Toxic Substances from Coal Combustion - Forms of Occurrence Analyses

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Abstract

In a cooperative agreement with DOE (Contract No. DE-AC22-95101), the USGS has participated with Physical Sciences, Inc. (PSI) in a project entitled "Toxic Substances From Coal Combustion - A Comprehensive Assessment". Samples from the Pittsburgh, Elkhorn/Hazard, Illinois No. 6, and Wyodak program coals were examined to determine the mode of occurrence of selected trace elements (As, Se, Cr, Hg, and Ni) using selective leaching, scanning electron microscopy, electron microprobe analysis, and X-ray diffraction techniques. Among other findings, our results indicate that the bulk of the arsenic in the Pittsburgh and Illinois No. 6 coals is in pyrite. High percentages (60-80%) of arsenic were leached by nitric acid, and microprobe data confirm the presence of arsenic in pyrite in each of these coals (concentrations ranging from <0.01 to 0.09 wt.% of the pyrite grains). In the Elkhorn/Hazard coal, arsenic may have several modes of occurrences. About 30 percent of the arsenic in the Elkhorn/Hazard coal was leached by hydrochloric acid, possibly indicating the presence of arsenates that were formed by the oxidation of pyrite. About 25 percent of the arsenic in the Elkhorn/Hazard coal was leached by nitric acid, suggesting an association with pyrite. Only sixty percent of the total arsenic in the Elkhorn/Hazard coal was leached. The low percentage of leachable arsenic may be accounted for by unleached pyrite grains, which were detected in solid residues from the nitric acid leach. In the Wyodak coal, arsenic probably occurs in iron oxides or carbonates (35 % arsenic leached by HCl) and clays (15% arsenic leached by HF). Arsenic in the Wyodak coal may also have an organic association, as indicated by low totals for leaching (50% unleached arsenic). In the four program coals 20 to 45 percent of the chromium was leached by hydrofluoric acid, suggesting an association with silicates (probably illite). Microprobe analysis of the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals confirmed the presence of chromium in illite and possibly in other clays, at concentrations that are near the detection limits. Results related to the forms of occurrence of the other trace elements (Se, Hg, and Ni) are varied; further work in Phase II is planned to determine their mode of occurrence.

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B) Nickel-in-pyrite mass-balance diagram. For each coal, diagram shows a sliding scale of fractions of whole-coal nickel accounted for by pyrite, in increments of 10% (0.1). Diagram also shows nickel-in-pyrite fractions indicated by selective leaching (HNO_3 fraction; open symbols), and mass-balances obtained by electron microprobe (EPMA; filled symbols). See text for discussion of results.

Executive Summary

In a cooperative agreement with DOE (Contract No. DE-AC22-95101), the USGS has participated with Physical Sciences, Inc. (PSI) in a project entitled "Toxic Substances From Coal Combustion - A Comprehensive Assessment". The Pittsburgh, Elkhorn/Hazard, Illinois No. 6, and Wyodak program coals have been examined to determine the mode of occurrence of selected trace elements (As, Se, Cr, Hg, and Ni) using selective leaching, scanning electron microscopy (SEM), electron microprobe analysis (EMPA), and X-ray diffraction (XRD) techniques. An integrated approach using these methods has been valuable for several reasons: (1) this approach has provided a visual characterization of textural relationships (SEM and EMPA analysis), (2) we have used this approach to examine trace elements such as selenium that are difficult to detect using other techniques, and (3) the methods used may be available in service laboratories.

Our results indicate that the bulk of the arsenic in the Pittsburgh and Illinois No. 6 coals is in pyrite. High percentages (60-80%) of arsenic were leached by nitric acid, and microprobe data confirm the presence of arsenic in pyrite in each of these coals (concentrations ranging from <0.01 to 0.09 wt.% of the pyrite grains). In the Elkhorn/Hazard coal, arsenic may have several modes of occurrences. About 30 percent of the arsenic in the Elkhorn/Hazard coal was leached by hydrochloric acid, possibly indicating the presence of arsenates that were formed by the oxidation of pyrite. About 25 percent of the arsenic in the Elkhorn/Hazard coal was leached by nitric acid, suggesting an association with pyrite. Only sixty percent of the total arsenic in the Elkhorn/Hazard coal was leached. The low percentage of leachable arsenic may be accounted for by unleached pyrite grains, which were detected in solid residues from the nitric acid leach. In the Wyodak coal, arsenic probably occurs in iron oxides or carbonates (35% arsenic leached by HCl) and clays (15 % arsenic leached by HF). Arsenic in the Wyodak coal may also have an organic association, as indicated by low totals for leaching (50% unleached arsenic). In the four program coals, 20 to 45 percent of the chromium was leached by hydrofluoric acid, indicating some association with silicates (possibly illite). Microprobe analysis of the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals confirmed the presence of chromium in illite and possibly in other clays, at concentrations that are near the detection limits. Results related to the forms of occurrence of the other trace elements (Se, Hg, and Ni) were varied; further work in Phase II is planned to determine their mode of occurrence.

Introduction

In a cooperative agreement with DOE (Contract No. DE-AC22-95101), the USGS has participated with Physical Sciences, Inc. (PSI) in a project entitled "Toxic Substances From Coal Combustion - A Comprehensive Assessment". In support of this effort, the United States Geological Survey (USGS) has analyzed a number of coal samples utilizing the techniques described below, to provide information necessary to achieve a better understanding of toxic element behavior.

Phase I

As a complement to the analyses being performed by PSIT under DOE Contract No. DE-AC22-95PC95101, data from a unique protocol developed by the USGS have been used to analyze selected coal size and density fractions for trace element modes of occurrence. In Phase I, the four Phase I coals have been analyzed. The protocol incorporates the methods described below.

All of the samples have been treated by a selective leaching procedure, a powerful technique for approximating modes of occurrence using differing solvents at various temperatures and concentrations. Splits of the coal have been leached with these solvents (ammonium acetate, hydrochloric acid, hydrofluoric acid, nitric acid) according to the methods developed at the USGS. Results from these leaching tests provide essential information on chemical bonding of the elements present: elements that are leached by hydrofluoric acid are generally associated with silicates, those that are leached by nitric acid generally occur in sulfides, and those that are leached by hydrochloric acid generally occur in carbonates and monosulfides. Ammonium acetate will leach water-soluble elements or elements weakly attached to exchangeable sites.

The above procedures provided indirect evidence, or approximations of the modes of occurrence of the trace elements in coal. These techniques were complemented by direct procedures such as operator-controlled scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX) of polished pellets of coal. The operator manually selected the appropriate phases for analysis by EDX and interpreted textural relations of the phases being analyzed. The mineralogical, geological, and geochemical expertise of the USGS personnel provided unique and essential insights. For a more sensitive and quantitative analysis, an electron microprobe analyzer was used.

Tests were made for volatility of trace elements. Volatility was determined by heating the coal samples to 550° C and 1000°C. Results for the samples ashed at these temperatures were compared.

The Agency shall not proceed with any of the work under the Phase II program until formal notification is provided.

Phase II Plans

A new set of study coals will be designated and anlyzed in Phase II. Detailed analysis of coal splits (size and density fractions) from both Phase I and Phase II coals will also be conducted, as required. The standard protocol to be used in Phase II is nearly identical to that used in Phase I; the most significant difference is in the samples to be analyzed. Some samples may be subjected to separation procedures and subsequent analysis. Separates may be prepared by using density or magnetic separations techniques or by handpicking specific mineral grains to obtain a high-purity sample. The protocol to be followed in Phase II incorporates the techniques described below.

Using a methodology similar to that of Phase I, all of the samples will be treated by a selective leaching procedure, using four solvents: ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid. Experiments to determine the volatility of the elements will also be conducted by heating the coal samples to 200°C, 550° C, and 1000°C, using the same procedures as described in Phase I.

These procedures will provide indirect evidence, or approximations of the modes of occurrence of the trace elements in coal. As in Phase I, they will be complemented by direct determinations on polished pellets of coal using conventional SEM analysis with the EDX analyzer. For a more sensitive and quantitative analysis, an electron microprobe analyzer will be used. Other methods such as analytical transmission electron microscopy, secondary ion mass spectrometry, and infrared spectroscopy will be used as necessary. Where direct mode-of-occurrence information is difficult to obtain (e.g. for Hg), indirect results, using statistical correlations with other coal-quality parameters, will be used.

Methods

Grinding, Sulfur Form Analysis, and Chemical Analysis

After the USGS received the program coals, they were shipped to Geochemical Testing of Somerset, Pennsylvania (May, 1996) for grinding of samples to -20 mesh splits (to be used in petrographic, SEM, and microprobe analysis) and -60 mesh splits (for analysis by ICP-MS, ICP-AES, hydride generation, and cold vapor atomic absorption). Samples were purged with argon and carefully packaged before shipping to avoid chemical contamination. Geochemical Testing also performed analysis of forms of sulfur in accordance with ASTM D2492-90 (1994). The USGS received the Pittsburgh and Elkhorn/Hazard coals in May, 1996; the Illinois No. 6 coal in June, 1996; and the Wyodak coal in February, 1997. Forms of sulfur form data for the Pittsburgh, Elkhorn/Hazard, Illinois No. 6, and Wyodak coal samples are given in Appendix I. Chemical analyses (ICP-MS, ICP-AES, hydride generation, and cold vapor atomic absorption, INAA) for the four raw coals have been completed.

Leaching Procedures

The sequential selective leaching procedure used in this study is similar to that described by Palmer et al. (1993) and Finkelman et al. (1990). In this procedure, duplicate 5g samples were sequentially leached in 50 ml polypropylene tubes using 35 ml each of 1N ammonium acetate (CH_3COONH_3), 3N hydrochloric acid (HCl), concentrated hydrofluoric acid (HF; 48%), and 2N (1:7) nitric acid (HNO_3). Each tube was shaken for 18 hrs on a Burrell[1] wrist action shaker. Because of the formation of gas during some of the leaching procedures, it was 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. Approximately 0.5 g of residual solid was removed from each tube for instrumental neutron activation analysis (INAA). The solutions were saved for inductively coupled argon plasma (ICP-AES) analysis and inductively coupled argon plasma mass spectroscopy (ICP-MS) analysis.

Leaching experiments were completed for the four program coals and the resulting leachate solutions and solid residues were submitted for chemical analysis. Leachate solutions were analyzed by ICP-AES and ICP-MS; solid residues were analyzed by INAA. For each analytical method, chemical data were processed to derive the mean percentages of each element leached by each of the four leaching agents, as compared to the original concentration of each element in the unleached coal. A single value for the percent leached for each element was then determined, based on the potential uncertainty of each technique (Table 1) and reproducibility of analytical results. The resulting calculated percentages were used as an indirect estimate of the mode of occurrence of specific trace elements in the coals. We estimate an error of up to ±25 percent for the calculated leached percentages.

Leaching procedures were completed for the Pittsburgh, Elkhorn/Hazard, Illinois No. 6, and Wyodak coal samples and analytical data for leachates and solid residues were processed.

SEM, Microprobe, and XRD Analysis

<u>Coal pellet casting and polishing</u>

The pellet formation procedure follows the ASTM D2797-85 technique for anthracite and bituminous coal (ASTM, 1997). In the casting procedure, approximately 7-8 grams of crushed sample are impregnated, under pressure, with epoxy and poured into a cylindrical mold which is cured overnight at 60° C. A label is incorporated with the sample.

The cylindrical pellet is ground and polished using ASTM D2797-85 procedures. In this process, one end of the pellet is ground with a 15 μm diamond platen and 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 between and after the various steps insures a final product free of extraneous abrasive material.

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[1] 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.

Two pellets are prepared from each sample. Wafers about 2 mm in thickness are sliced from the polished end of the pellet and carbon-coated for SEM and microprobe analysis.

Scanning electron microscope analysis.

A JEOL-840[1] scanning electron microscope equipped with a Princeton Gamma-Tech. energy-dispersive X-ray analytical system. and/or an Autoscan ETEC[1] with Kevex EDX[1] were used for SEM examination of project coals. Mineral identifications were made on the basis of grain morphology and major-element composition. 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 high-atomic number trace phases can be revealed. Samples were scanned initially to obtain an overall view of the phases present, as with a petrographic microscope. This initial scanning 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 approximately a tenth-of-weight-percent level or greater. Typical operating conditions for SEM analysis were: accelerating potential of 10-30 kV, magnifications of ~50 to >10,000 times and working distances ranging from 15 to 20 mm (ETEC) and 25 or 39 mm (JEOL).

Scanning electron microscopy preceded electron microprobe analysis. SEI or 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. Images at higher magnifications commonly reveal the presence of interstices or other imperfections in mineral grains that are not visible in reflected light microscopy. SEI/BSE mapping enabled us to avoid features that would adversely affect the quantitative analysis using the microprobe.

Electron microprobe analysis.

A fully-automated 5-spectrometer instrument (JEOL JXA 8900L Superprobe[1]) was used to quantitatively determine element concentrations in sulfides and clay minerals in program coals by the wavelength-dispersive technique. For sulfides, the following elements were measured: Fe, S, As, Ni, Cu, Zn, Se, Co, and Cd. For clay minerals illite and kaolinite, the elements reported as oxides (K_2O, CaO, Na_2O, Al_2O_3, SiO_2, MgO, Cr_2O_3, MnO, FeO, and TiO_2) were measured. Natural and synthetic standards were used. For sulfides, an accelerating potential of 20 KeV was used, at beam currents of 2.0×10^{-8} or 3.0×10^{-8} amps. For clays, an accelerating potential of 15 KeV was used, at a beam current of 2.0×10^{-8} amps. All analyses were done using a focused beam (beam diameter setting = 1 μm), giving an actual working diameter of about 2-3 micrometers.

Detection limits for each of the minor or trace elements determined are estimated to be about 100 ppm in sulfides and 200 ppm in clays. Long counting times, at least 60 seconds for peak and 30 seconds for each background, were used to achieve these detection limits. For example, to measure arsenic in pyrite, a peak counting time of 90 seconds, and a 45 second count for each background were used. Because many of the trace elements of interest are present at levels that are at or near the detection limits of the probe, counting statistics for these elements have large uncertainties.

Microprobe data for pyrite grains (Appendix II) and clays (Appendix III) have been completed. For pyrite grains, only analyses totaling ≥ 95% were accepted. For clays, most analyses have totals in the 87-90% range, reflecting the presence of water in the structures of these phases. In addition to quantitative analyses, JEOL 8900 wavelength-dispersive spectrometry was used to produce color maps of elemental distribution in project sulfides. This technique was used to delineate arsenic heterogeneity in high-arsenic pyrite of the Elkhorn/Hazard coal (Fig. 1).

In order to obtain additional mode of occurrence information for chromium in the Elhorn/Hazard coal, three density separates (float, middling, and sink fractions) were examined using the SEM.

X-ray diffraction analysis

To obtain semi-quantitative information on minerals present in the study coals, samples of low-temperature (< 200°C) ash were pressed onto powdered plastic backings to form wafers which were X-rayed using an automated diffractometer. The samples were analyzed over an interval from 4° to 60° 2θ at a step interval of 0.02° 2θ. Counts were collected for 0.5 sec. per step. 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 Analyses

SEM analyses indicate the presence of the major minerals illite, kaolinite, quartz, calcite, and pyrite in the Pittsburgh and Illinois No. 6 coals (Appendix IB). The Elkhorn/Hazard coal contains the same major phases, with the exception of calcite. (However, trace amounts of calcite were detected in the Elkhorn/Hazard with XRD analysis, Appendix IC). Iron oxides were also found to be a major constituent of the Pittsburgh coal. Other minerals were found in minor or trace amounts in each of the coals. In the Wyodak coal, major minerals detected include quartz, illite, kaolinite, and possibly mixed-layer clays. Pyrite was found only in very minor amounts in the Wyodak coal.

A range of pyrite morphologies was observed in the program coals using the SEM, including subhedral, euhedral, composite, and framboidal grains.

.Microprobe Analyses

1- Microprobe analysis of Iron-Sulfides

Microprobe data for most pyrite grains indicate trace-element concentrations that are at or below the detection limit of ~100 ppm (Appendix II). Of the seven trace elements determined (Se, Cu, Ni, As, Zn, Cd, and Co), only Cu, As, and Ni are commonly present at levels that exceed the detection limit. Concentrations of these three elements were determined for all of the pyrite grains analyzed.

Microprobe data indicate that the arsenic contents of pyrite grains in the Illinois No. 6 (<0.01 to 0.03 weight percent) and Pittsburgh (<0.01 to 0.09 weight percent) samples are similar, and that pyrite grains in these two coals are not distinguishable based on arsenic concentrations. The arsenic concentrations of the pyrite grains in these coals do not appear to vary according to grain size, however, non-framboidal pyrite grains commonly have higher arsenic concentrations than framboidal pyrite grains (Figs. 2a and 2b). Arsenic content of pyrites in the Elkhorn/Hazard coal is much more variable than that in the other program coals, ranging from below the detection limit to greater than 2.0 weight percent. As in the Pittsburgh and Illinois No. 6 coals, non-framboidal pyrite grains commonly have higher arsenic concentrations than framboidal pyrite grains and the arsenic concentrations do not appear to vary according to grain size (Fig. 2c). The presence of scattered high-arsenic pyrite grains in the Elkhorn /Hazard coal makes it difficult to determine a representative arsenic composition for pyrites in this coal (see "Mass Balance Calculations" section). Elemental mapping of one such grain in the Elkhorn/Hazard coal also reveals fine-scale variation in arsenic content (Fig. 1).

Overall, the Illinois No. 6 coal has higher concentrations of nickel in pyrite grains (mean = 0.035 wt. %) than the Pittsburgh coal (0.01 wt.%) or Elkhorn/Hazard coal (0.02 wt.%; Appendix II). In the Pittsburgh and Elkhorn/Hazard coals, the nickel concentrations of pyrite grains do not appear to vary according to the size of grains or according to pyrite morphology (framboidal vs non-framboidal, Figs. 3a and 3c). In the Illinois No. 6, framboidal pyrite grains are more likely to show enrichment in nickel, but there is considerable overlap in values (Fig. 3b). The highest nickel concentrations determined are 0.26 and 0.40 wt.% in two separate Illinois No. 6 framboids.

The concentrations of arsenic in pyrite vs. nickel in pyrite are plotted in Figures 4a-c. These elements appear to show independent enrichment trends, particularly for nickel in the Illinois No. 6 coal (Fig. 4b) and arsenic in the Elkhorn/Hazard coal (Fig. 4c).

Maximum selenium concentrations of 0.01 to 0.02 wt.% were found for pyrite in each coal, but most selenium values were below the detection limit of ~100 ppm (Appendix II).

In the Wyodak coal, one pyrite grain was analyzed (Appendix II). Arsenic concentrations are near or below the detection limit (below detection limit (0.01) to 0.03 wt. %). Nickel concentrations are below the detection limit.

2 - Microprobe Analysis of Clay Minerals

Microprobe analyses of the clay minerals illite and kaolinite are given in Appendix III. For the Elkhorn/Hazard and Illinois No. 6 coals, the average Cr_2O_3 concentration of illites is below the detection limit (about 200 ppm). For the Pittsburgh coal, only one illite gave an acceptable analysis, based on its oxide sum and stoichiometry. This illite (PITTS illite1) has a Cr_2O_3 content (0.02 to 0.03 weight percent) that is marginally above the detection limit, and is therefore subject to a large uncertainty.

The grains that we have identified as illites probably also contain mixed-layer clays and finely disseminated quartz, as indicated by the large variations in SiO_2, K_2O and FeO (Appendix III). Unlike the illites, the kaolinites show little chemical variation. The kaolinites are essentially stoichiometric $Al_2Si_2O_5(OH)_4$, with minor substitution by Fe and K, possibly from adjacent illites (Appendix III). Some kaolinites give a response for Cr_2O_3, possibly indicating the presence of a small amount of chromium in this clay mineral as well as illite.

Analysis totals for kaolinite and illite are less than 100 percent because of structural water in these clays.

Semi-quantitative Mineralogy of the Low-Temperature Ash

Results of X-ray diffraction analysis of low-temperature ash are presented in Appendix IC, together with semi-quantitative estimates of the mineral content of the coal on a whole-coal dry basis. Quartz and kaolinite are dominant in each of the four program coals. Illite is dominant in the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals; however, it occurs only in trace amounts in the Wyodak coal. Bassanite (a form of calcium-sulfate), which is formed from calcium and sulfur in the ashing process, is dominant only in the Wyodak coal. XRD analysis indicates pyrite concentrations of 1.5 and 2.1 percent on a whole-coal basis in the Pittsburgh and Illinois No. 6 coals, respectively. In the Elkhorn/Hazard coal, only trace amounts of pyrite were detected by XRD. Although pyrite was not detected by XRD analysis in the Wyodak coal, it was observed with SEM analysis. Trace amounts of calcite are present in the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals.

