# Photochemical aging enhances the viscosity of Biomass Burning Organic Aerosol (BBOA)

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# Introduction: Biomass Burning Organic Aerosol (BBOA)

Wildfires are a major source of organic aerosols, which can affect the climate and our health.

Wildfire frequency and intensity is increasing in many parts of the world due to climate change.[1]

The amount of land burned by extreme fires is expected to increase by 50% by 2100.[2]

We need to understand the physical properties of BBOA to model them properly and get accurate predictions of air quality and climate.

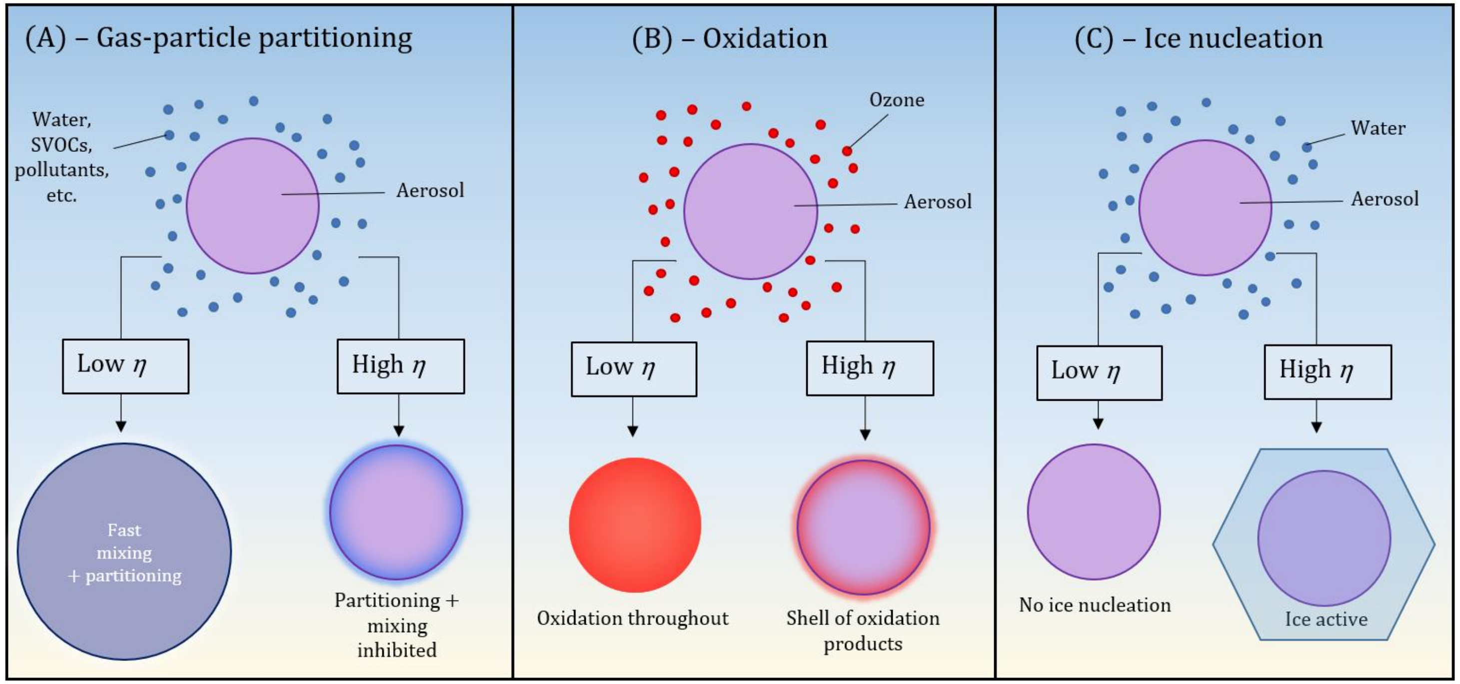
[1] IPCC AR6, 2021
[2] UN Environment Programme report, 2022

# The Importance of Aerosol Viscosity

Viscosity ($\eta$) is a fluid's resistance to flow, inversely related to diffusion rates.

High $\eta$ slows down many aerosol processes, and reactions can become diffusion limited.

In glassy particles, heterogenous reaction can be limited to the surface.




Viscosity (Pa s): $10^{-3}$ $10^{2}$ $10^{12}$

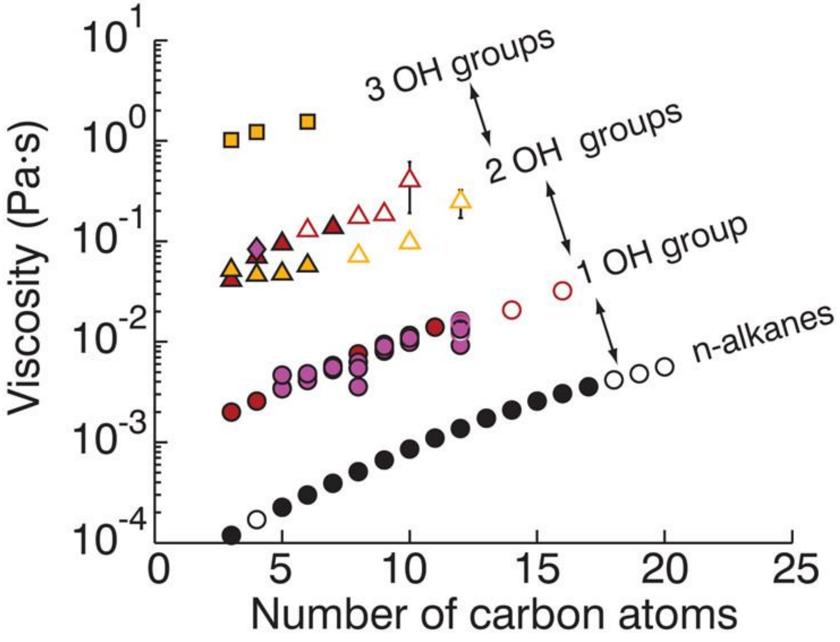
water

Liquid Semi-solid Solid/glass

# What influences viscosity in an organic aerosol?

<u>Chemical properties</u>

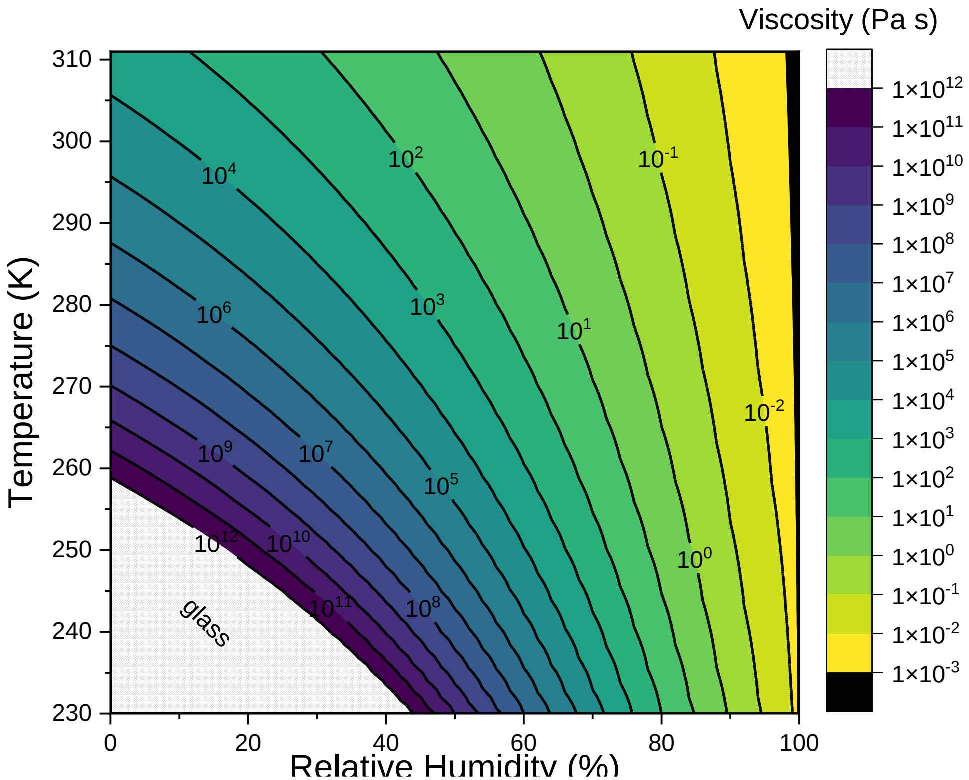
- Average molecular weight
  - larger molecules = higher viscosity
- Functional groups
  - more polar groups = higher viscosity




Rothfuss and Peters, *ES&T* 2016

<u>Environmental factors</u>

- Relative humidity: high RH = low viscosity
  - Influenced by hygroscopicity
- Temperature: high T = low viscosity




Schnitzler et al., *PNAS.* 2022

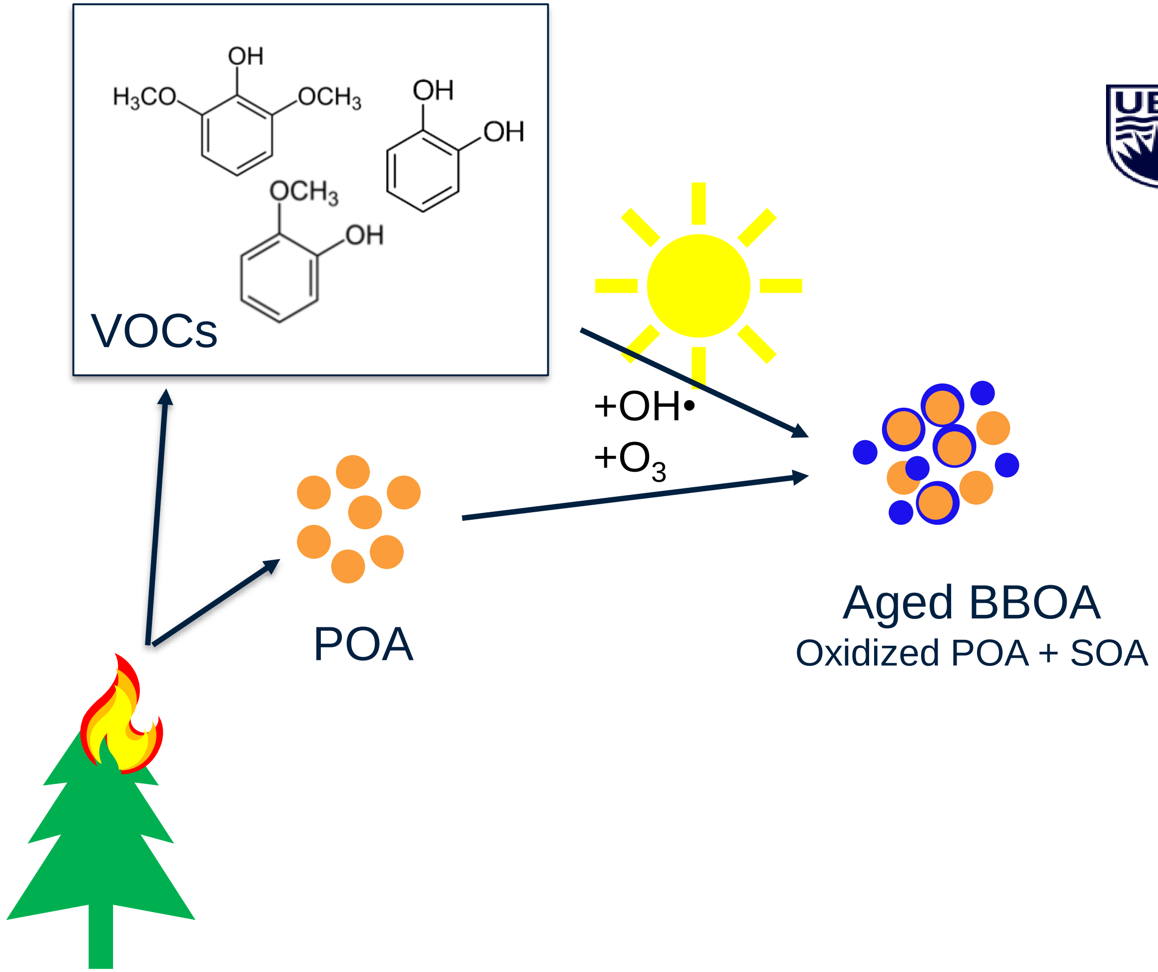
# Atmospheric aging

Organic aerosols are “aged” in the atmosphere by photochemical reactions.

