Studies of Particle Formation, Growth, and Chemistry Using Aerosol Mass Spectrometry

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Workshop on Techniques for High-Pressure Combustion

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Atmospheric chemistry

Conditions: $P \leq 1$ bar, $T \leq 320$ K, $\chi \leq$ ppb, ppt

Relation to combustion chemistry:

1) Emissions

2) Similarities in terms of (organic) chemistry

- Radical-initiated oxidation of species to form low-volatility (particulate) material
- Multiphase processes: homogeneous reactions, heterogeneous reactions, partitioning between phases
- Many reactants, intermediates, products → immensely complex chemical mechanisms

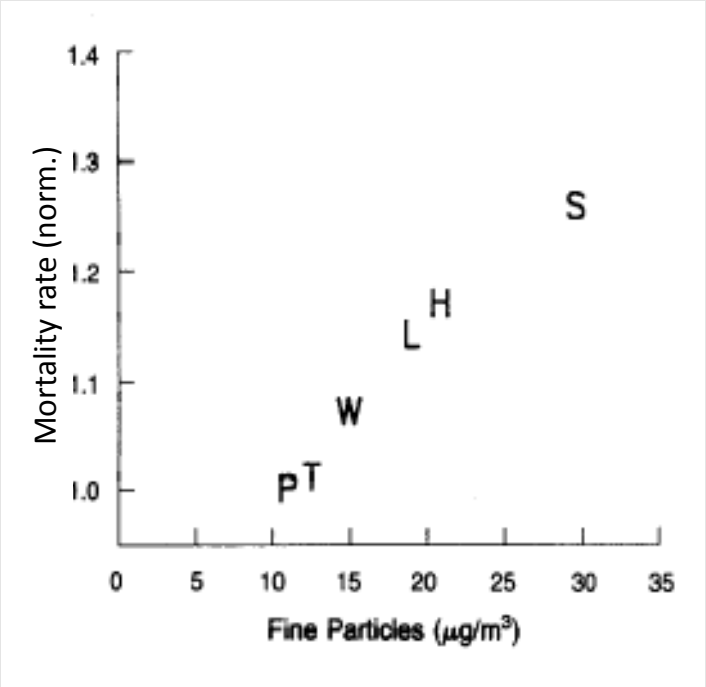
Outline

1) Atmospheric aerosol, aerosol mass spectrometry
2) Flow tube studies of aerosol chemistry
3) Carbon oxidation state of organics
4) Connection with combustion chemistry

Atmospheric aerosol

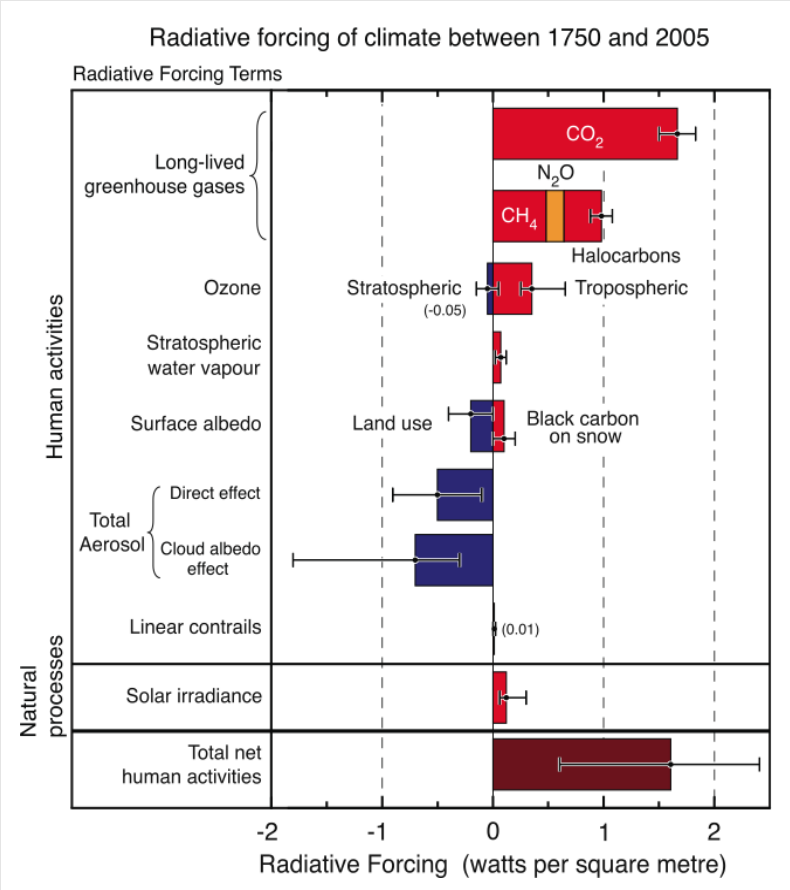
Fine particles: diameter ≤ 1μm

1) Human health



D. W. Dockery et al., *New Engl. J. Med.* 329, 1753-1759 (1993)

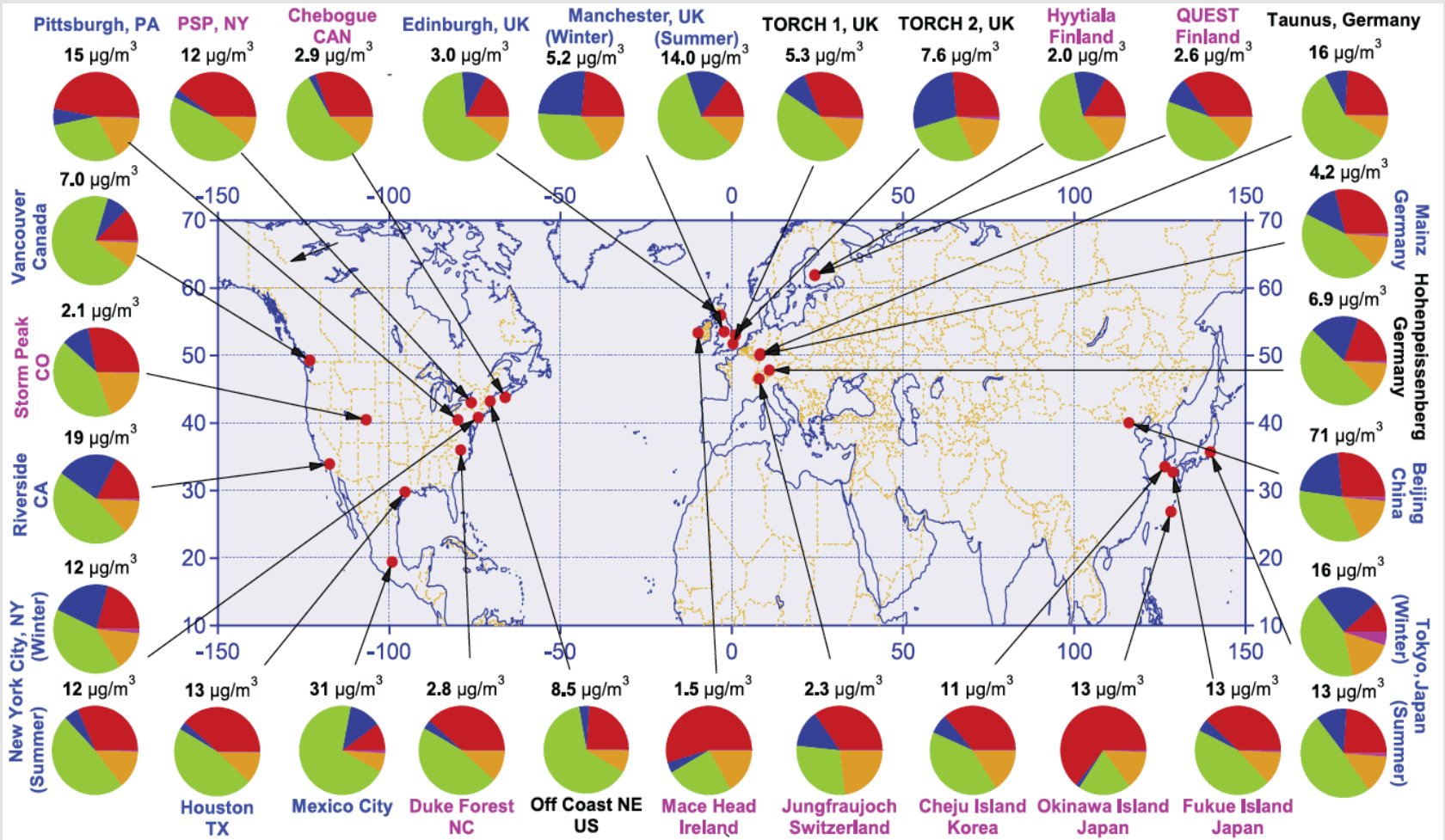
2) Global climate



IPCC: *Climate Change 2007: The Physical Science Basis* (2007).

Atmospheric aerosol loadings/composition

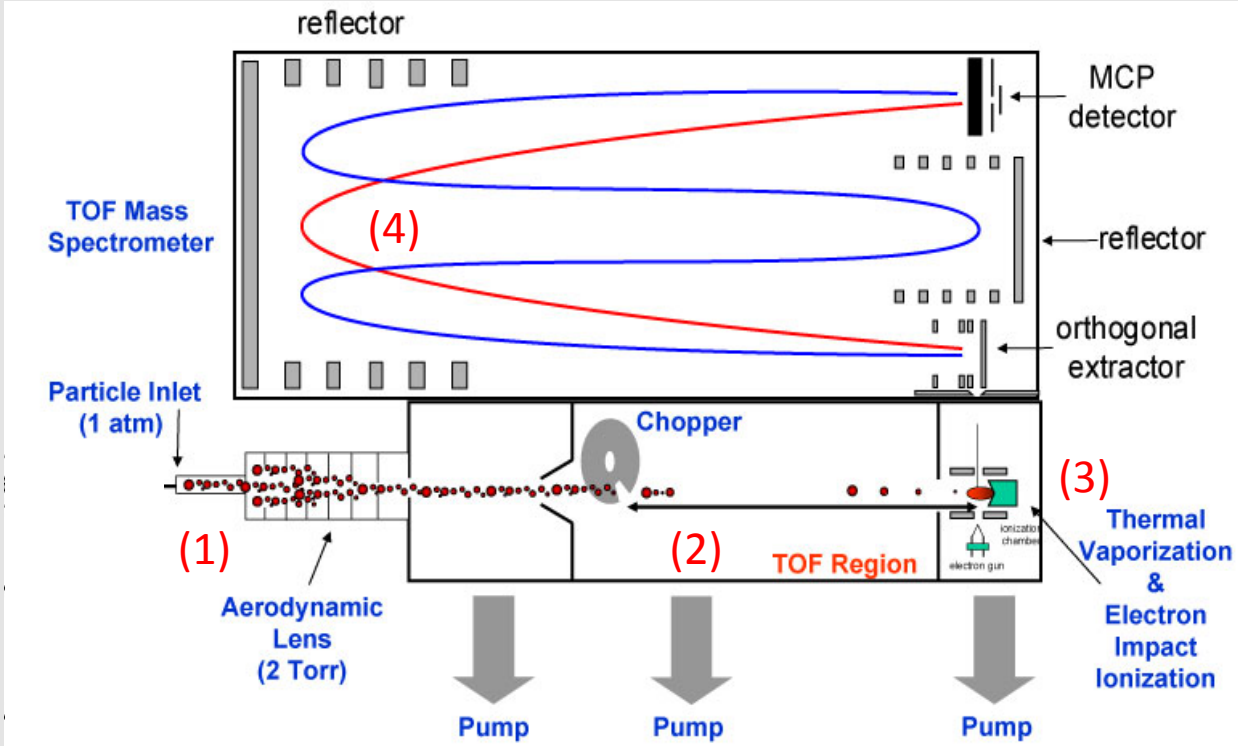
Fine particles ("aerosols"): $d_p \leq 1\ \mu m$



organic sulfate nitrate ammonium

Zhang et al. 2007

Aerodyne Aerosol Mass Spectrometer (AMS)



