Predicting Mobilization & Bioaccumulation of Trace Elements from Coal Fly Ash using Speciation Analysis

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TVA Fly Ash Release Environmental
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NC STATE University

TVA

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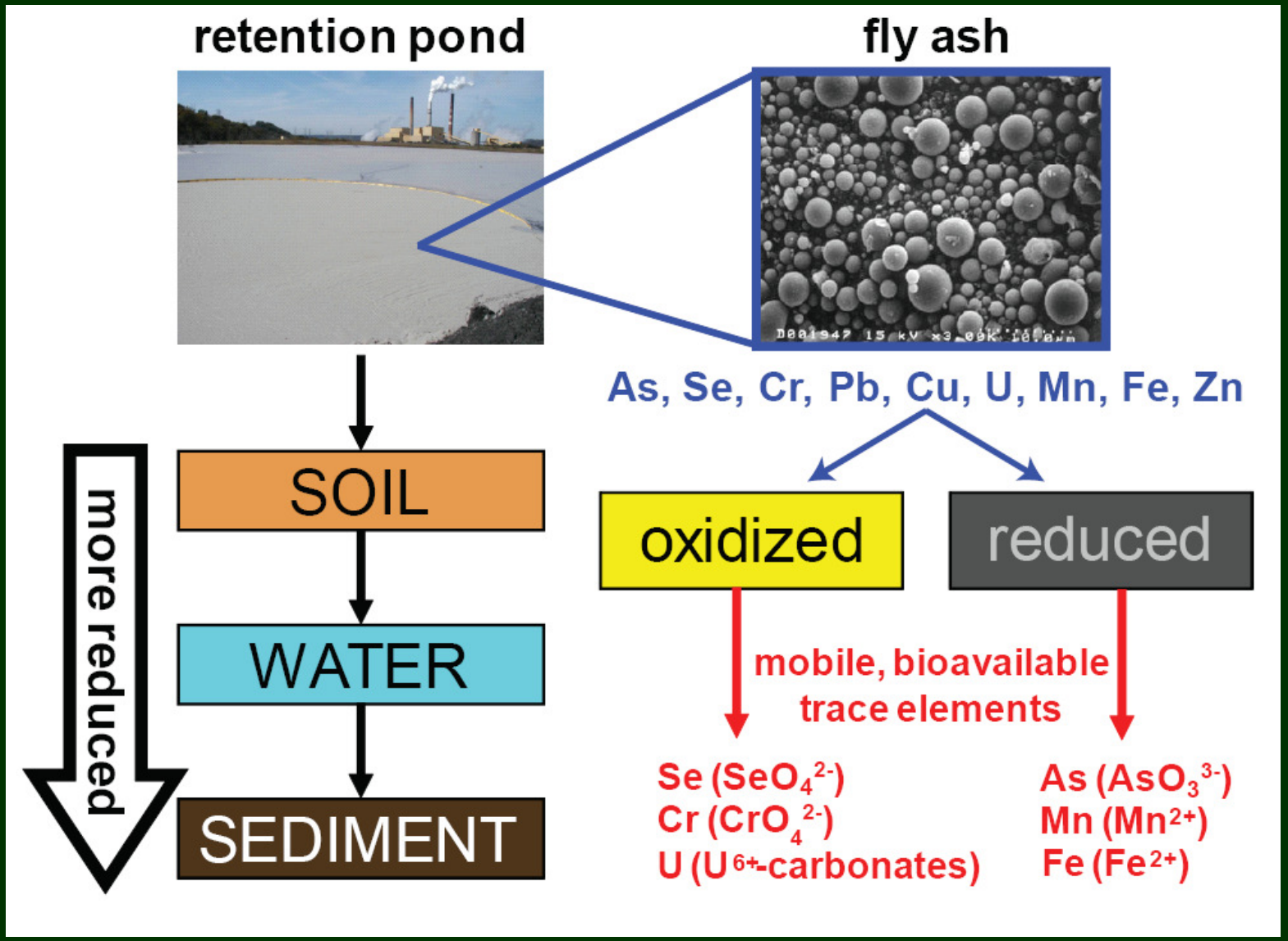
OAK RIDGE ASSOCIATED UNIVERSITIES

Conceptual Schematic of the Proposed Research



(Image: United States Department of Transportation)

Objectives

1. Characterization of fly ash-
   - Chemical composition
   - Mineralogical compositions
   - Trace element speciation
2. Weathering of fly ash-
   - Quantification of toxic trace element dissolution
3. Bioaccumulation of trace element-
   - Periphyton biofilms

Objectives

1. Characterization of fly ash-
   - Chemical composition
   - Mineralogical compositions
   - Trace element speciation

Material & Methods

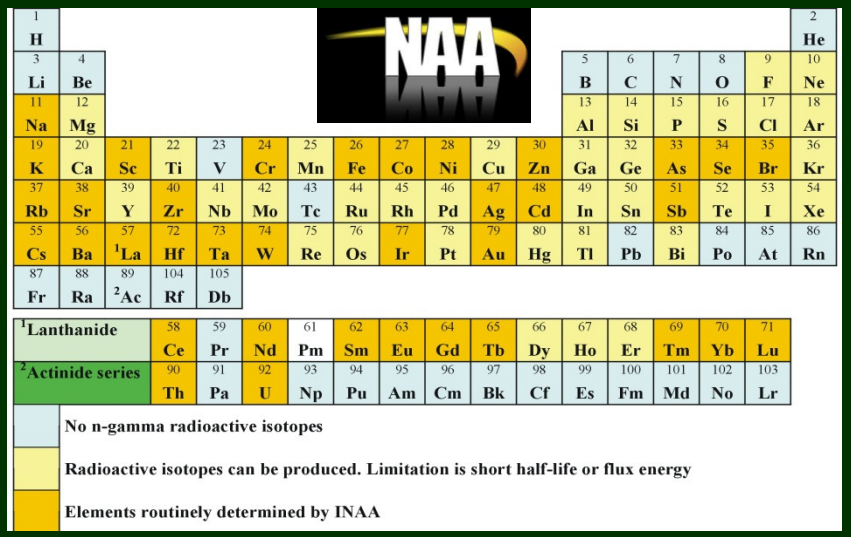
- **Kingston power plant:**
  - **TVA-KIF-110110-F……*KIF***
  - **TVA-122208-7-7-J ……*Pre-KIF***
- **Johnsonville power plant:**
  - **TVA-JVL-101910-A ……*JVL***

Chemical Composition of Fly Ash

Acid Digestion
(Al, Si, Fe, Ca, Cr, Mn, Zn, Cu, Cd, Pb, S, Mg, Sr, P)

Direct
(As, Se, U)

