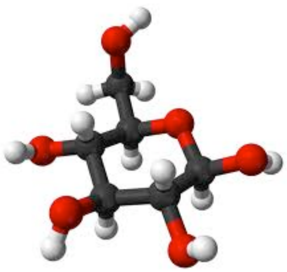
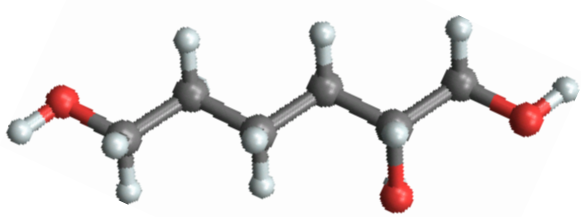
adapted from Knopf et al., 2010



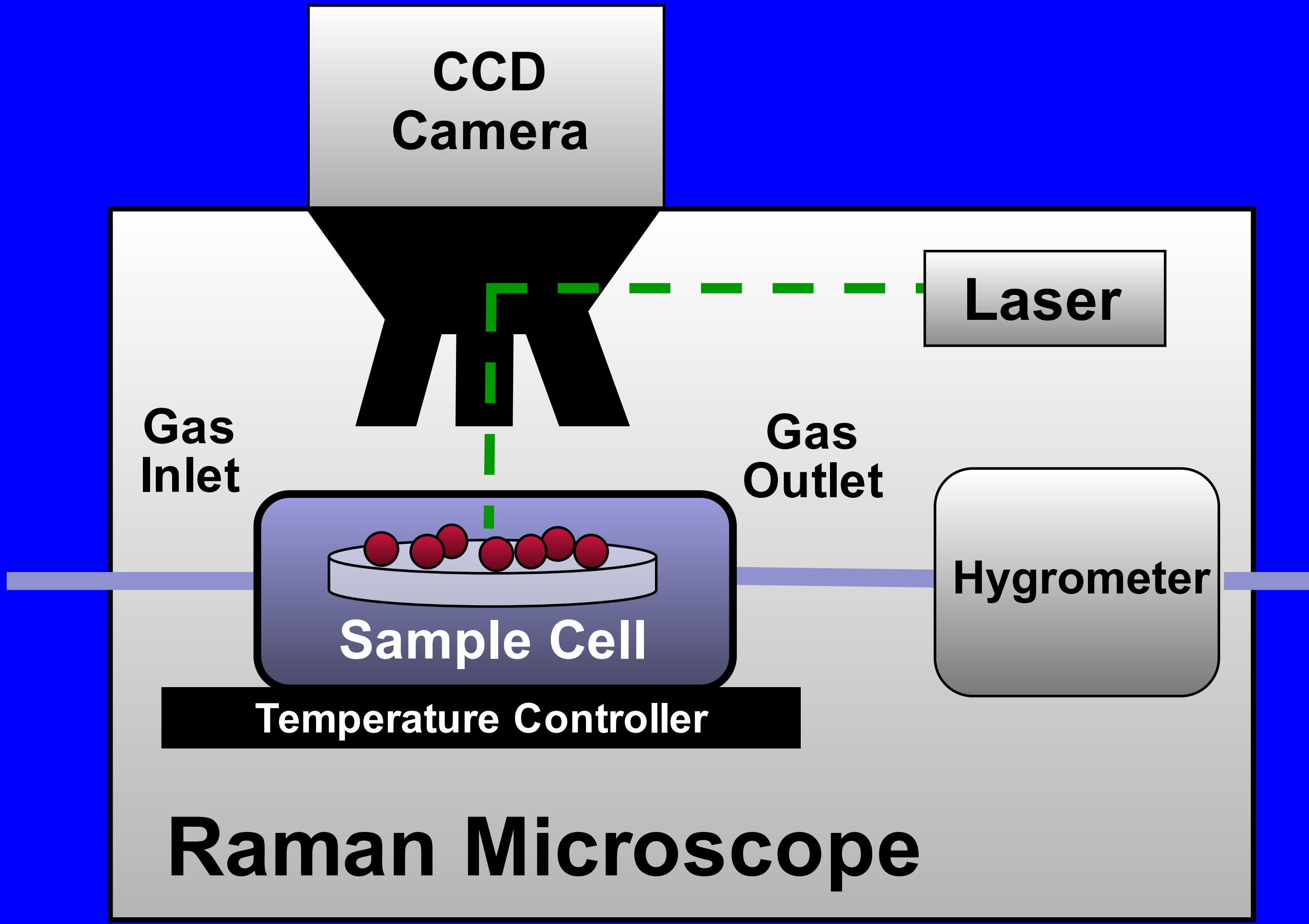
More types of information may help clarify the role of organics

Laboratory studies: role of organics uncertain

Organics Studied in Present Work

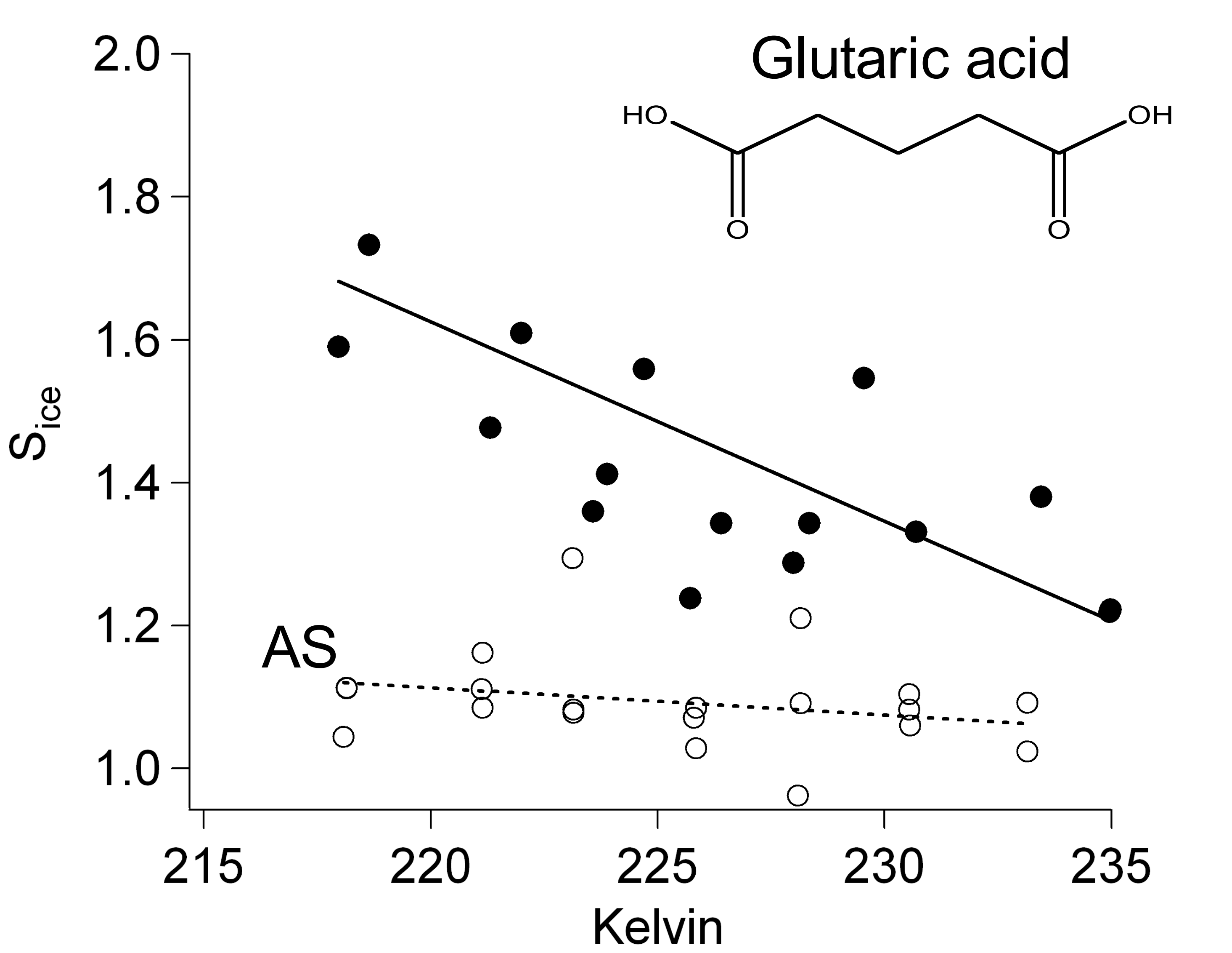
	glutaric acid	soluble, low vp
	Glucose	forms a glass
	1,2,6-hexanetriol	phase separates

