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Chemical analysis and modes of occurrence of selected trace elements in a Powder River Basin coal and its corresponding simulated cleaned coal:

A Technical Report by the U.S. Geological Survey

CRADA No. OT8562W with CQ Inc.

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Abstract

This report provides semi-quantitative data on modes of occurrence of 19 elements in as-mined Powder River Basin coal and its corresponding simulated cleaned coal. 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. 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 40 percent of the elements Co, U, Be, Ca, Fe, Mn, Ba, Zn, Cd, Pb are associated with HCl-soluble carbonates, iron oxides, or monosulfides, greater than 40 percent of the Al, Cr and Mo are associated with HF-soluble silicates, greater than 40 percent of the Ni, Cu, As and Sb are associated with acid-insoluble phases and/or organic matter, and greater than 50 percent of the Hg is associated with HNO_3-soluble pyrite. Thirty percent of the Th was leached by HCl and 30 percent of this element was leached by HF. Scanning electron microscopy indicates that quartz, kaolinite, illite and iron oxide, possibly hematite, are the major minerals present. X-ray diffraction analysis confirmed that quartz, kaolinite and hematite are present, but did not determine illite, indicating that illite in these coals is of low abundance or is poorly crystalline. Electron microprobe data indicate that concentrations of 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 in both the as-mined coal and its corresponding simulated cleaned coal product. 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. to better understand how modes of occurrence of elements in coal affect their performance during physical coal cleaning. Previous work (Raleigh and others, 1998; Palmer and others, 1997, 1998) 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 during commercial coal cleaning operations. Herein we report on the modes of occurrence of 19 elements in a Powder River Basin (PRB) coal and a corresponding simulated cleaned coal product.

The sub-bituminous PRB coal examined in this study was collected from the Antelope Mine in the Powder River Basin, Wyoming, by CQ, Inc. A commercial laboratory produced a simulated cleaned coal by combining various float-sink fractions according to CQ, Inc.'s specifications. Initial project tasks included (1) obtaining semi-quantitative information on trace element modes of occurrence in PRB and other coal types, and (2) assembling the information in a form that can be used by industry to

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

enhance the potential of coal cleaning technologies for reducing hazardous air pollutants (HAPs). This phase of the project concentrated on a subbituminous PRB coal that is not currently being cleaned. The as-mined coal and a simulated cleaned coal were subjected to a series of direct and indirect methods for determining modes of occurrence of trace elements. This resulted in reproducible semi-quantitative information on the modes of occurrence of 19 elements, including all those currently considered as potential HAPs.

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). Quadruplicate 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). CH_3COONH_4 removes elements bonded onto exchangeable sites, water-soluble compounds, and some carbonates. HCl dissolves carbonates, iron oxides, monosulfides and certain 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 the formation of gas during some of the leaching steps, it is necessary to enclose each tube in double polyethylene bags, each 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, 1998a). 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 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 analysis by inductively coupled argon plasma-atomic emission spectromentry (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 technique for anthracite and bituminous coal, as modified by Pontolillo and Stanton (1994). The casting procedure impregnates, under pressure, approximately 7-8 grams of crushed

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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.

sample with Armstrong C4 epoxy. The resultant mold is cured overnight at 60° C. A label is incorporated with the sample.

The 2.5 cm diameter circular pellet block is ground and polished using ASTM D2797-85 procedure (ASTM, 1998b) as modified by Pontolillo and Stanton (1994). The epoxy-coal pellet is 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. Ultrasonic cleaning after each steps insures a final product free of extraneous abrasive material.

Two pellets were prepared from each sample. Each pellet was sectioned with a thin, slow-speed diamond saw and carbon coated for SEM and microprobe analysis.

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 coals. Mineral identifications are based on morphology, and major-element composition of grains. Both secondary electron imaging (SEI) and backscattered electron imaging (BSE) modes were used in coal sample characterization. The BSE mode is especially sensitive to variation in mean atomic number and is useful for showing 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 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.

The SEI and BSE images taken at low magnification were used as a guide to locate phases of interest for microprobe analysis. SEM images taken at higher magnifications provided records of the points analyzed, and were helpful in avoiding interstices and inclusions in mineral grains that would adversely affect the quantitative microprobe analysis.

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. The beam currents used were from 3.0 x10^{-8} amps and the voltage was 20 KeV. 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 was about 100 ppm for each of the trace elements analyzed, using counting times of 60 seconds for peak and 30 seconds for background for most of the elements. For Co, the detection limit is only to about 500 ppm (0.05 weight percent) due to an interference with Fe giving a constant background in pyrite of 400-500 ppm. Co results shown in Appendix 2 are background corrected. Counting statistics have a large uncertainty as the detection limit is approached. Microprobe data are shown in Appendix 2.

X-Ray Diffraction Analysis

To obtain semi-quantitative information on the minerals present in the coals, samples of low- temperature (<200° C) ash were pressed into pellets and analyzed using an automated X-ray diffractometer. Diffraction of Cu KA 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

SEM analyses on samples ground to –60 mesh (< 250 µm diameter) show that the major minerals quartz, illite, and kaolinite are present in both the as-mined and the simulated cleaned PRB coal (Table 1). In addition to these three minerals, major amounts of an Fe-oxide phase (possibly hematite) were found in the as-mined sample. Other minerals were found in minor and trace amounts (Table 1, 2). Although, illite is listed as a major mineral in the cleaned coal and the as-mined coal, a discernable reduction in the proportion of illite (vs. kaolinite) and in the proportion of iron-oxide, in the clean coal vs. the as-mined coal was observed using the SEM. The significantly lower concentrations of K, Al and Si in the simulated cleaned coal as compared to the as-mined coal (Table 3) also indicate that the concentration of illite is lower in the cleaned coal, but Fe does not show a similar reduction. A coarse (-20 mesh; 850 µm diameter) fraction of the as-mined coal was also examined to better establish mineral-mineral and maceral-mineral relationships.

Microprobe data for 9-10 pyrite grains in both the as-mined and cleaned samples (Appendix 2) show that, for most analyses, the concentrations of most elements are below the 100-200 ppm detection limits. An exception is grain 5 in the as-mined sample, in which the Ni content is about 10-15 times the detection limit. The data indicate that the average concentrations of these elements in the pyrite are below the microprobe detection limits, with the possible exception of Ni.

Table 1. Mineralogy- Powder River Basin coal, Antelope Mine (SEM Analysis)

Phases	As-mined -60 mesh	As-mined -20 mesh	Cleaned - 60 mesh
Quartz	M	M	M
Illite	M	M	M
Kaolinite	M	M	M
Fe oxide phase (hematite?)	M	m	m
Pyrite	m	m	M
Calcite		m	m
Zircon	m		m
Barite	m	m	m
Ti oxide phase (rutile?)	m	m	m
Apatite	m		
Crandellite	m		m
Sphalerite	m		m
Chalcopyrite	M	m	m
Chromite	m		
Ilmenite	?		

M = Major phase m = Minor or trace phase ? = presence uncertain
blank =none detected

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). About 30-35 percent of each LTA sample consists of quartz and 35 to 40 percent is kaolinite. Bassanite ($CaSO_4$ $\frac{1}{2}H_2O$), likely an artifact of the ashing process, constitutes 20-35 percent of the LTA. Illite was not detected by XRD but was detected as a major phase by SEM, perhaps indicating that it is poorly crystalline. Siderite, ankerite, hematite, sphalerite, and possibly pyrite, were detected as trace phases (<5 percent) by XRD. Of these minerals, sphalerite, pyrite and Fe_2O_3 (hematite?) were also detected by SEM. Calcite was not detected by XRD.

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

Sample	QTZ	KOL	ILL	BAS	SID	ANK	HEM	PY	SPH	DOL	APA
As-mined	35	40	?	20	≤ 5	≤ 5	?	?	≤ 5	?	?
Clean	30	35		35	?		≤ 5		?		?

QTZ = quartz; KOL = kaolinite; ILL = illite; BAS = bassanite; SID = siderite; ANK = ankerite; HEM = hematite; PY = pyrite; SPH = sphalerite; DOL = dolomite; and APA = apatite. ? =Trace constituent (≤ 5 %) that could not be resolved with certainty. Blank = not detected. Weight percentages listed are on an ash basis. Frank T. Dulong analyst.

Elemental Analysis— Quality Control

In addition to the PRB as-mined and simulated cleaned coals, CQ, Inc. submitted three blind standards for quality control purposes. All samples were chemically analyzed by multiple techniques. Concentrations of 30 elements were determined by INAA, using techniques described by Palmer (1997). 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 (Cl; Gent and Wilson, 1985) at the USGS laboratories in Denver, Colorado. Table 3 shows the average or "best" (as defined below) results for 53 elements in the as-mined and simulated cleaned coal samples, including19 elements that were determined by both INAA and other techniques. These values typically represent either 1) the average of values determined by all techniques for a given element; 2) in a few cases an average of results from multiple techniques, weighted according to the reliability of techniques for a given element; or 3) in 2 cases, specific determinations were chosen where mass balance considerations excluded the value for the alternate analysis. For example, the concentration of Pb in duplicates of the simulated cleaned coal is 0.88 and 1.7 ppm. If 0.88 ppm were chosen as the correct value, many of the leaching fractions would have totals that exceed 100 percent. Furthermore, a Pb value of 1.7 ppm for the simulated cleaned coal gives a reduction of Pb from the as-mined coal that is similar in magnitude to that of the other elements. Therefore, 1.7 ppm was selected as the "best" value for Pb in this sample. Similarly, a value of 0.08 ppm for Hg was chosen as a best value for Hg for the as-mined sample; 0.4 ppm was not averaged based on mass balance considerations. Individual determinations, best values for each technique, and the overall best values for each sample are given in Appendix 3, which is color-coded to show the type of analysis for each determination. Excessively high Br contents were found by INAA in the simulated cleaned coal, due to contact with brominated heavy liquids used in the density separation of this sample. Additional duplicates of the cleaned coal were analyzed by INAA after washing the sample with acetone, but the results for Br remain anomalous. The high Br concentrations should only affect results determined by INAA.

Table 3. Average Values for Elements in Powder River Basin Coal (As-mined) and the Corresponding Simulated Cleaned Coal (Cleaned) except as noted

variables:	Hg	As	Cr	Pb	Co	Ni	Mn	Ba
units:	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
As- mined	0.08*	0.65**	4.1**	1.9	2.5**	4.0**	12	390**
Cleaned	0.08	0.5**	3.6**	1.7*	2.5**	3.7**	11	370**

variables:	Be	Cd	Cu	Mo	Zn	Sb	Th	U
units:	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
As- mined	0.19	0.069	14	0.42	16.4**	0.15**	1.1**	0.46**
Cleaned	0.17	0.059	12	0.49	23**	0.14**	1.1**	0.5**

variables:	Al	Ca	Fe	Na	Mg	Si	K	Ti
units:	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
As- mined	0.58	0.96	0.25**	0.076**	0.22	1.10	0.025**	0.055
Cleaned	0.49	0.95	0.23**	0.070**	0.21	0.84	0.016**	0.049

variables:	Li	B	P	Cl	Sc	V	Ga	Ge
units:	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
As- mined	1.9	28	490	< 150	1.4**	14	1.9	0.35
Cleaned	2.0	25	460	***	1.35**	13	1.5	0.31

variables:	Se	Br	Rb	Sr	Y	Zr	Sn	Cs
units:	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
As- mined	0.25**	4.7	1.2**	221**	2.7	16	0.5	0.16**
Cleaned	0.4**	***	0.5**	210**	2.5	15	0.6	0.16**

variables:	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
units:	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
As- mined	4.1	6.8	< 8	0.67	0.15	0.07	0.26	0.04
Cleaned	3.9	5.8	< 16	0.68	0.14	0.080	0.27	0.040

variables:	Hf	Ta	W	Au	Tl
units:	ppm	ppm	ppm	ppm	ppm
As- mined	0.45	0.15	0.67	< 0.002	0.06
Cleaned	0.42	0.12	0.08	< 0.016	0.04

wt.=weight

*One value eliminated due to mass balance considerations (see Appendix 3)

**weighted average of multiple techniques

*** = Contaminated by heavy liquids used in density separation

Element concentrations for the as-mined coal and the simulated cleaned are very similar. The average concentrations of elements in the simulated cleaned coal were about 6 percent lower than the as-mined coal. The average ash yields determined at 525° C were almost identical at 5.95 weight percent for the as-mined coal, compared to 5.9 weight percent for the simulated cleaned coal.

