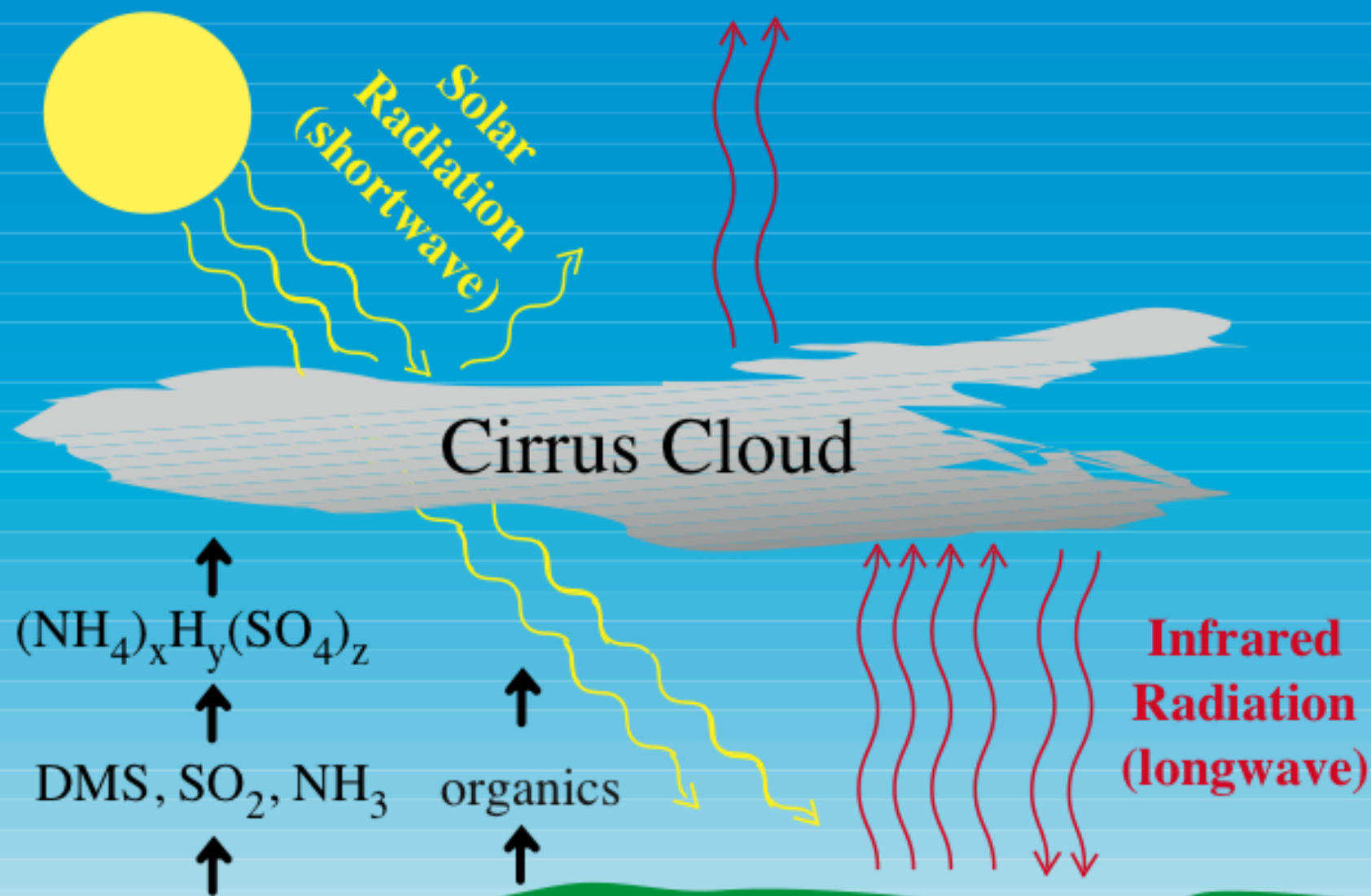


As cold as ice: cirrus cloud formation in the upper troposphere

Margaret A Tolbert



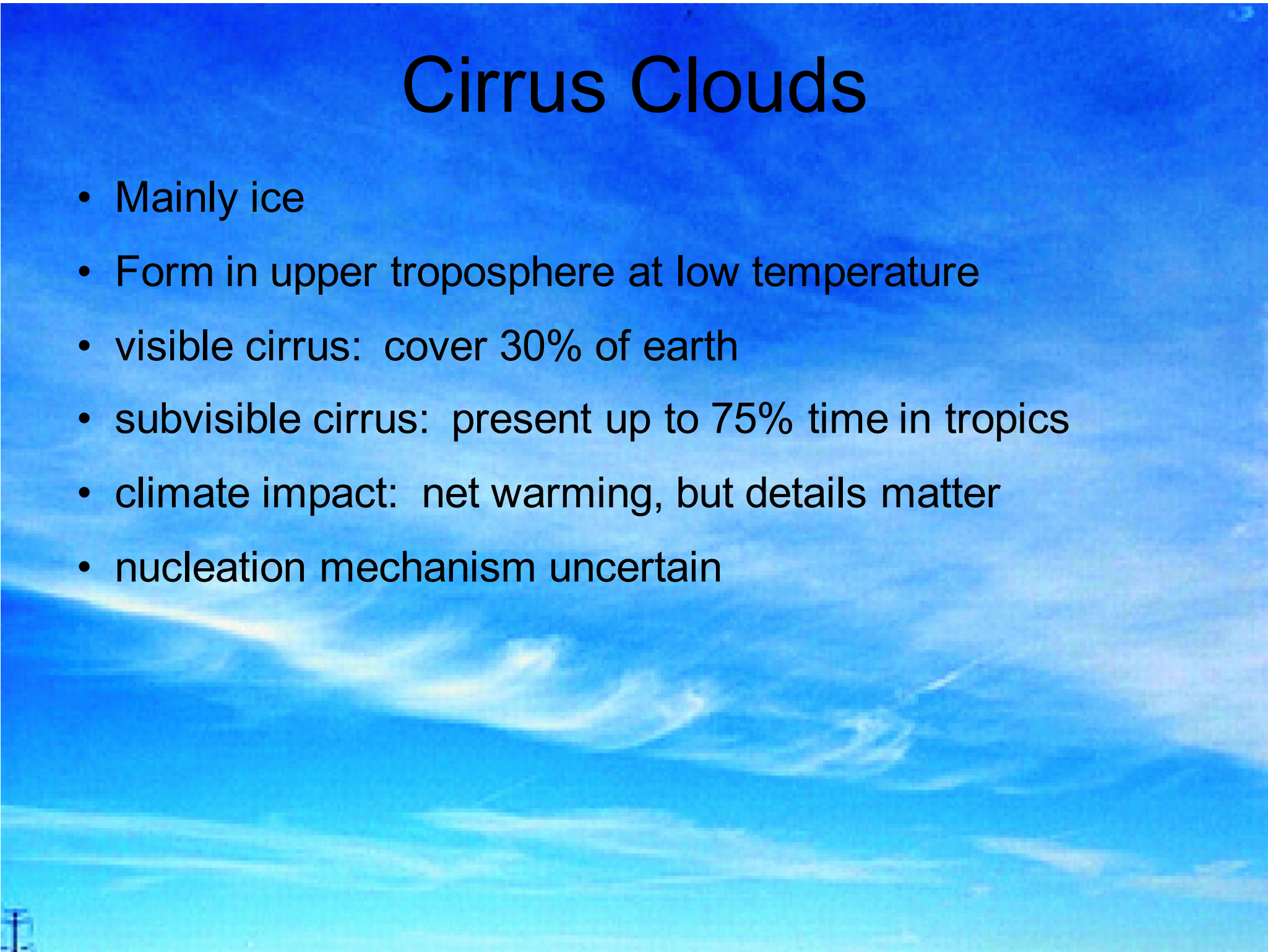
Cirrus Clouds and Climate



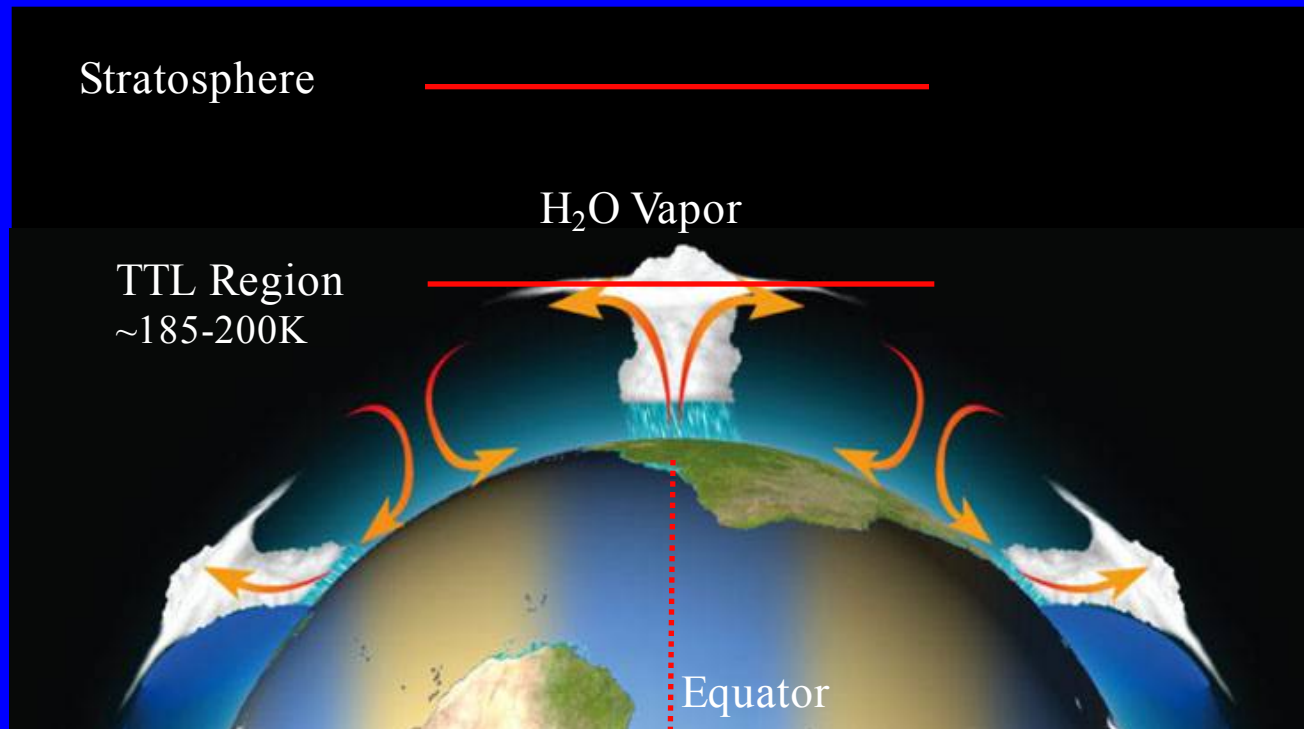
- » Large uncertainties in climate forcing
- » Cloud properties depend on nucleation

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

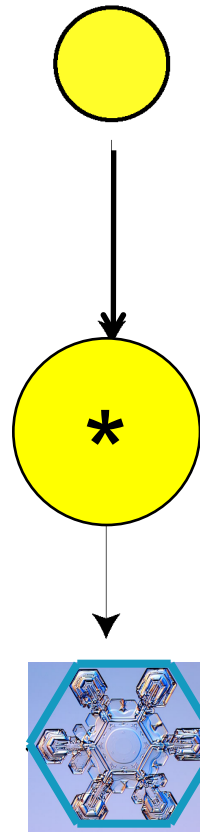


Freeze-dry air ascending into the stratosphere

Cirrus nucleation impacts water (ex//increase saturation ratio from 1.0 to 1.2 causes 10-15% increase in stratospheric H₂O).

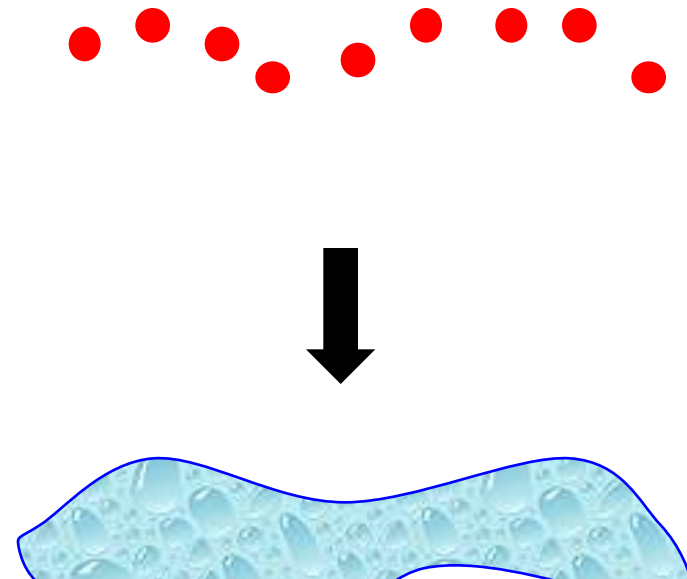
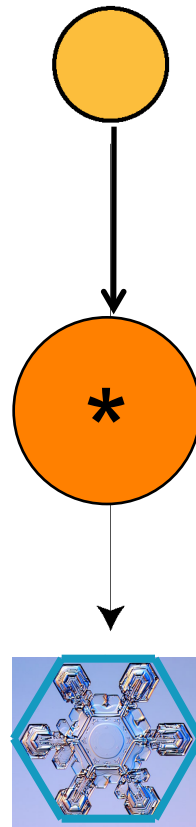
Ice Saturation Ratio: $S = P_{H_2O}/VP_{ice}$

