EPFL

Thermodynamics of Earth systems

Lecture 11:
CCN and INP activity

Material covered in Lecture

Part 2: Framework

Phase Equilibria

- Gibbs phase rule: thermodynamic degrees of freedom, phases and components
- Energy in phase changes and chemical reactions

Part 3: Applications

Physical chemistry of water solutions – solution thermodynamics

- Colligative properties (freezing point depression, boiling point elevation)
- Phase diagram (for single and multiple component system); Clausius-Clapeyron equation;

Nucleation and Diffusional Growth

- Surface energy, surface tension - Kelvin effect
- Nucleation of the liquid and ice phase
- Adsorption effects of water

Thermodynamics of droplets: Köhler equation

Apply Kelvin equation to a pure water droplet (i.e., σ_w and $v_l = \frac{M_w}{\rho_w}$)

$$P = P^* \exp\left(\frac{4M_w\sigma}{RT\rho_w D_p} \right)$$

Dissolved substances in the drop depress water vapor pressure.
Assume $\sigma_w, v_l \sim$ **const.** then only P^* changes (given by Raoult's law)

$$\frac{P}{P^{sat}} = x_w \gamma_w \exp\left(\frac{4M_w\sigma}{RT\rho_w D_p} \right)$$

Köhler Equation

The above is the full form of the equation, without simplifications

Thermodynamics of droplets: Köhler equation

One can invoke simplifying assumptions:

$$x_w = \frac{n_w}{n_w + i n_s} = 1 - \frac{i n_s}{n_w + i n_s} \approx 1 - \frac{i n_s}{n_w} = 1 - \frac{i n_s}{\frac{\pi}{6} D_p^3 \frac{\rho_w}{M_w}} = 1 - \frac{\frac{6}{\pi}\frac{M_w}{\rho_w} i n_s}{D_p^3}$$

$$= 1 - \frac{B}{D_p^3} \quad \text{where} \quad B = \frac{6}{\pi}\frac{M_w}{\rho_w} i n_s$$

n_s: Moles of solute in droplet

i: van't Hoff factor of solute in droplet

$$\gamma_w \approx 1 \quad \text{and} \quad \exp\left(\frac{4 M_w \sigma}{R T \rho_w D_p}\right) \approx 1 + \frac{A}{D_p} \quad \text{where} \quad A = \frac{4 M_w \sigma}{R T \rho_w}$$

Substitution into full Köhler equation, and considering leading terms:

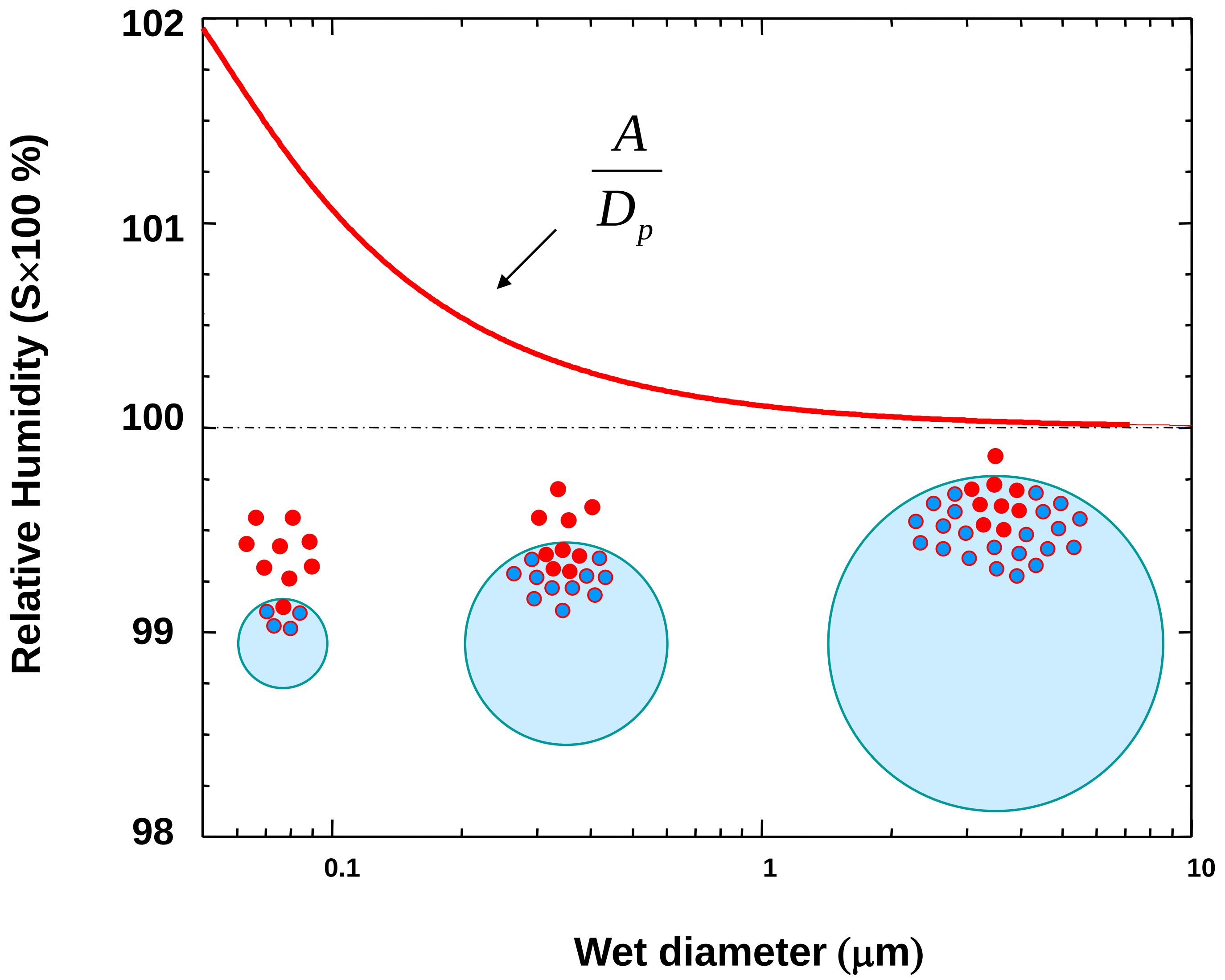
$$S = \frac{P}{P^{sat}} = 1 + \frac{A}{D_p} - \frac{B}{D_p^3}$$

Simplified Köhler equation

- $S = \frac{P}{P^{sat}}$: Saturation ratio
- $\frac{A}{D_p}$: "Kelvin" term
- $\frac{B}{D_p^3}$: "Raoult" term

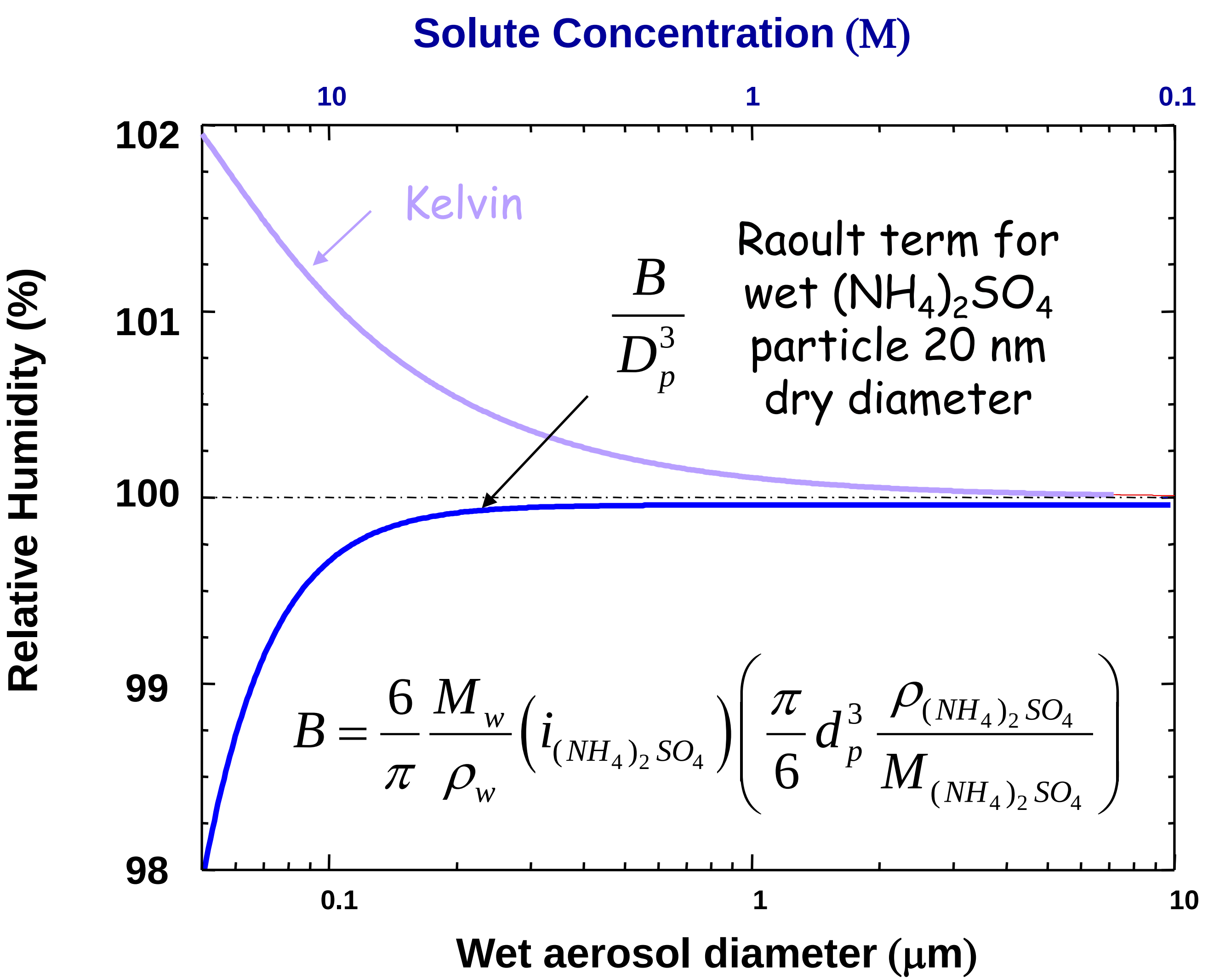
Thermodynamics of droplets: Köhler equation

First plot the Kelvin term



Thermodynamics of droplets: Köhler equation

Take same drop and add some solute



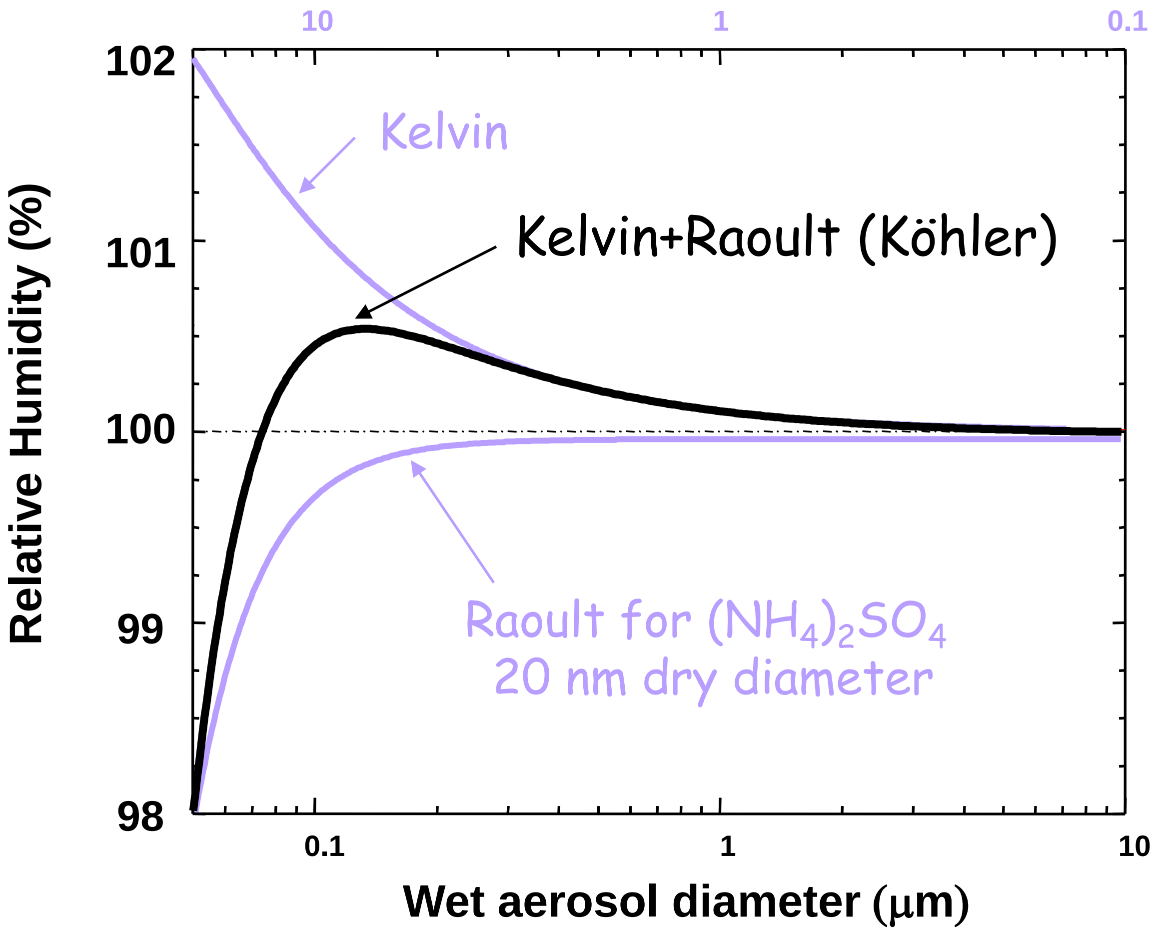
$$\frac{B}{D_p^3}$$

$$B = \frac{6}{\pi}\frac{M_w}{\rho_w}\left(i_{(NH_4)_2SO_4}\right)\left(\frac{\pi}{6}d_p^3\frac{\rho_{(NH_4)_2SO_4}}{M_{(NH_4)_2SO_4}}\right)$$

Thermodynamics of droplets: Köhler equation

Both effects together: equilibrium vapor pressure of a wet aerosol.

$$S = \frac{P}{P^{sat}} = 1 + \frac{A}{D_p} - \frac{B}{D_p^3}$$

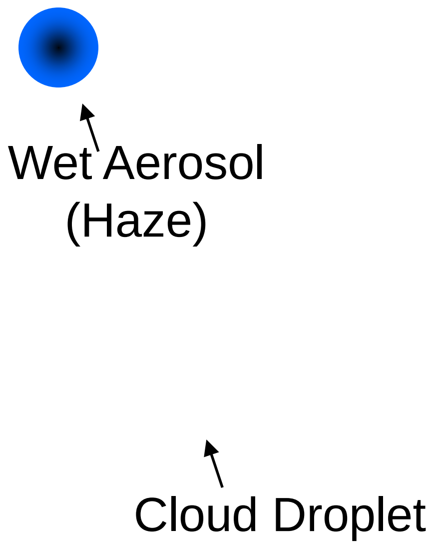


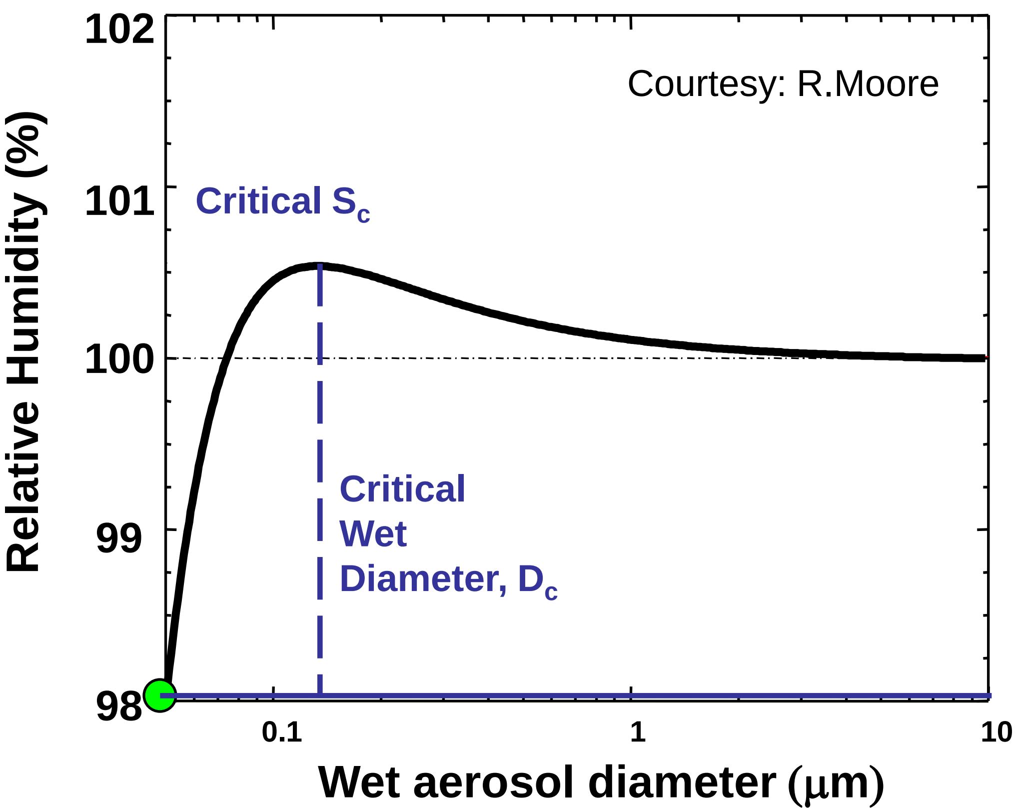
The combined Kelvin and Raoult effects is the simplified **Köhler equation**.

You can be in equilibrium **even if you are above saturation**.

Regions of stability/instability of ambient droplets

Dynamical behavior of an aerosol particle in a variable RH environment.



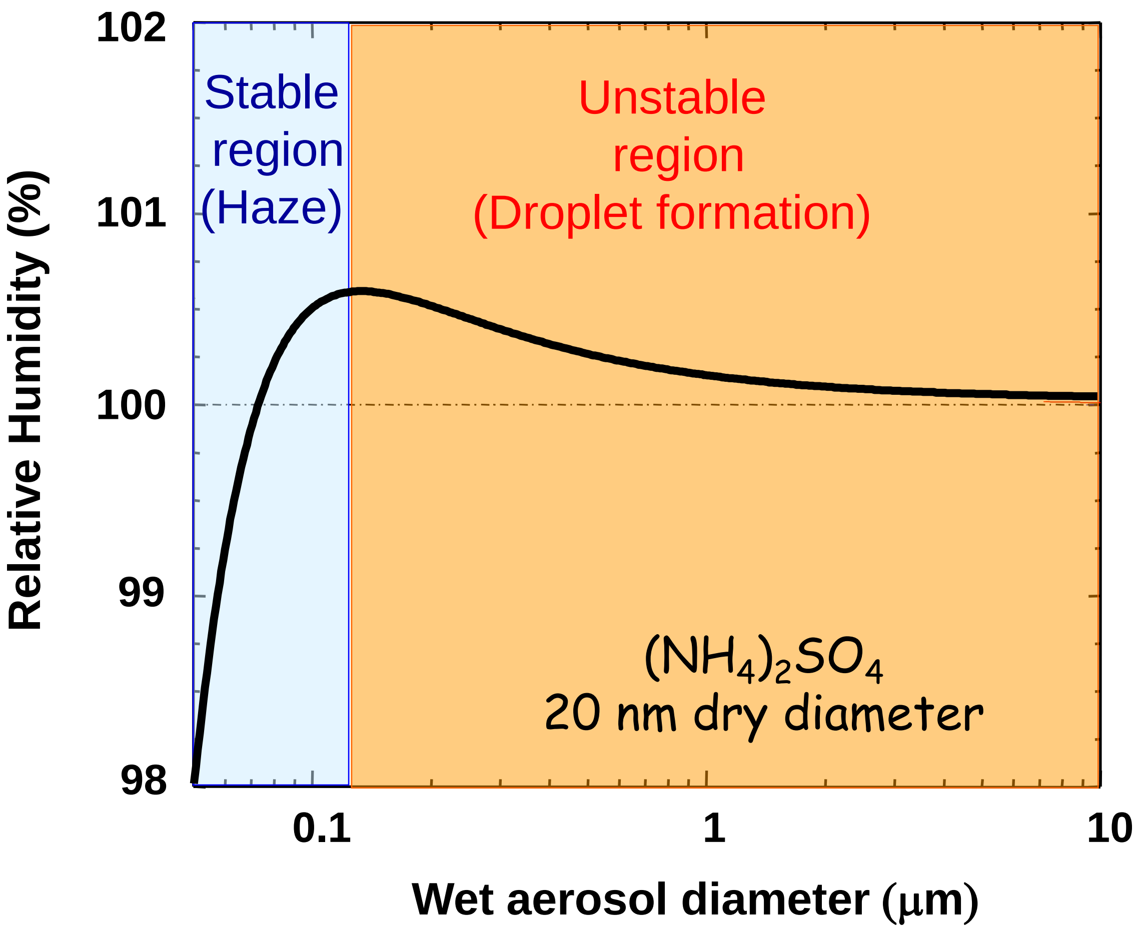


If ambient S exceeds the maximum, particles grow uncontrollably. They are said to act as Cloud Condensation Nuclei (CCN)

Thermodynamics of droplets: Köhler equation

When the ambient saturation ratio $S > S_c$ AND the wet size is larger than D_c, it acts as a CCN. ($S > S_c$ sufficient).

