# How well can we generate, characterized, and predict black carbon soot particle optical properties?

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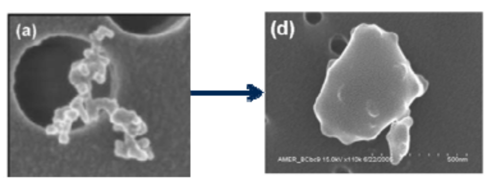
# Atmospheric Black Carbon

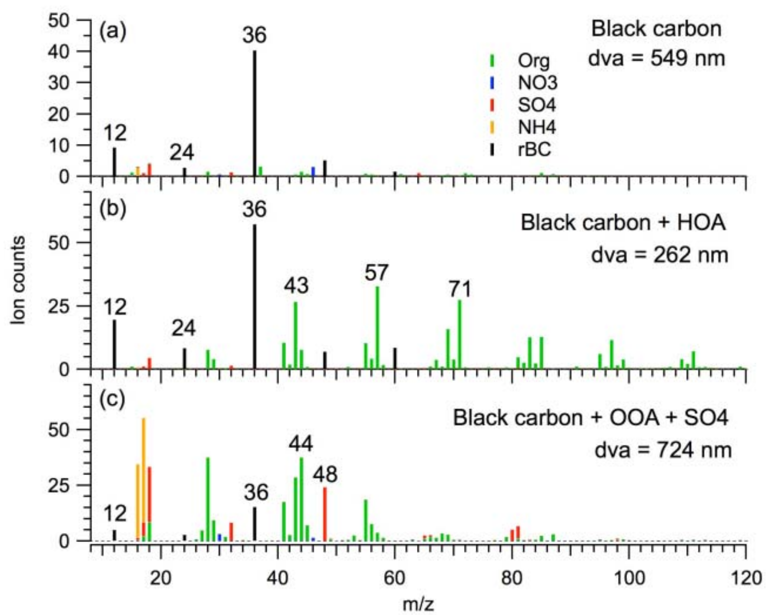
- Product of incomplete combustion
- Emissions as high as 8 TgC/yr
  - ~60% fossil fuel and biofuel consumption
  - ~40% open biomass burning
- Non-spherical shape that depends on chemical processing
- Absorbs light strongly; depends upon coating material
- IPCC Fifth Assessment Report direct RF for fossil fuel

  BC= +0.40 W $m^{-2}$ (+0.05 to 0.80 W $m^{-2}$)

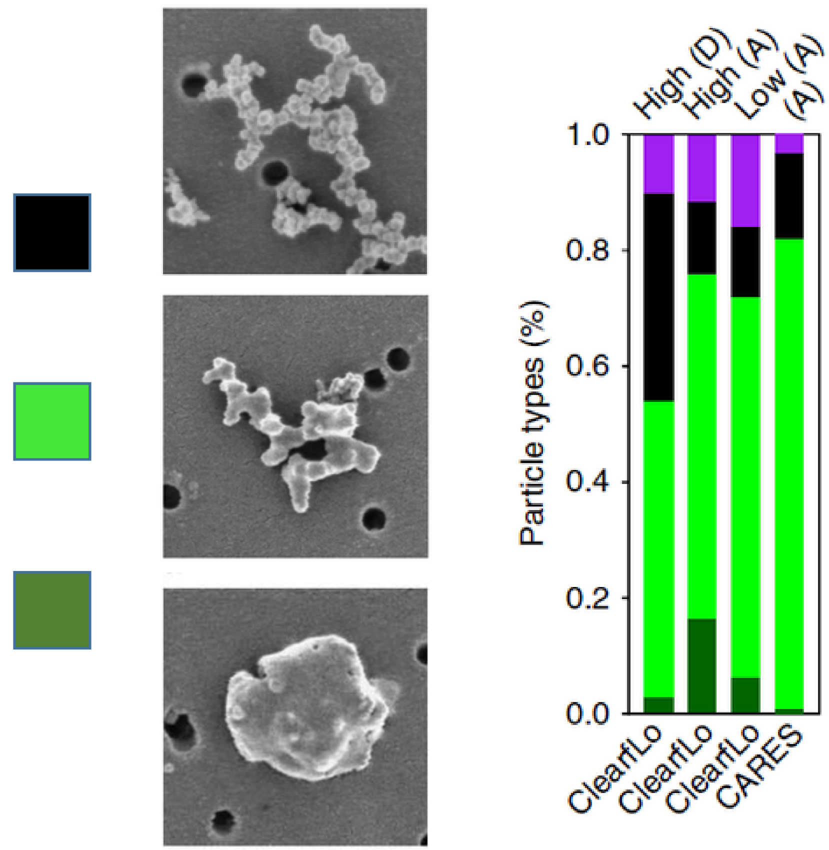


# Particle mixing state

- In urban and rural environments, BC is found internally mixed to varying extents with organics (POA and SOA) and inorganics ($SO_4$ and $NO_3$).



