



# Soot Nanostructure: Definition, Quantification and Implications

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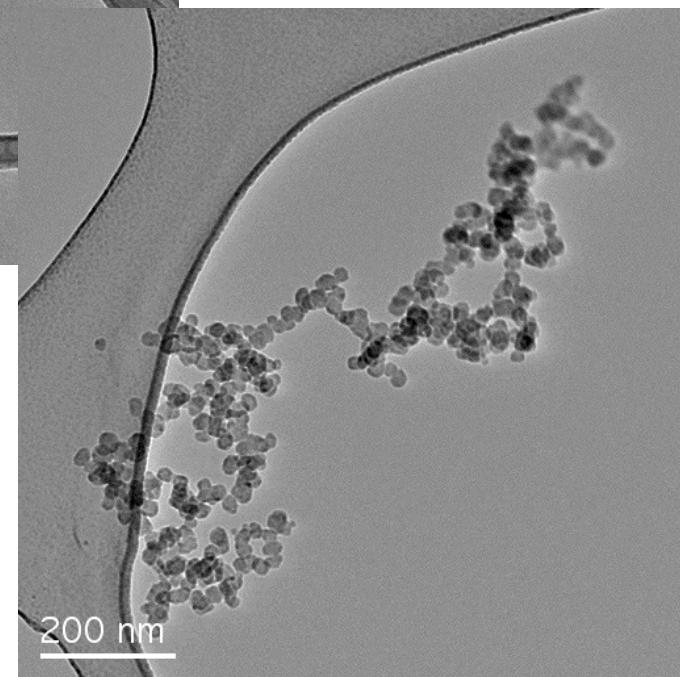
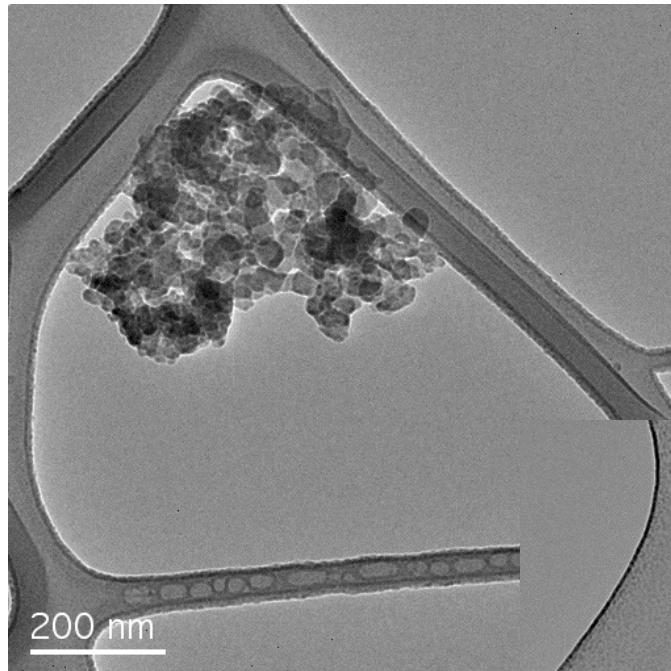
William K. Thompson

## Acknowledgements:

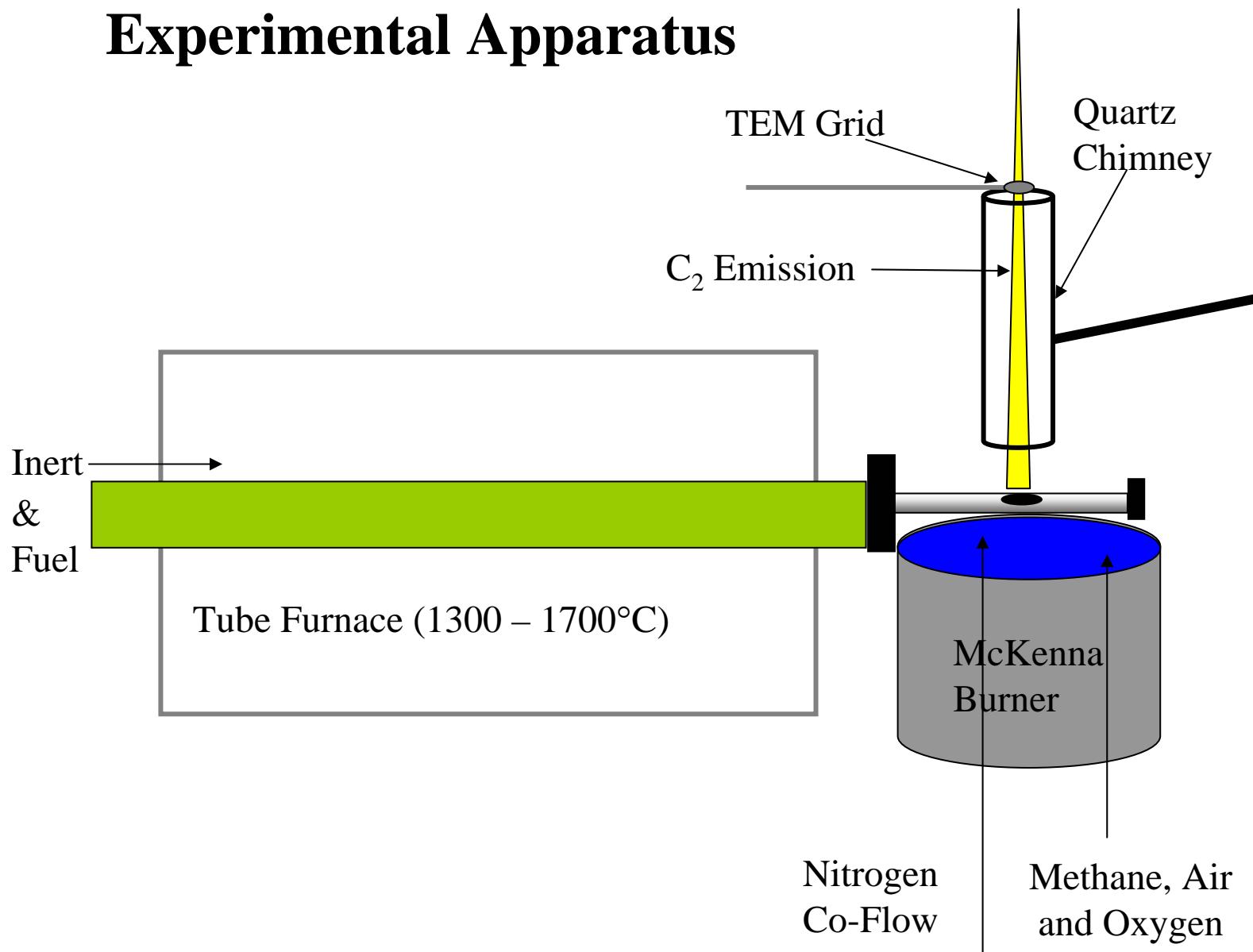
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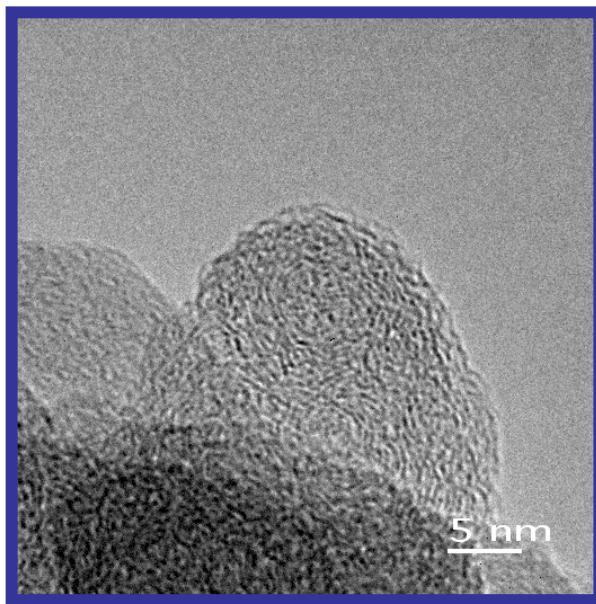
# Soot Macrostructure: Aggregate Size and Morphology



