



Toxic Substances From Coal Combustion- A Comprehensive Assessment, Phase II: Element Modes of Occurrence for the Ohio 5/6/7, Wyodak, and North Dakota Coal Samples

By Allan Kolker¹, Stanley J. Mroczkowski¹, Curtis A. Palmer¹, Kristen O. Dennen¹, Robert B. Finkelman¹, and John H. Bullock, Jr.²

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"Toxic Substances from Coal Combustion- A Comprehensive Assessment, Phase II"

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**U.S. Department of the Interior
U.S. Geological Survey**

¹U.S. Geological Survey, 956 National Center, Reston, VA 20192

²U.S. Geological Survey, Denver Federal Center MS 973, Denver, CO 80225

Executive Summary

This study reports on the second phase (Phase II) of USGS research activities in support of DOE contract DE-AC22-95PC95101 "Toxic Substances From Coal Combustion- A Comprehensive Assessment", funded under DOE Interagency Agreement DE-AI22-95PC95145. The purpose of the study was to provide a quantitative and semi-quantitative characterization of the modes of occurrence of trace elements in coal samples investigated under Phase II, including 1) Ohio 5/6/7, an Ohio bituminous coal sample blended from the #5, #6, and #7 beds; 2) North Dakota, a lignite sample from the Falkirk Mine, Underwood, ND, and 3) Wyodak, a sub-bituminous coal sample from the Cordero Mine, Gillette, WY. Samples from these coal beds were selected for their range in rank and commercial applicability. Results of this research provide basic information on the distribution of elements in Phase II coal samples, information needed for development of a commercial predictive model for trace-element behavior during coal combustion.

The analytical approach used in this study combines an iterative, 4-solvent selective leaching procedure for determination of 44 elements, and mineral identification/quantification, using microanalysis of individual mineral grains. For a given element, the leaching procedure gives the proportions of coal constituents leached by ammonium acetate ($\text{CH}_3\text{COONH}_4$), hydrochloric acid (HCl), hydrofluoric acid (HF), nitric acid (HNO_3), and a fifth fraction inferred to be in an organic association. Bulk analysis of whole coals by inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and element specific methods for selenium, and mercury, provide the basis for calculating elemental fractions removed by each solvent. At each stage of the leaching procedure, leaching solid residues were saved for analysis by X-ray absorption fine structure (XAFS), to compare that approach to determining element speciation with the USGS procedure. Mineral identification was accomplished by scanning electron microscopy (SEM) and X-ray diffraction (XRD) of low-temperature ash. Microanalysis procedures used include electron microprobe, SHRIMP-RG ion microprobe and laser-ablation ICP-MS. Microanalysis concentrated primarily on determination of minor and trace elements in pyrite and illite/smectite, important inorganic constituents of each coal. The overall approach used in this study is similar to that used by the USGS in the Phase I study (Senior and others, 1997). Significant improvements vs. Phase I result from determination of a greater number of elements (44 vs. 6), and introduction of new procedures, including mercury analysis by direct mercury analyzer (DMA), and use of the ion microprobe and laser ablation ICP-MS for quantitative microanalysis of trace metals at levels not attainable with the electron microprobe.

Leaching results for the Ohio 5/6/7 coal sample show that the proportions of chalcophile elements (elements having a geochemical affinity for sulfur) such as arsenic, lead, selenium, residing in pyrite, are much greater than in the lower rank Wyodak and North Dakota coal samples. The Wyodak and North Dakota coal samples have a greater proportion of chalcophile elements in organic or HCl-leachable forms, a distribution typical of lower-rank coal. An exception to this is mercury. Each of the three coal samples has a large (60-80%) fraction of mercury residing in pyrite, even though the proportion of pyrite in the two lower rank coal samples is considerably less. Laser ablation ICP-MS analysis confirms the association of Hg and pyrite for the Ohio 5/6/7 sample, and for 2 other bituminous coal samples studied in Phase I. Comparison of leaching data and XAFS determinations for the same leaching splits show similar proportions of pyritic arsenic by the two methods, and that arsenate resulting from pyrite oxidation is HCl-leachable (Huggins and others, in press). Electron microprobe data for pyrite show concentrations of trace elements mostly at or near detection limits (~100 ppm). In each of the Phase II coal samples, isolated domains within pyrite are enriched in one or more chalcophile elements. In the

Ohio 5/6/7 coal sample, arsenic in pyrite is as much as 2.0 weight percent on the scale of a 3 μm analysis spot, without appreciable enrichment in associated elements. Enrichment of cadmium and selenium shows some correlation with arsenic in pyrite present in the Wyodak and North Dakota coal samples. Concentrations of chromium, and other transition metals in the clay minerals illite/smectite, determined using the SHRIMP-RG ion microprobe, support selective leaching results that show silicate-hosted portions of these metals in each of the Phase II coal samples.

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INTRODUCTION

To understand and predict trace element emissions from coal-fired power plants, it is essential to determine the trace-element transformations that take place during coal combustion. As a first step to making such predictions, the distribution and host of trace elements in coal must be determined. The USGS has developed quantitative and semi-quantitative methods for determining the modes of occurrence of elements in coal. Results reported here provide basic information on the element forms present in three selected coal samples, in support of DOE contract DE-AC22-95PC95101 "Toxic Substances From Coal Combustion- A Comprehensive Assessment" awarded to Physical Sciences, Inc. (PSI), of Andover, MA. The overall goal of the contract is to generate a commercial predictive model for trace-element behavior during coal combustion. USGS activities in support of this contract are funded under DOE Interagency Agreement DE-AI22-95PC95145. These activities have a direct bearing on the predictive equations being developed by PSI as the primary product of this program. Results presented here were obtained during the second phase of this program (Phase II), conducted from March, 1998 through June, 2001. The results and interpretations follow from procedures developed for the initial phase of the contract (Phase I) conducted from 1995 to 1997, but are considerably expanded in the number of elements investigated and the techniques applied, especially for microanalysis of mineral phases present in the coal samples studied.

Coal samples investigated in Phase II are as follows: 1) Ohio bituminous coal blended from the #5, #6, and #7 beds, prepared for McDermott Technologies, Inc.; 2) North Dakota lignite from the Falkirk Mine, Underwood, ND, and 3) Wyodak sub-bituminous coal from the Cordero Mine, Gillette, WY. Splits of these samples were provided to all program participants in pulverized form at the outset of the study. The samples are intended to represent commercial pulverized coals used in electric utilities. The three coal samples investigated were selected for their variation in rank, commercial applicability, and availability. These samples are intended to provide information on trace-element transformations that take place during coal combustion, using coals of differing rank. Whereas the samples are taken from important commercial coal beds, they are not intended to be representative of these coal beds in a geologic sense.

METHODS

Approach

The approach used in this study combines an iterative, 4-solvent selective leaching procedure for bulk coal samples, with mineral identification and microanalysis of specific mineral phases in coal, such as illite/smectite and pyrite. Bulk analysis of the whole coal samples is completed as part of the leaching procedure, in order to compare the fraction a given element leached in each step of the procedure to that in original coal sample. The leaching procedure is devised to sequentially attack specific minerals or groups of minerals, thereby providing information on the fraction of an element residing in that portion of the coal sample. The overall approach is similar to that used by the USGS in the Phase I study. Improvements in Phase II include determination of a greater number of elements (44 vs. 6), introduction of new procedure for mercury analysis, and quantitative microanalysis of trace metals at low levels not attained in Phase I.

At each stage of the leaching procedure, leaching solid residues were saved for analysis by X-ray absorption fine structure (XAFS), by our colleagues at the University of Kentucky, to compare the XAFS

approach to element forms determined by the leaching procedure. This study demonstrates that the two approaches used on the same material are complementary (Huggins and others, 2000a; Huggins and others, in press). The leaching technique provides additional information for elements such as Se and Hg, whose concentrations are commonly too low to obtain XAFS spectra, and for elements with atomic numbers beyond the routine XAFS atomic number range of about 20 to 42 (Ca to Mo). For elements that are common to the two approaches, such as arsenic and chromium, comparison of results is generally good (Kolker and others, 2000a; Huggins and others, 2000b).

Procedures Introduced in Phase II

The USGS approach to the Phase II investigation is similar to that used in Phase I (Senior and others, 1997), with some fundamental additions. In Phase I, leaching data were obtained for 6 elements: Fe, As, Se, Cr, Ni, and Hg, in the Pittsburgh, Illinois #6, and Elkhorn/Hazard Phase I coal samples. In the Phase II investigation, leaching data have been obtained for more than 40 elements in the Ohio 5/6/7, North Dakota, and Wyodak Phase II coal samples. Leaching results are presented in similar detail to those reported in Phase I for only 6 elements.

Phase II tested and confirmed procedures developed in Phase I. Pyrite digestion problems encountered in the HNO₃ step of the leaching procedure in Phase I and early in Phase II, were corrected by adopting a new procedure, the flask method, for this stage of the process. To help integrate the leaching and X-ray absorption fine-structure (XAFS) portions of this project, XAFS splits were taken from solid residues at each of the leaching steps conducted. Arsenic XAFS spectra were obtained by Frank Huggins (University of Kentucky) for leached residues of the Ohio and North Dakota samples. A series of leaching experiments was also devised to test the possibility that the leaching process itself results in in-situ pyrite oxidation. In these experiments, baseline HCl leaching experiments for the Wyodak and North Dakota samples were repeated after heating the coal to 75 °C in air, or wet-dry cycling of the coal while heating.

A new method for mercury analysis, using a direct mercury analyzer (DMA) was introduced as part of this study. Compared to the cold-vapor atomic absorption (CVAA) method used for all parts of the leaching procedure in Phase I, the DMA method offers lower detection limits for small solid samples having low mercury concentrations, such as our leached solid residues. CVAA remains a reliable method for bulk samples having mercury concentrations ≥ 100 ppb. Leaching results for mercury in Phase II are based on whole-coal CVAA, and DMA for the leaching solid residues.

Microanalysis of Phase II coal samples by electron microprobe was conducted using a similar approach to the Phase I work, but in Phase II, these analyses were followed by trace-element microanalysis with the USGS SHRIMP-RG ion microprobe at Stanford University, and the USGS laser ablation ICP-MS system in Denver. The ion probe analyses confirm the residence of transition metals and other elements of interest in illite/smectite, an important clay mineral present in each of the three Phase II coal samples. This mode of occurrence is indicated by HF-soluble leaching fractions, and by Phase I and II electron microprobe analyses, indicating that elements such as chromium are present in illite/smectite at levels that approach the detection limit of this method. Detailed electron microprobe studies of sulfides in the three Phase II coal samples was followed by semi-quantitative SHRIMP-RG ion microprobe work and reconnaissance laser ablation ICP-MS analysis. The laser ablation ICP-MS provides quantitative results for a range of chalcophile elements, including mercury, the first direct determinations we have made for mercury in organic or inorganic constituents of coal.

Coal Testing

Upon receipt of the 3 Phase II coal samples, splits of each coal were prepared and sent to Geochemical Testing, Inc., of Somerset, PA. for coal analyses not available at the USGS. These tests included proximate analysis, ultimate analysis, heating value, forms of sulfur, free swelling index, and ash fusion temperature. Because of the large difference in moisture in the 3 Phase II coal samples, these results, and all USGS analyses, are reported on a dry basis.

Low Temperature Ash/X-ray Diffraction

To prepare mineral concentrates for X-ray diffraction analysis (XRD), the coal samples were subjected to a low temperature (< 200 °C) ashing procedure in which the bulk of the organic matter is slowly consumed in an oxygen plasma, without altering the mineralogy by phase transformations that generally occur at higher temperatures. To obtain semi-quantitative information on the minerals present in the coal samples, the low-temperature ash was pressed into pellets and analyzed using an automated X-ray diffractometer. Diffraction of Cu K α X-rays was measured over the interval from 4° to 60° 2 θ . Counts were collected at 0.5 seconds per step. The data were processed using a computer program for semi-quantitative mineral analysis by X-ray diffraction (Hosterman and Dulong, 1985).

The low rank of the North Dakota sample required slight modifications to the standard LTA procedure. Lignites tend to have a high concentration of cations associated with carboxyl groups. These cations neutralize the oxygen plasma during ashing, thus significantly reducing the rate at which ashing occurs. An additional problem with lignites is that the fixation of sulfur as sulfate is much greater than in bituminous coals. As the ashing progresses, this fixed sulfate coats the remaining particles, shielding the surfaces from the oxygen plasma and further hampering the ashing process. Increased formation of sulfates also may obscure the X-ray diffractogram, making it difficult to interpret. To prevent these complications, prior to the ashing procedure, the North Dakota sample was treated with an ammonium acetate leach to remove the carboxyl-bound cations, and prevent fixation of the oxidized organic sulfur as sulfate.

Bulk Analysis and Leaching Procedure

Bulk coal analyses utilize a combination of techniques that have been optimized by the USGS for multi-element analysis of coal (Palmer, 1997). In this procedure, ground coal is ashed at 525 °C, and analyzed by ICP-AES and ICP-MS. Acid digestions are used for analysis of Li, Be, Na, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, Sr, Y, and Th, by ICP-AES, and for analysis of Ga, Ge, As, Rb, Nb, Mo, Ag, Cd, Sn, Sb, Te, Cs, Au, Tl, Pb, Bi, and U, by ICP-MS. Sinter digestions are used for analysis of B, Mg, Al, Si, K, Ca, Ti, Fe, Zr, and Ba, by ICP-AES, and for analysis of Hf, Ta, and W, by ICP-MS. Element-specific methods on whole ground coal are used for Se (hydride generation), Cl (ion selective electrode), and Hg (Cold Vapor Atomic Absorption).

The sequential selective leaching procedure used in this study is similar to that described by Palmer and others (1993), which was modified from that of Finkelman and others (1990). Duplicate 5 g aliquots of the three Phase II samples were sequentially leached with 35 ml each of 1N ammonium acetate (CH₃COONH₄), 3N hydrochloric acid (HCl), concentrated hydrofluoric acid (HF; 48 percent), and 2N (1:7) nitric acid (HNO₃). Each of these solvents digest a specific portion of the coal sample. Ammonium

acetate removes elements bonded onto exchangeable sites, water-soluble compounds, and some carbonates. Hydrochloric acid dissolves carbonates, iron oxides, monosulfides, and certain chelated organic compounds. Hydrofluoric acid digests silicates, and nitric acid dissolves disulfides, especially pyrite. Additionally, information on elements hosted by minor or trace phases, such as phosphates, sulfates, and oxides, can be obtained with knowledge of the leaching behavior of these phases.

For the first three leaching stages ($\text{CH}_3\text{COONH}_4$, HCl , and HF) solid coal samples and corresponding solvents were placed in conical-bottom 50 ml polypropylene centrifuge tubes and shaken for 18 hours on a Burrell¹ wrist-action shaker. The solid samples consist of the leached solid residue from each previous step of the procedure, the exception of the first ($\text{CH}_3\text{COONH}_4$) stage, in which the original coal sample is leached. Formation of gas during some leaching steps requires that the tube be enclosed in double polyethylene bags, closed with plastic-coated wire straps. The bags allow gas to escape, but prevent the release of liquid. The final (HNO_3) digestion was carried out in an Erlenmeyer flask, similar to the method for the determination of pyritic sulfur (ASTM, 1998a). This "flask method" is more effective at dissolving pyrite than digestion in centrifuge tubes, because the partially de-mineralized coal from the three previous leaching steps has a very low density, forming a protective layer of sediment covering pyrite that concentrates at the bottom of the conical tubes.

At each stage of the leaching procedure, approximately 0.5 g of residual solid was removed for instrumental neutron activation analysis (INAA) and mercury analysis. Mercury concentrations of the residual solids were determined using a direct mercury analyzer (DMA). Each of the leachate solutions was collected and analyzed by ICP-AES and ICP-MS. Chemical data for the leachates and the solid residues were processed to derive the mean percentages of each element leached by each of the four solvents. The analytical uncertainties were estimated to be ± 2 to ± 25 percent for these data, but uncertainties are generally within ± 5 percent, absolute (Palmer and others, 1998).

Some portion of each element present may not be leached by any of the four reagents. These unleached fractions may be present in the organic portions of the coal, or in insoluble phases such as zircon or titanium dioxide. Additionally, where mineral grains are completely encased in the organic matrix, these "shielded" grains may not be completely digested. As an internal check, analytical results are obtained for both the solid residues (by INAA, or mercury-specific method) and leachates (by ICP-MS and ICP-AES).

At each step of the leaching process, the samples were leached in duplicate. Early on in Phase II a problem with the normality of the HNO_3 used in that step of the leaching process necessitated re-leaching of the North Dakota and Ohio samples (in duplicate). Later, adoption of the flask method for the HNO_3 step of the procedure necessitated a second round of re-leaching for each of the samples. Results for the first 3 steps of the procedure ($\text{CH}_3\text{COONH}_4$, HCl , HF) were not affected by these modifications. As a result, leaching results given in this report are based on 3 duplicate leachings (6 samples total) for the North Dakota and Ohio samples, and 2 duplicate leachings (4 samples total) for the Wyodak sample, with the exception of the HNO_3 step. Results for the HNO_3 step are based on the final duplicate leaching, using the flask method (2 samples for each Phase II coal sample).

Electron Microprobe and SEM

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Electron microprobe analysis and scanning microscopy were conducted on pellets prepared from the sample powders provided for each Phase II coal sample. In this procedure, approximately 7-8 g of crushed sample is impregnated under pressure with Armstrong C4 epoxy. The resultant mold is cured overnight at 60 °C. The pellet is ground and polished using the ASTM D2797-85 procedure (ASTM, 1998b) as modified by Pontolillo and Stanton (1994). The epoxy-coal pellet is first ground until flat and smooth, with a 15- μm diamond platen, and then with 600-grit SiC paper. Rough polishing is done with 1- μm alumina, and final polishing is completed with 0.06- μm -colloidal silica. Ultrasonic cleaning after each step insures a final product free of extraneous abrasive material.

A JEOL-840 scanning electron microscope (SEM) equipped with a Princeton Gamma-Tech. energy-dispersive X-ray analytical system (EDX) and/or an ETEC Autoscan SEM with a Kevex EDX, was used for SEM examination of the coal samples. Mineral identifications were 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 abundances of the phases were assessed. This approach allows the operator to select phases for analysis by EDX and to interpret textural relations. EDX analysis provides information on elements having concentrations at roughly the tenth-of-percent level or greater. Typical operating conditions for SEM analysis are: accelerating potential of 15 or 20 keV and working distances ranging from 15 to 20 mm (ETEC Autoscan) and 15, 25 or 39 mm (JEOL-840). SEI and BSE images were used as a guide to select phases for electron microprobe analysis.

A fully-automated, 5 spectrometer microprobe instrument (JEOL JXA 8900R Superprobe) was used to determine element concentrations in pyrite, illite, and carbonates, by the wavelength-dispersive technique. In our microprobe analysis of pyrite the following elements were measured: Fe, S, As, Ni, Cu, Zn, Se, and Co. Natural and synthetic standards were used. A beam current of 3.0×10^{-8} amps and a voltage of 20 KeV was used in the analysis of sulfides. For quantitative analysis, the probe beam diameter was fully focused, giving an actual working diameter of about 3 μm .

The minimum detection limit for microprobe analysis of pyrite was about 100 ppm for each of the trace elements analyzed, using peak counting times of 60 seconds and 30-second upper and lower backgrounds. For Co, the detection limit is about 500 ppm (0.05 weight percent) due to an interference with Fe giving a constant background concentration in pyrite of 400-500 ppm. Co results shown in Appendix 1 are background-corrected. Analysis counting statistics have a large uncertainty as the detection limit is approached.

SHRIMP-RG ion microprobe

Analyses of transition metals and other elements in illite/smectite in the Phase II coal samples were obtained using the Stanford-USGS SHRIMP-RG ion microprobe at Stanford University. A procedure was developed for analyzing illites using the O_2^- duoplasmatron ion source. Calibration was achieved using aluminosilicate standard glasses that included National Institute of Standards and Technology (NIST) SRM 610 and 612, and USGS standards GSE and GSD, synthetic standards prepared for the USGS by Corning Glass Works, Inc., and glass prepared from powdered USGS rock standard BHVO-1.

Element concentrations in illite/smectite were determined by comparing the raw counts obtained for our unknowns to raw counts/ppm determined for aluminosilicate standards approximating the bulk composition of the illites. Analysis points were initially subjected to a 1-3 minute burn-in to stabilize the response. The burn-in was followed by a "short" analysis of 4, 7, or 8 elements, to confirm the identity of the grains selected and minimize the contribution of overlapping grains. This was followed by a "long" analysis in which the initial group of elements was repeated with about 10 additional elements or masses. In August 1999, the "short" analyses were followed directly by "long" analyses in which the initial 7 elements (Mg, Al, Ca, Si, ^{52}Cr , K, and Fe) were re-determined and combined with analyses of Sc, Ti, V, ^{53}Cr , Mn, Co, Ni, Cu, Zn, Rb, and Sr. The same procedure was used to measure these elements in reference standards. A similar procedure was followed in February 2000, except that all the short runs were conducted successively, followed by a series of long runs for illite/smectite grains confirmed by the short runs. This modification minimized magnet instability caused by changes to its within-run scan range.

In addition to trace element results for illite/smectite, SHRIMP-RG data were obtained for pyrite in the three Phase II coal samples and in the Illinois #6 and Pittsburgh coal samples from Phase I of the program. Minor or trace elements determined included Ti, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, Sb, and Pb, using the oxygen duoplasmatron source. Because suitable standards were not available, quantitative results were not obtained. However, the results show relative differences among the samples, when the response for trace elements is plotted as ratios vs. ^{32}S or ^{57}Fe , whose content in pyrite is assumed to be nearly uniform by stoichiometry. Because the ionization efficiency differs for each element, and relative sensitivity factors (a measure of ionization efficiency) for pyrite are not well known, the ratios determined cannot be used to compute concentrations using Fe or S as an internal standard.

The capabilities of the SHRIMP-RG instrument for determining Hg in sulfides, and arsenic on the surfaces of ash particles, were also investigated.

Laser Ablation ICP-MS

Reconnaissance laser ablation ICP-MS data were obtained for pyrite in the Ohio 5/6/7 coal sample, and in the Illinois #6 and Pittsburgh samples from Phase I. The laser ablation system consists of a pulsed Nd(YAG) laser coupled to a dedicated ICP-MS. In order to obtain results for Hg at the 0.5 ppm level, instrument conditions included a 50 μm spot, and a laser pulse rate of 20 Hz at 75% energy. These conditions gave an excavation rate of about 3 $\mu\text{m}/\text{sec}$. NIST SRM 2710 was used for analysis of Hg, and USGS standard GSE was used to determine other elements, including Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, and Pb. Fe was used as an internal standard, and its concentration was fixed at the Fe content of stoichiometric pyrite. Ablated material was introduced into the ICP-MS analyzer as an argon plasma, therefore, the matrix match between standards and unknowns is not critical. Laser ablation ICP-MS data were not obtained for pyrite in the Wyodak and North Dakota samples, because these samples do not contain pyrite grains large enough to analyze with the 50 μm spot.

PHASE II RESULTS

Coal Testing

Results for ash content, moisture, and forms of sulfur are given in Table 1. Compared to the two lower rank coal samples, the Ohio 5/6/7 sample has a much lower moisture content, and a higher sulfur content,

especially pyritic sulfur. More complete coal testing results, including ultimate analysis, heating value, volatile matter, fixed carbon, etc., are given in Appendix 1, reported on an as-received basis, on a dry basis, and on a dry ash-free basis.

Low Temperature Ash/X-ray Diffraction

X-ray diffraction results for low-temperature ash (LTA) are shown in Table 2. Results show that quartz is more abundant than clay minerals (illite + kaolinite) in the North Dakota sample, whereas clays are the most abundant inorganic phases in the Wyodak and Ohio 5/6/7 samples. Pyrite is present in each of the 3 coal samples and is most abundant in the Ohio 5/6/7 sample. Trace phases indicated include feldspar (Ohio 5/6/7, North Dakota), siderite (North Dakota), pyrite (North Dakota, Wyodak), marcasite (Ohio 5/6/7), sphalerite (all 3 samples), and hematite (North Dakota).

SEM

Mineralogy of the three phase II coal samples determined by SEM/EDX is summarized in Table 3. The Ohio 5/6/7 coal sample contains all of the 5 most common coal mineral phases (quartz, illitic clay, kaolinitic clay, pyrite and calcite). The illite grains in this sample are large (some larger than 50 μm) and well formed. The North Dakota and Wyodak samples appear to lack calcite. From the XRD results, it is likely that kaolinite is present in the North Dakota sample. SEM and XRD also show that the Ohio 5/6/7 and North Dakota samples have sub-equal amounts of illite and kaolinite, whereas kaolinite is by far the dominant clay mineral in the Wyodak sample. Pyrite was observed in all three coal samples, and is most abundant in the Ohio 5/6/7 sample (Table 2 and 3).

The minor or trace mineral phases common to each of the coal samples include a TiO_2 phase (probably rutile), monazite (REE phosphate) and sphalerite (ZnS ; Table 3). Barite (BaSO_4) and an iron-oxide or hydroxide phase are common in both the North Dakota and Wyodak samples. An interesting suite of accessory silicates is present in the North Dakota sample, including epidote, chlorite, and probably, alkali-feldspar. The presence of these phases may indicate a detrital metamorphic contribution to the coal basin.

Leaching Studies

Leaching results were obtained for 44 elements, ranging from Li to U, in each of the Phase II coal samples. The leaching results show excellent recoveries, totaling 50-100% in most cases. Recoveries less than 100% are acceptable because the procedure does not digest organic portions of the coal, which may be host to a significant fraction of metallic elements, especially in the two low rank coal samples. As a check of the whole coal results, a series of blind replicate analyses was performed (Table 5). Agreement was considered acceptable for all elements of interest.

Leaching results are reported in Table 6, with the results expressed as a percentage fraction of a given element removed in each stage of the leaching procedure. This compilation is based on weighted averages of replicate analyses of leachate solutions and solid residues. Results are discussed below by coal, and by element. Leaching data are also shown in Figure 1, in which results are grouped by element affinity (e.g. chalcophile, lithophile, exchangeable, etc.), and for the remainder of the elements determined, in order of atomic number. Finally, in Table 7, we interpret the elemental proportions

residing in various constituents of the 3 Phase II coal samples, based on integrating the results of leaching studies, other results in this study, and our experience with other samples. Assumptions used in interpreting the results are given in the section on results by element.

Description of the leaching data is facilitated by using the following definitions: **Dominant** element associations are indicated where the amount of an element leached by a given solvent exceeds that of any other solvent, and that of the unleached fraction, and is $\geq 35\%$. **Significant** element associations are indicated for any leached fraction $\geq 25\%$. Where no leached fraction exceeds the unleached fraction, and the unleached fraction is $>50\%$, that element is said to be **organic dominant**. **Subsidiary** associations are cases where the fraction of an element leached is $\geq 10\%$. **Mixed** associations refer to cases where there are multiple subsidiary associations. **Bimodal** associations are cases where the element occurs almost entirely in two forms whose proportion is subequal. These definitions are intended to help us provide consistent descriptions of the results, and do not replace the quantitative or semi-quantitative determinations.

Leaching results by coal sample

Ohio 5/6/7: The Ohio 5/6/7 coal sample has a dominant silicate association for Li, Be, Na, Mg, Al, K, Ti, Rb, Sr, Zr, Cs, and Ba. Significant silicate associations in the Ohio 5/6/7 coal sample are indicated for Sc, V, Cr, Sn, Ta, and W. Many elements partition into clay minerals such as kaolinite and/or illite-smectite, as confirmed by microanalysis. Non-clay silicate-hosted elements include a dominant fraction of Zr and a significant fraction of U, both of which are present in zircon. A dominant sulfide association is indicated for Fe, Cu, As, Hg, Tl, and Pb. Each of these trace elements has been found in pyrite, although Cu more commonly occurs as chalcopyrite (CuFeS_2 ; Kolker and Finkelman, 1998). Several elements that generally do not occur in pyrite (REE, Th) were also found to be HNO_3 leachable, possibly due to silicate-encapsulated phosphates. Significant sulfide associations were found for Mn, Ni, Zn, Se, Mo, and Cd. Bimodal element associations are indicated for Se (sulfide/organic) and Hf (silicate/organic). Se is known to occur in pyrite, whereas Hf can substitute for Zr in zircon. Mn, Co, Ni, Zn, Mo, and Cd show mixed associations in the Ohio 5/6/7 sample, and Sc, V, Cr, Sn, Sb, Yb, Lu, Ta, W, and U are organic dominant.