Raman Microscopy: One Particle at a Time



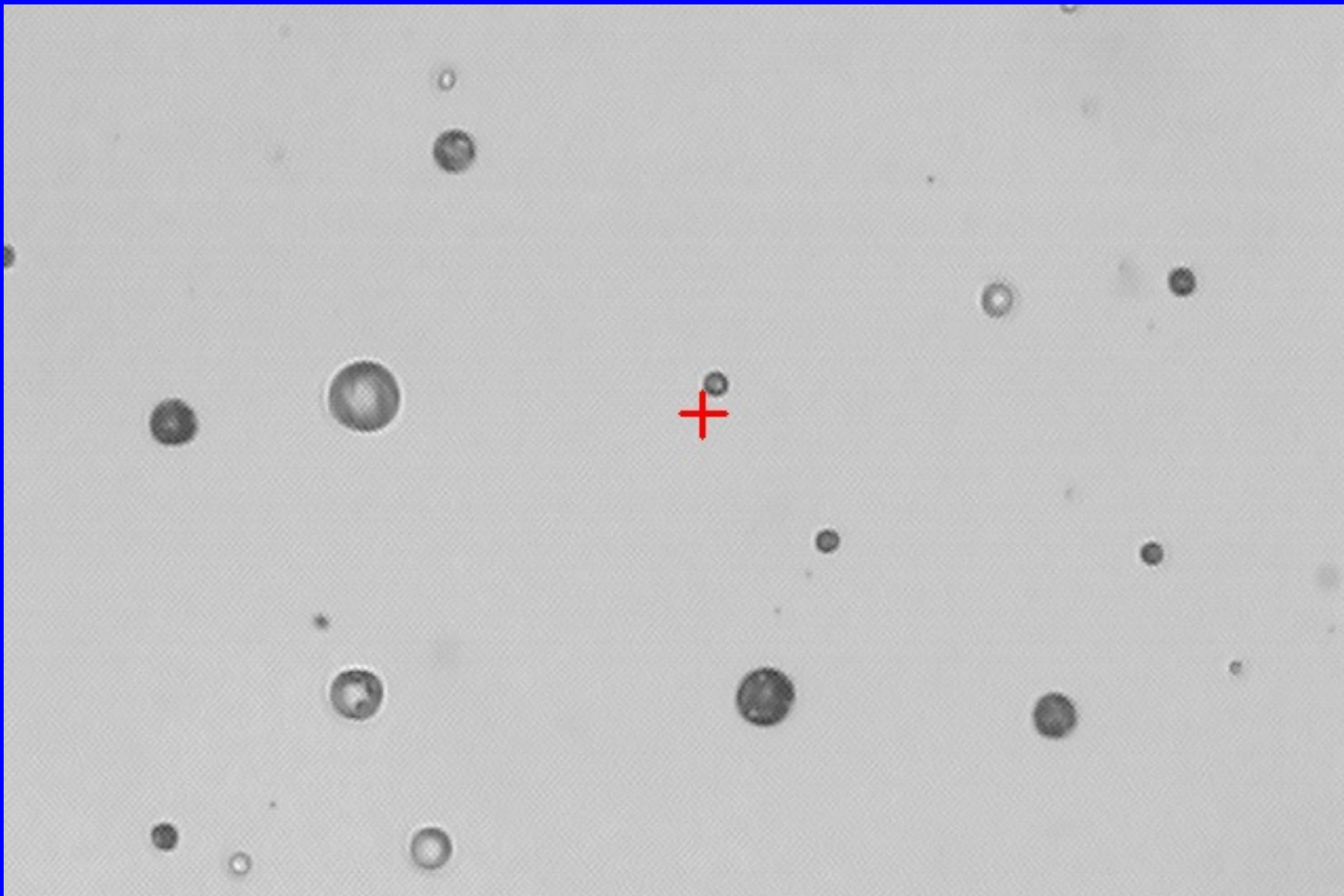
$$S_{ice} = P_{H2O}/VP_{ice}$$

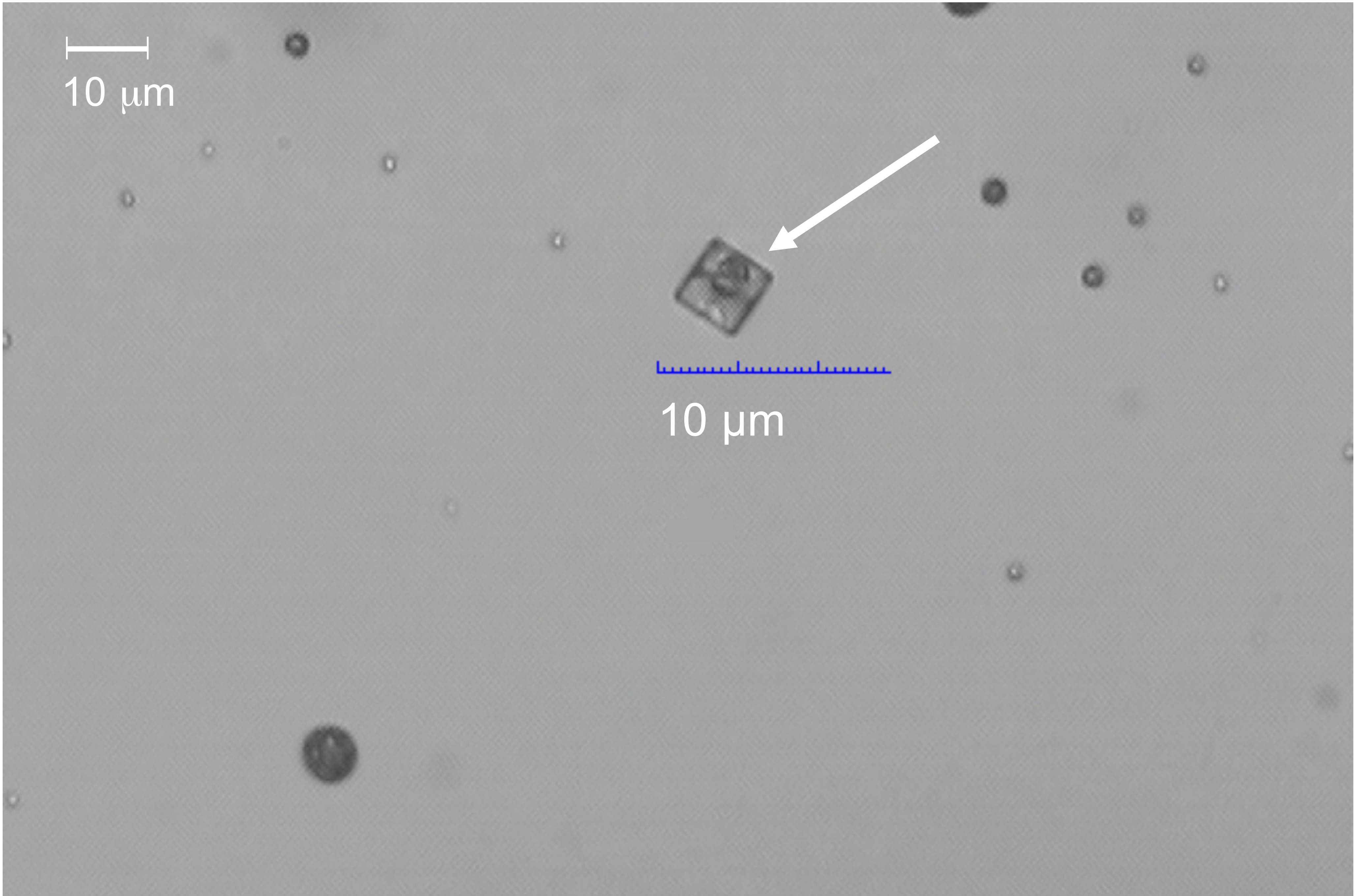
Comparison of heterogeneous ice nucleation



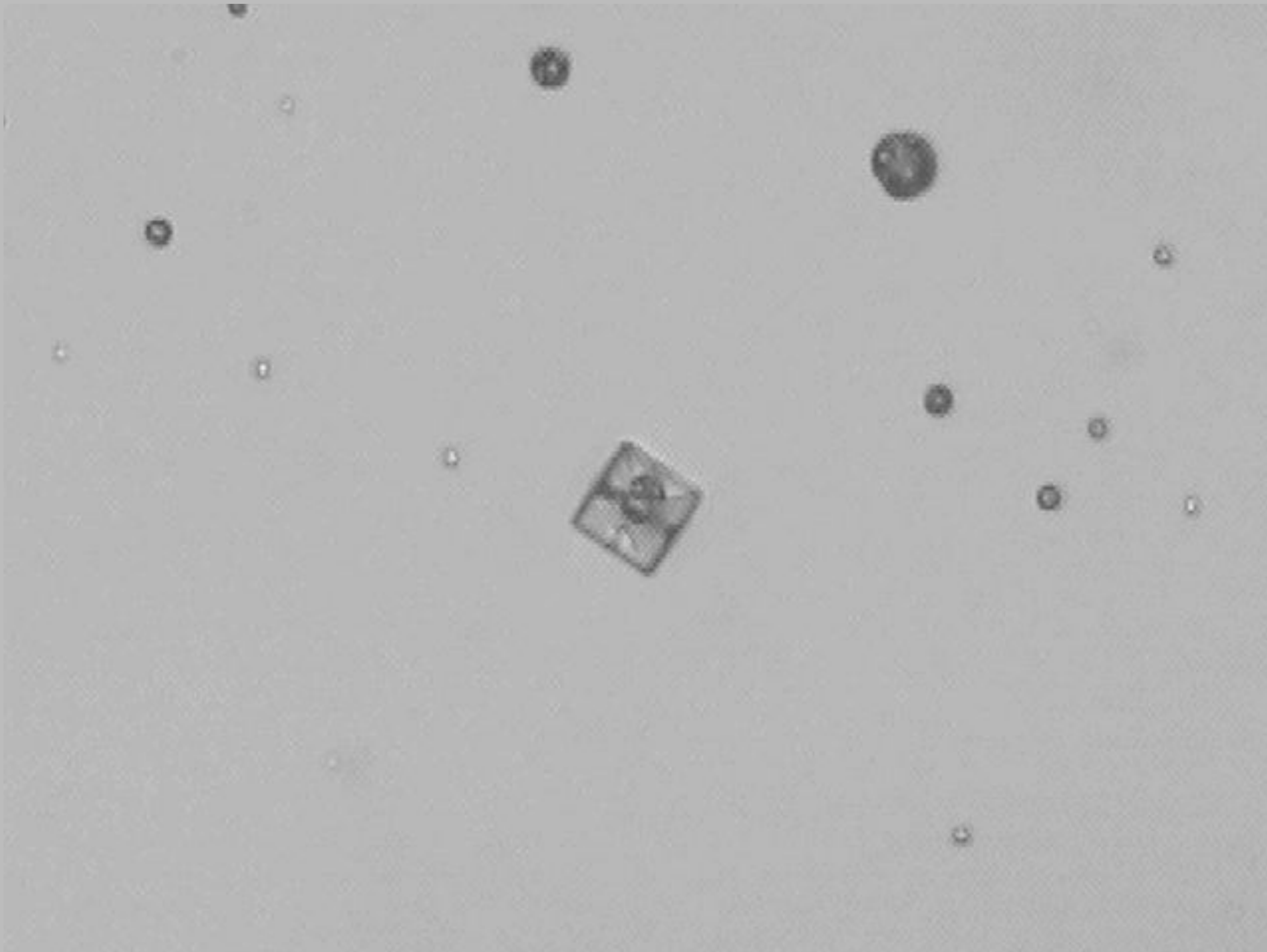
Glutaric acid less effective ice nucleator than AS

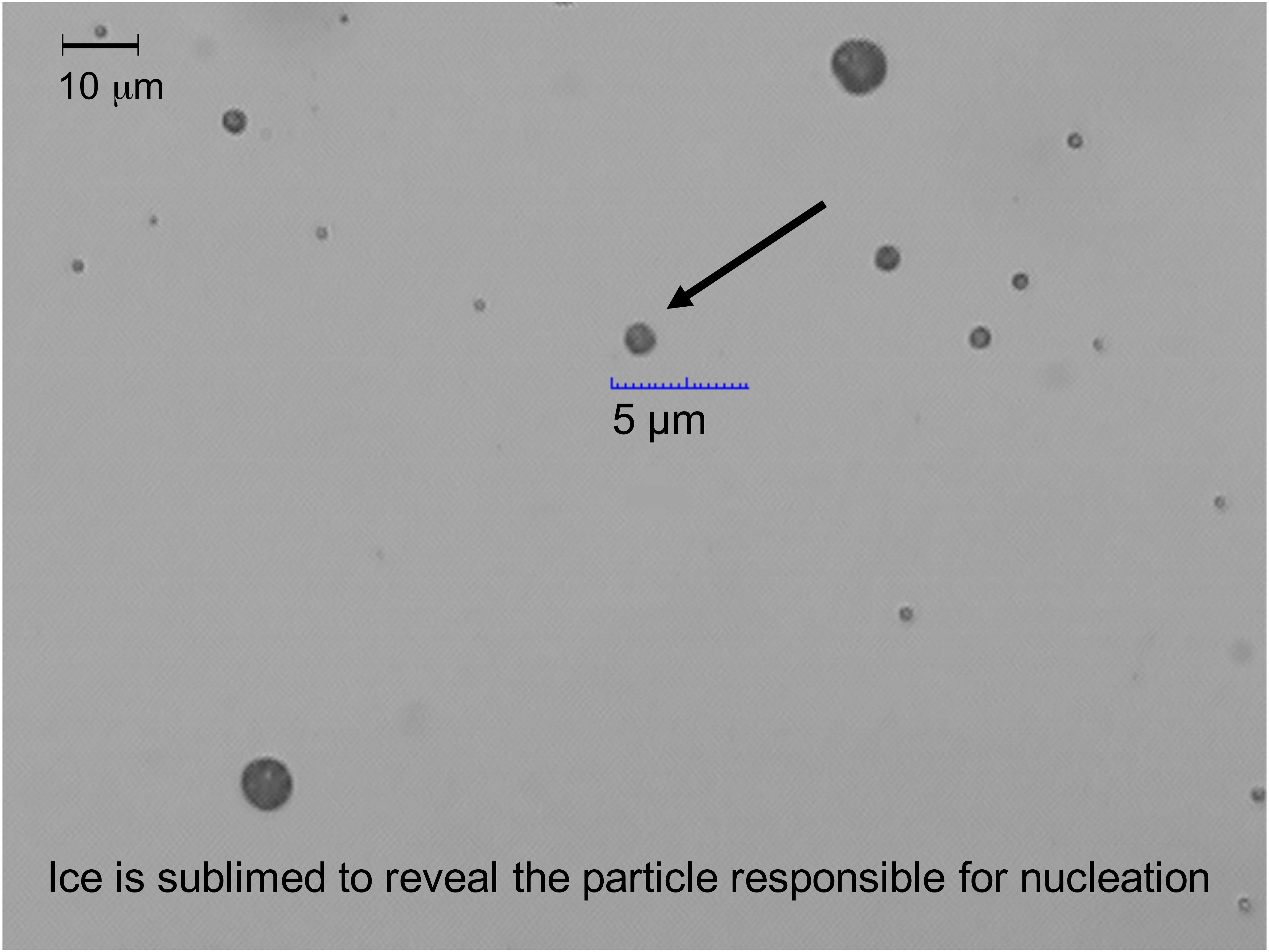
Mixed Grid of externally mixed AS and Glutaric Acid