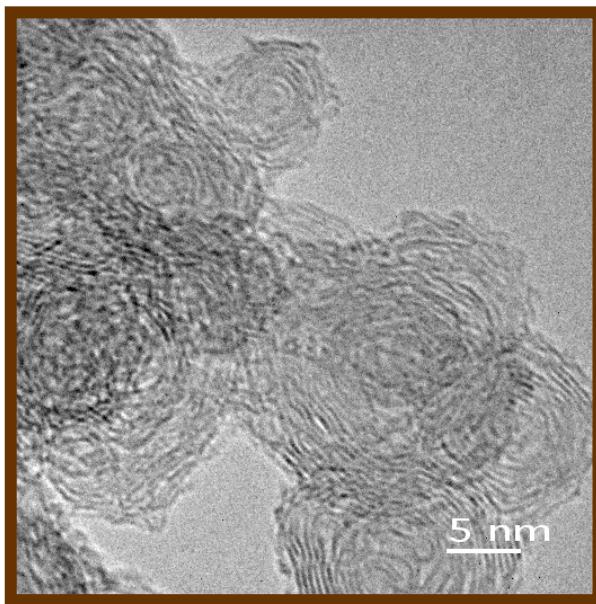
# Soot Nanostructure: Experimental Apparatus



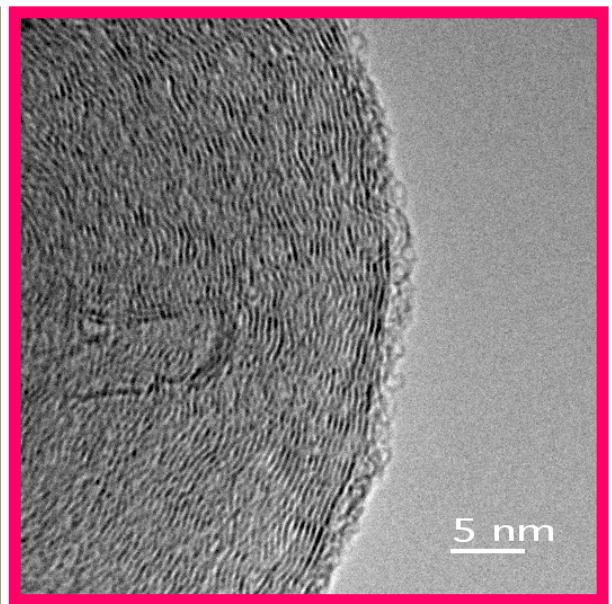
# Soot Nanostructure: Definition using HRTEM Images of Primary Particle (Internal) Structure



