Chemical analysis and modes of occurrence of selected trace elements in a coal sample from eastern Kentucky coal bed: White Creek Mine, Martin County, Kentucky

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Abstract

This report provides semi-quantitative data on modes of occurrence of 20 elements in a sample collected from an eastern Kentucky coal from the White Creek Mine, Martin County, Kentucky. The data are in support of the project "Prediction of Trace Element Removal from Coal" --a Cooperative Research and Development Agreement (CRADA) with CQ Inc. The purpose of this CRADA is to apply modes of occurrence information to coal cleaning procedures, specifically a low sulfur central Appalachian coal for this study. Techniques used in this study include sequential selective leaching procedures, scanning electron microscopy, X-ray diffraction analysis, and electron microprobe analysis. Selective leaching results indicate that greater than 50 percent of the elements Ca, Cd, Mn, Pb, and Zn are associated with HCl- or ammonium acetate-soluble carbonates, iron oxides, or monosulfides; greater than 40 percent of the Al, Be and Cr are associated with HF-soluble silicates; greater than 40 percent of the Co, Cu, Ni, Se, Sb, Th and U are associated with HCl, HF and HNO_3 acid-insoluble phases and/or organic matter; and greater than 50 percent of the As and Hg is associated with HNO_3-soluble pyrite. Due to the high clay content and relatively low pyrite content in this sample, 35 percent of the Fe was associated with the HF-soluble silicates while only 25 percent was associated with the pyrite. Thirty-five percent of the Ba is associated with the HF-soluble silicates whereas 40 percent of the Ba was associated with HCl-soluble (and ammonium acetate-soluble) barite. Thirty-five percent of the Mo was associated with the HF soluble clays. The major minerals present in this sample are quartz, kaolinite, and illite, as indicated by scanning electron microscopy and confirmed by X-ray diffraction analysis. The chalcophile elements As, Se, Cu, Ni, Zn, and Cd in most pyrite grains are at or below the detection limit of about 100-200 ppm based on electron microprobe analysis, but two pyrite grains locally showed As concentrations of greater than one weight percent. One of these grains also had over a weight percent of each of the following elements: Co, Cu, Ni, and Se. Lead and Cu were also higher in this grain than in any other grains measured.

The results of this project should aid in the development of models for predicting the response of potentially toxic trace elements in commercial coal cleaning procedures.

Introduction

The United States Geological Survey (USGS)[1] is collaborating with CQ Inc. a coal research laboratory in Homer City Pennsylvania, to better understand how modes of occurrence of elements in coal affect partitioning of elements during physical coal cleaning. Previous work (Raleigh and others, 1998; Palmer and others, 1997, 1998, 2000) describes semi-quantitative methods for determining modes of occurrence of elements in coal or coal-cleaning separates. The eventual goal of this collaborative project is to develop models for predicting the removal efficiency of potentially toxic trace elements from a variety of coals from different US coal basins during commercial coal cleaning operations. Herein, we report on the modes of occurrence of 20 elements in a sample collected from an eastern Kentucky coal bed from the Addington Energy Inc

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[1] A complete listing of the many abbreviations, chemical symbols, and mineral names used throughout this paper of the is given in Appendix 1.

(AEI)'s White Creek mine in Martin County, in the central Appalachian Basin. This coal sample is believed to be a run of mine Broaz Seam coal shipped by barge and collected by personnel at Tennessee Valley Authority's Widow's Creek Fossil Plant barge unloading facilities.

The overall goal of this project is to assess the technical and economic potential for using the most promising advanced coal cleaning technologies to reduce emissions of mercury and other hazardous air pollutants (HAPs) when coal is burned. The objectives included: (1) obtaining semi-quantitative information on trace element modes of occurrence in the sample; and (2) assembling the information in a form that can be used by industry to enhance the potential of coal cleaning technologies for reducing hazardous air pollutants (HAPs). Previous work funded by EPRI and DOE concentrated on understanding the effectiveness of removing Hg and other HAPs-forming elements from bituminous coal feedstocks that are currently being cleaned (Northern Appalachian Basin, the Southern Appalachian basin, the Illinois basin) (Palmer and others, 1997a) and the Powder River basin subbituminous coal that is not currently being cleaned. These previous studies included samples of feed stock coal, coal from various coal-cleaning streams and simulated cleaned coal.. This previous work indicated that the success of using physical coal cleaning techniques to reduce the potential HAP's emissions was highly dependent on: 1) understanding the modes of occurrence of trace elements in coal including what minerals are present and what trace elements are associated with these minerals and applying appropriate cleaning procedures; 2) liberatation of discrete particles of trace element-bearing mineral matter including mineral size and associations; and 3) type, amount, and level of intensity of physical treatment . This paper provides data on the modes of occurrence of 20 elements, including all those considered as potential HAPs. This data will be used to develop models to determine the most effective coal cleaning procedures for specific coals.

Methods

Sequential Leaching

The sequential selective leaching procedure used in this study is similar to that described by Palmer and others (1993), which was modified from that of Finkelman and others (1990). Duplicate 5 g samples were sequentially leached with 35 ml each of 1N ammonium acetate (CH_3COONH_4), 3N hydrochloric acid (HCl), concentrated hydrofluoric acid (HF; 48 percent), and 2N (1:7) nitric acid (HNO_3). Ammonium acetate removes elements bonded onto exchangeable sites, water-soluble compounds, and some carbonates. HCl dissolves carbonates, iron oxides, monosulfides and some chelated organic compounds. HF solublizes silicates, and nitric acid dissolves disulfides, especially pyrite. For the first three leaching stages (CH_3COONH_4, HCl, and HF), each sample was shaken in conical bottom 50 ml polypropylene tubes for 18 hours on a Burrell[2] wrist action shaker. Because of gas formation during some of the leaching steps, it is necessary to enclose each tube in double polyethylene bags each

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[2] Use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U. S. Geological Survey.

closed with plastic coated wire straps. The bags allow gas to escape, but prevent the release of liquid. The HNO_3 leach was carried out in an Erlenmeyer flask similar to the method for the determination of pyritic sulfur (ASTM, 2001a). We have found that this "flask method" is more effective at dissolving pyrite than shaking in tubes, because the partially demineralized coal resulting from the first three leaches has a very low density and forms a protective layer of sediment above the pyrite concentrated at the bottom of the conical tubes. Approximately 0.5 g of residual solid was removed from each tube for instrumental neutron activation analysis (INAA) and cold vapor atomic absorption analysis (CVAA) for mercury. Leachate solutions were saved for analyzed by inductively coupled argon plasma-atomic emission spectrometry (ICP-AES) and inductively coupled argon plasma-mass spectrometry (ICP-MS).

Scanning Electron Microscope (SEM) and Microprobe Analysis

1 - Coal pellet casting and polishing

The pellet formation procedure follows the ASTM D2797-85 (ASTM, 2001b) technique for anthracite and bituminous coal, as modified by Pontolillo and Stanton (1994). The casting procedure impregnates, under pressure, approximately 7-8 g of 20 (850μm) or 60 mesh (250μm) crushed sample with Armstrong C4 epoxy. The resultant mold is cured overnight at 60E C. The 2.5 cm diameter circular pellet block is ground and polished using ASTM D2797-85 procedure (ASTM, 2001b) as modified by Pontolillo and Stanton (1994). The epoxy-coal pellet is first ground with a 15-μm -diamond platen and then 600-grit SiC paper until flat and smooth. Rough polishing is done with 1 μm alumina and final polishing is completed with 0.06-μm-colloidal silica.

2 - SEM analysis.

A JEOL-840 scanning electron microscope (SEM) equipped with a Princeton Gamma-Tech. energy-dispersive X-ray analytical system (EDX) and/or an ETEC Autoscan SEM with a Kevex EDX, was used for SEM examination of the coal. Mineral identifications inferred from morphology, and major-element composition of grains. Both secondary electron imaging (SEI) and backscattered electron imaging (BSE) modes were used in coal characterization. The BSE mode is especially sensitive to variation in mean atomic number and is useful for determining within-grain compositional variation. By optimizing the BSE image, the presence of trace phases containing elements with high-atomic number can be revealed. Samples were scanned initially to obtain an overall view of the phases present. This was followed by a series of overlapping traverses in which the relative abundance of the phases was assessed. EDX analysis provides information on elements having concentrations at roughly the tenth-of-percent level or greater. Typically, operating conditions for SEM analysis are: accelerating potential of 10-30 kV, magnifications of ~50->10,000 times and working distances ranging from 15 to 20 mm (ETEC Autoscan) and 15, 25, or 39 mm (JEOL-840). The advantage of the conventional SEM methods over automated, computer-controlled SEM is that the operator can select appropriate phases for analysis by EDX and can apply instantaneous interpretation of the textural relations of the phases being analyzed.

3 - Electron microprobe analysis.

A fully-automated, 5 spectrometer microprobe instrument (JEOL JXA 8900R Superprobe) was used to quantitatively determine element concentrations in pyrite by the wavelength-dispersive technique. In our preliminary microprobe analysis of pyrite the following elements were measured: Fe, S, As, Ni, Cu, Zn, Se, and Co. Natural and synthetic standards were used. A beam current used of 3.0 x10^{-8} amps and a voltage of 20 KeV was used in the determinations. The probe diameter was set as a focused beam; the actual working diameter was about 3 micrometers. In this study, the minimum detection limit for microprobe analysis of trace elements was about 100 ppm, using counting times of 60 seconds for peak and 30 seconds for upper and lower background. Counting statistics have a large uncertainty as the detection limit is approached. For Co (only), the detection limit is about 700 ppm (0.07 weight percent) due to an interference with Fe giving a constant background in pyrite of 700-800 ppm. Results for Co shown in Appendix 2 are background-corrected. Microprobe data are shown in Appendix 2.

X-Ray Diffraction Analysis

To obtain semi-quantitative information on the minerals present in the coal a split of the sample was low-temperature (<200° C) ashed. Duplicate samples of low-temperature ash were pressed into pellets and analyzed using an automated X-ray diffractometer. Diffraction of Cu Kα X-rays was measured over the interval from 4° to 60° 2θ. Counts were collected for 0.5 seconds per step (0.02 degrees). The data were processed using a computer program for semi-quantitative mineral analysis by X-ray diffraction (Hosterman and Dulong, 1985).

Results and Discussion

SEM and Microprobe Analysis

1- SEM Analysis of Raw Coal

SEM analyses show that the major minerals in the eastern Kentucky coal (kaolinite, illite, and quartz) were generally present as large quartz/clay intergrowths in some cases more than 100 microns in their largest dimension (Table 1). Subhedral and frambodial pyrite, including some particles larger than 10 microns and calcite were present, but not very abundant. A crandelite group mineral (goyazite?; see appendix 1) was commonly observed, but Fe oxide and barite rare. In addition, rutile or anatase (grains analyzed as Ti only) was found in the raw coal as micron to several micron-sized particles commonly in quartz/clay intergrowths.

2- SEM Analysis of Leached Residue

Two hundred and six (206) mineral grains were analyzed by SEM. These grains ranged in size from less than a micron to 10 microns in the leached residue (material remaining after sequential leaching). In order to estimate the percent of residual minerals present, the area of the mineral grains were estimated by assuming either a rectangular or circular shape. This analysis showed that the composition of 85 percent of the mineral grains analyzed, representing about two thirds of the total area of these mineral grains, were TiO_2. Figure 1 shows an area of unusually high concentration of mineral matter in one of the leached residue pellets. Except for two zircon grains, all particles on figure 1 b were TiO_2 grains. Most of these were elongated grains, typical of rutile. Both rutile and zircon are resistant tot the leaching process. Generally, as can be seen in figure 1a there is very little mineral matter present in the residual sample.

Four percent of the particles examined, ranging in size from sub-micron to 10 microns (representing 26 percent of the area) were pyrite completely encapsulated by organic material. In addition, 3 percent of the particles found in coal after leaching were chalcopyrite but all these particles were less than 2 microns in size and represented only 2 percent of the total area. Trace amounts of illite, kaolinite, quartz and goyazite were also found to be completely encapsulated in the coal matrix representing the remaining 8 percent of the particles and 5 percent of the total mineral area. Except goyazite, these minerals are less dense than pyrite and rutile so that they represent even a smaller percentage of the total mineral matter by weight than their area suggests.

3 -Microprobe Data

Microprobe data for 26 pyrite grains in coal sample are given in Appendix 2. Two to six different points on each grain were analyzed. The average concentration of Fe was 47 ± 1.4 weight percent and the average was 53 ± 1.2 weight percent for S; results expressed on an atomic basis give acceptable soichiometry for FeS_2. Cd is below the detection limit for all analyses and is not shown in Appendix 2. Zn is consistently less than 0.02 weight percent for all analyses. The other six elements (As, Co, Cu, Ni, Pb and Se) show more variability but in general are less than 0.1 weight percent.

