Influence of photooxidation and oligomerisation on the hygroscopicity and volatility of 1,3,5-TMB SOA

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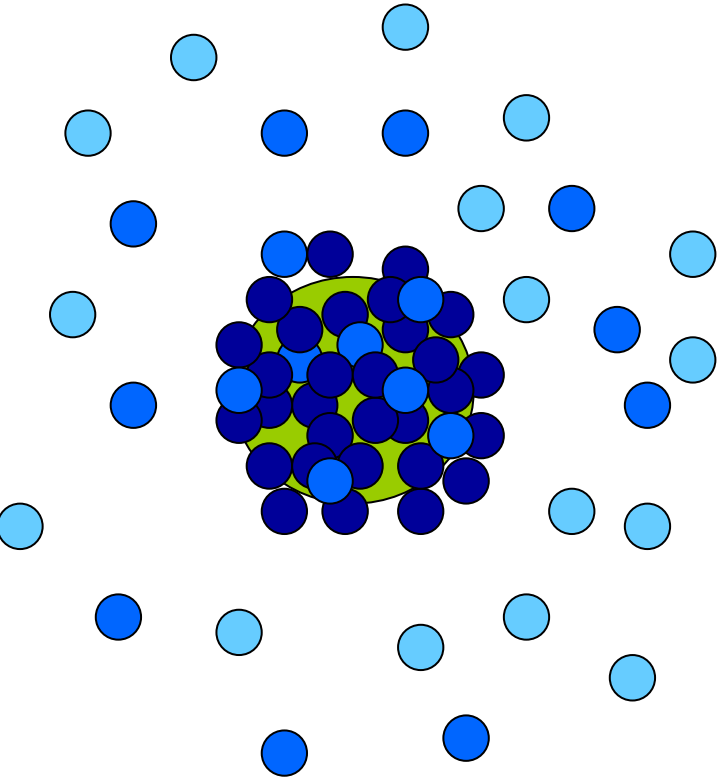
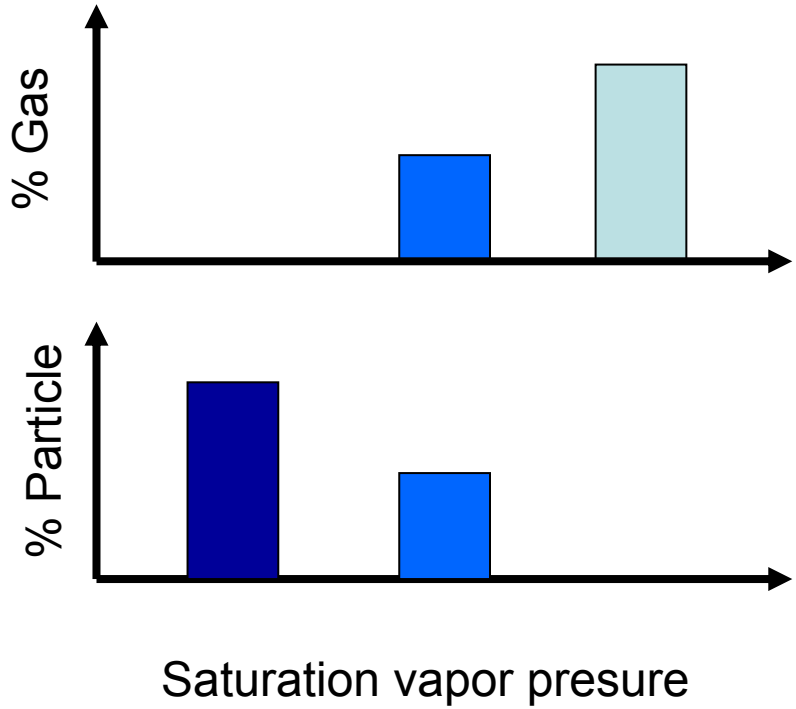
Definitions

- Primary Organic Aerosol (POA)
  - Aerosol particles which are directly emitted into the atmosphere.
- Secondary Organic Aerosol (SOA)
  - Aerosol particles which are formed in the atmosphere from gas phase by chemical reaction.

Partitioning theory

Case 1: Low aerosol mass



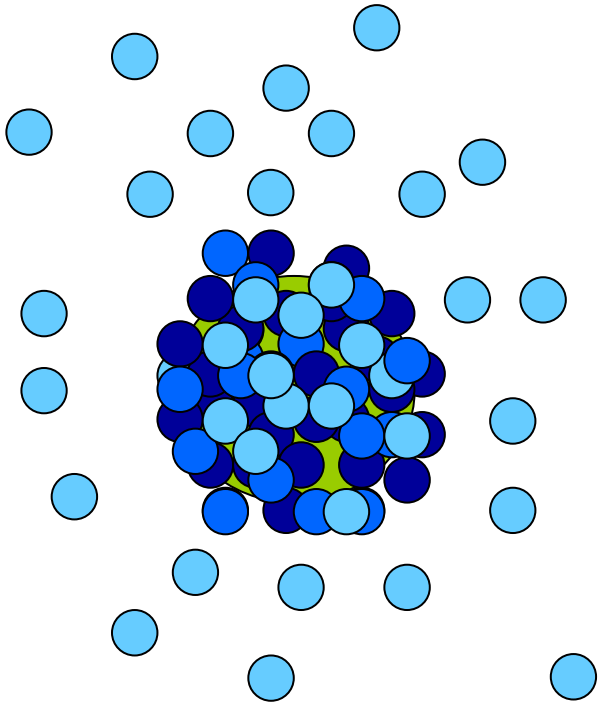


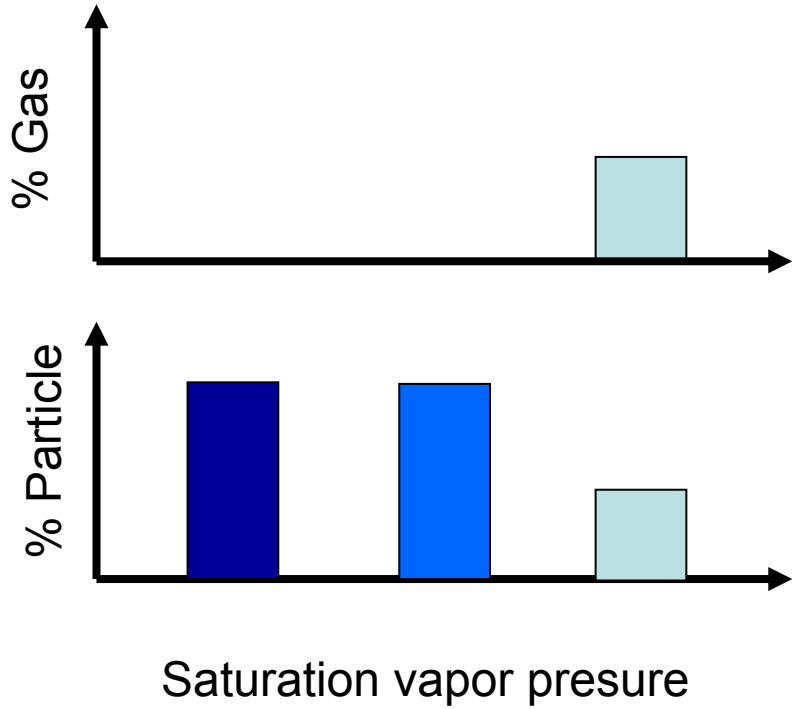
Saturation vapor pressure = Volatility

Low Medium High

Partitioning theory

Case 2: High aerosol mass

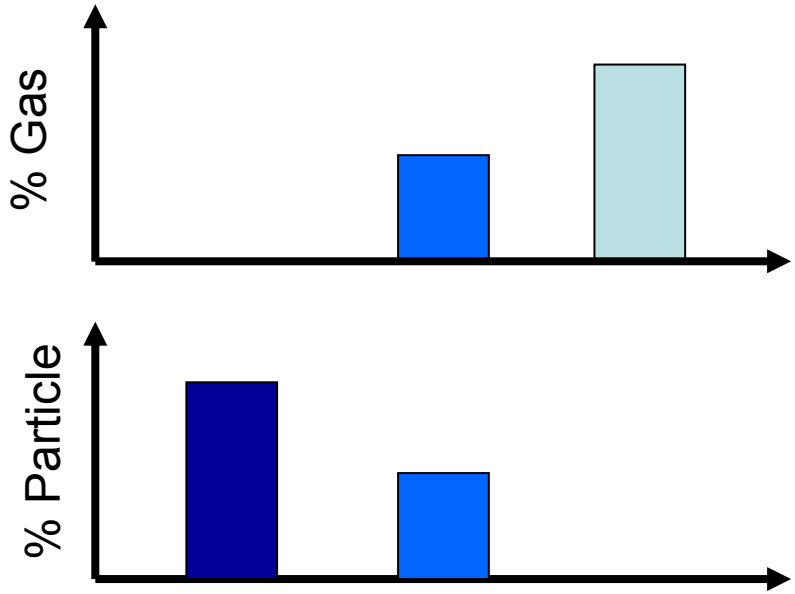




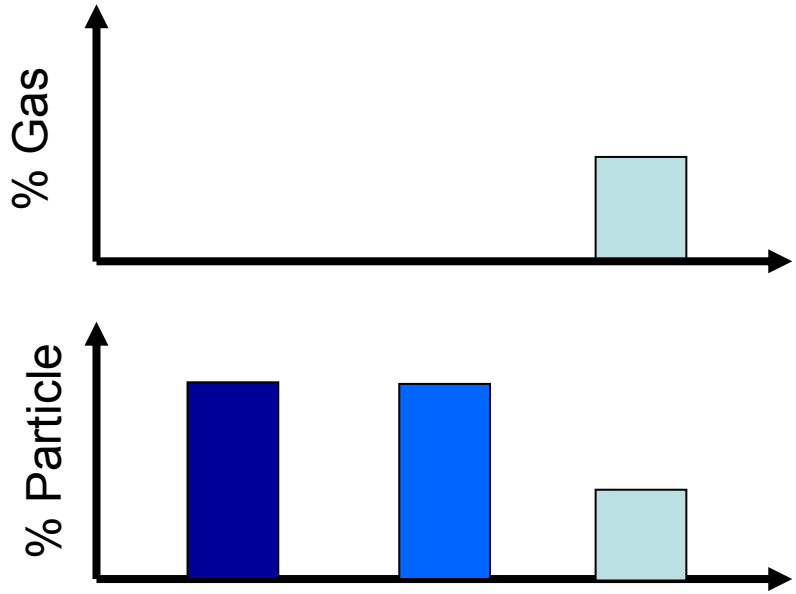
Saturation vapor pressure = Volatility

Partitioning theory

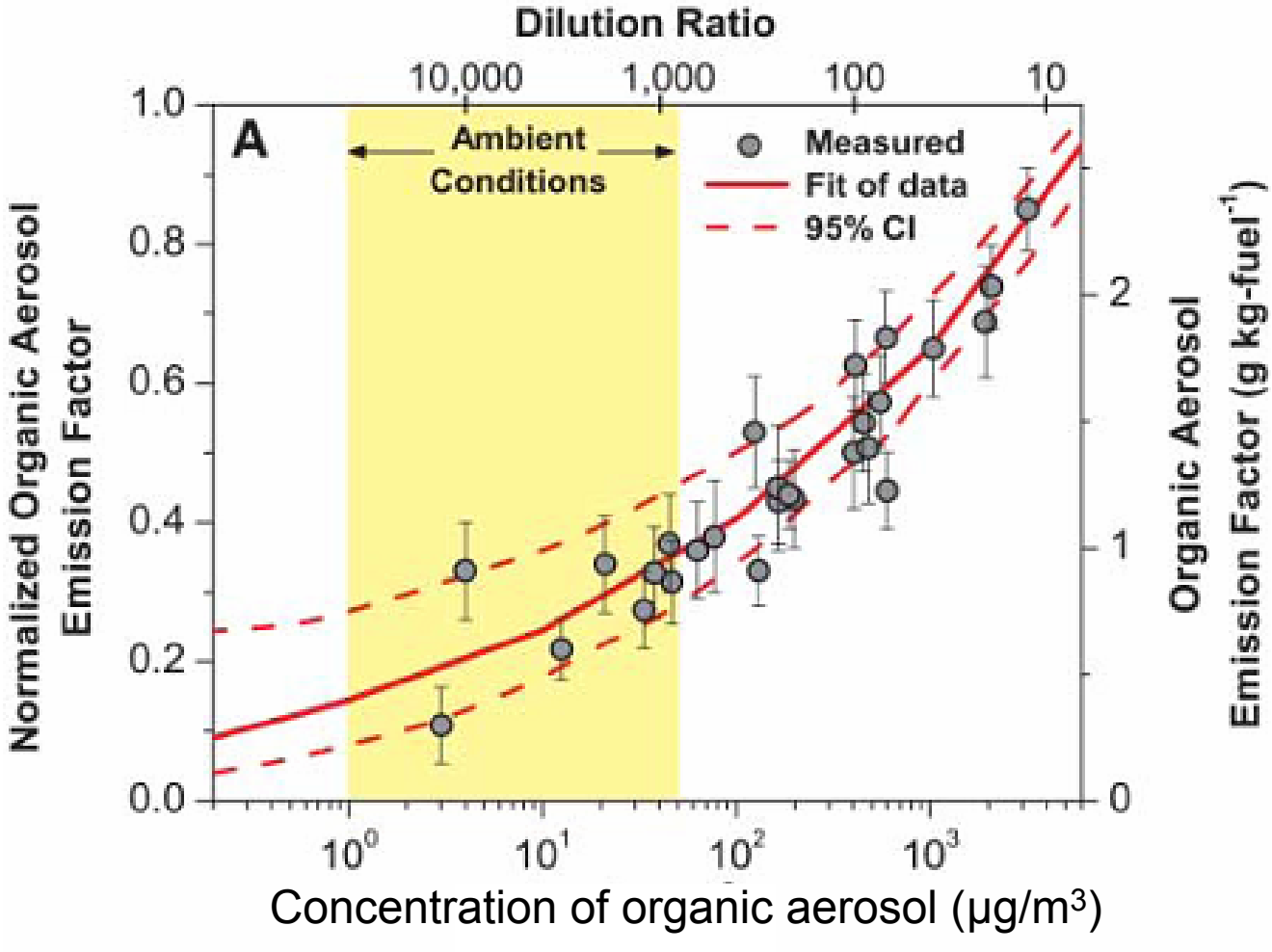
Low aerosol mass



High aerosol mass

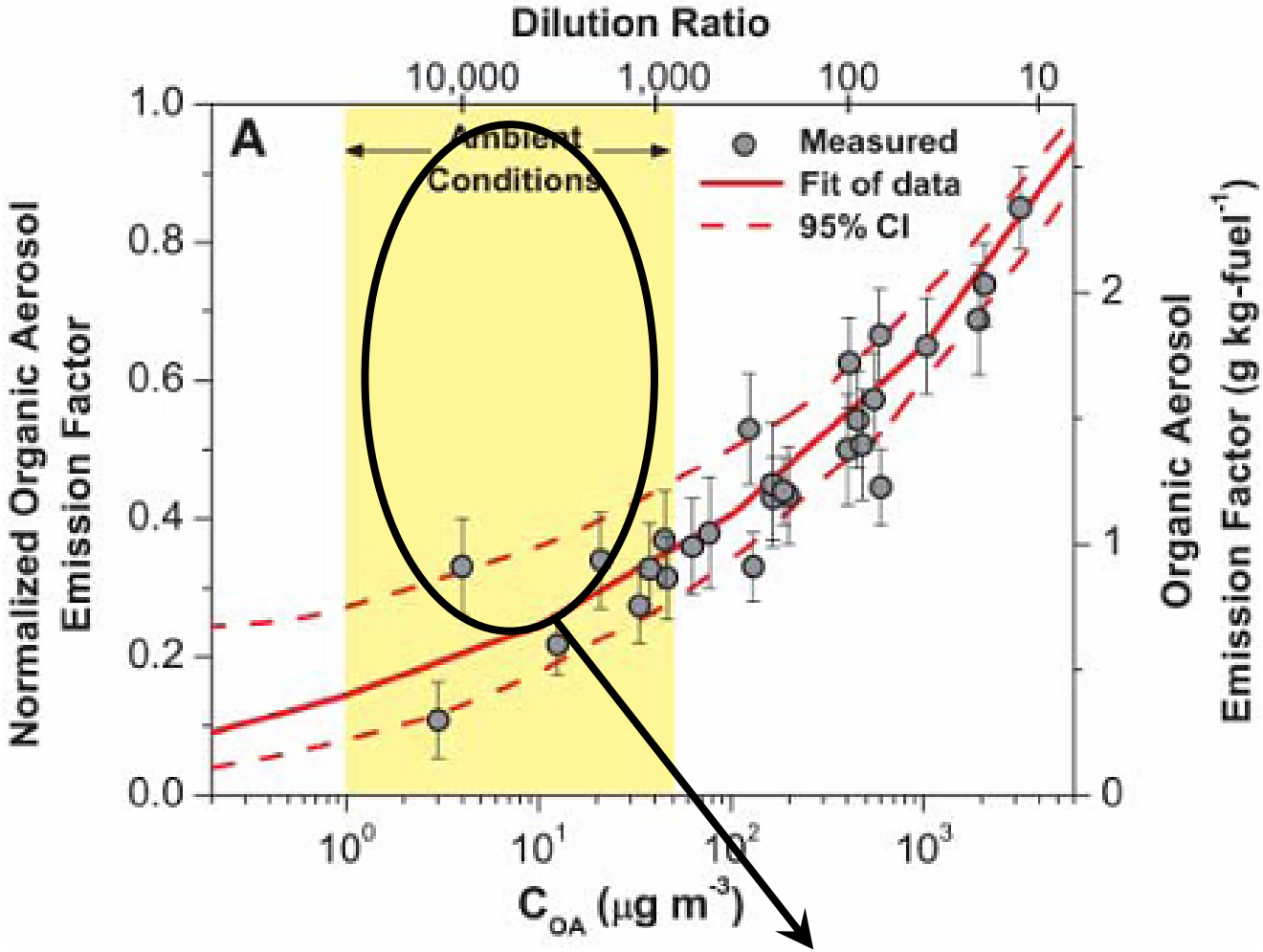


Partitioning changes with the mass loading



•Evaporation of POA with increasing the dilution (i.e. decreasing the mass loading)
•At ambient condition only 25% of POA exist

