PAUL SCHERRER INSTITUT PSI

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SWISS NATIONAL SCIENCE FOUNDATION

European Commission

Dr. Peter A. Alpert :: Paul Scherrer Institut

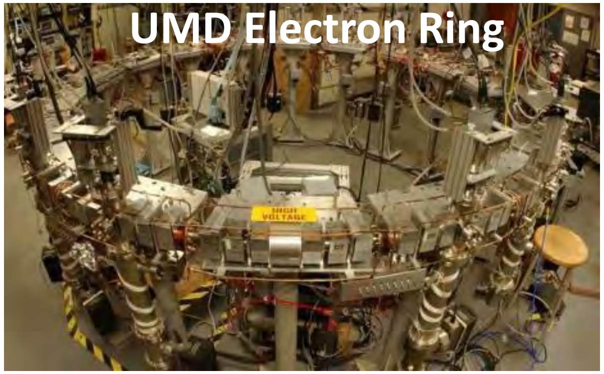
Advances in Understanding Ice Nucleation with Microanalytical Methods

Laboratory of Environmental Chemistry - Labor für Umweltchemie

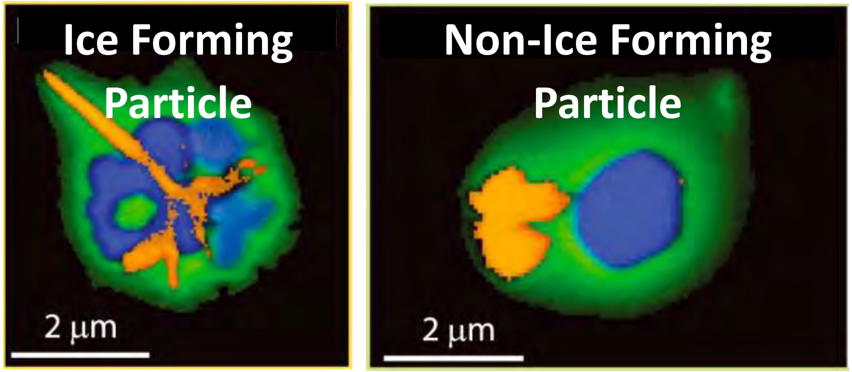
Ice Nucleation Colloquium

Thu 06.07.23 17:00 CET

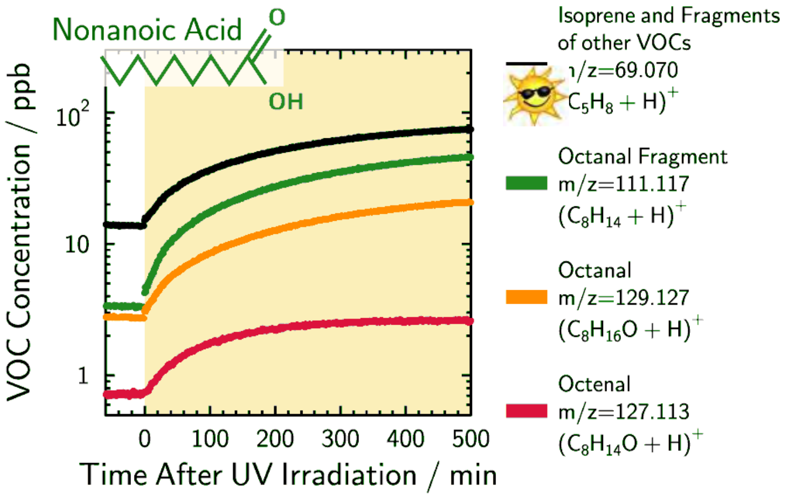
About me...



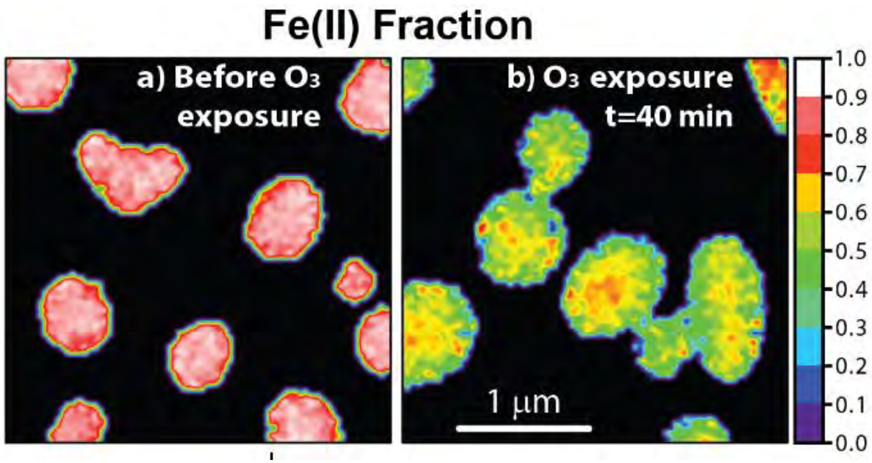
B.S. Physics - University of Maryland (UMD) College Park



Ph. D. Marine and Atmospheric Sciences with Daniel Knopf - Stony Brook University (SBU)

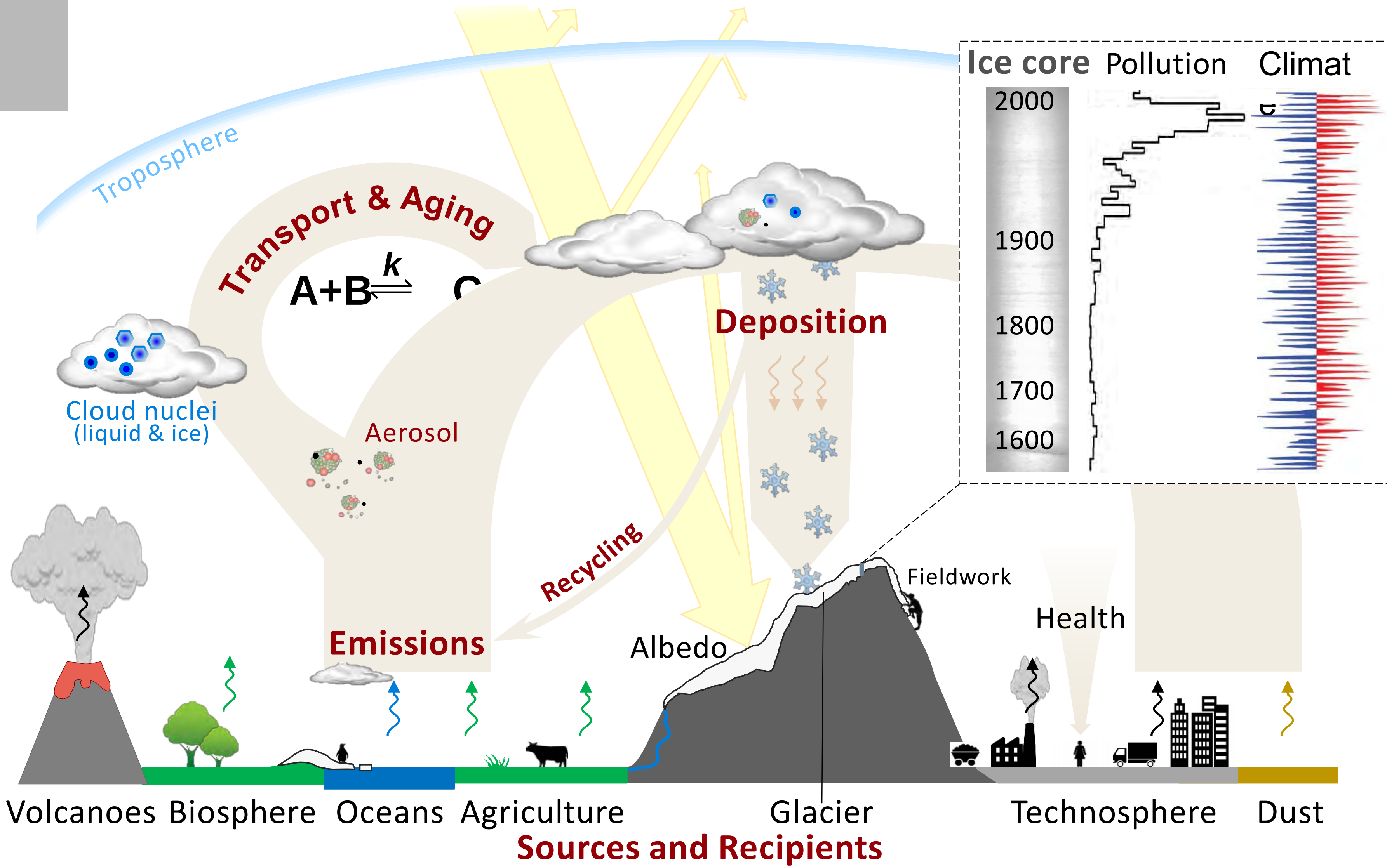


Post Doc with Christian George - Centre national de la recherche scientifique (CNRS), Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), Université Claude Bernard Lyon 1, Lyon, France.



Post Doc/Project Scientist with Markus Ammann - Paul Scherrer Institut

Laboratory for Environmental Chemistry - From multiphase chemistry and pollutant cycles to ice core paleo records



Luckily we have Rock Stars to help us with some aspects of it.

GALLERY

Music at PSI

Sounds coming from technical devices and scientific research processes are the order of the day at PSI. We already presented a tiny excerpt of the PSI soundscape in the 1/2022 issue. Now and then, though, completely different sounds ring out on both sides of the Aare campus, because many of our researchers are also musicians. Let us introduce you to some of them.

Text: Christian Heid

The band

When Robert Sobota (drums), Ludmila Leroy (bass and vocals), and Peter Alpert (guitar) cut loose, a powerful, groovy sound reverberates from the PSI research building. They came together with their own respective preferences: the guitarist, founder of the PSIchedelics, goes for grunge; the singer especially loves the songs of Freddie Mercury, the long-deceased lead singer of the group Queen; the drummer has a soft spot for progressive and art-rock. Their research interests, too, are different. Ludmila Leroy works in solid-state physics at the X-ray free-electron laser SwissFEL and at the Swiss Light Source SLS. Peter Alpert works with airborne particles at the SLS. And for Robert Sobota the focus is on next-generation superconductors. Yet anyone who has heard them immediately knows: on the musical level, they're in perfect harmony!

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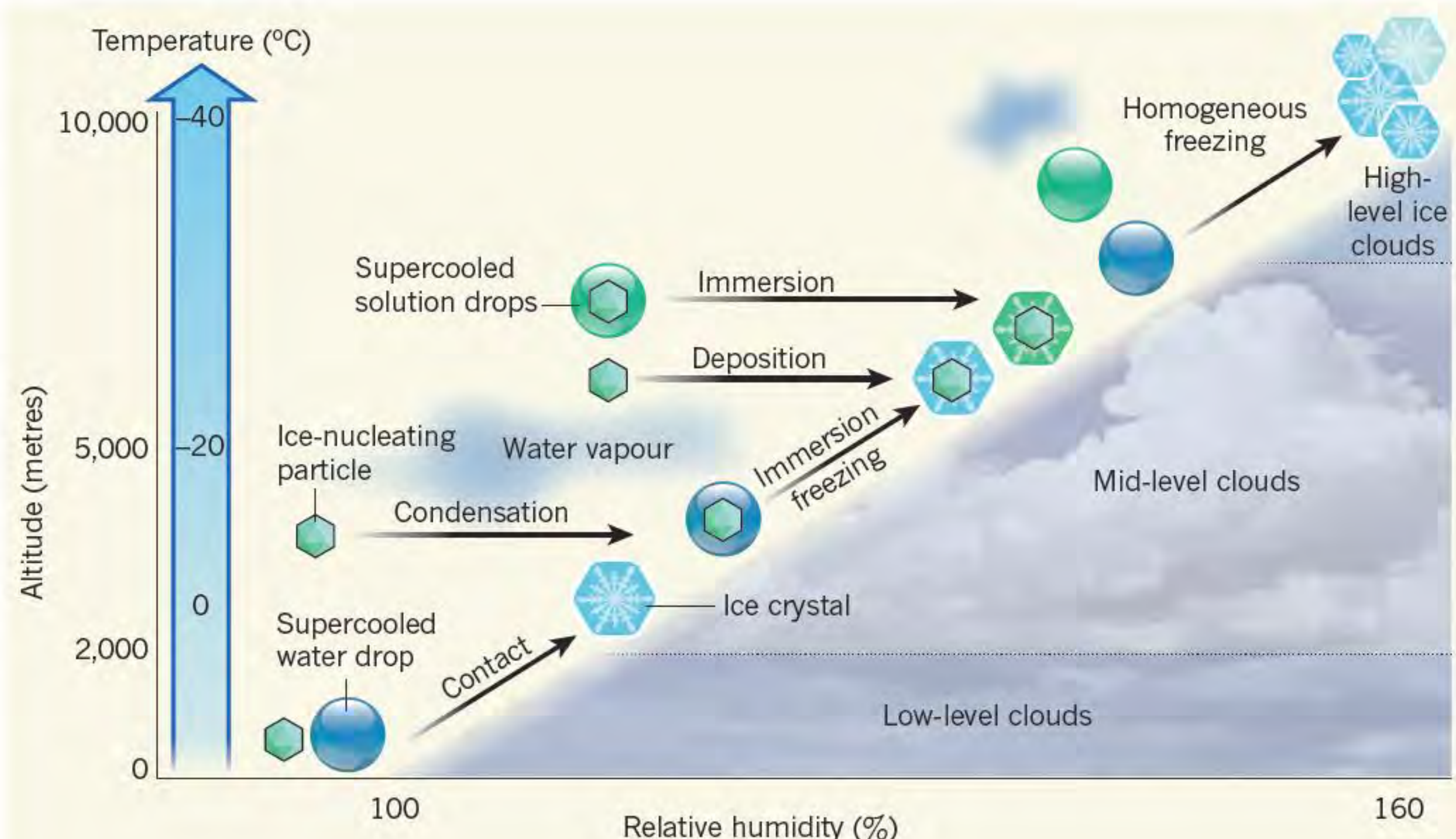
5232 The magazine of the Paul Scherrer Institute 29

[5232 Magazine - Click to go to issue]

Atmospheric Ice Nucleation Represents One of the Least Understood Processes (IPCC 2013)



Russel, *Nature,* 2015

…maybe due to i) various ice formation pathways

ii) small fraction of ice nucleating particles, <10^{-5} L (air)

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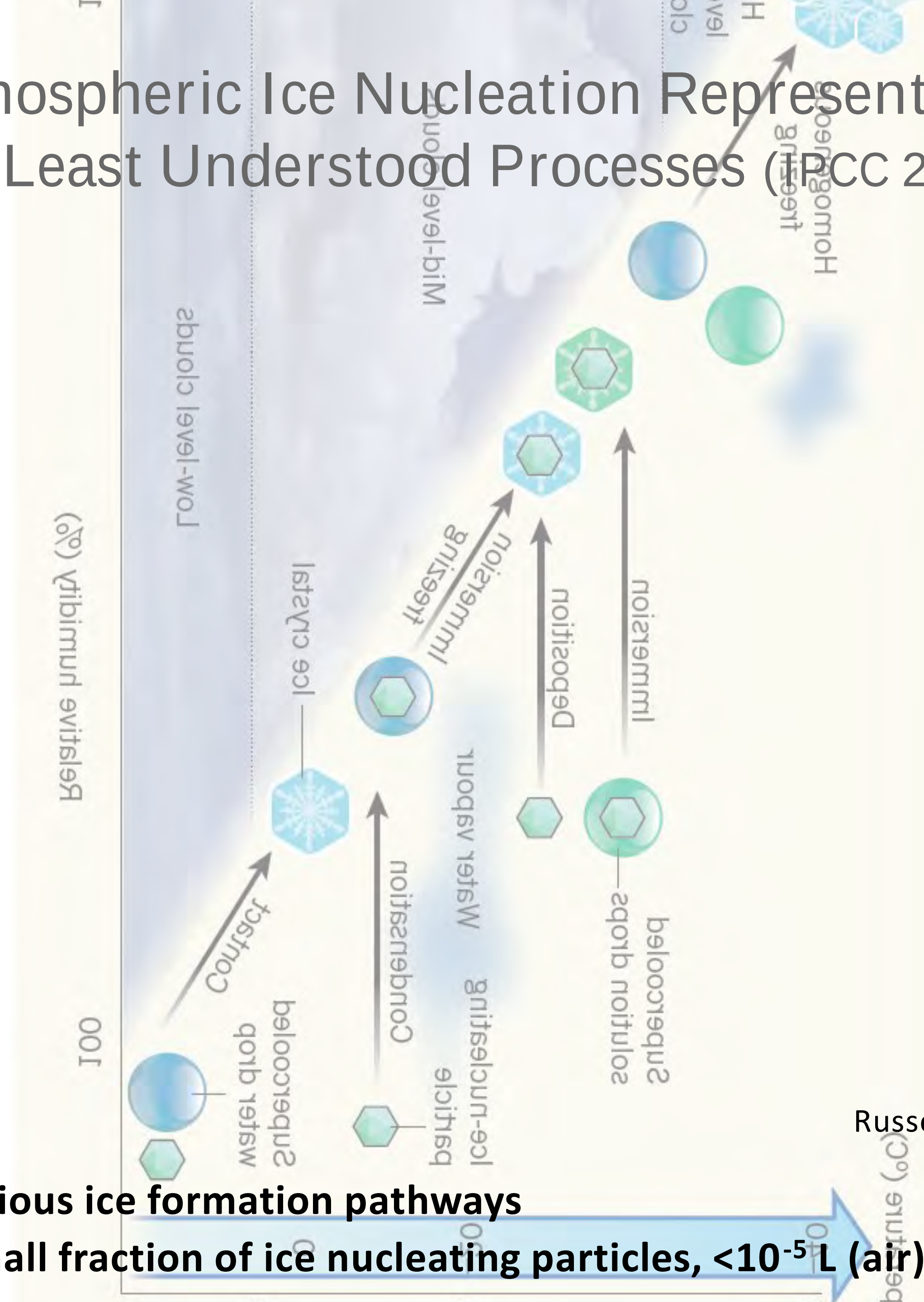

