Towards a reference material for soot/LAC measurement: Evaluation of candidates with electron microscopy, SP2 and thermal-optical analysis

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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

Measurement Instrumentation

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

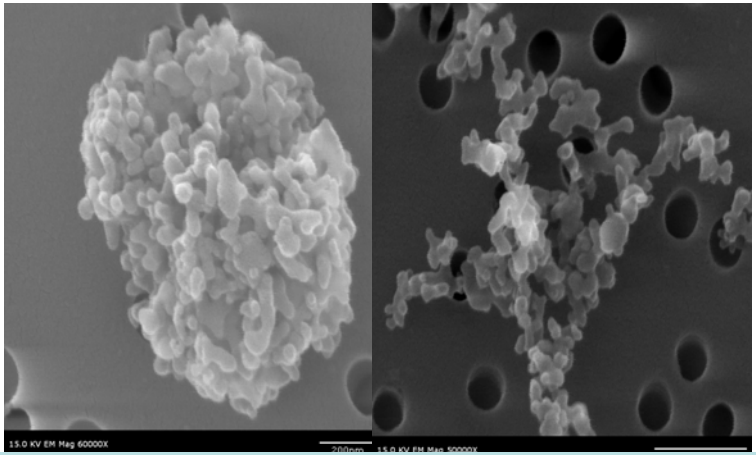
LAC reference material: requirements

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

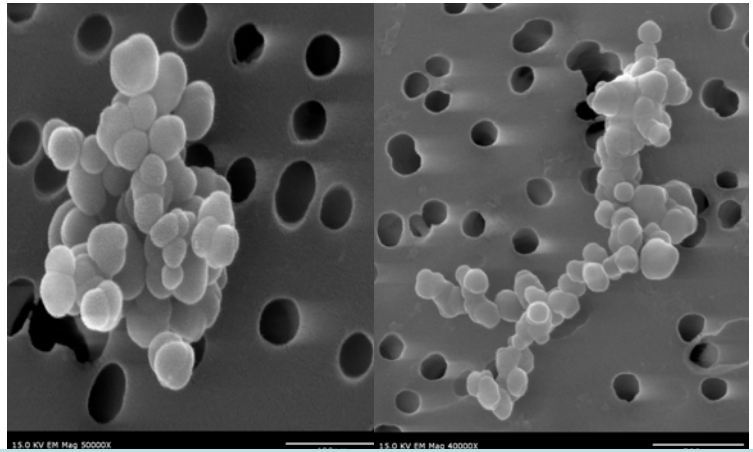
Candidates

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

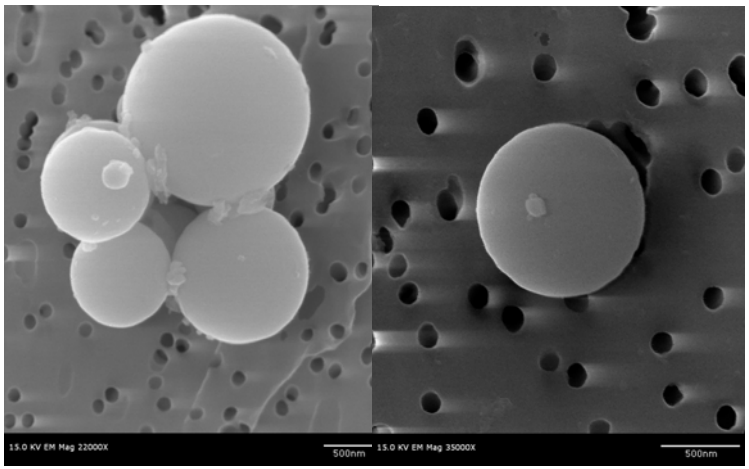
Soot-like aggregates, spherules and agglomerated spherules



