

SP-AMS of rBC Particles From 6 Sources:

Refractory Carbon Clusters (C_x^+) and Oxygenated Ions (rCO_x^+)

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³IAST, FHNW, Switzerland

⁴DLR, Germany

⁵Aerodyne

Soot Sources

1. CAST "Black"

- Propane soot (C/O = 0.25)
~10% thermal OC¹

2. CAST "Brown"

- Propane soot (C/O = 0.41)
~30% thermal OC¹

6. Airplane-turbine soot

- Sampled at Zurich Airport from a short-range civil-aviation engine.

3. Spark-generated soot

- PALAS GFG 1000, diesel-like morphology²

4. "Regal Black"

- Carbon black (SP-AMS calibration)³

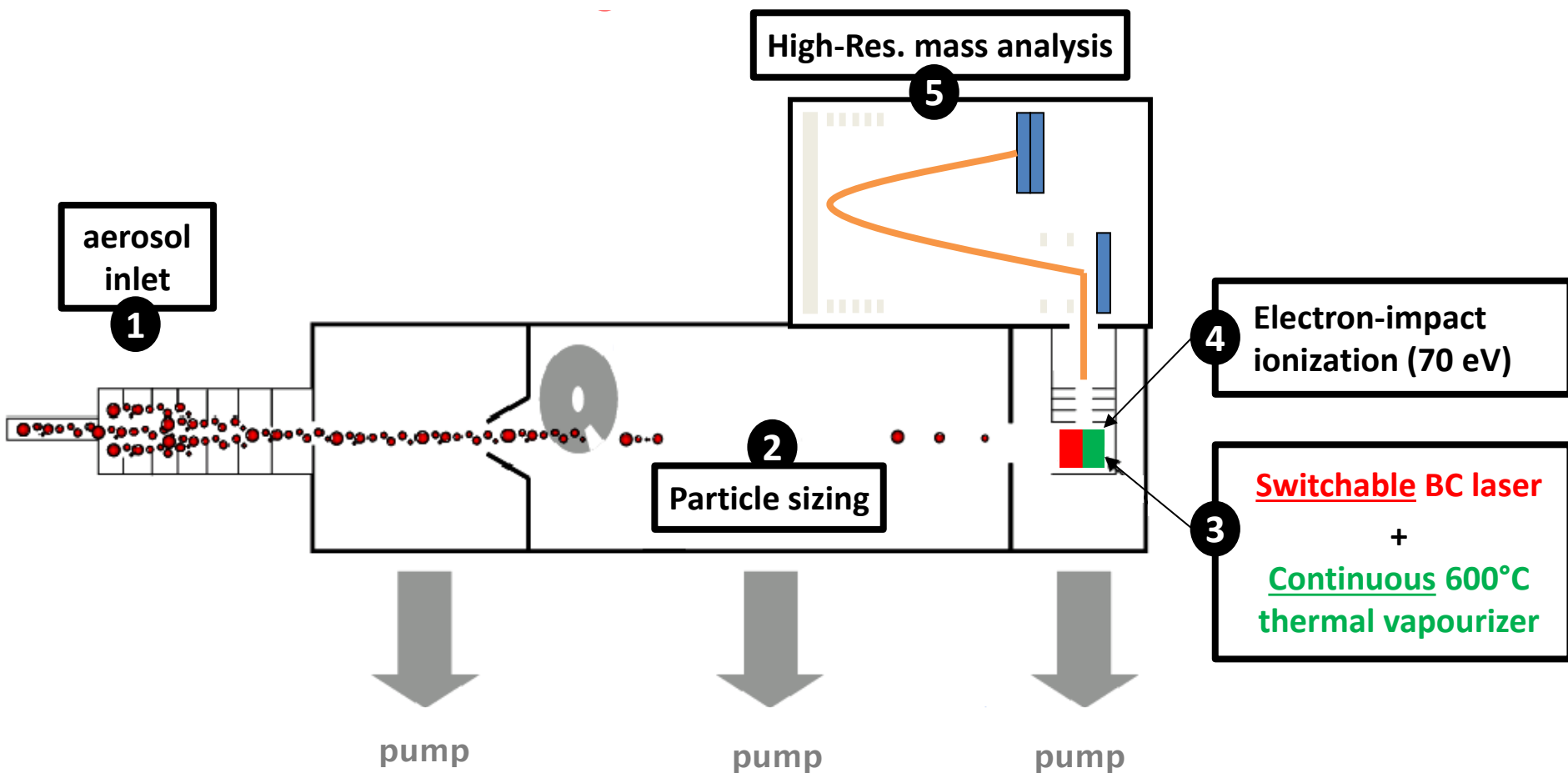
5. Fullerene-enriched soot

- C₆₀ and C₇₀ (6 and 1% each) enriched soot.⁴
- SP2 calibration.⁵

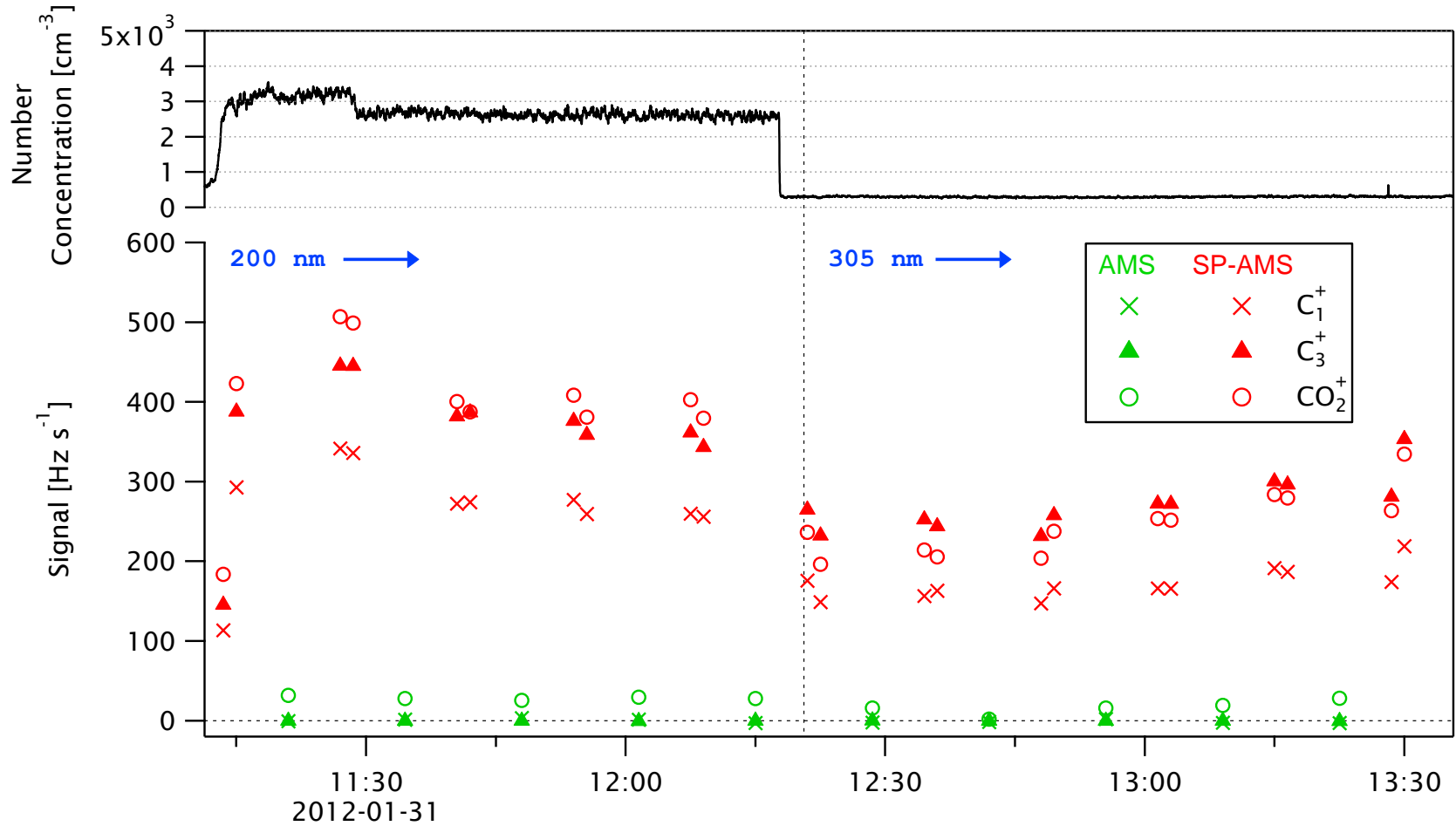
¹Schnaiter et al., 2006 ACP; ²Helsper et al., 1993; ³Onasch et al., AST 2012;

