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Project # DE-FE0031739

Elucidating Arsenic and Selenium Speciation in Coal Fly Ashes

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EPRI ELECTRIC POWER RESEARCH INSTITUTE

Research background

- Recent EPA CCR and ELG regulations – First federal boundaries on the amount of toxic metals (e.g. Hg, As, Se, Cr) and other pollutants that steam electric power plants are allowed to discharge to their waste streams (e.g. bottom ash, fly ash, FGD purge).

- Addressing compliance with these regulations can present a significant financial and environmental burden to the coal industry.

Toxic metals: total content vs speciation

Speciation
Chemical state
Physical state

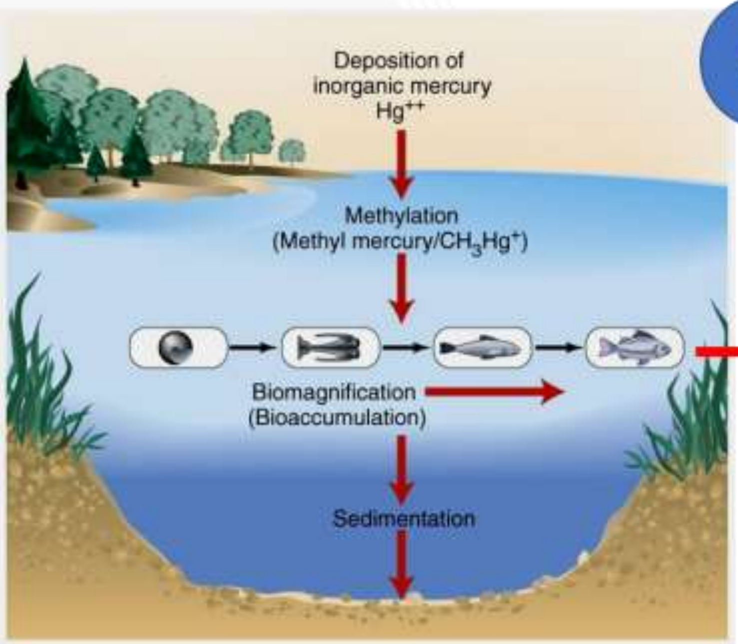
→

Mobility
Bioavailability
Toxicity

→

Fate
Transport
Remediation

Hg



Cr

Cr(III)
- Relatively insoluble
- Low mobility
- Low bioavailability
- Essential micronutrient

Cr(VI)
- Highly soluble
- High mobility
- High bioavailability
- Toxic and carcinogenic

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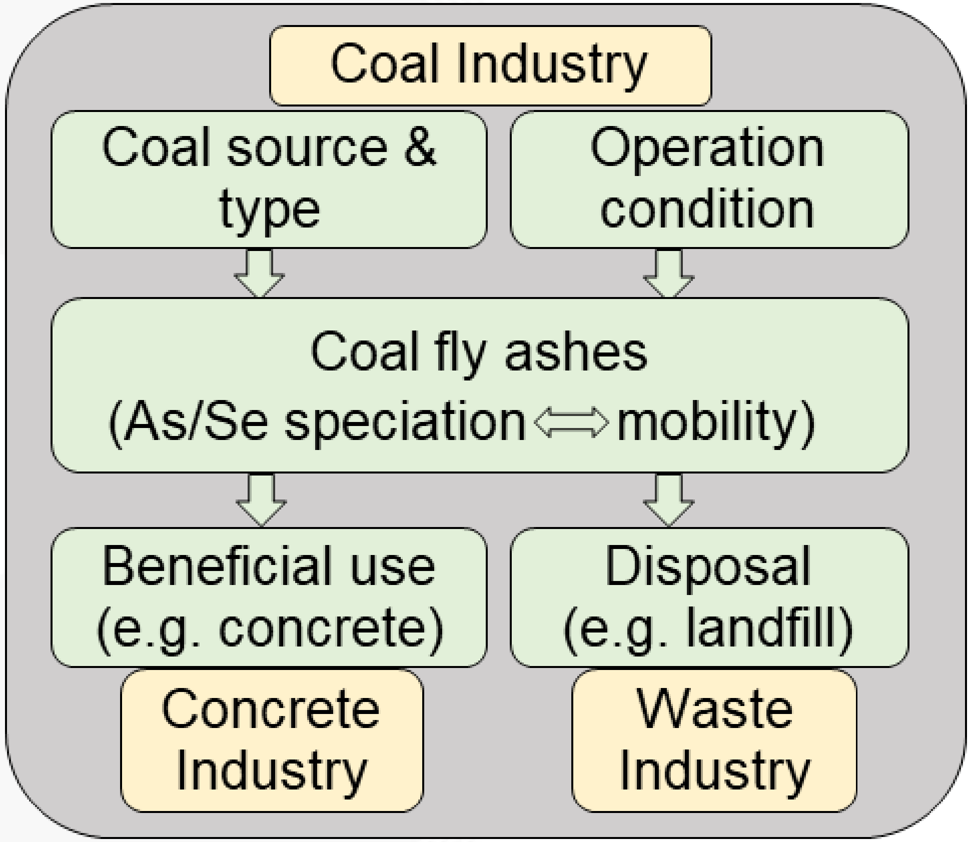
Challenges



- What is the speciation of As and Se in coal fly ashes? — **Characterization**
- How do coal source/type and utility operation conditions affect As/Se speciation? — **Survey**
- How do As/Se speciation affect their subsequent mobility? — **Mobility**

Project goals

- To systematically characterize As and Se speciation within a representative matrix of coal fly ashes.

- To develop correlations for coal source/type, generation condition, As/Se speciation, and As/Se mobility.

Current techniques and proposed solution

Method	Method Type	Risk of Speciation Alteration	Detection Limit	Spatial Resolution	Chemical Speciation		Matrix Effect
					Oxidation State	Mineralogy / Phase	
Digestion, HPLC, ICP-MS	Chemical	High, ex situ	ppm	Bulk	Yes	No	High
Sequential extraction, ICP-MS	Chemical	High, ex situ	ppm	Bulk	No	Yes, empirical	High
LA-ICP-MS	Physical, chemical	No to low, ex situ	ppb	Micron to submicron	No	Based on composition	Mid
SEM-EDS	Physical	No to low, in situ	100s ppm	Micron	No	Based on composition	Mid
Bulk XAS	Physical	No, in situ	ppm	Bulk	Yes	Yes	No
μ-XRF/XAS	Physical	No, in situ	ppb–ppm	Micron	Yes	Yes	No

