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

<table>
<thead>
<tr>
<th>Element</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Boiler Fouling</td>
</tr>
<tr>
<td>Iron</td>
<td>Boiler Slagging</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Corrosion; Hg capture</td>
</tr>
<tr>
<td>Si (Quartz)</td>
<td>Erosion of Combustors</td>
</tr>
</tbody>
</table>
### Trace Element Averages

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

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

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

* 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 occurrence.
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

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Minor Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (SiO$_2$)</td>
<td>Negligible</td>
</tr>
<tr>
<td>Clays</td>
<td></td>
</tr>
<tr>
<td>Illite/Illite-smectite</td>
<td>Fe, Cr, Mn, V, Mn, As, Hg, Co, Ni</td>
</tr>
<tr>
<td>Kaolinite Al$_4$(Si$<em>4$O$</em>{10}$)(OH$_8$)</td>
<td>Negligible (?)</td>
</tr>
<tr>
<td>Carbonates</td>
<td></td>
</tr>
<tr>
<td>Calcite (CaCO$_3$)</td>
<td></td>
</tr>
<tr>
<td>Siderite (FeCO$_3$)</td>
<td></td>
</tr>
<tr>
<td>Ankerite Ca(Mg,Fe,Mn)(CO$_3$)$_2$</td>
<td>Sr, Mn</td>
</tr>
<tr>
<td>Pyrite (Marcasite)</td>
<td>As, Hg, Co, Ni</td>
</tr>
<tr>
<td>(FeS$_2$)</td>
<td></td>
</tr>
</tbody>
</table>
Forms of pyrite in Donets Basin (Ukraine) coal samples (SEM/BSE).
# Minor/Trace Phases

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Major Components</th>
<th>Minor Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galena</td>
<td>(PbS)</td>
<td></td>
</tr>
<tr>
<td>Sphalerite</td>
<td>(ZnS)</td>
<td>Cd</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>(CuFeS$_2$)</td>
<td></td>
</tr>
<tr>
<td>Clausthalite</td>
<td>(PbSe)</td>
<td></td>
</tr>
<tr>
<td>Crandallite Group</td>
<td>(Ca, Al, P)</td>
<td>Ba, Sr, REE</td>
</tr>
<tr>
<td>Monazite</td>
<td>(REE, P)</td>
<td>Th</td>
</tr>
<tr>
<td>Xenotime</td>
<td>(YPO$_4$)</td>
<td>REE</td>
</tr>
<tr>
<td>Apatite</td>
<td>(Ca, P)</td>
<td>REE</td>
</tr>
<tr>
<td>Zircon</td>
<td>(ZrSiO$_4$)</td>
<td>U, Pb, Th</td>
</tr>
<tr>
<td>Rutile</td>
<td>(TiO$_2$)</td>
<td></td>
</tr>
<tr>
<td>Barite</td>
<td>(BaSO$_4$)</td>
<td></td>
</tr>
<tr>
<td>Feldspars</td>
<td>(Ca, Na, K, Al, Si)</td>
<td></td>
</tr>
<tr>
<td>Micas</td>
<td>(K, Fe, Mg, Ti, Al, Si)</td>
<td></td>
</tr>
<tr>
<td>Zeolites</td>
<td>(Ca, Na, K, Al, Si)</td>
<td></td>
</tr>
</tbody>
</table>
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.).

<table>
<thead>
<tr>
<th>Jiaole Township</th>
<th>Haizi Township</th>
<th>Xingyi City-Dadi area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>As</td>
<td>Sb</td>
</tr>
<tr>
<td>A</td>
<td>2223</td>
<td>55</td>
</tr>
<tr>
<td>B</td>
<td>1591</td>
<td>132</td>
</tr>
<tr>
<td>C</td>
<td>7391</td>
<td>165</td>
</tr>
<tr>
<td>D</td>
<td>607</td>
<td>40</td>
</tr>
<tr>
<td>E</td>
<td>405</td>
<td>29</td>
</tr>
<tr>
<td>F</td>
<td>419</td>
<td>22</td>
</tr>
<tr>
<td>G</td>
<td>239</td>
<td>38</td>
</tr>
<tr>
<td>H</td>
<td>313</td>
<td>68</td>
</tr>
<tr>
<td>I</td>
<td>2286</td>
<td>142</td>
</tr>
</tbody>
</table>

