Tar Balls: An Important Class of BrC

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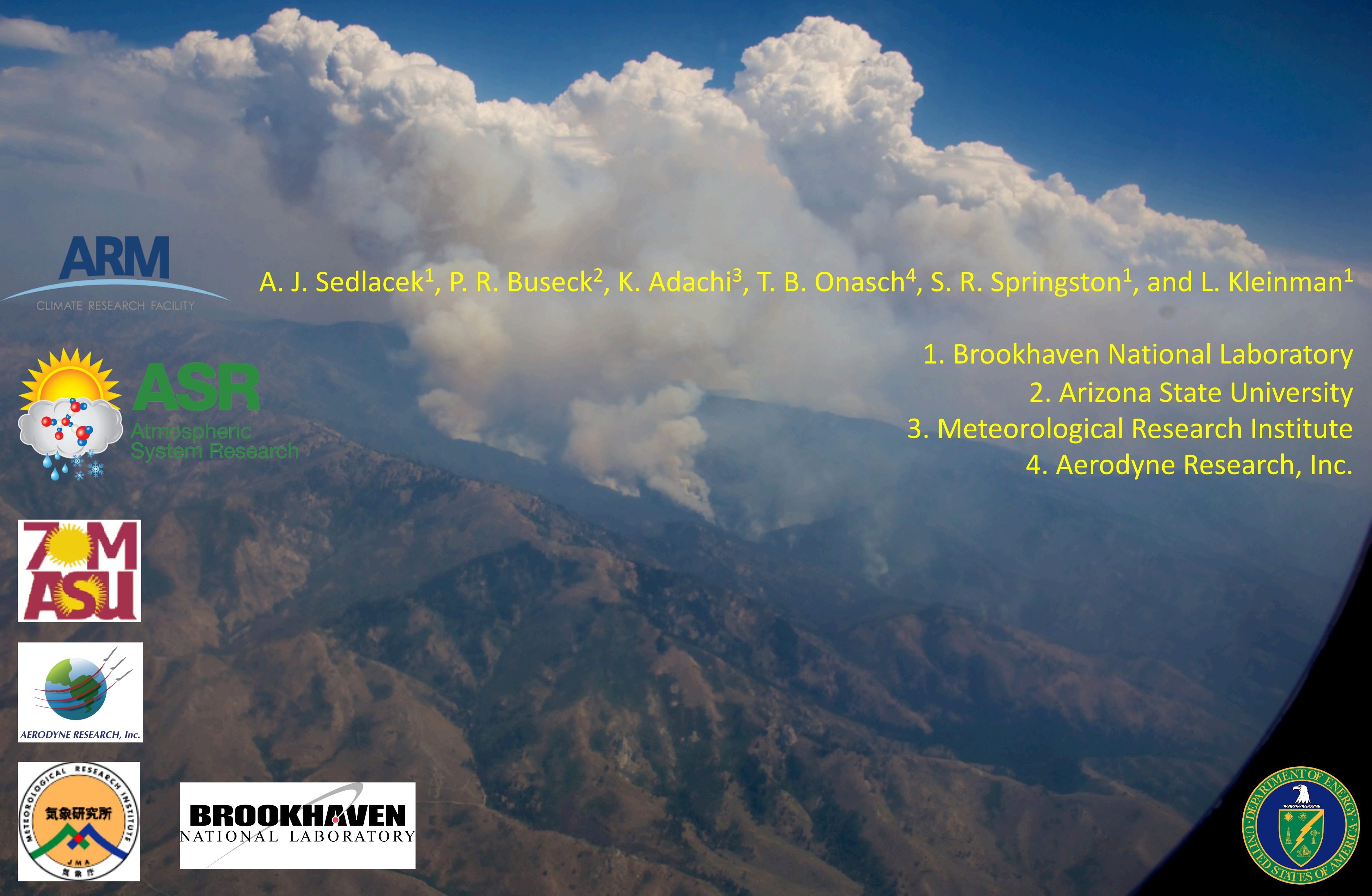
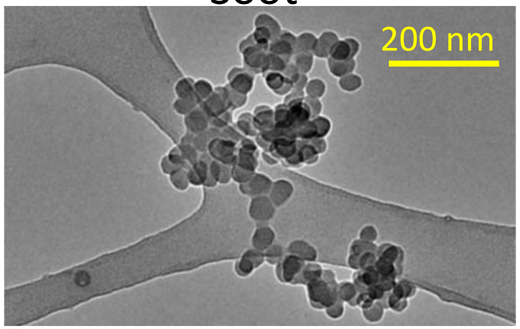


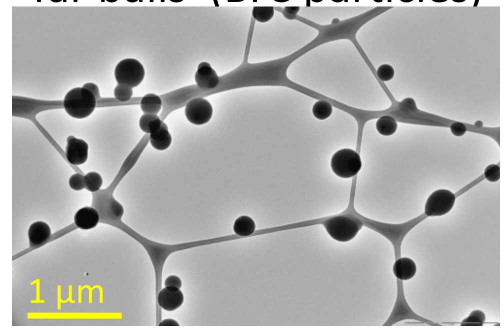
Type of Spherical Carbonaceous Solids

Soot

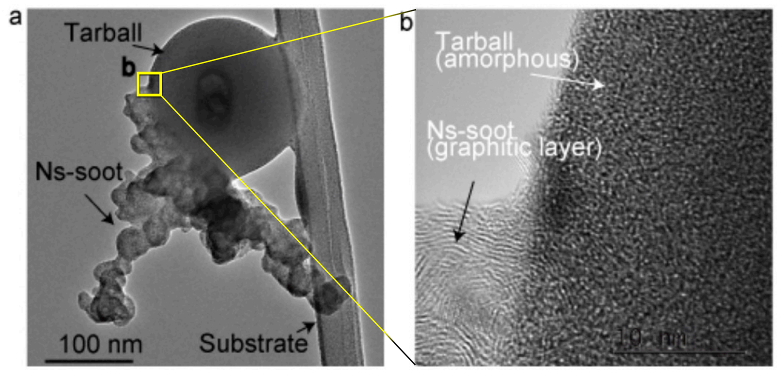


Pawlyta and Hercman Ann. Soc. Geo. Pol. 2016

Tar balls (BrC particles)



