

Quantitative Scanning Electron Microscopy Methods to Characterize Ambient Air PM_{2.5}

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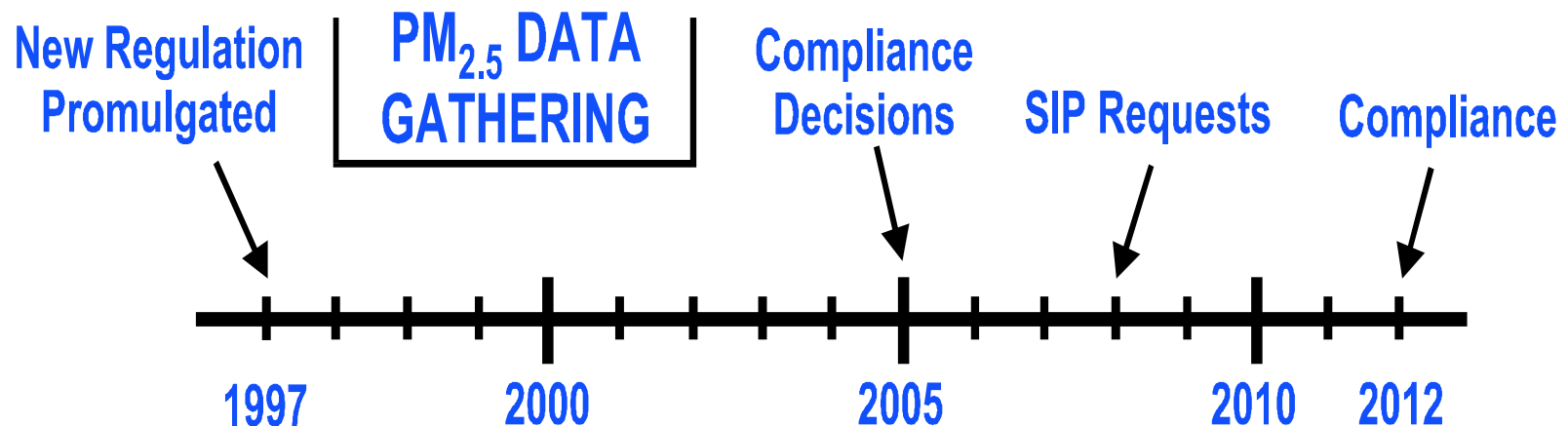
Different Missions

- **EPA – Protect the public health**
- **DOE – Assist the private sector in supplying clean, abundant, and affordable energy**



PM_{2.5} Regulatory Process

- **1997 National Ambient Air Quality Standards (NAAQS) for PM_{2.5} based on “health effects”**
 - Mean annual concentration < 15 µg/m³
 - Maximum concentration < 65µg/ m³



PM_{2.5} TIME LINE



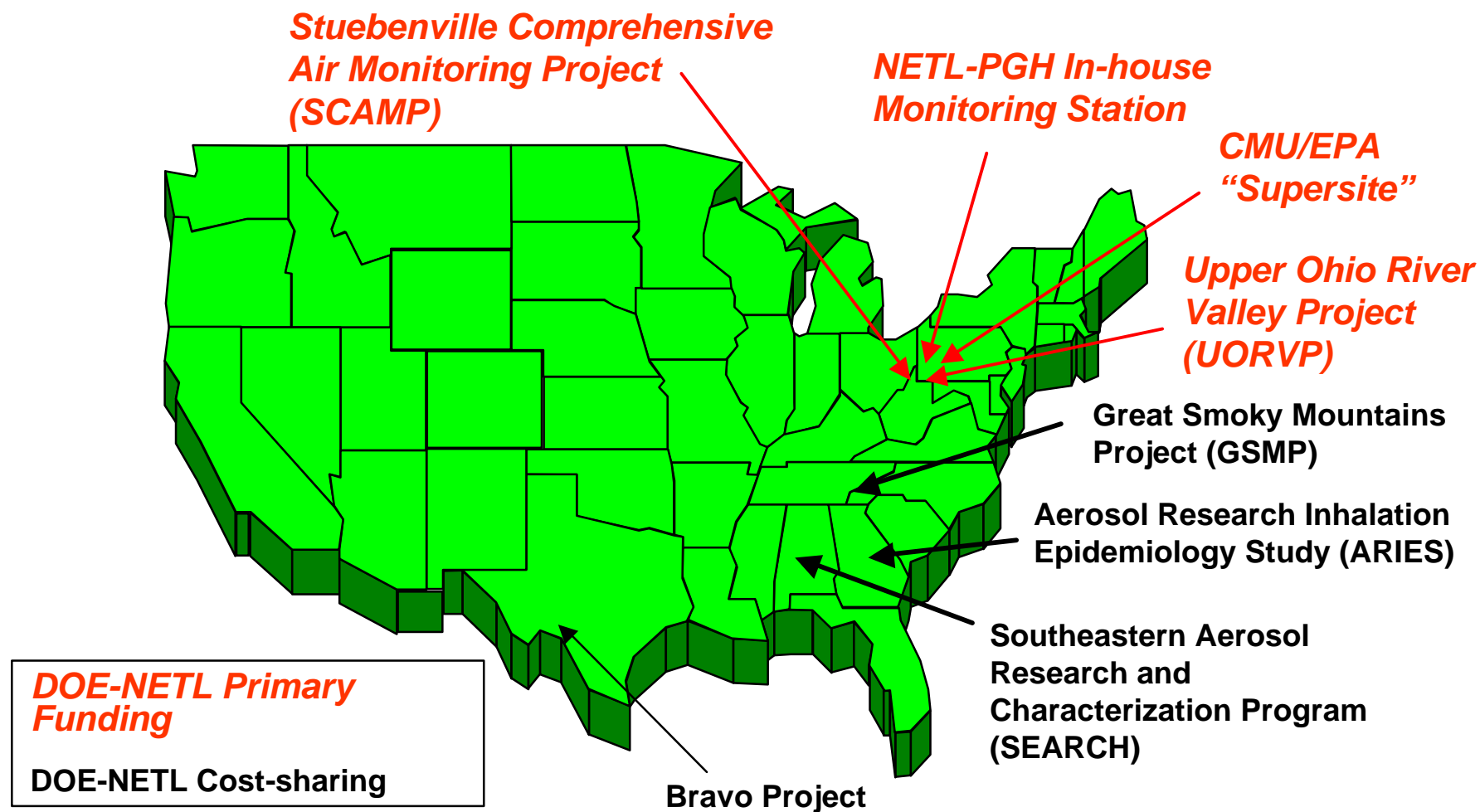
Why Is DOE Concerned About PM_{2.5}?

- **Coal-based power systems contribute to PM_{2.5}**
 - Primary particles:
 - Ultra-fine fly-ash (Spherical Alumino-silicates, SAS), carbon soot
 - Gaseous precursors:
 - SO₂, SO₃, NO_x
 - React with NH₃ in the atmosphere to form ammonium sulfate and ammonium nitrate particles
- **SIPs will likely restrict emissions from coal power plants.**

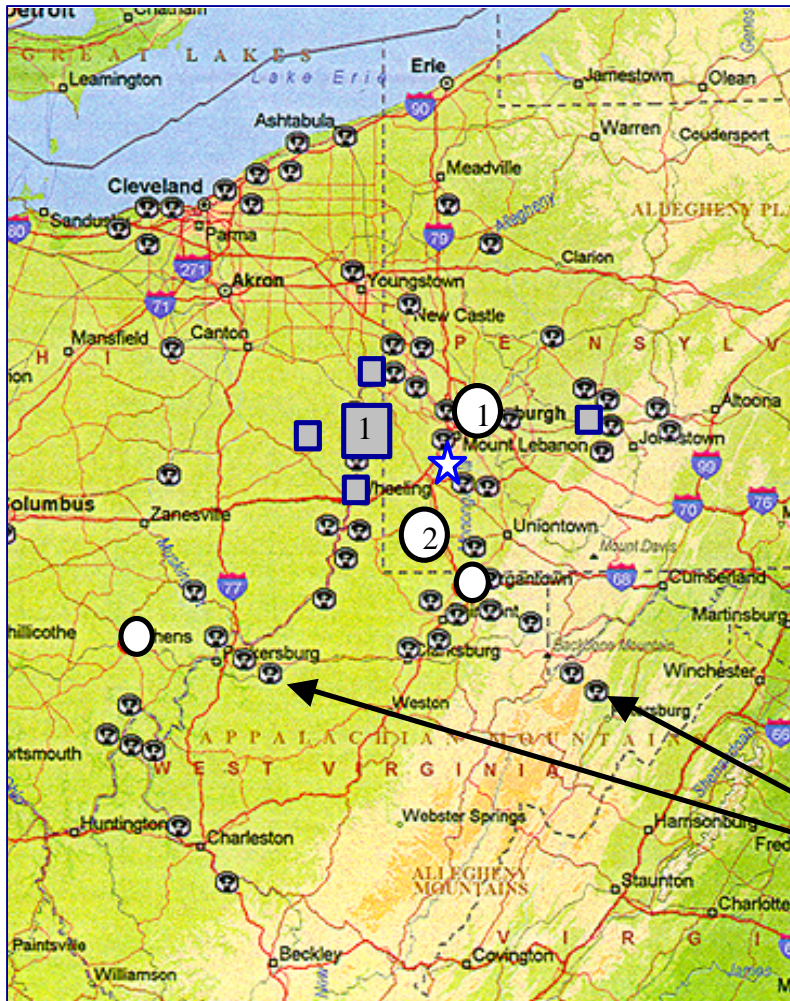


Ambient PM Monitoring and Characterization

Current Project Portfolio



Regional Ambient PM Monitoring Sites



UORVP Sites

- ① - Lawrenceville
- ② - Holbrook
- - Satellites

SCAMP Sites

- 1 - Primary
- - Satellites

★ - NETL In-house site

**Coal-fired
power plants**



Project Objective

- **Measure the degree that coal-fired utilities contribute to the primary fine-particulate matter load in ambient air.**