The XRD data are in general agreement with SEM analysis, with several exceptions. For example, trace amounts of feldspar were detected in the Pittsburgh and Elkhorn/Hazard coals with XRD analysis, but not detected with SEM analysis. In the Pittsburgh coal, iron metal or iron oxide was detected with SEM analysis, however, it was not detected by XRD analysis. Because the XRD is dependent on the degree of crystallinity of minerals, iron oxides are not easily detected. Both the XRD data and SEM data suggest the dominance of kaolinite over illite in each of the four program coals. However, mixed layer clays are not easily detected by XRD and may also be present in the program coals.

Leaching Experiments and Comparison to Other Data

In the following section, the leaching behavior of arsenic, selenium, chromium, mercury, and nickel (Table 1, Figs. 5a-f) are discussed and compared to the results from microprobe and SEM analysis. Final modes of occurrence (Figs. 6a-d) are determined for each element based on integration of data from leaching experiments, SEM analysis, electron microprobe analysis, and XRD data.

<u>Arsenic</u>

Pittsburgh and Illinois No. 6 coals: The bulk of the arsenic in the Pittsburgh and Illinois No. 6 coals is in pyrite, as indicated by high percentages of arsenic leached by HNO_3 (60-80%, Fig. 5a). Microprobe data confirms the presence of arsenic in pyrite and shows typical concentration ranges to be from <0.01 to 0.09 wt.% in the Pittsburgh coal and from <0.01 to 0.03 wt.% in the Illinois No. 6 coal. The high total percentage of arsenic leached in the Pittsburgh and Illinois No. 6 coals (80-90%) suggests little or no organic association. Minor amounts of arsenic (10-20%) were leached by HCl, which may indicate an association with mono-sulfides (such as sphalerite or galena) or possibly iron sulfates. However, these mono-sulfides and iron sulfates were not observed with SEM analysis. Percentages for the mode of occurrence diagram (Fig. 6a) were derived directly from the leaching percentages (Fig. 5a).

Elkhorn/Hazard Coal: The Elkhorn/Hazard coal may have several modes of occurrence for arsenic. In contrast to the Pittsburgh and Illinois No. 6 coals, 30 percent of arsenic in the Elkhorn/Hazard coal was leached by HCl and 25 percent of arsenic was leached by HNO_3. A minor amount of arsenic was leached by HF (5%). Leaching of arsenic by HCl may indicate the presence of arsenates that were formed by the oxidation of pyrite. It is also possible that HCl-soluble arsenic-bearing monosulfides (such as sphalerite or galena) or iron sulfates are present, however, these minerals were not observed with SEM analysis.

Because only sixty percent of the total arsenic in the Elkhorn/Hazard coal was leached, an organic association for arsenic or the presence of organically encapsulated (shielded) arsenic-bearing pyrite might be suggested. However, petrographic and SEM analysis of solid residues from the nitric acid leach have identified the presence of both shielded and unshielded pyrite grains in the solid residues, indicating that nitric acid leaching was incomplete. Work in Phase II will include an investigation of the leaching process, to determine why leaching of pyrite grains by nitric acid is incomplete in the Elkhorn/Hazard coal. The amount of unleached pyrite observed may be sufficient to account for the low percentage of leachable arsenic in the Elkhorn/Hazard coal. To estimate the total amount of arsenic present in pyrite, we adjusted the amount of nitric acid leached arsenic (25%) by adding the amount of unleached arsenic (40%), to obtain the total arsenic in pyrite (65%, Fig. 6a). Work in Phase II will include examination of unleached pyrite grains in Elkhorn/Hazard residue to determine why they were not dissolved in nitric acid.

Wyodak Coal: Similar to the Elkhorn/Hazard coal, the Wyodak coal has more than one mode of occurrence for arsenic. 35 percent of arsenic in the Wyodak coal was leached by HCl; 15 percent of the arsenic was leached by HF. Leaching by HCl may indicate an association of arsenic with iron oxides;

leaching by HF probably indicates an association with clays (possibly illite). 50 percent of the total arsenic was not leached in the Wyodak coal. Because most of the iron was leached (see next section), some of the arsenic may be associated with organics. Percentages for the mode of occurrence diagram (Fig. 6a) were derived directly from the leaching percentages (Fig. 5a).

Iron

The leaching behavior of arsenic was also compared to that of iron in the Pittsburgh, Elkhorn/Hazard, Illinois No. 6, and Wyodak coals. In the Pittsburgh and Illinois No. 6 coals, the leaching behavior of iron is similar to that of arsenic (Fig. 5b). Iron was leached primarily by HNO_3 (85-90%). Percentages given in the iron mode of occurrence diagram (Fig. 6b) were derived directly from the leaching data. For the Illinois No. 6 coal, we assume that there is little or no organic iron, because the cumulative amount of iron leached by the four solvents is 100 percent.

In the Elkhorn/Hazard coal, only 75 percent of the total iron was leached, and only a small portion of iron (15%) was leached by HNO_3 (Fig. 5b). Based on our observations of unleached pyrite grains in the nitric acid solid residue, we have estimated that the sum of leachable iron in pyrite (15%) and unleached iron (25%) is approximately equivalent to the total amount of iron in pyrite (40%) (Fig. 6b). The assumption that the Elkhorn/Hazard coal contains little or no organically-bound iron is inherent in this estimate. The ratio of leachable iron in pyrite to total iron in pyrite (15/40) is approximately 38%. Because the ratio of leachable arsenic in pyrite to total arsenic in pyrite (25/65=38%) is equal to the ratio found for iron (38%), we infer that the leaching behavior of iron is similar to the leaching behavior of arsenic. HCl-soluble iron may possibly be associated with iron sulfates, that were formed by the oxidation of pyrite.

In the Wyodak coal, sixty-five percent of the iron was leached by HCl and twenty-five percent was leached by HF. In contrast to arsenic, nearly all of the iron was leached (90 percent). We infer that the iron is primarily associated with iron oxides or carbonates (as indicted by leaching with HCl) and clays (as indicated by leaching with HF).

Selenium

In the Pittsburgh coal, selenium was leached to a large degree by nitric acid (90%), suggesting an association with pyrite (Fig. 5c). An association of selenium with pyrite is also evident in the Elkhorn/Hazard coal, where selenium was leached primarily by nitric acid (50%). In the Elkhorn Hazard coal and Illinois No. 6 coals, because the total amount of selenium leached is fairly low (45% and 60%, respectively), we infer an association with the organics. In the Pittsburgh and Elkhorn/Hazard coals, selenium was leached to some degree (5% and 15%, respectively) by HCl. The HCl-soluble selenium may be in accessory mono-sulfides such as sphalerite (ZnS) and galena (PbS).

Selenium concentrations in pyrite grains were generally below the microprobe detection limit (~100 ppm) in the Pittsburgh, Illinois No. 6, and Elkhorn/Hazard coals. Isolated values of 100 or 200 ppm were obtained for selenium in pyrite in each of these coals. Microprobe data for the Wyodak coal are not sufficient to estimate selenium content in pyrite (Appendix II). In the Elkhorn/Hazard coal, concentrations of selenium in pyrite were near the detection limit of selenium (100 ppm). To estimate the total organic selenium in the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals (Fig. 6c), we have added the ammonium acetate-leached selenium to the unleached selenium.

In the Wyodak coal, selenium was leached primarily by ammonium acetate (20 percent). Only 30 percent of the total selenium was leached, suggesting an association with organics. To estimate the total organic selenium in the Wyodak coal (Fig. 6c), we have added the ammonium acetate-leached selenium to the unleached selenium.

<u>Chromium</u>

The leaching behavior of chromium is varied (Fig. 5d). Chromium is leached to some extent by HF (20-25%) in the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals. In the Wyodak coal, 45 percent of the chromium is leached by HF. Leaching by HF suggests an association with silicates (possibly illite). In the Elkhorn/Hazard and Illinois No. 6 coals, totals for leaching of chromium are low (45%). In the Wyodak coal, the total leached chromium is fairly low (70%). The low leaching totals possibly suggest an organic association for chromium. It is also possible that the unleached chromium is due to the presence of shielded (organically encapsulated) illite grains. In the Pittsburgh coal, chromium is leached to some degree by HCl (20%), suggesting an association with carbonates or HCl-soluble sulfides. Chromium is also leached by HNO_3 (30%) in the Pittsburgh coal, indicating an association with pyrite. Because the leaching data for chromium are inconclusive, we did not make a final determination for its forms of occurrence.

Huggins and Huffman (University of Kentucky) have identified the mode of occurrence of chromium in density separates of the program coals, based on XAFS data. Their results indicate the presence of CrOOH in the float fractions of the coals, chromium in silicates of the middling fractions, and chromite in the sink fractions of the coals. We examined float, middling, and sink density fractions of the Elkhorn/Hazard coal with the SEM to determine the forms of occurrence of chromium. Overall, our findings present no evidence to conflict with the observations of Huggins and Huffman. In the sink fraction, we detected chromite in 2 out of 21 grains analyzed, a relatively high proportion of chromite. Although we did not observe any species of chromium in the float fraction of the coal, identification of the amorphous CrOOH grains by SEM is difficult and concentrations may have been below detection limits. We also did not observe any species of chromium in the middling fraction of the coal. However, as discussed earlier, our microprobe analysis of the raw coal indicates the presence of chromium in illite, at concentrations that are near the detection limits of the microprobe.

<u>Nickel</u>

The leaching behavior of nickel is also varied (Fig. 5e). In each of the four program coals, nickel is leached to some degree by each of the four leaching agents (ammonium acetate, HCl, HF, and HNO_3). In the Elkhorn/Hazard coal, total leaching levels are low (35%). In each of the coals, nickel leached by

HNO_3 is probably associated with pyrite. The presence of nickel in pyrite in the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals is confirmed by microprobe data. Nickel leached by HCl may possibly be in nickel-oxides, however, nickel-oxides were not observed with the SEM. Modes of occurrence for nickel, as indicated by leaching data, are shown in Fig. 6d.

Mercury

The leaching behavior of mercury in the four program coals is highly varied (Fig. 5f). In the Pittsburgh and Elkhorn/Hazard coal, mercury is leached primarily by HCl (25-40%). HCl-leachable mercury in these coals may be associated with oxidized pyrite or HCl-soluble sulfides. Overall, a total of forty to fifty percent of mercury is leached in the Pittsburgh and Elkhorn Hazard beds. In the Illinois No. 6 coal, a total of only five percent of the mercury is leached. In the Wyodak coal, leaching data suggest that mercury was not leached at all. Work planned for Phase II will allow us to gain a better understanding of the behavior of mercury in the program coals. Because the leaching data for mercury are inconclusive, we did not make a final determination of its forms of occurrence.

Mass Balance Calculations

Using the mean arsenic and nickel concentrations obtained for pyrite by electron microprobe analysis, mass-balance calculations were done for the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals. The contribution of pyrite to the mass balance of arsenic and nickel was calculated by multiplying the concentration of each element in pyrite by the amount of pyrite (Appendix IV). The amount of pyrite (in weight percent) was calculated from pyritic sulfur values (Appendix IA). The calculated concentration of each element is expressed as a percentage of the whole-coal value. Results for arsenic and nickel are shown in Figures 7a and 7b, in which mass-balance fractions obtained by microprobe are compared with the mode of occurrence percentages based primarily on leaching data with an estimated error of ± 25% (figs. 6a-d).

Mass-balances were calculated on the basis of microprobe data. These calculations indicate that 60 percent of arsenic in the Pittsburgh coal can be accounted for by pyrite, comparing well (within the inferred leaching data error of ± 25%) with our final mode of occurrence determination, which indicates that 80% of arsenic is associated with pyrite (Fig. 7a). In the Illinois No. 6 coal, microprobe data indicate a higher proportion of arsenic associated with pyrite (100%) than our final mode of occurrence determinations (60%, Fig. 7a). This result is also within uncertainty, because the leaching value (60%) requires an average arsenic concentration in pyrite of about 50 ppm, which is about half of the microprobe detection limit. The microprobe result may be high, because the mass-balance calculation includes many below-detection-limit values that are taken to be at 70% of the detection limit (70 ppm) in the calculation.

Microprobe data for the Elkhorn/Hazard coal indicate that only about 20% of arsenic is associated with the pyrite. These data do not compare well to our final mode of occurrence estimates (65% percent total arsenic associated with pyrite), as derived from the sum of arsenic leached by nitric acid (25%) and the fraction of unleached arsenic (40%; Fig. 7a). However, because arsenic has a heterogeneous distribution in pyrites of the Elkhorn/Hazard coal, it is difficult to obtain an accurate mean value for arsenic and the mass balance approach based on microprobe data may not be appropriate.

Mass-balance for nickel calculated from microprobe analyses of pyrite is in fairly good agreement (within the leaching data error of ± 25%) with leaching data for the Pittsburgh, Illinois No. 6, and Elkhorn/Hazard coals (Fig. 7b). Microprobe data indicate the following percentages of nickel associated with pyrite: Pittsburgh (17%), Elkhorn/Hazard (3%), and Illinois No. 6 (50%). These data compare fairly well with final values based primarily on leaching: Pittsburgh (20%), Elkhorn/Hazard (5%), and Illinois No. 6 (30%).

The number of illite analyses with detectable concentrations of chromium was not sufficient to calculate mean values for chromium concentrations in illite based on microprobe data. If an average Cr_2O_3 value of 0.025 weight percent (equivalent to about 170 ppm Cr) in illite is assumed, mass balance calculations indicate that about ten percent of the chromium in the Pittsburgh, Illinois No. 6, and Elkhorn/Hazard coals can be accounted for by illite. This percentage is fairly close to percentages (20 to 25 percent) obtained in the HF stage of leaching.

Selenium concentrations in pyrite are generally below the microprobe detection limit (Appendix II) for the Pittsburgh or Illinois No. 6 coals. On the basis of mass-balance calculations, if all selenium is assumed to be in pyrite in the Pittsburgh and Illinois No. 6 coals, concentration levels in pyrite would still be lower than the detection limit (100 ppm). For the Elkhorn/Hazard coal, the mean selenium concentration in pyrite is marginally above the detection limit (about 110 ppm, based on 11 pyrite grains, Appendix II). A mass-balance calculation based on these data indicates that only about 8 percent of the selenium in the Elkhorn/Hazard coal is in pyrite. The rest of the selenium may be associated with the organics.

Experiments to Determine the Volatility of Trace Elements

Experiments were conducted to determine the volatility of trace elements by heating the coal samples to 550°C and 1000°C. Analytical data indicate that the concentrations of arsenic, chromium, and nickel are not affected by heating samples to temperatures of up to 1000°C within the analytical errors of the experiment, which are generally less than 10 percent.

Conclusion

Work on Phase I is essentially complete. The USGS has analyzed the Pittsburgh, Elkhorn/Hazard, Illinois No. 6, and Wyodak coals to determine the mode of occurrence of arsenic, selenium, chromium, nickel, and mercury using (1) trace element analysis (ICP-AES, ICP-MS, cold vapor atomic absorption, hydride generation, INAA), (2) leaching experiments, (3) scanning electron microscopy, (4) electron microprobe analysis, and (5) X-ray diffraction.

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Finkelman, R.B. Palmer, C.A., Krasnow, M.R., Aruscavage, P.J. Sellers, G.A., and Dulong, F.T., 1990, Combustion and leaching behavior of elements in Argonne Premium Coal Samples: *Energy and Fuels* 4(5) 755-766.

Hosterman, J. W., and Dulong, F. T., 1985, A computer program for semi-quantitative mineral analysis by X-ray diffraction: In, Pevear, D. R., and Mumpton, F. A., eds., Qualitative mineral analysis of clays: CMS Workshop, Lectures, vol. 1, The Clay Minerals Society, Evergreen Colorado, p. 38-50.

Palmer, C.A., Krasnow, M.R., Finkelman, R.B., and D'Angelo, W.M., 1993, An evaluation of leaching to determine modes of occurrence of selected toxic elements in coal: *Journal of Coal Quality* 12 (4) 135-141.

Figures

Figure 1

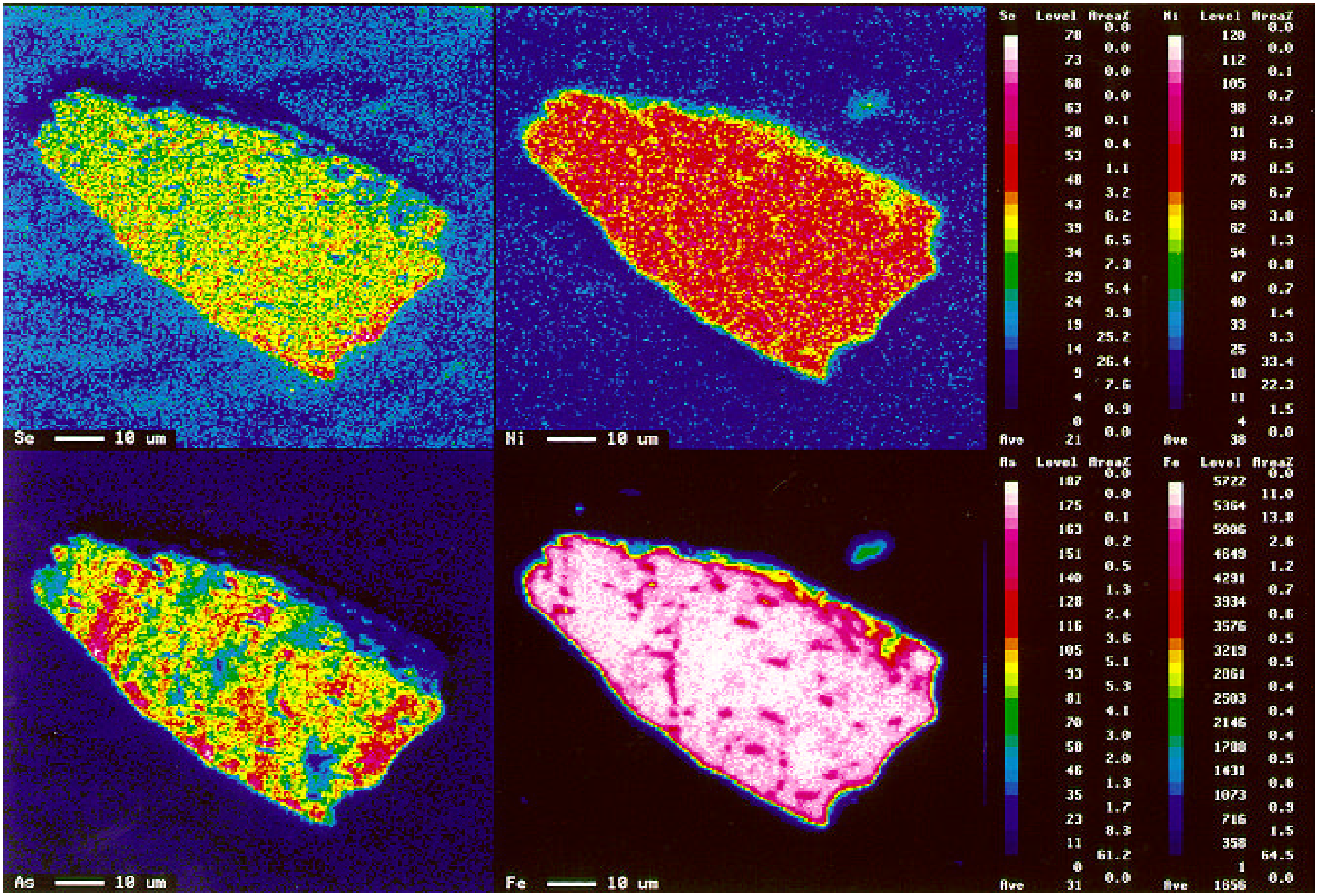
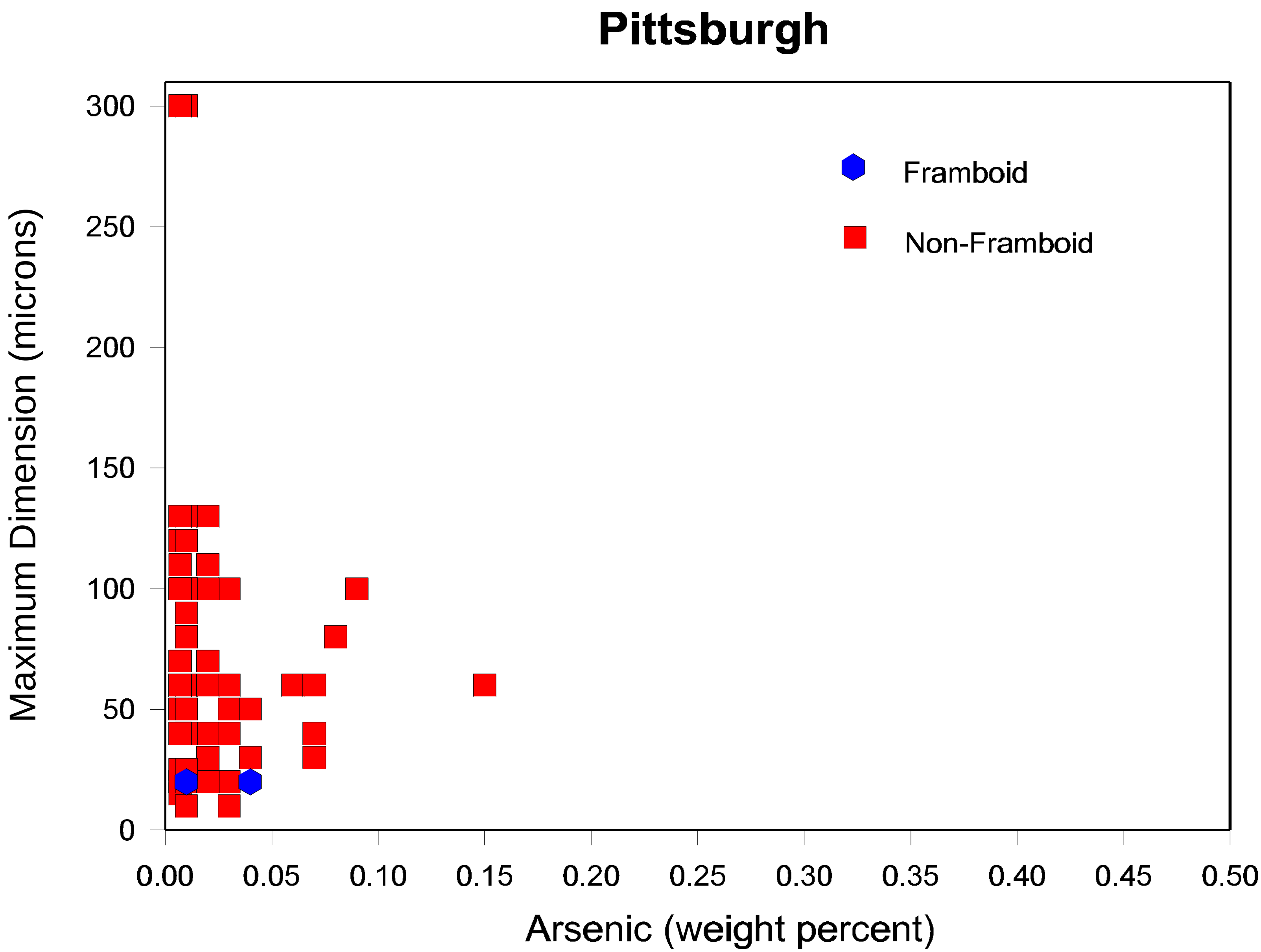

