

Prepared in cooperation with Servicio Geológico Colombiano, Bogotá, Colombia

## **Topics in Coal Geochemistry—Short Course**

Open-File Report 2018–1145



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By Allan Kolker

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## Preface

This short course consists of material presented by Allan Kolker at Servicio Geológico Colombiano (SGC), the Geological Survey of Colombia, in Bogotá, Colombia, November 28–30, 2016, and November 27–30, 2017. The material is organized into five sessions, prepared at the invitation of the SGC as a training module for its research staff. The material presented is primarily based on studies conducted by the author and his collaborators during previous USGS investigations.

Colombia is a major coal producer, primarily of export coal, and the module provides information needed by SGC on coal quality and environmental issues related to coal production and use. Some examples given are specific to Colombian coal, but the overall principles discussed are relevant to the topic of coal geochemistry and should be useful for general application. Slide headings in English and Spanish are included in presentation slides (appendix 2).

## Acknowledgments

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## Abbreviations

|                 |   |
|-----------------|---|
| Al              | aluminum  |
| AMD             | acid mine drainage  |
| APCD            | air pollution control device  |
| As              | arsenic   |
| ASTM            | American Society for Testing and Materials (now ASTM International) |
| atm             | atmosphere  |
| Au              | gold  |
| Be              | beryllium   |
| Boiling PTS     | boiling points  |
| Br              | bromine   |
| BSE             | backscattered electron (image)                                      |
| Btu             | British thermal unit  |
| Btu/lb          | British thermal unit per pound                                      |
| CCP             | coal combustion product   |
| Cd              | cadmium   |
| cESP            | cold side electrostatic precipitator                                |
| Cl              | chlorine  |
| CLR/clr         | centered log-ratio transformation                                   |
| Co              | cobalt  |
| CO <sub>2</sub> | carbon dioxide  |
| COALQUAL        | U.S. Geological Survey coal quality database                        |
| CPP             | Clean Power Plan  |
| Cr              | chromium  |
| Cu              | copper  |
| CVAA            | cold vapor atomic absorption  |
| CVAFS           | cold vapor atomic fluorescence                                      |
| °C              | degrees Celsius   |
| DMA             | direct mercury analysis/analyzer                                    |
| D,mmf           | Dry, mineral matter free  |
| DOE             | U.S. Department of Energy   |
| EDX             | energy dispersive X-ray spectroscopy/analyzer                       |
| EERSC           | USGS Eastern Energy Resources Science Center                        |
| EIA             | U.S. Energy Information Administration                              |
| EPA             | U.S. Environmental Protection Agency                                |

|                  |   |
|------------------|---|
| EPMA             | electron probe microanalysis  |
| Eskom            | South Africa national electric utility  |
| ESP              | electrostatic precipitator  |
| eV               | electronvolts   |
| FA               | fly ash   |
| Fe               | iron  |
| FeS <sub>2</sub> | pyrite, marcasite, or iron disulfide  |
| FF               | fabric filter   |
| FGD              | flue-gas desulfurization  |
| °F               | degrees Fahrenheit  |
| GWh              | gigawatt hours  |
| HCl              | hydrochloric acid   |
| hESP             | hot side electrostatic precipitator   |
| HF               | hydrofluoric acid   |
| Hg               | mercury   |
| Hg <sup>0</sup>  | elemental mercury   |
| Hg <sub>p</sub>  | particulate mercury   |
| HNO <sub>3</sub> | nitric acid   |
| HR               | high resolution   |
| HREE             | heavy rare earth elements   |
| ICP-MS           | inductively coupled plasma-mass spectrometry                                      |
| ICR              | Information Collection Request  |
| IEA              | International Energy Agency   |
| ILR/ilr          | isometric log-ratio transformation  |
| INAA             | instrumental neutron activation analysis  |
| IUPAC            | International Union of Pure and Applied Chemistry                                 |
| km               | kilometer   |
| kt               | thousand tonnes   |
| LA-ICP-MS        | laser ablation-inductively coupled plasma-mass spectrometry                       |
| LNLS             | Laboratório Nacional de Luz Síncrotron, Brazilian National Synchrotron Laboratory |
| LOI              | loss on ignition  |
| LREE             | light rare earth elements   |
| MATS             | Mercury and Air Toxics Standards  |
| mg/kg            | milligram per kilogram  |
| mg/L             | milligram per liter   |

|                          |  |
|--------------------------|--|
| mi                       | mile   |
| MJ/kg                    | Megajoules per kilogram  |
| m,mmf                    | Moisture containing, mineral matter free                             |
| Mn                       | manganese  |
| MREE                     | middle rare earth elements   |
| Mt                       | million tonnes   |
| $\mu\text{g}/\text{m}^3$ | microgram per cubic meter  |
| $\mu\text{m}$            | micrometer   |
| n                        | number   |
| na                       | not applicable   |
| NASC                     | North American shale composite                                       |
| Ni                       | nickel   |
| NIST                     | National Institute of Standards and Technology                       |
| Norm.                    | normalized   |
| $\text{NO}_x$            | nitrogen oxides  |
| $\text{O}_3$             | ozone  |
| Pb                       | lead   |
| PbS                      | galena   |
| PbSe                     | lead selenide  |
| PC                       | pulverized coal  |
| PCD                      | particulate control device   |
| PIXE                     | proton induced X-ray emission  |
| $\text{PM}_{2.5}$        | fine particulate matter $\leq 2.5$ micrometers                       |
| ppb                      | parts per billion  |
| ppm                      | parts per million  |
| PTS                      | points   |
| Rb                       | rubidium   |
| REE                      | rare earth elements  |
| Ref                      | EIA Annual Energy Outlook 2016 Reference with Clean Power Plan (CPP) |
| RGM                      | reactive gaseous mercury   |
| Sb                       | antimony   |
| SCR                      | selective catalytic reduction  |
| SDA                      | spray dry absorber   |
| Se                       | selenium   |
| SEM                      | scanning electron microscope/microscopy                              |

|                 |   |
|-----------------|---|
| SGC             | Servicio Geológico Colombiano               |
| SO <sub>2</sub> | sulfur dioxide                              |
| SOP             | standard operating procedure                |
| SRM             | standard reference material                 |
| SXRF            | synchrotron X-ray fluorescence              |
| TCLP            | Toxicity Characteristic Leaching Procedure  |
| TEM             | transmission electron microscope/microscopy |
| Ti              | titanium                                    |
| UNEP            | United Nations Environment Programme        |
| USGS            | U.S. Geological Survey                      |
| V               | vanadium                                    |
| wt. %           | weight percent                              |
| XAFS            | X-ray absorption fine structure             |
| XANES           | X-ray absorption near-edge structure        |
| XRD             | X-ray diffraction                           |
| Y               | yttrium                                     |
| Zn              | zinc  |
| Zr              | zirconium                                   |

# Topics in Coal Geochemistry—Short Course

By Allan Kolker

## Introduction

This short course was prepared at the request of Servicio Geológico Colombiano (SGC) as a module for staff training. Prior to the short course, the SGC expressed interest in receiving training in (1) geochemistry and quality of coal; (2) geochemistry of trace elements in coal; (3) mercury and halogens in coal; (4) characterization and cycling of atmospheric mercury; (5) mercury, trace elements, and organic constituents in atmospheric fine particulate matter; (6) mercury in coal and the effect of coal quality on mercury emissions from combustion systems; (7) environmental and health effects related to coal use; and (8) related topics in coal combustion processes. A five-session short course was prepared that addressed all but the engineering aspects of coal use. In the sections that follow, topic overviews are given for the material that was presented. Brief descriptions of each slide are given in appendix 1, and the actual short course material, presented as a series of PowerPoint slides, is included in Portable Document Format (PDF) as appendix 2.

## Session 1

The goal of this session is to present the larger context of coal geochemistry, before discussing specific details. World coal production is examined as well as dependence on coal for power generation. Columbia has extensive hydroelectric resources and, as a result, exports most of its coal production. Also in this session, basic parameters applicable to coal characterization are reviewed. Emerging limits for mercury and carbon dioxide (CO<sub>2</sub>) emissions from coal-burning utility power stations are discussed from global and U.S. perspectives, updated to their status as of November 2017.

### 1.1 Global Coal Production and Use

In this section, available information about global coal production is discussed from Colombian and U.S. perspectives based on the most recent International Energy Agency (IEA) and U.S. Energy Information Administration (EIA) data. Colombia is highlighted as the 11th largest coal producer and the 4th largest coal exporter in the world. The United States is 1st in terms of coal reserves, and Colombia is 12th (World Energy Council, 2013). Because of its abundant hydroelectric resources, Colombia is among the lowest in the world in its dependency on coal for electric power generation (only about 10 percent). By contrast, the United States is slightly below the world average in terms of dependence on coal for power generation, but this dependence has been steadily decreasing due to the abundance of shale gas (World Bank, 2013; EIA, 2016). International Energy Agency data on coal production show increasing production of Colombian coal for nearly three decades with almost all of that produced for export (IEA, 2016; appendix 2, slide 1.1-5). The La Guajira and Cesar Departments of Colombia are the largest producers of coal relative to other parts of the country (World Coal, 2011), but smaller coal mines are present over a large part of both the eastern and western basins (Tewalt and others, 2006; appendix 2, slide 1.1-6).

In a series of slides, the U.S. energy mix for power generation is compared to that of Colombia. Coal production in the United States increased steadily for three decades up until about 2010, when it began to decline (EIA, 2016). This decline was most pronounced in the two largest U.S. coal-producing regions: the Appalachian Basin and the Powder River Basin. At the same time, coal production in the Illinois Basin was increasing, due in large part to the increased use of flue-gas desulfurization (FGD) scrubbers in the United States, because high-sulfur coal is needed to operate the scrubbers efficiently. As a result, sulfur emissions were no longer an impediment to the use of high-sulfur coal (EIA, 2016; appendix 2, slide 1.1-10). The larger trends of increasing gas-fired power generation and decreasing coal-fired power generation in the United States mirror the increase in U.S. shale gas production (EIA, 2016; appendix 2, slides 1.1-11, 1.1-14). In the current (2015) U.S. energy mix, coal and gas each account for 33 percent of net electric generation. Trends projected by the EIA show an increase in renewables and a continued increase in gas in the United States, with a corresponding decrease in the proportion of coal used for power generation. The extent of reduction in coal use depends on whether the proposed U.S. Environmental Protection Agency (EPA) Clean Power Plan (CPP; EPA, 2015) is adopted (EIA, 2016; section 1.3).

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To conclude this section, U.S. Geological Survey (USGS) studies about shale gas production and its effects and about CO<sub>2</sub> storage capacity in U.S. saline reservoirs are discussed (USGS, 2013). Shale gas topics include studies of pore structure in shales to understand gas distribution, sampling of water produced together with gas (produced water) and testing of produced water for additives used in hydraulic fracturing. The USGS assessment of CO<sub>2</sub> storage capacity shows the largest capacity in the Gulf Coast, Rocky Mountains, northern Great Plains, and Alaska. The assessment of CO<sub>2</sub> storage capacity shows that the largest storage capacity for CO<sub>2</sub> is not near the greatest concentration of U.S. coal-fired power stations in the Midwestern States, requiring substantial addition of pipeline infrastructure to take advantage of this storage capacity (USGS, 2013; appendix 2, slide 1.1-16).

### 1.2 Review of Basic Coal Data

In this section, basic approaches to coal characterization are reviewed, and more detailed information specific to trace elements in coal and coal ash is presented later in the short course. To begin this section, basic concepts such as coal rank, heating value, moisture, and mineral matter (ash) are reviewed. Important American Society for Testing and Materials (ASTM) approaches for coal characterization are described, including how to collect coal samples and prepare them for analysis, and what is included in essential ASTM determinations such as Proximate Analysis (ASTM D3172), Ultimate Analysis (ASTM D3176), Forms of Sulfur (ASTM D2492), and Rank Classification (ASTM D388). An example of ASTM D388 Rank Classification is given in appendix 2, slide 1.2-6, for four Colombian coal samples based on proximate analyses reported by Tewalt and others (2006). Three examples of sulfur forms determinations are provided, including a freshly collected low-sulfur South African coal and a freshly collected U.S. Illinois Basin high-sulfur coal, each having different total and pyritic sulfur contents. The third example is a weathered, moderate-sulfur Ukrainian coal sample collected from an outcrop, showing characteristic sulfate formation (appendix 2, slide 1.2-10). Useful publications are highlighted, including USGS Circular 1143 (Schweinfurth, 2003), which provides an introduction to coal science and coal quality, and USGS Open-File Report 2012–1205 (East, 2013), which shows the distribution of U.S. coal basins and illustrates the ASTM D388 Rank Classification for coal.