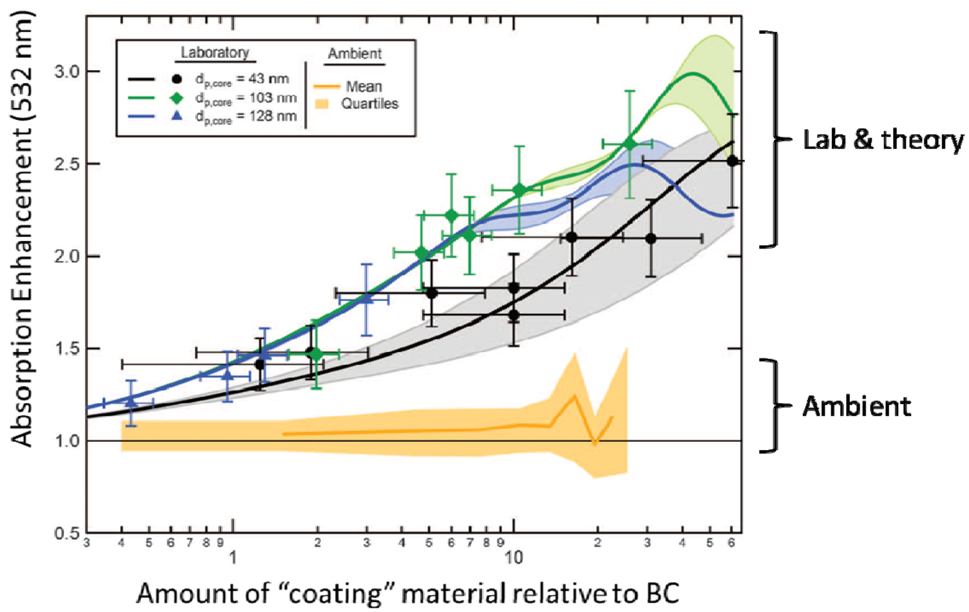

*Alex Lee et al., 2015 - U. Toronto*



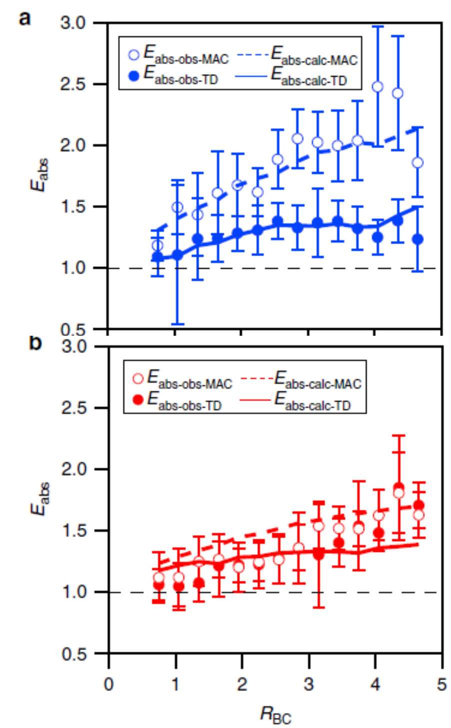

*Liu et al., 2015 - Mich. Tech. Univ.*

# Radiative impact of internal mixing

*Cappa et al., 2012*




*Liu et al., 2015*




California urban summer

- Mainly urban (traffic, etc.) sources with little/no biofuels
- Measurements lower than shell-core Mie theory

UK suburban winter

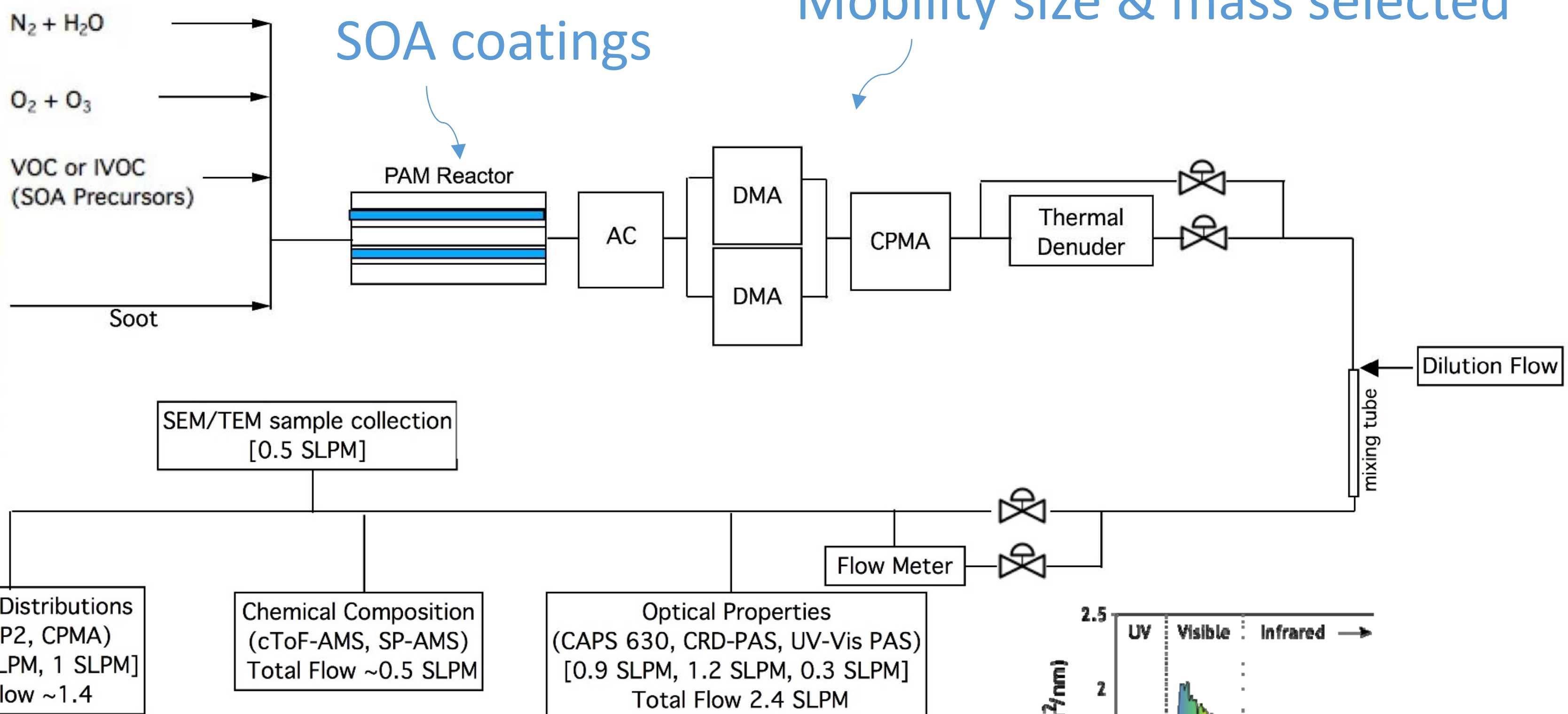
- Mixed sources including solid fuel burning
- Measurements match shell-core Mie theory