Se 10 um
Ni 10 um
As 10 um
Fe 10 um
Se Level Area%
78 73 68 63 58 53 48 43 39 34 29 24 19 14 9 4 0
0.0 0.0 0.0 0.0 0.0 0.1 0.4 1.1 3.2 6.2 6.5 7.3 5.4 9.9 25.2 26.4 7.6 0.9 0.0
Ave 21
Ni Level Area%
120 112 105 98 91 83 76 69 62 54 47 40 33 25 18 11 4
0.0 0.0 0.1 0.7 3.0 6.3 8.5 6.7 3.0 1.3 0.8 0.7 1.4 9.3 33.4 22.3 1.5 0.0
Ave 38
As Level Area%
187 175 163 151 140 128 116 105 93 81 70 58 46 35 23 11 0
0.0 0.0 0.1 0.2 0.5 1.3 2.4 3.6 5.1 5.3 4.1 3.0 2.0 1.3 1.7 8.3 61.2 0.0
Ave 31
Fe Level Area%
5722 5364 5006 4649 4291 3934 3576 3219 2861 2503 2146 1788 1431 1073 716 358 1
0.0 11.0 13.8 2.6 1.2 0.7 0.6 0.5 0.5 0.4 0.4 0.4 0.5 0.6 0.9 1.5 64.5 0.0
Ave 1858

Figure 2a



Pittsburgh
Framboid
Non-Framboid
Maximum Dimension (microns)
300
250
200
150
100
50
0
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
Arsenic (weight percent)

Figure 2b

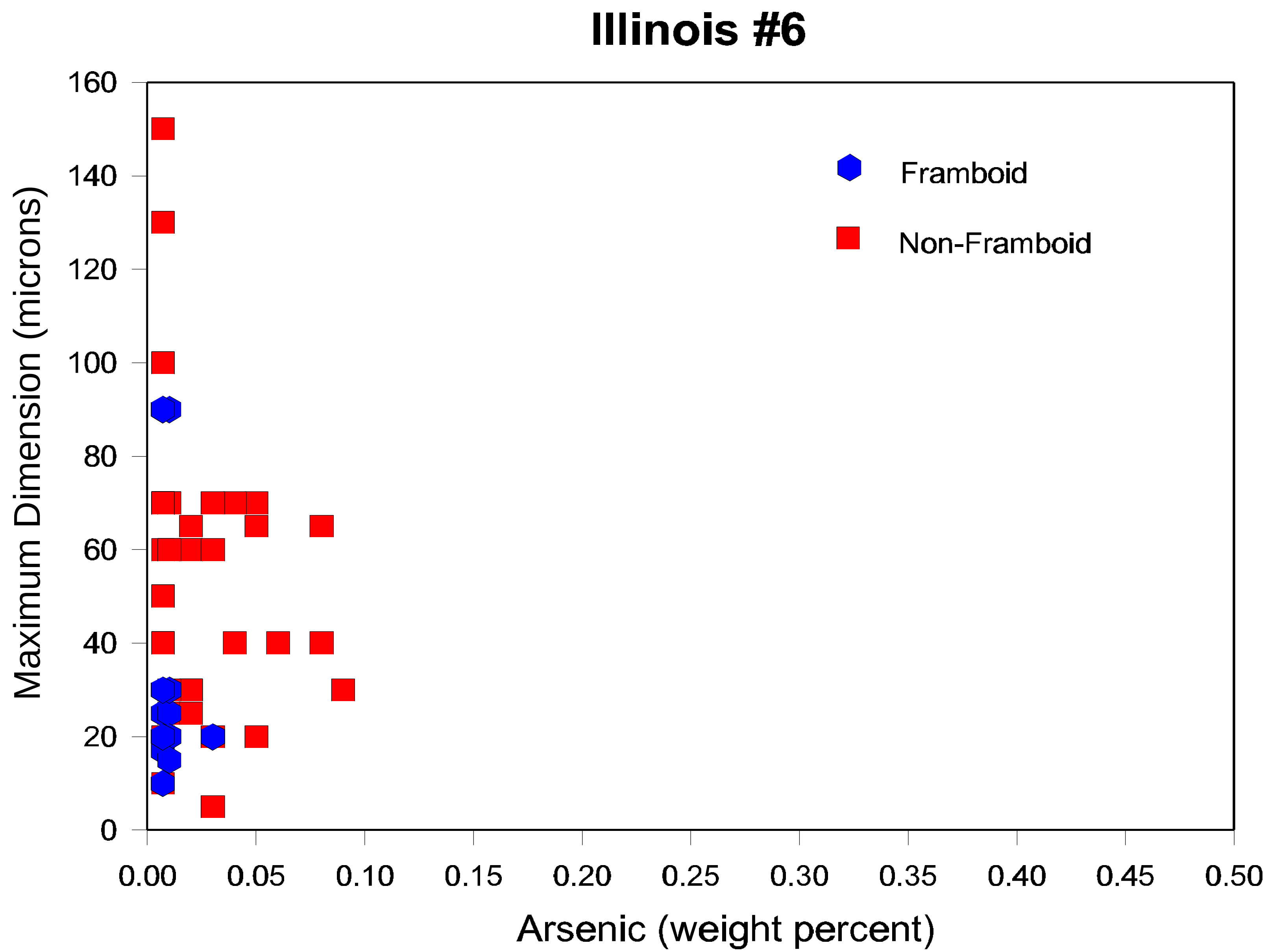

Illinois #6
160
140
120
100
80
60
40
20
0
Maximum Dimension (microns)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
Arsenic (weight percent)
Framboid
Non-Framboid

Figure 2c

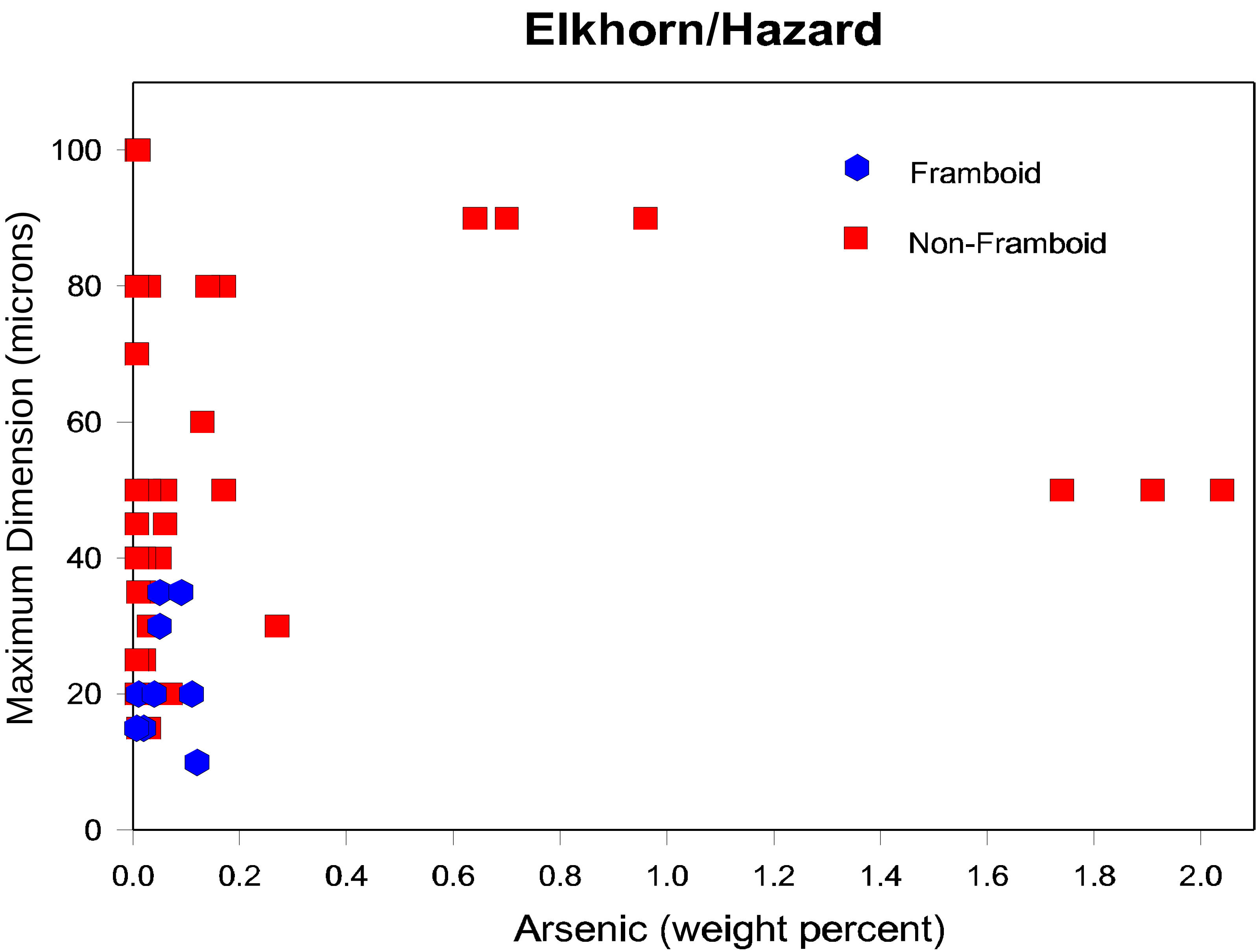

Elkhorn/Hazard
Framboid
Non-Framboid
Maximum Dimension (microns)
100
80
60
40
20
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Arsenic (weight percent)

Figure 3a

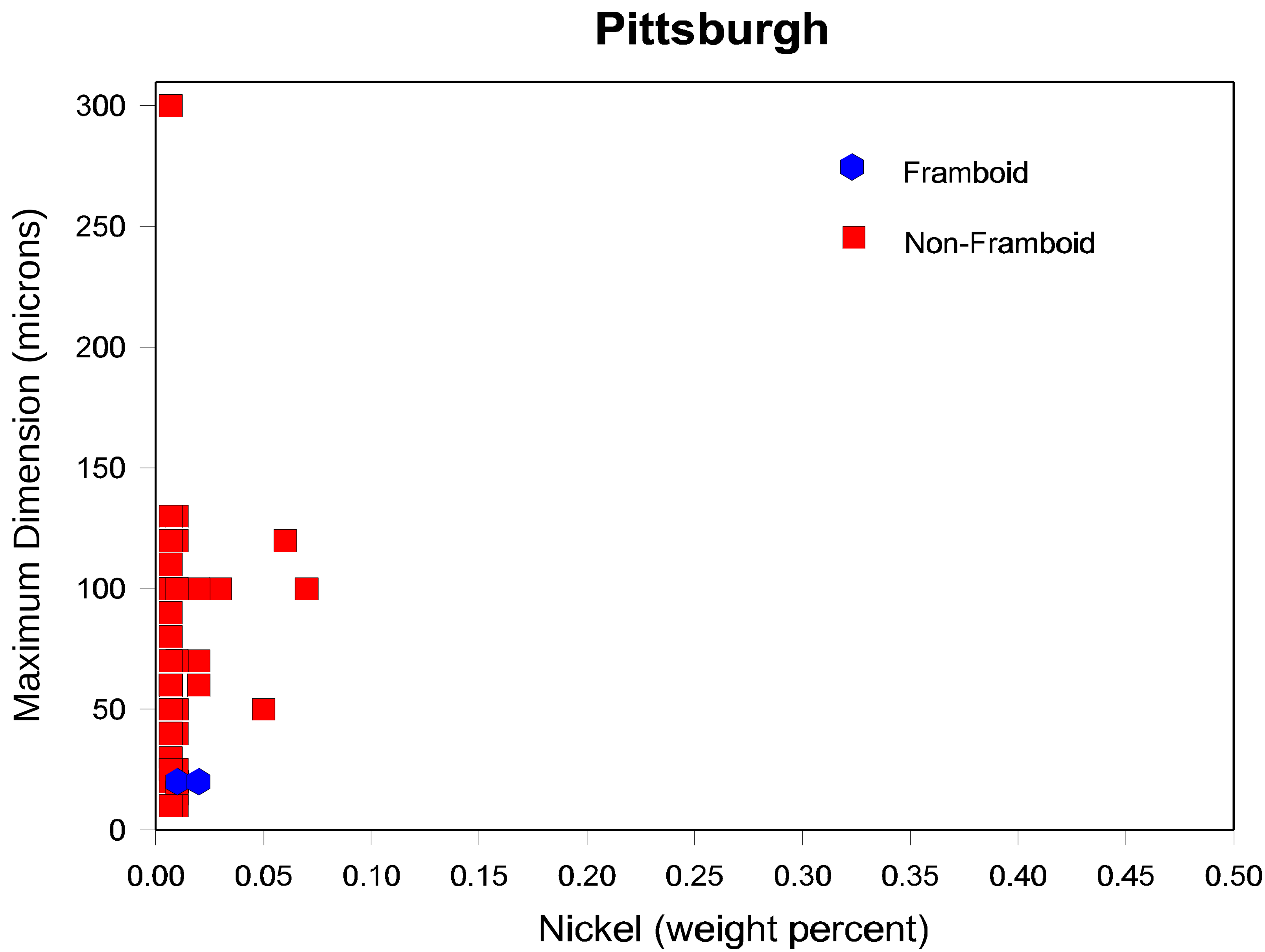
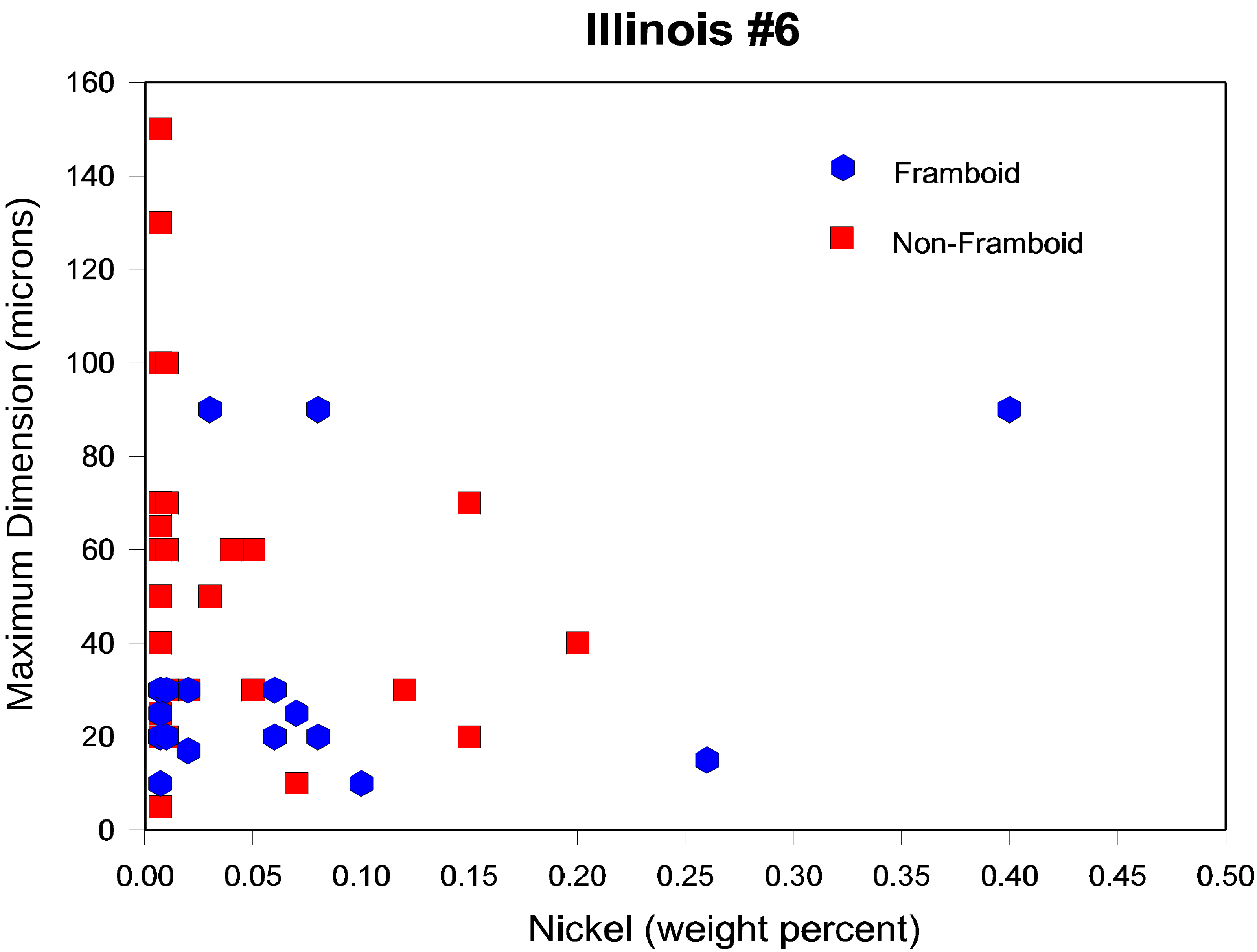

Pittsburgh
Framboid
Non-Framboid
Maximum Dimension (microns)
0
50
100
150
200
250
300
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
Nickel (weight percent)

