SHORT COURSE C

Modes of Occurrence of Trace Elements in Coal:

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MODES OF OCCURRENCE OF TRACE ELEMENTS IN COAL

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Introduction

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Impact of Trace Metals

Understanding of trace-metal distribution is needed to:

- Develop models for power plant emissions.
- Predict coal behavior upon cleaning.
- Control release of metals from coal and coal combustion materials to ground water.
- Minimize health consequences of coal use in domestic settings.

Effects of Inorganic Components on Coal Utilization

Element	Effects
Sodium	Boiler Fouling
Iron	Boiler Slagging
Chlorine	Corrosion; Hg capture
Si (Quartz)	Erosion of Combustors

Trace Element Averages

Element	Mean Value (ppm)	Standard deviation	Maximum value	Number of samples
Beryllium	2.2	4.1	330	7,484
Chromium	15	15	250	7,847
Manganese	43	84	2,500	7,796
Cobalt	6.1	10	500	7,800
Nickel	14	15	340	7,900
Arsenic	24	60	2,200	7,676
Selenium	2.8	3.0	150	7,563
Cadmium	0.47	4.6	170	6,150
Antimony	1.2	1.6	35	7,473
Mercury	0.17	0.24	10	7,649
Lead	11	37	1,900	7,469
Thorium	3.2	3.0	79	6,866
Uranium	2.1	16	1,300	6,923

Average concentrations of elements of environmental interest in U. S. Coals (results from USGS COALQUAL database, Bragg et al., 1998; after Finkelman, 1993; Kolker and Finkelman, 1998).

About Moisture

- Generally, calorific value increases and moisture decreases with increasing rank. Need to know moisture content to accurately express elemental concentrations in coal.
- Moisture contents range from about 2% in bituminous coals to as much as 30% in low rank coals. Perfect analyses determined on a dry basis can be off by as much as 30% if moisture is not taken into account.

Mode of Occurrence Concept

- Definition- Understanding the chemical form of an element present in coal.
- Importance- Determines element behavior during coal combustion and potential for removal. Determines environmental impact, technological behavior and byproduct potential. Can provide information on geologic history.

Element Modes of Occurrence

Organic Association (Maceral)

- Ionic bound to maceral
- Covalent bound to maceral
- Moisture

Inorganic Association (Mineral)

- Solid solution (e.g As for S in pyrite; Cr in illite/smectite; Cd in sphalerite)
- Essential Structural Constituent (e.g. Galena - PbS)

Results for Elements of Environmental/Human Health Interest

Element	Mode of Occurrence	Confidence*
Antimony	Pyrite; accessory sulfides	Moderate
Arsenic	Pyrite	High
Beryllium	Organic association; silicates	Low/moderate
Cadmium	Sphalerite	High
Chromium	Illlite; organic association; chromite	Moderate/high
Cobalt	Pyrite; accessory sulfides	Moderate
Lead	Galena; selenides	High
Mercury	Pyrite	Moderate/high
Manganese	Carbonates, illite	High
Nickel	Pyrite; organic; other	Moderate
Selenium	Organic; pyrite; selenides	High

* Interpretative index assigned by the authors; i.e. "High" indicates a high confidence in the results by the authors for the specified element mode of occurence.

Geologic Factors Influencing Coal Chemistry

- Burial and diagenetic changes.
- Stratigraphic and lateral variation.
- Interaction with mineralizing fluids (e.g. Alabama, China, western Washington).
- Movement of fluids along fractures.
- Cleat (fracture-filling) mineralization during coal formation.

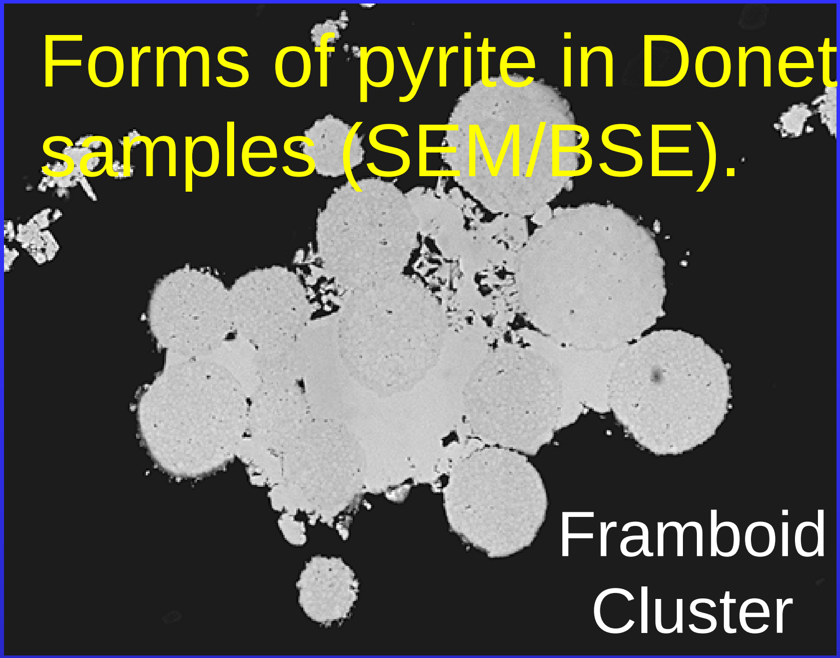
Coal Mineralogy and Mineral Chemistry

Allan Kolker

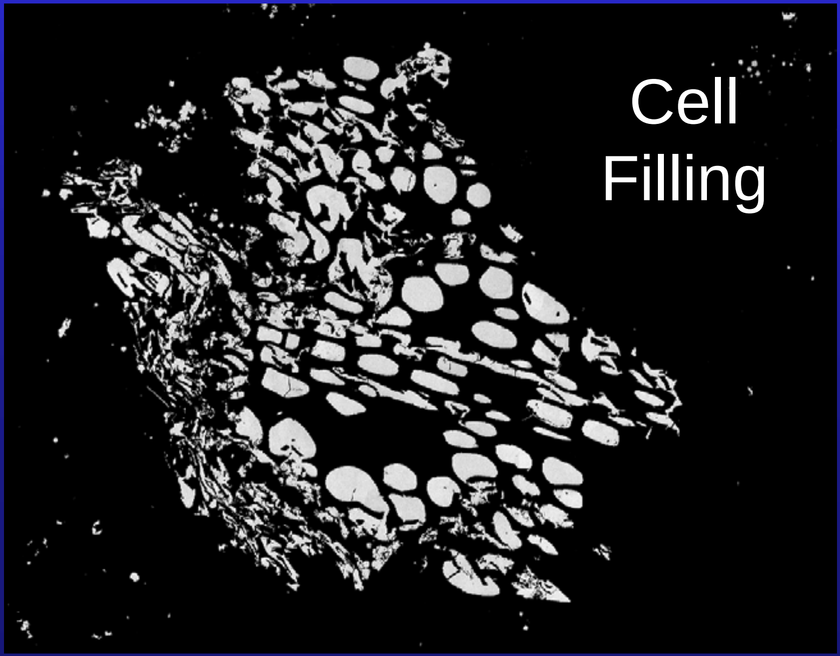
Coal Mineralogy

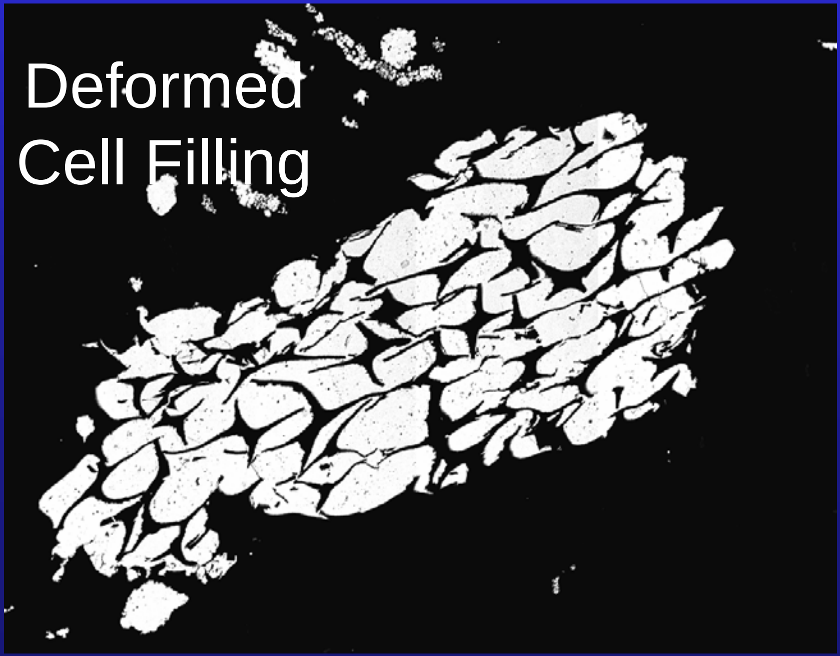
Mineral	Minor Elements
Quartz (SiO$_2$)	Negligible
Clays	
Illite/Illite-smectite	Fe,Cr,Mn,V,
Kaolinite Al$_4$(Si$_4$O$_{10}$)(OH$_8$)	Negligible (?)
Carbonates	
Calcite (CaCO$_3$)	Sr, Mn
Siderite (FeCO$_3$)	Mn
Ankerite Ca(Mg,Fe,Mn)(CO$_3$)$_2$	Sr
Pyrite (Marcasite) (FeS$_2$)	As,Hg,Co,Ni

Forms of pyrite in Donets Basin (Ukraine) coal samples (SEM/BSE).


Framboid Cluster


Micro-Cleat


Cell Filling


Deformed Cell Filling

Minor/Trace Phases

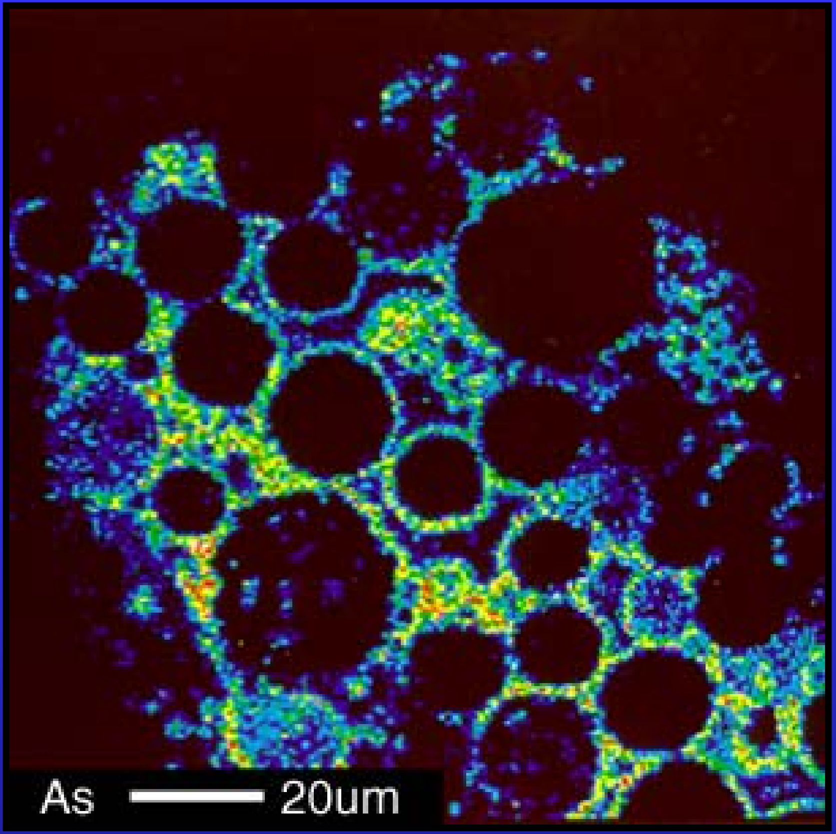
Mineral	Formula or Major Components	Minor Elements
Galena	(PbS)	
Sphalerite	(ZnS)	Cd
Chalcopyrite	($CuFeS_2$)	
Clausthalite	(PbSe)	
Crandallite Group	(Ca, Al, P)	Ba, Sr, REE
Monazite	(REE, P)	Th
Xenotime	(YPO_4)	REE
Apatite	(Ca, P)	REE
Zircon	($ZrSiO_4$)	U, Pb, Th
Rutile	(TiO_2)	
Barite	($BaSO_4$)	
Feldspars	(Ca, Na, K, Al, Si)	
Micas	(K, Fe, Mg, Ti, Al, Si)	
Zeolites	(Ca, Na, K, Al, Si)	

Low Temperature Ashing/XRD

- Method for determining coal mineralogy.
- Concentrate mineral matter by slowly consuming organic matter at 175°C.
- Mineral I.D. by X-Ray diffraction of LTA.
- Mixture of minerals solved by computer.
- Computer-controlled SEM is an alternate approach. Both techniques are semi-quantitative.

Arsenic in Coal

- Pyrite is primary host of arsenic in bituminous coals; Arsenopyrite is rare
- Arsenic contents vary widely within and between pyrite grains.
- In low rank coals, pyrite is a less important host of arsenic.



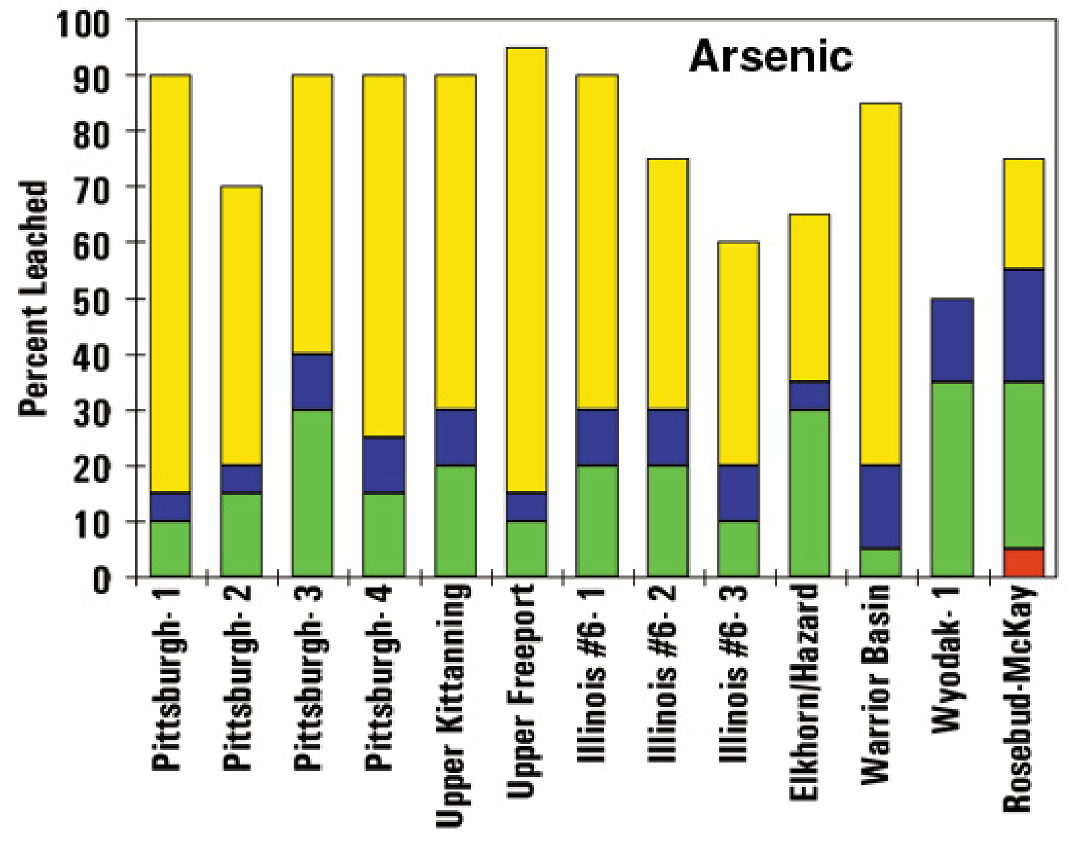
Arsenic-rich pyrite overgrowths on pyrite framboids in an Alabama bituminous coal.

Source: Goldhaber et al., 2003

Arsenic in Coal - continued

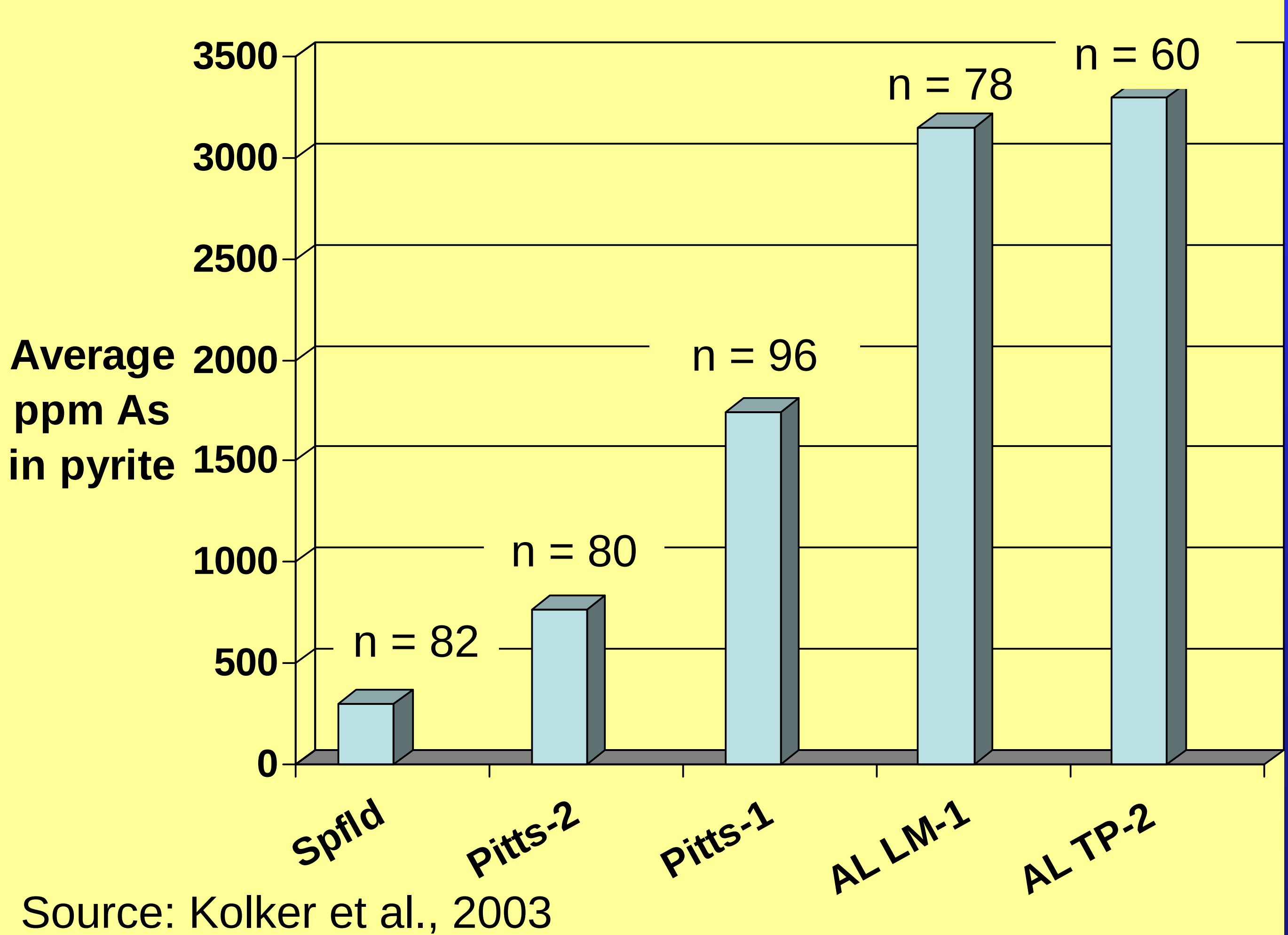
- Coal cleaning reduces pyrite content, but framboids may remain in organic fraction.
- Pyrite oxidation releases arsenic to the environment and changes arsenic oxidation state.
- Documented health effects from arsenic are rare: 1) Guizhou, Province, China: Domestic use of ultra-high-arsenic coals (up to 30,000 ppm). 2) Central Slovakia, 1970's: Arsenic toxicity from use of local coals in power plant.

Arsenic selective leaching results for 13 coal samples showing pyrite association (yellow) for 11 bituminous samples.

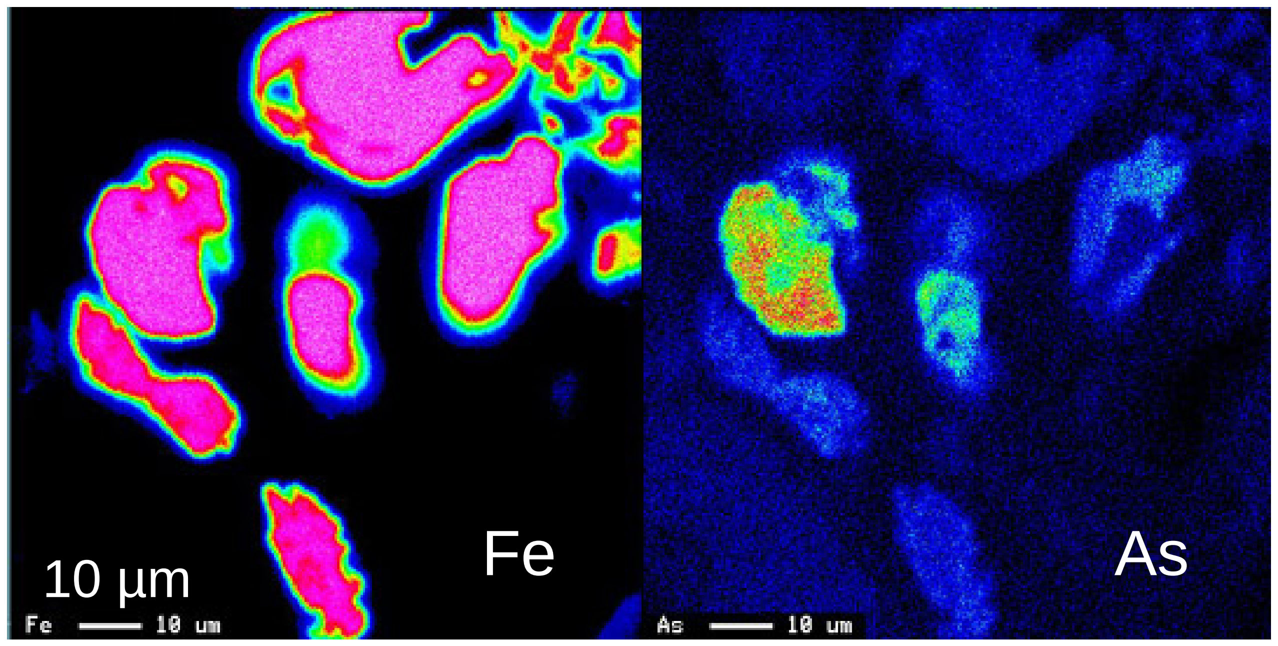


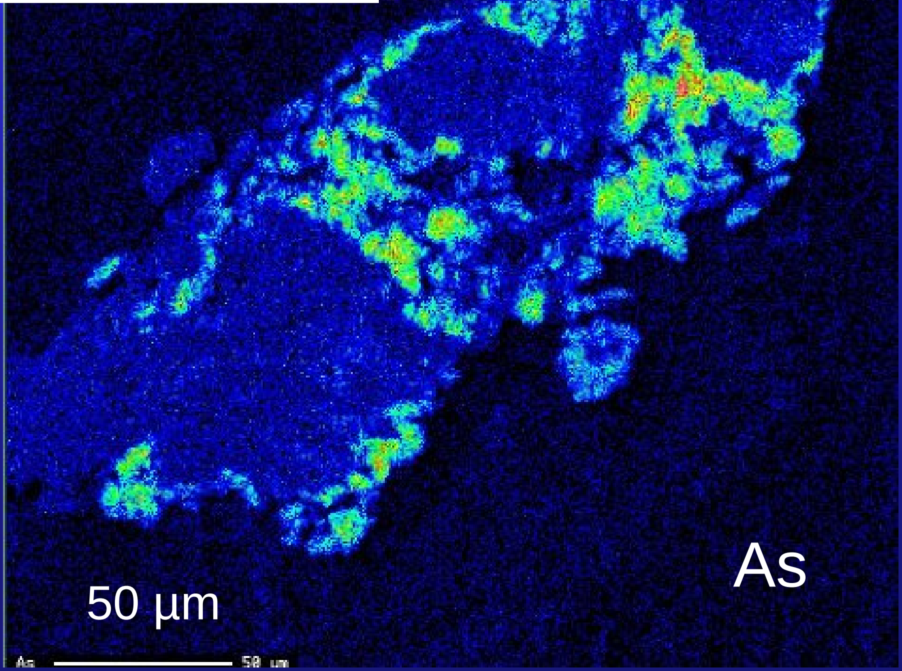
Source: Palmer et al., 1998

Relative Concentration of As in Pyrite



Source: Kolker et al., 2003





Wavelength-dispersive electron microprobe elemental maps of pyrite in Alabama samples LM-1 (above) and TP-1 (right) showing arsenic-enriched domains.

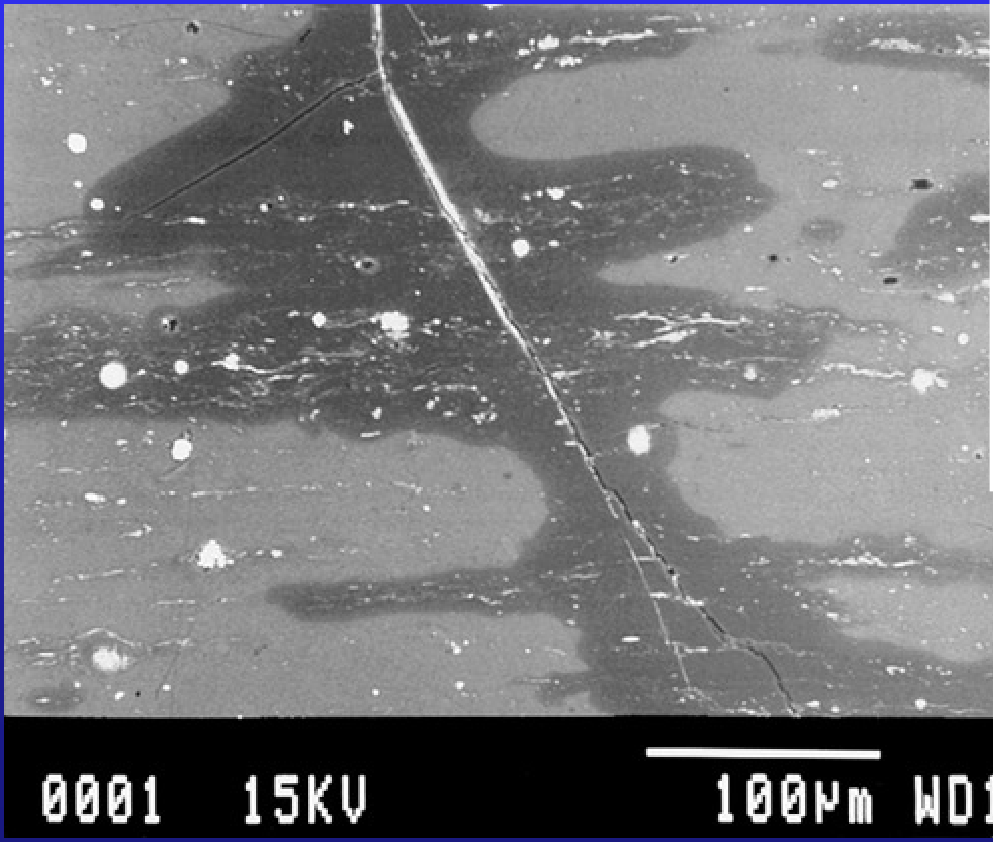
Coals used domestically in areas of pervasive arsenic poisoning, southwest Guizhou Province, China (Belkin et al.).