Sedlacek et al., 2018



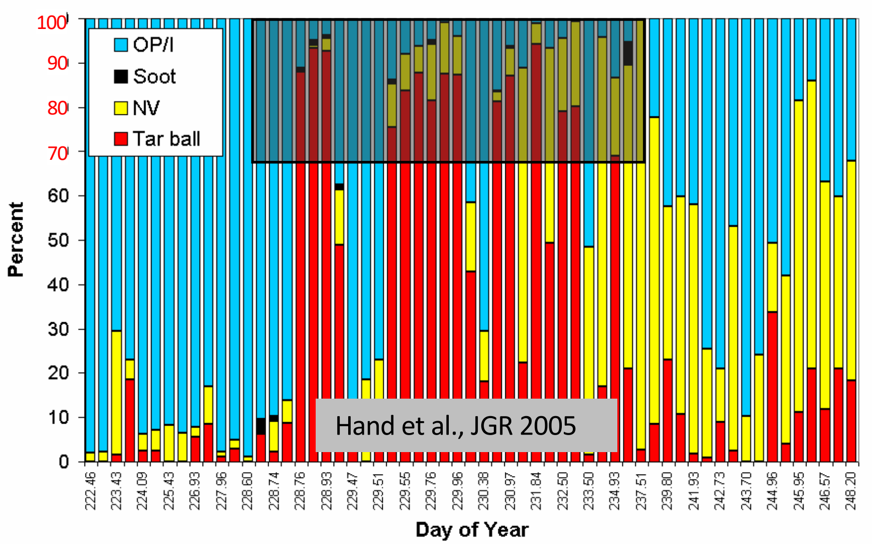
Adachi et al., (*under review*)

Tar Balls (TBs)

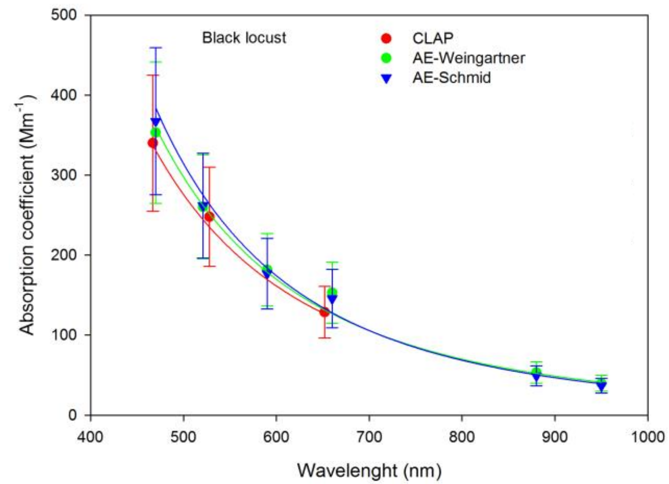
- Spherical shape
- Particle diameter between 200 - 500 nm
- High viscosity
- Lack of crystallinity and absence of graphitic fine structure
- Composed primarily of carbon and oxygen
- Low volatility
- Recognized only through transmission electron microscopy (TEM)

TBs as Major Aerosol Type with a Broad Absorption Spectrum

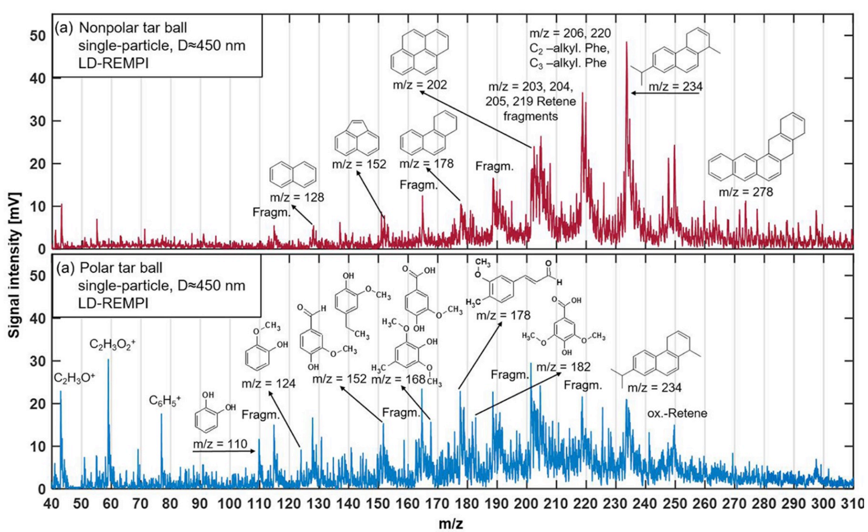
Yosemite Aerosol Characterization Study observed several wildfires that contained > 70% TBs.



Hoffer et al., (2016) reported that TBs absorb from visible to the near-IR



Evidence for 2 Flavors of TBs.

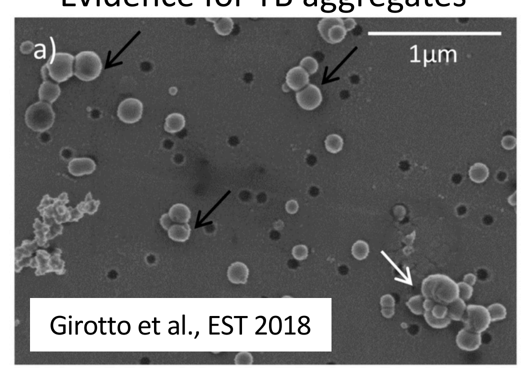


Li et al., ACP 2019

Radiative forcing impact of TBs could be significant:

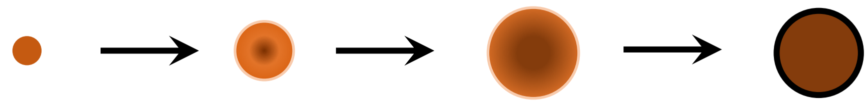
- BB events produce a lot of these particles
- TBs appear to possess a wide absorption spectrum

Evidence for TB aggregates



How are Tar Balls Formed?

- TB formation involving secondary gas-to-particle polymerization
- Followed by dehydration.