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 ($\text{FeS}_2$) 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, $\text{HgSe}$, $\text{HgS}$ (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

<table>
<thead>
<tr>
<th>Basin</th>
<th>Average Cl in Coal (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northern Appalachian</td>
<td>850</td>
</tr>
<tr>
<td>Central Appalachian</td>
<td>950</td>
</tr>
<tr>
<td>Southern Appalachian</td>
<td>310</td>
</tr>
</tbody>
</table>

*Results for Bragg et al., 1991*
# Chlorine Stratigraphic Variation

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

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.
• **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.
Coal Formation and Diagenesis

Geologic Controls on Coal Chemistry
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
Climate

Controls the type of peat, the type and rate of vegetation, and sediment input into the mire or peat swamp.
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
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 Upper Pennsylvanian Appalachian basin coals).

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

**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*

www.noaa.gov
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
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 °C to 200 °C in about 1 hour
  – Samples heated at 200 °C for 1.5 hrs
  – Temperature increased to 350 °C and held 2 hrs
  – Temperature increased to 525 °C and held 36 hrs
  – Samples slowly cooled (1-2 hr)
  – Samples examined and re-ignited at 525 °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 °C with Na₂O₂)
    » 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$_2$O
- 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 Chromatography**
    
    • Single element Cl
    • Requires dissolution
    • Less than 5 percent of coals below detection limit of 150 ppm
    • Reliable and accurate
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 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
- Hydrochloric Acid 2N leaches: leached coal step 1 (sequential)
- Hydrofluoric Acid 48% leaches: leached coal step 2 (sequential)
- Nitric Acid 2N leaches: leached coal step 3 (sequential)

Step 1: Exchangable Organic Bound Material (Carbonates)
Step 2: Acid Soluble Salts (Carbonates, Sulfates and Acid Soluble Sulfides)
Step 3: Silicates Including Quartz and Clays
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 (HNO₃):
  – 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 \( \text{HNO}_3 \) (nitric acid)
Concentrations of As in the original coal samples in parts per million

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>7.4</td>
</tr>
<tr>
<td>P2</td>
<td>4</td>
</tr>
<tr>
<td>P3</td>
<td>10</td>
</tr>
<tr>
<td>P4</td>
<td>3.5</td>
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<td>P5</td>
<td>13</td>
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<td>P6</td>
<td>4.5</td>
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<tr>
<td>K1</td>
<td>13</td>
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<tr>
<td>K2</td>
<td>4.7</td>
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<td>F1</td>
<td>45</td>
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<tr>
<td>F2</td>
<td>2</td>
</tr>
<tr>
<td>EH</td>
<td>4.4</td>
</tr>
<tr>
<td>SA</td>
<td>20</td>
</tr>
<tr>
<td>E1</td>
<td>7.2</td>
</tr>
<tr>
<td>E2</td>
<td>2.3</td>
</tr>
<tr>
<td>R1</td>
<td>1.5</td>
</tr>
<tr>
<td>R2</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Nitric Acid
Hydrochloric Acid
Hydrofluoric Acid
Ammonium Acetate

Mercury

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

Legend:
- Ammonium Acetate
- Hydrochloric Acid
- Hydrofluoric Acid
- Nitric Acid
Results

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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Be (ppm)</th>
</tr>
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<tbody>
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<td>P2</td>
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<td>P3</td>
<td>0.9</td>
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<tr>
<td>P4</td>
<td>0.8</td>
</tr>
<tr>
<td>P5</td>
<td>0.7</td>
</tr>
<tr>
<td>K1</td>
<td>2</td>
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<td>K2</td>
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<td>F2</td>
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<tr>
<td>EH</td>
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<tr>
<td>SA</td>
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<tr>
<td>E1</td>
<td>1</td>
</tr>
<tr>
<td>E2</td>
<td>1</td>
</tr>
<tr>
<td>R1</td>
<td>0.5</td>
</tr>
<tr>
<td>R2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Legend:
- Red: Ammonium Acetate
- Green: Hydrochloric Acid
- Blue: Hydrofluoric Acid
- Yellow: Nitric Acid
Chromium

Percent leached

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

- Ammonium Acetate
- Hydrochloric Acid
- Hydrofluoric Acid
- Nitric Acid

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
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<tbody>
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<td>P2</td>
<td>9.7</td>
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<tr>
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<td>R1</td>
<td>3.9</td>
</tr>
<tr>
<td>R2</td>
<td>6</td>
</tr>
</tbody>
</table>
Results