Figure 3b



Illinois #6
Framboid
Non-Framboid
Maximum Dimension (microns)
Nickel (weight percent)
0
20
40
60
80
100
120
140
160
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50

Figure 3c

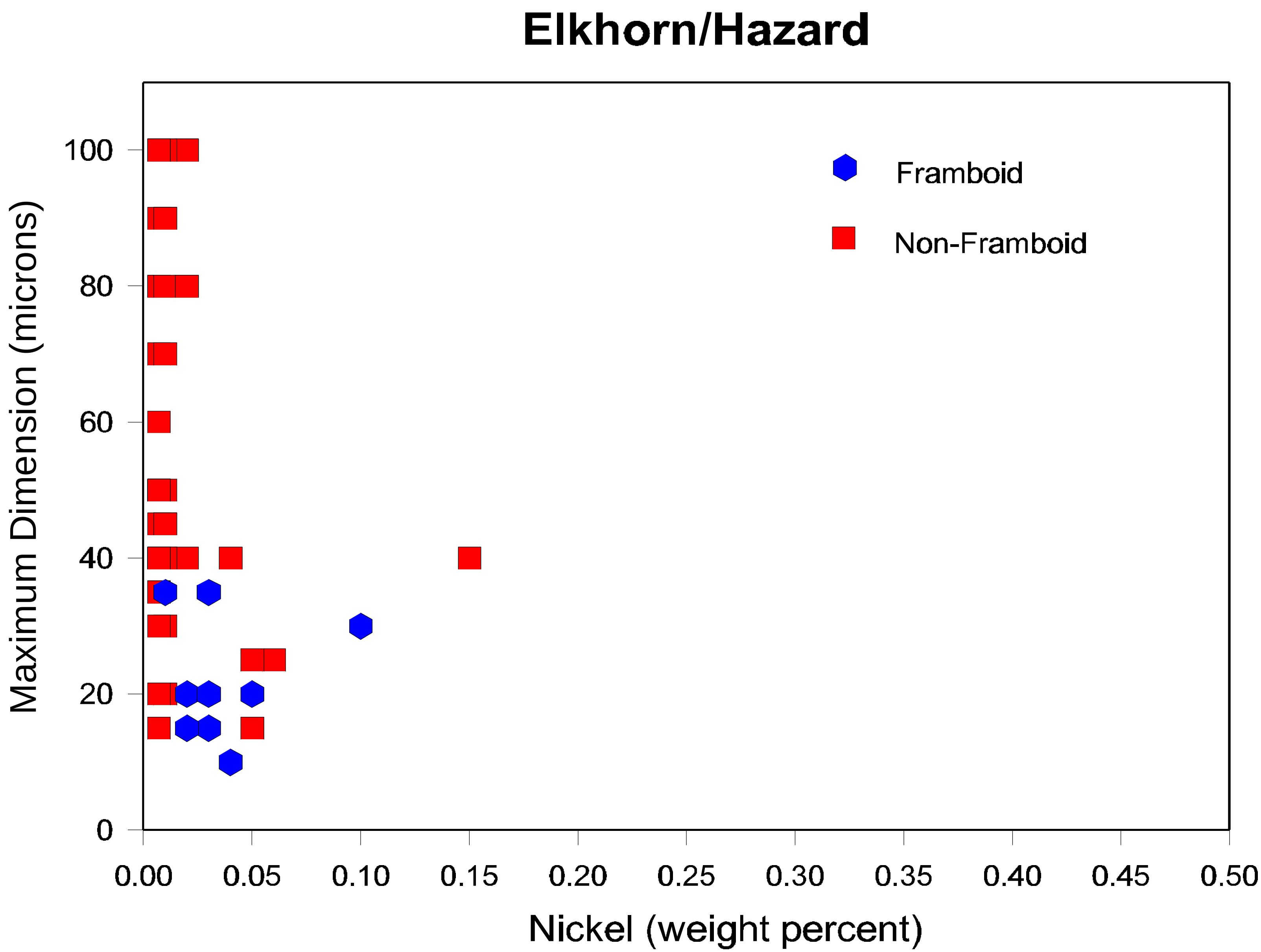

Elkhorn/Hazard
Framboid
Non-Framboid
Maximum Dimension (microns)
0
20
40
60
80
100
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
Nickel (weight percent)

Figure 4a

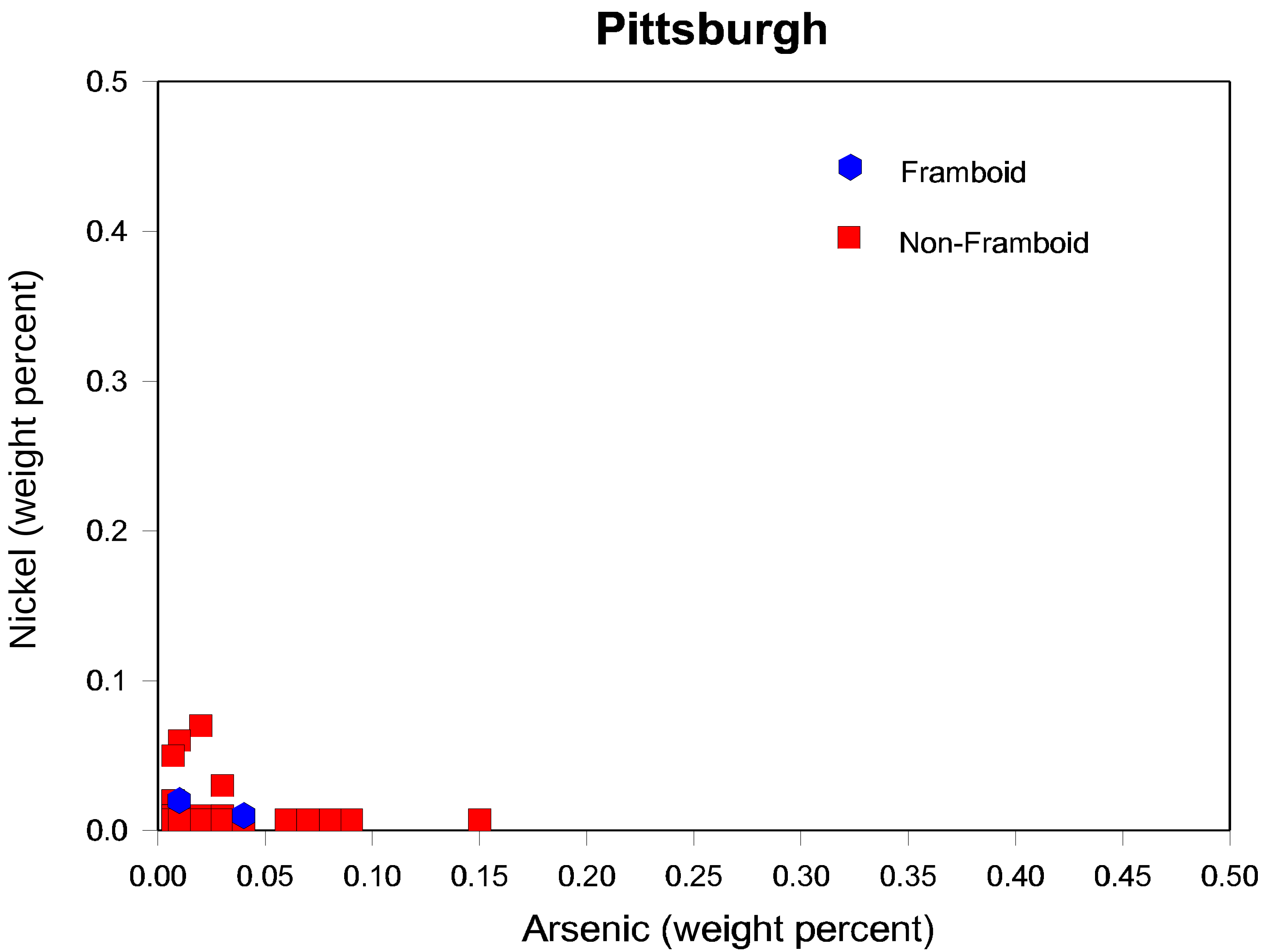
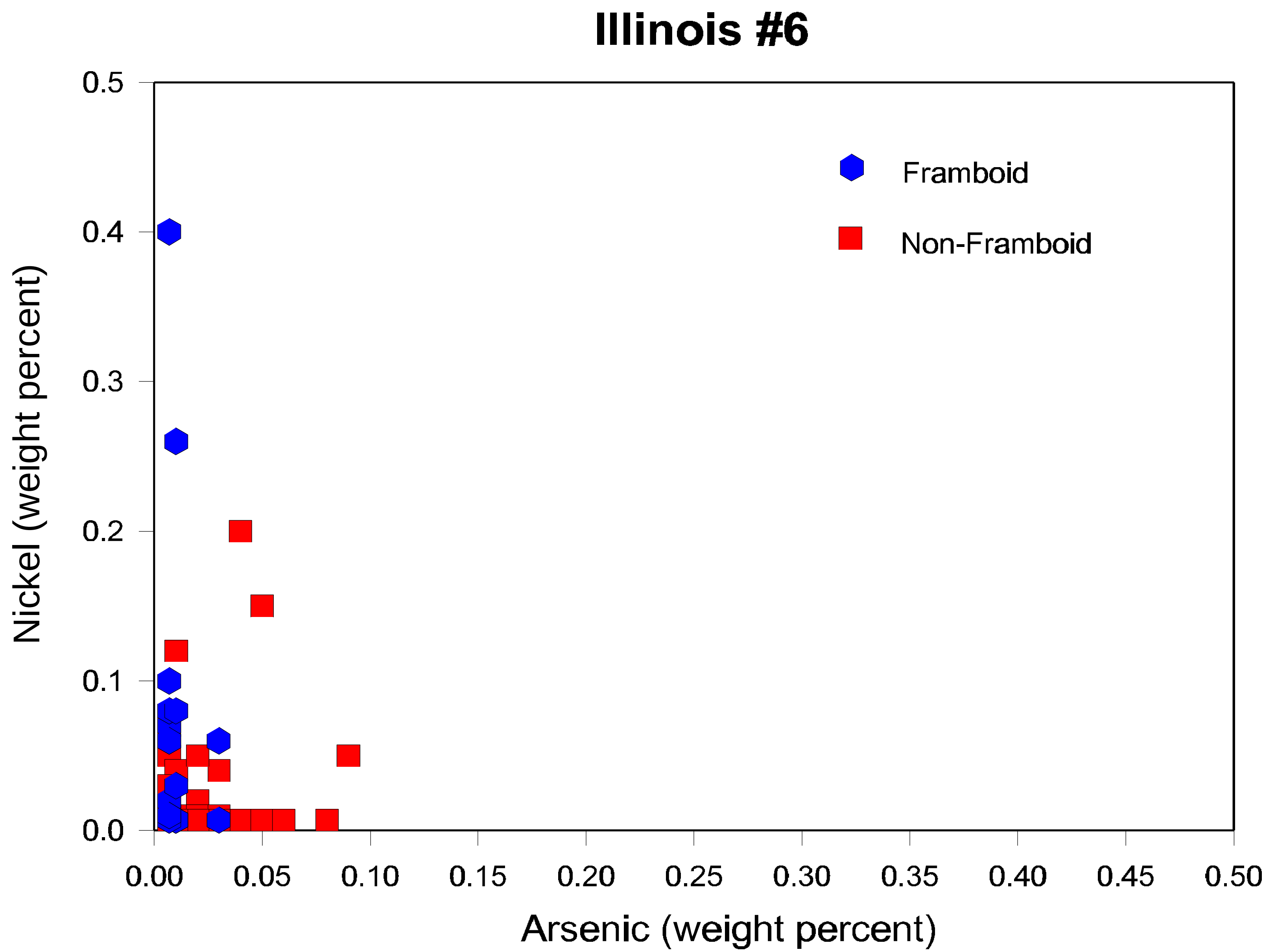
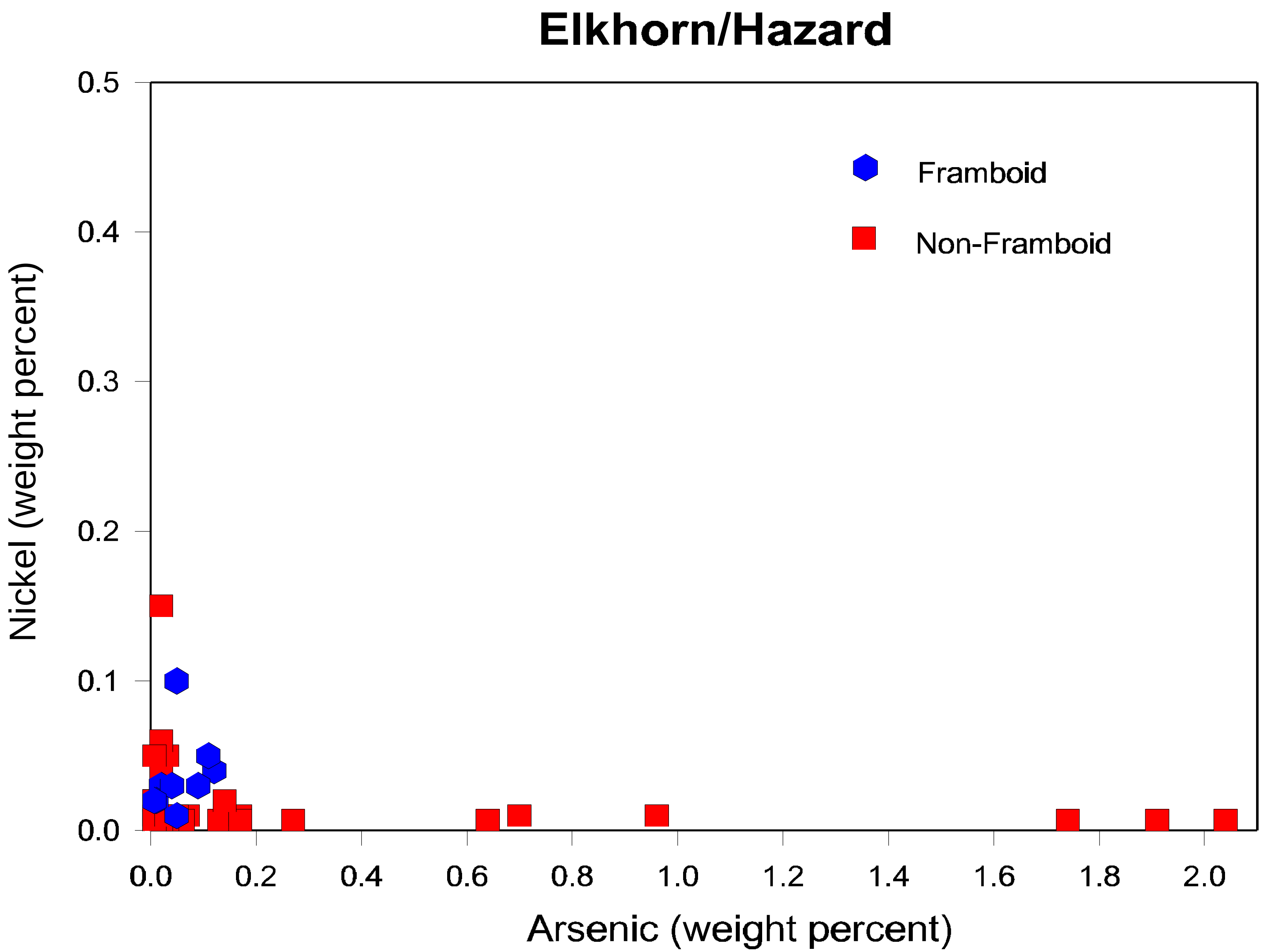

Pittsburgh
0.5
0.4
0.3
0.2
0.1
0.0
Nickel (weight percent)
Framboid
Non-Framboid
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
Arsenic (weight percent)

Figure 4b



Illinois #6
Framboid
Non-Framboid
Nickel (weight percent)
Arsenic (weight percent)
0.0
0.1
0.2
0.3
0.4
0.5
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50

Figure 4c



Elkhorn/Hazard
Framboid
Non-Framboid
Nickel (weight percent)
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Arsenic (weight percent)

Figure 5a

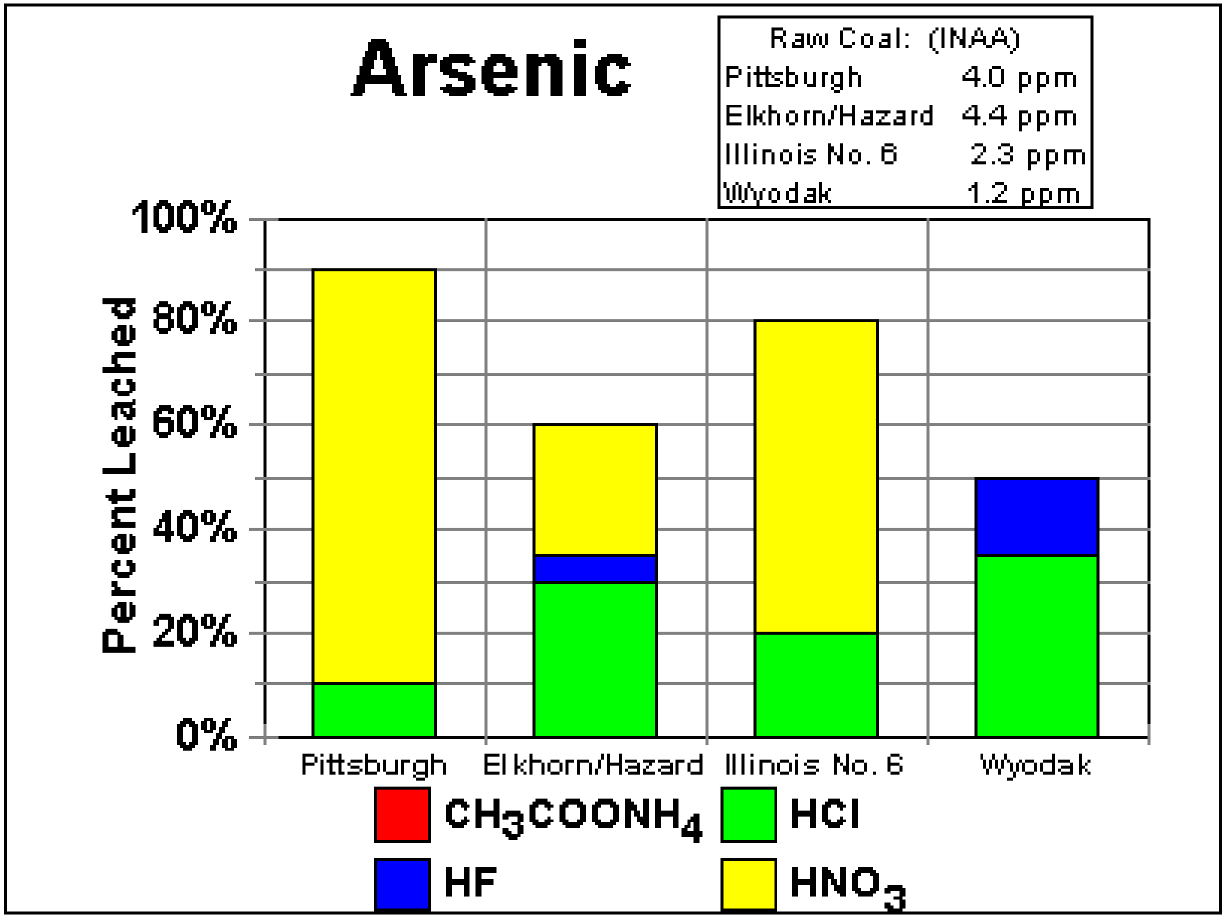
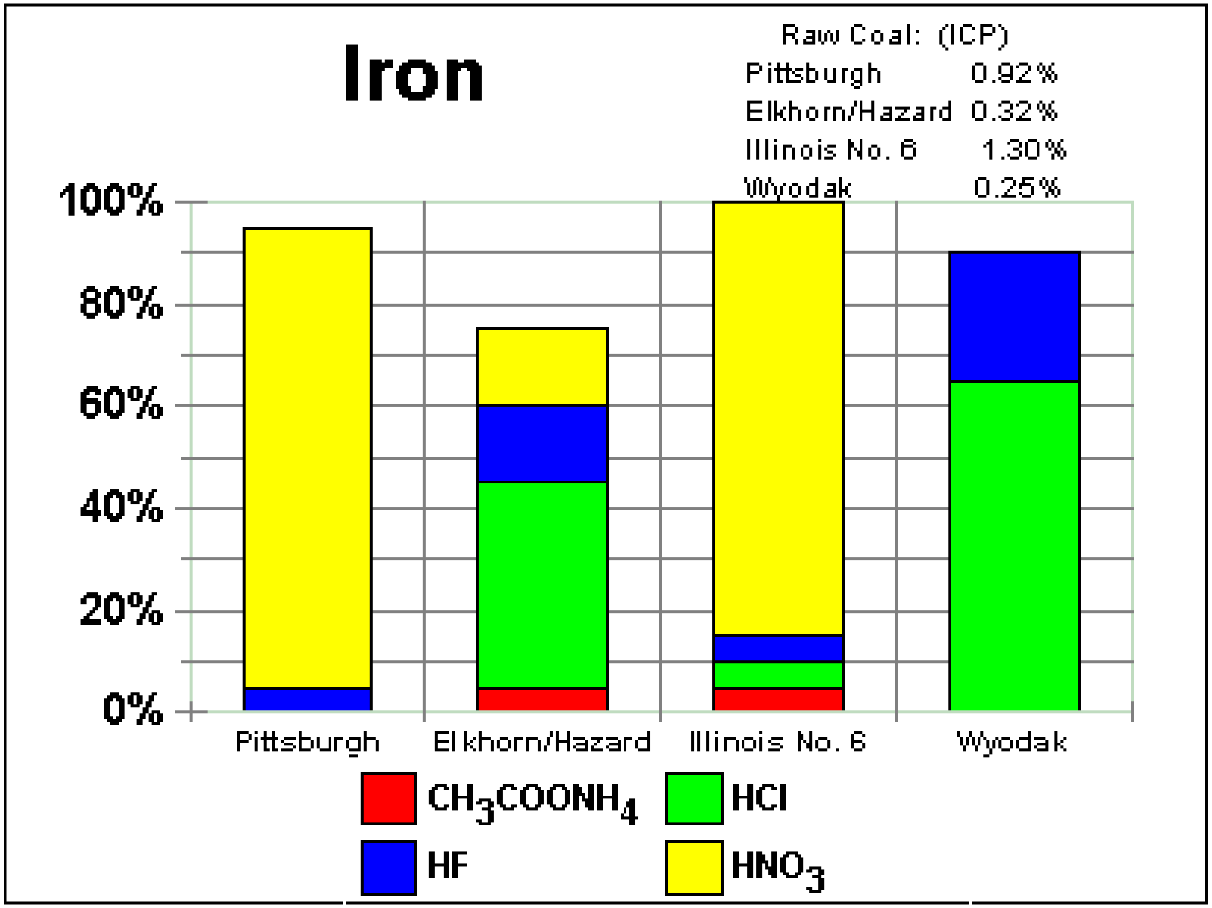