Gas-to-particle formation Polymerization and dehydration

Indirect

Pósfai et al., 2004

- Upon initial plant burning a liquid tar droplet is released from the pores of plants
- Transformation of tar droplet to tar balls occurs upon rapid heating (600 C)

Tar-water emulsion Tar ball

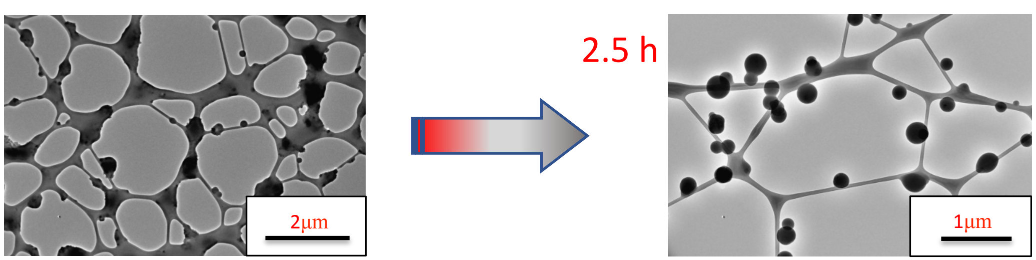
Direct

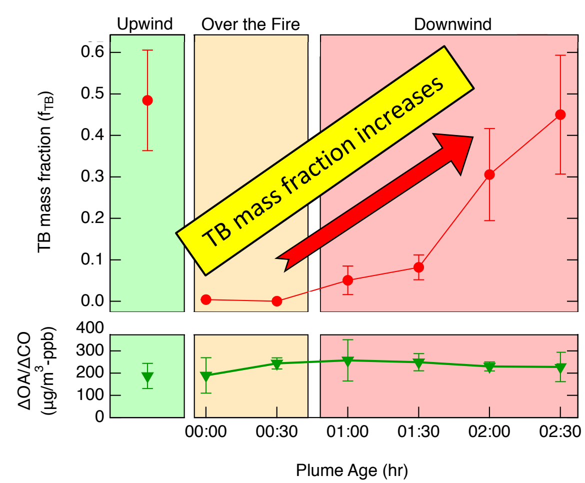
Toth et al., (2014)

BBOP demonstrated that TBs are a processed primary particles (Sedlacek ACP et al., 2018)

0 h

2.5 h

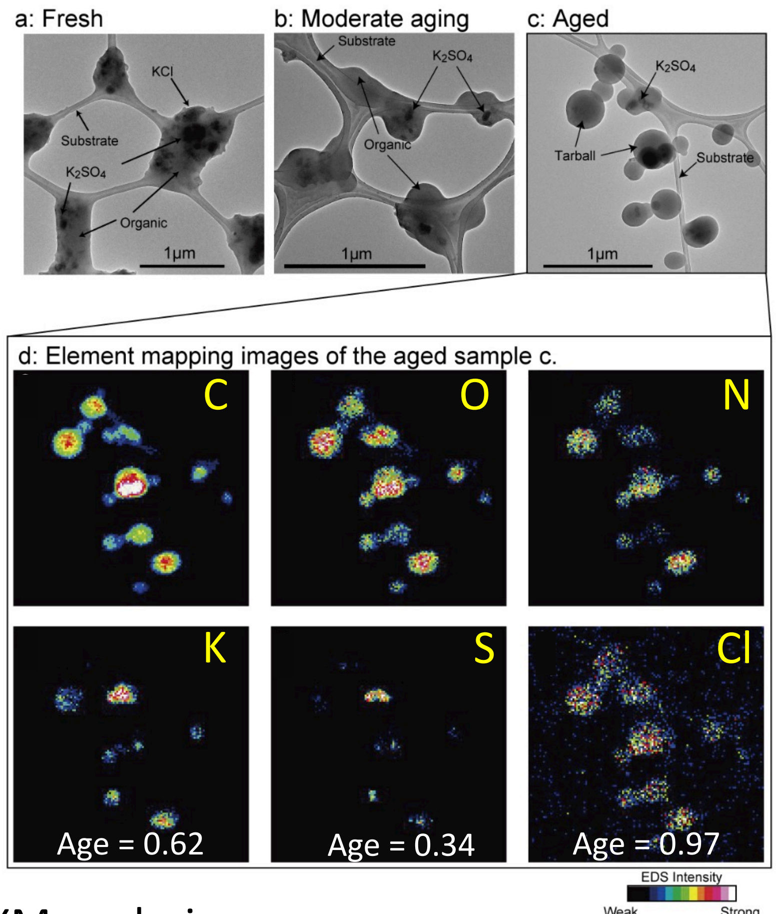




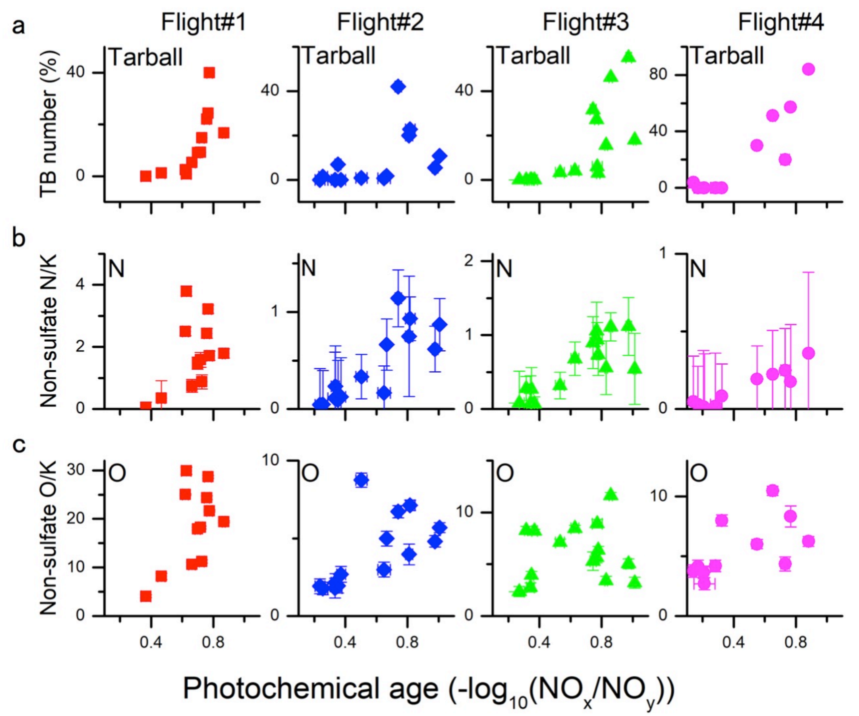
Compositional and Microphysical Changes Support Indirect Mechanism

Adachi et al., (*under review*)

Changes in particle shape and element distributions



Changes in (a) tarball number fractions, (b) non-sulfate N/K, and (c) non-sulfate O/K with photochemical age.



