Heterogeneous ice nucleation of soot particles: measurements, predictions and implications

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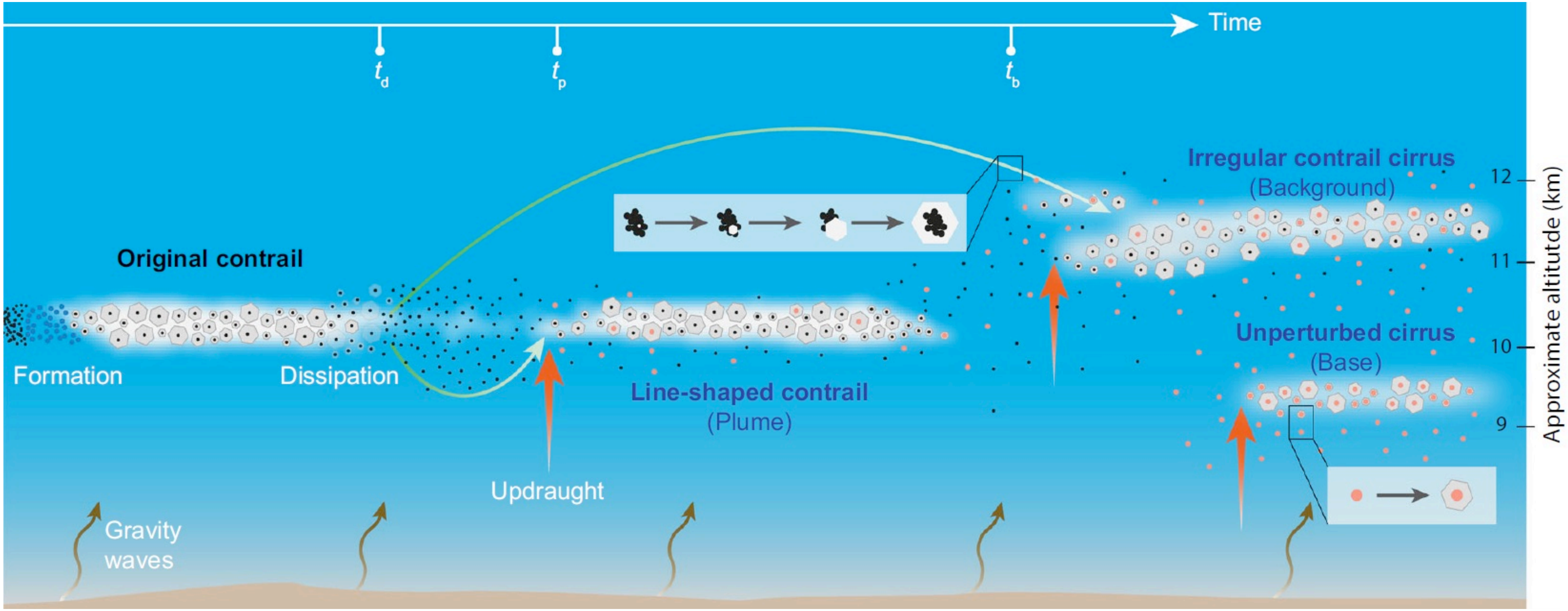
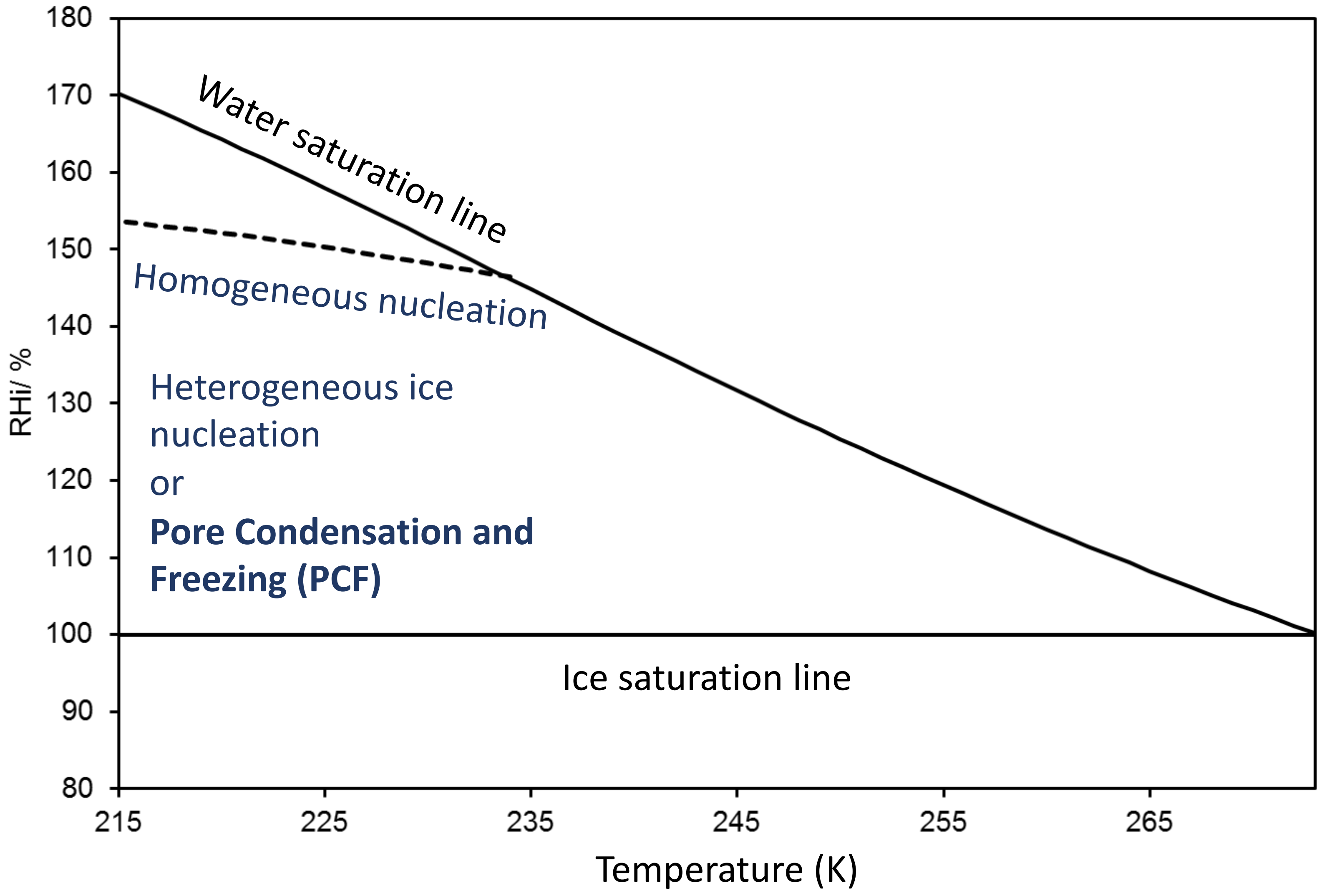
Overview



Kärcher et al., Nature Comm., 2021

RH/T conditions for the different ice nucleation modes



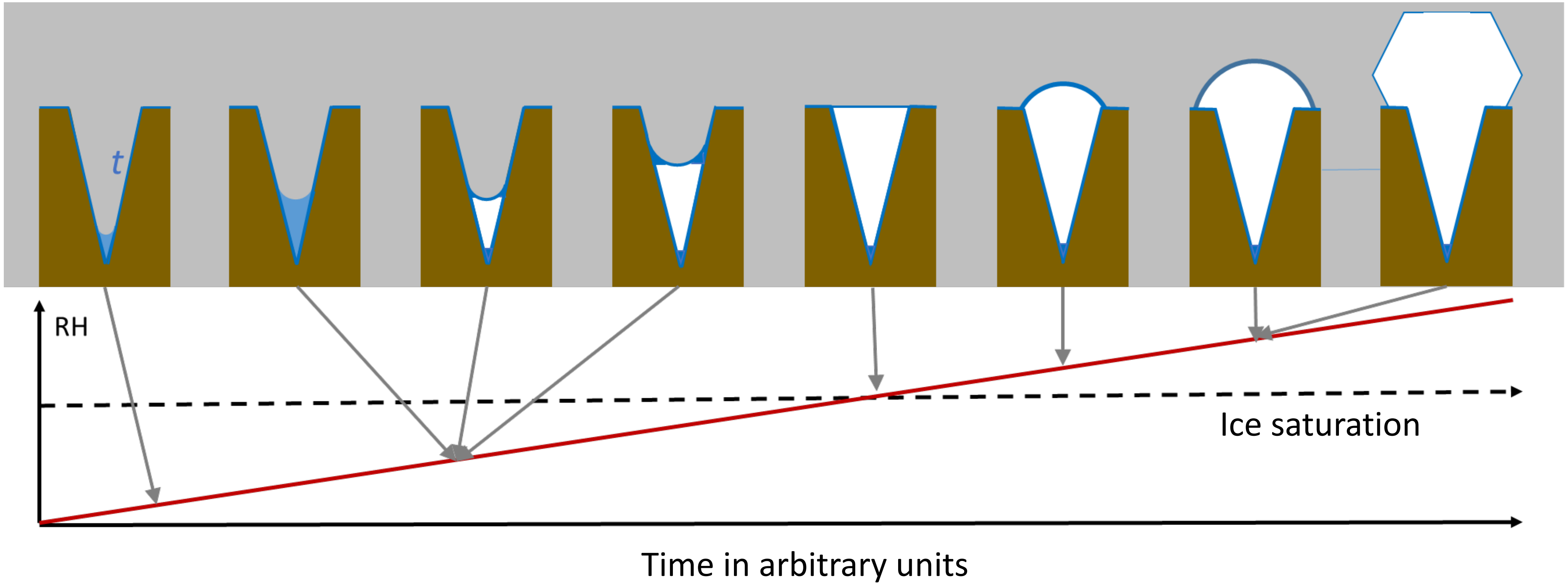
Homogeneous ice nucleation:
Occurring on ubiquitous solution droplets