Dept. of Soil Science, NCSU



Dept. of Nuclear Engineering, NCSU

NIST Standard (#2689) used for analytical accuracy

Mineralogical composition: Synchrotron X-ray diffraction

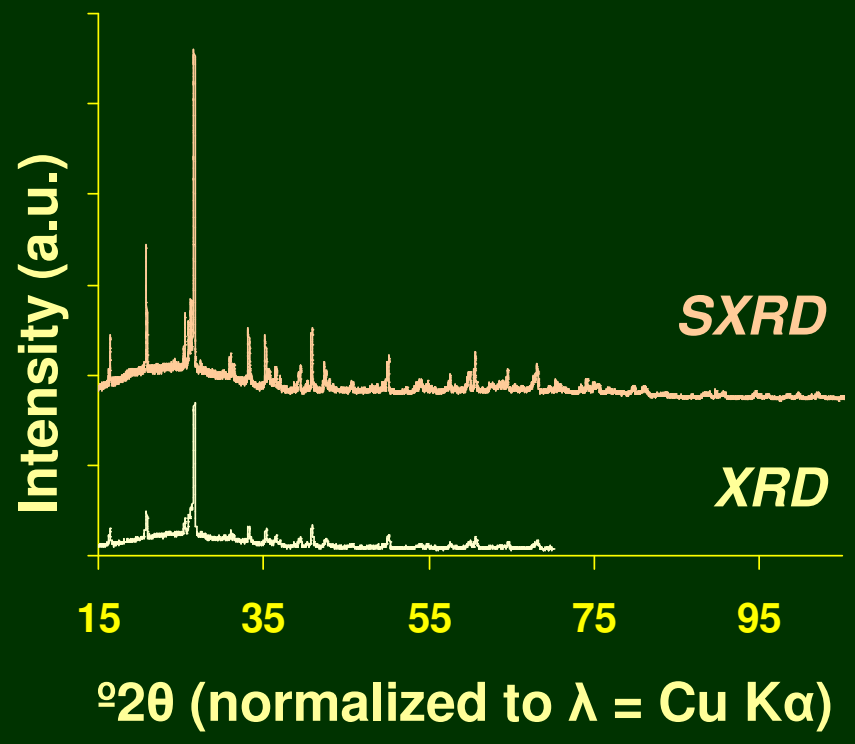
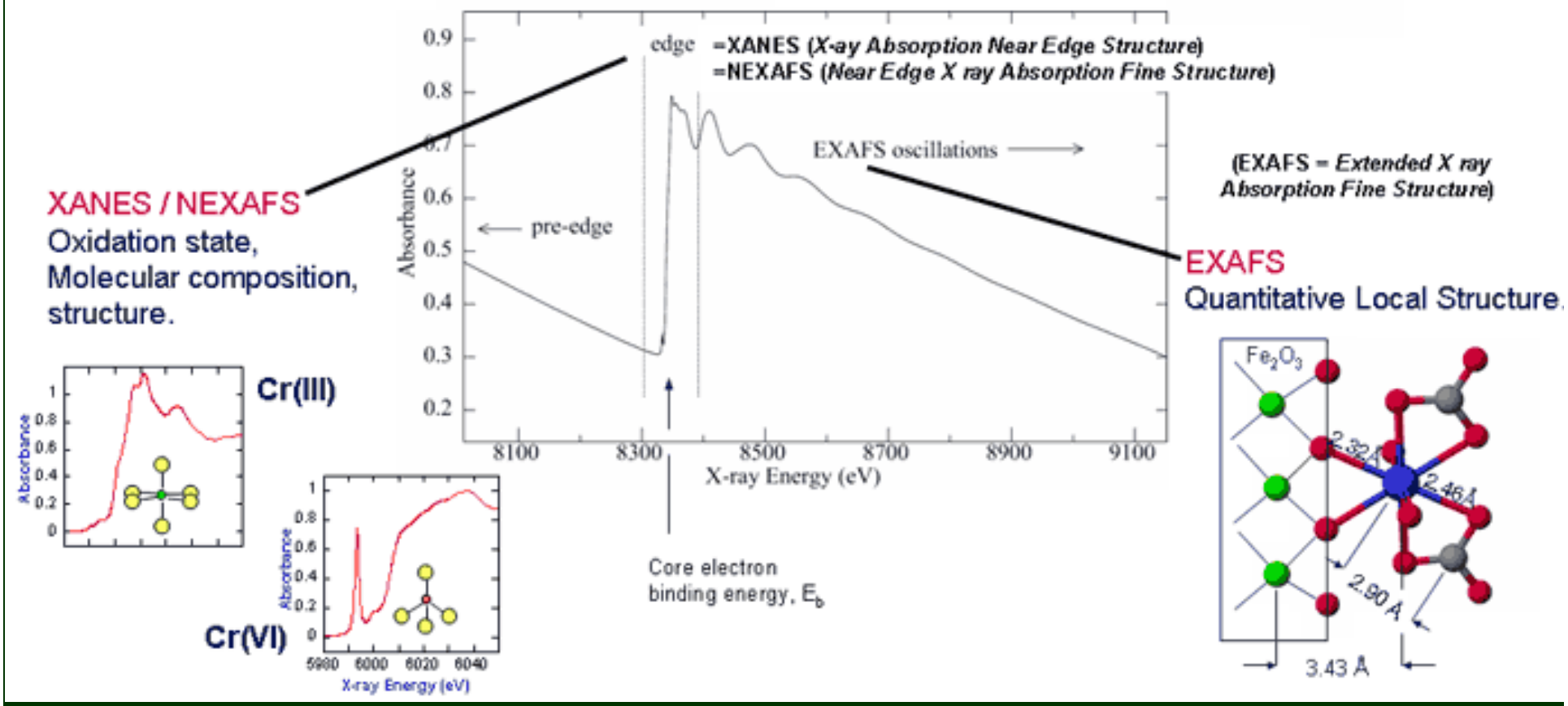


Fig. SXRD vs. conventional XRD for KIF

Elemental Speciation:
X-ray Absorption Spectroscopy



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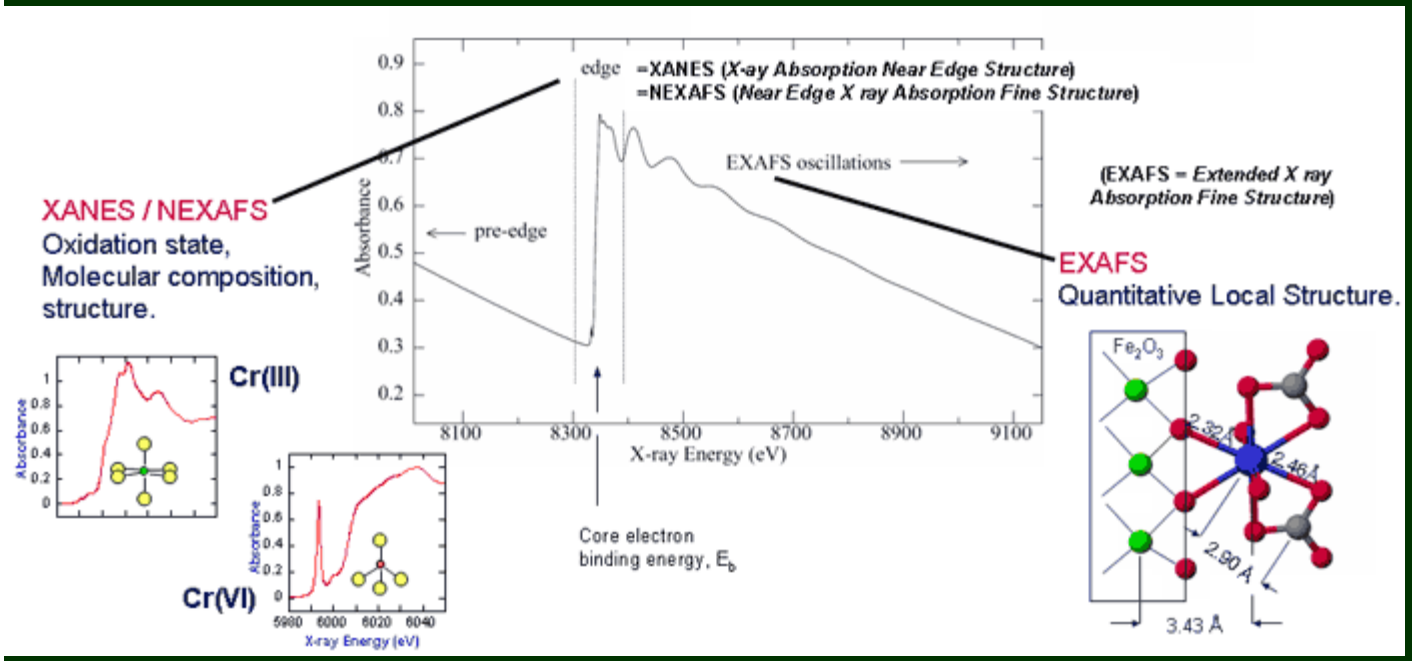


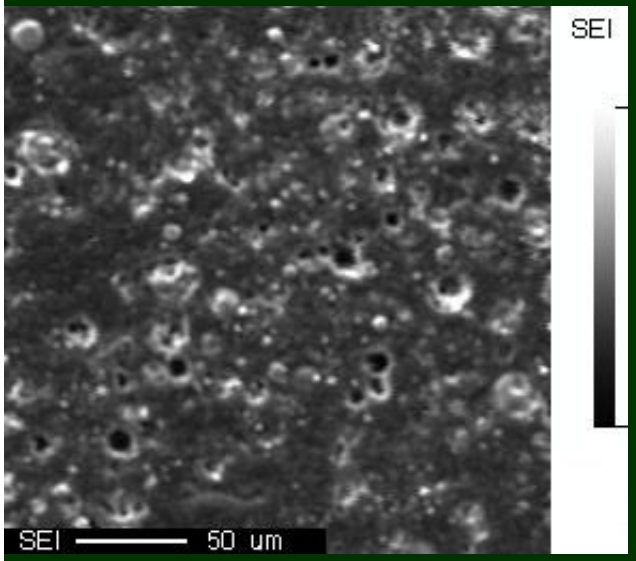
National Syn. Light Source, BNL, NY

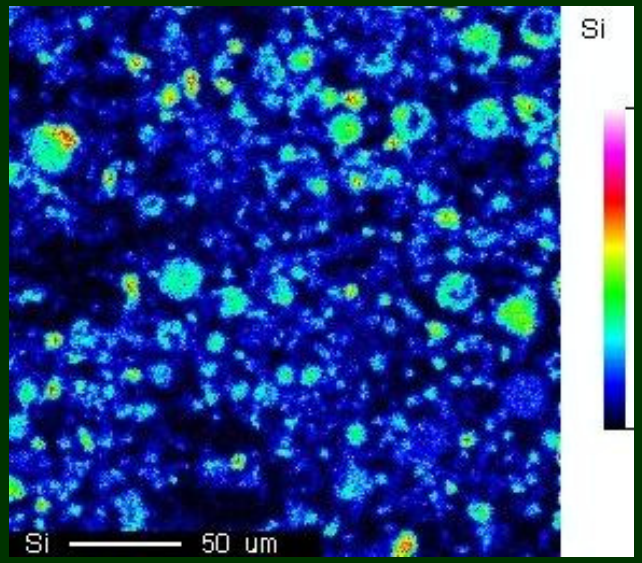
Stanford Syn. Radiation Light Source, CA