This is the direct microphysical link between aerosols and clouds



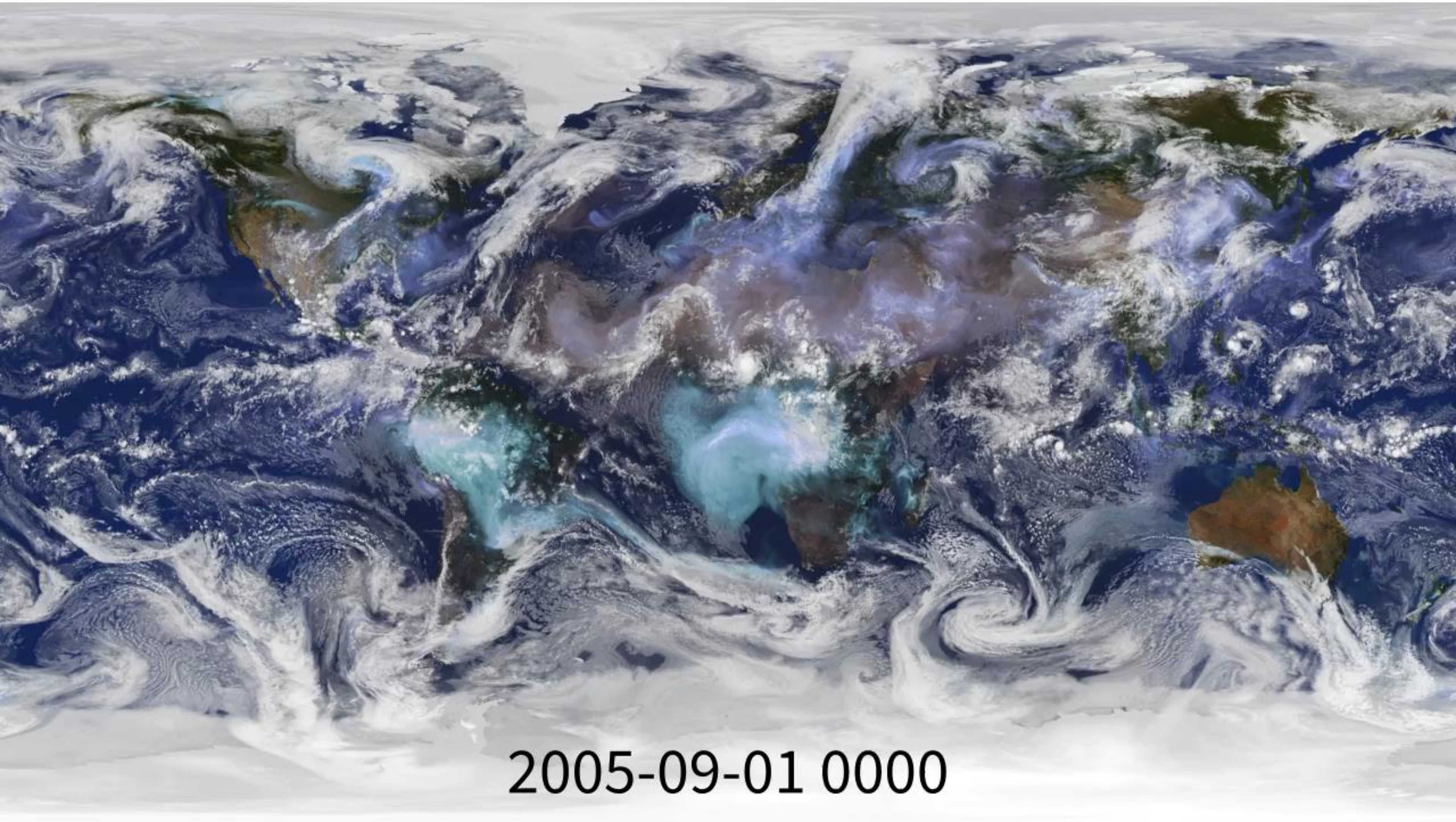
Köhler theory:

$$s_c = \left(\frac{4A^3}{27B} \right)^{1/2}$$

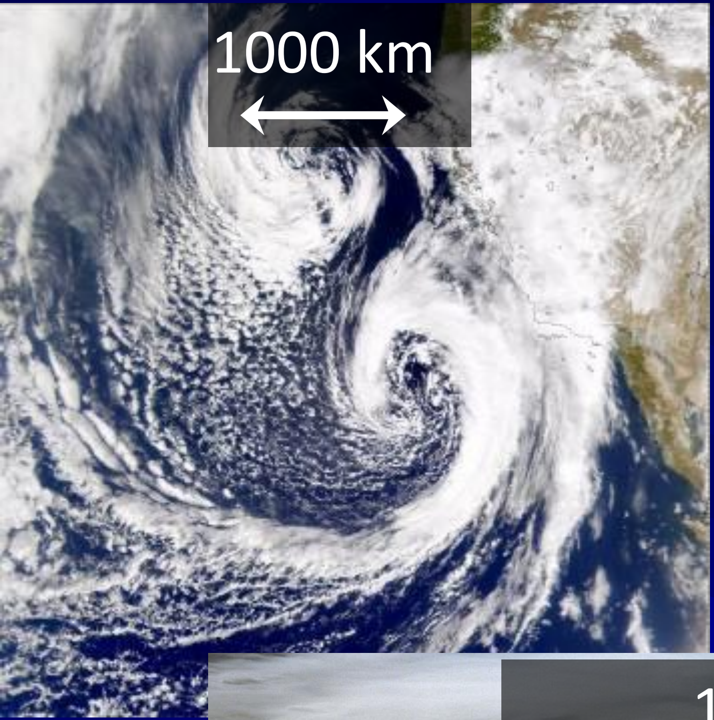
$$s_c \sim d_{dry}^{-3/2}, \varepsilon_{\mathbf{soluble}}^{-1/2}$$

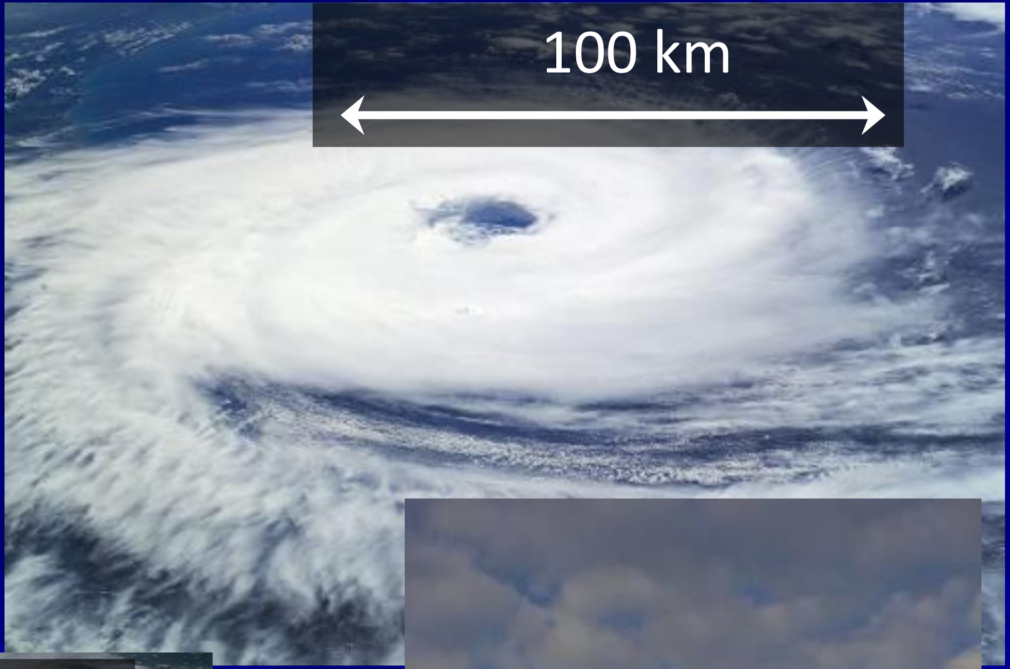
Size is more important than composition

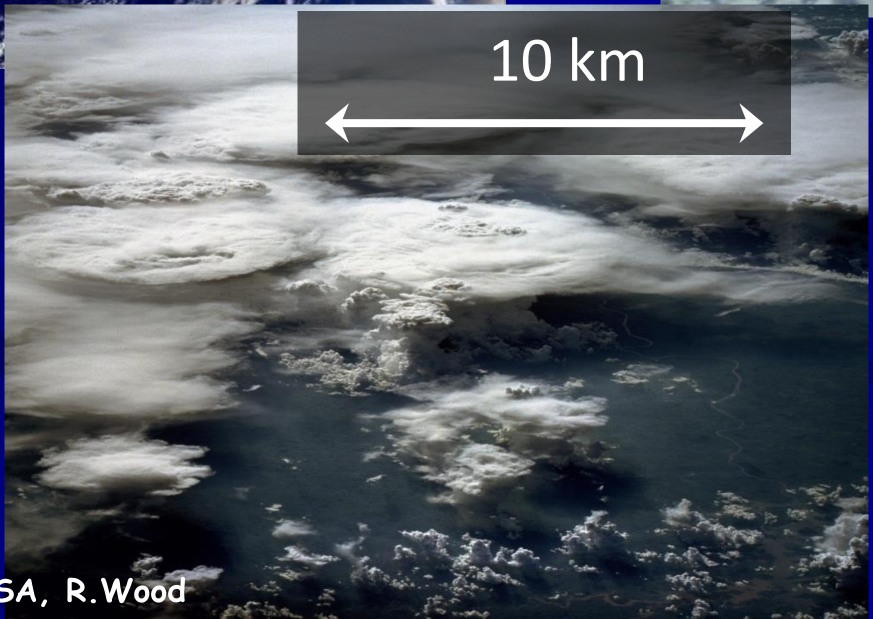
Clouds are everywhere and at all scales…



Clouds are everywhere and at all scales…







Photos: NASA, R.Wood

Clouds have an important radiative impact.

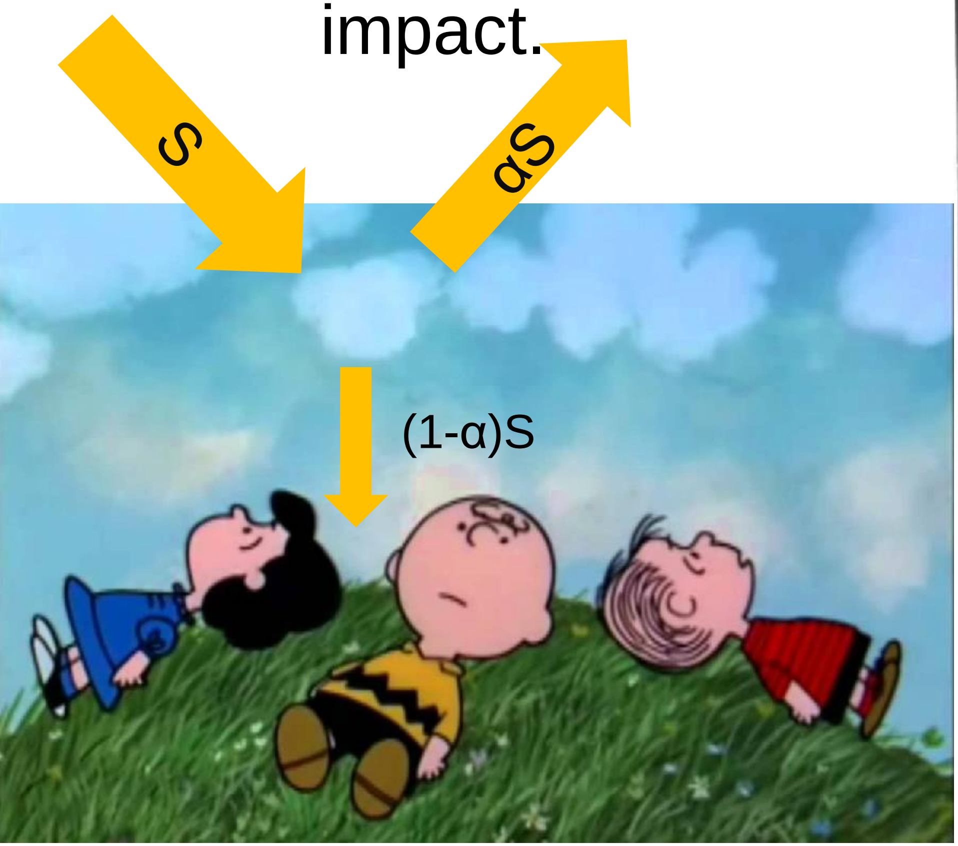


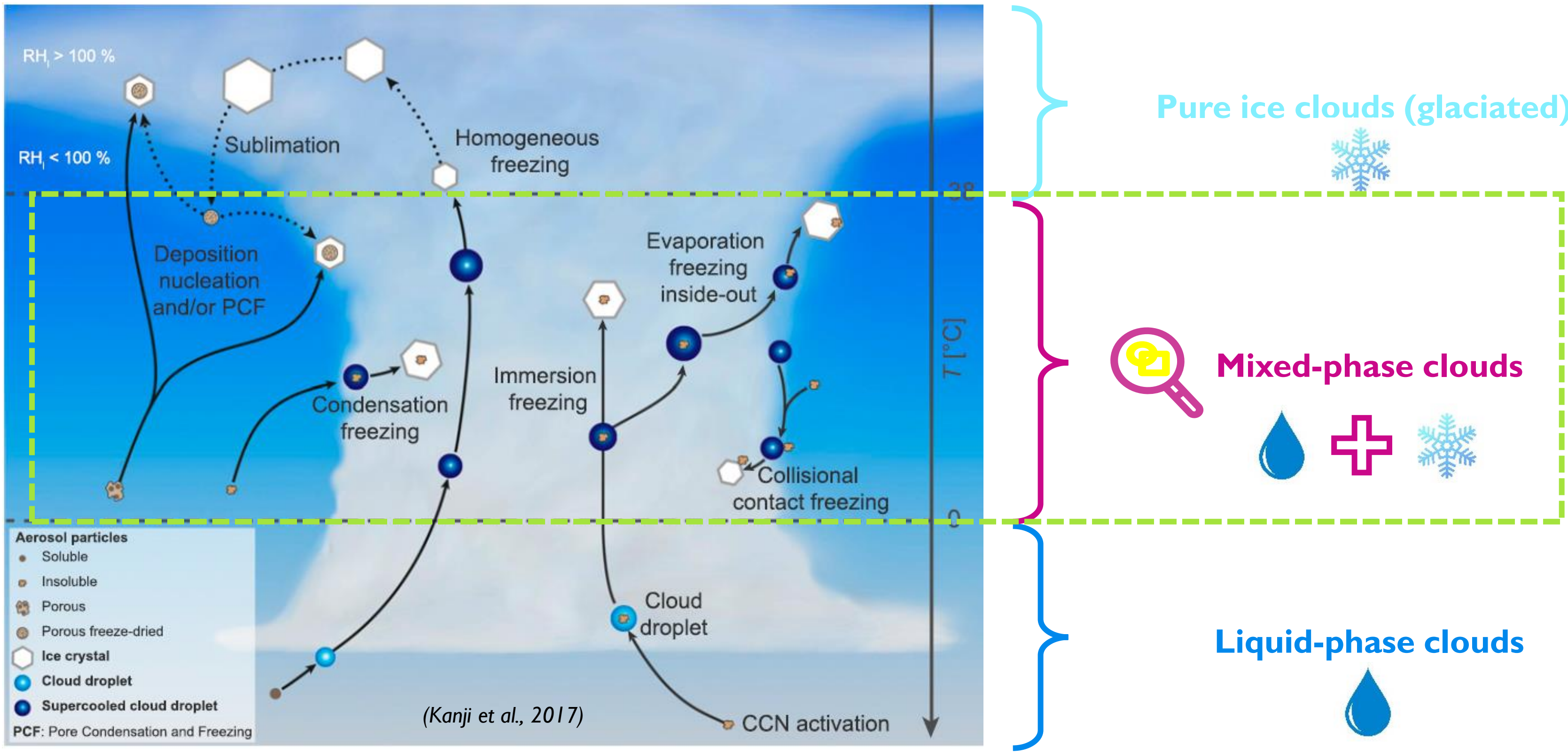
Photo from Wynn Bullock

Clouds also have an important hydrological impact.

Both critically important for regional and global climate

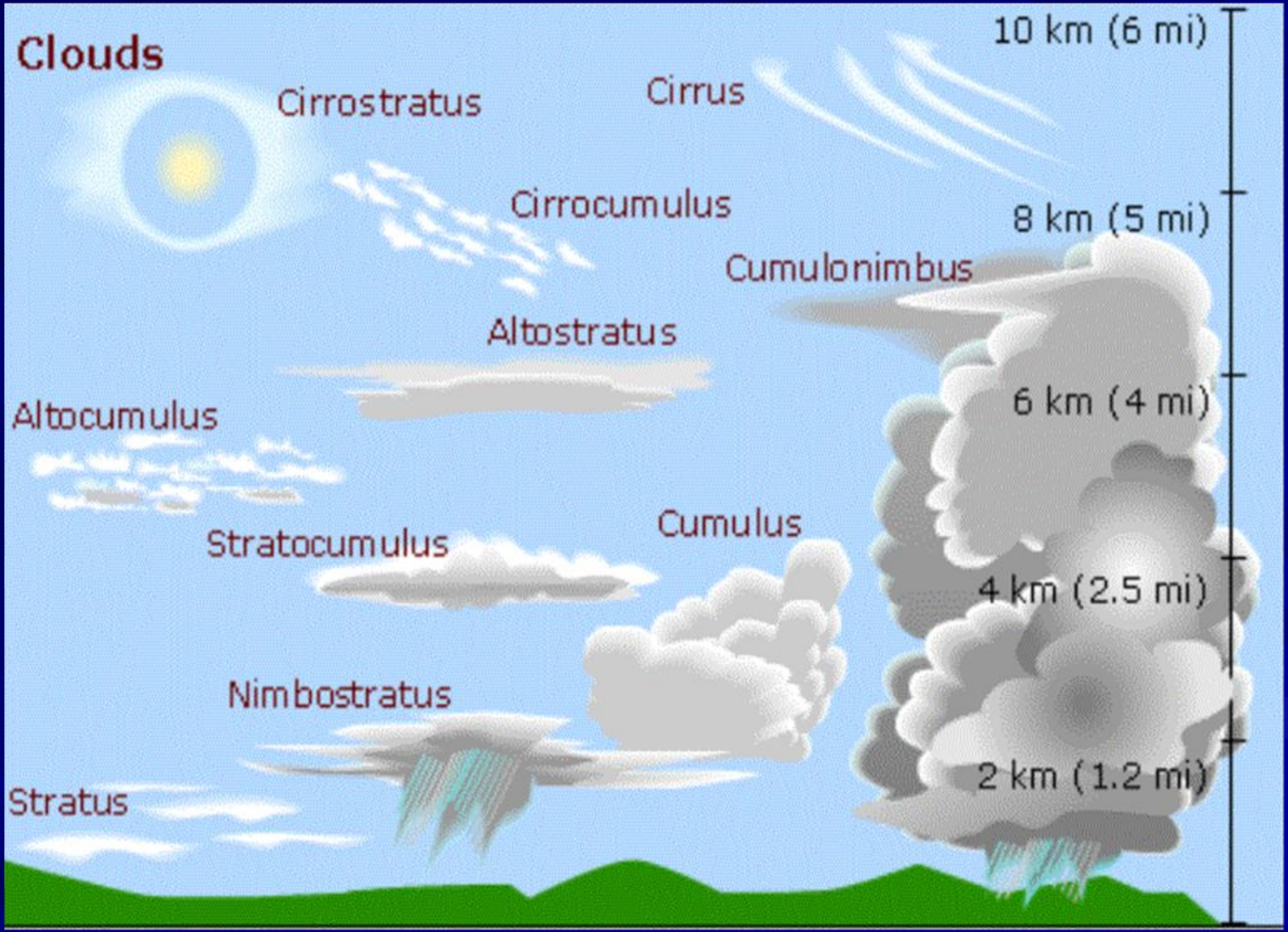
Courtesy: S.Sullivan

Clouds types in the atmosphere



Atmospheric Particles ("aerosol") are the seeds for cloud formation
Aerosol/Cloud/Climate interactions are a major source of uncertainty in climate projections

Cloud impacts vary alot



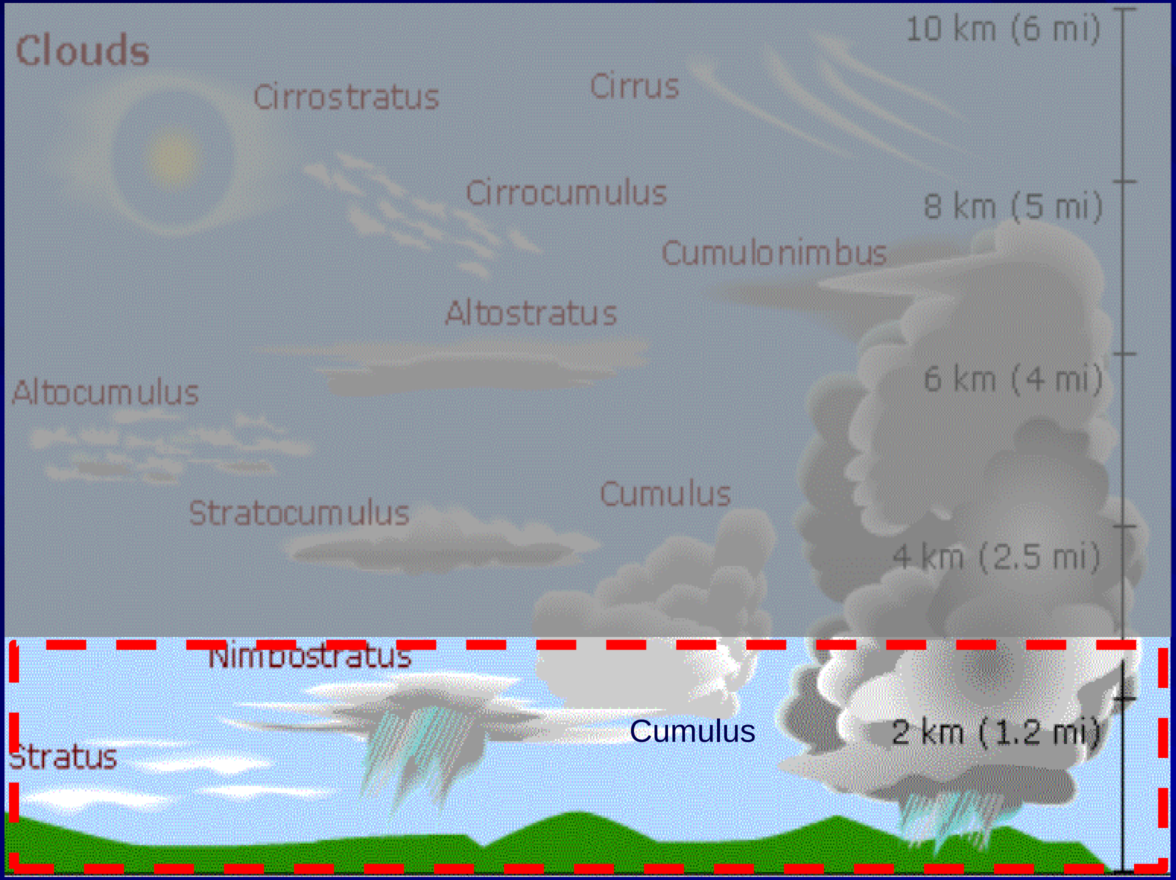
High clouds (ice crystals): *warm* climate