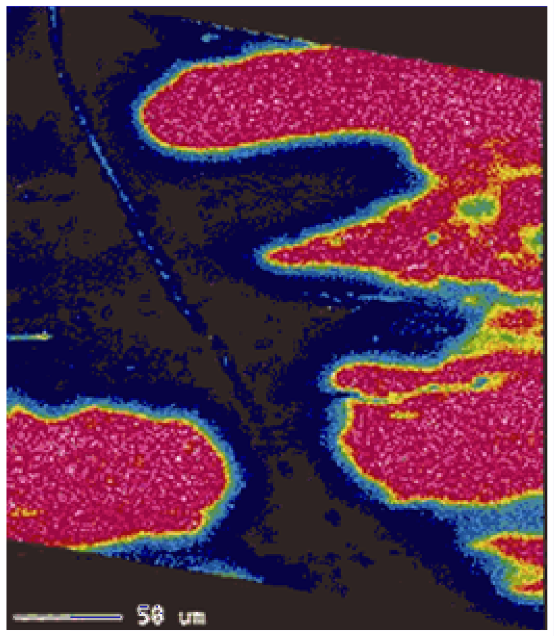
Jiaole Township				Haizi Township				Xingyi City-Dadi area			
Sample	As	Sb	Hg	Sample	As	Sb	Hg	Sample	As	Sb	Hg
A	2223	55	14	A	35037	209	4.1	A	5.2	0.4	0.1
B	1591	132	45	B	32316	140	5.8	B	274	0.7	0.48
C	7391	165	8.5	C	48	8	0.32	C	386	0.5	0.41
D	607	40	29	D	318	13	0.48	D	1100	1.6	0.26
E	405	29	2.0	E	53	16	0.9	E	5.5	0.4	0.7
F	419	22	6.9	F	22	16	0.32	F	925	0.6	0.24
G	239	38	17.6	G	7817	364	5.2	G	26	0.4	0.18
H	313	68	46	H	85	5	0.53	H	4.8	0.6	0.34
I	2286	142	30.2	I	315	16	1.4				

As and Sb by INAA, Hg by Cold-Vapor AA (USGS Labs, Denver). Values are in ppm.

Guizhou (China) Coal Samples

Back-Scattered Electron Image





Arsenic Microprobe Map

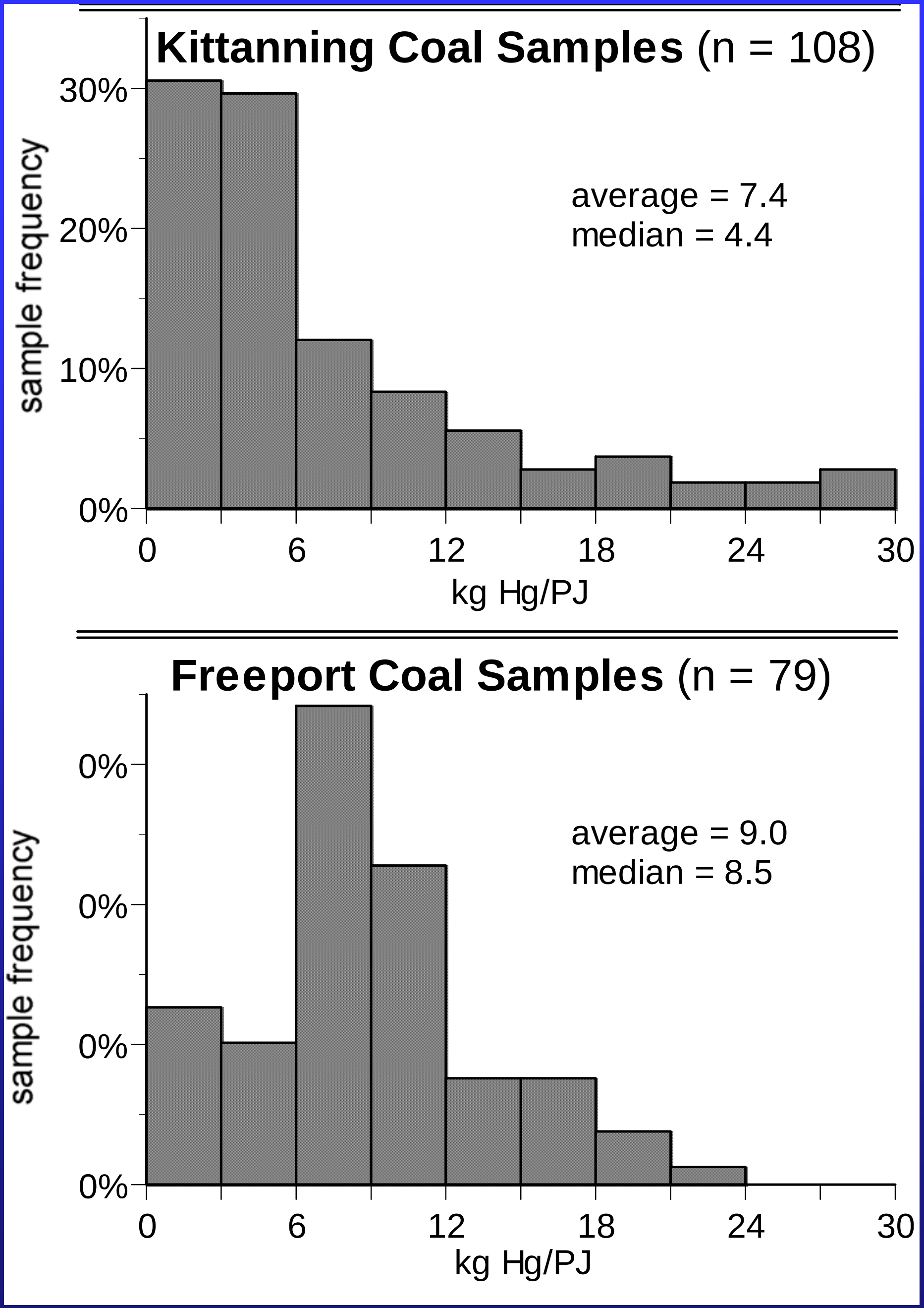
Images from Belkin et al.

Arsenic Field Tests

- Test kit developed in China to identify arsenic-rich coals in the field.
- Commercial version (left) being introduced by U.S. manufacturer.
- Testing has resulted in closure of “mines” with highest As coal.

Mercury in Coal

- Pyrite (FeS_2) is the most common mercury association in bituminous coals.
- Mercury content of pyrite is variable and can be correlated with arsenic and other air toxics.
- In low rank coals, an organic association is common.
- In very mercury-rich coals, HgSe, HgS (cinnabar), and/or native mercury may be present.

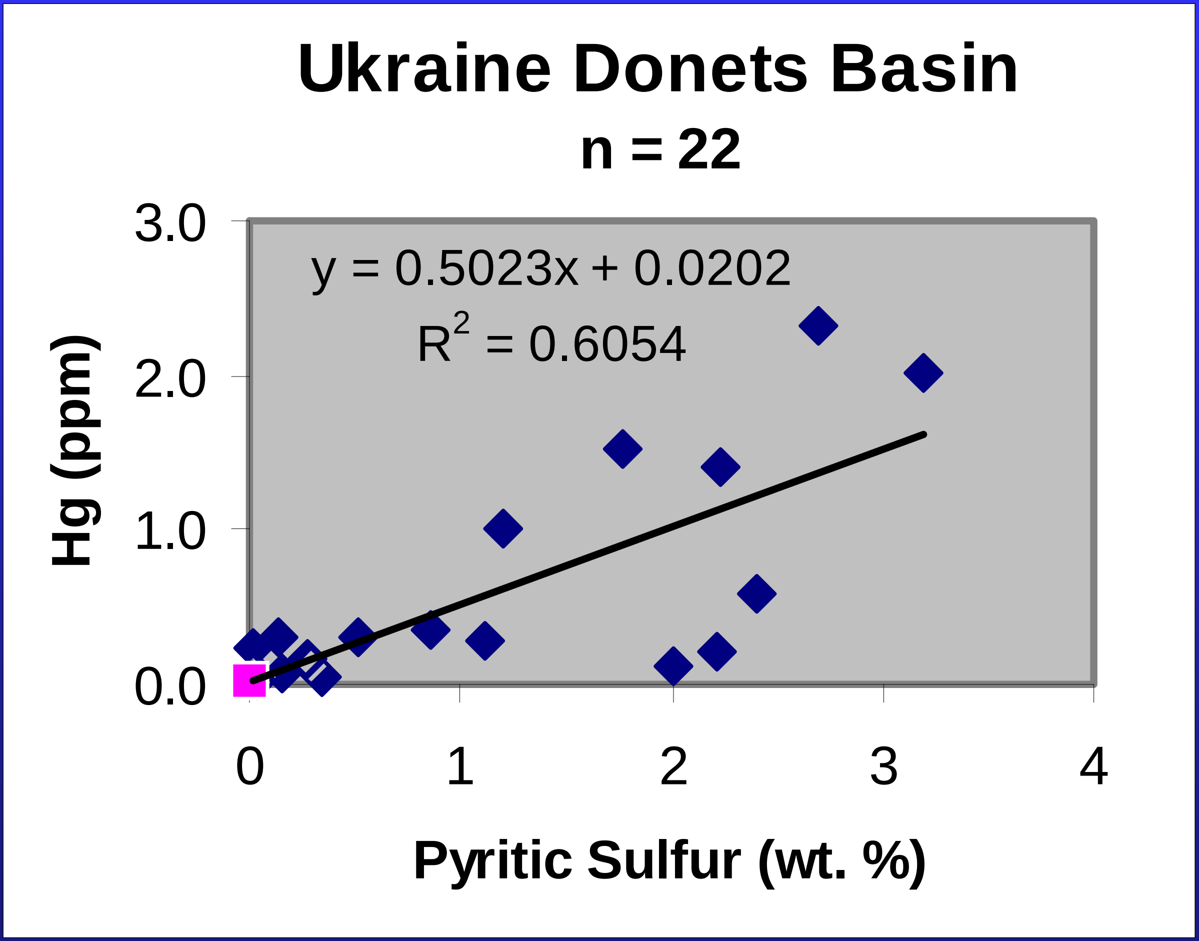


Comparison of mercury distribution in Kittanning and Freeport Coals.

From: Quick et al. , *2003, Environmental Geology*

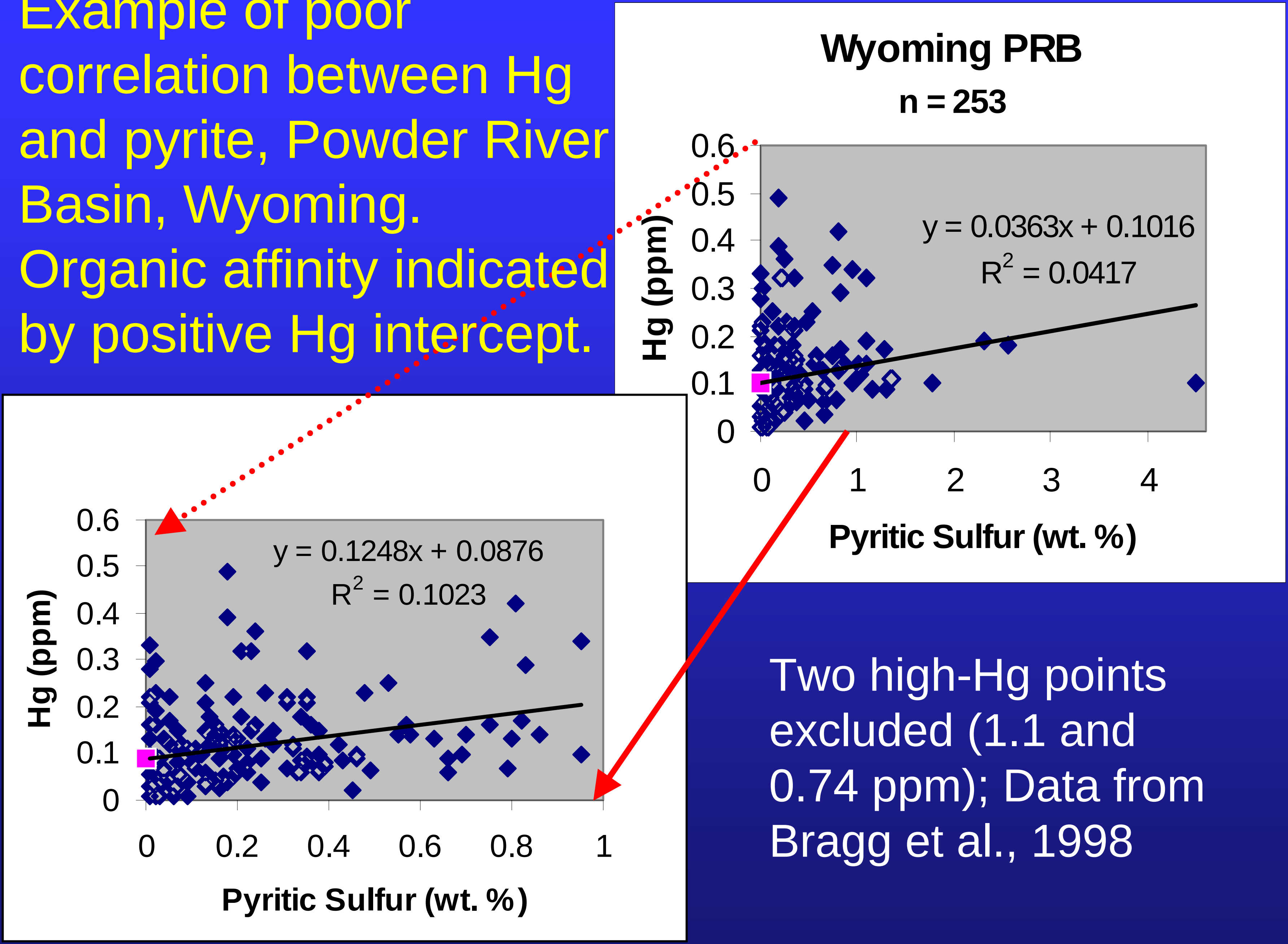
Example of Hg variation controlled by pyrite

One outlier (Hg = 4.5 ppm) removed



Source: Modified from Kolker et al., 2002

Example of poor correlation between Hg and pyrite, Powder River Basin, Wyoming. Organic affinity indicated by positive Hg intercept.



Two high-Hg points excluded (1.1 and 0.74 ppm); Data from Bragg et al., 1998

Selenium in Coal

- Important organic association indicated by most studies.
- Measurable Se in some pyrite; May contribute Se to ground water upon pyrite oxidation.
- Selenides (eg. PbSe) common in coal, unlike other sediments.
- Sensitive to in-situ oxidation, but less so than As.

Chromium in Coal

- Silicate (illite) and organic-hosted forms are dominant.
- Cr may also occur in Fe-Ti-Cr oxide minerals, if present.
- Not prone to in-situ oxidation in coal, unlike Fe, As, Se.

Source: Huggins et al., 2002

Chlorine in Coal

- Chlorine content is an important parameter because of corrosive effects of HCl and Hg-Cl complexing in coal-fired power plants.
- Chlorine contents are strongly influenced by salinity or paleo-salinity.
- Salinity increases with depth or paleo-depth.

Chlorine in Appalachian Coal

Basin	Average Cl in Coal (ppm)*
Northern Appalachian	850
Central Appalachian	950
Southern Appalachian	310

*Results for Bragg et al., 1991

Chlorine Stratigraphic Variation

Age	Formation	Number of Samples	Mean Cl (ppm)
Lower Permian (?)	Dunkard Group	44	162
Upper Pennsylvanian	Monongahela Formation	73	477
Upper Pennsylvanian	Conemaugh Formation	41	828
Middle Pennsylvanian	Allegheny Formation	709	1097
Middle Pennsylvanian	Kanawha Formation	36	1408
Lower Pennsylvanian	New River Formation	56	1503

Results for Bragg et al., 1991

Trace Metals in Coal Macerals

- Limited number of determinations, in-situ or on maceral separates.
- Information on vitrinite, liptinite and inertinite groups.
- Large variation within and between coals:
  sub-ppm: Hg
  sub-ppm to few ppm: Sb, Th, U
  ppm to 10’s ppm: Cr, Ni, As, V
  ppm to 100’s ppm: Fe, Mn

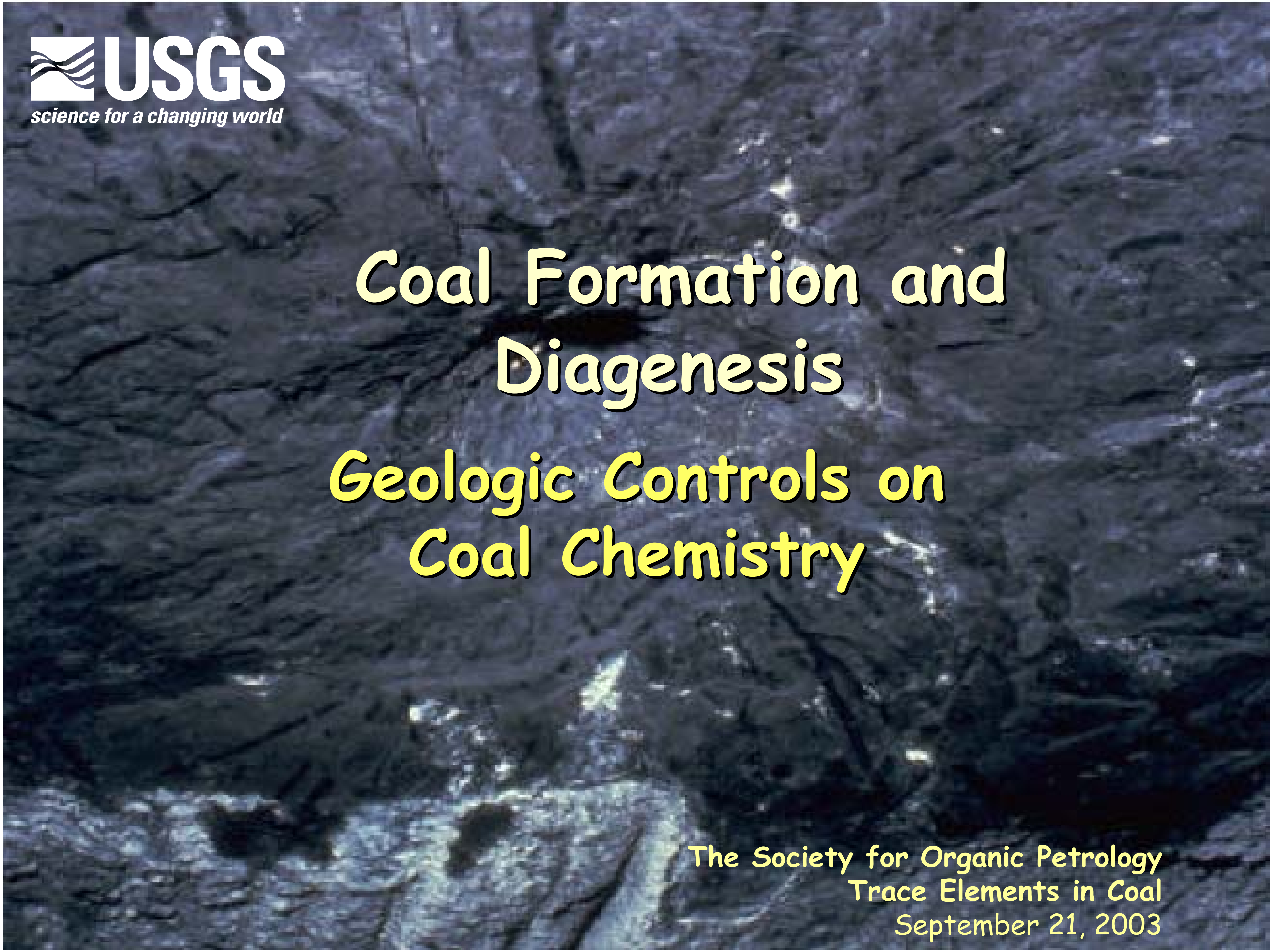
Source: Kolker and Finkelman, 1998

Summary - Trace Metals in Coal

- Arsenic:
  - Arsenic-bearing pyrite is dominant form in fresh bituminous coals.
  - Oxidized form (arsenate) is a function of the degree of pyrite oxidation.
  - Greater organic fraction in low-rank coals.
- Chromium:
  - Illite and organic forms are dominant.
  - Oxidation state all Cr(III) in coal; rare Cr(VI) in ash.
- Mercury:
  - Pyrite is most significant host of Hg.
  - Organic fraction is greater in low-rank coals.

Trace Metals in Coal- continued

- Selenium:
  - Exhibits multiple forms; common to have a significant organic fraction, even in bituminous coals.
  - Oxidation state changes with pyrite decomposition, but less so that Fe, As.
- Chlorine:
  - Chlorine content variable; controlled by salinity or paleo-salinity.
  - Affects Hg emissions by Hg-Cl complexing.
- Macerals:
  - Largest fraction of trace elements in low-rank coals.
  - May be a significant host of transition metals.



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Coal Formation and Diagenesis

Geologic Controls on Coal Chemistry

The Society for Organic Petrology
Trace Elements in Coal
September 21, 2003

Conclusions

The concentration, variation (both laterally and vertically), and modes of occurrence of trace elements are controlled by geologic and geochemical processes that begin in the peat stage of coalification and continue thru coalification and exploitation.

If we understand the processes that control elements we have a good chance of predicting: 1) where elements are; 2) how they are bound; and 3) what will happen to elements during coal utilization.

What controls coal quality?

Allogenic controls

- Climate
- Tectonism
- Eustasy

Autogenic controls

- Depositional environment
- Hydrology
- Sediment influx
- Alteration within peat body
- Diagenetic reactions
- Rank
- Weathering

Allogenic Control 1

Climate

Controls the type of peat, the type and rate of vegetation, and sediment input into the mire or peat swamp.

Allogenic Control 1

Domed (convex upward) peat:

- *Ever-wet, tropical climates* - domed, rain-fed (ombrogenous) peat bodies. (Sumatra foreland basin, L. Mississippian to mid-Middle Pennsylvanian Central Appalachian Basin coals: includes Pocahontas, Fire Clay, Winifred/Stockton coals.)

Doming, radial drainage, flushing.
Low in nutrients: eolian input, dissolved solids minimal.
Limited buffering capacity, rapid peat development.
Minimal degradation of organic matter.
Upland soils anchored

Allogenic Control 1

Planar (flat-lying) peats

Seasonally-wet, more temperate climates–planar, ground-water and rainwater-fed (rheotrophic) peat bodies. (U.S. coastal swamps; late Middle to U. Pennsylvanian Appalachian basin coals).

High sediment/nutrient input – eolian, fluvial, and groundwater.
Leaching can be high.
Relatively high pH (>4); organics degraded.

Allogenic Control 2

Tectonism

Controls rate of base level change – climatic fluctuations may raise or lower water table but need base level rise to build up thick peat.

Fluctuations in base level dependent on tectonic subsidence, eustasy, and compaction.

For the preservation of economic coals need a continuous rise in groundwater (subsidence) and relatively low relief of hinterlands to restrict sediment influx. These conditions occur in foreland basins.

Model for Cretaceous coals of western U.S.

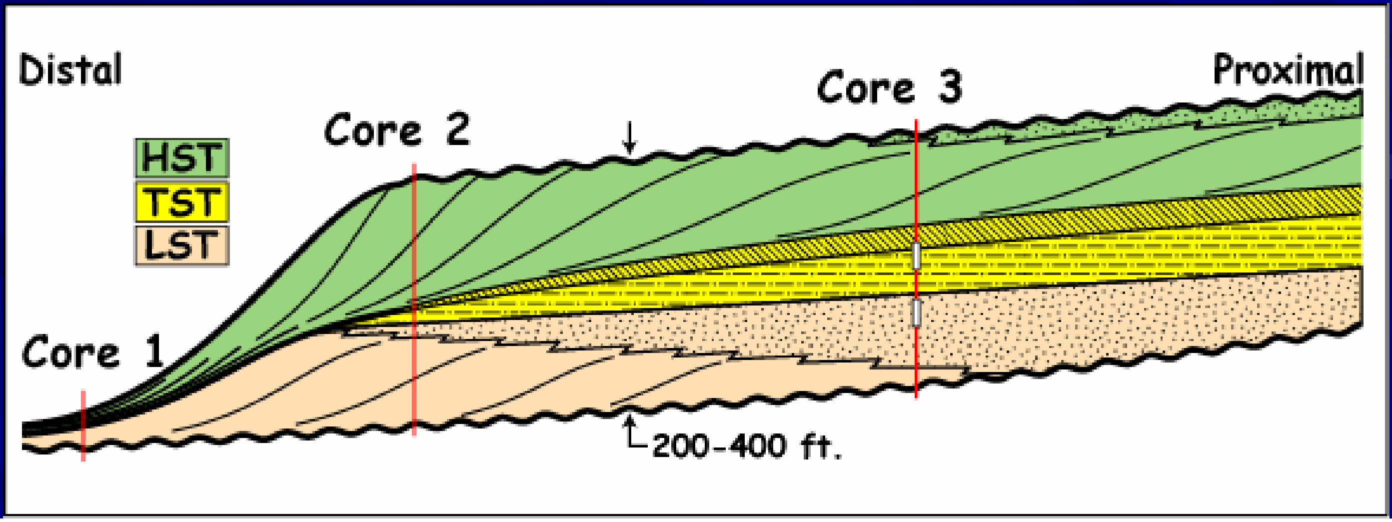
Allogenic Control 3

Eustasy

Increased water depths with marine flooding elevates water tables in non-marine and continental settings.

Elevated fresh water tables allow for plant growth, peat development, and coal preservation in the accommodation space.

Sequence stratigraphy concepts.



What controls coal chemistry?

Autogenic controls

Depositional environment
Hydrology
Sediment influx
Burial
Alteration within peat body
Diagenetic reactions
Rank
Weathering

Depositional Environment & Geologic Setting

Affects geometry, extent, and boundaries of peat bodies.

Affects bed and dissolved load of streams and peat swamp.

Controls underlying substrate.

Exerts a control on ground-water chemistry.

Autogenic Controls

Hydrology

CONTROLS, TO A LARGE EXTENT, GEOMETRY

Ombrotrophic peats (rainwater-fed)

Low in ash – few dissolved solids.
Often domed – limits detrital influx.
Sediment input-eolian volcanics and dust.
Highly acidic.
Low diversity of plants, stunted in middle.