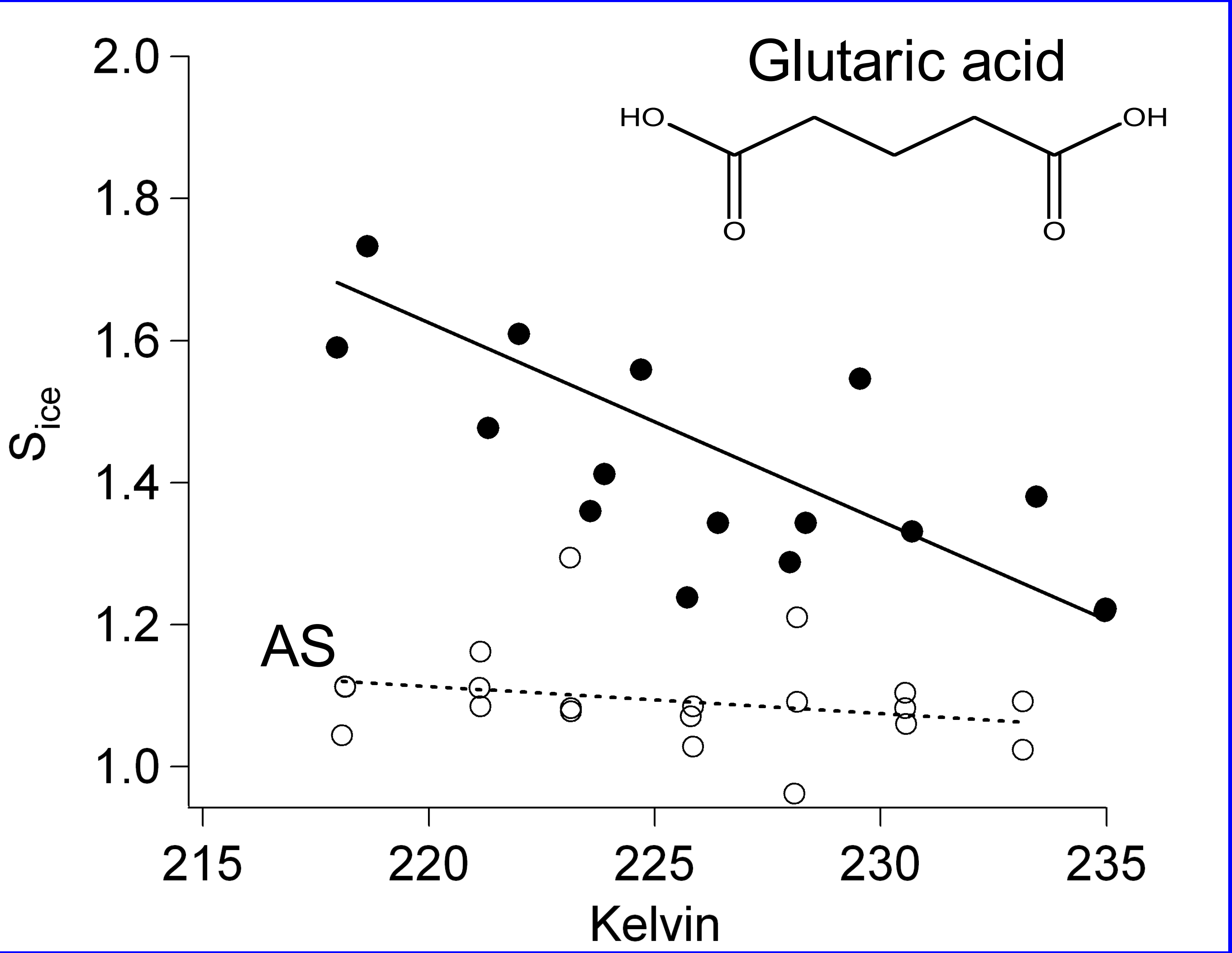


Ice nucleation on external mixture of glutaric acid and AS



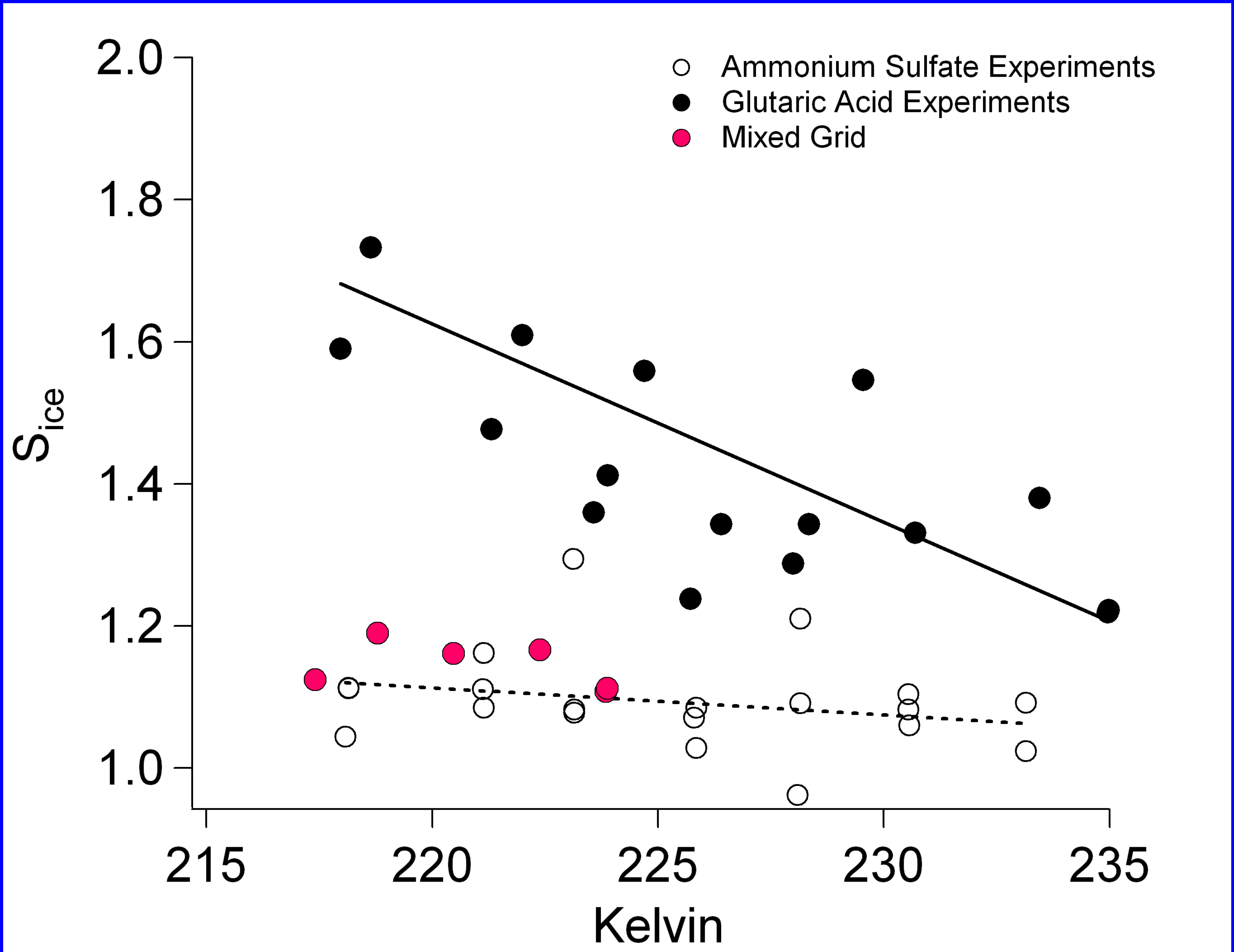

10 μm
5 μm
Ice is sublimed to reveal the particle responsible for nucleation

Comparison of heterogeneous ice nucleation



Glutaric acid less effective ice nucleator than AS

Ice Nucleation on Externally Mixed Particles

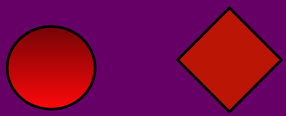
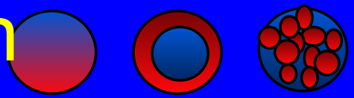


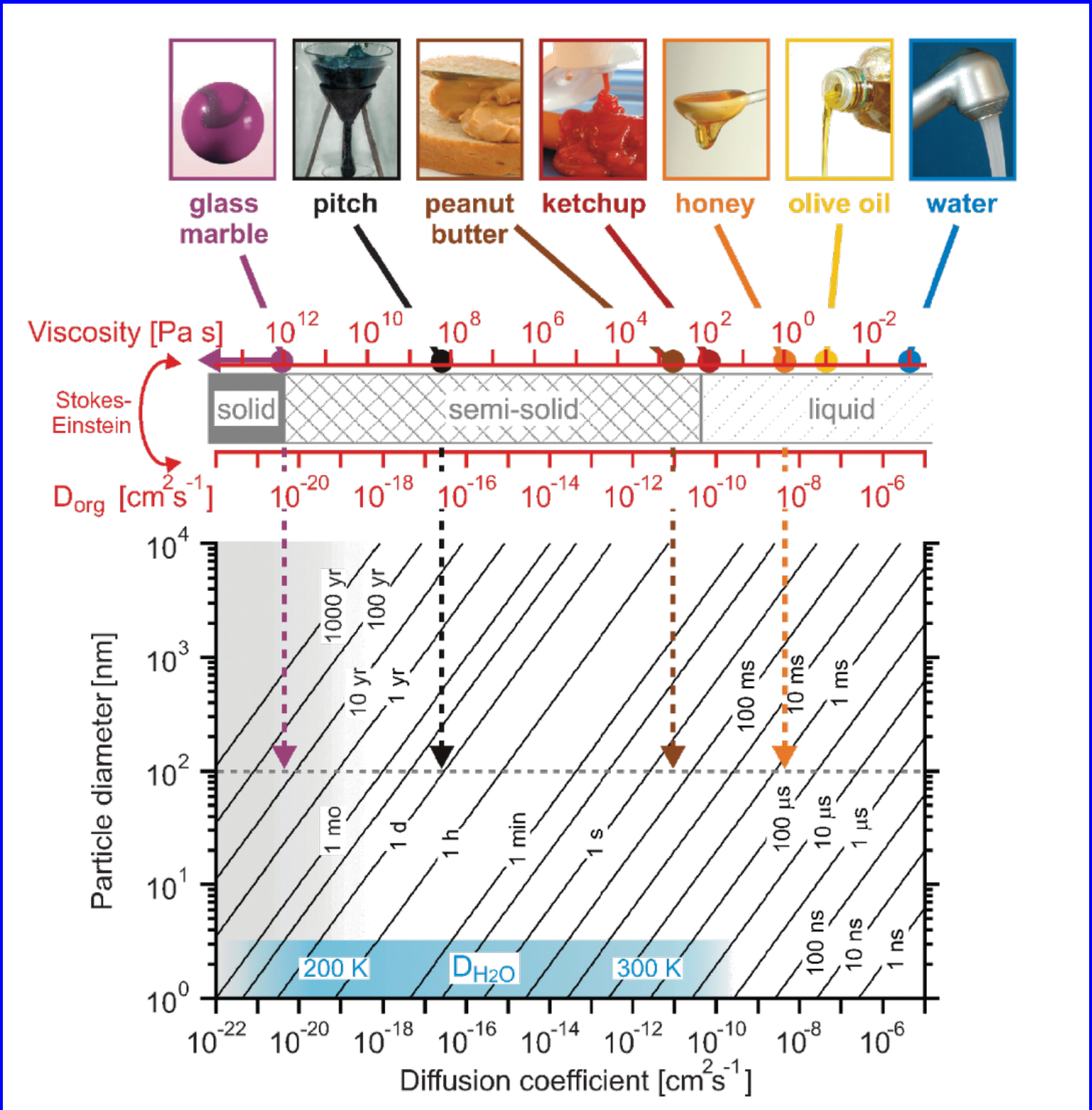
Ice preferentially nucleates on ammonium sulfate!

Factors important for Ice Nucleation

Cirrus: Optically thin due to low ice concentration

Only 1 in ~10000 particles act as IN

1. Particle size — Larger better
2. Composition — Minerals/salts good; Organics poor
3. Phase 
4. Chemical Distribution 

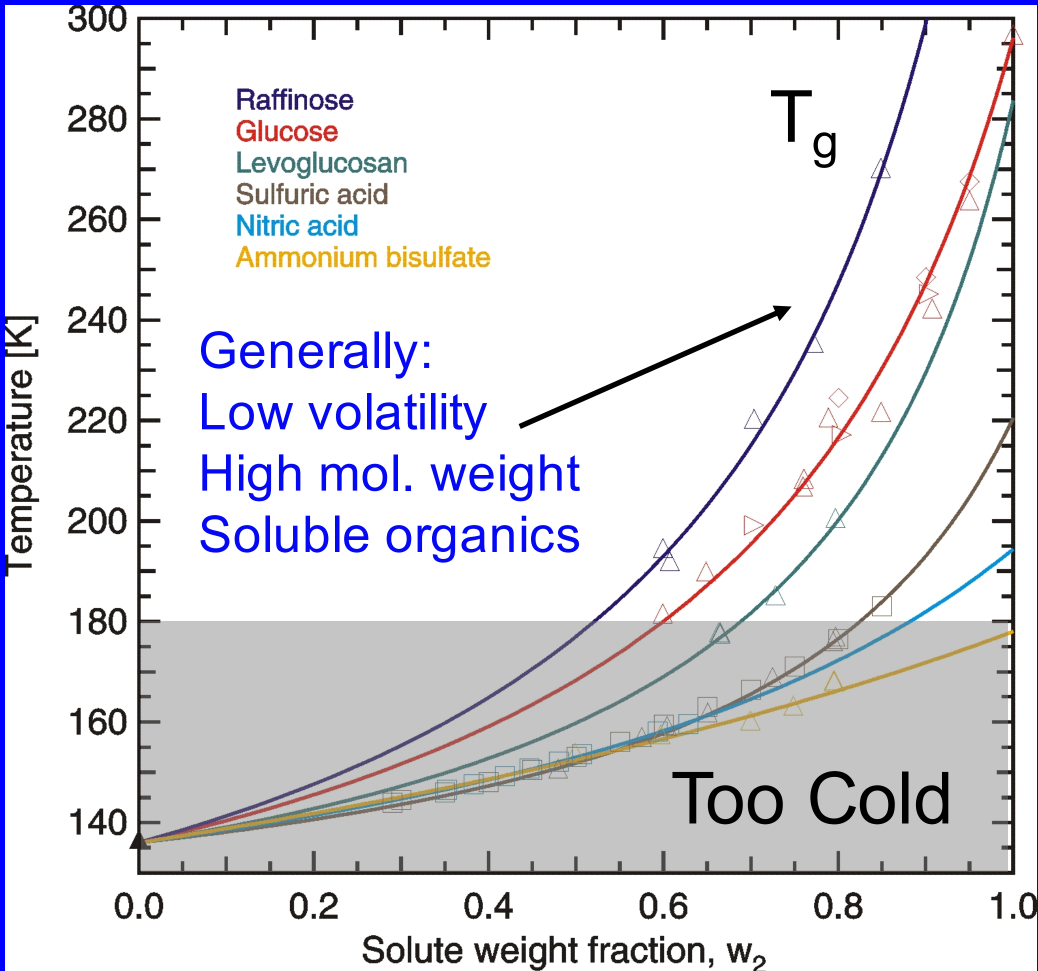


Glasses:

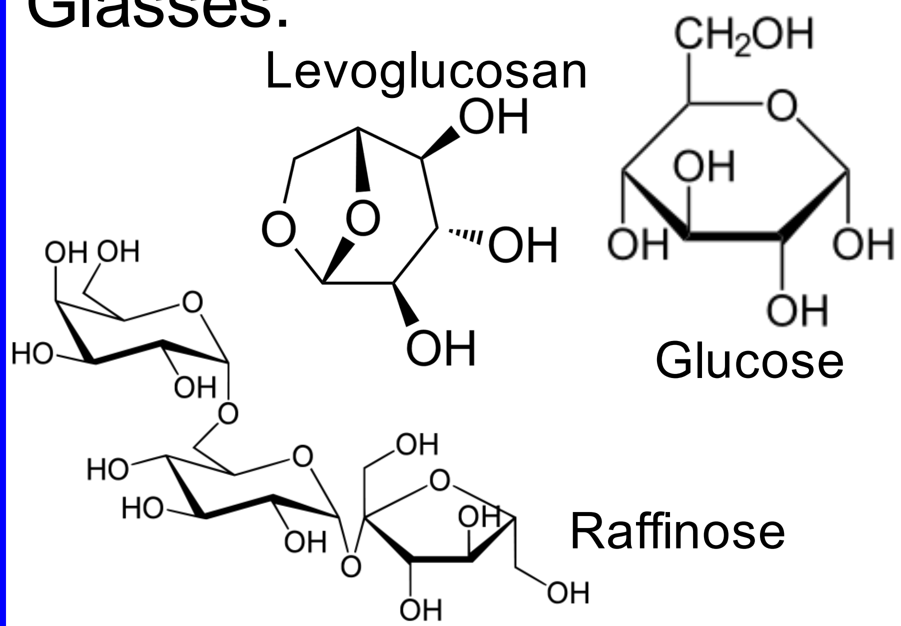
High viscosity
Low diffusion

Koop PCCP 2011

Atmospheric Glasses



Glasses:



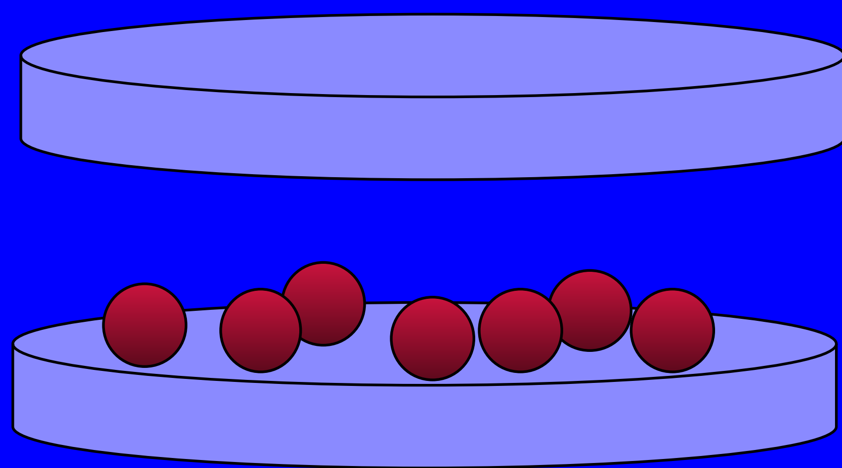
Not glasses:

$(NH_4)HSO_4$ H_2SO_4 HNO_3

Zobrist et al., (2008)

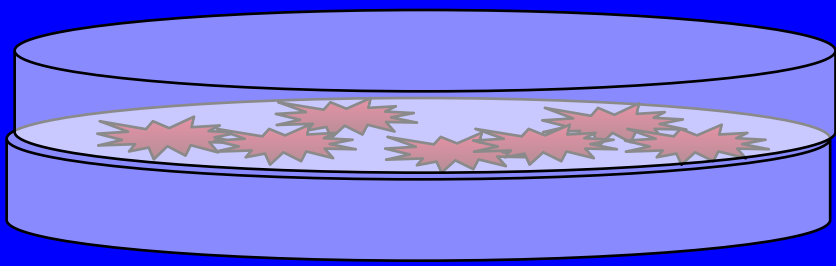
Organic aerosol can exist as highly viscous amorphous glasses
High MW and high O content favors glass formation

Smash Experiment

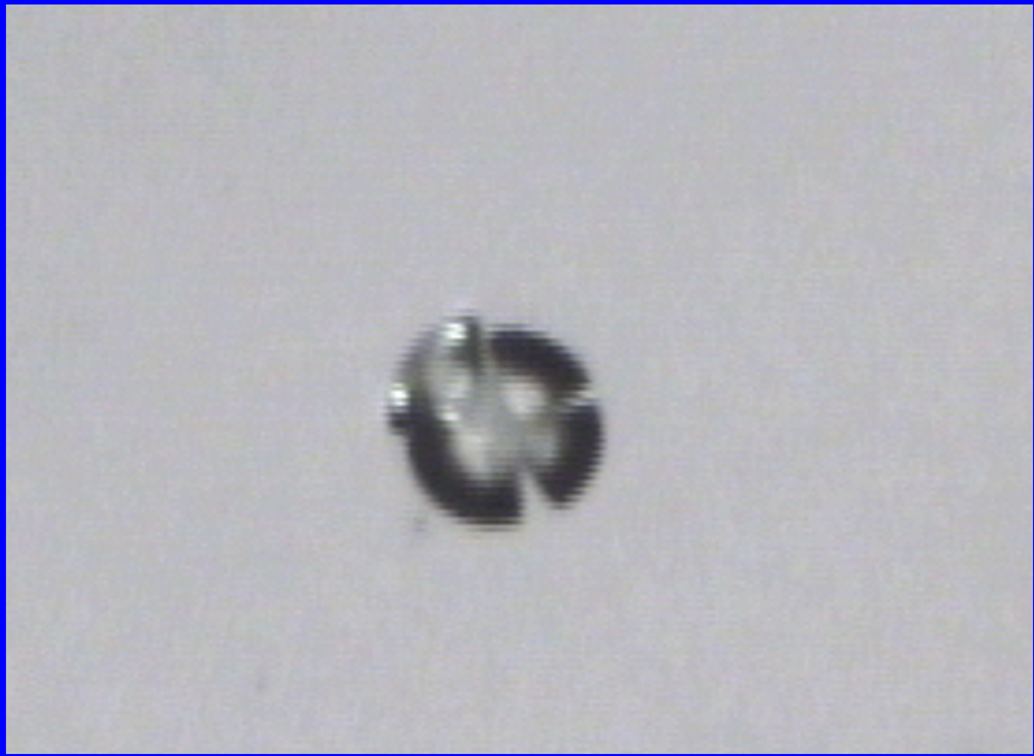


Adapted from
Murray ACP 2011

Smash Experiment



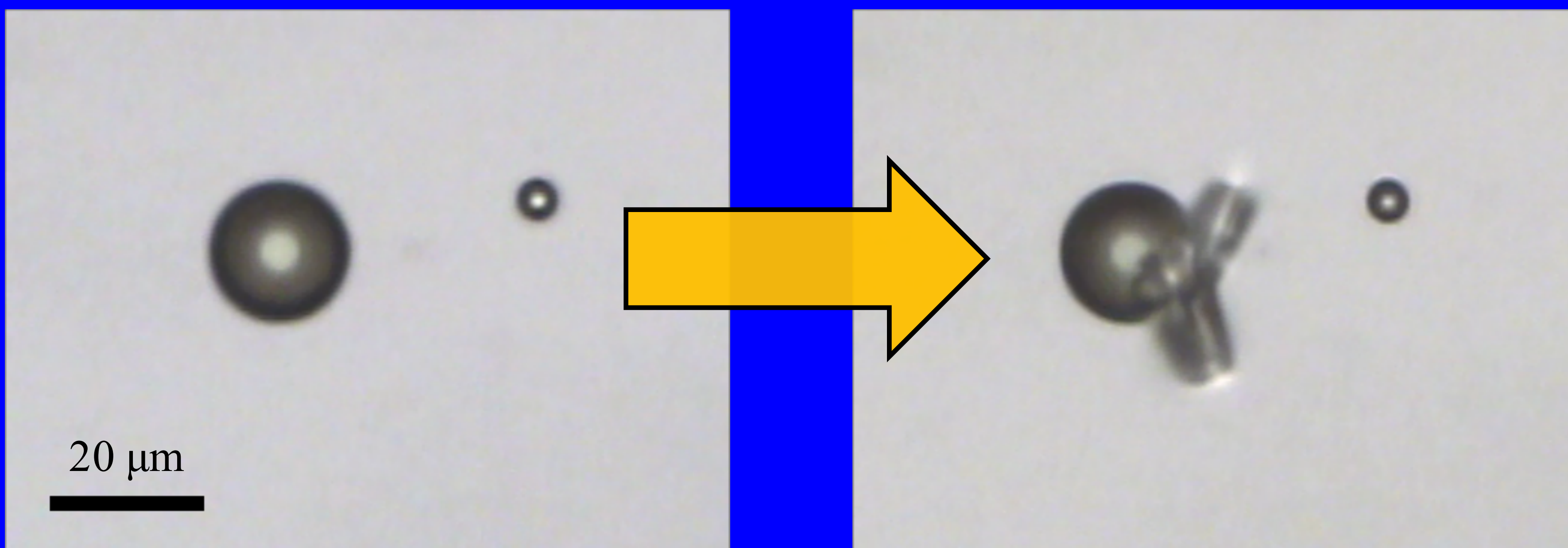
Adapted from
Murray ACP 2011



“Smoosh” → Liquid

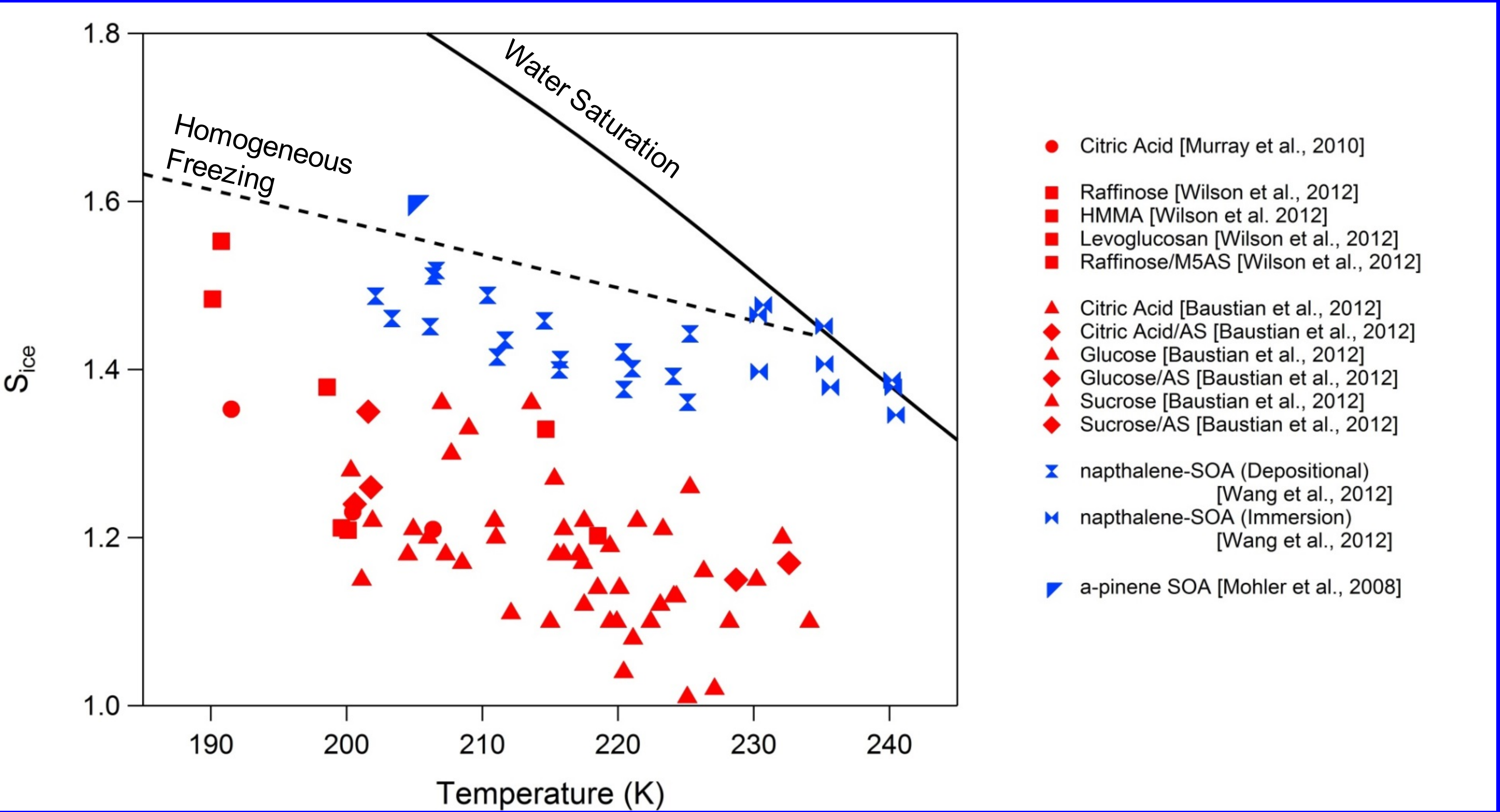
Shatter → highly viscous (semi-)solid or glassy state

Depositional Ice Nucleation on (un-smashed) Glassy organic



Before they liquefy, glassy particles can nucleate ice depositionally

Heterogeneous Ice Nucleation on Organic Glasses



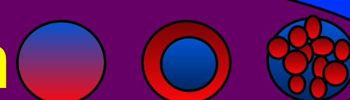
Simples organic glasses – good IN

Complex glassy organic (SOA) a poor ice nucleus?