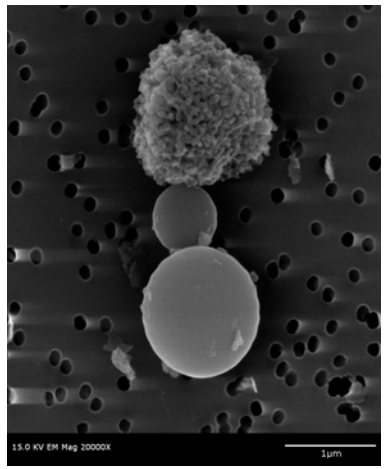
Fullerene soot: 400 & 110 nm



Tokai GC: solubilized & air-blown

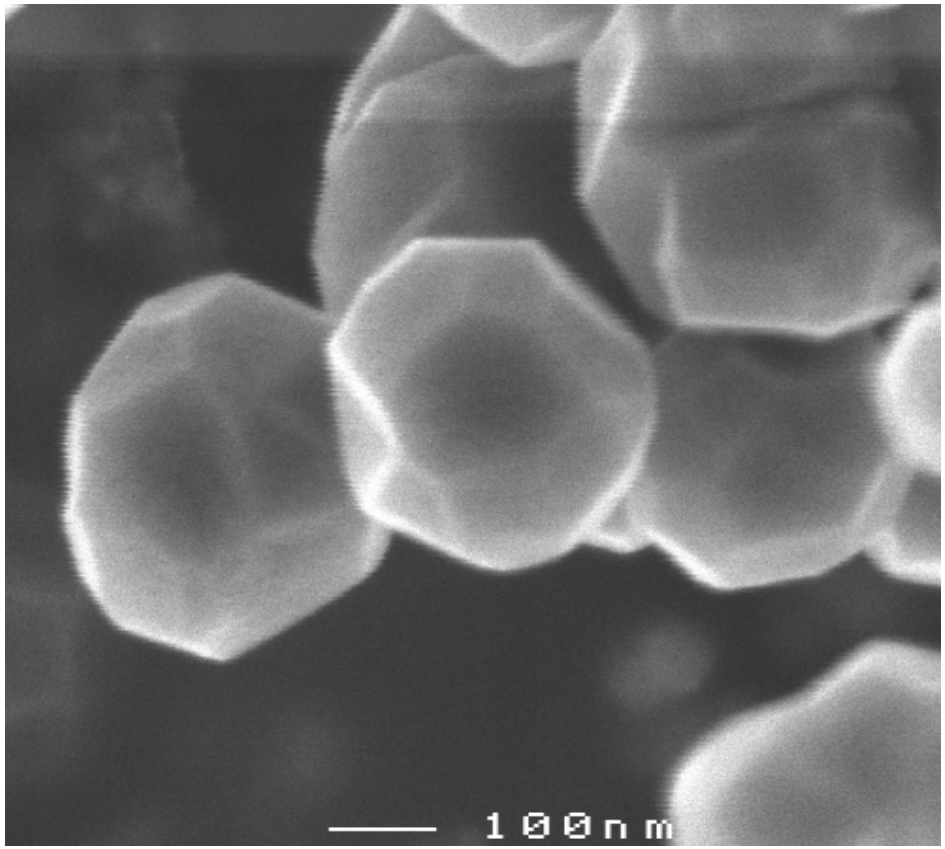


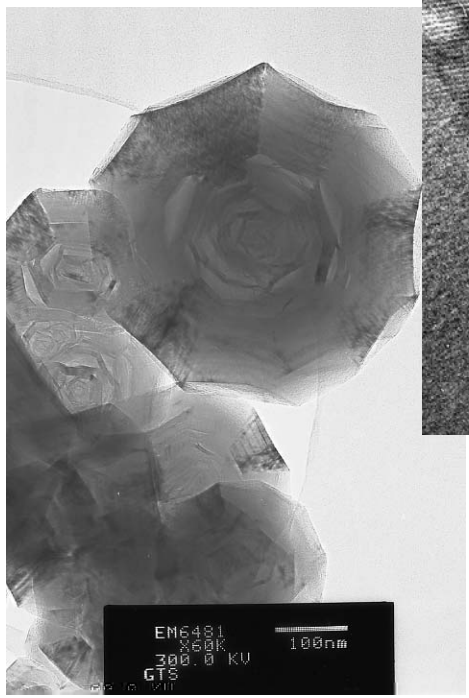
Alfa glassy carbon

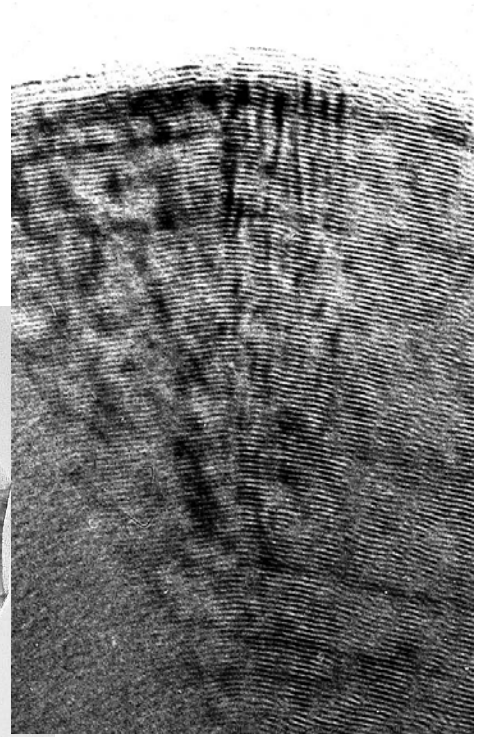


Aquadag (contaminated?)

Graphitized thermal soot (GTS)

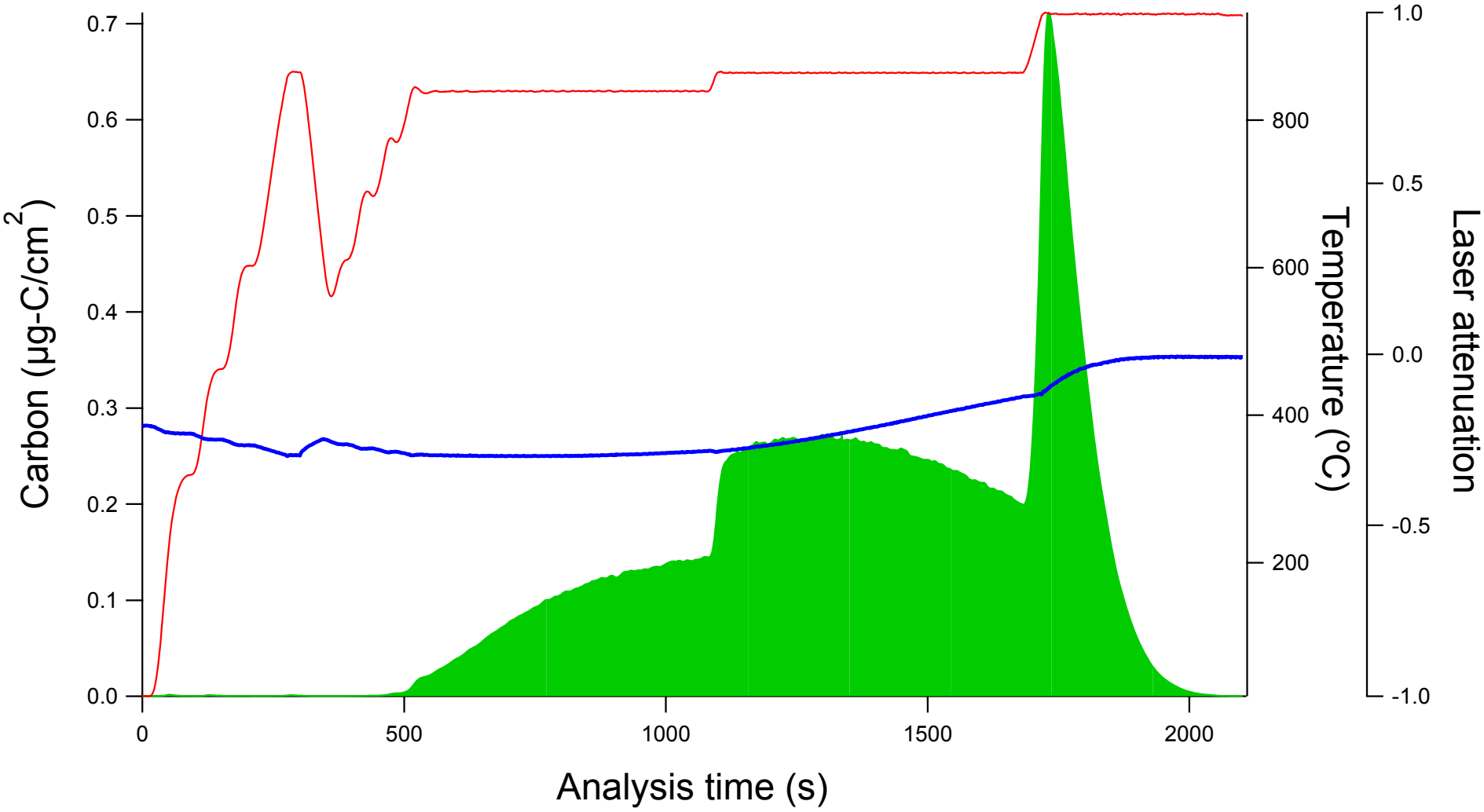




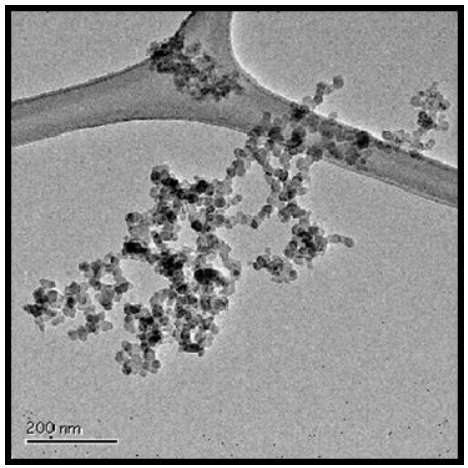


Popovicheva et al. (2008)