Experimental Approach

- **Use Spherical Alumino-Silicates (SAS) as the measure of coal-fired utilities' contribution to the primary fine-particulate matter load in ambient air.**

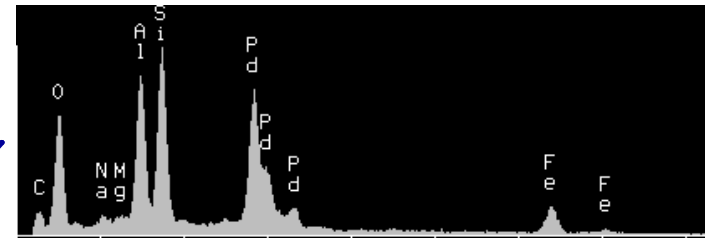
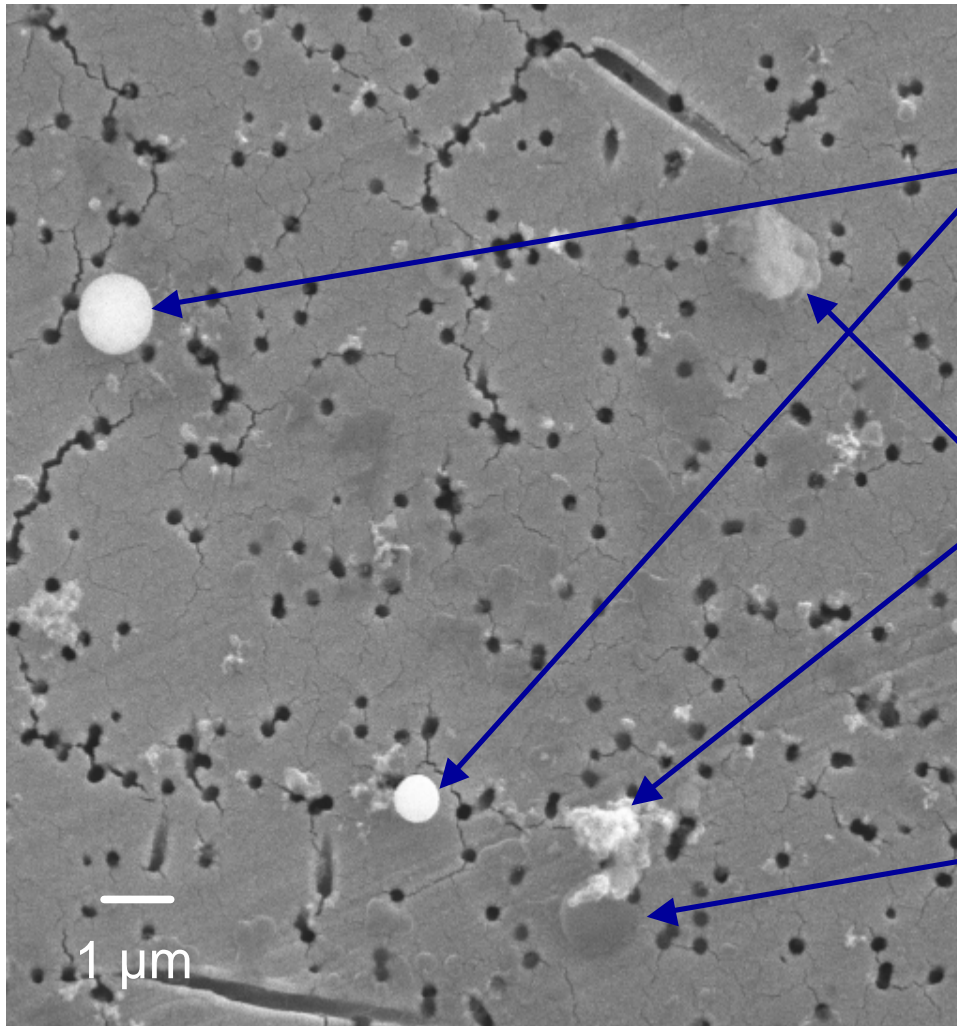


Experimental Objectives

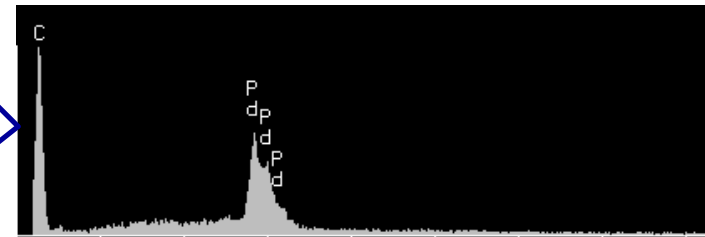
- **Quantitatively validate the SEM methods.**
 - Assess comparability of polycarbonate filters to FRM teflon filters.
- **Improve methods to account for most particle species on the filters.**
 - Identify particle species including SAS, sulfates, and carbonaceous.



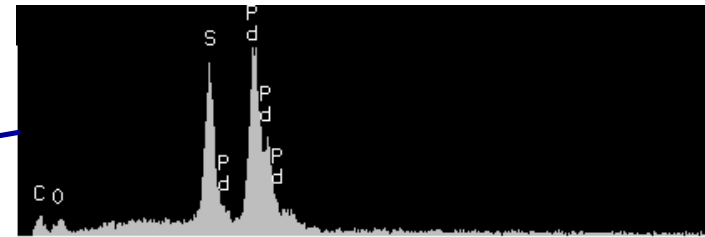
Secondary Electron Image



SAS Particle



Carbon-rich Particle



Sulfur Droplet



Experimental – Sample Collection



Experimental – Sample Collection

- Andersen RAAS[®] 400 Speciation Sampler
- Four flow channels
 - One at 16.7 L/m, teflon filter for FRM comparison
 - Two at 7 L/m, polycarbonate filters for SEM
 - One at 16.7 L/m, ‘quartz’ filter for EC/OC



Experimental – Sample Collection

- **Channel configurations**
 - 1: **FRM teflon filter**
 - 2: **Carbon denuder, Pd coated polycarbonate filter, Nylasorb[®] filter**
 - 3: **Carbon denuder, uncoated polycarbonate filter, Nylasorb[®] filter**
 - 4: **Carbon denuder, ‘quartz’ filter, carbon filter**



Experimental – Sample Collection

- **Pre-weigh and post-weigh filters.**
- **Sample SEM flow channels at 7 L/m found to produce good particle dispersion at typical $15\mu\text{g}/\text{m}^3$ ambient air loading.**
- **Sample ambient air for 24 hours.**
- **Analyze SEM filters ASAP after sampling or store particle filters under controlled conditions.**



Comparison of Gravimetric Filter Loading Variation: RAAS Polycarbonate versus FRM and RAAS Teflon versus FRM

Filter Type	Number of Filters	Avg. abs. difference, %	Standard Deviation
Polycarbonate	46	9.6	6.8
Teflon	163	5.6	6.8



Scanning Electron Microscopy (SEM)

- **SEM analysis can provide both morphology and composition information for use in individual particle species determination.**