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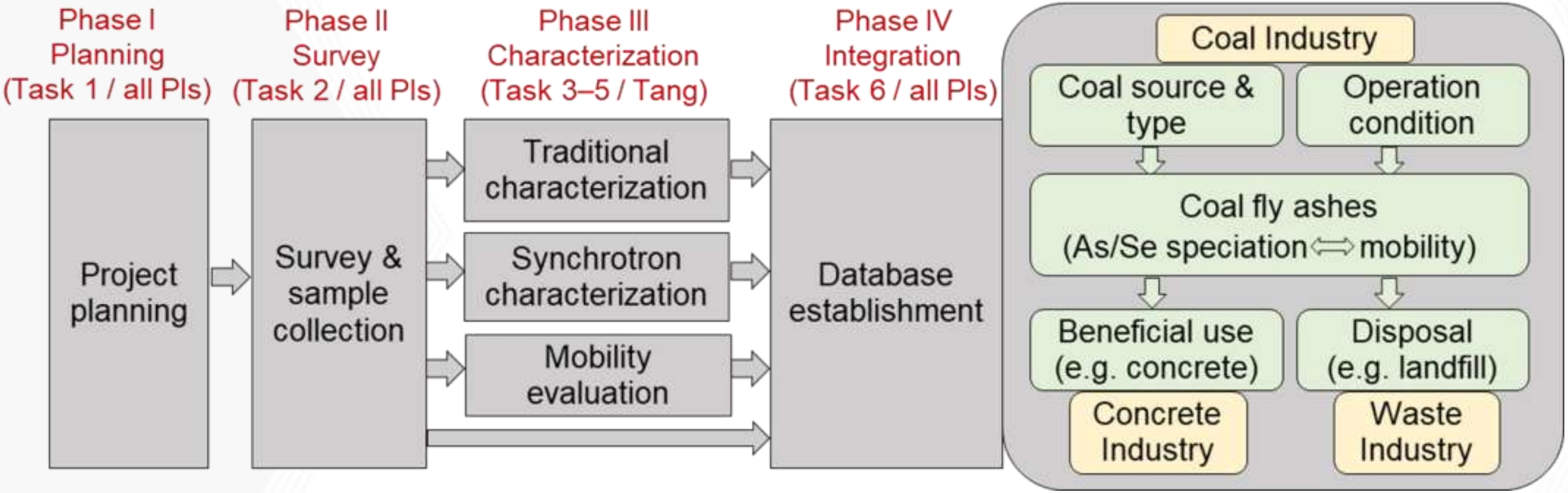
Survey study and sample collection

- A survey of fossil power generating units as a function of coal source/type, operating conditions, environmental control systems, additive use, and fly ash handling methods
- Representative subset of candidate units to collect fly ash samples from existing particulate control devices

Multi-scale characterization of As and Se speciation

- Elemental composition: ICP-MS
- Surface area, particle size, and particle morphology: BET, SEM-EDS
- Mineralogy: XRD
- Oxidation state, structure, elemental association: Synchrotron X-ray microscopy and spectroscopy
- Mobility: EPA Method 1311 (Toxicity Characteristic Leaching Procedure)
- Mobility and phase: Sequential chemical extraction
  - Acid-soluble phases (e.g. carbonates)
  - Reducible phases (e.g., Fe-Mn oxides)
  - Oxidizable phases (e.g. organic matter and sulfide)
  - Residual phase (e.g. silicates)

Project tasks and timeline



Project updates: Survey of current operating plants

- Determine the current outlook of Coal-Fired EGUs generating fly ash across the U.S. and classify according to:
  - Coal source
  - Capacity
  - Installed emission controls: particulate matter, NOx, SOx, Hg

- Compilation and cross-check of various databases
  - Review of EPRI internal databases (as of Dec. 2019)
  - EPA Public Databases (as of Dec. 2018)
  - S&P Global Electrical Generating Units (as of Dec. 2019)

Major coal regions in the U.S.

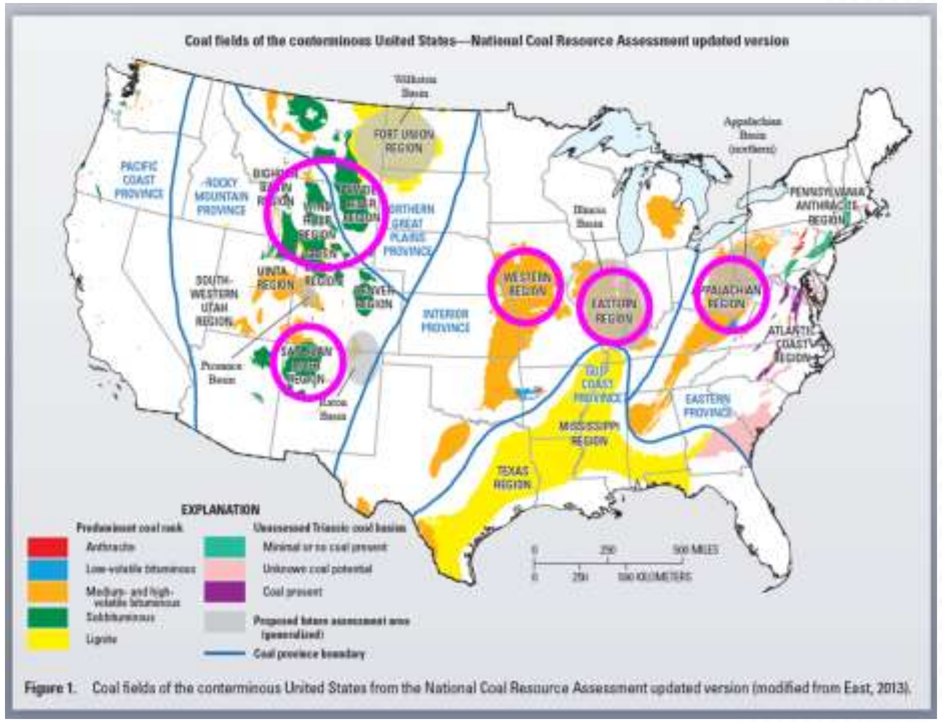


Figure 1. Coal fields of the conterminous United States from the National Coal Resource Assessment updated version (modified from East, 2013).

