### Colockum Tarps Wildfire: June 30, 2013





Orthogonal transects roughly represent 30-minutes of aging starting from 0 hours over the fire ( $B_{ext}$ : A. Freedman)

#### ASU: TEM Sampler

Lacy-Carbon grid One collection/transect



## **Types of Spherical Carbonaceous Solids**

Ns-soot



Li, Pósfai, Hobbs, Buseck (JGR 2003)

#### Tar balls (BrC particles)



Li, Pósfai, Hobbs, Buseck (JGR 2003)

100x

### Tar Balls (TBs)

- Organic particles distinguished by shape, composition, high viscosity, lack of crystallinity, and possibly refractory character
- Uniquely recognized through electron microscopy; overlooked by other measurement (?)
- Size Range: 100 300 nm
- Can contain up to 10 mol % of non-carbon elements, mainly H, O, S
- Are one of the major identified components of brown carbon (BrC) (e.g., Andreae & Geléncser 2006)
- Refractive Index
  - o  $RI_{TB} = 1.27 0.27i$  (Alexander et al. 2008) &  $RI_{TB} = 1.84 0.21i$  (Hoffer et al., 2015)
  - $RI_{TB} = 1.56 0.02i$  (Hand et al., 2005)
  - RI<sub>TB</sub> = 1.75 0.002i (Chakrabarty et al., 2010)

## **Evolution of Tar Balls**

Lingering uncertainty about TB Formation mechanism

- Primary: rapid heating of primary plant emissions
- Secondary: oxidation/photolysis of POA

BBOP data shows increase in TBs number as a function of plume age





# **TB Fraction in a Wildfire Plume**

Conclusive detection of TBs is still limited to electron microscopy (e.g., TEM) Several TEM studies have reported very high TB fractions (>50%)

However:

Loss of volatile material can occur during storage and electron beam interrogation TEM-derived TB fractions overestimate the true contribution of TBs

Combine TEM, AMS, and SP2 to provide estimate the TB mass fraction in the plume



Plume Age

Sedlacek et al., manuscript in prep

### **Thermal Robustness of Tar Balls**

n = 8 TBs

500

600



## **Take Home Messages**

Tar balls are observed to increase in number fraction as a function of plume age

- TB formation proceeds through a secondary process.
- First time that high-temporal-resolution data has documented this formation.
- Growth in TBs means increase of an absorbing component in the plume contrary to commonly observed increase in SSA
- TB mass fraction estimated in plume
  - Combining the ratio of TB mass to ns-soot mass derived from TEM with rBC mass fraction (from SP2 & AMS), the mass fraction of TBs in plume is estimated to be ~0.30.
  - First time the mass fraction of TBs in a smoke plume has been estimated.

Thermal Robustness of TBs

- Heating experiments reveal that TBs exhibit a degree of thermal robustness (refractory character)
- Implications to AMS detection efficiency (600° C) must be understood.

Likely that biomass burn inventory is underestimated due to the difficulty of measuring TBs.

- BBOP derived TB mass fractions suggests this underreporting could be 25-30%
- Help in closing the top-down/bottom-up discrepancy (2-4x; see Kaiser et al., 2012)