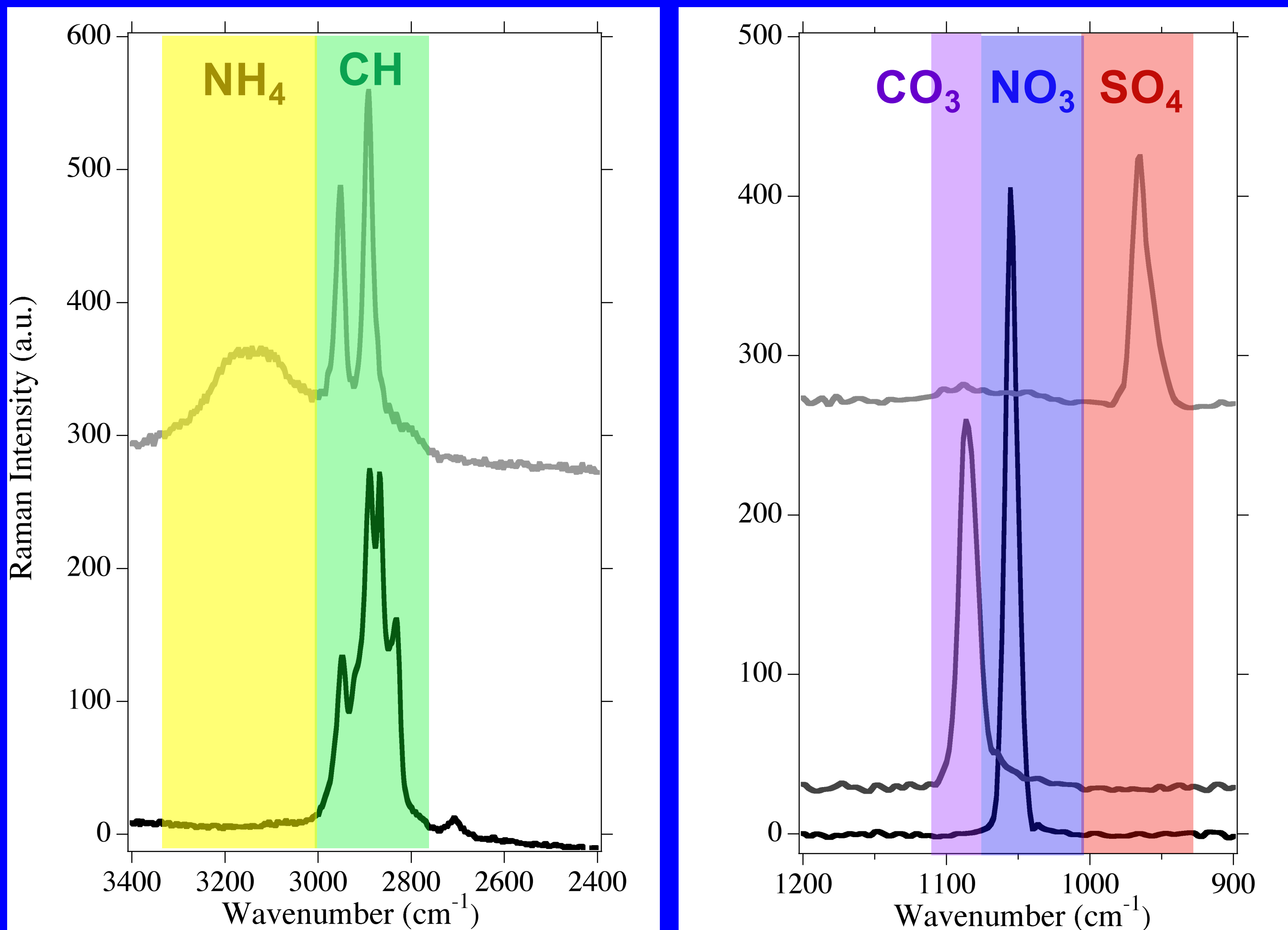
Factors important for Ice Nucleation

Cirrus: Optically thin due to low ice concentration

Only 1 in ~10000 particles act as IN

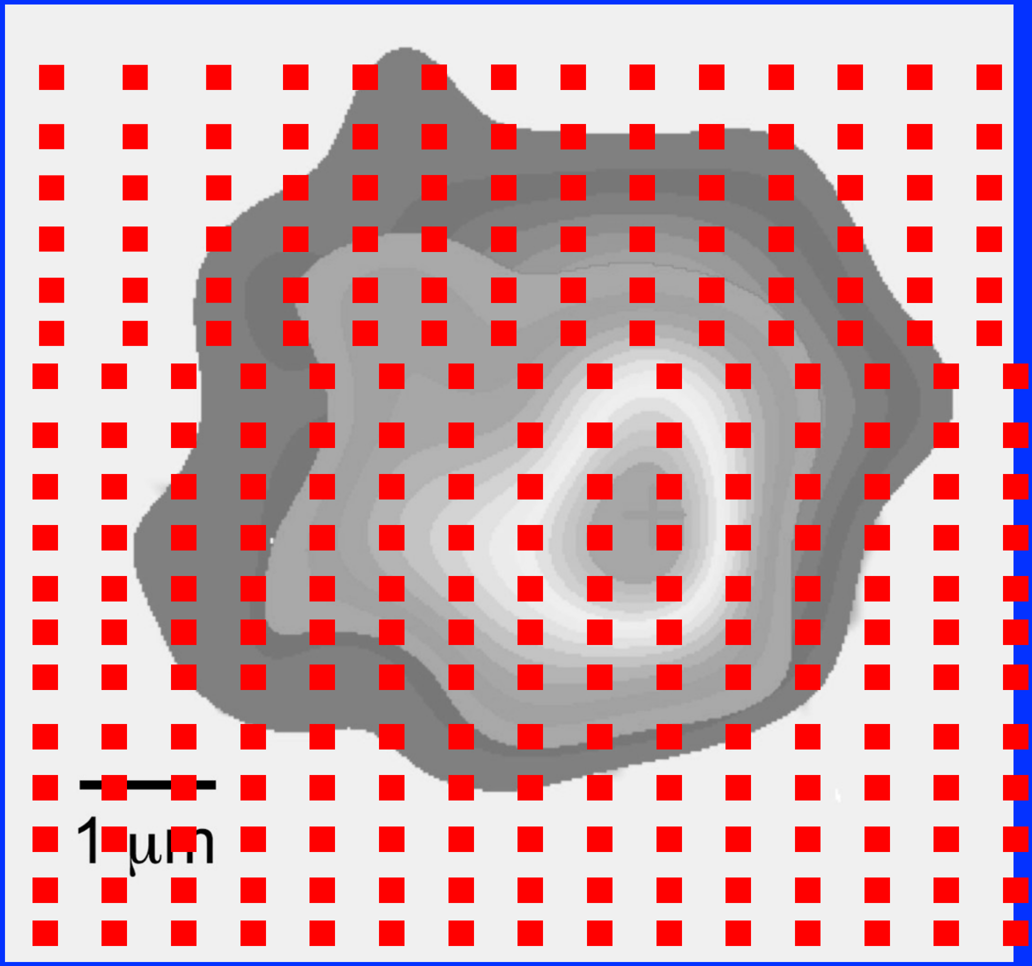
1. Particle size — Larger better
2. Composition — Minerals/salts good; Organics poor
3. Phase — Glasses mixed
4. Chemical Distribution 

Spectral Classification for Raman Mapping

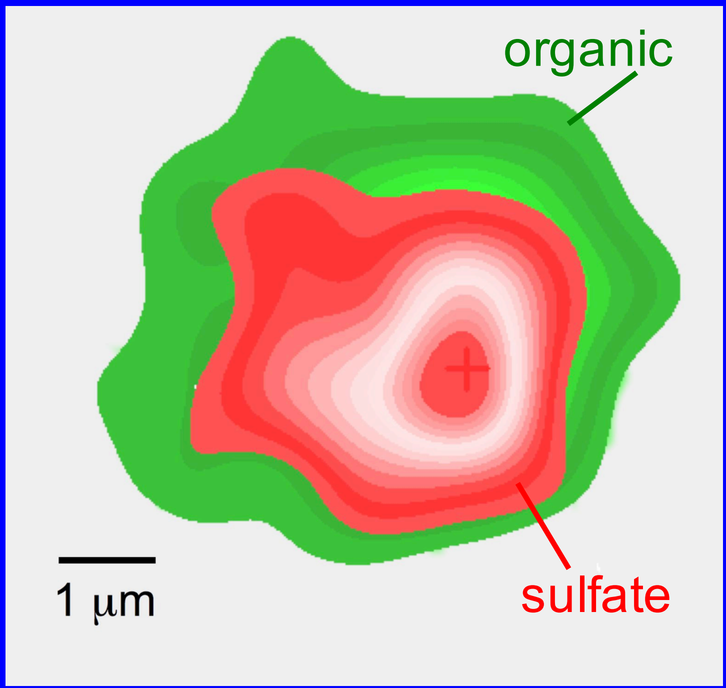


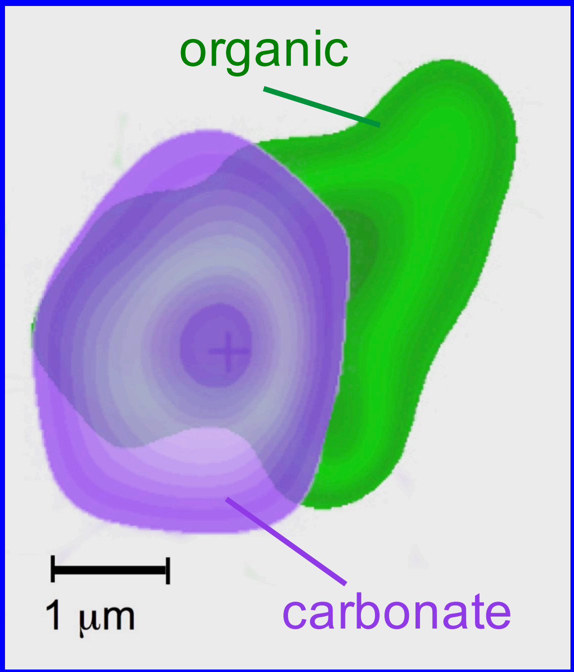
Spectra were classified using characteristic frequencies: Organics, Sulfates, Nitrates (aged sea salt), Carbonates (mineral dust), Ammonium.