Rheotrophic peats – (groundwater-fed)

High in dissolved solids.
Often planar.
Sediment-rich.

Mesotrophic peats (ground-and rainwater)

Intermediate in ash.

Autogenic Controls

Sediment Input

www.noaa.gov

Eolian Sources (domed and planar)

Dust

Volcanic ash-fall material – amphibole, pyroxene, quartz, feldspar, glass, etc.

Cosmic dust

Sea-spray

Water-born sources (predominantly planar, edges of domes)

Dependent on geologic setting

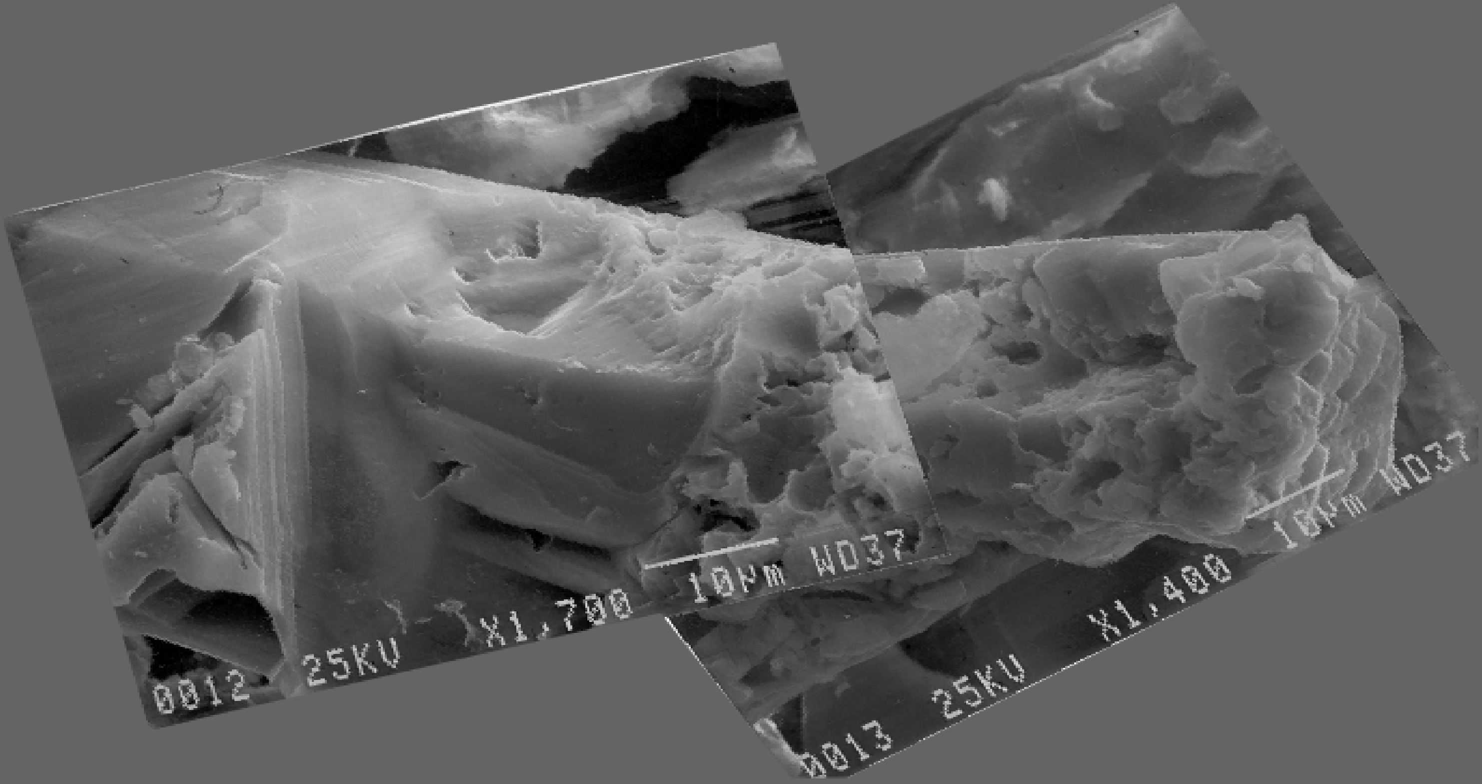
Rate and amount must be low

What gets into the peat doesn't necessarily stay there:

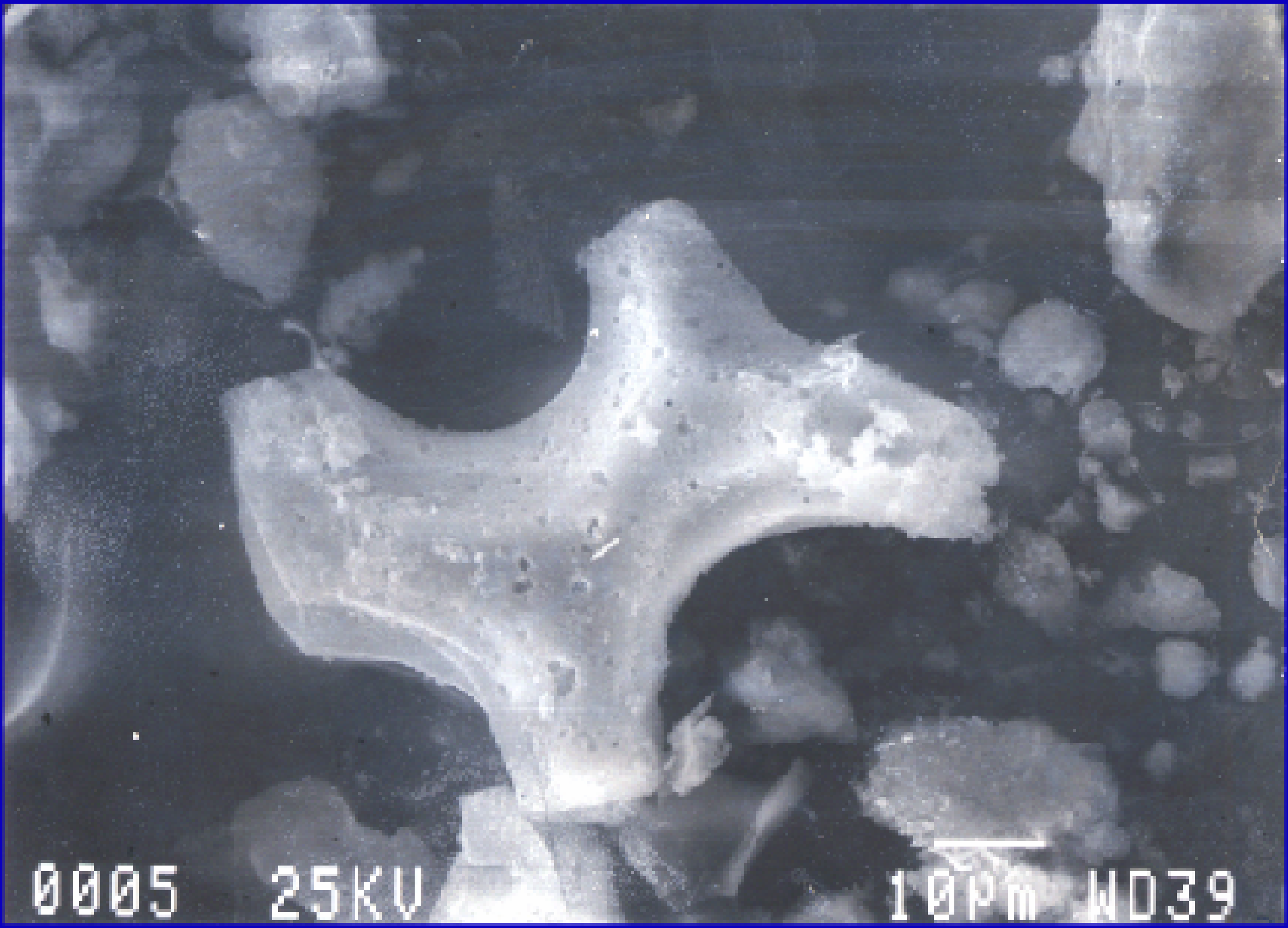
With production of multiple organic acids:

- Dissolution and alteration of mineral matter.
- Loosely bonded organic and inorganic complexes can break.
- Inorganic elements can bond with different organic complexes or become incorporated in syngenetic mineral phases.
- Ions available from ground and surface waters can be incorporated in minerals.

* Organically-associated elements are the most likely to be mobilized during diagenesis. These elements can be leached from the system or re-precipitated into epigenetic mineral phases. *



Etching of an eolian, volcanic quartz grain from a domed Indonesian peat by organic acids.



Disassociated elements can recombine into other authigenic phases, be flushed from the system, or bond to organics.

Peat Preservation and Burial

To preserve peat you need:

Anoxic conditions - control the rate and degree of humification (decay within peat profile).

Very acidic conditions - generation of humic acid from organics.

Burial must be rapid.

Subsidence must be rapid.

What gets into the peat doesn't necessarily stay there:

After burial:

As rank increases, organic bonds weaken, releasing elements.

Elements continue to be moved around.

Elements added, subtracted, and moved within the system.

Epigenetic mineral phases form.

Leaching continues.

Cleat

Two types of cleating:

1 – Moisture/volatile loss – occurs once moisture falls below about 20% (sub-bituminous range).

2 – Tectonic forces/differential compaction.

Cleats can be coated with minerals, then further infilled.

Cleat infilling – pyrite, kaolinite, sphalerite, calcite, gypsum, etc.

Multi-generational cleat infilling not uncommon.

Faults

Faults can act as conduits for fluid flow in coals and coal basins.

Example – Warrior Basin, Alabama

Credit: M. Goldhaber, USGS

Weathering

Atmospheric weathering and action of ground waters effect the elemental and mineral composition of coal beds.

Development of new suites of minerals
- oxidation (pyrite to sulfate);
- inclusion of water in clay lattice – (allophane)

Removal of some remaining organically-bound minerals.

Removal of some organics concentrating inorganic elements.

Conclusions:

1 – Coal quality results from a continuum of processes that start in the peat stage and continue through coalification.

2 – Geometry of a peat body (planar vs. domed) factors heavily in the quality of the resulting coal.

The concentration, variation (both laterally and vertically), and mode of occurrence of elements are controlled by geologic and chemical processes that start during peat development and continue through coalification. Understanding those processes will allow us to predict coal quality trends before mining.

Overview of Bulk Analytical Methods and USGS Selective Leaching Procedure

Curtis Palmer

U.S. Geological Survey

Bulk Analytical Methods: Coal Quality Characterization

- ASTM Procedures
  - USGS uses contract labs such as Geochemical Testing and Wyoming Analytical Laboratories
- Major and Trace Elements
  - Uses procedures developed by USGS some of these are included in ASTM procedures and are preformed by USGS personnel

ASTM Procedures

- Ultimate analysis:
  - ASTM D3176-D3179
  - Moisture, C, H, O, N, total S
- Proximate analysis
  - ASTM D3172-D3175
  - Moisture, volatile matter, fixed carbon and ash
- Other techniques
  - Sulfur forms, calorific values,
  - Hardgrove grindability free swelling index, ash fusability,
  - Specific gravity, equilibrium moisture

Analytical Methods Overview and Relative Merits

- Methods to be covered (Elemental Analysis)
  - Routine Methods
    - Multi-Element Techniques
      - Inductively Coupled Plasma- Atomic Emission Spectroscopy (ICP-AES)
      - Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS)
    - Single Element Techniques
      - Cold Vapor Atomic Absorption (CVAA; Hg)
      - Hydride Generation Atomic Absorption (HGAA; Se)
  - Non-Routine Methods
    - Instrumental Neutron Activation analysis (INAA)

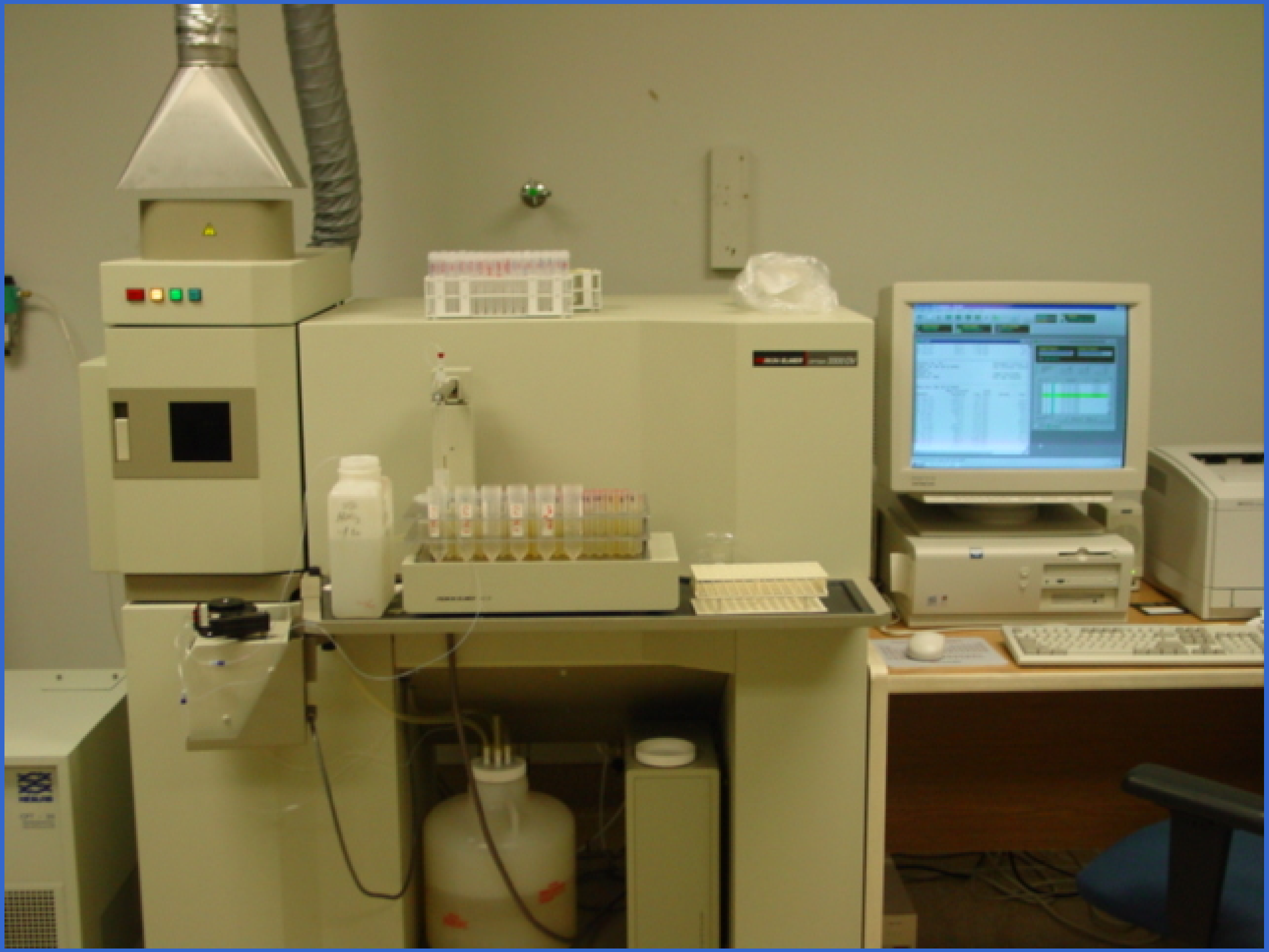
- Sample Preparation:To Ash or Not to Ash
  - – Advantages of Ashing
    - Increases concentration and apparent detection limits
    - Makes it easier to place many elements into solution
    - Ash is more stable for long term storage (Archiving)
    - Can improve homogeneity

- Disadvantages of Ashing
  - Some elements may volatilize
    - Volatility may be matrix dependent
    - Amounts volatilized may be different for each sample and element
    - Occasionally elements not normally considered volatile are volatile for a given sample
    - Potential of cross-contamination of volatile components
  - Larger sample needed
  - Additional steps and time
    - Elements may need to be recalculated to a whole coal basis
    - Care must be taken to ensure ashing is complete
  - Mechanical losses can effect results

- Ashing Procedure– USGS – Similar to ASTM
  - Samples heated from 25 ^{o}C to 200 ^{o}C in about 1 hour
  - Samples heated at 200 ^{o}C for 1.5 hrs
  - Temperature increased to 350 ^{o}C and held 2 hrs
  - Temperature increased to 525 ^{o}C and held 36 hrs
  - Samples slowly cooled (1-2 hr)
  - Samples examined and re-ignited at 525 ^{o}C if necessary
  - Samples homogenized

- Methods requiring ashing
  - ICP-AES
    - Advantages
      - Rapid
      - Low Cost
      - Multi-element
    - Disadvantages
      - Requires dissolution of ash
      - Moderate sensitivity

USGS ICP-AES



- Two dissolution procedures (sinter and acid digest)
  - Sinter (Ash fused at 445 ^{o}C with Na_2O_2)
    - » Advantages
      - -- Dissolves species difficult by acid dissolution
      - -- Conserves volatile elements during acid dissolution
    - » Disadvantages
      - -- High dissolution ratio reduces sensitivity
      - -- High salt content can cause instrument problems
    - » Elements Determined
      - -- Major elements in ash except Na
      - -- Trace elements: B, Ba, Zr

–Acid Digest

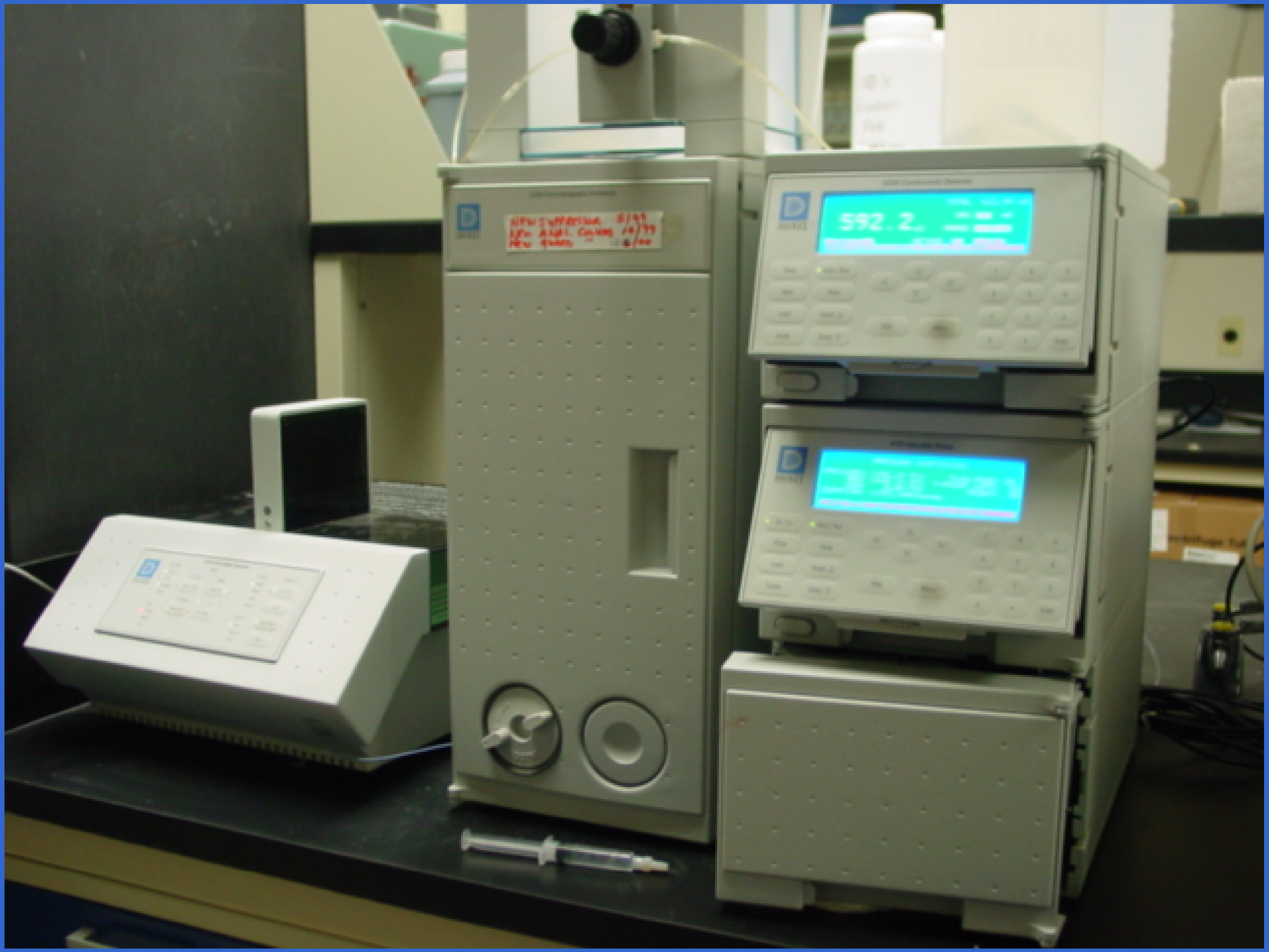
- » Advantages
  - --Low dissolution ratio--Higher sensitivity
  - --Low salt content no Na contamination
- » Disadvantages
  - --Some elements are volatile, eg. B, Se, Cl
  - --Some elements are associated with insoluble minerals, eg. Zr, Ba
- » Elements Determined
  - -- Major element: Na_2O
  - -- Trace elements: Be, Co Cr, Cu, Li, Mn, Ni, Sc, Sr, Th, V, Y, Zn

- ICP-MS
  - Much higher sensitivity (10 to 1000 times)
  - Higher cost instrument
  - Some elements have interferences– poorer results than ICP-AES; Others similar results to ICP-AES
  - Same dissolutions as ICP-AES but sinter dissolution is not routinely analyzed because the use of the highly ionic solution requires special setup and require additional maintenance
  - Acid digest: Ag, As, Au, Bi, Cd, Cs, Ga, Ge, Mo, Nb, Pb, Rb, Sb, Sn, Te, Tl, U
  - Sinter: 13 Rare earth elements, Hf, Ta and W

USGS ICP-MS

- Whole Coal Techniques
  - Cold Vapor Atomic Absorption (CVAA)
    - Single element (Hg)
    - Requires dissolution
    - 5 to 10 percent of coals below detection limit of 0.02 ppm
    - Reliable and accurate (ASTM method)
  - Ion Chromotography
    - Single element Cl
    - Requires dissolution
    - Less than 5 percent of coals below detection limit of 150 ppm
    - Reliable and acurate

USGS Ion chromotragraph



- Hydride generation atomic absorption (HGAA)
    - Single element (Se)
    - Requires dissolution
    - Several elements (especially heavy and transition metals) in high concentrations can interfere with results
- Instrumental neutron activation analysis (INAA)
    - Time consuming multi-element technique
    - Highly linear—few interferences
    - Small sample size
    - No ashing or dissolution required
    - High sensitivity
    - High cost– requires nuclear reactor
    - Elements include: Na, K, Fe, Sc, Cr, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th, U
    - Other elements possible Al, Ca, Mg, Ti, S, V, Cl, I, Mn, Dy, Hg

Quality Control and Quality Assurance

- Accuracy – degree of agreement between the measured value to the “true” or proposed value
- Standard Reference Materials
    1. CLB-1 – coal
    2. NIST 1632b – coal (bituminous)
    3. NIST 1633a – coal fly ash
- Certified Calibration Standards
- Precision – degree of agreement between measured values under repetitive testing of a sample; reproducibility of results
- Duplicate samples

- References
  - Visit our web site: energy.er.usgs.gov/products/papers
    - Click Palmer, C.A., 1997, The chemical analysis of Argonne Premium Coals: U.S. Geological Survey Bulletin 2144 or enter energy.er.usgs.gov/products/papers/B2144
    - Click Golightly, D.W., and Simon, F.O., 1989, Methods for Sampling and Inorganic Analysis of Coal: USGS Bulletin 1823 or enter energy.er.usgs.gov/products/papers/B1893
    - Click Swanson, V.E. and Huffman, C., Jr. 1976, Guidelines for sample collecting and analytical methods used in the U.S. Geological Survey for determining chemical composition of coal: United States Geological Survey Circular 735 or enter energy.er.usgs.gov/products/papers/C735

Summary

- Multi-element techniques provide methods to obtain a large and varied amount of data in a relatively short time.
- Cost of instruments for multi-element techniques can be very high.
- Some elements in coal can not be determined using multi-element techniques due to volatility and problem matrices.