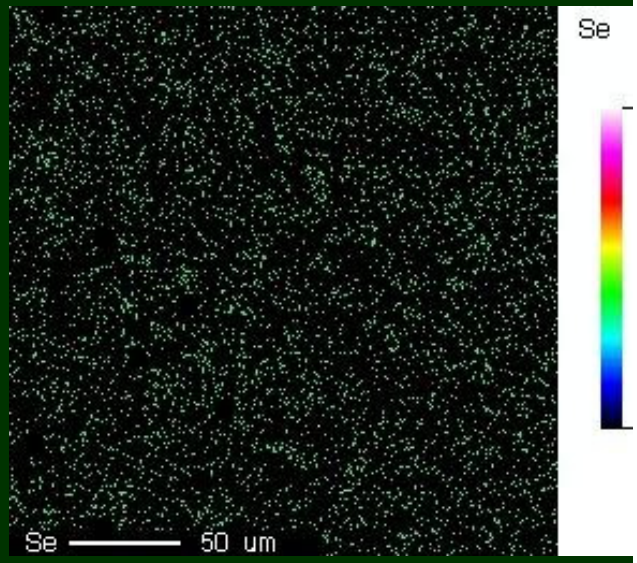
Fly Ash samples, Mineral & Glass Standards

- **EXAFS: Fe- & Sr- K edge**
- **XANES: Cu-, Zn-, As-, Se-, Ca- & S- K edge**

Elemental Mapping:
HyperProbe



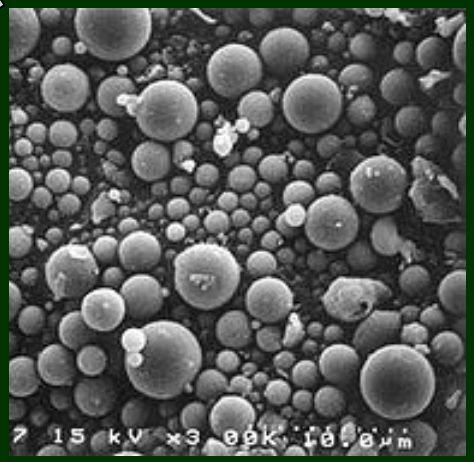




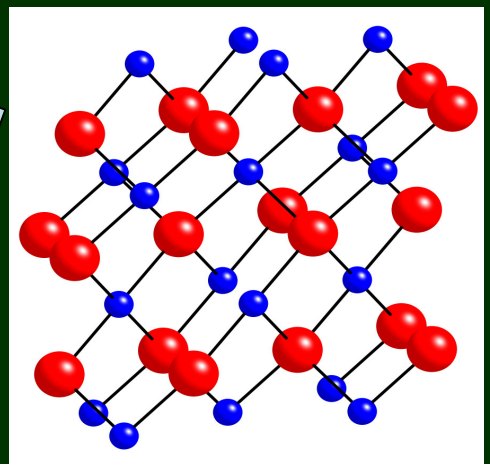
Southeastern NC Regional Microanalytical & Imaging Center, FSU

KIF: Fe, Si, Al, Ca, Sr, Se, As, Zn, Mn, Cr, U, S, Mg

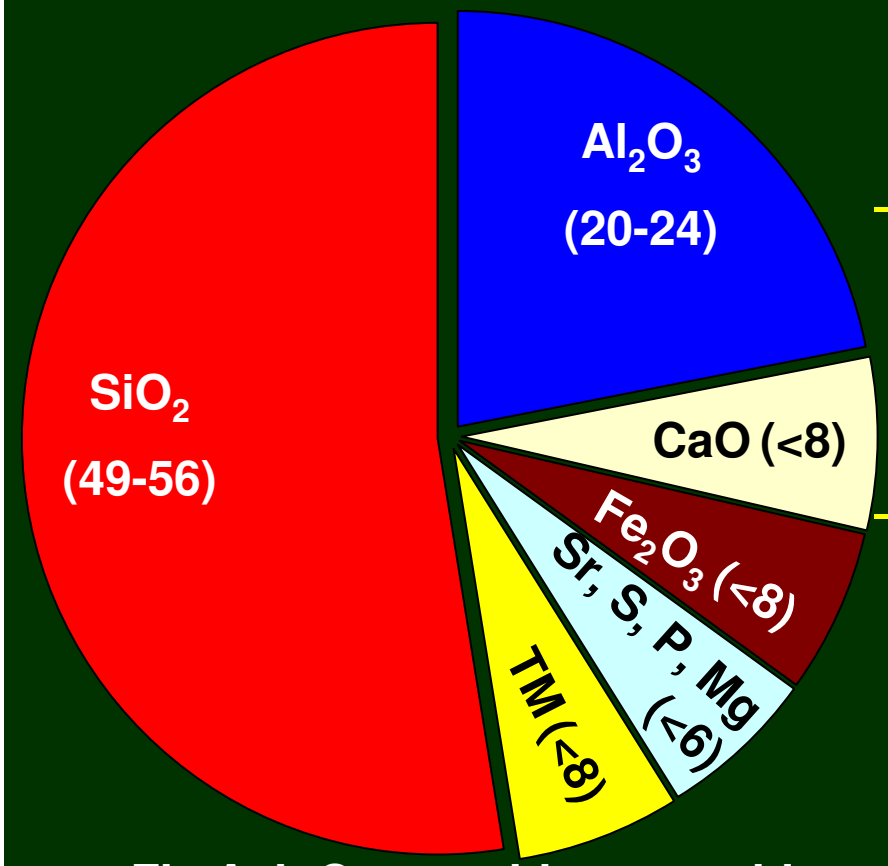
JVL & Pre-KIF: Pending



Results



Main Fly Ash Matrix Constituents: Si, Al, Ca, Fe



Fly Ash Composition on oxide basis (% w/w)

- ASTM (1988) utilitarian system
  - Class F
    - pozzolanic
- Ternary classification system‡
  - Alkaline modic
    - pH (9-12)

ASTM: American Society for Testing Materials, ‡Roy & Griffin (1982)

Fly Ash Contains Hazardous Elements in Significant Extractable Amounts

Element	Conc. ($\mu g\ g^{-1}$)
Se	4.1-5.5
U	6-7
As	26-43
Cr	50-70
Zn	80-117
Cu	57-130
Mn	105-130
Cd	2-2.5
Pb	26-31