Raman Mapping



Raman Mapping to Probe Mixing State





not an IN

IN

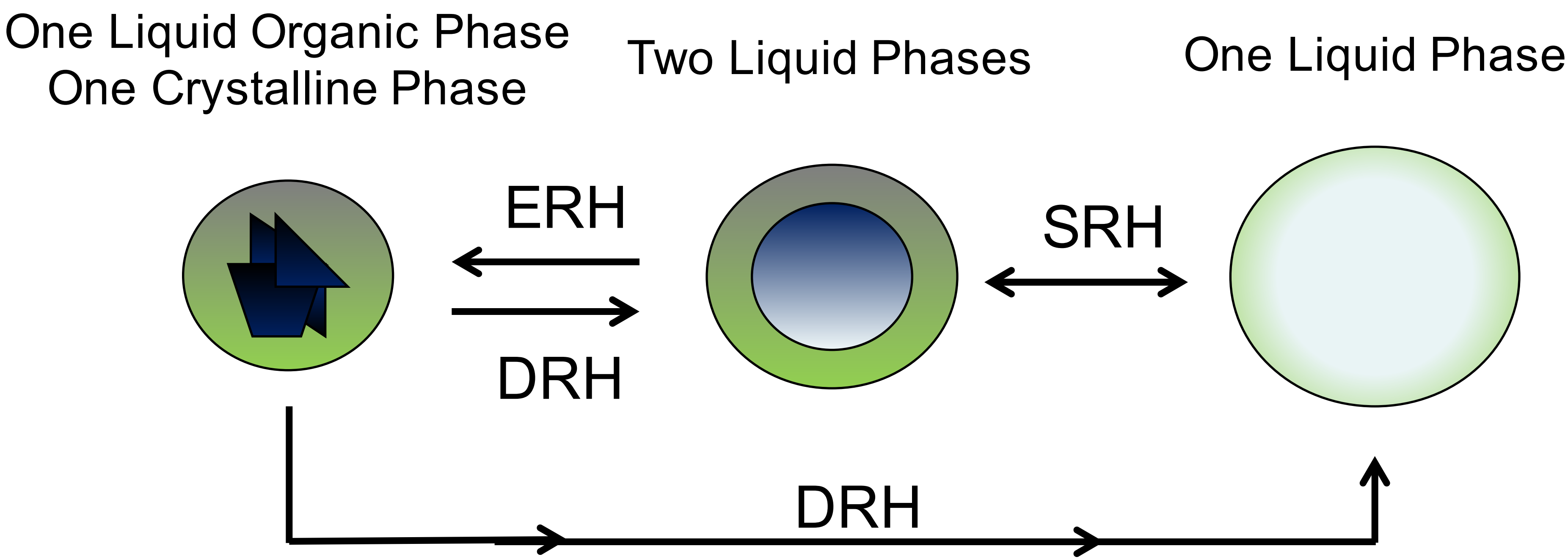
Collected at Storm Peak

Almost all contained at least trace organics

14% were coated with organics

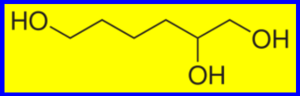
Liquid-Liquid Phase Separation

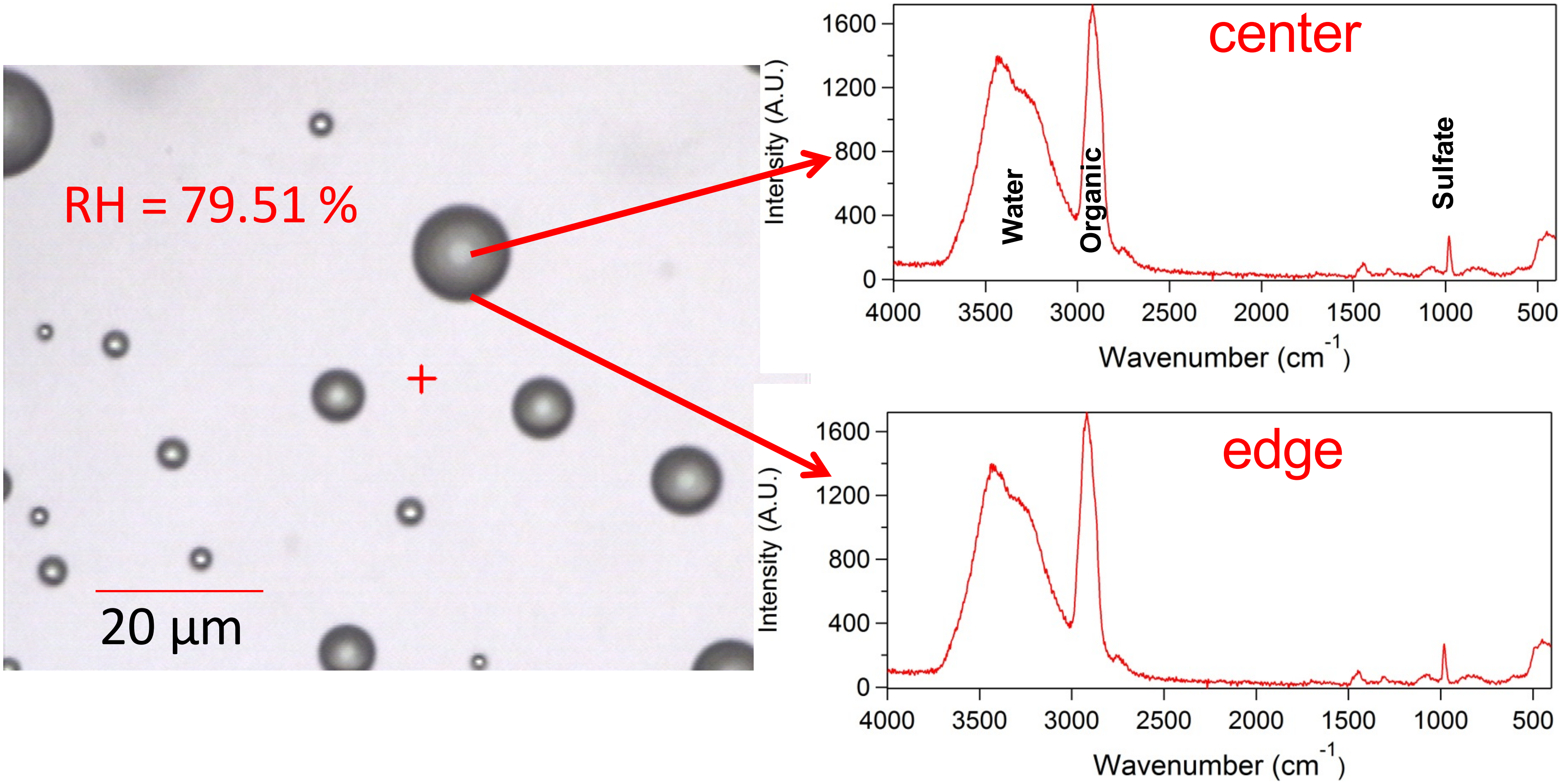
O:C < 0.7 will Liquid-Liquid Phase Separate mixed with AS



Increasing RH

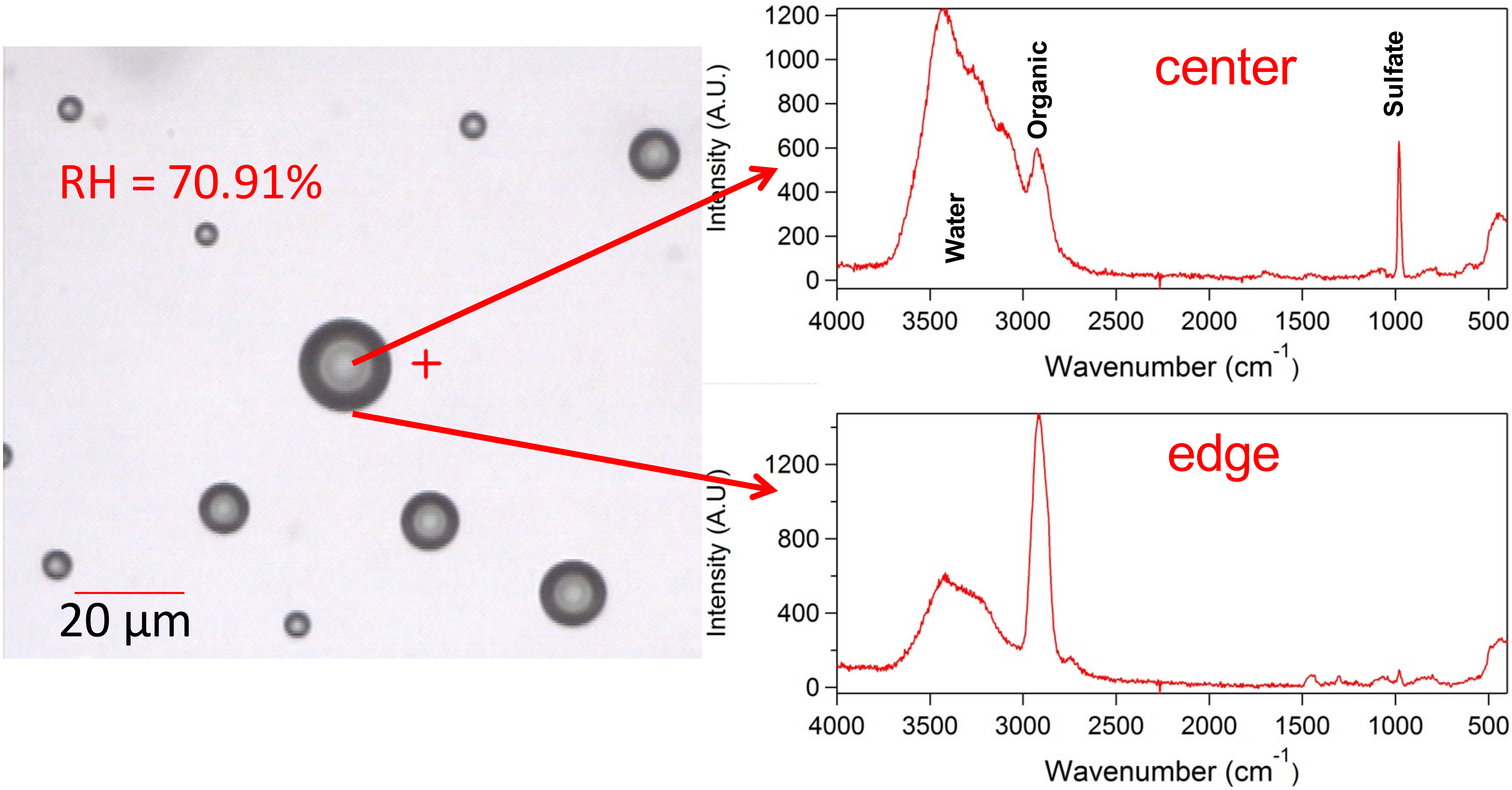
Bertram ACP 2012

Deliquesced 1,2,6-Hexanetriol ()
+ Ammonium Sulfate at 260 K



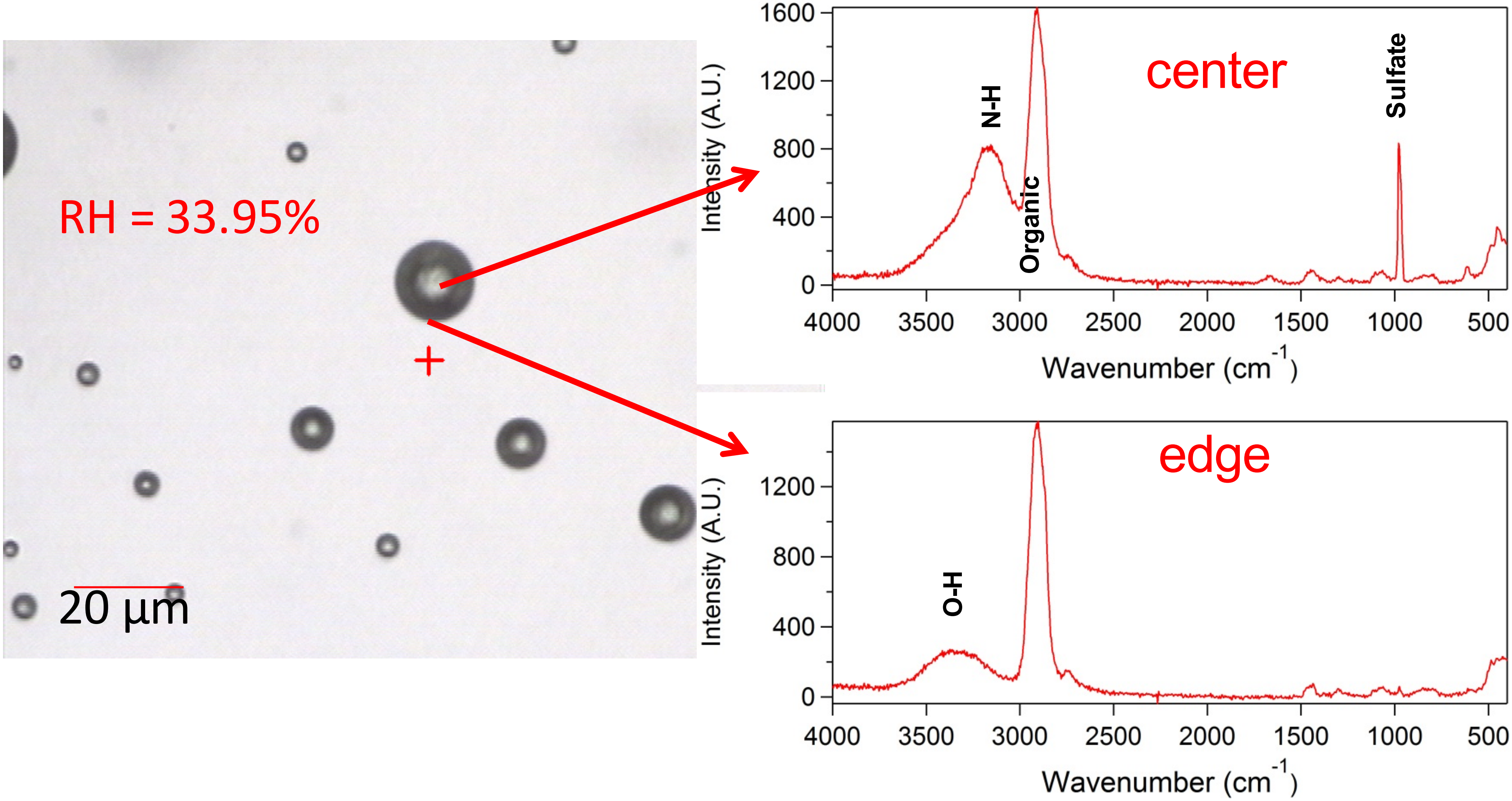
Particle composition same interior and exterior