Heterogeneous ice nucleation:
Occurring on ice-nucleating particles (INPs) with nucleation sites

PCF:
Occurring on porous particles through homogeneous ice nucleation of pore water

Pore condensation and freezing (PCF)

- Capillary condensation of water into pores (Kelvin equation)
- Nucleation of ice within the pores (Classical nucleation theory)
- Growth of ice out of the pores (Kelvin equation)

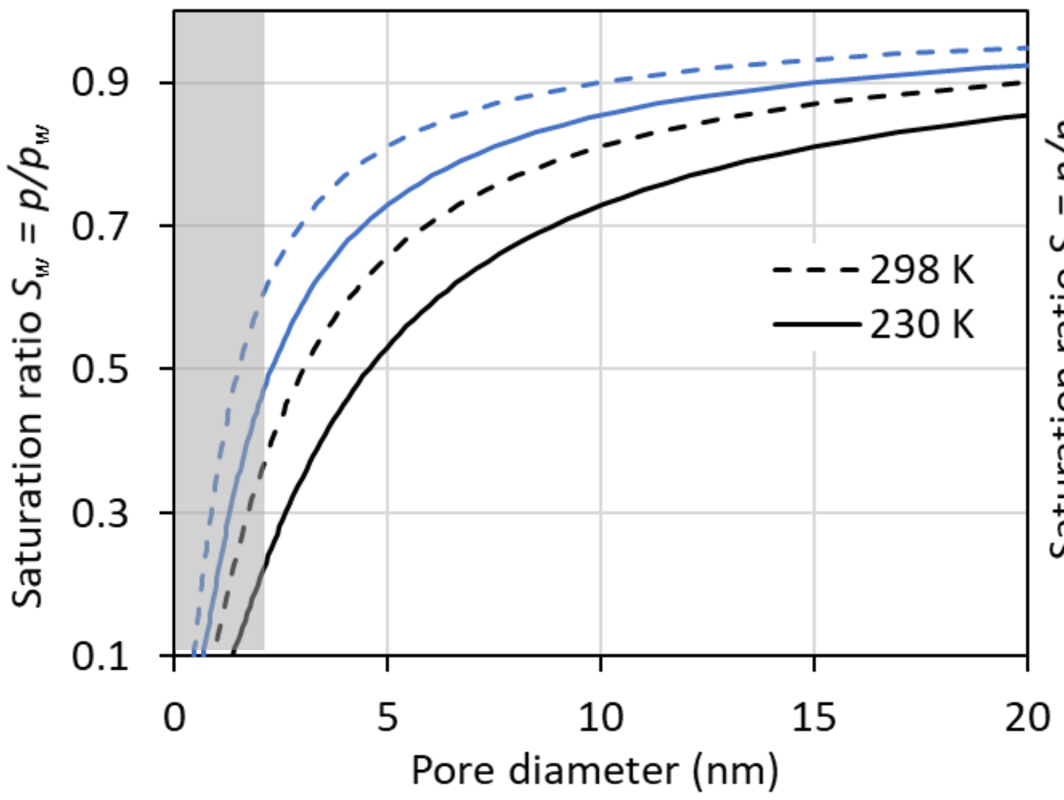


Marcolli, ACP, 2020

What is the relevant diameter range for PCF?