The elemental concentrations of a series of "blind" samples, submitted by CQ, Inc. to various laboratories to determine the comparability of data between laboratories, are included in Appendix 4, Table A4-1. It was later revealed that these samples, labeled 67799, 67999 and 60899, were standard reference materials, NIST 1635, 1632b and USGS CLB-1, respectively. Each of these standards was analyzed in duplicate by INAA, but sample availability limited the ICP-AES/ICP-MS analysis to a single determination. Independently, the USGS analyzed CLB-1 as a control (Appendix 4, Table A4-2) with every sample set (2 for ICP-AES/ICP-MS and 5 for INAA). Certified, recommended, and informational values are given in Appendix 4 for each reference sample. For elements determined by more than one method, a "best overall value" was determined in the same manner as the best values given in Appendix 3.

Leaching Experiments

Leachate solutions were analyzed by ICP-AES and ICP-MS, and solid residues were determined 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 coals. The analytical uncertainties were estimated to be ±2 to ±25 percent for these data, but uncertainties are generally within ±5 percent, absolute.

Data for the as-mined PRB coal and its corresponding simulated cleaned coal were determined in quadruplicate leaching experiments. Reproducibility is generally within the expected analytical uncertainties, and is generally better within a given technique than among techniques. Figure 1 shows an example of the quadruplicate analysis for Co, determined by INAA, ICP-AES, and ICP-MS. Cobalt concentrations are below the ICP-AES detection limit in all HNO_3 fractions except for one replicate of the as-mined coal. Cobalt was not determined by ICP-MS on the whole coal fractions, and the percent leached by ICP-MS is compared to ICP-AES whole coal Co concentrations. Nevertheless, the agreement of INAA and ICP-MS values is quite good and appears to be better than the agreement of either INAA or ICP-MS results with ICP-AES. These results were combined in figure 2 to show the average percent Co leached, based on the INAA replicates (on the solid residue) compared with the average percent Co leached based on analysis of the solution. The results agree within 5 percent absolute. The greatest difference is that the portion of Co removed by HF, as determined in the solutions, is greater than that determined in the solids by about 5 percent. The additional ICP-MS data on the solutions increases the confidence in the data in general especially the INAA data.

The leaching results are further combined to yield a single stacked bar chart for each element for each sample. The values are rounded to the nearest increment of 5 percent for each leached fraction. The results for Co and other elements are shown in figure 3. The leaching behavior of Co in the as-mined coal and the simulated cleaned coal are the same within the analytical uncertanity of the procedure.

All the elements shown in figure 3 (Mo, Th, Co, Cr, U, Be, and Al) have greater than 25 percent of the leached fractions associated with the silicate (HF leachable) fraction. Be, Co, Cr, Th, and U also have significant HCl-soluble fractions. In rocks, Be is generally associated with Al minerals (Goldschmidt, 1954). In bituminous coals, Be is leached mainly by HF but in lower rank coals some Be is also soluble in HCl (Palmer and others, 1998). The same is true for Al (Mroczkowski, 1998, unpublished data).

In this study, 55 percent of the Be and 30 percent of the Al in the as-mined coal is HCl soluble, and 60 percent of the Be and 35 percent of the Al in the simulated cleaned coal is HCl soluble. The presence of HF-soluble Be indicates some association with the silicates (probably clays) but the Be/Al ratio appears to be lower in the HF leachate (silicates) than the HCl leachate (oxide/hydroxides). Only, a relatively small amount of Be (5-15 percent) is acid insoluble and therefore most likely organically associated, but it is possible that some of the HCl soluble Be is also organically associated. These results differ from data for bituminous coal reported by Palmer and others (1998) showing 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 in their coals was organically associated based on float-sink procedures. To date, the exact modes of occurrence of Be are unresovled, but there is an international effort to resolve the exact modes of occurrence of Be in coals.

Cobalt has mixed modes of occurrence. Forty to forty-five percent of the Co is leached by HCl, indicating an association with carbonates, Fe-oxides, and/or HCl-soluble mono-sulfides. Twenty percent of the Co is associated with silicate minerals, and 10 percent of the Co is associated with pyrite. This leaves 25-30 percent of the Co in insoluble phases, presumably residual organic matter.

Forty to forty-five percent of the Cr in each sample is leached by HF and is probably associated with illite and mixed layer clays (Fig. 3; Palmer and others, 1998). Only 15 percent of the Cr is HCl-soluble and may be associated with Cr oxy-hydroxides (Huffman and others, 1994). Thirty percent of the Cr is not leached. Some of this may be organically associated but some may be in trace insoluble species such as chromite, identified by SEM (table 1).

Forty to fifty-five percent of the Mo is HF-soluble, indicating a silicate (clay) association. Mo was not leached by any other solvent. The large amount of unleached Mo indicates an organic association.

Thirty percent of the Th is leached by HF, from both the as-mined and the simulated cleaned coal. Thorium is probably associated with the clays, although some HF leachable Th may be from zircons (detected by SEM). HCl-soluble Th (30 percent) is probably derived from trace amounts of apatite or monazite. Thirty to thirty-five percent of the Th remains unleached. Some of this unleached Th could reside in insoluble or partially soluble minerals such as zircon (table 4) or may be organically bound. The small amount of HNO_3 leachable Th may be from phosphates shielded by

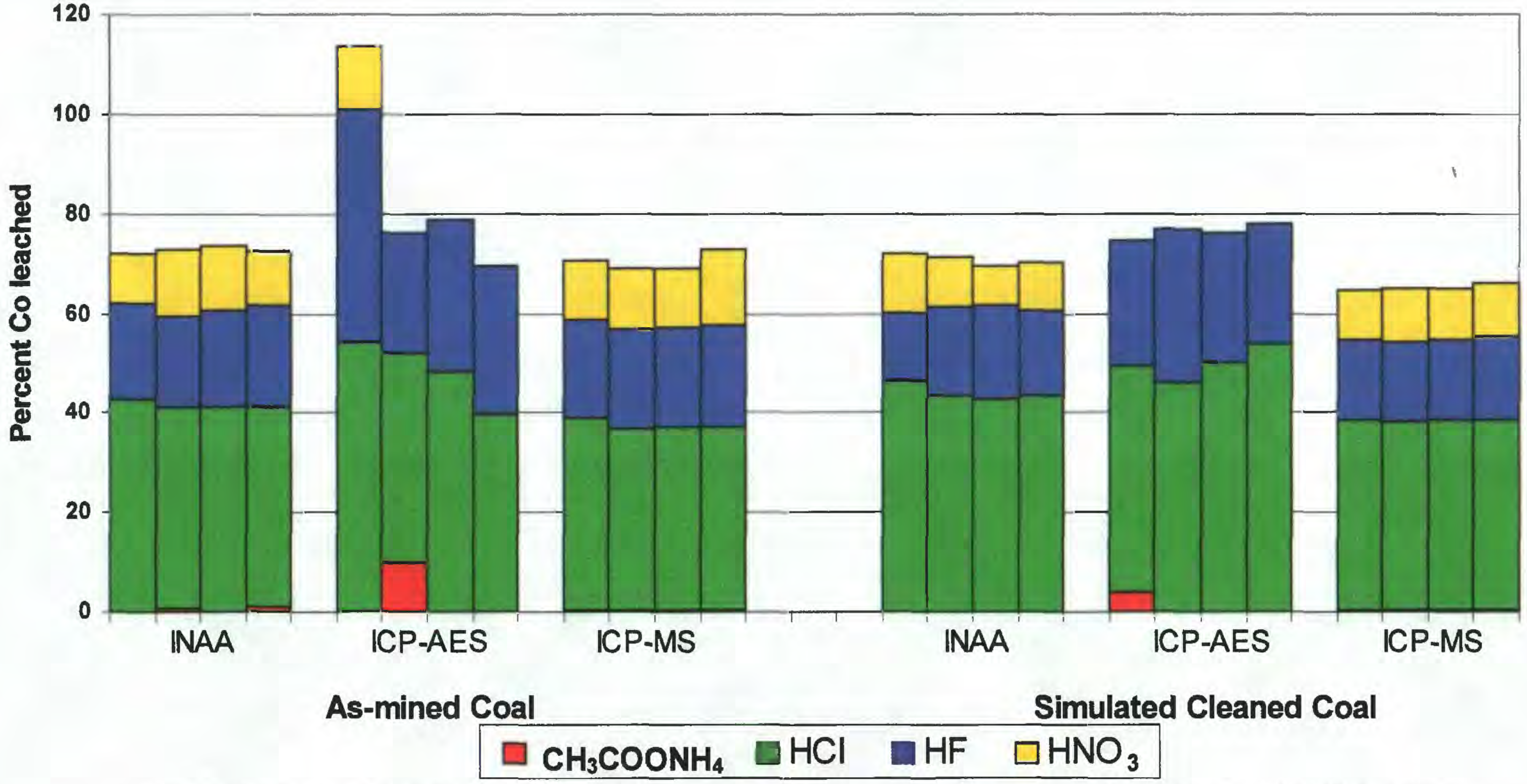

Figure 1. Comparison of all replicates of INAA on the solids, and all replicates of ICP-AES and ICP-MS on the solution for Co in the as-mined and simulated cleaned coal samples.

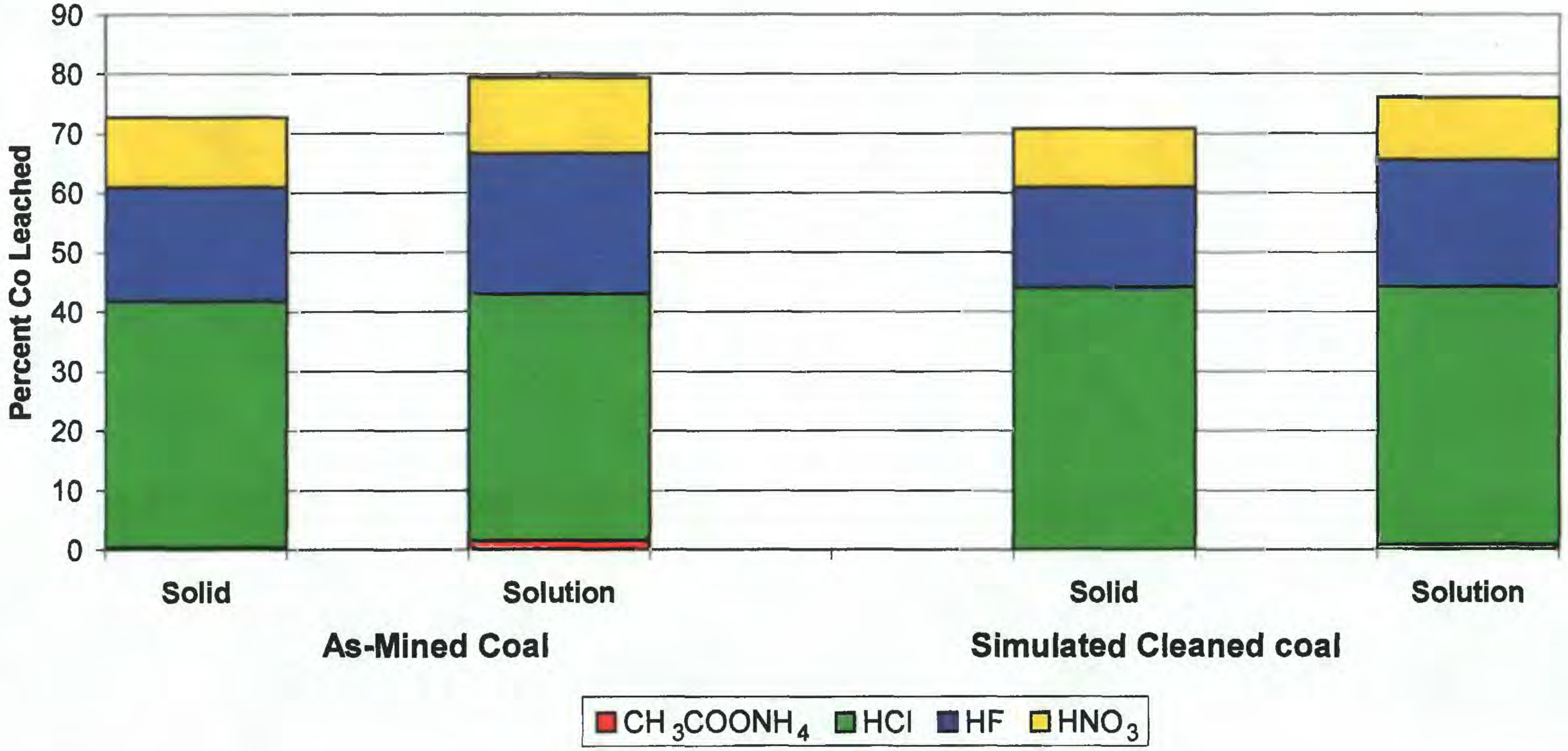

Figure 2. Comparison of average percent Co leached as determined in the solid residues by INAA and as determined by ICP-AES and ICP-MS on the solutions for the as-mined and simulated cleaned coal samples.