Liquid-Liquid Phase Separation



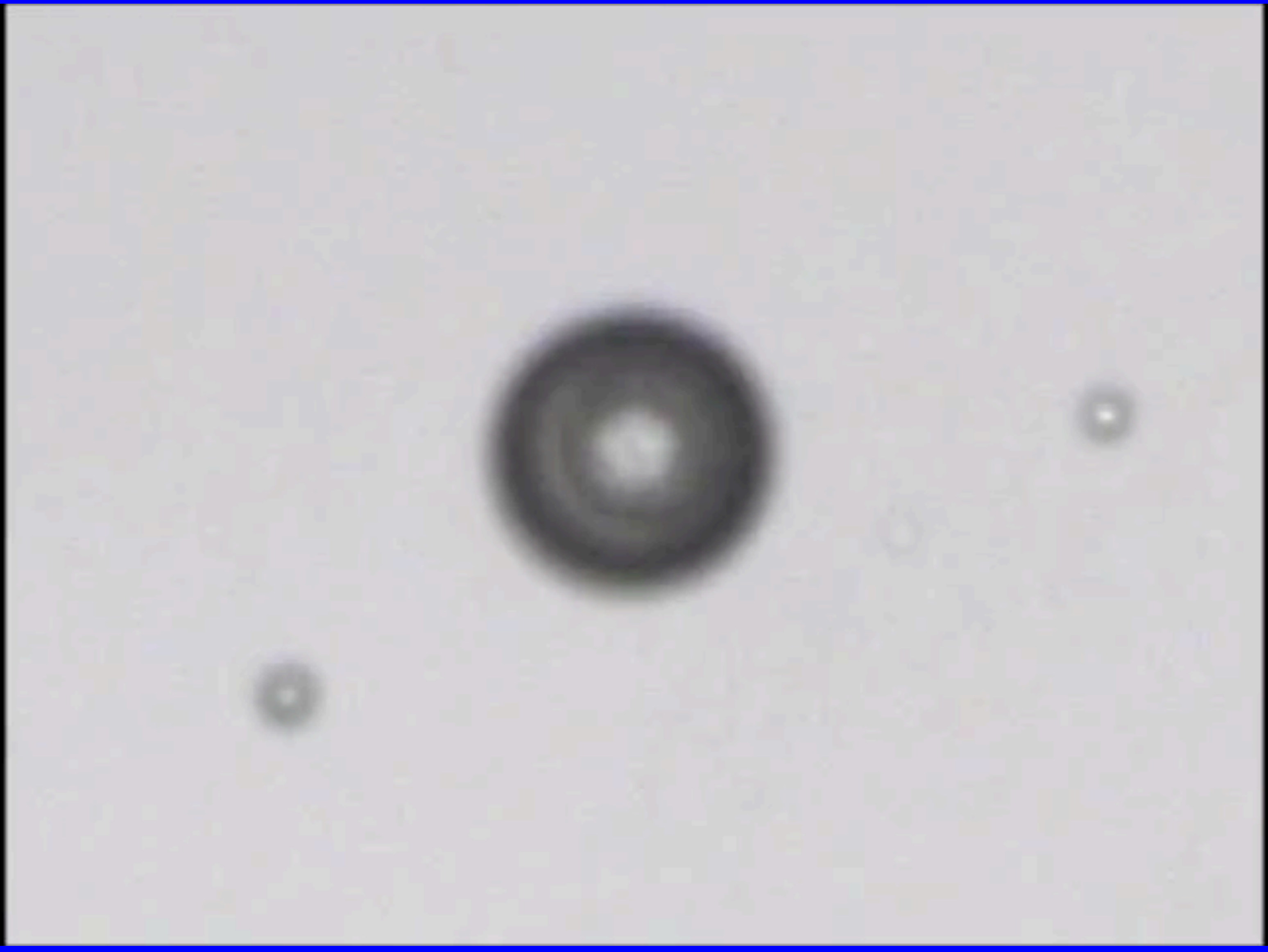
Aqueous ammonium sulfate core with organic coating

