OH• Aging of Organic Aerosols

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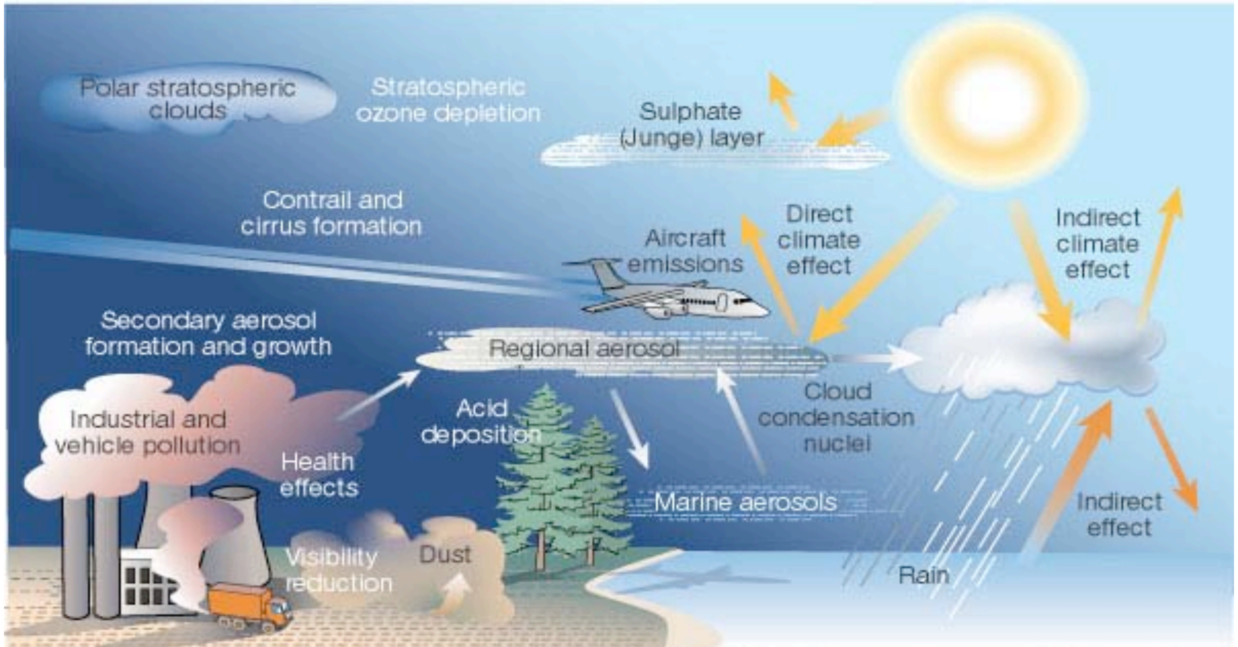
Introduction



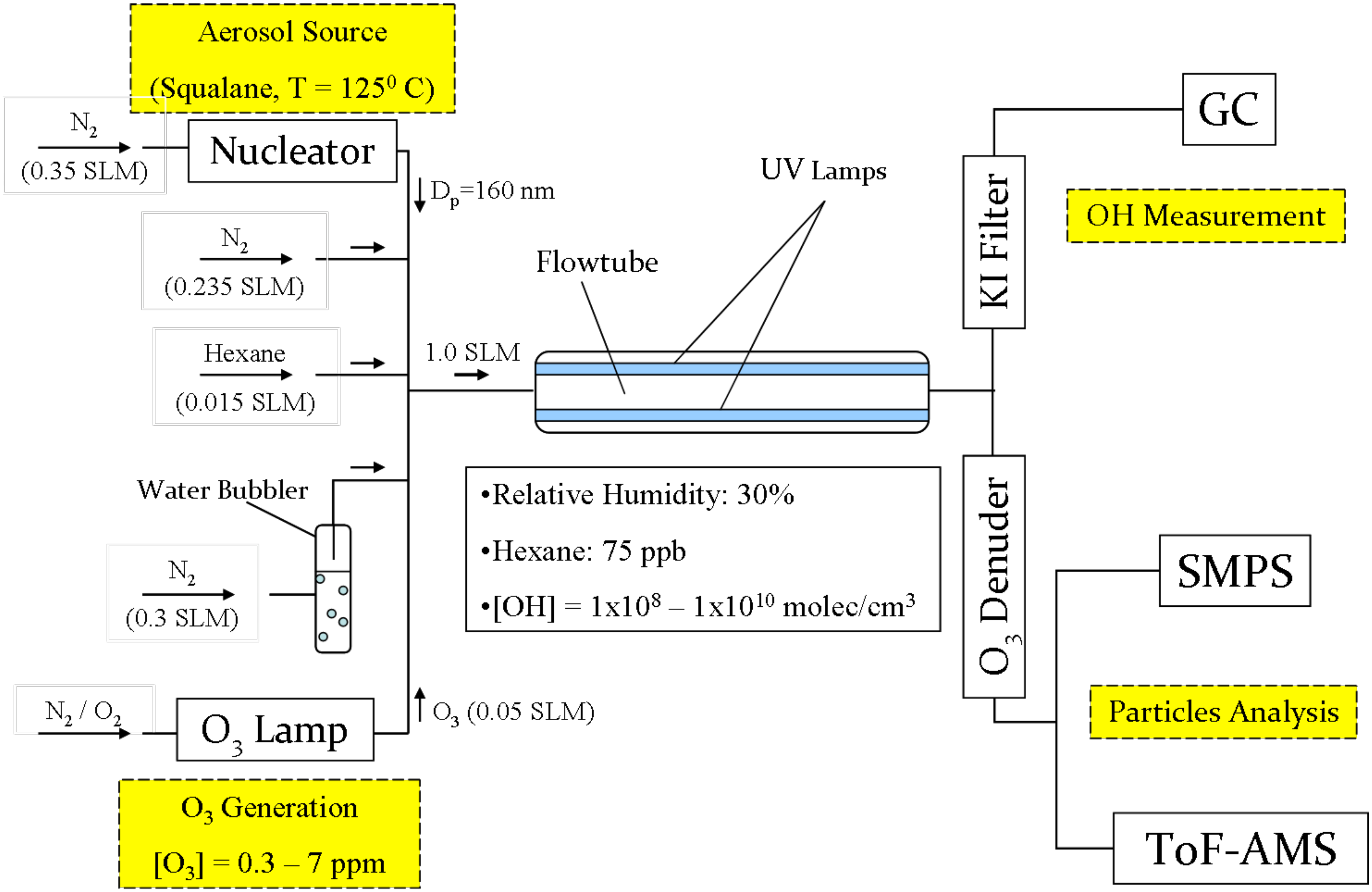
C. E. Kolb, Nature **417**, 597 (2002)