Wyodak: For the Wyodak coal sample, a dominant silicate association is indicated for Al, K, Ti, Co, Rb, Zr, and Cs, and W. Significant silicate associations are indicated for Li, Be, Sc, V, Cr, Mo, Sb, Hf, Ta, Th, and U. Only Hg shows a dominant (60%) sulfide (pyrite) element association in the Wyodak coal, and Zn is the only element that shows a significant (25%) pyrite association. Many elements are dominantly HCl-leachable in the Wyodak sample, including Be, P, Ca, Sc, V, Mn, Fe, Zn, As, Sr, Y, Cd, Ba, REE, Pb, and U. No one phase is responsible for this behavior. Elements such as Mg, Ca, Mn, Fe, and Sr, are present in carbonate minerals that undergo some dissolution in ammonium acetate, and more complete digestion in HCl (Palmer and others, 1998). For example, Sr is 30% ammonium acetate leachable and 65% HCl leachable. Other HCl-dominant elements such as Zn and Pb, occur in HCl-soluble monosulfides such as sphalerite (ZnS) and galena (PbS). Cadmium (70% HCl leachable) is known to substitute in the sphalerite structure (Gluskoter and Lindahl, 1973). Significant HCl leachable fractions found for elements such as Co (30%) and Ni (25%), which do not occur in common monosulfides, probably reflect limited substitution of these elements in carbonates. Overall, Ni shows a mixed association, as does Th. The dominant (50%) fraction of HCl-leachable As found for the Wyodak coal is likely an arsenate phase, as shown by XAFS study of our Phase II leached residues (see section on XAFS). Organic dominant elements in the Wyodak sample include Li, Cu, Se, Mo, and Ta.

North Dakota: Dominant silicate associations in the North Dakota sample include Al, K, Sc, Ti, V, Rb, Zr, Mo, Cs, Hf, W, and Th. Significant silicate associations are Cr, Co, Ni, Sb, Ta, and U. Uranium shows a bimodal silicate/HCl-leachable distribution. Like the Wyodak sample, only Hg shows a dominant (80%) pyrite association in the North Dakota sample. Only Se shows a significant (25%) sulfide association. As in the Wyodak sample, the North Dakota sample contains many HCl-leachable element forms. Dominant HCl-leachable elements include Be, P, Ca, Mn, Fe, Co, Ni, Zn, As, Sr, Y, Ba, REE, and Pb. Significant HCl-leachable elements include Mg, Al, V, Cu, and U. The behavior of Li and Se is organic dominant.

Leaching results by element

Lithium: Lithium has a dominant (65%) silicate association in the Ohio 5/6/7 coal sample and significant (35% each) fractions in the Wyodak and North Dakota samples, which both show organic dominant (65%W, 55%ND) forms of lithium (Fig. 1e).

Beryllium: Beryllium has a dominant (50%) silicate association in the Ohio 5/6/7 coal sample. The Wyodak and North Dakota samples show dominant HCl-leachable forms (55%W, 70%ND) and subsidiary (35%W, 20%ND) silicate associations (Fig. 1v).

Sodium: Sodium has a dominant (40%) silicate association and a subsidiary exchangeable association (25%) in the Ohio 5/6/7 sample. In the two lower rank coal samples, sodium has a dominant exchangeable association (90% in W, 85% in ND; Fig. 1i).

Magnesium: Magnesium has a dominant (70%) silicate association in the Ohio 5/6/7 coal sample. In the Wyodak and North Dakota samples, magnesium is dominantly exchangeable (55% in W, 50% in ND), and has a subsidiary HCl-leachable form (30% in W, 35% in ND; Fig. 1j).

Aluminum: Aluminum has a dominant (100%) silicate association in the Ohio 5/6/7 coal sample. In the Wyodak and North Dakota samples, aluminum has a dominant silicate association (55% in W, 65% in ND), and a subsidiary (25% in W and ND) HCl-leachable association (Fig. 1f).

Phosphorus: In the Ohio 5/6/7 sample, phosphorus has a bimodal HF-leachable (50%) and HCl-leachable (50%) association. The HCl-leachable form probably represents phosphate minerals such as apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$), whereas the HF-leachable form may be explained by phosphate minerals encased in silicates, rather than the presence of phosphorus in solid solution in silicates. In the Wyodak and North Dakota samples, phosphorus shows a dominant HCl-leachable form (80% in W, 85% in ND), indicating a phosphate association (Fig. 1w).

Potassium: Potassium has a dominant (90%) silicate association in the Ohio 5/6/7 blend. In the Wyodak and North Dakota samples, potassium has a dominant (50% in W, 80% in ND) silicate association, and a subsidiary (30% in W, 10% in NA) exchangeable fraction (Fig. 1k).

Calcium: In each of the Phase II coal samples, calcium has a dominant carbonate and/or exchangeable association. This is expressed for the Ohio 5/6/7 by a mixed ammonium acetate (30%), HCl (30%) and unleached (30%) association. For the two lower rank coal samples calcium occurs as bimodal association of ammonium acetate leachable (45% in W, 40% in ND) and HCl-leachable Ca (55% in W, 60% in ND; Fig. 1p).

Scandium: The Ohio 5/6/7 coal sample shows a significant (40%) silicate association for scandium, which is organic-dominant (55% unleached) in this sample. The Wyodak sample shows a dominant (60%) HCl-leachable form of scandium and a subsidiary (35%) silicate association. The North Dakota sample has a dominant (80%) silicate association, and a subsidiary (15%) HCl-leachable fraction (Fig. 1x).

Titanium: Titanium shows a dominant silicate association in each of the samples (65% in O, 60% in W and ND). Some of the HF-leachable titanium may be due to inclusions of titanium dioxide in silicates. SEM of leached residues shows that TiO_2 minerals are not completely digested by the leaching procedure. Each of the two lower rank coal samples show subsidiary (20%) HCl-leachable titanium forms (Fig. 1g).

Vanadium: The Ohio 5/6/7 coal sample shows a significant (35%) silicate association for vanadium, which is organic-dominant (65% unleached) in this sample. The Wyodak sample shows a dominant (65%) HCl-leachable form and a subsidiary (25%) silicate-hosted form. The North Dakota sample contains vanadium dominantly as silicates (45%), but with a subsidiary (35%) HCl-hosted form (Fig. 1y).

Chromium: The Ohio 5/6/7 coal sample shows a significant (30%) silicate association for chromium, which is organic-dominant (70% unleached) in this sample. The Wyodak sample shows a bimodal distribution of silicate (45%) and organic (45% unleached) forms, as well as a subsidiary HCl-leachable (10%) form. The North Dakota sample has a significant (35%) silicate form of chromium, a subsidiary (10%) HCl-leachable form, and is organic dominant (50% unleached; Fig. 1h).

Manganese: Manganese has a mixed association (15-30% for each solvent) in the Ohio 5/6/7 sample. The significant fraction of manganese in pyrite in this sample (20%) may reflect the fact that the manganese content of this sample is low (20 ppm), less than half the average for U.S. coals (43 ppm; Bragg and others, 1998). In the two lower rank coal samples, manganese is dominantly carbonate-hosted, with HCl-leachable fractions of 80% (W) and 75% (ND; Fig. 1q).

Iron: Iron shows a dominant (80%) sulfide (pyrite) association in the Ohio 5/6/7 sample, and subsidiary (10% each) HCl-leachable and HF-leachable forms, probably Fe in carbonates and in illite/smectite. In the two low rank coal samples, a dominant (75% in W, 65% in ND) HCl-leachable form of iron is present, probably carbonate. Each of the two low rank coal samples shows subsidiary (10% in W, 15% in ND) HF-leachable forms, probably illite/smectite, and subsidiary (10% in each) HNO_3 -leachable iron, representing pyrite-hosted iron (Fig. 1a). Pyritic sulfur contents of the 3 coal samples (1.42 wt. % in O, 0.05 wt. % in W, 0.28 wt. %) broadly reflect the differences in pyrite-associated Fe indicated by the leaching data.

Cobalt: Cobalt shows a mixed association in the Ohio 5/6/7 sample, with the fraction leached by each of the 4 solvents, and the unleached fraction, all exceeding 10%. The HCl fraction (30%) and the HNO_3 fraction (20%) are the two most abundant leached fractions in the Ohio 5/6/7 sample. These data indicate that carbonate, silicate (illite), organic, and pyritic forms of cobalt are present. The two lower rank coal samples each show roughly bimodal distributions of HCl-leachable (30% in W, 55% in ND) and HF-leachable (60% in W, 40% in ND) Co (Fig. 1l).

Nickel: Nickel shows a mixed association in each of the 3 coal samples. Only the North Dakota sample shows a dominant leached fraction (45%), an HCl-leachable form. Significant nickel (25%) is leached by HF in the Wyodak sample. A significant pyrite association is indicated by HNO_3 -leachable nickel (25%) in the Ohio 5/6/7 sample, as confirmed by microanalysis (Fig. 1m).

Copper: In the Ohio 5/6/7 sample, copper is dominantly (65%) leached by HNO_3 , with subsidiary (10%) HCl-leachable copper, and a 20% unleached fraction. These results indicate a dominant pyrite association and a subsidiary chalcopyrite and organic associations. The Wyodak sample, copper is organic dominant (55% unleached). Both lower rank coal samples have equal or subequal fractions (20% in W, 30% in ND) of HCl-leachable Cu (chalcopyrite) and HNO_3 -leachable (20% in W, 20% in ND) copper in pyrite (Fig. 1b).

Zinc: In the Ohio 5/6/7 coal sample, zinc shows a mixed association in which there are significant (30% each) HCl- and HNO_3 -leachable fractions, corresponding to sphalerite and pyrite associations, and a subsidiary (25%) organic association. In the two lower rank coal samples zinc is dominantly in sphalerite (50% in W, 65% in ND), with subsidiary silicate (10%), pyrite (25%), and organic (15%) associations in the Wyodak sample, and subsidiary silicate (10%) and organic (20%) associations in the North Dakota sample (Fig. 1r).

Arsenic: The distribution of arsenic in the 3 coal samples is similar to that for iron. In the Ohio 5/6/7 sample, arsenic is dominantly (60%) in pyrite, with a subsidiary (25%) HCl-leachable form, probably arsenate. In the two lower rank coal samples, the arsenate(?) form is dominant (40% in W, 50% in ND), with subsidiary organic (30% in W, 20% in ND) and pyrite-hosted (15% in each) As. The two lower rank coal samples also show subsidiary (15% in each) HF-leachable arsenic. XAFS study of leached residues shows that HF removes arsenate not removed by HCl, rather than arsenic that is structurally bound in silicates (Huggins and others, in press). However, some of this arsenic may be interstitial to finely disseminated clays and released by their digestion in HF (Fig. 1c).

Selenium: Selenium shows a bimodal pyritic (50%) and organic (50%) association in the Ohio 5/6/7 coal sample. In the two lower rank coal samples, selenium is organic-dominant (70% in W, 60% in ND) with a subsidiary (20%) pyrite association in the Wyodak sample, and a significant (25%) pyrite association in the North Dakota sample (Fig. 1d).

Rubidium: Rubidium is dominantly (65-70%) hosted by silicates in each of the 3 Phase II coal samples (Fig. 1z).

Strontium: Strontium is dominantly (60%) silicate-hosted in the Ohio 5/6/7 sample. In the two lower rank coal samples, strontium is dominantly carbonate-hosted. The sum of ammonium-acetate and HCl-leachable fractions in these samples is 95% (W) to 100% (ND). The ammonium-acetate leachable fraction ranges from 30% (W) to 40% (ND), permitting a subsidiary portion of exchangeable strontium (Fig. 1aa).

Yttrium: In the Ohio 5/6/7 sample, yttrium follows a mixed distribution, with a significant (25%) fraction leached by HNO_3 . In the two lower-rank coal samples, HCl-leachable forms are dominant (65% in W, 80% in ND), probably phosphates such as apatite, the crandallite group $(\text{Ca,Ba,Sr})\text{Al}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$, or xenotime (YPO_4 ; Fig. 1bb).

Zirconium: Zirconium is dominantly (60-70%) hosted by silicates (zircon) in each of the 3 Phase II coal samples (Fig. 1cc).

Molybdenum: Molybdenum shows a mixed association in the Ohio 5/6/7 sample, with significant (25%) sulfide-hosted Mo. The Wyodak sample is organic dominant (55%) with a significant (45%) HF-

leachable component, probably in clays. The North Dakota sample shows a dominant HF-leachable component (60%) with a significant (40%) organic component (Fig. 1dd).

Cadmium: In the Ohio 5/6/7 coal sample, cadmium has 3 major forms, including pyrite (35%), organic (35%), and a subsidiary (20%) HCl-leachable form, likely representing Cd in sphalerite. In the Wyodak sample, the HCl-leachable form is dominant. Cadmium leaching data were not determined for the North Dakota sample, as its whole coal cadmium concentration is below the detection limit (<0.1 ppm; Fig. 1ee).

Tin: For the Ohio 5/6/7 coal sample, tin is organic dominant (60% unleached), and there is a significant (35%) silicate association. Tin leaching data were not determined for the Wyodak and North Dakota samples, as their whole-coal tin concentrations are each below the detection limit (Fig. 1ff).

Antimony: Antimony is organic dominant (60% unleached) in the Ohio 5/6/7 coal sample, with subsidiary HF- (20%) and HNO₃-leachable (15%) forms. The Wyodak sample shows a mixed association with significant (35%) silicate-hosted antimony. The North Dakota sample has a bimodal silicate (40%) and organic (50%) Sb, with a subsidiary (10%) sulfide-hosted form (Fig. 1n).

Cesium: Cesium shows a dominant (75% in O, 60% in W, 75% in ND) silicate association in each of the 3 Phase II coal samples. The data indicate a subsidiary (10% in O, 25% in W, 15% in ND) organic cesium fraction in each sample (Fig. 1gg).

Barium: Leaching results for the Ohio 5/6/7 sample shows a dominant (90%) silicate association. In the two lower rank coal samples, barium has a dominant (80% in each) HCl-leachable association, probably barium in barite (BaSO₄; Fig. 1hh).

Light REE (La, Ce): In the Ohio 5/6/7 sample, lanthanum and cerium are dominantly leached by HNO₃ (55% La, 60% Ce). In the Wyodak sample, these elements are dominantly leached by HCl (60% La, 65% Ce). Lanthanum and cerium in the North Dakota sample are also dominantly leached by HCl (55% La, 60% Ce; Fig 1 ii-jj).

Middle REE (Sm, Eu, Tb): Middle REE show a mixed association in the Ohio 5/6/7 sample, whereas an HCl-leachable form is dominant in the Wyodak and North Dakota coal samples (60-70% for each element in each coal; Fig. 1kk-1mm).

Heavy REE (Yb, Lu): In the Ohio sample, the heavy REE are organic dominant (55% unleached Lu, 60% unleached Yb), with significant (25-30%) HNO₃-leachable fractions, and a subsidiary (10%) HF-leachable fraction. The Wyodak sample has a dominant (40-45%) HCl-leachable fraction, and a significant organic component (25% for each). The North Dakota sample shows a dominant HCl-leachable form for ytterbium and lutetium (60% each; Fig. 1nn-oo).

The predominance of HCl-leachable REE forms in the Wyodak and North Dakota samples vs. the Ohio 5/6/7 is attributable to their lower rank (Fig. 2).

Hafnium: Hafnium shows a similar bimodal silicate (50-45%)/organic (50% in each) association for the Ohio and Wyodak samples. In the North Dakota sample, the silicate form of hafnium is dominant (60%), with a significant (35%) organic hafnium component (Fig. 1pp).

Tantalum: The occurrence of tantalum is similar for each of the 3 Phase II coal samples. In each sample, tantalum is organic dominant (50-60%), with a significant (35-45%) silicate fraction (Fig. 1qq).

Tungsten: In the Ohio 5/6/7 sample, tungsten is organic dominant (60%), with a significant silicate fraction (25%), and a subsidiary (10%) HCl-leachable fraction. In the two lower rank coal samples, the silicate fraction of tungsten is dominant (45% in W, 50% in ND), with a significant (35% in W, 25% in ND) organic fraction (Fig. 1rr).

Mercury: A dominant pyrite association (60%) is shown for the Ohio sample, and surprisingly, for both the Wyodak and North Dakota coal samples (60%-80%), even though these contain much smaller pyrite fractions, and show a much less pronounced pyrite association for other chalcophile elements such as arsenic, copper, and selenium. The Ohio 5/6/7 sample also shows subsidiary exchangeable (10%), and unleached (20%) fractions. Subsidiary (20%) unleached and exchangeable mercury fractions are present in the Wyodak sample. For the North Dakota sample, CVAA results for the whole coal are below 100 ppb (Table 4, 5), and at these levels, DMA results are considered more reliable. DMA results for the whole coals are not available, but comparison of whole-coal CVAA replicates, and DMA results for the North Dakota fraction leached by ammonium acetate, show excellent agreement. The fraction of Hg leached by ammonium acetate in the North Dakota sample is inferred to be negligible.

Thallium: A pyrite association is dominant (50%) for thallium in the Ohio sample, with subsidiary (10-15%) amounts of thallium leached by each of the other solvents. Thallium leaching results were not determined for the two lower rank coal samples because the whole-coal thallium values of these samples are below the detection limit.

Lead: Lead shows a mixed distribution for the Ohio sample, in which the main modes of occurrence are as HNO₃ leachable lead (40%, in pyrite), and as HCl-leachable lead (35%, likely as galena). HCl-leachable lead is the dominant lead form in the two lower rank coal samples (70% in W, 85% in ND; Fig. 1ss).

Thorium: Thorium shows a mixed association in each of the 3 phase II coal samples. The Ohio sample has a significant HNO₃-leachable (35%), and unleached (45%) fractions. The Wyodak coal sample has significant HCl- and HF-leachable thorium fractions. In the North Dakota sample, the silicate thorium fraction is dominant (45%; Fig. 1t).

Uranium: Uranium shows a strongly organic dominant mode (70%) in the Ohio sample, with a subsidiary (20%) silicate fraction. The Wyodak sample shows a dominant HCl-leachable uranium mode, with a significant (30%) silicate fraction, and a subsidiary (10%) exchangeable form. The North Dakota sample has a bimodal HCl (45%) and silicate (45%) distribution of uranium forms (Fig. 1u).

Comparison with XAFS

XAFS results for leached residues show that HCl removes arsenate, HF has little effect on As, and that HNO₃ removes pyritic arsenic (results for Ohio 5/6/7 only; Huggins and others, in press). The XAFS data show that a small amount of residual arsenic remains after leaching. Arsenate forms extracted by HCl and ammonium acetate are believed to be oxidation products from the other major arsenic forms, resulting from exposure of the powdered coal samples to air. These results are consistent with Phase I XAFS results for bituminous coal samples (Kolker and others, 2000a), showing that significant fractions of arsenate can result from in-situ oxidation.

Coal Oxidation Experiments

Experiments testing the possibility that the leaching process itself results in pyrite oxidation compare baseline HCl leaching values (for Fe) vs. results after heating the coal to 75 °C in air, and wet-dry cycling of the coal while heating. The results are within analytical uncertainty for all determinations, indicating that neither heating or wetting and drying, both of which take place during the leaching procedure, has a measurable effect on the fraction of Fe leached by HCl (Fig. 3). This fraction should increase if pyrite is being oxidized by the leaching procedure.

Electron Microprobe Analyses

Microprobe studies concentrated on pyrite, illite-smectite, and carbonate minerals. Complete analytical results are given in Appendix 1. Results for pyrite are plotted in Figure 4, and representative analyses are shown in Table 8. In the Ohio 5/6/7 coal sample, with the exception of 1 pyrite grain, whose arsenic content ranges for 0.02 to 1.79 %, arsenic contents of pyrite grains determined are below 0.4 weight percent and there is no correlation between arsenic content and concentrations of other chalcophile elements (Fig. 4a-d). In the Wyodak coal sample, arsenic in pyrite ranges from negligible to about 0.5 weight percent, with some correlation between abundance of As and other chalcophile elements, especially Se (Fig. 4d). Arsenic in North Dakota pyrite is generally below 0.40 weight percent with the exception of 1 subhedral grain whose arsenic content ranges from 0.18 to 0.84 weight percent (Fig. 4). This grain is also enriched in Se (0.02 to 0.07 wt. %) and Ni (0.00 to 0.12 wt %; Fig. 4).

Microprobe data for illite/smectite show considerable major element variability in the contents of K, Mg, Fe, and to a lesser degree, Al, and Si. This is due to fine-scale intergrowth of clay minerals, overlap with adjacent grains, and differing degrees of substitution of these elements in the illite structure (Table 9; Appendix 1). Prior electron microprobe elemental mapping and the presence of Fe, Mg, and K, were used to identify illite/smectite grains during SHRIMP-RG analyses (Fig. 5; see following section). In most grains, SiO₂ in illite/smectite averages about 50% weight percent and Al₂O₃ averages about 30 weight percent (Table 9). Compared to the Ohio 5/6/7 sample, the North Dakota illites have slightly lower Al₂O₃ contents, and the Wyodak sample has a greater fraction of kaolinite. Unlike the illite/smectite, kaolinite shows little or no solid solution, and is essentially stoichiometric Al₄Si₄O₁₀(OH)₈, giving an Al₂O₃ content of about 40 weight percent and an SiO₂ content of about 50 weight percent (Table 9). The clay mineral analyses do not sum to 100% because of structural water and/or hydroxyls, that are not determined.

Electron microprobe data were also obtained for calcite in the Ohio 5/6/7 coal sample. The following elements were determined (as oxides)- Mn, Mg, Pb, Ca, Sr, Ba, and Zn. The results confirm that Mg, Fe, Sr, and Mn are commonly present at trace to minor element levels in calcite, and measurable concentrations of Ba, Pb, and Zn were found in a few cases. Results for calcite in the Phase 2 Ohio 5/6/7 sample are given in Appendix 1.

SHRIMP-RG Ion Microprobe

SHRIMP-RG results for Mg, V, Cr, Mn, and Ni, in illite/smectite are shown in Figure 6. Contents of transition metals are correlated with Mg content, a proxy for the illite (ferromagnesian) component in clays that show both solid solution to smectite and fine-scale intergrowth with other clay minerals, such as kaolinite. Contents of V and Cr show similar ranges in the illite/smectites, and appear to be correlated (Fig. 6e). Quantifying the concentration of Cr was the highest priority, and therefore, Cr was determined twice, as ^{52}Cr and as ^{53}Cr . Using this approach, the natural ratio of $^{53}\text{Cr}/^{52}\text{Cr}$ (0.1134) was easily reproduced to three decimal places. Concentrations obtained using the two chromium isotopes were generally within 1% (absolute), for calibrations obtained using the same standard (Fig. 6g; Kolker and others, 2000b,c).

Comparison of results using different standards for the same Ohio 5/6/7 illite/smectite, is given in Table 10. For most elements, the GSE standard gives the lowest concentrations, and these can be considered minima. GSE is the only standard determined in both illite/smectite SHRIMP-RG runs, providing a uniform basis for comparing data. Table 11 shows the reproducibility of counts/concentration for the GSE standard in 4 runs over a 2-day period in February, 2000. Total deviation ranges from 5.8 to 12.5%, except for Rb (20.9%) and Sr (17.9%).

Semi-quantitative determinations of transition and chalcophile elements in pyrite were obtained, including Cd, whose contents are generally below the electron microprobe detection limit. Results are expressed as a ratio of the counts for elements of interest, vs. counts for ^{32}S , whose concentration in pyrite is assumed to be uniform (Fig. 7). Results for Cd, Se, and possibly other elements, show enrichment in pyrite present in the two low rank coal samples (North Dakota and Wyodak) relative to pyrite in the Ohio 5/6/7 sample, and two other bituminous coal samples from Phase I (Fig. 7a, 7c). Note that count rates for Cd, Sb, and As are all similar, even though arsenic in pyrite is generally more abundant than the other two elements. This suggests that relative sensitivity factors (RSF's) in pyrite, which determine the count rate for a given concentration, are like those in silicate matrices, in which RSF's for Cd and Sb are similar, and the RSF for As is lower (Wilson and others, 1989).

Laser Ablation ICP-MS

Results of reconnaissance laser ablation ICP-MS analysis of pyrite in the Ohio 5/6/7 sample are given in Table 12. Pyrite in the Wyodak and North Dakota coal samples was found to be too fine-grained to determine using the 50 μm spot, chosen to maximize sensitivity for Hg. As in the SHRIMP-RG determination of Cr in illite, Hg was determined using two isotopes, ^{200}Hg (23.1% of Hg) and ^{202}Hg (29.9% of Hg). Each isotope provided acceptable results; there is a slight bias towards higher contents using the more abundant isotope (Fig. 8a). The data show that the most mercury-rich pyrites are also enriched in other metals (Fig 8b-c).

DISCUSSION

Trace element variation by rank

The three coal samples in this study show a distinct rank dependence in their trace-element distribution. In the Ohio 5/6/7 sample chalcophile elements (As, Cu, Se, Hg, etc.) occur primarily in pyrite, as observed for the Illinois #6 and Pittsburgh bituminous coal samples in Phase 1 (Kolker and others,

2000a; Kolker and others, 2000d). In the Wyodak and North Dakota samples, chalcophile elements in organic or HCl-soluble forms generally exceed those in pyrite (e.g. As, Fig. 1c).

An exception is mercury, which has a distinct sulfide association, even in the Wyodak and North Dakota samples. Based on their HNO₃ leaching fractions and their whole coal mercury contents (60% of 0.18 ppm, 60% of 0.13 ppm, and 80% of 0.08 ppm) the total amount of mercury residing in pyrite in the three Phase II coal samples is estimated to range from about 0.06 ppm in the North Dakota sample to about 0.11 ppm in the Ohio 5/6/7 sample. Because the pyritic sulfur content of the Ohio 5/6/7 coal is 5 (North Dakota) to 28 (Wyodak) times that of the other samples, we expect individual pyrite grains in the lower rank coal samples to have higher mercury contents than those we measured for the Ohio 5/6/7 sample by laser ablation ICP-MS.

Elements such as Co, Ni, Mn, Mo, which show some pyrite association in the Ohio 5/6/7 sample, have little or no pyrite association in the Wyodak and North Dakota coal samples, and in low rank coal samples in general. The Wyodak and North Dakota coal samples also show markedly different modes of occurrence for Sr, Ba, and REE than the Ohio 5/6/7 bituminous coal sample. In the Ohio 5/6/7 sample, a silicate association is indicated for Sr and Ba, whereas leaching results for the Wyodak and North Dakota samples suggest association of Sr with carbonates, or Sr-bearing phosphates, and Ba with barite. The proportion of HCl-soluble REE, probably as REE phosphates, is far greater in the Wyodak and North Dakota samples than in the Ohio 5/6/7 sample.

Summary

Iterative selective leaching using ammonium acetate, HCl, HF, and HNO₃ used in conjunction with mineral identification/quantification, and microanalysis of individual mineral grains, has allowed delineation of modes of occurrence for 44 elements in the Ohio 5/6/7, Wyodak, and North Dakota Program coal samples. These results provide basic information on the distribution of elements in these coal samples, information needed for characterization and combustion model development.