Russel, *Nature,* 2015

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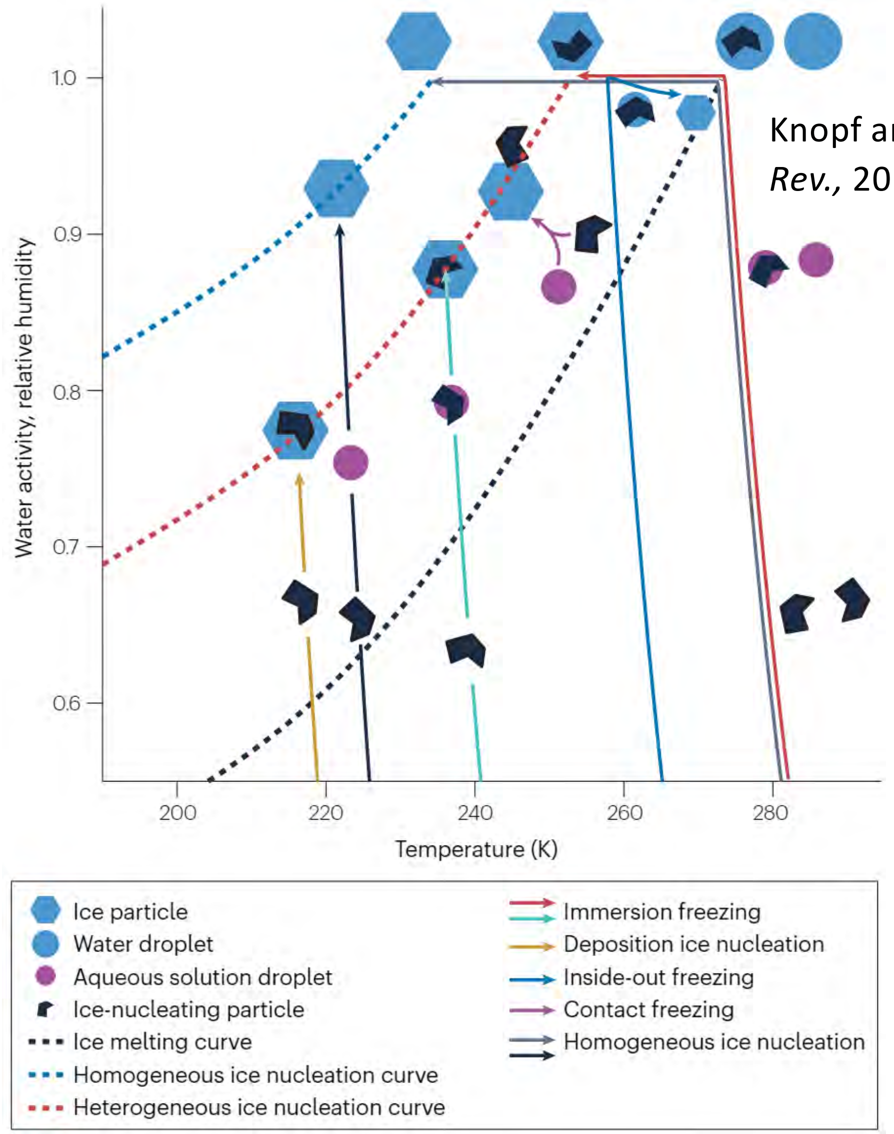
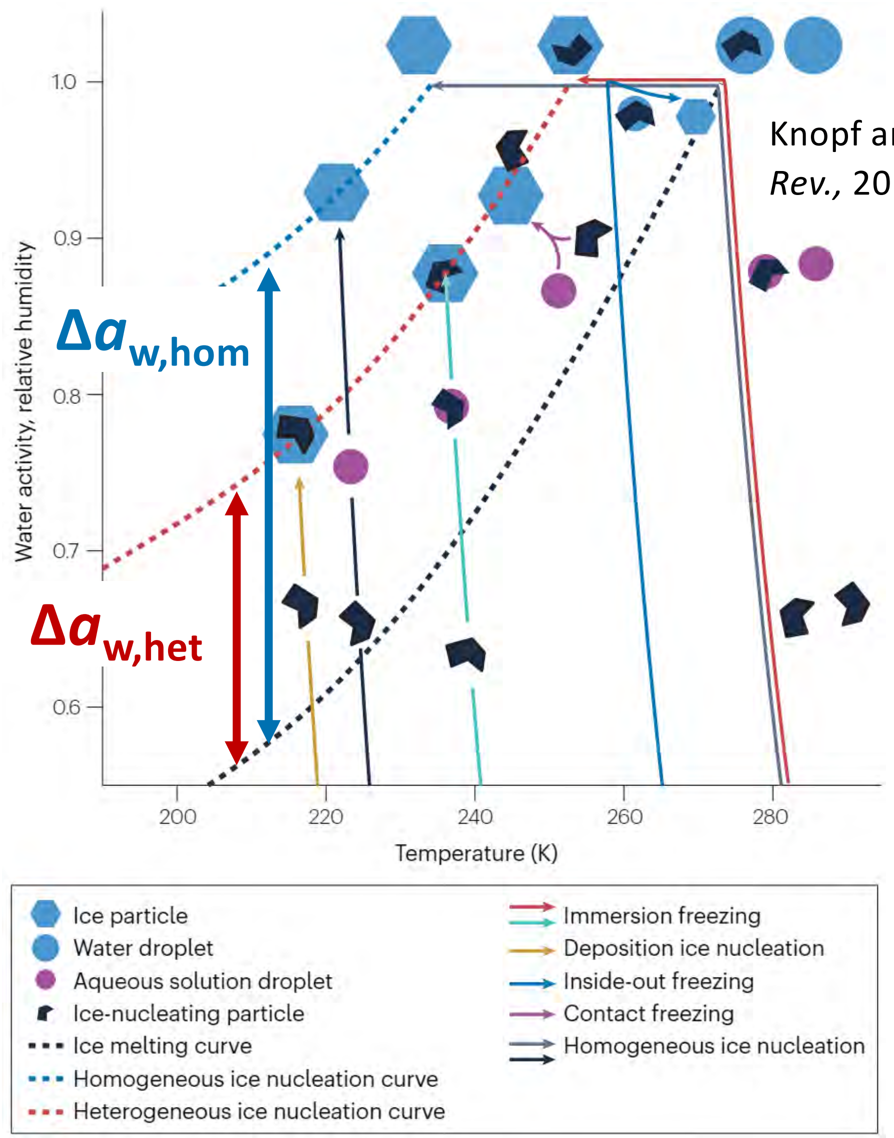
Phase diagram of ice nucleation



Knopf and Alpert, *Nat. Phys. Rev.*, 2023

Phase diagram of ice nucleation

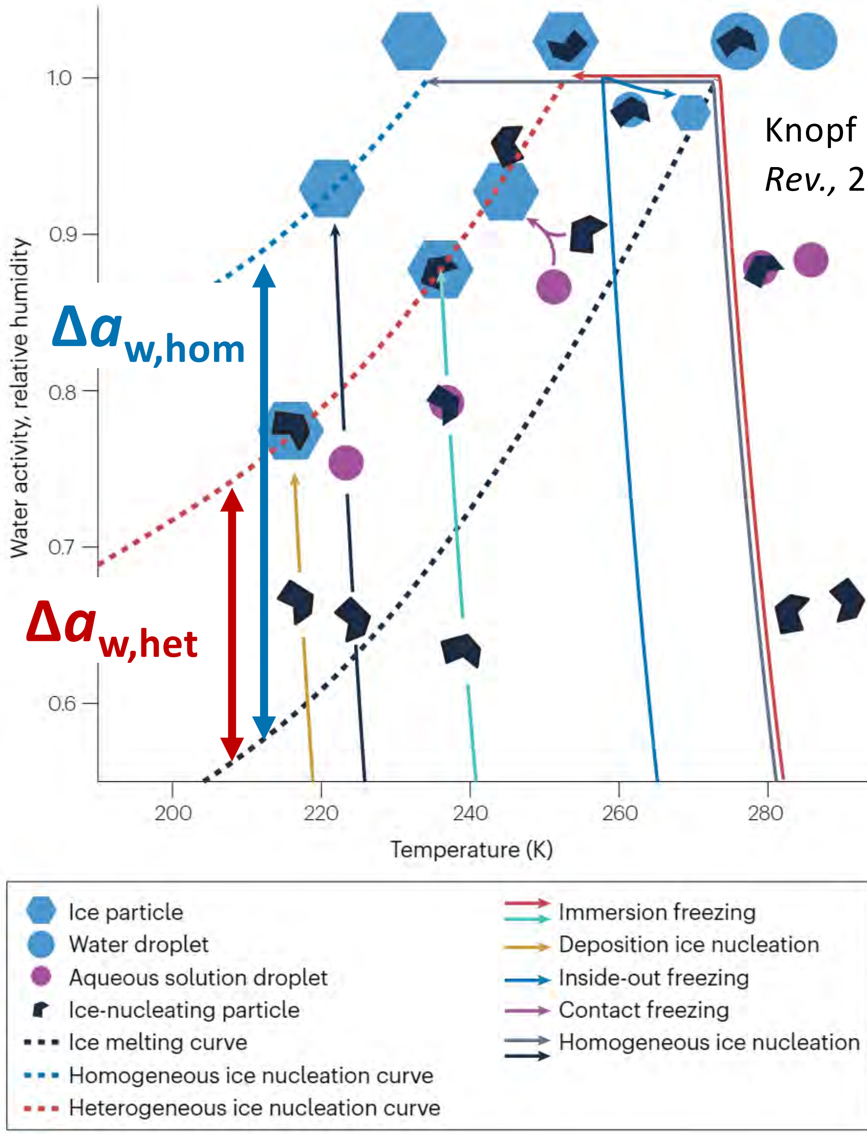


Knopf and Alpert, *Nat. Phys. Rev.*, 2023

Phase diagram of ice nucleation

Δa_w quantifies…

- **pairs of *T* and *RH* for any freezing point.**
- **the a_w at freezing when compressibility is maximum.**
- **the a_w at freezing when low/high density amorphous water are in equilibrium.**



Knopf and Alpert, *Nat. Phys. Rev.*, 2023

Bullock and Molinero, *Faraday Discuss.*, 2013

Baker and Baker, Geophys. Res. Lett., 2004

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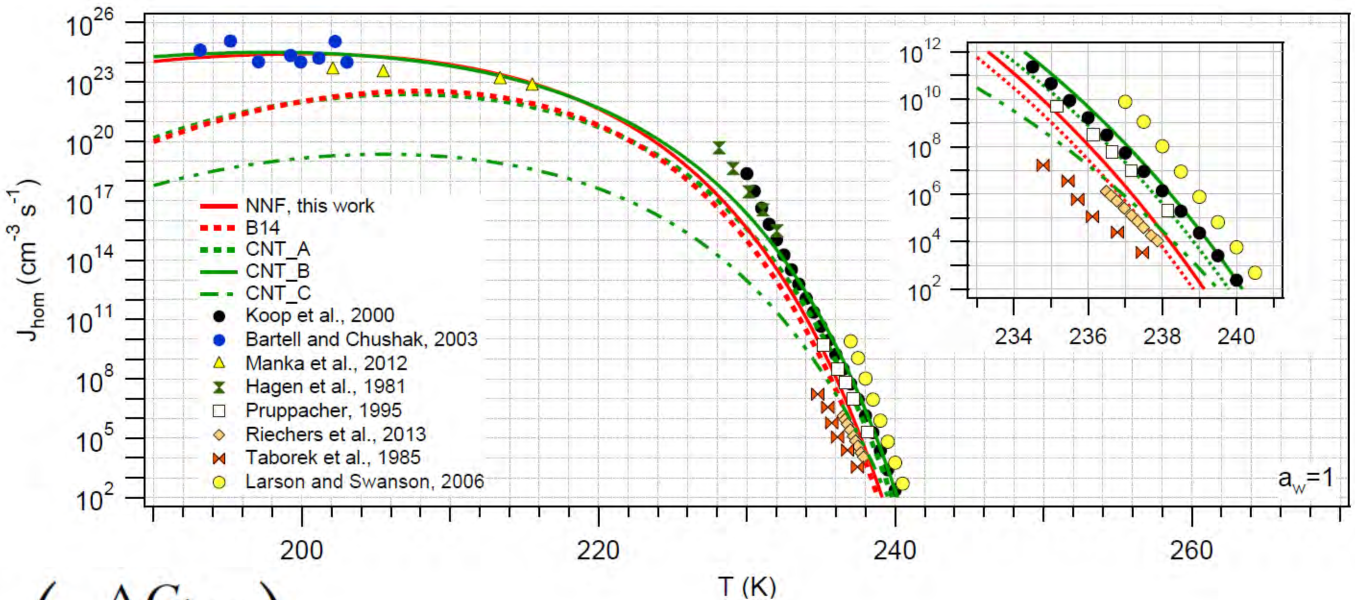
One theory exists explaining water activity and temperature dependence on homogeneous ice nucleation rate coefficients.