Heterogeneous OH oxidation of organic aerosols

- **Timescales for oxidation?**
  - **Uptake measurements range from 0.3 to 2.0**
- **Role of secondary chemistry?**
  - **Uptake coefficient >1 ?**
- **Does oxidation lead to volatilization?**
  - **Conflicting evidence from recent measurements.**
- **Chemical Mechanism?**

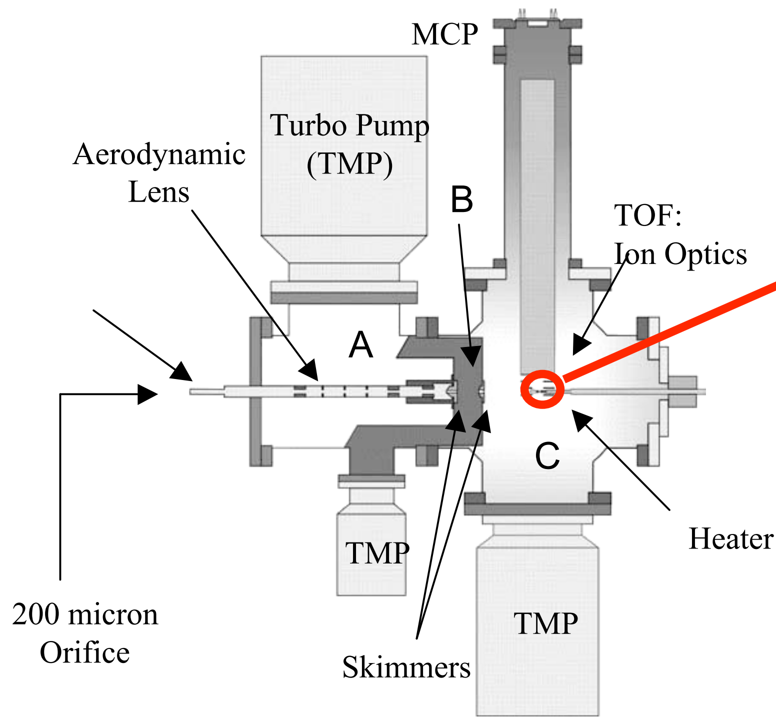
Molina *et al.* (2004), Hearn *et al*. (2007), George *et al*. (2007), McNeil *et al.* (2008)

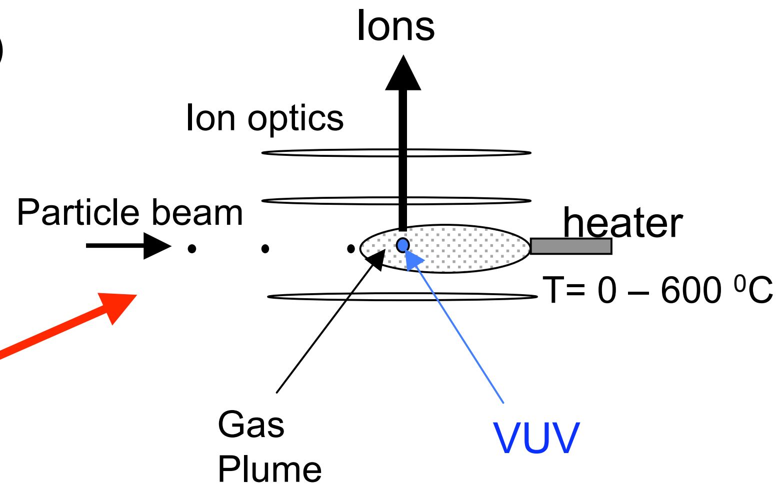
Experimental Set-up



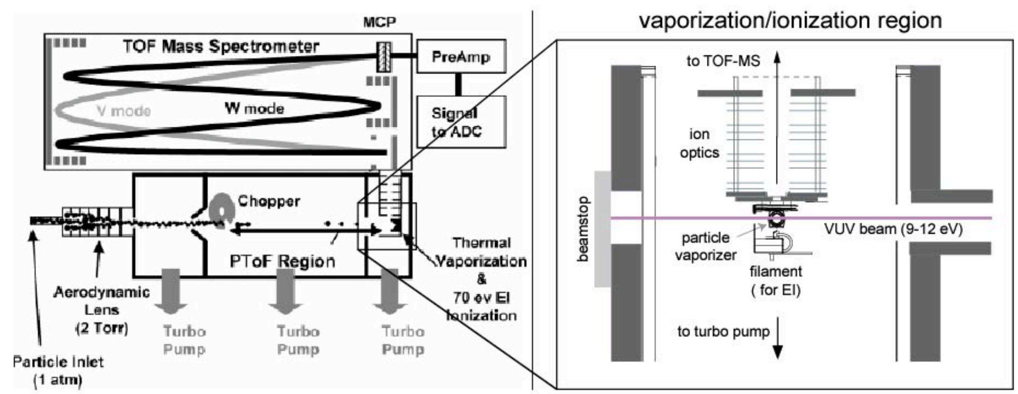
Aerosol Mass Spectrometry

Mass Spectrometer at
the Chemical Dynamics Beamline (ALS)



