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JÜLICH FORSCHUNGSZENTRUM

Novel method of generation of $Ca(HCO_3)_2$ and $CaCO_3$ aerosols.

Determination of hygroscopic and cloud condensation nuclei activation properties.

D. F. Zhao, A. Buchholz, Th. F. Mentel, K.-P. Müller, J. Borchardt, A. Kiendler-Scharr, C. Spindler, R. Tillmann, A. Trimborn, T. Zhu, A. Wahner

Achievements so far

We build / developed / modified

•Hygroscopicity Tandem DMA
•Scanning CCN-Spectrometer
•CCN-Spectrometer layout for Zeppelin flights

PhD thesis, Angela Buchholz (August 2010)
Diploma thesis (FH), Linda Strathmann (September 2009)

Applications / Publications :

LACIS (CCN, HTDMA)
AIDA (CCN, HTDMA)
JPAC (CCN, HTDMA, AMS) -> Lang-Yona et al., ACPD 2010
$CaCO_3$ (CCN, HTDMA, AMS) -> Zhao et al., ACPD 2010

Open: experiments of IN modification in SAPHIR
(long term natural chemical ageing).

Introduction

Task:
Generate sufficient $CaCO_3$ particles in the x100 nm size range to fill the Jülich Large Aerosol Chamber (V ~ 250 m^3) in a reasonable time (1h).

Goal:
Substrate for chemical studies and physico-chemical studies

Analytical tools:
HG, hygroscopicity tandem differential mobility analyzer
CCN, scanning CCN-spectrometer
„Composition“: Q-AMS

Chemistry and Thermal Composition

$$CaCO_3(s) + CO_2 + H_2O \rightleftarrows Ca(HCO_3)_2(aq)$$ **weathering of rocks**

$Ca(HCO_3)_2$ becomes instable at 300°C

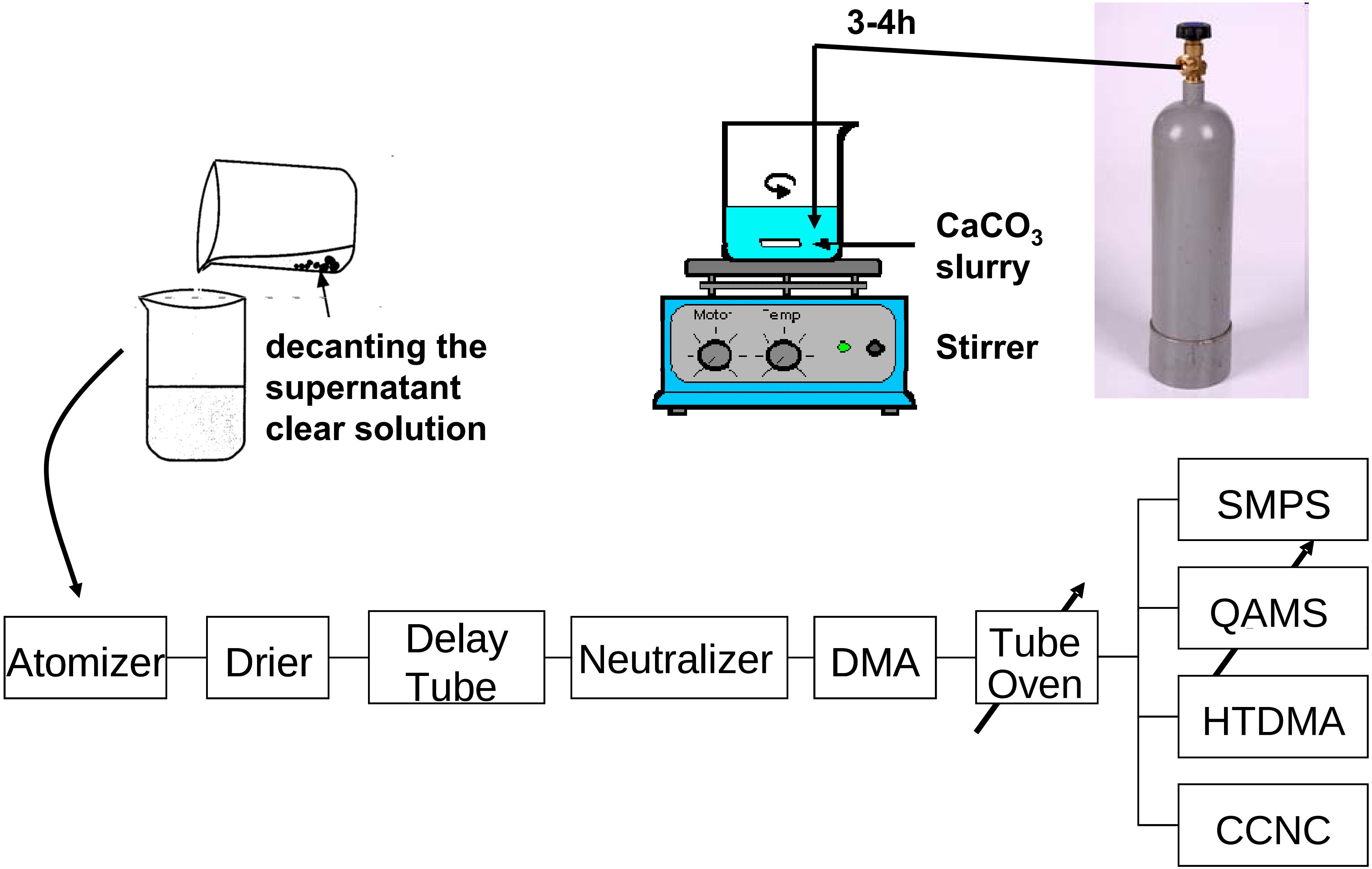
$$Ca(HCO_3)_2(s) \longrightarrow CaCO_3(s) + CO_2 + H_2O$$ **decay at 300°C**

$CaCO_3$ becomes instable at 900°C

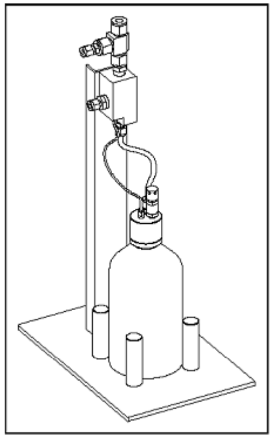
$$Ca(HCO_3)_2(s) \longrightarrow CaO(s) + 2CO_2 + H_2O$$ **decay at 900°C**