sulfuric acid/water ammonium sulfate/water



Homogeneous nucleation
 $S=1.5$

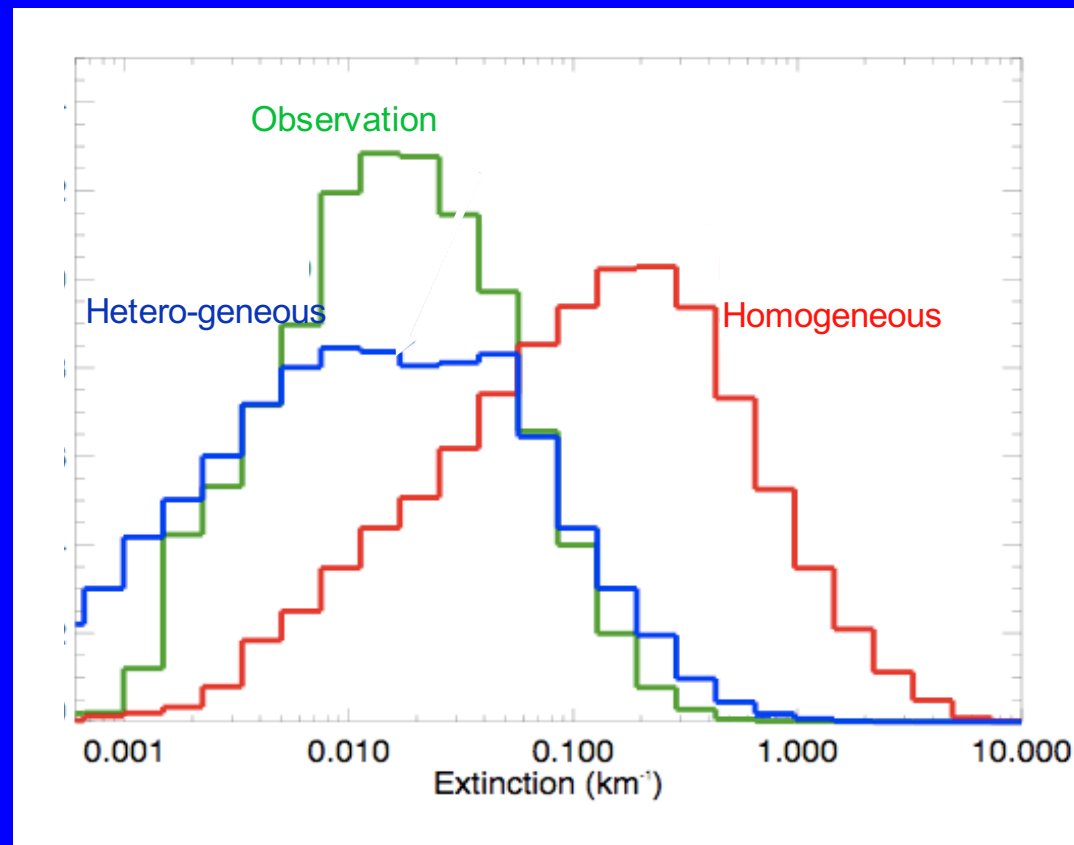
ice germ



This study:
heterogeneous
nucleation, $S=??$

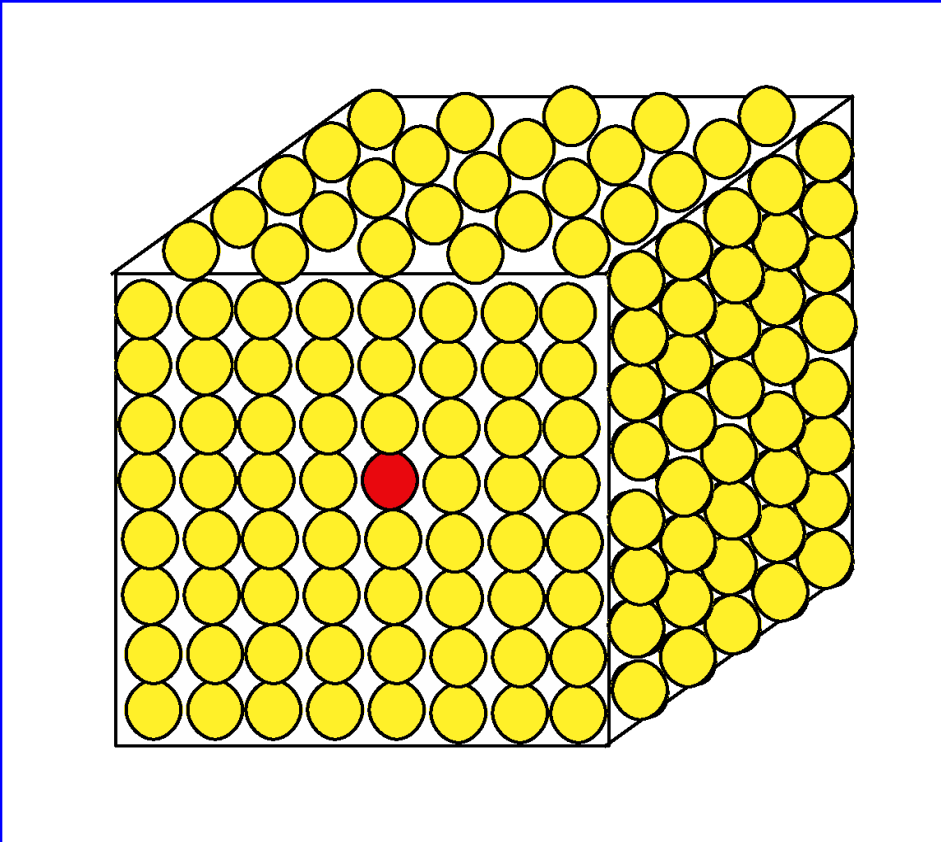
Ice Nucleation in the Upper Troposphere

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



Some observations and modeling studies do not support homogeneous ice nucleation

Cirrus Cloud Nucleation Selective



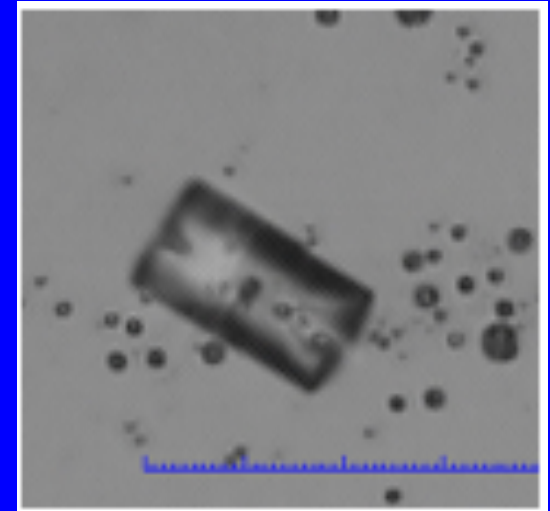
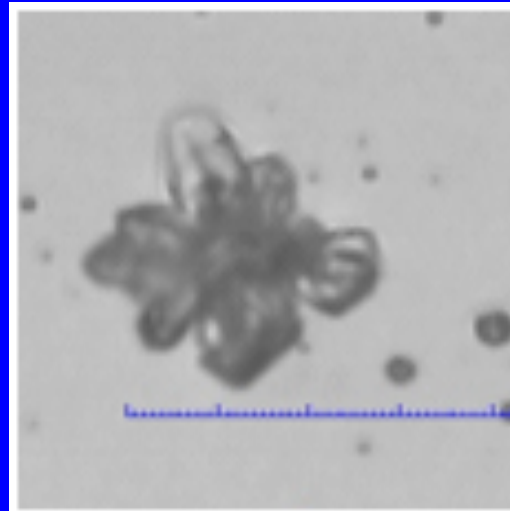
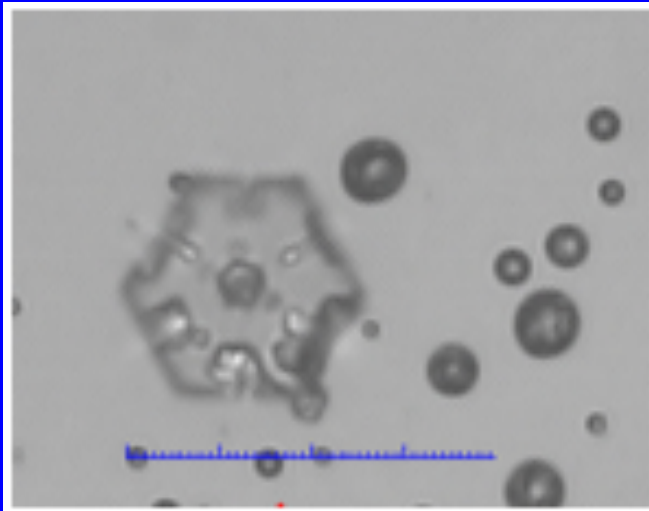
Only 1 in 10^4
aerosol particles
nucleate ice!

Selective Ice Nucleation

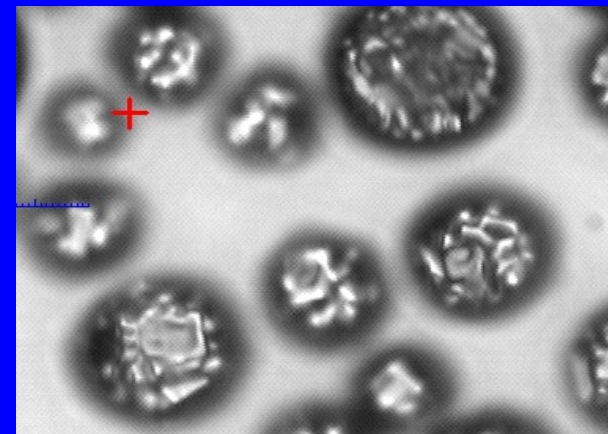


Heterogeneous Ice Nucleation Selective

Heterogeneous nucleation:



Homogeneous nucleation:



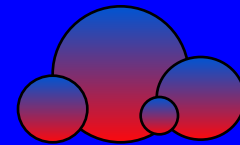
Factors important for Ice Nucleation

Cirrus: Optically thin due to low ice concentration

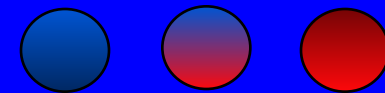
Only 1 in ~10000 particles act as IN



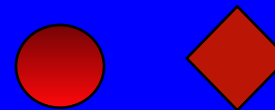
1. Particle size



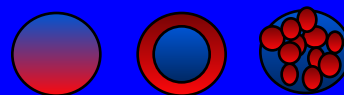
2. Composition



3. Phase



4. Chemical Distribution

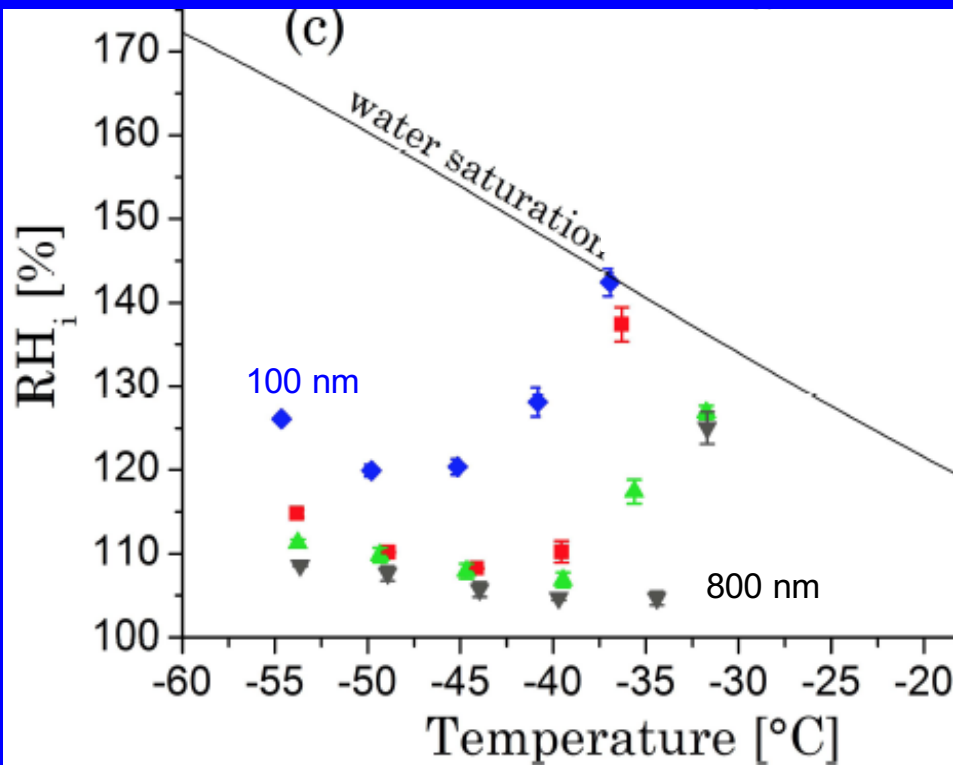


Increasingly difficult to measure

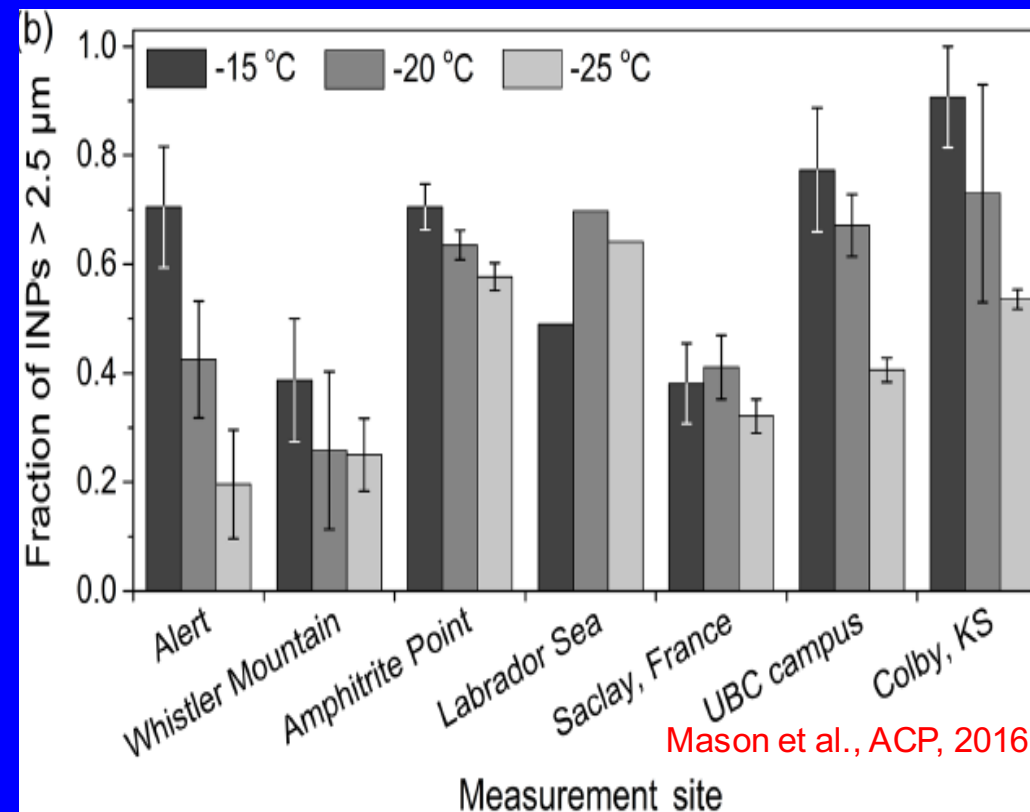
Large particles better ice nuclei

Lab (S_{ice} on illite)

Field (size of residual)



Welti et al., ACP, 2009



Mason et al., ACP, 2016

Small particles require higher S_{ice} 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



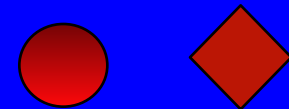
1. Particle size

Larger better

2. Composition



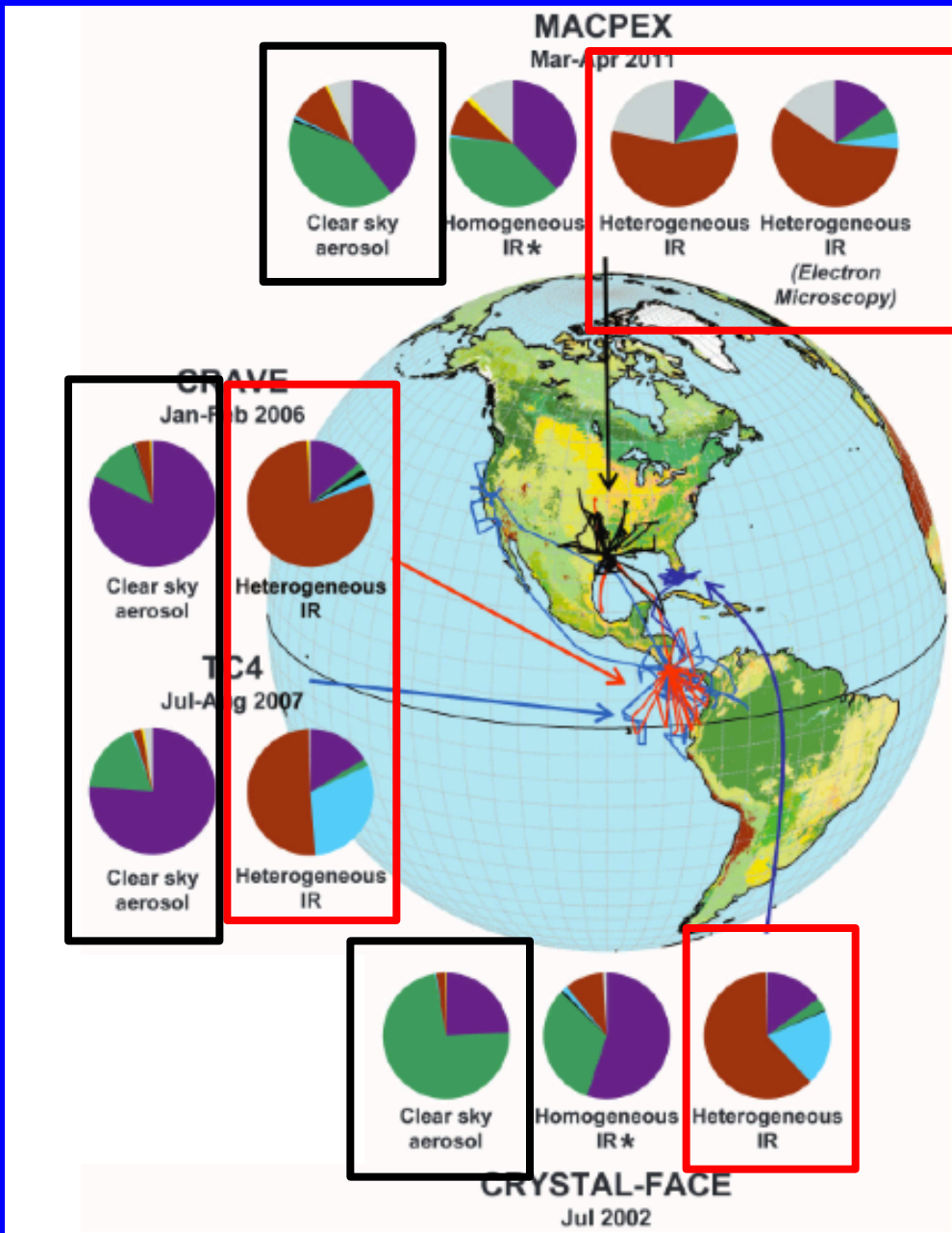
3. Phase



4. Chemical Distribution



Mineral Dust Excellent IN

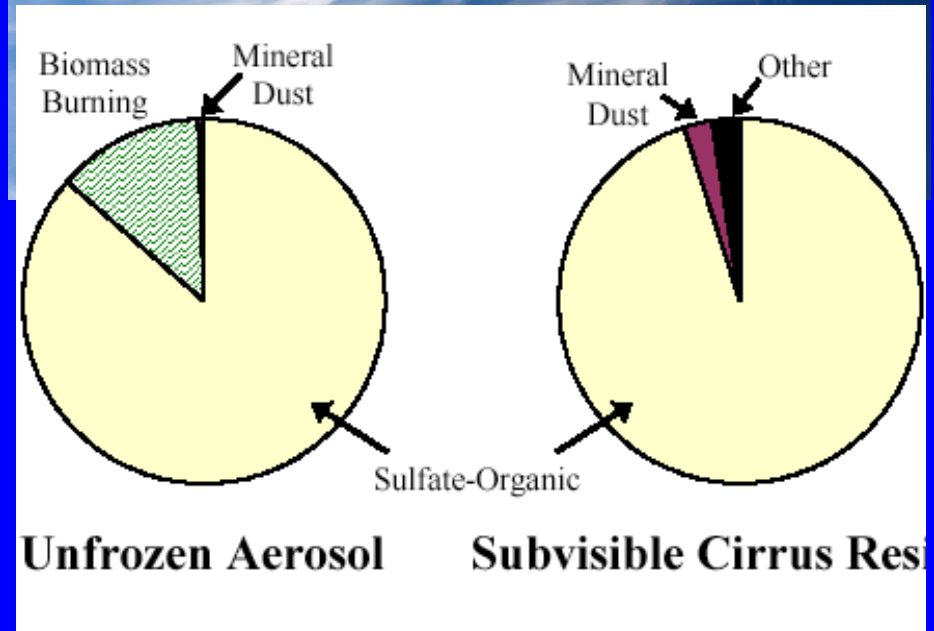


- 1000-3000 Tg/yr mineral aerosol emitted in the atmosphere

Cirrus IN in the Tropical Tropopause Layer (TTL)