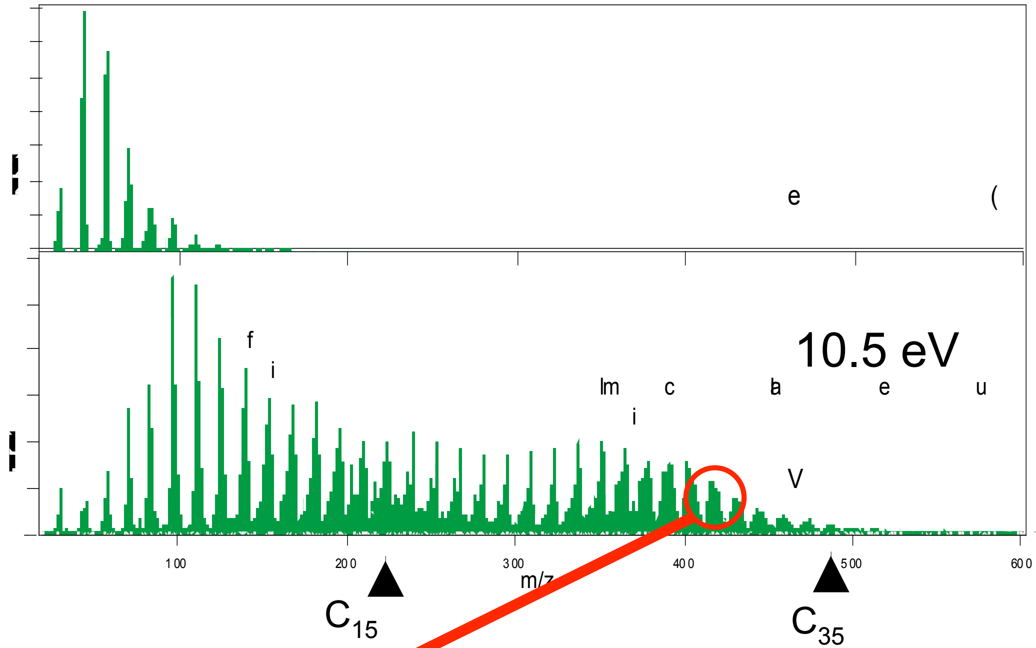


Aerodyne AMS

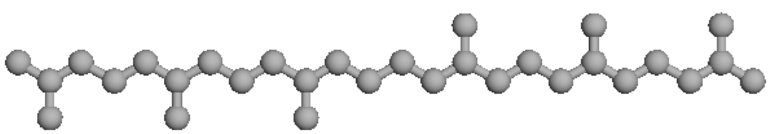


Ionization by electron impact (EI) or vacuum ultraviolet (VUV) photoionization [Northway et al., 2007]

Diesel Particles are Chemically Complex



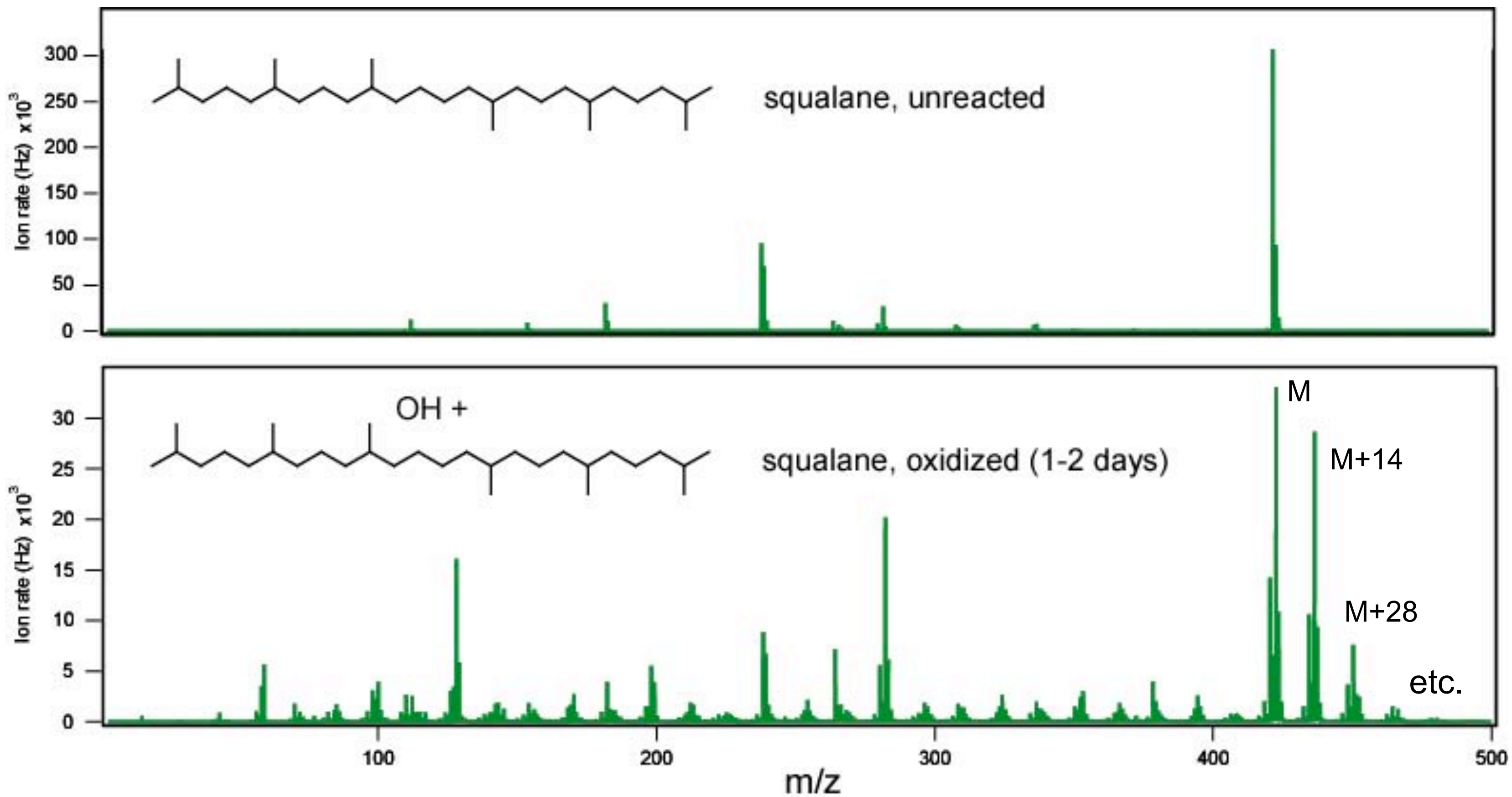
Squalane
($C_{30}H_{62}$)