Quantitative, real-time measurement of aerosol mass, composition

(1) Particle focusing/concentration

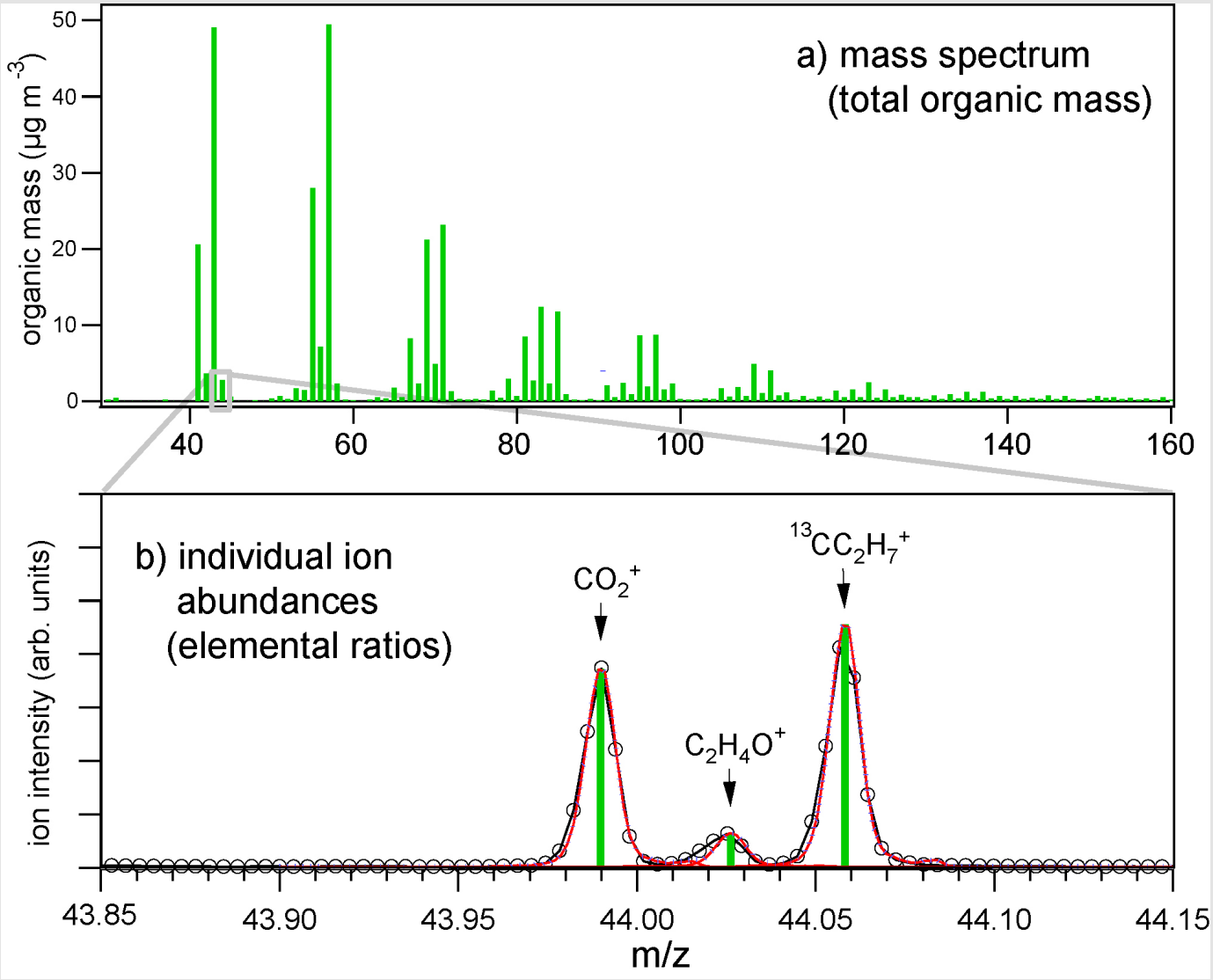
(2) Particle sizing

(3) Vaporization at 600°C, electron impact ionization at 70 eV (ion fragmentation)

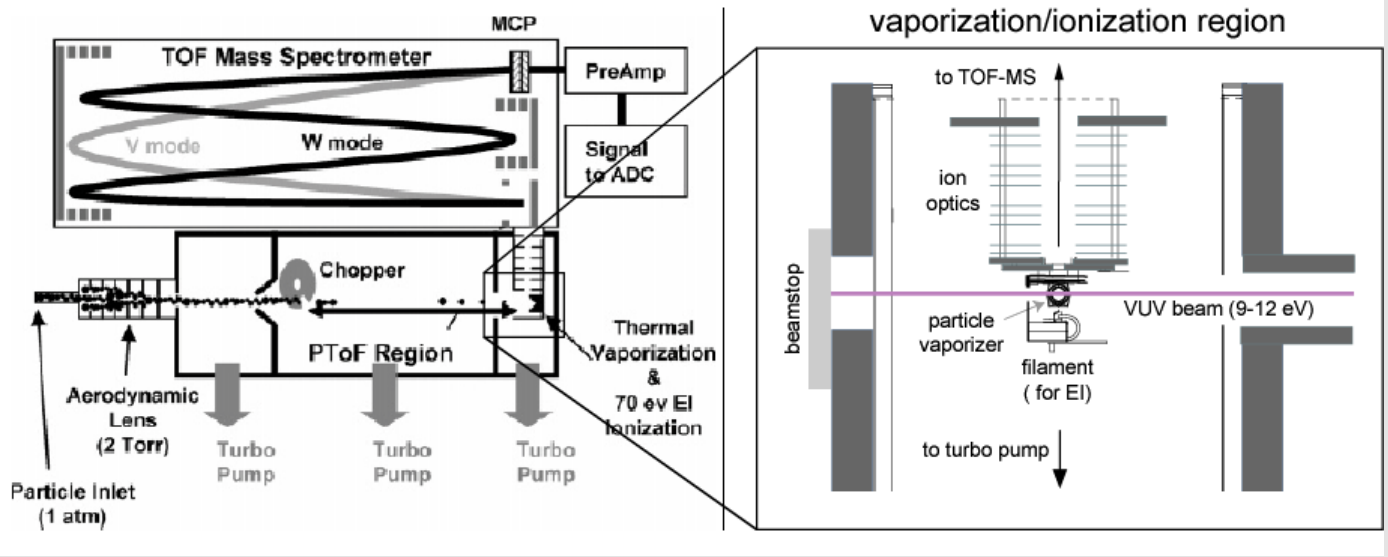
(4) High-resolution (5000) time-of-flight mass spectrometry

Jayne et al., *Aerosol Sci. Technol.*, 2000, Canagaratna et al., *Mass Spectrom. Rev.*, 2007

High-resolution electron impact AMS



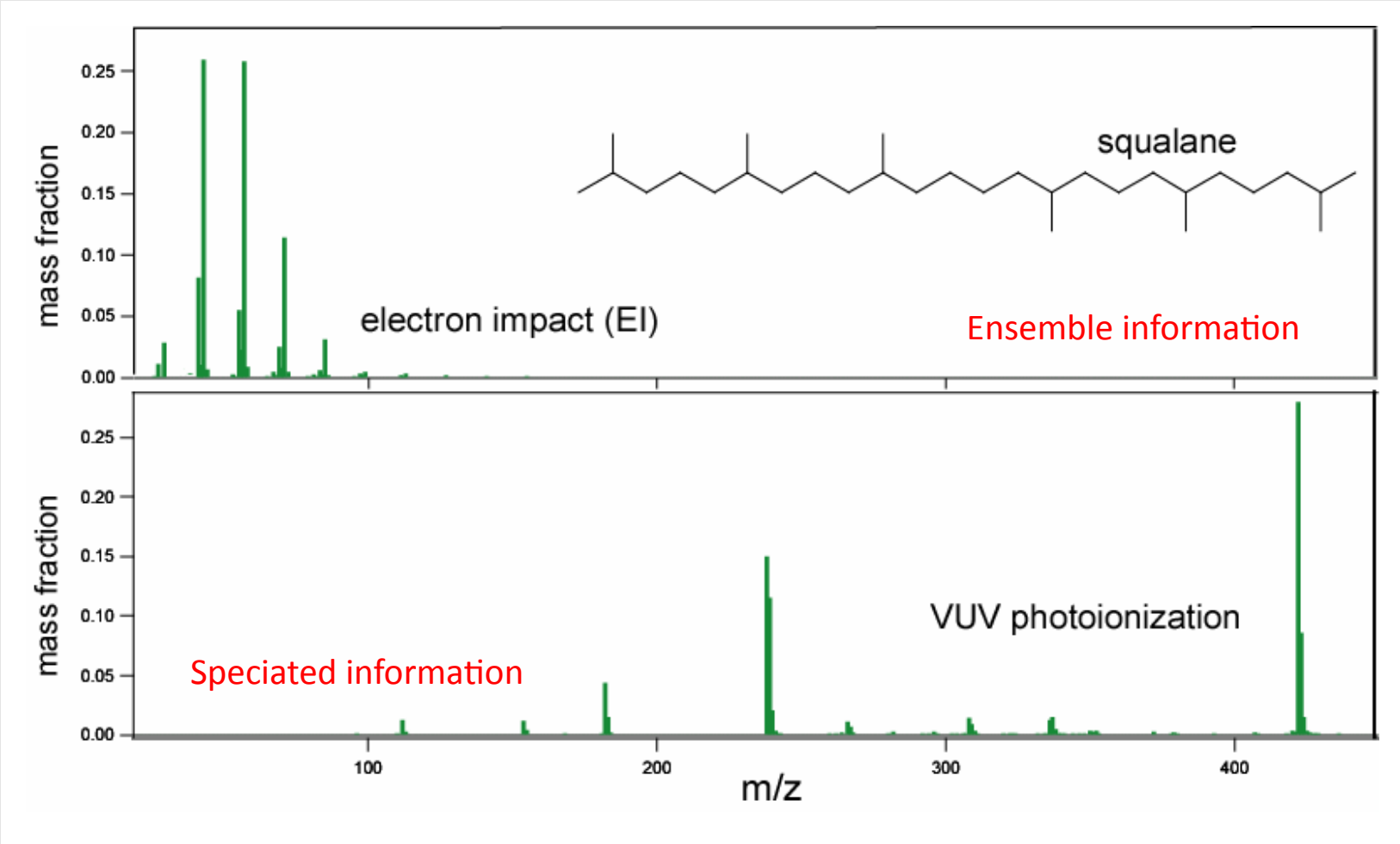
Vacuum ultraviolet photoionization (VUV) AMS



