Individual Particle Analysis of Ambient $PM_{2.5}$ Using Advanced Electron Microscopy Techniques

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NETL UCR Review Conference
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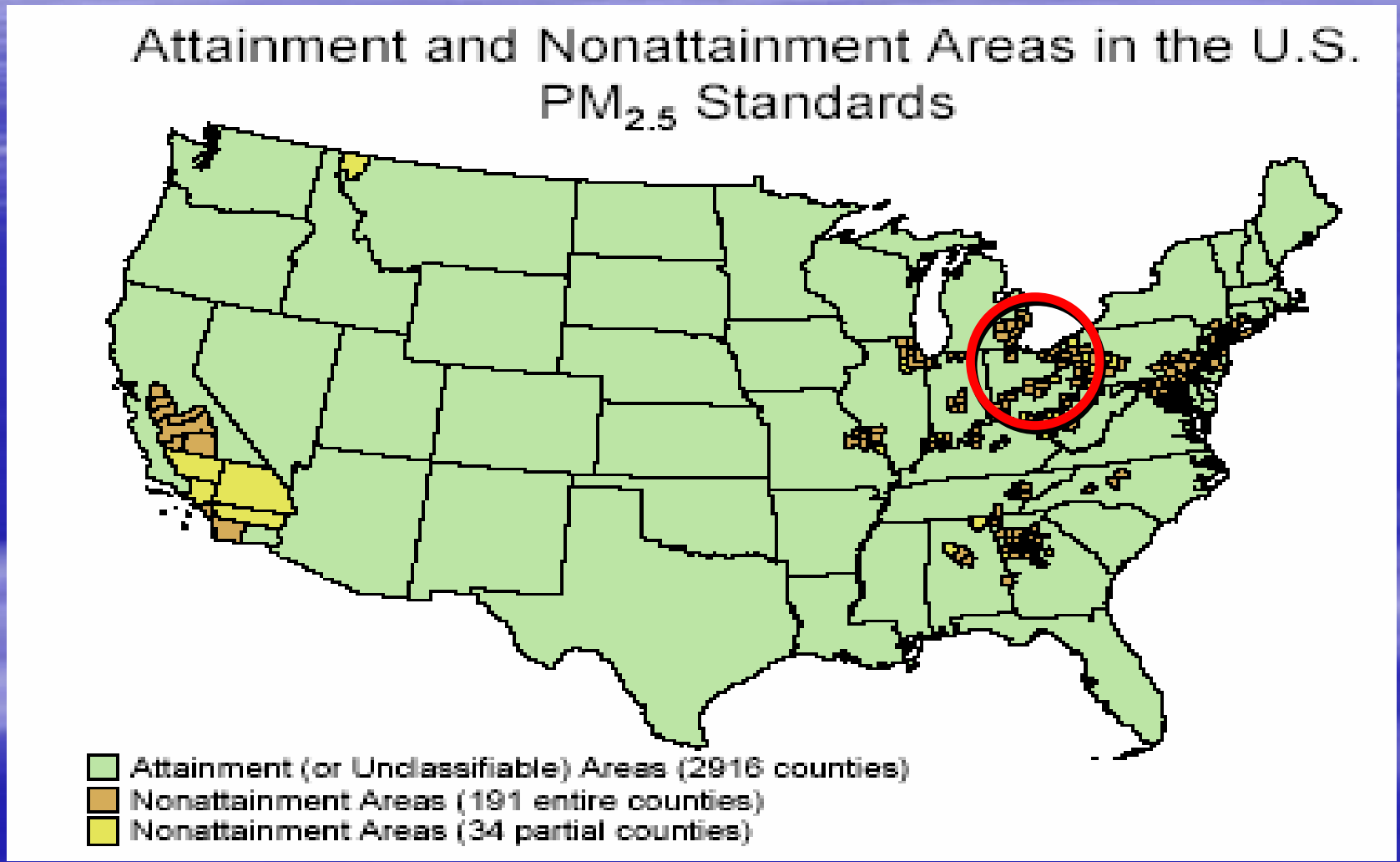
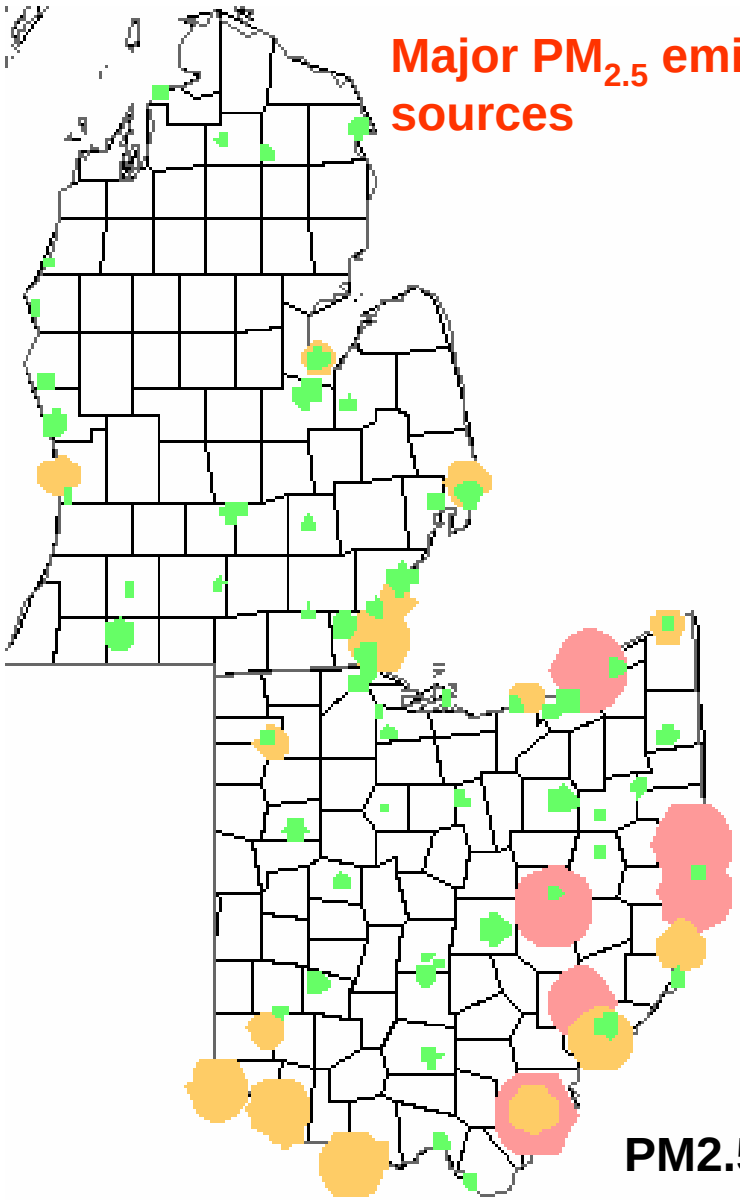
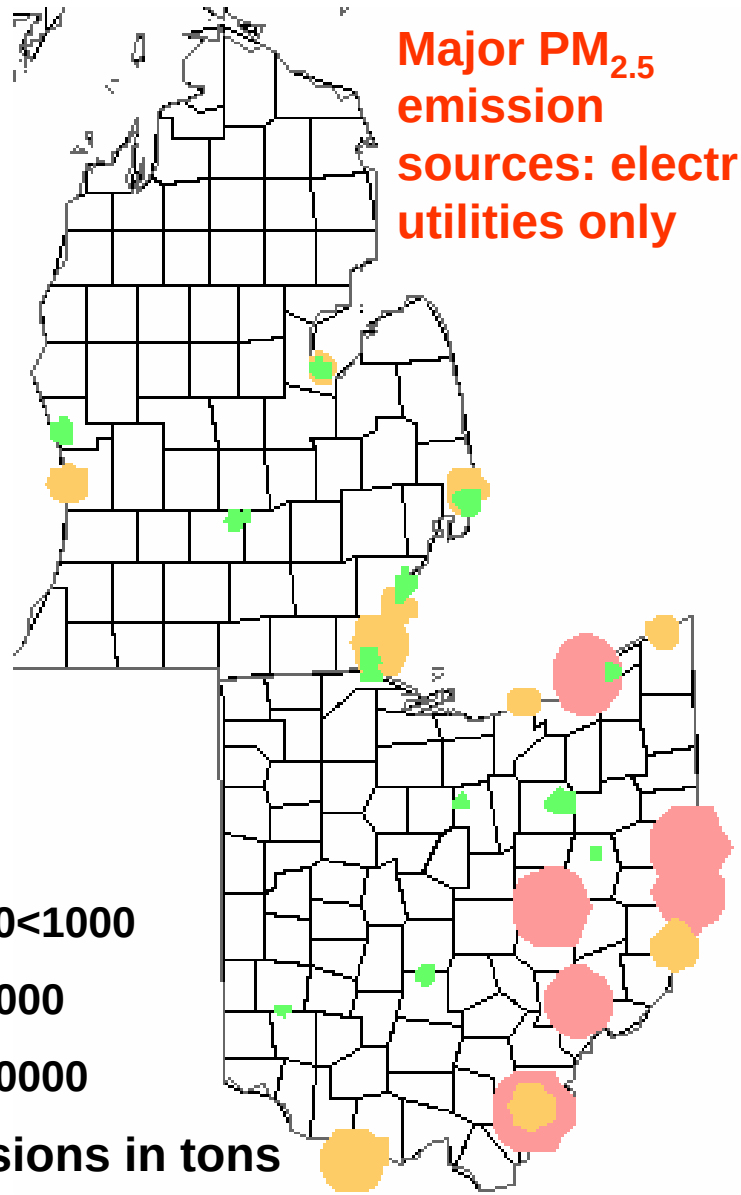
National Ambient Air Quality Standard



$PM_{2.5}$ emission sources





100<1000

>5000

>10000

PM2.5 emissions in tons

Source: EPA Facility Map

Assisting source apportionment

- Bulk chemical analysis
  - Difficult to differentiate transported PM from freshly emitted PM especially from coal-fired power plants.
- Scanning electron microscopy analysis
  - Challenging to find nano-scale particles which are freshly generated from fossil fuel combustion sources

➢ Analytical techniques for individual ultrafine particle that are capable of providing information on size, morphology, elemental composition can improve source apportionment analysis.

Objectives

- To demonstrate a combination of advanced electron microscopy techniques that can be effectively used to identify and characterize individual fine and ultrafine (nano-scale) particles, and their sources

Approach
Aim1

- To collect a series of ambient $PM_{2.5}$ samples in:
  - **Southwestern Detroit, MI**

    close to multiple sources, including motor vehicle/diesel, incinerators, and coal combustion
  - **Steubenville, OH**

    close to several coal-fired utility boilers

Industrial and Motor Vehicle Sources of Particulate Air Pollution in Southwest Detroit

Key:

- A — Automotive Plant
- C — Cement Plant
- O — Oil Refinery
- P — Power Plant
- S — Steel Industry
- WI — Waste Incinerator
- Bridge with Heavy Diesel Truck Traffic

NETL Air Quality Research

- **CARDIOPULMONARY TOXICITY INDUCED BY AMBIENT PARTICULATE MATTER**

-TRI CITY CONCENTRATED AMBIENT PARTICLE STUDY-

Principal Investigator: Annette Rohr

DOE Project Manager: Bill Aljoe

Project Teams

–Michigan State University (Jack Harkema)

–University of Michigan (Jerry Keeler)

Objectives:

Evaluate the potential for adverse cardiopulmonary effects from exposure to environmentally relevant coal-fired power plant and traffic-related PM

Cooperative Agreement: DE-FC26-05NT42303

AirCARE 1

Mobile Air Research Lab

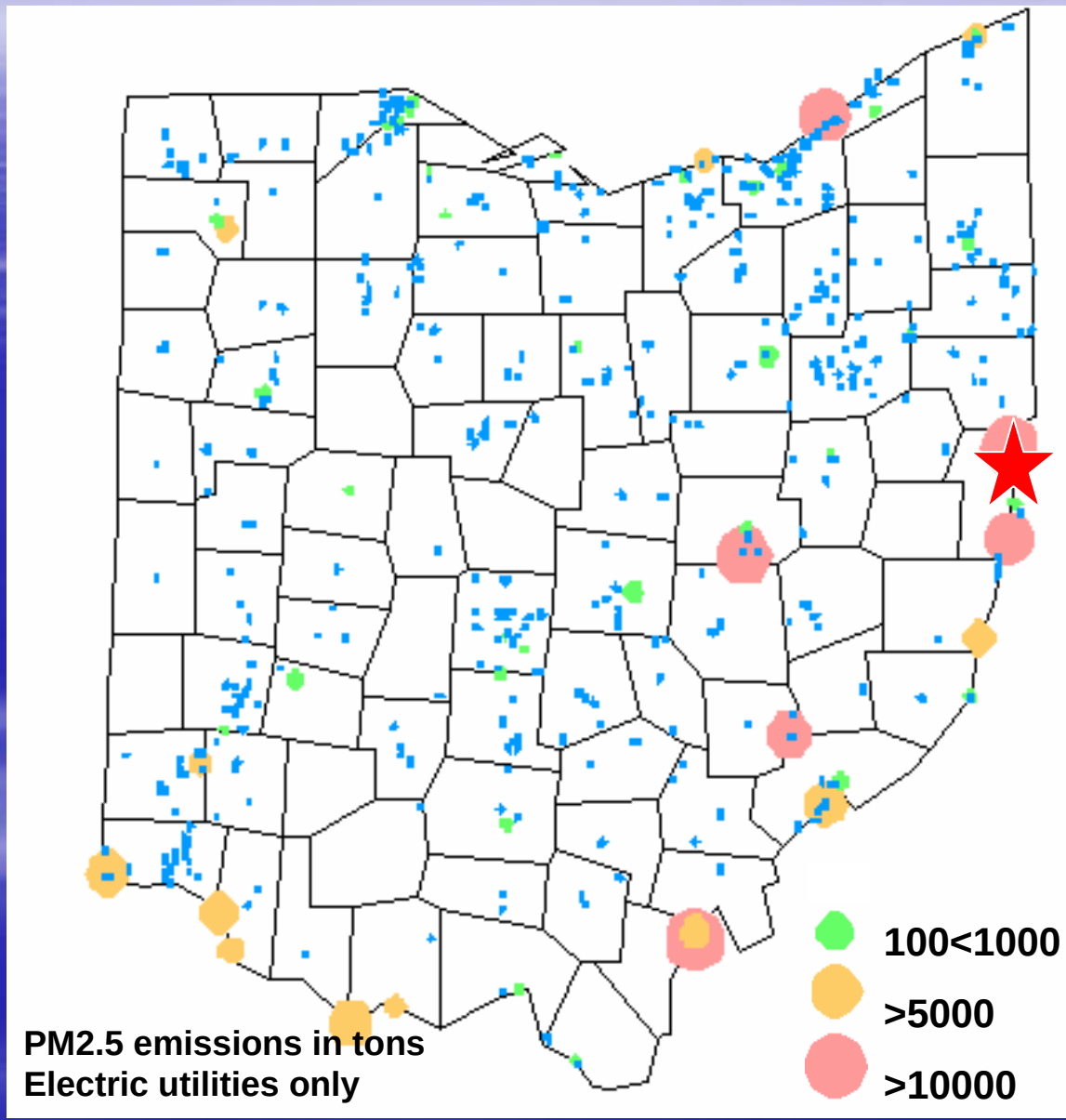
Additional trace element analysis using ICP-MS

Three fixed resolutions

- Low Resolution
  - Rb, Sr, Mo, Cd, Sb
  - Ba, La, Ce, Sm, Pb, U
- Medium Resolution
  - Na, Mg, Al, P, S, Ca, Ti, V, Cr
  - Mn, Fe, Co, Ni, Cu, Zn
- High Resolution
  - K, As, Se

Finnigan ELEMENT2

Steubenville, OH



Approach
Aim2

- To utilize high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), STEM energy dispersive X-ray spectrometry (EDX), and energy-filtered TEM to provide information on the size, morphology, structure, and elemental composition of individual particles collected in Detroit and Steubenville.