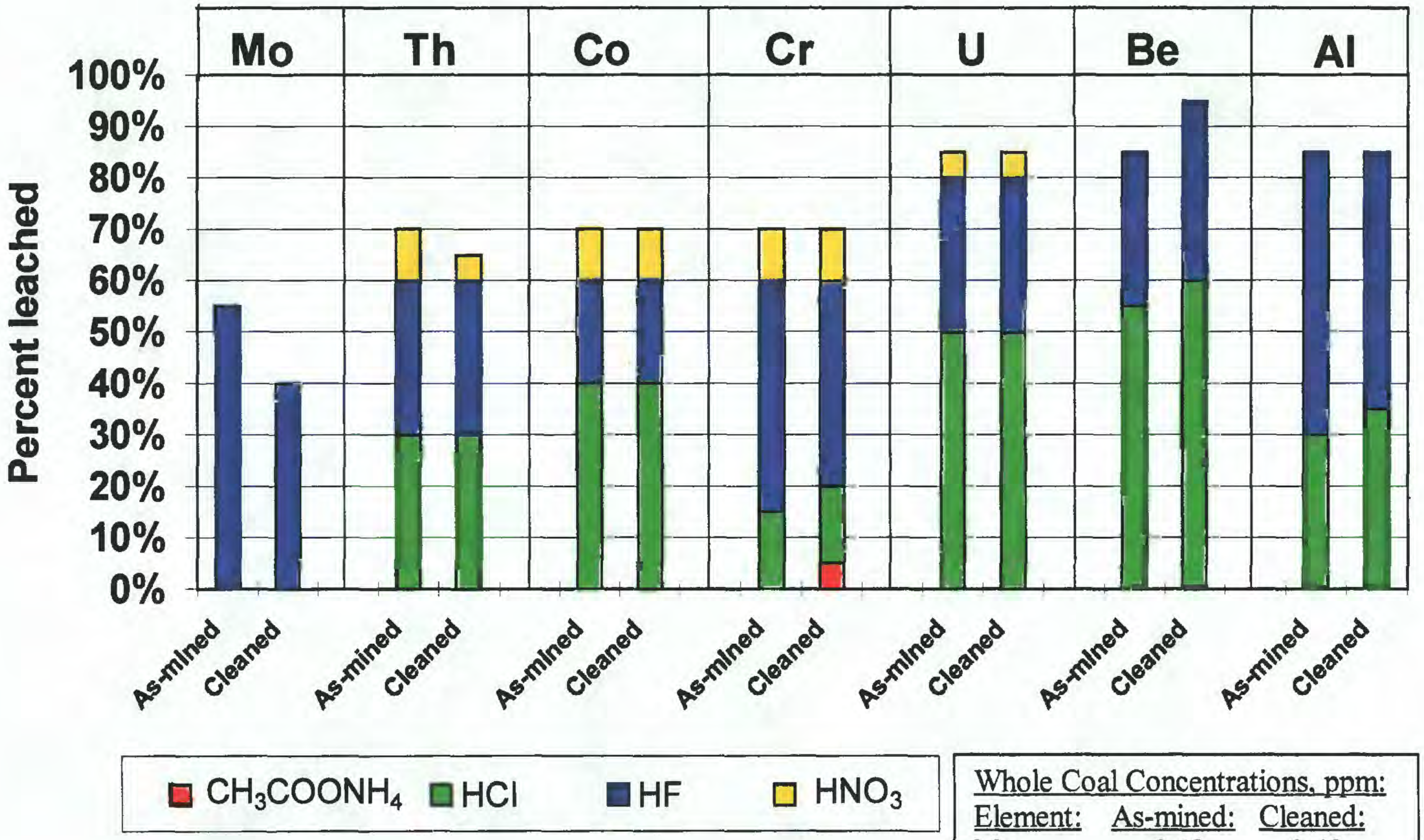

Figure 3: Leaching Data for Mo, Th, Co, Cr, U, Be, and Al. Values rounded to nearest 5 percent

Whole Coal Concentrations, ppm:

Element:	As-mined:	Cleaned:
Mo	0.42	0.49
Th	1.1	1.1
Co	2.5	2.5
Cr	4.1	3.6
U	0.46	0.50
Be	0.19	0.17
Al	5800	4900

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 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 modes of occurrence of U in the as-mined and the simulated cleaned coal are identical. Fifty percent of the U is HCl soluble in both samples, perhaps due to U present in carbonates, iron oxides or chelates. Thirty percent of the U is HF soluble, and is likely present in clays and zircon. Five percent of the U is HNO_3 soluble, perhaps indicating dissolution of U-bearing phosphates, which may be exposed following HF dissolution of encapsulating silicates. Like Th, 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 above discussion of Th). Only 15 percent of the U is unleached, and may be due to partly soluble minerals such as zircon (Table 4), or may be organically bound. The low percentage of organically bound U is somewhat surprising considering its uptake in peat swamps (Zielinski and Meier, 1988), but the total concentration of U is only about 0.5 ppm (Table 3). Some of the HCl soluble U may be in organic chelates so that the total percentage of organically associated U may be higher than indicated by the 15 percent unleached U.

More than 50 percent of each of the seven elements in figure 4 (Ca, Fe, Mn, Ba, Zn, Cd, and Pb), was removed by HCl. An additional 50 percent of the Ca was removed by ammonium acetate. For Fe, Mn, Zn, Ba, Cd, and Pb, less than 25 percent was removed by ammonium acetate, HF and HNO_3. Two major modes of occurrence are proposed for elements removed in the HCl-soluble fractions. For Ca, Fe, Mn, and Ba, HCl-soluble fractions are probably derived from carbonates, although some of the HCl-soluble Fe may be from Fe oxides (identified by SEM, table 1). Although barite was detected by SEM (table 1), less than 2 percent of the Ba in the HCl-soluble fraction can be attributed to barite based on its low solubility (Weast, 1971). The HCl-soluble Zn, Cd, and Pb are likely due to the monosulfides sphalerite (identified by SEM, table 1) and galena, not detected in these coals but commonly found in trace amounts in coal.

Some of the Ca leached by the ammonium acetate is from carbonates, as indicated by Palmer and others (1998). The small amounts of ammonium-acetate-soluble Fe and Mn may also be derived from carbonates. The larger percentages of ammonium-acetate-soluble Ba (20-25 percent) and Ca (50 percent) indicate that portions of these elements are exchangeably bound to organic sites, as is common in low rank coal. Calcite was not detected by XRD

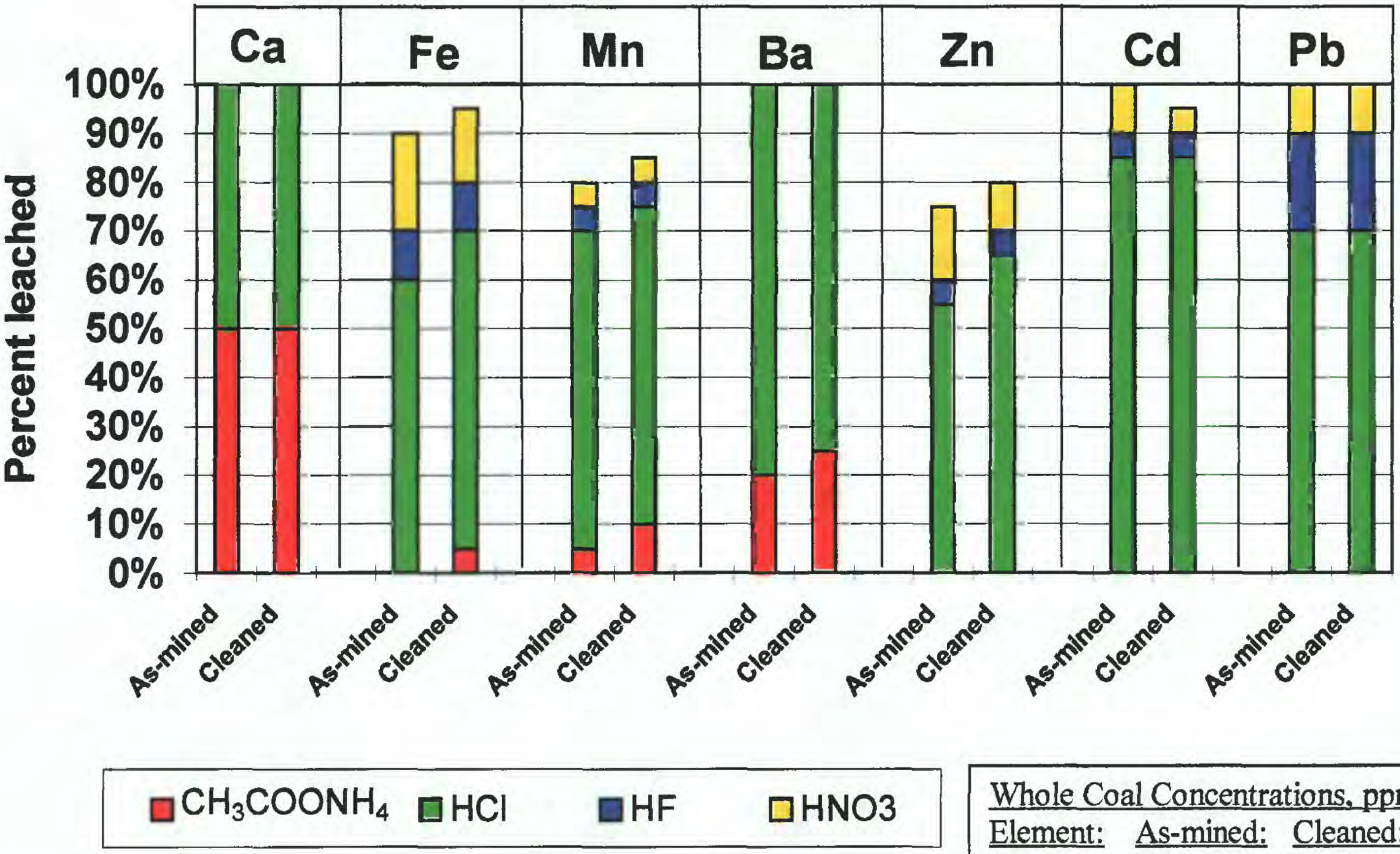

Figure 4: Leaching Data for Ca, Fe, Mn, Ba, Zn, Cd, and Pb. Values rounded to nearest 5 percent

Whole Coal Concentrations, ppm:

Element:	As-mined:	Cleaned:
Ca	9600	9500
Fe	2500	2300
Mn	12	11
Ba	390	370
Zn	16	23
Cd	0.069	0.059
Pb	1.9	1.7

and was only found by SEM in trace amounts in the cleaned coal, indicating that a significant amount of the Ca must be organically associated. A few grains of a Ca-bearing phase, possibly CaF_2 formed by re-precipitation following the HF stage, were by found in the leached residuals (table 4).

The HNO_3-soluble fractions for Fe, Mn, Zn, Cd, and Pb (5 to 20 percent) indicate that these elements are partly associated with pyrite and chalcopyrite, both identified by SEM (table 1).