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2$$ **decay at 900°C**

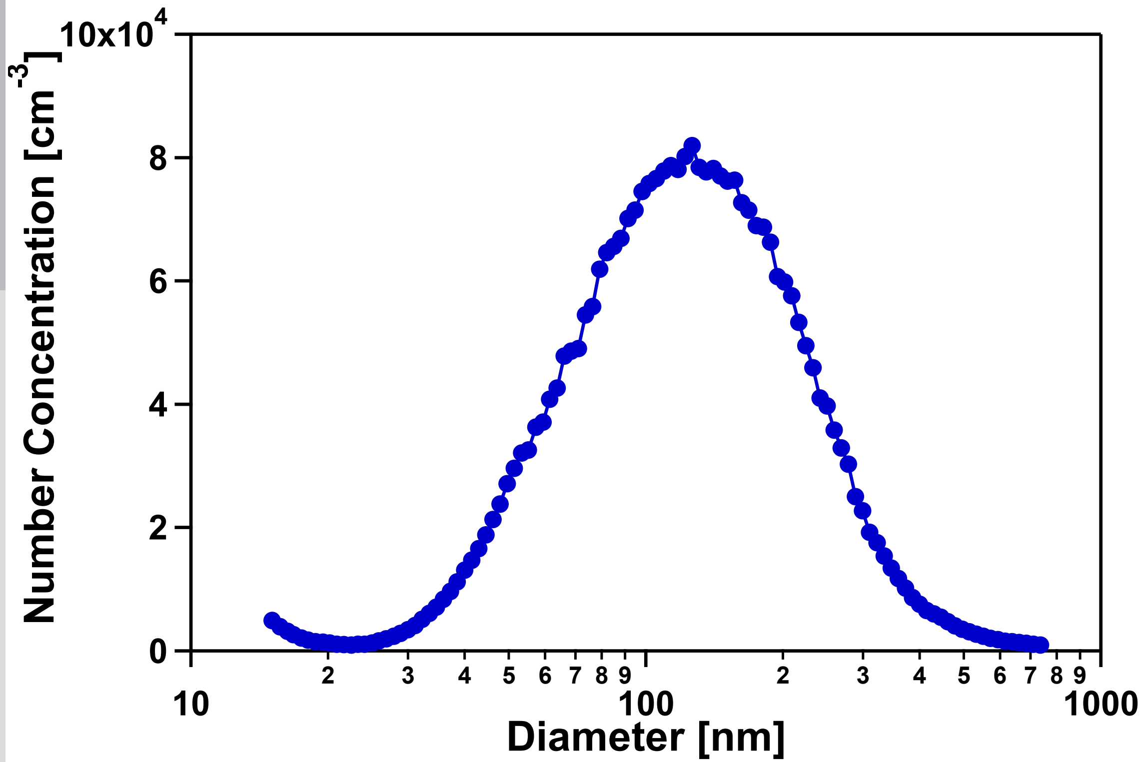
The $Ca(HCO_3)_2$ Solution and Setup

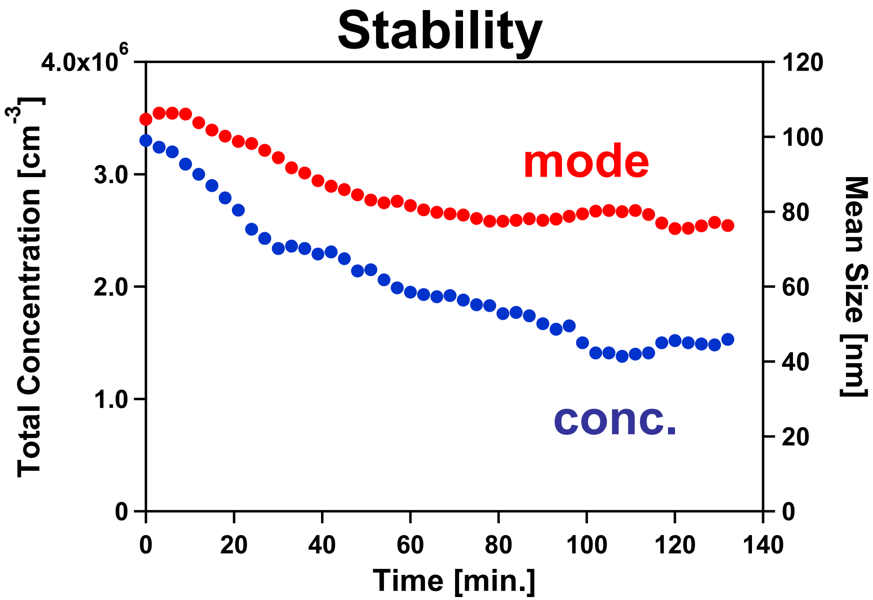


The Fresh $Ca(HCO_3)_2$ Aerosol



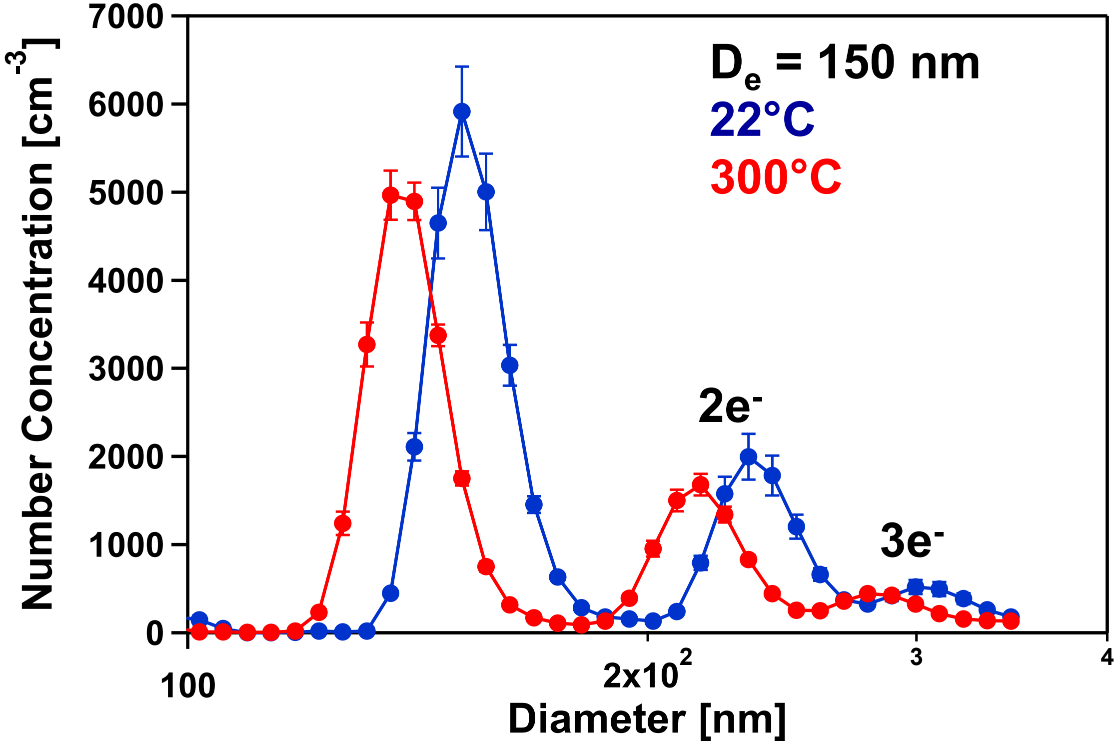
TSI3076 Atomizer
4 bar
$Ca(HCO_3)_2$ solution





a white precipitation appared, probably $CaCO_3$, since we deplete CO_2 on spraying with synth. air

