SOA Volatility Evolution: Formation and Oxidation Over the Lifecycle of PM2.5

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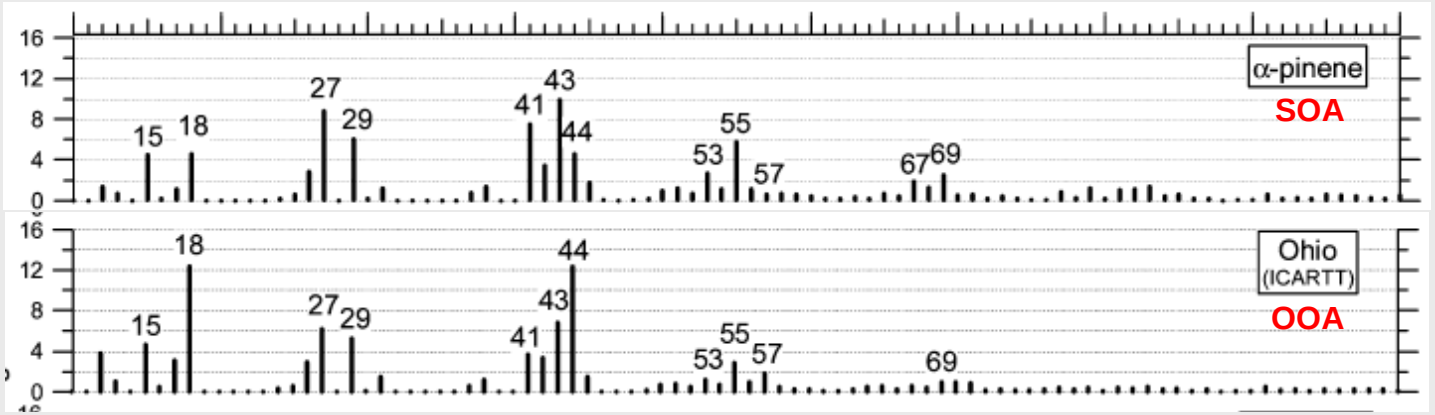
Laboratory vs. atmosphere

Fundamental differences between secondary organic aerosol (SOA) generated in the laboratory (chambers) and oxidized organic aerosol (OOA) measured in the ambient atmosphere:

1) *Amount*. Measured loadings of ambient organic aerosol are higher than inferred from chamber yield measurements [Heald et al., 2005; De Gouw et al., 2005; Volkamer et al., 2006; Kleinman et al., 2008…]

Laboratory vs. atmosphere

2) *Composition*. Aerosol mass spectrometer (AMS) measurements show chamber-SOA is less oxidized than ambient OOA:

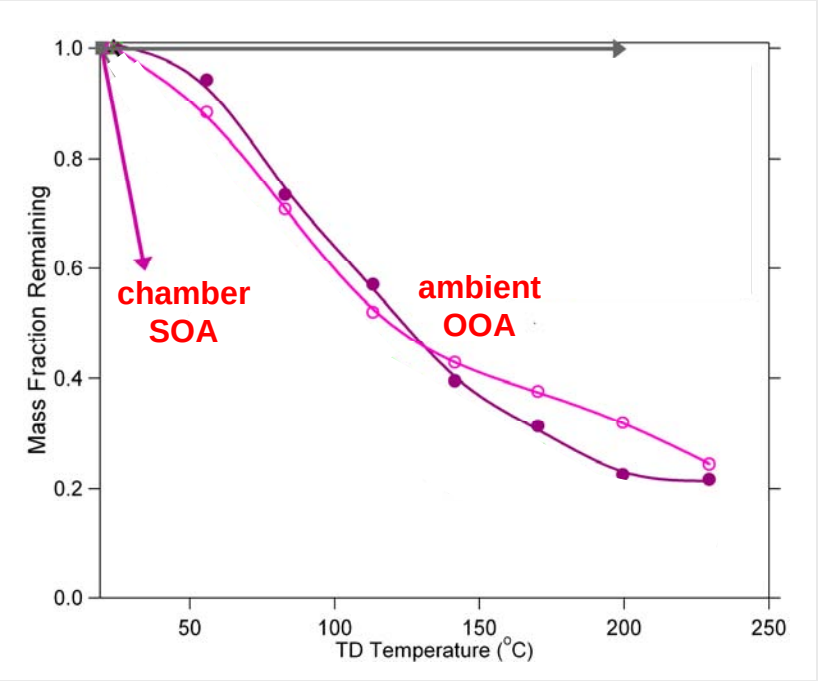


[Bahreini et al., *ES&T*, 2005]

m/z 44 (CO_2^+): marker for highly oxidized organics

Laboratory vs. atmosphere

3) *Volatility*. Thermal denuder measurements show that ambient OOA is much less volatile than chamber SOA:



[Huffman, Jimenez, et al., *ES&T*, submitted]

Atmospheric processing ("aging")

Gas-phase organic compounds: lost by deposition after days/weeks

Tropospheric [OH]: ~ 2×10^{6} OH/cm^{-3}

OH rate constant (k_{OH}): ~ 3×10^{-11} cm^{3} $molec^{-1}$ s^{-1}

Chemical lifetime of a gas-phase organic in the troposphere:

$\tau_{OH} = (k_{OH} [OH])^{-1} = 5$ hours

→ an organic compound in the troposphere can undergo several generations of gas-phase oxidation prior to loss by deposition

→ only a fraction of these reactions will occur within the timescale of a single laboratory (chamber) experiment

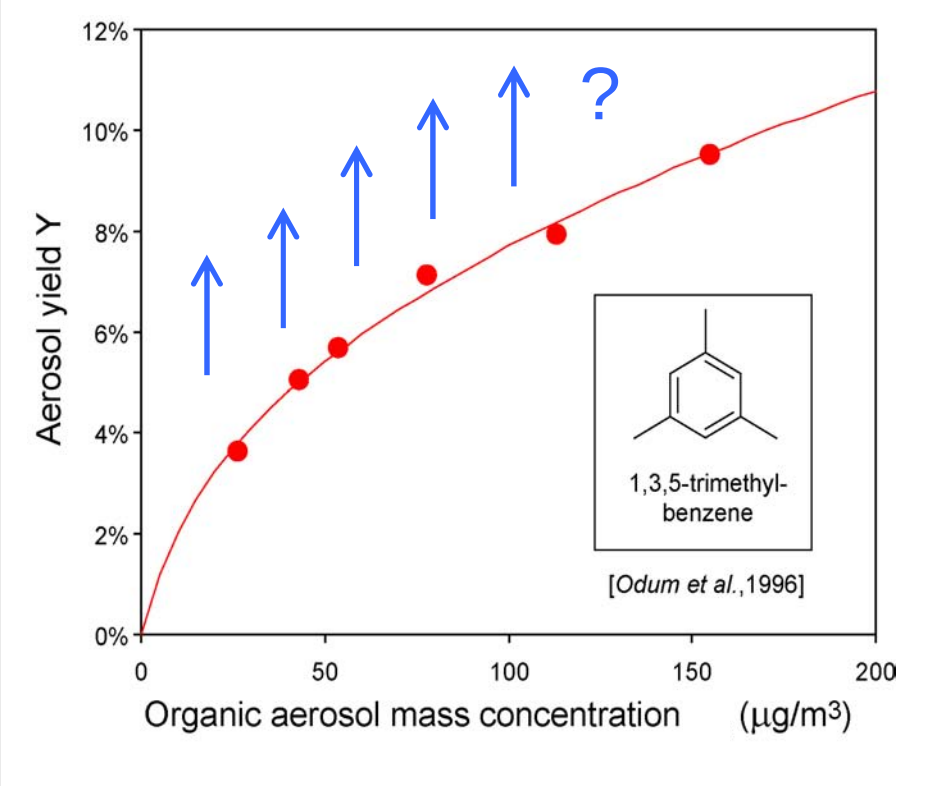
Atmospheric processing and SOA

SOA formation typically described in terms of a "volatility distribution": formation yields and vapor pressures of reaction products

