Towards a reference material for soot/LAC measurement: Evaluation of candidates with electron microscopy, SP2 and TOA

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9th International Conference on Carbonaceous Particles in the Atmosphere
August 2008

Acknowledgments

- Civilian Research and Development Fund

Motivation

- Strongly light-absorbing carbon (LAC)/soot an important player in climate change, air quality, health effects and visibility
- LAC measurements often operationally-defined
  - Thermal-optical methods can produce 2x different results
- Lack of reference material impeding progress on understanding method biases

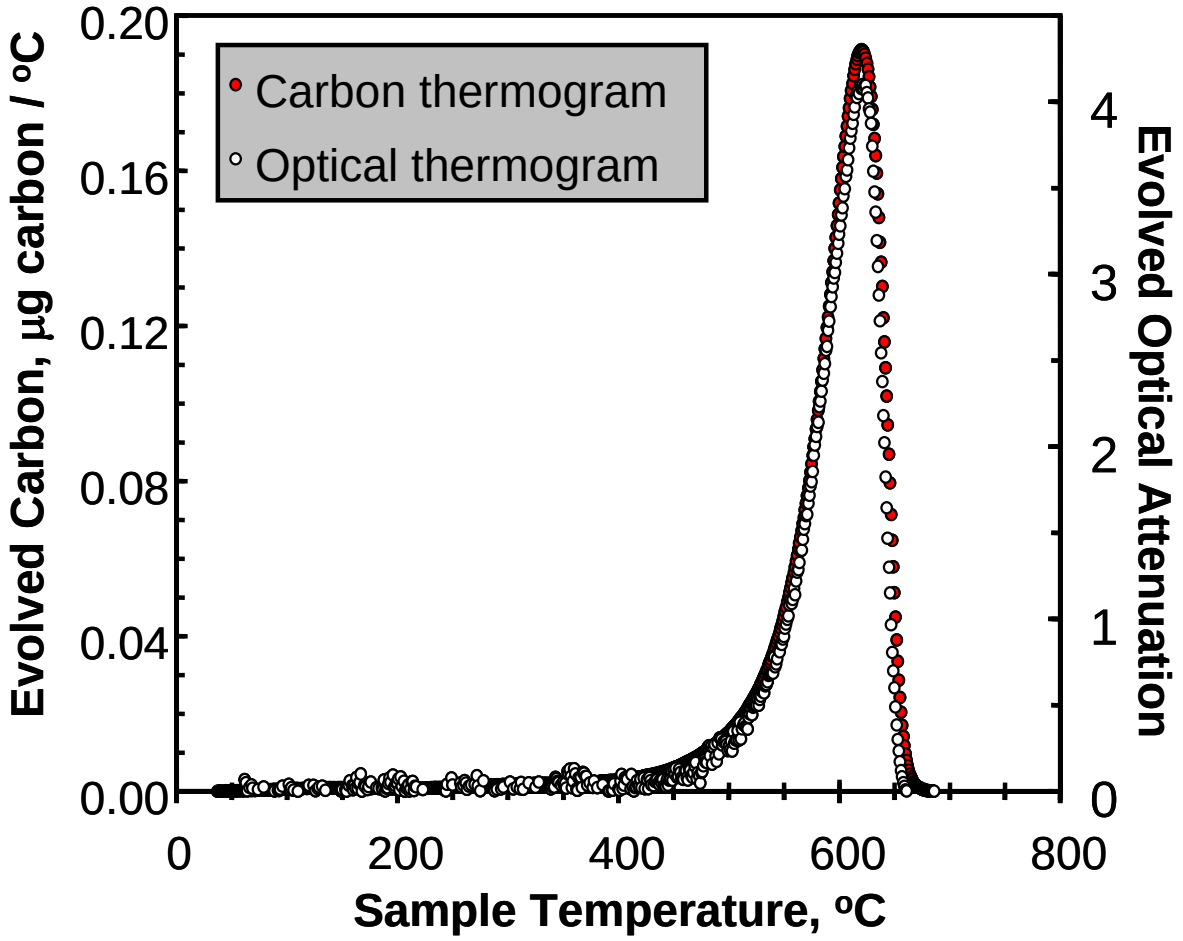
LAC reference material: requirements

- Known composition and density
- Well-characterized shape
  - Helps correctly identify mass of particles selected through a DMA
- Physical characteristics similar to LAC
  - Refractory
  - Optical properties
- Manufacturing:
  - Reproducible size distribution, easily obtained
  - Size-controlled (monodisperse) production
- Usability:
  - Stable over extended periods of time
  - Dispensable (easily mixes with water)
- Previous work: Black Carbon Steering Committee
  - http://www.geo.unizh.ch/phys/bc/
  - n-hexane soot
  - Wood and grass chars

Candidates

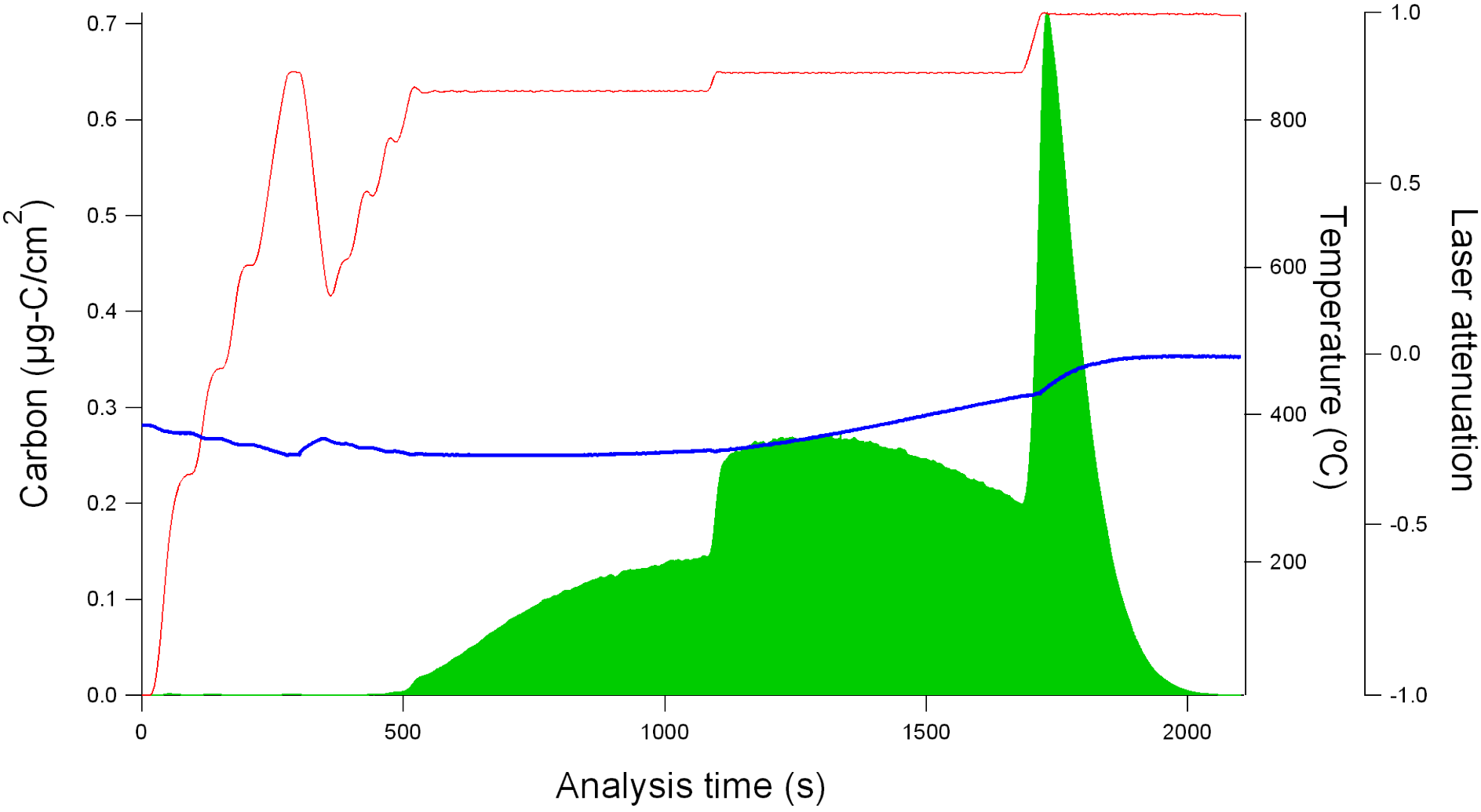
- Glassy carbon
  - Alfa Aesar©, Tokai©
- Fullerene soot
  - Alfa Aesar©
- Acheson Aquadag©
- Graphitized thermal soot (GTS)
  - Moscow State University
- Diffusion flame-generated (“Magic”) soot
  - Lawrence Berkeley National Laboratory

Magic soot: All EC



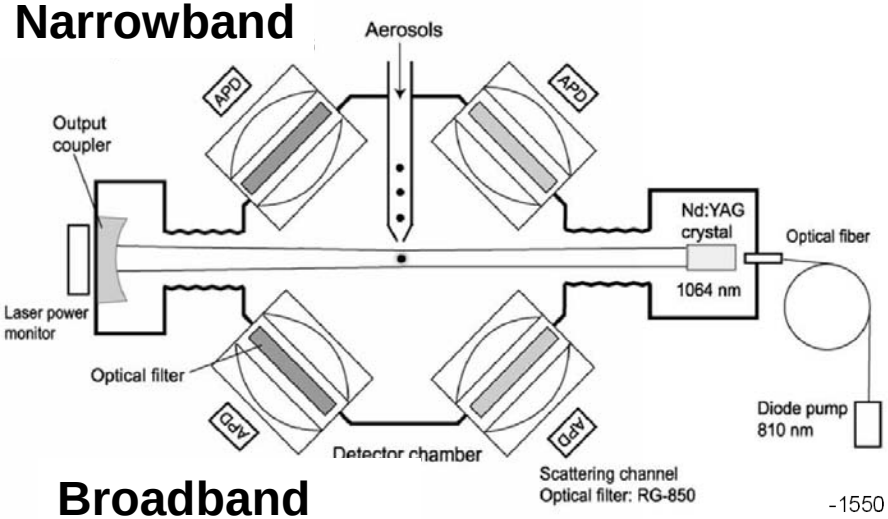
Kirchstetter & Novakov, “Evaluating and Improving Measurements of Black Carbon.” American Geophysical Union, 2007.