Source: USGS Fact Sheet 2017-3067

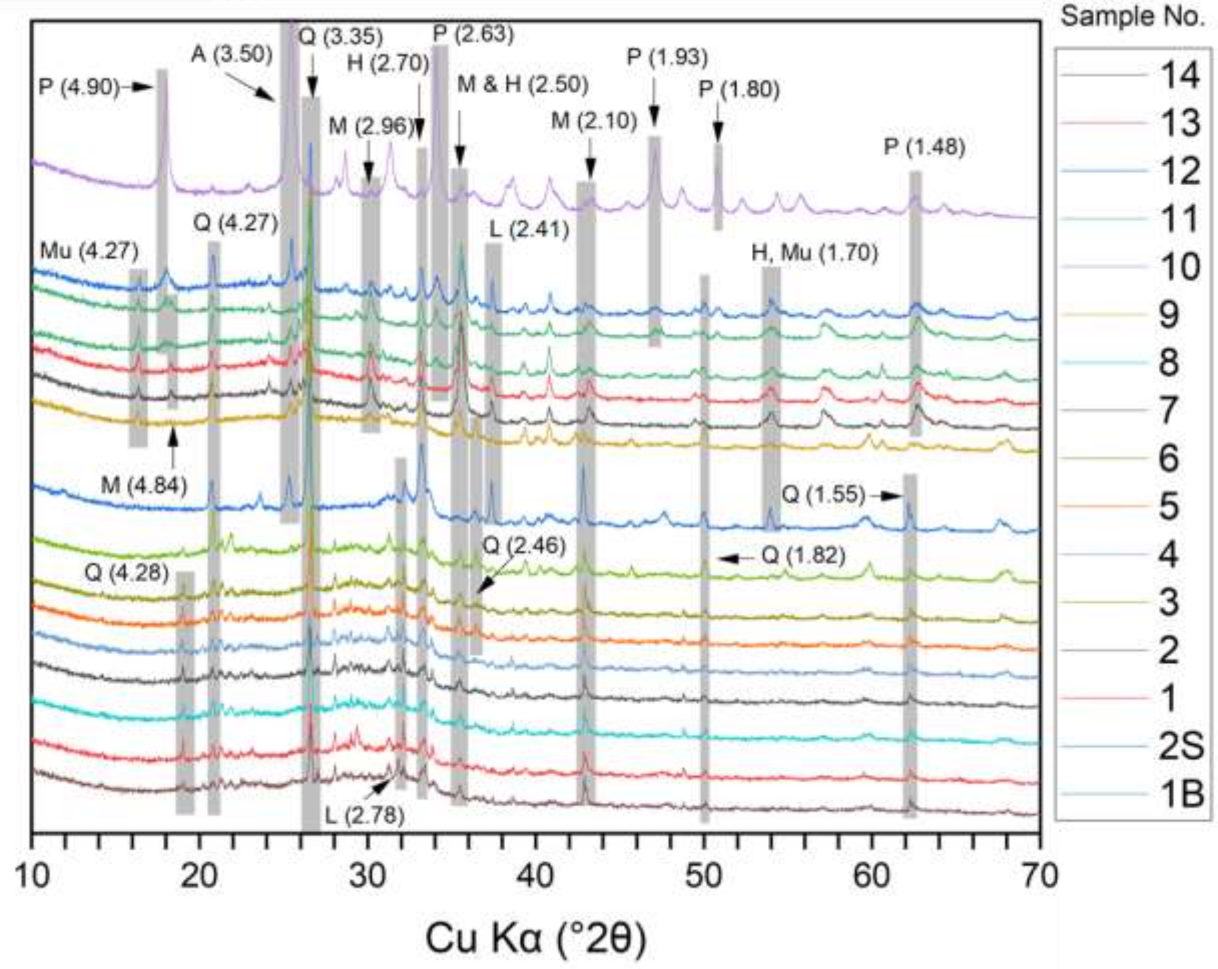
Capacity	Focus on EGUs >90MWg nameplate capacity. Units retired as of Dec 2019 were removed
Furnace burner design	atmospheric circulating fluidized bed, cyclone or slagging boiler, front-wall fired boiler, opposed-wall fired boiler, turbo-fired opposed boiler, tangential or corner fired boiler
Fuels	bituminous coal, subbituminous coal, lignite, blend of coals
NOx controls	selective catalytic reduction, selective non-catalytic reduction, combustion controls
SOx controls	coal blending / compliance fuel, dry flue gas desulfurization (FGD), wet FGD, Semi-dry FGD
Particulate matter controls	baghouse, electrostatic precipitator (ESP), cold-side ESP, hot-side ESP

Preliminary samples for consideration

Unit A	Bit - ILB	Tang. + SCR + ESPc or BH + WFGD
Unit B	Sub - PRB	Tang. + SCR + BH + WFGD
Units C & D	Sub - PRB	OPP + ESPc
Unit E	Sub-PRB 85% + Bit-MSW 15%	Tang. + ESPc
Unit F	Bit-ILB	Tang. + ESPc + BH + WFGD
Unit G	Bit-ILB	OPP + ESPc + BH + WFGD

Total 16 samples collected

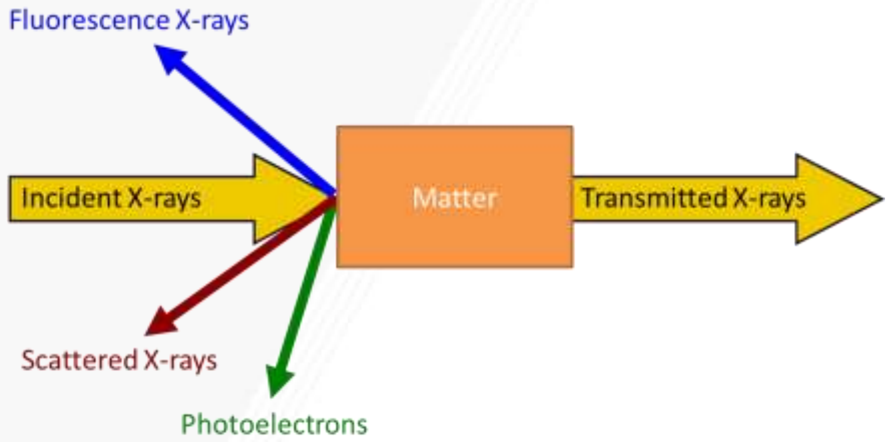
Mineralogical analysis



P: Portlandite $Ca(OH)_2$
A: Anhydrite
Mu: Mullite
M: Magnetite
H: Hematite
Q: Quartz
L: Lime

Speciation analysis by synchrotron techniques

- Bulk X-ray absorption spectroscopy (XAS)
- Micro-X-ray fluorescence microscopy (µ-XRF) and µ-XAS

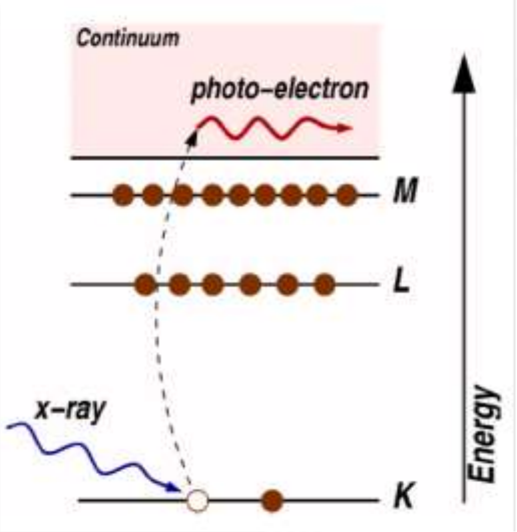


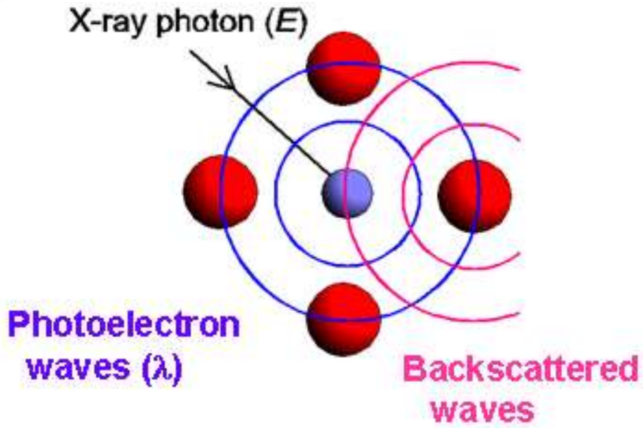
- Non-destructive
- In situ
- Spatially resolved (micron scale)
- High resolution (ppb – ppm)
- Highly desired for complex heterogeneous samples

