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Soot Aerosols as a Source for Ice Nucleating Particles in the Cirrus Regime

the Role of Soot Particle Properties

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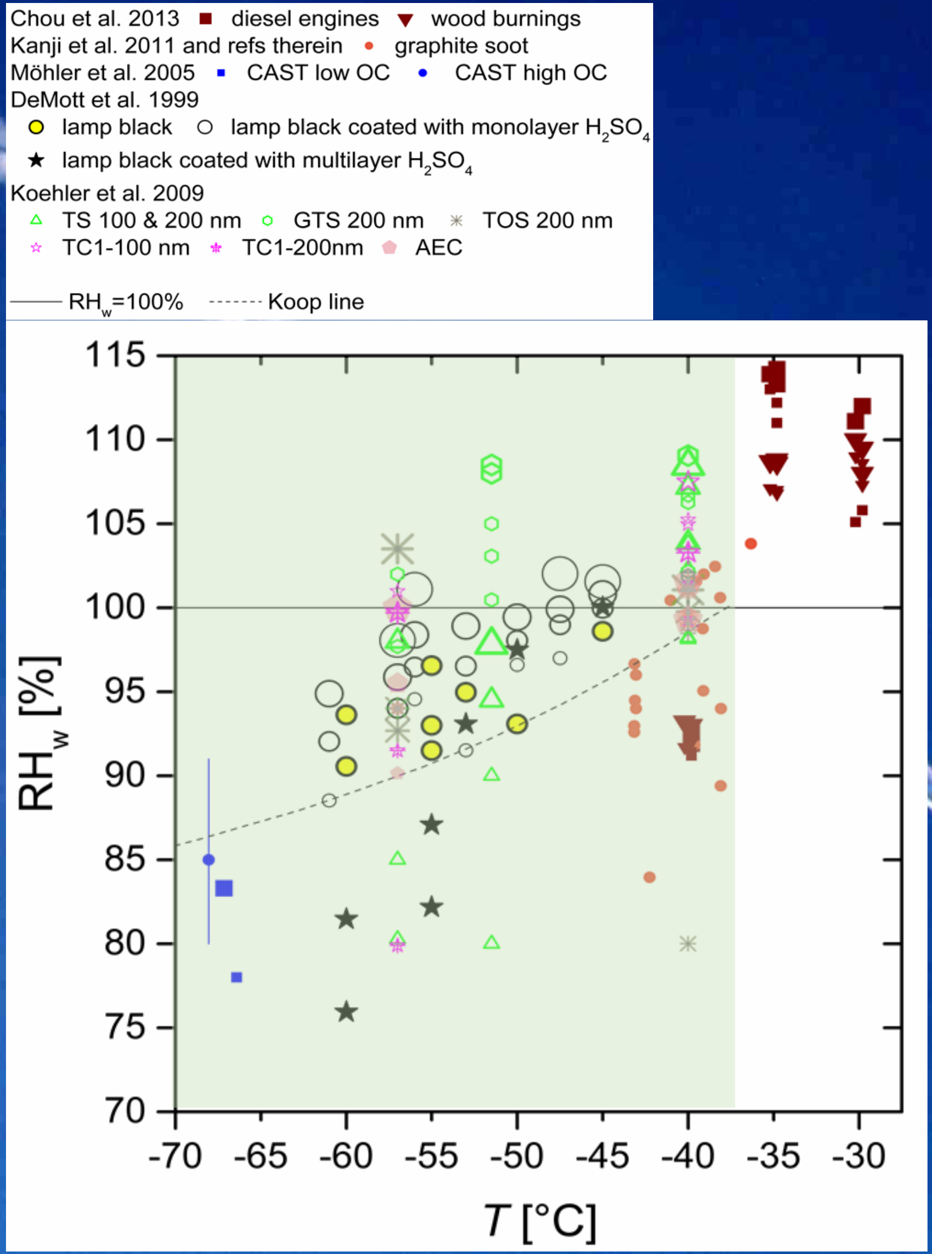
Acknowledgment:
H. Wydler, J. Aerni, L. Lacher, F. Friebel, J. Atkinson, S. Brunamonti, U. Krieger, J. Wong, M. Plötze and I. Burgert

Supporting information can also be found at:
https://doi.org/10.5194/acp-2018-557



Kanji, Z. A., et al. (2017). "Overview of Ice Nucleating Particles." Meteorological Monographs **58**(0): 1.1-1.33.

... uncertainties in net climate forcing from black-carbon-rich sources are substantial, largely due to lack of knowledge about cloud interactions with both black carbon and co-emitted organic carbon.

Bond et al. (2013)