### 1.3 Toward Global Emissions Standards

In this section, implications of coal use for the global environment are considered in a status report on the state of efforts to limit carbon and mercury emissions, both globally and in the United States. For carbon emissions, the global effort is the Paris Agreement on Climate Change adopted on December 12, 2015 (United Nations, 2017). In the Paris Agreement, each participating country is expected to have a plan to reduce carbon emissions. At the time of the first short course in November 2016, ratification status of the agreement had been reached. Since then, in June 2017, the United States has sought to withdraw from the agreement. Current status of the Paris Agreement on Climate Change is given at [http://unfccc.int/paris\\_agreement/items/9485.php](http://unfccc.int/paris_agreement/items/9485.php). The U.S. plan to limit powerplant carbon emissions is the EPA Clean Power Plan (CPP), introduced in 2015 (EPA, 2015). The CPP has a goal of a 32-percent carbon reduction relative to 2005 emissions by 2030 (appendix 2, slide 1.3-3). However, at the time of the first short course, implementation of the CPP was on hold by the U.S. Supreme Court, and more recently, the EPA has proposed to repeal it.

The Minamata Convention on Mercury (United Nations Environment Programme [UNEP], 2016) is a global effort to control the release of mercury and limit its use. The convention includes controls on air emissions of mercury as well as a ban on new mercury mines, phase-out of existing ones, and regulation of mercury used in small-scale gold mining. At the time of the first short course in November 2016, more than 100 countries had signed the convention, but it had not reached the 50 ratifications required for it to go into effect. Since then, the minimum needed for ratification has been reached, and in August 2017, the Minamata Convention entered into force. The current status of the Minamata Convention is given at <http://mercuryconvention.org/>.

In the United States, the EPA Mercury and Air Toxics Standards (MATS) were introduced to limit emissions of mercury [Hg], other harmful trace elements (Beryllium [Be], Chromium [Cr], Manganese [Mn], Cobalt [Co], Nickel [Ni], Arsenic [As], Selenium [Se], Antimony [Sb], and Lead [Pb]), listed in order of increasing atomic number, and acid gases (hydrofluoric acid [HF], and hydrochloric acid [HCl]; EPA, 2011a). These standards apply to all coal- and oil-fired power generating units greater than 25 megawatts, which is essentially all power generation at the utility scale. Rationale for MATS is given in a series of slides showing that (1) powerplants are the largest source of U.S. mercury emissions; (2) other toxic metals from powerplants such as arsenic, chromium, and nickel can cause cancer; (3) fish consumption advisories for mercury are in effect in every State; (4) substantial health benefits, including avoidance of premature deaths and hospitalizations for respiratory and cardiovascular diseases, are projected to result from MATS (EPA, 2011b); and (5) compared to other industrial sectors that have become regulated, the unregulated utility sector has shown minimal reduction in mercury emissions (appendix 2, slide 1.3-6, 1.3-7). Finalization of MATS in April 2016 preceded the first short course. The current status of the MATS program is given at <https://www.epa.gov/mats>.

## Session 2

In this session, detailed information on the distribution and controls of trace elements in coal is presented. Emphasis is given to iron disulfides pyrite and marcasite (both  $\text{FeS}_2$ ) because these minerals host many of the elements of environmental interest, such as As, Se, Sb, Hg, and Pb in coal. Results are presented on the basis of published determinations by the author using microanalysis and by other results from the literature. The goal of this session is to provide a better understanding of the occurrence and effect of trace elements in coal as a foundation for a later session on the behavior of trace elements in coal combustion (Session 4).

### 2.1 Trace Elements in Coal

This section begins by providing the rationale for understanding trace element distribution in coal. Reasons include effects on power station operation, prediction of emissions, prediction of element behavior in coal preparation, control of metals release from coal and coal combustion products to groundwater, and minimizing health consequences. This discussion is followed by an introduction to the mode of occurrence concept, which is the form that a chemical element takes within coal. The mode of occurrence of an element determines its behavior during coal combustion and its environmental impact. Mode of occurrence is a function of geologic setting and can also provide information on the geologic history of a sample. In a broad sense, elements in coal may have primary organic and inorganic associations. Among inorganic associations, minor and trace elements may substitute for major constituents, such as chromium in illite-smectite, or occur as discrete trace phases, such as lead selenide ( $\text{PbSe}$ ; Finkelman, 1981; Kolker and Finkelman, 1998). Summaries of mineral matter in coal, trace phases, and modes of occurrence of potentially toxic metals in coal are given in a series of slides (appendix 2, slides 2.1-6 to 2.1-8). An overview of analytical approaches for investigating trace elements is given in this session but is expanded in Session 5. In both Session 2 and Session 5, the importance of moisture determination in accurately expressing the concentration of elements in coal is discussed.

The topic of arsenic in coal is introduced in this section by USGS Fact Sheet 2005–3152, “Arsenic in Coal” (Kolker and others, 2006a; appendix 2, slide 2.1-11). Past USGS studies used a selective chemical leaching approach to infer the mode of occurrence of elements, such as arsenic, in coal (Palmer and others, 1998; Finkelman and others, 2018). On the basis of the removal of arsenic in the nitric acid leaching step of the multi-stage leaching procedure, arsenic shows a predominant pyritic association in bituminous coals. Leaching studies also indicated a less pronounced pyritic association for arsenic in lower rank coals. The occurrence of arsenic as an abundant minor constituent in coal pyrite was confirmed by direct determinations, using electron microprobe analysis (Kolker and others, 2000; Kolker, 2012).

Using a spectroscopic approach, Huffman and others (1994) recognized that a portion of the arsenic associated with coal pyrite is converted spontaneously to arsenate, an oxidized arsenic form, over time. Huggins and others (2002) compared this spectroscopic approach to USGS selective leaching results to monitor progressive arsenic oxidation in the same coal samples. Both methods give similar proportions of arsenate if the HF and HCl leaching fractions combined are assumed to represent the arsenate fraction in coal. In a series of experiments over 18 months, Kolker and Huggins (2007) investigated the extent of arsenic substitution in pyrite on the rate of formation of arsenate in coal. Results showed similar rates of progressive arsenic oxidation under dry conditions regardless of the initial amount of pyritic arsenic. As an analogue for development of acid mine drainage in samples that were wetted, arsenic oxidation is much more rapid, leading to nearly 100 percent arsenate, a highly mobile arsenic form, by the end of the experiment (appendix 2, slide 2.1-15; Kolker and Huggins, 2007).

### 2.2 Trace Elements in Iron Disulfides

Iron disulfides are common components of coal and are known to contain harmful elements such as arsenic, selenium, and mercury. Studying the distribution of these constituents is especially helpful in understanding dispersion of air and water pollutants and in optimizing approaches for their reduction by coal preparation. In this section, the extents and modes of substitution of minor constituents into iron disulfides is reviewed together with the growth history of iron disulfides in coal. Divalent cations such as  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  generally substitute for  $\text{Fe}^{2+}$ , whereas monovalent anions such as  $\text{As}^-$ ,  $\text{Se}^-$ , and  $\text{Sb}^-$  generally substitute for  $\text{S}^-$  (Deditius and others, 2008). Coupled substitution has been recognized most notably as a mechanism for hosting gold in pyrite as  $\text{As}^{3+}$  plus  $\text{Au}^+$ . Substitution of minor constituents in iron disulfides is compiled from the literature, with emphasis on the occurrence of arsenic and mercury in pyrite (appendix 2, slide 2.2-3; Kolker, 2012).

Backscattered electron (BSE) imaging and wavelength-dispersive elemental mapping reveal similar growth histories and patterns of element enrichment in iron disulfides occurring in widely dispersed coals. Framboidal pyrite is always the earliest iron disulfide generation and is almost always arsenic poor. Single framboids or composite framboid masses are commonly overgrown by a later pyrite generation that is distinguished by a subhedral texture. Overgrowths on framboids may also be

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distinct compositionally, often showing enrichment in arsenic or other constituents relative to the earlier framboïd as shown in appendix 2, slides 2.2-7 to 2.2-9, and in Kolker (2012). In some cases, framboïds were found to have preferential nickel enrichment at or near their centers, which may indicate nickel availability in earliest diagenesis when its precursor existed in a monosulfide form (slide 2.2-10; discussed in Kolker, 2012). At the other extreme of the coal-forming sequence, cleat or vein-filling pyrite is always the last iron disulfide generation, based on crosscutting relations and, in some cases, by contrasting trace element contents.

### 2.3 Introduction to Mercury in Coal

In this section, common forms of mercury occurrence in coal are reviewed as an introduction to Session 3, which goes into this topic in greater detail. A brief discussion is provided about how we know that certain minerals, such as pyrite, are common hosts for mercury in bituminous coals. This section also compares available results for mercury in U.S. coals published in a USGS database (Bragg and others, 1997; updated by Palmer and others, 2015) and by the EPA, following extensive surveys of U.S. coal used in power generation conducted in 1999 (EPA, 2003) and again in 2010 (EPA, 2011c). Mean mercury contents (0.17 parts per million [ppm]) are higher in the USGS database than in the EPA databases (0.11 and 0.12 ppm, respectively) primarily because the USGS data represent coals as mined whereas the EPA databases represent delivered coals that may have undergone some degree of preparation prior to delivery (appendix 2, slide 2.3-3). This difference also reflects a greater proportion of low-mercury western coals included in the EPA databases. Mercury and arsenic in coals exported to the Netherlands are shown in appendix 2, slide 2.3-4, from the compilation by Meij and te Winkel (2009). The plots show a large range in values for each element in coal from different international sources and that coal exported from Colombia is below average for both mercury and arsenic.

Also in this section, approaches are reviewed that show how the occurrence of mercury in iron disulfides in coal is known (slide 2.3-5). In most cases, the mercury content of iron disulfides is below the detection limit of electron-beam instruments, such as an electron microprobe, but can be determined by using more sensitive instruments, such as laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). In addition, the occurrence of mercury in pyrite is inferred in selective leaching studies of coal and in bulk elemental analysis by correlation of mercury with iron disulfide proxies such as total iron contents. Different pyrite populations can have different mercury contents, as shown in slide 2.3-6. Coals with similar pyritic sulfur contents from the U.S. Illinois Basin are compared to coals from Donets Basin of eastern Ukraine, a known mercury-enriched province. A plot showing bulk mercury content versus pyritic sulfur for coals from these locations shows strongly diverging trends despite similar pyrite contents. The trend for the Ukraine samples reflects greater substitution of mercury in pyrite compared to the Illinois Basin samples.

## Session 3

This session focuses on the distribution of mercury and halogens in coal and their behavior in determining mercury emissions and promoting mercury capture in coal-fired boilers. The session also emphasizes inexpensive approaches for improving mercury capture from utility boilers on the basis of past EPA and USGS field studies and recommendations of UNEP. Past USGS studies, measuring ambient mercury contents and speciation, and using trace elements in fine particulate matter for source apportionment, are also discussed in Session 3.

### 3.1 Mercury and Halogens in Coal

This section begins with a review of the introductory material on mercury in coal presented in section 2.3 of the previous session. To introduce the effect of halogens in combustion systems, slide 3.1-3 shows that halogens can have positive effects by helping to improve mercury capture but can also have negative effects on boiler operation if the concentration of halogens, especially chlorine, is too high. Kolker and others (2012) reviewed the effect of halogens on mercury capture and showed how mercury, halogens, and particulates interact in the boiler. On a mass basis, bromine is more effective than chlorine in oxidizing elemental mercury in power station flue gas, thereby promoting mercury capture. On a mass basis, bromine is typically 1–4 percent of the chlorine content of U.S. coals (Vosteen and others, 2010; Kolker and others, 2012). Halogen contents of U.S. coals vary with rank and are lowest in low-rank coals and anthracite (Kolker and Quick, 2015; appendix 2, slide 3.1-6). The mode of occurrence of halogens in coal was investigated by Huggins and Huffman (1995), using spectroscopic approaches, which showed that halogens in coal are associated with the organic fraction, indicating a predominant association where halogens present in coal moisture are loosely bound to maceral surfaces or retained in pore spaces. In addition to rank variation,



halogen contents are controlled by geologic factors, including depth of burial, chemistry of associated formation waters, and proximity to geologic structures, such as fault zones, that may provide pathways for halogen-bearing fluids to interact with coal. Examples of the variation of chlorine content of U.S. coals with depth are presented for the U.S. Illinois Basin (from Gluskoter and Rees, 1964; appendix 2, slides 3.1-9, 3.1-10) and for the central Appalachian Basin (Bragg and others, 1991; appendix 2, slides 3.1-11, 3.1-12).