The Phase II coal samples show rank-dependent differences in trace-element modes of occurrence. For example, the Ohio 5/6/7 sample shows a greater proportion of chalcophile elements such as As, Se, Pb, etc., residing in pyrite, compared to the Wyodak and North Dakota samples. The Wyodak and North Dakota samples have a greater proportion of chalcophile elements in organic or HCl-leachable forms, a distribution typical of lower-rank coal samples. An exception to this rank dependence is mercury. Each of the three coal samples has a large (60-80%) fraction of its mercury residing in pyrite, even though the overall pyrite content of the Ohio 5/6/7 sample is much greater than that of the lower rank coal samples. The association of mercury and pyrite was confirmed using laser ablation ICP-MS, for the Ohio 5/6/7 sample, and for the Illinois #6 and Pittsburgh coal samples studied in Phase I.

Comparison of leaching data and XAFS determinations for the same leaching splits show similar proportions of pyritic arsenic by the two methods, and that arsenate resulting from pyrite oxidation is HCl-leachable (Huggins and others, in press). Microanalysis shows that each of the Phase II coal samples have pyrite containing sub grain-scale domains enriched in one or more chalcophile elements. Pyrite in the Ohio 5/6/7 coal sample has the most arsenic-rich pyrite, approaching 2.0 weight percent As, on the scale of an individual (3 μ m) microprobe analysis. Arsenic-rich pyrite in the Ohio 5/6/7 sample shows little or no enrichment in associated chalcophile elements. Grain-scale concentrations of other chalcophile elements (e.g. Cd, Se) show some correlation with arsenic, in pyrite found in the Wyodak

and North Dakota samples. Chromium and other transition metals in illite/smectite determined using the SHRIMP-RG ion microprobe, support our leaching results indicating silicate-hosted fractions of these metals in each of the three Phase II coal samples.

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[*indicates publications resulting from Phase II of "Toxic Substances from Coal Combustion"]

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Table 1. Summary of Coal Characteristics, Phase II Coal Samples (in weight percent, dry basis)

	Ohio 5/6/7	North Dakota	Wyodak
Ash	9.93	14.64	8.13
Pyritic Sulfur	1.42	0.28	0.05
Organic Sulfur	1.24	0.56	0.37
Sulfate Sulfur	0.02	0.14	0.01
Moisture	2.33	35.88	25.81
Rank	Bituminous	Lignite	Subbituminous

Results from Geochemical Testing, Inc. of Somerset, PA.

Table 2. Semi-quantitative determination of sample mineralogy by X-ray diffraction (XRD) of low-temperature ash (LTA)

Sample	QTZ	FLD	SID	ILL	KOL	PY	BAS	SPL	MAR	HEM
N. Dakota	38	tr	tr	12	16	tr	28			tr
N. Dakota*	47	tr	tr	12	12	tr	20	tr		tr
Wyodak	26				46		28	tr		
Wyodak*	30				46	tr	23			
Ohio 5/6/7	19	tr		21	43	12	tr	tr	tr	

Where QTZ = quartz; FLD = feldspar; SID = siderite; ILL = illite; KOL = kaolinite; CHL = chlorite; PY = pyrite; BAS = bassanite; SPL = sphalerite; MAR = marcasite; and HEM = hematite. Values listed as trace (tr) range from <1 to 3%; values $\leq 5\%$ are considered trace constituents by this method. Samples with an asterisk were treated with ammonium acetate prior to ashing. Bassanite ($\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$) is probably an artifact of the ashing process, formed by combination of organic Ca and S, but may also form by dehydration of gypsum. Other possible trace constituents that could not be resolved with certainty are listed below. Phases are listed in boldface where they also have been found in SEM. For the North Dakota sample, these phases are **chlorite**, **apatite**, **rutile**, and anatase (not distinguishable from rutile in SEM). For the Wyodak sample, these phases are siderite, apatite, and **rutile**. For the Ohio sample, these phases are **calcite**, siderite, chlorite, hematite, **apatite**, **rutile**, and barite. Values are listed on an ash-basis.

Table 3. Mineralogy of PSI Phase II Coal samples determined by SEM. Mineral phases observed in SEM are indicated by an X.

		Ohio	North Dakota	Wyodak
Major Phases				
Quartz		X	X	X
Illite		X	X	X
Kaolinite		X		X
Pyrite		X	X	X
Calcite		X		
Minor or Trace Phases				
Epidote	<i>Fe-Mg-Ca-Al silicate</i>		X	
Chlorite	<i>Fe-Mg-Al silicate</i>		X	
Alkali-feldspar	<i>K-Al-silicate</i>		X	
Zircon	$ZrSiO_4$			X
Barite	$BaSO_4$		X	X
Fe-O(OH) phase			X	X
TiO ₂ phase		X	X	X
Apatite	<i>Ca-phosphate</i>	X	X	
Crandellite	<i>Ca-Al phosphate</i>			X
Goyazite	<i>Sr-Al-REE phosphate</i>		X	
Monazite	<i>REE phosphate</i>	X	X	X
Sphalerite	ZnS	X	X	X
Chalcopyrite	$CuFeS_2$			X

Table 4: Elemental Concentrations of Phase II whole coal samples.
Values are in ppm on a dry basis.

Element	OHIO	WYODAK	ND	Element	OHIO	WYODAK	ND
Li	11	3.7	5.1	Te	<0.2	<0.2	<0.3
Be	2.6	0.3	0.8	Cs	0.75	0.136	0.58
B	86	42	130	Ba	66	450	590
Na	280	860	3800	La	9.82	5.60	4.96
Mg	340	1900	4000	Ce	18.4	9.3	7.8
Al	9100	7400	9000	Sm	2.17	0.96	0.75
Si	19000	13000	25000	Eu	0.427	0.193	0.149
P	270	570	170	Tb	0.319	0.11	0.111
K	1600	190	1700	Yb	0.98	0.42	0.49
Ca	1100	11000	15000	Lu	0.137	0.049	0.070
Sc	3.8	1.9	1.9	Hf	0.61	0.59	0.61
Ti	580	670	410	Ta	0.20	0.159	0.137
V	25	18	15	W	1.1	0.48	2.99
Cr	15.3	7.9	11.5	Au	<1.0	<0.9	<1.5
Mn	20	8.2	59	Hg	0.18	0.13	0.08
Fe	14700	3030	7870	Tl	1.3	<0.2	<0.3
Co	4.91	5.66	9.1	Pb	9.1	1.9	1.5
Ni	18	4.8	4.3	Bi	<0.2	<0.2	<0.3
Cu	9.6	14	5.5	Th	2.14	1.85	1.67
Zn	21	8.2	12	U	1.25	0.73	1.12
Ga	6.0	2.5	2.3				
Ge	9.8	0.37	1.3				
As	17.8	1.74	10				
Se	1.78	1.31	0.97				
Br	18.7	1.1	2.58				
Rb	11.3	2.1	7.2				
Sr	100	260	420				
Y	9.7	3.5	4.8				
Zr	14	18	26				
Nb	3.0	2.8	3.1				
Mo	4.9	1.1	2.3				
Ag	<0.2	<0.2	<0.3				
Cd	0.1	0.1	<0.1				
Sn	1.0	<0.9	<1.5				
Sb	1.94	0.23	0.70				

Table 5: Replicate analyses of Ohio 5/6/7, Wyodak, and North Dakota coal samples. Only analyses done by the same method are compared.

Element	Analysis 1 OHIO	Analysis 2 OHIO	Analysis 1 WYODAK	Analysis 2 WYODAK	Analysis 1 ND	Analysis 2 ND
Li	11	9.5	3.7	3.2	5.1	4.6
Be	2.6	2.6	0.3	0.3	0.8	0.8
B	86	100	42	56	130	160
Na	280	270	860	910	3800	3900
Mg	340	360	1900	2000	4000	4500
Al	9100	10000	7400	6500	9000	8900
Si	19000	19000	13000	8200	25000	21000
P	270	290	570	570	170	160
Ca	1100	1000	11000	10000	15000	16000
Ti	580	600	670	530	410	400
V	25	24	18	18	15	16
Mn	20	20	8.2	8.5	59	62
Ni	18	21	4.8	5.8	4.3	5.5
Cu	9.6	7.4	14	13	5.5	4.0
Zn	21	22	8.2	7.9	12	12
Ga	6.0	5.5	2.5	2.1	2.3	2.5
Ge	9.8	10	0.37	0.34	1.3	1.6
Sr	100	97	260	280	420	430
Y	9.7	9.7	3.5	3.5	4.8	4.9
Zr	14	19	18	15	26	28
Nb	3.0	3.4	2.8	2.9	3.1	2.7
Mo	4.9	3.2	1.1	0.65	2.3	1.4
Ag	<0.2	0.1	<0.2	<0.1	<0.3	-0.2
Cd	0.1	0.078	0.1	0.084	<0.1	0.072
Sn	1.0	1.4	<0.9	0.35	<1.5	0.78
Te	<0.2	0.045	<0.2	0.13	<0.3	0.10
Ba	66	71	450	430	590	560
Au	<1.0	<1.0	<0.9	<1.0	<1.5	-2.0
Hg	0.18	0.15	0.13	0.09	0.08	0.09
Tl	1.3	1.2	<0.2	0.1	<0.3	0.11
Pb	9.1	8.1	1.9	1.5	1.5	1.6
Bi	<0.2	0.1	<0.2	0.074	<0.3	0.087

Table 6: Un-interpreted leaching results.

Leaching Results for OHIO 5/6/7 Coal Sample

Element	NH4Ac	HCl	HF	HNO3	Total	Element	NH4Ac	HCl	HF	HNO3	Total
Li	0%	0%	65%	0%	65%	Sn	0%	5%	35%	0%	40%
Be	0%	5%	50%	0%	55%	Sb	0%	5%	20%	15%	40%
Na	25%	10%	40%	10%	85%	Cs	5%	5%	75%	5%	90%
Mg	10%	5%	70%	0%	85%	Ba	5%	0%	90%	5%	100%
Al	0%	0%	100%	0%	100%	La	0%	5%	5%	55%	65%
P	0%	50%	50%	0%	100%	Ce	0%	5%	5%	60%	70%
K	0%	5%	90%	0%	95%	Sm	0%	25%	5%	35%	65%
Ca	30%	30%	5%	5%	70%	Eu	5%	25%	5%	30%	65%
Sc	0%	5%	40%	0%	45%	Tb	5%	20%	5%	25%	55%
Ti	0%	0%	65%	0%	65%	Yb	0%	5%	10%	25%	40%
V	0%	0%	35%	0%	35%	Lu	0%	5%	10%	30%	45%
Cr	0%	0%	30%	0%	30%	Hf	0%	0%	50%	0%	50%
Mn	15%	30%	20%	30%	95%	Ta	0%	0%	35%	5%	40%
Fe	0%	10%	10%	80%	100%	W	5%	10%	25%	0%	40%
Co	15%	30%	10%	20%	75%	Hg	10%	5%	5%	60%	80%
Ni	5%	15%	10%	25%	55%	Tl	10%	15%	15%	50%	90%
Cu	0%	10%	5%	65%	80%	Pb	0%	35%	10%	40%	85%
Zn	5%	30%	10%	30%	75%	Th	0%	10%	10%	35%	55%
As	0%	25%	5%	60%	90%	U	0%	5%	20%	5%	30%
Se	0%	0%	0%	50%	50%						
Rb	0%	5%	70%	10%	85%						
Sr	5%	5%	60%	5%	75%						
Y	0%	20%	10%	25%	55%						
Zr	0%	5%	70%	25%	100%						
Mo	5%	10%	20%	25%	60%						
Cd	5%	20%	5%	35%	65%						

Leaching Results for North Dakota Coal Sample

Element	NH4Ac	HCl	HF	HNO3	Total	Element	NH4Ac	HCl	HF	HNO3	Total
Li	10%	0%	35%	0%	45%	Ce	0%	60%	10%	20%	90%
Be	0%	70%	20%	0%	90%	Sm	5%	70%	10%	15%	100%
Na	85%	5%	5%	0%	95%	Eu	0%	60%	15%	10%	85%
Mg	50%	35%	10%	0%	95%	Tb	0%	60%	15%	10%	85%
Al	0%	25%	65%	0%	90%	Yb	0%	60%	20%	10%	90%
P	0%	85%	10%	0%	95%	Lu	0%	60%	15%	0%	75%
K	10%	5%	80%	0%	95%	Hf	0%	0%	60%	5%	65%
Ca	40%	60%	0%	0%	100%	Ta	5%	0%	45%	0%	50%
Sc	0%	15%	80%	5%	100%	W	10%	10%	50%	5%	75%
Ti	0%	20%	60%	0%	80%	Hg	0%	5%	5%	80%	90%
V	0%	35%	45%	0%	80%	Tl	ND	ND	ND	ND	ND
Cr	0%	10%	35%	5%	50%	Pb	0%	85%	10%	5%	100%
Mn	15%	75%	10%	0%	100%	Th	0%	20%	45%	15%	80%
Fe	0%	65%	15%	10%	90%	U	0%	45%	45%	5%	95%
Co	0%	55%	40%	0%	95%	Th	0%	20%	45%	15%	80%
Ni	0%	45%	25%	15%	85%	U	0%	45%	45%	5%	95%
Cu	0%	30%	10%	20%	60%						
Zn	0%	65%	10%	5%	80%						
As	0%	50%	15%	15%	80%						
Se	10%	5%	0%	25%	40%						
Rb	0%	5%	70%	0%	75%						
Sr	40%	60%	0%	0%	100%						
Y	0%	80%	10%	5%	95%						
Zr	0%	5%	65%	0%	70%						
Mo	0%	0%	60%	0%	60%						
Cd	ND	ND	ND	ND	ND						
Sn	ND	ND	ND	ND	ND						
Sb	0%	0%	40%	10%	50%						
Cs	0%	5%	75%	5%	85%						
Ba	0%	80%	15%	5%	100%						
La	0%	55%	10%	20%	85%						

Leaching Results for WYODAK Coal Sample

Element	NH4Ac	HCl	HF	HNO3	Total	Element	NH4Ac	HCl	HF	HNO3	Total
Li	0%	0%	35%	0%	35%	Ba	5%	80%	5%	0%	90%
Be	0%	55%	35%	0%	90%	La	0%	60%	5%	15%	80%
Na	90%	5%	0%	0%	95%	Ce	0%	65%	5%	15%	85%
Mg	55%	30%	0%	0%	85%	Sm	0%	70%	5%	10%	85%
Al	0%	25%	55%	0%	80%	Eu	0%	60%	10%	10%	80%
P	0%	80%	10%	0%	90%	Tb	0%	70%	5%	10%	85%
K	30%	5%	50%	0%	85%	Yb	5%	40%	15%	15%	75%
Ca	45%	55%	0%	0%	100%	Lu	5%	45%	15%	10%	75%
Sc	0%	60%	35%	0%	95%	Hf	0%	0%	45%	5%	50%
Ti	0%	20%	60%	0%	80%	Ta	0%	0%	40%	5%	45%
V	0%	65%	25%	0%	90%	W	10%	5%	45%	5%	65%
Cr	0%	10%	45%	0%	55%	Hg	20%	0%	0%	60%	80%
Mn	5%	80%	5%	5%	95%	Tl	ND	ND	ND	ND	ND
Fe	0%	75%	10%	10%	95%	Pb	0%	70%	20%	10%	100%
Co	0%	30%	60%	5%	95%	Th	0%	30%	25%	15%	70%
Ni	0%	25%	15%	20%	60%	U	10%	50%	30%	5%	95%
Cu	0%	20%	5%	20%	45%						
Zn	0%	50%	10%	25%	85%						
As	0%	40%	15%	15%	70%						
Se	5%	5%	0%	20%	30%						
Rb	10%	0%	65%	0%	75%						
Sr	30%	65%	5%	0%	100%						
Y	0%	65%	10%	10%	85%						
Zr	0%	5%	60%	0%	65%						
Mo	0%	0%	45%	0%	45%						
Cd	0%	70%	5%	10%	85%						
Sn	ND	ND	ND	ND	ND						
Sb	0%	5%	35%	15%	55%						
Cs	5%	5%	60%	5%	75%						

Table 7. Interpreted Leaching Results.

Element	OHIO	WYODAK	NORTH DAKOTA
Li	65% Silicates 35% Organic	35% Silicates 65% Organic	35% Silicates 65% Organic (15%) ¹
Be	50% Silicates 5% Gibbsite (?) 45% Organic	35% Silicates 55% Gibbsite (?) 10 % Organic	20% Silicates 70% Gibbsite 10 % Organic
Na	25% Exchangable 10% HCl Soluble 40% Silicates 10% HNO ₃ Soluble	90 % Exchangable 5% HCl Soluble	85% Exchangable 5% HCl Soluble 5% Silicates
Mg	70% Silicates 25% Organic (10%) ¹ 5% Carbonates	70% Organic (55%) ¹ 30 % Carbonates	10% Silicates 55% Organic (50%) ¹ 35% Carbonates
Al	100% Silicates	55% Silicates 25% Gibbsite (?) 20% Organic	65% Silicates 25% Gibbsite (?) 10% Organic
P	50% Phosphates 50% Silicates	80% Phosphates 10% Silicates 10% Organic	85% Phosphates 10% Silicates 5% Organic
K	90% Silicates	50% Silicates 45% Organic (30%) ¹	80% Silicates 15% Organic (10%) ¹
Ca	60% Carbonates 5% Silicates 30% Organic	100% Carbonates	100% Carbonates
Sc	40% Silicates 5% Fe-Oxides 55% Insolubles ²	35% Silicates 60% Fe-Oxides 5% Insolubles ²	80% Silicates 15% Fe-Oxides
Ti	65% Silicates 35% Insoluble (TiO ₂)	60% Silicates 20% Insoluble (TiO ₂) 20% Fe-Oxides	60% Silicates 20% Insoluble (TiO ₂) 20% Fe-Oxides
V	35% Silicates 65% Organic	25% Silicates 10% Organic 65% Fe-Oxides	45% Silicates 20% Organic 35% Fe-Oxides
Cr	30% Silicates 70% Insolubles ²	45% Silicates 45% Insolubles ² 10% Fe-Oxides	35% Silicates 50% Insolubles ² 10% Fe-Oxides
Mn	45% Carbonates ³ 20% Silicates 30% Pyrite	85% Carbonates ³ 5% Silicates 5% Pyrite	90% Carbonates ³ 10% Silicates
Element	OHIO	WYODAK	NORTH DAKOTA

Fe	80% Pyrite 10% Fe-Oxides ⁴ 10% Silicates	10% Pyrite 75% Fe-Oxides ⁴ 10% Silicates	10% Pyrite 65% Fe-Oxides ⁴ 15% Silicates
Co	10% Silicates 30% HCl Soluble ⁵ 40% Organic (15%) 20% Pyrite	60% Silicates 30% HCl Soluble ⁵ 5% Organic 5% Pyrite	40% Silicates 55% HCl Soluble ⁵ 5% Organic
Ni	25% Pyrite 10% Silicates 15% HCl Soluble ⁵ 50% Organic (5%)	20 Pyrite 15% Silicates 25% HCl Soluble ⁵ 40% Organic	15% Pyrite 25% Silicates 45% HCl Soluble ⁵ 15% Organic
Cu	65% Pyrite ⁶ 5% Silicates 10% HCl Soluble ⁵ 20% Organic	20% Pyrite ⁶ 5% Silicates 20% HCl Soluble ⁵ 55% Organic	20% Pyrite ⁶ 10% Silicates 30% HCl Soluble ⁵ 40% Organic
Zn	30% Sphalerite 30% Pyrite 10% Silicates 30% Organic (5%) ¹	50% Sphalerite 25% Pyrite 10% Silicates 15% Organic	65% Sphalerite 5% Pyrite 10% Silicates 20% Organic
As	60% Pyrite 25% Arsenate 5% Silicates 10% Organic	15% Pyrite 40% Arsenate 15% Silicates 30% Organic	15% Pyrite 50% Arsenate 15% Silicates 20% Organic
Se	50% Pyrite 50% Organic	20% Pyrite 75% Organic (5%) ¹	25% Pyrite 70% Organic (10%) ¹
Rb	70% Silicates 15% Organic	65% Silicates 35% Organic (10%)	70% Silicates 25% Organic
Sr	10% Carbonates 60% Silicates	95% Carbonates 5% Silicates	100% Carbonates
Y	45% Phosphates 10% Silicates 45% Organic	75% Phosphates 10% Silicates 15% Organic	85% Phosphates 10% Silicates 5% Organic
Zr	70% Silicates (Zircon) 5% HCl Soluble ⁷ 25% HNO ₃ Soluble ⁷	60% Silicates (Zircon) 5% HCl Soluble ⁷ 35% Insoluble (Zircon)	65% Silicates (Zircon) 5% HCl Soluble ⁷ 30% Insoluble (Zircon)
Mo	20 % Silicate 45% Organic (5%) ¹ 25% Pyrite	45% Silicates 55% Organic	60% Silicates 40% Organic

Element	OHIO	WYODAK	NORTH DAKOTA
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Cd	20% Sphalerite	70% Sphalerite	ND
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	35% Pyrite 40% Organic (5%) ¹	10% Pyrite 15% Organic	ND ND
Sn	35% Silicates 60% Organic	ND ND	ND ND
Sb	20% Silicates 60% Organic 15% Pyrite	35% Silicates 45% Organic 15% Pyrite	40% Silicates 50% Organic 10% Pyrite
Cs	75% Silicates 10% Insolubles ⁸ 5% HCl Soluble	60% Silicates 25% Insolubles ⁸ 5% HCl Soluble	75% Silicates 15% Insoluble ⁸ 5% HCl Soluble
Ba	5% Barite 90% Silicates 5% Organic (5%) ¹	80% Barite 5% Silicates 15% Organic (5%) ¹	85% Barite 15% Silicates
La	55% HNO ₃ Soluble ⁹ 5% HCl Soluble ⁹ 5% Silicates 35% Organic	15% HNO ₃ Soluble ⁹ 60% HCl Soluble ⁹ 5% Silicates 20% Organic	20% HNO ₃ Soluble ⁹ 55% HCl Soluble ⁹ 10% Silicates 15% Organic
Ce	60% HNO ₃ Soluble ⁹ 5% HCl Soluble ⁹ 5% Silicates 30% Organic	15% HNO ₃ Soluble ⁹ 65% HCl Soluble ⁹ 5% Silicates 15% Organic	20% HNO ₃ Soluble ⁹ 60% HCl Soluble ⁹ 10% Silicates 10% Organic
Sm	35% HNO ₃ Soluble ⁹ 25% HCl Soluble ⁹ 5% Silicates 35% Organic	10% HNO ₃ Soluble ⁹ 70% HCl Soluble ⁹ 5% Silicates 15% Organic	15% HNO ₃ Soluble ⁹ 70% HCl Soluble ⁹ 10% Silicates
Eu	30% HNO ₃ Soluble ⁹ 25% HCl Soluble ⁹ 5% Silicates 40% Organic (5%)	10% HNO ₃ Soluble ⁹ 60% HCl Soluble ⁹ 10% Silicates 20% Organic	10% HNO ₃ Soluble ⁹ 60% HCl Soluble ⁹ 15% Silicates 15% Organic
Tb	25% HNO ₃ Soluble ⁹ 20% HCl Soluble ⁹ 5% Silicates 40% Organic (5%)	10% HNO ₃ Soluble ⁹ 70% HCl Soluble ⁹ 5% Silicates 15% Organic	10% HNO ₃ Soluble ⁹ 60% HCl Soluble ⁹ 15% Silicates 15% Organic
Yb	25% HNO ₃ Soluble ⁹ 5% HCl Soluble ⁹ 10% Silicates 60% Organic	15% HNO ₃ Soluble ⁹ 40% HCl Soluble ⁹ 15% Silicates 30% Organic (5%)	10% HNO ₃ Soluble ⁹ 60% HCl Soluble ⁹ 20% Silicates 10% Organic
Element	OHIO	WYODAK	NORTH DAKOTA
Lu	30% HNO ₃ Soluble ⁹ 5% HCl Soluble ⁹ 10% Silicates	10% HNO ₃ Soluble ⁹ 45% HCl Soluble ⁹ 15% Silicates	60% HCl Soluble ⁹ 15% Silicates

	55% Organic	30% Organic (5%)	25% Organic
Hf	50% Silicates 50% Organic	45% Silicates 50% Organic	60% Silicates 35% Organic
Ta	35% Silicates 60% Organic	40% Silicates 55% Organic	45% Silicates 55% Organic (5%) ¹
W	25% Silicates 10% HCl Soluble 65% Organic (5%) ¹	45% Silicates 5% HCl Soluble 45% Organic (10%) ¹	50% Silicates 10% HCl Soluble 35% Organic (10%) ¹
Hg	60% Pyrite 20% Organic 10% Exchangeable	60% Pyrite 20% Exchangeable 20% Organic	80% Pyrite 10% Organic
Tl	50% Pyrite 15% Silicates 15% Monosulfides 10% Organic	ND ND ND ND	ND ND ND ND
Pb	35% Galena 40% Pyrite 10% Silicates 15% Organic	70 Galena 10% Pyrite 20% Silicates	85% Galena 5% Pyrite 10% Silicates
Th	45% Phosphates 10% Silicates 45% Organic	45% Phosphates 25% Silicates 30% Organic	35% Phosphates 45% Silicates 20% Organic
U	20% Silicates 5% HCl Soluble ¹⁰ 70% Organic ¹¹	30% Silicates 50% HCl Soluble ¹⁰ 15% Organic (10%) ^{1,11}	45% Silicates 45% HCl Soluble ¹⁰ 15% Organic ¹¹

NOTES:

¹Number in parentheses after Organic % indicates percent in exchangeable sites.

²Organic association or insoluble species (such as chromite).

³May also include Fe oxides, oxidized pyrite, and mono-sulfides.

⁴May also include oxidized pyrite, carbonates and mono-sulfides.

⁵No evidence for any particular species. May be associated with carbonates, sulfates, oxides, or mono-sulfides.

⁶Includes pyrite and most chalcopyrite.

⁷Zircon may be partially soluble in HCl and HNO₃.

⁸Species unknown—may be organically associated.

⁹Likely associated with phosphates, especially rare earth bearing phosphates. There is conflicting evidence as to whether HCl-soluble and HNO₃-soluble rare earth elements are associated with different species.

¹⁰Species unknown, may be associated with organic chelates, and/or with zircon.

¹¹Small amounts may be associated with zircon.

Table 8. Representative Electron Microprobe Analyses for Pyrite in Phase II Coal samples.

	1	2	3	4	5	6	7	8	9
S	53.07	53.22	53.19	53.07	53.35	52.78	51.97	52.90	54.23
Fe	47.36	46.48	46.94	45.63	47.06	47.43	46.10	47.43	44.61

Co*	0.00	0.00	0.03	0.01	0.00	0.01	0.01	0.01	0.11
Ni	0.00	0.06	0.02	0.29	0.01	0.00	0.10	0.00	0.49
Cu	0.00	0.02	0.00	0.15	0.02	0.03	0.03	0.00	0.01
Zn	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.01
As	0.00	0.11	1.74	0.11	0.00	0.02	0.83	0.01	0.27
Se	0.01	0.00	0.00	0.00	0.00	0.01	0.05	0.00	0.08
Cd	0.02	0.01	0.01	0.02	0.00	0.00	0.00	0.04	0.01
Pb	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.17
Total	100.48	99.90	101.94	99.28	100.44	100.30	99.09	100.40	99.99

1- 5 Ohio 5/6/7; 6 -7 North Dakota; 8 - 9 Wyodak.

*Results for Co are background-subtracted and analyses are re-calculated to original totals.

Table 9. Representative electron microprobe analyses for illite/smectite in Phase II coal samples.

	1	2	3	4*	5	6	7	8	9
SiO ₂	49.15	50.44	50.19	49.61	49.42	51.89	50.30	46.99	48.20
TiO ₂	0.35	0.04	0.24	0.00	0.02	0.24	0.70	0.44	0.09
Al ₂ O ₃	29.69	31.83	34.39	41.67	31.62	29.67	29.69	35.13	36.45
Cr ₂ O ₃	0.03	0.01	0.01	0.00	0.01	0.02	0.01	0.00	0.00
MgO	2.60	1.38	1.29	0.02	2.13	1.74	2.30	0.40	0.87
CaO	0.02	0.07	0.12	0.02	0.13	0.32	0.08	0.11	0.08
MnO	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.03	0.00
FeO	4.67	2.32	1.71	0.13	2.85	4.26	4.57	0.72	2.20
Na ₂ O	0.11	0.08	0.17	0.00	0.14	0.10	0.10	0.89	0.06
K ₂ O	8.20	1.73	4.75	0.00	6.53	4.96	6.30	7.45	3.75
Total	94.83	87.91	92.86	91.45	92.85	93.21	94.06	92.16	91.70

1- 4 Ohio 5/6/7; 5 -7 North Dakota; 8 - 9 Wyodak.