Arsenic
Raw Coal: (INAA)
Pittsburgh 4.0 ppm
Elkhorn/Hazard 4.4 ppm
Illinois No. 6 2.3 ppm
Wyodak 1.2 ppm
Percent Leached
100%
80%
60%
40%
20%
0%
Pittsburgh
Elkhorn/Hazard
Illinois No. 6
Wyodak
CH3COONH4
HCl
HF
HNO3

Figure 5b



Iron
Raw Coal: (ICP)
Pittsburgh 0.92%
Elkhorn/Hazard 0.32%
Illinois No. 6 1.30%
Wyodak 0.25%
100%
80%
60%
40%
20%
0%
Pittsburgh
Elkhorn/Hazard
Illinois No. 6
Wyodak
CH_3COONH_4
HCl
HF
HNO_3

Figure 5c

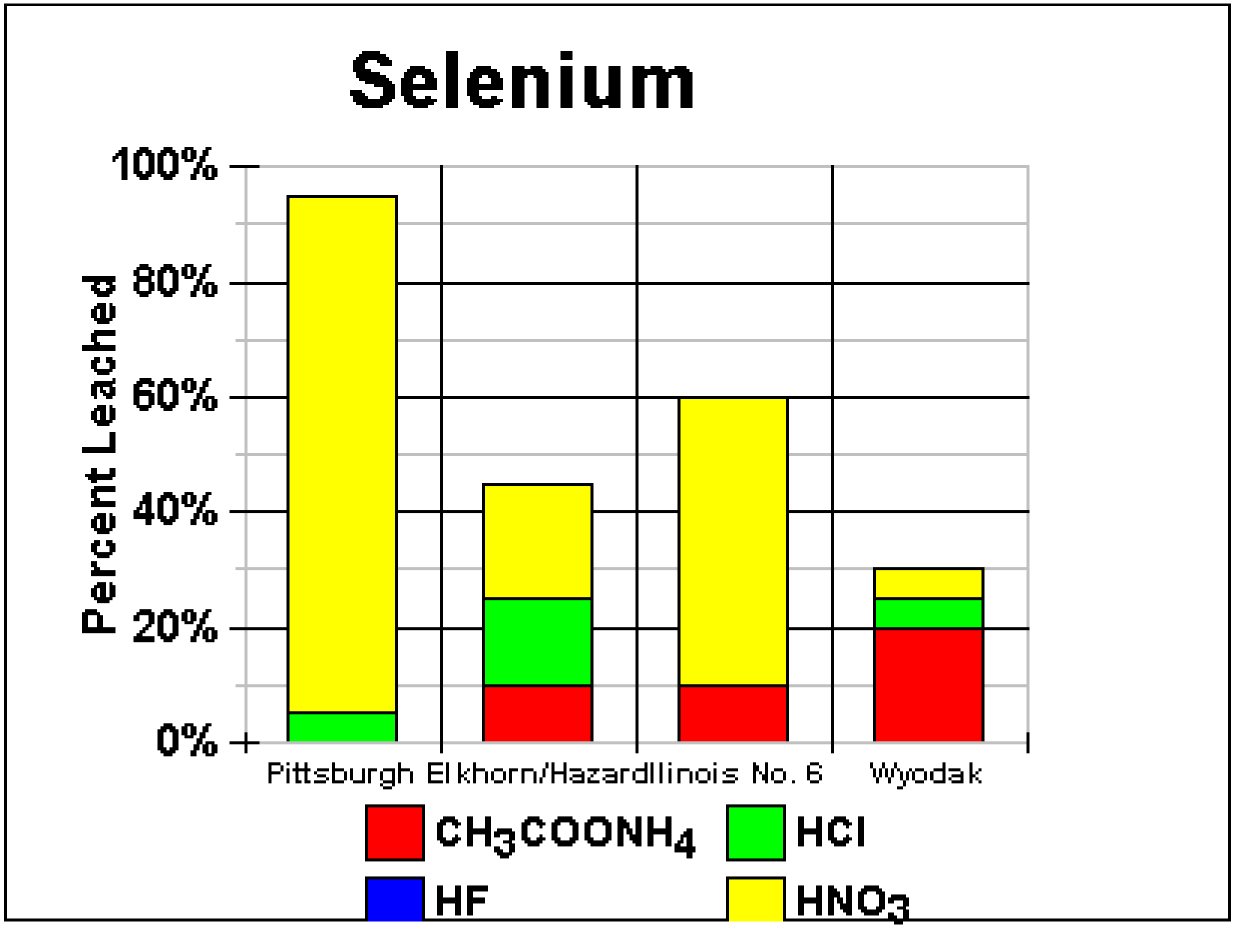

Selenium
Percent Leached
100%
80%
60%
40%
20%
0%
Pittsburgh
Elkhorn/Hazard
Illinois No. 6
Wyodak
CH_3COONH_4
HCl
HF
HNO_3

Figure 5d

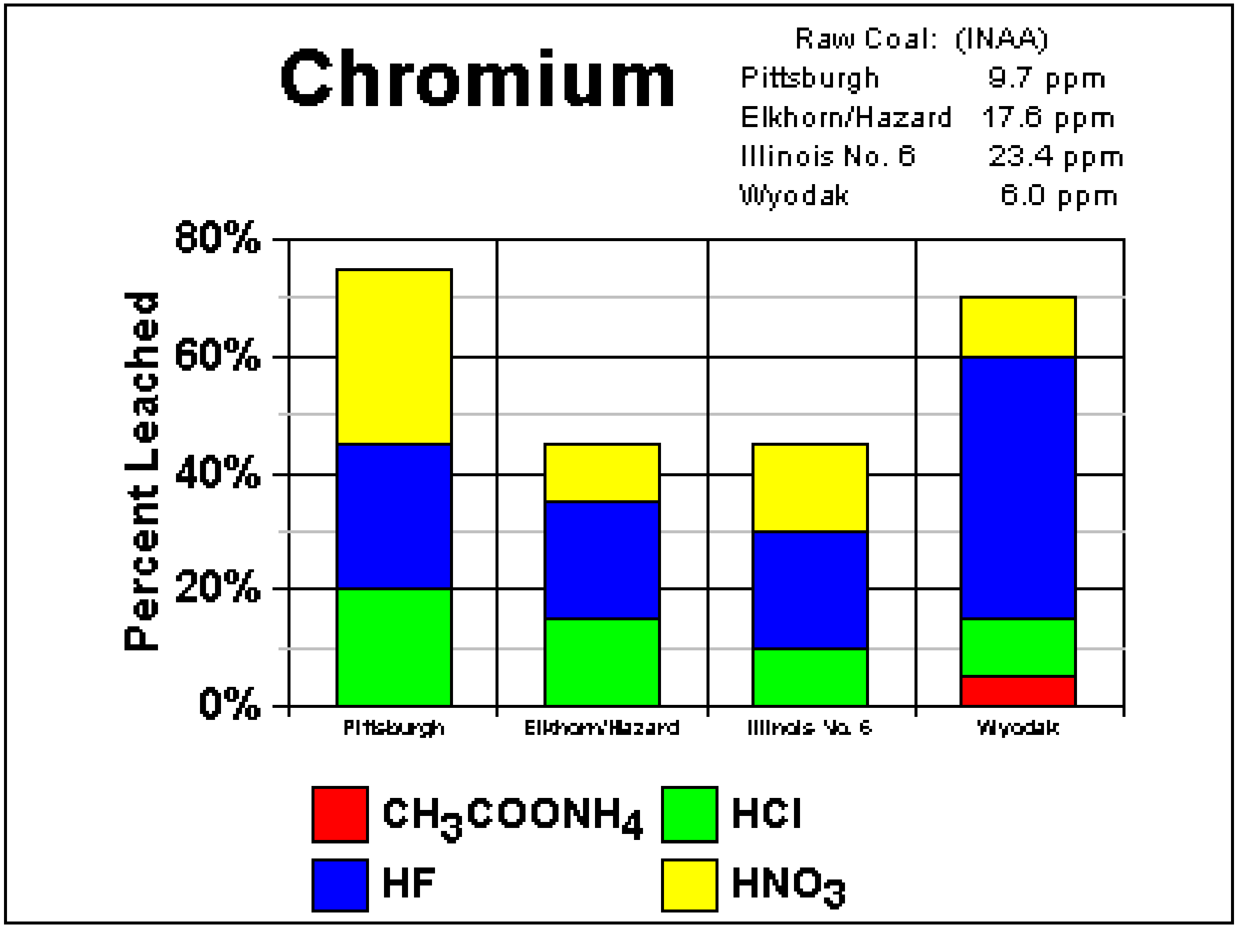
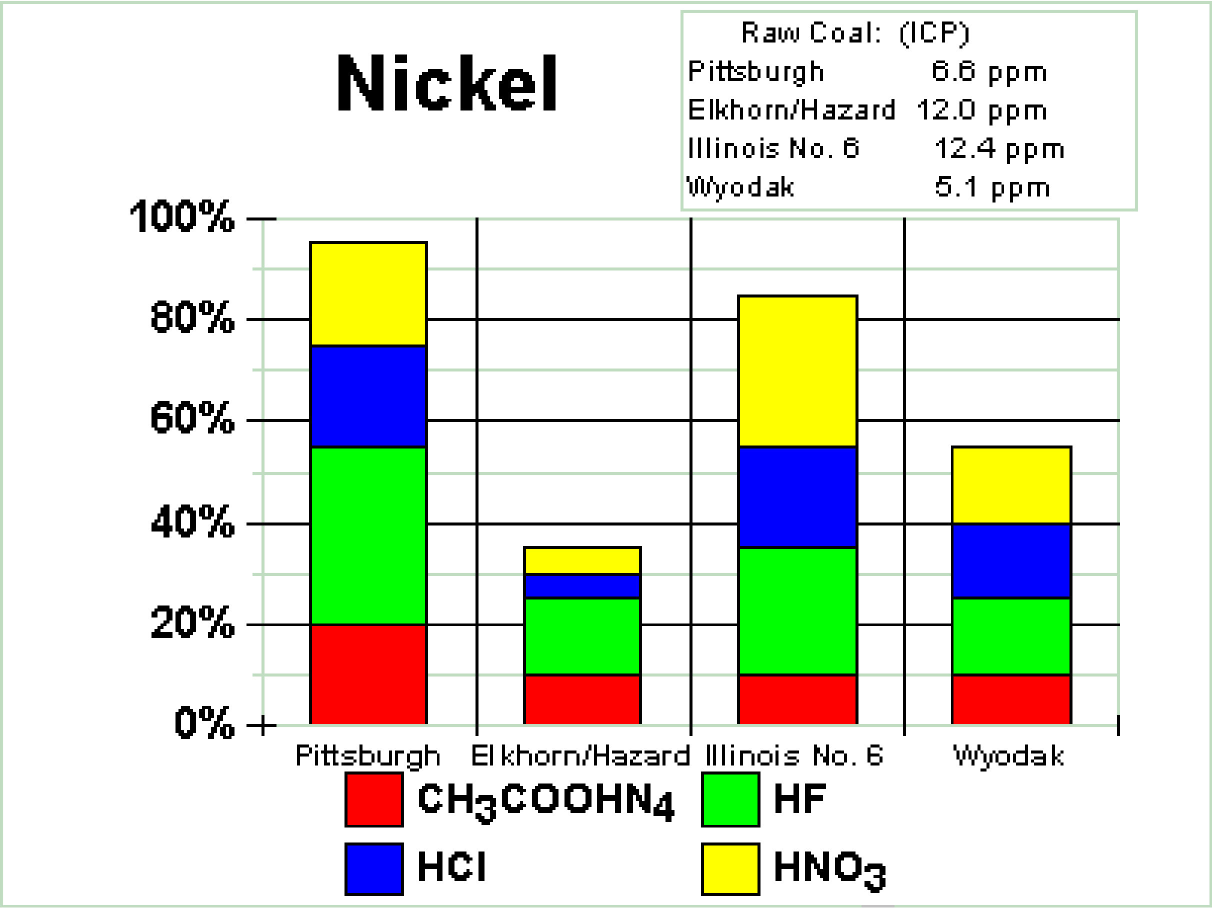

Chromium
Raw Coal: (INAA)
Pittsburgh 9.7 ppm
Elkhorn/Hazard 17.6 ppm
Illinois No. 6 23.4 ppm
Wyodak 6.0 ppm
Percent Leached
80%
60%
40%
20%
0%
Pittsburgh
Elkhorn/Hazard
Illinois No. 6
Wyodak
CH_3COONH_4
HCl
HF
HNO_3

Figure 5e



Nickel
Raw Coal: (ICP)
Pittsburgh 6.6 ppm
Elkhorn/Hazard 12.0 ppm
Illinois No. 6 12.4 ppm
Wyodak 5.1 ppm
100%
80%
60%
40%
20%
0%
Pittsburgh
Elkhorn/Hazard
Illinois No. 6
Wyodak
CH_3COOHN_4
HF
HCl
HNO_3

Figure 5f

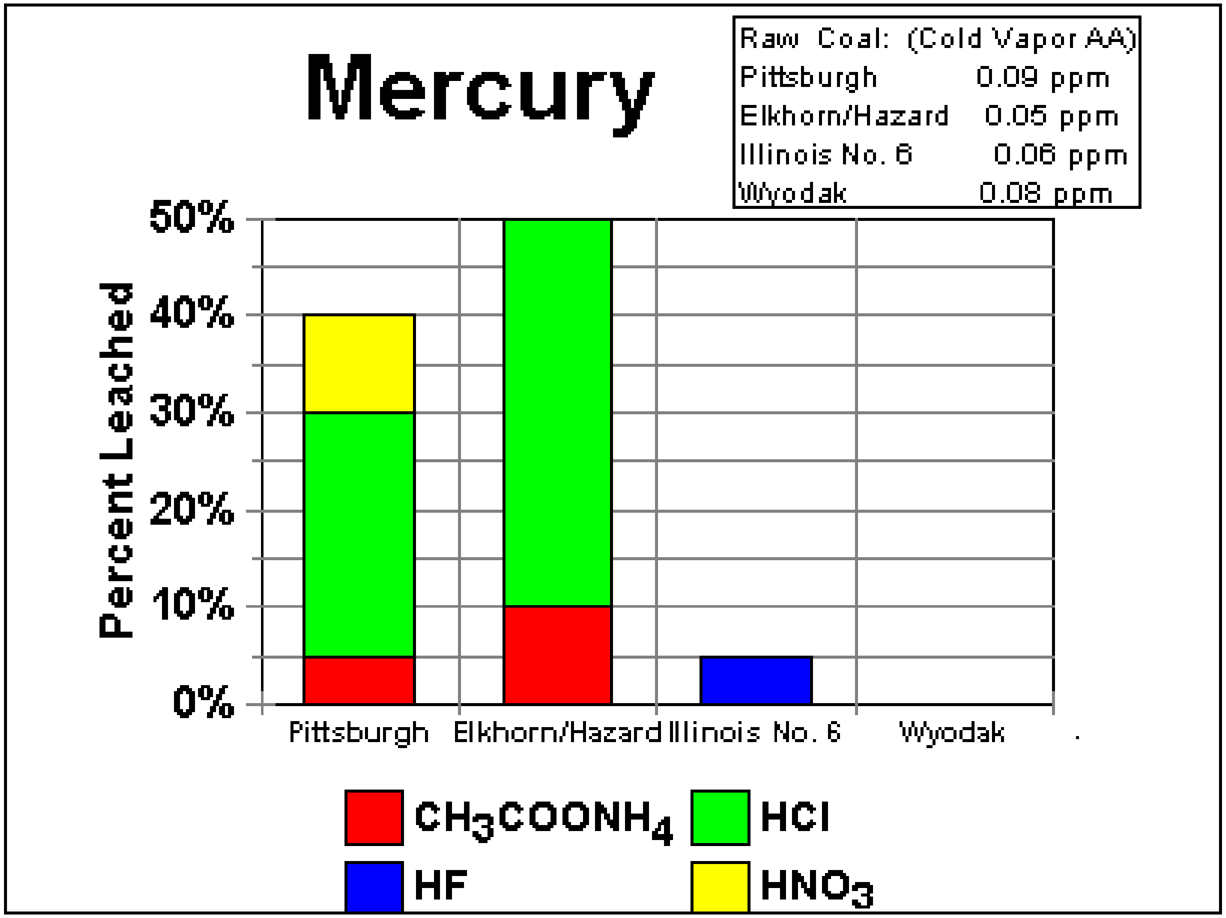
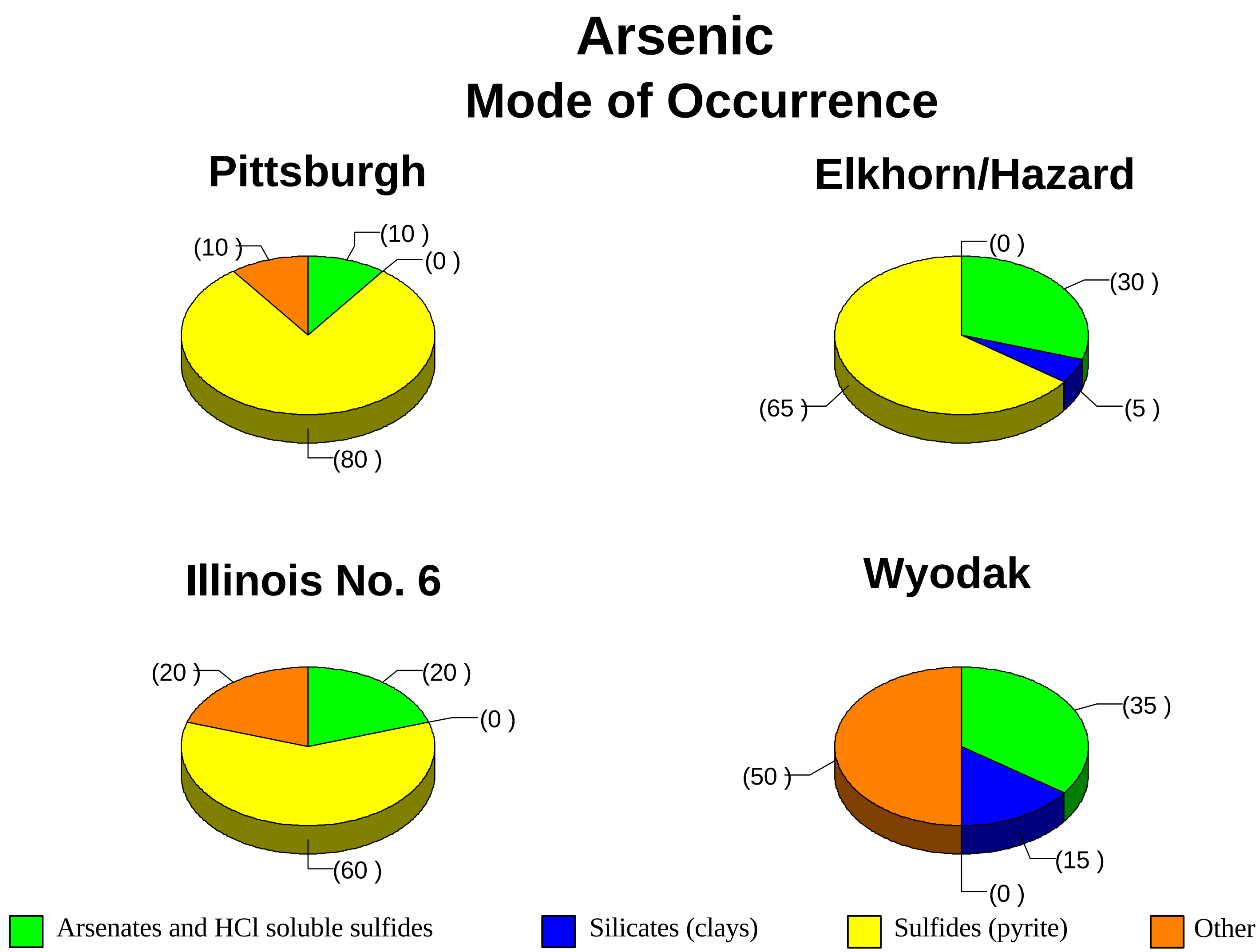