⁴Krätschmer et al., 1990 Chem. Phys. Lett., ⁵Laborde et al. AMT 2012

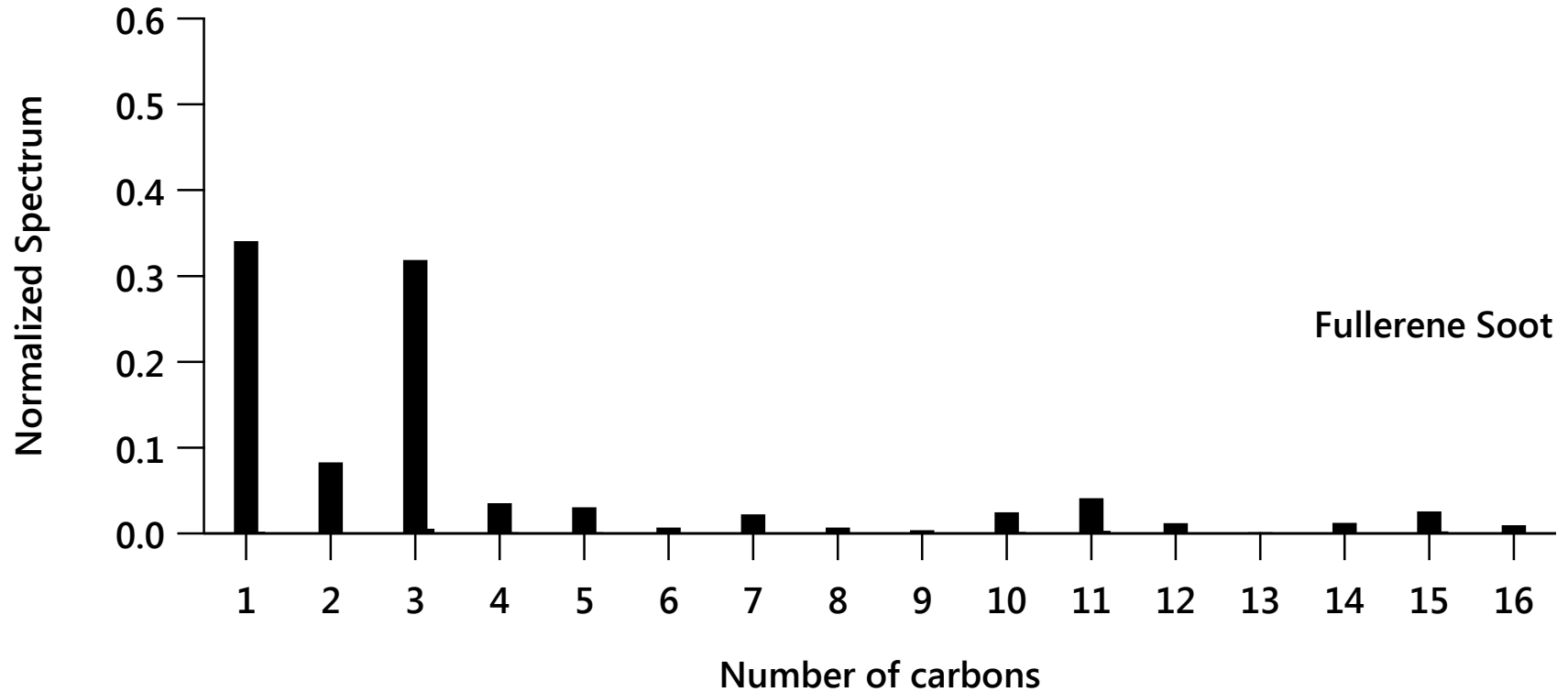
The **Soot-Particle** Aerosol Mass Spectrometer: **SP-AMS**



