Topics in Coal Geochemistry
Short Course

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U.S. Department of the Interior
U.S. Geological Survey
Global Coal Production and Use
Review of Basic Coal Data
Toward Global Emissions Standards

SESSION I
GLOBAL COAL PRODUCTION AND USE
Global Coal Production and Export
Producción y exportaciones mundiales de carbón

Production data by country, includes steam coal, coking coal, lignite, and recovered coal, production in million tonnes (Mt), 2016 provisional data.

<table>
<thead>
<tr>
<th>COAL PRODUCERS</th>
<th>Mt</th>
<th>% of world total</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>3,242</td>
<td>44.6</td>
</tr>
<tr>
<td>India</td>
<td>708</td>
<td>9.7</td>
</tr>
<tr>
<td>United States</td>
<td>672</td>
<td>9.2</td>
</tr>
<tr>
<td>Australia</td>
<td>503</td>
<td>6.9</td>
</tr>
<tr>
<td>Indonesia</td>
<td>460</td>
<td>6.3</td>
</tr>
<tr>
<td>Russian Federation</td>
<td>365</td>
<td>5.0</td>
</tr>
<tr>
<td>South Africa</td>
<td>257</td>
<td>3.5</td>
</tr>
<tr>
<td>Germany</td>
<td>176</td>
<td>2.4</td>
</tr>
<tr>
<td>Poland</td>
<td>131</td>
<td>1.8</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>98</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>Colombia</strong></td>
<td>91</td>
<td>1.3</td>
</tr>
<tr>
<td>Canada</td>
<td>60</td>
<td>0.8</td>
</tr>
<tr>
<td>Rest of the World</td>
<td>506</td>
<td>7.0</td>
</tr>
<tr>
<td>World</td>
<td>7,269</td>
<td>99.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COAL EXPORTERS</th>
<th>Mt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>389</td>
</tr>
<tr>
<td>Indonesia</td>
<td>367</td>
</tr>
<tr>
<td>Russian Federation</td>
<td>147</td>
</tr>
<tr>
<td><strong>Colombia</strong></td>
<td>83</td>
</tr>
<tr>
<td>South Africa</td>
<td>76</td>
</tr>
<tr>
<td>United States</td>
<td>46</td>
</tr>
<tr>
<td>Mongolia</td>
<td>26</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>26</td>
</tr>
<tr>
<td>Canada</td>
<td>24</td>
</tr>
<tr>
<td>DPR of Korea</td>
<td>21</td>
</tr>
<tr>
<td>Others</td>
<td>8</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>1,213</td>
</tr>
</tbody>
</table>

1.1-2
### World Coal Proved Reserves

**Reservas probadas de carbón en el mundo**

<table>
<thead>
<tr>
<th>Rank</th>
<th>Country</th>
<th>Total Reserves (Mt)</th>
<th>Rank distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>United States</td>
<td>237,295</td>
<td>All</td>
</tr>
<tr>
<td>2.</td>
<td>Russian Federation</td>
<td>157,010</td>
<td>All</td>
</tr>
<tr>
<td>3.</td>
<td>China</td>
<td>114,500</td>
<td>All</td>
</tr>
<tr>
<td>4.</td>
<td>Australia</td>
<td>76,400</td>
<td>Bituminous, lignite</td>
</tr>
<tr>
<td>5.</td>
<td>India</td>
<td>60,600</td>
<td>Bituminous, lignite</td>
</tr>
<tr>
<td>6.</td>
<td>Germany</td>
<td>40,548</td>
<td>Lignite</td>
</tr>
<tr>
<td>7.</td>
<td>Ukraine</td>
<td>33,873</td>
<td>Bituminous, sub-bituminous</td>
</tr>
<tr>
<td>8.</td>
<td>Kazakhstan</td>
<td>33,600</td>
<td>Bituminous, lignite</td>
</tr>
<tr>
<td>9.</td>
<td>South Africa</td>
<td>30,156</td>
<td>Bituminous</td>
</tr>
<tr>
<td>10.</td>
<td>Indonesia</td>
<td>28,017</td>
<td>Sub-bituminous</td>
</tr>
<tr>
<td>11.</td>
<td>Serbia</td>
<td>13,411</td>
<td>Lignite</td>
</tr>
<tr>
<td>12.</td>
<td>Colombia</td>
<td>6,746</td>
<td>Bituminous</td>
</tr>
<tr>
<td>13.</td>
<td>Brazil</td>
<td>6,630</td>
<td>Sub-bituminous</td>
</tr>
<tr>
<td>14.</td>
<td>Canada</td>
<td>6,582</td>
<td>All</td>
</tr>
<tr>
<td>15.</td>
<td>Poland</td>
<td>5,465</td>
<td>Bituminous, lignite</td>
</tr>
</tbody>
</table>


Electricity from Coal
Generación de energía eléctrica usando carbón

- France is lowest due to reliance on nuclear power.
- Colombia, Canada each have significant hydro-electric power and rely on coal for only about 10% of their electric power.
- U.S. fraction slightly below world average.
- Countries with high reliance on coal (e.g., Poland, South Africa) lack alternatives.

http://data.worldbank.org/indicator/EG.ELC.COAL.ZS.
Colombian Coal Production
Producción colombiana de carbón

Colombia coal production and exports by year in thousand tonnes (kt).

Coal production for La Guajira (Guajira) and Cesar compared to other departments of Colombia (Other), in tonnes.
Source: World Coal, 2011
Coal Fields of Colombia

Yacimientos colombianos de carbón

Source: Tewalt and others, 2006
Colombia – Power Generation by Source

Fuentes colombianas de energía

Generation in gigawatt hours (GWh).

U.S. Coal Production (1980 – 2015)
Producción de carbón de Estados Unidos

Source: U.S. Energy Information Administration, 2016

Source: U.S. Energy Information Administration, 2016
U.S. Coal Basins

Cuencas carboníferas en Estados Unidos

Source: East, 2013, USGS Open-File Report 2012-1205
U.S. Coal Production by Coal Basin
Producción carbonífera de EE.UU. por cuenca

- Production declining in Appalachian Basin and Powder River Basin, the two largest producers.
- Production increasing (through 2013) or steady in Illinois Basin due to low transportation costs and increased use of FGD scrubbers in nearby power stations.

Source: U.S. Energy Information Administration, 2016
In the U.S., gas-fired power generation has replaced some of the coal-fired capacity:
U.S Electric Power Generation (1990 – 2040)
Generación de energía eléctrica en EE.UU.

2015 U.S. Energy Mix
Coal – 33%
Nat. Gas – 33%
Nuclear – 20%
Renewable – 13%
  Hydro – 6%
  Wind – 4.7%
  Biomass – 1.6%
  Solar – 0.6%
Total ---------------99%

U.S. Power Generation by Region

Generación de energía eléctrica en EE.UU. por regiones

Source: U.S. Energy Information Administration, 2016
Producción de gas de lutita en EE.UU.

Source: U.S. Energy Information Administration, 2016
USGS Shale Gas Studies
Gas de lutita en EE.UU.: bibliografía

• U.S. Energy Information Administration projects continued increase in U.S. shale gas production from 2020 to 2040.
• USGS fundamental studies of pore structure in gas shales to better understand gas occurrence and distribution.
• Sampling and analysis of wastewater produced with oil and gas wells (produced water) and related environmental studies.
• Can we see chemicals from hydraulic fracturing in wastewater produced from gas wells?
Carbon Capture and Storage
Captura y almacenamiento de carbono

- **Geologic carbon storage** addressed in USGS assessment of storage capacity in underground **saline reservoirs**.
- The regions with the largest storage resources are the Coastal Plains (mostly in Gulf Coast, 65%); Rocky Mountains and N. Great Plains (9%); and Alaska (9%; mostly North Slope).
- Related questions—
  - Environmental risks of storing CO₂ in underground reservoirs?
  - Potential for CO₂ leakage, its impacts to drinking water, and induced seismicity?
  - Largest storage capacity not near greatest concentration of coal-fired powerplants.

Source: USGS, 2013, Circular 1386
https://pubs.usgs.gov/circ/1386/
• Colombia is the 11th largest coal producer and the 4th largest exporter of coal in the world.
• Coal production and exports have increased by about a factor of four in the last 20 years.
• In Colombia only about 10% of electricity comes for coal which is among the lowest in the world.
• Colombian coals are produced for export without preparation due to their low ash and sulfur contents.
• Colombian coals are also much below world average contents of mercury.
Summary – Topic 1: Global Coal Production and Use

- U.S. is the 3rd largest coal producer and the 6th largest coal exporter in the world.
- U.S. coal production increased steadily until the mid-2000s, but has now begun to decline.
- Currently, about 33% of U.S. electric power generation comes from coal, which is slightly below the world average and has decreased from about 50% in the last decade.
- With discovery of large shale gas resources in the U.S., coal-fired generating capacity has been replaced by gas-fired generation.
- The USGS has completed a national assessment of underground storage capacity for CO$_2$. 


REVIEW OF BASIC COAL DATA
Some Basic Points About Coal

Generalidades sobre carbones

- Coal rank: *Lignite, sub-bituminous, bituminous, anthracite*, listed in order of increasing rank.

- Generally, *heating value* increases and *moisture* decreases with increasing rank.

- Noncombustible mineral matter in coal is referred to as *ash* or as mineral matter. Ash content is important in determining coal combustion characteristics and element mass-balance.

- Generally, trace element concentrations in coal are greater in ash than in the organic fraction.
Coal – A Complex Natural Resource

• Circular 1143 (2003) is a good introduction to coal science.
• Publication reviews coal quality and coal use in the U.S. with sections on coal origins, coal formation, mineral matter in coal, and health effects.

Important ASTM Methods for Coal
Normas ASTM para carbones

<table>
<thead>
<tr>
<th>Method</th>
<th>What it Does</th>
</tr>
</thead>
<tbody>
<tr>
<td>• D2234, 4596 Sample collection</td>
<td>• How to collect coal samples.</td>
</tr>
<tr>
<td>• D2013 Sample preparation</td>
<td>• Grinding of coal for analysis.</td>
</tr>
<tr>
<td>• D5865 Calorific value</td>
<td>• Gives heating value of coal.</td>
</tr>
<tr>
<td>• D3172 Proximate analysis</td>
<td>• Gives percent ash, fixed carbon, moisture, volatiles.</td>
</tr>
<tr>
<td>• D3176 Ultimate analysis</td>
<td>• Gives percent ash, and total C, H, N, O, and S.</td>
</tr>
<tr>
<td>• D2492 Forms of Sulfur</td>
<td>• Gives amount of S in pyrite, as organic S, or as sulfate.</td>
</tr>
<tr>
<td>• D388 Rank Classification</td>
<td>• Classifies coal according to fixed carbon and heating value (D5865 and D3172).</td>
</tr>
</tbody>
</table>

ASTM Coal Rank (ASTM D388)
Calidades ASTM de carbones

- Rank classification is based on coal heating value (HV) or fixed carbon (FC) if FC is greater than 69%.
- HV is adjusted to a mineral matter-free (MMF) basis.
- FC is adjusted to a dry, MMF basis.
- Most Colombian coals are high volatile bituminous.

Source: East, 2013
USGS Open-File Report 2012-1205, from ASTM D388
Example of ASTM D388 Rank Classification

Ejemplo de clasificación ASTM D388

As-received determination for four Colombian coal samples (in percent except HV)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formation/Bed</th>
<th>Ash (A)</th>
<th>Moisture (M)</th>
<th>Fixed Carbon (FC)</th>
<th>Sulfur (S)</th>
<th>Heating Value (HV) (Btu/lb)</th>
<th>Heating Value (HV) (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGM 1077</td>
<td>Guaduas</td>
<td>5.86</td>
<td>0.85</td>
<td>60.26</td>
<td>0.73</td>
<td>14,690</td>
<td>34.2</td>
</tr>
<tr>
<td>IGM 0073C</td>
<td>Cerrejón 75</td>
<td>1.01</td>
<td>3.66</td>
<td>49.15</td>
<td>0.47</td>
<td>13,770</td>
<td>32.0</td>
</tr>
<tr>
<td>IGM 0067C</td>
<td>Cerrejón 115</td>
<td>0.53</td>
<td>3.89</td>
<td>55.76</td>
<td>0.63</td>
<td>13,520</td>
<td>31.4</td>
</tr>
<tr>
<td>IGM 1238</td>
<td>Cerrito y Cienaga de Oro</td>
<td>2.92</td>
<td>12.81</td>
<td>43.22</td>
<td>0.58</td>
<td>10,610</td>
<td>24.7</td>
</tr>
</tbody>
</table>

FORMULAE (ASTM D388)*

Fixed Carbon (FC) Dry-MMF: 100(FC-0.15S)/(100-(M + 1.08A + 0.55S))

Heating Value (HV) Moist-MMF, Btu/lb: 100(Btu-50S)/(100- (1.08A + 0.55S))

To convert Btu/lb to MJ/kg, multiply by 0.0023255

*Assumes no S as sulfate

Values adjusted for ASTM D388 Rank determination

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formation/Bed</th>
<th>FC (Dry MMF)</th>
<th>HV (Moist MMF, Btu/lb)</th>
<th>HV (Moist MMF, MJ/kg)</th>
<th>ASTM Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGM 1077</td>
<td>Guaduas</td>
<td>65.08</td>
<td>15,711</td>
<td>36.5</td>
<td>High Volatile A Bituminous</td>
</tr>
<tr>
<td>IGM 0073C</td>
<td>Cerrejón 75</td>
<td>51.67</td>
<td>13,935</td>
<td>32.4</td>
<td>High Volatile B Bituminous</td>
</tr>
<tr>
<td>IGM 0067C</td>
<td>Cerrejón 115</td>
<td>58.48</td>
<td>13,614</td>
<td>31.7</td>
<td>High Volatile B Bituminous</td>
</tr>
<tr>
<td>IGM 1238</td>
<td>Cerrito y Cienaga de Oro</td>
<td>51.52</td>
<td>10,962</td>
<td>25.5</td>
<td>High Volatile C Bituminous or Subbituminous A</td>
</tr>
</tbody>
</table>

Source: Tewalt and others, 2006
Coal Sampling
Muestreo de carbones

- **ASTM D4596** Standard Practice for Collection of Channel Samples of Coal in a Mine.
- **ASTM D2234** Standard Practice for Collection of a Gross Sample of Coal.

- Used to sample an entire coal bed. Top, bottom, and partings are commonly included.
- Used for general sampling run of mine coals or from a stopped belt. Sample across entire belt if moving or stopped.