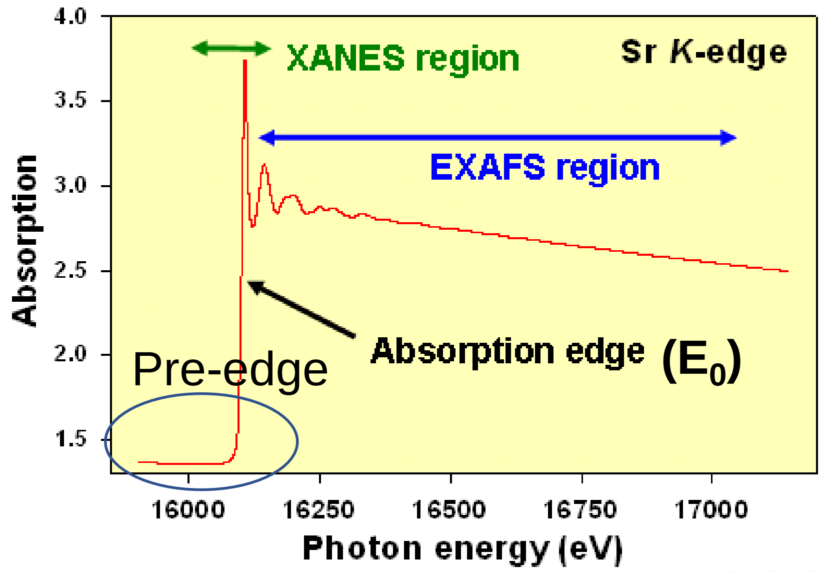
Advanced Photon Source (APS)

X-ray absorption spectroscopy (XAS)

- Scattering of the photo-electron ejected from the absorbing atom
- Element specific
- Probes local structure
  - Oxidation state
  - Identity, distance, and number of neighbor atoms





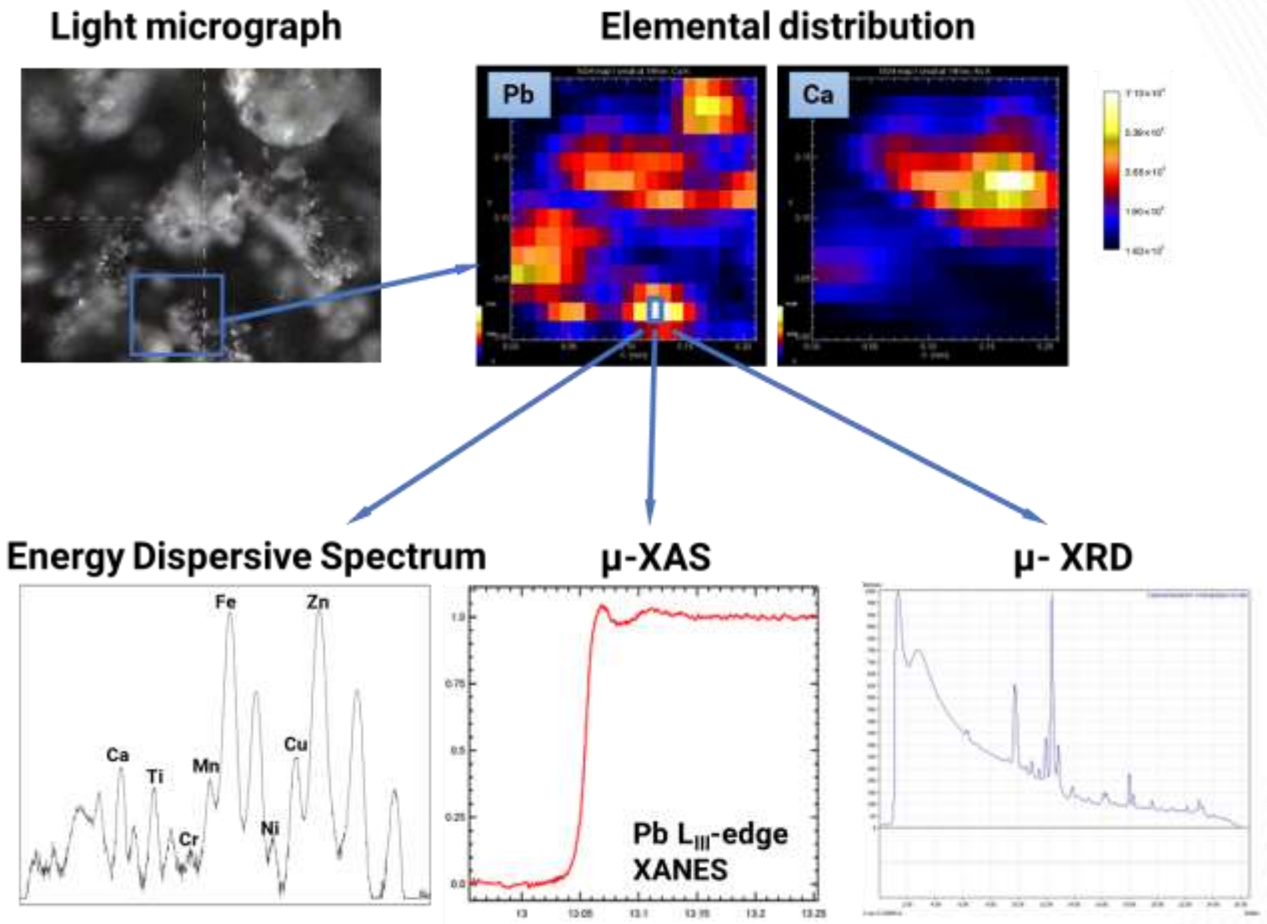


XANES (X-ray absorption near edge structure)

EXAFS (Extended X-ray absorption fine structure)

Micro-X-ray fluorescence microscopy (μ-XRF) and μ-XAS

- μ-XRF: element distribution and correlation
- μ-XANES: micro-scale oxidation state, phase, and structure information
- X-ray beam size: μm to nm
- Suitable for samples with low bulk concentration and heterogeneous distribution



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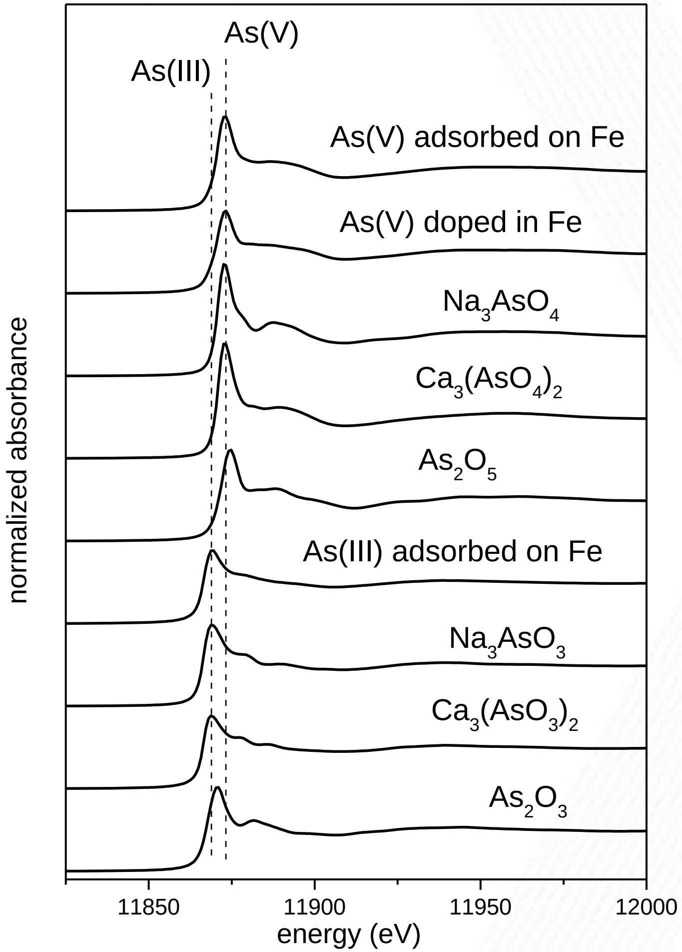
As: bulk XANES