For two pyrite grains, As concentrations for one or more points were one weight percent or higher. Grain 16 (Appendix 2) was significantly enriched in several trace elements. In addition, As, Ni, Se, and Co were all found to have concentrations of one weight percent or more in spot analyses. Pb concentrations were as high as 0.48 percent and Cu concentrations were 0.15-0.18 weight percent. Concentration maps of this grain as well as the backscattered electron image are shown in figure 2. In backscatter mode (fig. 2d) the grain looks like a half of a framboid and is clearly zoned. This zoning is also evident in the elemental maps generated for Se (fig. 2a), Ni (fig. 2b) and As (fig. 2c) although the areas of highest concentration are different for each element. However, the elemental maps show the entire form of the framboid, indicating that the remaining portion of the framboid lies just below the surface. The weaker backscatter electrons cannot penetrate the surface and therefore do not produce an image. The stronger x-rays used to generate the elemental maps penetrate the surface but are attenuated producing an image with an apparent lower concentration for each of the elements in the upper right hand corner of figures 2a-c where the backscatter image of the framboid is missing.

Table 1. Phases found in the coal sample and the leached residue using SEM analysis

Phases	Raw Coal -60 mesh	Residual - 60 mesh
Quartz	M	m
Illite	M	m
Kaolinite	M	m
Fe oxide phase (hematite?)	m	
Pyrite	m	m
Chalcopyrite		m
Calcite	m	
Barite	m	
Ti oxide phase (rutile?)	m	M
Zircon		m
Crandellite	m	m

M = Major phase (estimated to be greater than 10 percent of mineral grains present in the sample)
m = Minor or trace phase (estimated to be less than 10 percent of the mineral grains present in the sample)
blank =none detected

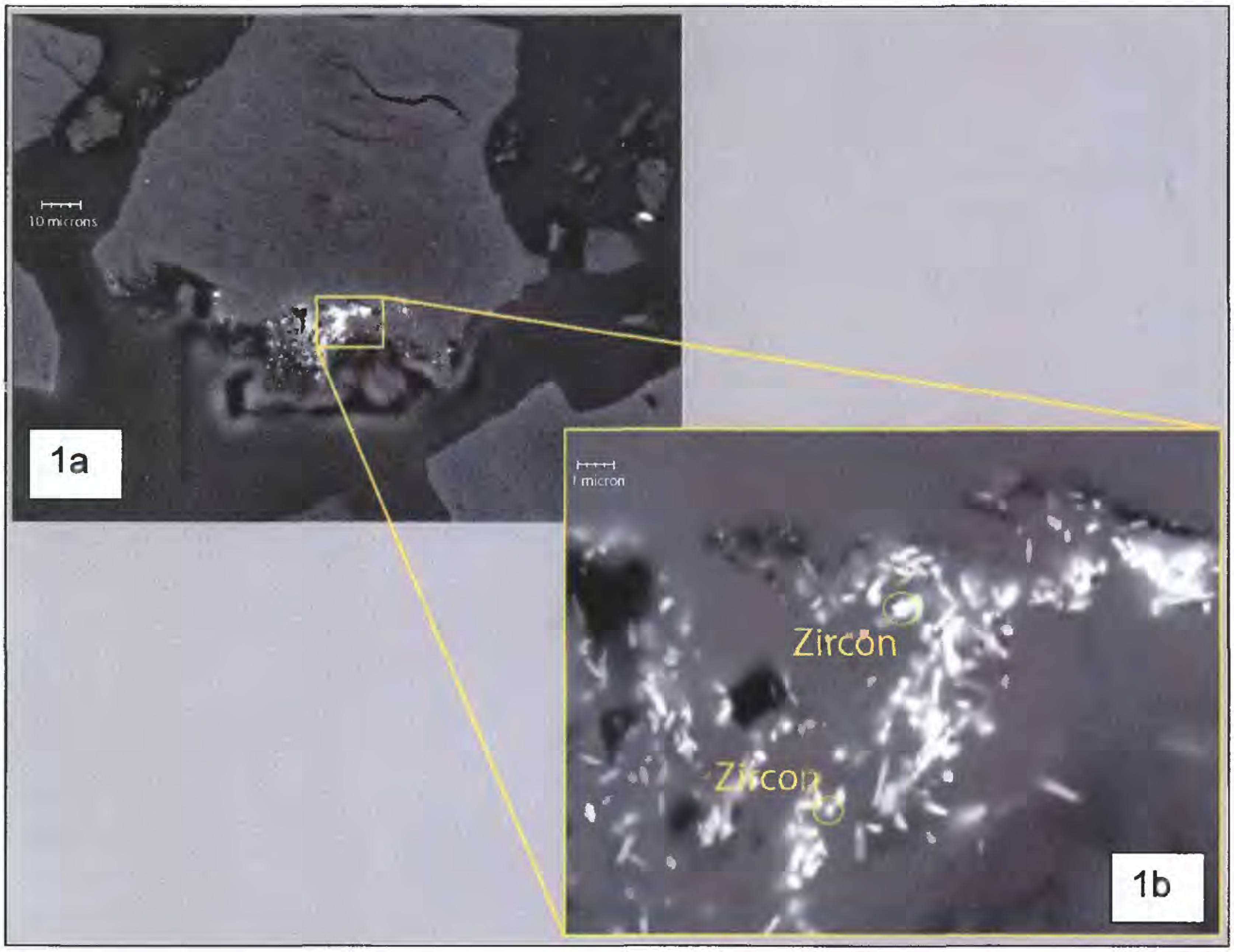

Figure 1. a) SEM micrograph of a coal particle with an unusually high concentration of sub-mircon mineral grains in a relatively small area. b) shows that most particles are elongated rutile (TiO_2) grains. The rounded particles are either rutile grains in cross section or anatase (also TiO_2 identified by XRD, Table 2) except for two rounded particles labeled as zircon.

Grain 22 (Appendix 2) also showed high As (1.72 weight percent) for one electron mcroprobe analysis point whereas a second point showed an As concentration of only 0.09 weight percent. For this grain, As showed a significant enrichment, so only its elemental map and the corresponding backscattered electron image are shown in figure 3. One area of the grain is clearly high in arsenic whereas the other areas are much lower in concentration. This As-rich zonation appears on the backscattered electron image as a brighter patch in the lower right portion of the grain.

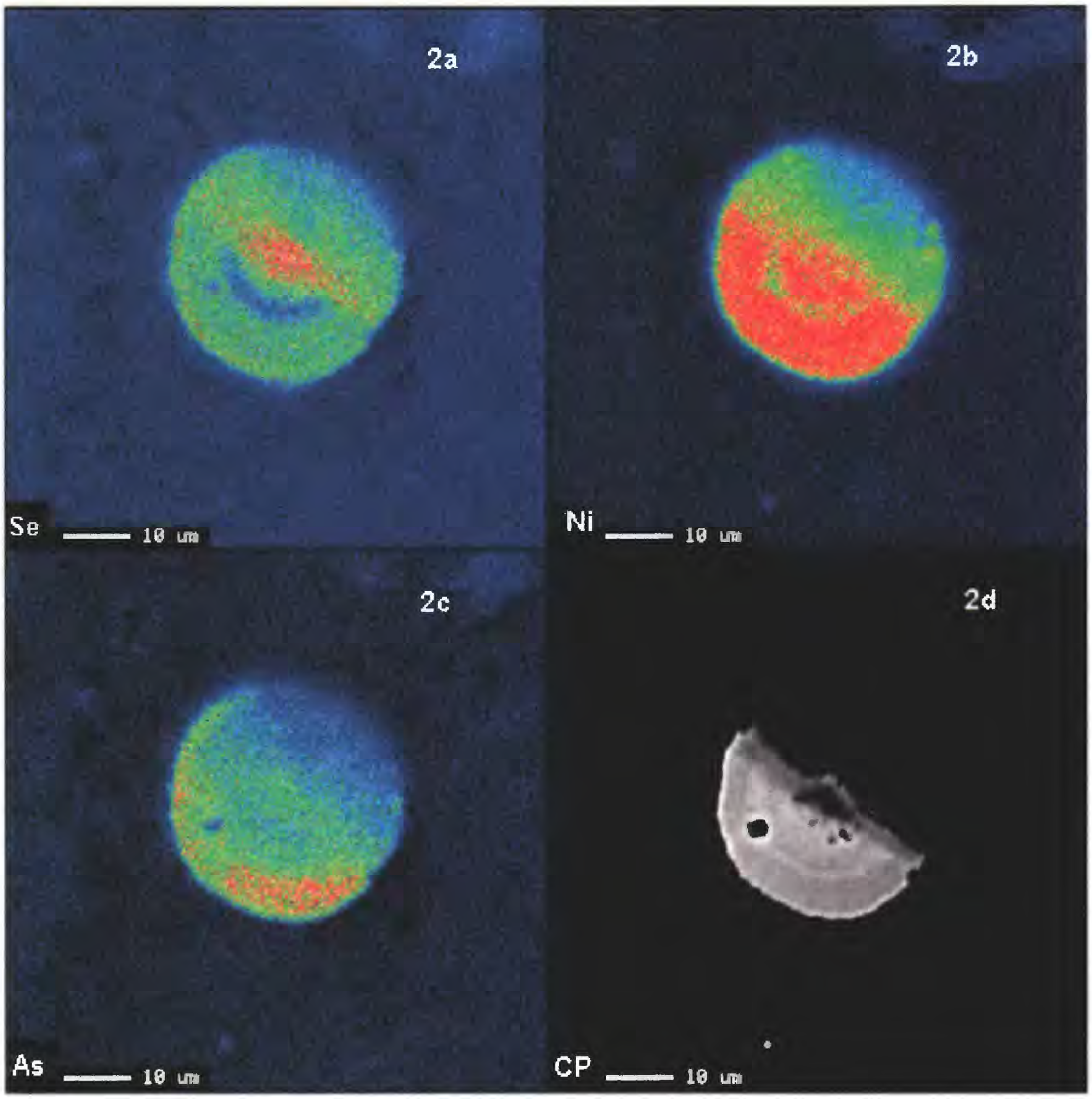

Figure 2. Electron microprobe wavelength-dispersive elemental maps for Se, Ni and As, and backscattered electron image (CP) for a framboidal pyrite in CQ sample CQ-352 (Grain 16 in Appendix 2). Maps show differing regions of enrichment for each of these elements. Scale bar is 10 micrometers; width of field of view is 80 micrometers. Red to orange indicates relatively high concentrations. Yellow to green indicate intermediate concentrations and blue to black indicate low concentrations for figures 2a through 2c. For the backscattered electron image (figure 2d) areas of higher mean atomic number are brighter.

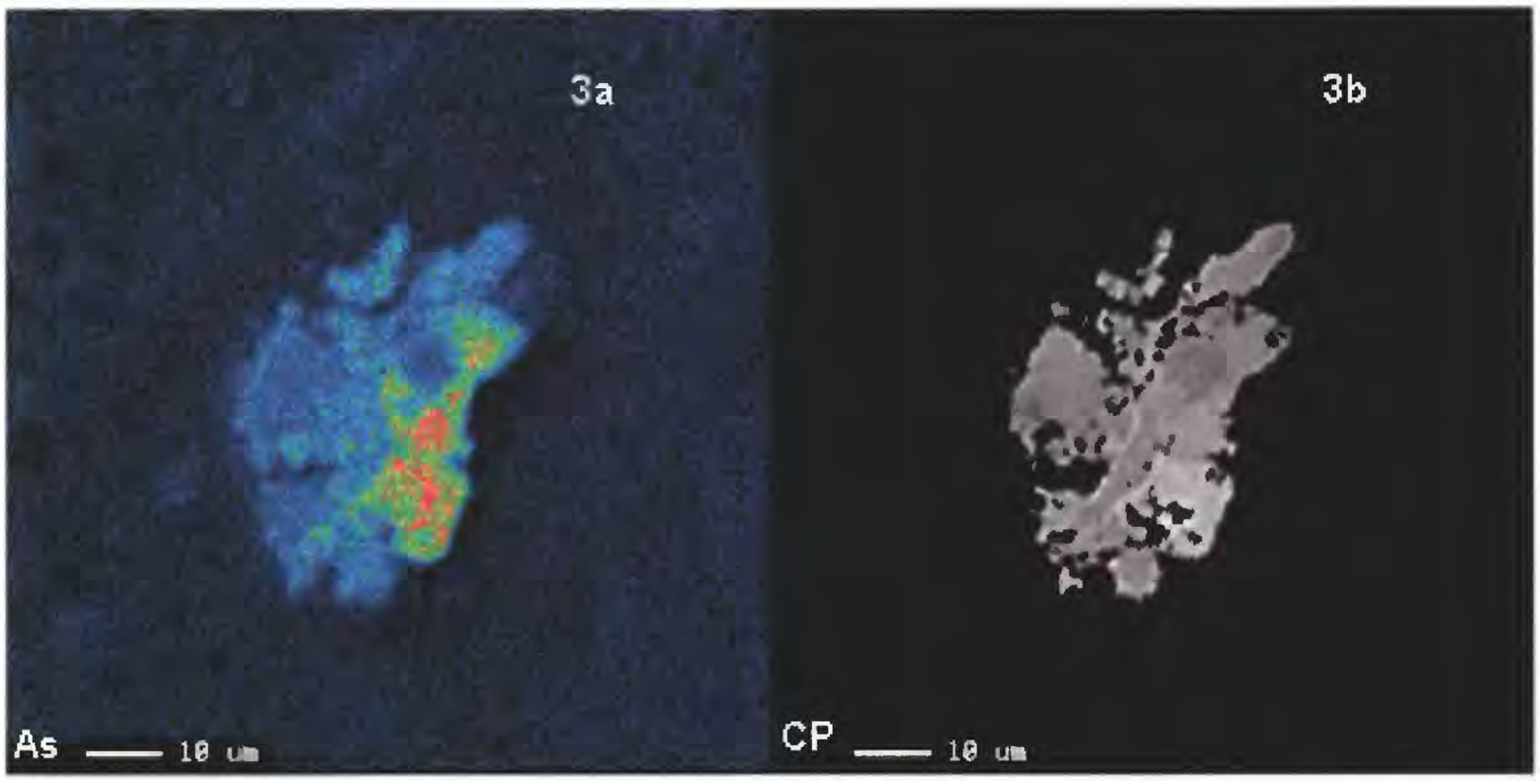

Figure 3. Electron microprobe wavelength-dispersive elemental map for As (3a), and backscattered electron image (CP; 3b) for a subhedral pyrite in CQ sample CQ-352 (Grain 22 in Appendix 2). Arsenic-rich zone corresponds to brighter areas of the backscattered image. Scale bar is 10 micrometers; width of field of view is 100 micrometers.