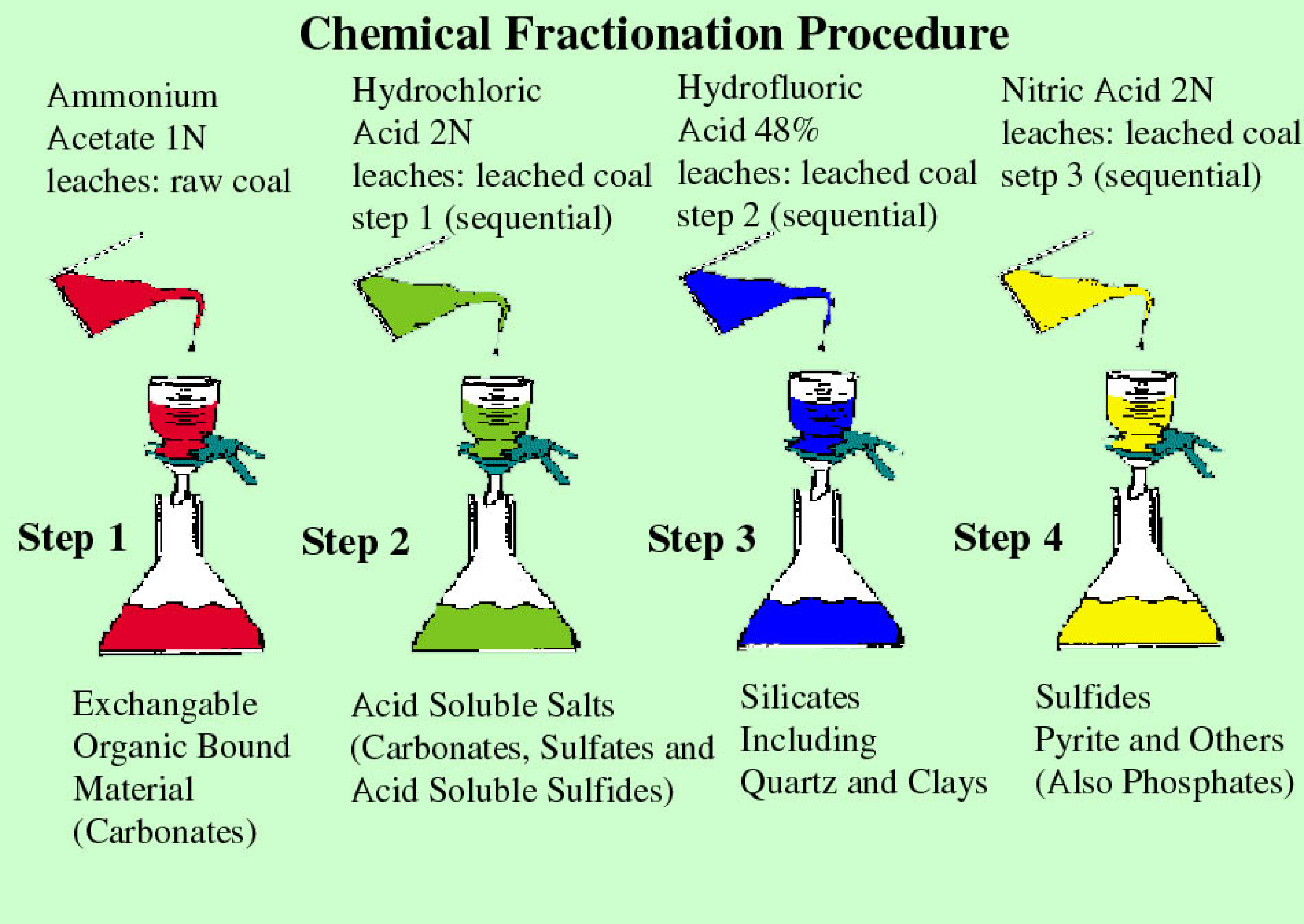
Modes of Occurrence of Elements in Coal

- Selective leaching
- Scanning electron microscopy
- Microprobe Analysis

Overview of Leaching Procedure

- A Multi-Element Semi-Quantitative Approach
  - Semi-Quantitative Leaching Results
  - Microprobe Analysis– Concentration of elements in minerals
  - Qualitative SEM– Mineral identification in whole samples and leached residues
  - Semi-quantitative XRD– Concentration of minerals in coal

Leaching Procedure



Chemical Fractionation Procedure

Ammonium
Acetate 1N
leaches: raw coal

Step 1

Exchangable
Organic Bound
Material
(Carbonates)

Hydrochloric
Acid 2N
leaches: leached coal
step 1 (sequential)

Step 2

Acid Soluble Salts
(Carbonates, Sulfates and
Acid Soluble Sulfides)

Hydrofluoric
Acid 48%
leaches: leached coal
step 2 (sequential)

Step 3

Silicates
Including
Quartz and Clays

Nitric Acid 2N
leaches: leached coal
setp 3 (sequential)

Step 4

Sulfides
Pyrite and Others
(Also Phosphates)

Sequential Leaching

- Duplicate, 5 gram 60 mesh samples are shaken in a centrifuge tube with 35 ml of Ammonium Acetate for 18 hrs
  - The resulting solution is saved for analysis by ICP-AES and ICP-MS
  - A 300 mg split of the resulting solid is analyzed by INAA and a 200 mg split is analyzed by CVAA for Hg. Additional splits may be taken for specialized experiments (XAFS, SEM, etc)

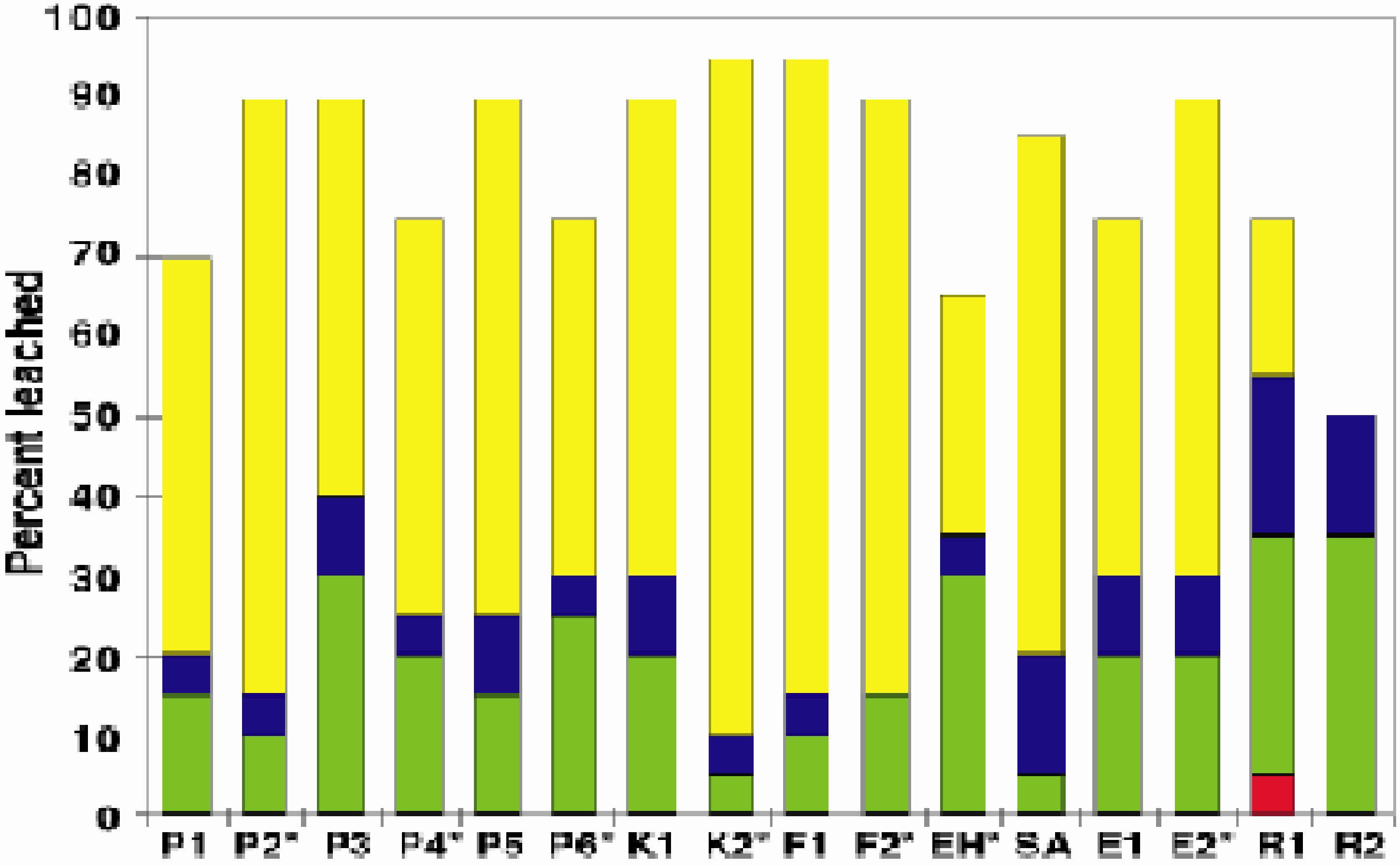
Sequential Leaching

- The remaining solid from each sample is leached in the same manner with hydrochloric acid (HCl) and subsequently with hydrofluoric acid (HF) with splits taken
- The remaining solid after leaching with HF is leached in a flask with nitric acid (HNO_3)
  - Procedure is similar to ASTM method for determining pyritic sulfur
  - Solutions and solid samples are analyzed as in other steps

Results

- Several Elements Are mainly associated with Pyrite as demonstrated by a large percentage of the element leached by HNO_3 (nitric acid)

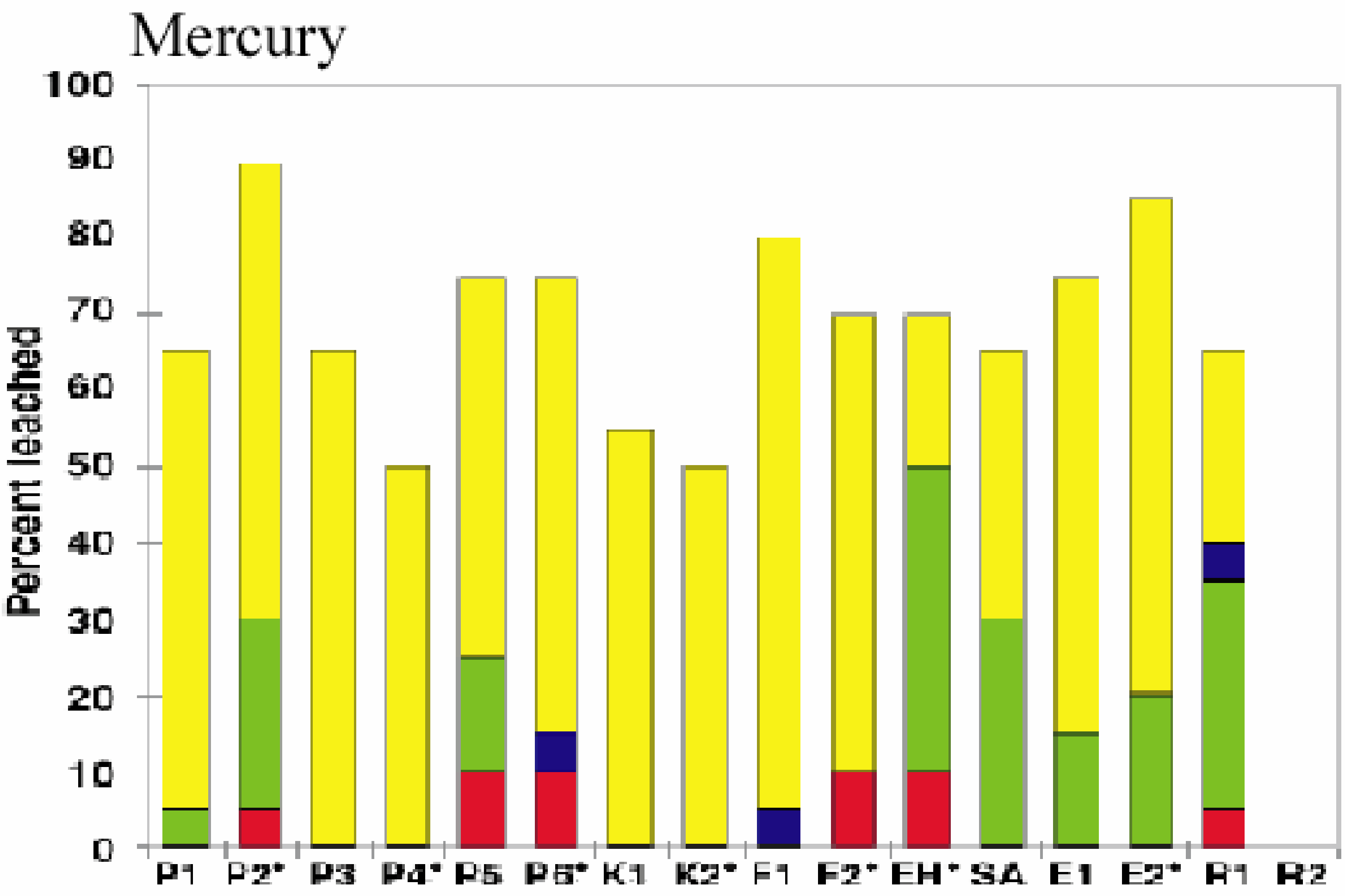
Arsenic



🟥 Ammonium Acetate
🟩 Hydrochloric Acid
🟦 Hydrofluoric Acid
🟨 Nitric Acid

Concentrations of As in the original coal samples in parts per million

P1	7.4	P5	13	F1	45	E1	7.2
P2	4	P6	4.5	F2	2	E2	2.3
P3	10	K1	13	EH	4.4	R1	1.5
P4	3.5	K2	4.7	SA	20	R2	1.2



🟥 Ammonium Acetate

🟩 Hydrochloric Acid

🟦 Hydrofluoric Acid

🟨 Nitric Acid

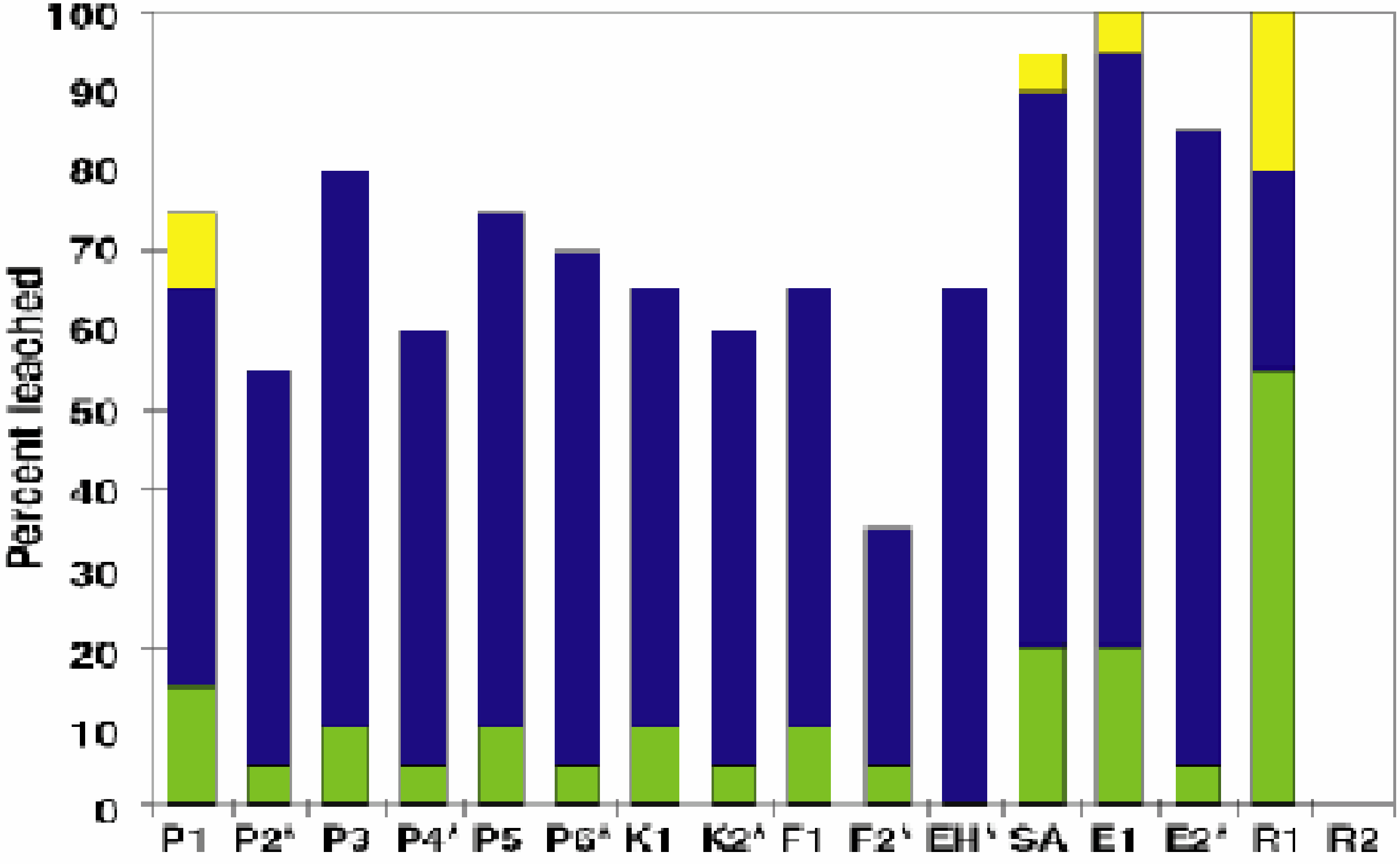
Concentrations of Hg in the original coal samples in parts per million

P1	0.09	P5	0.15	F1	0.5	E1	0.09
P2	0.09	P6	0.08	F2	0.4	E2	0.06
P3	0.13	K1	0.25	EH	0.05	R1	0.07
P4	0.06	K2	0.16	SA	0.1	R2	0.08

Results

- Other elements are mainly associated with silicates as demonstrated by a large percentage of the element leached by Hydrofluoric Acid.

Beryllium

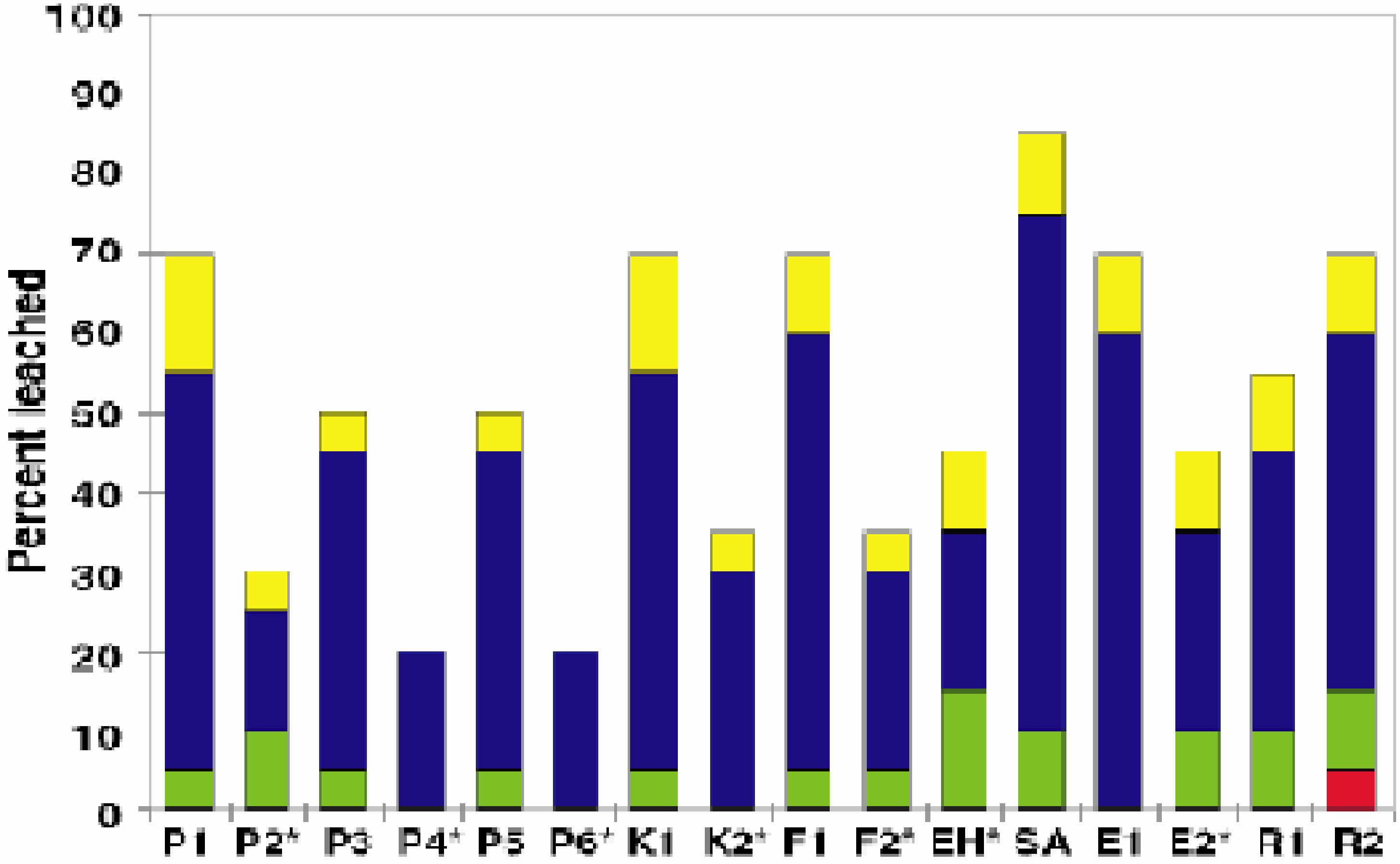


🟥 Ammonium Acetate
🟩 Hydrochloric Acid
🟦 Hydrofluoric Acid
🟨 Nitric Acid

Concentrations of Be in the original coal samples in parts per million

P1	1	P5	0.7	F1	3	E1	1
P2	0.6	P6	0.7	F2	2	E2	1
P3	0.9	K1	2	EH	12	R1	0.5
P4	0.8	K2	2	SA	31	R2	0.4

Chromium



🟥 Ammonium Acetate

🟩 Hydrochloric Acid

🟦 Hydrofluoric Acid

🟨 Nitric Acid

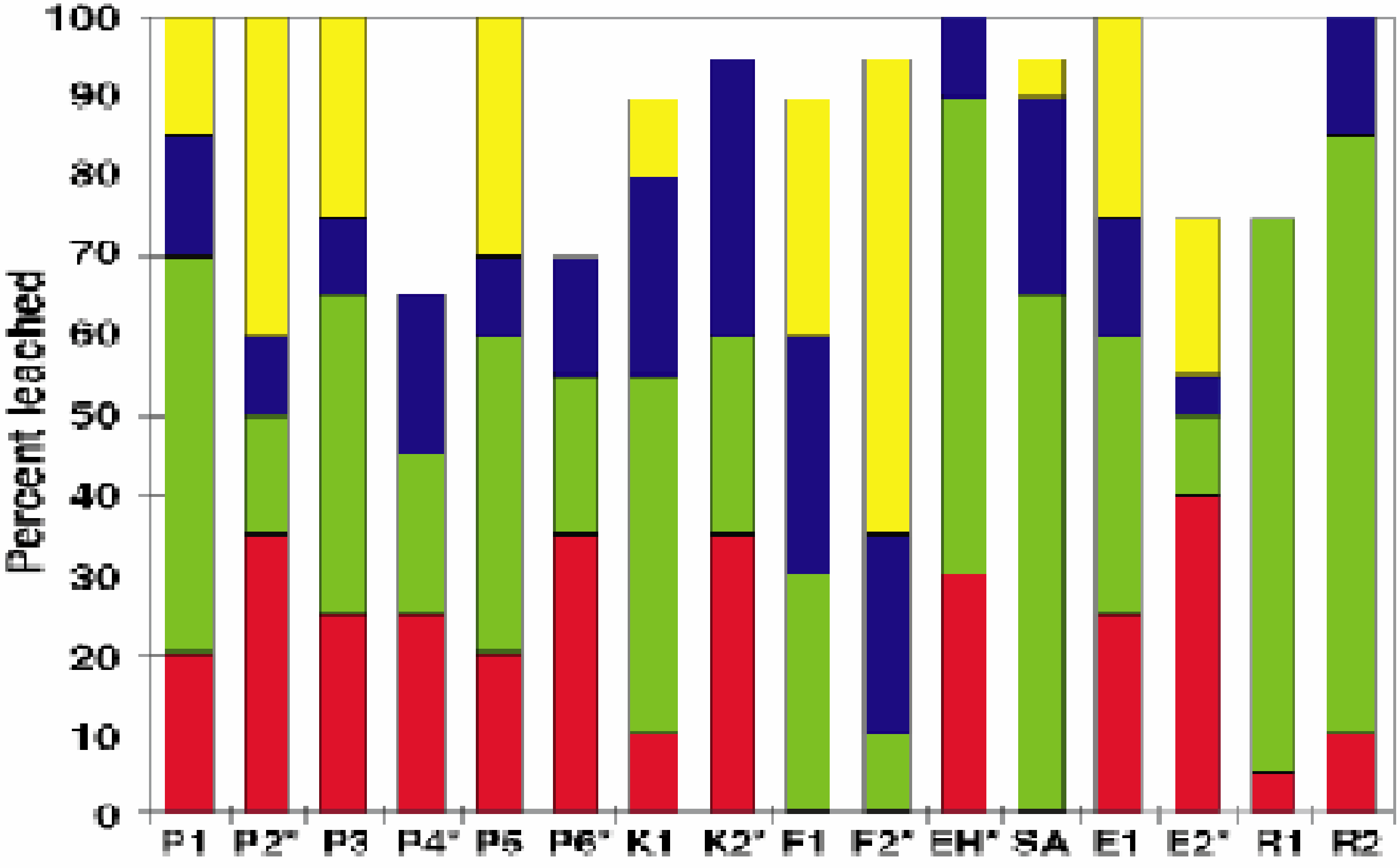
Concentrations of Cr in the original coal samples in parts per million

P1	31	P5	17	F1	33	E1	97
P2	9.7	P6	12	F2	15	E2	23
P3	20	K1	54	EH	18	R1	3.9
P4	12	K2	25	SA	62	R2	6

Results

- When the majority of a element is soluble with HCl then the element is likely associated with carbonates or monosulfides.
- Elements associated with calcite are partially soluble in ammonium acetate.