Robinson et al. 2007 Science



More volatile compound stay in the gas phase, and then this could form SOA after Oxydation / Oligomerisation (chemistry transformation) in the gas phase

Robinson et al. 2007 Science

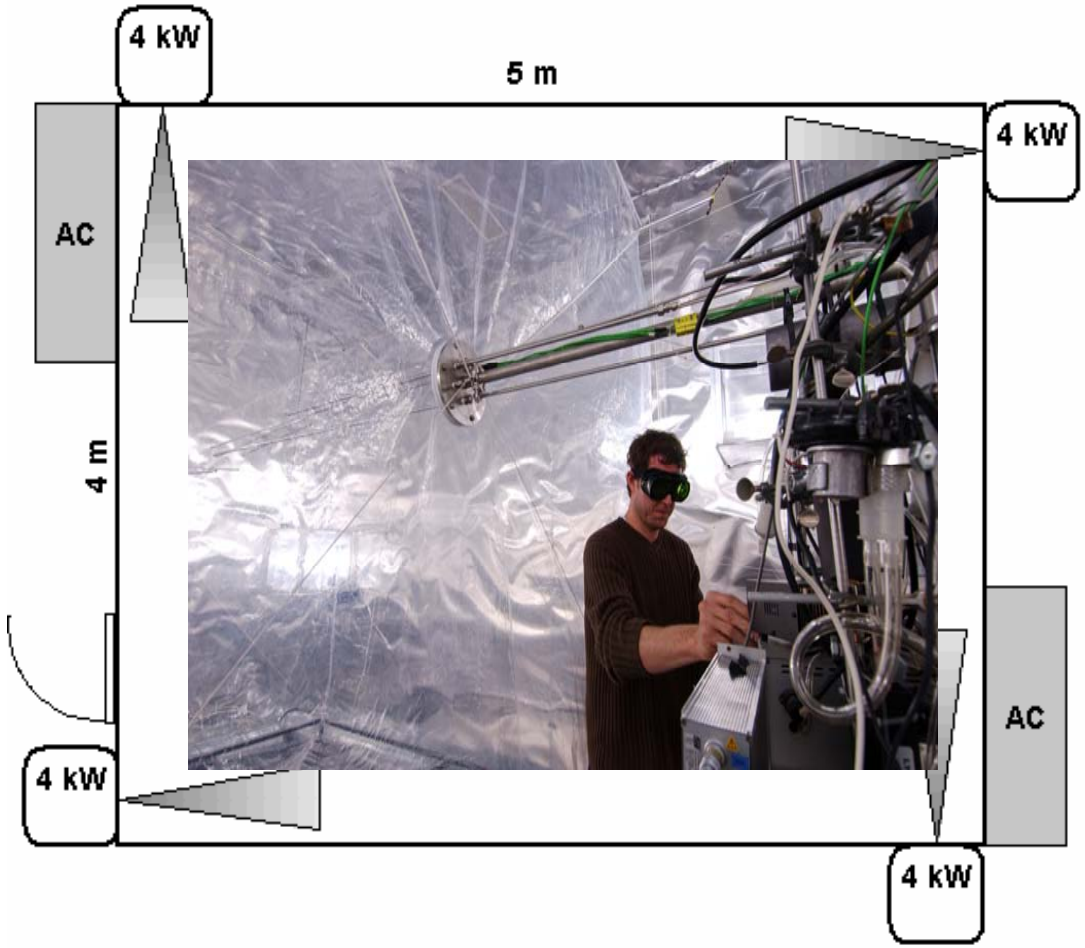
Outline

- Experimental setup description

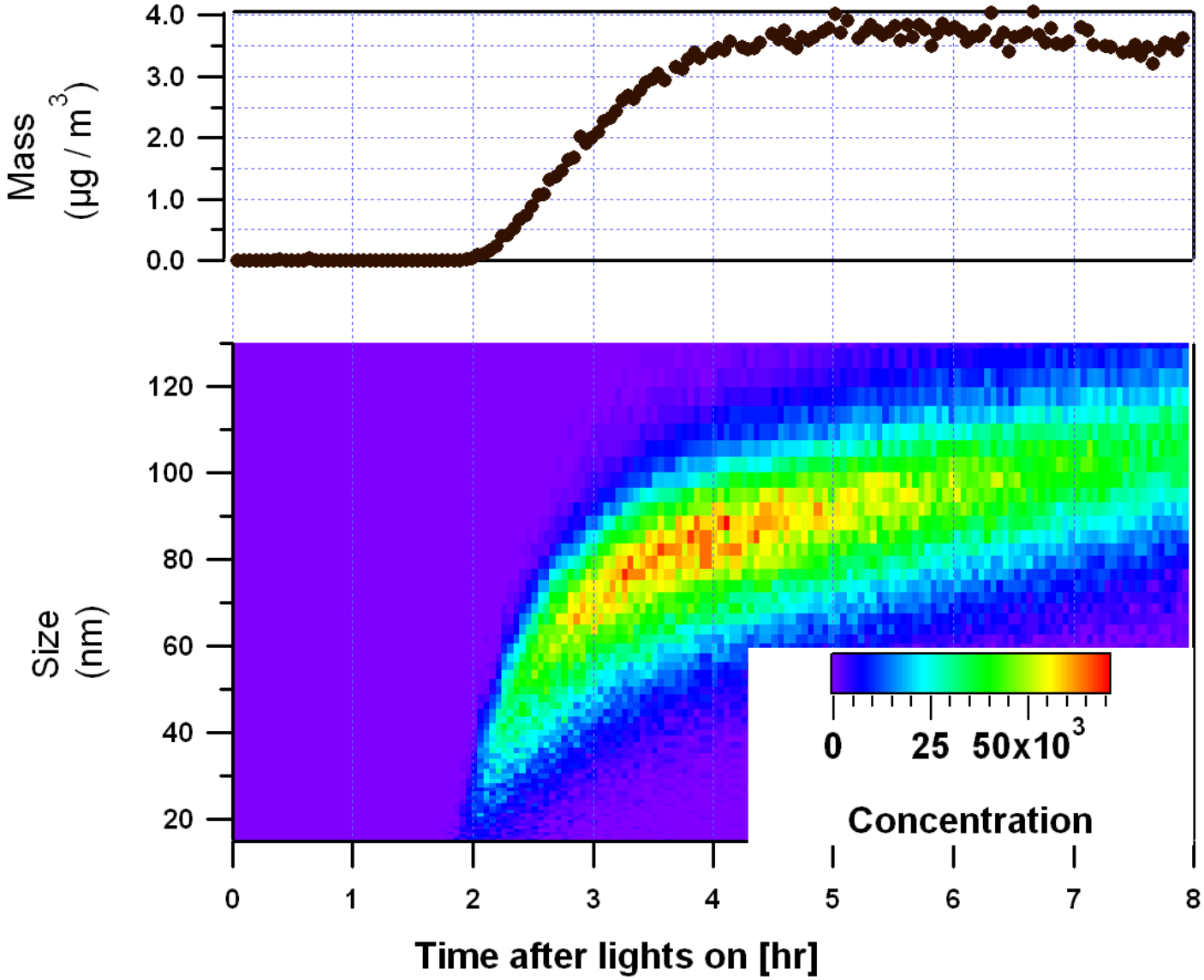
- Hygroscopicity and volatility of SOA produced using **low (60 ppb)** and **high (1200 ppb)** initial precursor (TMB) concentrations.

Smog Chamber facility

- Temperature Control
- RH = 50%
- Gas input facilities NO_x,VOC
- 4 xenon lamps

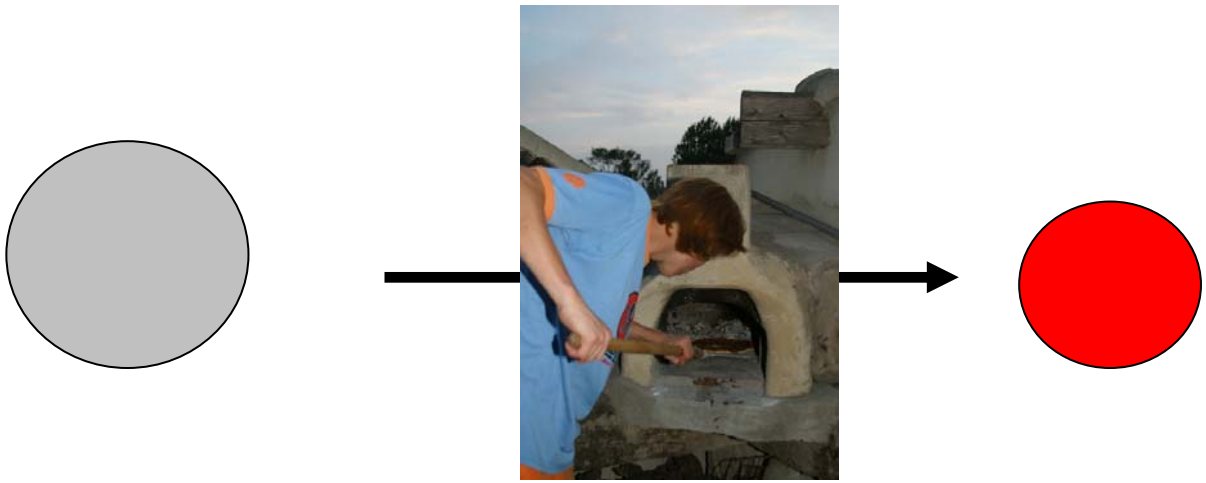


Typical experiment at the Smog Chamber



Instruments

- **V**TDMA → measures the **V**olatility properties

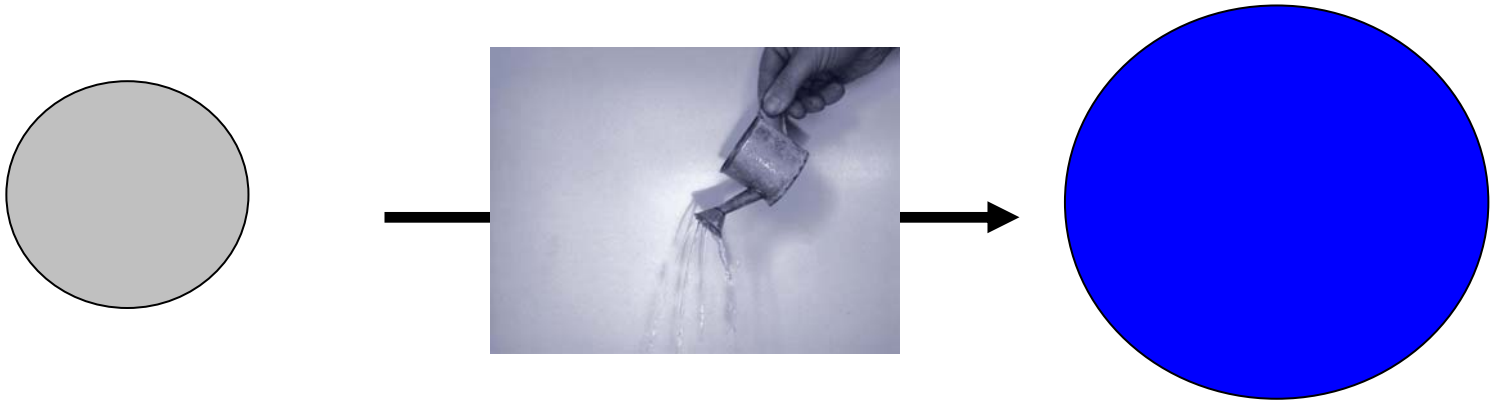


$$VFR(T,Time) = \frac{\textbf{Volume after heating}}{\textbf{Volume at 25°C dry}}$$

VFR(T) = Volume Fraction Remaining (expressed in %)

Instruments

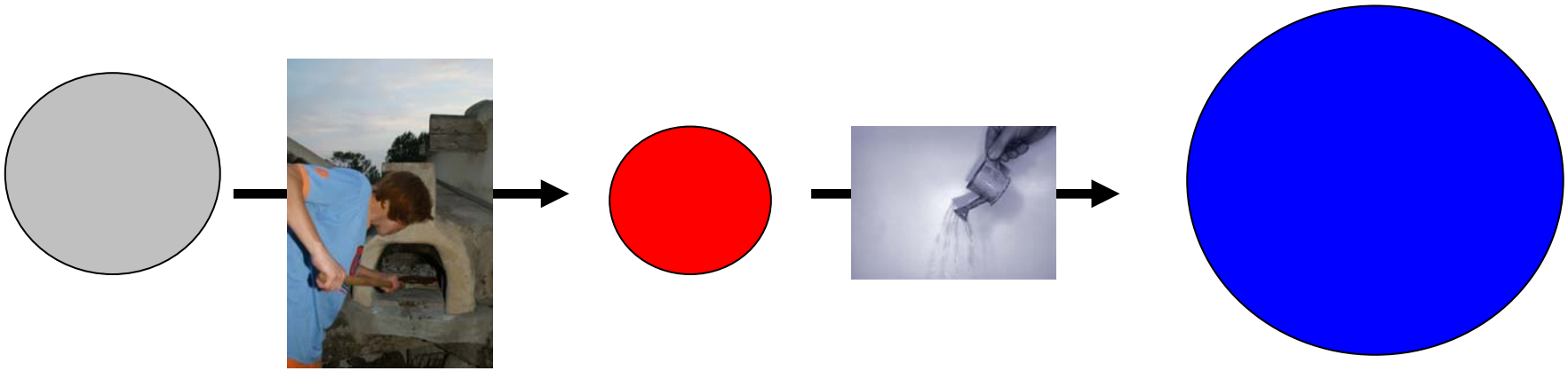
- **H**TDMA → measures **H**ygroscopic properties



$$GF(RH) = \frac{\text{Diameter humid (RH)}}{\text{Diameter dry}}$$

Instruments

- **VH**TDMA → measures the **H**ygroscopic properties of the residual aerosol remaining after the oven

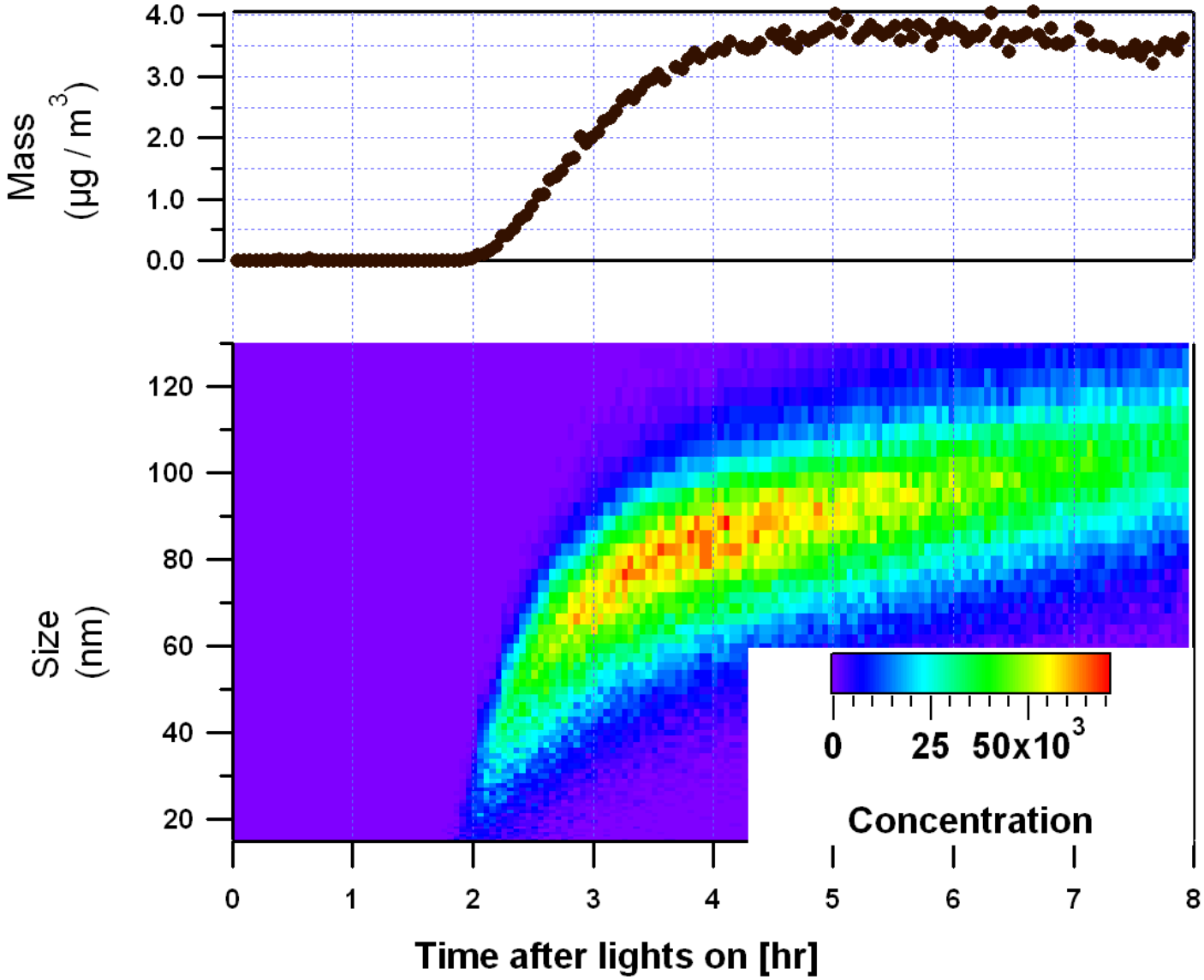


$$VH\_GF(RH,T) = \frac{\text{Diameter humid (RH)}}{\text{Diameter after heating}}$$