The small amount of insoluble Fe (5-10 percent) may be due to chemically resistant minerals such as chromite and ilmenite that were found in the unleached coals (table 1), and possibly to chalcopyrite found in the unleached coal and its residue (table 4, fig. 5). Pyrite was not found in the residues. The unleached Mn (15 to 20 percent) and unleached Zn (20-25 percent) in this experiment indicate an organic association for these elements. It is possible that small discrete sphalerite grains could be completely encapsulated by the coal, making them insoluble in this procedure. However, scanning electron microscopy of the leached residues did not detect sphalerite grains (table 4).

More than 50 percent of the Ni and As are insoluble, indicating an organic association (figure 5). The detection of encapsulated chalcopyrite (figure 6) in the residues may account for all of the unleached Cu. The total concentrations of Ni, given in table 3 (about 4 ppm) and As (about 0.5 ppm), are very low compared to the average for U.S. coals. There is usually a finite organic association for most elements in coal. If the total concentration of an element is low, the fraction that is organically bound may be high. Lyons and others (1989) found about 1 ppm As and 2 ppm Ni in vitrinite concentrates with ash yields less than 1 percent. The elements in these concentrates were assumed to be nearly 100 percent organically associated.Forty to sixty percent of the Sb in the PRB samples is organically bound, similar to results from previous studies (Palmer and others, 1998). All elements in figure 5 (Ni, Cu, As, Sb, and Hg) have a significant HNO_3 fraction, indicating a pyrite (or chalcopyrite) association. Up to 55 percent of the Hg and 10 to 15 percent of the Ni, As, and Sb is associated with pyrite. Less than 15 percent of the Ni, As, and Hg is associated with silicates (probably the clays) but 30 percent of the Sb is associated with silicates.

Table 4. SEM examination of leached residues

Sample	R-1	R-2	R-3	R-4	C-1	C-2	C-3	C-4
Leaching effectivness	Very Clean	Clean	Very Clean	Clean	Very Clean	Very Clean	Very Clean	Very Clean
Minerals								
TiO_2	X	X		X	X	X	X	X
Zircon	X			X		X		
Chalcopyrite	X	X	X		X	X	X	X
Barite			X		X			

X = present; Leaching effectiveness:Clean= less than approximately 1 percent of original mineral matter; Very Clean= very much less than 1 percent of original mineral matter. Blank = mineral not present.

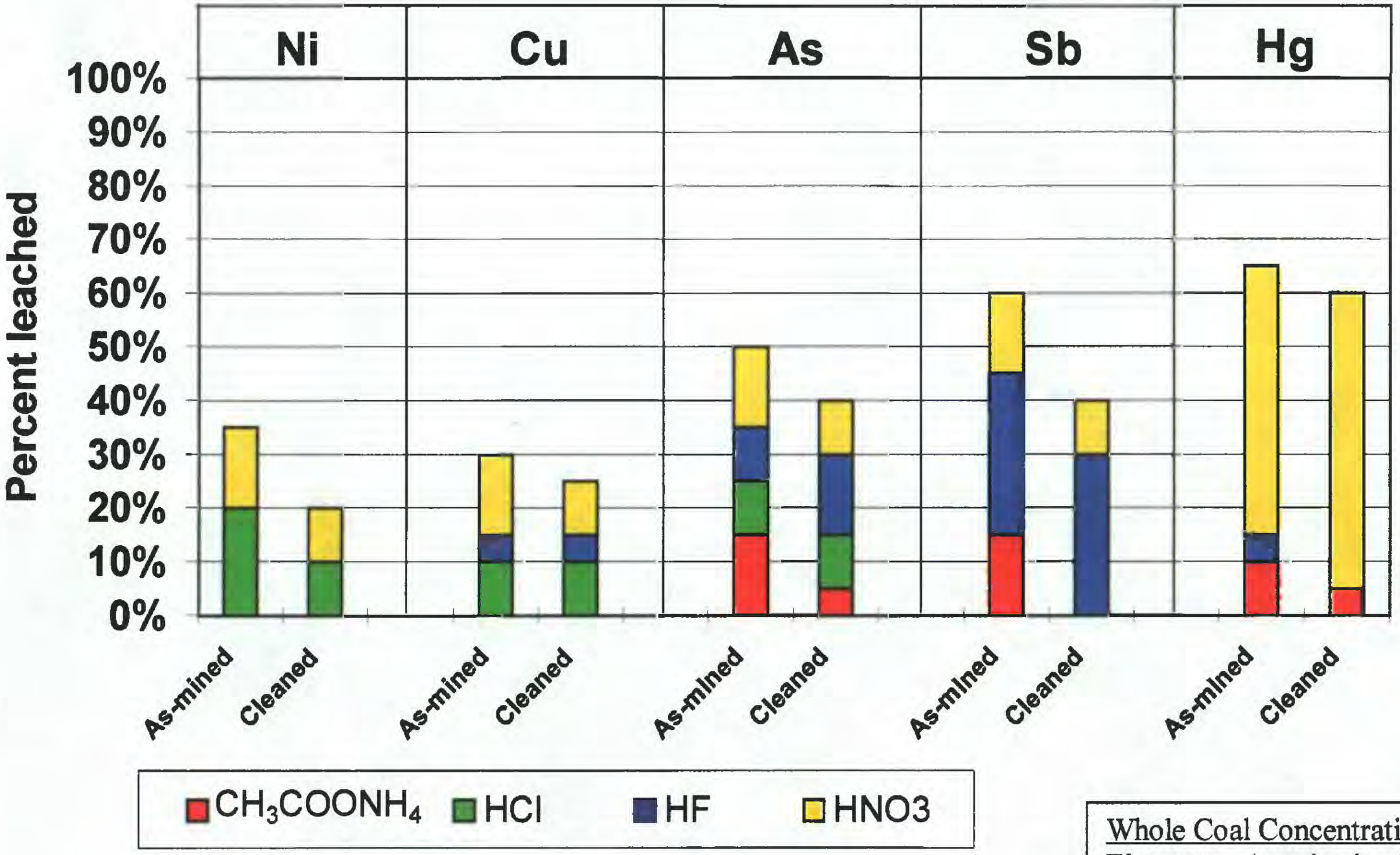

Figure 5: Leaching Data for Ni, Cu, As, Sb, and Hg. Values rounded to nearest 5 percent.

Whole Coal Concentrations, ppm:

Element:	As-mined:	Cleaned:
Ni	4.0	3.7
Cu	14	12
As	0.65	0.50
Sb	0.15	0.14
Hg	0.08	0.08

Examination of residual leached material

Sample pellets made from solid residues of the HNO_3 leach were examined using SEM to determine if any mineral matter survived the leaching process. Table 4 shows the results of SEM examination of each of the as-mined (R-1 through R-4), and simulated cleaned (C-1 through C-4) solid residue sample splits. The effectiveness of the leaching procedure was assessed qualitatively, and samples were described as "clean" if less than 1 percent of the original mineral matter was estimated to be present and "very clean" if much less than 1 percent of the original mineral matter was estimated to be present. Figure 6 is a SEM view of the as-mined residual, showing a rare chalcopyrite grain in a matrix that has no other visible mineral grains. Based SEM analysis, TiO_2 (rutile or anatase), zircon, chalcopyrite, and barite are the most common phases to survive the leaching process. Zircon and TiO_2 are known to be highly insoluble. Trace amounts of KCl and CaF_2, thought to be formed during leaching with HCl and HF, respectively, were also observed, in addition to occasional materials added in the polishing process such as Al_2O_3, SiC, and/or colloidal Si.

Figure 6. SEM backscattered electron image of leached residue of the as-mined sample R-1 (table 4) showing a grain of chalcopyrite (white) in a field of organic matter (dark gray)

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 5 shows the percentage of 19 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.

Comparison of results with PRB samples studied previously.

Table 6 shows a comparison of the as-mined coal investigated in this study with two as-mined PRB coals (R1 and R2) reported by Palmer and others, (1998). The general uniformity of composition is somewhat remarkable considering that the samples are from two different seams and from three different locations in the basin and have different ash contents. For the 13 elements common to both studies, concentrations of the elements are generally within a factor of 2 or 3 of one another, except the concentration of Mn in R1, which is more than 10 times higher than in the other samples. The as-mined coal in this study is from the Wyodak seam as is R2 from the previous study. R1 has the highest ash yield, 11.3 weight percent, and is from the Rosebud seam in the northern part of the basin. R1 has the highest concentrations of Fe, As, Pb, Ni, Mn, Be, Sb, Th, and U, and the lowest concentrations of Cr and Zn. The as-mined sample in this study has the lowest ash yields, the lowest concentrations of Fe, As, Pb, Ni, Mn, Be, Sb, Th, and U, and the highest concentrations of Cr and Zn. Hg has essentially the same values for all samples. The concentrations of Co in R1 and R2 are essentially the same but the concentration of Co in the as-mined sample is higher.

For Fe, Cr, Co, Mn, Be, and Sb, the amount leached from the as-mined coal was within 20 percent (absolute) of the amount leached by each solvent for R1 and R2. This indicates that the modes of occurrence of these elements in these samples are very similar. Other elements were not as consistent in their leaching behavior. The modes of occurrence were generally not related to ash yields or location within the basin.

Conclusions

There is little difference in the concentration or the modes of occurrence of trace elements between the as-mined coal and the corresponding simulated cleaned coal. The concentration of most elements was about 6 percent higher in the PRB as-mined coal than the simulated cleaned coal product and the ash yields were almost identical.

Table 5. Modes of Occurrence of Trace Elements in Powder River Basin Coal

Molybdenum

	Silicates	Organics
As-Mined	55%	45%
Simulated cleaned coal	40%	60%

Thorium

	Phosphates	HCl Soluble	Silicates	Insoluble
As-Mined	10%	30%	30%	30%
Simulated cleaned coal	5%	30%	30%	35%

Cobalt

	Pyrite	HCl Soluble	Silicates	Organics
As-Mined	10%	40%	20%	30%
Simulated cleaned coal	10%	45%	20%	30%

Chromium

	Pyrite	Oxyhydroxides	Illite	Organics
As-Mined	10%	10%	45%	30%
Simulated cleaned coal	10%	10%	40%	35%

Uranium

	Oxides	HCl Soluble	Silicates	Organics
As-Mined	5%	50%	30%	15%
Simulated cleaned coal	5%	50%	30%	15%

Beryllium

	Oxides/Hydroxides	Silicates	Organics
As-Mined	55%	10%	10%
Simulated cleaned coal	60%	10%	15%

Table 5. Modes of Occurrence of Trace Elements in Powder River Basin Coal (Continued).

Aluminum

	Oxides/Carbonates	Silicates	Organics
As-Mined	30%	55%	15%
Simulated cleaned coal	35%	50%	15%

Calcium

	Exchangeable/Carbonates
As-Mined	100%
Simulated cleaned coal	100%

Iron

	Pyrite	Oxides/Carbonates	Silicates	Organics
As-Mined	20%	60%	10%	10%
Simulated cleaned coal	15%	70%	10%	5%

Manganese

	Pyrite	Carbonates	Silicates	Organics
As-Mined	5%	70%	5%	20%
Simulated cleaned coal	5%	75%	5%	15%

Barium

	Oxides/Carbonates	Barite
As-Mined	100%	< 1%
Simulated cleaned coal	100%	< 1%

Zinc

	Pyrite	Sphalerite	Silicates	Organics
As-Mined	15%	55%	5%	25%
Simulated cleaned coal	10%	65%	5%	20%

Table 5. Modes of Occurrence of Trace Elements in Powder River Basin Coal (continued).