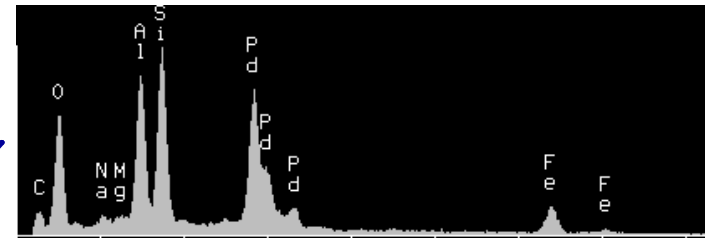
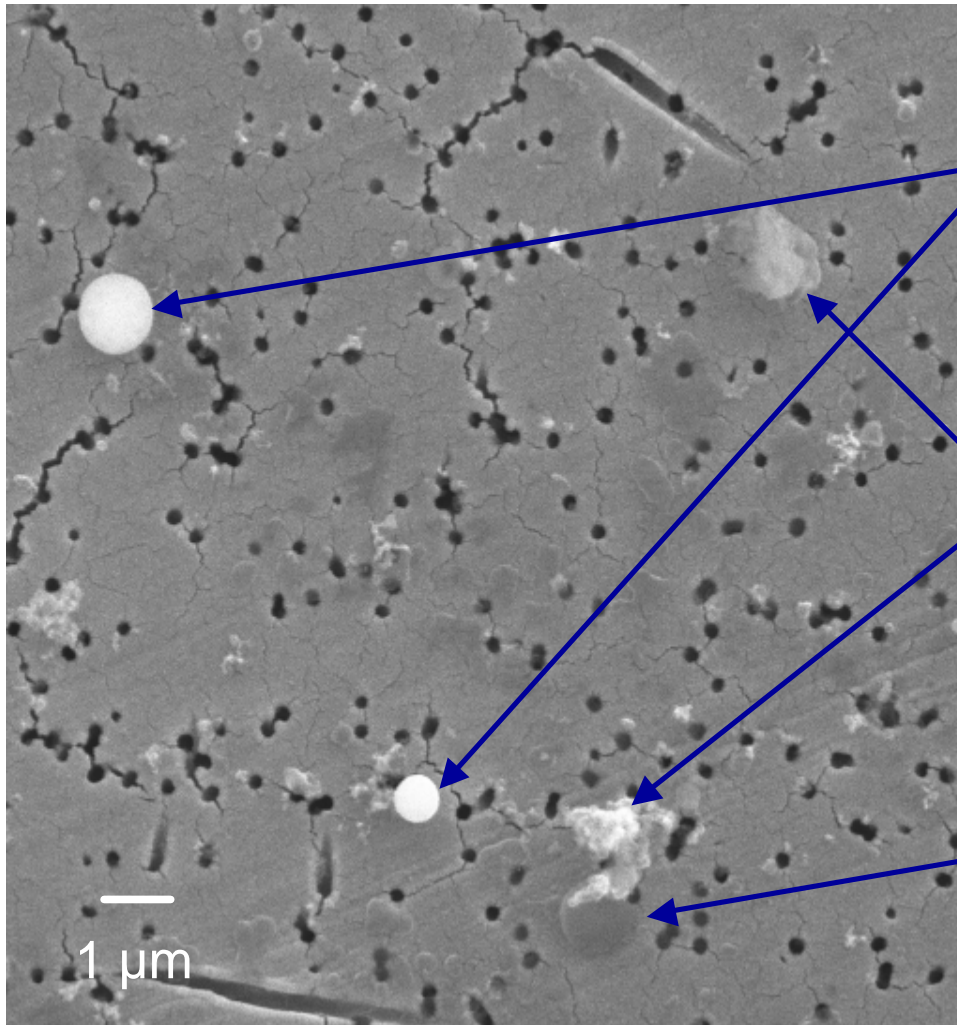


Scanning Electron Microscopy (SEM)

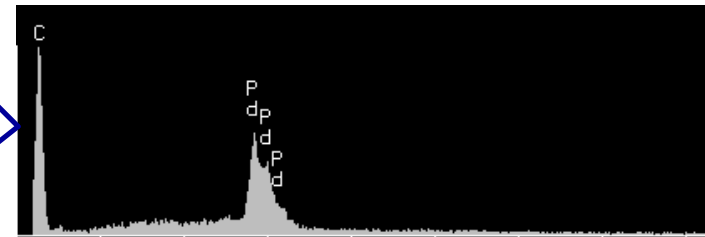
- **Image information**
 - **Secondary Electron (SE): Morphology**
 - **Backscattered Electron (BSE): Chemistry, Morphology**
- **Composition information**
 - **X-ray (EDX/EDS): Chemistry**



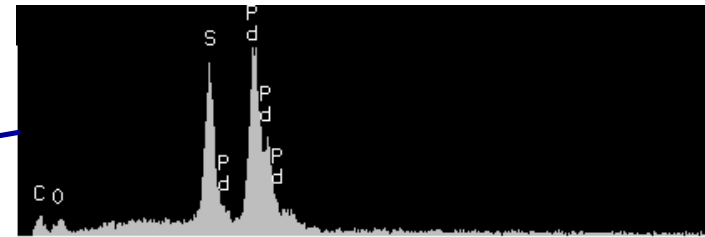
Secondary Electron Image



SAS Particle

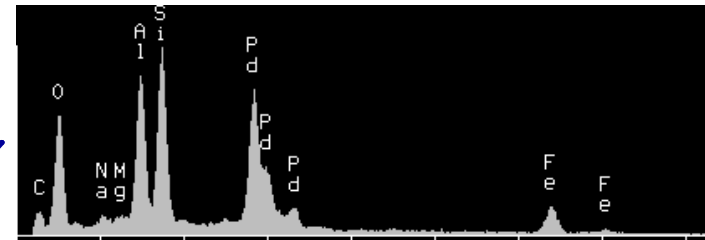
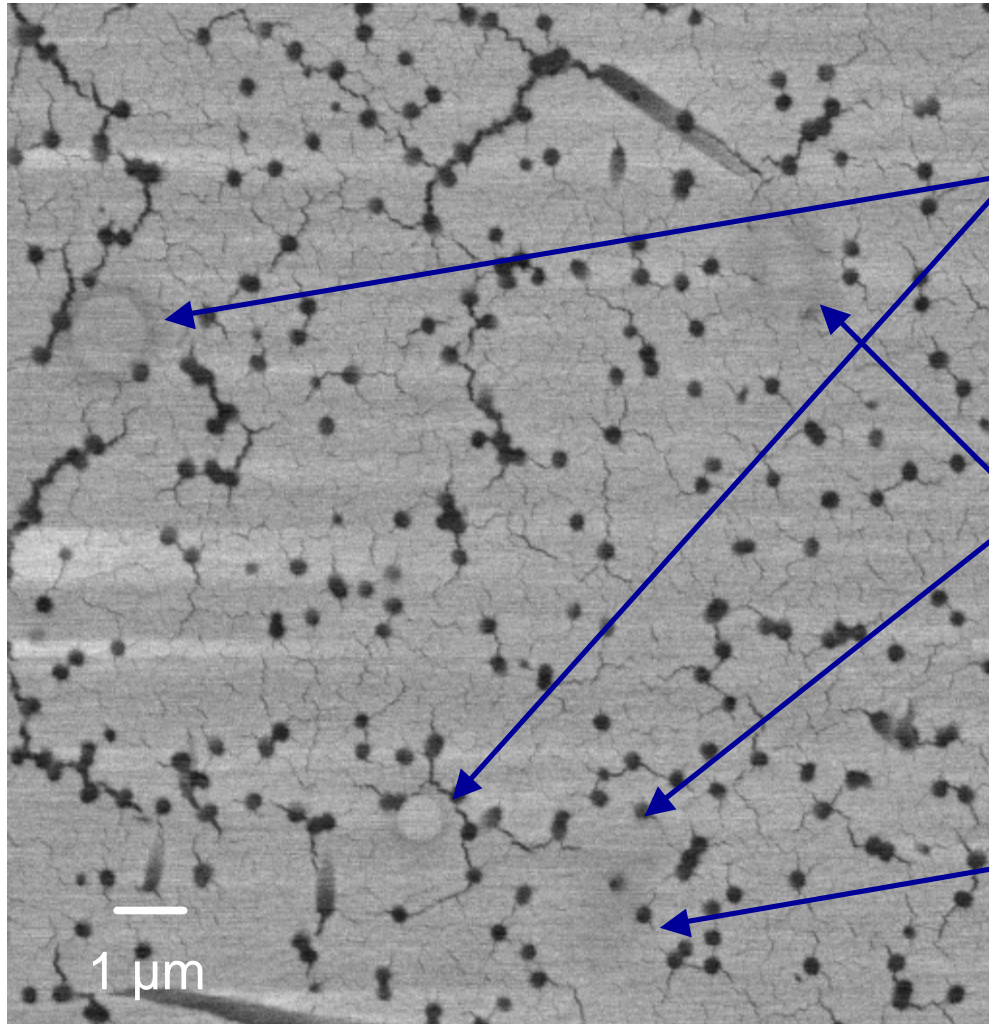