Semi-Quantitative Mineralogy of Low-Temperature Ash

Table 2 gives semi-quantitative estimates of mineralogy based on X-ray diffraction analysis (XRD) of low-temperature ash (LTA) of duplicate samples of the eastern Kentucky coal sample. About 55 to 60 percent of each LTA sample consists of kaolinite, 15-20 percent of each sample is composed of illite and 15 percent, quartz. Bassanite ($CaSO_4 \cdot ½H_2O$), likely an artifact of the ashing process, constitutes ≤ 5 percent of the LTA and may be formed from calcite (which was detected by SEM but not by XRD) reacting with organic sulfur in the sample. Siderite, hematite, sphalerite, and pyrite, were detected as trace phases (<5 percent) by XRD. Of these minerals, sphalerite, pyrite and an iron oxide (hematite?) were also detected by SEM. Both rutile and anatase (TiO_2) were detected by XRD. Anatase was only detected in one of the duplicate samples, but was detected at the 5 to 10 percent level, whereas rutile was found to be less than 5 percent in both of the duplicate samples. The relatively high percentage of anatase found in one duplicate sample and the non detection of anatase in the other duplicate sample suggests that anatase is not homogeneously distributed in the original coal sample.

Table 2. Semi-quantitative determination of minerals by X-ray diffraction (XRD) of low-temperature ash (LTA; values in weight percent on an LTA basis)

Sample	KOL	ILL	QTZ	PY	SID	RUT	ANA	HEM	SPH	BAS	BOE	CHL	FLD	APA
Duplicate analysis														
CQ353A1	60	20	15	≤5	≤ 5	≤ 5		≤ 5	≤ 5	≤ 5		?		≤ 5
CQ352B2	55	15	15	≤ 5	≤ 5	≤ 5	>5<10	≤ 5		≤ 5	≤ 5	?	≤ 5	≤ 5

QTZ = quartz; KOL = kaolinite; ILL = illite; BAS = bassanite; SID = siderite; ANA= anatase; HEM = hematite; PY = pyrite; SPH = sphalerite;FLD= feldsbar; CHL= chlorite; BOE= boehmite. ? =Trace constituent (≤ 5 %) that could not be resolved with certainty. Blank entry = not detected. Weight percentages listed are on a low-temperature ash basis. Frank T. Dulong, analyst.

Elemental Analysis— Quality Control

In addition to the eastern Kentucky coal sample, CQ, Inc. submitted five blind standards for quality control purposes. The Eastern Kentucky coal was chemically analyzed by multiple techniques. Concentrations of 30 elements were determined by INAA, using techniques described by Palmer (1997) on duplicate sample splits. Results were also obtained by ICP-AES (sinter and acid dissolution procedures; Briggs, 1997) ICP-MS (Meier, 1997), hydride generation AA (Se), cold vapor AA (Hg; O'Leary, 1997) and ion chromatography (IC; Gent and Wilson, 1985) on triplicate sample splits at the USGS laboratories in Denver, Colorado. Table 3 shows the average results for 53 elements in the Eastern Kentucky coal sample.

The elemental concentrations of a series of 5 "blind" samples were submitted by CQ, Inc. to various laboratories to determine the comparability of data among laboratories. These samples were determined only by INAA because the limited quantity of sample provided did not allow for our standard ICP-AES and ICP-MS analysis. The first two samples, labeled CQO11202 and CQO111208 appear to be duplicates. There was no significant difference between the samples for any of the 30 elements determined by INAA. The next two samples CQO111211 and CQO111214 are probably different splits of the same sample. The only element that differs from the first two samples is Br. The average concentration of Br was determined to be 54.9 ±1.3 ppm for CQO11202 and 54.6±1.3 ppm for CQO11208 compared to 21.1±0.53 for CQO111211 and 21.0±0.53 for CQO111214. All of these samples appear to be splits of the eastern Kentucky coal sample analyzed in this study. The Br concentration in the sample used for this study was 21.0±0.53: the same as CQO111211 and CQO11214. The final blind sample CQO111218 is significantly different than the other four control samples. However, it is not significantly different than the 1632C control sample that was run with all of the samples in this study. Certified, recommended, and informational values are given in Appendix 4-2 for each reference sample.

Table 3. Average Values for 53 Elements in the Eastern Kentucky coal sample (CQ352)

Variables:	Hg	As	Cr	Pb	Co	Ni	Mn	Ba
units:	Ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
CQ352	0.15	6.4	22	9.2	9.8	17	14	130

Variables:	Be	Cd	Cu	Mo	Zn	Sb	Th	U
units:	Ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
CQ352	2.0	0.058	17	1.8	18	0.63	3.7	1.3

Variables:	Al	Ca	Fe	Na	Mg	Si	K	Ti
units:	wt. %	Wt. %	wt. %	wt. %	Wt. %	wt. %	wt. %	Wt. %
CQ352	2.4	0.095	0.48	0.023	0.080	3.8	0.31	0.12

Variables:	Li	B	P	Cl	Sc	V	Ga	Ge
units:	Ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
CQ352	31	43	76	610	5.2	35	5.9	2.1

Variables:	Se	Br	Rb	Sr	Y	Zr	Sn	Cs
units:	Ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
CQ352	6.2	21	20	71	9.3	31	1.5	1.4

Variables:	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
units:	Ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
CQ352	14	26	< 5	2.8	0.52	0.075	0.12	0.04

Variables:	Hf	Ta	W	Au	Tl
units:	Ppm	ppm	ppm	ppm	ppm
CQ352	1.1	0.32	0.86	< 0.002	0.07

wt.=weight

These values typically represent the average of values determined by all techniques for a given element. Individual determinations, average values for each technique, and the overall values (which may be weighted averages depending on the reliability of the different techniques for a given element) for each sample are given in Appendix 3, which is color-coded to show the type of analysis for each determination.

Leaching Experiments

Leachate solutions were analyzed by ICP-AES and ICP-MS, and solid residues were analyzed by CVAA (Hg) and INAA. Chemical data for the leachates and the solid residues have been processed to derive the mean percentages of each element leached by each of the four solvents. The calculated percentages were then used as an indirect estimate of the mode of occurrence of individual trace elements in the coal sample. The analytical errors were estimated to be ± 2 to ± 25 percent for these data, but errors are generally within ±5 percent, absolute.

Results for the Kentucky coal sample were determined in duplicate leaching experiments. Reproducibility is generally within the expected analytical errors, and is generally better within a given technique than among techniques. Figure 4 shows an example of the duplicate analyses of Co, determined by INAA, ICP-AES, and ICP-MS. Cobalt was not determined by ICP-MS on the whole coal fractions, therefore, the percent leached by ICP-MS is compared to ICP-AES whole coal, which might explain some of the differences of ICP-AES and ICP-MS. The results for each leached fraction agree within 10 percent absolute, but the ICP-MS is consistently higher than the other two techniques. The total amount leached is about 15 percent higher (or the unleached Co is 15 percent lower) as determined by ICP-MS. By averaging the various data for the duplicate individual analysis and rounding to the nearest 5, percent best values for each technique are determined. These results are then combined into a single stacked bar by further averaging, giving more weight to more accurate numbers and rounding to the nearest 5 percent to give the "overall best values".

Figure 5 shows the overall values for Ca, Mn, Cd, Zn, Pb, Cu and Ba. These results are grouped together because the combined amounts of each of these elements leached by ammonium acetate and HCl are greater than the amount leached by any other solvent. Palmer and others, (1998) have shown that calcite (found in this sample by SEM; table 1) is partially soluble in ammonium acetate as well as being soluble in HCl. They also suggest that other carbonates, especially siderite, may be soluble in ammonium acetate. Mn and Ca have been shown to be primarily associated with carbonates (Palmer and others, 1998). Mn is also associated with silicates, particularly clays, as 30 percent of the Mn is HF leachable. These results are consistent with our previous leaching experiments (Palmer and others, 1998).

Forty to fifty percent of the Cd, Zn and Pb are leached by HCl with small amounts of Cd and Zn leached by ammonium acetate. Generally, these elements are associated with the monosulfides (galena and sphalerite). We did not identify either of these minerals by SEM in this sample. However, the concentrations of Cd, Zn and Pb are very low in this sample. Twenty to twenty-five percent of these elements are leached by HNO_3 suggesting that these elements also have an association with pyrite. Thirty percent of the Zn was leached by HF; consistent with Zn concentrations in illite and kaolinite found in coal. (Palmer and Lyons, 1996).

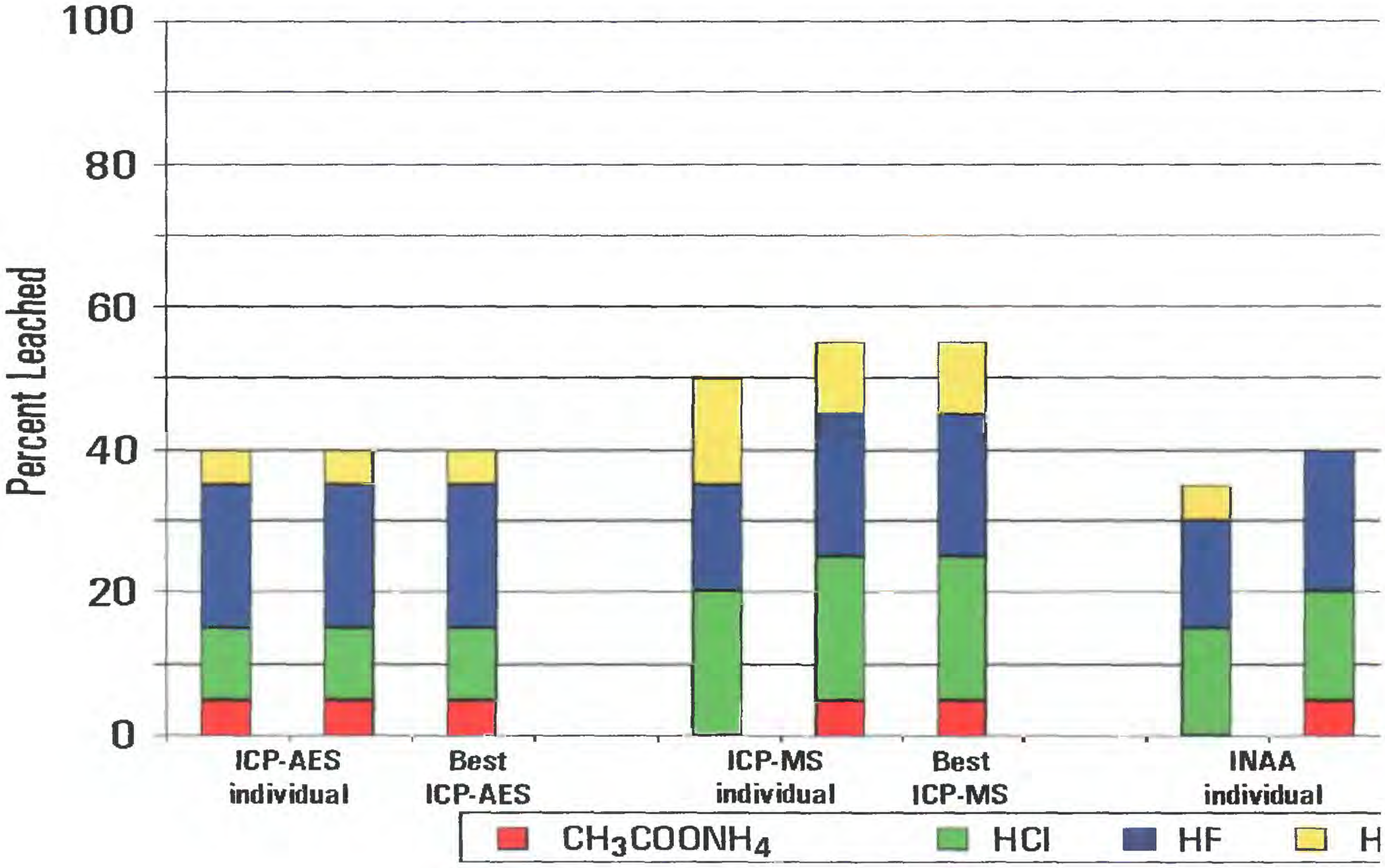

Figure 4. Percent cobalt (rounded to ± 5 percent) leached by selected solvents for two "individual" sample splits and "Best" (average values rounded to ± 5 percent) for ICP-AES,ICP-MS and INAA as well as "Best Overall" (weighted average of all values for all techniques rounded to ± 5 percent.)