In the remainder of this section, a series of slides is presented from a USGS collaborative study of coals used for power generation in South Africa (Kolker and others, 2014). In this study, funded by UNEP and conducted in cooperation with Eskom, the national electric utility of South Africa, the USGS was provided with 42 samples of composite feed coals, representing all 13 operating coal-fired power stations in South Africa. A separate group of eight density separates of South African Highveld #4 coal was provided to study mercury and trace element partitioning expected during coal preparation. The mean mercury content of the South African feed coals, determined in USGS laboratories, is more than twice that of U.S. feed coals and approximately four times that of South African coal produced for export (appendix 2, slide 3.1-14). Investigation of the Highveld #4 density separates shows a strong correspondence of pyrite contents with ash and mercury. Results show that the lowest ash and mercury contents are in the lowest density separates that approximate the values of South African export coals (Kolker and others, 2017b). In situ determination of arsenic and mercury in pyrite by LA-ICP-MS confirms enrichment of these elements in pyrite relative to whole coal values and shows considerable grain-scale variation (Kolker and others, 2017b). On the basis of values for the bulk separates of the Highveld #4 coal used in South Africa, mercury contents would be expected to vary by a factor of about eight between exported coal and its discarded stone (Kolker and others, 2017b; appendix 2, slide 3.1-19).

## 3.2 Improving Mercury Capture

Mercury capture in coal-fired utility power stations is a function of coal quality, including rank, mercury content, and coal halogen content, as well as plant operations, including type and positioning of air pollution control devices (APCDs), the amount of unburned carbon in the particulate fraction, and whether there are specific controls for nitrogen oxides ( $\text{NO}_x$ ) and (or) mercury (UNEP, 2011; Senior, 2015). For power stations with conventional APCDs, a minimum of about 300 ppm chlorine is optimal to promote mercury capture, whereas concentrations of significantly more than 1,000 ppm have a diminishing benefit and may result in corrosion of the boiler (Quick and others, 2005; Kolker and others, 2006b; appendix 2, slide 3.2-3). In the boiler, gas-phase and gas-particle reactions promote oxidation of elemental mercury to form mercury-halogen complexes or bind mercury species to particles to form particulate mercury. Each of these mercury forms is easier to capture by APCDs than elemental mercury. Low rank coals typically do not have high enough halogen contents to promote oxidation and capture of elemental mercury. In this case, activated carbon may be injected upstream from the particulate control devices, or halogen-based sorbents may be added to the coal (Kolker and others, 2012; appendix 2, slide 3.2-4). Simple ways to lower mercury emissions include (1) preparing coal to reduce input mercury by removing pyrite-associated elements such as mercury and (2) adjusting power station operating conditions to increase the amount of unburned carbon in the ash, thereby improving mercury capture from the flue gas. The latter may have unwanted effects, though, such as decreasing boiler efficiency and affecting the quality of ash for marketing. Among widely used particulate controls, fabric filters (FFs) generally capture a higher proportion of mercury from the flue gas than electrostatic precipitators (ESPs). Where regulations require reductions in powerplant sulfur dioxide ( $\text{SO}_2$ ) emissions, the addition of FGD to reduce sulfur emissions should have a co-benefit of capturing a high proportion of any gaseous-oxidized mercury present.

In the remainder of this section, a case study of the Kendal and Duvha power stations in South Africa is presented. These stations were sampled in 2010 by the EPA for stack emissions, feed coal, and fly ash in each of the six boiler units for each power station (Scott, 2011; Kolker and others, 2014). Emissions measurements show lower total emissions and a higher fraction of oxidized mercury from three units in the Duvha station equipped with FFs compared to the other three units at Duvha and to all six units at the Kendal station, which are equipped with ESPs. The three Duvha units with FFs have the highest mercury capture efficiency, and USGS results show that fly ash from these units also has the highest mercury content (Kolker and others, 2014; appendix 2, slide 3.2-10). The section concludes by referring to the UNEP guidance document for reducing mercury emissions from coal combustion in powerplants. The UNEP document gives best practices for improving mercury control at a range of costs (UNEP, 2011).

## 3.3 Ambient Mercury and Fine Particulate Matter

This section gives a brief introduction to sampling ambient mercury and fine particulate matter, based primarily on recent USGS studies. Sampling mercury in the environment relates to coal geochemistry because coal-fired power stations are among the largest point-source emitters of ambient atmospheric mercury (EPA, 2011a, b). Measurement of ambient atmospheric mercury includes three operationally defined species: (1) reactive gaseous mercury (RGM), including all charged gaseous mercury

species; (2) particulate mercury ( $\text{Hg}_p$ ), including all mercury bound to particles; and (3) elemental mercury ( $\text{Hg}^\circ$ ), the dominant form of mercury in the atmosphere. Elemental mercury has a long residence time in the atmosphere and, as a result, can be transported globally, whereas RGM is deposited locally or regionally and has a shorter residence time. Residence time of  $\text{Hg}_p$  varies depending on particle size, composition, and solubility (Kolker and others, 2007).

The USGS Mobile Mercury Laboratory (Mobile Lab) has been deployed in a variety of settings to investigate ambient mercury species and associated parameters, such as fine particulate ( $\text{PM}_{2.5}$ ) mass, and ancillary gases, such as  $\text{SO}_2$ ,  $\text{NO}_x$ , and ozone ( $\text{O}_3$ ; Kolker and others, 2007, 2008, 2010; Engle and others 2008, 2010). In one such study, the Mobile Lab was deployed to Woods Hole, Massachusetts, for more than a year (Kolker and others, 2013). Mercury species in this northern coastal setting were compared to previous Mobile Lab deployments along the U.S. Gulf Coast and other southern locations to assess controls on atmospheric mercury deposition in coastal environments (Engle and others, 2008, 2010). During the Woods Hole deployment, and in previous studies (Edgerton and others, 2006; Kolker and others, 2008), transient RGM plumes were found to occur together with elevated  $\text{SO}_2$  and  $\text{NO}_x$ , indicating these plumes have coal combustion sources.

During the Woods Hole study, fine particulate matter was collected over several months, using filter-based samplers external to the Mobile Lab (Kolker and others, 2013; appendix 2, slide 3.3-4). Trace elements in  $\text{PM}_{2.5}$  were determined by extraction of particulate matter from the filters together with analysis by inductively coupled plasma-mass spectrometry (ICP-MS). Sources contributing to the observed trace element distributions were investigated by using a matrix factorization approach together with air mass back trajectories (Kolker and others, 2013). Results of the factorization analysis give weighted proportions of four probable source categories contributing to each element measured and to the total mass of  $\text{PM}_{2.5}$  collected. Among sources identified, an energy generation source was determined to be the largest contributor to  $\text{PM}_{2.5}$  mass with lesser contributions from crustal and marine sources and a possible metal smelting source. Elements such as vanadium (V), Cr, Ni, As, Se, molybdenum (Mo), Sb, and Hg are characteristic of coal combustion for energy generation whereas aluminum (Al), titanium (Ti), iron (Fe), yttrium (Y), zirconium (Zr), and the rare earth elements (REE) are characteristic of crustal sources (Duce and others, 1975; Pacyna and Pacyna, 2001; Song and others, 2001; appendix 2, slide 3.3-8). Surprisingly, some crustal-sourced material was contributed by air masses having offshore back trajectories. This determination supports the observed transport of Saharan dust across the Atlantic in the summer months combined with northward transport along the Atlantic coast by clockwise circulation of the summer Bermuda high (Perry and others, 1997; Kolker and others, 2013). These studies demonstrate how sampling and analysis of fine particulate matter can be used for source apportionment and to identify the contribution of energy sources to the ambient environment.

## Session 4

This session emphasizes fundamentals of coal combustion products (CCPs) and recent CCP-related USGS research. A recent EPA ruling upholds the designation of CCPs as nonhazardous waste, allowing the continued beneficial use of CCPs in construction materials and in other applications, while eliminating the need for more stringent (and expensive) handling requirements if CCPs were reclassified (EPA, 2014). This session examines the mineralogy of CCPs and mineral transformations that take place during coal combustion, together with trace element variation in CCPs, and between CCPs and coal. Current beneficial use of CCPs is reviewed together with the potential for new uses, such as a source of valuable elements. In the last part of this session, the potential for mobility of coal ash and its trace constituents is considered.

### 4.1 Introduction to Coal Ash

Coal combustion products primarily include fly ash, bottom ash, and, in plants equipped with FGD, flue-gas desulfurization sludge. The classification of coal ash in ASTM C618 for construction purposes is based on its major element characteristics expressed as the sum of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  compared to other major constituents. Where  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  is greater than or equal to 50 percent of the total on a weight basis, the ash is called “cementitious” and is classified as Class C. Where  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  is greater than or equal to 70 percent of the total on a weight basis, the ash is called “pozzolanic” and is classified as Class F. Each classification has specific properties for use in concrete.

Common minerals in coal, such as quartz, clays, carbonates and pyrite, either break down, react, or undergo phase transformations at boiler temperatures. Clays, such as illite-smectite and kaolinite, are either replaced in coal fly ash by aluminosilicate minerals, such as mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), or they enter the melt, forming aluminosilicate glass upon cooling. Pyrite in coal is oxidized in the boiler to form iron oxides, whereas quartz undergoes a phase transformation to the high-temperature  $\beta$  form (appendix 2, slide 4.1-6). Aluminosilicate glass is the most abundant constituent of coal fly ash, making up about 70 to more than 90 percent of most samples. Unburned carbon in fly ash may be present as various forms of coke or as coal constituents, which have survived the combustion process, such as inertinite (slide 4.1-8). In slides 4.1-9 and 4.1-10, examples show the

use of electron beam methods to characterize constituents of coal ash. Methods shown include BSE and wavelength-dispersive elemental mapping. These methods are discussed further in section 5.1

## 4.2 Trace Elements in Coal Ash

The behavior of trace elements in pulverized-coal-fired boilers is highly dependent on relative element volatilities (Ratafia-Brown, 1994; appendix 2, slide 4.2-3). Elements such as selenium, mercury, and the halogens are extremely volatile, leading to concerns over emission of these constituents. Conversely, elements such as manganese (Mn), rubidium (Rb), Zr, and the REE, are highly retained in the ash fraction and, as a result, are considered to be potential resources if they can be effectively recovered (see the following section). Most elements have more intermediate behavior and are both emitted and retained to some degree. Elements such as Be, Cr, Ni, As, Sb, and Pb fall into this category. However, concern over their emission is sufficient for them to be included with elements whose emissions are limited under the EPA MATS regulations (EPA, 2011a). Retention or partial retention of elements of environmental interest in coal ash results in pronounced overall enrichment in these elements relative to concentrations present in coal, because the mass fraction of ash is much smaller than that of the feed coal (Deonarine and others, 2015; appendix 2, slide 4.2-5). In addition to a general enrichment of trace elements in fly ash relative to coal, fly ash trace element contents vary by location within APCDs as flue-gas temperature and particle size decrease downstream from the boiler, resulting in greater element capture. As a result, concentrations of elements such as arsenic, mercury, and lead tend to be higher in the back rows of ESPs where the finest size fractions are collected (Mardon and Hower, 2004; James Hower, unpub. data, 2004; appendix 2, slides 4.2-7, 4.2-8).

## 4.3 Beneficial Uses of Coal Ash

The affirmation of nonhazardous waste status by the EPA allows the continued beneficial use of CCPs, with specified procedures for proper handling, transport, and storage of these materials. In 2016, the rate of CCP re-use in the United States reached 52 percent, an all-time high (American Coal Ash Association, not dated; appendix 2, slide 4.3-3). The increased rate of re-use is important because CCPs that are not re-used must be stored in landfills or impoundments, which is costly and could release coal ash into the environment in the event of a catastrophic failure (see the following section). Primary uses of coal ash and FGD sludge include raw material in concrete products, feedstock in the production of cement, waste stabilization, and road construction. FGD sludge is a component of synthetic gypsum for use in construction and agriculture.