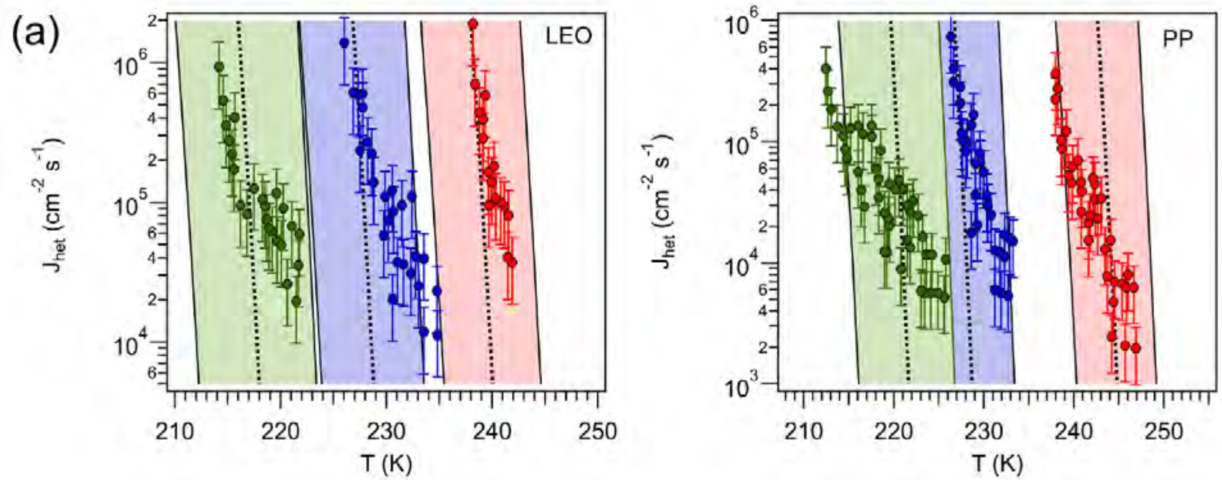
$$J_{\text{hom}} \propto \exp\left(-\frac{\Delta G_{\text{hom}}}{k_B T}\right)$$

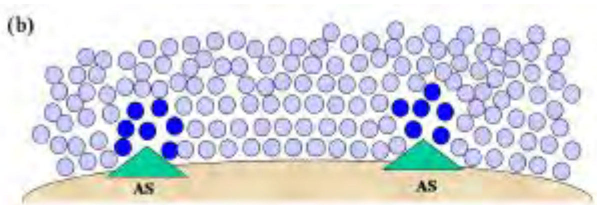
$$\Delta G_{\text{hom}} = \frac{4}{27}\frac{\left[\Gamma_w s\left(\Delta h_f - \Gamma_w k_B T \ln a_w\right)\right]^3}{\left[k_B T \ln\left(\frac{a_w^2}{a_{w,eq}}\right)\right]^2}$$

Barahona, *Atmos. Chem. Phys.*, 2014
Barahona, *Atmos. Chem. Phys.*, 2015
Barahona, *Atmos. Chem. Phys.*, 2018

Γ_w	Molecular surface excess of at the interface, 1.46 (Barahona, 2014; Spaepen, 1975)
s	Geometric constant of the ice lattice, 1.105 mol$^{2/3}$ (Barahona, 2014)
Δh_f	Heat of fusion of water, J mol^{-1}, J(Barahona, 2014; Johari et al., 1994)*

One theory exists explaining water activity and temperature dependence on heterogeneous ice nucleation rate coefficients.





$$\mu_{vc} = (1-\zeta)\hat{\mu}_{LL} + \zeta\hat{\mu}_{IL}$$

$$\mu_{vc} = \mu_w$$

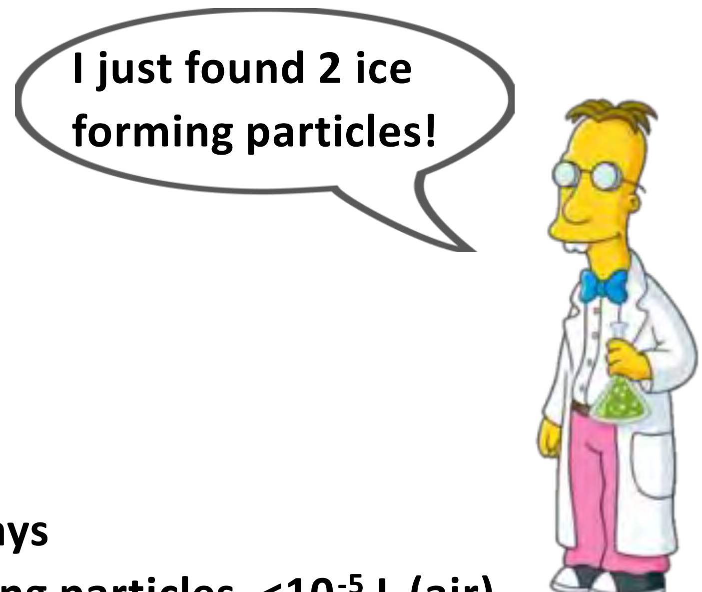
$$J_{het} \propto \exp\left(-\frac{n_{het}\Delta\mu_i|_{a_{w,eff}}}{2k_B T}\right)\left[1+\left(\frac{a_w}{a_{w,eq}}\right)^{n_t(1-\zeta)}\right]^{-1}$$

μ_w, μ_s, μ_{vc}	Chemical potential of water, ice and vicinal water, respectively J
n_{het}	Critical germ size for heterogeneous ice nucleation
$a_{w,eff}$	Effective water activity
$a_{w,eq}$	Equilibrium a_w between bulk liquid and ice (Koop and Zobrist, 2009)
n_t	Number of formation paths of the transient state, 16 (Barahona, 2015)
ζ	Templating factor

Barahona, *Atmos. Chem. Phys.*, 2014
Barahona, *Atmos. Chem. Phys.*, 2015
Barahona, *Atmos. Chem. Phys.*, 2018

Atmospheric ice nucleation research is challenging for various reasons

Divisions	Match	Odds to win
1 Prize	5+1	1:31,474,716
2 Prize	6	1:6,294,943
Grand Prize	**2 ice forming particles**	**1:10,000,000,000**

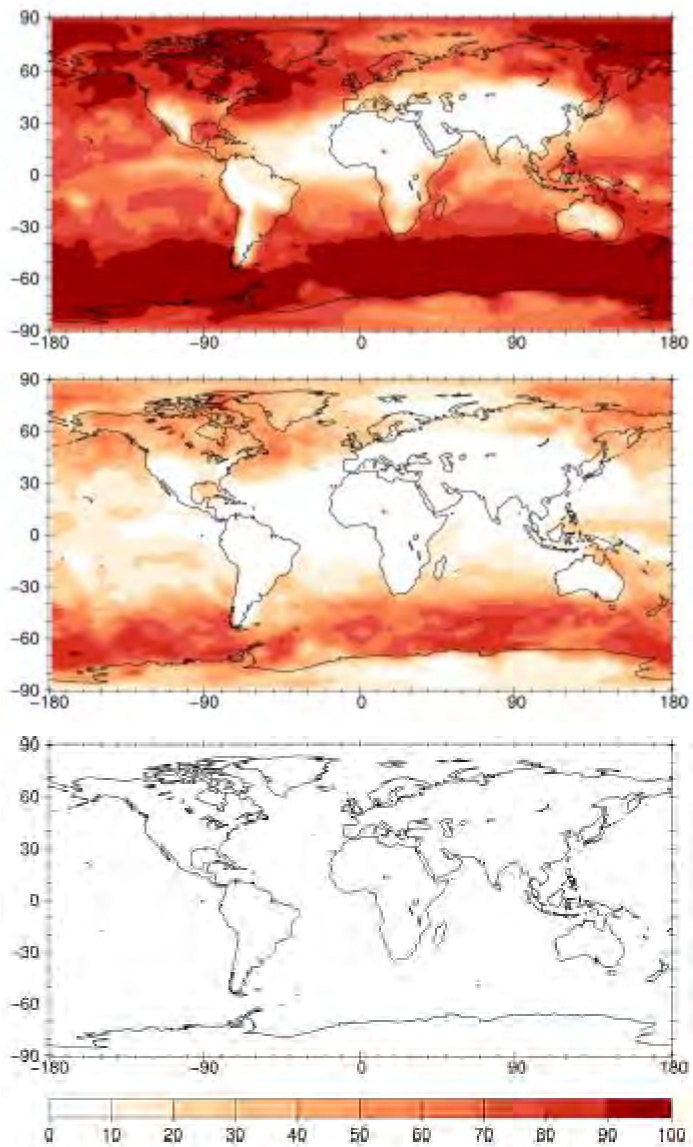


…maybe due to

i) various ice formation pathways
ii) small fraction of ice nucleating particles, <10^{-5} L (air)
iii) various type of particles that nucleate ice
iv) lack of universal heterogeneous ice nucleation theory

Marine organic aerosol (sea spray aerosol (SSA) particles) uncertainty for ice nucleation

Fraction of ice that is from sea spray (red) Or dust (white).



High Estimate

Medium Estimate

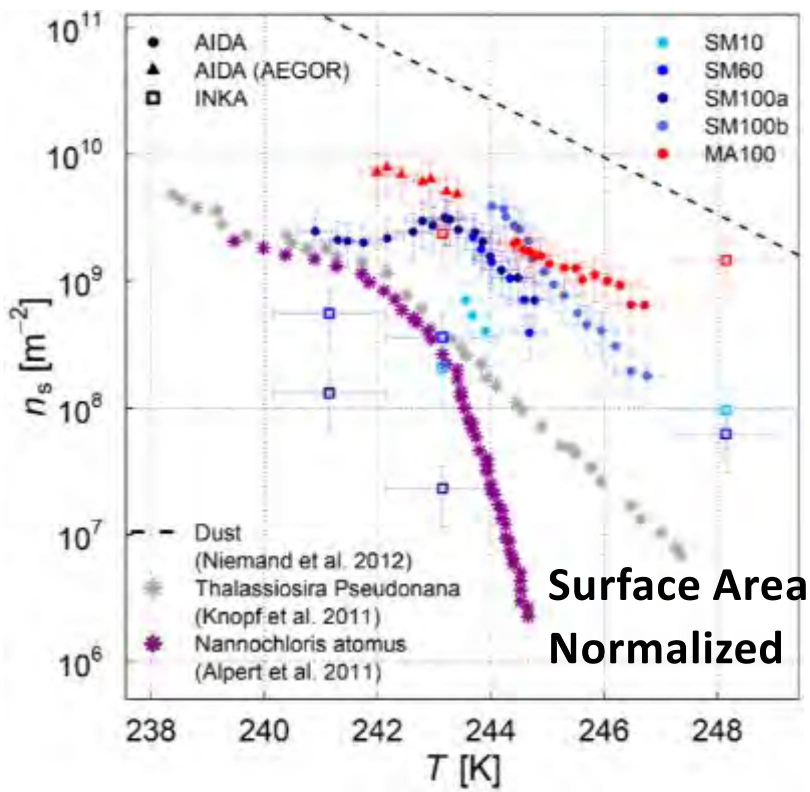
Low Estimate

…uncertainties in the predicted aerosol number concentration and the predicted ice nucleation efficiency from the Phillips parameterization.

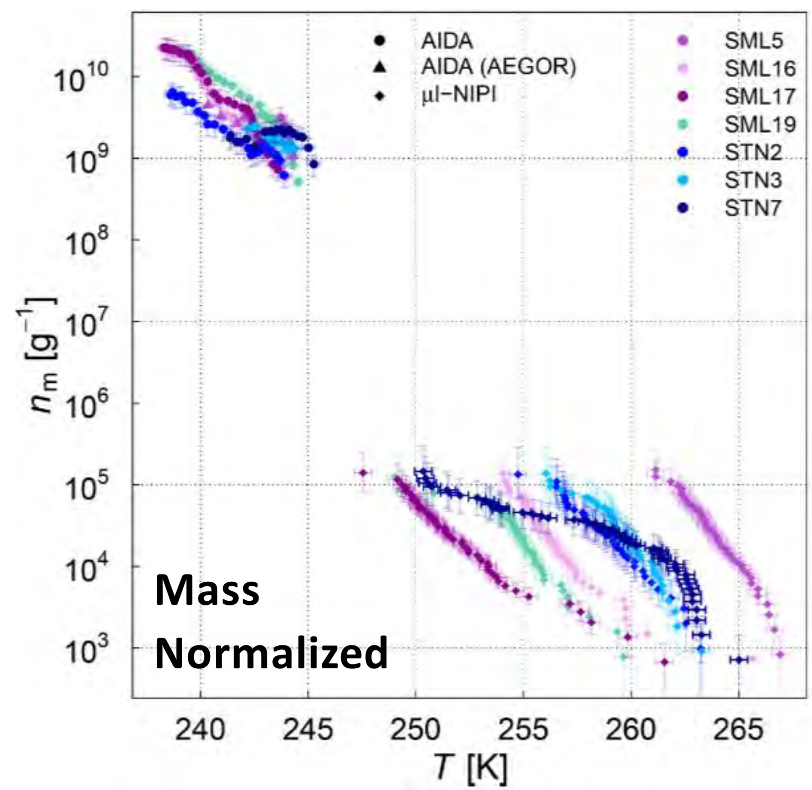
Burrows et al., *Atmos. Chem. Phys.*, 2013
Yun and Penner, *Geophys. Res. Lett.*, 2013

Many studies show sea water, surface seawater (microlayer), sea spray particles and phytoplankton cultures nucleate ice