Size Selection and Annealing in Tube Furnace



Effective density: comparison with mass modal diameter in Q-AMS measurements

$\rho_{p22°C}$ = 1.8 g/cm^3

$\rho_{p300°C}$ = 1.8 g/cm^3

$\rho_{Calcite}$ = 2.71 g/cm^3

$\rho_{Aragonite}$ = 2.83 g/cm^3

TEM Images: Spheres

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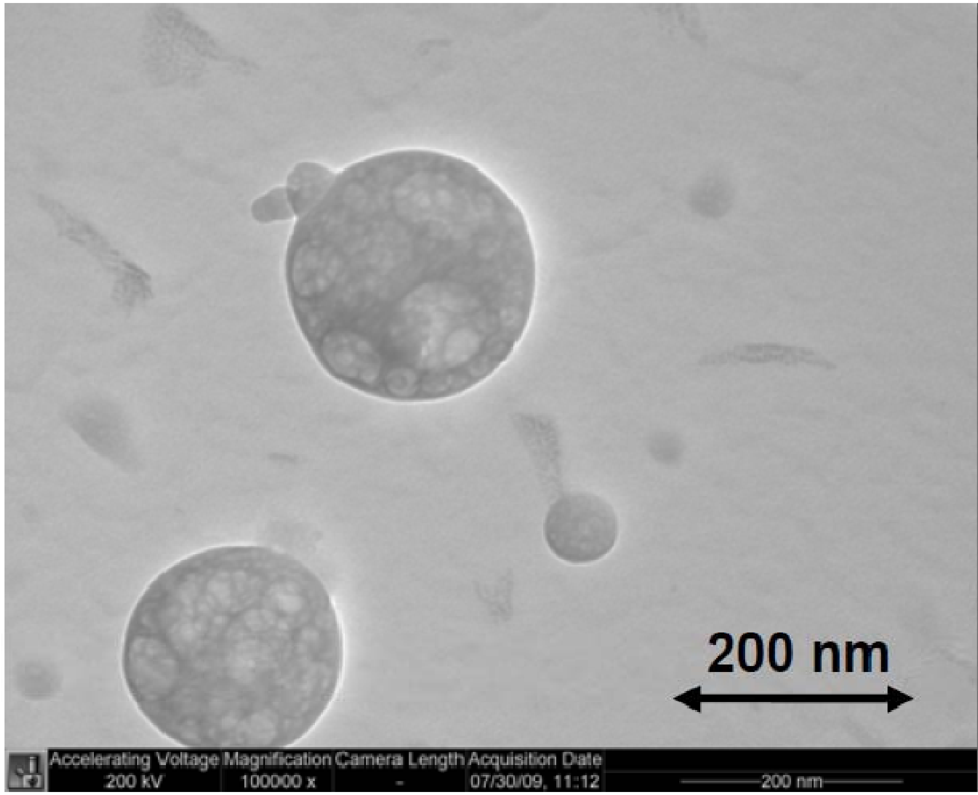
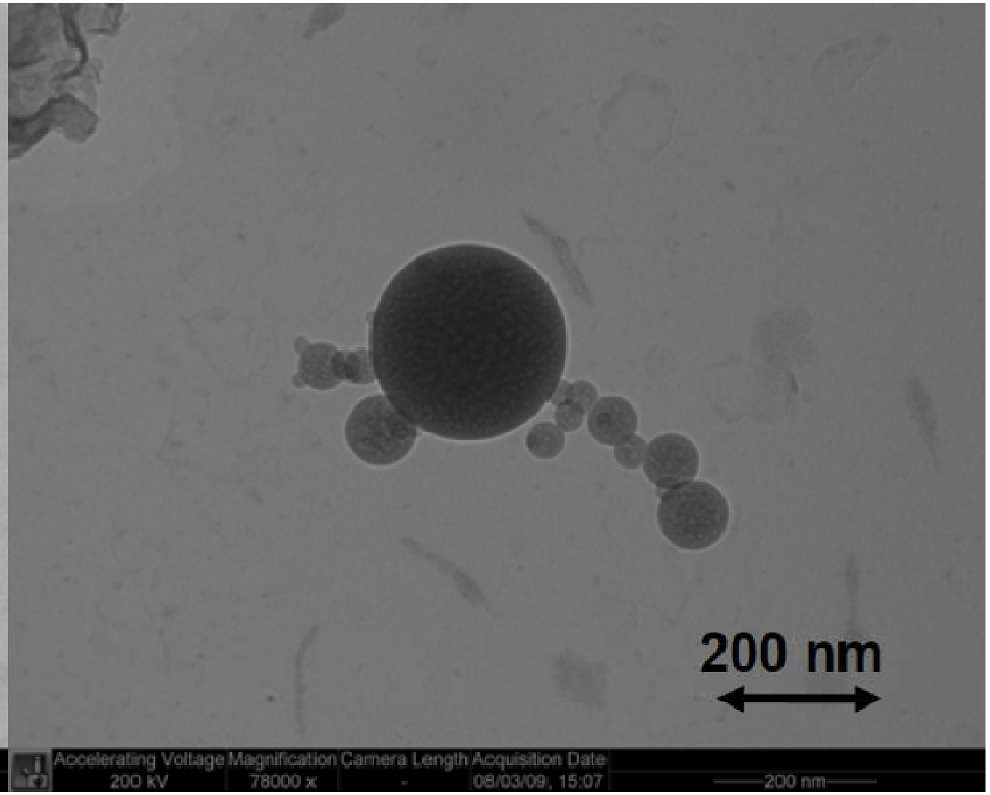
After Drying



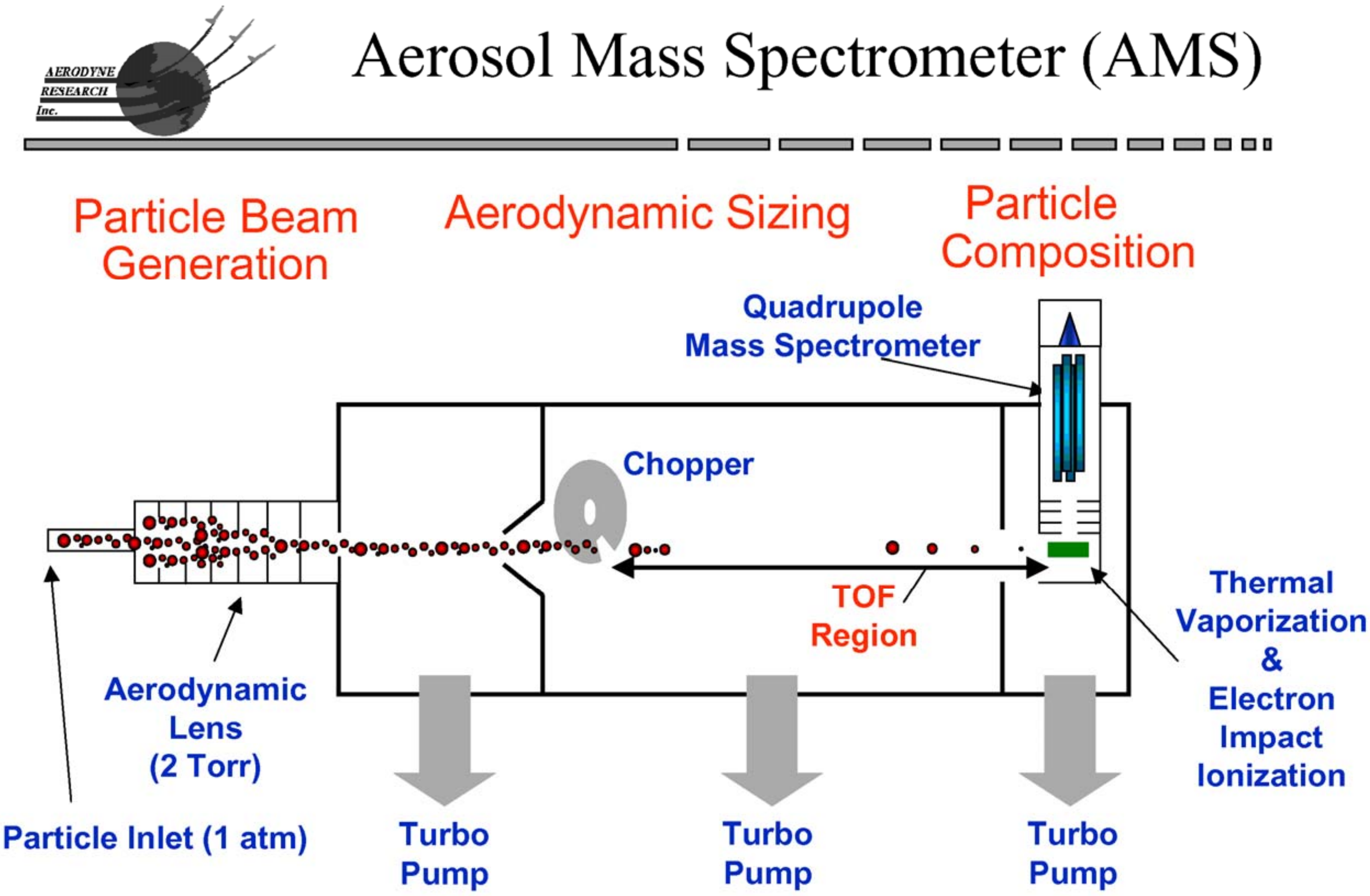
(a)