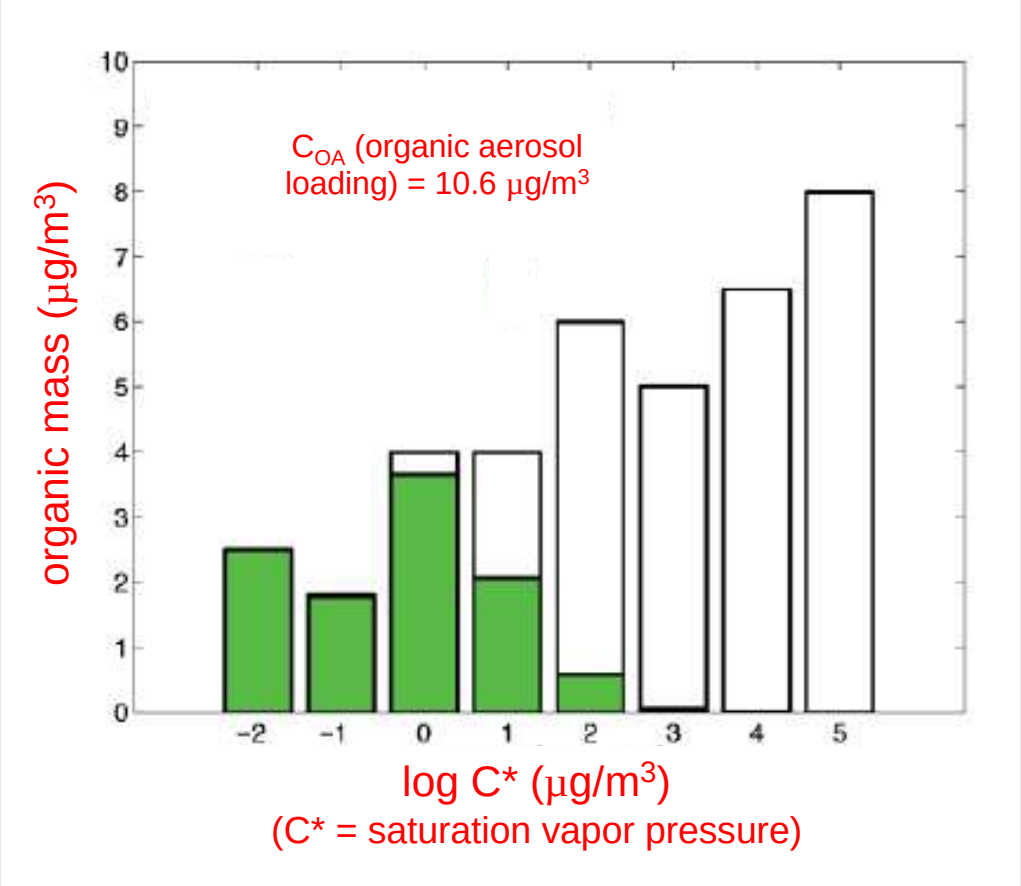
"two-product model"

$$HC + ox \rightarrow \alpha_1 P_1 + \alpha_2 P_2$$

? ?



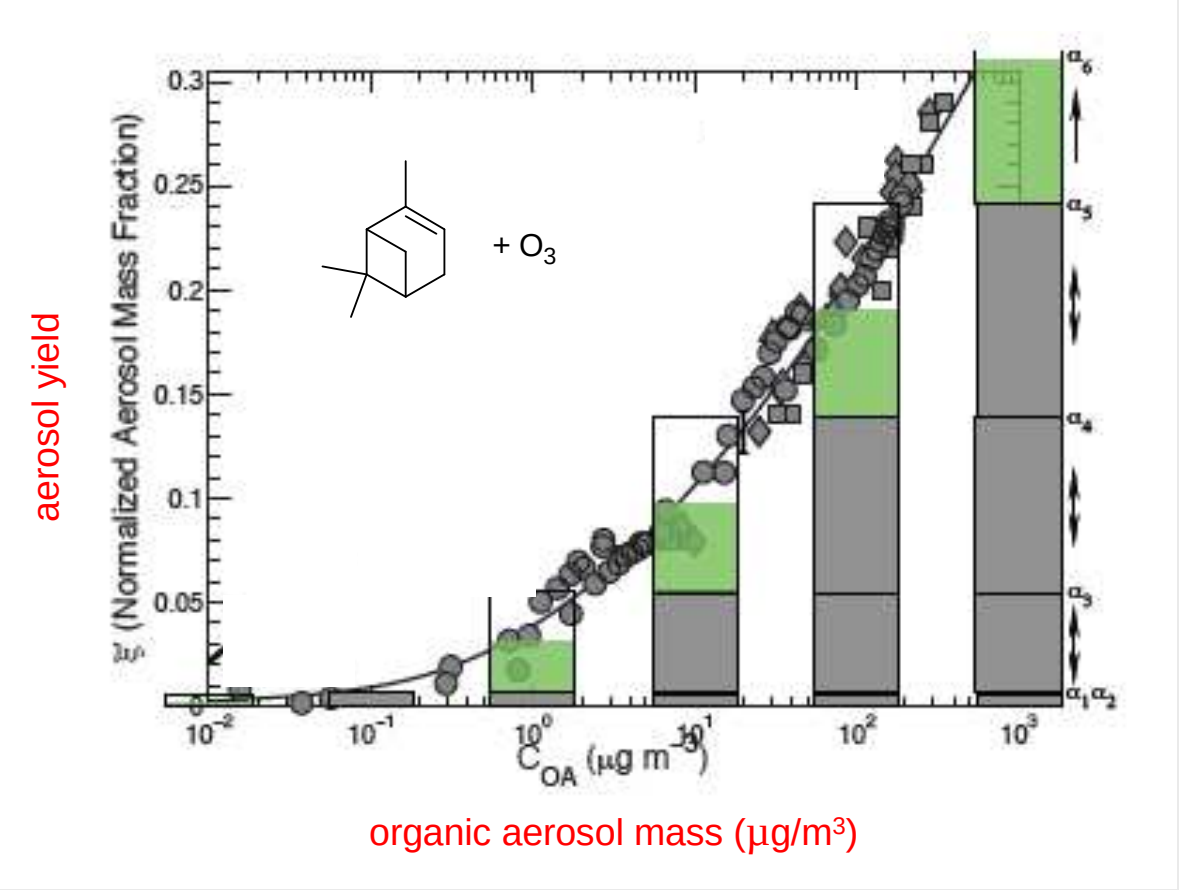
Volatility basis set



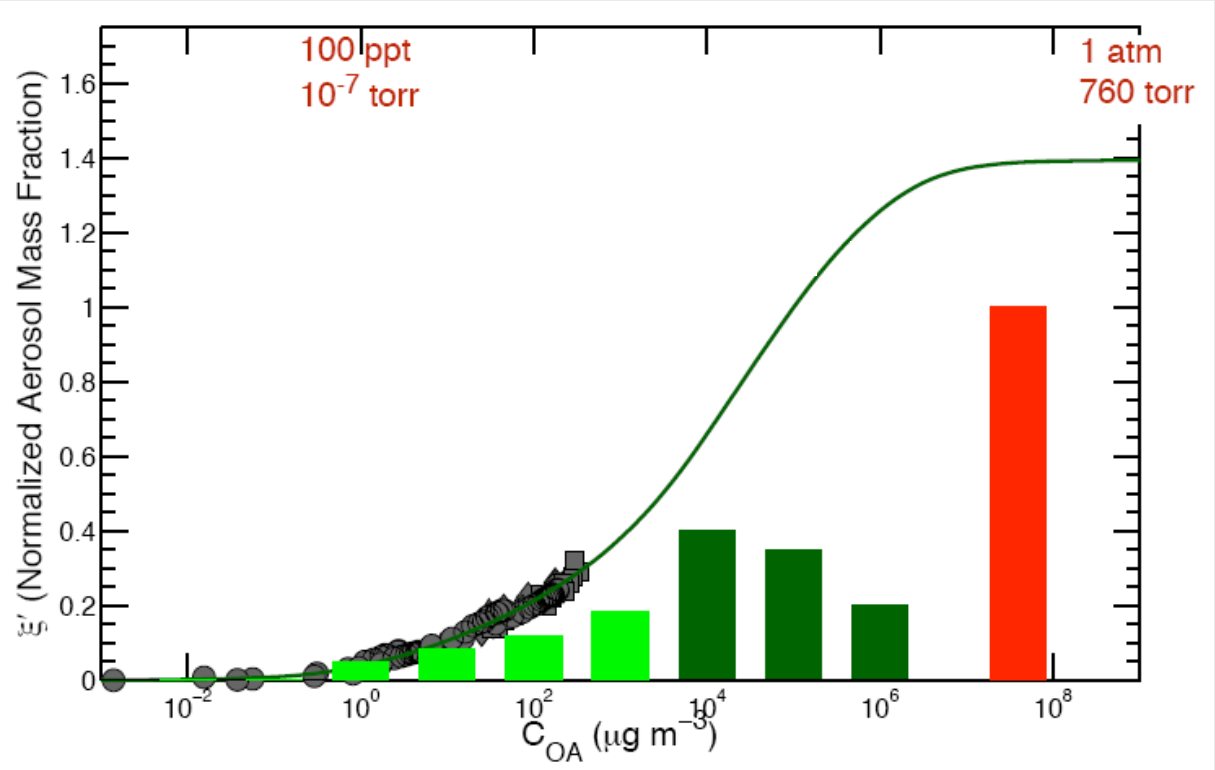
[Donahue et al., *ES&T*, 2006]