Mid-level: Warm/cool

Low clouds (liquid drops): *cool* climate

http://www.ucar.edu/news

Let's focus on LIQUID clouds first



- **Ice (cold) clouds**: Ice crystals, T<235 K. Warm climate
- **Mixed Phase clouds**: Liquid droplets & ice, 235K < T < 273K Warm/cool climate
- **Liquid (warm) clouds**: Liquid droplets T >273 K Cool climate

Cloud particles are formed on **aerosol particles.**
These aerosol-cloud interactions affect climate

http://www.ucar.edu/news

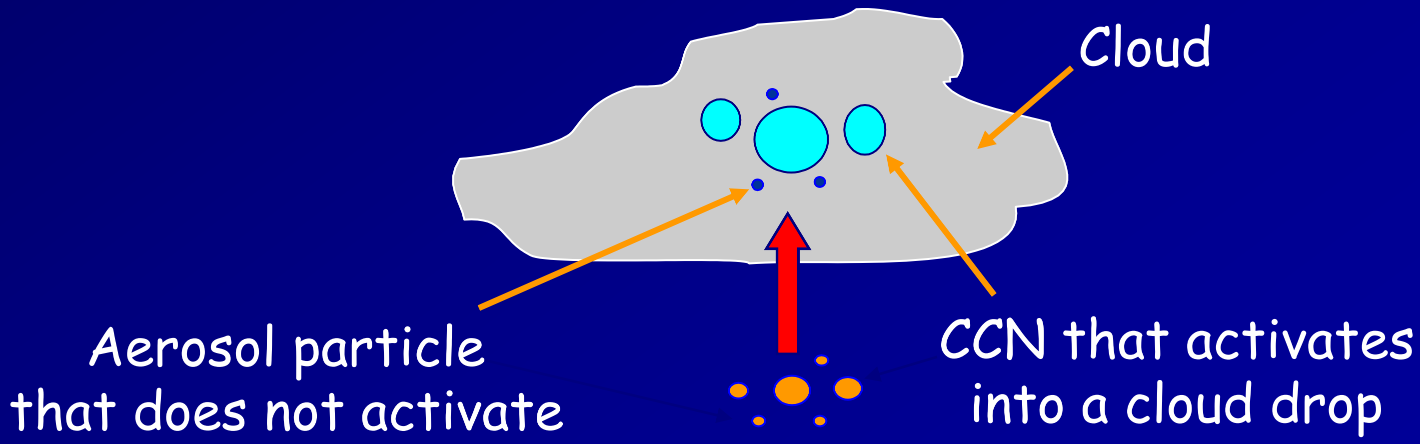
How do (liquid water) clouds form?

Clouds form in regions of the atmosphere where there is too much water vapor (it is “supersaturated”).

This happens when air is cooled (primarily through expansion in updraft regions and radiative cooling).

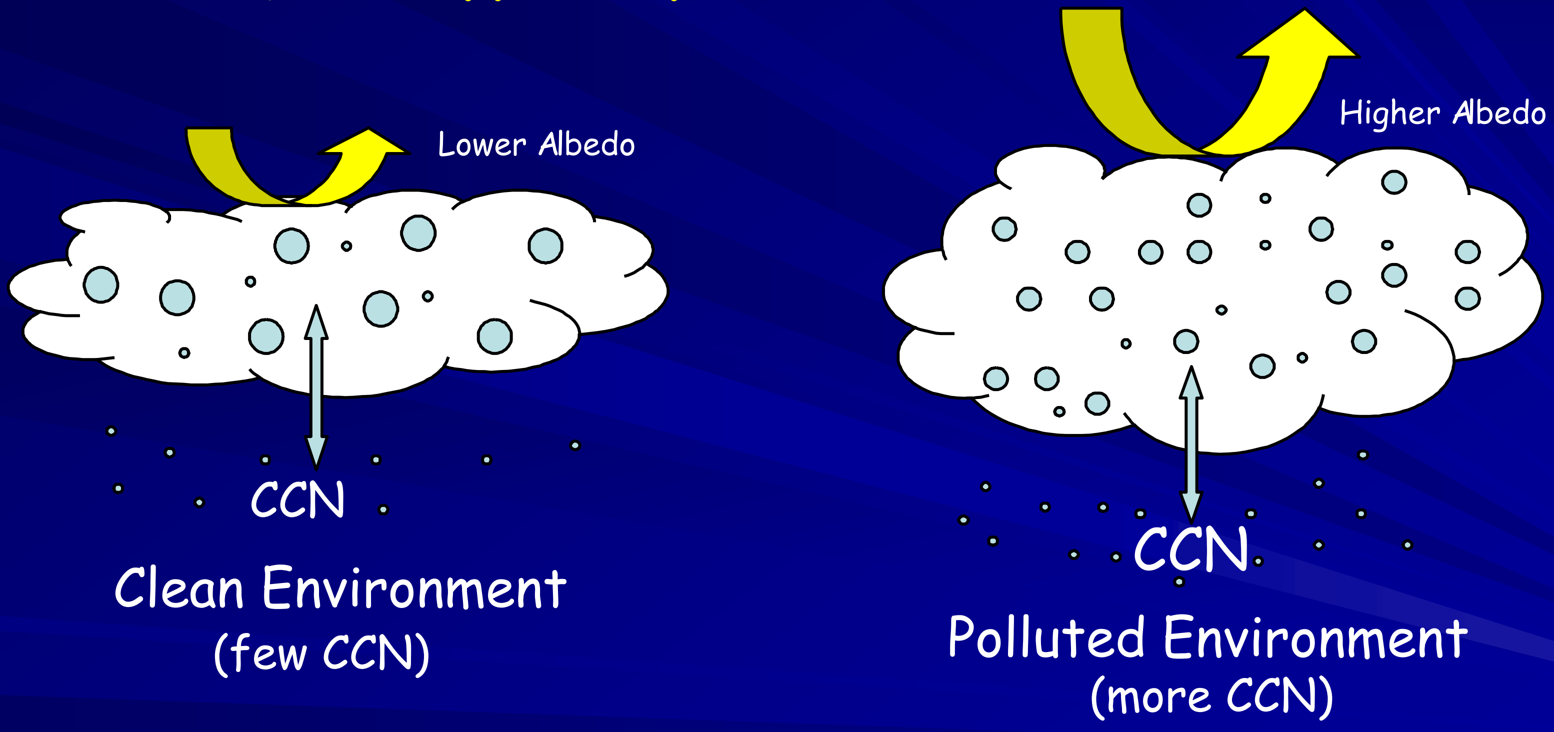
Cloud droplets nucleate on pre-existing particles found in the atmosphere (aerosols) with ~ 0.1μm diameter.

Aerosols that can become droplets are called cloud condensation nuclei (CCN).



Increases in aerosol affects warm clouds

You make clouds that are "whiter", precipitate less (persist longer) and potentially cover larger areas of the globe. This is thought to yield a net cooling on climate and is termed as the "**indirect climatic effect of aerosols**".

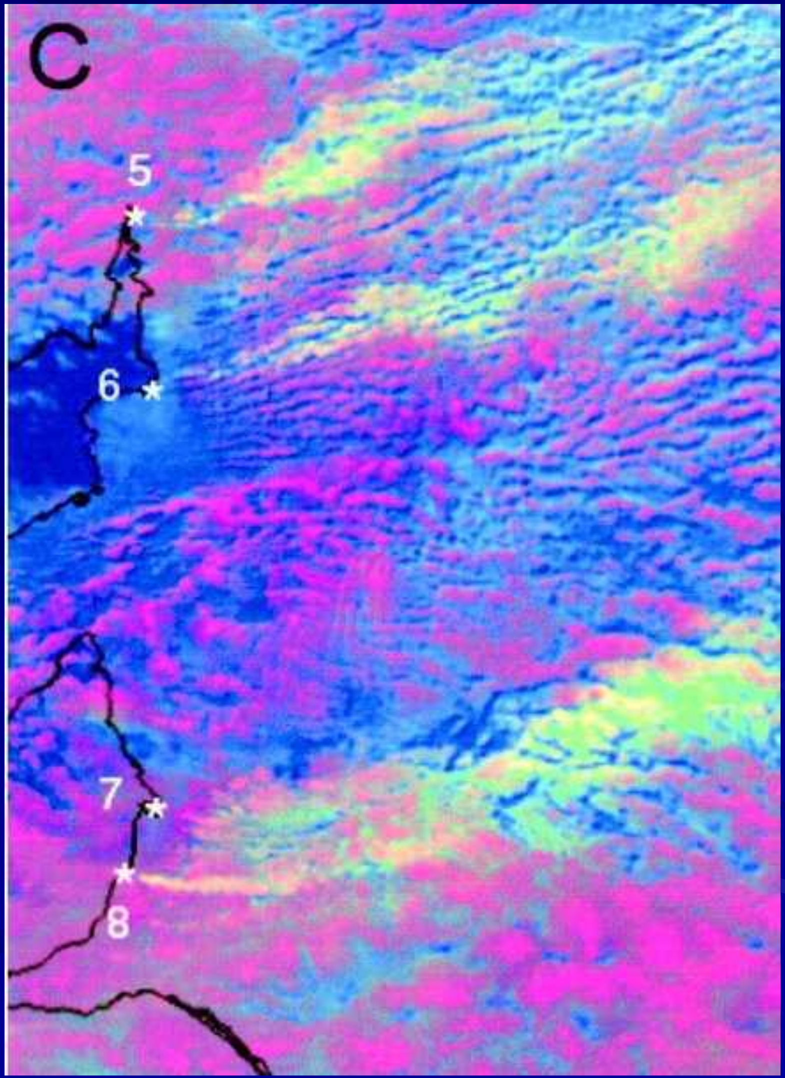


Increasing particles tends to cool climate (potentially alot).

Quantitative assessments done with climate models.

Observational evidence of indirect effect

Satellite observations of clouds off W. Australia.



Red: Clouds with low reflectivity.

White: Clouds that reflect alot.

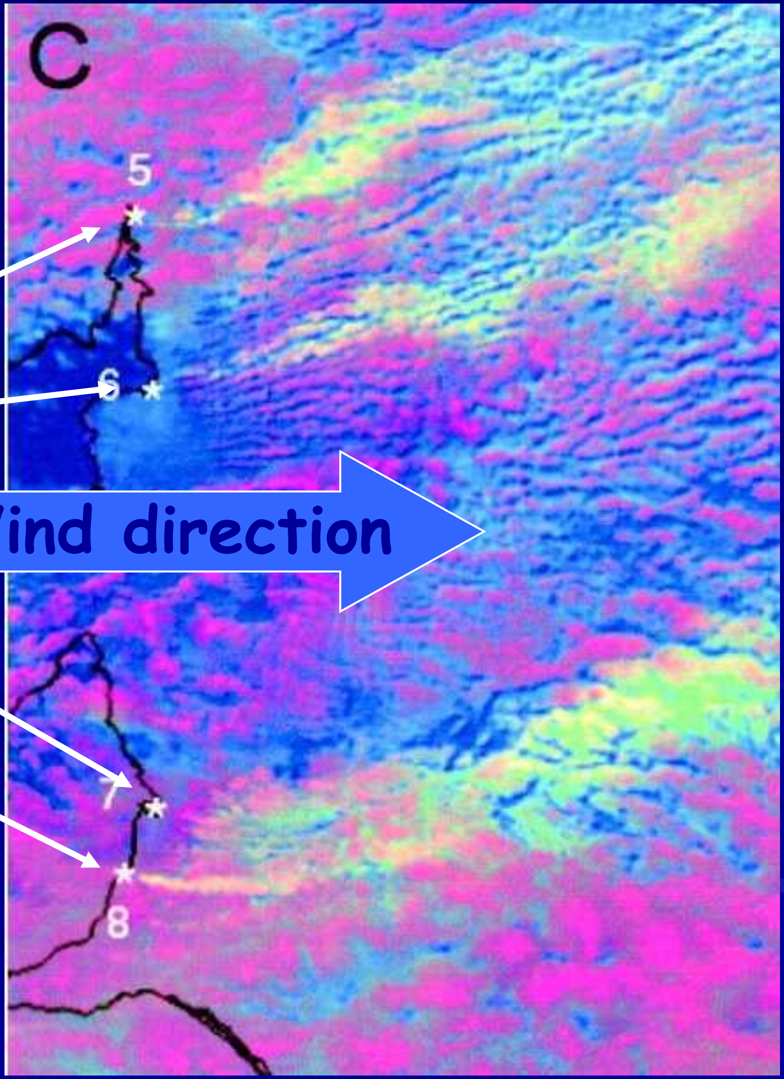
Blue: Clear sky.

Rosenfeld et al., Science

Observational evidence of indirect effect

Air pollution can affect cloud properties

Satellite observations of clouds off W. Australia.



Power plant

Lead smelter

Port

Oil refineries

Red: Clouds with low reflectivity.

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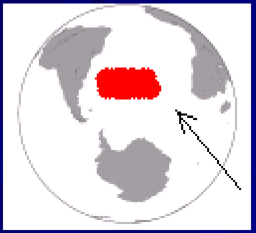
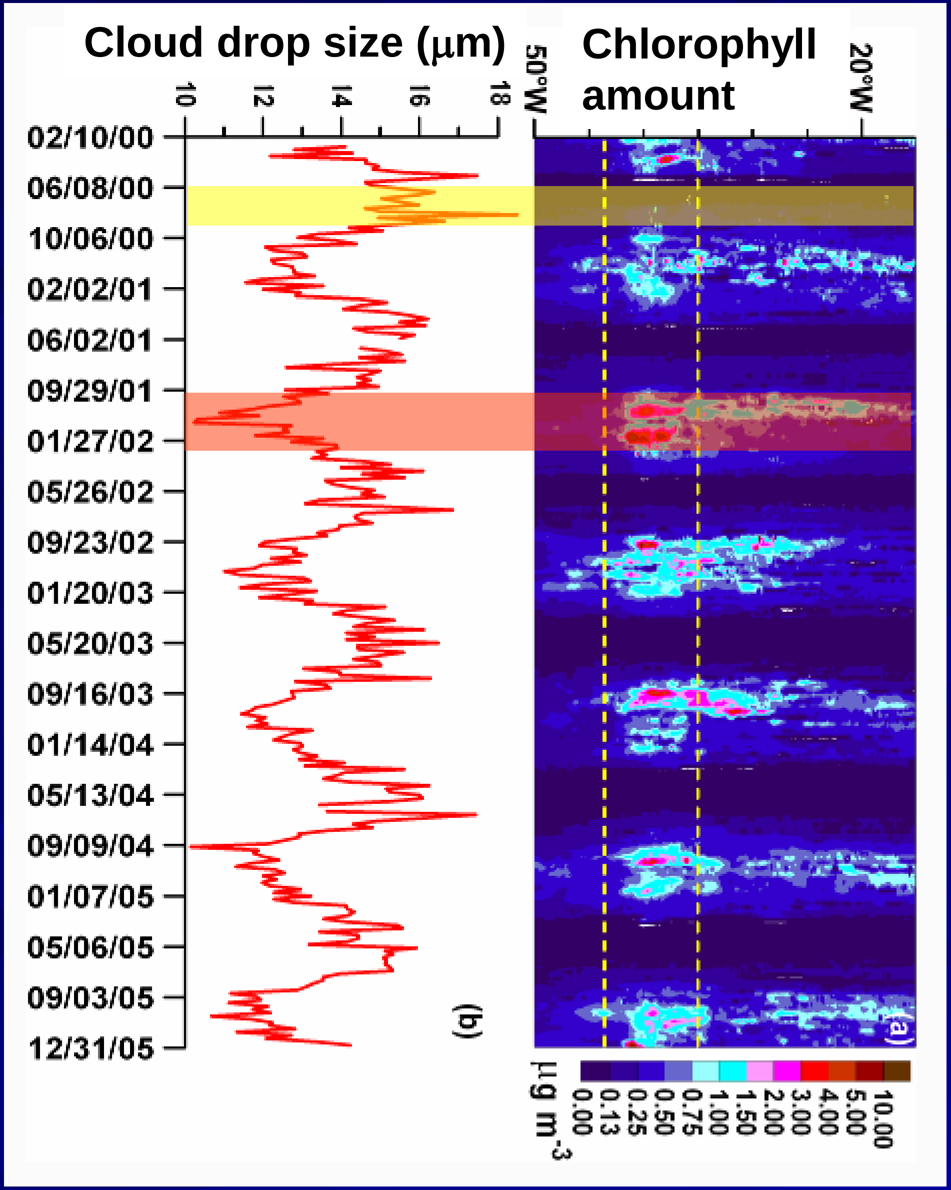
Rosenfeld et al., Science

Phytoplankton affect clouds too…

Location: East of Patagonia (South America)





Low chlorophyll period, clouds have large drops (not very reflective)

High Chlorophyll period, Clouds have small drops (very reflective)

Meskhidze and Nenes, Science, 2006

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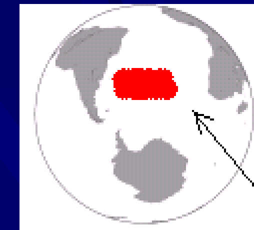
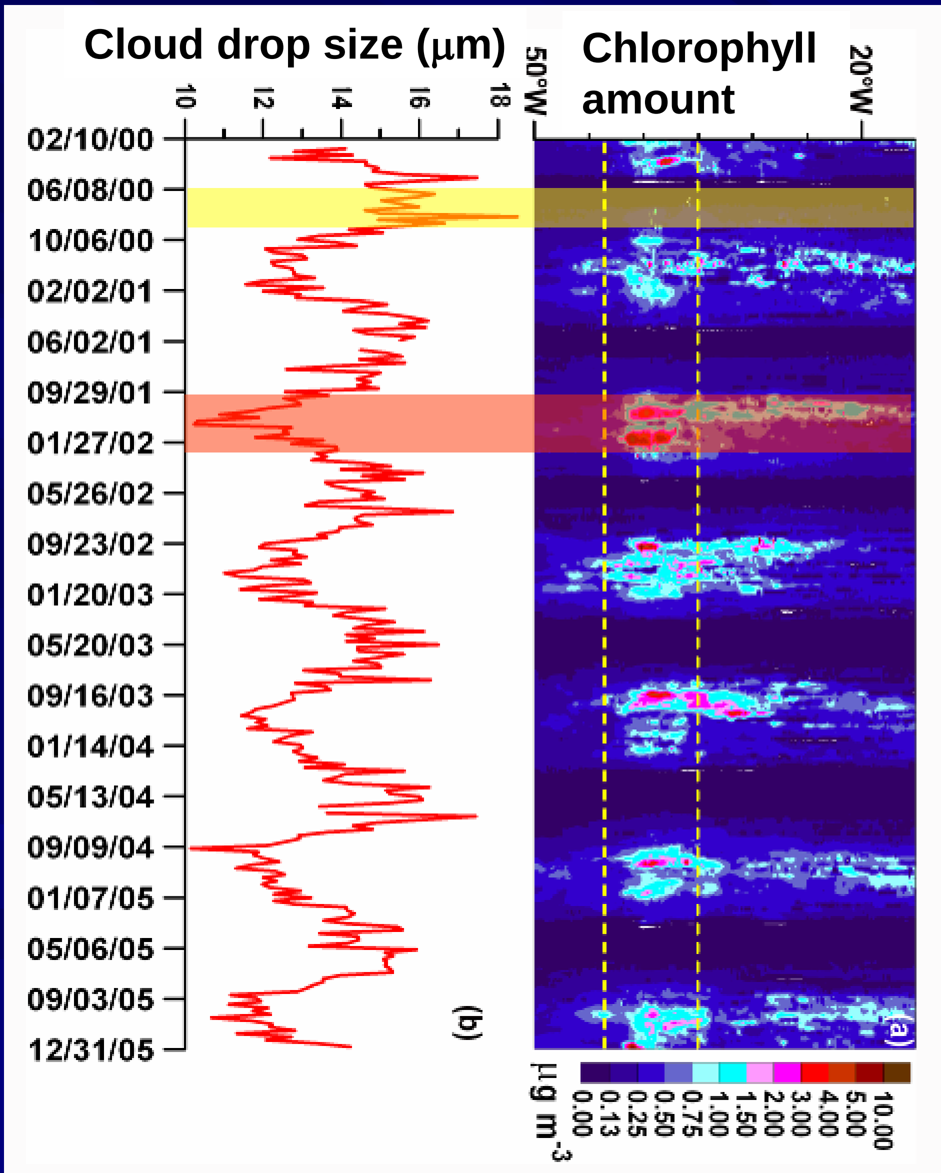




Low chlorophyll period, clouds have large drops (not very reflective)

High Chlorophyll period, Clouds have small drops (very reflective)

Phytoplankton emissions increase particle loads, and strongly impact clouds.