- During the day, OH chemistry dominates.

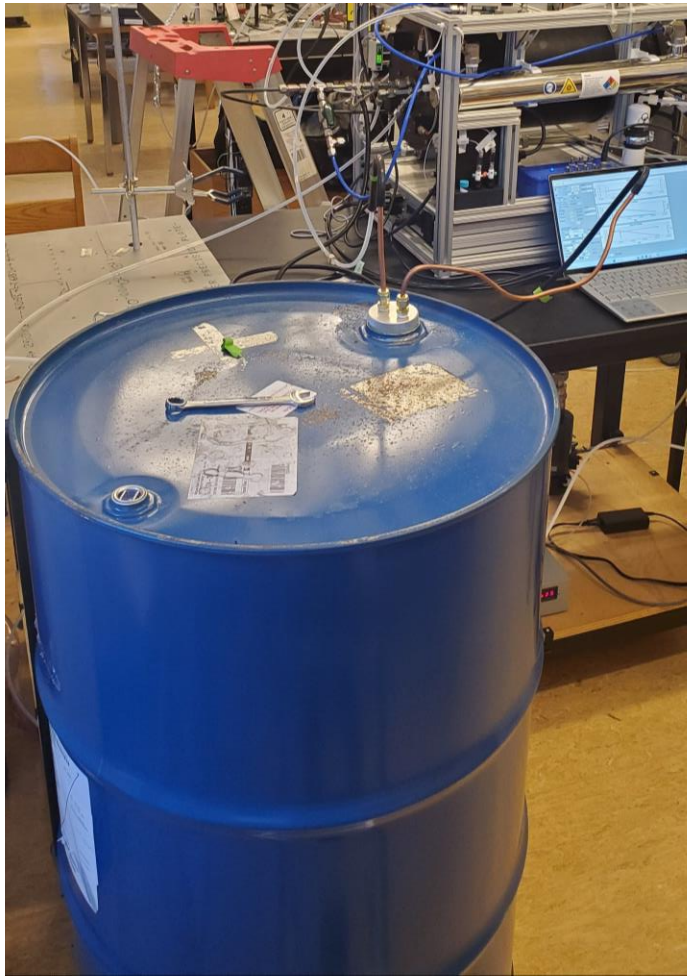
Oxidation can change the viscosity of particles.

- More oxygen = more polar groups = higher viscosity and hygroscopicity
- Oxidation can cause fragmentation or oligomerization.
- Oxidation causes secondary organic aerosol (SOA) formation, which is often more viscous than primary (POA).



# BBOA production

Pine wood was smoldered at ~300° C in our flow-tube furnace, and pumped into a 200 L steel drum.

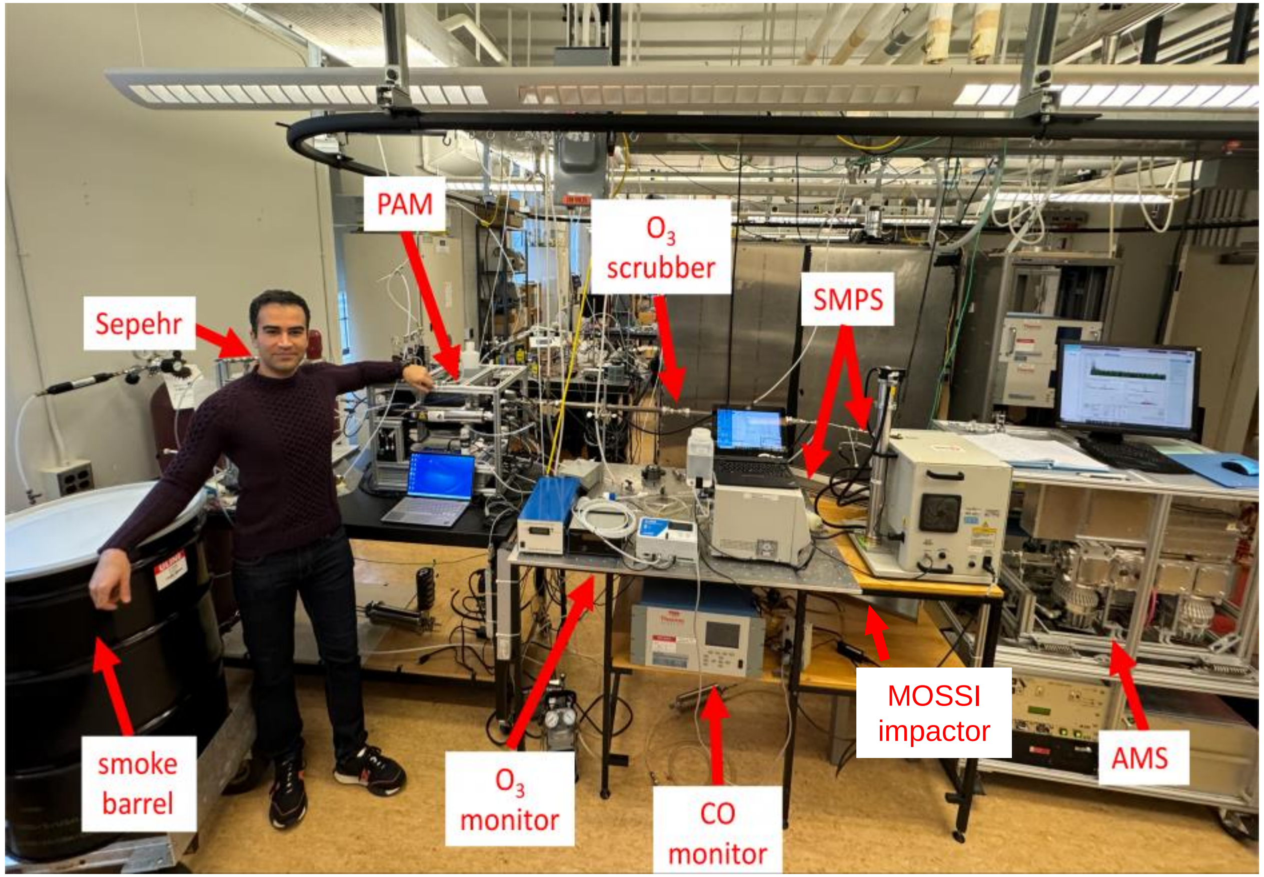


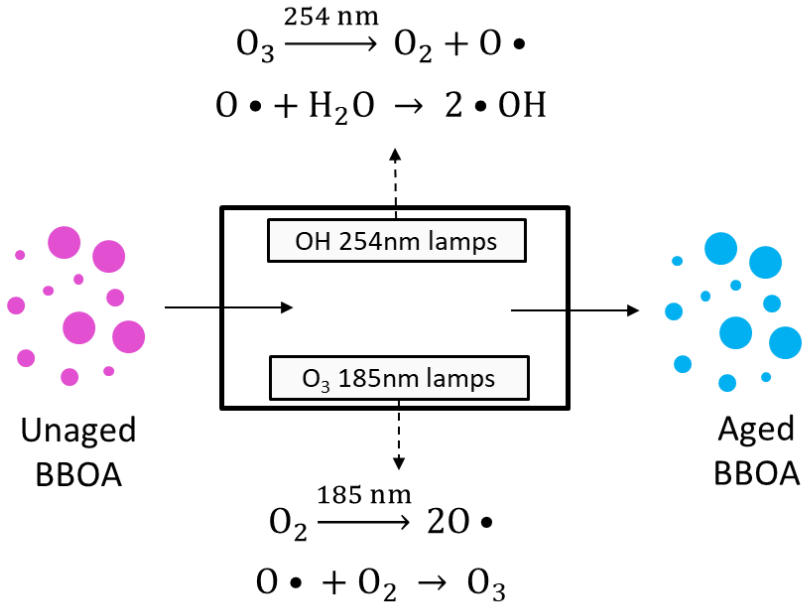
# Oxidation of BBOA

BBOA was pulled into the PAM oxidative flow reactor with a 600 × dilution.

Residence time in the chamber is 173 seconds.

"Age" of a particle through PAM = $\frac{[\mathrm{OH}]_{PAM} t_{PAM}}{[\mathrm{OH}]_{troposphere}}$



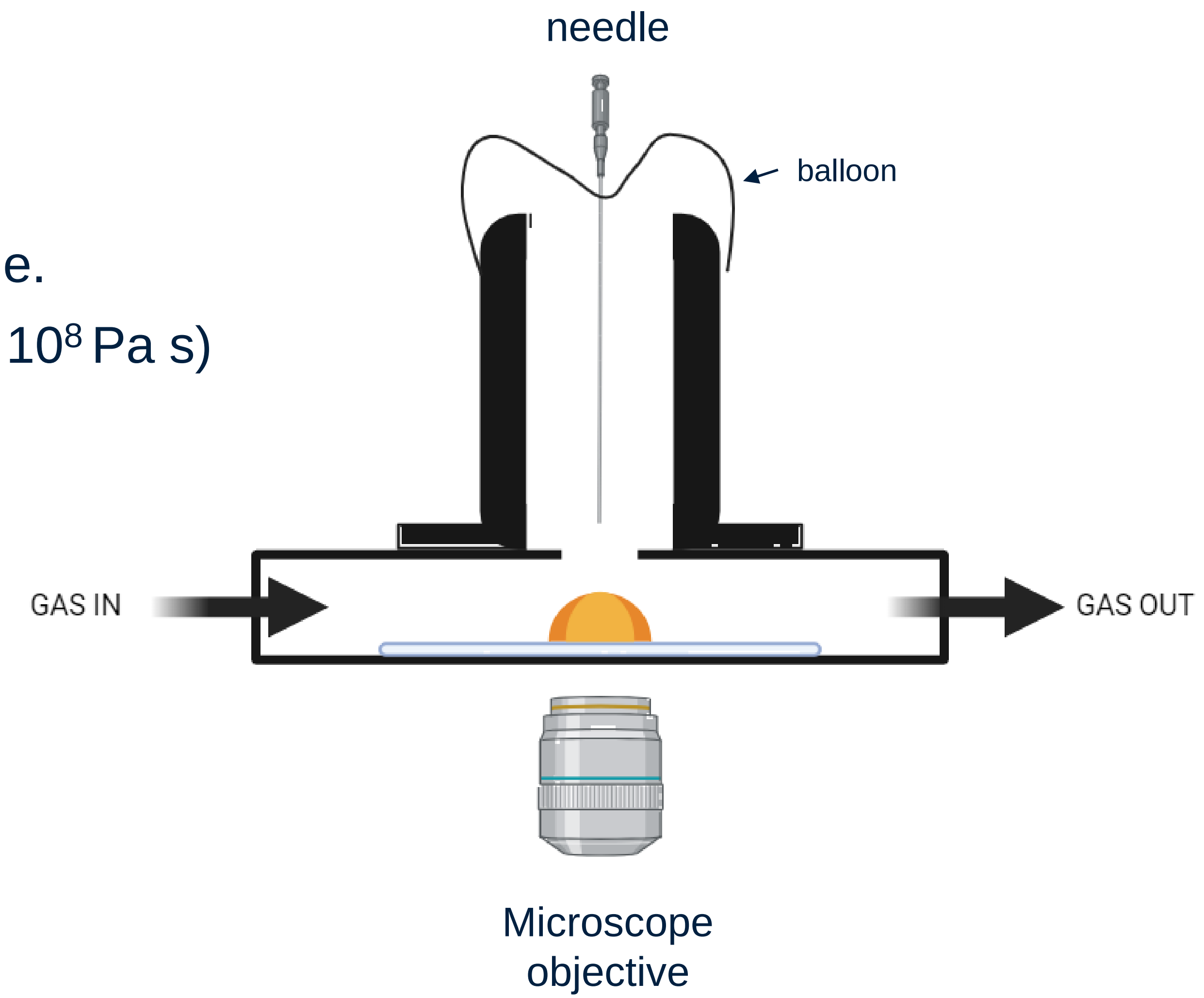

Aerodyne "Potential Aerosol Mass" oxidative flow reactor

# Viscosity measurements with the poke-flow method

Particles were collected with a single-stage impactor for 60-90 minutes, creating large (>50 µm) droplets on microscope slides.

