Aerosol particle formation in the atmosphere: the CLOUD experiment at CERN, the possible influence of galactic cosmic rays, and comparison to field observations

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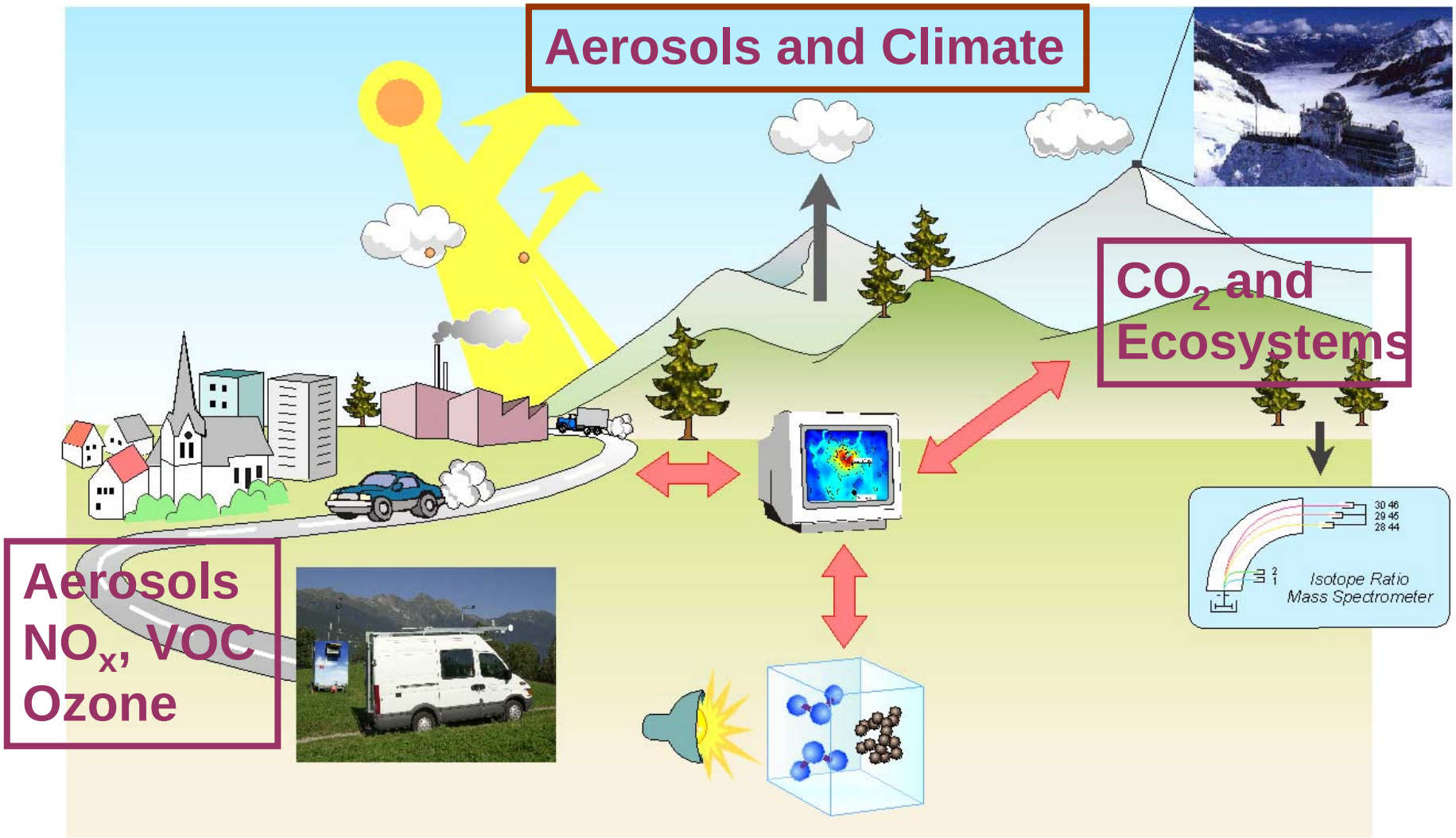
Geneva, 16 April 2014

The Laboratory of Atmospheric Chemistry at the Paul Scherrer Institute

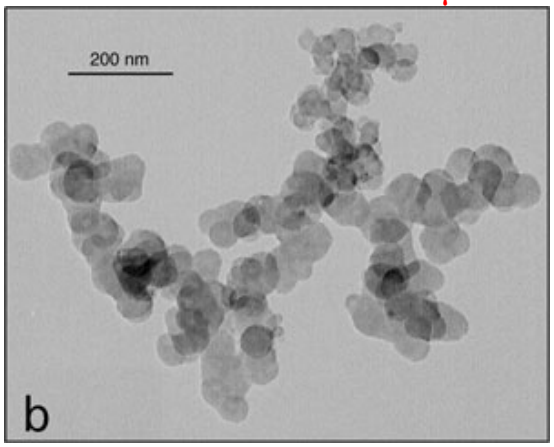


Primary and secondary aerosols

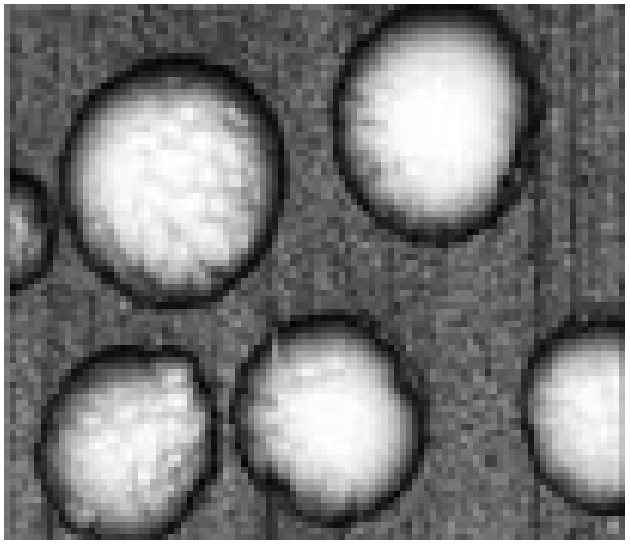
Definition: PM10 =
Particles with aerodynamic diameter <10μm

Examples:

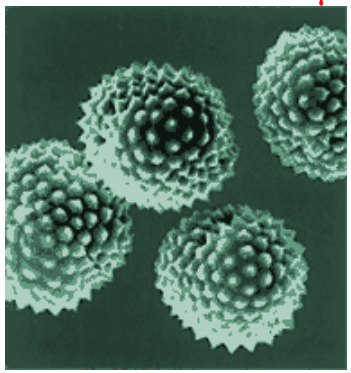
Diesel soot: ca. 0.1 μm



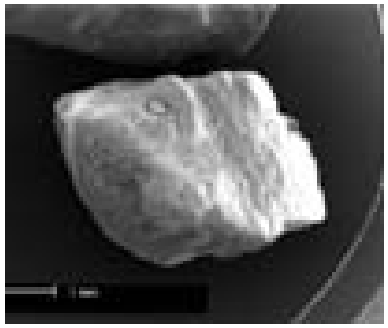
Ammonium sulfate: ca. 0.1 μm



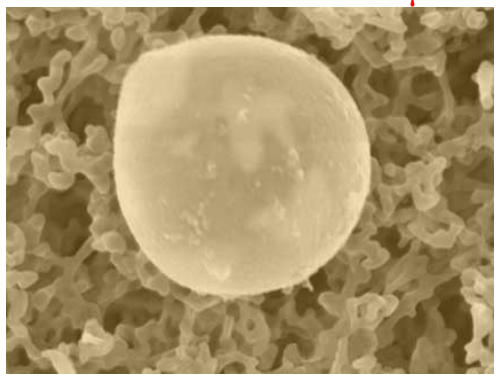
Pollen: 10 - 100 μm



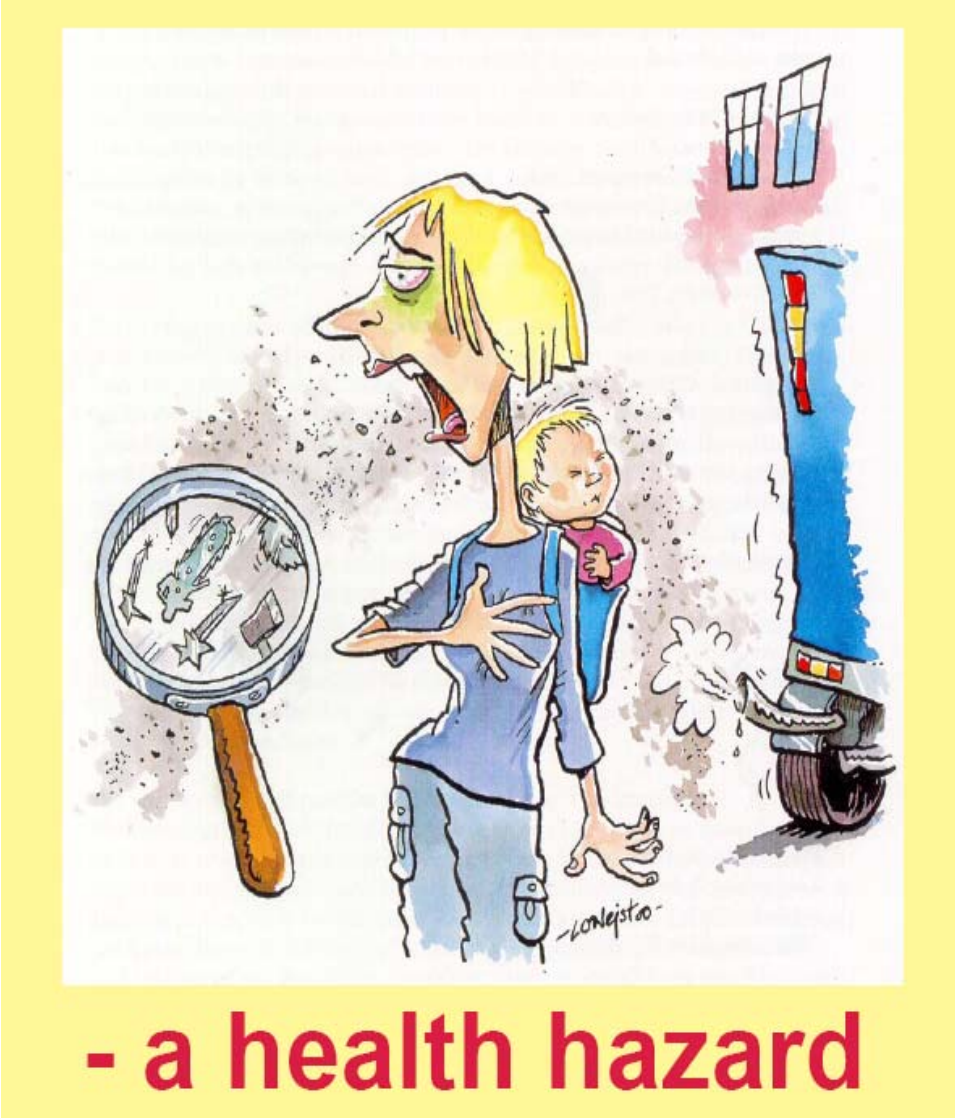
Sea salt: 0.2 - 10 μm



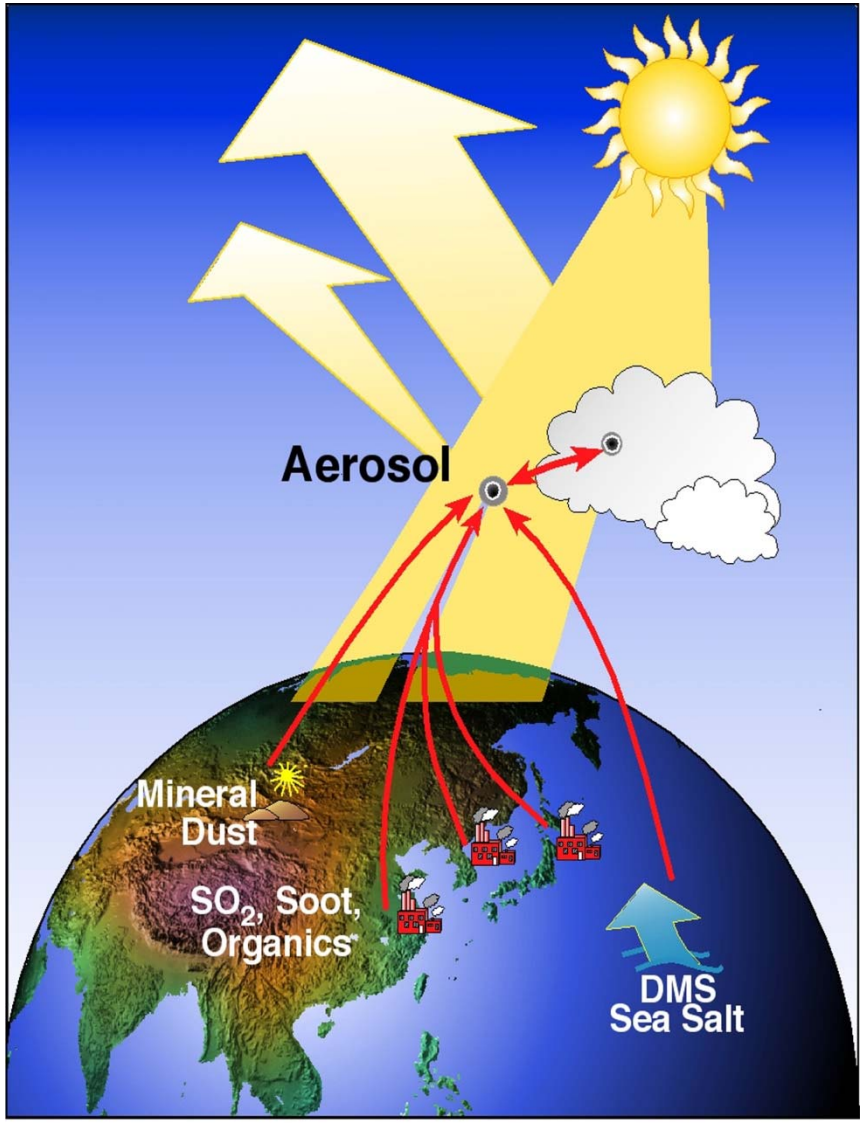
Mineral dust: 0.2 - 10 μm



Aerosols affect our health and have an impact on climate

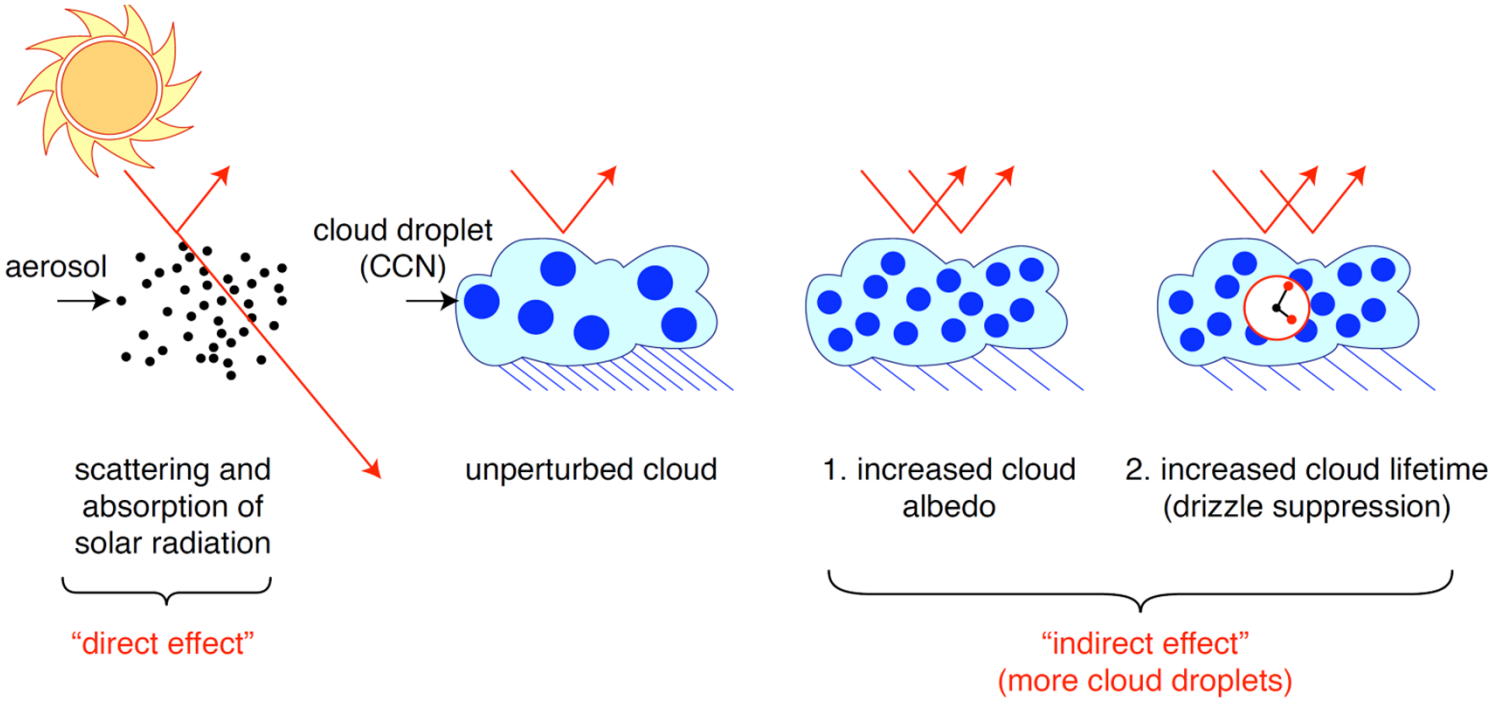


Source: www.ecocouncil.dk

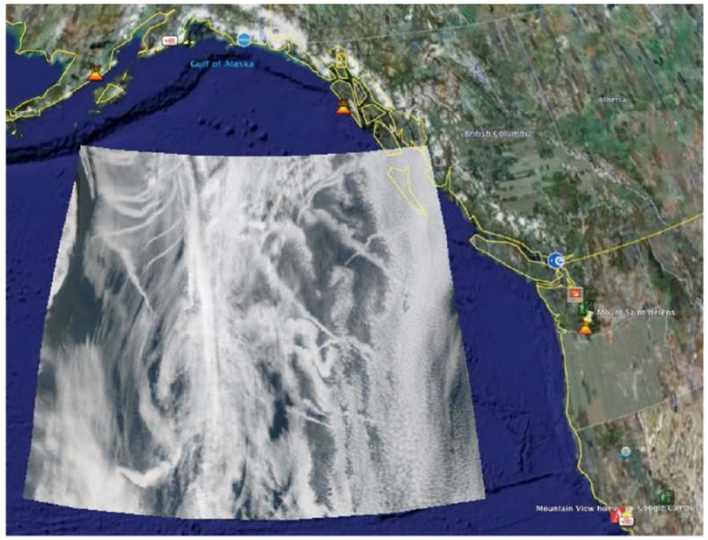


http://saga.pmel.noaa.gov/aceasia/

The radiative forcing of aerosols



- Aerosols are tiny liquid or solid particles suspended in the atmosphere
- Above 50nm size they provide Cloud Condensation Nuclei (CCN)



ship tracks forming stratocumulus deck in North Pacific

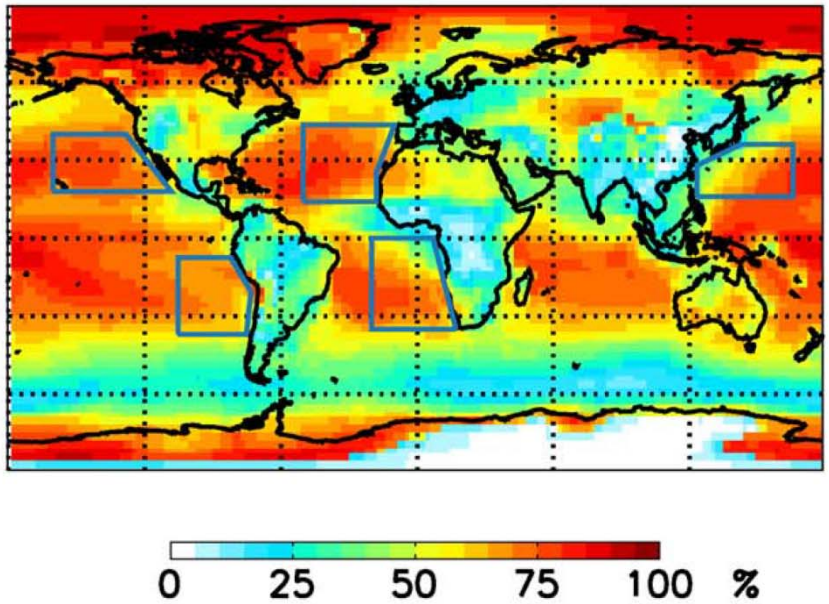
Courtesy: J. Kirkby, CERN

Atmospheric aerosol nucleation is important for cloud formation

Origin of global cloud condensation nuclei, CCN, 500-1000 m above ground level

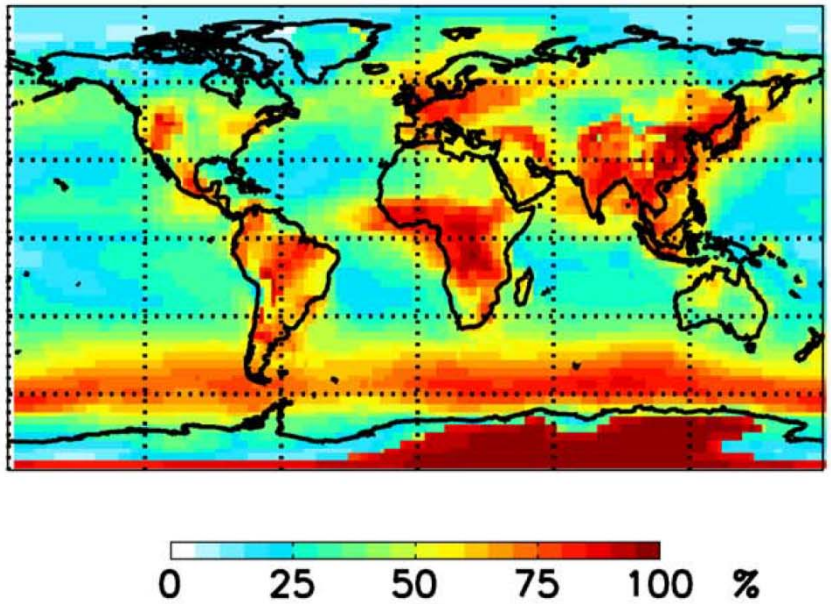
Secondary production - nucleation
(gas-to-particle conversion)

A: CCN(0.2%) contribution from nucleation



Primary production
(dust, sea-spray, biomass burning)

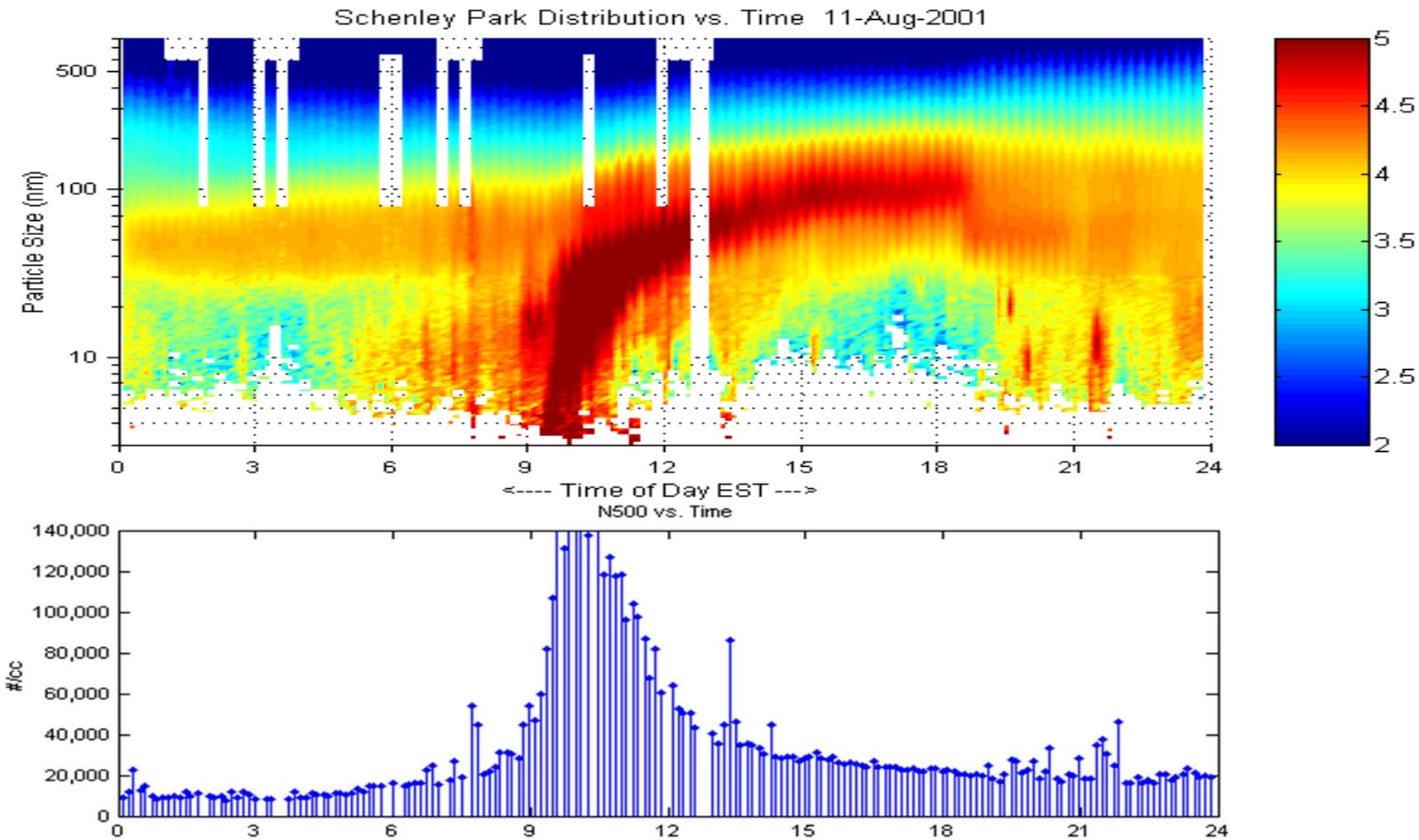
B: CCN(0.2 %) contribution from Primaries



45% of global CCN attributed to nucleation

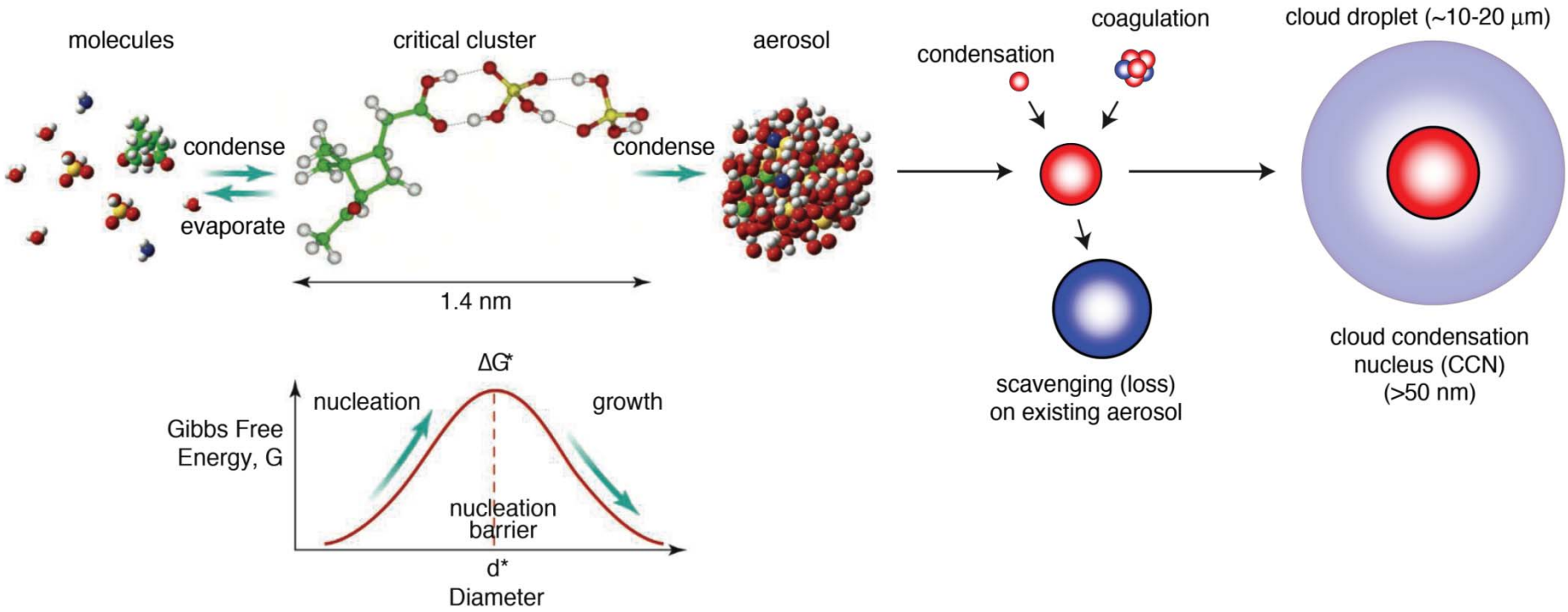
Merikanto et al., ACP 2009

Nucleation
Example: Pittsburgh (August 11, 2001)