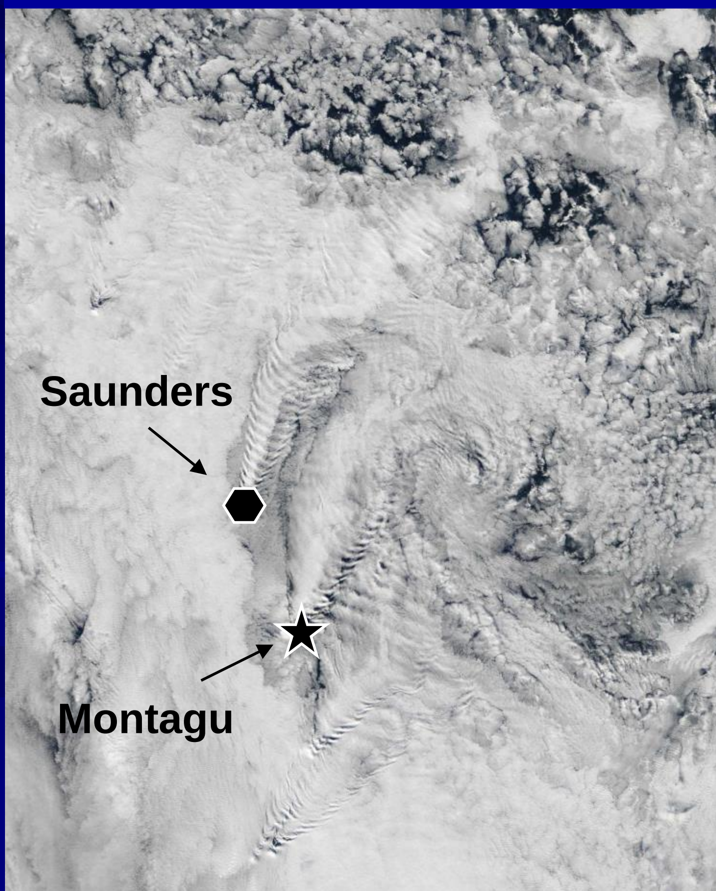
Biology-cloud interactions affect radiation in the region.

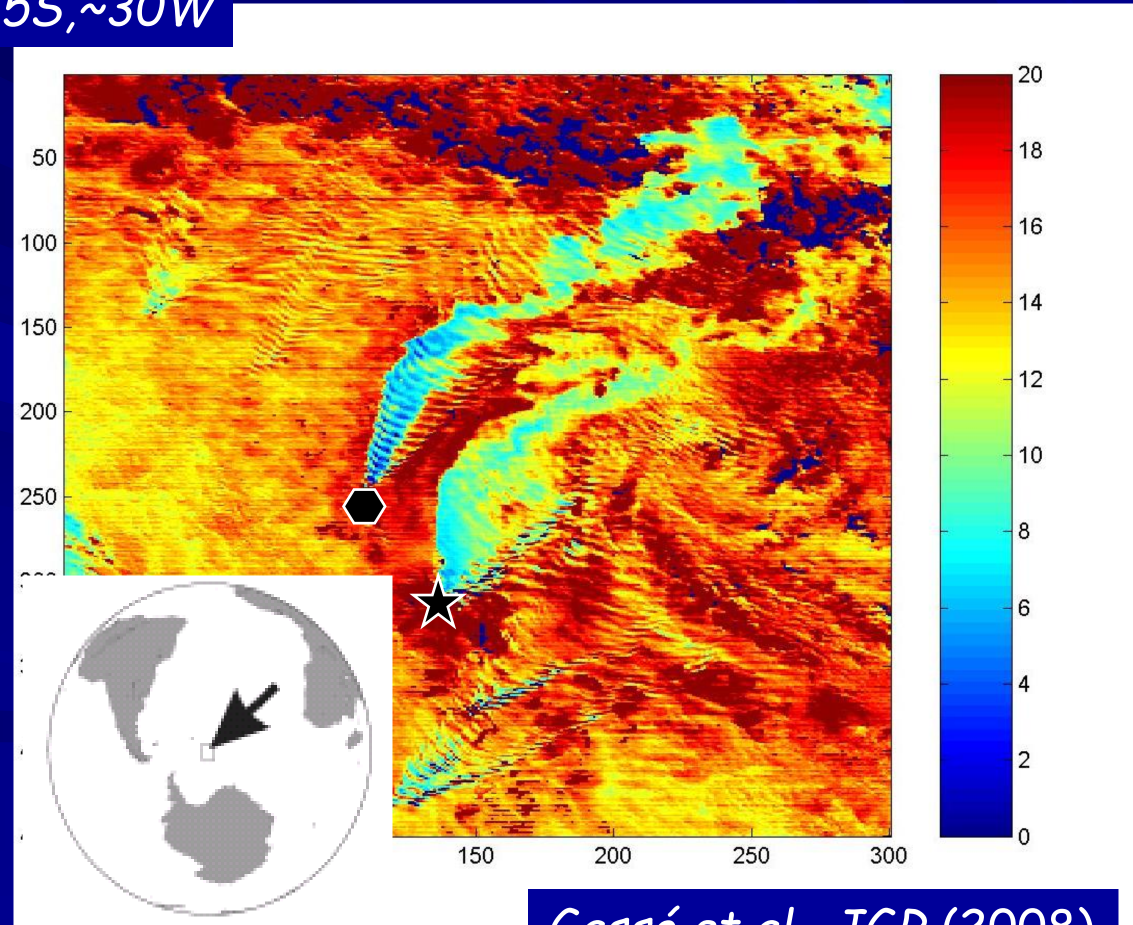
Meskhidze and Nenes, Science, 2006

So do volcanoes (even when “sleeping”) …

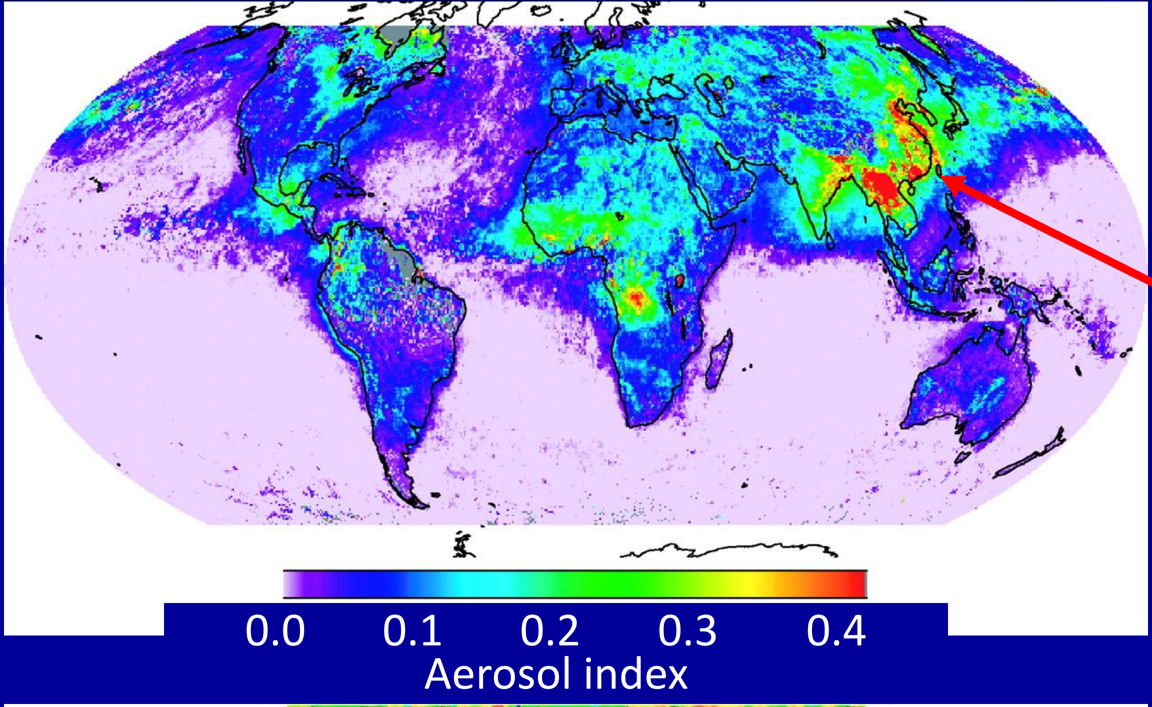
Volcanoes continuously emit SO_2 which becomes sulfate aerosol.
The aerosol can substantially increase CCN in volcanic plumes.
Clouds in the plume are much more reflective than outside.

Location: Sandwich Islands , ~55S,~30W





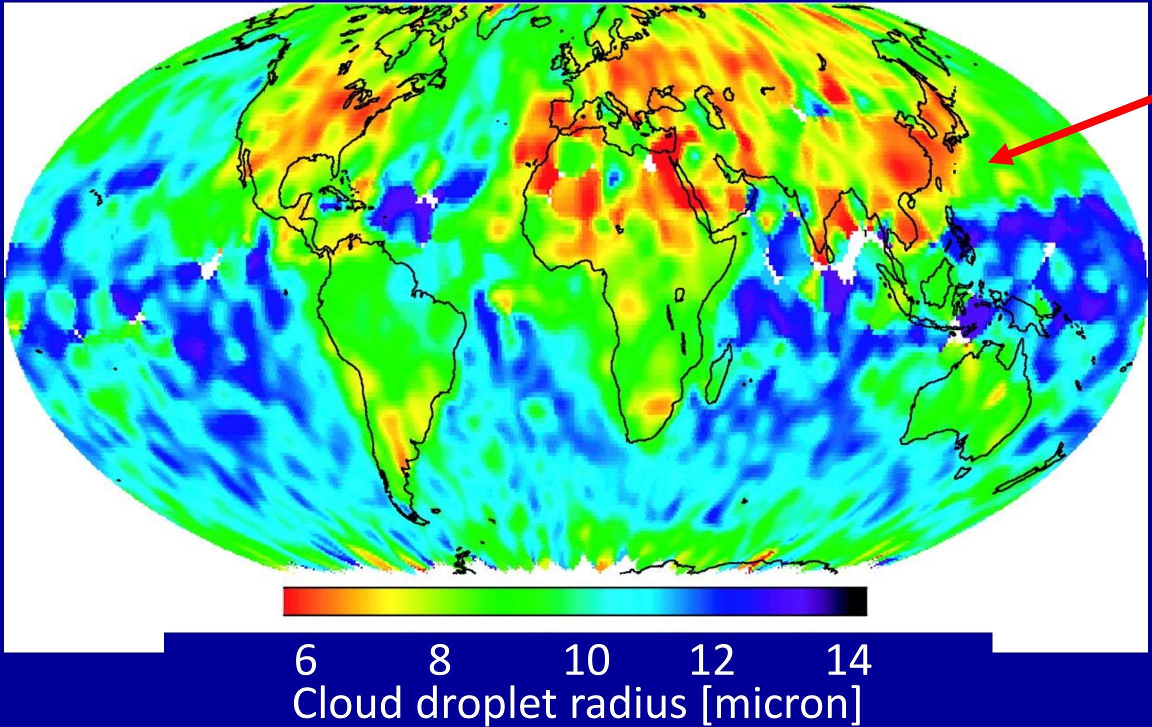
Gassó et al., JGR (2008)



A remote sensing global picture…

A lot of aerosol…

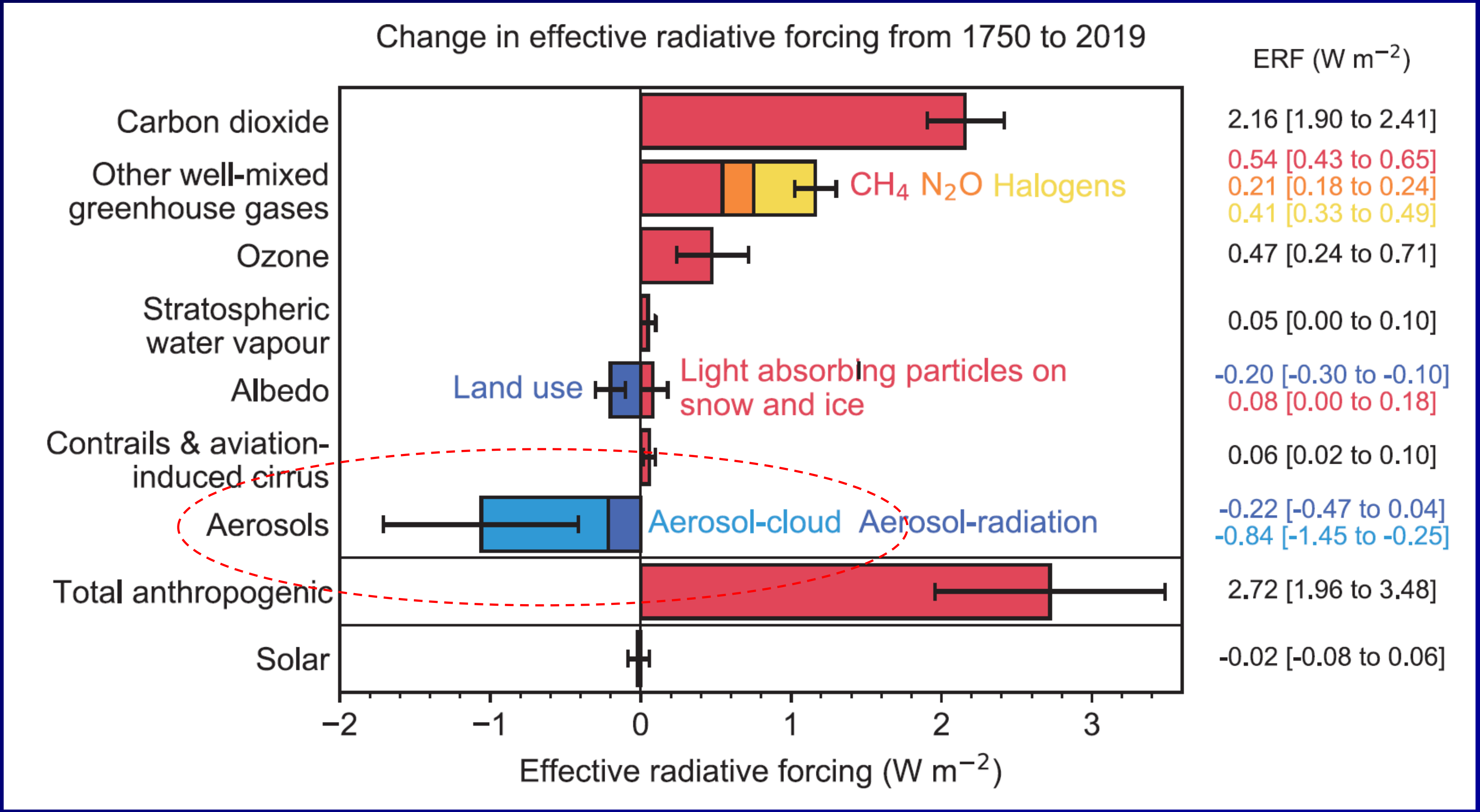
…gives smallest cloud droplets



We see the same on all satellite platforms…

Breón et al. (2002)

Aerosol-cloud interactions are important for climate - but highly uncertain



Forster et al. (2021), IPCC AR6

LIQUID cloud microphysics

- **Ice (cold) clouds**: Made of ice crystals at T < 235 K.
- **Mixed Phase clouds**: Mixture of liquid droplets and ice for T between 235 and 273K
- **Liquid (warm) clouds**: Made of liquid droplets at T >273 K

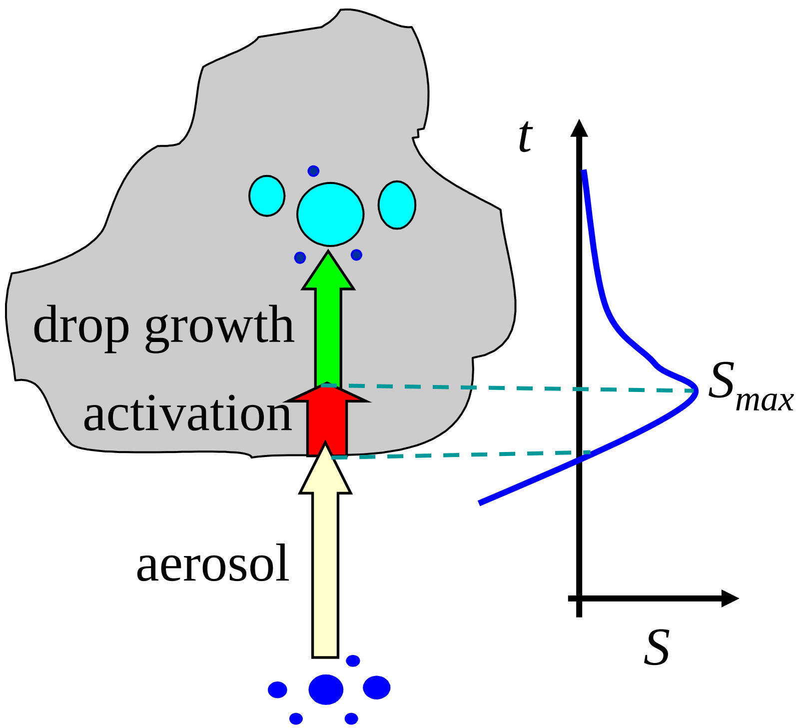
Cloud particles are not created directly from the vapor phase but from **suspended aerosol particles**

http://www.ucar.edu/news

Droplet formation: The essence

Goal: Link cloud droplet concentration with precursor aerosol

Approach: Use the "simple story of cloud formation".

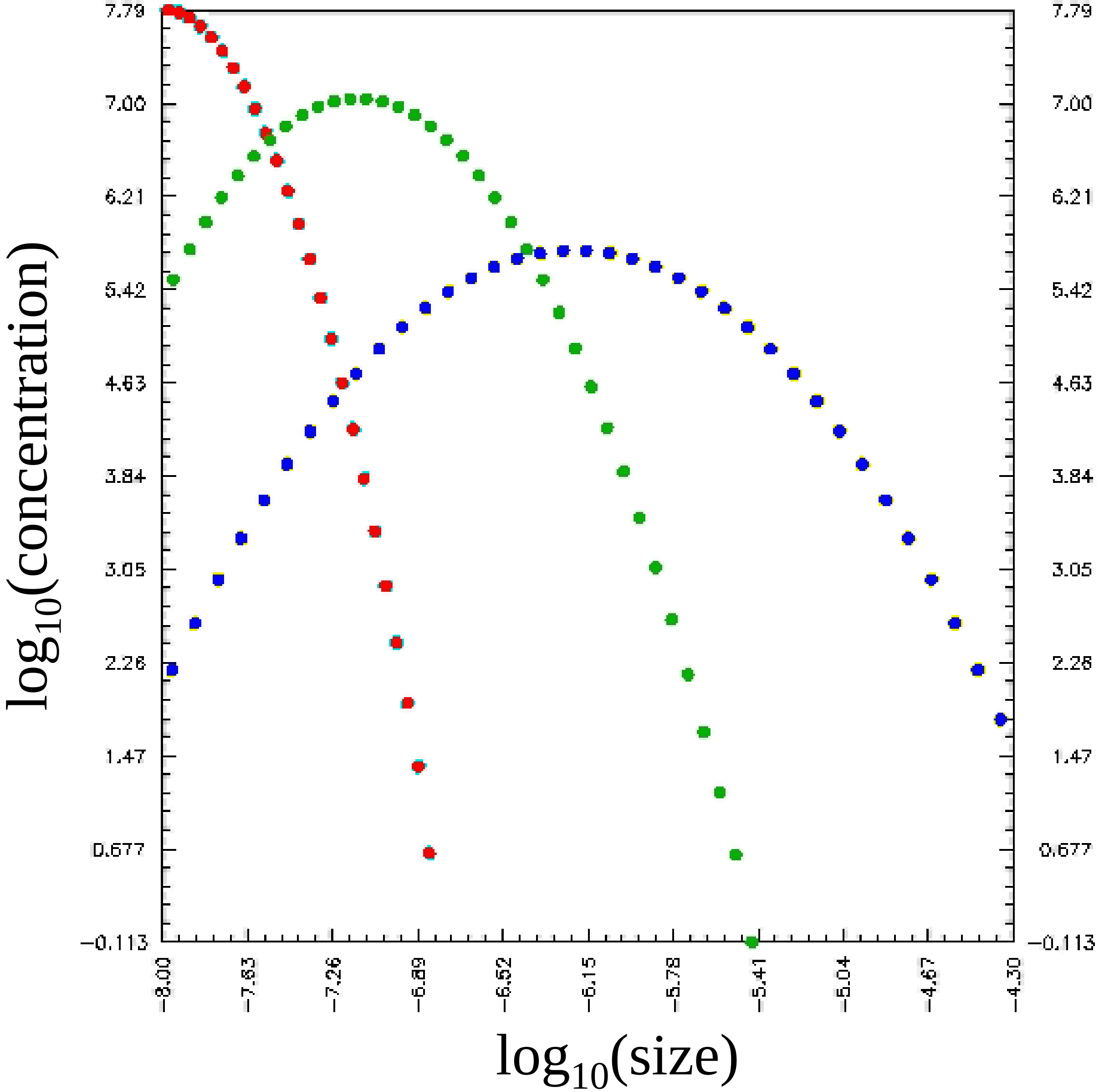


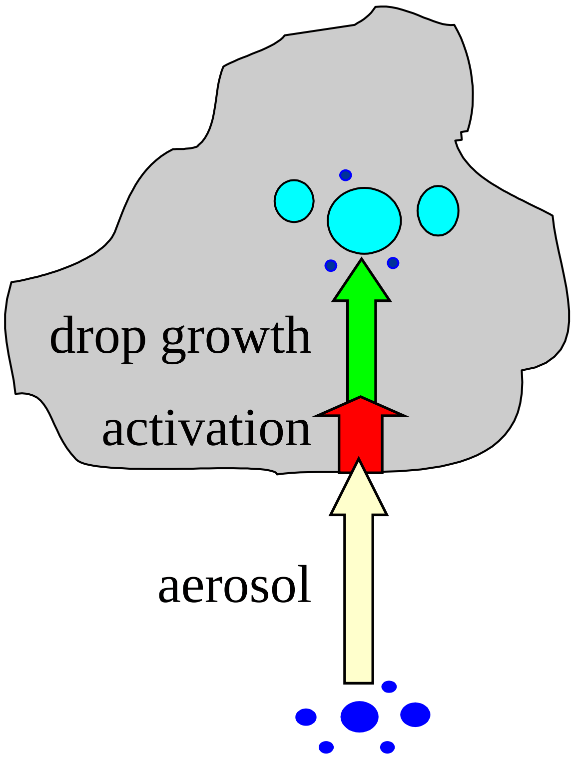
Conceptual steps are:

- Air parcel cools, reaches 100% humidity.
- Water vapor is **supersaturated**
- Droplets start forming on existing CCN.
- Condensation of water on droplets becomes intense.
- Humidity reaches a **maximum**
- No more additional drops form