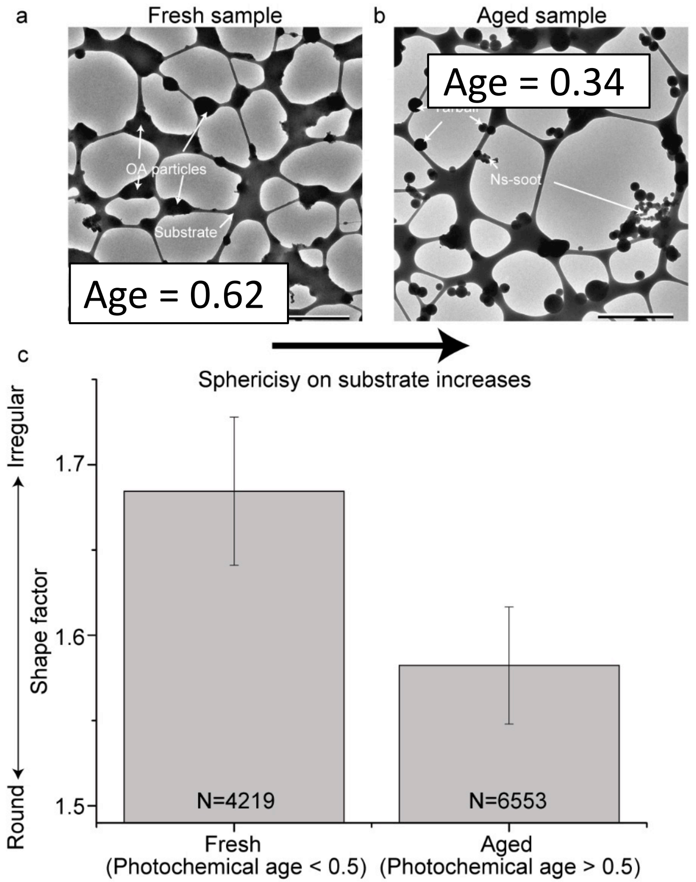
STXM analysis

- Particles become spherical and the TB number fraction increases.
- C, O, N, and Cl occur in all particles.
- K is a conserved tracer.

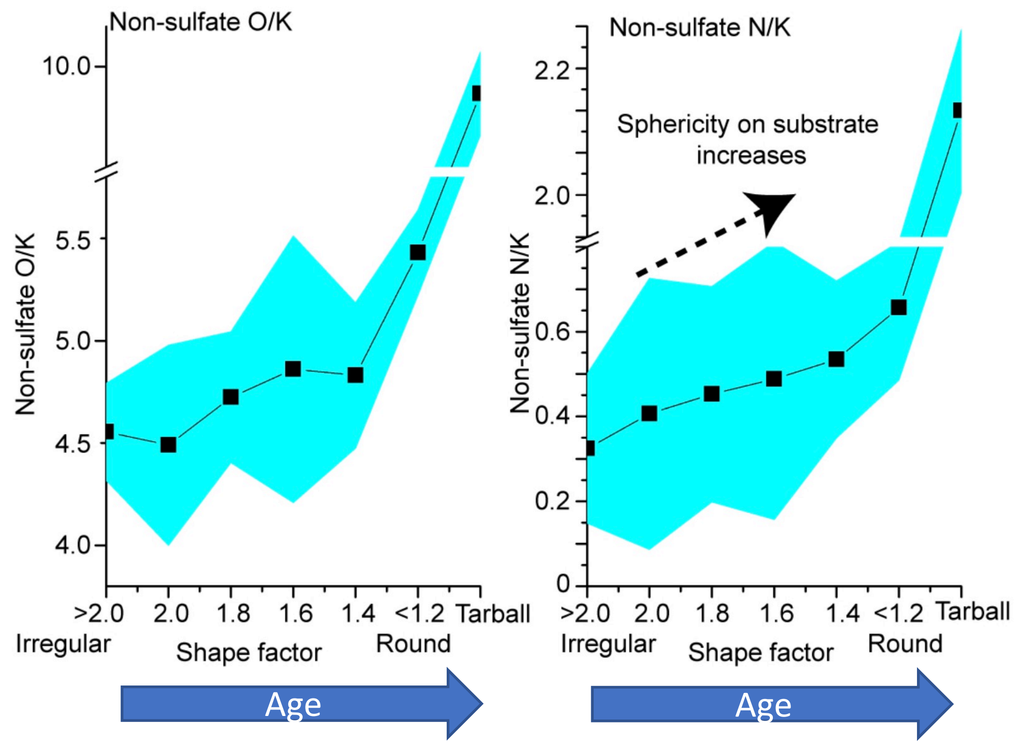
Compositional and Microphysical Changes Support Indirect Mechanism

Adachi et al., (*under review*)

Particle shape becomes more spherical with age.



Increase in O and N associated with increased sphericity.



Retention of spherical shape upon impact on the substrate indicates particles possess higher viscosity and surface tension.

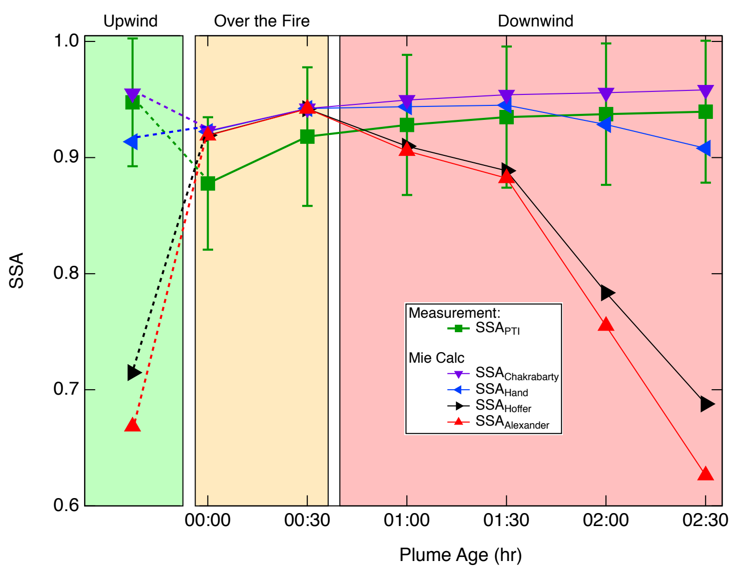
Constraint on Optical Properties of Tar Balls