# BC4 experimental details

Diffusion flame

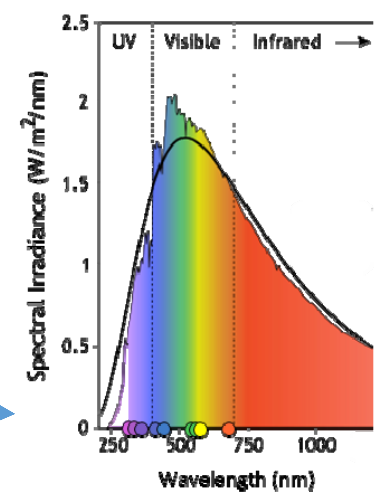
SOA coatings

Mobility size & mass selected





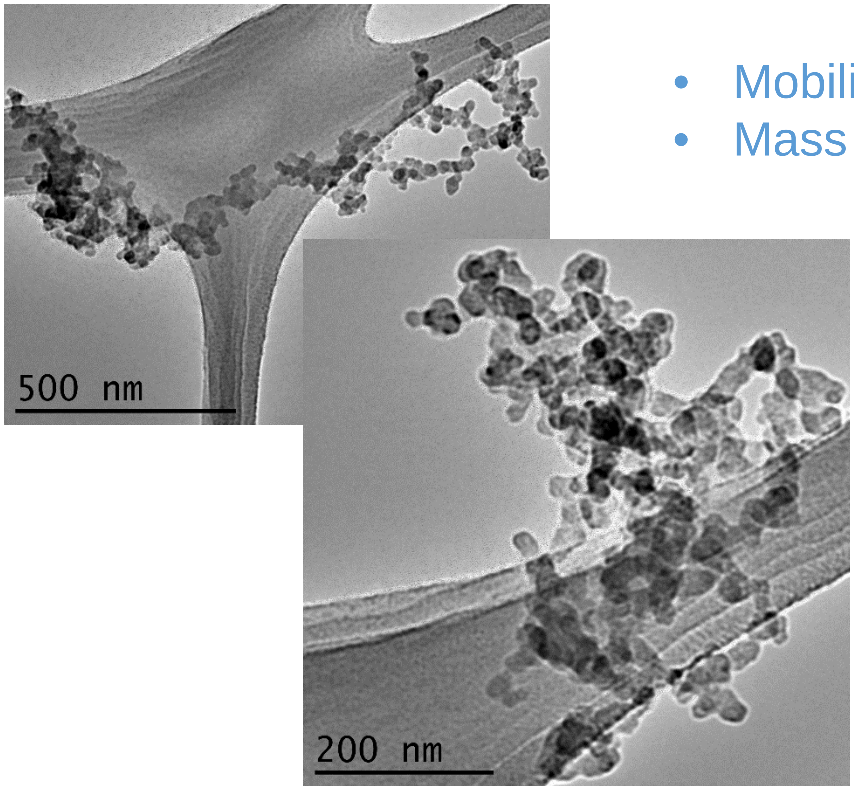
Optical properties measured across UV-Vis range!

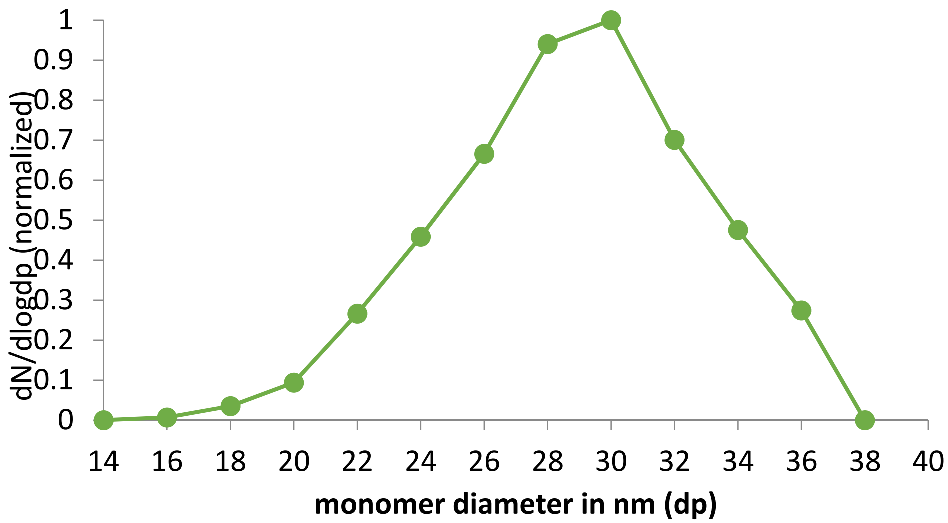


# Flame generated nascent soot

Methane diffusion flame – ‘mature’ soot

- Mobility selected 300 nm (DMA)
- Mass selected 3.3 fg/particle (CPMA)