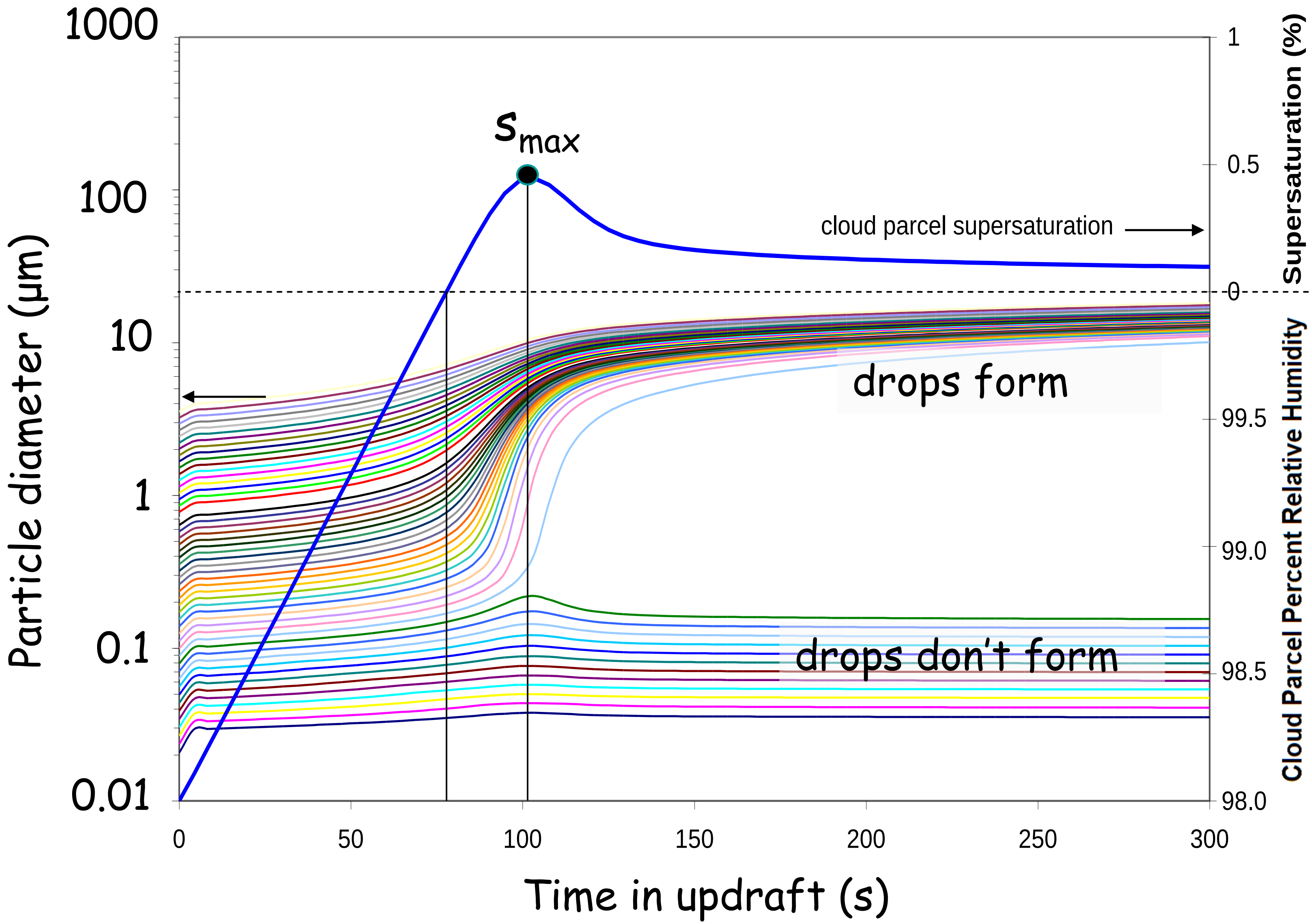
A "classical" nucleation/growth problem

Simulation of cloud droplet formation





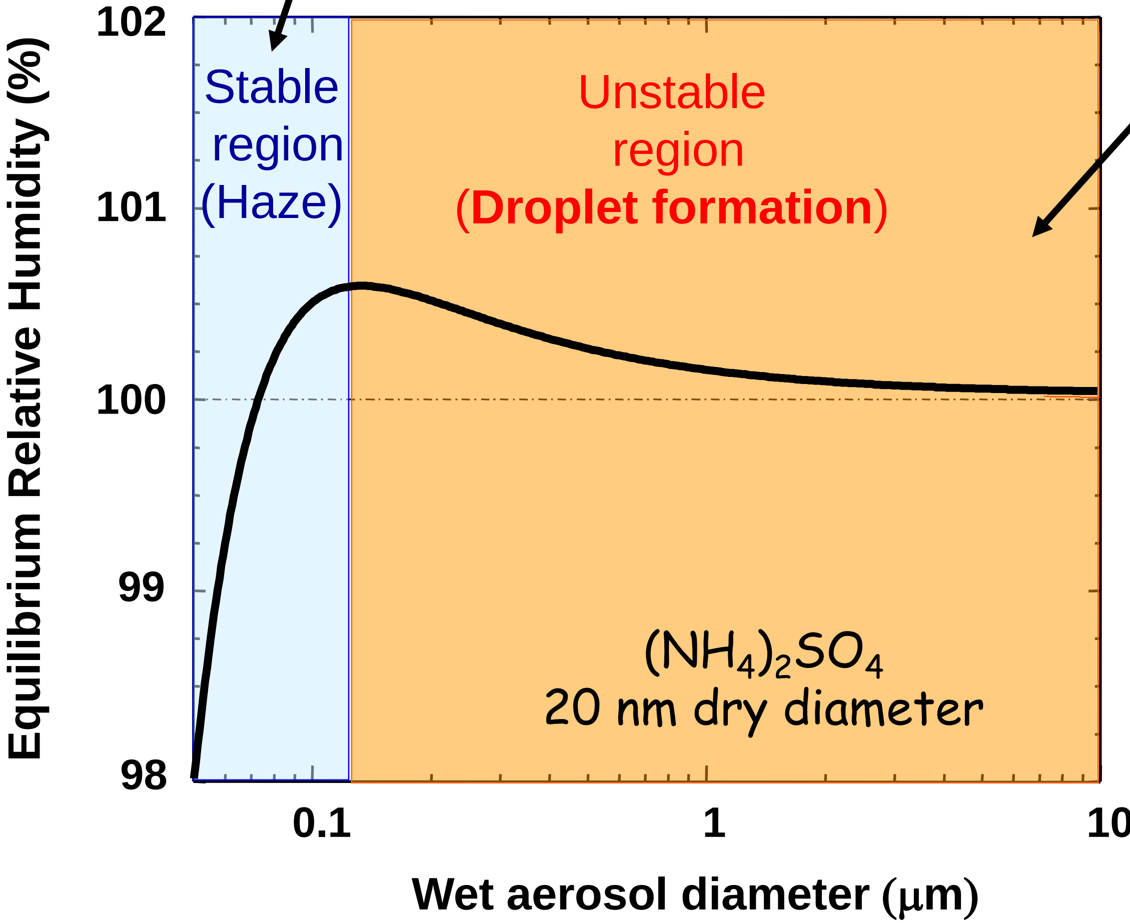
Now we understand droplet formation



When does an aerosol particle act as a CCN ?

Ambient RH **less** than S_c -> *stable* equilibrium.

Ambient RH **above** S_c -> unstable equilibrium. Particles act as CCN and make droplets



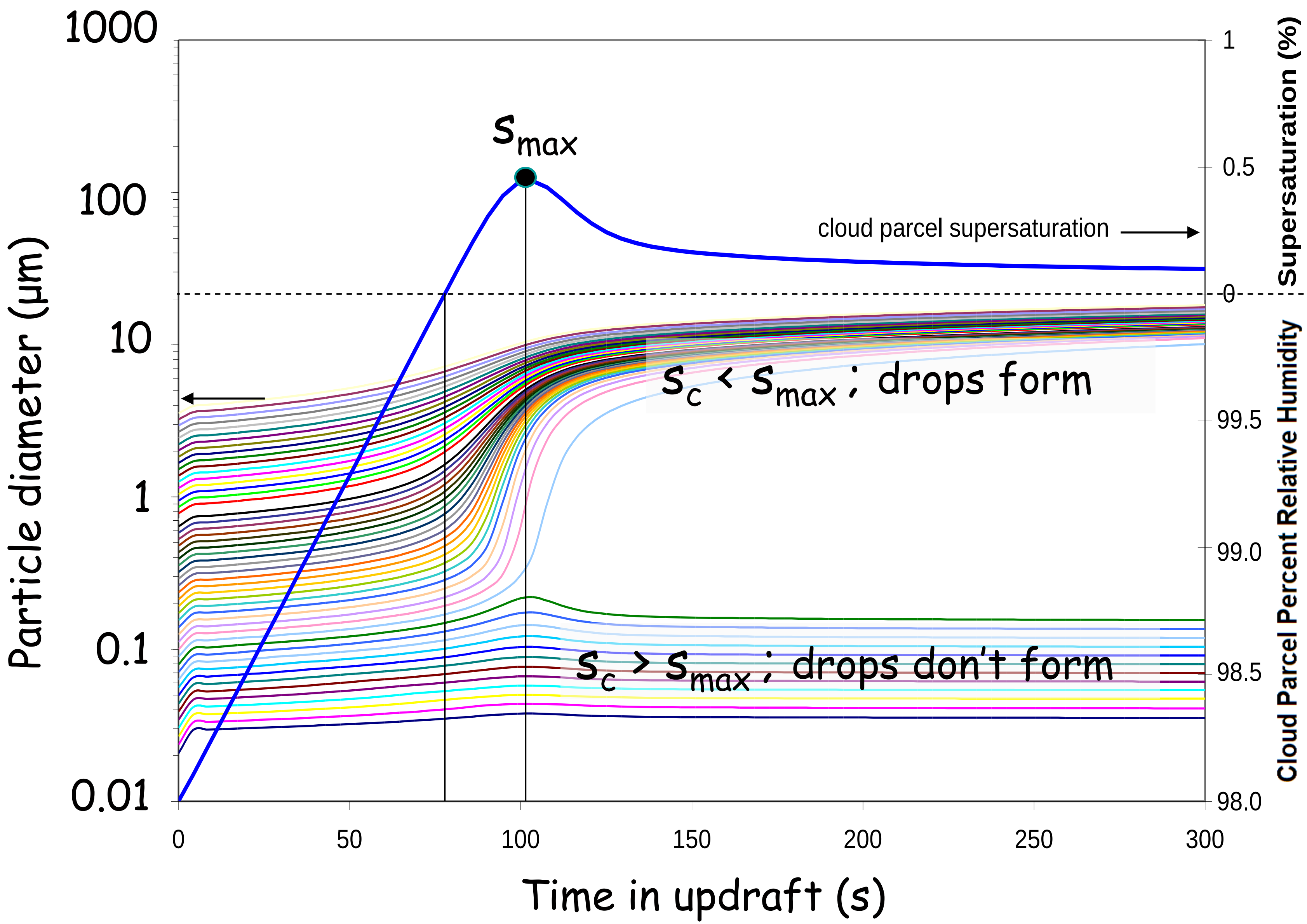
Köhler theory:

$$s_c = \left(\frac{4A^3}{27B} \right)^{1/2}$$

$$s_c \sim d_{dry}^{-3/2}, \varepsilon_{\mathbf{soluble}}^{-1/2}$$

Size is more important than composition

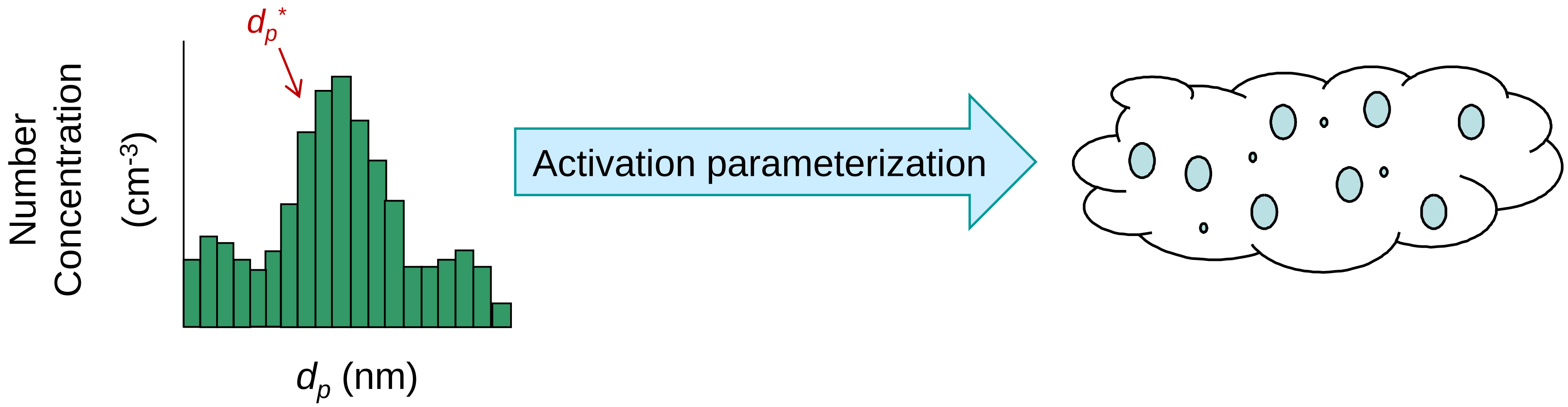
Now we understand droplet formation



Describing droplet formation in models…

Droplet calculation in models then is:

Calculated size distribution + κ + vertical velocity

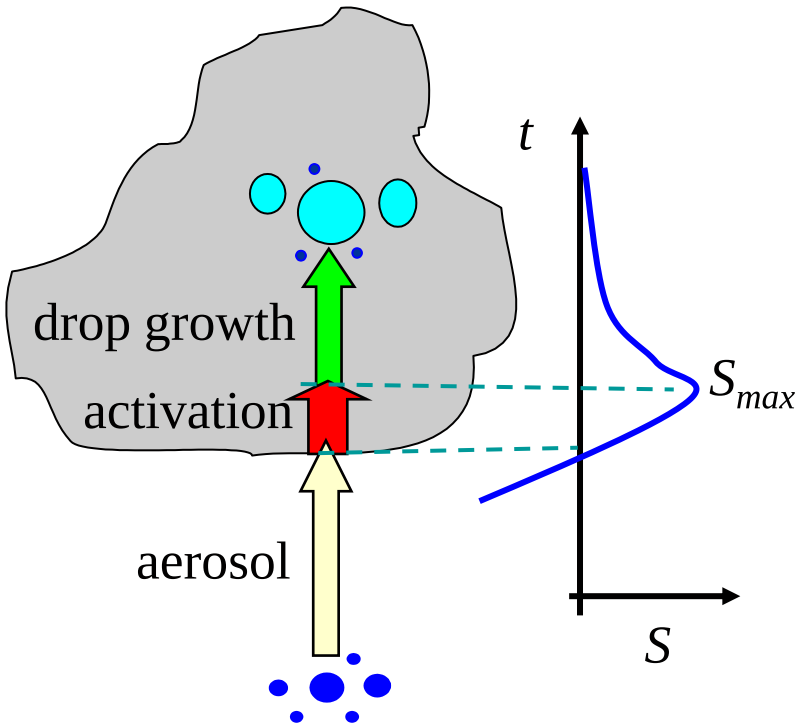


Activation parameterization is either a correlation or a solution to the parcel model equations that describe the activation process in clouds.

Droplet number needs CCN and max.cloud RH…

Algorithm for calculating N_d (Mechanistic parameterization):

1. Calculate s_{max} (approach-dependent)
2. N_d is equal to the CCN with $s_c \leq s_{max}$



Mechanistic Parameterizations: Twomey (1959); Abdul-Razzak et al., (1998); Nenes and Seinfeld, (2003); Fountoukis and Nenes, (2005); Kumar et al. (2009), Morales and Nenes (2014), and others.

Input: P,T, vertical wind, particle size distribution,composition.

Output: Cloud properties (droplet number, size distribution).

Comprehensive review & intercomparison:
Ghan, et al., *JAMES* (2011); Morales and Nenes (2014)

Is this description of droplet formation real

Evaluate with in-situ data from airborne platforms

CIRPAS Twin Otter

Observed Aerosol size distribution & composition

Observed Cloud updraft Velocity (PDF)

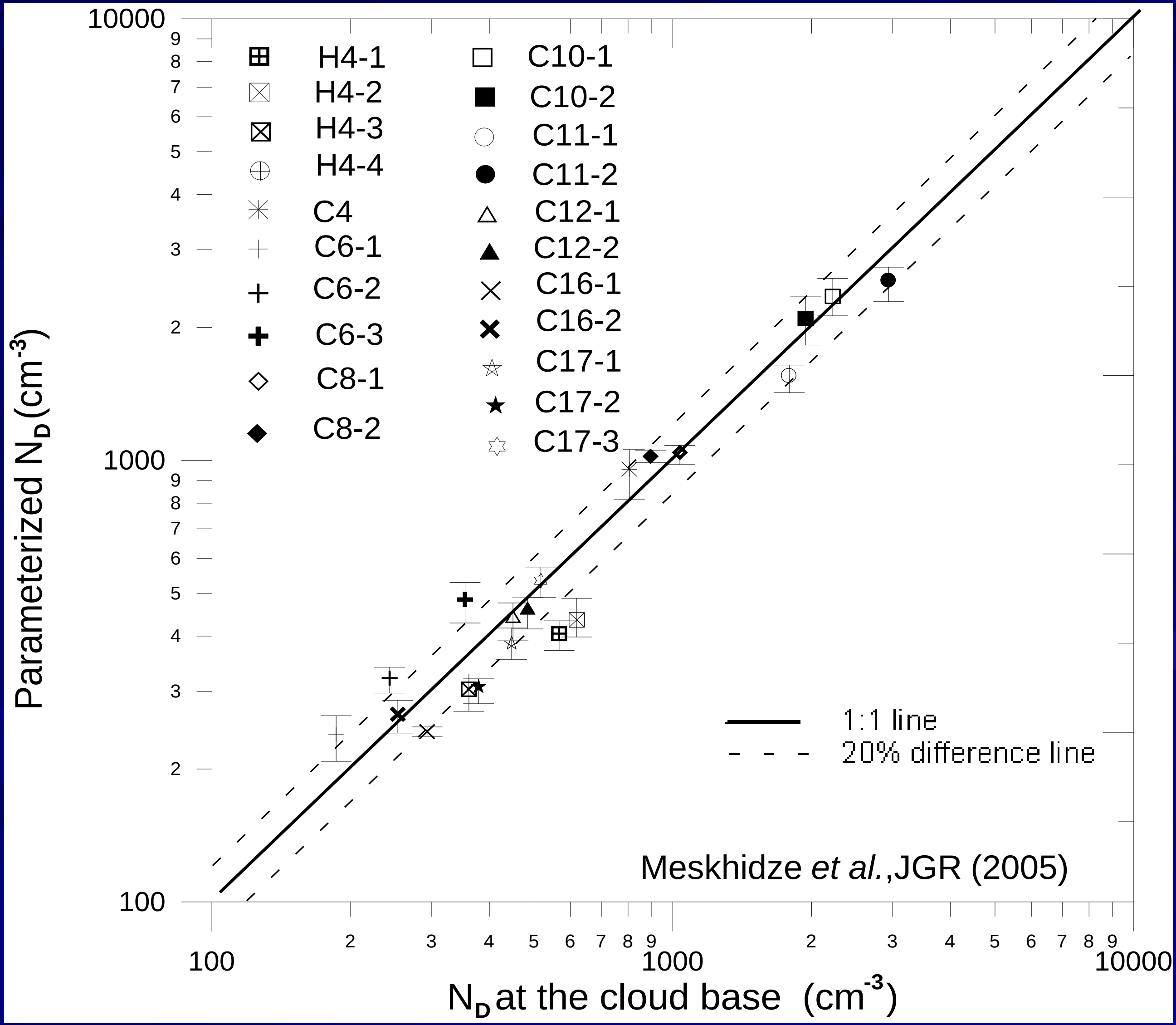
Predicted Drop Number (Parameterization)

Compare

Observed Drop Number Concentration

CRYSTAL-FACE (2002) Cumulus clouds

CIRPAS Twin Otter



Paramet'n agrees with observed cloud droplet number

Agreement to within a few % (on average)!

…when aerosol composition and size, AND cloud dynamics is known

Issue: aerosols are complex

Primary emissions

Automobiles, industry, domestic, vegetation, forest fires, seasalt, ...

Secondary transformations

Oxidation of precursors (by O_3, H_2O_2, OH, NO_3, etc.) generates organic compounds.

Reaction of volatile bases (NH_3) with acids, dust and seasalt form salts like $(NH_4)_2SO_4$.