Carbon-rich Particle

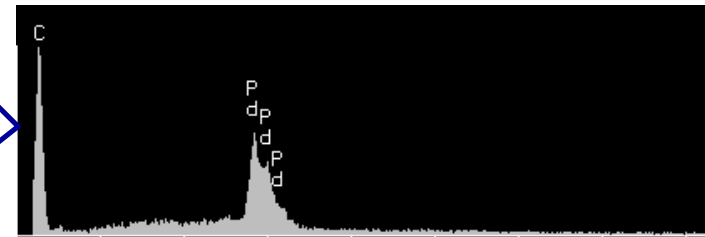


Sulfur Droplet

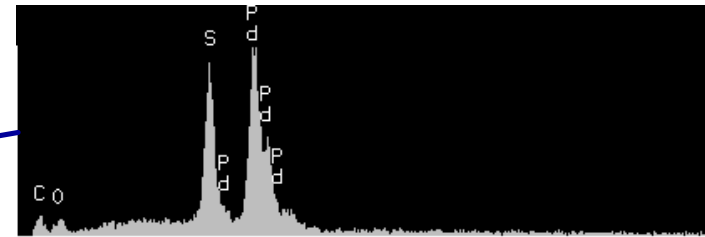
Backscattered Electron Image



SAS Particle



Carbon-rich Particle



Sulfur Droplet

SEM Technique Validation

- **Test for uniform particle dispersion over the filter surface.**
- **Test for reasonable particle size distributions within measured fields.**



Experimental – SEM Analysis

- Mount filters with double-sided silver tape; no filter post sampling coating with carbon or metals
- SEM conditions: 15kV; stable beam current; fixed WD
- SE image fields at 1000x; center to perimeter of filter wedge analyzed; particle ID threshold monitored
- Reference spectra used; 7 sec spectra acquisition
- Pd coated filters for carbon particle identification
 - C:Pd EDX ratio used for ID particle threshold



Comparison of Filter Area required to Obtain 1000 Particle Images from filter Center and filter Perimeter

Section Location	Perim. of filter	Center of filter
Area Analyzed	0.0234 mm ²	0.0288 mm ²

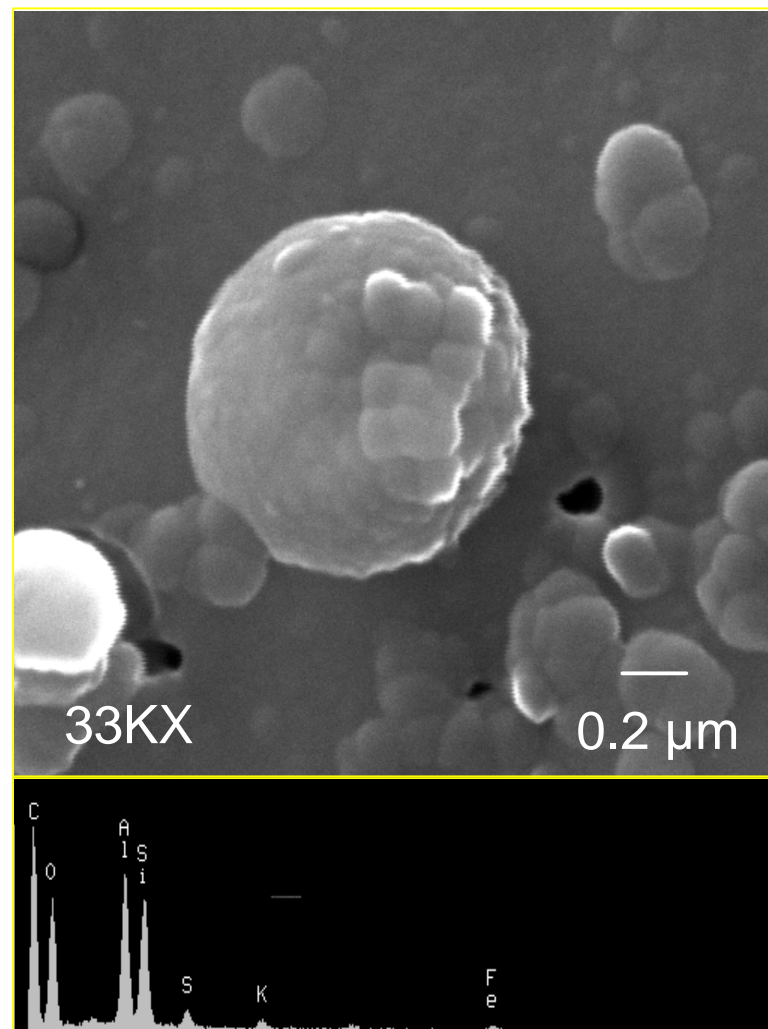
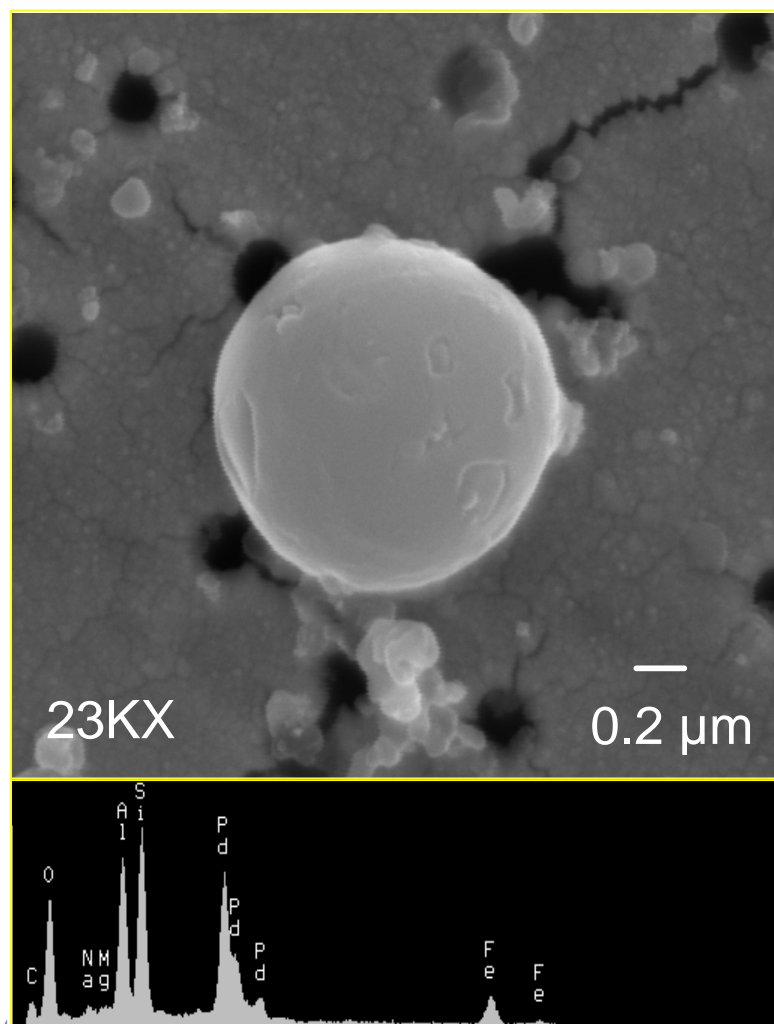


Comparison of Particle Species from filter Center and filter Perimeter, Excluding Ammonium Sulfate “Blobs”