VUV from the chemical dynamics beamline (9.0.2) at the Advanced Light Source, Lawrence Berkeley National Laboratory [Kevin Wilson, Steve Leone, et al.]

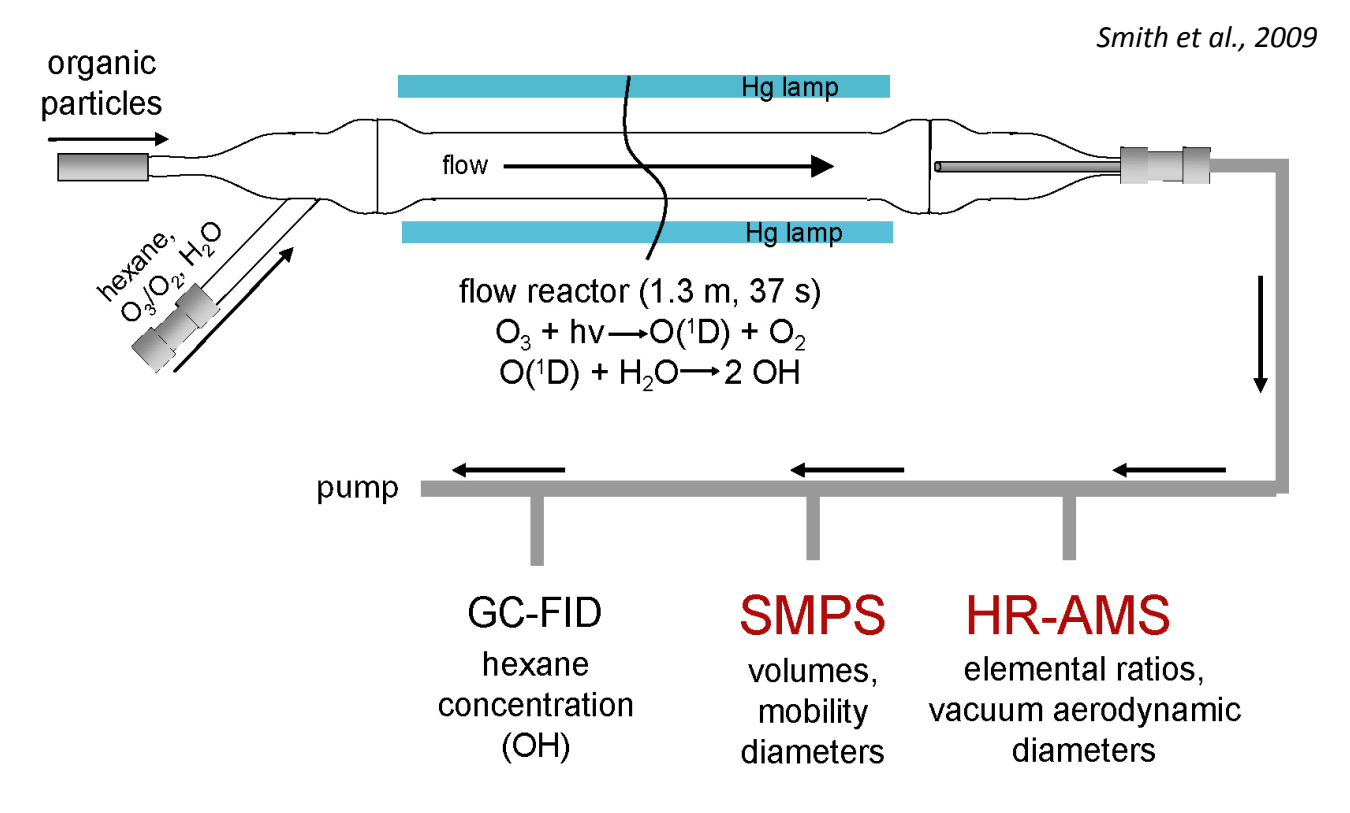
"Soft ionization" approach: vaporizer at <100°C, photon energy (8-12 eV) just above ionization threshold (~9-10 eV for large organics)

AMS: Hard (EI) vs. soft (VUV) ionization



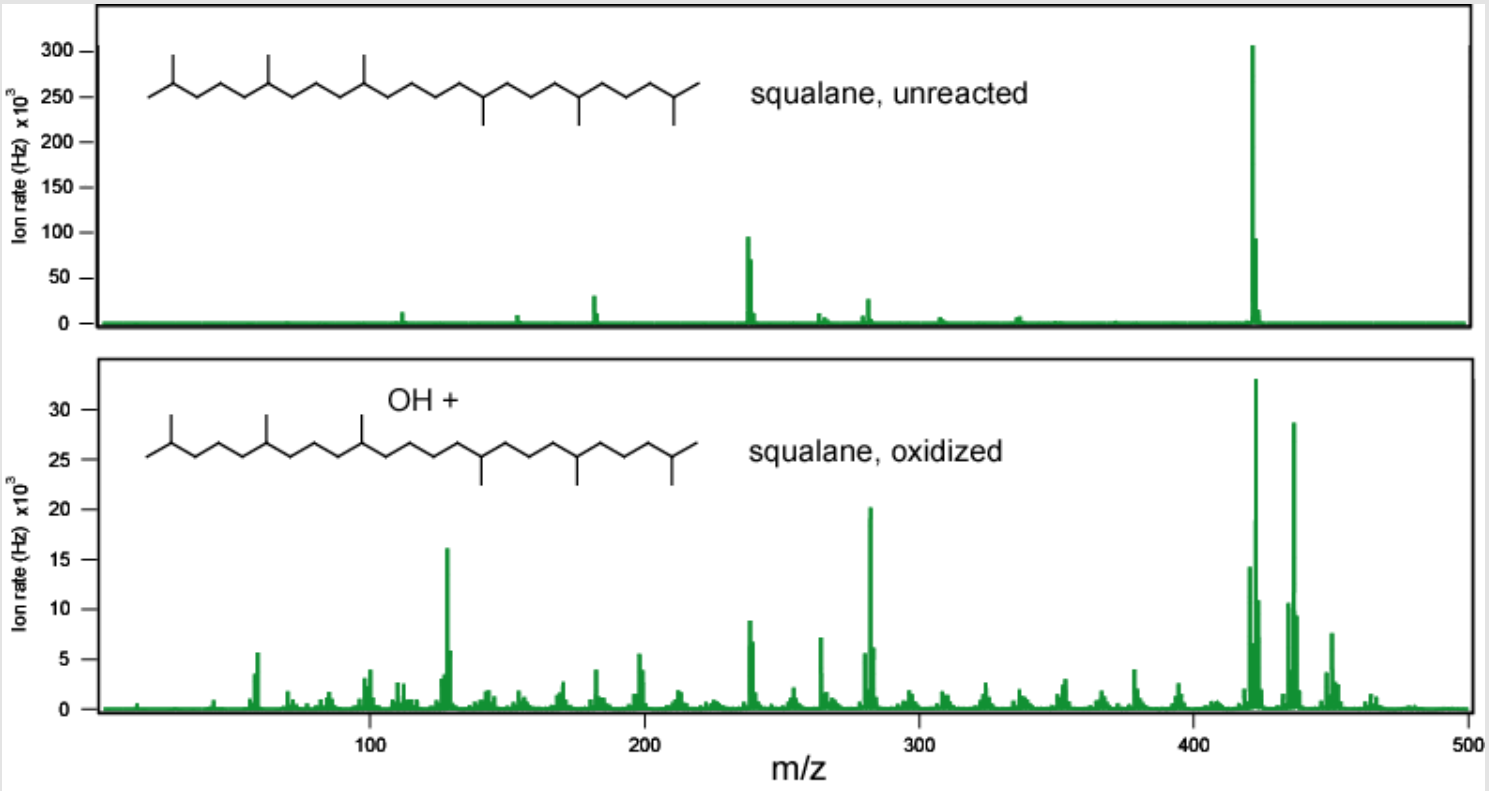
Flow tube experiments (heterogeneous oxidation)

Flow reactor at Lawrence Berkeley National Laboratory (PI: Kevin Wilson):



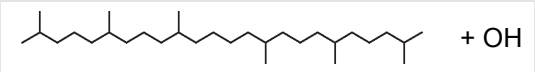
- AMS + scanning mobility particle sizer (SMPS): elemental ratios, particle volume, density, mass
- [OH] varied by changing [O_3]: can access hours to weeks of atmospheric oxidation