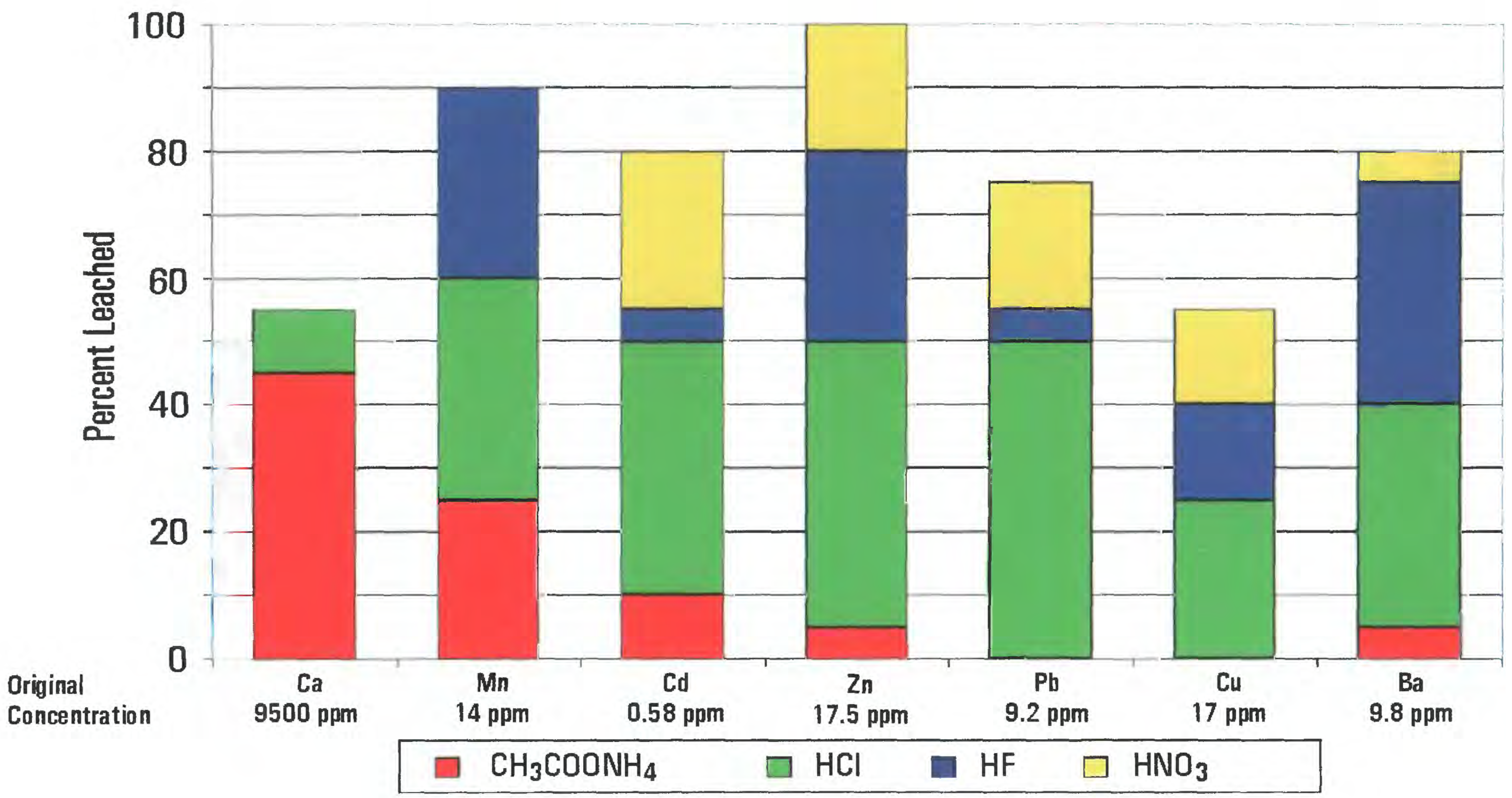

Figure 5. Leaching results for elements leached primarily with ammonium acetate and HCl.

Barite ($BaSO_4$) was detected with the SEM. Barite is only partially soluble with HCl, and at most, only about 20 percent of the total Ba dissolved in the HCl could be due to barite, according to solubility data given by Linke (1958). The remaining HCl-leachable Ba could be due to Ba in carbonate minerals. The ammonium acetate-soluble Ba also suggests that some Ba may be in carbonate minerals. Thirty-five percent of the barium is associated with the silicates (HF soluble), most likely clays (Palmer and others, 1996) and twenty percent is unleached which may be insoluble barite or organically associated Ba.

The modes of occurrence of Cu are less certain than other elements in this group. Fifteen percent of the Cu is associated with pyrite and and an equal percentage associated with the silicates. Twenty-five percent of the copper is HCl soluble. This copper could exist as copper sulfate minerals many of which are HCl soluble, or copper oxides that are also HCl soluble.

HF leached a greater percentage of the elements shown in figure 6 (Al, Be Cr, Sb, U, Mo, and Co) than any other single solvent, suggesting a silicate association. However, except for Al, 35 to 55 percent of these elements remain unleached suggesting an organic association. In addition, all of these elements (except Al) have small, but significant HCl-soluble fractions. In rocks, Be is generally associated with Al minerals (Goldschmidt, 1954) such as boehmite found to be present in trace amounts by XRD. In previous leaching experiments, Palmer and others, (1998) found that Be is leached mainly by HF in bituminous coal, with significant organic (unleached) Be, whereas, in lower rank coal some Be is also soluble in HCl with much smaller percentage of organic Be.

In the sample investigated in this study, 50 percent of the Be and 100 percent of the Al is HF soluble. Abundant kaolinite and Illite account for the majority of the Al. The presence of HF-soluble Be indicates significant association with the silicates (probably clays) but the large unleached fraction (45 percent) indicates a significant organic association as well. Palmer and others (2000) suggest that some HCl soluble Be may also be also be organically associated. Data for bituminous coal reported by Palmer and others (1998) show that 20-65 percent of the Be was insoluble and therefore organically-associated, and less than 20 percent of the Be was soluble in HCl. Querol and Heurta (1998) found nearly all of the Be was organically-associated (based on float-sink procedures) even for samples jointly analyzed by their group and the USGS, which were shown by USGS techniques to have significant silicate association. To date the exact modes of occurrence of Be are unresolved.

Forty-five percent of the Cr in each sample is leached by HF and this Cr is probably associated with illite and mixed-layer clays (fig. 6; Palmer and others, 1998). Only 10 percent of the Cr is HCl-soluble and may be associated with Cr oxy-hydroxides (Huffman and others, 1994). Thirty-five percent of the Cr is not leached. Some of this may be organically associated, but some may be present in insoluble trace phases such as chromite.

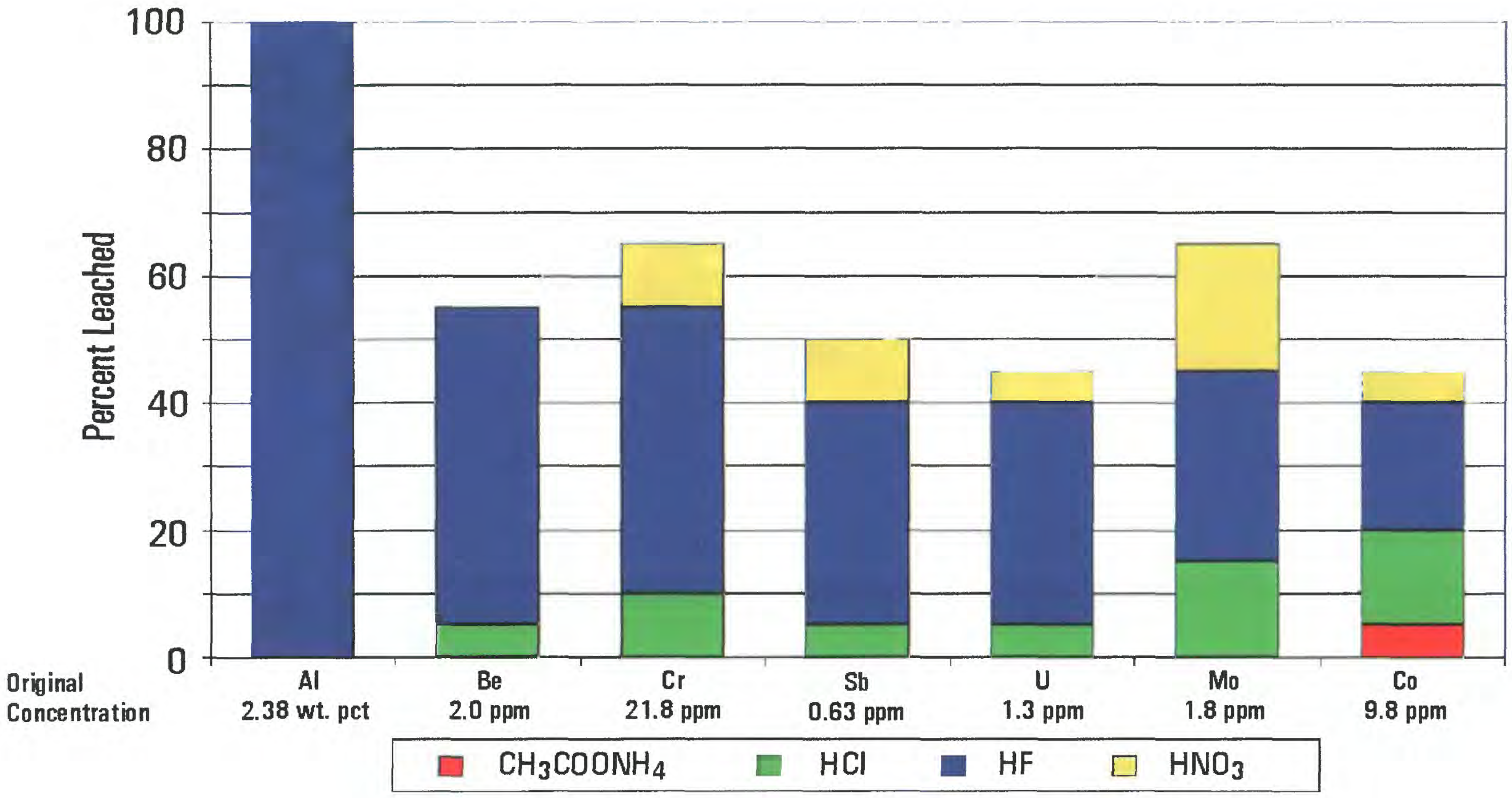

Figure 6. Leaching results for elements leached primarily with HF. Except for Al these elements have significant unleached portions.

Thirty-five percent of the Sb and U in the eastern Kentucky coal sample is leached by HF indicating a silicate association (clay minerals and zircon). Fifty percent of the Sb and 55 percent of the U is unleached, suggesting that it is organically bound. The percentage of HF leached Sb is higher than in bituminous coal studied previously (10-20 percent), but the portion of unleached Sb is remarkably similar to results from previous studies (Palmer and others, 1998). The high percentage of organically-bound U is not surprising considering its uptake into the organic matrix in peat swamps (Zielinski and Meier, 1988), however some of the unleached U may be due to the presence of insoluble zircon in the sample (fig. 1)

Five percent of the Sb and U is HCl-soluble in both samples, perhaps due to Sb and U present in carbonates, iron oxides or chelates. Some of the HCl-soluble U may be in organic chelates increasing the total percentage of organically associated U.