**Amorphous  
(Benzene)**

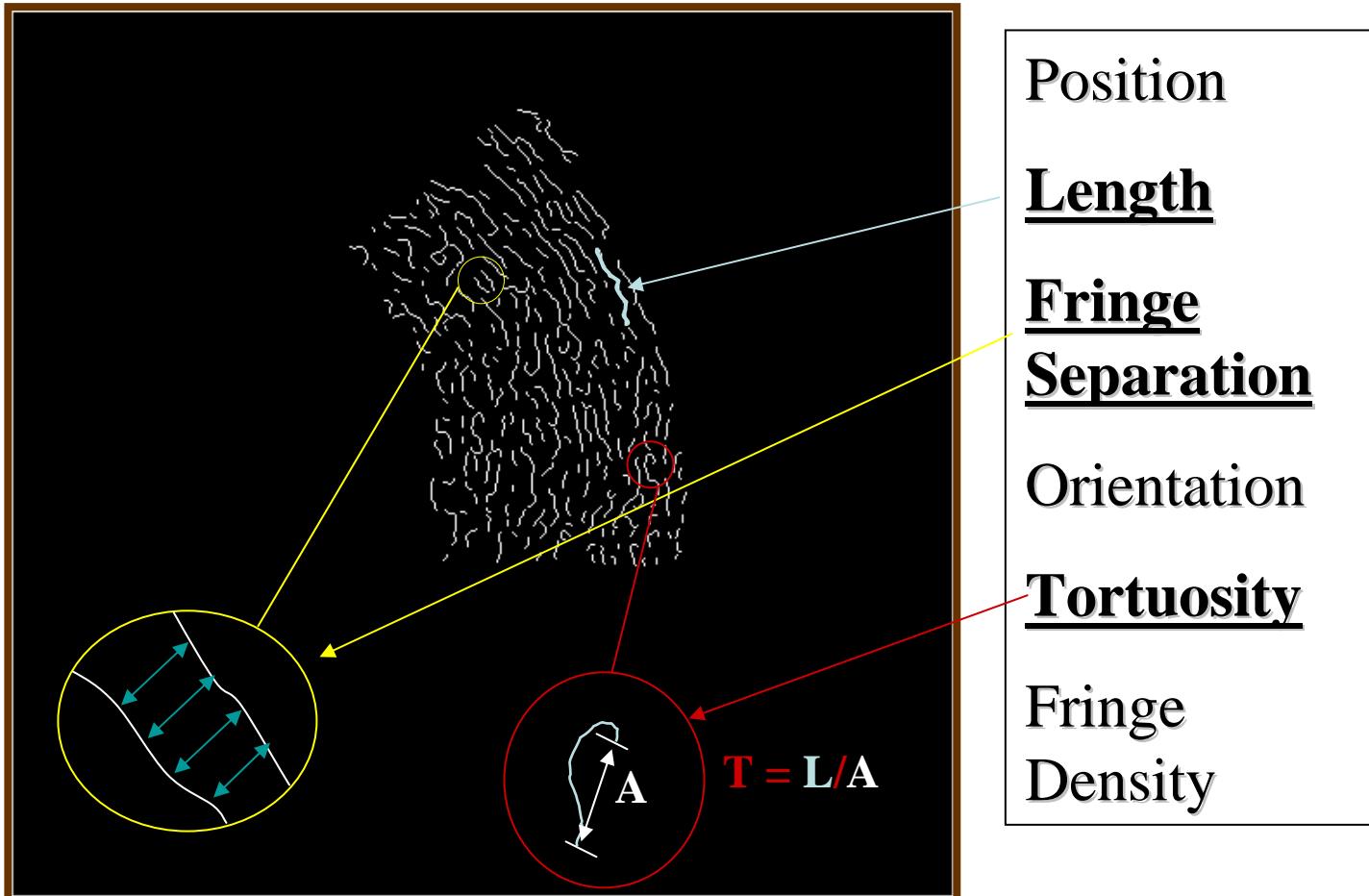


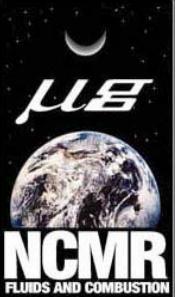
**Fullerenic  
(Ethanol)**



**Graphitic  
(Acetylene)**

# Statistical Properties Extracted From HRTEM Images (of soot nanostructure)





# Soot Nanostructure: Quantification via Fringe Analysis

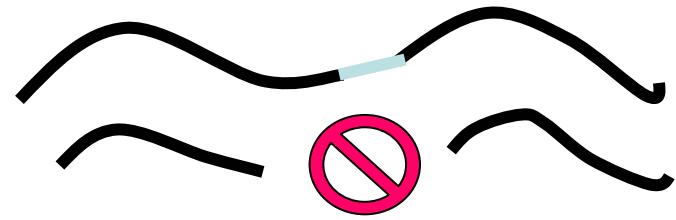
Algorithm-Optimas® Version 6.5

## Operations:

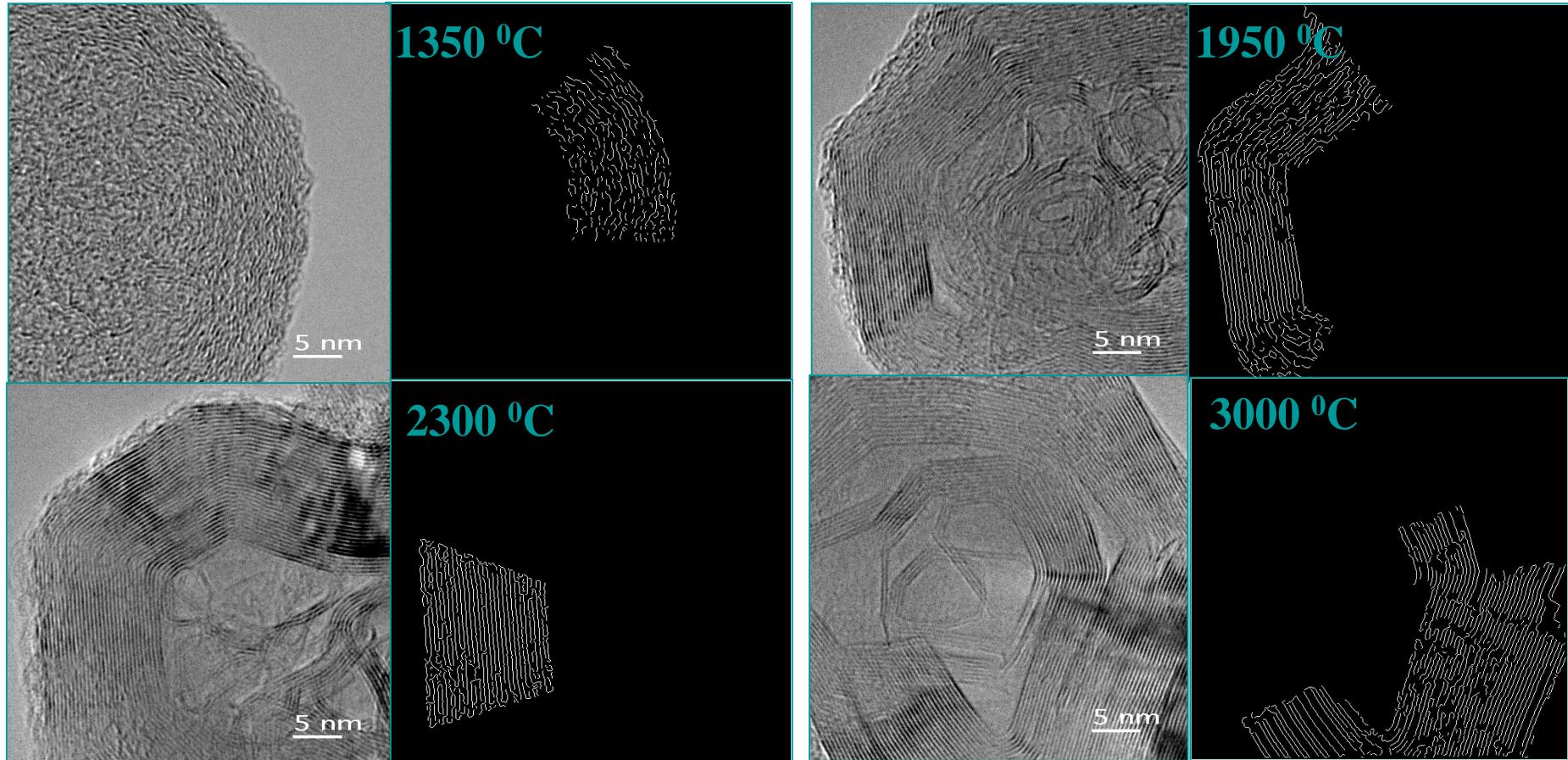
1. Switches 256 grayscale image to binary
2. Removes all pixels not above threshold
3. Removes remaining pixels and groups of pixels that do not form extended lines
4. Uses position of pixels within lines to determine length, curvature, etc. of fringes

# Soot Nanostructure: Quantification via Fringe Analysis

- \* **Image refinements - To overcome HRTEM image limitations**
  - Region of interest
  - Spatial filtering
  - Binary thresholding
  