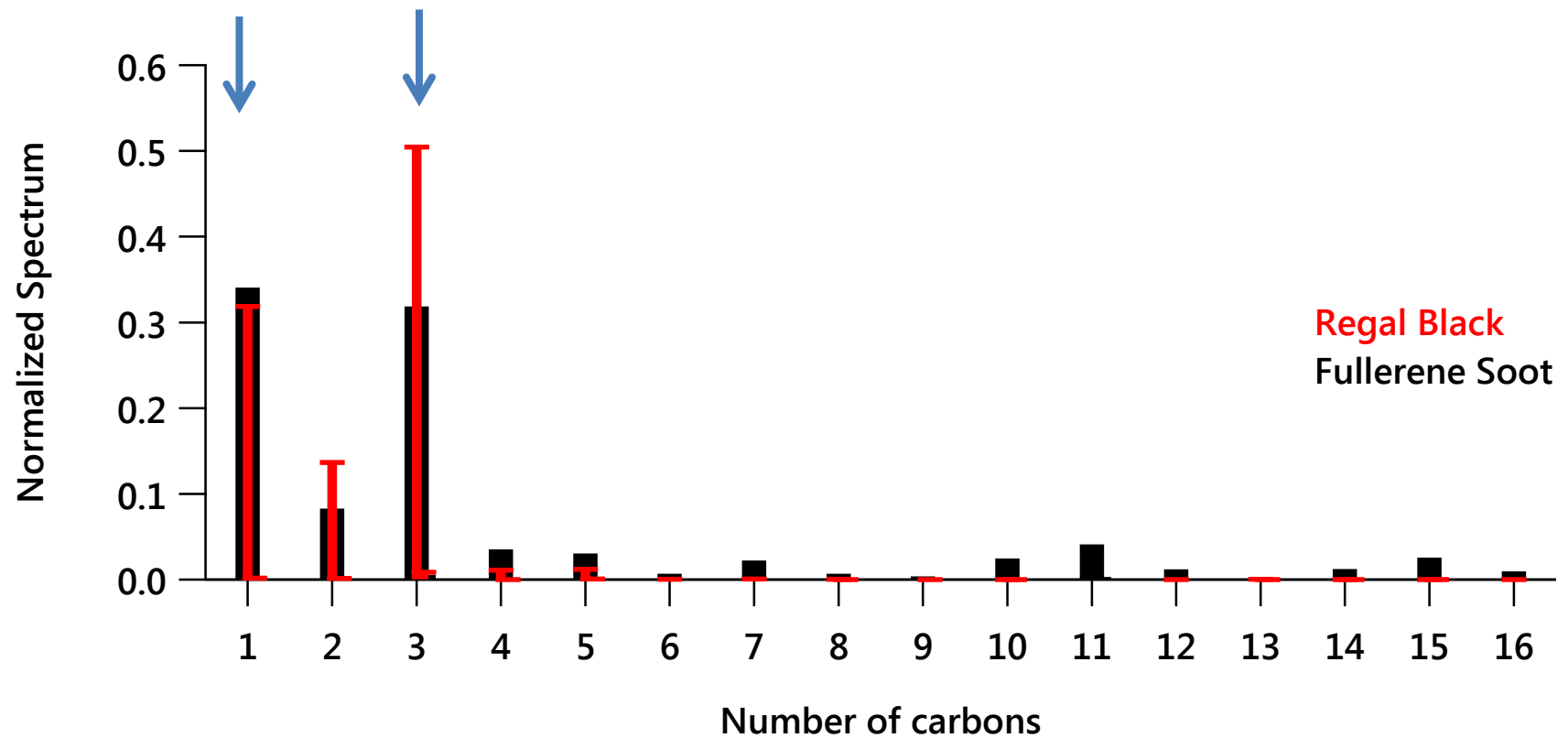
Switching between SP-AMS and AMS modes



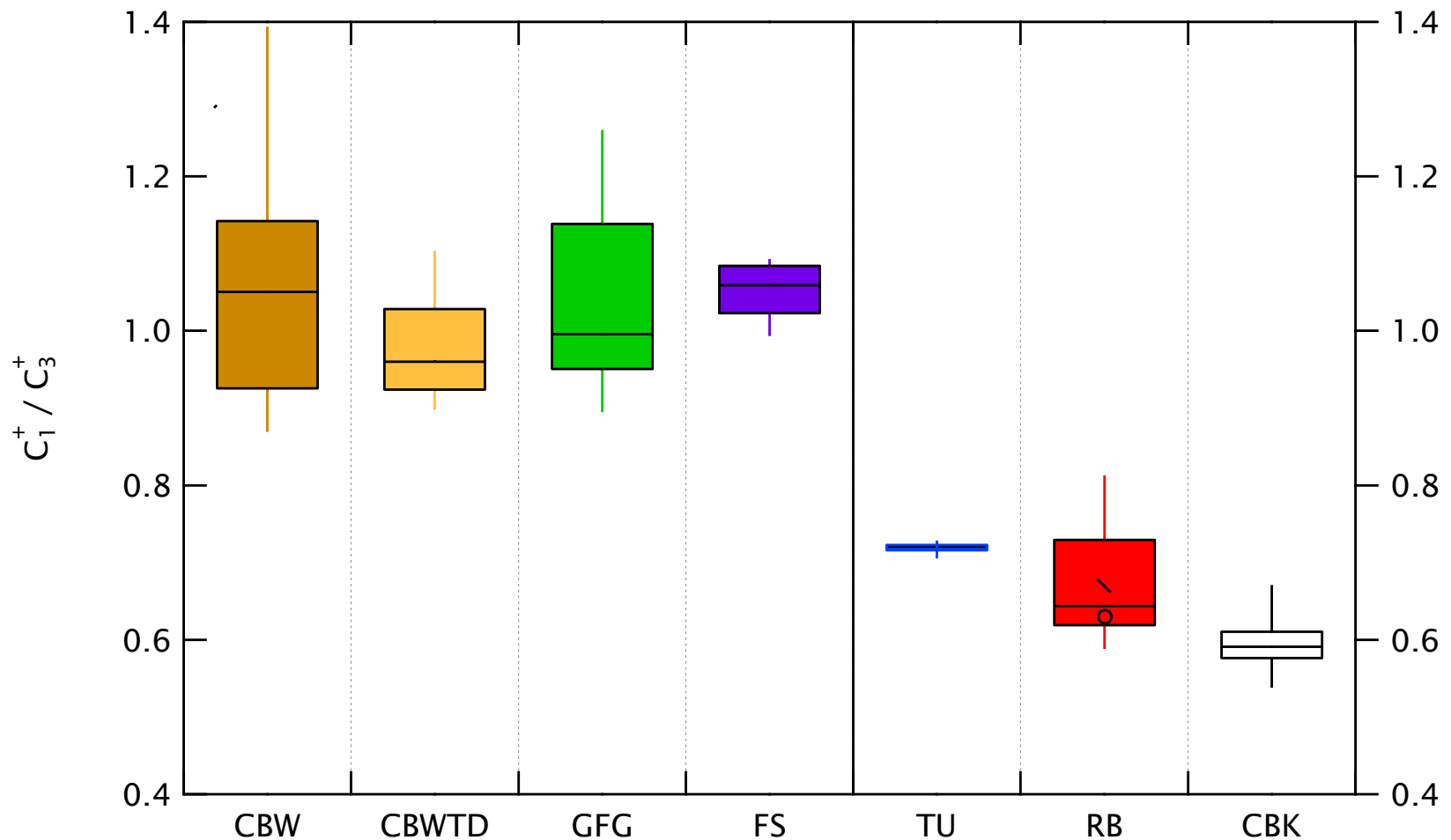
Carbon-cluster (C_x) MS ($m/z < 200$)