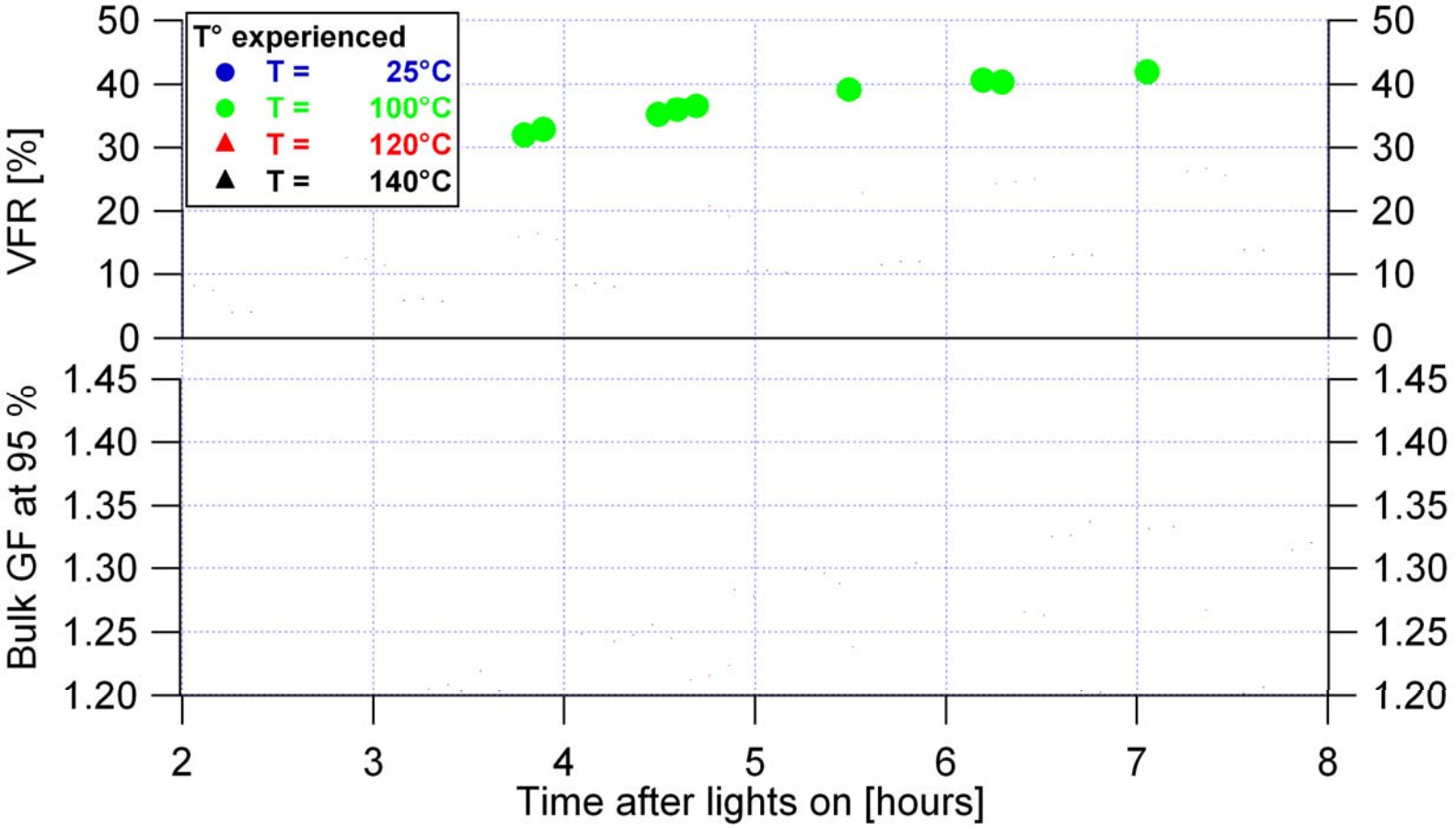
SOA from 1,3,5-Trimethylbenzene (TMB)

- Low precursor concentration experiment
  - 60 ppb TMB
  - 30 ppb NO_x
  - 400 ppt SO_2
- High precursor concentration experiment
  - 1200 ppb TMB
  - 600 ppb NO_x
  - 400 ppt SO_2

Low initial precursor concentration

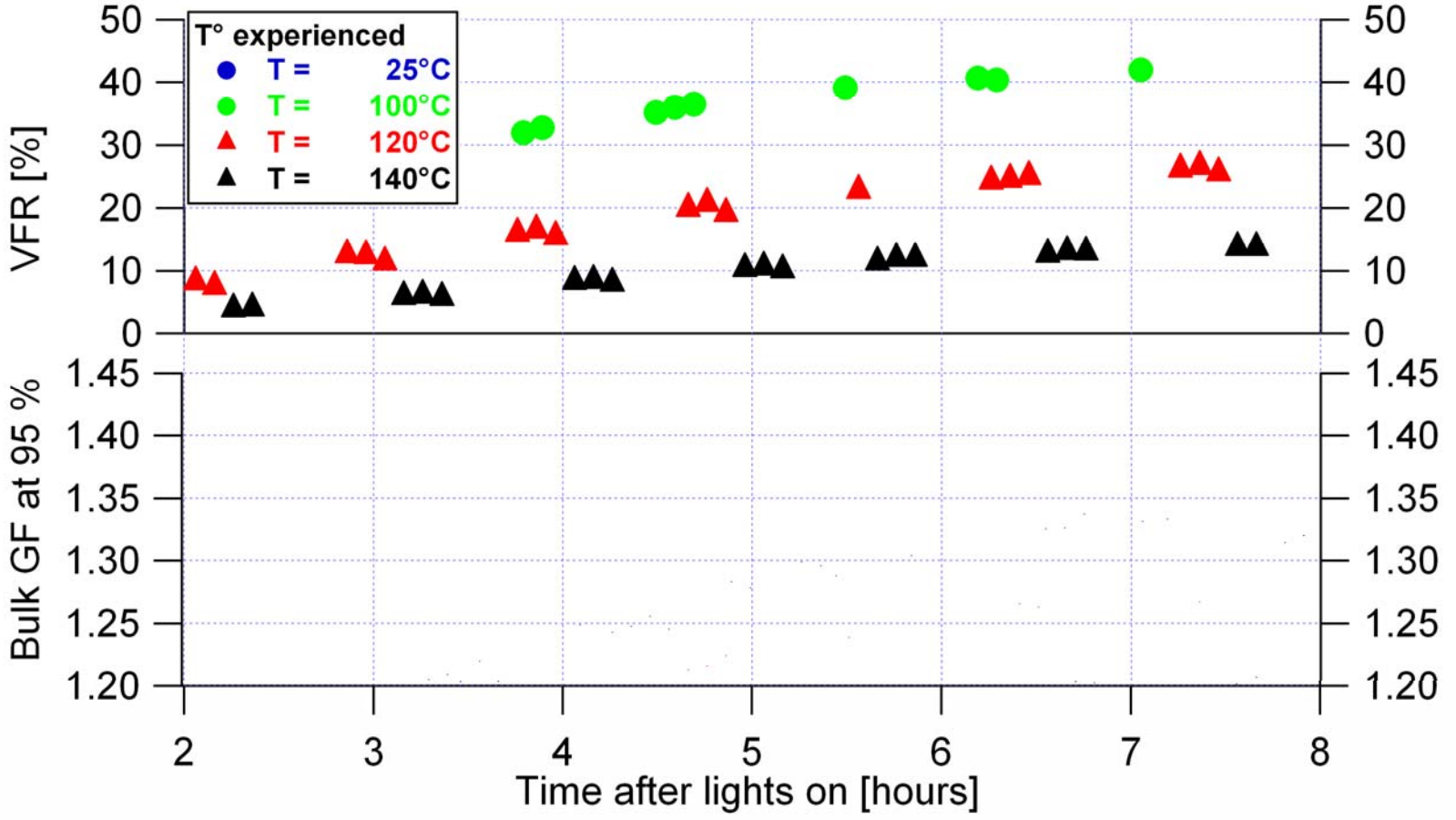


Low initial precursor concentration



•At a specific temperature, the VFR increases with time i.e. the particles become less and less volatile: This can be explained either by oligomerisation or oxidation or both.

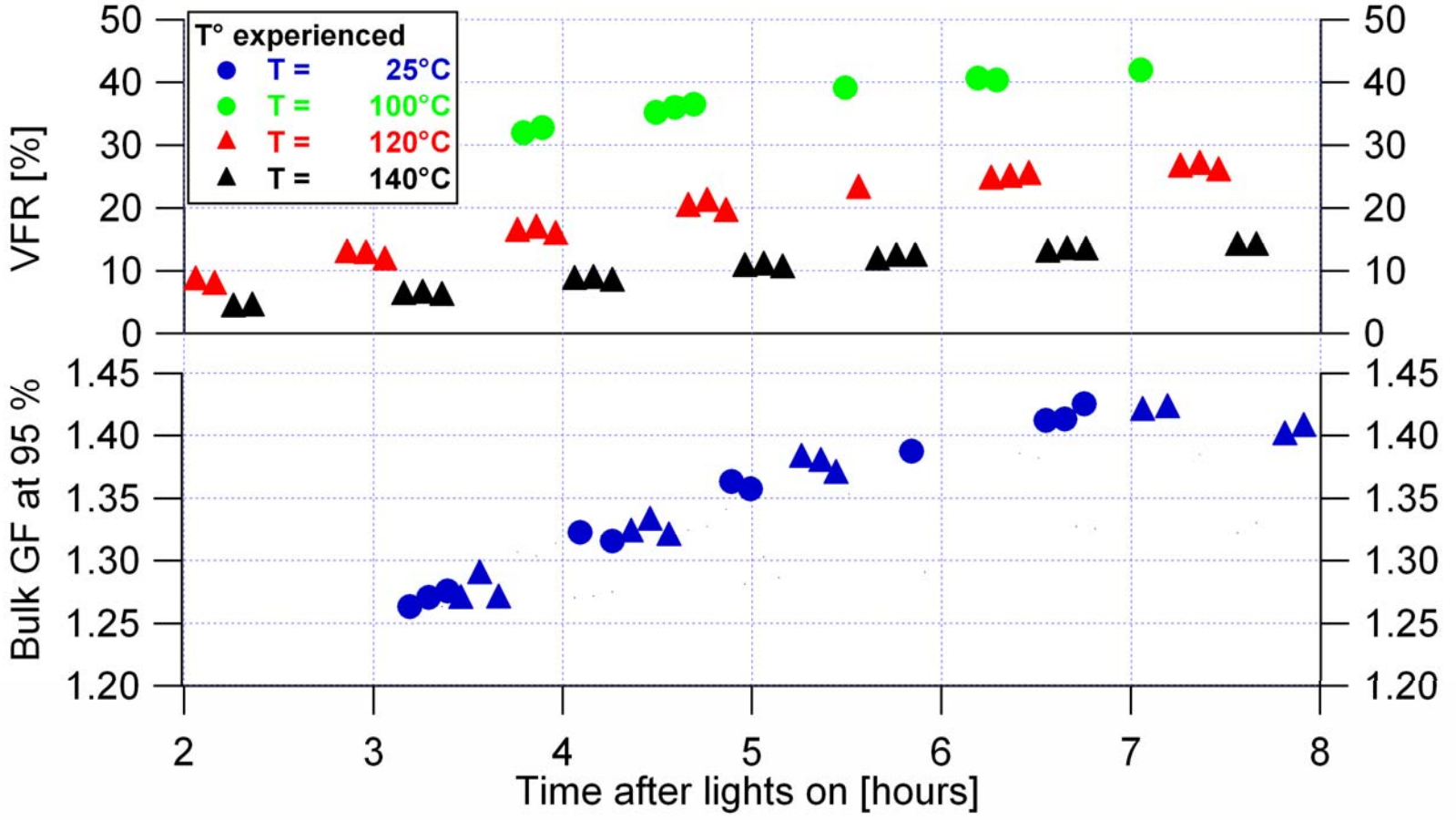
Low initial precursor concentration



• At higher temperature, the VFR is lower. More compounds evaporate at higher temperature.

•At 120ºC and at 140ºC the VFR increases with time. This can be explained either by oligomerisation or oxidation or both.

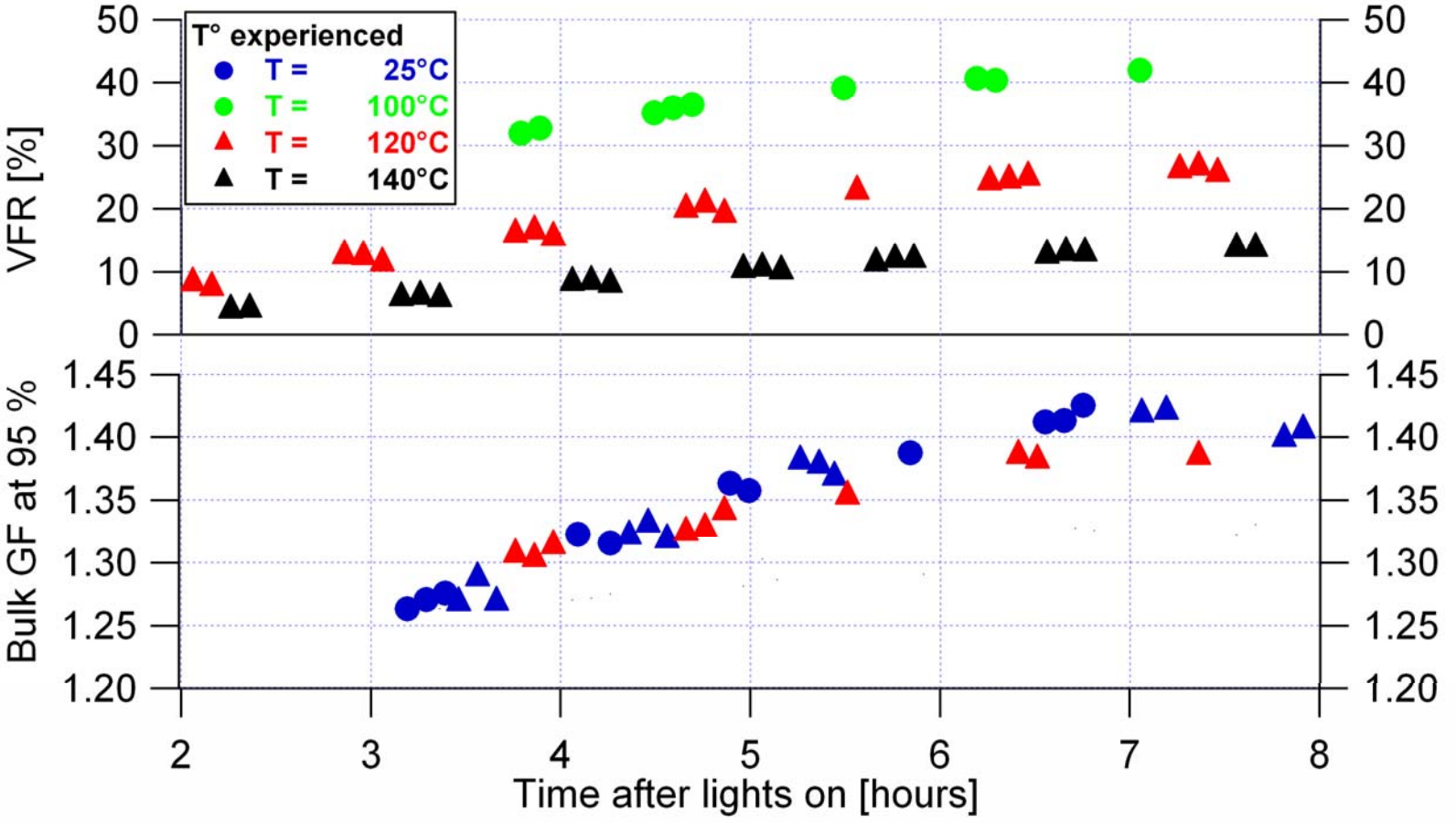
Low initial precursor concentration



Increase of the hygroscopic property with time:

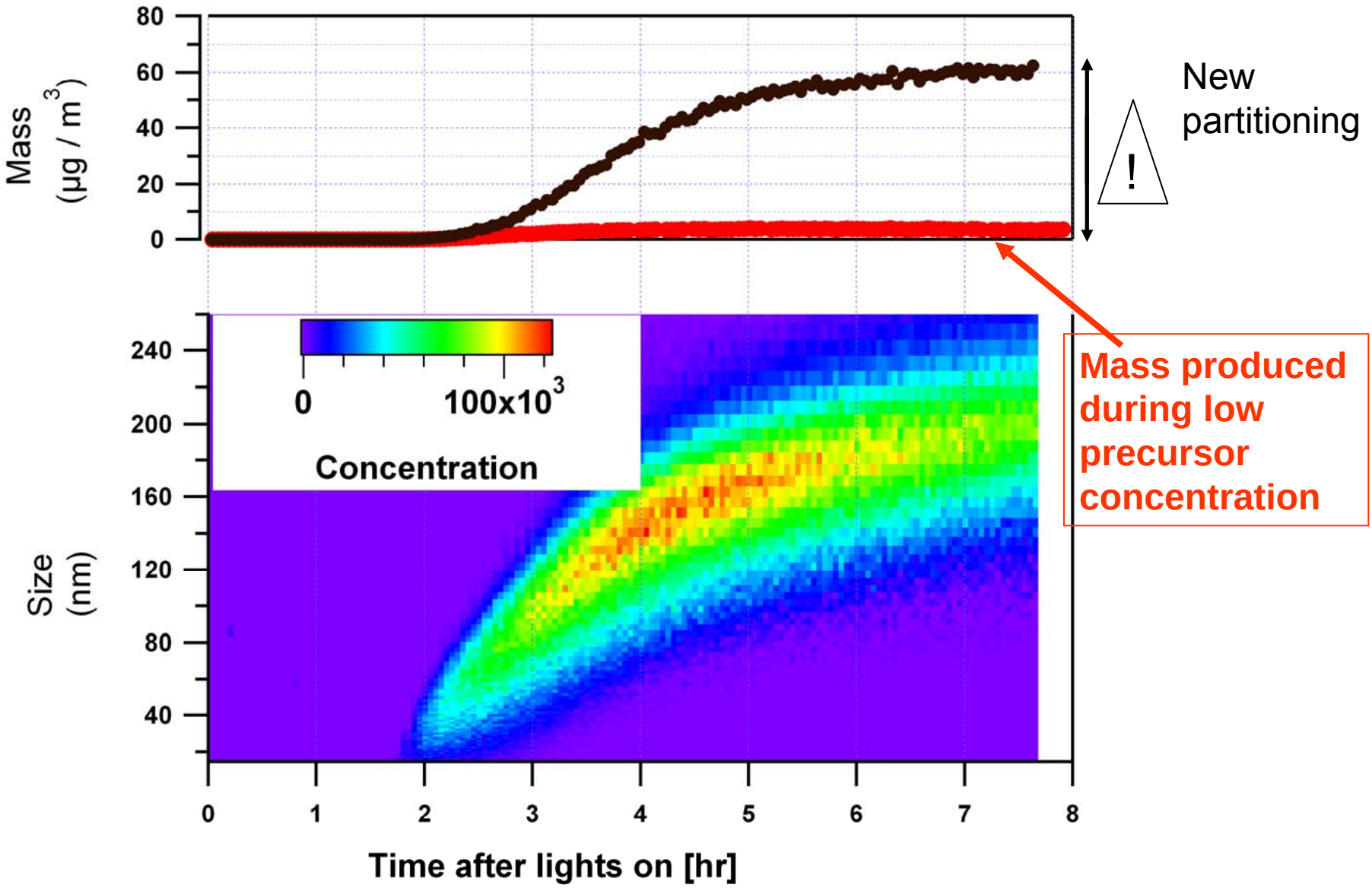
Oxidation has a stronger effect on hygroscopicity than oligomerisation

Low initial precursor concentration

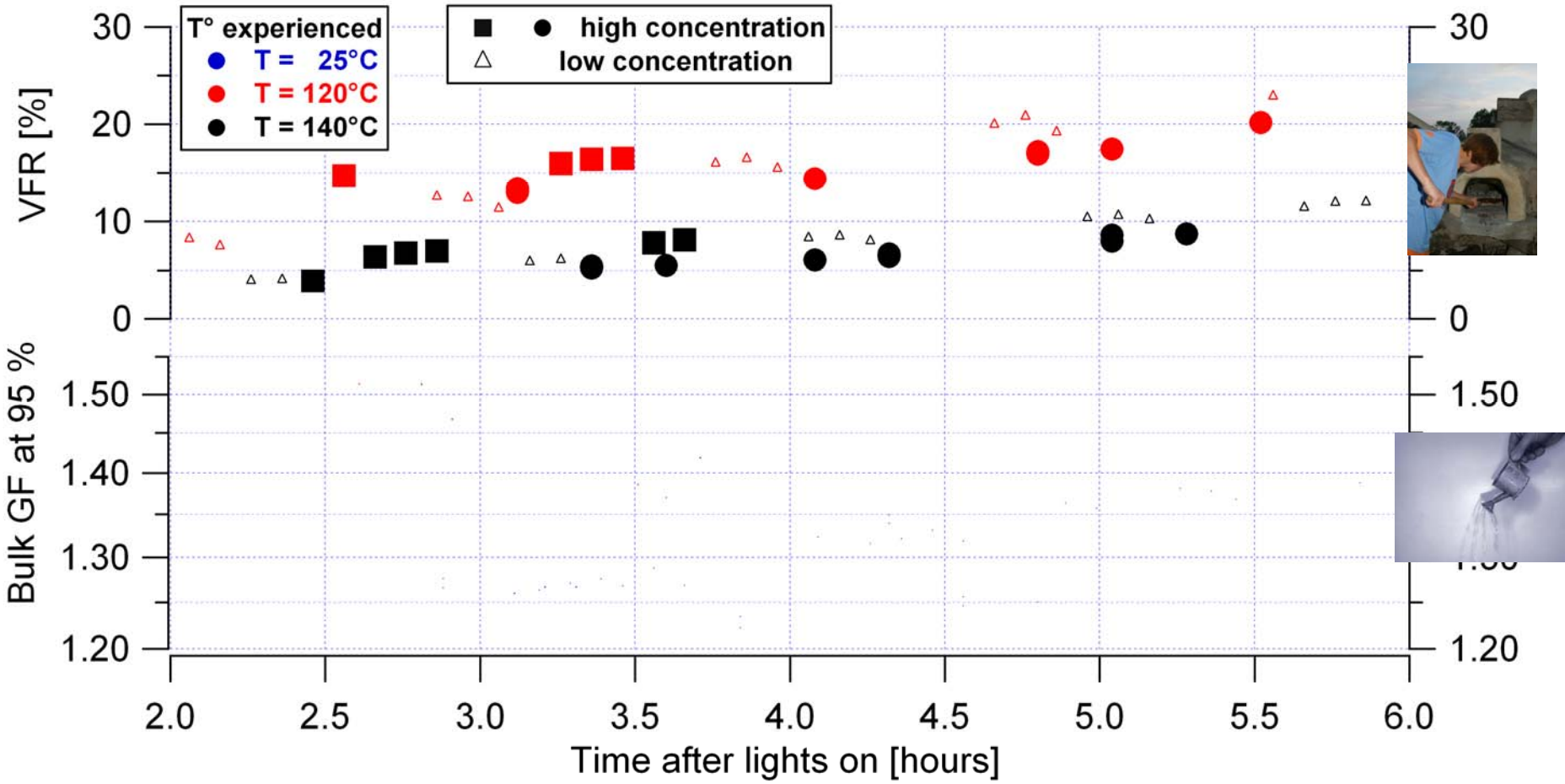


- **At 120 ºC the remaining particle have the same GF of the non-heated particle.**
- **The GF of the remaining particle increases with time.**

High initial precursor concentration



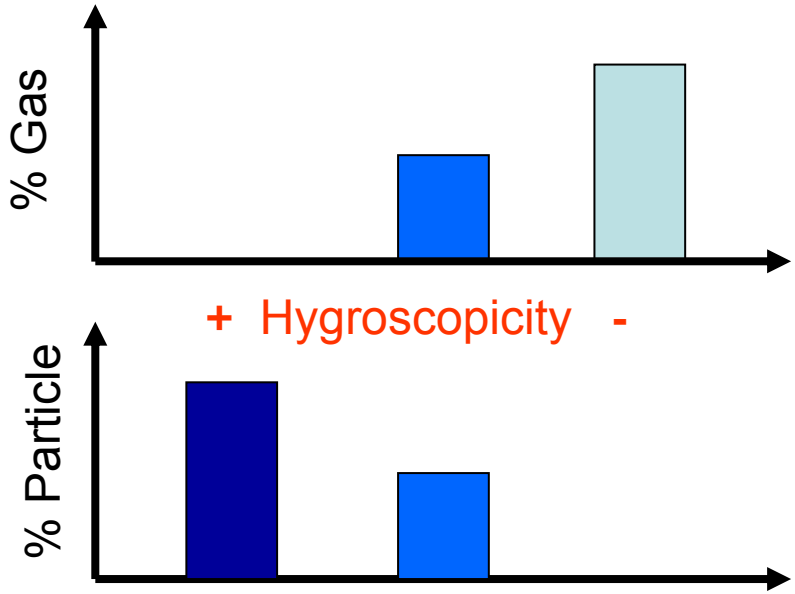
High initial precursor concentration



- At higher temperature, the VFR is lower.
- VFR increases with time (Oxidation or oligomerisation or both).
- Compared to low concentration, we have the same trend and value of the VFR.

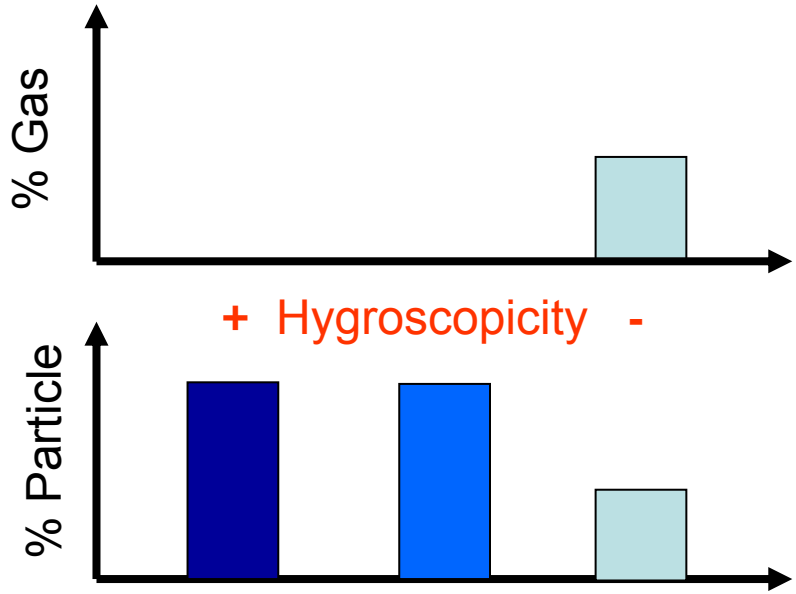
Partitioning …

Low aerosol mass



Saturation vapor presure

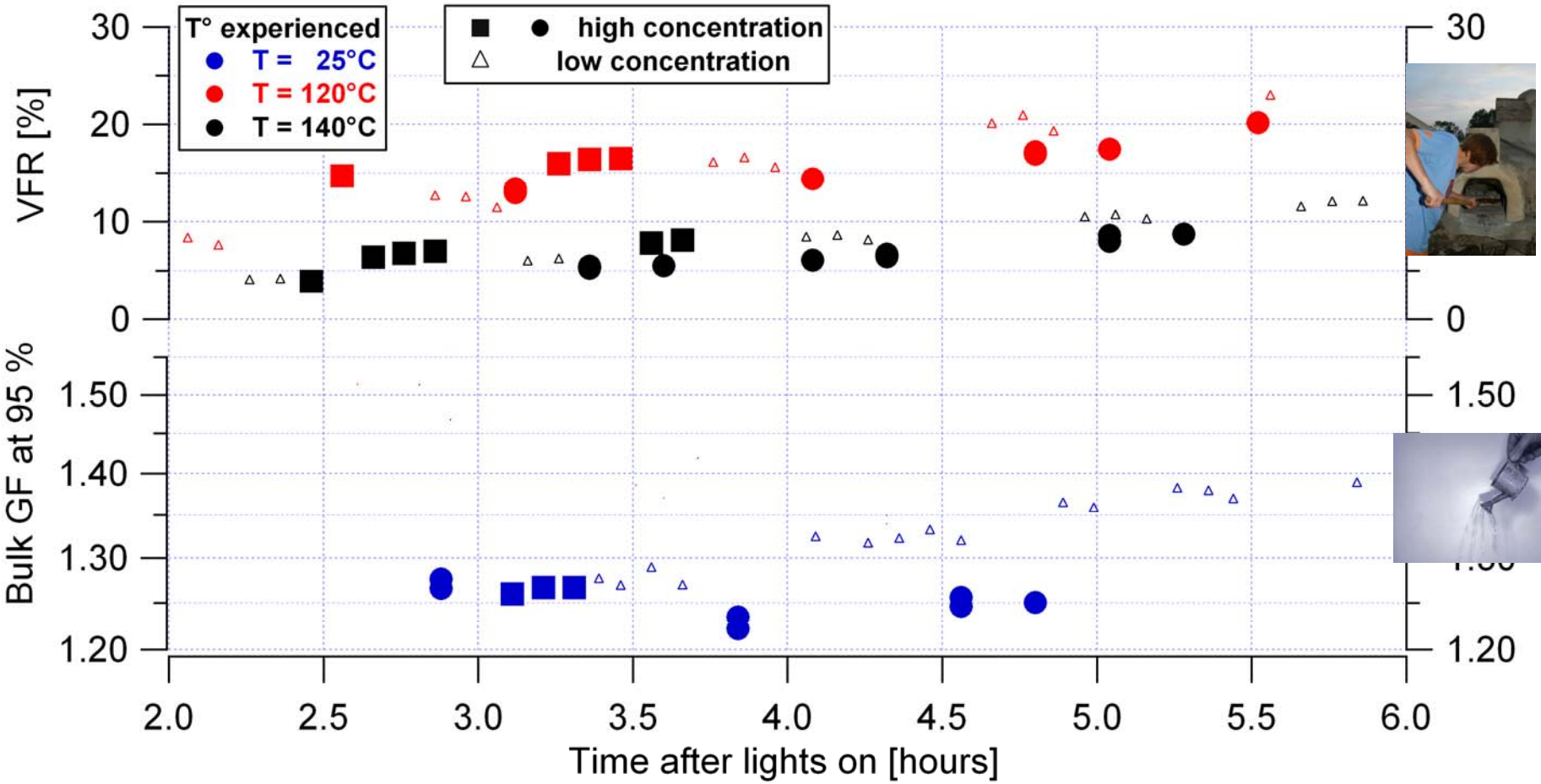
High aerosol mass



Saturation vapor presure

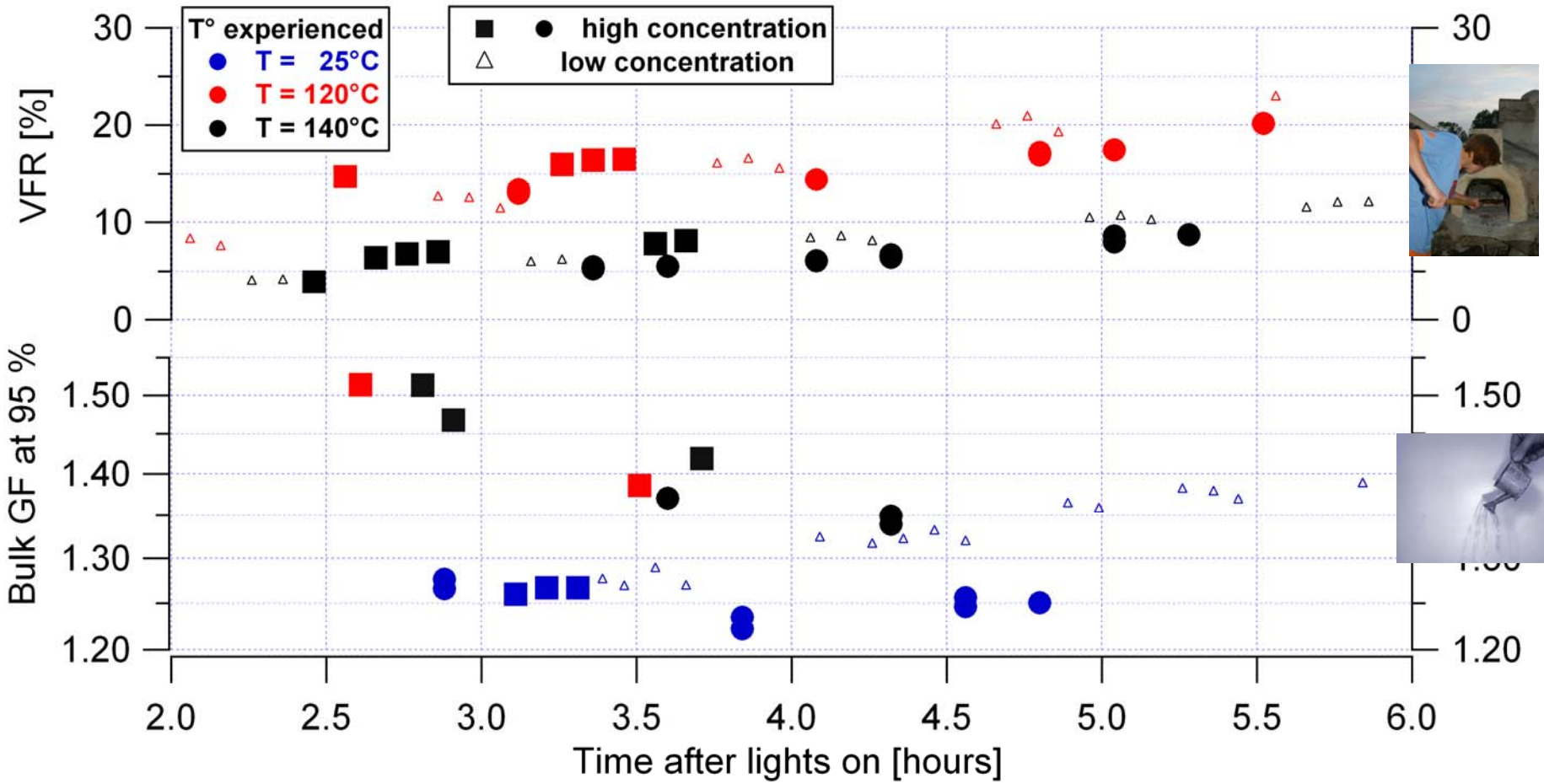
Partitioning changes with the mass loading

High initial precursor concentration



- For high precursor concentration, **we expect partitioning of more volatile species** (less oxidized) into the particle phase **which should decrease the hygroscopicity.**
- The GF stays more or less stable with time.