Viscosity was investigated with the poke-flow method:

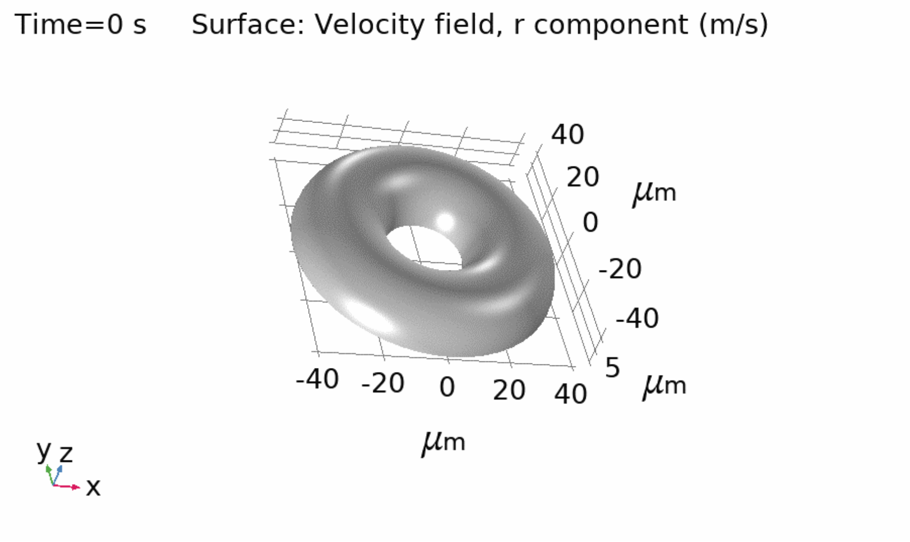
- Particles are poked with a fine needle.
  - Highly viscous particles (>2.5 × $10^8$ Pa s) shatter
  - Liquids flow

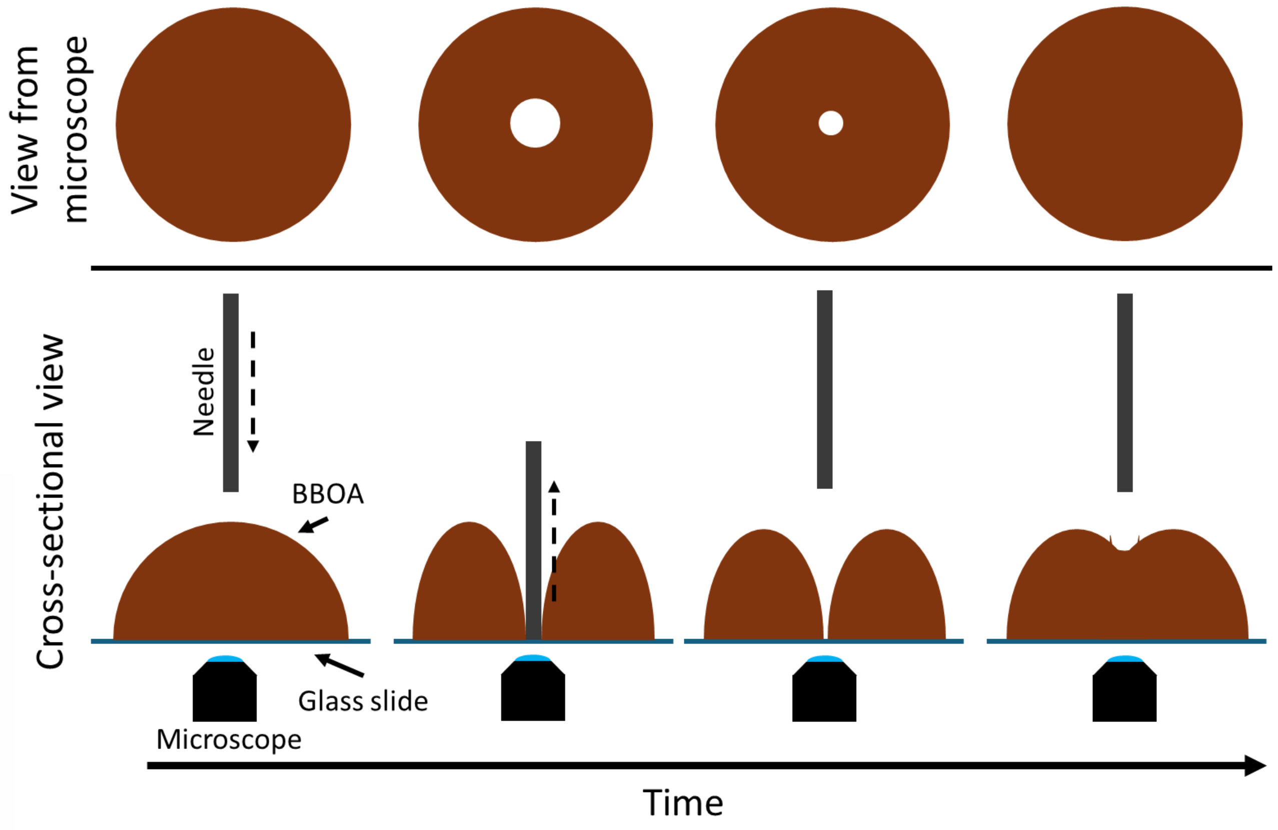


# Viscosity measurements with the poke-flow method

Based on the time it takes for the hole to close, we can calculate viscosities from $10^3$ to $>10^8$ Pa s

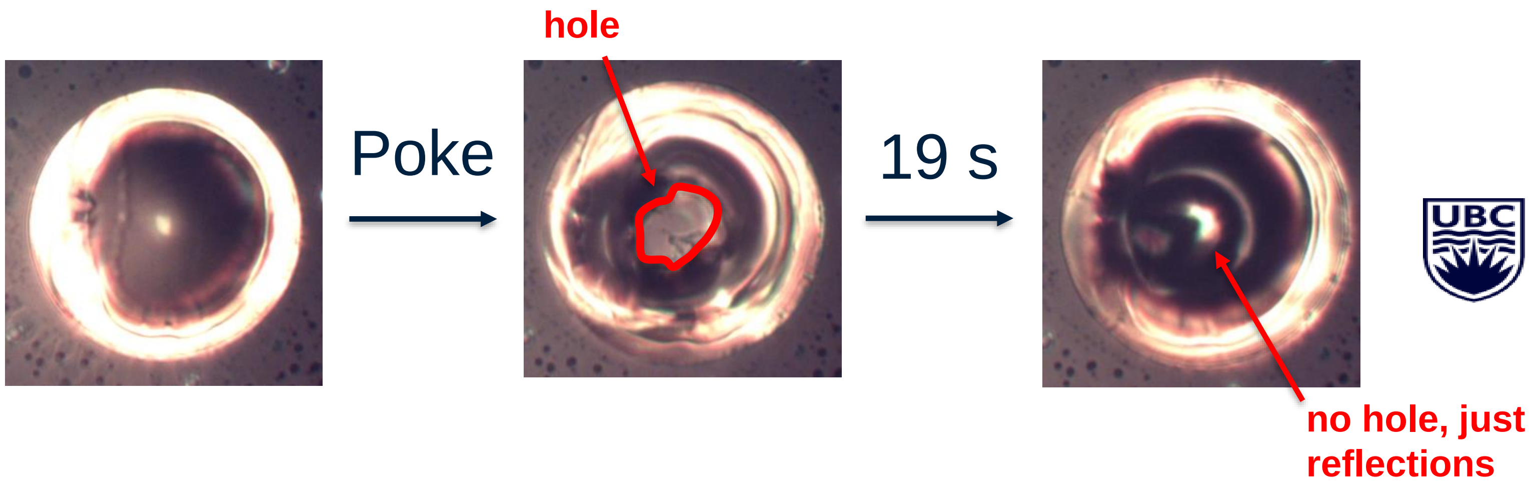
- COMSOL Multiphysics
  - Navier-Stokes momentum equation
  - continuity equation



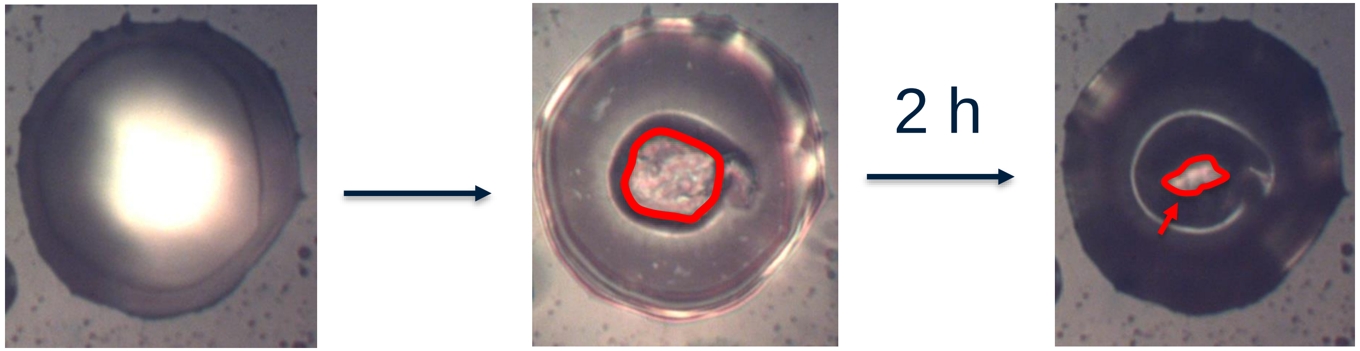



# Poke-flow results (dry)

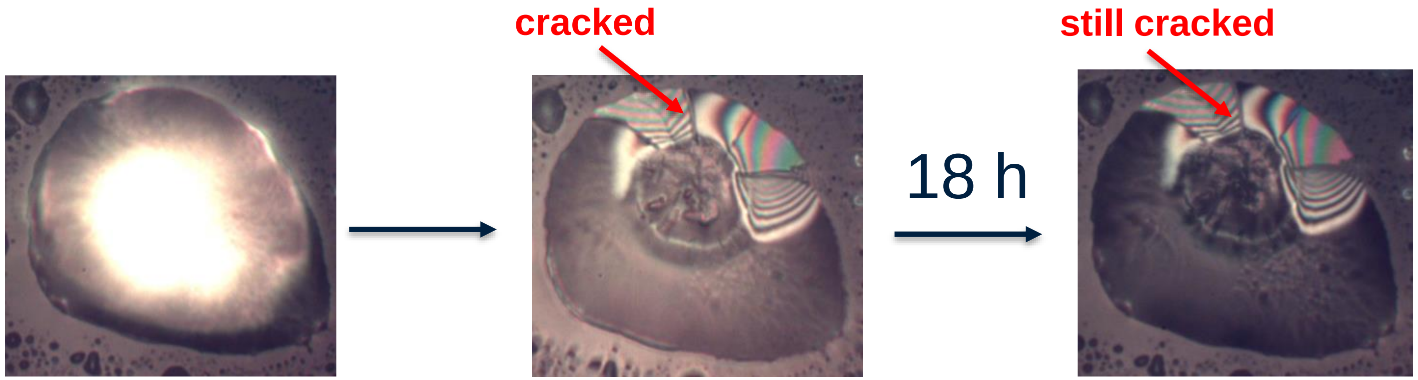
Unaged particles behave like a liquid, recovering in seconds.