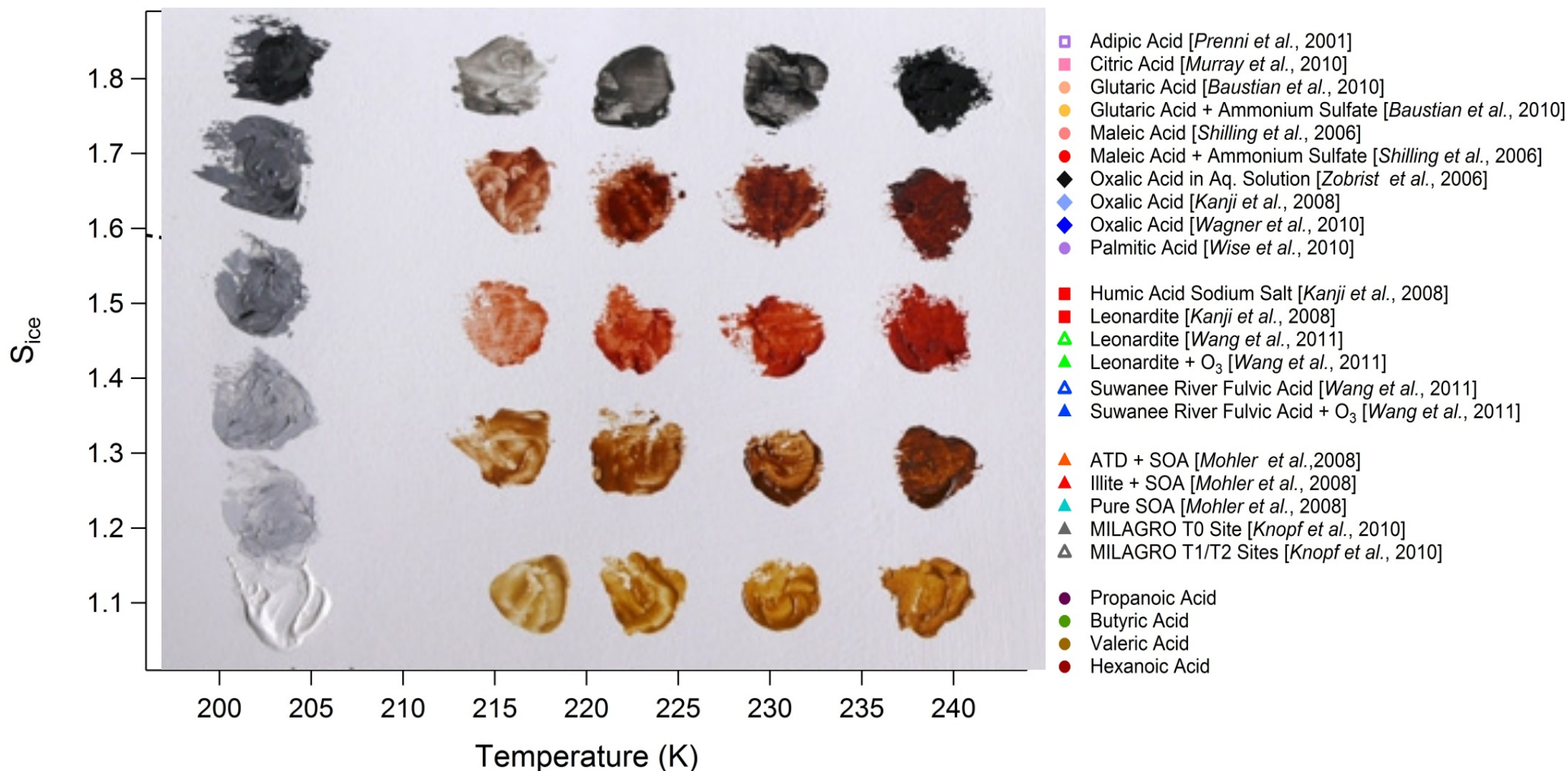
Species considered
good heterogeneous
IN are
not present in TTL

- sulfate/organic main IN in TTL



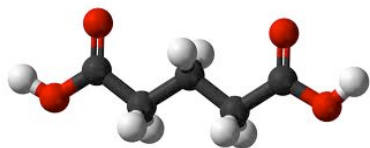
Heterogeneous Ice Nucleation on Organics

adapted from Knopf et al., 2010



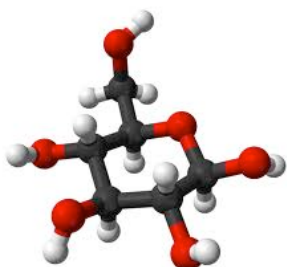
More types of information may help clarify the role of organics
Laboratory studies: role of organics uncertain

Organics Studied in Present Work



glutaric acid

soluble, low vp



Glucose

forms a glass

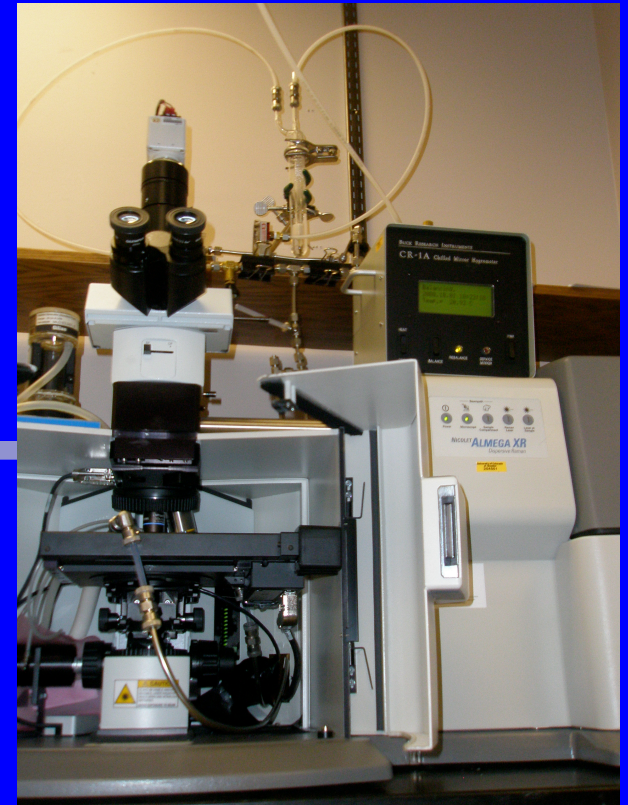
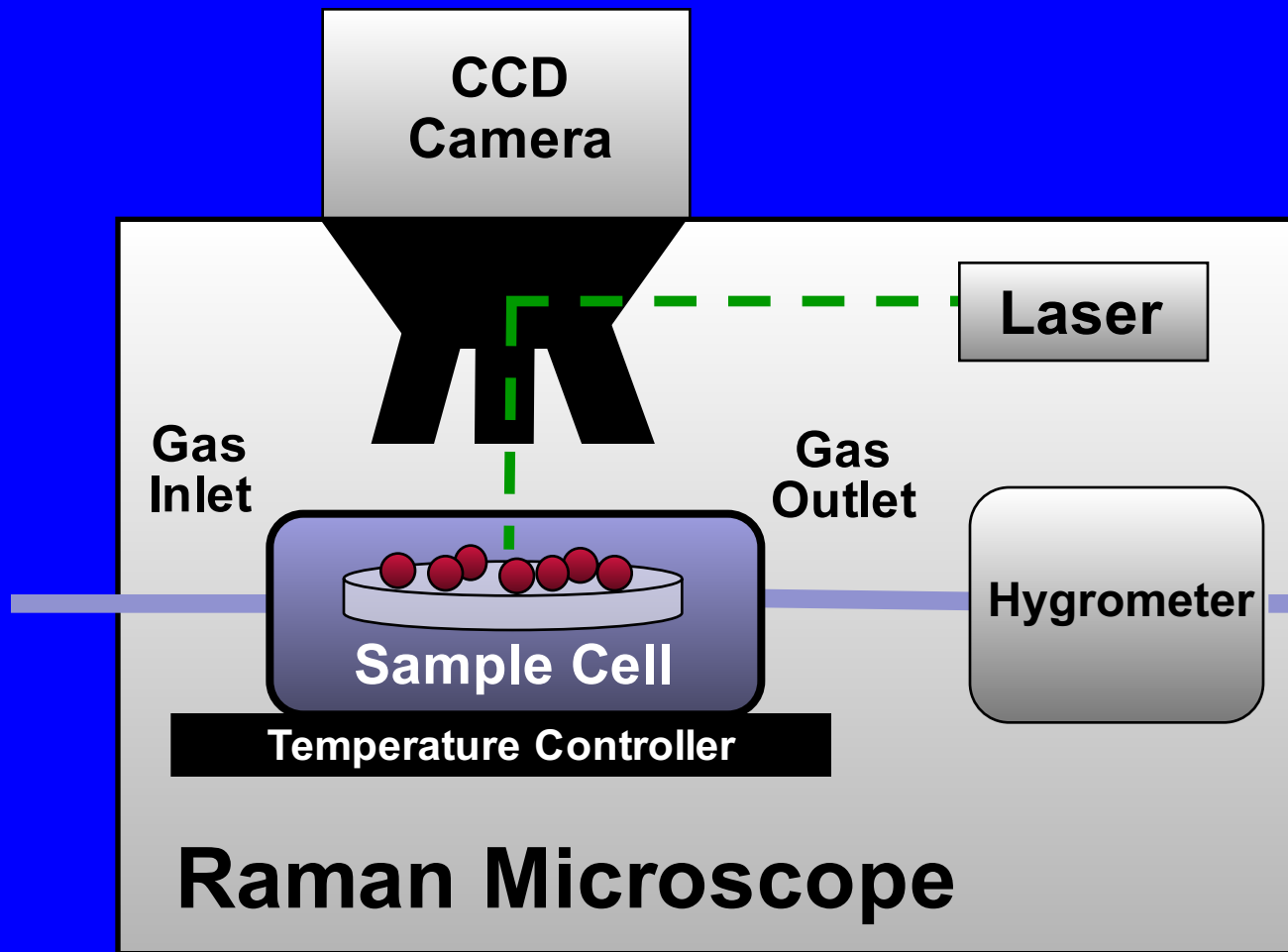