Five percent of the U and 10 percent of the Sb is HNO_3 soluble. The HNO_3 soluble U may indicate dissolution of U-bearing phosphates, which may be exposed following HF dissolution of encapsulating silicates. The concentration of U in pyrite is very low (about 1 ppm; Palmer and others, 1996) and U has been found to be HCl soluble after the HF leach (see discussion of Th below). The total Sb concentration is very low, 0.63 ppm, and it is possible that even with the low pyrite concentration in this sample (less than 1 percent), 10 percent of the Sb could be in the pyrite.

Thirty-five percent of the Mo is in HF-soluble silicates, most likely clay minerals. The 35 percent of unleached Mo indicates a significant organic association. Twenty percent of the Mo has a pyrite association and 15 percent was leached by HCl.

Cobalt appears to have mixed modes of occurrence. Results for Co are included in figure 6 because the 20 percent of the Co leached by HF is greater than that leached by HCl (15 percent) or that leached by either HNO_3 or Ammonium Acetate (5 percent each). The HF soluble Co is associated with the silicates, probably clay minerals, HCl- and ammonium acetate-soluble Co is probably associated with carbonates, Fe-oxides and/or HCl-soluble monosulfides and the nitric acid soluble Co is associated with pyrite. This leaves 55 percent of the Co unleached, presumably associated with organic matter.

At least 25 percent of each element in figure 7 (Fe, As, Hg, Ni, Se, and Th) was leached by nitric acid indicating a pyrite association. However, pyrite is not the primary mode of occurrence of all of these elements. This is partly because the total concentration of pyrite is small (on the order of about 0.25 weight percent). Thirty-five percent of the Fe is leached by HF indicating a silicate association. Table 1 shows that illitic clays are abundant with large quartz/clay intergrowths in some cases over 100 mircons in their longest dimension. Energy dispersive analyses of illitic clay particles by SEM show Fe to be a major component of these clays.

Fe oxides identified in SEM pellets (table 1) account for the 20 percent fraction of the Fe dissolved by HCl. Some of this Fe oxide may be due to the oxidation of pyrite. In addition, about 20 percent of the Fe was unleached. SEM examination of the leached solid residue found eight pyrite grains of the 206 grains analyzed (4 submicron framboids, 2-1 micron framboids, 1 subhedral grain 3X5 micrometers in size and 1-10 micrometer framboid, always completely surrounded by organic material). In addition, four particles of chalcopyrite were found ranging from 0.3 microns to 2 microns in their longest dimension. If one assumes that all of the unleached Ti is due to rutile and or anatase then (based on the area of other unleached minerals and appropriate density corrections) approximately 25 percent of the unleached Fe is due to pyrite or 5 percent of the total Fe in the sample and the amount of Fe due to unleached chalcopyrite and kaolinite is much less than 1 percent of the total Fe.

A larger percentage of the As (50 percent) than Fe (25 percent) is leached by nitric acid, indicating that much of the As is in pyrite. About the same percentage of Arsenic as iron was dissolved by HCl. This is consistent with the observation above that some of the Fe oxide may be due to pyrite oxidation. About 15 percent of the original As is in the silicates as determined by the leaching of As by HF. This is consistent with As found in illite (2.35 ppm) and kaolinite (0.52 ppm) by Palmer and others, (1996). Fifteen percent of the As was unleached suggesting an organic association. However, we calculate that most of the unleached As is due to unleached pyrite or about 5 percent of the total As, so that the remaining unleached (organically associated As) is less than 5 percent.

Seventy percent of the Hg was leached by nitric acid suggesting a strong pyrite association in this coal. Assuming that Hg is homogeneously distributed throughout the pyrite and calculating the amount of unleached pyrite, we calculate that 17 percent of the unleached Hg or about 15 percent of the total Hg is due to unleached pyrite. The remaining 15 percent of the unleached Hg may be organically associated. The total concentration of Hg was 0.15 ppm (table 3).

Equal percentages (25 percent) of Ni were associated with silicates and pyrite. However, as silicates represent a much larger percentage of the whole coal, the average concentration of Ni in the pyrite is much larger than the concentration in the clays. Ten percent of the Ni is HCl-soluble and may be associated with the Fe-oxides, or associated with carbonates. About 5 percent of the Ni is due to unleached pyrite using the assumptions above, and the remaining 35 percent of the Ni is unleached and is likely organically bound.

Twenty-five percent of the Se was nitric acid soluble and therefore associated with pyrite. An additional 5 percent of the Se may be due to unleached pyrite but the remaining 50 percent of the unleached Se is probably organically associated. Ten percent of the Se was leached by HF (silicate associated; probably clays) and by HCl (may be due to oxidized pyrite).

Thirty percent of the Th is leached by HNO_3 suggesting a pyrite association. However, the HNO_3 leachable Th may be from phosphates shielded by silicates, rather than in pyrite, as the samples in this study have very little pyrite, and concentrations of Th in pyrite have been found to be less than 0.5 ppm (Palmer et al. 1996). Thorium-bearing minerals such as monazite are detrital, and

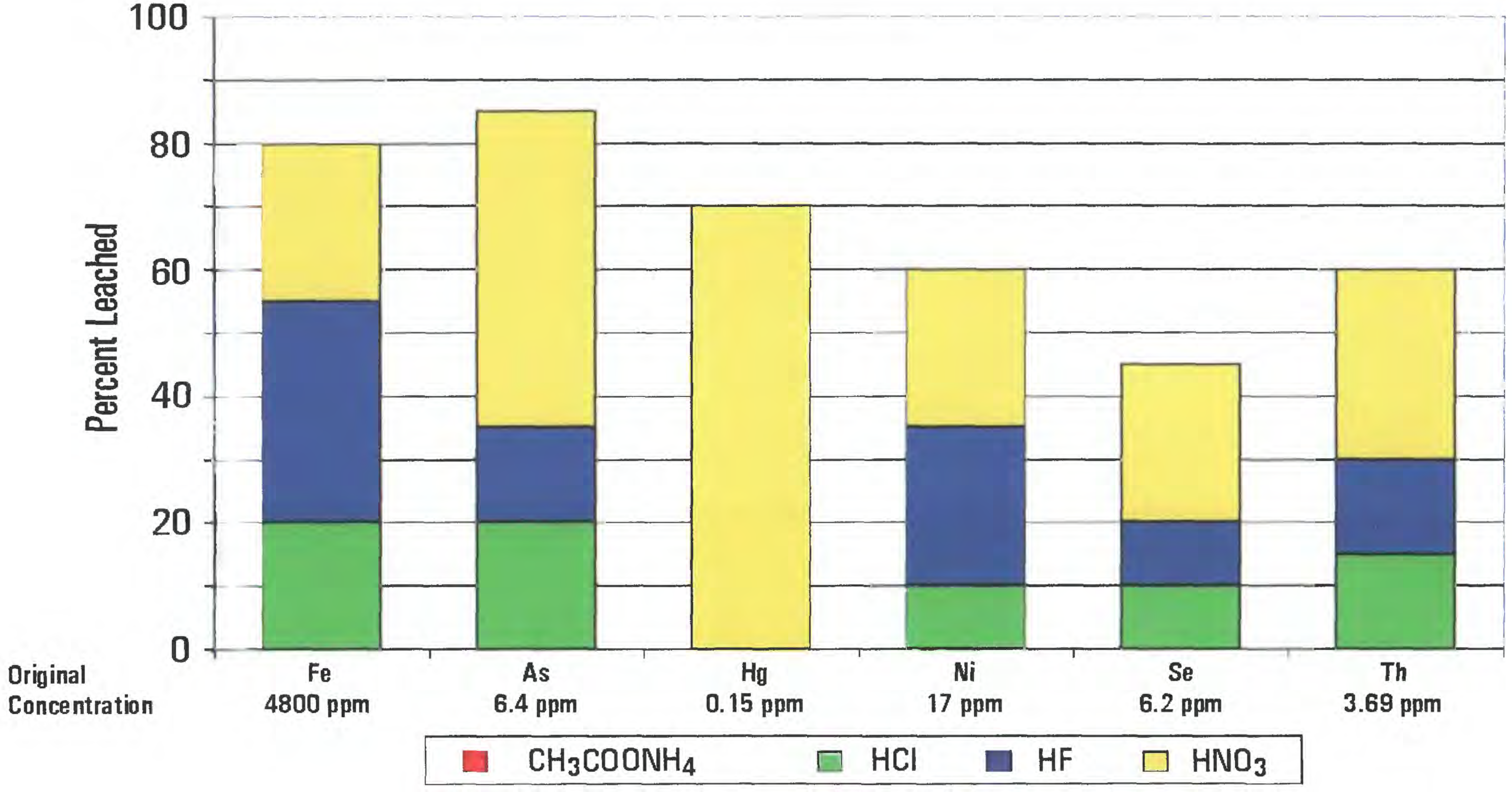

Figure 7. Leaching results for selected elements leached to a significant degree by HNO_3.

are commonly associated with silicates. Experiments on a high pyrite coal (Palmer et al., 1999) show that 40 percent of the Th was removed by HCl, whereas an additional 20 percent was released by a second HCl leach, conducted following the HF step instead of leaching with nitric acid.

The result of the second HCl leaching for this coal is equal to the 20 percent Th leached by nitric acid using the standard leaching protocol, again suggesting that nitric acid leachable Th does not necessarily reside in pyrite. Similar results were found for U, but elements generally associated with pyrite such as As and Hg, were not found to be HCl-soluble after the HF leach. The 15 percent of the Th leached by HF, is probably associated with the clays, although some HF leachable Th may be from zircon (detected by SEM). HCl-soluble Th (15 percent) is probably derived from trace amounts of apatite or monazite. Forty percent of the Th remains unleached. Some of this unleached Th could reside in insoluble or partially soluble minerals such as zircon (table 1), or may be organically bound.

Semi-quantitative Modes of Occurrence

Semi-quantitative assessments of each trace-element's modes of occurrence have been determined by combining all of the information available. This includes leaching results, electron microprobe analysis, scanning electron microscopy, X-ray diffraction analysis and chemical analyses, as well as knowledge of the geochemical characteristics of each element. Table 4 shows the percentage of 20 elements in each of three or four major phases or minerals. In cases where there is supporting direct evidence for a particular mode of occurrence, the host form of the mineral is given, such as As in pyrite, Zn in sphalerite or Cr in illite. In cases where there is strong geochemical evidence and strong indirect evidence, classes of minerals are given, such as sulfides, silicates, oxides or arsenates. In the remaining cases a descriptor is used, such as HCl-soluble.

Conclusions

The sample of eastern Kentucky coal in this study is lower in pyrite than most eastern US bituminous coal. Most of the 14 percent ash yield is due to quartz and clay minerals particularly kaolinite and illite. This leads to higher percentages of elements that are normally chalcophilic associated with the silicates. Greater than 15 percent of 15 of the 20 elements presented in this study were associated with silicates. Only Hg and As were primarily (greater than 50 percent) associated with pyrite.

For 9 of the 20 elements, greater than 40 percent of the original material was unleached. Although some of the unleached material can be accounted for by unleached pyrite, chalcopyrite and other minerals, except for Cu and Ti (not included in this study), the residual minerals represented only a small amount of the unleached element and most of the unleached elements were assumed to be organically associated. Except for Al, all elements had multiple modes of occurrence, although Hg and Ca had only two modes of occurrence.

Table 4. Modes of Occurrence of Trace Elements the Eastern Kentucky Coal Sample

Calcium

	Exchangeable/Carbonates	Organics
CQ352A	55%	45%

Manganese

	Carbonates	Silicates	Organics
CQ352A	60%	30%	10%

Cadmium

	Pyrite	Sphalerite	Silicates	Organics
CQ352A	25%	40%	5%	30%

Zinc

	Pyrite	Sphalerite	Silicates	Organics
CQ352A	20%	50%	30%	5%

Lead

	Pyrite	Galena	Silicates	Organics
CQ352A	20%	50%	5%	25%

Copper

	Chalcopyrite/pyrite	Oxides/Carbonates	Silicates
CQ352A	60%	25%	15%

Barium

	Barite	Silicates	HNO_3- Soluble	Organics
CQ352A	35%	35%	5%	25%

Aluminum

	Silicates
CQ352A	100%

Table 4. Modes of Occurrence of Trace Elements the Eastern Kentucky Coal Sample (Continued).