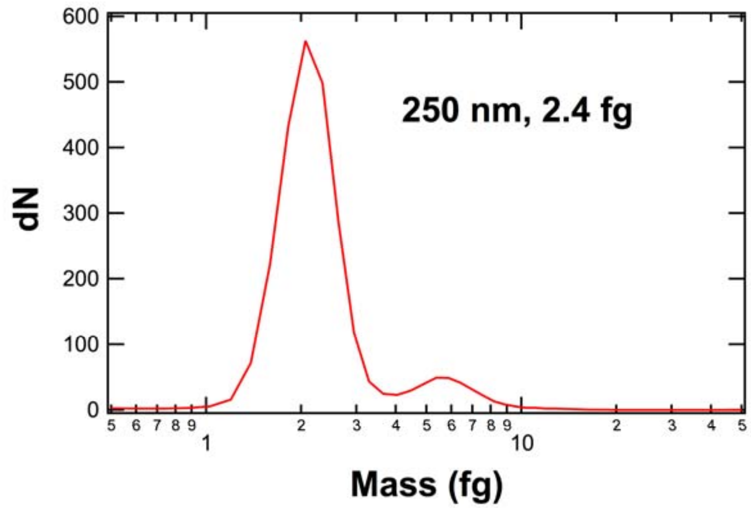



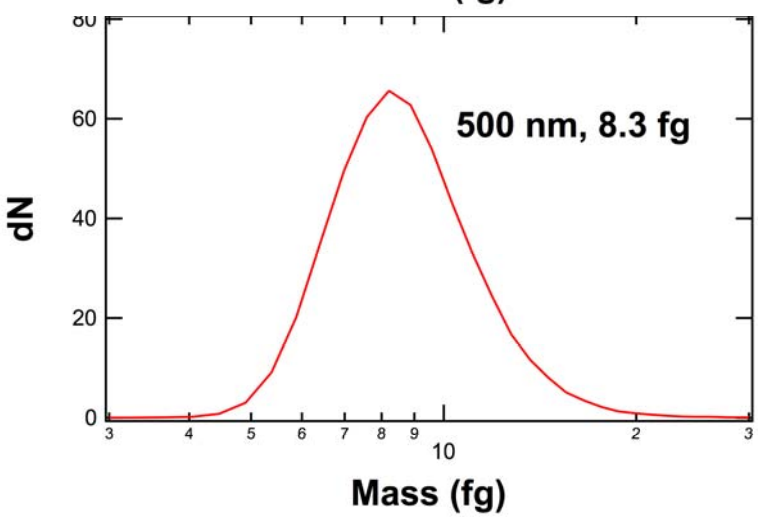

- Fractal particles composed of ~30 nm spherules
- Variety of geometries, including more linear and compact

*Janarjan Bhandari, Swarup China, Claudio Mazzoleni – Michigan Technical University*

# Mass Corrections Using SP2

## Effects of $Q^{+}$ and $Q^{++}$




- 250 nm, 2.4 fg
  Two Mass Peaks
  Q1 = 2.1 fg
  Q2 = 5.4 fg
  <m> = 2.80 fg

- 500 nm, 8.3 fg
  Single Valued
  Q1= Measured Mass

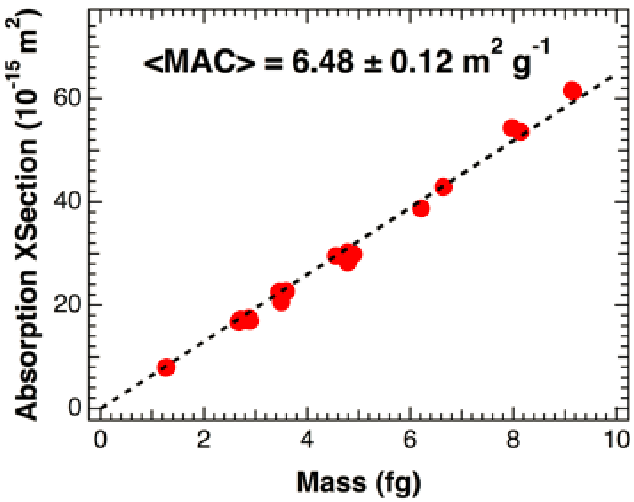
***Acknowledge DOE ARM SP2***

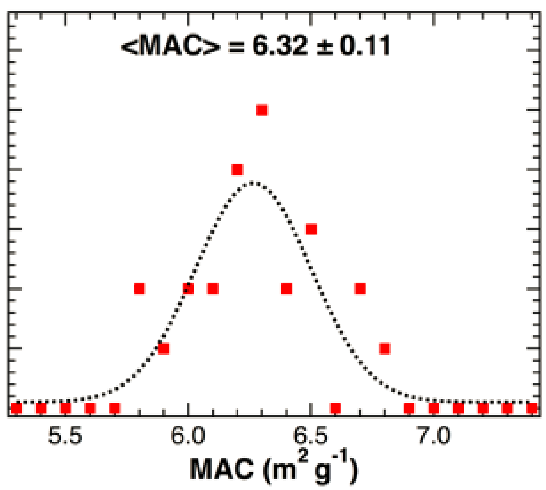
*Arthur Sedlacek– Brookhaven National Laboratory*

# MAC

Mass Absorption Coefficient (Absorption Cross Section Per Unit Mass)