1,2,6-
hexanetriol

phase separates

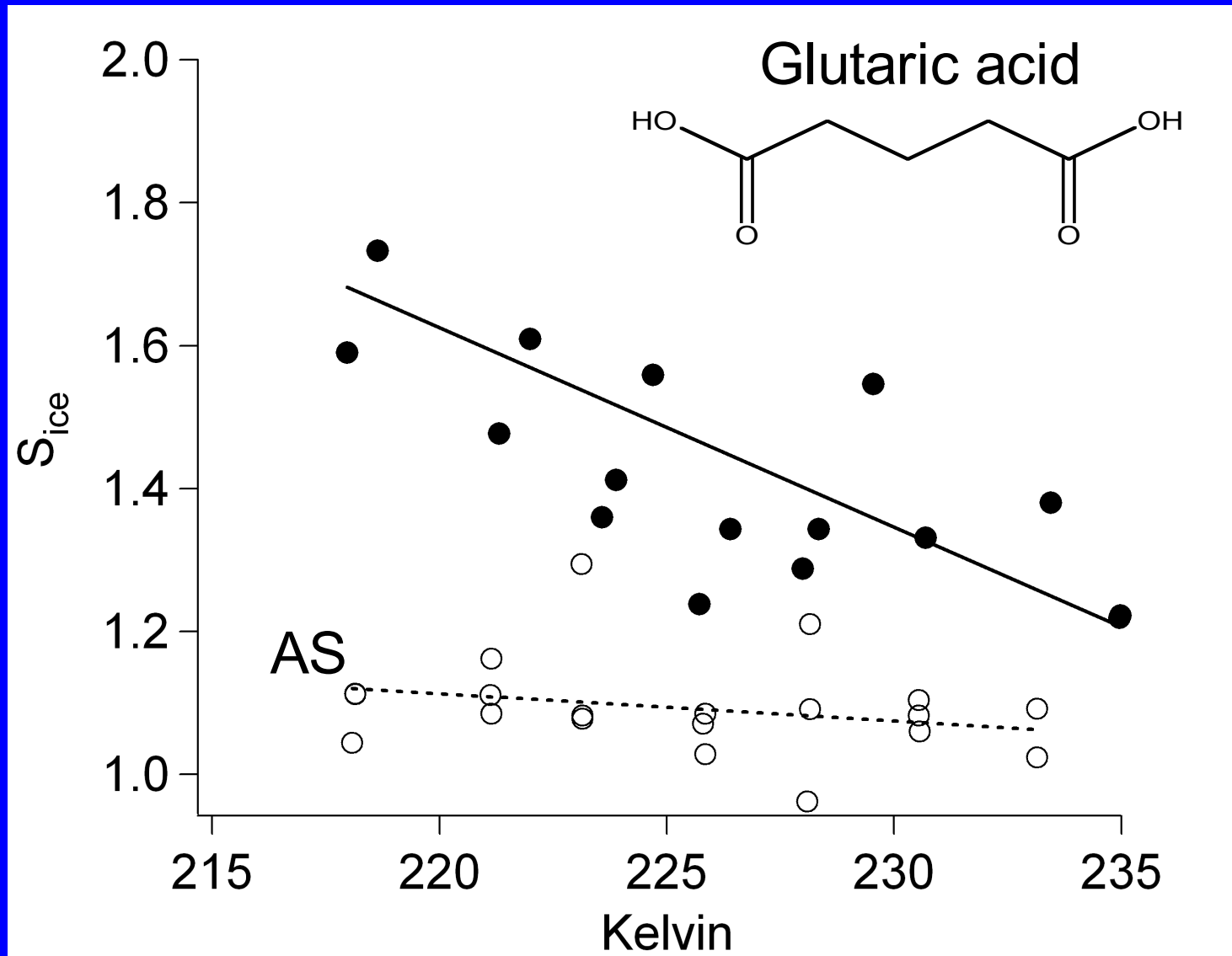


Raman Microscopy: One Particle at a Time



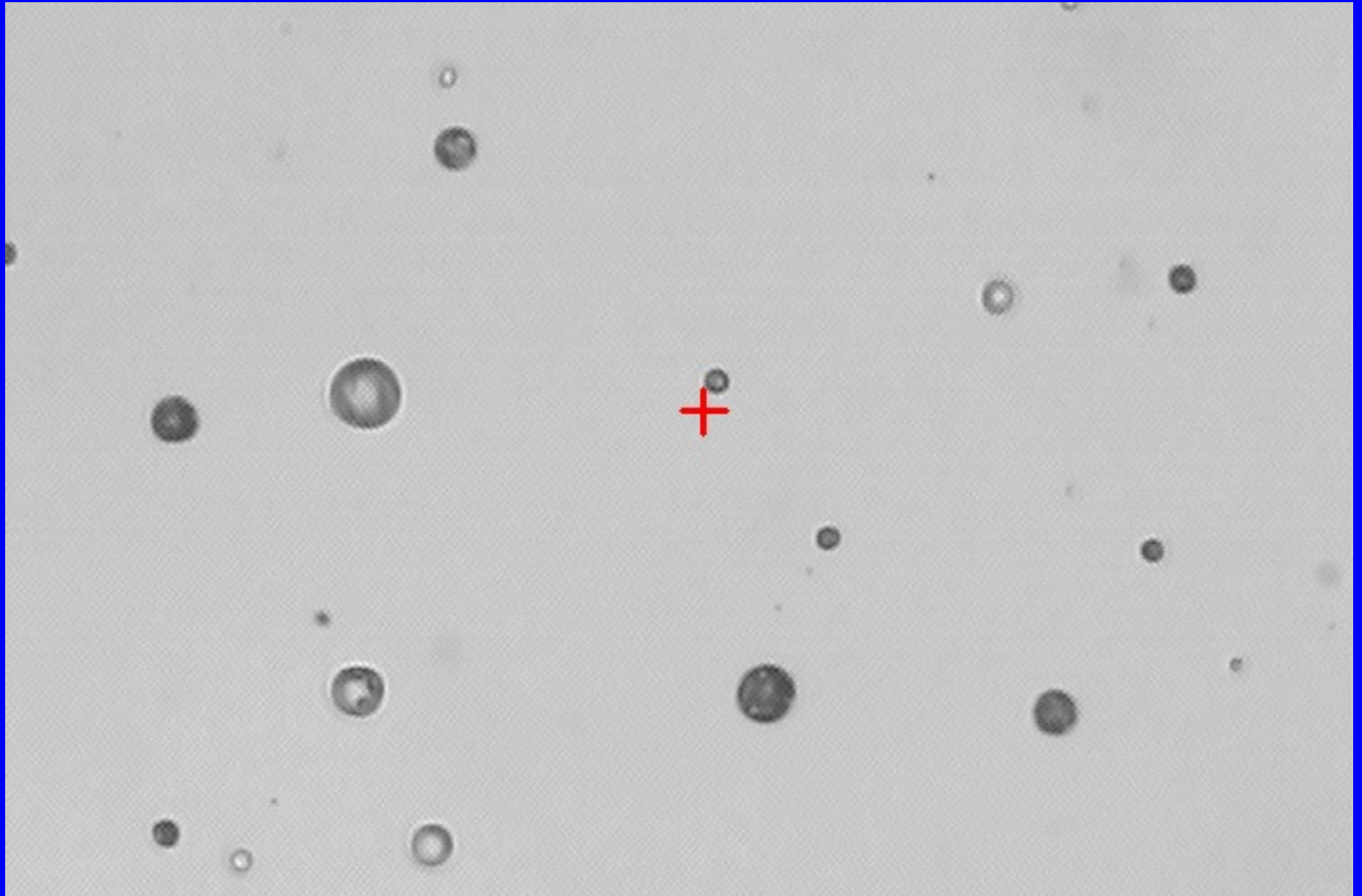
$$S_{ice} = P_{H_2O} / VP_{ice}$$

Comparison of heterogeneous ice nucleation



Glutaric acid less effective ice nucleator than AS

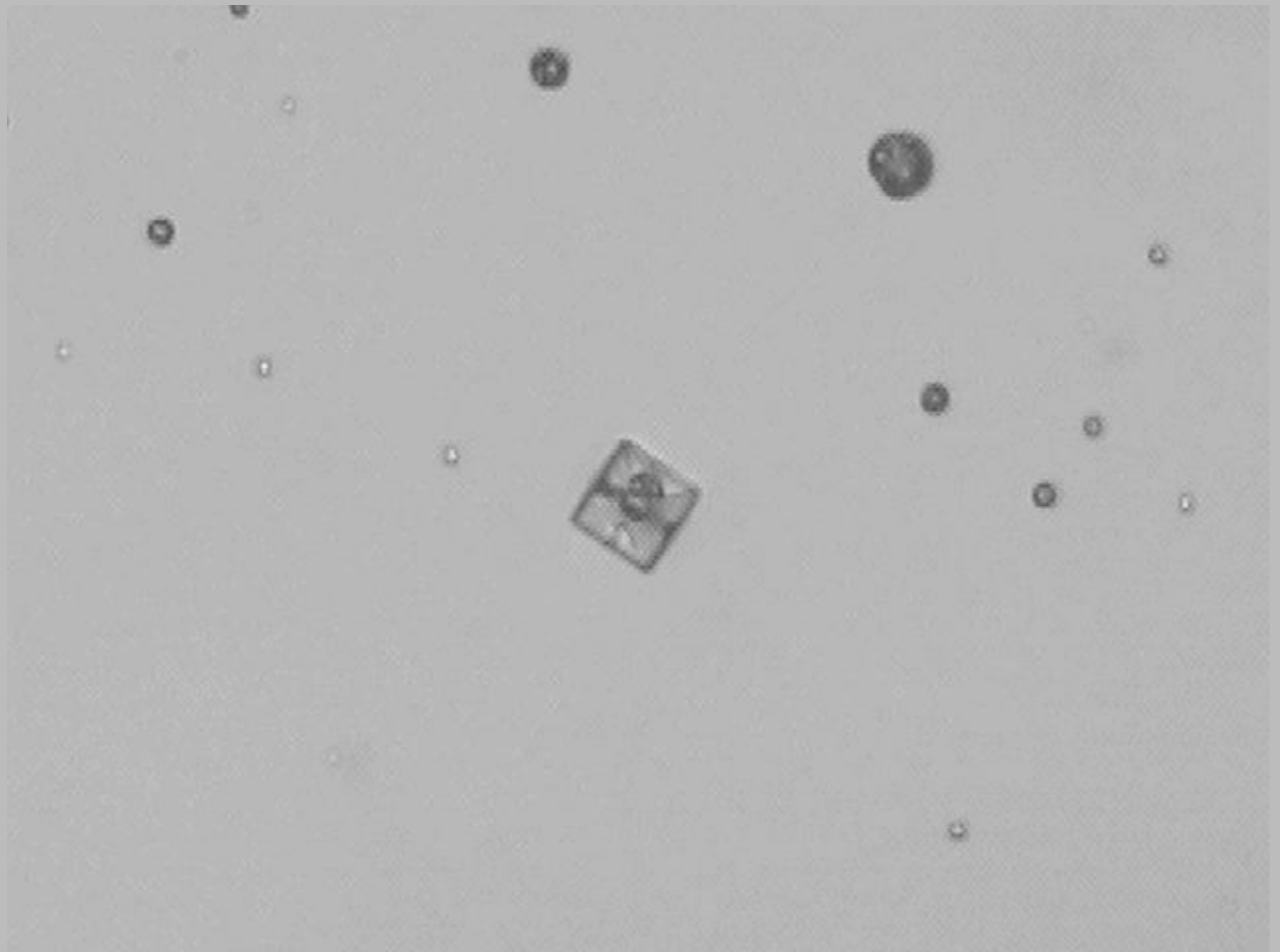
Mixed Grid of externally mixed AS and Glutaric Acid

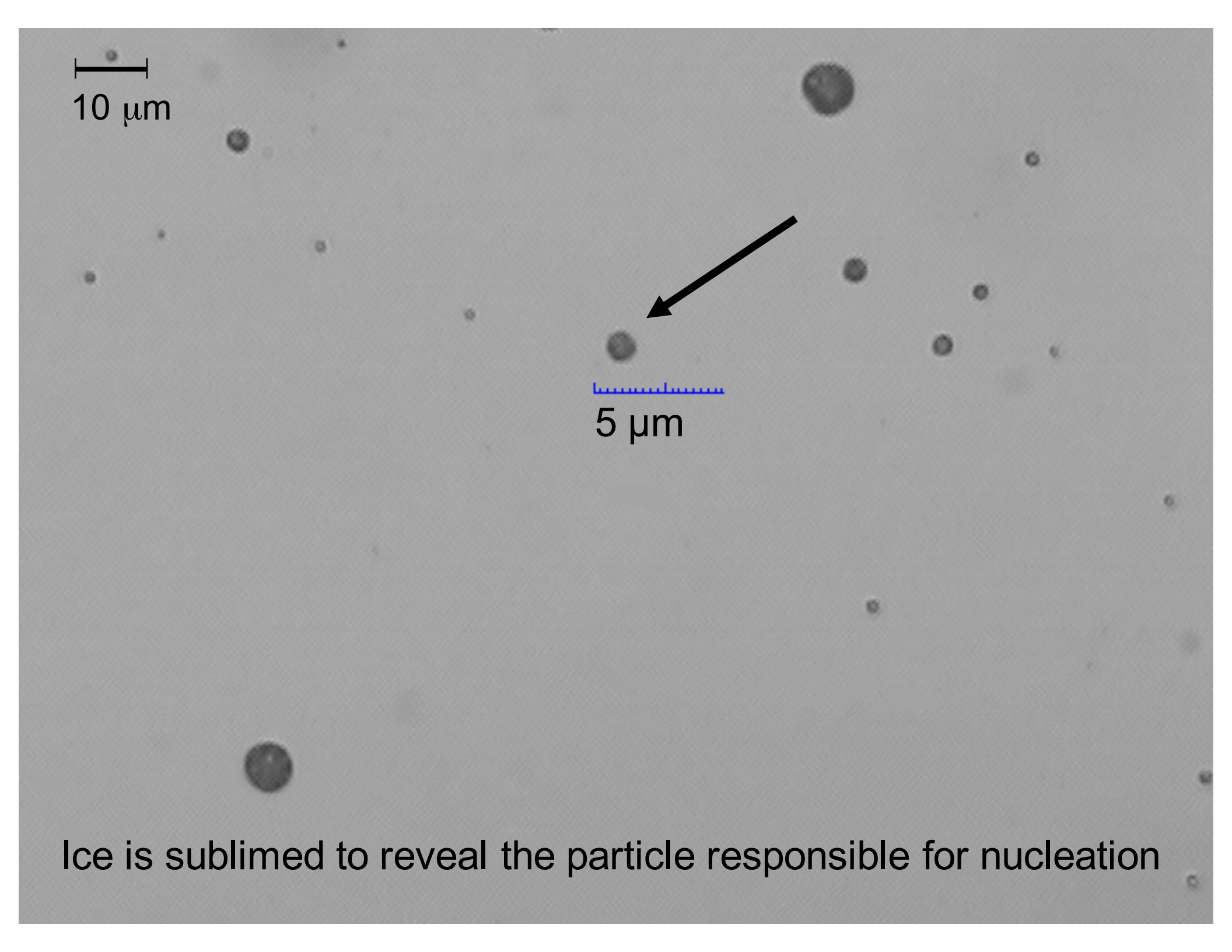


10 μm

10 μm

Ice nucleation on external mixture of glutaric acid and AS





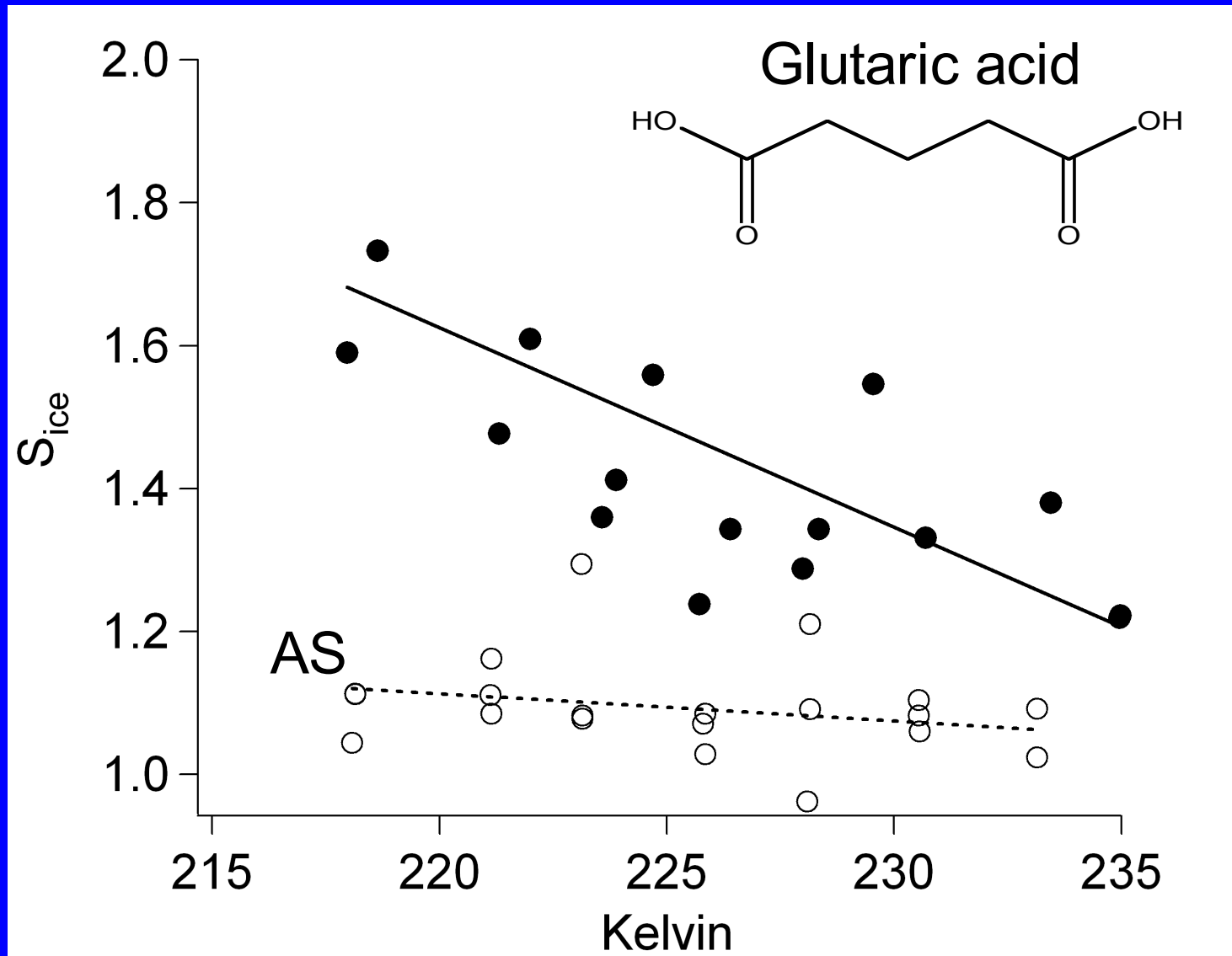
A grayscale micrograph showing numerous small, dark, spherical particles of varying sizes scattered across a light gray background. Some particles are significantly larger and more prominent than others. A black arrow points from the upper right towards a specific particle in the center. Two scale bars are present: a black one in the top left and a blue one in the center.

10 μm

5 μm

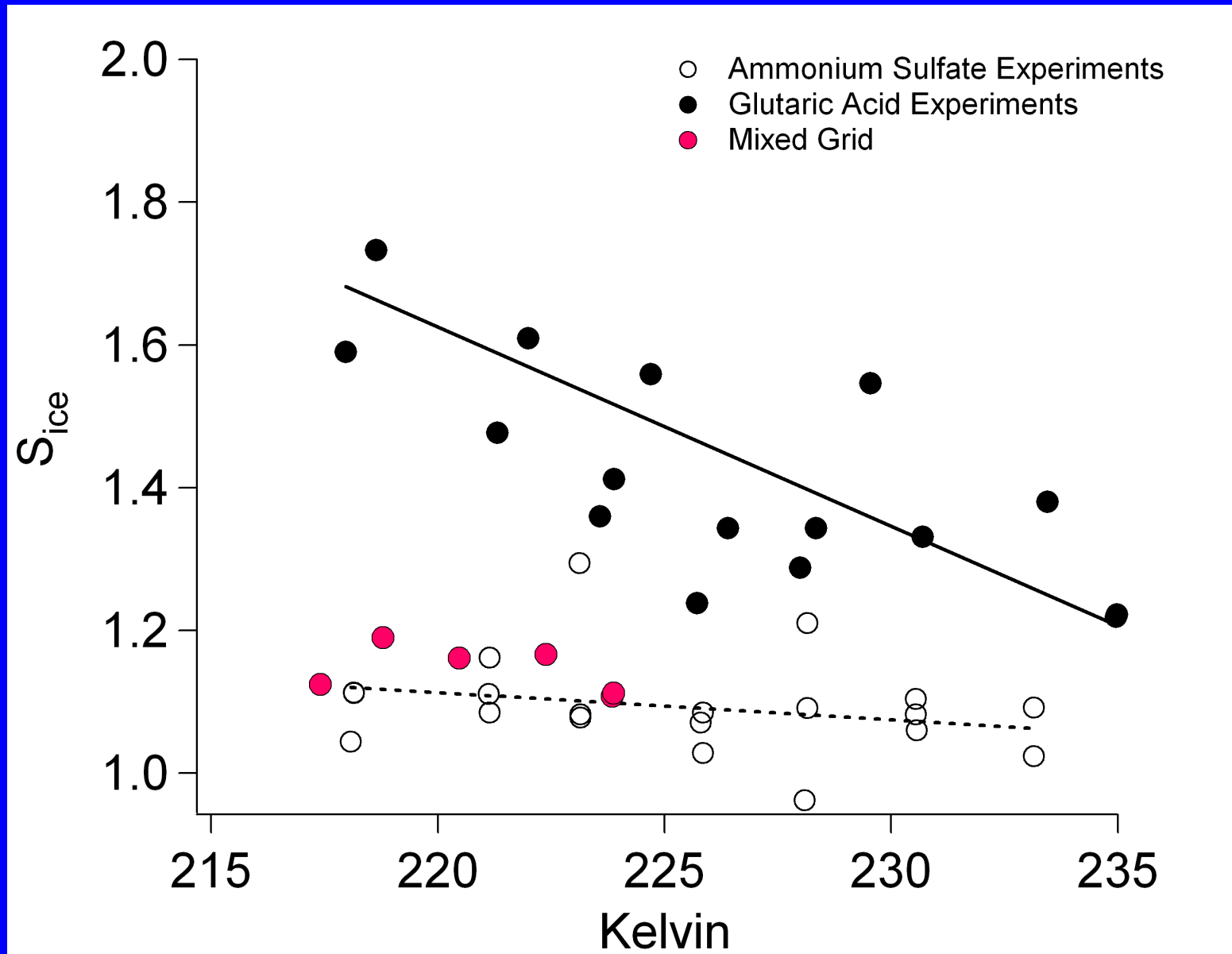
Ice is sublimed to reveal the particle responsible for nucleation