Sampling Coal Ash
Muestreo de cenizas

- ASTM methods are not available for geochemical sampling of ash.
- Collect fly ash samples in cans or rigid jars having a sealable airtight lid.
- Collect from front, middle, and rear ESP hoppers.
- Collect economizer fly ash and bottom ash if available.
- Avoid putting hot ash directly into plastic containers!!

Source: James Hower, University of Kentucky
Forms of Sulfur (ASTM D2492)
Distinctos tipos de azufre

• Sulfur in coal has three forms- **organic**, **pyritic**, and **sulfate**.

• Total sulfur is determined in **D4239**.

• **D2492** determines **pyritic sulfur** and **sulfate sulfur**. **Organic sulfur** is calculated by the difference as (total sulfur) – (pyritic sulfur + sulfate sulfur).

• Freshly collected samples of unweathered coal should have **little or no sulfate sulfur**.
Examples of Sulfur Forms (ASTM D4239 + D2492)

Ejemplos de distintos tipos de azufre

South African Power Station Feed Coal
(Low-Sulfur Coal; as-received basis)

<table>
<thead>
<tr>
<th>Sample</th>
<th>KFC 2B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Sulfur (%)</td>
<td>0.69</td>
</tr>
<tr>
<td>Sulfate Sulfur</td>
<td>0.06</td>
</tr>
<tr>
<td>Pyritic Sulfur</td>
<td>0.31</td>
</tr>
<tr>
<td>Organic Sulfur (by difference)</td>
<td>0.32</td>
</tr>
</tbody>
</table>

U.S. Illinois Basin
(High-Sulfur Coal; as-received basis)

<table>
<thead>
<tr>
<th>Samples</th>
<th>IL-1 Raw</th>
<th>IL-8 Cleaned</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Sulfur (%)</td>
<td>5.39</td>
<td>2.37</td>
</tr>
<tr>
<td>Sulfate Sulfur</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Pyritic Sulfur</td>
<td>4.46</td>
<td>0.88</td>
</tr>
<tr>
<td>Organic Sulfur (by difference)</td>
<td>0.92</td>
<td>1.48</td>
</tr>
<tr>
<td>Heating value (Btu/lb)</td>
<td>7,141</td>
<td>11,745</td>
</tr>
</tbody>
</table>

Ukraine coal from outcrop
in abandoned mine (as-received basis)

<table>
<thead>
<tr>
<th>Sample</th>
<th>N-4A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Sulfur (%)</td>
<td>3.08</td>
</tr>
<tr>
<td>Sulfate Sulfur</td>
<td>0.39</td>
</tr>
<tr>
<td>Pyritic Sulfur</td>
<td>1.37</td>
</tr>
<tr>
<td>Organic Sulfur (by difference)</td>
<td>1.32</td>
</tr>
</tbody>
</table>

- Proportions of **pyritic** and **organic sulfur** in coal are highly **variable**.
- In coal preparation, **pyritic sulfur is reduced** while **organic sulfur is retained**.
- As organic fraction is increased, so is **heating value**.
- Sulfate sulfur is minimal in unweathered samples; higher in samples from outcrop.
Summary – Topic 2: Review of Basic Coal Data

• Standardized analysis and reporting methods for coal quality parameters are available using ASTM methods.
• Important parameters include mineral matter (ash) content, heating value, fixed carbon, sulfur content, and moisture.
• Heating value and (or) fixed carbon expressed on a dry, ash-free basis determines ASTM coal rank.
• Low rank coals have low heating values and high moisture contents.
• Higher rank coals have higher heating values and lower moisture contents.
• Sulfur forms include organic, pyritic, and sulfate. Proportions of organic and pyritic vary; sulfate is low in fresh coal samples and higher in weathered samples.
References – Topic 2: Review of Basic Coal Data


TOWARD GLOBAL EMISSIONS STANDARDS
Paris Agreement on Climate Change
Acuerdo de Paris sobre cambio climático

- **Paris Agreement** adopted on 12 December, 2015. Every country is expected to have a plan to reduce carbon emissions.

- Plans will be revisited every 5 years and countries are required to monitor their progress in reducing carbon emissions using a specified uniform approach.

- Agreement goes into effect 30 days after at least 55 signers representing an estimated 55% of emissions ratify the treaty.

- Currently (Nov., 2017), 197 parties have signed the agreement and it has been ratified or accepted by 169 countries.

- 55/55 status was reached on 5 October, 2016 so the agreement went into effect on 4 November, 2016.

- June 1, 2017, U.S. President announces intent to withdraw from the Paris Agreement.

Limiting U.S. Carbon Emissions
Reducción de emisiones por carbones en EE.UU.

- National emissions standards with some flexibility in State approaches to compliance.
- Benefit in emissions reduction and health impacts.
- 32% carbon reduction goal relative to 2005 emissions by a 2030 time frame.
- October, 2017, EPA proposes repealing the CPP following Executive order calling for its review.

Source: U.S. Environmental Protection Agency, 2015
https://www.epa.gov/cleanpowerplan.
Minamata Convention on Mercury
Tratado de Minamata sobre mercurio

• 2013 global treaty to protect human health and the environment from the adverse effects of mercury.
• Controls anthropogenic release of mercury and limits other mercury uses.
• Includes a ban on new mercury mines, phase-out of existing ones, controls on air emissions, and regulation of mercury used in artisanal and small-scale gold mining.
• 128 countries are signatory with 84 ratifications (min. 50).
• Treaty entered into force on 16 August, 2017.

Source: United Nations Environment Programme (UNEP), 2016
U.S. EPA Mercury and Air Toxics Standards (MATS)
Normas sobre contaminación atmosférica en EE.UU.

- Standards limit emissions of mercury, other trace elements (Be, Cr, Mn, Co, Ni, As, Se, Sb, and Pb), and acid gasses, including HF and HCl.
- Standards apply to coal- and oil-fired generating units $\geq 25$ megawatts.
- MATS implementation went into effect in 2016.

Rationale For U.S. EPA MATS
Justificación de las normas

- Power plants are the largest source of U.S. mercury emissions.
- People are exposed to mercury by eating contaminated fish.
- Other toxic metals from power plants, such as arsenic, chromium and nickel, can cause cancer.
- EPA estimates that implementation of MATS will have health benefits avoiding:
  4,200 to 11,000 premature deaths
  4,700 nonfatal heart attacks
  2,600 hospitalizations for respiratory and cardiovascular diseases


### Sources of U.S. Mercury Emissions

<table>
<thead>
<tr>
<th>Industrial Category</th>
<th>1990 Emissions (tons per year)</th>
<th>2005 Emissions (tons per year)</th>
<th>Percent Reduction</th>
<th>2016 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Plants</td>
<td>59</td>
<td>53</td>
<td>10%</td>
<td>Not Regulated</td>
</tr>
<tr>
<td>Municipal Waste Combustors</td>
<td>57</td>
<td>2</td>
<td>96%</td>
<td>Regulated</td>
</tr>
<tr>
<td>Medical Waste Incinerators</td>
<td>51</td>
<td>1</td>
<td>98%</td>
<td>Regulated</td>
</tr>
</tbody>
</table>

Source: U.S. EPA, 2011a
[https://www.epa.gov/mats](https://www.epa.gov/mats)

Map Showing U.S Fish Consumption Advisories for Mercury (2010)

Source: Kolker and others, 2012.
Summary – Topic 3: Global Emissions Standards

• Global emissions limits for CO₂ through the Paris Agreement, and mercury, through the Minamata Convention, are being adopted.

• Conditions for ratification the Paris Agreement have been met, but after ratifying the Agreement, the U.S. announced its intent to withdraw from the Paris Agreement. The Agreement allows flexibility in the approach each country may take to reduce their CO₂ emissions.

• The Minamata Convention has now entered into force. The Convention includes limits on primary mercury production, mercury used in gold mining, and mercury emissions from coal. The U.S. was the first country to ratify the Minamata Agreement and remains a party to the Convention.

• The U.S. EPA has introduced plans to limit U.S. carbon and mercury emissions from coal combustion by its Clean Power Plan and its Mercury and Air Toxics Standards, respectively. The MATS standards are being implemented at U.S. utility power stations, but the EPA has now proposed repealing the Clean Power Plan.


TRACE ELEMENTS IN COAL
Why Study Trace Elements in Coal?

Justificación del estudio de elementos traza

• Differences in coal quality affect operation of coal-fired utility power stations and their emissions.

• An understanding of trace-metal distribution in coal is needed to:
  – Predict powerplant emissions.
  – Predict element behavior in coal preparation.
  – Control release of metals from coal and coal combustion materials to groundwater.
  – Minimize health consequences of coal use.
### Effects of Inorganic Substances on Coal Utilization

<table>
<thead>
<tr>
<th>Element</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Boiler <em>Fouling</em></td>
</tr>
<tr>
<td>Iron</td>
<td>Boiler <em>Slagging</em></td>
</tr>
<tr>
<td>Chlorine</td>
<td><em>Corrosion</em>; Mercury Capture</td>
</tr>
<tr>
<td>Silicon (Quartz)</td>
<td><em>Erosion</em> of Combustors</td>
</tr>
</tbody>
</table>

*USGS*  
2.1-3
Mode of Occurrence Concept

Modo de ocurrencia de los elementos químicos

• **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

Modo de ocurrencia de los elementos químicos

**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])
Generalized Minerals in Coal
Presencia de minerales en carbones

**Major constituents**

- **Quartz**: (SiO$_2$)
- **Clays**:
  - Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$)
  - Illite-smectite (K,Al,Si,Fe,Mg)
- **Fe-disulfides**:
  - Pyrite, marcasite (both FeS$_2$)
- **Carbonates**:
  - Calcite (CaCO$_3$) dolomite (Ca,Mg), ankerite (Ca,Fe,Mg,Mn), siderite (FeCO$_3$)
- **Trace phases**:
  - Chalcopyrite (CuFeS$_2$), sphalerite (ZnS), galena (PbS), clausthalite (PbSe), zircon (ZrSiO$_4$), allanite (Ca,REE,Al,Fe,Si).

**Trace constituents**

- **Quartz**: None measured
- **Clays**:
  - Kaolinite: None measured
  - Illite-smectite: Cr, V
- **Fe-disulfides**: As, Hg, Se, Sb, Ni. Arsenopyrite (FeAsS) very rare.
- **Carbonates**: Divalent alkaline earths (Sr, Ba).
- **Trace phases**: Are sources of their respective constituents. No common Cd trace phase but present at percent level in sphalerite. All but PbSe are common in rocks.

Sources: Finkelman, 1981; Kolker and Finkelman, 1998; Finkelman and others, 2018
### Minor/Trace Phases

**Elementos menores y elementos traza**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula or 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>Chalcopryrite</td>
<td>(CuFeS$_2$)</td>
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</tr>
<tr>
<td>Clausthalite</td>
<td>(PbSe)</td>
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<tr>
<td>Crandallite Group</td>
<td>(Ca, Al, P)</td>
<td>Ba, Sr, REE</td>
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<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>
Metals in Coal
Elementos metálicos en carbones

• Emissions of Sb, As, Be, Cd, Cr, Co, Pb, Hg, Mn, Ni, Se regulated under EPA Mercury and Air Toxics Standards.

• As, Sb, Se, Cd, Hg, Co, Pb commonly have a sulfide association in bituminous coals.

• Mn, Cr, Ni, Be can have mixed associations:
  - Cr, Ni in illite-smectite clays and organics
  - Mn in carbonates, clays, and organics
  - Be in silicates (clays) and possibly organics

• Mineral-associated elements can be reduced by coal preparation (washing).
How to Study Trace Elements in Coal
Cómo estudiar elementos traza

**Bulk Methods**

**Whole Sample**
- **Chemical Analysis** - Element distribution, e.g., by **ICP-MS**.
- **Selective leaching** - Element forms (species) inferred from leaching behavior.
- **X-ray absorption fine structure (XAFS)** - Element species determined directly by structure of X-ray absorption edge.

**Microanalysis**

**Specific Minerals**
- **Scanning Electron Microscope (SEM)** - Texture and distribution of minerals in coal individually.
- **Electron microprobe** - Most abundant elements in individual minerals.
- **Laser Ablation ICP-MS and Ion Microprobe** - Trace elements in individual minerals.
- **Transmission Electron Microscope (TEM)** - Minerals in coal individually at very fine scale.
About Moisture

Humedad

• Generally, **heating 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.

• **Moisture** content can change if samples are not analyzed promptly after collection.
Arsenic in Coal

• Arsenic is a persistent toxin that occurs in trace amounts in rocks, sediments, and coal. 

• All coals contain some arsenic. Arsenic contents vary considerably by coal basin.

• In bituminous coals, arsenic occurs primarily in pyrite, with lesser amounts in organic portions of coal.

• A small fraction of arsenic present in coal is emitted to the atmosphere during coal combustion.

• Direct exposure to arsenic in coal may occur where coal is used in the home for cooking and heating.

Source: Kolker and others, 2006a, USGS Fact Sheet 2005-3152
https://pubs.usgs.gov/fs/2005/3152/
Leaching Procedure for Coal Samples
Lixiviación de carbones

4-step leaching procedure for:
1) Ion-exchangeable organic-bound
2) Acid-soluble salts
3) Silicates
4) Sulfides

Selective Leaching of Arsenic in U.S. Coals
Lixiviación de arsénico en carbones en EE.UU.

- Results from selective leaching studies of bulk coal show a predominant pyritic (nitric acid leached) association.
- Pyritic association is less pronounced in two low-rank coals.
- Unleached fraction interpreted to be arsenic in the organic portion of coal.

Arsenic Oxidation
Oxidación del arsénico

• Over time arsenic in coal undergoes oxidation to an arsenate ($\text{AsO}_4^{3-}$) form that is analogous to sulfate ($\text{SO}_4^{2-}$).
• What happens when pyrite is enriched in As?
• Experimental study over 18 months comparing behavior of five U.S. bituminous coals having different extents of arsenic substitution in pyrite.
• Monitoring of arsenic species by As-XANES, a spectroscopic method.

Mean values for As in pyrite based on quantitative electron microprobe analysis of about 100 analysis points per sample.

Source: Kolker and Huggins, 2007
Applied Geochemistry
Monitoring by As-XANES

- Arsenate forms gradually with time under dry conditions.
- Under wet conditions, arsenate forms much more rapidly.

Source: Kolker and Huggins, 2007
Applied Geochemistry
Selective Leaching vs. XAFS for Arsenic Species

Dos técnicas para el análisis de arsénico

- Proportion of arsenic in the arsenate form was compared using synchrotron As XANES (XAFS) vs. selective leaching.