Understanding & parameterizing CCN activity…

Petters and Kreidenweis (2007) expressed the solute parameter in terms of a "hygroscopicity parameter", κ

$$s_c = \left(\frac{4A^3}{27B}\right)^{1/2} \Rightarrow s_c = \left(\frac{4A^3}{27\kappa}\right)^{1/2} d^{-3/2}$$

$\kappa \sim 1$ for NaCl, ~ 0.6 for $(NH_4)_2SO_4$, ~ 0-0.3 for organics

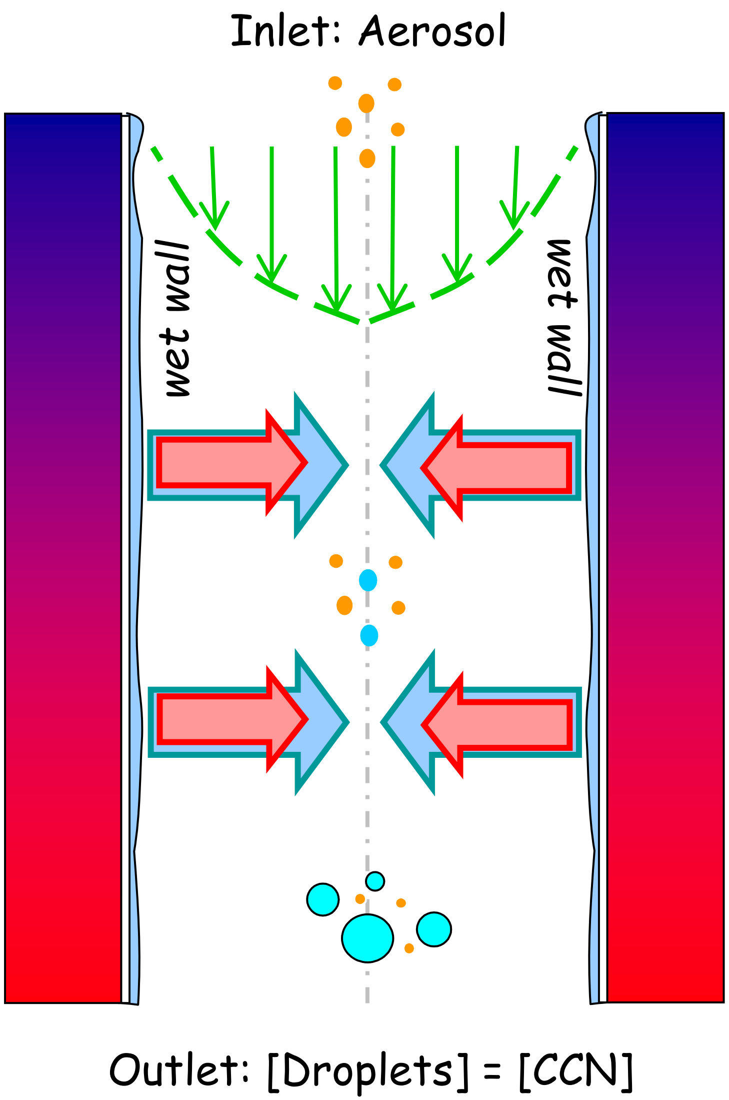
κ rarely exceeds 1 in atmospheric aerosol

Simple way to think of κ: the "equivalent" volume fraction of NaCl in the aerosol (the rest being insoluble).

$\kappa \sim 0.6$ ⇨ particle behaves like 60% NaCl, 40% insoluble

Measuring CCN activity of ambient particles:

Continuous-Flow Streamwise Thermal Diffusion Chamber



Metallic cylinder with walls wet. Apply T gradient, and flow air.

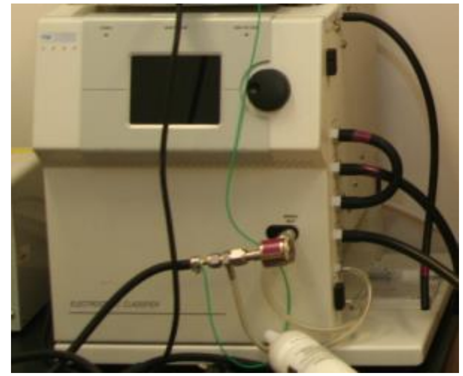
- Wall saturated with H_2O.
- H_2O diffuses faster than heat and arrives at centerline first.
- The air is supersaturated with water vapor at the centerline.
- Flowing aerosol at center would activate some into droplets.

Count the **concentration** and **size** of droplets that form with a 1 s resolution.

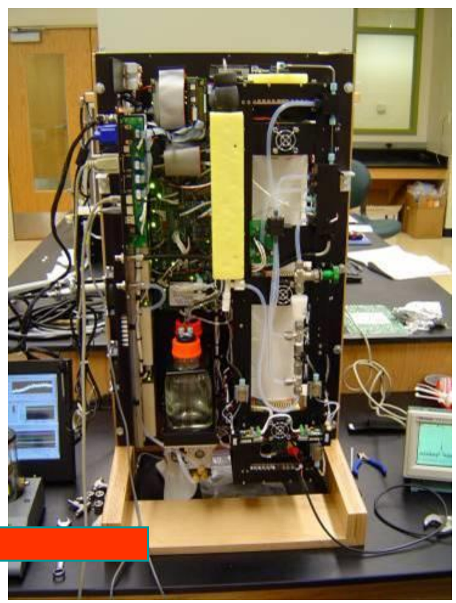
Roberts and Nenes (2005), US Patent 7,656,510

Measuring hygroscopicity, κ

size-resolved CCN measurements



Size Selection



Count CCN

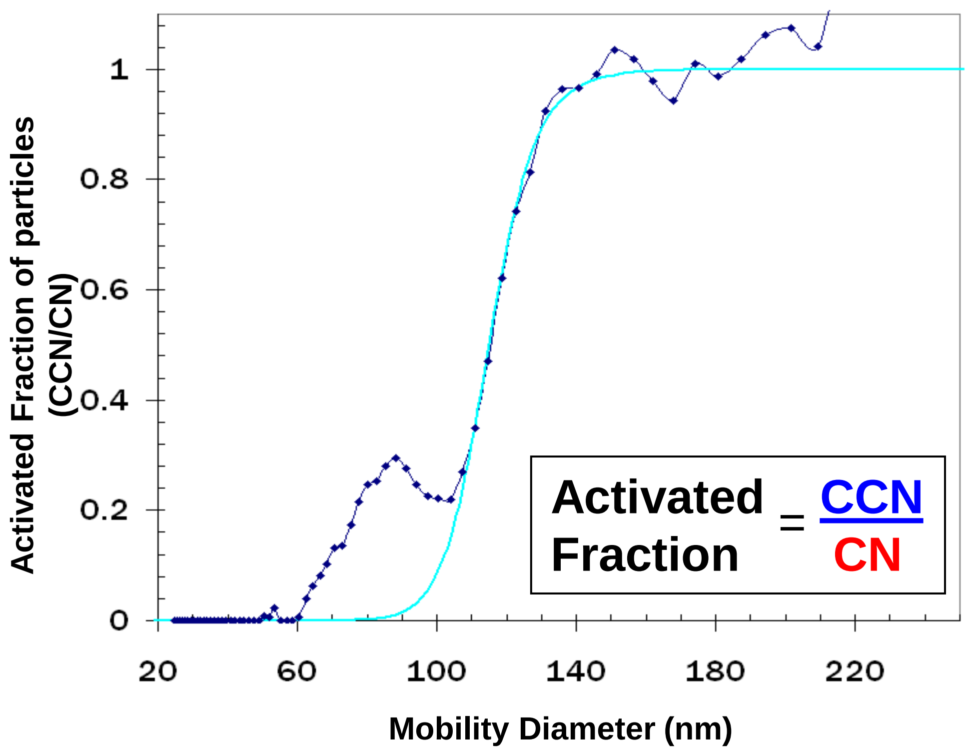
Particle Detection

Count CN

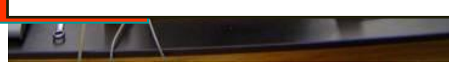
Measuring hygroscopicity, κ

size-res

Results: “activation curves”
CCN/CN as a function of *d*



e Selection



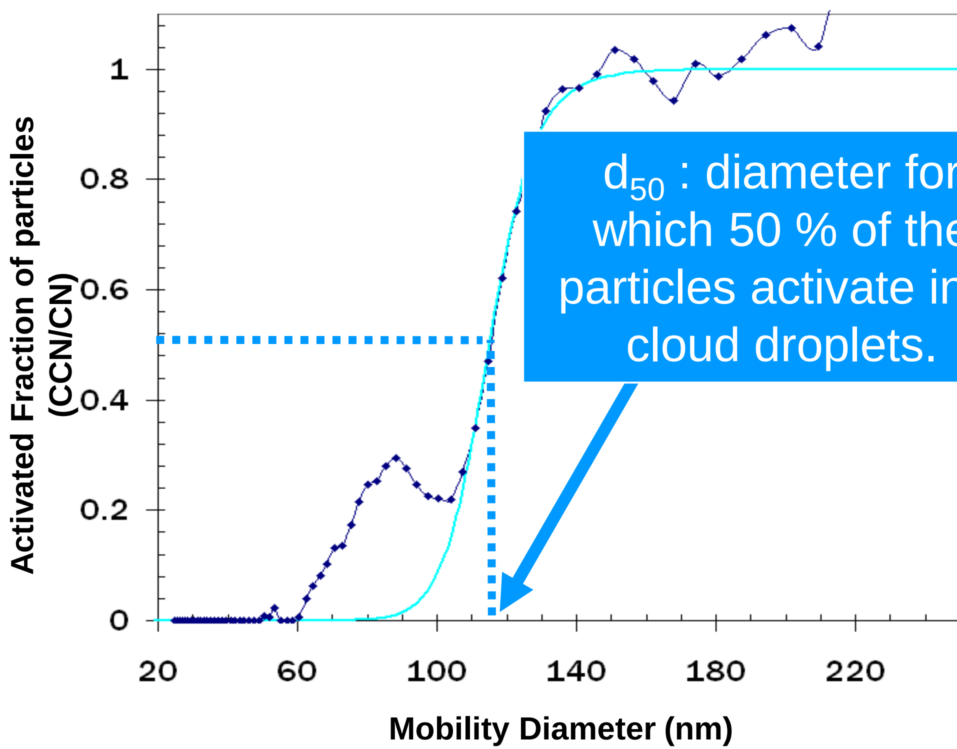
Count CCN

Count CN

Measuring hygroscopicity, κ

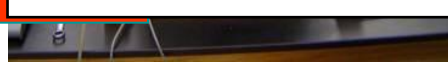
size-res

Results: “activation curves” CCN/CN as a function of *d*



d_{50} : diameter for which 50 % of the particles activate into cloud droplets.

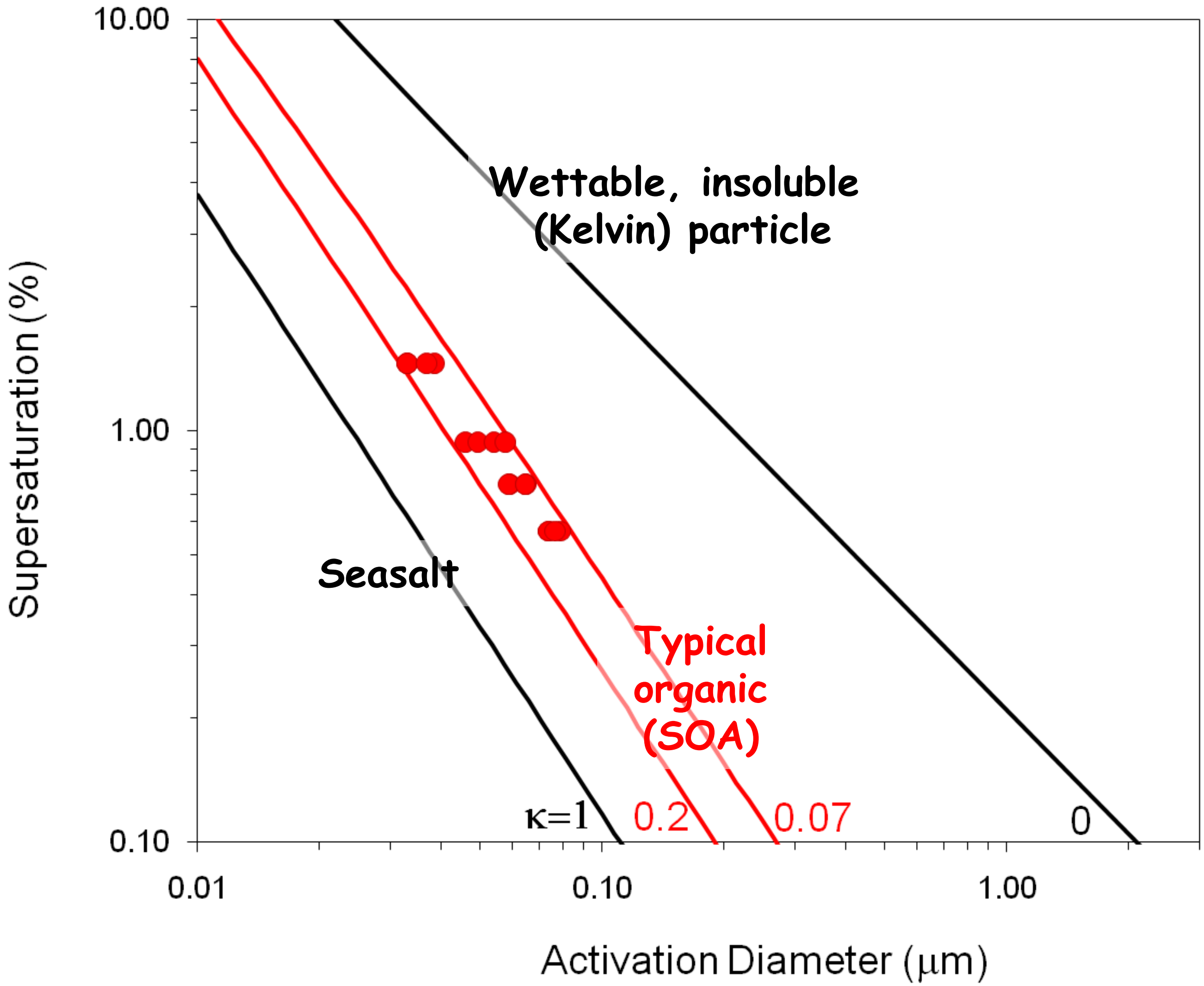
e Selection



Count CCN

Count CN

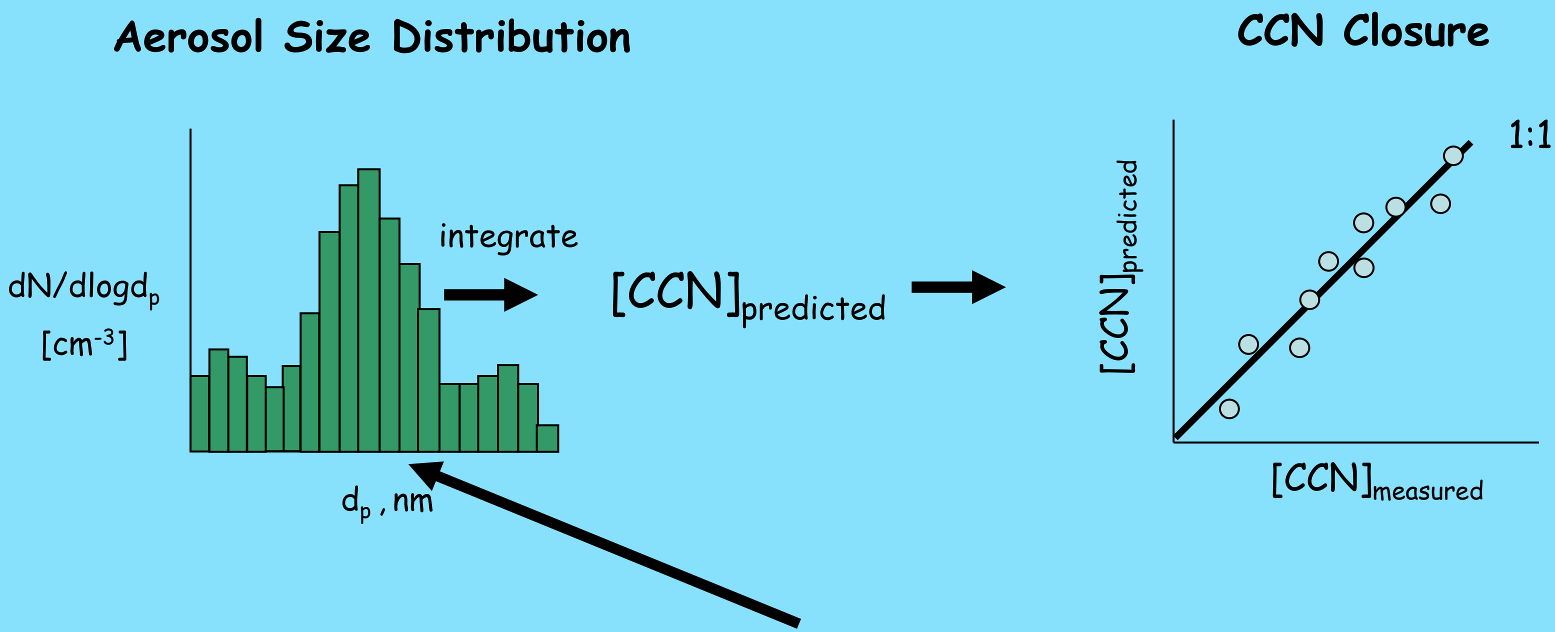
Hygroscopicity parameter for organics



Petters and Kreidenweis, ACP (2007); Figure adopted from Engelhart et al.,(2011)

CCN "Closure": test of Köhler theory

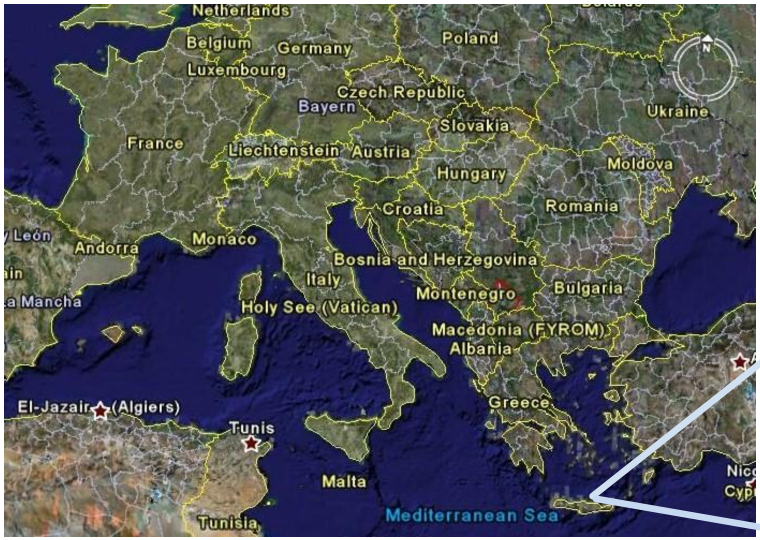
Compare measurements of CCN to predictions using Köhler activation theory and κ description



Use theory to predict the particles that can act as CCN based on measured <u>chemical composition</u> and CCN instrument <u>supersaturation.</u>

Finokalia Aerosol Measurement Campaign

(FAME-07) – Summer 2007



DMT CCN counter
Supersaturation range: 0.2-1.0%

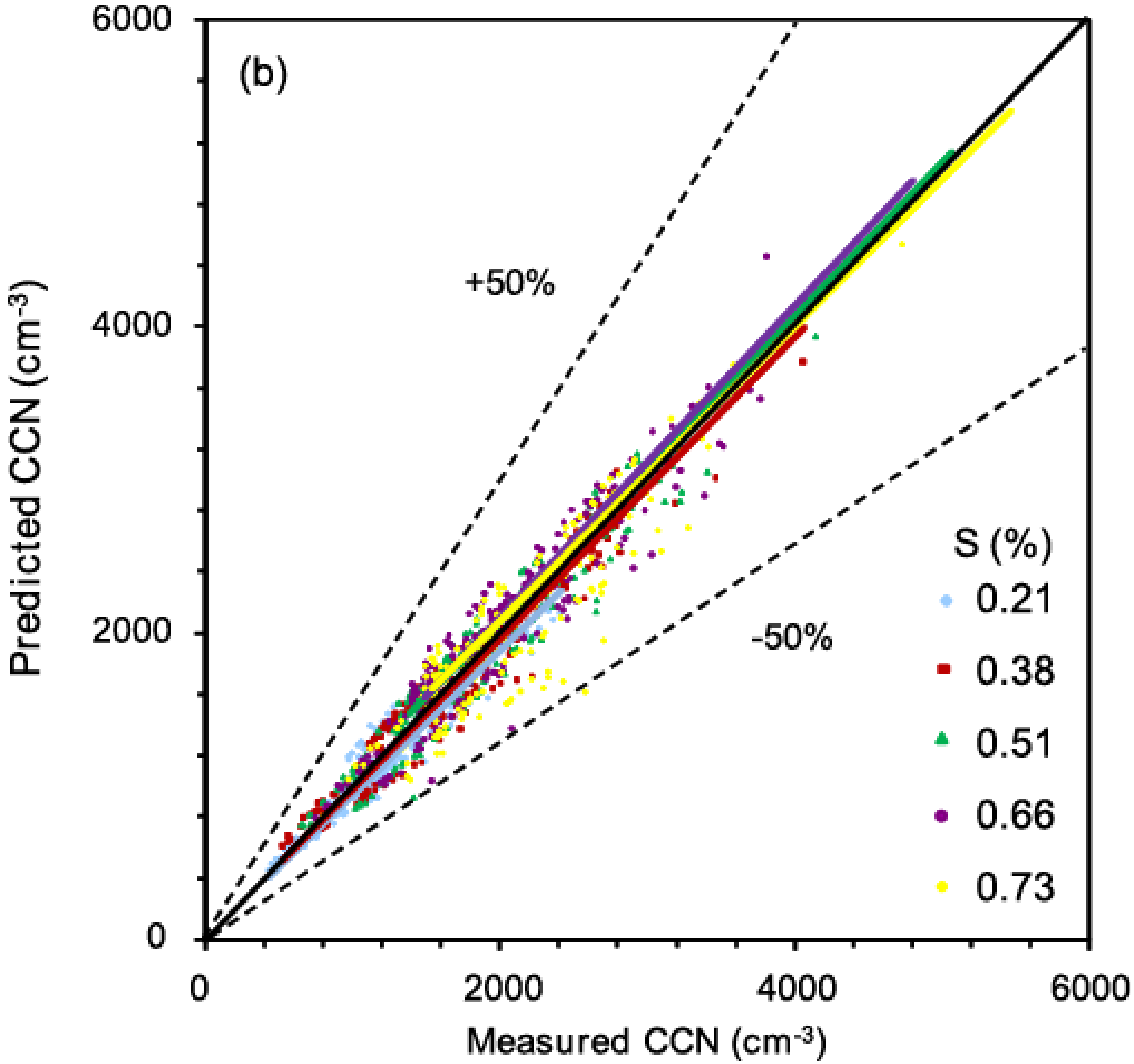
TSI 3080 SMPS
Size range: 20-460 nm

Low-vol impactor
Ionic composition measured via IC

WSOC/EC/OC also measured

(Bougiatioti et al., ACP, 2009)

FAME-07 CCN closure study



2% overprediction (on average).

Introducing compreshensive composition into CCN calculation gives excellent CCN closure.

Köhler (CCN activation) theory *really* works.