Carbon-cluster (C_x) MS: two trends

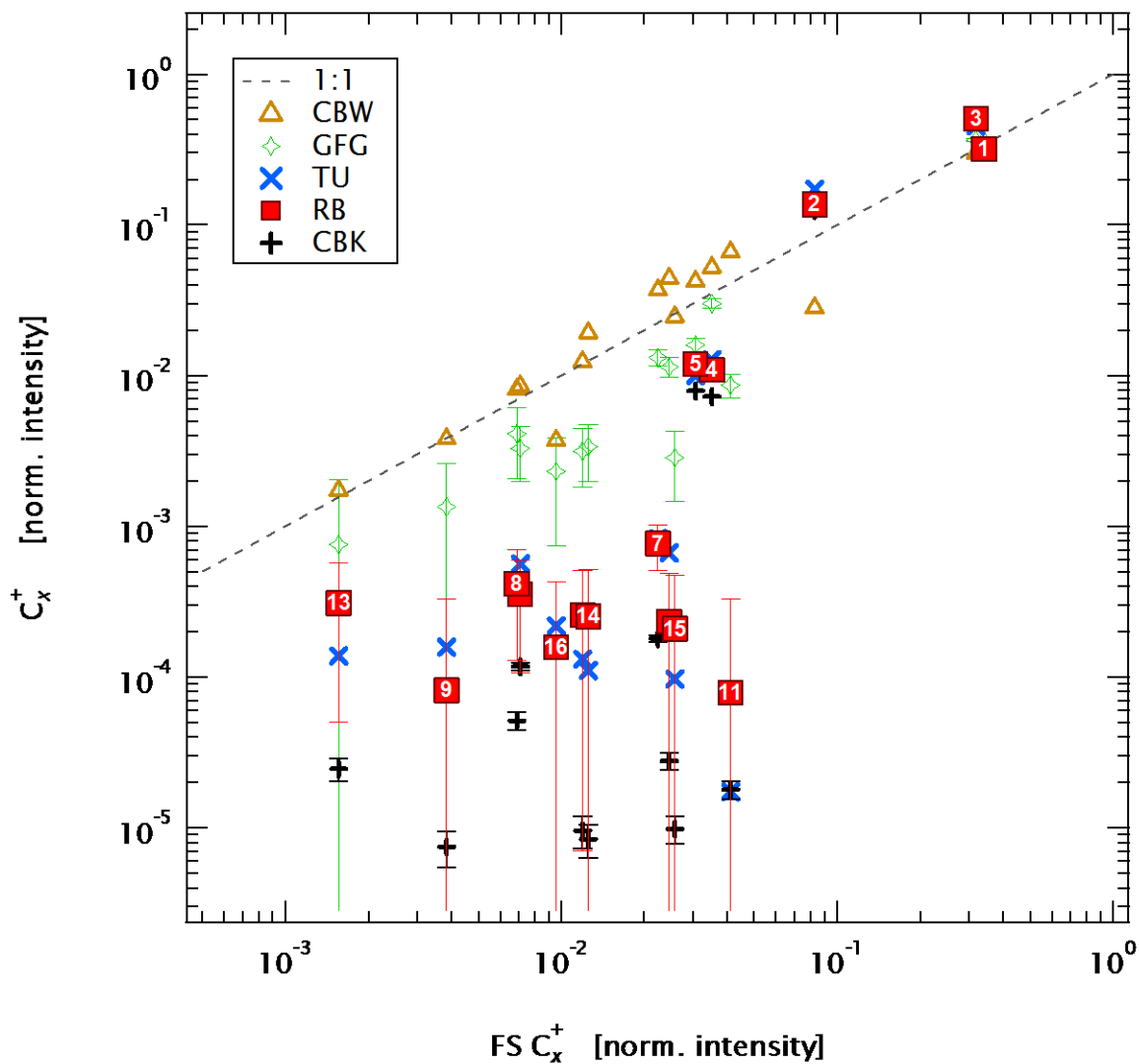


C_1^+ / C_3^+ ratio: two regimes (~ 0.7 , ~ 1.0)



*CBW = fuel-rich propane CAST; CBWTD = thermodenuded CBW; GFG = spark-generated
FS = Fullerene-enriched soot; TU = aircraft turbine; RB = Regal Black; CBK = CAST black*

Carbon-cluster (C_x) MS: two trends



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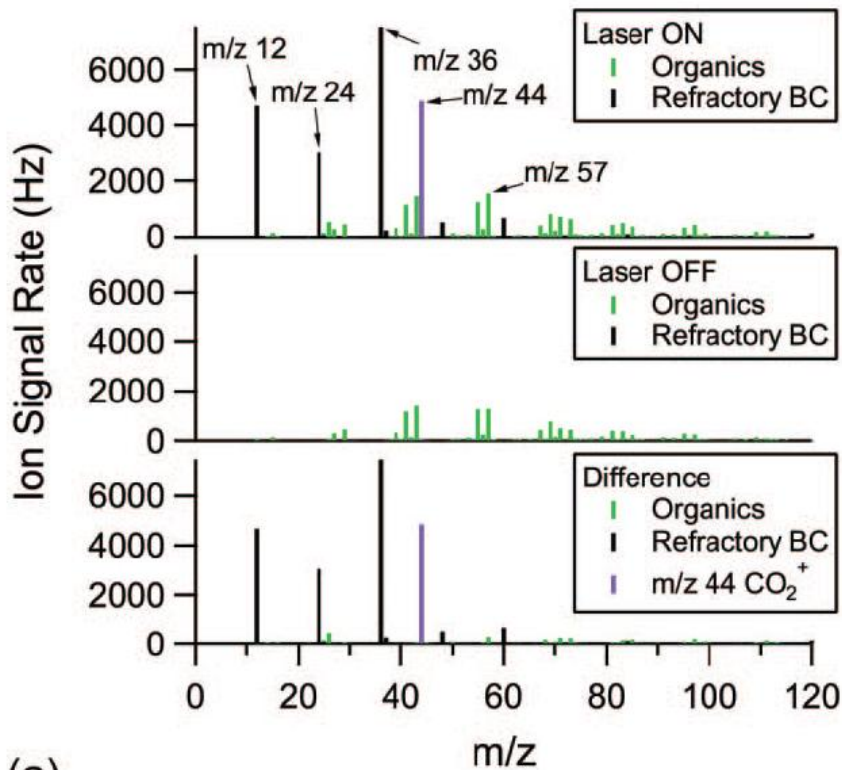
²LAC, PSI, Switzerland

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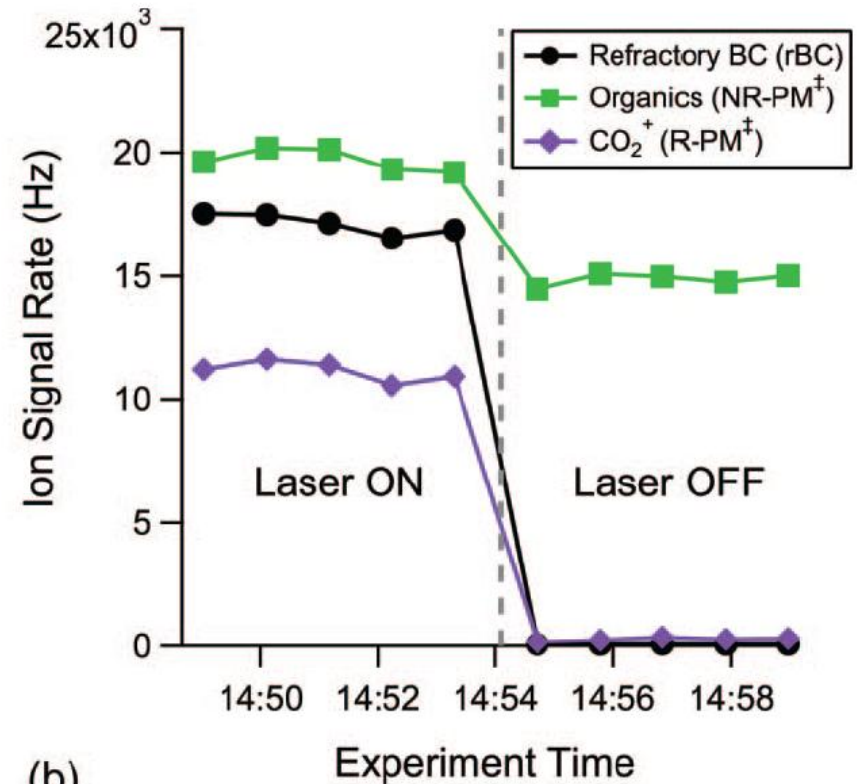
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RB rCO₂⁺ already established by Onasch et al. [2012]