GTS composition: ~100% EC



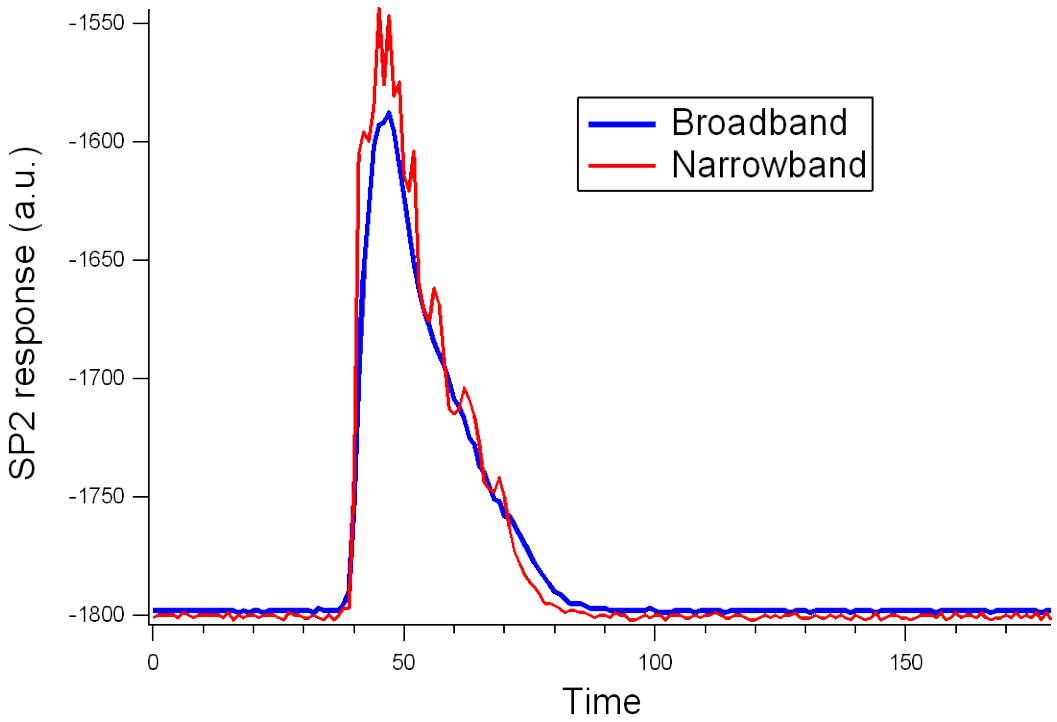
Identifying LAC with the SP2

Narrowband

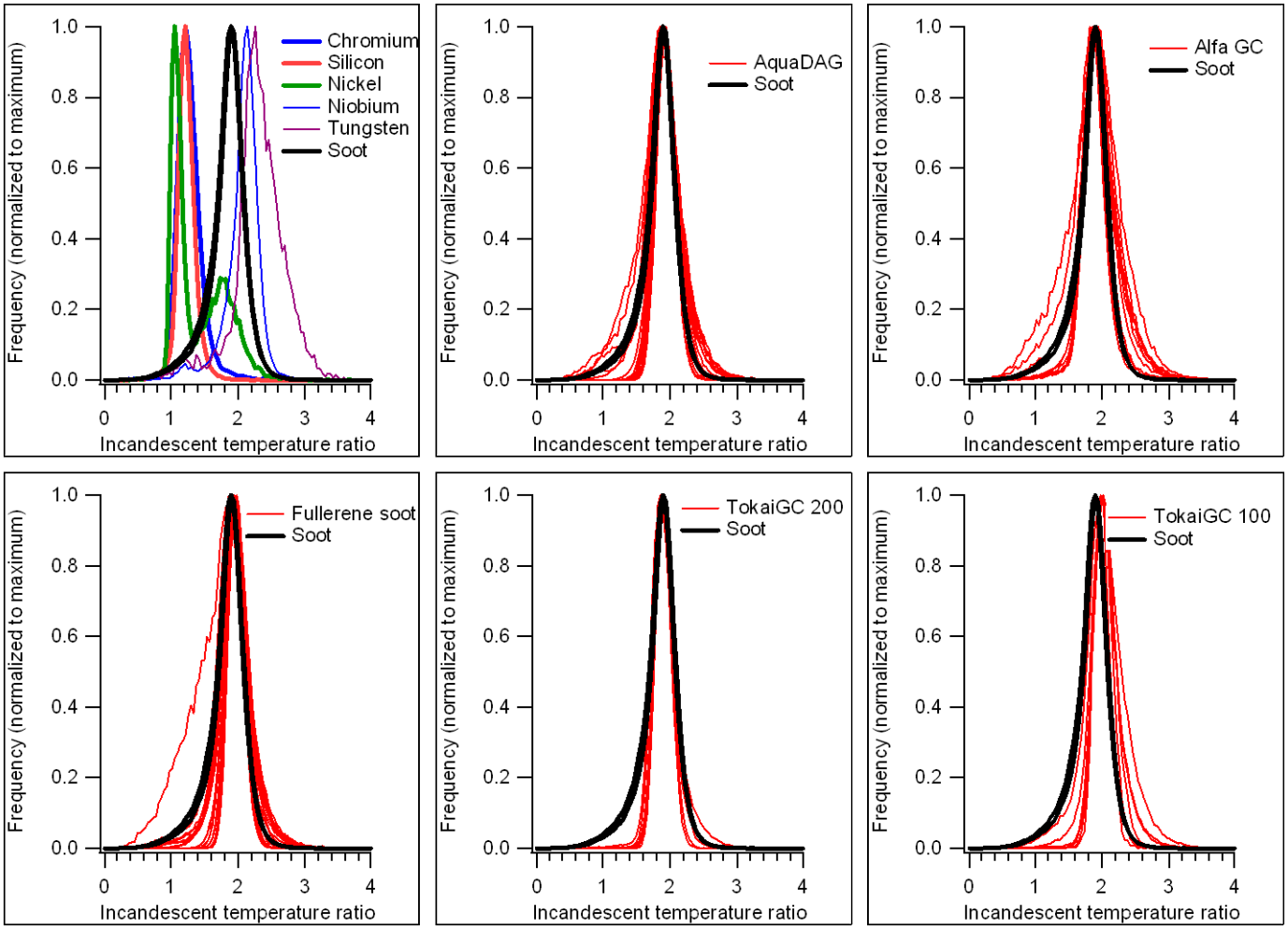


Broadband incandescence

Schematic from Moteki & Kondo (2007)