- Leaching arsenate fraction obtained by combining arsenic leached in the HCL and HF fractions.

- Both methods give similar arsenate proportions and show progressive increase with time.

Source: Huggins and others, 2002, Energy and Fuels
Selective Leaching of Arsenic in U.S. Coals
Lixiviación de arsénico en carbones de EE.UU.

- Results from selective leaching studies of bulk coal show a predominant pyritic association.
- Pyritic association is less pronounced in two low-rank coals.
- Un-leached fraction interpreted to be arsenic in the organic portion of coal.
- HF + HCl fraction interpreted as the arsenate fraction.

Summary – Topic 1: Trace Elements in Coal

Resumen – Tema 1: Elementos traza en carbones

• Trace elements can have an organic, an inorganic, or a combined association, but in bituminous coals, the inorganic (mineral) association is predominant.

• Bulk analysis gives the total amount of an element present in all associations.

• Direct (e.g., microanalysis, spectroscopic methods) or indirect (e.g., selective leaching) methods are needed to determine element mode of occurrence in coal.
Summary – Topic 1: Trace Elements in Coal
(continued)

Resumen – Tema 1: Elementos traza en carbones

• Arsenic commonly occurs in trace amounts in coal.

• A portion of the arsenic present in coal is emitted during coal combustion and some is retained in coal combustion products.

• Arsenic occurs primarily in pyrite in bituminous coals with a greater portion or organic-associated arsenic in low rank coals.

• Arsenic in coal undergoes oxidation to arsenate similar to sulfur oxidation to sulfate.
References – Topic 1: Trace Elements in Coal


TRACE ELEMENTS IN FE-DISULFIDES IN COAL
Why Study Fe-Disulfides (FeS$_2$) in Coal?

Justificación del estudio de disulfuros de hierro

- Fe-disulfides (pyrite, marcasite) are common minerals in coal, controlling the distribution of As, Hg, Se, etc., especially in bituminous coals. A source of air and water pollutants.

- Knowing the distribution of minor elements in pyrite can help optimize strategies for coal preparation.

- Minor element variation shows differences resulting from changes in fluid chemistry during diagenesis.

- Minor element substitution can influence the stability of Fe-disulfides, affecting the rate of pyrite oxidation and formation of acid mine drainage (AMD).
<table>
<thead>
<tr>
<th>Sulfide</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Se</th>
<th>Sb</th>
<th>Hg</th>
<th>Pb</th>
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<td>dl - 1.5%</td>
<td>dl - 0.20 %</td>
<td>EPMA</td>
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<td>dl – 0.05%</td>
<td>dl – 0.79%</td>
<td>dl – 0.92%</td>
<td>dl – 0.14%</td>
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<td>dl – 590</td>
<td>dl – 140</td>
<td>dl – 104</td>
<td>dl – 18</td>
<td>LA ICP-MS2</td>
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<tr>
<td>Pyrite</td>
<td>dl – 1.2%</td>
<td>dl – 250</td>
<td>dl – 39</td>
<td>227</td>
<td>LA ICP-MS</td>
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<td>dl - 4,500</td>
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<td>dl - 39</td>
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<td>dl - 250</td>
<td>dl - 39</td>
<td>227</td>
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<td>dl - 1.2%</td>
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<td>dl - 39</td>
<td>227</td>
<td>LA ICP-MS</td>
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<tr>
<td>Pyrite</td>
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<td>dl - 2,300</td>
<td>dl - 1.2%</td>
<td>dl - 250</td>
<td>dl - 39</td>
<td>227</td>
<td>LA ICP-MS</td>
<td></td>
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<tr>
<td>Marcasite</td>
<td>4.8</td>
<td>227 – 1,210</td>
<td>32.2 - 45</td>
<td>2.5 -2.5</td>
<td>43 - 4,100</td>
<td>SXRF</td>
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<tr>
<td>Marcasite</td>
<td>25 - 2,740</td>
<td>30 - 3.4 %</td>
<td>2 - 452</td>
<td>43 - 4,100</td>
<td>SXRF</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

From Kolker, 2012, Int. J. of Coal Geology; values in ppm and (or) wt. %
Substitution of Minor Elements in FeS₂

Substitution for Fe²⁺
- Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺
- Poor fits: Pb²⁺, *Hg²⁺, etc.
- Coupled substitution:
  As³⁺ and Au⁺
  Other trivalent plus monovalent combinations

Substitution for S⁻
- As⁻, Se⁻, Sb⁻, etc.

*Oxidation state of Hg is assumed to be Hg²⁺, but is uncertain.

Source: Deditius and others, 2008, Geochimica et. Cosmochimica Acta
Generations of Iron Disulfides in Coal
Formación de disulfuros de hierro en carbones

- **Multiple generations** are commonly present and each may show minor element variation.
- **Framboidal pyrite** is always the earliest generation, commonly overgrown by subhedral pyrite.
- **Cleat- or vein-filling** pyrite are the latest pyrite generations as shown by crosscutting relations and compositional differences.
Framboids and their Overgrowths
Desarrollo de estructuras cristalinas

1) Staunton Formation, Indiana, USA;  2) Pittsburgh, West Virginia, USA
3) Donets Basin, Ukraine;    4) Staunton Formation, Indiana, USA
5) Donets Basin, Ukraine;    6) Illinois #6, Indiana, USA

Backscattered Electron (BSE) Images

Source: Kolker, 2012
International Journal of Coal Geology
2.2-6
Alabama, USA Warrior Basin Coal

Carbones en la cuenca Warrior, Alabama, EE.UU.

Warrior Basin is enriched in arsenic:

Arsenic enrichment seen in:

A. Subhedral frambooid overgrowths
B. Oscillatory-zoned aresenian pyrite
C. Cleat pyrite

Typically, framboidal pyrite is arsenic poor

Wavelength–dispersive electron microprobe element maps

Source: Goldhaber and others, 2003
Arsenic in Ground Water

USGS

2.2-7
Donetsk-Makeevka District, Ukraine
Distrito Donetsk-Makeevka, Ucrania

Donetsk is enriched in Hg and As:

Source: Kolker and others, 2009
International Journal of Coal Geology
As and Se Enrichment in Fe-disulfides
Enriquecimiento en As y Se de disulfuros de hierro

Wavelength–dispersive electron microprobe element maps:

A. Alabama, USA
B. Ukraine
C. Alabama, USA
D. West Virginia, USA
E. West Virginia, USA
F. Ukraine

Source:
Kolker, 2012
International Journal of Coal Geology
Nickel Enrichment in Framboids

Enriquecimiento en niquel

A. Pittsburgh Coal, Appalachian Basin, West Virginia, USA
B. Raccoon Creek Group Coal, Illinois Basin, Indiana, USA
C. H10 Middle Coal Bed, Donets Basin, Ukraine

Source: Kolker, 2012
International Journal of Coal Geology
Summary – Topic 2: Fe-Disulfides in Coal

Resumen – Tema 2: Disulfuros de hierro en carbones

• Fe-disulfides in coal contain trace elements of environmental interest such as **As, Se, Ni, and Hg**.

• **Multiple generations** of Fe-disulfides are common. Framboidal pyrite is always the earliest generation and cleat (fracture-filling) pyrite is latest.

• Different Fe-disulfide generations may have different trace element characteristics. **Framboidal pyrite** is commonly **Ni rich but As poor**.

• Overgrowths on framboidal pyrite may be **As or Se** enriched, especially if coals have interacted with fluids enriched in these elements.

• Removal of Fe-disulfides in coal preparation will help reduce the concentrations of harmful elements such as As and Se.
References – Topic 2: Trace Elements in FeS₂


Kolker, A., Senior, C.L., and Quick, J.C., 2006b, Mercury in coal and the impact of coal quality on mercury emissions from combustion systems: Applied Geochemistry, v. 21, no. 11, p. 1821–1836. [Also available at https://doi.org/10.1016/j.apgeochem.2006.08.001.]


INTRODUCTION TO MERCURY IN COAL
Mercury in Coal
Mercurio en carbones

- Mercury in **Fe-disulfides** and **organics** are the most common Hg forms in bituminous coals; organic association is more common in low rank coals.

- There are **few direct determinations** of Hg in pyrite on a grain scale, primarily by laser-ablation ICP-MS.

- Presence of Hg in Fe-disulfides is indicated by selective leaching studies and correlation of Hg with **pyrite proxies** such as Fe content or pyritic sulfur.

- Differences in trace element content of different pyrite forms, as seen for As, are likely for Hg.
U.S Coal Databases: Mercury Results

Mercurio en bases de datos de EE.UU.

From: Kolker and others, 2012
Mercury in World Export Coals
Mercurio en carbones de exportación

- Meij and te Winkel (2009) Compared Hg and As in coals imported to the Netherlands.
- World averages for bituminous coals\(^1\):
  \[ \text{Hg} = 0.10 \pm 0.01 \text{ ppm} \]
  \[ \text{As} = 9.0 \pm 0.7 \text{ ppm} \]
- Colombian coal is well below average for Hg and As, similar to Australian export coal.

\(^1\)Ketris and Yudovich, 2009, Int. J. Coal Geol.

Mercury in Iron Disulfides
Mercurio en disulfuros de hierro

• Detection limit generally below electron microprobe detection on individual grains and XAFS on whole coal.

• Limited microanalysis determinations, for example, by laser-ablation ICP-MS.

• Presence of Hg indicated by selective leaching studies and by correlation of bulk mercury with proxies such as iron or pyritic sulfur.

• Imaging showing generational changes in composition, such as that seen for arsenic and selenium, is generally not available.
Hg-rich coals in Ukraine vs. U.S. Illinois Basin coals

Carbones con alto contenido de Hg en Ucrania y EE.UU.

- Whole-coal samples have similar pyritic sulfur but much different Hg contents.
- Impurities in pyrite differ: Pyrite-rich coals ≠ Hg-rich.
- Coals formerly produced at Nikitovka Hg-mines have extreme Hg contents due to presence of cinnabar (HgS).

Kolker and others, 2009 – Ukraine and Bragg and others, 1997, COALQUAL - Herrin #6 and Springfield #5 Illinois Basin coals.
Summary – Topic 3: Introduction to Hg in Coal
Resumen – Tema 3: Fundamentos de Hg en carbones

• **Pyrite** is most common mercury mode of occurrence in **bituminous coals**. Organic-hosted mercury is more likely in low rank coals.

• Mercury content of pyrite varies. Can have high pyrite coals with only moderate mercury contents (e.g., U.S. Illinois Basin) and high mercury coals with only moderate pyrite contents (e.g., Donets Basin, Ukraine).

• Mean mercury content of U.S. coals used for power generation (0.11 to 0.12 ppm) is close to the world average for Hg (0.10 ± 0.01 ppm).

• Hg and As contents of exported Colombian coals are below world averages for both elements.


Mercury and Halogens in Coal
Improving Mercury Capture
Measuring Ambient Mercury and Fine Particulate Matter

SESSION 3
Session 3  Topic 1

MERCURY AND HALOGENS IN COAL
Mercury in Coal - Session 2 Review

Mercurio en carbones: revisión de la Sesión 2

• Mercury in **Fe-disulfides** and **organics** are the most common Hg forms; **organic association** is more common in **low rank coals**.

• There are few direct determinations of **Hg in pyrite** on a grain scale, primarily by **laser-ablation ICP-MS**.

• Presence of Hg in Fe-disulfides is indicated by **selective leaching** studies and correlation of Hg with **pyrite proxies** such as Fe content or pyritic sulfur.

• Differences in trace element content of different pyrite forms, as seen for As, are **likely for Hg**.
Halogenes in Coal – Cl, F, Br, I
Halógenos en carbones: Cl, F, Br, I

**Good**

- Halogens in sufficient amounts **promote capture of mercury** from power station flue gas by forming mercury-halogen complexes.
- These complexes are easier to capture in power station air pollution control devices than elemental mercury present in the boiler.

**Bad**

- Too high concentrations of alkalis and halogens in coal can cause **boiler fouling**, boiler tube **deposits**, and **corrosion** of boiler components.
U.S. fish consumption advisories have driven efforts by the EPA to limit emissions of mercury and other toxic substances from coal-fired utility power stations.

USGS studies show the impact of coal quality on mercury emissions from coal combustion.

Halogen emissions are also regulated as acid gases under EPA MATS.

Kolker and others, 2012, USGS Fact Sheet 2012-3122
https://pubs.usgs.gov/fs/2012/3122/
Halogen content in U.S. coals:

- Bromine is 1-4% of Cl content on a weight basis.
- Iodine contents are typically ≤ Br.
- Fluorine is ≤ Cl.

U.S. county-average Cl and Br contents (USGS data).
Rank Dependence of Halogens

Halógenos y calidad de carbones

Results show U.S. county-average Cl and Br contents with ASTM coal rank and origin. Cl data from 1999 EPA ICR; Br results from USGS COALQUAL.

Source: Kolker and Quick, 2015
Mode of Occurrence of Halogens in Coal

Halógenos y su forma de ocurrencia en carbones

- Cl and Br K-edge XANES (X-Ray Absorption Near-Edge Structure) spectra show an association with coal macerals but not bound as organohalogen compounds.

- Cl and Br are primarily associated with coal moisture and are loosely bound to maceral surfaces or retained in pore spaces.

Source: Huggins and Huffman, 1995, Fuel
Geologic Factors Influencing Coal Halogen Contents

Dependencia entre factores geológicos y halógenos

- **Rank** - Halogen contents increase with rank for low-rank and bituminous coals.
- **Depth** - Halogen contents increase with depth or paleo (stratigraphic) depth.
- **Groundwater chemistry** - Deep basin fluids are more saline and have higher halogen contents.
- **Geologic structures** - Proximity to structures such as faults that have acted as conduits for saline or hydrothermal fluids.
Chlorine in U.S. Coal

Cloro en carbones de EE.UU.

<table>
<thead>
<tr>
<th>Ibs Chlorine per Billion Btu</th>
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</thead>
<tbody>
<tr>
<td>3 - 25</td>
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<tr>
<td>25 - 50</td>
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<tr>
<td>50 - 75</td>
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<tr>
<td>75 - 100</td>
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<tr>
<td>100 - 200</td>
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<tr>
<td>200 - 326</td>
</tr>
</tbody>
</table>

U.S. County Averages

1999 EPA ICR Data,

Source: Quick and others, 2005
Example 1: U.S. Illinois Basin

Ejemplo 1: La cuenca de Illinois, EE.UU.

- 1964 study in Illinois motivated by fouling and corrosion of boilers by coals with high alkali chloride contents.

- Recognized that the highest Cl contents were found in the deepest coals and that Cl in coal was correlated with Cl in groundwater.