Beryllium

	Oxides/Hydroxides	Silicates	Organics
CQ352A	5%	50%	45%

Chromium

	Pyrite	Oxyhydroxides	Illite	Organics
CQ352A	10%	10%	45%	35%

Antimony

	HCl-soluble	Pyrite	Silicates	Organics
CQ352A	5%	10%	35%	50%

Uranium

	Oxides/Phosphates/Chelates	Silicates	Organics
CQ352A	10%	35%	55%

Molybdenum

	Oxides	Silicates	Pyrite	Organics
CQ352A	15%	30%	20%	35%

Cobalt

	Pyrite	HCl Soluble	Silicates	Organics
CQ352A	5%	15%	20%	60%

Iron

	Pyrite	Oxides/Carbonates	Silicates	Organics
CQ352A	30%	20%	35%	15%

Arsenic

	Pyrite	Arsenates	Silicates	Organics
CQ352A	55%	20%	15%	10%

Table 4. Modes of Occurrence of Trace Elements the Eastern Kentucky Coal Sample (Continued)

Mercury

	Pyrite	Organic
CQ352A	80%	20%

Nickel

	Sulfides	Ni oxides	Silicates	Organics
CQ352A	25%	10%	65%	40%

Selenium

	Sulfides	HCl-Soluble	Silicates	Organics
CQ352A	25%	10%	10%	55%

Thorium

	Phosphates	Silicates	Insoluble
CQ352A	45%	15%	40%

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Appendix 1. Chemical symbols, mineral names, and abbreviations used in this report

Chemical symbols

Al	aluminum	Ga	Gallium	S	Sulfur
As	arsenic	Ge	Geranium	Sb	antimony
Au	gold	H	Hydrogen	Sc	scandium
B	boron	Hg	Mercury	Se	selenium
Ba	barium	K	Potassium	Si	Silicon
Be	beryllium	La	Lanthanum	Sm	samarium
Br	bromine	Li	Lithium	Sn	Tin
C	carbon	Mg	Magnesium	Sr	strontium
Ca	calcium	Mn	Manganese	Tb	terbium
Cd	cadnium	Mo	Molybdenum	Th	thorium
Ce	cerium	N*	nitrogen	Ti	titanium
Cl	chlorine	Na	Sodium	Tl	thallium
Co	cobalt	Nd	Neodymium	U	uranium
Cr	chromium	Ni	Nickel	V	vanadium
Cs	cesium	O	oxygen	W	tungsten
Cu	copper	P	phosphorus	Y	Yttrium
Eu	europium	Pb	Lead	Zn	Zinc
F	fluorine	Rb	rubidium	Zr	zirconium
Fe	iron				

*differs from abbreviation for **normal** (see below) because it is part of a chemical formula

Major Minerals

Quartz	SiO_2
Kaolinite	$Al_2(Si_2O_{15})(OH)_4$
Illite	A group of mica-clay minerals with the general formula: $(K,H_3O)(Al, Mg, Fe)_2(Si,Al)_4O_{10}[(OH)_2H_2O]$

Trace Minerals

Anatase	TiO_2	Feldspar	XR_4O_8***
Apatite	$Ca_5((F,Cl,OH)(PO_4)_3$	Galena	PbS
Barite	$BaSO_4$	Goyazite	$SrAl_3(PO_4)_2(OH)_5 \cdot H_2C$
Bassanite	$CaSO_4θ½ H_2O$	Hematite	Fe_2O_3
Boehmite	$AlO(OH)$	Molybdite	MoO_3
Calcite	$CaCO_3$	Monazite	$(Ce,La,Y, Th)PO_4$
Chalcopyrite	$CuFeS_2$	Pyrite	FeS_2
Chromite	$FeCr_2O_4$	Rutile	TiO_2
Chlorite	$A_{5-6}Z_4O_{10}(OH)_8$**	Siderite	$FeCO_3$
Crandelite	$CaAl_3(PO_4)_2(OH)_5θH_2O$	Sphalerite	ZnS
		Zircon	$ZrSiO_4$

**A=Al,Fe^{2+},Fe^{3+},Li, Mg, Mn^{2+},Ni; Z=Al, Fe^{3+},Si

***X=Ba,Ca,K,Na,NH_4,Sr;R=Al,B,Si

Appendix 1. Chemical symbols, mineral names, and abbreviations used in this report

(continued)

Abbreviations

-60	less than 60
K∀	K alpha (line intensities for X-rays)
µm	micrometer
<	less than
1:7	(one part acid and 7 parts water)
°C	degrees Centigrade (refers to temperature)
° 22	degrees 2 theta (measurement of angle of x-ray peaks in XRD)
AA	atomic absorption
amp	ampere
ANA	anatase (See mineral list above)
ASTM	American Society for Testing Materials
BAS	bassanite (See mineral list above)
BOE	boehmite (See mineral list above)
BSE	backscattered electron imaging
CVAA	cold vapor atomic absorption
CHL	chlorite (See mineral list above)
CRADA	Cooperative research and development agreement
CH_3COONH_4	ammonium acetate
EDX	Energy Dispersive X-ray
ETEC Autoscan	model of a scanning electron microscope used in this study
FLD	feldspar (See mineral list above)
g	grams
HAPs	hazardous air pollutants
HCl	hydrochloric acid
HEM	hematite (See mineral list above)
HF	hydrofluoric acid
HNO_3	nitric acid
IC	ion chromotography: used to analyze for Cl
ICP-AES	inductively coupled argon plasma- atomic emission spectrometry
ICP-MS	inductively coupled argon plasma- mass spectrometry
ILL	illite (See mineral list above)
INAA	instrumental neutron activation analysis
JEOL-840	model number of a scanning electron microscope used in this study
JEOL JXA 8900R	model number of microprobe used in this study
KeV	kilo-electron volt (unit of energy)
KOL	kaolinite (See mineral list above)
ml	milliliters
M	major phase
m	minor or trace phase

Appendix 1. Chemical symbols, mineral names, and abbreviations used in this report (continued)

N****	normality
ppm	parts per million
PY	pyrite (see mineral list above)
QTZ	quartz (See mineral list above)
RUT	rutile (see mineral list above)
SID	siderite (See mineral list above)
SEI	secondary electron imaging
SEM	scanning electron microscope
SPH	sphalerite (see mineral list above)
SiC	silicon carbide
U.S.	United States
USGS	United States Geological Survey
XRD	X-ray diffraction

**** Concentration of a solution in equivalents per liter; differs from the chemical symbol for **nitrogen** in that it is preceeded by a number and followed by a chemical formula or chemical name.

Appendix 2: Quantitative microprobe analyses of 26 pyrite grains

Where possible, pyrite classifications having genetic significance are used. such as cleat or framboidal pyrite. In many cases, the genesis of the pyrite is uncertain and descriptive terms are used. These include: *irregular-* an irregular mass consisting of smaller, generally well-formed crystals. For individual crystals, descriptive terms include *euhedral-* referring to a complete crystal form defined by well-formed crystal faces; *subhedral* an approximate crystal form that may include some well-formed faces; and *anhedral-* a grain that lacks obvious crystal form. d.l.=detection limit.

Appendix 2: Quantitative microprobe analyses of 26 pyrite grains in sample CQ352
(values in weight percent;d.l.=detection limit)

Grain	Se	Ni	Co	Cu	Zn	As	Pb	Fe	S	Total	Comment	Form (size) (microns)
1	0.16	0.03	0.04	0.51	0.01	0.25	d.l.	47.00	53.67	101.74	CQ#1Ap1.1	Subhedral (20x20)
1	0.13	d.l.	0.01	0.59	d.l.	0.27	d.l.	46.91	53.85	101.83	CQ#1Ap1.2	
2	d.l.	0.01	0.01	0.01	0.01	0.01	d.l.	46.70	52.27	99.10	CQ#1Ap2.1	Subhedral (30x40)
2	d.l.	0.01	d.l.	0.02	d.l.	0.01	d.l.	46.91	52.07	99.08	CQ#1Ap2.2	
2	d.l.	0.06	0.01	0.03	0.02	0.02	d.l.	46.60	52.00	98.79	CQ#1Ap2.3	
3	d.l.	d.l.	0.01	0.01	0.02	d.l.	d.l.	46.10	51.48	97.69	CQ#1Ap3.1	Subhedral (30x30)
3	d.l.	d.l.	0.01	0.01	0.02	0.02	d.l.	45.83	51.46	97.41	CQ#1Ap3.2	
3	d.l.	0.01	0.02	0.01	d.l.	0.02	d.l.	46.06	51.84	98.03	CQ#1Ap3.3	
4	d.l.	0.02	0.04	0.01	d.l.	0.02	d.l.	45.19	50.13	95.48	CQ#1Ap5.1	Framboid (15)
5	d.l.	0.05	0.04	0.01	d.l.	0.07	d.l.	47.43	52.66	100.32	CQ#1Ap5.2	Framboid (15)
6	0.01	0.03	0.03	0.01	d.l.	0.04	d.l.	46.83	52.55	99.56	CQ#1Ap5.3	Framboid (15)
7	d.l.	d.l.	0.01	0.01	d.l.	0.07	0.32	44.61	50.43	95.52	CQ#1Ap6.1	Subhedral (30x40)
7	d.l.	0.01	0.01	0.01	d.l.	0.04	0.20	46.13	52.76	99.23	CQ#1Ap6.2	
8	d.l.	0.03	0.01	d.l.	d.l.	0.01	d.l.	48.02	53.81	101.94	CQ#1Ap7.1	Subhedral (30x40)
8	d.l.	0.03	0.01	d.l.	d.l.	0.02	d.l.	45.75	52.13	98.02	CQ#1Ap7.2	
8	0.01	0.03	0.02	d.l.	d.l.	0.01	d.l.	47.94	53.81	101.89	CQ#1Ap7.3	
9	d.l.	d.l.	0.01	d.l.	d.l.	0.02	d.l.	45.90	51.02	97.02	CQ#1Ap8.2	Framboid (20)
10	d.l.	0.03	d.l.	0.01	d.l.	0.08	d.l.	47.47	53.58	101.23	CQ#1Ap9.1	Subhedral (25x40)
10	d.l.	0.02	0.02	0.01	d.l.	0.07	d.l.	47.54	53.51	101.24	CQ#1Ap9.2	
11	d.l.	d.l.	0.02	d.l.	0.02	0.01	d.l.	47.80	53.83	101.75	CQ#1Ap10.1	Subhedral (25x40)
11	d.l.	d.l.	0.02	0.01	0.01	d.l.	d.l.	48.02	53.77	101.90	CQ#1Ap10.2	
11	d.l.	0.01	0.02	d.l.	0.01	0.05	d.l.	47.79	53.96	101.92	CQ#1Ap10.3	

Appendix 2 (continued): Quantitative microprobe analyses of 26 pyrite grains for sample CQ352
(values in weight percent; d.l.= detection limit

No.	Se	Ni	Co	Cu	Zn	As	Pb	Fe	S	Total	Comment	Form (size) (microns)
12	0.01	0.05	0.02	0.02	0.02	0.30	0.01	46.26	51.47	98.22	CQ#1Ap11.1	Framboid (20)
12	d.l.	0.03	0.02	0.01	d.l.	0.17	d.l.	47.90	53.27	101.47	CQ#1Ap11.2	
12	d.l.	0.05	0.03	0.02	0.02	0.20	d.l.	47.24	52.54	100.17	CQ#1Ap11.3	
13	0.01	0.04	0.04	0.03	0.02	0.05	d.l.	47.85	53.80	101.90	CQ#1Ap12.1	Framboid (20)
13	0.03	0.03	0.04	0.05	d.l.	0.05	d.l.	47.64	52.90	100.80	CQ#1Ap12.2	
13	0.02	0.03	0.02	0.03	0.01	0.04	d.l.	47.74	53.16	101.12	CQ#1Ap12.3	
14	d.l.	d.l.	0.01	0.02	0.01	0.04	d.l.	46.42	51.92	98.48	CQ#1Ap13.1	Subhedral (20x20)
14	d.l.	0.01	0.01	0.01	0.01	0.06	d.l.	46.66	52.26	99.09	CQ#1Ap13.2	
15	d.l.	d.l.	0.02	d.l.	d.l.	0.03	d.l.	47.93	53.23	101.28	CQ#1Ap14.1	Subhedral (30x50)
15	0.01	d.l.	0.02	d.l.	d.l.	0.02	d.l.	48.21	54.18	102.51	CQ#1Ap14.2	
15	0.01	d.l.	0.01	d.l.	d.l.	0.01	d.l.	48.08	54.68	102.87	CQ#1Ap14.3	
16	0.52	1.52	0.40	0.16	0.01	1.00	d.l.	43.38	51.54	98.59	CQ#1Ap15.1	Half framboid (25)
16	0.66	1.54	0.51	0.18	d.l.	0.61	0.36	43.52	52.04	99.48	CQ#1Ap15.2	
16	1.24	1.25	1.30	0.15	0.01	0.82	0.48	38.86	46.83	91.02	CQ#1Ap15.3	
17	d.l.	d.l.	0.02	d.l.	d.l.	0.03	d.l.	48.70	53.82	102.65	CQ#1Bp1.1	Subhedral (25x70)
17	d.l.	0.01	d.l.	d.l.	0.01	0.08	d.l.	48.29	53.67	102.13	CQ#1Bp1.2	
17	d.l.	d.l.	0.01	d.l.	d.l.	0.07	d.l.	48.13	53.42	101.70	CQ#1Bp1.3	
17	d.l.	d.l.	0.01	d.l.	0.01	0.05	d.l.	48.12	53.26	101.52	CQ#1Bp1.4	
18	d.l.	d.l.	0.02	d.l.	d.l.	0.02	d.l.	47.08	52.37	99.55	CQ#1Bp2.1	Framboid (25)
18	d.l.	0.01	0.03	d.l.	d.l.	d.l.	d.l.	47.00	51.37	98.49	CQ#1Bp2.2	
18	d.l.	d.l.	0.03	d.l.	d.l.	0.02	d.l.	46.86	51.41	98.38	CQ#1Bp2.3	
19	0.02	0.04	0.02	0.06	d.l.	0.08	d.l.	46.61	52.74	99.62	CQ#1Bp3.1	Framboid 20
19	0.02	0.03	0.01	0.06	d.l.	0.06	d.l.	46.38	52.33	98.97	CQ#1Bp3.2	