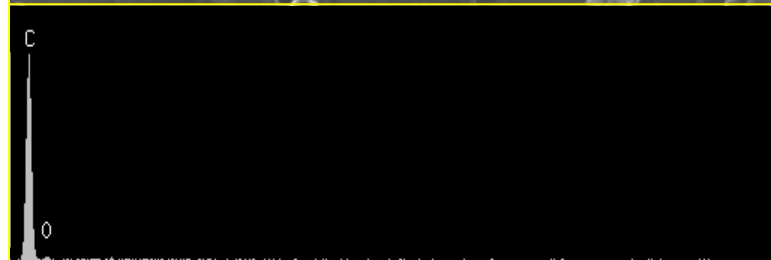
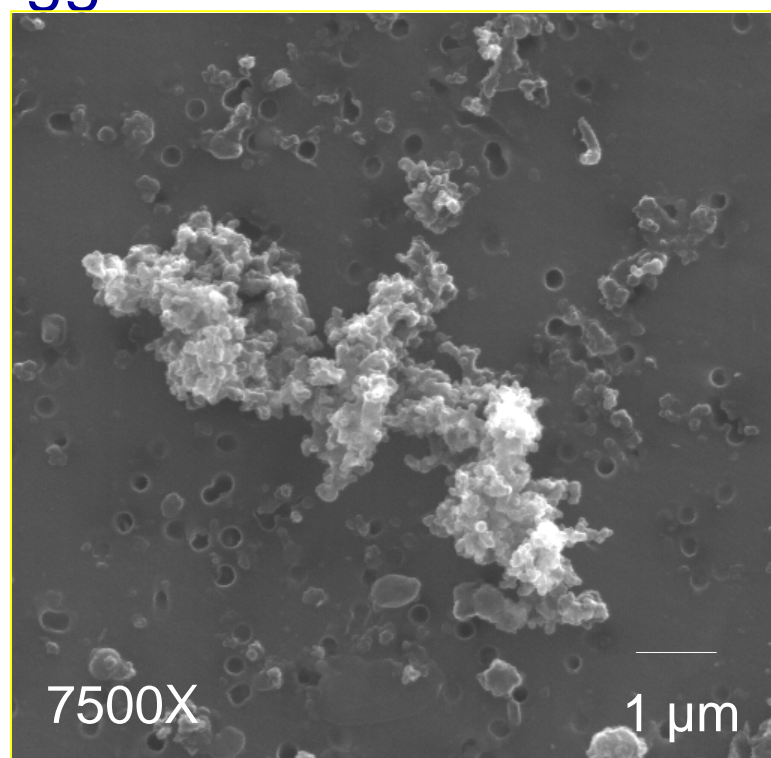
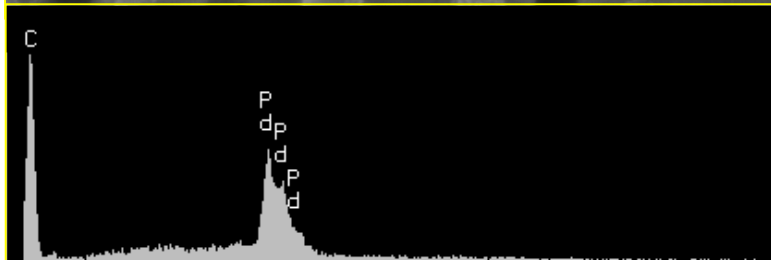
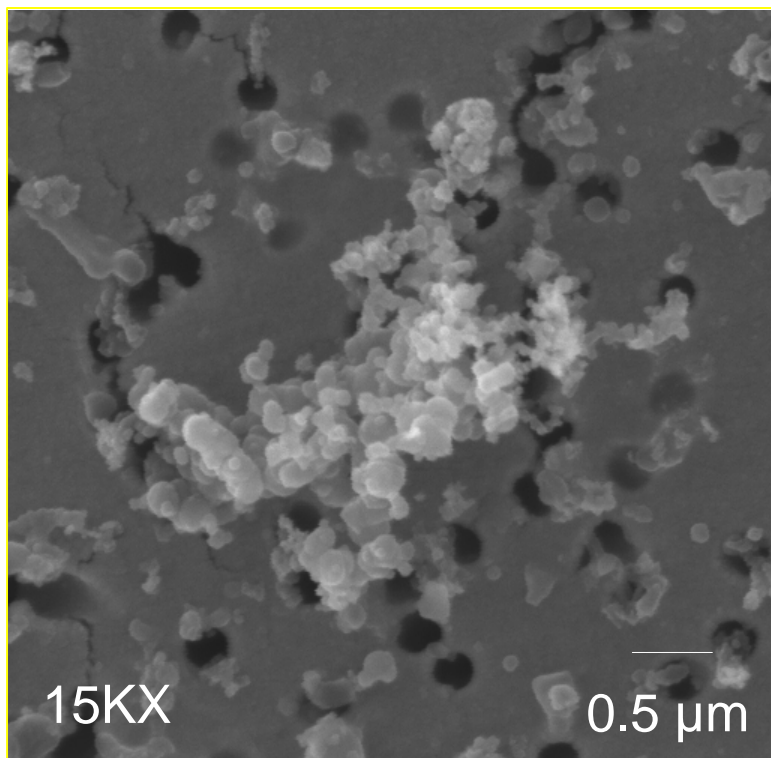
Particle Type	Perim.	Center	Perim.	Center
	Number %	Number %	Volume %	Volume %
SAS	1.8	1.4	4.1	4.3
C-rich	85.5	79.6	69.7	68.8
Crustal	8.6	14.4	21.3	23.8
S-rich	4.1	4.6	4.9	3.1



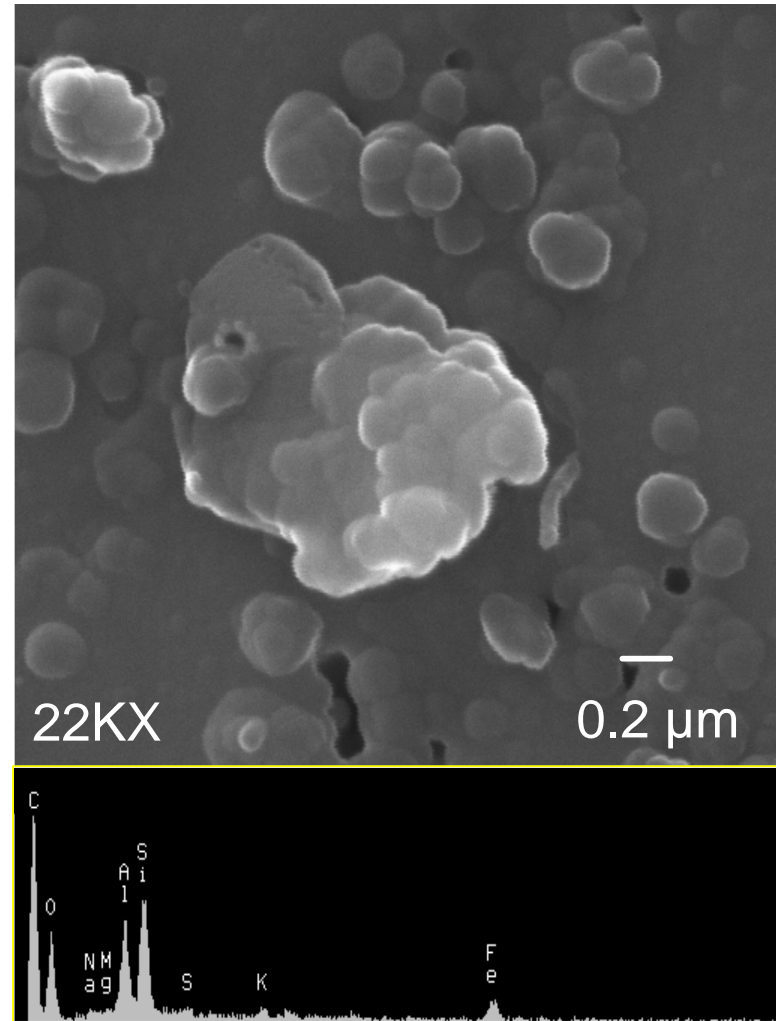
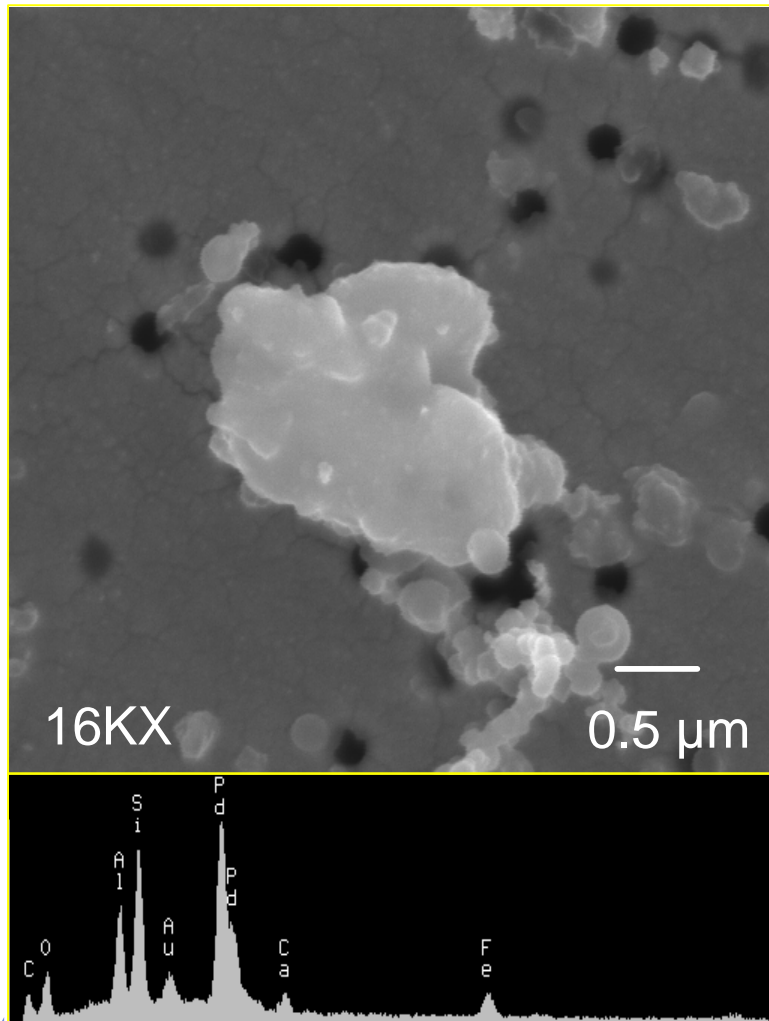
Secondary Electron Images SAS