• When the majority of an 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

Percent leached

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

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>P5</th>
<th>F1</th>
<th>E1</th>
<th>P2</th>
<th>P6</th>
<th>F2</th>
<th>E2</th>
<th>P3</th>
<th>K1</th>
<th>EH</th>
<th>R1</th>
<th>R2</th>
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<td></td>
<td>8.1</td>
<td>7.4</td>
<td>230</td>
<td>R2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Ammonium Acetate
- Hydrochloric Acid
- Hydrofluoric Acid
- Nitric Acid
Nitric Acid
Hydrochloric Acid
Hydrofluoric Acid
Ammonium Acetate

Zinc

Percent leached

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
</tr>
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<tbody>
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<tr>
<td>F2</td>
<td>13</td>
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<tr>
<td>EH</td>
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<td>SA</td>
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<td>E1</td>
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<tr>
<td>E2</td>
<td>70</td>
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<tr>
<td>R1</td>
<td>6.8</td>
</tr>
<tr>
<td>R2</td>
<td>8.1</td>
</tr>
</tbody>
</table>

Ammonium Acetate
Hydrochloric Acid
Hydrofluoric Acid
Nitric Acid
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

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

- Ammonium Acetate
- Hydrochloric Acid
- Hydrofluoric Acid
- Nitric Acid

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
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<td>F2</td>
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<td>0.31</td>
</tr>
<tr>
<td>R2</td>
<td>0.24</td>
</tr>
</tbody>
</table>
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
Results

• Leaching of some elements are not dominated by a single solvent
  – Multiple modes of occurrence
  – Said to by mixed modes of occurrence
Nitric Acid
Hydrochloric Acid
Hydrofluoric Acid
Ammonium Acetate

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

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
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<th>F2</th>
<th>E1</th>
<th>E2</th>
<th>R1</th>
<th>R2</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>5.9</td>
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<td>24</td>
<td>16</td>
<td>48</td>
<td>12</td>
<td>5.7</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Legend:
- Red: Ammonium Acetate
- Green: Hydrochloric Acid
- Blue: Hydrofluoric Acid
- Yellow: Nitric Acid
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
Electron-beam Instruments (SEM and Electron Microprobe)

- **Secondary Electrons** (imaging)
- **Back Scattered Electrons** (imaging + comp.)
- **Characteristic X-rays** (elemental composition)

Signals produced by electron beam/sample interaction

Diagram showing the interaction of an incident electron beam with a sample, resulting in various types of signals such as secondary electrons, back-scattered electrons, characteristic X-rays, and continuum X-rays.
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**

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

**Sensitive High-Resolution Ion Microprobe Reverse Geometry**
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 \( \mu \text{m} \) 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.
XAFS Experiment

NSLS Beamline X23 A2

As$_2$O$_3$ Reference

Sample Chamber

Incident Beam

(Li)Ge Detector
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:
  - $\text{Cr}^{3+}$/illite
  - Org. associated Cr (Amorph. CrOOH)
- Chromite- Common only in coals unusually rich in Cr.
- **Oxidation State**- Always $\text{Cr}^{3+}$ in coal (rare $\text{Cr}^{6+}$ 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coal Bed</th>
<th>Location</th>
<th>Arsenic Content (ppm)</th>
<th>Pyritic Sulfur&lt;sup&gt;1&lt;/sup&gt; (wt. %)</th>
<th>Arsenic in Pyrite (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitts #1</td>
<td>Pittsburgh</td>
<td>West Virginia</td>
<td>23.0</td>
<td>1.32</td>
<td>d.l. to 0.34</td>
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<td>Pittsburgh</td>
<td>West Virginia</td>
<td>12.0</td>
<td>1.58</td>
<td>d.l to 0.14</td>
</tr>
<tr>
<td>Spfd</td>
<td>Springfield</td>
<td>Indiana</td>
<td>6.5</td>
<td>2.13</td>
<td>d.l. to 0.06</td>
</tr>
<tr>
<td>TP1-1.0</td>
<td>Warrior</td>
<td>Alabama</td>
<td>8.2</td>
<td>0.26</td>
<td>d.l. to 2.46</td>
</tr>
<tr>
<td>LM1-2.0</td>
<td>Warrior</td>
<td>Alabama</td>
<td>8.9</td>
<td>0.27</td>
<td>d.l. to 2.72</td>
</tr>
</tbody>
</table>