Source: Gluskoter and Rees, 1964
Chlorine in U.S. Coal

Cloro en carbones de EE.UU.

Source: Quick and others, 2005

U.S. County Averages
1999 EPA ICR Data,

Example 2
Example 2: Chlorine Variation with Depth

<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>1,097</td>
</tr>
<tr>
<td>Middle Pennsylvanian</td>
<td>Kanawha Formation</td>
<td>36</td>
<td>1,408</td>
</tr>
<tr>
<td>Lower Pennsylvanian</td>
<td>New River Formation</td>
<td>56</td>
<td>1,503</td>
</tr>
</tbody>
</table>

Central Appalachian Basin, USA
Source: Bragg and others, 1991
2014 USGS study in cooperation with Eskom and United Nations Environment Programme (UNEP).

Eskom provided USGS a suite of 42 feed coal samples including all 13 operating coal-fired utility power stations in South Africa.

Eskom also provided 8 density separates of Highveld #4 coal.

Study helps show mercury content of coal used for power generation in South Africa and the potential for mercury reduction.

Source: Kolker and others, 2014, USGS Open-File 2014-1153
https://pubs.usgs.gov/of/2014/1153/
Mercury Distribution by Power Station
Fluctuaciones en el contenido de mercurio

• Hg contents vary by power station due to differences in coal supply.
• Mean Hg content of 42 South African feed coals is about 4x that of typical export coals.
• Matimba station # 11 burns washed Waterburg coals; others use partly washed or unwashed coals.

Source: Kolker and others 2014, USGS Open-File 2014-1153
https://pubs.usgs.gov/of/2014/1153/
Impact of Coal Preparation on Mercury

Impacto de la preparación sobre el mercurio

• **Reduces mineral matter** and sulfur associated with minerals such as pyrite.
• **Increases energy content** by concentrating organic fractions.
• **Mercury reduction varies** typically 0-35% on a concentration basis, higher on equivalent energy basis.
• **Potential for mercury reduction** depends on the fraction of mercury present as pyrite vs. organic association and efficiency of washing process.
South African Highveld #4 Coal
Carbón sudafricano Highveld #4

• **Highveld #4** coal is being tested to produce low ash, washed export coal.

• Remaining fractions are used for power generation, unless export yield is low, then run-of-mine or destoned (discard fraction removed) coal is burned.

• **Density separates** simulate the behavior of Highveld #4 coal during coal washing.

• The separation process is effective in concentrating pyrite in the high-ash, higher density fractions.

Source: Kolker and others, 2017b
More pyrite is present in separates taken at higher densities.

• Raw coal ~35% ash, 0.29 ppm Hg.
• Export product 11.5% ash, 0.06 ppm Hg.
• Results show pyritic mercury association confirmed by laser ablation ICP-MS.

Source: Kolker and others, 2017b, Int. J. Coal Geology
Pyrite by Laser Ablation ICP-MS
Espectrometría de piritas

South Africa Highveld #4 Coal

- Results show As, Hg are enriched in pyrite.
- Element contents are highly variable on a grain scale.

Source: Kolker and others, 2017b, Int. Journal Coal Geol.
## Coal Products Predicted from Density Separates

**Productos de separaciones por densidad**

<table>
<thead>
<tr>
<th>Product</th>
<th>Samples averaged</th>
<th>Ash (wt. %)</th>
<th>Hg (ppm)</th>
<th>As (ppm)</th>
<th>Se (ppm)</th>
<th>Approx. cut point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Export</td>
<td>1.4F</td>
<td>11.5</td>
<td>0.06</td>
<td>0.5</td>
<td>0.5</td>
<td>Cut at 1.4</td>
</tr>
<tr>
<td>De-stoned</td>
<td>1.4F-1.9F</td>
<td>26.6</td>
<td>0.24</td>
<td>1.4</td>
<td>1.0</td>
<td>Cut at 1.9</td>
</tr>
<tr>
<td>Middling</td>
<td>1.5F-1.9F</td>
<td>29.7</td>
<td>0.27</td>
<td>1.5</td>
<td>1.1</td>
<td>1.4 to 1.9</td>
</tr>
<tr>
<td>Run-of-mine</td>
<td>14F-2.0S</td>
<td>35.2</td>
<td>0.29</td>
<td>2.0</td>
<td>1.1</td>
<td>No washing</td>
</tr>
<tr>
<td>Middling + discard</td>
<td>1.5F-2.0S</td>
<td>38.6</td>
<td>0.32</td>
<td>2.2</td>
<td>1.2</td>
<td>&gt; 1.4</td>
</tr>
<tr>
<td>Stone (discard)</td>
<td>2.0F, 2.0S</td>
<td>60.9</td>
<td>0.46</td>
<td>3.8</td>
<td>1.4</td>
<td>&gt; 2.0</td>
</tr>
</tbody>
</table>

Source: Kolker and others, 2017b, Int. J. Coal Geol.

Used in South Africa for power generation
Coal preparation is an effective means of reducing mercury input to the boiler where mercury-specific controls are lacking.

Halogens in coal (e.g., Cl, F, Br) help reduce the fraction of Hg emitted by promoting its oxidation and capture.

Halogen content is a function of coal rank, depth of burial, and (or) proximity to geologic structures, allowing saline or hydrothermal fluids to interact with coal.

Br/Cl ratio of many commercial coals ranges from 0.01 to 0.04, regardless of rank. On a mass basis, Br is more effective than Cl in promoting Hg oxidation and capture.
References – Topic 1: Mercury and Halogens in Coal


Session 3   Topic 2

IMPROVING MERCURY CAPTURE
Factors that Influence Mercury Capture
Factores que contribuyen a la captura de mercurio

- **COAL QUALITY**
  - Coal rank
  - Coal mercury content
  - Coal halogen content
  - Coal sulfur content

- **PLANT OPERATIONS**
  - Type and positioning of air pollution control devices.
  - Unburned carbon in particulate fraction.
  - NO$_x$ control (post-combustion, SCR).
  - Mercury-specific controls.

Sources: UNEP, 2011; Senior, 2015
Impact of Chlorine on Mercury Capture

Influencia del cloro en captura de mercurio

- Figure shows predicted impact of Cl on Hg capture for various controls.
- Results are calculated for U.S. county averages from 1999 EPA ICR data and published best-fit equations for each control technology.

Sources: Quick and others, 2005; Kolker and others, 2006b

1With conventional air pollution control devices (APCDs)
Role of Halogens in Mercury Capture
Papel de los halógenos en la captura de mercurio

Cartoon showing gas phase and gas-particle reactions in the boiler.

- Halogens promote oxidation of elemental mercury to form mercury-halogen complexes or mercury bound to particles.
- These forms are easier to capture than gaseous elemental mercury.

Source: Kolker and others, 2012, USGS Fact Sheet 2012-3122
https://pubs.usgs.gov/fs/2012/3122/
Improving Mercury Capture\textsuperscript{1}

Mejorar en la captura de mercurio

- **Coal selection and coal washing:** Can reduce contents of elements bound in pyrite such as Hg. Ash, Hg, and S contents of Colombian coals are generally low and coals are not washed.

- **Optimize operating conditions:** Lowering air preheater exit temperature can increase the amount of unburned carbon, improving Hg capture. This change may affect boiler efficiency and may impact marketing of ash for other uses.

\textsuperscript{1}With Conventional Emission Controls

Effect of ash unburned carbon (LOI) on % Hg removal across ESP air pollution controls.

Source: Senior and Johnson, 2005 Energy and Fuels
Improving Mercury Capture
Mejoras en la captura de mercurio

• **Addition of Fabric Filters (FFs):** FFs are generally more efficient than electrostatic precipitators (ESPs) in removing mercury. FFs can be added within an existing ESP unit or by bypassing the ESP with a separate FF unit.

• **Use of sorbents:** Addition of sorbents can improve mercury capture. For low Cl coals, such as Colombian export coals, addition of halogens (Cl, Br) to the fuel or the boiler will improve Hg capture. Injection of activated carbon upstream from particulate controls is a common approach to increasing Hg capture. Less sorbent is required if the unit has an FF instead of an ESP.

![Effect of coal Cl on % elemental Hg at inlet to particulate controls](image)

Source: Senior and Johnson, 2005 Energy and Fuels

1With Conventional Emission Controls
Improving Mercury Capture\textsuperscript{1}

Mejorar en la captura de mercurio

- **Addition of Flue-Gas Desulfurization (FGD):** FGD scrubbers remove gaseous oxidized Hg with an efficiency of 90\% or higher. The cost of adding FGD is probably too high to be justified on the grounds of Hg removal alone. However, if future regulations require reductions in the emissions of SO\textsubscript{2} and FGDs are installed, there will be additional reduction in Hg emissions.

\textsuperscript{1}With Conventional Emission Controls

Kendal and Duvha Power Stations, South Africa
Centrales termoeléctricas de Kandal y Duvha, Sudáfrica

• 2010 UNEP, Eskom, EPA, South Africa collaborative study to measure mercury stack emissions for each station using EPA methods¹.

• Samples of feed coal and fly ash were also collected by EPA from each boiler unit.

• Coal and fly ash samples were obtained by USGS and studied as part of 2012 UNEP, Eskom, USGS collaborative study of all 13 South African coal-burning power stations².

Case Study

## Mercury Mass Balance, Kendal and Duvha Power Station, South Africa

<table>
<thead>
<tr>
<th>Power Station</th>
<th>Unit Number</th>
<th>Air Pollution Controls</th>
<th>Avg. Hg. In Feed Coal (ppm)</th>
<th>Avg. Hg. In Fly ash (ppm)</th>
<th>Emissions Avg. % Hg, μg/m³ @ 3% O₂</th>
<th>Emissions Percent oxidized Hg (Hg²⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duvha</td>
<td>1</td>
<td>Fabric Filter</td>
<td>0.14</td>
<td>0.18</td>
<td>13.81</td>
<td>89%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Fabric Filter</td>
<td>0.18</td>
<td>0.63</td>
<td>4.65</td>
<td>73%</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Fabric Filter</td>
<td>0.16</td>
<td>0.68</td>
<td>4.09</td>
<td>88%</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>ESP</td>
<td>0.28</td>
<td>0.13</td>
<td>35.49</td>
<td>56%</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>ESP</td>
<td>0.21</td>
<td>0.21</td>
<td>29.01</td>
<td>54%</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>ESP</td>
<td>0.26</td>
<td>0.19</td>
<td>40.37</td>
<td>55%</td>
</tr>
<tr>
<td>Kendal</td>
<td>1</td>
<td>ESP</td>
<td>0.18</td>
<td>0.09</td>
<td>39.20</td>
<td>70%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>ESP</td>
<td>0.22</td>
<td>0.09</td>
<td>43.45</td>
<td>54%</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>ESP</td>
<td>0.20</td>
<td>0.06</td>
<td>49.13</td>
<td>52%</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>ESP</td>
<td>0.18</td>
<td>0.15</td>
<td>46.03</td>
<td>52%</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>ESP</td>
<td>0.36</td>
<td>0.08</td>
<td>39.47</td>
<td>48%</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>ESP</td>
<td>0.35</td>
<td>0.03</td>
<td>46.34</td>
<td>54%</td>
</tr>
</tbody>
</table>

Source: Kolker and others, 2014; Scott, 2011
Kendal and Duvha Power Stations, South Africa

Source: Kolker and others, 2014
Kendal and Duvha Power Stations, South Africa
Centrales termoeléctricas de Kendal y Duvha, Sudáfrica

- Capture efficiency for Hg varies by utility boiler according to setup and operating conditions.
- Duvha units 1-3 equipped with fabric filters have a much higher capture efficiency for Hg than units with ESPs, as shown by:
  1) Total Hg in flue gas
  2) Percent Hg$^{2+}$ in flue gas
  3) Hg captured in fly ash.
- Hg capture efficiency in Kendal station and in Duvha units 4-6 equipped with ESPs is typically $\leq 20\%$.

Source: Kolker and others, 2014
Improving Mercury Capture
Mejoras en la captura de mercurio

• UNEP 2010 Guidance Document for **reducing mercury emissions** from coal-burning powerplants.

• **Recommendations and best practices** for improving mercury capture generally without mercury-specific controls.

• Approaches range from inexpensive to more cost intensive.

Summary- Topic 2: Improving Hg Capture

Resumen—Tema 2: Captura de mercurio

- In the boiler, Hg is present as elemental Hg that is difficult to capture using conventional air pollution controls (e.g., ESPs).

- Halogens in coal or in added sorbents convert some of the Hg to oxidized species that can be captured from flue gas by air pollution controls.

- Unburned carbon in ash and (or) activated carbon-based sorbents also effect Hg capture.

- Fabric filters are more efficient than ESPs in capturing mercury.

- FGD, if added to reduce sulfur emissions, will also improve Hg capture.
References – Topic 2: Improving Mercury Capture


Kolker, A., Senior, C.L., and Quick, J.C., 2006b, Mercury in coal and the impact of coal quality on mercury emissions from combustion systems: Applied Geochemistry, v. 21, no. 11, p. 1821–1836. [Also available at https://doi.org/10.1016/j.apgeochem.2006.08.001.]


USGS
MEASURING AMBIENT MERCURY AND FINE PARTICULATE MATTER
Speciation of Ambient Mercury
Especiación del mercurio en la atmósfera

• Coal-fired power stations are among the largest point-source emitters of ambient atmospheric Hg.

• Operationally defined species:
  - Elemental Mercury (Hg°)
  - Reactive Gaseous Mercury (RGM)
  - Particulate Mercury (Hgp)

• RGM (also known as gaseous oxidized Hg) includes all charged Hg species (e.g., HgCl2(g)); Hgp includes all Hg bound to particulates.

• Hg° is the dominant Hg form in the atmosphere and has a long residence time, resulting in global Hg transport.

• RGM has a shorter residence time and is deposited locally to regionally.

• Atmospheric residence time of Hgp varies depending on size, composition, and solubility of particles.
USGS Mobile Mercury Lab
Laboratorio para análisis de mercurio del USGS

• Near continuous $\text{Hg}^0$, RGM, $\text{Hg}_{\text{PM2.5}}$ measurements in the field with trapping of Hg species and analysis by cold vapor atomic fluorescence.

• Mobile lab can also measure fine particulate mass ($\text{PM}_{2.5}$), and gaseous $\text{SO}_2$, $\text{NO}_x$, and $\text{O}_3$.

• Separate PM collectors are needed to collect $\text{PM}_{2.5}$ for analysis, including trace elements.

Source: Kolker and others, 2007
USGS Fact Sheet 2007-3071
Particulate samplers on rooftop. Particulates are collected on filters and extracted for analysis.