- \* **Other inputs**
  - Maximum join distance
  - Minimum fringe length



# Comparison of Input (HRTEM) and Output (Binary-Fringe) Images

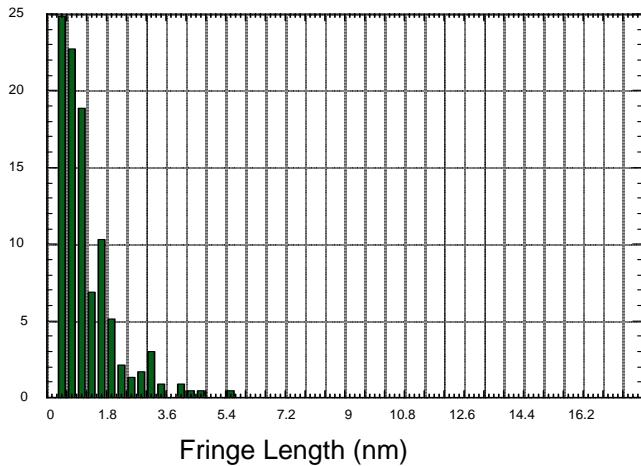


Selected samples of heat-treated carbon black

# Fringe Analysis Output Data - Fringe Length Histograms

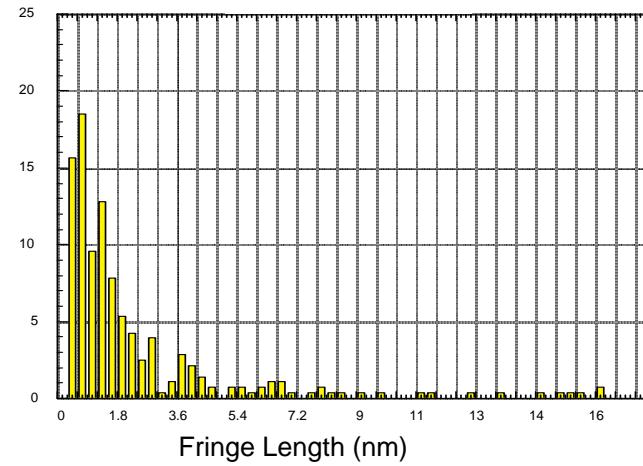
**1350 °C**

% of Fringes



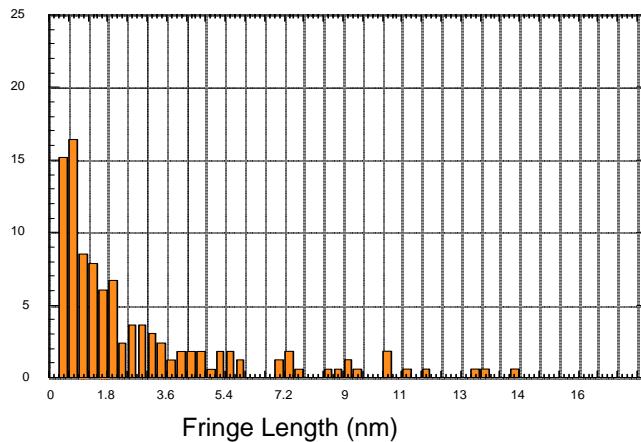
**1950 °C**

% of Fringes



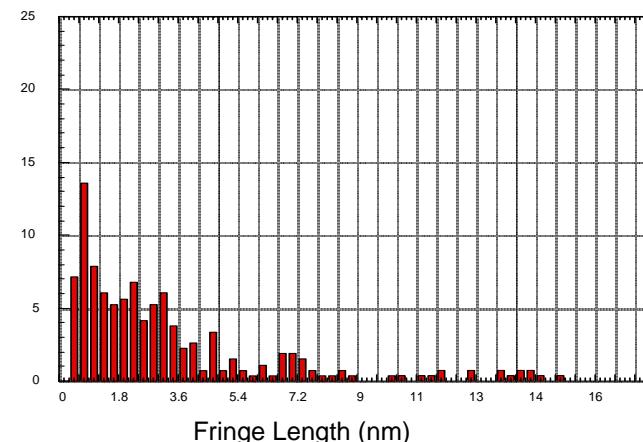
**2300 °C**

% of Fringes



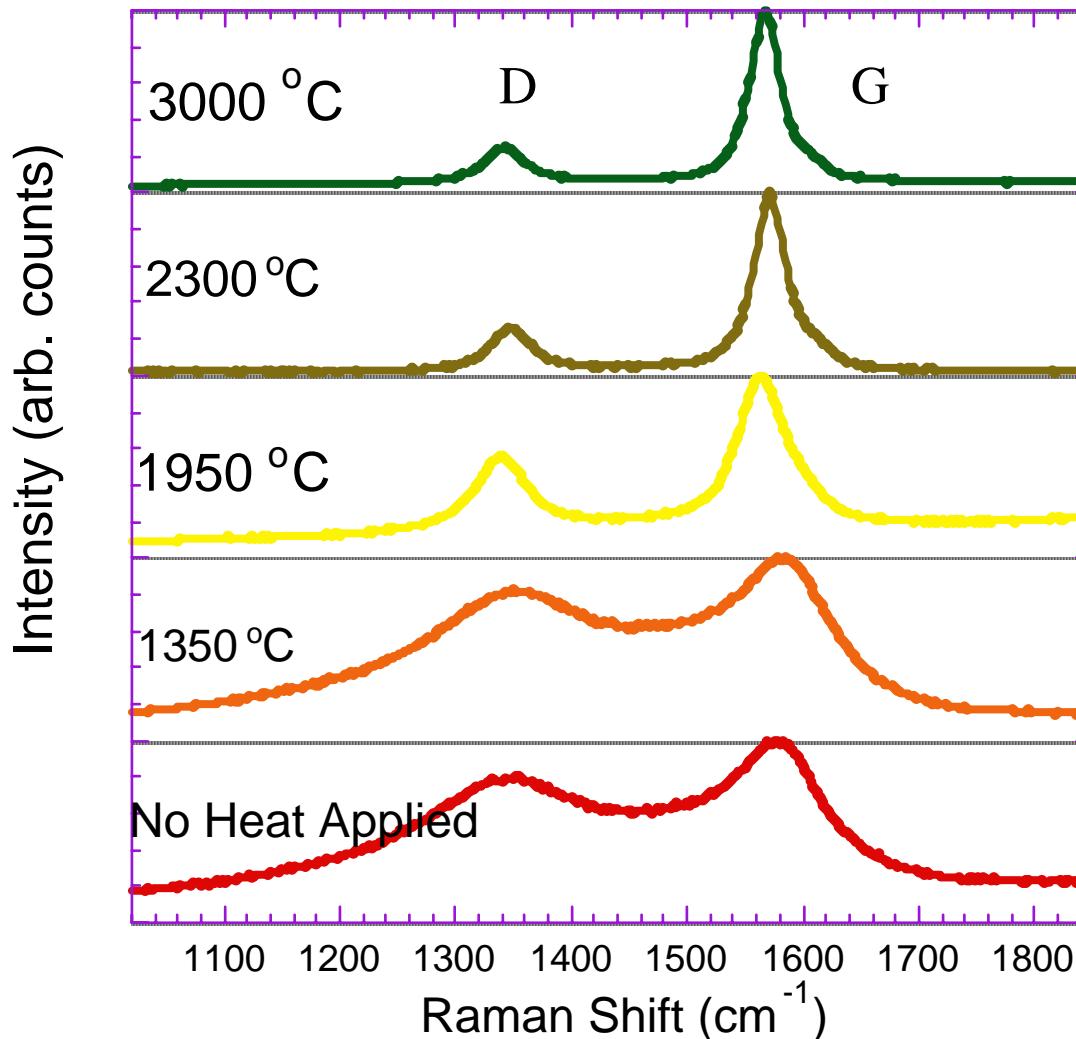
