The detection and identification of extremely low-volatilty organic species during SOAS and FIXCITCIT using an NO_3^--CIMS

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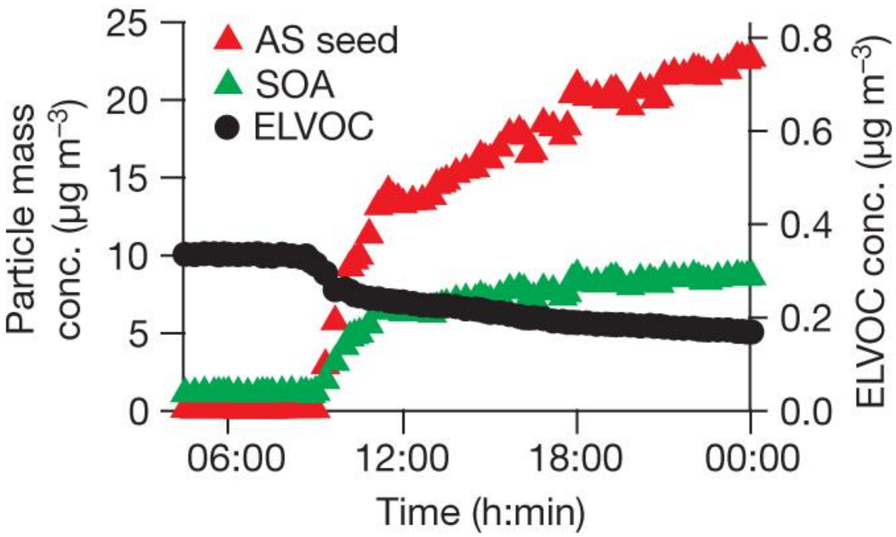
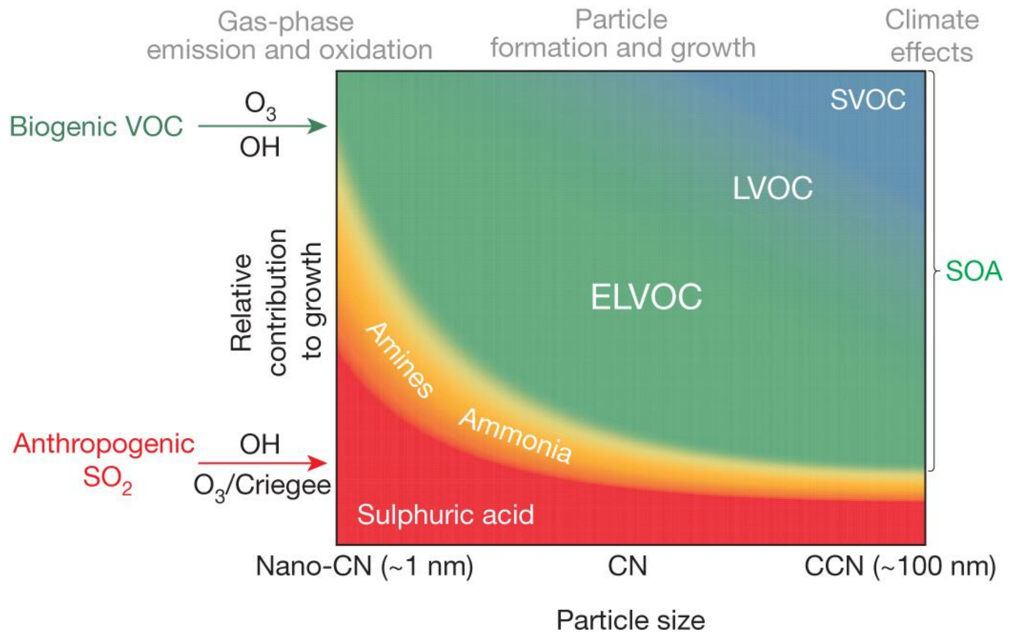
Motivation: Extremely Low Volatility Organic Compounds (ELVOCs) are important for new particle growth in a-Pinene dominated environments

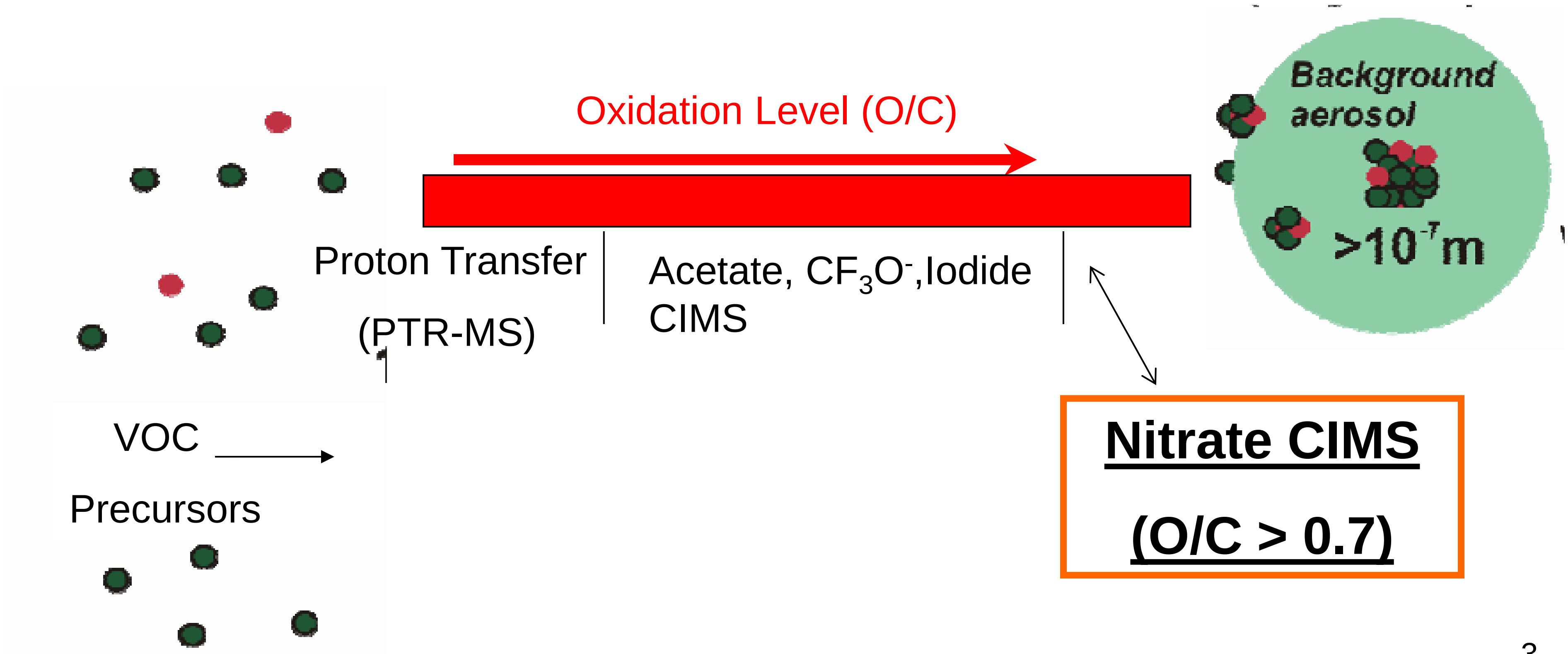




From: Ehn, M. *et al.* A large source of low-volatility secondary organic aerosol. *Nature* **506**, 476–479 (2014).

METHOD: Detection of Oxidized Organics in the gas phase via Chemical Ionization Mass Spectrometry (CIMS)

- Selective method via specific ionization schemes
- Molecular identification via high resolution mass spectrometry



Nitrate Ion (NO_3^-) Ionization Scheme for Oxidized Organic Molecules

X-rays

$$(n+1)HNO_3 \rightarrow (HNO_3)_n NO_3^- + H^+$$

Deprotonation:

$$(HNO_3)_n NO_3^- + HX \rightarrow (HNO_3)_n + HNO_3 + X^-$$

ELVOC detection

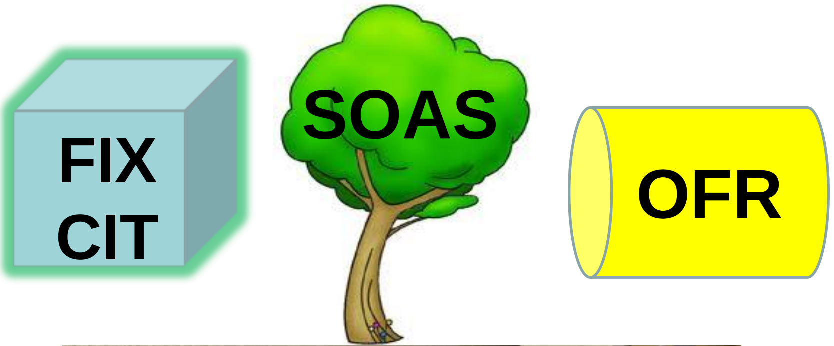
Clustering:

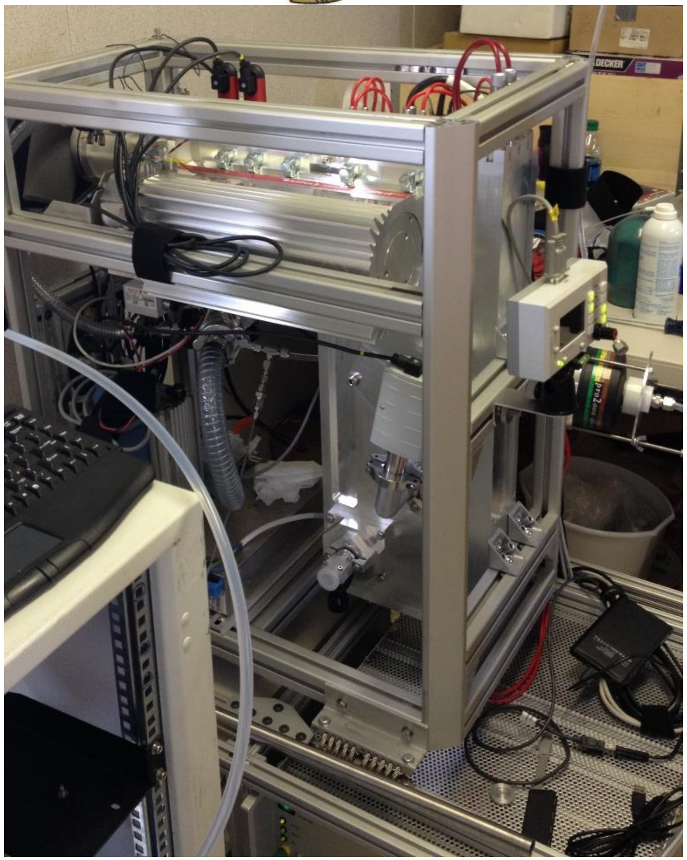
$$(HNO_3)_n NO_3^- + HX \rightarrow (HNO_3)_n + (NO_3^-)H$$

Sensitivity = ppt levels (low background, high S/N)

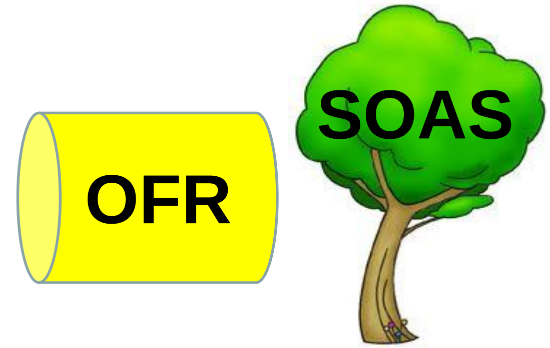
Calibration = obtained for H_2SO_4 based on inlet geometry (flows) (*Mauldin et al., JGR, 1999; Jokinen et al., ACP, 2012*)