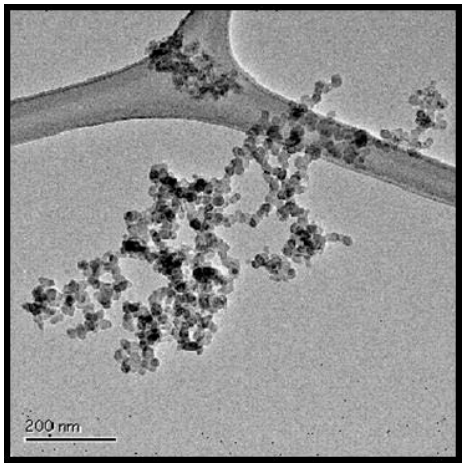


Reference materials and combustion (magic) soot behave similarly in the SP2

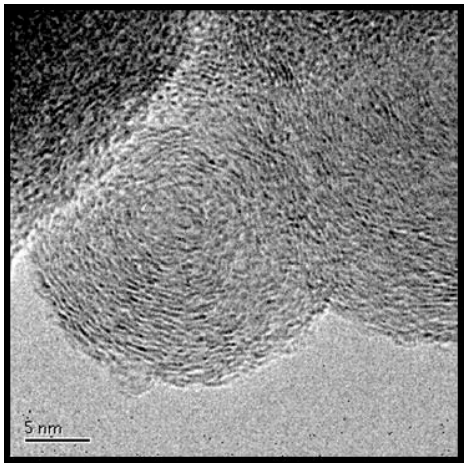


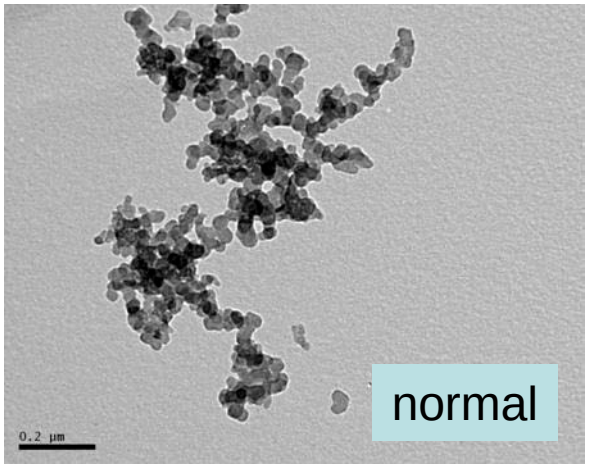
Thick black curve: Magic soot

Magic soot

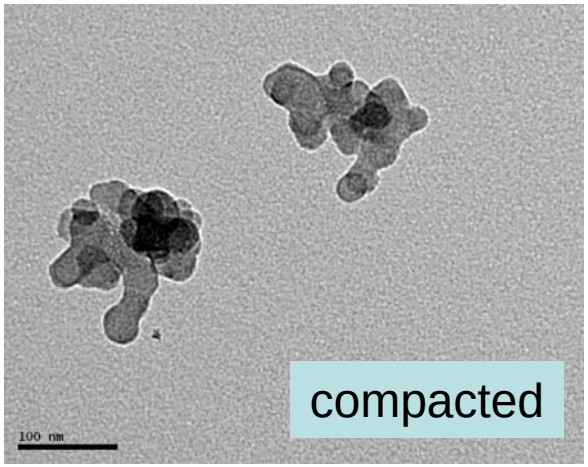


Untreated soot*



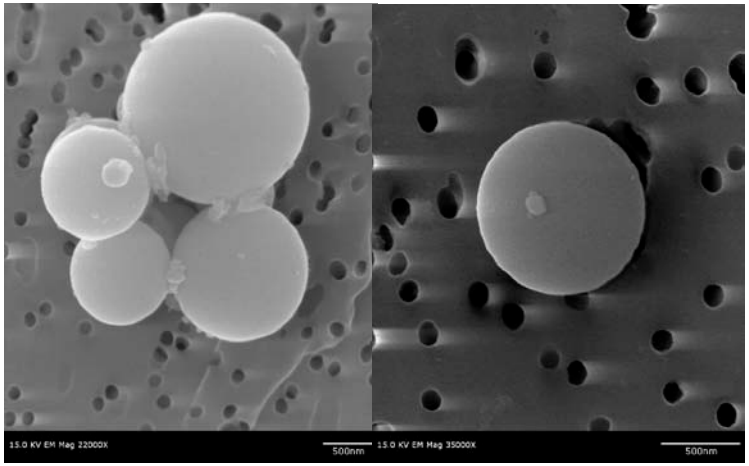


Soot, oxidized and exposed to water

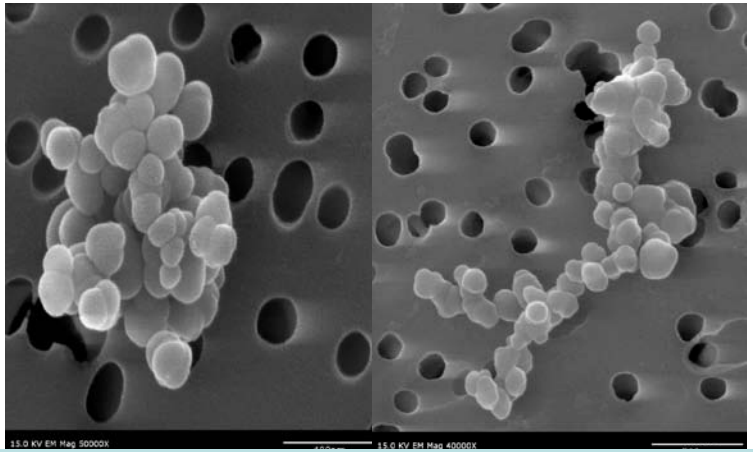


(*Top two TEM Images courtesy of Randy VanderWal (NASA Glen Research Center), from Kirchstetter & Novakov, “Evaluating and Improving Measurements of Black Carbon.” AGU 2007.)

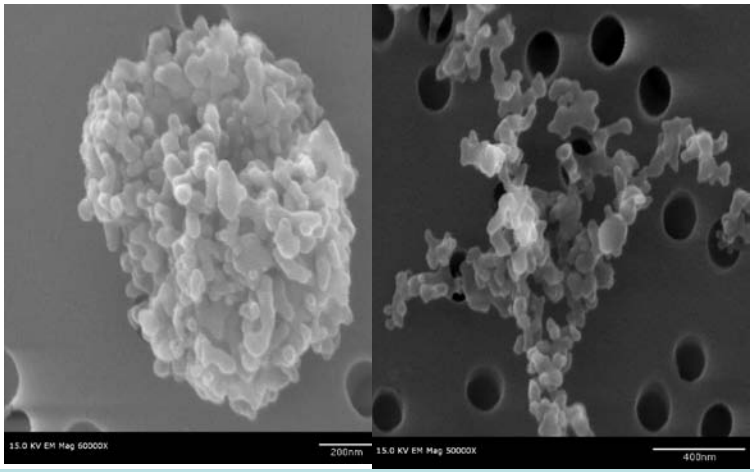
Soot-like aggregates, spherules and agglomerated spherules



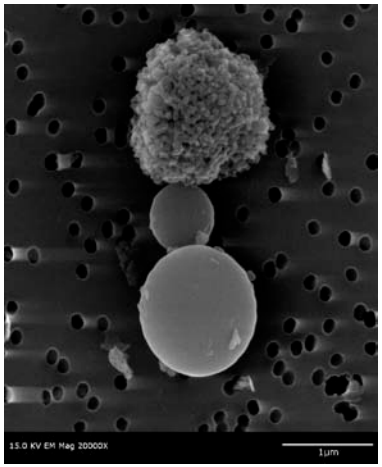
Alfa glassy carbon



Tokai GC: solubilized & air-blown

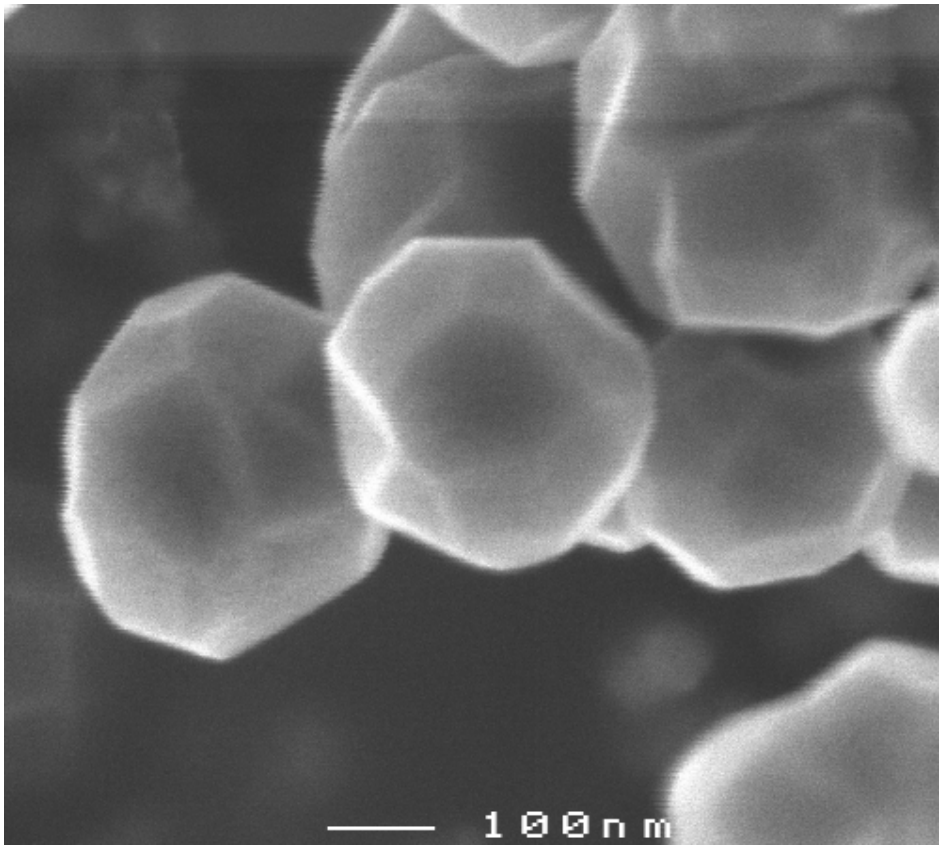


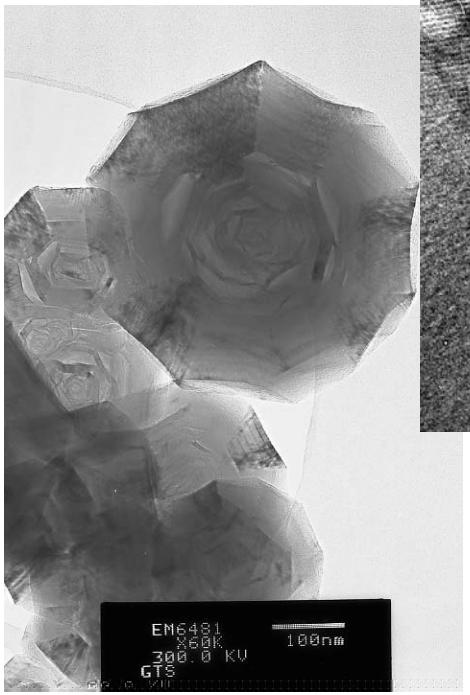
Fullerene soot: 400 & 110 nm

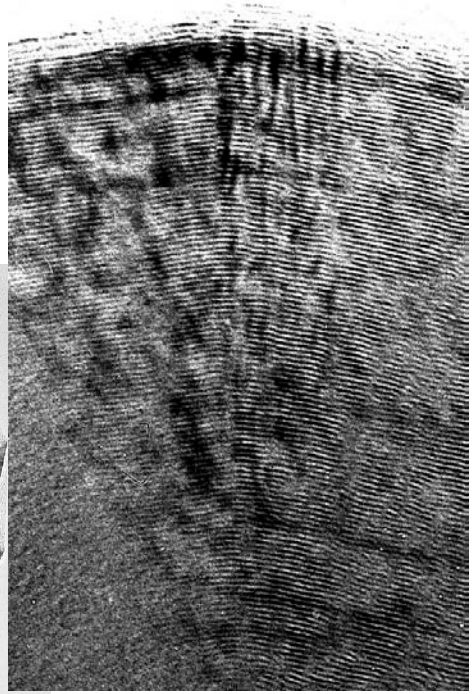


Aquadag (contaminated?)