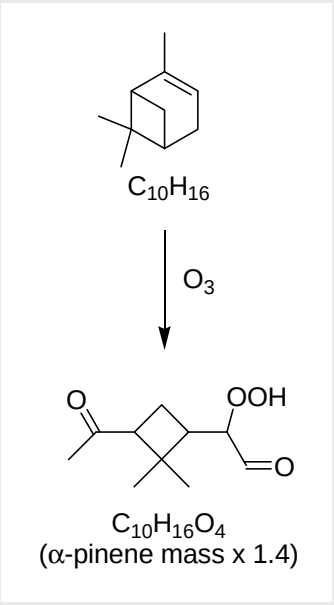
Fitting chamber SOA growth data

α-pinene ozonolysis [Presto et al., ES&T 2006]:



Non-particulate products



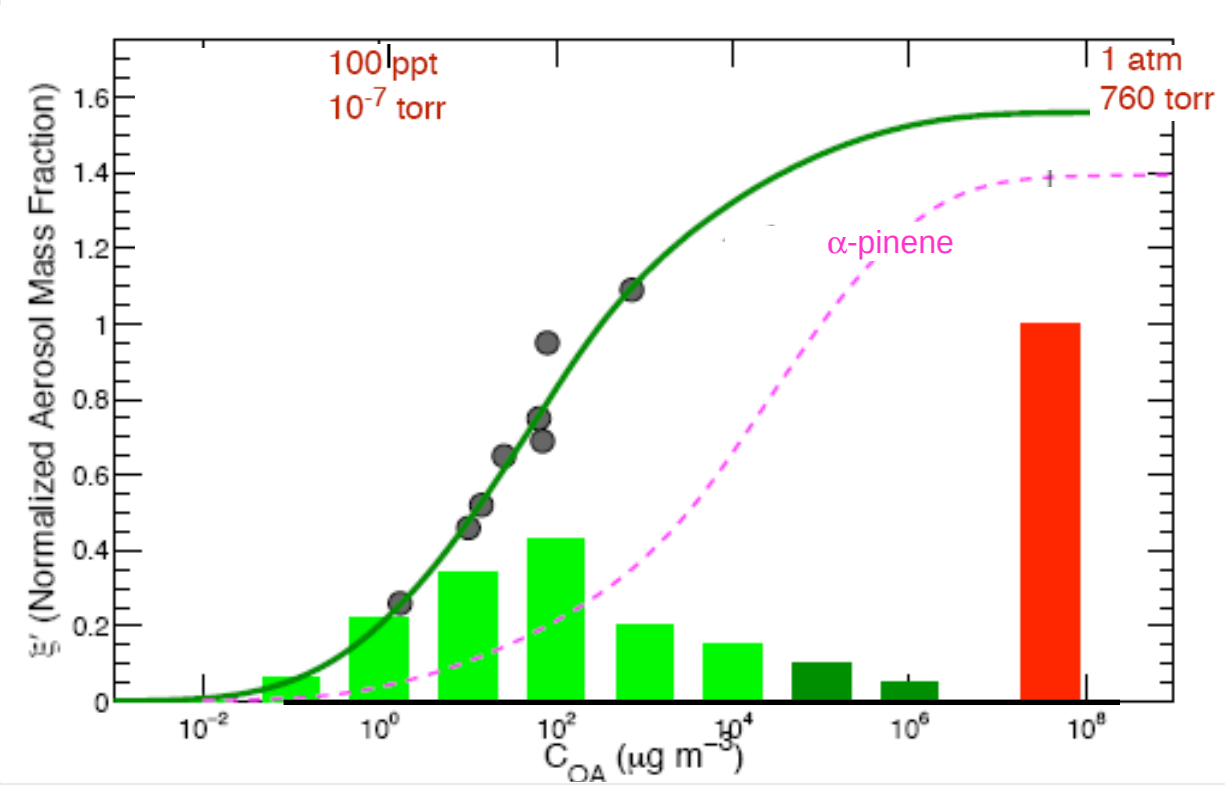


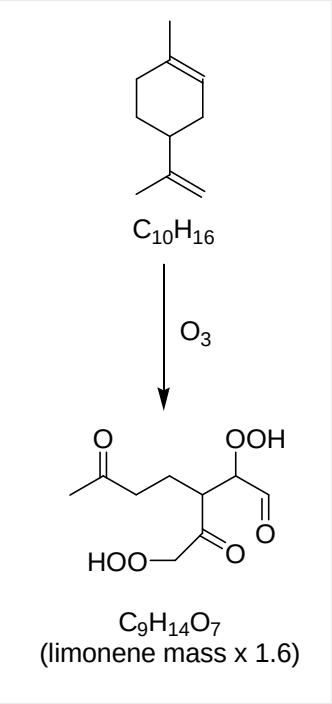
α-pinene (precursor)

semivolatiles

inferred gas-phase products (“intermediate volatility”)

Two generations of oxidation: limonene



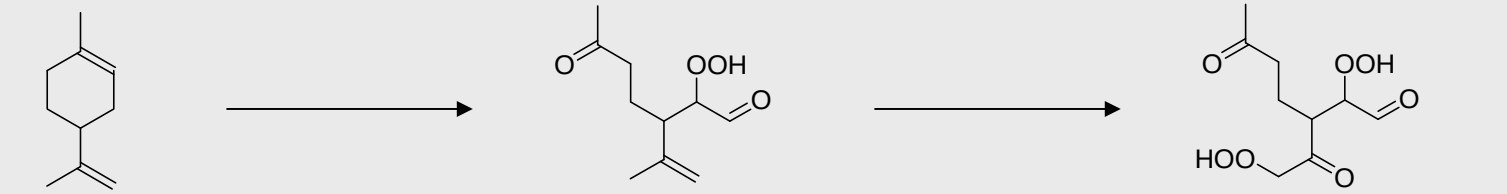


limonene (precursor)

semivolatiles

inferred gas-phase products (“intermediate volatility”)

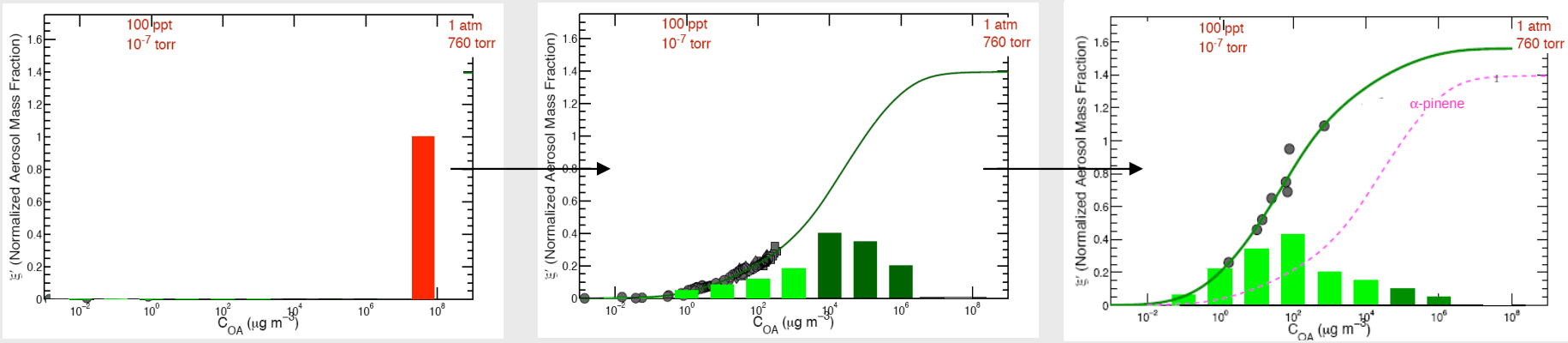
Multiple generations of oxidation



limonene

first generation product
(analogous to α-pinene + O_3)