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



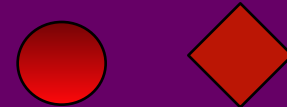
1. Particle size

Larger better

2. Composition

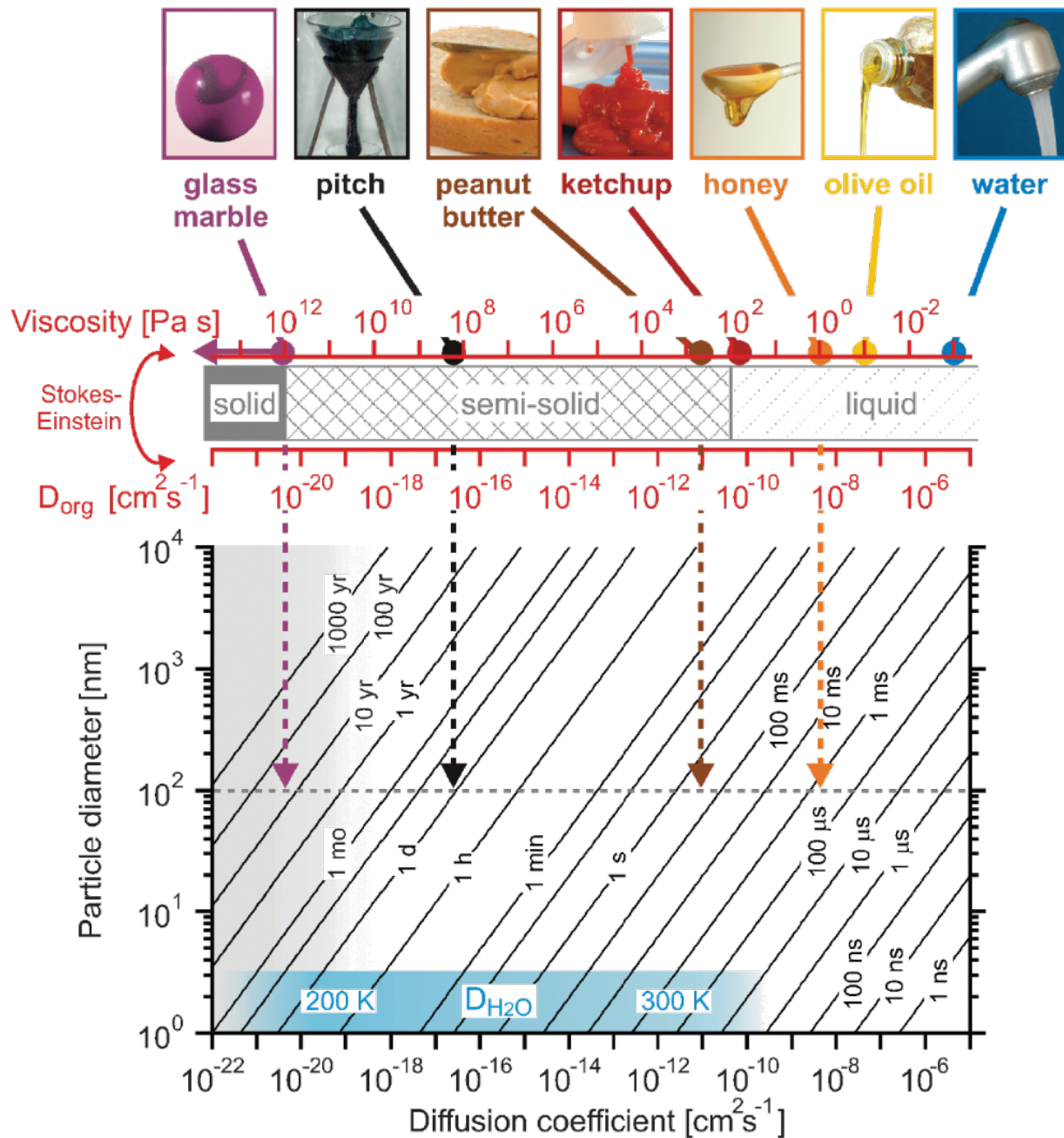
Minerals/salts good
Organics poor

3. Phase



4. Chemical Distribution



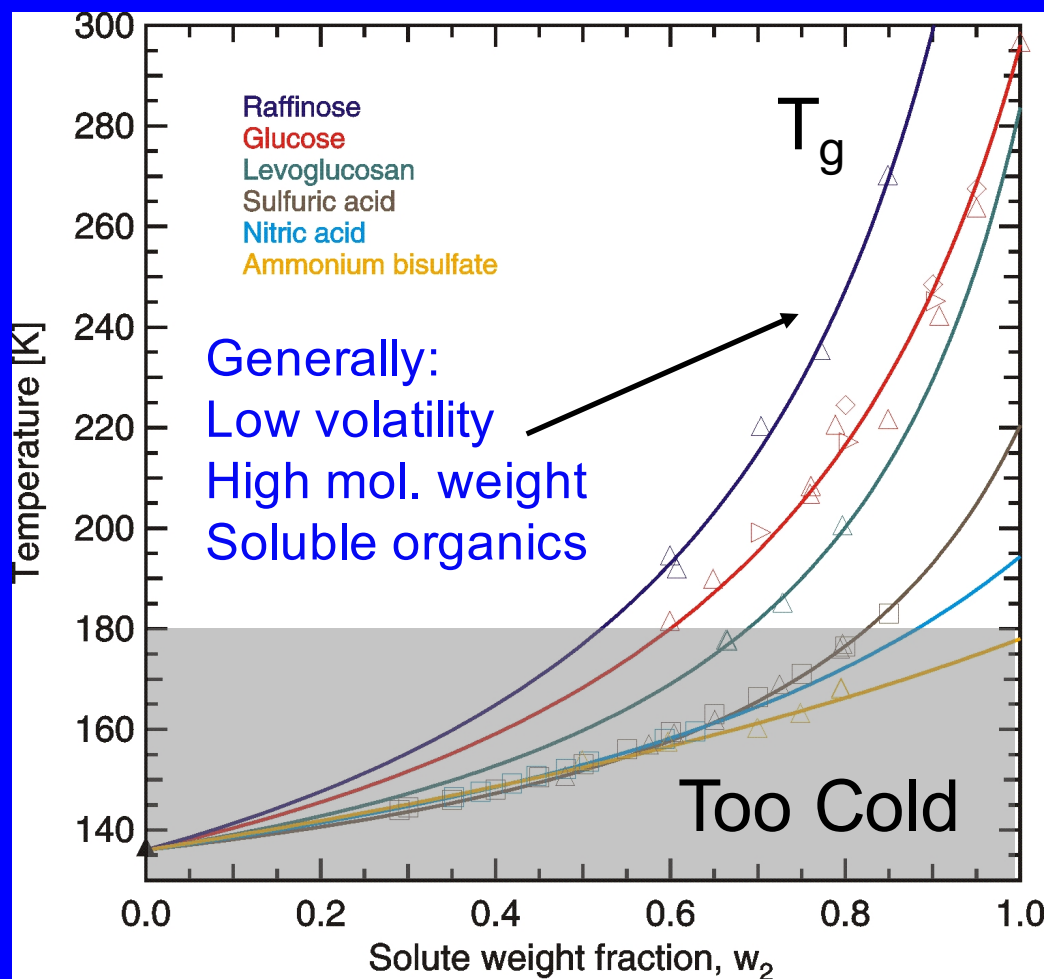


Glasses:

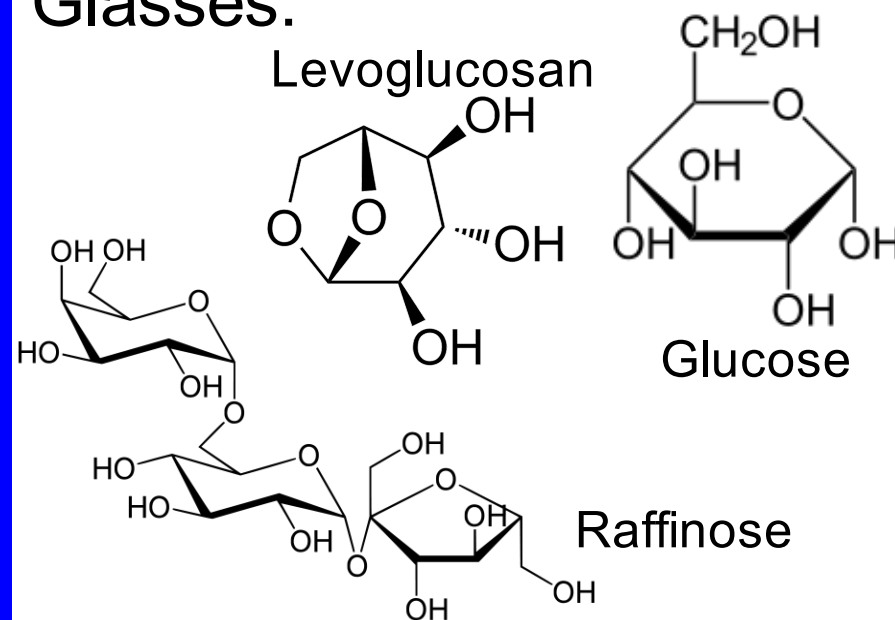
High viscosity
Low diffusion

Koop PCCP 2011

Atmospheric Glasses



Glasses:



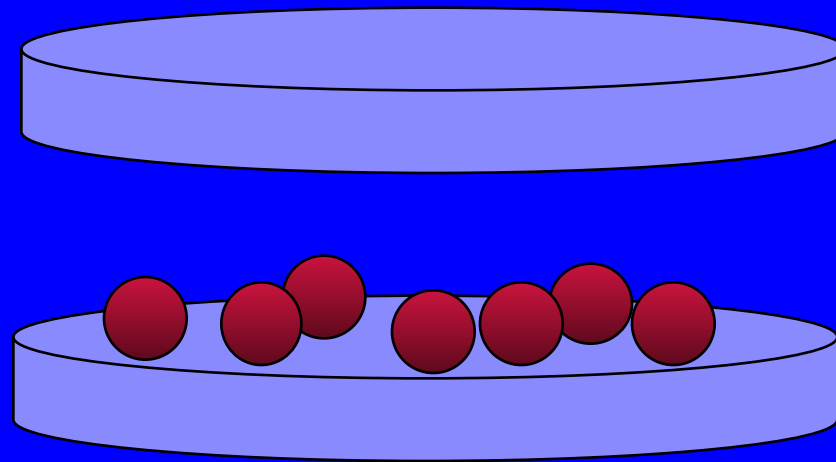
Not glasses:



Zobrist et al., (2008)

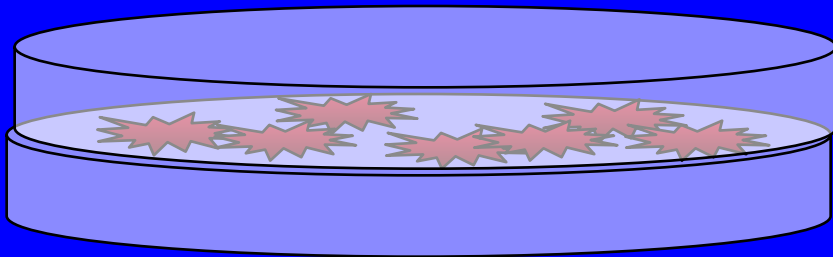
Organic aerosol can exist as highly viscous amorphous glasses
High MW and high O content favors glass formation

Smash Experiment

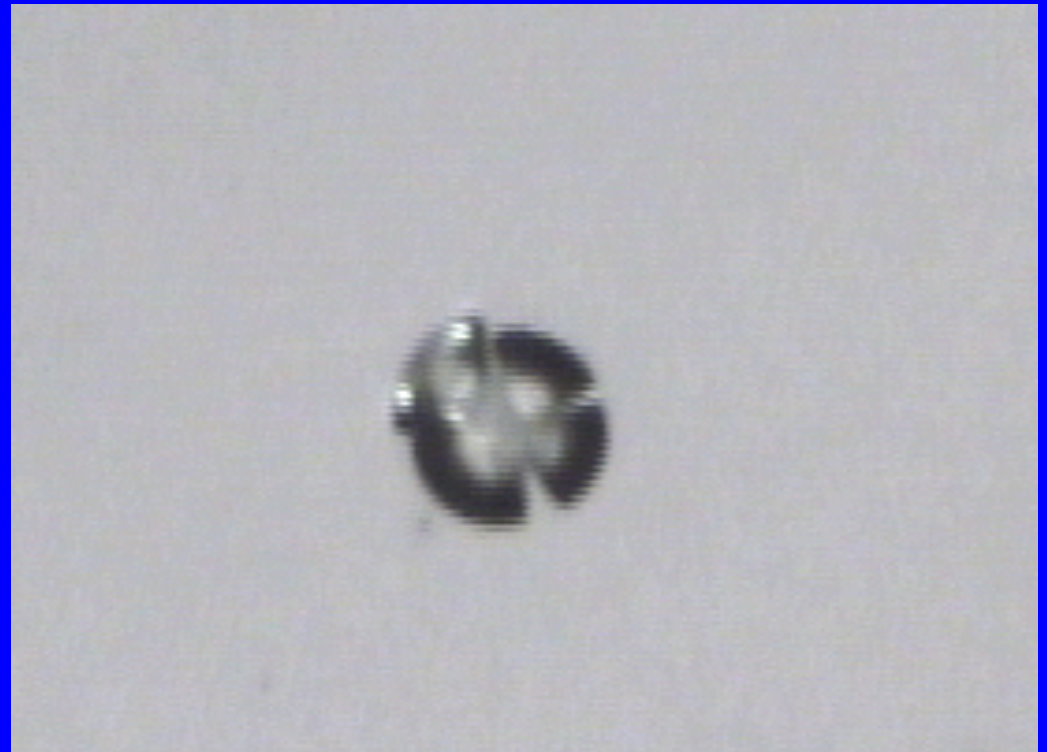


Adapted from
Murray ACP 2011

Smash Experiment



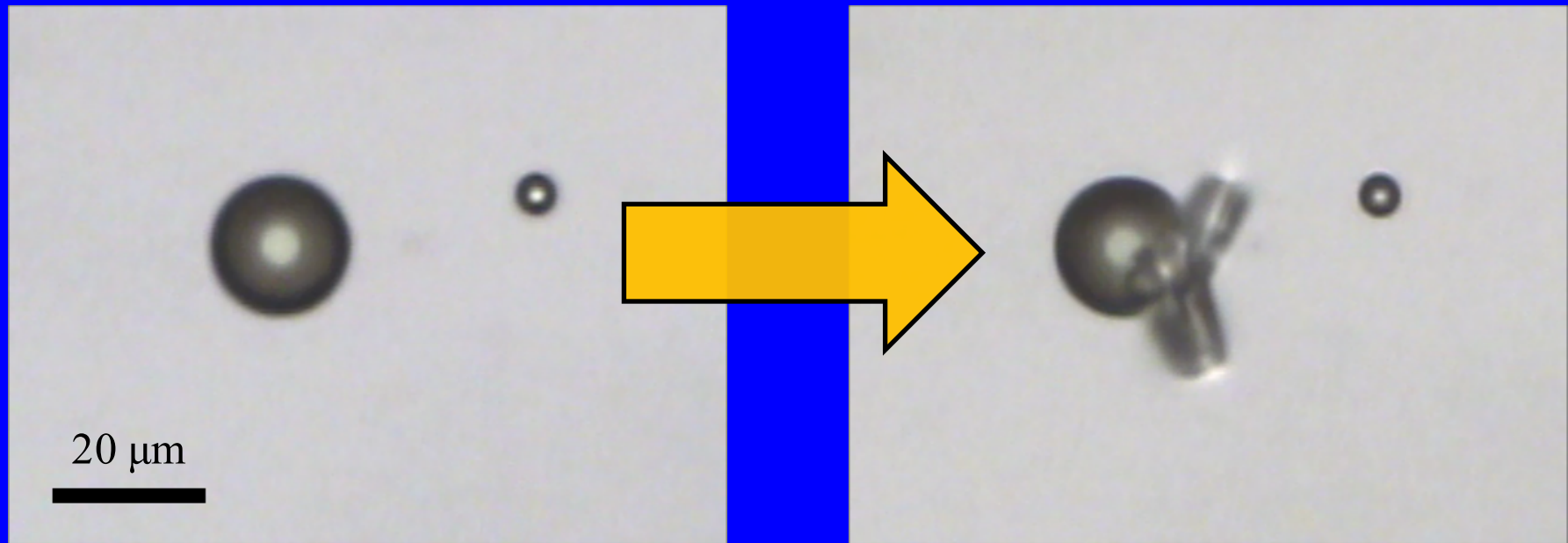
Adapted from
Murray ACP 2011



“Smooosh” → Liquid

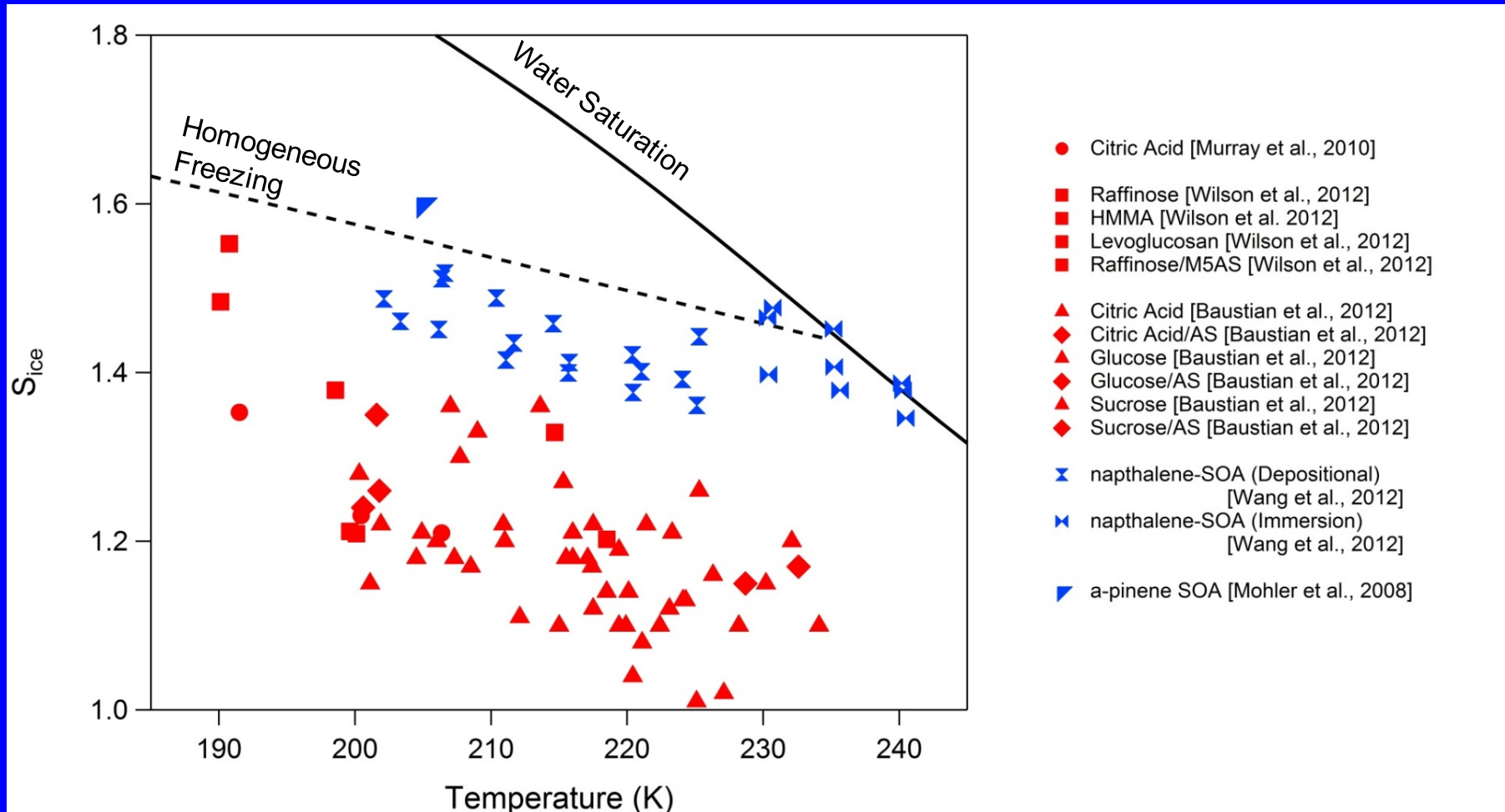
Shatter → highly viscous
(semi-)solid or glassy state