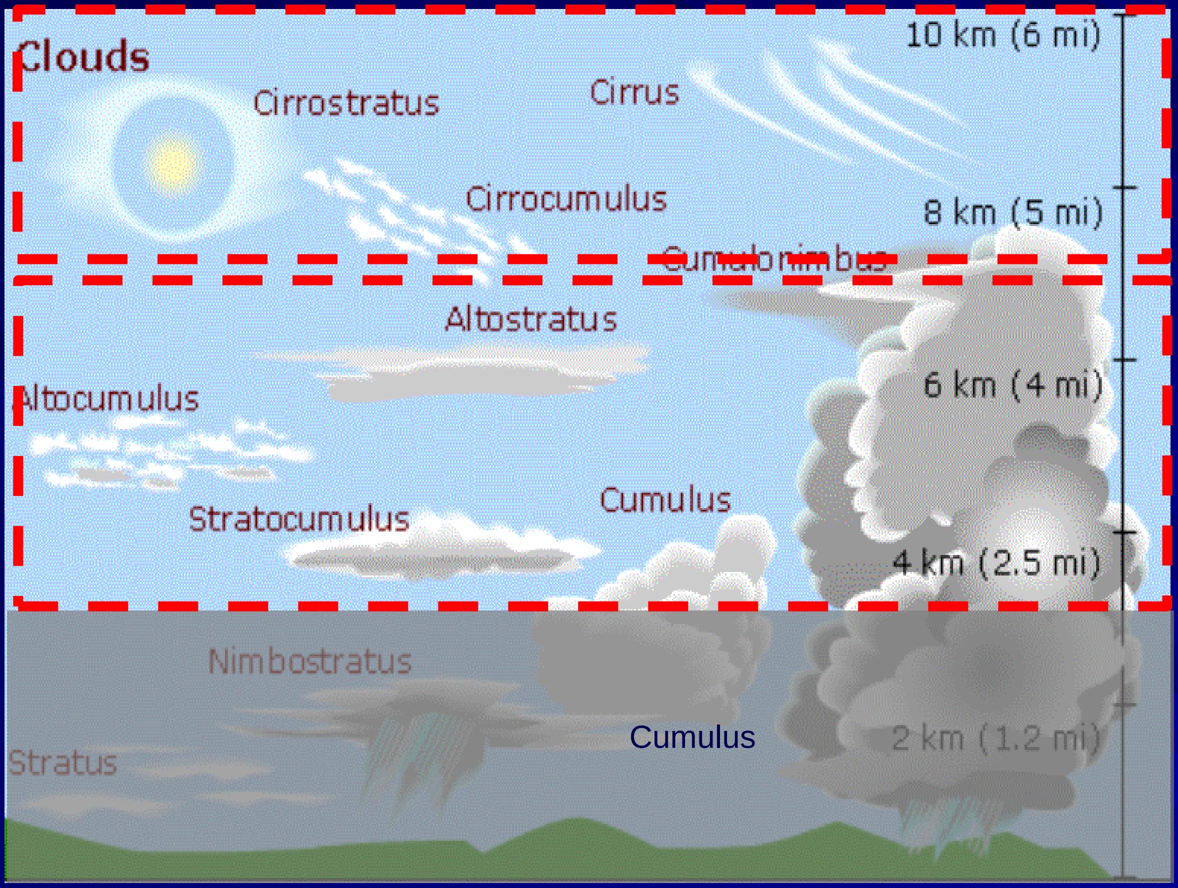
(Bougiatioti et al., ACP, 2009)

Some "take-home" messages

- Physically based formulations for description of CCN activity and the cloud droplet formation in atmospheric models rely heavily on thermodynamics.
- Single-parameter ("kappa") Köhler theory is adequate for describing the CCN of aerosol.
- Size-resolved measurements of CCN activity are very useful for constraining the extent and sources of aerosol hygroscopicity on cloud droplet formation.
- The water-soluble fraction of oxidized organics is very hygroscopic, and is surprisingly constant.
- The cumulative effect of organics on CCN activity can likely be described by simple relationships of the form:

$$\kappa_{org} = (0.25 \pm 0.05)\,\varepsilon_{sol} \quad \text{or} \quad \kappa_{org} \sim 0.1$$

Focus on "Slush" and Ice clouds now

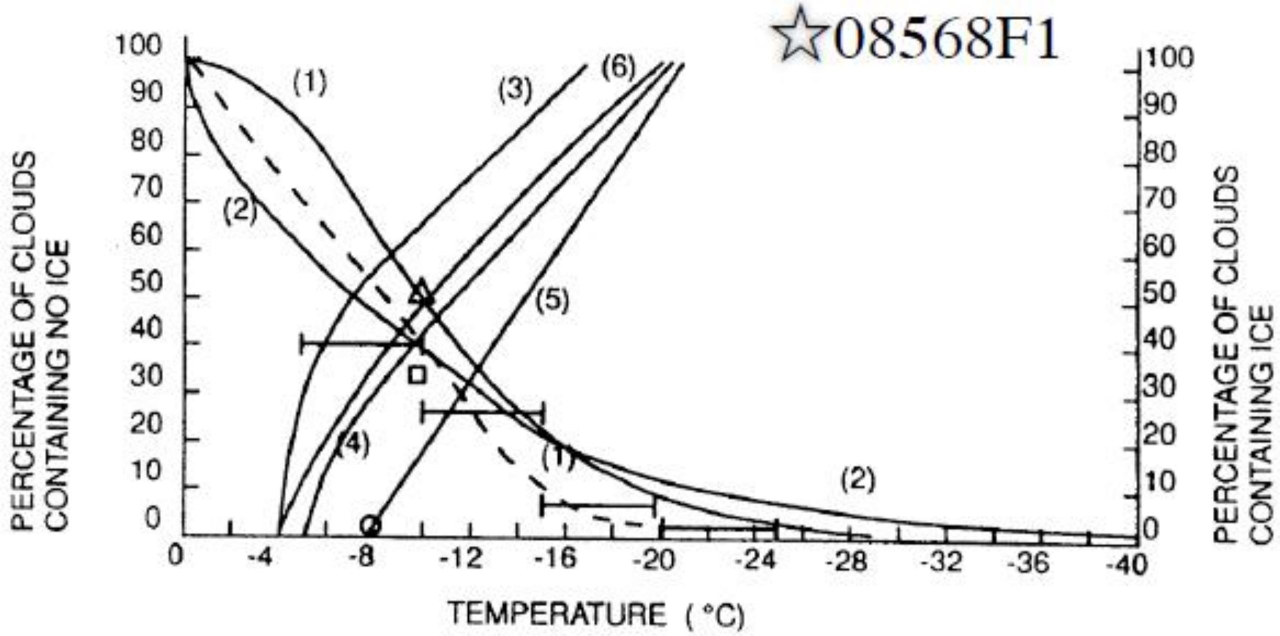


- **Ice (cold) clouds**: Made of ice crystals at $T < 235$ K.
- **Mixed Phase clouds**: Mixture of liquid droplets and ice for T between 235 and 273K
- **Liquid (warm) clouds**: Made of liquid droplets at $T > 273$ K

Cloud particles are not created directly from the vapor phase but from **suspended aerosol particles**

http://www.ucar.edu/news

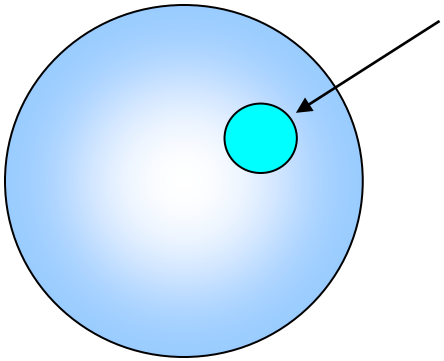
When do atmospheric clouds freeze?



- At the nominal freezing point of water nearly all cloud contain no ice
- Below -4 C or so, clouds start containing ice
- Below -20 C or so all clouds contain some ice
- Below -40 C or so all clouds are ice clouds

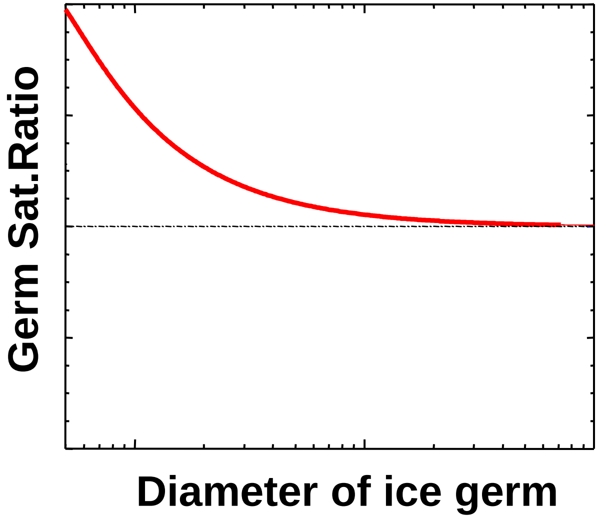
Surprise! It takes *a lot* of cooling to freeze

Curvature effect: the basis of nucleation



Ice Germs: generated in supercooled droplets

If you are cool enough – the ice germ will be around long enough to grow into a stable crystal.



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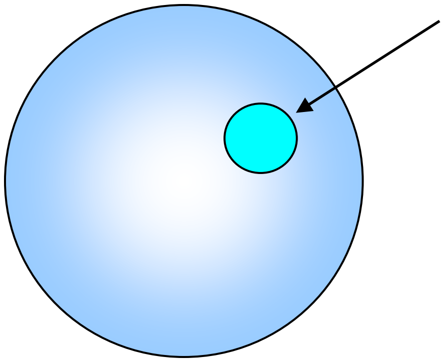

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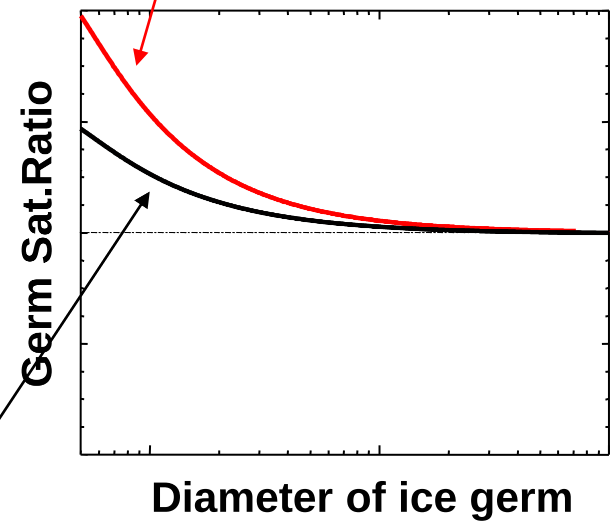
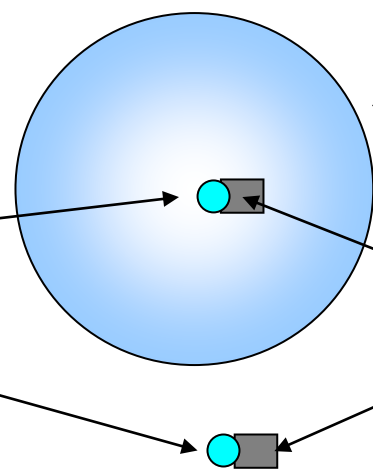


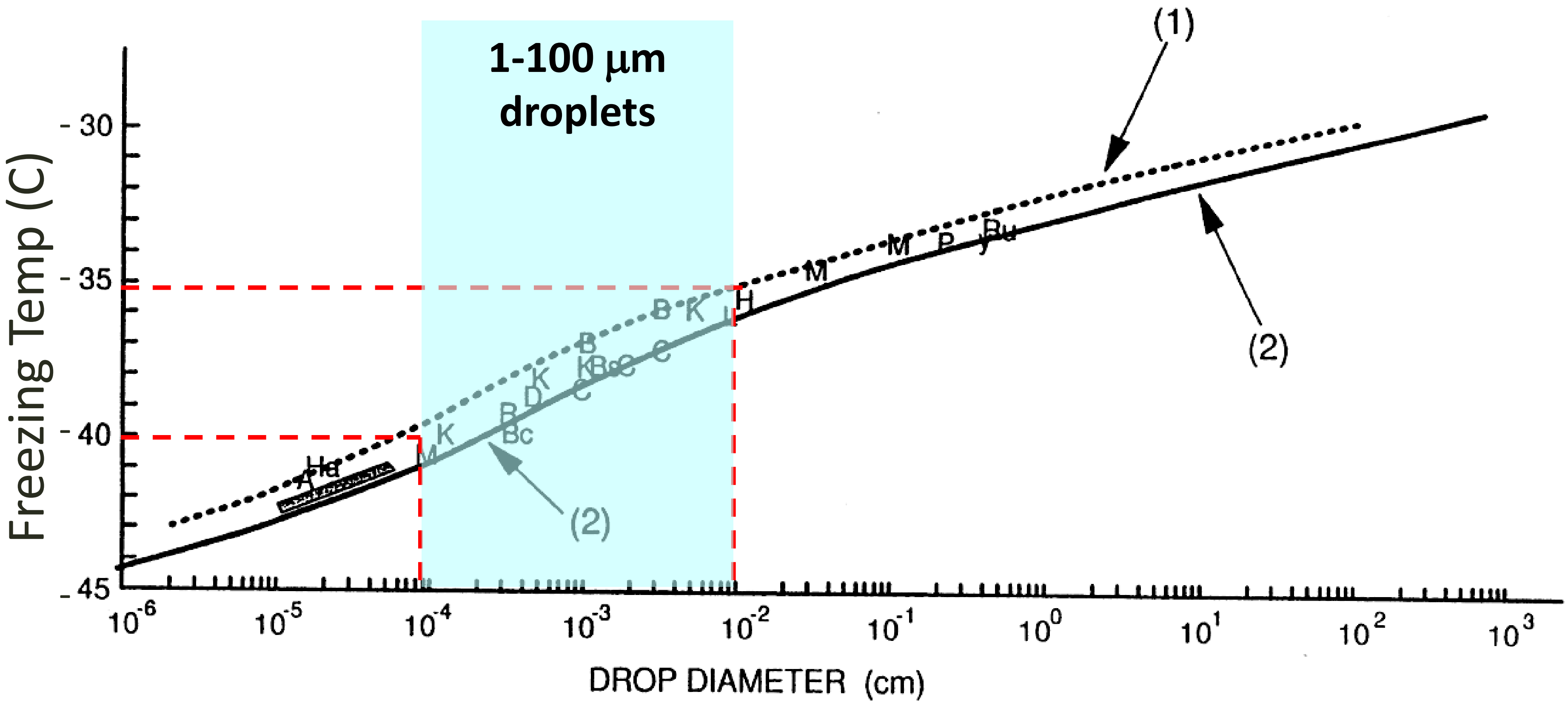


Ice Germs: generated on insoluble particles inside of superscooled droplets or suspended in air

Insoluble particle

(why do insolubles help?)

Maximum supercooling of extrapure water

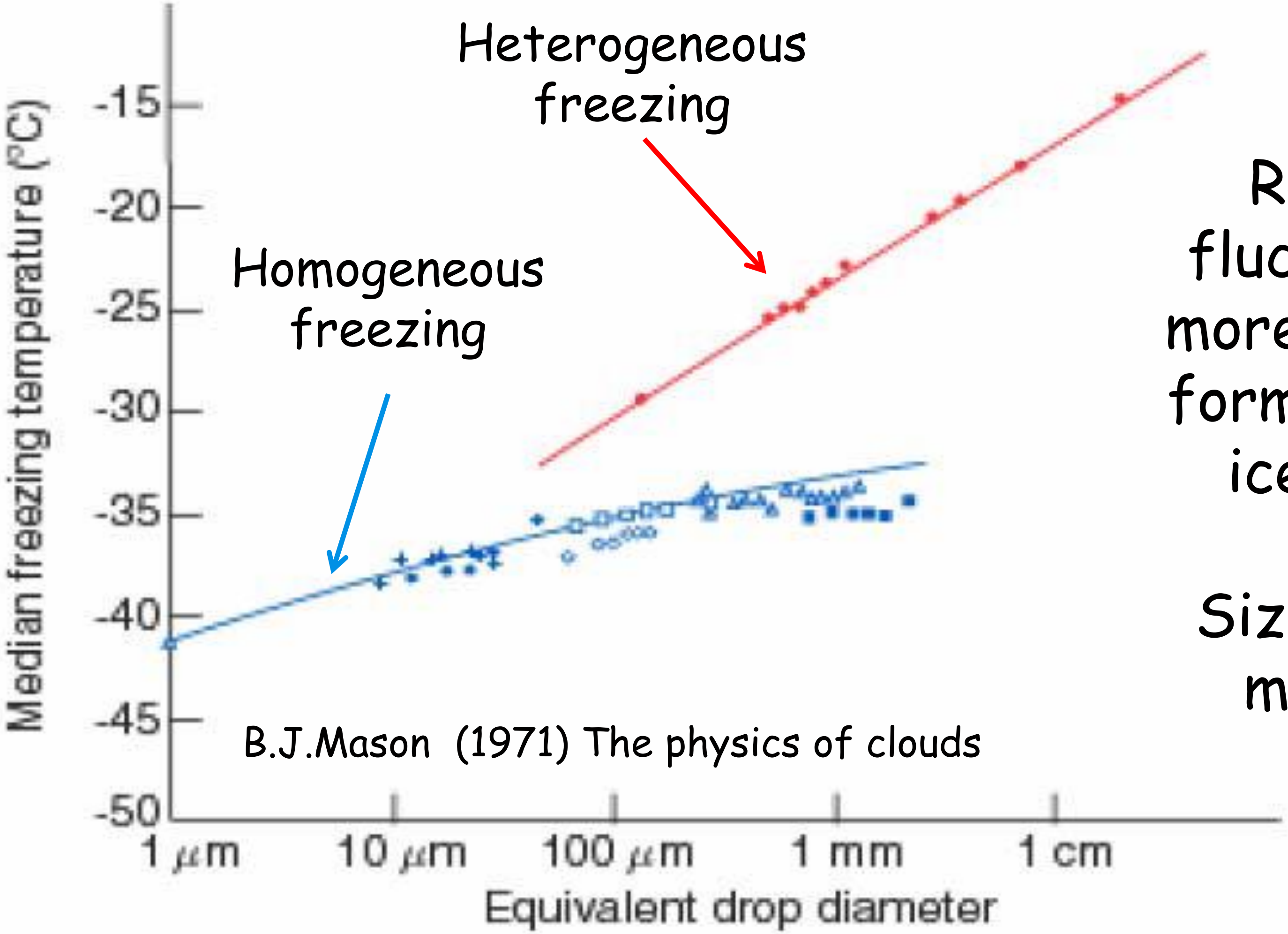


Result: Pure water cloud droplets in the atmosphere effectively start freezing at around -35°C

Problem: Why do ice cubes form in our freezer? Are the gods “bending the rules” so we can enjoy **ούζο**, **frappe** or your favorite drink?

Median freezing T of water samples

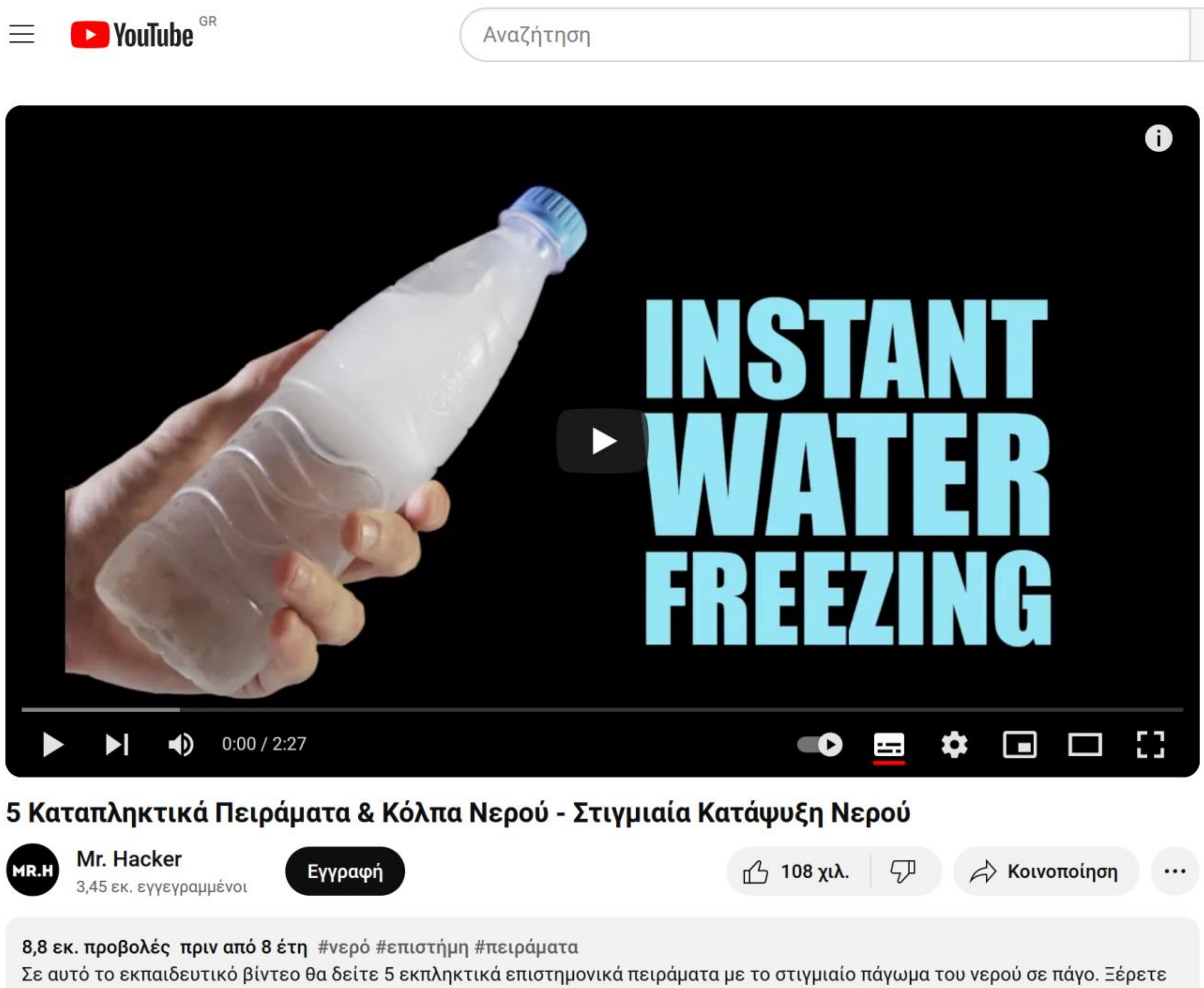
Not really…. Heterogeneous Freezing Greatly Facilitates Ice Formation