The U.S. Department of Energy (DOE) is supporting a range of promising research approaches to recover REE from coal and coal-related materials. These materials include coal itself, coal fly ash, and even acid mine drainage from past coal mining (DOE, 2017a, b). This effort resulted from the need for REE in a wide range of modern applications ranging from cell phones to rare earth magnets used in wind-powered electric generation (Van Gosen and others, 2014). The need for REE is also reflected in the fact that one country, China, provides much of the REE commodity supplied to the world (Gambogi, 2017; slide 4.3-5).

The USGS is currently investigating the distribution of REE in coal fly ash as an alternative source of REE to conventional mining. REE are strongly retained in the coal ash after coal combustion, leading to enrichment relative to their concentrations in coal and shale (appendix 2, slide 4.3-8). Normalization of REE concentrations to chondritic meteorites (chondrite normalization) is a convenient way to compare REE results for different samples and to compensate for the Oddo-Harkins effect, apparent in REE, in which even-numbered elements are more abundant than odd-numbered elements (appendix 2, slide 4.3-9). Although discrete REE-bearing trace mineral phases are apparent in coal (appendix 2, slides 4.3-11 and 4.3-12), these minerals are much less common in coal ash (Hower and others, 2013).

Using an ion microprobe (section 5.1; <https://shrimprg.stanford.edu/>), REE distribution within constituents of coal ash was investigated on a grain scale (Kolker and others, 2017a). Results indicate that glasses formed at boiler temperatures have similar REE distributions as the bulk ash samples. REE are also contained in iron oxide-glass intergrowths but are much less abundant in quartz, which constitutes a small portion of some samples. Results for bulk REE distribution in a larger group of samples (Taggart and others, 2016) show a good correlation of REE content with  $Al_2O_3$ , consistent with USGS findings on a grain scale that REE are partitioned into aluminosilicate glasses in coal fly ash (appendix 2, slide 4.3-14).

## 4.4 Coal Ash Environmental Issues

The continued designation of coal ash as nonhazardous waste (EPA, 2014) has allowed a wide range of beneficial uses of coal ash to continue and has eliminated the need to store a large portion of ash in U.S. landfills and impoundments. For ash that is stored, standard tests, such as the EPA Toxicity Characteristic Leaching Procedure (TCLP), help ensure that harmful elements are not readily mobilized (EPA, 1992). Recently, several large releases of stored coal ash into the environment occurred in the

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United States, including ash stored at Kingston, Tennessee, in December 2008 and Eden, North Carolina, in February 2014 (appendix 2, slide 4.4-3). The Kingston spill resulted in the transport of harmful constituents, such as arsenic and mercury, from coal ash to river sediments, and these sediments continued to be affected by the spill even after concentrations of trace metals in river water returned to normal levels (Ruhl and others, 2010; Deonarine and others, 2015).

Leaching tests, such as the TCLP, assume that coal ash is stored at the land surface or in surface impoundments, under oxic conditions, where oxygen is available. This is not always the case in landfills and impoundments, especially at depth, where oxygen may be unavailable and, thus, conditions may be anoxic. Fly ash leaching experiments by Deonarine and others (2015, 2016), conducted under controlled conditions, show that leaching behavior of elements, such as chromium and arsenic, can be much different depending on the availability of oxygen. Although arsenic was leachable in all cases studied, in one sample, it was more leachable under anoxic conditions than if oxygen had been available (appendix 2, slide 4.4-6). These experiments show that additional leaching tests that more accurately reflect the conditions where coal ash is stored are needed to ascertain the potential for mobility of trace constituents from coal ash into the environment. The design of ash storage facilities is also an important factor. Lined landfills are much less likely to release constituents to the environment than unlined landfills (Deonarine and others, 2015; appendix 2, slide 4.4-5).

## Session 5

In this session, analytical methods used to study trace elements in coal are reviewed, including bulk analytical methods and methods for microanalysis. Each method is discussed from the standpoint of its advantages and common pitfalls. This discussion is followed in section 5.2 by the examination of data affected by common analytical problems, especially bulk analysis by ICP-MS. The short course concludes by introducing, in section 5.3, mathematical concepts underlying compositional data analysis. The purpose of this section is to help data users avoid potential problems, such as spurious correlation and contradictory results, encountered when statistical approaches are applied to data that sum to a constant as in results expressed as a percentage and (or) parts per million. Section 5.3 describes tools needed to avoid these problems.

### 5.1 Laboratory Methods

This section gives methods for bulk analysis and microanalysis of coal, in large part from the authors' experience with all but transmission electron microscopy (TEM) and instrumental neutron activation analysis (INAA). Some approaches, such as X-ray diffraction (XRD), are used to identify which minerals are present in the whole (bulk) coal sample, whereas microanalysis generally provides compositional information for individual grains within a sample (slide 5.1-2). Bulk analysis is used to determine the element distribution in a whole sample. Methods for bulk chemical analysis include ICP-MS, INAA, X-ray fluorescence, and isotope dilution. Advantages and disadvantages of each method are shown in appendix 2, slide 5.1-3. ICP-MS is the most common multi-element bulk analytical method currently in use but requires that a solid sample be digested to get it into solution. Prior to sample digestion, coal samples are "ashed" in a laboratory furnace to consume the organic fraction, leaving behind all but the most volatile elements in the inorganic fraction. Volatile elements such as mercury and selenium should be run on whole coal samples rather than on laboratory ash. Care should be taken in ICP-MS analysis to avoid or correct for interferences for the elements of interest. An example is given in section 5.2 showing how one or more isotopes having the same mass as the element of interest can interfere with the determination and how to avoid or correct for these isobaric interferences. Here and previously in section 2.1, the importance of accurately determining moisture contents, especially for low-rank coals, is emphasized to express elemental concentrations in coal. To eliminate variability resulting from differences in moisture content and the proportion of ash present in coal, expression of concentrations on a moisture-free whole coal basis is recommended, requiring accurate determination of moisture in coal together with bulk analysis and knowledge of the proportion of ash present (slide 5.1-5). National Institute of Standards and Technology (NIST) standard reference material (SRM) 1632d (Trace Elements in Bituminous Coal) and SRM 1633c (Trace Elements in Coal Fly Ash) are useful for analysis of coal and coal ash. NIST SRMs are produced in batches having expiration dates, and values with three levels of certainty are given: certified, reference, and informational. Where certified values are unavailable, reference and informational values may be useful, but generally, these two values should not be used for primary instrument calibration (slide 5.1-6).

In appendix 2, slide 5.1-7, methods for bulk mercury analysis are compared. The most widely used methods are (1) thermal decomposition together with amalgamation and measurement by atomic absorption spectrophotometry, an EPA method also known as direct mercury analysis (DMA; EPA, 2007); (2) cold vapor atomic absorption (CVAA); and (3) cold vapor atomic fluorescence (CVAFS). DMA is the most common method currently in use because of its flexibility to run solid or liquid samples



and the availability of relatively inexpensive, ready-to-use analyzers. CVAA has a similar range of determination as DMA but requires solid samples to be brought into solution. CVAFS has lower detection limits than either DMA or CVAA but is used primarily in studies of low-level ambient mercury rather than mercury in coal. Portable atomic absorption units with Zeeman background corrections are useful in field applications to measure real-time vapor phase mercury, especially in areas where sources of mercury emissions are nearby.

In the next part of section 5.1, microanalysis methods used in the characterization of coal and coal combustion products are discussed, including methods that are useful in determining major constituents, such as scanning electron microscopy (SEM), electron microprobe, and TEM, and methods specific to trace element microanalysis, such as LA-ICP-MS, ion microprobe, and synchrotron-based approaches (slides 5.1-8 to 5.1-20). Examples showing laboratory setups and results generated by micro-beam instruments, such as SEM, electron microprobe, and TEM, are given in slides 5.1-9 to 5.1-13. Electron beam instruments are useful in imaging samples using secondary electrons, obtaining combined imaging and compositional data using BSE, and obtaining compositional data and element mapping using wavelength dispersive or energy dispersive analysis (slides 5.1-9 to 5.1-12). Examples illustrating trace element microanalysis using LA-ICP-MS, ion microprobe, and synchrotron-based methods are shown in slides 5.1-15 to 5.1-20. Laser ablation and ion microprobe analysis primarily offer point analyses at much lower detection limits than electron beam instruments. Both methods offer concentration and isotopic determination on the same spots. Synchrotron-based methods are primarily used for bulk sample determinations of element speciation but have been adapted to do combined concentration mapping and element speciation of the same sample areas (slides 5.1-14 and 5.1-20). TEM analysis is especially useful in revealing characteristics of particle surfaces (slide 5.1-13) and in determining sample mineralogy on a nanometer scale, which in many cases has proven to be very different than micro- or macromineralogy.

## 5.2 Laboratory Quality Assurance

Increasingly, laboratories such as the USGS are adopting formal quality management procedures, requiring written standard operating procedures (SOPs) for analysis methods, and enhanced review and record keeping for laboratory data. Although this process is an important aspect of laboratory operation, it is not covered in this short course. Instead, this section emphasizes common problems with bulk trace element analysis using ICP-MS and how to recognize them from ICP-MS results. As noted in section 5.1, ICP-MS is the most widely used method of bulk sample analysis, including laboratories at the SGC.

Incomplete sample digestion, especially for insoluble minerals such as zircon and monazite, is a common problem in ICP-MS if acid digestion is used. Using a sinter digestion, where sample material is mixed with sodium peroxide and sintered in a crucible at high temperature, generally gives a more complete sample digestion (appendix 2, slide 5.2-3), but acid digestion is commonly used in metals analysis, where trace phase digestion is not critical. In the example shown in appendix 2, slide 5.2-5, REE analysis of USGS standard GXR-4 after sinter digestion and acid digestion, performed by the same commercial laboratory, is compared. Results by acid digestion give much lower material recoveries for the REE, suggesting some REE-bearing phases were not dissolved. In the next example, REE analysis of NIST SRM 1633c in two sinter digestions by two laboratories is compared. Whereas there are no certified values for the REE in this SRM, it is difficult to assess the quality of the two analyses. If the results are plotted on a chondrite-normalized plot, however, the result from Lab 1 gives a smooth pattern whereas the result for Lab 2 has a kinked pattern for the heavy rare earth elements, especially ytterbium, suggesting there may be a problem with the result. Because of their low abundance, analysis of odd-numbered heavy REE such as holmium, thulium, and lutetium can often be problematic, although not in this example. Plotting results on a chondrite-normalized plot can help distinguish possible analytical problems for the REE.

In the next series of slides (appendix 2, slides 5.2-10 to 5.2-13), the problem of ICP-MS isobaric interferences is discussed and an example is given showing a correction for isobaric interferences for  $^{75}\text{As}$ , the only isotope of arsenic. This correction uses the polyatomic species  $^{37}\text{Cl}^{40}\text{Ar}$  to determine the interference of  $^{35}\text{Cl}^{40}\text{Ar}$ , after correcting for an interference by  $^{77}\text{Se}$  at mass 77 with any selenium present (appendix 2, slide 5.2-13). A newer approach to arsenic and selenium determination by ICP-MS uses a collision/reaction cell to minimize spectral interferences (Li and others, 2014).

Other potential problems with ICP-MS include extrapolation of results beyond the calibrated range and carryover from a previous high-concentration sample if wash time is insufficient. Internal checks on data quality include running standards as unknowns, running total analytical blanks, and, for major elements, determining if the analysis sum is near 100 percent. For coal, sulfur is a major element and should be included in the summation. For rare earth elements, results plotted on a chondrite-normalized plot should give a smooth pattern. If not, there may be a problem. And finally, as a check, can you replicate results obtained previously or in another laboratory? The section concludes with a mercury analysis example where the same sample materials were determined at USGS laboratories in Reston, Virginia, and Denver, Colorado. Agreement generally was good, but a few samples needed multiple runs by the two laboratories for values to converge (appendix 2, slide 5.2-16; Kolker and others, 2014). This difference is a result of the concentration of mercury in pyrite contributing to variability of mercury analysis.