*Analysis 4 is kaolinite.

Table 10. Example of SHRIMP-RG data reduction for grain 1-2L, a representative Ohio5/6/7 illite/smectite. Table shows raw counts for this illite, counts per ppm (Al_2O_3 , CaO, SiO_2 are in counts/per weight percent) for standards SRM 610, GSE, and BHVO, and concentration results for this illite obtained by each standard.

	Raw Counts	Counts/ppm or wt. % (Al_2O_3 , CaO, SiO_2)			Illite concentration by standard		
		SRM 610	GSE	BHVO	Conc. 610	Conc. GSE	Conc. BHVO
Mg	21391	9.44	13.00	13.06	2266	1645	1637
$^1\text{Al}_2\text{O}_3$	325487	10252	16810	11708	31.75	19.36	27.80
^1CaO	5442	90615	111287	104267	0.06	0.05	0.05
$^1\text{SiO}_2$	1059325	18292	27723	19627	57.91	38.21	53.97
Sc	4163	362.6	240.5	349.6	11.48	17.31	11.91
Ti	29024	18.13	20.55	17.24	1601	1413	1683
V	13766	175.0	190.0	129.8	78.68	72.47	106.04
^{52}Cr	14022	180.2	215.9	163.0	77.82	64.95	86.01
^{53}Cr	1587	20.25	24.53	18.53	78.37	64.72	85.65
Mn	7009	200.6	303.2	253.2	34.94	23.12	27.69
Co	173	108.3	186.0	165.0	1.60	0.93	1.05
Ni	687	21.94	43.81	34.70	31.30	15.67	19.79
Rb	68370	617.4	718.8	584.2	110.74	95.12	117.02
Sr	11821	239.3	280.4	233.1	49.40	42.15	50.70

Results for Al_2O_3 , CaO, and SiO_2 are determined in weight percent to facilitate comparison with electron microprobe results known to be approximately 30 wt. %, <0.5 wt. % and 50 wt. %, respectively, for illite/smectite.

Table 11. Reproducibility of SHRIMP-RG results obtained in 5 runs of the GSE standard (in counts per ppm or weight percent).

Mass Determined	Counts per ppm or weight percent (AlO, SiO, Ca)				
	2 Feb 00	2 Feb 00	3 Feb 00	3 Feb 00	3 Feb 00
	GSE_L1	GSE_L2	² GSE_L1	GSE_L2	GSE_L3
²⁶ Mg	236.5	227.5	241.7	230.0	222.7
⁴³ AlO ¹	48462	46832	47833	50470	47871
⁴⁴ Ca ¹	320743	307322	310075	333787	315280
⁴⁴ SiO ¹	81609	79356	81572	85734	81213
⁴⁵ Sc	762.3	738.3	700.7	798.6	728.8
⁴⁷ Ti	63.08	60.09	59.64	66.63	61.58
⁵¹ V	608.0	572.0	552.0	644.1	585.8
⁵² Cr	650.5	611.0	588.9	668.6	618.6
⁵³ Cr	72.98	68.83	64.97	75.45	69.67
⁵⁵ Mn	864.3	844.1	723.5	897.6	827.7
⁵⁵ KO	7.17	6.97	6.22	7.20	6.71
⁵⁹ Co	475.9	474.3	370.9	493.0	446.3
⁶⁰ Ni	103.8	104.1	77.93	107.07	96.12
⁶³ Cu	165.3	166.7	118.0	170.9	151.2
⁶⁴ Zn	84.54	87.33	57.32	85.92	76.38
⁷² FeO	15.82	15.67	10.46	16.33	14.67
⁸⁵ Rb	1673.3	1673.4	741.2	1926.4	1523.8
⁸⁸ Sr	736.0	723.9	405.7	866.0	710.6

¹Results for AlO, Ca, and SiO are determined in weight percent to facilitate comparison with electron microprobe results.

²Results were excluded from computation of average counts/ppm for GSE standard.

Table 12. Laser Ablation ICP-MS data for pyrite in Ohio 5/6/7 coal sample (in ppm). Data are corrected for in-run drift. Fe content is fixed and assumed to be stoichiometric.

	ohio1 py1.1	ohio1 py1.2	ohio1 py4.1	ohio2 py6.1	ohio2 py6.1a	ohio2 py6.2	ohio2 py1.1	ohio2 py5.1	ohio2 py5.2
Cr	4.1	8.4	25	720	1.2	9.2	0.77	1.2	0.37
Mn	304	523	501	833	141	473	92	336	368
Fe	465500	465500	465500	465500	465500	465500	465500	465500	465500
Co	135	255	12	57	9.1	7.6	1.7	12	16
Ni	889	974	941	420	15	13	22	75	95
Cu	314	339	298	361	63	52	88	27	8.4
Zn	16	26	14	42	2.8	4.3	5.3	14	17
As	735	835	47	471	171	166	44	176	247
Se	720	898	86	596	12	31	67	133	161
Mo	7.1	12	6.9	46	5.3	10	0.24	41	45
Cd	1.8	1.6	0.30	0.45	0.30	0.52	0.29	0.68	0.92
Sb	23	94	12	55	0.94	3.3	0.53	1.9	2.3
¹ Hg	24	23	1.7	9.0	0.59	0.97	0.98	14.6	18
² Hg	29	27	2.1	12	0.65	0.98	1.1	16.3	20
Tl	183	140	8.3	4.1	23	19	0.54	24	29
Pb	547	1268	273	518	70	91	27	3.6	4.8

¹Hg determined as ²⁰⁰Hg.

²Hg determined as ²⁰²Hg.

-Figures-

Figure 1a-d. Selective leaching results for Fe, Cu, As, and Hg, showing a chalcophile association (primarily in Ohio 5/6/7).

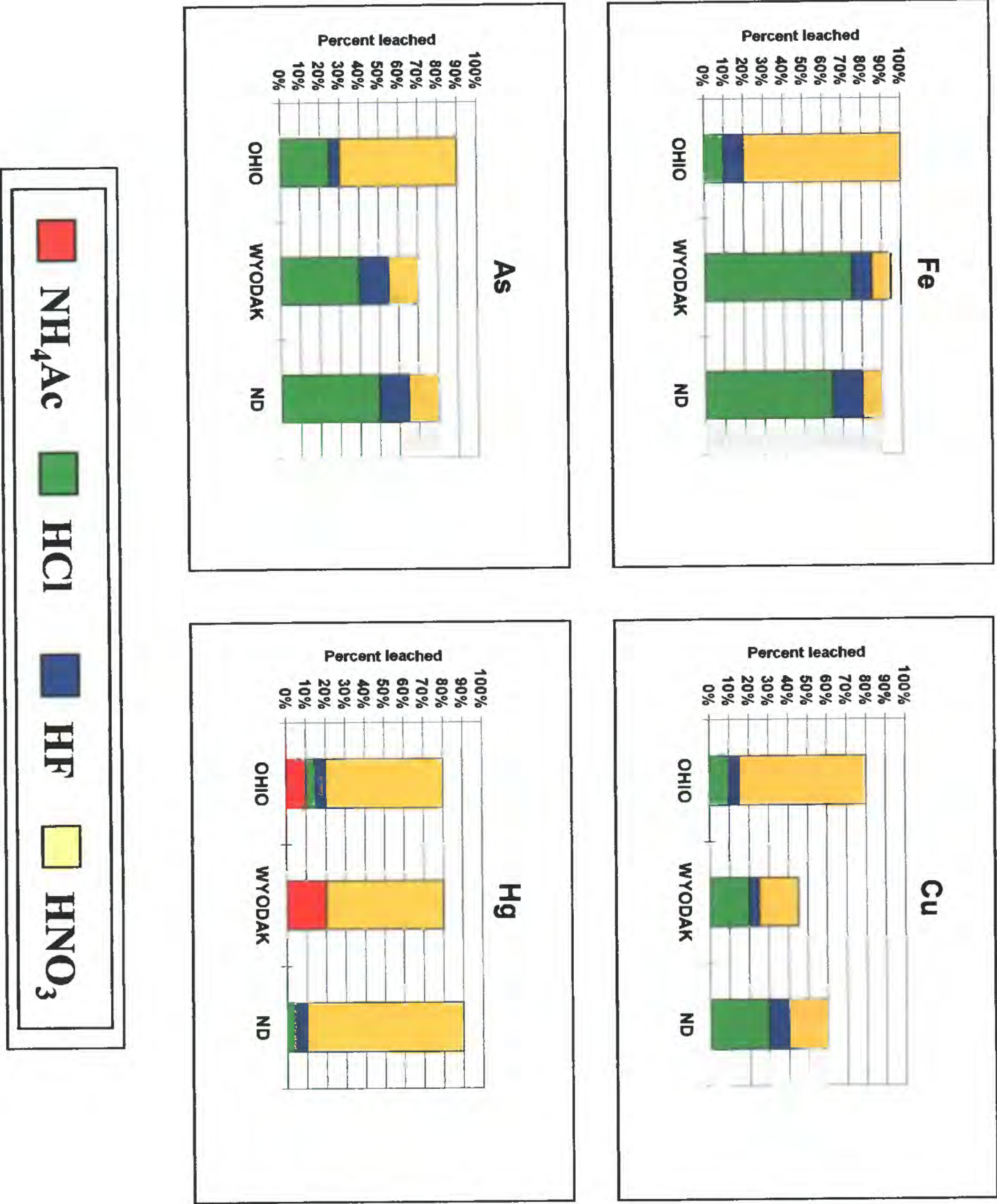


Figure 1e-h. Leaching data for elements Li, Al, Ti, Cr, showing lithophile association.

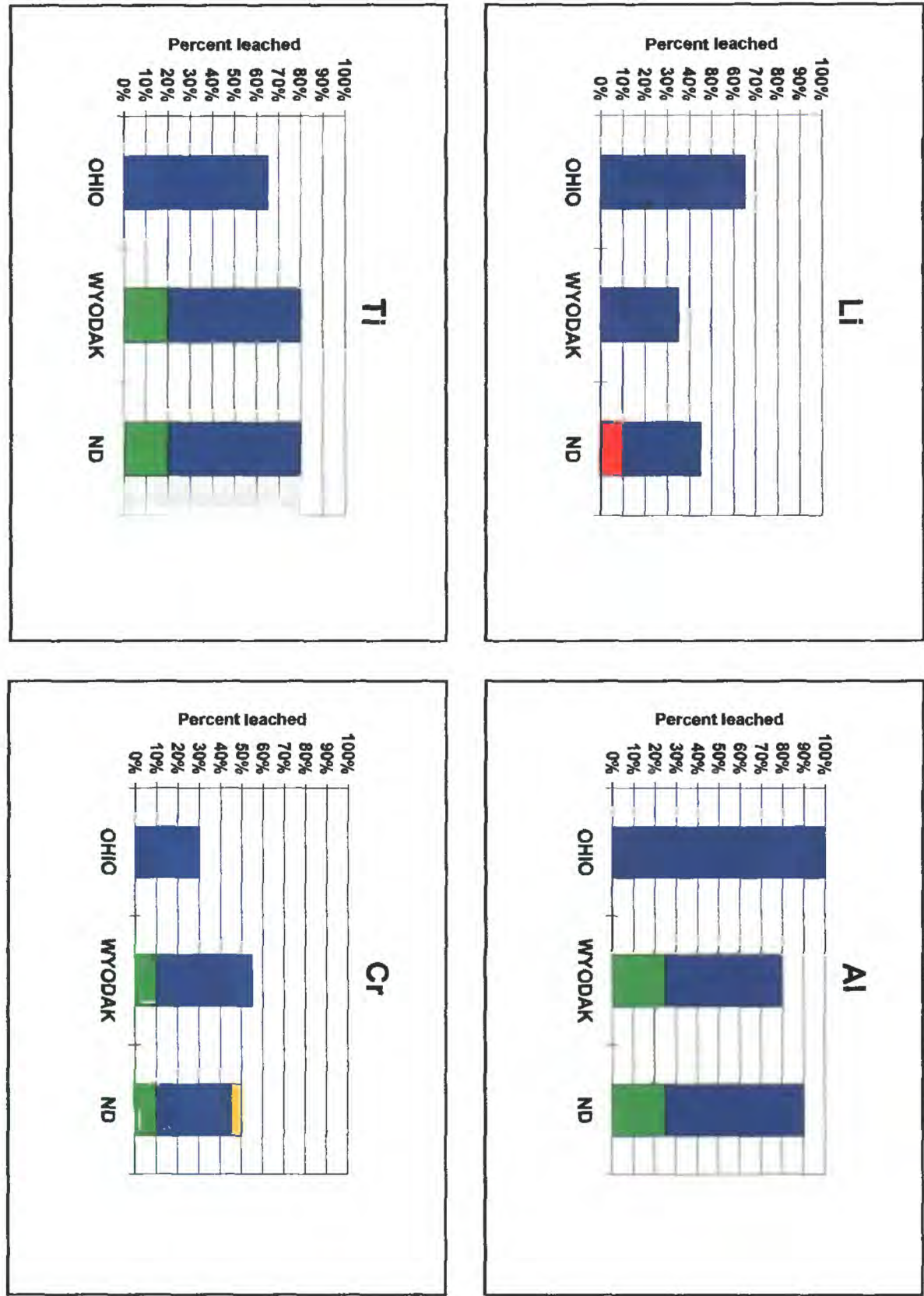


Figure 11-k. Selective leaching results for elements Na, Mg, K, showing exchangeable component.

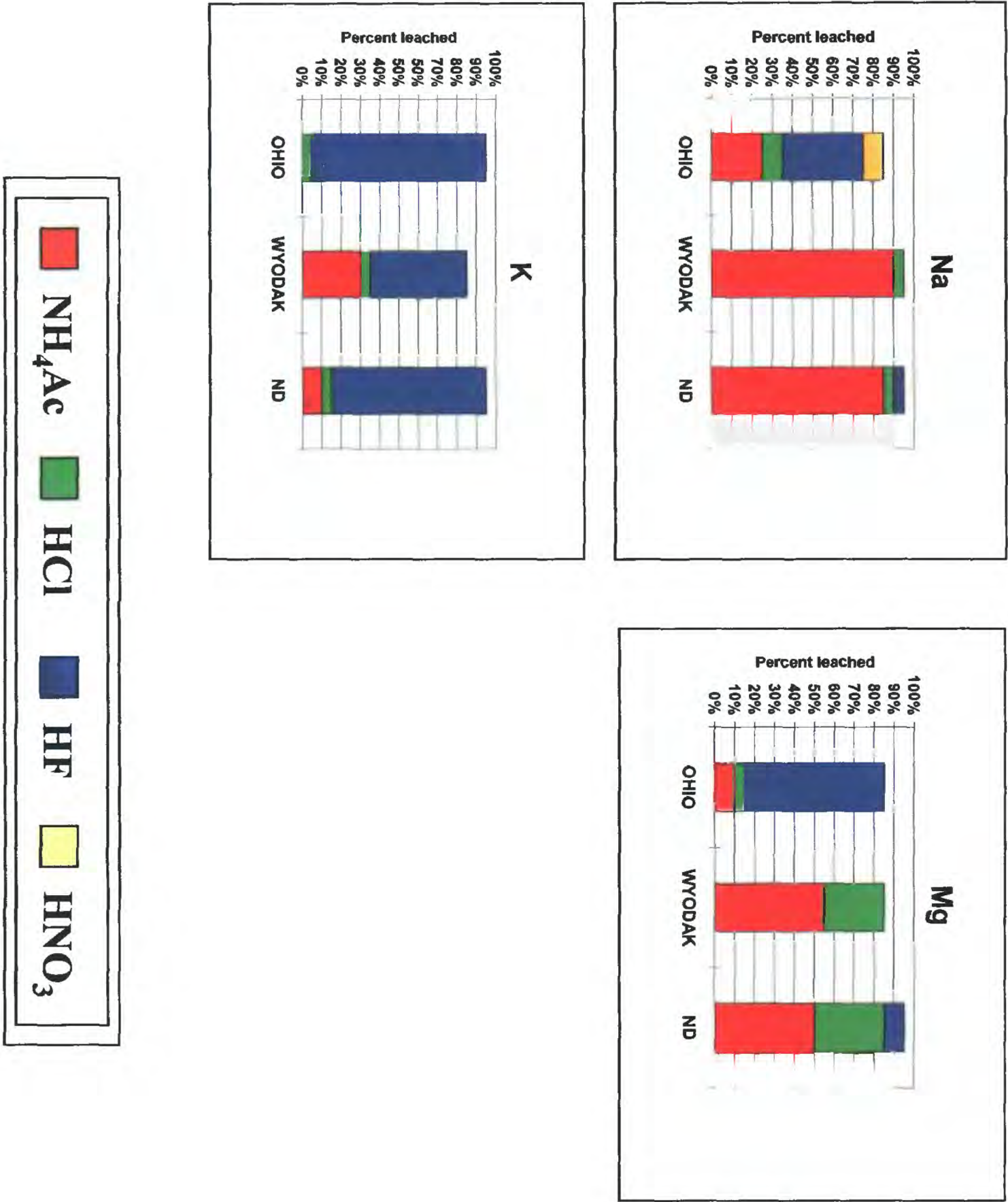


Figure 11-n. Selective leaching results for elements Co, Ni, Se, and Sb, showing a mixed association

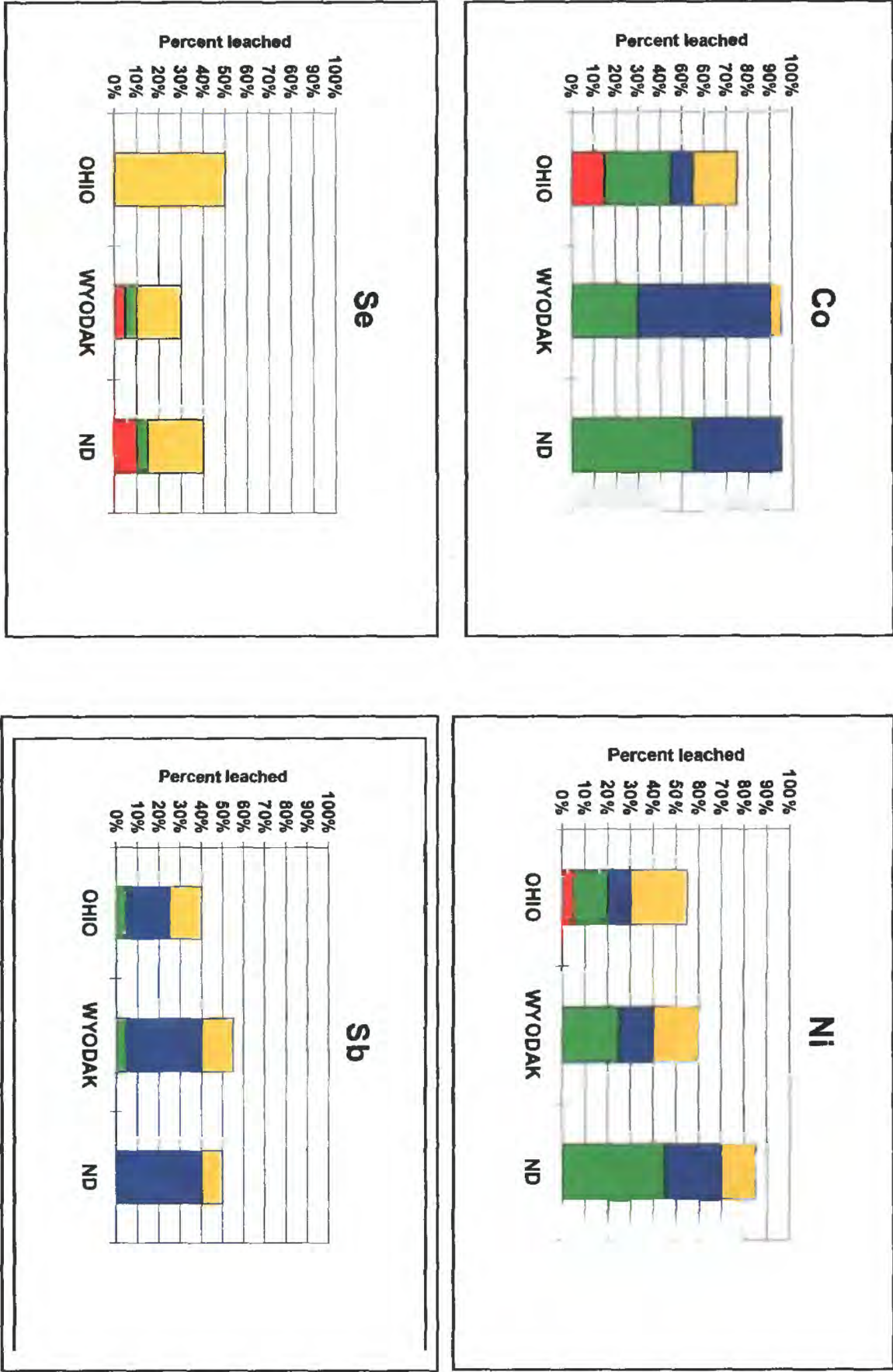


Figure Fig 1p-s. Selective leaching results for selected elements showing a carbonate (Ca, Mn) or monosulfide (Zn, Pb) association.

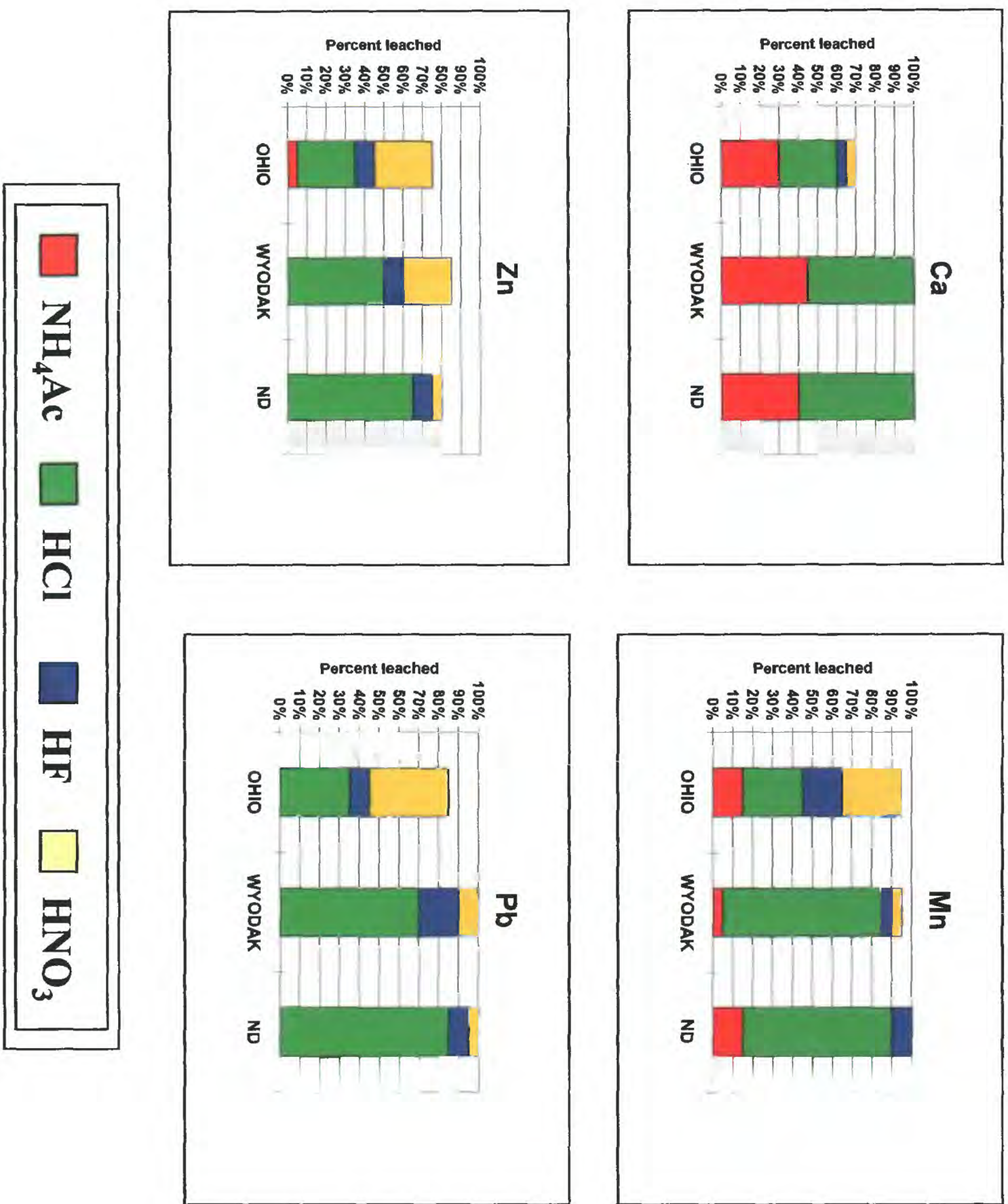


Figure 1t-u. Selective leaching results for radionuclides Th and U

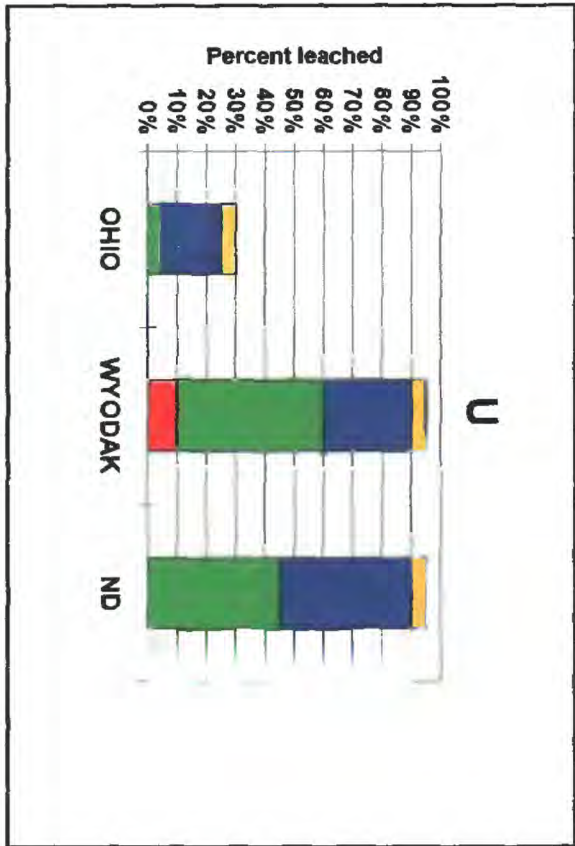
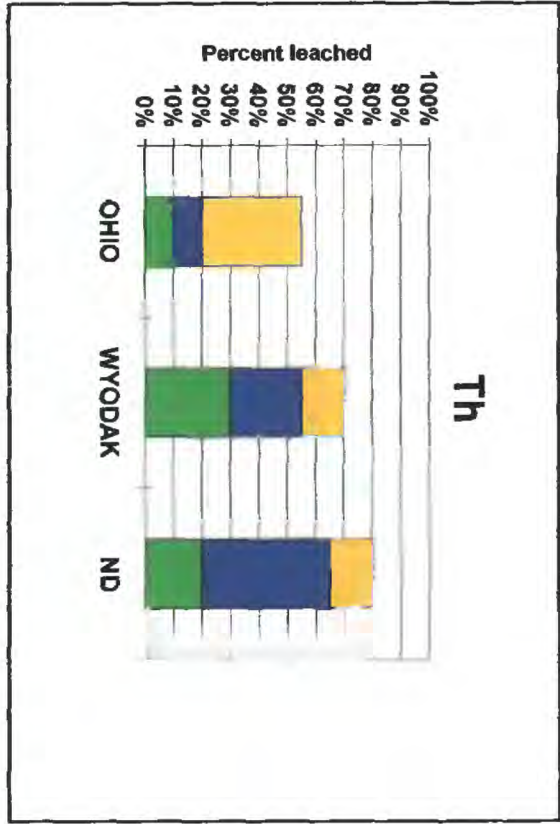


Figure 1v-y. Selective leaching results for elements Be, P, Sc, V, not shown in Fig 1a to Fig. 1u (by atomic number).