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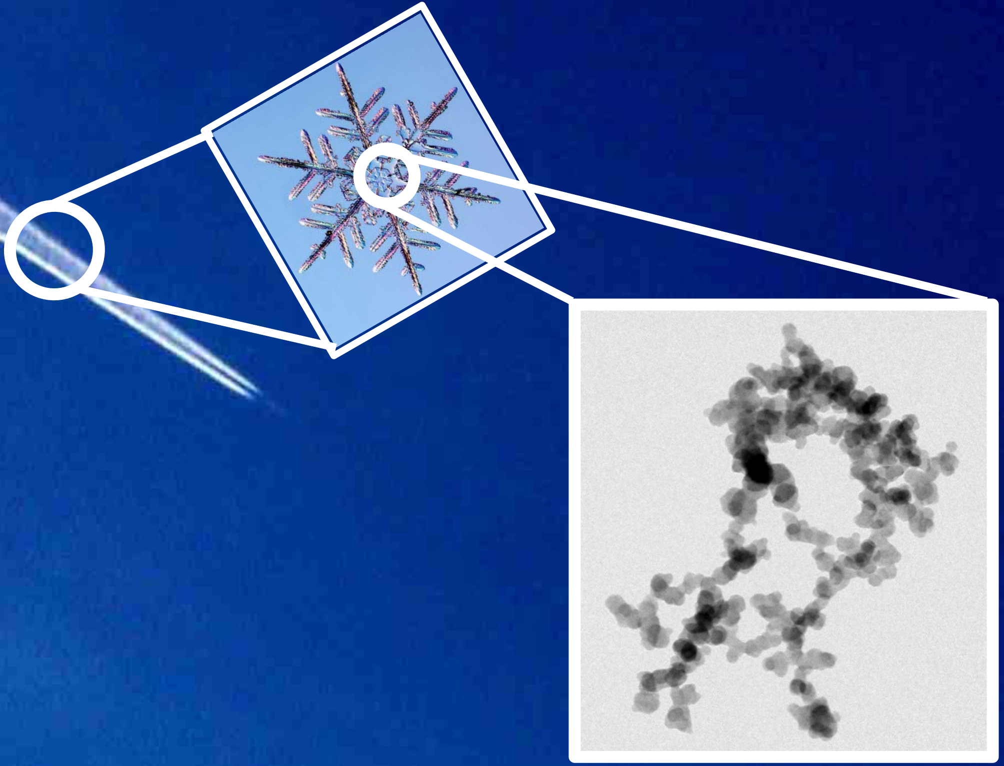
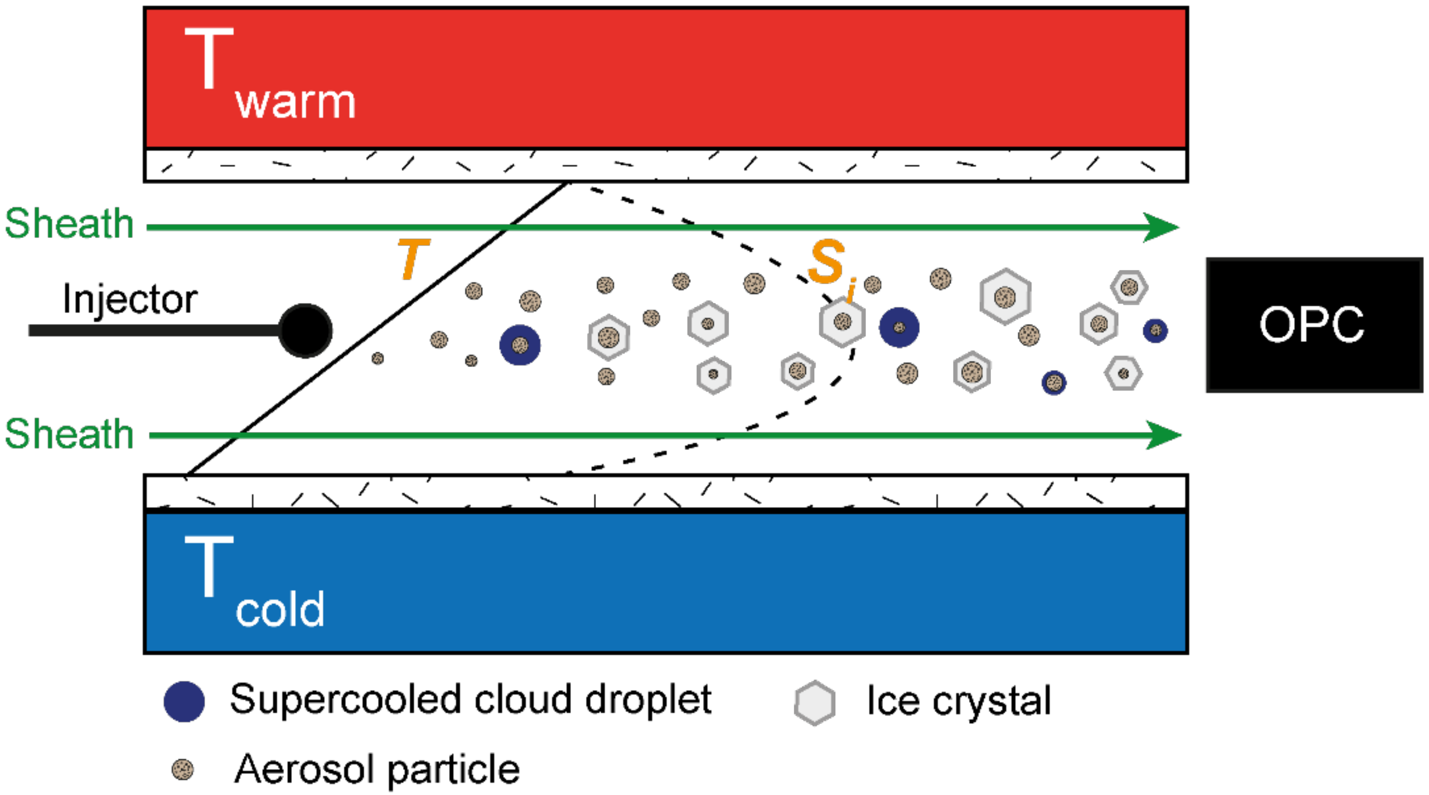
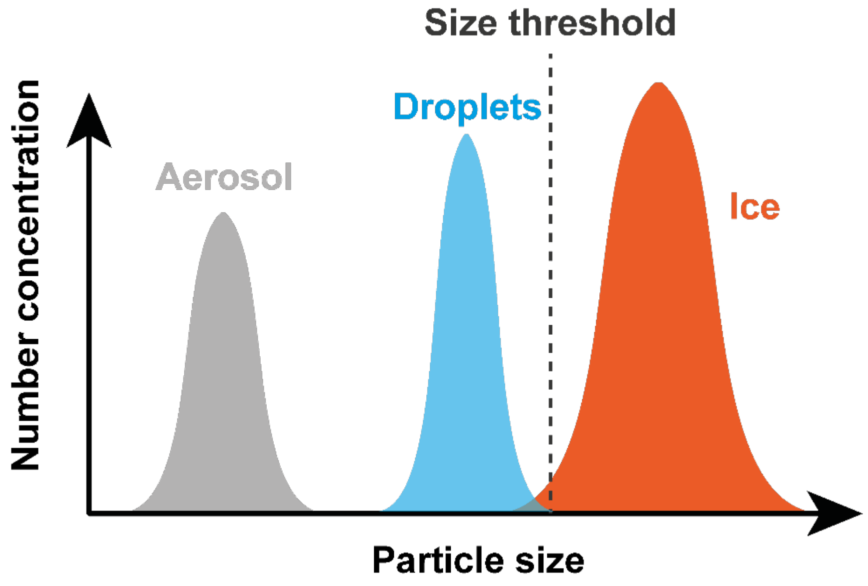


Method: Ice nucleation measurements

The Horizontal Ice Nucleation Chamber (HINC)[1,2]

A Continuous Flow Diffusion Chamber (CFDC)