### 5.3 Introduction to Compositional Data Analysis

This section introduces basic concepts of compositional data analysis, a mathematical approach to compositional data analysis, and data interpretation. The approach is gaining acceptance in the geosciences with recognition that spurious correlations (and misinterpretation) can result from the application of conventional statistics to compositional data that are constrained to a constant sum (Aitchison and Pawlowsky-Glahn, 1997; Filzmoser and Hron, 2008; Pawlowsky-Glahn and others, 2015). Examples where compositional data are constrained to a constant sum include major element data expressed in percent and trace element data expressed in parts per million. Together, these are the primary datasets used by geochemists.

The section begins by comparing data that are mathematically limited to a constant sum, such as percent, and data that are inherently unconstrained, such as speed and molar concentrations. Closure of constrained compositional data requires that proportions of the whole must be positive or zero. This constraint sets compositional data apart from variables with absolute scales such as speed, mass, and time. In a given dataset, mathematical covariance of results can lead to spurious correlations, giving misleading or contradictory results. An example is given that is an analogue to proximate analysis of coal expressed in moisture-containing and dry states. In the moist state, there is an apparent correlation between components  $X_1$  and  $X_2$ . However, moisture ( $X_4$ ) expressed in percent is constrained to be no more than 100 percent. When this variable is removed by drying, the sign of the covariation between components  $X_1$  and  $X_2$  is reversed (appendix 2, slide 5.3-5). Problems with compositionally constrained data apply even where only a few of many components are measured, such as in trace element data, where values add up to be much less than the total.

To avoid problems inherent in constrained compositional data, a series of approaches is given whereby these data are converted into forms that can be used in unconstrained space where conventional statistical approaches are applicable. The first step is to compute ratios of variables and determine the logarithms of the ratios (log ratios; appendix 2, slide 5.3-8). As shown in appendix 2, slide 5.3-9, log ratios are then mathematically transformed to give calculated variables that include isometric log-ratio transformations (ilr) and centered log-ratio transformations (clr). These transformed variables can then be used to explore controlling dependencies of the dataset. One such approach is to use a two-dimensional biplot showing principal components and transformed log-ratio variables of the dataset in an unconstrained space (Otero and others, 2005; Thió-Henestrosa and Comas, 2016; appendix 2, slide 5.3-10). Log-ratio transformations can also be mapped to display transformed data in a geo-spatial context as shown in appendix 2, slide 5.3-11; Olea and Luppens, 2015). Both the biplot and the map show that among a range of coal parameters for the dataset examined, ash yield exerts the greatest overall control on the distribution of values obtained. Once constraints are removed, as shown in appendix 2, slide 5.1-13, compositional data can be used to test or describe processes such as variation of constituents with time, as shown, and (or) other geologically relevant processes.

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## Appendix 1. Short Course Slide Descriptions

### Session 1

#### 1.1 Global Coal Production and Use

1.1-1 Title slide Session 1, Topic 1: Global Coal Production and Use

1.1-2 Global Coal Production and Export. Compilation showing top ranking global coal producers and exporters based on IEA (2016) data. Colombia is highlighted as the #11 producer and the #4 coal exporter.

1.1-3 World Coal Proved Reserves. World Energy Council (2013) compilation showing the top 15 countries listed in order of proved coal reserves. The United States is #1 and Colombia is #12.

1.1-4 Electricity from Coal. Plot showing World Bank (2013) data for relative dependence on coal for electric power generation. France is lowest due to reliance on nuclear power. Poland and South Africa are among the highest. The United States is slightly below the world average coal dependence.

1.1-5 Colombian Coal Production. Plots showing increasing production of Colombian coal and coal produced for export. The two trends are nearly identical because most coal in Colombia is produced for export (IEA, 2016). Plot at right shows the proportion of coal produced in Guajira and Cesar Departments of Colombia, where the largest mines are located, relative to other parts of the country (World Coal, 2011).

1.1-6 Coal Fields of Colombia. Map at left showing the administrative Departments of Colombia and the locations of coal fields. Map at right shows simplified geologic base (from Tewalt and others, 2006).

1.1-7 Colombia—Power Generation by Source. Plot showing electric power generation in Colombia over time and that hydroelectric power generation predominates. Coal use constitutes a relatively small portion of electric power generation and this proportion has been fairly constant.

1.1-8 U.S. Coal Production (1980–2015). Graph showing declining U.S. coal production starting in about 2010. This is the first in a series of slides comparing the U.S. energy mix to that of Colombia (EIA, 2016).

1.1-9 U.S. Coal Basins. Map showing the distribution of U.S. coal basins and the location of the Appalachian Basin, Powder River Basin, and Illinois Basin discussed in slide 1.1-10 (from East, 2013).

1.1-10 U.S. Coal Production by Coal Basin. Plot showing production data, with time, of major coal producers—the Appalachian Basin, Powder River Basin, and Illinois Basin.

1.1-11 U.S. Electric Power Sector (1980–2015). Plot showing long-term U.S. trends in electric power generation by energy source. Plot shows decrease in the proportion of coal used for power generation beginning about 2010 and a corresponding increase in natural gas-fired power generation. Data are from EIA (2016).

1.1-12 U.S. Electric Power Generation (1990–2040). Plot showing current and projected trends in U.S. electric power generation by source. In current (2015) energy mix, coal- and gas-fired power generation are each 33 percent of net electric generation. Projected trends show increase in renewables and continued increase in gas-fired power generation and a decrease in the proportion of coal used for power generation. The extent of reduction in coal use depends on whether the proposed EPA Clean Power Plan (CPP) is adopted. Data are from EIA (2016).

1.1-13 U.S. Power Generation by Region. Map showing differences in the U.S. energy mix for electric power generation by region in 2015 and projected variation to 2030. Proportion of coal used for power generation is lowest in California and the Northeastern States and highest in the Northern Plains region. U.S. average from slide 1.1-13 is shown as inset in lower left. Data are from EIA (2016).

1.1-14 U.S. Shale Gas Production (2007–2014). Plot showing U.S. production of shale gas since 2007. Increasing gas production has compensated for the decline in coal production as U.S. coal-fired powerplants have increasingly adopted gas-fired power generation. Data are from EIA (2016).

1.1-15 USGS Shale Gas Studies. Summary slide listing ongoing USGS shale gas research and projection from EIA (2016) that U.S. shale gas production is expected to continue to increase between 2020 and 2040. USGS research topics include studies of pore structure in shales to understand gas distribution, sampling of produced water, and testing of produced water for constituents added in hydraulic fracturing.

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1.1-16 Carbon Capture and Storage. Summary slide describing a recent USGS study of the capacity for geologic carbon dioxide (CO<sub>2</sub>) storage in underground saline reservoirs. The largest capacity is in the Gulf Coast, Rocky Mountains, northern Great Plains, and Alaska. The study does not address how to capture and store CO<sub>2</sub>. The study shows that the largest storage capacity for CO<sub>2</sub> is not near the greatest concentration of U.S. coal-fired power stations in the Midwestern States. Results are from USGS (2013).

1.1-17 Summary—Topic 1: Global Coal Production and Use. Summary of Topic 1.1 with emphasis on Colombian coal production, the energy mix in Colombia, and characteristics of Colombian coals.

1.1-18 Summary—Topic 1: Global Coal Production and Use (Continued). Summary of Topic 1.1 with emphasis on U.S. coal production, the energy mix in the United States, growth of U.S. shale gas production, and USGS work on assessing the underground storage capacity for CO<sub>2</sub> in the United States.

1.1-19 References—Topic 1: Global Coal Production and Use.

## 1.2 Review of Basic Coal Data

1.2-1 Title slide Session 1, Topic 2: Review of Basic Coal Data

1.2-2 Some Basic Points About Coal. Review slide defining basic properties of coal such as rank, heating value, moisture, and ash.

1.2-3 Coal—A Complex Natural Resource. Slide showing USGS Circular 1143 (Schweinfurth, 2003), which is an introduction to coal quality and coal science.

1.2-4 Important ASTM Methods for Coal. Summary slide showing commonly used ASTM International methods for characterizing coal, including the name for each method and what it does.

1.2-5 ASTM Coal Rank (ASTM D388). Plot showing coal rank as defined by ASTM D388, based on variation in heating (calorific) value and percent fixed carbon. Figure is from East, (2013).

1.2-6 Example of ASTM D388 Rank Classification. Example showing application of ASTM D388 formulae for fixed carbon and heating value used to determine rank classification for four Colombian coal samples using results in Tewalt and others (2006).

1.2-7 Coal Sampling. Summary slide showing ASTM methods for coal sampling and what each method is used for.

1.2-8 Sampling Coal Ash. Summary slide showing recommendations for sampling coal ash at a power station. There are no ASTM methods for geochemical sampling of coal ash.

1.2-9 Forms of Sulfur (ASTM D2492). Summary slide showing what goes into ASTM D2492 (sulfur forms), what these forms are, and how they are determined.

1.2-10 Examples of Sulfur Forms (ASTM D4239 + D2492). Slide showing three examples of sulfur forms determinations using ASTM methods. South African example is low sulfur, un-weathered; Illinois Basin example is high sulfur with corresponding sulfur reduction and increase in heating value by coal preparation. Ukraine example is moderate sulfur with sulfate fraction contributed by weathering.

1.2-11 Summary—Topic 2: Review of Basic Coal Data. Review listing of basic coal parameters and variation in coal characteristics with these parameters.

1.2-12 References—Topic 2: Review of Basic Coal Data.

## 1.3 Toward Global Emissions Standards

1.3-1 Title slide Session 1, Topic 3: Toward Global Emissions Standards.

1.3-2 Paris Agreement on Climate Change. Summary slide showing basic elements of the Paris Agreement to reduce carbon emissions adopted on December 12, 2015.

1.3-3 Limiting U.S. Carbon Emissions. Summary slide showing elements of the EPA CPP to limit U.S. carbon emissions.

1.3-4 Minamata Convention on Mercury. Summary slide showing elements of the United Nations Minamata Convention to limit, regulate, and phase out global mercury use, including controls on air emissions of mercury.

1.3-5 U.S. EPA Mercury and Air Toxics Standards (MATS). Slide showing basic elements of the EPA for U.S. coal- and oil-fired generating units.

1.3-6 Rationale for U.S. EPA MATS. Slide showing rationale for implementing EPA MATS in the United States and their projected health benefits. EPA estimates that 50 percent of U.S. atmospheric mercury is derived from emissions from U.S. coal-fired power stations (EPA, 2011b).



1.3-7 Rationale for U.S. EPA MATS. Further rationale for EPA MATS is shown in a map of U.S. fish consumption advisories for mercury and in a table showing reduction in mercury emissions in industrial sectors that have become regulated versus coal-fired utility powerplants, which were unregulated prior to implementation of MATS in 2016.

1.3-8 Summary—Topic 3: Global Emissions Standards.

1.3-9 References—Topic 3: Global Emissions Standards.

## Session 2

### 2.1 Trace Elements in Coal

2.1-1 Title slide Session 2, Topic 1: Trace Elements in Coal.

2.1-2 Why Study Trace Elements in Coal? Slide summarizing rationale for understanding trace element distribution in coal. Reasons include effects on power station operation, prediction of emissions, prediction of element behavior in coal preparation, control of metals release for coal and coal combustion products to groundwater, and minimizing health consequences.

2.1-3 Effects of Inorganic Constituents on Coal Utilization. Summary slide showing inorganic constituents that affect power station operations and their effects.

2.1-4 Mode of Occurrence Concept. Introduction to the concept that the form of a chemical element in coal determines its behavior during coal combustion and other characteristics, including its environmental effect. Mode of occurrence is a function of geologic setting and can provide information on the geologic history of a sample.

2.1-5 Element Modes of Occurrence. Slide summarizing primary organic and inorganic associations of trace elements in coal.

2.1-6 Generalized Mineral Matter in Coal. Compilation of the mineral constituents of coal including major constituents such as clay minerals and trace constituents such as lead selenide. Compilation also shows trace elements substituting in major constituents, such as chromium in illite-smectite. From Finkelman, 1981; Kolker and Finkelman, 1998; Finkelman and others, 2018.

2.1-7 Minor/Trace Phases. Compilation of minor and trace mineral phases in coal and their constituents.

2.1-8 Metals in Coal. Compilation of potentially toxic metals in coal and their modes of occurrence.

2.1-9 How to Study Trace Elements in Coal. Compilation of analytical methods used to study the distribution of trace elements in coal on a bulk sample basis and in microanalysis. These methods are discussed in greater detail in section 5.1.