US-EPA Method 3051A

Fly Ash Matrix = Glass + Minerals

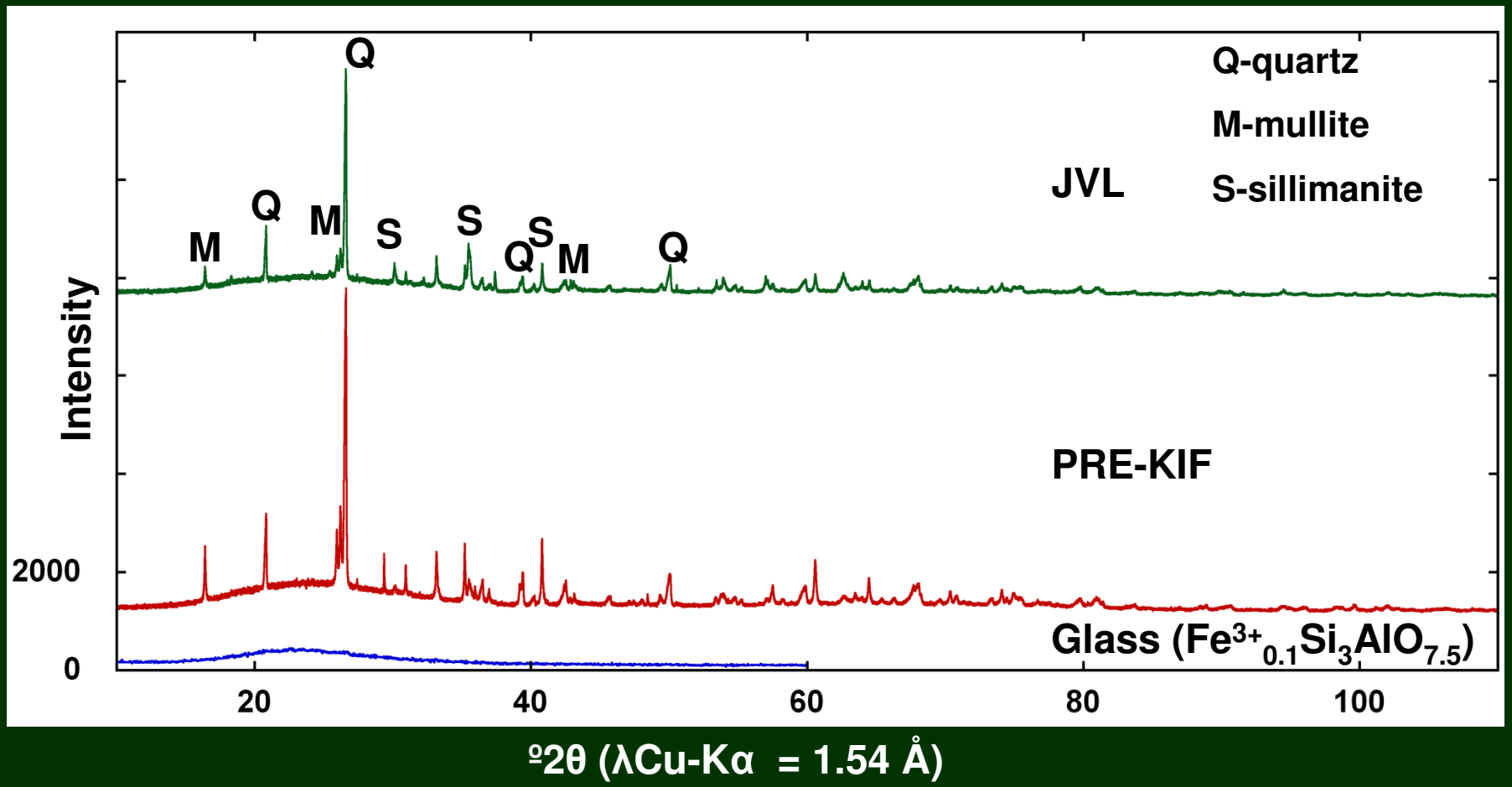
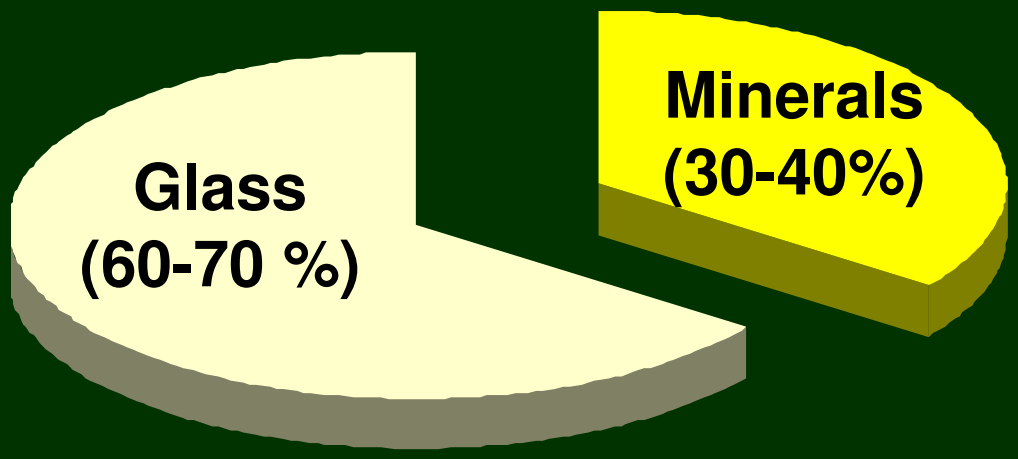
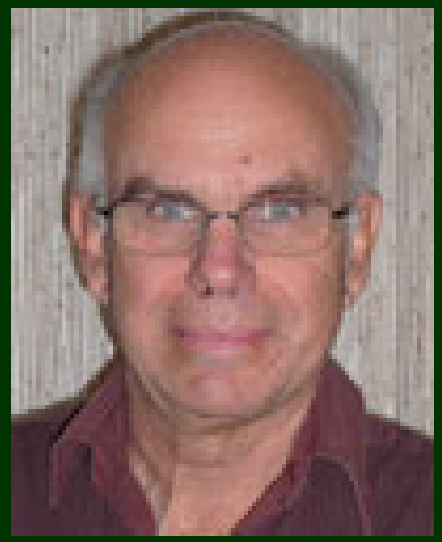