second generation product

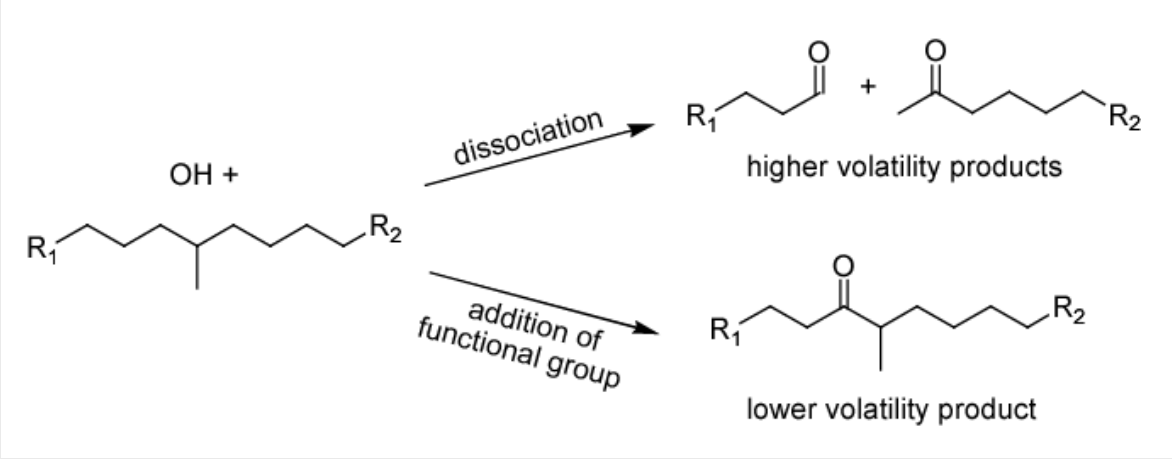


→ measurement of changes to volatility distribution upon oxidation allows for the determination of "*volatility operators*"

→ these can be used to include atmospheric processing in models

Changes in volatility

Atmospheric oxidation can increase the volatility of organics by cleavage of carbon-carbon bonds, or decrease volatility by addition of polar functional groups:



aerosol mass decreases

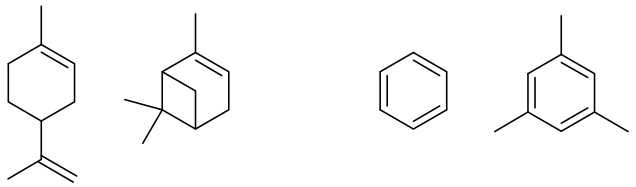
aerosol mass increases

What controls this branching?

- details of carbon skeleton (branched, cyclic)
- degree of oxidation
- etc.

Multigeneration oxidation experiments

Volatile organic compounds
("traditional SOA precursors"):



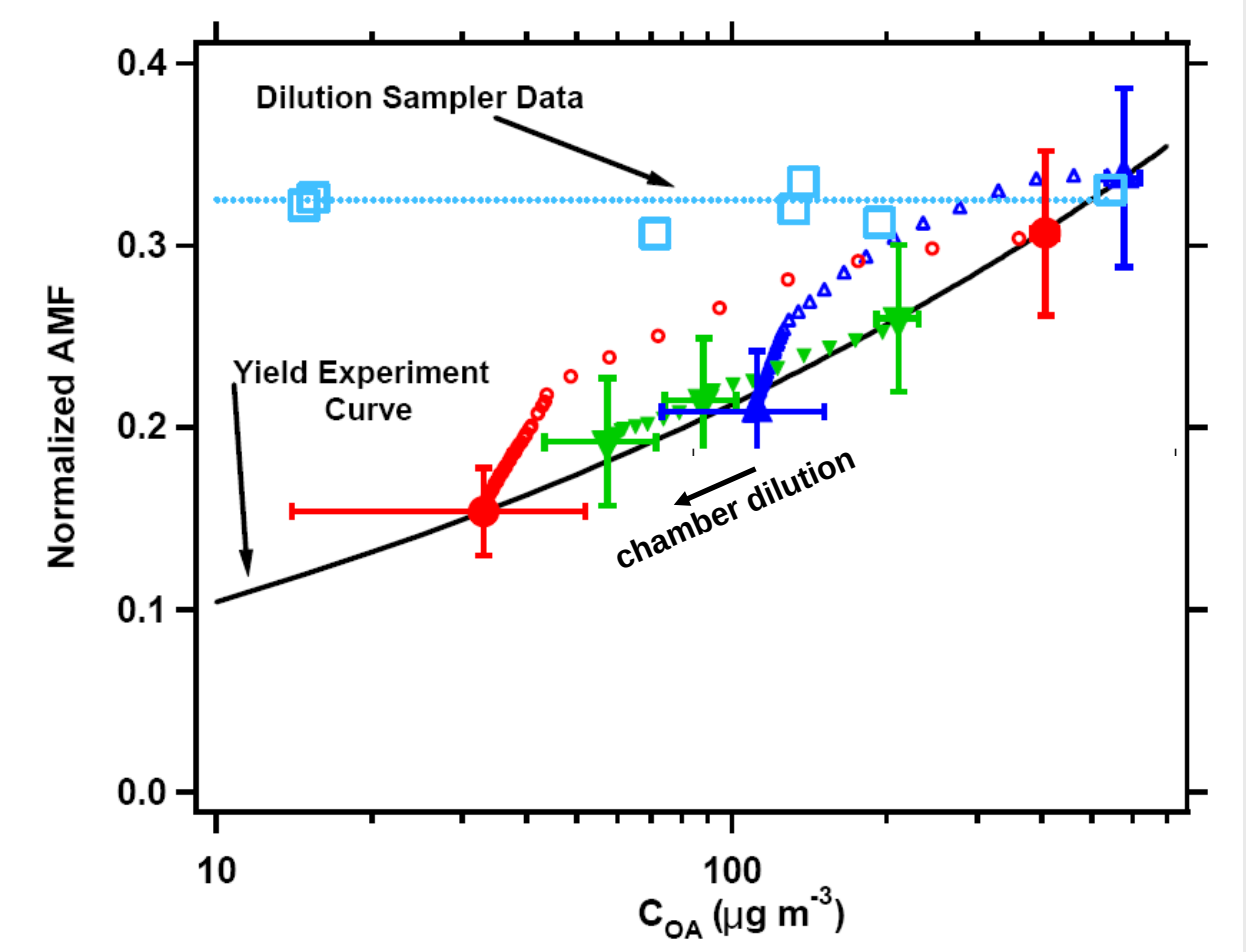
Oxidize over several well-defined generations:

- Sequential oxidation: O_3, then OH; *or*
- Sustained oxidation: continual addition of oxidants [Lambe et al., *ES&T*, 2007]

For all experiments, real-time measurements of:

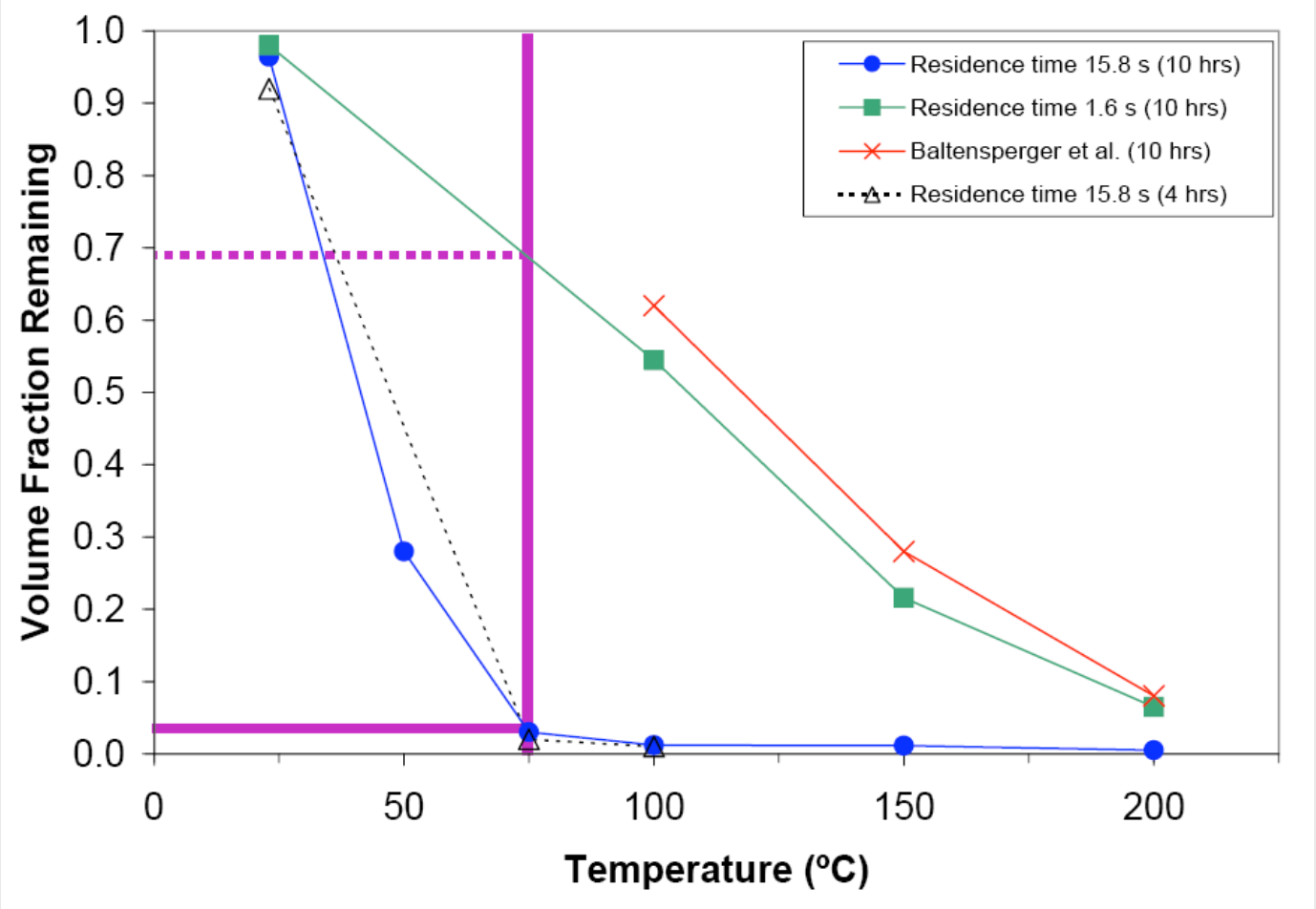
- particle volume (SMPS),
- chemical composition in the gas phase (GC-FID, PTRMS),
- chemical composition in the particle phase (AMS), and
- ***particle volatility***

Measurement of volatility: (1) dilution



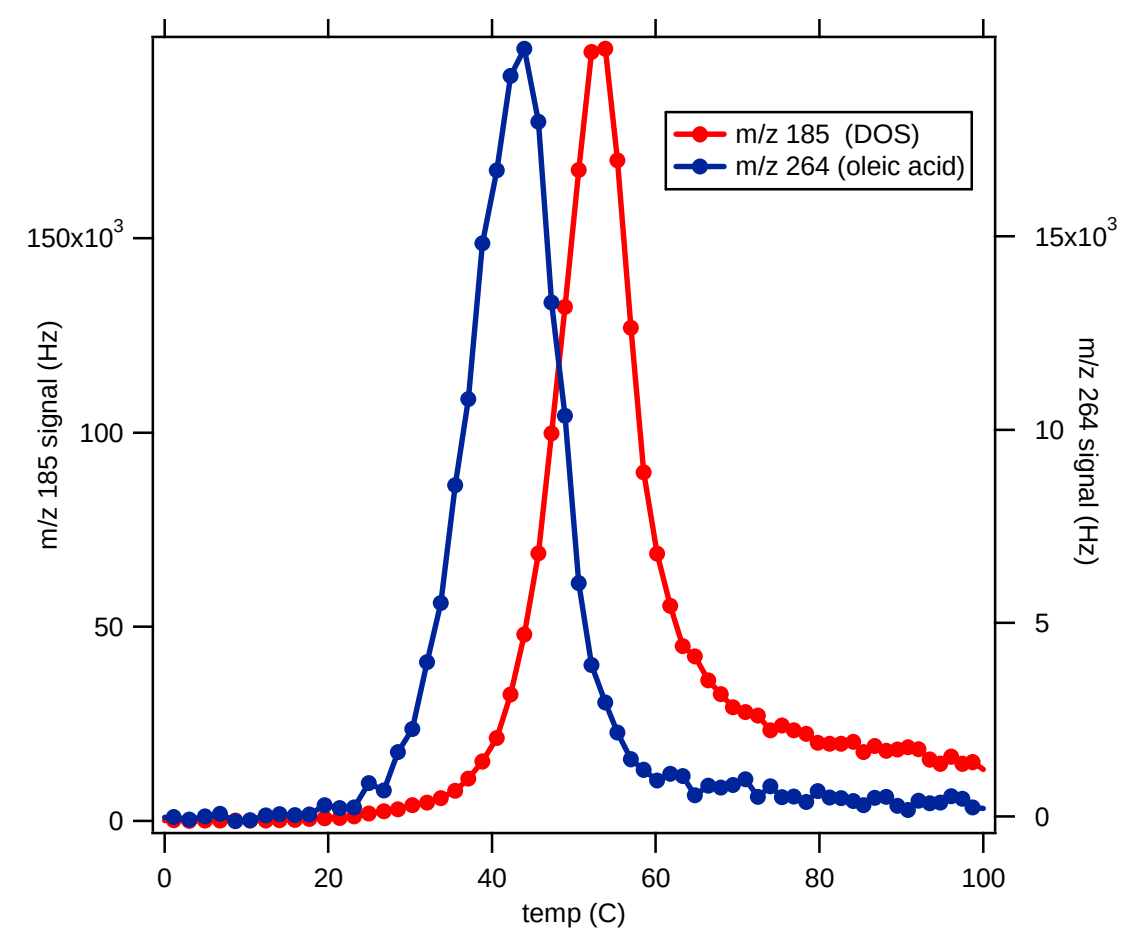
[Grieshop et al., *GRL*, 2007]

Measurement of volatility: (2) thermal denuding

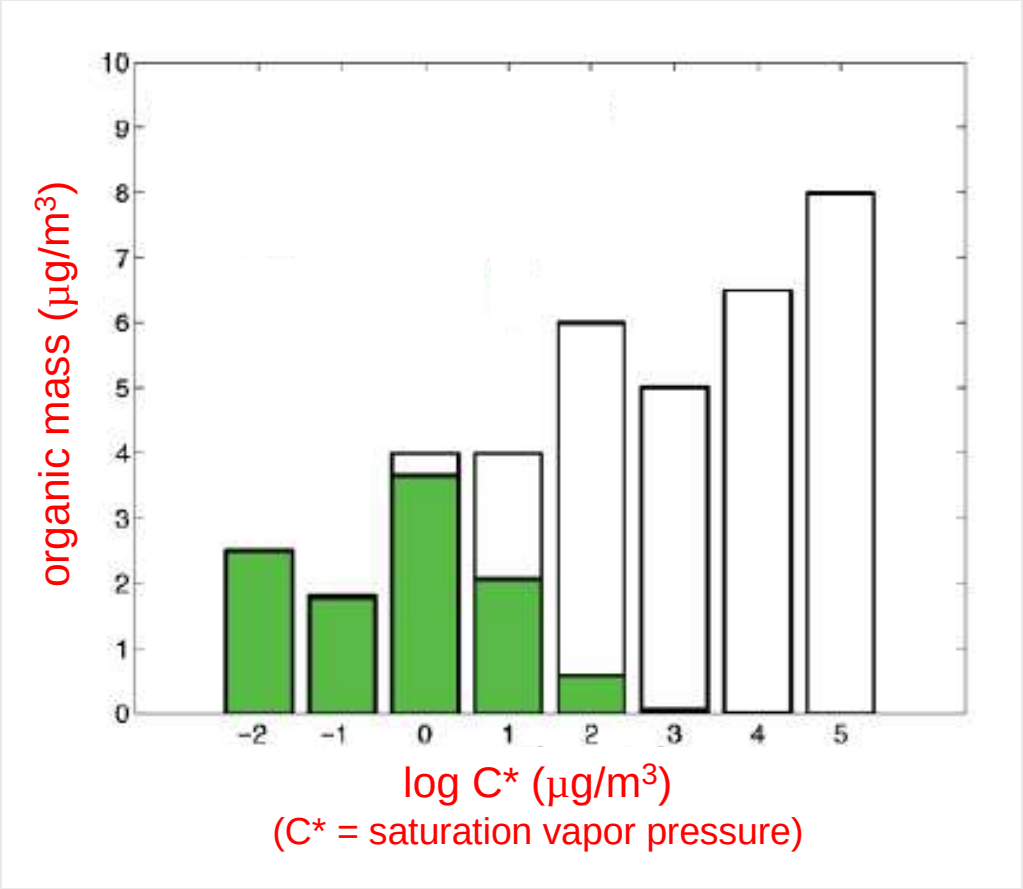


[An et al., *J. Aerosol Sci.*, 2007]