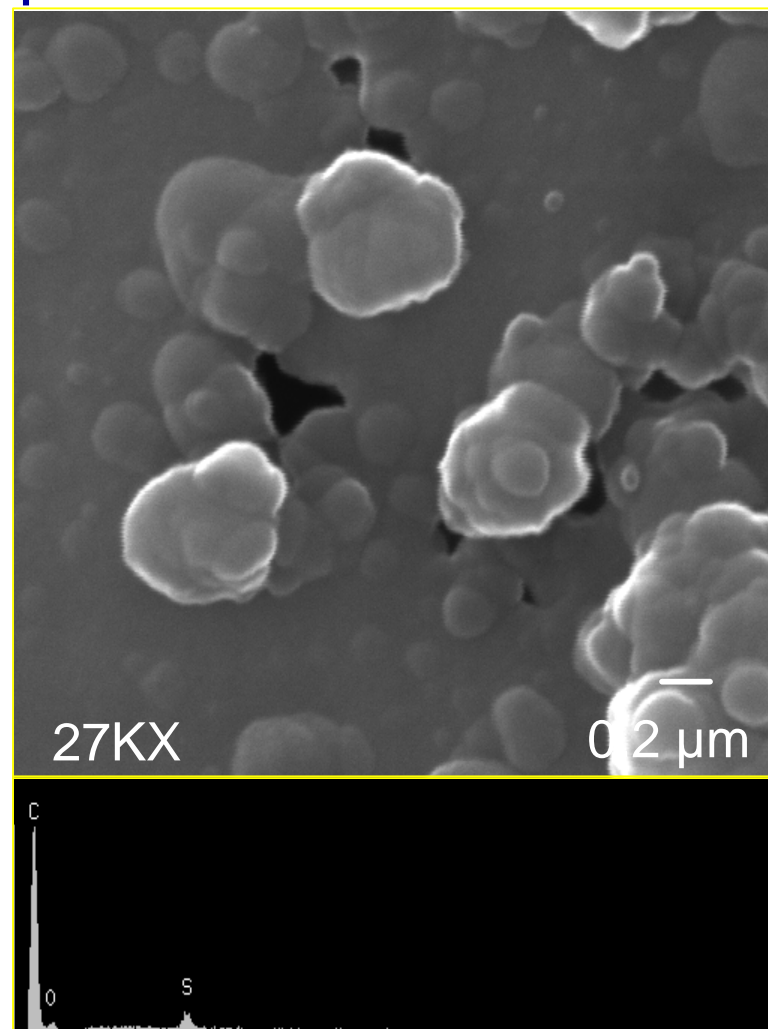
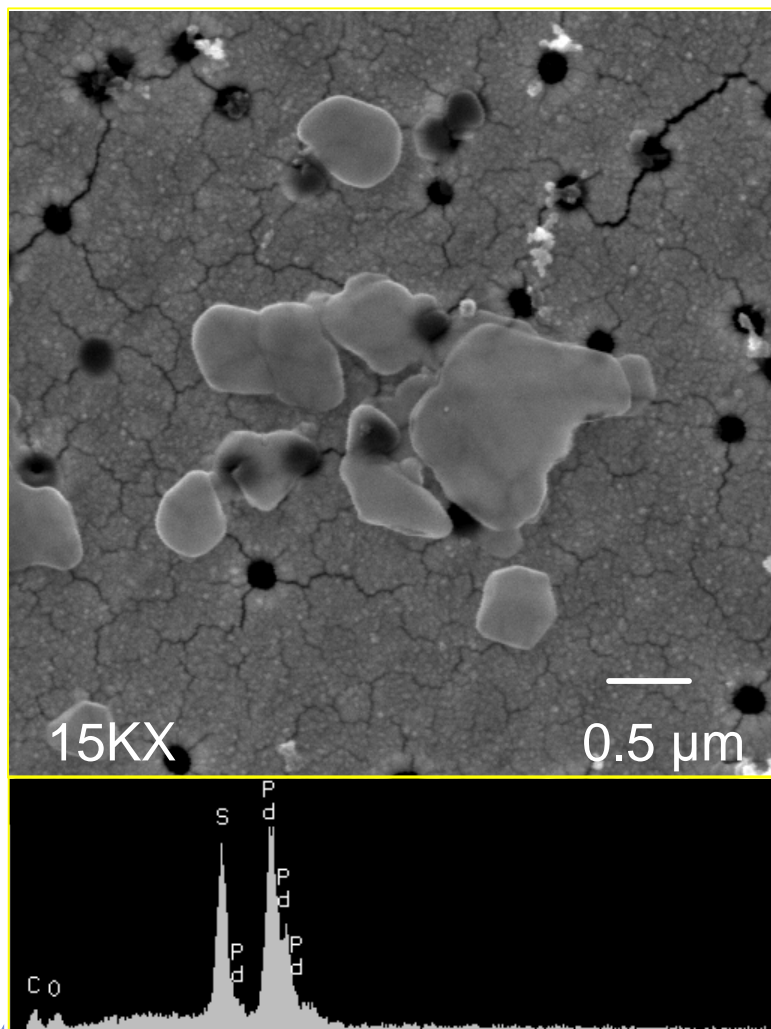
Secondary Electron Images Carbon Chain Agglomerates



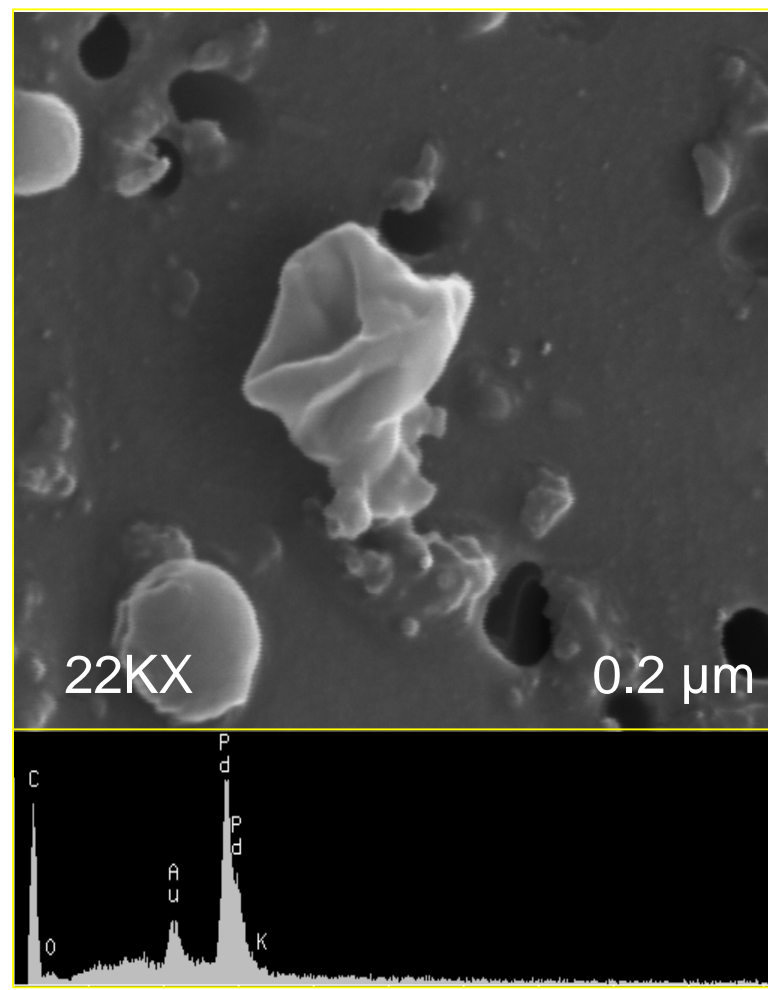
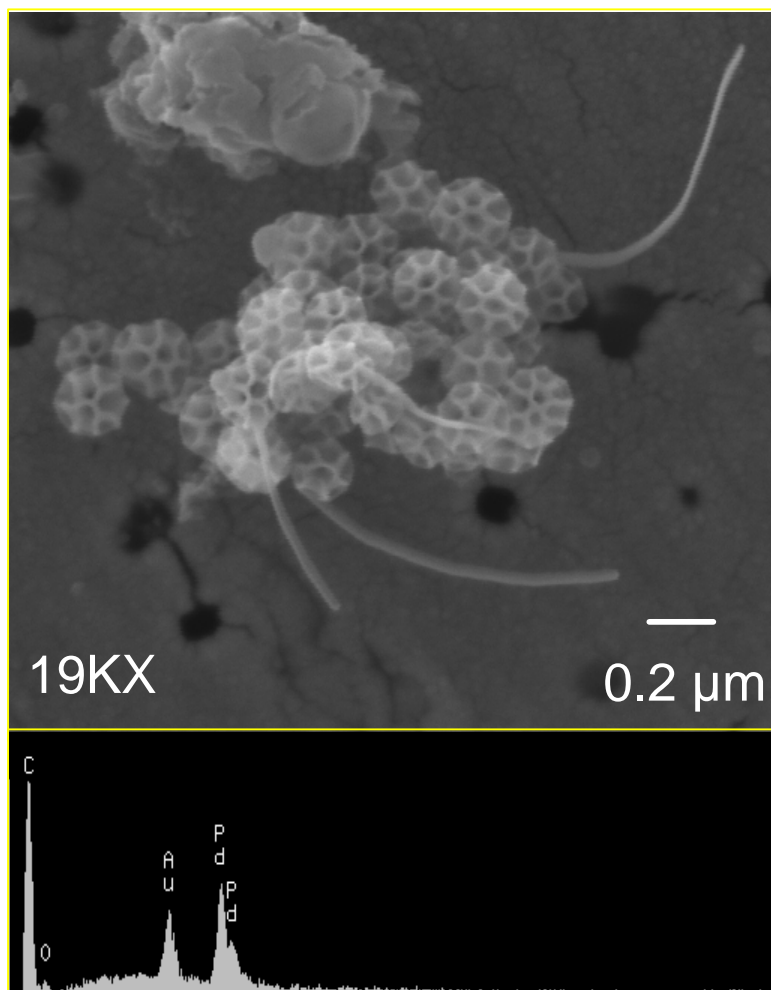
Secondary Electron Images Crustal