Fig. SXRD & XRD for samples & glass, respectively

Quantification of Glass in Fly Ash



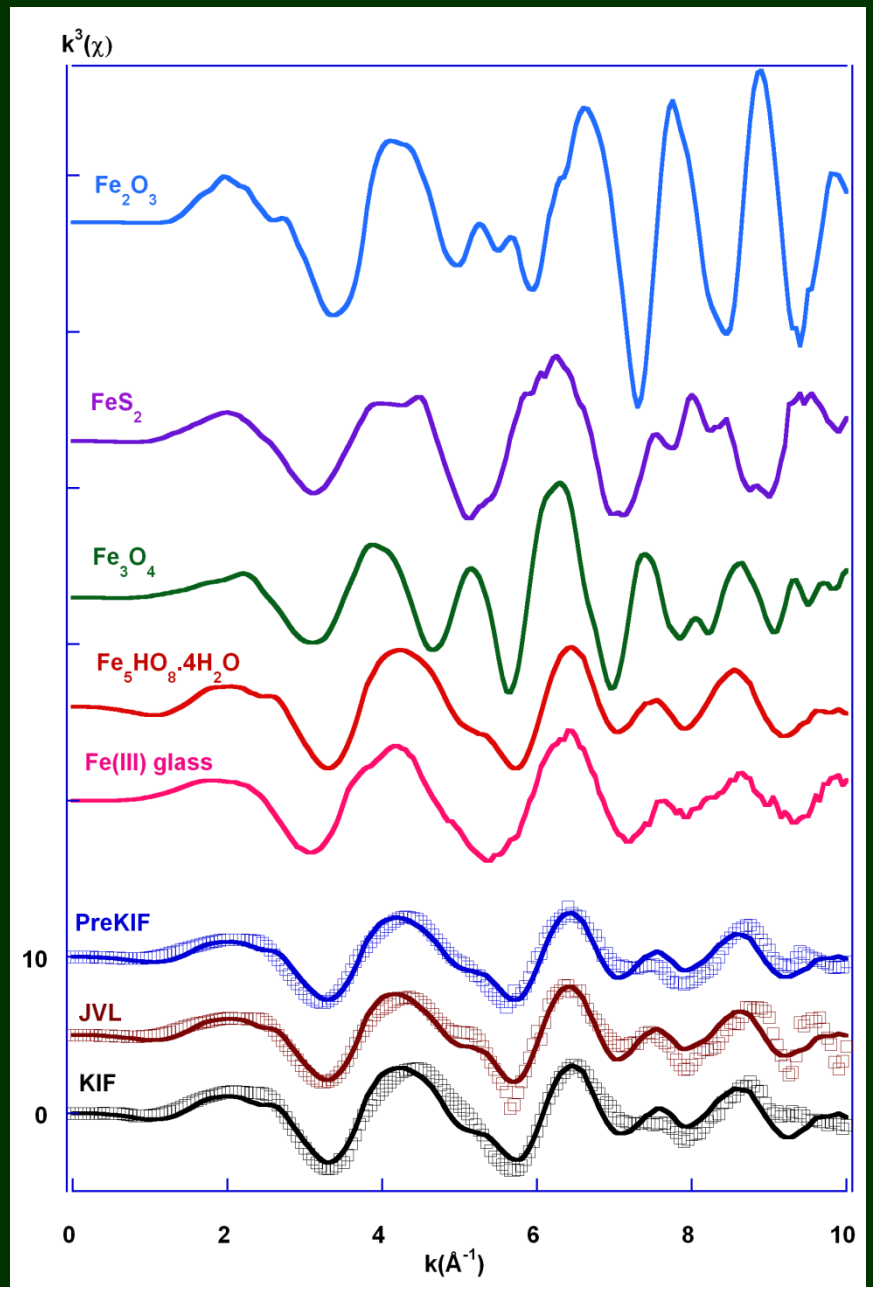


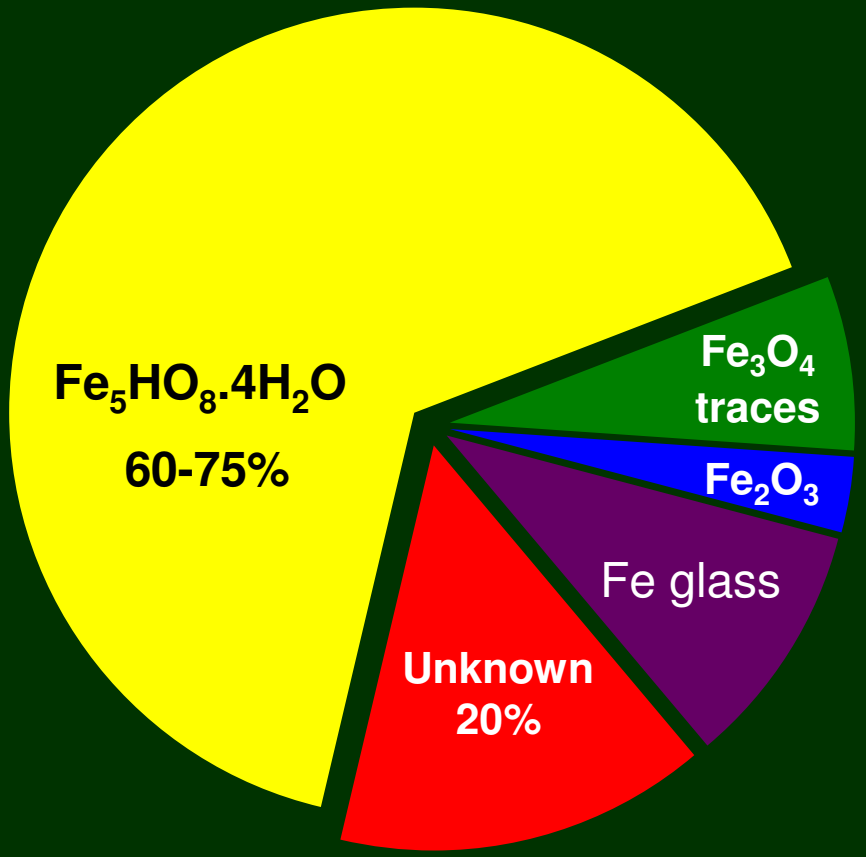
Ward, C.R. & French, D.; Fuel 85 (2006) 2268–2277

Colin R Ward, UNSW, Australia

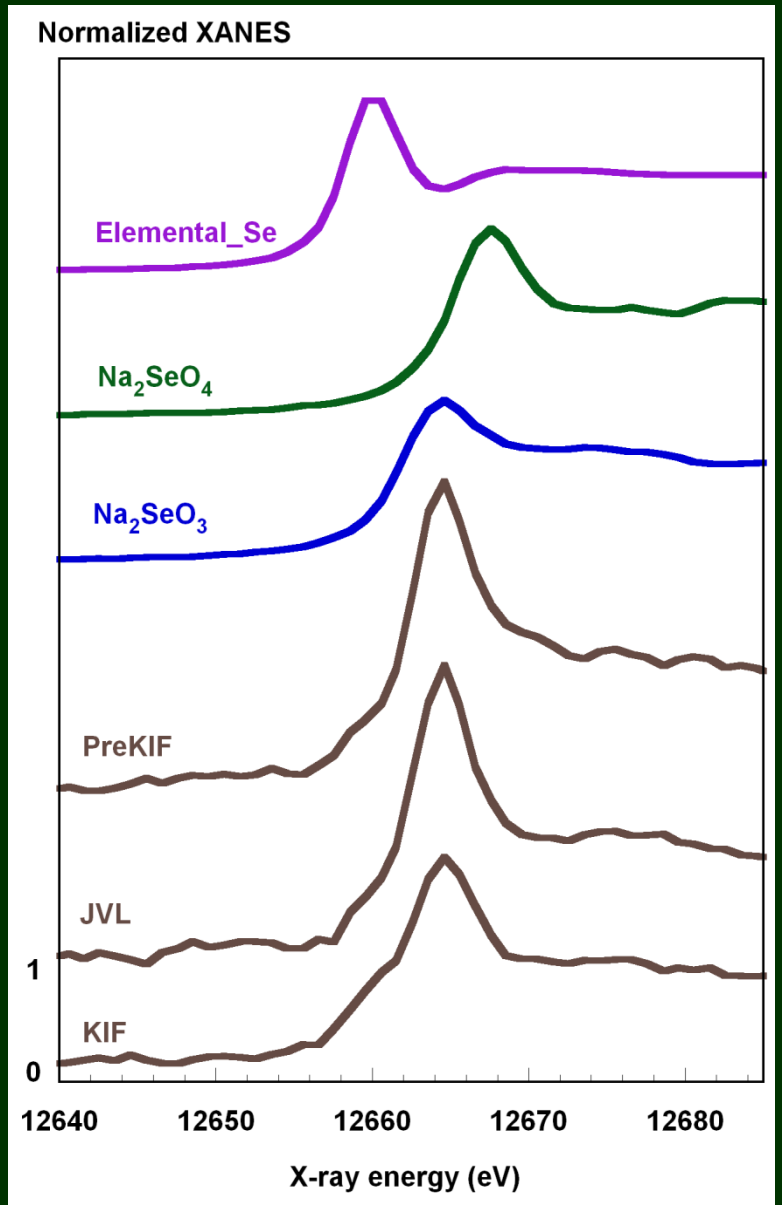
Recipient of 2010 Gilbert H. Cady Award , The Geological Society of America

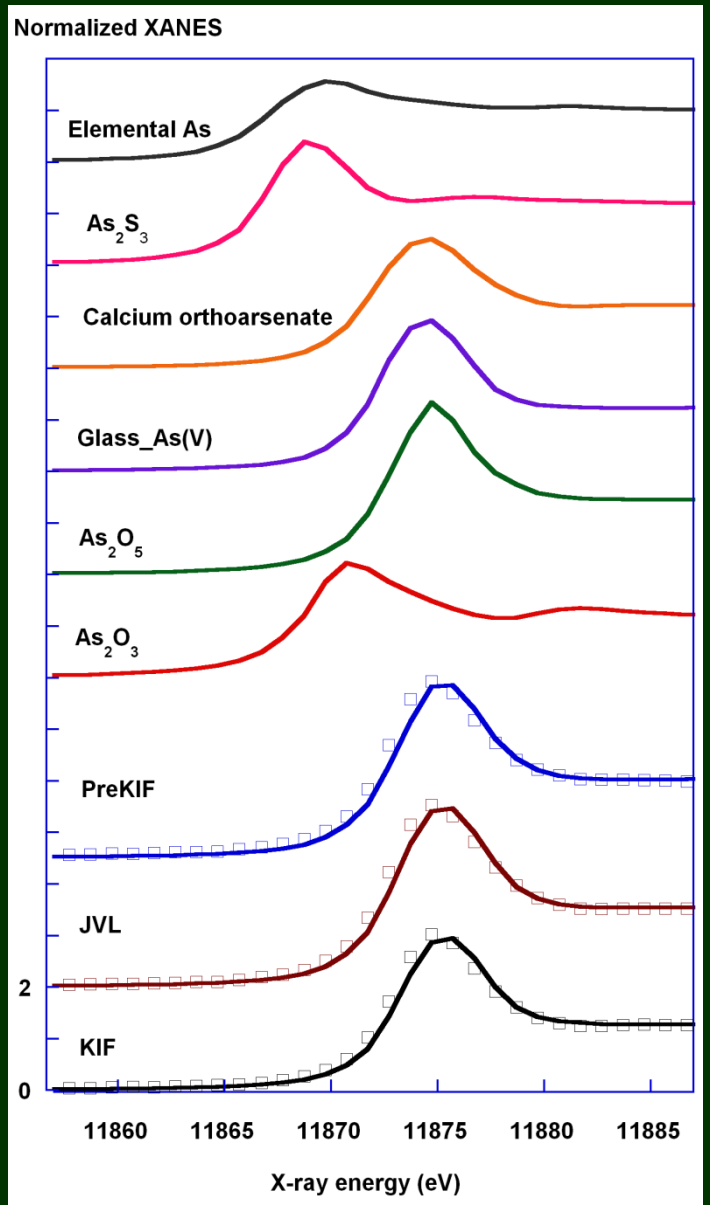
Fe-EXAFS Spectra fits best with Ferrihydrite