*Used With Soot Emission Inventories in GCMs to Calculate Radiative Forcing*

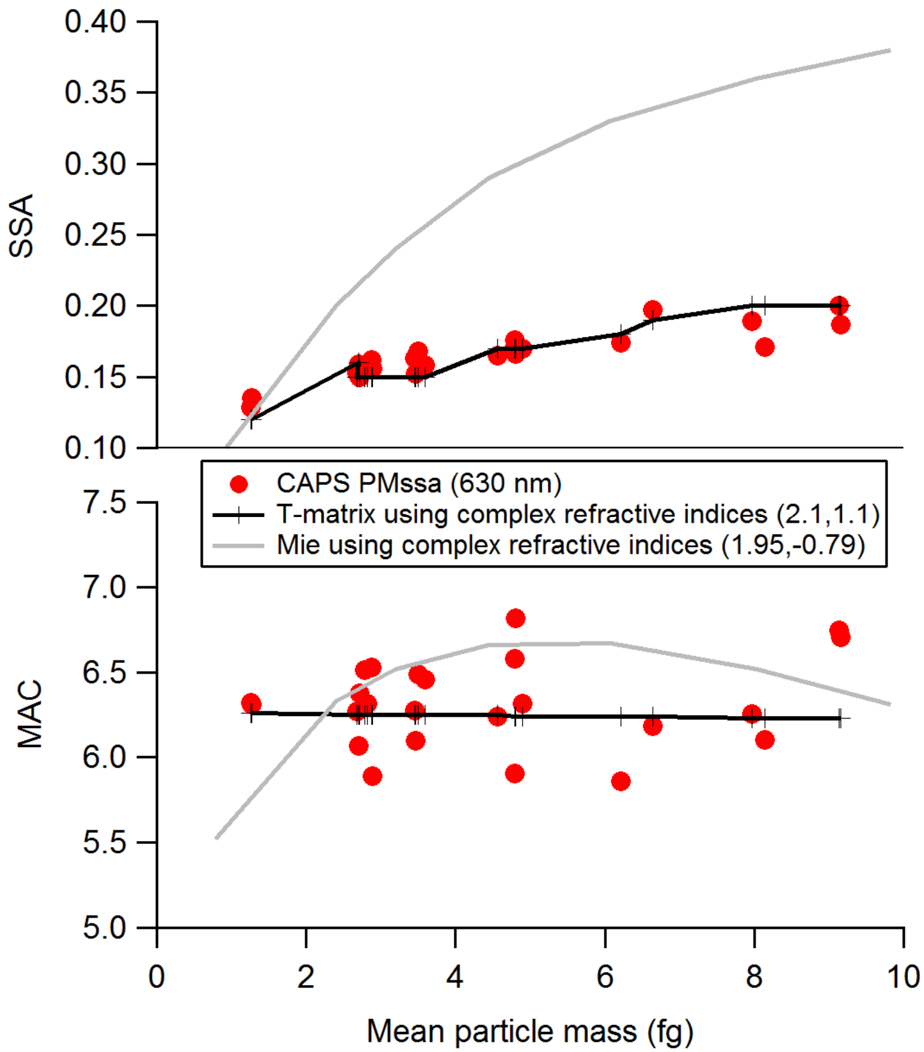



$\lambda$ = 630 nm

- MAC= 6.40 ± 0.22 $m^2$ $g^{-1}$
  (2$\sigma$ precision)
- Total Uncertainty = ±10%
  (Accuracy + Precision)
- Literature
  6.5±1.0 $m^2$ $g^{-1}$ (Bond and Bergstrom, 2006)
  6.5±1.0 $m^2$ $g^{-1}$ (Petzold and Schönlinner, 2004)

# Predictive optical theories




Mie theory

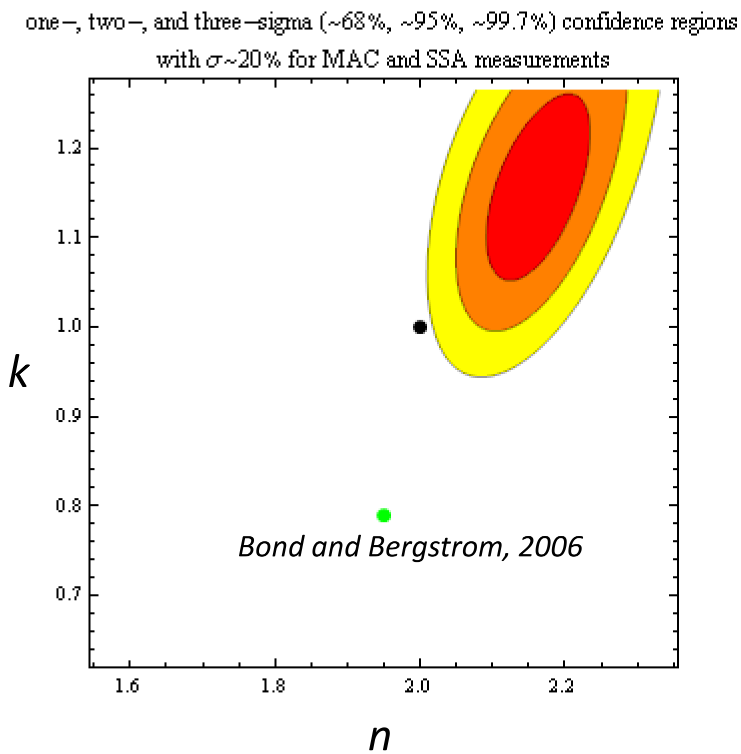
- assuming mass-equivalent sphere
- material density = 1.8 g cm-3
- RI (1.95, -0.79) (Bond and Bergstrom, 2006)

T-Matrix theory

- assuming constant size primary spherules, no overlap of spherules, and no necking
- exact results for a given geometry
- simulated representative aggregate geometries created with cluster-cluster (CC) and diffusion limited aggregation (DLA) methods

Mie theory does not match measurements well for both absorption and scattering!