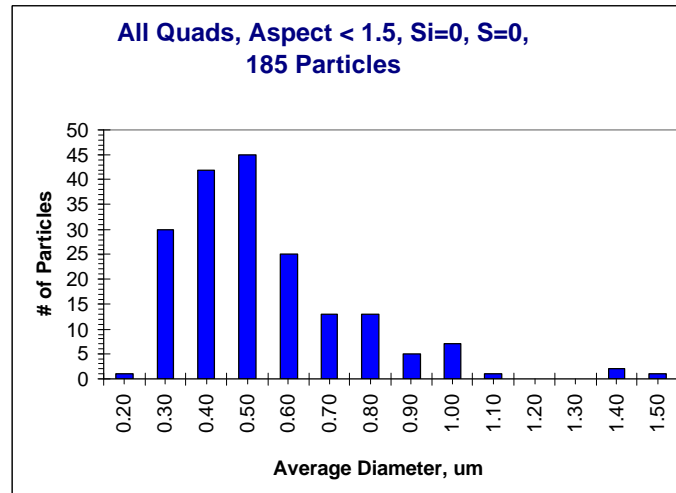
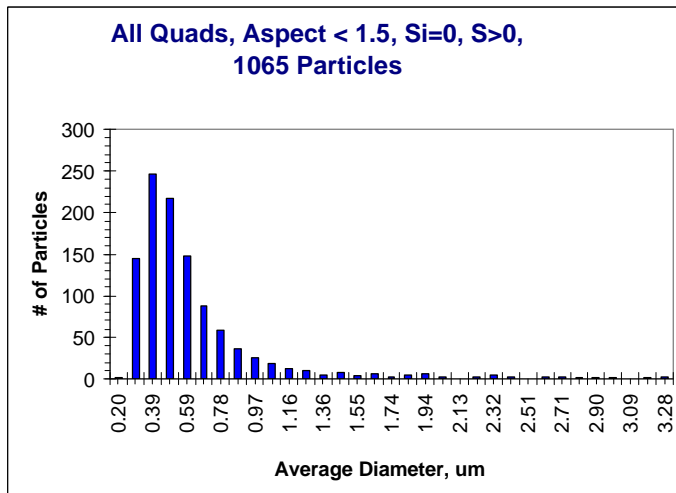
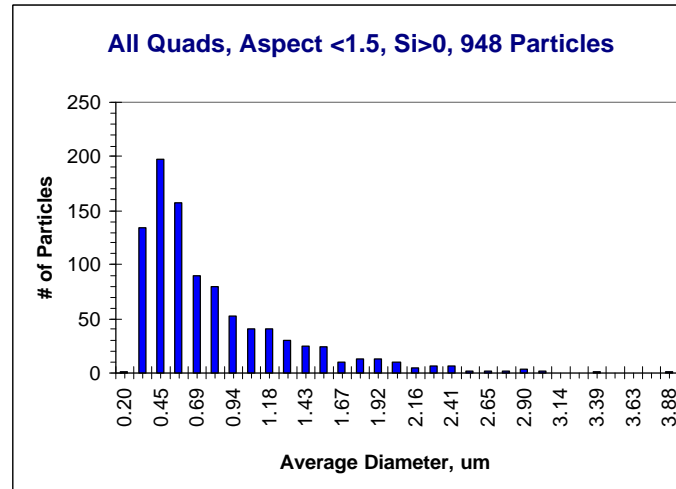
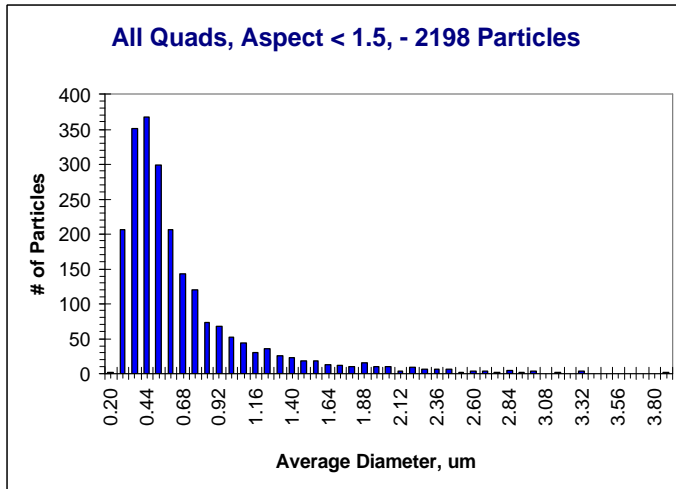
Secondary Electron Images Sulfur Deposits



Secondary Electron Images Plant Material

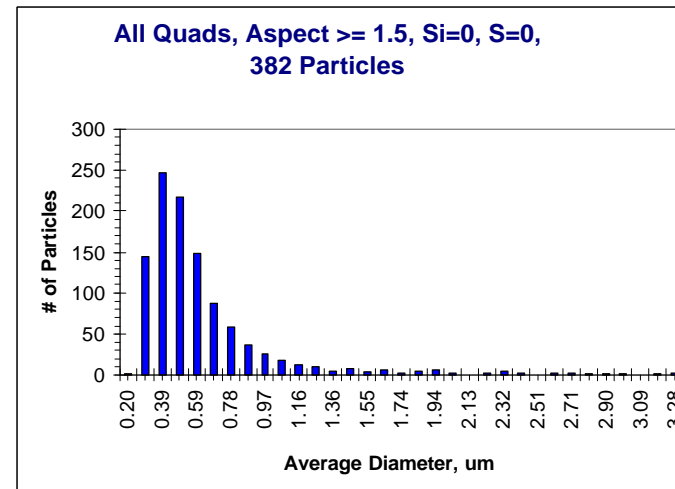
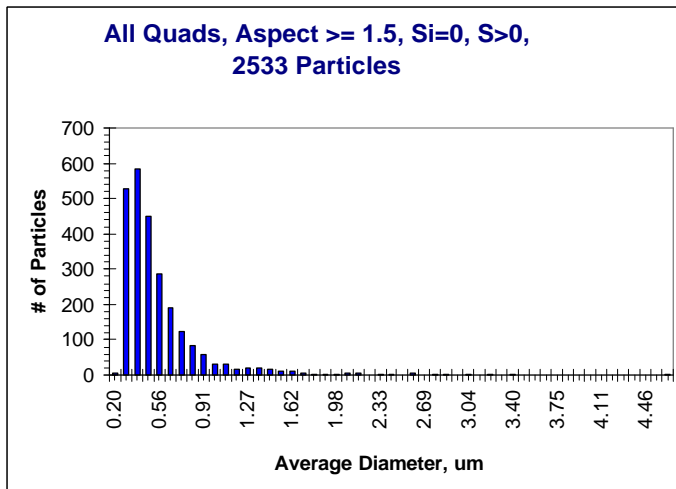
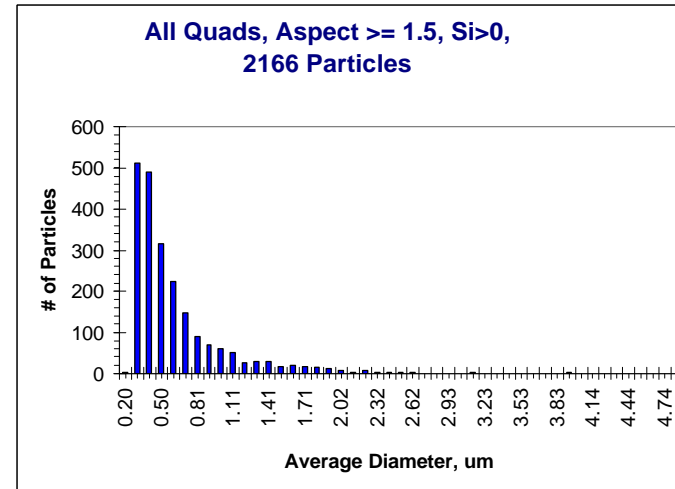
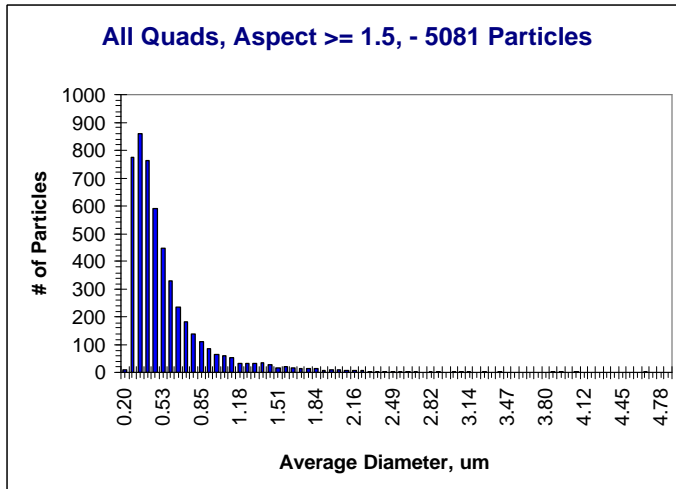