Major chemical composition of fine and ultrafine particles in eastern coal fly ash

For an eastern U.S. bituminous coal fly ash:

- Spherical aluminosilicate particles are often used as a tracer for primary PM emissions from coal-fired boilers (Giere et al., 2003; Chen et al., 2004)
- The dominant single-element inorganic particles are Iron oxides (Chen, et al., 2005).
- Titanium oxide particles are commonly observed in coal ash (Huggins, et al., 1997).

Major chemical composition of UF particles in eastern coal fly ash

Categories	Elements	%
Ti-Al-Fe	Ti-Al-Fe-Si-S-Ca	19
Fe-Si-Al	Fe-Si-Al-Ti-S	15
Ti-Si-Al	Ti-Si-Al-S-Si-Fe	14
Fe-rich	Fe-Al-Si-Ti	13
Ti-rich	Ti-Al-Fe-Si	7
Al-Ti	Al-Ti-S-Ti-Ca-Fe	5

(Chen, Y. et al., ES&T, 2005)

Trace element particles in eastern coal

EPA, 1995	Chow et al., 2004	Giere et al., 2003	Goodarzi, 2006
HAPs in coal	coal fly ash (<0.1% abundances)	coal fly ash	coal fly ash
As	Rb	As	As
Be	Cu	Be	Ni
Cd	Se	Pb	Cr
Cr	V	Tl	Mo
Hg	Mo	Zn	Hg
Ni	Mn	U	Pb
Pb	Pb		
U	Zn		

Results

Detroit

Industrial and Motor Vehicle Sources of Particulate Air Pollution in Southwest Detroit

Key:

- A — Automotive Plant
- C — Cement Plant
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- S — Steel Industry
- WI — Waste Incinerator
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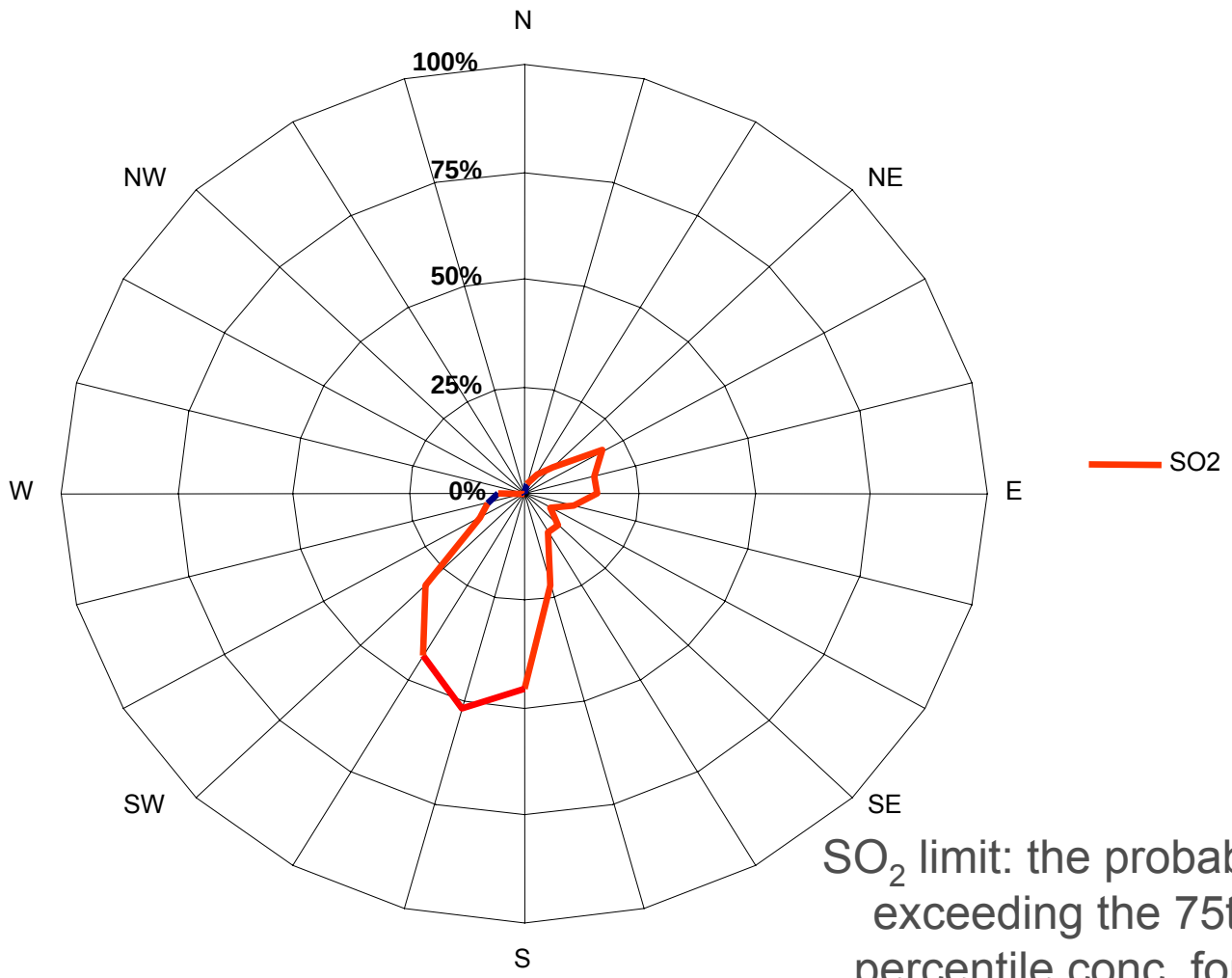
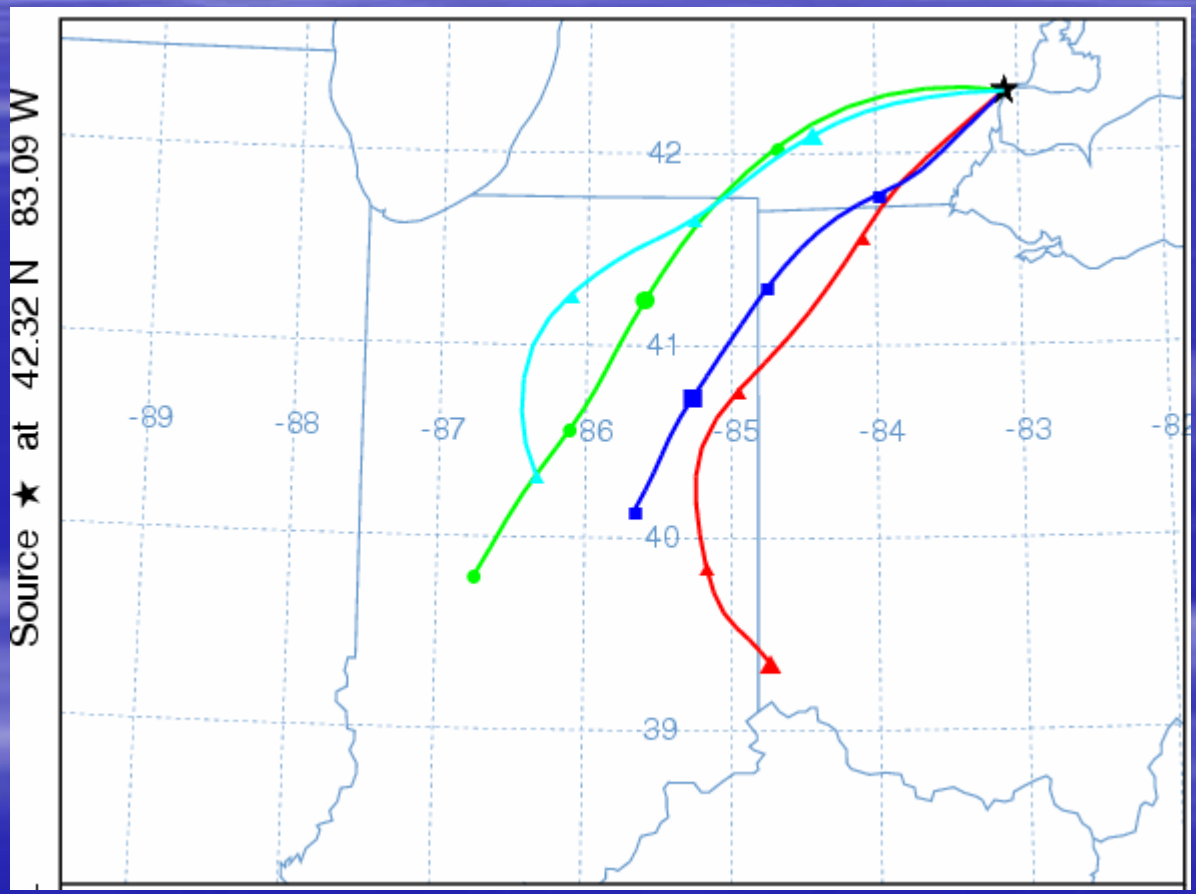
Elevated SO_2: frequency vs. wind direction

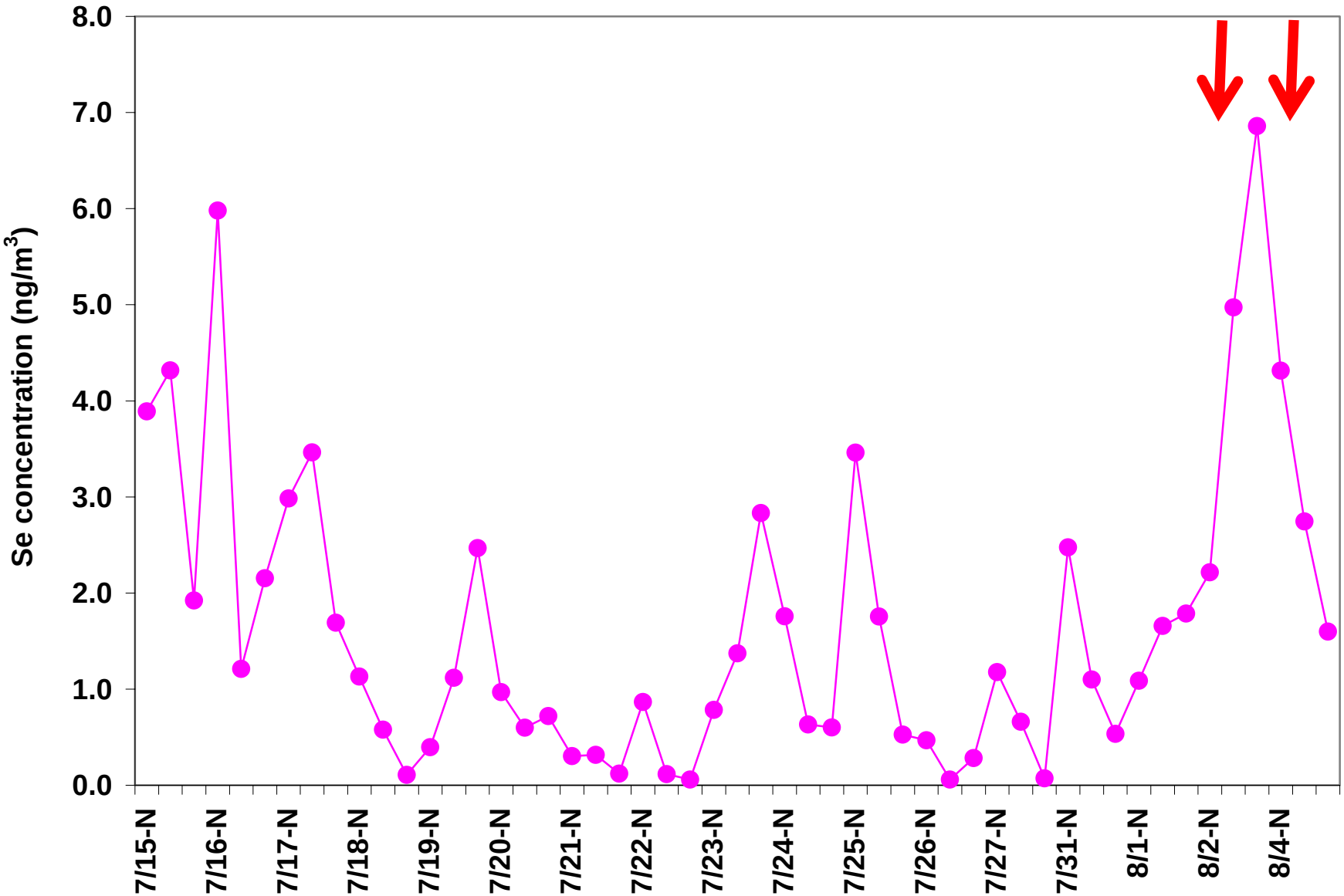


SO_2 limit: the probability exceeding the 75th percentile conc. for a given wind direction.