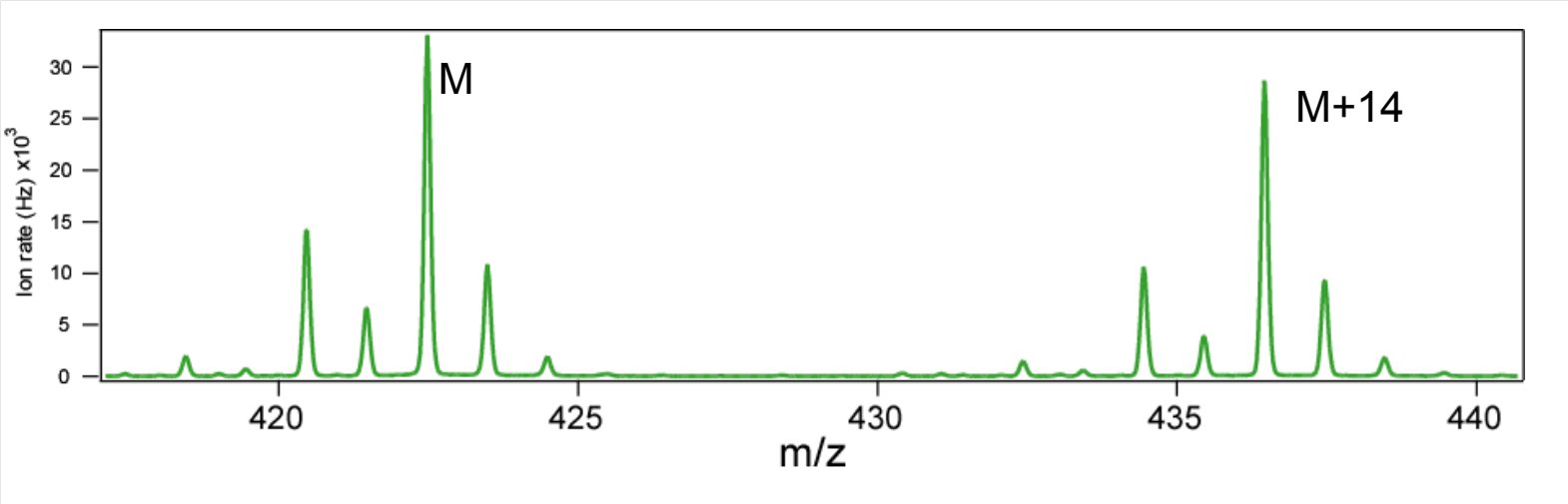
VUV-AMS spectrum: Oxidized squalane



Smith et al., *Atmos. Chem. Physics*, 2009

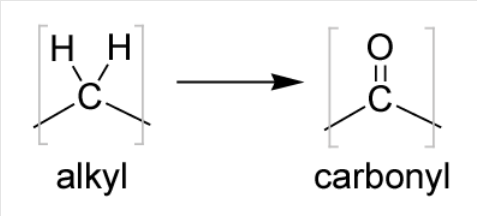
VUV-AMS spectrum: Oxidized squalane





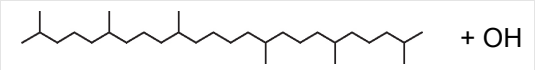
$\Delta m/z = 13.97$

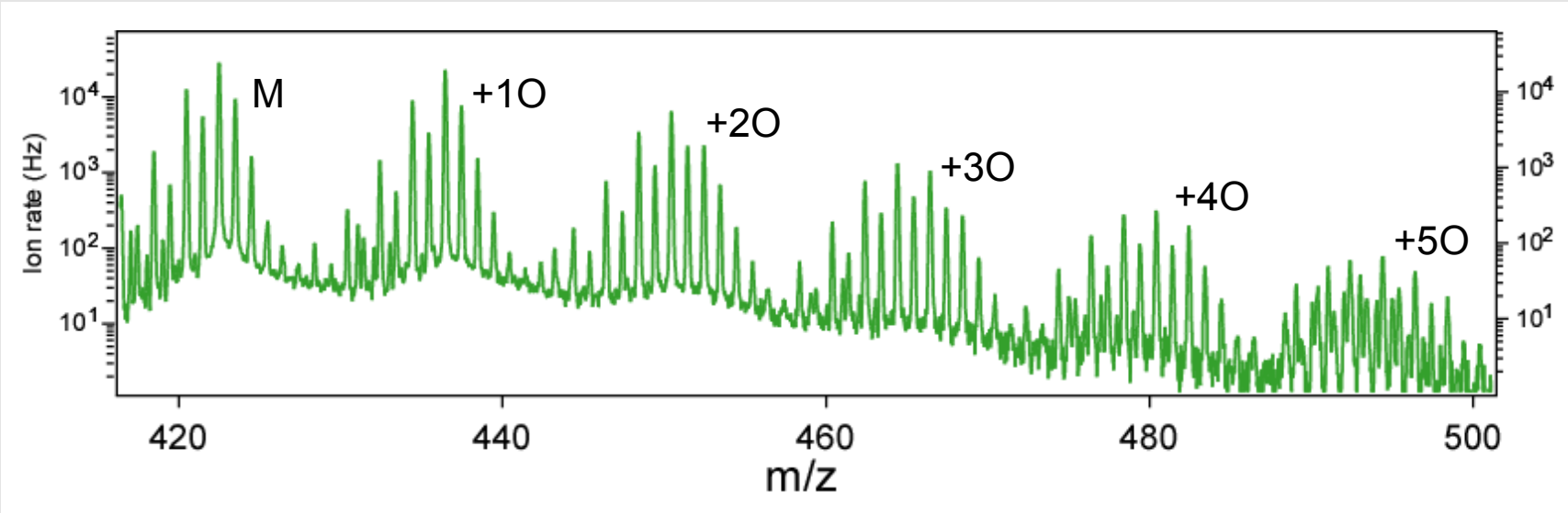
+1O, -2H



Smith et al., *Atmos. Chem. Physics*, 2009

VUV-AMS spectrum: Oxidized squalane

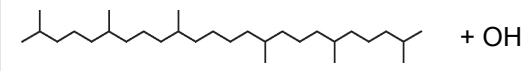




Some fraction of the aerosol becomes highly oxygenated (>5 O atoms) very quickly

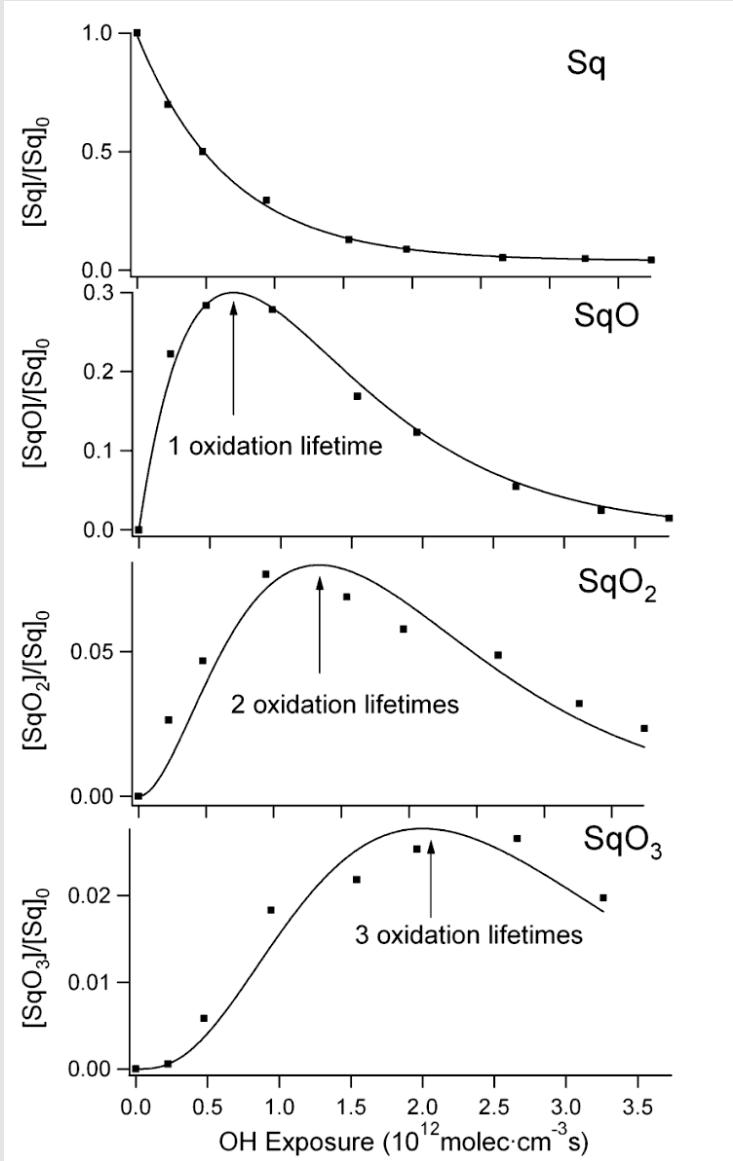
Smith et al., *Atmos. Chem. Physics*, 2009

Sequential oxidation



$$Sq + OH \rightarrow SqO$$
$$SqO + OH \rightarrow SqO_2$$
$$SqO_2 + OH \rightarrow SqO_3$$
$$\ldots$$
$$SqO_n + OH \rightarrow SqO_{n+1}$$

$$\frac{[SqO_n]}{[Sq]_0} = B_n \frac{(k \cdot \langle OH \rangle \cdot t)^n}{n!} \mathrm{Exp}(-k \cdot \langle OH \rangle_t \cdot t)$$