Particles aged for ~1 equivalent day are much more viscous, showing limited movement after a couple hours.



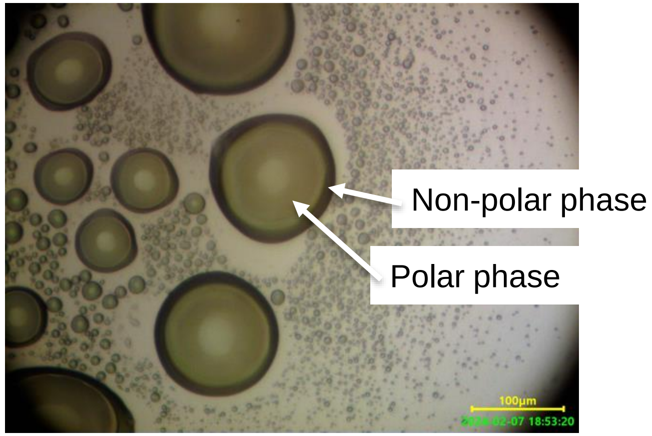

Older particles (5+ days) shatter after being poked, behaving like a glass.

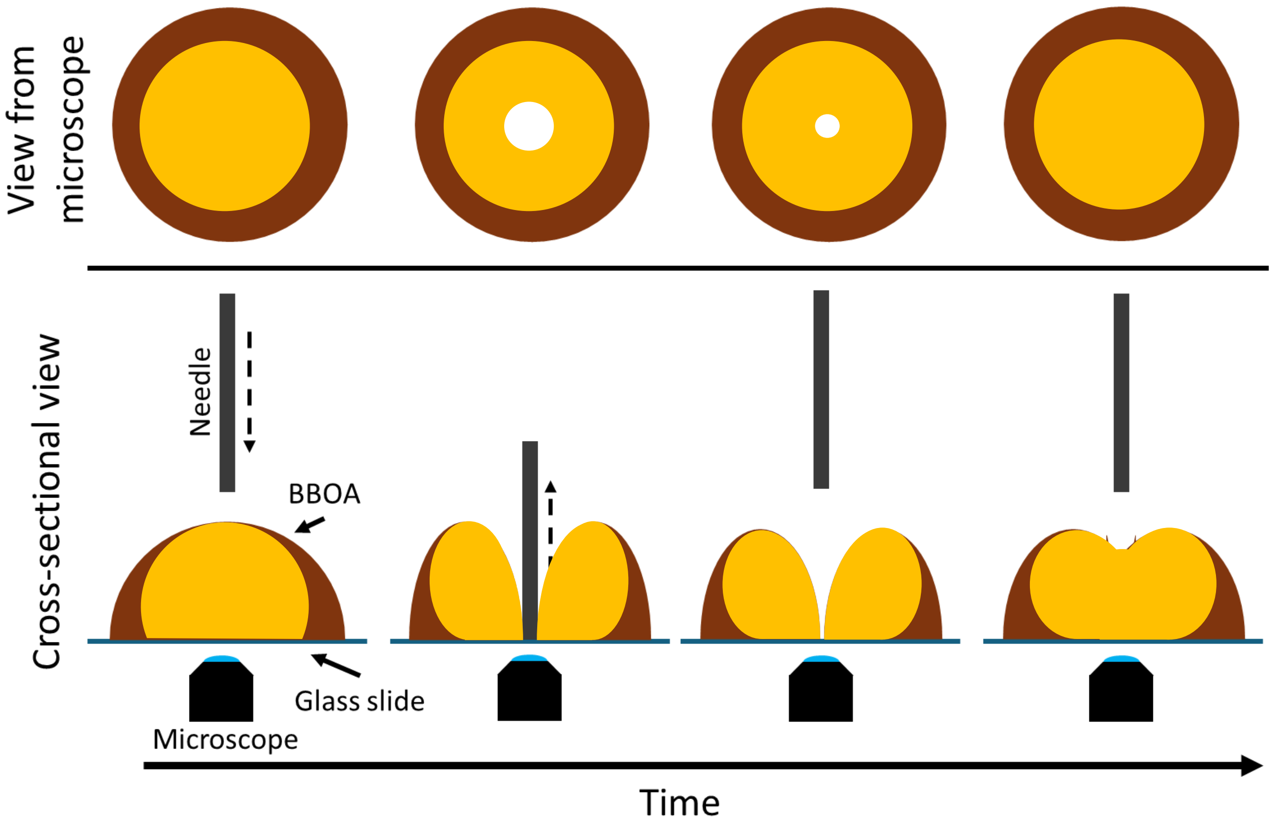


# Viscosity measurements with the poke-flow method

- Based on the time it takes for the hole to close, we can estimate viscosities from $10^3$ to $>10^8$ Pa s

- Caveat: poke-flow is designed and validated for a single-phase system.
  - The effects of the interactions between the phases are unknown



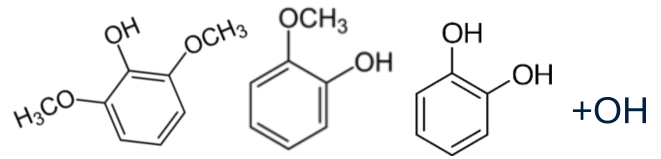
# (Apparent) Viscosity of Aged BBOA

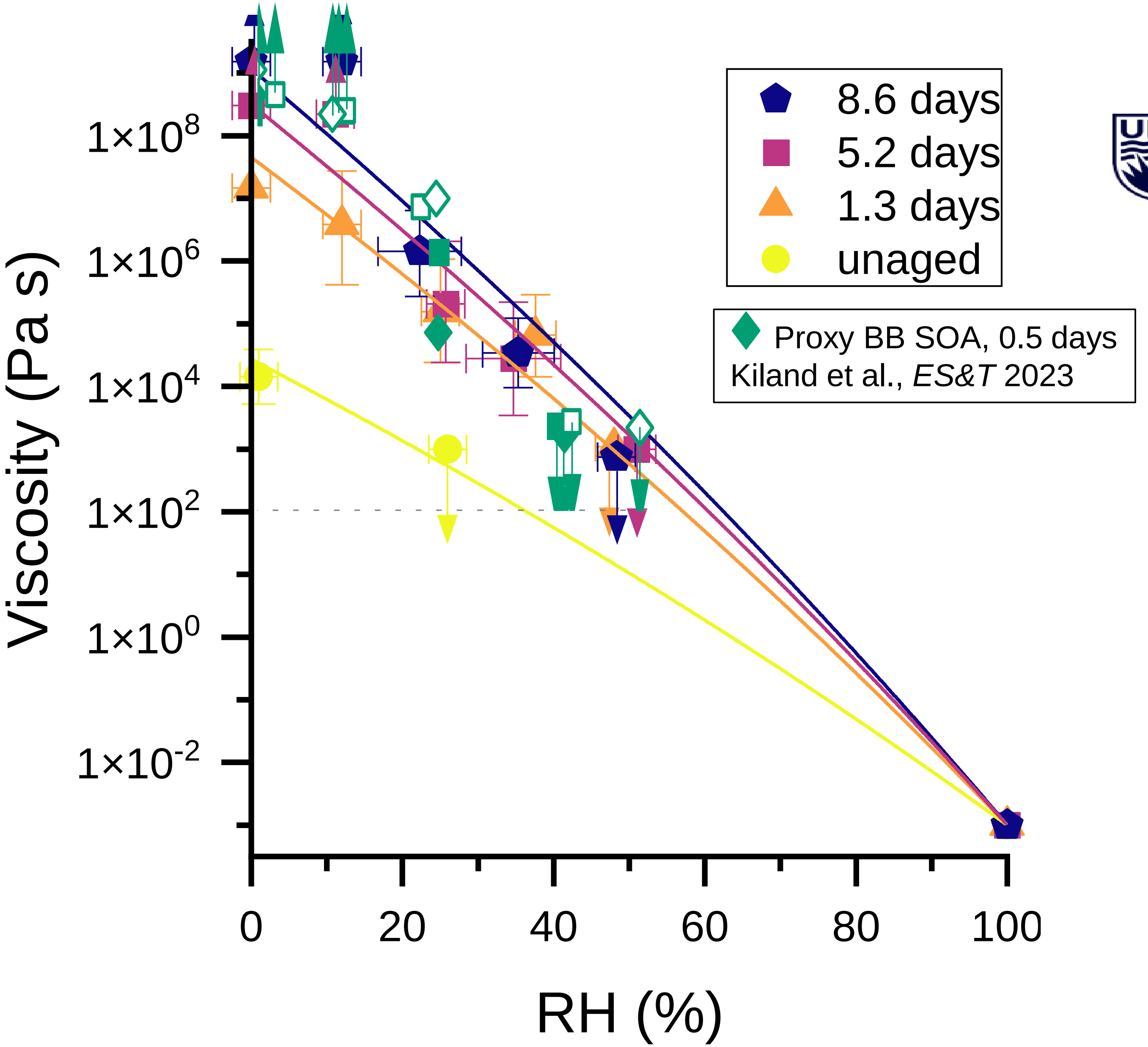
BBOA viscosity increases rapidly over the **first day** of aging.

Changes slow down after the first day.

After **5 days**, BBOA exhibits glassy behaviour under low RH conditions. **8 days** is the same.

Aged BBOA looks similar to "**BBOA-like SOA proxies**" we generated from OH + phenolic compounds in a smog chamber.