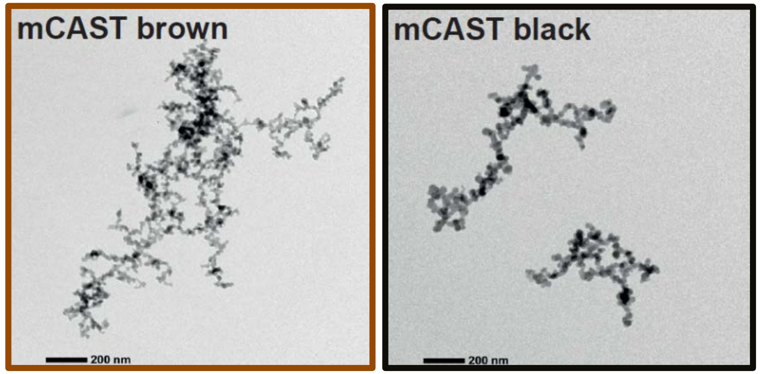
$$\text{Active Fraction} = \frac{N(Ice)}{N(Aerosol)}$$

[1] Lacher, L., et al. (2017). "The Horizontal Ice Nucleation Chamber (HINC): INP measurements at conditions relevant for mixed-phase clouds at the High Altitude Research Station Jungfraujoch." Atmospheric Chemistry and Physics **17**(24): 15199-15224.

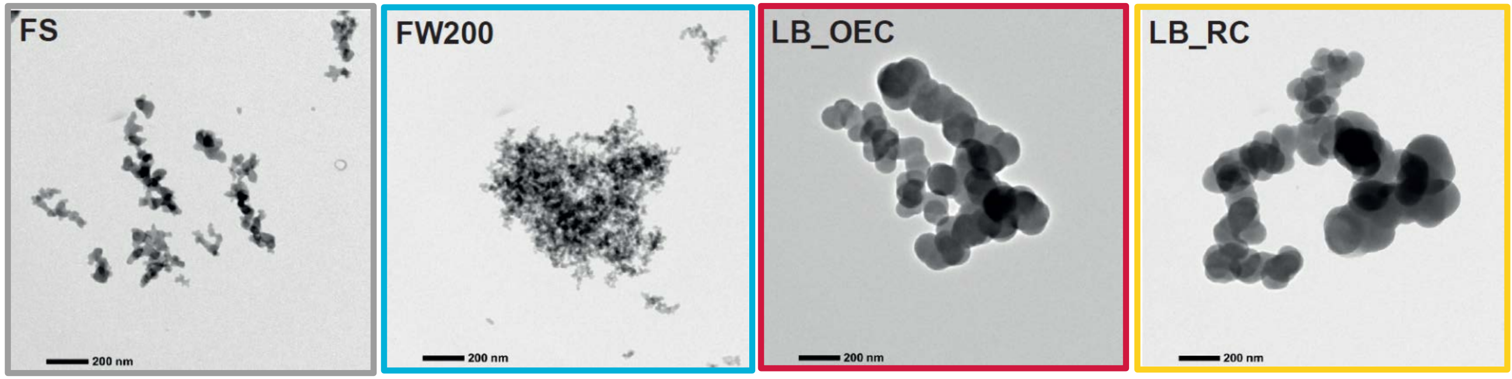
[2] Mahrt, F., et al. (2018). "Ice nucleation abilities of soot particles determined with the Horizontal Ice Nucleation Chamber." Atmos. Chem. Phys. Discuss. **2018**: 1-41.