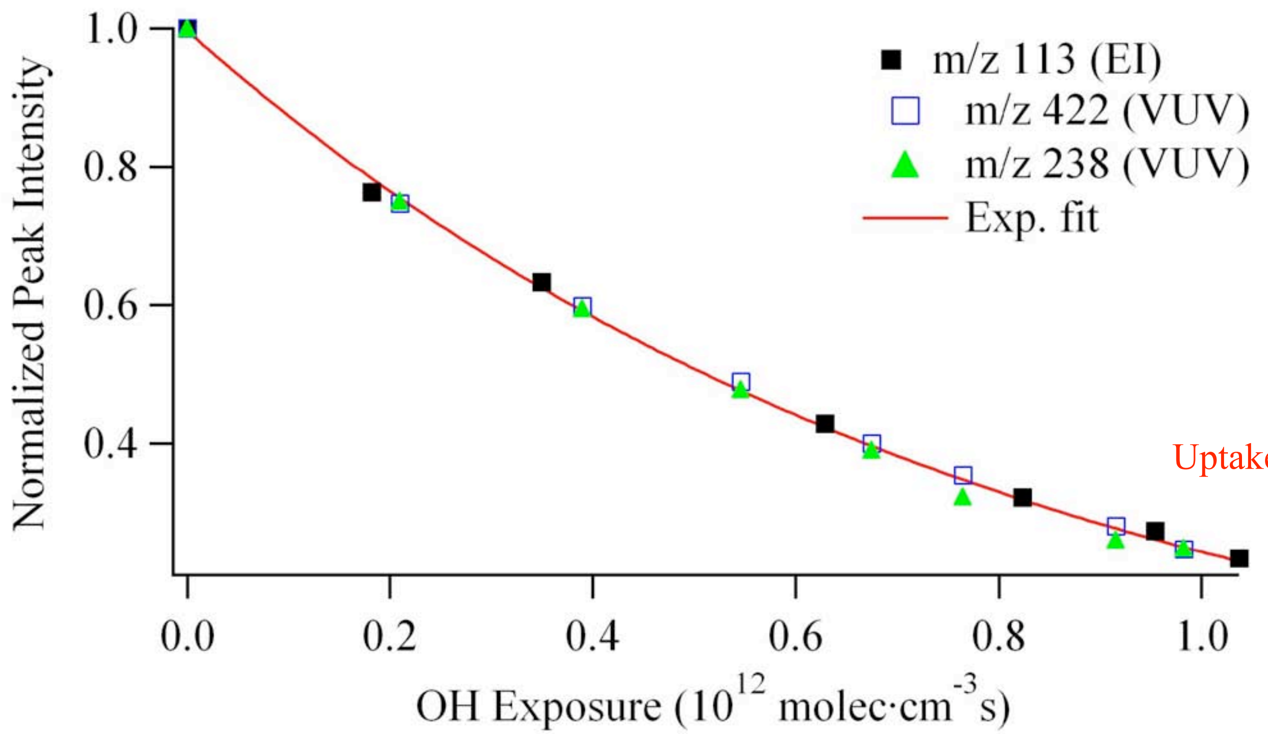
+ OH• →

- **Kinetics**
- **Chemical Composition**
- **Mechanism**
- **Secondary Chemistry**
- Product Partitioning
- CCN Activity

Heterogeneous Kinetics



Heterogeneous Kinetics



$$\gamma_{Squal.} = \frac{k \cdot 4 \cdot D \cdot \rho}{\bar{c} \cdot 6} = 0.35 \pm 0.1$$