High initial precursor concentration



- The hygroscopicity of the remaining particle (120 and 140 ºC) is higher than the non-heated particle.
- The partitioning of more volatile species (less oxidized) into the particle phase decreases the hygroscopicity. By removing this volatile species (which lower the hygroscopicity), the remaining particles gains a higher hygroscopic property. **The concentration of the precursor does have an important impact on the hygroscopic property of SOA.**

Conclusions

- Due to partitioning, precursor concentration has an effect on the particle physical properties (hygroscopicity).
- The particle chemistry changes with time (becomes more oxidized and more oligomerised) which leads to a change of the hygroscopic and volatile properties.
- The VHTDMA technique is well suited to the investigation of such phenomena

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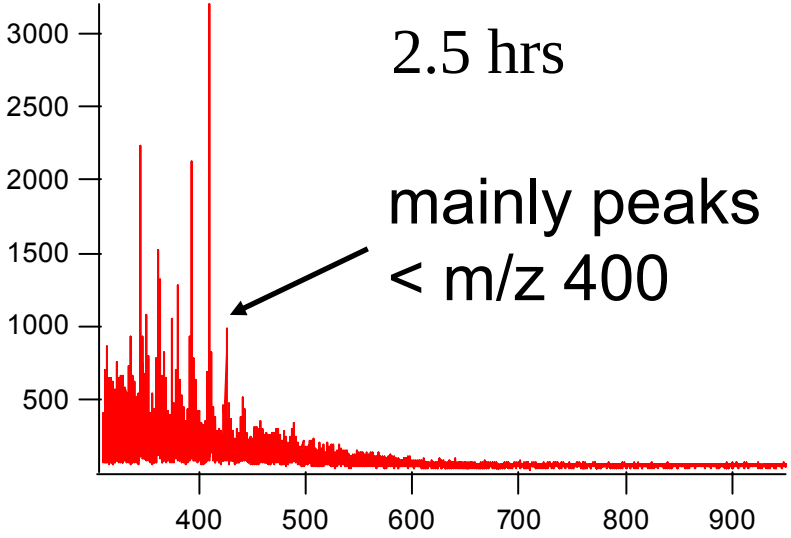
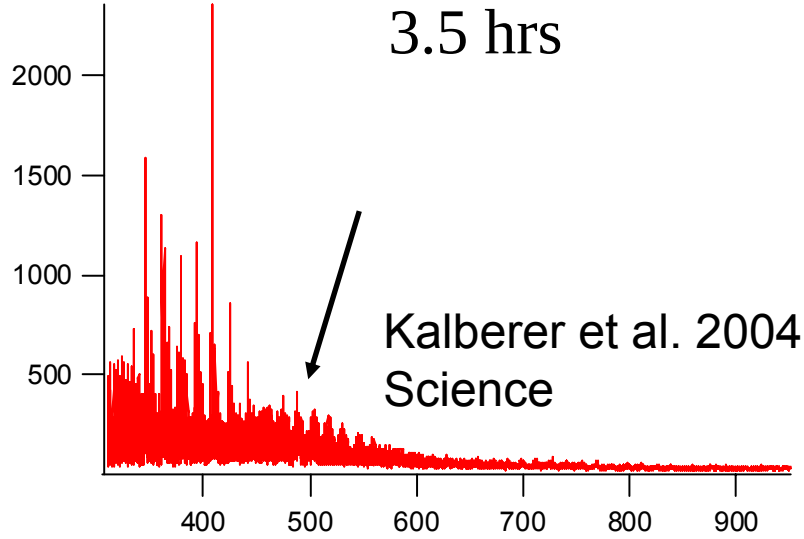
Thanks for your attention

Oligomerisation seen from the LDI-MS



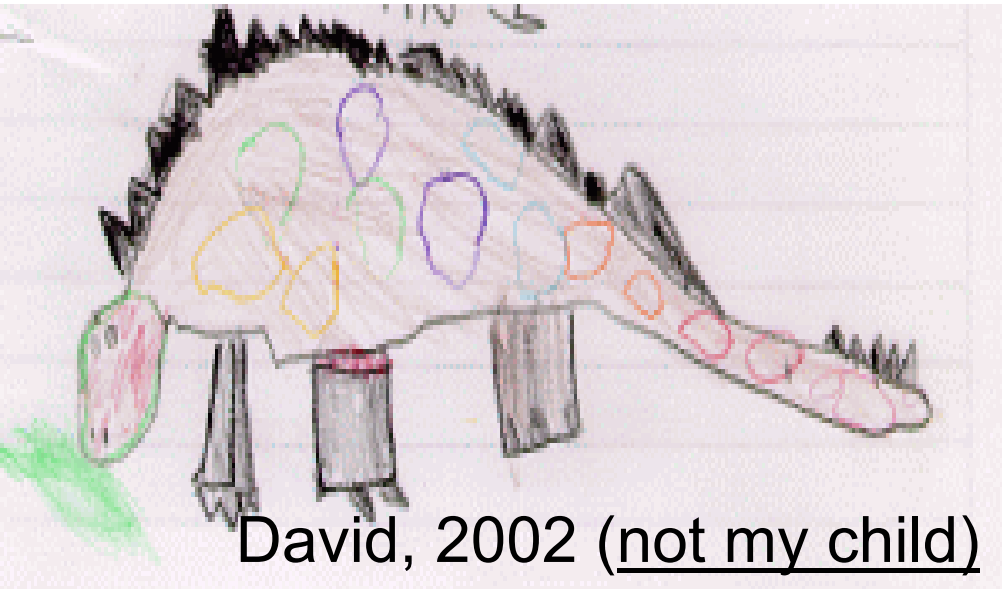
2.5 hrs

mainly peaks
< m/z 400

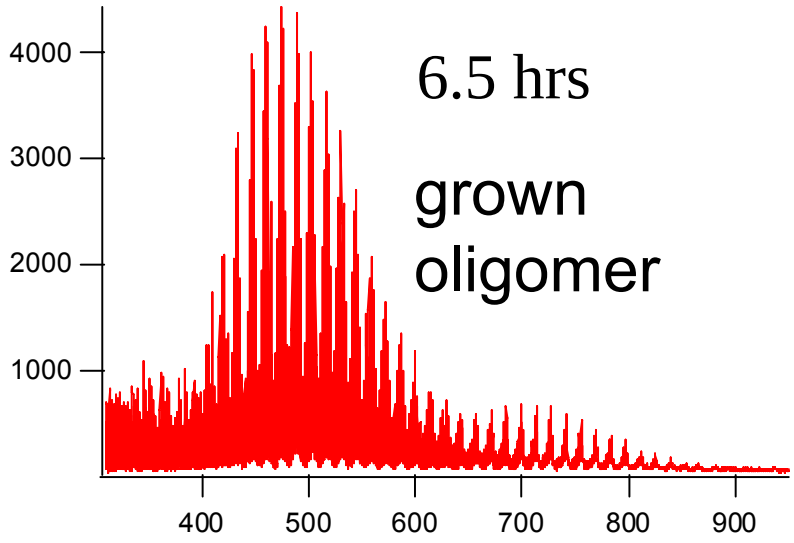


3.5 hrs

Kalberer et al. 2004
Science



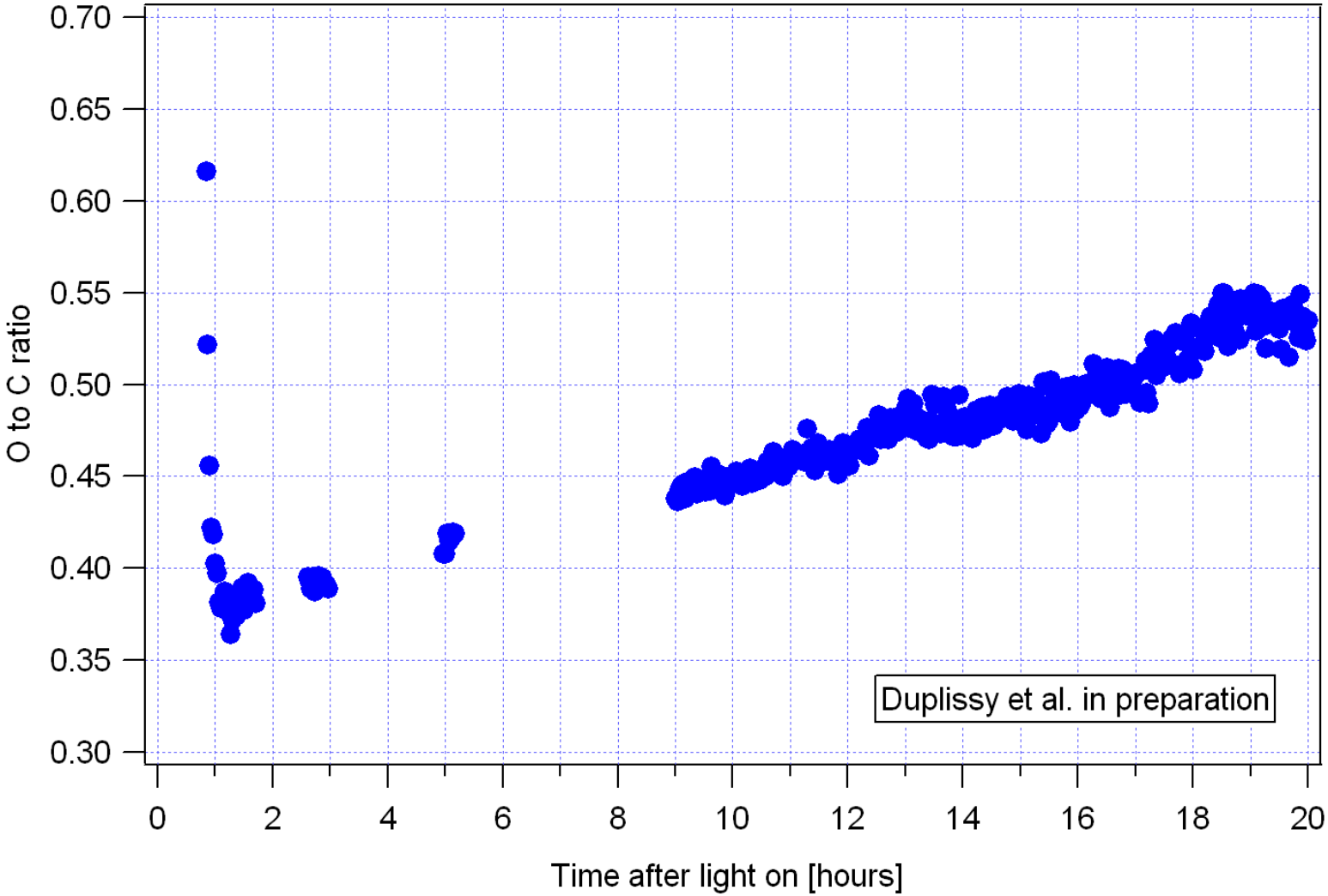
David, 2002 (not my child)