Materials and methods
Soot samples and experimental set up

miniCAST/propane flame soot



Commercial and industrial carbon blacks

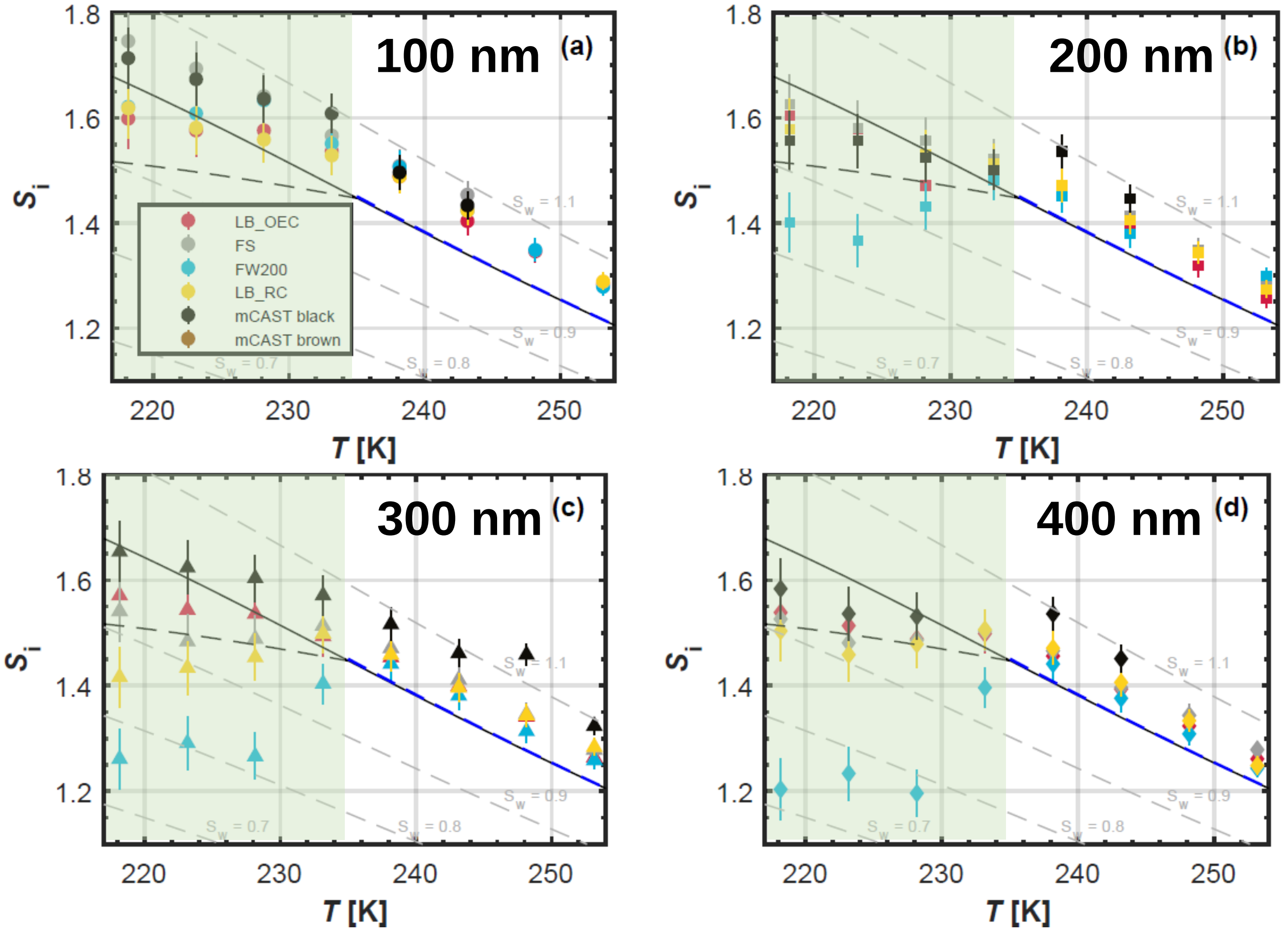


- miniCAST soot with different organic matter content were used as surrogates for soot emitted from jet engines.[1]
- Fullerene soots (FS) have previously been attributed to Diesel engines.[2]
- FW200 is an industrial carbon used as surrogate of atmospherically aged soot.
- Lamp Blacks are frequently used in pigment applications and have been investigated for ice nucleation.[3]

[1] Bescond, A., et al. (2014). "Automated Determination of Aggregate Primary Particle Size Distribution by TEM Image Analysis: Application to Soot." Aerosol Science and Technology **48**(8): 831-841.
[2] Muller, J. O., et al. (2005). "Morphology-controlled reactivity of carbonaceous materials towards oxidation." Catalysis Today **102**: 259-265.
[3] DeMott, P. J., et al. (1999). "Ice formation by black carbon particles." Geophysical Research Letters **26**(16): 2429-2432.

Results: Ice nucleation of size selected soot particles

Onset conditions for 1% of the particles to activate into ice crystals and/or cloud droplets



- 100 nm soot particles do not heterogeneously nucleate ice.
- Dependence on homogeneous nucleation temperature (HNT = 235 K) [2] suggest involvement of liquid water[3].

Cirrus regime (T < 235 K)

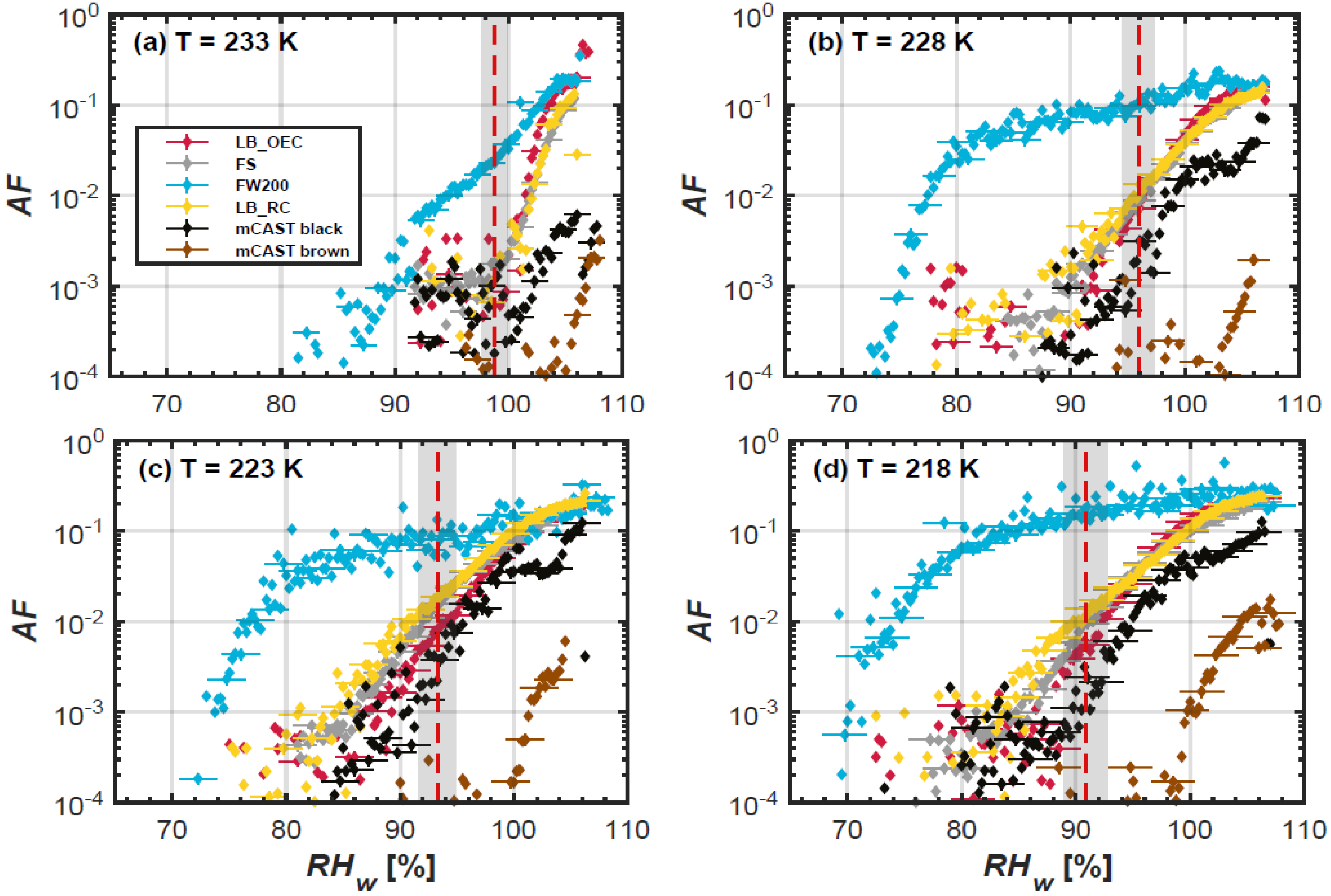
Water saturation

Koop et al. (2000)[1]

WDS

[1] Koop, T., et al. (2000). "Water activity as the determinant for homogeneous ice nucleation in aqueous solutions." Nature **406**(6796): 611-614.
[2] Friedman, B., et al. (2011). "Ice nucleation and droplet formation by bare and coated soot particles." Journal of Geophysical Research-Atmospheres **116**.
[3] Welti, A., et al. (2009). "Influence of particle size on the ice nucleating ability of mineral dusts." Atmospheric Chemistry and Physics **9**(18): 6705-6715.