2.1-10 About Moisture. Slide emphasizing the importance of determining the moisture content of coal samples and the effect of moisture in determining the concentration of elements in coal.

2.1-11 Arsenic in Coal. Summary slide on the distribution and behavior of arsenic in coal, referring to Kolker and others (2006a).

2.1-12 Leaching Procedure for Coal Samples. Diagram showing selective chemical leaching of coal samples used in past USGS studies to indirectly determine the mode of occurrence of elements in coal (from Palmer and others, 1998).

2.1-13 Selective Leaching of Arsenic in U.S. Coals. Slide showing selective leaching results for arsenic in 13 U.S. coal samples, including 11 bituminous samples and 2 subbituminous coals. Plot shows a predominant pyritic (nitric-acid leached) association in the bituminous samples and a less pronounced pyritic association for arsenic in lower rank coals.

2.1-14 Arsenic Oxidation. Slide describing Kolker and Huggins (2007) study of coals with different extents of arsenic substitution in pyrite to see if this substitution affects the rate of formation of arsenate, the oxidized form of arsenic.

2.1-15 Spontaneous Arsenic Oxidation in Coal. Slide showing results of Kolker and Huggins (2007) study in which arsenic oxidation was monitored using arsenic X-ray absorption near-edge structure (XANES). Results show progressive arsenic oxidation under dry conditions regardless of starting pyritic arsenic. In samples that were wetted, arsenic oxidation was much more rapid, leading to nearly 100 percent arsenate by the end of the experiment.

2.1-16 Selective Leaching vs. X-Ray Absorption Fine Structure (XAFS) for Arsenic Species. Slide describing Huggins and others (2002) study comparing USGS selective leaching results for arsenic forms versus XANES, an XAFS approach, as a monitor for progressive arsenic oxidation in coal. Both methods give similar proportions of arsenate, but the leaching approach is indirect and requires interpretation that arsenate is removed in both the hydrochloric (HCl) and hydrofluoric (HF) acid leaching fractions.

2.1-17 Selective Leaching of Arsenic in U.S. Coals. Repeat of slide 2.2-13 included here to show combined results for the HF and HCl acid leaching fractions interpreted to represent the arsenate fraction in coal.

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2.1-18 Summary—Topic 1: Trace Elements in Coal.

2.1-19 Summary—Topic 1: Trace Elements in Coal (Continued).

2.1-20 References—Topic 1: Trace Elements in Coal.

### 2.2 Trace Elements in Fe-Disulfides in Coal

2.2-1 Title slide Session 2, Topic 2: Trace Elements in Fe-Disulfides in Coal.

2.2-2 Why Study Fe-Disulfides (FeS<sub>2</sub>) in Coal? Slide stating the benefits of studying pyrite and marcasite in coal. Benefits include understanding the source of air and water pollutants in coal use, reducing harmful constituents in coal preparation, showing diagenetic history, and predicting the formation of acid mine drainage (AMD).

2.2-3 Compilation of Minor Elements in Fe-disulfides in Coal. Compilation showing extents of minor and trace element substitution in pyrite and marcasite in coal. Compilation from various sources included in Kolker (2012).

2.2-4 Substitution of Minor Elements in FeS<sub>2</sub>. Compilation from Deditius and others (2008) showing elements that substitute for iron and those that substitute for sulfur in iron disulfides (FeS<sub>2</sub>).

2.2-5 Generations of Iron Disulfides in Coal. Slide stating that iron disulfides can be present in multiple generations in coal and that framboidal pyrite is earliest and cleat- or vein-filling pyrite is latest.

2.2-6 Framboids and their Overgrowths. Scanning electron microscope backscattered electron (BSE) images from Kolker (2012), showing framboidal pyrite overgrown by a later pyrite generation. Similar textures are found in widely dispersed coals.

2.2-7 Alabama, USA Warrior Basin Coal. Examples from Warrior Basin coal samples, showing differences in arsenic contents in different generations of pyrite in coal (Goldhaber and others, 2003).

2.2-8 Donetsk-Makeevka District, Ukraine. BSE image and wavelength-dispersive elemental maps showing arsenic-enriched pyrite overgrowths on arsenic-poor framboids in coal from Ukraine. Texture and genesis are very similar to that shown in slide

2.2-9 Arsenic and Selenium Enrichment in Iron Disulfides. Enrichment of arsenic and selenium in iron disulfides in coal, shown by wavelength-dispersive electron microprobe elemental maps for coal samples from the United States and Ukraine. From Kolker (2012).

2.2-10 Nickel Enrichment in Framboids. Wavelength-dispersive electron microprobe elemental maps for nickel in coal samples from the United States and Ukraine, showing preferential concentration of nickel at the core or mantle of pyrite framboids. From Kolker (2012).

2.2-11 Summary—Topic 2: Trace Elements in Fe-Disulfides in Coal.

2.2-12 References—Topic 2: Trace Elements in FeS<sub>2</sub>.

### 2.3 Introduction to Mercury in Coal

2.3-1 Title slide Session 2, Topic 3: Introduction to Mercury in Coal.

2.3-2 Mercury in Coal. Summary slide listing the most common forms of mercury occurrence in coal and how we know that pyrite is the most common form of mercury occurrence in bituminous coals.

2.3-3 U.S. Coal Databases: Mercury Results. Comparison of mercury results in USGS and EPA U.S. coal databases. USGS COALQUAL database represents coal in the ground and has a higher mean mercury content than what is included in EPA databases, which contain data on coal delivered to power stations. This difference is a function of coal preparation prior to delivery and a greater proportion of low-mercury western coals included in the EPA databases. From Kolker and others (2012).

2.3-4 Mercury in World Export Coals. Plots of mercury and arsenic concentrations in coals imported to the Netherlands from various sources. Slide gives world averages for mercury and arsenic in coal and shows that Colombian export coals are well below the world averages for these elements. From Meij and te Winkel (2009).

2.3-5 Mercury in Iron Disulfides. Summary slide showing how it is known that mercury resides in iron disulfides in coal.

2.3-6 Mercury-Rich Coals in Ukraine versus U.S. Illinois Basin Coals. Plots of mercury and pyritic sulfur, comparing mercury-rich coals in Ukraine with U.S. Illinois Basin coals, each group having similar pyritic sulfur contents. The trend for active mines in Ukraine is shown in the upper plot (from Kolker and others, 2009). Ukraine data are shown in the lower plot together with the trend for U.S. Illinois Basin coals (Bragg and others, 1997). The lower plot shows that mercury content of the whole coal is a function of both the amount of pyrite and the mercury content of that pyrite.

2.3-7 Summary—Topic 3: Introduction to Mercury in Coal.

2.3-8 References—Topic 3: Introduction to Mercury in Coal.

## Session 3

### 3.1 Mercury and Halogens in Coal

- 3.1-1 Title slide Session 3, Topic 1: Mercury and Halogens in Coal.
- 3.1-2 Mercury in Coal—Session 2 Review. Review of key points noted in previous session introducing the topic of mercury in coal.
- 3.1-3 Halogens in Coal—Cl, F, Br, I. Summary slide listing positive effects of halogens in coal to promote mercury capture and negative effects on boiler operation if the concentration of halogens, especially chlorine, is too high.
- 3.1-4 Mercury and Halogens in Coal. Slide listing major points about mercury and halogens in coal given in Kolker and others (2012).
- 3.1-5 Halogens in U.S. Coals. Plot of chlorine versus bromine contents of U.S. coals averaged by county. Plot shows that bromine content of U.S. coals typically is 1–4 percent of chlorine content on a mass basis. Plot is from Kolker and others (2012), modified from Vosteen and others (2010).
- 3.1-6 Rank Dependence of Halogens. Plots showing county-average distribution of chlorine and bromine contents in U.S. coals as a function of ASTM coal rank. Plots show depletion of halogens in low-rank coals. From Kolker and Quick (2015).
- 3.1-7 Mode of Occurrence of Halogens in Coal. Investigation by Huggins and Huffman (1995), using XANES for chlorine and bromine. Their results show association of halogens in coal with organic fraction but not bound as organohalogen complexes. Huggins and Huffman (1995) concluded that chlorine and bromine are present in coal moisture and are loosely bound to maceral surfaces or retained in pore spaces.
- 3.1-8 Geologic Factors Influencing Coal Halogen Contents. Summary slide listing geologic factors determining halogen content of coals. Factors include rank, depth of burial or paleodepth, chemistry of associated formation waters, and proximity to geologic structures.
- 3.1-9 Chlorine in U.S. Coal. Map showing the distribution of chlorine in U.S. coal by county average, used as an introduction to the case study of chlorine in coal in the U.S. Illinois Basin (example 1). Map from Quick and others (2005).
- 3.1-10 Example 1: U.S. Illinois Basin. Study describing the progressive increase of chlorine in formation water with depth in the Illinois Basin and a corresponding increase in the chlorine content of coal associated with those waters. From Gluskoter and Rees (1964).
- 3.1-11 Chlorine in U.S. Coal. Map showing distribution of chlorine in U.S. coal by county average, used as an introduction to the case study of chlorine in coal in the U.S. Appalachian Basin (example 2). Map from Quick and others (2005).
- 3.1-12 Example 2: Chlorine Variation with Depth. Example 2 showing controls of chlorine variation in coal. Compilation from Bragg and others (1991) showing variation in chlorine content of Appalachian Basin coals with stratigraphic depth.
- 3.1-13 Mercury in South African Feed Coals. Introduction to the case study by Kolker and others (2014) for mercury in South African coals used in power generation.
- 3.1-14 Mercury Distribution by Power Station. Plot of mercury content for 13 coal-fired utility power stations operating in South Africa. The mean value for these coals is compared to U.S. feed coals from EPA databases and South African coals prepared for export. The mean mercury content of coals used for domestic power generation in South Africa is about four times the mercury content of South African export coals. From Kolker and others (2014).
- 3.1-15 Impact of Coal Preparation on Mercury. Summary slide showing benefits of coal preparation to improve coal quality on mercury reduction.
- 3.1-16 South African Highveld #4 Coal. Introduction to the case study on tests of density separates of South African Highveld #4 coal as a source of export coal (Kolker and others, 2017b).
- 3.1-17 Density Separates. Plots showing variation in pyritic sulfur with mercury and ash contents for density separates of South African Highveld #4 coal. Plots show correspondence of pyrite contents with ash and mercury. Results show the lowest ash and mercury contents are in the low density separates that approximate export coals (Kolker and others, 2017b).
- 3.1-18 Pyrite by Laser Ablation ICP-MS. In situ determination of arsenic and mercury in pyrite from density separates of South African Highveld #4 coal. Results show enrichment of both elements in pyrite relative to the whole coal and a large extent of grain-scale variation in mercury and arsenic contents within individual pyrite grains (Kolker and others, 2017b).
- 3.1-19 Coal Products Predicted from Density Separates. Table showing ash, mercury, arsenic, and selenium contents predicted in coal products used in South Africa, exported, or discarded, based on simple combinations of results for density separates from Highveld #4 coal. Mercury contents would be expected to vary by about a factor of 8 in these materials (Kolker and others, 2017b).

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3.1-20 Summary—Topic 1: Mercury and Halogens in Coal.

3.1-21 References—Topic 1: Mercury and Halogens in Coal.

### 3.2 Improving Mercury Capture

3.2-1 Title Slide Session 3, Topic 2: Improving Mercury Capture.

3.2-2 Factors that Influence Mercury Capture. Summary slide listing coal quality factors and plant operation factors influencing mercury capture in coal-fired powerplants. From United Nations Environment Programme (UNEP; 2011) and Senior (2015).

3.2-3 Impact of Chlorine on Mercury Capture. Plot showing extent of mercury capture in coal-fired utility power stations equipped with various conventional air pollution control devices (APCDs). Results show the optimal range for chlorine to promote mercury capture, above which additional halogen contents are less beneficial. Results are based on U.S. county averages and available best-fit equations for each control technology. Plot is from Kolker and others (2006b), using county averages from Quick and others (2005).

3.2-4 Role of Halogens in Mercury Capture. Diagram showing gas phase and gas-particle reactions in the boiler involving mercury, halogens, and particulate matter. Halogens promote mercury oxidation to form mercury-halogen complexes or mercury bound to particles. These forms are easier to capture than gaseous elemental mercury. Diagram is from Kolker and others (2012).

3.2-5 Improving Mercury Capture. Plot showing mercury removal across an electrostatic precipitator (ESP) as a function of unburned carbon content (represented by loss on ignition [LOI]) of the ash. Results from Senior and Johnson (2005).