Cadmium

	Pyrite	Sphalerite	Silicates	Organics
As-Mined	10%	85%	5%	0%
Simulated cleaned coal	5%	85%	5%	5%

Lead

	Pyrite	Galena	Silicates
As-Mined	10%	70%	20%
Simulated cleaned coal	10%	70%	20%

Nickel

	Sulfides	Ni oxides	Organics
As-Mined	15%	20%	65%
Simulated cleaned coal	10%	10%	80%

Copper

	Chalcopyrite/pyrite	Oxides/Carbonates	Silicates
As-Mined	85%	10%	5%
Simulated cleaned coal	85%	10%	5%

Arsenic

	Pyrite	Arsenates	Silicates	Organics
As-Mined	15%	10%	10%	65%
Simulated cleaned coal	10%	10%	15%	65%

Antimony

	Pyrite	Silicates	Organics
As-Mined	15%	30%	55%
Simulated cleaned coal	10%	30%	60%

Mercury

	Pyrite	Organic	Silicates
As-Mined	50%	45%	5%
Simulated cleaned coal	55%	45%	0%

Table 6. Element concentrations and modes of occurrence of the as-mined coal sample in this study ("As-mined") compared to similar data for the as-mined Powder River Basin samples ("R1" and "R2") previously reported by Palmer and others (1998).

	Fe	Hg	As	Cr	Pb	Co	Ni	Mn	Be	Zn	Sb	Th	U
Original Concentration (ppm)													
As-Mined	2500	0.07	0.65	4.1	1.9	2.5	4	12	0.19	16.4	0.15	1.1	0.46
R1	4500	0.07	1.5	3.9	2.3	1.6	5.7	150	0.5	6.8	0.31	2.2	1.2
R2	2500	0.08	1.2	6	1.6	1.5	5.1	8.7	0.4	8.1	0.24	1.8	0.66
Percent leached by CH_3COONH_4													
As-Mined	0	10	15	0	0	0	0	5	0	0	15	0	0
R1	5	5	5	0	0	0	0	5	0	10	0	0	0
R2	0	0	0	0	---	0	10	10	---	10	5	5	0
Percent leached by HCl													
As-Mined	60	0	10	15	70	40	20	65	55	55	0	30	50
R1	65	30	30	10	25	60	40	70	55	25	0	20	40
R2	60	0	35	10	---	40	10	75	---	35	5	5	25
Percent leached by HF													
As-Mined	10	5	10	45	20	20	0	5	30	5	30	30	30
R1	25	5	15	45	5	15	30	0	25	35	40	35	30
R2	10	0	10	45	---	20	15	15	---	20	40	10	50
Percent leached by HNO_3													
As-Mined	20	50	15	10	10	10	15	5	0	15	15	10	5
R1	0	25	15	10	5	5	20	0	20	10	15	10	5
R2	20	0	0	10	---	5	10	0	---	0	0	40	5
Percent unleached													
As-Mined	25	35	50	30	0	20	65	20	15	25	40	30	15
R1	20	35	35	35	65	20	10	25	0	20	45	35	25
R2	10	100	55	35	---	35	55	0	---	35	50	40	20

All three samples were ashed at 550° C to determine elemental concentrations by ICP-AES and ICP-MS. The ash yield for the as-mined coal was 5.95 percent, for R1, 11.3 percent, and for R2, 7.3 percent.

For 13 of the 19 elements, greater than 40 percent of the amount leached was removed by HCl, which indicated carbonate and monosulfide associations. Greater than 20 percent of the Mo, Th, Co, Cr, U, Be, Pb and Sb were associated with silicates. Greater than 40 percent of the Mo, Ni, As, Sb, and Hg were organically associated. Very little of the As was associated with the pyrite, but more than 50 percent of the Hg was associated with pyrite.

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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: $(K,H_3O)(Al, Mg, Fe)_2(Si,Al)_4O_{10}[(OH)_2H_2O]$
Pyrite	FeS_2

Trace Minerals

Ankerite	$Ca(Fe,Mg)(CO_3)_2$	Fluorite	CaF_2
Apatite	$Ca_5((F,Cl,OH)(PO_4)_3$	Gibbsite	$Al(OH)_3$
Barite	$BaSO_4$	Hematite	Fe_2O_3
Bassanite	$CaSO_4 \cdot ½ H_2O$	Illmenite	$FeTiO_3$
Calcite	$CaCO_3$	Monazite	$(Ce,La,Y, Th)PO_4$
Chalcopyrite	$CuFeS_2$	Siderite	$FeCO_3$
Chromite	$FeCr_2O_4$	Sphalerite	ZnS
Crandelite	$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$	Zircon	$ZrSiO_4$
Dolomite	$(Ca,Mg)(CO_3)_2$		

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

Abbreviations

$K\alpha$	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)
$^{\circ}2\theta$	degrees 2 theta (measurement of angle of x-ray peaks in XRD)
AA	atomic absorption
amp	ampere
ANK	ankerite (See mineral list above)
APA	apatite (See mineral list above)
ASTM	American Society for Testing Materials
BAS	bassanite (See mineral list above)
BSE	backscattered electron imaging
CVAA	cold vapor atomic absorption
CONT.	contamination
CRADA	Cooperative research and development agreement
CH_3COONH_4	ammonium acetate
CVAA	cold vapor atomic absorption
DOL	dolomite (See mineral list above)
EDX	Energy Dispersive X-ray
ETEC Autoscan	model of a scanning electron microscope used in this study
g	grams
HAPs	hazardous air pollutants
HCl	hydrochloric acid
HEM	hematite (See mineral list above)
HF	hydrofluoric acid
HGAA	hydride generation atomic absorption
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
PRB	Powder River Basin
PY	pyrite (see mineral list above)
QTZ	quartz (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

Weight % Group : Kolker Dec 10, 1999 Pyrite

Grain	Fe	S	As	Ni	Se	Zn	Co	Cu	Total	Comment	Size micrometers Form
1	47.10	52.45	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	99.60	60meshAs-mined 1.1	15x25
1	46.90	55.58	d.l.	d.l.	0.01	d.l.	d.l.	d.l.	102.54	60meshAs-mined 1.2	subhedral
2	45.61	51.85	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	97.51	60meshAs-mined 2.1	25x30
2	46.83	51.06	d.l.	0.01	0.01	d.l.	0.02	d.l.	97.97	60meshAs-mined 2.2	irregular
2	43.91	50.10	d.l.	d.l.	d.l.	0.01	d.l.	d.l.	94.06	60meshAs-mined 2.3	
3	46.58	55.20	d.l.	0.01	d.l.	d.l.	d.l.	d.l.	101.83	60meshAs-mined 4.1	30x90
3	46.64	55.32	d.l.	d.l.	d.l.	0.02	d.l.	d.l.	102.02	60meshAs-mined 4.2	subhedral
3	46.83	55.44	d.l.	0.01	d.l.	d.l.	d.l.	d.l.	102.31	60meshAs-mined 4.3	
3	47.23	55.79	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	103.07	60meshAs-mined 4.4	
3	47.01	55.64	d.l.	d.l.	0.02	d.l.	0.01	d.l.	102.71	60meshAs-mined 4.5	
4	45.52	55.36	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	100.93	60meshAs-mined 5.1	10x15
4	46.20	55.68	d.l.	0.01	d.l.	d.l.	d.l.	d.l.	101.93	60meshAs-mined 5.2	anhedral
5	45.55	54.22	d.l.	0.11	d.l.	d.l.	d.l.	0.01	99.95	60meshAs-mined 7.1	10x40
5	44.19	54.05	0.01	0.17	d.l.	d.l.	d.l.	0.02	98.48	60meshAs-mined 7.2	cleat
5	43.42	54.46	d.l.	0.16	0.01	d.l.	d.l.	0.01	98.11	60meshAs-mined 7.3	
6	46.25	54.27	d.l.	d.l.	d.l.	0.01	d.l.	d.l.	100.58	60meshAs-mined 8.1	30x60
6	46.43	54.39	0.01	d.l.	0.02	d.l.	d.l.	d.l.	100.89	60meshAs-mined 8.2	subhedral
6	46.65	53.70	0.01	d.l.	d.l.	0.02	0.01	0.01	100.45	60meshAs-mined 8.3	
6	47.01	54.24	d.l.	0.01	d.l.	0.01	d.l.	d.l.	101.33	60meshAs-mined 8.4	
6	46.72	54.28	d.l.	d.l.	d.l.	0.02	d.l.	d.l.	101.08	60meshAs-mined 8.5	
7	47.12	53.88	d.l.	0.03	0.01	d.l.	0.01	d.l.	101.09	60meshAs-mined 9.1	20x40
7	46.39	54.09	d.l.	0.03	d.l.	0.01	d.l.	d.l.	100.57	60meshAs-mined 9.2	subhedral

Appendix 2: Quantitative microprobe analyses (continued).

Grain	Fe	S	As	Ni	Se	Zn	Co	Cu	Total	Comment
8	47.05	55.73	d.l.	0.01	d.l.	d.l.	0.01	d.l.	102.84	60mesh As-mined 10.1 15x50
8	47.65	55.54	d.l.	d.l.	d.l.	0.01	d.l.	d.l.	103.24	60mesh As-mined 10.2 cleat?
8	46.68	56.08	d.l.	0.01	0.01	d.l.	d.l.	0.01	102.84	60mesh As-mined 10.3
9	41.90	48.10	d.l.	d.l.	d.l.	0.01	d.l.	d.l.	90.05	60mesh As-mined 11.1 10x20
9	45.34	53.17	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	98.56	60mesh As-mined 11.2 cleat?
10	46.80	54.30	d.l.	d.l.	d.l.	0.02	d.l.	d.l.	101.17	60mesh As-mined 12.1 50x90
10	46.50	53.67	0.01	0.01	d.l.	d.l.	0.01	d.l.	100.25	60mesh As-mined 12.2 anhedral
10	46.76	53.48	d.l.	d.l.	0.02	0.01	0.02	d.l.	100.34	60mesh As-mined 12.3 (oval)
10	47.03	53.31	d.l.	0.01	d.l.	0.01	d.l.	d.l.	100.41	60mesh As-mined 12.4
10	46.92	54.22	0.01	d.l.	d.l.	d.l.	d.l.	d.l.	101.20	60mesh As-mined 12.5
10	47.24	53.75	d.l.	0.02	d.l.	0.02	d.l.	0.01	101.07	60mesh As-mined 12.6
1C	46.91	53.65	d.l.	d.l.	d.l.	d.l.	0.01	0.02	100.64	60mesh Cleaned 2.1 10x60
1C	46.49	53.69	d.l.	d.l.	0.01	d.l.	d.l.	d.l.	100.24	60mesh Cleaned 2.2 irregular or
1C	46.41	55.07	d.l.	d.l.	d.l.	0.01	0.01	d.l.	101.57	60mesh Cleaned 2.3 cleat
2C	45.39	52.77	d.l.	d.l.	0.01	d.l.	d.l.	0.01	98.22	60mesh Cleaned 3.1 20x20
2C	46.13	53.13	d.l.	d.l.	0.01	0.01	0.01	0.02	99.35	60mesh Cleaned 3.2 subhedral
3C	46.55	54.37	d.l.	d.l.	d.l.	0.02	d.l.	0.01	100.99	60mesh Cleaned 4.1 30x70
3C	46.41	54.51	d.l.	d.l.	d.l.	d.l.	0.02	d.l.	100.99	60mesh Cleaned 4.2 subhedral
3C	46.17	53.91	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	100.13	60mesh Cleaned 4.3
3C	46.81	54.28	d.l.	d.l.	d.l.	0.01	d.l.	d.l.	101.15	60mesh Cleaned 4.4
4C	45.15	56.20	d.l.	d.l.	d.l.	0.02	d.l.	d.l.	101.41	60mesh Cleaned 6.1 7x15
4C	44.42	55.61	d.l.	0.02	d.l.	0.01	d.l.	d.l.	100.11	60mesh Cleaned 6.2 cleat?

Appendix 2: Quantitative microprobe analyses (continued).