Instrument controls in Mobile Lab.
Study Area: Woods Hole, Massachusetts, USA

Source: Kolker and others, 2013, Atmospheric Environment
Hg Species and Other Gases, Woods Hole

Mercurio y otros gases en la atmósfera de Woods Hole

Source: Kolker and others, 2013
Distinguishing Sources of Ambient Mercury
Fuentes de contaminación atmosférica con mercurio

- Ambient mercury species defined as elemental mercury ($\text{Hg}^0$), reactive gaseous mercury ($\text{RGM}$), and particulate mercury ($\text{Hg}_p$).
- Monitoring of mercury species, fine particulate matter, and ancillary gasses can help distinguish mercury sources.
- Correlation of $\text{RGM}$ with $\text{SO}_2$ and (or) $\text{NO}_x$ peaks indicates plumes from coal combustion such as in powerplants.
- Lack of corresponding $\text{SO}_2$ and (or) $\text{NO}_x$ peaks indicates non-coal sources, such as chlor-alkali plants.
- Use of elemental mercury in small-scale gold mining generates no $\text{RGM}$, $\text{Hg}_p$, or corresponding ancillary gases.

Sources: Edgerton and others, 2006; Kolker and others, 2008, 2010
Source
- **Crustal** (natural source)
- **Marine** (natural source)
- **Coal Combustion** (anthropogenic source)
- **Metal Smelting** (anthropogenic source)

**Typical Elements**
- Al, Ti, La, Ce, REE, Y, Fe, Zr
- Na, Mg, Ca, Sr, Cl
- Ni, V, Mo, Sb, As, Hg, Cr, Se
- Pb, Zn, Cu, Cd

Anthropogenic source is indicated where ratio of anthropogenic element/crustal element is $\geq 10$ times crustal proportion for these elements.

Sources:
- Duce and others, 1975
- Pacyna and Pacyna, 2001
- Song and others, 2001
Trace Elements in PM$_{2.5}$
Trazas y PM-2.5

Factorization analysis indicates four probable source categories at Woods Hole site.
(Percent of PM$_{2.5}$ mass):

1) **Crustal** (18.4%)
2) **Marine** (23.1%)
3) **Metal smelter?** (13.0%)
4) **Energy generation** (45.5%)

Source: Kolker and others, 2013, Atmospheric Environment
Summary – Topic 3: Ambient Mercury and Fine Particulates

Resumen – Tema 3: Mercurio y partículas en suspensión

- Operationally defined species: Elemental Mercury ($\text{Hg}^0$); Reactive Gaseous Mercury ($\text{RGM}$); Particulate Mercury ($\text{Hg}_p$)

- $\text{RGM}$ includes all charged Hg species; $\text{Hg}_p$ includes all Hg bound to particulates.

- $\text{RGM}$ has local to regional sources such as power stations and chlor-alkali plants. $\text{RGM}$ from combustion sources is present in plumes with other gaseous species such as $\text{SO}_2$ and $\text{NO}_x$.

- $\text{Hg}^0$ has long residence times leading to global transport. As a result, there are fish consumption advisories for Hg in remote areas of the United States where there are no local Hg sources.

- EPA regulations limit U.S. $\text{PM}_{2.5}$ concentrations based on average mass concentrations. USGS and others have used trace elements in $\text{PM}_{2.5}$ to distinguish source input. Coal combustion sources are indicated by $\text{Ni}$, $\text{V}$, $\text{Mo}$, $\text{Sb}$, $\text{As}$, $\text{Cr}$, etc., in addition to $\text{Hg}$. 

USGS

3.3-10


SESSION 4

Introduction to Coal Ash
Trace Elements in Coal Ash
Beneficial Uses of Coal Ash
Coal Ash Environmental Issues
INTRODUCTION TO COAL ASH
Coal Combustion Products (CCPs)  
Productos de la combustión del carbón

- Coal combustion products are produced in large quantities during coal combustion for power generation.
- Coal combustion products consist primarily of fly ash, bottom ash, and, in plants with flue-gas desulfurization (FGD), sludge from FGD scrubber.
- In 2016, 52% of U.S. coal fly ash was beneficially used, primarily in construction.
- Classification of coal ash for construction purposes is based on its major element composition, expressed as the sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ vs. other major constituents.
- These characteristics are a function of the chemistry, rank, and mineralogy of the feed coal.

Fly ash backscattered electron image, 1000x, USGS Reston labs.

Source: American Coal Ash Association, not dated https://www.acaa-usa.org/
Coal Combustion Products (CCPs)
Productos de la combustión del carbón

Diagram showing typical range of CCPs generated in a coal-fired powerplant equipped with an electrostatic precipitator (ESP) and flue-gas desulfurization scrubber (FGD).

Source: Deonarine and others, 2015
USGS Fact Sheet 2015-3037
https://pubs.usgs.gov/fs/2015/3037/


**ASTM C618 Fly Ash Classification**

**Clasificación de cenizas de acuerdo a ASTM C618**

- **Class C** – “cementitious” = more calcium rich.
  \[ \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 50\% \]

- **Class F** – “pozzolanic” = more aluminosilicate rich.
  \[ \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70\% \]

- Each class has different properties for use in concrete.

Source: ASTM International C618-17, 2017a
In the Boiler
En el horno

• Peak temperatures in PC boilers generally ~1,700 °C.

• Temperature in flue gas is reduced to ~200 °C within seconds.

• Some boilers (e.g., fluidized bed) have lower operating temperatures.

Source: Senior, 2015, Chap. 7, in Mercury Control for Coal-derived Gas Streams
## Mineral Transformations in Powerplants

### Transformación de minerales por combustión

**Coal**

- Quartz \((\text{SiO}_2)\)
- Clays
  - Illite-smectite
  - Kaolinite \(\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8\)
- Carbonates
  - Calcite \((\text{CaCO}_3)\)
  - Siderite \((\text{FeCO}_3)\)
  - Ankerite \(\text{Ca}(\text{Mg,Fe,Mn})(\text{CO}_3)_2\)
- Pyrite (Marcasite; \(\text{FeS}_2\))

**Fly Ash**

- Quartz (beta form)
- Aluminosilicates
  - Mullite \(\text{Al}_6\text{Si}_2\text{O}_{13}\)
- Aluminosilicate glass
- Ca, Mg phases (Class C ash)
  - Ca-aluminosilicates
  - Anhydrite \((\text{CaSO}_4)\)
  - Lime \((\text{CaO})\); Periclase \((\text{MgO})\)
- Fe oxides (pyrite breakdown)
  - Hematite \((\text{Fe}_2\text{O}_3)\)
  - Magnetite \((\text{Fe}_3\text{O}_4)\)
Examples of Fly Ash Constituents

Ejemplos de partículas en suspensión

Glassy Cenosphere [SEM]

Mullite [reflected light]

Partially Combusted Coal [reflected light]

Magnetite [reflected light]

Source: James Hower, Univ. of Kentucky
Fly Ash Petrography
Petrografía de partículas en suspensión

Inorganic

- **Neoformed** [formed in the boiler]
  - Glass, 70 to >90% of most FA
  - Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$)
  - Spinel (magnetite)

- **Coal derived**
  - Quartz

Organic

- **Neoformed** [formed in the boiler]
  - isotropic coke
  - anisotropic coke

- **Coal (or fuel) derived**
  - inertinite
  - petroleum coke
Fly Ash Microanalysis

Microanálisis

- Backscattered electron image (BSE) is a function of mean atomic number.

- **BSE** shows distribution of glassy areas and Fe-oxides in ash sample.

- Wavelength-dispersive electron microprobe **map** shows distribution of specific elements.

- Maps shows that **Ni** is concentrated in Fe-oxide phases relative to glass.
Fly Ash Microanalysis

Microanálisis de partículas en suspensión

Backscattered electron imaging (BSE, above) and wavelength-dispersive elemental mapping (right) shows composition.

Source: Kolker and others, 2017a
Summary – Topic 1: Introduction to Coal Ash

Coal ash consists of material formed during coal combustion and uncombusted material from coal remaining after coal combustion.

Ash constituents include glass, residual minerals such as quartz, new-formed minerals such as mullite, and unburned carbon.

Coal ash is classified by its major constituents. Bulk composition of fly ash from low-rank coals differs from that of bituminous coals.

ASTM classification of coal ash for construction purposes is based on its properties and the sum of SiO₂ + Al₂O₃, + Fe₂O₃. These components are largely a function of the chemistry, rank, and mineralogy of the feed coal.

Coal quality parameters determine ash chemistry. Reactions during coal combustion involve high temperature breakdown of clays and carbonates, and oxidation of pyrite.


TRACE ELEMENTS IN COAL ASH
Trace Elements in Coal Ash

Elementos traza en cenizas de carbones

- At boiler temperatures, minerals in feed coal melt, react, or undergo phase transformations, with redistribution of major and trace elements.

- Trace metal content of ash is controlled by minor constituents in minerals from the coal such as clays, the presence of trace phases, and boiler conditions.

- **Volatile elements** such as mercury and selenium are partitioned into the gas phase during coal combustion and are emitted or condense on ash particles.

- **Refractory elements** such as zirconium and the rare earths are retained in the ash.

- Element concentrations in fly ash are higher than in feed coals due to mass reduction, capture, and retention of gas phase constituents.
Behavior of Elements During Coal Combustion

Volatilidad de los elementos en la combustión

<table>
<thead>
<tr>
<th>Boiling PTS, °C</th>
<th>INCREASING VOLATILITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-188.1</td>
</tr>
<tr>
<td>Cl</td>
<td>-34.1</td>
</tr>
<tr>
<td>Se</td>
<td>217</td>
</tr>
<tr>
<td>SeO₂</td>
<td>317</td>
</tr>
<tr>
<td>Hg</td>
<td>357</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>465</td>
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<td>As</td>
<td>613</td>
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<tr>
<td>MoO₃</td>
<td>795</td>
</tr>
<tr>
<td>Zn</td>
<td>907</td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>1155</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>1800</td>
</tr>
<tr>
<td>CoO</td>
<td>1800</td>
</tr>
<tr>
<td>Mn</td>
<td>1960</td>
</tr>
<tr>
<td>Cu</td>
<td>2570</td>
</tr>
<tr>
<td>Ni</td>
<td>2730</td>
</tr>
<tr>
<td>Co</td>
<td>2870</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>3000-4000</td>
</tr>
<tr>
<td>Mo</td>
<td>4660</td>
</tr>
</tbody>
</table>

Very Volatile

Hg
Br Cl F

Not Volatile

Eu Hf La Mn Rb
Sc Sm Th Zr

Class III
Volatized and Emitted fully in the Vapor-phase not Enriched on the Fly Ash

Class II
Enriched in the Fly Ash and Depleted in the Bottom Ash

Class I
Equally Distributed between Bottom Ash and Fly Ash

From the Flue Gas
Gases de combustión

• Capture of elements from the gas phase occurs as the flue gas cools, primarily by adhering of constituents onto ash particle surfaces. Hg and Se are the most volatile and the proportion these elements captured is lowest (or emitted is highest).

• Highest trace metal concentrations occur in the finest size fractions of ash. These fractions have the greatest surface area with which to capture volatiles from the gas phase.

• Most elements are associated with inorganic fly ash constituents, but as shown in the section on Hg capture, Hg has an affinity for residual unburned carbon.
Element Enrichment in Coal Ash

Enriquecimiento de elementos en las cenizas

Plot showing element enrichment in three U.S. coal fly ash samples, in relation to average element contents in U.S. coals (Bragg and others, 1997).

Source: Deonarine and others, 2015
USGS Fact Sheet 2015-3037
https://pubs.usgs.gov/fs/2015/3037/
Variation in Fly Ash Chemistry
Fluctuaciones químicas de las partículas

• Concentrations of many volatile trace elements vary within the ash-collection system.

• Flue-gas temperature and particle size decrease away from the boiler, resulting in greater element capture.

• Arsenic, lead and other elements tend to be more highly concentrated in back rows of electrostatic precipitators (ESP).

Source: Keith Holbert
Arizona State University
Fly Ash Chemistry – Arsenic
Arsénico y partículas en suspensión

• Example showing arsenic variation in a ESP hoppers in a powerplant in Kentucky, USA.

• Diagram shows arsenic enrichment in hoppers toward the rear of the ESP array.

• Powerplant is burning medium sulfur, high volatile A bituminous coal.

Source: James Hower, University of Kentucky, unpublished data, 2004
Fly Ash Chemistry – Mercury
Mercurio y partículas en suspensión

- Example showing mercury variation in ESP hoppers in a powerplant in Kentucky, USA.
- Diagram shows mercury enrichment in hoppers toward the rear of the ESP array.
- Powerplant is burning a single-seam/single-mine coal burned at a 220-MW utility boiler.

Source: Mardon and Hower, 2004, Int. J. Coal Geology
Mercury Capture
Captura de mercurio

• On average, ~36% of mercury in feed coal is retained in coal ash in U.S. power stations.

• In high-temperature regions of the boiler, only gaseous elemental mercury is present.

• As the flue gas cools to ~150 to 250 °C, some elemental mercury is converted to oxidized gas-phase mercury and particulate mercury, which are much more readily captured in coal ash.

• Mercury capture can be increased if halogens are present in the feed coal or if unburned carbon is present in coal ash.

• Sorbents containing halogens or activated carbon can be added to increase Hg capture.

Source: Kilgrove and others, 2002, EPA-600/R-01-109
Summary – Topic 2: Trace Elements in Coal Ash

Resumen – Tema 2: Elementos traza en cenizas

- Elements such as arsenic, mercury, and selenium are partitioned into the gas phase, with capture occurring primarily by adhering onto ash particle surfaces as the flue gas cools or is emitted.

- Highest trace metal concentrations occur in the finest size fractions of ash at the rear of ESP arrays.

- Mercury and selenium are especially volatile, with the smallest fractions of the amount present in feed coal retained in the fly ash.

- Refractory elements such as the rare earths do not enter the gas phase and are retained in the ash.
References – Topic 2: Trace Elements in Coal Ash


BENEFICIAL USES OF COAL ASH
Beneficial Uses of Coal Combustion Products
Aprovechamiento de las cenizas de carbonos

- A 2014 review by the EPA upheld existing classification of U.S. coal ash as nonhazardous waste.
- Nonhazardous status allows continued beneficial use of coal ash, but also specifies procedures for proper handling, transfer, and storage.
- The rate of re-use of coal combustion products in the U.S. is now 52%, which is an all-time high.
- If coal ash is not re-used, it must be stored in landfills or impoundments.