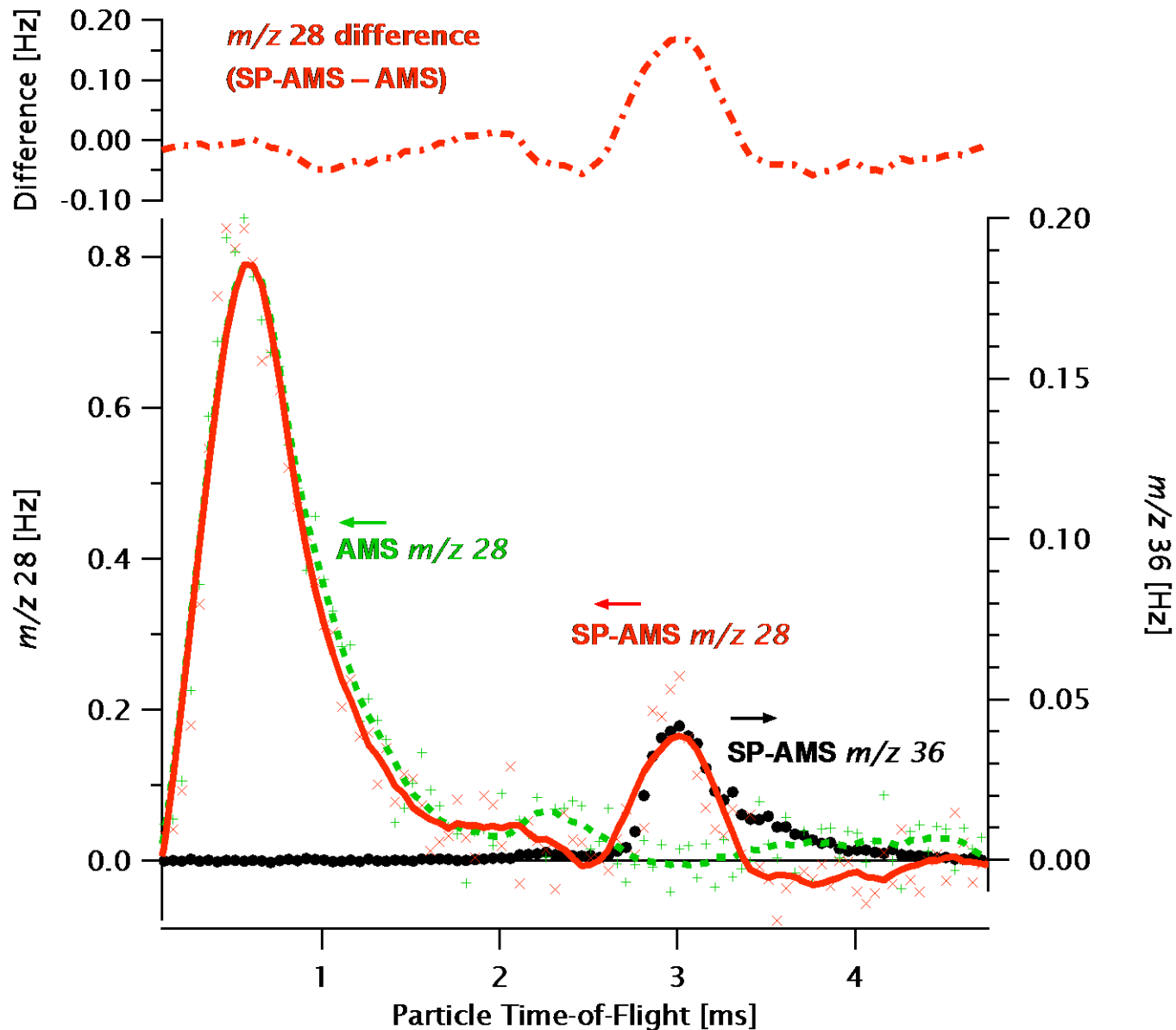


(a)

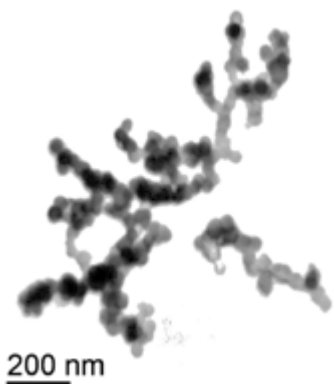


(b)

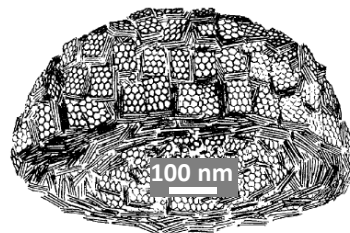
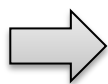
Refractory CO⁺ signals from RB



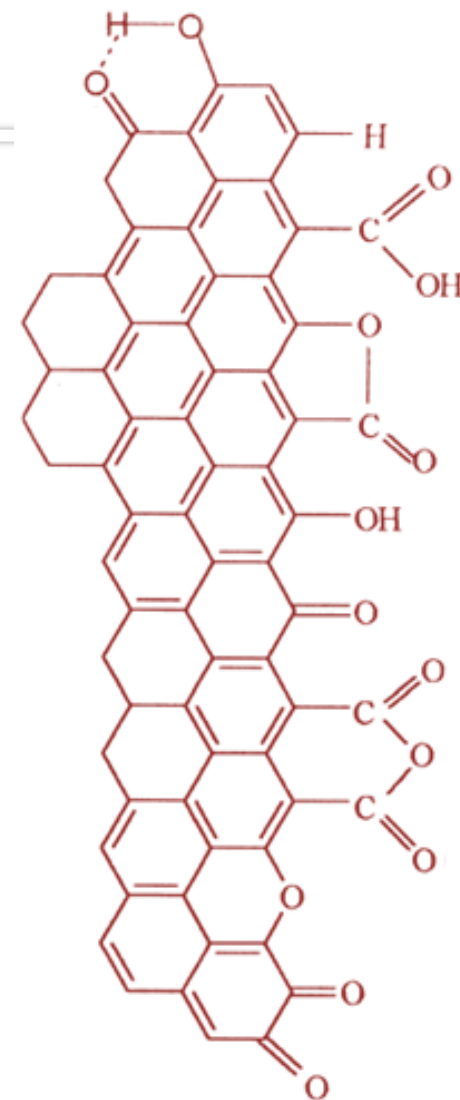
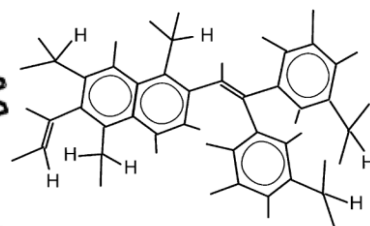
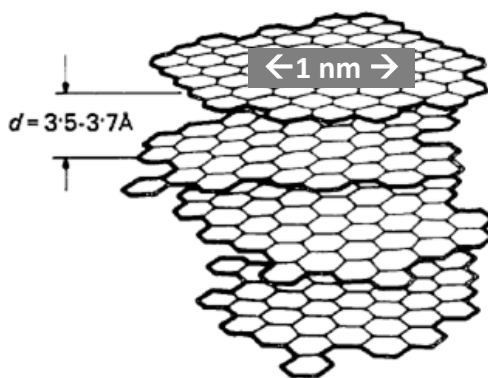
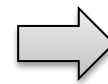
Proposed origin of refractory CO⁺