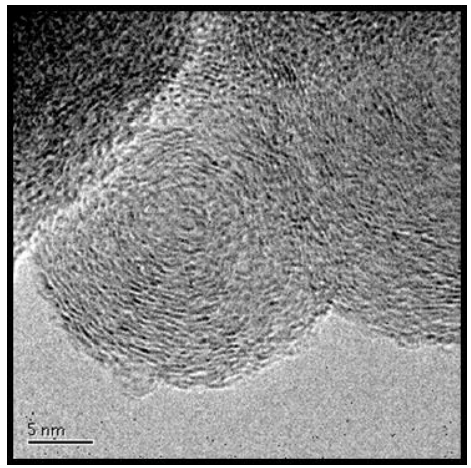
GTS composition: ~100% EC

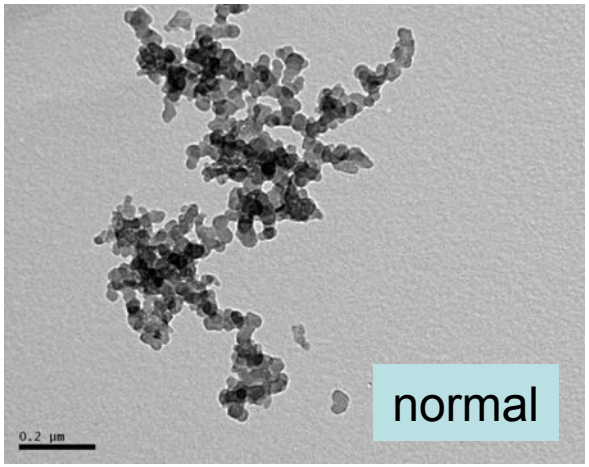


Methane/air diffusion-flame-generated soot

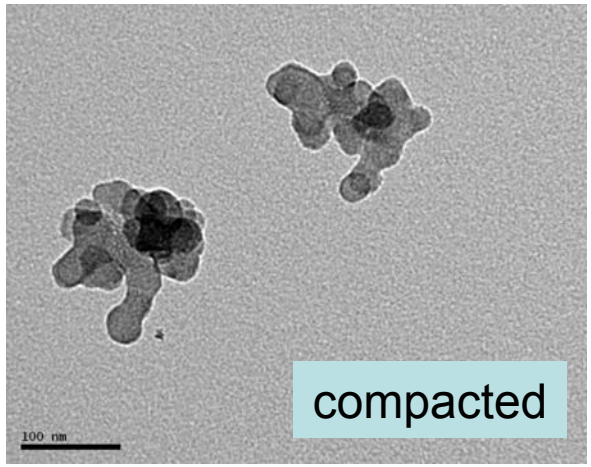


Untreated soot*



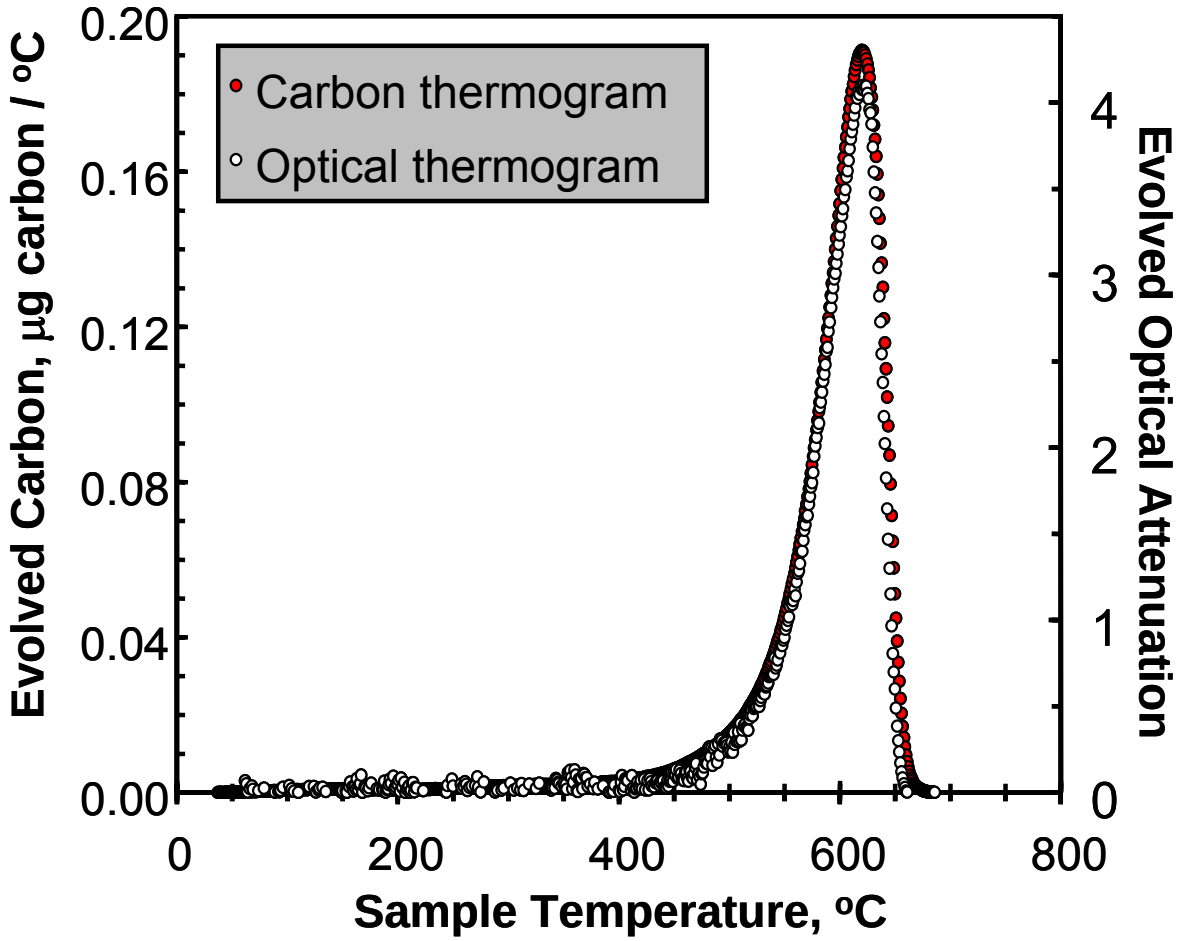


Soot, oxidized and exposed to water



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

Diffusion-flame-generated soot: All EC

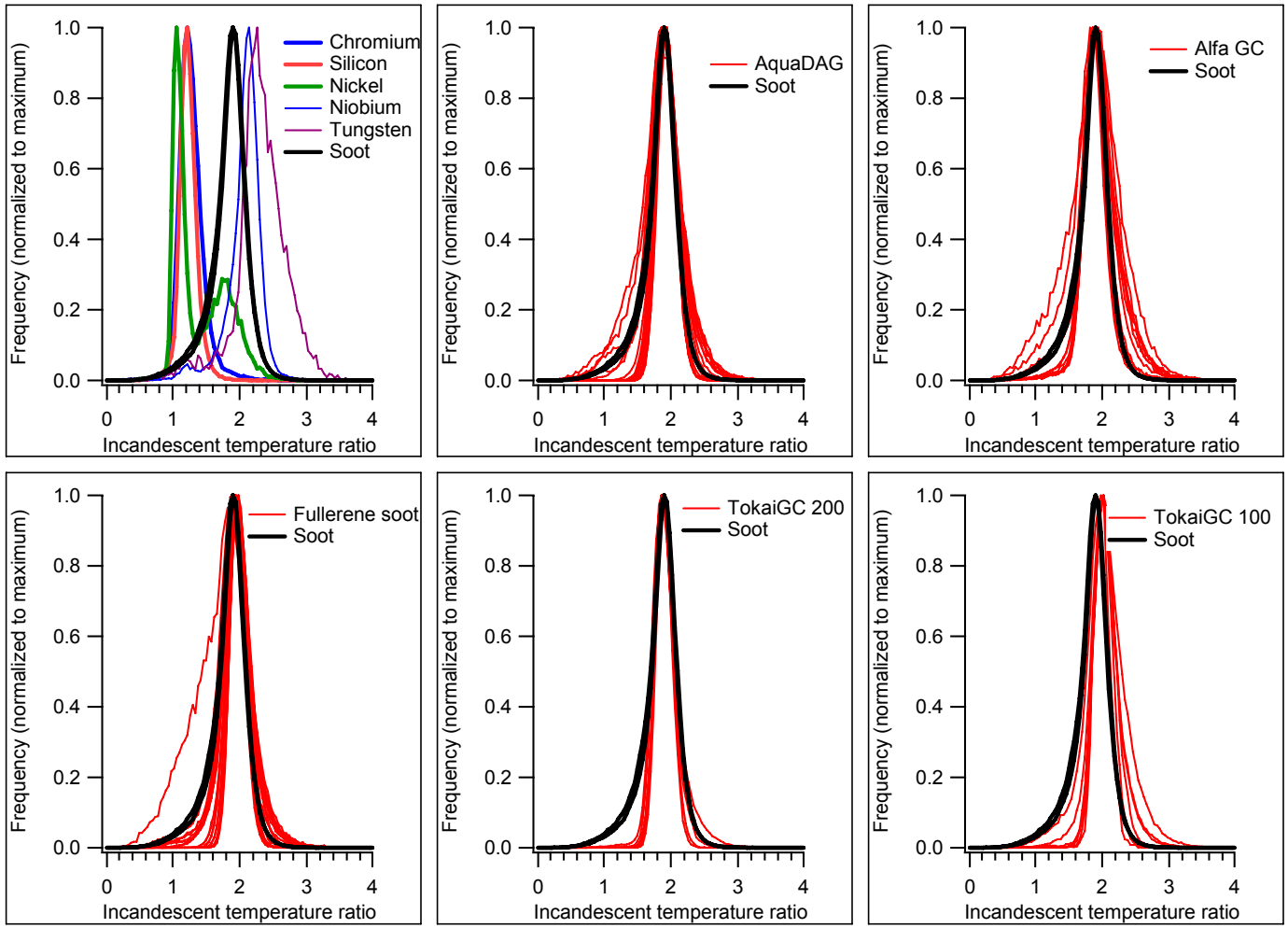