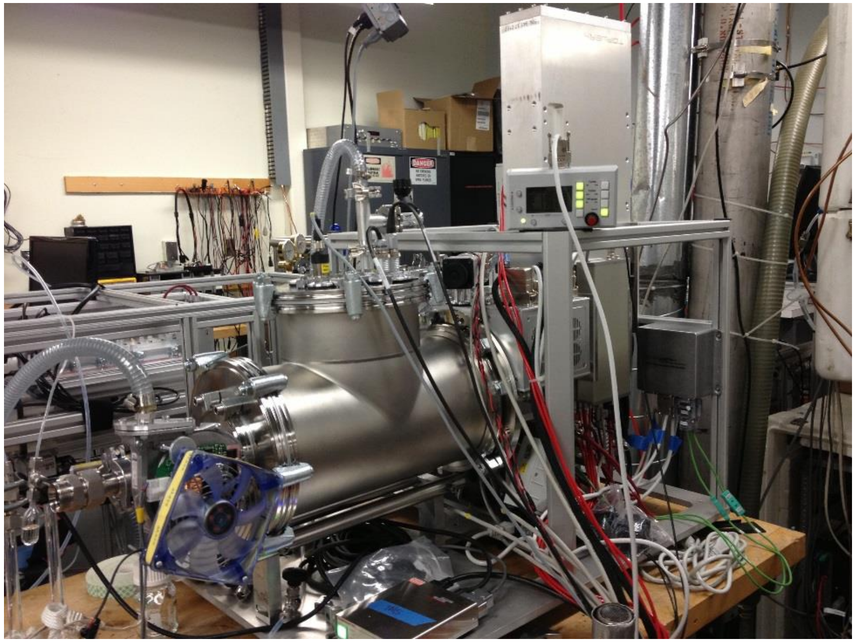
NO_3^--CIMS





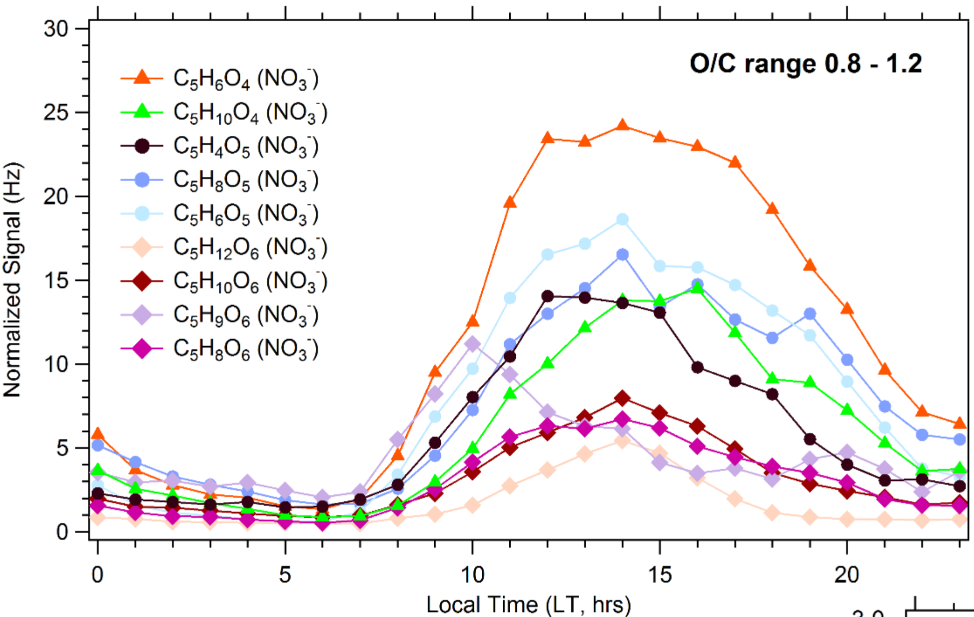
IMS-TOF





C_5 compounds observed

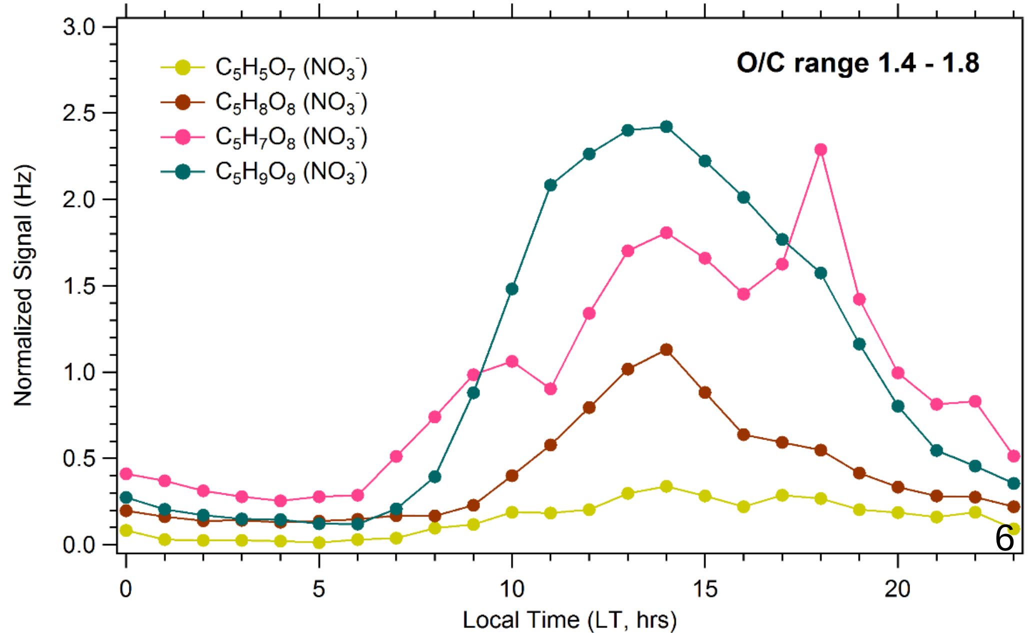
SOAS



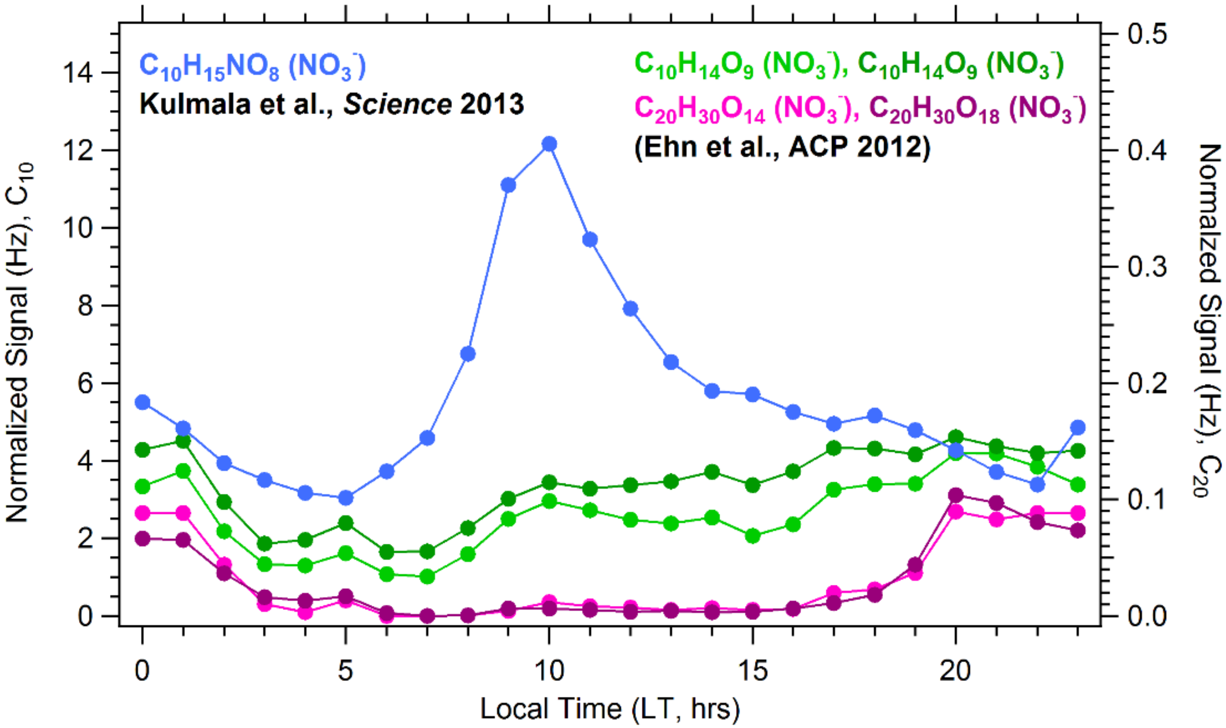
- O/C values ranging from of 0.8 to 1.8

NOTE: A day-to-day variability depending on rain rate and cloudiness is observed for all of these compounds

(Massoli, AGU 2013)



Diurnal Cycles of α-pinene known oxidation products



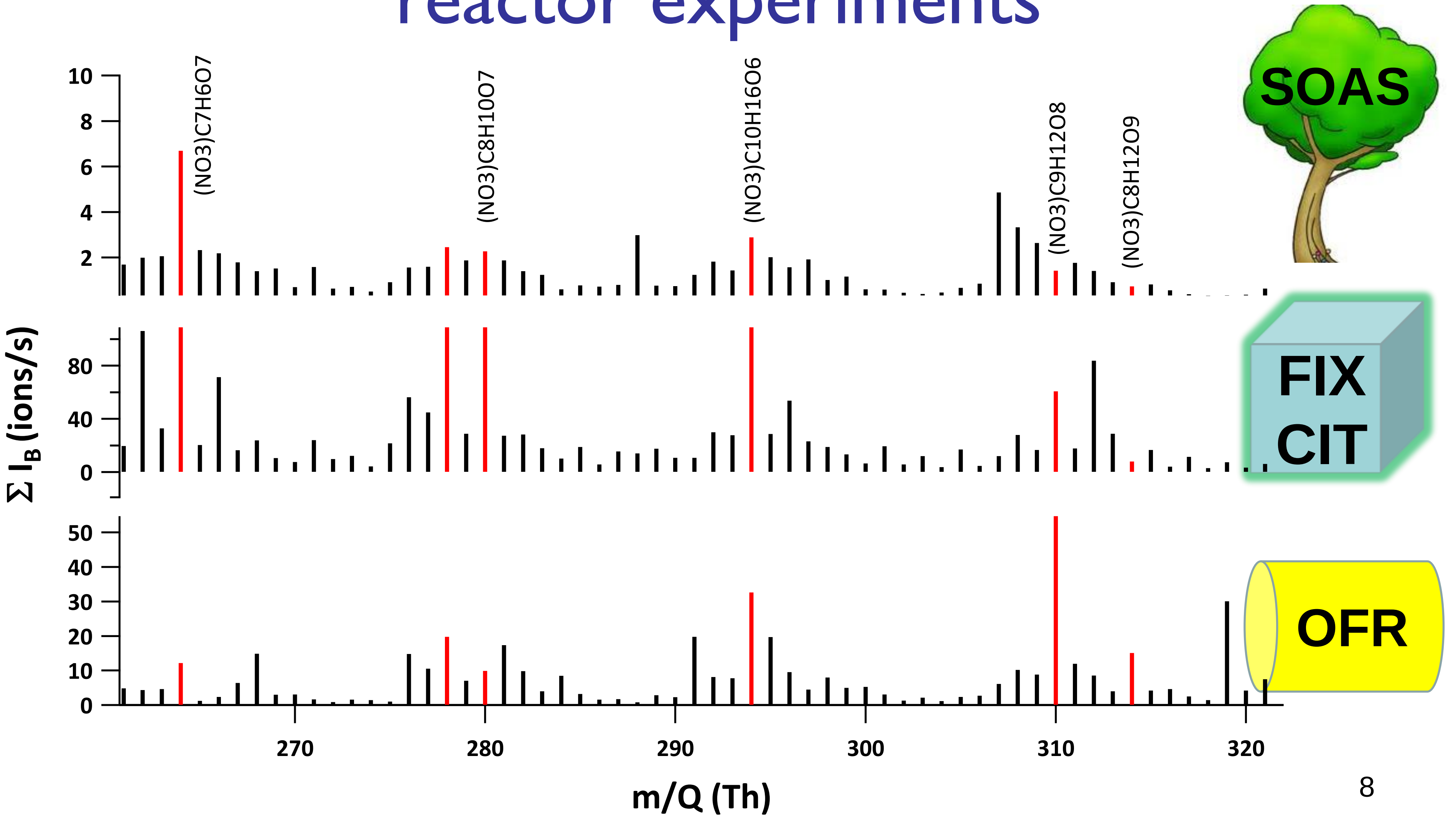
- **α-pinene products (C_{10}, C_{20})**