No.	Fe	S	As	Ni	Se	Zn	Co	Cu	Total	Comment	
5C	46.55	54.34	d.l.	d.l.	0.01	d.l.	d.l.	0.02	100.95	60mesh Cleaned 7.1	25x70
5C	46.85	54.53	d.l.	0.01	d.l.	d.l.	d.l.	d.l.	101.45	60mesh Cleaned 7.2	cleat?
5C	46.91	54.75	d.l.	d.l.	d.l.	0.02	d.l.	0.01	101.74	60mesh Cleaned 7.3	
5C	46.62	54.41	d.l.	d.l.	0.01	0.02	d.l.	0.02	101.12	60mesh Cleaned 7.4	
5C	46.94	54.56	d.l.	d.l.	0.01	d.l.	0.01	d.l.	101.56	60mesh Cleaned 7.5	
6C	44.66	51.35	d.l.	0.01	d.l.	0.02	d.l.	0.01	96.09	60mesh Cleaned 8.2	5X50 cleat
7C	46.14	55.10	d.l.	0.01	d.l.	d.l.	d.l.	d.l.	101.30	60mesh Cleaned 9.1	12x100
7C	45.99	52.01	d.l.	0.01	0.01	0.02	d.l.	0.01	98.09	60mesh Cleaned 9.2	cleat
7C	46.17	52.04	d.l.	0.02	d.l.	0.02	0.01	d.l.	98.30	60mesh Cleaned 9.3	
7C	46.39	53.00	d.l.	0.01	d.l.	0.03	d.l.	d.l.	99.47	60mesh Cleaned 9.4	
8C	46.00	53.66	d.l.	0.01	d.l.	d.l.	d.l.	d.l.	99.72	60mesh Cleaned 10.1	20x45
8C	44.73	53.78	d.l.	0.01	d.l.	0.01	d.l.	0.01	98.59	60mesh Cleaned 10.2	cleat?
8C	45.96	54.17	d.l.	d.l.	d.l.	0.01	d.l.	d.l.	100.18	60mesh Cleaned 10.3	
9C	46.62	53.85	d.l.	0.01	d.l.	d.l.	0.01	0.01	100.55	60mesh Cleaned 11.1	15x40
9C	47.29	53.87	d.l.	d.l.	d.l.	0.01	d.l.	0.01	101.22	60mesh Cleaned 11.2	irregular
9C	46.17	53.71	d.l.	d.l.	d.l.	0.04	0.01	d.l.	99.98	60mesh Cleaned 11.3	

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 3: Data from individual splits

For quality control purposes, the samples in Appendix 3 are identified by the two digit sample set number after the sample name so that individual samples can be matched with blind quality control samples (table A4-1) and USGS quality control samples (table A4-2) analyzed in the same sample set. For example, As-mined 56, were analyzed with 67799 56, 67999 56, 68099 56 (table A4-1) and CLB-1 56 (table A4-2). A letter after the run number identifies a split for samples run in duplicate in the same sample set. For example "Cleaned 46a and Cleaned 46b are duplicate simulated cleaned coal samples analyzed in the same sample set "46".

The "best as-mined" values and the "best cleaned" 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.

APPENDIX 3. Data for individual splits.

Variables:	Si	Al	Fe	Mg	Ca	Na	K	Ti	P
units (%= weight percent):	%	%	%	%	%	%	%	%	%
Powder River Basin Coal (as-mined)									
As- Mined 56			0.248			0.072	0.033		
Analytical uncertanity 56:			0.009			0.002	0.005		
As-Mined 57			0.236			0.073	0.025		
Analytical uncertanity 57:			0.012			0.002	0.003		
Best Value INAA	ND	ND	0.24	ND	ND	0.072	0.029	ND	ND
Estimated INAA analytical uncertanity			0.012			0.002	0.004		
As-Mined 46	1.12	0.58	0.26	0.22	0.92	0.085	0.027	0.055	0.050
As-Mined 31	1.08	0.58	0.26	0.23	0.99	0.081	0.024	0.056	0.047
Best Value other techniques	1.10	0.58	0.26	0.22	0.96	0.085	0.025	0.055	0.049
Estimated other techniques analytical uncertanity	0.11	0.06	0.03	0.02	0.10	0.008	0.003	0.006	0.005
Best as-mined value	1.10	0.58	0.25	0.22	0.96	0.076	0.025	0.055	0.049
Estimated as-mined Analytical uncertanity	0.11	0.06	0.02	0.02	0.10	0.09	0.004	0.006	0.005
Simulated cleaned coal									
Cleaned 62a			0.216			0.072	0.017		
Analytical uncertanity 62a:			0.005			0.001	0.002		
Cleaned 62b			0.217			0.073	0.014		
Analytical uncertanity 62b:			0.005			0.002	0.002		
Cleaned 60			0.213			0.070	<0.11		
Analytical uncertanity 60:			0.005			0.002			
Cleaned 61			0.216			0.070	<0.1		
Analytical uncertanity 61:			0.006			0.002			
Best Value INAA	ND	ND	0.215	ND	ND	0.071	0.015	ND	ND
Estimated INAA analytical uncertanity			0.005			0.002	0.002		
Cleaned 46a	0.86	0.50	0.24	0.21	0.94	0.067	0.017	0.050	0.045
Cleaned 46b	0.81	0.48	0.24	0.21	0.96	0.065	0.016	0.048	0.047
Best Value Other Techniques	0.84	0.49	0.24	0.21	0.95	0.066	0.016	0.049	0.046
Estimated other technique analytical uncertanity	0.08	0.05	0.02	0.02	0.10	0.007	0.002	0.005	0.005
Best cleaned value	0.84	0.49	0.23	0.21	0.95	0.070	0.016	0.049	0.046
Estimated cleaned analytical uncertanity	0.08	0.05	0.02	0.02	0.10	0.006	0.002	0.005	0.005

Key: ND=Not determined; CONT.= Contaminated; Analytical uncertanity= ± absolute ICP-acid ICP-sinter ICP-MS HGAA CVAA INAA IC

APPENDIX 3. Data for individual splits (continued).

Variables:	Li	Be	B	Cl	Sc	V	Cr	Mn	Co
units (ppm =parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Powder River Basin Coal (As-Mined)									
As- Mined 56					1.41		3.88		2.38
Analytical uncertanity 56:					0.04		0.61		0.07
As-Mined 57					1.40		4.25		2.45
Analytical uncertanity 57:					0.028		0.71		0.07
Best Value INAA	ND	ND	ND	ND	1.41	ND	4.1	ND	2.42
Estimated INAA analytical uncertanity					0.034		0.66		0.068
As-Mined 46	1.9	0.19	29	< 200	1.5	14	4.0	12	2.9
As-Mined 31	2.0	0.19	28	< 200	1.5	14	4.0	12.3	2.9
Best Value Other Techniques	1.9	0.19	28	< 150	1.5	14	4.1	11.6	3.1
Estimated other technique analytical uncertanity	0.19	0.019	3			1.4	0.4	1.2	0.3
Best as-mined value	1.9	0.19	28	< 150	1.4	14	4.1	12	2.5
Estimated as-mined analytical uncertanity	0.08	0.02	3		0.1	0.7	0.3	0.5	0.6
Simulated Cleaned Coal									
Cleaned 62a					1.34		3.78		2.40
Analytical uncertanity 62a:					0.02		0.18		0.04
Cleaned 62b					1.35		3.71		2.42
Analytical uncertanity 62b:					0.02		0.35		0.06
Cleaned 60					1.40		3.76		2.58
Analytical uncertanity 60:					0.02		0.22		0.06
Cleaned 61					1.38		3.71		2.54
Analytical uncertanity 61:					0.03		0.27		0.06
Best Value INAA	ND	ND	ND	ND	1.35	ND	3.7	ND	2.41
Estimated INAA analytical uncertanity					0.02		0.3		0.05
Cleaned 46a	1.9	0.18	25	2543	1.35	14	3.6	11	3.1
Cleaned 46b	2.0	0.17	25	2083	1.24	13	3.6	10	3.0
Best Value Other techniques	2.0	0.60	25	CONT.	1.35	13	3.6	11	3.1
Estimated other technique analytical uncertanity	0.2	0.02	2		0.14	1	0.36	1	0.3
Best cleaned value	2.0	0.17	25	CONT.	1.35	13	3.6	11	2.5
Estimated cleaned analytical uncertanity	0.2	0.02	2		0.02	1	0.3	1	0.6

Key: ND=Not determined; CONT.= Contaminated; Analytical uncertinity= ± absolute ICP-acid ICP-sinter ICP-MS HGAA CVAA INAA IC

APPENDIX 3. Data for individual splits (continued).

variables:	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb
units (ppm =parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Ppm
Powder River Basin Coal									
As- Mined 56	< 8		15			0.59	< 1.2	5.02	< 2
Analytical uncertanity 56:			1			0.06		0.17	
As-Mined 57	< 10		17			0.647	< 1.3	4.39	< 3
Analytical uncertanity 57:			2			0.050		0.14	
Best Value INAA	< 8	ND	16.5	ND	ND	0.62	< 1.2	4.7	< 2
Estimated INAA analytical uncertanity			1.5			0.056		0.32	
As-Mined 46	3.9	13	16.3	1.9	0.4	0.72	0.25		1.2
As-Mined 31	4.0	13.7	16.4	1.9	0.36	0.75	< 0.13		1.2
Best Value Other Techniques	4.0	13.5	16.3	1.9	0.35	0.73	0.25	ND	1.2
Estimated Other technique analytical uncertanity	0.4	1.4	1.6	0.1	0.02	0.037	0.01		0.06
Best as-mined value	4.0	14	16.4	1.9	0.35	0.65	0.25	4.7	1.2
Estimated as-mined analytical uncertanity	0.4	1	1.5	0.1	0.2	0.09	0.01	0.3	0.06
Simulated cleaned coal									
Cleaned 62a	5		22			0.59	0.57	386	< 1.2
Analytical uncertanity 62a:	2		1.2			0.06	0.17	6	
Cleaned 62b	<12		23			0.60	0.35	372	< 1.2
Analytical uncertanity 62b:			1.4			0.10	0.11	9	
Cleaned 60	<9		23			<1.4	<0.6	1730	< 1.6
Analytical uncertanity 60:			1			0		44	
Cleaned 61	<10		26			<1	<0.6	1623	<2.1
Analytical uncertanity 61:			1			0		43	
Best Value INAA	5.0	ND	22.5	ND	ND	0.59	0.46	CONT.	< 2
Estimated INAA analytical uncertanity	1.6		1.3			0.08	0.14		
Cleaned 46a	3.7	13	24	1.5	0.31	0.284	0.40		0.49
Cleaned 46b	3.7	12	23	1.5	0.31	0.389	0.26		0.50
Best Value Other Techniques	3.7	12	24	1.5	0.31	0.34	0.33	ND	0.5
Estimated Other technique analytical uncertanity	0.4	1.2	2.4	0.08		0.02	0.08		
Best cleaned value	3.7	12	23	1.5	0.31	0.5	0.4	CONT.	0.5
Estimated cleaned analytical uncertanity	0.5	1.2	1	0.08		0.2	0.1		

Key: ND=Not determined, CONT.= Contaminated; Analytical uncertanity =± absolute ICP-acid ICP-sinter ICP-MS HGAA CVAA INAA IC

APPENDIX 3. Data for individual splits (continued).

variables:	Sr	Y	Zr	Mo	Cd	Sn	Sb	Cs	Ba
units (ppm =parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Powder River Basin Coal									
As- Mined 56	236			< 3			0.16	0.16	397
Analytical uncertanity 56:	14						0.04	0.01	26
As-Mined 57	238			< 0.16			0.14	0.225	377
Analytical uncertanity 57:	20						0.02	0.037	19
Best Value INAA	237	ND	ND	< 0.16	ND	ND	0.15	0.19	387
Estimated INAA analytical uncertanity	17						0.029	0.034	22
As-Mined 46	221	2.7	16	0.44	0.073	< 0.2	0.16	0.13	391
As-Mined 31	222	2.7	16	0.40	0.064	0.5	0.14	0.12	394
Best Value Other Techniques	221	2.7	16	0.42	0.069	0.51	0.15	0.13	392
Estimated Other technique analytical uncertanity	22	0.3	2	0.02	0.005	0.03	0.01	0.01	39
Best as-mined value	221	2.7	16	0.42	0.069	0.51	0.15	0.16	390
Estimated as-mined analytical uncertanity	22	0.3	2	0.02	0.005	0.03	0.007	0.04	30
Simulated cleaned coal									
Cleaned 62a	240			<1.3			0.13	0.16	405
Analytical uncertanity 62a:	10						0.01	0.01	13
Cleaned 62b	240			<1.4			0.16	0.17	374
Analytical uncertanity 62b:	14						0.02	0.02	25
Cleaned 60	259			ND			<0.22	0.17	399
Analytical uncertanity 60:	14							0.02	21
Cleaned 61	245			<5			0.17	0.20	407
Analytical uncertanity 61:	14						0.02	0.02	21
Best Value INAA	240	ND	ND	< 1.3	ND		0.14	0.16	389
Estimated INAA analytical uncertanity	12						0.02	0.01	19
Cleaned 46a	206	2.5	16	0.48	0.058	0.35	0.12	0.15	369
Cleaned 46b	212	2.4	15	0.50	0.06	0.84	0.13	0.16	363
Best Value Other Techniques	210	2.5	15	0.49	0.059	0.6	0.13	0.16	366
Estimated Other technique analytical uncertanity	21	0.2	2		0.005	0.3	0.1	0.008	37
Best cleaned value	210	2.5	15	0.49	0.059	0.6	0.14	0.16	370
Estimated cleaned analytical uncertanity	21	0.2	1.550		0.005	0.3	0.1	0.01	20

