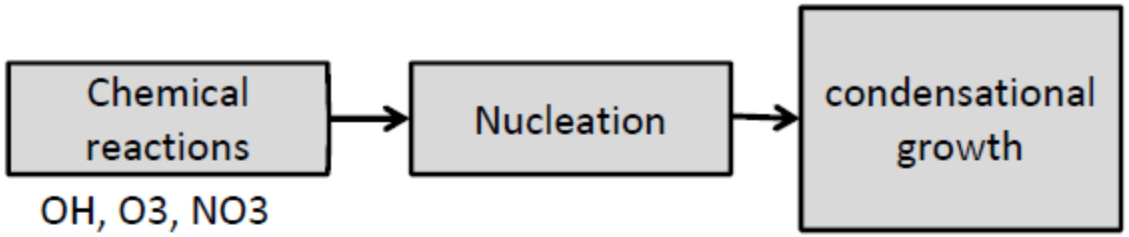
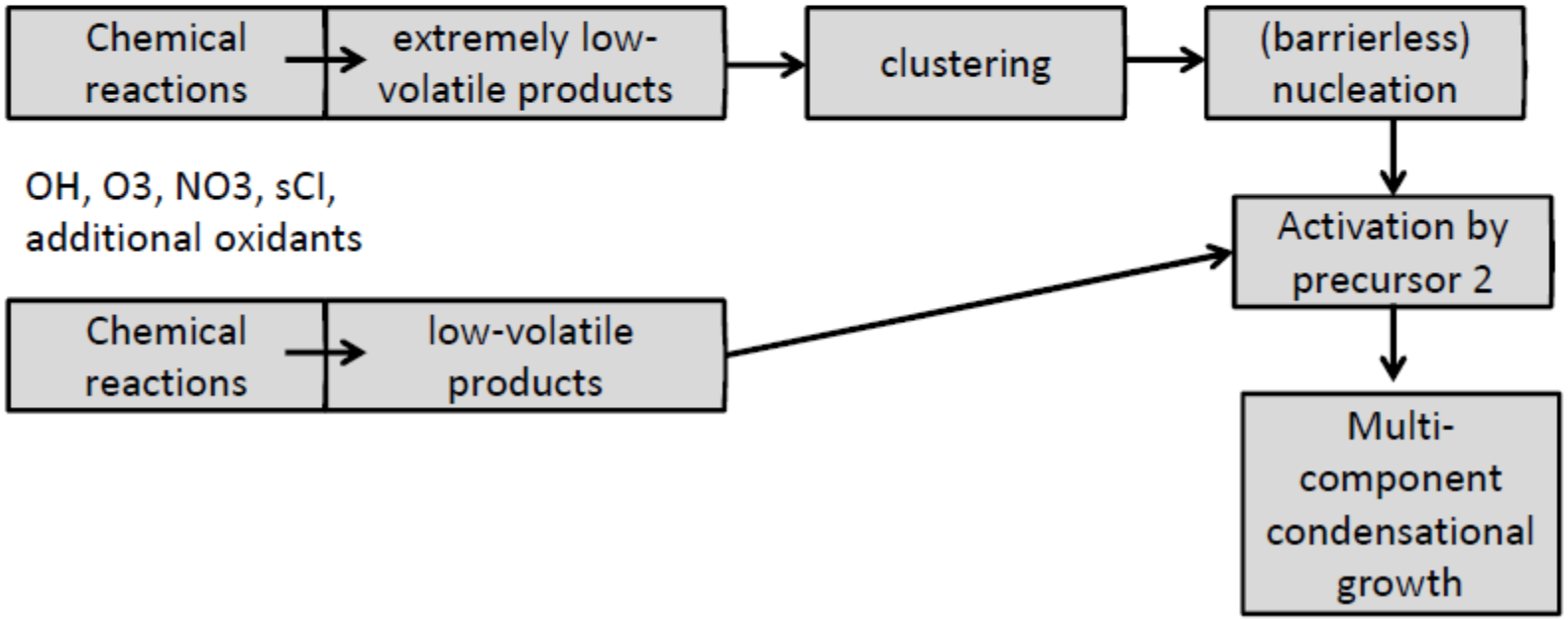
Atmospheric New Particle Formation

Markku Kulmala et al.
University of Helsinki

Traditional view:

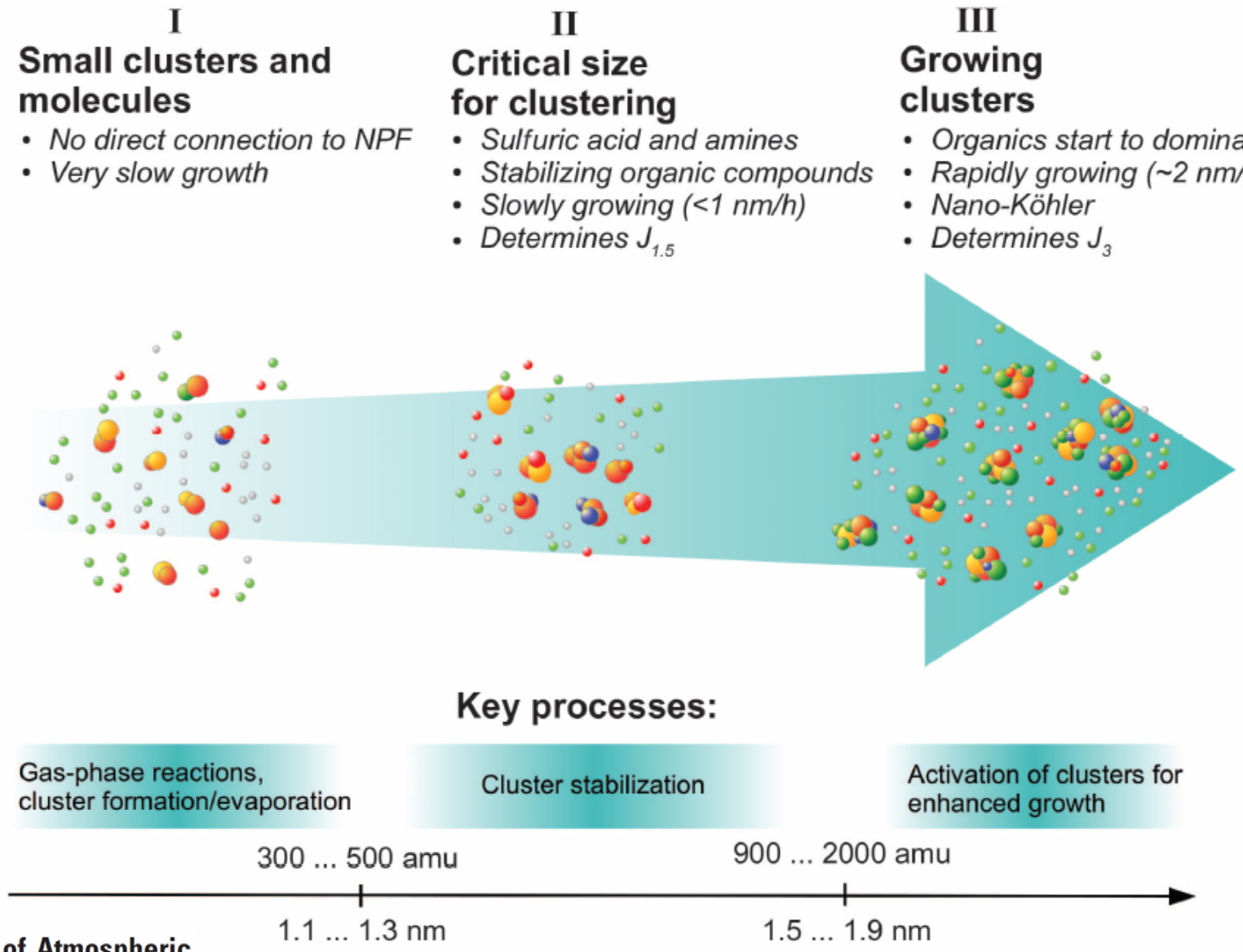


Current view:



Kulmala et al., 2014, accepted

Science
AAAS



Direct Observations of Atmospheric Aerosol Nucleation

Markku Kulmala,[1*] Jenni Kontkanen,[1] Heikki Junninen,[1] Katrianne Lehtipalo,[1] Hanna E. Manninen,[1] Tuomo Nieminen,[1,14] Tuukka Petäjä,[1] Mikko Sipilä,[1] Siegfried Schobesberger,[1] Pekka Rantala,[1] Alessandro Franchin,[1] Tuija Jokinen,[1] Emma Järvinen,[1] Mikko Äijälä,[1] Juha Kangasluoma,[1] Jani Hakala,[1] Pasi P. Aalto,[1] Pauli Paasonen,[1] Jyri Mikkilä,[2] Joonas Vanhanen,[2] Juho Aalto,[3] Hannele Hakola,[4] Ulla Makkonen,[4] Taina Ruuskanen,[1] Roy L. Mauldin III,[1,5] Jonathan Duplissy,[1] Hanna Vehkamäki,[1] Jaana Bäck,[6] Aki Kortelainen,[7] Ilona Riipinen,[8] Theo Kurtén,[1,9] Murray V. Johnston,[10] James N. Smith,[7,11] Mikael Ehn,[1,12] Thomas F. Mentel,[12] Kari E. J. Lehtinen,[4,7] Ari Laaksonen,[4,7] Veli-Matti Kerminen,[1] Douglas R. Worsnop[1,4,7,13]

Direct Observations of Atmospheric Aerosol Nucleation
Markku Kulmala *et al.*
Science **339**, 943 (2013);
DOI: 10.1126/science.1227385

1. Atmospheric oxidation

LETTER

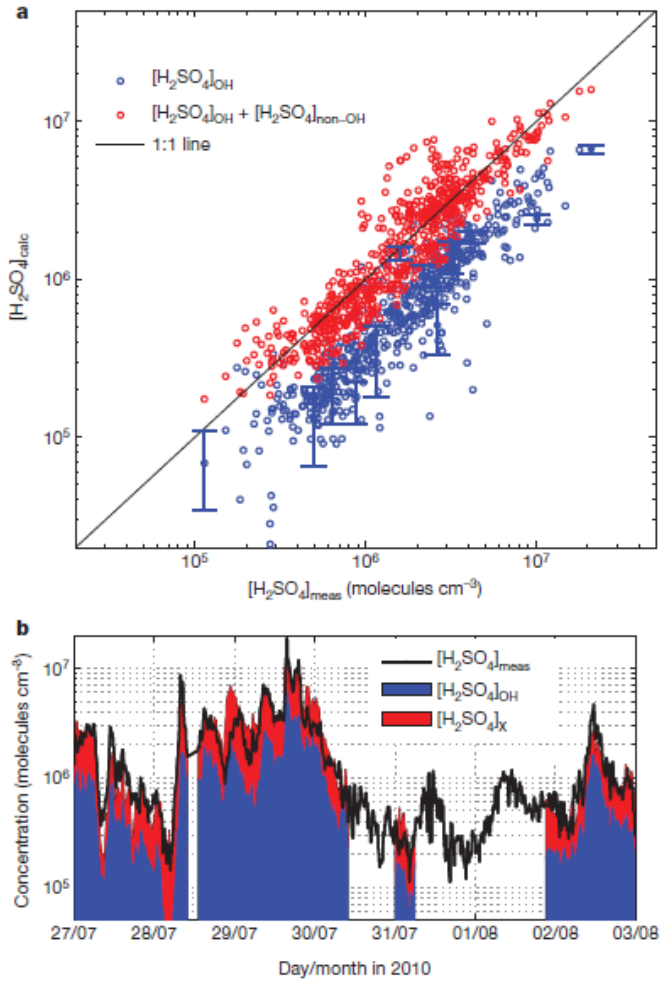
RESEARCH LETTER

doi:10.1038/nature11278

A new atmospherically relevant oxidant of sulphur dioxide

R. L. Mauldin III[1,2,3], T. Berndt[4], M. Sipilä[1,4,5], P. Paasonen[1], T. Petäjä[1], S. Kim[2], T. Kurtén[1,6], F. Stratmann[4], V.-M. Kerminen[1] & M. Kulmala[1]

Oxidation of SO_2 to sulfuric acid by Stabilized Criegee intermediates (SCI) has a significant contribution to sulfuric acid concentrations in boreal environment.



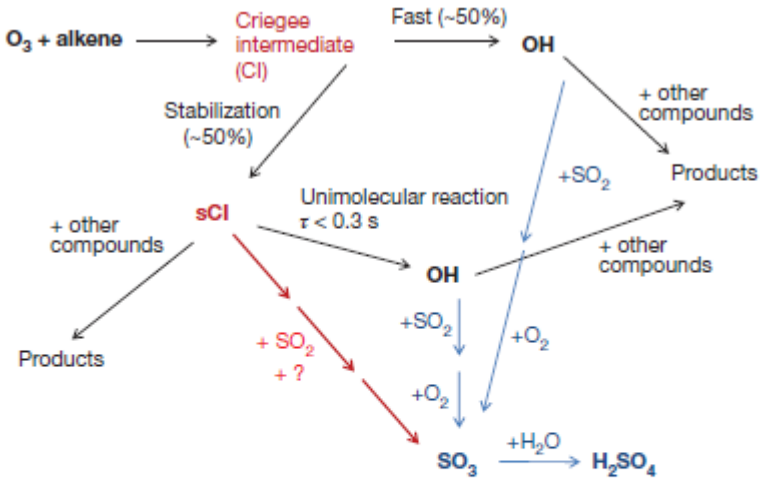


Figure 3 | Proposed mechanism for the formation of oxidant X. Of the Criegee intermediates (CI) formed during ozonolysis, ~50% decompose to produce OH on a subsecond timescale while the other 50% are stabilized, producing stabilized Criegee radicals, sCI. These sCI can then decompose over a much longer lifetime, τ. Our observations suggest that sCI, or non-OH derivatives of sCI, can also oxidize at least SO_2 (red arrows), thus altering the known view of oxidation chemistry in the atmosphere. Typical OH chemistry is depicted in blue.