Depositional Ice Nucleation on (un-smashed) Glassy organic



Before they liquefy, glassy particles can nucleate ice
depositionally

Heterogeneous Ice Nucleation on Organic Glasses



Simple 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

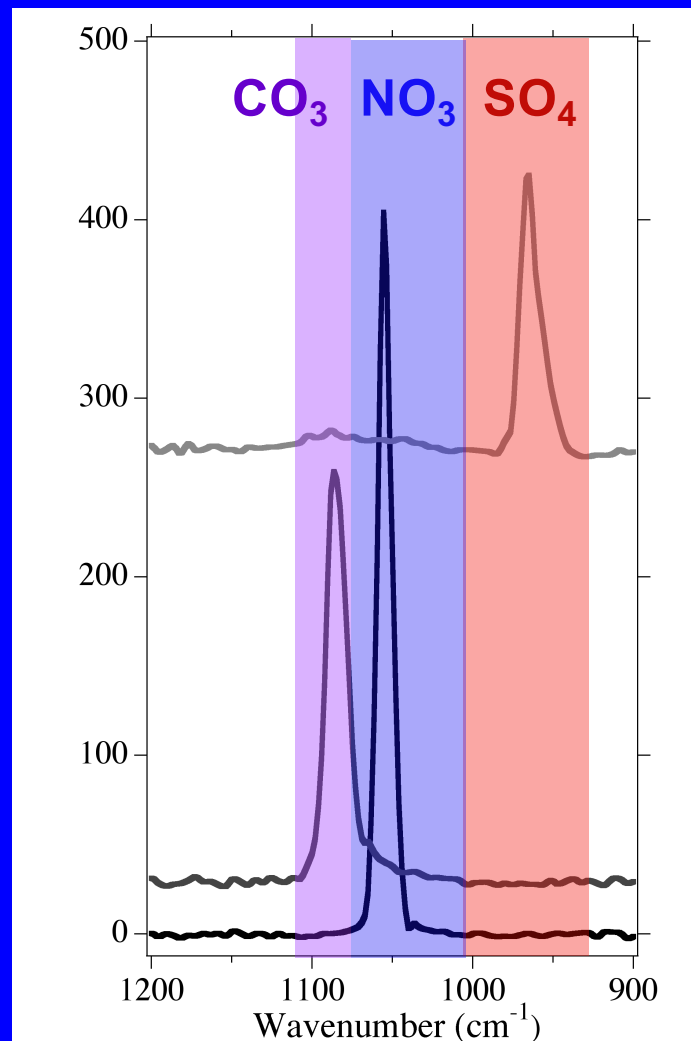
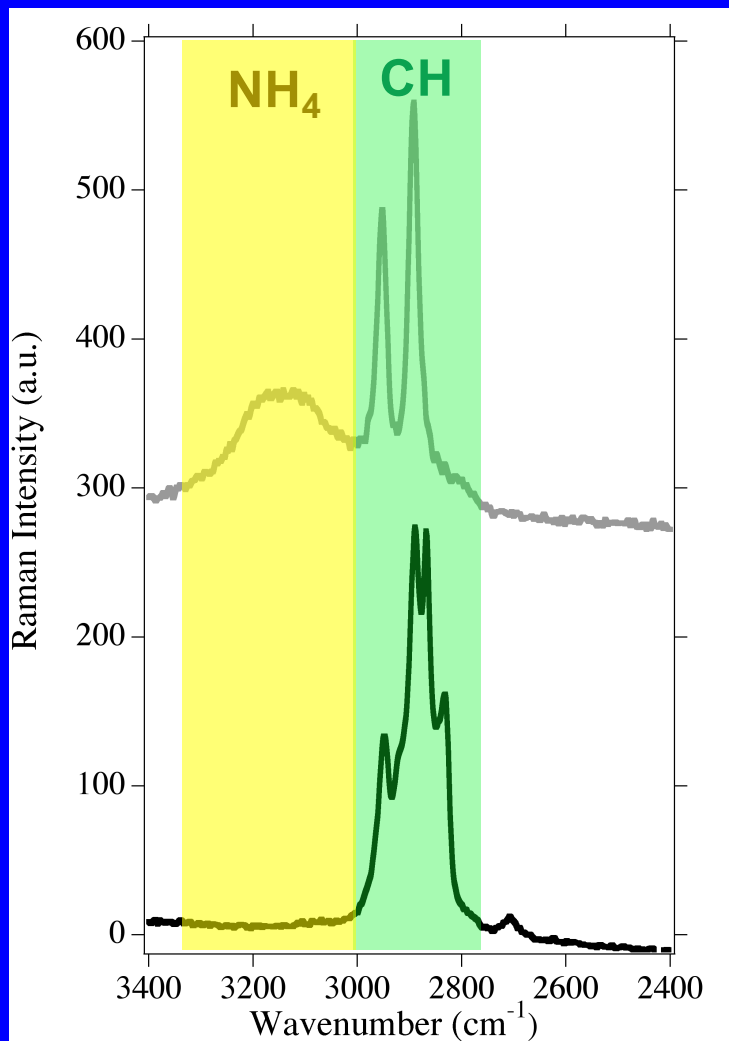
3. Phase

Glasses mixed

4. Chemical Distribution

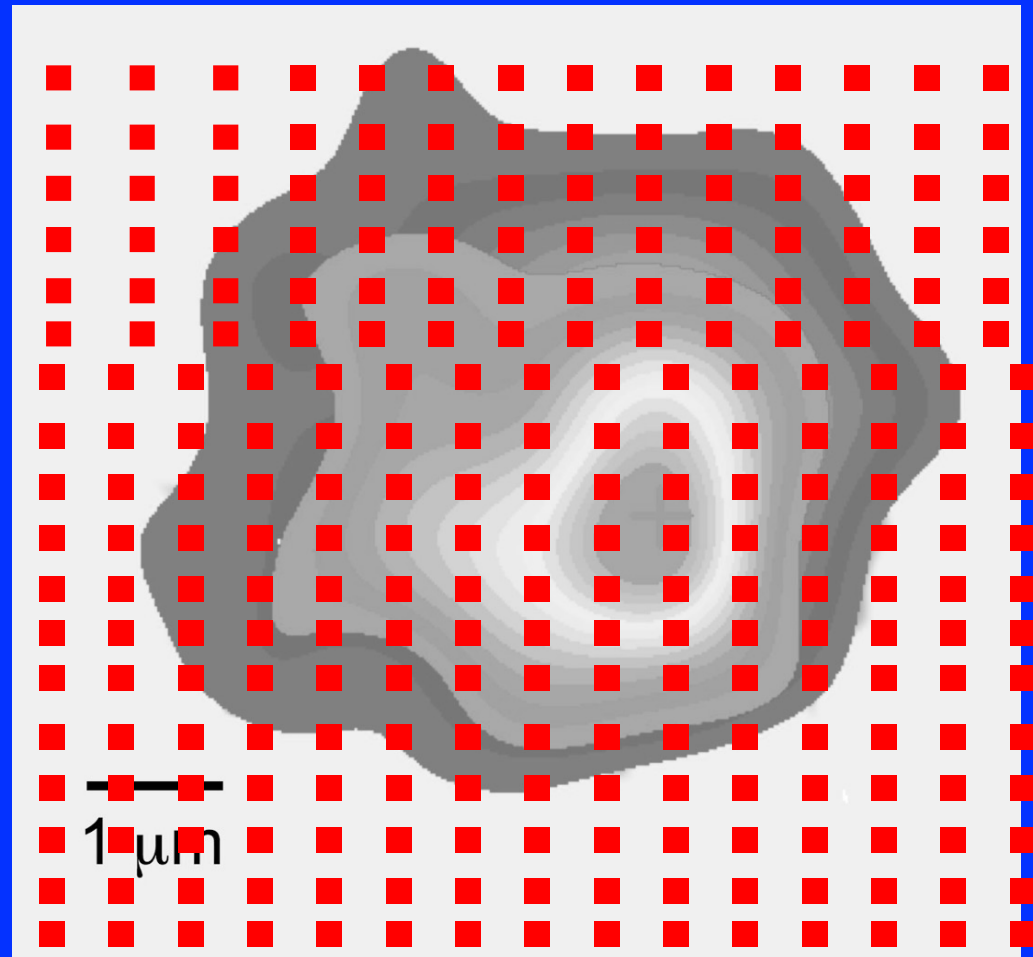


Spectral Classification for Raman Mapping

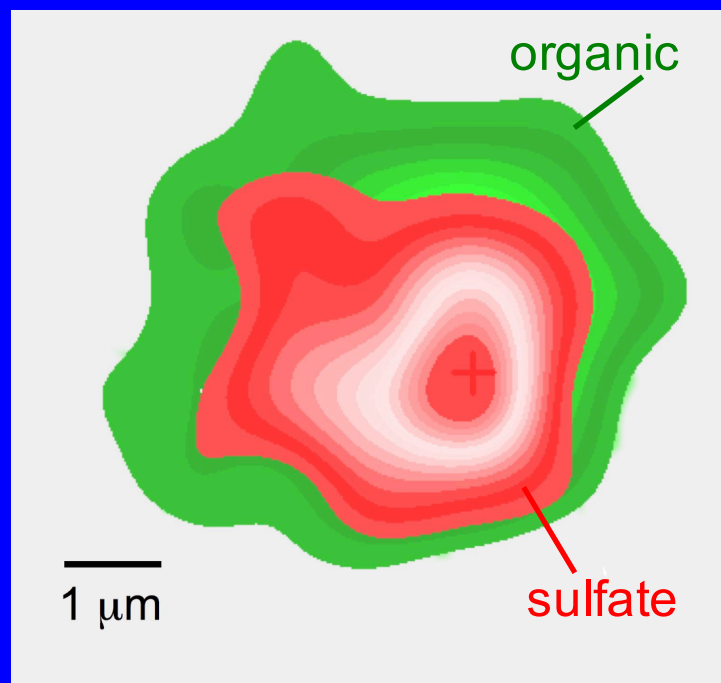


Spectra were classified using characteristic frequencies:
Organics, Sulfates, Nitrates (aged sea salt), Carbonates
(mineral dust), Ammonium.

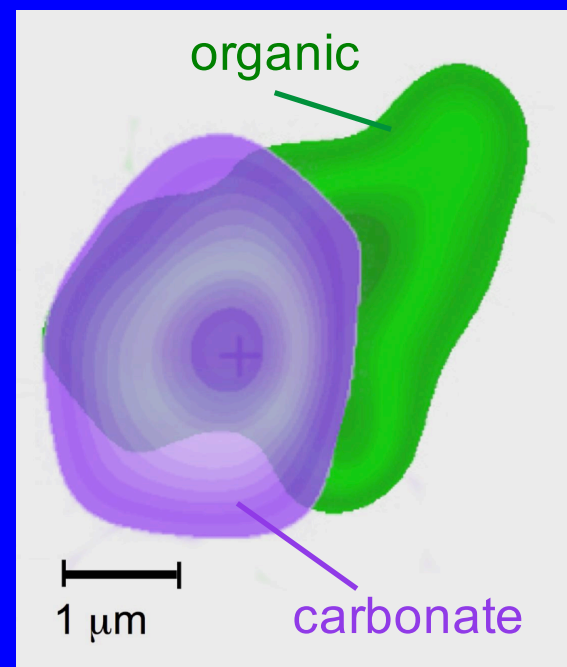
Raman Mapping



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

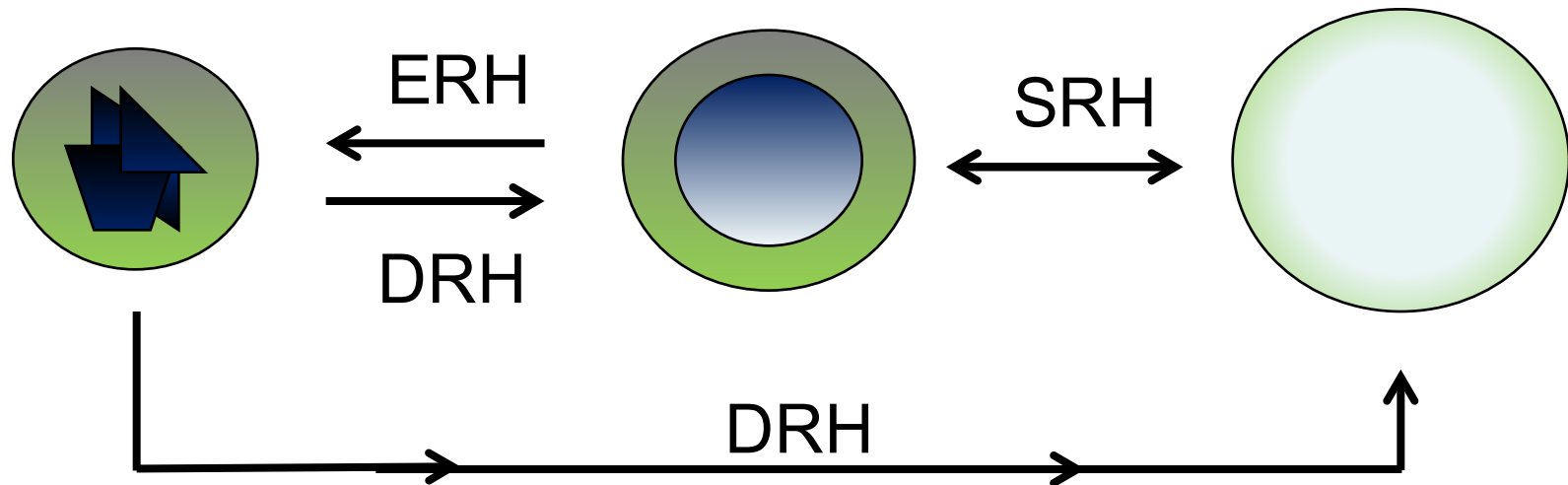
Liquid-Liquid Phase Separation

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

One Liquid Organic Phase
One Crystalline Phase

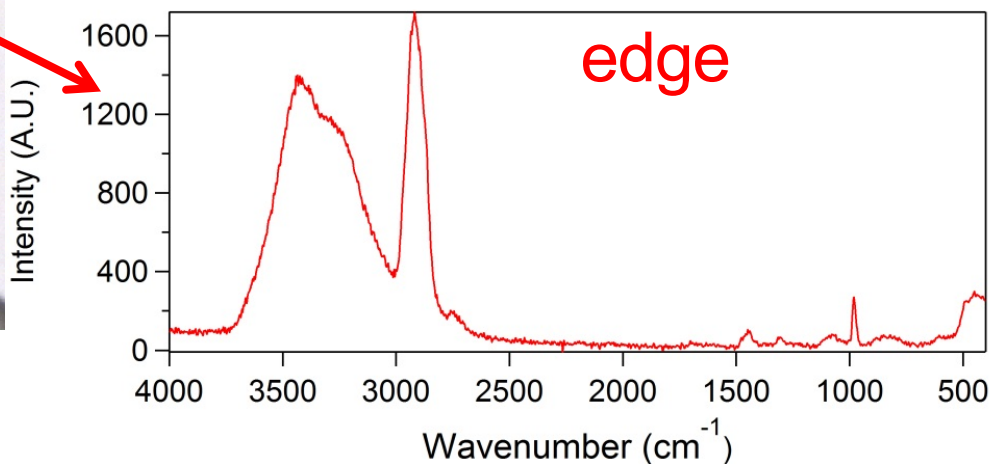
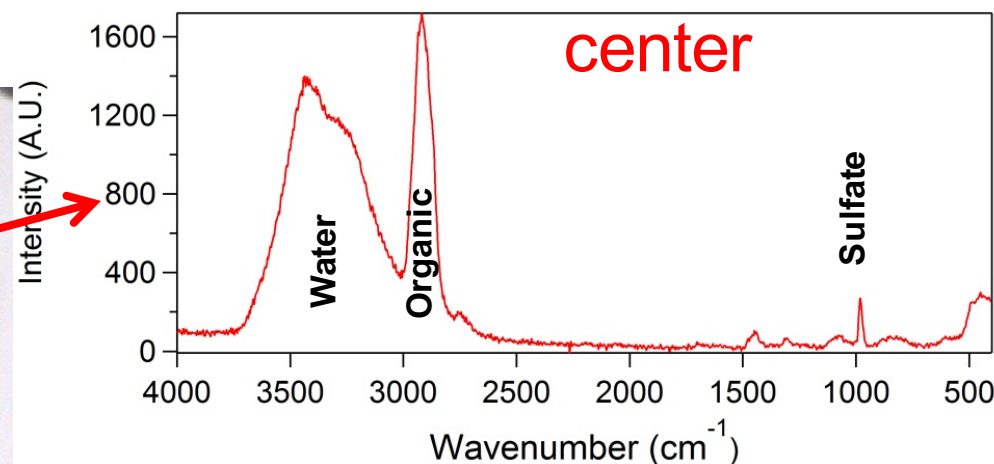
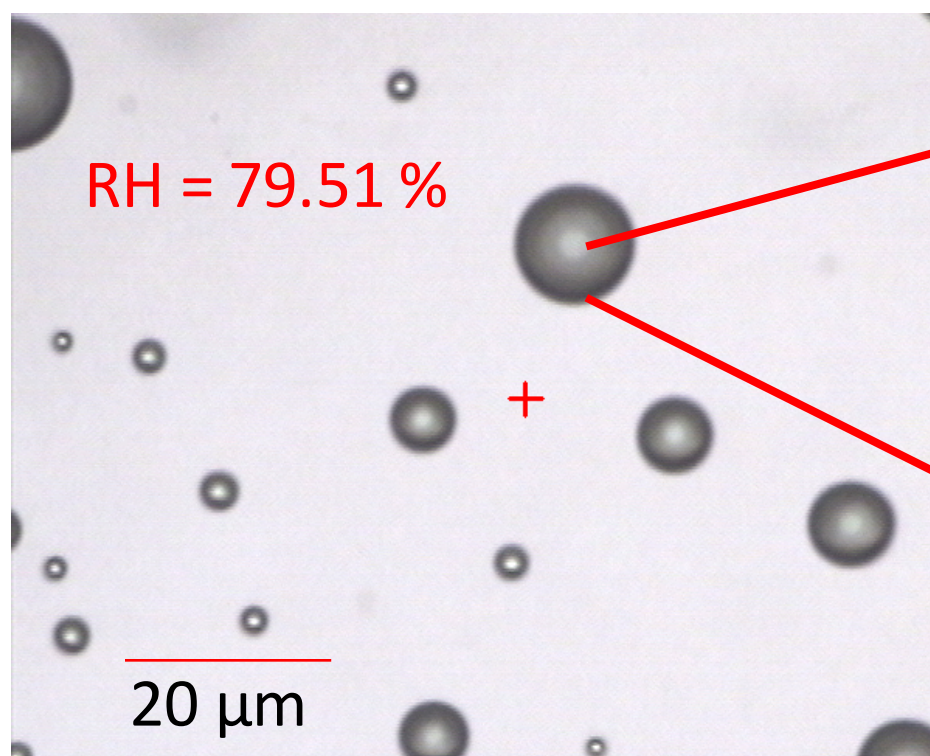
Two Liquid Phases