Manganese

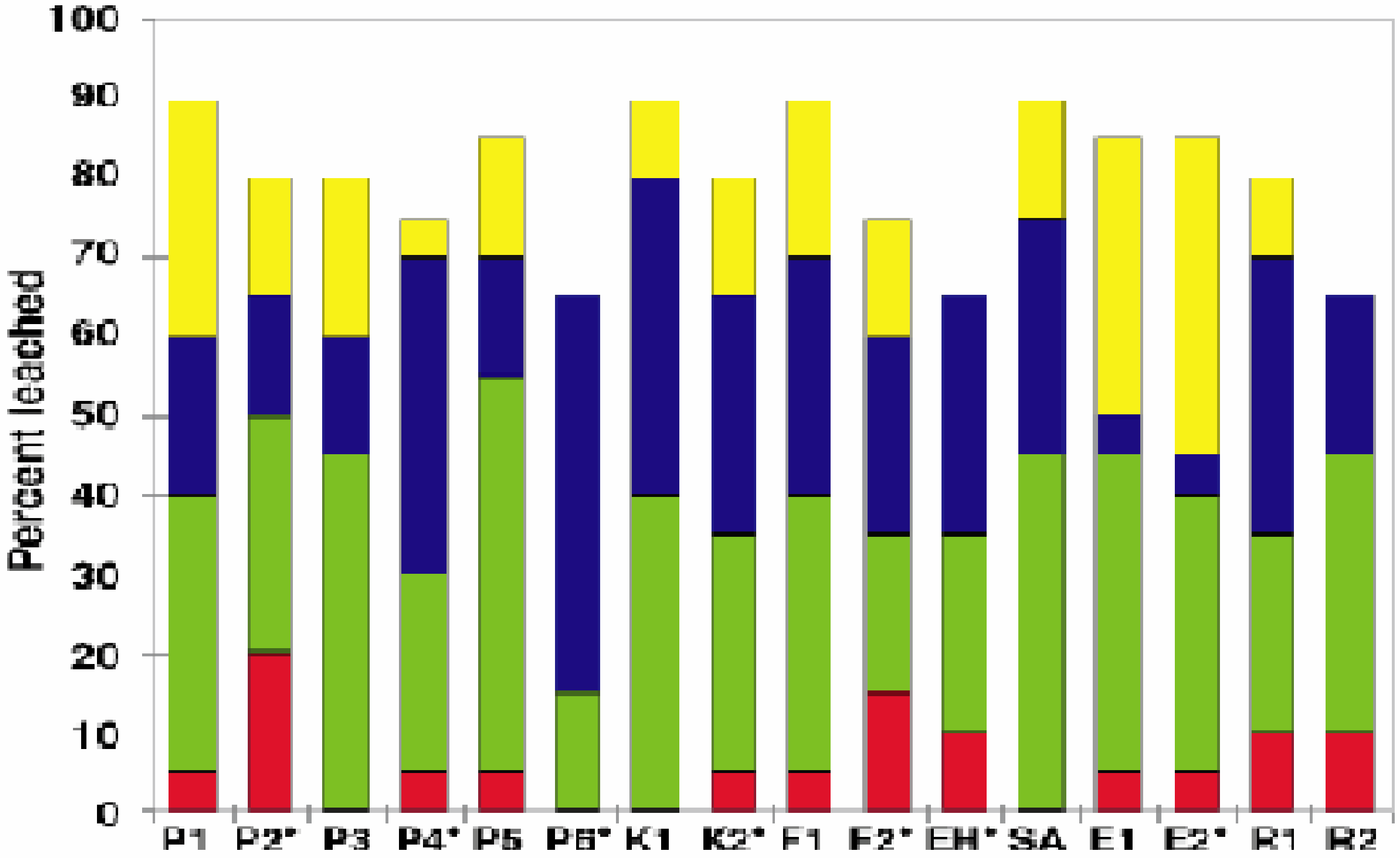


🟥 Ammonium Acetate
🟩 Hydrochloric Acid
🟦 Hydrofluoric Acid
🟨 Nitric Acid

Concentrations of Mn in the original coal samples in parts per million

P1	29	P5	35	F1	39	E1	94
P2	13	P6	16	F2	10	E2	37
P3	23	K1	57	EH	14	R1	150
P4	8.1	K2	7.4	SA	230	R2	8.7

Zinc



🟥 Ammonium Acetate
🟩 Hydrochloric Acid
🟦 Hydrofluoric Acid
🟨 Nitric Acid

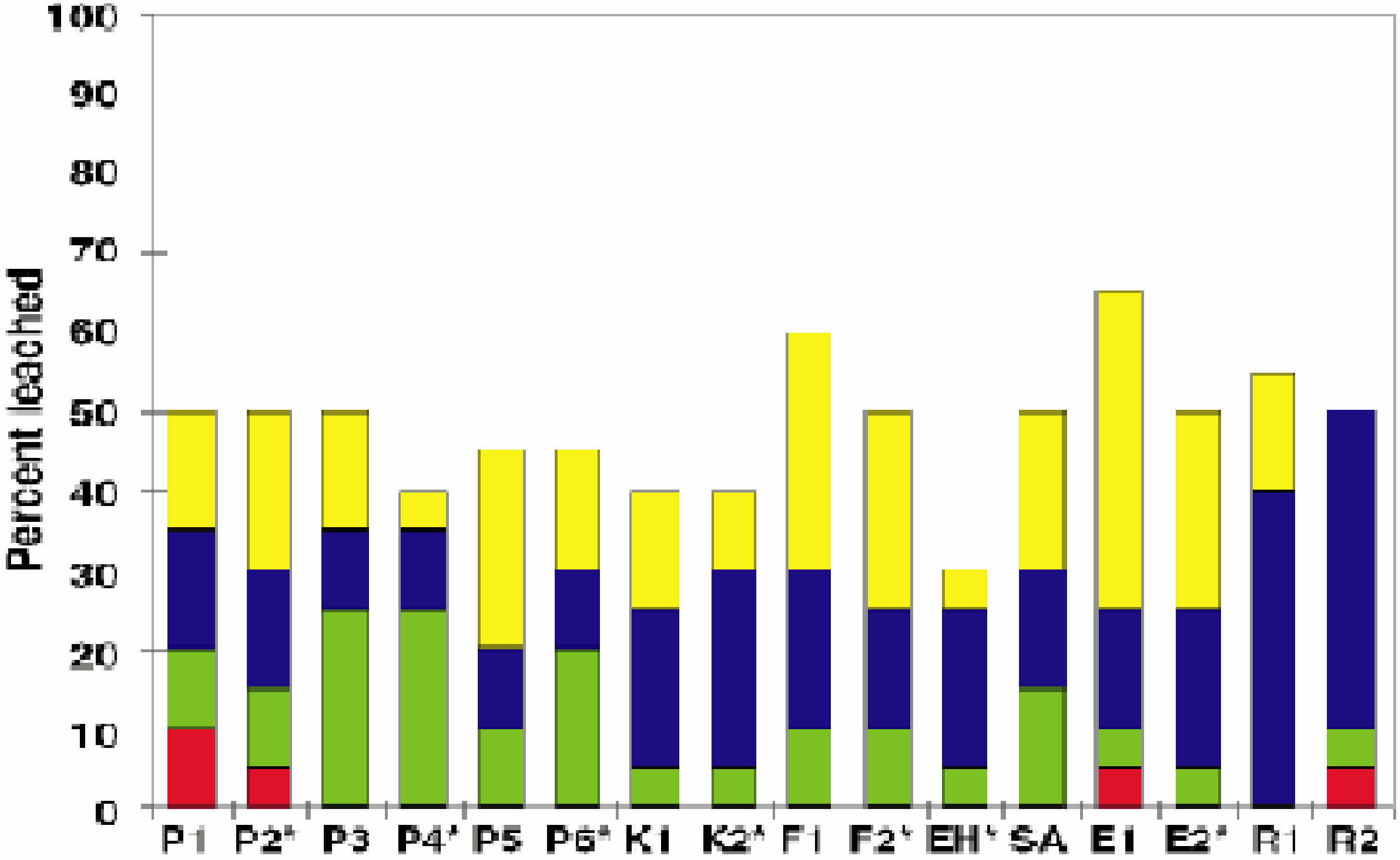
Concentrations of Zn in the original coal samples in parts per million

P1	25	P5	18	F1	34	E1	190
P2	9.3	P6	5.1	F2	13	E2	70
P3	18	K1	52	EH	6.6	R1	6.8
P4	7.6	K2	15	SA	60	R2	8.1

Results

- For some elements a significant fraction is unleached indicating that the element is organically associated
- In some cases mineral species are encapsulated or insoluble.
  - Examination by SEM can usually be used to determine encapsulated or insoluble species.

Antimony



🟥 Ammonium Acetate

🟩 Hydrochloric Acid

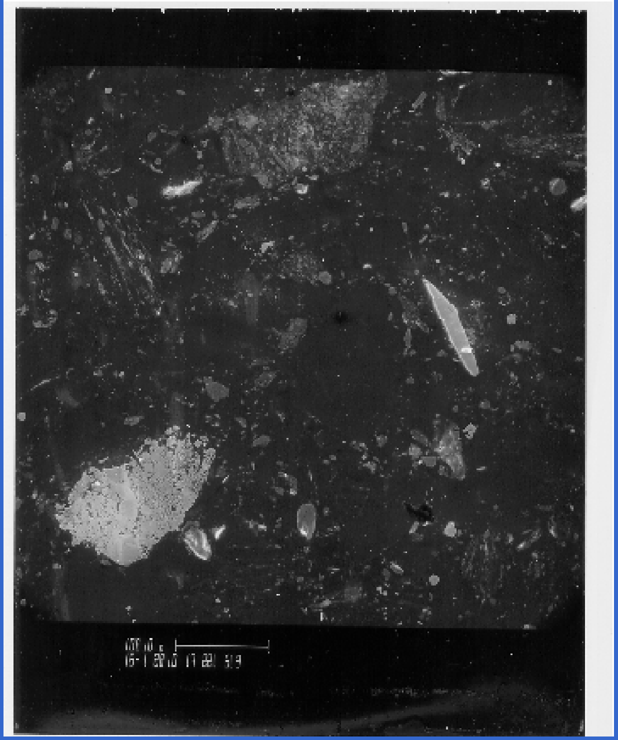
🟦 Hydrofluoric Acid

🟨 Nitric Acid

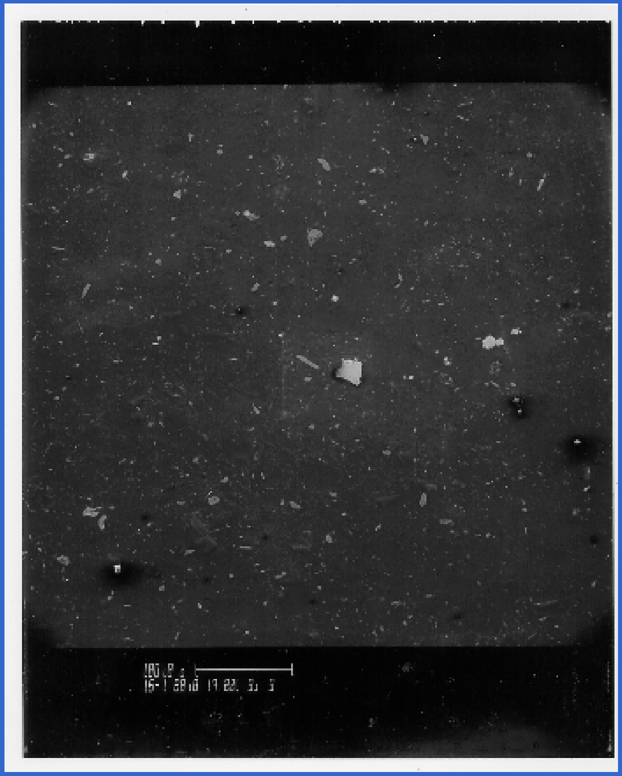
Concentrations of Sb in the original coal samples in parts per million

P1	0.72	P5	0.56	F1	0.62	E1	1.2
P2	0.29	P6	0.26	F2	0.48	E2	0.44
P3	0.49	K1	1.8	EH	1.1	R1	0.31
P4	0.31	K2	2.1	SA	1.6	R2	0.24

SEM comparison of original coal to leached coal



- Raw
- Minerals of all sizes



Demineralized

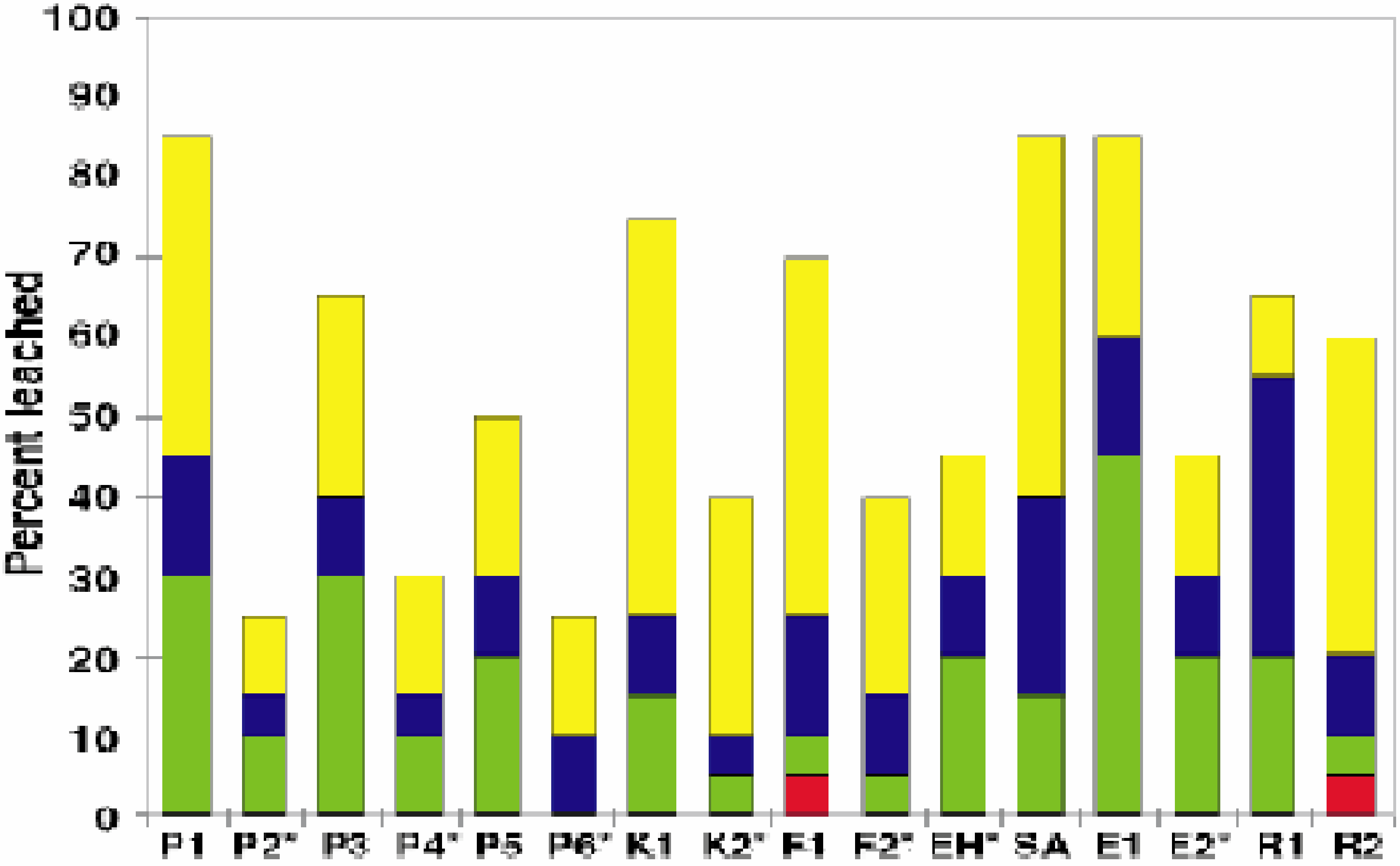
Small mineral grains

(mostly grinding compound)

Results

- Phosphates are also soluble in HCl
- Some elements can be in mineral forms especially phosphates encapsulated by silicates.
  - Produces significant amounts of element leached by HNO_3
  - Can be tested by leaching with HCl after HF leach

Thorium



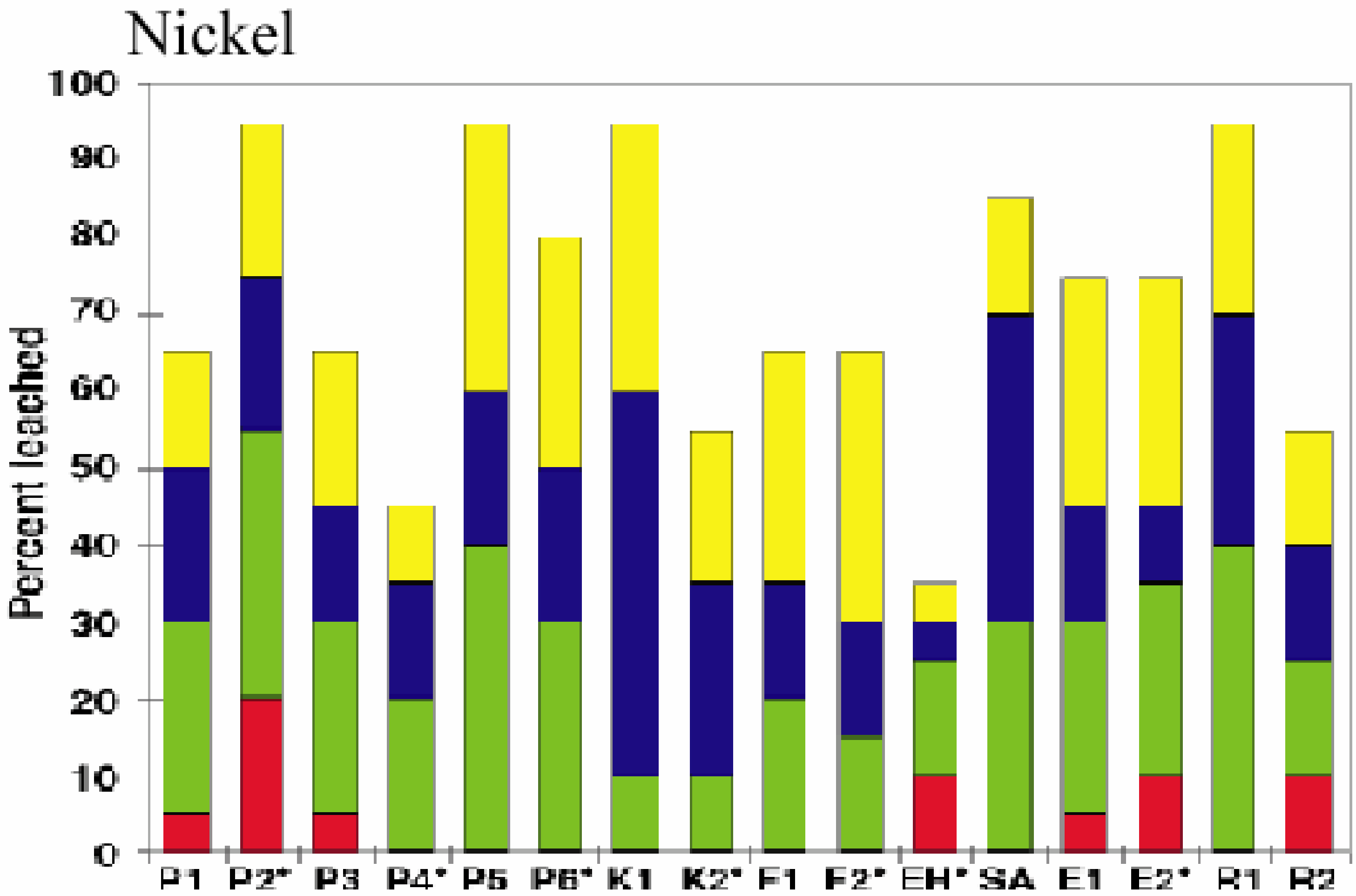
🟥 Ammonium Acetate
🟩 Hydrochloric Acid
🟦 Hydrofluoric Acid
🟨 Nitric Acid

Concentrations of Th in the original coal samples in parts per million

P1	4.3	P5	2.5	F1	4.5	E1	4.5
P2	1.2	P6	1.7	F2	1.9	E2	1.6
P3	2.9	K1	8.1	EH	3.8	R1	2.2
P4	1.5	K2	4	SA	8.7	R2	1.8

Results

- Leaching of some elements are not dominated by a single solvent
  - Multiple modes of occurrence
  - Said to by mixed modes of occurrence



🟥 Ammonium Acetate
🟩 Hydrochloric Acid
🟦 Hydrofluoric Acid
🟨 Nitric Acid

Concentrations of Ni in the original coal samples in parts per million

P1	22	P5	13	F1	24	E1	48
P2	6.6	P6	5.9	F2	16	E2	12
P3	15	K1	30	EH	12	R1	5.7
P4	7.9	K2	22	SA	31	R2	5.1

Conclusions

- The mode of occurrence can be semi-quantitatively determined by selective leaching
- Since each solvent dissolves more than one species supporting techniques (SEM, Microprobe etc.) are needed to determine exact mode of occurrence
- There is a great deal of consistency within a given rank of coal

Microanalysis and Spectroscopic Methods

Allan Kolker

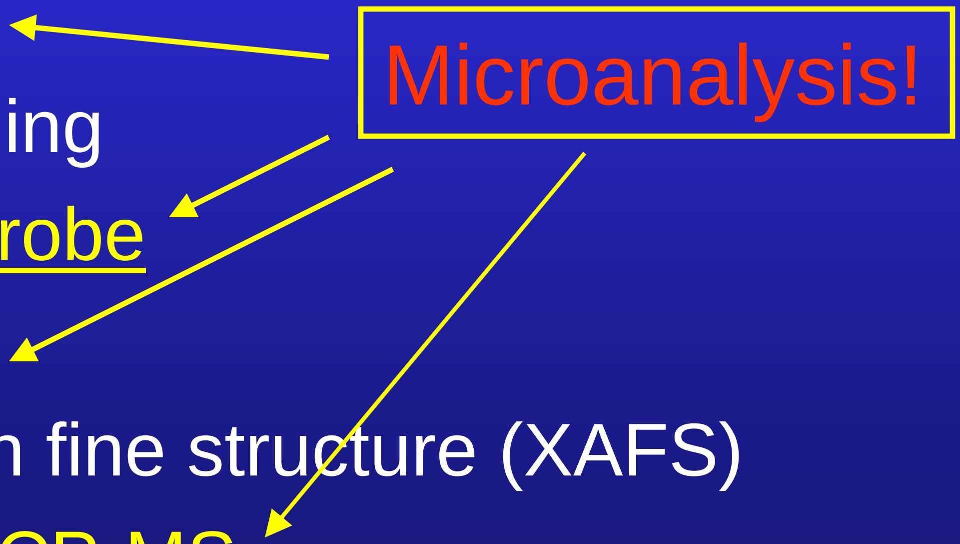
Leaching vs. Microanalysis

- Selective leaching is a bulk multi-element method.
- Interpretation is based on known or inferred leaching behavior.
- Leaching is constrained by element mass-balance.

- Microanalysis selects phases of interest on a microns scale.
- Microanalysis gives a direct analysis, where an appropriate method can be found.
- Not intended to achieve a mass balance.

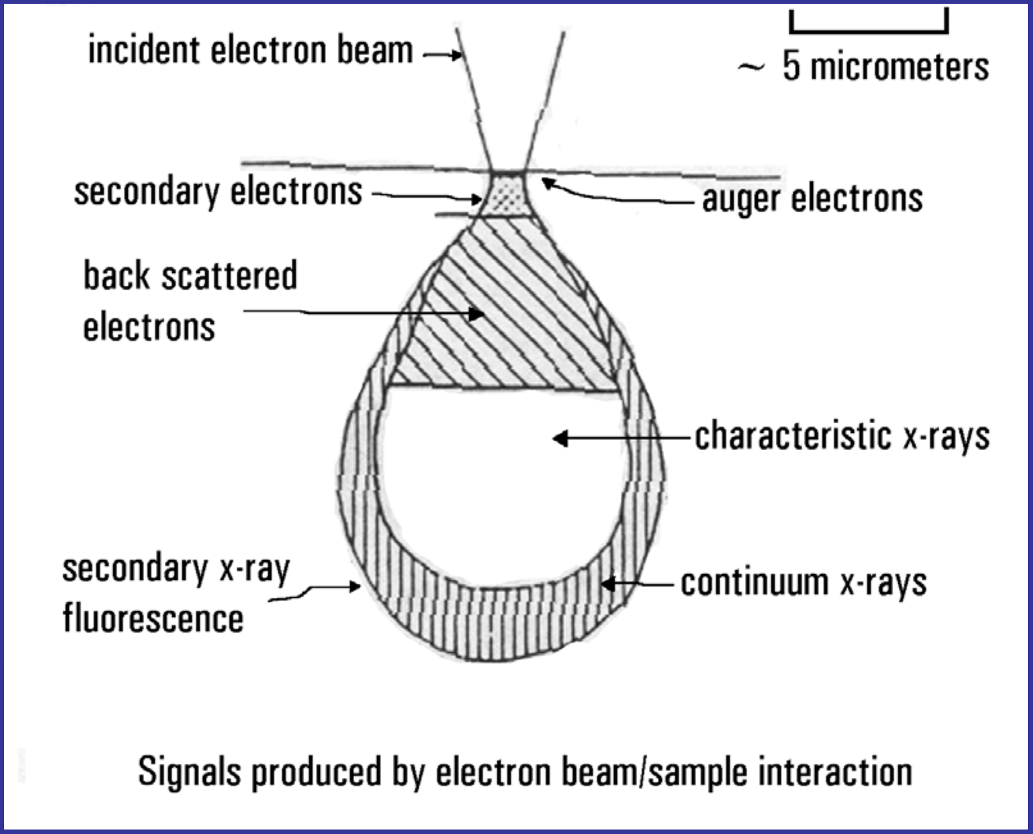
Methods of Determining Element Associations in Coal

- XRD Mineralogy
- Bulk Chemical Testing (INAA, ICP-AES, ICP-MS, XRF, etc.)
- SEM with BSE
- Selective Leaching
- Electron Microprobe
- Ion Microprobe
- X-ray absorption fine structure (XAFS)
- Laser Ablation ICP-MS



Microanalysis!

Electron-beam Instruments (SEM and Electron Microprobe)



Signals produced by electron beam/sample interaction

Secondary Electrons

(imaging)

Back Scattered Electrons

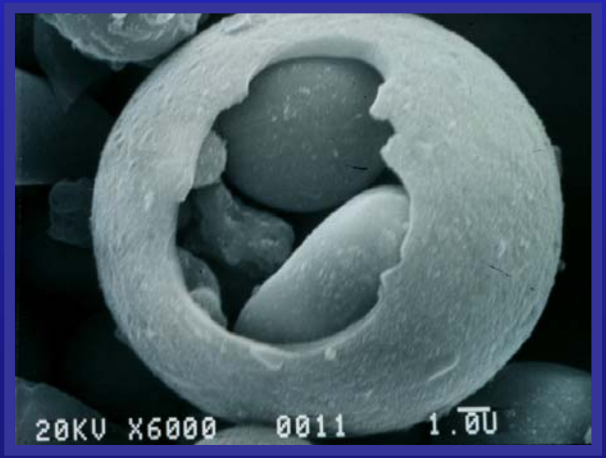
(imaging + comp.)

Characteristic X-rays

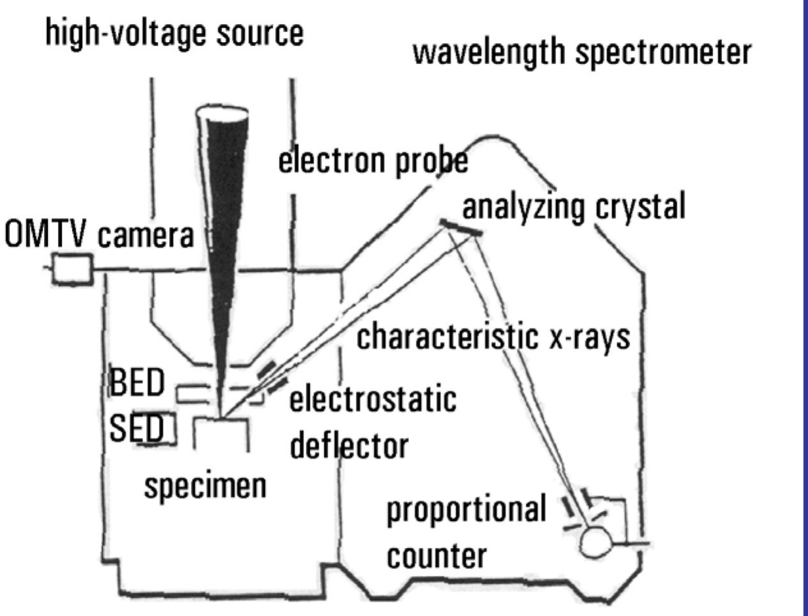
(elemental composition)

Scanning Electron Microscope

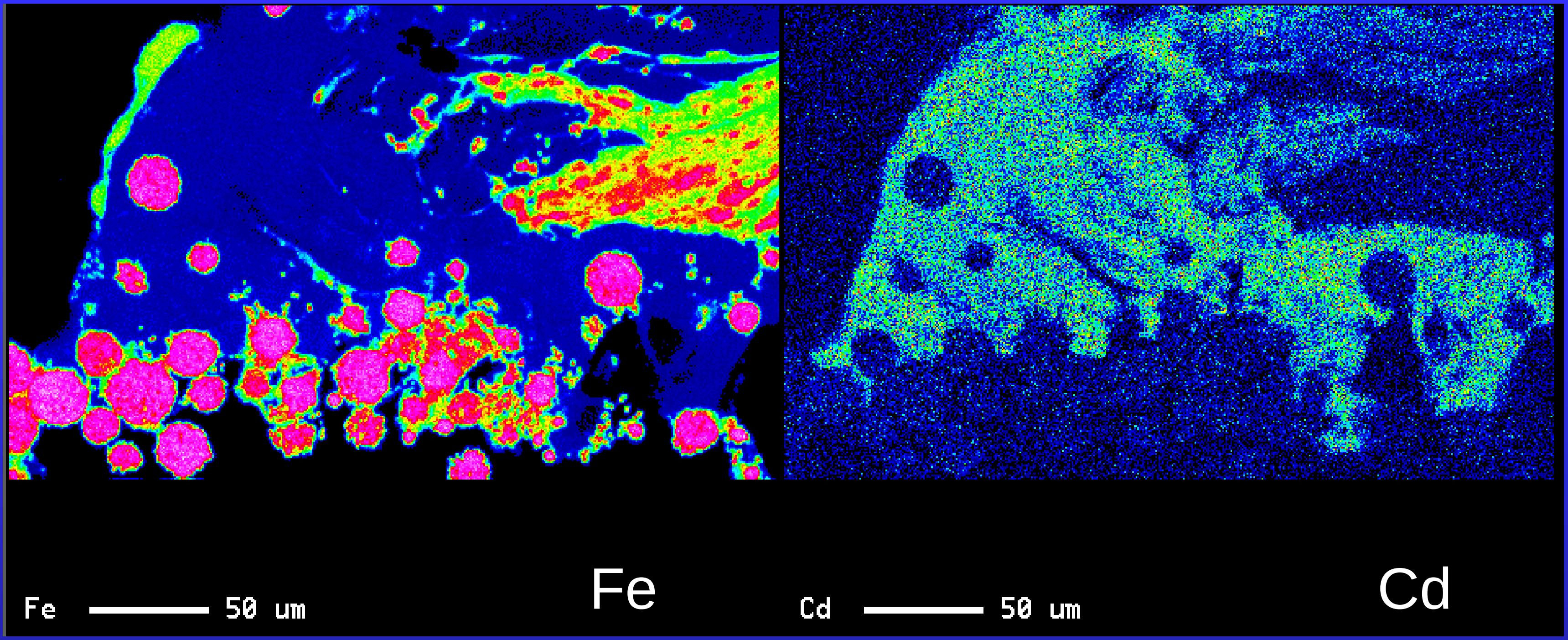
SEM Image of Fly Ash Particle



Electron Microprobe



Microprobe schematic
SED = secondary electron detector
BED = backscattered electron detector
OMTV = optical microscope viewer/camera



Electron microprobe elemental maps of Fe (left) and Cd (right) showing Cd-bearing sphalerite enclosing pyrite framboids, 458.2’ WV#7 core. Host is sandstone above coal-bearing interval in Allegheny Formation. Scale bar is 50 micrometers.