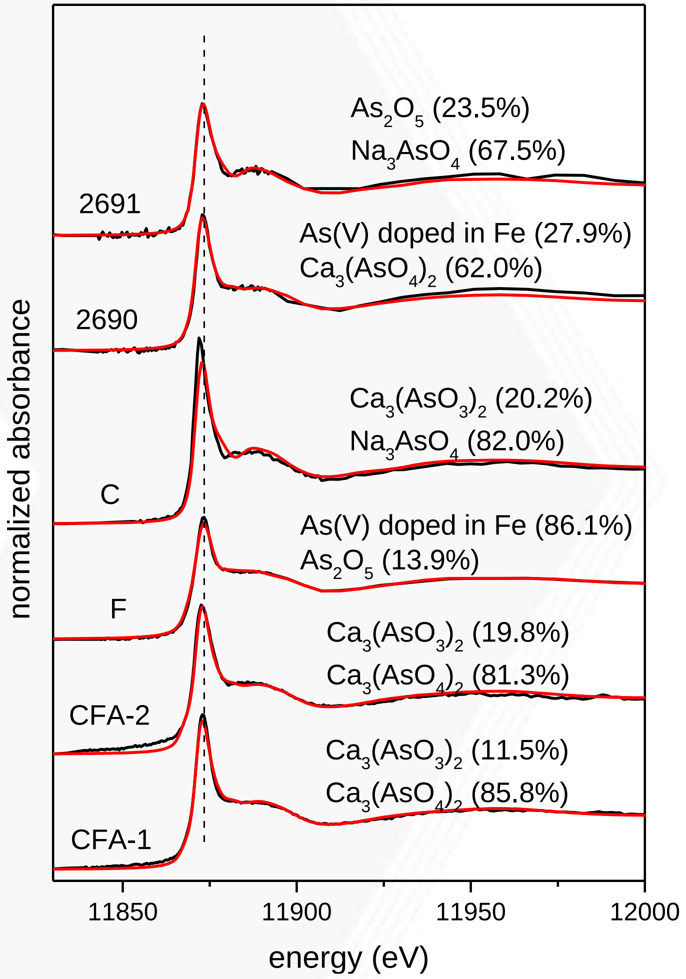
- We have collected bulk XAS data for
  - 9 standard compounds
  - 10 fly ash samples

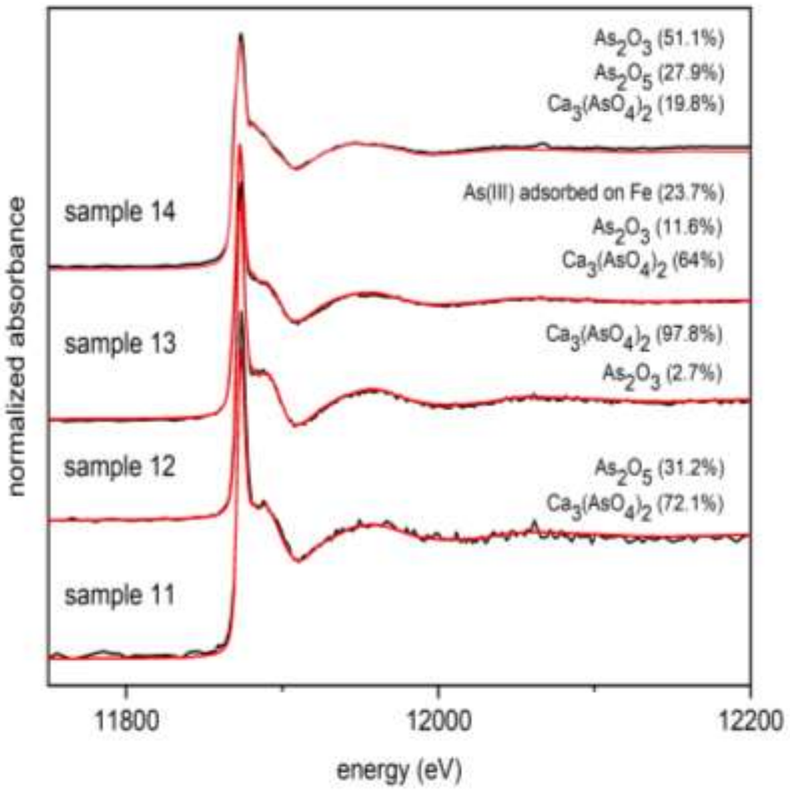
- We have conducted principal component analysis (PCA), target transformation, and linear combination fitting (LCF) to identify the dominant As species and their relative contribution