After Annealing at 300°C



(b)

Analysis by Q-AMS



300°C
or
900°C

100% transmission (60-600 nm), aerodynamic sizing, linear mass signal.

Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles. Jayne et al., Aerosol Science and Technology 33:1-2(49-70), 2000.

Analysis by Q-AMS

CO_2: m/z=44

H_2O: m/z=18

mass(CO_2) -> mole number CO_2
mass(H_2O) -> mole number H_2O

Take Advantage of Thermal Properties of $Ca(HCO_3)_2$ / $CaCO_3$ System

$$Ca(HCO_3)_2(s) \longrightarrow CaCO_3(s) + CO_2 + H_2O$$ **decay at 300°C**

$$Ca(HCO_3)_2(s) \longrightarrow CaO(s) + 2CO_2 + H_2O$$ **decay at 900°C**

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2$$ **decay at 900°C**

Normalization of Q-AMS data to SMPS data

Q-AMS does not evaporate CaO – no measure of total mass

To compensate for fluctuations during generation:
normalizing to SMPS volume !

SMPS volume – ρ_p -> particle mass

Particle mass -> molar Ca content
- fresh: $Ca(HCO_3)_2$
- annealed: $CaCO_3$

Normalization to Ca -> collection effiency of the Q-AMS

$$Ca(HCO_3)_2(s) \longrightarrow CaCO_3(s) + CO_2 + H_2O$$

decay at 300°C

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2$$

decay at 900°C

$$Ca(HCO_3)_2(s) \longrightarrow CaO(s) + 2CO_2 + H_2O$$

decay at 900°C

Analysis by Q-AMS

300°C

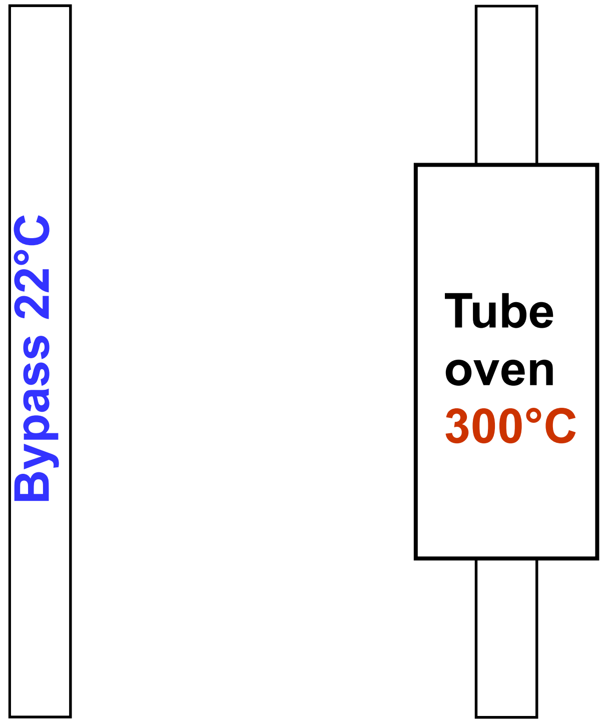
$$Ca(HCO_3)_2(s) \longrightarrow CaCO_3(s) + CO_2 + H_2O$$

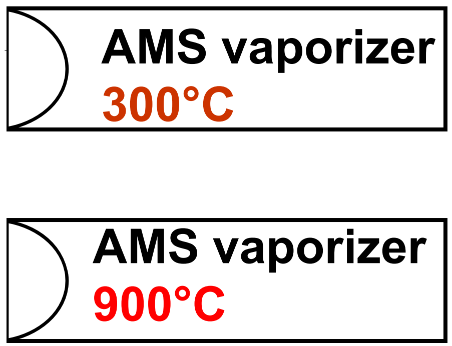
900°C

$$Ca(HCO_3)_2(s) \longrightarrow CaO(s) + 2CO_2 + H_2O$$

900°C

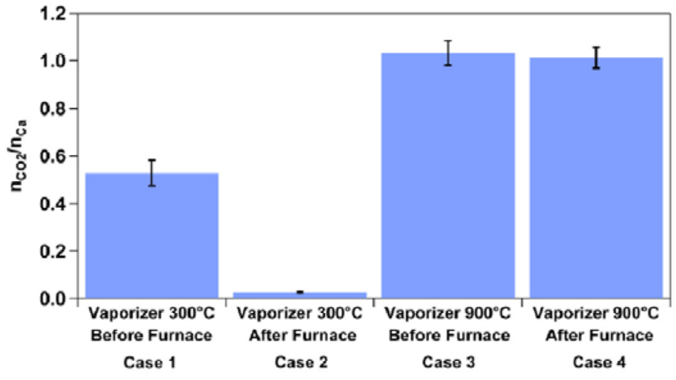
$$CaCO_3(s) \longrightarrow CaO(s) + CO_2$$



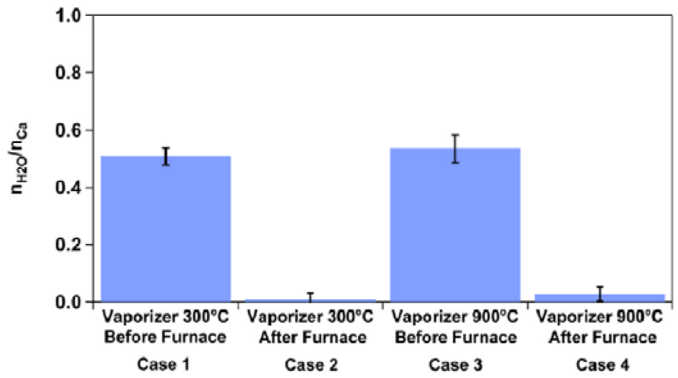


Case 1 **$H_2O:CO_2$ – 1 : 1**	Case 2 **$H_2O:CO_2$ – 0 : 0**
Case 3 **$H_2O:CO_2$ – 1 : 2**	Case 4 **$H_2O:CO_2$ – 0 : 1**