Kirchstetter & Novakov, “Evaluating and Improving Measurements of Black Carbon.” American Geophysical Union, 2007.

Reference material density

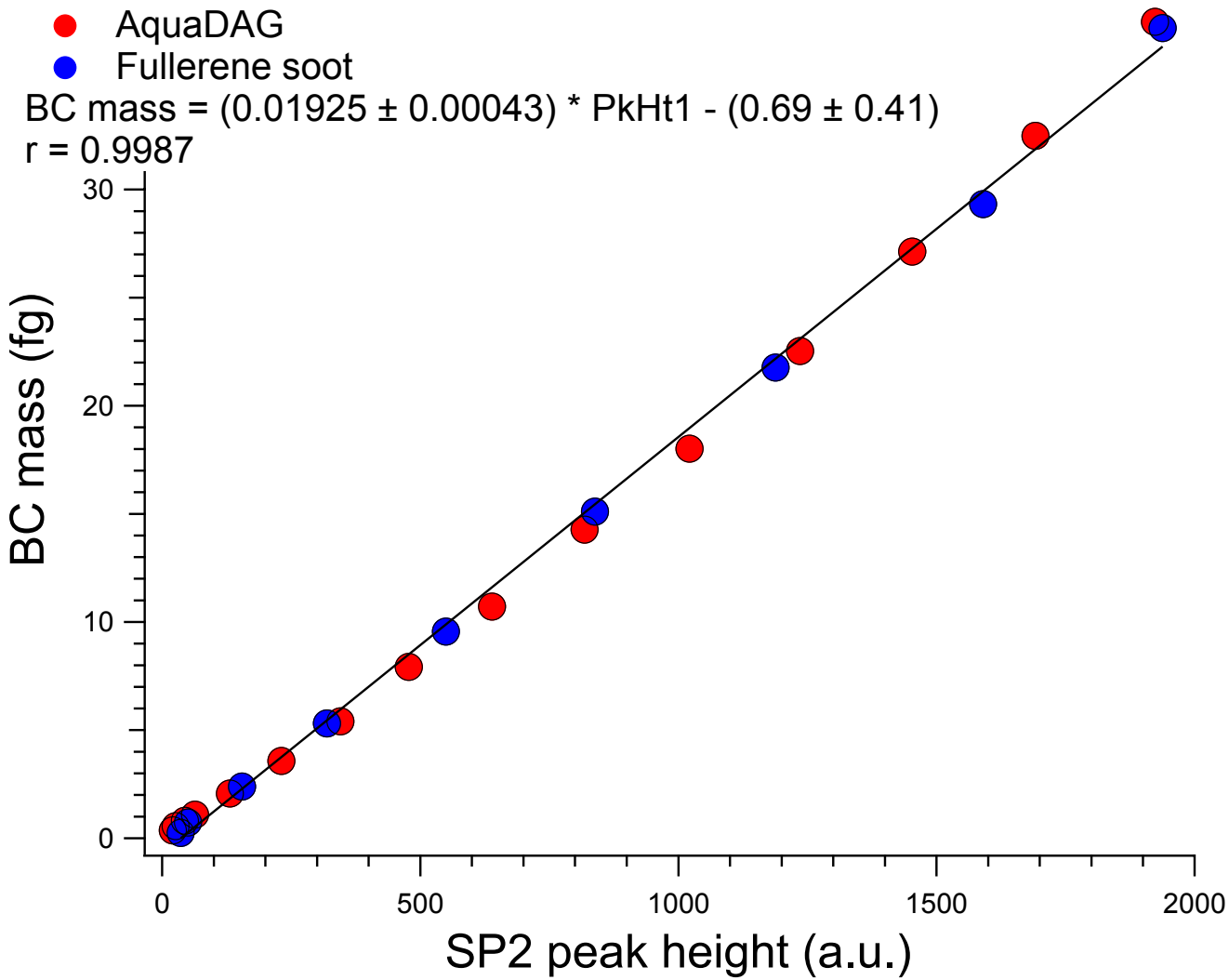
- Tokai GC: 1.85 g/cm^3
- Alfa GC: 1.42 g/cm^3
- Fullerene soot: 0.35 g/cm^3? (mobility density)
- Aquadag: 1 g/cm^3? (mobility density)
  - Not specified by manufacturer
- Graphitized thermal soot (GTS): ~2 g/cm^3?
  - assuming density of graphite
- Diffusion-flame-generated (DFG) soot: ~1.9 g/cm^3?
  - 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