Various Phytoplankton Species

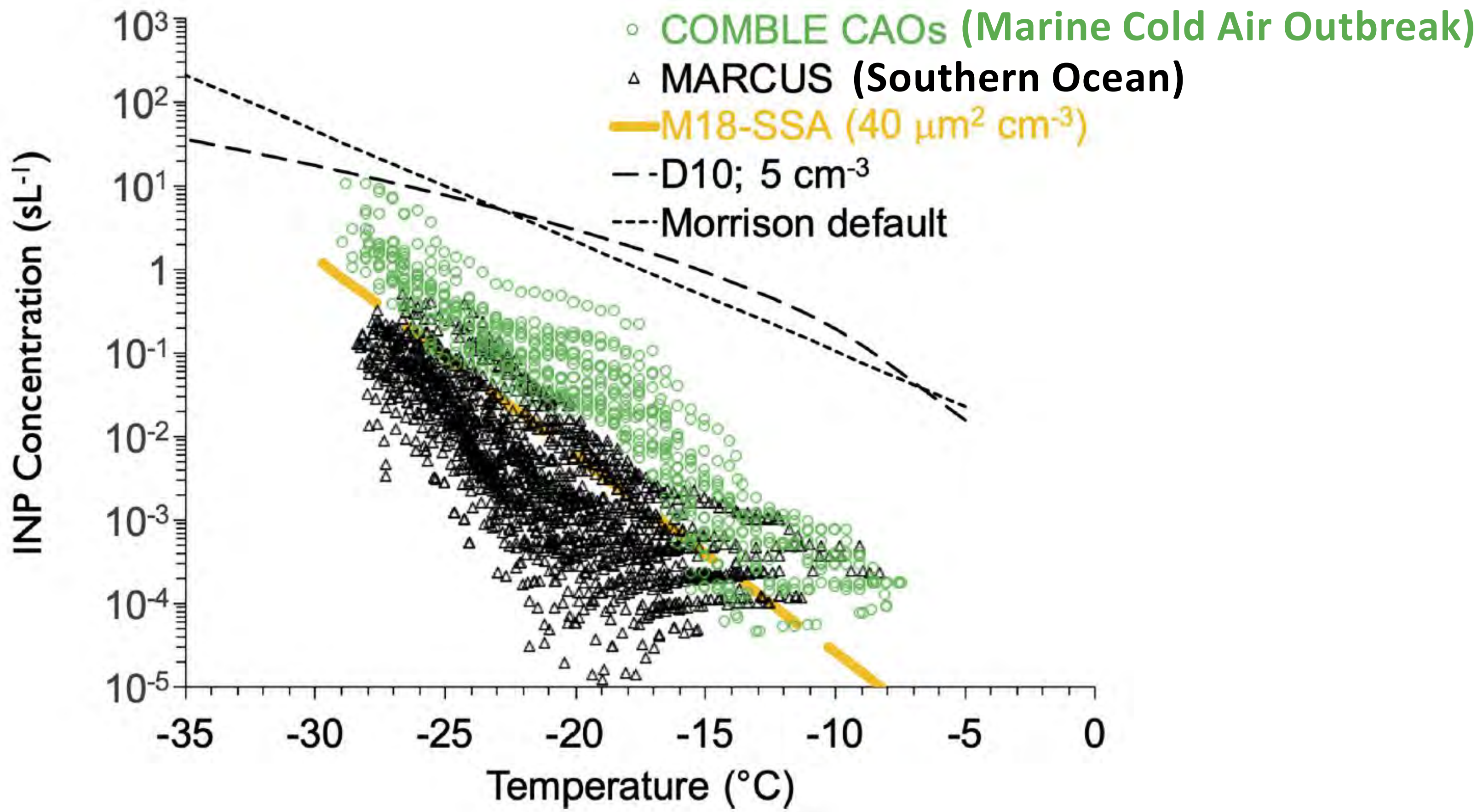


Microlayer Seawater



Ickes et al., *Atmos. Chem. Phys.*, 2020

Ambient studies and complex particle types nucleating ice



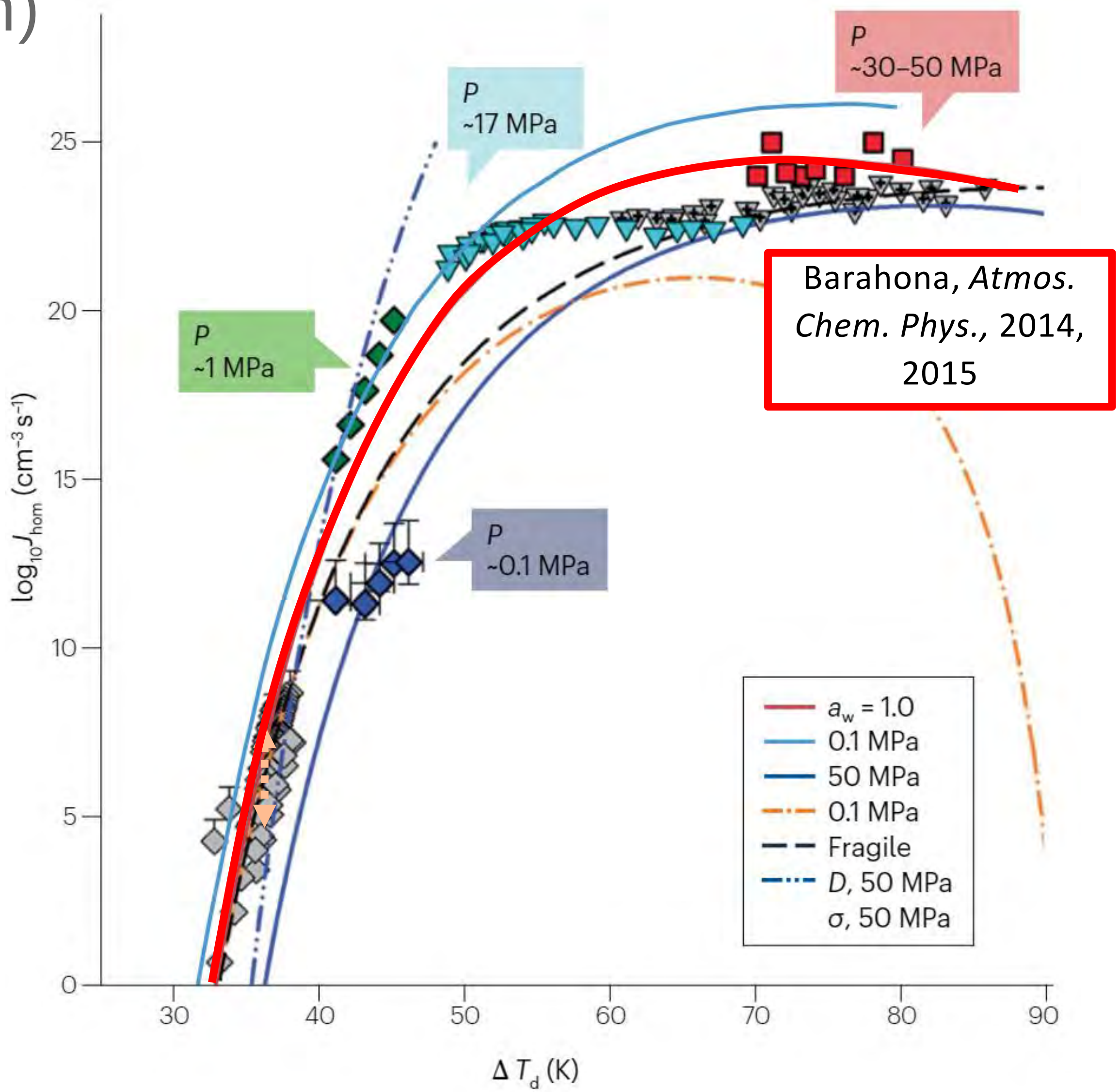
Geerts et al., *B. Am. Meteorol. Soc.*, 2022

McCluskey et al., *J. Atmos. Sci.*, 2018

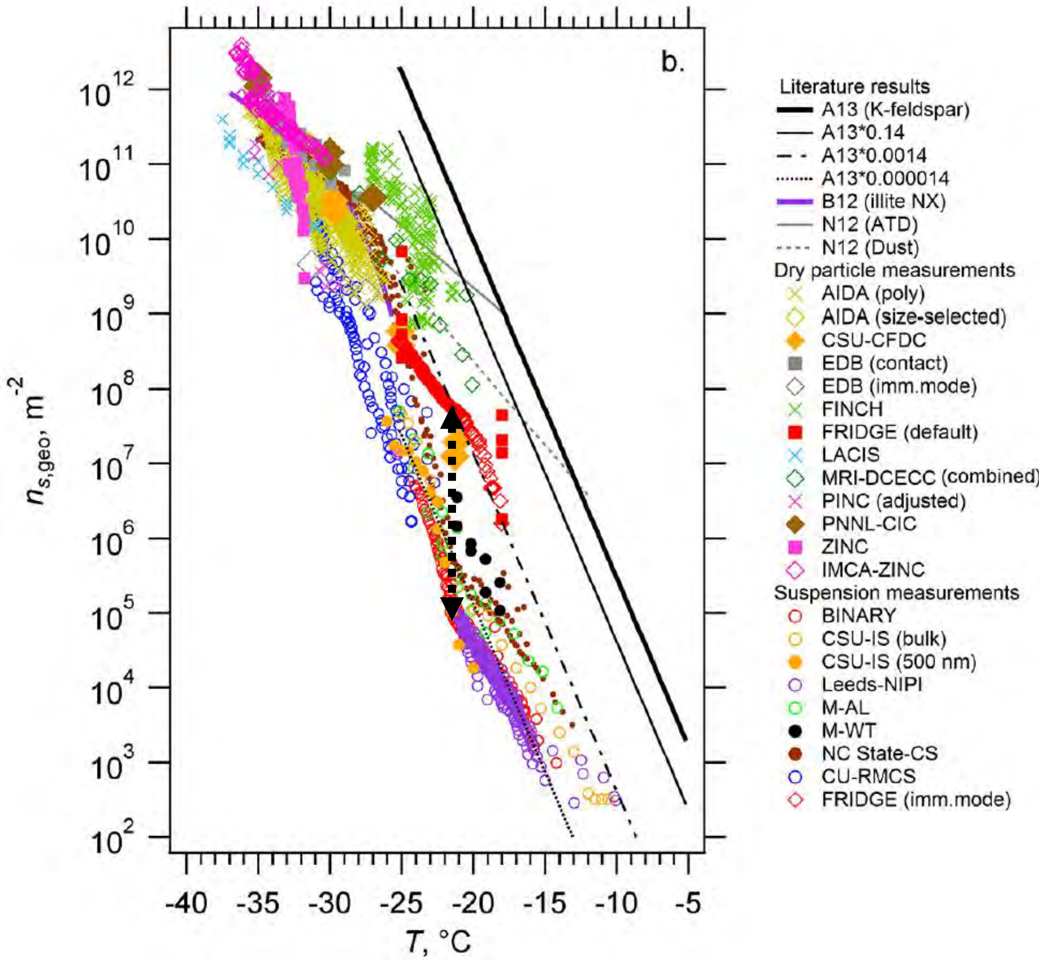
“Non-aerosol-aware parameterizations can be a source of uncertainty.”

Uncertainties from theoretical based parameterizations (homogeneous ice nucleation)

- Knopf and Alpert, *Nat. Phys. Rev.*, 2023
- Murray et al., *Phys. Chem. Chem. Phys., 2010*
- Riechers et al., *Phys. Chem. Chem. Phys.*, 2013
- Stöckel et al., *J. Phys. Chem. A*, 2005
- Stan et al., *Lab on a Chip*, 2009
- Laksmono et al., *J. Phys. Chem. Lett.*, 2015
- Hagen et al., *J. Atmos. Sci.*, 1981
- Amaya and Wyslouzil, *J. Chem. Phys.*, 2018
- Bhabhe et al., *J. Phys. Chem. A*, 2013
- Bartell and Chushak, Water in Confining Geometries, Springer, 2003



Non-theoretical-aware parameterizations can be a source of uncertainty (heterogenous ice nucleation)



Within 3 orders of magnitude uncertainty – counting ice and normalizing to surface area is good enough?

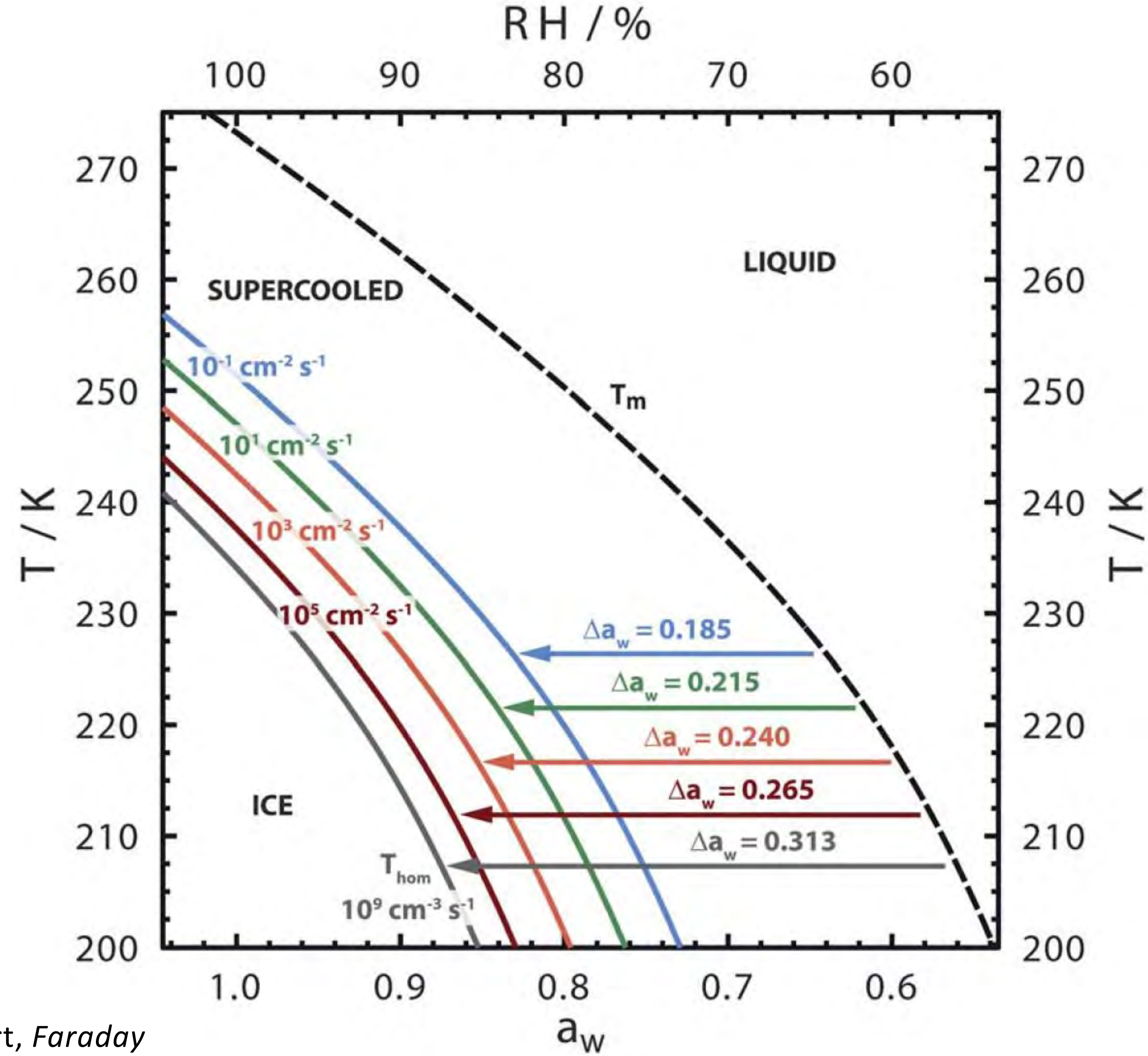
Time and surface area scales are equally important for ice nucleation theory.

Minimum cooling rate = 0.3 K min^{-1} or 500 cm s^{-1}. Competition with homogeneous ice nucleation starts only far < 100 cm s^{-1}.

Hiranuma et al., *Atmos. Chem. Phys.*, 2023

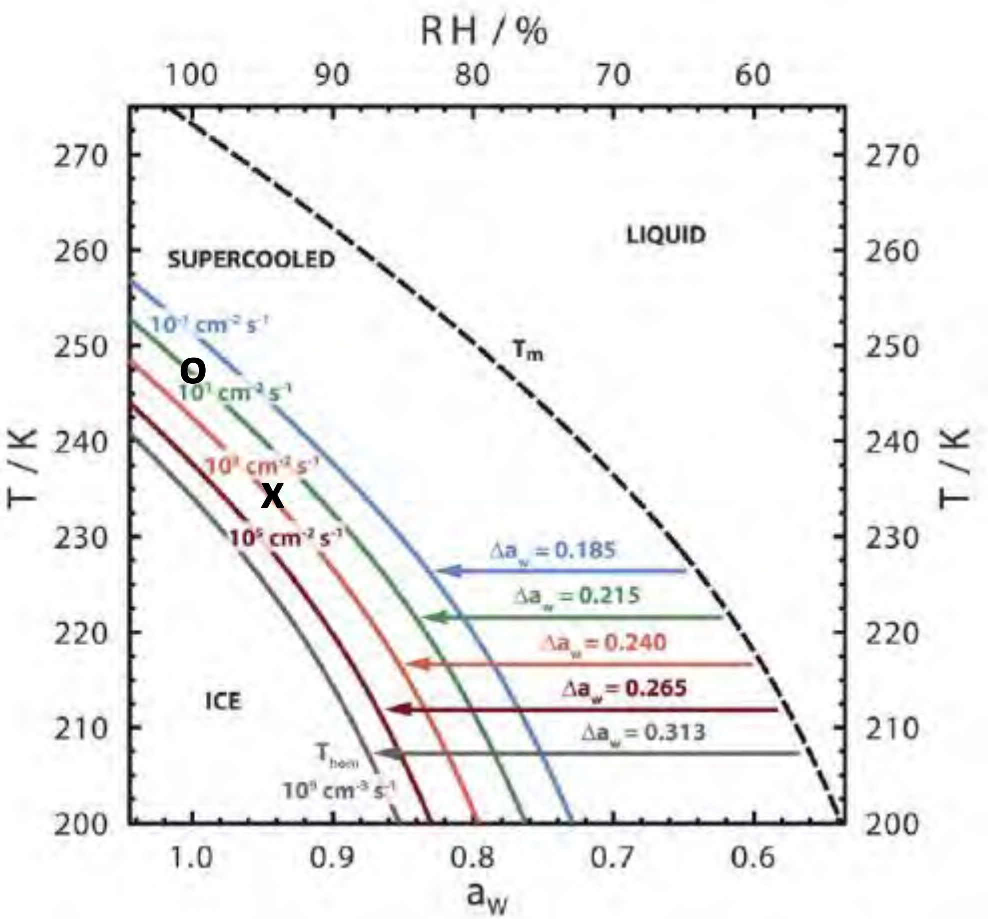
Lacher et al., *preprint*, 2023 – ambient INP concentrations within 1 order of magnitude! Great!

Aerosol-theory-aware parameterization



Knopf and Alpert, *Faraday Discuss.*, 2013

Using the ice-water phase diagram to derive ice nucleation rate coefficients, J_{het} and the water activity criterion, Δa_w.



Example:

o – a particle at 248 K that made a cloud droplet (100% RH, a_w = 1.0) has Δa_w = 0.215 and J_{het} = 10 cm^{-2} s^{-1}.