Results: Ice nucleation of d_m = 400 nm soot particles
Cirrus temperature regime[1]



AF curves

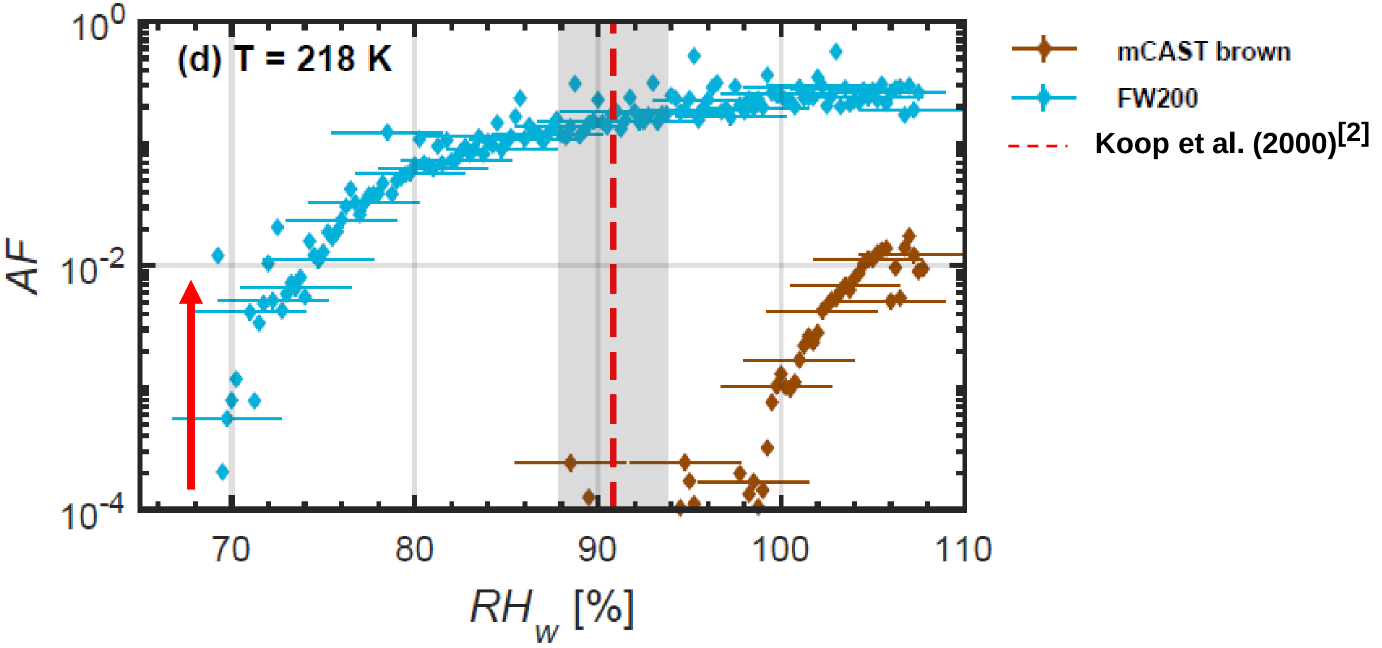
What particle characteristics can explain difference in ice nucleation ability?

Koop et al. (2000)[2]

[1] Mahrt, F., et al. (2018). "Ice nucleation abilities of soot particles determined with the Horizontal Ice Nucleation Chamber." Atmos. Chem. Phys. Discuss. **2018**: 1-41.
[2] Koop, T., et al. (2000). "Water activity as the determinant for homogeneous ice nucleation in aqueous solutions." Nature **406**(6796): 611-614.

Ice nucleation mechanism

Can soot nucleate ice via Pore Condensation and Freezing (PCF)[1]?



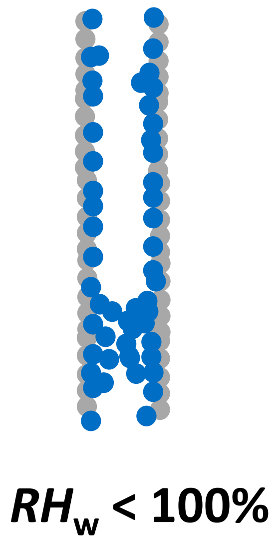


Figure: R. O. David

Inverse Kelvin effect:

$$p_{lc} = p_l \cdot exp\left(\frac{-4\gamma v_l}{\frac{D_p}{cos\theta}RT}\right)$$

D_p: Pore diameter
θ: Contact angle
T: Temperature
p_{lc}: water vapor pressure - concave surface
p_l: water vapor pressure - flat surface
γ: surface tension of water
v_l: molar volume of water
R: dry gas constant

Steep activation curve of FW200 suggests **homogeneous** freezing type mechanism.

PCF mechanism :

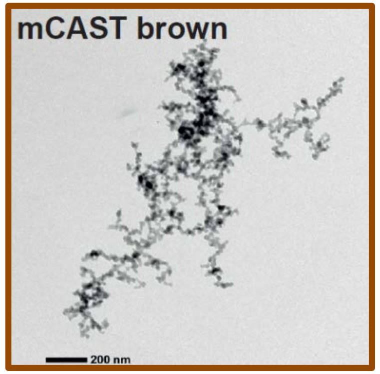
- Water uptake at RH_w < 100%
  - Inverse Kelvin effect
- Pore water freezes

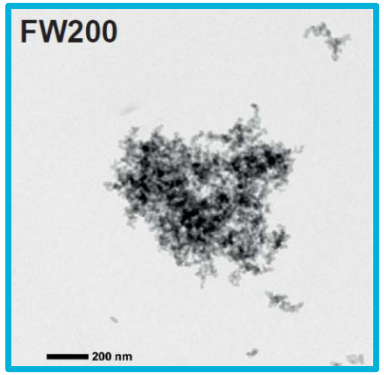
[1] Marcolli, C. (2014). "Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities." Atmos. Chem. Phys. **14**(4): 2071-2104.
[2] Koop, T., et al. (2000). "Water activity as the determinant for homogeneous ice nucleation in aqueous solutions." Nature **406**(6796): 611-614.