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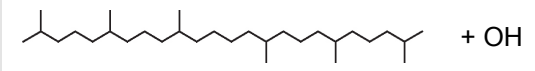
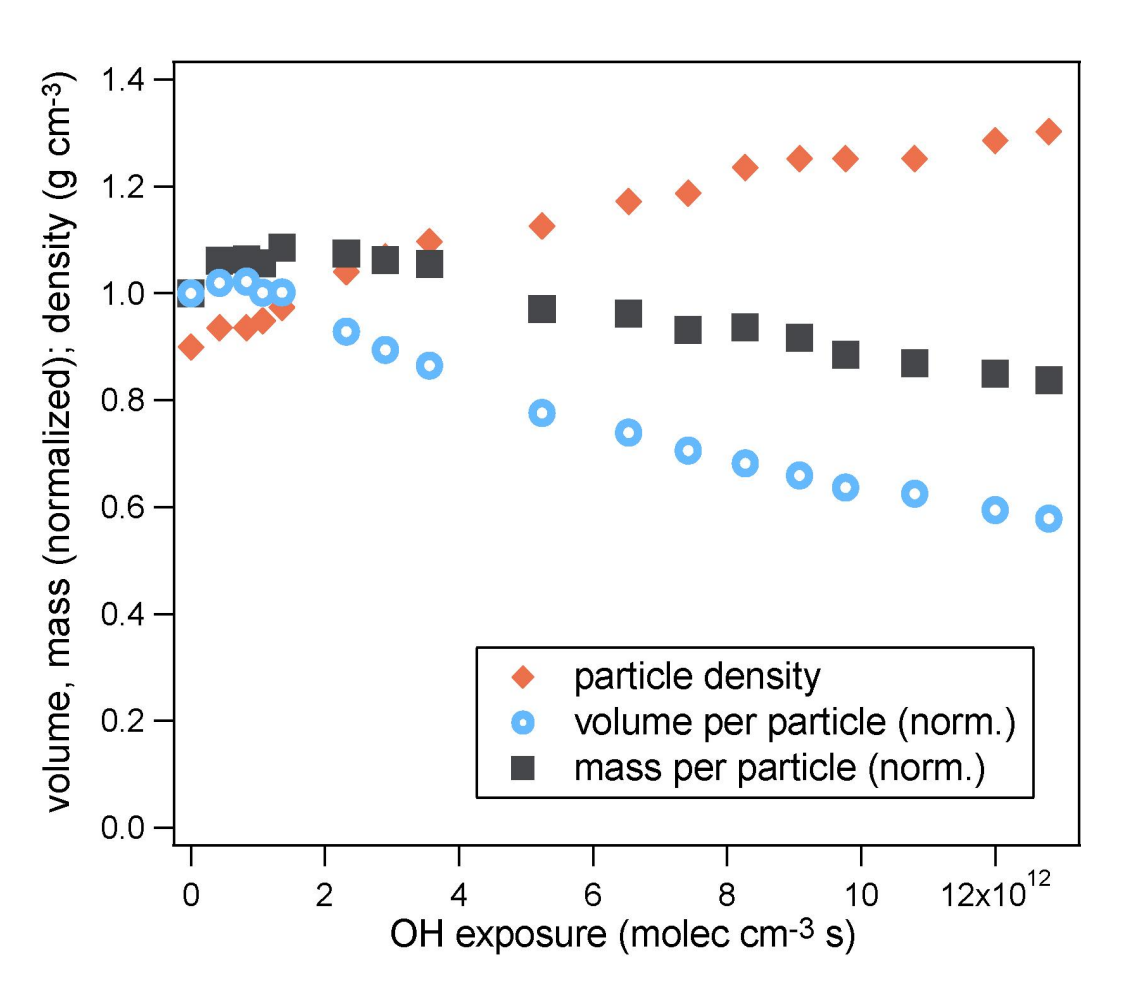
Ensemble measurements: Physical changes