# Derived complex RI's



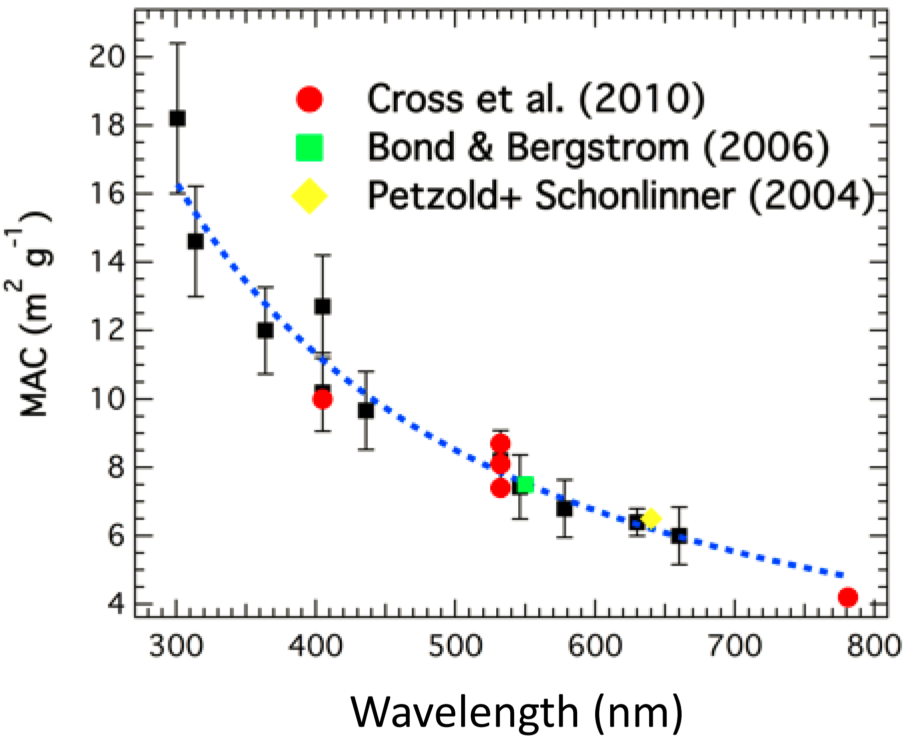

## High Dimension Model Representation

- HDMR meta-model of T-matrix results
- One-, two-, and three-sigma confidence regions for refractive index based on the HDMR meta-model and MAC and SSA measurements

| **HDMR input parameter** | **Range** |
|---|---|
| fractal prefactor, $k_0$ | 0.68 - 1.50 |
| fractal dimension, $D_f$ | 1.60 - 2.01 |
| real refractive index, *n* | 1.56 – 2.34 |
| imaginary refractive index, *k* | 0.632 – 1.264 |
| primary spherule radius, *a* | 10 - 20 nm |
| density, *ρ* | 1.6 - 1.9 g/cm$^3$ |
| mass, *m* | 0.11 - 16 fg |