**3000 °C**

% of Fringes



# Comparison to Benchmark Methods

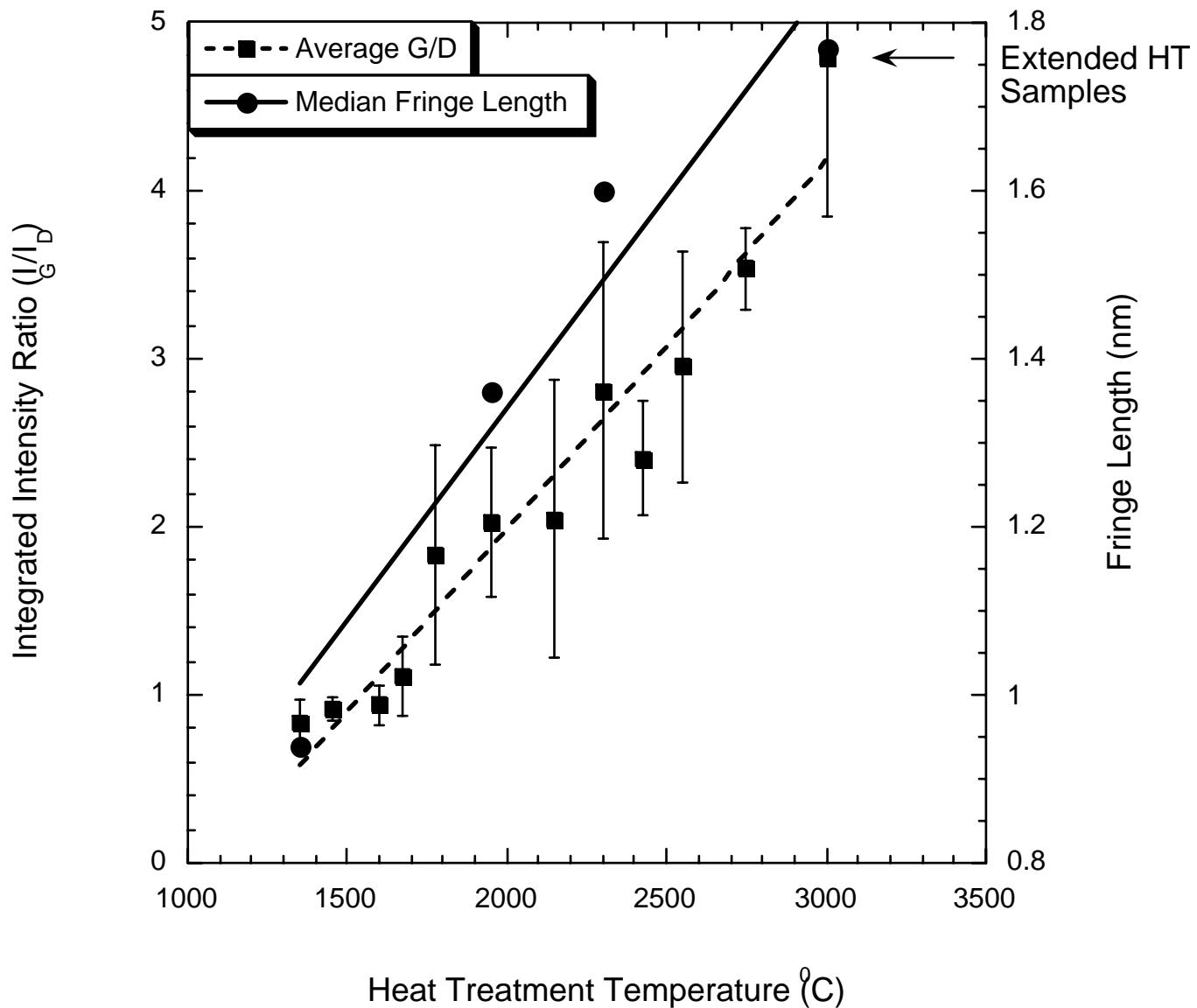
## Raman Spectra of Heat Treated Soot



- $E_{2g}$  or (G) peak at  $1580 \text{ cm}^{-1}$  (Graphitic)
- $A_{1g}$  or (D) peak at  $1360 \text{ cm}^{-1}$  (Disordered)
- Intensity ratio have been used to measure in-plane dimensions

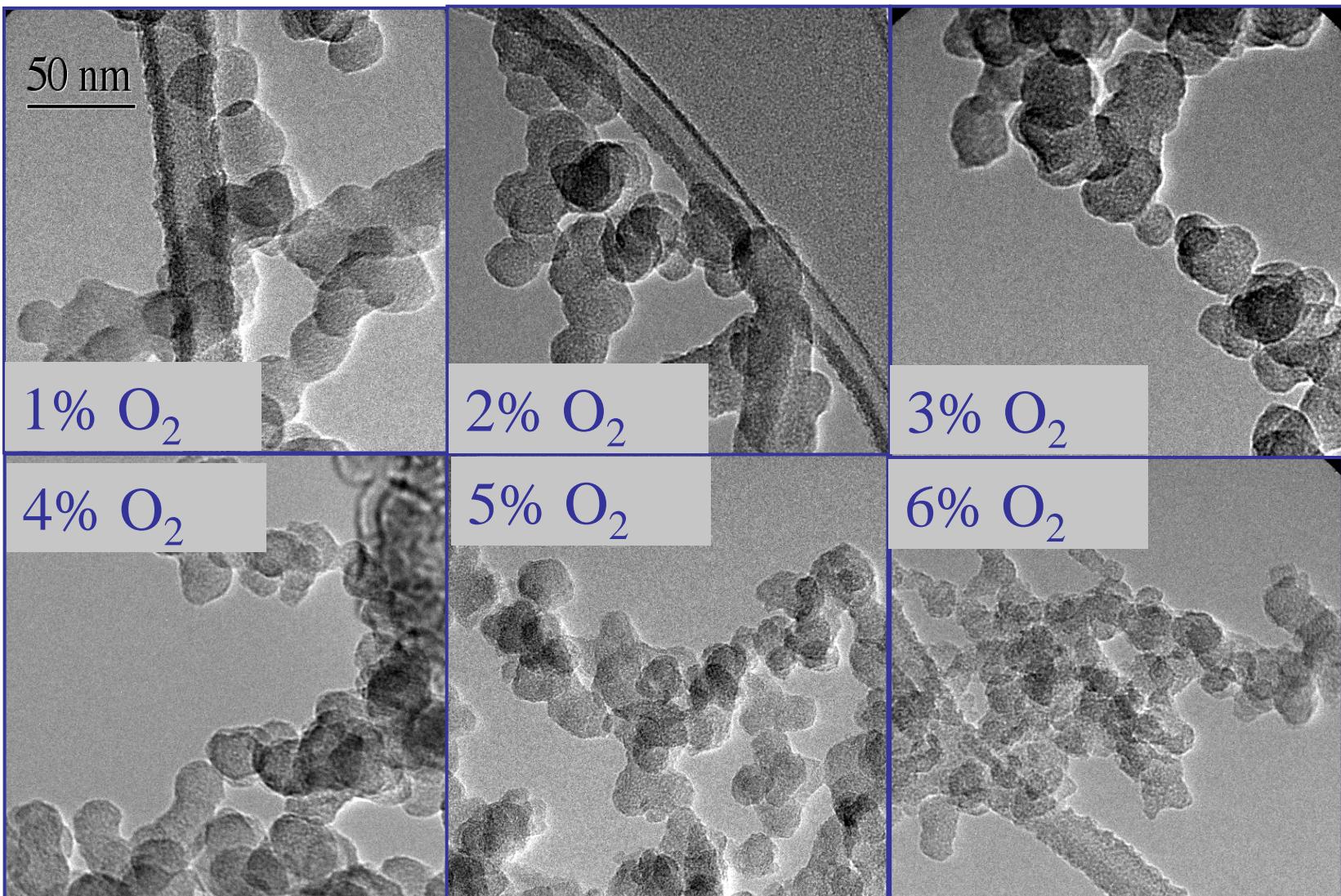


## Ratios of Integrated Raman Intensities for Heat Treated Carbon Soots



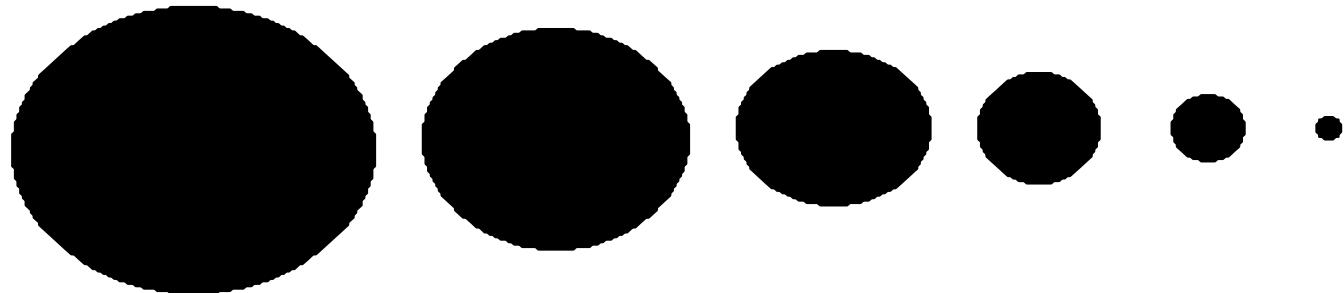
# Soot Nanostructure and Implications: Reactivity