- O/C = 0.8 – 1

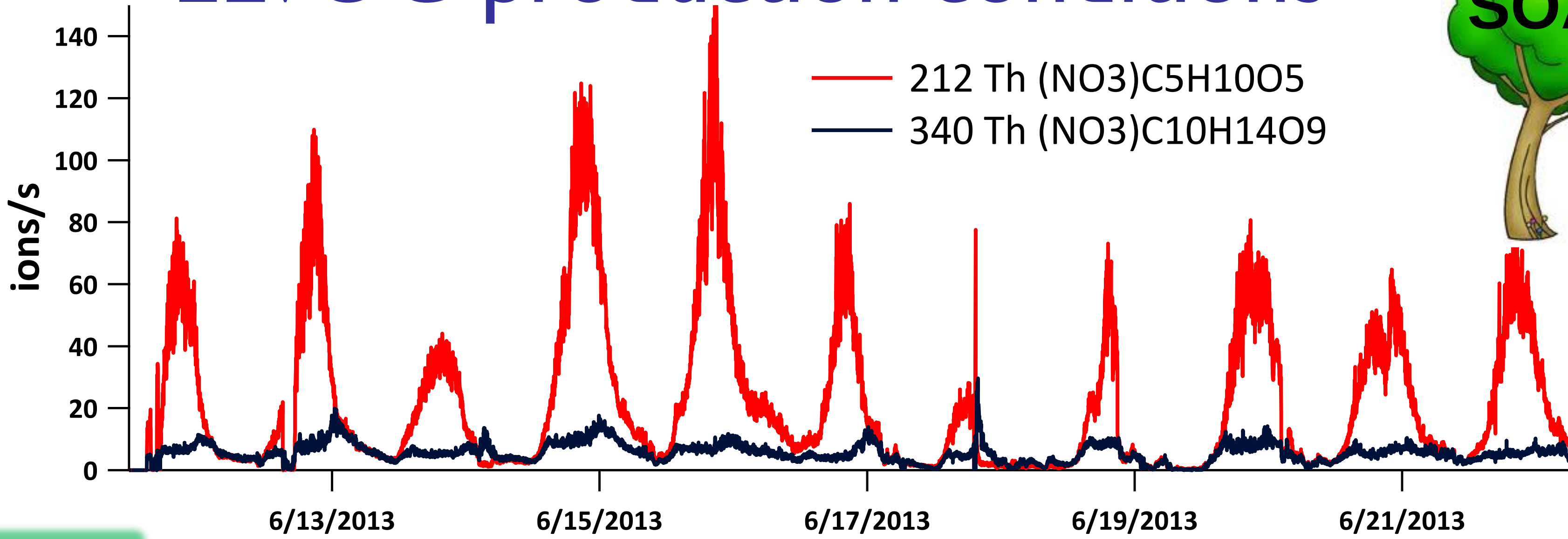
- Night time peak (O_3) except for $C_{10}H_{15}NO_8$ (NO_3^-), observed during the day (O_3 and OH) as in Hyytiala (role for NPF and growth)

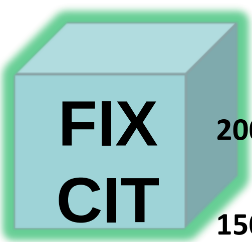
(Massoli, AGU 2013)

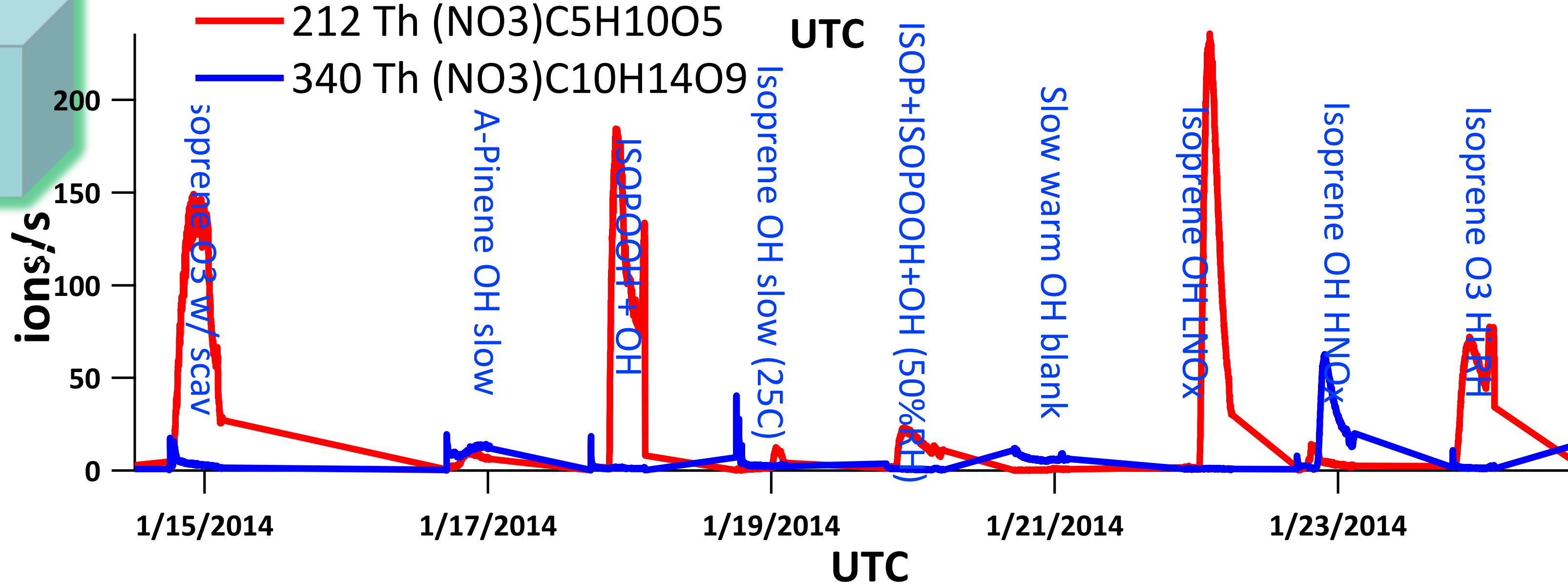
α-pinene Ions observed during SOAS match ions generated in chamber and flow reactor experiments



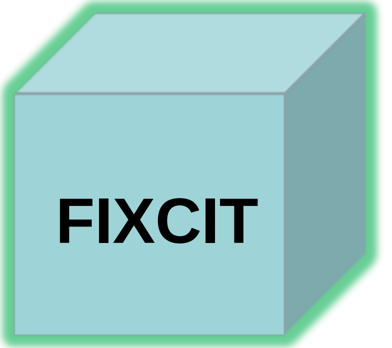
Use FIXCIT NO_3^--CIMS to identify SOAS ELVOC production conditions