Key: ND=Not determined, CONT.= Contaminated; Analytical uncertanity = ± absolute ICP-acid ICP-sinter ICP-MS HGAA CVAA INAA IC

APPENDIX 3. Data for individual splits (continued).

variables:	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
units (ppm =parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Powder River Basin Coal								
As- Mined 56	4.03	6.53	< 8	0.66	0.14	0.085	0.27	0.037
Analytical uncertainty 56:	0.12	0.47		0.02	0.01	0.007	0.04	0.006
As-Mined 57	4.14	7.04	< 8	0.687	0.154	0.057	0.256	0.041
Analytical uncertainty 57:	0.12	0.38		0.021	0.011	0.009	0.037	0.005
Best Value INAA	4.1	6.8	< 8	0.671	0.149	0.071	0.26	0.039
Estimated INAA Analytical uncertanity	0.12	0.43		0.021	0.010	0.016	0.04	0.006
As-Mined 46								
As-Mined 31								
Best Value Other Techniques	ND	ND	ND	ND	ND	ND	ND	ND
Estimated Other technique analytical uncertanity								
Best as-mined value	4.1	6.8	< 8	0.67	0.15	0.07	0.26	0.04
Estimated as-mined analytical uncertanity	0.1	0.4		0.02	0.01	0.02	0.04	0.01
Simulated cleaned coal								
Cleaned 62a	3.84	5.68	< 23	0.68	0.14	0.078	0.25	0.041
Analytical uncertanity 62a:	0.08	0.18	0.00	0.02	0.00	0.004	0.03	0.003
Cleaned 62b	3.92	5.85	<19	0.68	0.13	0.081	0.30	0.039
Analytical uncertanity 62b:	0.12	0.32		0.03	0.01	0.006	0.05	0.004
Cleaned 60	3.9	6.7	<16	0.65	0.150	0.072	<1.4	0.043
Analytical uncertanity 60:	0.2	0.3		0.06	0.007	0.005		0.008
Cleaned 61	3.9	7.0	<21	0.68	0.144	0.081	<0.4	0.030
Analytical uncertanity 61:	0.2	0.4		0.04	0.008	0.007		0.005
Best Value INAA	3.88	5.77	< 16	0.68	0.136	0.080	0.27	0.040
Estimated INAA analytical uncertanity	0.10	0.25		0.02	0.006	0.005	0.04	0.003
Cleaned 46a								
Cleaned 46b								
Best Value Other Techniques	ND	ND	ND	ND	ND	ND	ND	ND
Estimated Other technique analytical uncertanity								
Best cleaned value	3.88	5.77	< 16	0.68	0.136	0.080	0.27	0.040
Estimated cleaned analytical uncertanity	0.10	0.25		0.02	0.006	0.005	0.04	0.003

Key: ND=Not determined, CONT.= Contaminated; Analytical uncertanity=± absolute ICP-acid ICP-sinter ICP-MS HGAA CVAA INAA IC

APPENDIX 3. Data for individual splits (continued).

variables:	Hf	Ta	W	Au	Hg	Tl	Pb	Th	U
units (ppm =parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Powder River Basin Coal									
As- Mined 56	0.49	0.13	0.59	< 0.002				1.14	0.45
Analytical uncertanity 56:	0.04	0.01	0.07					0.09	0.08
As-Mined 57	0.416	0.168	0.744	< 0.002				1.18	0.44
Analytical uncertanity 57:	0.038	0.019	0.064					0.04	0.08
Best Value INAA	0.45	0.15	0.67	< 0.002	ND	ND	ND	1.16	0.44
Estimated INAA analytical uncertanity	0.04	0.020	0.093					0.066	0.08
As-Mined 46				< 0.8	0.08	0.065	1.9	1.4	0.46
As-Mined 31				<0.8	0.04	0.048	1.9	0.8	0.47
Best Value Other Techniques	ND	ND	ND	< 0.8	0.07	0.056	1.9	1.1	0.40
Estimated other technique analytical uncertanity					0.02	0.090	0.5	0.3	0.02
Best as-mined value	0.45	0.15	0.67	< 0.002	0.07	0.06	1.9	1.1	0.46
Estimated as-mined analytical uncertanity	0.04	0.02	0.09		0.02	0.09	0.5	0.2	0.02
Simulated cleaned coal									
Cleaned 62a	0.42	0.12	<0.21					1.10	0.80
Analytical uncertanity 62a:	0.01	0.01						0.02	0.20
Cleaned 62b	0.41	0.13	0.08					1.09	0.62
Analytical uncertanity 62b:	0.02	0.01	0.06					0.04	0.18
Cleaned 60	0.41	0.13	<1.4	< 0.024				1.13	<2.4
Analytical uncertanity 60:	0.02	0.02						0.05	
Cleaned 61	0.42	0.13	<1.3	< 0.016				1.11	<9
Analytical uncertanity 61:	0.03	0.01						0.04	
Best Value INAA	0.42	0.12	0.08	< 0.016	ND	ND	ND	1.10	0.71
Estimated INAA analytical uncertanity	0.02	0.01	0.06					0.03	0.19
Cleaned 46a				< 0.7	0.08	0.038	0.88	0.83	0.42
Cleaned 46b				< 0.7	0.07	0.040	1.7	1.13	0.43
Best Value Other Techniques	ND	ND	ND	< 0.7	0.075	0.04	1.7	1.0	0.43
Estimated Other technique analytical uncertanity					0.02	0.01	0.8	0.2	0.02
Best cleaned value	0.42	0.12	0.08	< 0.016	0.08	0.04	1.7	1.1	0.5
Estimated cleaned analytical uncertanity	0.02	0.01	0.06		0.02	0.01	0.8	0.1	0.2

Key: ND=Not determined; CONT.= Contaminated; Analytical uncertanity = ± absolute ICP-acid ICP-sinter ICP-MS HGAA CVAA INAA IC

Appendix 4. Quality Control Data

Control samples in Appendix 4 were submitted as blind samples. The blind sample numbers are followed by the sample set number so that individual samples can be matched with samples in Appendix 3 in the same sample set. For example, with Blind quality control samples 67799 56, 67999 56, 68099 56 (Table A4-1) and CLB-1 56 (Table A4-2) were analyzed with As-mined 56 (Appendix 3).

Table A4-1. CQ "Blind" Quality Control Samples

variables:	Si	Al	Fe	Mg	Ca	Na	K	Ti	P
units (%= weight percent):	%	%	%	%	%	%	%	%	%
67799 (NIST 1635)									
67799 56			0.233			0.253	<0.28		
Analytical uncertanity 56:			0.005			0.006			
67799 57			0.238			0.264	<0.3		
Analytical uncertanity 57:			0.006			0.006			
67799 31	0.78	0.34	0.28	0.093	0.51	0.252	0.015	0.021	0.0069
Certified/informational			**0.239**			0.24			
Analytical uncertanity			0.005						
67999 (NIST 1632b)									
67999 56			0.765			0.051	0.087		
Analytical uncertanity 56:			0.019			0.001	0.006		
67999 57			0.765			0.051	0.077		
Analytical uncertanity 57			0.015			0.001	0.004		
67999 31	1.62	0.94	0.81	0.039	0.21	0.046	0.073	0.045	0.0059
Certified/informational	1.4	**0.855**	**0.759**	**0.0383**	**0.204**	**0.0515**	**0.0748**	**0.0454**	ND
Analytical uncertanity		0.019	0.045	0.0008	0.006	0.0011	0.0028	0.0017	
68099 (USGS CLB-1)									
68099 56			0.884			0.018	0.070		
Analytical uncertanity 56:			0.016			0.000	0.005		
68099 60			0.880			0.017	0.066		
Analytical uncertanity 60:			0.045			0.000	0.005		
68099 31	1.32	0.86	0.96	0.028	0.16	0.014	0.070	0.047	0.037
Recommended/informational	1.17	0.799	**0.874**	**0.0283**	**0.16**	**0.017**	**0.063**	0.047	0.031
Analytical uncertanity	0.098	0.021	0.35	0.0018	0.0071	0.002	0.004	0.0018	0.004

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-1. CQ "Blind" Quality Control Samples

variables:	Li	Be	B	Cl	Sc	V	Cr	Mn	Co
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
67799 (NIST 1635)									
67799 56					0.627		2.42		0.67
Analytical uncertanity 56:					0.012		0.22		0.02
67799 57					0.635		2.66		0.70
Analytical uncertanity 57:					0.021		0.37		0.04
67799 31	2.7	0.45	120	< 200	0.66	4.6	2.3	20.3	1.4
Certified/informational					0.63	**5.2**	**2.5**	**21.4**	0.65
Analytical uncertanity						1	0.30	1.5	
67999 (NIST 1632b)									
67999 56					1.98		10.6		2.19
Analytical uncertanity 56:					0.03		0.6		0.06
67999 57					1.98		10.3		2.20
Analytical uncertanity 57					0.06		0.5		0.14
67999 31	9.8	0.60	50	1016	1.9	13	10.6	11.1	3.3
Certified/informational	10		ND		1.9	14	11	12.4	**2.29**
Analytical uncertanity								1	0.17
68099 (USGS CLB-1)									
68099 56					2.06		9.47		6.93
Analytical uncertanity 56:					0.05		0.38		0.15
68099 60					2.10		9.48		7.32
Analytical uncertanity 60:					0.05		0.41		0.20
68099 31	7.9	1.08	4.2	993	1.9	12	10	8.2	6.9
Recommended/informational	8				2.0	**12**	**9.7**	8	**7.0**
Analytical uncertanity					0.1	1	1.2		0.7

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-1. CQ "Blind" Quality Control Samples

variables:	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
67799 (NIST 1635)									
67799 56	< 8		4.5			0.514	0.77	1.44	< 3
Analytical uncertanity 56:			0.5			0.084	0.11	0.12	
67799 57	< 12		5.7			0.622	1.20	1.6	< 2
Analytical uncertanity 57:			1.2			0.081	0.17	0.1	
67799 31	1.7	1.0	5.1	1.0	0.87	0.11	0.57		0.69
Certified/informational	**1.74**	3.60	**4.70**	1.05		**0.42**	**0.90**		
Analytical uncertanity	0.10	0.3	0.5			0.15	0.3		
67999 (NIST 1632b)									
67999 56	< 9		10.7			3.42	1.16	23.6	5.18
Analytical uncertanity 56:			1.0			0.15	0.20	0.6	0.71
67999 57	< 19		31.3			3.29	1.56	23.6	5.62
Analytical uncertanity 57			2.7			0.13	0.23	0.6	0.77
67999 31	6.1	3.1	11	2.5	2.63	3.8	1.12		5.2
Certified/informational	**6.1**	**6.28**	**11.89**			**3.72**	**1.29**	17	**5.5**
Analytical uncertanity	0.27	0.3	0.78			0.09	0.11		0.01
68099 (USGS CLB-1)									
68099 56	15		51			13	2	69	4.38
Analytical uncertanity 56:	3		2			1	0	2	0.76
68099 60	13		45			12	3	70	4.79
Analytical uncertanity 60:	2		5			0	0	2	0.60
68099 31	18	9.7	49	3.1	13.9	16	1.9		5.2
Recommended/informational	**18**	10	**48**	3		13	**2.1**		**5.2**
Analytical uncertanity	2		4				0.39		0.9