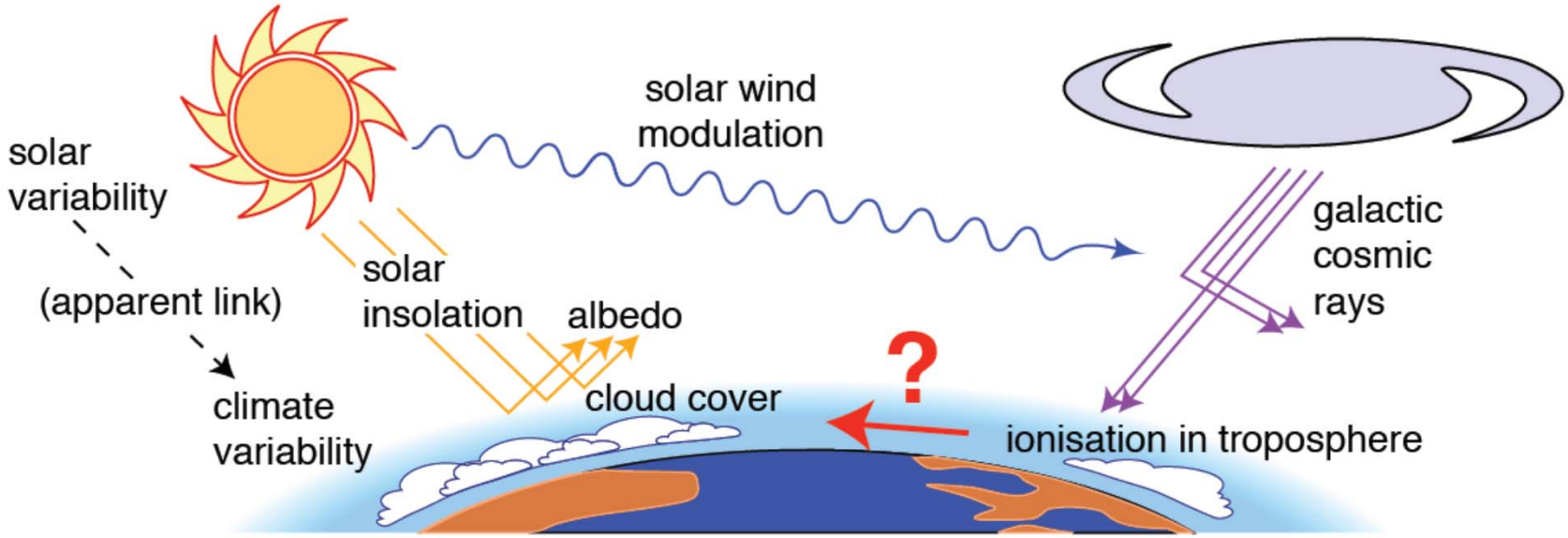
Courtesy: S. Pandis

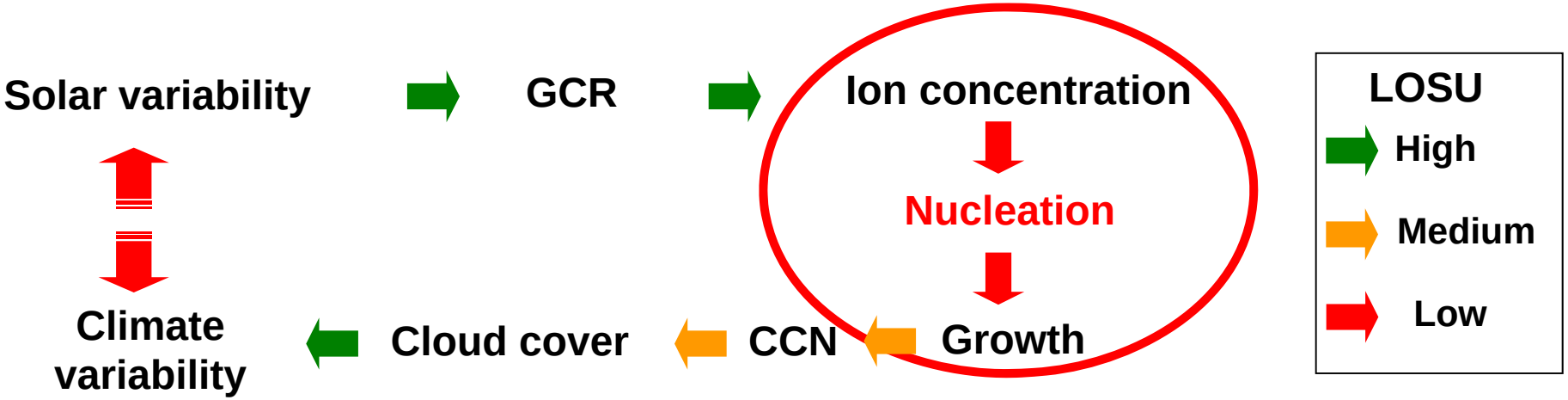
Atmospheric aerosol nucleation (gas-to-particle conversion)



Adapted from Zhang (2010)

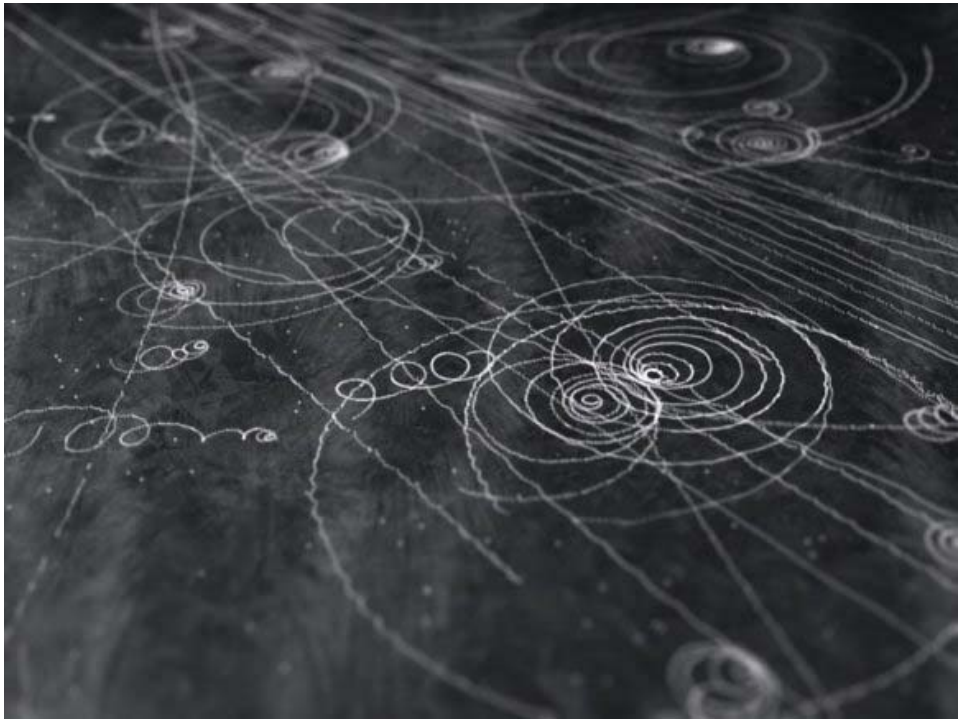
A big current debate:
Do galactic cosmic rays influence clouds and climate?