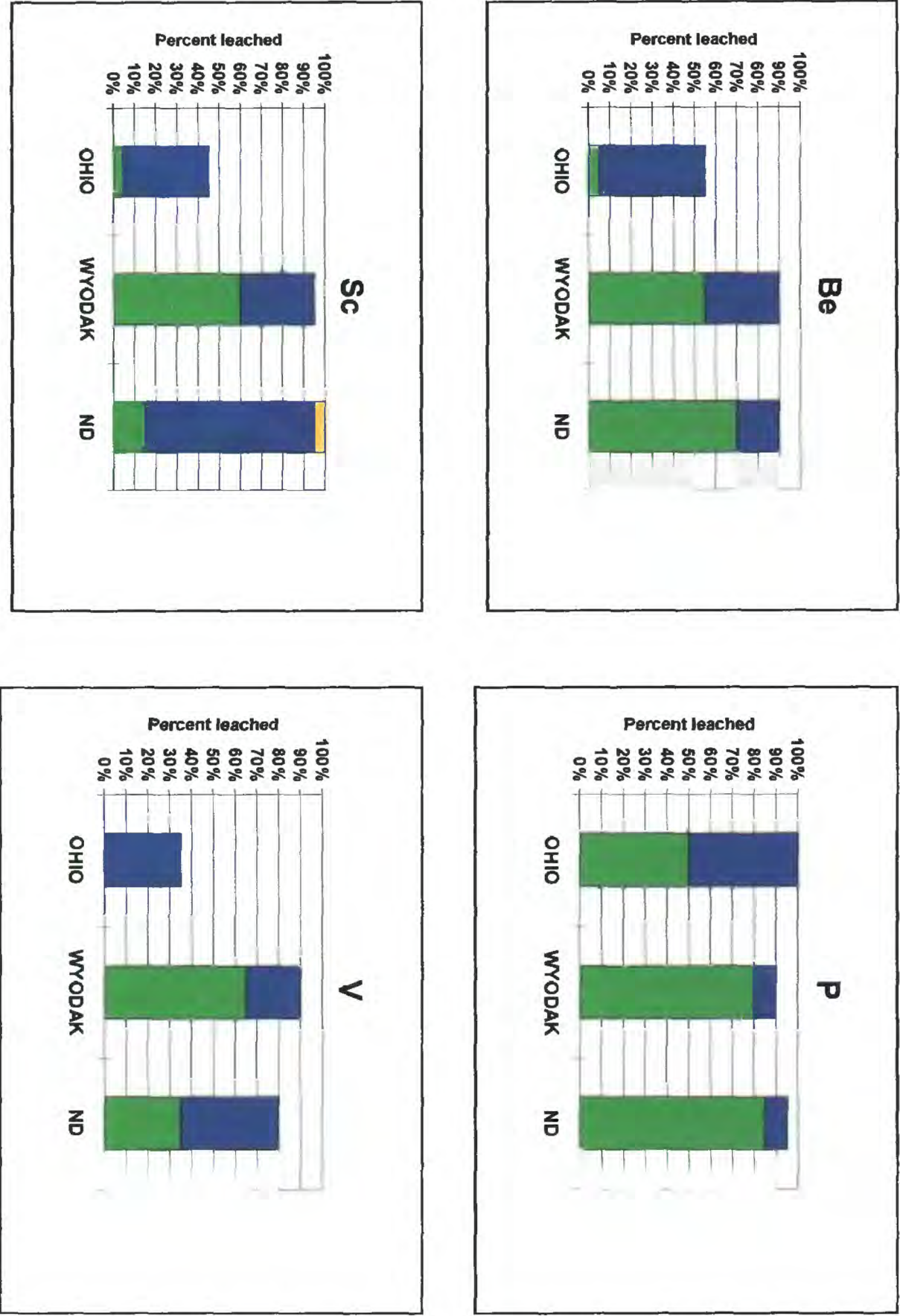


Figure 1z to 1cc. Selective leaching results for Rb, Sr, Y, Zr.

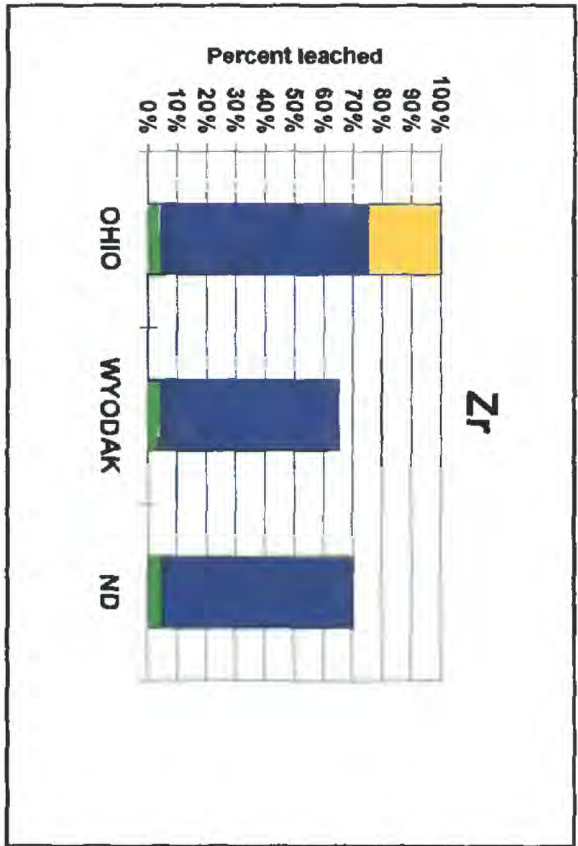
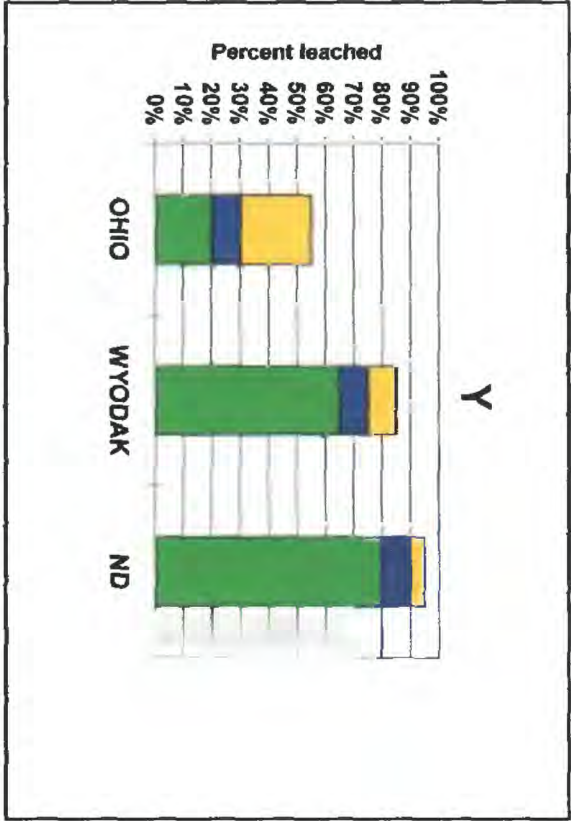
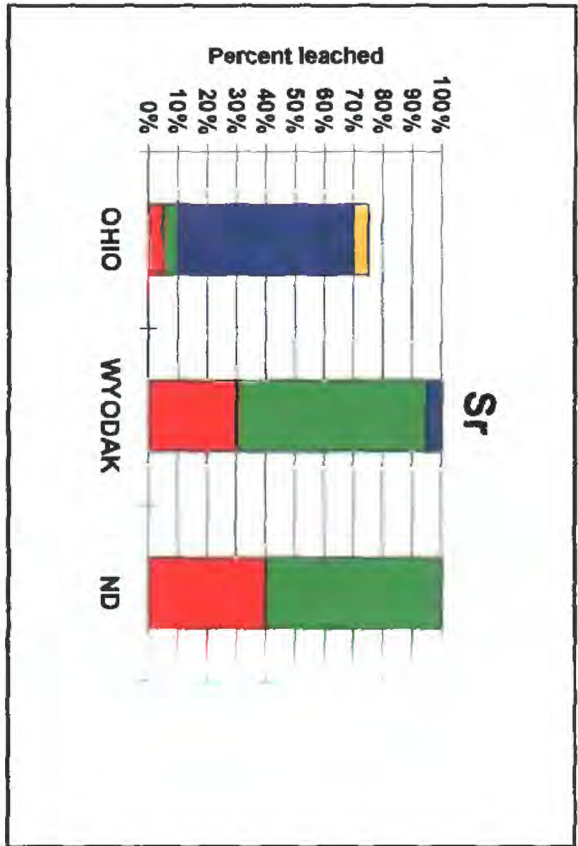
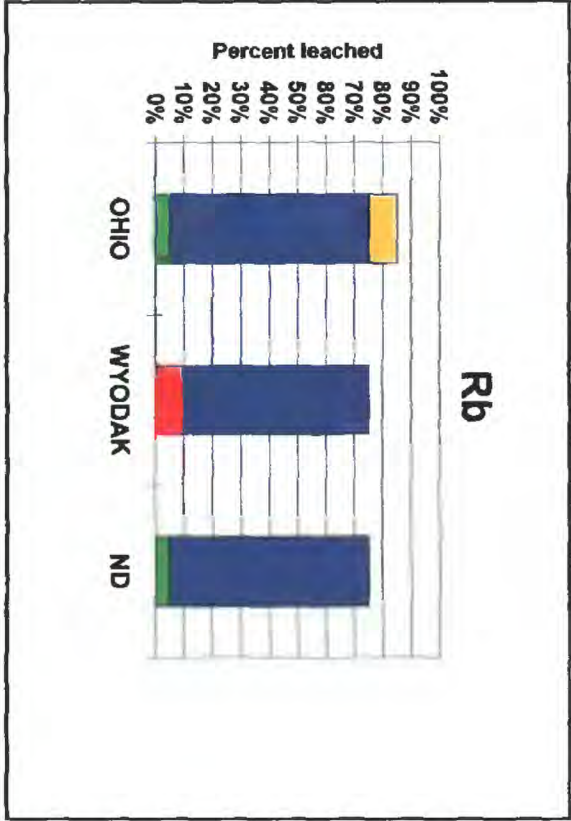


Figure 1dd-1gg . Selective leaching results for Mo, Cd, Sn, Cs.

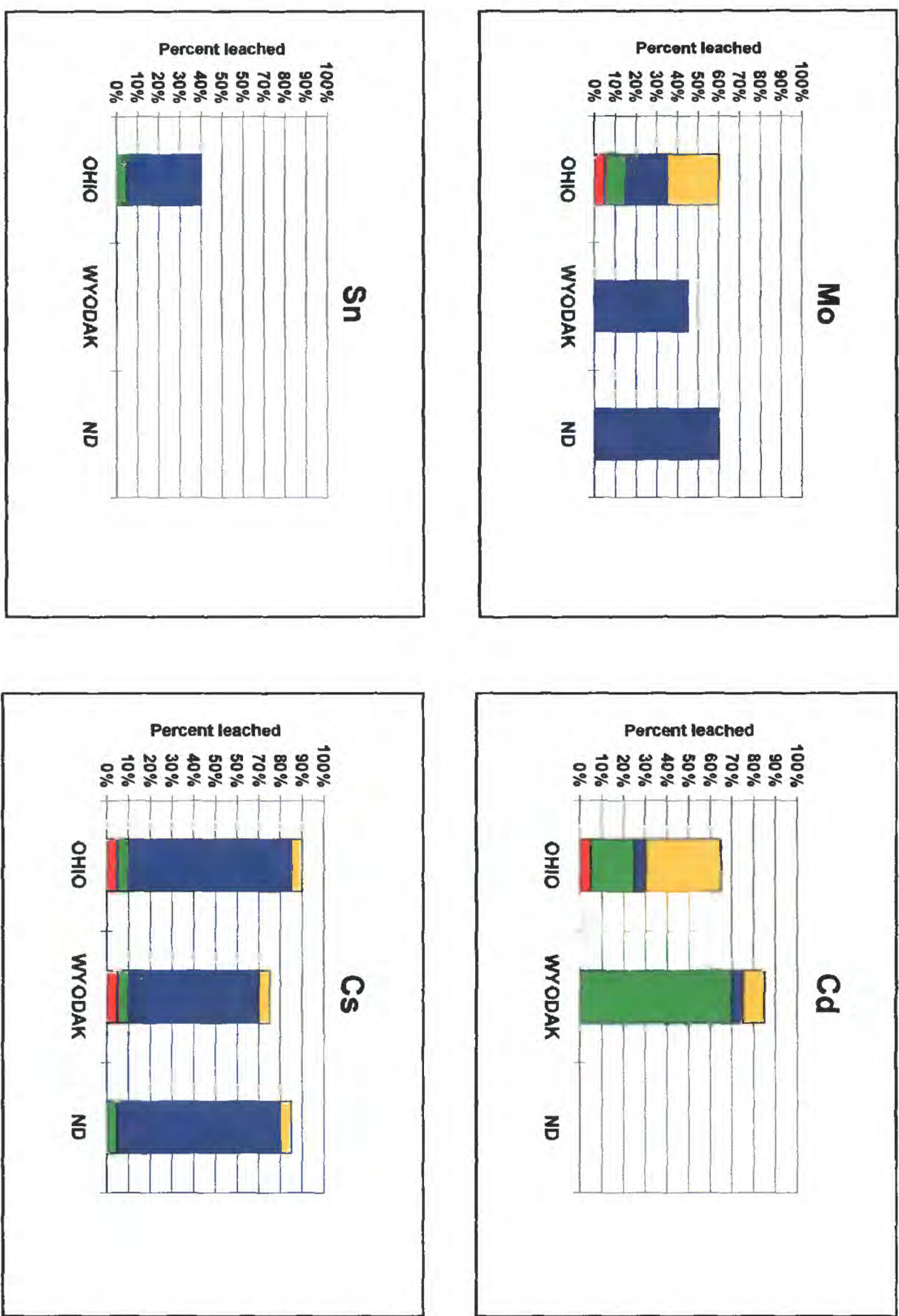


Figure 1hh – 1kk. Selective leaching results for Ba, La, Ce, Sm.

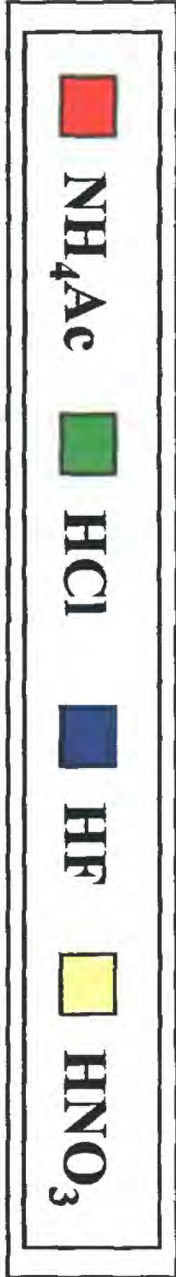
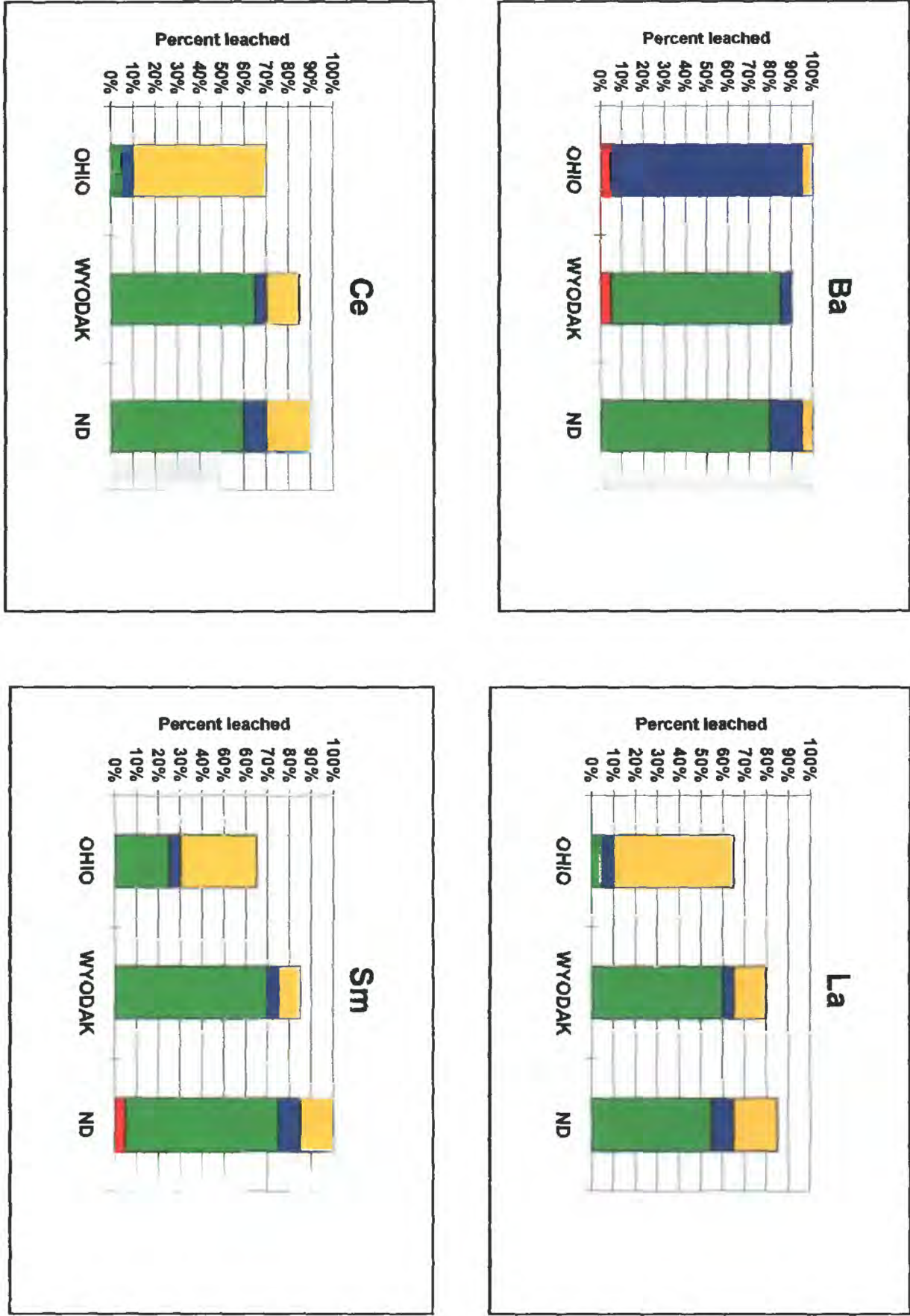


Figure 111 – 100. Selective leaching results for Eu, Tb, Yb, Lu.

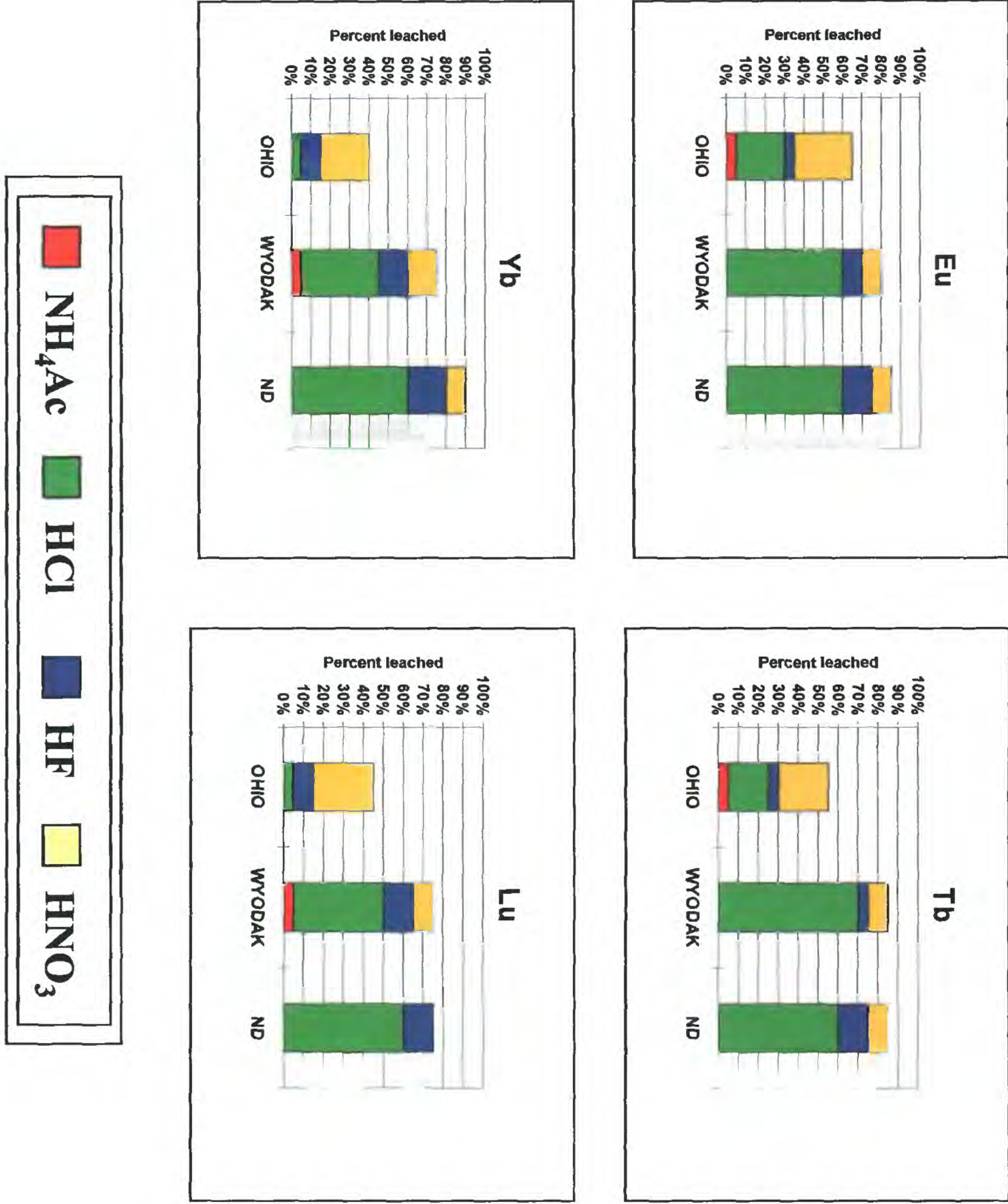


Figure 1 pp – 1ss. Selective leaching results for Hf, Ta, W, W, TI.

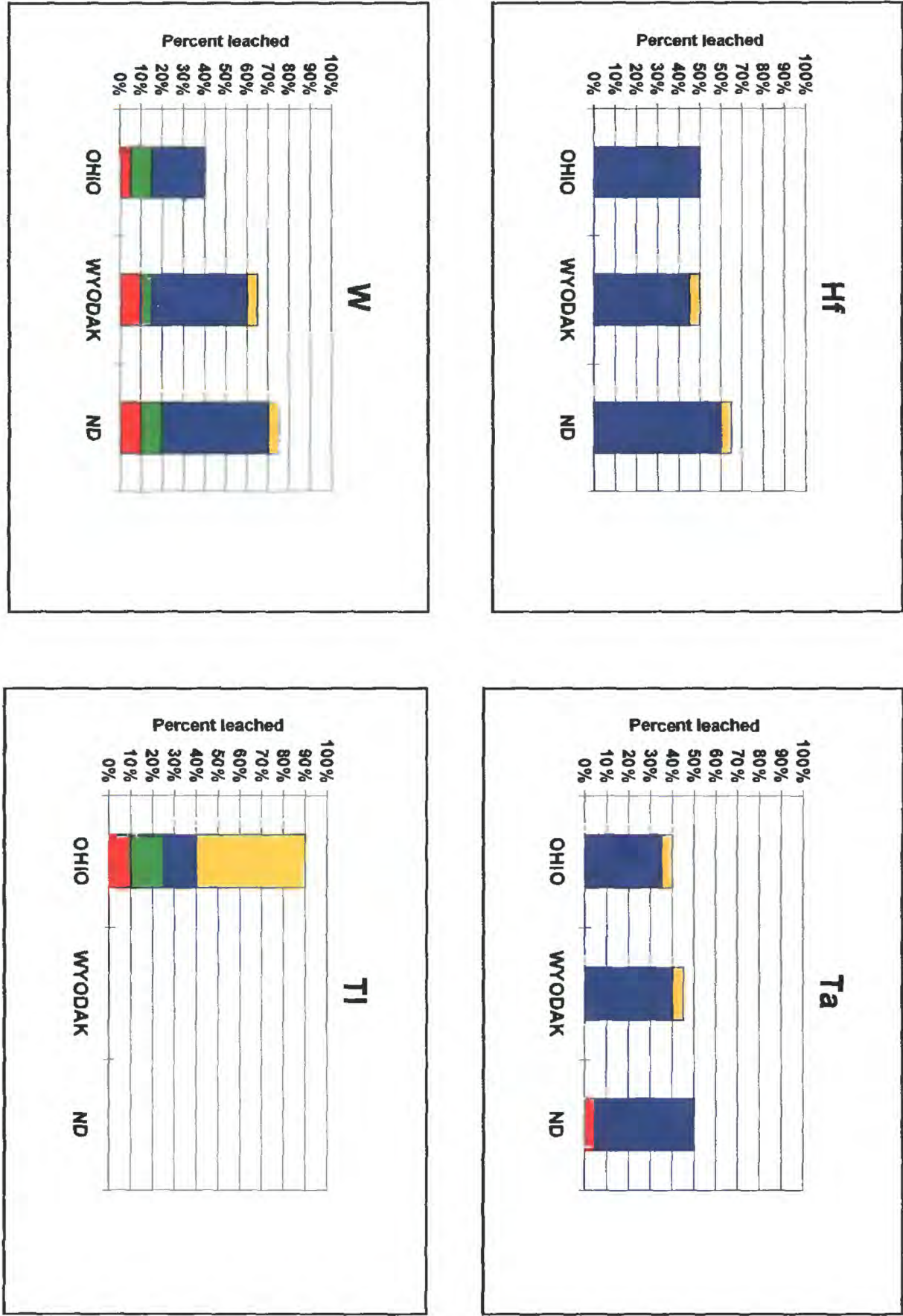


Figure 2. Selective leaching results for rare earth elements (REE) showing chondrite-normalized pattern for whole coal samples Fig. 2a) and rank dependence of HCl fraction (blue curve in Fig 2b-d). REE fraction leached by HCl is greatest in Wyodak and North Dakota samples (Fig 2c-d).