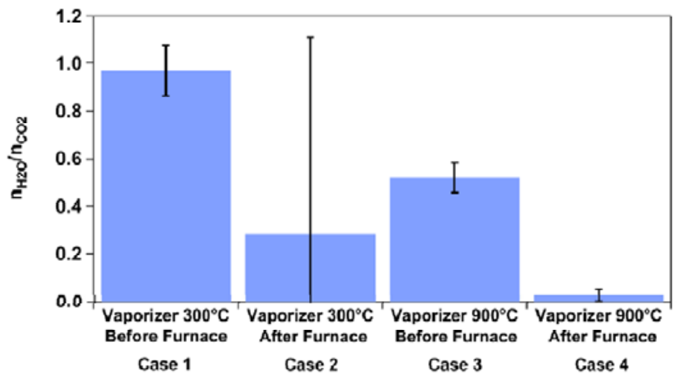
Analysis by Q-AMS



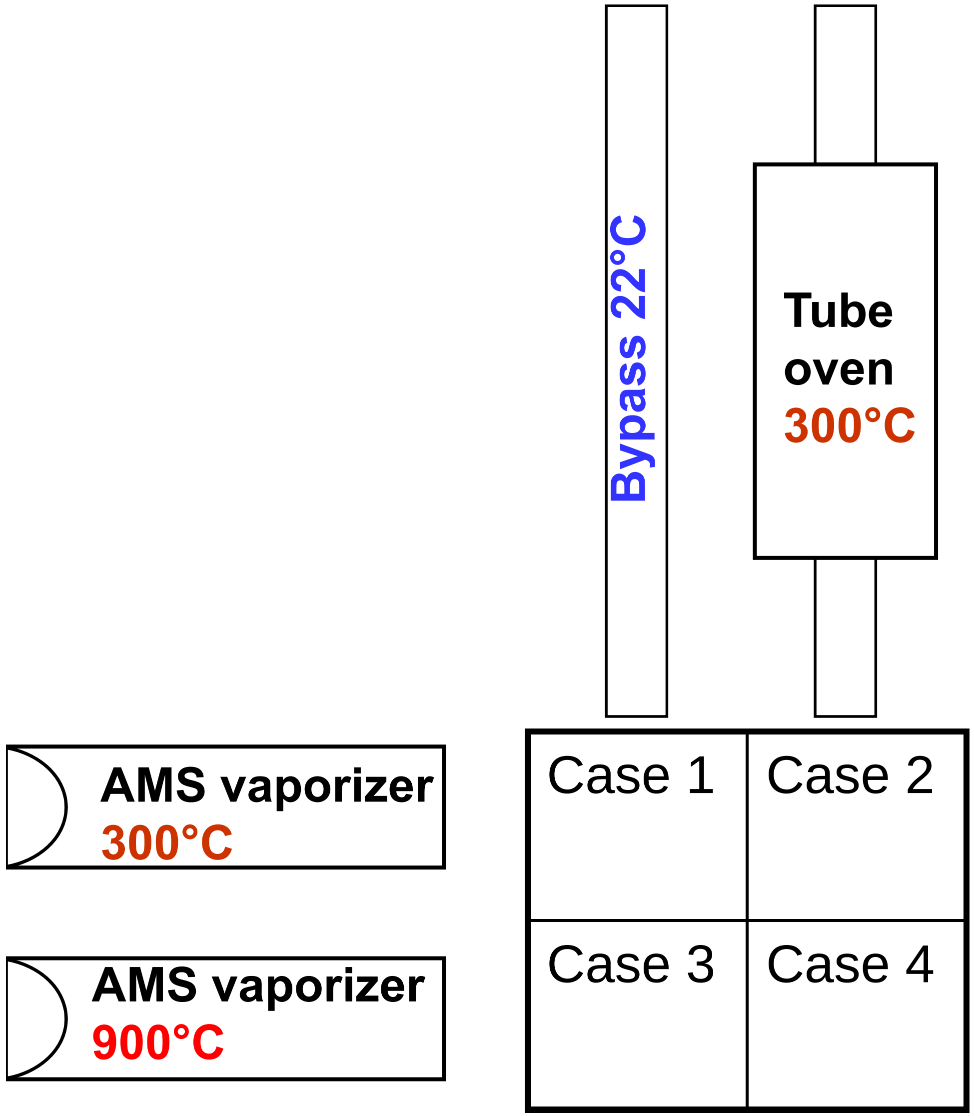
(a)



(b)



(c)