Sedlacek et al., 2018

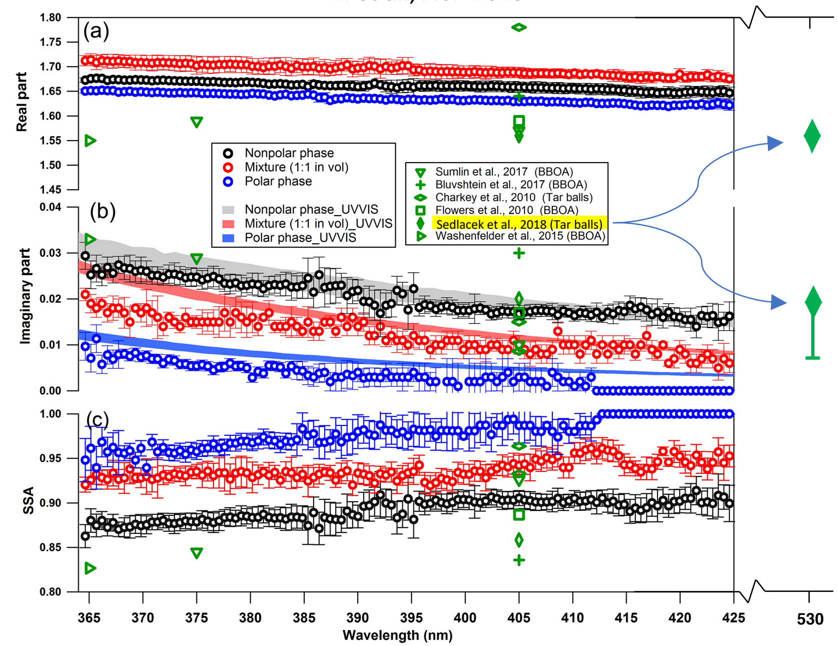
Previous reported values of Tar Ball refractive index:

- m =1.67 – 0.27i (Alexander et al., 2008)
- m =1.84 – 0.21i (Hoffer et al., 2015)
- m =1.56 – 0.02i (Hand et al., 2005)
- m =1.80 – 0.007i (Chakrabarty et al., 2010)
- m =1.75 – 0.002i (Chakrabarty et a., 2010)

100x range in imaginary component

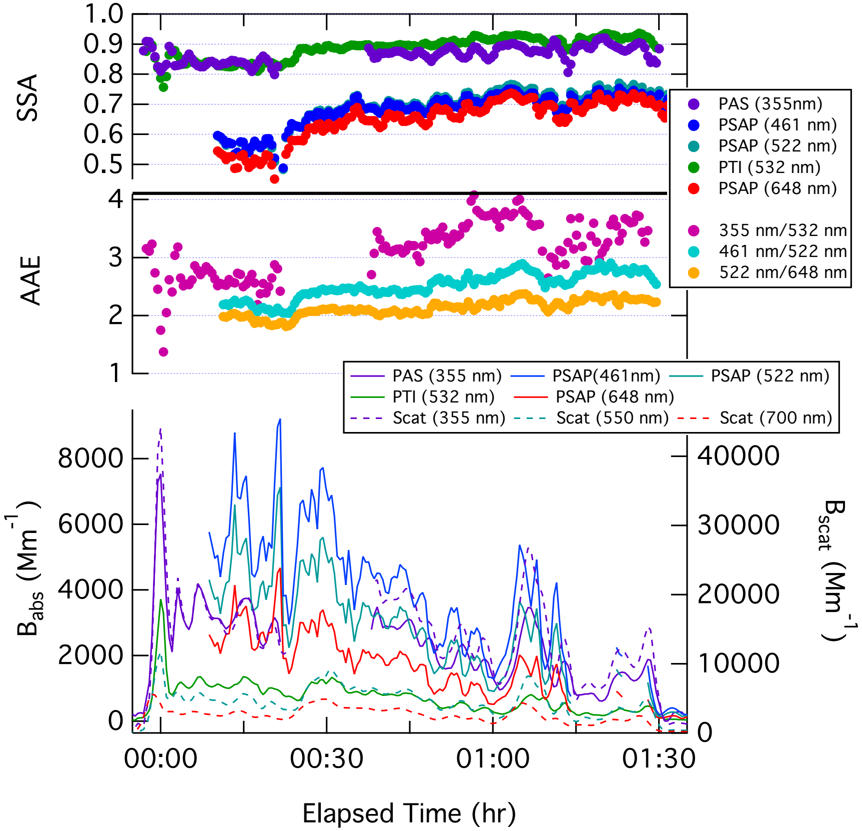


Li et al., ACP 2019



m=1.56 – 0.02i, based on SSA consistency between calculations and BBOP field measurements. (Sedlacek et al., 2018)

Evolution of Brown Carbon (BrC) Absorption



AAE

Wavelength pair	Near source	Downwind	%Δ
355/532 nm	2.6	3.5	36
464/522 nm	2.2	2.7	23
522/648 nm	1.9	2.3	13

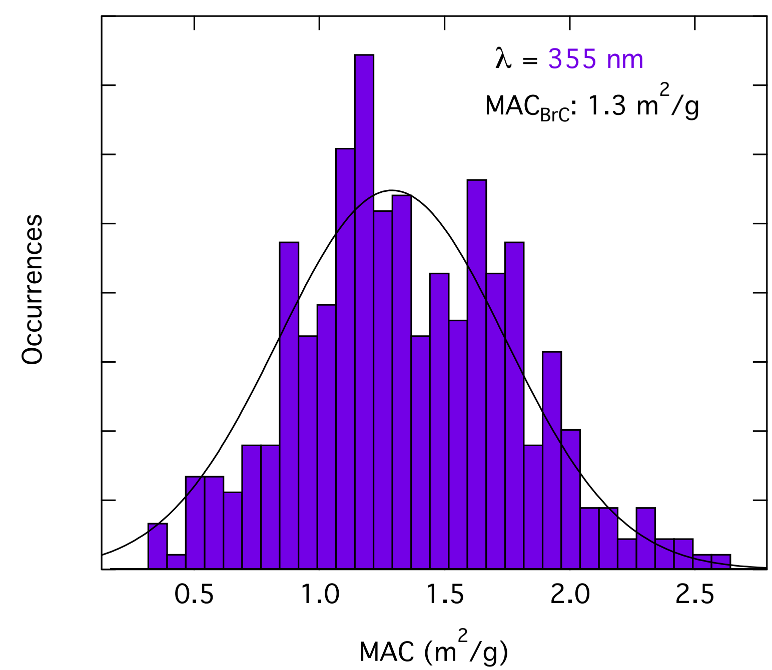
Absorption apportionment

	Near source	Downwind	%Δ
532 nm $B_{abs\text{-}BrC}/B_{abs\text{-}total}$	19%	28%	45
355 nm $B_{abs\text{-}BC}/B_{abs\text{-}total}$	40%	30%	-25