*Greg Magoon – Aerodyne Research, Inc.*

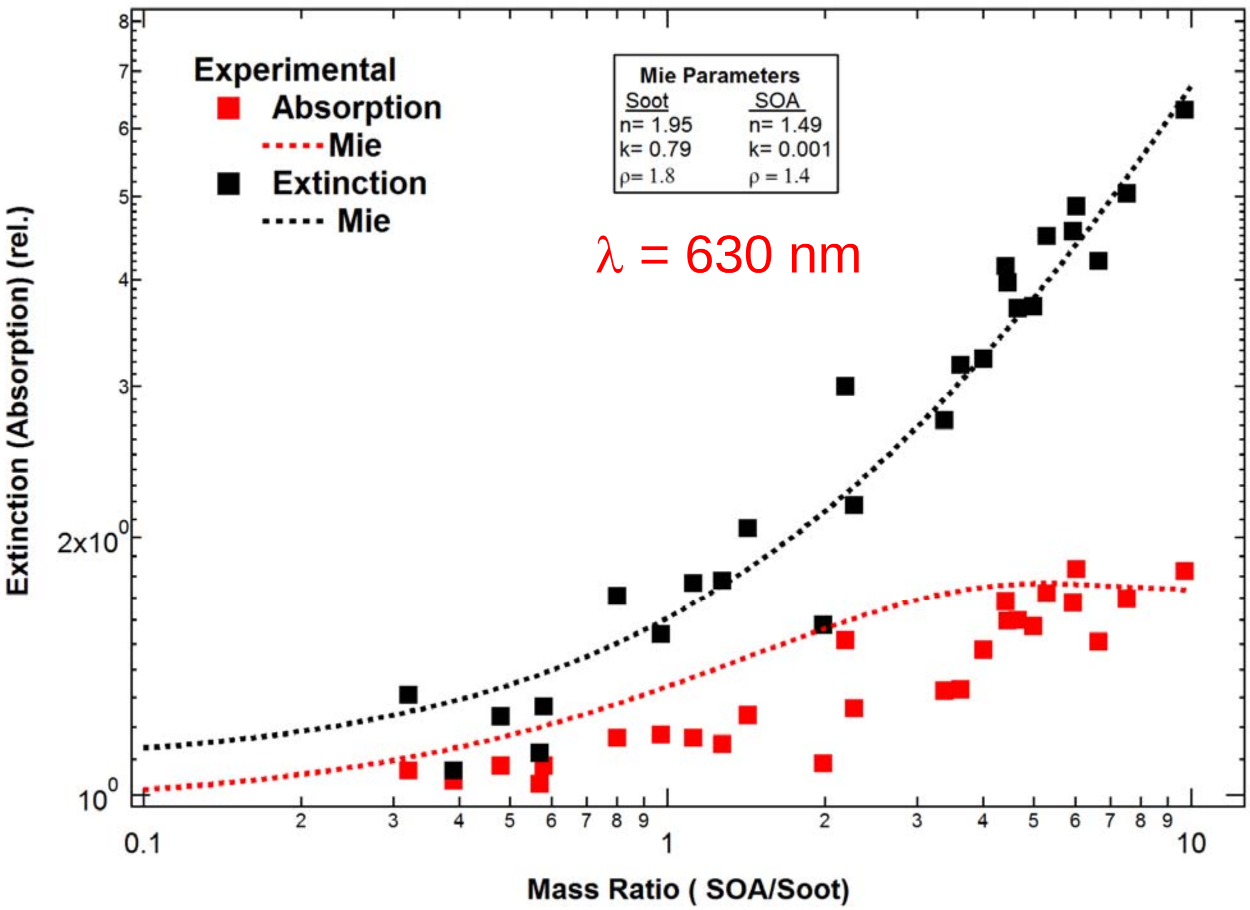
# Ångström Coefficient Determination




- AAE = 1.25 ± 0.24
- Uncertainties reflect accuracies of absorption measurements
- Uncertainties in Number Density and Mass cause points to shift up and down in concert
- Fits are Weighted by Error Bars

  Essentially Pinned to CAPS Value at 630 nm

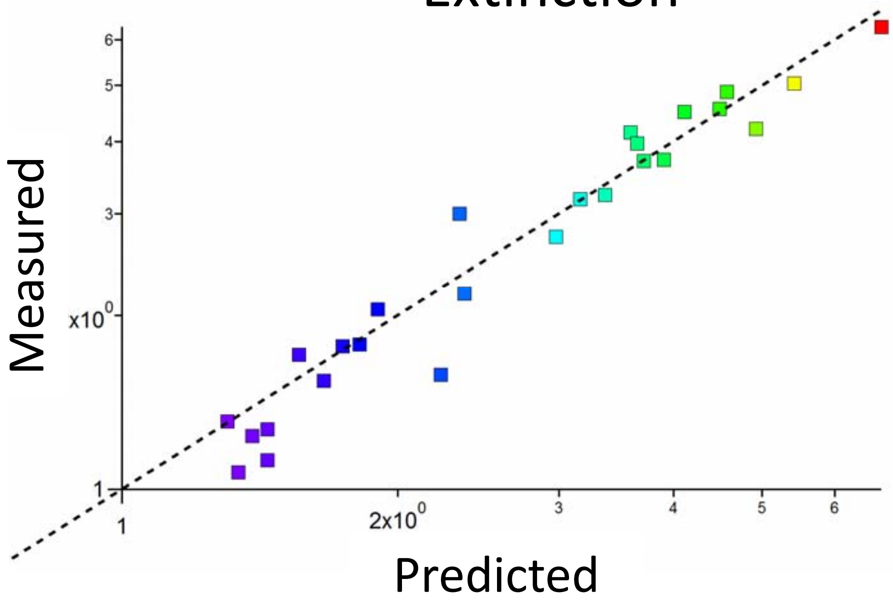
# Impacts of coatings on optical properties



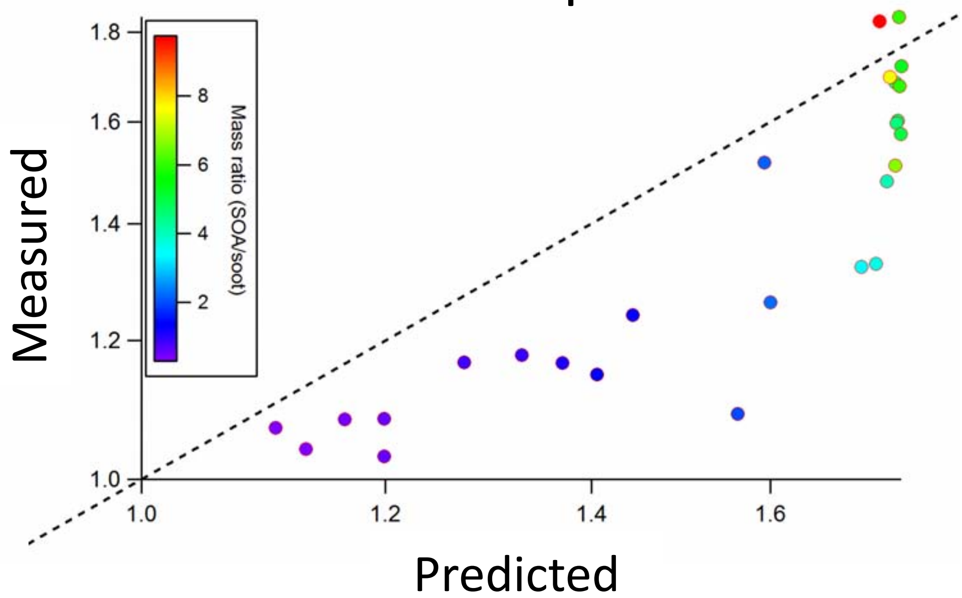

- ABS increases by ~1.8 and plateaus
- EXT (really SCAT) increases more rapidly than ABS and does not plateau