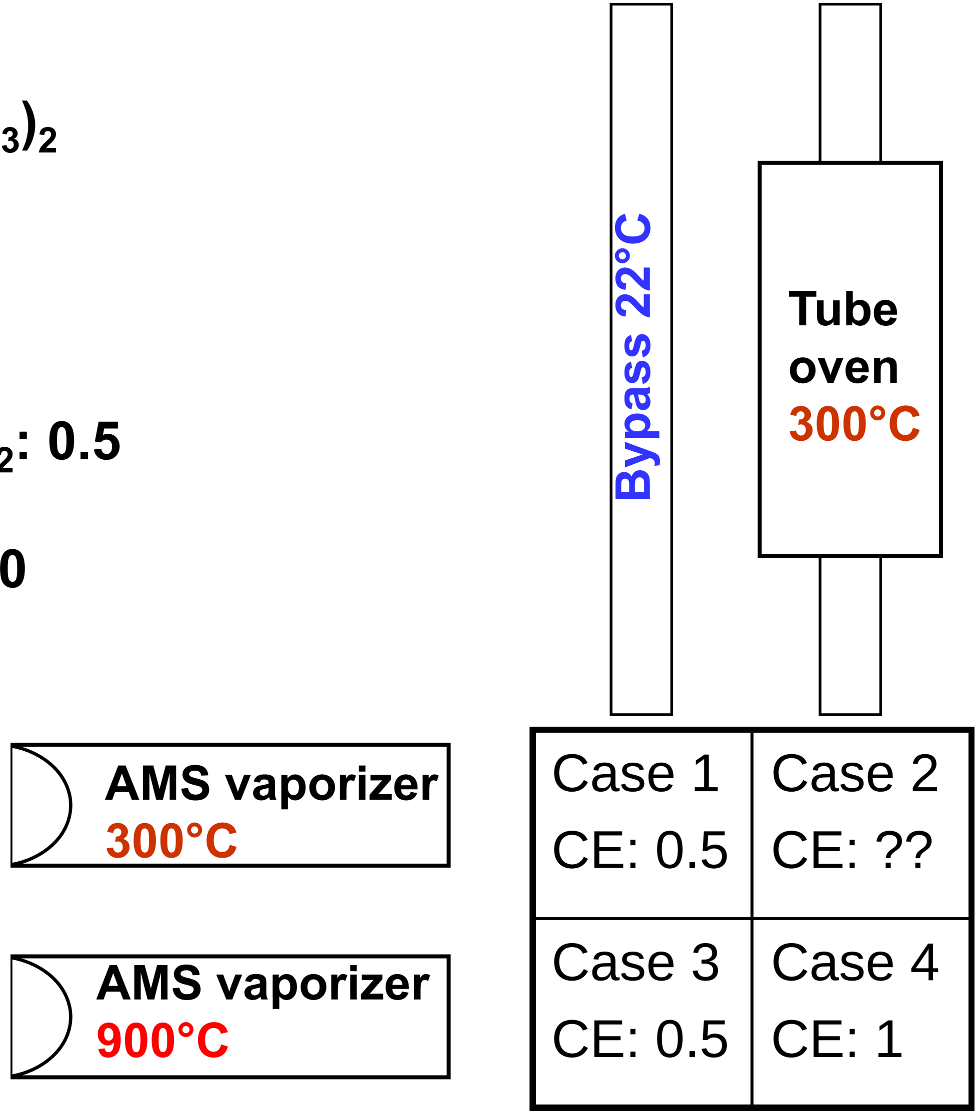
Results Q-AMS Analysis

fresh, dry aerosol: $Ca(HCO_3)_2$

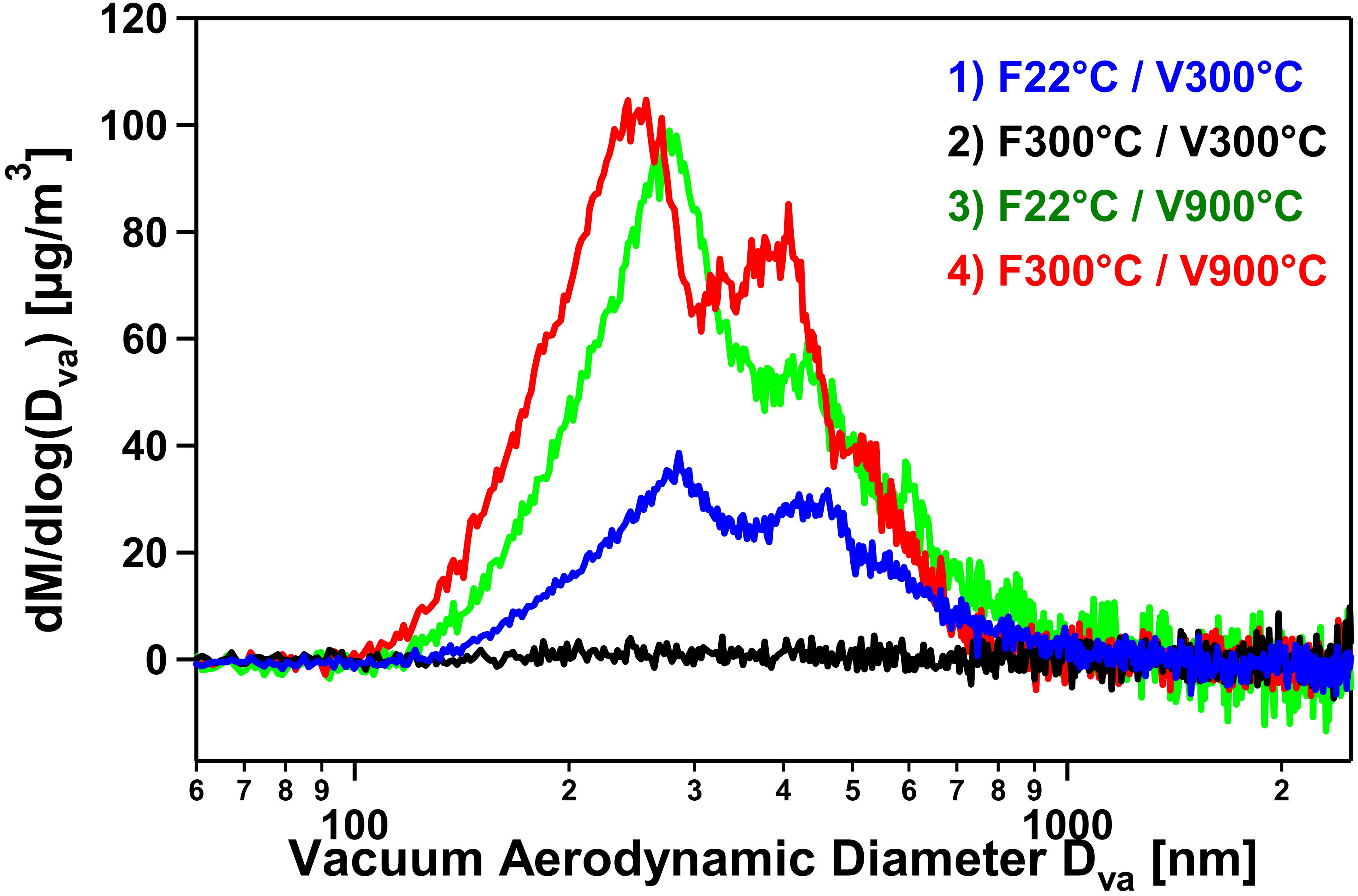
annealed aerosol: $CaCO_3$

Collection efficiency $Ca(HCO_3)_2$: 0.5

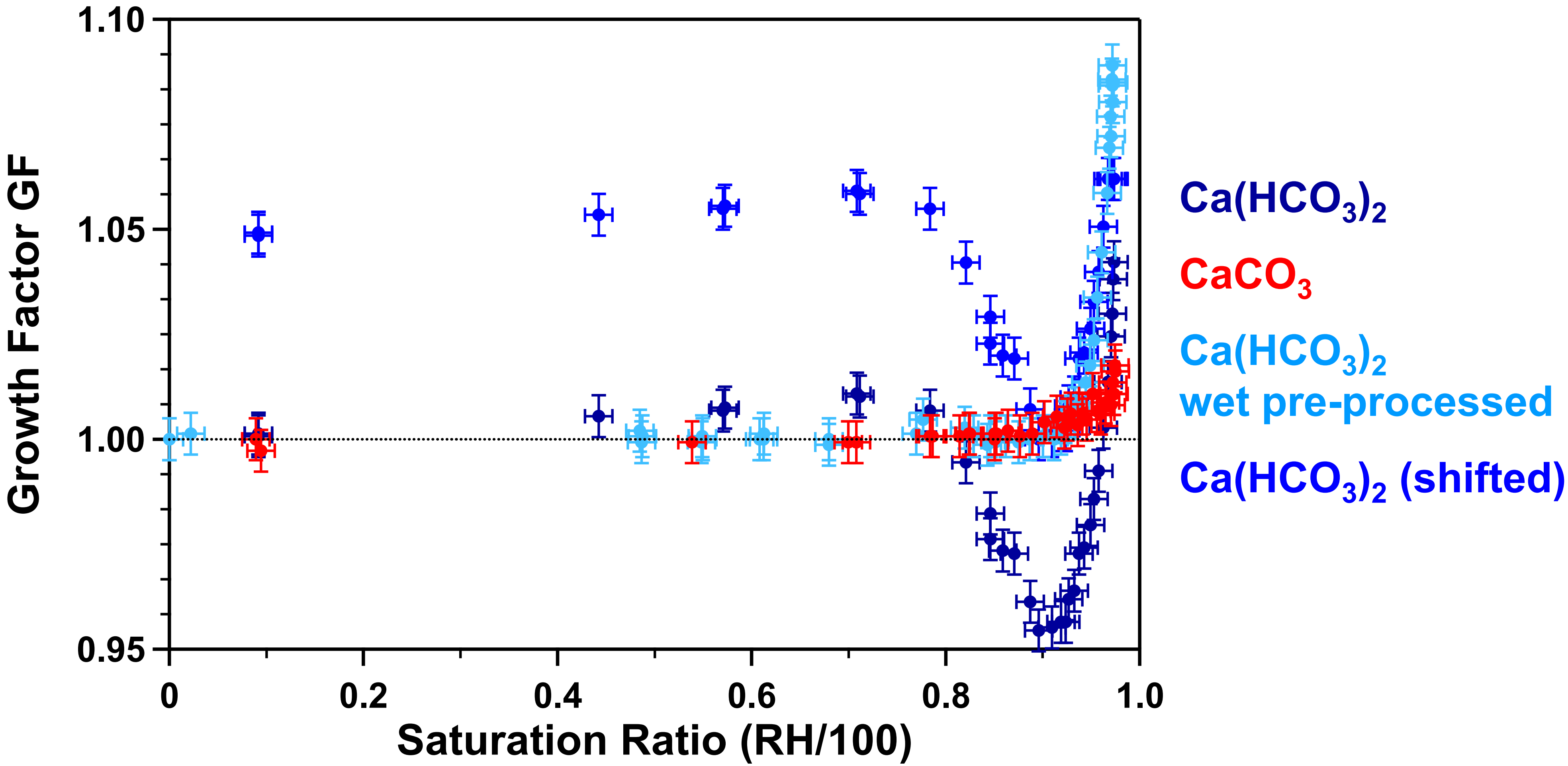
Collection efficiency $CaCO_3$: 1.0



Results Q-AMS Analysis

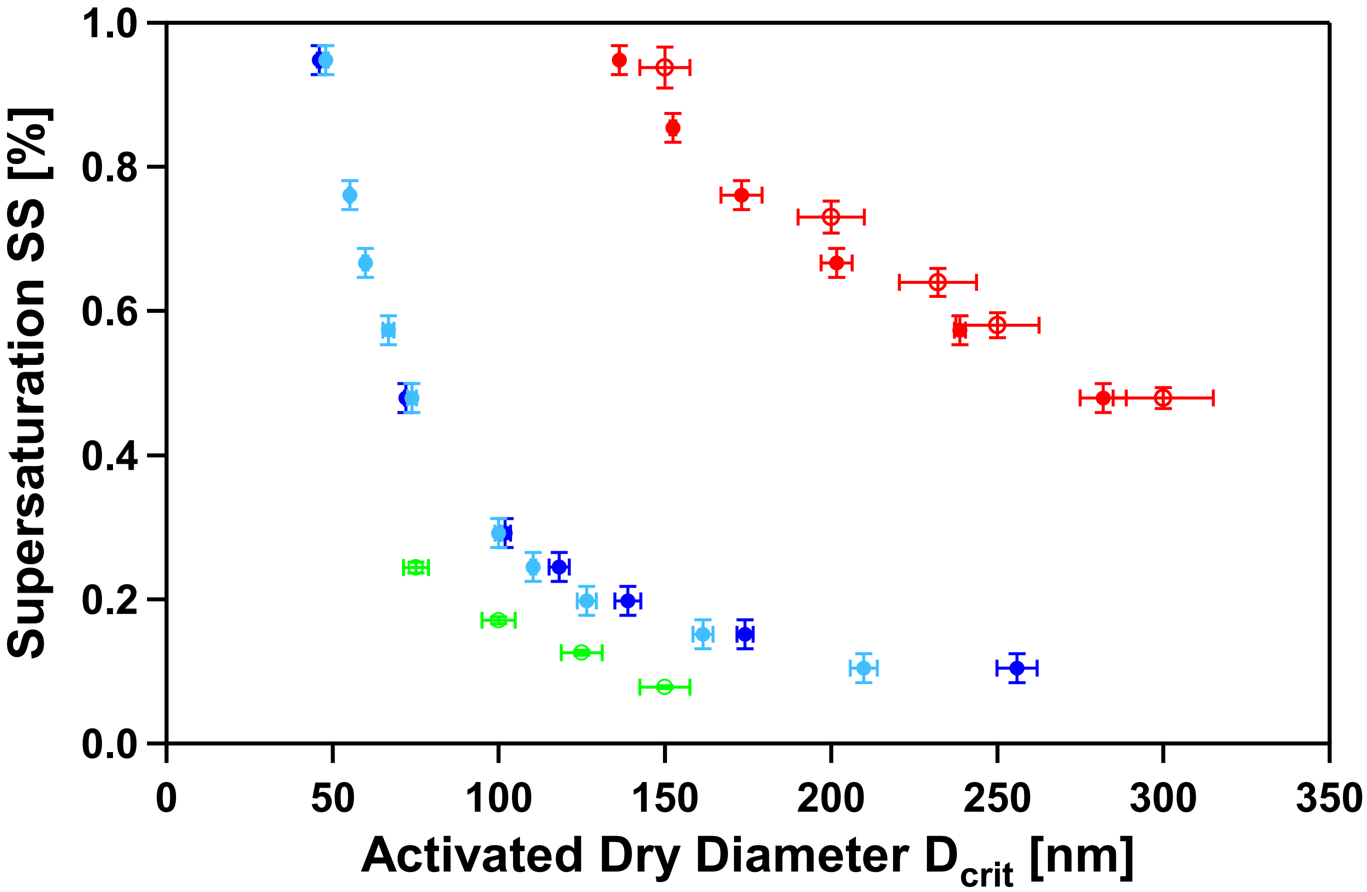


Hygroscopic Growth of $Ca(HCO_3)_2$ and $CaCO_3$



D_e = 150 nm, measurement errors: saturation ratio ±0.014, GF ±0.005

Droplet Activation of $Ca(HCO_3)_2$ and $CaCO_3$