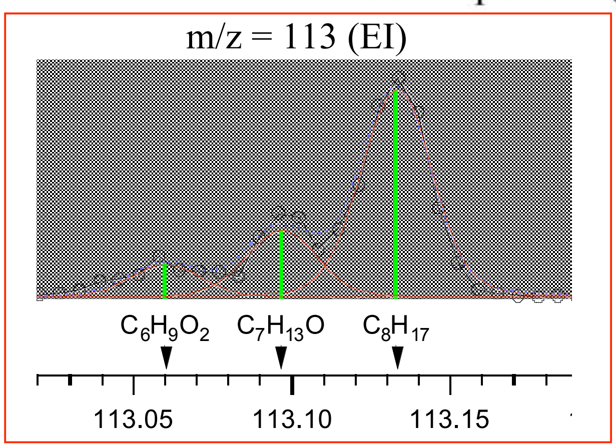
decay constant

particle diameter

Uptake coefficient

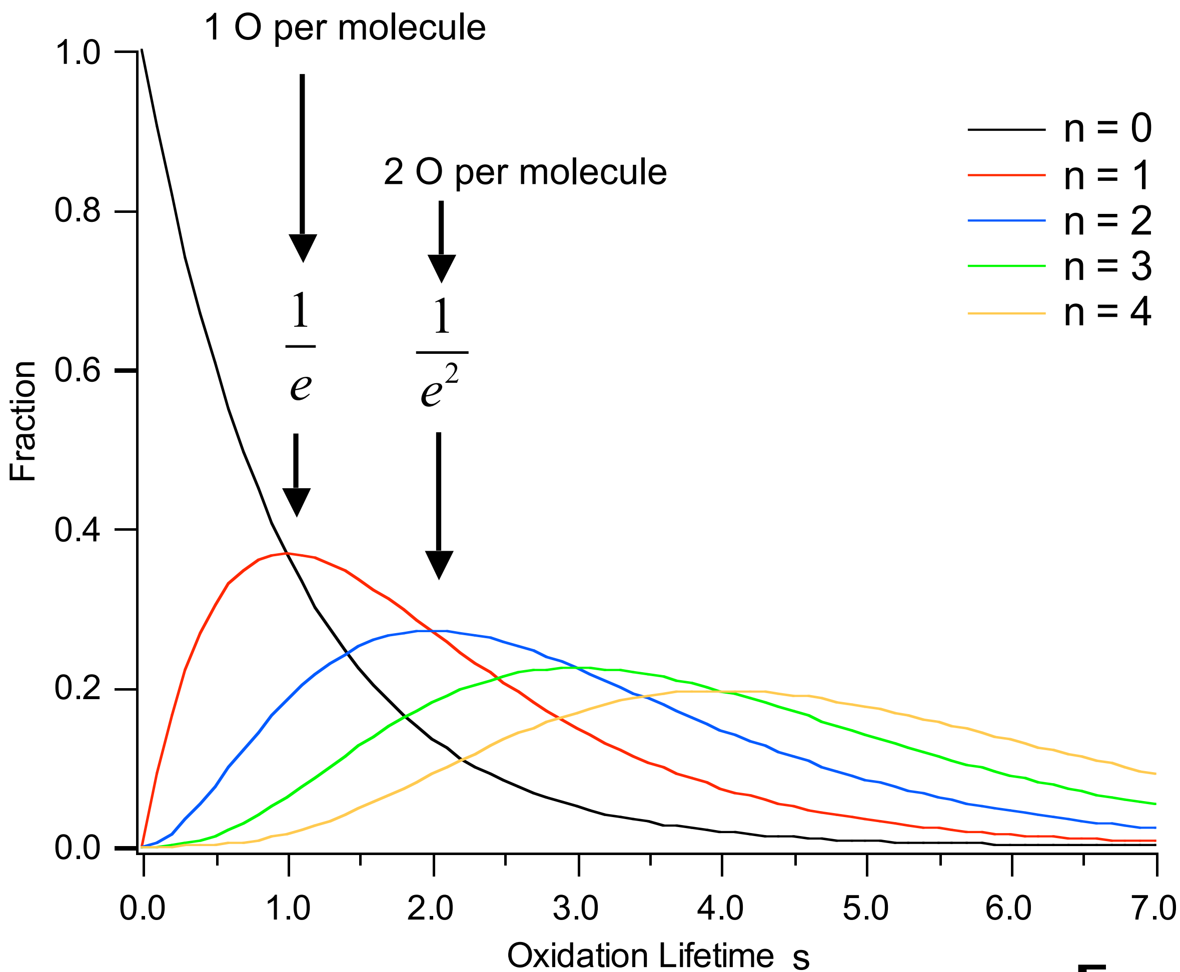
molecular density

mean speed of OH



High resolution ToF-AMS necessary for kinetic measurements in EI mode.