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

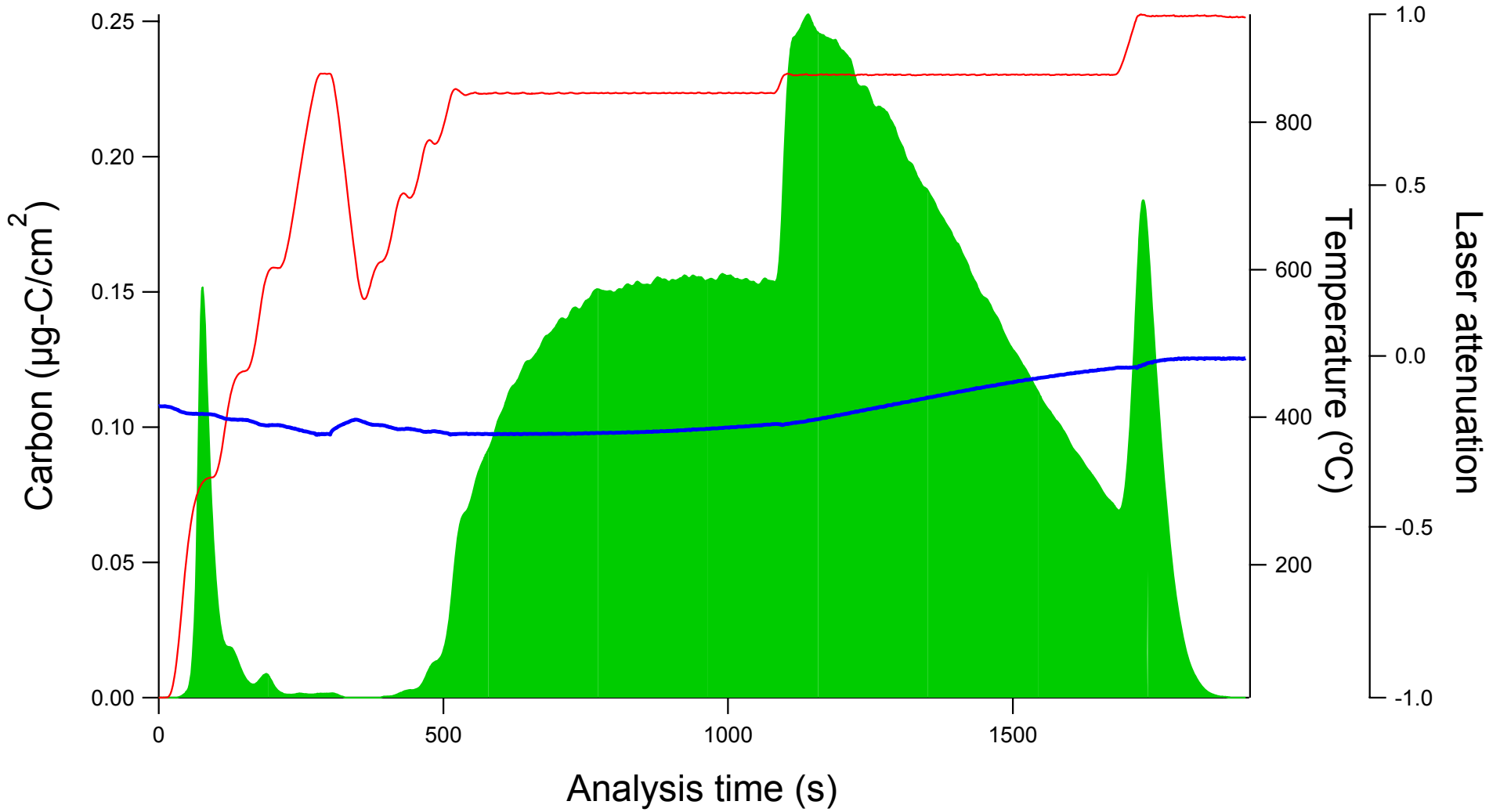


Thick black curve: Flame soot

Calibration of SP2 using Aquadag and fullerene soot



Organic-coated GTS: Soot standard?



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

Fresh combustion soot is likely LAC thinly coated with organic matter

Summary

- Glassy carbon and GTS have spherical/ spheroidal shape
  - good for DMA size selection (mass is known)
  - Fullerene soot, Aquadag, DFG soot are more fractal, so DMA-selected mass not certain
- Alfa glassy carbon and Aquadag behave nicely in DMA
- GTS is ~100% EC
  - Can be coated with organic matter (currently up to 10% of EC mass)
- Reference material candidates tested behave similarly in the SP2
- ***Need*** to confirm (mobility) density of fullerene soot, GTS, DFG soot and Aquadag
- ***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
  - DFG soot is freshly-generated LAC

Do the candidates meet our requirements?