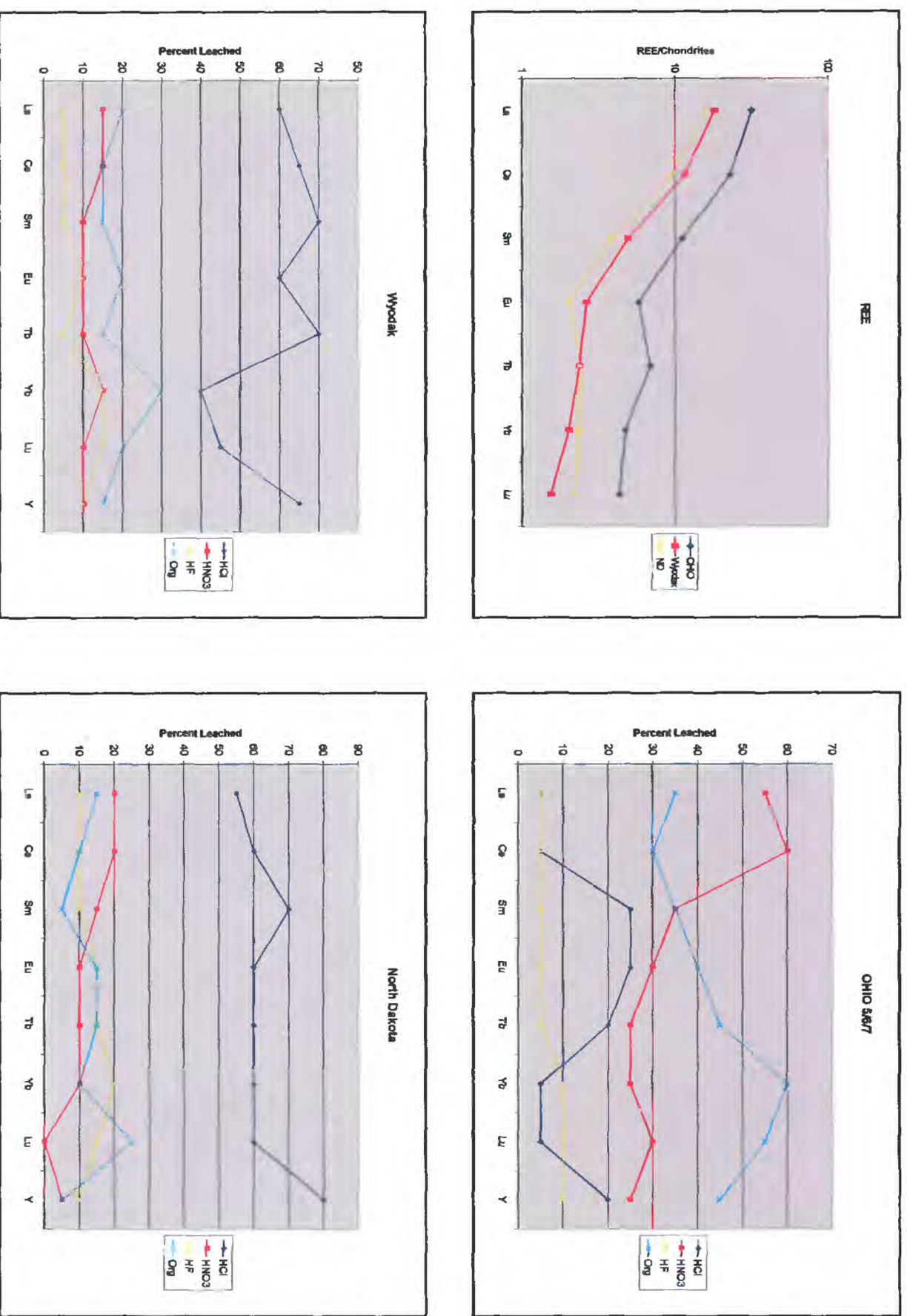


Figure 3 a-d. Percent of iron leached by HCl during heating and wet-dry cycling experiments.

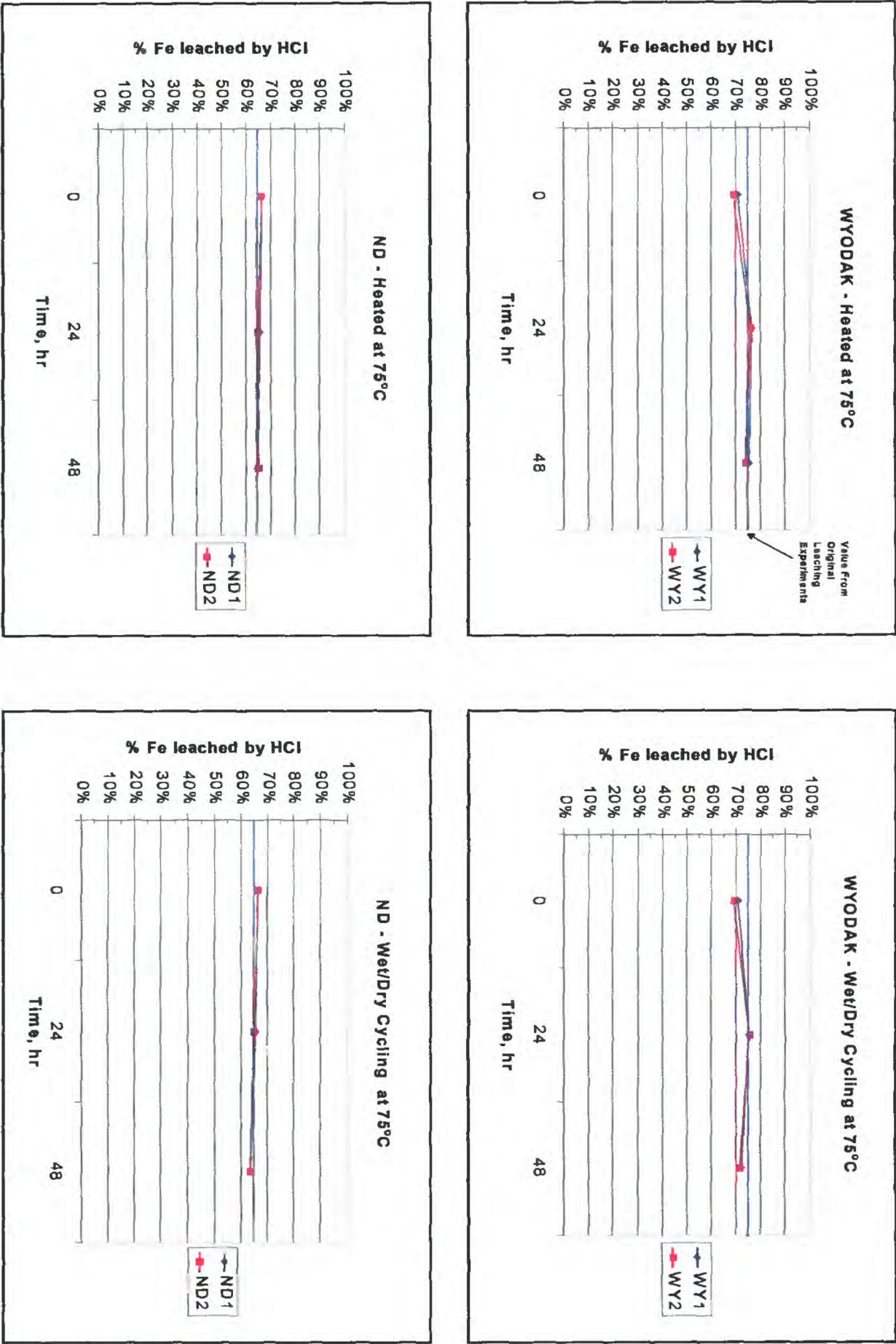


Figure 4 a-d. Selected element associations in pyrite from the Ohio 5/6/7, North Dakota, and Wyodak samples, determined by electron microprobe.

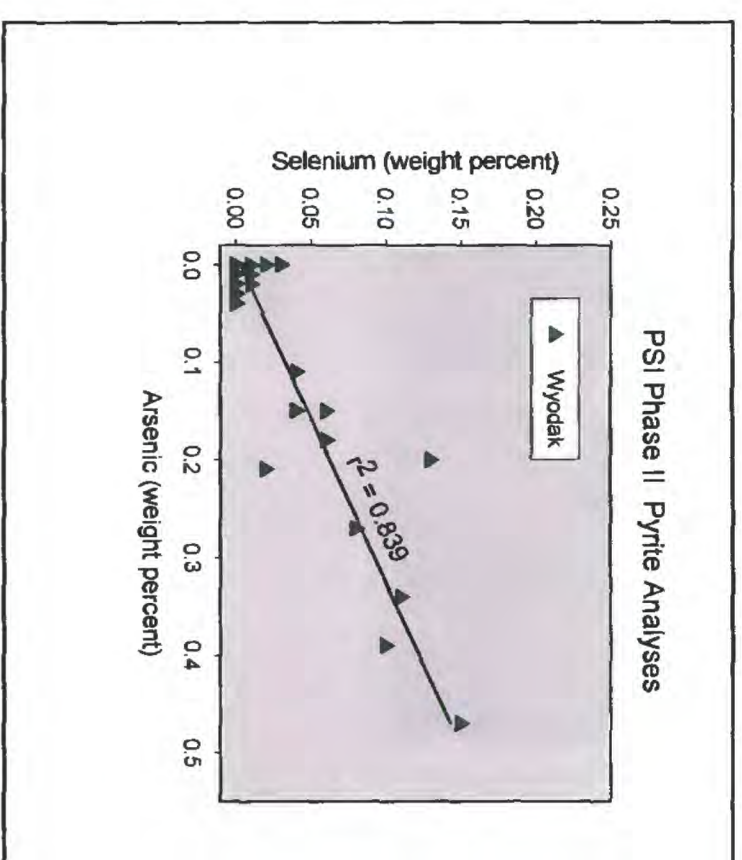
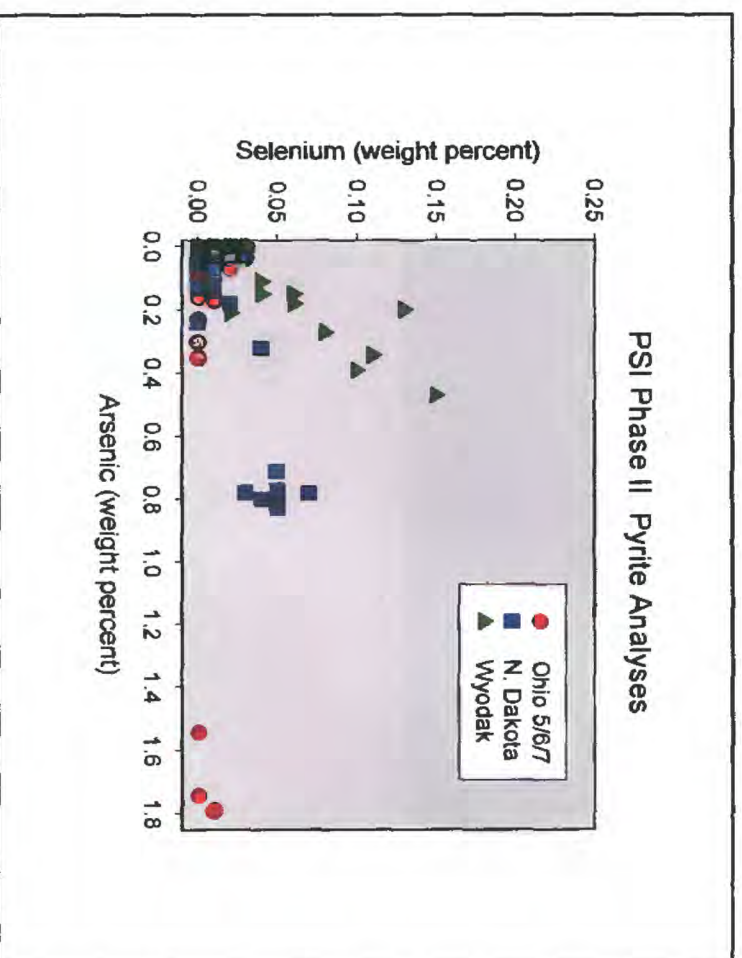
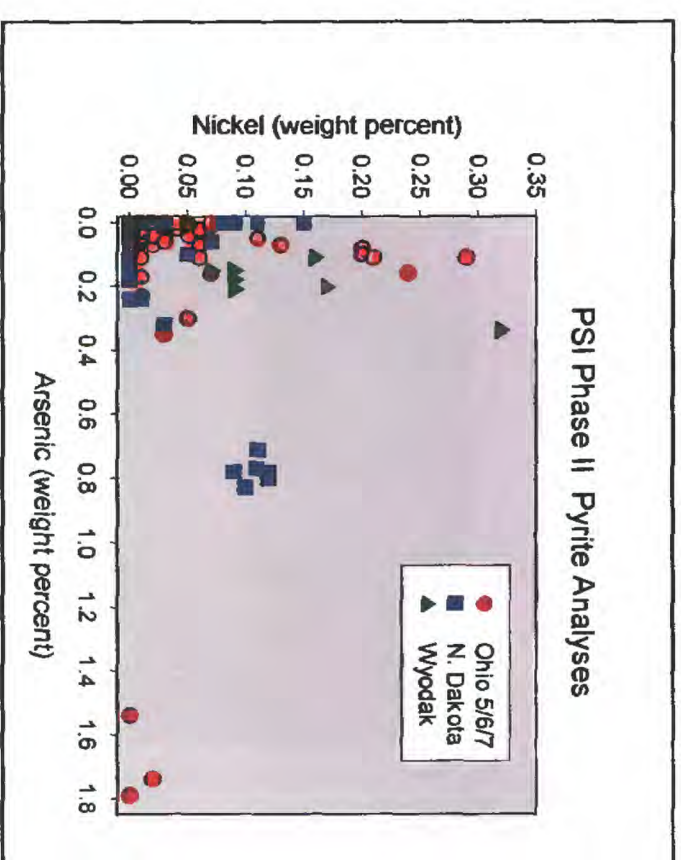
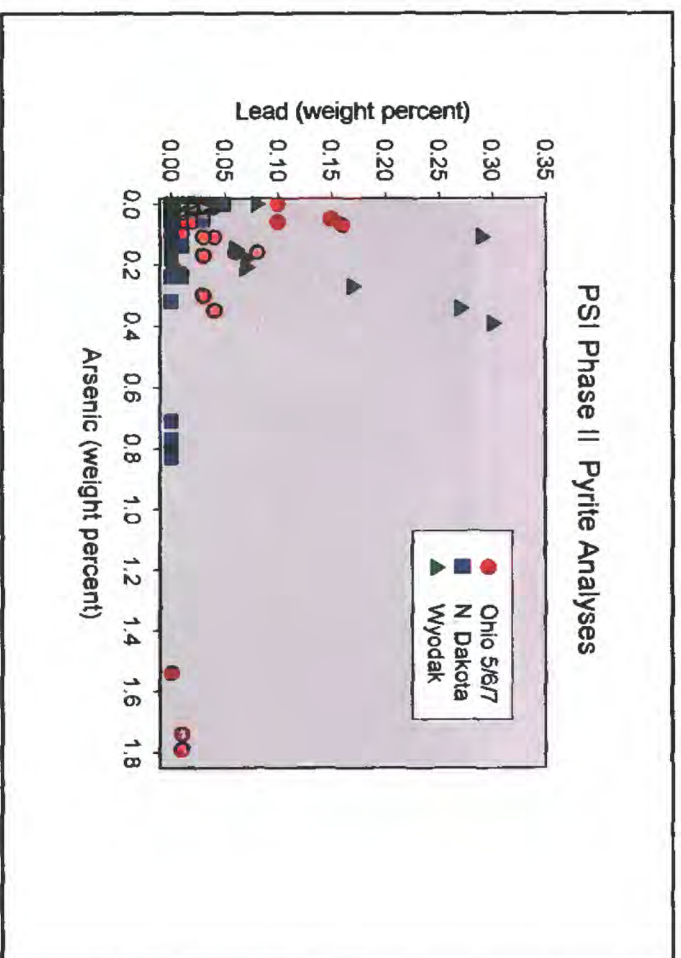
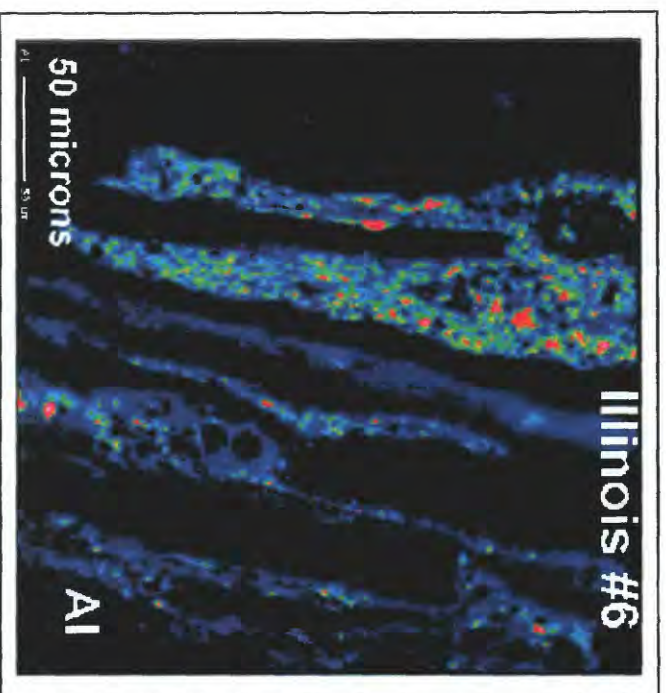
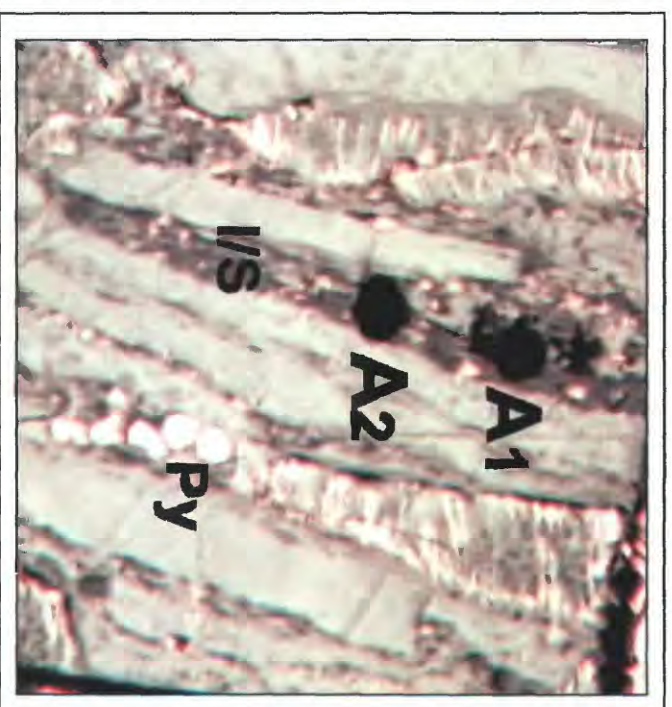


Figure 5 a. Electron microprobe aluminum map of a portion of the Phase I Illinois #6 coal sample. Map shows distribution of Al-rich clay minerals, used to locate targets for SHRIMP-RG analysis of illite/smectite. Figure 5 b. Reflected-light image of the same area showing distribution of illite/smectite and SHRIMP-RG analysis points.



(a)



(b)

Key:

A1, A2 = analysis points

I/S = illite/smectite

Py = pyrite

Figure 6 a-d. Transition metal contents in illite/smectite in Phase II samples and Phase I Illinois #6 and Pittsburgh samples, determined by SHRIMP-RG ion microprobe.

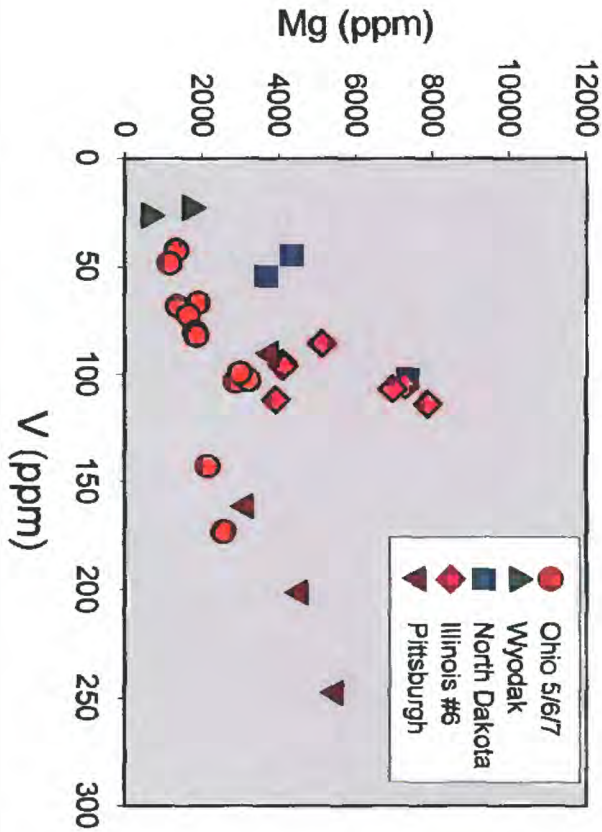
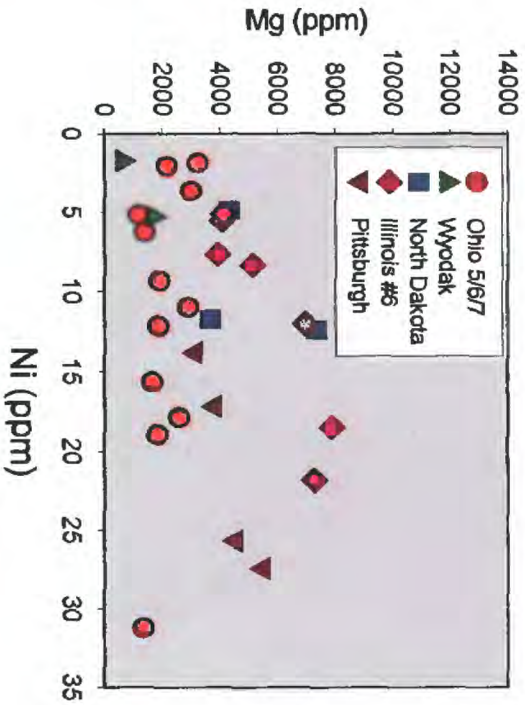
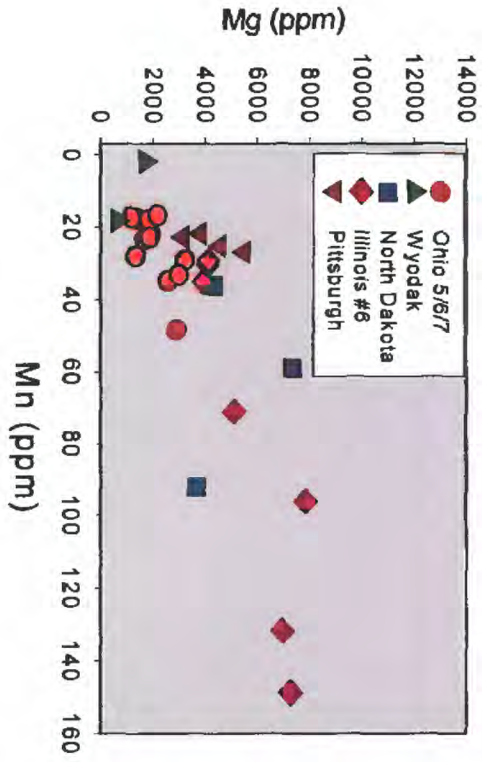
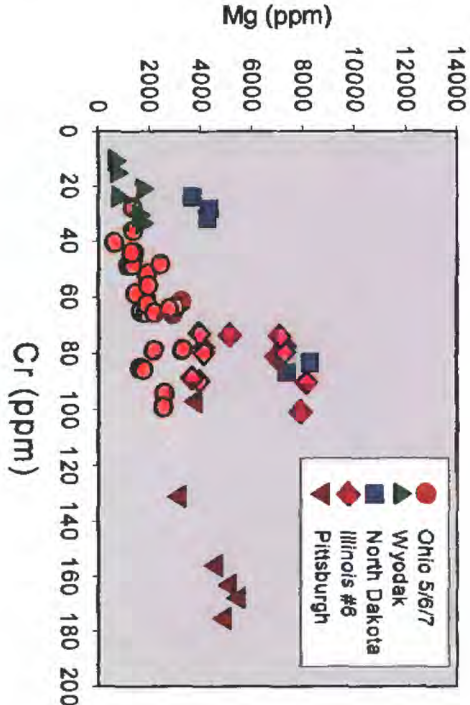


Figure 6 (continued) e-g. Additional element associations and results for illite/smectite (Fig 6e,f) and reference standards (Fig. 6g), determined by SHRIMP-RG ion microprobe.

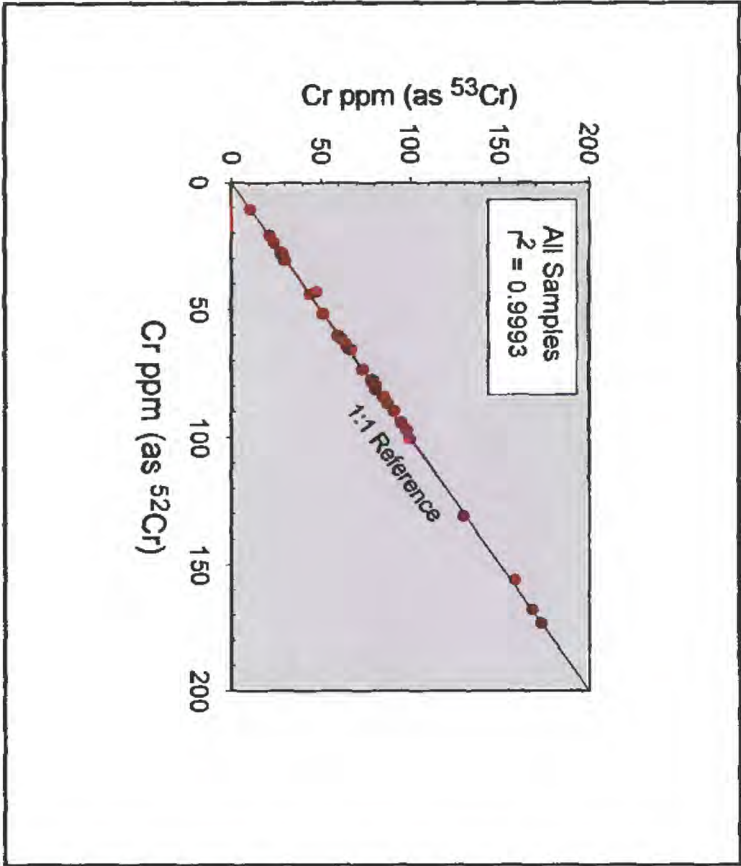
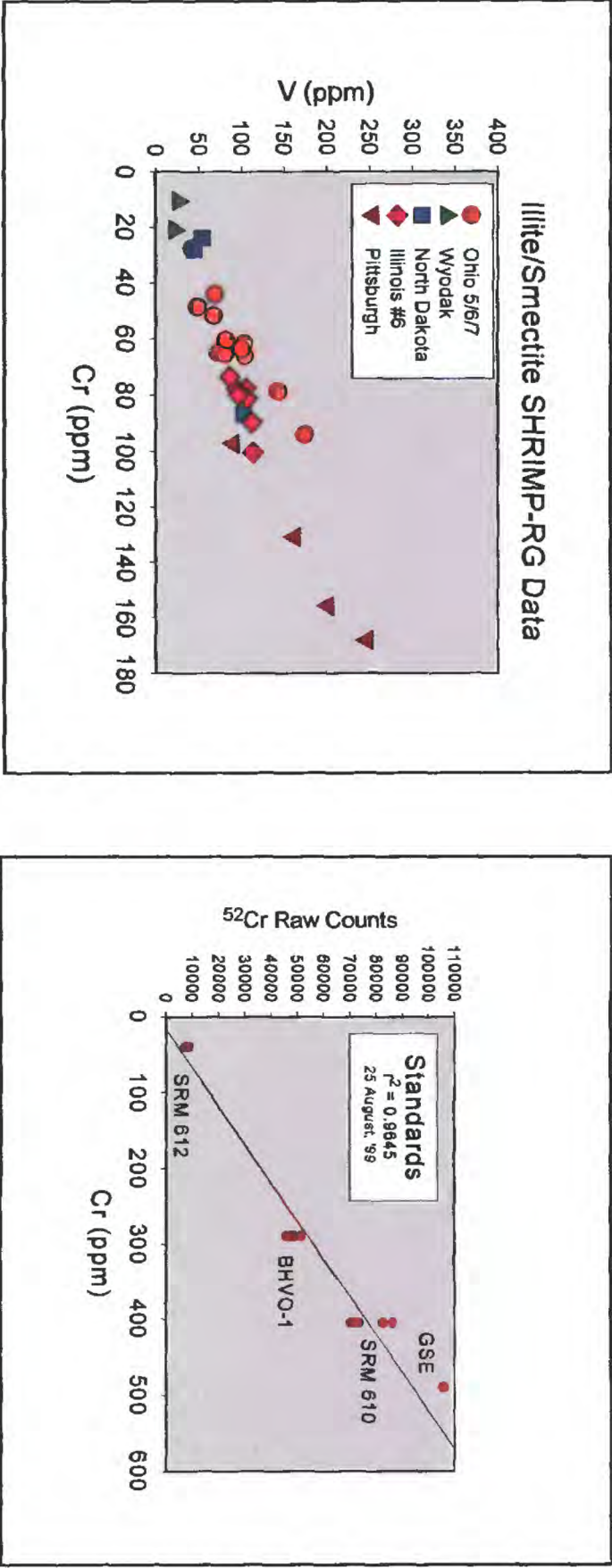


Figure 7 a-d. Relative abundances of selected isotopes in pyrite in Phase II samples and Phase I Illinois #6 and Pittsburgh samples, determined by SHRIMP-RG ion microprobe. Results are normalized to ^{32}S .