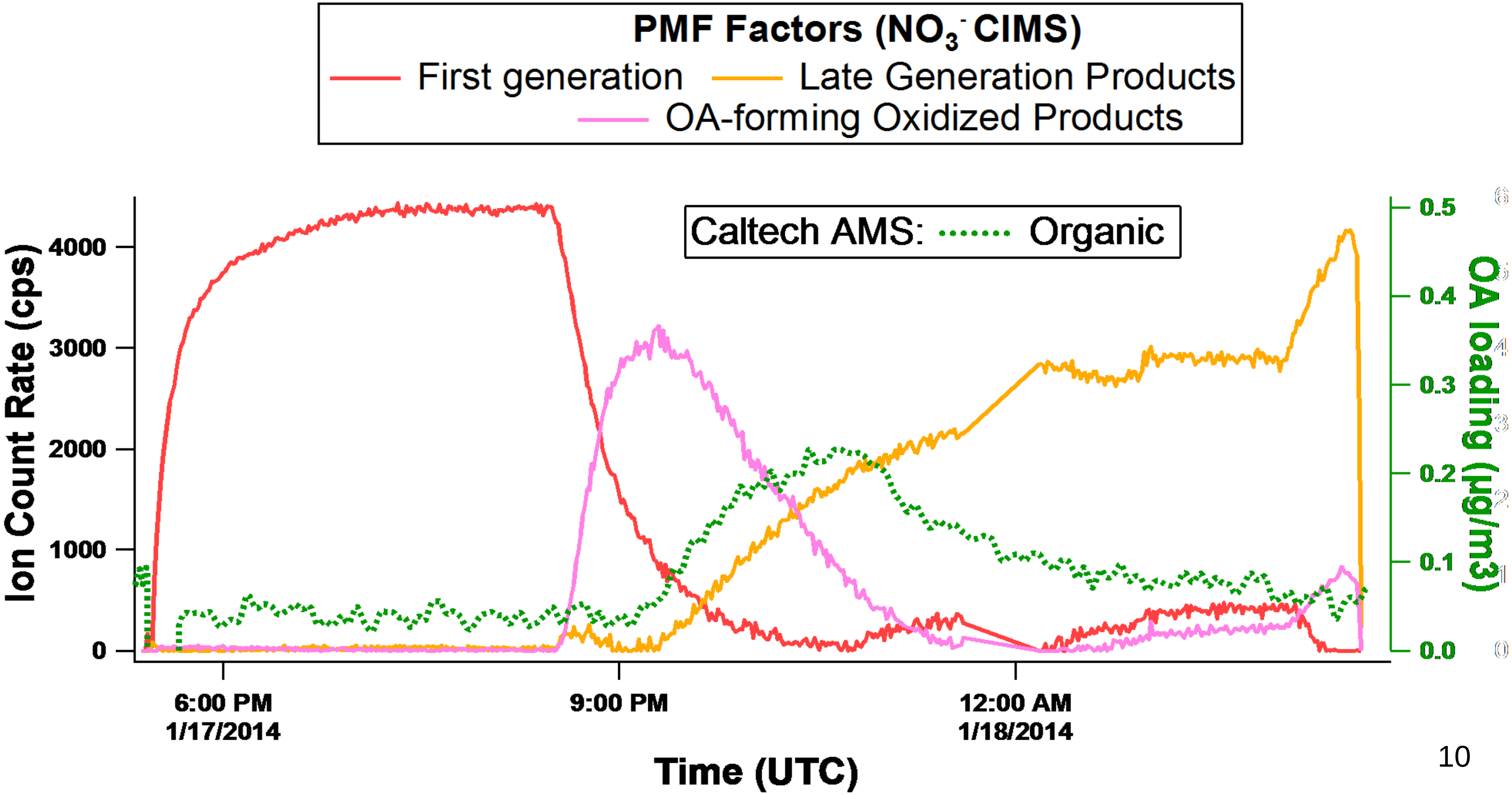






Isoprene ELVOCs correlate w/ OA growth and formation in chamber





N-containing species also condense onto seed aerosol

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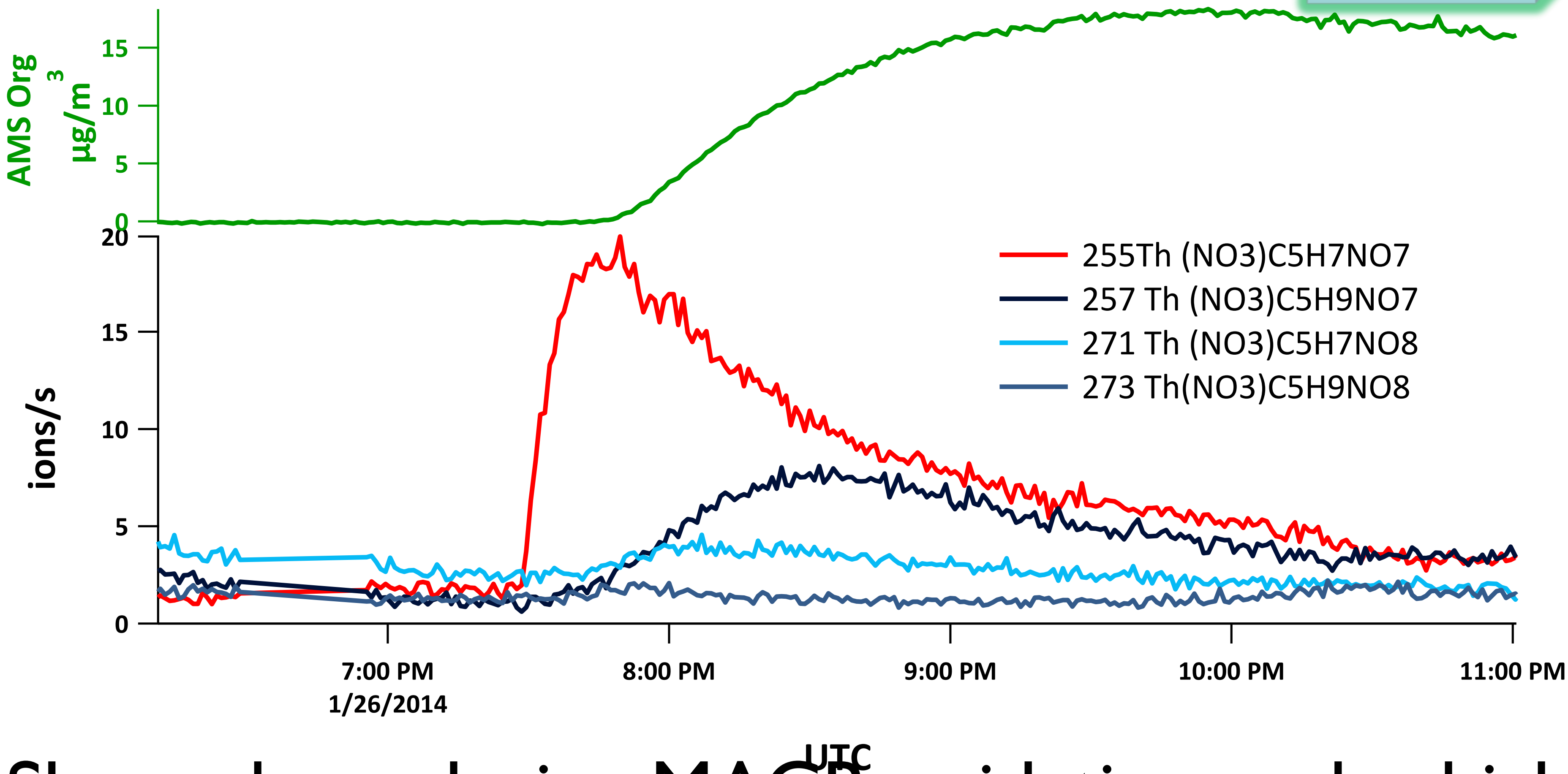
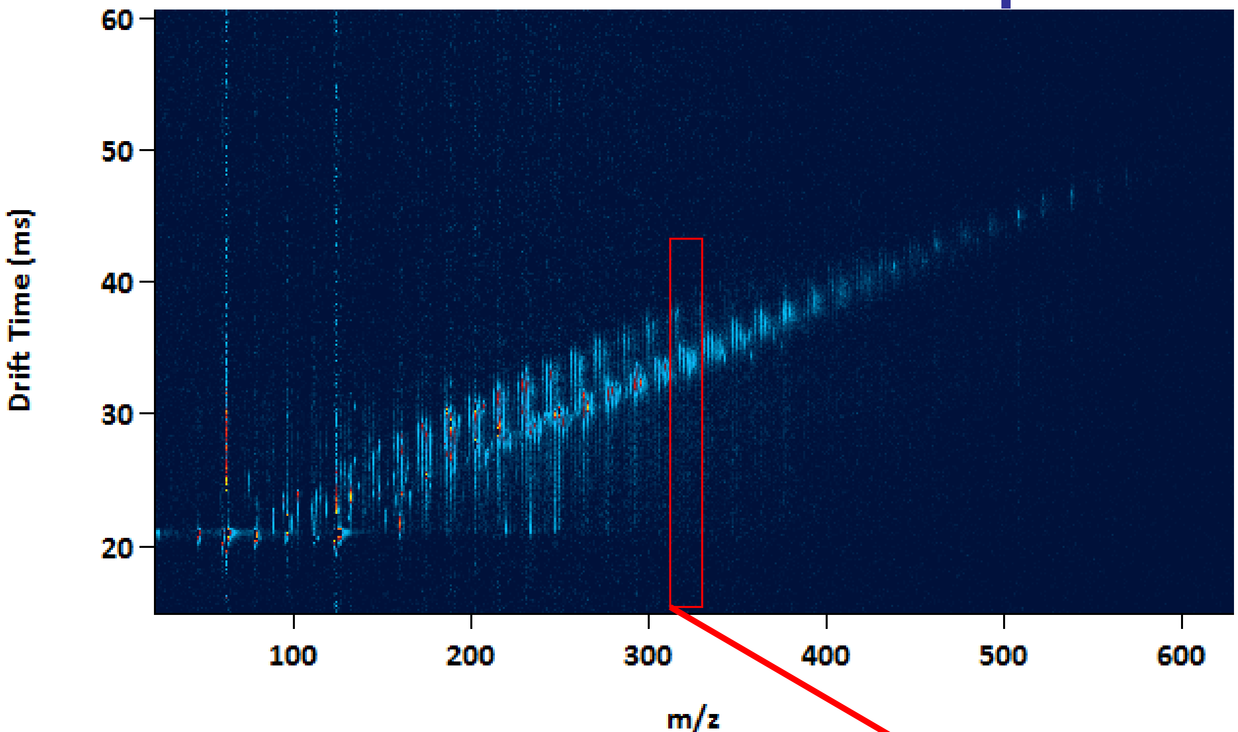