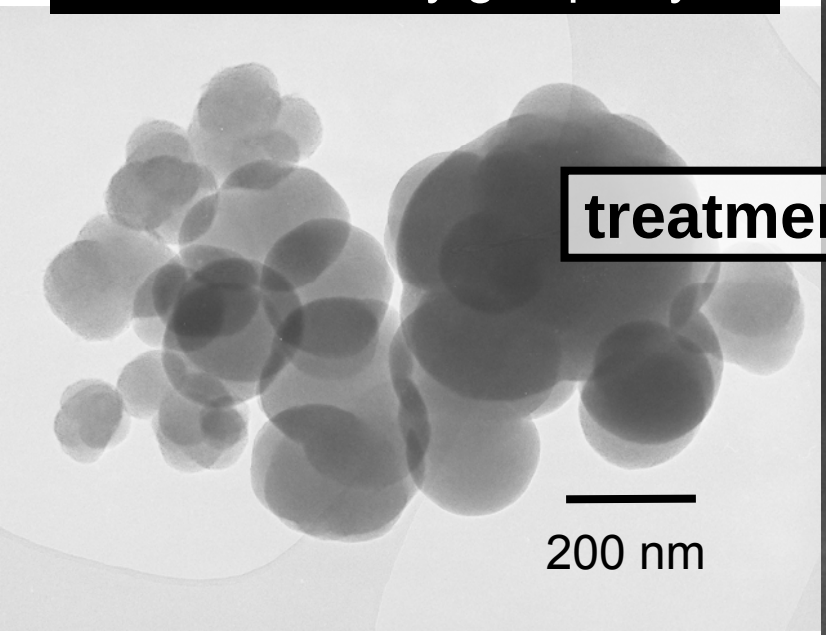
Requirement	Alfa GC	Tokai GC	Fullerene soot	Aquadag	GTS	DFG soot
Shape (for DMA)	●	●	+	+	●	nt
Density (mobility)	+	+	●	●	●	●
Size distribution	-	●	+	+	●	●†
Monodisperse		?			?	
Long-term stability	nt	nt	nt	●	nt	nt
Water dispersion	●	●	+	+	+	●
Optical properties	nt	nt	nt	nt	●	●
SP2 behavior	+	+	+	+	+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

†Kirchstetter and Novakov, *Atmos. Env.*, **41** (2007). nt: not tested

Extra slides follow

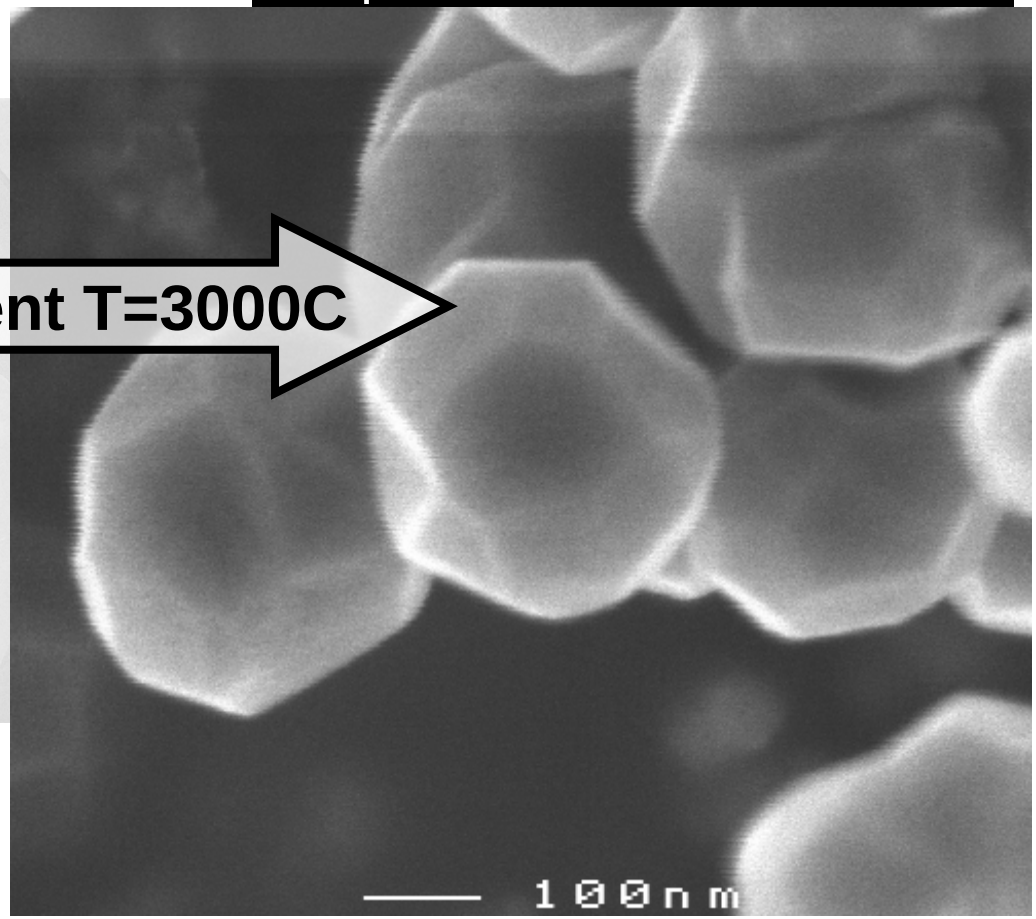
Production of Elemental Carbon Reference Material