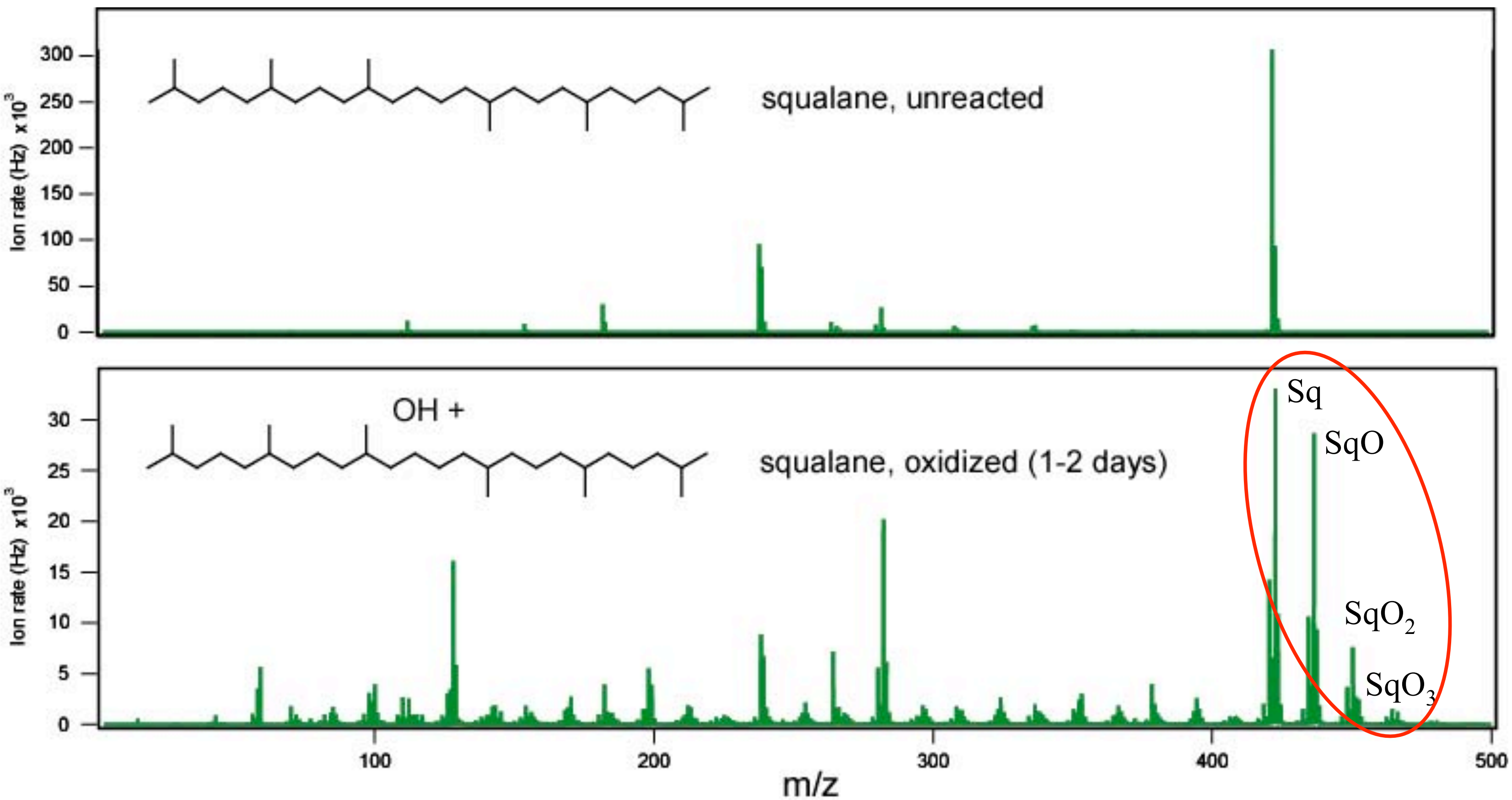
Oxidation Model



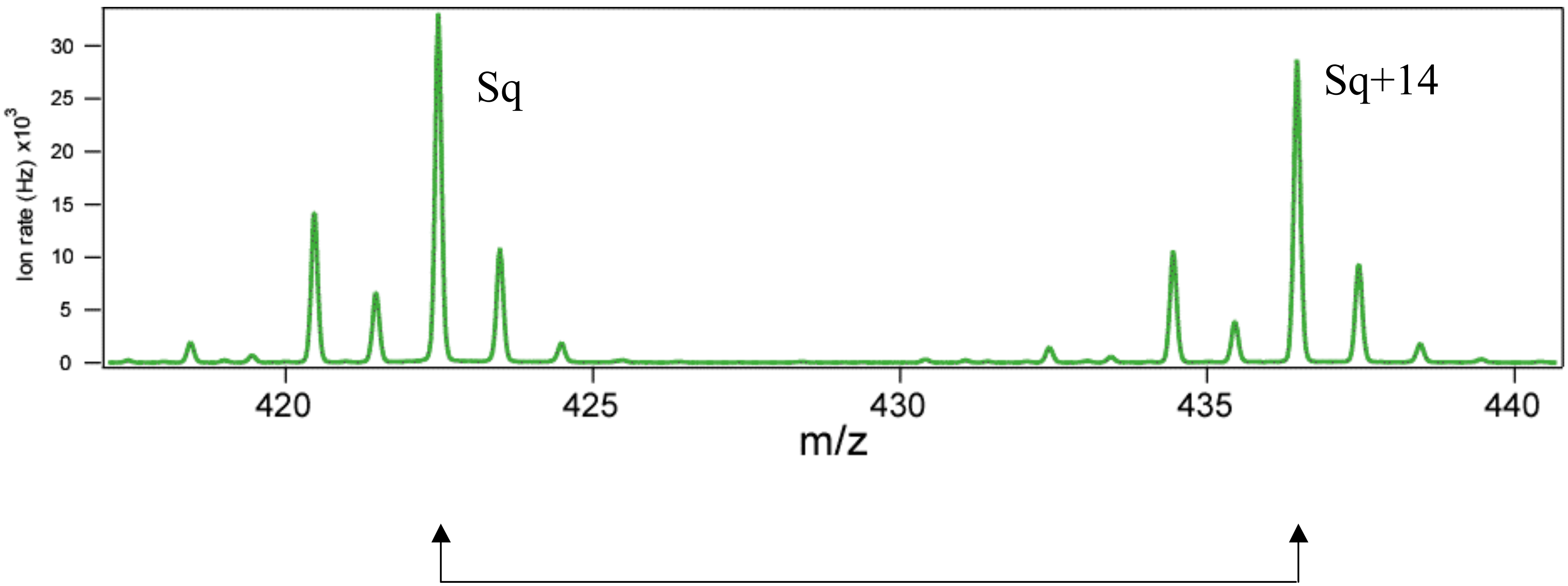
$$Sq \xrightarrow{k} SqO$$
$$SqO \rightarrow SqO_2$$
$$SqO_2 \rightarrow SqO_3$$
$$\bullet$$
$$\bullet$$
$$SqO_{n-1} \rightarrow SqO_n$$