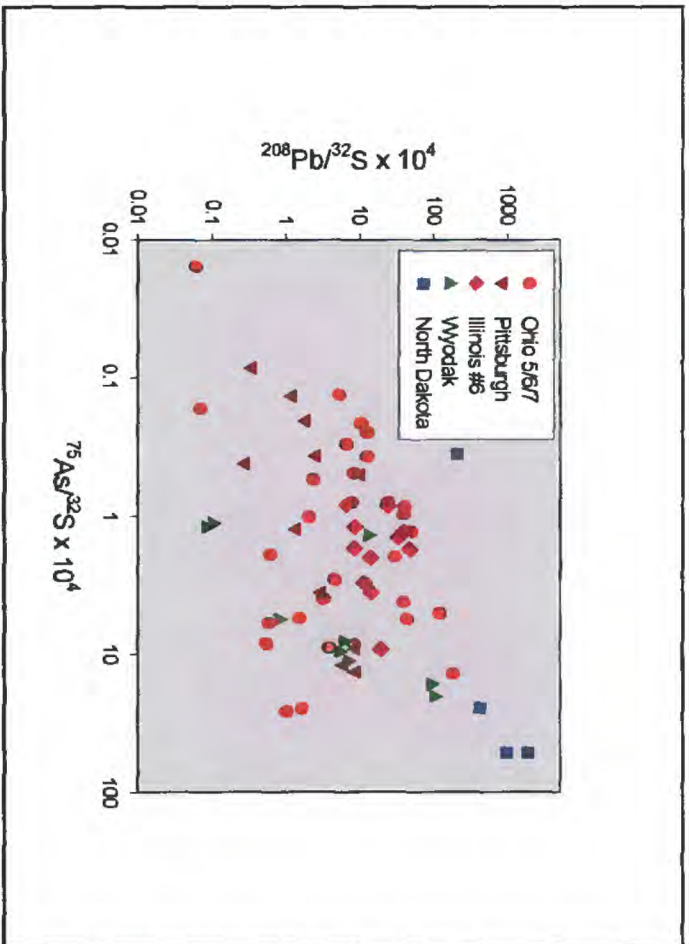
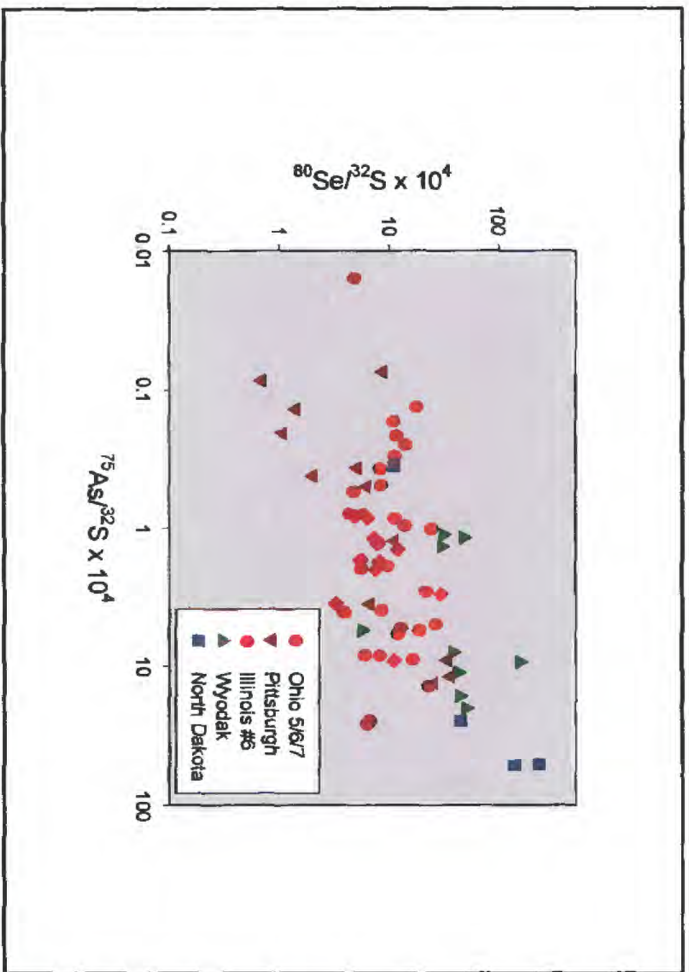
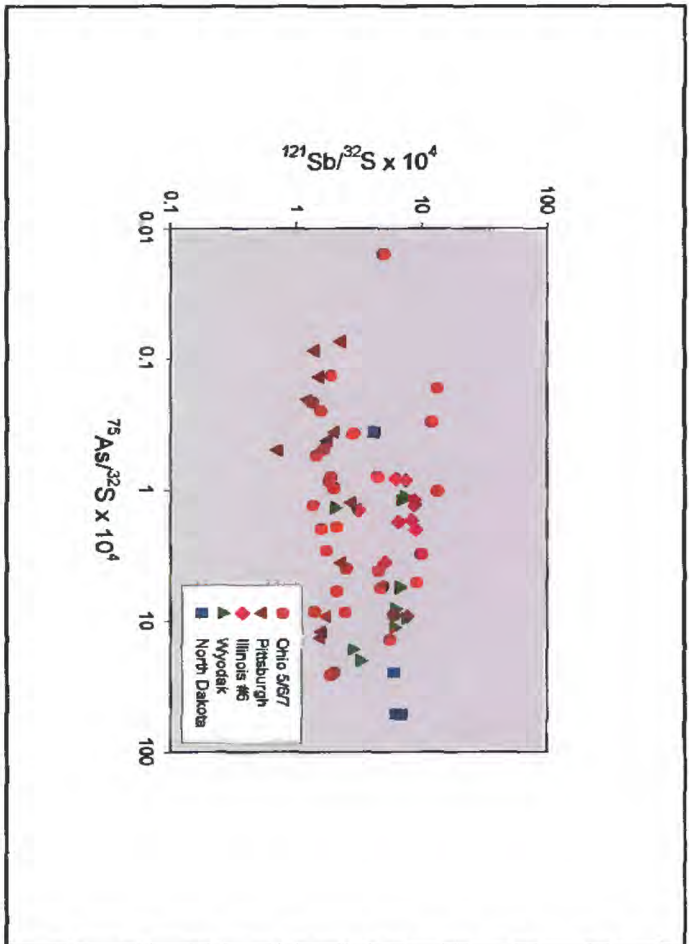
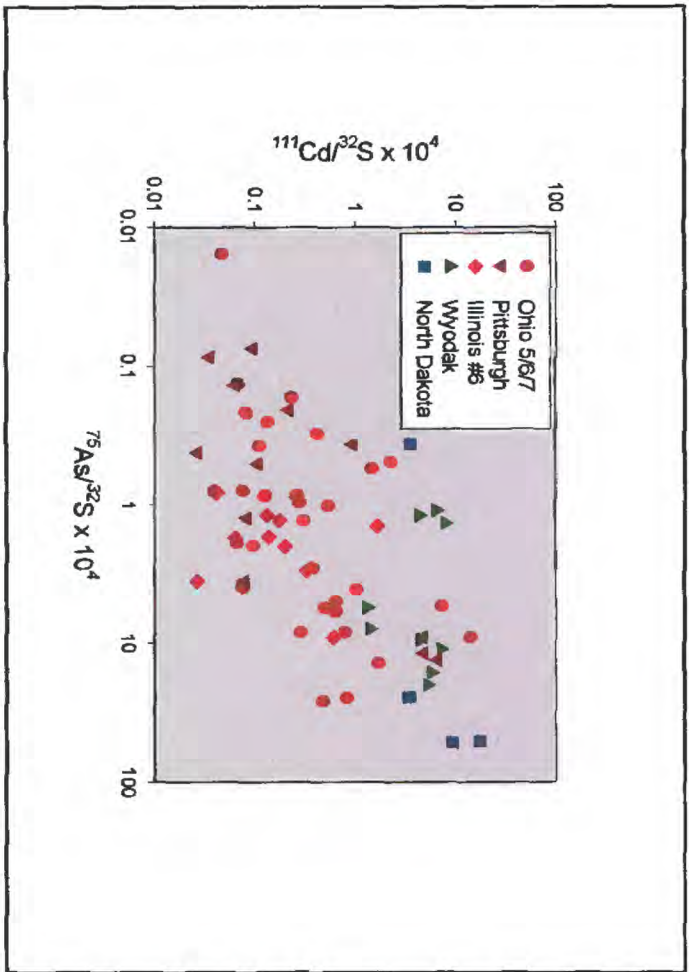
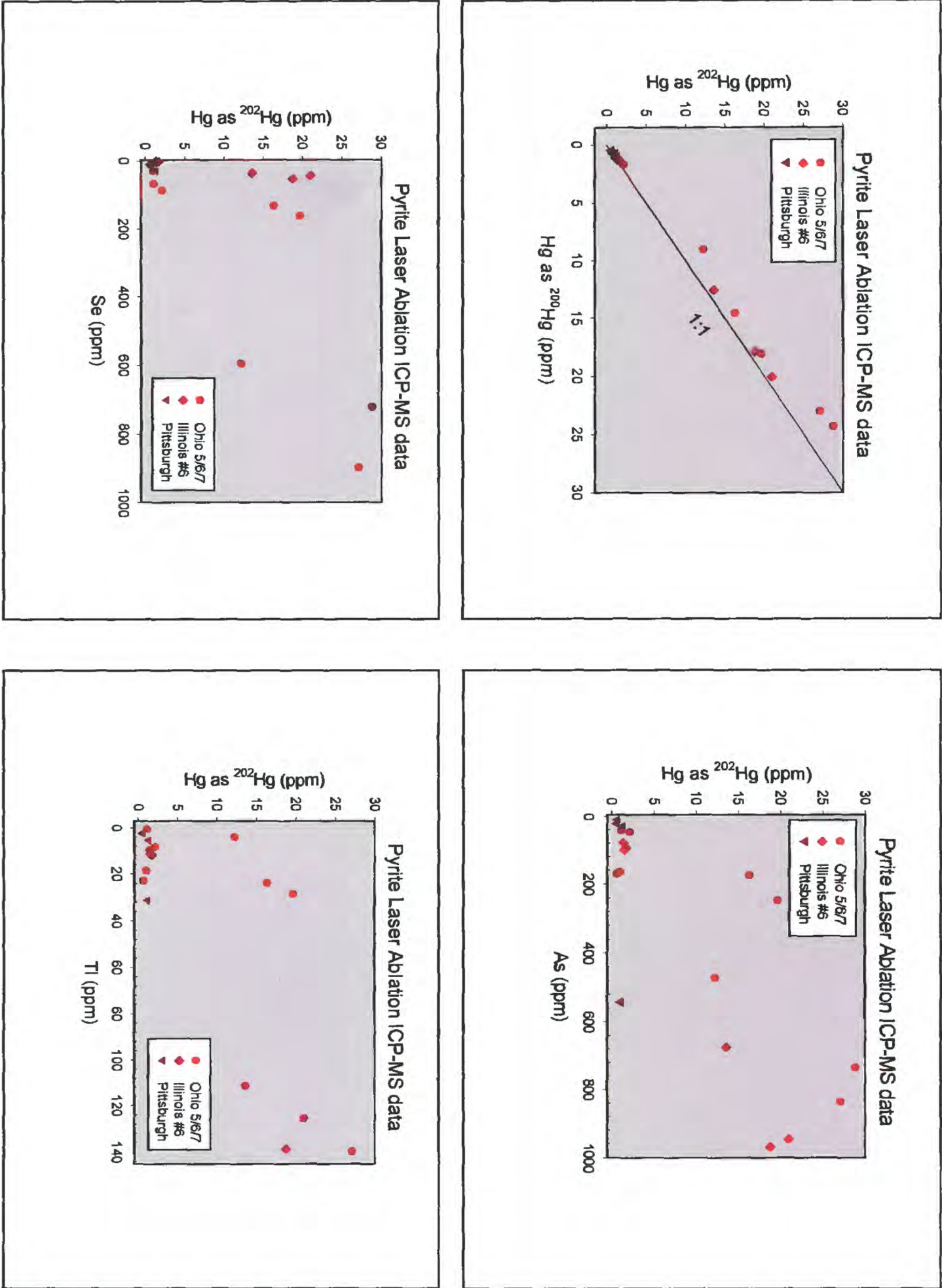


Figure 8 a-d. Mercury associations for pyrite in Phase II Ohio 5/6/7 sample and Phase I Illinois #6 and Pittsburgh samples, determined by laser ablation ICP-MS analysis.



Appendix 1. Coal Test Results

COAL ANALYSIS REPORT—Ohio 5/6/7

Analyzed on: 06/17/98

Air Dry Loss.....0.00 %

Residual Moisture.....2.33 %

	As Received	Dry	Dry Ash-Free
PROXIMATE ANALYSIS D3172			
Moisture.....	2.33		
Ash.....	9.70	9.93	
Volatile Matter.....	39.19	40.12	44.55
Fixed Carbon.....	48.78	49.95	55.45
	-----	-----	-----
	100.00	100.00	100.00

ULTIMATE ANALYSIS D3176			
Hydrogen.....	5.07	4.92	5.47
Carbon.....	71.07	72.77	80.79
Nitrogen.....	1.37	1.40	1.56
Sulfur.....	2.62	2.68	2.98
Oxygen.....	10.17	8.30	9.20
Ash.....	9.70	9.93	
	-----	-----	-----
	100.00	100.00	100.00

Heating Value (btu/Lb) D1989	12865	13172	14624
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FORMS OF SULFUR D2492			
Sulfate Sulfur.....	0.02	0.02	0.02
Pyritic Sulfur.....	1.39	1.42	1.58
Organic Sulfur.....	1.21	1.24	1.38

Free Swelling Index D720	4.0
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Ash Fusion (Reducing Atmosphere)				
	Initial D.	Softening T.	Hemi T.	Fluid T.
Temp F	2130	2240	2390	2490

COAL ANALYSIS REPORT---North Dakota

Analyzed on: 06/17/98

Air Dry Loss.....25.22 %

Residual Moisture.....14.25 %

	As Received	Dry	Dry Ash-Free
PROXIMATE ANALYSIS D3172			
Moisture.....	35.88		
Ash.....	9.38	14.64	
Volatile Matter.....	28.15	43.90	51.42
Fixed Carbon.....	26.59	41.46	48.58
	-----	-----	-----
	100.00	100.00	100.00

ULTIMATE ANALYSIS D3176			
Hydrogen.....	6.59	4.02	4.71
Carbon.....	38.57	60.15	70.46
Nitrogen.....	0.42	0.65	0.77
Sulfur.....	0.63	0.98	1.15
Oxygen.....	44.41	19.56	22.91
Ash.....	9.38	14.64	
	-----	-----	-----
	100.00	100.00	100.00

Heating Value (btu/Lb) D1989	6392	9969	11678
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FORMS OF SULFUR D2492			
Sulfate Sulfur.....	0.09	0.14	0.16
Pyritic Sulfur.....	0.18	0.28	0.33
Organic Sulfur.....	0.36	0.56	0.66

Free Swelling Index D720	0.0
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Ash Fusion (Reducing Atmosphere)				
	Initial D.	Softening T.	Hemi T.	Fluid T.
Temp F	2050	2070	2090	2110

COAL ANALYSIS REPORT---Wyodak

Analyzed on: 10/06/98

	As Received	Dry	Dry Ash-Free
PROXIMATE ANALYSIS D3172			
Moisture.....	25.81		
Ash.....	6.03	8.13	
Volatile Matter.....	34.85	46.97	51.13
Fixed Carbon.....	33.31	44.90	48.87
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

ULTIMATE ANALYSIS D3176			
Hydrogen.....	6.51	4.88	5.31
Carbon.....	51.19	69.00	80.10
Nitrogen.....	0.72	0.97	1.06
Sulfur.....	0.32	0.43	0.47
Oxygen.....	35.23	16.59	18.06
Ash.....	6.03	8.13	
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

Heating Value (btu/Lb) D1989	8869	11955	13013
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FORMS OF SULFUR D2492			
Sulfate Sulfur.....	0.01	0.01	0.01
Pyritic Sulfur.....	0.04	0.05	0.06
Organic Sulfur.....	0.27	1.37	0.40

Free Swelling Index D720	0.0
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Ash Fusion (Reducing Atmosphere)				
	Initial D.	Softening T.	Hemi T.	Fluid T.
Temp F	2100	2120	2140	2230

Appendix 2. Electron Microprobe Data

Electron Microprobe Results for Pyrite in the Ohio 5/6/7 coal sample.

No.	Pb	Se	Cu	Cd	As	Ni	Zn	Co*	Fe	S	Total	Comment	Size/Form
10	0.02	0.01	0.00	0.02	0.00	0.00	0.00	0.05	47.34	53.04	100.48	OhioB1.1	30
11	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.05	42.22	52.38	94.65	OhioB1.2	subhedral
13	0.00	0.00	0.05	0.03	0.07	0.13	0.00	0.06	44.40	50.13	94.86	OhioB3.1	10x25
14	0.06	0.01	0.03	0.01	0.16	0.24	0.00	0.06	44.05	50.01	94.63	OhioB3.2	subhedral
15	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.05	46.99	52.94	100.01	OhioB4.1	80x80
16	0.00	0.00	0.00	0.00	0.07	0.02	0.00	0.06	47.08	51.81	99.04	OhioB4.2	subhedral
18	0.00	0.00	0.00	0.01	0.11	0.01	0.00	0.05	47.19	51.83	99.19	OhioB4.4	
19	0.00	0.00	0.00	0.01	0.04	0.01	0.00	0.06	47.35	51.88	99.35	OhioB4.5	
20	0.01	0.01	0.00	0.03	0.00	0.00	0.00	0.05	46.81	52.75	99.66	OhioB5.1	90x90
21	0.00	0.01	0.00	0.02	0.00	0.00	0.01	0.04	46.67	53.32	100.07	OhioB5.2	round
22	0.02	0.02	0.02	0.02	0.00	0.00	0.00	0.07	46.08	53.06	99.29	OhioB5.3	
23	0.10	0.02	0.02	0.04	0.00	0.00	0.00	0.04	45.82	51.73	97.76	OhioB5.4	
24	0.03	0.01	0.00	0.01	0.01	0.00	0.00	0.05	46.51	51.18	97.80	OhioB6.1	35x120
25	0.00	0.02	0.00	0.04	0.01	0.00	0.00	0.05	46.75	51.17	98.03	OhioB6.2	subhedral
26	0.00	0.01	0.01	0.01	0.02	0.01	0.00	0.05	46.49	52.00	98.60	OhioB6.3	
27	0.04	0.00	0.03	0.04	0.35	0.03	0.00	0.05	45.54	50.62	96.70	OhioB7.1	60x60
28	0.04	0.00	0.01	0.04	0.01	0.03	0.01	0.04	46.22	50.24	96.65	OhioB7.2	round
29	0.03	0.00	0.01	0.01	0.30	0.05	0.00	0.06	45.82	49.33	95.60	OhioB7.3	
30	0.02	0.00	0.01	0.00	0.04	0.05	0.00	0.06	46.30	50.30	96.78	OhioB7.4	
39	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.05	47.54	51.80	99.43	OhioB10.1	120x170
40	0.00	0.01	0.04	0.01	0.04	0.06	0.00	0.06	47.07	51.90	99.17	OhioB10.2	subhedral
41	0.00	0.00	0.04	0.03	0.02	0.04	0.00	0.05	47.37	51.59	99.13	OhioB10.3	
42	0.03	0.00	0.00	0.00	0.01	0.00	0.00	0.06	47.39	51.41	98.90	OhioB10.4	
43	0.01	0.00	0.03	0.03	0.04	0.03	0.01	0.05	46.78	51.55	98.52	OhioB10.5	
44	0.00	0.01	0.03	0.01	0.04	0.01	0.00	0.05	45.44	49.55	95.14	OhioB11.1	70x190
45	0.00	0.02	0.03	0.03	0.03	0.00	0.00	0.05	45.22	50.02	95.39	OhioB11.2	oval
46	0.01	0.00	0.04	0.00	0.03	0.01	0.01	0.06	45.20	49.26	94.63	OhioB11.3	
47	0.00	0.02	0.03	0.03	0.04	0.00	0.00	0.05	46.13	50.41	96.70	OhioB11.4	
48	0.01	0.02	0.00	0.03	0.03	0.01	0.00	0.05	46.82	51.76	98.73	OhioB11.5	
No.	Pb	Se	Cu	Cd	As	Ni	Zn	Co*	Fe	S	Total	Comment	Size/Form

49	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.06	46.89	51.24	98.22	OhioB12.1	70x120
50	0.00	0.00	0.00	0.02	0.03	0.00	0.00	0.05	46.79	51.02	97.90	OhioB12.2	subhedral
51	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.06	46.72	50.85	97.67	OhioB12.3	
52	0.00	0.00	0.00	0.07	0.02	0.06	0.00	0.06	46.46	50.93	97.60	OhioB12.4	
53	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.04	46.15	51.12	97.32	OhioB12.5	
54	0.04	0.00	0.01	0.11	0.01	0.01	0.00	0.03	45.97	50.39	96.58	OhioB13.1	50x60
55	0.03	0.01	0.00	0.17	0.02	0.01	0.00	0.06	45.43	50.63	96.35	OhioB13.2	irregular
10	0.02	0.00	0.00	0.02	0.01	0.00	0.00	0.04	46.75	55.25	102.09	OhioA1.1	35x80
11	0.02	0.01	0.00	0.02	0.01	0.00	0.01	0.06	46.45	55.64	102.21	OhioA1.2	subhedral
12	0.01	0.01	0.00	1.79	0.02	0.00	0.00	0.06	47.20	53.43	102.51	OhioA1.3	
13	0.00	0.00	0.01	1.54	0.01	0.00	0.00	0.06	46.81	54.69	103.13	OhioA1.4	
14	0.01	0.00	0.00	1.74	0.01	0.02	0.00	0.08	46.92	53.16	101.93	OhioA1.5	
15	0.02	0.01	0.00	0.00	0.01	0.00	0.02	0.06	47.50	55.85	103.46	OhioA2.1	35x60
16	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.05	47.82	54.72	102.62	OhioA2.2	composite
17	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.05	46.86	54.59	101.53	OhioA2.3	subhedral
18	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.04	47.49	55.32	102.86	OhioA2.4	
19	0.02	0.02	0.01	0.00	0.01	0.00	0.00	0.05	46.70	54.52	101.32	OhioA2.5	
20	0.01	0.00	0.01	0.05	0.00	0.03	0.00	0.05	45.75	52.53	98.42	OhioA3.1	50x100
21	0.01	0.00	0.00	0.04	0.01	0.02	0.00	0.06	44.79	50.96	95.88	OhioA3.2	composite
22	0.02	0.00	0.00	0.04	0.00	0.05	0.01	0.06	45.40	52.64	98.24	OhioA3.3	zoned
23	0.02	0.01	0.00	0.01	0.02	0.00	0.01	0.05	43.82	50.81	94.74	OhioA3.4	subhedral
24	0.02	0.00	0.00	0.03	0.00	0.00	0.00	0.05	44.43	51.33	95.86	OhioA3.5	
25	0.04	0.01	0.00	0.00	0.01	0.01	0.00	0.06	46.87	55.71	102.71	OhioA3.6	
26	0.03	0.00	0.01	0.00	0.01	0.00	0.00	0.04	46.79	53.26	100.13	OhioA4.1	45
27	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.06	47.92	54.57	102.56	OhioA4.2	framboid?
28	0.01	0.02	0.01	0.00	0.00	0.01	0.00	0.05	46.39	53.47	99.95	OhioA4.3	
29	0.00	0.00	0.01	0.05	0.02	0.00	0.00	0.05	46.71	54.11	100.95	OhioA5.1	45x60
30	0.00	0.00	0.01	0.04	0.00	0.01	0.00	0.05	46.38	54.83	101.32	OhioA5.2	zoned
31	0.00	0.03	0.00	0.04	0.01	0.01	0.00	0.05	46.85	54.66	101.64	OhioA5.3	subhedral
32	0.01	0.00	0.00	0.23	0.01	0.01	0.00	0.04	46.72	54.56	101.58	OhioA5.4	
33	0.00	0.00	0.02	0.00	0.02	0.01	0.00	0.05	46.72	53.89	100.71	OhioA5.5	
No.	Pb	Se	Cu	Cd	As	Ni	Zn	Co*	Fe	S	Total	Comment	Size/Form

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67	0.00	0.00	0.04	0.02	0.00	0.02	0.00	0.05	45.86	55.17	101.15	OhA13.1	175x150
68	0.00	0.00	0.06	0.01	0.00	0.01	0.00	0.05	47.10	56.27	103.49	OhA13.2	composite
69	0.00	0.01	0.01	0.01	0.00	0.02	0.00	0.04	46.60	55.41	102.10	OhA13.3	subhedral
70	0.01	0.01	0.01	0.00	0.00	0.02	0.00	0.05	47.24	55.35	102.69	OhA13.4	
71	0.01	0.00	0.01	0.01	0.00	0.09	0.00	0.05	46.77	55.74	102.67	OhA13.5	
72	0.01	0.01	0.03	0.01	0.00	0.02	0.00	0.05	46.76	54.47	101.36	OhA13.6	
54	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.04	46.69	52.59	99.38	OH-1 1.1	190x150
55	0.00	0.01	0.04	0.00	0.03	0.00	0.01	0.06	46.47	52.06	98.68	OH-1 1.2	composite
56	0.00	0.00	0.05	0.00	0.04	0.00	0.01	0.04	45.89	51.99	98.02	OH-1 1.3	subhedral
57	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.04	45.68	51.80	97.57	OH-1 1.4	
58	0.00	0.03	0.04	0.00	0.01	0.00	0.01	0.05	42.77	52.11	95.02	OH-1 1.5	
60	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.05	47.10	52.60	99.77	OH-1 2.1	90x50
61	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.06	46.59	53.24	99.91	OH-1 2.2	subhedral
62	0.00	0.00	0.03	0.00	0.00	0.00	0.01	0.04	46.53	52.49	99.10	OH-1 2.3	
66	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.05	47.28	52.54	99.88	OH-1 4.1	140x40
67	0.00	0.00	0.04	0.00	0.00	0.07	0.01	0.04	46.64	50.71	97.51	OH-1 4.2	framboid
68	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.05	47.23	52.55	99.84	OH-1 4.3	cluster
70	0.00	0.01	0.03	0.00	0.00	0.01	0.00	0.05	45.23	52.66	97.99	OH-1 4.5	
71	0.00	0.00	0.06	0.00	0.00	0.01	0.00	0.05	46.40	52.23	98.74	OH-1 4.6	
72	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.05	46.57	51.65	98.29	OH-2 1.1	170x150
73	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.04	46.06	51.99	98.12	OH-2 1.2	composite
74	0.00	0.02	0.04	0.00	0.00	0.01	0.00	0.05	46.61	51.49	98.21	OH-2 1.3	subhedral
75	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.06	43.10	52.10	95.26	OH-2 1.4	
76	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.06	47.14	51.83	99.04	OH-2 1.5	
77	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.05	47.36	52.33	99.75	OH-2 1.6	
78	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.05	45.09	51.03	96.20	OH-2 1.7	
80	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.05	45.76	52.10	97.93	OH-2 2.2	75x60
81	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	47.81	52.72	100.58	OH-2 2.3	subhedral
82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	47.32	52.53	99.91	OH-2 2.4	
83	0.00	0.02	0.01	0.00	0.04	0.01	0.00	0.04	43.63	51.72	95.47	OH-2 5.1	150x90
84	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.05	46.49	51.34	97.90	OH-2 5.2	framboid
85	0.00	0.05	0.03	0.00	0.07	0.01	0.00	0.05	45.90	51.81	97.91	OH-2 5.3	cluster
86	0.00	0.03	0.03	0.00	0.09	0.01	0.00	0.04	45.84	51.95	97.99	OH-2 5.4	
87	0.00	0.03	0.04	0.00	0.04	0.00	0.00	0.05	44.77	51.56	96.48	OH-2 5.5	
No.	Pb	Se	Cu	Cd	As	Ni	Zn	Co*	Fe	S	Total	Comment	Size/Form

88	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.05	46.01	50.66	96.75	OH-2 5.6	
89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.05	47.29	50.94	98.29	OH-2 5.7	
90	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.06	46.98	52.35	99.40	OH-2 6.1	140x120
91	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.05	0.05	45.42	52.50	97.98	OH-2 6.2	composite
92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.05	47.60	52.52	100.18	OH-2 6.3	subhedral
93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.05	46.94	52.24	99.23	OH-2 6.4	
94	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.04	0.04	43.78	52.54	96.37	OH-2 6.5	
95	0.00	0.00	0.01	0.00	0.03	0.00	0.00	0.00	0.05	0.05	47.74	52.79	100.61	OH-2 6.6	

*Cobalt data reflect a constant background of 0.05 ± 0.02 wt. %, due to an interference with iron. Results for Co are not background-subtracted.