3.2-6 Improving Mercury Capture. Slide listing other options for improving mercury capture in coal-fired power stations equipped with conventional air pollution controls. These options include the addition of fabric filters (FFs) and the use of sorbents with an affinity for mercury.

3.2-7 Improving Mercury Capture. Slide showing addition of flue-gas desulfurization (FGD) as an option for improving mercury capture. FGD is a more expensive option, and its primary use would be to reduce sulfur emissions. If FGD is added, these devices can remove mercury in its gaseous oxidized form with high efficiency.

3.2-8 Kendal and Duvha Power Stations, South Africa. Introduction to the UNEP, Eskom, EPA, and USGS collaborative study (Scott, 2011; Kolker and others, 2014) of feed coal and fly ash from the Kendal and Duvha power stations.

3.2-9 Kendal and Duvha Power Stations, South Africa. Table showing total mercury emissions and proportion of oxidized mercury emitted from each boiler unit at Kendal and Duvha power stations. Measurements are from 2010 EPA field visit (Scott, 2011). Also shown is the concentration of mercury in fly ash as a function of the air pollution controls present. Results show that mercury oxidation is higher and more mercury is captured in the fly ash in units equipped with fabric filters (Kolker and others, 2014).

3.2-10 Kendal and Duvha Power Stations, South Africa. Plots showing that the extent of mercury capture and mercury content of fly ash is higher in Duvha boiler units equipped with fabric filters relative to Duvha and Kendal units equipped with electrostatic precipitators (ESPs). Coal and fly ash samples shown in the left plot were collected in duplicate with total sampling and analytical variation as shown (Kolker and others, 2014).

3.2-11 Kendal and Duvha Power Stations, South Africa. Summary slide showing findings with respect to variation in mercury capture in Kendal and Duvha boiler units equipped with ESPs versus FFs.

3.2-12 Improving Mercury Capture. Slide showing UNEP guidance document giving best practices for mercury emissions reduction and improving mercury capture without mercury-specific controls.

3.2-13 Summary—Topic 2: Improving Mercury Capture.

3.2-14 References—Topic 2: Improving Mercury Capture.

### 3.3 Measuring Ambient Mercury and Fine Particulate Matter

3.3-1 Title slide Session 3, Topic 3: Measuring Ambient Mercury and Fine Particulate Matter.

3.3-2 Speciation of Ambient Mercury. Summary slide defining measurable mercury species in the atmosphere, including elemental mercury ( $\text{Hg}^0$ ), reactive gaseous mercury (RGM), and particulate mercury ( $\text{Hg}_p$ ), and the characteristics of each.

3.3-3 USGS Mobile Mercury Laboratory. Slide showing USGS Mobile Mercury Laboratory and its capabilities for measuring mercury species; ancillary gases such as sulfur dioxide ( $\text{SO}_2$ ), nitrous oxides ( $\text{NO}_x$ ), and ozone ( $\text{O}_3$ ); and fine particulate mass ( $\text{PM}_{2.5}$ ). From Kolker and others (2007).

3.3-4 Ambient Mercury and Fine Particulate Matter. View of the interior of the USGS Mobile Mercury Laboratory showing instrument controls and view of the particulate sampler external to the Mobile Laboratory deployed to collect fine particulate matter for trace element analysis.

3.3-5 Ambient Mercury, Woods Hole, Massachusetts. Results of study by Kolker and others (2013), showing correspondence of RGM peaks with transient elevation of  $\text{SO}_2$  and  $\text{NO}_x$ . Correspondence of all three parameters is indicative of plumes from coal-burning emission sources such as coal-fired powerplants.

3.3-6 Mercury Species and Other Gases, Woods Hole. Plots showing longer term correspondence between mercury species and ancillary gas concentrations, Woods Hole, Mass. (Kolker and others, 2013).

3.3-7 Distinguishing Sources of Ambient Mercury. Summary slide for distinguishing plumes from coal combustion versus other mercury sources such as chlor-alkali plants and the use of mercury in small-scale gold mining. Results are based on studies by Edgerton and others (2006) and by Kolker and others (2008 and 2010).

3.3-8 Trace Elements in  $\text{PM}_{2.5}$ . Summary slide showing generalized source categories of element groupings in fine particulate matter. From Duce and others (1975); Pacyna and Pacyna (2001); and Song and others (2001).

3.3-9 Trace Elements in  $\text{PM}_{2.5}$ . Results from the Kolker and others (2013) study of fine particulate matter at Woods Hole, Mass., showing crustal, marine, smelter, and energy- source categories and the calculated proportions of each.

3.3-10 Summary—Topic 3: Measuring Ambient Mercury and Fine Particulate Matter.

3.3-11 References—Topic 3: Measuring Ambient Mercury and Fine Particulate Matter.

## Session 4

### 4.1 Introduction to Coal Ash

4.1-1 Title Slide Session 4, Topic 1: Introduction to Coal Ash.

4.1-2 Coal Combustion Products (CCPs). Summary slide with background information and definitions for coal combustion products.

4.1-3 Coal Combustion Products (CCPs). Diagram showing the range of coal combustion products produced in power generation and where in the plant they are generated. Diagram is from Deonarine and others (2015).

4.1-4 ASTM C618 Fly Ash Classification. Slide showing characteristics of ASTM Class C (“cementitious”) and Class F (“pozzolanic”) fly ash based on major element chemistry. From ASTM C618-17.

4.1-5 In the Boiler. Plot showing the range of temperature conditions in the boiler during coal combustion. From Senior (2015).

4.1-6 Mineral Transformations in Powerplants. Slide showing the mineralogical differences between coal and fly ash produced during coal combustion.

4.1-7 Examples of Fly Ash Constituents. SEM and microscopic images of coal fly ash showing constituents of the ash, including glass cenospheres, mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), and partially combusted coal. Images courtesy of James Hower, University of Kentucky.

4.1-8 Fly Ash Petrography. Summary of organic and inorganic constituents of fly ash that are newly formed in the boiler (neoformed), such as glassy material, and those that are inherited from the feed coal, such as quartz and inertinite.

4.1-9 Fly Ash Microanalysis. Electron microprobe BSE images and wavelength dispersive elemental maps of iron oxide particle in glass and skeletal iron oxides with interstitial glass in fly ash. Nickel maps suggest an association of nickel with the iron oxide phase.

4.1-10 Fly Ash Microanalysis. Electron microprobe BSE and wavelength dispersive elemental maps of Fe, Ca, Al, and Si distribution in a coal fly ash sample. Images show glassy aluminosilicate cenospheres, iron oxides, and calcium-enriched zones in this sample area.

4.1-11 Summary—Topic 1: Introduction to Coal Ash.

4.1-12 References—Topic 1: Introduction to Coal Ash.

### 4.2 Trace Elements in Coal Ash

4.2-1 Title Slide Session 4, Topic 2: Trace Elements in Coal Ash.



- 4.2-2 Trace Elements in Coal Ash. Summary slide listing generalized behavior of trace elements in coal fly ash including volatile elements such as mercury that are emitted during coal combustion and refractory elements such as the rare earths that are retained in the ash fraction.
- 4.2-3 Behavior of Elements During Coal Combustion. Diagram showing relative volatility of elements during coal combustion. Volatile elements are emitted whereas refractory (not volatile) elements are retained in a smaller mass fraction. From Ratafia-Brown (1994).
- 4.2-4 From the Flue Gas. Slide summarizing the capture of volatile elements from the flue gas.
- 4.2-5 Element Enrichment in Coal Ash. Plot showing trace element enrichment in three U.S. coal fly ash samples relative to mean concentrations for these elements in U.S. coal from Bragg and others (1997). Plot is from Deonarine and others (2015).
- 4.2-6 Variation in Fly Ash Chemistry. Slide summarizing the variation in trace element content of fly ash within the ash collection system as a function of decreasing particle size and temperature.
- 4.2-7 Fly Ash Chemistry—Arsenic. The variation of arsenic content from front to rear in ESP hoppers in a Kentucky powerplant. From James Hower, University of Kentucky (unpub. data, 2004).
- 4.2-8 Fly Ash Chemistry—Mercury. The variation of mercury content from front to rear and from side to side in ESP hoppers in a Kentucky powerplant. From Mardon and Hower (2004).
- 4.2-9 Mercury Capture. Summary of the status of mercury capture in U.S. coal-fired utility power stations. Outline of factors that influence the process and extent of mercury capture in power stations that burn coal.
- 4.2-10 Summary—Topic 2: Trace Elements in Coal Ash.
- 4.2-11 References—Topic 2: Trace Elements in Coal Ash.

### 4.3 Beneficial Uses of Coal Ash

- 4.3-1 Title Slide Session 4, Topic 3: Beneficial Uses of Coal Ash.
- 4.3-2 Beneficial Use of Coal Combustion Products. Summary slide giving the status of EPA regulation of coal ash for beneficial use and the status of the use of coal combustion products in the United States. Sources: EPA (2014); American Coal Ash Association (not dated).
- 4.3-3 Use of U.S. Coal Combustion Products (CCPs). Plot showing amounts of CCPs produced and used by year and proportion used as a percentage. In 2016, proportion used exceeded 50 percent for the first time. Source: American Coal Ash Association (not dated).
- 4.3-4 Some Current Use of Coal Ash and FGD. Summary slide listing primary uses of coal ash and FGD materials. Source: American Coal Ash Association (not dated).
- 4.3-5 Recovery of Rare Earth Elements from Coal Ash? Summary slide listing the need for alternative sources of rare earth elements (REE), characteristics of coal ash that make it a possible source of REE, and the potential for REE recovery from coal ash.
- 4.3-6 Advantages of Coal Ash as a Source of REE. Summary of the advantages of coal ash as a potential source of REE, continued from previous slide.
- 4.3-7 Behavior of Elements During Coal Combustion. Slide emphasizing the nonvolatile behavior of REE during coal combustion. Slide is repeated from slide 4.2-3, which emphasized very volatile behavior of elements such as mercury and is the opposite of the behavior of REE during coal combustion. From Ratafia-Brown (1994).
- 4.3-8 REE in Coal Ash vs. Coal and Upper Continental Crust. Slide comparing REE enrichment of U.S. average coal (Bragg and others, 1997, Palmer and others, 2015; Upper Continental Crust (Taylor and McLennan, 1985), and a series of coal fly ash samples (Kolker and others, 2017a). Plot illustrates relative REE enrichment in fly ash relative to other materials. Chondrite-normalized plot, with normalizing values from from Korotev (2009).
- 4.3-9 Oddo-Harkins Effect. Slide illustrating the Oddo-Harkins effect in which even-numbered elements are more abundant than odd-numbered elements. Normalization to chondrites eliminates the appearance of a sawtooth abundance pattern resulting from the Oddo-Harkins effect.
- 4.3-10 Possible Modes of Occurrence of REE in Coal Ash. Summary slide explaining the uncertainty in mode of occurrence of REE in coal ash and giving possibilities that have been proposed for this occurrence.
- 4.3-11 REE-Bearing Trace Phases in Coal. Table listing REE-bearing trace phases found in coal and their melting temperatures as pure phases. These melting temperatures are similar to or exceed peak temperatures attained in coal-fired utility boilers.
- 4.3-12 REE-Bearing Trace Phases in Coal. Additional forms of REE occurrence in coal. Some are present only in mineralized coals.

- 4.3-13 Investigation of Fly Ash for REE. Outline of ongoing USGS studies of fly ash to determine the distribution of REE and preliminary results using ion microprobe analysis described in Session 5 of this short course.
- 4.3-14 REE in Coal Fly Ash. Results from Kolker and others (2017a) showing the distribution on a chondrite-normalized plot of REE in two bulk fly ash samples and their constituents.
- 4.3-15 Summary—Topic 3: Beneficial Uses of Coal Ash.
- 4.3-16 References—Topic 3: Beneficial Uses of Coal Ash.
- 4.3-17 References (Continued)—Topic 3: Beneficial Uses of Coal Ash.