Graphitized thermal soot (GTS)





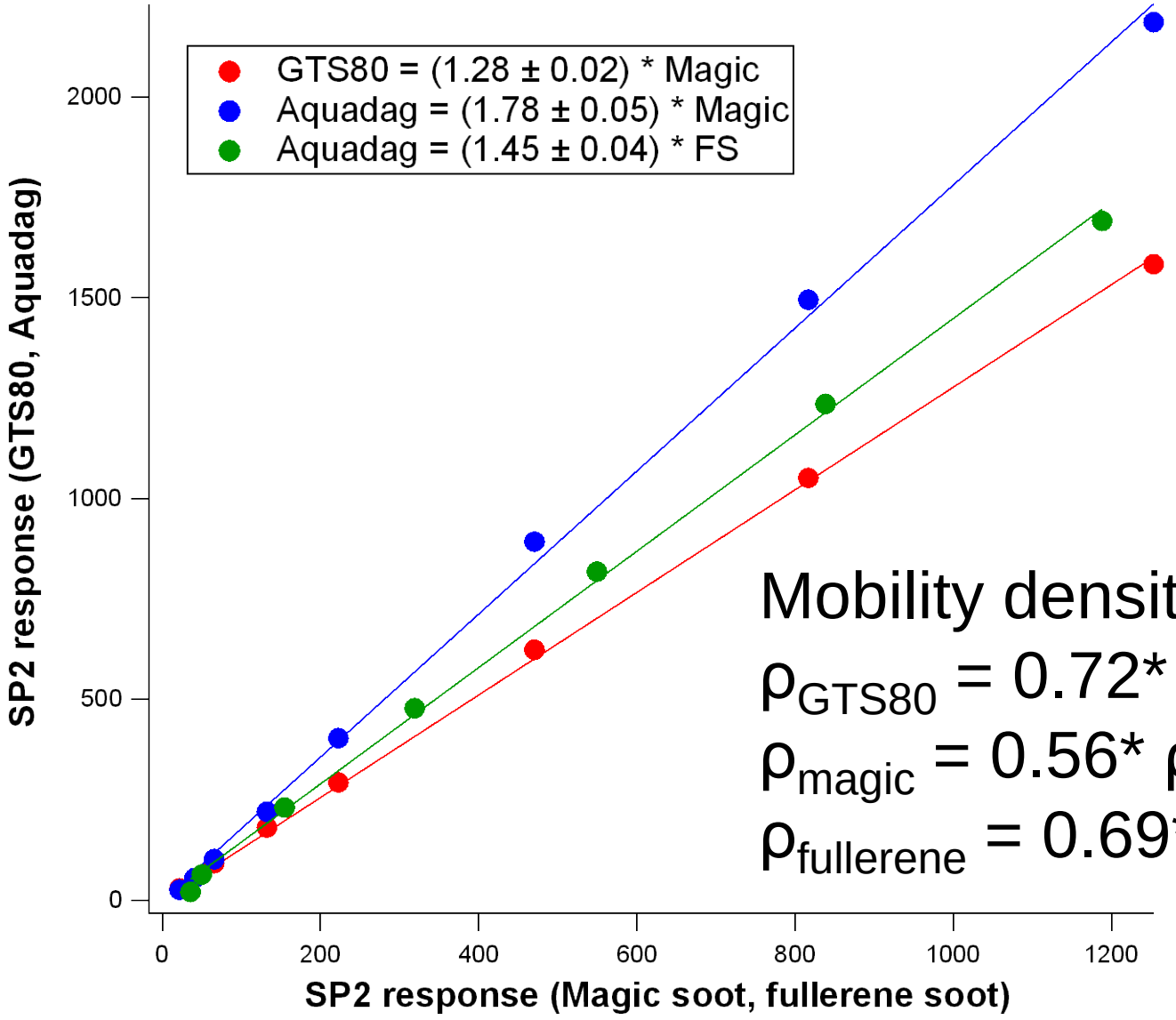


Popovicheva et al. (2008)

Reference material density

- Tokai GC: 1.85 g/cm^3
- Alfa GC: 1.42 g/cm^3
- Fullerene soot: ?
- Aquadag: 1 g/cm^3? (mobility density)
  - Not specified by manufacturer
- Graphitized thermal soot (GTS): ~2 g/cm^3?
  - assuming density of graphite
- Magic soot: ~1.9 g/cm^3?
  - assuming density of fresh LAC
- **Material density not the same as *mobility* density**
  - Hard spherical particles are OK (like *individual* glassy carbon particles)
  - Fractal agglomerates may have a different effective density in a DMA due to non-spherical shape factors

Comparing Aquadag, GTS80, magic soot and fullerene soot



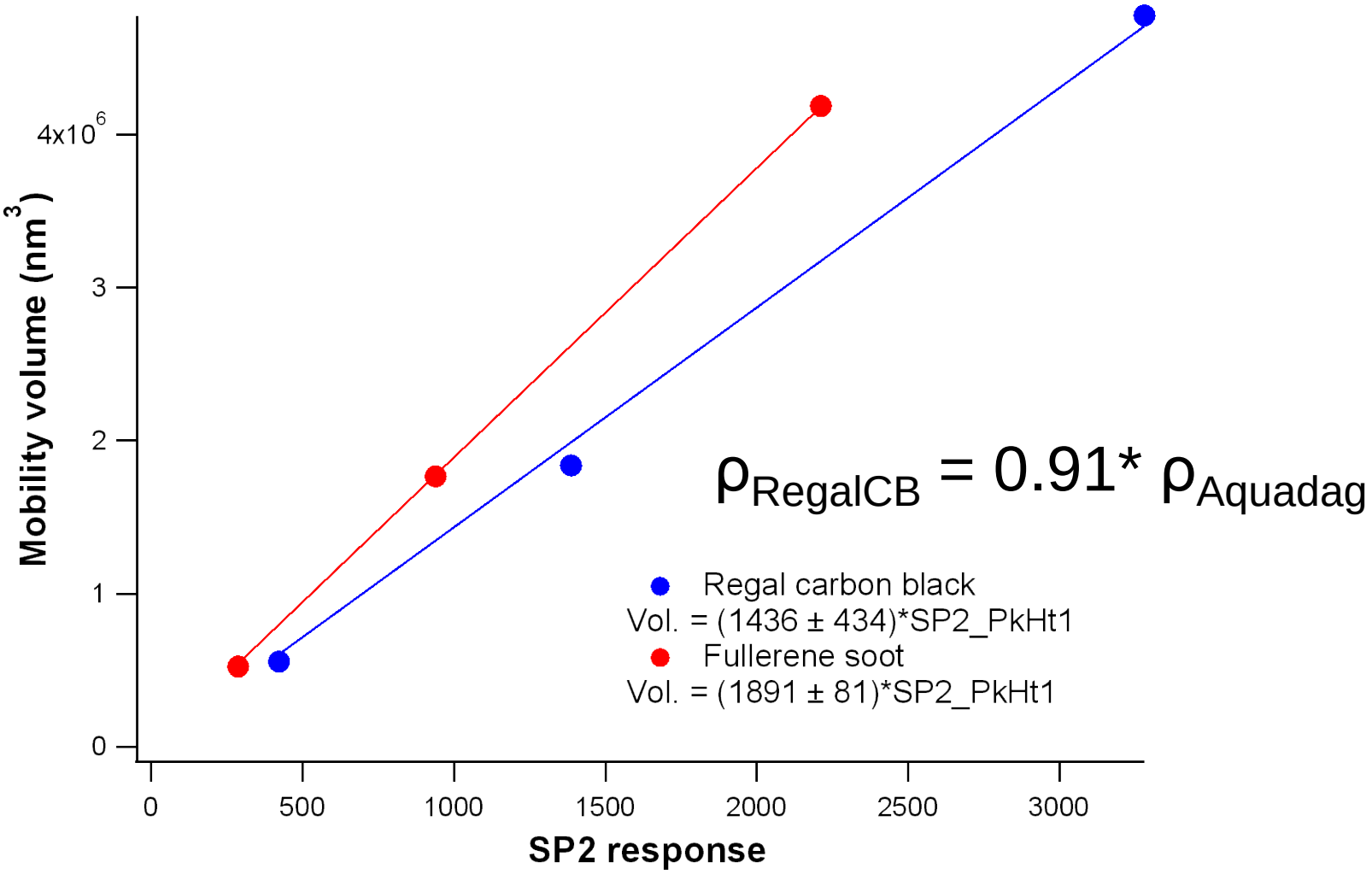
Mobility density:

$\rho_{GTS80} = 0.72^* \rho_{Aquadag}$

$\rho_{magic} = 0.56^* \rho_{Aquadag}$

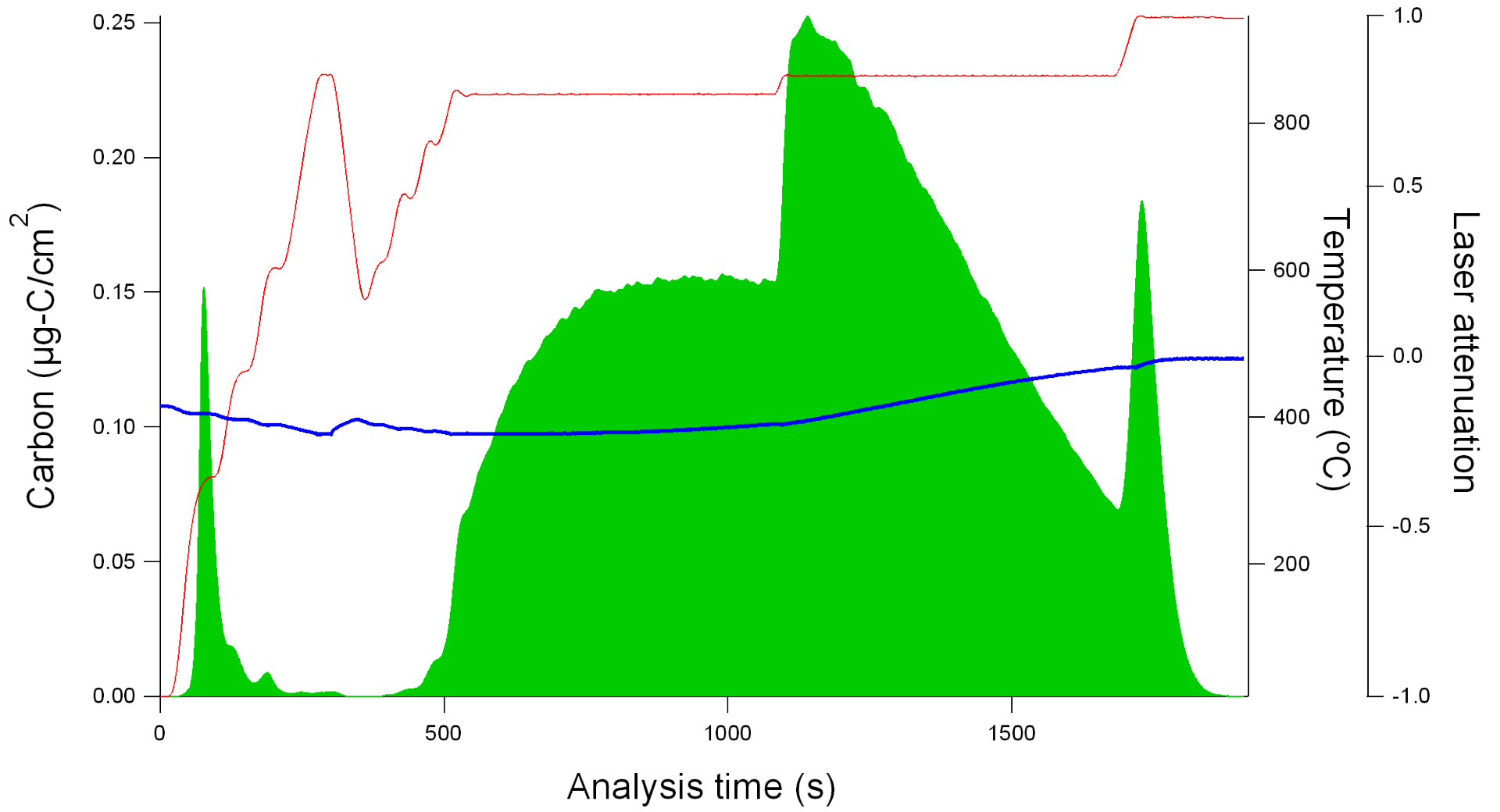
$\rho_{fullerene} = 0.69^* \rho_{Aquadag}$