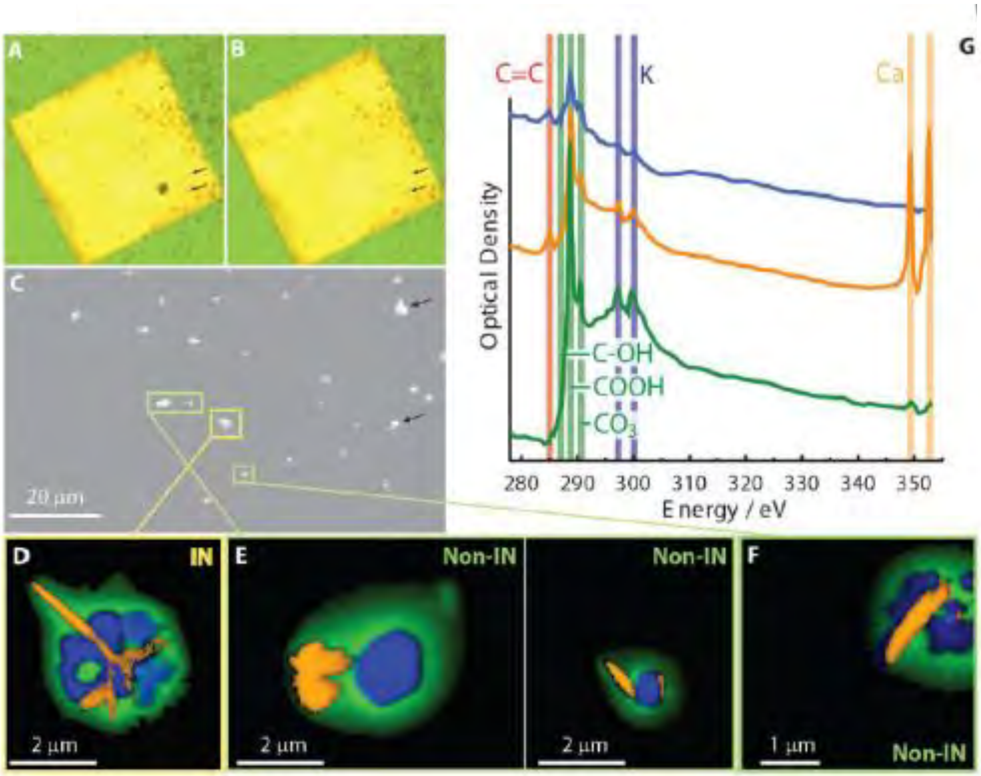
Example:

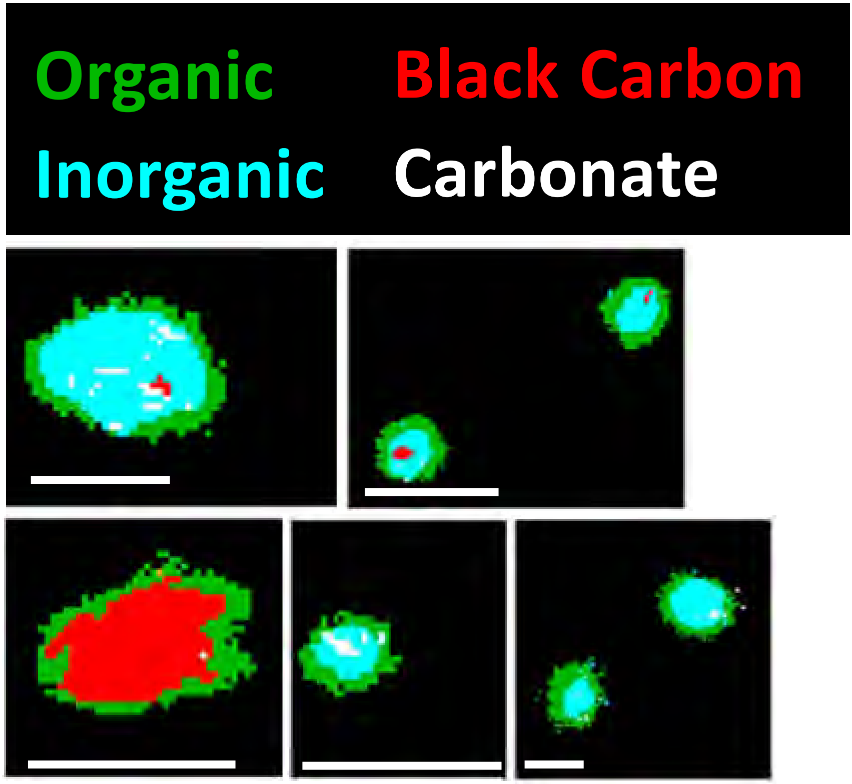
x – a particle at 234 K without a cloud (94% RH, aw = 0.94) has Δa_w = 0.265 and J_{het} = 10^3 cm^{-2} s^{-1}.

Ambient particles that nucleated ice have been identified with X-ray microscopy. Balancing the nanometer scale and chemical selectivity.

Knopf et al., *J. Geophys. Res.-Atmos.*, 2014

Hiranuma et al., *J. Geophys. Res.-Atmos.*, 2013

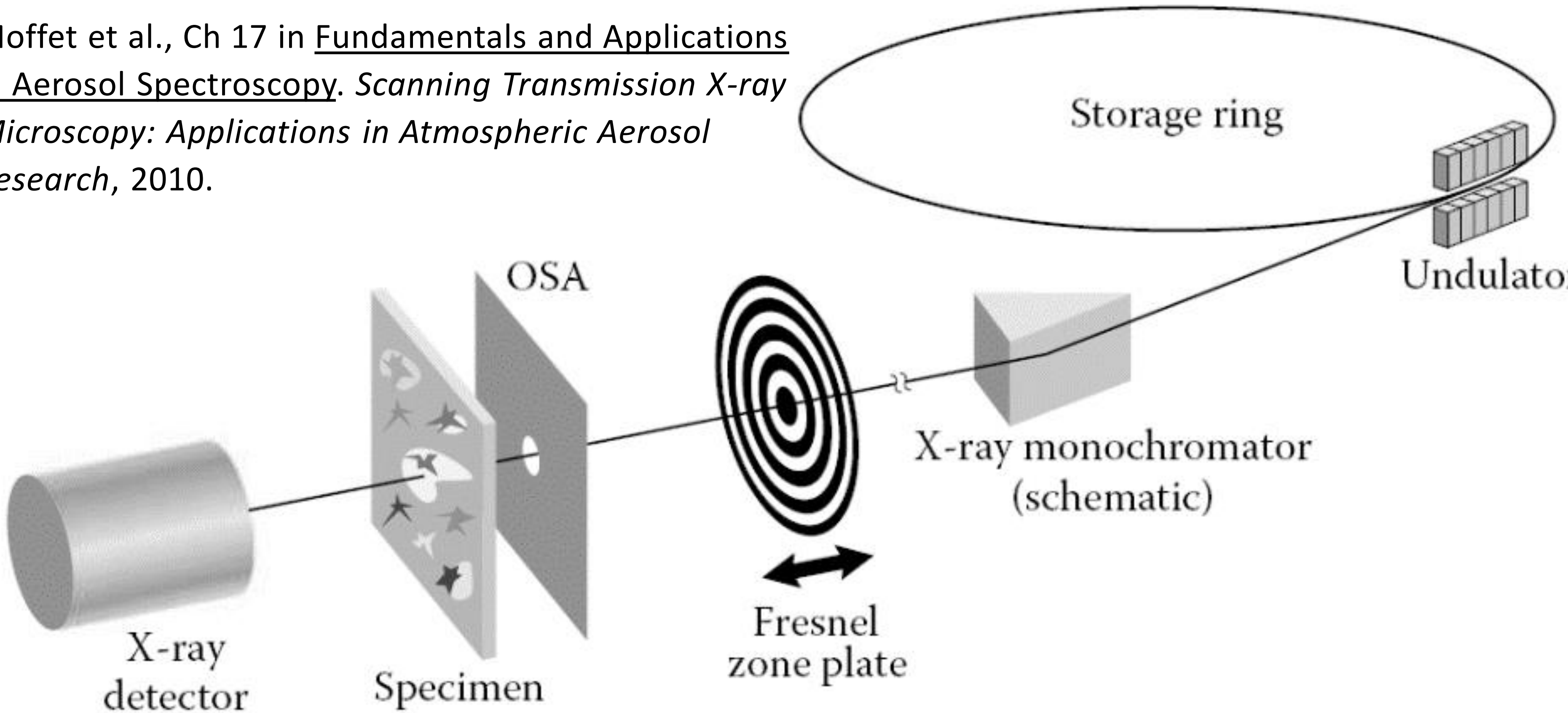




Wang et al., *J. Phys. Chem. Chem. Phys.*, 2016

Scanning Transmission X-ray Microscopy coupled with Near-Edge X-ray Absorption Fine Structure Spectroscopy (STXM/NEXAFS)

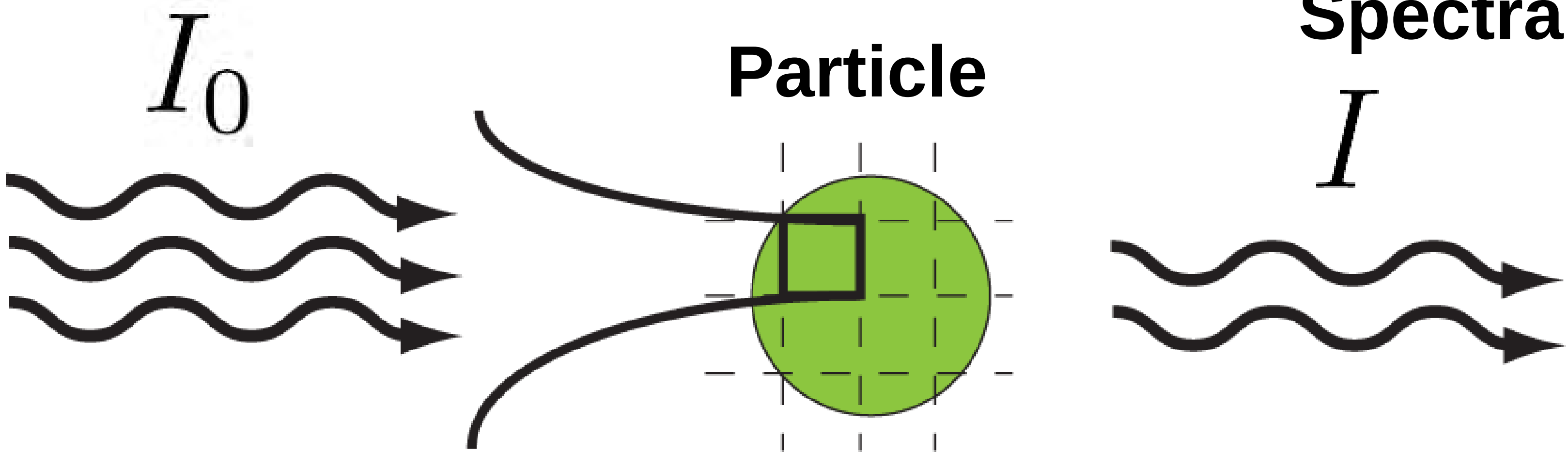
Moffet et al., Ch 17 in Fundamentals and Applications in Aerosol Spectroscopy. *Scanning Transmission X-ray Microscopy: Applications in Atmospheric Aerosol Research*, 2010.



STXM/NEXAFS Measures Optical Density

Single Energy X-Rays

Measure Absorption Spectra



$$I = I_0 e^{-\mathrm{OD}}$$

$$\mathrm{OD} = -\ln \frac{I}{I_0} = \rho \mu d$$

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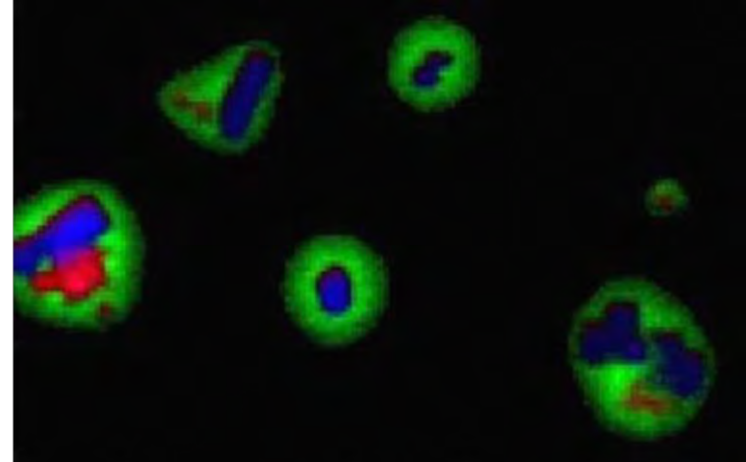
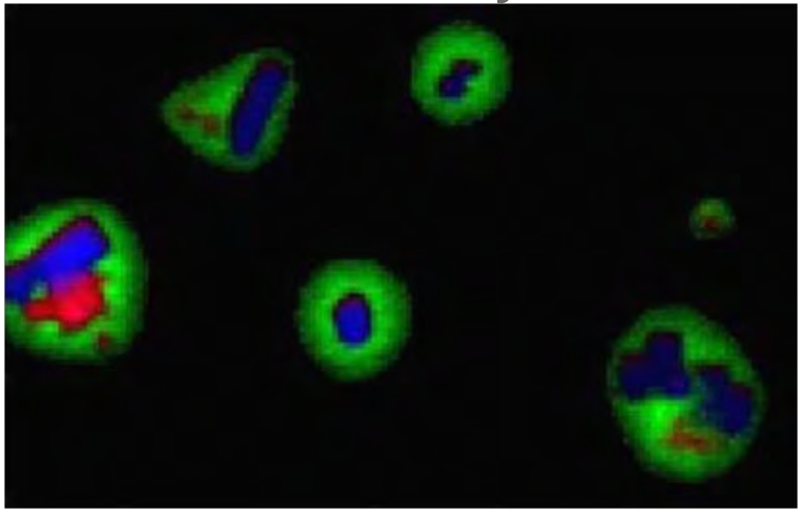
Inorganic

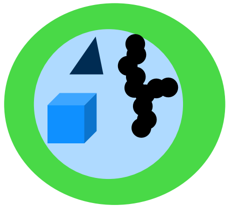
C=C

COOH



How To Get Mixing State Out of STXM/NEXAFS Analysis





Functional Group/Compound		Peak Energy / eV
Double Bond	R(C=C)R	285.1
Phenolic-Hydroxyl	phenolic(C-OH)	286.5
Hydroxyl	R(C-OH)	287.0
Aliphatic	C-H	287.7
Carboxyl	R(C=O)OH	288.5
Carbonyl	R(C=O)R	289.1-289.8
Carbonate	CO_3	290.4
Potassium	K L-Edge	299.7 & 297.1
Calcium	Ca L-Edge	346.2 & 349.7

Moffet et al., *Anal. Chem.*, 2010.

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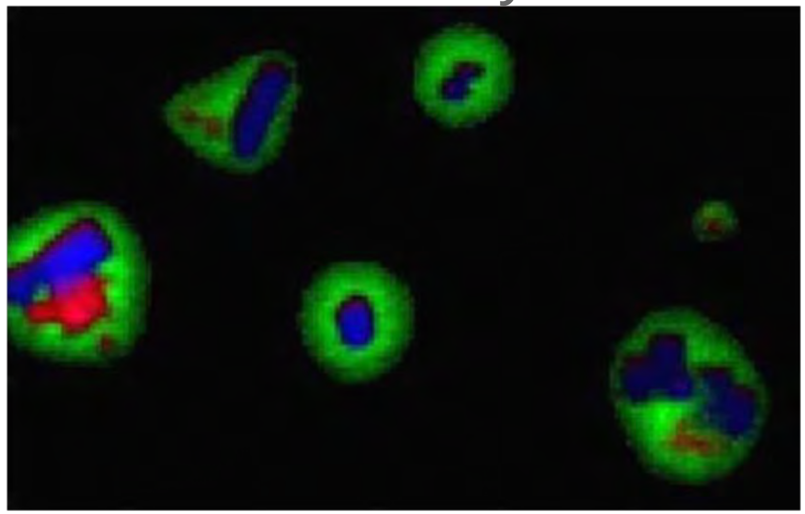

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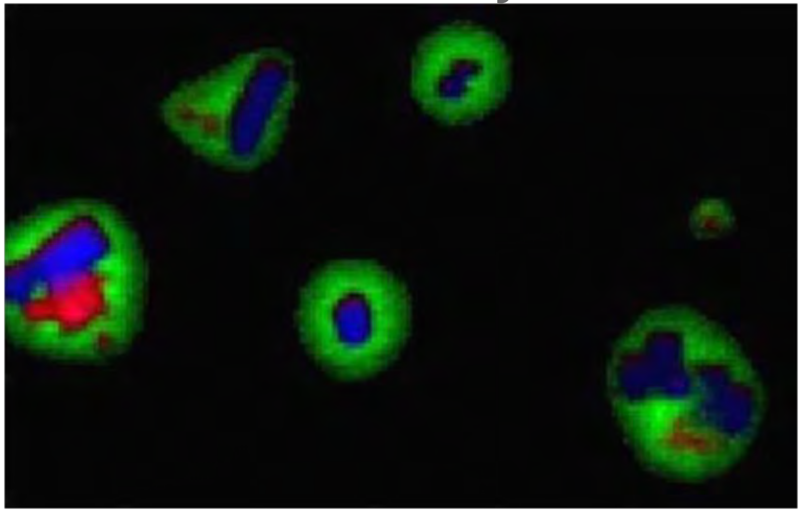