Use B_{BC}^{532nm} to estimate B_{BC}^{355nm}

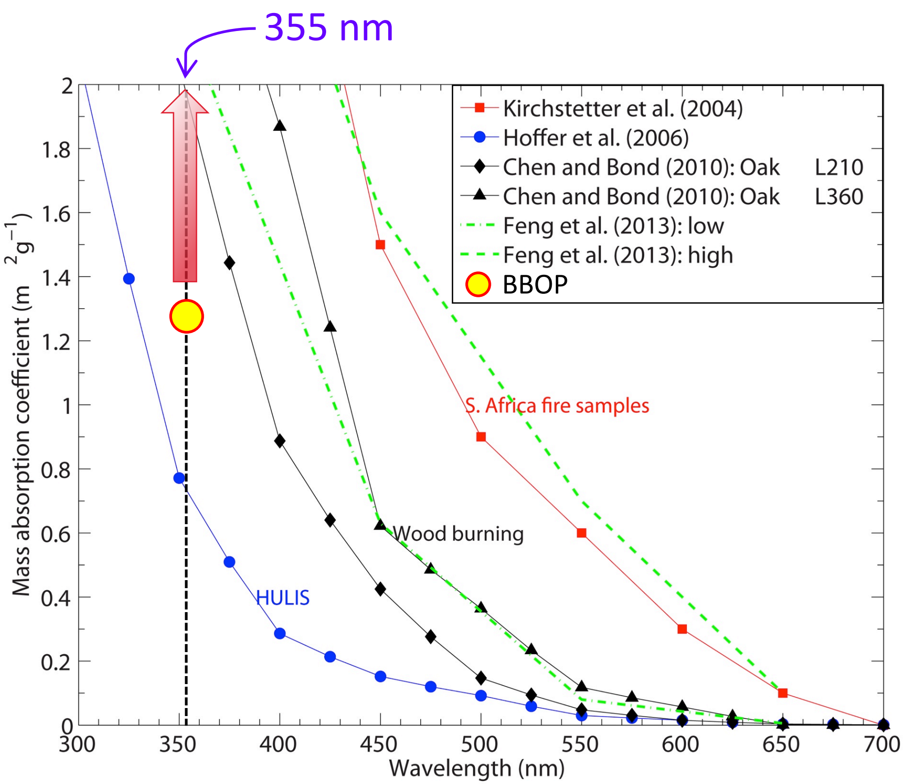
$$B_{BrC}^{355nm} = B_{expt}^{355nm} - B_{BC}^{355nm}$$

OA loading from SP-AMS



BrC Mass Absorption Cross-Section (MAC_{BrC})

MAC_{BrC} (1.3 m^2/g @ 355 nm) compares very favorable with MAC_{TB} = 1.1 m^2/g reported by Li et al., (2019)



Plot courtesy of Y. Feng (ANL)

Core assumption: all ORG contributes to BrC absorption

Order-of-magnitude range

Barnard et al., 2008

MAC_{BrC} (350 nm): ~7.7 m^2/g

Kirchstetter et al., 2004

MAC_{BrC} (350 nm): 5 m^2/g

Sun et al., 2007

MAC_{BrC} (350 nm): ~ 5.4 m^2/g

Chen and Bond, 2010

MAC_{BrC} (360 nm): ~ 2.2 m^2/g

Li et al., 2019

MAC_{BrC-TB} (360 nm): 1.1 m^2/g

Hoffer et al., 2006

MAC_{BrC} (350 nm): ~ 0.9 m^2/g

Lin et al., 2015

$MAC_{BrC-bulk}$ (365 nm): ~ 0.8 m^2/g

Microphysical Properties of Tar Balls

AEROSOL SCIENCE AND TECHNOLOGY
2018, VOL. 52, NO. 1, 46–56
https://doi.org/10.1080/02786826.2017.1373181

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Check for updates

Volume changes upon heating of aerosol particles from biomass burning using transmission electron microscopy

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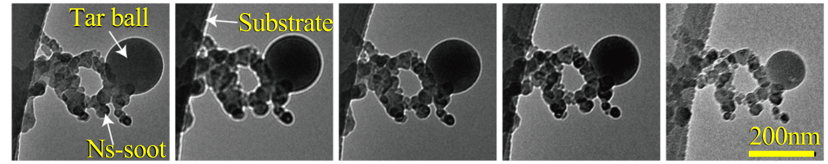
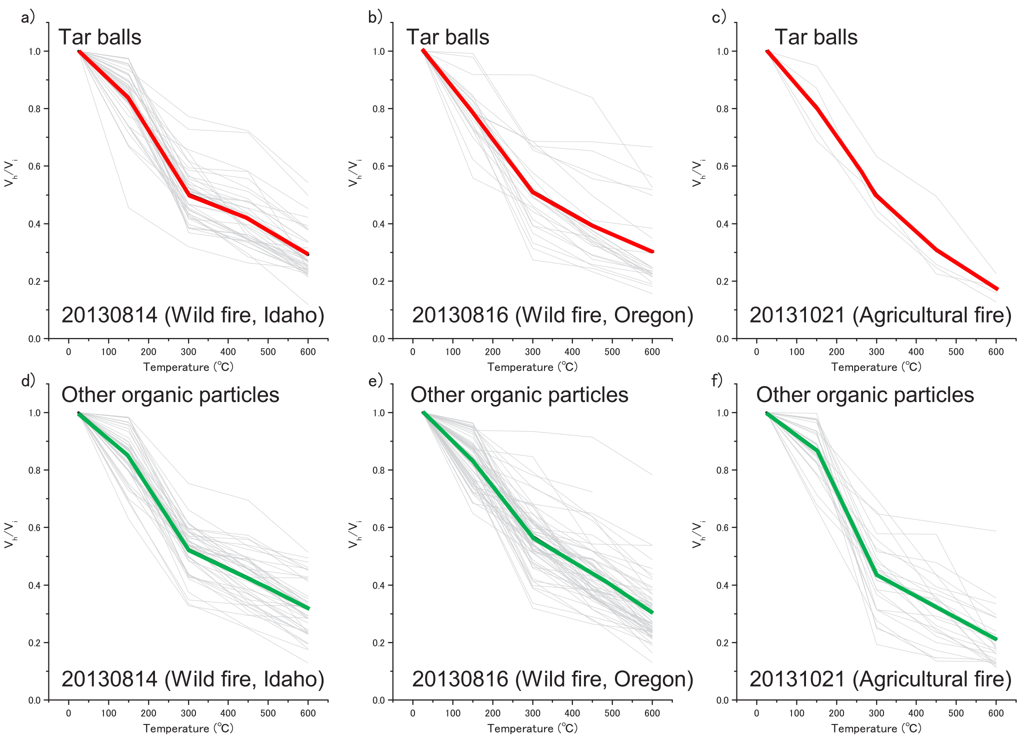


25 C 150 C 300 C 450 C 600 C



- Chemical analysis reveals that K and Na remain in the residues, whereas S and O were lost.
- Some organic particles exhibit significant thermal stability.
- Results suggest caution assuming complete loss of organic material with thermal denuders.