Fullerene soot and Regal carbon black (BC/Aerodyne Soot Project 2)



Measured soot masses ~0.4 to 3.4 fg-LAC

Organic-coated GTS: Soot standard?



GTS80 + 4.88% 1,2,4-benzene tricarboxylic acid

Summary

- Magic soot and GTS are ~100% EC
  - GTS can be coated with organic matter as a “soot” proxy
- All materials behave like LAC in the SP2
- Glassy carbon and GTS have spherical/ spheroidal shape
  - good for DMA size selection (mass is known)
  - Fullerene soot, Aquadag, magic soot are more fractal, so DMA-selected mass not certain
- Aquadag behaves nicely in DMA, over a wide range of mobility diameters (0.5 – 100 fg)
- *Need* to confirm mobility density of fullerene soot, GTS, magic soot and Aquadag
  - **DMA/SP2 response differentiated only by mobility density**
- *Need* to test optical properties of most materials
  - Previously, tests have shown discrepancies between PSAP and PASS absorption for GTS
  - GTS microstructure similar to graphite, so optical properties could be similar to graphite
  - Magic soot is freshly-generated LAC

Do the candidates meet our requirements?

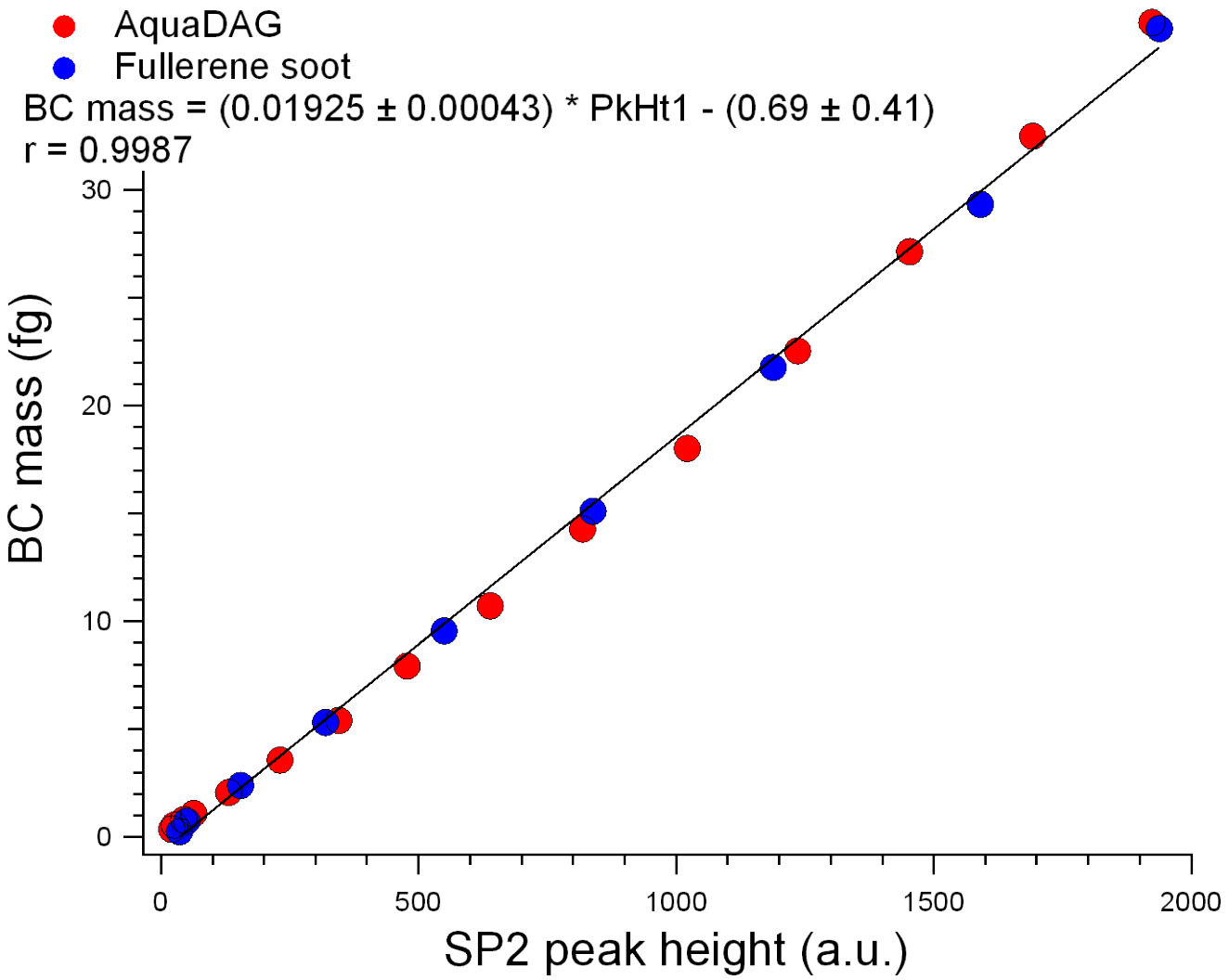
Requirement	Alfa GC	Tokai GC	Fullerene soot	Aquadag	GTS	Magic soot
Shape (for DMA)						nt
Density (mobility)	+	+	+	+	+	+
Size distribution	+		+	+		†
Monodisperse						
Long-term stability						
Water dispersion			+		+	
Optical properties	nt	nt	nt	nt	+	
SP2 behavior	+	+	+	+	+	+
OC/EC	nt	nt	nt	nt	EC	EC†

†Kirchstetter and Novakov, *Atmos. Env.*, **41** (2007).