Shown here during MACR oxidation under high NOx conditions

SOAS 2013: IMS-TOF Spectra



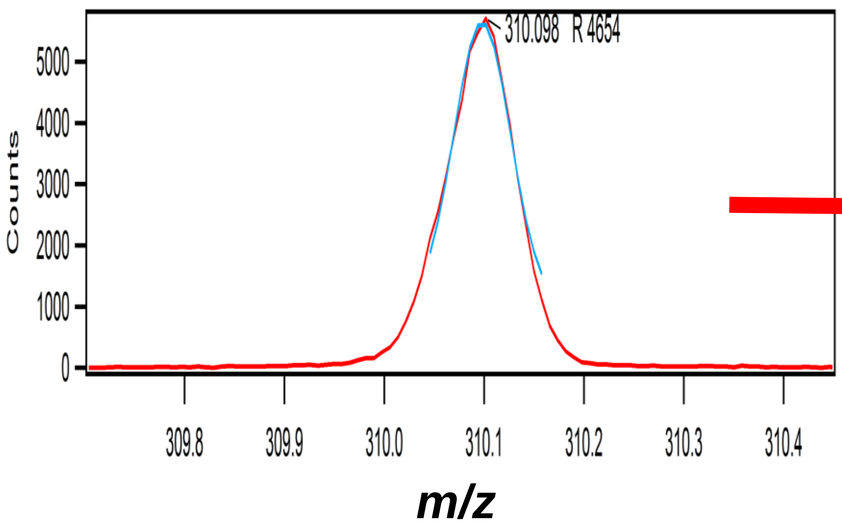
2-D Data every 5 minutes

IMS

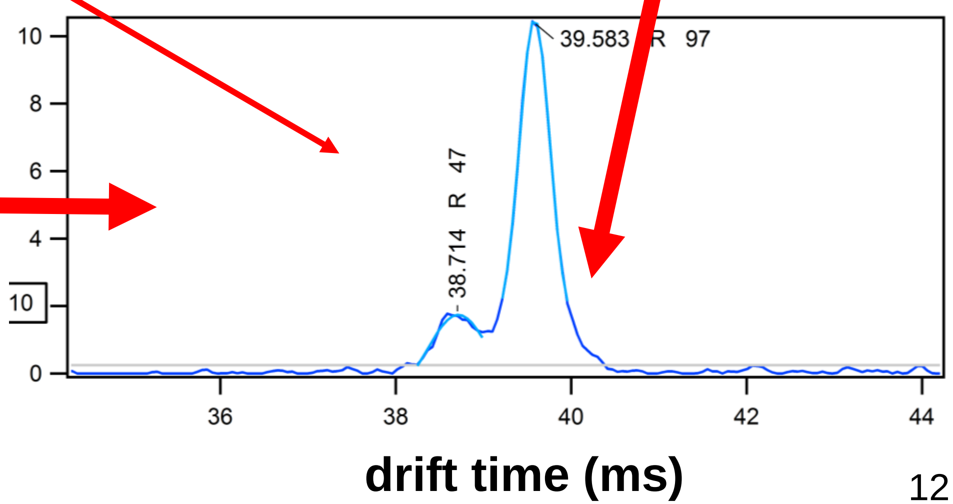
Two distinct species

$C_9H_{12}O_8$ and $C_{10}H_{16}O_7$

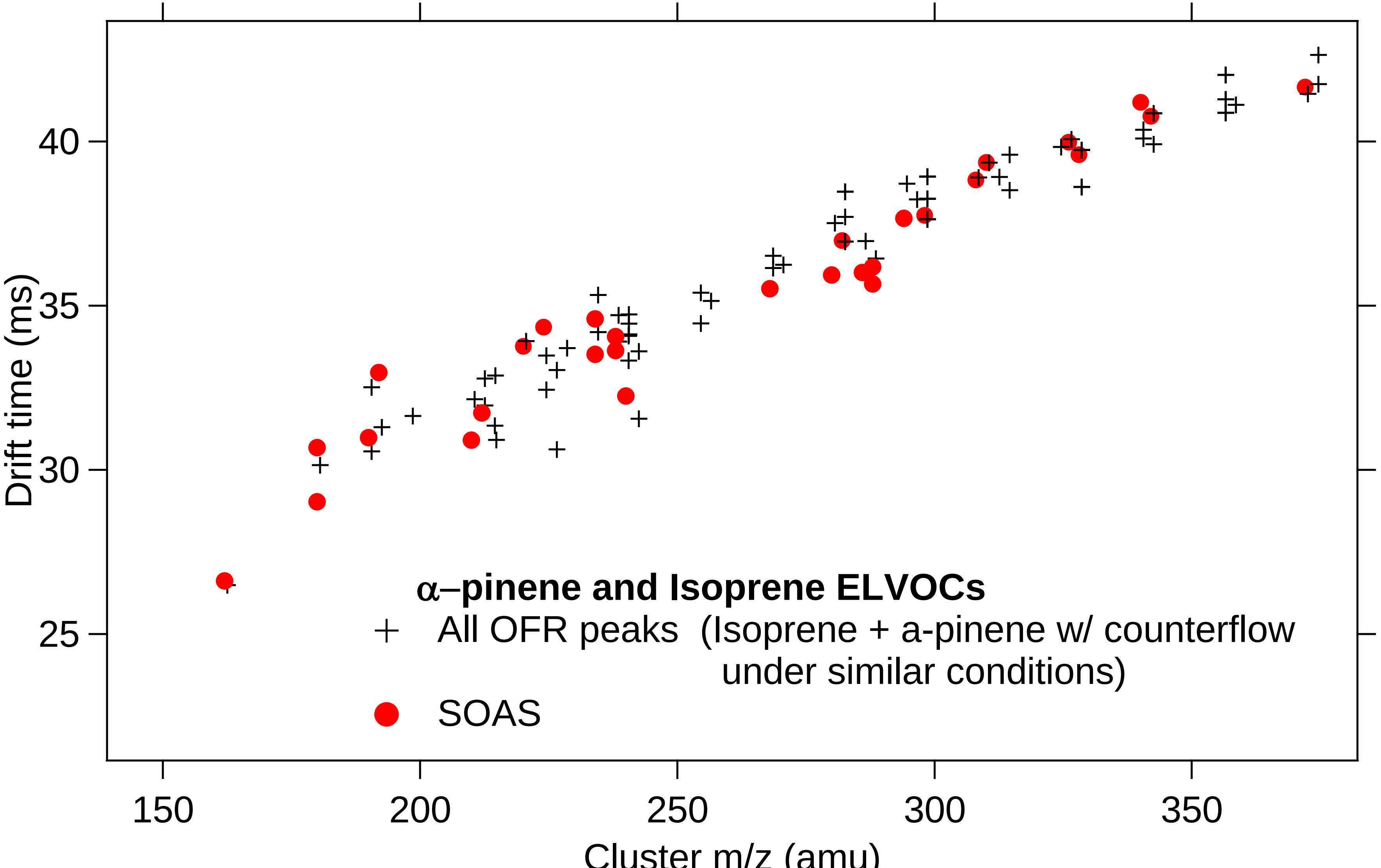
Dimension 1: HR- TOF-MS



Dimension 2: Ion Mobility Separation of Isobars



Lab and field IMS measurements for α-pinene-O3 monomers agree well



Initial Conclusions & Future Work

- We see isoprene and α-pinene ELVOCs throughout SOAS
- We can produce ELVOCs in chamber and laboratory
- Isoprene ELVOCs correlate with aerosol growth in lab experiments

- Quantitation of Isoprene ELVOCs
- Confirm molecular assignments (with IMS)
- Finalizing Isoprene peak list
- Application to SOAS organic aerosol growth: Is condensation of isoprene ELVOCs atmospherically relevant?

Thanks for your attention!