$$\left[SqO_n\right] \propto \frac{1}{n!} Exp(-kt)\, t^n$$

Product Evolution

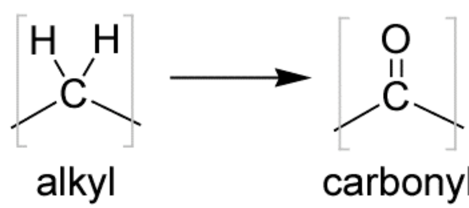


Product Evolution

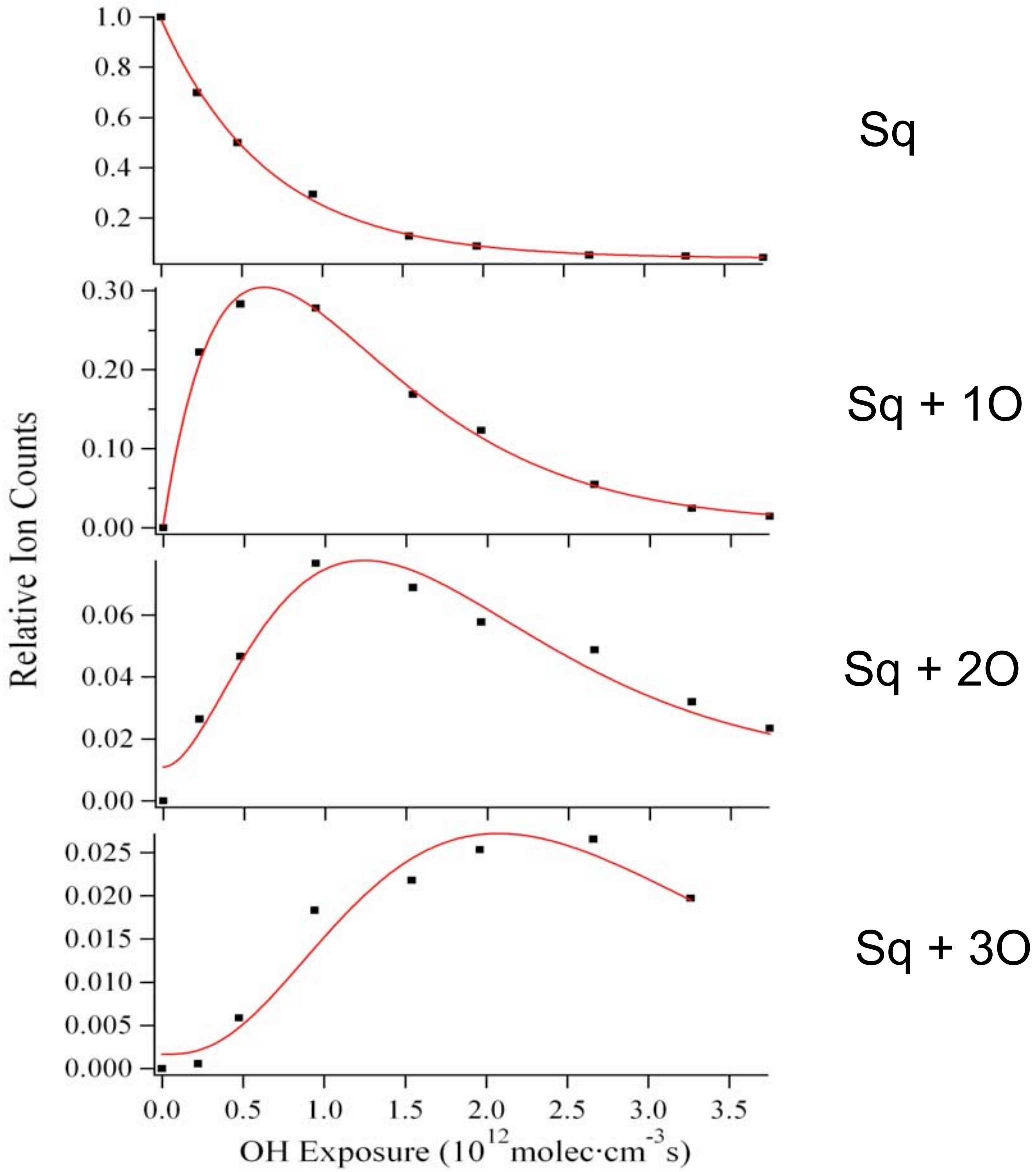


Δm/z = 13.97

+1O, -2H



Product Evolution

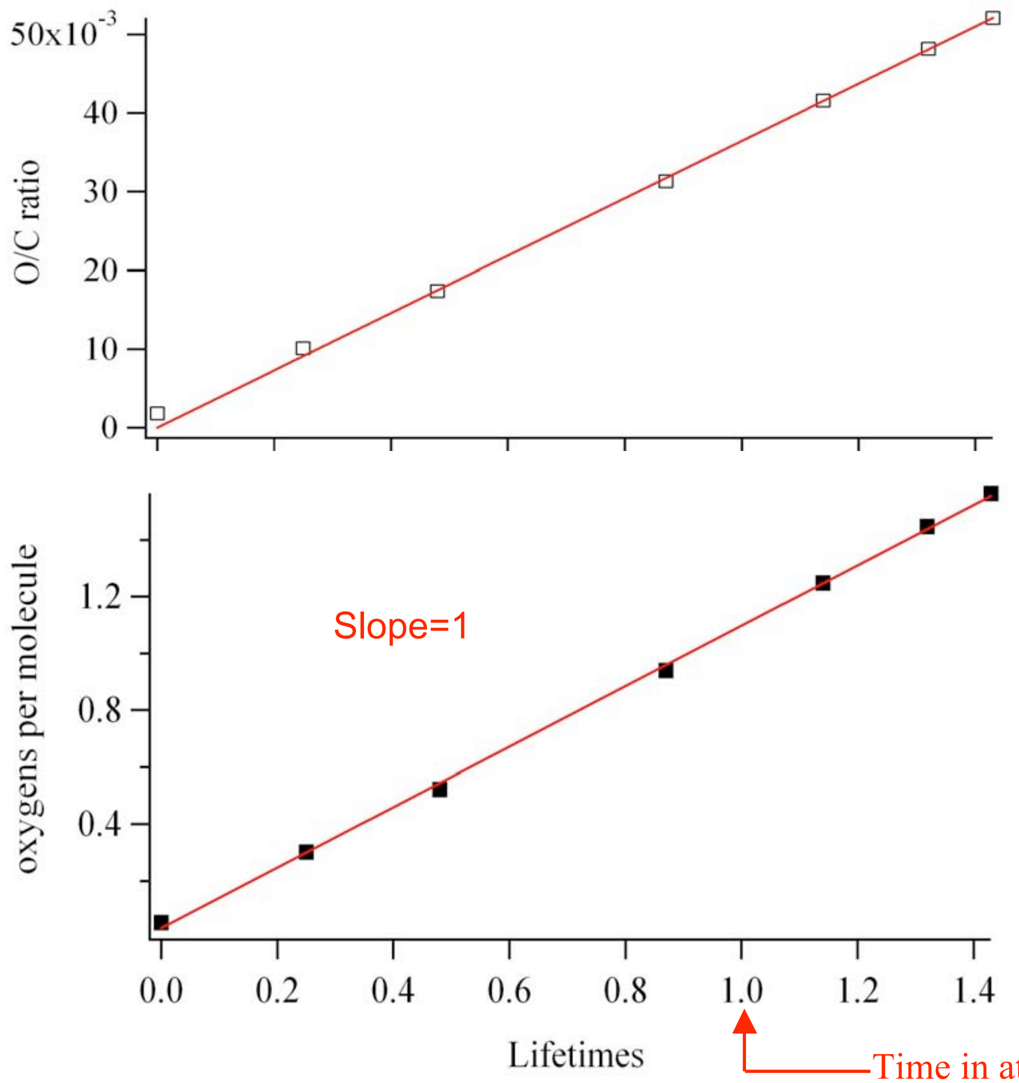


$$[SqO_n] \propto \frac{1}{n!} Exp(-kt)\, t^n$$

- Product evolution supports sequential oxidation mechanism.
- Oxidation products react at the same rate as parent compound
- Distribution of products could potentially be an important consideration (CCN, volatilization, etc.).

Oxygen Addition

$$\text{lifetimes} = \frac{\#\text{ of OH reactions}}{\#\text{ of molecules in particle}} = \frac{[OH]\cdot t\cdot \gamma \cdot \bar{c}\cdot 6}{4\cdot D\cdot \rho}$$



Time in atmosphere = 6 – 8 days (depends on MW and D_p)

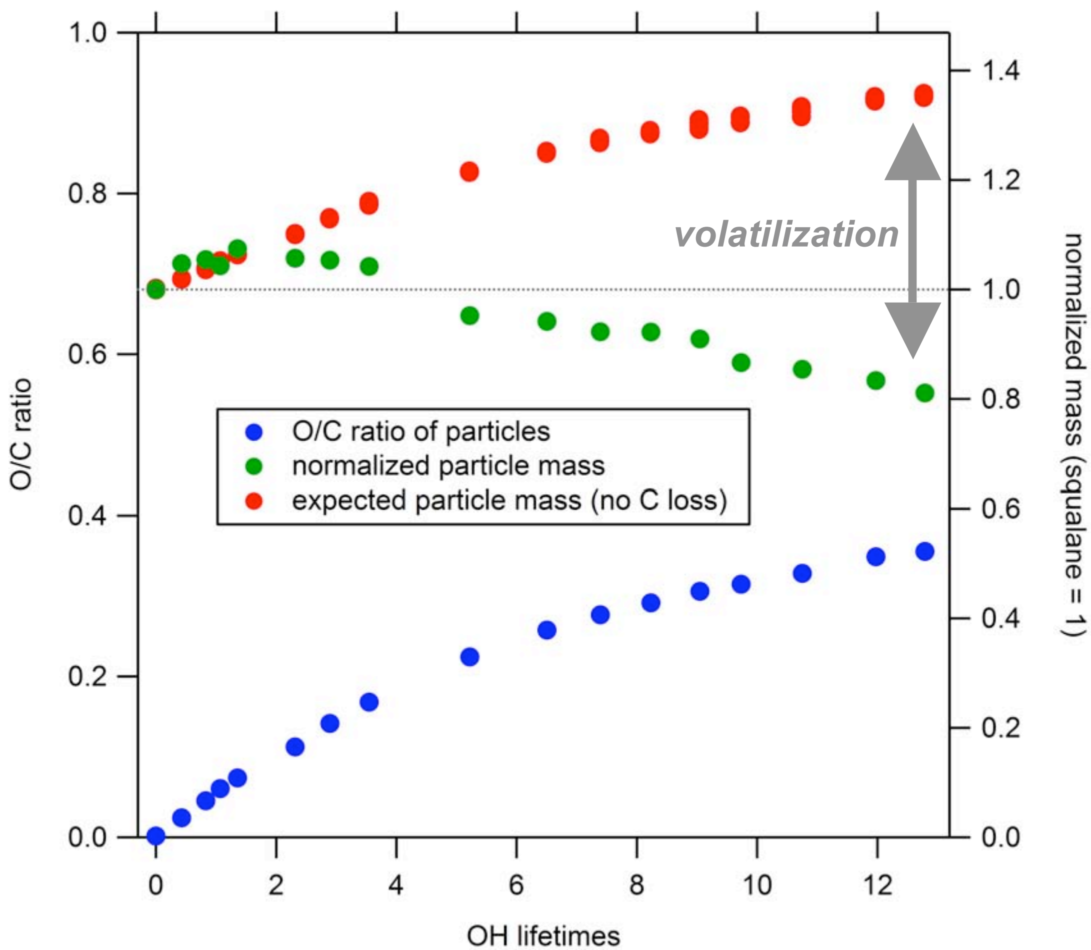
O/C ratios measured with high resolution ToF-AMS (Aiken *et al.* (2008))

Kinetics expressed in terms of “OH lifetimes”: average fraction of molecules which have reacted with an OH.

No secondary chemistry necessary.

Increases confidence in uptake coefficient.

Particle Volatilization



mass calculated from SMPS volume multiplied by particle density (AMS pToF)

Simple oxidation model breaks down at high oxidation. Volatilization becomes important

Conclusions

Heterogeneous OH oxidation of organic aerosols

- **Timescales for oxidation?**
  - Uptake coefficient = 0.35 ± 0.1 (one lifetime = 6 – 8 days)
- **Role of secondary chemistry?**
  - Strong correlation between parent and subsequent products
  - Secondary chemistry not necessary
- **Does oxidation lead to volatilization?**
  - Volatilization only results at very high oxidation.
- **Chemical Mechanism?**
  - Oxidation mechanism captures peak evolutions and O/C ratios.

Acknowledgements

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Daphne Che
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