Wood-stove particle¹



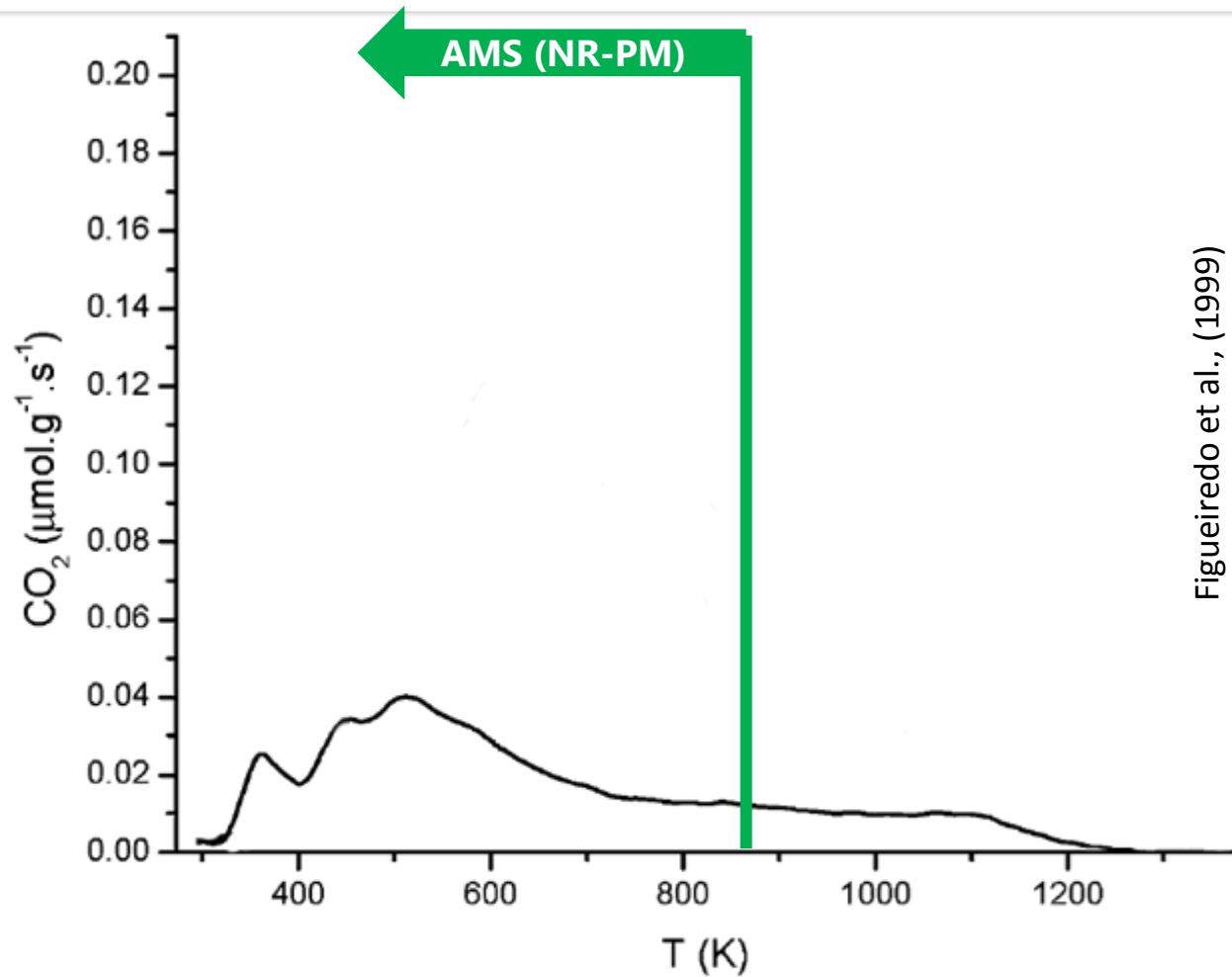
graphitic/amorphous-carbon backbone^{2,3}



Oxidized surface groups
decomposition^{4,5} into CO and CO₂
at 500–1200 K [5 K min⁻¹]

- (1) Zelenay et al., ACP 2011
- (2) Heidenreich et al., JAC 1968
- (3) Robertson, MSER 2002
- (4) Figueiredo et al., Carbon 1999
- (5) Corbin et al., 2013

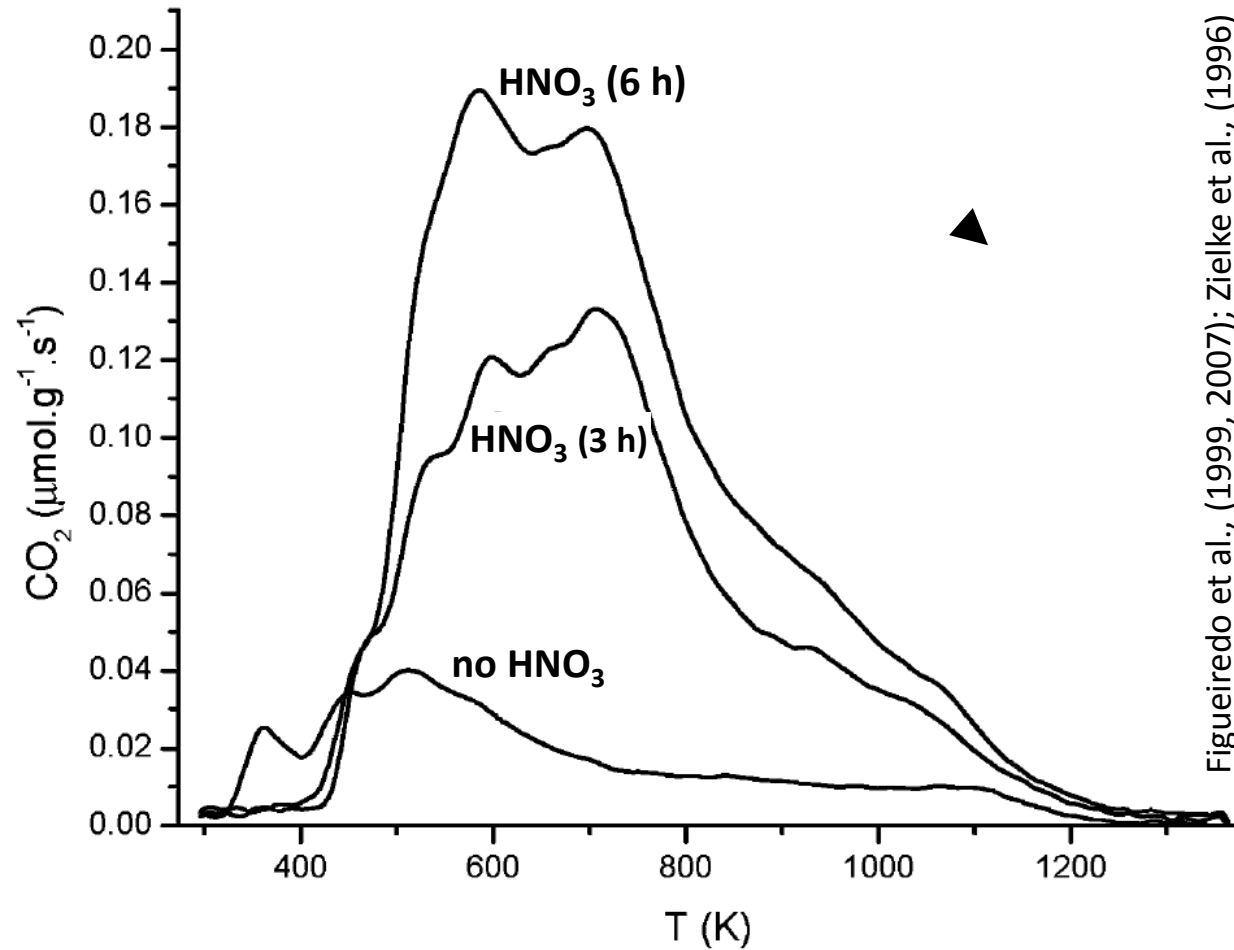
rCO₂ observed from soot heated at 5 K min⁻¹