Source: Kolker et al., 2001

Stanford/USGS

SHRIMP-RG Ion Microprobe

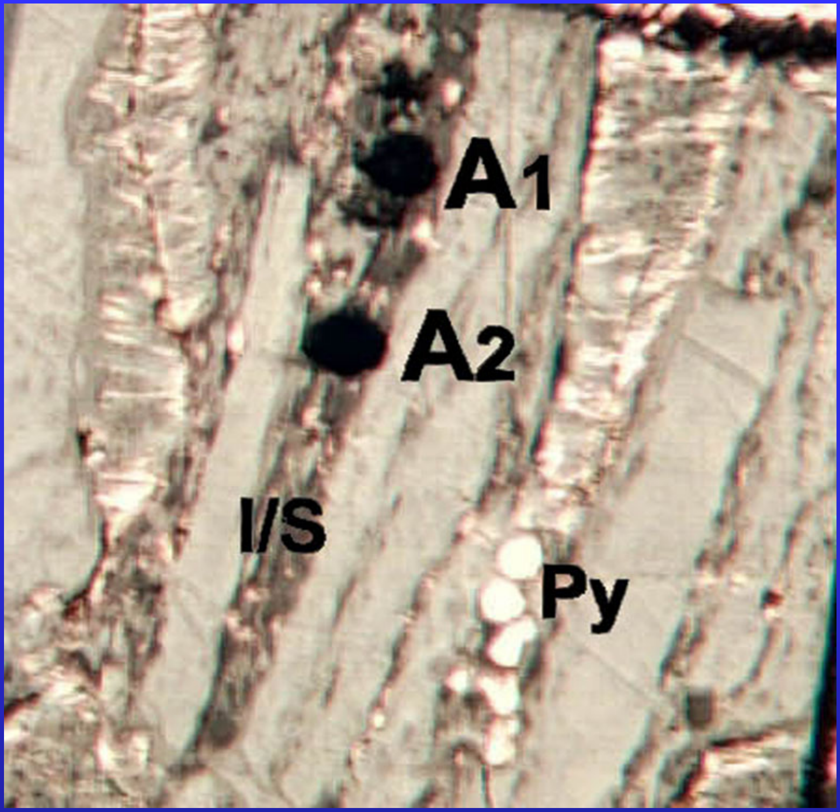
Sensitive High-Resolution Ion Microprobe Reverse Geometry

- Primary beam of O_2^- or Cs^+ ions
- Detection in the ppm range
- 10-15 micron spot size
- Determine isotope ratios

Cr in Coal

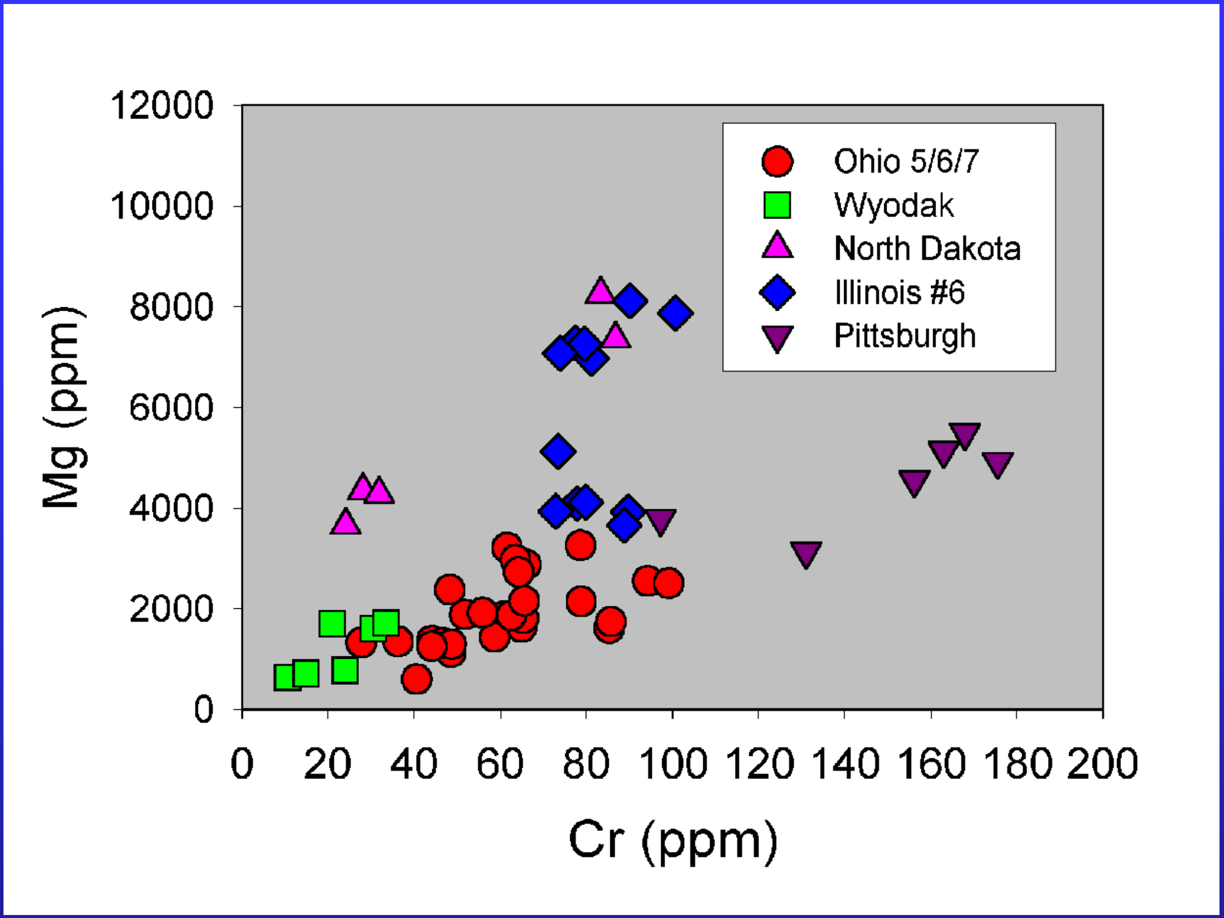
- Silicate and organic hosted forms.
- Quantitative results for illite/smectite using Stanford-USGS SHRIMP-RG ion microprobe.
- Concentrations in illite:

  Cr = 11 to 176 ppm
  Mn = 2 to 149 ppm
  V = 23 to 248 ppm
- Confirms leaching results and electron microprobe data.



Reflected-light image of illite-smectite band in Illinois coal and two 15 μm SHRIMP-RG analysis points.

SHRIMP-RG results for chromium in illite-smectite in 5 U.S. coal samples. Results confirm selective leaching studies commonly indicating a silicate association for Cr.

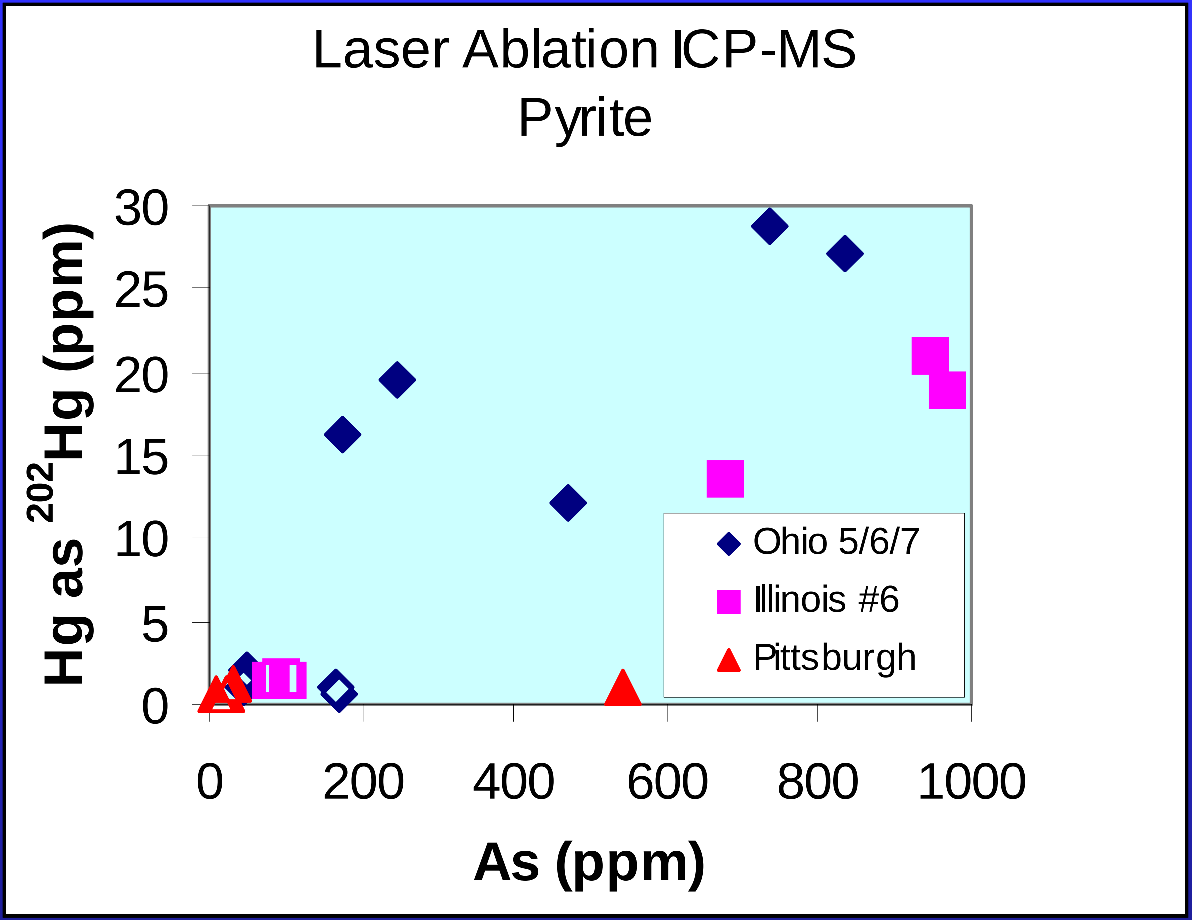


Source: Kolker et al., 2000

Laser Ablation ICP-MS

- Pulsed Nd (YAG) laser coupled to dedicated ICP-MS. Excavation rate is about 3 μm/sec.
- Results for Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, and Hg, in pyrite.
- Sample/standard matrix match not critical as both are introduced into ICP-MS in an argon plasma.
- Best results for Hg with 50 μm beam (about 3 times that of SHRIMP-RG).

Laser ablation ICP-MS confirms mercury association with pyrite in selected bituminous coal samples.



Source: Kolker et al., 2002.

Element Speciation

- Different forms of an element can have very different behavior.

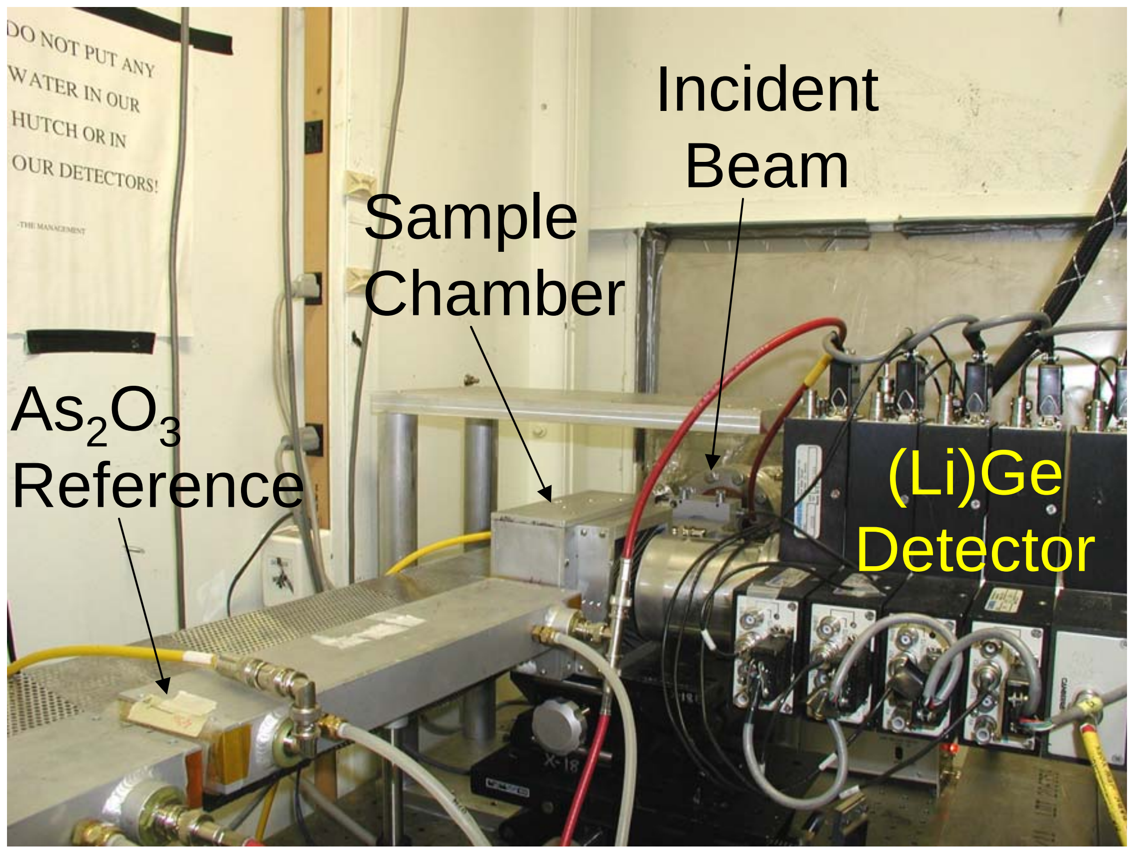
  Examples:
- Trivalent chromium is an essential nutrient; hexavalent chromium is a carcinogen.
- Trivalent arsenic (arsenite) is more toxic than pentavalent arsenic (arsenate).

Approaches to Speciation Determinations

- Classical approach using ion-exchange column chemistry.
- Spectroscopic methods such as X-ray absorption fine structure (XAFS) and ^{57}Fe Mössbauer analysis (primarily solids)
- Selective leaching, where leached form of an element corresponds to a particular species.
- Coupled ion-chromatography-ICP/MS.

XAFS

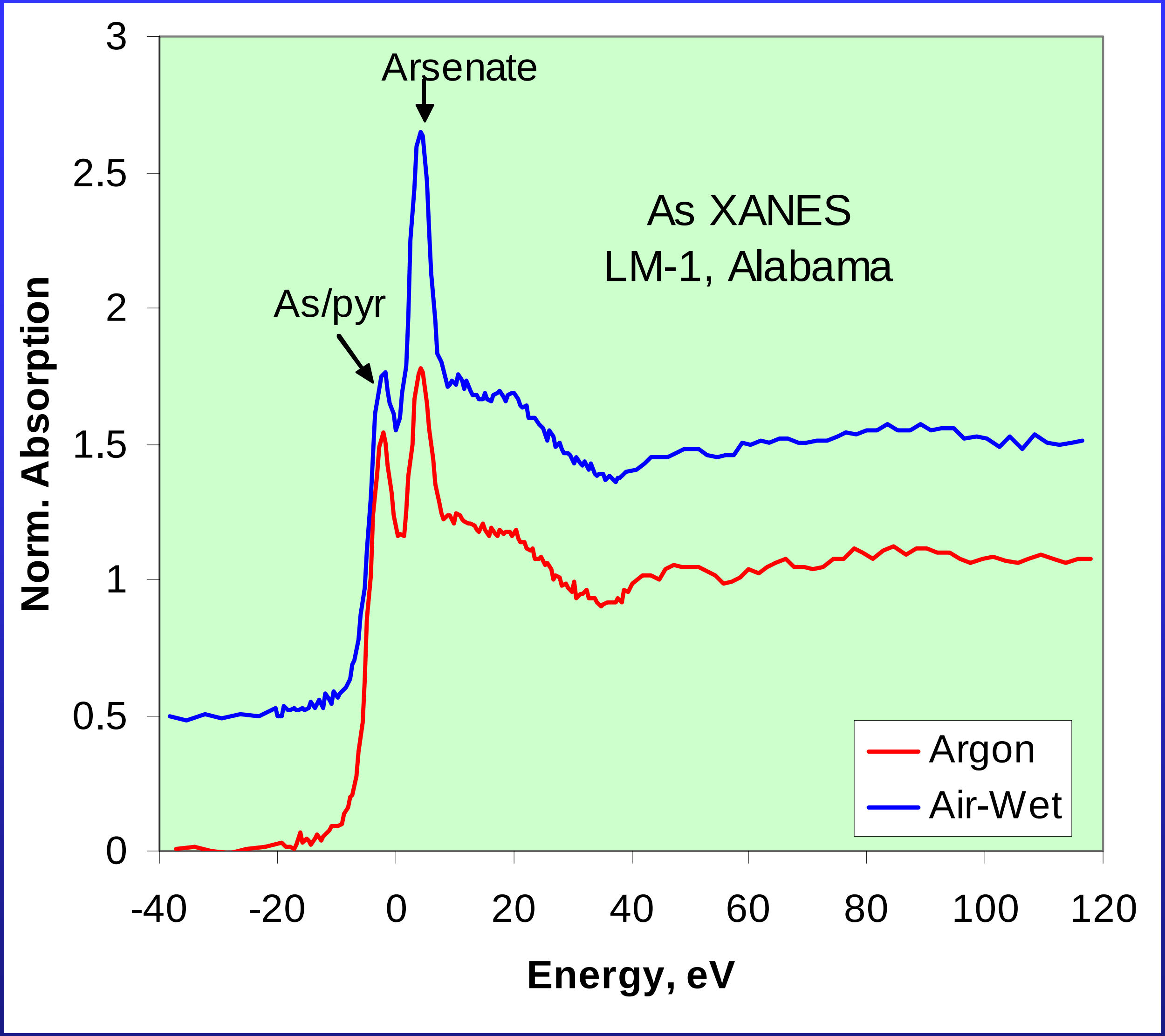
- Can determine elemental species in powdered coal samples using high-energy synchrotron radiation.
- Need samples with several ppm of an element; limited atomic number range, best for transition metals, As, Se.
- To be quantitative, need to do least-squares fitting of spectra for unknowns to spectra of calibration standards.



NSLS
Beamline
X23 A2

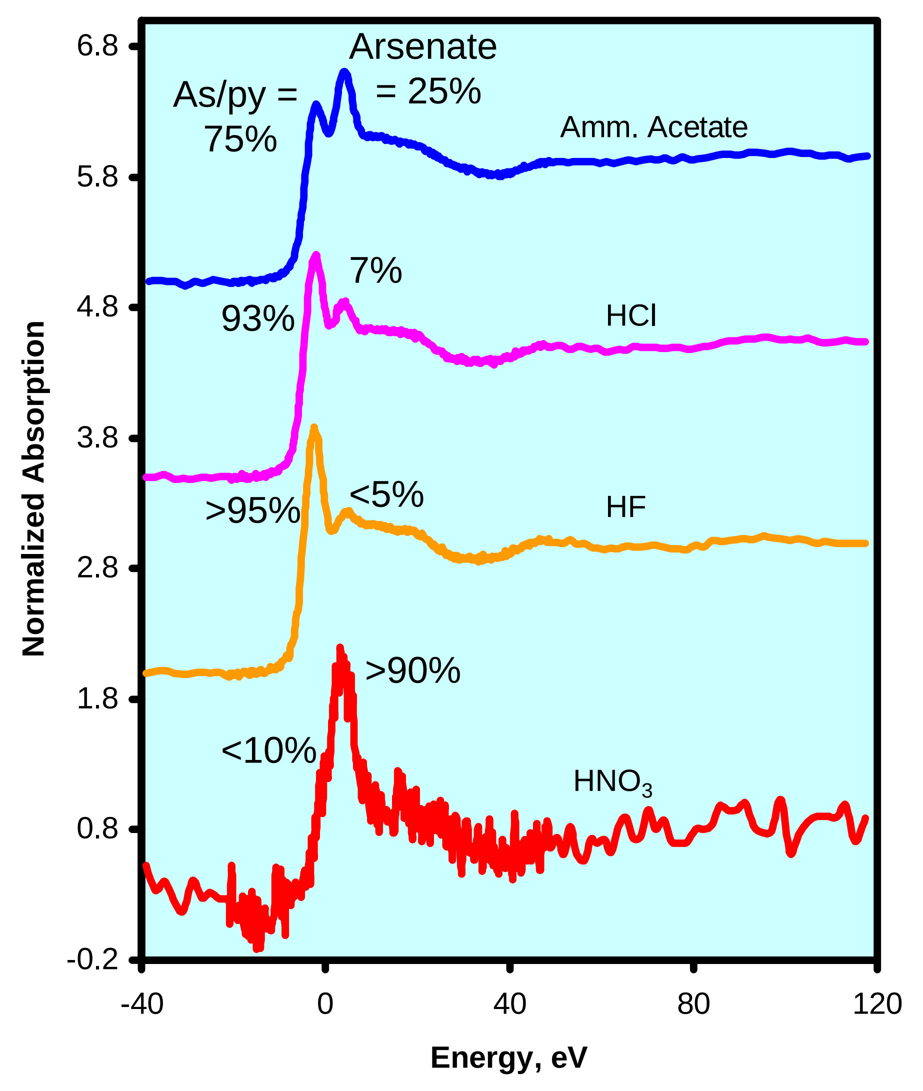
XAFS
Experiment

XAFS spectra of Alabama coal sample showing pyritic arsenic and arsenate forms.



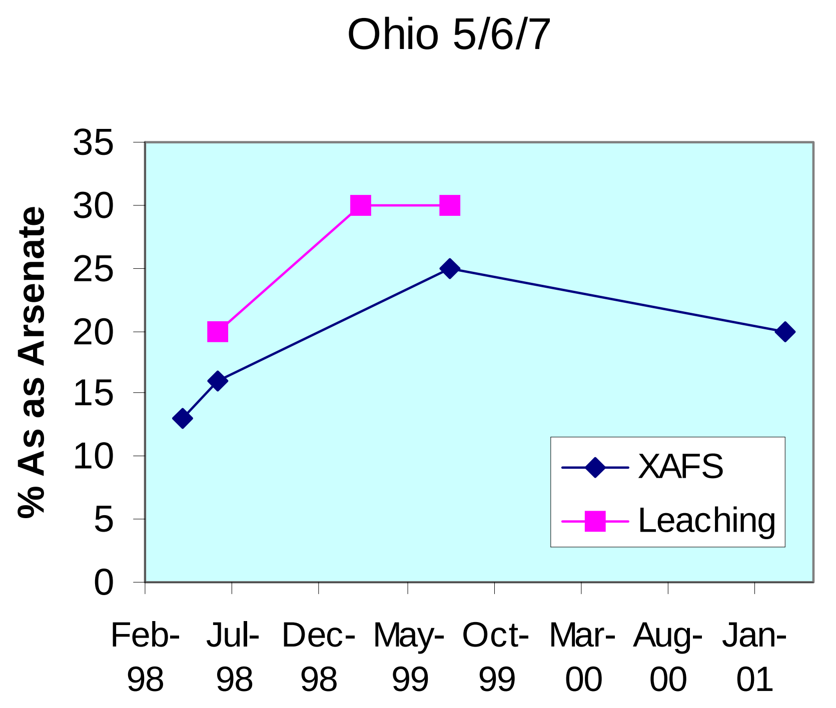
As XAFS of Leached Residues

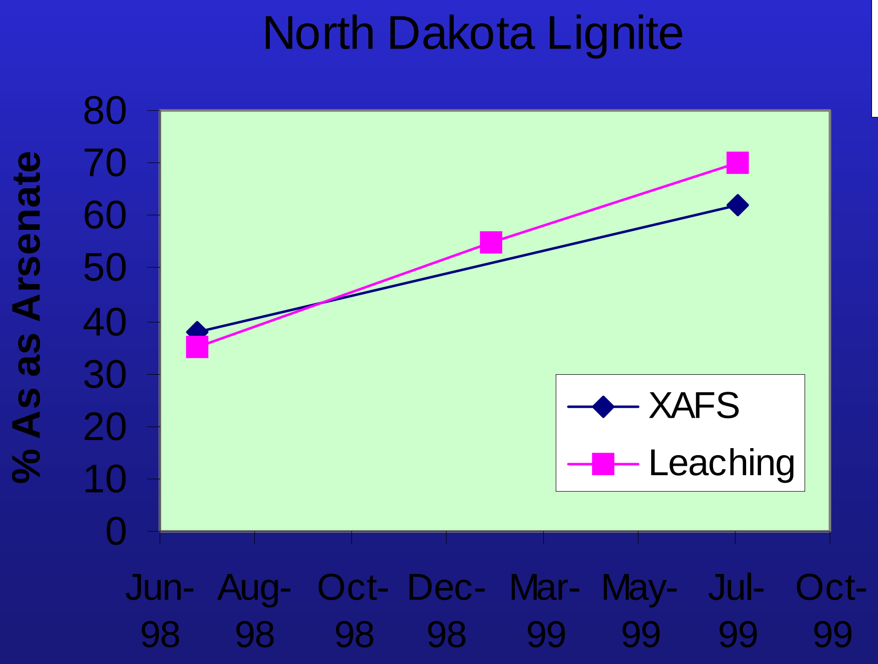
- Pyrite and arsenate are main forms of arsenic in Ohio5/6/7 (bituminous) coal.
- HCl removes arsenate but does not remove significant pyritic arsenic.
- HF removes arsenate not removed by HCl (no As-bearing silicates).
- Fraction of arsenate is primarily a function of pyrite oxidation.