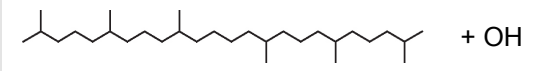


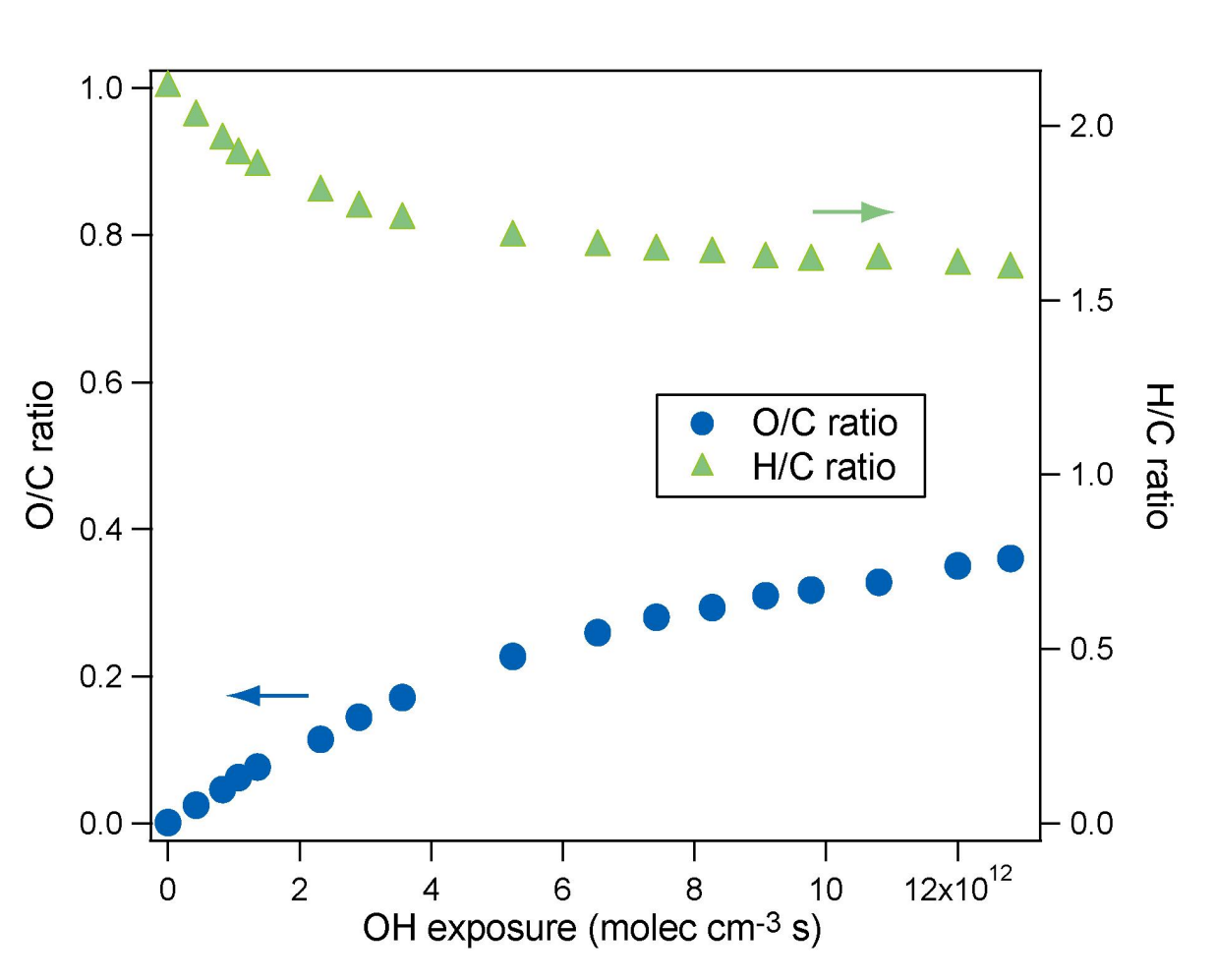


density increases
volume decreases
→ net decrease in mass

Kroll et al., PCCP 2009

Ensemble measurements: Chemical changes

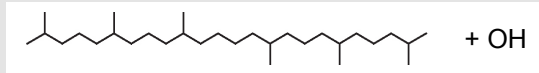


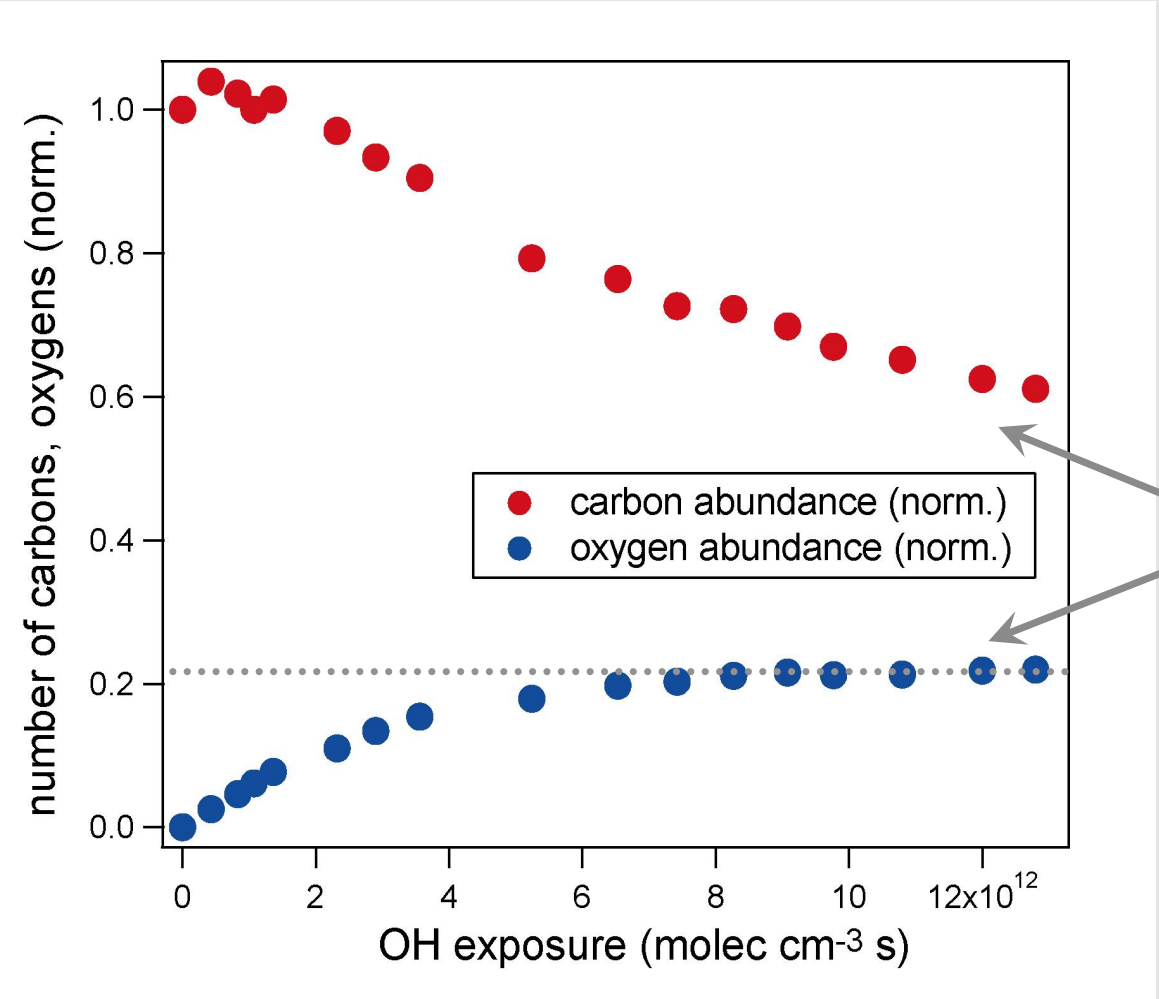


O/C increases
H/C decreases
→ oxidation state increases

Kroll et al., PCCP 2009

Elemental abundances



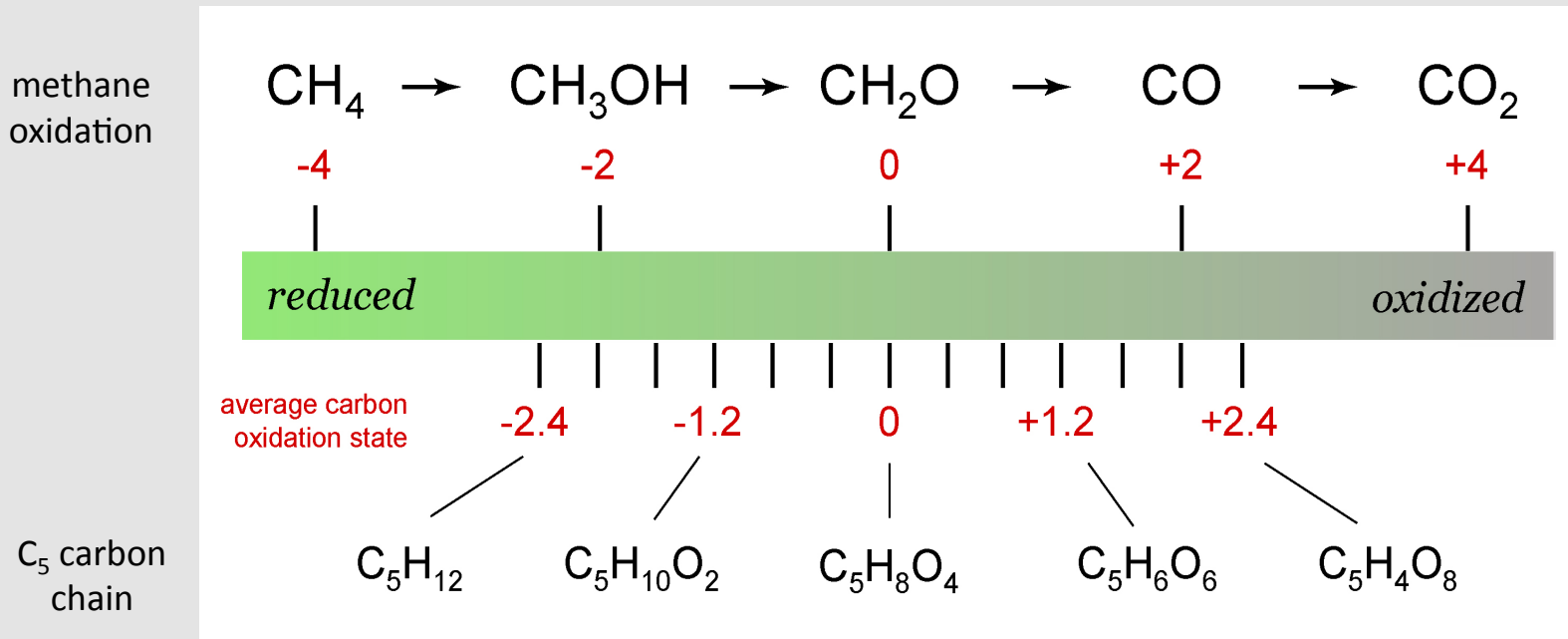


increase in O/C ratio not from net addition of oxygen (functionalization), but from loss of carbon (fragmentation)

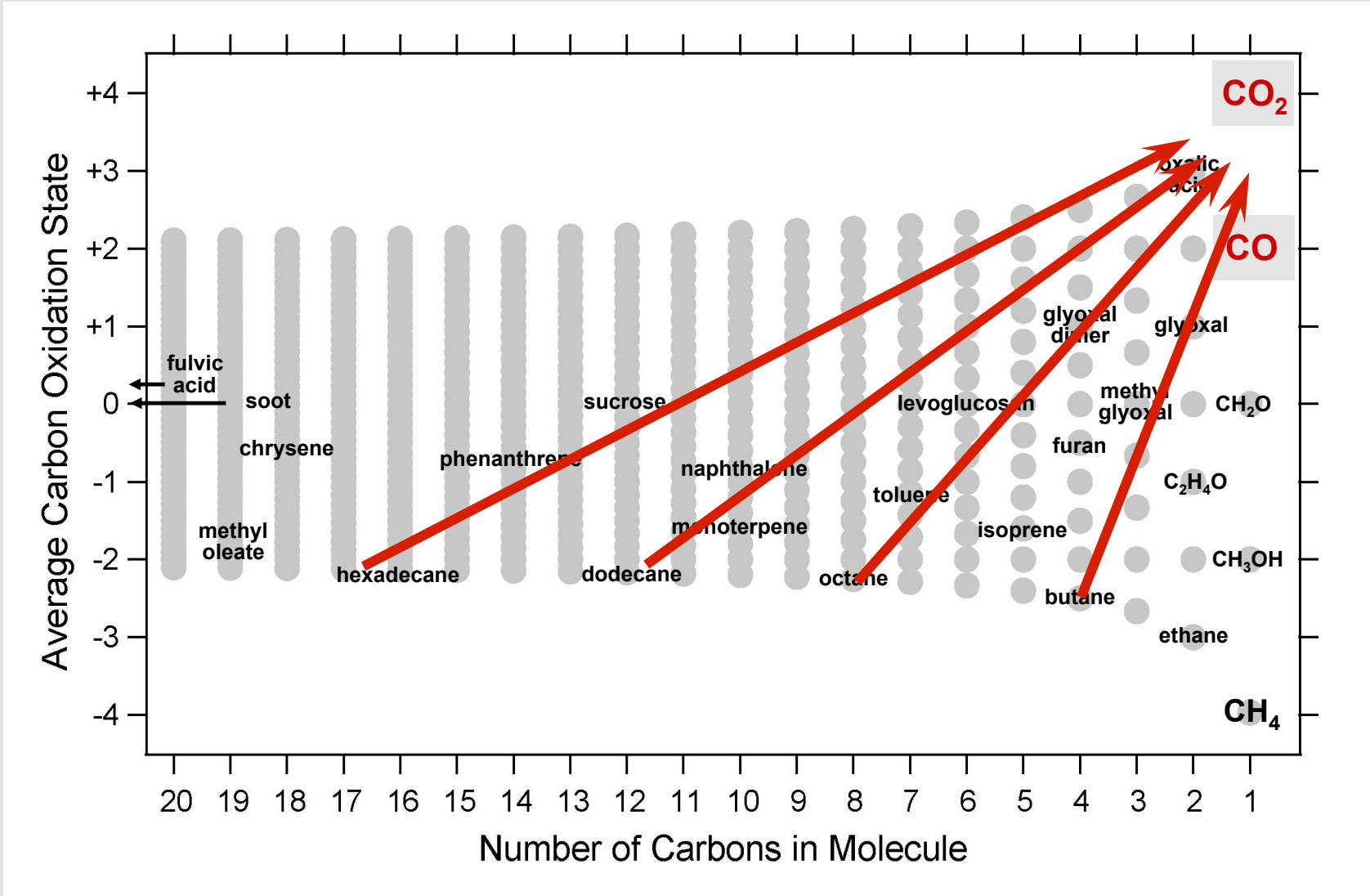
Kroll et al., PCCP, 2009

Oxidation of organic species

In an oxidizing environment, the oxidation state of carbon increases:



Carbon oxidation state vs. carbon number



Kroll et al., Nature Chem., 2011

Measuring carbon oxidation state

Trivial for speciated measurements

Can also be determined for complex mixtures:

$$\overline{\mathrm{OS}}_{\mathrm{C}} = -\sum_i \mathrm{OS}_i \frac{n_i}{n_C}$$

OS_i = oxidation state of atom *i*

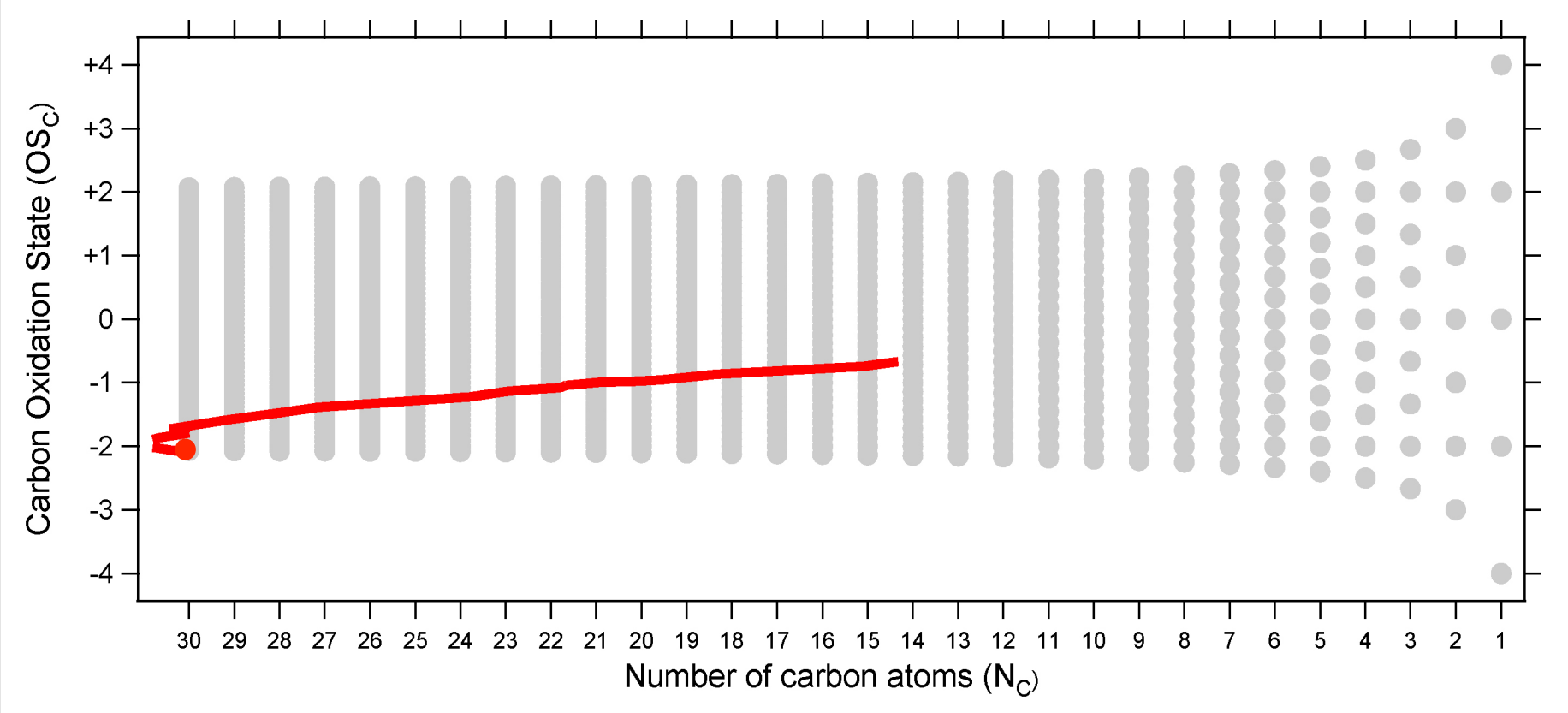
n_i = number of atom *i*

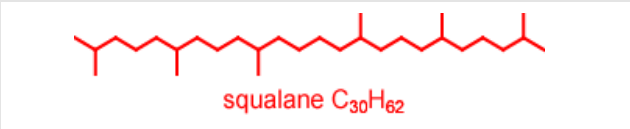
Organic aerosol is made up largely of carbon, hydrogen (OS=+1) and reduced oxygen (OS=-2) :

$$\overline{\mathrm{OS}}_{\mathrm{C}} \approx 2 \times \mathrm{O/C} - \mathrm{H/C}$$