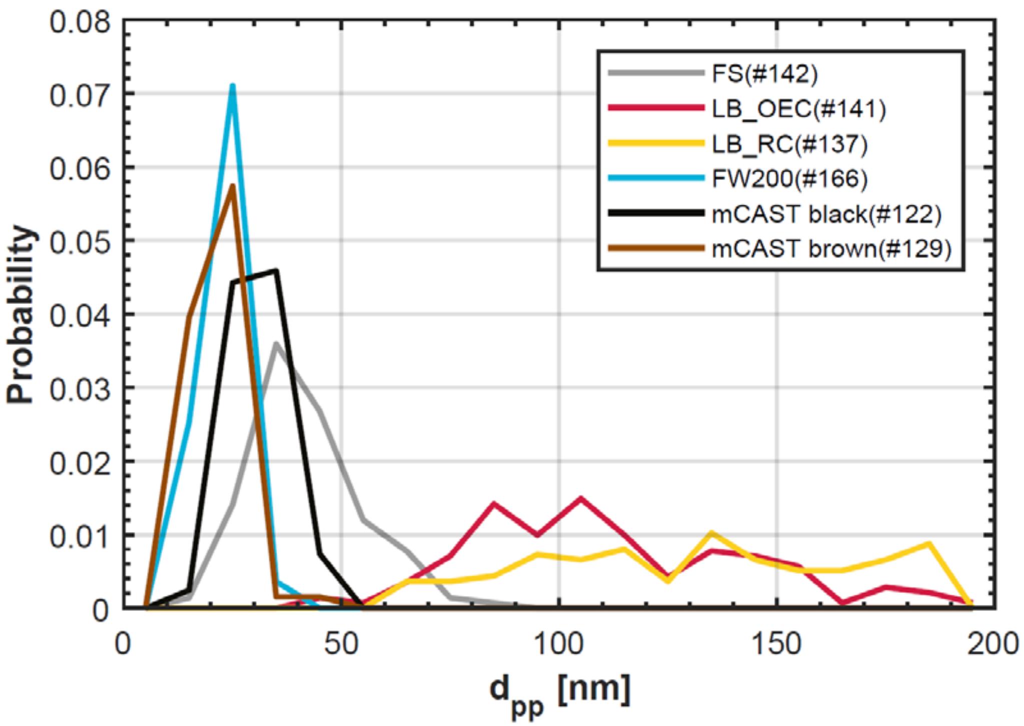
Porous and fractal structure of soot particles

What can TEM evaluation tell us about particle morphology?

Overall aggregate structure & primary particle size







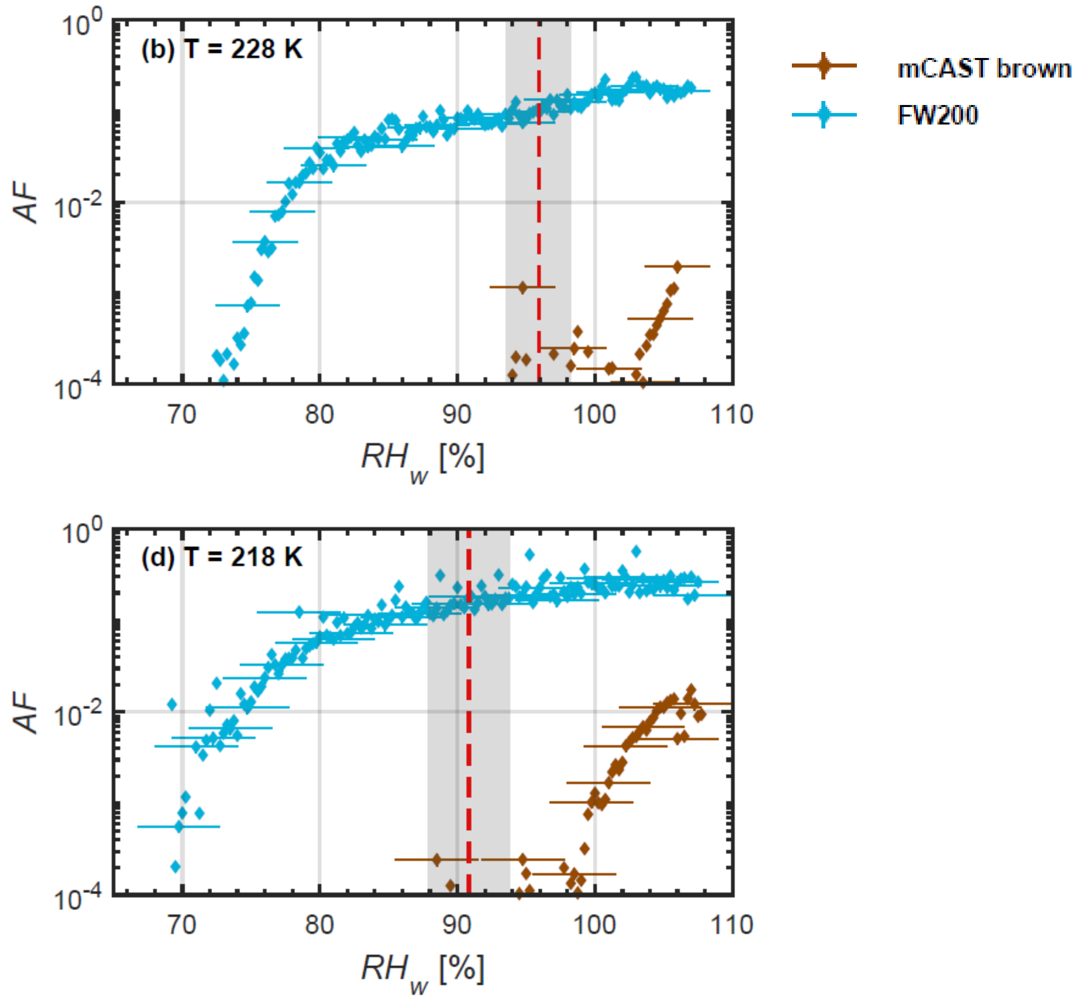
- Pores formed in between sintered primary particles.
- TEM evaluation reveals mesopores with diameters between 2 – 8 nm.
- Soot with smaller primary particles are more likely to nucleate ice via PCF due to the higher propensity of pores.
- Macroscopic ice only grows out of pores if they are closely spaced[1].