Appendix 2 (continued): Quantitative microprobe analyses of 26 pyrite grains for sample CQ352
(values in weight percent; d.l.= detection limit)

No.	Se	Ni	Co	Cu	Zn	As	Pb	Fe	S	Total	Comment	Form (size) (microns)
20	0.02	d.l.	0.01	d.l.	d.l.	0.27	d.l.	48.03	54.07	102.47	CQ#1Bp4.1	Subhedral (60x80)
20	d.l.	d.l.	0.01	0.01	0.01	0.20	d.l.	48.33	54.45	103.09	CQ#1Bp4.2	
20	d.l.	d.l.	0.02	d.l.	d.l.	0.12	d.l.	48.26	53.98	102.45	CQ#1Bp4.3	
20	d.l.	d.l.	0.02	d.l.	d.l.	0.04	d.l.	47.57	53.77	101.47	CQ#1Bp4.4	
20	d.l.	d.l.	0.01	0.01	d.l.	0.11	d.l.	48.00	53.53	101.74	CQ#1Bp4.5	
20	d.l.	d.l.	d.l.	0.01	d.l.	0.12	d.l.	47.85	52.90	100.94	CQ#1Bp4.6	
21	d.l.	d.l.	0.01	d.l.	d.l.	0.11	d.l.	47.48	53.45	101.12	CQ#1Bp5.1	Subhedral (60x90)
21	0.01	d.l.	0.02	d.l.	0.01	0.07	d.l.	47.87	53.13	101.17	CQ#1Bp5.2	
21	d.l.	0.01	0.02	d.l.	d.l.	0.10	d.l.	47.43	53.05	100.66	CQ#1Bp5.3	
21	d.l.	d.l.	0.02	d.l.	d.l.	0.08	d.l.	47.02	53.53	100.73	CQ#1Bp5.4	
22	0.01	0.04	0.01	0.01	d.l.	0.09	d.l.	46.45	52.54	99.22	CQ#2AP1.1	Subhedral (35x50)
22	0.01	d.l.	0.02	0.01	d.l.	1.72	d.l.	47.55	52.94	102.31	CQ#2AP1.3	
23	0.02	d.l.	0.01	d.l.	0.01	0.01	d.l.	47.33	53.66	101.10	CQ#2AP2.2	Subhedral (45x100)
23	d.l.	0.01	d.l.	d.l.	d.l.	d.l.	d.l.	48.21	53.85	102.15	CQ#2AP2.3	
23	d.l.	0.01	0.01	d.l.	d.l.	0.04	d.l.	47.75	53.62	101.49	CQ#2AP2.4	
24	d.l.	d.l.	0.01	d.l.	d.l.	0.09	d.l.	47.29	52.82	100.27	CQ#2AP3.1	Subhedral (40x70)
24	d.l.	d.l.	0.02	d.l.	d.l.	0.03	d.l.	47.79	52.60	100.50	CQ#2AP3.2	
25	d.l.	d.l.	0.01	0.03	d.l.	0.01	d.l.	46.75	52.18	99.05	CQ#2AP4.1	Subhedral (45x45)
25	d.l.	d.l.	d.l.	0.04	d.l.	0.02	d.l.	46.86	52.29	99.28	CQ#2AP4.2	
25	d.l.	0.01	d.l.	0.01	d.l.	0.03	d.l.	46.29	51.97	98.38	CQ#2AP4.3	
25	d.l.	d.l.	d.l.	0.01	d.l.	0.03	d.l.	46.44	52.01	98.56	CQ#2AP4.4	
26	d.l.	0.01	0.02	d.l.	d.l.	0.31	d.l.	47.39	53.63	101.44	CQ#2AP5.1	Subhedral (20x40)
26	d.l.	d.l.	0.02	d.l.	d.l.	0.27	d.l.	47.14	53.88	101.38	CQ#2AP5.2	
26	d.l.	0.01	0.01	d.l.	d.l.	0.48	d.l.	46.85	53.15	100.57	CQ#2AP5.3	
26	0.01	d.l.	0.01	0.01	0.01	0.32	d.l.	46.07	53.30	99.79	CQ#2AP5.4	

Appendix 3: Data from individual splits

The "best overall values" in Appendix 3 are also reported in Table 3. Appendix 3 also gives separate "best values" for INAA and for "other techniques" because some elements determined by INAA were also determined by other techniques but there is no duplication of results between the other techniques.

All INAA values were determined in the same irradiation with quality control samples submitted by CQ (Appendix 4-1) and quality control standards: USGS standard reference material CLB-1 and National Institute for Standards and Technology (NIST) certified reference material 1632C (Appendix 4-2). The quality control standards for "other techniques" (Appendix 4-2) were also run together with the sample splits in Appendix 3. Samples CQ353A and CQ352B were submitted as blind duplicates. CQ352BA was a lab duplicate of CQ352B.

Appendix 3. Data for individual splits in ppm except as noted.

	Si (%)	Al (%)	Fe (%)	Mg (%)	Ca (%)	Na (%)	K (%)	Ti (%)	P (%)	Cl (%)
CQ352A			0.462			0.024	0.312			
Error A			0.009			0.001	0.013			
CQ352B			0.459			0.024	0.305			
Error B			0.009			0.001	0.014			
Best INAA	ND	ND	0.460	ND	ND	0.024	0.308	ND	ND	ND
Estimated INAA errror			0.009			0.001	0.013			
CQ352A (233)	3.86	2.42	0.51	0.081	0.10	0.022	0.32	0.13	0.0080	0.06
CQ352B (233)	3.72	2.35	0.49	0.080	0.09	0.022	0.30	0.12	0.0073	0.07
CQ352BA (233)	3.61	2.27	0.46	0.076	0.09	0.022	0.30	0.12	0.0067	
Best Value other techniques	3.73	2.35	0.48	0.079	0.09	0.022	0.31	0.12	0.0074	0.06
Estimated other techniques error	0.19	0.12	0.02	0.004	0.005	0.001	0.02	0.01	0.0004	0.00
Best overall value	3.73	2.35	0.47	0.079	0.09	0.023	0.31	0.12	0.01	0.06
Estimated overall error	0.19	0.12	0.02	0.004	0.005	0.001	0.02	0.01	0.0004	0.00

	Li	Be	B	Sc	V	Cr	Mn	Co	Ni	Cu
CQ352A				5.21		22.4		9.93	18.9	
Error A				0.076		1.0		0.19	3.1	
CQ352B				5.20		22.3		9.84	13.3	
Error B				0.076		0.7		0.29	2.6	
Best INAA	ND	ND	ND	5.21	ND	22.3	ND	9.88	16.1	ND
Estimated INAA errror				0.076		0.8		0.24	2.840	
CQ352A	31	2.0	47	5.3	35	22	14	9.4	17	18
CQ352B	31	2.0	39	5.1	35	21	14	9.9	18	17
CQ352BA	31	2.0	39	5.2	35	21	15	9.6	16	17
Best Value other techniques	31	2.0	41	5.2	35	21	14	9.6	17	17
Estimated other techniques error	1.5	0.10	2.1	0.26	2	1.07	0.72	0.48	0.85	0.86
Best overall value	31	2.0	41	5.2	35	22	14.45	10	17	17
Estimated overall error	1.5	0.10	2.1	0.3	2	1	0.72	0.48	3.5	0.86

Key: ND=Not Determined; INAA=instrumental neutron activation analyis.Other techniques include:inductivly coupled plasma (ICP) atomic emisson spectroscopy (AES)-acid d

ICP-AES sinter digest, ICP-mass spectroscopy-acid digest; hydride generation (HG) atomic absorption (AA); Cold vapor AA; Ion chromotography Error in grey

Appendix 3. Data for individual splits in ppm (continued)

	Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y
CQ352A	18			6.7	6.2	20.9	20.9	72	
Error A	1			0.2	0.5	0.5	1.6	13	
CQ352B	18			6.5	5.9	21.3	21.0	77	
Error B	1			0.2	0.4	0.5	1.6	12	
Best INAA	18	ND	ND	6.6	6.1	21.1	21.0	74	ND
Estimated INAA errror	1			0.2	0.5	0.5	1.6	13	
CQ352A	16	43	15	6.4	6.0		20	67	9.4
CQ352B	17	42	15	6.4	6.8		19	67	9.1
CQ352BA	17	43	15	6.3	ND		20	69	9.3
Best Value other techniques	17	43	15	6.4	6.4	ND	20	68	9.3
Estimated other techniques error	0.84	2.1	0.75	0.32	0.32		0.98	3.39	0.46
Best overall value	17	43	15	6.5	6.3	21.1	20.5	69	9.28
Estimated overall error	1	2.1	0.75	0.3	0.5	0.5	1.5	7	0.46

	Zr	Nb	Mo	Cd	Sn	Sb	Cs	Ba
CQ352A			2.5			0.612	1.43	124
Error A			0.6			0.023	0.07	12
CQ352B			1.3			0.598	1.42	128
Error B			0.4			0.023	0.05	13
Best INAA	ND	ND	1.9	ND	ND	0.605	1.43	126
Estimated INAA errror			0.5			0.023	0.06	12
CQ352A	33	3.2	1.6	0.062	1.7	0.68	1.4	138
CQ352B	30	2.7	1.6	0.055	1.2	0.64	1.3	132
CQ352BA	28	2.8	1.6	0.060	1.4	0.63	1.4	131
Best Value other techniques	30	2.9	1.6	0.059	1.5	0.65	1.4	133
Estimated other techniques error	1.5	0.14	0.08	0.003	0.07	0.03	0.07	6.67
Best overall value	30.3	2.88	1.6	0.06	1.45	0.61	1.4	130
Estimated overall error	1.5	0.14	0.5	0.003	0.07	0.05	0.07	8

Key: ND=Not Determined; INAA=instrumental neutron activation analyis.Other techniques include:inductivly coupled plasma (ICP) atomic emisson spectroscopy (AES)-acid d ICP-AES sinter digest, ICP-mass spectroscopy-acid digest; hydride generation (HG) atomic absorption (AA); Cold vapor AA; Ion chromotography Error in grey

Appendix 3. Data for individual splits in ppm (continued)

	La	Ce	Sm	Eu	Tb	Yb	Lu	Hf
CQ352A	14.1	26.1	2.76	0.525	0.34	1.28	0.17	1.02
Error A	0.3	0.6	0.07	0.017	0.01	0.07	0.01	0.08
CQ352B	14.1	25.7	2.76	0.510	0.35	1.22	0.17	1.01
Error B	0.3	0.8	0.07	0.016	0.02	0.08	0.01	0.04
Best INAA	14.1	25.9	2.7	0.518	0.344	1.251	0.17	1.01
Estimated INAA errror	0.342	0.710	0.066	0.017	0.015	0.075	0.012	0.057
CQ352A								
CQ352B								
CQ352BA								
Best Value other techniques	ND	ND	ND	ND	ND	ND	ND	ND
Estimated other techniques error								
Best overall value	14.1	25.9	2.8	0.52	0.34	1.25	0.17	1.01
Estimated overall error	0.3	0.7	0.1	0.017	0.015	0.075	0.012	0.06

	Ta	W	Tl	Hg	Pb	Bi	Th	U
CQ352A	0.32	1.0					3.75	1.4
Error A	0.01	0.1					0.08	0.1
CQ352B	0.32	0.73					3.63	1.3
Error B	0.03	0.07					0.08	0.1
Best INAA	0.32	0.86	ND	ND	ND	ND	3.69	1.352
Estimated INAA errror	0.021	0.074					0.080	0.105
CQ352A			0.75	0.15	9.4	0.18	3.6	1.4
CQ352B			0.70	0.14	8.8	0.17	3.5	1.3
CQ352BA			0.71	0.15	9.2	0.17	3.4	1.3
Best Value other techniques	ND	ND	0.72	0.15	9.1	0.17	3.5	1.3
Estimated other techniques error			0.04	0.008	0.46	0.01	0.18	0.07
Best overall value	0.32	0.86	0.72	0.15	9.14	0.17	3.6	1.4
Estimated overall error	0.02	0.07	0.04	0.008	0.46	0.01	0.18	0.10

Key: ND=Not Determined; INAA=instrumental neutron activation analyis.Other techniques include:inductivly coupled plasma (ICP) atomic emisson spectroscopy (AES)-acid d ICP-AES sinter digest, ICP-mass spectroscopy-acid digest; hydride generation (HG) atomic absorption (AA); Cold vapor AA; Ion chromotography Error in grey

Appendix 4. Quality Control Data

Control samples in Appendix 4-1 were submitted as blind samples. Due to limited sample size elemental concentrations in these samples were determined only by INAA. Elemental concentrations of standard reference material USGS CLB-1 and certified reference material NIST 1632C (Appendix 4-2) were determined with the samples in Appendix 3 for all techniques. Elemental concentrations of certified reference materials, NIST 1633b and NIST 1632b, were also determined for selected techniques (Appendix 4-2).