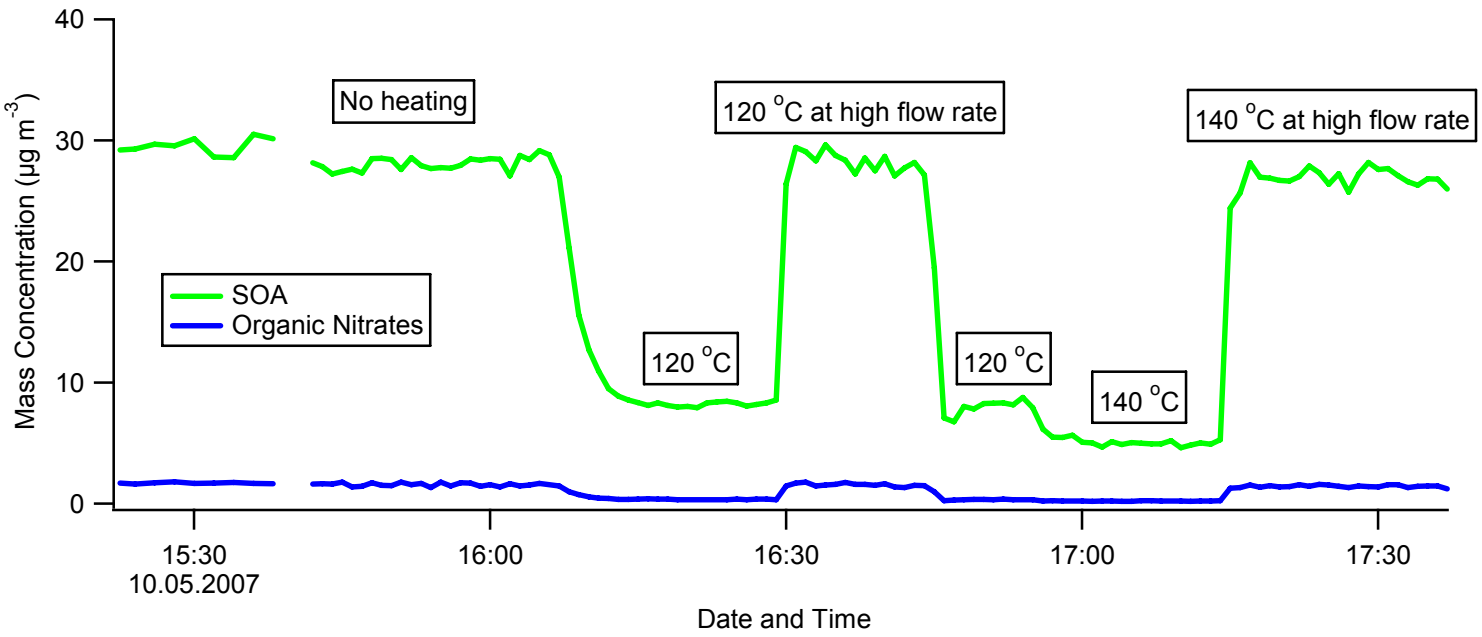


6.5 hrs

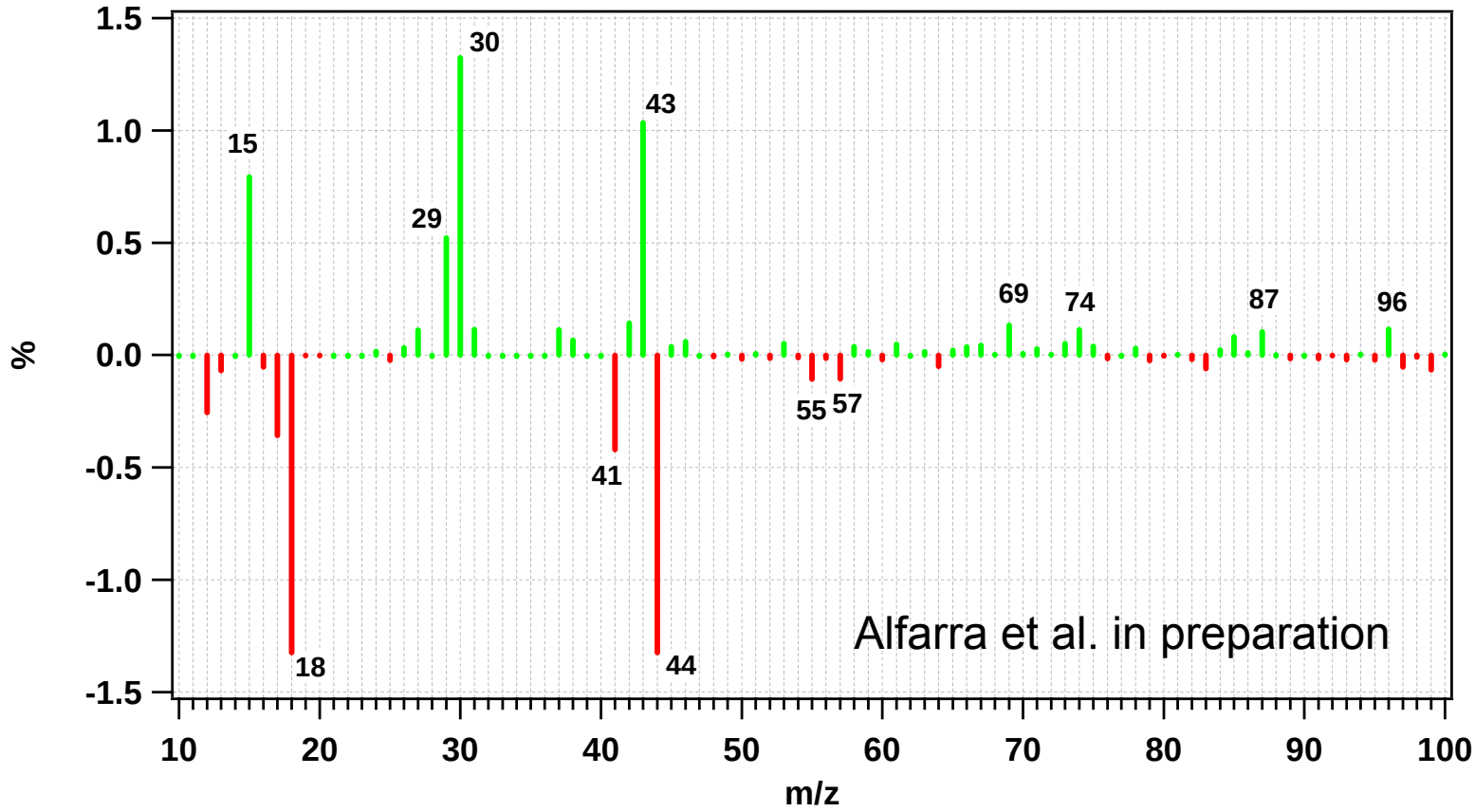
grown
oligomer

Evidence of Oxydation from the W-TOF AMS



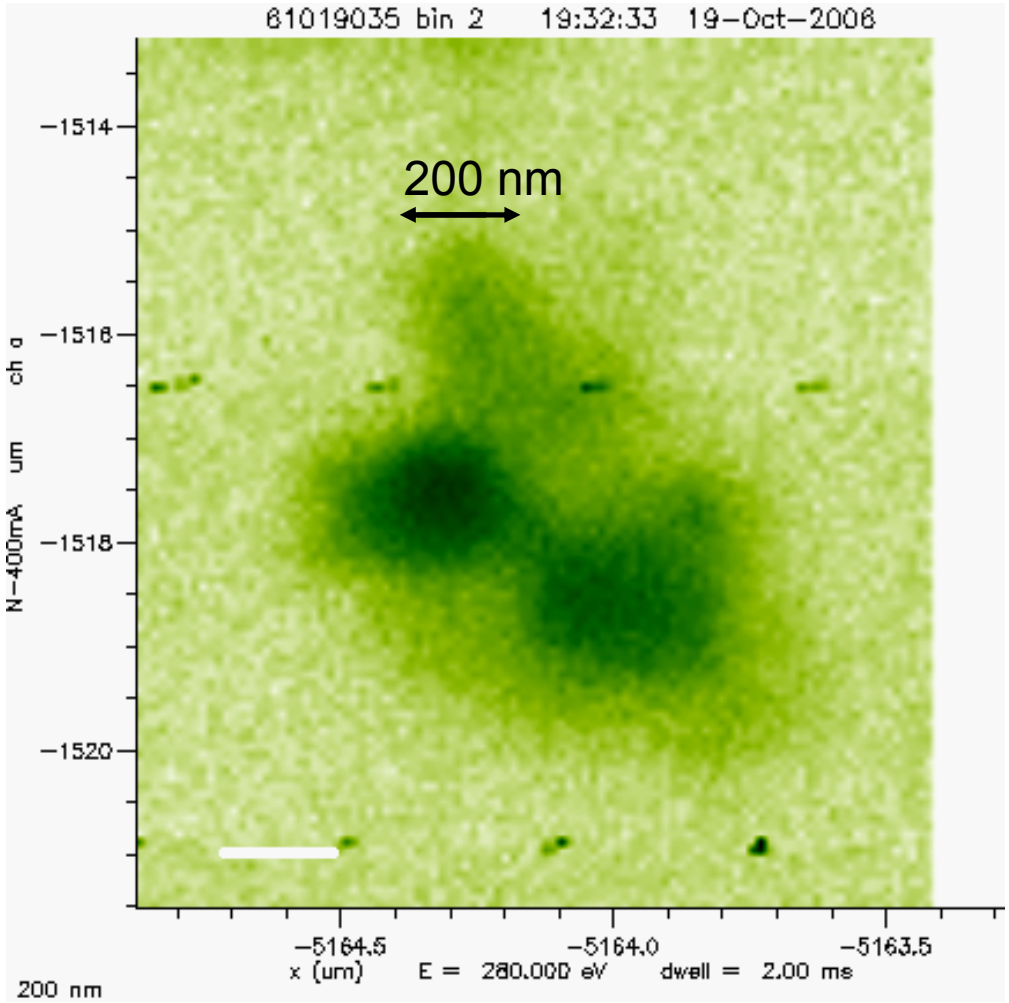

40
30
20
10
0
Mass Concentration (µg m-3)
No heating
120 °C at high flow rate
140 °C at high flow rate
SOA
Organic Nitrates
120 °C
120 °C
140 °C
15:30
10.05.2007
16:00
16:30
17:00
17:30
Date and Time

Partitioning from the Q-AMS

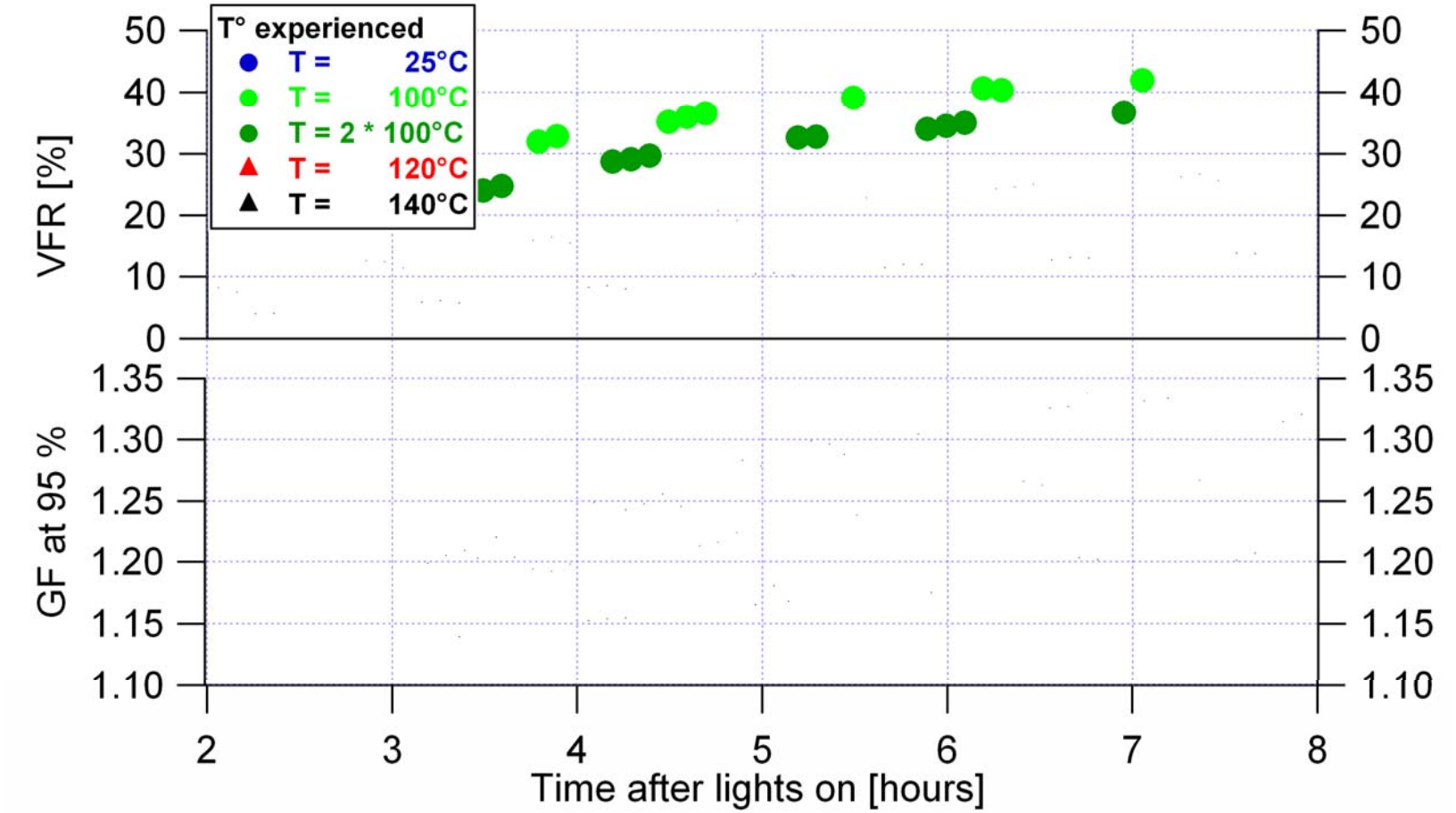


This results supports our understanding that more volatile material partition into SOA at high mass concentrations.

My talk will be about SOA: How does it look like?



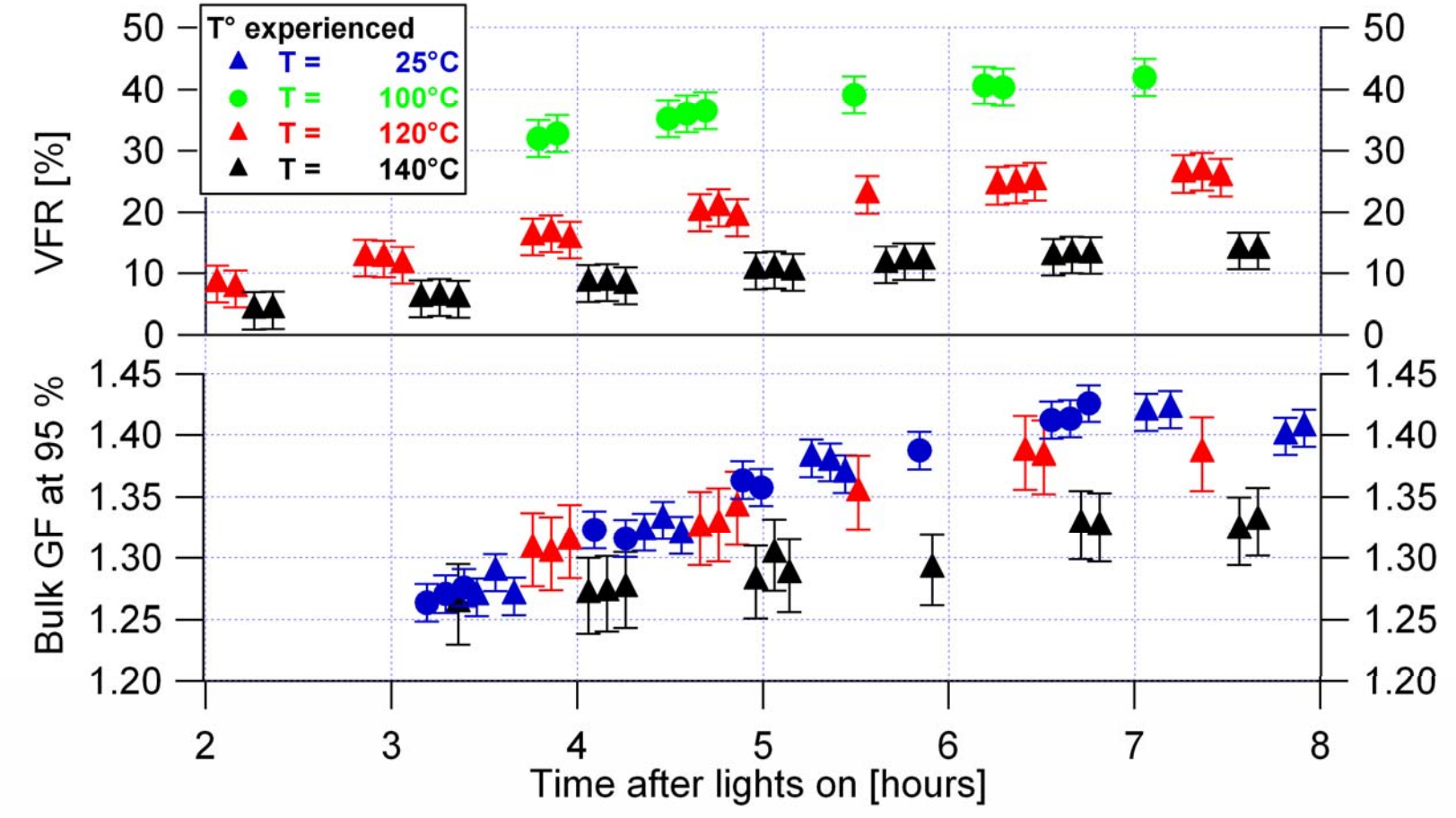
Low initial precursor concentration



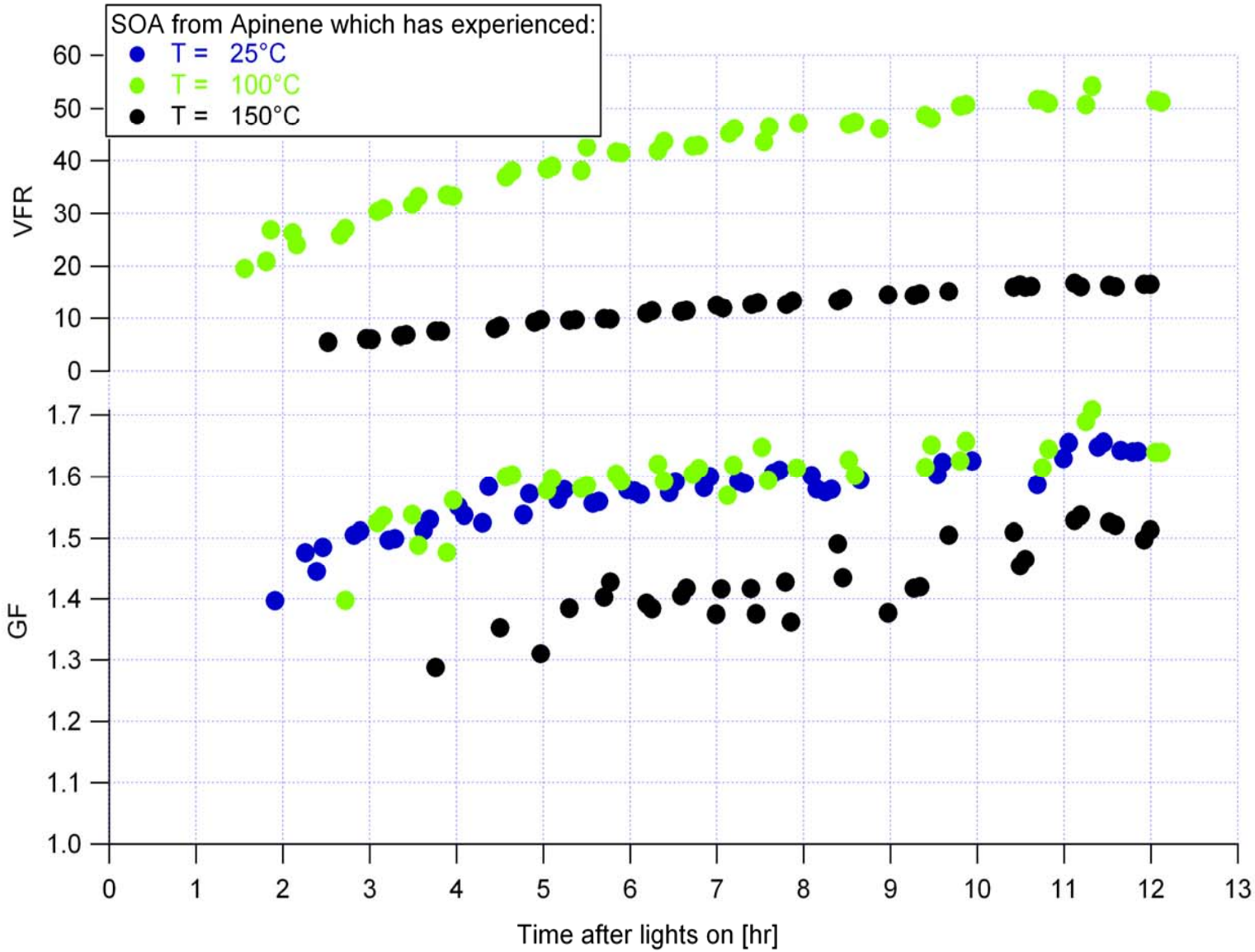
•Residence time effect: At the same temperature a higher residence time allows further volatilisation (Woo *et al.,* 2007): Oven of my VTDMA not well suited to study volatility of a specific coumponds.