Source: Huggins et al., 2002

Comparison of XAFS and leaching results for Ohio (bituminous) and North Dakota (lignite) coal samples. Determinations show formation of arsenate from As/pyrite over time.





Leaching results are sum of arsenic leached by HCl and HF. Data from Huggins et al., 2002.

XAFS Summary

Arsenic

- Pyrite and arsenate (equivalent to HCl + HF-leached As) are main forms in bituminous coals.
- Arsenate and As (III) are main forms in low rank coals.
- Fraction of arsenate is primarily a function of pyrite oxidation.

Chromium

- Two major forms identified:
  - Cr^{3+}/illite
  - Org. associated Cr (Amorph. CrOOH)
- Chromite- Common only in coals unusually rich in Cr.
- Oxidation State- Always Cr^{3+} in coal (rare Cr^{6+} in some fly ash)

Coal-use Issues and Case Studies

Allan Kolker

Trace elements and coal use

- Mercury emissions balance potential health effects vs. multi-billions cost of controls.
- Fine particulate matter ($PM_{2.5}$) concentrate trace metals relative to coarser ash fractions, and are more readily inhaled.
- Water quality issues:
  Acid mine drainage (AMD).
  Disposal of coal preparation wastes.
  Use of coal combustion products- considered non-hazardous under RCRA.

Pyrite Oxidation

- Oxidation of pyrite results in acid mine drainage and releases metals such as arsenic into the environment.
- Oxidation of pyrite in coal occurs spontaneously over time. Arsenic oxidation proceeds more rapidly than iron oxidation.
- Pyrite oxidation has important implications for coal transport and handling, potentially resulting in leaching of metals from coal piles.

Background- Coal Oxidation Experiments

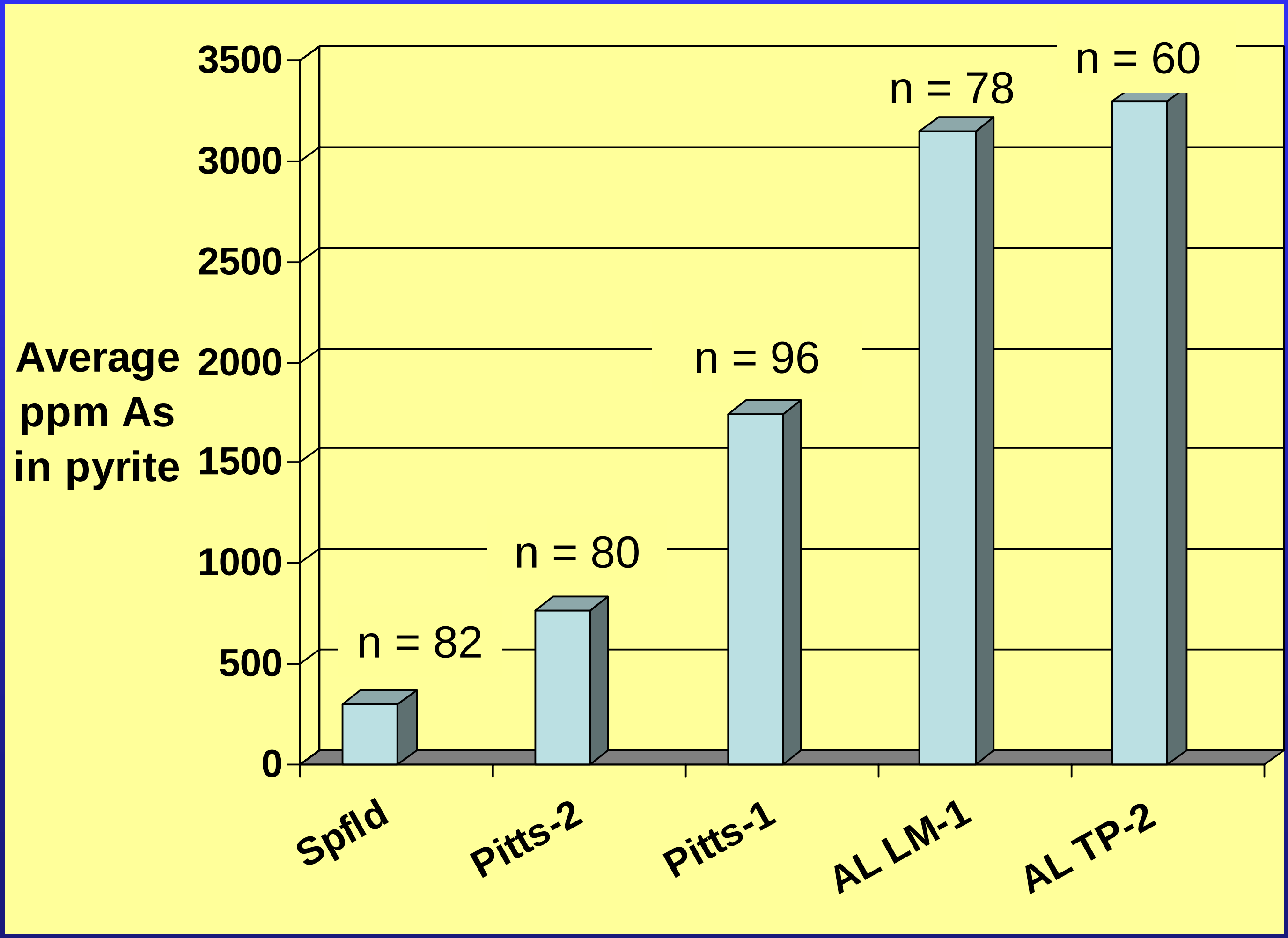
- Huggins et al. (2002), using As XANES showed that arsenate forms from pyritic arsenic in coal samples over time.
- We use As XANES and Fe-Mössbauer analysis to monitor pyrite oxidation in coal under controlled conditions.
- Experiments test the hypothesis that arsenic-rich pyrite is more susceptible to oxidation than pyrite with little or no arsenic.

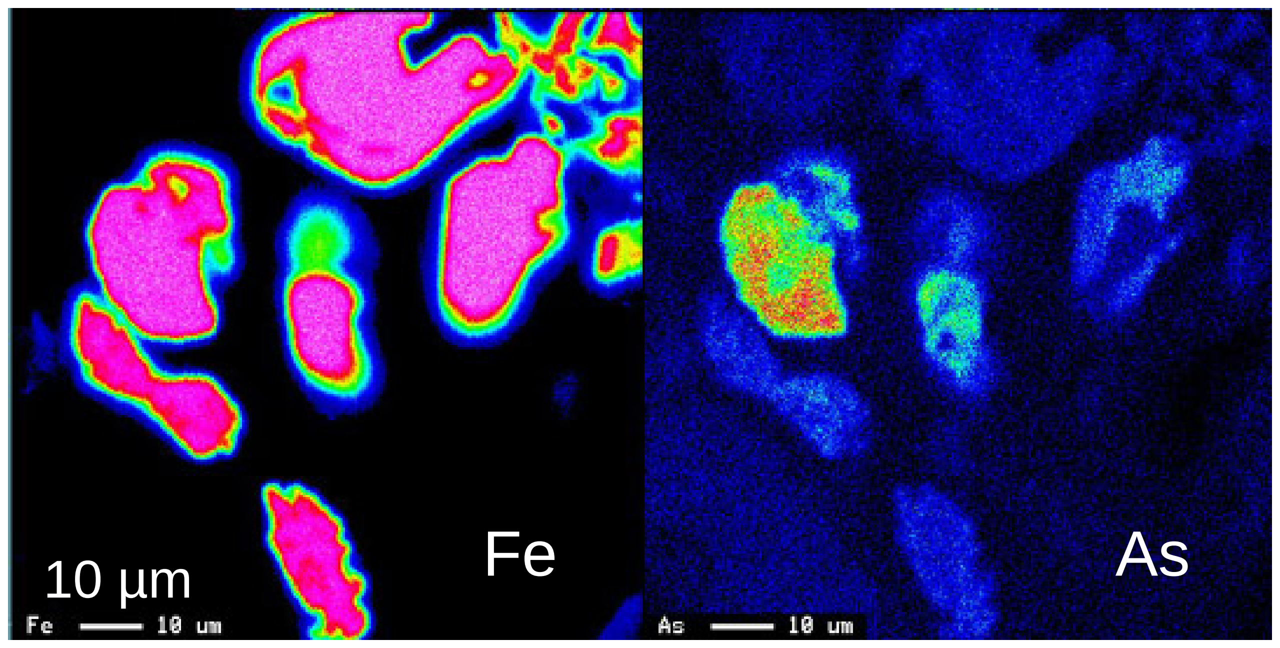
Comparison of Coal Samples Investigated

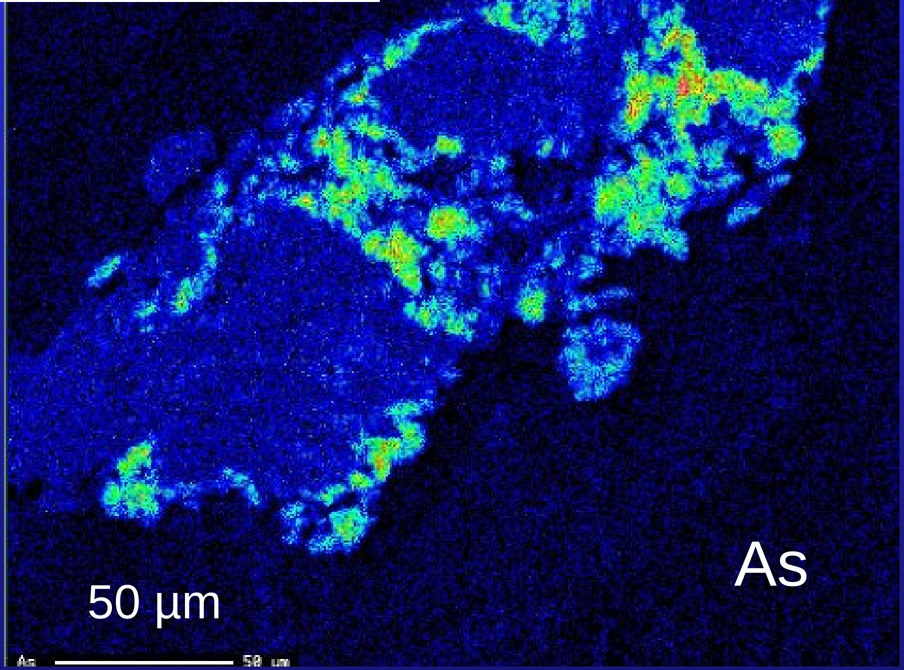
Sample	Coal Bed	Location	Arsenic Content (ppm)	Pyritic Sulfur[1] (wt. %)	Arsenic in Pyrite (wt. %)
Pitts #1	Pittsburgh	West Virginia	23.0	1.32	d.l.[2] to 0.34
Pitts #2	Pittsburgh	West Virginia	12.0	1.58	d.l to 0.14
Spfd	Springfield	Indiana	6.5	2.13	d.l. to 0.06
TP1-1.0	Warrior	Alabama	8.2	0.26	d.l. to 2.46
LM1-2.0	Warrior	Alabama	8.9	0.27	d.l. to 2.72

[1] Dry Basis; [2] Microprobe detection limit approximately 0.01 weight percent.

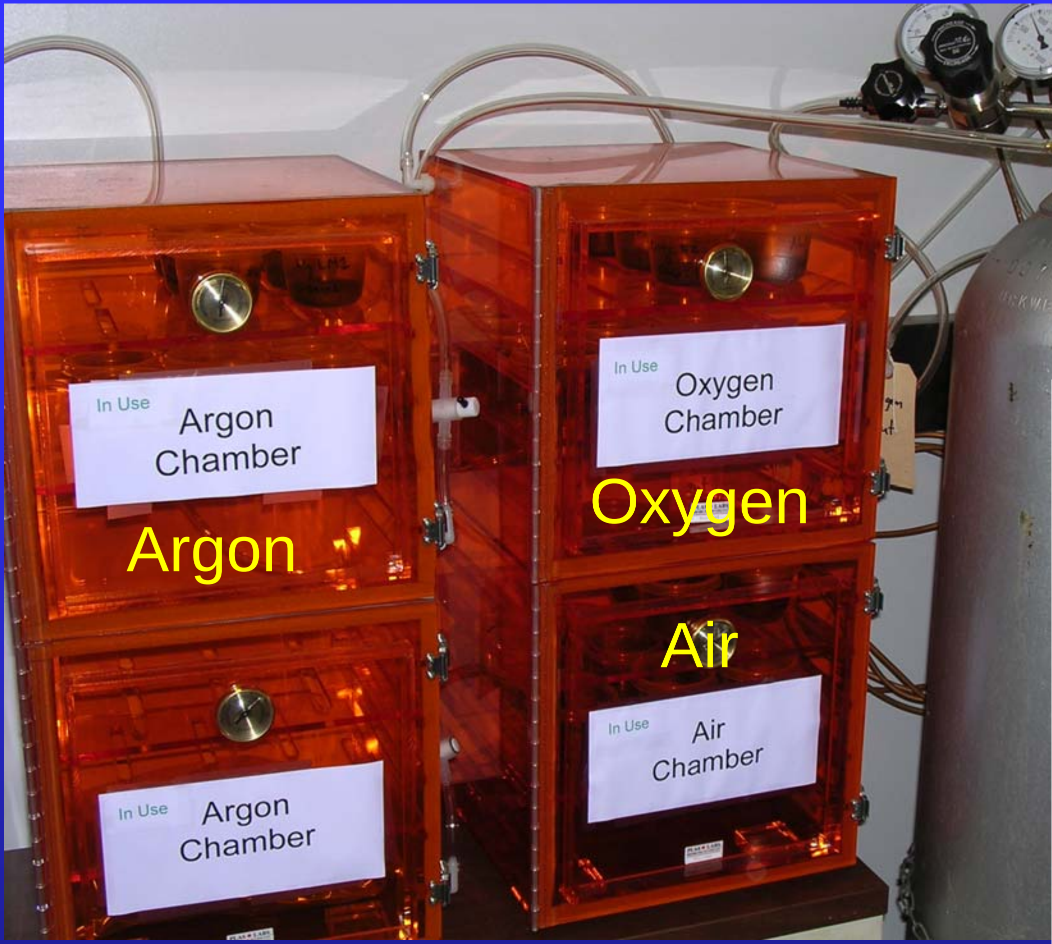
Relative Concentration of As in Pyrite







Wavelength-dispersive electron microprobe elemental maps of pyrite in Alabama samples LM-1 (above) and TP-1 (right) showing arsenic-enriched domains.



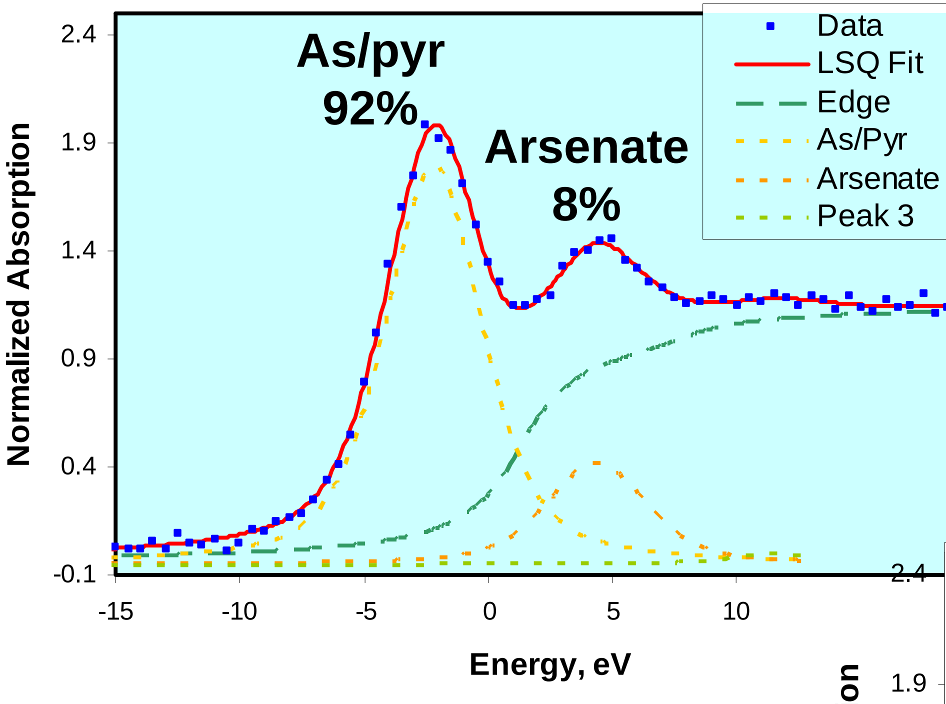
Controlled Atmosphere Experiment
(Argon, Oxygen, Air)

Air-wet Experiment

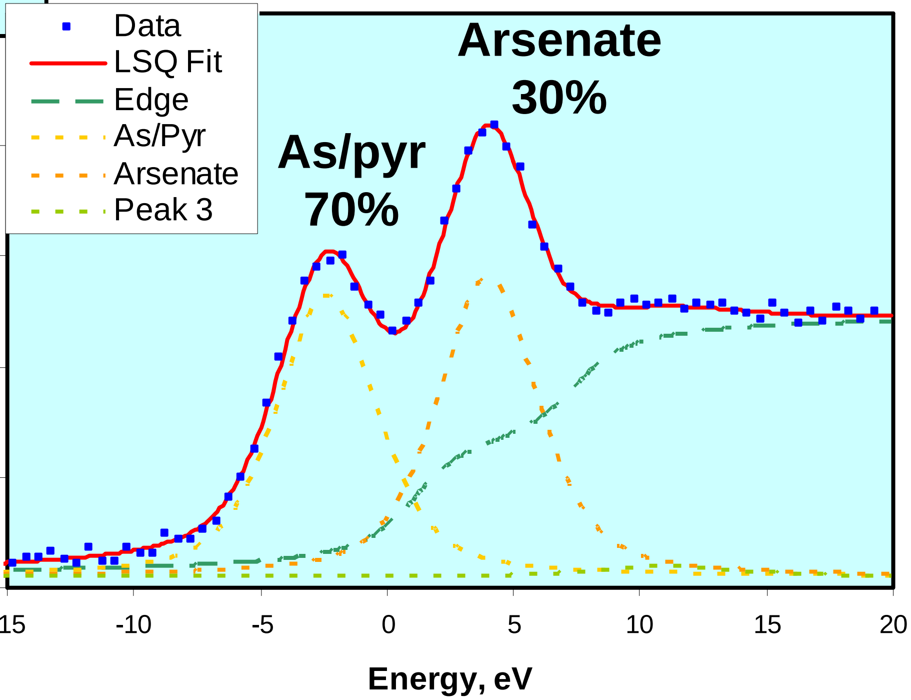
XAFS PROJECT TIMELINE

Results of least-squares fitting of As XANES spectra

Springfield No. 2 Indiana Argon



Springfield No. 2 Indiana Air-Wet



Examples from Stage 1 XAFS November, 2002

Results of least-squares fitting of As XANES spectra, Stage 1 analysis, November, 2002

Sample	Ala. LM-1		Ala. TP-1		Springfield		Pitts #1		Pitts #2	
	Pyrite	Arsenate	Pyrite	Arsenate	Pyrite	Arsenate	Pyrite	Arsenate	Pyrite	Arsenate
Argon	77	23	82	18	92	8	93	7	92	8
Oxygen	76	24	81	19	91	9	92	8	91	9
Air Dry	75	25	81	19	91	9	93	7	91	9
Air Wet	61	39	69	31	70	30	81	19	77	23

Data are %As of total As in sample that is associated with pyrite or arsenate
Estimated error ±3%

Comparison of As XANES and ^{57}Fe Mössbauer Results (Stage 1 Data)

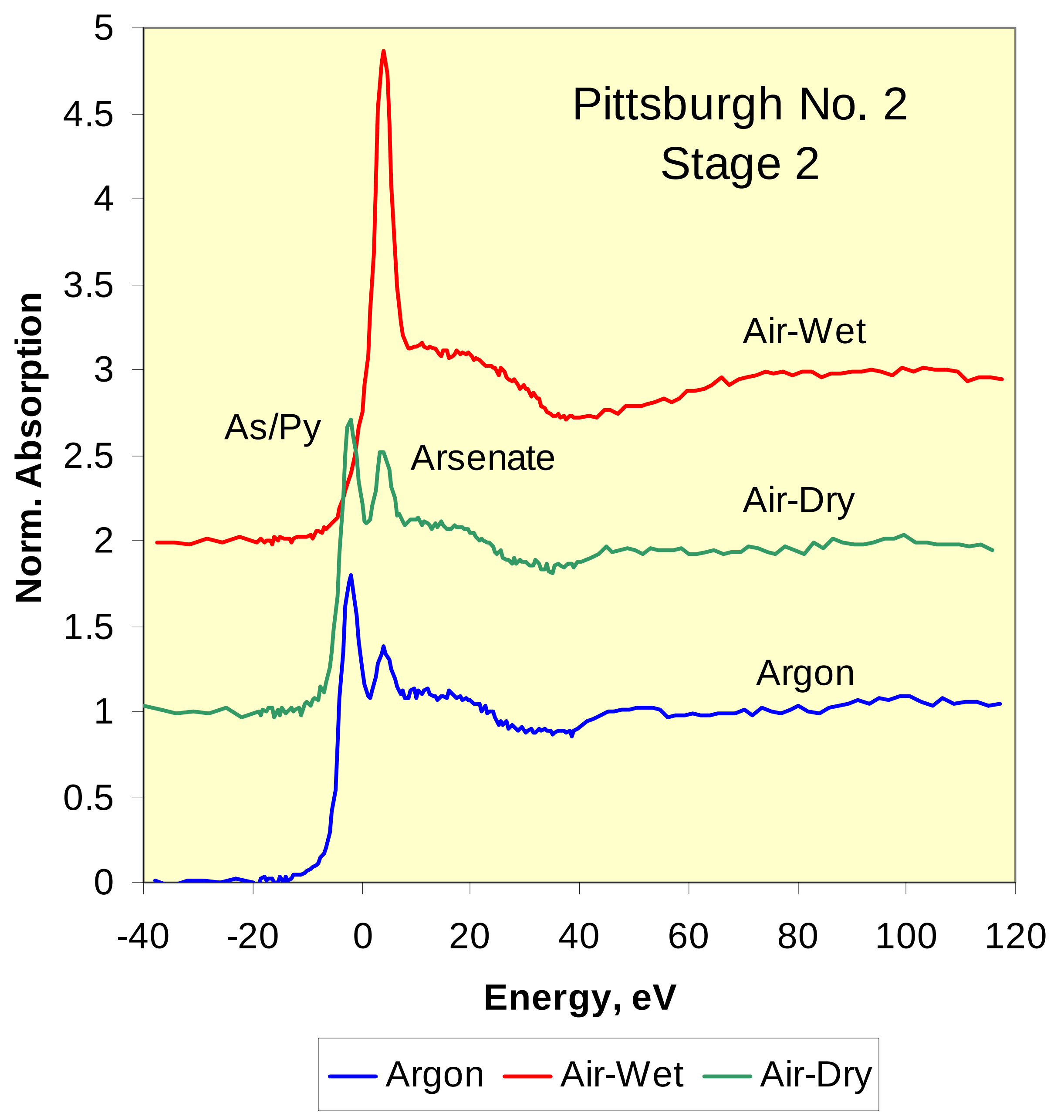
	Springfield			
	Arsenic		Iron	
	Pyrite	Arsenate	Pyrite	Jarosite
Argon	92	8	91	8
Air Wet	70	30	82	16
	Pittsburgh #1			
Argon	93	7	98	2
Air Wet	81	19	86	14

Stage 2 Experiments

- Little or no difference between samples stored under dry gasses (argon & oxygen).
- Unlike Stage 1, samples stored in air are more oxidized than those kept in dry gas.
- Air-wet samples:

Pitts #2 and Ala TP-1 (no As/py (<5%) remaining); Ala LM-1, Springfield, Pitts #1, 10 to 50% As/py remaining (estimated).

Example of Stage 2 XAFS Results, July, 2003



Summary- Coal Oxidation Experiments

- Nearly complete range of arsenic oxidation is produced by experimental conditions. Arsenic and iron show parallel oxidation.
- Humidity and/or presence of water, and oxygen availability are most important factors controlling oxidation state.
- Complete results are needed to evaluate rates of pyrite oxidation as a function of pyrite arsenic content.

Mercury Emissions from Coal-Fired Power Plants

- December, 2000, EPA determines to limit mercury emissions from coal-fired power plants; timetable superceded by Clear Skies.
- Clear Skies*- Multi-pollutant plan links Hg, SO2 and NOx. Reduces 1999 Hg emissions (48 tons) to 26 tons by 2010 and 15 tons by 2018.
- Boiler MACT- Multi-pollutant plan for industrial/commercial boilers. Limits new boilers to 3 lbs Hg/trillion BTU and existing plants to 7 lbs/trillion BTU. Legislation sought by early 2004 and compliance in 3 years.