2) atmospheric nucleation

Discovering the world below 3 nm

Size scale

1µm

aerosol particles

3nm

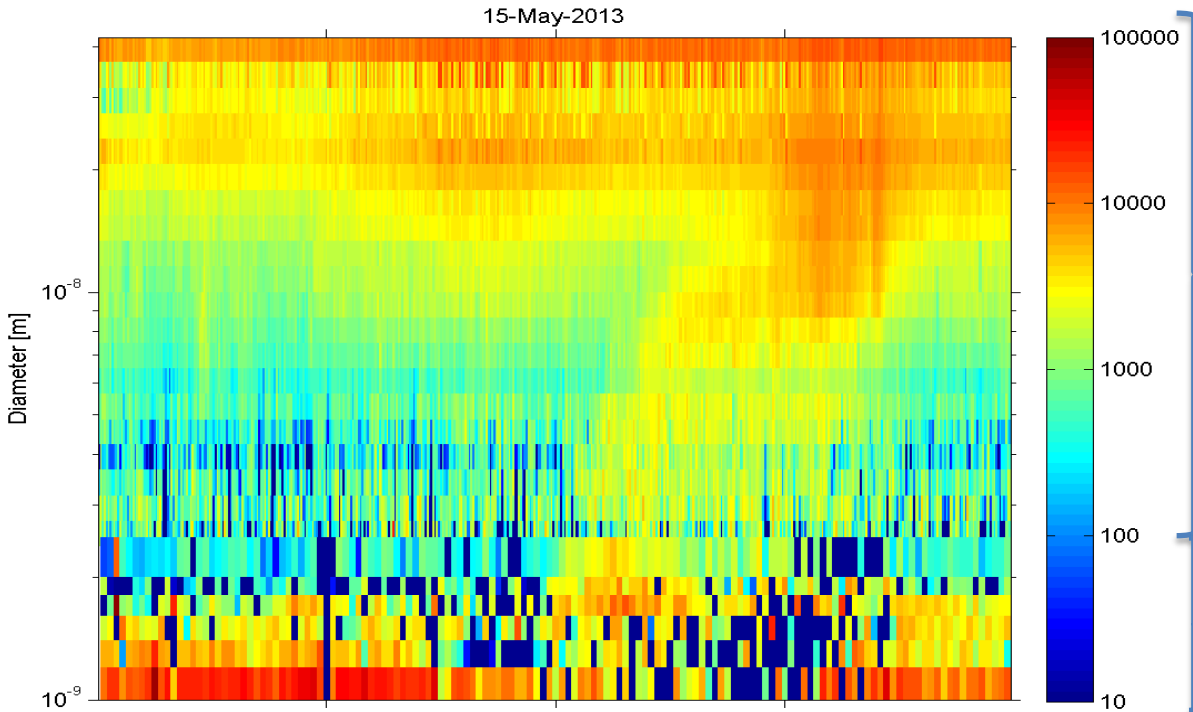
clusters

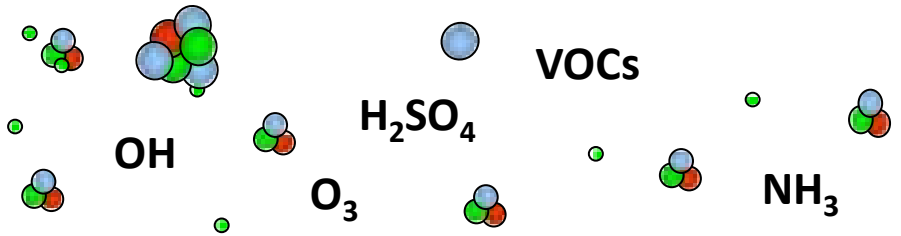
1nm

1Å

gas molecules

Hyytiälä 15th May 2013:





Measured with:

NAIS

PSM

Mass specs

Slide courtesy of Katrianne Lehtipalo

First paper on nucleation in Hyytiälä…

GEOPHYSICAL RESEARCH LETTERS, VOL. 24, NO.10, PAGES 1219-1222, MAY 15, 1997

Observations of ultrafine aerosol particle formation and growth in boreal forest

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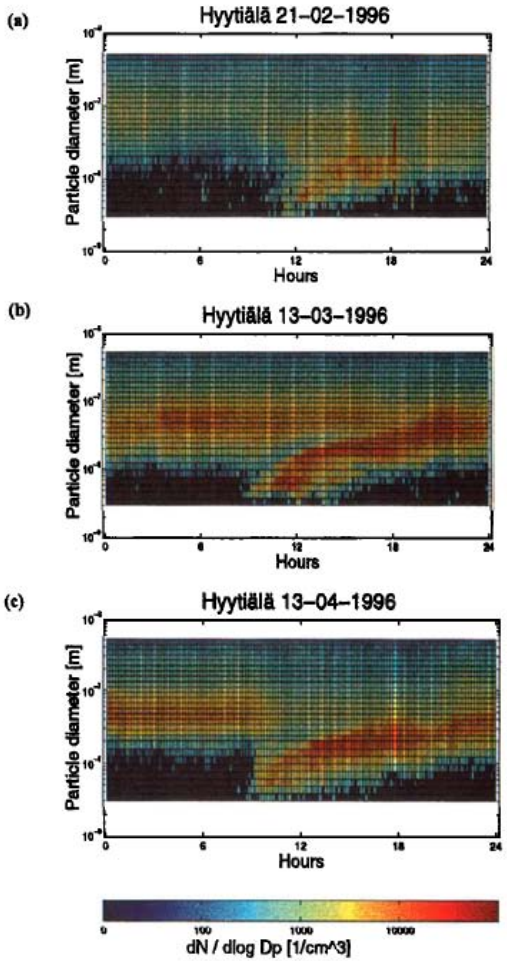
A. Nissinen, S. Palmroth
Department of Forest Ecology, University of Helsinki, FINLAND

T. Markkanen, K. Seitsonen, H. Lihavainen, M. Kulmala
Department of Physics, University of Helsinki, FINLAND

…and the first Bananas



ELVOCs predicted

Tellus (1998), 50B, 449–462
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TELLUS
ISSN 0280–6509

Analysis of the growth of nucleation mode particles observed in Boreal forest

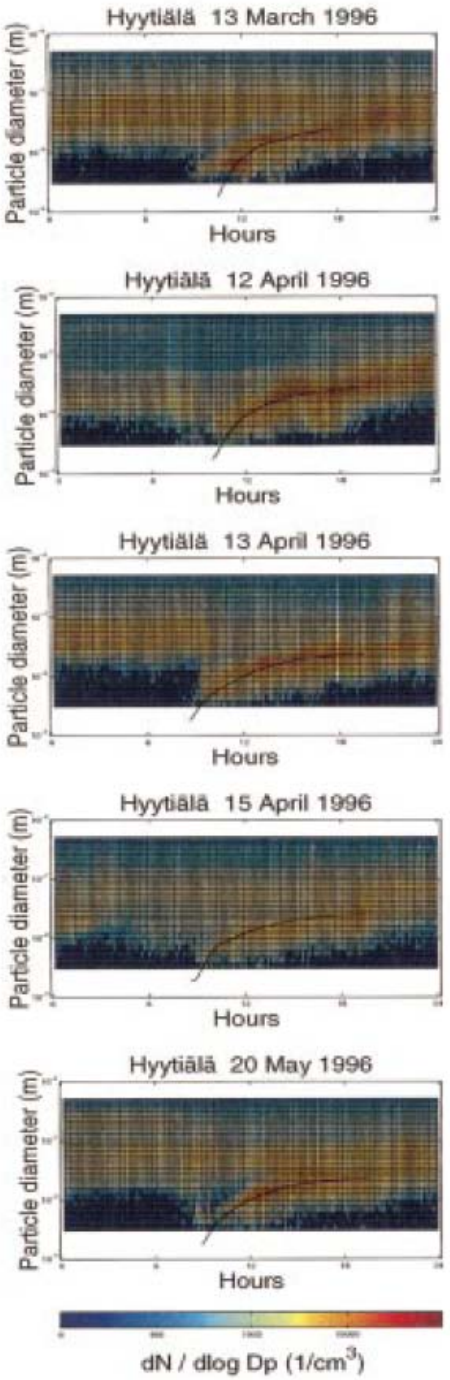
By MARKKU KULMALA, ANNE TOIVONEN, JYRKI M. MÄKELÄ and ARI LAAKSONEN*[1],
Department of Physics, POB 9, 00014 University of Helsinki, Finland; [1]University of Kuopio, Department of Applied Physics, POB 1627, 70211 Kuopio, Finland

(Manuscript received 21 July 1997; in final form 27 August 1998)