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-1. CQ "Blind" Quality Control Samples

variables:	Sr	Y	Zr	Mo	Cd	Sn	Sb	Cs	Ba
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
67799 (NIST 1635)									
67799 56	127			< 2			< 0.4	0.103	71
Analytical uncertanity 56:	11							0.011	7
67799 57	151			< 0.3			0.15	0.130	128
Analytical uncertanity 57:	13						0.03	0.028	9
67799 31	133	2.0	8.9	0.33	0.027	0.26	0.18	0.071	87
Certified/informational					**0.03**		0.14		
Analytical uncertanity					0.01				
67999 (NIST 1632b)									
67999 56	106			< 0.5			0.23	0.43	66
Analytical uncertanity 56:	16						0.04	0.03	8
67999 57	107			< 0.6			0.255	0.441	77
Analytical uncertanity 57	16						0.019	0.027	11
67999 31	92	3.0	13	0.71	0.057	1.2	0.28	0.52	61
Certified/informational	102			0.9	**0.0573**		0.24	0.44	**67.5**
Analytical uncertanity					0.0027				2.1
68099 (USGS CLB-1)									
68099 56	86			9.23			1.39	0.37	51
Analytical uncertanity 56:	12			2.33			0.10	0.04	8
68099 60	83			8.86			1.46	0.30	40
Analytical uncertanity 60:	11			1.65			0.10	0.02	5
68099 31	64	4.9	13	11	0.091	0.69	1.8	0.38	39
Recommended/informational				9			1.5		**34**
Analytical uncertanity									5

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-1. CQ "Blind" Quality Control Samples

variables:	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
67799 (NIST 1635)								
67799 56	2.16	3.42	< 10	0.308	0.07	0.041	0.392	0.032
Analytical uncertainty 56:	0.08	0.27		0.015	0.01	0.006	0.082	0.006
67799 57	2.31	3.41	< 10	0.333	0.09	0.043	<0.13	0.033
Analytical uncertainty 57:	0.08	0.49		0.015	0.01	0.007		0.007
67799 31								
Certified/informational		3.6			0.06			
Analytical uncertanity								
67999 (NIST 1632b)								
67999 56	4.93	8.79	< 7	0.86	0.18	0.11	< 0.6	0.046
Analytical uncertanity 56	0.14	0.30		0.02	0.01	0.01		0.006
67999 57	4.98	9.26	< 6	0.886	0.170	0.089	0.385	0.052
Analytical uncertanity 57	0.14	0.74		0.026	0.010	0.010	0.054	0.006
67999 31								
Certified/informational	5.1	9		0.87	0.17			
Analytical uncertanity								
68099 (USGS CLB-1)								
68099 56	6.00	11.3	< 9	1.15	0.24	0.16	0.49	0.07
Analytical uncertanity 56:	0.17	0.4		0.03	0.01	0.01	0.09	0.01
68099 60	6.16	11.1	< 6	1.19	0.24	0.15	0.59	0.07
Analytical uncertanity 60:	0.17	0.4		0.03	0.01	0.01	0.05	0.01
68099 31								
Recommended/informational	5	**10**	5					
Analytical uncertanity		1.6						

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-1. CQ "Blind" Quality Control Samples

variables:	Hf	Ta	W	Au	Hg	Tl	Pb	Th	U
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
67799 (NIST 1635)									
67799 56	0.269	0.062	< 0.3	< 0.003				0.58	< 0.3
Analytical uncertanity 56:	0.019	0.009						0.03	
67799 57	0.264	0.105	< 0.3	0.004				0.65	0.57
Analytical uncertanity 57:	0.026	0.024		0.001				0.04	0.12
67799 31				< 0.6	< 0.02	0.033	1.5	0.81	0.24
Certified/informational	0.29						**1.9**	**0.62**	**0.24**
Analytical uncertanity							0.2	0.04	0.02
67999 (NIST 1632b)									
67999 56	0.39	0.15	0.39	< 0.002				1.32	0.38
Analytical uncertanity 56:	0.02	0.02	0.06					0.10	0.07
67999 57	0.437	0.190	0.421	< 0.002				1.36	0.326
Analytical uncertanity 57	0.027	0.017	0.046					0.08	0.059
67999 31				< 0.7	0.07	0.12	4.0	1.10	0.45
Certified/informational	0.43		0.48				**3.67**	**1.342**	**0.436**
Analytical uncertanity							0.26	0.036	0.12
68099 (USGS CLB-1)									
68099 56	0.35	0.12	0.67	< 0.003				1.40	0.45
Analytical uncertanity 56:	0.02	0.01	0.08					0.05	0.10
68099 60	0.45	0.14	0.90	<0.003				1.39	0.50
Analytical uncertanity 60:	0.02	0.01	0.14					0.05	0.09
68099 31				< 0.7	0.13	0.69	5.4	<0.6	0.51
Recommended/informational					0.2		5	1.4	0.55
Analytical uncertanity									

Key: Analytical uncertanity = ± absolute   INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-2. USGS Quality Control Samples

variables:	Si	Al	Fe	Mg	Ca	Na	K	Ti	P
units (%= weight percent):	%	%	%	%	%	%	%	%	%
QC STD (USGS CLB-1)									
CLB-1 56			0.896			0.017	0.067		
Analytical uncertanity 56:			0.016			0.000	0.004		
CLB-1 57			0.861			0.017	0.068		
Analytical uncertanity 57:			0.017			0.000	0.004		
CLB-1 60			0.873			0.017	0.067		
Analytical uncertanity 60:			0.030			0.000	0.004		
CLB-1 61			0.881			0.017	0.069		
Analytical uncertanity 61:			0.035			0.000	0.004		
CLB-1 62			0.913			0.018	0.073		
Analytical uncertanity 62:			0.040			0.000	0.004		
CLB-1 31	1.27	0.82	0.86	0.027	0.15	0.014	0.065	0.047	0.031
CLB-1 46	1.33	0.81	0.95	0.026	0.15	0.015	0.071	0.043	0.032
Recommended/informational	1.17	0.799	**0.874**	**0.0283**	**0.16**	**0.017**	**0.063**	0.047	0.031
Analytical uncertanity	0.098	0.021	0.35	0.0018	0.0071	0.002	0.004	0.0018	0.004

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-2. USGS Quality Control Samples continued.

variables:	Li	Be	B	Cl	Sc	V	Cr	Mn	Co
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
QC STD (USGS CLB-1)									
CLB-1 56					2.08		9.81		6.90
Analytical uncertanity 56:					0.04		0.48		0.15
CLB-1 57					2.06		10.52		6.96
Analytical uncertanity 57:					0.06		0.56		0.16
CLB-1 60					2.10		9.42		7.24
Analytical uncertanity 60:					0.04		0.37		0.20
CLB-1 61					2.10		9.69		7.17
Analytical uncertanity 61:					0.03		0.37		0.16
CLB-1 62					2.05		9.66		6.78
Analytical uncertanity 62:					0.04		0.38		0.14
CLB-1 31	7.5	1.06	< 1.3	1033	1.8	12	9.9	7.9	6.8
CLB-1 46	8.0	1.10	2.1	1024	1.8	12	10	8.0	6.8
Recommended/informational	8				2.0	**12**	**9.7**	8	**7.0**
Analytical uncertanity					0.1	1	1.2		0.7

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-2. USGS Quality Control Samples continued.

variables:	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
QC STD (USGS CLB-1)									
CLB-1 56	20		50.0			13.8	2.44	70.5	5.85
Analytical uncertanity 56:	3		2.0			0.5	0.21	1.7	0.78
CLB-1 57	26		48.0			12.8	2.77	70.8	5.75
Analytical uncertanity 57:	5		2.8			0.5	0.25	1.7	0.99
CLB-1 60	23		43.3			12.2	2.82	69.8	5.12
Analytical uncertanity 60:	3		9.7			0.4	0.28	1.6	0.52
CLB-1 61	21		54.7			12.8	2.20	70.3	4.64
Analytical uncertanity 61:	3		2.6			0.4	0.24	1.6	0.79
CLB-1 62	19		47.2			14.7	1.77	71.5	5.11
Analytical uncertanity 62:	3		1.8			0.5	0.30	1.7	0.51
CLB-1 31	18	8.6	47	3.1	13.9	13	2.3		4.7
CLB-1 46	18	9.0	48	3.1	13.8	15	2.5		5.2
Recommended/informational	**18**	10	**48**	3		13	**2.1**		**5.2**
Analytical uncertanity	2		4				0.39		0.9

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-2. USGS Quality Control Samples continued.

variables:	Sr	Y	Zr	Mo	Cd	Sn	Sb	Cs	Ba
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
QC STD (USGS CLB-1)									
CLB-1 56	89			9.69			1.41	0.35	46
Analytical uncertanity 56:	11			2.45			0.12	0.02	9
CLB-1 57	83			5.63			1.38	0.35	33
Analytical uncertanity 57:	17			0.96			0.05	0.03	9
CLB-1 60	86			7.65			1.42	0.32	38
Analytical uncertanity 60:	12			1.42			0.06	0.02	5
CLB-1 61	77			7.34			1.48	0.34	26
Analytical uncertanity 61:	8			1.08			0.09	0.02	6
CLB-1 62	71			8.41			1.51	0.35	37
Analytical uncertanity 62:	9			2.47			0.05	0.03	4
CLB-1 31	65	4.7	11	9.2	0.084	0.66	1.46	0.28	37
CLB-1 46	65	4.9	12	11	0.086	0.64	1.8	0.38	35
Recommended/informational				9			1.5		**34**
Analytical uncertanity									5

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-2. USGS Quality Control Samples continued.

variables:	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
QC STD (USGS CLB-1)								
CLB-1 56	6.13	10.7	< 9	1.15	0.23	0.15	0.55	0.08
Analytical uncertanity 56:	0.17	0.3		0.03	0.01	0.01	0.06	0.01
CLB-1 57	6.12	11.0	< 7	1.19	0.24	0.14	0.56	0.08
Analytical uncertanity 57:	0.17	0.4		0.03	0.03	0.01	0.05	0.01
CLB-1 60	6.09	10.9	< 5	1.19	0.24	0.14	0.50	0.06
Analytical uncertanity 60:	0.16	1.0		0.03	0.01	0.01	0.04	0.01
CLB-1 61	6.20	10.9	< 3	1.18	0.24	0.15	0.55	0.07
Analytical uncertanity 61:	0.16	0.5		0.03	0.01	0.01	0.05	0.01
CLB-1 62	6.29	10.7	<12	1.24	0.22	0.15	0.46	0.07
Analytical uncertanity 62:	0.17	0.5		0.03	0.01	0.01	0.04	0.00
CLB-1 31								
CLB-1 46								
Recommended/informational	5	**10**	5					
Error		1.6						

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC

Table A4-2. USGS Quality Control Samples continued.

variables:	Hf	Ta	W	Au	Hg	Tl	Pb	Th	U
units (ppm= parts per million):	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
QC STD (USGS CLB-1)									
CLB-1 56	0.36	0.11	0.66	< 3				1.36	0.55
Analytical uncertanity 56:	0.02	0.01	0.08					0.07	0.11
CLB-1 57	0.38	0.16	0.77	< 3				1.39	0.57
Analytical uncertanity 57:	0.03	0.02	0.07					0.06	0.09
CLB-1 60	0.37	0.13	0.95	< 3				1.42	0.50
Analytical uncertanity 60:	0.02	0.01	0.12					0.05	0.09
CLB-1 61	0.39	0.13	0.71	< 2				1.38	0.48
Analytical uncertanity 61	0.02	0.01	0.05					0.06	0.07
CLB-1 62	0.37	0.12	0.72					1.41	0.54
Analytical uncertanity 62	0.02	0.01	0.08					0.04	0.11
CLB-1 31				< 0.7	0.16	0.73	4.8	1.10	0.52
CLB-1 46				< 0.7	0.15	0.67	5.4	0.75	0.51
Recommended/informational					0.2		5	1.4	0.55
Analytical uncertanity									

Key: Analytical uncertanity = ± absolute INAA ICP-acid ICP-sinter ICP-MS HGAA CVAA IC