<sup>1</sup>Dry Basis; <sup>2</sup>Microprobe detection limit approximately 0.01 weight percent.
Relative Concentration of As in Pyrite

Average ppm As in pyrite

- Spfld: n = 82
- Pitts-2: n = 80
- Pitts-1: n = 96
- AL LM-1: n = 78
- AL TP-2: n = 60
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)
XAFS PROJECT TIMELINE

Stage 1
November, 2002

Stage 2
July 2003

Stage 3
April 2004

Start
October, 2002
Results of least-squares fitting of As XANES spectra

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ala. LM-1</th>
<th>Ala. TP-1</th>
<th>Springfield</th>
<th>Pitts #1</th>
<th>Pitts #2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pyrite</td>
<td>Arsenate</td>
<td>Pyrite</td>
<td>Arsenate</td>
<td>Pyrite</td>
</tr>
<tr>
<td>Argon</td>
<td>77</td>
<td>23</td>
<td>82</td>
<td>18</td>
<td>92</td>
</tr>
<tr>
<td>Oxygen</td>
<td>76</td>
<td>24</td>
<td>81</td>
<td>19</td>
<td>91</td>
</tr>
<tr>
<td>Air Dry</td>
<td>75</td>
<td>25</td>
<td>81</td>
<td>19</td>
<td>91</td>
</tr>
<tr>
<td>Air Wet</td>
<td>61</td>
<td>39</td>
<td>69</td>
<td>31</td>
<td>70</td>
</tr>
</tbody>
</table>

Data are %As of total As in sample that is associated with pyrite or arsenate. Estimated error ±3%
Comparison of As XANES and $^{57}\text{Fe}$ Mössbauer Results (Stage 1 Data)

<table>
<thead>
<tr>
<th></th>
<th>Springfield</th>
<th></th>
<th>Pittsburgh #1</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Arsenic</td>
<td>Iron</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyrite</td>
<td>Arsenate</td>
<td>Pyrite</td>
<td>Jarosite</td>
</tr>
<tr>
<td>Argon</td>
<td>92</td>
<td>8</td>
<td>91</td>
<td>8</td>
</tr>
<tr>
<td>Air Wet</td>
<td>70</td>
<td>30</td>
<td>82</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Argon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>93</td>
<td>7</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>Air Wet</td>
<td>81</td>
<td>19</td>
<td>86</td>
<td>14</td>
</tr>
</tbody>
</table>
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/

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

- 86.9% Combustion Sources (e.g., coal-fired boilers)
- 10.0% Manufacturing Sources (Chlor-alkali, cement, batteries)
- 2.2% Area Sources (e.g., fluorescents, dental)
- 0.9% Miscellaneous Sources (e.g., Geothermal)

*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]
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

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

*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)

\[
\frac{1 \text{ lb Hg}}{10^7 \text{ lb coal}} \times \frac{1 \text{ lb coal}}{1.35 \times 10^5 \text{ Btu}} = \frac{7.4 \text{ lbs Hg}}{10^{12} \text{ Btu}}
\]
**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).

<table>
<thead>
<tr>
<th></th>
<th>Calorific value raw coal (Btu/lb)</th>
<th>Hg content raw coal (ppm)</th>
<th>Calorific value cleaned coal (Btu/lb)</th>
<th>Hg content cleaned coal (ppm)</th>
<th>Percent Hg reduction (equal energy basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10,704</td>
<td>0.23</td>
<td>13,730</td>
<td>0.16</td>
<td>37</td>
</tr>
</tbody>
</table>

Reducing Mercury Loading

• Example- Coal Cleaning for average Central Appalachian coal:

Other Ways To Reduce Hg:
• Selective Mining
• Increase Hg capture with ESP, FGD, etc.
• Unburned Carbon

<table>
<thead>
<tr>
<th>Raw Coal (lbs Hg/10^12 Btu)</th>
<th>Estimated Cleaned Coal (37% reduction)</th>
<th>MACT (existing boilers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.3</td>
<td>7.1</td>
<td>7.0</td>
</tr>
</tbody>
</table>

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 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 (Kilgrove 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.
National Atmospheric Deposition Program
Mercury Deposition Network

MDN 2003

VA-08 & VA-28
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.

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