”it seems unlikely that the condensing molecule X is sulphuric acid”

”one possibility is that the growth is caused by some organic acid(s)”

”The growth seems to be limited by a species with gas-phase concentration above 10^7 and saturation vapour density below 10^5 molecules per cc”



The first explanation …

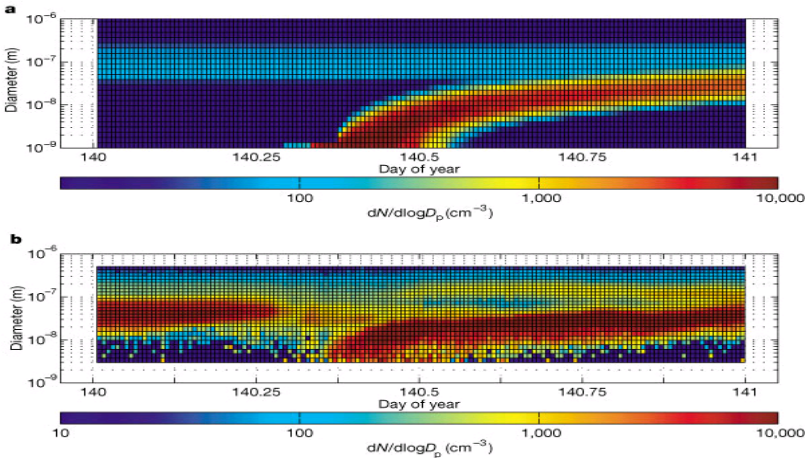
and prediction of atmospheric cluster pool

Letters to Nature

Nature **404**, 66-69 (2 March 2000) | Received 5 July 1999; Accepted 10 January 2000

Stable sulphate clusters as a source of new atmospheric particles

Markku Kulmala, Liisa Pirjola and Jyrki M. Mäkelä



"...ambient sulphuric acid (H2SO4) levels are typically lower than required for binary nucleation, but are sufficient for ternary nucleation (sulphuric acid–ammonia–water). Here we present results from an aerosol dynamics model with a ternary nucleation scheme which indicate that nucleation in the troposphere should be ubiquitous, and yield a reservoir of thermodynamically stable clusters 1–3 nm in size."

Nano-Köhler

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 109, D04205, doi:10.1029/2003JD003961, 2004

Organic aerosol formation via sulphate cluster activation

Markku Kulmala,[1] Veli-Matti Kerminen,[2] Tatu Anttila,[1,2] Ari Laaksonen,[3] and Colin D. O'Dowd[4]

Received 8 July 2003; revised 18 November 2003; accepted 11 December 2003; published 25 February 2004.

[1] The formation of aerosols, and subsequent cloud condensation nuclei, remains one of the least understood atmospheric processes upon which global climate change critically depends. Under atmospheric conditions, the process of homogeneous nucleation (formation of stable clusters $\sim$ 1 nm in size), and their subsequent growth into new particles (>3 nm), determines the aerosol and cloud nuclei population, yet, hitherto, no theory has elucidated the new particle formation phenomenon in detail. In this study, we present a new theory which provides a mechanistic explanation for new particle formation via activation of stable inorganic clusters by organic vapors. The new nano-particle activation theory is analogous to Köhler theory which describes cloud formation in a supersaturated water vapor field but differs in that it describes the activation of inorganic stable nano-clusters into aerosol particles in a supersaturated organic vapor which initiates spontaneous and rapid growth of clusters. Inclusion of the new theory into aerosol formation models predicts that increases in organic vapor densities lead to even greater increases in particle production, which, in turn, will influence the global radiative cooling effect of atmospheric aerosols. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions

Citation: Kulmala, M., V.-M. Kerminen, T. Anttila, A. Laaksonen, and C. D. O'Dowd (2004), Organic aerosol formation via sulphate cluster activation, *J. Geophys. Res.*, *109*, D04205, doi:10.1029/2003JD003961.

Nano-Köhler

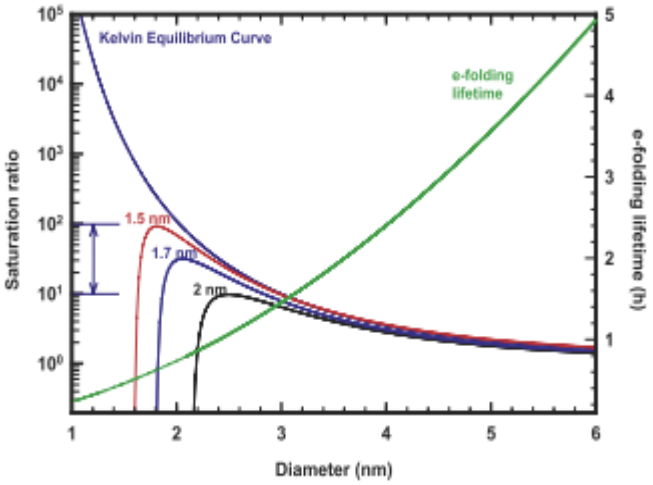


Figure 1. Comparison of Kelvin equilibrium curve for a pure organic droplet and nano-particle equilibrium curves for clusters with initial nuclei sizes of 1.5, 1.7 and 2 nm. The range of saturation ratios expected for condensable organic vapors based on analytical estimates is highlighted. Also shown is the e-folding lifetime, i.e., the inverse of the coagulation sink, of nanometer-size particles.