LOSU: Level of Scientific Understanding

The Wilson cloud chamber, 1911

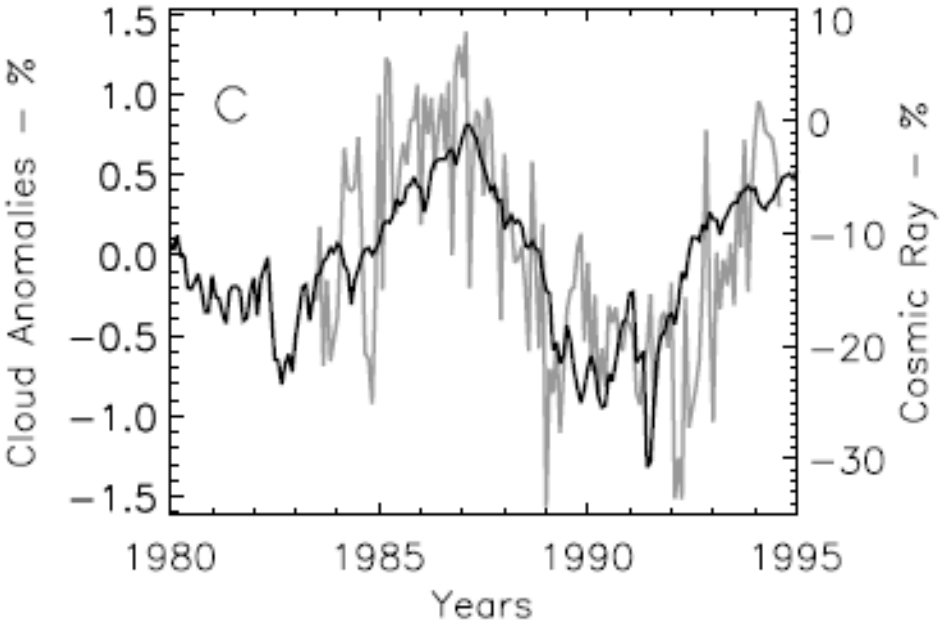


Milano

Cosmic rays and cloud cover

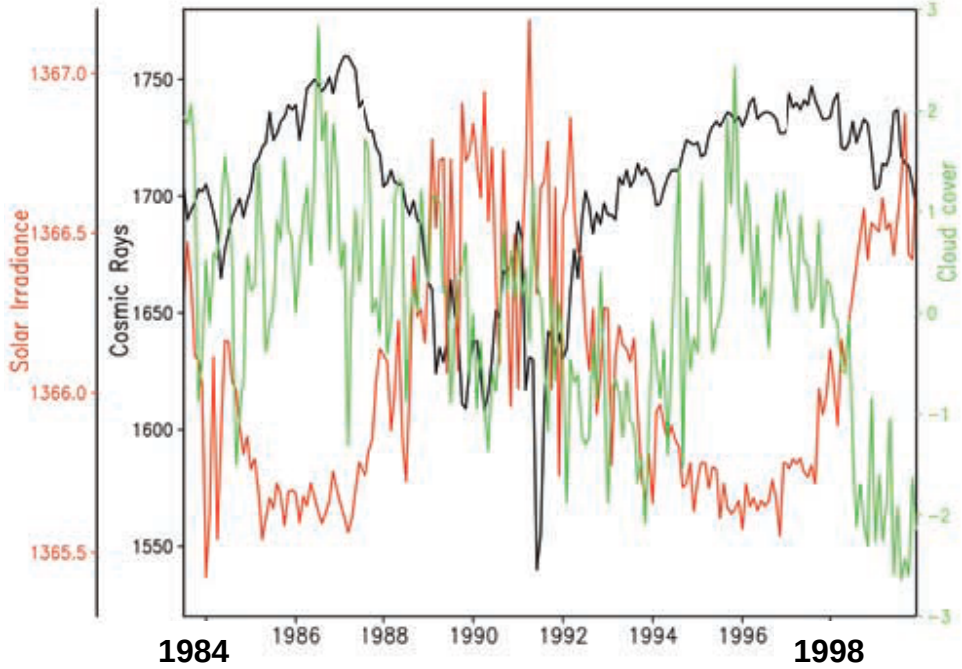
Conflicting data

Cosmic rays
Cloud cover



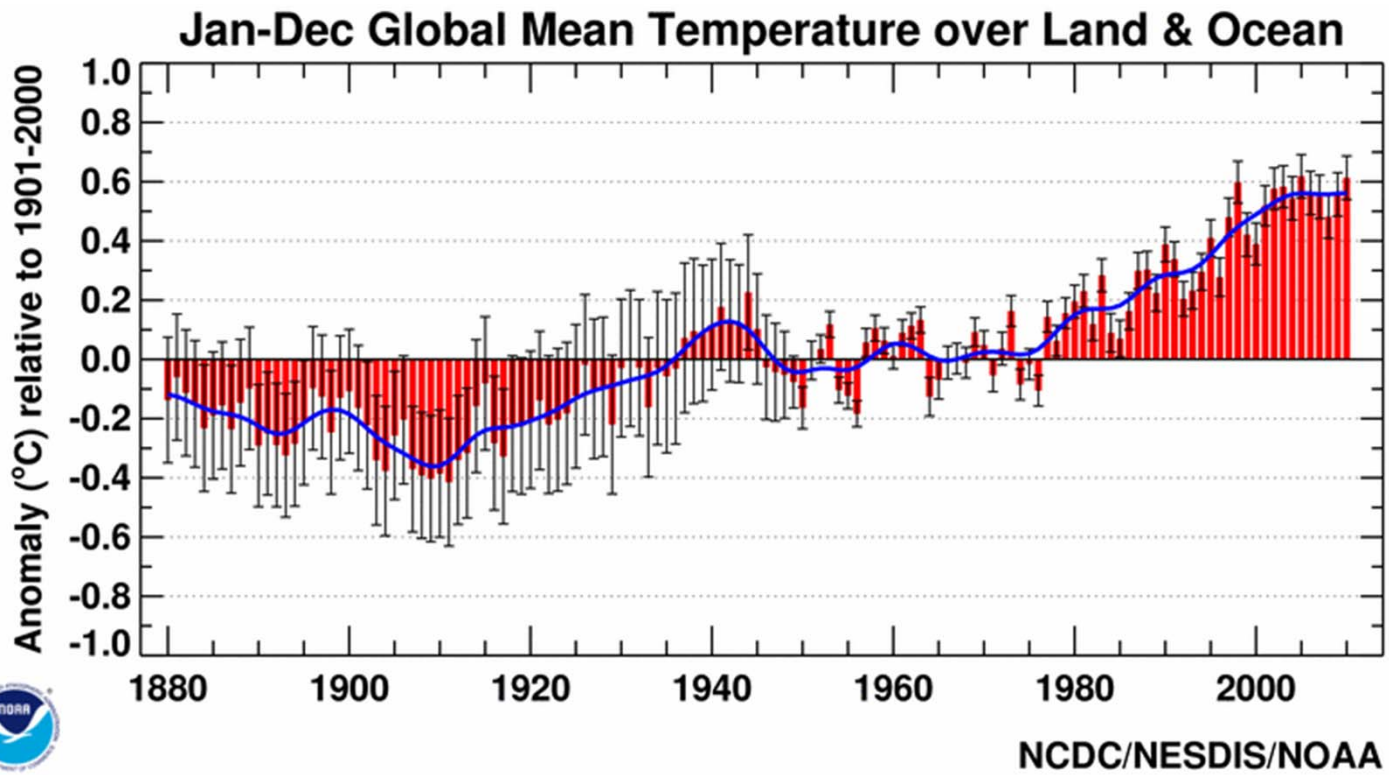
Marsh and Svensmark, 2000

Solar irradiance
Cosmic rays
Cloud cover



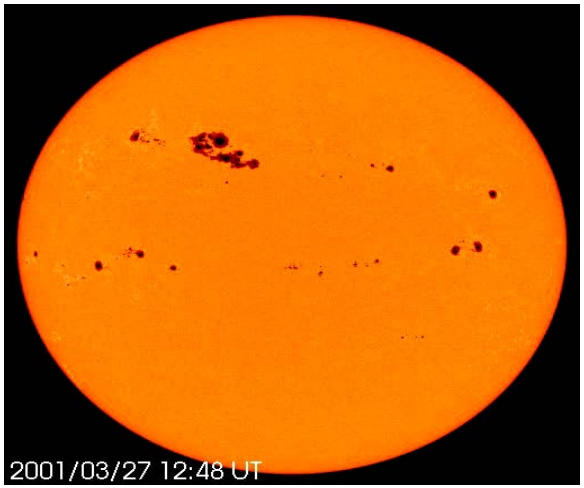
Kristjansson et al., 2002

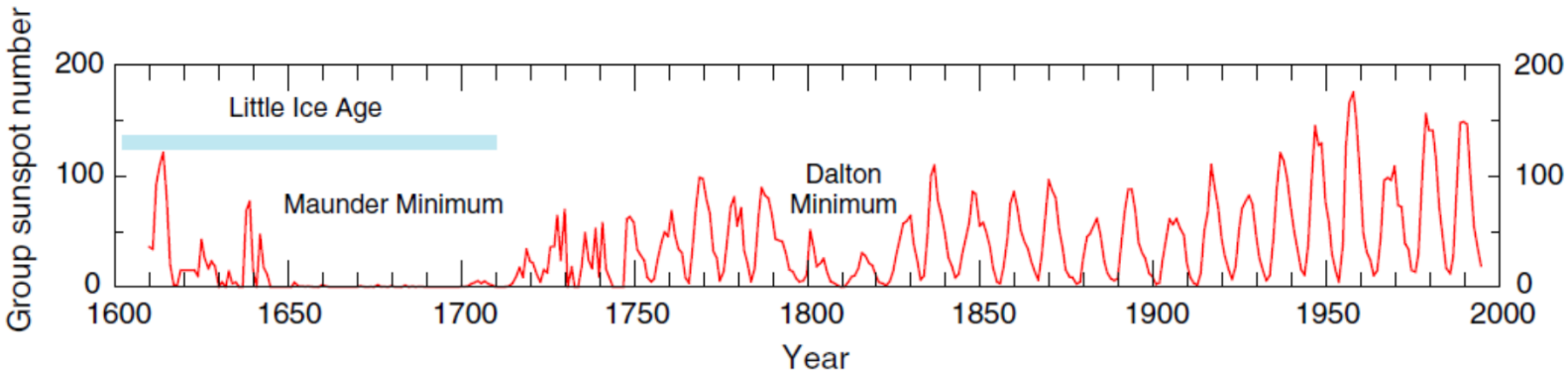
Global mean temperature anomalies



Solar activity and temperature I

Sunspot number

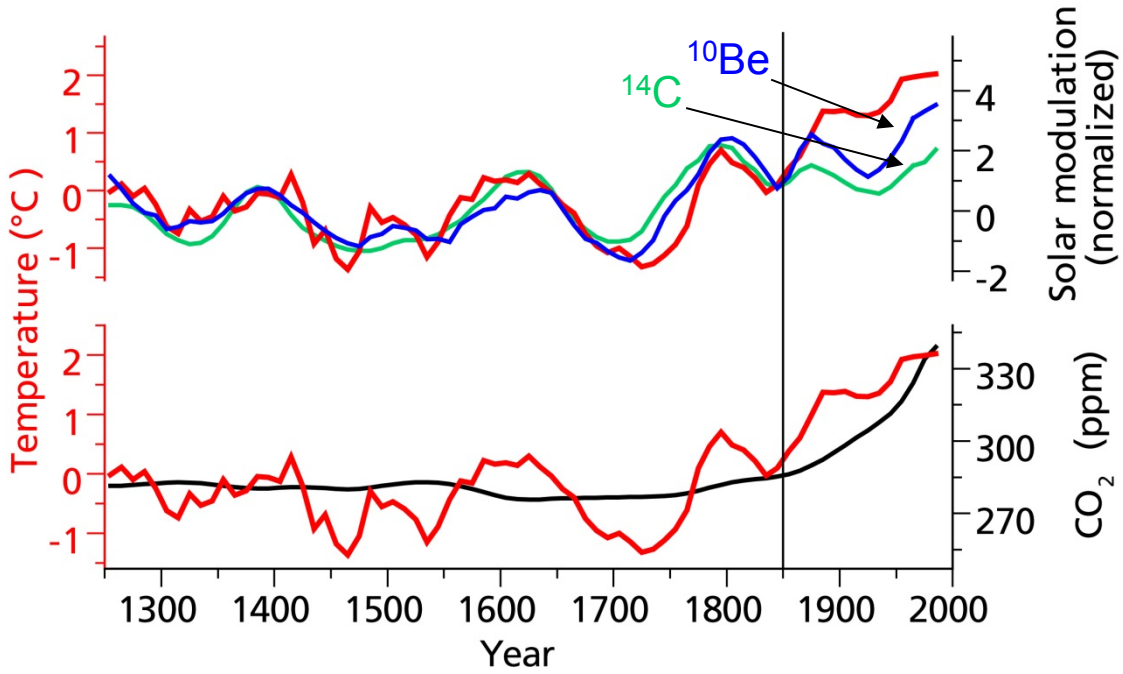




Solar activity and temperature II

http://www.psi.ch/media/temperature#

Eichler et al. GRL 36 (2009)



Temperature proxy: ice core oxygen isotope

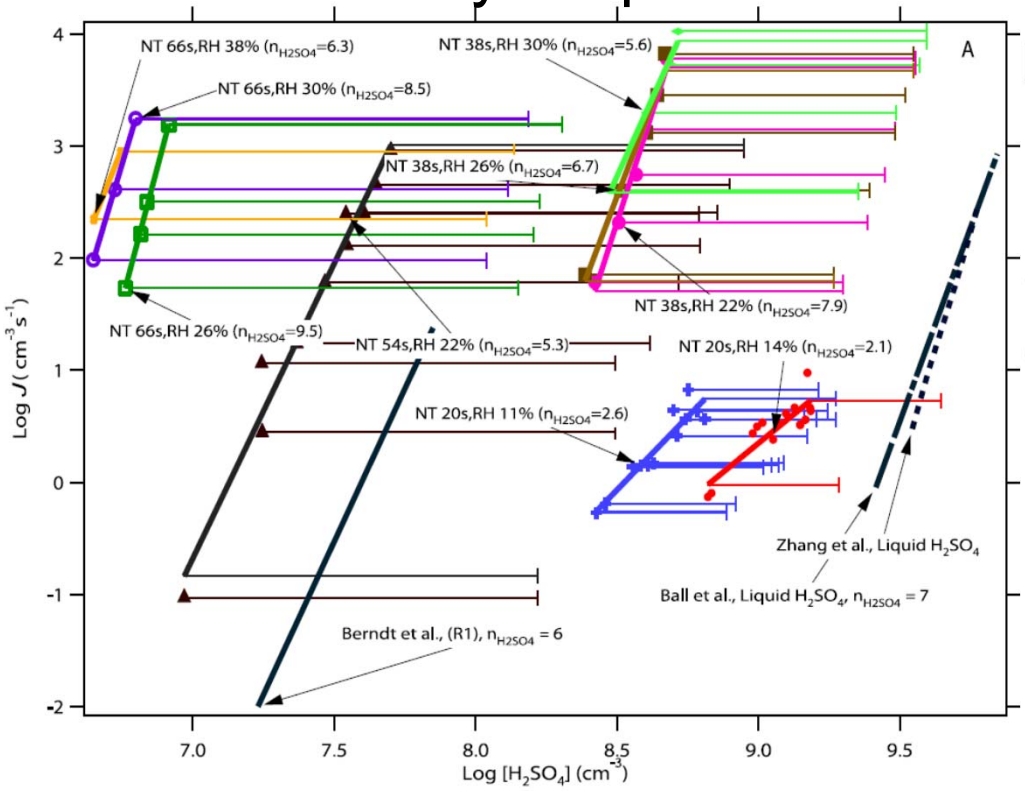
Nucleation:

Very large discrepancies between different laboratory experiments, and between lab and field

Steeper slopes and/or higher conc. in lab expts

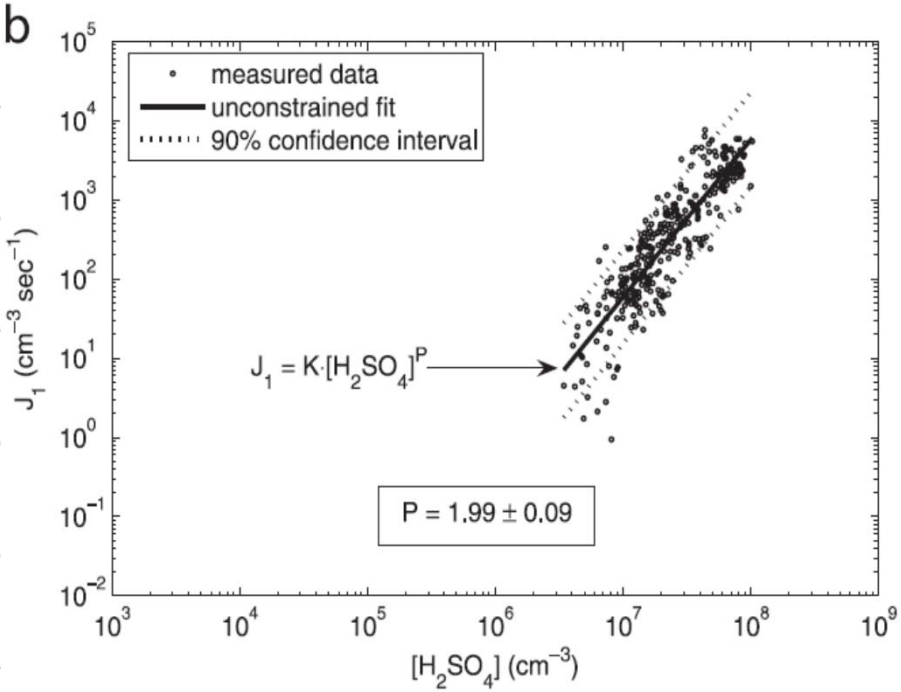
slope: number of sulfuric acid molecules in the critical cluster

Laboratory: slope = 2 to 9



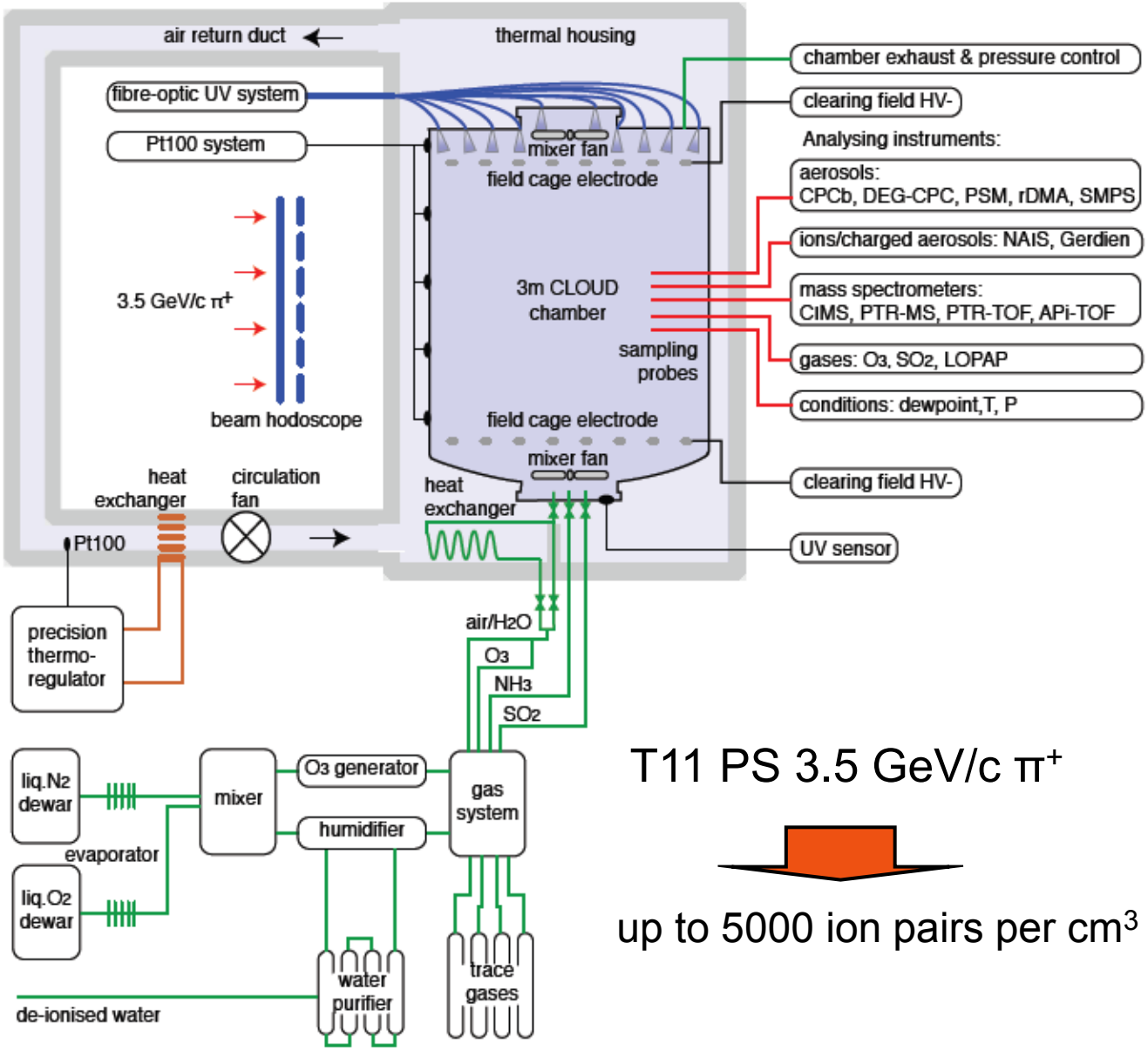
Benson et al., 2008

Field: slope ≅ 2



Kuang, McMurry et al., 2008

The CLOUD chamber at CERN



T11 PS 3.5 GeV/c π^+

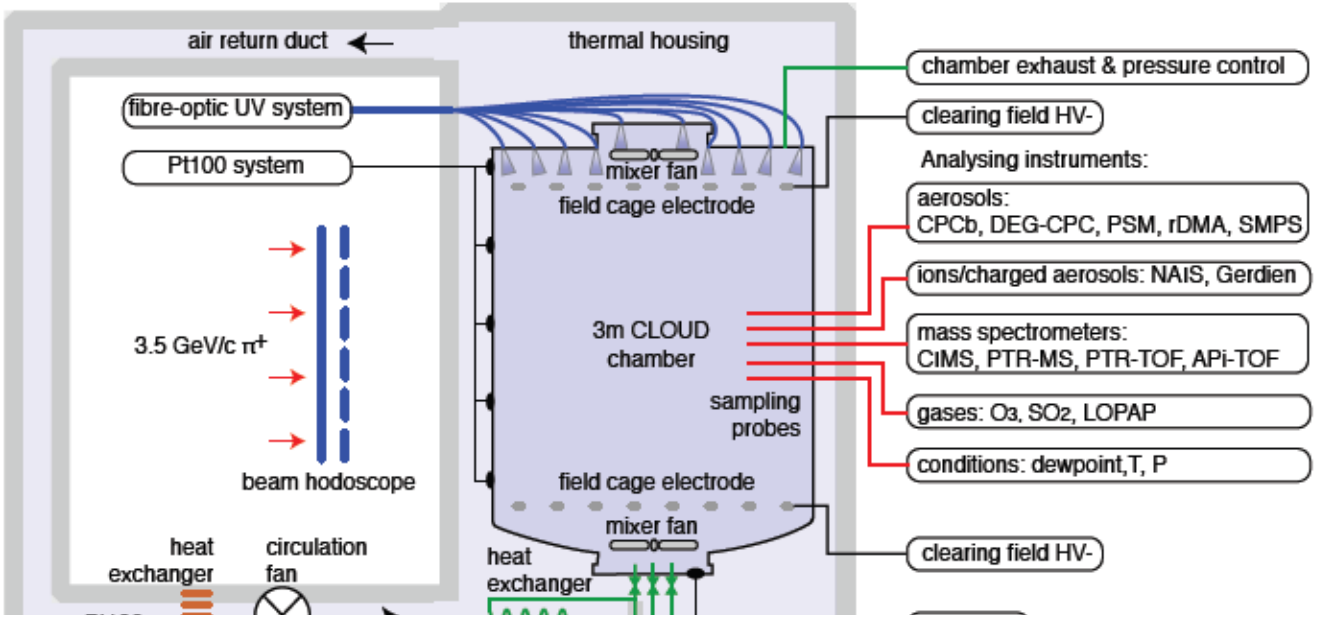
up to 5000 ion pairs per cm^3

OH from photolysis of ozone (and ozonolysis of double bonds)