Random fluctuations more likely to form a stable ice germ:

Size always matters

The need to supercool and the role of perturbations in ice formation

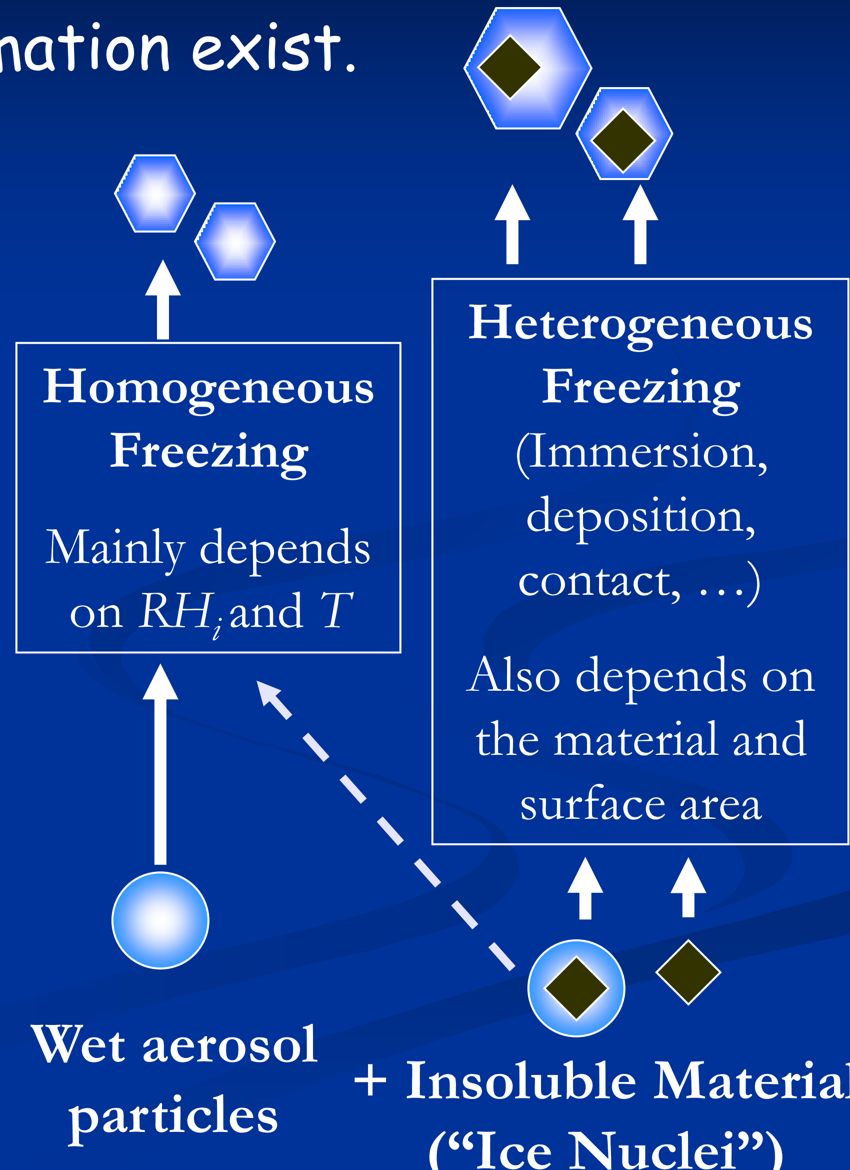


https://www.youtube.com/watch?v=kEHdyiBMgAg

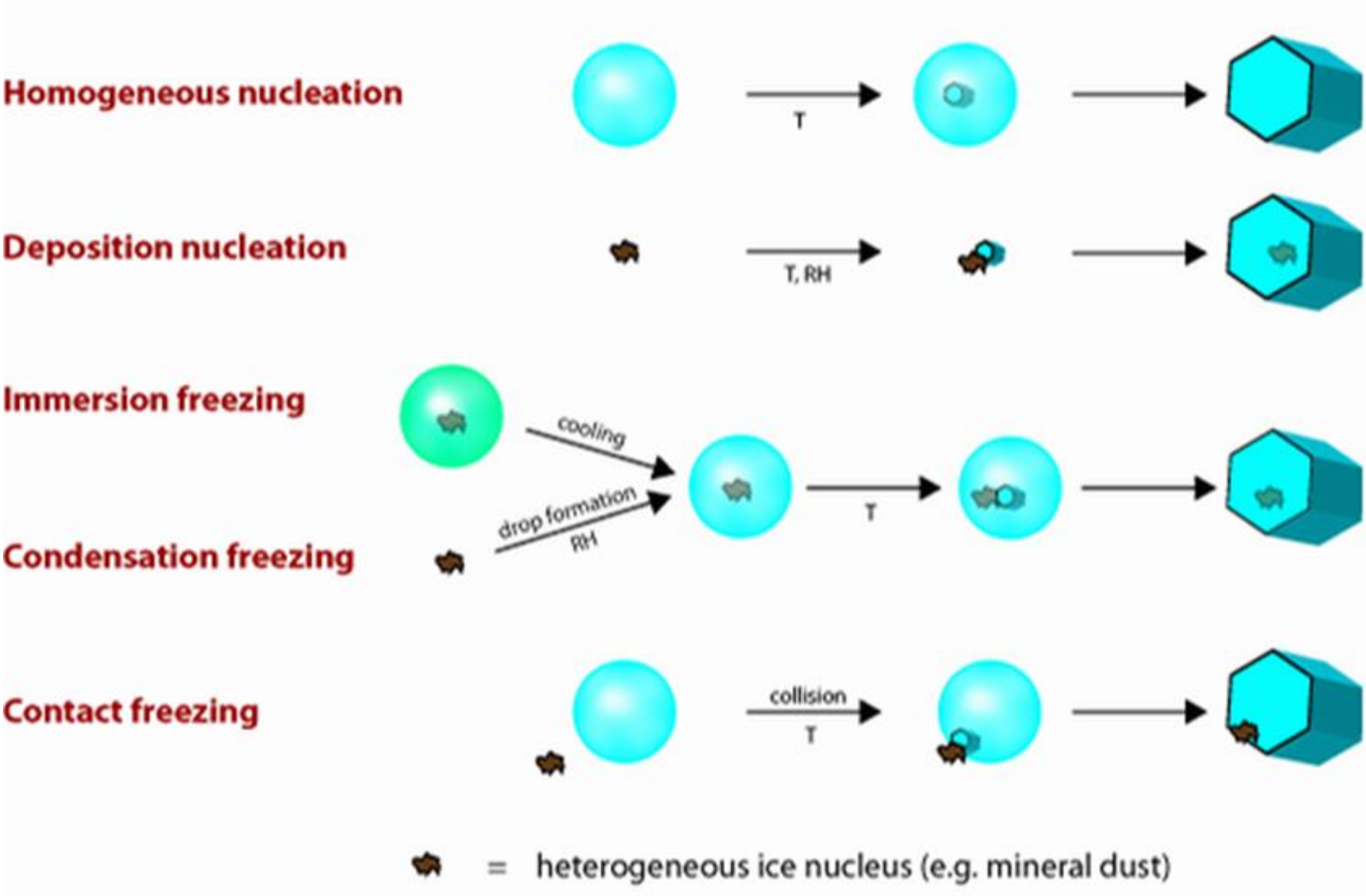
How do (ice water) clouds form?

Ice crystals also form on preexisting particles.

Multiple mechanisms for ice formation exist.

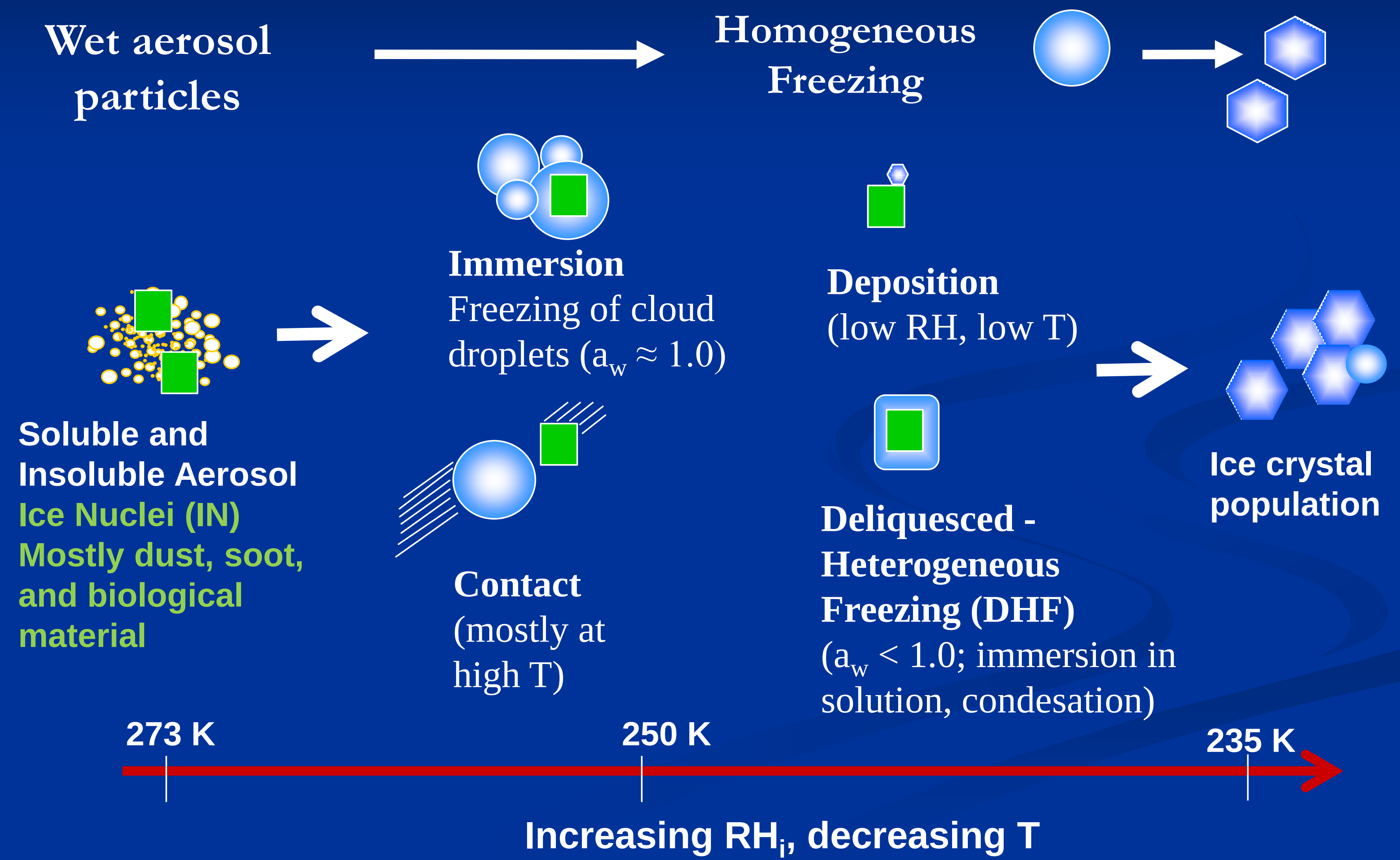


Heterogeneous ice nuclei: freezing modes

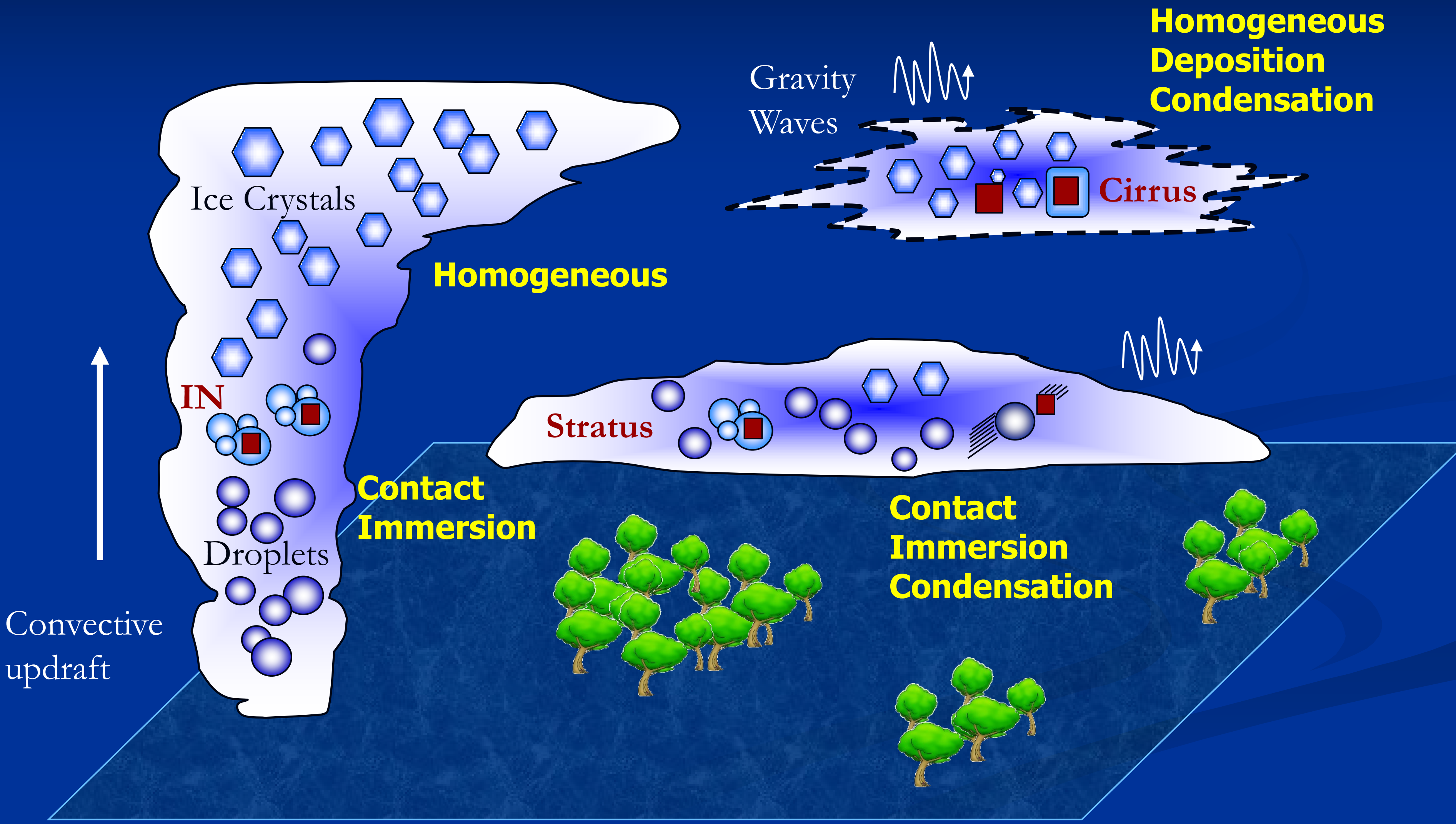


Heterogeneous ice nuclei: freezing modes

Multiple mechanisms for ice formation can be active.



Ice formation "modes" depends on cloud conditions (T, RH) and IN

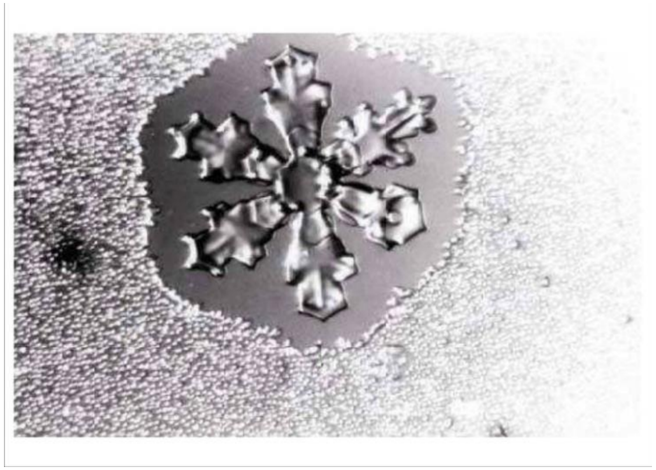


IN vs CCN: implications for clouds

IN are far less abundant than CCN. (1 in a million!)
CCN: 100-1000 cm^{-3} vs IN: 0.001-0.01 cm^{-3}

Hence, in an ice cloud, cloud water is typically distributed on ***orders of magnitude fewer*** cloud particles than in a liquid cloud.

Consequently, the ice crystals are much larger than cloud droplets and therefore much more likely to fall out as precipitation.



Most precipitation on the planet is initiated from the ice phase.

Heterogeneous ice nuclei: requirements

Insolubility: A rigid substrate is needed for the ice ”germ” formation.

Size: Larger particles are better IN (more active sites for forming a germ).

Chemical bond/Chrystallography: A similar bond as the ice crystal lattice is beneficial. Geometry of aerosol (surface steps/imperfections) is important.

Coatings: worsens the IN activity, because it depresses the water activity of the aerosol, and may deactivate the ice-forming sites on the particle.

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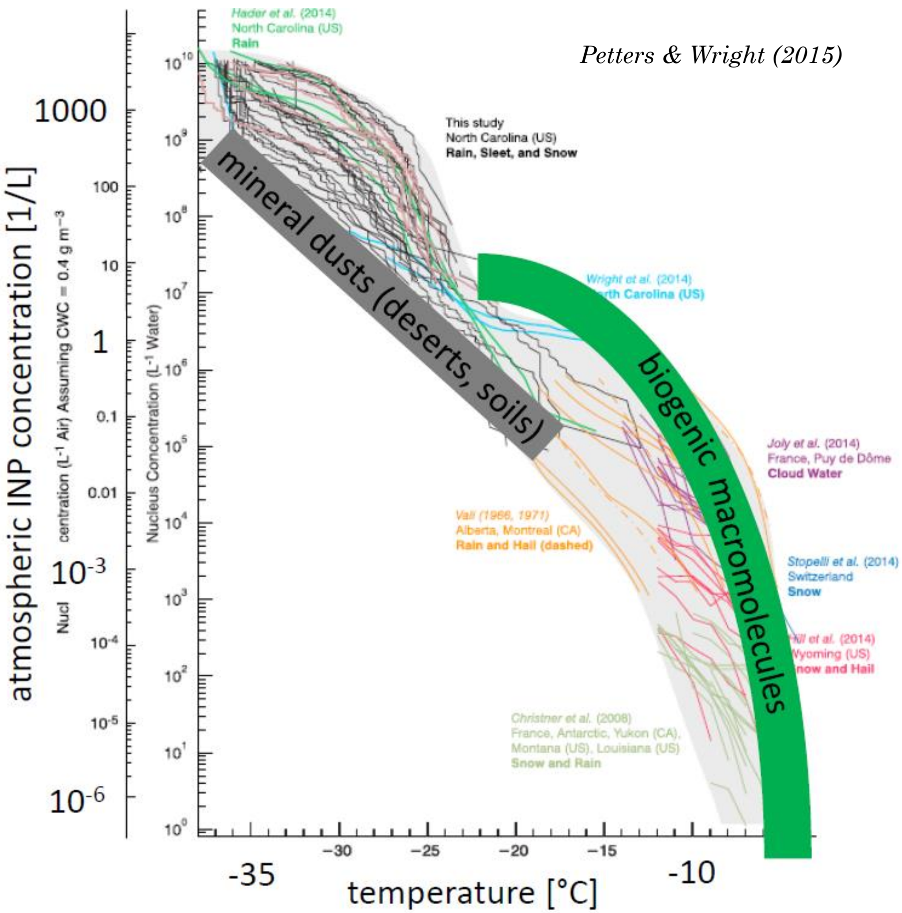
Table 2. Activation Temperatures T_a and Median Freezing Temperatures T_m Determined From Laboratory Experiments[a]

	Immersion Freezing		Contact Freezing	
Particle Type	T_a	T_m	T_a	T_m
Bacteria	−4°C,[b] a = 250 μm	−7°C,[b] a = 250 μm	−3°C[h]	−4.5°C[h]
Leaf litter	−5°C,[c] a = 350 μm	−9°C,[c] a = 350 μm	−5°C[c]	−10°C[c]
Pollen	−9°C,[d] a = 250 μm	−14°C,[d] a = 250 μm	−5°C[d]	−10°C[d]
Montmorillonite	−12°C,[e] a = 350 μm	−19°C,[e] a = 350 μm, and −24°C,[f] a = 50 μm	−3°C[e]	−8°C[e]
Kaolinite	−14°C,[e] a = 350 μm	−23°C,[e] a = 350 μm, and −32.5°C,[f] a = 50 μm	−5°C[e]	−12°C[e]
Soot	−18°C,[g] a = 350 μm	−28°C,[g] a = 350 μm		−18°C[h] (extrapolated)

[a]Immersion freezing temperatures are for defined drop radii a, and contact freezing temperatures are for arbitrary drop sizes.
[b]*Levin and Yankofsky* [1983].
[c]*Diehl et al.* [2001b].
[d]*Diehl et al.* [2002].
[e]*Pitter and Pruppacher* [1973].
[f]*Hoffer* [1961].
[g]*Diehl and Mitra* [1998].
[h]*Gorbunov et al.* [2001].

Observed concentrations of INPs around the globe



- ✓ Ice nuclei are **rare** compared to CCN (one in **10^5** to **10^6** aerosol particles at T> −38 °C)
- ✓ In the atmosphere, mainly two main INP types contribute:
  mineral dust particles and **biological particles** (e.g., pollen or bacteria)
- ✓ Microorganisms have macromolecules causing the ice activity (proteins or polysaccharides)
  -They are very ice active, but VERY rare
  -Heat can destroy bio INP (proteins)
- ✓ Mineral dust particles have ice active sites
  -They are ice active at lower temperatures but are more abundant, however, still rare
  -**K-feldspar** is the most ice active mineral dust


THANK YOU !!