Mercury
Raw Coal: (Cold Vapor AA)
Pittsburgh 0.09 ppm
Elkhorn/Hazard 0.05 ppm
Illinois No. 6 0.06 ppm
Wyodak 0.08 ppm
Percent Leached
50%
40%
30%
20%
10%
0%
Pittsburgh
Elkhorn/Hazard
Illinois No. 6
Wyodak
CH3COONH4
HCl
HF
HNO3

Figure 6a



Arsenic
Mode of Occurrence
Pittsburgh
(10)
(10)
(0)
(80)
Elkhorn/Hazard
(0)
(30)
(65)
(5)
Illinois No. 6
(20)
(20)
(0)
(60)
Wyodak
(35)
(50)
(15)
(0)
Arsenates and HCl soluble sulfides
Silicates (clays)
Sulfides (pyrite)
Other

Figure 6b

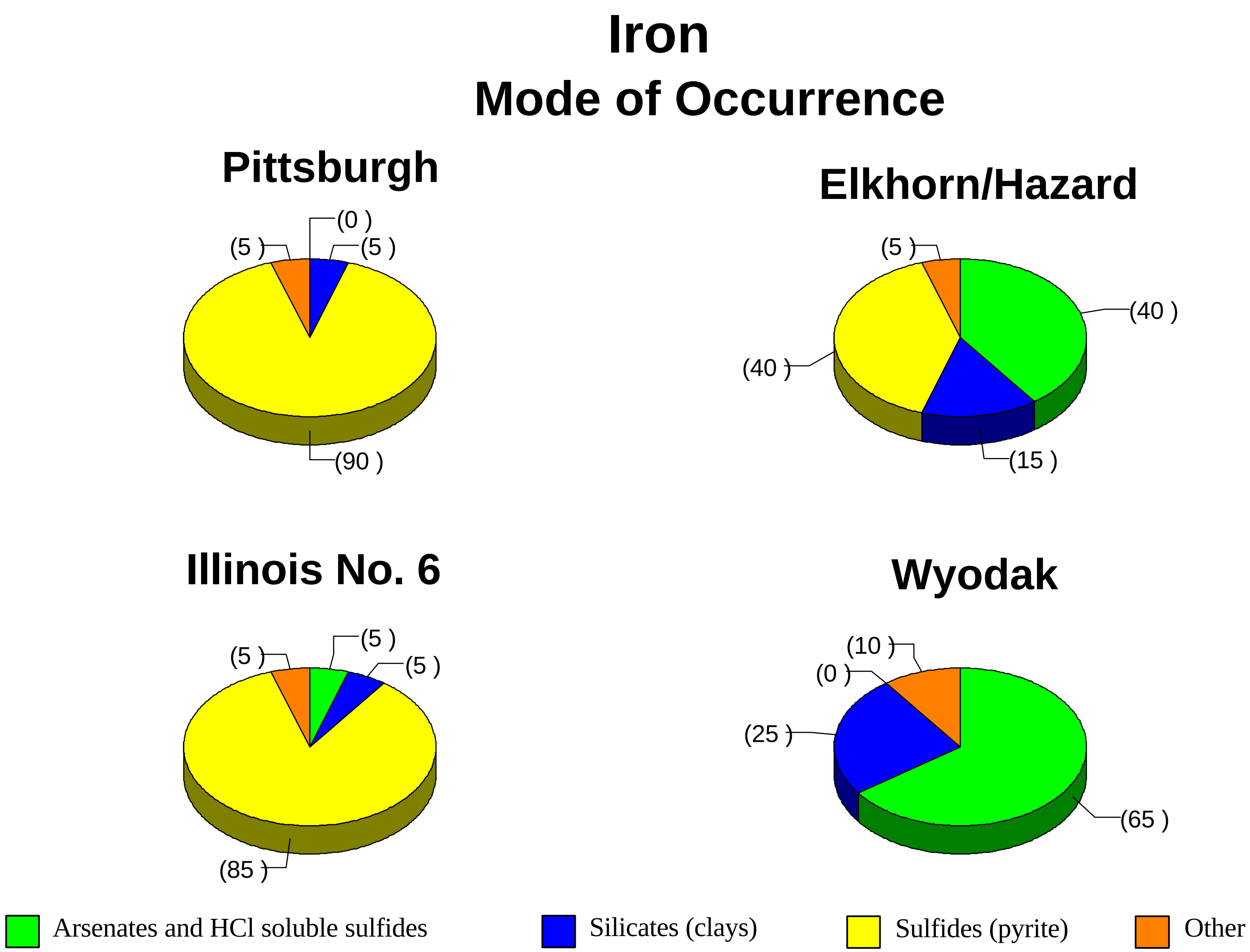

Iron
Mode of Occurrence
Pittsburgh
(0)
(5)
(5)
(90)
Elkhorn/Hazard
(5)
(40)
(40)
(15)
Illinois No. 6
(5)
(5)
(5)
(85)
Wyodak
(10)
(0)
(25)
(65)
Arsenates and HCl soluble sulfides
Silicates (clays)
Sulfides (pyrite)
Other

Figure 6c

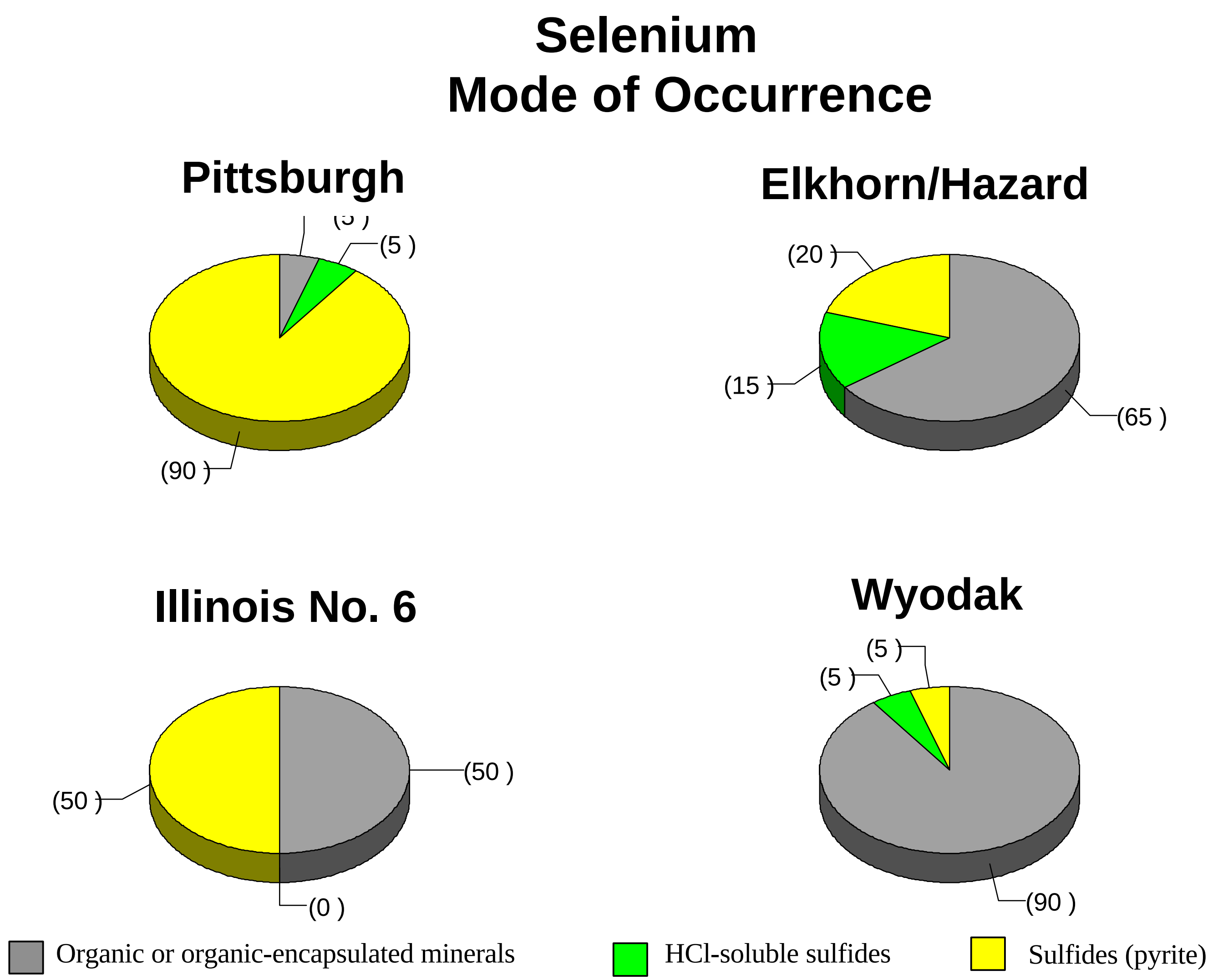

Selenium
Mode of Occurrence
Pittsburgh
(5)
(5)
(90)
Elkhorn/Hazard
(20)
(15)
(65)
Illinois No. 6
(50)
(50)
(0)
Wyodak
(5)
(5)
(90)
Organic or organic-encapsulated minerals
HCl-soluble sulfides
Sulfides (pyrite)

Figure 6d

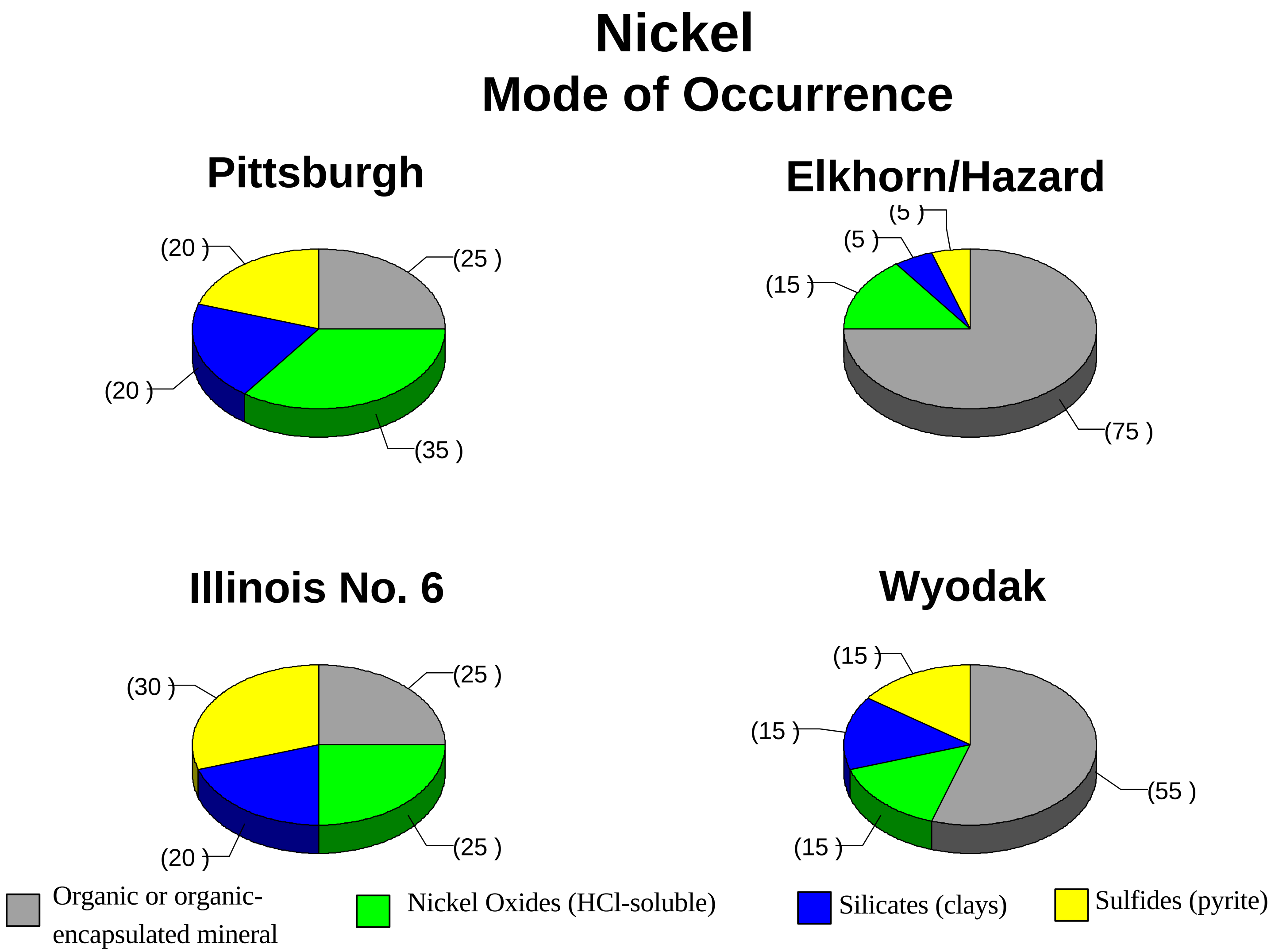

Nickel
Mode of Occurrence
Pittsburgh
(20)
(25)
(20)
(35)
Elkhorn/Hazard
(5)
(5)
(15)
(75)
Illinois No. 6
(30)
(25)
(20)
(25)
Wyodak
(15)
(15)
(55)
(15)
Organic or organic-encapsulated mineral
Nickel Oxides (HCl-soluble)
Silicates (clays)
Sulfides (pyrite)

Figure 7a

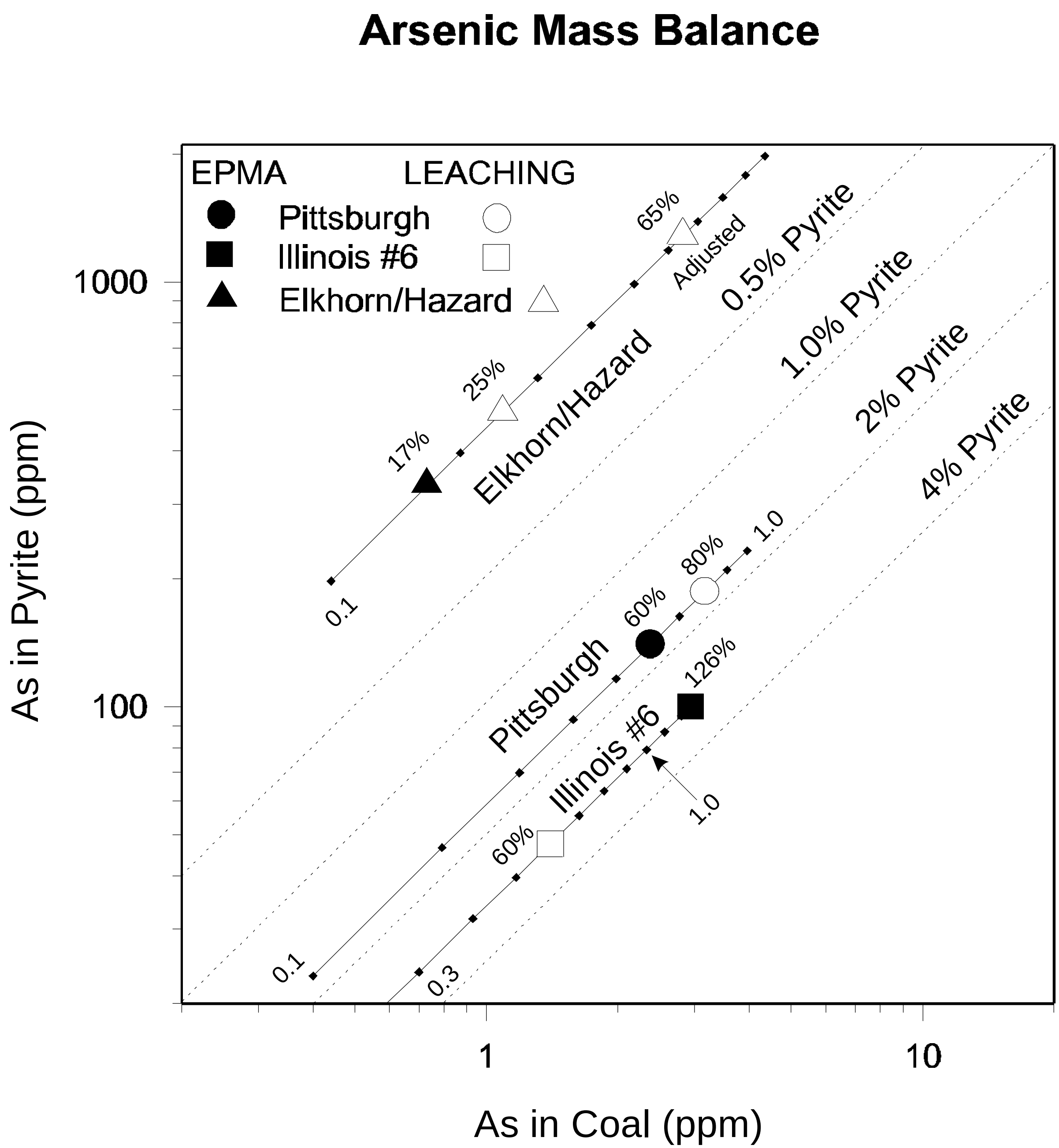
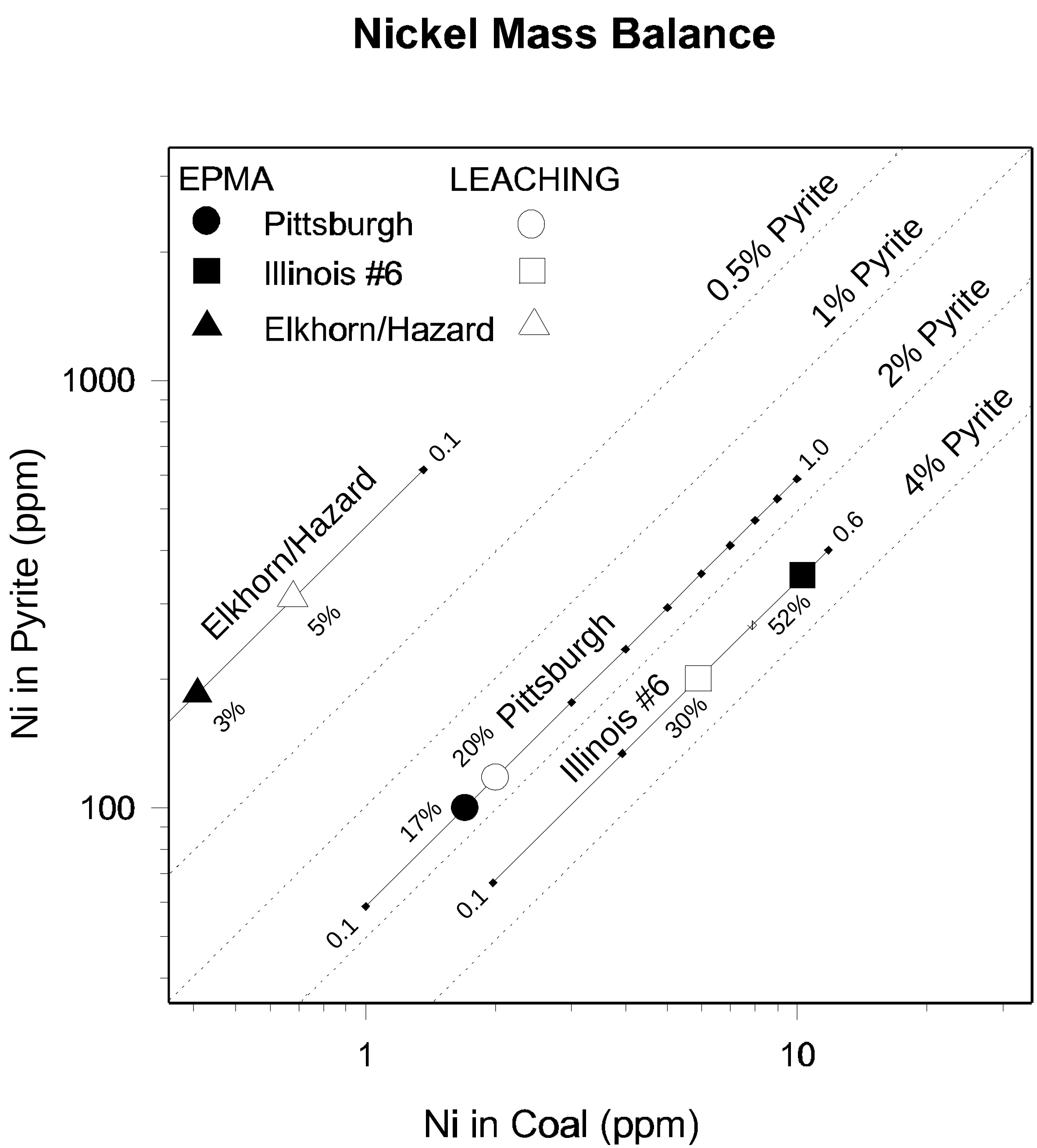