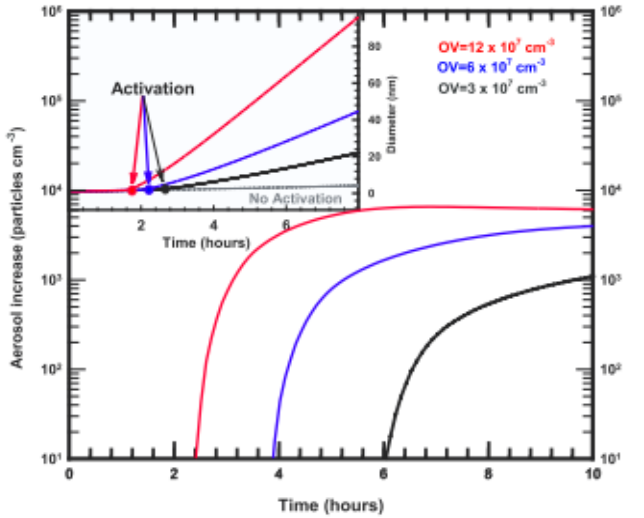
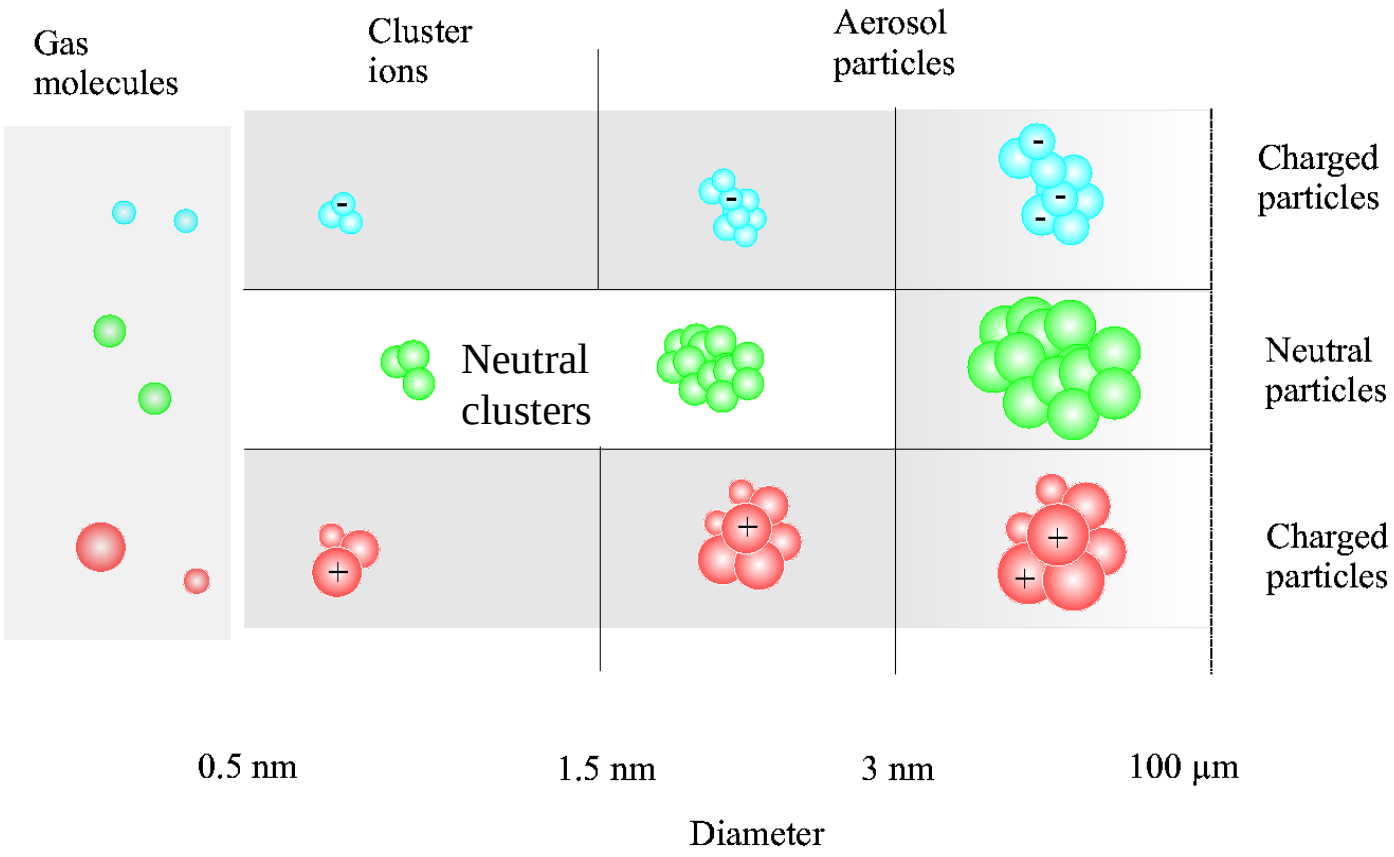


Figure 2. Growth of sulphate clusters and resulting nanoparticles as a function of time for organic vapor (OV) concentrations 3, 6 and 12 $\times$ 10^7 molecules cm^{-3} (inset). The point of activation is highlighted by the dot on the curve. Also shown is the time evolution of the cluster size without nano-particle equilibrium theory incorporated into the dynamics model. The time evolution of the increase in concentration for particle sizes greater than 15 nm is shown in the main plot for the three organic vapor scenarios.