Standard compounds

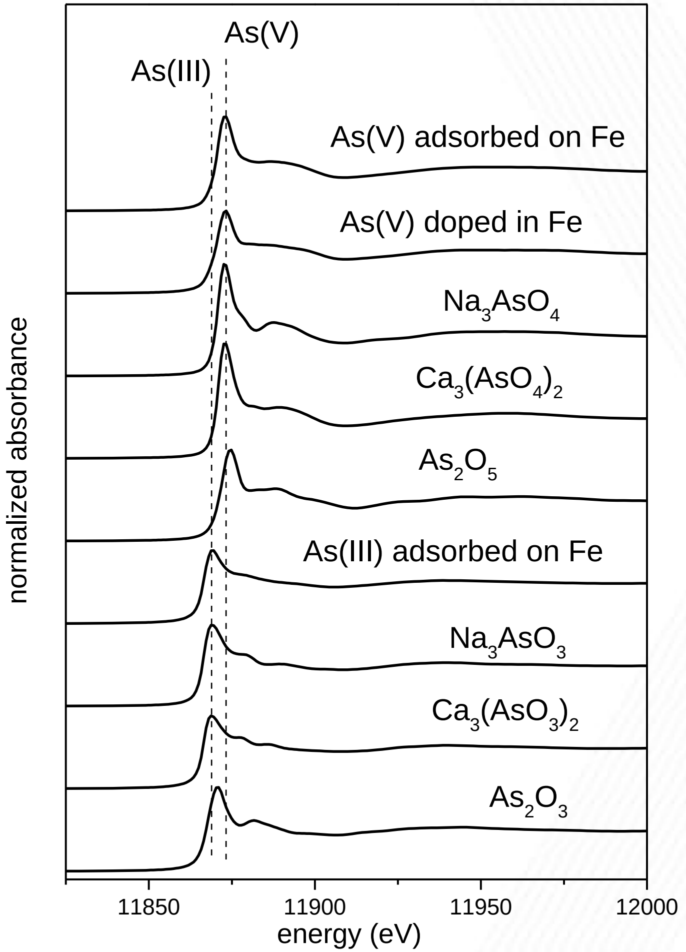


Fly ash samples: Linear combination fitting results



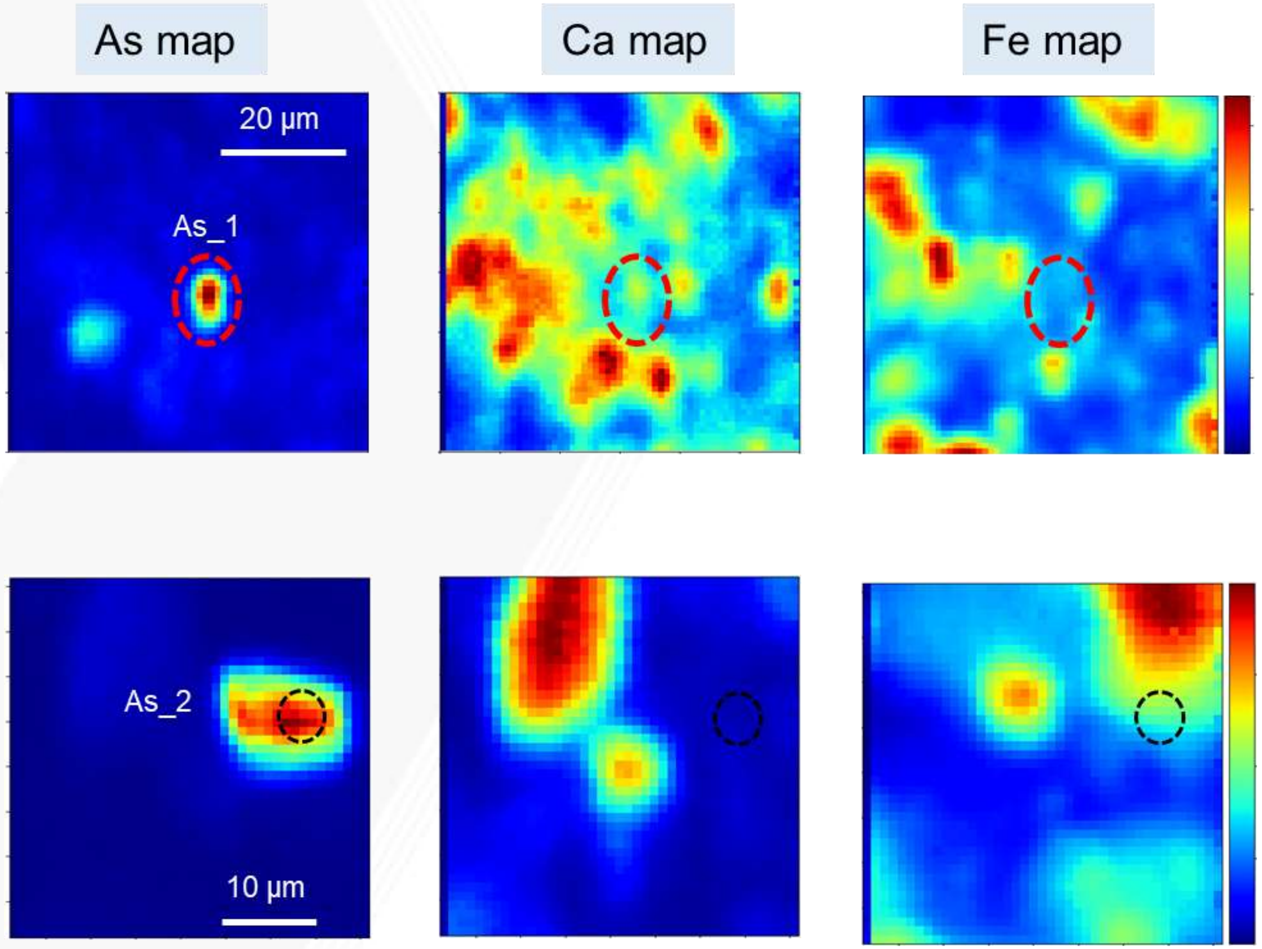


Standard compounds



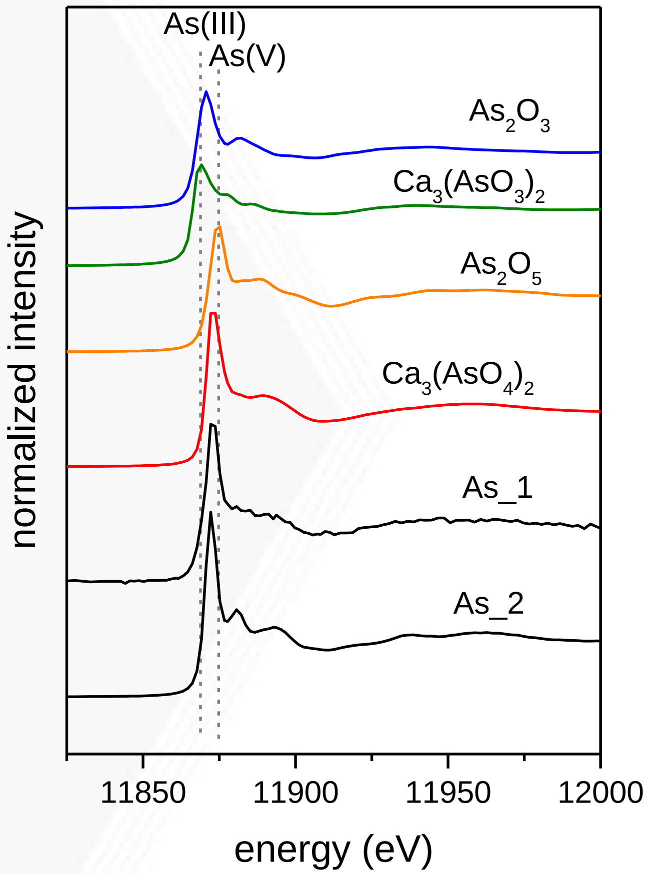
Sample ID	As(III) species (%)			As(V) species (%)			
	As_2O_3	As(III) sorb FeOx	$Ca_3(AsO_3)_2$	As_2O_5	Na_3AsO_4	As(V) doped FeOx	$Ca_3(AsO_4)_2$
2691				23.5	67.5		
2690						27.9	62
C			20.2		82		
F				13.9		86.1	
CFA-2			19.8				81.3
CFA-1			11.3				85.8
14	51.1			27.9			19.8
13	11.6	23.7					64
12	2.7						97.8
11				31.2			72.1

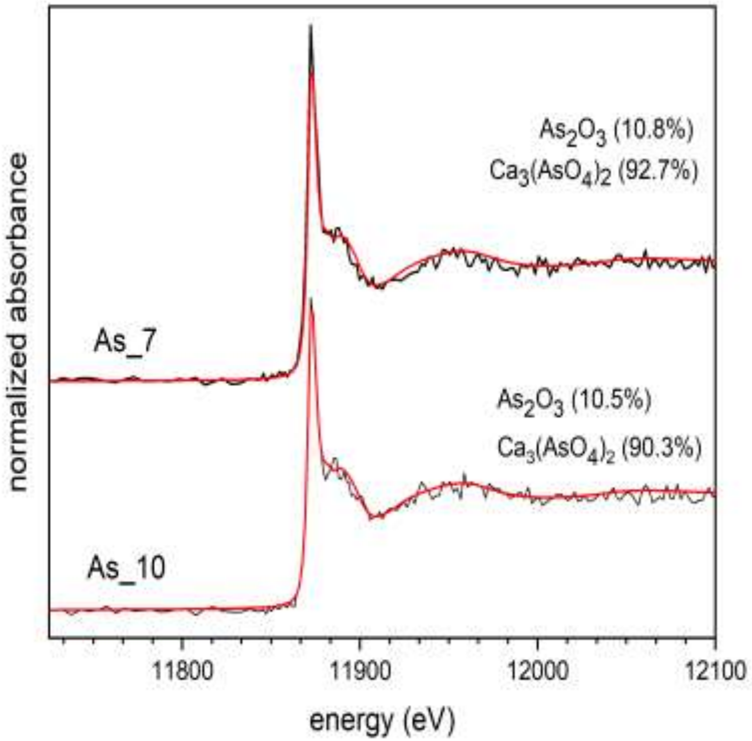
As: XRF and µ-XANES



Particle As_1:
- 10 µm x 5 µm particle
- As co-localized with Ca
- 20% As(III) and 80% As(V)