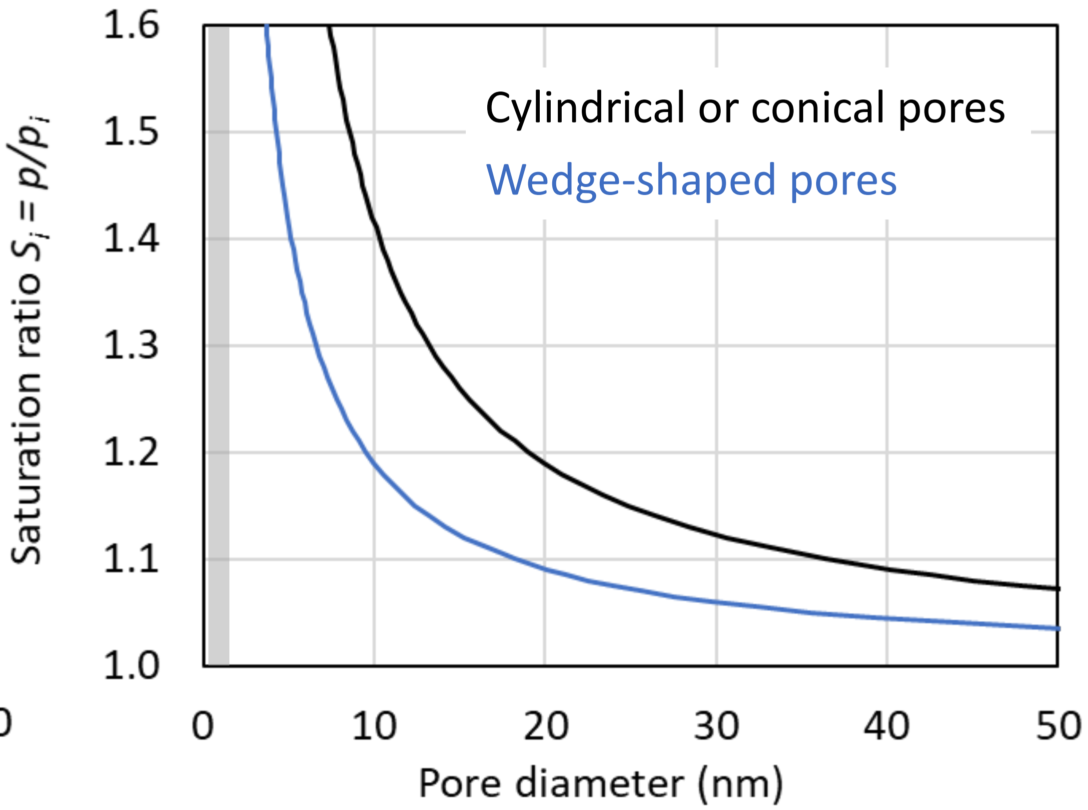
Pore filling with water

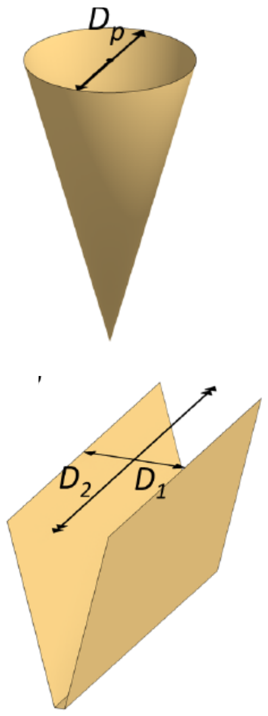
Too narrow to freeze



Ice growth out of the pores

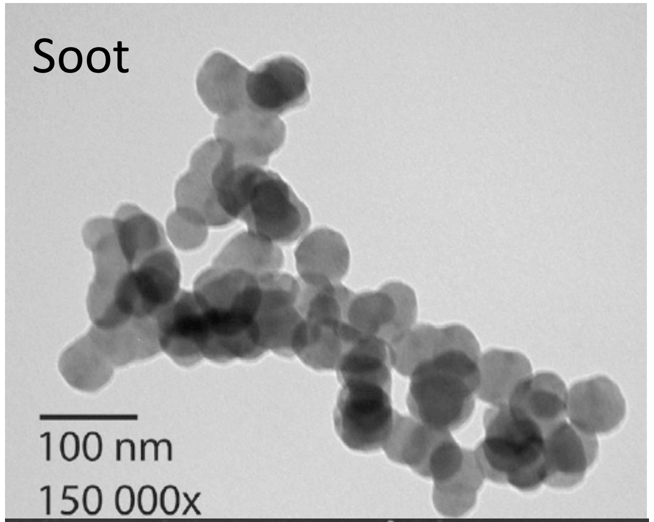
Too narrow to freeze

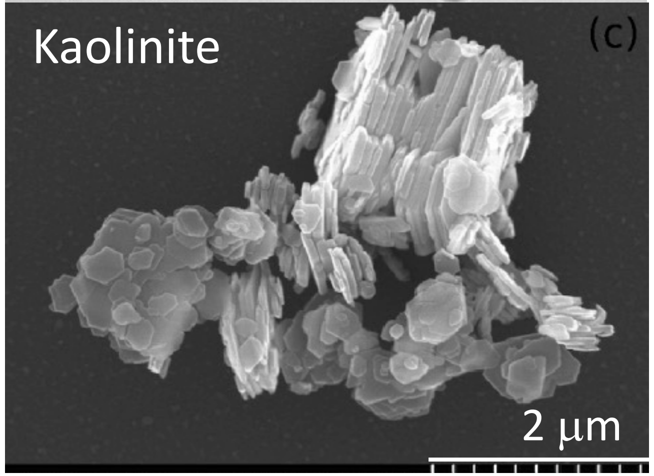




Marcolli, ACP, 2020

What is the porosity of aerosol particles?





Soot

Porosity arising between primary particles

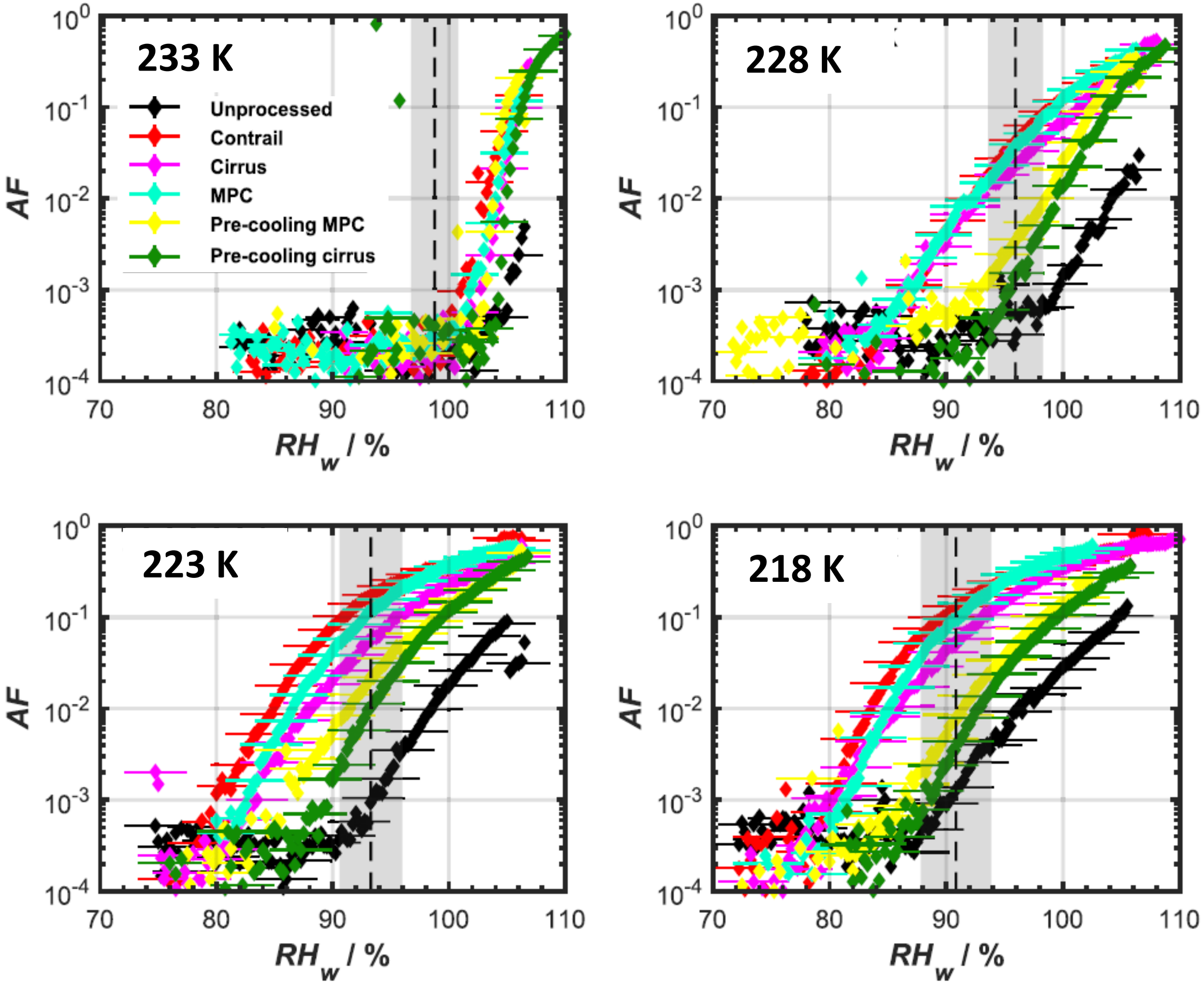
Mineral dust

Porosity arising:

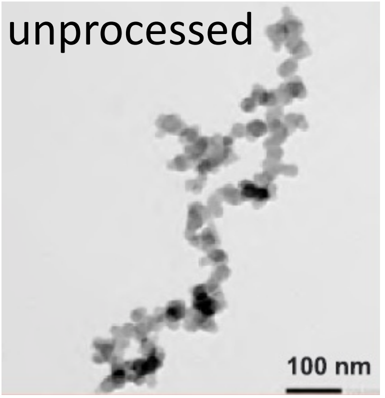
- in aggregates of crystallites
- At edges of clay minerals

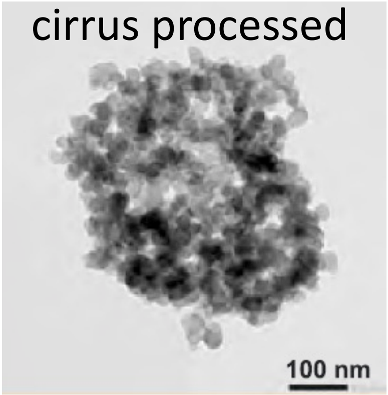
SEM images: Joo et al., Fuel, 2018; Wheeler et al., JPC A, 2015

Activated fraction of processed miniCAST black



	Preprocessing	Evaporation
Unprocessed	–	–
contrail	104 % RH_w 228 K	38 % RH_w 233 K
cirrus	96 % RH_w 228 K	38 % RH_w 233 K
MPC	108 % RH_w 243 K	30 % RH_w 253 K
Precool MPC	96 % RH_w 243 K	30 % RH_w 253 K
Precool cirrus	65 % RH_w 228 K	38 % RH_w 233 K