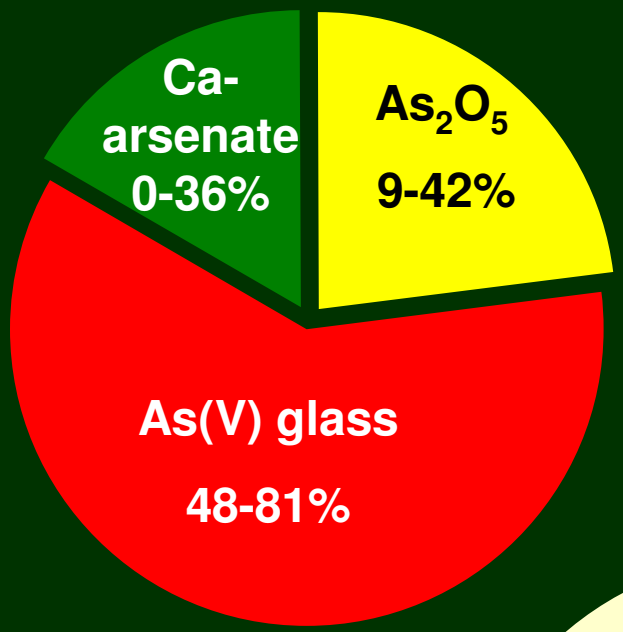


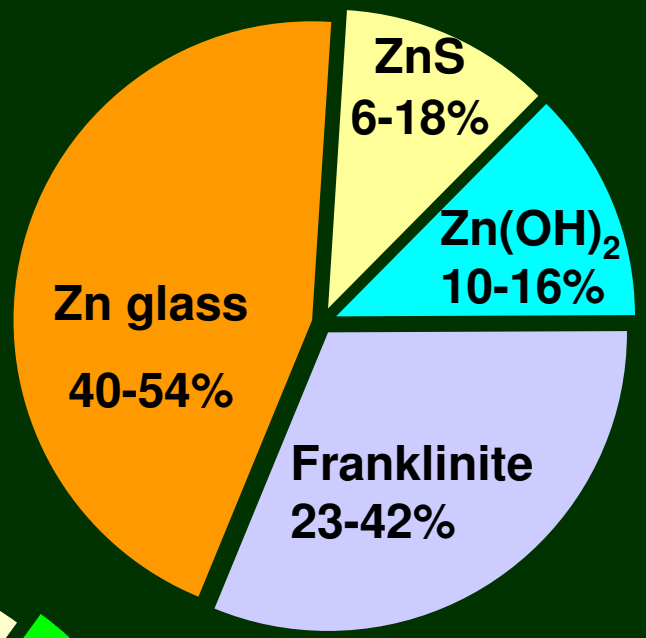
Selenium and Arsenic are Present Mainly as Se(IV) & As(V)

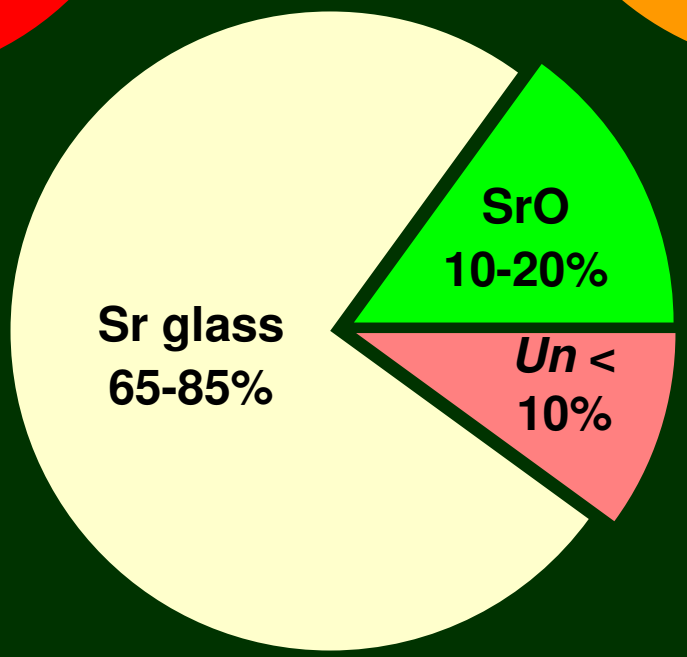




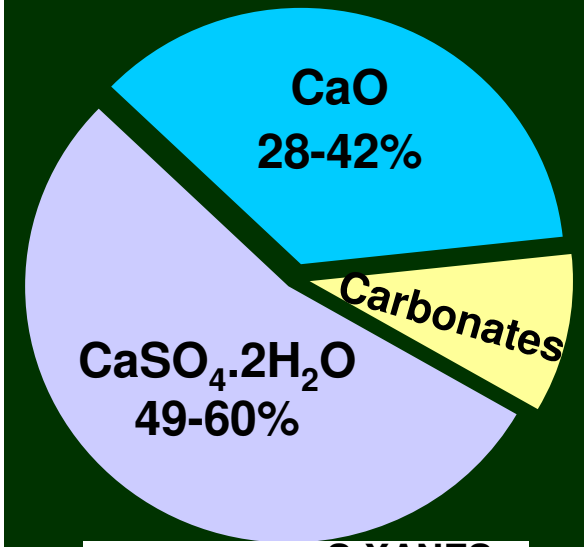
XAS fits included significant fractions of Glass