Ions, clusters and aerosol particles



New instruments (PSM, CI-Api-ToF) to detect neutral clusters

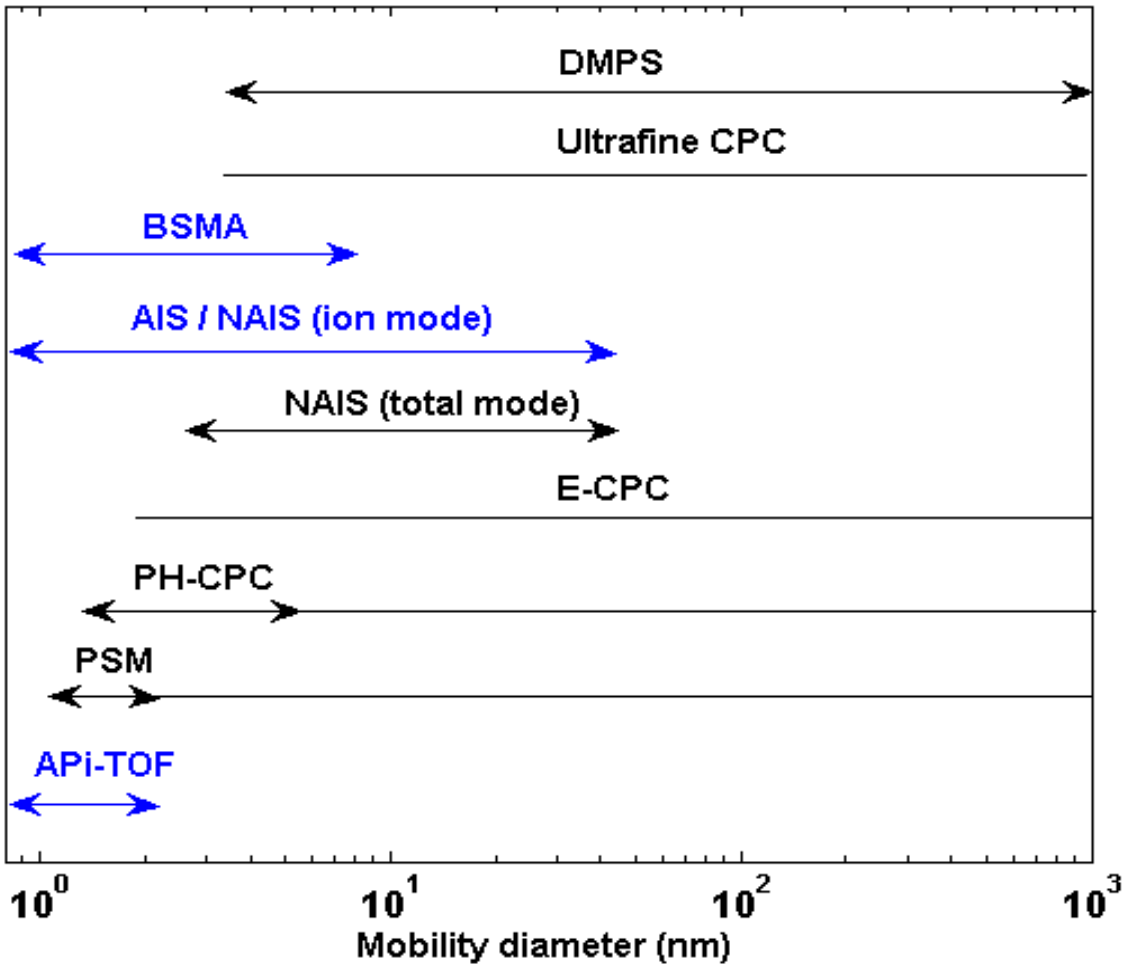
Figure by L. Laakso

The development of measurement techniques

Blue=ions
Black=total

Measurement range

Size distribution



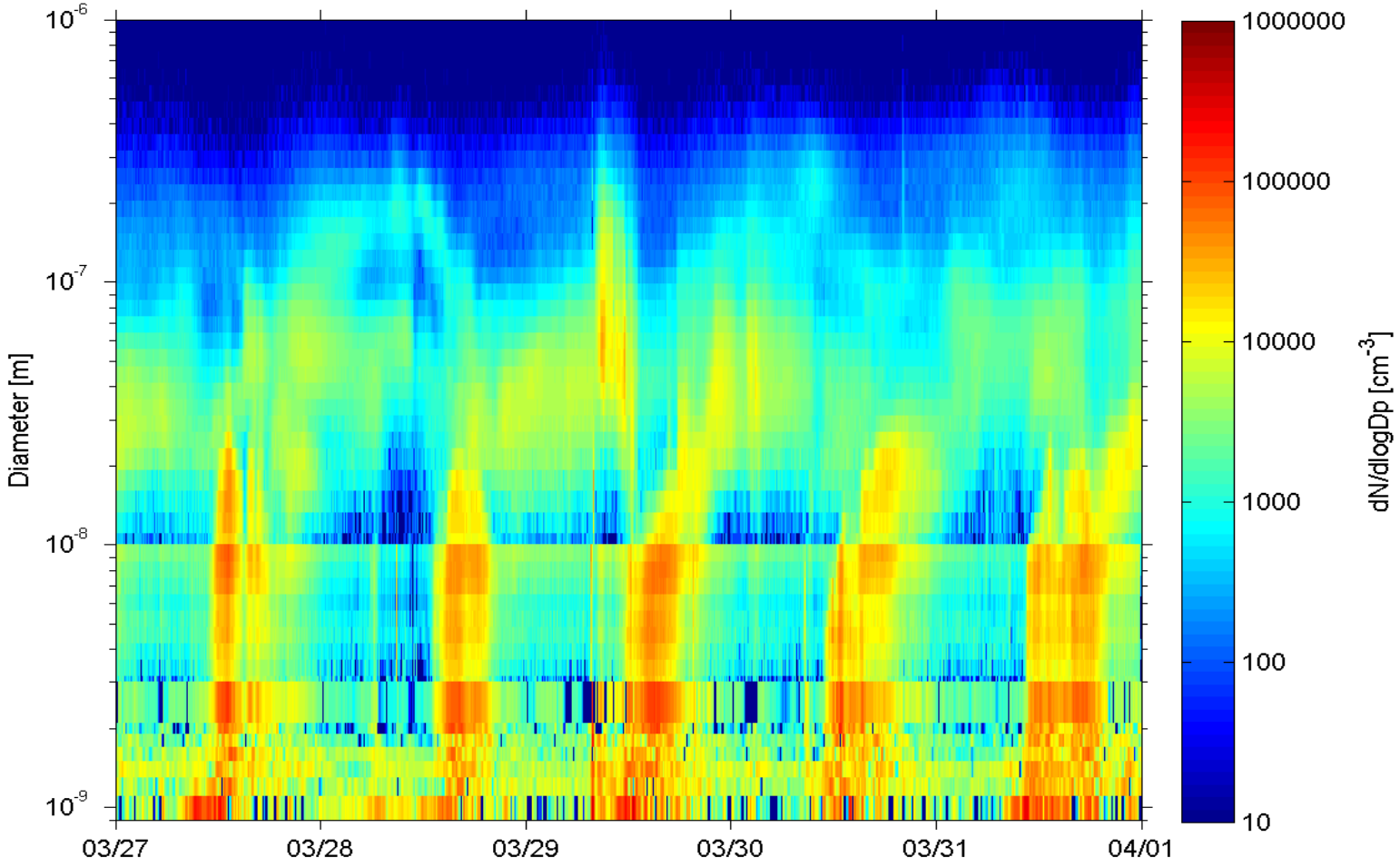
In Hyytiälä

1996→
1996→
2003→
2003→
2006→
2007-2008
2007-2009
2009→
2009→

Lehtipalo, 2011

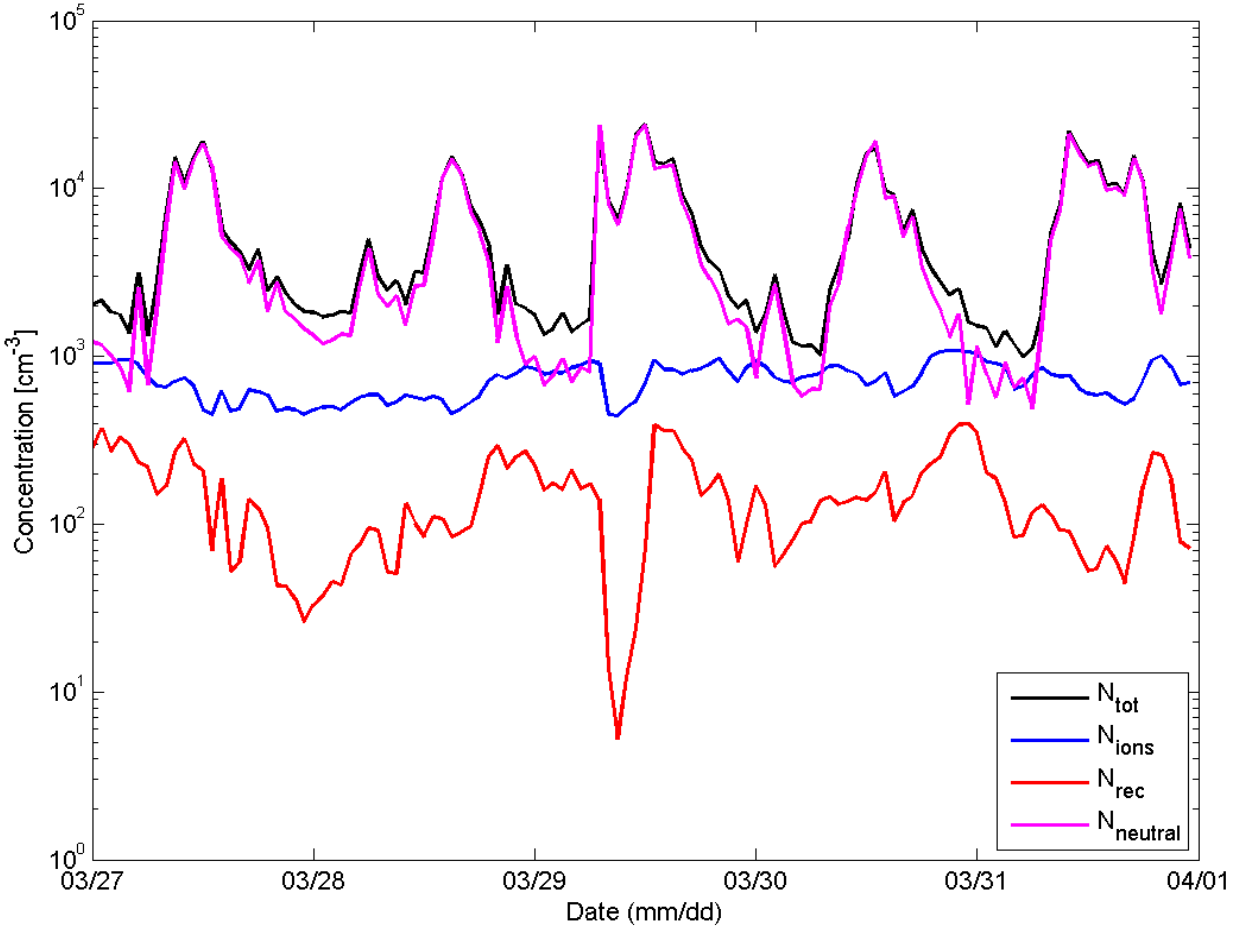
Atmospheric clusters

- AIS/NAIS/BSMA
  - ion concentration, mobility diameter
- PSM: total concentration as a function of size
  - Ammonium sulphate equal mobility diameter
- CIMS: H2SO4
- Api-ToF: +/- ion composition
- CI-Api-ToF: neutral composition/ size in amus
- PTR-MS: VOCs
- Others: NH3, UV, Meteorology etc.
- Measurements:
  - March 14th to May 16th 2011 at the SMEAR II station in Hyytiälä
  - Several other measurements at different locations