•At a specific temperature, the VFR increase with time i.e. the particles become less and less volatile: This can be explained either by oligomerisation or oxidation or both.

Low initial precursor concentration

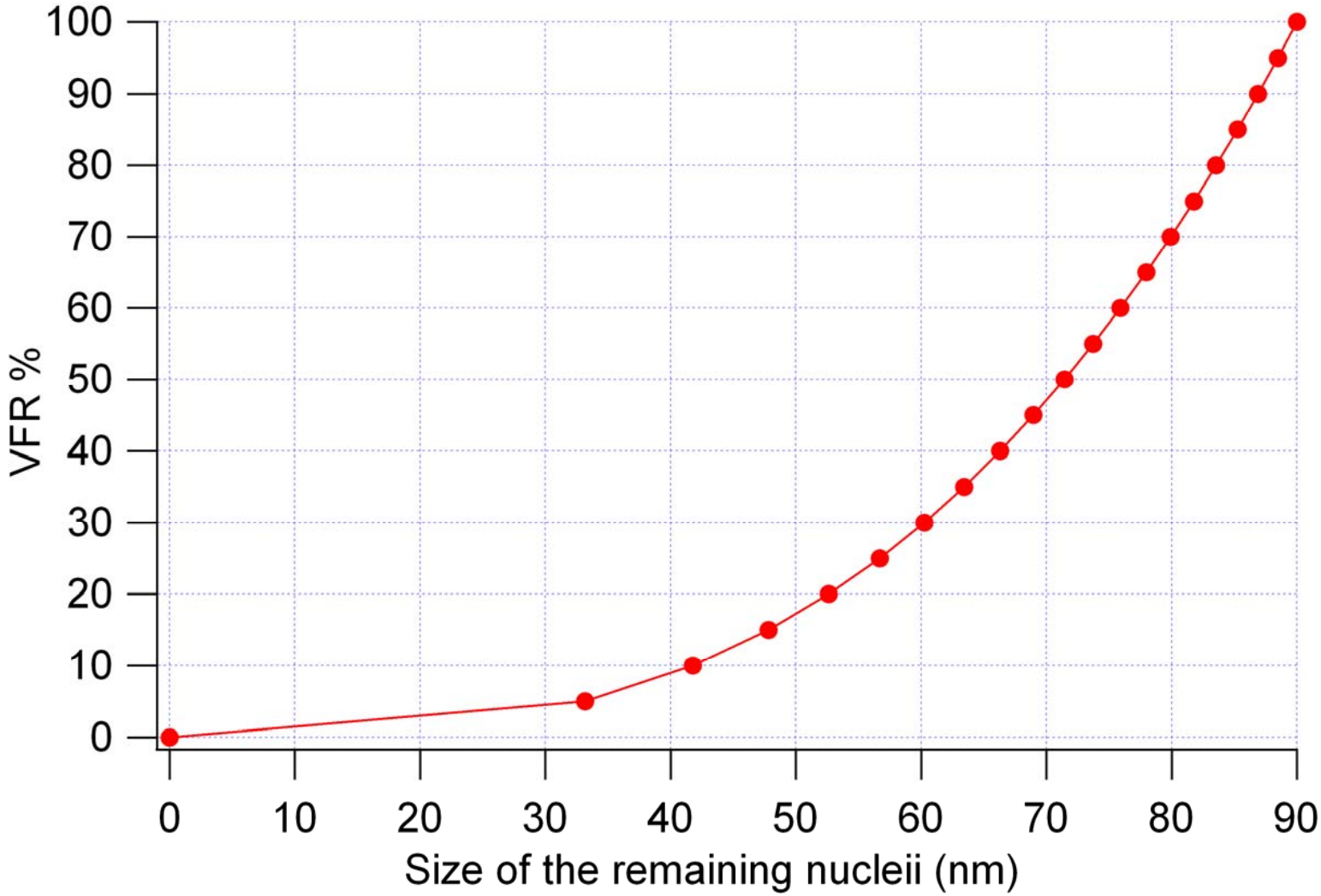


- **At 140 ºC, the hygroscopicity of the remaining particle is a bit lower, within the error bar.**

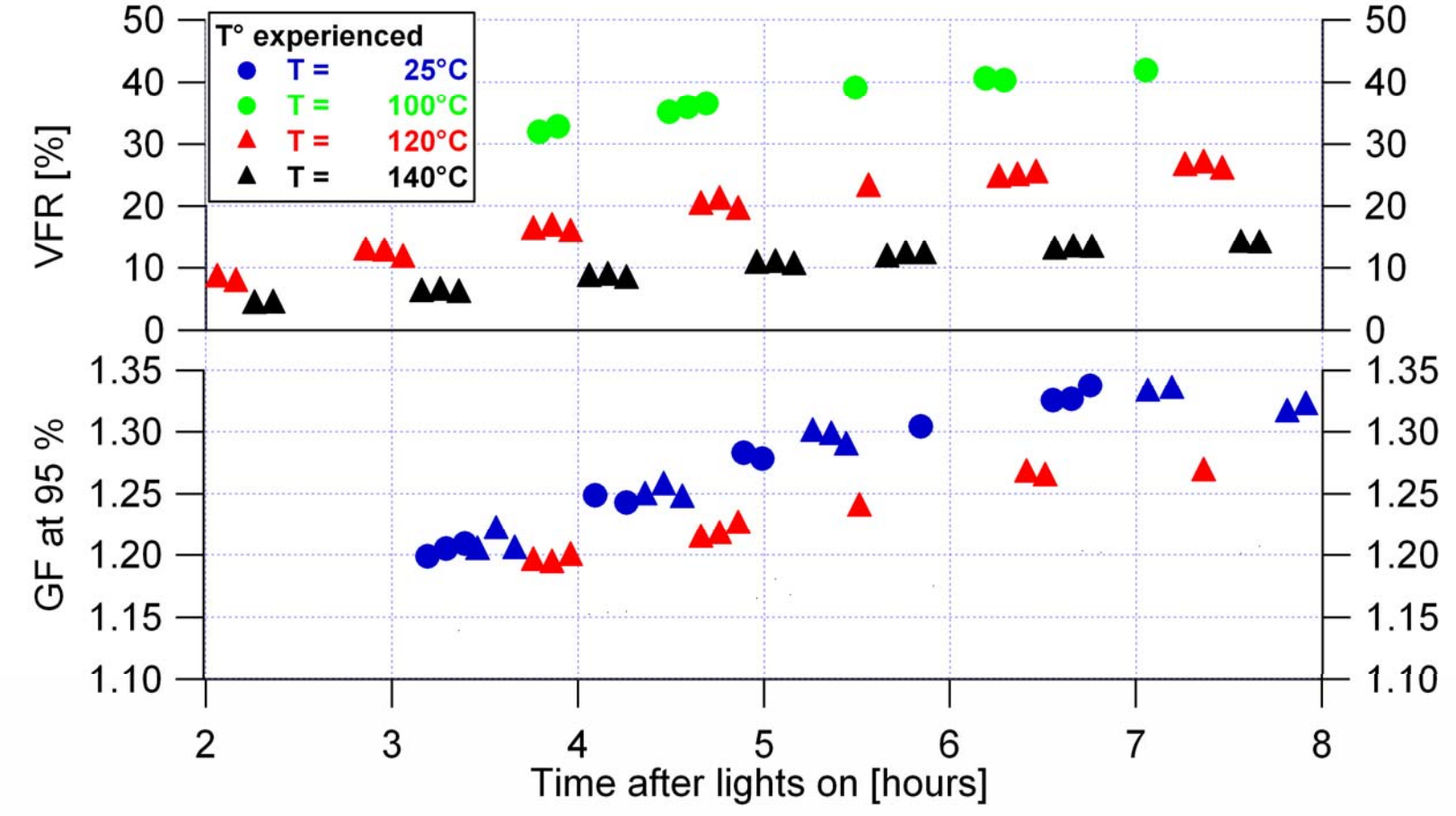


Need to show size and correct for Kelvin effect….

With 90 nm particle



Low initial precursor concentration



- **Is it due to Kelvin effect?**

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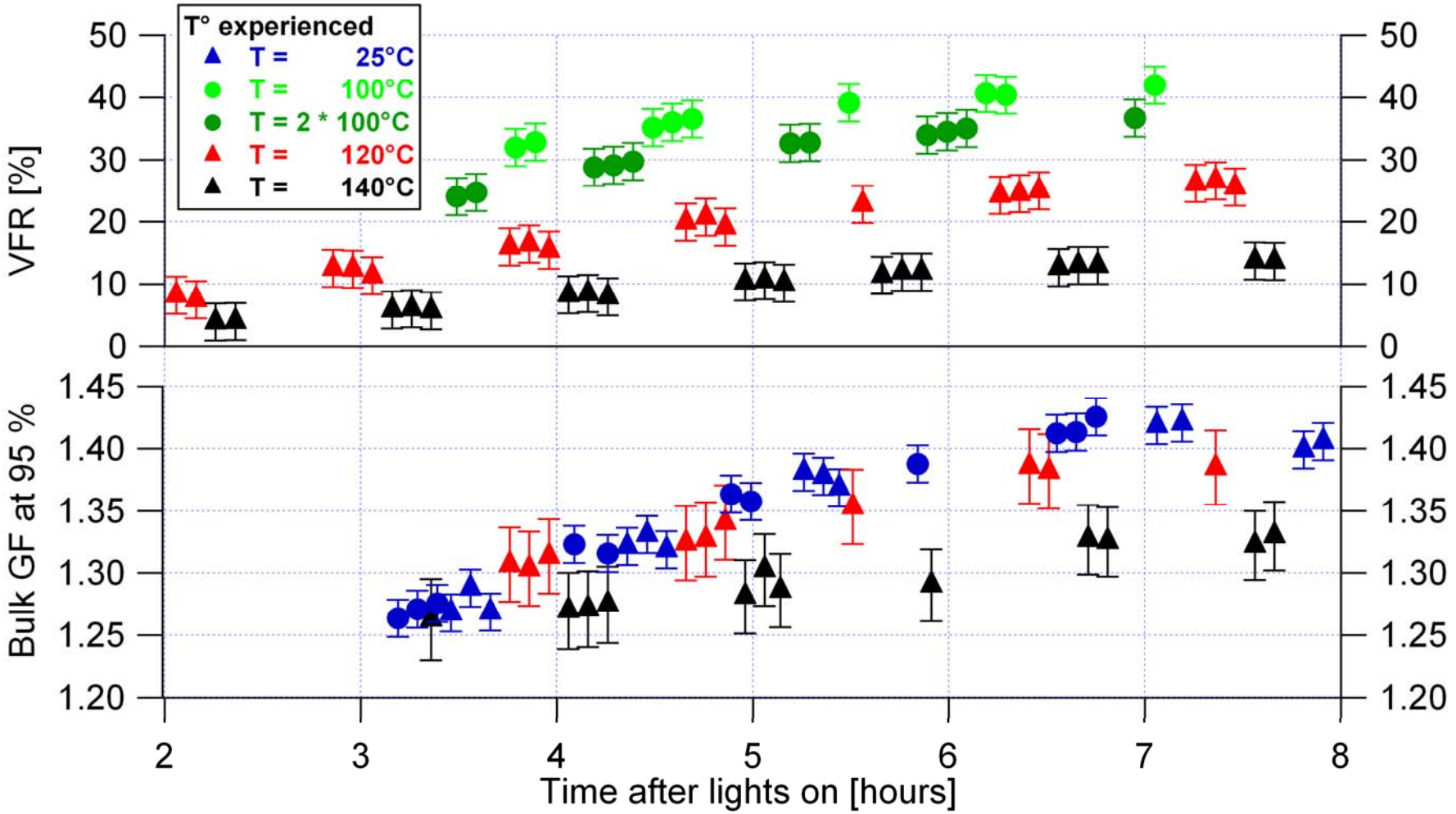
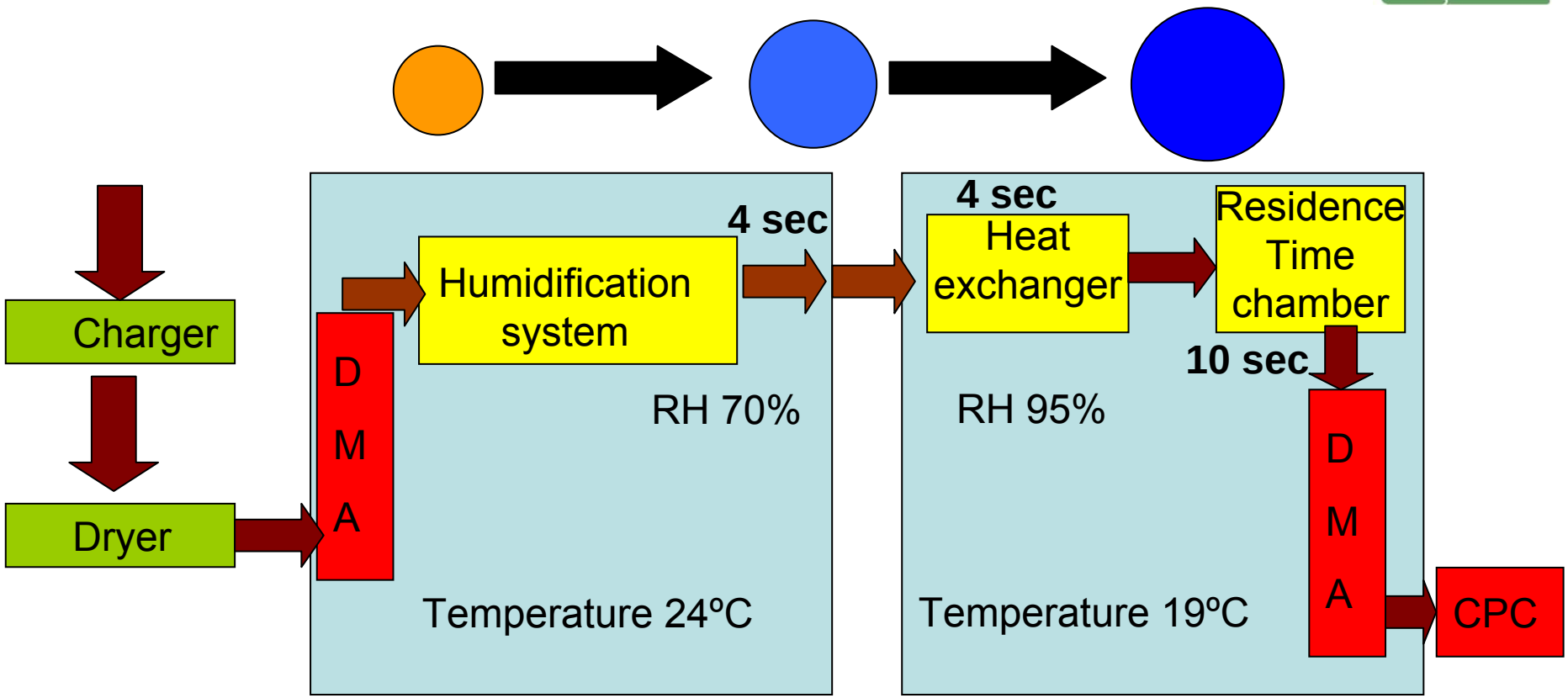
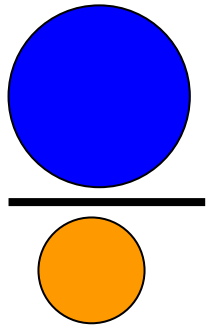
Error Plot