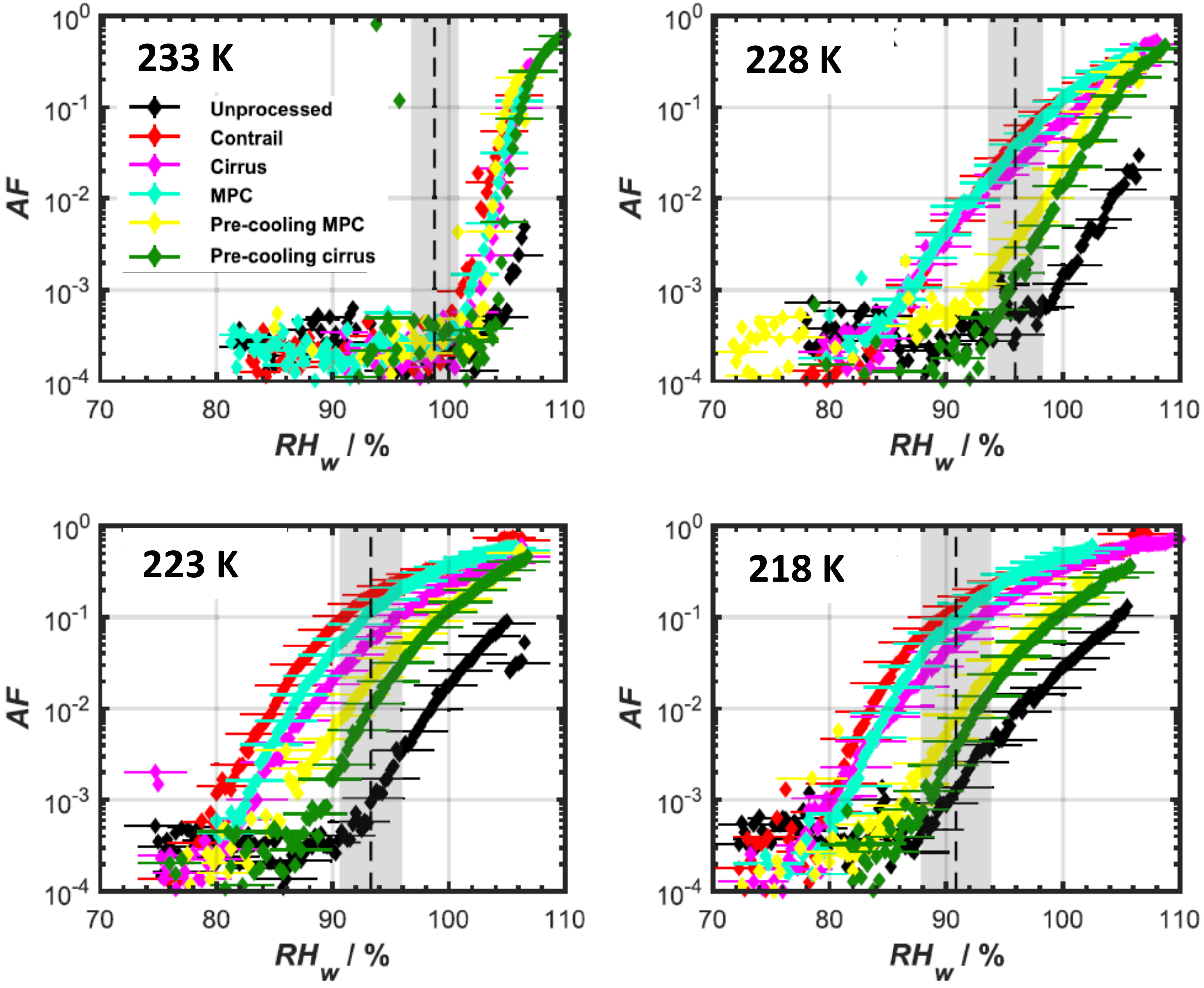




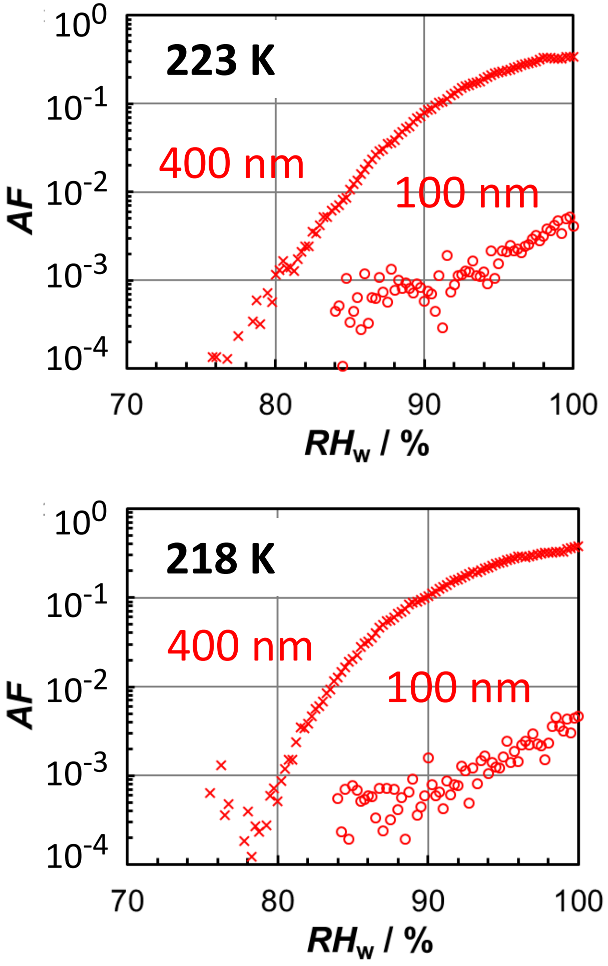
Mahrt et al., JGR, 2020

Activated fraction of processed miniCAST black

400 nm diameter



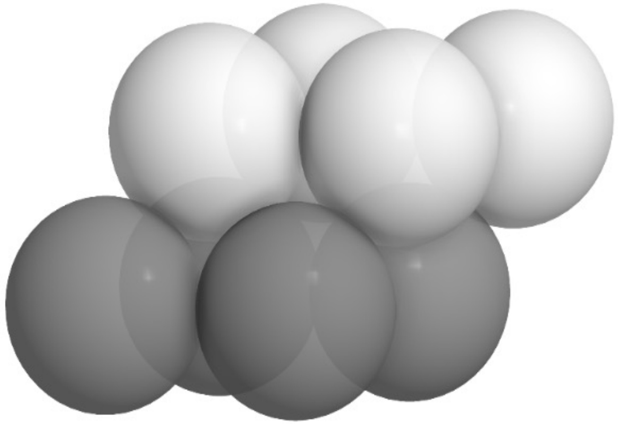
Size dependence

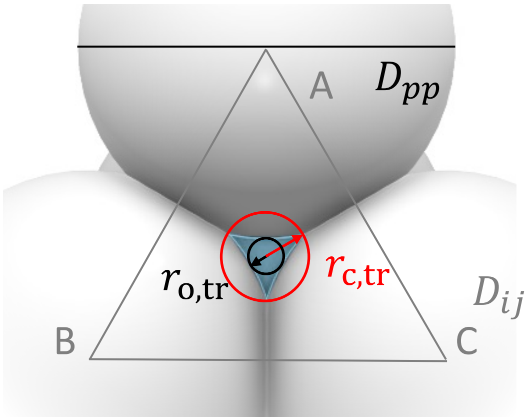


Mahrt et al., JGR, 2020

Pores within soot aggregates

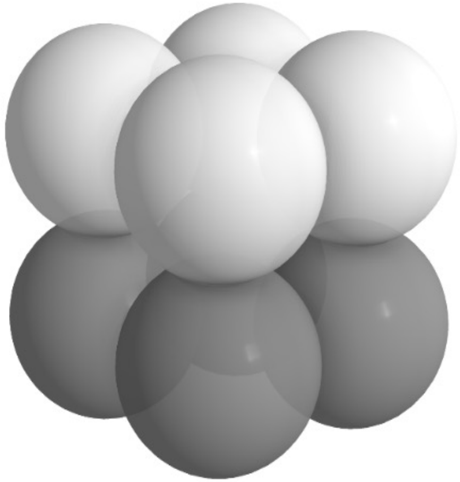
Tetrahedral packing

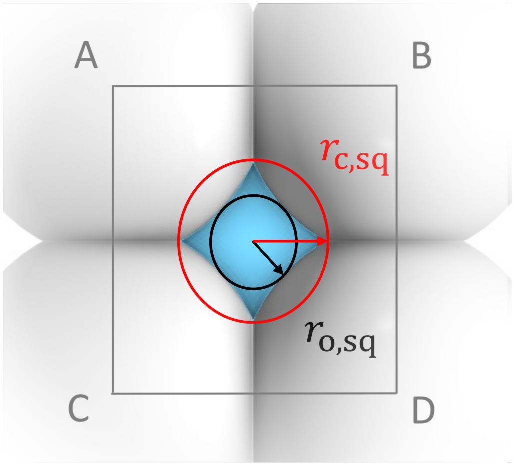




Three-membered ring pore

Cubic packing





Four-membered ring pore

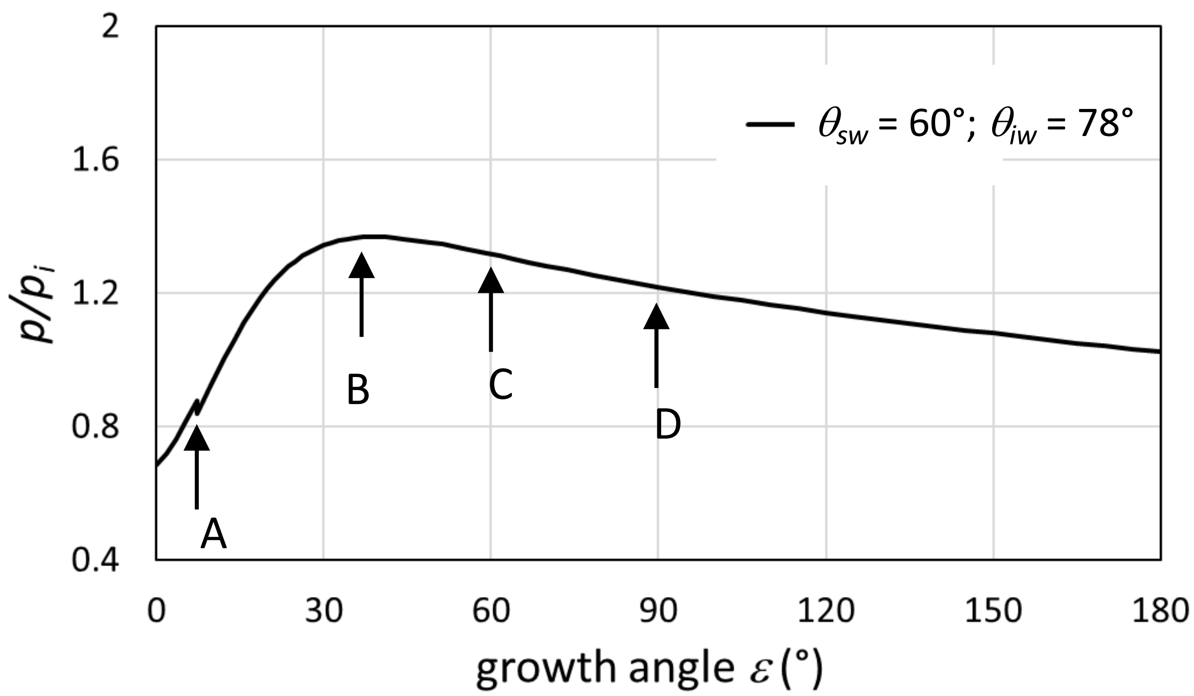
Spherical primary particles with typical diameters D_{pp} = 10–30 nm

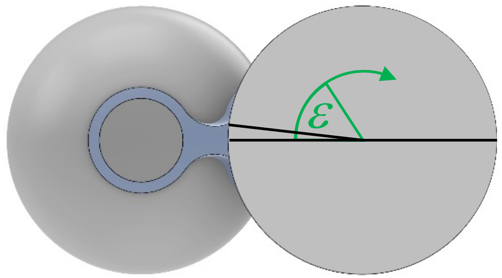
Overlap $C_{ov} = \frac{D_{pp} - D_{ij}}{D_{pp}}$ = 0.01–0.2