Distributions - Spherical Particles



From "Quantitative Scanning Electron Microscopy of Ambient Air 2.5 μ m Particles Using", *Air Quality II Conference*, McLean, Virginia, September 19-21, 2000.

Non-spherical Particles



From "Quantitative Scanning Electron Microscopy of Ambient Air 2.5 μ m Particles Using", *Air Quality II Conference*, McLean, Virginia, September 19-21, 2000.

Analysis Results

FRM and SEM particle class data normalized to $\mu\text{g}/\text{m}^3$

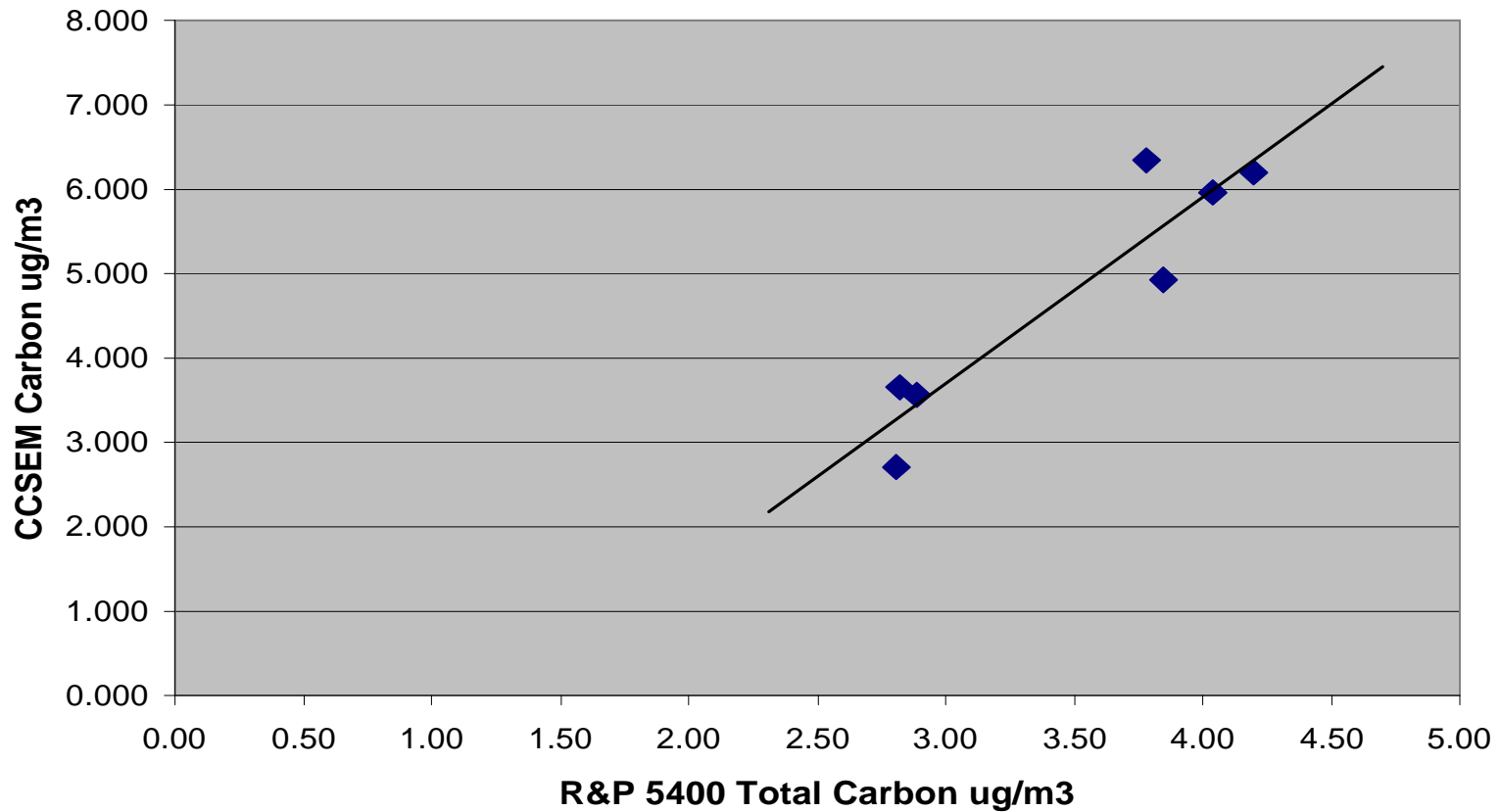
Sample Start Date	24 Hour FRM $\mu\text{g}/\text{m}^3$	SEM Ammonium Sulfate	SEM Carbon Particles	SEM All Crustal Particle Types	SEM Spherical Alumino-Silicates	SEM Crustal	SEM Ca/S Rich	SEM Fe Rich Spheres	SEM Metal Oxide Particles	SEM Misc. Particles
08/06/00	20.8	9.77	5.97	5.06	0.87	3.79	0.30	0.06	0.02	0.03
08/08/00	23.4	13.95	4.93	4.51	0.24	3.67	0.51	0.00	0.01	0.07
08/10/00	15.7	7.94	6.34	1.37	0.03	0.92	0.00	0.09	0.30	0.03
08/12/00	7.6	2.08	3.57	1.95	0.09	1.10	0.07	0.09	0.39	0.21
08/14/00	17.8	9.07	6.20	2.53	0.08	2.04	0.03	0.22	0.15	0.01
08/16/00	9.5	4.76	2.72	2.02	0.26	0.60	0.67	0.00	0.37	0.13
08/18/00	14.0	8.17	3.66	2.17	0.07	1.17	0.41	0.22	0.24	0.07

FRM and SEM particle class data normalized to $\mu\text{g}/\text{m}^3$ (SEM particle class volume fraction x daily FRM). SEM data normalized to IC ammonium sulfate analysis. From "Quantitative Analysis of Ambient Air 2.5 μm Particles Using Scanning Electron Microscopy", 11th International Conference on Coal Science, San Francisco, Oct. 2001.



R&P Carbon versus SEM Carbon

Carbon Values



From "Quantitative Analysis of Ambient Air 2.5 μ m Particles Using Scanning Electron Microscopy", *11th International Conference on Coal Science*, San Francisco, Oct. 2001.



Conclusions

- **SEM sampling methodology is reasonably comparable to the FRM, based on $\mu\text{g}/\text{m}^3$ filter loading.**
- **The SEM technique provides satisfactory results to continue the method development.**
- **Although the methodology may be subject to improvement, it is of sufficient quality to apply it to the comparative measurement of SAS particles in a more comprehensive study.**



Future Work

- **Correlate the SEM results with bulk analyses of companion filters.**
- **Analyze more filters to develop statistics on distributional analysis of particle classes.**
- **Use the palladium coating as an internal standard for quantifying the particle species.**
- **Revisit uncoated filters (check validity of calculating carbon by difference).**



Acknowledgements

- **Dr. Elias J. George – NETL Environmental Safety and Health Division**
- **Traci Lersch – R.J. Lee Group**
- **The other PM_{2.5} Sampling and Analysis team members**
- **Mr. Thomas J. Feeley – Product Manager: Environmental and Water Resources, NETL**