Detection limit for other elements is 0.01 wt. %. Grain sizes are in micrometers. Different runs are indicated by normal, italicized, and underlined analysis numbers, respectively.

Electron microprobe results for pyrite in the North Dakota coal sample.

No.	Pb	Se	Cu	Cd	As	Ni	Zn	Co*	Fe	S	Total	Comment	Size/Form
57	0.00	0.01	0.02	0.01	0.08	0.00	0.00	0.04	46.63	52.26	99.06	NDakA2.1	35x35
59	0.03	0.01	0.00	0.02	0.05	0.00	0.00	0.05	46.90	50.69	97.74	NDakA2.3	irregular
60	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.05	44.56	49.41	94.03	NDakA3.1	10x25
62	0.00	0.00	0.02	0.02	0.00	0.15	0.00	0.06	46.61	48.75	95.60	NDakA4.1	subhedral
63	0.02	0.00	0.00	0.01	0.00	0.08	0.00	0.06	46.58	52.17	98.92	NDakA4.2	20x25
64	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.05	45.42	48.47	93.98	NDakA5.1	subhedral
66	0.00	0.01	0.00	0.01	0.10	0.05	0.00	0.07	46.23	52.79	99.25	NDakA6.1	20x20
67	0.01	0.00	0.00	0.02	0.06	0.07	0.00	0.06	46.00	51.49	97.70	NDakA6.2	irregular
68	0.05	0.00	0.00	0.02	0.00	0.00	0.00	0.05	46.29	50.50	96.92	NDakA7.1	15x20
70	0.00	0.01	0.00	0.04	0.07	0.00	0.00	0.05	46.91	52.08	99.15	NDakA8.1	subhedral
71	0.00	0.00	0.00	0.02	0.13	0.00	0.00	0.07	46.86	50.37	97.45	NDakA8.2	30x50
72	0.00	0.01	0.01	0.03	0.14	0.00	0.00	0.05	46.41	51.59	98.25	NDakA8.3	irregular
73	0.00	0.00	0.00	0.00	0.24	0.00	0.00	0.06	46.04	52.33	98.67	NDakA9.1	30x35
74	0.01	0.00	0.01	0.02	0.24	0.01	0.01	0.06	46.57	51.63	98.56	NDakA9.2	subhedral
75	0.00	0.00	0.00	0.02	0.24	0.00	0.00	0.05	46.34	51.82	98.47	NDakA9.3	
81	0.00	0.00	0.00	0.05	0.00	0.09	0.00	0.06	46.29	50.37	96.86	NDak11.1	60x70
83	0.00	0.01	0.00	0.01	0.00	0.11	0.00	0.06	45.64	51.06	96.89	NDak11.3	irregular
84	0.01	0.01	0.01	0.02	0.14	0.00	0.00	0.06	46.28	49.01	95.53	NDak12.1	15
86	0.01	0.00	0.00	0.01	0.03	0.00	0.00	0.05	45.81	52.16	98.08	NDak13.2	framoboid
87	0.04	0.01	0.02	0.02	0.00	0.00	0.00	0.06	46.15	50.17	96.45	NDak13.3	35x40
75	0.00	0.00	0.01	0.02	0.07	0.00	0.00	0.05	47.73	48.89	96.77	NDakB2.1	irregular
76	0.00	0.00	0.01	0.01	0.01	0.03	0.00	0.07	47.56	53.29	100.97	NDakB2.2	40x50
77	0.00	0.02	0.00	0.01	0.03	0.00	0.00	0.06	48.02	48.59	96.72	NDakB2.3	multiple
78	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.06	47.06	55.41	102.58	NDakB3.1	framoboid
79	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.06	47.00	56.73	103.80	NDakB3.2	15x15
No.	Pb	Se	Cu	Cd	As	Ni	Zn	Co*	Fe	S	Total	Comment	Size/Form
80	0.00	0.01	0.00	0.00	0.03	0.00	0.00	0.06	44.69	52.03	96.81	NDakB4.1	subhedral
81	0.00	0.03	0.02	0.00	0.03	0.01	0.01	0.04	44.75	53.36	98.25	NDakB4.2	Size/Form
82	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.04	46.04	54.48	100.58	NDakB4.3	40x40

89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	48.74	54.84	103.67	NDakB7.1	15x15
90	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	47.78	56.46	104.31	NDakB7.2	subhedral
91	0.00	0.00	0.00	0.00	0.03	0.02	0.00	0.00	0.00	0.05	47.06	55.89	103.05	NDakB8.1	30x35
92	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.06	45.99	54.24	100.32	NDakB8.2	subhedral
93	0.00	0.00	0.00	0.00	0.03	0.01	0.00	0.00	0.00	0.05	46.52	54.35	100.96	NDakB8.3	
94	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.04	46.97	56.23	103.25	NDakB9.1	17x35
95	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.06	46.37	55.51	101.95	NDakB9.2	cleat?
99	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.04	47.89	47.19	95.15	NDkB10.3	35
100	0.02	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.00	0.05	45.86	53.62	99.59	NDkB11.1	euohedral
101	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.02	0.00	0.05	47.66	54.78	102.54	NDkB11.2	30x60
104	0.01	0.00	0.00	0.00	0.03	0.03	0.00	0.01	0.00	0.05	47.66	55.81	103.57	NDkB12.1	irregular
107	0.01	0.00	0.00	0.00	0.02	0.02	0.02	0.00	0.00	0.04	47.67	51.82	99.57	NDkB13.1	40x40
42	0.00	0.03	0.03	0.03	0.00	0.00	0.78	0.12	0.00	0.05	45.56	51.95	98.53	ND-2 3.1	35x35
43	0.00	0.04	0.02	0.02	0.00	0.00	0.80	0.12	0.00	0.05	45.72	52.01	98.76	ND-2 3.2	subhedral
44	0.00	0.05	0.03	0.03	0.00	0.00	0.83	0.10	0.00	0.06	46.08	51.94	99.09	ND-2 3.3	65x40
45	0.00	0.07	0.03	0.03	0.00	0.00	0.78	0.09	0.01	0.04	45.14	51.85	98.01	ND-2 3.4	subhedral
46	0.00	0.05	0.02	0.02	0.00	0.00	0.78	0.12	0.00	0.05	45.60	52.23	98.85	ND-2 3.5	
47	0.00	0.05	0.01	0.01	0.00	0.00	0.77	0.11	0.02	0.06	45.72	52.03	98.78	ND-2 3.6	
48	0.00	0.05	0.02	0.02	0.00	0.00	0.71	0.11	0.02	0.06	45.88	52.10	98.95	ND-2 3.7	
49	0.00	0.04	0.02	0.02	0.00	0.00	0.32	0.03	0.02	0.05	46.28	52.47	99.23	ND-2 3.8	
50	0.00	0.02	0.03	0.03	0.00	0.00	0.18	0.00	0.00	0.05	46.72	52.44	99.44	ND-2 3.9	
51	0.00	0.01	0.03	0.03	0.00	0.00	0.02	0.00	0.02	0.06	47.41	52.75	100.28	ND-2 4.1	70x30
52	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.06	47.73	52.76	100.59	ND-2 4.2	subhedral
53	0.00	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.06	46.56	52.39	99.04	ND-2 4.3	

*Cobalt data reflect a constant background of 0.05 ± 0.02 wt.%, due to an interference with iron. Results for Co are not background-subtracted.

Detection limit for other elements is 0.01 wt. %. Grain sizes are indicated by normal, italicized, and underlined analysis numbers, respectively.

Electron microprobe results for pyrite in the Wyodak coal sample.

No.	Pb	Se	Cu	Cd	As	Ni	Zn	Co	Fe	S	Total	Comment	Size/Form
88	0.06	0.04	0.17	0.04	0.15	0.07	0.01	0.06	45.26	50.21	96.06	WdakB1.1	30x40
89	0.07	0.02	0.14	0.03	0.21	0.09	0.00	0.07	44.61	49.93	95.17	WdakB1.2	framboid
90	0.07	0.06	0.17	0.02	0.18	0.09	0.00	0.07	44.17	50.70	95.52	WdakB1.3	cluster
92	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.07	47.68	52.88	100.65	Wdak2.1	30x30
94	0.00	0.00	0.01	0.02	0.01	0.00	0.01	0.07	48.04	52.63	100.78	Wdak2.3	subhedral
95	0.01	0.00	0.00	0.04	0.01	0.00	0.00	0.06	47.41	52.87	100.39	Wdak3.1	15x25
96	0.03	0.00	0.00	0.03	0.01	0.00	0.00	0.06	48.10	52.58	100.81	Wdak3.2	subhedral
97	0.04	0.00	0.00	0.03	0.00	0.00	0.00	0.06	46.32	51.71	98.15	Wdak4.1	60x80
98	0.00	0.01	0.01	0.02	0.00	0.00	0.00	0.05	46.36	51.28	97.73	Wdak4.2	subhedral
99	0.02	0.00	0.00	0.03	0.00	0.00	0.00	0.05	46.42	51.20	97.72	Wdak4.3	
100	0.00	0.01	0.00	0.03	0.00	0.00	0.00	0.05	46.30	51.45	97.84	Wdak4.4	
101	0.00	0.02	0.00	0.02	0.00	0.00	0.00	0.07	45.50	51.99	97.60	Wdak4.5	
102	0.02	0.00	0.01	0.02	0.00	0.00	0.00	0.06	45.21	51.16	96.46	Wdak4.6	
104	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.07	45.91	51.43	97.43	Wdak5.2	40x50
106	0.00	0.06	0.03	0.04	0.15	0.09	0.00	0.06	44.32	49.15	93.89	Wdak6.1	irregular
108	0.01	0.03	0.00	0.01	0.00	0.00	0.00	0.04	47.01	53.85	100.95	Wdak7.1	subhedral
109	0.00	0.00	0.01	0.04	0.00	0.00	0.00	0.06	45.95	53.65	99.70	Wdak7.2	15x25
111	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.05	46.44	54.87	101.37	WydkA2.1	subhedral
112	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.04	46.09	55.12	101.26	WydkA2.2	15x30
114	0.29	0.04	0.45	0.01	0.11	0.16	0.00	0.10	46.27	53.71	101.15	WydkA3.2	10
115	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.07	47.15	55.39	102.64	WydkA4.1	framboid
119	0.40	0.15	0.12	0.02	0.47	0.47	0.00	0.10	45.18	56.50	103.40	WydkA6.1	10
120	0.27	0.11	0.09	0.03	0.34	0.32	0.00	0.10	45.65	55.93	102.83	WydkA6.2	framboid
121	0.30	0.10	0.11	0.02	0.39	0.39	0.00	0.09	45.79	55.71	102.88	WydkA6.3	35x50
122	0.17	0.08	0.01	0.01	0.27	0.49	0.01	0.16	44.59	54.20	100.00	WydkA6.4	cleat?

No.	Pb	Se	Cu	Cd	As	Ni	Zn	Co*	Fe	S	Total	Comment	Size/Form
124	0.08	0.01	0.00	0.01	0.00	0.00	0.00	0.05	43.68	55.23	99.06	WydkA7.2	20x30
127	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.04	45.77	56.95	102.76	WydkA8.2	subhedral
128	0.00	0.13	0.01	0.00	0.20	0.17	0.02	0.08	46.72	47.77	95.09	WydkA9.1	10x15
131	0.00	0.02	0.02	0.01	0.00	0.02	0.00	0.06	47.05	56.41	103.59	WydkA10.2	irregular
133	0.04	0.00	0.04	0.01	0.00	0.05	0.00	0.07	46.21	55.91	102.33	WydkA11.1	20x25
134	0.03	0.01	0.04	0.02	0.01	0.05	0.00	0.07	46.56	56.17	102.96	WydkA11.2	subhedral
30	0.00	0.00	0.02	0.00	0.03	0.01	0.00	0.05	46.30	52.36	98.77	WY-1 1.1	20
31	0.00	0.01	0.01	0.00	0.02	0.01	0.00	0.06	44.96	52.07	97.13	WY-1 1.2	framboid
32	0.00	0.00	0.02	0.00	0.04	0.00	0.00	0.06	47.05	51.96	99.13	WY-1 1.3	20
33	0.00	0.00	0.04	0.00	0.02	0.00	0.00	0.05	47.46	52.04	99.62	WY-1 1.4	framboid
34	0.00	0.00	0.01	0.00	0.03	0.01	0.00	0.05	44.60	51.99	96.69	WY-1 1.5	20
35	0.00	0.00	0.03	0.00	0.01	0.00	0.00	0.06	44.35	52.00	96.44	WY-1 1.6	framboid
36	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.05	46.82	51.67	98.57	WY-1 2.1	120x45
37	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.03	46.86	51.84	98.75	WY-1 2.2	irregular
38	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.06	46.25	51.82	98.14	WY-1 2.3	20
39	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.05	44.78	51.37	96.21	WY-1 2.4	framboid
41	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.04	44.54	52.52	97.12	WY-1 2.6	20

*Cobalt data reflect a constant background of 0.05 ± 0.02 wt.%, due to an interference with iron. Results for Co are not background-subtracted.

Detection limit for other elements is 0.01 wt. %. Grain sizes are indicated by normal, italicized, and underlined analysis numbers, respectively.

Electron microprobe data for illite/smectite and kaolinite¹

No.	Na ₂ O	K ₂ O	CaO	MgO	FeO	MnO	TiO ₂	Cr ₂ O ₃	Al ₂ O ₃	SiO ₂	Total ²	Comment
						Ohio 5/6/7						
14	0.22	3.13	0.03	0.27	0.42	0.00	0.17	0.01	34.93	42.68	81.87	Map2Ohio2.1
15	0.11	8.20	0.02	2.60	4.67	0.01	0.35	0.03	29.69	49.15	94.82	Map2Ohio2.2
16	0.18	5.09	0.06	0.84	1.38	0.00	0.85	0.00	27.46	45.85	81.72	Map2Ohio2.3
182	0.16	4.83	0.24	1.15	1.66	0.01	0.98	0.01	27.62	44.54	81.20	Ohio(a) gr1 1.2
186	0.18	4.89	0.23	1.14	1.63	0.00	0.84	0.02	27.64	45.55	82.11	Ohio(a)gr1 1.6
191	0.47	8.01	0.00	1.38	2.20	0.01	0.16	0.02	33.29	48.81	94.35	Ohio(a)gr3 3.1
192	0.17	4.75	0.12	1.29	1.71	0.00	0.24	0.01	34.38	50.19	92.85	Ohio(a)gr3 3.2
193	0.01	0.02	0.02	0.04	0.10	0.02	0.03	0.01	39.69	47.94	87.87	Ohio(a)gr4 4.1
195	0.10	1.19	0.10	0.26	0.62	0.00	0.00	0.00	27.13	52.11	81.51	Ohio(a) 6.1
196	0.81	8.15	0.04	0.37	1.67	0.01	0.13	0.01	33.16	43.13	87.49	Ohio(a) 7.1
197	0.03	0.05	0.06	0.11	0.40	0.00	0.03	0.00	39.77	47.63	88.08	Ohio(a) 8.1
198	0.03	0.04	0.04	0.07	0.26	0.00	0.00	0.00	39.35	47.89	87.68	Ohio(a) 8.2
199	0.16	5.96	0.13	2.30	1.94	0.03	0.29	0.04	28.58	47.29	86.72	Ohio(a) 9.1
200	0.31	3.98	0.01	0.36	0.73	0.01	0.30	0.01	33.84	49.96	89.50	Ohio(a) 9.2
51	0.32	8.54	0.02	0.30	0.90	0.00	0.17	0.01	39.09	47.12	96.48	Map12Ohio12.1
58	0.17	4.29	0.20	0.87	0.85	0.00	0.09	0.00	31.51	49.42	87.40	Map13Ohio13.3
59	0.06	2.07	0.03	0.63	0.50	0.00	0.04	0.01	37.87	48.44	89.63	Map13Ohio13.4
60	0.11	0.74	0.11	0.20	0.19	0.00	0.02	0.00	36.49	47.23	85.09	Map13Ohio13.5
61	0.03	0.41	0.01	0.07	0.13	0.00	0.00	0.00	39.82	48.00	88.48	Map13Ohio13.6
62	0.12	2.64	0.00	0.19	0.30	0.02	0.03	0.00	39.44	48.08	90.81	Map13Ohio13.7
63	0.04	0.52	0.13	0.12	0.14	0.00	0.02	0.00	37.70	46.54	85.21	Map13Ohio13.8
83K	0.00	0.05	0.06	0.08	0.16	0.01	0.00	0.00	41.20	49.74	91.31	Ohio(b)gr1 1.1
84K	0.00	0.02	0.01	0.01	0.16	0.00	0.01	0.00	40.91	48.97	90.09	Ohio(b)gr1 1.2
85K	0.00	0.11	0.05	0.09	0.15	0.01	0.01	0.00	40.77	48.97	90.15	Ohio(b)gr1 1.3
89K	0.00	0.00	0.02	0.02	0.13	0.00	0.00	0.00	41.67	49.61	91.46	Ohio(b)gr1 1.7
No.	Na ₂ O	K ₂ O	CaO	MgO	FeO	MnO	TiO ₂	Cr ₂ O ₃	Al ₂ O ₃	SiO ₂	Total*	Comment

96	0.92	5.26	0.04	0.77	1.30	0.00	1.56	0.02	33.35	49.49	92.72	Ohio(b)gr3 3.1
97	0.58	4.58	0.17	0.99	1.35	0.00	0.69	0.00	31.49	44.04	83.89	Ohio(b)gr3 3.2
100	0.40	4.51	0.05	0.89	1.53	0.01	0.21	0.03	30.30	43.00	80.93	Ohio(b)gr3 3.5
107	0.03	0.20	0.02	0.14	0.31	0.00	0.02	0.00	40.34	49.47	90.54	Ohio(b)gr5 5.1
108	0.02	0.26	0.02	0.18	0.45	0.00	0.05	0.01	40.39	49.89	91.27	Ohio(b)gr5 5.2
117	0.08	1.73	0.07	1.38	2.32	0.01	0.04	0.01	31.83	50.44	87.91	Ohio(b)gr6 6.5
						North Dakota						
39	0.18	5.60	0.22	3.85	10.56	0.05	0.06	0.02	16.91	46.80	84.25	Map8ND8.1
40	0.15	6.76	0.18	1.96	1.88	0.00	0.00	0.01	32.19	51.85	94.97	Map8ND8.2
41	0.14	6.53	0.13	2.13	2.85	0.00	0.02	0.01	31.62	49.42	92.85	Map8ND8.3
42	0.16	4.19	0.15	3.78	6.97	0.06	0.00	0.01	32.30	48.55	96.16	Map8ND8.4
126	0.37	3.13	0.42	2.91	3.97	0.01	0.13	0.03	18.89	53.39	83.27	ND(b) gr1 1.1
128	0.14	2.83	0.49	2.02	2.85	0.04	0.02	0.00	18.09	59.35	85.83	ND(b) gr1 1.3
129	0.11	2.01	0.44	2.53	3.56	0.00	0.35	0.01	19.49	50.72	79.22	ND(b) gr1 1.4
130	0.11	2.43	0.55	1.95	4.51	0.04	0.26	0.02	15.29	58.28	83.42	ND(b) gr1 1.5
131	0.13	1.93	0.57	1.20	2.62	0.01	0.22	0.01	14.09	61.89	82.67	ND(b) gr2 2.1
132	0.12	3.20	0.41	1.49	2.45	0.01	0.19	0.01	16.96	61.80	86.64	ND(b) gr2 2.2
133	0.16	2.74	0.54	1.31	2.42	0.02	0.40	0.02	16.24	56.42	80.27	ND(b) gr2 2.3
135	0.14	1.67	0.34	1.05	3.01	0.02	0.15	0.02	25.16	54.39	85.95	ND(b) gr3 3.1
136	0.13	2.53	0.54	2.46	6.38	0.00	0.44	0.01	18.07	48.50	79.05	ND(b) gr3 3.2
138	0.10	4.96	0.32	1.74	4.26	0.01	0.24	0.02	29.67	51.89	93.20	ND(b) gr3 3.4
139	0.29	1.88	0.84	1.63	4.05	0.01	2.80	0.03	16.78	52.73	81.01	ND(b) gr4 4.1
141	0.13	4.60	0.16	1.05	1.33	0.03	0.35	0.01	26.86	57.87	92.39	ND(b) gr4 4.3
142	0.34	5.94	0.56	1.13	3.05	0.02	0.13	0.01	18.16	58.60	87.95	ND(b) gr4 4.4
145	0.63	2.96	0.51	2.51	5.23	0.04	0.13	0.01	19.53	55.74	87.28	ND(b) gr5 5.2
147	0.10	2.73	0.49	2.27	3.65	0.02	0.96	0.02	16.12	55.53	81.88	ND(b) gr5 5.4
152	0.12	3.48	0.21	0.97	1.78	0.00	0.15	0.01	20.00	60.13	86.85	ND(b) gr6 6.4
154	0.11	8.08	0.06	2.38	5.36	0.01	0.43	0.02	26.49	47.33	90.27	ND(b) gr7 7.1
155	0.15	1.49	0.70	1.58	4.58	0.00	0.15	0.01	17.40	55.55	81.60	ND(b) gr7 7.2
158	0.10	6.30	0.08	2.30	4.57	0.01	0.70	0.01	29.69	50.30	94.06	ND(b) gr7 7.5
No.	Na2O	K2O	CaO	MgO	FeO	MnO	TiO2	Cr2O3	Al2O3	SiO2	Total*	Comment
159	0.13	2.31	0.58	1.16	1.59	0.00	0.15	0.01	17.10	57.54	80.56	ND(b) gr8 8.1

207	0.09	6.78	0.15	2.62	2.91	0.00	0.10	0.01	28.20	49.74	90.58	NDak(a) 4.1
						Wyodak						
165	0.12	1.44	0.71	0.95	2.69	0.00	0.68	0.00	24.70	50.98	82.26	Wdk(b) gr1 1.4
168	0.03	0.27	0.27	0.20	0.34	0.00	0.16	0.00	37.21	45.87	84.34	Wdk(b) gr2 2.3
169	0.07	0.50	0.44	0.38	0.43	0.01	0.21	0.00	37.06	47.16	86.26	Wdk(b) gr2 2.4
178	0.09	1.50	0.64	0.78	1.00	0.02	1.27	0.02	28.79	47.42	81.52	Wdk(b) gr4 4.2
21	0.06	3.75	0.08	0.87	2.20	0.00	0.09	0.00	36.45	48.20	91.69	Map4Wyodak4.1
22	0.04	1.80	0.22	0.43	0.89	0.01	0.13	0.00	39.18	47.02	89.73	Map4Wyodak4.2
26	0.01	0.01	0.17	0.02	0.30	0.01	0.06	0.00	39.53	46.35	86.45	Map5Wyodak5.1
27	0.04	0.04	0.16	0.05	0.35	0.00	0.00	0.00	38.71	42.00	81.35	Map5Wyodak5.2
210	0.00	0.00	0.03	0.02	0.03	0.00	0.00	0.00	39.12	47.23	86.44	Wyodak(a) 1.1
211	0.00	0.01	0.02	0.01	0.02	0.00	0.03	0.00	39.51	46.70	86.31	Wyodak(a) 1.2
214	0.89	7.45	0.11	0.40	0.72	0.03	0.44	0.00	35.13	46.99	92.17	Wyodak(a) 4.1
215	0.67	6.15	0.18	0.29	0.56	0.00	0.25	0.01	33.93	45.63	87.69	Wyodak(a) 4.2
216	0.00	0.05	0.59	0.05	0.06	0.01	0.00	0.00	37.56	42.53	80.85	Wyodak(a) 5.1

¹Kaolinite analysis numbers are followed by a K.

²Totals 85-95% due to the presence of structural water and/or hydroxyl, which are not determined.

Electron microprobe analyses of calcite in Ohio 5/6/7

No.	MnO	MgO	PbO	CaO	FeO	SrO	BaO	ZnO	Total ¹	Comment
39	0.39	0.38	0.03	55.71	0.37	0.20	0.06	n.d.	57.14	OhioB clc1.1
40	0.47	0.47	0.00	55.53	0.49	0.30	0.00	n.d.	57.26	OhioB clc1.2
41	0.81	0.21	0.00	57.66	1.53	0.02	0.04	n.d.	60.27	OhioB clc2.1
42	0.67	0.22	0.03	58.02	1.67	0.07	0.00	n.d.	60.67	OhioB clc2.2
43	0.80	0.19	0.01	57.01	1.37	0.02	0.00	n.d.	59.40	OhioB clc2.3
141	0.50	0.23	0.01	54.35	0.86	0.08	0.04	0.01	56.08	OhioBclc2.4
142	0.54	0.20	0.01	51.13	0.89	0.05	0.00	0.00	52.81	OhioBclc2.5
44	0.00	0.39	0.01	59.16	2.05	0.06	0.00	n.d.	61.66	OhioB clc4.1
45	0.03	0.63	0.03	56.74	1.89	0.06	0.00	n.d.	59.37	OhioB clc4.2
46	0.32	0.41	0.00	56.88	1.04	0.17	0.00	n.d.	58.82	OhioB clc5.1
47	0.32	0.43	0.00	56.32	1.25	0.20	0.00	n.d.	58.52	OhioB clc5.2
48	0.29	0.43	0.02	56.76	1.30	0.22	0.00	n.d.	59.01	OhioB clc5.3
49	0.22	0.49	0.00	55.86	1.23	0.19	0.05	n.d.	58.03	OhioB clc5.4
143	0.26	0.40	0.00	54.67	0.75	0.28	0.00	0.00	56.35	OhioBclc5.5
144	0.32	0.35	0.03	54.64	0.85	0.20	0.00	0.00	56.38	OhioBclc5.6

¹Carbon not determined. Optimal total for pure CaCO₃ is 56.0 wt. % CaO.