Figureiredo et al., (1999)

“Temperature-Programmed Desorption”

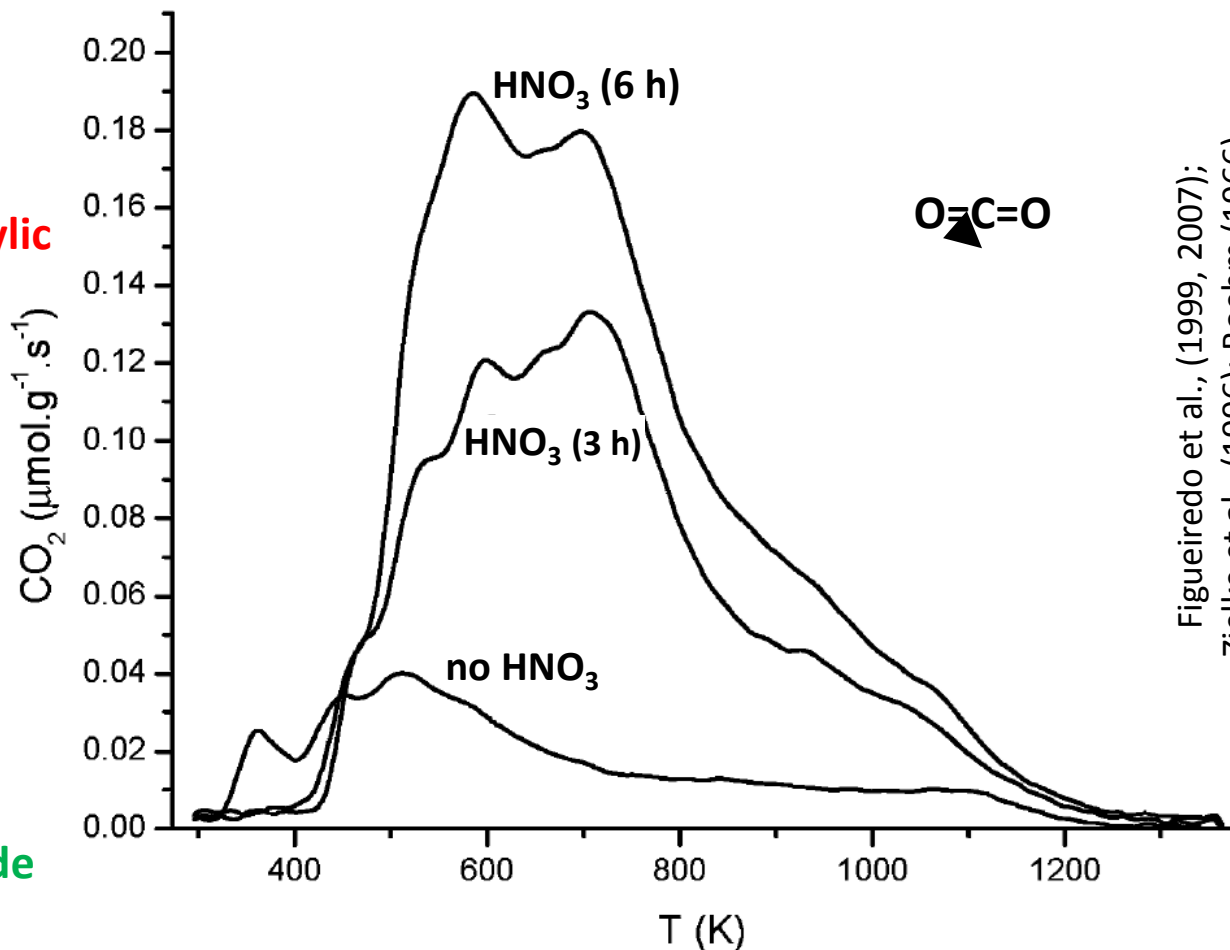
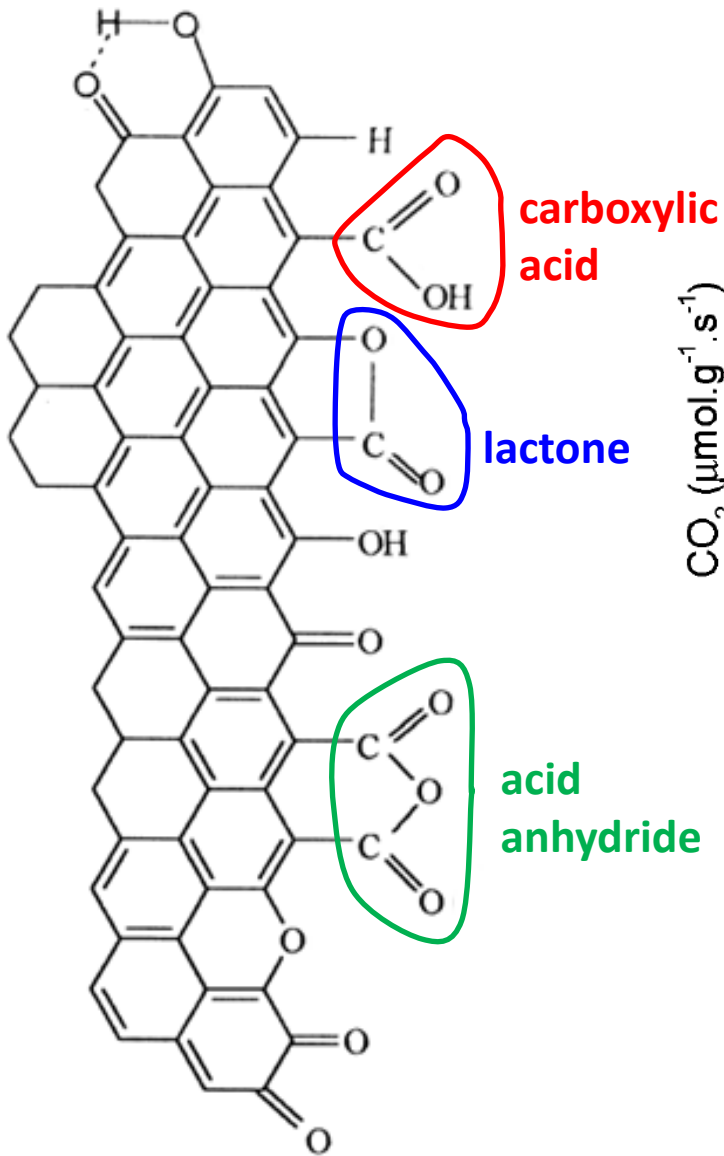
rCO₂ observed from soot heated at 5 K min⁻¹



Our Regal Black sample is HNO₃-treated

Figueiredo et al., (1999, 2007); Zielke et al., (1996)