OSc vs C# and map isoprene, a-pinene, and organonitrate

Many of these oxidized organics condense on $(NH_4)_2SO_4$ seed

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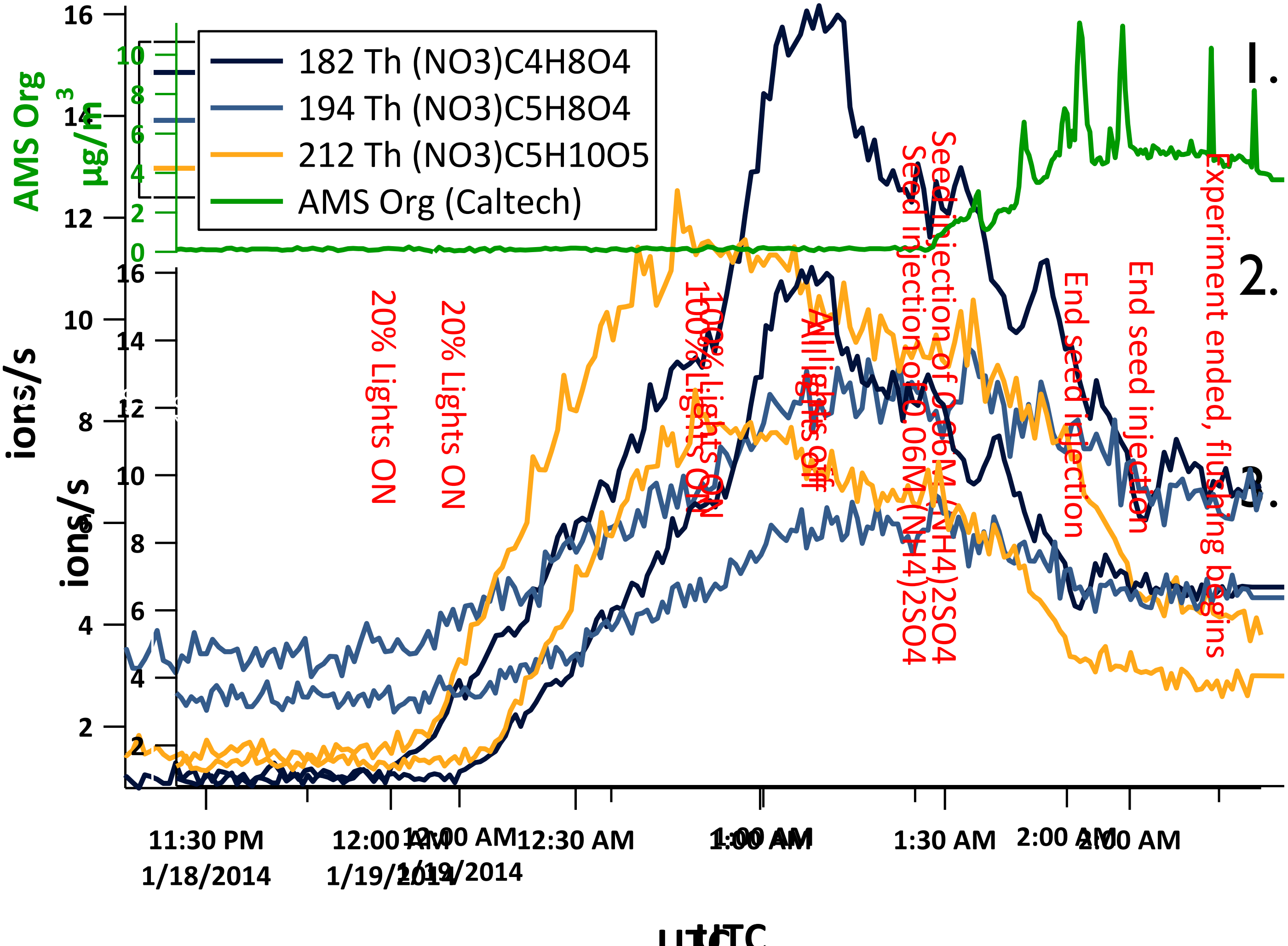
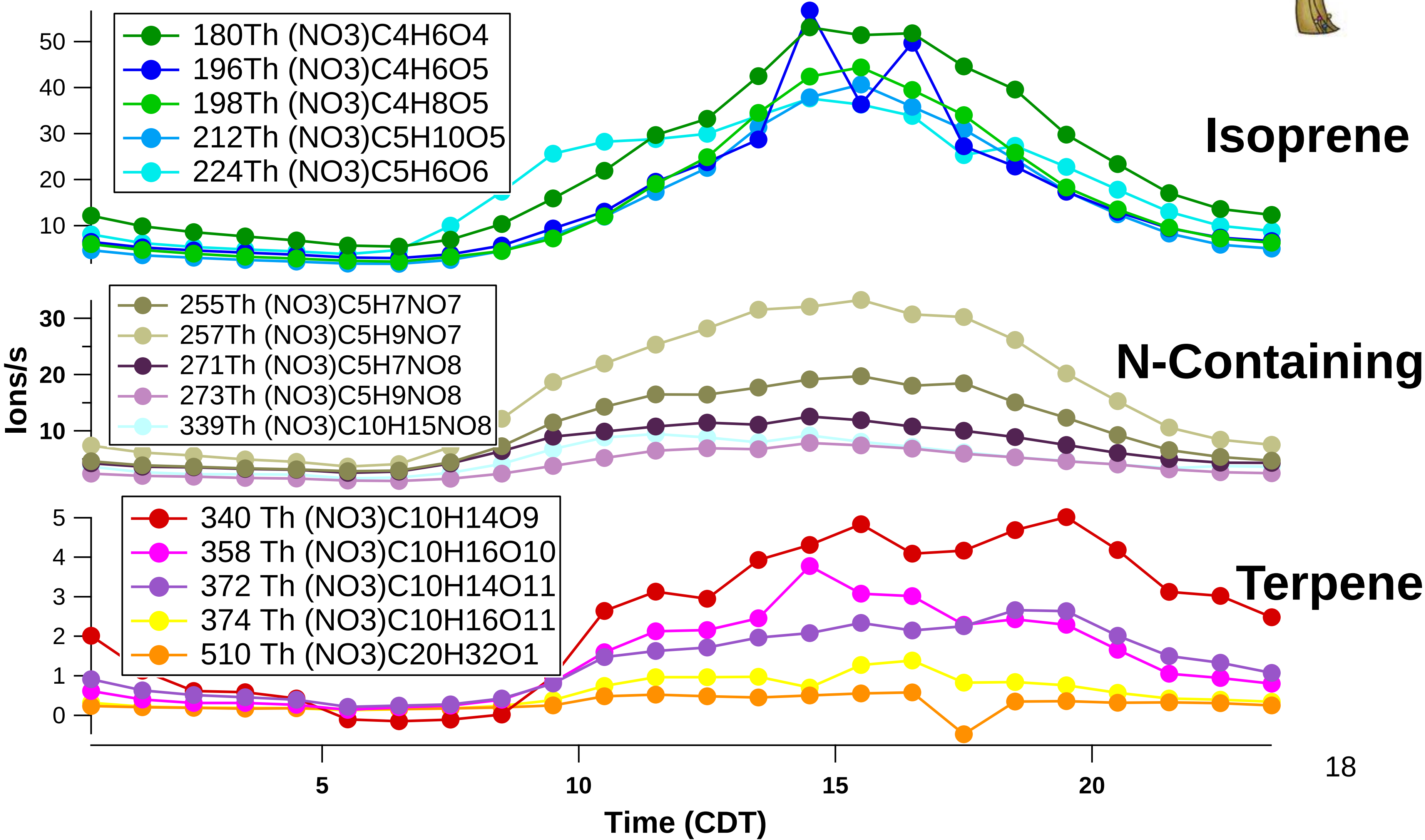
From Isoprene OH oxidation:

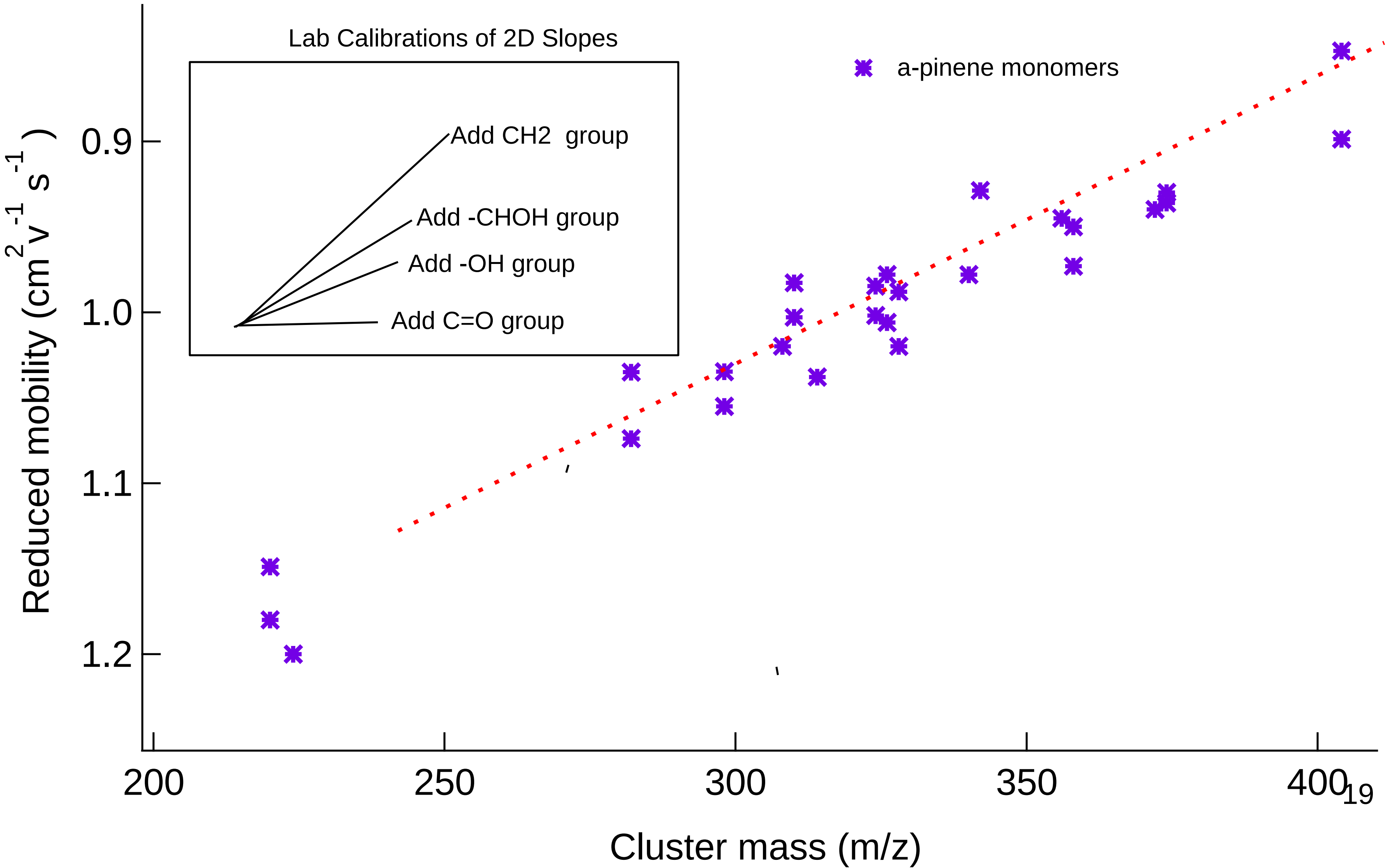


1. Isoprene ELVOCs are produced rapidly
2. Ammonium sulfate is injected into the chamber
3. ELVOC concentration declines and organic aerosol increases