Kroll et al., Nature Chem., 2011

Oxidation state evolution





Kroll et al., Nature Chem., 2011

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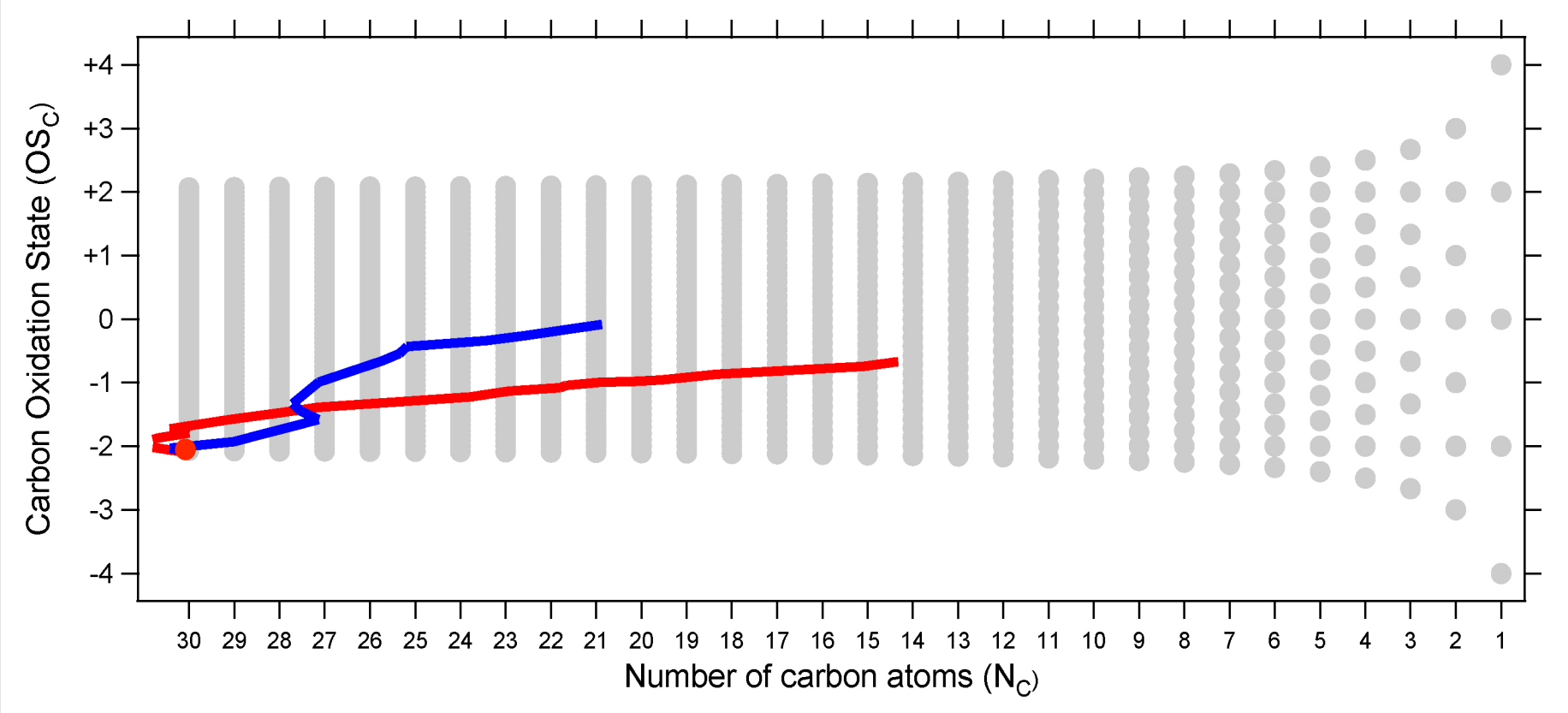

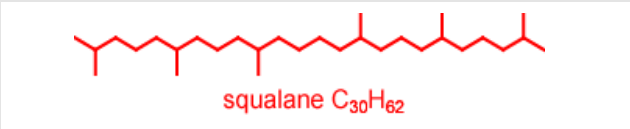

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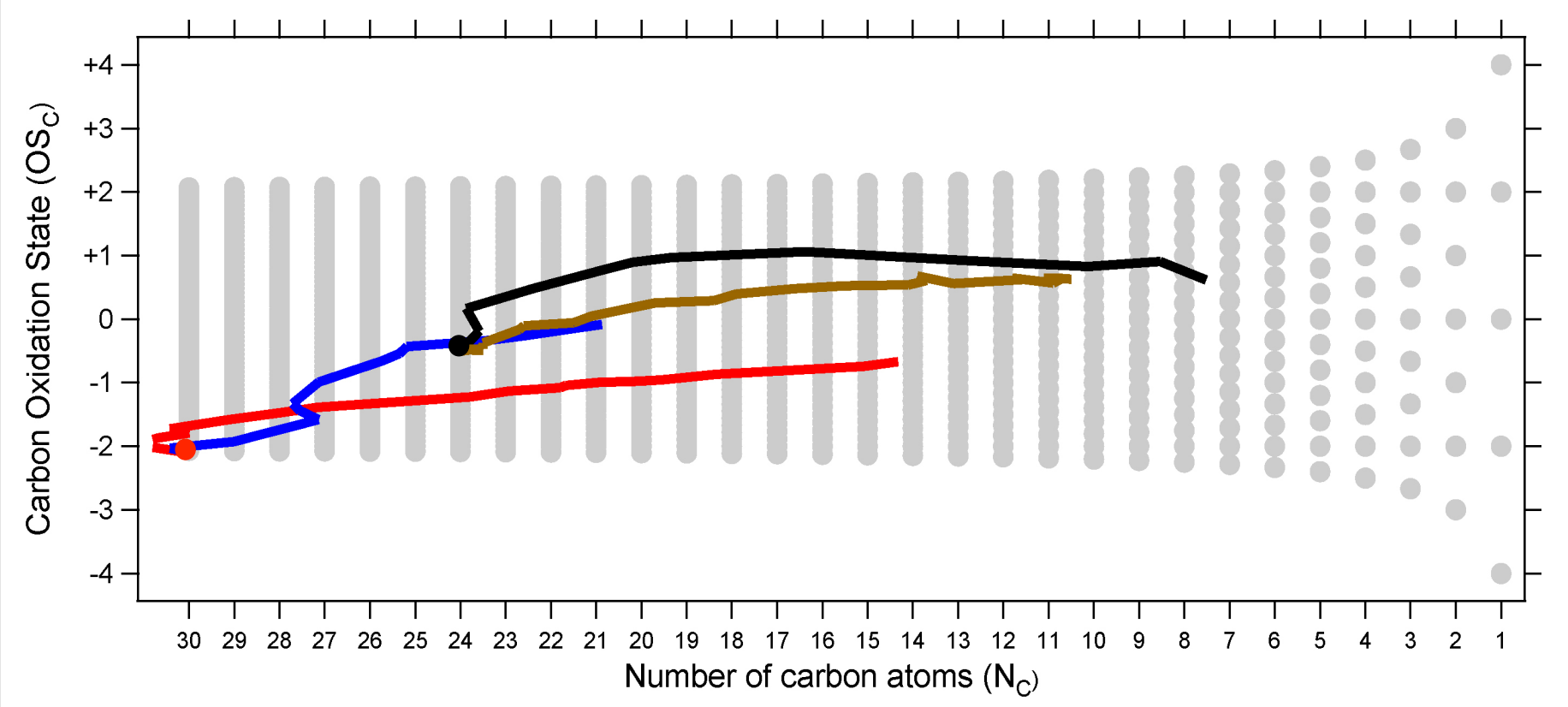