Refractory moieties



↑
strong acid

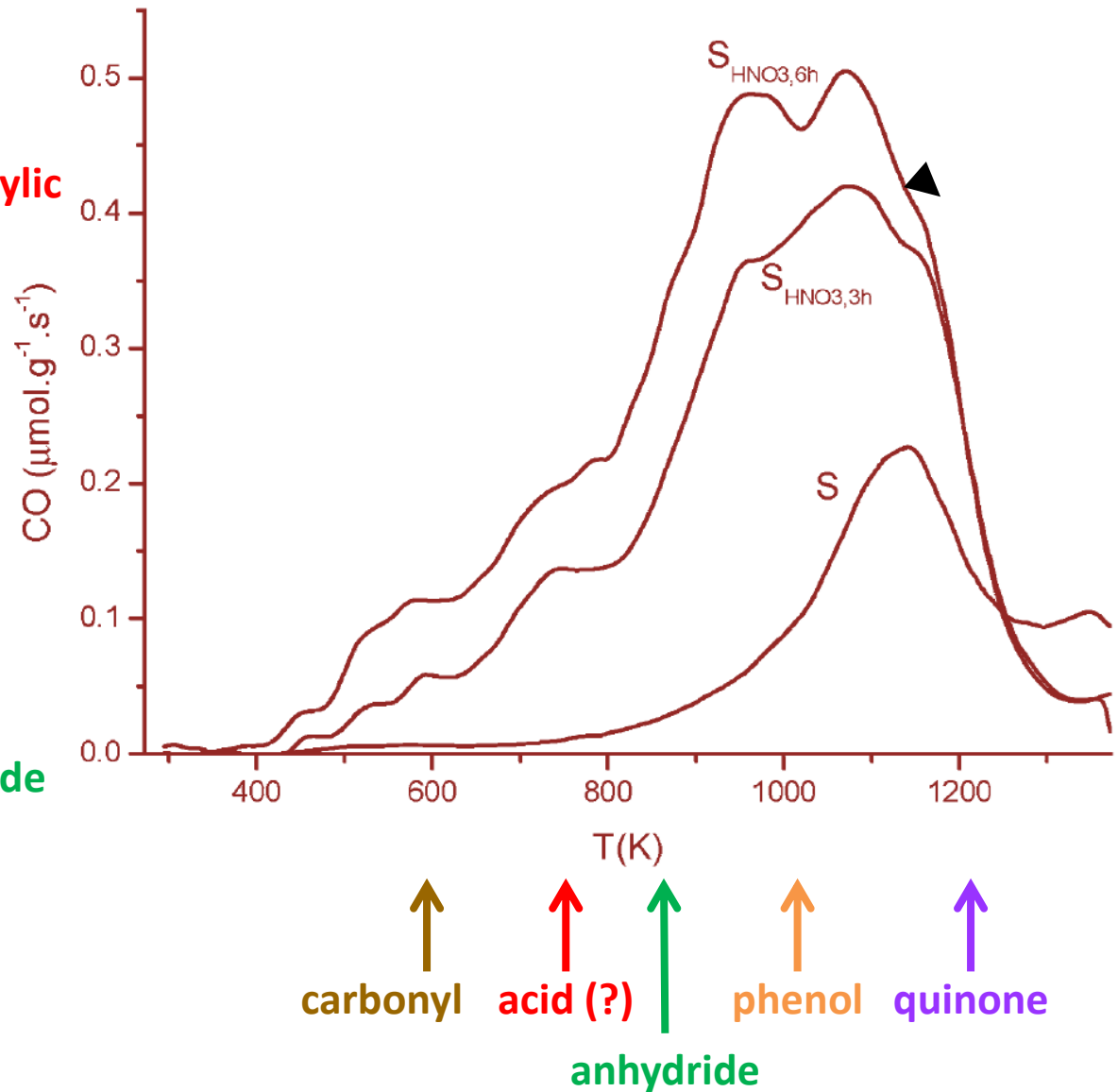
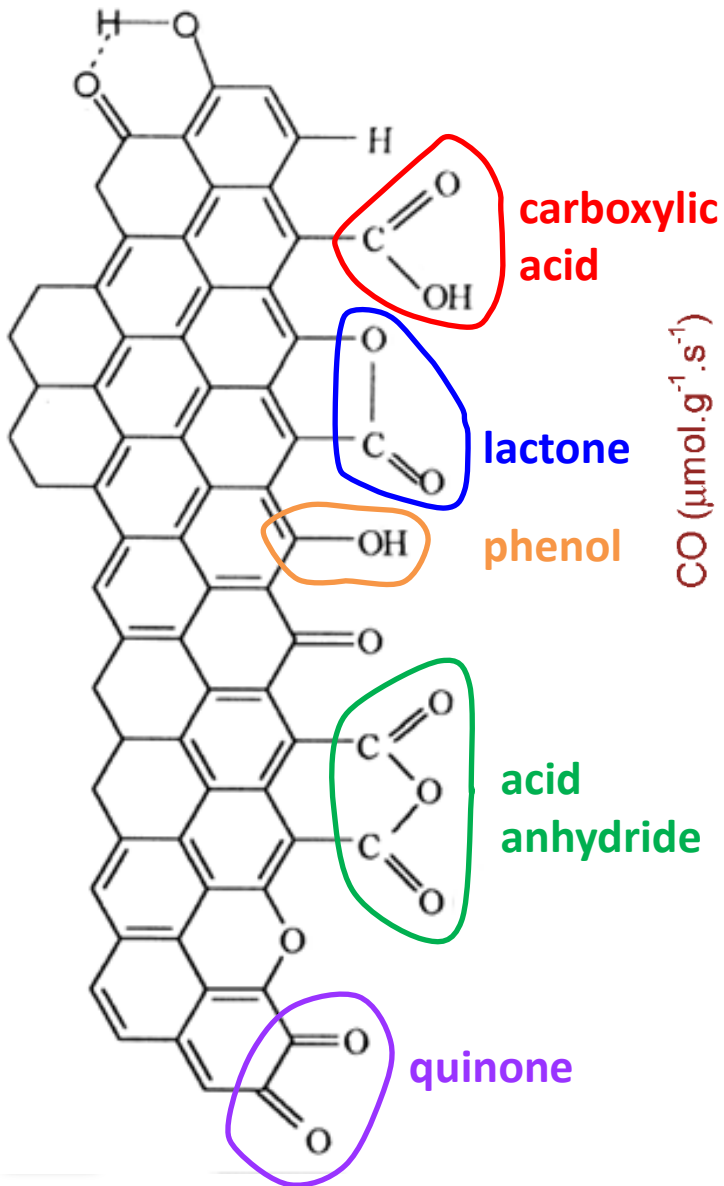
↑
weak acid

↑
anhydride

↑
lactone

Figueiredo et al., (1999, 2007);
Zielke et al., (1996); Boehm (1966)

Refractory moieties



Figueiredo et al., (1999, 2007);
Zielke et al., (1996); Boehm (1966)

Take-home messages

1. $\{C_1^+\}$ is not universally $= 0.625 * \{C_3^+\}$
 1. PIKA frag should be checked
2. Carbon fragmentation patterns may distinguish soot sources, as expected
3. TPD results indicate that rCO_x should vapourize at $\ll 4000$ K
 - Different RIE?