American Coal Ash Association, not dated, https://www.acaa-usa.org/
Use of U.S. Coal Combustion Products (CCPs)

Aprovechamiento de cenizas en EE.UU.

All CCPs Production and Use with Percent

Source: American Coal Ash Association, not dated
https://www.acaa-usa.org/
Some Current Uses of Coal Ash and FGD
Usos principales de cenizas de carbones

• Raw material in **concrete** products and grout.
• Feedstock in the production of **cement**.
• Fill material for **structural applications** and embankments.
• Ingredient in **waste stabilization** and (or) solidification.
• Ingredient in soil modification and (or) stabilization.
• Component in road bases, sub-bases, and pavement.
• Produce **synthetic gypsum** for use in construction and agriculture (FGD).

Source: American Coal Ash Association, not dated
[https://www.acaa-usa.org/](https://www.acaa-usa.org/)
Recovery of Rare Earth Elements from Coal Ash?
Extracción de tierras raras en las cenizas

• **Rare earth elements** (REE) are increasingly needed in commercial and military applications, including energy applications such as in the magnets of wind turbines.

• Global supply of REE is strongly controlled by a single international source—China.

• U.S. REE production (one mine with operations currently on hold) is not sufficient to keep up with U.S. demand.

• **REE from coal** are strongly retained in coal ash during coal combustion for power generation.

• Alternative REE sources, including coal and coal ash, and new methods of REE extraction from these sources, are currently being investigated in the U.S. and elsewhere.

Source: U.S. Department of Energy, 2017a,b
Advantages of Coal Ash as a Source of REE
Ventajas de la obtención de tierras raras de cenizas

• In 1935, V.M. Goldschmidt proposed recovering rare elements, including REE, from coal ash.

• Coal ash (fly ash, bottom ash) is produced in large quantities by utilities during coal combustion for power generation.

• REE are strongly enriched in the ash fraction compared to REE contents of feed coals.

• Fly ash is produced in a powdered form, eliminating the need for crushing of ores.

Source: Goldschmidt, 1935
Behavior of Elements During Coal Combustion

Volatilidad de los elementos en la combustión

REE in Coal Ash vs. Coal and Upper Continental Crust
Abundancia de tierras raras

- Plot compares REE for fly ash samples vs. average continental crust and U.S. average coal.

- REE patterns of coal ash and coal are similar, but REE contents are higher in coal ash. REE are also higher in coal ash than in Upper Continental Crust.

Sources: Kolker and others, 2017a (Compilation of fly ash sample data) Taylor and McLennan, 1985 (Upper Continental Crust) Bragg and others, 1997; Palmer and others, 2015 (U.S. Average Coal) Korotev, 2009 (Chondrite normalization)
• Elements with an even atomic number are more abundant than those with an odd atomic number.

• Effect is apparent in the distribution of the REE.

• Normalization to chondritic meteorites (chondrites) eliminates the effect.

• Effect occurs because pairing of protons results in greater stability by each one offsetting the spin of the other.

Sources: Taylor and McLennan, 1985 (North American Shale Composite (NASC))
Korotev, 2009 (Chondrite normalization)
Possible Modes of Occurrence of REE in Coal Ash

Presencia de tierras raras en cenizas de carbones

• Retention of trace phases in coal whose melting temperature may exceed boiler temperatures (e.g., monazite, xenotime). But these are much less common in coal ash than in coal.

• Retention of trace phases in coal with size reduction by thermal shock.

• Breakdown of trace phases with partitioning of REE into the melt. Melt is quenched to form glass phase that may host REE and other constituents.

• Occurrence of REE in coal ash as nanoparticles.
### REE-Bearing Trace Phases in Coal

#### Fuentes minerales de tierras raras en carbones

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Predominant REE</th>
<th>Melting Temp. (°C, 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apatite</td>
<td>Ca$_5$(PO$_4$)$_3$(OH,F,Cl)</td>
<td>MREE</td>
<td>1,644 (fluorapatite)</td>
</tr>
<tr>
<td>Zircon</td>
<td>ZrSiO$_4$</td>
<td>HREE</td>
<td>1,690</td>
</tr>
<tr>
<td>Monazite</td>
<td>(Ce,La,Nd,Th)PO$_4$</td>
<td>LREE, MREE</td>
<td>2,000+</td>
</tr>
<tr>
<td>Xenotime</td>
<td>YPO$_4$</td>
<td>Y, HREE</td>
<td>2,000+</td>
</tr>
<tr>
<td>Allanite</td>
<td>(Ce,Ca,Y)$_2$(Al,Fe$^{3+}$)$_3$(SiO$_4$)$_3$(OH)</td>
<td>LREE, Y</td>
<td>No Data</td>
</tr>
</tbody>
</table>
### REE Occurrence in Coal

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Predominant REE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhabdophane</td>
<td>(Ce,La,Y)PO₄·H₂O</td>
<td>LREE, Y</td>
<td>Dai and others, 2014</td>
</tr>
<tr>
<td>Florencite</td>
<td>CeAl₃(PO₄)₂(OH)₆</td>
<td>LREE</td>
<td>Dai and others, 2016</td>
</tr>
<tr>
<td>Bastnäsite</td>
<td>(Ce,Nd,La)CO₃F</td>
<td>LREE, MREE</td>
<td>Zhao and others, 2017; Dai and others, 2016</td>
</tr>
<tr>
<td>Organic hosted</td>
<td></td>
<td>MREE, HREE</td>
<td>Eskanazy, 1987; Eskanazy, 1999</td>
</tr>
</tbody>
</table>

- Rhabdophane, florencite in some Chinese coals;
- Bastnäsite in mineralized Chinese coals.
- Organic-hosted REE recognized in Bulgarian coals.
Investigation of Fly Ash for REE
Analisis de cenizas y tierras raras

• USGS obtained a suite of U.S. and International coal ash samples to determine REE mode of occurrence.

• Preliminary characterization using microanalysis to determine the distribution of materials in coal ash samples.

• Trace element microanalysis using an ion microprobe.

• Preliminary results indicate occurrence of REE in fly ash glass phase.

• Analytical approach described further in Session 5.
REE in Coal Fly Ash

Tierras raras en partículas en suspensión

- **Aluminosilicate glass** has similar REE distribution as bulk sample.
- Glasses containing Ca, Fe trend toward higher REE contents than pure Al-Si glasses.
- REE are much less abundant in quartz, which makes up a small portion of the samples.
- REE are also present in Fe-oxides.
- Results suggest glasses are the primary REE hosts, as suggested by Taggart and others (2016), who found REE correlated with Al in bulk ash and difficulty extracting REE in HNO₃.
- Fly ash glass is a potential REE source.

Source: Kolker and others, 2017a
Summary – Topic 3: Beneficial Uses of Coal Ash

Beneficial use of coal combustion products is allowed by its EPA designation as nonhazardous.

Coal combustion products are primarily used in construction materials.

Coal and coal ash are being considered as unconventional sources of needed rare elements, including rare earth elements (REE).

REE are strongly retained in the ash fraction during coal combustion, but REE-bearing trace phases are less common in coal ash than in coal.

Preliminary results suggest that REE enter the melt and might be recoverable from coal ash by fully digesting the glass phase.

Normalization of bulk REE data to chondritic values or to sample composites are useful ways of comparing and interpreting results.
References – Topic 3: Beneficial Uses of Coal Ash

Referencias – Tema 3: Aprovechamiento de cenizas


Eskenazy, G.M., 1987, Rare earth elements and yttrium in lithotypes of Bulgarian coals: Organic Geochemistry, v. 11, no. 2, p. 83–89. [Also available at https://doi.org/10.1016/0146-6380(87)90030-1.]


References – Topic 3: Beneficial Uses of Coal Ash


Mobility of Constituents from Coal Ash?
Lixiviación de los componentes de las cenizas

- Beneficial use of coal ash is permitted in the U.S. because coal ash has been designated as a nonhazardous waste by the U.S. EPA.
- If not used, U.S. coal ash is stored in landfills or impoundments often along rivers and streams.
- Standardized leaching tests, such as the EPA Toxicity Characteristic Leaching Procedure (TCLP), are used to test for element mobility from coal ash.

Sources: EPA, 1992 (TCLP)
Deonarine and others, 2015 (diagram)
Mobility of Constituents From Coal Ash?

Lixiviación de los componentes de las cenizas

- Recent U.S. coal ash spills from storage facilities, with considerable environmental impact:

  **Kingston, Tennessee**, December 2008, 5.4 million cubic yards of coal ash was released into the Emory and Clinch Rivers. After the spill, river sediments contained elevated levels of arsenic and mercury even after river water trace metals returned to normal levels.

  **Eden, North Carolina**, February 2014, 39 thousand tons of coal ash was released into the Dan River.

- Other ash impoundments have been identified by the EPA as having potential for hazardous impacts in the event of a spill.

- Ash utilization in construction materials and other uses can help reduce the need for storage of coal ash.

Sources: Ruhl and others, 2010; Deonarine and others, 2015
Mobility of Constituents From Coal Ash?
Lixiviación de los componentes de las cenizas

Coal ash spill site, Kingston, TN, December 2009
Sources: U.S. EPA, 2014; Deonarine and others, 2015, 2016

Immediate Area Impacted by Ash Spill
Potential for Mobility of Trace Elements

Lixiviación de los componentes de las cenizas

- Potential mobility of trace elements from coal ash differs by element.
- Availability of oxygen effects degree of element leaching.
- Standardized leaching test protocols only consider case where oxygen is available.

Deonarine and others, 2015, USGS Fact Sheet 2015-3037 4.4-5
Leaching Experiments for As and Cr in Fly Ash
Lixiviación de As y Cr en cenizas de carbones

- Coal ash leaching experiments up to **28 days** to test for trace metal mobility with redox conditions controlled.
- **Arsenic is leachable** under all conditions.
- **Chromium is partly leachable** in one sample under oxic conditions and not leachable in other cases.

Source: Deonarine and others, 2015, 2016
Summary – Topic 4: Environmental Issues

Resumen – Tema 4: Problemas ambientales

- U.S. coal ash is classified as a nonhazardous waste, permitting its beneficial use.
- When not used, coal ash is stored in landfills and (or) impoundments. With failure, ash or constituents from ash may be released into the environment.
- Standardized leaching protocols, such as TCLP, generally indicate that trace constituents are not readily leachable from coal ash, but the test only applies to surface (oxygenated) conditions.
- Availability of oxygen varies with depth in landfills and impoundments, and these differences in redox conditions can influence the mobility of trace constituents.


Laboratory Methods
Laboratory Quality Assurance
Introduction to Compositional Data Analysis

SESSION 5
Session 5  Topic 1

LABORATORY METHODS
How to Study Trace Elements in Coal
Métodos de estudio de elementos traza en carbones

### Bulk Methods

**Whole Sample**

- **Chemical Analysis** - Element distribution, e.g., by **ICP-MS**.
- **Selective leaching** - Element forms (species) inferred from leaching behavior.
- **X-ray absorption fine structure (XAFS)** - Element species determined directly by structure of X-ray absorption edge.

### Microanalysis

**Specific Minerals**

- **Scanning Electron Microscope (SEM)** - Texture and distribution of minerals in coal individually.
- **Electron microprobe** - Most abundant elements in individual minerals.
- **Laser Ablation ICP-MS and Ion Microprobe** - Trace elements in individual minerals.
- **Transmission Electron Microscope (TEM)** - Minerals in coal individually at very fine scale.
### Common Methods for Bulk Trace Element Analysis

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-MS</td>
<td>Precision and Detection Limits; All Elements Determined at Once; Most Common Method</td>
<td>Must Get Sample Entirely Into Solution; Isobaric Interferences must be Avoided or Corrected.</td>
</tr>
<tr>
<td>Neutron Activation (INAA)</td>
<td>Precision and Detection Limits; All Elements Determined at Once; Digestion not Required</td>
<td>Access to a Reactor Facility; Handling of Radioactive Samples; Not as Widely Used as ICP-MS</td>
</tr>
<tr>
<td>Isotope Dilution</td>
<td>Very High Precision (1-2%)</td>
<td>Requires Column Chemistry for Separation of Elements or Groups of Elements. Used in Specialized Applications where High Precision is Needed.</td>
</tr>
</tbody>
</table>
About Moisture
Humedad de carbones

• Generally, **heating 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.

• Moisture content can change if samples are not analyzed promptly after collection.
Whole Coal vs. Ash Basis
Componentes en el total de la muestra o en sus cenizas

- For inorganic analysis, coal samples are “ashed” in a laboratory furnace.
- Ashing concentrates inorganic matter in coal for sample digestion and analysis.
- Trace element results obtained are on an ash basis, but concentrations in the ash are a function of 1) whole coal element concentration; 2) proportion of ash present in coal; and 3) proportion of moisture present in coal.
- To eliminate variability in 2) and 3), results need to be converted to a common basis—moisture-free whole coal.
Standards for Coal and Coal Ash Analysis

Normas sobre análisis de carbones y sus cenizas


• **SRM 1632d** Trace Elements in Bituminous Coal
  
  *Elements Certified:* H, Na, S, Cl, K, Ti, V, Fe, Co, Cu, Rb, Sr, Sb, Ba, Hg, Pb, U.