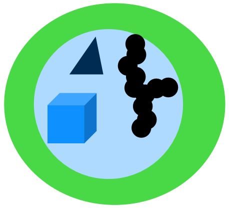

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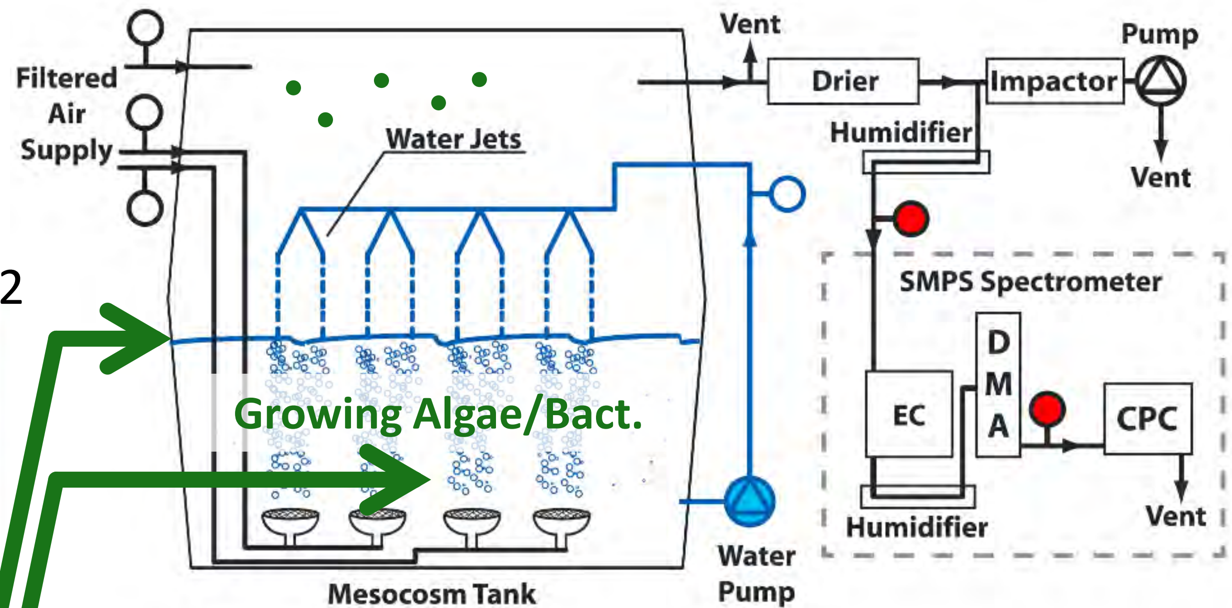
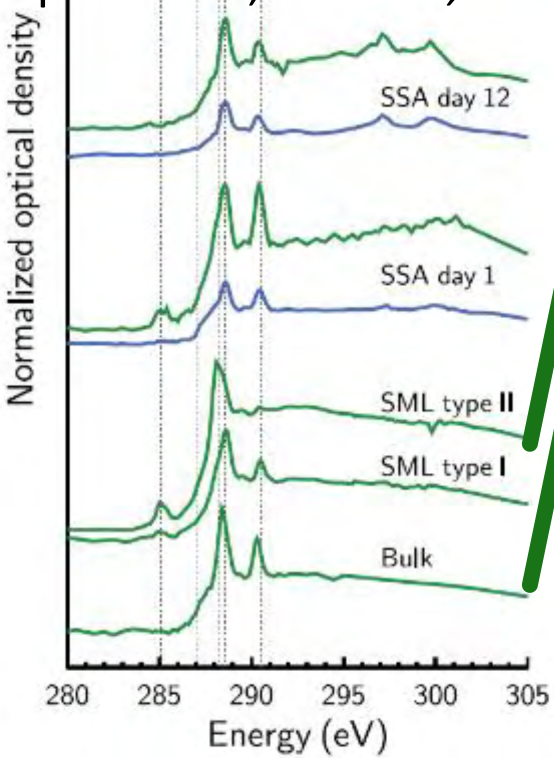
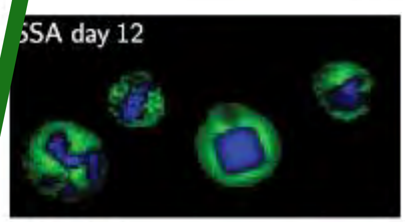
Generated sea spray aerosol (SSA) particles are fairly identical having organic acid and unsaturated functionalities.

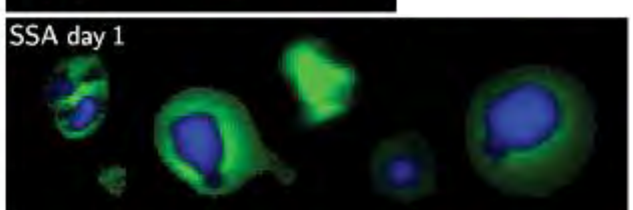
Alpert et al., *J. Geophys. Res.*, 2015

Alpert et al., *Sci. Adv.*, 2022





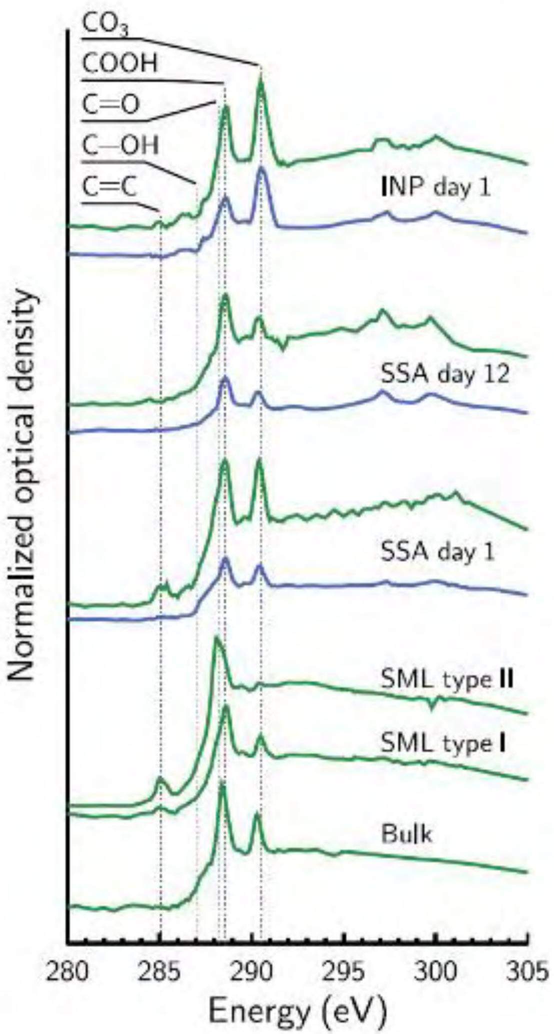


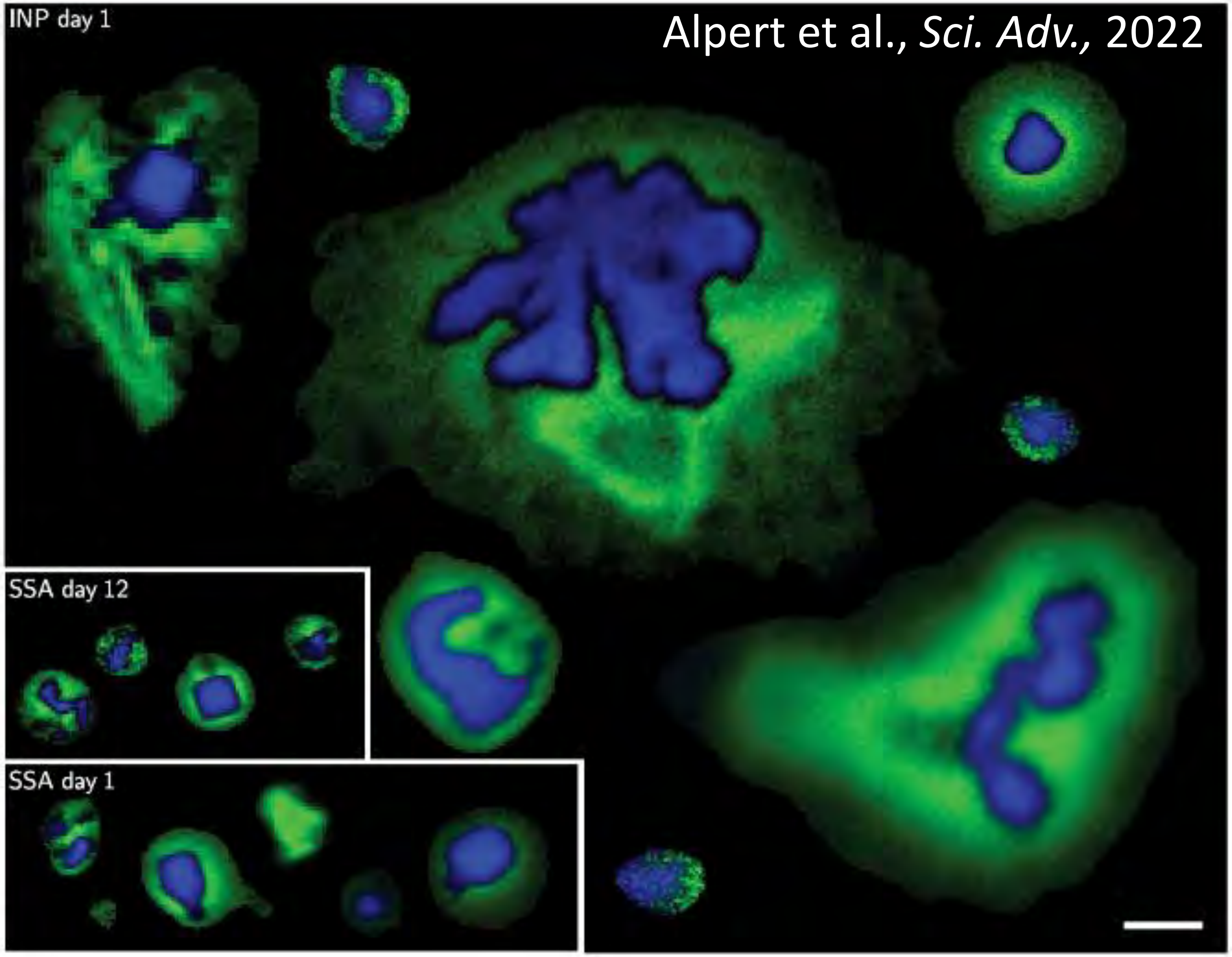


…fatty acids, mono-/ poly-saccharides.

Cochran et al., *Chem. 2* 2017

Ice formed on particles with the same composition, and mostly larger. This implies all SSA particles are ice nucleating particles (INP).



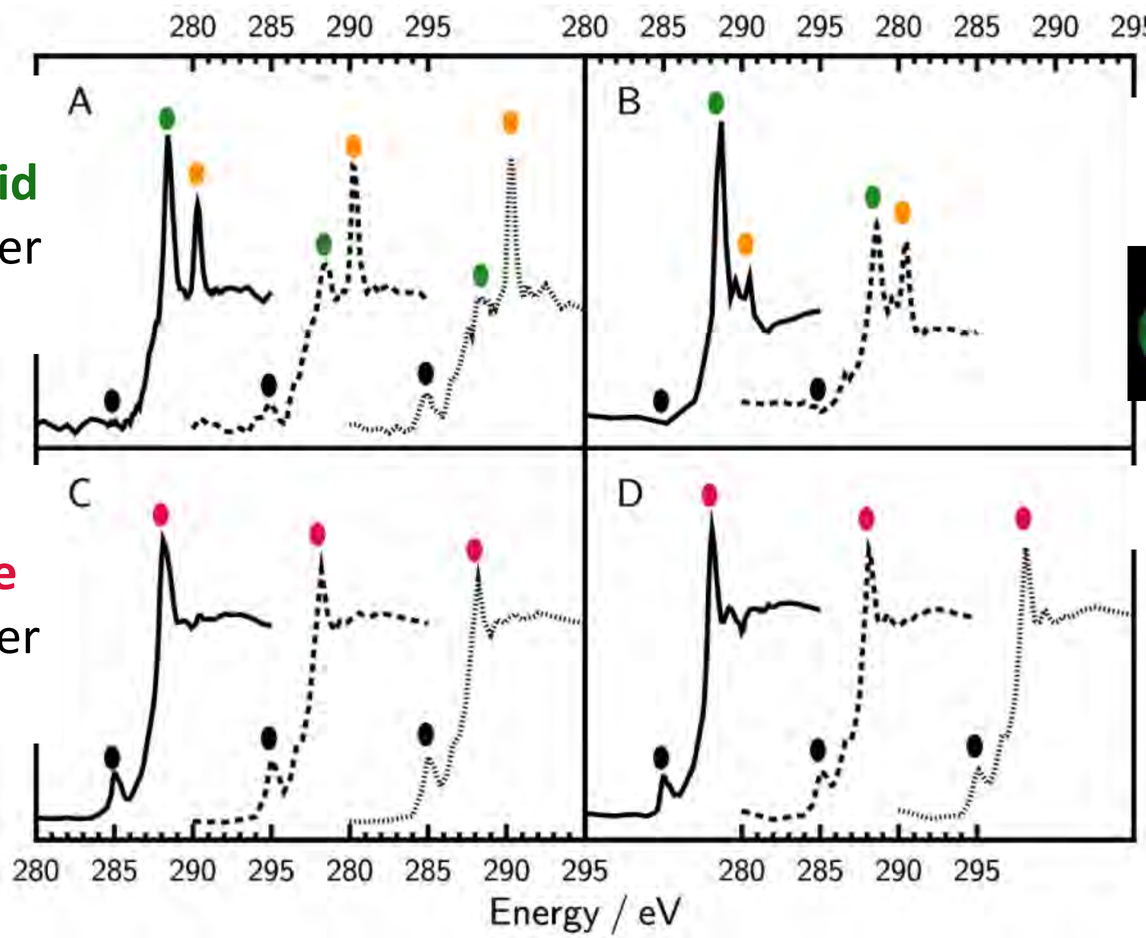


Alpert et al., *Sci. Adv.*, 2022

X-ray's damage particles. I can avoid it, or do it on purpose to indirectly identify similarities in composition.

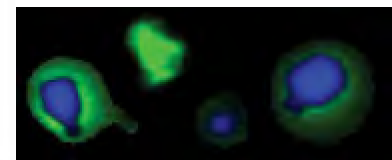
Exudate Organic Acid in Microlayer Seawater

Exudate Saccharide in Microlayer Seawater



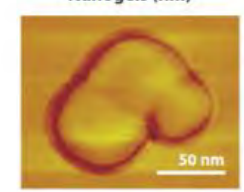
Alpert et al., *Sci. Adv.*, 2022

SSA particles and INPs

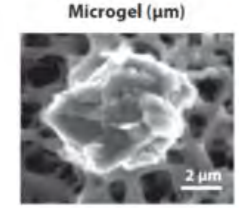


Xanthan Gum

Nanogels (nm)



Microgel (µm)

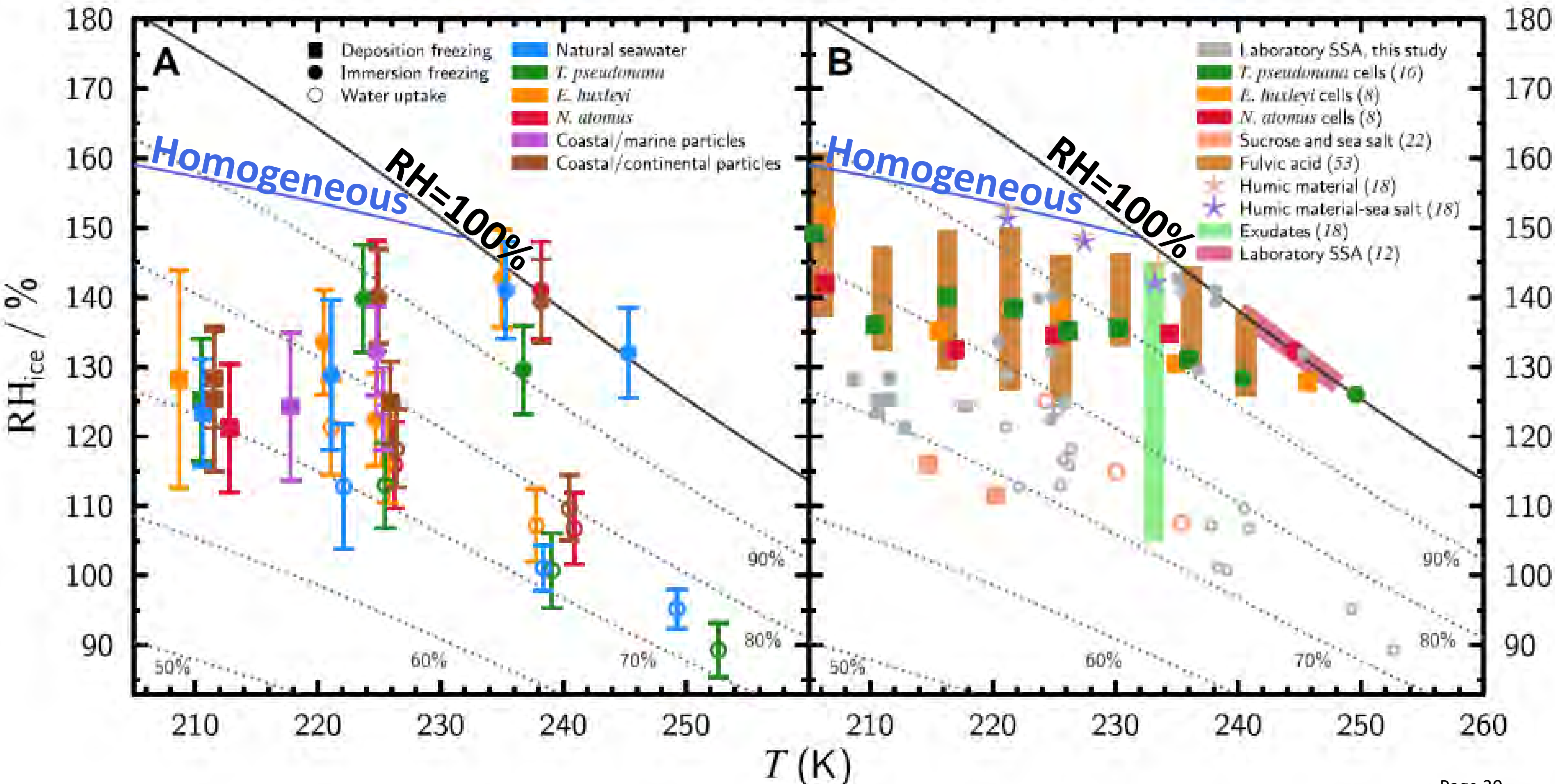


Verdugo, *Annul. Rev. Mar. Sci.*, 2012

SSA particles → sea salt and microbial exudates of polysaccharidic and proteinaceous particles.