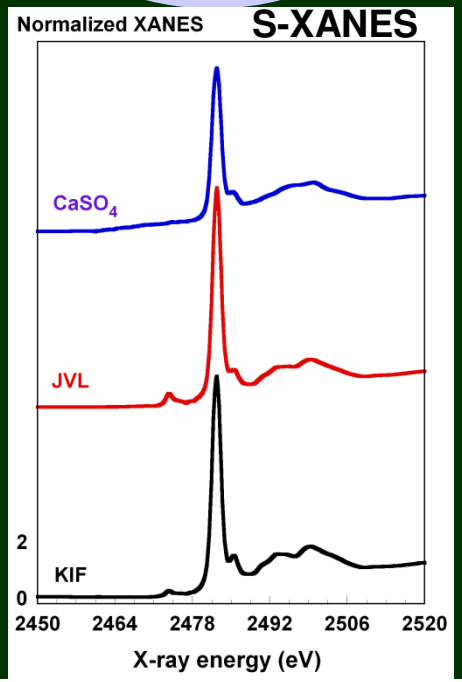


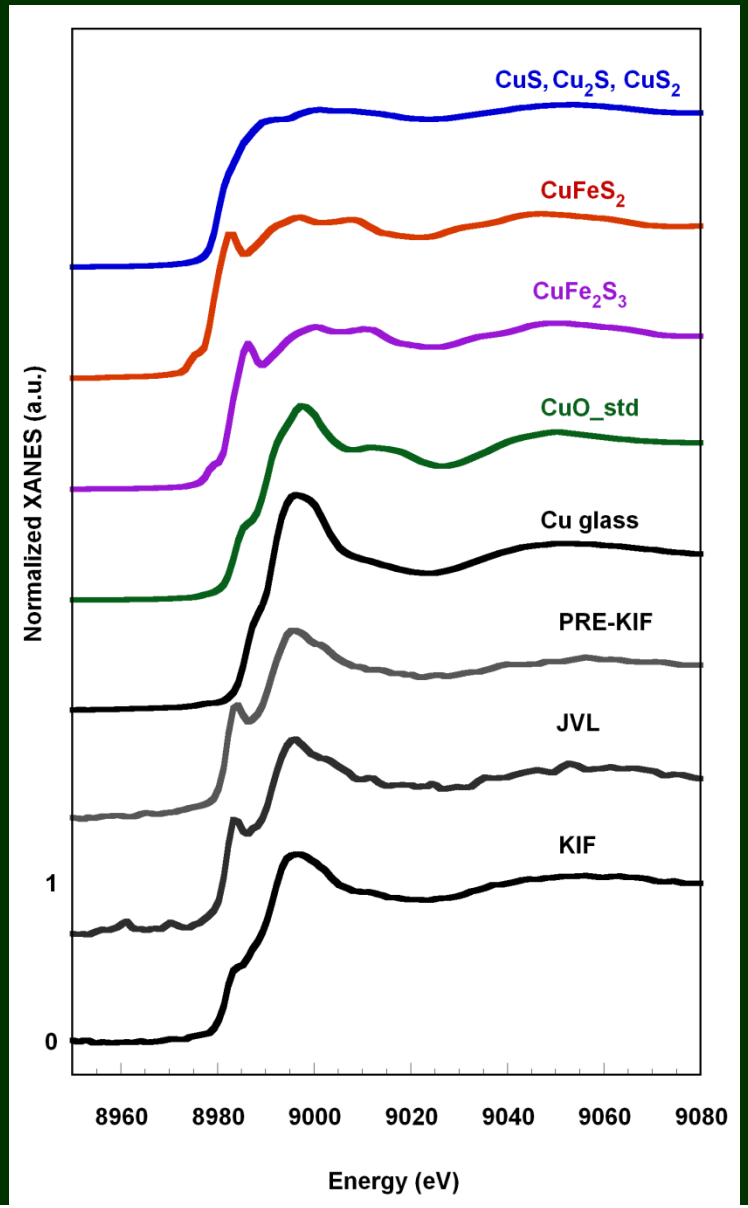


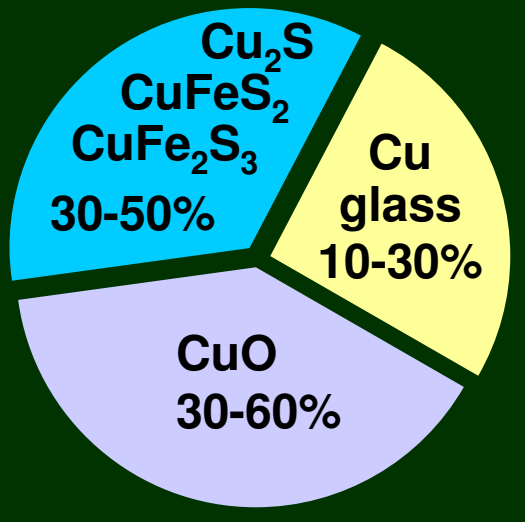


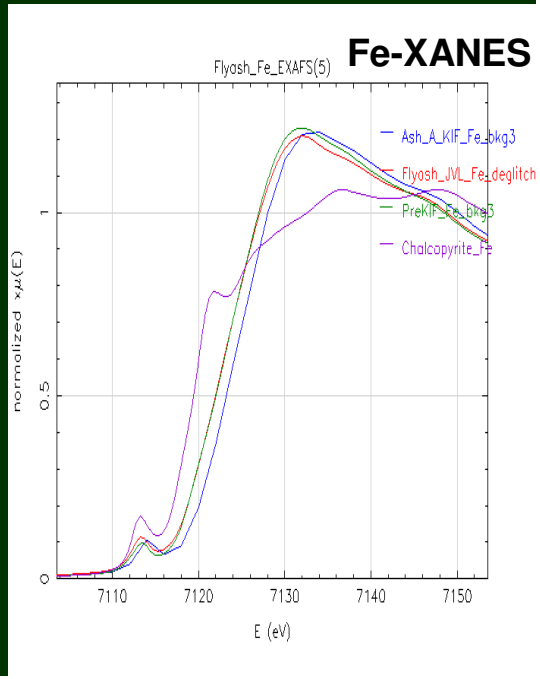
Ca, S, Cu, Fe XANES: Indication of S^{2-}