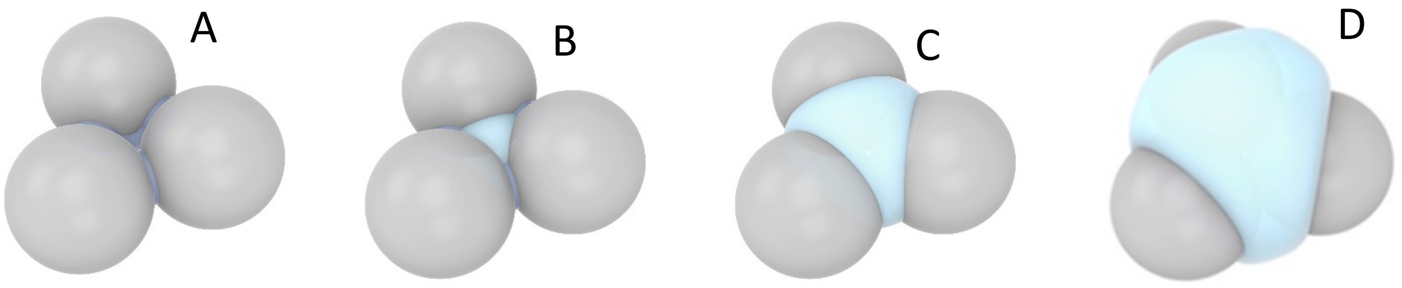
Marcolli et al., ACP, 2021

Soot PCF on three-membered ring pore

primary particle diameter: 20 nm, C_{ov} = 0.05



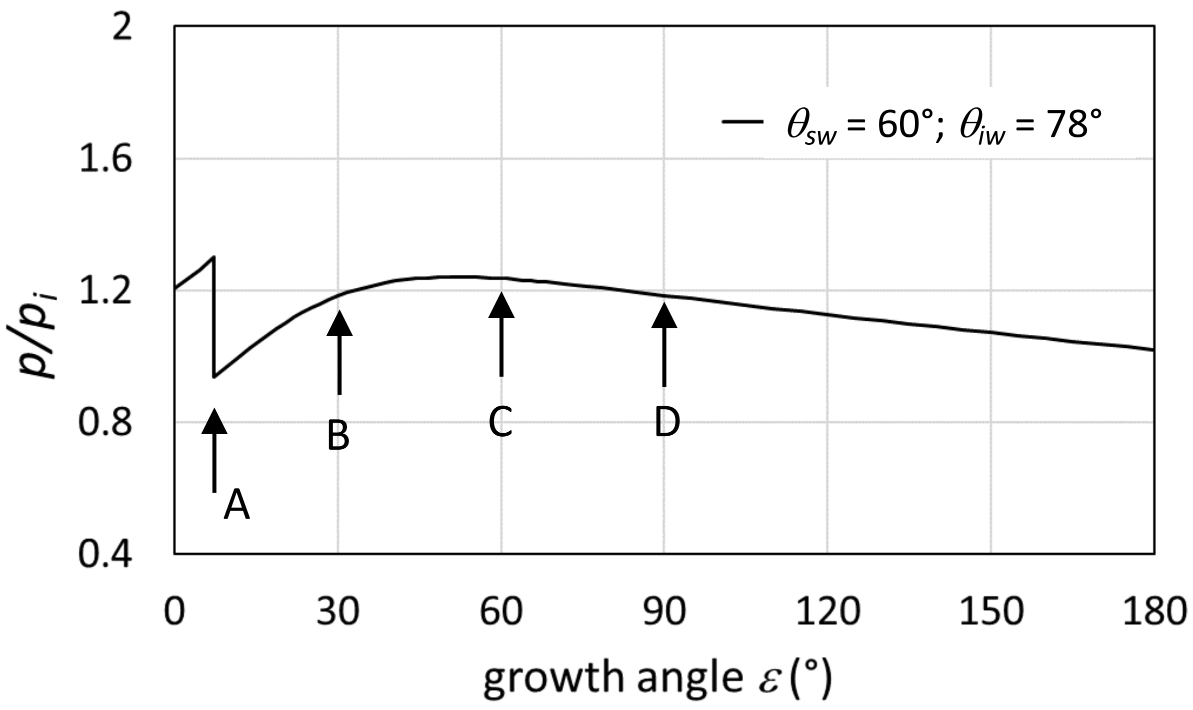


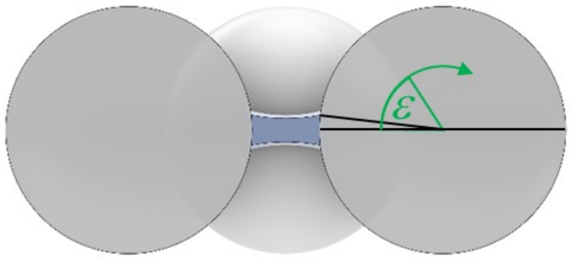


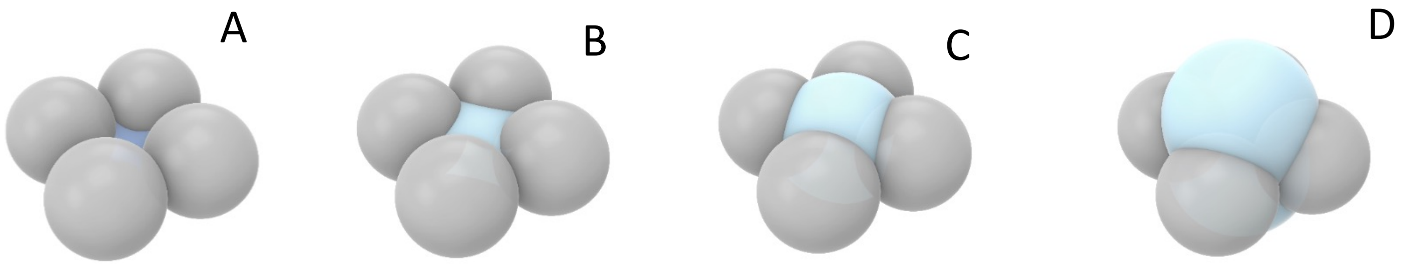
Marcolli et al., ACP, 2021

Soot PCF on four-membered ring pore

primary particle diameter: 20 nm, $C_{ov} = 0.1$

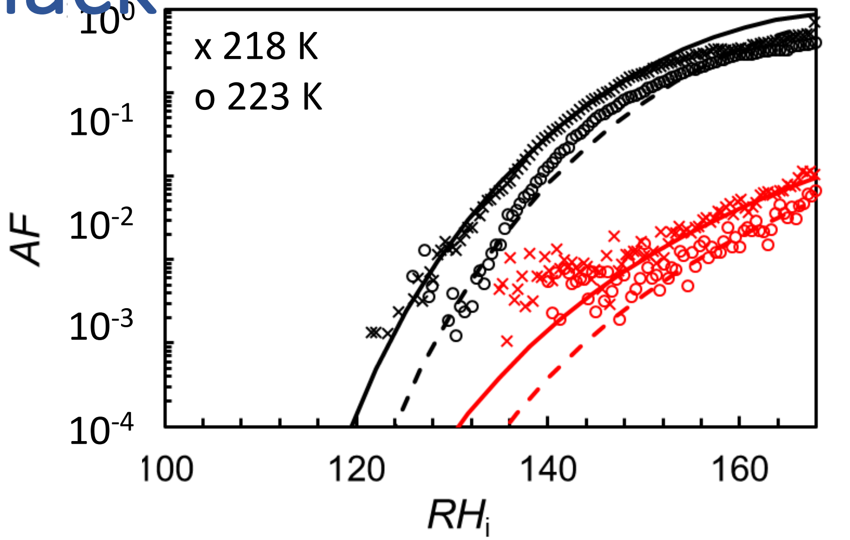