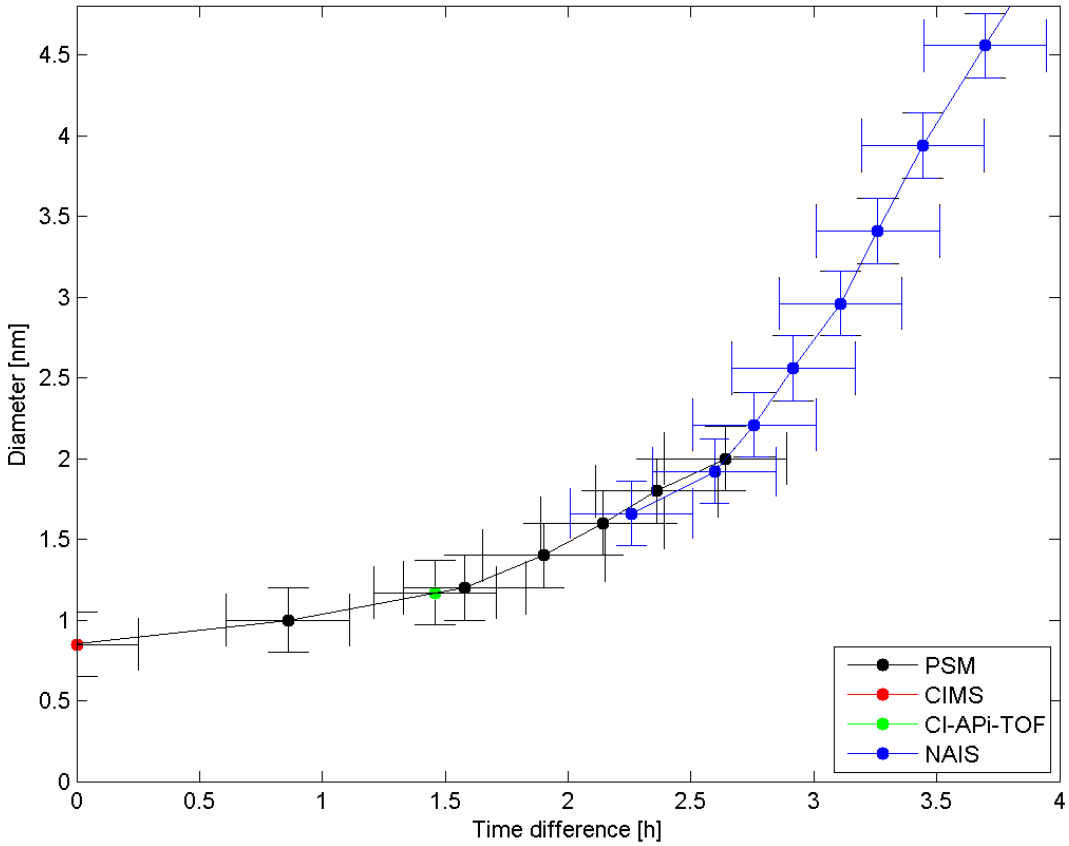


Kulmala et al., 2013, Science, SOM

Neutral vs ion clusters

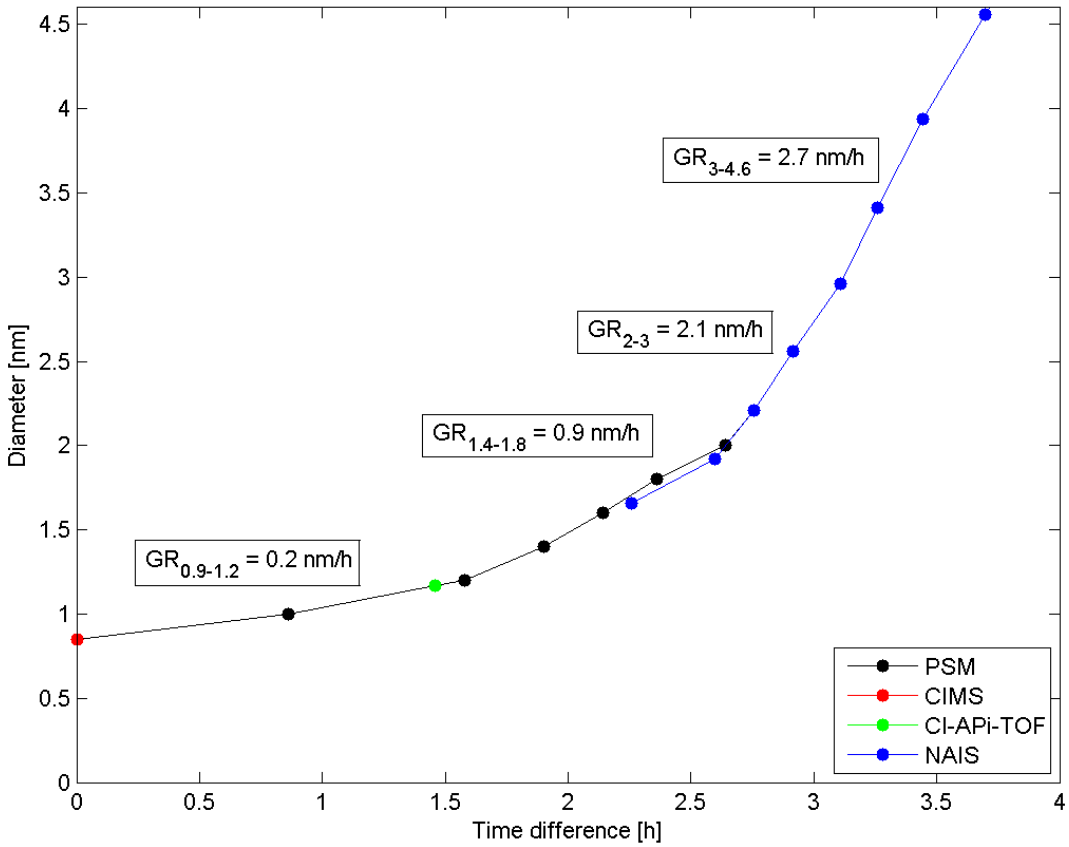


Size as a function of time



Kulmala et al., Science, 22.2. 2013

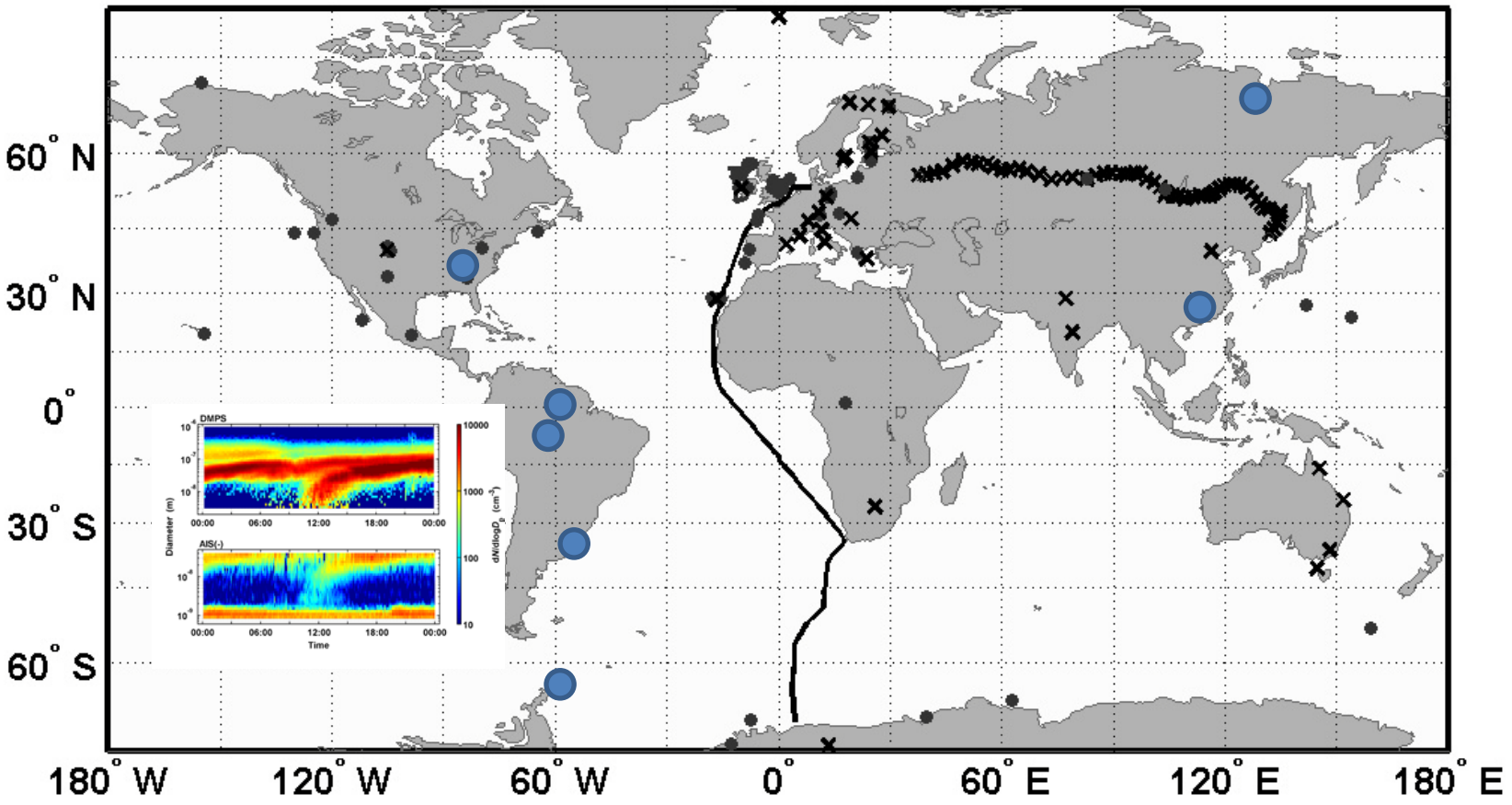
Growth rate



Kulmala et al., Science, 22.2. 2013

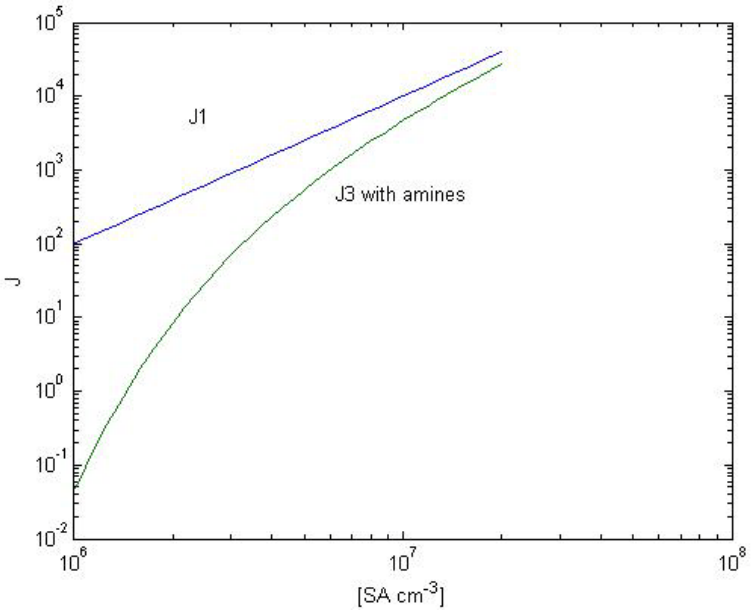
Global measurement activities

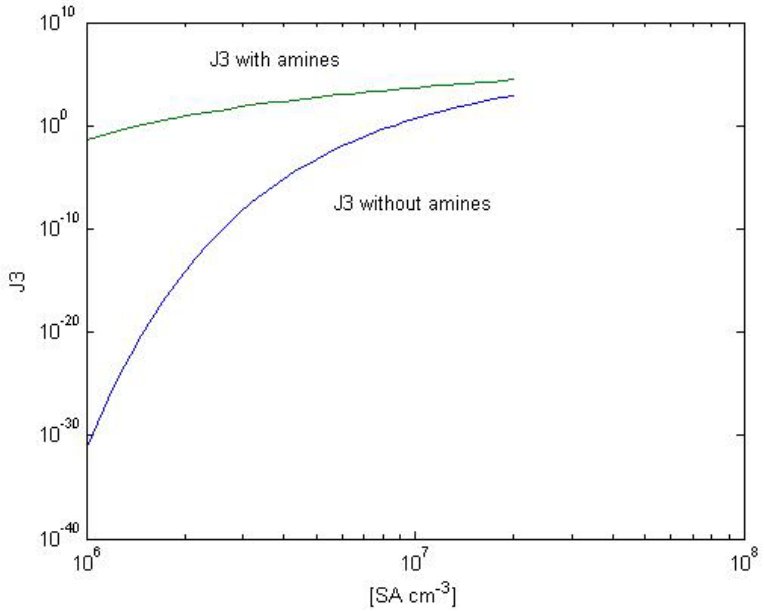
Particle formation and growth is a global phenomenon (Kulmala et al., JAS 2004)



- Contributes significantly to global particle and CCN numbers
  (Spracklen et al., 2006; 2008; Carslaw, ICNAA 2009)

Effect of saturation vapour concentration





Gas-to-particle conversion

- Traditional view
  1. Chemical reactions in gas phase to produce low volatile vapour(s)
  2. Nucleation
  3. Subsequent condensational growth

- New view
  1. Like traditional step 1
  2. Clustering
  3. Nucleation or barrierless nucleation
  4. Activation with the second group of vapour(s)
  5. Like traditional step 3
- All steps are active simultaneously although (i-1) is needed before step (i)

Kulmala et al., 2014, accepted