Measurement of volatility: (3) thermal desorption



Chemistry within a volatility-based model



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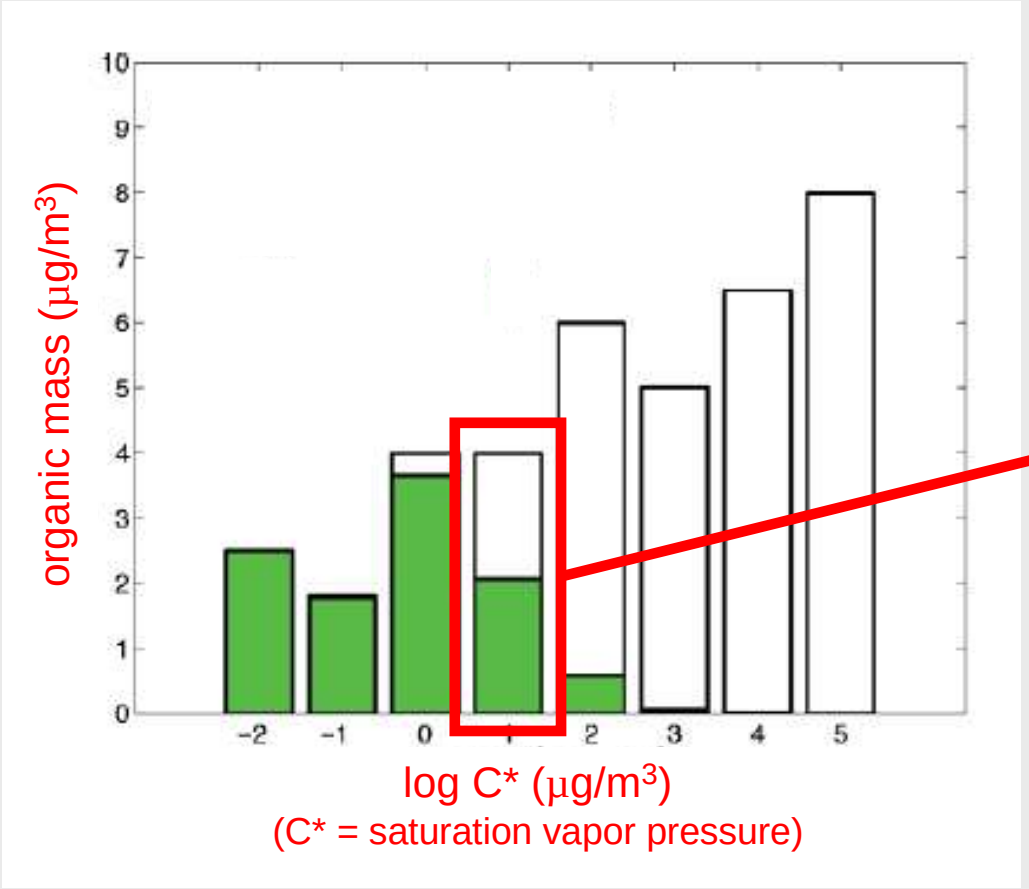
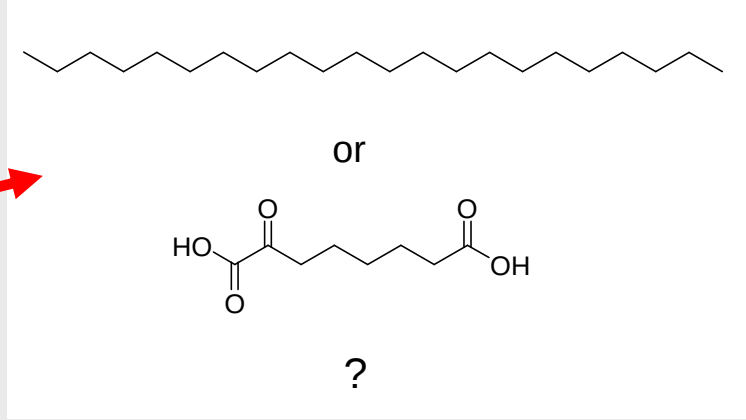
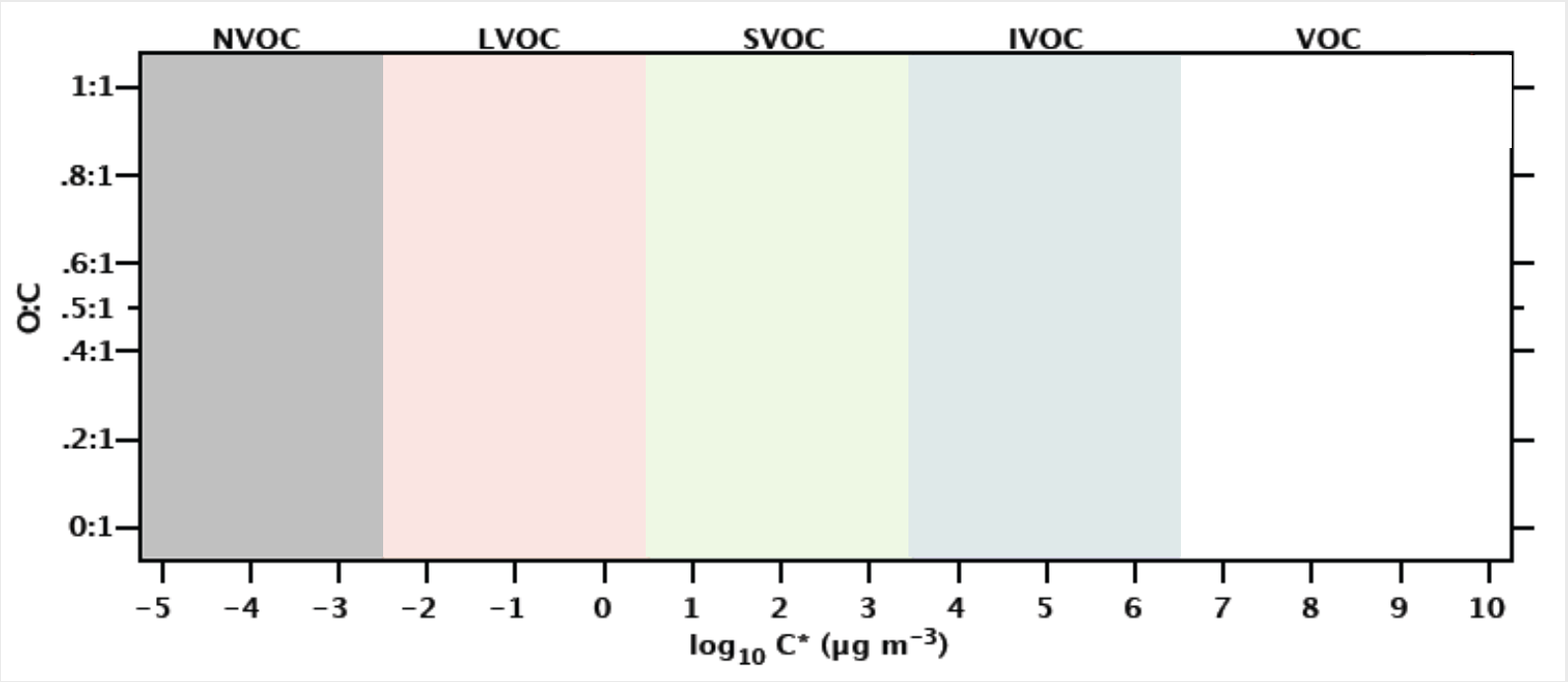