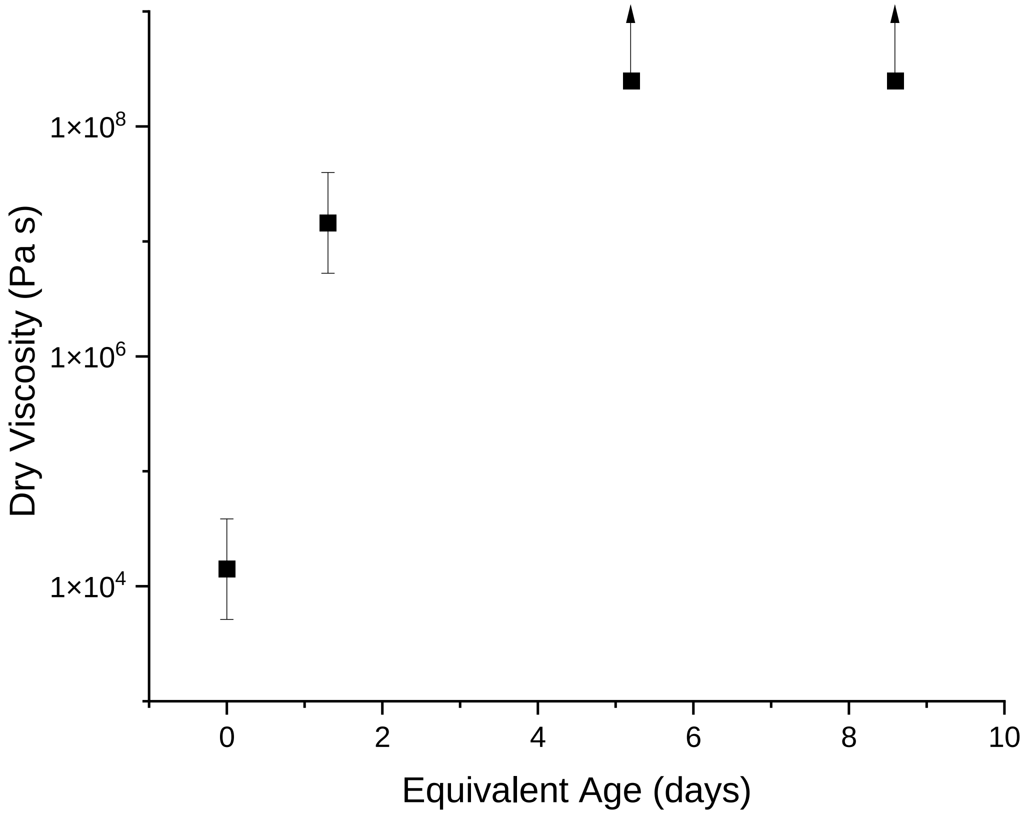


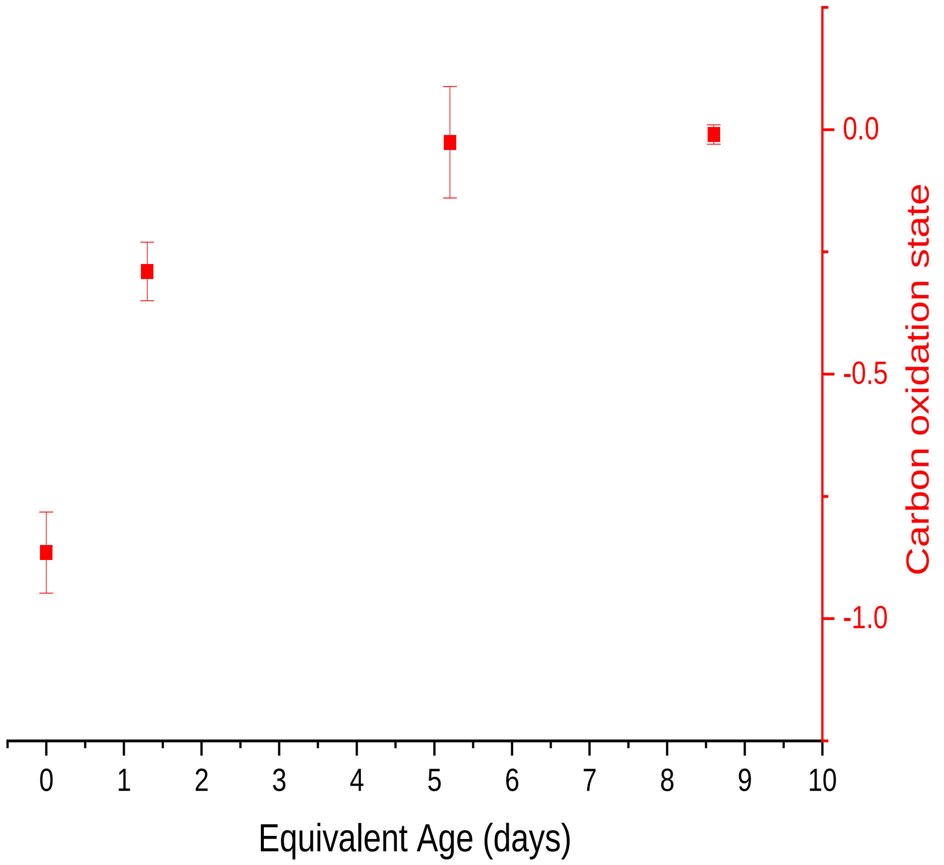



# Viscosity and Oxidation

Carbon oxidation state ($\overline{OS}_C \approx 2\mathrm{O{:}C} - \mathrm{H{:}C}$) was measured with an Aerosol Mass Spectrometer.

Trends in log(viscosity) and oxidation state look similar as BBOA age increases.



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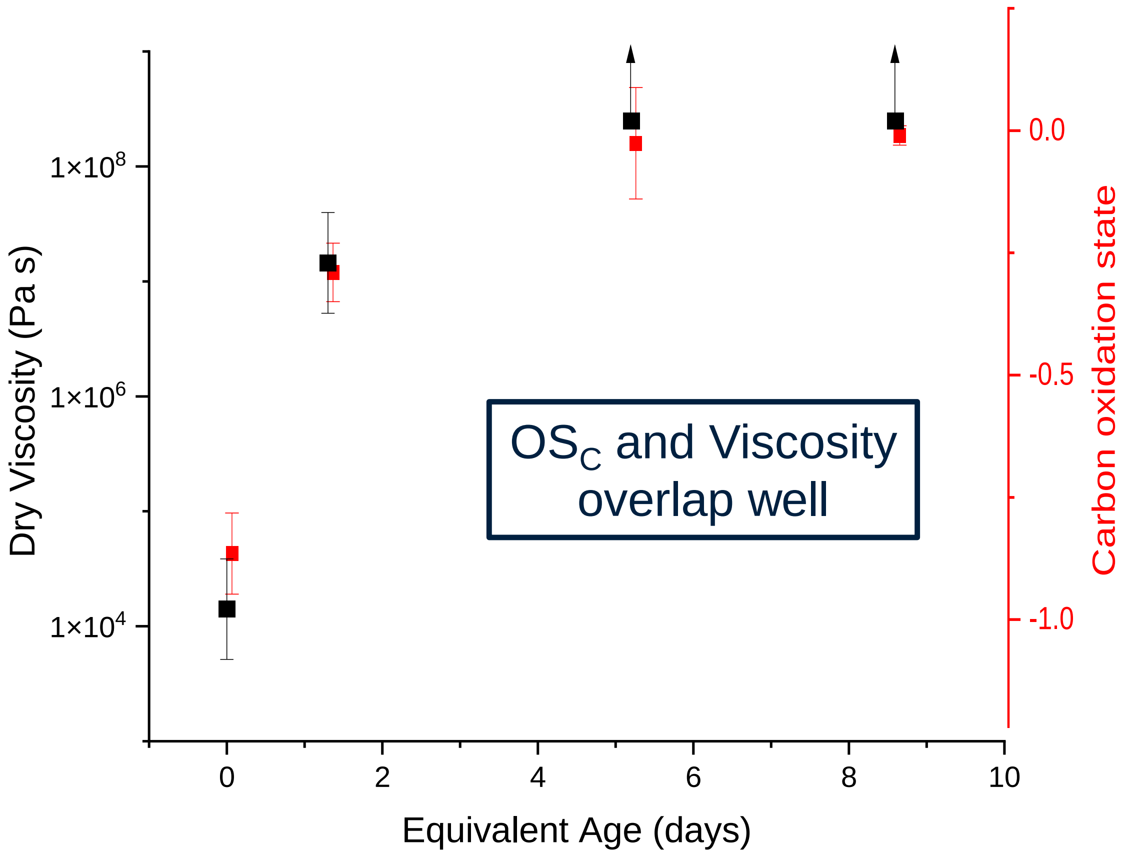
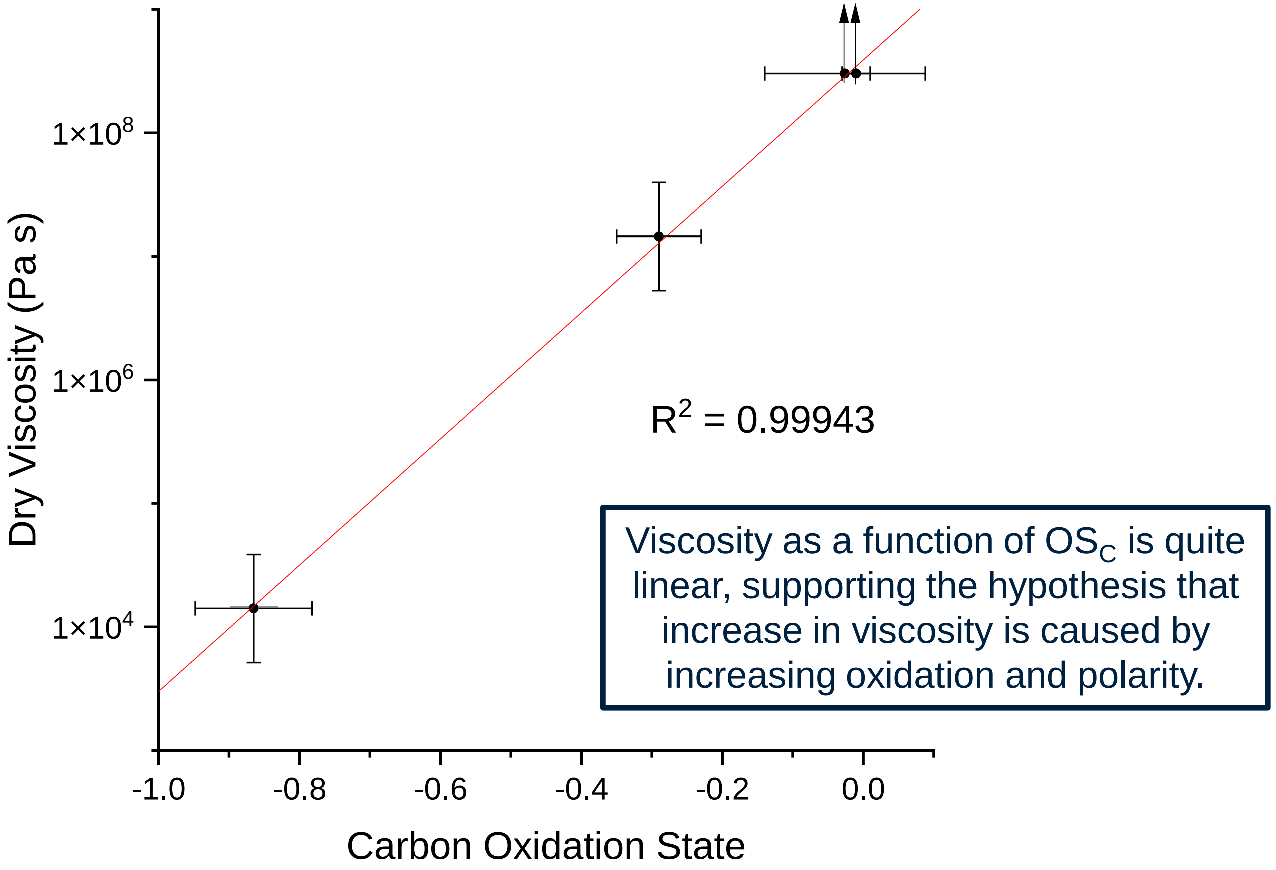
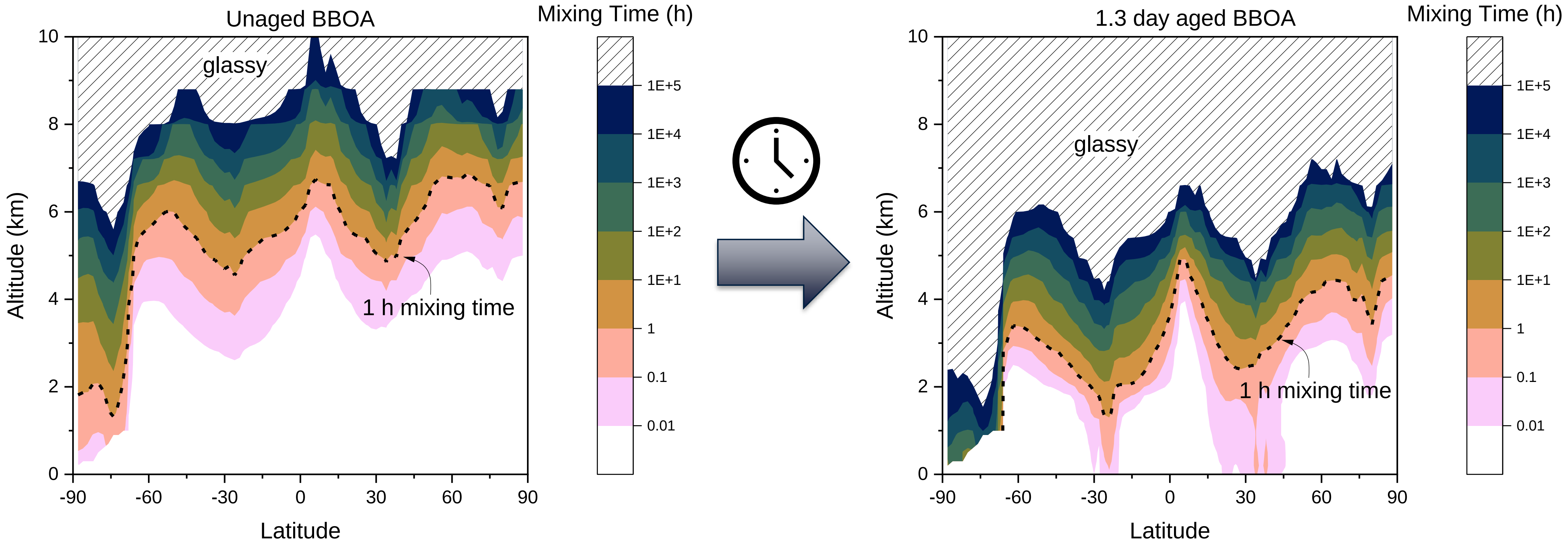