TEM images of partially oxidized benzene soot



# Oxidation Analysis

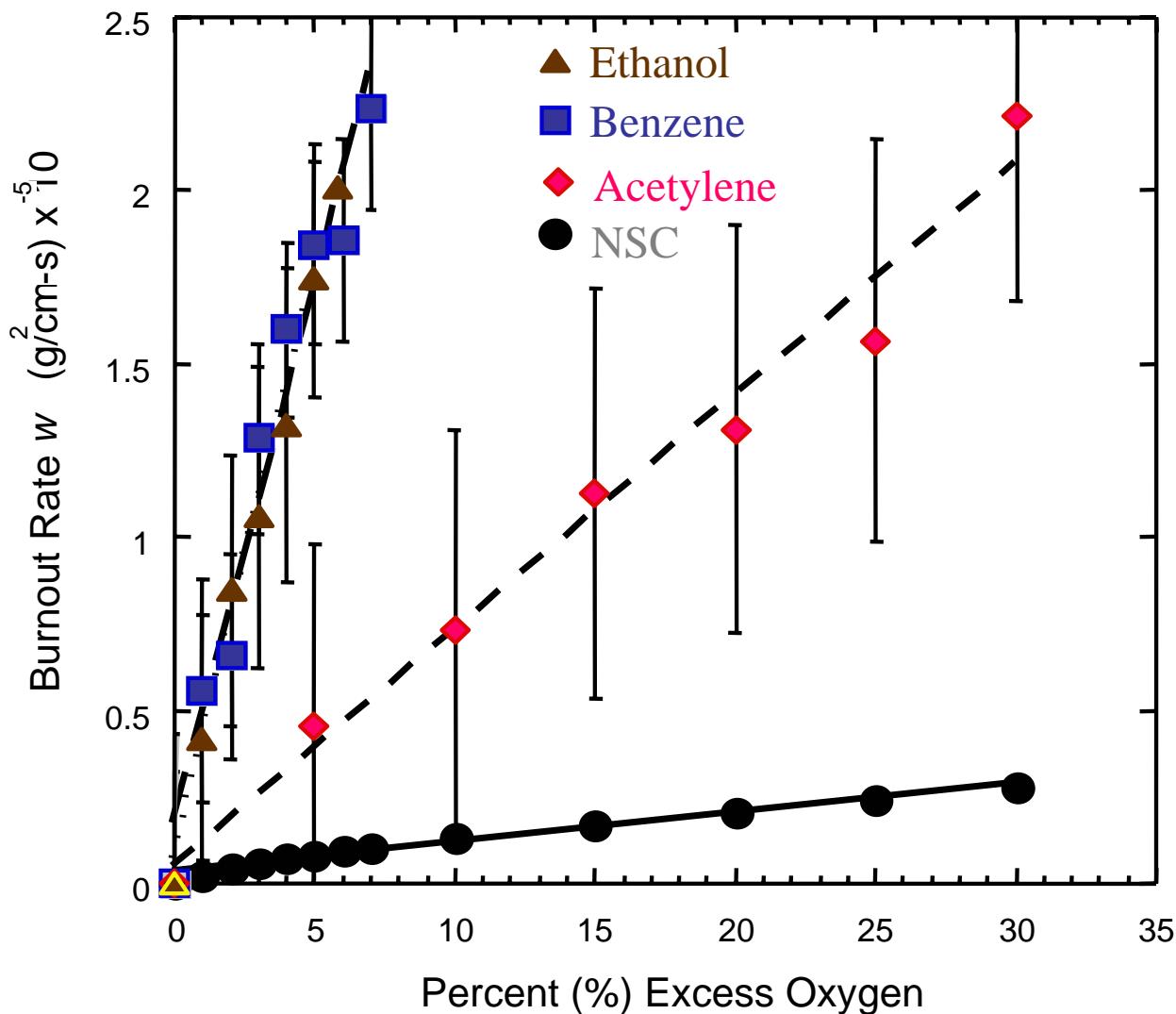
- Shrinking Spheres Model



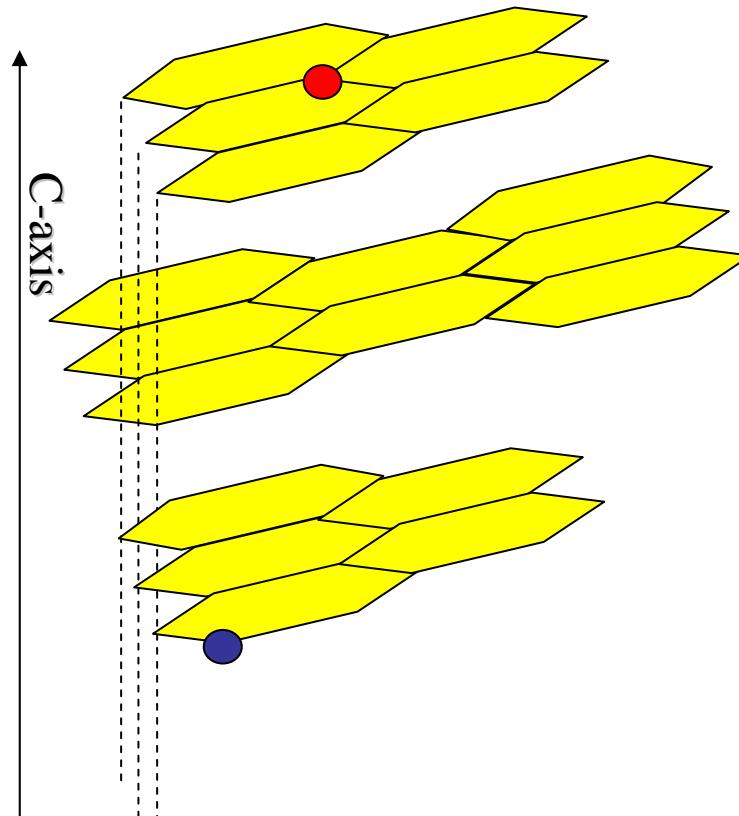
- Soot Burnout Rate Expression

$$\omega(kg / m^2 s) = \frac{\rho r_0}{t} \left(1 - \frac{r_t}{r_0}\right) = \frac{1}{A} \frac{dm}{dt}$$