Good; + further testing needed; nt: not tested

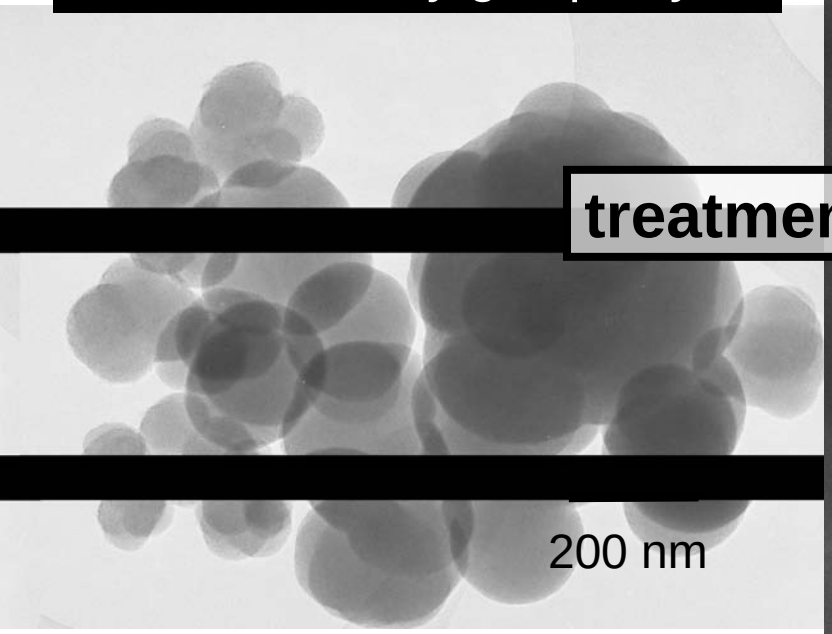
Extra slides follow

Calibration of SP2 using Aquadag and fullerene soot



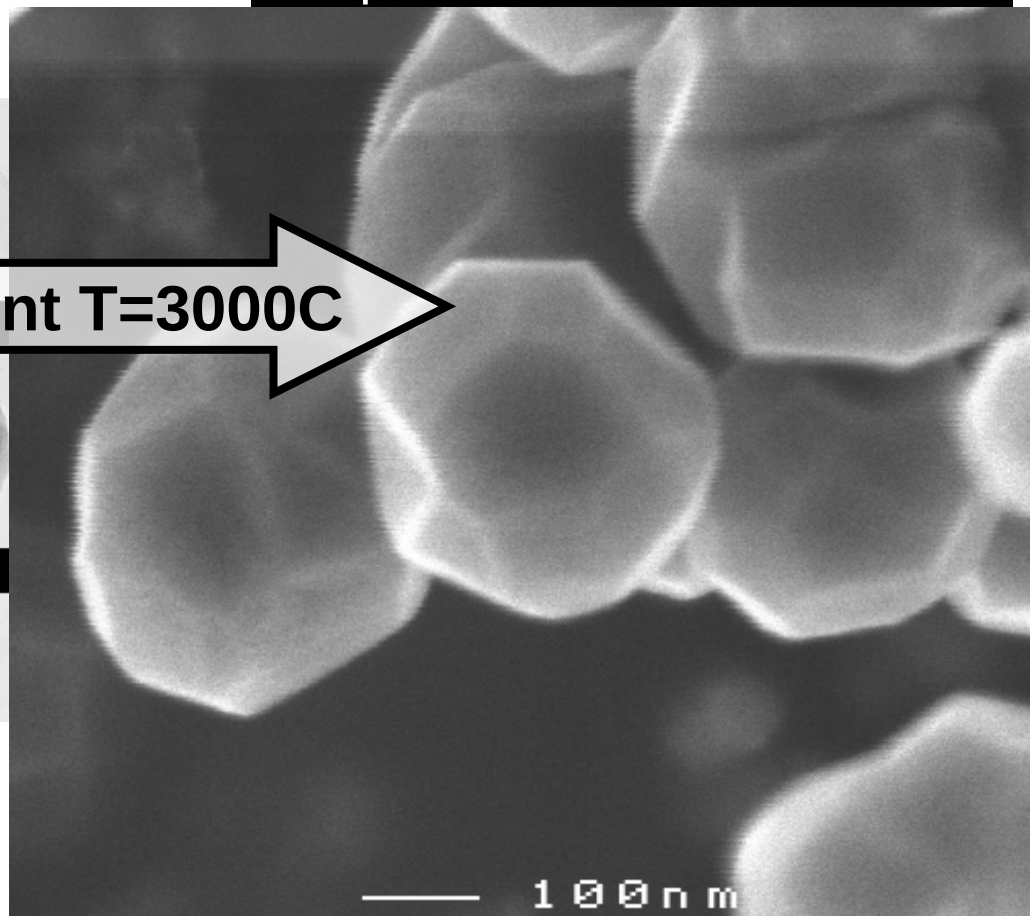
Production of Elemental Carbon Reference Material

Thermal soot by gas pirolysis



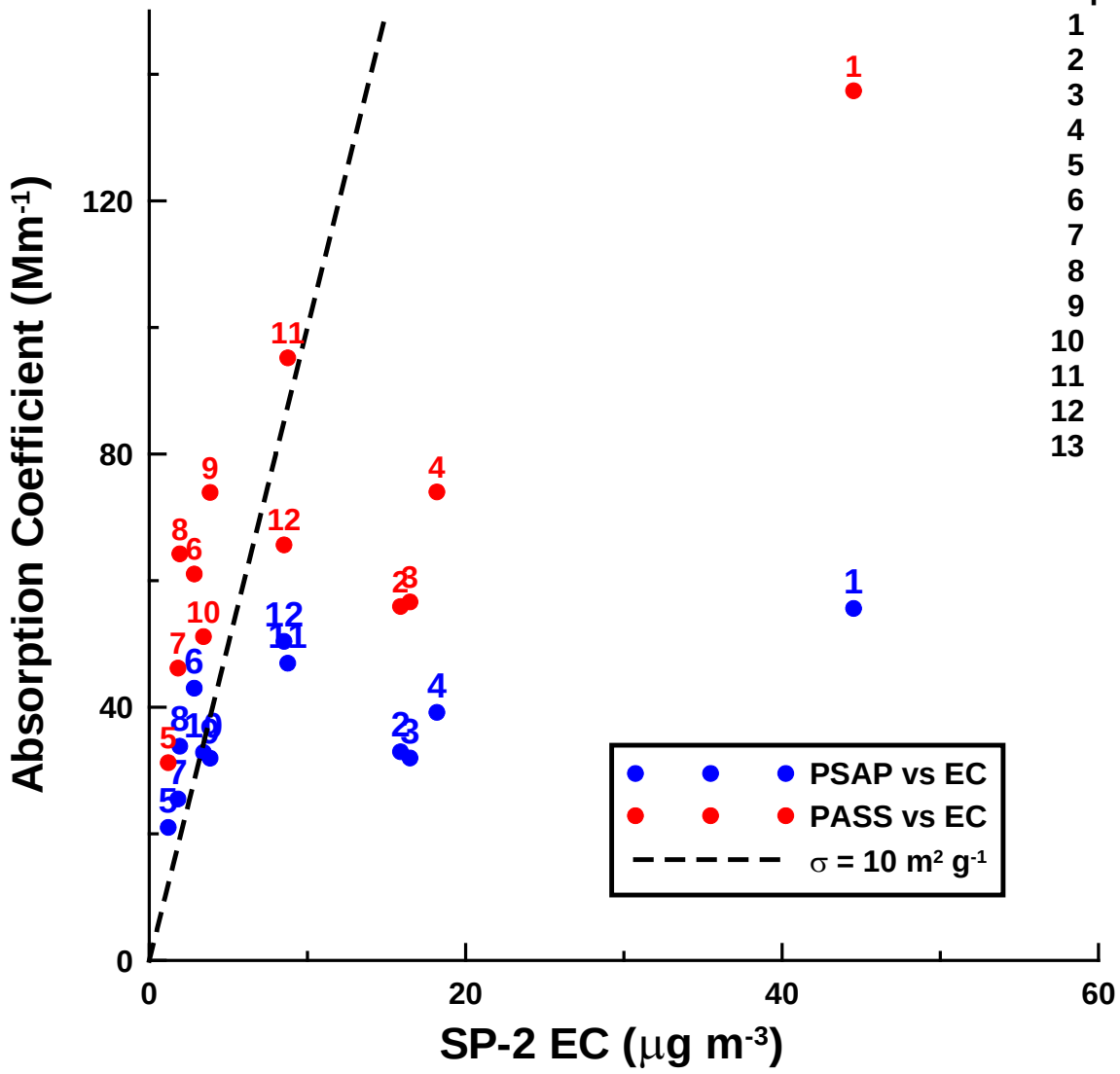
treatment T=3000C

Graphitized Thermal soot GTS

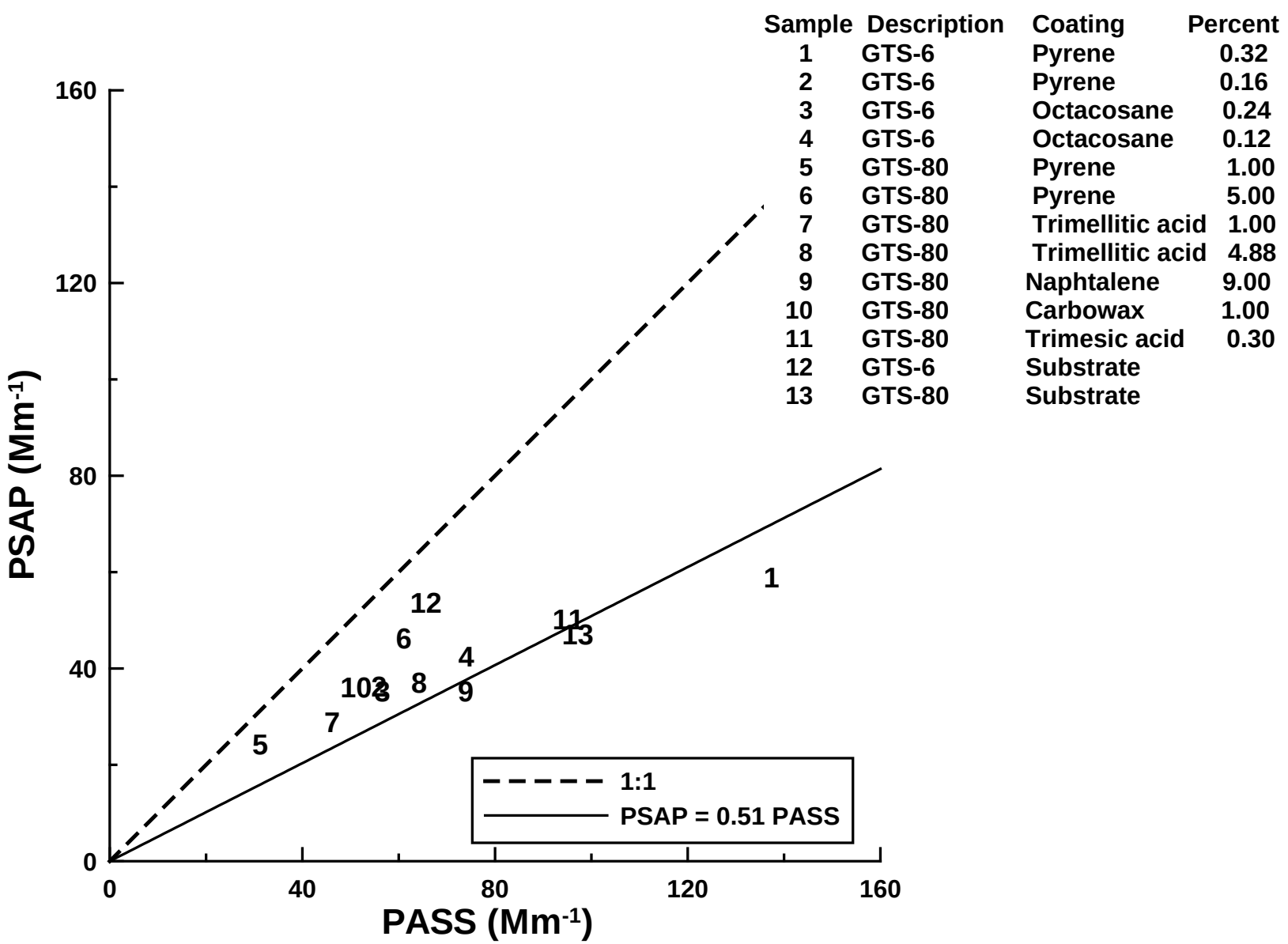


- **Cleaning from**
  - **organic coverage,**
  - **inorganics, ash.**
- **Production of well-graphitized structure,**

  perfect chemically uniform surface.