# Why do we care?

Increased viscosity leads to increased mixing times in aerosols.

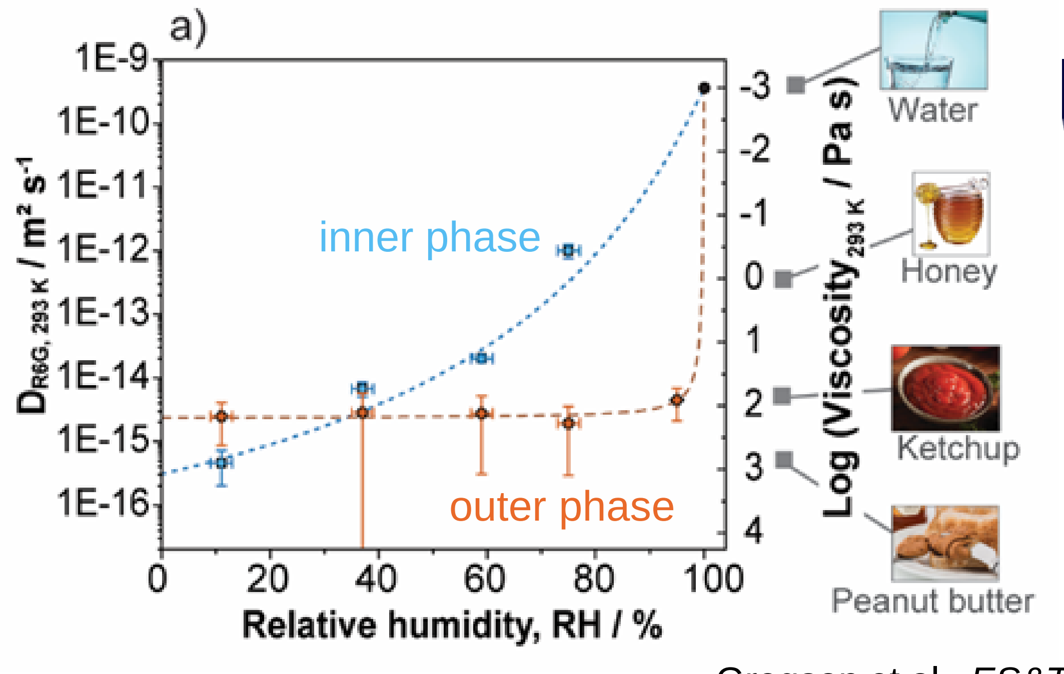
Traditionally it is assumed that mixing times in aerosols are fast, but this is not true for viscous particles.




After aging, longer mixing times happen lower in the troposphere.
Chemistry will slow down.
Ice might nucleate - check out poster 9CC.3, Mei Fei (Janice) Zeng tomorrow.

# Next steps:

- Validating the application of poke-flow to 2-phased particles using Fluorescence Recovery After Photobleaching (FRAP)
  - Previously showed that the inner and outer phases of unaged BBOA have different viscosity
- Connect aging-induced viscosity changes to molecular information from mass spectrometry




Gregson et al., *ES&T* 2023

# Acknowledgements

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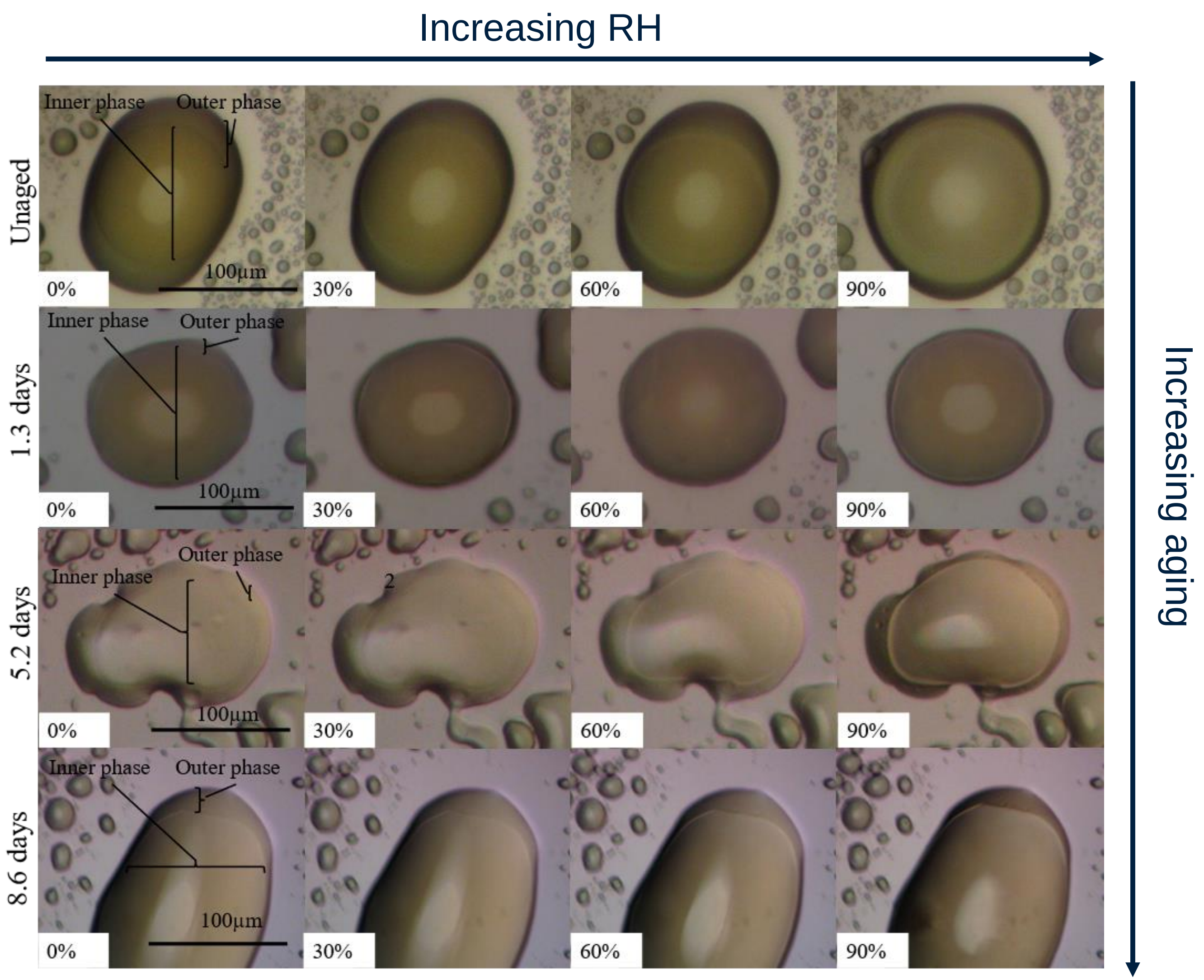
NSERC CRSNG

# Phase behaviour

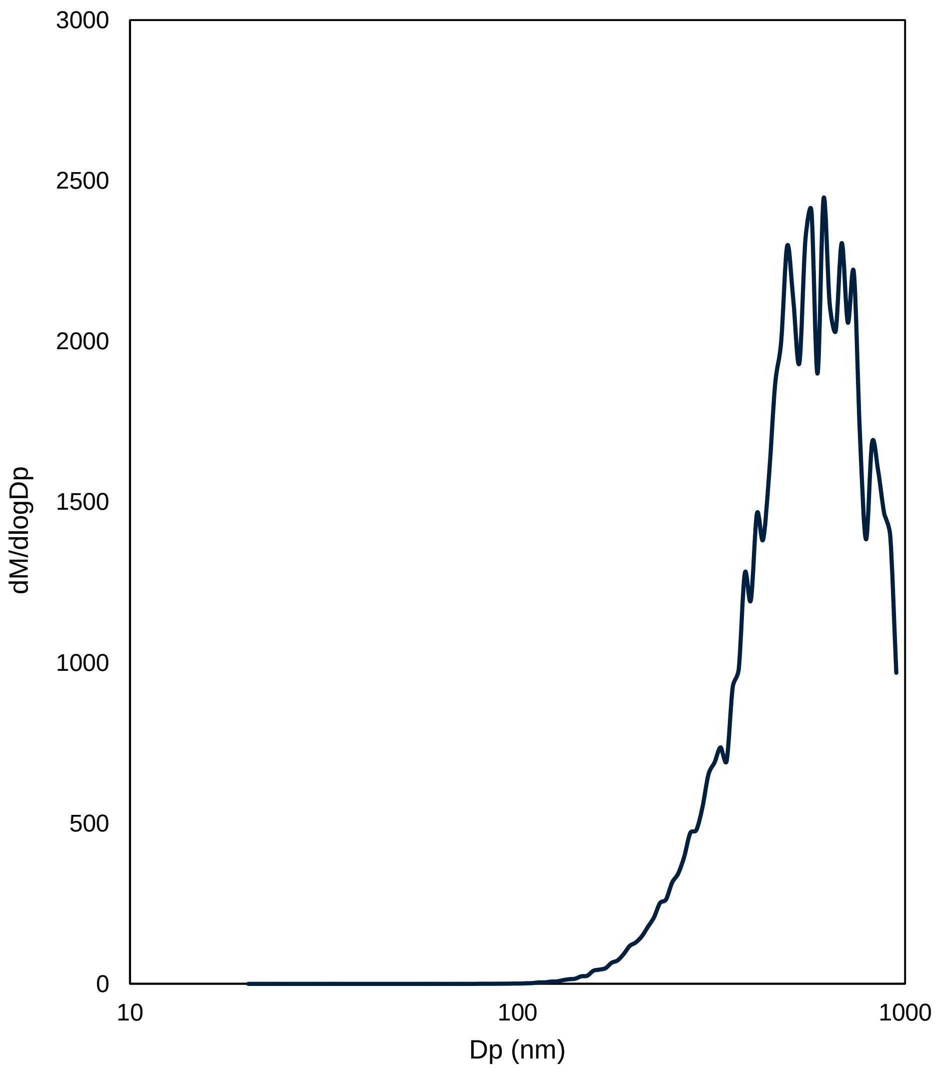
BBOA particles have two organic phases:

- Polar, hydrophilic on the inside.
- Non-polar, hydrophobic on the inside.
- *Does not* depend on aging for the range we investigated here.
- Same as field-sampled BBOA we have investigated previously.