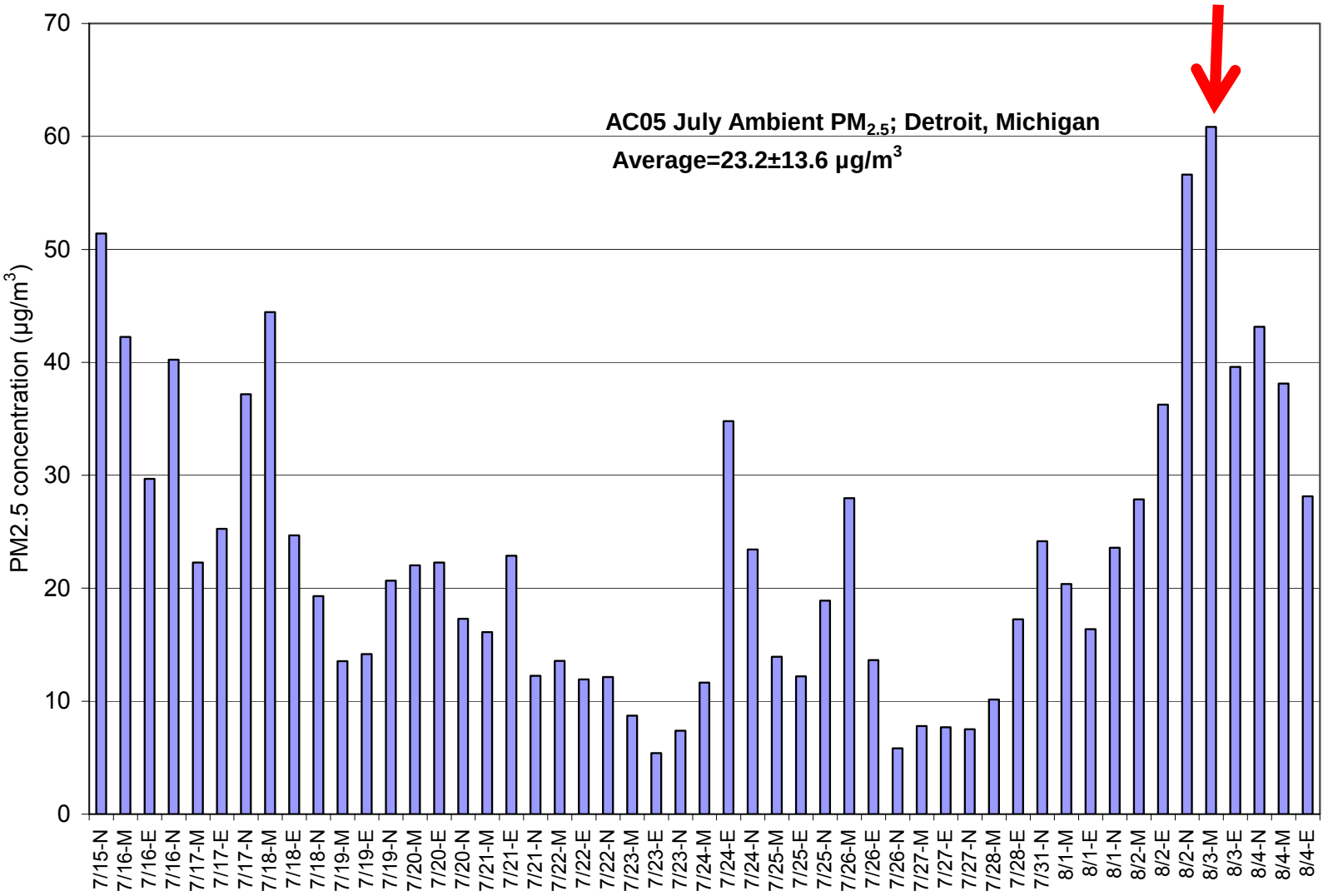
NOAA HYSPLIT MODEL
24 hr Backward trajectories
Detroit site - August 4, 2005



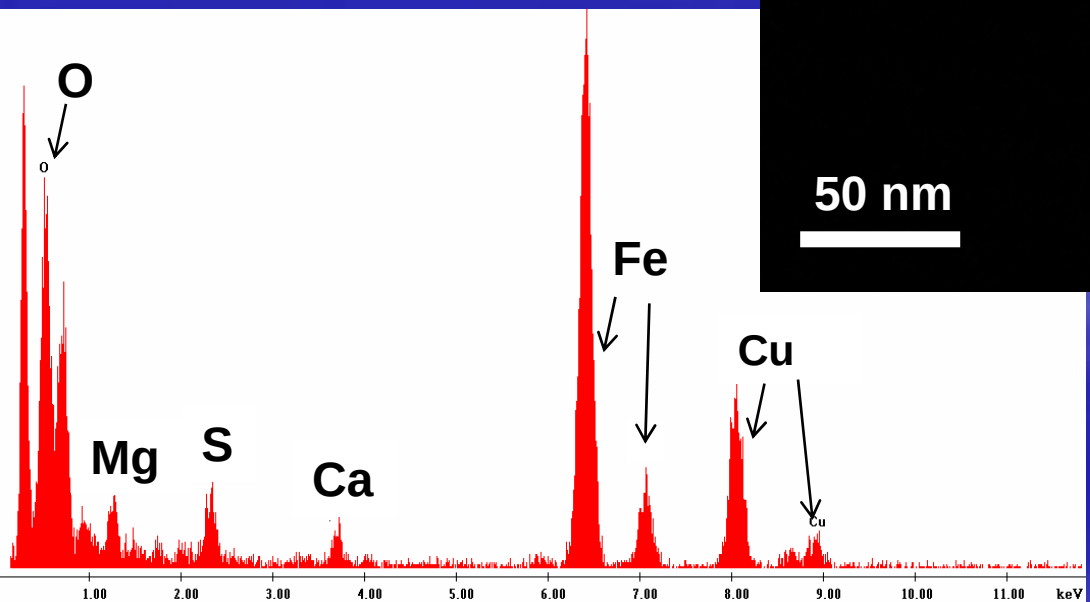
Selenium in Detroit

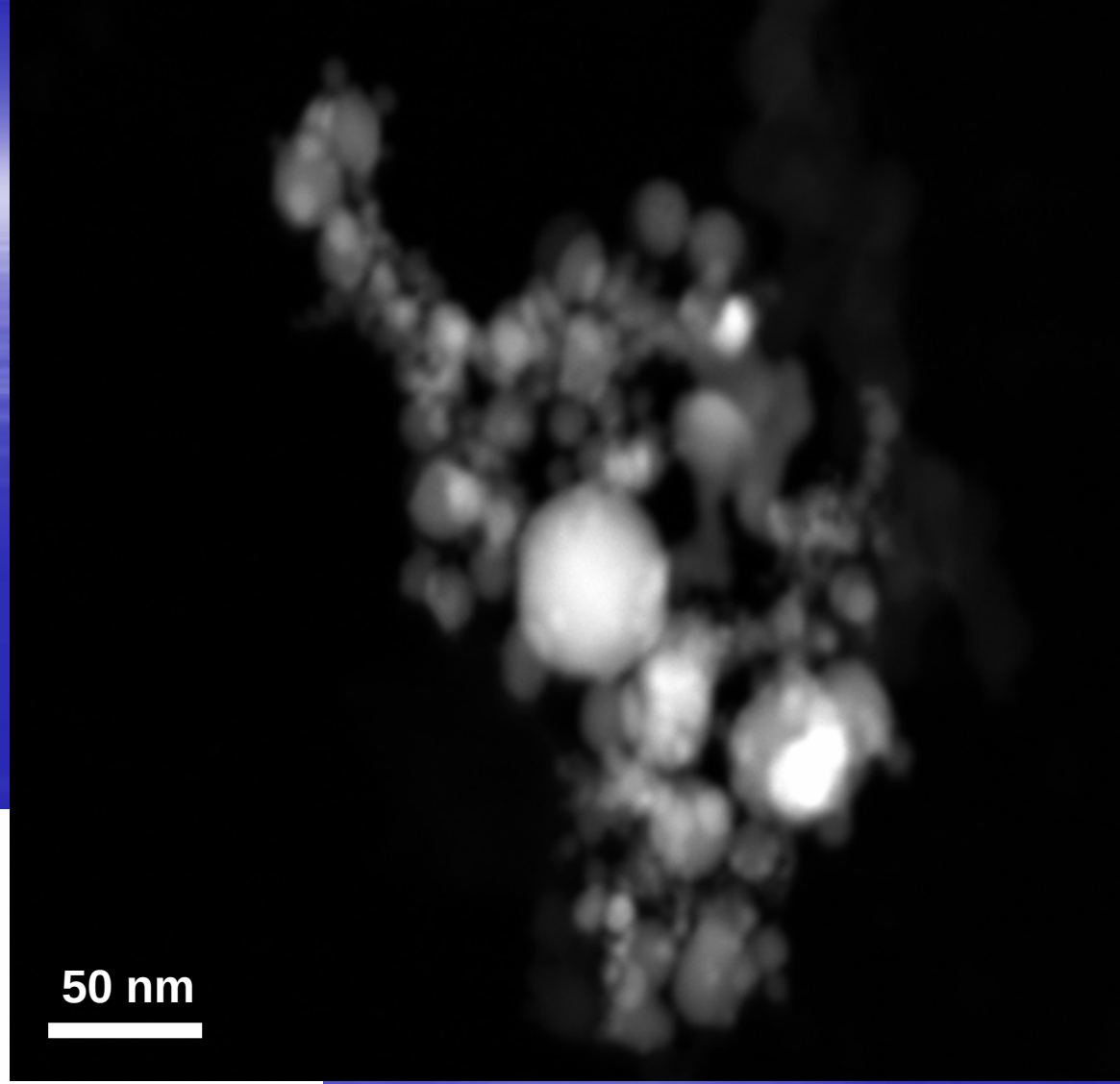


Ambient $PM_{2.5}$
2005 Summer in Detroit, Michigan

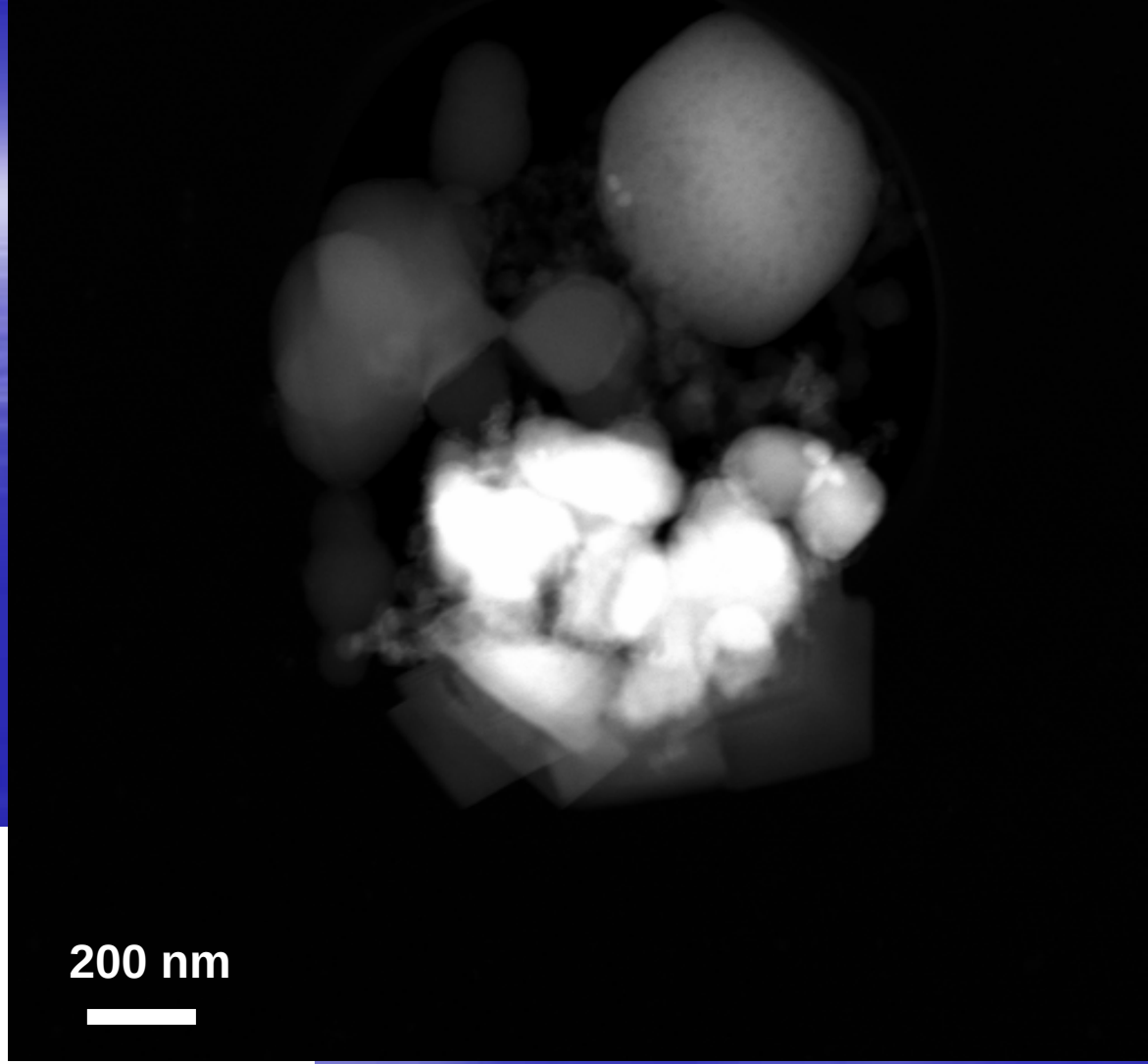


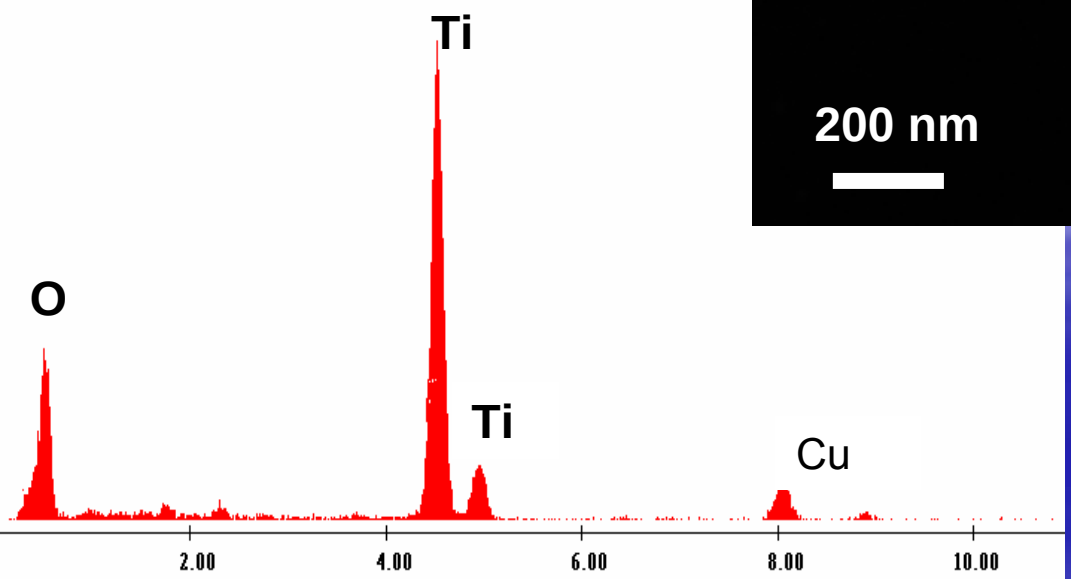
- Iron oxide-rich UF particles and soot aggregates