H_2SO_4 from reaction of SO_2 with OH

Kirkby et al., Nature 2011

The CLOUD chamber at CERN



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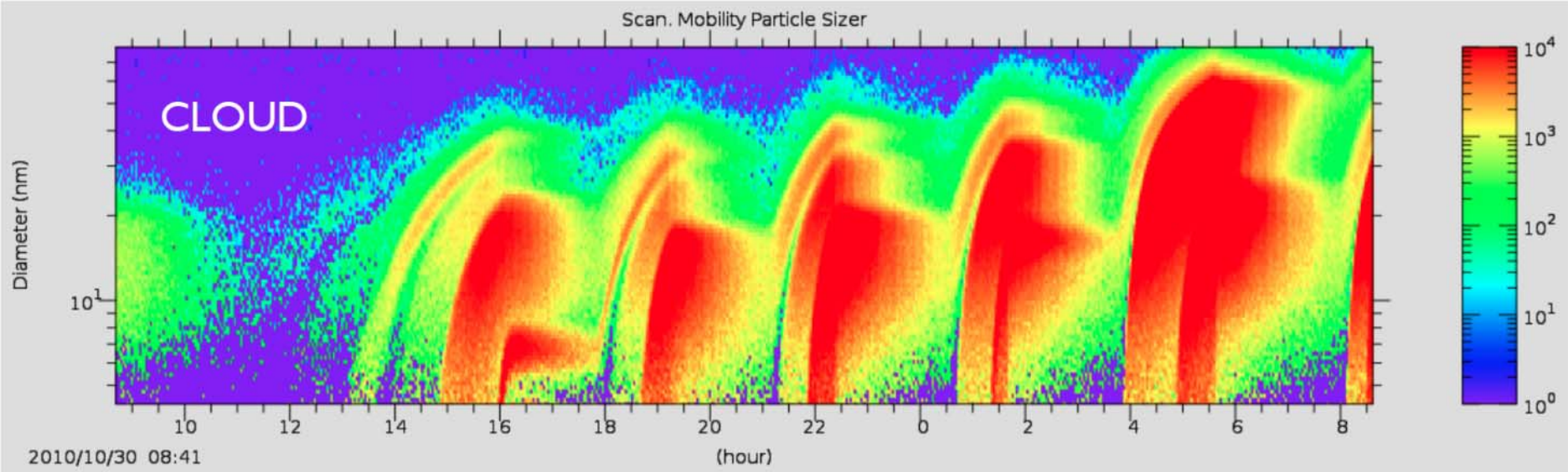
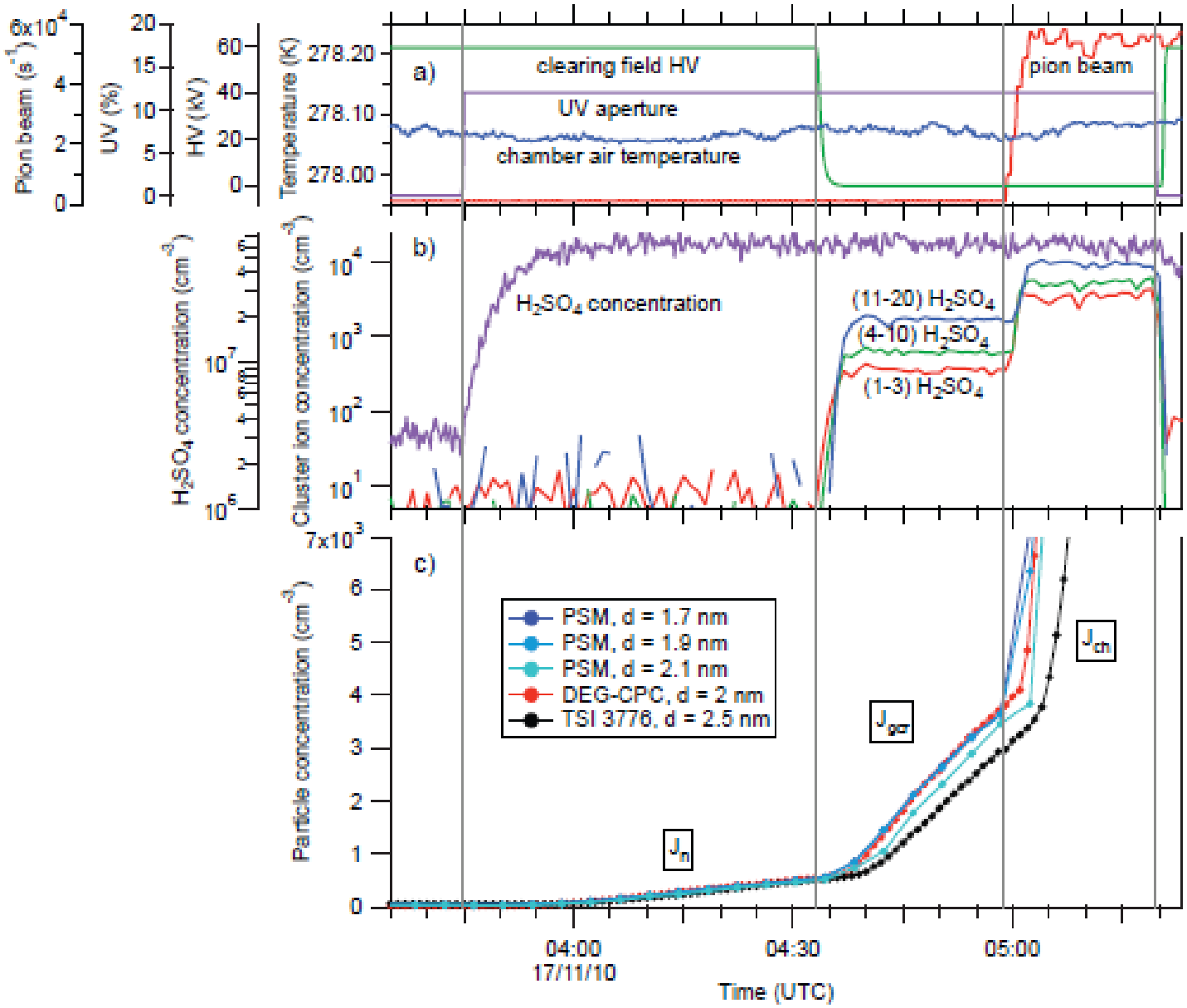
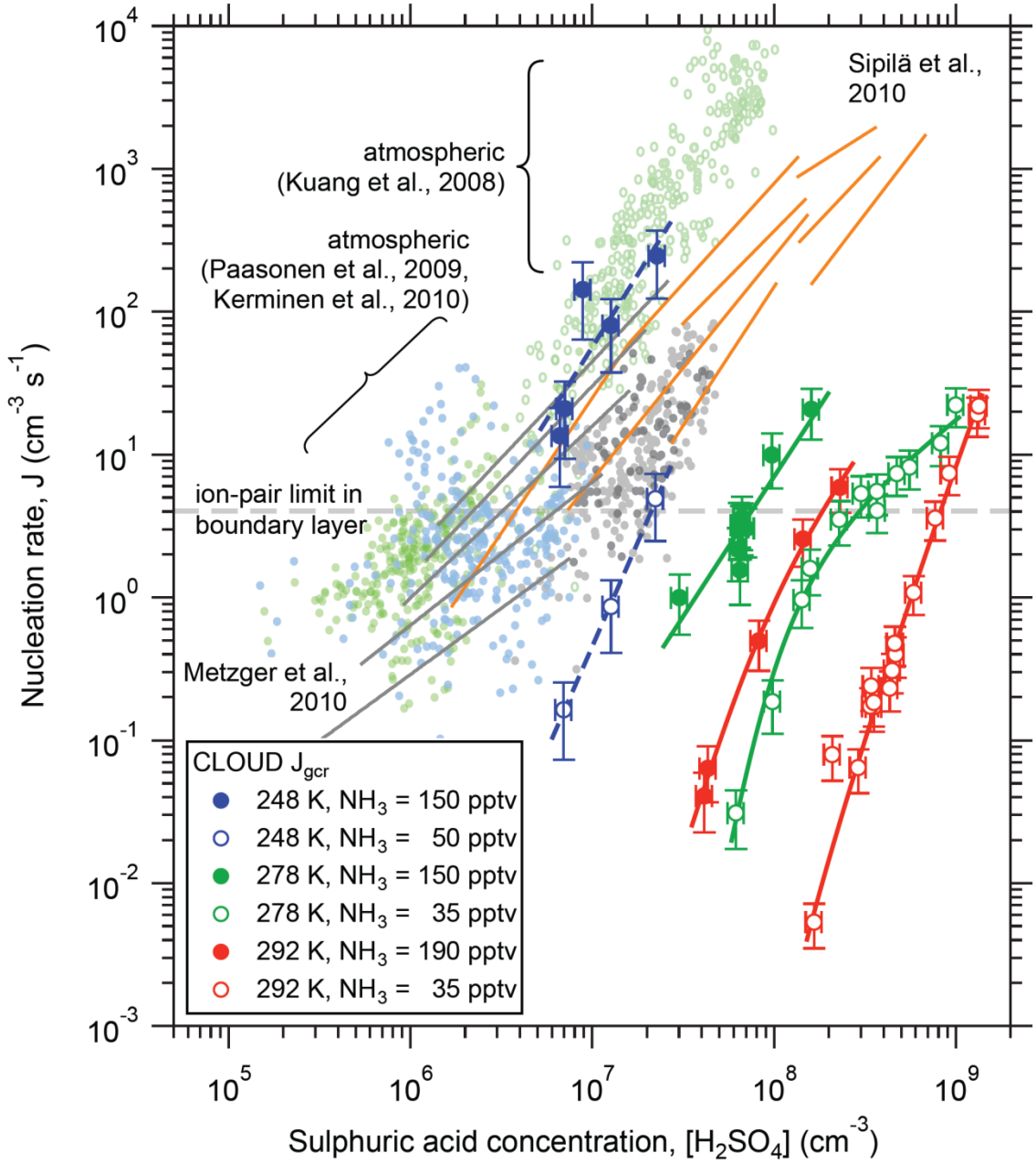


A typical experiment



Kirkby et al., Nature 2011

Nucleation rate of H_2SO_4 (and NH_3)



Boundary layer nucleation cannot be explained either by binary (H_2SO_4-H_2O) or by ternary nucleation with ammonia

Even with ion enhancement, ternary NH_3-H_2SO_4-H_2O is too low by a factor 10-1000

➔ Other ingredients needed to explain atmospheric data

Kirkby et al., Nature 2011

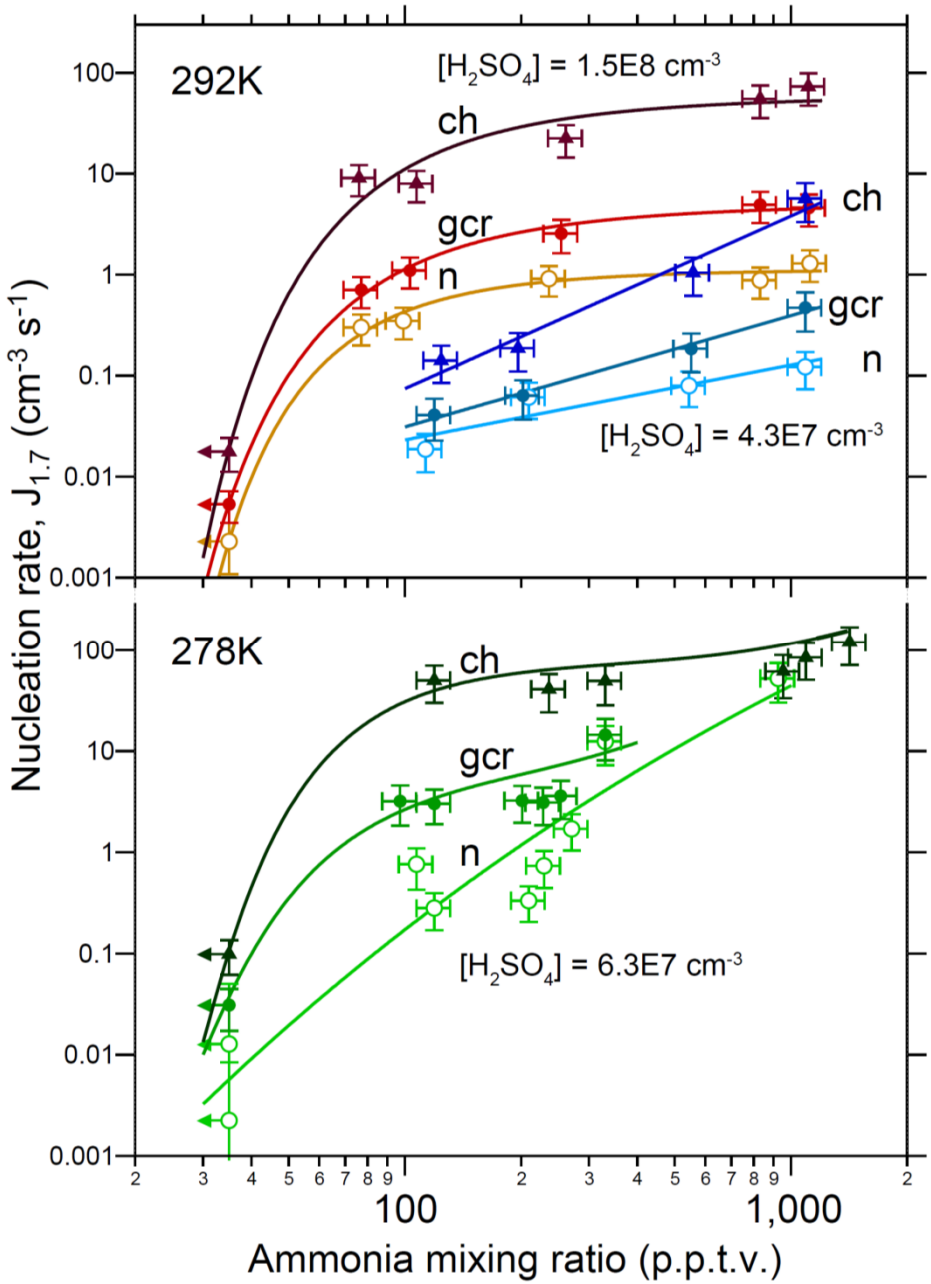
The influence of ammonia

Very small amounts of ammonia (and similar molecules, amines, urea) result in a very high increase in the nucleation rate (1000 x at 100 ppt) Above ~100 ppt: saturation

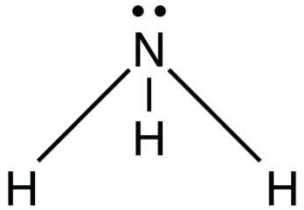
(NH_3 intentionally added)

Contaminants play a crucial role!