HTDMA Principle

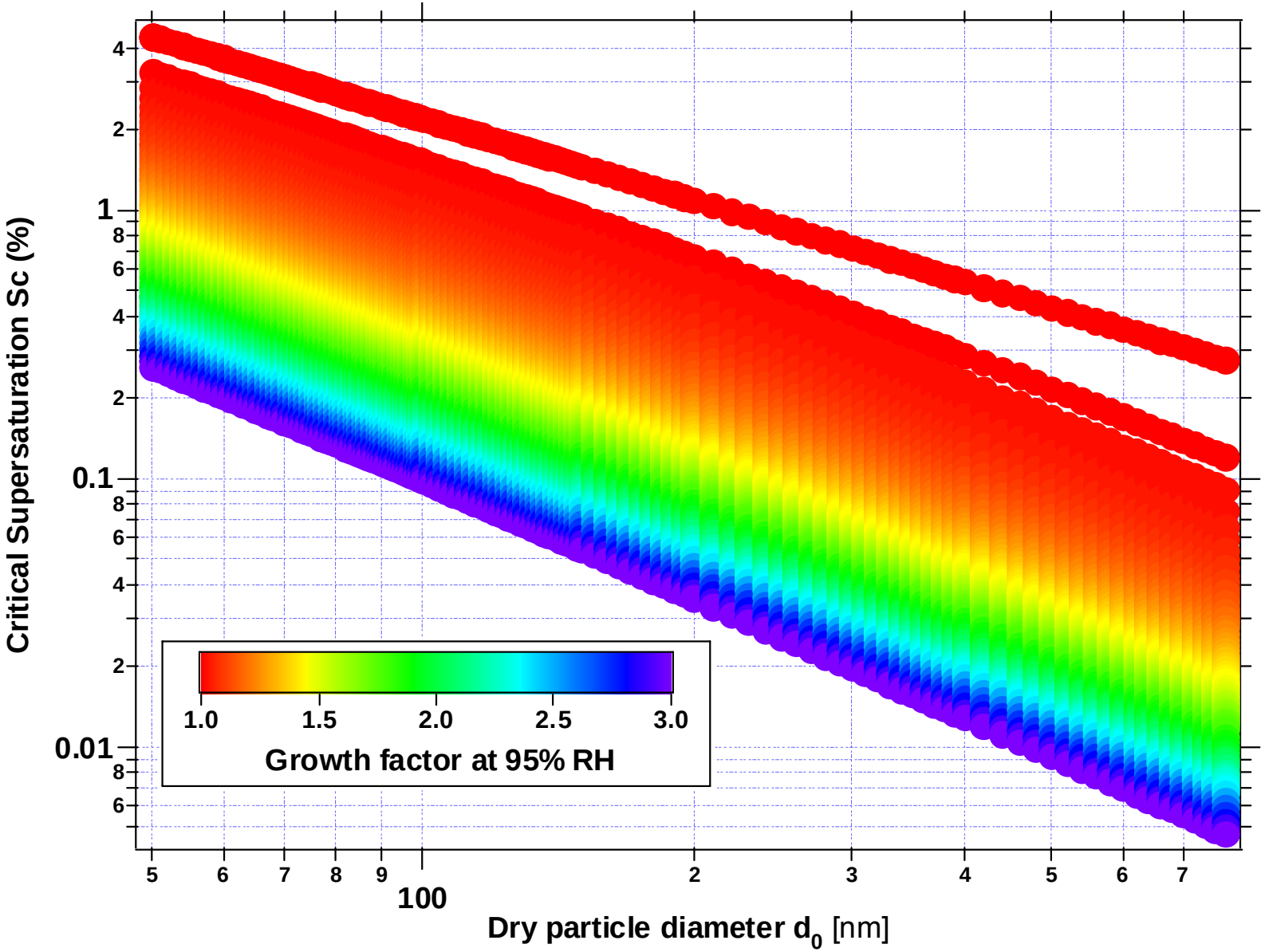


$$GF(RH) = \frac{\text{Size at a certain RH}}{\text{Size when it is dry}} =$$

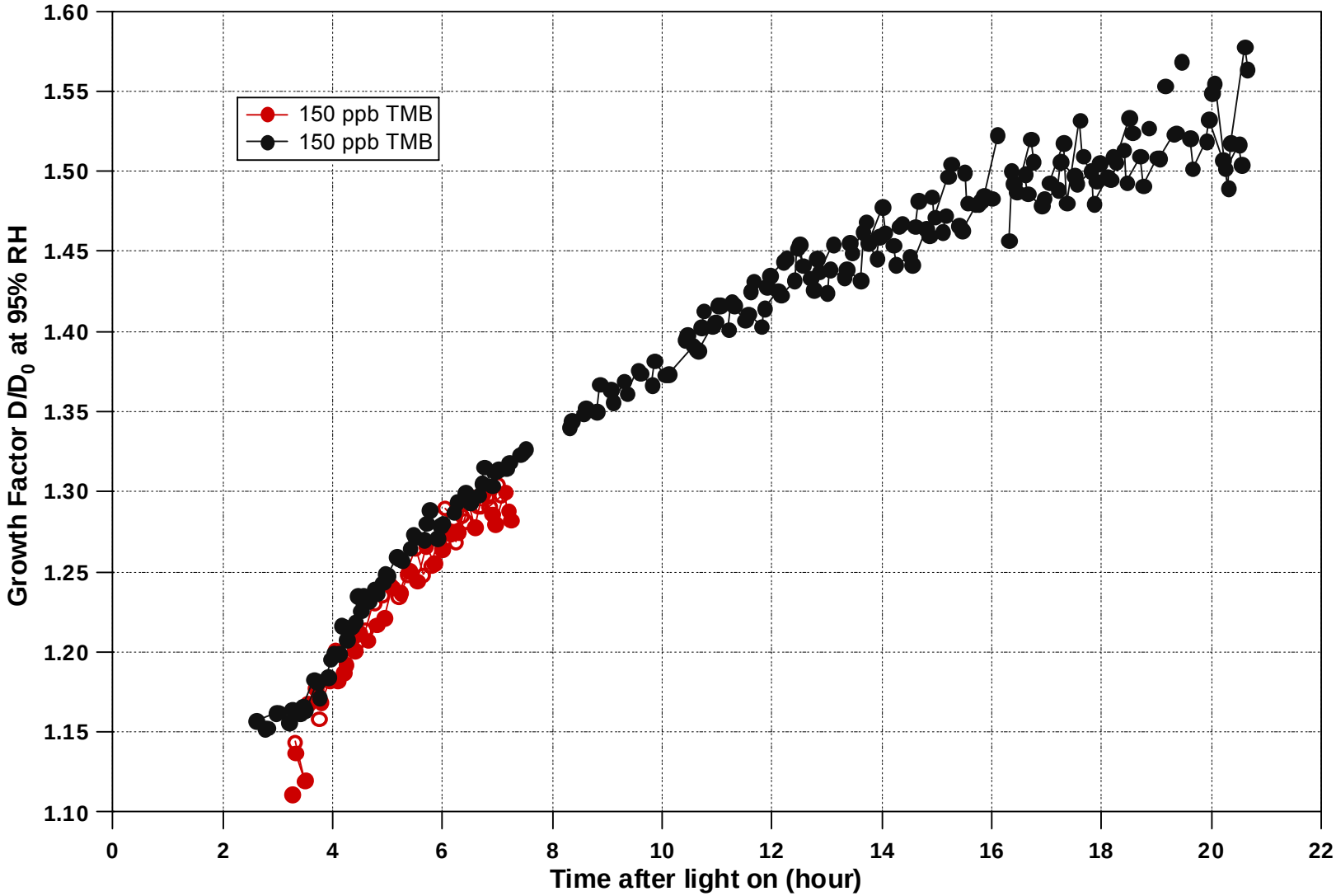


Allowed accurate measurement up to 95% RH

GF, size influence CriticalSuperSaturation?



TMB



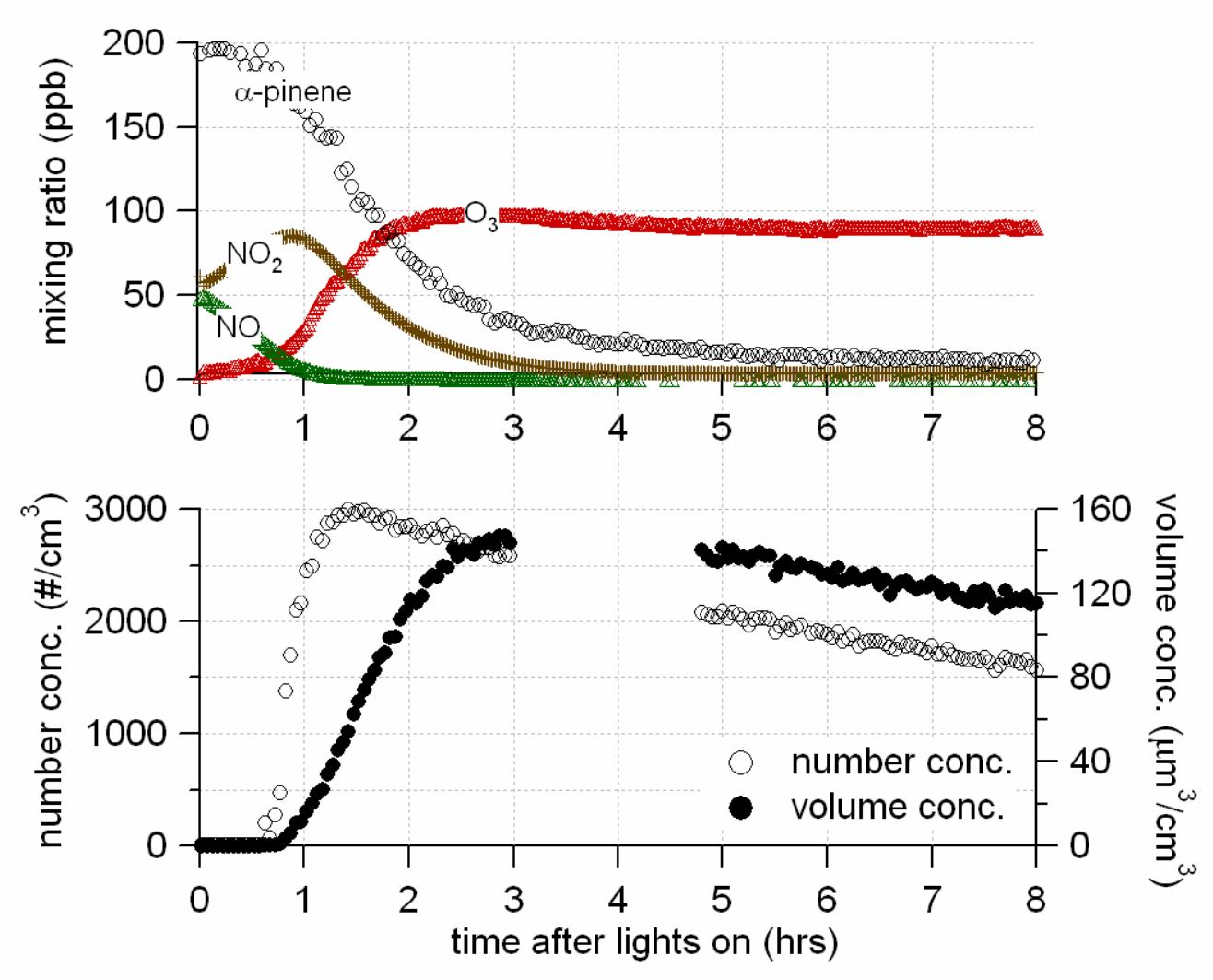
Continual increase of the growth factor with time during 20 hours,

Oxydation processing

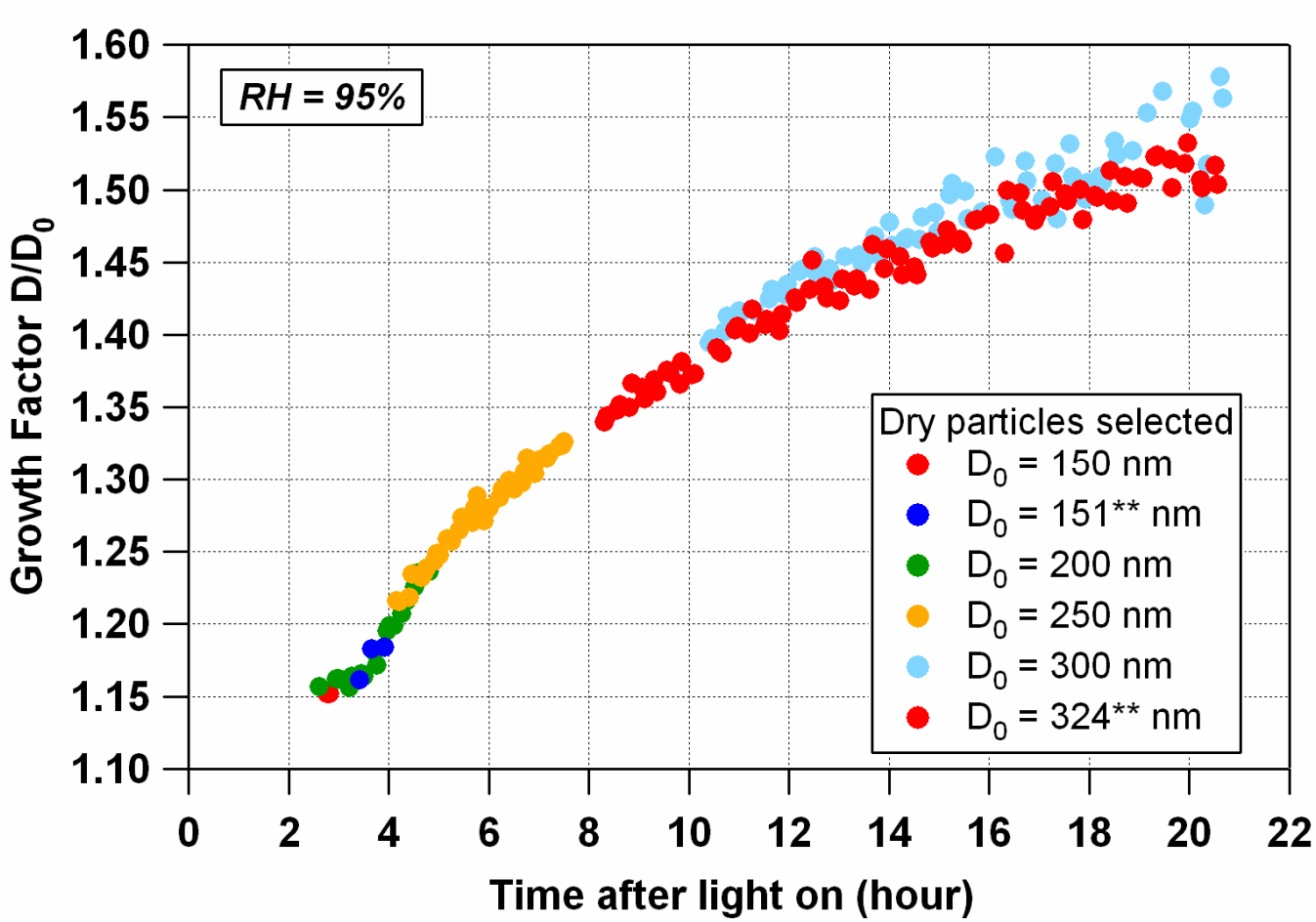
Typical Experiment

Gas phase

Particle phase



TMB (150 ppb, 75ppb NO_2)



- Continuous increase of the growth factor during 20 hours (Oxidation)
- No size dependence of hygroscopic growth (also observed for α-pinene and isoprene)

Prepared answer for question...

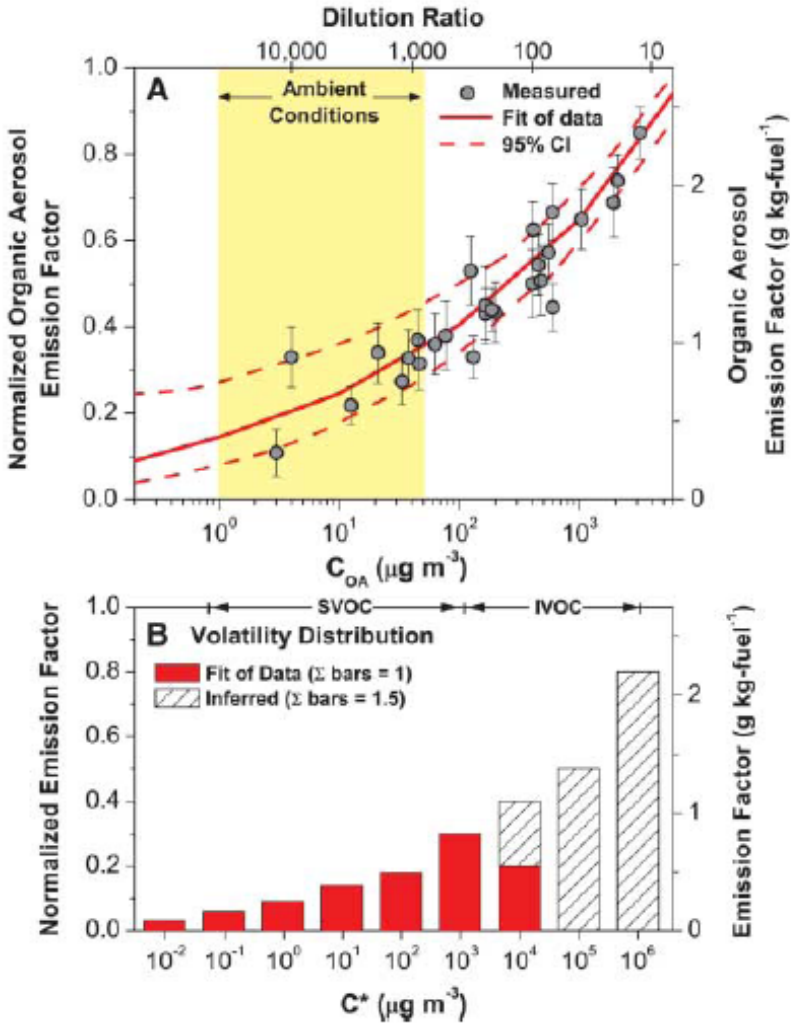
- Why do not you use longer residence time?
  - We would like to study the oligomere, not the monomers out of the oligomere distroyed by the Oven (Woo Jin An paper)
  - We would like to avoid polymerisation artifact which could also occurs in the oven. For example Methyl glioxide in an oven for polymers. (Ref???)
- Are the VFR measured absolute value?
  - No because not enough residence time. But can be use as a relative value.
- Oven change properties of aerosol??
- Sulfate influence the hygroscopicity??

Remaining Question and informations

- Does Oligomeres hydrolyse at 95% RH
- Polygomeres are made from assembling monomeres. During this assembling, monomeres loss Oxygen (H2O is released).

Remember list

- Talk about Woo Jin An residence time studies (read the paper...)
- Show one graph with VFR and GF vs temperature



POA emission factor decreases with increasing dilution
i.e. the AMF decreases

POA EF are determined at low dilution
→ if dilution takes place a new volatility distribution is formed.

Red: POA as measured
Hatched: one assumes that there are IVOCs between the non-volatiles (POA) and the highly volatile species (e.g. toluene)