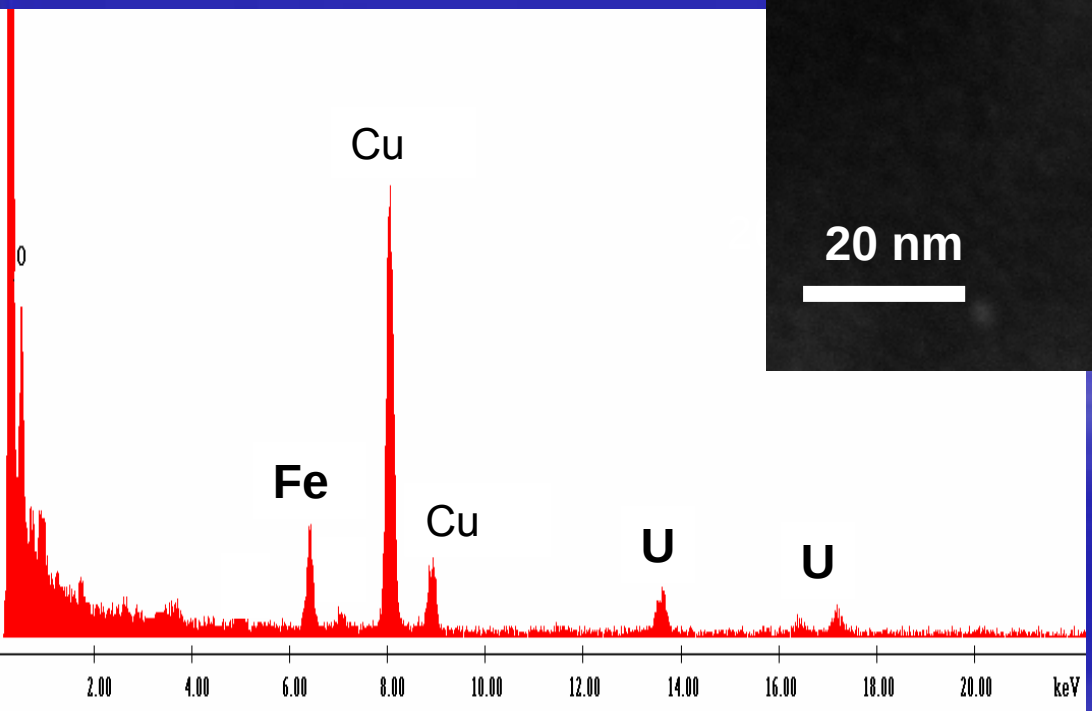


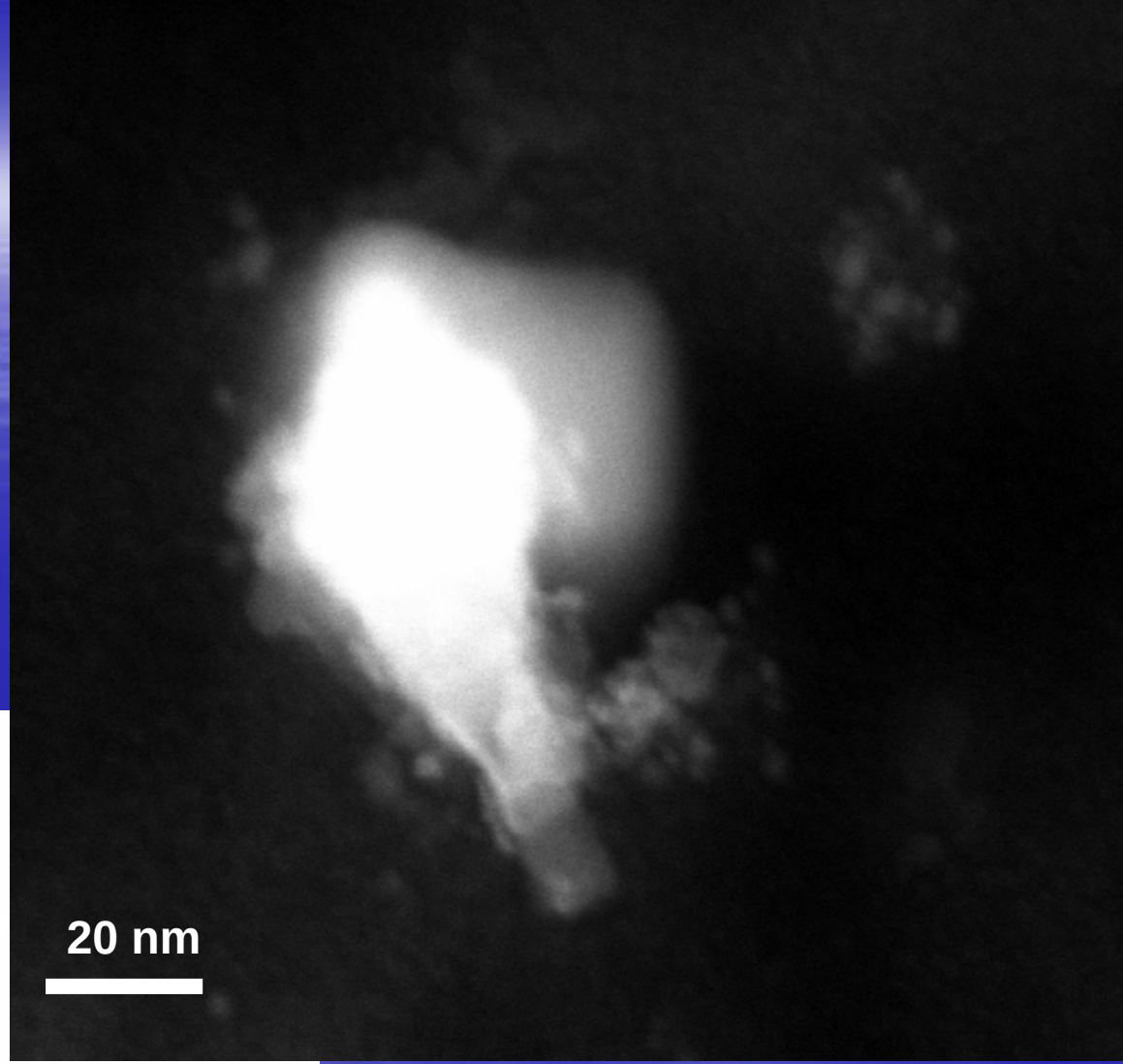
- Titanium oxide-rich UF particles



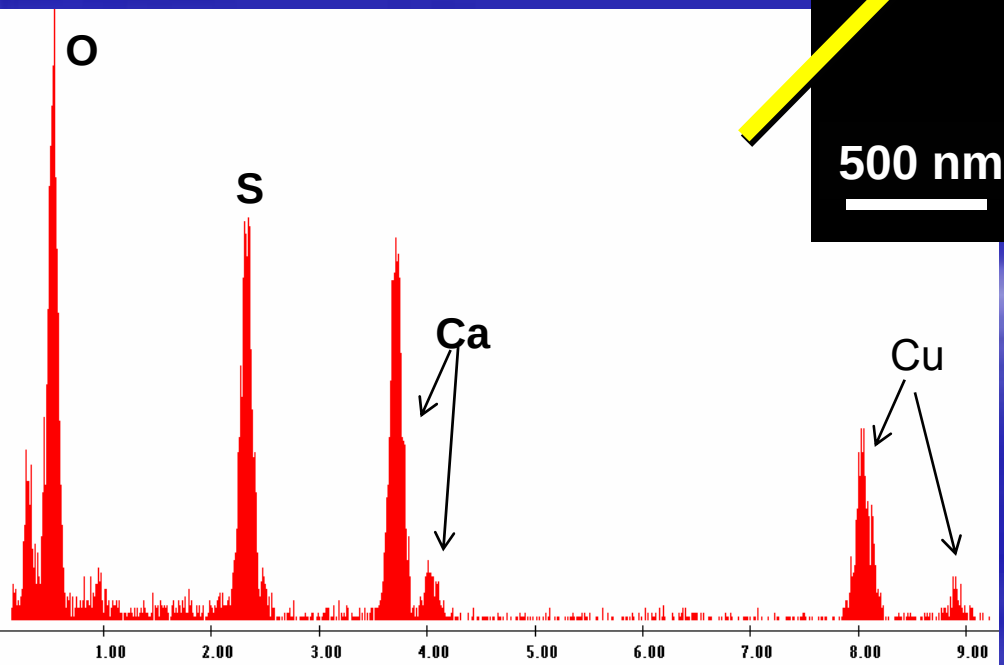


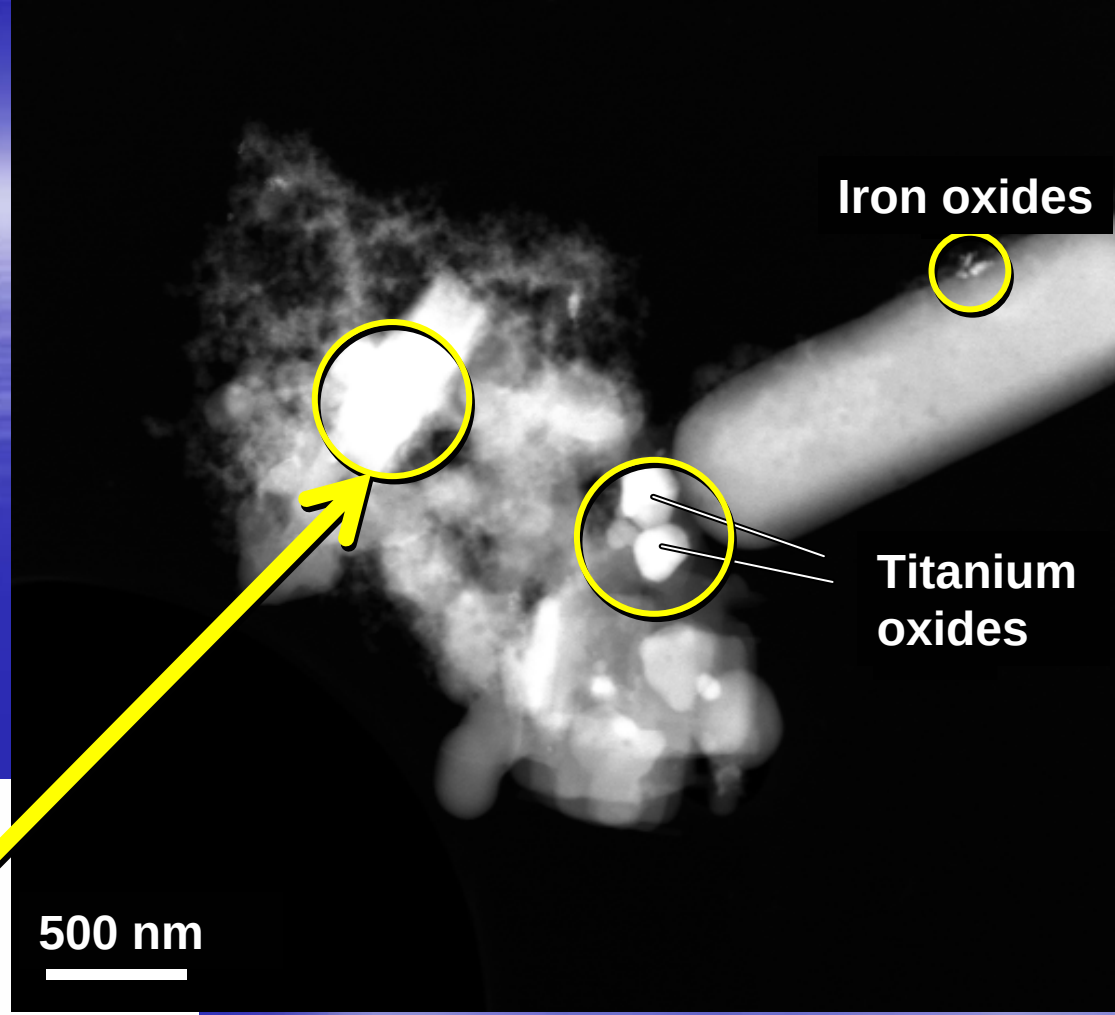
- ✓ Uranium and Iron oxide UF particles

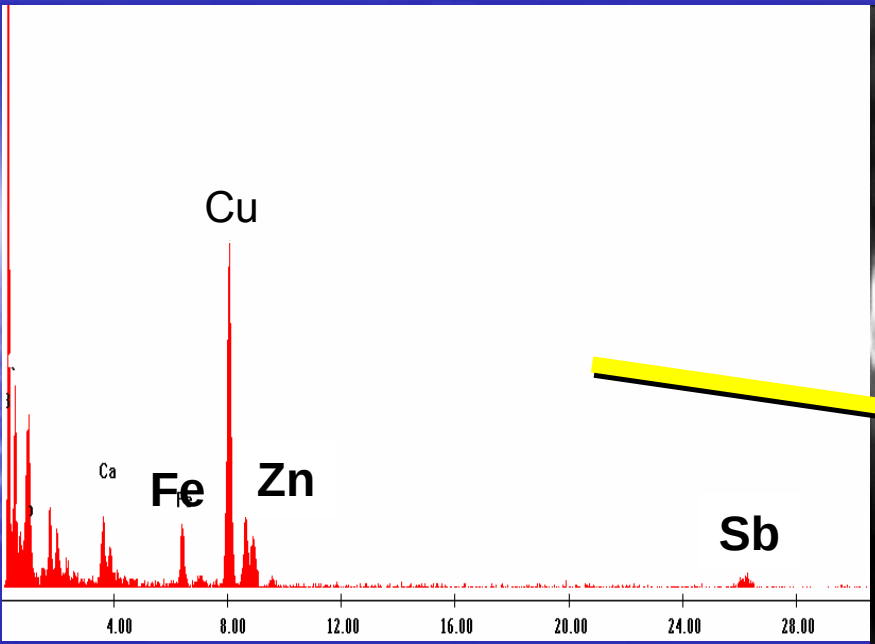


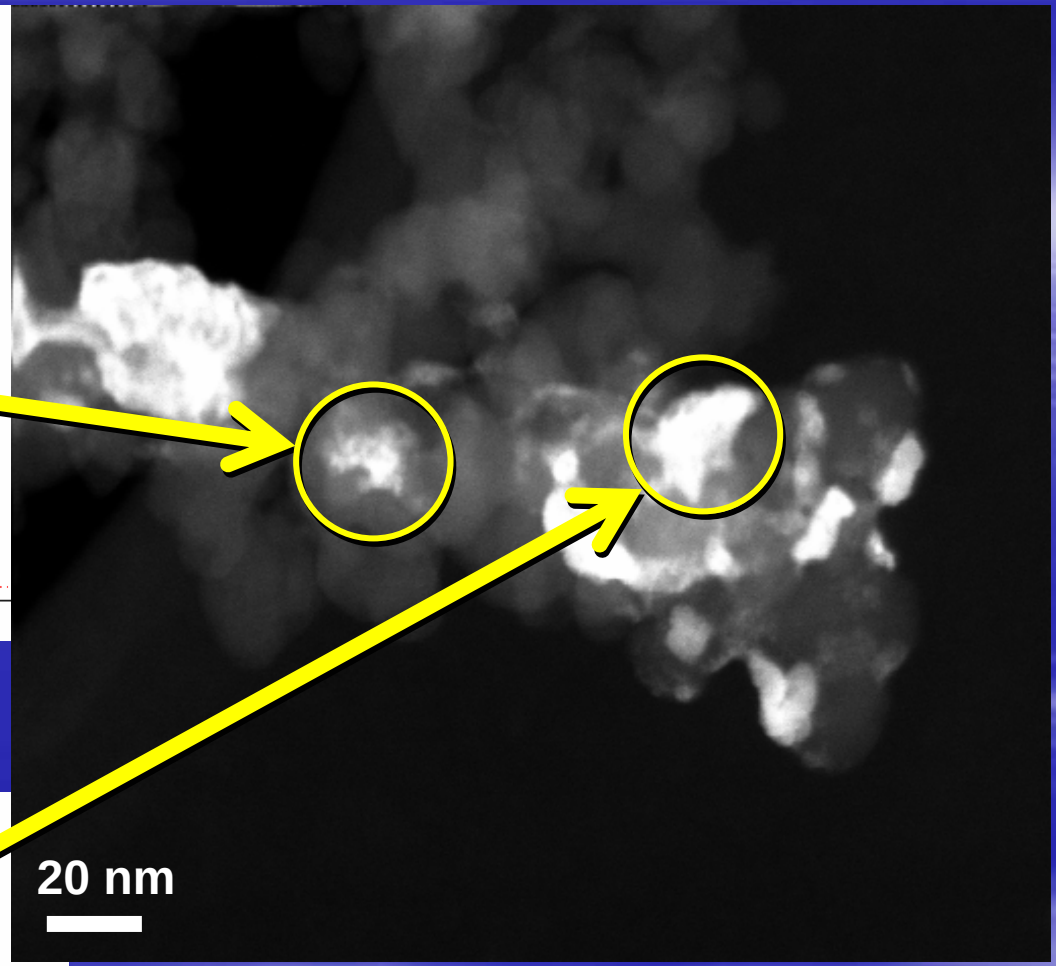