- Single-particle results imply that many individual organic particles consist of multiple types of organic matter having different thermal stabilities.
- Potentially under report measurements of carbonaceous particles using thermal/optical carbon analyzers

Evidence for Charring of Tar Balls

AEROSOL SCIENCE AND TECHNOLOGY
https://doi.org/10.1080/02786826.2018.1531107

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AEROSOL RESEARCH LETTER

Formation of refractory black carbon by SP2-induced charring of organic aerosol

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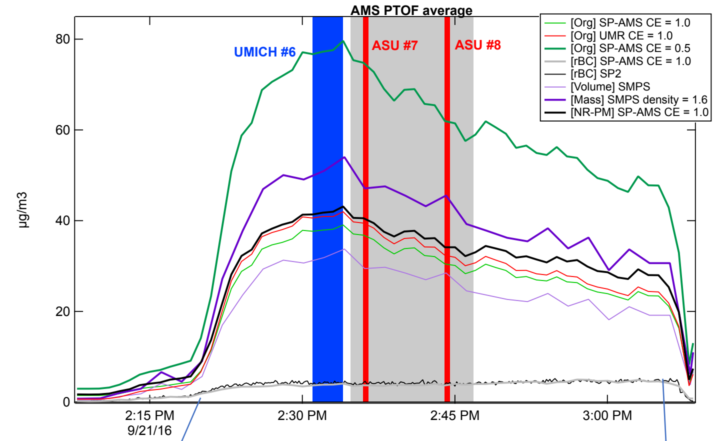
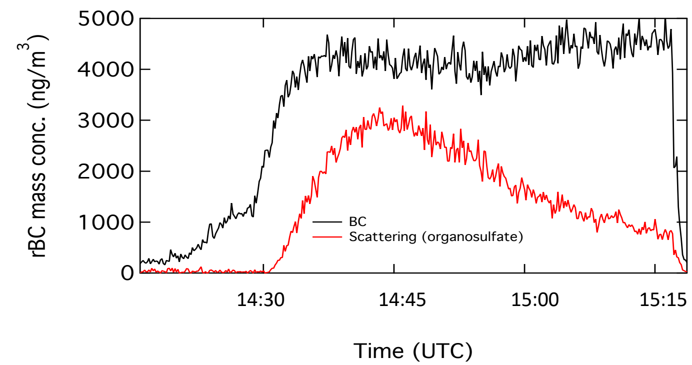


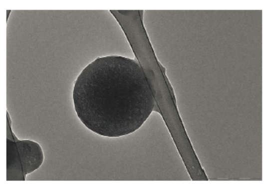
In 2016, Aerodyne and Brookhaven pyrolyzing pine twigs to generate TBs and found these TBs to contain hydrocarbons and rBC. The latter a very puzzling result.

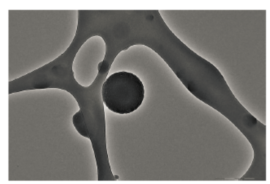
Onasch et al., 2017



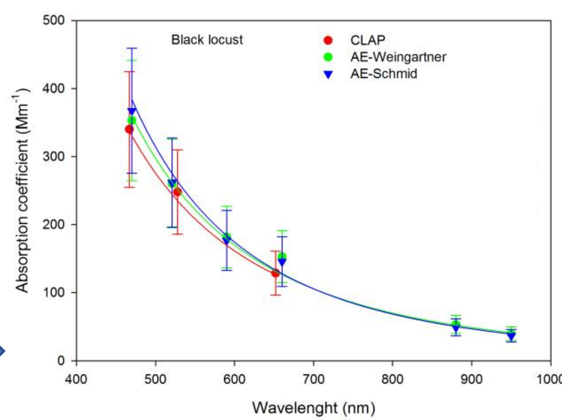
Pyrolysis of pine twigs

Lab-generated TBs similar





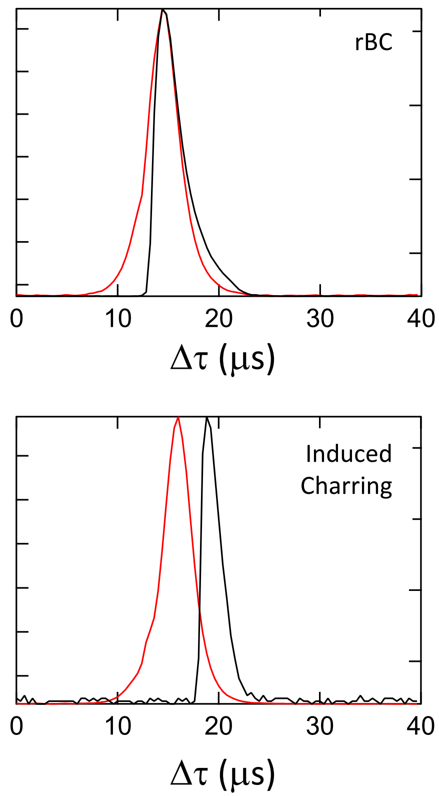
Hoffer et al., (2016) that SP2 can induce charring and rBC production in those materials possessing a near-IR absorption