Kirkby et al., Nature 2011

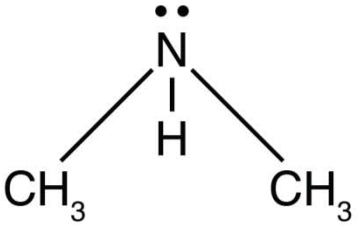


Addition of amines and terpenes



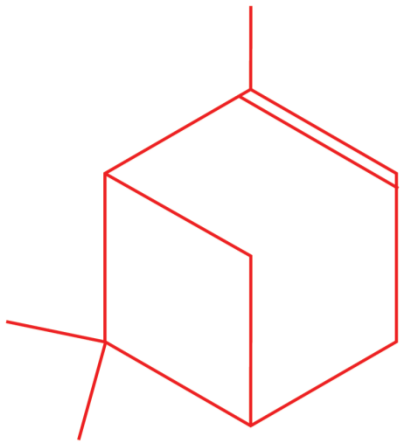
ammonia
(NH3, MWt. 17.03)

Kirkby et al., Nature 2011



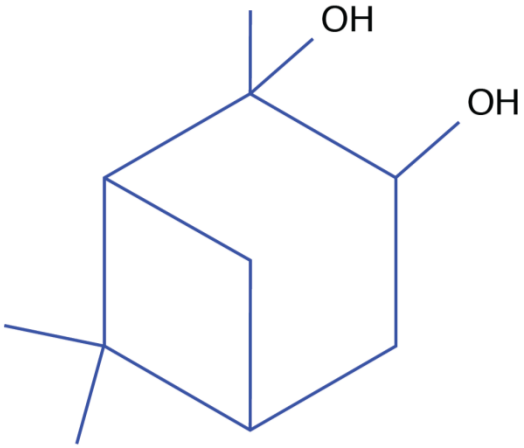
dimethylamine
(C2H7N, MWt. 45.08)

Almeida et al., Nature 2013



alpha-pinene
(C10H16, MWt. 136.23)

Analysis ongoing



pinanediol
(C10H18O2, 170.25)

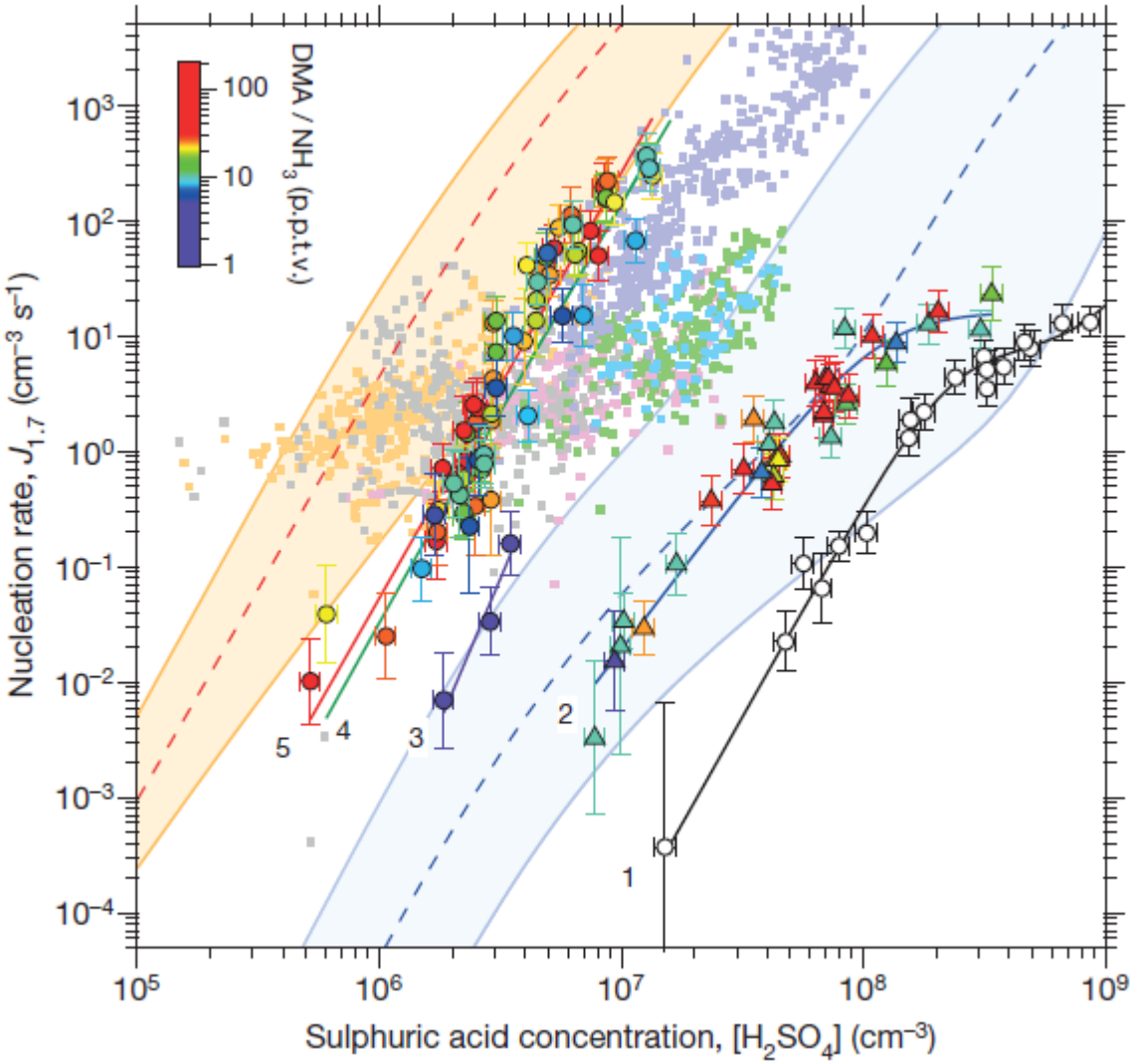
Schobesberger et al., PNAS 2013
Riccobono et al., Science 2014, in press

(Note: the results of Riccobono et al. are excluded from the current pdf as required by Science)

alpha-pinene globally most abundant monoterpene

pinanediol is closely related but has no C=C bond so is unreactive with O_3 - only OH

Ternary nucleation with dimethyl-amine (DMA): enough to explain rates observed in the ambient atmosphere



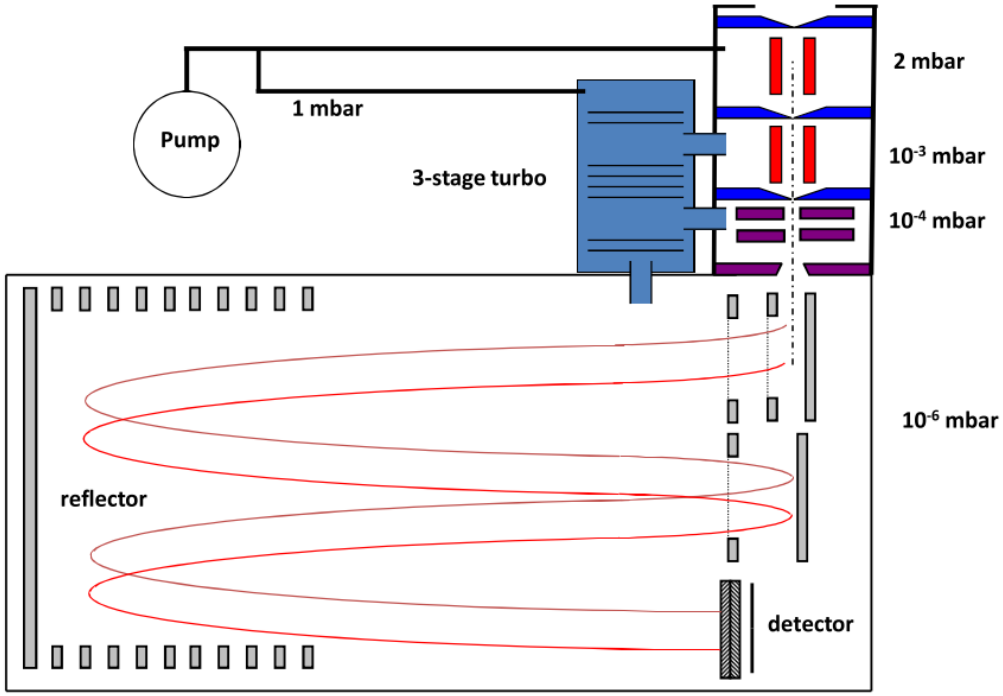
1: pure H_2SO_4 / water
2: plus NH_3
3: plus low DMA (3-5 ppt)
4,5: plus high DMA (6-140 ppt)

But:
Gas-phase amines are expected to be lost rapidly to aerosol phase
➔ Only gas phase concentration relevant for nucleation
➔ Amines are expected to influence nucleation rates only in the vicinity of sources

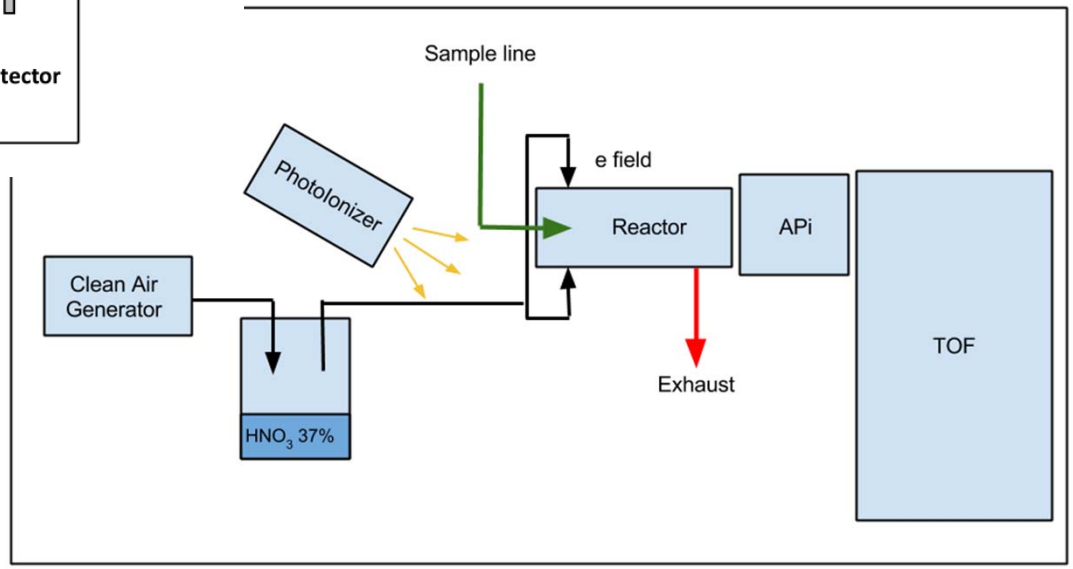
Almeida et al., Nature 2013

The cluster chemical composition

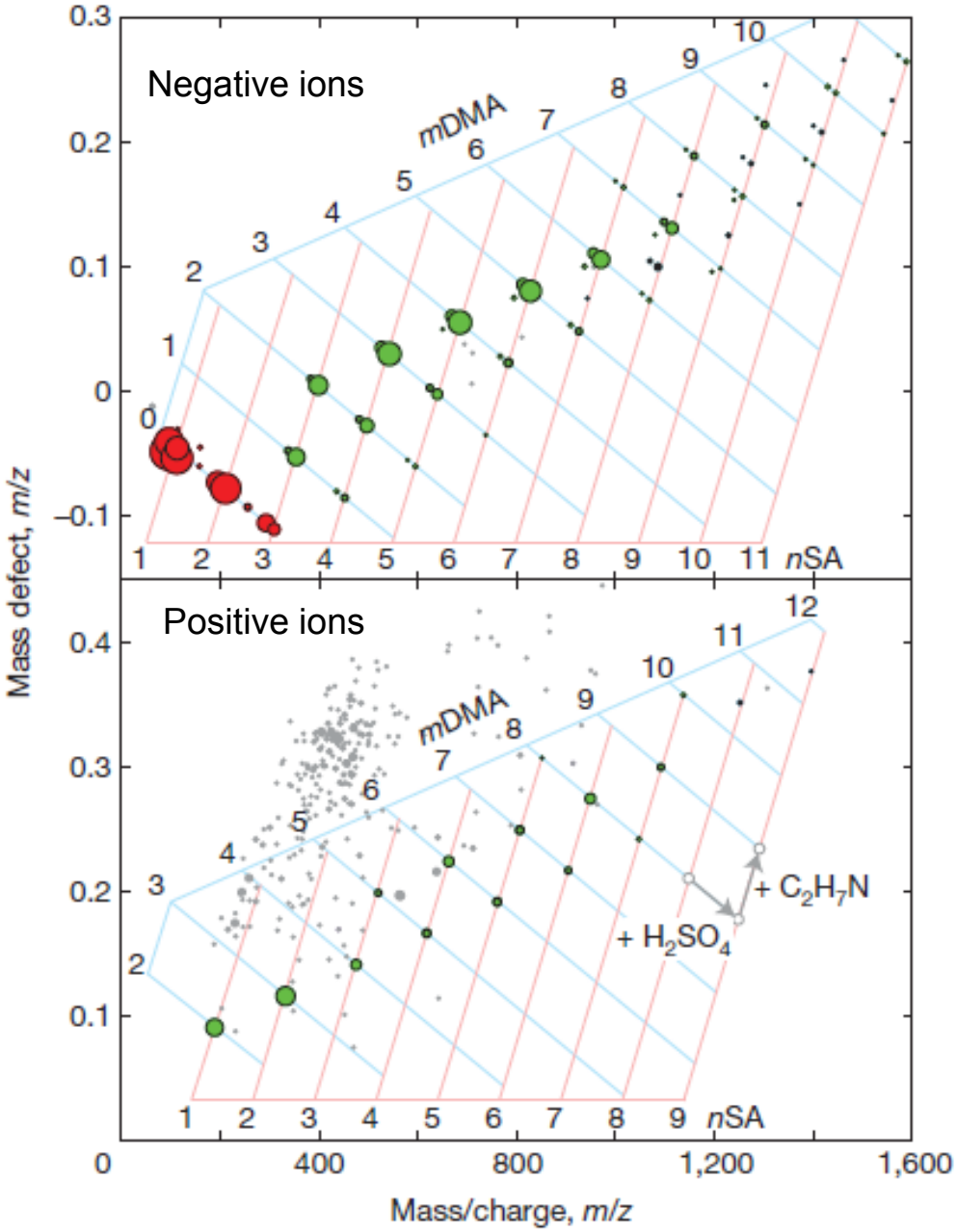
The APi-TOF
Only ions (pos. or neg.)