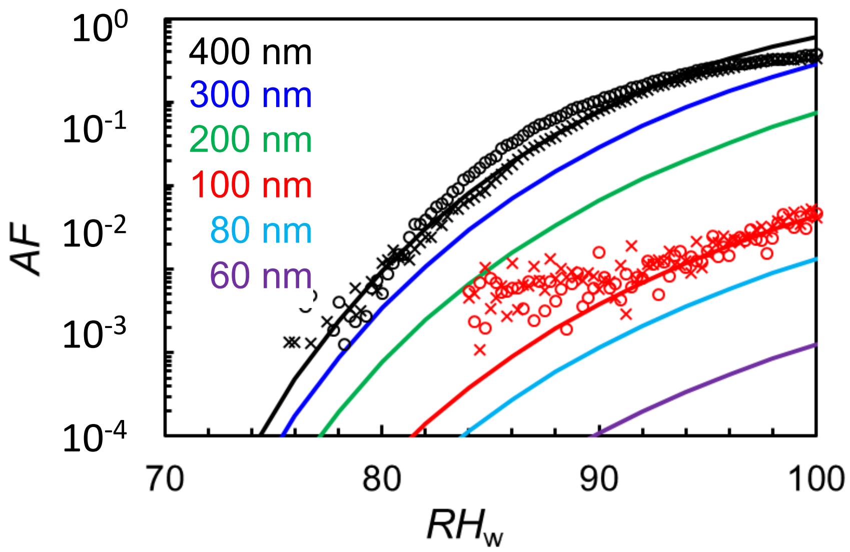




Marcolli et al., ACP, 2021

Activated fraction (AF) parameterization of miniCAST black





$$AF = 1 - \left(1 - P_N(RH)\right)^{\left((N_p - 2)^{1.86}\right)}$$

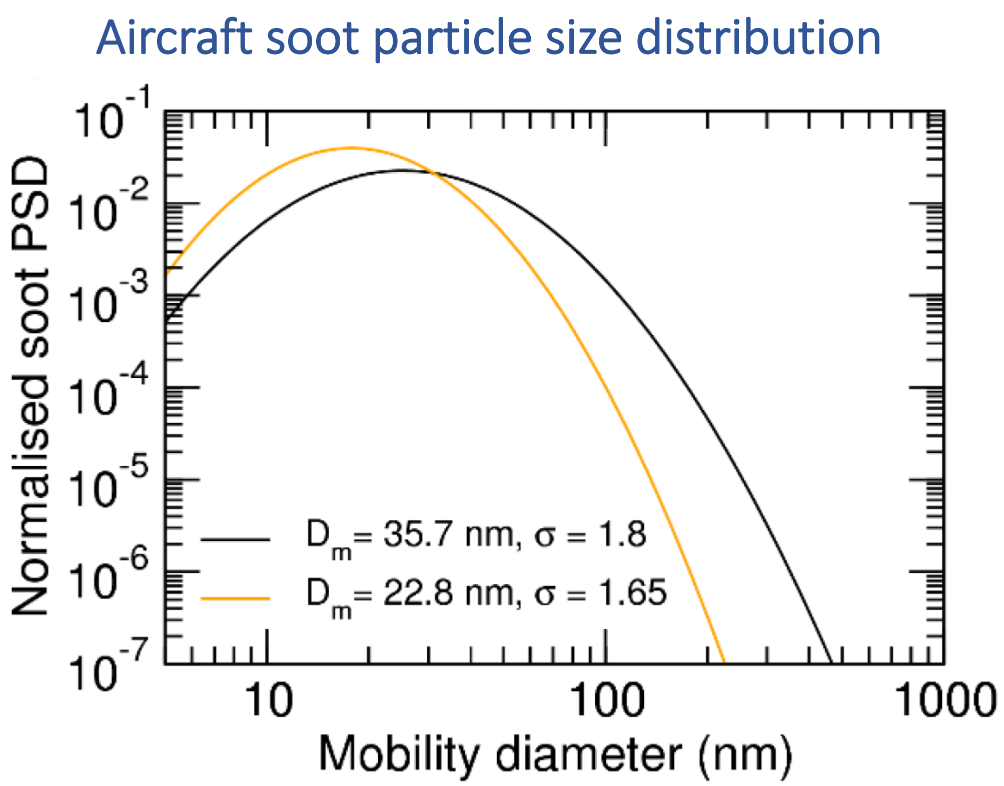
$$P_N(RH_w) = 10^{\left(\frac{1}{0.3374 - 0.006091 RH_w}\right)}$$

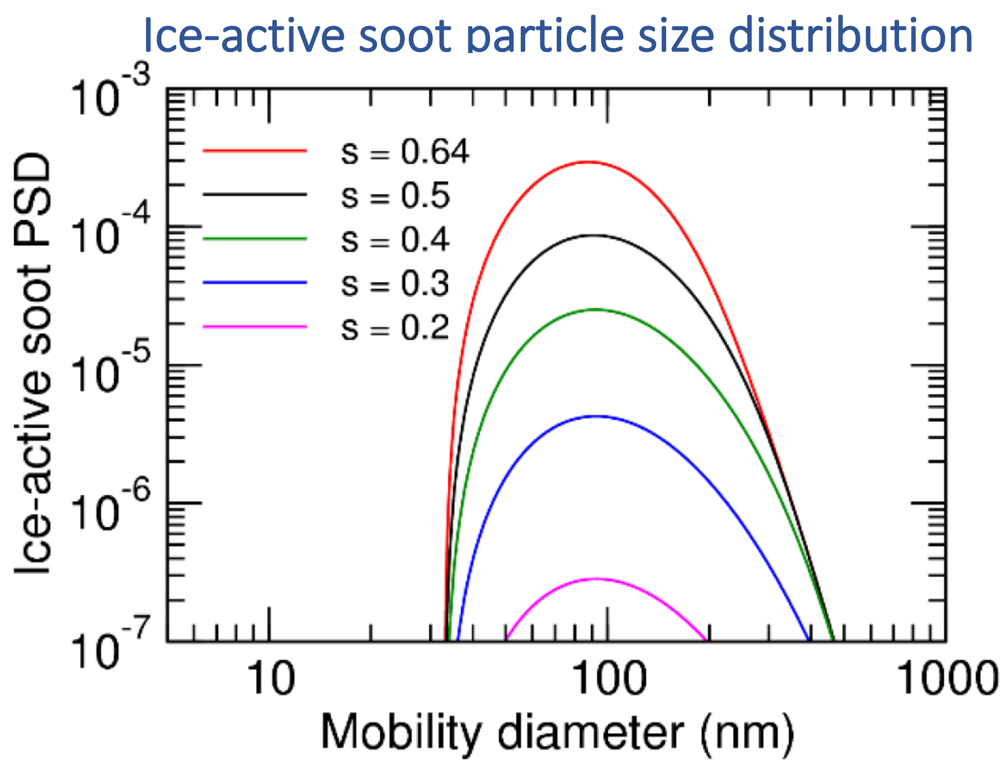
Primary particle diameter: D_{pp} = 31 nm
Fractal dimension: 1.86
→ Number of particles (N_p) in aggregate with diameter D_m