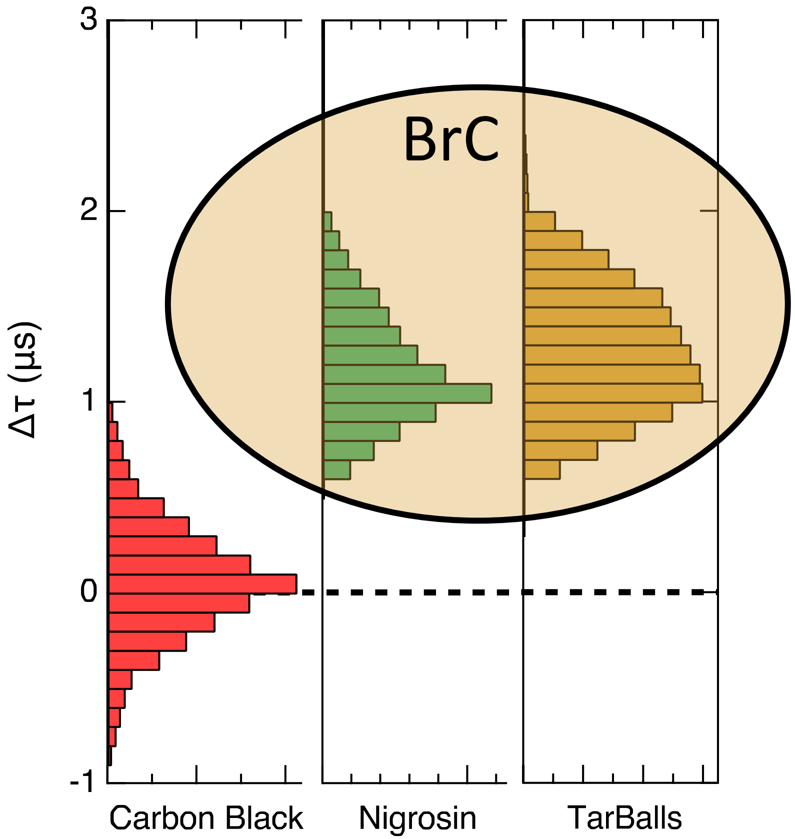


It is estimated that ~10% of the TBs generated underwent SP2 laser-induced charring.

Non-Microscopy Measurement of TBs

Sedlacek AS&T et al. 2018





Sedlacek et al., 2018 demonstrates that rBC production via laser-induced charring of near-IR light absorbing OA

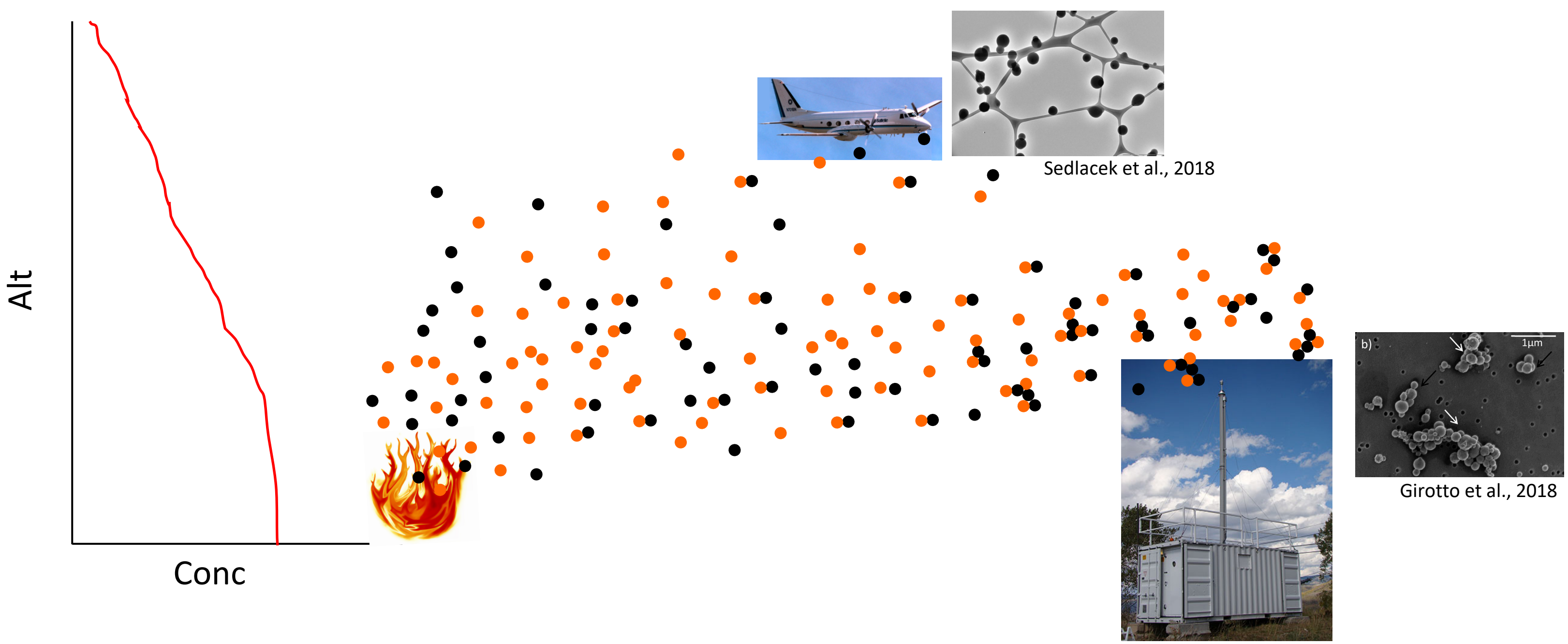
- TBs possess requisite near-IR (NIR) light absorption: ~ 10% charring efficiency.
- Potentially technique to provide particle-resolved measurement of NIR light absorbing BrC.

Observation of Coagulated and Uncoagulated Tar Balls

Aircraft-based measurements see little evidence for coagulated TBs
Ground-based measurements report presence for coagulated TBs

One explanation to reconcile these two observations

- Smoldering conditions are lower temperature translating to lower injection height of emissions.
- Resulting concentration gradient would favor high concentrations lower to the ground.
- Higher concentrations favor coagulation.



Summary

Tar balls are an important class of aerosol that can (*should*) be treated as uniquely as soot is is treated in models of wildfire plumes.

- Detected by several groups throughout the world representing several different fire source.
- These aerosols can represent a sizable contribution to BB aerosol mass.
- Light absorption spans the entire spectral range from UV to near-IR.
- Refractive index is closer to that of BrC ($i \sim 0.02$) and not $i \sim 0.2$.
- Primary processed particles (low-viscosity OA → high-viscosity, spherical particle).
- Evidence that TBs can be uniquely detected via online techniques (SP-LD-REMPI; AMS; SP2).

Outstanding questions

- How representative are laboratory-generated TBs to those measured in the field.
- What are the hygroscopic properties of these particles.