*http://www.epa.gov/clearskies/

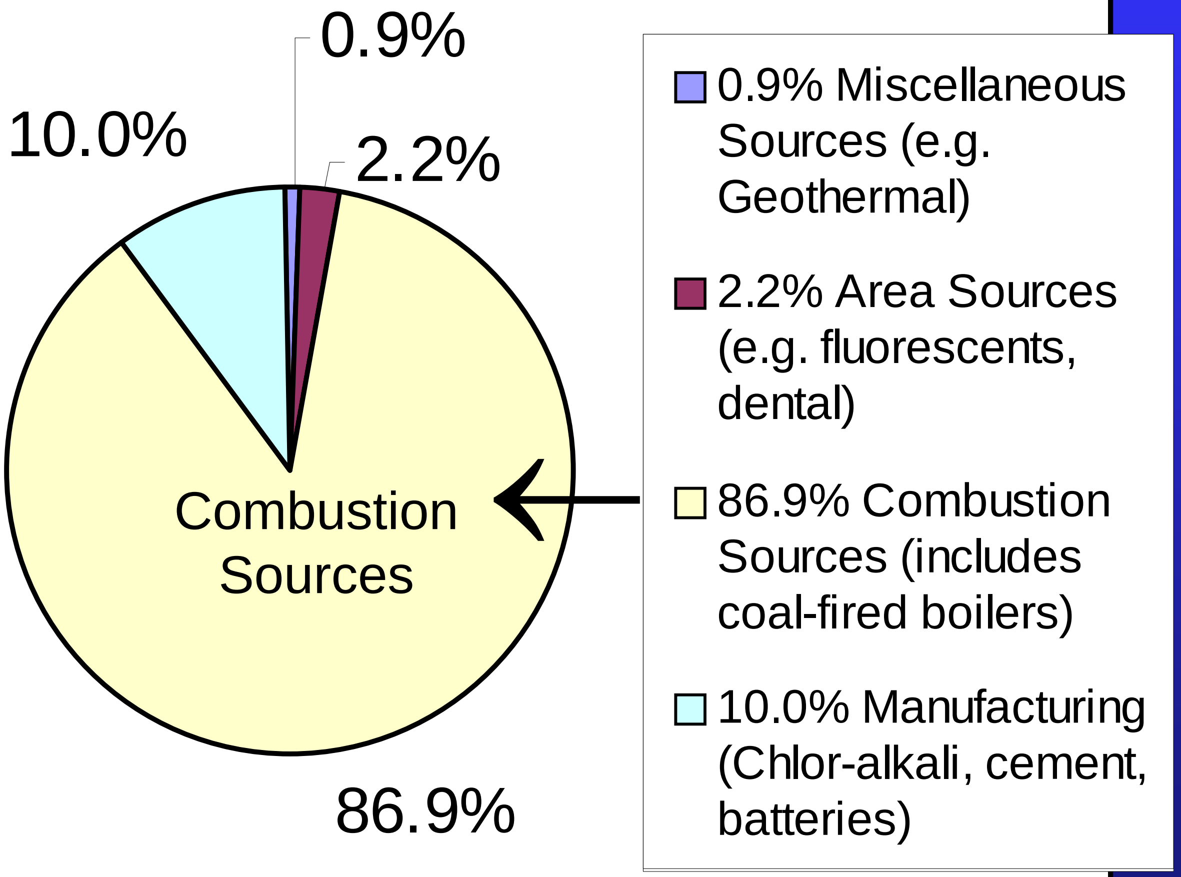
Estimates of U.S. Point-Source Mercury Emission Rates (1994-1995*)

Regulated or Proposed Regulations

Medical Waste
Municipal Waste
Hazardous Waste
Non-Utility Boilers

Not Regulated:

Coal-Fired Utilities (about 33% of U.S. emissions)

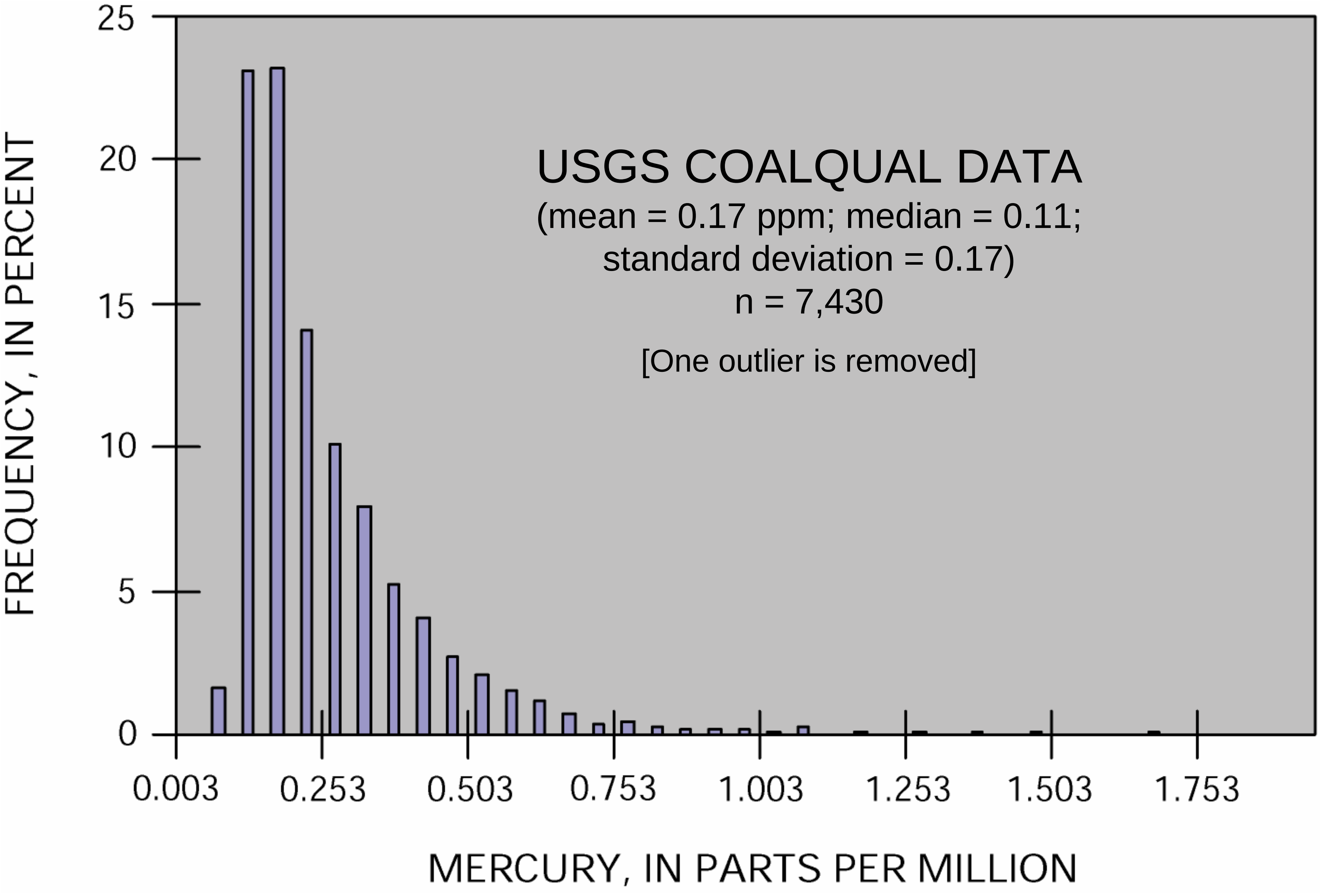


Source: EPA-PB98-124738

*Latest Figures Available

Health Risks from Mercury

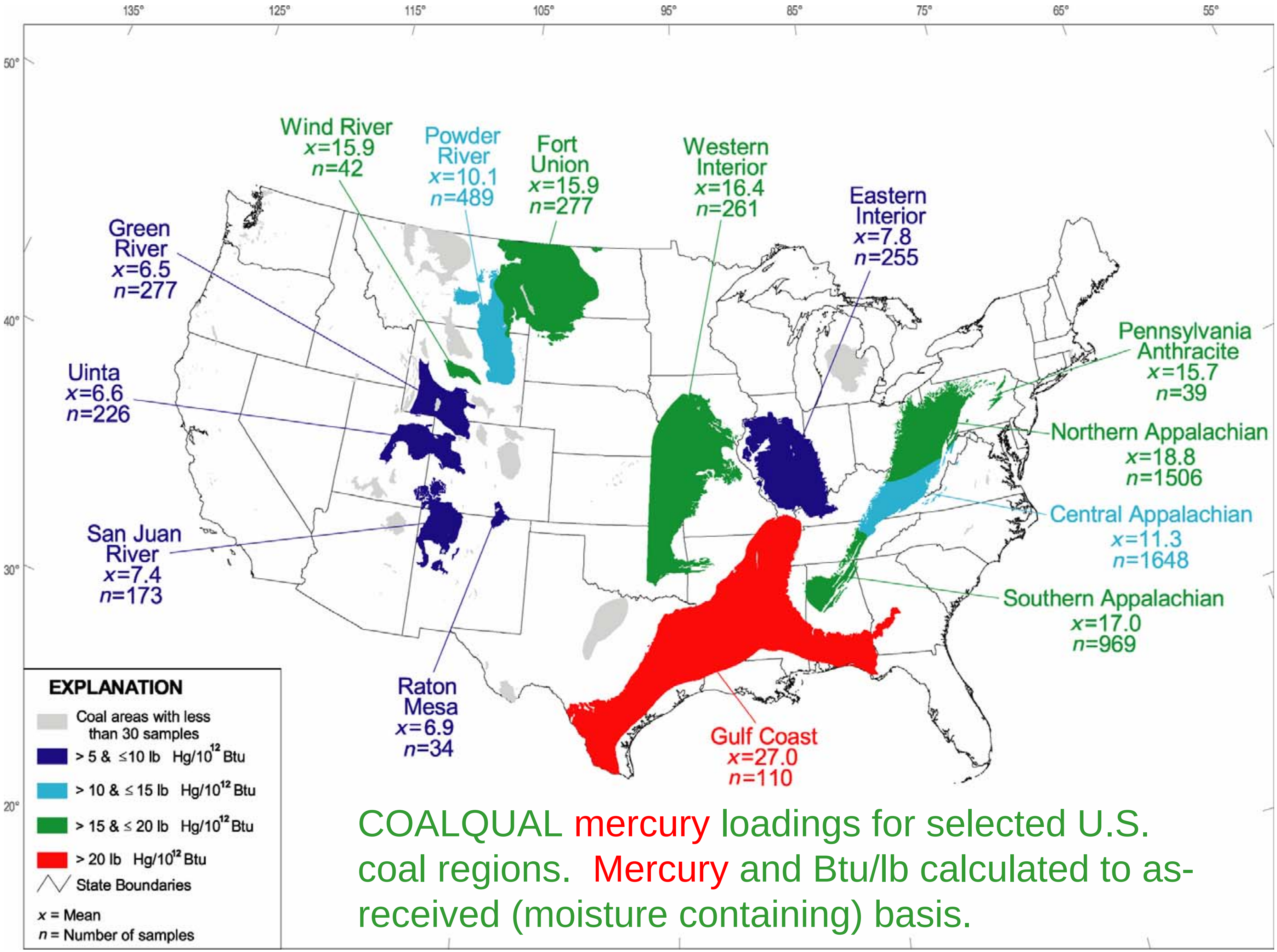
- Exposure due to consumption of methyl-mercury in fish.
- Nervous system effects and developmental disorders. Documented effects of chronic exposure at low levels. Risk to fetuses and infants is greatest.
- Strong association with kidney damage and disease.
- Likely association with increases in lung cancer, and possible cardiovascular effects.


USGS COALQUAL DATA
(mean = 0.17 ppm; median = 0.11;
standard deviation = 0.17)
n = 7,430
[One outlier is removed]
FREQUENCY, IN PERCENT
25
20
15
10
5
0
0.003
0.253
0.503
0.753
1.003
1.253
1.503
1.753
MERCURY, IN PARTS PER MILLION

Comparison of
USGS and EPA ICR Data Sets

- EPA ICR database reflects mercury content of commercial coals delivered in 1999 to U.S. power plants ≥ 25 MW.
- USGS database includes data for about 40 elements and many coal-use parameters.
- Subsets[1] give averages of 0.10 ppm for ICR and 0.17 ppm for COALQUAL. Difference reflects cleaned vs. in-ground values, and increased use of low-S western coals.

[1] Quick et al. , *2003, Environmental Geology*



COALQUAL mercury loadings for selected U.S. coal regions. Mercury and Btu/lb calculated to as-received (moisture containing) basis.

Average Mercury Loadings Appalachian Coal Regions

Coal Region	**Mean Hg** (ppm)	**Mean Calorific Value** (Btu/lb)	**Mean Hg Loading*** (lbs Hg/10^{12} Btu)
Northern Appalachian	0.24	12,440	18.8
Central Appalachian	0.15	13,210	11.3
Southern Appalachian	0.21	12,760	17.0

*as-received basis

USGS Results from Tewalt et al., 2001

Calculating Mercury Loading

Example:

High-volatile B Bituminous Coal

Calorific value = 13,500 Btu/lb

Hg = 0.1 ppm Hg (equivalent basis)

$$\frac{1\text{ lb Hg}}{10^{7}\text{ lb coal}}\ \text{X}\ \frac{1\text{ lb coal}}{1.35\text{ x }10^{5}\text{ Btu}} = \frac{7.4\text{ lbs Hg}}{10^{12}\text{ Btu}}$$

Benefit of Coal Cleaning

Table shows calorific value and mercury contents for raw and cleaned coal averages for 24 eastern bituminous coal samples (dry, equal-energy basis).

Calorific value raw coal (Btu/lb)	Hg content raw coal (ppm)	Calorific value cleaned coal (Btu/lb)	Hg content cleaned coal (ppm)	Percent Hg reduction (equal energy basis)
10,704	0.23	13,730	0.16	37

Results from B. Toole-O'Neil et al., *Fuel*, v. 78, p. 47-54, 1999.

Reducing Mercury Loading

- Example- Coal Cleaning for average Central Appalachian coal:

Raw Coal (lbs Hg/10^{12} Btu)	**Estimated Cleaned Coal** (37% reduction)	**MACT** (existing boilers)
11.3	7.1	7.0

Other Ways To Reduce Hg:

- Selective Mining
- Increase Hg capture with ESP, FGD, etc.
- Unburned Carbon

Eastern coal producers practice coal cleaning and selective mining; Delivered Hg contents are lower than USGS in-ground averages.

Estimating Yearly Mercury Loading to U.S. Power Plants

- Need to accurately know tonnages and moisture contents of coals having a particular mercury content.
- Estimates:

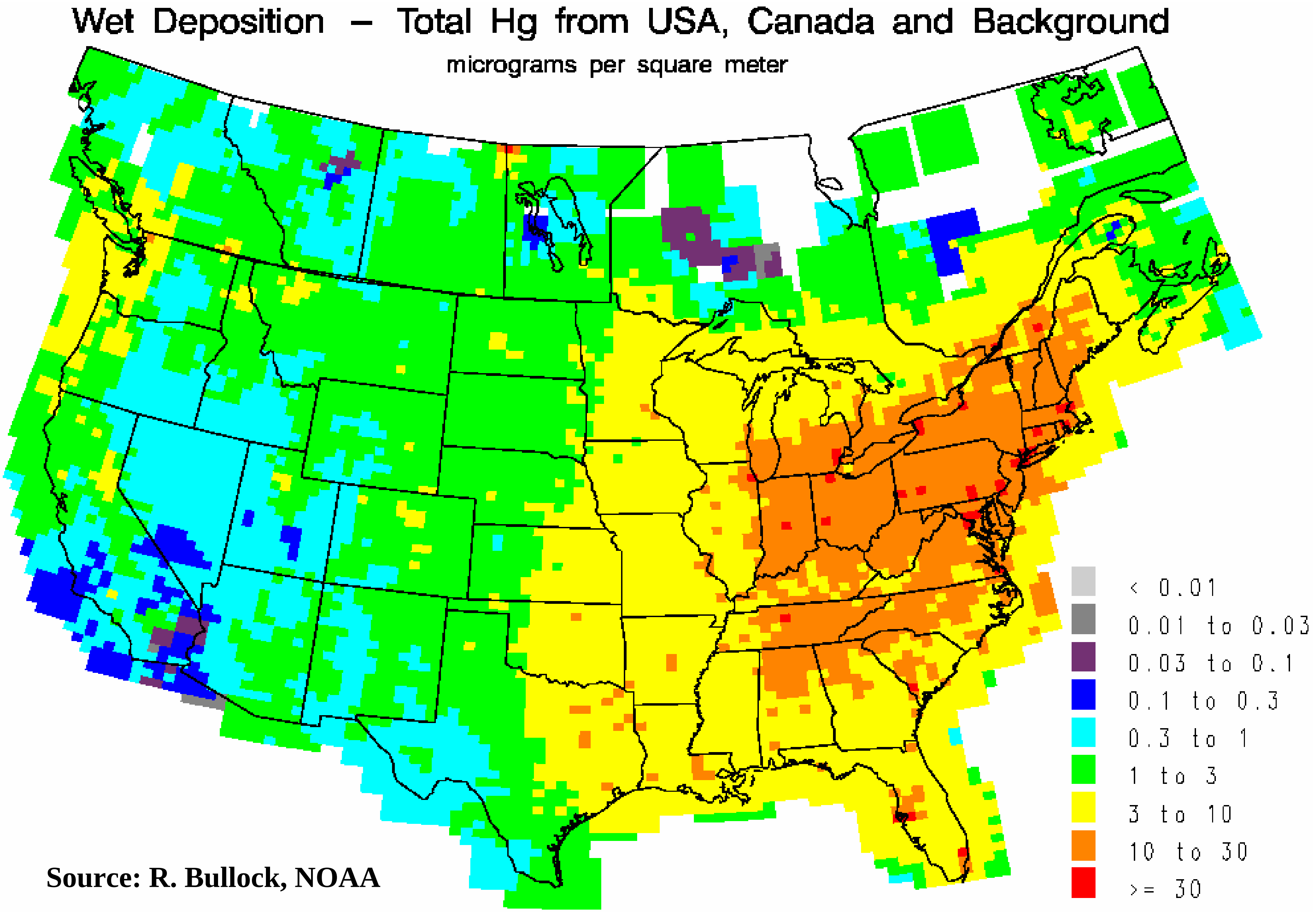
1) 63 [1]Mg, based on ICR state averages, EIA tonnage data, for power plants ≥ 50 MW only (Quick et al.).

2) 68 Mg, based entirely on ICR data ([2]Kilgroe et al.).

3) 111 Mg, based on COALQUAL state averages (Quick et al.). Reduced to about 70 Mg with estimated 37% reduction by cleaning (equal energy basis).

[1] Mg is one metric ton; 1 metric ton = 1.1023 U.S. tons

[2] EPA-600/R-01-109, April 2002



Wet Deposition – Total Hg from USA, Canada and Background

micrograms per square meter

Source: R. Bullock, NOAA

Mercury Deposition Network

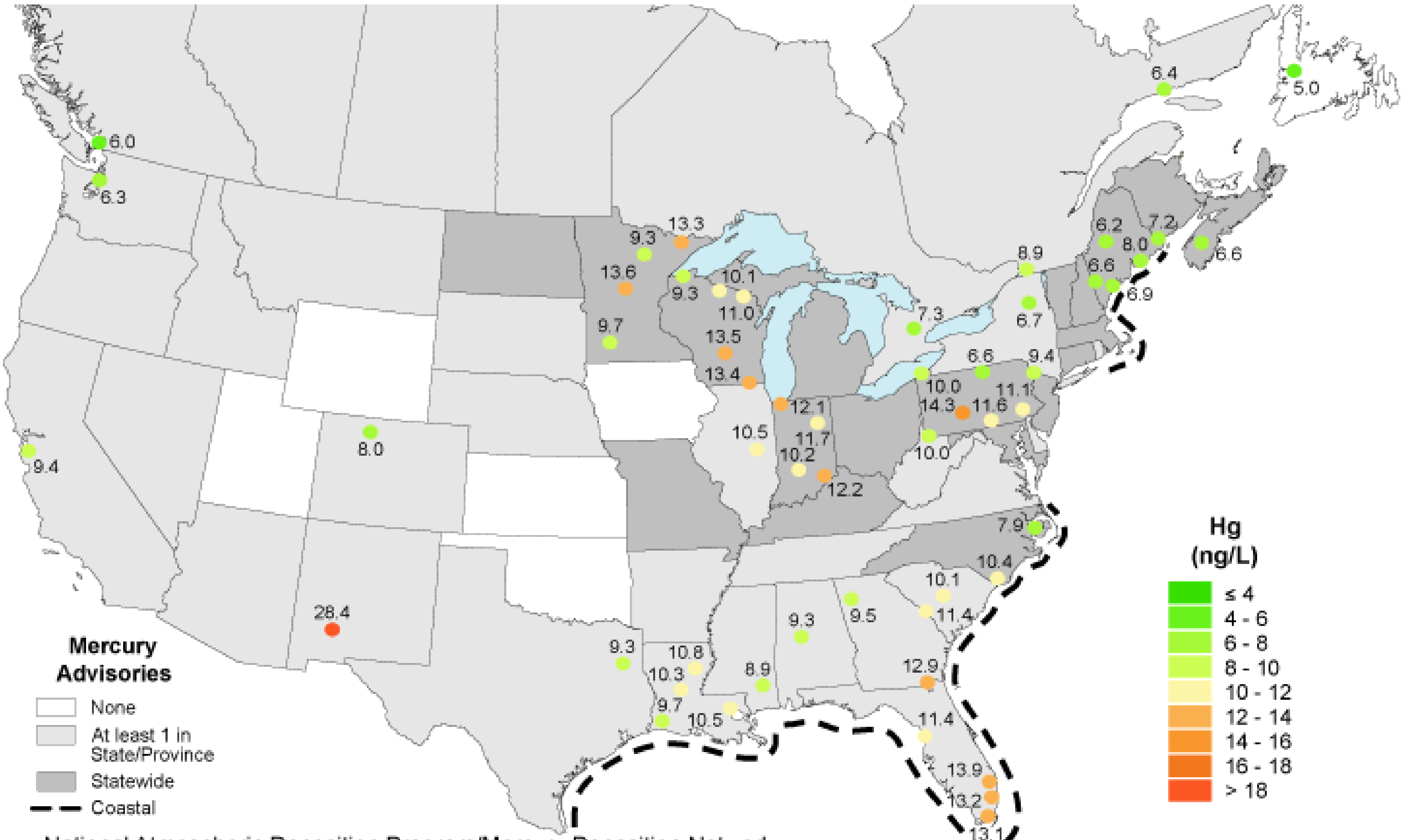
- Subprogram of National Atmospheric Deposition Program initiated in 1995 to monitor mercury levels in precipitation.
- Current network consists of about 80 standardized sites in U.S. and Canada.
- Weekly wet deposition samples are determined by cold vapor atomic fluorescence at Frontier Geosciences, Inc.
- Data distribution and program management by Illinois State Water Survey.

Data available at: http//:nadp.sws.uiuc.edu

Background

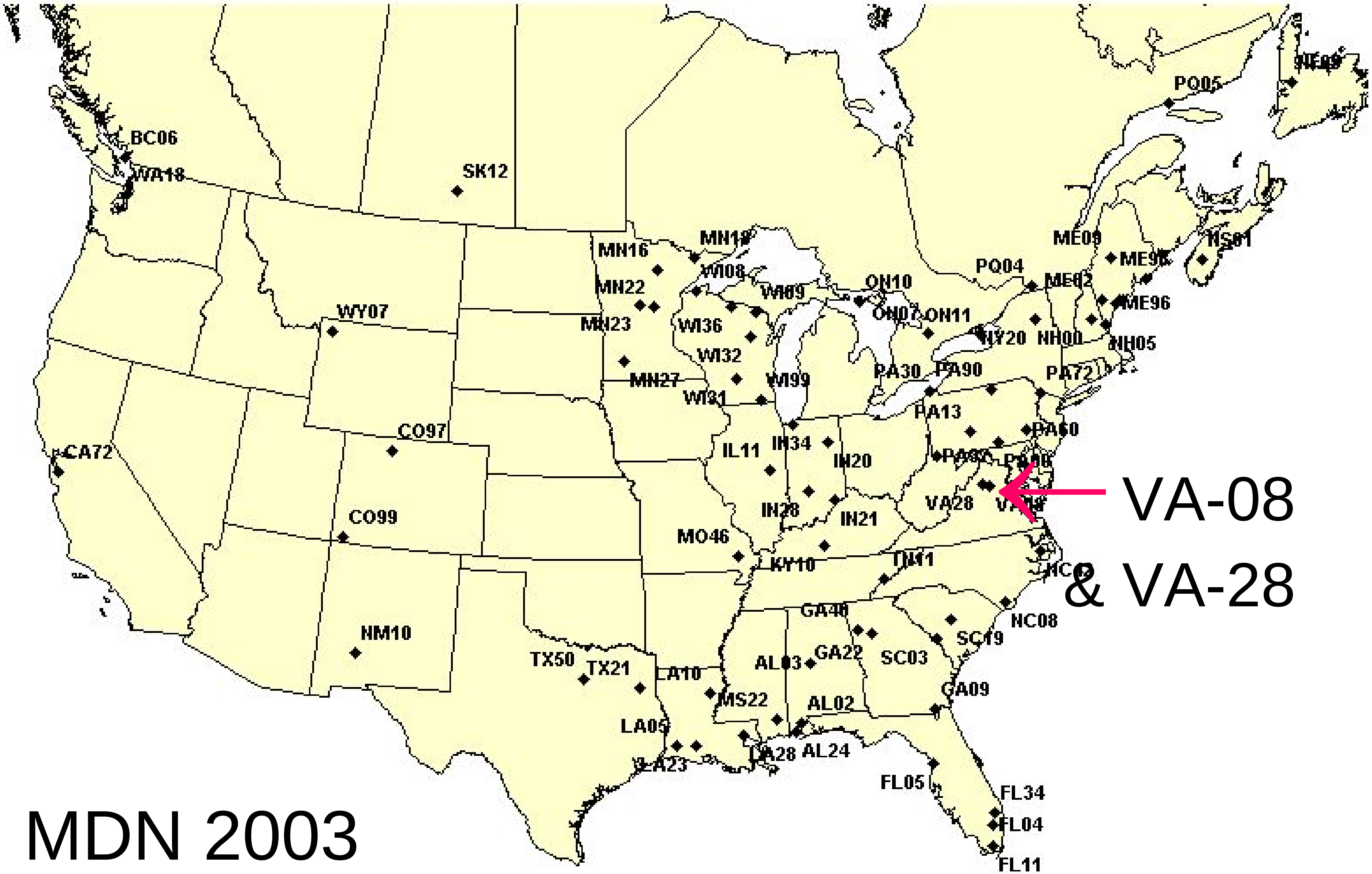
- Highest projected rates of mercury deposition in the eastern third of U.S.
- Nonetheless, no operating MDN sites in DE, MD, VA, or WV as of 2002 (2 inactive sites).
- VA-08 Culpeper (USGS/GMU) and VA-28 SNP Big Meadows (National Park Service) started in Oct./Nov. 2002 to help fill the void.
- VA-28: Reference for ecological and water quality studies in Shenandoah National Park.
- VA-08 and VA-28: Regional background for mercury emissions prior to mandated changes.

Total Mercury Concentration, 2001



National Atmospheric Deposition Program/Mercury Deposition Network

National Atmospheric Deposition Program
Mercury Deposition Network



VA-08

& VA-28

MDN 2003

Views of new MDN stations

VA-28 Shenandoah National Park Big Meadows

VA-08 Culpeper

Preliminary results- Quarterly volume-averaged mercury concentrations, VA-08, VA-28 and nearest active sites.

Site	*VA-08*	*VA-28*	*PA-37*	*PA-13*	*PA-00*	*PA-47*
Name	Culpeper	SNP Big Meadows	Holbrook	Allegheny Portage NHS	Arendtsville	Millersville
Latitude	38.42	38.52	39.82	40.50	39.92	39.99
Longitude	-78.10	-78.44	-80.29	-78.55	-77.31	-76.39
Elevation (m)	163	1074	1140	739	269	85
Dist. VA-08 (km)	----	31	245	235	180	229
1 Qtr 2003	**4.25**	**2.76**	**6.31**	**5.09**	**5.43**	**4.05**
2 Qtr 2003	**7.02**	**6.37**	**10.58**	**7.98**	**8.79**	**7.16**