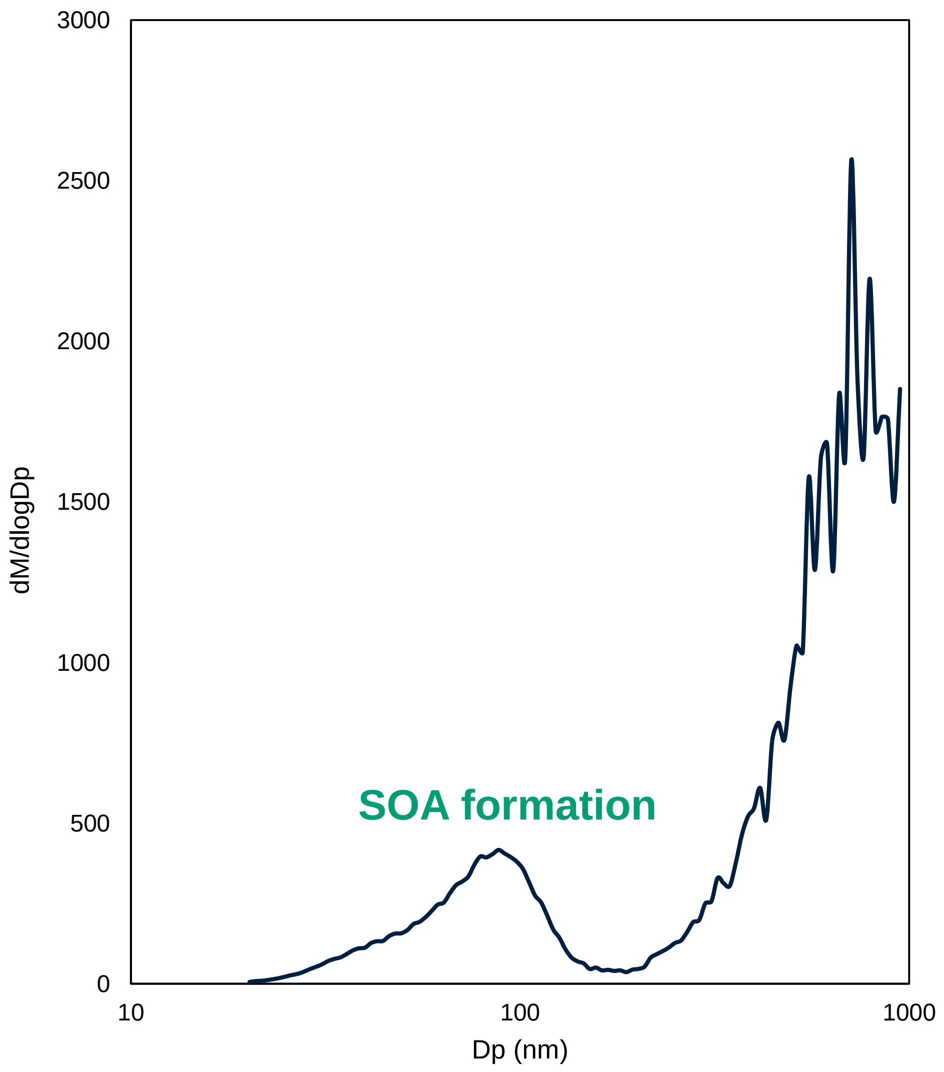
# Effects of oxidation on particle size (mass distribution)

BBOA Mass, PAM **OFF**

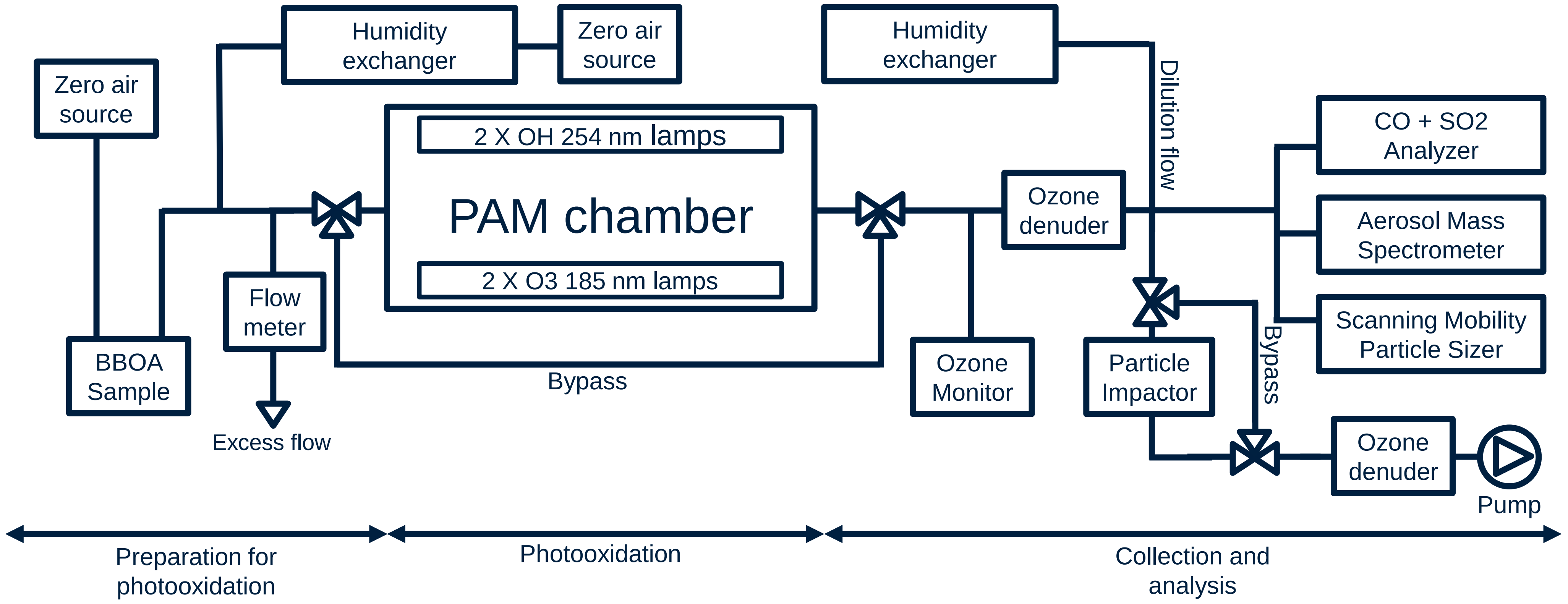



OH oxidation

BBOA Mass, PAM **ON**



# Schematic



Zero air source
Humidity exchanger
Zero air source
Humidity exchanger
Dilution flow
2 X OH 254 nm lamps
PAM chamber
2 X O3 185 nm lamps
CO + SO2 Analyzer
Ozone denuder
Aerosol Mass Spectrometer
Scanning Mobility Particle Sizer
Flow meter
BBOA Sample
Bypass
Excess flow
Ozone Monitor
Particle Impactor
Bypass
Ozone denuder
Pump
Preparation for photooxidation
Photooxidation
Collection and analysis

# OH Exposure to Equivalent aging time

- $SO_2$ and CO react with OH in a pseudo-first-order reaction
- Consumption of $SO_2$ and CO within PAM is used to find OH exposure and equivalent aging times

Reaction with OH

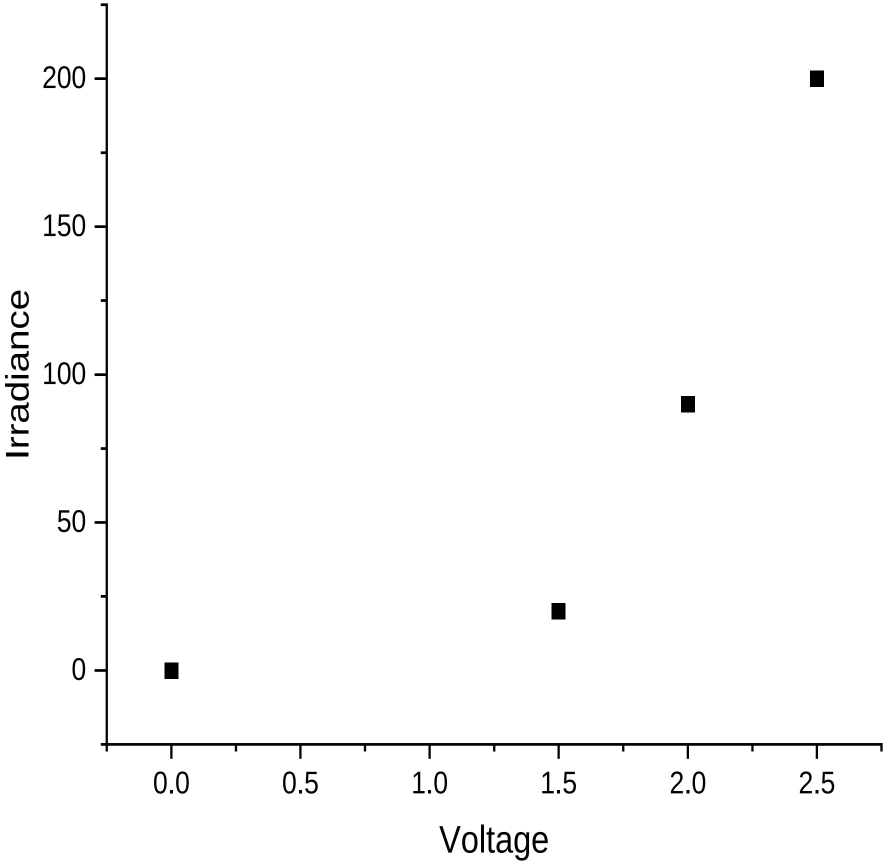
$$\bullet OH + CO \rightarrow H\bullet + CO_2 \longrightarrow \mathrm{OH}\ exposure = \frac{1}{k_{\mathrm{CO+OH}}} \times \ln \frac{[\mathrm{CO}]\ lights\ off}{[\mathrm{CO}]\ lights\ on}$$

$$\bullet OH + SO_2 \rightarrow HOSO_2\bullet \longrightarrow \mathrm{OH}\ exposure = \frac{1}{k_{\mathrm{SO_2+OH}}} \times \ln \frac{[\mathrm{SO_2}]\ lights\ off}{[\mathrm{SO_2}]\ lights\ on}$$