Efflorescence

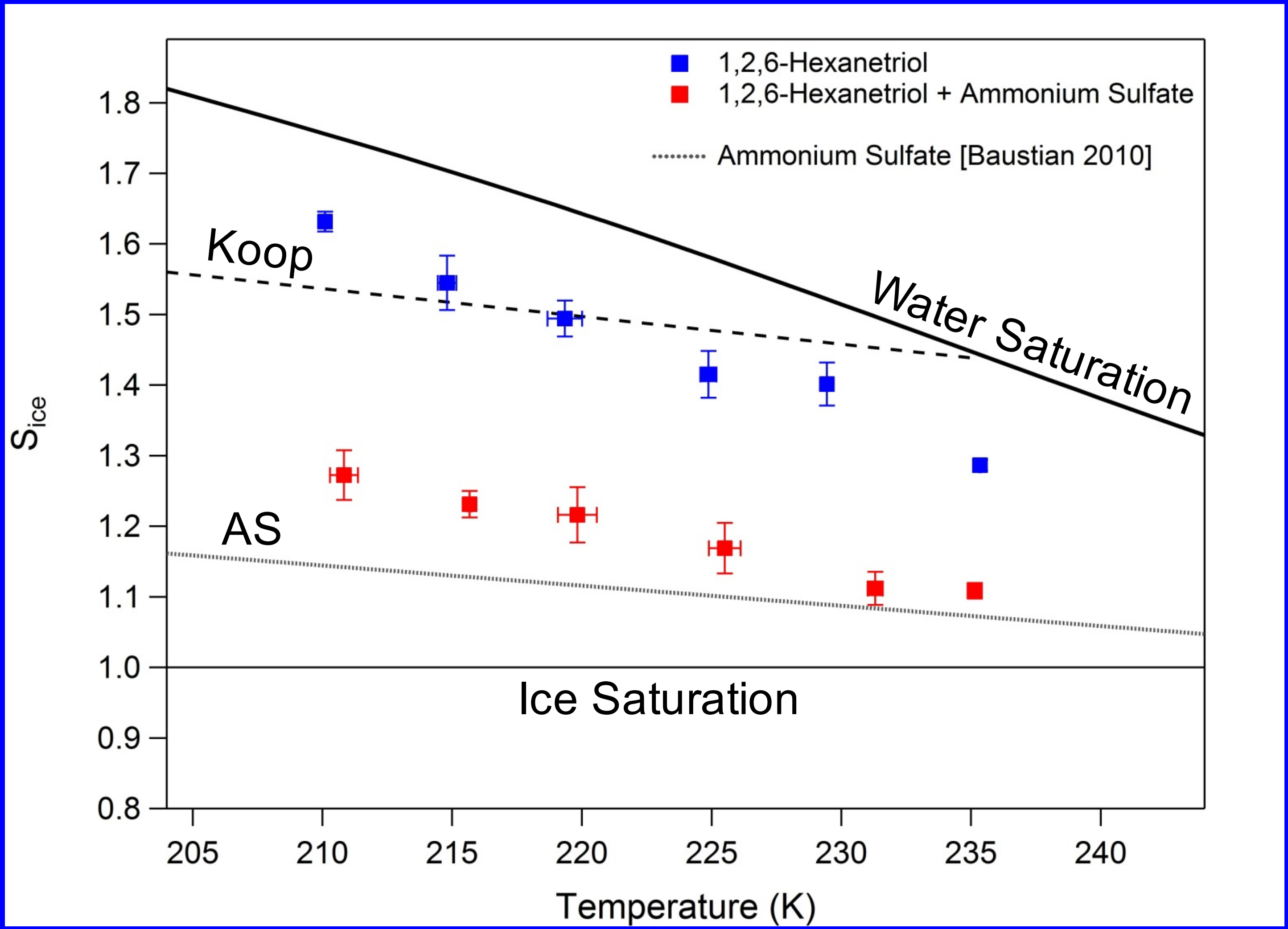


Solid ammonium sulfate core with organic coating

Ice Nucleation inside out

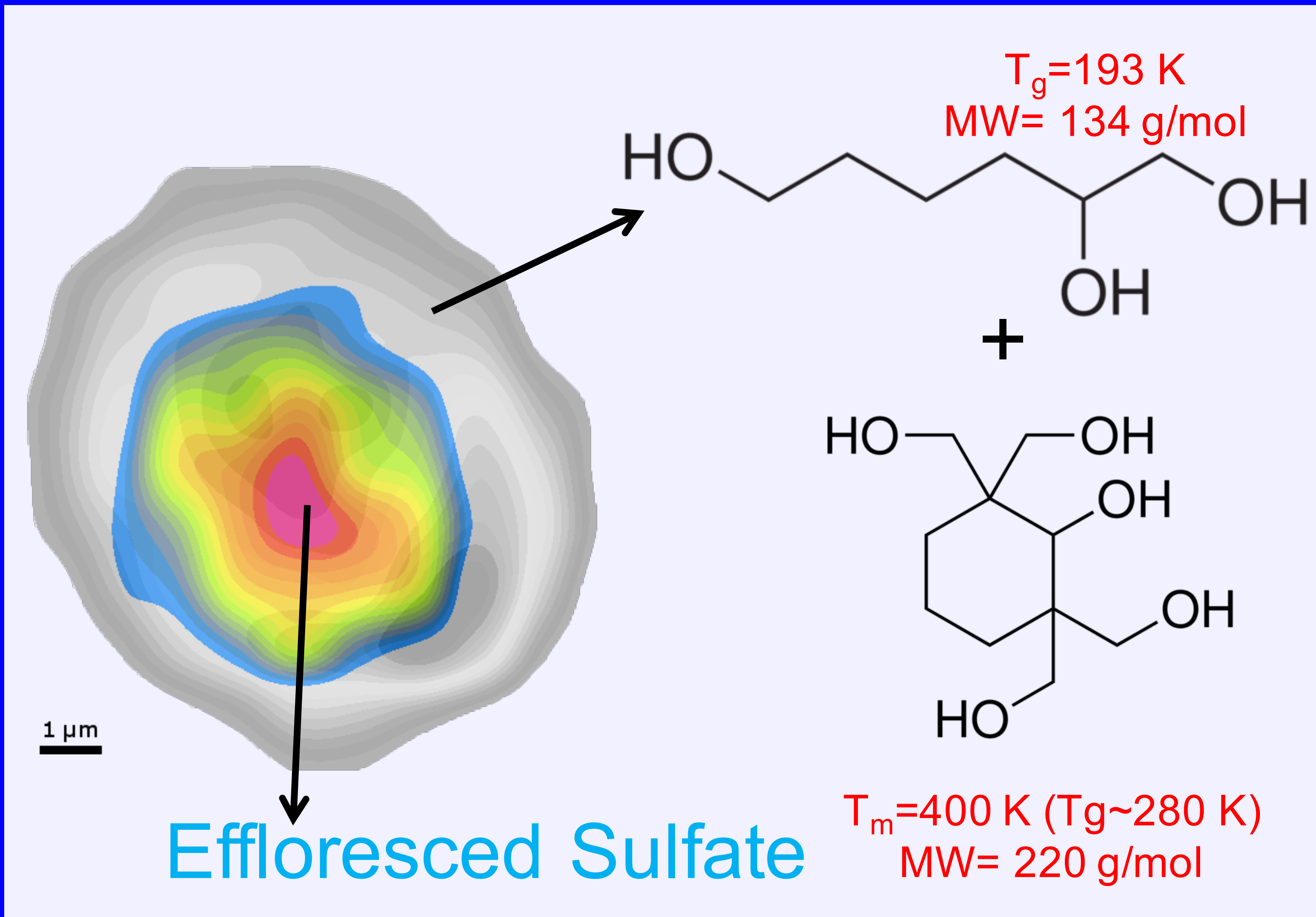


S_{ice} for inside-nucleated ice



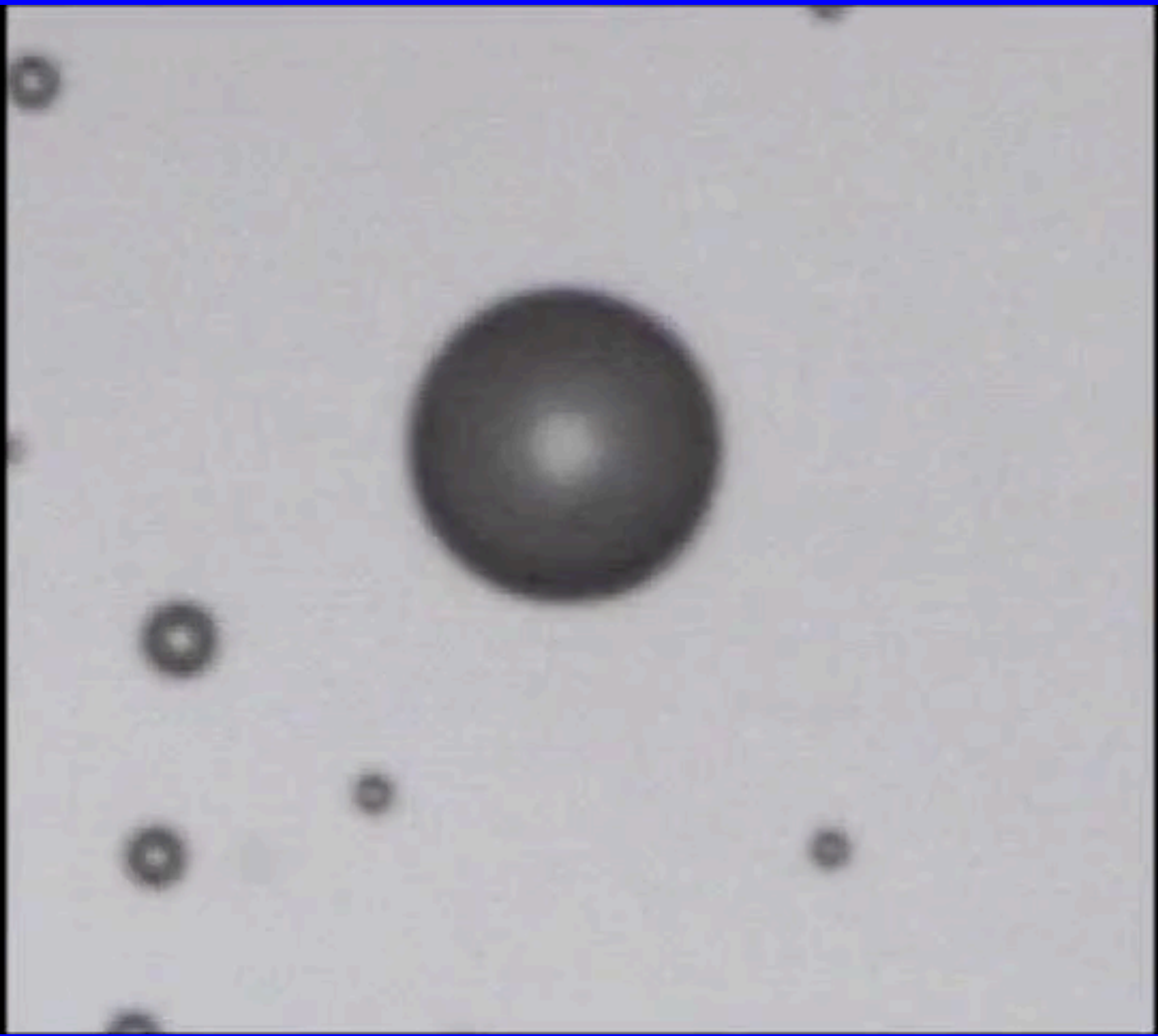
Coated AS almost as good IN as pure AS

Ice Nucleation for Glassy Coating

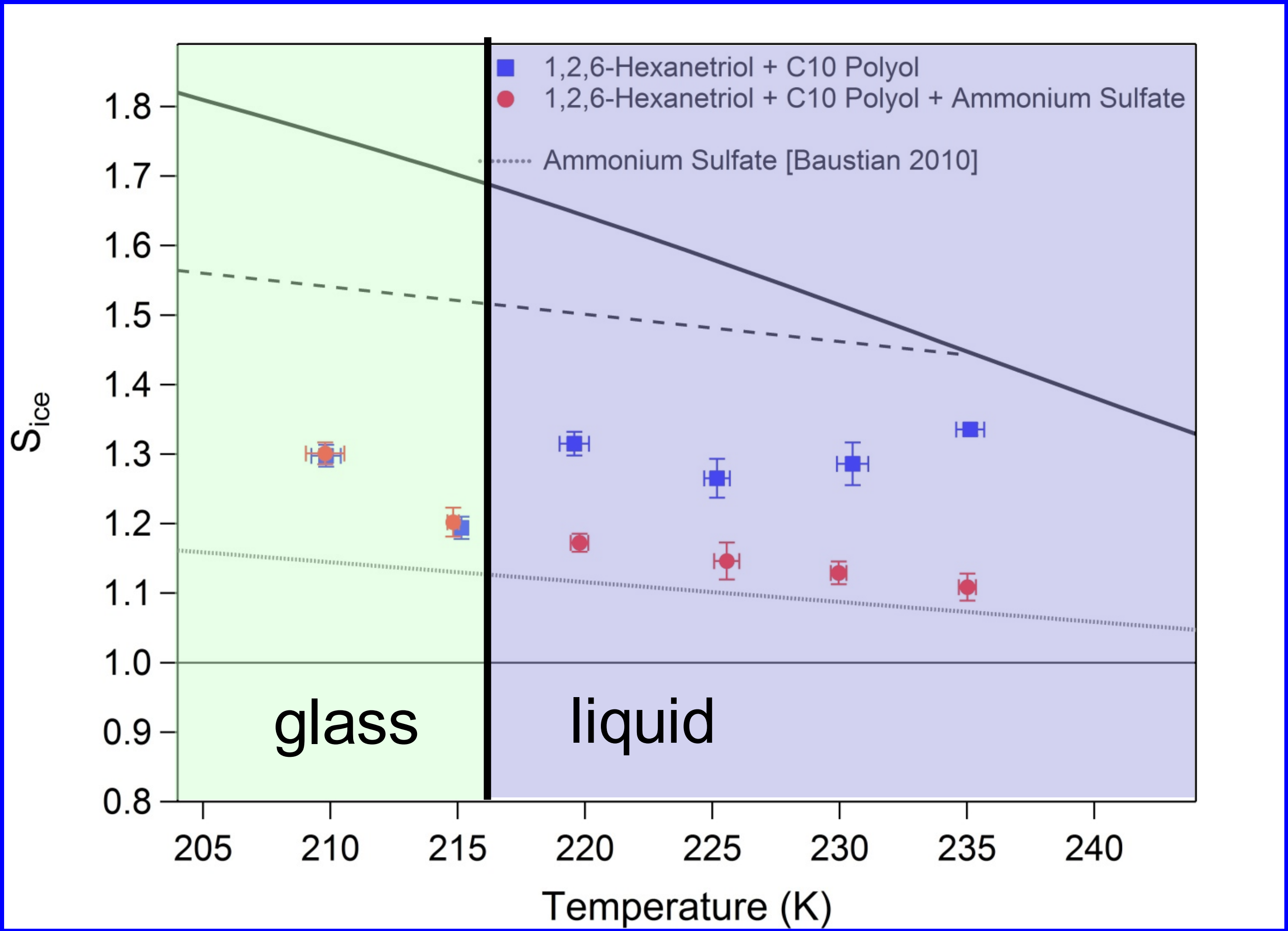


Goal: Liquid at 250 to phase separate, lower T to form glass

Ice Nucleation on Glassy Organics

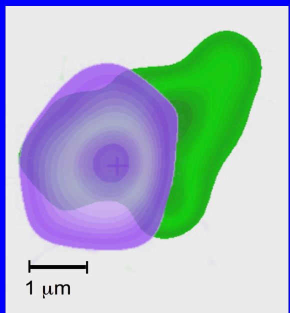


S_{ice} for Mixed Organic

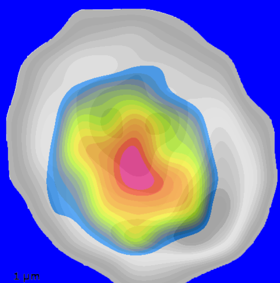


Good IN over entire range for different reasons

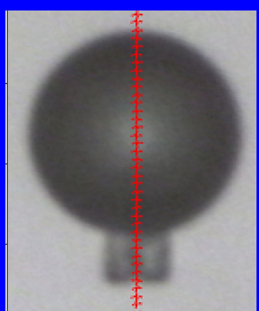
Atmospheric IN with organics



Minerals, salts: excellent IN
Partial organic coating...still good IN



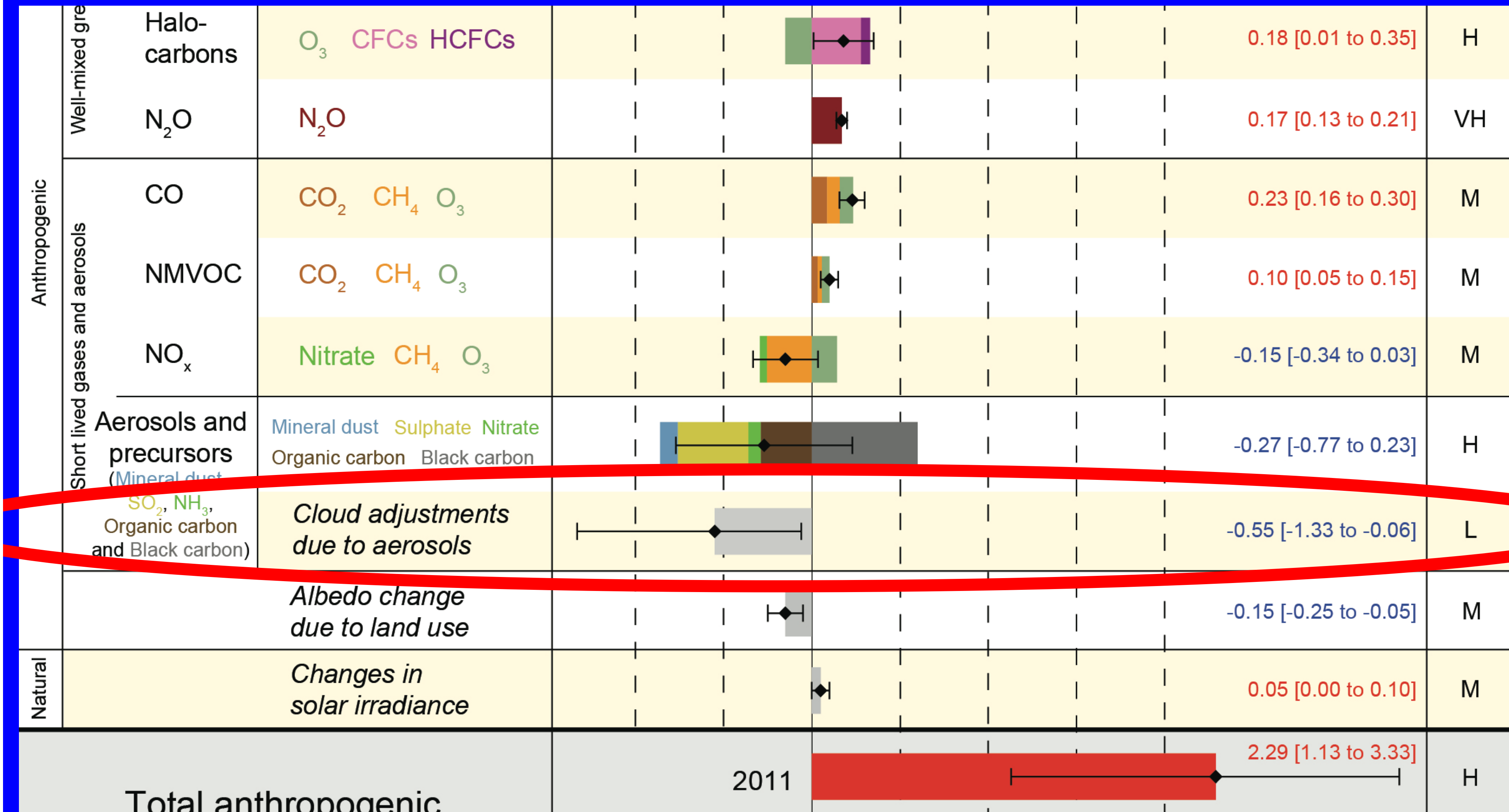
Liquid organic coating: can be good IN



Some glassy organics good IN

Inorganics still good IN even when mixed with organics
Consistent with sulfate/organic IN at TTL

Aerosol size, composition, phase and distribution all important for ice nucleation



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Acknowledgements