# Soot Burnout Rates



# Carbon Soot Nanostructure



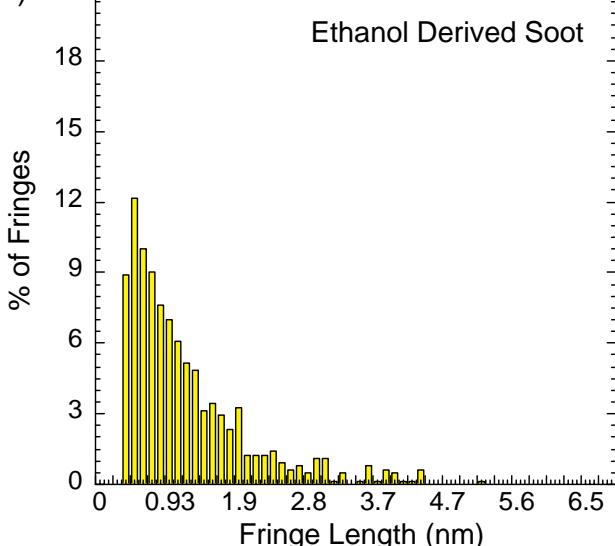
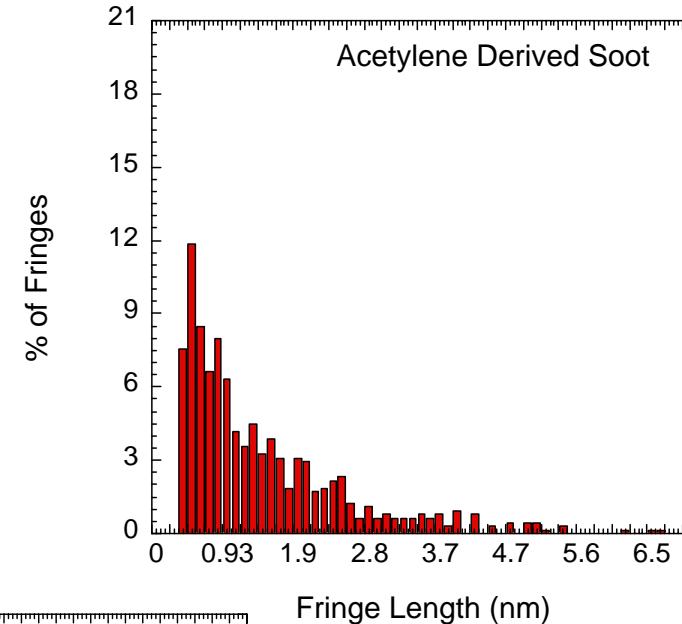
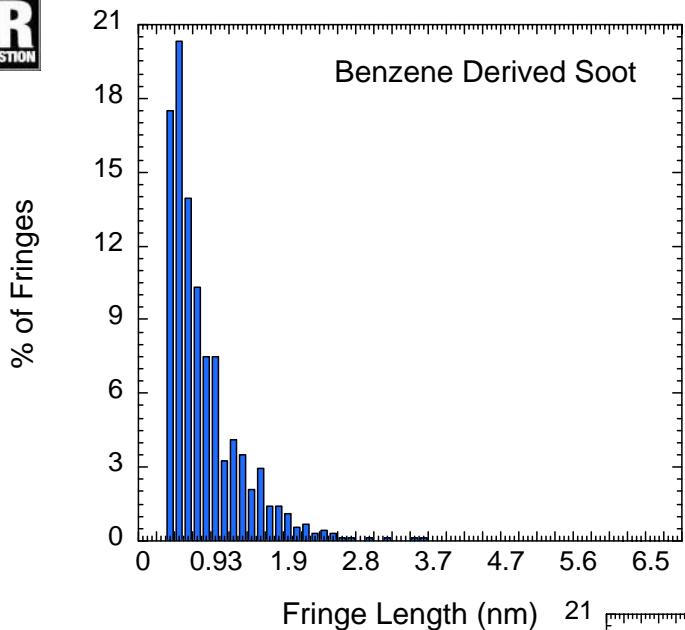
- Edge Site Carbon
- Basal Plane Carbon

- Soot oxidation rates are different. What is the cause?
- Previous studies ignored nanostructure.
- Graphitic carbons are less reactive than amorphous carbons.
- Is it just fringe length?



# Nanostructure and Implications: Reactivity

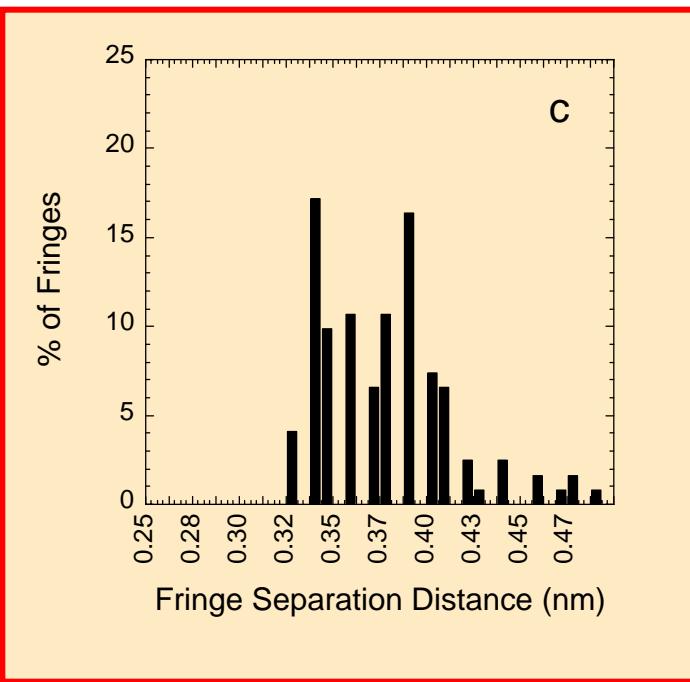
## Fringe Length Histograms



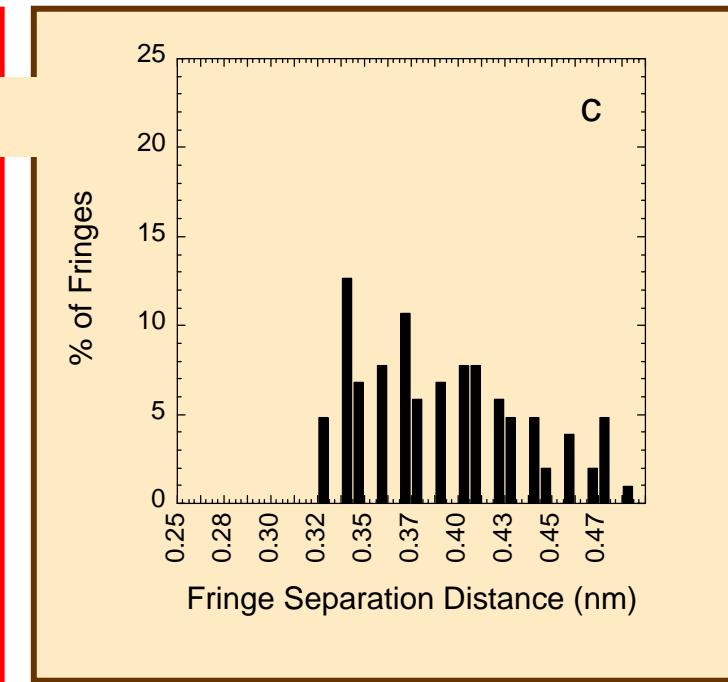
# Nanostructure and Implications: Reactivity