[1] David et al. (in prep.), "Is Deposition Ice Nucleation Real? The Role of Pore Condensation and Freezing on Atmospheric Ice Nucleation"

Data: E. Barthazy Meier

Results: Ice nucleation of d_m = 400 nm soot particles

Cirrus temperature regime



Question:

- Pure availability of porous structures seems to be insufficient.
- What are we missing?

Inverse Kelvin effect:

$$p_{lc} = p_l \cdot exp\left(\frac{-4\gamma v_l}{\frac{D_p}{cos\theta}RT}\right)$$

D_p: Pore diameter

θ: Contact angle

T: Temperature

Results: Wettability of soot particles

Water Adsorption Isotherms

Gravimetric technique: Dynamic Vapor Sorption (DVS)

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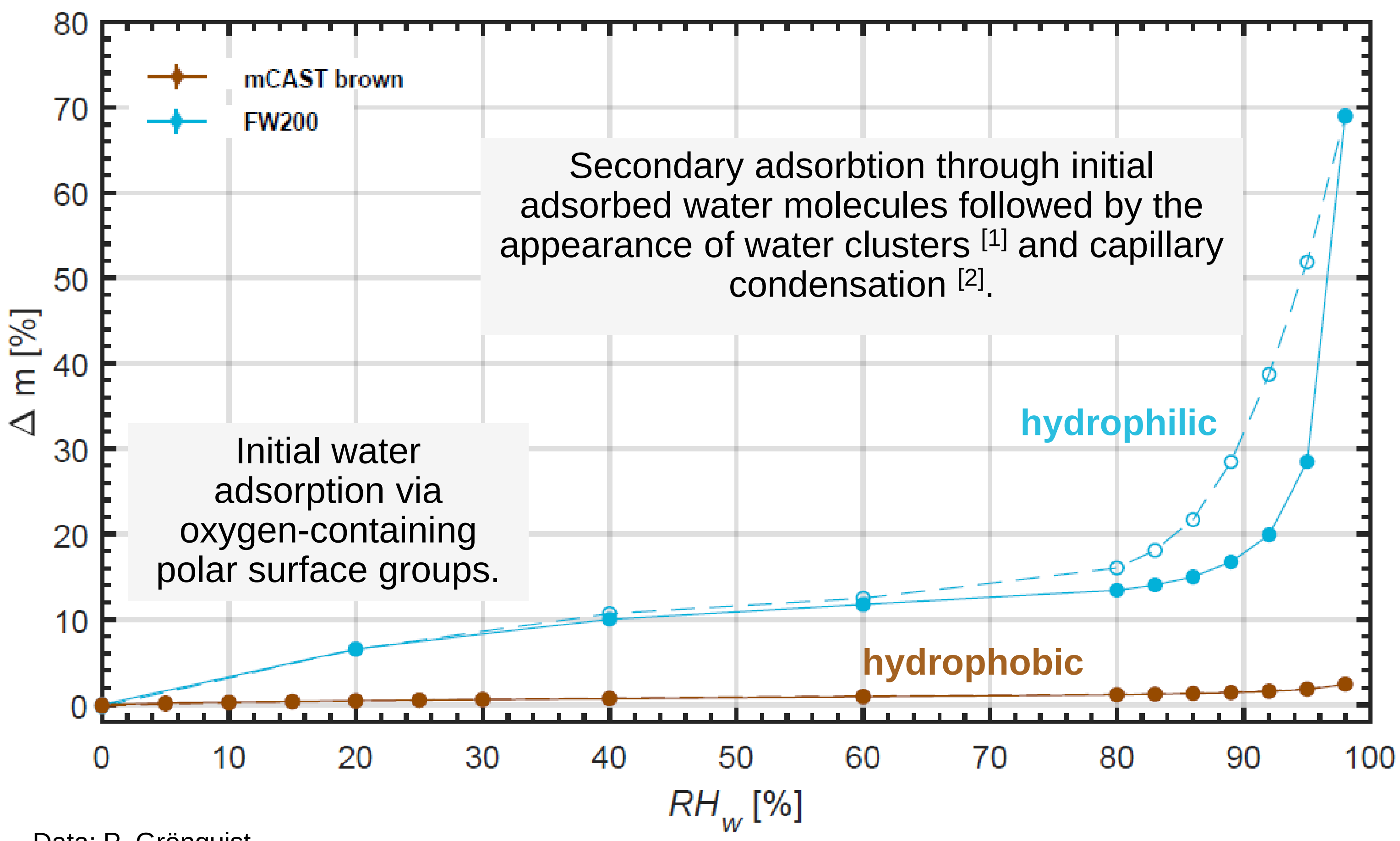

Data: P. Grönquist

- More ice active soot shows enhanced water adsorption
- Strong water uptake at high RH_w indicates presence of mesopores on FW200, needed for PCF
- Strong water uptake indicative of low soot-water contact angle
- DVS results support a PCF ice nucleation mechanism

[1] Ferry, D., et al. (2002). "Water adsorption and dynamics on kerosene soot under atmospheric conditions." Journal of Geophysical Research-Atmospheres **107**(D23)

[2] Thommes, M., et al. (2015). "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)." Pure and Applied Chemistry **87**(9-10): 1051-1069.

[3] David, R. O., et al. (in prep.). "The Role of Contact Angle and Pore Width on Pore Condensation and Freezing."

Pore filling conditions

Can PCF estimates explain results?