Arsenic Mass Balance
EPMA
LEACHING
Pittsburgh
Illinois #6
Elkhorn/Hazard
65%
Adjusted
25%
17%
0.1
Elkhorn/Hazard
0.5% Pyrite
1.0% Pyrite
2% Pyrite
4% Pyrite
1.0
80%
60%
126%
Pittsburgh
Illinois #6
1.0
60%
0.1
0.3
1000
100
1
10
As in Pyrite (ppm)
As in Coal (ppm)

Figure 7b


Nickel Mass Balance
EPMA
LEACHING
Pittsburgh
Illinois #6
Elkhorn/Hazard
0.5% Pyrite
1% Pyrite
2% Pyrite
4% Pyrite
Elkhorn/Hazard
0.1
5%
3%
Pittsburgh
1.0
20%
17%
0.1
Illinois #6
0.6
52%
30%
0.1
1000
100
1
10
Ni in Pyrite (ppm)
Ni in Coal (ppm)

Tables

Table 1. Percentages of elements leached by ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid as compared to the total concentration of the element in the unleached coal.

	CH3COONH3	HCl	HF	HNO3	Total
Arsenic					
Pittsburgh	0%	10%	0%	80%	90%
Elkhorn/Hazard	0%	30%	5%	25%	60%
Illinois No. 6	0%	20%	0%	60%	80%
Wyodak	0%	35%	15%	0%	50%
Iron					
Pittsburgh	0%	0%	5%	90%	95%
Elkhorn/Hazard	5%	40%	15%	15%	75%
Illinois No. 6	5%	5%	5%	85%	100%
Wyodak	0%	65%	25%	0%	90%
Chromium					
Pittsburgh	0%	20%	25%	30%	75%
Elkhorn/Hazard	0%	15%	20%	10%	45%
Illinois No. 6	0%	10%	20%	15%	45%
Wyodak	5%	10%	45%	10%	70%
Mercury					
Pittsburgh	5%	25%	0%	10%	40%
Elkhorn/Hazard	10%	40%	0%	0%	50%
Illinois No. 6	0%	0%	5%	0%	5%
Wyodak	0%	0%	0%	0%	0%
Selenium					
Pittsburgh	0%	5%	0%	90%	95%
Elkhorn/Hazard	10%	15%	0%	20%	45%
Illinois No. 6	10%	0%	0%	50%	60%
Wyodak	20%	5%	0%	5%	30%
Nickel					
Pittsburgh	20%	35%	20%	20%	95%
Elkhorn/Hazard	10%	15%	5%	5%	35%
Illinois No. 6	10%	25%	20%	30%	85%
Wyodak	10%	15%	15%	15%	55%

Appendices

Appendix I.

Forms of Sulfur Data, Mineralogy of the four program coals based on SEM analysis, and Semi-quantitative ash mineralogy by XRD

Appendix IA. Forms of Sulfur Data (all data in percent on a dry basis).

	Sulfate Sulfur	Pyritic Sulfur	Organic Sulfur	Total S
Pittsburgh	0.01	0.91	1.20	2.12
Elkhorn/Hazard	0.03	0.12	0.72	0.87
Illinois No. 6	0.04	1.57	2.21	3.82
Wyodak	0.02	0.03	0.41	0.46

Appendix 1B. Mineralogy of the three program coals based on SEM analysis.

Pittsburgh

Major:	Illite, kaolinite, quartz, pyrite, calcite, iron oxide
Minor/trace:	Barite, TiO_2, calcium sulfate (probably gypsum)

Elkhorn/Hazard

Major:	Illite, kaolinite, quartz, pyrite
Minor/trace:	Iron oxide, chalcopyrite, TiO_2, barite, apatite, monazite (REE phosphate), zircon.

Illinois No. 6

Major:	Illite, kaolinite, quartz, pyrite, calcite
Minor/trace:	none observed

Wyodak

Major:	Quartz, illite, kaolinite, mixed layer clays
Minor/trace:	Pyrite

Appendix IC. Semi-Quantitative Ash Mineralogy by XRD*

Sample	% Ash	Quartz	Feldspar	Calcite	Siderite	Ankerite	Illite	Kaolinite	Pyrite	Gypsum + Bassanite	Sphalerite	Analcime	Hematite
Pittsburgh	7.3	20	trace	trace	trace	trace	10	45	20				
		[1.5]**					[0.7]	[3.3]	[1.5]				
Elkhorn/ Hazard	8.0	15	trace	trace	trace		10	65	trace				
		[1.2]					[0.8]	[5.2]					
Illinois #6	10.3	25		trace	trace		10	35	20	trace	trace		trace
		[2.6]					[1.0]	[3.6]	[2.1]				
Wyodak	7.9	30			<5		<5	60		10		<5****	
		[2.6]			[1.0]		[1.0]	[3.6]				[<0.4]	

*Analyst F. Dulong, USGS-Reston

**Numbers in brackets indicate percent values on a whole-coal basis.

***Analcime is indicated in a trace amount at the lowest level of probability.

Values less than 5 percent are termed “trace”.

Appendix II.

Quantitative Microprobe Analyses of Pyrite Grains in the Pittsburgh, Elkhorn/Hazard, Illinois No. 6 and Wyodak Coals

Pyrite Analyses.							PITTSBURGH						
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
3/22/97	64	dl	dl	0.01	dl	dl	dl	**dl**	45.28	51.14	96.46	PittsB.1	50x70 subhedral
	67	dl	dl	dl	dl	0.00	dl	**dl**	45.71	53.45	99.20	PittsC.1	100x120 composite-
	68	0.01	dl	dl	0.01	dl	dl	**dl**	45.77	51.78	97.60	PittsC.2	core
	69	0.01	dl	0.00	0.01	dl	dl	**dl**	45.14	52.76	97.96	PittsC.3	
	72	dl	dl	dl	0.00	dl	dl	**0.01**	45.10	51.93	97.08	PittsD.1	40x80 composite-core
	73	0.00	dl	dl	0.01	dl	dl	**dl**	44.66	51.58	96.29	PittsD.2	
	77	0.02	dl	dl	dl	dl	dl	**dl**	46.43	52.45	98.93	PittsE.1	30x70 subhedral
	78	dl	dl	0.02	dl	dl	dl	**dl**	44.91	52.70	97.66	PittsE.2	
	79	0.00	dl	dl	dl	dl	dl	**dl**	45.88	52.07	97.99	Pitts2.1	80x100 subhedral
	80	dl	dl	dl	0.09	dl	dl	**dl**	46.10	52.36	98.59	Pitts2.2	
	81	0.01	dl	0.01	0.01	dl	dl	**dl**	45.55	50.73	96.35	Pitts2.3	
	82	0.02	0.03	dl	0.02	0.01	dl	**dl**	45.16	51.11	96.39	Pitts3.1	40x40 euhedral
	83	dl	0.06	dl	0.01	dl	dl	**dl**	45.09	51.96	97.15	Pitts3.2	
	84	dl	dl	dl	dl	dl	dl	**dl**	44.67	51.52	96.22	Pitts4.1	20x20 euhedral
	85	dl	0.02	dl	0.02	dl	dl	**dl**	45.34	52.19	97.60	Pitts5.1	25x25 euhedral
													on framboid
	86	dl	0.01	dl	dl	dl	dl	**dl**	45.04	54.61	99.70	Pitts6.1	40x50 subhedral
	87	dl	0.03	dl	dl	0.01	dl	**dl**	44.60	51.84	96.50	Pitts6.2	
	88	dl	dl	dl	0.01	dl	dl	**dl**	45.17	50.34	95.54	PittsH.1	150x300 subhedral
	89	dl	dl	dl	0.00	dl	dl	**dl**	45.38	52.07	97.48	PittsH.2	
	90	dl	dl	dl	dl	dl	dl	**dl**	45.19	51.73	96.96	PittsH.3	
	91	dl	dl	dl	dl	dl	dl	**0.01**	45.44	50.66	96.14	PittsH.4	
	92	dl	dl	0.03	0.03	dl	dl	**0.01**	45.63	51.45	97.18	PittsI.1	60x100 composite
	93	dl	dl	0.07	0.02	dl	dl	**dl**	45.48	51.28	96.86	PittsI.2	
	96	0.01	dl	dl	dl	0.00	dl	**0.01**	45.80	51.48	97.33	PittsJ.1	100x110 subhedral
	97	dl	dl	dl	0.02	0.01	dl	**dl**	45.54	51.78	97.38	PittsJ.2	

					PITTSBURGH- continued								
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
11/27/96	54		dl	dl	0.08	0.01	dl		45.22	50.75	96.06	Pitts.2.3	60x80 subhedral
	55		dl	dl	0.00	dl	dl		46.06	52.03	98.11	Pitts.3.1	60x60 euhedral
	56		dl	dl	dl	0.01	dl		46.26	52.32	98.60	Pitts.3.2	
	57		0.01	0.02	dl	dl	dl		46.04	52.30	98.36	Pitts.3.3	
	58		dl	dl	dl	dl	dl		45.62	51.23	96.85	Pitts.4.1	40x60 subhedral
	59		dl	dl	dl	dl	dl		45.74	52.10	97.84	Pitts.4.2	
	60		0.01	dl	0.01	dl	dl		45.88	51.34	97.24	Pitts.5.1	25x60 subh./irreg.
	61		dl	dl	dl	dl	dl		46.21	51.48	97.69	Pitts.5.2	
	62		dl	0.01	dl	dl	dl		46.69	52.66	99.36	Pitts.6.1	60x100 subh./irreg.
	63		dl	dl	dl	dl	dl		46.55	52.41	98.96	Pitts.6.2	
	64		dl	dl	0.01	dl	dl		46.39	52.06	98.46	Pitts.6.3	
	65		0.03	dl	dl	dl	dl		46.56	53.84	100.43	Pitts.7.1	120 euhedral
	66		dl	0.06	0.01	dl	dl		45.18	51.51	96.75	Pitts.7.2	
	67		dl	0.02	dl	dl	dl		45.92	51.93	97.86	Pitts.8.1	20x60 cleat?
	68		dl	dl	dl	dl	dl		46.18	51.99	98.17	Pitts.8.2	
	69		0.02	0.01	0.02	dl	dl		46.75	52.76	99.55	Pitts.9.1	15x70 cleat?
	70		dl	dl	0.02	0.01	dl		46.76	52.49	99.28	Pitts.9.2	
	71		dl	dl	0.00	dl	dl		46.61	52.08	98.70	Pitt.10.1	100x100 comp. euh.
	72		0.02	0.02	dl	dl	dl		46.55	52.51	99.10	Pitt.10.2	
	73		0.03	0.01	dl	0.01	dl		46.08	51.68	97.82	Pitt.10.3	
	76		0.19	dl	0.03	0.02	dl		45.98	52.17	98.39	Pitt.13.1	20 euhedral
10/19/96	30		dl	0.01	**0.13**				45.32	52.10	97.56	Pitt.1.1	20x40 subhedral
	31		dl	dl	**0.11**				45.28	51.57	96.95	Pitts.2.1	90 irreg. (round)

					PITTSBURGH -continued								
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
10/19/96	33		0.02	0.01	**0.06**				44.06	51.78	95.93	Pitts.3.1	5x15 subhedral
continued													
	34		dl	0.01	**0.08**				44.88	53.07	98.04	Pitts.4.1	20 euhedral
	35		0.02	dl	**0.25**				45.32	52.03	97.61	Pitts.5.1	20x60 subhedral
	36		dl	dl	**0.16**				45.59	52.66	98.41	Pitts.5.2	
	37		0.02	0.01	**0.14**				45.88	52.84	98.90	Pitts.6.1	20 framboidal
	38		dl	dl	**0.12**				46.36	54.42	100.91	Pitts.7.1	50x60 irregular
	39		0.01	dl	**0.10**				45.78	53.70	99.59	Pitts.8.1	40x50 subhedral
	40		0.02	dl	**0.11**				45.63	53.38	99.13	Pitts.8.2	
	41		dl	0.05	**0.08**				43.50	54.30	97.93	Pitts.8.2	
	61		dl	dl	**0.08**				45.41	51.86	97.36	Pitts.9.1	50x60 subhedral
	62		dl	dl	**0.09**				45.19	51.77	97.05	Pitts.9.2	
	63		dl	dl	**0.12**				45.56	51.85	97.54	Pitts.10.1	20x30 euhedral
	64		0.02	dl	**0.10**				46.38	53.57	100.07	Pitts.11.1	25x40 subhedral
9/26/96	42		dl	dl	**0.12**				43.81	51.33	95.25	Pitts.1.3	60 irregular
	44		0.10	0.01	**0.05**				44.40	53.56	98.11	Pitts.3.1	20x20 subhedral
	45		0.11	dl	**0.07**				45.54	54.09	99.82	Pitts.3.2	
	47		dl	dl	**0.04**				45.80	54.60	100.44	Pitts.4.2	25x60 subhedral
	48		dl	dl	**dl**				45.89	54.44	100.36	Pitts.4.3	
	49		dl	dl	**0.08**				45.81	53.68	99.57	Pitts.5.1	40x60 subhedral
	50		dl	dl	**dl**				46.35	53.69	100.09	Pitts.5.2	
	51		dl	dl	**dl**				45.93	53.93	99.85	Pitts.5.3	
	56		0.01	dl	**dl**				44.34	51.48	95.83	Pitts.9.1	100x130 subhedral

					PITTSBURGH- continued								
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
9/26/96	57		dl	dl	**0.06**				45.03	52.28	97.37	Pitts.9.2	
contd.	58		0.01	dl	**dl**				45.63	52.96	98.61	Pitts.9.3	
	59		dl	0.01	**0.06**				45.81	53.12	99.00	Pitts.9.4	
	60		0.02	dl	**dl**				45.22	52.34	97.62	Pitts.9.5	
	61		dl	dl	**0.06**				46.05	54.01	100.12	Pitt. 10.1	30x40 subhedral
	62		0.02	dl	**dl**				45.61	53.36	99.04	Pitts 10.2	
	63		0.01	0.02	**0.06**				44.18	51.86	96.12	Pitts 11.1	20 framboidal
	64		0.04	0.01	**0.06**				44.16	52.19	96.46	Pitts.12.1	10 euhedral on 11.1
	65		dl	0.01	**0.05**				44.88	52.52	97.46	Pitts.13.1	15x20 subhedral
	66		0.04	dl	**0.12**				45.36	53.28	98.79	Pitts.14.1	15x40 subhedral
	67		0.01	dl	**0.09**				45.10	53.26	98.45	Pitts.14.2	
	68		dl	dl	**0.06**				45.37	53.29	98.72	Pitts.15.1	20x30 subhedral
9/13/96	33		0.02	0.01	**0.12**				45.22	52.54	97.91	Pitts.1.1	25 irregular
	45		dl	dl	**0.13**				45.74	53.21	99.09	Pitts.7.2	25 irregular
	46		0.02	dl	**0.13**				45.44	51.67	97.26	Pitts.8.1	30 subhedral
	47		0.03	dl	**0.18**				46.16	53.36	99.73	Pitts.8.2	
	48		0.02	dl	**0.18**				46.04	53.72	99.96	Pitts.8.3	
	50		dl	0.00	**0.13**				45.60	51.51	97.24	Pitts.9.2	20 subhedral
	51		dl	dl	**0.08**				44.52	50.60	95.20	Pitts.10.1	50 subhedral
	52		0.01	0.01	**0.10**				44.45	50.80	95.36	Pitts.10.3	
	53		0.01	dl	**0.12**				44.46	51.42	96.00	Pitts.10.2	
	56		dl	dl	**0.14**				46.38	53.79	100.30	Pitts.11.2	10 euhedral

					PITTSBURGH- continued								
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
	57		dl	dl	**0.12**				44.99	51.46	96.57	Pitts.12.1	25 subhedral
	58		dl	0.00	**0.09**				45.76	52.17	98.04	Pitts.12.2	
	59		dl	dl	**0.11**				45.54	52.28	97.93	Pitts.12.3	
	60		dl	dl	**0.12**				45.72	52.53	98.37	Pitts.12.4	
	65		dl	0.01	**0.14**				44.41	50.72	95.29	Pitts.14.1	50 cleat?
	66		dl	dl	**0.14**				45.33	51.80	97.28	Pitts.14.2	
	67		dl	dl	**0.15**				46.21	53.76	100.13	Pitts.14.3	

*dl= values below detection limit of 100 ± 100 ppm, except arsenic values listed in boldface (dl= 500 ± 500 ppm).

Values for Co include a 0.03 wt. percent empirical correction factor subtracted from measured values.