Particle As_2:
- 10 µm x 10 µm particle
- As co-localized with Fe
- 25% As(III) and 75% As(V)





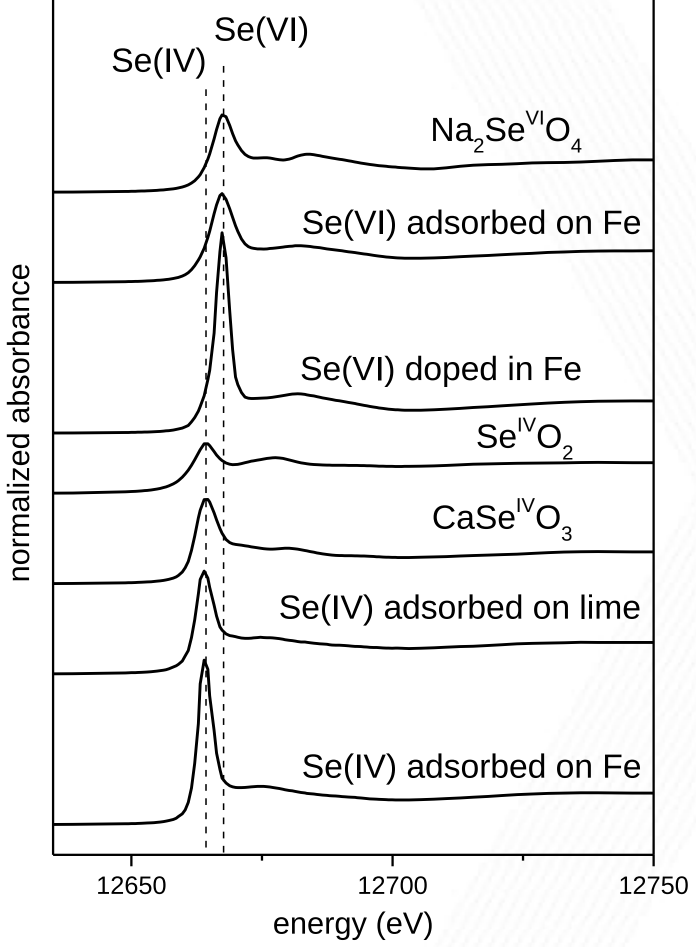
sample CFA-2C

Se: bulk XANES

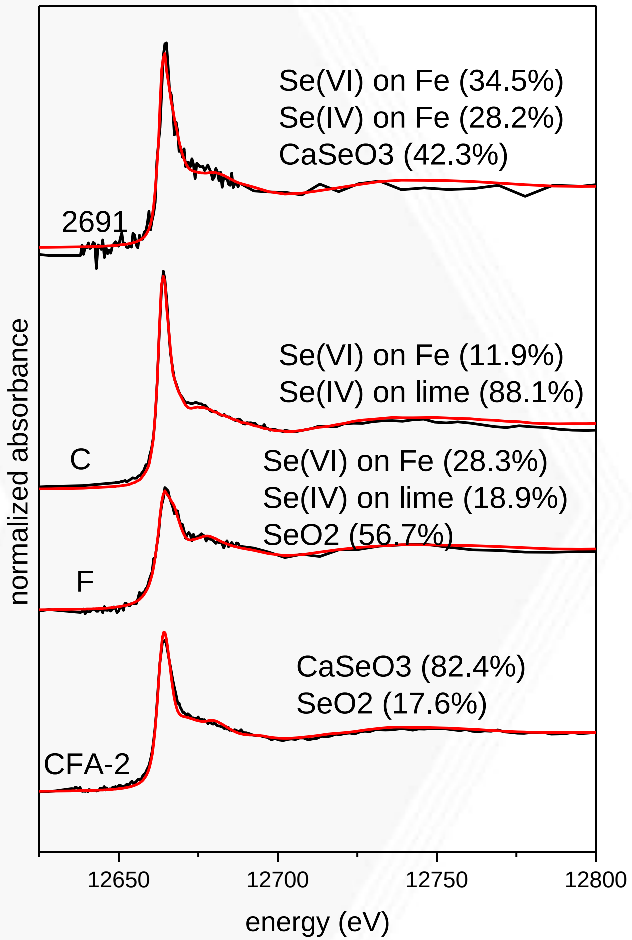
- We have collected bulk XANES data for
  - 7 standard compounds
  - 8 ash samples

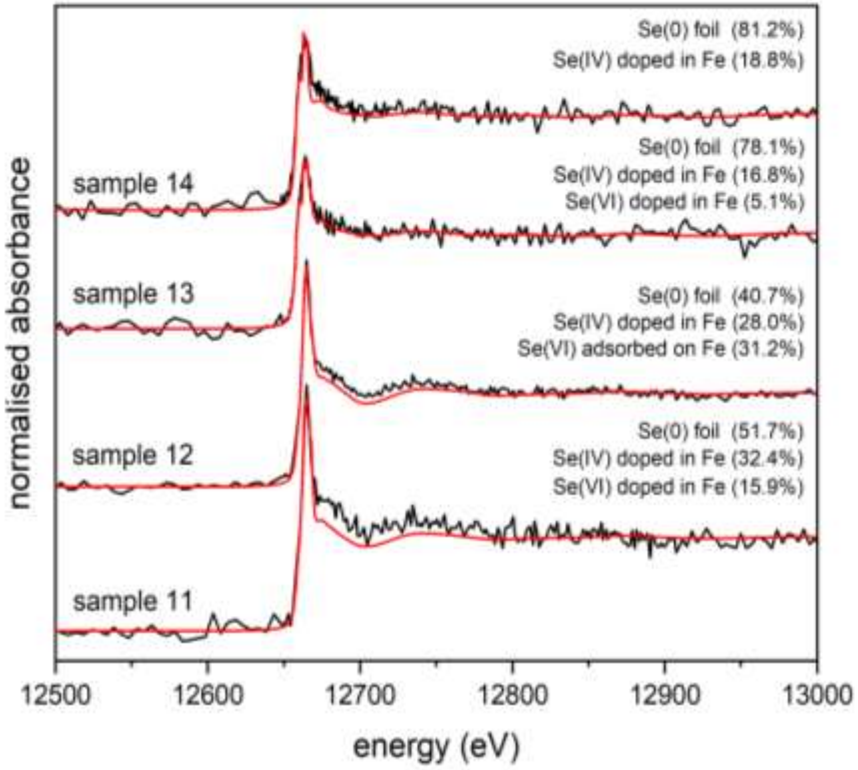
- Se concentrations in some samples are too low for bulk XAS analysis. These samples will be further analyzed using μ-XAS