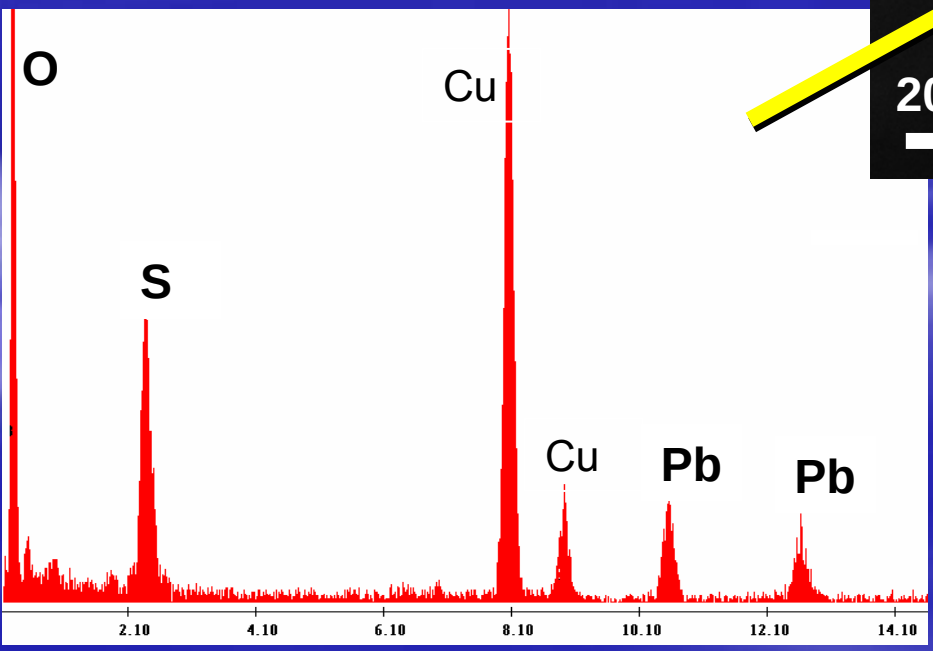
- ✓ Calcium sulfate and UF particles



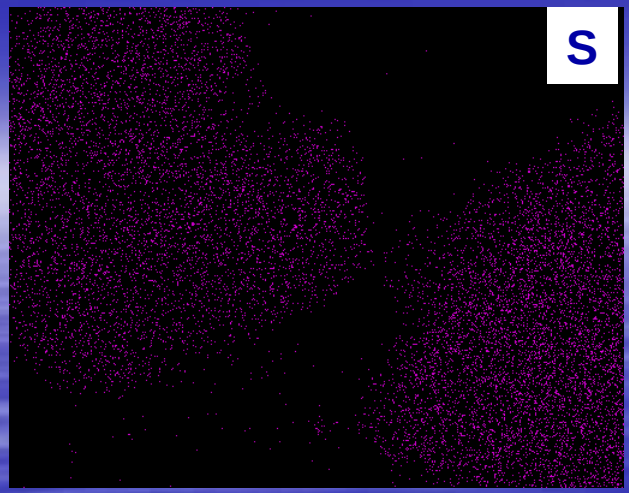


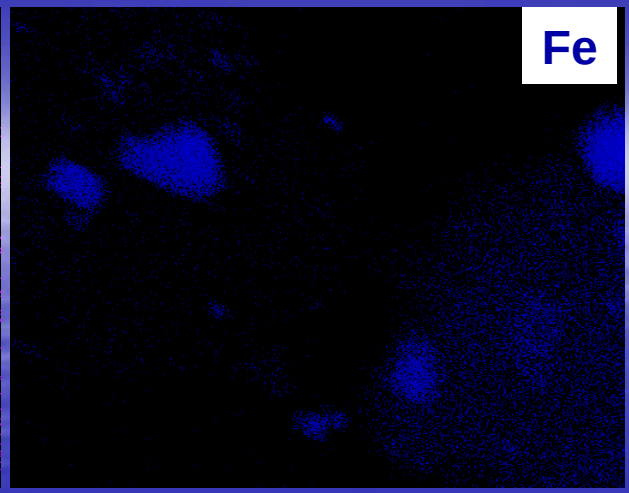


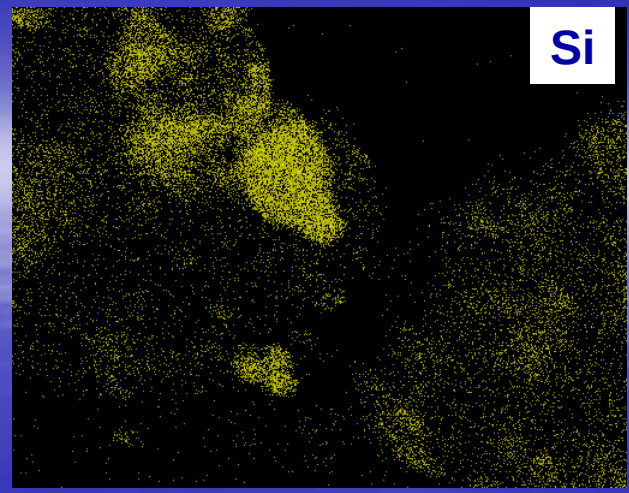




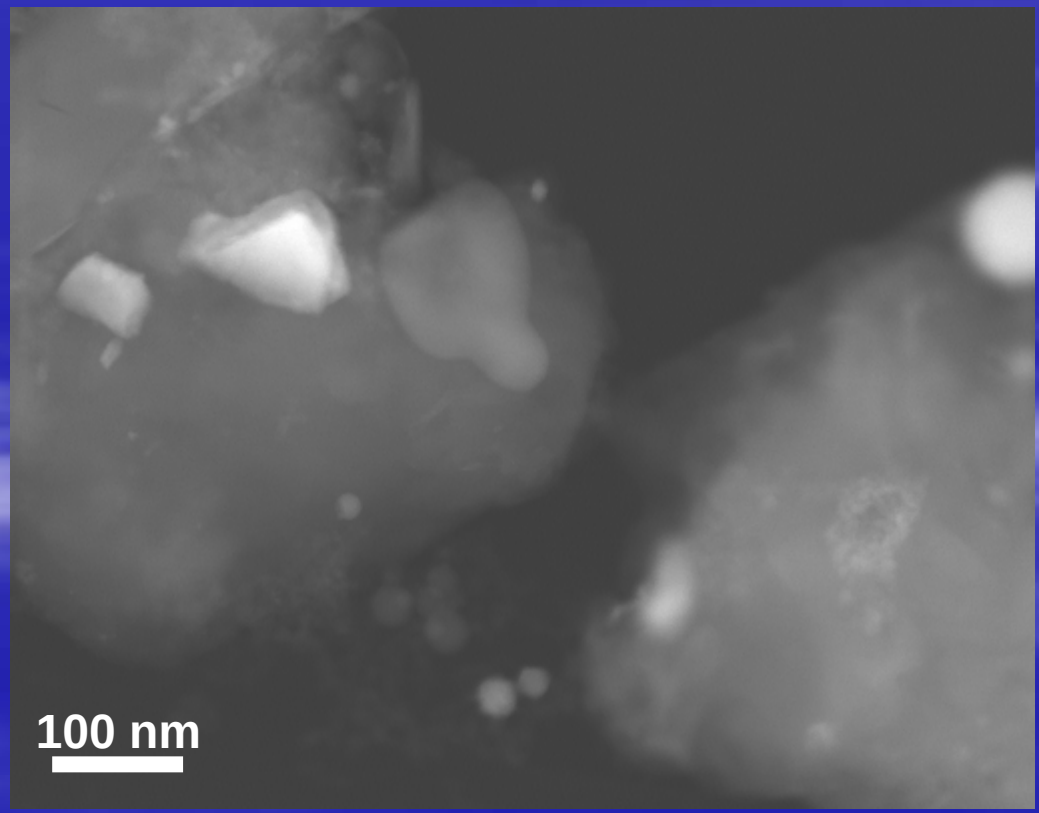
- ✓ S-rich Pb, Zn-Sb UF particles
- → motor vehicle/diesel and incinerator signature