D_m	N_p
400 nm	94
300 nm	55
200 nm	26
100 nm	7
80 nm	5
60 nm	3

Marcolli et al., ACP, 2021

PCF parameterization for aircraft soot



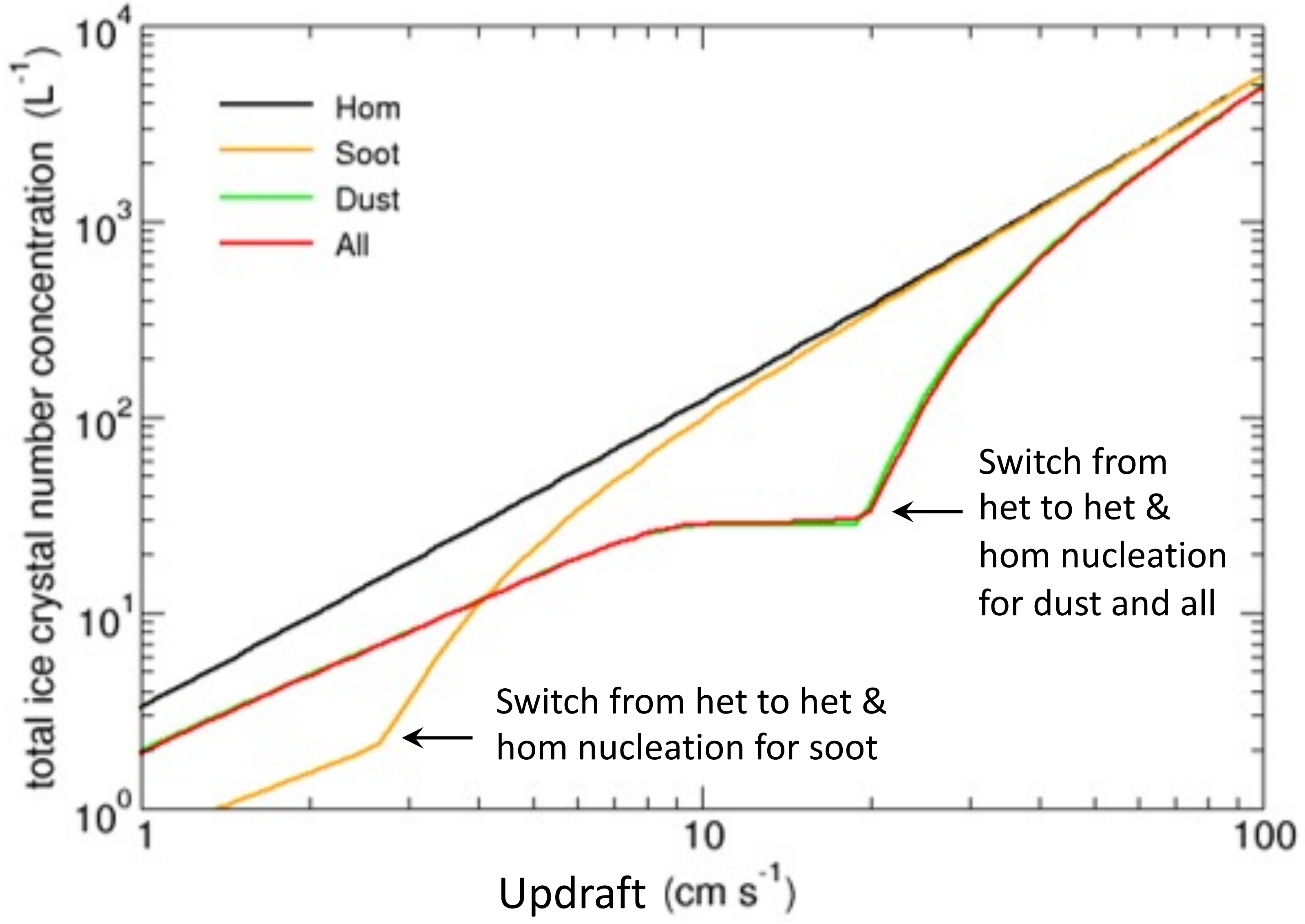


Ice nucleation activity of soot at cirrus conditions assuming:

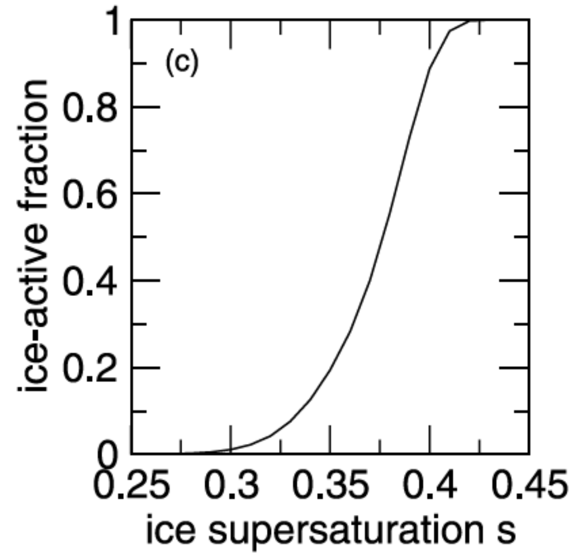
- bare soot aggregates (no caoting)
- a distribution of primary particle sizes from 5–40 nm with mean D_{pp} = 20 nm
- Primary soot particle overlap from 0.01–0.2
- soot-water contact angle of 60°

Kärcher et al., Nature Comm., 2021

Ice crystal formation at constant updraft



- 220 K, 250 hPa
- Liquid **background** aerosol particles: 500 000 L^{-1}
- **Soot**: 500 L^{-1} but only about 1 % are able to activate
- **Background dust**: 28 L^{-1}, all activate at about s = 0.4



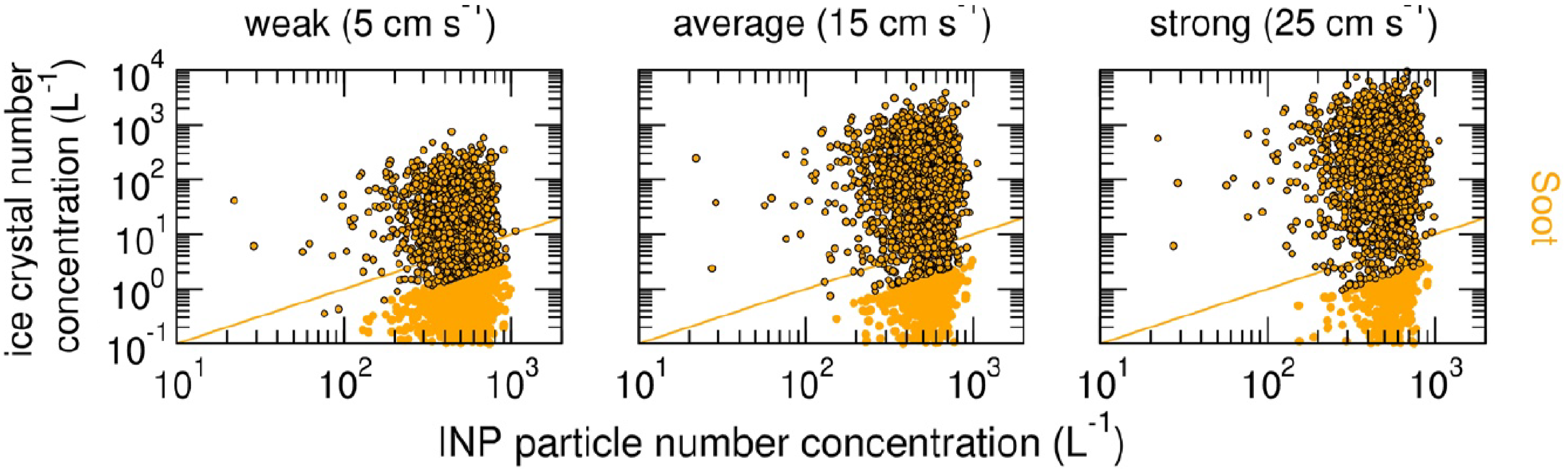
Kärcher et al., JGR., 2023

Ensemble simulations with high-resolution cirrus column model

- Typical upper tropospheric temperature (**220 K**) and pressure (**250 hPa**).
- Variable updraft speeds by random sampling from exponential distributions with standard deviations of **5 (weak), 15 (average), and 25 (strong) cm/s**.
- **Ice nucleation:**
  - **Homogeneously** on **constant** background aerosol: **500 000 L^{-1}** liquid 500 nm-particles (wet diameter)
  - On **variable** soot particles sampled from normal distributions in concentration (with n_s = **500 L^{-1}** and σ = 150 L^{-1}) and size (with D_m = **29.3 nm** and σ = 1.72 L^{-1})
  - On a **variable** background mineral dust particle concentration sampled from a normal distribution in concentration (with n_s = **28 L^{-1}** and σ = 12 L^{-1}) and constant size distribution.
- **Ice growth:** constant deposition coefficients of α = 0.3 (dust) and 0.7 (soot).