Standard compounds

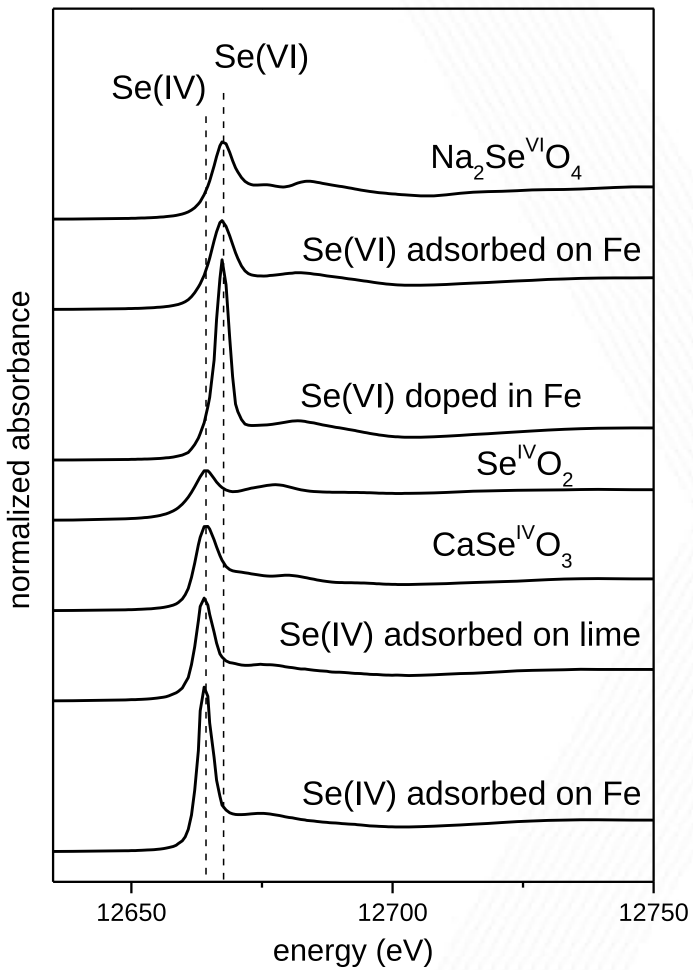


Fly ash samples: Linear combination fitting results



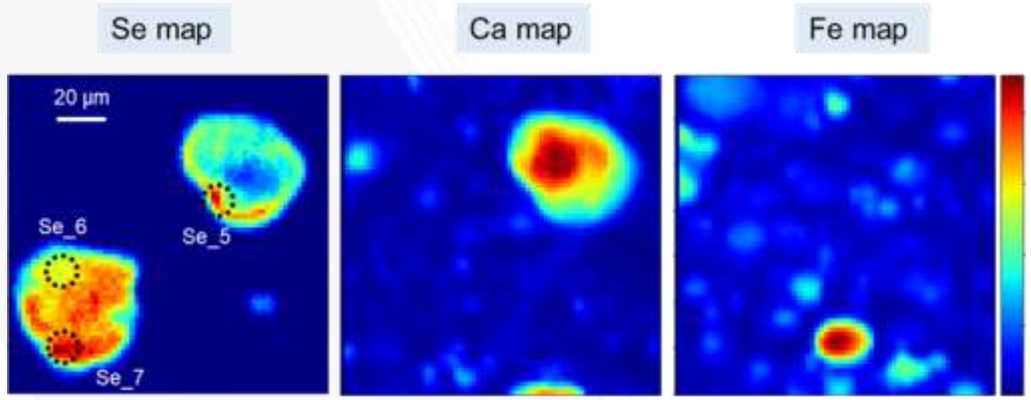


Standard compounds



Sample ID	Se(0) (%)	Se(IV) species (%)					Se(VI) species (%)	
		Se(IV) sorb FeOx	Se(IV) doped FeOx	Se(IV) sorb lime	SeO_2	$CaSeO_3$	Se(VI) sorb FeOx	Se(VI) doped FeOx
2691		28.2				42.3	34.5	
C				88.1			11.9	
F				18.9	56.7		28.3	
CFA-2					17.6	82.4		
14	81.2		18.8					
13	78.1		16.9					5.1
12	40.7		28				31.2	
11	51.7		32.4					15.9

Se XRF map and μ-XANES



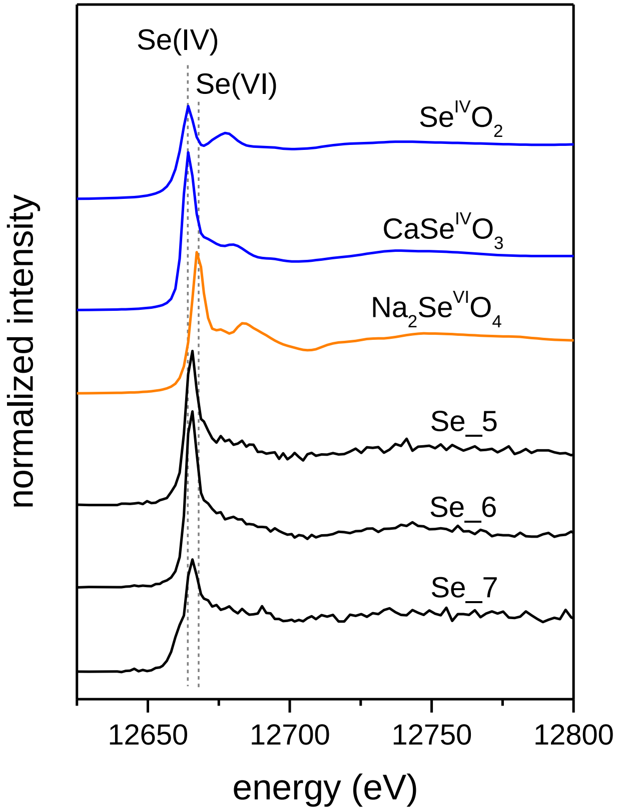
Particle size: two 40 μm x 40 μm particles

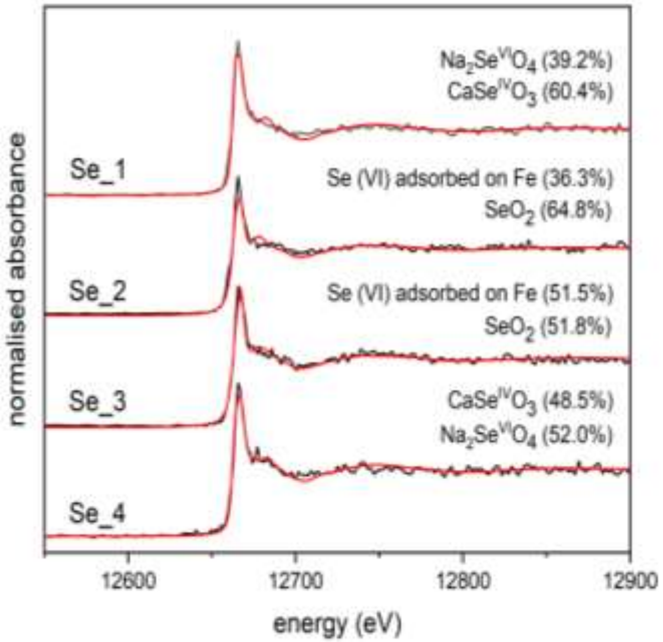
Se distribution:

- Se enriched on the surface of a Ca-rich particle
- Discrete Se-bearing particle with no other elements detected

Se oxidation:

- Se_5: ~70% Se(IV) and ~30% Se(VI)
- Se_6: ~40% Se(IV) and ~60% Se(VI)
- Se_7: ~65% Se(IV) and ~35% Se(VI)





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Next Steps

- Continue sample identification and collection
- Continue sample characterization: composition, surface area, particle size, morphology, mineralogy
- As/Se speciation: synchrotron analyses
- As/Se mobility: leaching tests

Acknowledgements

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