Ice formed heterogeneous at RH=100% at higher temperature and RH<100% at lower temperature.

Alpert et al., *Sci. Adv.*, 2022



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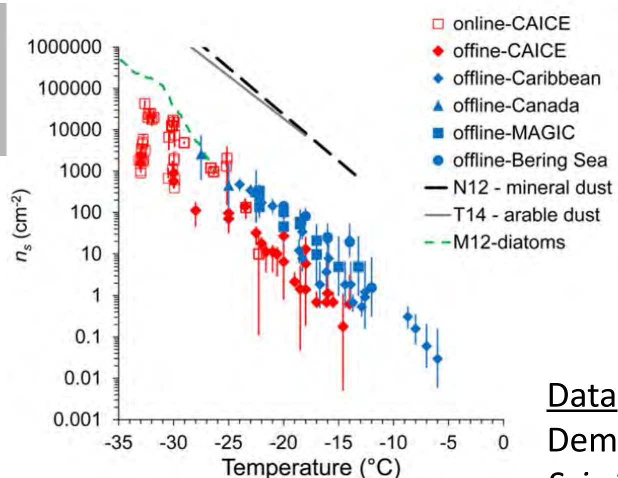
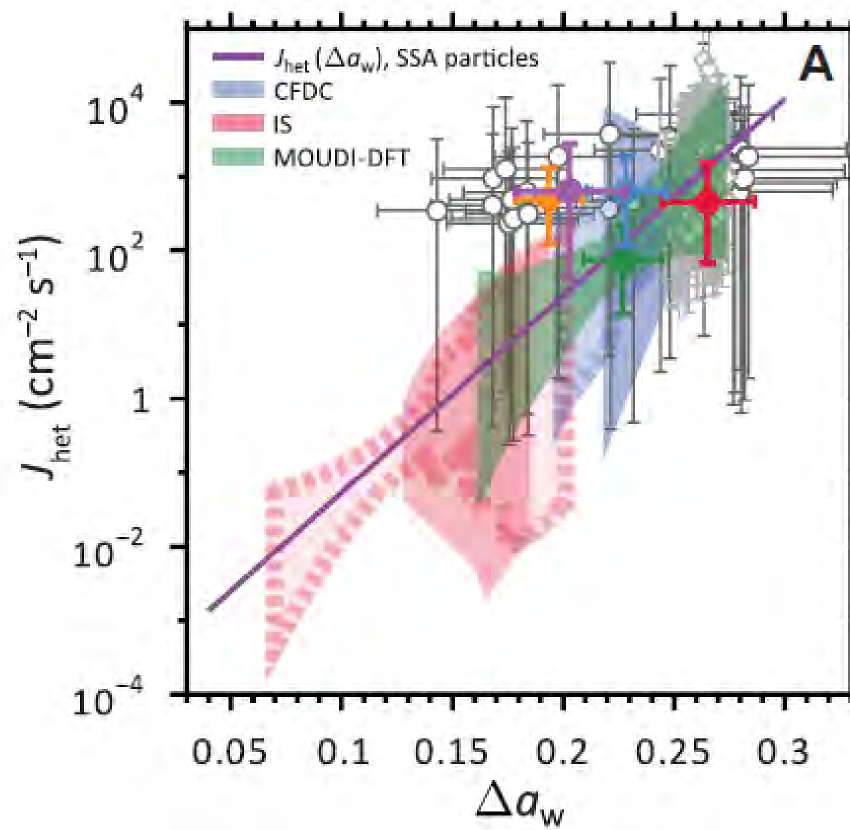


Continuous Flow Diffusion Chamber
Micro-Orifice Uniform Deposit Impactor - Droplet Freezing Technique
Ice Spectrometer

Alpert et al., *Sci. Adv.*, 2022



<u>Data</u> from this study and Demott et al., *Proc. Natl. Acad. Sci.,* 2016

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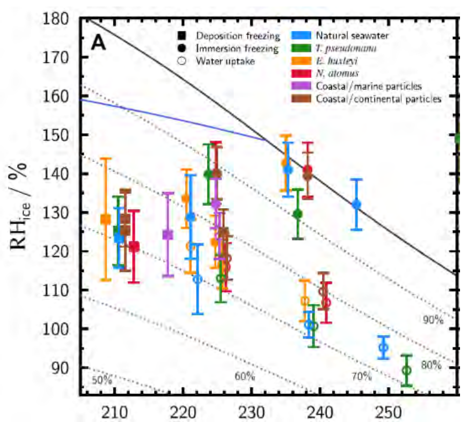
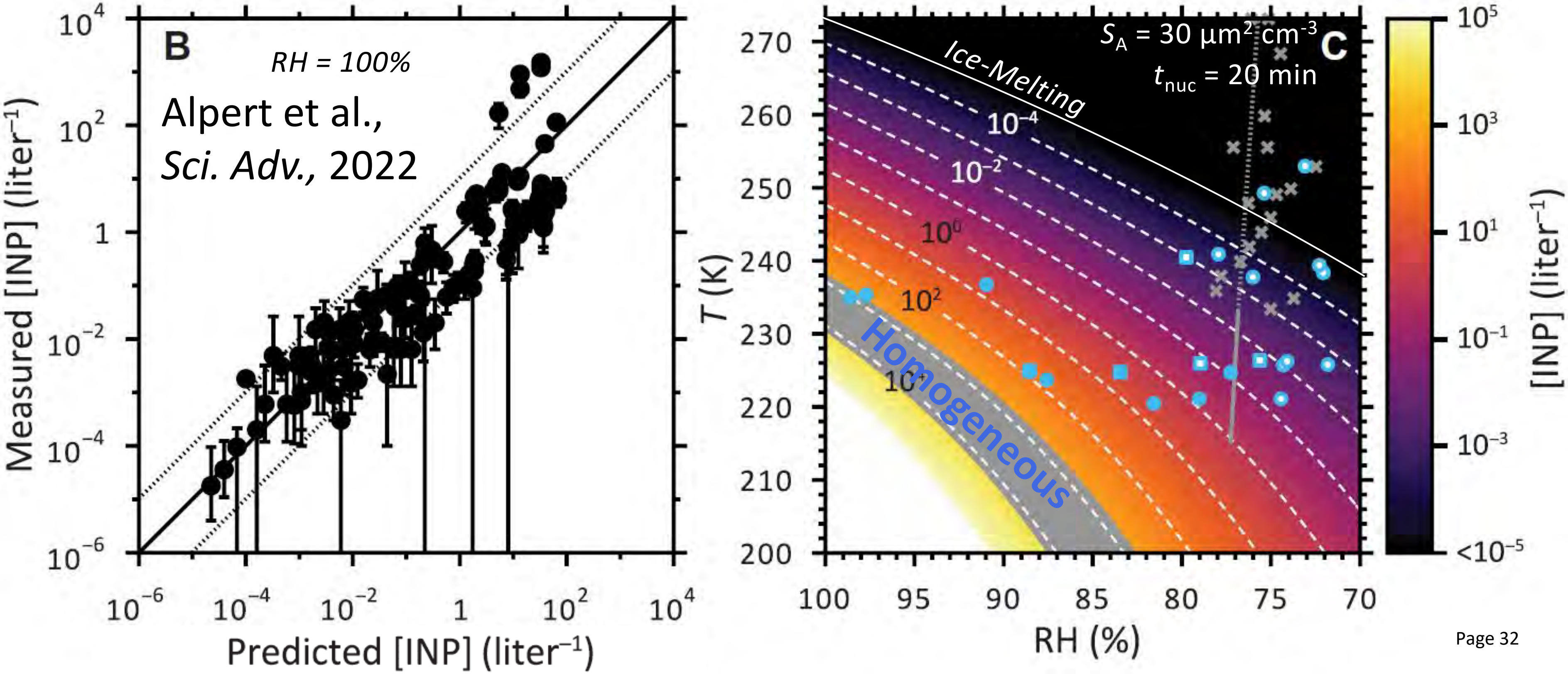


<u>Ice nucleation simulation to calculate J_{het} and uncertainties.</u>

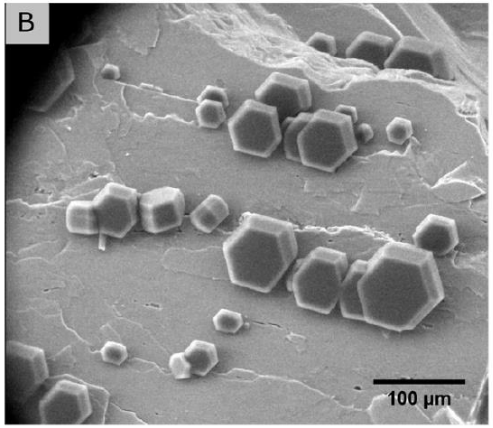
<u>Valid for field studies</u> by, Cornwell et al., *Geophys. Res. Lett.*, 2016 and Knopf et al., *B. Am. Meteorol. Soc.*, 2021.

Ice nucleation from laboratory and field studies can all be predicted with a single heterogeneous ice nucleation rate coefficient, J_{het}.

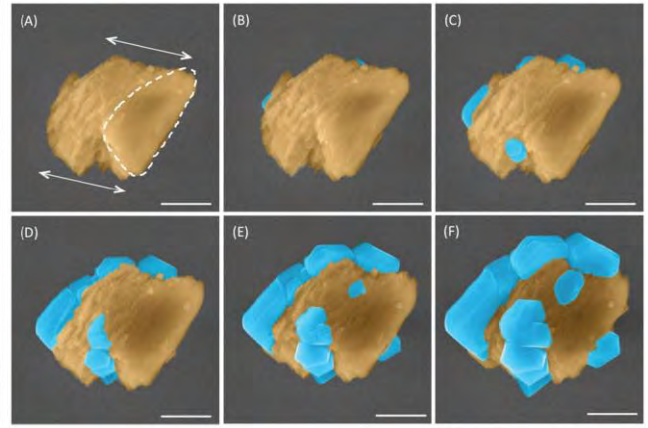


Temperature:	205 K – 267 K	Surface area:	6 – 930 µm² cm⁻³ (air)
Relative humidity:	60% – 100%	Particle numbers:	0.03 – 4.7 ×10³ cm⁻³ (air)
Timescale:	5 s – 30 min	Total particle area:	7.3×10^{-5} – 1.6×10^{2} cm²

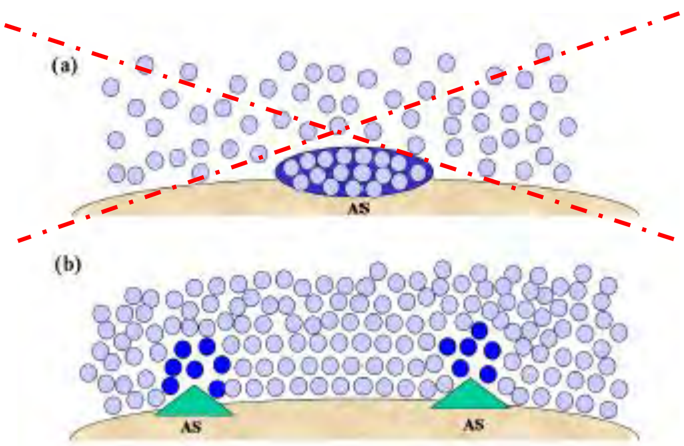
Active site-aware experiments and theory for immersion and deposition ice nucleation



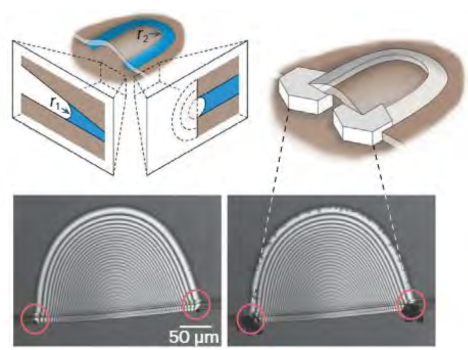
Kiselev et al., *Science,* 2016



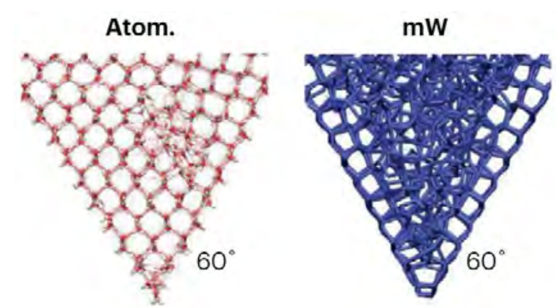
Wang et al., *Phys. Chem. Chem. Phys.,* 2016



Barahona, *Atmos. Chem. Phys.,* 2018 Nucleation in low density amorphous water. Bullock and Molinero, *Faraday Discuss.*, 2013



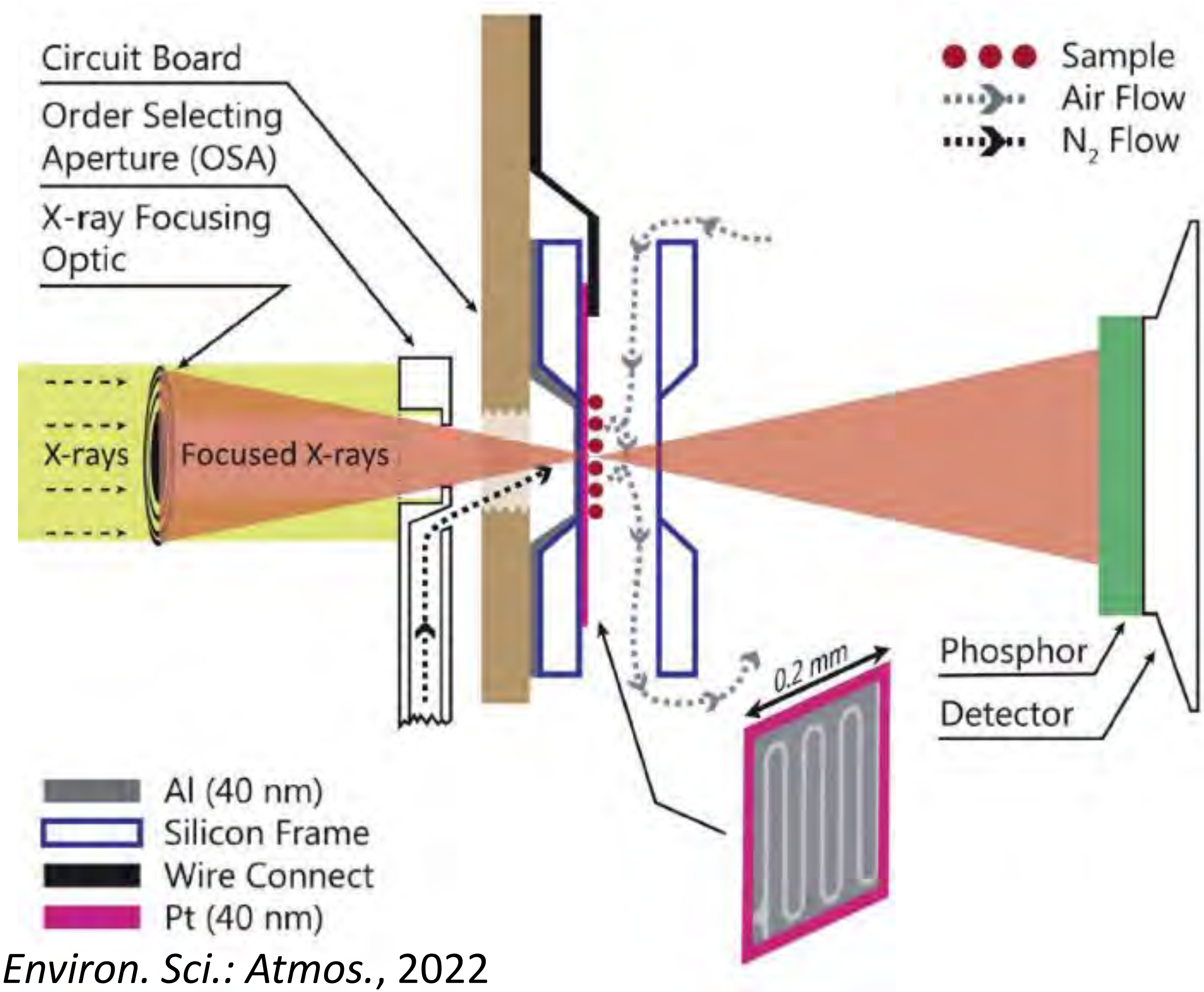
Campbell and Christenson, *Phys. Rev. Lett.,* 2018



Roudsari et al., *Atmos. Chem. Phys.,* 2022: Ice nucleation out of a single wedge.