Example: FW200 particles d_m = 400 nm

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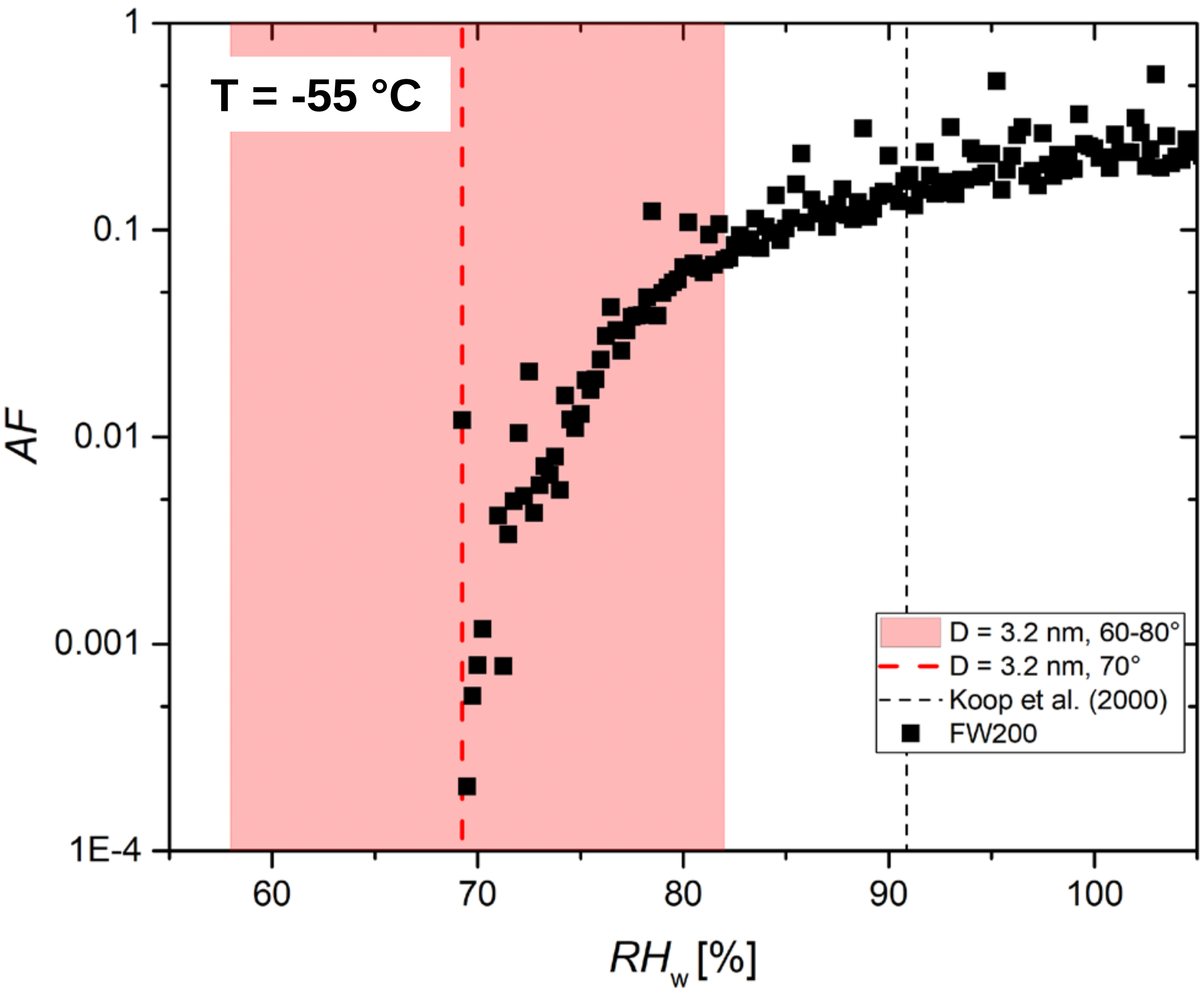

- Soot-water contact angles reported in literature range from 60 to 80°[1,2].
- Ice formation of FW200 falls within expected range, using pore sizes (from TEM and DVS) and contact angles (from literature).
- Nevertheless, better experimental determination of both contact angles and pore sizes needed.

[1] Persiantseva, N. M., et al. (2004). "Wetting and hydration of insoluble soot particles in the upper troposphere." Journal of Environmental Monitoring **6**(12): 939-945.
[2] Wei, Y., et al. (2017). "The Wetting Behavior of Fresh and Aged Soot Studied through Contact Angle Measurements." Atmospheric and Climate Sciences **Vol.07No.01**: 12.

Summary and Conclusions

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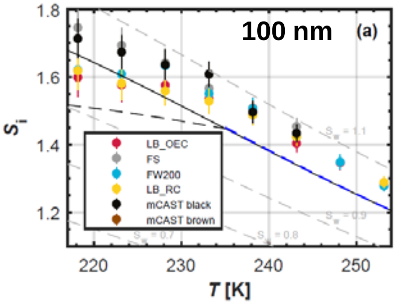
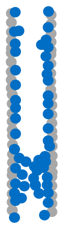


(1) Soot particles can contribute to ice formation below homogeneous freezing of solution droplets only for d_m > 100 nm.

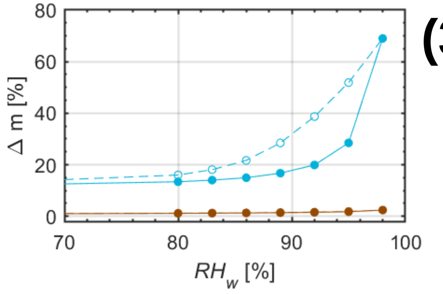
- Larger soot particles mainly sourced from biomass burning and wildfires[1]
- Soot particles from aviation emissions generally found to be < 100 nm[2,3]



RH_w < 100%

(2) Distinct dependence on HNT suggests involvement of liquid water in ice nucleation process on soot particles.

- Ice formation in cirrus regime and absence for MPC temperatures
- Best described by a PCF mechanism[4,5]



(3) Soot particle properties determine freezing ability by PCF.

- Cavities/pores are available, but their size and propensity is important
- Wettability/Soot-water contact angle as driving factor to inhibit and/or trigger ice formation.

[1] Chakrabarty, R. K., et al. (2014). "Soot superaggregates from flaming wildfires and their direct radiative forcing." Scientific Reports **4**: 5508.
[2] Moore, R. H., et al. (2017). "Biofuel blending reduces particle emissions from aircraft engines at cruise conditions." Nature **543**(7645): 411-+.
[3] Yu, Z. H., et al. (2017). "Evaluation of PM emissions from two in-service gas turbine general aviation aircraft engines." Atmospheric Environment **160**: 9-18.
[4] Higuchi, K. and N. Fukuta (1966). "Ice in capillaries of solid particles and its effect on their nucleating ability." Journal of the Atmospheric Sciences **23**(2): 187-&.
[5] Marcolli, C. (2014). "Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities." Atmos. Chem. Phys. **14**(4): 2071-2104.