						ELKHORN-HAZARD							
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
3/22/97	102	0.02	0.02	0.01	**0.03**	dl	dl	**dl**	44.29	50.96	95.36	ELKH B.2	25x30 subhedral
	103	dl	dl	dl	**0.64**	0.01	dl	**dl**	45.26	50.45	96.38	ELKH C.1	50x90 subhedral
	104	dl	dl	0.00	**0.96**	dl	dl	**0.01**	45.30	51.10	97.40	ELKH C.2	
	105	dl	0.01	0.01	**0.70**	dl	dl	**dl**	45.32	49.81	95.88	ELKH C.3	
	106	dl	dl	0.02	**dl**	dl	dl	**dl**	46.24	52.09	98.38	ELKH D.1	65x100 subhedral
	107	0.01	dl	0.01	**0.01**	dl	dl	**0.01**	46.01	51.84	97.93	ELKH D.2	
	108	dl	dl	0.02	**dl**	dl	dl	**dl**	46.04	52.09	98.18	ELKH D.3	
	109	0.02	0.02	0.01	**dl**	dl	dl	**dl**	46.44	51.44	97.96	ELKH D.4	
	110	dl	0.26	dl	**0.01**	0.02	dl	**0.01**	46.23	51.59	98.14	ELKH E.1	40x40 subhedral
	111	dl	0.02	dl	**dl**	dl	dl	**dl**	44.95	51.67	96.67	ELKH E.2	
	112	0.02	dl	0.03	**0.02**	0.01	dl	**dl**	46.03	51.60	97.74	ELKH 1.1	15 framboidal
11/27/96	29		0.01	dl	**0.13**	dl	dl		44.46	50.81	95.41	ELk-H.1.1	40x60 irregular
	31		0.02	0.01	**0.02**	dl	dl		44.95	50.84	95.84	ELk-H.2.1	10x20 irregular
	32		0.02	0.04	**0.12**	dl	dl		44.98	50.74	95.92	ELk-H.3.1	10 framboidal
	33		0.03	0.04	**0.02**	dl	dl		45.74	51.57	97.40	ELk-H.4.1	irregular
	34		0.04	0.15	**0.02**	dl	dl		45.90	52.22	98.32	ELk-H.4.2	
	35		0.01	0.02	**0.01**	dl	dl		45.64	51.34	97.03	ELk-H.5.1	20 framboidal
	36		0.01	0.02	**0.04**	dl	dl		45.27	50.38	95.72	ELk-H.5.2	
	38		0.06	0.10	**0.05**	dl	dl		44.68	51.13	96.03	ELk-H.6.2	30 framboidal
	39		dl	dl	**0.01**	dl	dl		45.08	50.97	96.06	ELk-H.7.1	15 subhedral
	40		0.03	dl	**0.27**	dl	dl		45.70	52.14	98.13	ELk-H.8.1	5x30 cleat

ELKHORN/HAZARD- continued													
Date	Anal #	Se	Cu	Ni	**As**	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
11/27/96	41		dl	dl	**0.01**	dl	dl		45.93	52.12	98.06	ELk-H.9.1	70x80 subhedral
continued	42		0.01	dl	**dl**	dl	dl		45.54	51.20	96.75	ELk-H.9.2	
	43		dl	dl	**0.01**	dl	dl		46.37	52.49	98.88	ELkH.10.1	80x100 subhedral
	44		dl	dl	**dl**	dl	dl		46.72	53.48	100.20	ELkH.10.2	
	45		dl	dl	**0.01**	dl	dl		46.60	52.51	99.12	ELkH.10.2	
	46		0.02	0.02	**dl**	dl	dl		45.30	51.18	96.52	ELkH.11.1	30x40 subhedral
	48		dl	dl	**0.02**	0.01	dl		45.51	51.24	96.79	ELkH.12.1	20x35 subhedral/euh.
	49		dl	dl	**0.01**	dl	dl		45.10	51.46	96.57	ELkH.12.2	
10/19/96	21		0.08	0.01	**0.17**				45.99	52.44	98.69	ELKH.1.1	35 framboidal
	22		0.08	0.02	**0.21**				45.67	52.53	98.52	ELKH.1.2	
	23		0.09	0.02	**0.10**				44.88	52.96	98.05	ELKH.2.1	15 framboidal
	24		dl	0.01	**0.19**				44.93	52.37	97.51	ELKH.3.1	20x20 subhedral
	27		0.04	0.05	**0.23**				45.45	53.26	99.03	ELKH.6.1	20 framboidal
	28		dl	dl	**0.11**				45.55	52.84	98.49	ELKH.7.1	30x70 irregular
	29		dl	0.01	**0.08**				45.37	52.89	98.34	ELKH.7.2	
	53		0.06	dl	**0.10**				45.45	53.86	99.48	ELKH.8.1	20 subhedral
	56		0.12	0.05	**0.15**				44.22	51.26	95.79	ELKH.11.1	15 detrital?
9/26/96	26		dl	dl	**1.80**				45.05	52.00	98.85	ElkH.2.1	30x50 subhedral/euh.
	27		0.01	dl	**1.97**				44.95	51.78	98.71	ElkH.2.2	
	28		dl	dl	**2.10**				44.82	51.74	98.66	ElkH.2.3	
	31		dl	dl	0.06				45.65	54.40	100.11	ElkH.4.1	30x40 euhedral
	32		0.01	0.01	0.05				45.53	54.27	99.87	ElkH.4.2	

ELKHORN/HAZARD-continued													
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
9/26/96	37		0.04	0.01	**0.11**				44.18	51.18	95.52	ElkH.8.1	35x40 euhedral
continued													
	74		0.04	dl	**0.12**				44.38	51.80	96.35	ElkH.11.1	40x50 subhedral
	75		0.05	0.01	**0.23**				44.38	51.73	96.39	ElkH.11.2	
	76		dl	dl	**0.12**				44.44	52.03	96.59	ElkH.12.1	45 round
	77		0.02	0.01	**dl**				44.56	51.56	96.20	ElkH.12.2	
	78		0.00	0.01	**dl**				44.47	51.81	96.33	ElkH.12.3	
	81		0.01	0.06	**0.08**				45.52	53.48	99.16	ElkH.14.1	25 round
	82		0.02	0.05	**dl**				45.64	53.49	99.20	ElkH.14.2	
9/13/96	24		dl	dl	**0.23**				45.02	51.58	96.83	ELKH.1.1	50 irregular
	25		dl	dl	**0.19**				44.91	51.30	96.39	ELKH.1.2	
	68		dl	dl	**0.17**				45.25	51.67	97.10	ELKH.8.1	40 subhedral
	69		0.01	dl	**0.22**				45.48	52.03	97.73	ELKH.8.2	
	70		dl	dl	**0.16**				45.09	51.45	96.70	ELKH.8.3	
	77		0.01	dl	**0.37**				44.29	50.49	95.17	ELKH.11.3	80 round
	78		dl	0.01	**0.23**				45.49	51.37	97.09	ELKH.11.4	
	79		0.01	0.02	**0.19**				45.55	51.79	97.55	ELKH.11.5	
	80		0.02	0.02	**0.34**				45.21	51.63	97.22	ELKH.11.6	

*dl= values below detection limit of 100 ± 100 ppm, except arsenic values listed in boldface (dl= 500 ± 500 ppm).

Values for Co include a 0.03 wt. percent empirical correction factor subtracted from measured values.

							ILLINOIS #6						
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
3/22/97	23	dl	dl	0.06	**dl**	dl	dl	**0.01**	45.76	52.52	98.38	Ill6PyD.1	30 subhedral/framb.
	24	0.01	0.02	0.02	**dl**	dl	dl	**0.02**	45.48	49.75	95.33	Ill6PyD.2	
	27	dl	dl	dl	**0.01**	dl	dl	**0.01**	45.58	53.75	99.40	Ill6Py1.1	20x25 subhedral/euh.
	28	0.01	0.01	dl	**0.02**	dl	dl	**dl**	45.02	53.78	98.87	Ill6Py1.2	
	29	dl	dl	dl	**dl**	dl	dl	**0.01**	44.36	50.71	95.11	Ill6Py2.1	20 framboidal
	30	dl	0.02	0.02	**dl**	0.01	dl	**0.01**	44.40	51.89	96.38	Ill6Py3.1	17 framboidal
	31	dl	dl	dl	**0.00**	dl	dl	**0.02**	45.38	52.46	97.89	Ill6Py4.1	20 framboidal
	32	dl	dl	dl	**0.02**	0.01	dl	**0.01**	45.64	51.78	97.48	Ill6Py5.1	40x60 subhedral
	33	dl	dl	0.01	**0.02**	0.01	dl	**0.01**	45.37	53.00	98.45	Ill6Py5.2	
	34	dl	0.01	dl	**0.01**	dl	dl	**0.01**	45.40	52.02	97.48	Ill6Py6.1	30 framboidal
	35	dl		dl	**0.00**	0.01	dl	**0.01**	44.46	51.26	95.78	Ill6Py6.2	
	36	0.02	0.03	0.02	**0.02**	0.01	dl	**dl**	44.57	52.01	96.70	Ill6Py7.1	20x30 subhedral
	39	dl	dl	0.01	**0.01**	0.02	dl	**dl**	43.65	51.19	94.91	Ill6Py8.2	60x60 subhedral/euh.
	41	dl	0.03	0.07	**dl**	dl	dl	**0.01**	45.30	51.89	97.32	Ill6Py9.1	25 framboidal/euh.
	49	dl	dl	dl	**dl**	0.01	dl	**dl**	46.03	52.71	98.78	Ill6Py11.2	80x150 plumose
	51	dl	0.02	0.08	**dl**	dl	dl	**0.01**	45.23	52.24	97.61	Ill6Py12.1	80x90 framb. cluster
	52	dl	0.03	0.40	**dl**	dl	dl	**0.01**	45.11	51.74	97.32	Ill6Py12.2	
	53	dl	0.02	0.03	**0.01**	dl	dl	**dl**	45.04	49.72	94.85	Ill6Py12.3	
	54	dl	0.04	0.08	**dl**	dl	dl	**0.01**	44.95	51.90	97.01	Ill6Py12.4	
	55	dl	0.01	dl	**dl**	dl	dl	**0.01**	45.83	53.31	99.19	Ill6Py13.1	25x70 cleat?
	56	dl	dl	dl	**dl**	0.02	dl	**dl**	46.00	48.98	95.03	Ill6Py13.2	
	57	0.02	dl	dl	**0.00**	dl	dl	**dl**	43.69	52.99	96.73	Ill6Py13.3	

ILLINOIS # 6- continued

Date	Anal#	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
11/27/96	8		0.03	0.05	**dl**	dl	dl		45.96	51.45	97.48	ILL-6.1.1	50x60 subhedral
	9		dl	0.04	**0.03**	0.02	dl		46.17	51.77	98.03	ILL-6.1.2	
	10		0.02	0.04	**0.01**	dl	dl		45.79	52.38	98.24	ILL-6.1.3	
	11		0.01	dl	**0.01**	dl	dl		45.62	52.38	98.01	ILL-6.2.1	25 framboidal
	12		0.03	0.01	**dl**	dl	dl		44.19	51.88	96.11	ILL-6.3.1	20 framboidal
	13		dl	dl	**dl**	dl	dl		46.66	53.47	100.12	ILL-6.4.1	20x70 cleat?
	14		dl	dl	**dl**	dl	dl		46.54	53.77	100.31	ILL-6.4.2	
	18		dl	dl	**0.01**	dl	dl		46.49	53.08	99.59	ILL-6.7.1	20 framboidal
	23		dl	0.01	**dl**	dl	dl		46.80	53.53	100.34	ILL-6.11.1	20 subhedral
	24		0.01	dl	**0.01**	dl	dl		46.37	51.83	98.23	ILL-6.12.1	30 framboidal
	25		dl	0.01	**dl**	dl	dl		46.21	52.37	98.59	ILL-6.12.1	
	26		0.08	0.07	**dl**	dl	dl		44.27	51.28	95.70	ILL-6.13.1	10 euhedral
	27		0.01	0.06	**dl**	dl	dl		45.40	51.74	97.22	ILL-6.14.1	20 framboid core
10/19/96	7		0.01	0.02	**0.05**				45.40	53.07	98.56	Ill6.2.1	50 irregular
	8		0.02	0.08	**0.09**				44.75	51.74	96.67	Ill6.3.1	20 framboidal
	9		0.01	0.06	**0.11**				45.57	52.55	98.30	Ill6.3.1	
	10		dl	0.05	**0.17**				45.65	52.86	98.73	Ill6.4.1	30 round
	11		dl	0.05	**0.10**				45.70	52.74	98.60	Ill6.4.2	
	12		dl	dl	**0.08**				45.78	52.04	97.90	Ill6.5.1	130 irregular
	13		dl	dl	**0.08**				46.02	53.19	99.29	Ill6.5.2	
	14		0.02	dl	**0.11**				44.85	51.93	96.90	Ill6.6.1	20x20 subhedral

ILLINOIS #6-continued													
Date	Anal#	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
10/19/96	15		0.01	0.15	**0.13**				45.58	52.47	98.34	Ill6.7.1	20 x20 subhedral
continued													
	16		0.01	0.00	**0.10**				45.91	52.16	98.18	Ill6.8.1	20x30 subhedral
	17		0.01	0.20	**0.12**				44.99	52.69	98.00	Ill6.9.1	10x40 subhedral
	18		0.02	0.15	**0.13**				45.31	52.79	98.40	Ill6.10.1	10x70 subhedral
	19		dl	dl	**0.12**				46.37	53.66	100.15	Ill6.10.1	
	20		0.01	0.01	**0.10**				46.06	53.39	99.57	Ill6.10.2	
	46		0.01	0.12	**0.09**				45.79	53.14	99.15	Ill6.13.1	15x30 subhedral
	47		dl	dl	**0.11**				45.11	52.04	97.26	Ill6.14.1	euhedral on 13.1
	48		dl	dl	**0.11**				45.89	52.80	98.79	Ill6.15.1	20 framboid
	52		0.04	dl	**0.05**				44.97	51.86	96.92	Ill6.18.1	10 framboid
9/26/96	9		dl	dl	**0.10**				45.73	53.20	99.04	Ill6.3.1	20x65 euhedral
	10		0.01	dl	**0.13**				45.74	53.64	99.52	Ill6.3.2	
	11		dl	dl	**0.16**				45.69	53.25	99.10	Ill6.3.3	
	12		dl	dl	**0.08**				45.31	53.52	98.91	Ill6.4.1	20x20 euhedral
	14		dl	dl	**dl**				46.43	54.74	101.20	Ill6.6.1	30x100 subhedral
	15		dl	dl	**dl**				46.28	54.05	100.37	Ill6.6.2	
	16		dl	dl	**0.05**				46.55	54.08	100.68	Ill6.6.3	
	17		0.02	0.01	**0.06**				46.34	53.26	99.68	Ill6.6.4	
	20		0.04	0.26	**0.09**				43.80	52.54	96.74	Ill6.8.1	15 framboid
	83		dl	dl	**0.06**				46.14	54.31	100.52	Ill6.11.1	40x70 subhedral
	84		dl	dl	**0.09**				46.07	54.68	100.85	Ill6.11.2	
	85		dl	0.01	**dl**				45.46	53.14	98.65	Ill6.12.1	20 framboid

ILLINOIS #6-continued													
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
9/26/96	86		0.02	dl	**dl**				46.53	53.89	100.44	Ill6.13.1	40 euhedral
continued	87		0.01	dl	**0.06**				46.53	54.11	100.71	Ill6.13.2	
	88		0.04	0.10	**0.08**				44.23	51.94	96.38	Ill6.14.1	10 framboidal
	89		dl	dl	**dl**				46.00	53.82	99.83	Ill6.15.1	20x70 subhedral
	90		0.01	dl	**0.08**				45.88	54.38	100.35	Ill6.15.2	
	91		dl	0.01	**0.07**				46.26	54.86	101.19	Ill6.15.3	
9/13/96	12		dl	dl	**0.06**				44.21	51.18	95.45	ILL6.1.1	50 subhedral
	13		0.01	dl	**0.08**				44.38	51.75	96.22	ILL6.1.2	
	81		dl	dl	**0.06**				47.22	54.33	101.61	ILL6.10.1	40 cleat?
	82		dl	dl	**0.14**				47.09	54.30	101.52	ILL6.10.2	
	83		dl	dl	**0.16**				46.83	54.50	101.50	ILL6.10.3	
	*dl= values below detection limit of 100 ± 100 ppm, except arsenic values listed in boldface (dl= 500 ± 500 ppm).												
	Values for Co include a 0.03 wt. percent empirical correction factor subtracted from measured values.												

WYODAK													
Date	Anal #	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Grain	Size (microns)/Form
5/21/97	176	dl	dl	dl	dl	0.03	dl	**0.01**	46.25	51.96	98.28	Cord 1.1	25 x 25 irregular
	177	dl	dl	dl	0.03	0.01	dl	**dl**	45.19	49.04	94.30	Cord 1.2	(composite)
	*dl= values below detection limit of 100 ± 100 ppm, except arsenic values listed in boldface (dl= 500 ± 500 ppm).												
	Values for Co include a 0.03 wt. percent empirical correction factor subtracted from measured values.												

Appendix III.

Quantitative microprobe analyses of illite and kaolinite in the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals.

Appendix III. Illite and Kaolinite Analyses											
No.	K_2O	CaO	Na_2O	Al_2O_3	SiO_2	MgO	Cr_2O_3	MnO	FeO	TiO_2	Total	Comment
PITTSBURGH												
111	2.40	7.29	0.24	24.78	48.40	1.01	0.02	0.03	1.79	0.41	86.38	PITTS illite1.1
112	2.69	6.34	0.30	17.97	58.39	0.80	0.03	0.03	1.39	0.23	88.16	PITTS illite1.2
104	dl	0.04	0.05	40.43	48.00	0.10	dl	dl	0.04	dl	88.67	PITTS Kaol1.1
106	0.04	dl	0.02	40.15	47.17	0.02	dl	dl	0.07	dl	87.48	PITTS Kaol2.1
107	0.03	dl	dl	40.20	47.57	dl	0.03	dl	0.04	dl	87.89	PITTS Kaol2.2
108	0.10	dl	dl	40.89	48.22	0.02	0.03	0.02	0.06	0.03	89.38	PITTS Kaol2.3
109	dl	0.02	0.04	39.75	46.83	0.08	dl	dl	0.26	dl	87.01	PITTS Kaol3.1
110	dl	dl	dl	40.47	47.32	0.04	dl	dl	0.10	dl	87.98	PITTS Kaol3.2
115	0.02	0.02	0.04	40.33	47.49	0.04	dl	dl	0.05	dl	87.99	PITTS Kaol4.1
116	0.05	dl	0.05	40.28	47.39	0.02	0.02	dl	0.04	dl	87.85	PITTS Kaol4.2
ELKHORN/HAZARD												
119	1.78	0.06	0.19	38.06	46.91	0.65	dl	dl	1.25	0.04	88.95	ELKHAZ ill1.1
120	1.48	0.06	0.13	38.36	49.79	0.67	dl	0.02	1.27	0.04	91.82	ELKHAZ ill1.2
121	2.26	0.07	0.12	35.09	46.07	0.54	dl	dl	1.07	dl	85.22	ELKHAZ ill1.3
11	0.76	0.07	0.27	35.54	48.81	0.88	dl	dl	1.82	0.05	88.21	ELKHAZ ill1.3
22	1.26	0.15	0.13	37.59	47.15	0.53	0.02	dl	1.48	dl	88.31	ELKHAZ ill2.1
23	1.31	0.14	0.10	36.72	46.87	0.56	dl	dl	1.47	0.02	87.21	ELKHAZ ill2.2
124	0.15	0.02	0.04	40.59	46.74	0.06	dl	dl	0.32	dl	87.92	ELKHAZ Kaol2.1
125	0.05	dl	0.04	41.37	47.94	0.04	dl	0.02	0.28	dl	89.76	ELKHAZ Kaol2.2
25	0.12	0.03	0.03	39.90	48.42	0.03	0.02	dl	0.24	dl	88.79	ELKHAZ Kaol3.1
27	0.05	0.04	0.07	40.08	47.80	0.06	0.02	dl	0.46	dl	88.58	ELKHAZ Kaol3.3
ILLINOIS #6												
130	0.05	0.02	0.03	40.68	48.71	0.18	dl	dl	0.38	dl	90.05	IL#6 illite1.1
131	5.59	0.04	0.16	18.69	51.51	0.84	dl	dl	0.90	0.57	78.29	IL#6 illite1.2
126	dl	dl	0.02	40.23	47.38	dl	dl	0.02	0.07	dl	87.75	IL#6 Kaol1.1
127	dl	0.03	dl	40.66	49.08	0.04	dl	dl	0.14	dl	89.97	IL#6 Kaol1.2
128	dl	dl	dl	40.91	47.80	0.02	dl	dl	0.04	dl	88.79	IL#6 Kaol2.1

Appendix IV.

Example of a mass-balance calculation for arsenic in pyrite.

Appendix IV. Example of a mass-balance calculation for arsenic in pyrite, based on electron microprobe (EPMA) data.

Pittsburgh coal: As= 3.96 ppm (whole coal basis)

EPMA: Mean As = 140 + 165 ppm (n = 46)

Pyritic S = 0.91 wt. % * 1.87 = 1.70 wt. % pyrite

As contributed by pyrite = 140 * 0.0170 = 2.38 ppm

Fraction of As contributed by pyrite = 2.38 ppm/3.96 ppm = 60%