David et al., *Proc. Natl. Ac. Sci.*, 2019: A network of closely spaced pores required.

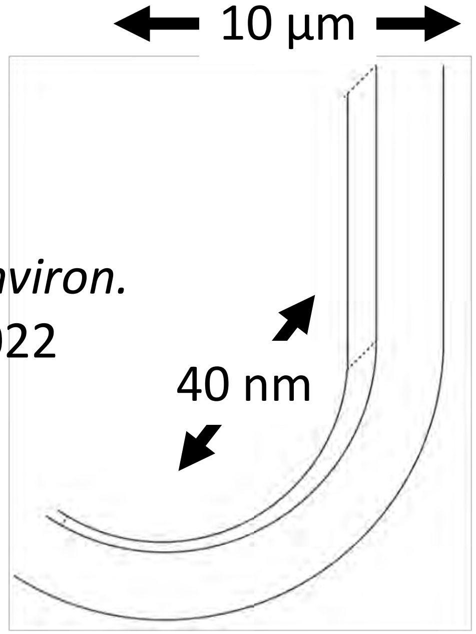
In situ ice nucleation experiment coupled to STXM for active sites and aerosol particles.



Alpert et al., *Environ. Sci.: Atmos.*, 2022

Lithography to create perfect step imperfections.

Alpert et al., *Environ. Sci.: Atmos.*, 2022



Fletcher, *Aust. J. Phys.*, 1960

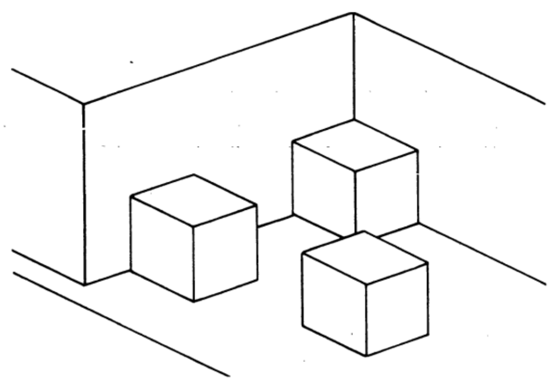
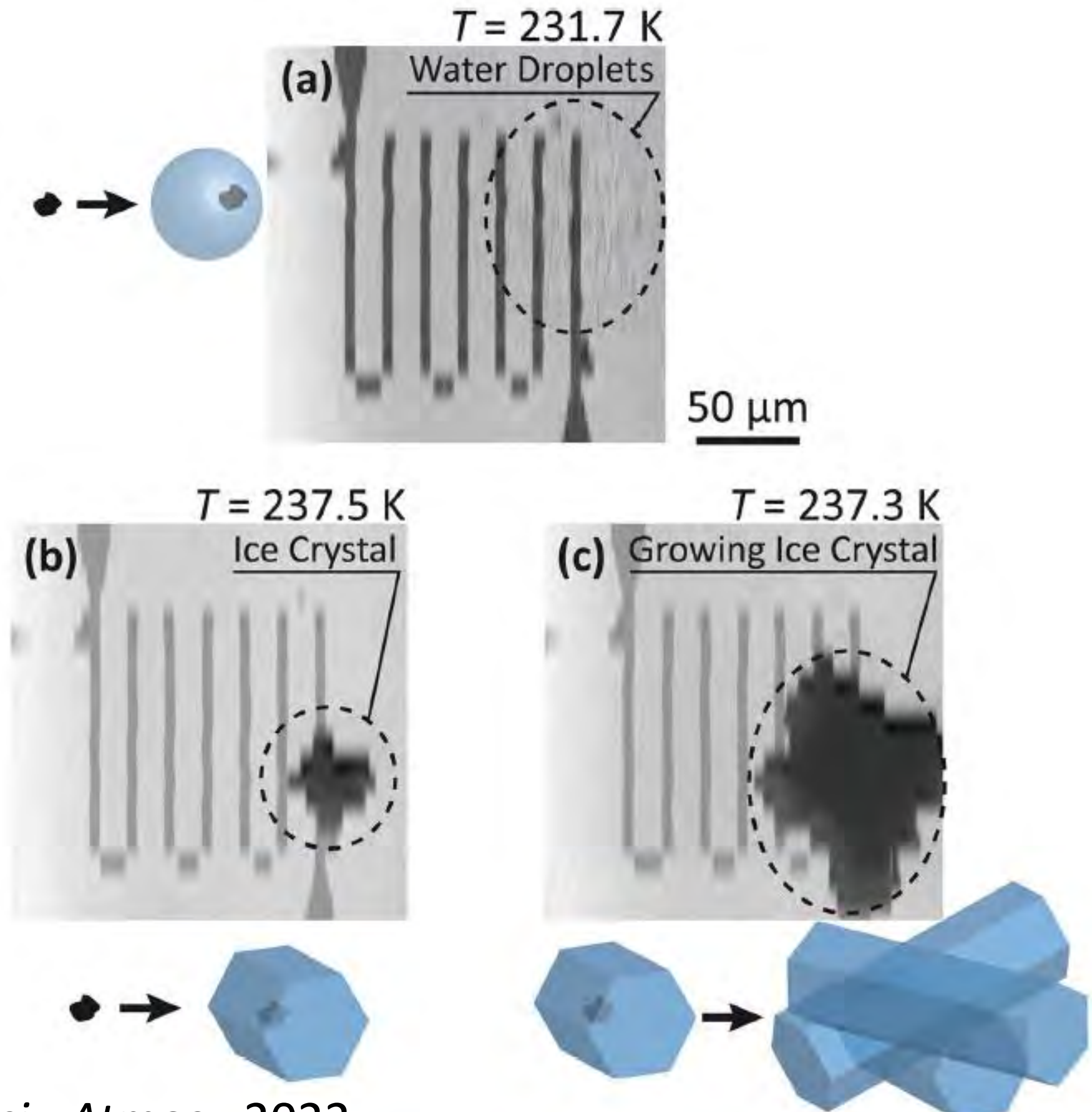


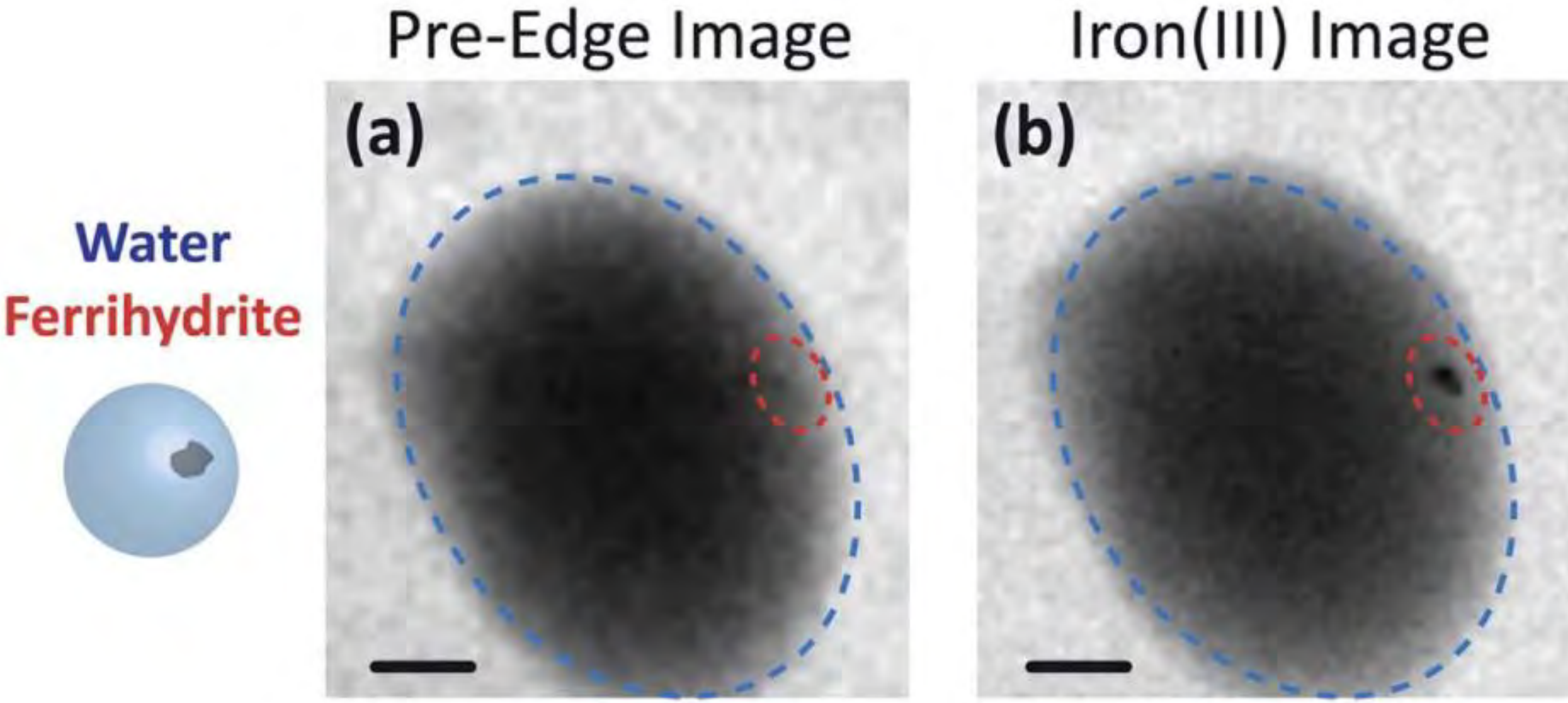
Fig. 4.—Nucleation of a simple cubic embryo on a plane surface, at a step, and in a corner.

Imaging particles in pure water droplets. Maintaining *RH* = 100%.



Alpert et al., *Environ. Sci.: Atmos.*, 2022

Imaging particles in pure water droplets. Maintaining $RH = 100\%$.



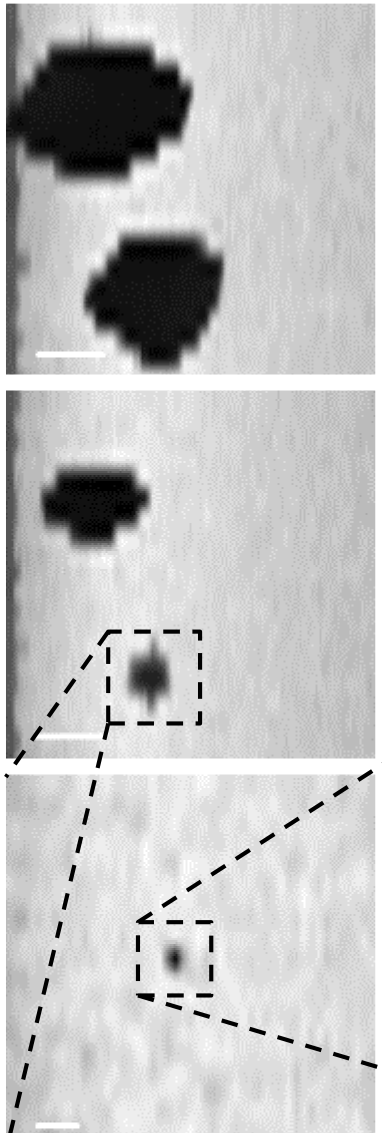
Alpert et al., *Environ. Sci.: Atmos.*, 2022

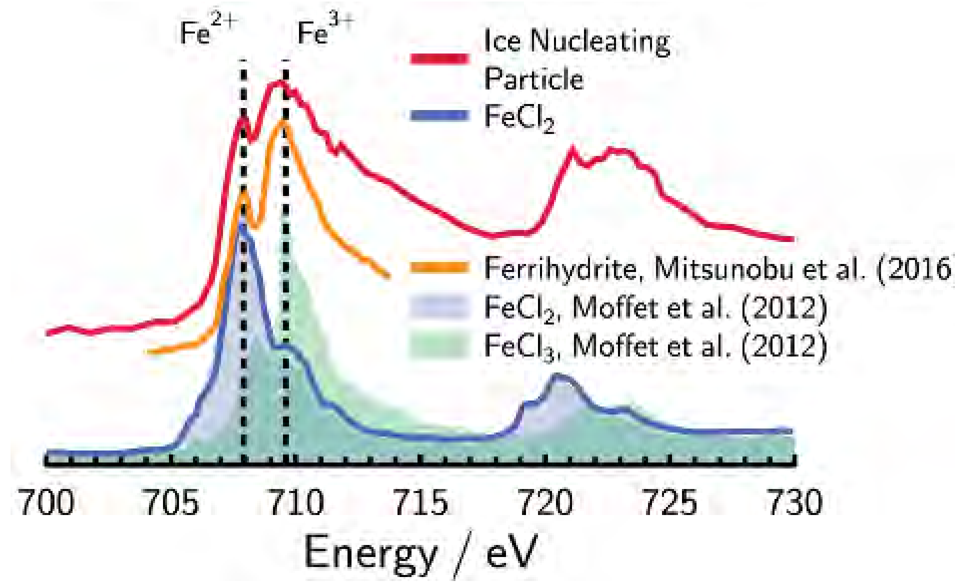
Sublimate a crystal and find out what is left behind.

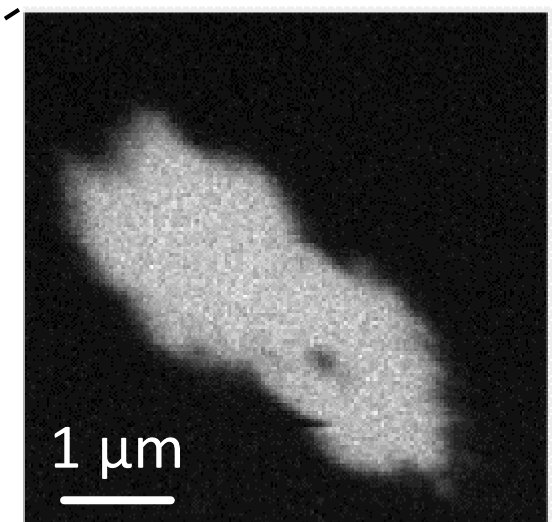
20 µm

20 µm

5 µm







Alpert et al., *Environ. Sci.: Atmos.*, 2022

Conclusions and Implications

- Ice nucleating particle composition and mapping in situ for chemically complex particles. X-ray Spectromicroscopy balances spatial resolution and chemical selectivity.
- Ferrihydrite (amprphous iron) can nucleation ice (deposition).
- All sea spray particles are ice nucleating particles.
- Aerosol- Theoretical- Active Site- aware may all be needed to reduce/explain uncertainties. Ice nucleation theory does this.

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