• **SRM 1633c** Trace Elements in Coal Fly Ash
  
  *Elements Certified:* Na, Mg, Al, K, Ca, Ti, Mn, Fe, Ni, Co, As, Rb, Sr, Cd, Sb, Ba, Hg, Pb

• Values given with three levels of certainty:
  1) **Certified**; 2) **Reference**; 3) **Informational**

• Produced in batches having an expiration date.
# Common Methods for Mercury Analysis

Méthodes de analisis geoquímico de mercurio

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal decomposition, amalgamation, and atomic absorption spectrophotometry, also called Direct Mercury Analysis (DMA), EPA, 2007</td>
<td>Good Precision and Detection Limits. Analysis Done on Solid Powdered Sample. Inexpensive Off the Shelf Analyzers Widely Available.</td>
<td>Somewhat Prone to Carry-over Effects After Runs of High-Hg Samples if Not Careful.</td>
</tr>
<tr>
<td>Cold Vapor Atomic Absorption (CVAA)</td>
<td>Precision and Detection Limits Comparable to DMA.</td>
<td>Requires getting sample into solution</td>
</tr>
<tr>
<td>Cold Vapor Atomic Fluorescence (CVAFS)</td>
<td>Better Detection Limits than DMA and CVAA.</td>
<td>Not as Widely Available as DMA, CVAA. Low levels of detection generally not needed for coal studies.</td>
</tr>
<tr>
<td>Portable atomic absorption spectrometer with Zeeman Background Correction</td>
<td>Real-time measurement of mercury in the vapor phase. Portable—excellent for field use. Amalgamation not required.</td>
<td>Generally not intended for bulk solid samples. Can be used for solids if other approaches are unavailable.</td>
</tr>
</tbody>
</table>
# Microanalysis Methods

## Microanálisis

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SEM/EDX</strong></td>
<td>Excellent spatial resolution and imaging capability. Newer models can operate at low vacuum conditions for environmental samples.</td>
<td>Results for trace elements are qualitative to semiquantitative with EDX. Need concentrations in the 10th’s of weight percent to determine trace elements.</td>
</tr>
<tr>
<td><strong>Electron Microprobe</strong></td>
<td>Good spatial resolution. Combines quantitative analysis and wavelength-dispersive elemental mapping capabilities.</td>
<td>Sensitivity for trace elements limited to ~100-200 ppm; can be improved by long count times.</td>
</tr>
<tr>
<td><strong>TEM/EDX &amp; HR TEM</strong></td>
<td>Spatial resolution in the nanometers range. Elemental data available if equipped with EDX. Excellent for imaging particle surfaces.</td>
<td>Not widely equipped with EDX analyzers. If EDX equipped, results for trace elements are semiquantitative, similar to SEM.</td>
</tr>
</tbody>
</table>
Scanning Electron Microscope (SEM) also has backscattered electron (BSE) mode. SEM is good for particle morphology. BSE is good for particle composition.

**EDX** - Energy Dispersive Analyzer
Used to identify major elemental constituents present and for qualitative analysis.

**SEM Image of Fly Ash Particle**
Electron Microprobe
Microsonda electrónica

Has wavelength dispersive spectrometers for quantitative analysis and element mapping in addition to SEM, BSE, and EDX
Electron-beam Instruments

Instrumentos de rayos catódicos

- Instruments include **SEM** and **electron microprobe**.

- **Modes include:**
  1) **Secondary electrons** for imaging.
  2) **Backscattered electrons** for imaging and composition.
  3) **Characteristic X-rays** for elemental composition.
Backscattered electron imaging (BSE, above) and wavelength dispersive elemental mapping (right) shows composition. Images from USGS electron microprobe in Reston.
High-resolution TEM shows nanometer-scale coating of carbonaceous material on fly ash particle surfaces.

Source: Deonarine and others, 2015
USGS Fact Sheet 2015-3037
## Trace Element Microanalysis Methods

### Microanálisis de elementos traza

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Ablation ICP-MS</td>
<td>Good spatial resolution (10-25 µm). <strong>Large range of elements determined with good detection limits.</strong> Measurement of isotopic ratios possible.</td>
<td>No mapping capability. Subject to isobaric interferences as in bulk ICP-MS. Destructive. Drills through sample grains in a few seconds.</td>
</tr>
<tr>
<td>Ion Microprobe</td>
<td>Good spatial resolution (10-25 µm). Large range of elements if they form secondary ions. <strong>Excellent precision for isotopic ratios.</strong> Used for radiometric dating of single zircons.</td>
<td>Not widely available due to high cost and complexity. No mapping capability. Ionization potential varies by element. Need standards that are a good matrix match to unknowns.</td>
</tr>
<tr>
<td>Synchrotron-based Microprobe</td>
<td>Good spatial resolution (10-25 µm). <strong>Can do element concentration, speciation, and mapping on the same areas.</strong></td>
<td>Beam time allocated by proposal. Nearest facility, LNLS Brazilian Synchrotron Light Laboratory. For mapping, may be better to use electron microprobe.</td>
</tr>
</tbody>
</table>
Laser Ablation ICP-MS
Ablación láser

- Trace element microanalysis method uses a focused laser source coupled to an ICP-MS analyzer.
- Good method for microanalysis of Hg.
- Good for showing variation in sample composition with depth.
- Method drills through samples in a few seconds.
Pyrite Analysis by Laser Ablation ICP-MS

Espectrometría de piritas

South Africa Highveld #4 Coal

Pyrite Backscattered Electron Image

Source: Kolker and others, 2017b, Int. Journal Coal Geol.
Ion Microprobe
Microsonda iónica

- Negative or positive primary ion beam (O$_2^-$ or Cs$^+$).
- Nominal spot size 15 microns.
- Calibration using NIST standard glasses or other trace element standards.
- Like laser ablation ICP-MS, ion microprobe standards must be homogeneous on the scale of analysis.
SHRIMP-RG Ion Microprobe
Microsonda iónica SHRIMP-RG

A mass spectrometer that uses an ion beam as the ion source.
Can determine isotope ratios in addition to trace element data.
Primary beam of $O_2^-$ or Cs$^+$ ions, with detection in the ppm range.
10-15 micron spot size.

Sources: Bacon and others, 2012; Stanford University, not dated (photo).
Ion microprobe allows selective trace element and (or) isotopic analysis of individual grains within a sample.

Results show aluminosilicate glass has similar REE distribution as bulk sample.

REE are also present in Fe-oxides.

REE are much less abundant in quartz, which makes up a small portion of most samples.

Source: Kolker and others, 2017a
Synchrotron Methods

Sincrotrón

- Spectroscopic method for trace element bulk analysis or microanalysis using high-energy X-rays from a synchrotron source.
- Compositional analysis and element speciation on same samples or sample areas.
- Requires beamline set up for XAFS (X-ray absorption fine structure) or XANES (X-ray absorption near-edge structure), a kind of XAFS.

Source: Deonarine and others, 2015, USGS Fact Sheet 2015-3037
Summary – Topic 1: Laboratory Methods

**Resumen – Tema 1: Métodos de laboratorio**

- **ICP-MS** is the most widely used bulk analysis method. Advantages include excellent detection limits and detection of a wide range of elements all at once.

- Trace element microanalysis complements bulk analysis by allowing **direct determination of trace element mode of occurrence**.

- Common approaches to trace element microanalysis include **electron-beam, laser, ion beam, and synchrotron X-ray methods**.

- Synchrotron-based methods can determine **element speciation** in addition to concentration or abundance.
References – Topic 1: Laboratory Methods


Stanford University, not dated, Stanford/USGS SHRIMP-RG lab, Sensitive, high resolution ion microprobe – reverse geometry, accessed July 9, 2018, at https://shrimprg.stanford.edu/.

Session 5    Topic 2

LABORATORY QUALITY ASSURANCE
Common Problems in ICP-MS Analysis
Problemas con el análisis ICP-MS

- **Incomplete sample digestion**, especially refractory trace phases such as zircon and monazite, resulting in incomplete recovery for some elements.

- **Interferences** having the same mass as elements of interest (isobaric interferences). These can be combinations of elements or elements plus argon used as carrier gas.

- **Calibration, baseline, and carry over** problems. Can be addressed by running standards and blanks and doing blank subtraction if necessary.
Sample Digestion for ICP-MS

Preparación de muestras para análisis ICP-MS

• Digestion in a heated 3-acid (HNO$_3$, HF, HCl) mixture is standard for metals analysis by ICP-MS.
• Can add perchloric acid (HClO$_4$), only if a perchloric hood is available.
• Acid digestion may not fully break down acid-resistant trace phases.
• Sinter digestion- sample is mixed with sodium peroxide and sintered in a crucible at high temperature.
• Sinter digestion generally used where total digestion is required, such as in REE determination.
### Common REE-Bearing Trace Phases in Coal and Rocks

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Predominant REE</th>
<th>Melting Temp. (°C, 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apatite</td>
<td>$\text{Ca}_5(\text{PO}_4)_3(\text{OH,F,Cl})$</td>
<td>MREE</td>
<td>1,644 (fluorapatite)</td>
</tr>
<tr>
<td>Zircon</td>
<td>$\text{ZrSiO}_4$</td>
<td>HREE</td>
<td>1,690</td>
</tr>
<tr>
<td>Monazite</td>
<td>$(\text{Ce,La,Nd,Th})\text{PO}_4$</td>
<td>LREE, MREE</td>
<td>2,000+</td>
</tr>
<tr>
<td>Xenotime</td>
<td>$\text{YPO}_4$</td>
<td>Y, HREE</td>
<td>2,000+</td>
</tr>
<tr>
<td>Allanite</td>
<td>$(\text{Ce,Ca,Y})_2(\text{Al,Fe}^{3+})_3(\text{SiO}_4)_3(\text{OH})$</td>
<td>LREE, Y</td>
<td>No Data</td>
</tr>
</tbody>
</table>
## Fusion digestion vs. 4-acid digestion for REE
Preparación de muestras para análisis de tierras raras

<table>
<thead>
<tr>
<th>USGS GXR-4 Standard</th>
<th>La</th>
<th>Ce</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Tb</th>
<th>Gd</th>
<th>Dy</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fusion (2012)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GXR-4 measured</td>
<td>65.1</td>
<td>109</td>
<td>42</td>
<td>5.9</td>
<td>na</td>
<td>0.5</td>
<td>na</td>
<td>2.6</td>
<td>0.2</td>
<td>1.5</td>
<td>na</td>
</tr>
<tr>
<td>GXR-4 certified</td>
<td>64.5</td>
<td>102</td>
<td>45</td>
<td>6.6</td>
<td>1.63</td>
<td>0.36</td>
<td>5.25</td>
<td>2.6</td>
<td>0.21</td>
<td>1.6</td>
<td>0.17</td>
</tr>
<tr>
<td>Recovery</td>
<td>1.01</td>
<td>1.07</td>
<td>0.93</td>
<td>0.89</td>
<td>na</td>
<td>1.39</td>
<td>na</td>
<td>1.00</td>
<td>0.95</td>
<td>0.94</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Acid (2015)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GXR-4 measured</td>
<td>31.2</td>
<td>67.4</td>
<td>26.3</td>
<td>4.4</td>
<td>1.01</td>
<td>0.4</td>
<td>3.4</td>
<td>2.1</td>
<td>0.1</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>GXR-4 certified</td>
<td>64.5</td>
<td>102</td>
<td>45</td>
<td>6.6</td>
<td>1.63</td>
<td>0.36</td>
<td>5.25</td>
<td>2.6</td>
<td>0.21</td>
<td>1.6</td>
<td>0.17</td>
</tr>
<tr>
<td>Recovery</td>
<td>0.48</td>
<td>0.66</td>
<td>0.58</td>
<td>0.67</td>
<td>0.62</td>
<td>1.11</td>
<td>0.65</td>
<td>0.81</td>
<td>0.48</td>
<td>0.50</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Comparison of fusion (sinter) digestion with 4-acid digestion (incl. perchloric) by a commercial lab
## Which analysis is better?

<table>
<thead>
<tr>
<th>Lab</th>
<th>1633c</th>
<th>Sinter</th>
<th>Digest</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>106</td>
<td>88.4</td>
<td>203</td>
<td>106</td>
<td>16</td>
<td>3.73</td>
<td>2.68</td>
<td>16.6</td>
<td>3.42</td>
<td>9.44</td>
<td>1.31</td>
<td>8.78</td>
<td>1.27</td>
</tr>
<tr>
<td>2</td>
<td>107</td>
<td>77.9</td>
<td>175</td>
<td>89.8</td>
<td>19.5</td>
<td>4.3</td>
<td>2.8</td>
<td>17</td>
<td>3.4</td>
<td>9.9</td>
<td>1.3</td>
<td>6.9</td>
<td>nd</td>
</tr>
<tr>
<td>Cert.</td>
<td>87</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref.</td>
<td></td>
<td>4.67</td>
<td>3.12</td>
<td>18.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.32</td>
</tr>
<tr>
<td>Inf.</td>
<td>180</td>
<td>87</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.7</td>
</tr>
</tbody>
</table>

Comparison of sinter digestions in two labs for NIST SRM 1633c fly ash trace elements (in ppm). Cert = Certified Value; Ref. = Reference Value; Inf. = Informational Value. Values in ppm.
Chondrite Normalization

Normalización de condritas

- Elements with an even atomic number are more abundant than those with an odd atomic number.
- Effect is apparent in the distribution of the rare earths.
- Normalization to chondrites or sample composites eliminates the effect.
- Effect occurs because pairing of protons results in greater stability by each one offsetting the spin of the other.

Sources: Taylor and McLennan, 1985 (North American Shale Composite (NASC)); Korotev, 2009 (Chondrite normalization).
Data Comparison using Chondrite Normalization

Normalization should give a smooth pattern except for Eu and in rare cases, Ce.

Kinks in normalized pattern suggest analytical problems for Lab 2.

Values in ppm

<table>
<thead>
<tr>
<th></th>
<th>1633c</th>
<th>Sinter</th>
<th>Digest</th>
<th>La</th>
<th>Ce</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab</td>
<td>Y</td>
<td>La</td>
<td>Ce</td>
<td>Nd</td>
<td>Sm</td>
<td>Eu</td>
<td>Tb</td>
<td>Dy</td>
<td>Ho</td>
<td>Er</td>
<td>Tm</td>
<td>Yb</td>
<td>Lu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>106</td>
<td>88.4</td>
<td>203</td>
<td>106</td>
<td>16</td>
<td>3.73</td>
<td>2.68</td>
<td>16.6</td>
<td>3.42</td>
<td>9.44</td>
<td>1.31</td>
<td>8.78</td>
<td>1.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>107</td>
<td>77.9</td>
<td>175</td>
<td>89.8</td>
<td>19.5</td>
<td>4.3</td>
<td>2.8</td>
<td>17</td>
<td>3.4</td>
<td>9.9</td>
<td>1.3</td>
<td>6.9</td>
<td>nd</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chondrite Normalization

Normalización de condritas

- No agreement on standard chondrite values to use.
- I use approach suggested by Korotev (2009).
- This approach uses data of Anders and Grevesse (1989) x 1.36 to give Sm = 0.200 ppm.
- Need factors because some chondrites are carbonaceous and some are ordinary.