## 4.4 Coal Ash Environmental Issues

- 4.4-1 Title Slide Session 4, Topic 4: Coal Ash Environmental Issues.
- 4.4-2 Mobility of Constituents from Coal Ash? Diagram showing possible pathways of migration of leachates from a coal ash impoundment where the impoundment is unlined. Slide also lists EPA TCLP leaching protocol used for testing potential element mobility from coal ash.
- 4.4-3 Mobility of Constituents From Coal Ash? Description of recent U.S. coal ash spills in Kingston, Tenn., and Eden, N.C., and the magnitudes of each spill.
- 4.4-4 Mobility of Constituents From Coal Ash? Photograph and map of the area affected by the 2009 Kingston, Tenn., coal ash spill. From Ruhl and others (2010), EPA (2014), and Deonarine and others (2015, 2016).
- 4.4-5 Potential for Mobility of Trace Elements. Slide showing USGS Fact Sheet 2015–3037 (Deonarine and others, 2015) and list of key findings: (1) Potential mobility of trace elements from coal ash differs by element; (2) Degree of oxygenation affects extent of element mobility; and (3) Standardized leaching tests only consider case where oxygen is available.
- 4.4-6 Leaching Experiments for Arsenic and Chromium in Fly Ash. Results from Deonarine and others (2015, 2016), showing leaching behavior of arsenic and chromium from two coal fly ash samples under oxic (with oxygen present) and anoxic (little or no oxygen present) conditions. Results show that arsenic is leachable under all conditions whereas chromium is partly leachable in one sample under oxic conditions and not leachable in the other cases.
- 4.4-7 Summary—Topic 4: Coal Ash Environmental Issues.
- 4.4-8 References—Topic 4: Coal Ash Environmental Issues.

## Session 5

### 5.1 Laboratory Methods

- 5.1-1 Title Slide Session 5, Topic 1: Laboratory Methods.
- 5.1-2 How to Study Trace Elements in Coal. Summary slide comparing whole sample (bulk) analysis methods versus microanalysis methods for selective analysis of individual minerals or constituents in coal.
- 5.1-3 Common Methods for Bulk Trace Element Analysis. Table listing bulk analysis method from slide 5.2-2 and giving advantages and disadvantages of each method. Methods include inductively coupled plasma-mass spectrometry (ICP-MS), instrumental neutron activation analysis (INAA), X-ray fluorescence, and isotope dilution. Compilation is based on experience by the author with each method except for INAA.
- 5.1-4 About Moisture. Slide emphasizing the importance of moisture determination for coal in bulk analysis on a whole-coal basis and on a dry basis.
- 5.1-5 Whole Coal versus Ash Basis. Slide explaining the difference between whole-coal and ash basis for bulk analysis of coal. Slide showing sources of variation in results expressed on an ash basis and how these can be eliminated by expressing results for bulk coal samples on a dry, whole-coal basis.
- 5.1-6 Standards for Coal and Coal Ash Analysis. Slide listing U.S. National Institute for Standards and Technology (NIST) standard reference materials (SRMs) for coal and coal ash analysis, including SRM 1632d, Trace Elements in Bituminous Coal, and SRM 1633c, Trace Elements in Coal Fly Ash. Also, the difference between certified, reference, and informational values in NIST SRMs is explained.

5.1-7 Common Methods for Bulk Mercury Analysis. Table listing bulk analysis methods for mercury giving advantages and disadvantages of each method. Compilation is based on experience by the author with the direct mercury analysis (DMA) method.

5.1-8 Microanalysis Methods. Table listing microanalysis methods and giving advantages and disadvantages of each method, including scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analyzer, electron microprobe, and transmission electron microscopy (TEM) or high resolution (HR) TEM. Compilation is based on experience by the author with each method except for TEM.

5.1-9 Scanning Electron Microscope SEM/EDX. Photographs of an SEM equipped with EDX analyzer and an SEM image of a fly ash particle.

5.1-10 Electron Microprobe. Photograph of an electron microprobe and diagram showing the cross section of a wavelength-dispersive spectrometer used to measure characteristic X-rays of elements generated by interaction of the sample with the electron beam.

5.1-11 Electron-beam Instruments. Diagram showing interaction of sample with the electron beam and source regions for secondary electrons used in SEM, backscattered electrons used in BSE, and characteristic X-rays used for compositional analysis.

5.1-12 Microanalysis. Images showing microanalysis of a fly ash sample including wavelength-dispersive elemental maps for Fe, Ca, Al, and Si, and BSE map of the same image area.

5.1-13 Transmission Electron Microscopy (TEM). Example of high-resolution TEM image of fly ash particle surfaces showing surface coating at nanometer scale. From Deonarine and others (2015).

5.1-14 Trace Element Microanalysis Methods. Table listing microanalysis methods capable of determining trace elements and advantages and disadvantages of each method. Methods include laser ablation ICP-MS (LA-ICP-MS), ion microprobe, and synchrotron-based microprobe. Compilation is based on experience by the author with each method.

5.1-15 Laser Ablation ICP-MS. Slide showing an LA-ICP-MS instrument and its characteristics.

5.1-16 Pyrite Analysis by Laser Ablation ICP-MS. Example of LA-ICP-MS analysis of arsenic and mercury in pyrite in South Africa Highveld #4 coal density separate. From Kolker and others (2017b).

5.1-17 Ion Microprobe. Summary slide for Stanford/USGS SHRIMP-RG ion microprobe used for USGS REE studies in coal fly ash.

5.1-18 SHRIMP-RG Ion Microprobe. Photograph showing Stanford/USGS SHRIMP-RG ion microprobe and additional information on its uses. This instrument is used to determine elements present at concentrations below detection by electron beam instruments, such as the REE (Bacon and others, 2012; Stanford University, not dated).

5.1-19 Ion Microprobe Data for the REE. Preliminary REE data for selective constituents of coal fly ash determined using the SHRIMP-RG ion microprobe. Concentrations are shown on a chondrite-normalized plot together with data for bulk sample from separate bulk analysis.

5.1-20 Synchrotron Methods. Example in coal fly ash showing arsenic composition map determined by synchrotron microanalysis and corresponding arsenic species (forms of arsenic) using X-ray absorption near-edge structure (XANES). Synchrotron source has the advantage of giving bulk trace element microanalysis together with element speciation. Example is from Deonarine and others (2015).

5.1-21 Summary—Topic 1: Laboratory Methods.

5.1-22 References—Topic 1: Laboratory Methods.

## **5.2 Laboratory Quality Assurance**

5.2-1 Title Slide Session 5, Topic 2: Laboratory Quality Assurance.

5.2-2 Common Problems in ICP-MS Analysis. Summary slide listing common problems that can affect bulk trace element analysis by ICP-MS.

5.2-3 Sample Digestion for ICP-MS. Summary slide listing approaches to digestion of solid samples for ICP-MS analysis and the requirements and limitations of each method.

5.2-4 REE-Bearing Trace Phases in Coal. Summary slide showing common REE-bearing trace phases in coal that may not be fully digested in acid digestion for REE analysis by ICP-MS.

5.2-5 Fusion Digestion vs. 4-Acid Digestion for REE. Comparison of measured and certified values for USGS standard GXR-4 in two separate ICP-MS runs by the same commercial laboratory. Using acid digestion, in most cases, recovery is only about 50 to 70 percent of the certified values. Using fusion digestion, recovery is near 100 percent.



5.2-6 Two Sinter Digestions for NIST SRM 1633c. Table showing separate ICP-MS runs for REE in NIST SRM 1633c, from two different laboratories, both using a sinter digestion procedure. Results obtained are similar in each case to available certified, reference, and informational values. Based on the values alone, it is not possible to determine which is the better analysis.

5.2-7 Chondrite Normalization. Chondrite normalization shows a smooth pattern for REE data subject to the Oddo-Harkins effect.

5.2-8 Data Comparison using Chondrite Normalization. Comparison of REE data from slide 5.2-6, using chondrite normalization. Data from Lab 1 give a smooth pattern whereas data from Lab 2 have a kinked pattern in Er and Yb, suggestive of analytical problems for the heavy REE.

5.2-9 Chondrite Normalization. Comparison of chondrite normalization approaches presented by Korotev (2009). Korotev suggests an approach using Anders and Grevesse (1989)  $\times 1.36$  to give Sm = 0.200 ppm. That approach has been adopted in this short course.

5.2-10 ICP-MS Isobaric Interferences. Summary slide showing potential isobaric interferences affecting trace element analysis by ICP-MS and ways to avoid, correct for, or eliminate them (Li and others, 2014).

5.2-11 IUPAC Periodic Table of the Isotopes. Table of the isotopes showing isotopic variation for arsenic and selenium discussed in the next slide.

5.2-12 Isotopes of Arsenic and Selenium. Table showing isotopes of arsenic and selenium needed to correct for isobaric interferences at  $^{75}\text{As}$ , the only isotope of arsenic, in ICP-MS determination of arsenic.

5.2-13 Example of Interference Correction for  $^{75}\text{As}$ . Example showing isobaric interferences for  $^{75}\text{As}$  and procedure to correct for these interferences.

5.2-14 Other Common Problems with ICP-MS. Summary slide describing calibration and carryover problems inherent in ICP-MS analysis.

5.2-15 Internal Checks on Data Quality. Summary slide listing internal checks on data quality in bulk analysis. Checks include running standards, blanks, and replicates, and, for major elements, summing to near 100 percent. For REE analyses, data should define a smooth pattern on a chondrite-normalized plot. If the checks are unsatisfactory, rerun the sample.

5.2-16 Run it Over Again. Example comparing DMA mercury analyses for the same samples run in USGS laboratories in Denver, Colo., and Reston, Va. Overall, results show good agreement between the two laboratories, with a few problem samples. Rerunning the problem samples resulted in convergence of initially disparate results for the two laboratories. Results from Kolker and others (2014).

5.2-17 Summary—Topic 2: Laboratory Quality Assurance.

5.2-18 References—Topic 2: Laboratory Quality Assurance.

### 5.3 Introduction to Compositional Data Analysis

5.3-1 Title Slide Session 5, Topic 3: Introduction to Compositional Data Analysis.

5.3-2 Compositional Data. Common examples where compositional data are constrained to a constant sum, such as values expressed in percent and parts per million, compared to unconstrained results, such as concentrations measured in milligrams per liter, micrograms per cubic meter, or molar concentrations.

5.3-3 Closure. Closure of compositional data means that proportions of a whole must be positive or zero. This sets compositional data apart from variables using absolute scales such as speed, mass, and time.

5.3-4 Correlations. In a given sample set, mathematical covariance of results can lead to misleading or contradictory results.

5.3-5 Subcompositional Incoherence. Correlations of components are compared in case A, a sample that contains moisture, and case B, where the sample material has been dried. The sign of the covariation between components  $X_1$  and  $X_2$  is reversed by drying. This example is similar to a coal proximate analysis expressed on a moisture-containing basis and on a dry basis.

5.3-6 Simplex. This example shows a set of values in D-dimensional noncompositional space where statistical techniques are valid and a set of values in (D-1)-dimensional space (a simplex) where compositional values add to a constant. The triangular D-1 simplex is a section within D-dimensional space.

5.3-7 Warnings. Some common fallacies pertaining to compositional data are given.

5.3-8 Solutions. An approach is given whereby compositional data constrained to a constant sum can be converted for use in unconstrained space where statistical approaches are applicable. This approach includes computing ratios of variables and taking the logarithms of the ratios (log ratios).

5.3-9 Log-Ratio Transformations using Geometric Means. Variable log ratios can be further transformed as shown and expressed as isometric log-ratio transformations (ilr) or centered log-ratio transformations (clr) These transformed variables can then be used to explore controlling dependencies of the dataset.

5.3-10 The Biplot: A Tool for Exploring Dependencies. Example using available software (Thió-Henestrosa and Comas, 2016) to generate plot showing principal components and variable log ratios in unconstrained space. Plot is useful in evaluating controls on data variability. Plot shows that the centered log ratio representing the ash (clr A) exerts the greatest control on the dataset.

5.3-11 Mapping. Log-ratio transformations can also be mapped to show data in a geospatial context. Here the data from the previous slide are mapped. The map also shows that where ash is highest, everything else is lower, as indicated in the previous slide.

5.3-12 Modeling of Compositional Processes. A process analogue is shown where each component has a different rate of change. This process can be applicable in cases where characterizing time series data is appropriate, such as production from different wells.

5.3-13 Summary—Topic 3: Compositional Data Analysis.

5.3-14 References—Topic 3: Compositional Data Analysis.

## Appendix 2. Short Course Slides

Short course material, presented in PDF as a series of PowerPoint slides, is available at <https://doi.org/10.3133/ofr20181145>.