Kärcher et al., JGR., 2023

Competition between homogeneous ice nucleation and ice nucleation on soot



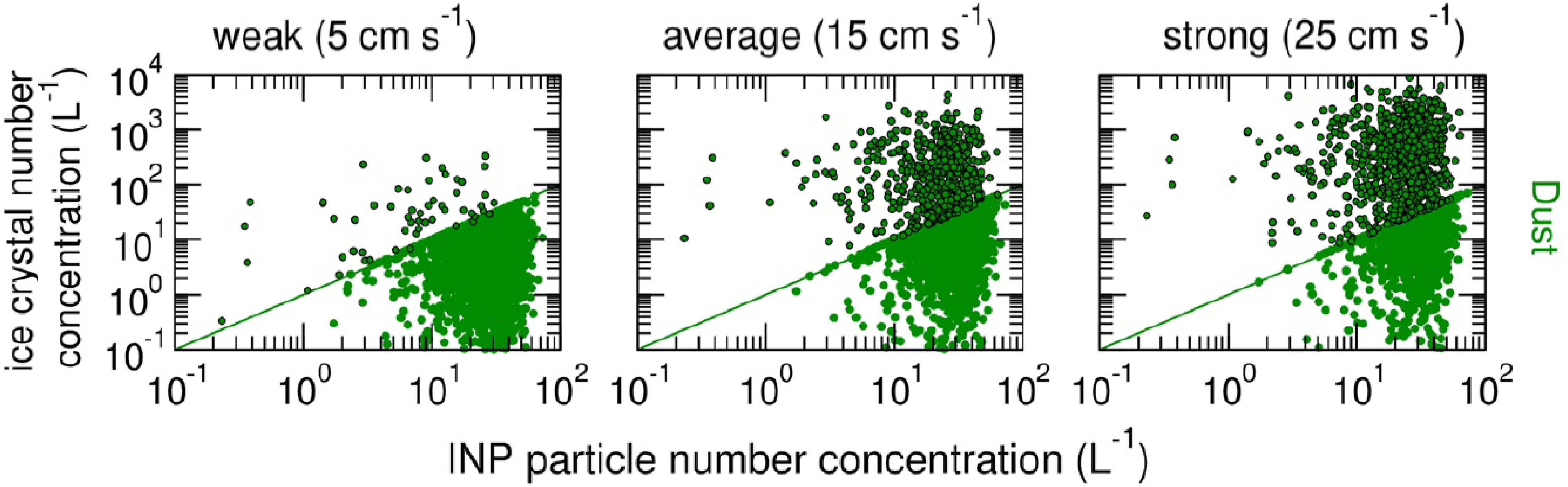
Filled yellow circles: ice formed only on soot particles (no homogeneous nucleation)

Yellow circles with black outlines: ice formed also homogeneously

Yellow line: ice crystal number concentration if all soot particles had activated to ice

Kärcher et al., JGR., 2023

Competition between homogeneous ice nucleation and ice nucleation on mineral dust



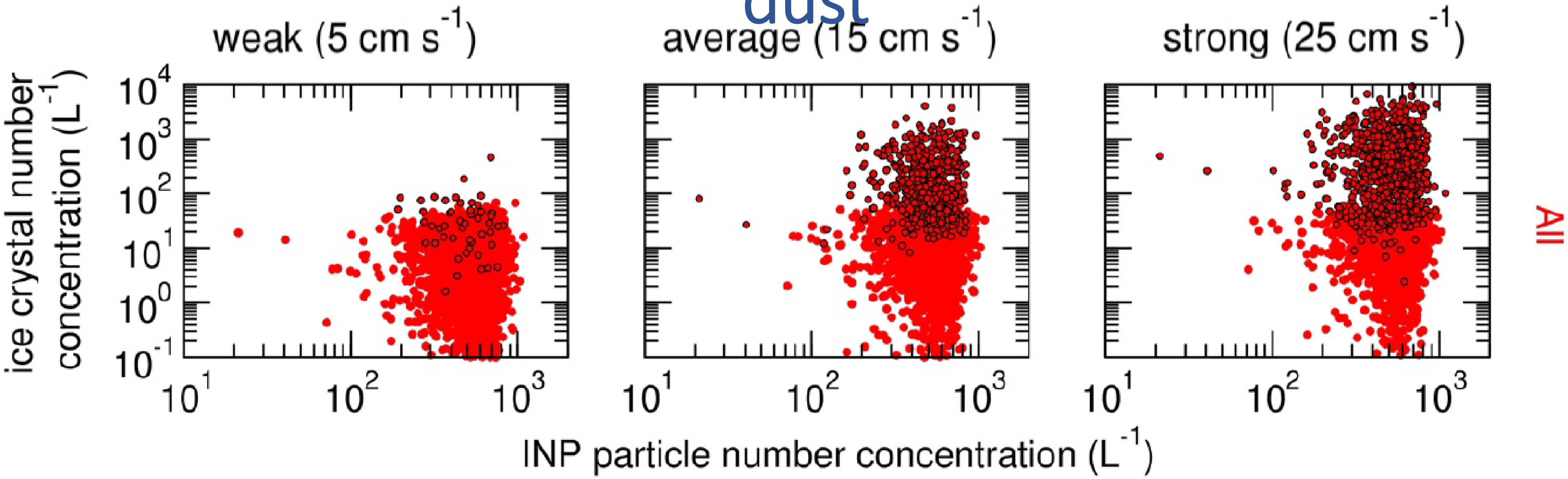
Filled green circles: ice formed only on background mineral dust (no homogeneous nucleation)

Green circles with black outlines: ice formed also homogeneously

Green line: ice crystal number concentration (ICNC) if all dust particles had activated to ice

Kärcher et al., JGR., 2023

Competition between homogeneous ice nucleation and ice nucleation on soot and mineral dust



Filled red circles: ice formed only on soot or dust particles (no homogeneous nucleation)

Red circles with black outlines: ice formed also homogeneously

Kärcher et al., JGR., 2023

Summary of all ensemble simulations

Case	Category	Updraft: 5 cm/s		Updraft: 15 cm/s		Updraft: 25 cm/s	
		Frequency	Median ICNC	Frequency	Median ICNC	Frequency	Median ICNC
Hom		100 %	14 L^{-1}	100 %	74 L^{-1}	100 %	164 L^{-1}
Soot	only het	49 %	0.73 L^{-1}	22 %	0.81 L^{-1}	14 %	0.9 L^{-1}
	Hom & het	51 %	22 L^{-1}	78 %	92 L^{-1}	86 %	215 L^{-1}
Dust	only het	97 %	6 L^{-1}	79 %	15 L^{-1}	62 %	18 L^{-1}
	Hom & het	3 %	21 L^{-1}	21 %	151 L^{-1}	38 %	272 L^{-1}
All	only het	98 %	6 L^{-1}	81 %	15 L^{-1}	63 %	19 L^{-1}
	Hom & het	2 %	22 L^{-1}	19 %	164 L^{-1}	37 %	275 L^{-1}

→ soot does hardly influence ice crystal number concentration (ICNC) considering the omnipresence of a background dust concentration

Kärcher et al., JGR., 2023

Conclusions

- Soot particles nucleate ice through a pore condensation and freezing process (PCF)
- Because of their tiny size, aircraft soot particles are poor INPs
- Upper tropospheric background concentrations of dust particles outcompete soot in cirrus cloud formation
- Aircraft soot does not seem to be relevant in cirrus cloud formation