The CI-Api-TOF
(neutral clusters)



Mass defect plots

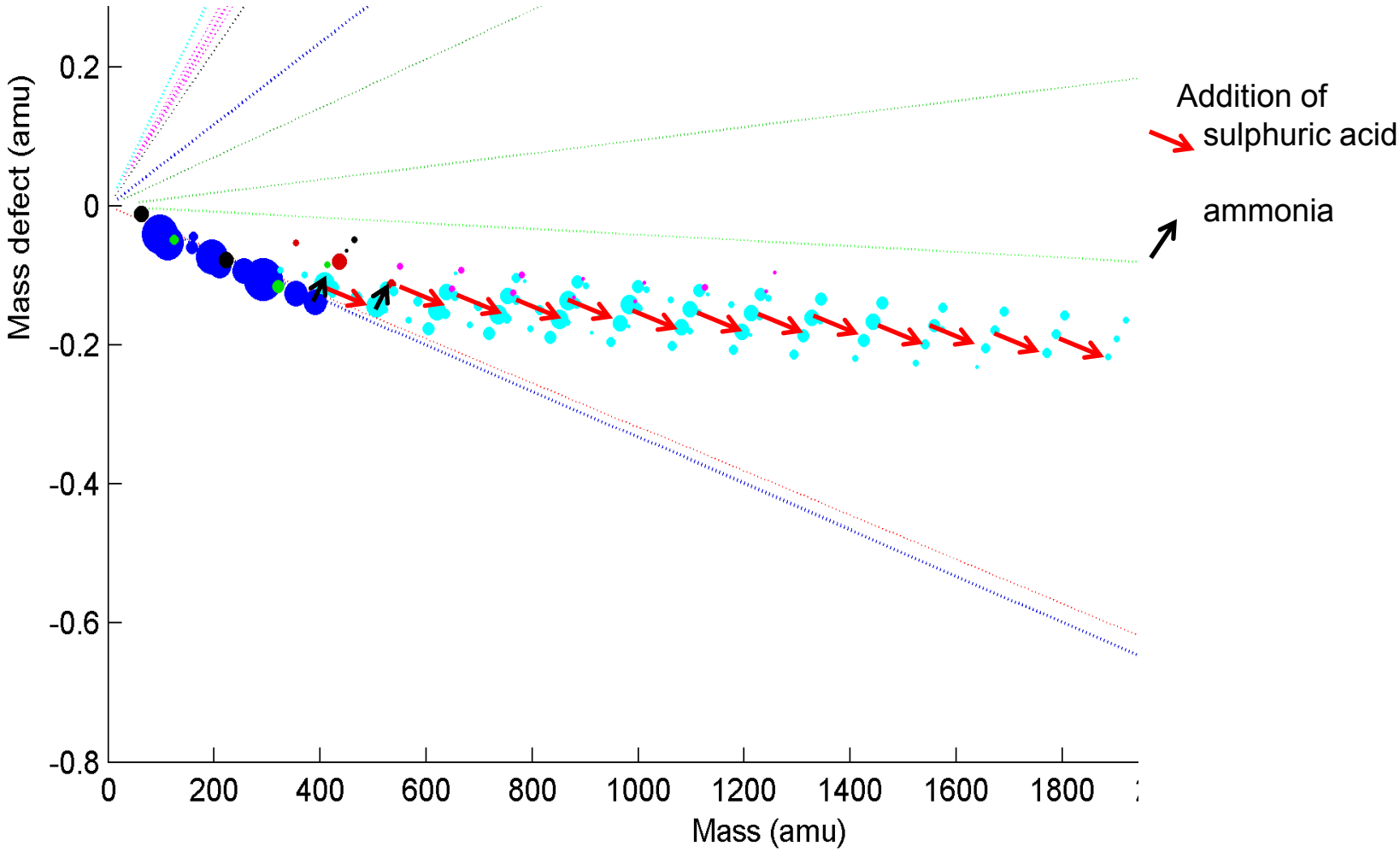


Mass-defect plot: the deviation from the nominal (integer) mass (i.e., the “mass defect”) of a compound is plotted versus the exact mass

~1:1 accretion (not 1:2 as one would expect for bulk conditions)

Almeida et al., Nature 2013

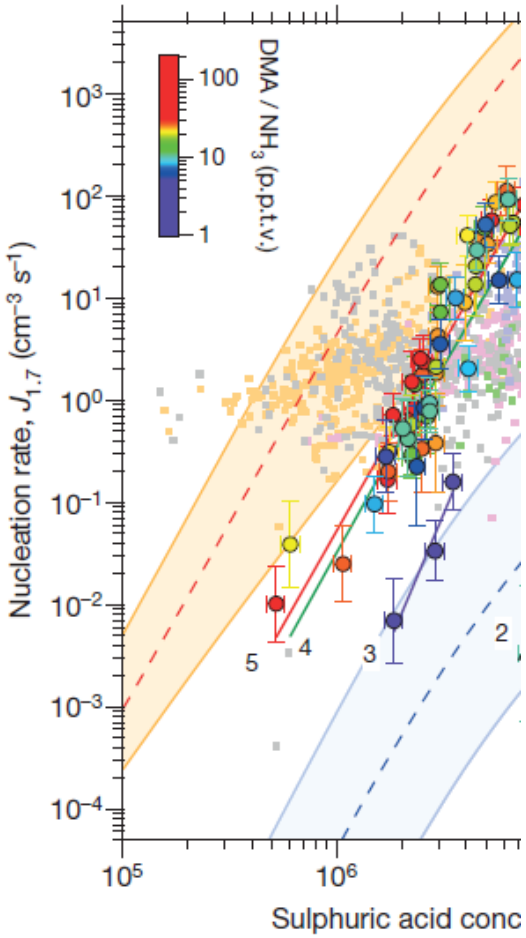
Same for ammonia:
1:1 addition of sulphuric acid and ammonia
(starting from tetramer)

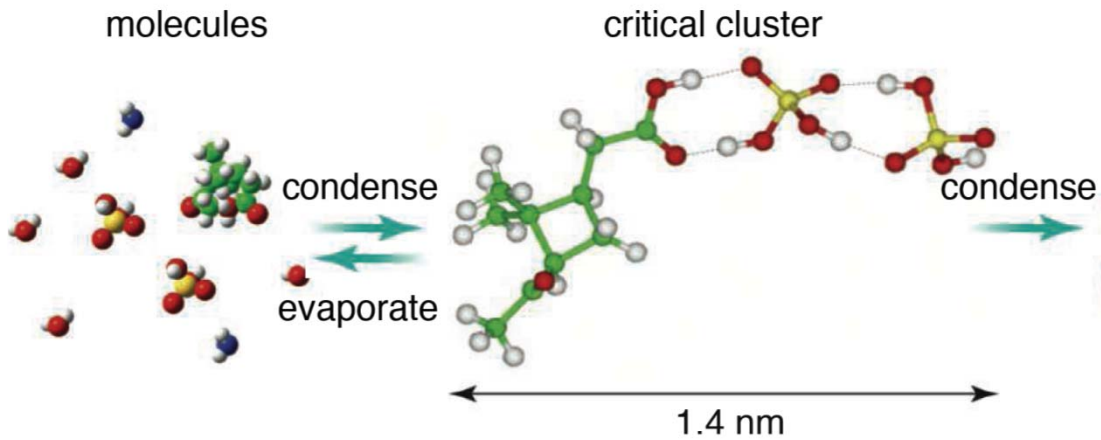


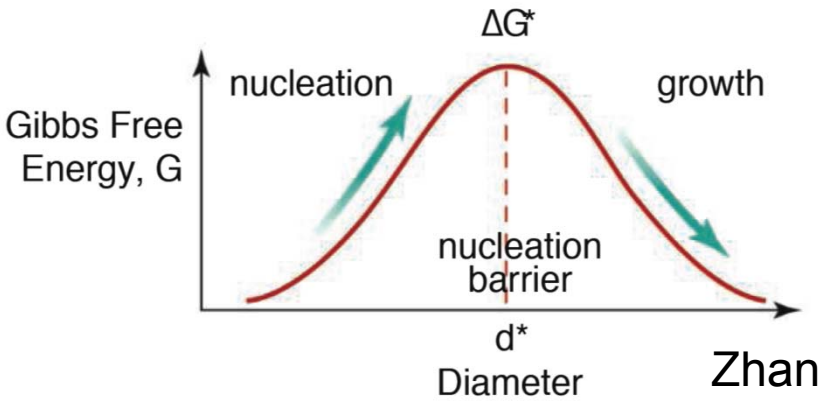
The critical cluster concept

1st nucleation theorem: slope = number of molecules in critical cluster. However, if stable clusters are formed loss mechanisms other than evaporation (wall losses, condensational sink) become more important

➔ slope will decrease with increasing *J*, slope = 4 in DMA case does not mean that there are 4 H_2SO_4 molecules in critical cluster







Zhang, 2010

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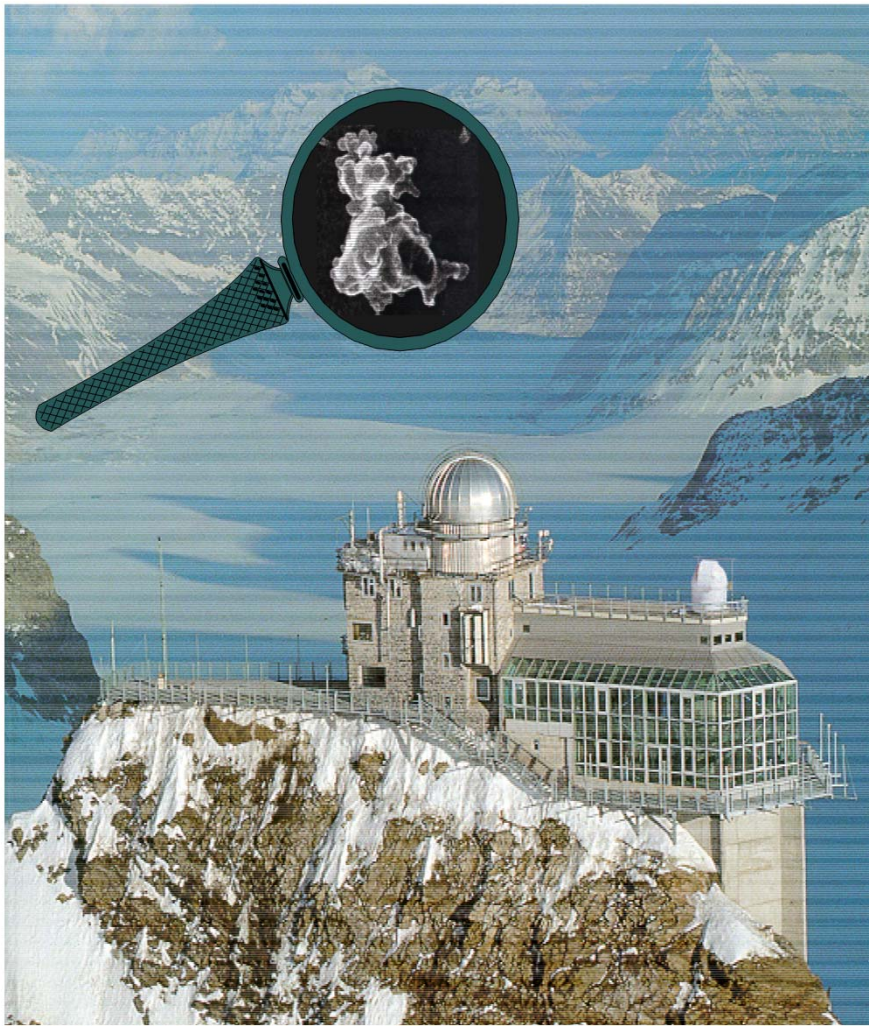
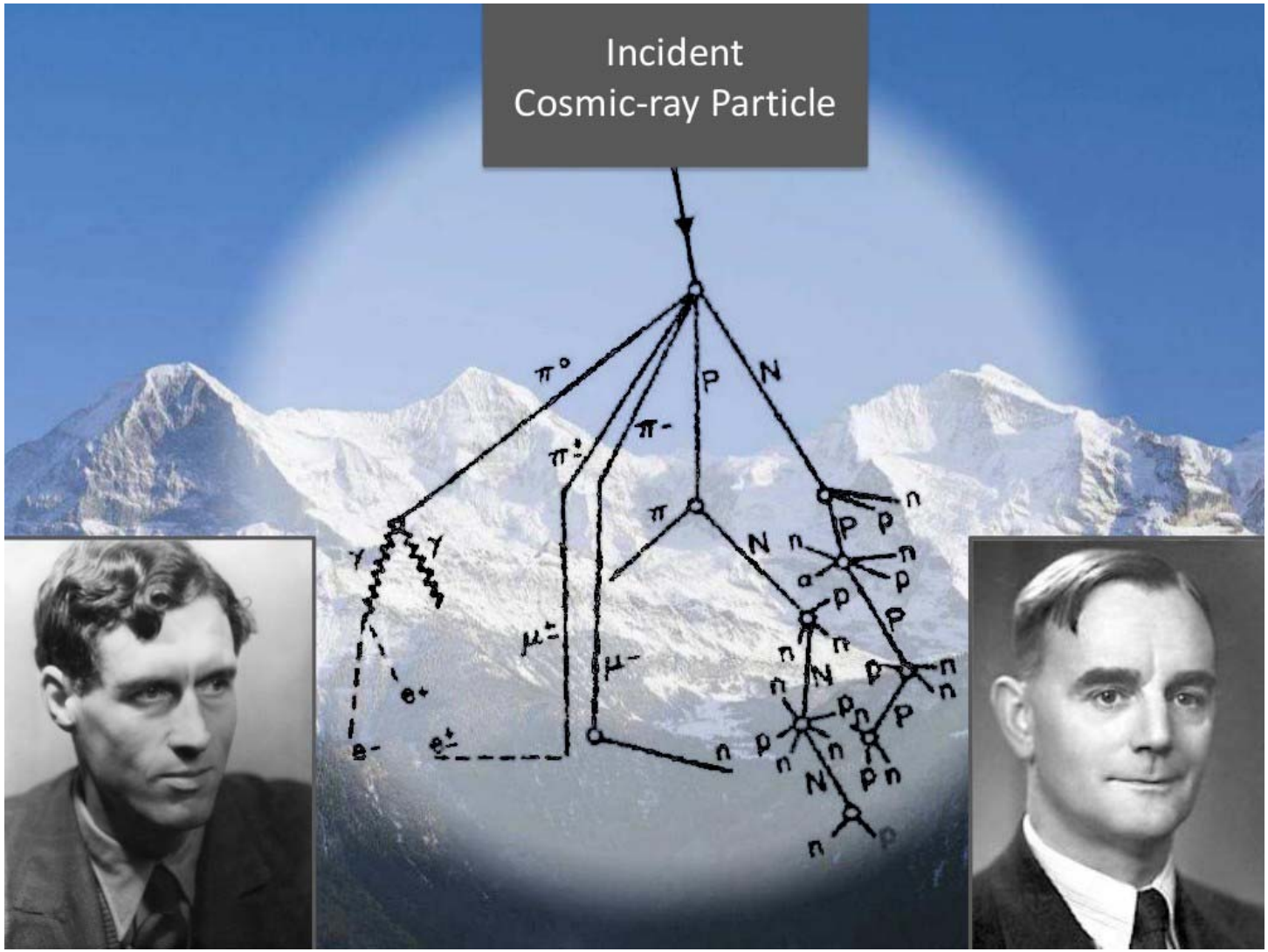
Measurements at the Jungfraujoch