Two-dimensional volatility basis set



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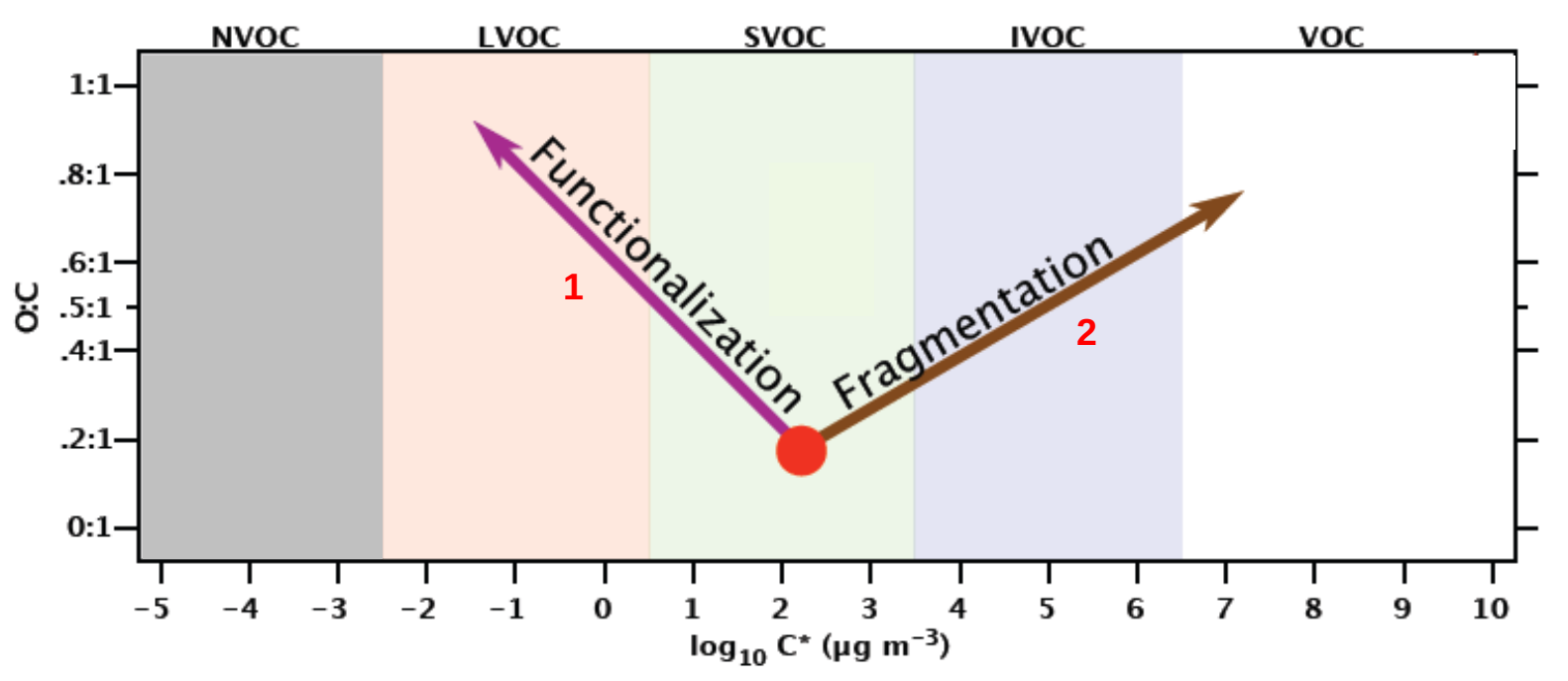
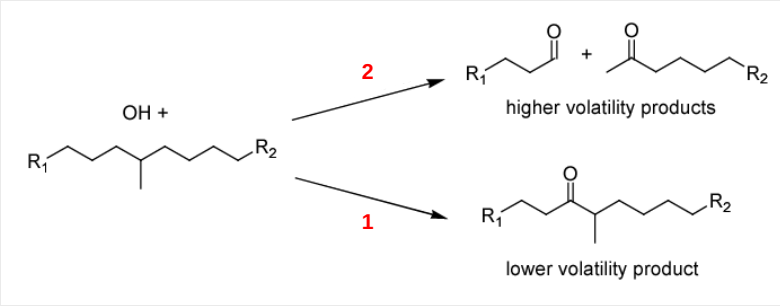
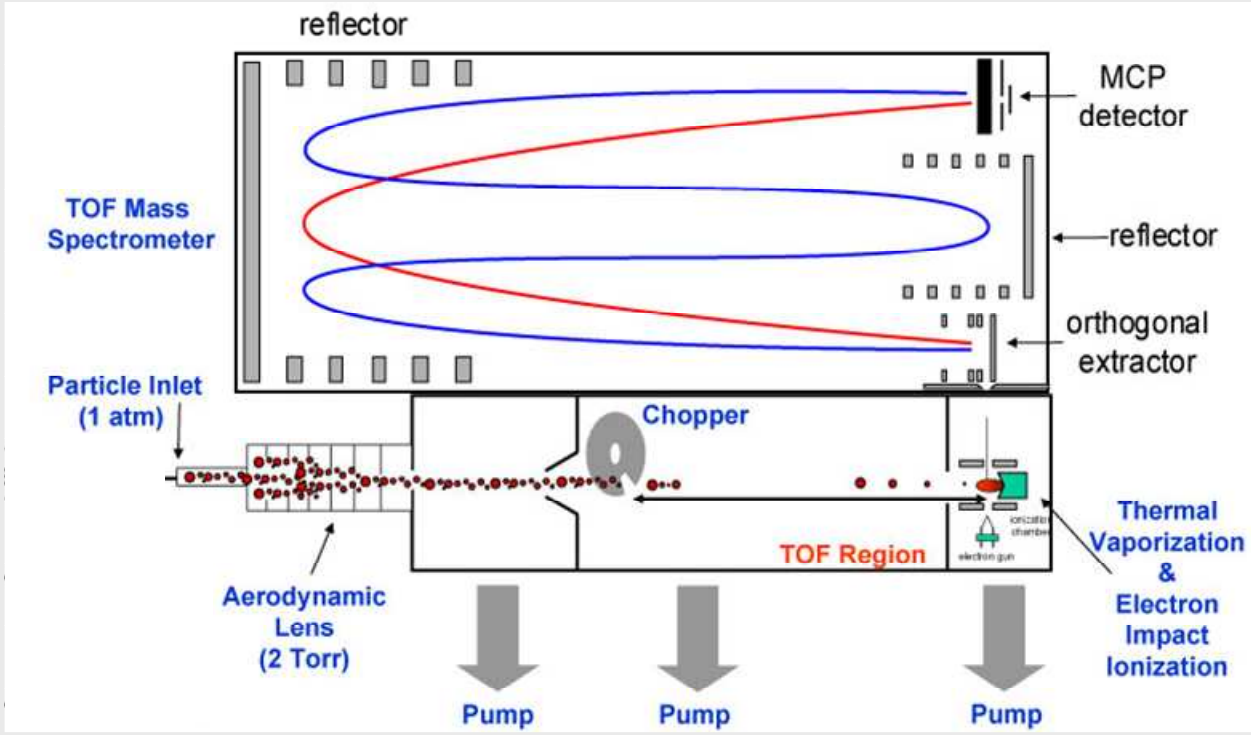


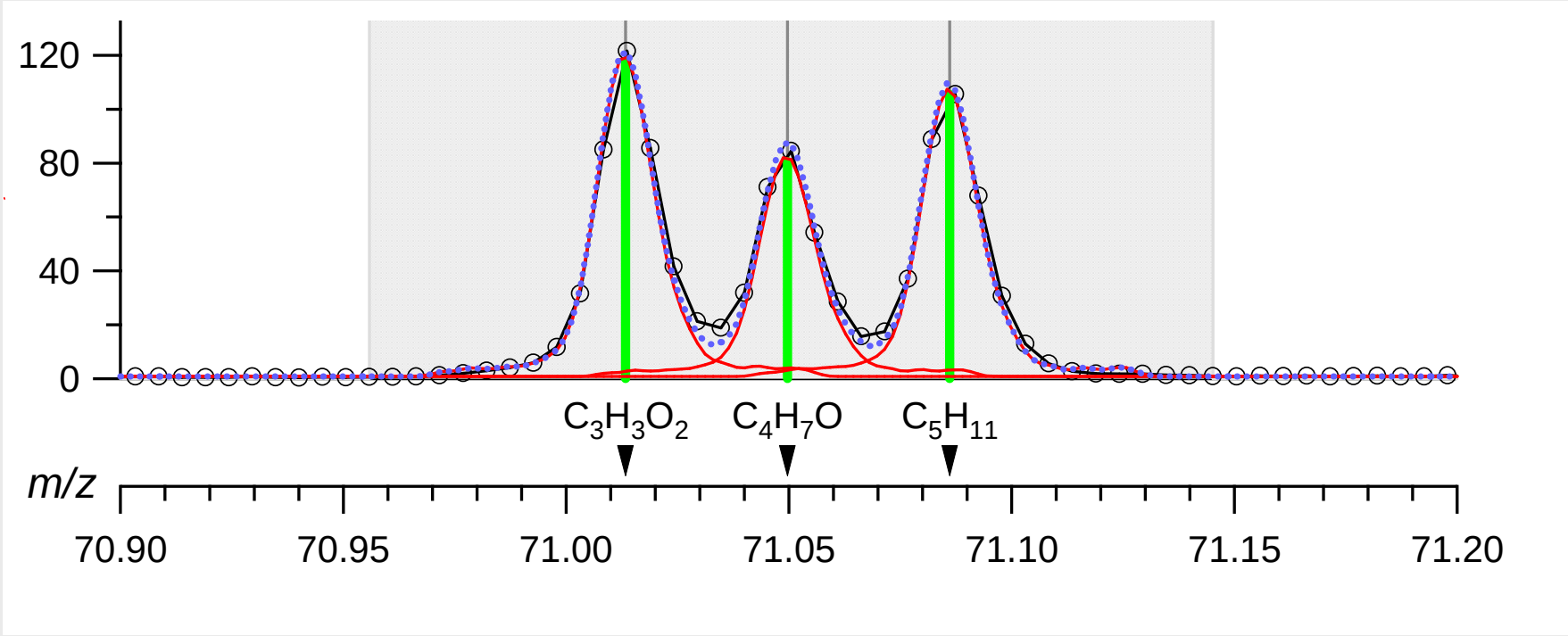


High-Resolution Aerosol Mass Spectrometer



Aerodyne HR-AMS: resolution of 3000 (V mode)-5000 (W mode)