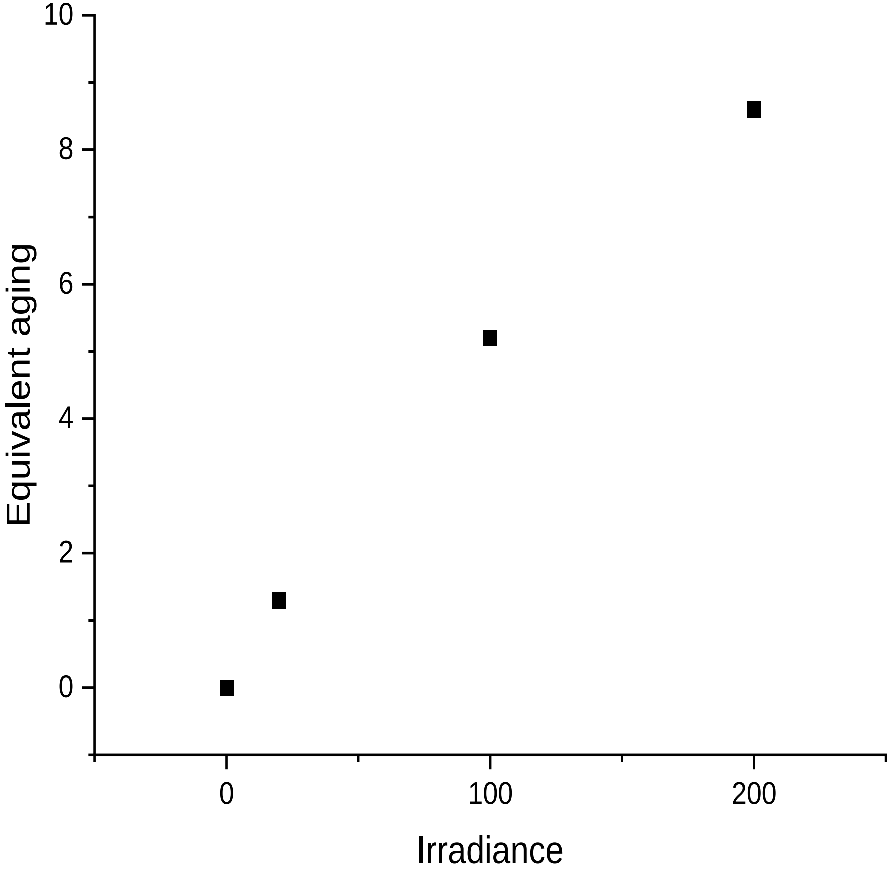
$$\frac{\mathrm{OH}\ exposure}{Average\ [\mathrm{OH}]\ in\ troposhere} = \text{“}equivalent\ aging\ time\text{”}$$

# Extra slides – PAM lamps, voltages, aging times

## Voltage vs Irradiance

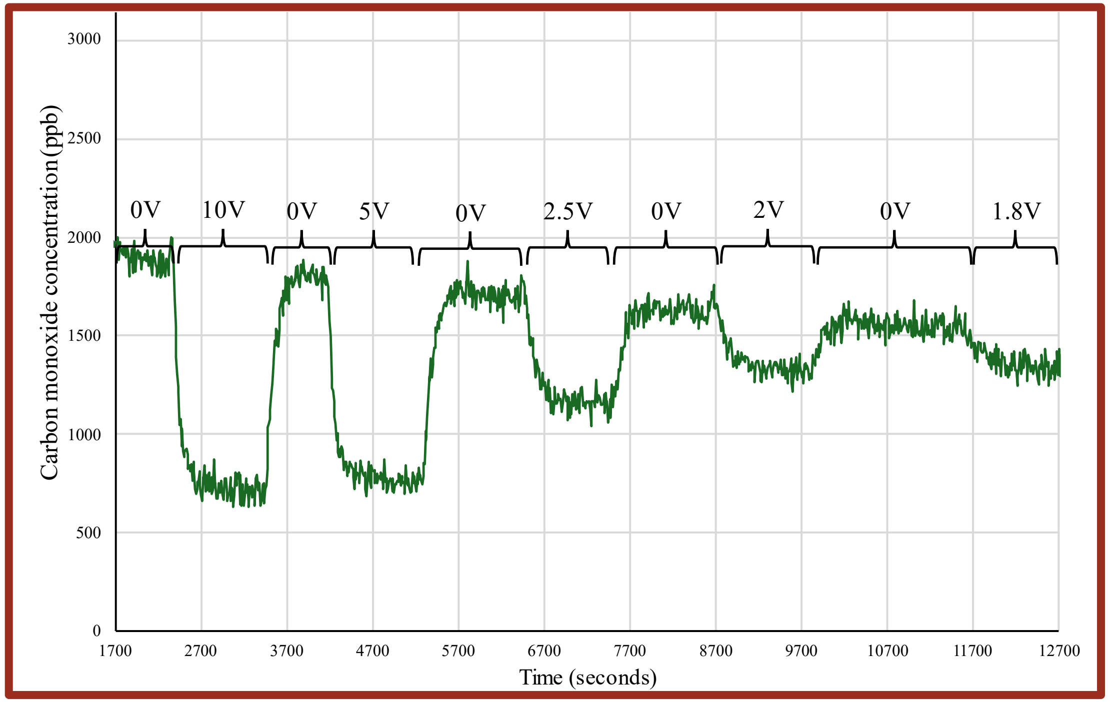



## Irradiance vs Aging time

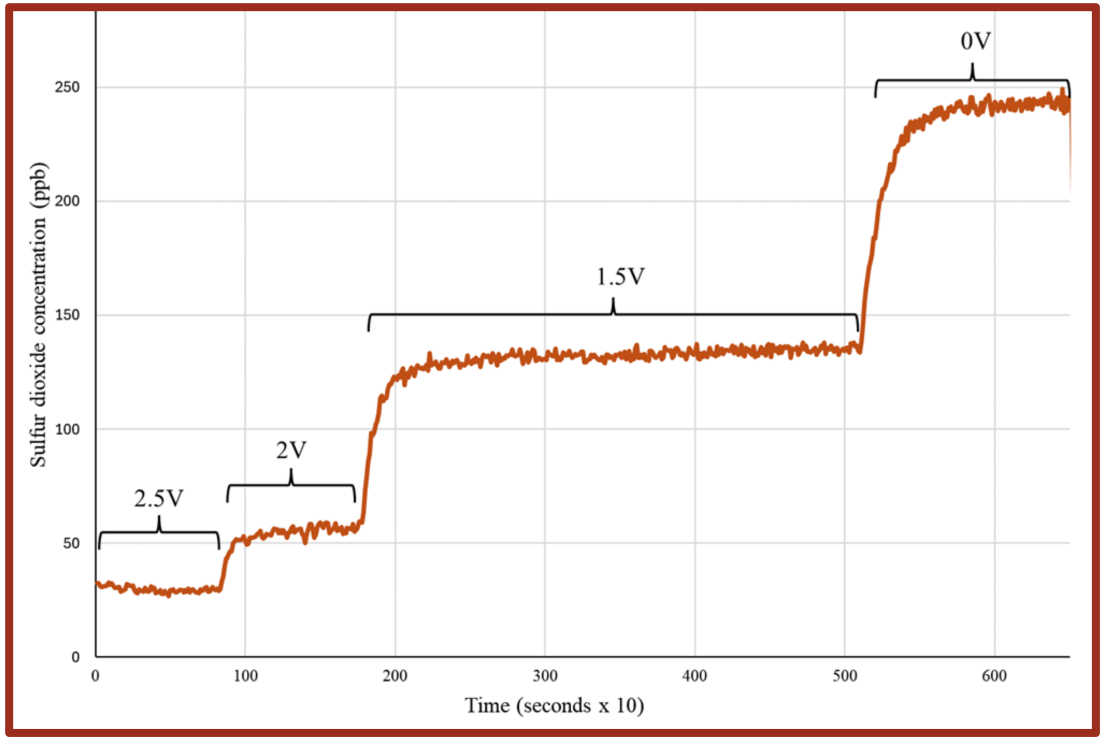


# OH exposure within the PAM chamber

## CO Trace

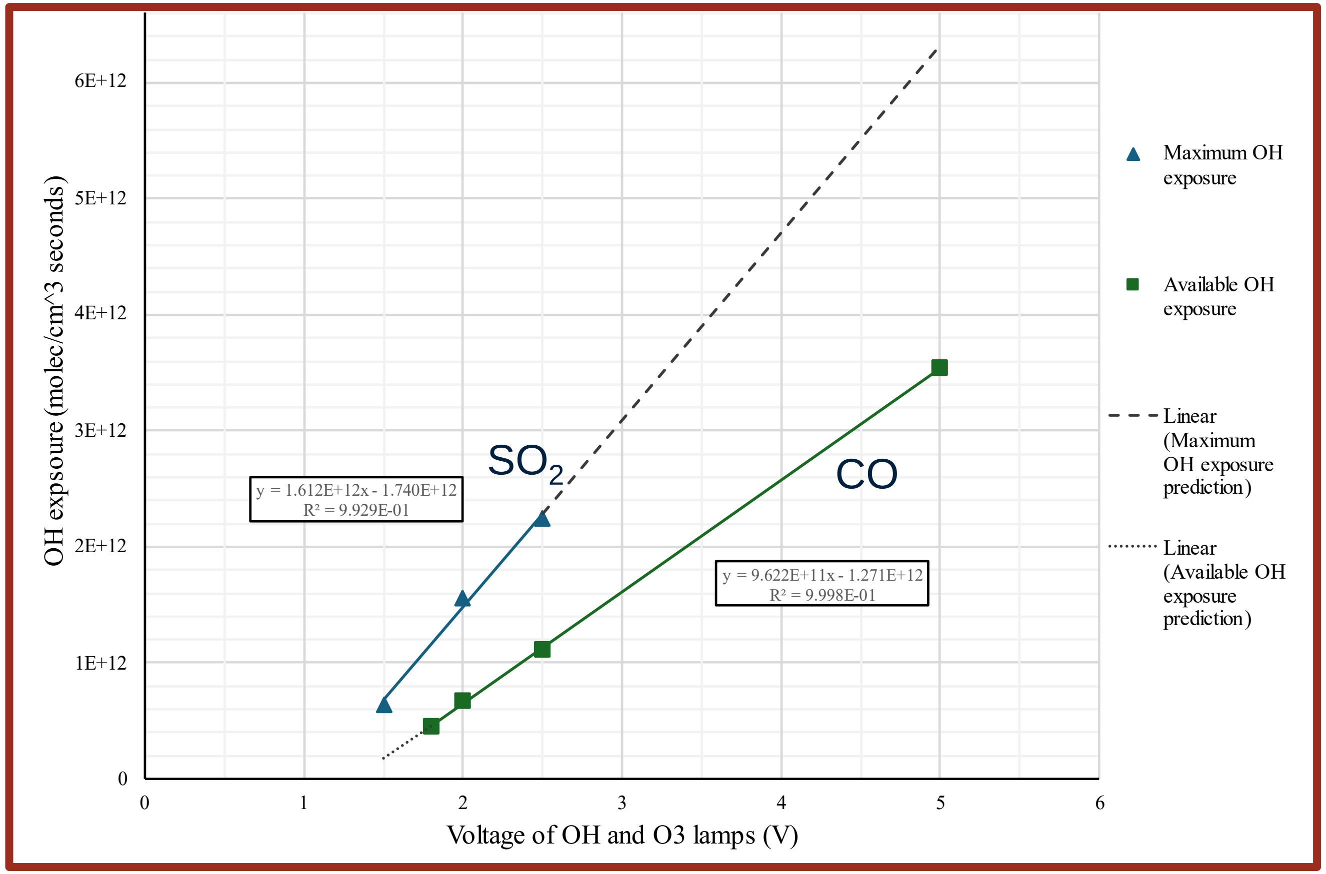



## $SO_2$ Trace



# Equivalent Aging Times Within the PAM Chamber

## OH exposure




## Equivalent Aging

| BBOA sample | PAM light voltage (V) | Equivalent aging (days) |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 1.5 | 1.3 |
| 3 | 2 | 5.2 |
| 4 | 2.5 | 8.6 |

CO was generated by biomass burning, particles were filtered out but VOCs were still present.