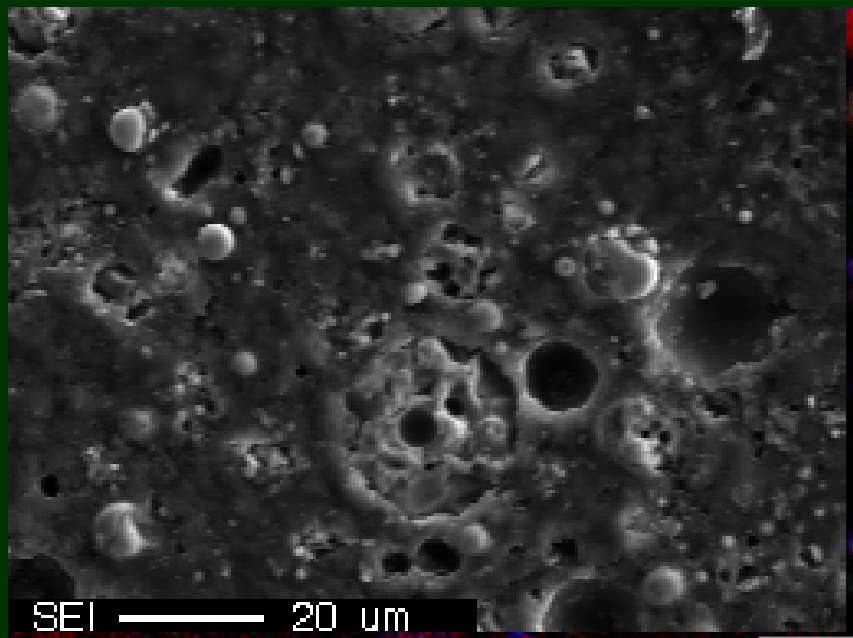


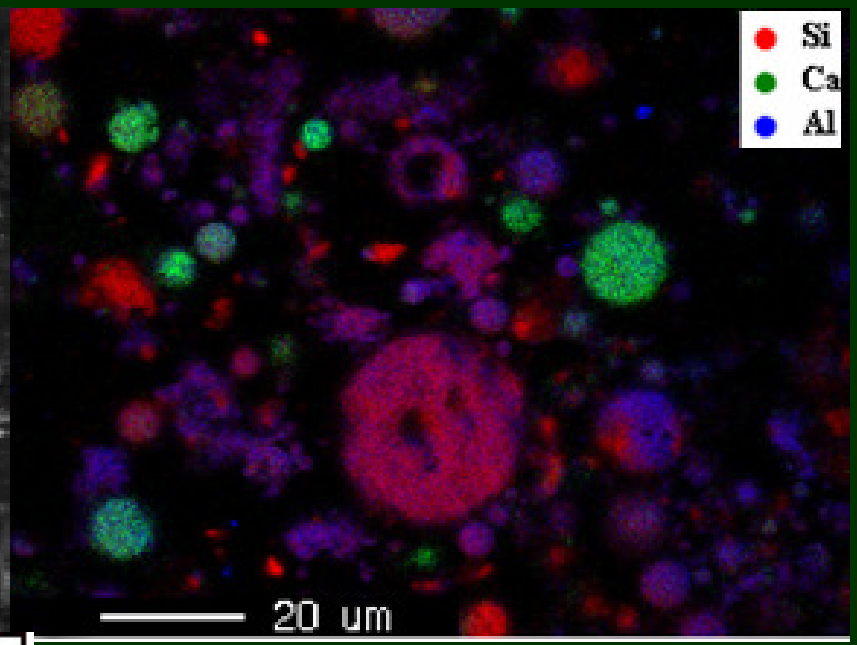


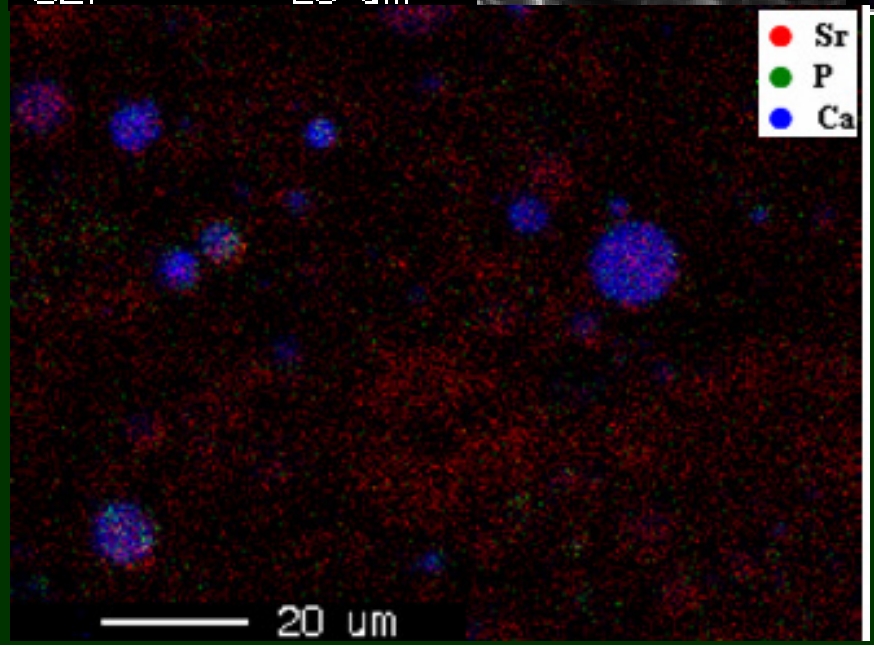




Composite HyperProbe Fly Ash Images







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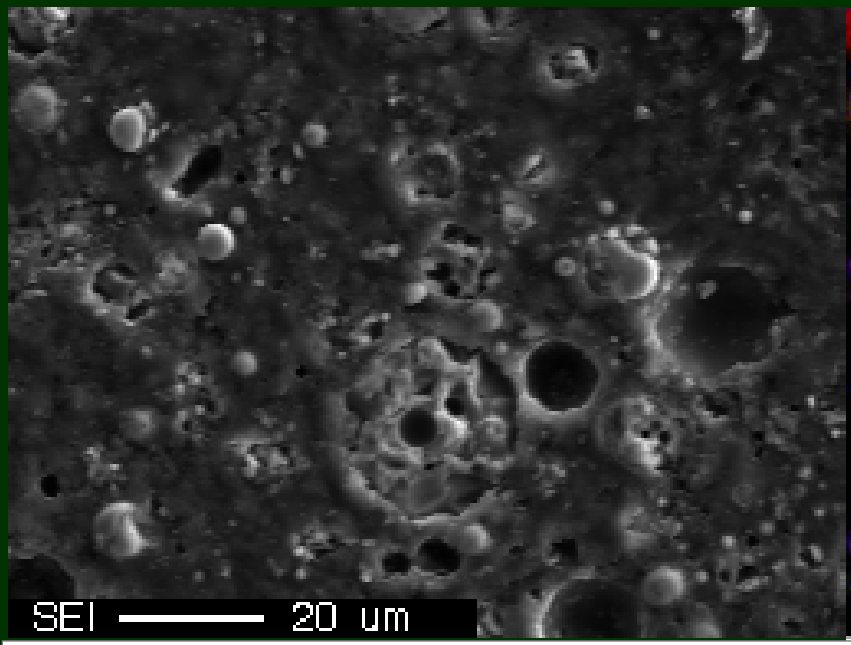

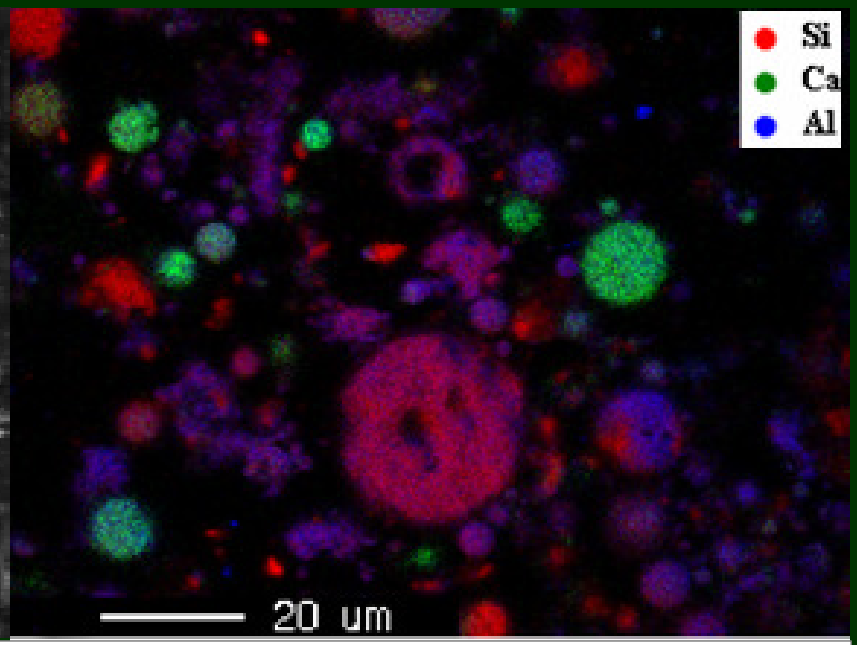

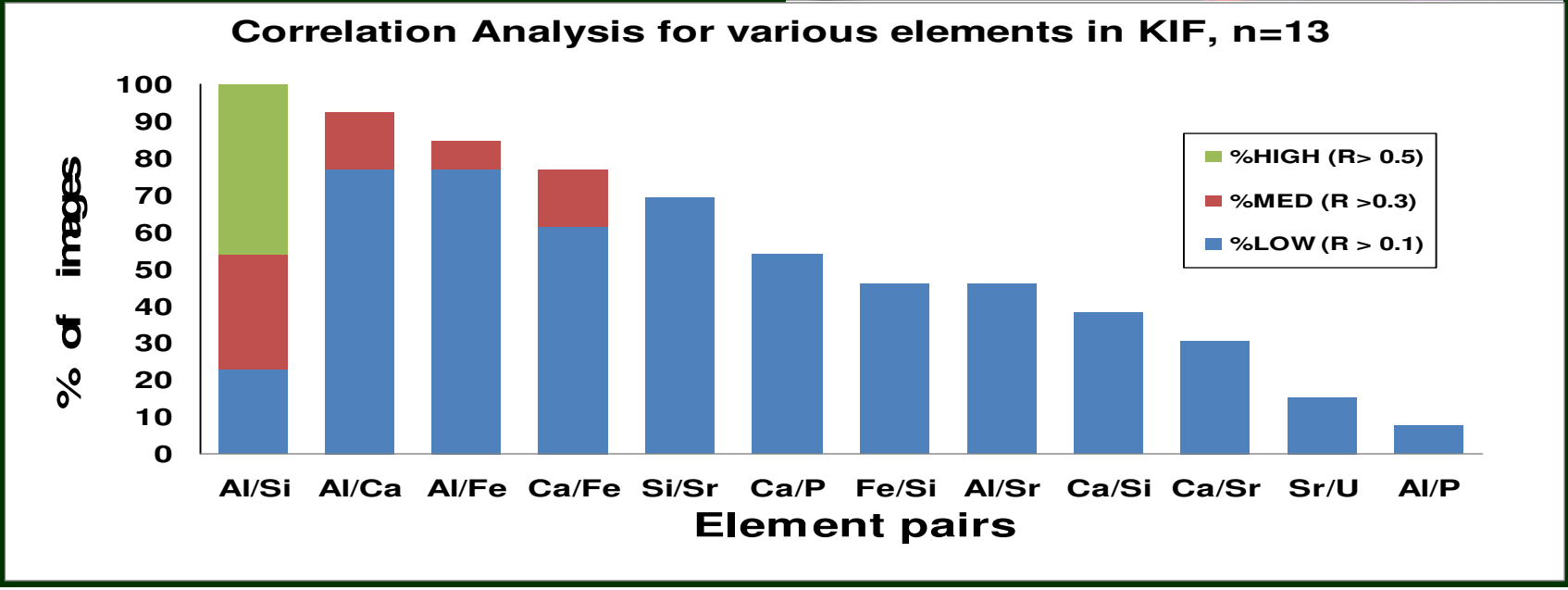

Conclusions

- Fly Ash matrix is highly heterogeneous and various phases, *viz.* glass and, Fe- and S-phases will dissolve differently under different conditions.
- Fe is present in poorly crystalline phases that may potentially release toxic metals.
- Large fractions of Sr, As, Se, Cu and Zn are in glass, which may weather easily in retention ponds because of alkaline pH of Ash.
- Se (IV) and As(V) are the main oxidation states in fly ash.
- SXRD, XAS and HyperProbe are the complimentary techniques to study heterogeneous material.

Future Planning

- Ash dissolution experiments
  - **pH**
  - **Organic matter**
  - **Reducing conditions**
- Biouptake experiments
  - **Periphyton biofilms**
  - **Mayfly life cycle analysis**

Funding & Resources

- TVA/ORAU Grant No. 7-22978
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- Dr. James Harrington (NC State)
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