Annual Review of Physical Chemistry

Atmospheric clusters present understanding

Theory / Predictions

- Existence of atmospheric clusters (K2000)
- Concentration: 1E5-1E6
- Nano-Köhler: size dependent growth (K2004)

Experiments

- Found (K2007)
- Concentration 1E3-1E5
  - Several observations
  - Something still missing ?
- Found (K2013)

Atmospheric nucleation rate

$$J_{1.5} = A \times [H_2SO_4] \cong k[H_2SO_4]N_n$$

$$\cong k'[H_2SO_4][Org]$$

$$OR$$

$$\cong k''[H_2SO_4][H_2SO_4] \cong k'''[Org][Org]$$

$$J(d_p) = J_{1.5} \exp\left\{\gamma\left(\frac{1}{d_p} - \frac{1}{1.5}\right)\frac{CS}{GR}\right\}$$

Summary

- New particle formation is globally significant
  - To CN, to CCN and to cloud droplets
- New instruments to detect
  - Size segregated size and composition
  - PSM, AIS/NAIS, (CI-)Api-ToF
    - Should be used simultaneously
- Theoretical predictions
  - From quantum chemistry to global models
  - Agree with observations
- In Planetary Boundary Layer
  - Neutral clustering dominates
  - Sulphuric acid crucial < 1.7 nm
  - At 1.7 nm +/- 0.2 nm organics will start to contribute significantly