Sample	Description	Coating	Percent
1	GTS-6	Pyrene	0.32
2	GTS-6	Pyrene	0.16
3	GTS-6	Octacosane	0.24
4	GTS-6	Octacosane	0.12
5	GTS-80	Pyrene	1.00
6	GTS-80	Pyrene	5.00
7	GTS-80	Trimellitic acid	1.00
8	GTS-80	Trimellitic acid	4.88
9	GTS-80	Naphtalene	9.00
10	GTS-80	Carbowax	1.00
11	GTS-80	Trimesic acid	0.30
12	GTS-6	Substrate	
13	GTS-80	Substrate	



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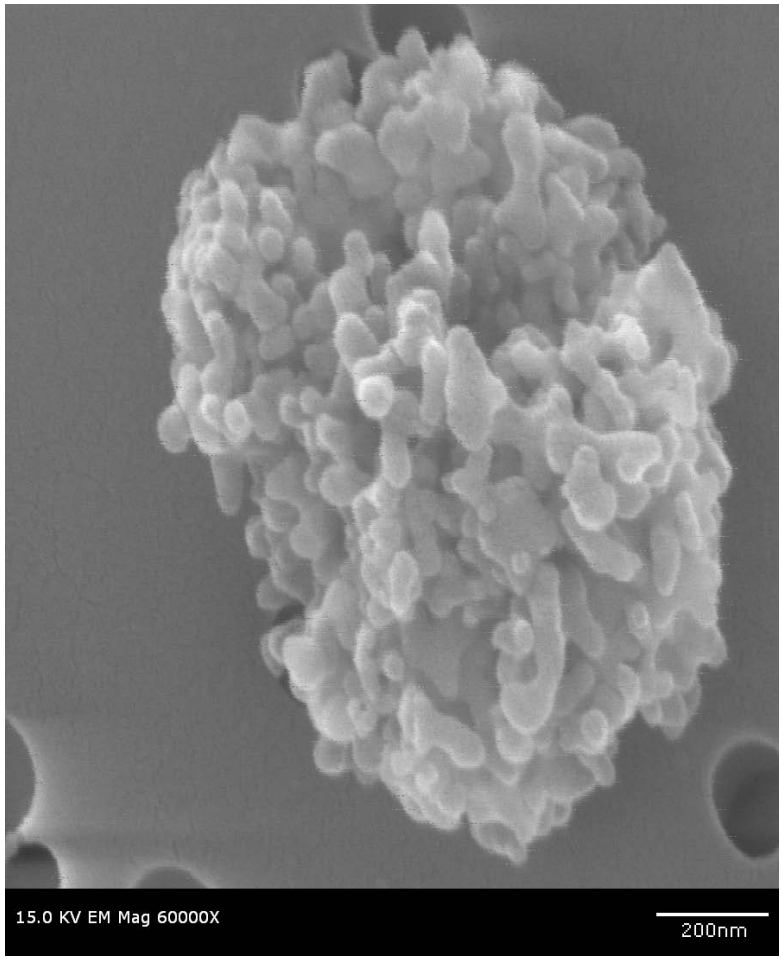
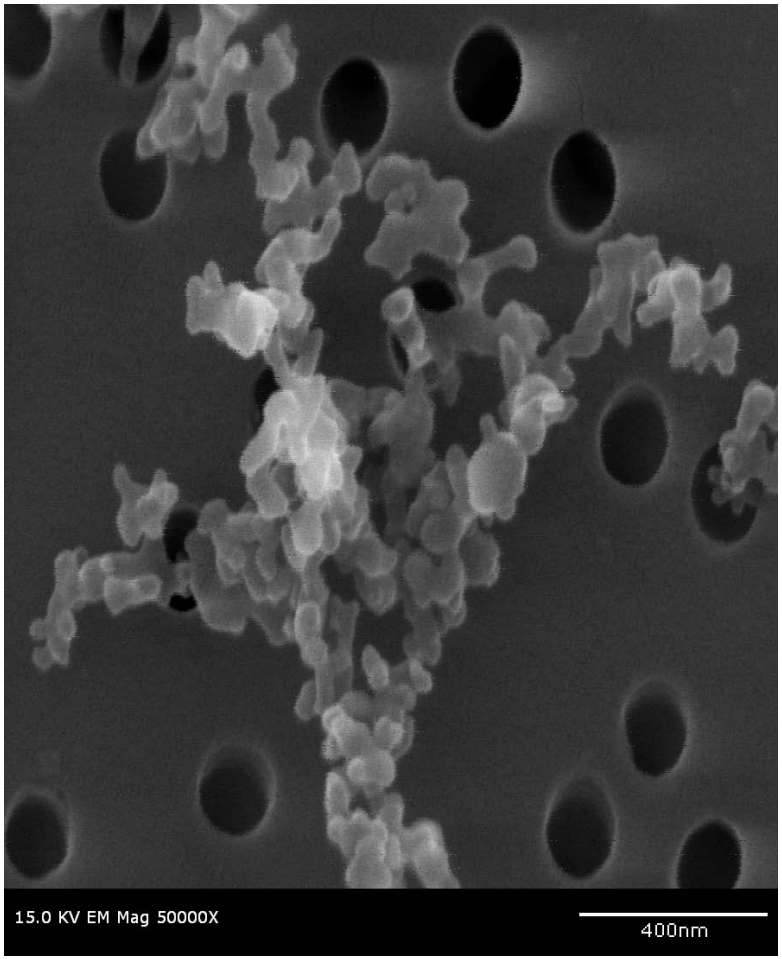
10	GTS-80	Carbowax	1.00
11	GTS-80	Trimesic acid	0.30
12	GTS-6	Substrate	
13	GTS-80	Substrate	