One Liquid Phase



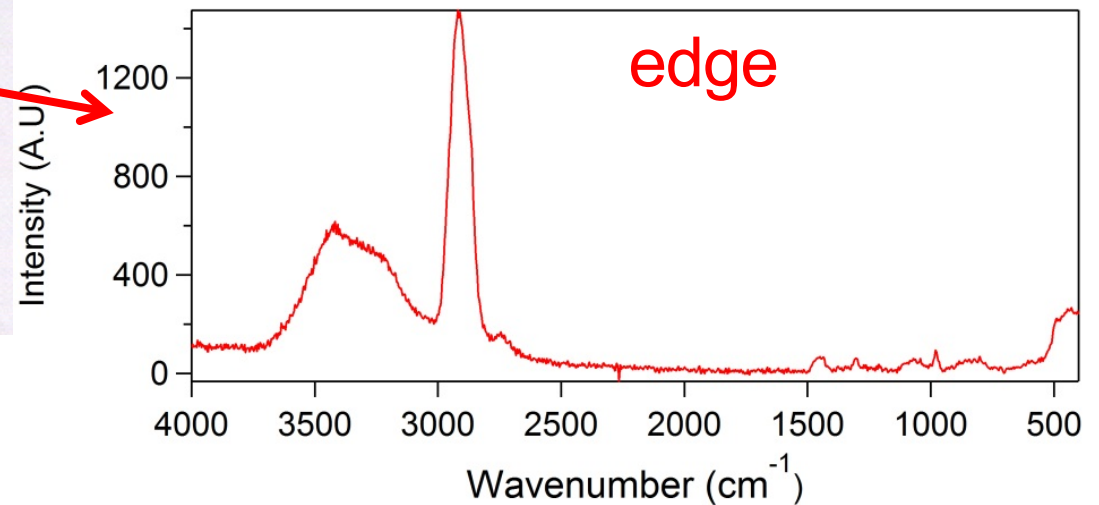
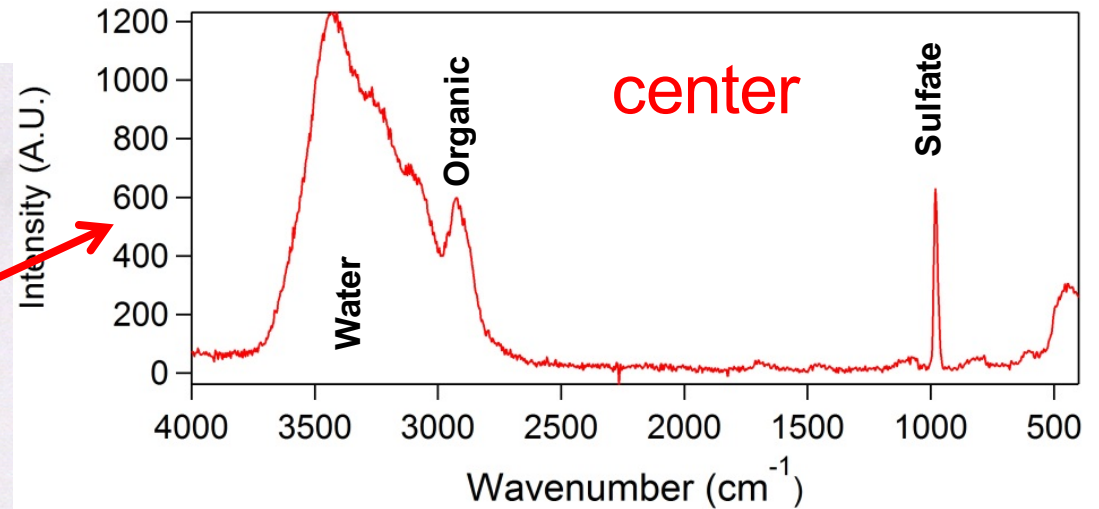
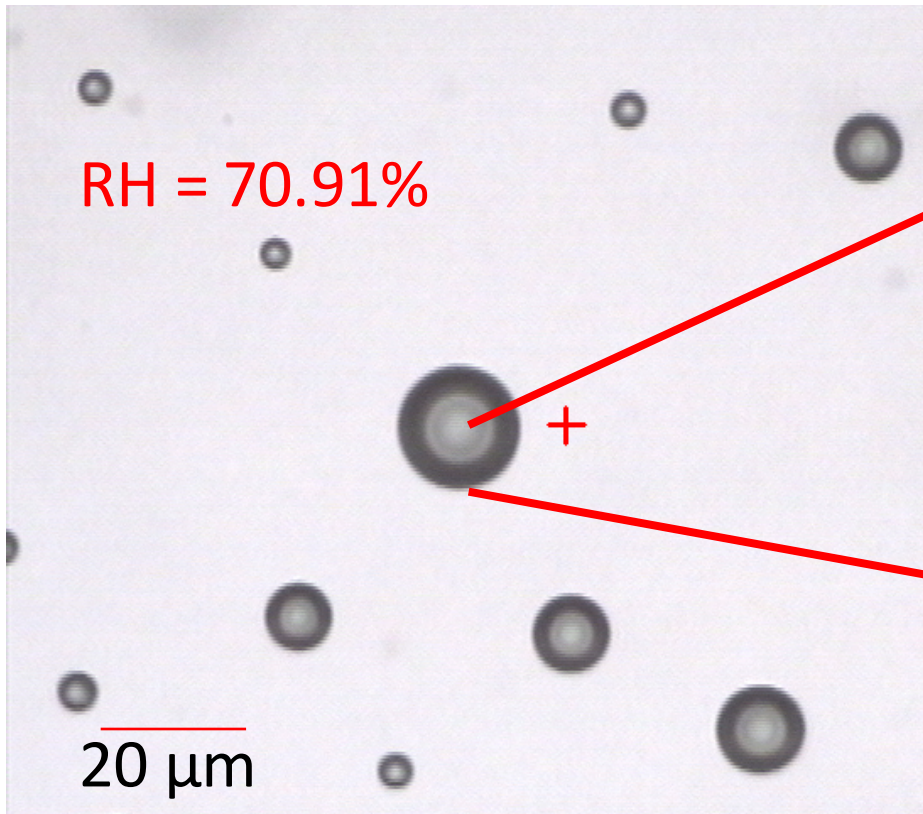
Increasing RH

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



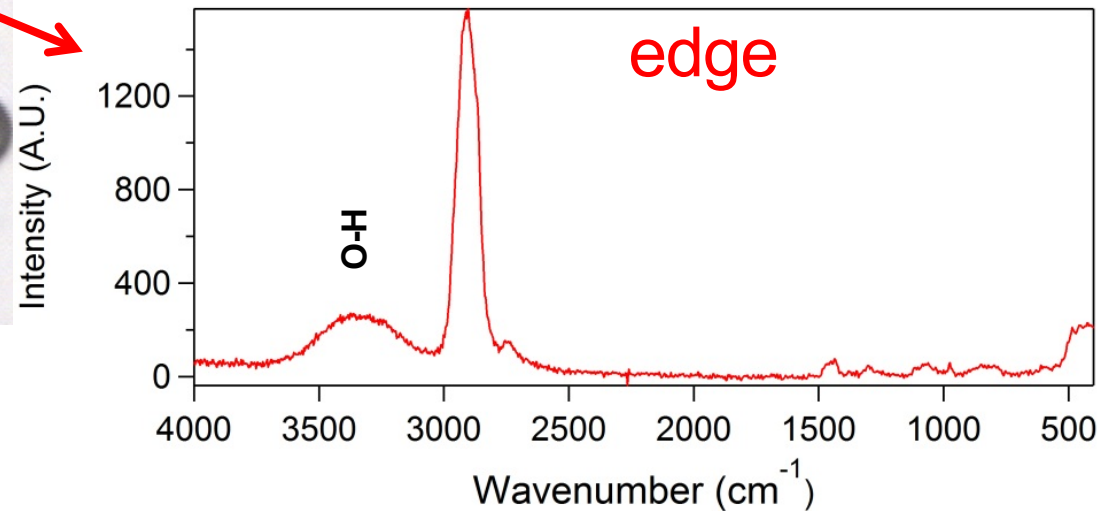
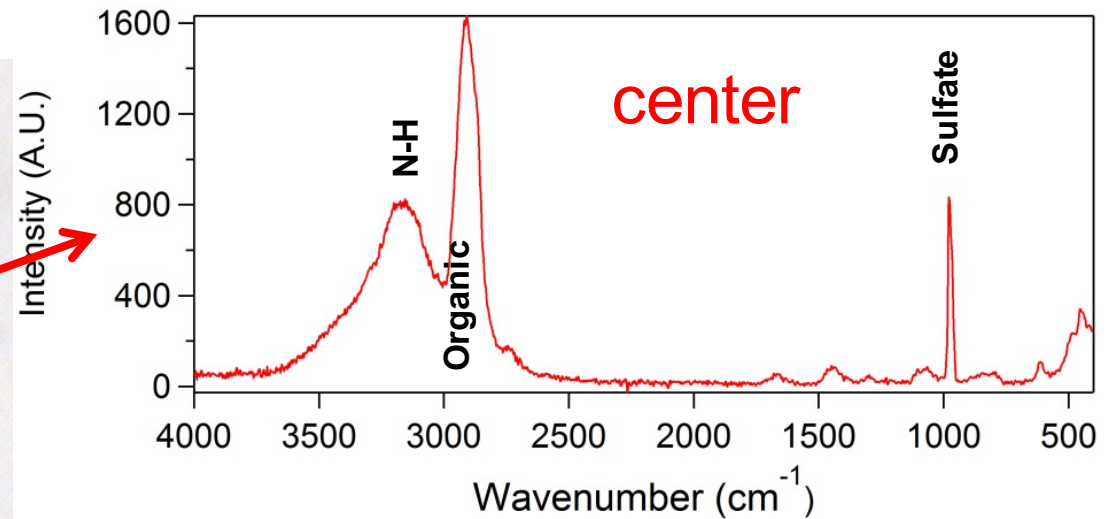
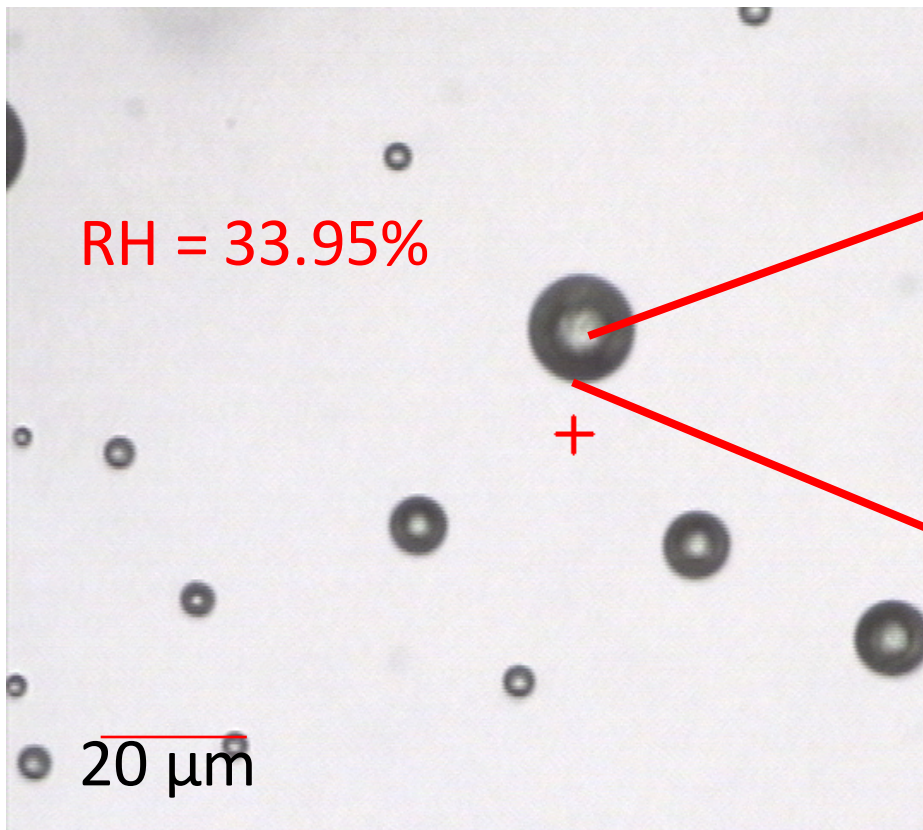
Particle composition same interior and exterior

Liquid-Liquid Phase Separation



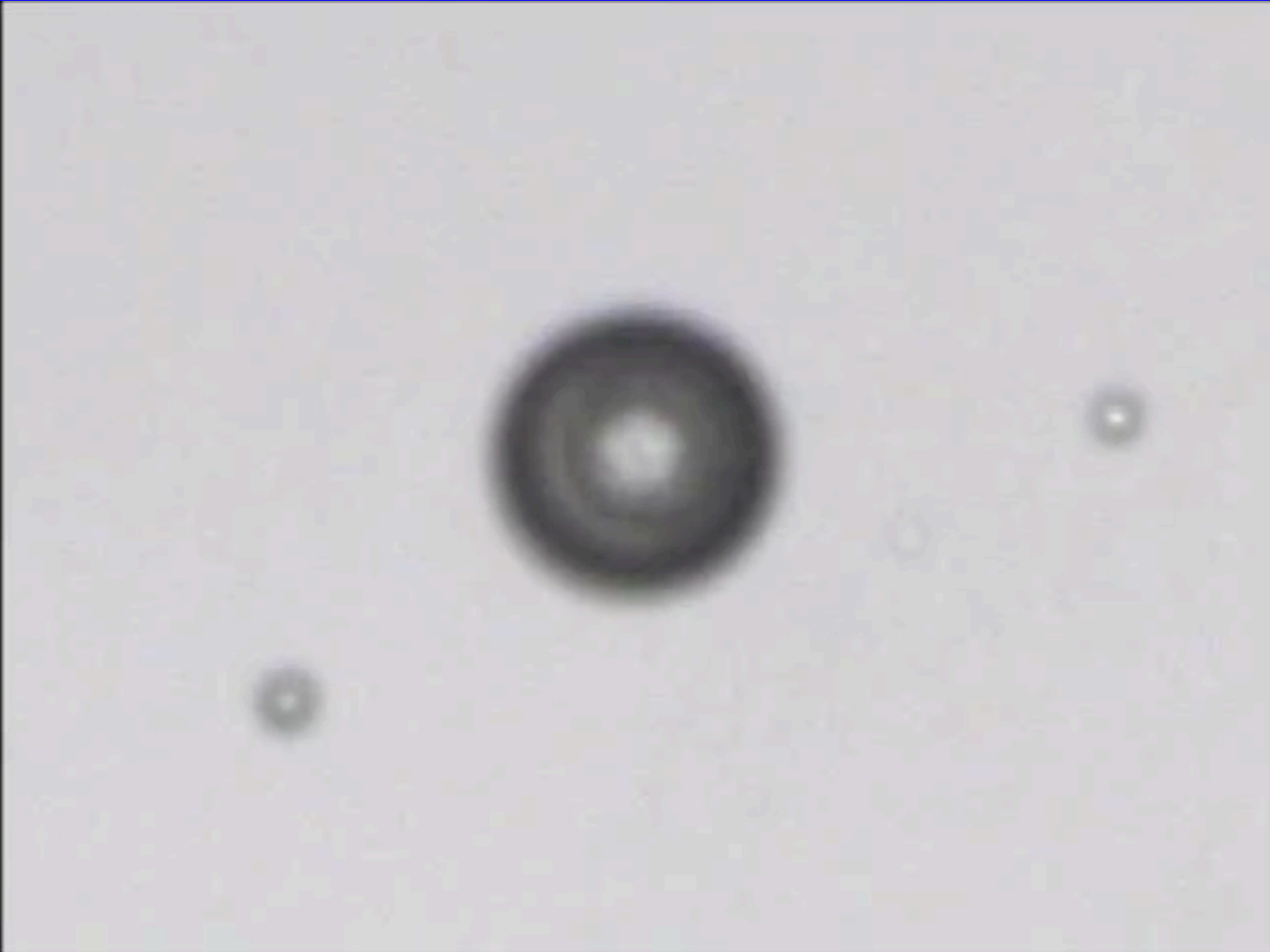
Aqueous ammonium sulfate core with organic coating