Table A4-1. CQ "Blind" quality control samples. Values in ppm except as noted.

variables:	Sc	Se	Sr	Ta	Th	U	W	Zn	La	Ce	Sm	Eu	Tb	Yb
CQO111202	5.26	5.70	82.8	0.35	3.89	1.20	0.73	32.4	14.7	27.0	2.80	0.51	0.36	1.32
Error:	0.08	0.57	11.7	0.01	0.08	0.10	0.06	1.7	0.35	0.58	0.066	0.018	0.013	0.083
CQ0111202	5.27	6.24	96.1	0.35	3.95	1.35	0.80	32.6	14.6	27.4	2.80	0.53	0.36	1.28
Error:	0.08	0.32	9.67	0.02	0.10	0.11	0.07	1.9	0.36	0.62	0.067	0.017	0.014	0.078
Average	5.26	5.97	89.5	0.352	3.92	1.28	0.765	32.5	14.6	27.2	2.80	0.522	0.361	1.30
Average Error	0.077	0.445	10.7	0.019	0.091	0.11	0.070	1.8	0.354	0.60	0.066	0.018	0.013	0.080
CQO111208	5.26	5.67	89.8	0.34	3.96	1.47	0.71	30.9	14.5	27.1	2.79	0.53	0.34	1.31
Error:	0.08	0.88	17.1	0.01	0.08	0.13	0.06	1.6	0.35	0.59	0.07	0.02	0.01	0.08
CQ0111208	5.30	6.02	82.3	0.35	3.88	1.25	0.99	33.7	14.7	27.3	2.81	0.55	0.36	1.16
Error:	0.08	0.56	10.9	0.02	0.08	0.10	0.11	1.6	0.36	0.61	0.07	0.02	0.01	0.08
Average	5.28	5.841	86.0	0.343	3.92	1.36	0.847	32.3	14.6	27.2	2.80	0.540	0.353	1.24
Average Error	0.077	0.719	14.0	0.016	0.083	0.113	0.088	1.6	0.35	0.60	0.067	0.020	0.013	0.077
CQO111211	5.19	5.32	78.4	0.34	3.74	1.35	0.83	19.2	14.0	26.0	2.75	0.53	0.36	1.30
Error:	0.08	0.92	10.9	0.02	0.08	0.10	0.09	1.3	0.34	0.57	0.06	0.02	0.01	0.12
CQ0111211	5.17	5.59	82.4	0.32	3.74	1.37	0.86	20.3	14.1	26.3	2.76	0.52	0.35	1.16
Error:	0.08	0.65	13.0	0.01	0.08	0.11	0.08	1.4	0.34	0.60	0.07	0.02	0.01	0.14
Average	5.18	5.452	80.4	0.327	3.74	1.36	0.844	19.7	14.0	26.2	2.75	0.528	0.356	1.23
Average Error	0.075	0.788	12.0	0.019	0.079	0.105	0.084	1.3	0.34	0.58	0.065	0.017	0.013	0.128
CQO111214	5.18	5.895	66.9	0.347	3.736	1.30	0.713	19.0	14.1	25.6	2.76	0.546	0.346	1.33
Error:	0.075	0.551	10.0	0.015	0.089	0.10	0.064	1.5	0.34	0.65	0.065	0.017	0.020	0.124
CQ0111214	5.12	5.447	73.2	0.329	3.76	1.39	0.836	16.8	14.1	26.2	2.77	0.532	0.361	1.28
Error:	0.079	0.838	8.6	0.015	0.083	0.11	0.077	2.4	0.34	0.58	0.066	0.017	0.014	0.076
Average	5.15	5.671	70.1	0.338	3.75	1.34	0.775	17.9	14.1	25.9	2.77	0.539	0.353	1.31
Average Error	0.077	0.694	9.3	0.015	0.09	0.10	0.070	1.9	0.34	0.62	0.066	0.017	0.017	0.100
CQO111218	2.80	1.206	68.8	0.142	1.35	0.538	0.421	10.9	6.50	11.4	1.10	0.221	0.135	0.492
Error:	0.043	0.143	11.0	0.011	0.040	0.071	0.061	0.85	0.17	0.52	0.029	0.011	0.012	0.056
CQ0111218	2.79	1.085	65.3	0.133	1.35	0.474	0.244	10.2	6.49	11.6	1.09	0.208	0.128	0.552
Error:	0.042	0.205	10.9	0.009	0.048	0.062	0.047	0.90	0.17	0.35	0.028	0.009	0.007	0.066
Average	2.80	1.145	67.0	0.137	1.35	0.506	0.333	10.5	6.50	11.5	1.10	0.215	0.131	0.522
Average Error	0.043	0.174	10.9	0.010	0.044	0.066	0.054	0.88	0.17	0.43	0.028	0.010	0.009	0.061

Table A4-2 USGS Quality Control Standards Values in ppm except as noted

	Si (%)	Al (%)	Fe (%)	Mg (%)	Ca (%)	Na (%)	K (%)	Ti (%)	P (%)	Cl (%)	I
CLB-1			0.895			0.0198	0.064				
Error			0.022			0.00086	0.0040				
CLB-1	1.20	0.79	0.86	0.03	0.15	0.0239	0.06	0.05	0.03	0.113	8
Recommended/Information	1.17	0.799	**0.874**	**0.0283**	**0.16**	**0.017**	**0.063**	0.047	0.031		8
Error (Recommended and information)	0.098	0.021	0.35	0.0018	0.0071	0.002	0.004	0.0018	0.004		
1632-C			0.755			0.031	0.106				
Error			0.012			0.00062	0.0057				
1632-C	1.61	0.91	0.74	0.03	0.14	0.0292	0.11	0.05	0.01	0.114	8
Certified/Reference/Informational	1.654	0.915	0.735	0.0384	0.145	**0.02988**	**0.1100**	0.0517	0.015	**0.1139**	8
Error (Certified and Reference values)	0.0034	0.00137	0.11	0.0032	0.030	0.00048	0.0033	0.0032		0.0041	
1633-B	23.1	15.1	6.5	0.5	1.6	0.19	2	0.77	0.24	ND	173
Certified/Noncertified	**23.02**	**15.05**	**7.78**	**0.482**	**1.51**	**0.201**	**1.95**	**0.791**	0.23	ND	
Error (Certified values)	0.08	0.27	0.23	0.008	0.06	0.003	0.03	0.014			
1632-B										0.107	
Certified/Noncertified										0.126	
Error (Certified values)											

	Be	B	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	C
CLB-1			2.04		10.2		6.97	13.6		50	
Error			0.029		0.41		0.14	3.4		3.5	
CLB-1	1.17	4.41	2.12	12	10.5	8.95	6.74	19.0	11.1	44.4	2
Recommended/Information	1.17		2.0	**12**	**9.7**	8	**7.0**	**18**	10	48.0	3
Error (Recommended and information)			0.1	1	1.2		0.7	2			
1632-C			2.83		13.9		3.43	10.7		10.5	
Error			0.039		0.79		0.18	2.9		0.92	
1632-C	1.01	61.72	2.86	22.4	14.4	13.0	3.79	10.10	5.93	13.6	3
Certified/Reference/Informational	1.0	62	2.905	23.72	13.73	**13.04**	**3.48**	9.32	6.01	**12.1**	3
Error (Certified and Reference values)		2	0.036	0.51	0.2	0.53	0.20	0.51	0.25	1.3	
1633-B (233)	12.6	61.9	41.8	288	182	129	50.0	108	108	192	51
Certified/Noncertified			41	**295.7**	**198.2**	**131.8**	50	**120.6**	**112.8**	210	
Error (Certified values)				3.6	4.7	1.7		1.8	2.6		

Key:ND=Not Determined; INAA=instrumental neutron activation analyis.Other techniques include:inductivly coupled plasma (ICP) atomic emisson spectroscopy (AES)-acid digest; ICP-AES sinter digest, ICP-mass spectroscopy-acid digest; hydride generation (HG) atomic absorption (AA); Cold vapor AA; Ion chromotography.

Table A4-2 USGS Quality Control Standards Values in ppm except as noted. (continued)

	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Cd
CLB-1		13.7	2.2	75.4	6.7	87.6				12.0	
Error		0.59	0.43	4.41	0.94	9.7				0.66	
CLB-1	13.8	13.9	2.55		5.25	70.6	4.93	10.96	1.07	9.89	0.088
Recommended/Information		13	**2.1**		**5.2**	67.1			1	9	
Error (Recommended and information)			0.39		0.9						
1632-C		5.93	1.31	24.4	7.47	67.1				< 1.2	
Error		0.14	0.17	0.44	1.1	10					
1632-C	4.7	6.16	1.32		7.37	64.7	3.95	16.25	1.23	0.77	0.072
Certified/Reference/Informational	5	6.18	**1.326**	18.7	**7.52**	**63.8**	4	16	1	0.8	0.072
Error (Certified and Reference values)		0.27	0.071	0.4	0.33	1.4					0.007
1633-B	17.0	128			140	1040	85.9	193	20.4	14.6	0.75
Certified/Noncertified		**136.2**			140	**1041**					**0.784**
Error (Certified values)		2.6				14					0.006
1632-B (233)			1.25								
Certified/Noncertified			**1.29**								
Error (Certified values)			0.11								

	Sn	Sb	Cs	Ba	La	Ce	Sm	Eu	Tb	Yb	Lu
CLB-1 (71)		1.55	0.359	42.0	5.94	10.6	1.17	0.225	0.156	0.557	0.075
Error		0.089	0.023	7.0	0.11	0.78	0.028	0.015	0.0086	0.035	0.0089
CLB-1 (233)	0.75	1.60	0.32	35.0							
Recommended/Information		1.5		**34**	5	**10**					
Error (Recommended and information)				5		1.6					
1632-C (71)		0.426	0.608	46.5	6.59	11.5	1.103	0.203	0.136	0.531	0.070
Error		0.016	0.029	7.1	0.12	0.32	0.021	0.0085	0.0079		
1632-C (233)	1.04	0.47	0.62	38.2							
Certified/Reference/Informational	1.00	**0.461**	0.594	**41.1**		11.9	1.078	0.1238			
Error (Certified and Reference values)		0.029	0.01	1.6		0.2	0.028	0.003			
1633-B (233)	12.1	5.6	10.5	688							
Certified/Noncertified		6	11	**709**							
Error (Certified values)				27							

Key:ND=Not Determined; INAA=instrumental neutron activation analyis.Other techniques include:inductivly coupled plasma (ICP) atomic emisson spectroscopy (AES)-acid digest; ICP-AES sinter digest, ICP-mass spectroscopy-acid digest; hydride generation (HG) atomic absorption (AA); Cold vapor AA; Ion chromotography.

Table A4-2 USGS Quality Control Standards Values in ppm except as noted. (continued)

	Hf	Ta	W	Tl	Hg	Pb	Bi	Th	U
CLB-1 (71)	0.445	0.106	0.691					1.40	0.580
Error	0.055	0.023	0.069					0.057	0.074
CLB-1 (233)				0.83	0.154	5.25	0.09	1.39	0.53
CLB-1 (248)					0.163				
Recommended/Information					0.2	5		1.4	0.55
Error (Recommended and information)									
1632-C (71)	0.495	0.123	0.418					1.40	0.520
Error	0.040	0.017	0.045					0.059	0.051
1632-C (233)				0.38	0.094	3.83	0.12	1.42	0.52
1632-C (248)					0.087				
Certified/Reference/Informational	0.585			0.4	**0.0938**	3.79	0.1	**1.40**	0.513
Error (Certified and Reference values)	0.1				0.0037	0.07		0.03	0.012
1633-B (233)				6.3	0.131	64.0	1.1	25.8	9.5
1633-B (248)					0.135				
Certified/Noncertified				5.9	**0.141**	**68.2**		**25.7**	**8.79**
Error (Certified values)					0.019	1.1		1.3	0.36
1632-B (233)					0.075				
1632-B (248)					0.069				
Certified/Noncertified									
Error (Certified values)									

Key:ND=Not Determined; INAA=instrumental neutron activation analyis.Other techniques include:inductivly coupled plasma (ICP) atomic emisson spectroscopy (AES)-acid digest; ICP-AES sinter digest, ICP-mass spectroscopy-acid digest; hydride generation (HG) atomic absorption (AA); Cold vapor AA; Ion chromotography.