Alfa fullerene soot: soot-like aggregates

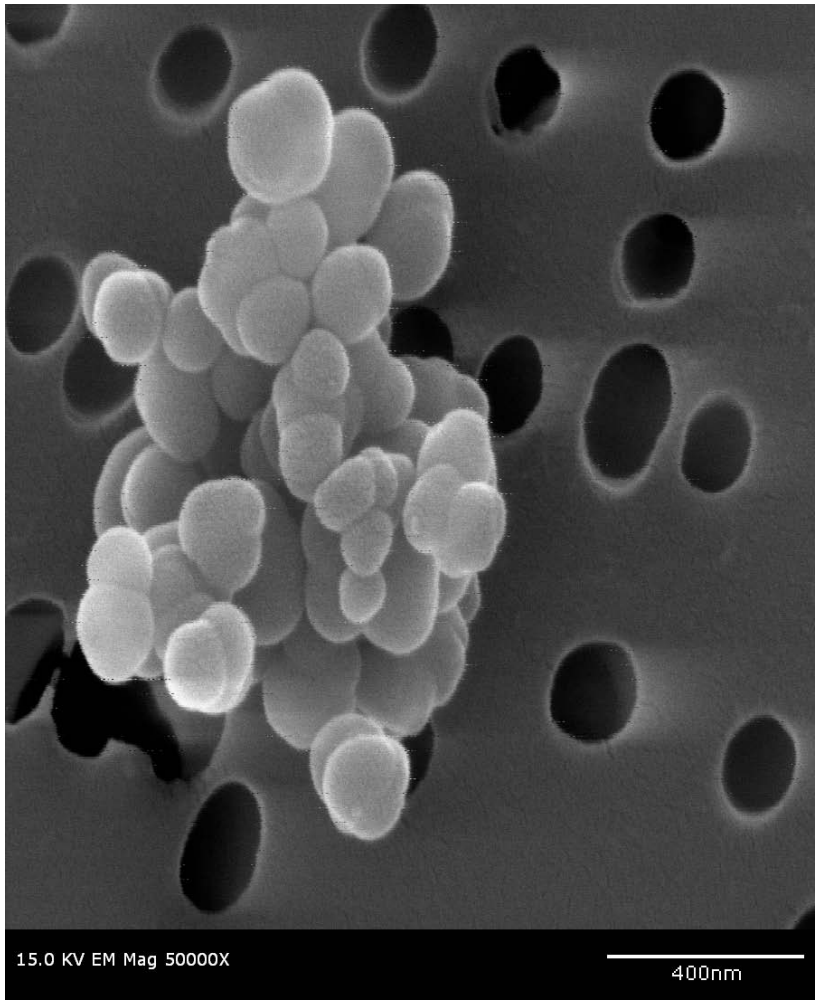


DMA @ 400 nm

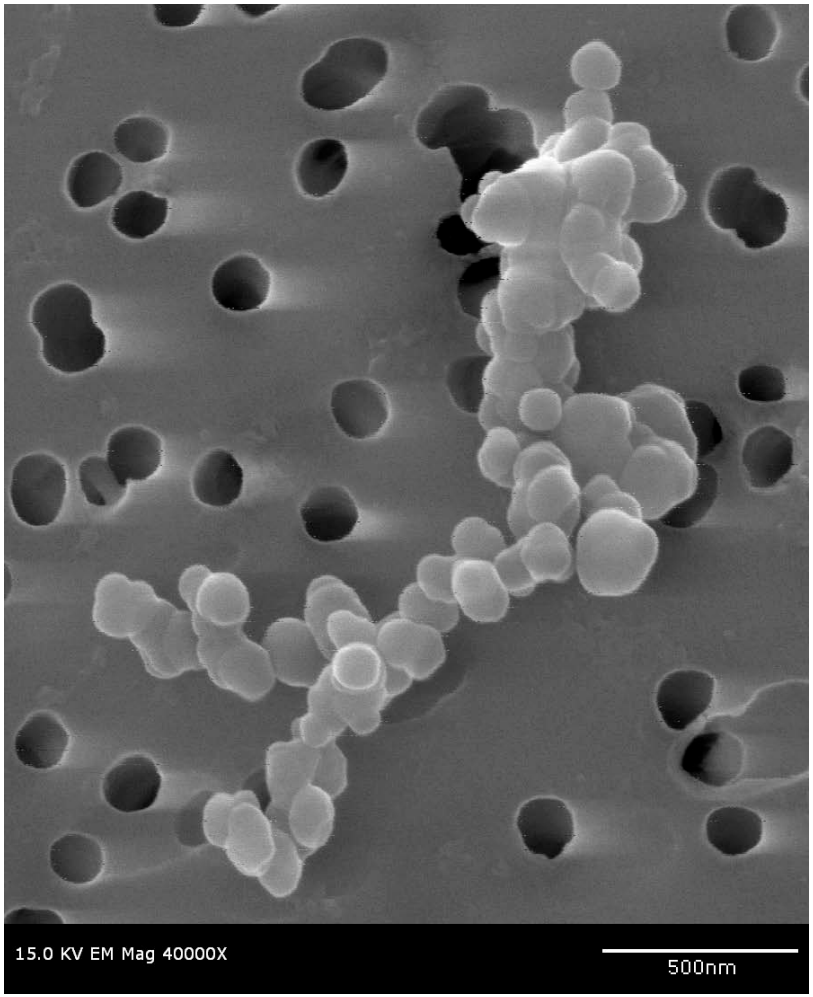


DMA @ 110 nm

Tokai glassy carbon: spherules and agglomerates

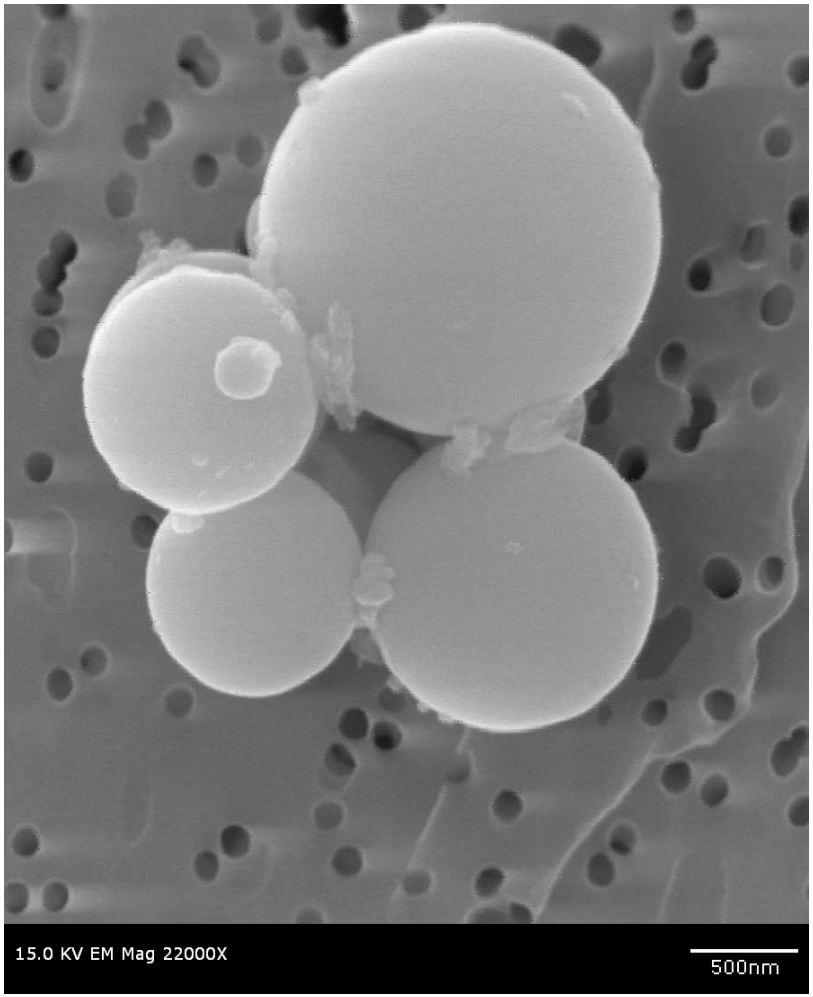


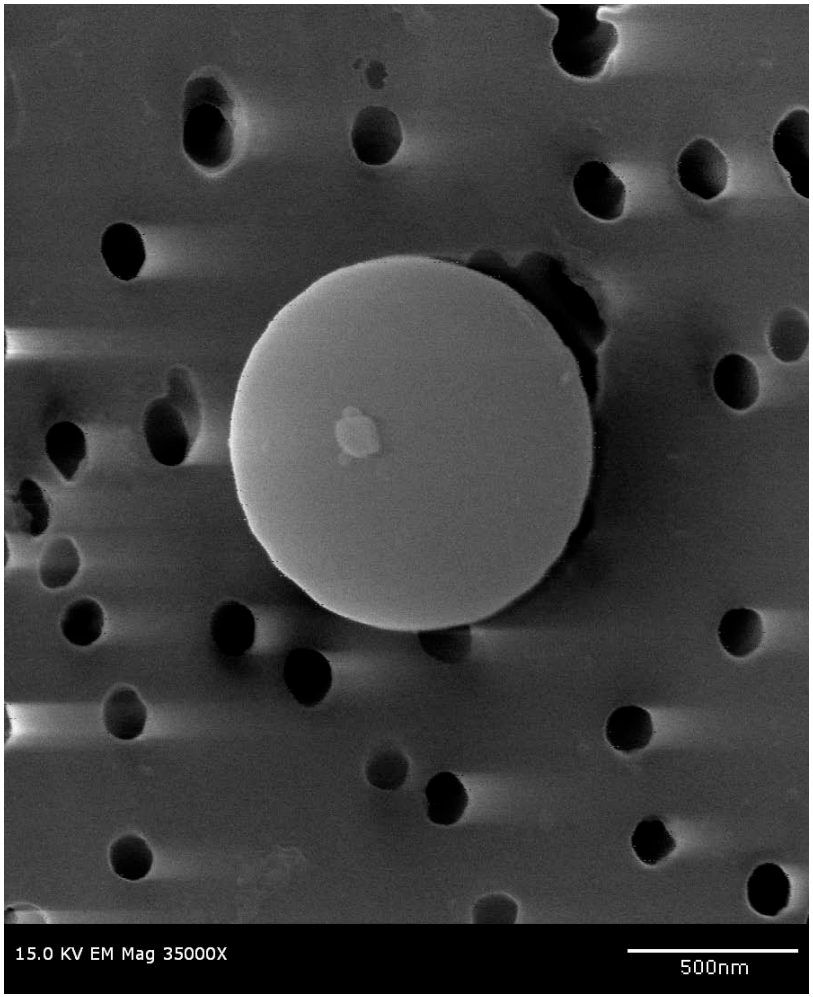
Tokai 200 nm



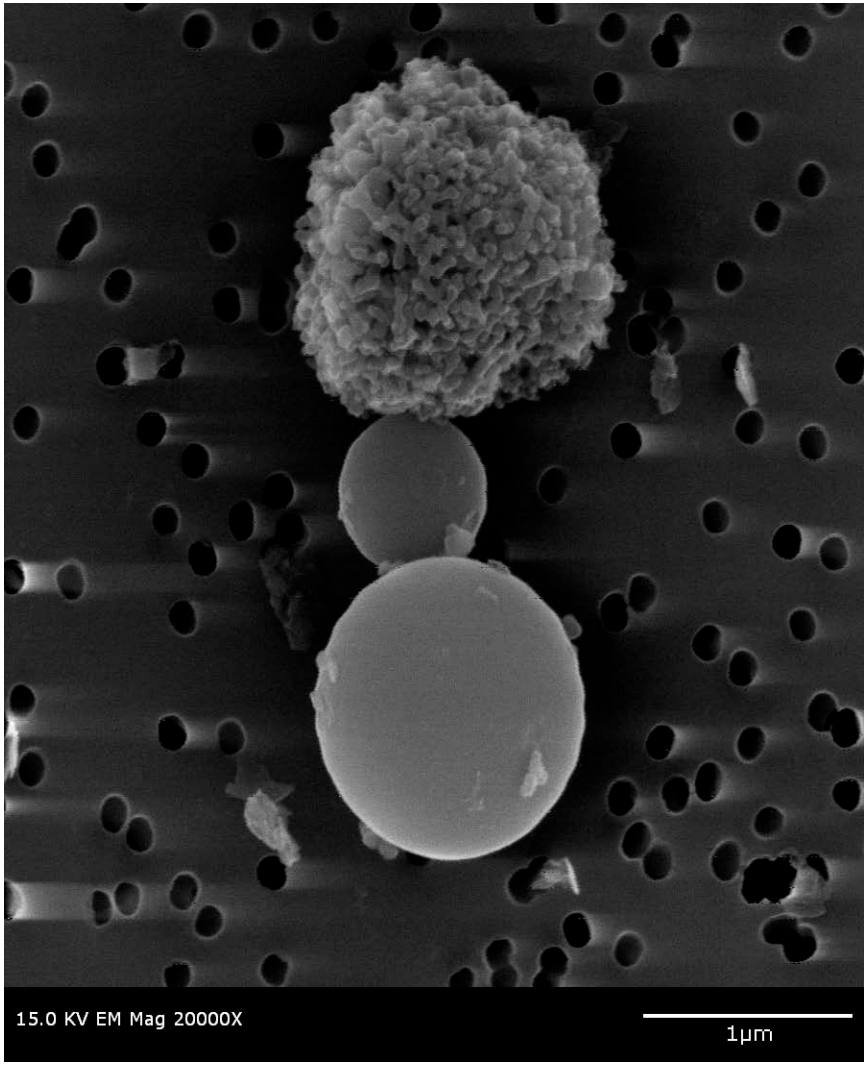
Tokai 200 nm, not solubilized

Alfa glassy carbon: single spheres and agglomerates





Acheson Aquadag: more aggregates like soot, but contaminated sample?



Measurement Instrumentation

- Single Particle Soot Photometer (SP2)
  --Individual particle mass measurement
- Thermal/Optical
  --elemental carbon/organic carbon
- Photoacoustic
  --*in-situ* particulate light absorption converted to mass
- Filter collection (aethelometer, PSAP, MAAP)
  --light absorption converted to mass