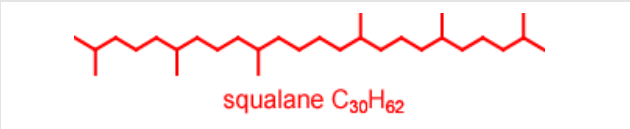

Kroll et al., Nature Chem., 2011

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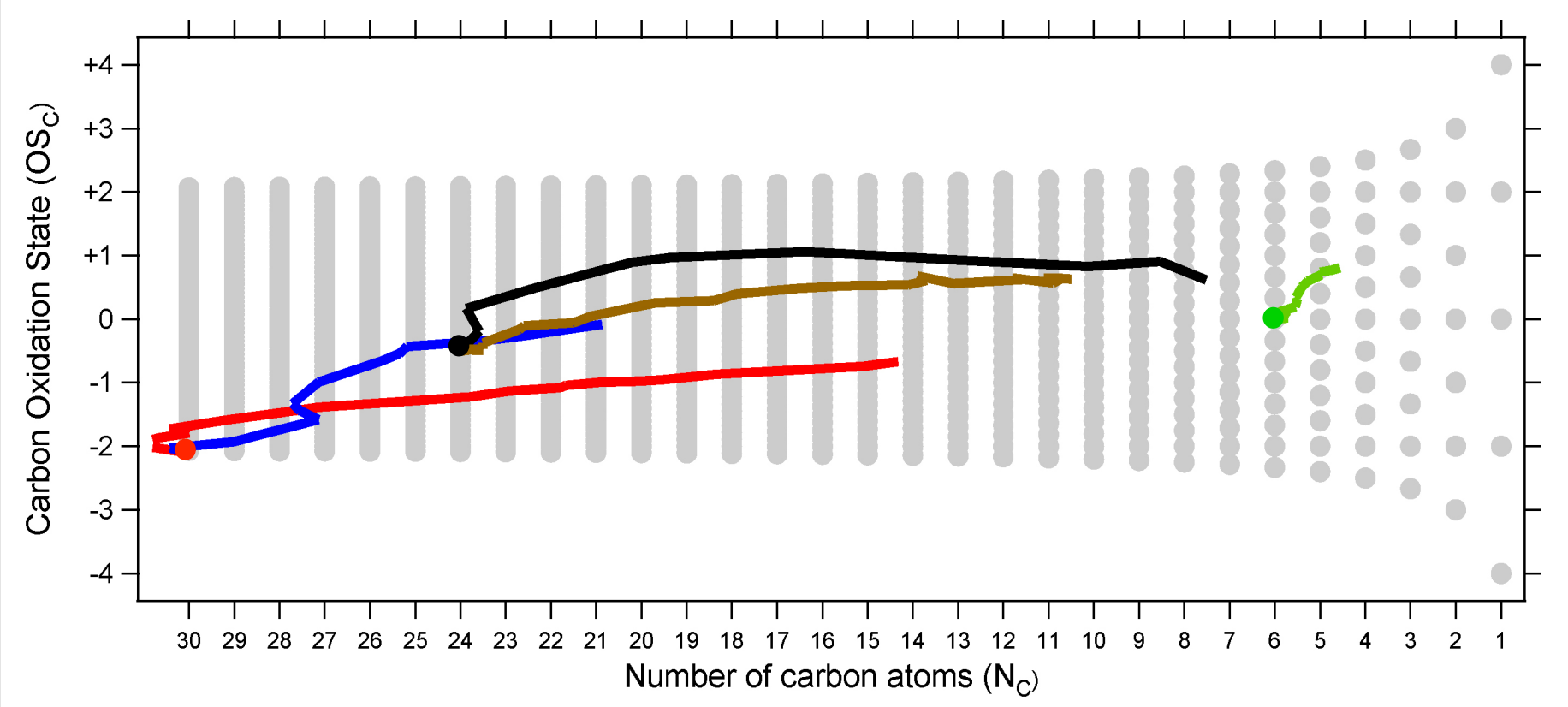
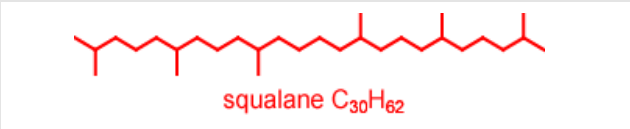
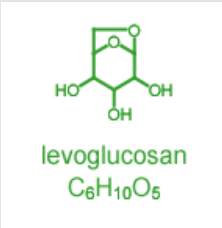
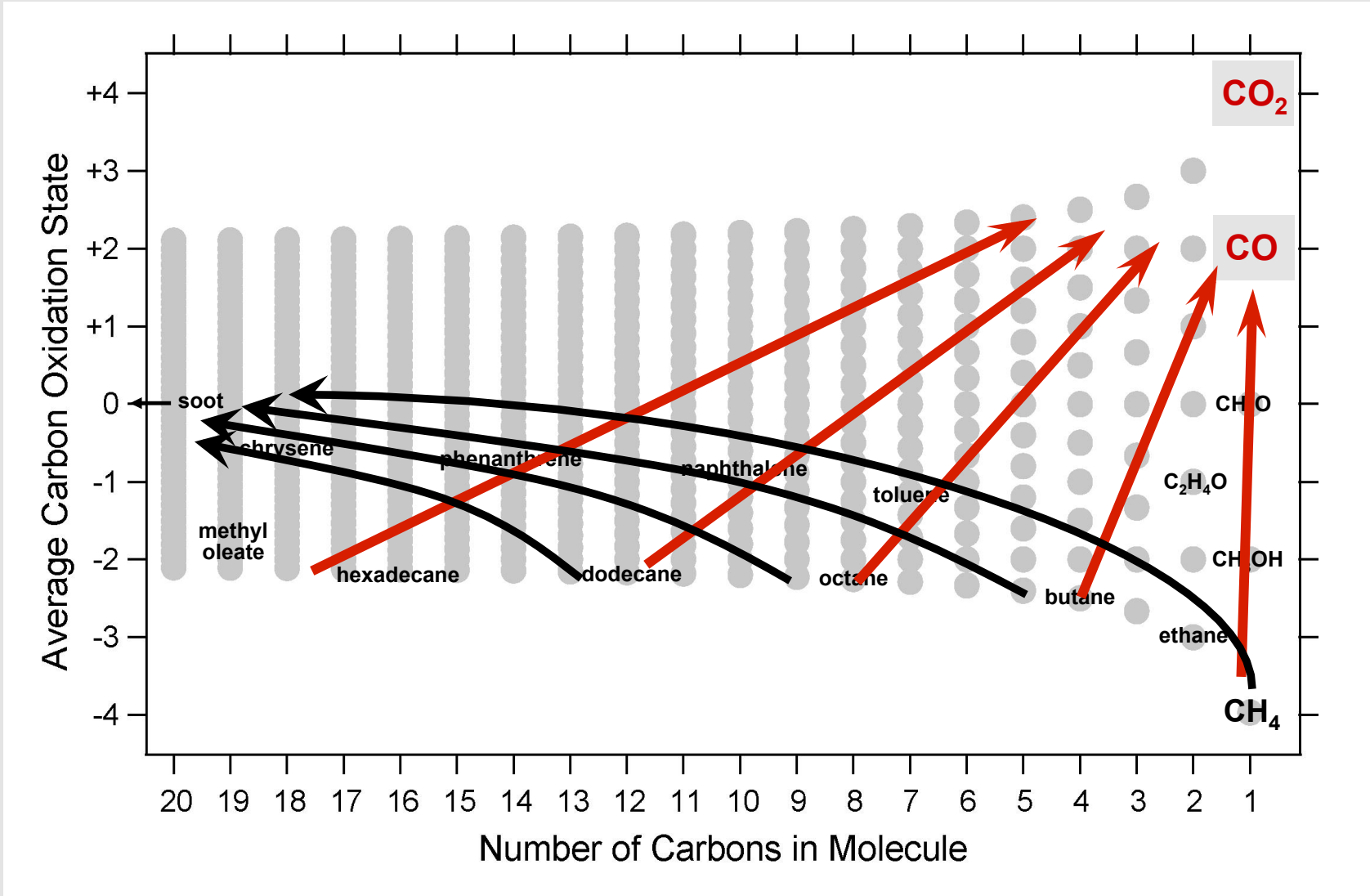






Kroll et al., Nature Chem., 2011

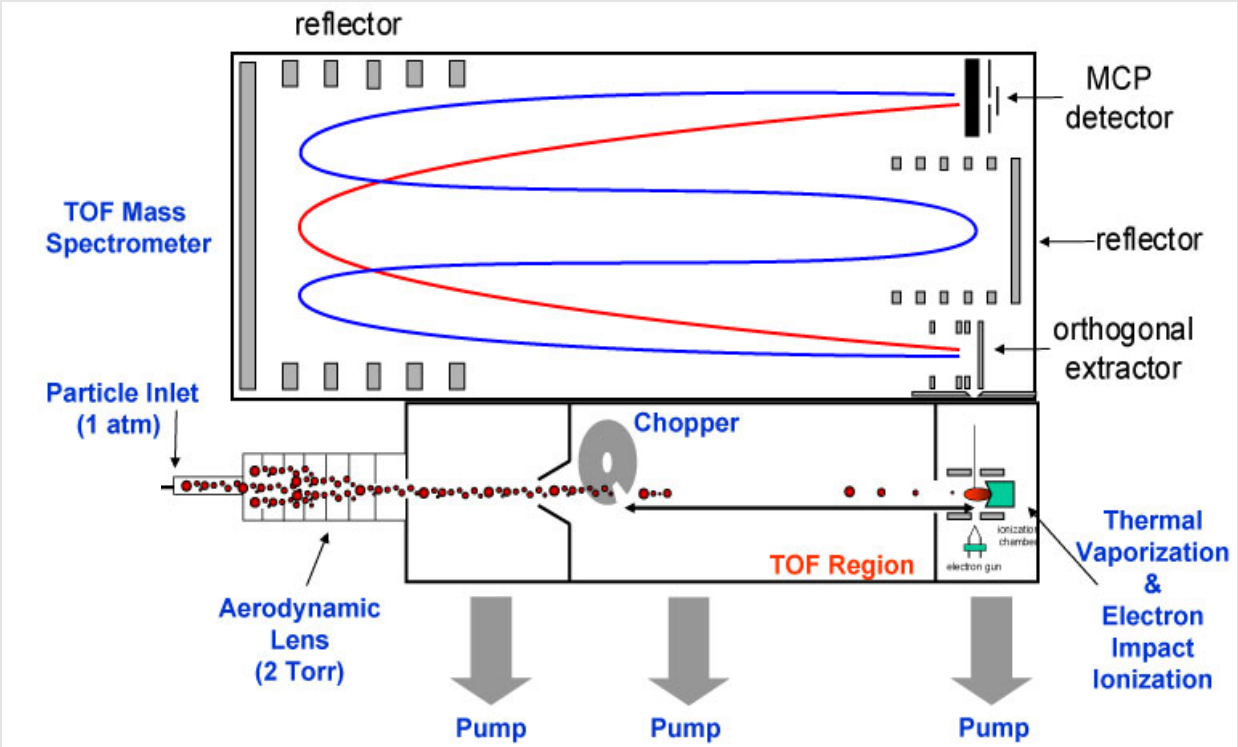
Combustion processes



AMS measurements of soot in combustion systems

Challenges:

1) Interface: high P, T
2) Refractory nature of soot: won't flash vaporize at 600°C
3) Very small particles (<10 nm): can't be focused in aerodynamic lens



Conclusions

Challenges in studying the chemistry of organic aerosol (OA) include:

- multistep, multiphase nature of the chemical mechanisms
- immense chemical complexity

We can understand key features of complex mechanisms and condensed-phase mixtures using *highly time-resolved aerosol mass spectrometry*:

- hard ionization (EI): ensemble measurements
- soft ionization (VUV): speciated measurements

Carbon oxidation state (OS_C) and carbon number (n_C) serve as a useful 'reduced representation" for describing atmospheric OA chemistry

Connections between atmospheric chemistry and combustion chemistry (and especially between OA and soot) → potential opportunities for both communities

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