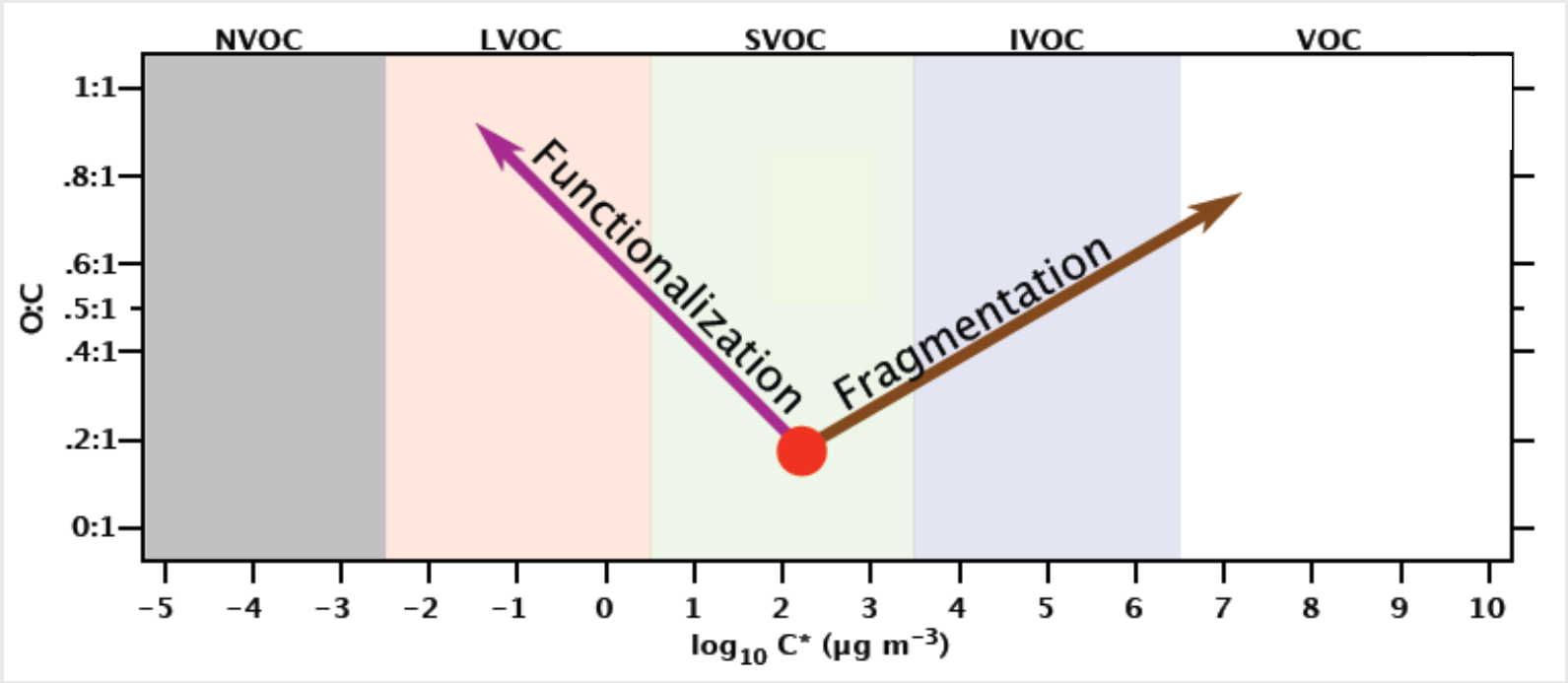
High resolution data



Allows for the measurement of elemental ratios (O/C, H/C, N/C)

[Aiken et al., *Anal. Chem.*, 2007;
Aiken et al., *ES&T*, in press]

Two-dimensional volatility basis set



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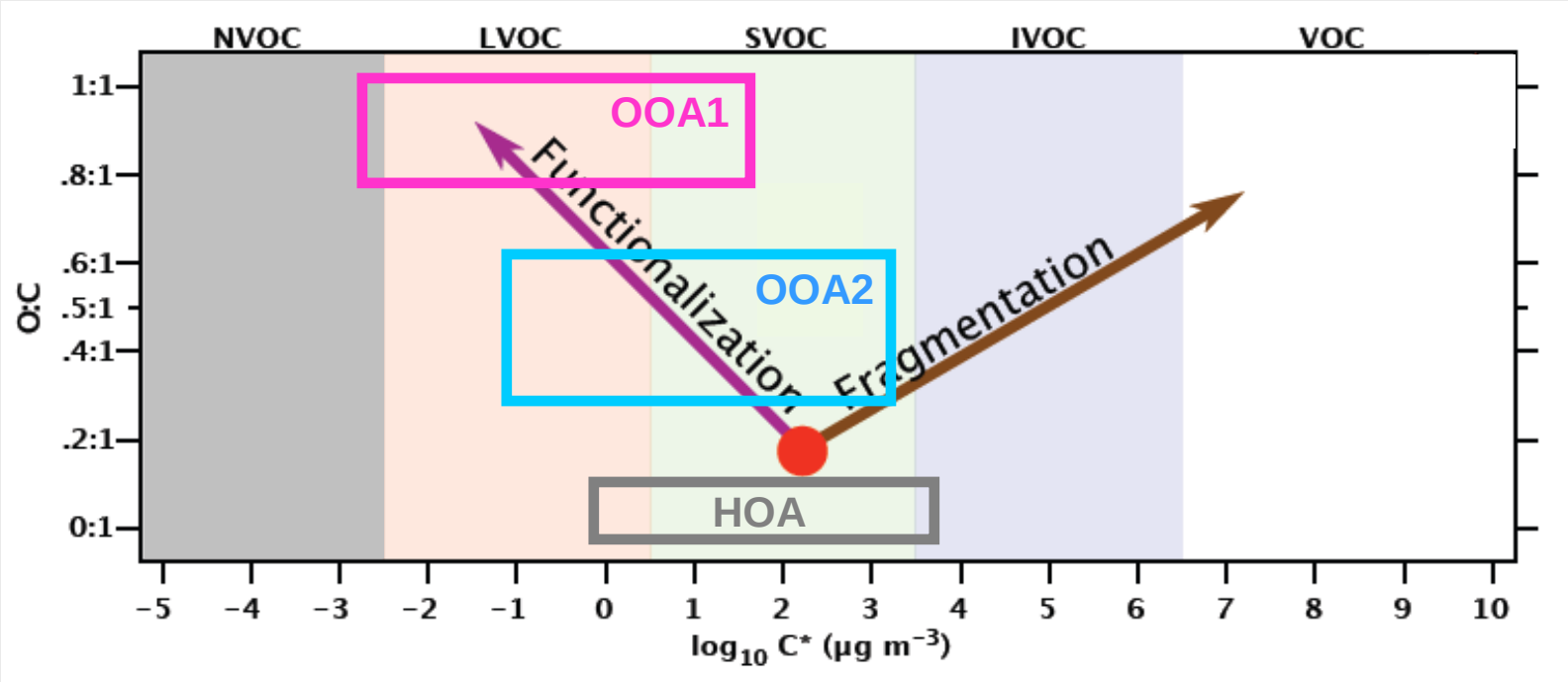

HOA: “Hydrocarbon-like Organic Aerosol”

OOAx: “Oxygenated Organic Aerosol”

[Zhang et al., *ES&T*, 2005;
Lanz et al. *ACP*, 2007]