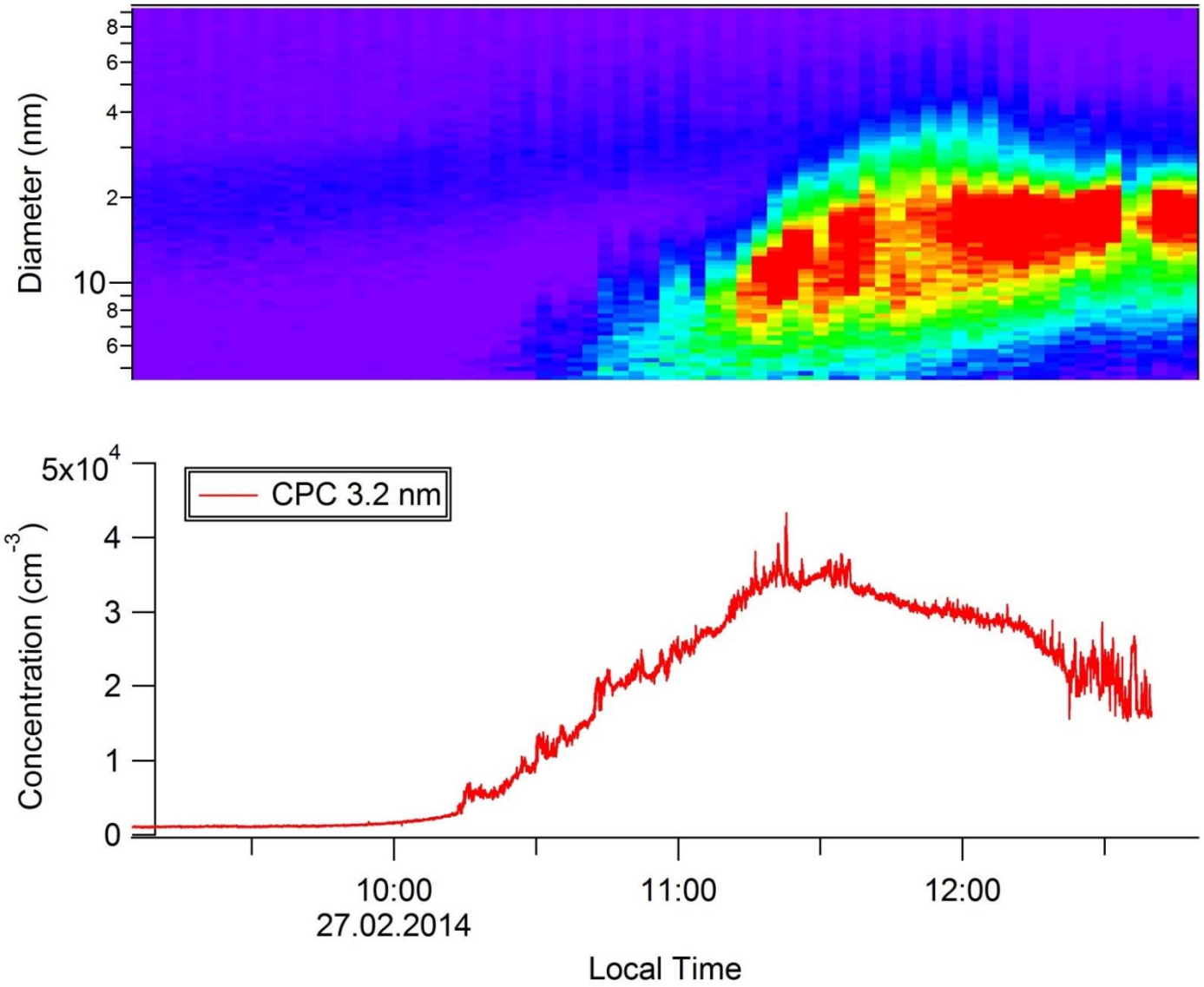
Measurements at the Jungfraujoch



The Physics Nobel Laureates of 1948 and 1950, P.M.S. Blackett (left) and C.F. Powell (right)

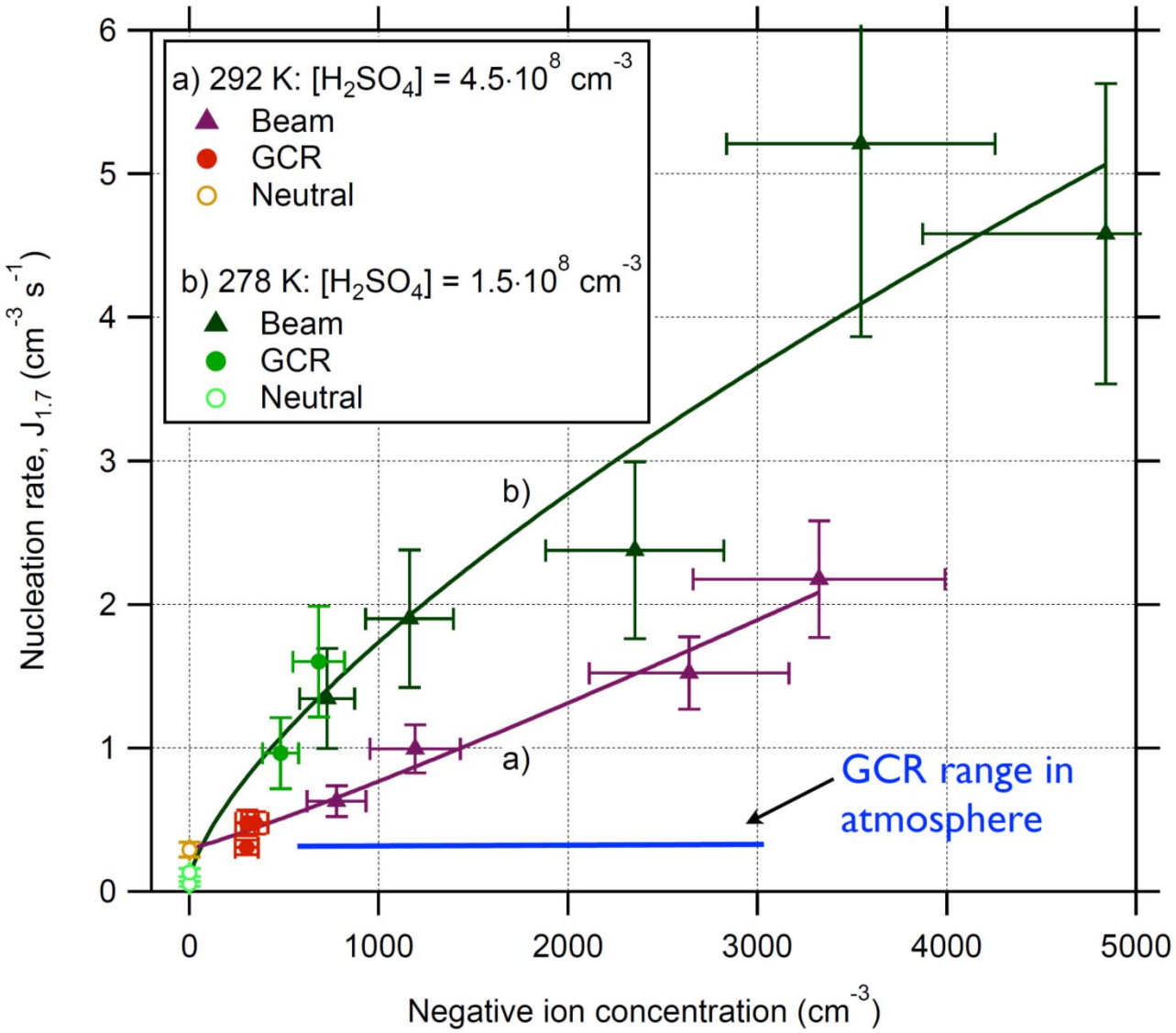
Where to measure ions at the JFJ?

A beautiful banana at the JFJ



Note: the other results from Jungfraujoch are excluded from the current pdf in order not to jeopardize a potential high impact paper.

Do charges influence nucleation rate? Nucleation rate vs [ion$^-$]



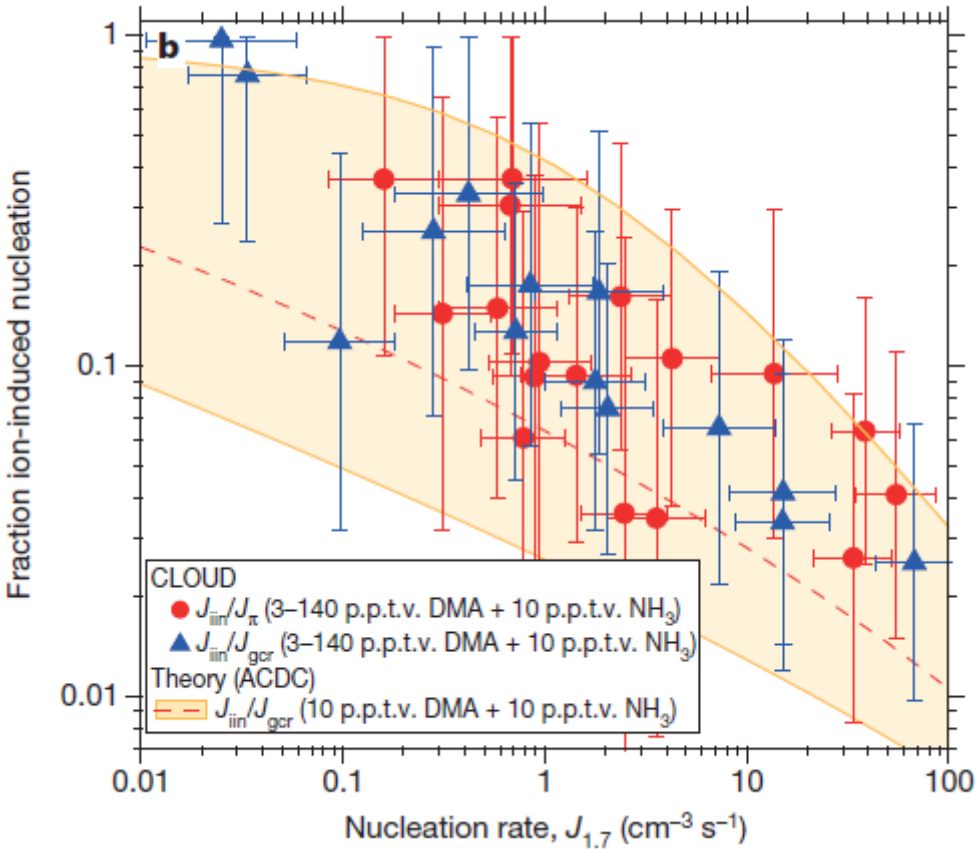
Nucleation rate at two different temperatures (278 and 292 K) with 35 pptv NH_3

$J = J_n + k[\text{Ion}^-]^p$
$p = 0.7–1.0$

Kirkby et al., Nature 2011

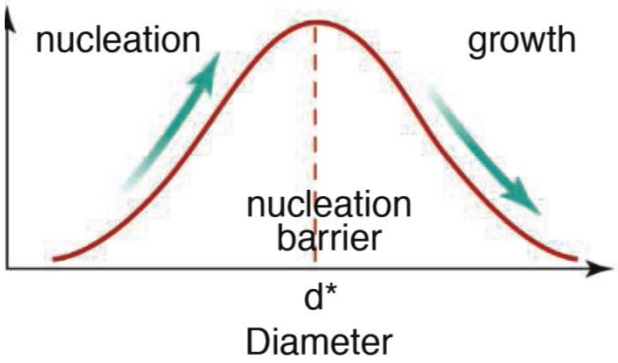
The effect of charges on nucleation

Depends on the nucleation rate:
the higher the nucleation rate,
the lower the ion induced fraction

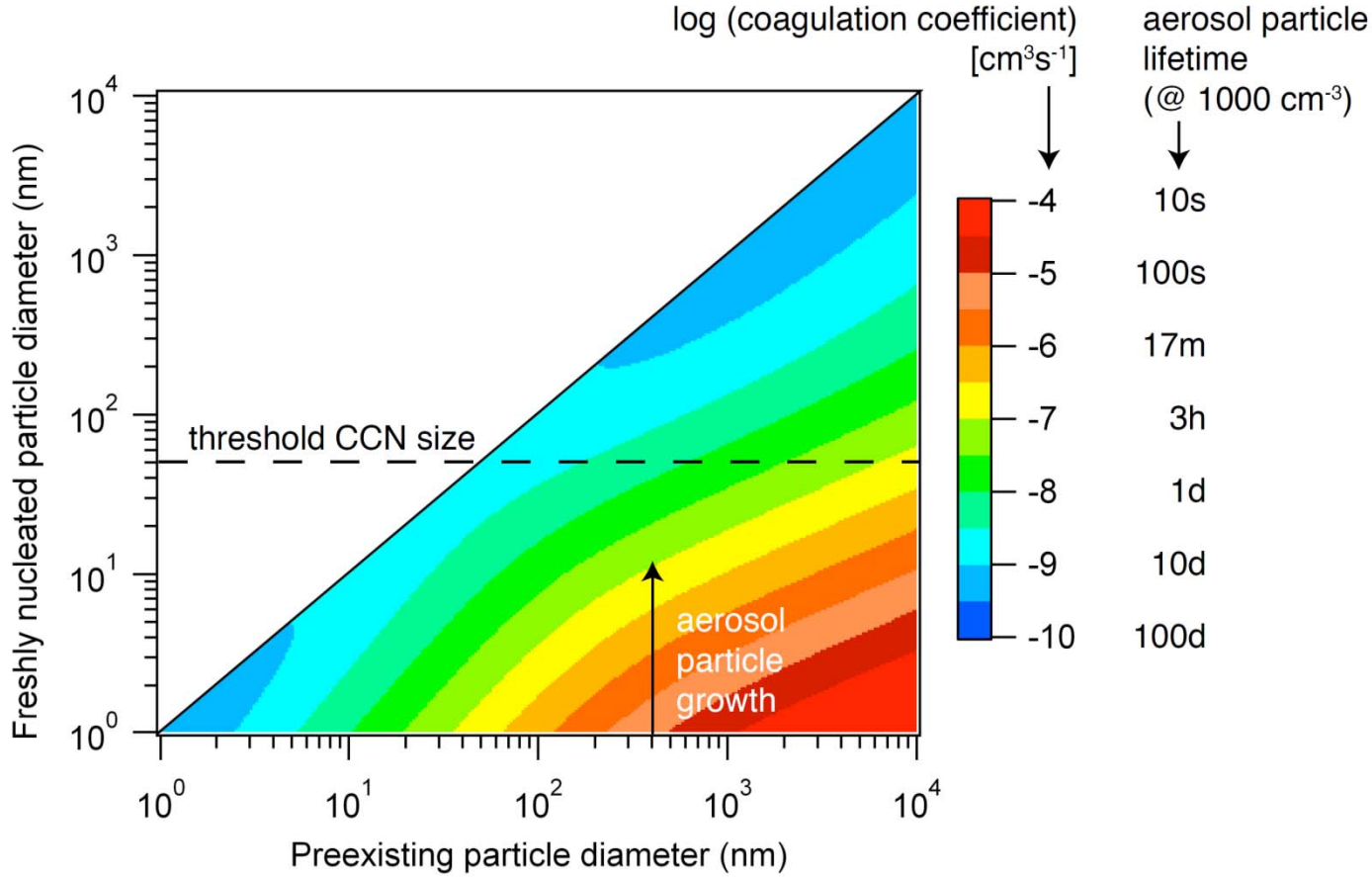


Almeida et al., Nature 2013

Also depends on the system:
The lower the evaporation rate of neutral clusters, the lower the possible impact by stabilization through charges



The fate of new particles: grow or die



- The fraction of freshly-nucleated particles that reach CCN size critically depends on their condensational growth rate
- 1 nm/h growth rate ≡ $[H_2SO_4] \sim 10^7$ cm^{-3}
- Pre-existing and freshly-nucleated aerosols compete for condensable vapours, and so:
  - Very few new particles may reach CCN size
  - Increase in CCN is generally much smaller than increase in nucleation rate

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THE WALL STREET JOURNAL.
WSJ.com

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Conclusions

- Nucleation experiments have a high chance of being affected by contamination
- The CLOUD experiment is the first ‚clean‘ laboratory experiment
- It will provide the solution of the nucleation conundrum
- Sulfuric acid appears to be a required player in most case, but other components are needed as well (ammonia, amines, oxidized organics)
- The Jungfraujoch is an excellent site for the investigation of the aerosol impact on climate, including nucleation


Thank you for your attention