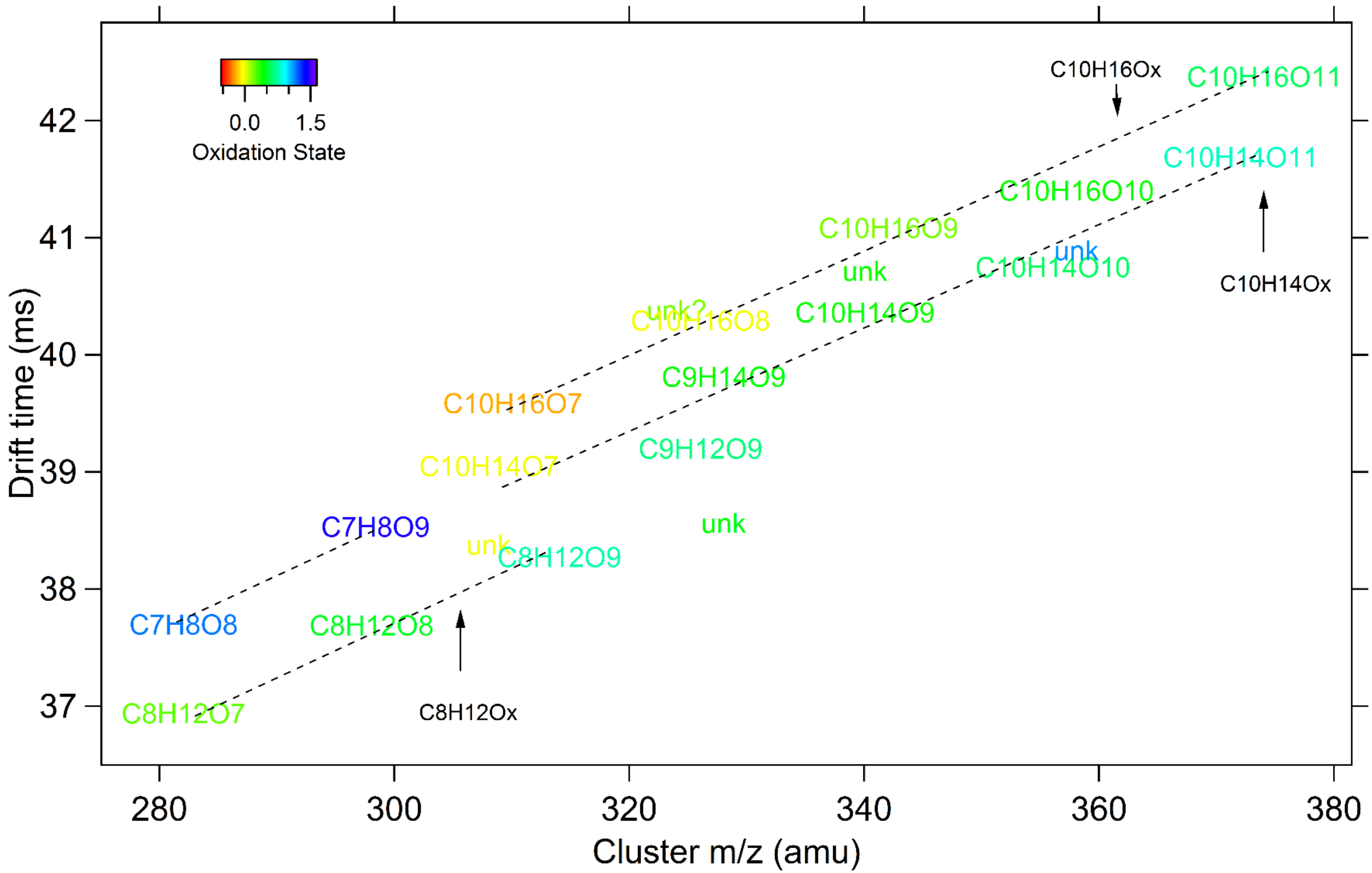
During SOAS we see three broad categories:



Ambient α-pinene trend lines



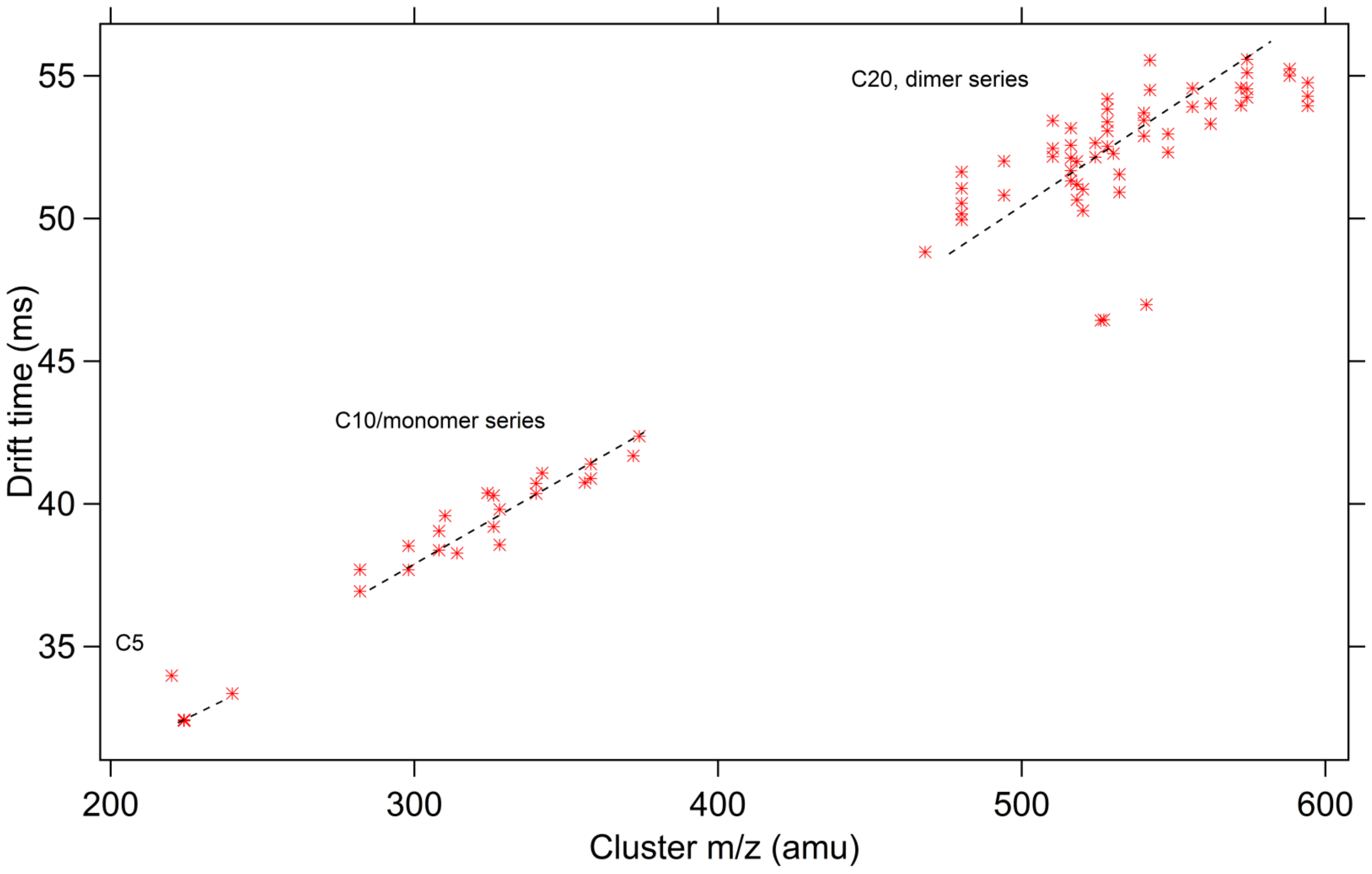
Ion Mobilities of Ehn et al. monomer Ions



Different ion series clearly separated according to drift times

Similar slopes indicate that species have similar chemical functionalities across all ion series|

All α-pinene peaks from Mikael



Ion mobilities measured for Dimers