Thermal soot by gas pirolysis



treatment T=3000C

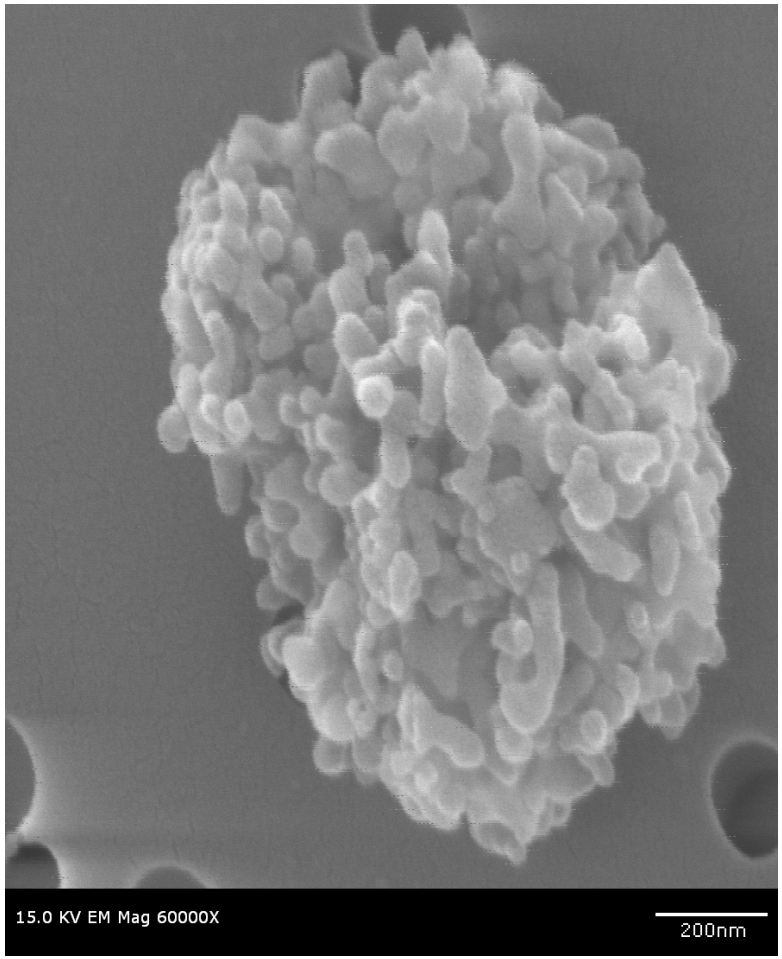
Graphitized Thermal soot GTS



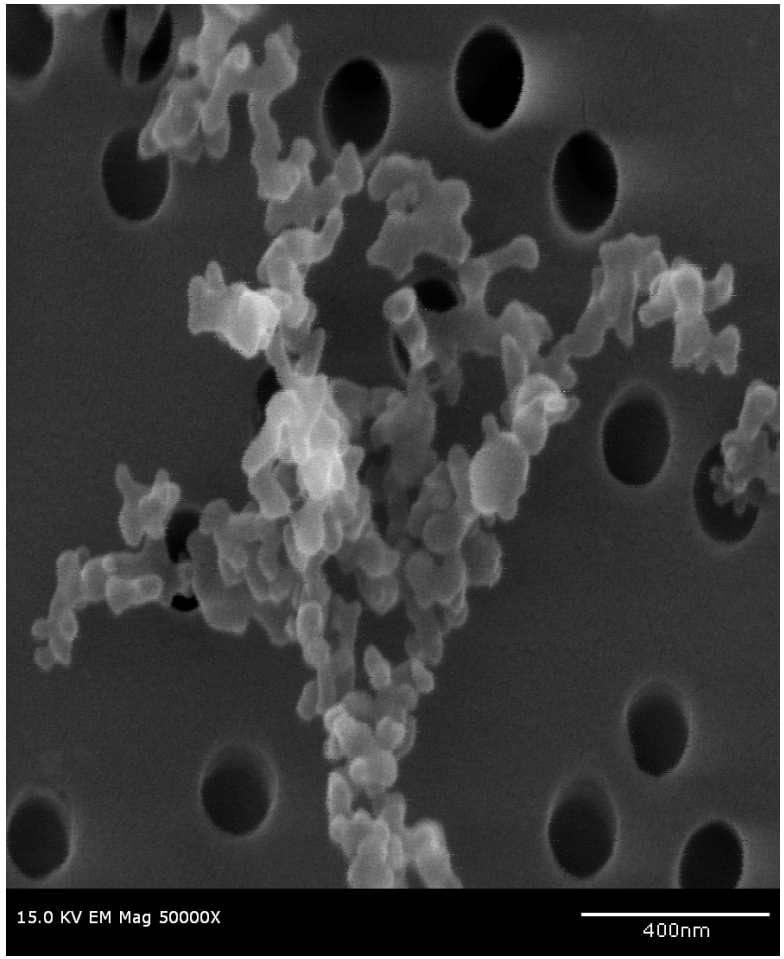
- **Cleaning from**
  - **organic coverage,**
  - **inorganics, ash.**
- **Production of well-graphitized structure,**

  perfect chemically uniform surface.