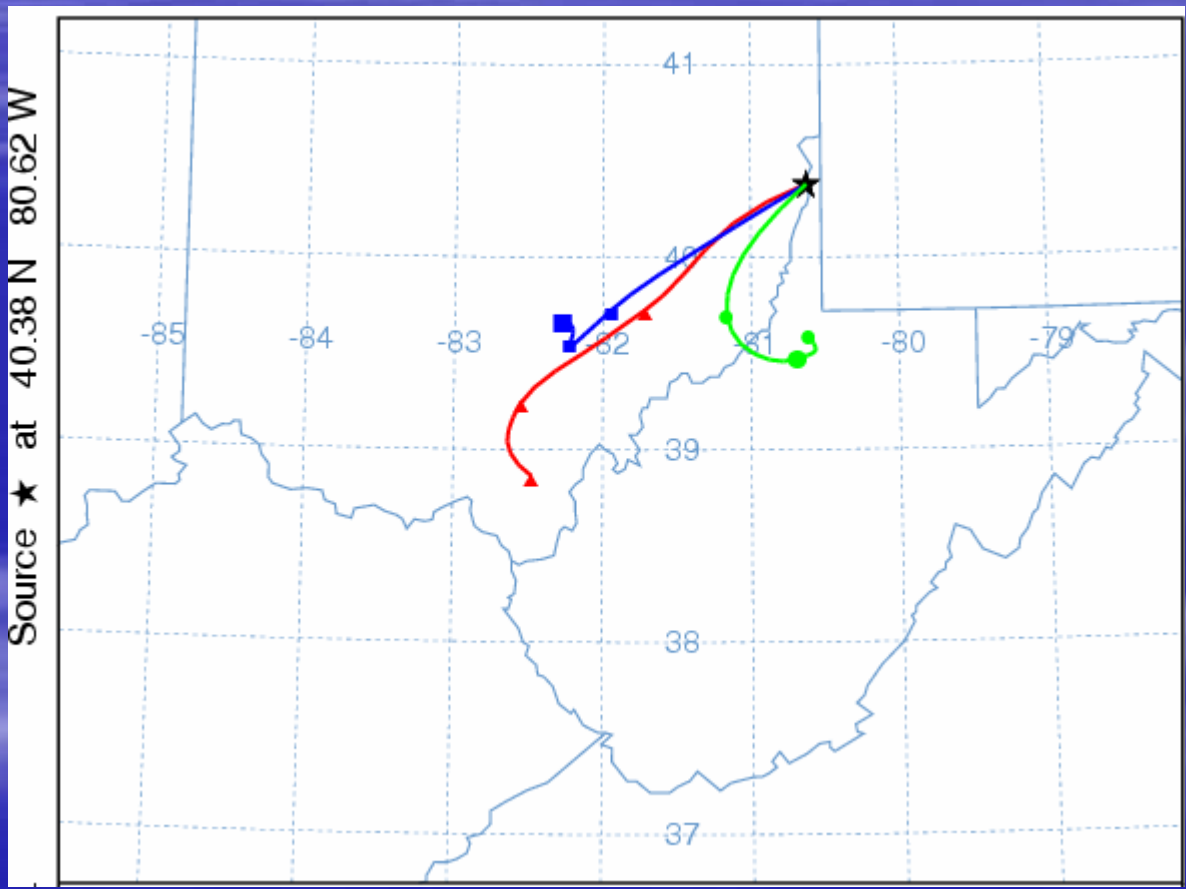
Detroit



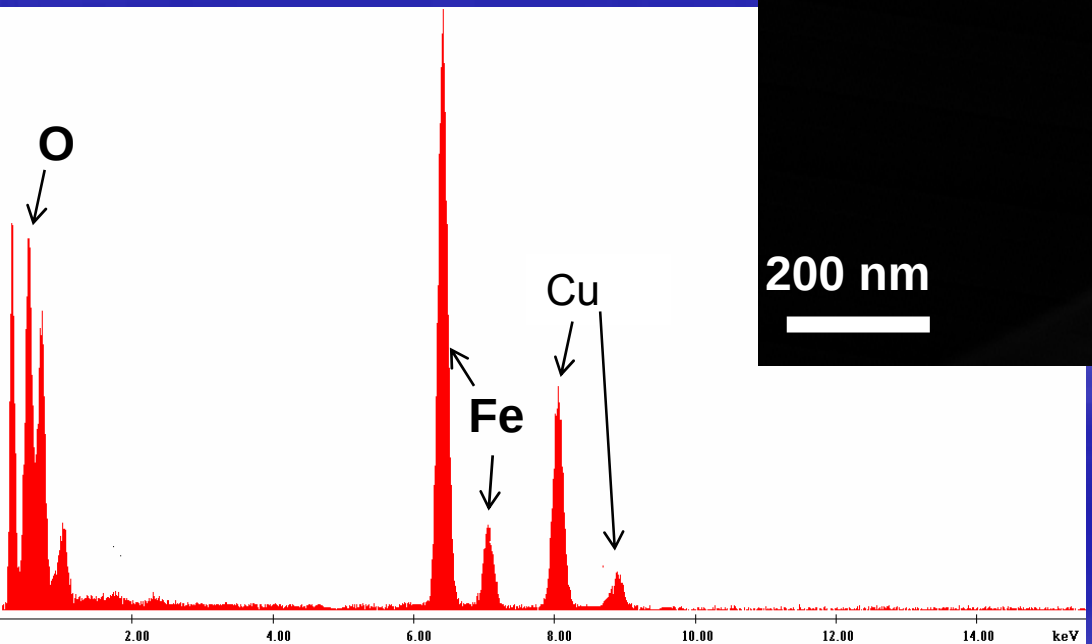
Results

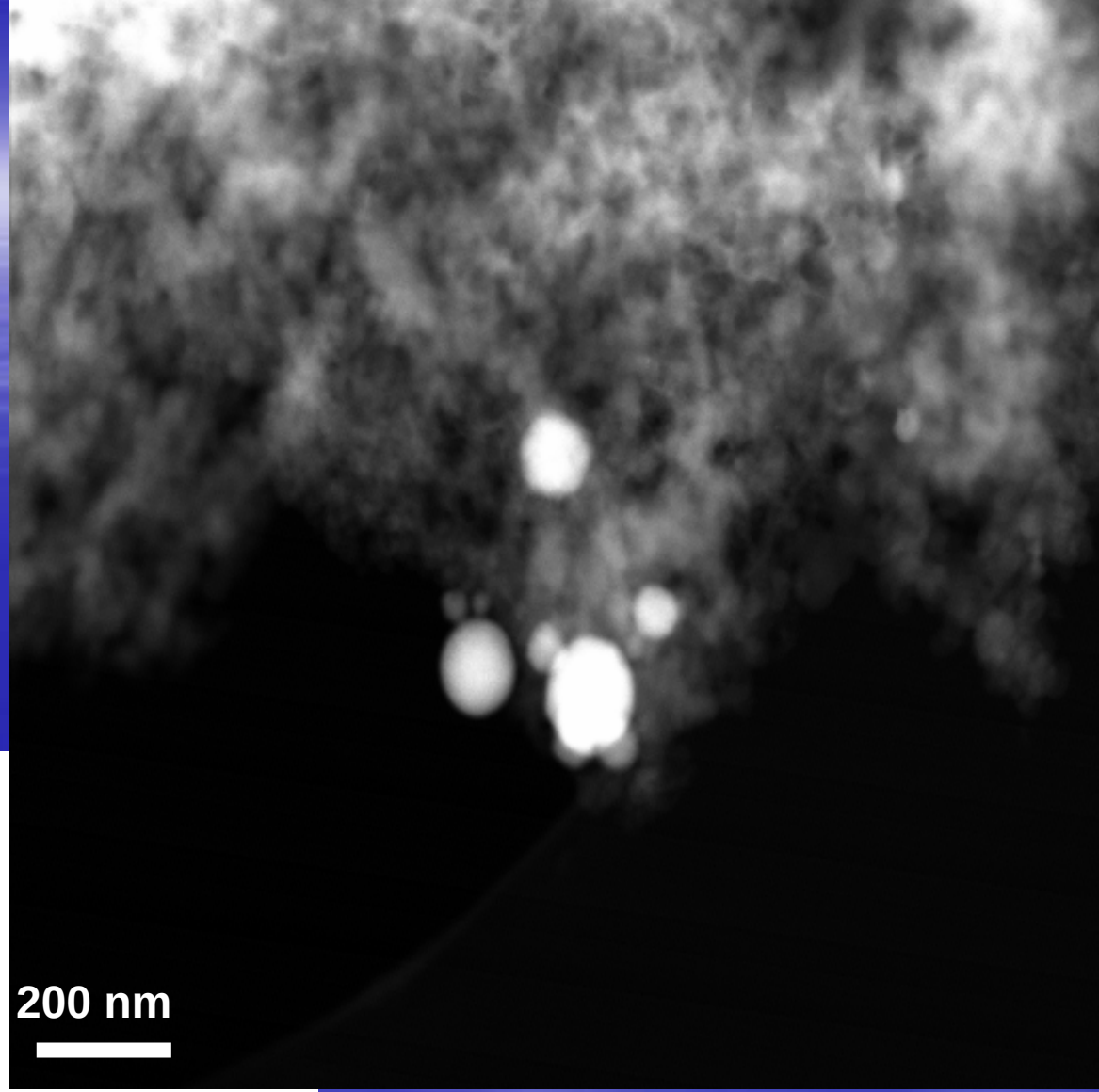
Steubenville

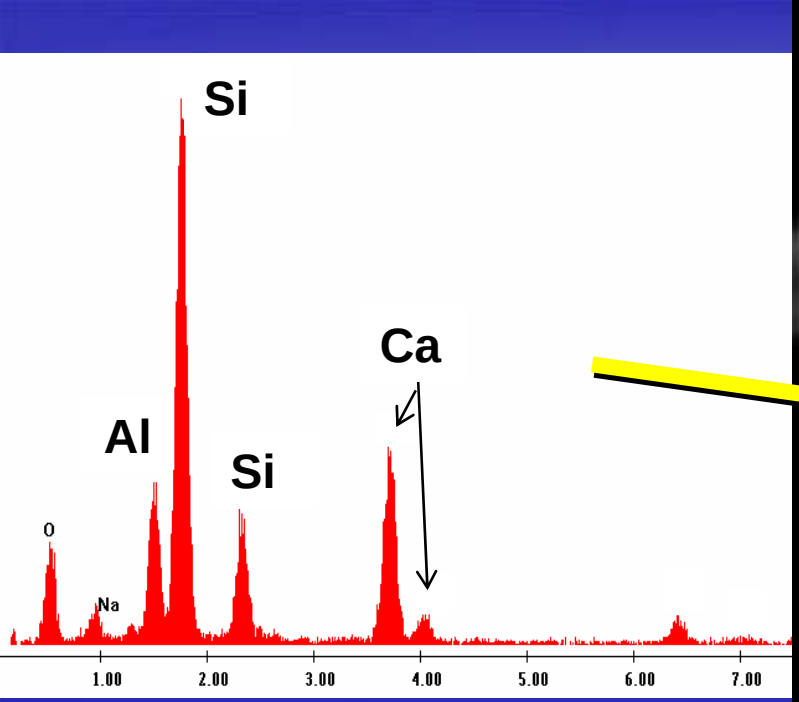
NOAA HYSPLIT MODEL
Backward trajectories
Steubenville site - August 4, 2005

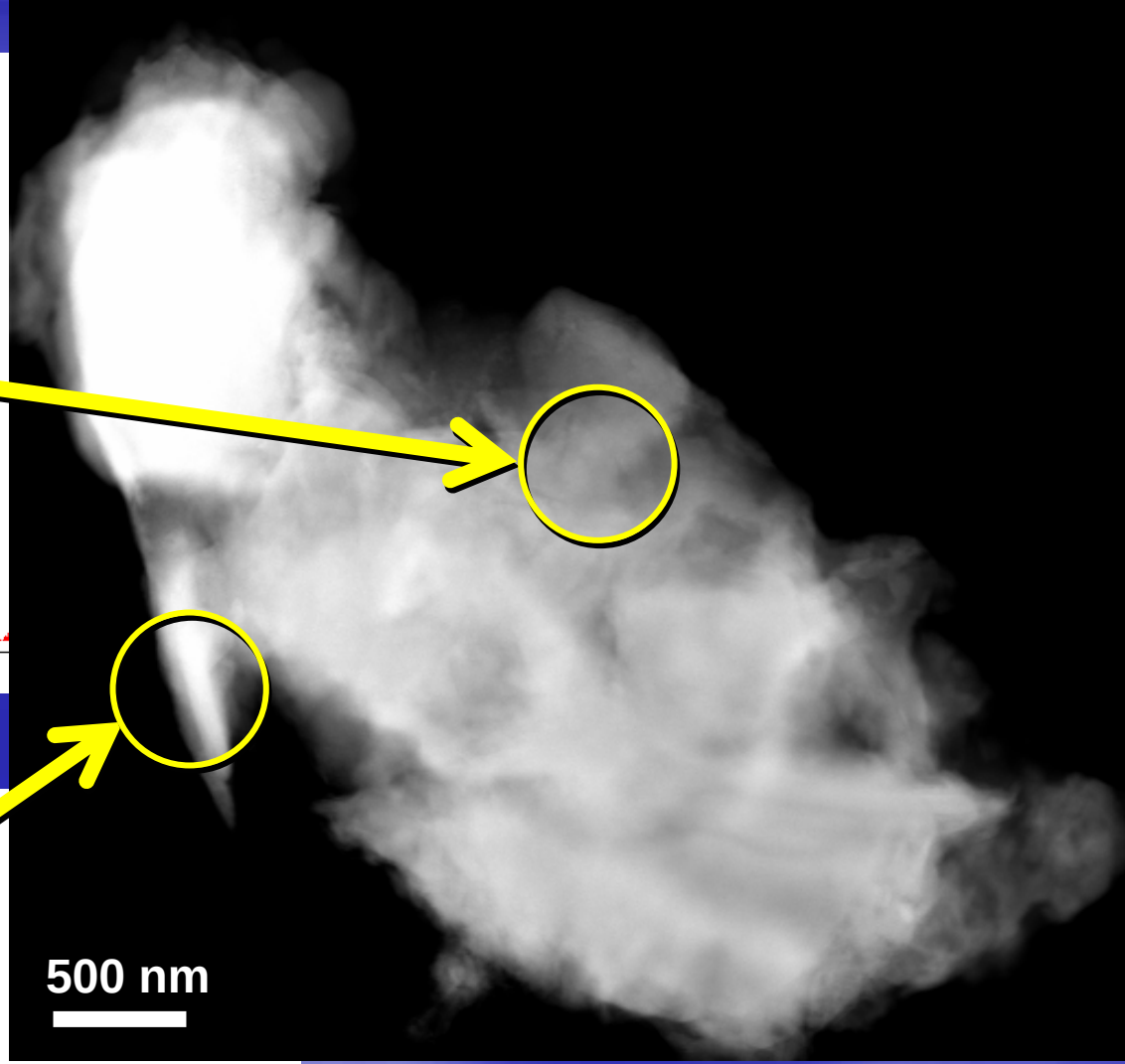


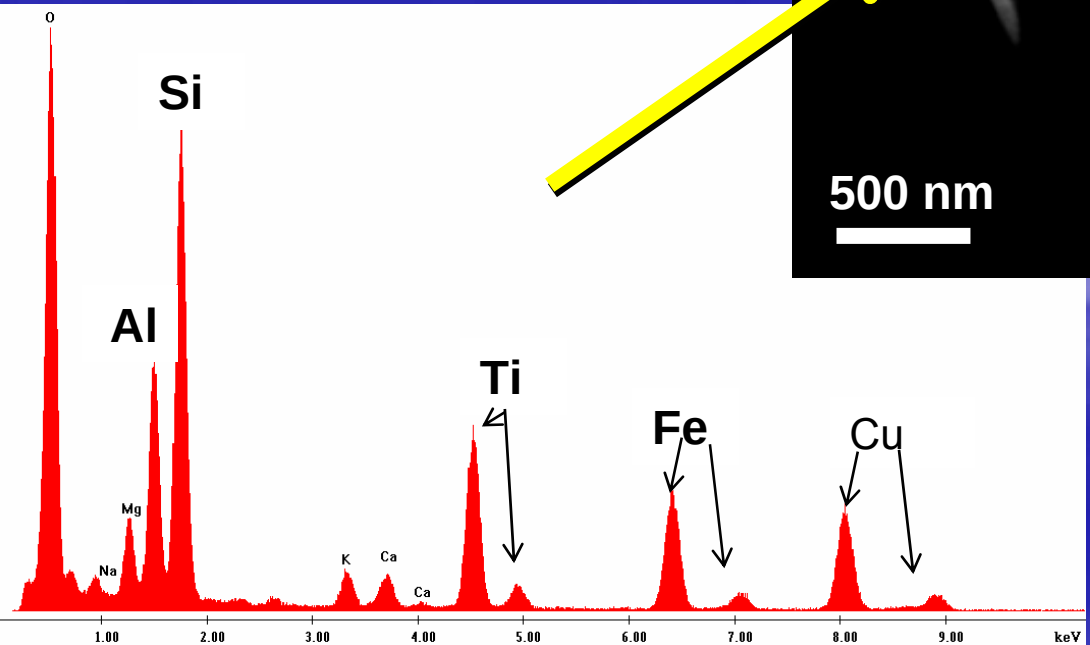
- ✓ Many Iron oxide UF particles and soot