# Predictive core-shell Mie Theory

Extinction



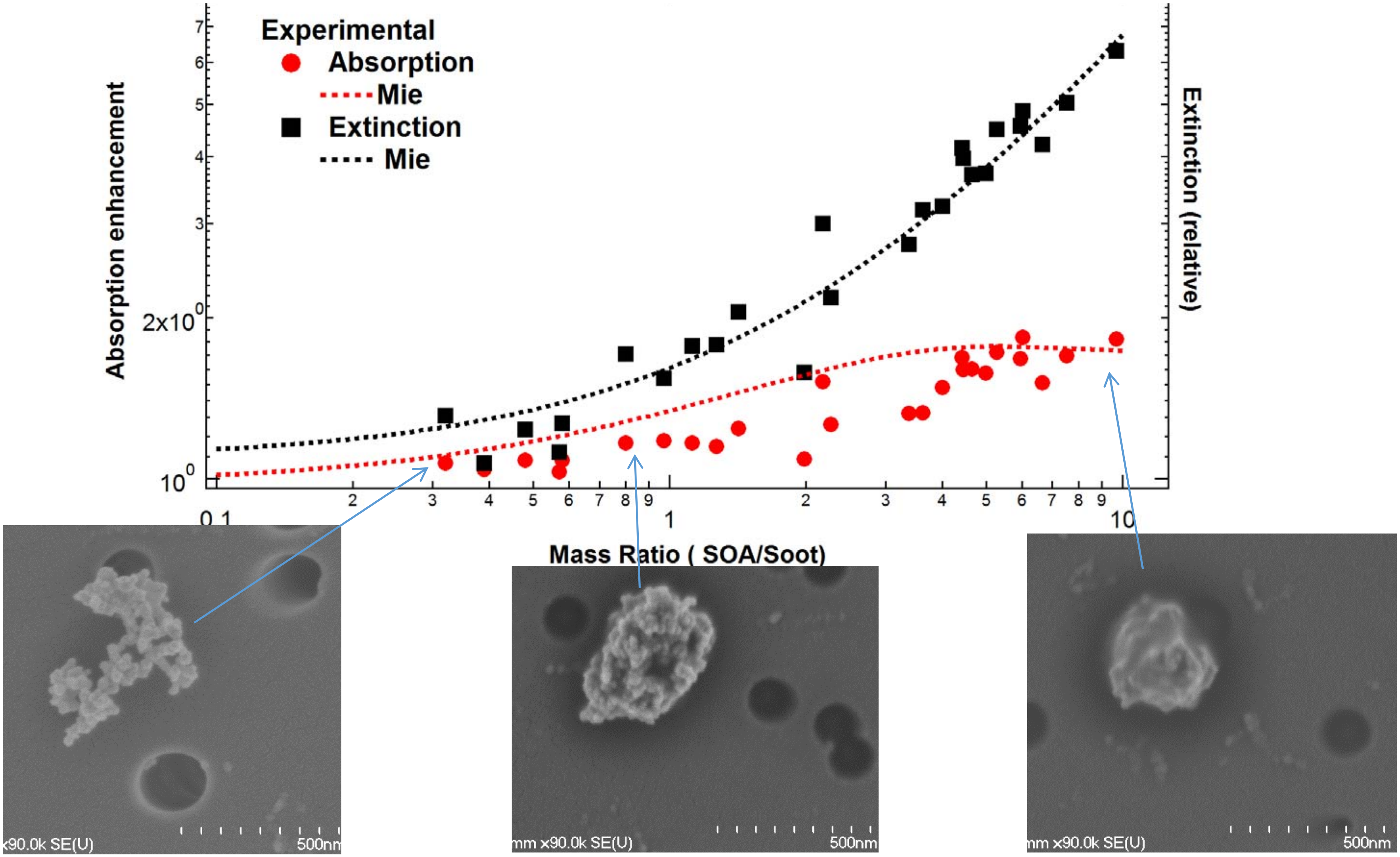

Absorption




Core-shell Mie theory

- over predicts EXT at small mass ratios ( < 0.7 )
- over predicts ABS at small to medium mass ratios ( < 5 )
- Adequately predicts EXT and ABS high mass ratios ( > 5 )

# Small mass ratios induce morphological changes which affect SCAT and ABS differently



# Conclusions

- Mie theory cannot predict both the scattering and absorption of nascent or uncoated soot particles
- Core-shell Mie theory over predicts the scattering and absorption for thinly coated soot particles, but appears to works well for thicker coatings
- Small amounts of SOA and $H_2SO_4$ mass condensation on fractal-like soot particles
  - Collapse the core soot structures for thin coatings, affecting the scattering more than absorption
  - Fill in interstitial regions initially, minimizing increases in cross-sections, leading to lower initial absorption enhancements
- More appropriate models, such as T-matrix or DDA, may be required for ‘freshly’ emitted and thinly coated soot particles in atmospheric models
  - HDMR may help incorporate these complex calculations into process, regional, and global models

# Acknowledgements


## DOE ASR funding – DOE ARM SP2

**BC4 study**

| Participating Institution | Instrumentation |
|---|---|
| Boston College | PAM, SMPS, O3 monitor, CPCs, AMS |
| Aerodyne Research | MCPC, SP-AMS, CPMA |
| Massachusetts Institute Of Technology | CAPS-SSA (630), CPMA |
| University of California Davis | CRD, PAS (405, 532nm) |
| University of GA | Broadband PAS (8 λ's) |
| Michigan Technological University | SEM/TEM analysis |
| Brookhaven National Labs | SP2 soot photometer |