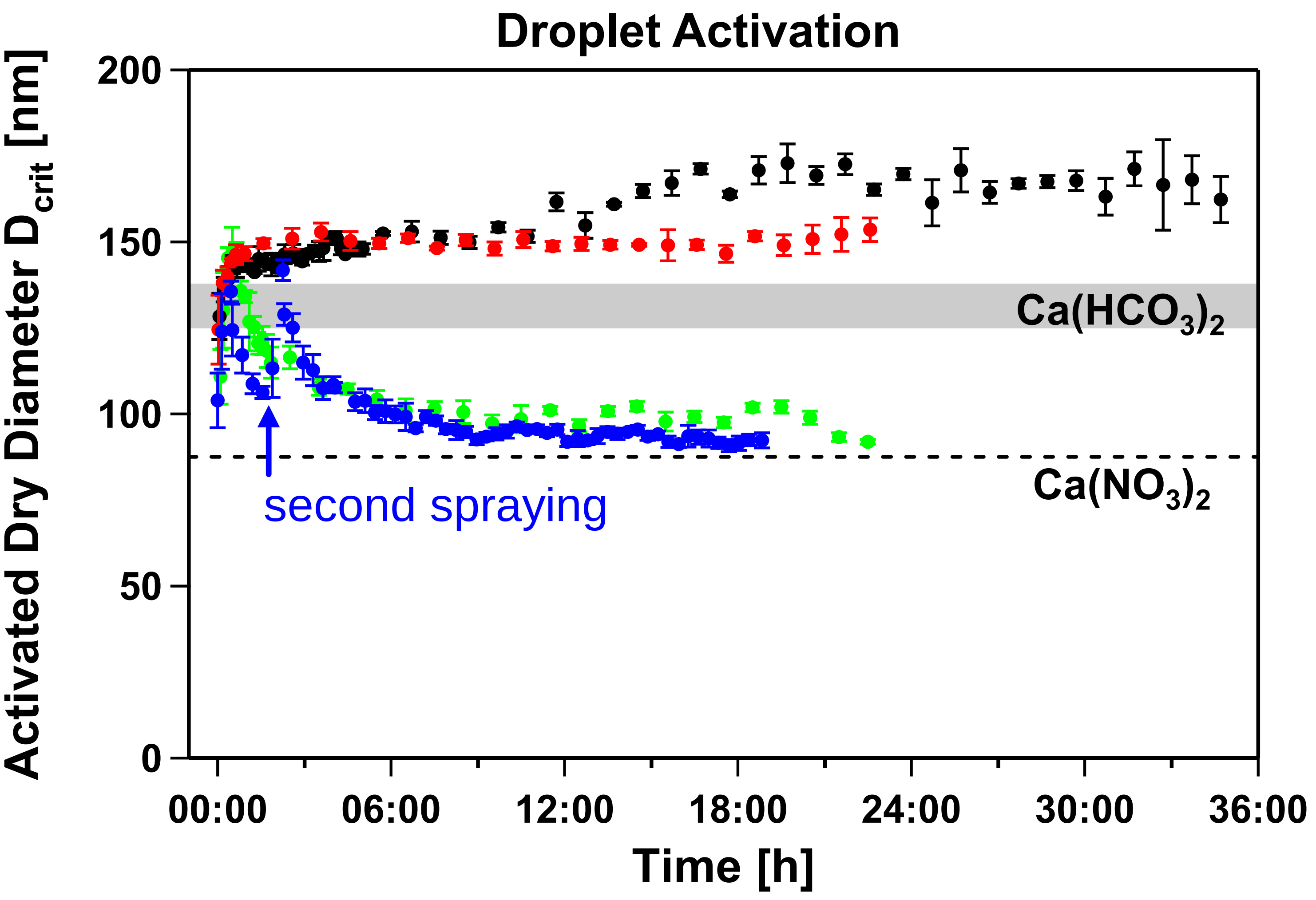
$Ca(HCO_3)_2$

filled: $CaCO_3$
open: Sullivan et al. 2009)

$Ca(HCO_3)_2$
wet pre-processed

$Ca(NO_3)_2$
(Sullivan et al. 2009)

Long Term Persistance of $Ca(HCO_3)_2$ and $CaCO_3$

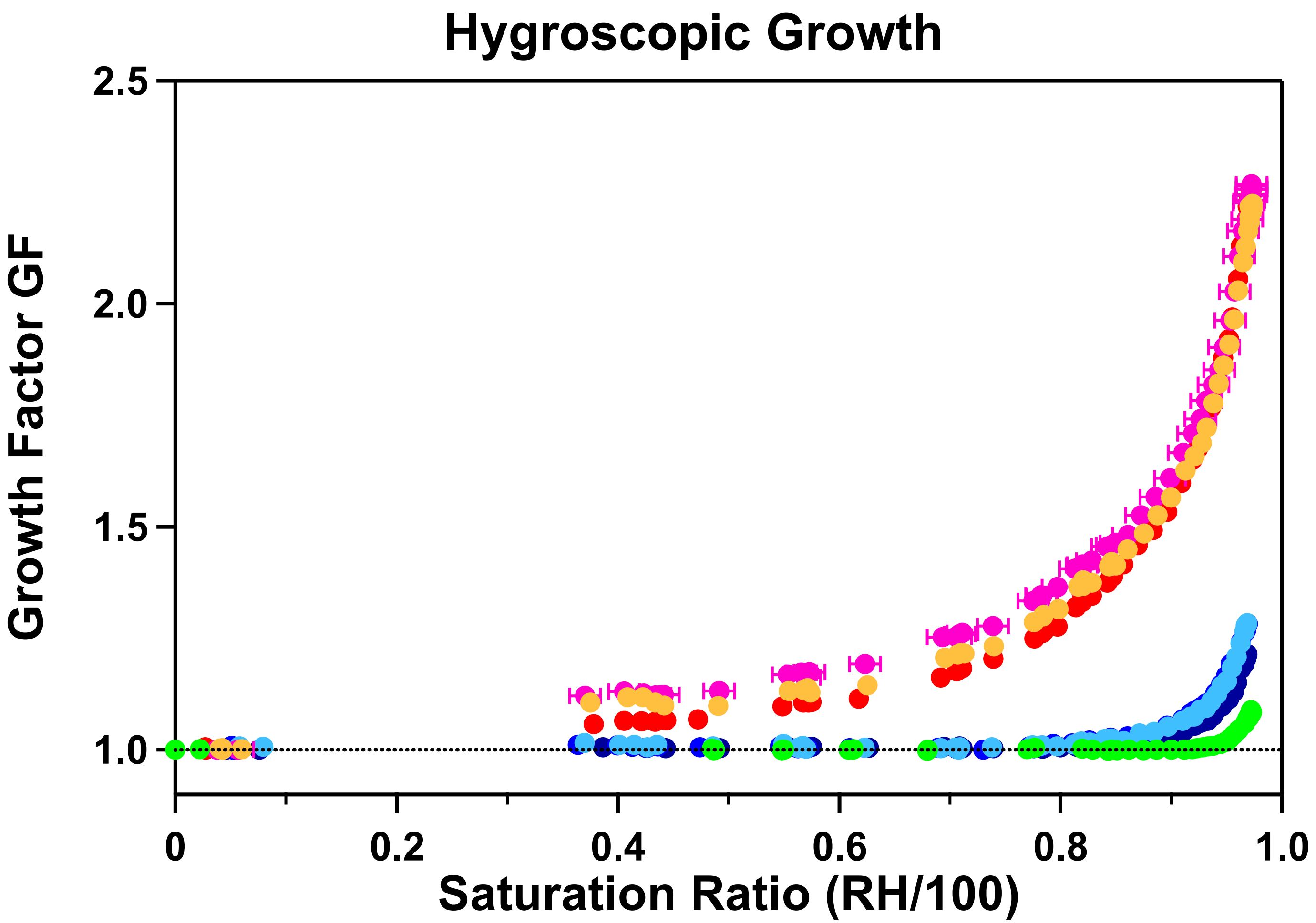


Dry experiments

Wet experiments (RH40%) & NO_X/NO_Y

Supersaturation: 0.2%, CaCO3

Long Term Persistance of $Ca(HCO_3)_2$ and $CaCO_3$



wet experiments (RH40%) & NO_X/NO_Y
3h, 18h, 20h

dry experiments
1h, 16h, 20h

D_e = 150 nm, measurement errors: saturation ratio ±0.014, GF ±0.005

Summary & Conclusion

- easy method to generate submicron $Ca(HCO_3)_2$, $CaCO_3$ (and CaO) particles in large amounts

- spherical particles with voids

- first determination of $Ca(HCO_3)_2$ hygroscopicity and CCN properties
  - -GF(95%) = 1.03 ±0.005 (non-hygroscopic)
  - -D_{act} = 130±5 nm at SS=0.2% (good CCN)

- $Ca(HCO_3)_2$ is persistant

-methods probably applicable for transition metal bicarbonates, -carbonates, and –oxides (under investigation)

- can we do systematic IN studies ?

Reference: Zhao et al., ACPD, 2010, 8009-8049