Efflorescence

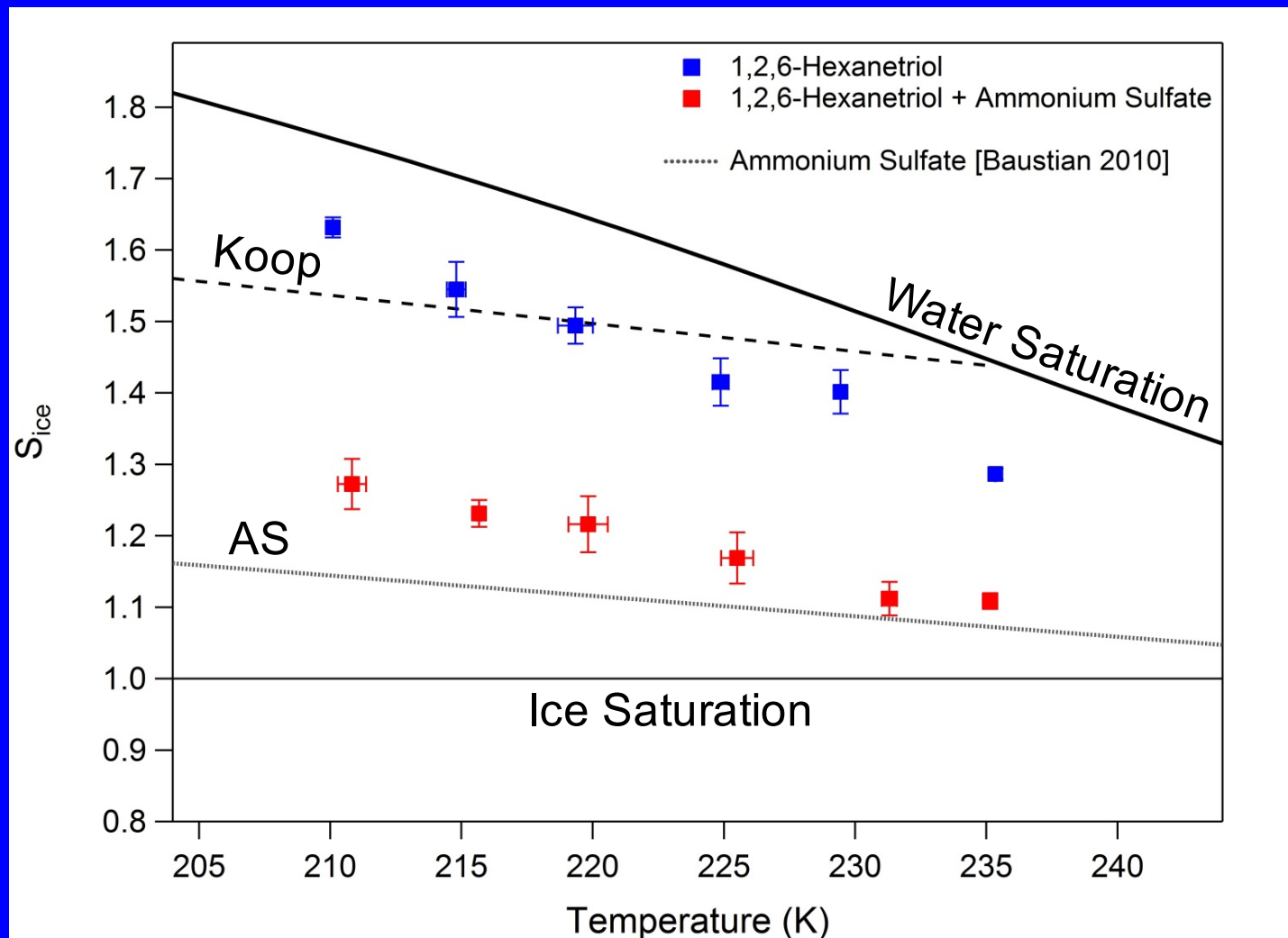


Solid ammonium sulfate core with organic coating

Ice Nucleation inside out

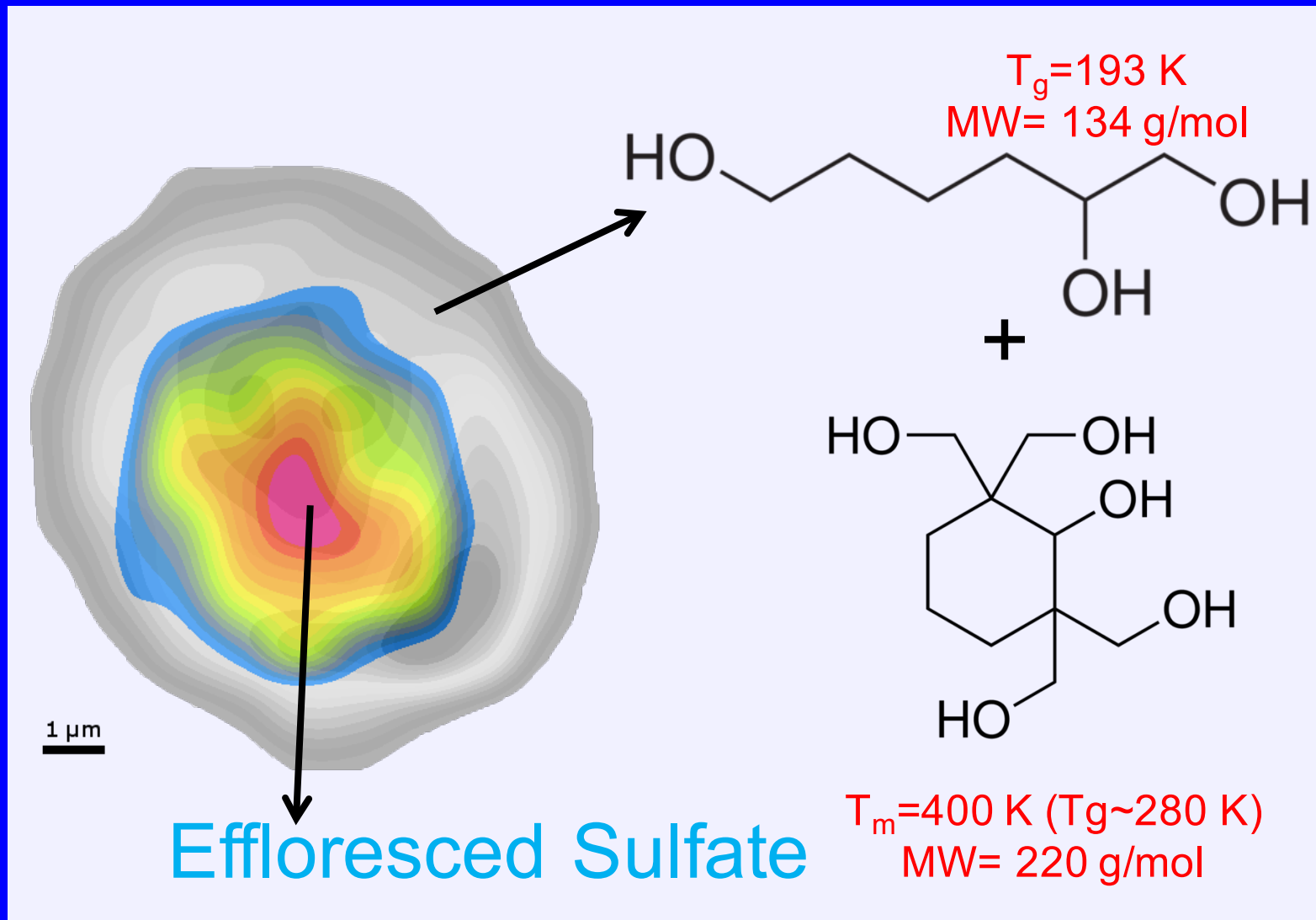


S_{ice} for inside-nucleated ice



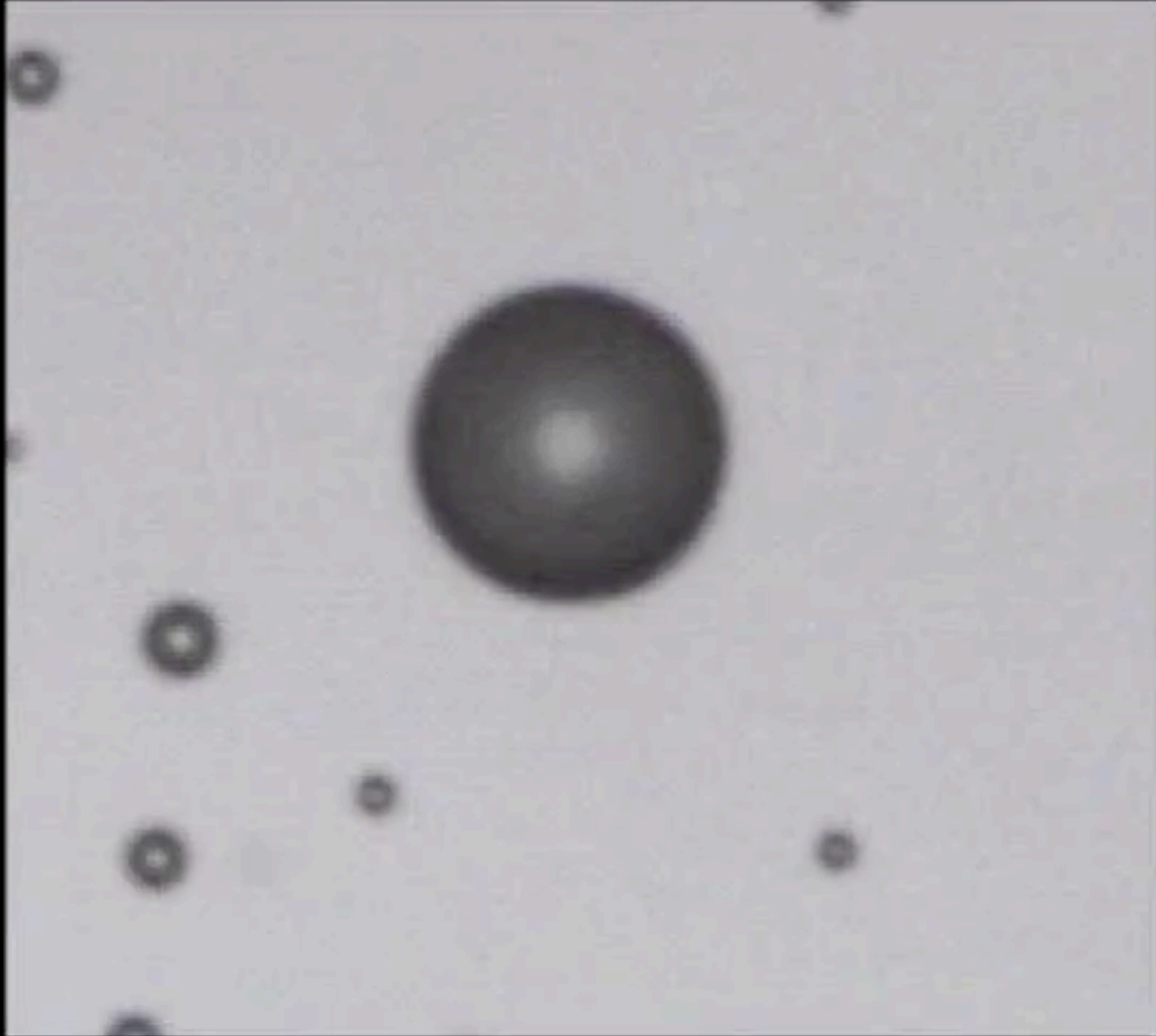
Coated AS almost as good IN as pure AS

Ice Nucleation for Glassy Coating

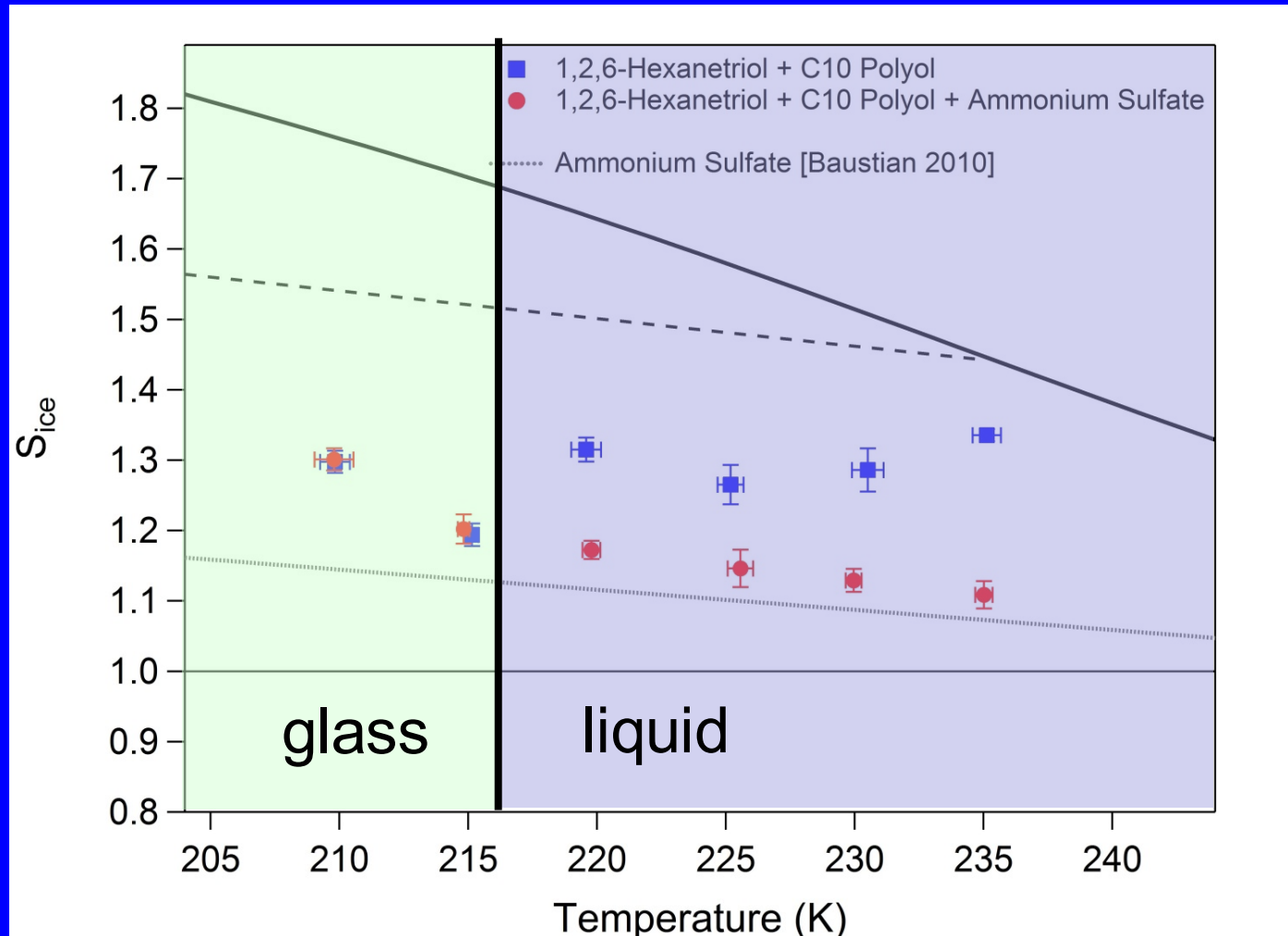


Goal: Liquid at 250 to phase separate, lower T to form glass

Ice Nucleation on Glassy Organics

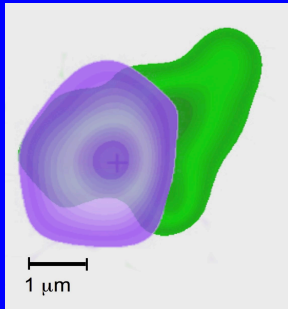


S_{ice} for Mixed Organic

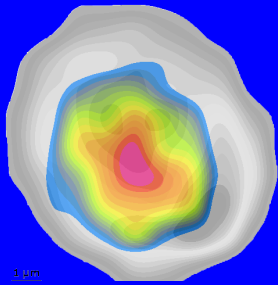


Good IN over entire range for different reasons

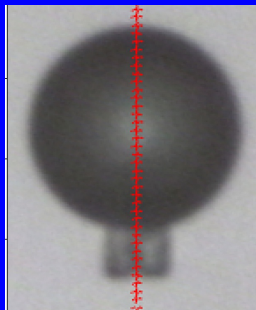
Atmospheric IN with organics



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

Anthropogenic	Well-mixed gases	Halo-carbons	O ₃ CFCs HCFCs		0.18 [0.01 to 0.35]	H
		N ₂ O	N ₂ O		0.17 [0.13 to 0.21]	VH
	Short lived gases and aerosols	CO	CO ₂ CH ₄ O ₃		0.23 [0.16 to 0.30]	M
		NMVOC	CO ₂ CH ₄ O ₃		0.10 [0.05 to 0.15]	M
		NO _x	Nitrate CH ₄ O ₃		-0.15 [-0.34 to 0.03]	M
	Natural	Aerosols and precursors (Mineral dust, Organic carbon, Black carbon)	Mineral dust Sulphate Nitrate Organic carbon Black carbon		-0.27 [-0.77 to 0.23]	H
SO ₂ , NH ₃ , Organic carbon and Black carbon)		Cloud adjustments due to aerosols		-0.55 [-1.33 to -0.06]	L	
		Albedo change due to land use		-0.15 [-0.25 to -0.05]	M	
		Changes in solar irradiance		0.05 [0.00 to 0.10]	M	
Total anthropogenic		2011		2.29 [1.13 to 3.33]	H	

Acknowledgements