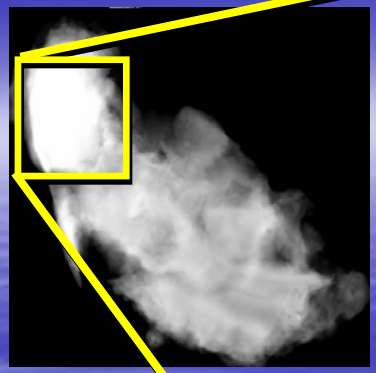


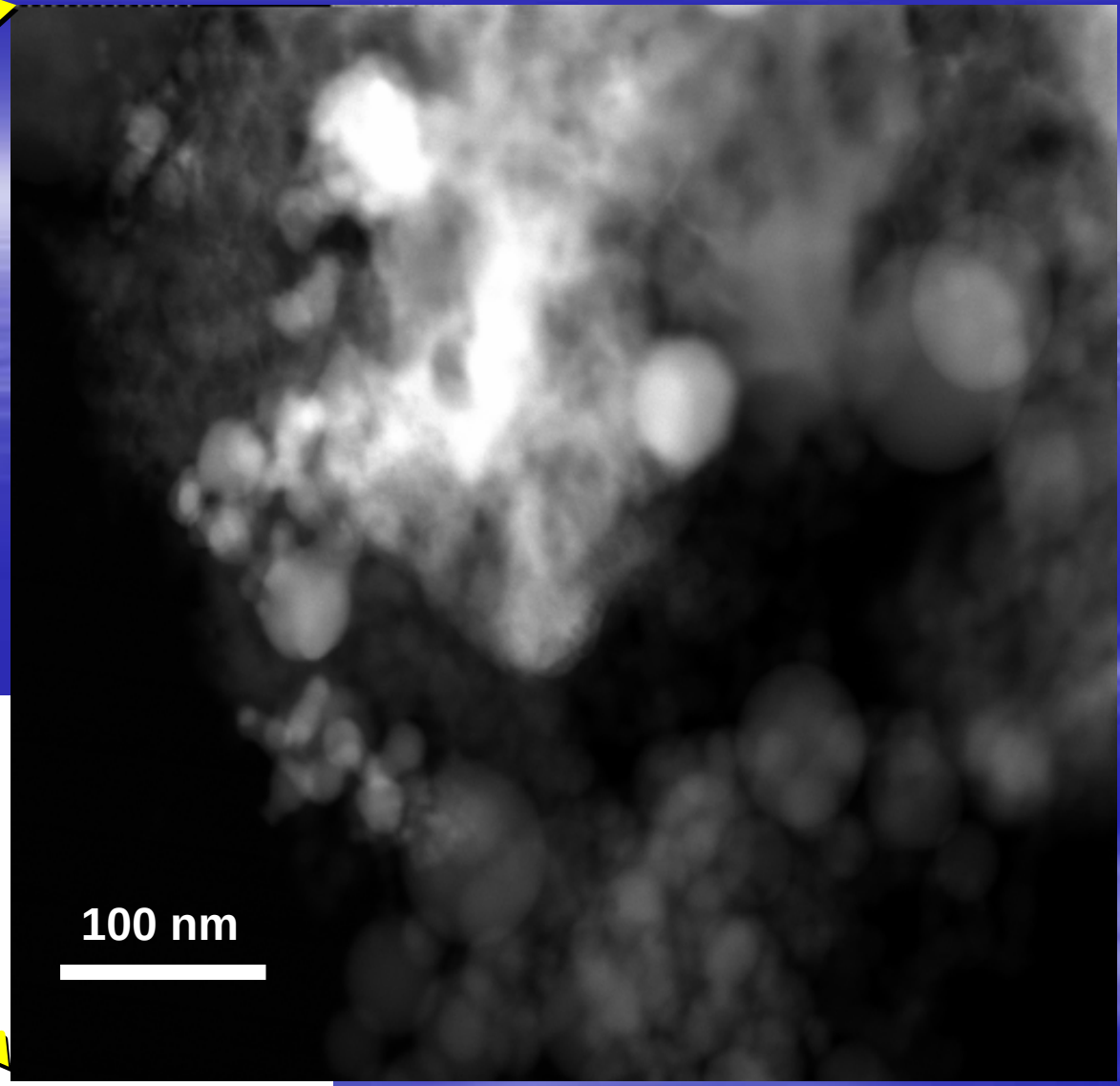


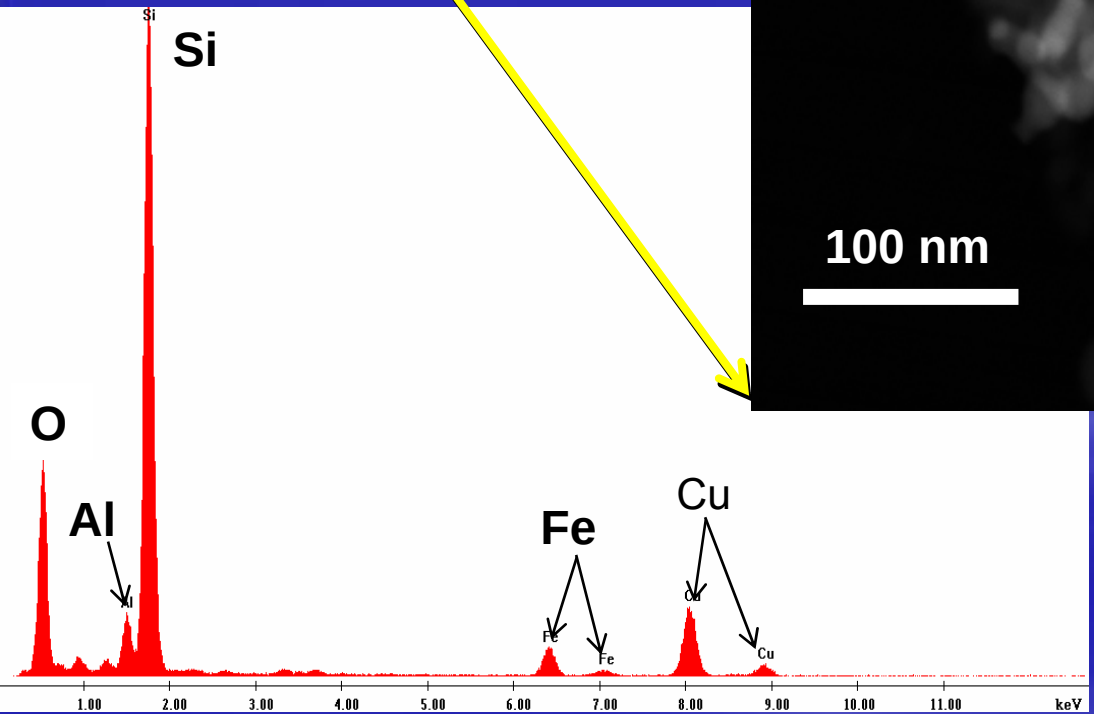




- ✓ Mostly Si-rich-Al-Ca & Si-rich-Al-Ti-Fe composition

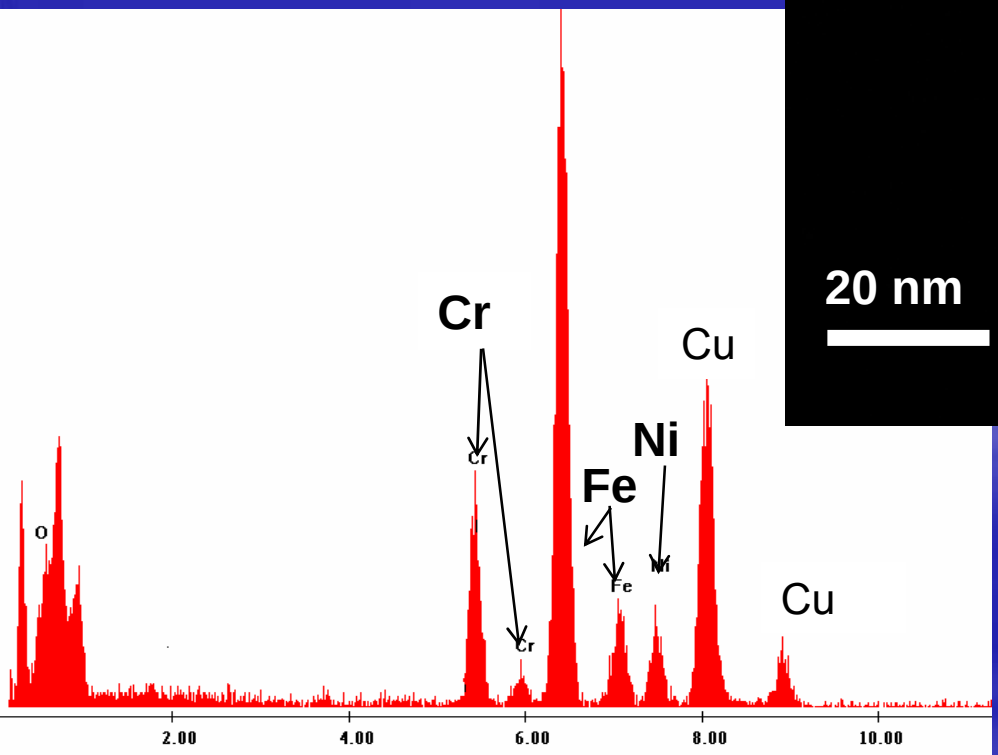


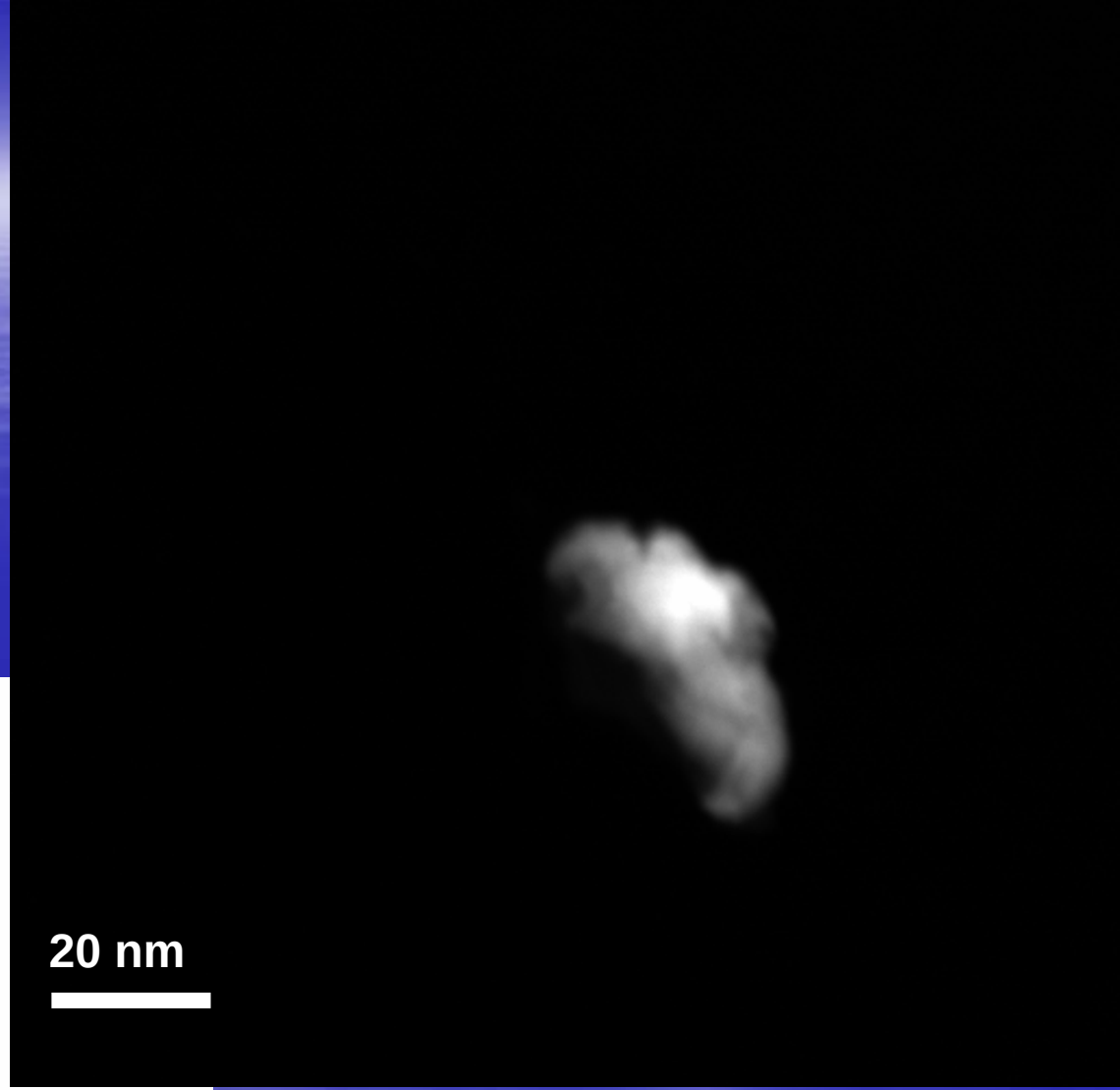


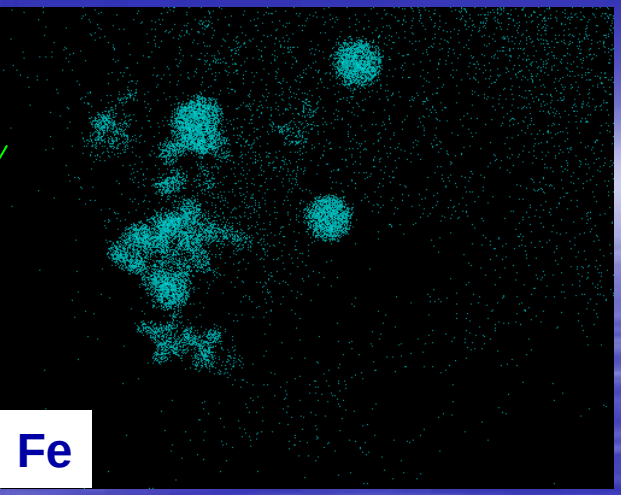


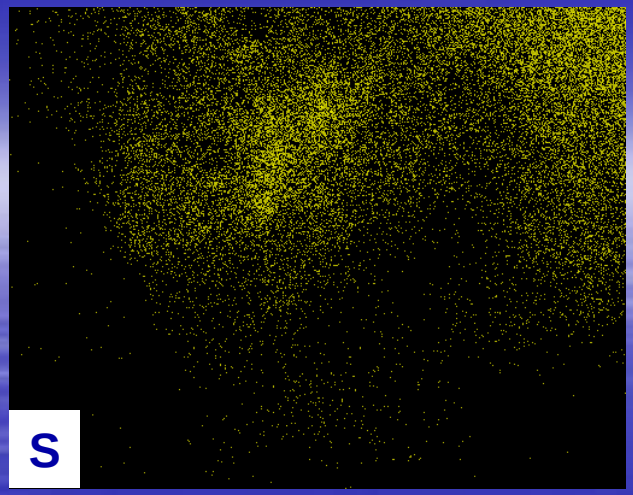
- ✓ Mostly Si-rich Al-Fe composition

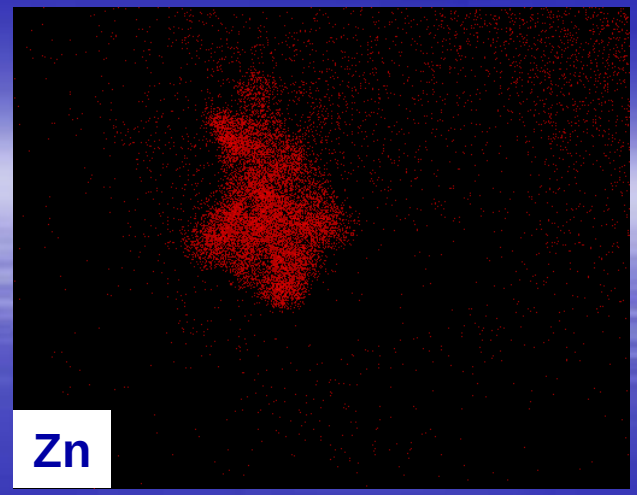
- Ni, Fe and Cr UF particles

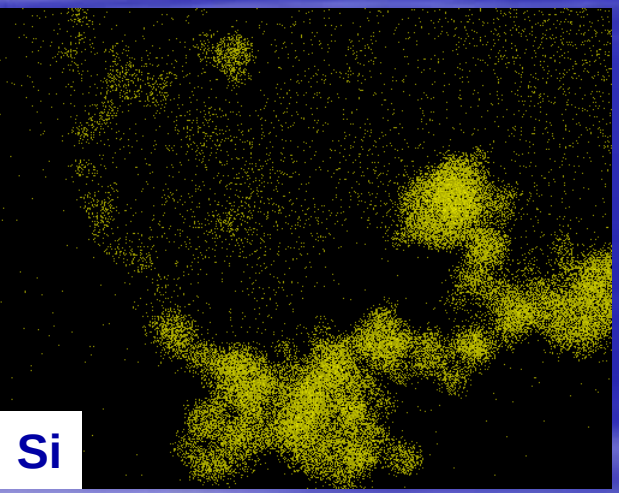


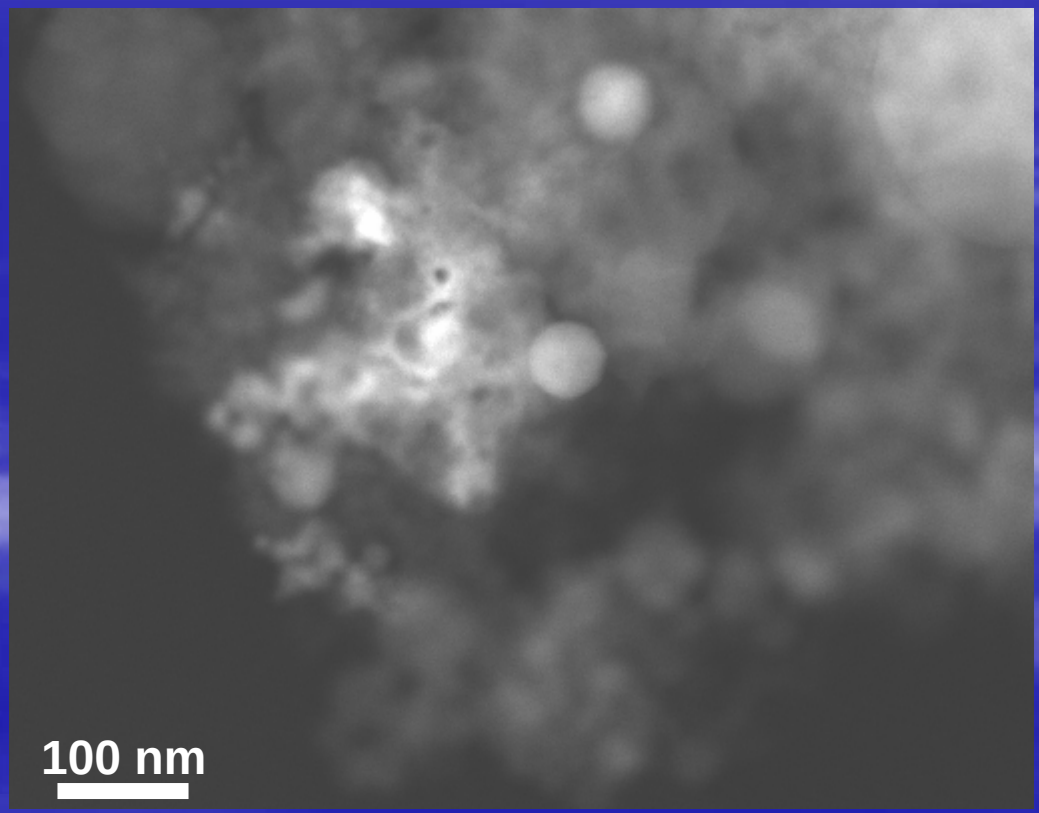




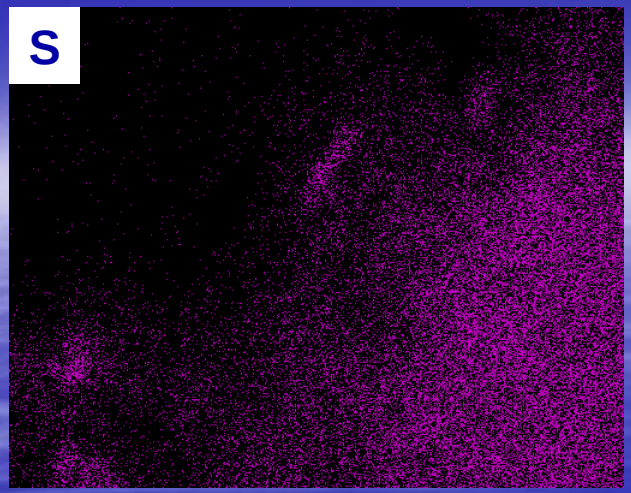


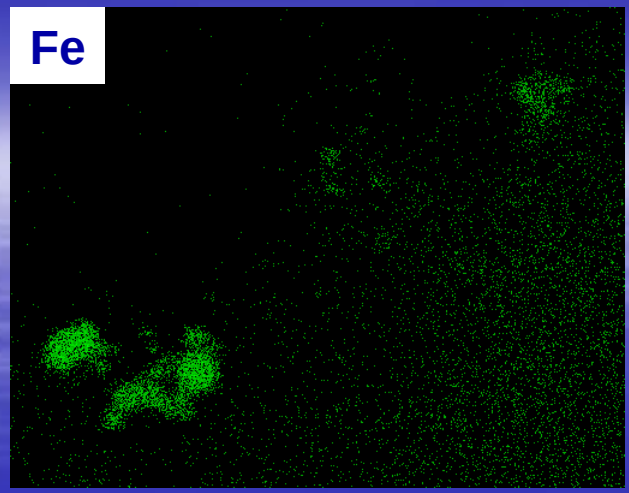


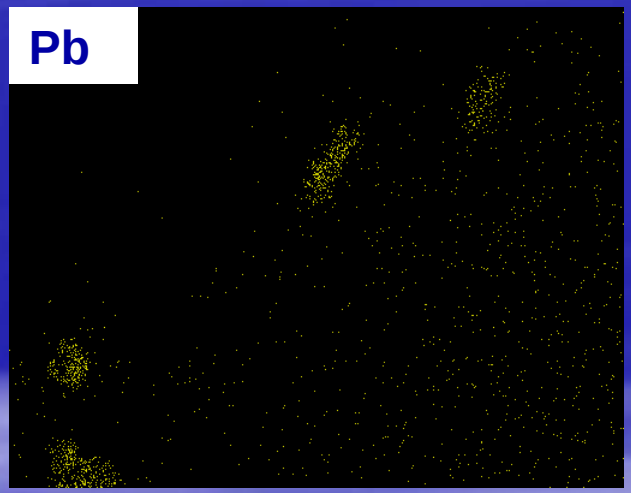


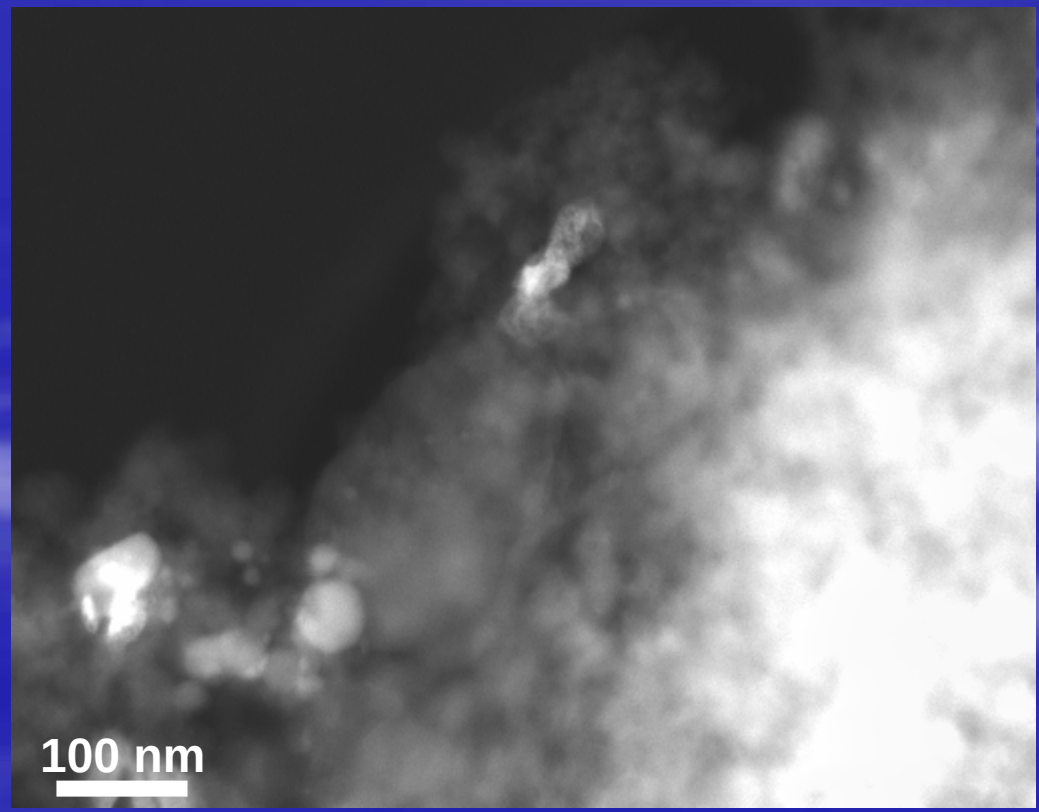


Steubenville









Steubenville

Correlation with Coal Combustion

Sampling Location	Elements found during this study	%	Connection to coal combustion
Detroit	Ca-rich	<5	Chen et al., 2005
	Ti-rich	<15	Chen et al., 2005
	Fe-rich	<20	Chen et al., 2005
	Pb, U	<5	EPA, 1995/Goodarzi, 2006
	Zn, Pb, Mn	<20	Chow, et al., 2004
Steubenville	Si-rich Al-Fe	<20	Chen et al., 2005
	Ti-Si-Al-Fe	<10	Chen et al., 2005
	Ti-Si-Al	<10	Chen et al., 2005
	Fe-rich	<25	Chen et al., 2005
	Pb, Ni, Cr	<5	EPA, 1995/Goodarzi, 2006
	Zn, Pb, Mn	<5	Chow, et al., 2004

Summary

- A combination of advanced electron microscopy techniques can be used to identify ambient $PM_{2.5}$ generated from coal-fired utilities at specific monitoring sites;
- Bulk chemical analysis and meteorological information are helpful in evaluating the impact of coal-fired utilities;
- Higher time-resolved sampling might be helpful to determine the impact of coal-fired utilities.

Support provided by:
Department of Energy,
Environmental Protection Agency, and
Electric Power Research Institute

THANK YOU