Normalization values (in ppm):

<table>
<thead>
<tr>
<th>57 La</th>
<th>58 Ce</th>
<th>59 Pr</th>
<th>60 Nd</th>
<th>62 Sm</th>
<th>63 Eu</th>
<th>64 Gd</th>
<th>65 Tb</th>
<th>66 Dy</th>
<th>67 Ho</th>
<th>68 Er</th>
<th>69 Tm</th>
<th>70 Yb</th>
<th>71 Lu</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.315</td>
<td>0.813</td>
<td>0.597</td>
<td>0.192</td>
<td>0.0722</td>
<td>0.259</td>
<td>0.325</td>
<td>0.213</td>
<td>0.208</td>
<td>0.0322</td>
<td>0.259</td>
<td>0.0761</td>
<td>0.267</td>
<td>0.0493</td>
<td>Masuda and others, 1973/1.2</td>
</tr>
<tr>
<td>0.319</td>
<td>0.820</td>
<td>0.121</td>
<td>0.615</td>
<td>0.200</td>
<td>0.0761</td>
<td>0.267</td>
<td>0.0493</td>
<td>0.330</td>
<td>0.0755</td>
<td>0.216</td>
<td>0.0329</td>
<td>0.221</td>
<td>0.033</td>
<td>Anders and Grevesse x 1.36</td>
</tr>
<tr>
<td>1.012</td>
<td>1.008</td>
<td>1.030</td>
<td>1.041</td>
<td>1.054</td>
<td>1.031</td>
<td>1.015</td>
<td>1.014</td>
<td>1.063</td>
<td>1.022</td>
<td>Proportion relative to Masuda and others, 1973/1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Others

| 0.31 | 0.808 | 0.122 | 0.6 | 0.195 | 0.0735 | 0.259 | 0.0474 | 0.322 | 0.0718 | 0.21 | 0.209 | 0.0322 | UMASS, 2005 |
| 0.367 | 0.957 | 0.137 | 0.711 | 0.231 | 0.087 | 0.306 | 0.058 | 0.381 | 0.0851 | 0.249 | 0.0356 | 0.248 | 0.0381 | Taylor and McLennan, 1985 |

ICP-MS Isobaric Interferences

Interferencias isobáricas en ICP-MS

- Interferences can be the result of: 1) Isotopes with overlapping mass ranges (e.g., $^{204}$Hg vs. $^{204}$Pb); 2) polyatomic species (e.g., $^{40}$Ar$^{16}$O vs $^{56}$Fe, $^{40}$Ar$^{40}$Ar vs. $^{80}$Se, $^{35}$Cl$^{40}$Ar vs. $^{75}$As); and 3) doubly charged species (e.g., 2x $^{69}$Ga$^+$ vs. $^{138}$Ba$^{2+}$).

- Can get around interferences by: 1) Choosing an isotope without interferences; 2) use of equations to correct for interferences; and 3) use of collision-reaction cell (CRC) technology, where the ion beam passes through a cell that contains an inert or a reactive gas to eliminate interferences (e.g., Li and others, 2014).
IUPAC Periodic Table of the Isotopes

Tabla periódica de los isótopos

Source: IUPAC, Chemistry International, 2011
<table>
<thead>
<tr>
<th>Isotopes of As and Se</th>
<th>Isótopos del arsénico y del selenio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Arsenic</strong> atomic number 33</td>
<td><strong>Selenium</strong> atomic number 34</td>
</tr>
<tr>
<td>$^{75}\text{As}$ 100%</td>
<td></td>
</tr>
<tr>
<td>$^{74}\text{Se}$ 0.89%</td>
<td></td>
</tr>
<tr>
<td>$^{76}\text{Se}$ 9.37%</td>
<td></td>
</tr>
<tr>
<td>$^{77}\text{Se}$ 7.63%</td>
<td></td>
</tr>
<tr>
<td>$^{78}\text{Se}$ 23.77%</td>
<td></td>
</tr>
<tr>
<td>$^{80}\text{Se}$ 49.61%</td>
<td></td>
</tr>
<tr>
<td>$^{82}\text{Se}$ 8.73%</td>
<td></td>
</tr>
</tbody>
</table>
Example of Interference Correction for $^{75}\text{As}$

Ejemplo de corrección de interferencia para $^{75}\text{As}$

- $^{35}\text{Cl}^{40}\text{Ar}$ interferes with $^{75}\text{As}$ used to measure As.
- Polyatomic species ($^{37}\text{Cl} + ^{40}\text{Ar}$) at mass 77 is used to give the contribution of ($^{35}\text{Cl} + ^{40}\text{Ar}$) at mass 75.
- This correction is adjusted for an interference at mass 77 with any selenium present.
- The contribution of $^{77}\text{Se}$ is determined by measuring $^{82}\text{Se}$, which has few interferences, and can be used to obtain the proportion of any isotope of Se present.
Other Common Problems with ICP-MS
Otros problemas frecuentes con ICP-MS

• **Calibration** - Instrument response for standards defines a calibration curve. If values for unknowns (samples) are too far removed from the calibration, response must be extrapolated, a source of error in the analysis. Fit to calibration curve should have a high correlation.

• **Carry over** - Occurs with insufficient wash-time between samples. If a sample with high concentration is run, some of this may carry over into the next run unless instrument response returns to its baseline.
Internal Checks on Data Quality
Revisión de la calidad de los datos

- Run **standards** for calibration and as unknowns. Are standard values reproduced?
- Run **total analytical blanks**. Does instrument response return to baseline or is there carry over? Is there a source of contamination? Especially important for trace elements.
- For major elements, do the analyses on an ash basis **sum to near 100%?** For coal, sulfur is a major element so this needs to be included in the analysis.
- For rare earths, do the results form a **smooth pattern** on a chondrite-normalized plot?
- Can you **replicate analyses**? If not, run it over again!
Repeticiones

• Replicate Hg analyses for feed coals and density separates were obtained using two different DMA analyzers at USGS labs in Denver and Reston.
• Results for 3 of 42 feed coals and 3 of 8 density separates showed poor agreement possibly due to Hg nugget effects. These were re-run (Table).
• Values converged after multiple runs.
• Averaged values were obtained for all density separates and the 3 feed coals (all values in ppb).

<table>
<thead>
<tr>
<th>Feed Coal</th>
<th>Reston Original</th>
<th>Denver Original</th>
<th>Denver Re-run 1</th>
<th>Denver Re-run 2</th>
<th>Reston Re-run</th>
<th>Mean (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9B</td>
<td>332</td>
<td>559</td>
<td>480</td>
<td>497</td>
<td>449</td>
<td>463 (5)</td>
</tr>
<tr>
<td>12A</td>
<td>211</td>
<td>312</td>
<td>310</td>
<td>271</td>
<td>285</td>
<td>278 (5)</td>
</tr>
<tr>
<td>12B</td>
<td>322</td>
<td>226</td>
<td>185</td>
<td>195</td>
<td>239</td>
<td>233 (5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Density Separate</th>
<th>Denver</th>
<th>Reston</th>
</tr>
</thead>
<tbody>
<tr>
<td>14A</td>
<td>44.6</td>
<td>76.5</td>
</tr>
<tr>
<td>14B</td>
<td>49.5</td>
<td>59.8</td>
</tr>
<tr>
<td>14C</td>
<td>78.4</td>
<td>115</td>
</tr>
<tr>
<td>14D</td>
<td>269</td>
<td>201</td>
</tr>
<tr>
<td>14E</td>
<td>224</td>
<td>392</td>
</tr>
<tr>
<td>14F</td>
<td>262</td>
<td>647</td>
</tr>
<tr>
<td>14G</td>
<td>226</td>
<td>614</td>
</tr>
<tr>
<td>14H</td>
<td>421</td>
<td>494</td>
</tr>
</tbody>
</table>

Linear regression excludes three samples in each plot. Perfect (1:1) correspondence also shown for each group of samples.

Source: Kolker and others, 2014, USGS Open-File 2014-1153
Summary – Topic 2: Laboratory Quality Assurance

Incomplete sample digestion and isobaric interferences are two of the most common problems in ICP-MS analysis.

REE-trace phases such as monazite, xenotime, allanite, and zircon are insoluble in multi-acid digestion used routinely for ICP-MS metals analysis. Sinter digestion is the best method for bulk determination of REE content.

Internal checks on data quality include running internal standards, blanks, and replicates.

For major elements, results should sum near 100% on an ash basis. REE data should give smooth patterns when plotted on a normalized plot.

If results are questionable, run them over again if possible.
References– Topic 2: Lab Quality Assurance

Referencias – Tema 2: Control de calidad


INTRODUCTION TO COMPOSITIONAL DATA ANALYSIS

Section Prepared by Ricardo Olea of USGS Eastern Energy Resources Science Center, rolea@usgs.gov.
Compositional data

Compositional data are measurements denoting proportional contributions of parts to a whole.

Depending on the units, the sum of all parts may add up to a constant. This is the most common case, happening, for example, when the units are percent, parts per million, or mg/kg.

Among the exceptions not adding to a constant, we have the case of concentrations measured in mg/L, μg/m³, or moles.
The relative information of compositional data sets them apart from conventional variables using absolute scales, such as speed, mass, and time.

For example, for every part \(j\), when the \(D\) parts \(x_j\) add to a constant \(\kappa\), one component always can be obtained from the others

\[
x_j = \kappa - \left( x_1 + x_2 + K + x_{j-1} + x_{j+1} + K + x_D \right),
\]

For example, the constant is 100 when the parts are measured as percentages.

Given the physical nature of parts, they cannot have negative values.
Correlations

In addition, even for those compositional data that do not add to a constant, the covariances are always related

\[
\text{Var}(x_j) = \text{cov}(x_1, x_j) + \text{cov}(x_2, x_j) + K + \text{cov}(x_{j-1}, x_j) + \text{cov}(x_j, x_{j+1}) + K + \text{cov}(x_j, x_D),
\]

where, if \( N \) is the sample size and \( m_j \) is the mean value of \( x_j \),

\[
\text{Var}(x_j) = \frac{1}{N-1} \sum_{i=1}^{N} (x_{ij} - m_j)^2
\]

\[
\text{cov}(x_j, x_k) = \frac{1}{N-1} \sum_{i=1}^{N} (x_{ij} - m_j)(x_{ik} - m_k)
\]

Not surprisingly, blind use of conventional statistics in the analysis of compositional data often leads to misleading or unacceptable results.
Subcompositional incoherence
Incoherencia subcomposicional

Denotes obtaining contradictory results after elimination of one or more components. A typical example would be: (A) analysis of the some specimens with moisture \( (x_4) \) versus (B) after drying them.

<table>
<thead>
<tr>
<th>Case A</th>
<th>( x_1 )</th>
<th>( x_2 )</th>
<th>( x_3 )</th>
<th>( x_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Case B</th>
<th>( x_1^* )</th>
<th>( x_2^* )</th>
<th>( x_3^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>0.50</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>0.40</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>3</td>
<td>0.43</td>
<td>0.43</td>
<td>0.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>corr A</th>
<th>( x_1 )</th>
<th>( x_2 )</th>
<th>( x_3 )</th>
<th>( x_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_1 )</td>
<td>1.00</td>
<td>0.50</td>
<td>0.00</td>
<td>-0.98</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>1.00</td>
<td>-0.87</td>
<td>-0.65</td>
<td></td>
</tr>
<tr>
<td>( x_3 )</td>
<td>1.00</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( x_4 )</td>
<td></td>
<td></td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>corr B</th>
<th>( x_1^* )</th>
<th>( x_2^* )</th>
<th>( x_3^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_1^* )</td>
<td>1.00</td>
<td>-0.57</td>
<td>-0.05</td>
</tr>
<tr>
<td>( x_2^* )</td>
<td>1.00</td>
<td>-0.79</td>
<td>1.00</td>
</tr>
<tr>
<td>( x_3^* )</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that drying resulted in a reversal in the sign of \( \text{cov}(x_1, x_2) \).
A set of values for $D$ non-compositional variables displays as a cloud in a $D$-dimensional Cartesian space.

A set of values for $D$ compositional variables lands inside a $(D-1)$-dimensional space (simplex).

Standard statistical techniques are valid for Euclidean distances in Cartesian coordinate systems, not in simplexes.
Warnings
Advertencias

• **Fallacy #1.** When only a few components are measured, sometimes there is the perception that all problems with compositional data vanish because, in this situation, the parts with measurements are far from adding to a constant.

• **Fallacy #2.** In the analysis of trace elements, typically the value of the concentrations are low. It is wrong to assume that the properties of compositional data disappear when all parts are small.

• **Fallacy #3.** It is false to assume that spurious effects of applying conventional statistics to compositional data are always negligible or predictable. It is like playing Russian roulette.
Solutions

Soluciones

- Develop a new form of statistics taking into account the properties of compositional data.
- **Represent compositional data in an unconstrained real space** (so it behaves like mass, time, or similar variables).

The most successful approach has been the latter. The dominant approach has been to transform the data and analyze the resulting new values. Common aspects are:
  - **Prepare ratios** of variables to consider the relative nature of the data, thus emphasizing scale invariance;
  - **Take natural logarithms of the ratios (log ratios)** to have absolute scale fluctuation in $(-\infty, +\infty)$, which sometimes also helps to have more symmetric probability distributions.
Log-ratio transformations using geometric means
Transformaciones log ratio usando medias geométricas

The geometric mean, \( g(x) \), of \( D \) parts is
\[
g(x) = \sqrt[\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!
The biplot: A tool for exploring dependencies

El biplot: Una herramienta para estudiar dependencias

- Length of the red rays is proportional to the standard deviation explained by PC1 and PC2. Here, clr A has the largest variability.
- Distance between ray ends away from the origin denotes difference in clrs. Clr M and clr V have quite similar variation.
- Because the rays extend in opposite directions, relative increases in ash for different samples are compensated with relative reductions of the other parts, and the reverse.

From Olea and Luppens (2015)

• Geostatistical processing of the information in the form of ilr transformations allows adequate mapping of parts.

• Area indicated shows a high-ash zone with corresponding reduction in fixed carbon and other parameters.
Modeling of compositional processes
Modelaje de procesos composicionales

Analogously to several other fields—such as time series analysis—analytical modeling of compositional data can be used to test or describe the nature of processes behind the observed value of the parts.

Evolution in time of three parts growing at different rates when the parameters are $\lambda_1 = 1; \lambda_2 = 2; \lambda_3 = 3$. 

From Pawlowsky-Glahn and others (2015)
Compositional Data Analysis

- When compositional data (parts) add up to a constant, use of conventional statistics in the analysis of these data can lead to misleading or conflicting results.
- Parts sometimes do not add to a constant, but still present the same problems.
- Compositional data expressed in percent are an obvious example of parts adding to a constant, which also applies to trace elements expressed in ppm.
- To represent compositional data in an unconstrained real space, take ratios of variables and natural logarithms of the ratios to create an unconstrained absolute variation in scale.
- Examples of log-ratio transformations include ilr (isometric log ratio), and clr (centered log ratio). Ilr gives coordinates in an unconstrained volume space. Clr is defined for each variable by dividing that variable by the geometric mean of all variables.
- Interdependencies among log-ratio transformed variables can be explored using bi-plots, 2-d mapping, or time variation.
- Use of compositional data analysis may or may not significantly change interpretation of compositional results, but it is more logical to play it safe.