## Fringe Separation Histograms

### Acetylene



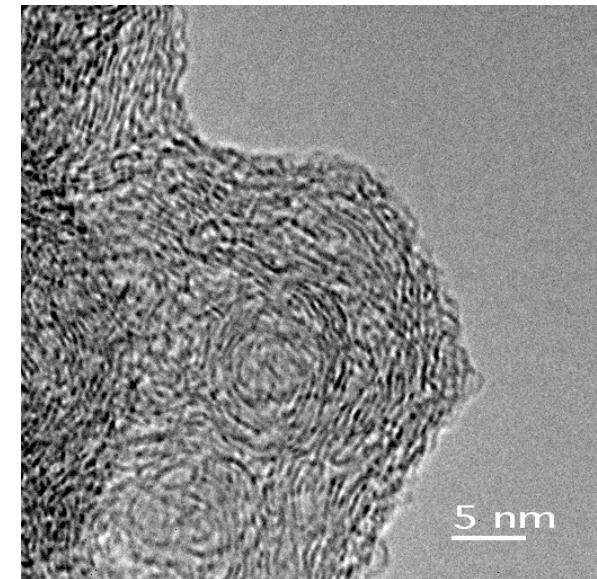
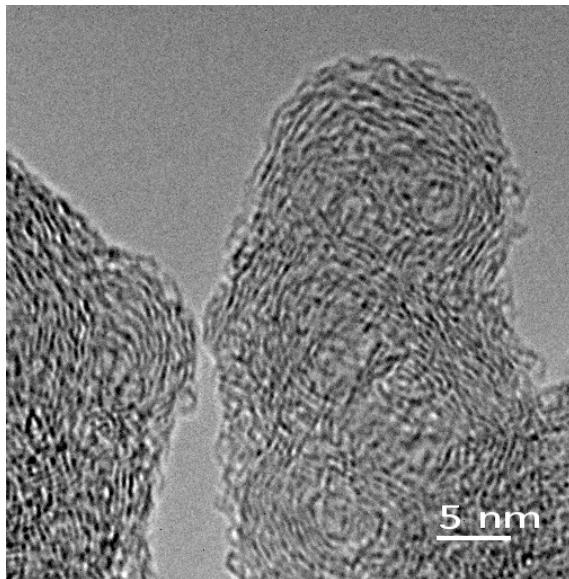
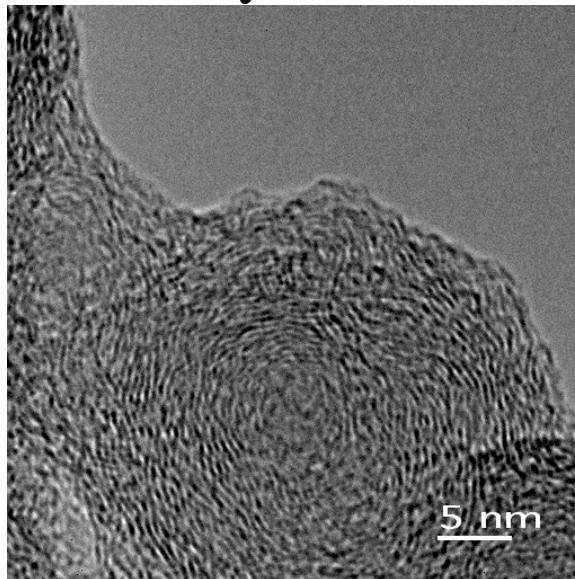
### Ethanol



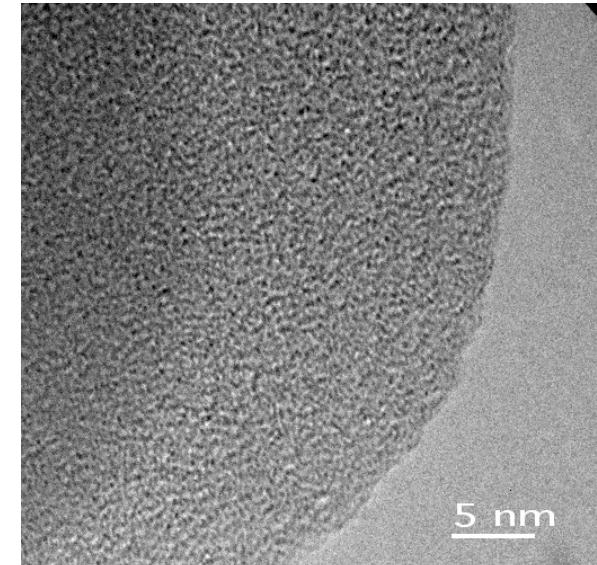
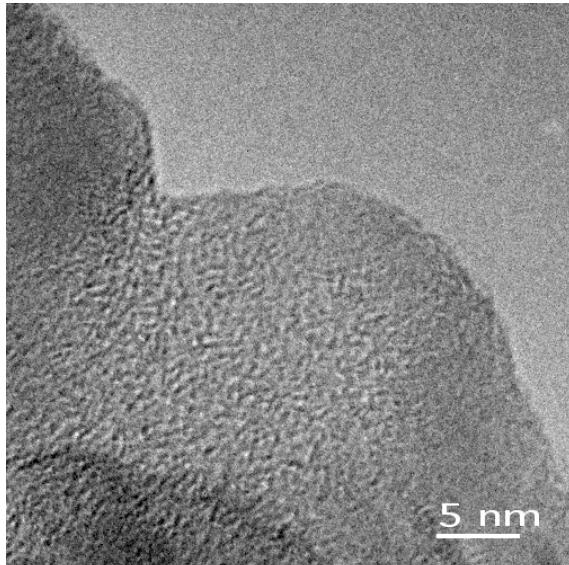
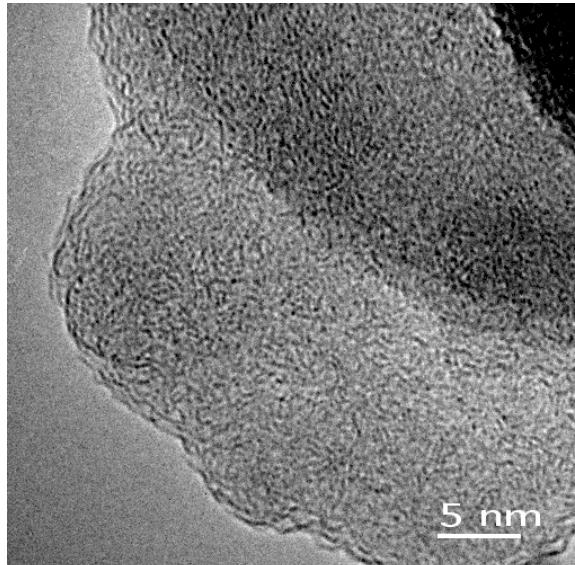
Average [ $\omega/\omega_{NSC}$ ]
17.9 Ethanol
6.7 Acetylene

Diesel Engine Soots  
Courtesy Sandia Nat. Labs

Reference Fuel - n-hexadecane + heptamethylnonane  
(CN 45-020926B)



Diethylene glycol diethyl ether (DGE)



# Conclusions

## Soot Nanostructure: (Definition)

- \* Soot Nanostructure refers to carbon lamella (layer plane) length, orientation, separation and tortuosity.
- \* Nanostructure is variable, dependent upon temperature, residence time and fuel identity.

## Fringe Analysis Algorithm: (Quantification)

- \* Lattice fringe analysis can be used to analyze HRTEM image data and quantify carbon nanostructure through statistical analysis.

## Oxidation Rates: (Implications)

- \* Oxidation rates are dependent upon nanostructure - suggests using nanostructure to control (accelerate) oxidation.
- \* Source apportionment via analysis of nanostructure?
- \* Health consequences related to nanostructure?
- \* Environmental impact dependent upon nanostructure?