Alfa fullerene soot: soot-like aggregates

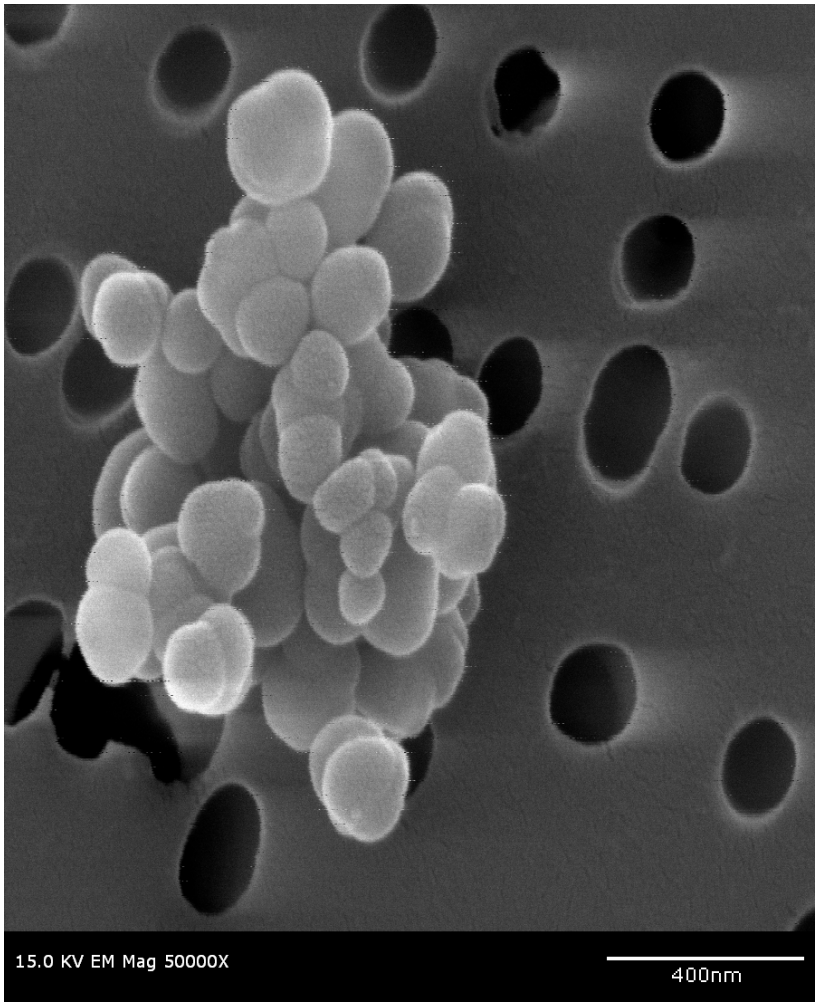


DMA @ 400 nm

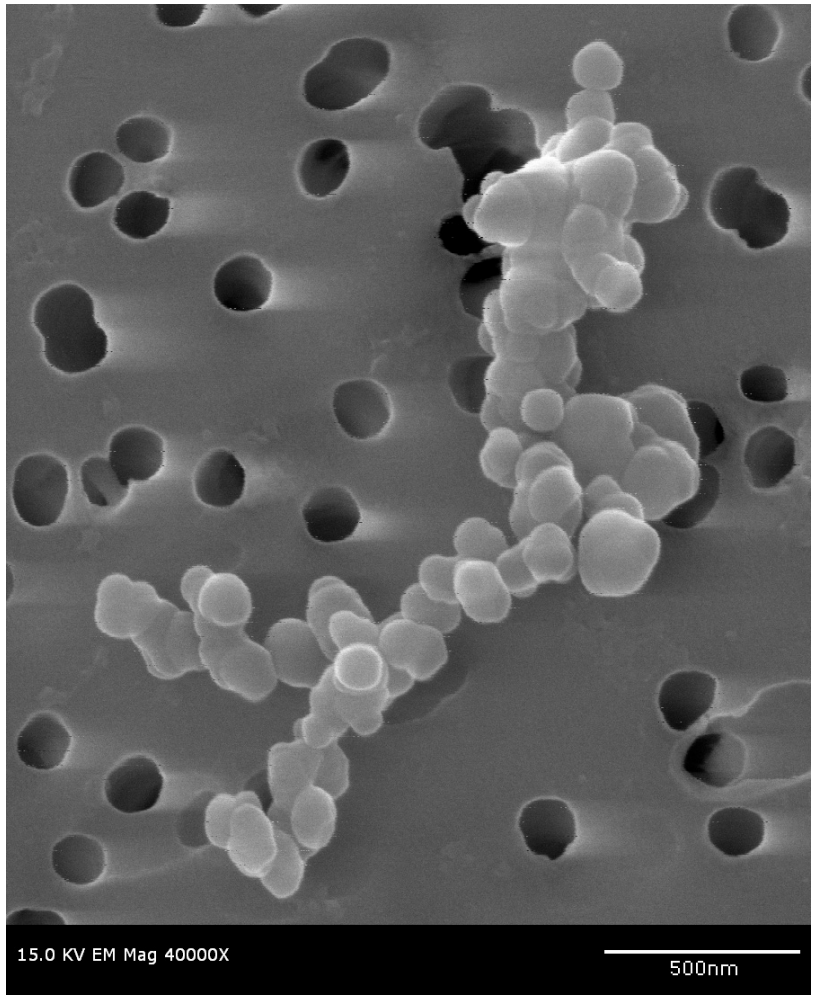


DMA @ 110 nm

Tokai glassy carbon: spherules and agglomerates

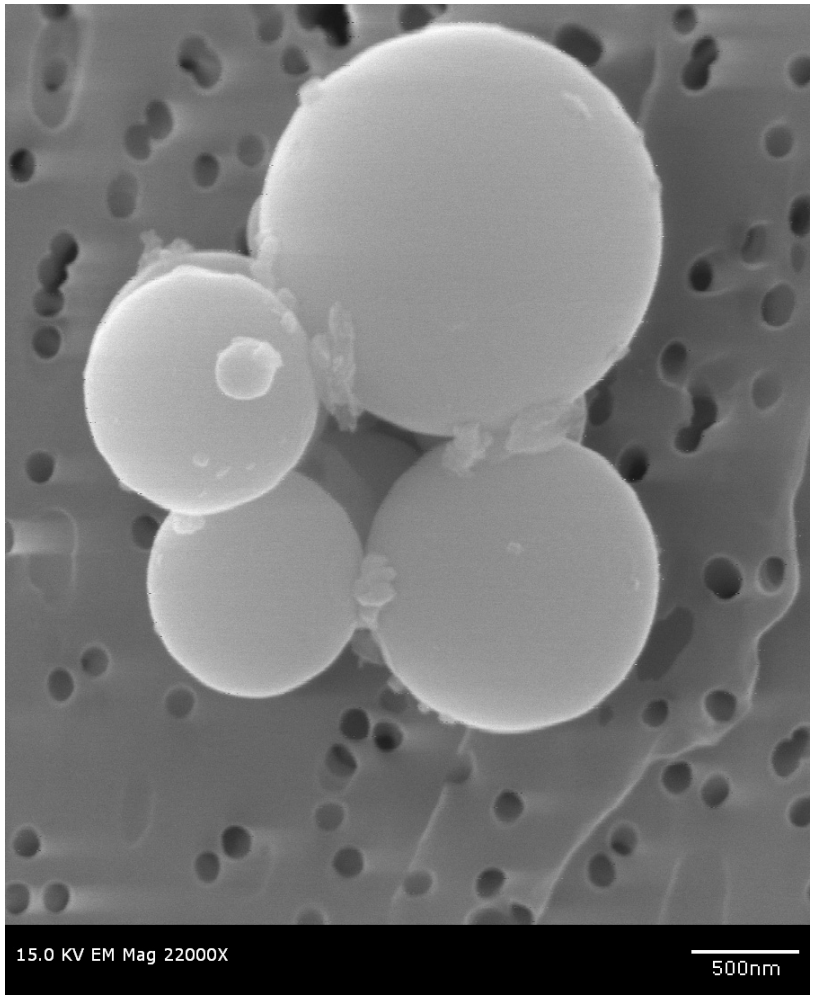


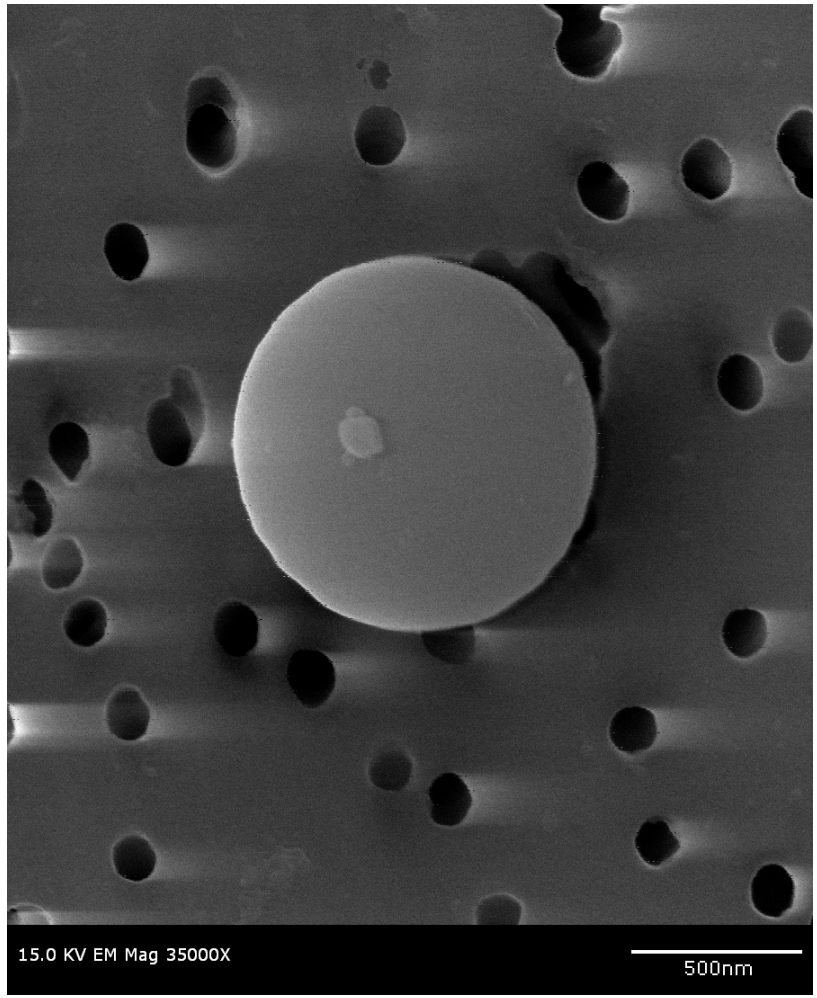
Tokai 200 nm



Tokai 200 nm, not solubilized

Alfa glassy carbon: single spheres and agglomerates





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